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Electronic Supplementary Information

Ligand effects on the stereochemistry of Stille couplings, as manifested in reactions of *Z*-alkenyl halides

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1. Experimental

1.1. General

All reactions were carried out a dry Ar atmosphere in flame-dried round bottom flasks or microwave vials. Column chromatography was preformed using Silicycle Silia-P 60 mesh flash silica gel. Thin-Layer-Chromatography analysis was conducted using commercially available EMD silica gel 60 F_{254} plates. *Z*-alkenyl halides and *Z*-alkenyl triflates were prepared following literature procedures.[1] Organotin reagents such as (*E*)-3-(tributylstannyl)prop-2-en-1-ol and (*E*)-3-(tributylstannyl)allyl acetate were synthesized according to known procedures.[2] All palladium catalysts were provided by Johnson Matthey Catalysts. Solvents and other reagents were all obtained from commercial vendors and used with no further purification. All known compounds were identified by appropriate technique such as ^{1}H NMR, ^{13}C NMR, GC/MS, and compared with previously reported data. All new compounds were identified by ^{1}H NMR, ^{13}C NMR and HRMS.

Nuclear Magnetic Resonance spectra were obtained on a Varian Inova system, in $CDCl_3$, with proton, carbon and HSQC resonances at 500 or 400, 125 and 600 MHz, respectively, and are referenced to the residual solvent signal at d 7.26 ppm for ^{1}H and d 77.00 ppm for ^{13}C. Data for ^{1}H are reported as follows: chemical shift (d ppm), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant and integration. Data for ^{13}C NMR are reported in terms of chemical shift. GC/MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). As capillary column a HP-5MS cross-linked 5% phenylmethyl- polysiloxanediphenyl column (30 m x 0.250 mm, 0.25 micron, Agilent Technologies) was employed. Helium was used as carrier gas at a constant flow of 1 mL/min. Retention times (tR) refer to the following temperature program: 70 °C for 0 min; heating rate 16°C/min; 300°C for 5.625 min; injection temperature 250 °C; detection temperature 280°C. High resolution mass spectral data were acquired on either a VF Autospec or an analytical VG-70-250 HF spectrometer.

1.2 Experimental Procedures

General Procedure A (Table 1) Catalyst (0.005 mmol or 0.010 mmol) was weighed into a microwave vial at room temperature, and β-bromostyrene (0.250 mmol), organotin reagent (0.275 mmol) and dry THF (1.0 mL) were then added by syringe. The resulting solution was allowed to stir at room temperature for 24 h. The homogeneous reaction mixture was then diluted with EtOAc (4 mL) and NEt_3 (0.3 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed in vacuo to afford the crude product which was determined by ^{1}H NMR and GC/MS to obtain the yield of *Z*-product and *Z*/*E* ratio. Further column chromatography on silica gel was needed to afford the pure desired product.

General Procedure B (Table 1) Catalyst (0.010 mmol) and K_2CO_3 (0.500 mmol) was weighed into a microwave vial at room temperature, and β-bromostyrene (0.250 mmol), organotin reagent (0.275 mmol) and dry DMF (1.0 mL) were then added by syringe. The

resulting solution was allowed to stir at room temperature for 24 h. The homogeneous reaction mixture was then diluted with EtOAc (4 mL) and NEt_3 (0.3 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed *in vacuo* to afford the crude product which was determined by ^{1}H NMR and GC/MS to obtain the yield of *Z*-product and *Z*/*E* ratio. Further column chromatography on silica gel was needed to afford the pure desired product.

General Procedure A (Table 2): Catalyst (0.010 mmol) was weighed into a round bottom flask at room temperature, and alkenyl halide (0.250 mmol), organotin reagent (0.275 mmol) and dry THF (1.0 mL) were then added by syringe. The resulting solution was allowed to stir under reflux for 24 h, and cooled to room temperature. The homogeneous reaction mixture was then diluted with EtOAc (4 mL) and NEt_3 (0.3 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed in vacuo to afford the crude product which was determined by ^{1}H NMR and GC/MS to obtain the yield of *Z*-product and *Z*/*E* ratio. Further column chromatography on silica gel was needed to afford the pure desired product.

General Procedure B (Table 2): Catalyst (0.010 mmol) and K_2CO_3 (0.500 mmol) were weighed into a microwave vial at room temperature, and alkenyl halide (0.250 mmol), organotin reagent (0.275 mmol) and dry DMF (1.0 mL) were then added by syringe. The resulting solution was allowed to stir at room temperature for 24 h. The homogeneous reaction mixture was then diluted with EtOAc (4 mL) and NEt_3 (0.3 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed in vacuo to afford the crude product which was determined by ^{1}H NMR and GC/MS to obtain the yield of *Z*-product and *Z*/*E* ratio. Further column chromatography on silica gel was needed to afford the pure desired product.

General Procedure C (Table 2): $Pd_2(dba)_3$ (2.5 μmol), P(*o*-Tol)$_3$ (0.010 mmol), K_2CO_3 (0.500 mmol) were weighed into a microwave vial at room temperature, and alkenyl halide (0.250 mmol), 2-furyltributyltin (0.275 mmol) and dry DMF (1.0 mL) were then added by syringe. The resulting solution was allowed to stir at 45 ^{o}C for 2 h or 8 h, and cooled to room temperature. The homogeneous reaction mixture was then diluted with EtOAc (4 mL) and NEt_3 (0.3 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed in vacuo to afford the crude product which was determined by ^{1}H NMR and GC/MS to obtain the yield of *Z*-product and *Z*/*E* ratio. Further column chromatography on silica gel was needed to afford the pure desired product.

General Procedure D (Table 2): Catalyst (0.01 mmol), K_2CO_3 (0.50 mmol) were weighed into a microwave vial at room temperature, and β-bromostyrene (0.25 mmol), organotin reagent (0.30 mmol) and dry DMF (1.0 mL) were then added by syringe. The resulting solution was allowed to stir at 100 ^{o}C for 24 h, and cooled to room temperature. The homogeneous reaction mixture was then diluted with EtOAc (4 mL) and NEt_3 (0.3 mL), filtered through a bed of silica gel layered over Celite, The volatiles were removed in vacuo to afford the crude product which was determined by ^{1}H NMR and GC/MS to obtain the yield of *Z*-product and *Z*/*E* ratio. Further column chromatography on silica gel was needed to

afford the pure desired product.

2. Characterization Data

(*Z*)-Buta-1,3-dienylbenzene (*Z*-**3**)[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20-5.25 (m, 1H), 5.36-5.40 (m, 1H), 6.24-6.30 (t, 1H), 6.47 (d, *J* = 11.6 Hz, 1H), 6.84-6.94 (m, 1H), 7.25-7.27 (m, 1H), 7.31-7.37 (m, 4H).

(*E*)-Buta-1,3-dienylbenzene (*E*-**3**)[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (d, *J* = 10.0 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 6.47-6.59 (m, 2H), 6.76-6.83 (m, 1H), 7.21-7.25 (m, 1H), 7.30-7.42 (m, 4H).

(*Z*)-2-Styrylfuran (*Z*-**5**)[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (d, *J* = 3.0 Hz, 1H,), 6.32-6.33 (dd, *J* = 3.5, 2.0 Hz, 1H), 6.38 (d, *J* = 12.5 Hz, 1H), 6.49 (d, *J* = 12.5 Hz 1H), 7.27-7.36 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H).

(*Z*)-2-(Oct-1-enyl)furan (*Z*-**6**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-0.91 (t, 3H), 1.28-1.51 (m, 8H), 2.42-2.47 (m, 2H), 5.54-5.59 (m, 1H), 6.18-6.21 (m, 1H), 6.25 (d, *J* = 3.0 Hz, 1H), 6.39-6.40 (m, 1H), 7.37 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 29.1, 29.3, 29.5, 31.7, 108.6, 111.0, 117.2, 131.5, 141.1, 153.4. HRMS (EI) Calcd. for $C_{12}H_{18}O$ 178.1358, found 178.1366.

(*E*)-2-(Oct-1-enyl)furan (*E*-**6**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.90 (t, 3H), 1.26-1.37 (m, 6H), 1.42-1.48 (m, 2H), 2.16-2.20 (m, 2H), 6.12 (d, *J* = 3.0 Hz, 1H), 6.15-6.23 (m, 2H), 6.34-6.35 (q, 1H), 7.30 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 31.7, 32.8, 105.8, 111.0, 118.4, 130.3, 141.1, 153.4. HRMS (EI) Calcd. for $C_{12}H_{18}O$ 178.1358, found 178.1360.

(*Z*)-Ethyl 3-(furan-2-yl)acrylate (*Z*-**7**)[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31-1.34 (t, *J* = 7.0 Hz, 3H), 4.21-4.26 (q, *J* = 2.0 Hz, 2H), 5.74 (d, *J* = 13.0 Hz, 1H), 6.51-6.52 (m, 1H), 6.79 (d, *J* = 13.0 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 3.5 Hz, 1H,).

(*Z*)-((Octa-5,7-dienyloxy)methyl)benzene (*Z*-**8**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46-1.52 (m, 2H), 1.62-1.67 (m, 2H), 2.19-2.23 (qd, *J* = 2.5, 1.5 Hz, 2H), 3.48-3.49 (t, *J* = 6.5 Hz, 2H), 4.50 (s, 2H), 5.08 (d, *J* = 10.0 Hz, 1H), 5.16-5.20 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.42-5.47 (dd, *J* = 18.5, 7.5 Hz, 1H), 5.98-6.03 (t, *J* = 11.0 Hz, 1H), 6.58-6.66 (m, 1H), 7.26-7.30 (m, 1H), 7.33-7.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2, 24.5, 29.3, 70.2, 72.9, 116.9, 127.5, 127.6, 128.3, 129.4, 132.2, 132.5, 138.6. HRMS (EI) Calcd. for $C_{15}H_{20}O$ 216.1514, found 216.1506.

(*Z*)-(4-Cyclohexenylbut-3-en-1-ynyl)benzene (*Z*-**9**)[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59-1.73 (m, 4H), 2.18-2.20 (m, 2H), 2.70-2.73 (m, 2H), 5.51 (d, *J* = 12.0 Hz, 1H), 6.00-6.02 (m, 1H), 6.20 (d, *J* = 12.0 Hz, 1H), 7.29-7.33 (m, 3H), 7.40-7.42 (m, 2H).

(*Z*)-(5-(Benzyloxy)pent-3-en-1-ynyl)benzene (**10**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39-4.41 (dd, *J* = 6.5, 1.5 Hz, 2H), 4.58 (s, 2H), 5.87-5.90 (dt, *J* = 11.0, 1.5 Hz, 1H), 6.13-6.18 (dt, *J* = 11.0, 6.5 Hz, 1H), 7.29-7.40 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 67.9, 72.4, 85.2, 95.2, 111.8, 123.2, 127.7, 127.9, 128.3, 128.4, 128.4, 131.5, 138.1, 139.2. HRMS (FI); Calcd. for $C_{18}H_{16}O$ 248.1201, found 248.1194.

(*Z*)-1,2-Diphenylethene (*Z*-**11**)[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (s, 2H), 7.20-7.30 (m, 10H).

(*Z*)-Hex-1-enylbenzene (*Z*-**12**)[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-0.92 (t, 3H), 1.30-1.48

(m, 4H), 2.32-2.36 (m, 2H), 5.56-5.70 (m, 1H), 6.41 (d, *J* = 11.5 Hz, 1H), 7.21-7.24 (m, 1H), 7.28-7.35 (m, 4H).

(2*E*,4*Z*)-Undeca-2,4-dien-1-ol (**13**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.90 (t, *J* = 7.0 Hz, 3H), 1.25-1.39 (m, 8H), 2.16-2.20 (m, 2H), 4.20-4.22 (td, *J* = 6.0, 1.0 Hz, 2H), 5.44-5.49 (m, 1H), 5.79-5.84 (dt, *J* = 15.0, 6.0 Hz, 1H), 5.97-6.02 (t, *J* = 11.5 Hz, 1H), 6.51-6.57 (ddq, *J* = 15.5, 11.0, 1.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 27.8, 28.9, 29.6, 31.7, 63.6, 127.0, 127.5, 131.5, 133.3. HRMS (EI); Calcd. for $C_{11}H_{20}O$ 168.1514, found 168.1514.

(*Z*)-2-Methylenedec-3-en-1-ol (**I**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.90 (t, 3H), 1.27-1.41 (m, 8H), 2.21-2.26 (m, 2H), 4.15 (d, *J* = 6.5 Hz, 2H), 5.03 (br, 1H), 5.27 (br, 1H), 5.58-5.63 (m, 1H), 5.81 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 29.0, 30.0, 31.7, 66.2, 113.3, 126.4, 134.8, 144.9. HRMS (EI); Calcd. for $C_{11}H_{20}O$ 168.1514, found 168.1508.

(2*E*,4*Z*)-9-(Benzyloxy)nona-2,4-dienyl acetate (*Z*-**14**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46-1.52 (m, 2H), 1.61-1.67 (m, 2H), 2.07 (s, 3H), 2.19-2.23 (qd, *J* = 8.5, 1.0 Hz, 2H), 3.46-3.49 (t, *J* = 6.3 Hz, 2H), 4.50 (s, 2H), 4.59 (d, *J* = 7.0 Hz, 2H), 5.47-5.52 (m, 1H), 5.70-5.75 (dt, *J* = 15.0, 6.5 Hz, 1H), 5.97-6.01 (t, *J* = 11.0 Hz, 1H), 6.52-6.58 (ddq, *J* = 15.5, 11.0, 1.0 Hz, 1H), 7.27-7.29 (m, 1H), 7.33-7.34 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 26.2, 27.6, 29.3, 65.0, 70.2, 72.9, 126.2, 127.5, 127.6, 127.6, 128.4, 129.8, 133.8, 138.6, 170.8. HRMS (EI); Calcd. for $C_{18}H_{24}O_3$ 288.1725, found $(M+Na)^+$ 311.1618.

(*Z*)-ethyl 3-(4-Methoxyphenyl)but-2-enoate (*Z*-**17**)[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12-1.15 (t, *J* = 7.0 Hz, 3H), 2.16 (d, *J* =1.5 Hz, 3H), 3.82 (s, 3H), 4.01-4.06 (q, *J* = 7.5 Hz, 2H), 5.87-5.88 (q, *J* = 1.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H).

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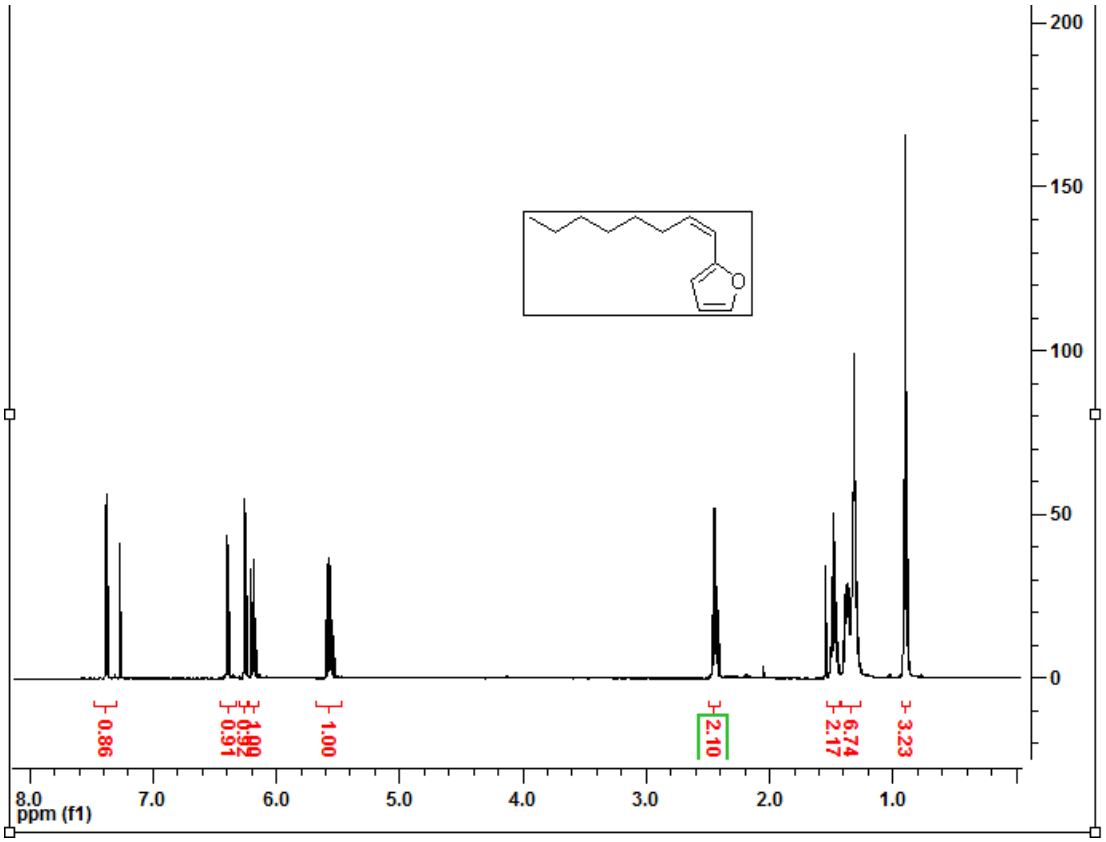
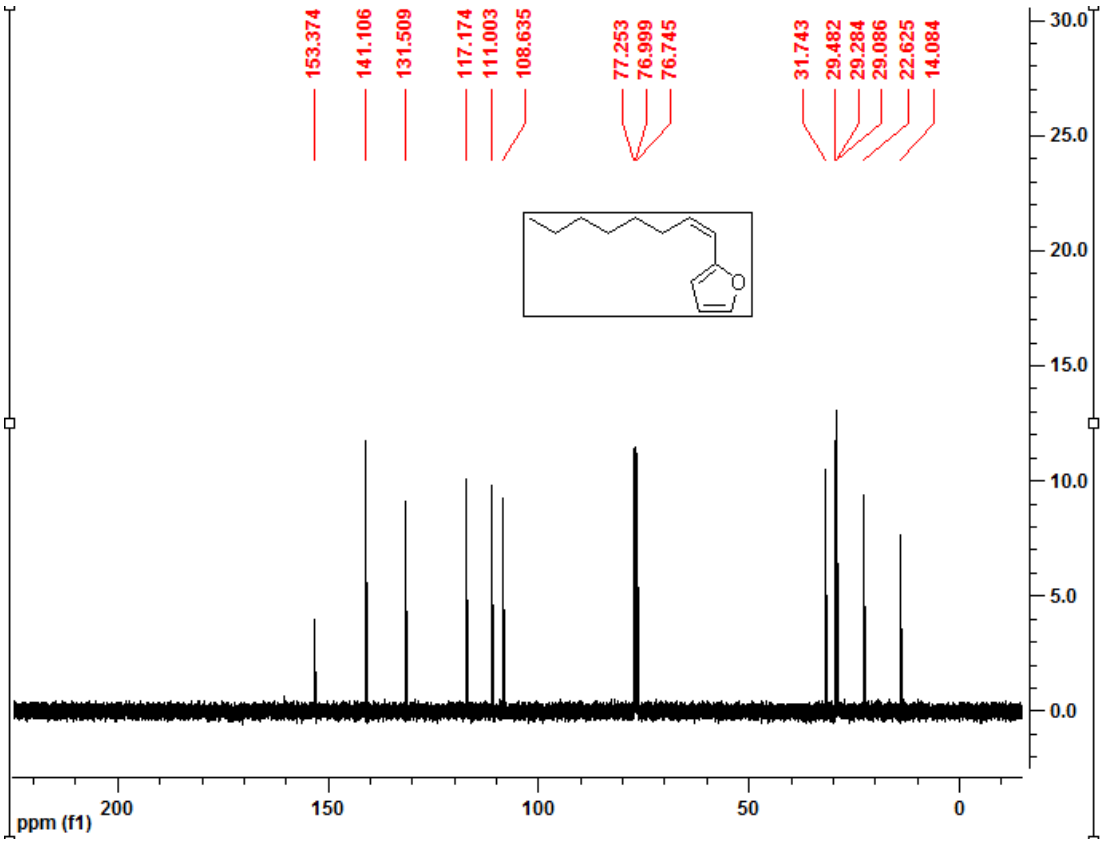
3. NMR Spectra of New Compounds

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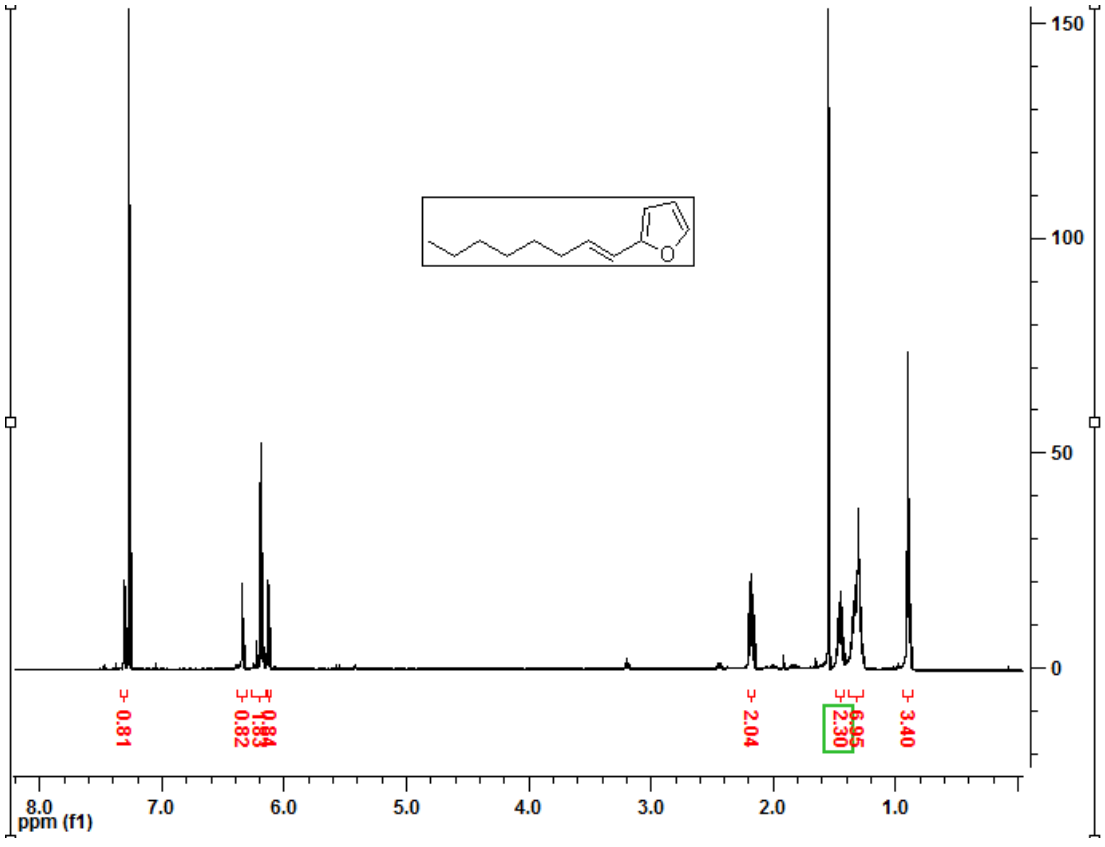
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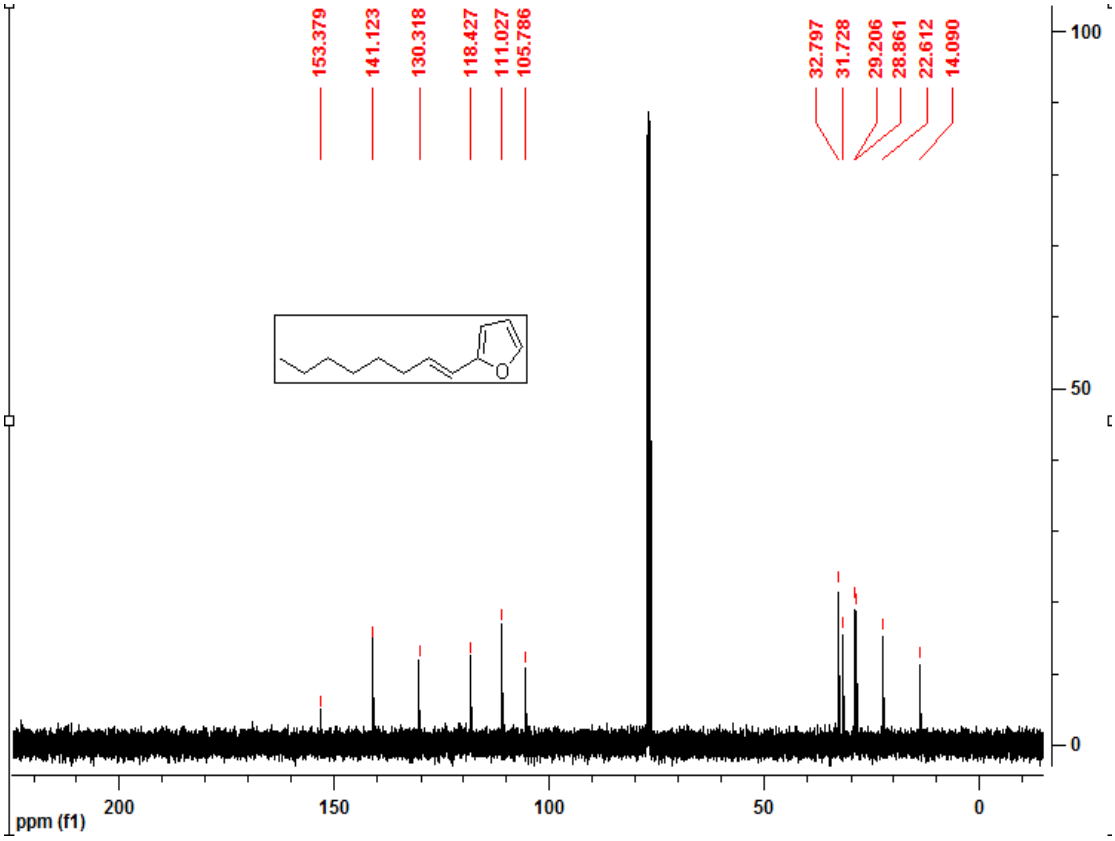
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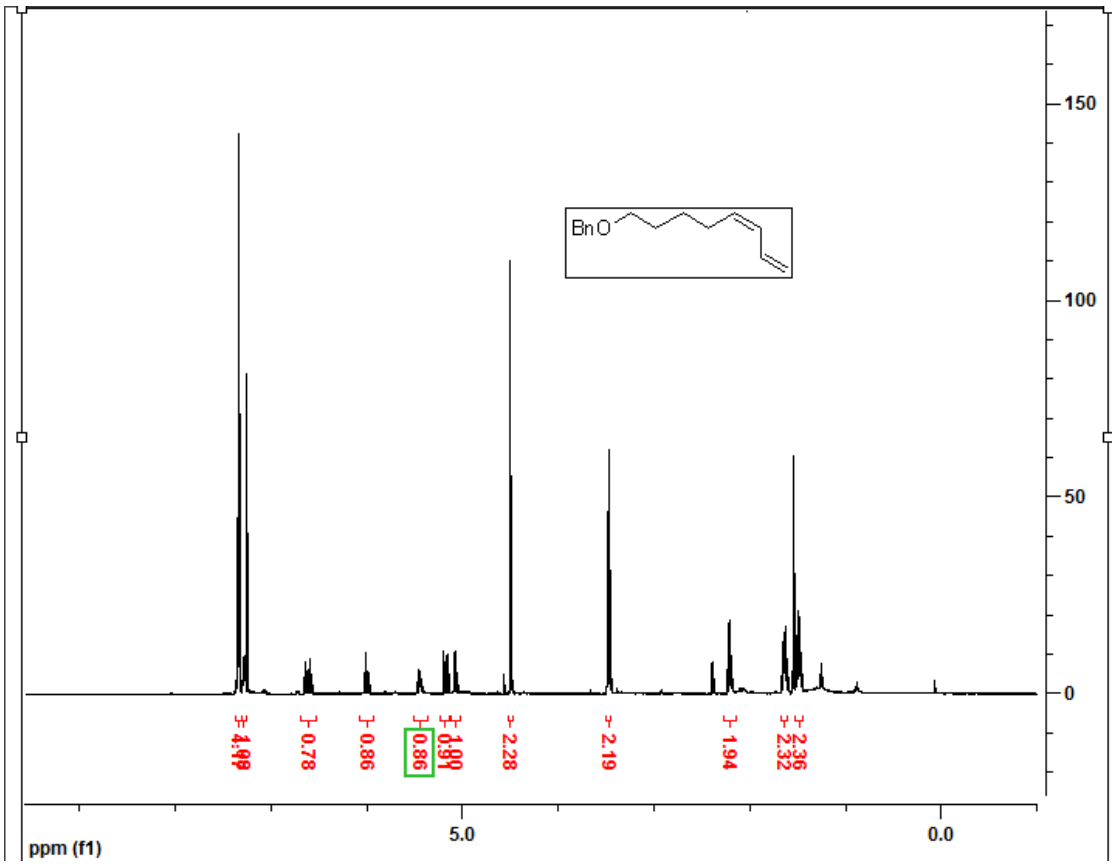
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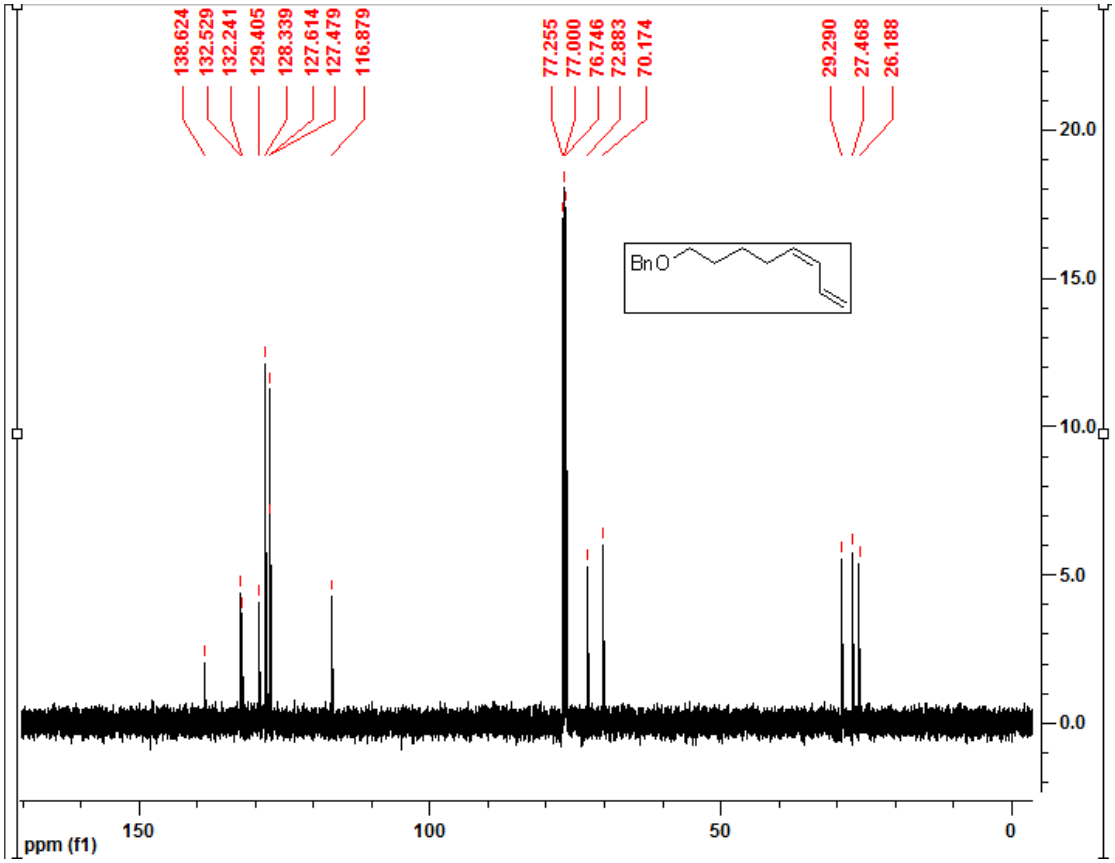
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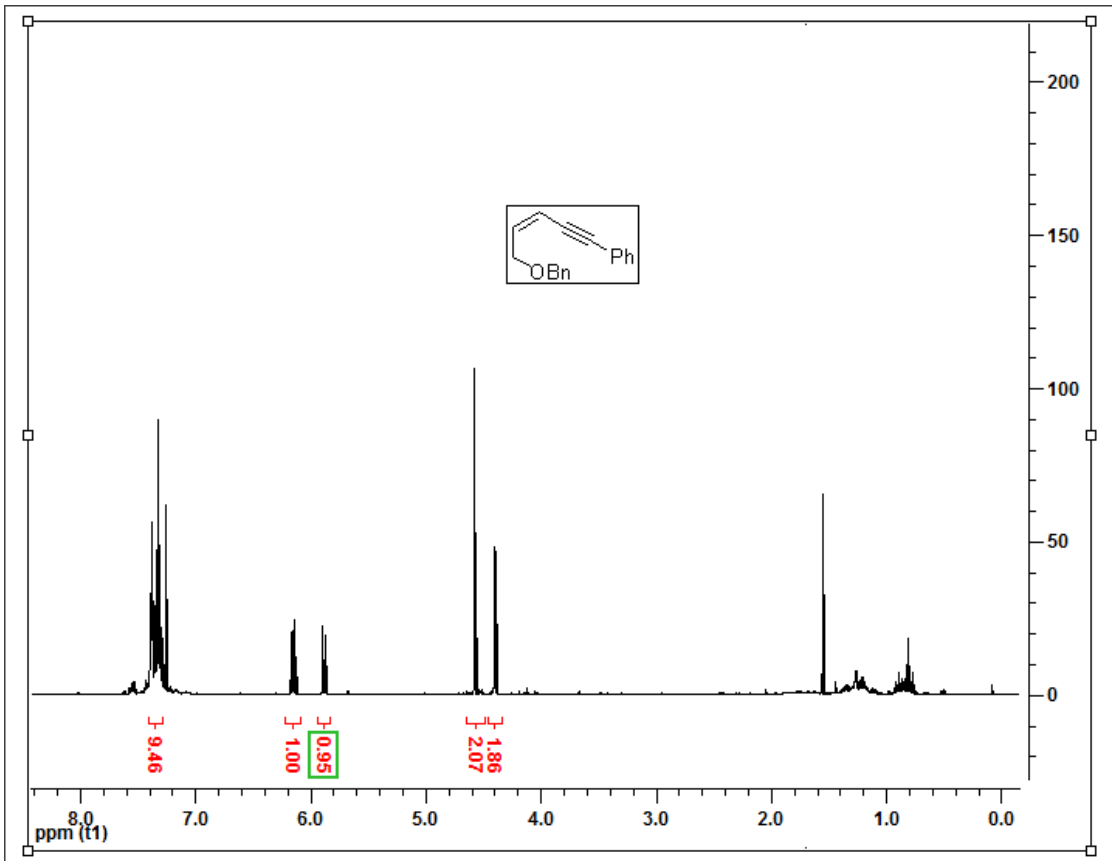
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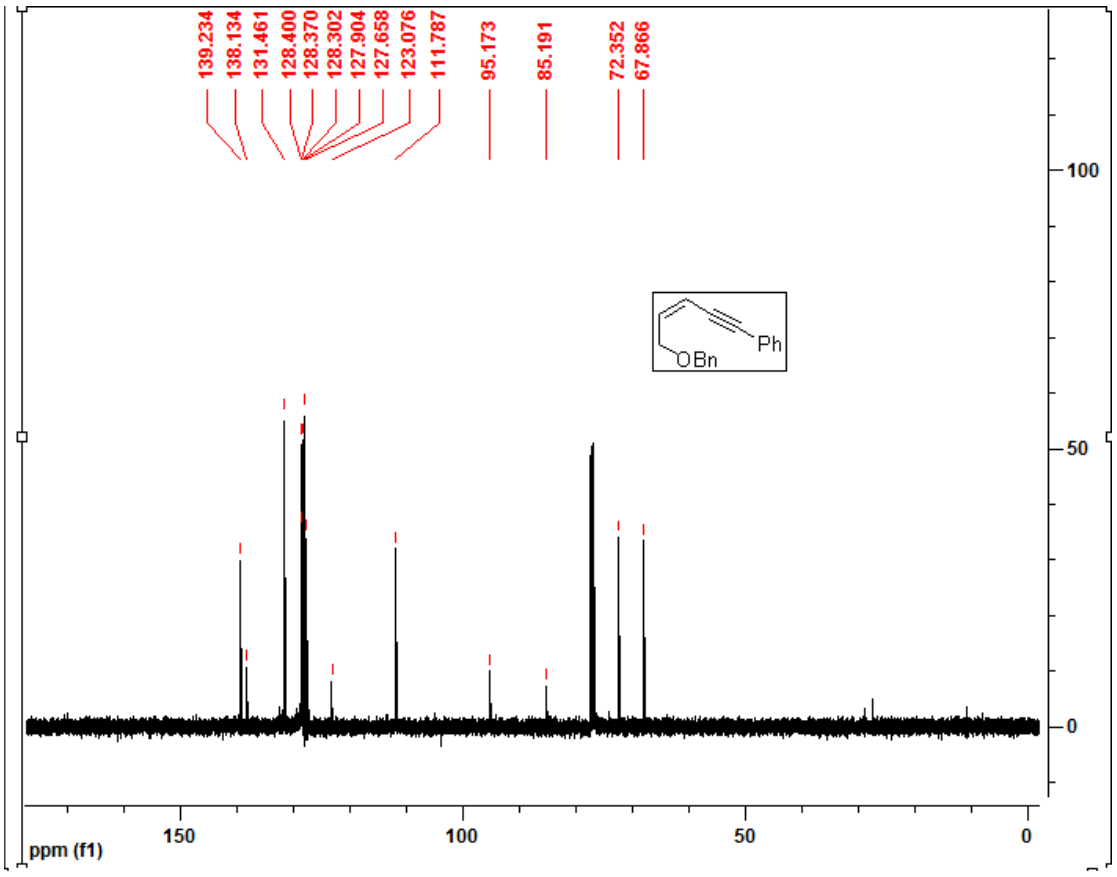
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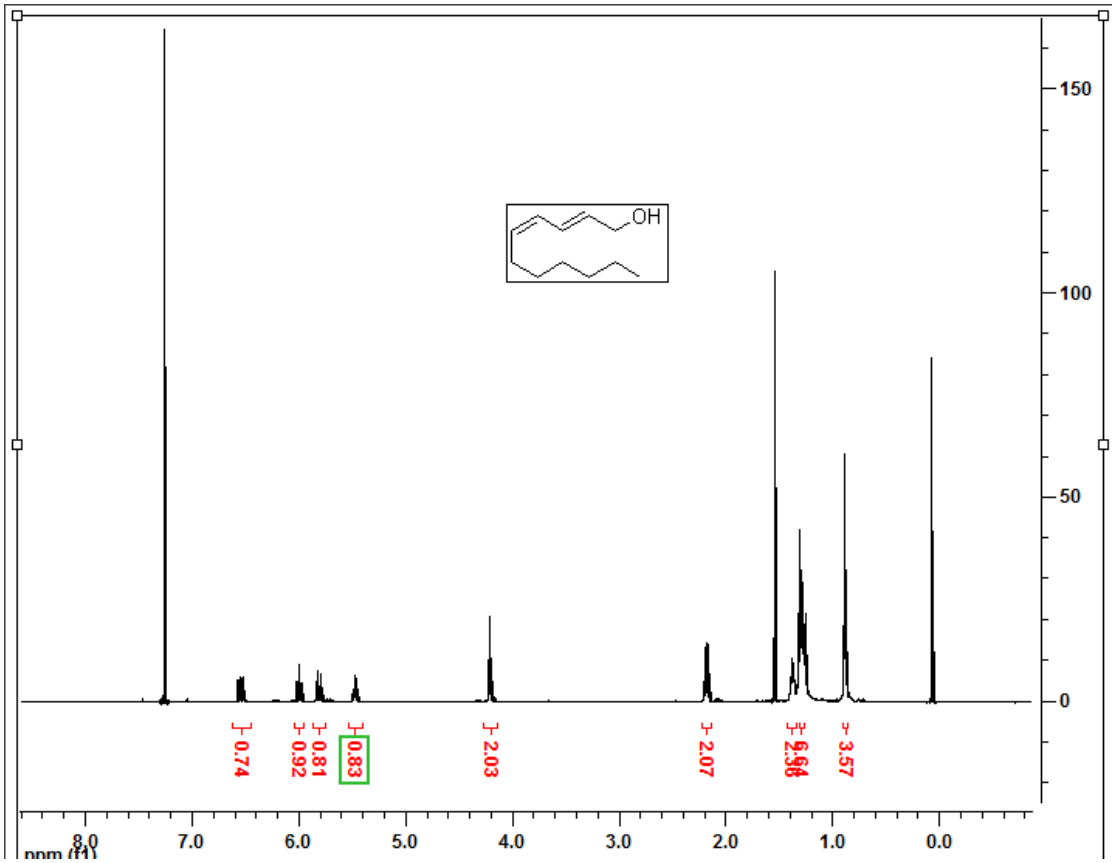
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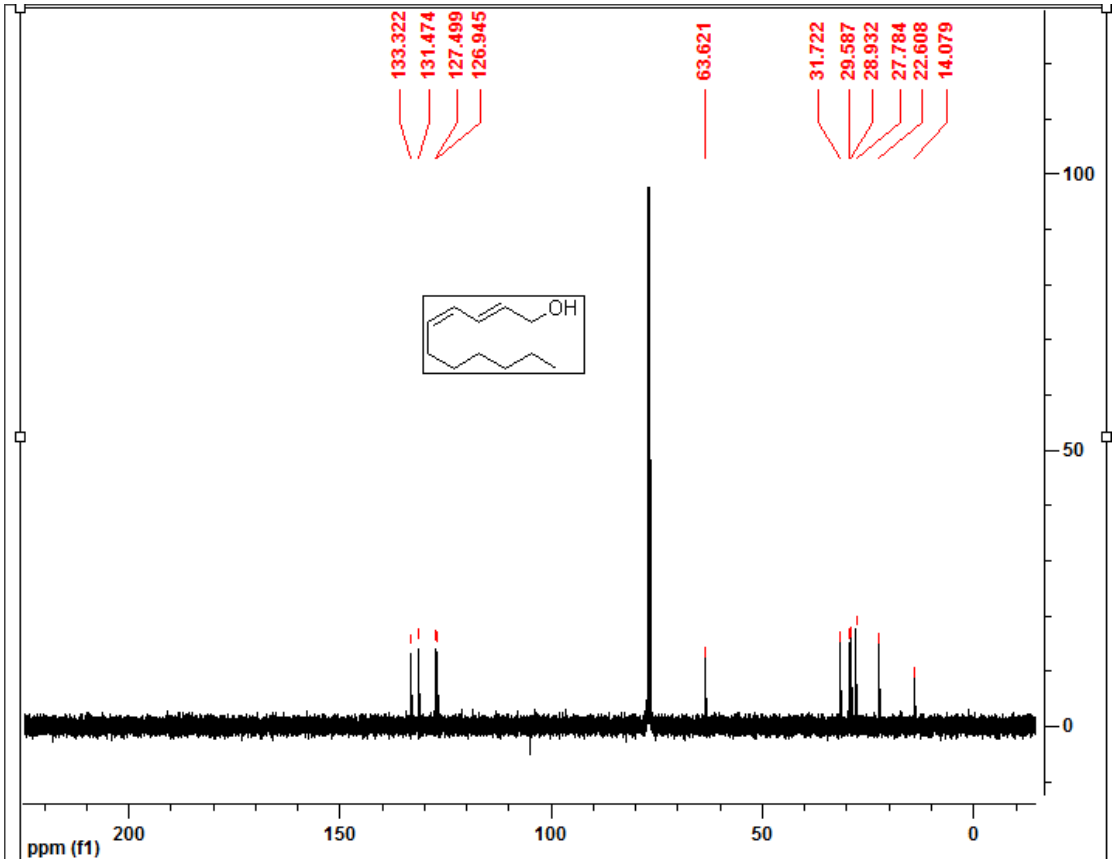
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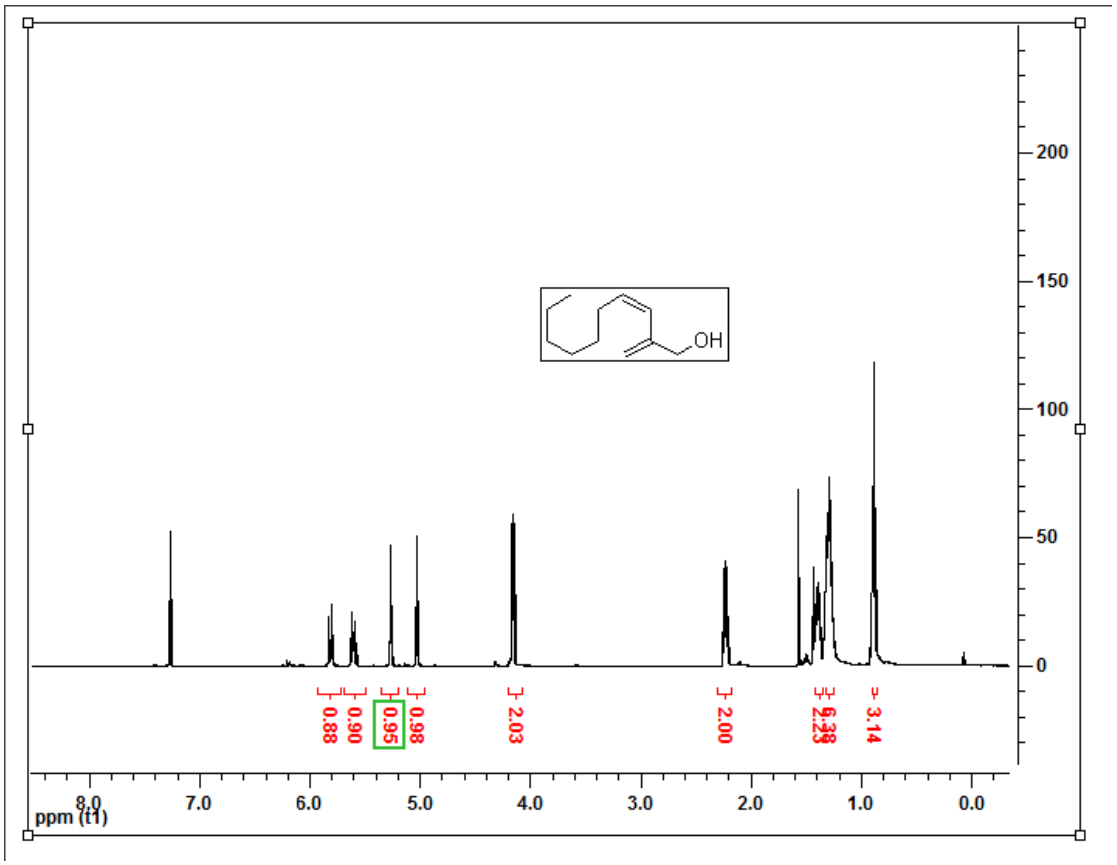
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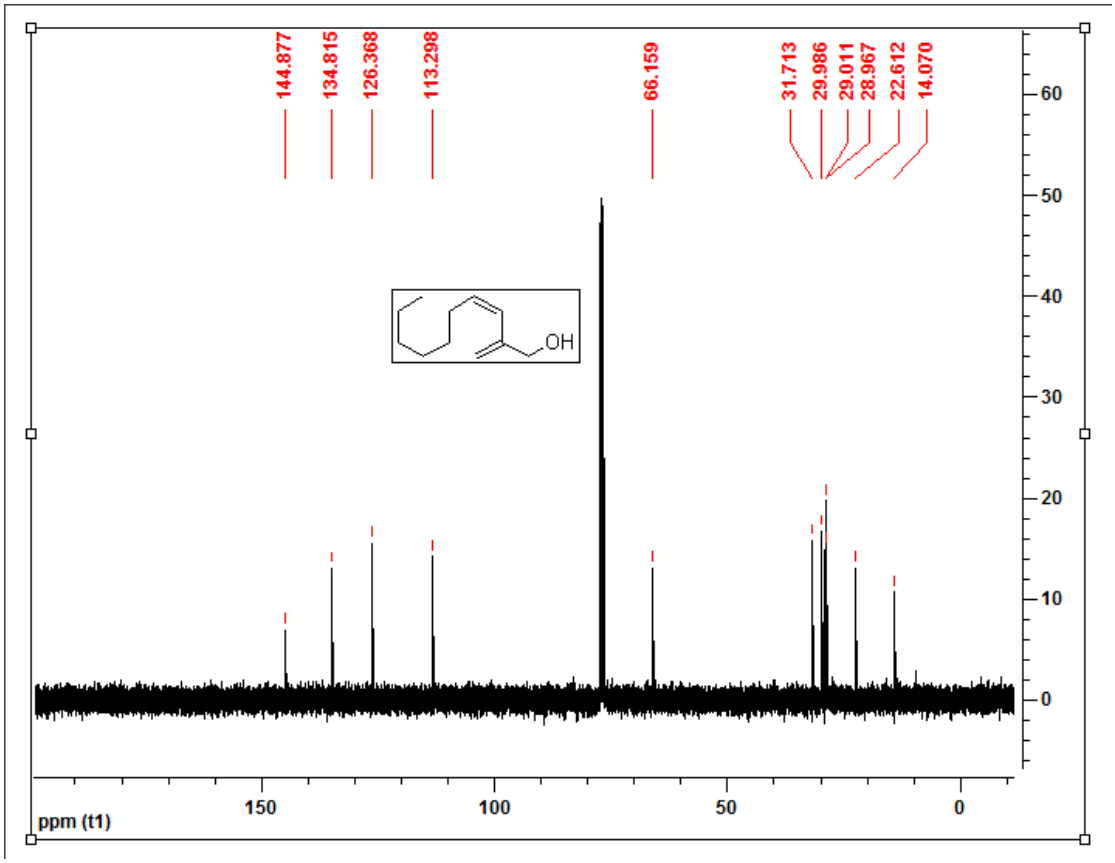
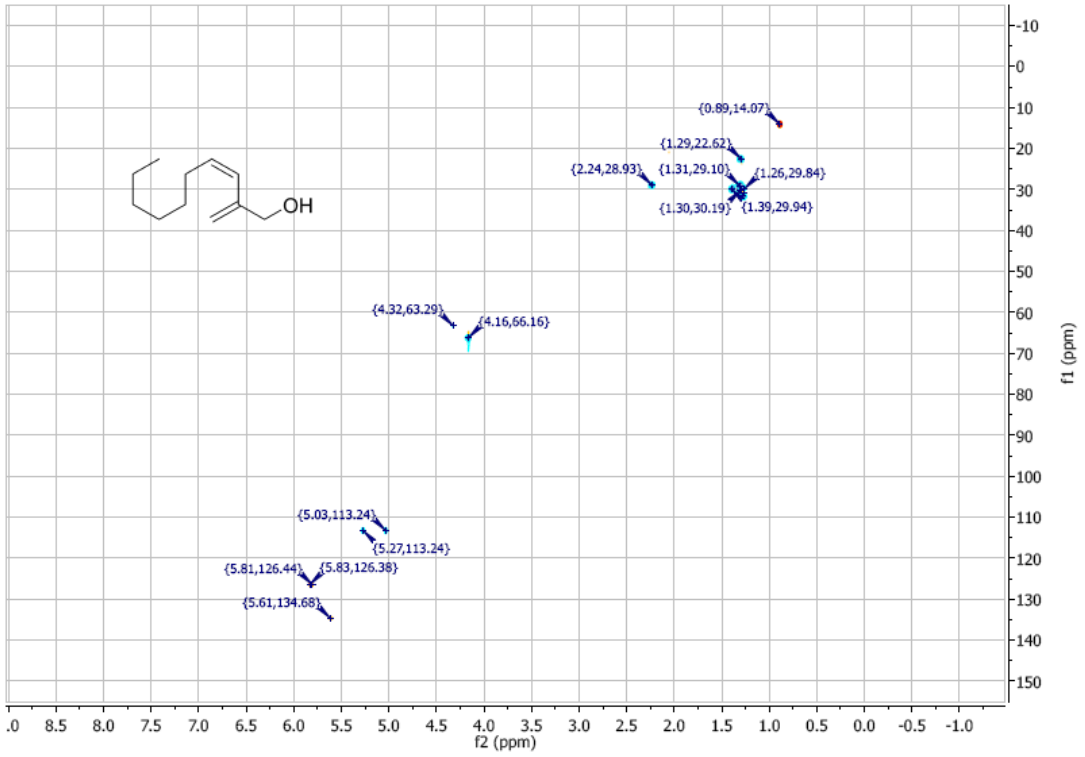
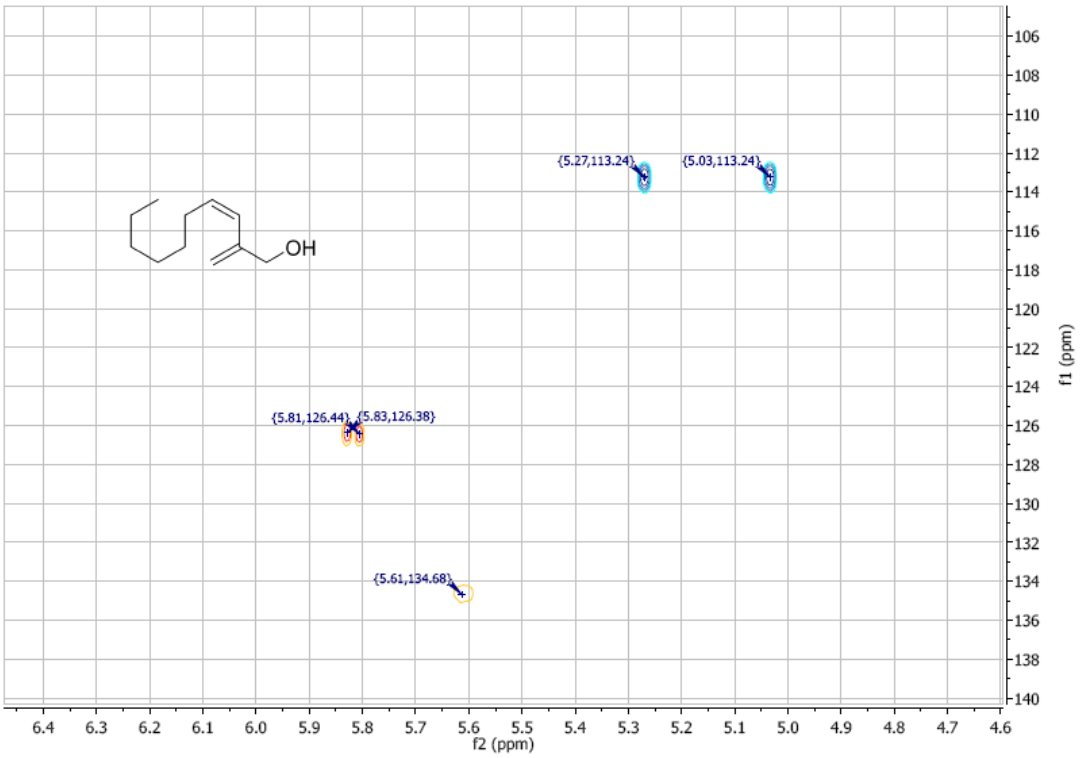
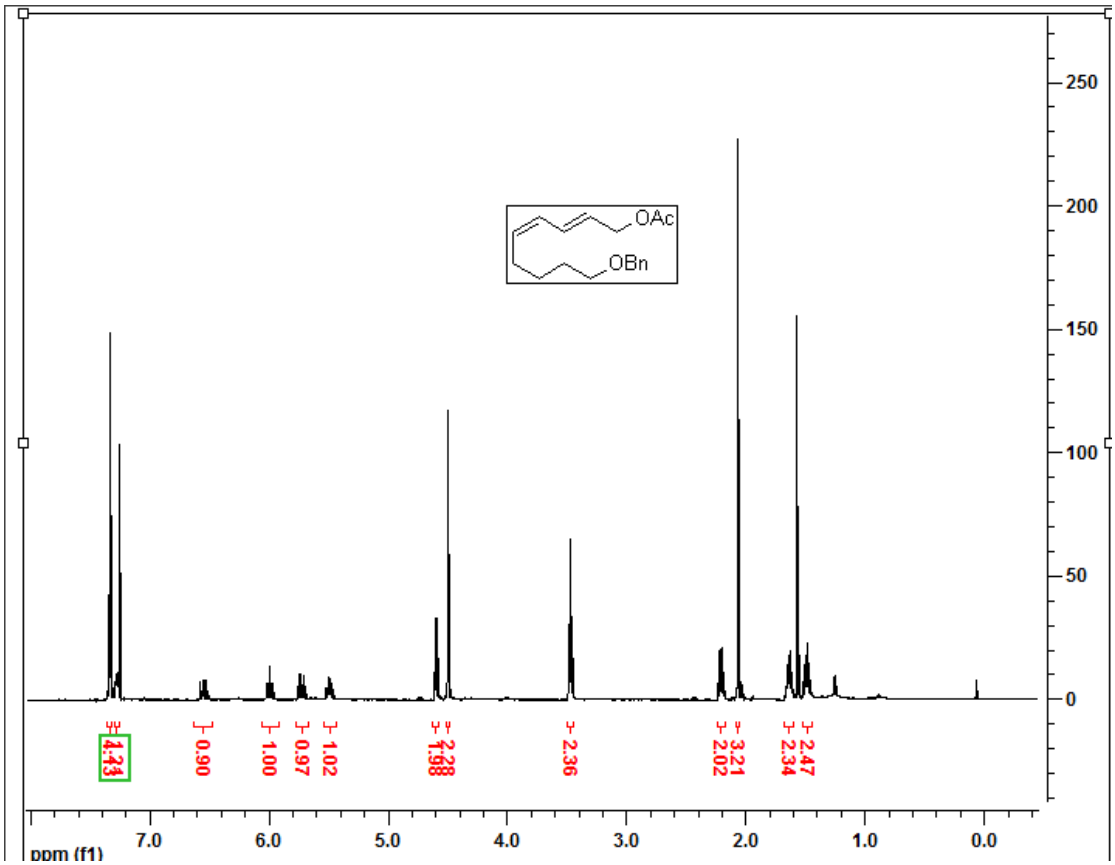
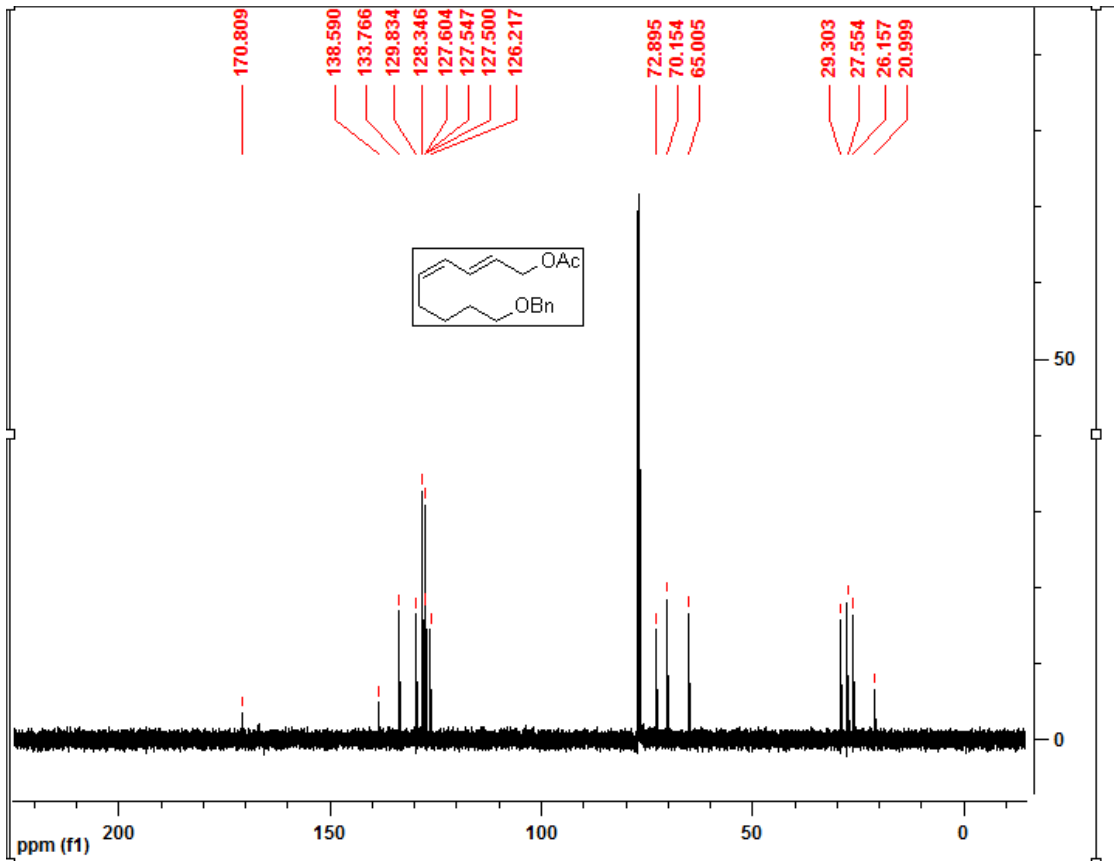
0.0
ppm (f1)


144.877
134.815
126.368
113.298
66.159
31.713
29.986
29.011
28.967
22.612
14.070
OH
ppm (t1)
150
100
50
0


OH
{0.89,14.07}
{1.29,22.62}
{2.24,28.93}
{1.31,29.10}
{1.26,29.84}
{1.30,30.19}
{1.39,29.94}
{4.32,63.29}
{4.16,66.16}
{5.03,113.24}
{5.27,113.24}
{5.81,126.44}
{5.83,126.38}
{5.61,134.68}
f2 (ppm)
f1 (ppm)


OH
{5.27,113.24}
{5.03,113.24}
{5.81,126.44}
{5.83,126.38}
{5.61,134.68}
f2 (ppm)
f1 (ppm)


OAc
OBn
4.43
0.90
1.00
0.97
1.02
1.98
2.28
2.36
2.02
3.21
2.34
2.47
ppm (f1)


170.809
138.590
133.766
129.834
128.346
127.604
127.547
127.500
126.217
72.895
70.154
65.005
29.303
27.554
26.157
20.999
OAc
OBn
50
0
ppm (f1)
200
150
100
50
0