Catalytic S_N2'-Selective Substitution of Allylic Chlorides With Aryl Boronic Esters

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General

All reactions were performed under a nitrogen atmosphere, using flame-dried glassware unless otherwise indicated. Column chromatography was performed on a Biotage Iso-1SV flash purification system using silica gel (Agela Technologies Inc., 60Å, 40-60 μm, 230-400 mesh). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum RX I spectrometer. IR peak absorbencies are represented as follows: s = strong, m = medium, w = weak, br = broad. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual $CHCl_3$ (7.26 ppm) or C_6D_6 (7.16 ppm). ^{13}C chemical shifts are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.2 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants in Hertz (Hz). Mass spectra were collected on a JEOL HX-110 Mass spectrometer, a Bruker Esquire 1100 Liquid Chromatograph – Ion Trap Mass Spectrometer or a Hewlett Packard 5971A gas chromatograph – Mass Spectrometer. Melting points were determined on a capillary MEL-TEMP melting point apparatus and are uncorrected. Regioselectivity was determined by GC analysis using Shimadzu GC-2010 with a flame ionization detector and a SHRXI-5MS column (15 m, 0.25 mm inner diameter, 0.25 μm film thickness). The following temperature program was used: 2 min @ 60 °C, 13 °C/min to 160 °C, 30 °C/min to 250 °C, 5.5 min @ 250 °C.

Materials

THF, CH_2Cl_2 and Et_2O and toluene were degassed and dried on columns of neutral alumina. 1,4-dioxane was distilled from purple Na/benzophenone ketyl, and stored over 4Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. 1,4-Dioxane-d^8 and THF- d^8 were distilled from purple Na/benzophenone ketyl. All other deuterated solvents degassed, and dried over 4Å molecular sieves. Commercial reagents were purchased from Sigma-Aldrich Co., VWR international, LLC., or STREM Chemicals, Inc., and were used as received.

Contents

I. Reaction optimization:

Catalyst Screen

In a glove box, a 1 dram vial was charged with a stir bar. To the vial was added NHC-Cu complex (0.10 equiv, 0.020 mmol), aryl boronic ester (1.25 equiv, 54 mg, 0.250 mmol), and KO*t*-Bu (1.00 equiv, 22 mg, 0.200 mmol). 1,3,5-trimethoxybenzene (5.0 mg, .030 mmol) was added as an internal standard. THF (0.97 mL) was added, and the resulting solution was stirred at room temperature for 10 minutes. (E)-2-hexenyl-1-chloride (1.00 equiv, 26.4 μL, 0.200 mmol) was added, and the solution was stirred at 45 °C for 24 h. The reaction progress was monitored by GC analysis of aliquots taken at 6 and 24 h.

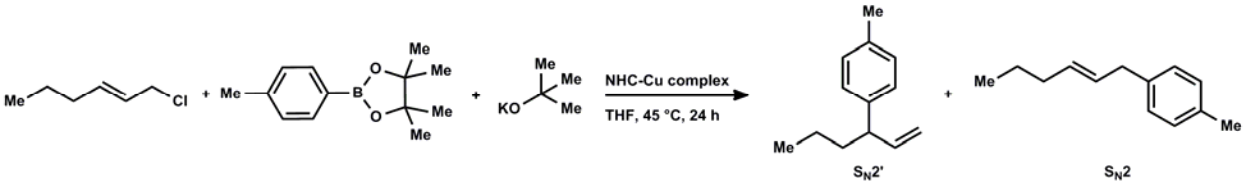
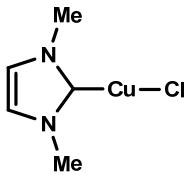
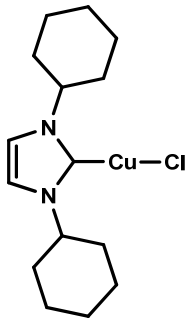


Table S1. Catalyst Screen in THF

NHC-Cu Complex	Loading (mol%)	T.P. (+h)	S_N2'/S_N2	Total (%)
IMeCuCl	10	6	8	97
		24	8	99
ICyCuCl	10	6	8	99
		24	8	99
IAdCuCl	10	6	3	92
		24	3	94
IMesCuCl	5	6	16	36
		24	15	95
	10	6	11	76
		24	10	95
IMesCuO*t*Bu	10	6	20	69
		24	20	99
	5	24	22	96
	1	24	30	43



IMeCuCl



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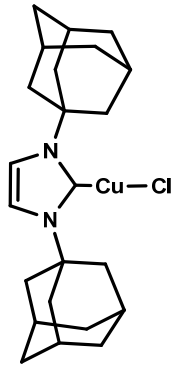
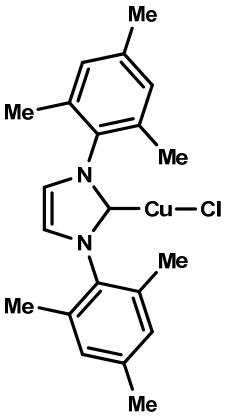
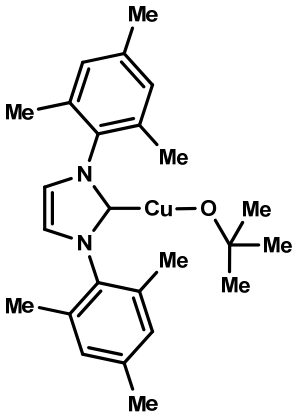


IAdCuCl



IMesCuCl



IMesCuO*t*Bu

Solvent Screen

In a glove box, a 1 dram vial was charged with a stir bar. To the vial was added IMesCuO*t*-Bu (0.10 equiv, 7.0 mg, 0.017 mmol), aryl boronic ester (1.25 equiv, 46.0 mg, 0.211 mmol), and KO*t*-Bu (1.00 equiv, 19.0 mg, 0.169 mmol). 1,3,5-trimethoxybenzene (TMB) was added as an internal standard. Solvent (0.84 mL) was added, and the resulting solution was stirred at room temperature for 10 minutes. (E)-2-hexenyl-1-chloride (1.00 equiv, 22.2 μL, 0.170 mmol) was added, and the reaction mixture was stirred at 45 °C for 24 h. The reaction progress was monitored by GC analysis of aliquots taken at 4 and 24 h.

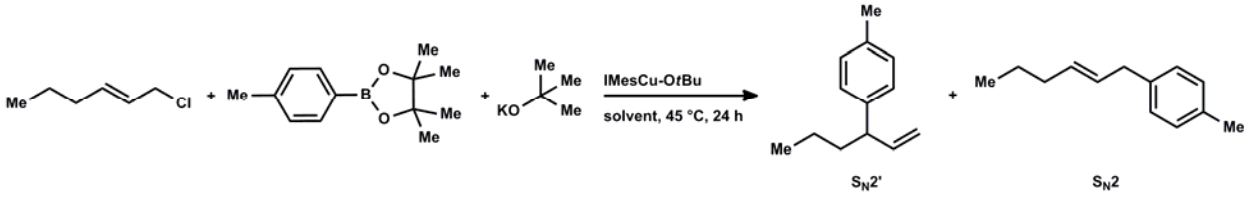


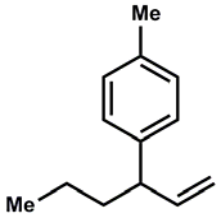
Table S2. Solvent Screen

Solvent	S_N2'/S_N2	Yield (%)[a]
1,4-dioxane	43	91
THF	19	92
Et_2O	21	94
Toluene	41	93
Pentane	13	93

[a]After 24 h at 45 °C

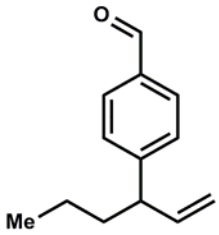
II. Allylic arylation:

General arylation procedure:
In a glove box, a scintillation vial was charged with a stir bar. To the vial was added boronic ester (1.25 equiv, 0.625 mmol), tert-butoxide (as specified in tables 2 and 3) (1.00 equiv, 0.500 mmol), and 1,4-dioxane (2.0 mL). After 10 minutes, IMesCuO*t*-Bu (0.05 equiv, 0.025 mmol) dissolved in 0.5 mL of 1,4-dioxane was added, and the mixture was stirred for another 10 min at ambient temperature. The allylic chloride was added (1.00 equiv, 0.500 mmol) in one portion and the scintillation vial was heated to 45 °C for 24 h. The vial was removed from the glove box, diluted with Et_2O, filtered through a plug of silica, concentrated in vacuo, and the crude reaction mixture was purified by silica gel chromatography.



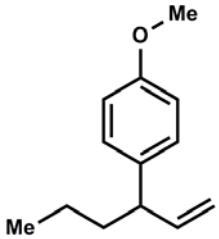
1-(hex-1-en-3-yl)-4-methylbenzene (8a)

Compound was isolated as a colorless oil (73.8 mg, 85% yield, 60:1 mixture of isomers) after purification by silica gel column using hexanes as an eluent. ^{1}H NMR (300 MHz, C_6D_6) δ 7.11 – 6.92 (m, 4H), 5.93 (ddd, *J* = 17.6, 10.3, 7.4 Hz, 1H), 5.15 – 4.84 (m, 2H), 3.17 (q, *J* = 7.4 Hz, 1H), 2.15 (s, 3H), 1.63 (m, 2H), 1.36 – 1.09 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 141.8, 135.6, 129.2, 127.6, 113.7, 49.3, 37.8, 21.1, 20.8, 14.1. HRMS calculated for $[M]^+$ 174.1409, found 174.1410. FTIR (neat, cm^{-1}): 3079 (w), 2927 (m), 1637 (m), 1513 (m), 1111 (w), 814 (m).



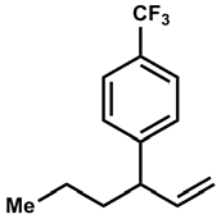
4-(hex-1-en-3-yl)benzaldehyde (8b)

Compound was isolated as a light yellow oil (91.7 mg, 97% yield, 20:1 mixture of isomers) after purification by silica gel column chromatography (5 → 15% EtOAc/hexanes). Major isomer; ^{1}H NMR (300 MHz, C_6D_6) δ 9.71 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 5.71 (ddd, *J* = 17.1, 10.3, 7.6 Hz, 1H), 5.02 – 4.73 (m, 2H), 3.03 (m, 1H), 1.51 – 1.39 (m, 2H), 1.18 – 0.99 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 152.4, 141.6, 135, 130.4, 128.7, 115.3, 50.2, 37.8, 21.0, 14.3. HRMS calculated for $[M+H]^+$ 189.1279, found 189.1281. FTIR (neat, cm^{-1}): 3081 (w), 2930 (m), 2733 (m), 1703 (s), 1576 (m), 1108 (w), 828 (m).



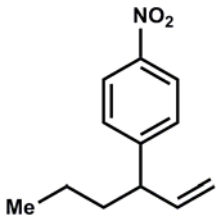
1-(hex-1-en-3-yl)-4-methoxybenzene (8c)

Compound was isolated as a colorless oil (80.6 mg, 85% yield, 58:1 mixture of isomers) after purification by silica gel column chromatography (5 → 20% EtOAc/hexanes). Major isomer; ^{1}H NMR (500 MHz, C_6D_6) δ 7.03 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.92 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.01 (m, 2H), 3.34 (s, 3H), 3.15 (m, 1H), 1.65 – 1.58 (m, 2H), 1.39 – 1.12 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 143.0, 136.8, 128.6, 113.9, 113.6, 55.3, 48.8, 37.8, 20.7, 14.1. HRMS calculated for $[M+H]^+$ 191.1434, found 191.1437. FTIR (thin film, cm^{-1}): 3077 (w), 2872 (m), 1636 (m), 1512 (s), 1249 (s), 1038 (m), 829 (m).



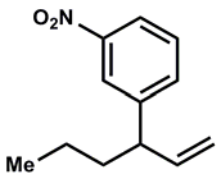
1-(hex-1-en-3-yl)-4-(trifluoromethyl)benzene (8d)

Compound was isolated as a colorless oil (85.5 mg, 75% yield, 24:1 mixture of isomers) after purification by silica gel column chromatography (0 → 15% EtOAc/hexanes). Major isomer; ^{1}H NMR (500 MHz, C_6D_6) δ 7.35 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 5.80 – 5.55 (m, 1H), 5.03 – 4.73 (m, 1H), 3.11 – 2.86 (m, 1H), 1.55 – 1.34 (m, 1H), 1.24 – 0.96 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9 (d, *J* = 1.0 Hz), 141.6, 128.6 (q, *J* = 32.3 Hz), 128.1, 125.5 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.8 Hz), 114.8 (s), 49.6, 37.6, 20.7, 14.1. HRMS calculated for $[M]^+$ 228.1128, found 228.1130. FTIR (thin film, cm^{-1}): 3082 (w), 2931 (m), 1327 (s), 1126 (m), 1609 (m), 917 (m), 839 (m).



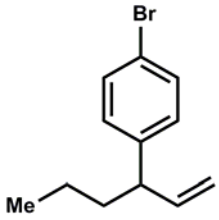
1-(hex-1-en-3-yl)-4-nitrobenzene (8e)

Compound was isolated as a light yellow oil (94.3 mg, 92% yield, 13:1 mixture of isomers) after purification by silica gel column chromatography (5 → 20% EtOAc/hexanes). Major isomer; ^{1}H NMR (500 MHz, C_6D_6) δ 7.84 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.59 (ddd, *J* = 17.6, 10.2, 7.6 Hz, 1H), 4.87 (m, 2H), 2.92 (m, 1H), 1.43 – 1.27 (m, 2H), 1.13 – 0.93 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 140.7, 128.4, 123.7, 115.4, 49.5, 37.4, 20.5, 13.9. HRMS calculated for $[M+H]^+$ 206.1179, found 206.1183. FTIR (thin film, cm^{-1}): 3080 (w), 2932 (m), 1637 (m), 1519 (s), 1346 (s), 1110 (m), 919 (m), 853 (m).



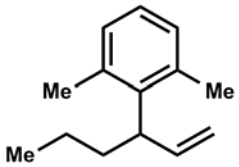
1-(hex-1-en-3-yl)-3-nitrobenzene (8f)

Compound was isolated as a light yellow oil (67.7 mg, 66% yield, 10:1 mixture of isomers) after purification by silica gel column chromatography (10 → 20% EtOAc/hexanes). Major isomer; ^{1}H NMR (500 MHz, C_6D_6) δ 7.95 (s, 1H), 7.79 – 7.66 (d, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.9 Hz, 1H), 5.67 – 5.48 (m, 1H), 4.87 (m, 2H), 2.95 (m, 1H), 1.36 (m, 2H), 1.17 – 0.90 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 148.9, 146.7, 141.1, 133.6, 129.2, 122.6, 121.4, 115.1, 49.4, 37.5, 20.7, 14.0. HRMS calculated for $[M+H]^+$ 206.1179, found 206.1186. FTIR (thin film, cm^{-1}): 3080 (w), 2931 (m), 1638 (m), 1530 (s), 1350 (s), 923 (m), 806 (m).



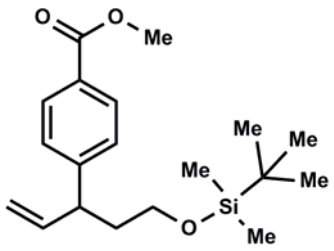
1-bromo-4-(hex-1-en-3-yl)benzene (8g)

Compound was isolated as a colorless oil (92.4 mg, 78% yield, 32:1 mixture of isomers) after purification by silica gel column chromatography using hexanes as an eluent. Major isomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 8.3 Hz, 2H), 5.81 – 5.59 (m, 1H), 4.97 – 4.82 (m, 2H), 2.95 (m, 1H), 1.55 – 1.32 (m, 2H), 1.21 – 0.91 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 142.1, 131.8, 129.7, 120.2, 114.2, 49.3, 37.7, 20.8, 14.1. HRMS calculated for $[M]^+$ 238.0357, found 238.0362. FTIR (thin film, cm^{-1}): 3079 (w), 2929 (m), 1637 (m), 1488 (m), 1106 (w), 1011 (m), 824 (m).



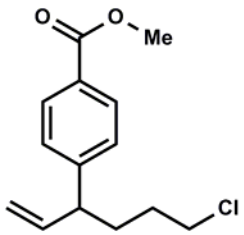
2-(hex-1-en-3-yl)-1,3-dimethylbenzene (8h)

Compound was isolated as a colorless oil (79.9 mg, 85% yield, 24:1 mixture of isomers) after purification by silica gel column chromatography (0 → 20% benzene/hexanes). ^{1}H NMR (500 MHz, C_6D_6) δ 7.02 - 6.92 (m, 3H), 6.01 (ddd, *J* = 17.3, 10.4, 5.0 Hz, 1H), 4.95 (m, 2H), 3.82 – 3.71 (m, 1H), 2.23 (s, 6H), 1.78 – 1.64 (m, 2H), 1.30 – 1.01 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 140.6, 136.8, 126.0, 113.8, 44.0, 35.3, 21.7, 21.5, 14.4. HRMS calculated for $[M]^+$ 188.1567, found 188.1566. FTIR (thin film, cm^{-1}): 3075(w), 2931 (m), 1633 (m), 910 (m), 768 (m).



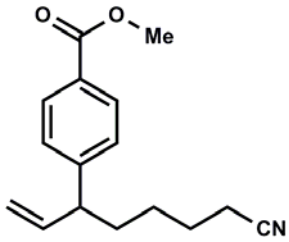
Methyl 4-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-en-3-yl)benzoate(Table 3, Entries 1 and 2)

Compound was isolated as a colorless oil (157.5 mg, 94% yield, 32:1 mixture of isomers, from Z alkene) (152.1 mg, 91%, 21:1 mixture of isomers, from E alkene) after purification by silica gel column chromatography (0 → 10% EtOAc in hexanes). Major isomer; ^{1}H NMR (500 MHz, C_6D_6) δ 8.13 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 5.77 (ddd, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.01 – 4.91 (m, 2H), 3.58 – 3.43 (m, 5H), 3.39 (dt, *J* = 10.0, 6.4 Hz, 1H), 1.80 (m, 2H), 0.96 (s, 9H), -0.01 (d, *J* = 5.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 149.6, 141.2, 129.9, 128.3, 127.9, 115.0, 60.5, 52.1, 45.8, 38.0, 26.0, 18.4, -5.3. HRMS calculated for $[M+H]^+$ 335.2041, found 335.2029. FTIR (neat, cm^{-1}): 3081 (w), 3000 (w), 2953 (s), 1725 (s), 1610 (m), 1278 (s), 1104 (s), 834 (s) 755 (m).



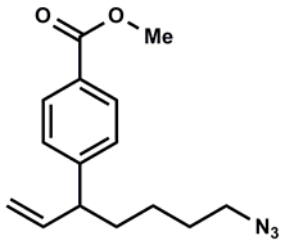
Methyl 4-(6-chlorohex-1-en-3-yl)benzoate(Table 3, Entry 3)

Compound was isolated as a colorless oil (106.1 mg, 90% yield, 20:1 mixture of isomers) after purification by silica gel column chromatography (30 → 80% benzene in hexanes). Major isomer; ^{1}H NMR (300 MHz, C_6D_6) δ 8.11 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 5.64 (ddd, *J* = 17.1, 10.3, 7.6 Hz, 1H), 5.00 – 4.74 (m, 2H), 3.53 (s, 3H) 3.03 (t, *J* = 6.4 Hz, 2H), 2.91 (q, *J* = 7.4 Hz, 1H), 1.62 – 1.17 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 149.3, 140.9, 130.0, 128.5, 127.7, 115.3, 52.1, 49.3, 44.9, 32.4, 30.6. HRMS calculated for $[M+H]^+$ 253.0996, found 253.1002. FTIR (neat, cm^{-1}):3082 (w), 3000 (w), 2953 (m), 1722 (s), 1609 (m), 1436 (m), 1280 (s), 912 (s), 733 (s).



Methyl 4-(7-cyanohept-1-en-3-yl)benzoate(Table 3, Entry 4)

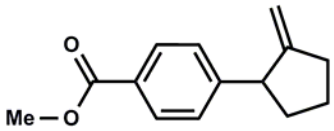
Compound was isolated as a colorless oil (118.4 mg, 92% yield, 21:1 mixture of isomers) after purification by silica gel column chromatography (10 → 40% EtOAc in hexanes). Major isomer; ^{1}H NMR (300 MHz, C_6D_6) δ 8.16 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 5.81 – 5.54 (m, 1H), 4.98 – 4.80 (m, 2H), 3.52 (s, 3H), 2.76 – 2.98 (m, 1H), 1.38 – 1.09 (m, 4H), 1.06 – 0.69 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 149.4, 140.9, 130.0, 128.4, 127.6, 119.6, 115.2, 52.1, 49.7, 34.4, 26.7, 25.3, 17.1. HRMS calculated for $[M+H]^+$ 244.1338, found 244.1333. FTIR (neat, cm^{-1}):3075 (w), 3000 (w), 2947 (m), 2241 (m), 1721 (s), 1609 (m), 1435 (m), 1281 (s), 919 (m).



Methyl 4-(7-azidohept-1-en-3-yl)benzoate(Table 3, Entry 5)

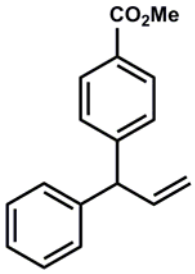
Compound was isolated as a light yellow oil (123.6 mg, 90% yield, 33:1 mixture of isomers) after purification by silica gel column chromatography (30 → 80% benzene in hexanes). Major isomer; ^{1}H NMR (300 MHz, C_6D_6) δ 8.16 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 5.83 – 5.55 (m, 1H), 5.00 – 4.82 (m, 2H), 3.52 (s, 3H), 2.95 (m, 1H), 2.59 (t, *J* = 6.8 Hz, 2H), 1.34 (m, 2H), 1.23 – 0.78 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 149.6, 141.2, 130.0, 128.4,

127.7, 115.1, 52.1, 51.3, 49.9, 34.9, 28.8, 24.7. HRMS calculated for $[M+H]^+$ 274.1553, found 274.1557. FTIR (neat, cm^{-1}):3079 (w), 2940 (m), 2095 (s), 1721 (s), 1609 (m), 1435 (m), 1279 (s).



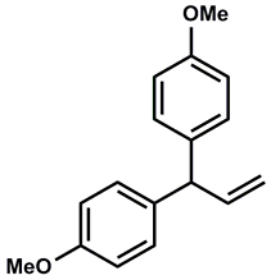
Methyl 4-(2-methylenecyclopentyl)benzoate(Table 3, Entry 6)

Compound was isolated as a white solid (69.1 mg, 64% yield, 30:1 mixture of isomers) after purification by silica gel column chromatography (0 → 10% EtOAc in benzene). mp 38 °C. Major isomer; ^{1}H NMR (300 MHz, C_6D_6) δ 8.15 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 4.97 (d, J = 2.0 Hz, 1H), 4.60 (d, *J* = 2.0 Hz, 1H), 3.52 (s, 3H), 3.32 (t, *J* = 7.4 Hz, 1H), 2.47 – 2.15 (m, 2H), 1.95 – 1.77 (m, 1H), 1.65 – 1.26 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 156.0, 150.8, 129.8, 128.4, 128.1, 107.8, 52.1, 51.3, 36.6, 33.6, 24.9. HRMS calculated for $[M+H]^+$ 217.1227, found 217.1236. FTIR (thin film, cm^{-1}): 3054 (w), 2987 (m), 1717 (s), 1610 (m), 1422 (m), 1265 (s), 896 (s).



Methyl 4-(1-phenylallyl)benzoate (Table 3, Entry 7)

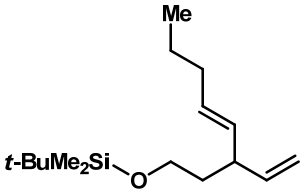
Compound was isolated as a clear liquid (114.2 mg, 90% yield, 17:1 mixture of isomers) after purification by silica gel column chromatography (0 → 20% benzene in hexanes).Major isomer; ^{1}H NMR (300 MHz, C_6D_6) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.35 – 6.95 (m, 7H), 6.18 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.06, 148.71, 142.54, 139.89, 129.82, 128.72, 128.62, 128.39, 126.71, 117.06, 54.98, 52.07. HRMS calculated for $[M+H]^+$ 253.1229, found 253.1232. FTIR (thin film, cm^{-1}):3061 (w), 3028 (w), 2952 (m), 1723 (s), 1610 (m), 1436 (m), 1281 (s), 1112.8 (s), 701.7 (m).



4,4`-(prop-2-ene-1,1-diyl)bis(methoxybenzene) (Table 3, Entry 8)

Compound was isolated as a clear liquid (108.3 mg, 85% yield, 15:1 mixture of isomers) after purification by silica gel column chromatography (0 → 20% benzene in hexanes). Major isomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 6.99 (m, 4H), 6.85 – 6.71 (m, 4H), 6.24 (ddd, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 4.97 (d, *J* = 17.1 Hz, 1H), 4.58 (d, *J* = 7.0 Hz, 1H), 3.39 – 3.21 (s, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 158.79, 141.93, 136.09, 129.97, 115.70, 114.20, 54.81, 53.83. HRMS calculated for $[M+H]^+$ 254.1306, found 254.1308. FTIR (thin film, cm^{-1}): 3054 (m), 3005 (m), 2958 (m), 1636 (m), 1035 (s), 739 (s).

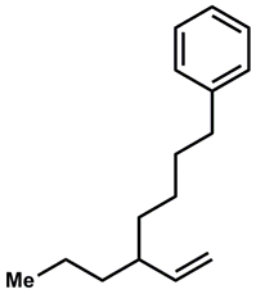
III. Allylic alkenylation:



(E)-tert-butyldimethyl((4-vinylnon-5-en-1-yl)oxy)silane (Equation 3)

In a glove box, a scintillation vial was charged with a stir bar. To the vial was added (E)-4,4,5,5-tetramethyl-2-(pent-1-en-1-yl)-1,3,2-dioxaborolane (1.25 equiv, 139 μL 0.625 mmol), sodium-*tert*-pentoxide (1.00 equiv, 55.0 mg, 0.500 mmol), and 1,4-dioxane (2.0 mL). The resulting solution was allowed to stir at 45 °C for 10 minutes. After 10 minutes, IMesCuO-*t*-Bu (0.05 equiv, 11.0 mg, 0.025 mmol) in 0.5 mL 1,4-dioxane was added and the mixture stirred for another 10 min at ambient temperature. (E)-*tert*-butyl((5-chloropent-3-en-1-yl)oxy)dimethylsilane was added (1.00 equiv, 118 mg, 0.500 mmol) in one portion and the scintillation vial was heated to 45 °C for 24 h. The vial was removed from the glove box, and the reaction mixture was diluted with Et_2O, filtered through a plug of silica, concentrated in vacuo and purified by silica gel chromatography. Compound was isolated as a colorless oil (116.2 mg, 86% yield) after purification by silica gel column chromatography (0 → 10% benzene/hexanes). ^{1}H NMR (300 MHz, C_6D_6) δ 5.85 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.68 – 5.33 (m, 2H), 5.27 – 4.93 (m, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 3.22 – 2.91 (m, 1H), 2.10 – 1.97 (m, 2H), 1.90 – 1.62 (m, 2H), 1.51 – 1.35 (m, 2H), 1.09 (s, 9H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.17 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.2, 133.1, 130.9, 114.0, 61.1, 43.5, 38.2, 35.2, 26.3, 23.1, 18.6, 13.9, -5.0. HRMS calculated for $[M+H]^+$ 269.2295, found 269.2298. FTIR (neat, cm-1): 3080 (w), 2859 (m), 1637 (m), 1102 (m), 969 (m).

IV. Allylic alkylation:

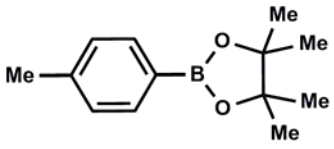


(5-vinyloctyl)benzene (Equation 4)

In a glove box, a scintillation vial was charged with a stir bar. To the vial was added but-3-en-1-ylbenzene (1.25 equiv, 83.0 mg, 0.625 mmol), 9-Borabicyclo[3.3.1]nonane dimer (0.63 equiv, 152 mg, 0.313 mmol), and 1,4-dioxane (0.5 mL). The resulting solution was stirred at 60 °C for 4 h. After 4 h, the solution was transferred to a scintillation vial containing IMesCuO*t*-Bu (0.05 equiv, 11.0 mg, 0.025 mmol), sodium-*tert*-pentoxide (1.00 equiv, 56.0 mg, 0.50 mmol), and 1,4-dioxane (2.0 mL). The resulting solution was allowed to stir at 25 °C for 10 minutes, and then (E)-2-hexenyl-1-chloride (1.00 equiv, 65.9 μL, 0.50 mmol) was added. The resulting solution was allowed to stir at 60 °C for 24 h. The vial was removed from the glove box, the reaction mixture was diluted with Et_2O, filtered through a plug of silica, and concentrated in vacuo. Compound was isolated as a colorless oil (89.0 mg, 82% yield, 32:1 mixture of isomers) after purification by silica gel chromatography (0 → 20% benzene/hexanes). Major isomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.01 (m, 5H), 5.57 (ddd, J = 16.9, 10.3, 8.9 Hz, 1H), 5.16 – 4.95 (m, 2H), 2.61 (t, J = 7.7 Hz, 2H), 2.13 – 1.91 (m, 1H), 1.80 – 1.55 (m, 2H), 1.52 – 1.14 (m, 8H), 0.99 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 142.9, 128.4, 128.2, 125.6, 113.9, 43.8, 37.3, 36.1, 34.9, 31.7, 27.0, 20.3, 14.2. HRMS calculated for $[M]^+$ 216.1879, found 216.1876. FTIR (neat, cm-1): 3064 (w), 2857 (m), 1639 (m), 956 (m), 745, (m), 698 (s).

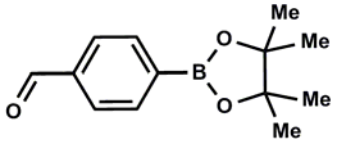
V. Synthesis of aryl boronic ester:

A flame-dried round bottom flask was charged with a stir bar and allowed to cool under N_2. Into the flask was added aryl boronic acid (1.0 equiv) and diol (1.0 equiv). Benzene was added (0.2 M solution of boronic acid) and the resulting solution was heated at the reflux for 1 h or until water layer separated. The solution was allowed to cool and $MgSO_4$ (0.5 equiv) was added. The solution was filtered, and the solvent volume was reduced by half under reduced pressure. The resulting solution was transferred to a separatory funnel and an equal volume of pentane was added. The organic layer was washed three times with H_2O, dried over $MgSO_4$ and filtered. Removal of the solvent under reduced pressure afforded the aryl boronic ester.



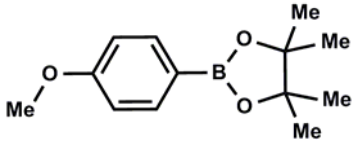
4,4,5,5-tetramethyl-2-p-tolyl-[1,3,2]dioxaborolane

Compound was isolated as a white solid (2.596 g, 85% yield). Spectral data matches the previously reported values.[1] ^{1}H NMR (300 MHz, C_6D_6) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.05 (dd, *J* = 8.1, 0.6 Hz, 2H), 2.06 (s, 3H), 1.13 (s, 12H).



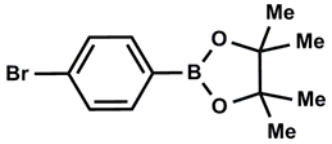
4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)benzaldehyde

Compound was isolated as a white solid (5.112 g, 86% yield). Spectral data matches the previously reported values.[2] ^{1}H NMR (300 MHz, C_6D_6) δ 9.64 (s, 1H), 8.05 (dd, *J* = 8.0, 3.0 Hz, 2H), 7.57 (dd, *J* = 8.2, 3.0 Hz, 2H), 1.08 (s, 12H).



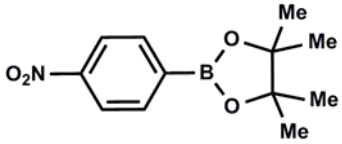
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane

Compound was isolated as a colorless oil (1.912 g, 82% yield). Spectral data matches the previously reported values.[3] ^{1}H NMR (300 MHz, C_6D_6) δ 8.16 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 3.22 (s, 3H), 1.15 (s, 12H).



2-(4-bromophenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane

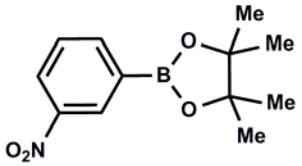
Compound was isolated as a white solid (2.733 g, 94% yield). Spectral data matches the previously reported values.3 ^{1}H NMR (300 MHz, C_6D_6) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 1.07 (s, 12H).



4,4,5,5-tetramethyl-2-(4-nitrophenyl)-[1,3,2]dioxaborolane

Compound was isolated as a yellow solid (538.8 mg, 72% yield). Spectral data matches the previously reported values.4 ^{1}H NMR (300 MHz, C_6D_6) δ 7.82 (m, 4H), 1.05 (s, 12H).

[1]Cameron, K. S.; Pincock, A. L.; Thompson, J.A. *J. Org. Chem.* **2004**, *69*, 4954.
[2]Yu, L.; Lindsey, J.S. *Tetrahedron* **2001**, *57*, 9285.
[3]Zhu, W.; Ma, D. *Org. Lett.* **2006**, *8*, 261.

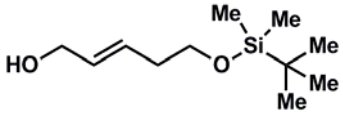


4,4,5,5-tetramethyl-2-(3-nitrophenyl)-[1,3,2]dioxaborolane
Compound isolated as a yellow solid (1.876 g, 75% yield). Spectral data matches the previously reported values.[4] ^{1}H NMR (300 MHz, C_6D_6) δ 8.84 (s, 1H), 8.13 – 7.71 (m, 2H), 6.93 – 6.58 (m, 1H), 1.06 (s, 11H).

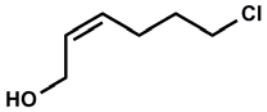
VI. Synthesis of allylic chlorides:

(E)-5-((*tert*-butyldimethylsilyl)oxy)pent-2-en-1-ol,[5] (Z)-6-chloro-hex-2-en-1-ol,[6](E)-7-chlorohept-2-en-1-ol,[7] (E)-8-hydroxyoct-6-enenitrile,[8] (E)-1-chlorohex-2-ene[9], (Z)-*tert*-butyl((5-chloropent-3-en-1-yl)oxy)dimethylsilane,[10] 1-(chloromethyl)cyclopent-1-ene9, and (E)-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene[11] were all synthesized according to literature procedures, and ^{1}H NMR data match literature values.

Allylic Alcohols:



(E)-5-((*tert*-butyldimethylsilyl)oxy)pent-2-en-1-ol
Compound was isolated as a colorless oil (1.570g, 82% yield) together with minor impurities containing TBS group. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 – 5.66 (m, 2H), 4.11 – 4.07 (m, 2H), 3.65 (t, *J* = 7.1 Hz, 2H), 2.31 – 2.24 (m, 2H), 1.34 (t, *J* = 5.8 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H).



(Z)-6-chloro-hex-2-en-1-ol Compound was isolated as a colorless oil (2.000 g, 93% yield).^{1}H NMR ($CDCl_3$) δ 5.68 (dt,J= 6.6, 9.9 Hz, 1H),5.47 (dt, J = 6.6, 10.7 Hz, 1H), 4.23 (d,J = 6.4 Hz, 2H), 3.56 (t, J = 7.1 Hz, 2H), 2.88 (s, 1 H), 2.13 – 2.47 (m, 2 H), 1.67 – 2.06 (m,2 H).

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[4]Oehlke, Alexander; Auer, Alexander A.; Schreiter, Katja; Hofmann, Katja; Riedel, Franziska; Spange, Stefan. *J. Org. Chem.* **2009**, *74*, 3316.
[5]Jensen, T.; Peders, H.; Bang-Andersen, B.; Madsen, R.; Joergensen, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 888.
[6]Holton, R. A.; Zoeller, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 2124.
[7]Zimmer, L. E.; Charette, A. B. *J. Am. Chem. Soc.* **2009**, *131*, 15624.
[8]Levine, S. G.; Bonner, M. P. *Tetrahedron Lett.* **1989**, *30*, 4767.
[9]Fox, R. J.; Lalic, G.; Bergman, R. G. *J. Am. Chem. Soc.* **2007**, *129*, 14144.
[10]Manning, P. T.; Misko, T. P. Combination Therapy with Inhibitors of Inducible Nitric Oxide Synthase and Alkylating Agents.*PCT Int. Appl.* WO 2005025620, March 24, 2005.
[11]Bouziane, A.; Helou, M.; Carboni, B.; Carreaux, F.; Demerseman, B.; Bruneau, C.; Renau J. *Chem. Eur. J.* **2008**, *14*, 5630.

(E)-7-chlorohept-2-en-1-ol

Compound was isolated as a colorless oil (4.638 g, 53% yield).^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 – 5.53 (m, 2H), 4.24 – 3.88 (m, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.16 – 1.97 (m, 2H), 1.88 – 1.68 (m, 2H), 1.61 – 1.47 (m, 2H), 1.29 (s, 1H).

(E)-8-hydroxyoct-6-enenitrile

Compound was isolated as a colorless liquid (1.351 g, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 – 5.47 (m, 2H), 4.03 – 4.17 (m, 2H), 2.35 (t, *J* = 6.9 Hz, 2H), 2.24 – 1.91 (m, 2H), 1.80 – 1.40 (m, 4H), 1.33 (s, 1H).

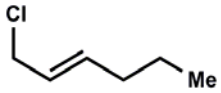
(E)-7-azidohept-2-en-1-ol (S1)

To a solution of 6-chloro-(2E)-heptene-1-ol (1.00 equiv, 1.00 mL, 6.817 mmol) in dry DMSO (14.0 mL) was added sodium iodide (0.10 equiv, 102.2 mg, 0.682 mmol) followed by sodium azide (2.00 equiv, 886.3 mg, 13.60 mmol). The reaction mixture was vigorously stirred for 16 h at 45 °C then cooled to room temperature, diluted with Et_2O, and washed with H_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The crude reaction mixture was purified by silica gel column chromatography (20 → 50% EtOAc/hexanes) and 6-azido-(2E)-hexen-1-ol was obtained as a light yellow oil (903.1 mg, 85% yield).^{1}H NMR (300 MHz, C_6D_6) δ 5.56 – 5.24 (m, 2H), 3.77 – 3.89 (m, 2H), 2.65 (t, *J* = 6.4 Hz, 2H), 1.66 – 1.82 (m, 2H), 1.25 – 0.98 (m, 4H), 0.77 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 132.3, 129.7, 63.7, 51.4, 31.7, 28.4, 26.2. ESI-MS (MeOH, *m/z*):178.1 $[M+Na]^+$. FTIR (neat, cm^{-1}): 3342 (m br), 2936 (m), 2097 (s), 1089 (m), 971 (m).

Allylic Chlorides:

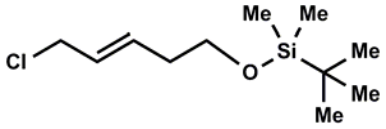
General

The allylic chlorides were synthesized according to a modified literature procedure:[5] Dimethyl sulfide (2.00 equiv) was added over 10 min to a flame dried flask containing N-chlorosuccinimide (2.00 equiv) in dry CH_2Cl_2 at 0 °C. The milky white solution was stirred for 1 h then cooled to -20 °C, and the allylic alcohol (1.00 equiv) in dry CH_2Cl_2 was added dropwise over 30 min. The reaction mixture was allowed to warm to 0 °C and after 2 h was allowed to warm to 25 °C. After complete consumption of the alcohol, solvent was removed in vacuo, and the crude mixture was diluted with pentane and washed with H_2O. The aqueous layer was extracted with pentane and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed under the reduced pressure. The product was passed through a plug of silica using a mixture of pentane and ethyl acetate as an eluent to afford the pure allylic chloride.



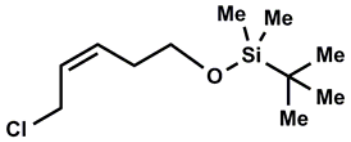
(E)-1-chlorohex-2-ene

Compound was isolated as a colorless liquid (1.841 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.69 – 5.53 (m, 1H), 4.03 (dd, *J* = 6.9, 0.8 Hz, 2H), 2.04 (m, 2H), 1.51 – 1.31 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).



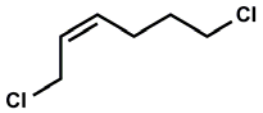
(E)-*tert*-butyl((5-chloropent-3-en-1-yl)oxy)dimethylsilane (S2)

Compound was isolated as a colorless liquid (1.327 g, 92% yield). ^{1}H NMR (300 MHz, C_6D_6) δ 5.55 – 5.34 (m, 2H), 3.62 (d, *J* = 5.9 Hz, 2H), 3.42 (t, *J* = 6.5 Hz, 2H), 2.09 – 1.97 (m, 2H), 0.96 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.6, 127.9, 62.5, 45.4, 35.8, 26.1, 18.5, -5.1. ESI-MS (MeOH, *m/z*): 257.1 $[M+Na]^+$. FTIR (neat, cm^{-1}): 3038 (w), 2956 (s), 1668 (w), 1472 (m) 1256 (m), 1104 (s), 837 (s).



(Z)-*tert*-butyl((5-chloropent-3-en-1-yl)oxy)dimethylsilane

Compound was isolated as a colorless liquid (1.458 g, 89% yield). ^{1}H NMR (300 MHz, C_6D_6) δ 5.58 – 5.32 (m, 2H), 3.62 (d, *J* = 5.9 Hz, 2H), 3.42 (t, *J* = 6.5 Hz, 2H), 2.12 – 1.97 (m, 2H), 0.96 (s, 9H), 0.02 (s, 6H).



(Z)-1,6-dichlorohex-2-ene (S3)

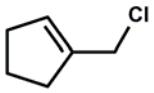
Compound was isolated as a colorless liquid (1.635 g, 73% yield) after filtration through a plug of silica using pentane as an eluent. ^{1}H NMR (300 MHz, C_6D_6) δ 5.41 (dtt, *J* = 10.6, 7.8, 1.5 Hz, 1H), 5.05 (dt, *J* = 10.6, 7.7 Hz, 1H), 3.67 (d, *J* = 7.8 Hz, 2H), 2.96 (t, *J* = 6.5 Hz, 2H), 1.82 – 1.67 (m, 2H), 1.35 – 1.23 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.2, 127.0, 44.3, 39.3, 31.9, 24.3.(GC-MS, EI, *m/z*): 152 $[M]^+$. FTIR (neat, cm^{-1}): 3027 (m), 2959 (s), 1653(m), 1251 (s), 756 (s), 650 (s).

(E)-8-chlorooct-6-enitrile (S4)

Compound was isolated as a colorless liquid (927.8 mg, 78% yield) after filtration through a plug of silica using 20% EtOAc in hexane as an eluent. ^{1}H NMR (300 MHz, C_6D_6) δ 5.47 – 4.95 (m, 2H), 3.61 (d, *J* = 6.5 Hz, 2H), 1.53 – 1.41 (m, 2H), 1.33 (t, *J* = 6.8 Hz, 2H), 1.00 – 0.73 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 127.0, 119.6, 45.2, 31.1, 27.7, 24.7, 17.0. HRMS calculated for $[M+Na]^+$ 180.0550, found 180.0546. FTIR (neat, cm^{-1}): 3036 (m), 2939 (s), 2247 (m), 1666 (m), 1251 (m), 969 (s), 674 (m).

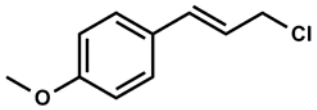
(E)-7-azido-1-chlorohept-2-ene (S5)

Compound was isolated as a light yellow liquid (639.7 mg, 93% yield) after filtration through a plug of silica using 10% EtOAc in hexane as an eluent. ^{1}H NMR (300 MHz, C_6D_6) δ 5.44 – 5.12 (m, 2H), 3.61 (d, *J* = 5.8 Hz, 2H), 2.60 (t, *J* = 6.6 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.17 – 0.87 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.2, 126.7, 51.4, 45.4, 31.6, 28.4, 26.0. HRMS calculated for $[M]^+$ 172.0636, found 172.0673. FTIR (neat, cm^{-1}): 3035 (w), 2939 (m), 2097 (s), 1666 (w), 1251 (m), 968 (m), 676 (m).



1-(chloromethyl)cyclopent-1-ene

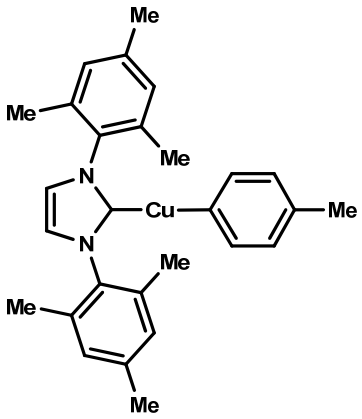
Compound was isolated as a colorless oil (816.2 mg, 86% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 – 5.78 (m, 1H), 4.15 (d, J = 0.8 Hz, 2H), 2.49 – 2.29 (m, 4H), 2.04 – 1.85 (m, 2H).



(E)-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene

Compound was isolated as a colorless oil (1.053g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.11 – 5.86 (m, 1H), 3.89 (d, *J* = 7.2 Hz, 2H), 3.38 (s, 3H).

VII. Synthesis of (IMes)Cu(4-methylbenzene) complex (Equation 5):



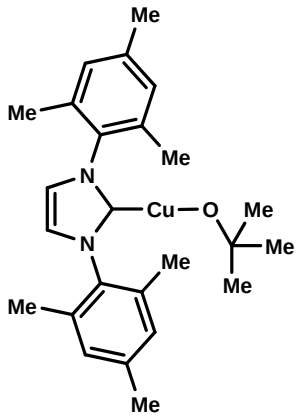
(IMes)Cu(4-methylbenzene)
(4-methylbenzene)[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene]-Copper (11)

A 100 mL Schlenk flask was charged with a stir bar and flame-dried under vacuum. The flask was then transferred into a glove box and was charged with IMesCuO-*t*Bu (1.1 equiv, 1.00 g, 2.27 mmol) and tolylboronicpinacolate ester (1.0 equiv, 0.45 g, 2.06 mmol). Toluene was added (50 mL, 0.05 M). The resulting solution was heated to 60 °C for 16 h and then filtered over a pad of Celite. The solvent was then removed until cloudy. An equal volume of pentane was added, and the flask was placed into the -20 °C freezer. After 24 h, the filtrate was removed by pipette and the crystals isolated by vacuum filtration. The crystals were then washed with pentane and transferred into a scintillation vial charged with a stir bar. Isooctane was added and the solution was vigorously stirred at room temperature for 0.5 h. The isooctane was then removed in vacuo. This process was repeated twice to yield the desired product as a white solid (575.5 mg, 61% yield). ^{1}H NMR (500 MHz, 1,4-dioxane-d^8) δ 7.22 (s, 2H), 7.07 (s, 4H), 6.80 (d, J = 7.4 Hz, 2H), 6.54 (d, J = 7.3 Hz, 2H), 2.35 (s, 6H), 2.17 (s, 12H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, THF-d^8) δ 184.5, 162.5, 140.8, 139.7, 137.2, 135.8, 131.9, 130.1, 126.8, 123.2, 21.8, 21.4, 18.4. The same compound was independently prepared by addition of 4-MePhMgBr to IMesCuCl. Attempts to obtain HRMS were not successful.

VIIa: Stoichiometric Reaction of (IMes)Cu(4-methylbenzene) with (E)-2-hexenyl-1-chloride (Equation 6)

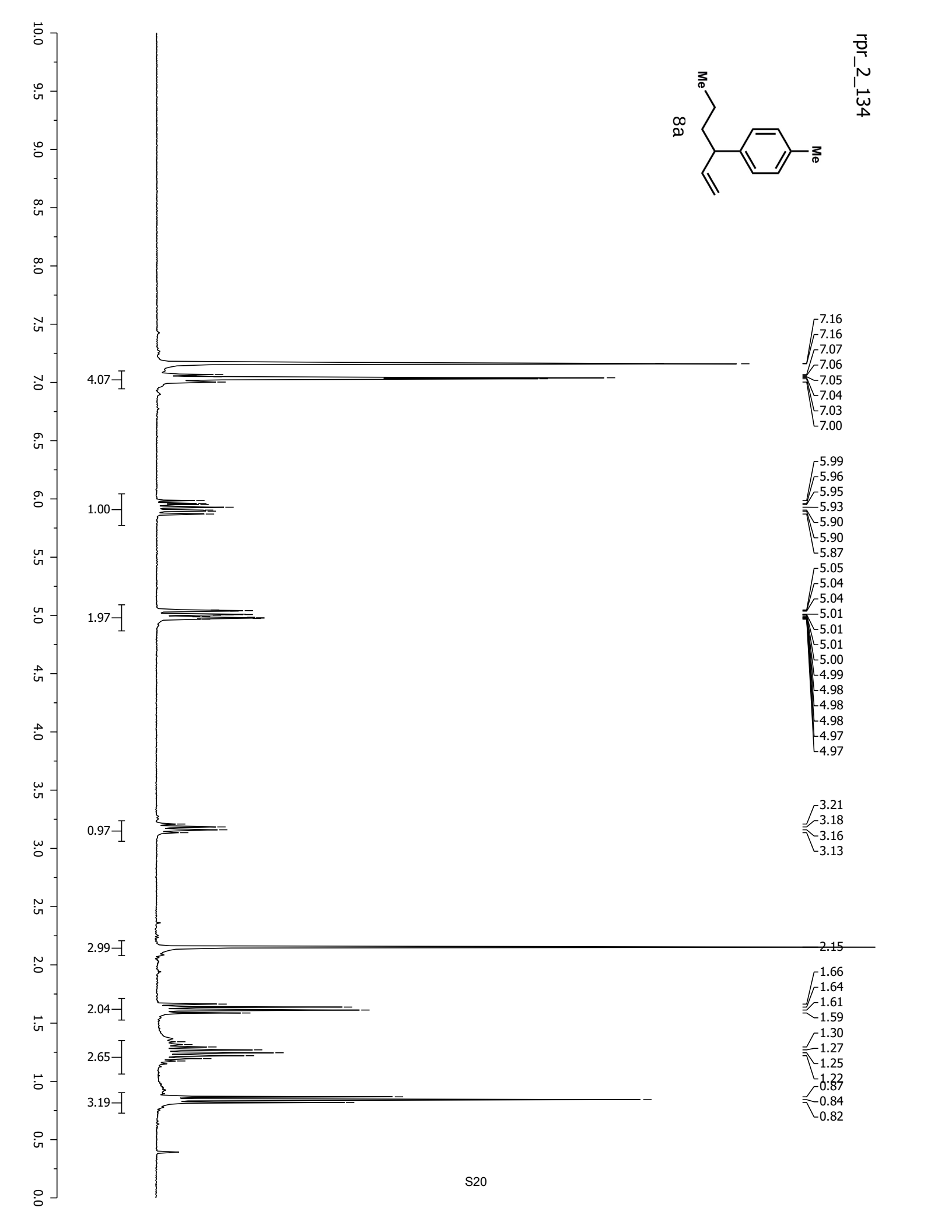
In a glove box, a 1 dram vial was charged with a stir bar. To the vial was added (E)-2-hexenyl-1-chloride (1.00 equiv, 6.6 μL, 0.05 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) in 1,4-dioxane (0.25 mL). Separately, a solution of (IMes)Cu(4-methylbenzene) (1.00 equiv, 23.0 mg, 0.05 mmol) in 1,4-dioxane (0.25 mL) was prepared. The solution of (IMes)Cu(4-methylbenzene)was added to a 1 dram vial containing (E)-2-hexenyl chloride and the resulting solution was stirred at 45 °C. After 5 minutes, an aliquot of the reaction analyzed by GC indicated complete conversion of (E)-2-hexenyl chloride. The arylation product was obtained in 79% yield (determined by GC analysis) as a mixture of isomers (30:1).

VIII. Catalyst synthesis:



IMesCuO*t*-Bu (10e)
(*t*-butoxy)[1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene]-Copper

A 200 mL Schlenk flask was charged with a stir bar and flame-dried under vacuum. The flask was then transferred into a glove box and was charged with 1,3-bis-(2,4,6-trimethylphenyl)-imidazolium chloride (IMes-chloride salt) (1.00 equiv, 3.41 g, 10.0 mmol), copper-*t*-butoxide tetramer $(CuO\textit{t}\text{-}Bu)_4$ (0.25 equiv, 1.37 g, 2.50 mmol), and sodium *t*-butoxide (NaO*t*-Bu) (1.00 equiv, 0.96 g, 10.0 mmol). With vigorous stirring, THF was added in one portion (0.1 M, 100.0 mL). The resulting pale-orange solution was allowed to stir at room temperature for 4 h. The flask was taken out of the glove box and the solvent was removed in vacuo. The flask was transferred to the glove box and the solid scraped and suspended in toluene. The resulting solution was filtered over a pad of Celite, and the pad was washed with two portions of toluene. The solvent was removed in vacuo to yield the product as a pale yellow solid (4.08 g, 92% yield). ^{1}H NMR (300 MHz, C_6D_6) δ 6.71 (s, 4H), 5.97 (s, 2H), 2.11 (s, 6H), 1.95 (s, 12H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, THF-d^8) δ 182.3, 139.7, 137.3, 135.9, 130.0, 123.2, 36.8, 21.3, 18.2.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Me
Me
7.16
7.16
7.07
7.06
7.05
7.04
7.03
7.00
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5.96
5.95
5.93
5.90
5.90
5.87
5.05
5.04
5.04
5.01
5.01
5.01
5.00
4.99
4.98
4.98
4.98
4.97
4.97
3.21
3.18
3.16
3.13
2.15
1.66
1.64
1.61
1.59
1.30
1.27
1.25
1.22
0.87
0.84
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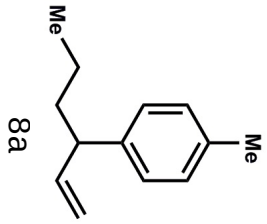
1.97
0.97
2.99
2.04
2.65
3.19

rpr_2_134_13C



8a

142.89
141.77
135.65
129.23
127.59
113.71
77.41
77.16
76.91
49.35
37.77
29.86
21.14
20.79
14.15

Analysis Date & Time : 3/31/2010 3:24:47 PM
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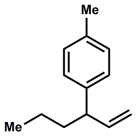

8a

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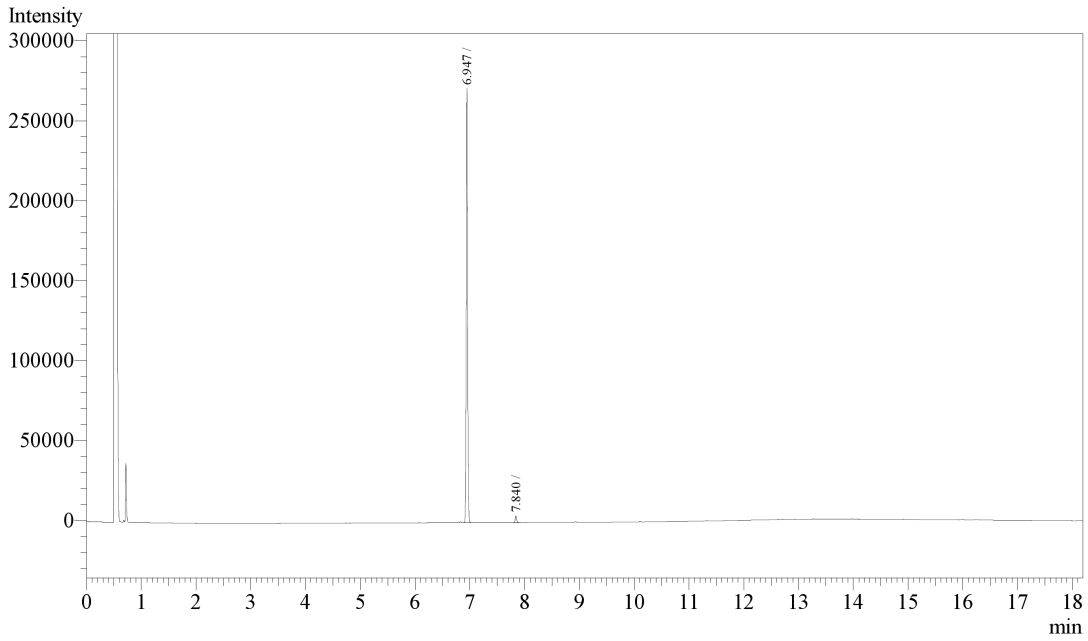

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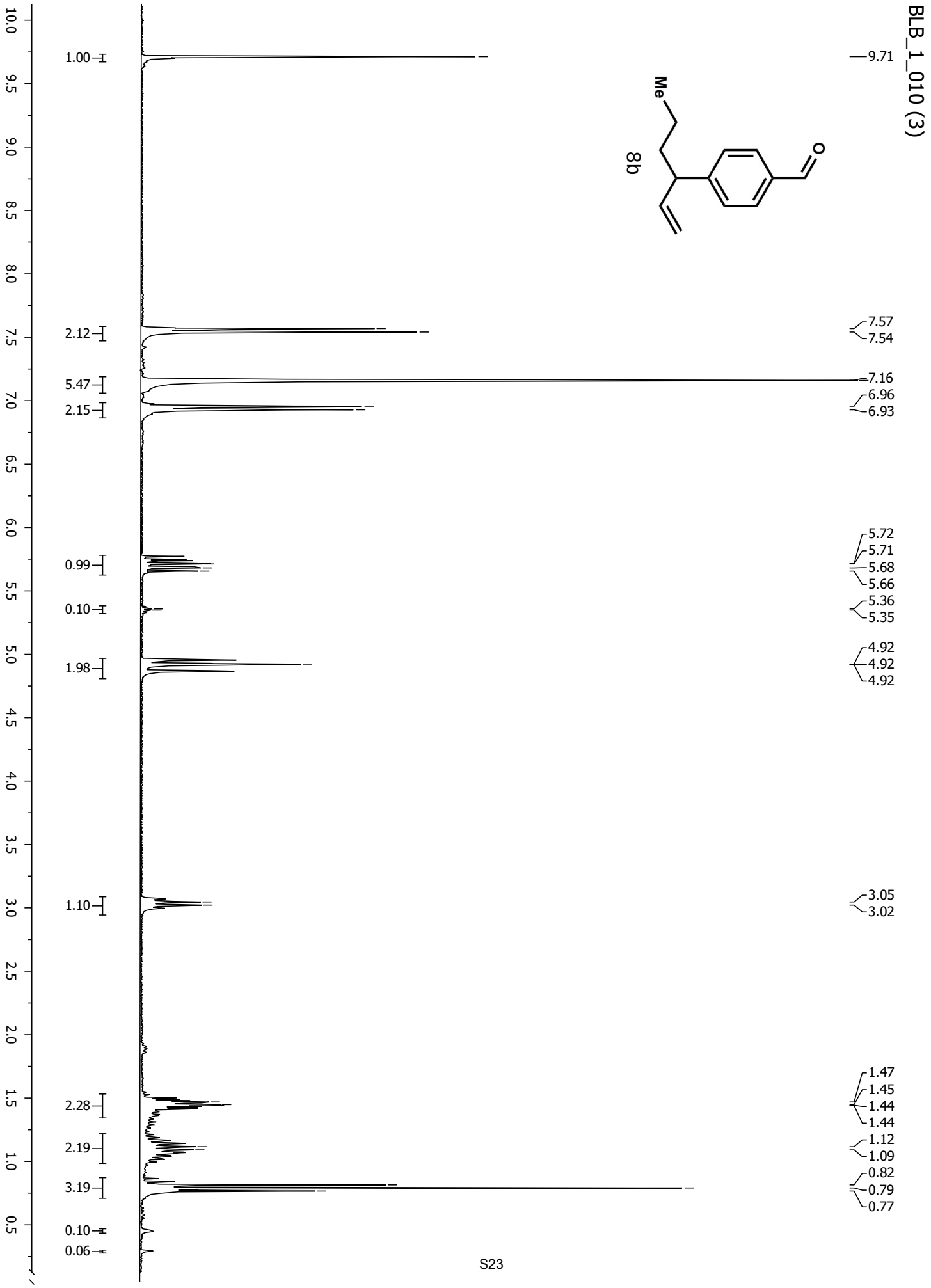
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8b
Me
O
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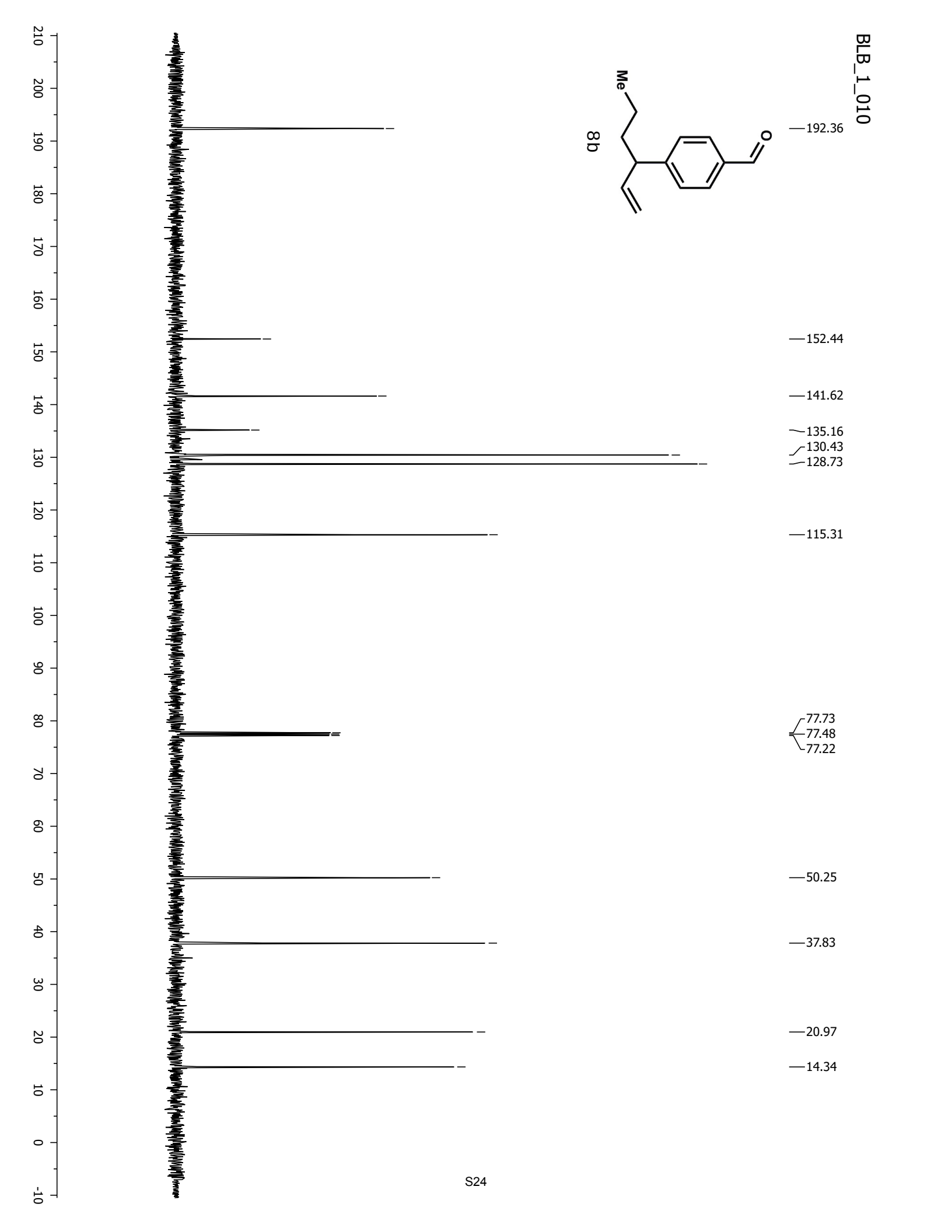
7.57
7.54
7.16
6.96
6.93
5.72
5.71
5.68
5.66
5.36
5.35
4.92
4.92
4.92
3.05
3.02
1.47
1.45
1.44
1.44
1.12
1.09
0.82
0.79
0.77
1.00
2.12
5.47
2.15
0.99
0.10
1.98
1.10
2.28
2.19
3.19
0.10
0.06


BLB_1_010
8b
Me
O
192.36
152.44
141.62
135.16
130.43
128.73
115.31
77.73
77.48
77.22
50.25
37.83
20.97
14.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Analysis Date & Time	: 3/25/2010 3:17:18 PM
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Sample Type	: Unknown
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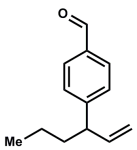
ISTD Amount	:



8b

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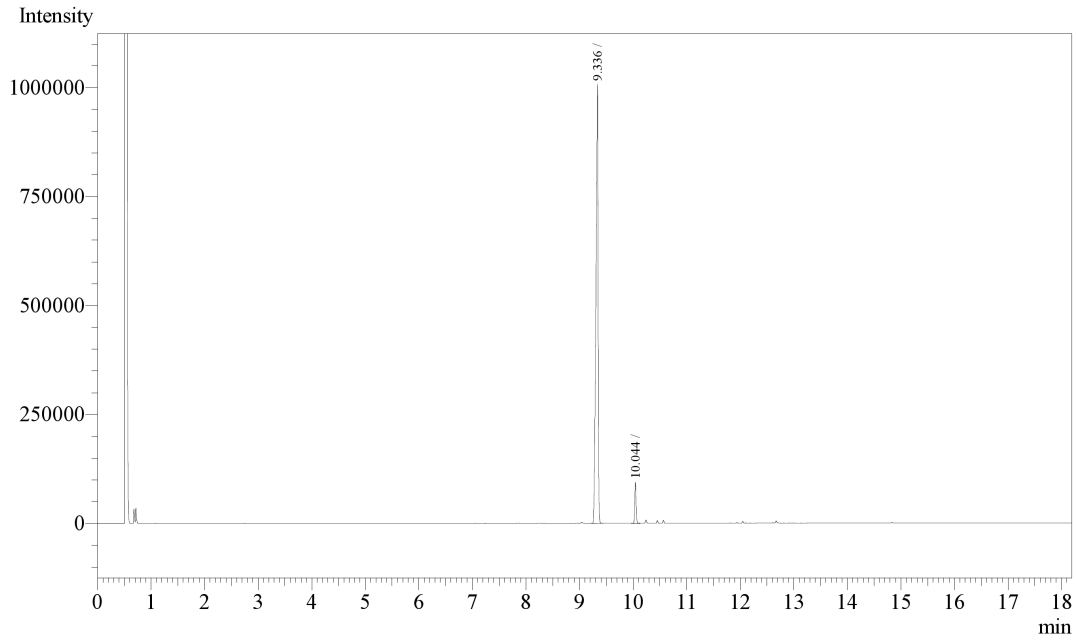

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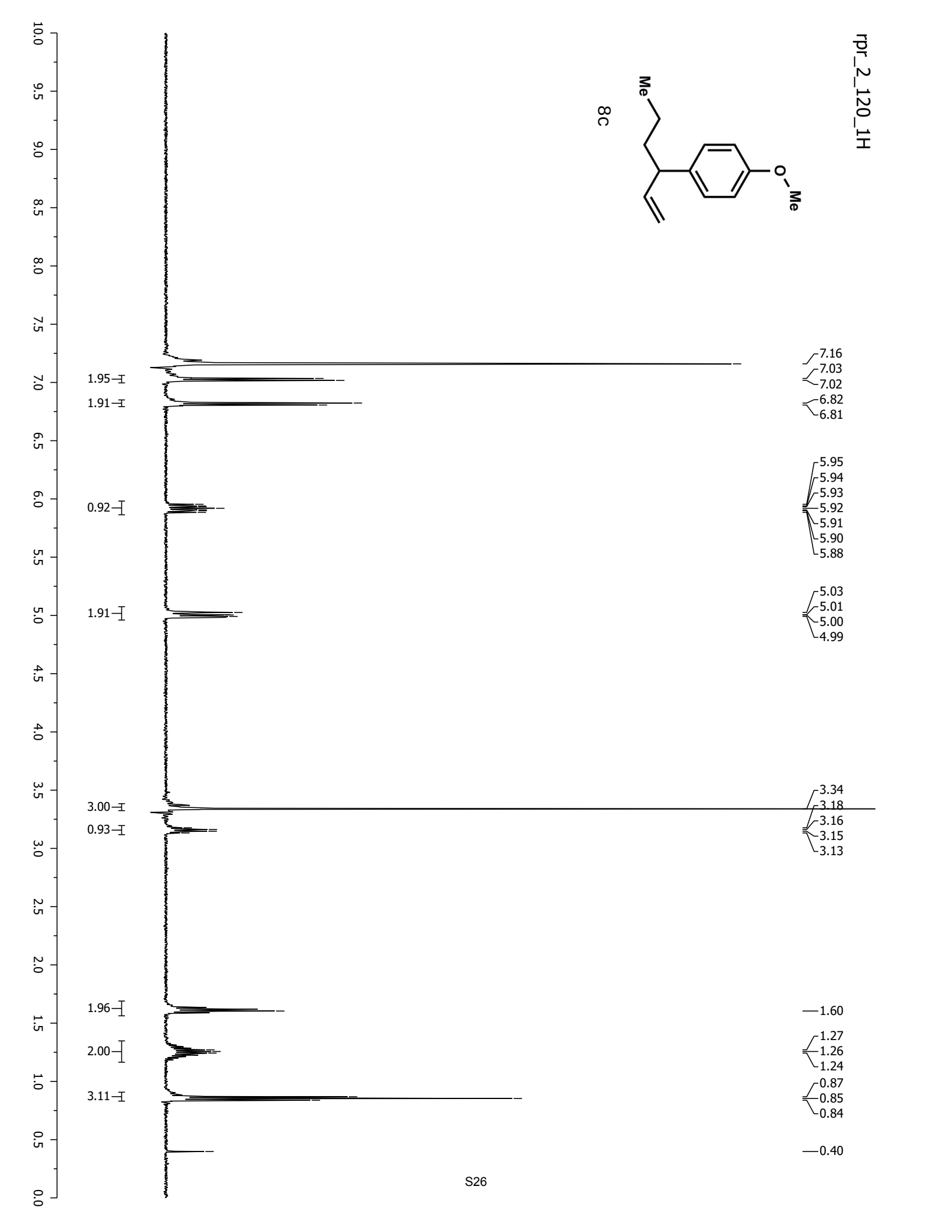
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O
Me
7.16
7.03
7.02
6.82
6.81
5.95
5.94
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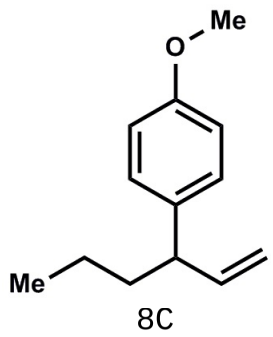
5.92
5.91
5.90
5.88
5.03
5.01
5.00
4.99
3.34
3.18
3.16
3.15
3.13
1.60
1.27
1.26
1.24
0.87
0.85
0.84
0.40
1.95
1.91
0.92
1.91
3.00
0.93
1.96
2.00
3.11

rpr_2_120_13C
13C NMR pMeOPh Sn2':Sn2 CDCl3



8C

Analysis Date & Time : 2/28/2010 7:45:50 PM
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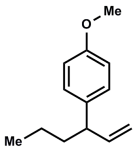
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :



8c

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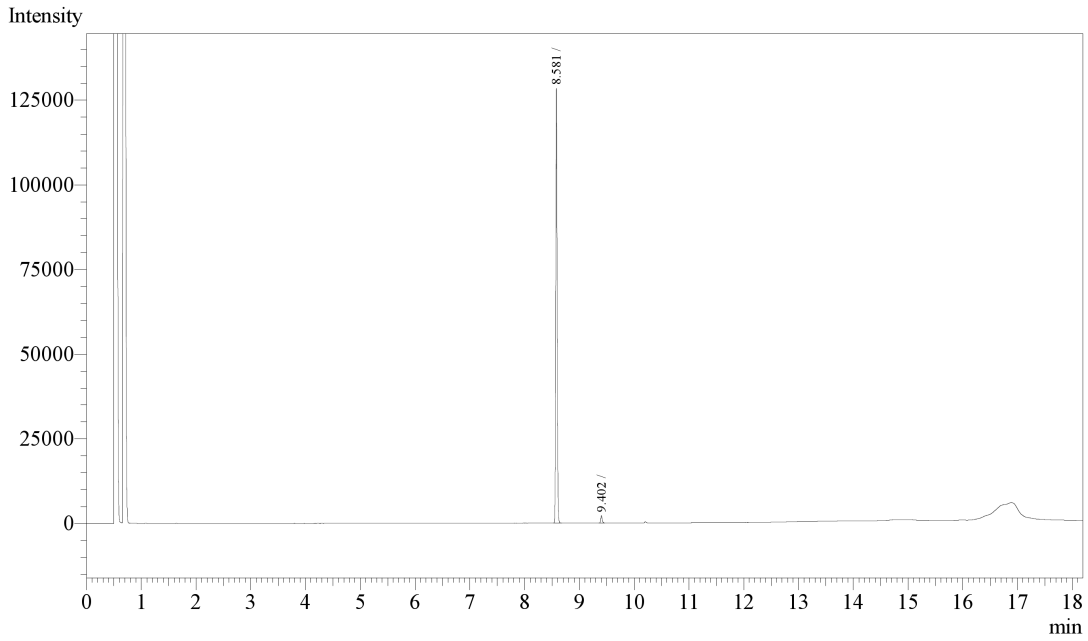

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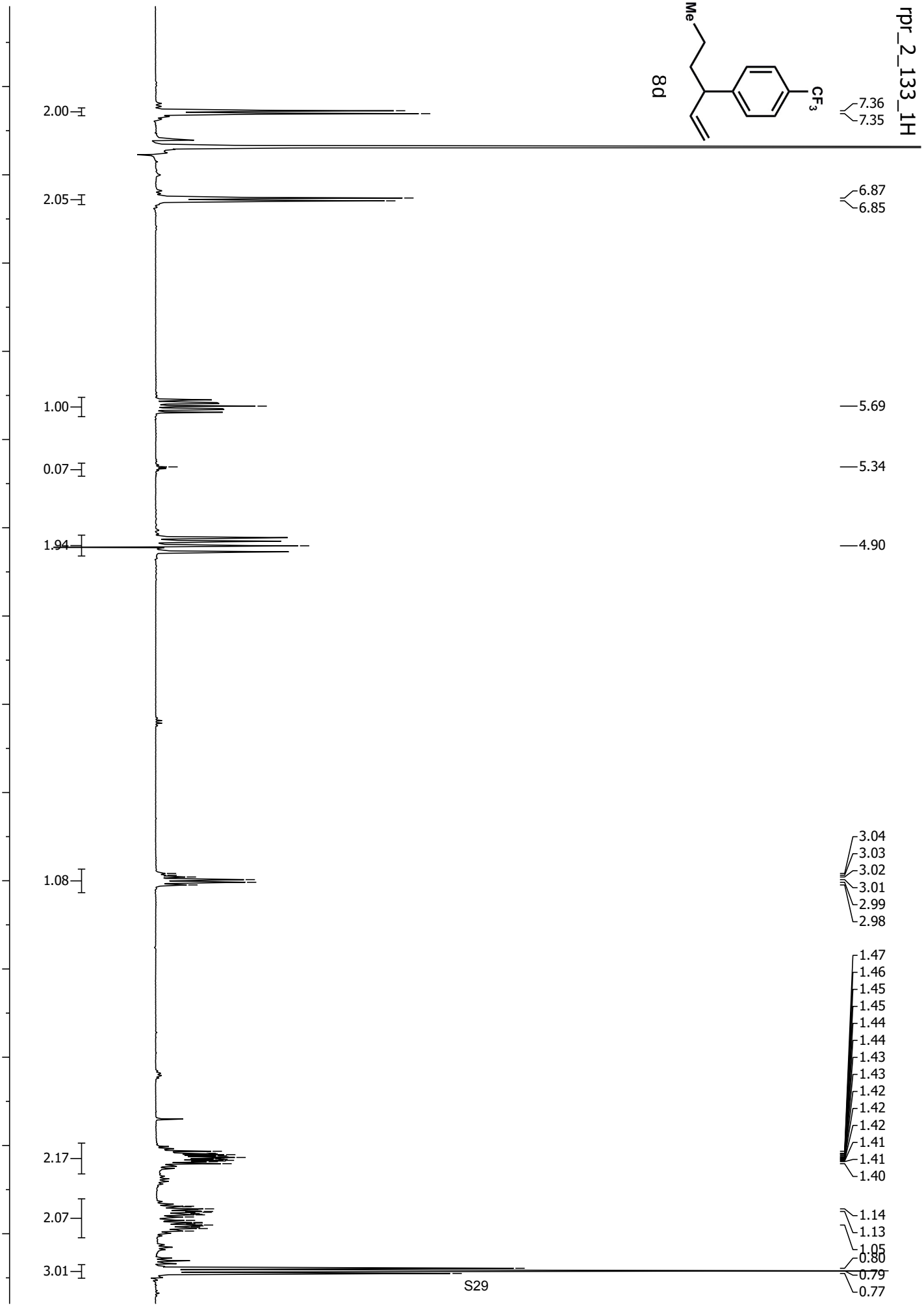
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6.85
5.69
5.34
4.90
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3.02
3.01
2.99
2.98
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.42
1.42
1.42
1.41
1.41
1.40
1.14
1.13
1.05
0.80
0.79
0.77
2.00
2.05
1.00
0.07
1.94
1.08
2.17
2.07
3.01
7.5
7.0
6.5
6.0
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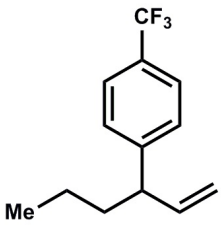
2.0
1.5
1.0

rpr_2_133_13C



8d

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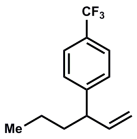

8d

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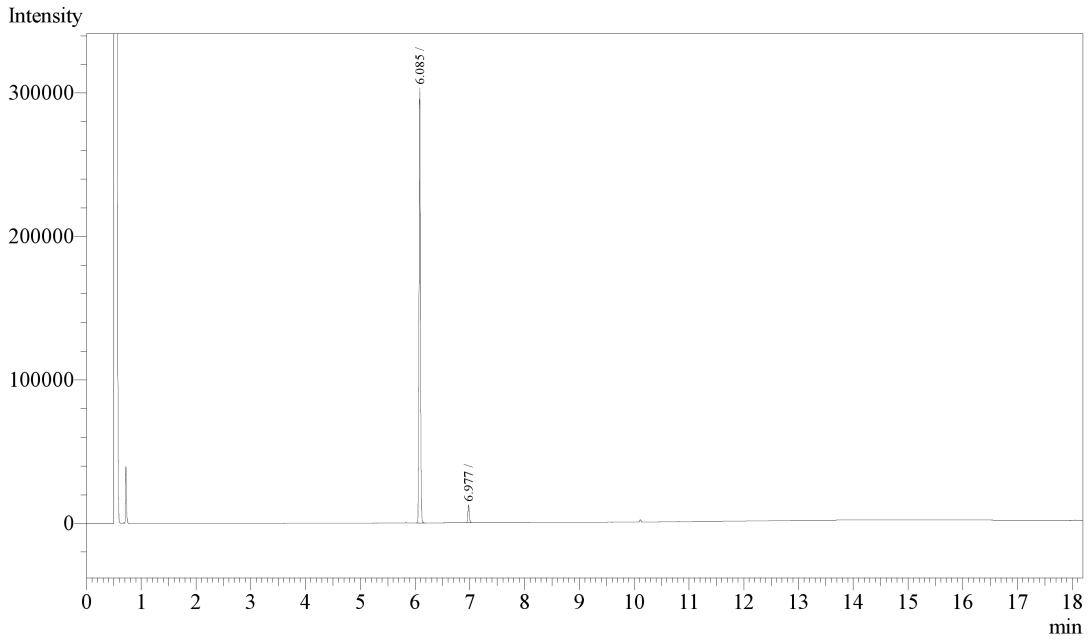

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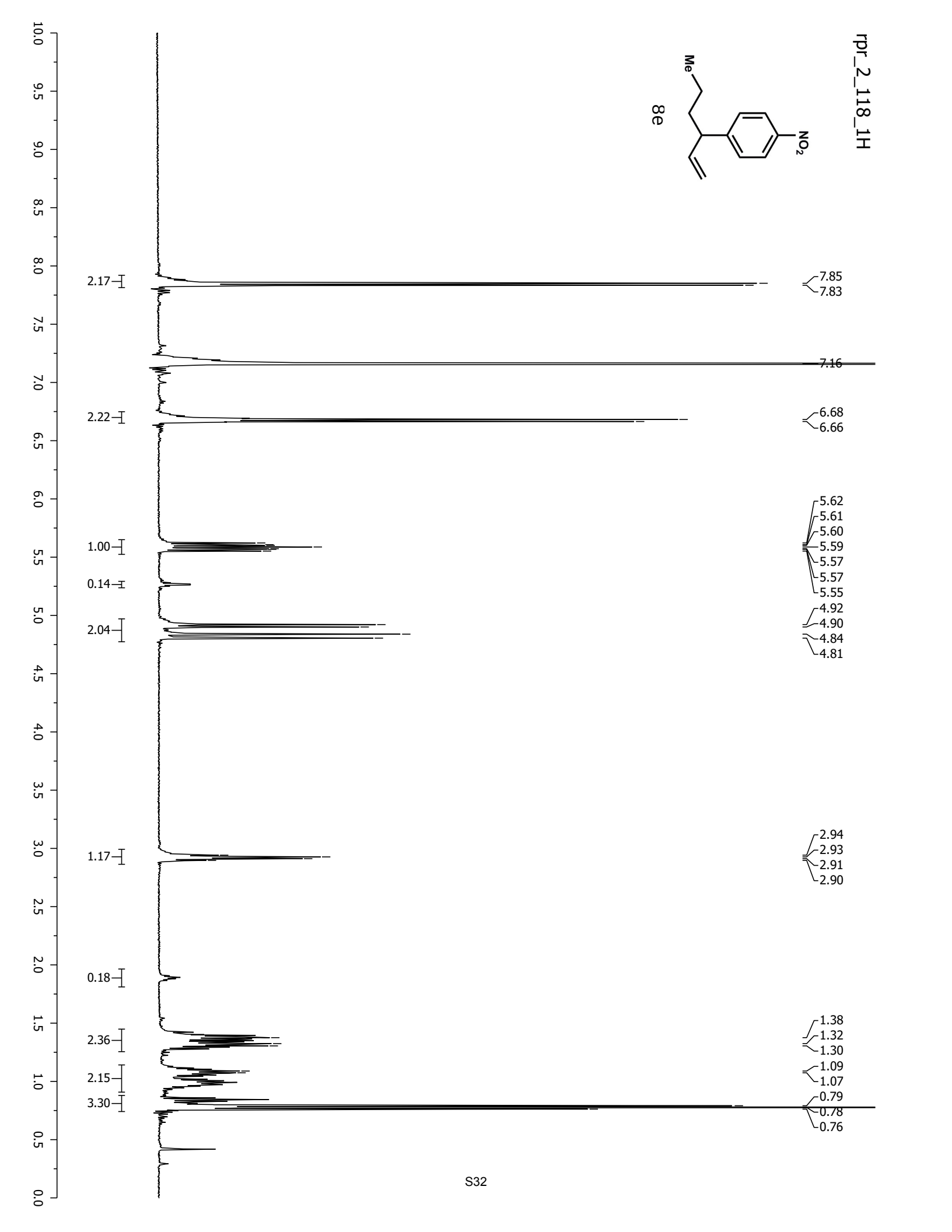
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NO2
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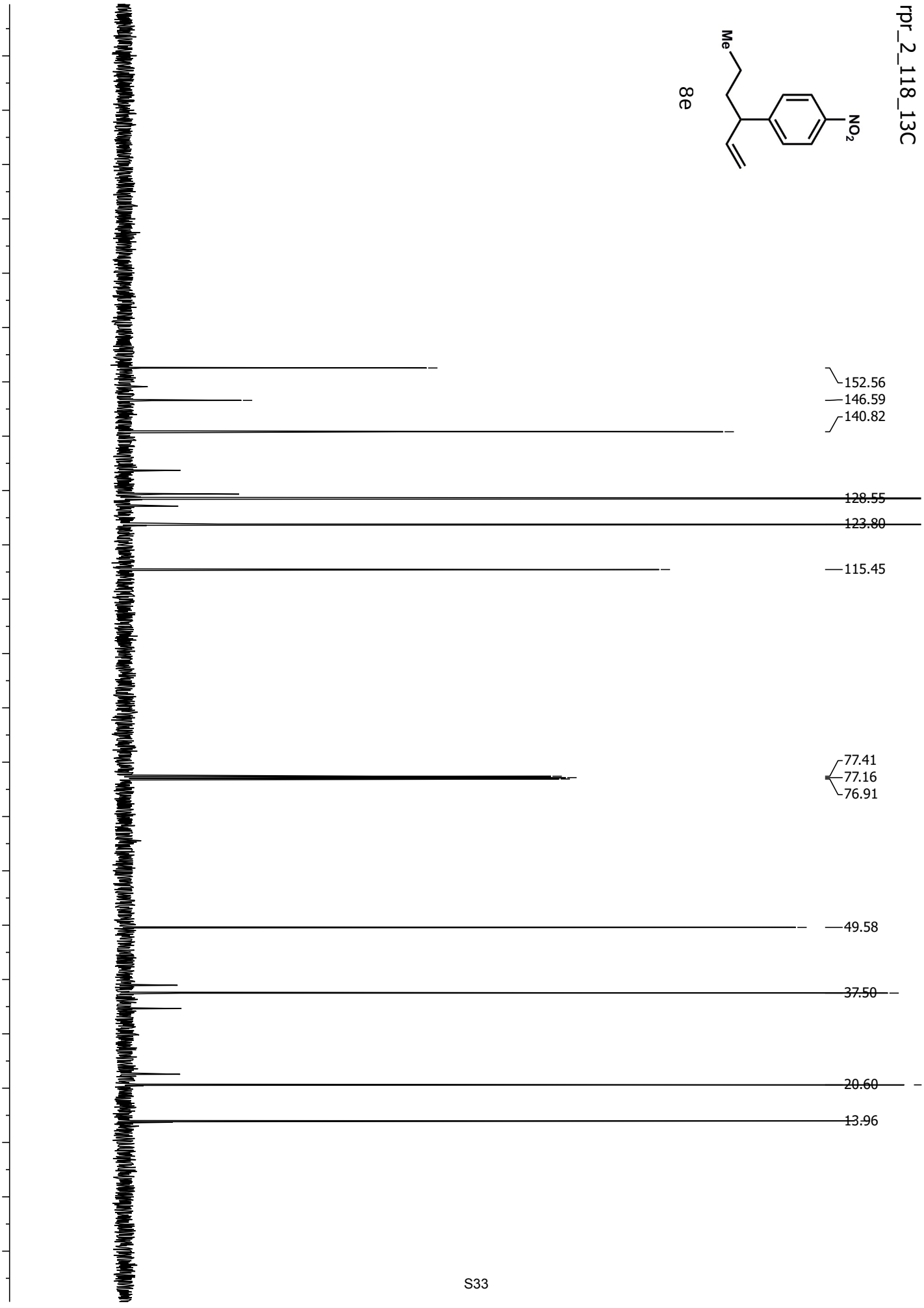
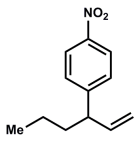
5.57
5.55
4.92
4.90
4.84
4.81
2.94
2.93
2.91
2.90
1.38
1.32
1.30
1.09
1.07
0.79
0.78
0.76
2.17
2.22
1.00
0.14
2.04
1.17
0.18
2.36
2.15
3.30

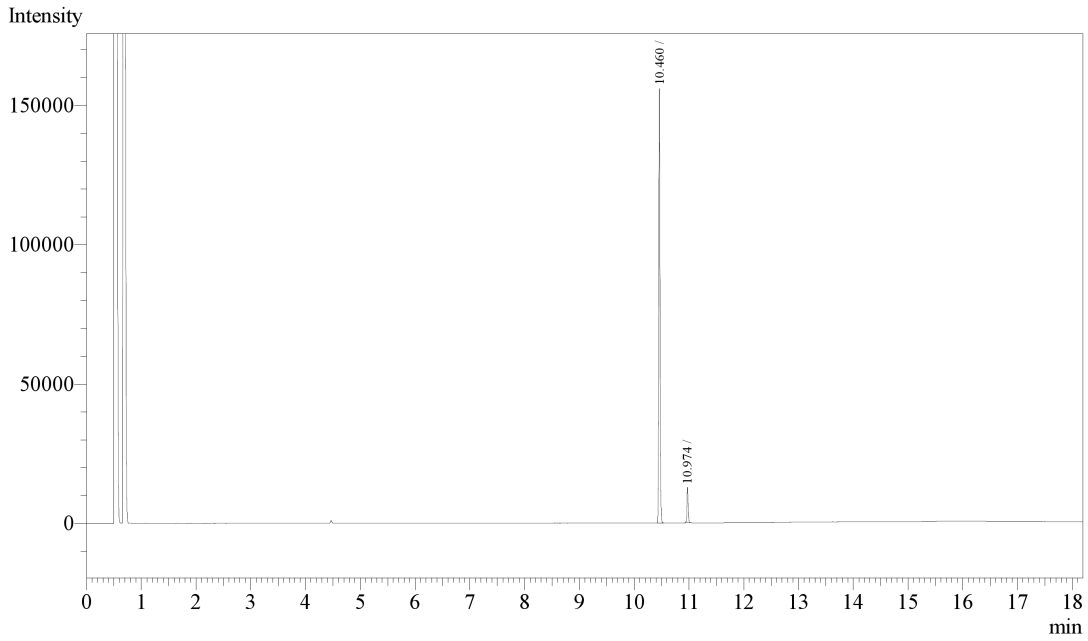

rpr_2_118_13C
8e
Me
NO2
152.56
146.59
140.82
128.55
123.80
115.45
77.41
77.16
76.91
49.58
37.50
20.60
13.96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Analysis Date & Time : 2/28/2010 7:20:36 PM
User Name : Admin
Vial# : 1
Sample Name : rpr_2_118_PURE
Sample ID : rpr_2_118_PURE
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

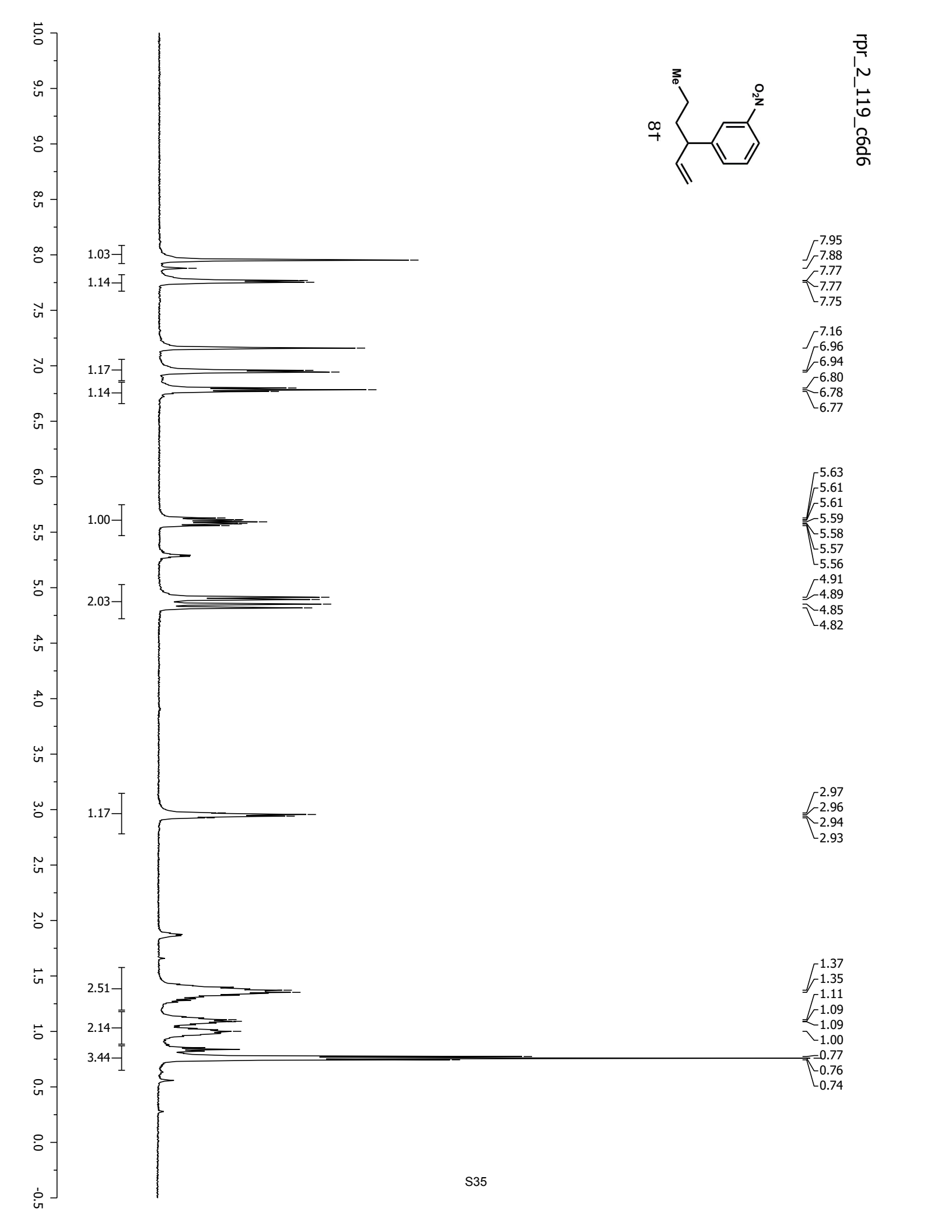


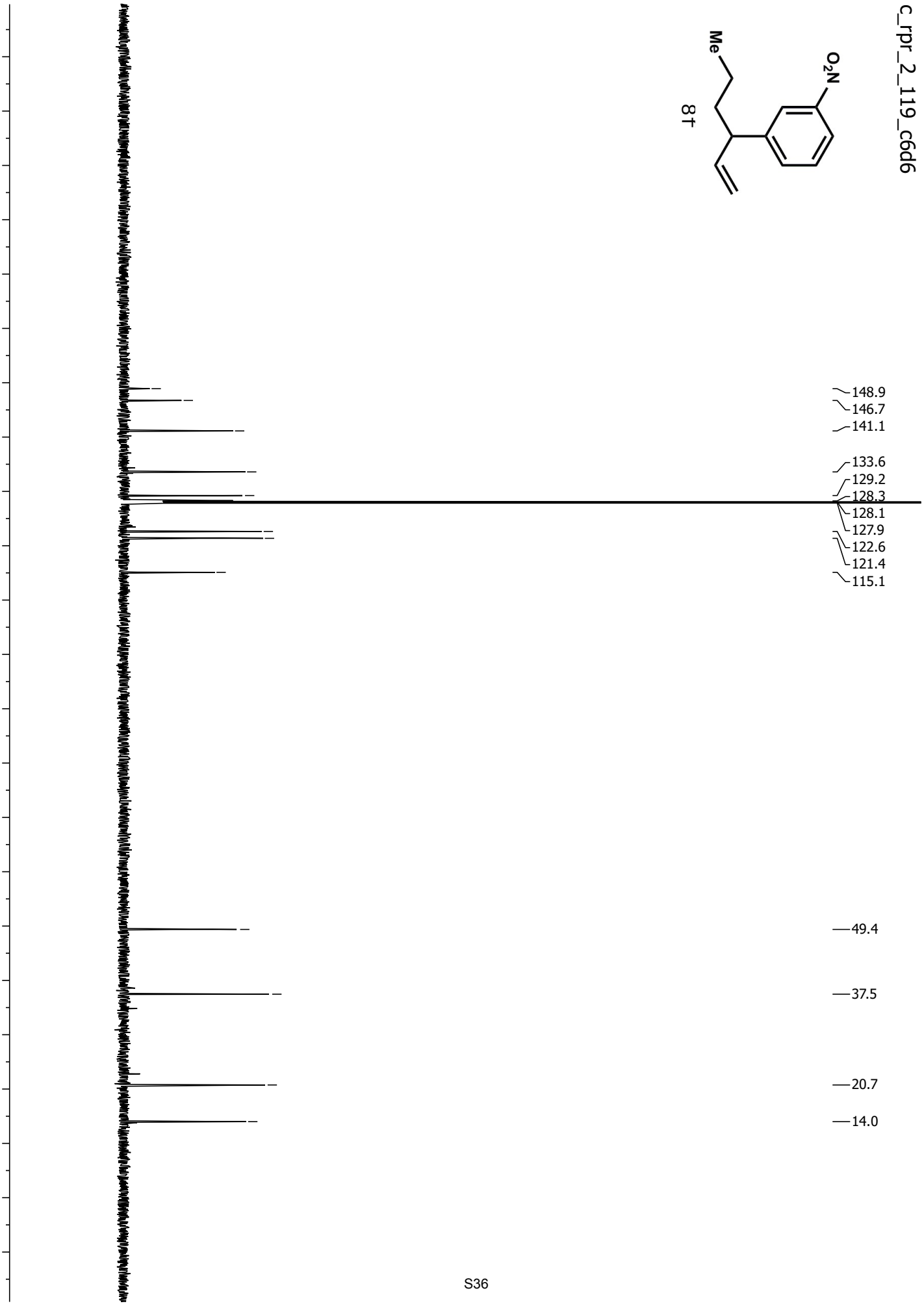
8e

Data Name : C:\GCsolution\Data\RPR_2\rpr_2_118\rpr_2_118_PURE.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm

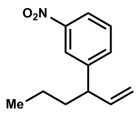


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	10.460	234557	153881	92.757				
2	10.974	18316	12548	7.243				
Total		252873	166429					


rpr_2_119_c6d6
8t
Me
O2N
7.95
7.88
7.77
7.77
7.75
7.16
6.96
6.94
6.80
6.78
6.77
5.63
5.61
5.61
5.59
5.58
5.57
5.56
4.91
4.89
4.85
4.82
2.97
2.96
2.94
2.93
1.37
1.35
1.11
1.09
1.09
1.00
0.77
0.76
0.74
1.03
1.14
1.17
1.14
1.00
2.03
1.17
2.51
2.14
3.44

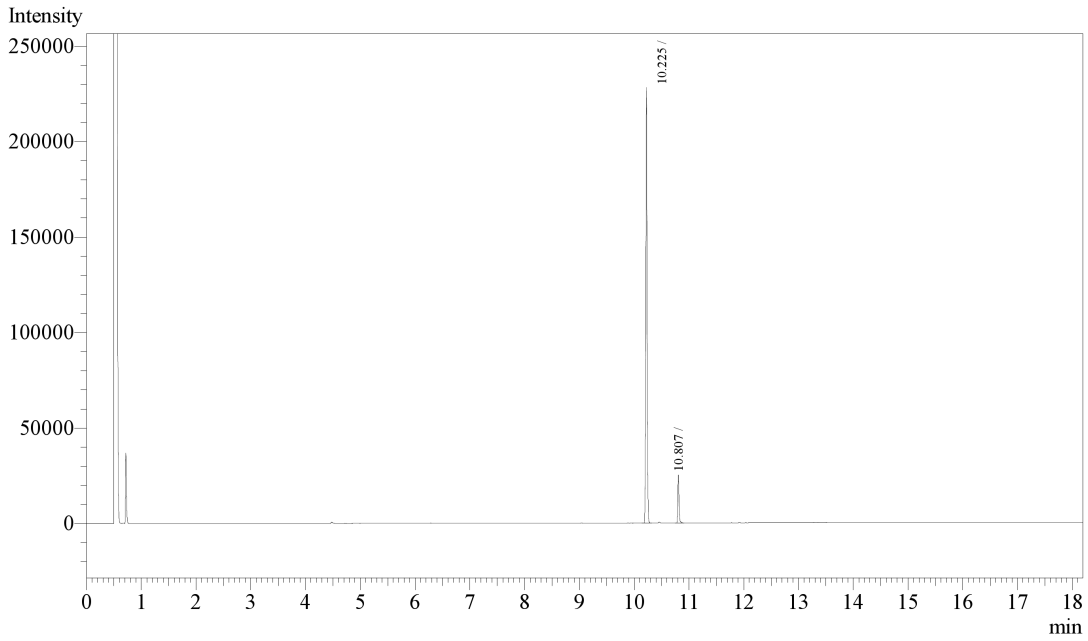

c_rpr_2_119_c6d6
Me
O2N
8t
148.9
146.7
141.1
133.6
129.2
128.3
128.1
127.9
122.6
121.4
115.1
49.4
37.5
20.7
14.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Analysis Date & Time : 4/5/2010 12:09:46 PM
User Name : Admin
Vial# : 1
Sample Name : rpr_2_119_pure
Sample ID : rpr_2_119_pure
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

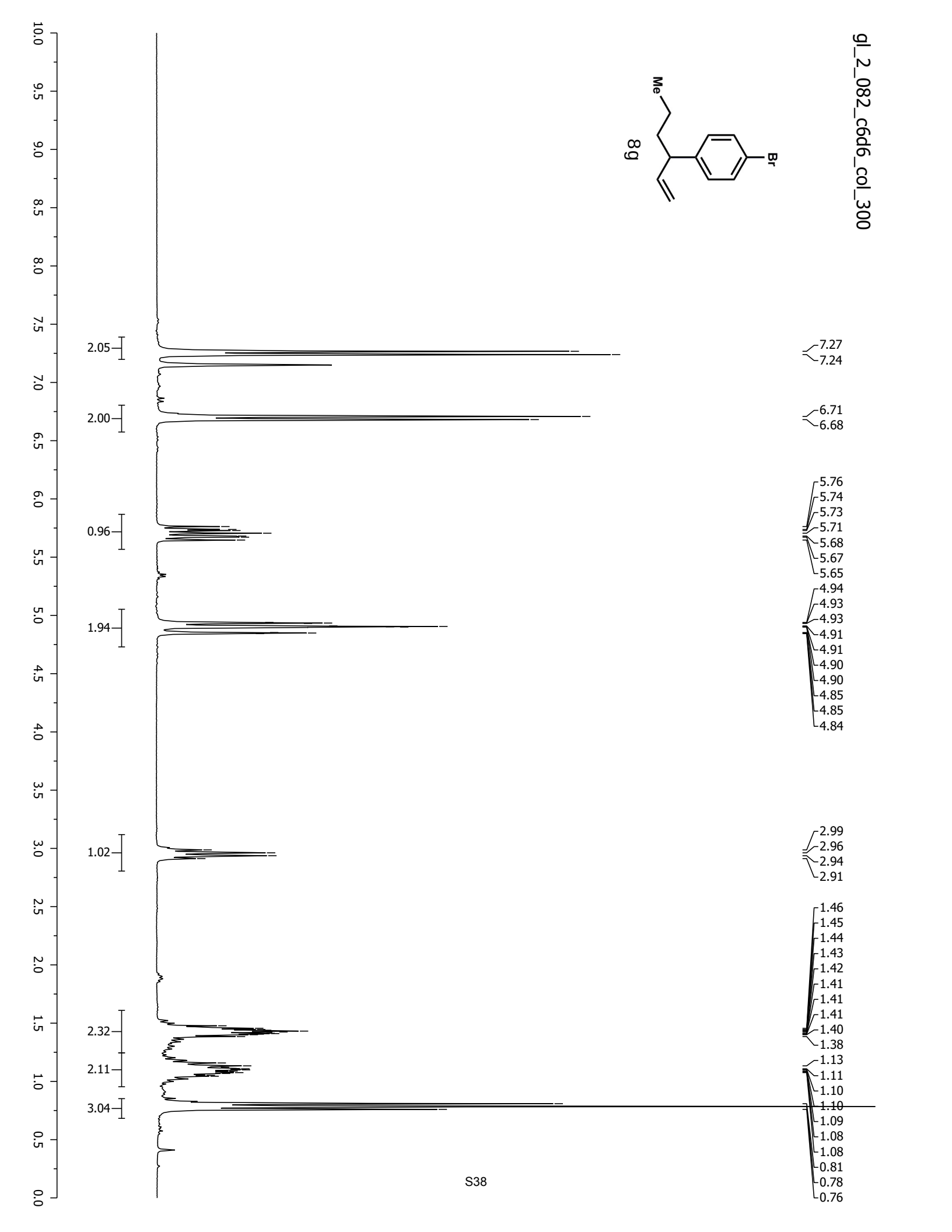


8f

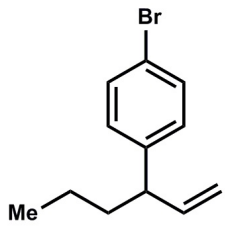
Data Name : C:\GCsolution\Data\RPR_2\rpr_2_119\rpr_2_119_pure.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	10.225	359095	220388	90.596				
2	10.807	37276	24762	9.404				
Total		396371	245150					


gl_2_082_c6d6_col_300
8g
Me
Br
7.27
7.24
6.71
6.68
5.76
5.74
5.73
5.71
5.68
5.67
5.65
4.94
4.93
4.93
4.91
4.91
4.90
4.90
4.85
4.85
4.84
2.99
2.96
2.94
2.91
1.46
1.45
1.44
1.43
1.42
1.41
1.41
1.41
1.40
1.38
1.13
1.11
1.10
1.10
1.09
1.08
1.08
0.81
0.78
0.76
2.05
2.00
0.96
1.94
1.02
2.32
2.11
3.04

c_gl_2_082_c6d6_col_300

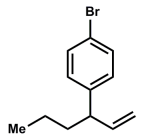


8g

143.7
142.1
131.8
129.8
128.4
128.1
127.7
120.2
114.2
49.3
37.7
20.8
14.1

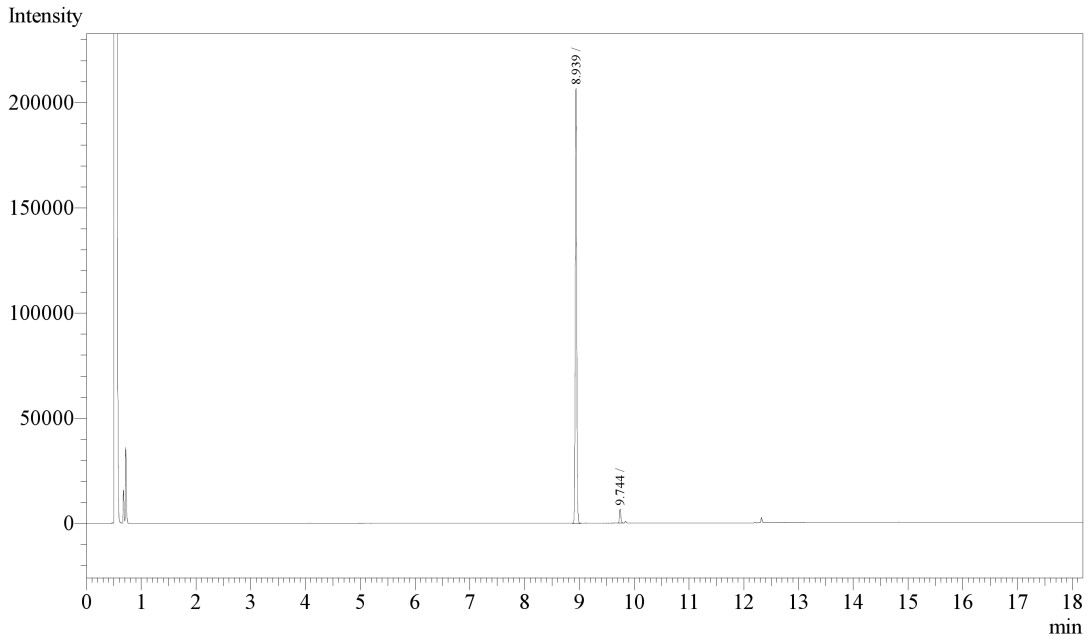
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Analysis Date & Time : 3/22/2010 11:30:51 AM
User Name : Admin
Vial# : 6
Sample Name : 2_082F
Sample ID : 2_082F
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

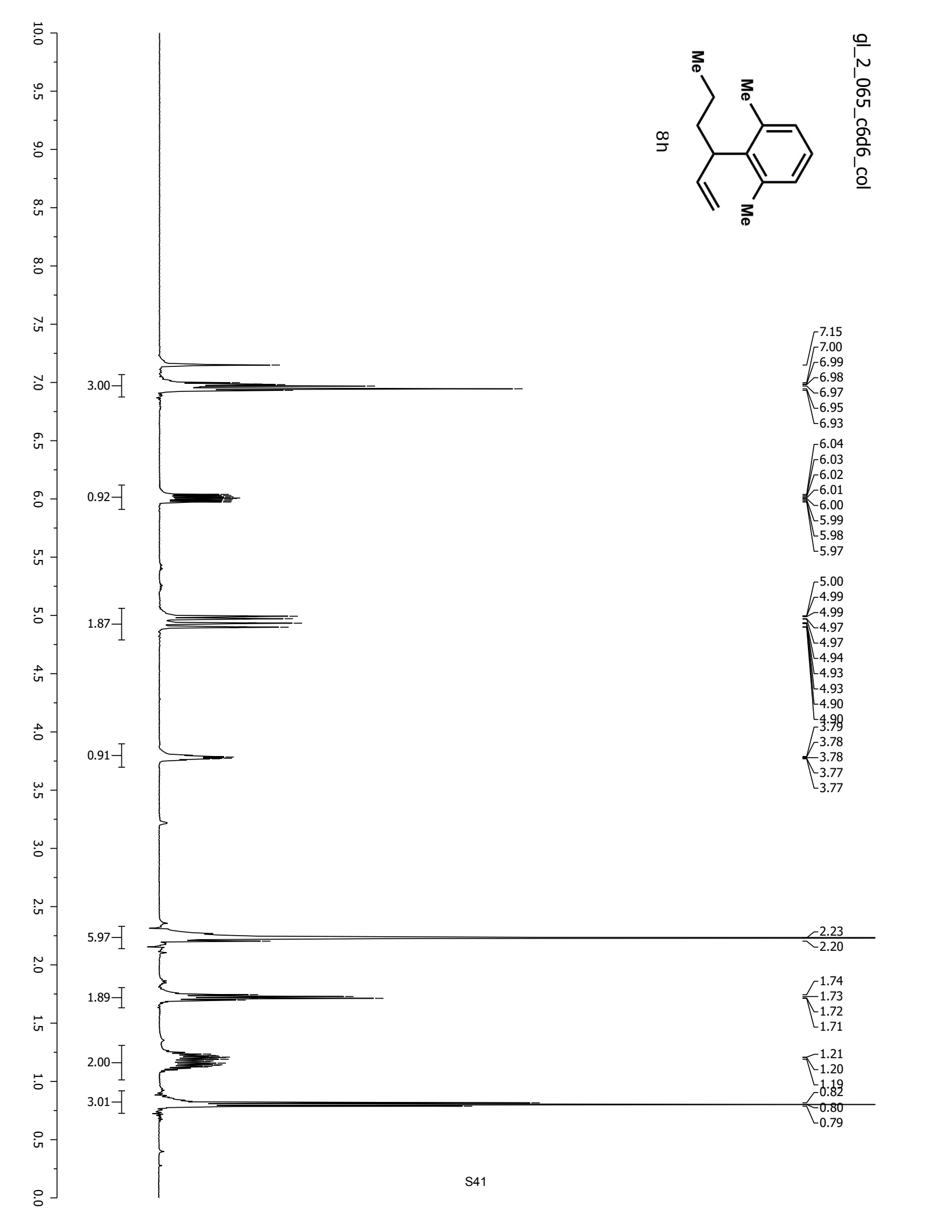


8g

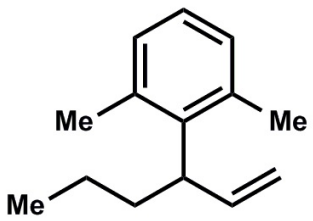
Data Name : C:\GCsolution\Data\Gojko\gl_2_081-82\2_082F.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	8.939	364759	204208	96.908				
2	9.744	11639	6605	3.092				
Total		376398	210813					


gl_2_065_c6d6_col
8h
Me
Me
Me
7.15
7.00
6.99
6.98
6.97
6.95
6.93
6.04
6.03
6.02
6.01
6.00
5.99
5.98
5.97
5.00
4.99
4.99
4.97
4.97
4.94
4.93
4.93
4.90
4.90
3.79
3.78
3.78
3.77
3.77
2.23
2.20
1.74
1.73
1.72
1.71
1.21
1.20
1.19
0.82
0.80
0.79
3.00
0.92
1.87
0.91
5.97
1.89
2.00
3.01

c_gl_2_065_cdcl3_col

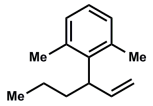


8h

141.05
140.63
136.77
125.98
113.80
44.03
35.30
21.72
21.58
14.42

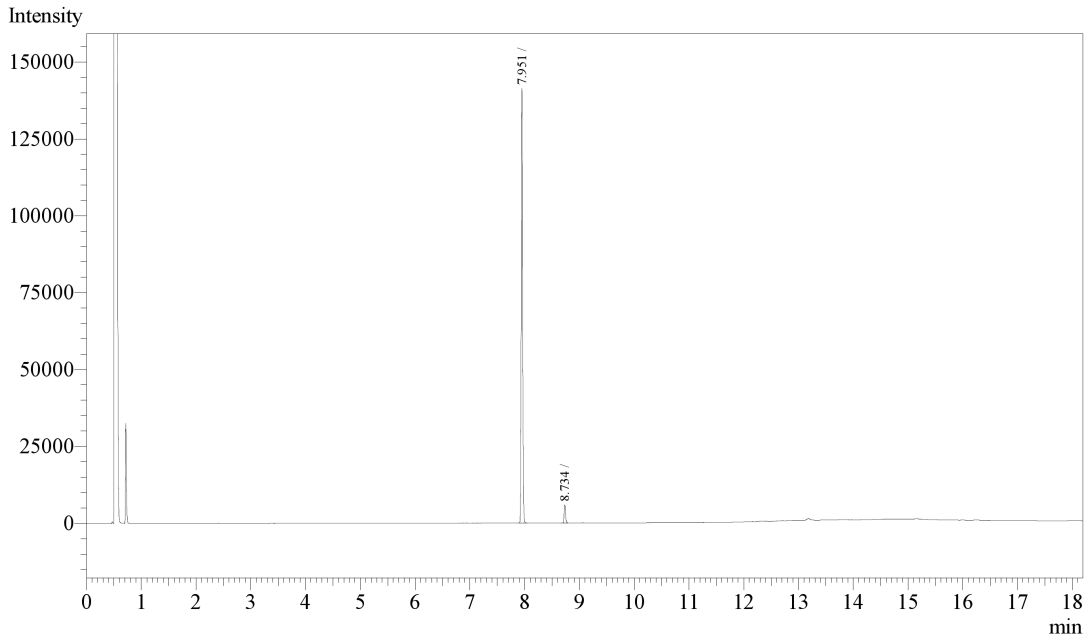
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Analysis Date & Time	: 3/2/2010 7:15:33 PM
User Name	: Admin
Vial#	: 1
Sample Name	: gl_2_065f
Sample ID	: gl_2_065f
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:



8h

Data Name	: C:\GCsolution\Data\Gojko\gl_2_064-065\2_065_f.gcd
Method Name	: C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	7.951	249081	140321	96.013				
2	8.734	10344	5789	3.987				
Total		259425	146110					

AW_3_049

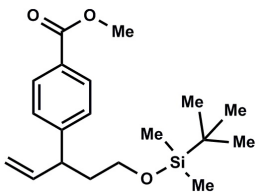


Table 3, Entries 1 and 2

AW_3_049

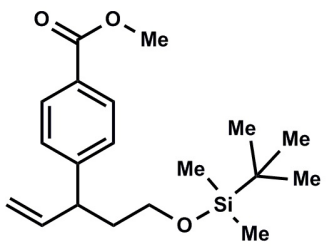


Table 3, Entries 1 and 2

Analysis Date & Time : 2/27/2010 4:07:25 PM
User Name : Admin
Vial# : 1
Sample Name : AW_3_049_2
Sample ID : AW_3_049_2
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

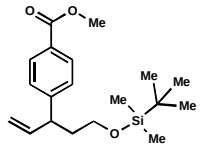
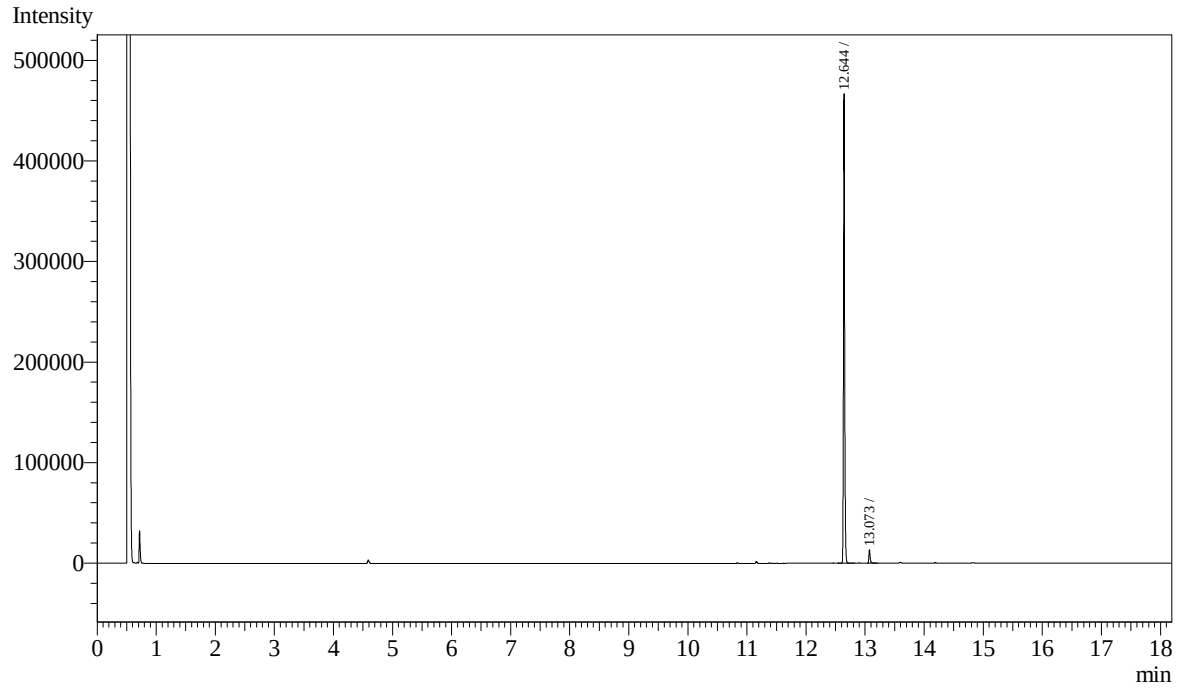


Table 3, Entries 1 and 2

Data Name : C:\GCsolution\Data\AW_book3\AW_3_049_2.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.644	632385	452189	96.958		V		
2	13.073	19841	13152	3.042		S		
Total		652226	465341					

AW_3_060

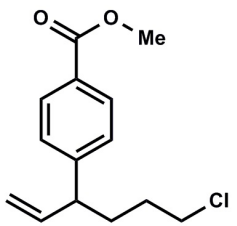


Table 3, Entry 3

CAW_3_060

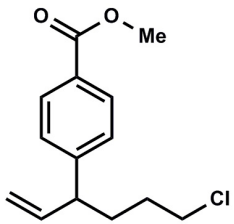


Table 3, Entry 3

Analysis Date & Time : 3/6/2010 5:46:18 PM
User Name : Admin
Vial# : 2
Sample Name : AW_3_056_2
Sample ID : AW_3_056_2
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

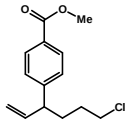
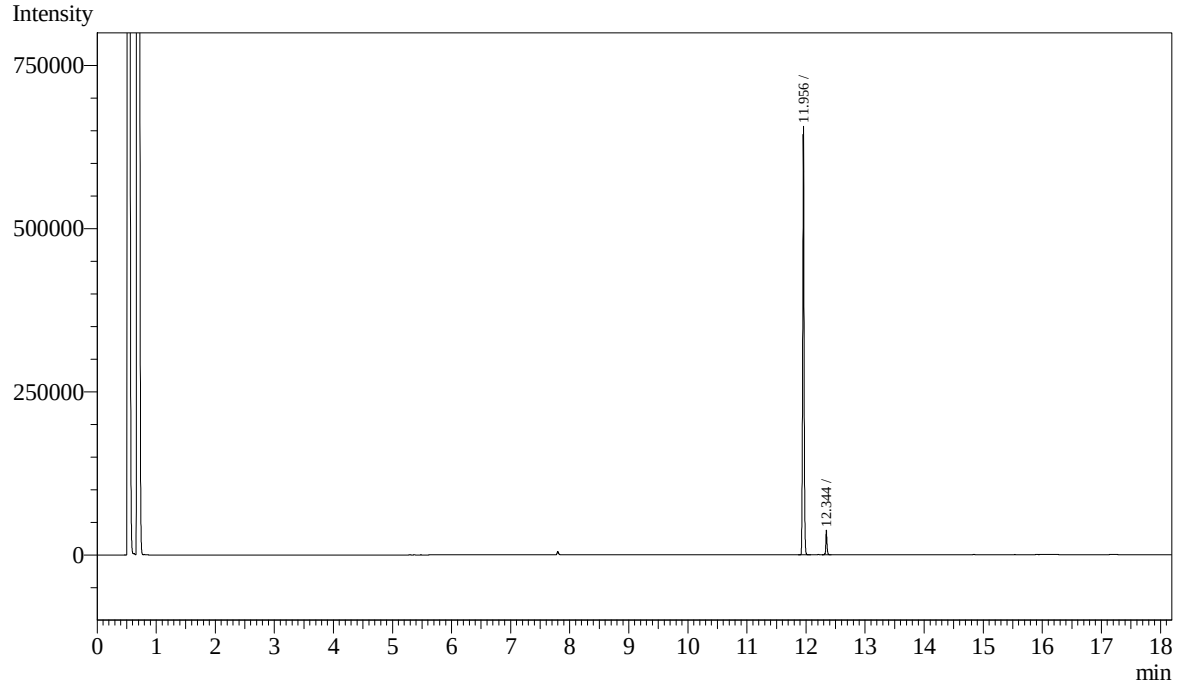
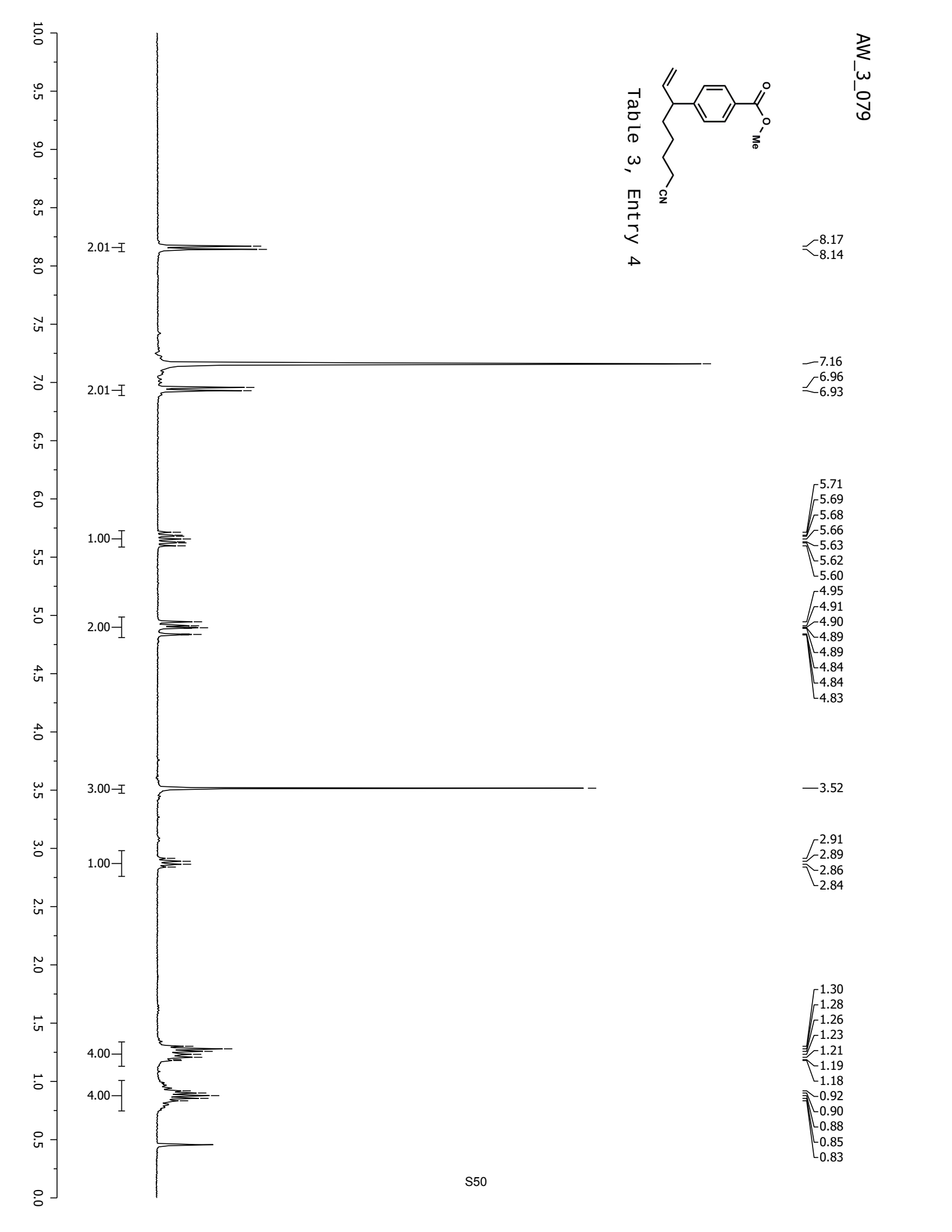


Table 3, Entry 3

Data Name : C:\GCsolution\Data\AW_book3\AW_3_056_2.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.956	1042566	626631	95.314		V		
2	12.344	51251	35655	4.686		V		
Total		1093817	662286					


AW_3_079
Table 3, Entry 4
Me
CN
8.17
8.14
7.16
6.96
6.93
5.71
5.69
5.68
5.66
5.63
5.62
5.60
4.95
4.91
4.90
4.89
4.89
4.84
4.84
4.83
3.52
2.91
2.89
2.86
2.84
1.30
1.28
1.26
1.23
1.21
1.19
1.18
0.92
0.90
0.88
0.85
0.83
2.01
2.01
1.00
2.00
3.00
1.00
4.00
4.00

CAW_3_079

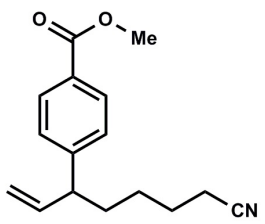


Table 3, Entry 4

Analysis Date & Time : 4/5/2010 10:54:15 AM
User Name : Admin
Vial# : 1
Sample Name : AW_3_079_2
Sample ID : AW_3_079_2
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

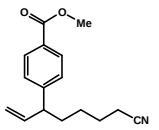
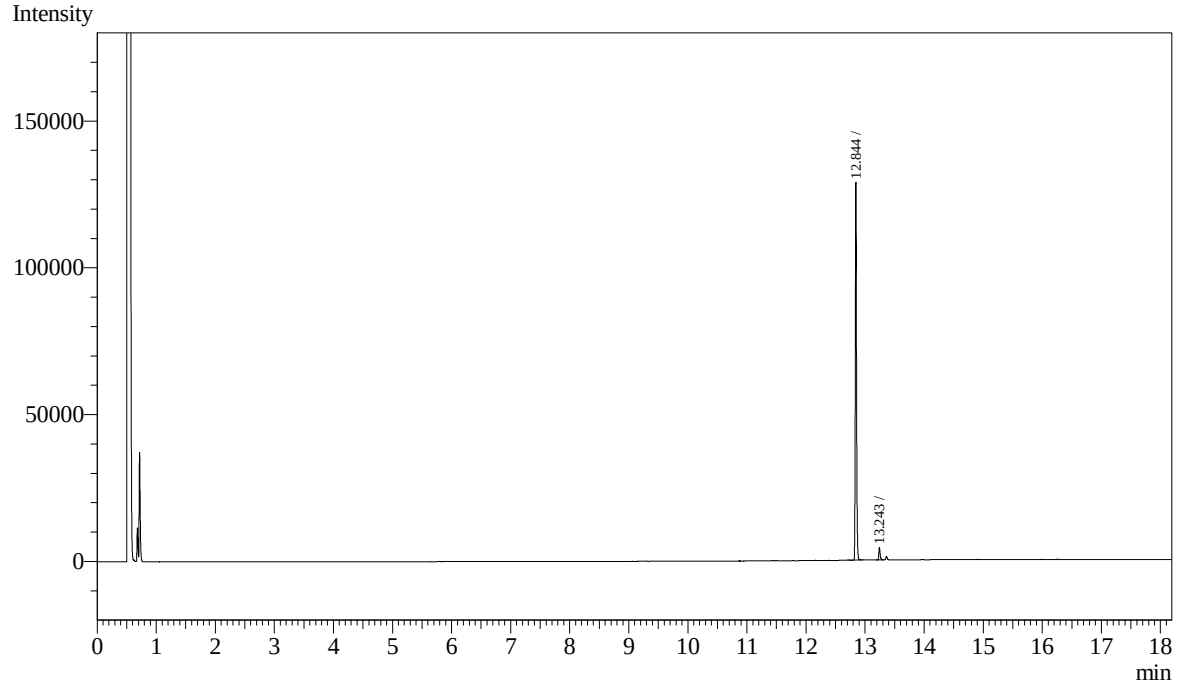
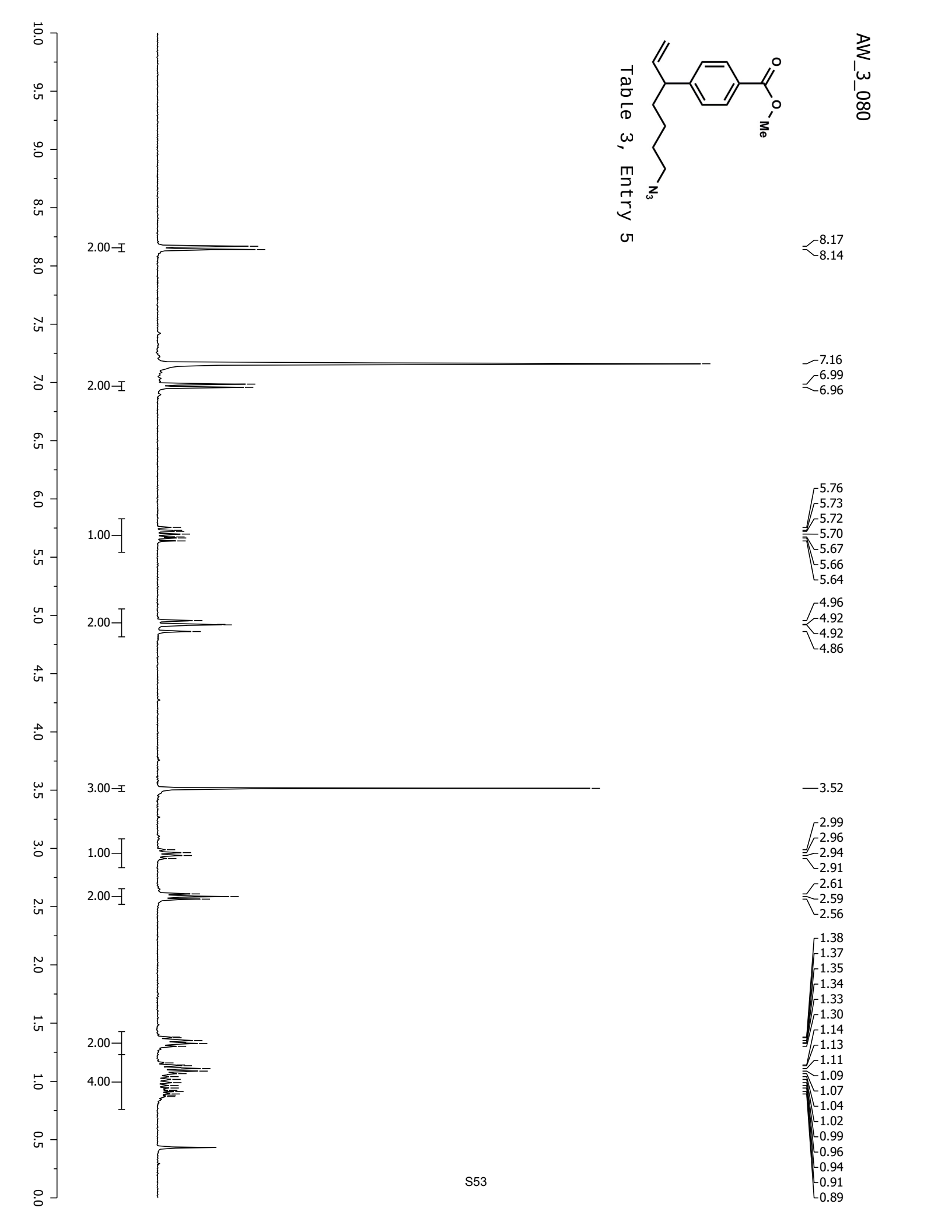


Table 3, Entry 4

Data Name : C:\GCsolution\Data\AW_book3\AW_3_079_2.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.844	178121	124267	96.436				
2	13.243	6583	4207	3.564				
Total		184704	128474					


AW_3_080
Table 3, Entry 5
N3
O
O
Me
8.17
8.14
7.16
6.99
6.96
5.76
5.73
5.72
5.70
5.67
5.66
5.64
4.96
4.92
4.92
4.86
3.52
2.99
2.96
2.94
2.91
2.61
2.59
2.56
1.38
1.37
1.35
1.34
1.33
1.30
1.14
1.13
1.11
1.09
1.07
1.04
1.02
0.99
0.96
0.94
0.91
0.89
2.00
2.00
1.00
2.00
3.00
1.00
2.00
2.00
4.00

CAW_3_080

167.1
149.6
141.2
130.0
128.4
127.7
115.1
52.1
51.3
49.9
34.9
28.8
24.7

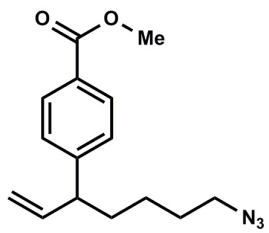


Table 3, Entry 5

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Analysis Date & Time : 4/5/2010 11:19:40 AM
User Name : Admin
Vial# : 2
Sample Name : AW_3_080_3
Sample ID : AW_3_080_3
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

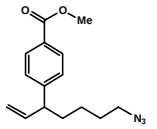
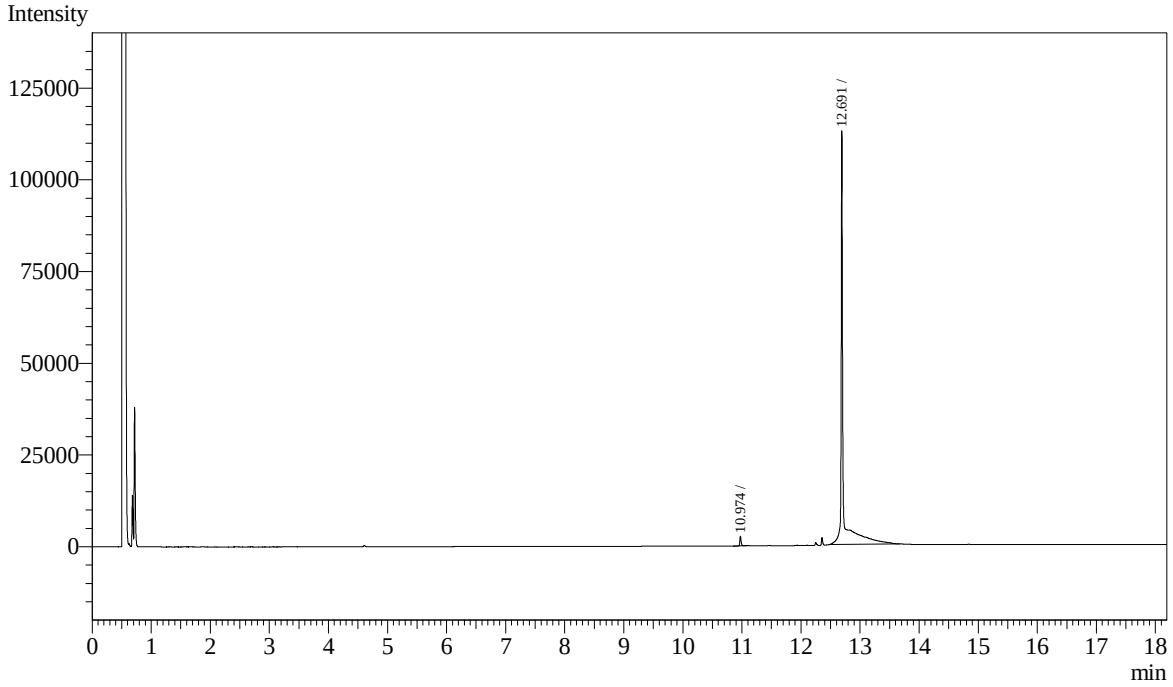


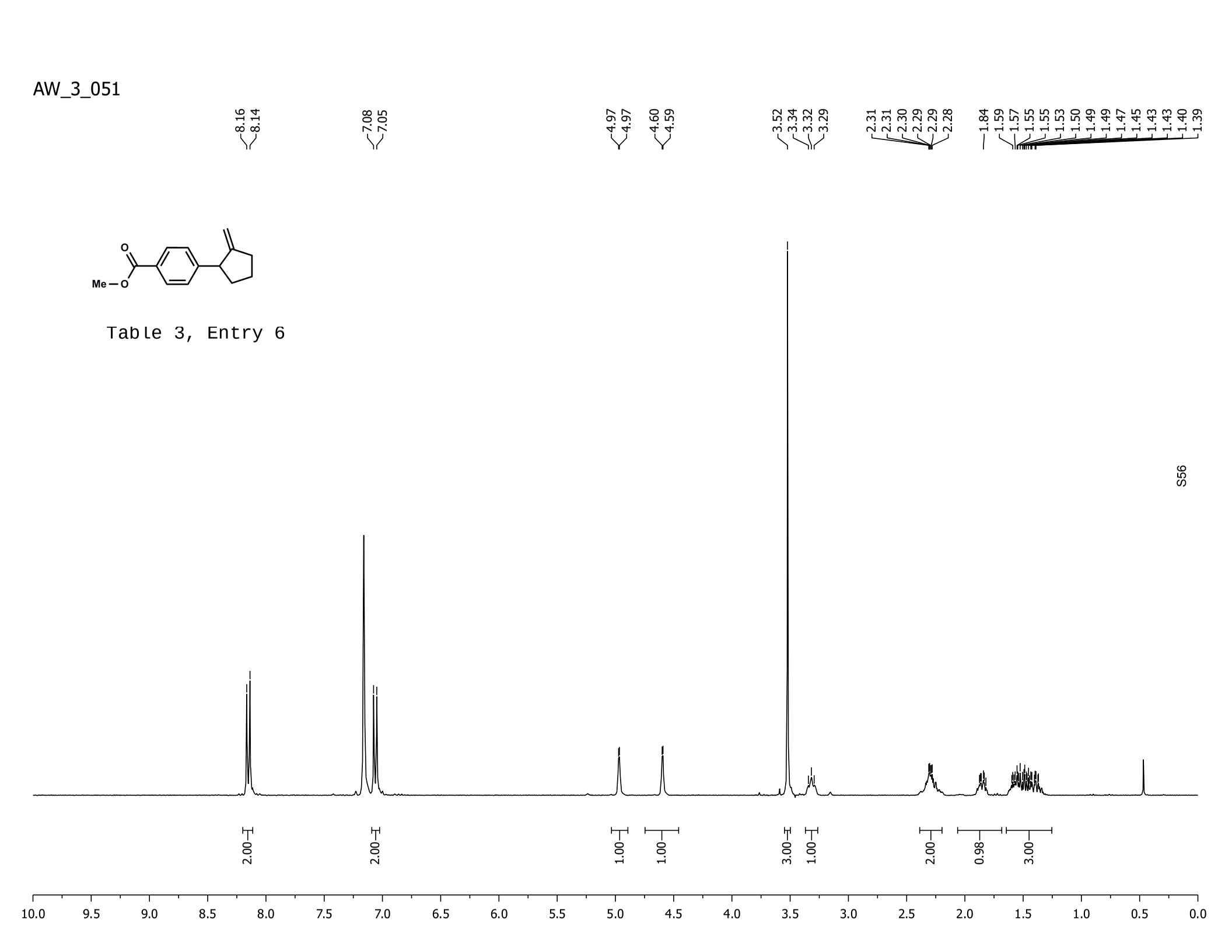
Table 3, Entry 5

Data Name : C:\GCsolution\Data\AW_book3\AW_3_080_3.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	10.974	3518	2598	1.265				
2	12.691	274497	110438	98.735				
Total		278015	113036					

AW_3_051


8.16
8.14
7.08
7.05
4.97
4.97
4.60
4.59
3.52
3.34
3.32
3.29
2.31
2.31
2.30
2.29
2.29
2.28
1.84
1.59
1.57
1.55
1.55
1.53
1.50
1.49
1.49
1.47
1.45
1.43
1.43
1.40
1.39
O
Me—O
Table 3, Entry 6
S56
2.00
2.00
1.00
1.00
3.00
1.00
2.00
0.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
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

CAW_3_051

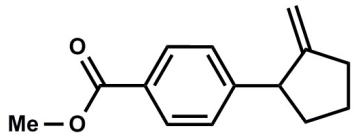


Table 3, Entry 6

Analysis Date & Time : 3/4/2010 10:19:14 AM
User Name : Admin
Vial# : 1
Sample Name : AW_3_051_2
Sample ID : AW_3_051_2
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

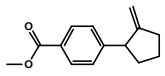
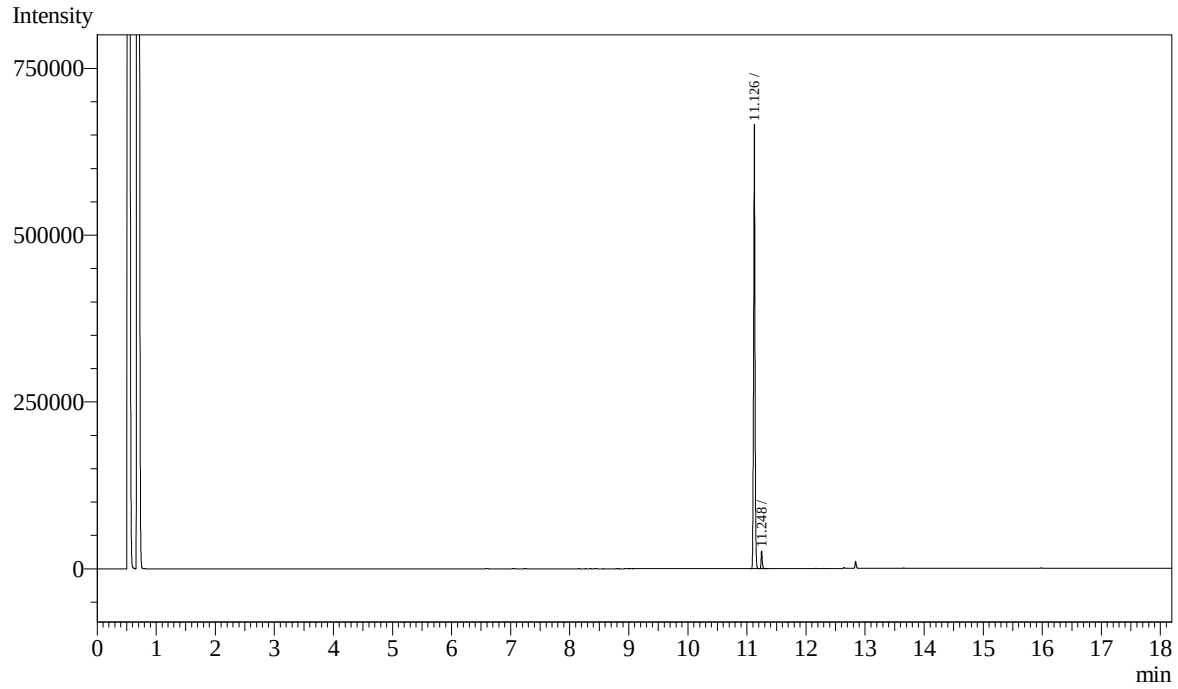


Table 3, Entry 6

Data Name : C:\GCsolution\Data\AW_book3\AW_3_051_2.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	11.126	1080370	635557	96.717				
2	11.248	36668	25820	3.283		V		
Total		1117038	661377					

gl_2_052B_c6d6_col

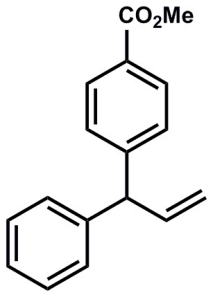


Table 3, Entry 7

c_gl_2_052B_col_cdcl3

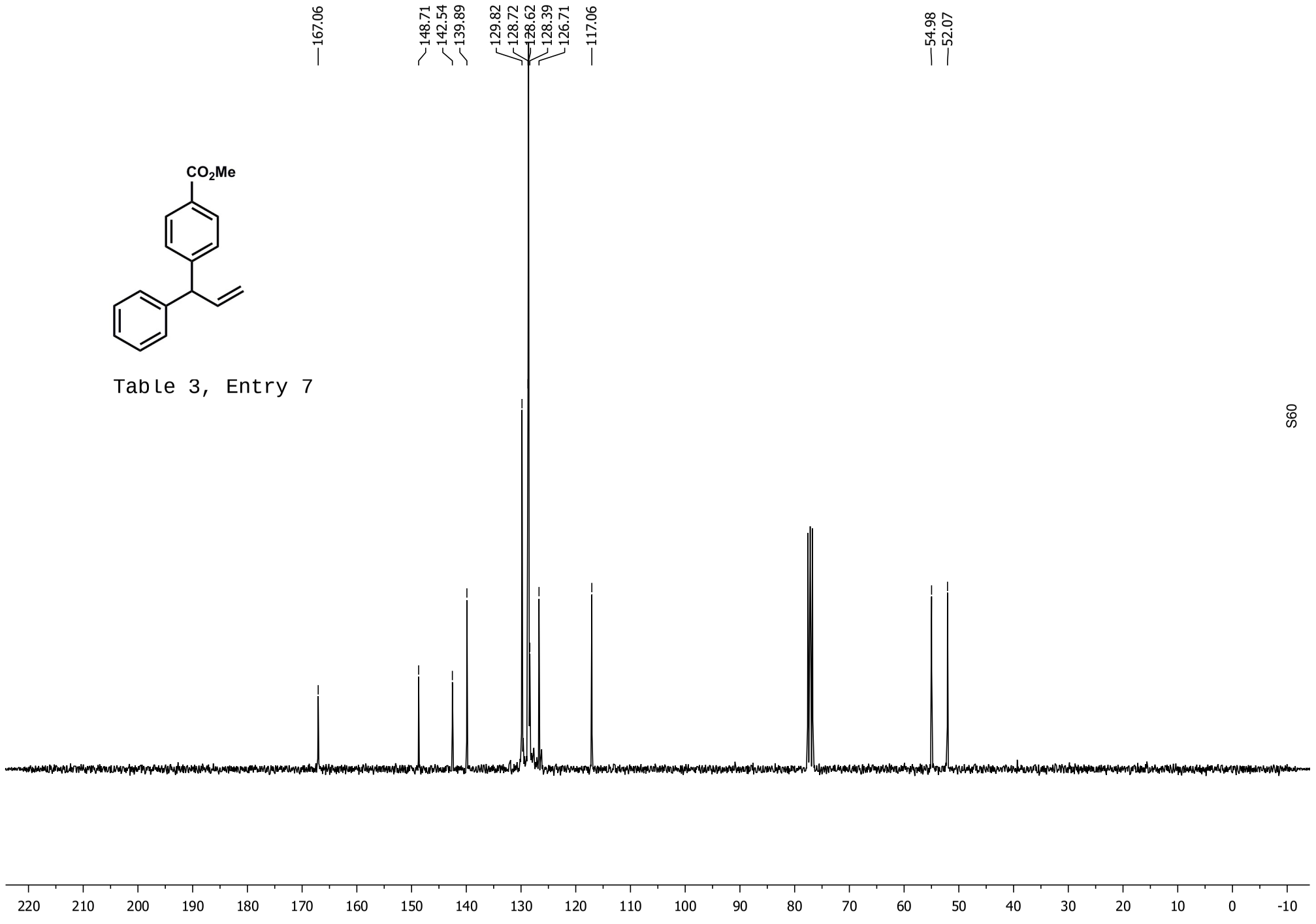
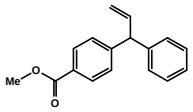


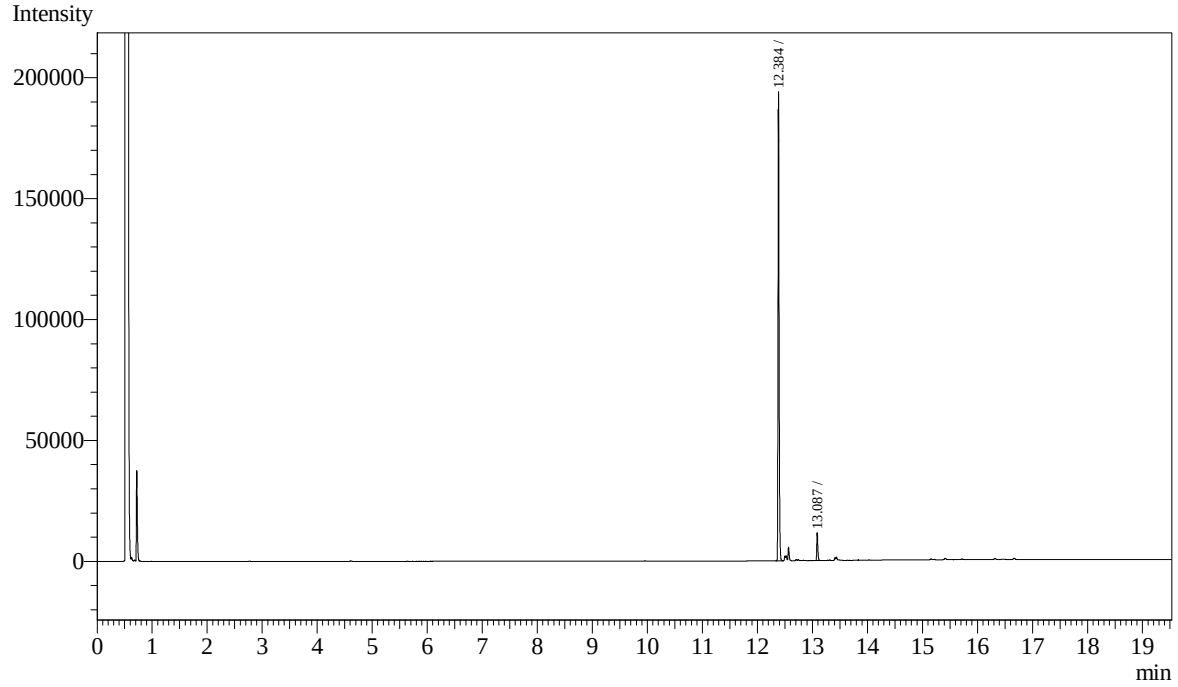
Table 3, Entry 7

Analysis Date & Time : 2/23/2010 4:22:28 PM
User Name : Admin
Vial# : 3
Sample Name : gl_2_052Bf
Sample ID : gl_2_052Bf
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :



Data Name : C:\GCsolution\Data\Gojko\gl_2_052\gl_2_052Bf.gcd
Method Name : C:\GCsolution\Data\Gojko\Methods\cinnamyl chlorides1.gcm

Table 3, Entry 7



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.384	257834	191131	94.416				
2	13.087	15249	11342	5.584				
Total		273083	202473					

gl_2_051a_c6d6

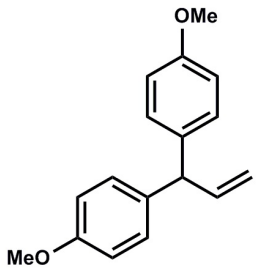


Table 3, Entry 8

S62

c_gl_2_051a_c6d6

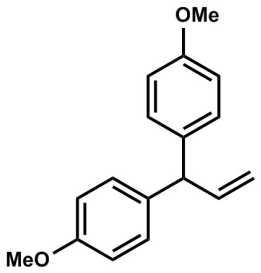


Table 3, Entry 8

Analysis Date & Time : 2/14/2010 4:05:48 PM
User Name : Admin
Vial# : 2
Sample Name : gl_2_051aF
Sample ID : gl_2_051aF
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

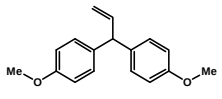
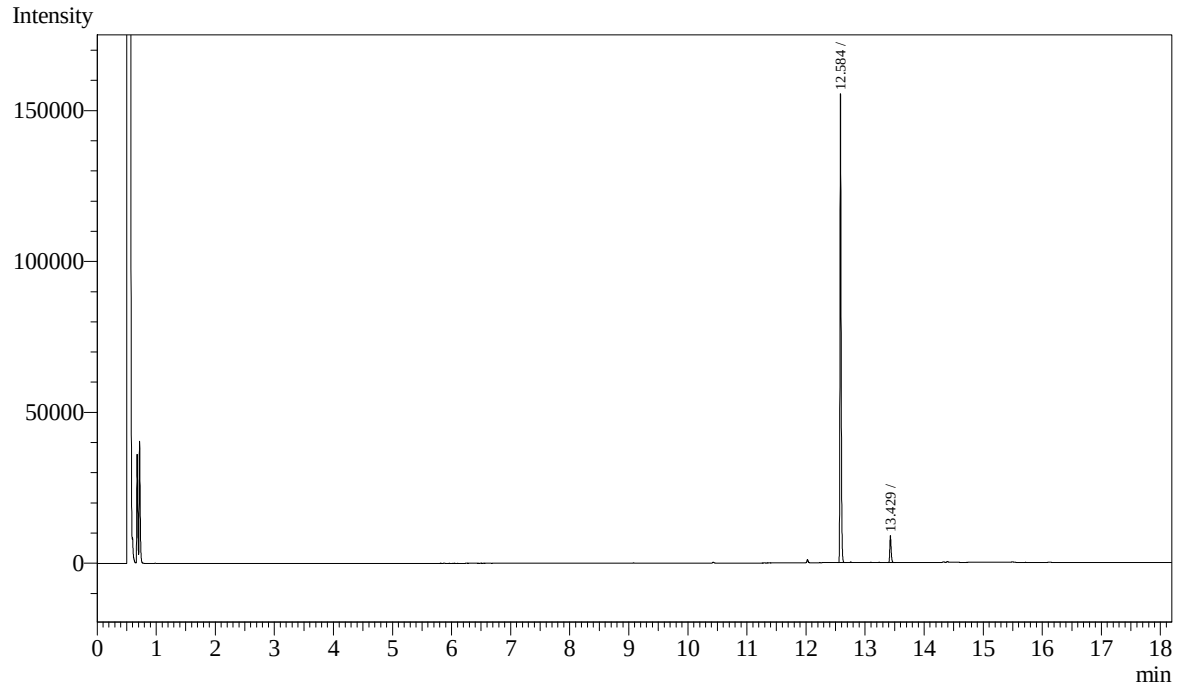


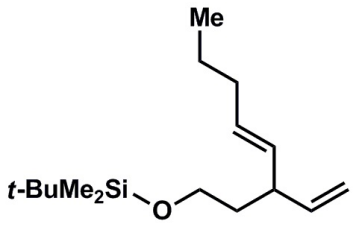
Table 3, Entry 8

Data Name : C:\GCsolution\Data\Gojko\gl_2_051\gl_2_051af.gcd
Method Name : C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



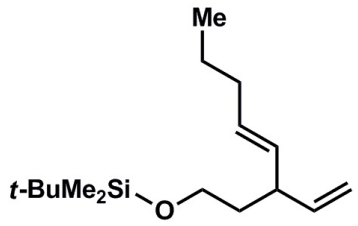
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	12.584	203741	151793	93.547				
2	13.429	14054	8856	6.453				
Total		217795	160649					

gl_2_076_1H



Equation 3

gl_2_076_13C

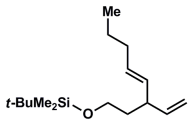


Equation 3

142.23
133.09
130.92
128.44
128.34
128.15
127.96
114.03
61.12
43.51
38.19
35.20
26.28
23.11
18.60
13.94
-5.03

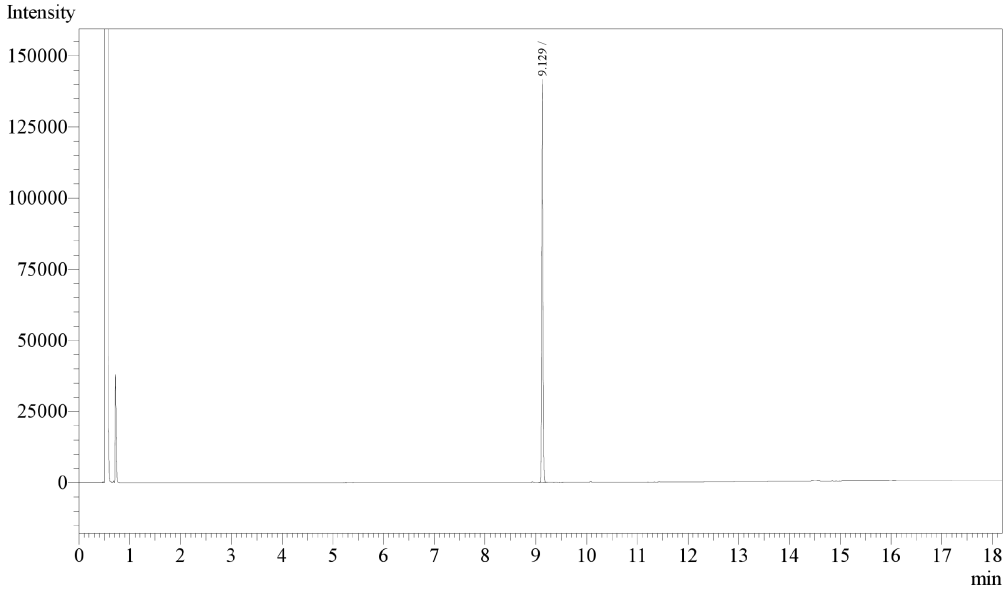
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Analysis Date & Time	: 3/15/2010 9:48:33 AM
User Name	: Admin
Vial#	: 2
Sample Name	: gl_2_76F
Sample ID	: gl_2_76F
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:

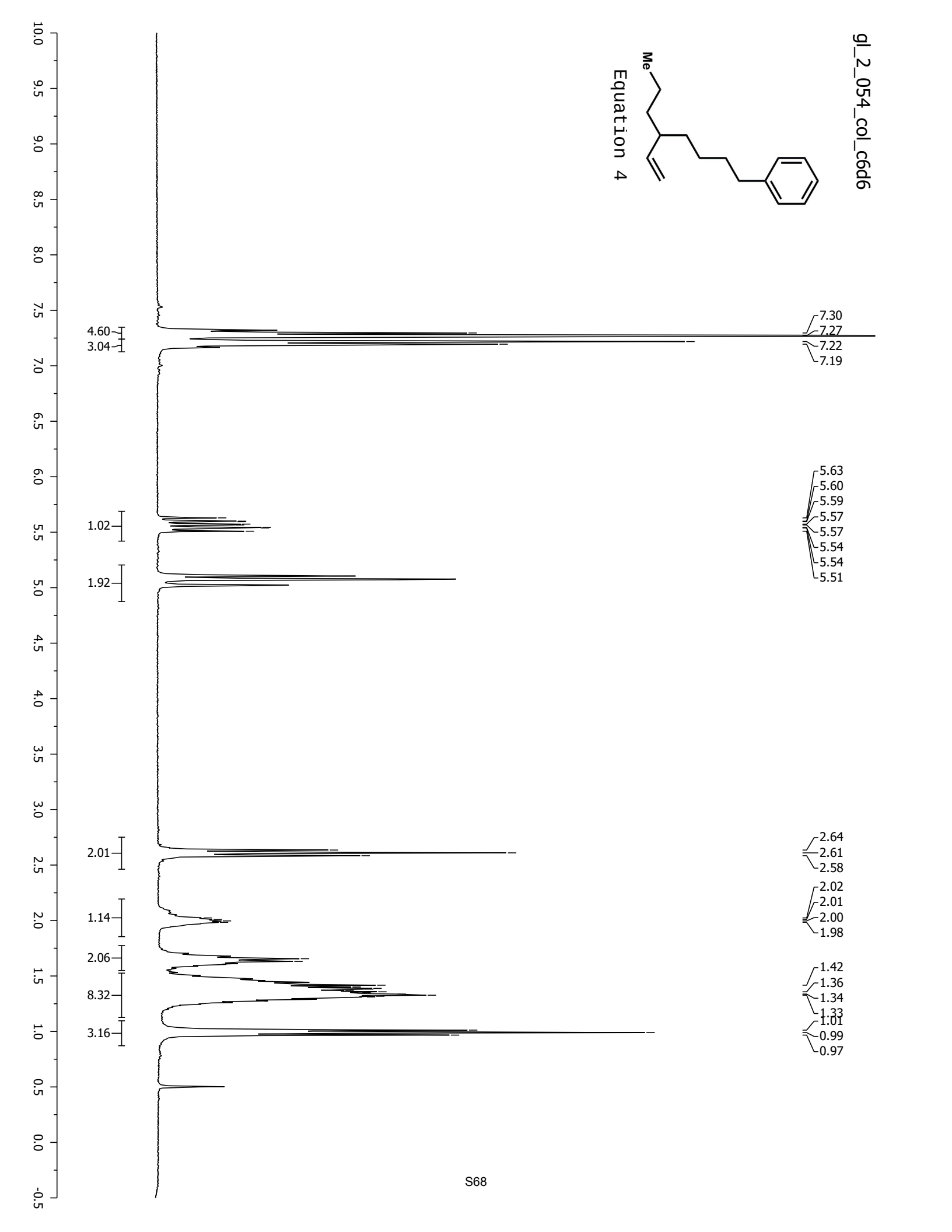


Equation 3

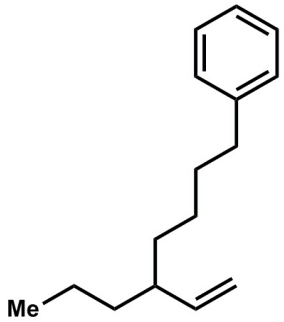
Data Name	: C:\GCsolution\Data\Gojko\gl_2_075-76\2_076F.gcd
Method Name	: C:\GCsolution\Data\Allylic Arylation\rpr_tolyl_sn2prime_sn2_shortened_II.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	9.129	254283	137504	100.000				
Total		254283	137504					


gl_2_054_col_c6d6
Equation 4
Me
7.30
7.27
7.22
7.19
5.63
5.60
5.59
5.57
5.57
5.54
5.54
5.51
2.64
2.61
2.58
2.02
2.01
2.00
1.98
1.42
1.36
1.34
1.33
1.01
0.99
0.97
4.60
3.04
1.02
1.92
2.01
1.14
2.06
8.32
3.16

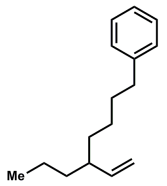
c_gl_2_054_cdcl3_col



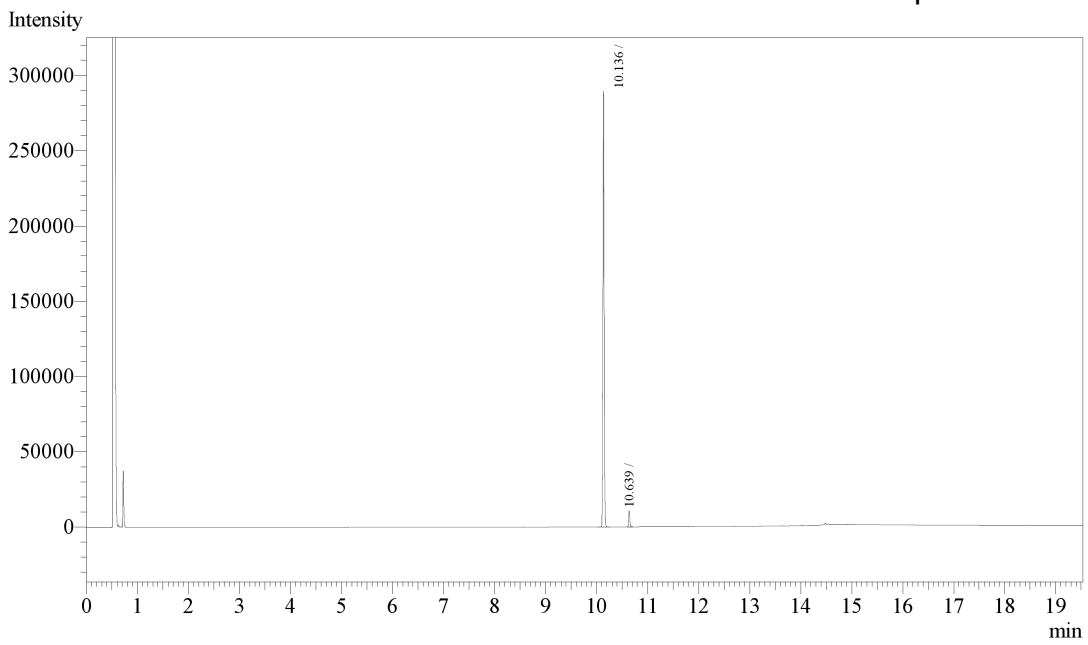
Equation 4

Analysis Date & Time : 2/23/2010 3:27:51 PM
User Name : Admin
Vial# : 1
Sample Name : gl_2_054F
Sample ID : gl_2_054F
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

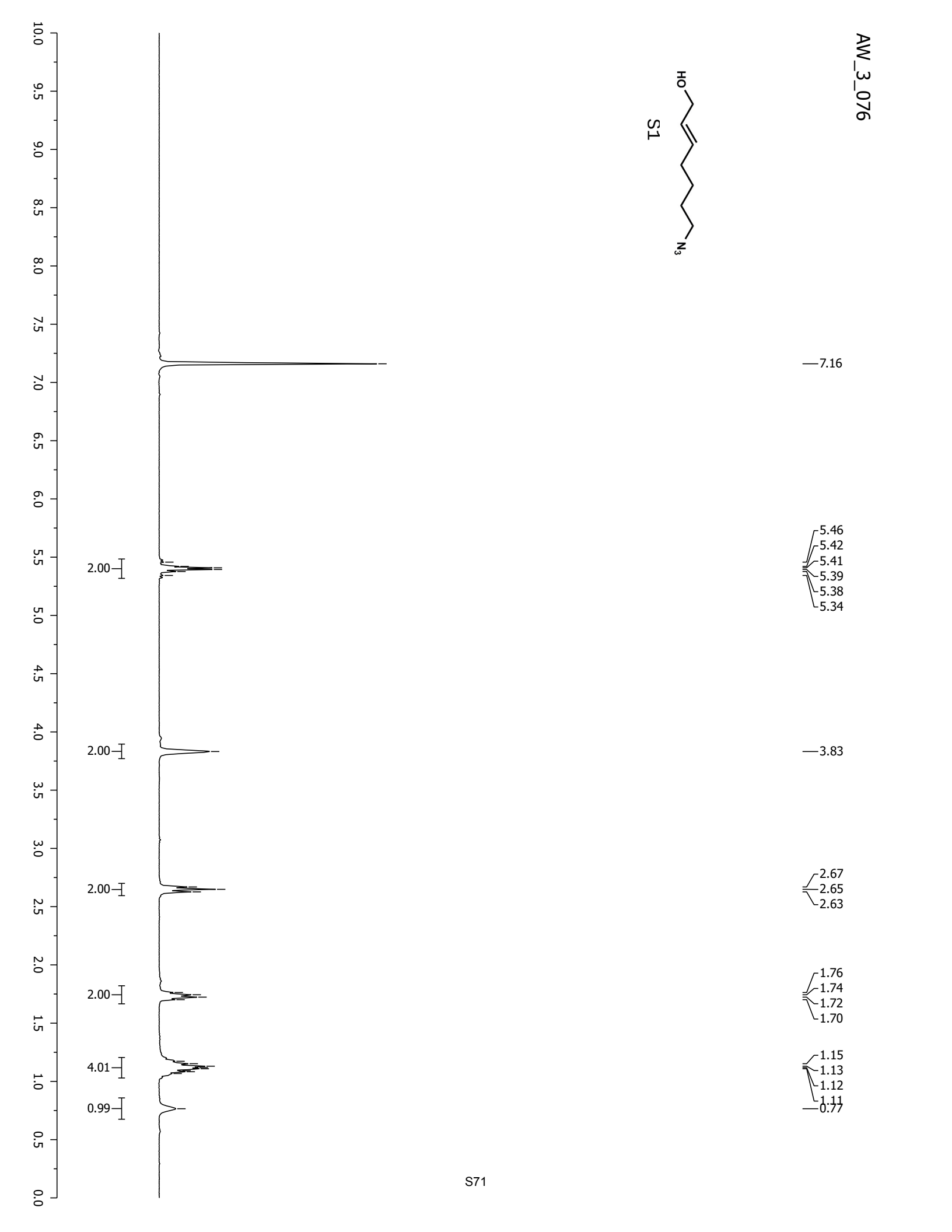
Data Name : C:\GCsolution\Data\Gojko\gl_054_055\gl_2_054F.gcd
Method Name : C:\GCsolution\Data\Gojko\Methods\cinnamyl chlorides1.gcm



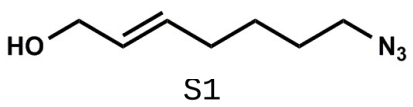
Equation 4



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	10.136	467477	280742	96.679				
2	10.639	16061	10543	3.321				
Total		483538	291285					

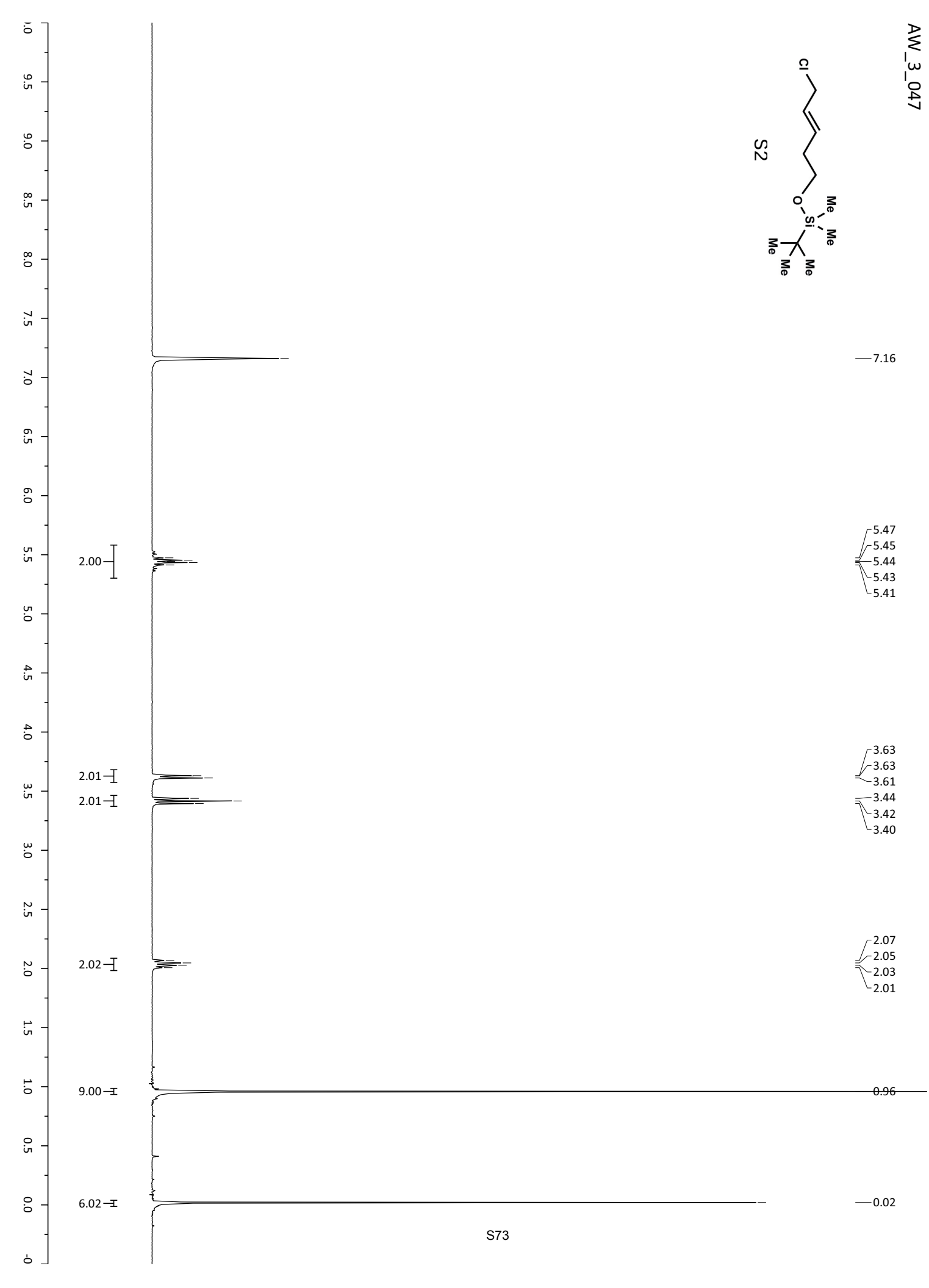

AW_3_076
S1
HO
N3
7.16
5.46
5.42
5.41
5.39
5.38
5.34
3.83
2.67
2.65
2.63
1.76
1.74
1.72
1.70
1.15
1.13
1.12
1.11
0.77
2.00
2.00
2.00
2.00
4.01
0.99

CAW_3_076

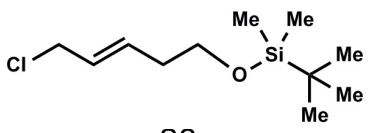

HO
N3

S1

132.3
129.7
63.7
51.4
31.7
28.4
26.2
S72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


AW_3_047
S2
Cl
O
Si
Me
Me
Me
Me
Me
7.16
5.47
5.45
5.44
5.43
5.41
3.63
3.63
3.61
3.44
3.42
3.40
2.07
2.05
2.03
2.01
0.96
0.02
2.00
2.01
2.01
2.02
9.00
6.02

CAW_3_047

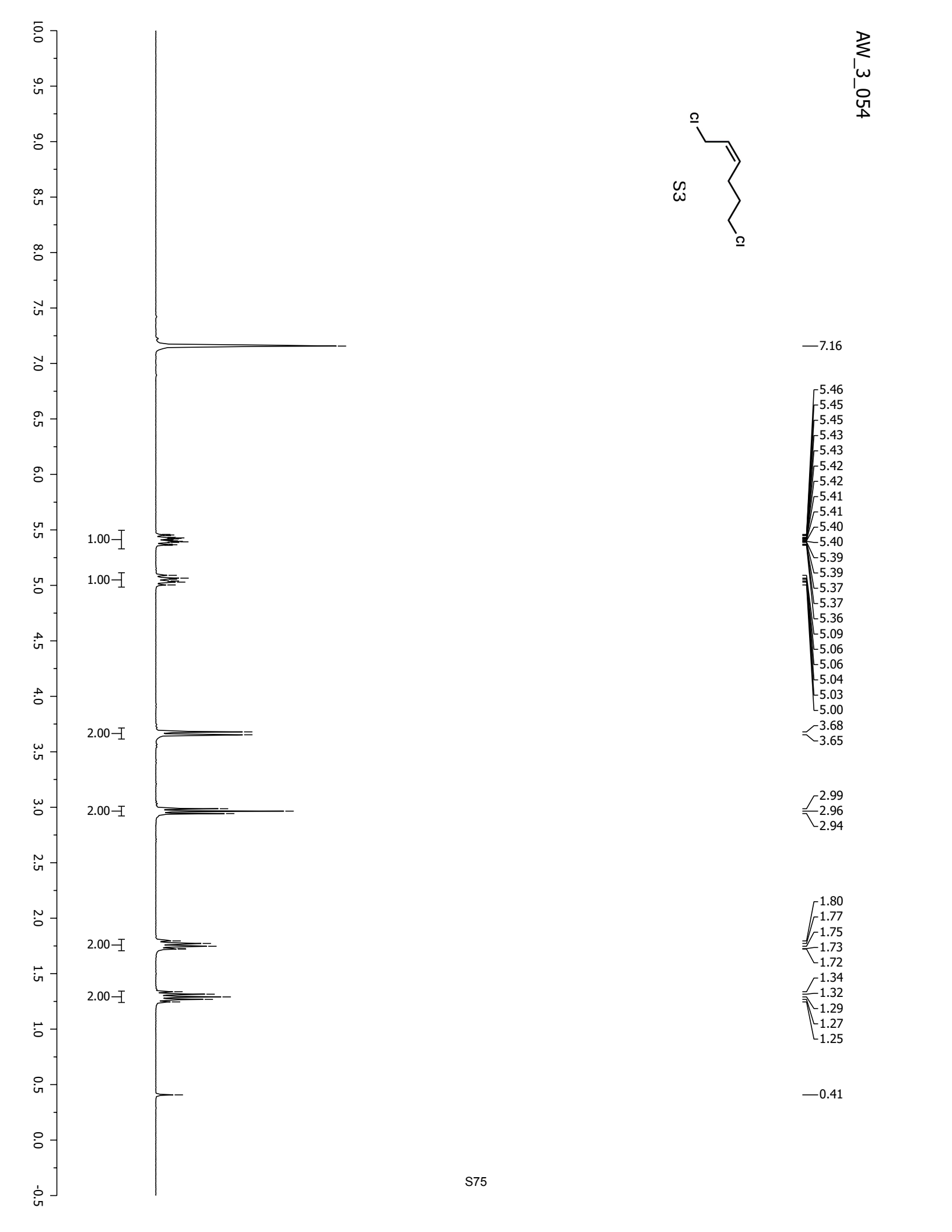


S2

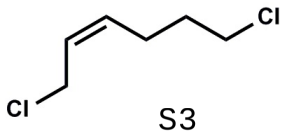
132.62
127.91
77.16
62.53
45.40
35.78
26.05
18.46
-5.15

S74

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

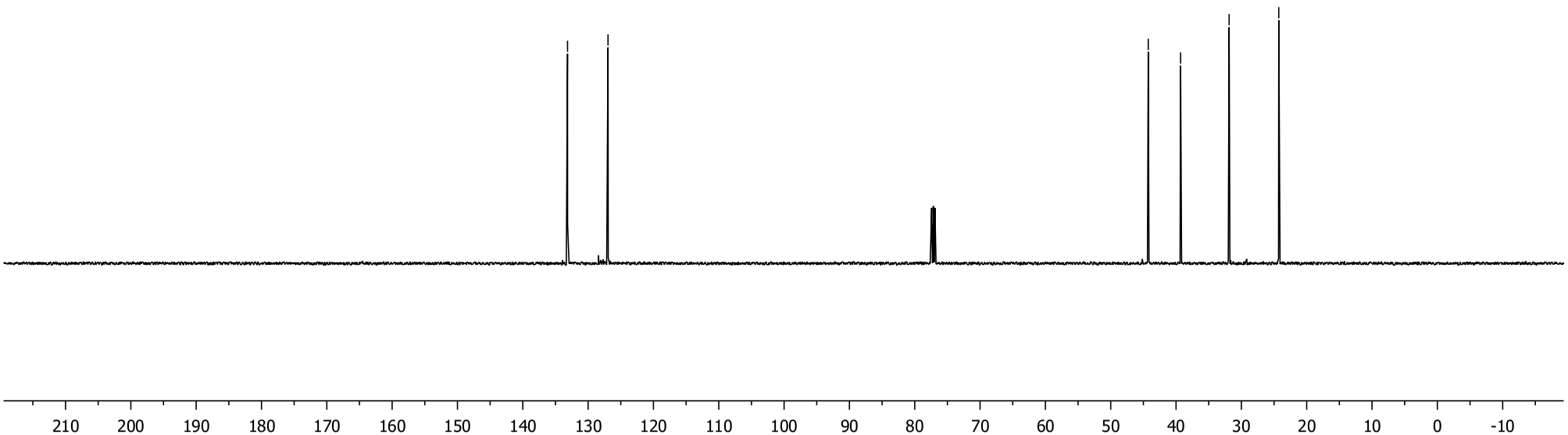

AW_3_054
S3
Cl
Cl
7.16
5.46
5.45
5.45
5.43
5.43
5.42
5.42
5.41
5.41
5.40
5.40
5.39
5.39
5.37
5.37
5.36
5.09
5.06
5.06
5.04
5.03
5.00
3.68
3.65
2.99
2.96
2.94
1.80
1.77
1.75
1.73
1.72
1.34
1.32
1.29
1.27
1.25
0.41
1.00
1.00
2.00
2.00
2.00
2.00

CAW_3_054

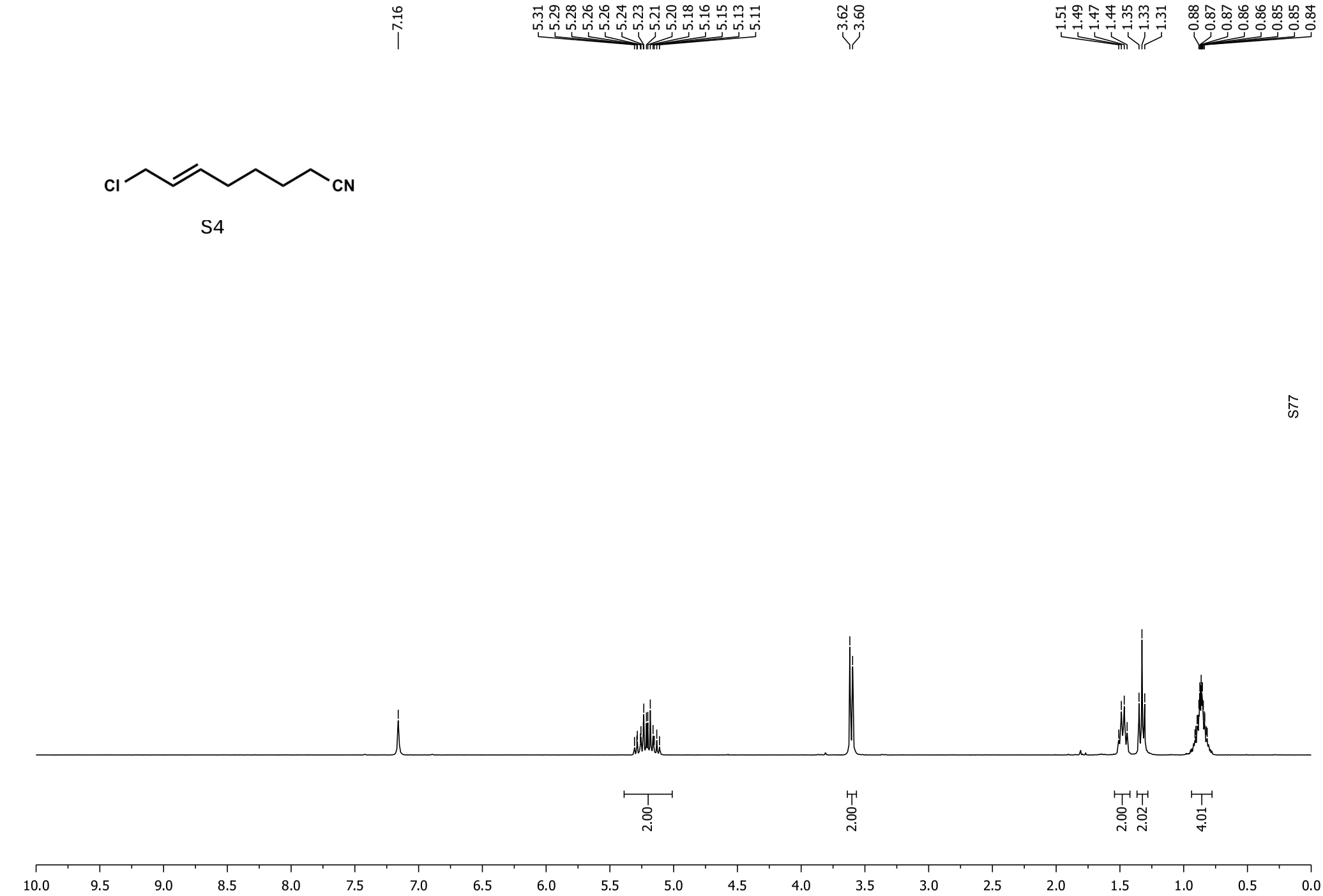


S3

133.2
127.0
44.3
39.3
31.9
24.3



AW_3_077

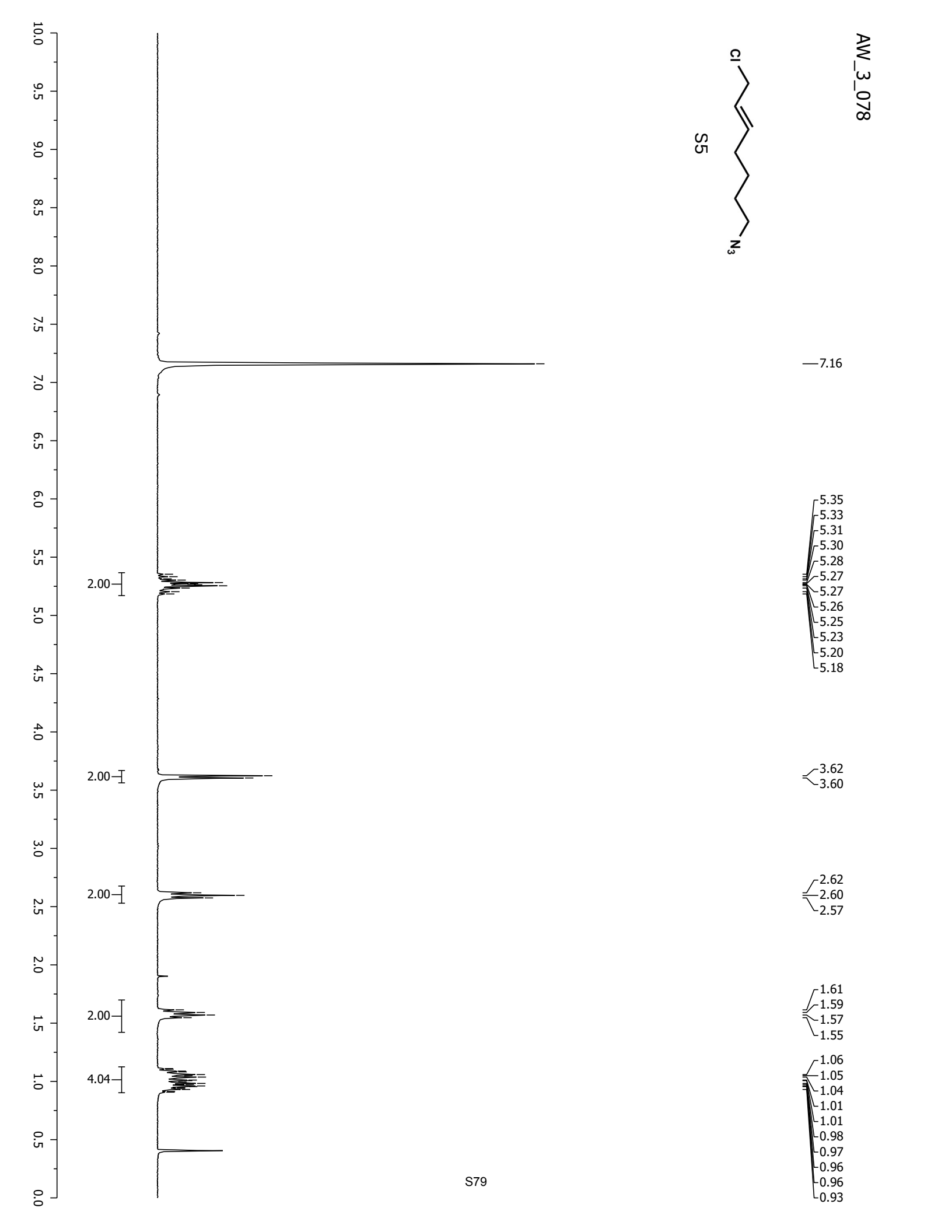

7.16
5.31
5.29
5.28
5.26
5.26
5.24
5.23
5.21
5.20
5.18
5.16
5.15
5.13
5.11
3.62
3.60
1.51
1.49
1.47
1.44
1.35
1.33
1.31
0.88
0.87
0.87
0.86
0.86
0.85
0.85
0.84
Cl
CN
S4
S77
2.00
2.00
2.00
2.02
4.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

CAW_3_077


Cl
CN

S4

134.5
127.0
119.6
45.1
31.1
27.7
24.7
17.0
S78
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


AW_3_078
S5
Cl
N3
7.16
5.35
5.33
5.31
5.30
5.28
5.27
5.27
5.26
5.25
5.23
5.20
5.18
3.62
3.60
2.62
2.60
2.57
1.61
1.59
1.57
1.55
1.06
1.05
1.04
1.01
1.01
0.98
0.97
0.96
0.96
0.93
2.00
2.00
2.00
2.00
4.04

CAW_3_078

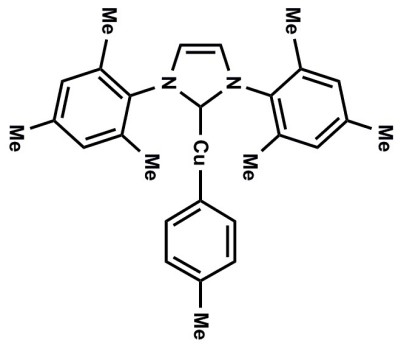

Cl
N3

S5

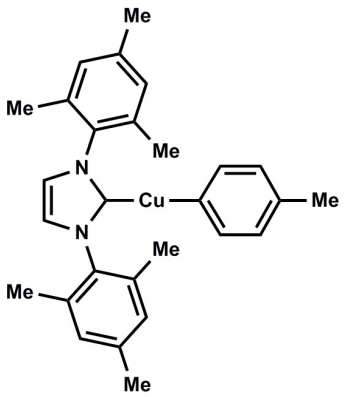
135.2
126.7
51.4
45.4
31.6
28.4
26.0
S80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

rpr_1_190_1H

11



rpr_2_13C_IMesCuTolyl_d8THF

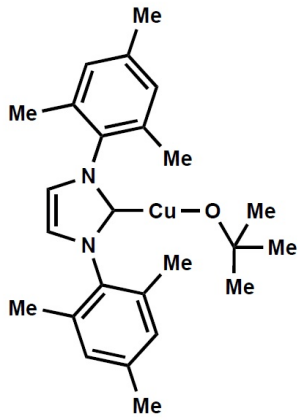


11

184.52
162.48
140.84
139.68
137.20
135.77
131.91
130.07
126.76
123.17
68.16
67.86
67.57
67.28
66.99
26.03
25.77
25.50
25.23
24.97
21.82
21.37
18.38

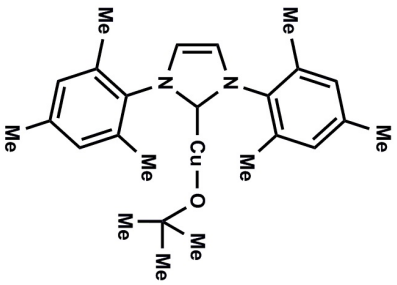
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

rpr_2_128_correctPgNo



10e

New folder



10e

182.31

139.67
137.31
135.92
130.00

123.20

67.92
67.75
67.57
67.39
67.22

36.85

25.99
25.82
25.66
25.50
25.34
25.18
21.33
18.24