Zr-CATALYZED ELECTROPHILIC CARBOMAGNESATION OF ARYL OLEFINS. MECHANISM-BASED CONTROL OF Zr-Mg LIGAND EXCHANGE

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Supporting Information

General. Infrared (IR) spectra were recorded on a Perkin-Elmer 781 spectrophotometer, υ_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on Varian Gemini 2000 (400 MHz) or Varian INOVA 500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; δ 7.26). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Gemini (100 MHz) or Varian INOVA 500 (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ77.7 ppm). Ratio of **2a** : **4a** and **3a** : **4a** were determined by integration of the benzylic proton (**2a** and **3a**; δ = 2.68) to the allylic proton (**4a**; δ = 2.45). Deuterium incorporation was determined by analysis of the m to the m + 1 ratio in the GC mass spectrum. Microanalyses were performed by Robertson Microlit Laboratories (Madison, NJ). High-resolution mass spectrometry was performed at the University of Illinois Mass Spectrometry Laboratories (Urbana, IL).

All reactions were conducted in oven- and flame-dried glassware under an inert atmosphere of dry nitrogen. Tetrahydrofuran and diethyl ether were purified by passage through two activated alumina columns under a positive pressure of inert gas (Ar). All Grignard reagents were prepared by using flame-dried Mg turnings purchased from Strem. Bis(cyclopentadienyl)zirconium dichloride (Boulder Scientific) was recrystallized from anhydrous toluene. Alkyl bromides (Aldrich) were distilled from anhydrous calcium chloride under nitrogen. Styrene and *p*-chlorostyrene (Aldrich) were distilled over calcium hydride. *o*-Methoxy- and *p*-methoxystyrene were prepared from the commercially available aldehydes through a Wittig reaction. Oxygen was passed through P_2O_5 and drierite as it was introduced into a reaction mixture. Benzaldehyde (Aldrich) was distilled from calcium hydride and N-bromosuccinamide (Aldrich) was recrystallized from water and subsequently dried over P_2O_5 under reduced pressure (0.2 mm).

Representative experimental procedure for the Zr-catalyzed alkylation of styrene with primary tosylates. A 10 mL flame-dried round bottom flask is charged with 1.00 x 10^2 mg (0.961 mmol) of styrene, 2.80 x 10^2 mg (1.09 mmol) of *n*-octyl tosylate and 3.80 mL of THF. Bis(cyclopentadienyl)zirconium dichloride (14.0 mg, 0.048 mmols) is then added in one portion, followed by the addition of 2-cyclohexylethyl magnesium chloride (1.92 mmol; 1.01 mL of a 1.81 M solution in THF). The resulting mixture is allowed to stir at 55 °C for 4.5 h. The mixture is then cooled to 0 °C and oxygen gas is gently introduced into the solution for 20 min (passed through a short column of drierite and P_2O_5). The resulting mixture is then diluted with 3.00 mL of water and washed with three 25 mL portions of diethyl ether. The combined organic layers are dried over $MgSO_4$, filtered and concentrated in vacuo to afford a pale yellow oil. This material was purified by silica gel chromatography (10:1 pentane : diethyl ether) to afford 146 mg of **10** as a colorless oil (0.623 mmol, 81.0% yield).

Representative experimental procedure for the Zr-catalyzed alkylation of styrene with secondary tosylates. (For secondary tosylates both the catalyst loading and Grignard reagent amount must be doubled for maximum efficiency.) A 10 mL flame-dried round bottom flask was charged with 1.00 x 10^2 mg (0.961 mmol) of styrene, 2.33 x 10^2 mg (1.09 mmol) of *i*-propyl tosylate, and 2.40 mL of THF. At this point, bis(cyclopentadienyl)zirconium dichloride (28.0 mg, 0.096 mmol) is added directly to the reaction solution in one portion, followed by 2-cyclohexylethyl magnesium chloride (3.82 mmol; 2.40 mL of a 1.59 M solution in THF). The resulting mixture is allowed to stir at 55 °C for 12 h. Typical aqueous workup affords a pale yellow oil, which is purified by silica gel chromatography (10:1 pentane : diethyl ether) to afford 115 mg of **13** as a colorless oil (0.700 mmol, 73.0% yield).

2-Phenyldecane (3a): IR (NaCl): 3027 (w), 2957 (s), 2925 (s), 2855 (s), 1604 (w), 1493 (m), 1453 (m), 1376 (w). ^{1}H NMR: δ 7.32-7.26 (2H, m), 7.21-7.15 (3H, m), 2.68 (1H, tq, *J* = 13.9, 7.0 Hz), 1.63-1.48 (2H, m), 1.34-1.10 (15H, m), 0.87 (3H, t, *J* = 6.8 Hz). ^{13}C NMR: δ 148.7, 128.9, 127.7, 126.4, 40.6, 39.1, 32.6, 30.4, 30.2, 30.0, 28.4, 23.4, 23.0, 14.8. HRMS Calcd for $C_{16}H_{26}$: 218.2035. Found: 218.2040. Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 88.18; H, 12.20.

2-(4-Methoxyphenyl)-decane (3b): IR (NaCl): 2955 (s), 2925 (s), 2855 (s), 1611 (m), 1584 (w), 1512 (s), 1464 (m), 1376 (w), 1301 (w), 1247 (s), 1177 (m). ^{1}H NMR: δ 7.10 (2H, d, *J* = 8.4 Hz), 6.84 (2H, d, *J* = 8.8 Hz), 3.79 (3H, s), 2.66-2.56 (1H, m), 1.76-1.60 (1H, m), 1.58-1.46 (2H, m), 1.34-1.14 (14H, m), 0.87 (3H, t, *J* = 7.0 Hz). ^{13}C NMR: δ 158.1, 140.7, 128.3, 114.2, 55.9, 39.8, 39.4, 32.7, 30.5, 30.4, 30.1, 28.5, 23.5, 23.4, 14.9. HRMS Calcd for $C_{17}H_{28}O$: 248.2140. Found: 248.2136. Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 81.87; H, 11.44.

2-(2-Methoxyphenyl)-decane (3c): IR (NaCl): 2962 (m), 2930 (s), 2855 (m), 1602 (w), 1495 (m), 1464 (w), 1287 (w), 1237 (m), 1036 (w). ^{1}H NMR: δ 7.20-7.12 (2H, m), 6.92 (1H, t, *J* = 7.3 Hz), 6.85 (1H, d, *J* = 8.0 Hz), 3.81 (3H, s), 3.22-3.12 (1H, m), 1.66-1.42 (3H, m), 1.34-1.08

(14H, m), 0.87 (3H, t, J = 6.8 Hz). ^{13}C NMR: δ 157.7, 137.0, 127.4, 127.1, 121.2, 111.1, 56.1, 37.8, 32.6, 32.4, 30.5, 30.3, 30.0, 28.4, 23.4, 21.7, 14.8. HRMS Calcd for $C_{17}H_{28}O$: 248.2140. Found: 248.2147. Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 81.86; H, 11.37.

2-(4-Chlorophenyl)-dec-1-ene (3d). IR (NaCl): 2925 (s), 2953 (m), 1492 (m), 1465 (w), 1094 (w), 1013 (w). ^{1}H NMR: δ 7.35-7.24 (5H, m), 5.24 (1H, s), 5.06 (1H, s), 2.45 (2H, t, J = 7.5 Hz), 1.47-1.15 (11H, m), 0.87 (3H, t, J = 6.9 Hz). ^{13}C NMR: δ 148.4, 140.6, 133.7, 129.0, 128.1, 113.2, 36.0, 32.5, 30.1, 30.0, 29.9, 28.6, 23.3, 14.8. HRMS Calcd for $C_{16}H_{23}Cl$: 250.1488. Found: 250.1488.

1-Bromo-2-phenyldecane (9). IR (NaCl): 3028 (w), 2925 (s), 1494 (w), 1453 (w). ^{1}H NMR: δ 7.33 (2H, t, J = 7.3 Hz), 7.29-7.22 (1H, m), 7.21-7.15 (2H, m), 3.56 (2H, d, J = 6.6 Hz), 2.97-2.89 (1H, m), 1.96-1.85 (1H, m), 1.68-1.57 (1H, m), 1.34-1.10 (12H, m), 0.86 (3H, t, J = 7.0 Hz). ^{13}C NMR: δ 143.1, 129.9, 128.2, 127.5, 48.9, 39.8, 34.9, 32.6, 30.3, 30.1, 30.0, 28.1, 23.5, 15.0. HRMS Calcd for $C_{16}H_{25}Br$: 296.1340. Found: 296.1140.

2-Phenyldecan-1-ol (10). IR (NaCl): 3347 (br), 2925 (s), 2855 (m), 1494 (w), 1453 (w), 1378 (w), 1042 (w). ^{1}H NMR: δ 7.35 (2H, dd, J = 7.8, 7.3 Hz), 7.28-7.21 (3H, m), 3.88-3.64 (2H, m), 2.80-2.71 (1H, m), 1.75-1.65 (1H, m), 1.63-1.54 (1H, m), 1.38-1.24 (12H, m), 0.88 (3H, t, J = 7.1 Hz). ^{13}C NMR: δ 143.2, 129.3, 128.7, 127.4, 68.3, 49.4, 32.7, 32.5, 30.4, 30.1, 29.9, 28.0, 23.3, 14.8. HRMS Calcd for $C_{16}H_{26}O$: 234.1984. Found: 234.1979. Anal. Calcd. for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.72; H, 10.99.

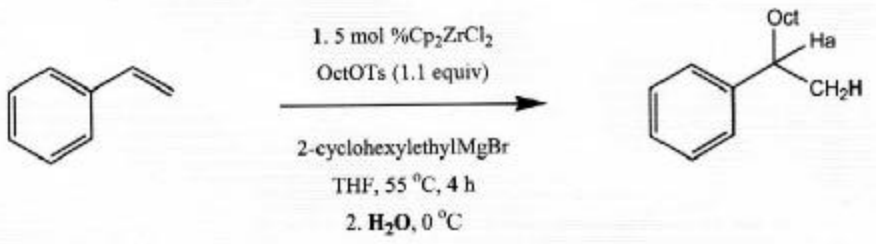
3-Phenylundecan-1-ol (11). IR (NaCl): 3323 (br), 3083 (w), 3062 (w), 3027 (m), 2925 (s), 2854 (s), 1603 (w), 1494 (m), 1454 (m), 1378 (w), 1051 (m). ^{1}H NMR: δ 7.31-7.24 (2H, m), 7.21-7.12 (3H, m), 3.56-3.40 (2H, m), 2.66 (1H, tt, J = 9.9, 4.9 Hz), 1.98-1.87 (1H, m), 1.83-1.73 (1H, m), 1.65-1.52 (2H, m), 1.31-1.05 (13H, m), 0.85 (3H, t, J = 7.0 Hz). ^{13}C NMR: 145.8, 128.9, 128.1, 126.6, 61.9, 43.3, 40.4, 37.8, 32.6, 30.5, 30.3, 30.0, 28.3, 23.4, 14.9. HRMS Calcd for $C_{17}H_{28}O$: 248.2140. Found: 248.2140. Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 81.88; H, 11.17.

1,3-Diphenylundecan-1-one (12).[1] IR (NaCl): 3061 (w), 3027 (w), 2923 (s), 2852 (s), 1721 (m), 1688 (s), 1598 (w), 1493 (w), 1449 (m), 1273 (m). ^{1}H NMR: δ 7.91-7.86 (2H, m), 7.54-7.49 (1H, m), 7.44-7.38 (1H, m), 7.29-7.14 (5H, m), 3.35-3.17 (3H, m), 1.75-1.56 (2H, m), 1.29-1.14 (12H, m), 0.84 (3H, t, J = 7.0 Hz). ^{13}C NMR: δ 199.9, 145.7, 138.0, 133.6, 129.2, 129.1, 128.7, 128.3, 126.9, 46.7, 42.0, 37.0, 32.5, 30.3, 30.1, 29.9, 28.2, 23.3, 14.8. HRMS Calcd for $C_{23}H_{30}O$: 322.2297. Found: 322.2295 Anal. Calcd. for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.34; H, 9.24.

1) After benzaldehyde is added, the reaction mixture is stirred for 12 h to allow complete oxidation to the ketone product (**12**).

3-Methyl-2-phenylbutan-1-ol (13). IR (NaCl): 3364 (br), 3028 (m), 2957 (s), 2927 (s), 2873 (s), 1607 (w), 1494 (m), 1451 (m), 1386 (m), 1367 (m), 1058 (s). ^{1}H NMR: δ 7.34-7.29 (2H, m), 7.26-7.13 (3H, m), 3.92 (1H, dd, *J* = 10.8, 4.8 Hz), 3.81 (1H, dd, *J* = 10.8, 9.0 Hz), 2.49 (1H, td, *J* = 8.8, 4.8 Hz), 1.92 (1H, 2dq, *J* = 8.7, 6.7 Hz), 1.00 (3H, d, *J* = 6.6 Hz), 0.73 (3H, d, *J* = 6.6 Hz). ^{13}C NMR: 142.4, 129.4, 129.2, 127.4, 65.9, 56.5, 30.8, 21.7. HRMS Calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1195. Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.44; H, 9.82.

2-Cyclohexyl-2-phenylethan-1-ol (14). IR (NaCl): 3371 (br), 3026 (w), 2924 (s), 2850 (m), 1493 (w), 1449 (w), 1045 (w). ^{1}H NMR: δ 7.33 (2H, t, *J* = 7.6 Hz), 7.24 (1H, t, *J* = 7.3 Hz), 7.21 (2H, d, *J* = 6.8 Hz), 3.98-3.95 (1H, m), 3.84 (1H, t, *J* = 10.0 Hz), 2.58 (1H, td, *J* = 8.8, 4.9 Hz), 1.89 (1H, d, *J* = 12.7 Hz), 1.75 (1H, d, *J* = 13.2 Hz), 1.66-1.54 (3H, m), 1.43 (1H, d, *J* = 11.7 Hz), 1.33-1.22 (1H, m), 1.20-1.10 (2H, m), 1.04 (1H, ddt, *J* = 12.7, 11.2, 3.5 Hz), 0.82 (1H, qd, *J* = 15.1, 2.9 Hz). ^{13}C NMR: δ 141.9, 129.0, 128.8, 126.9, 65.1, 55.0, 40.0, 31.6, 31.5, 26.7, 26.6, 26.5. HRMS Calcd for $C_{14}H_{20}O$: 204.1514. Found: 204.1508. Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.22; H, 9.78.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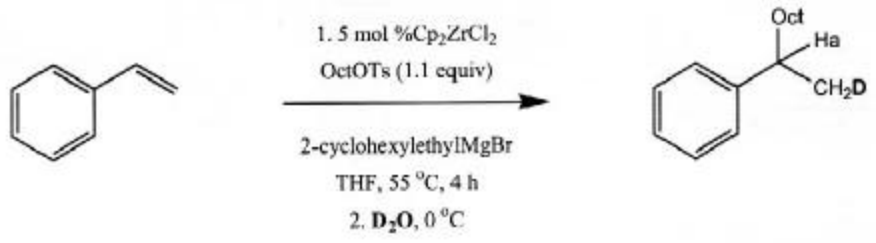
2. H2O, 0 °C
Oct
Ha
CH2H


C(Ha)
CH2H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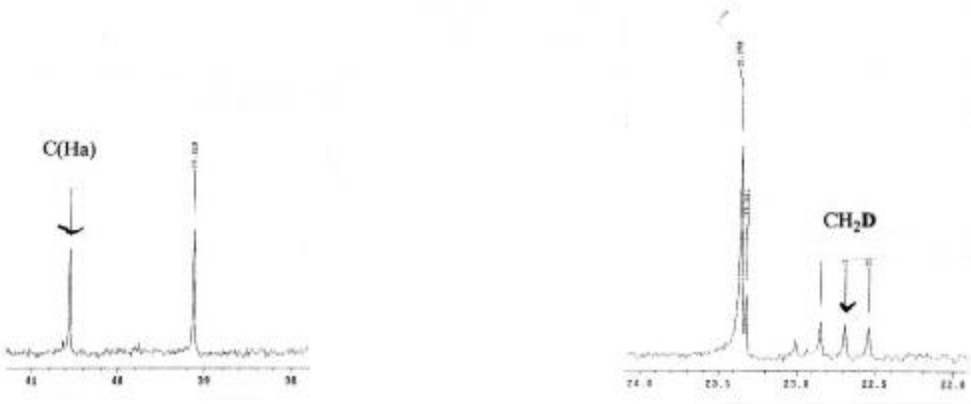
OctOTs (1.1 equiv)
2-cyclohexylethylMgBr
THF, 55 °C, 4 h
2. D2O, 0 °C
Oct
Ha
CH2D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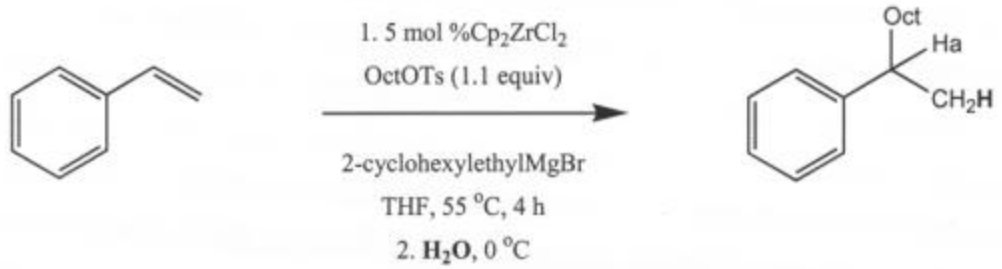
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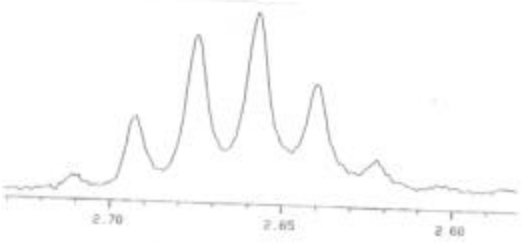
Oct
Ha
$CH_2\mathbf{H}$

Ha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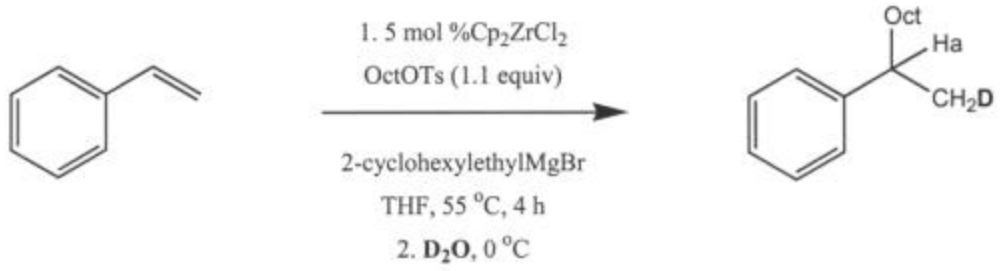
2.65
2.60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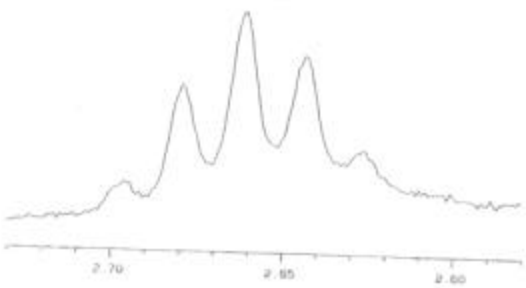
Oct
Ha
$CH_2\mathbf{D}$

Ha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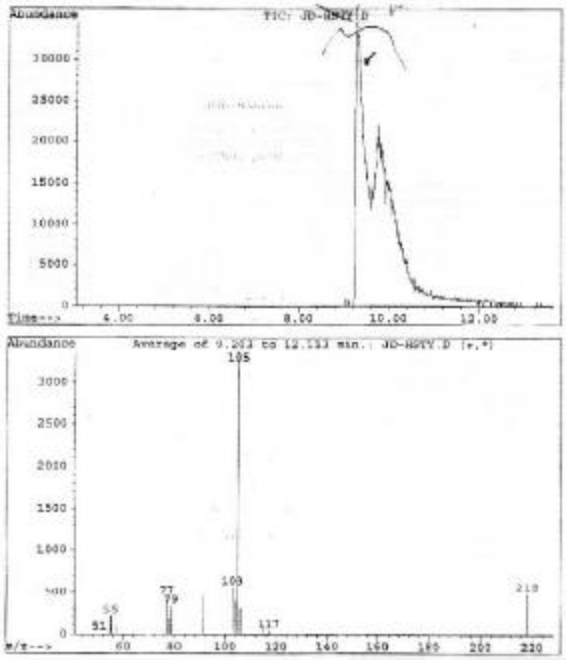
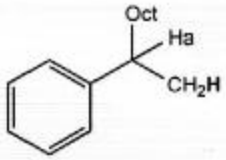
GC Mass Spectra of [1-^{1}H]-2-phenyldecane **(3a)**





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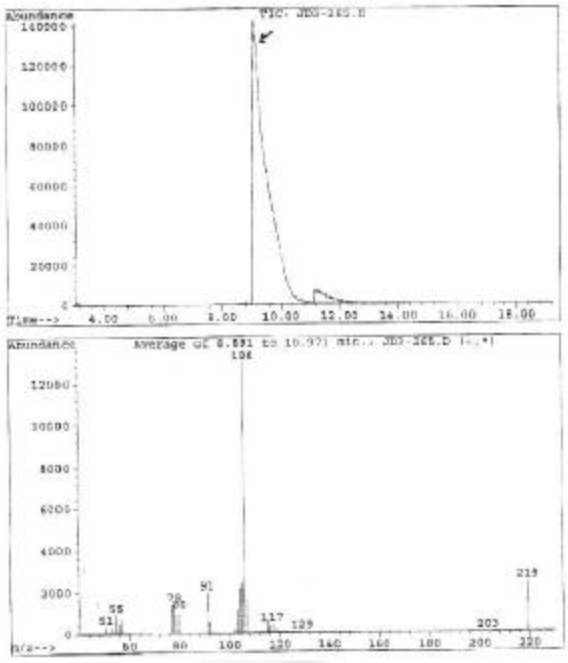
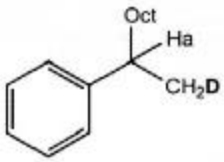
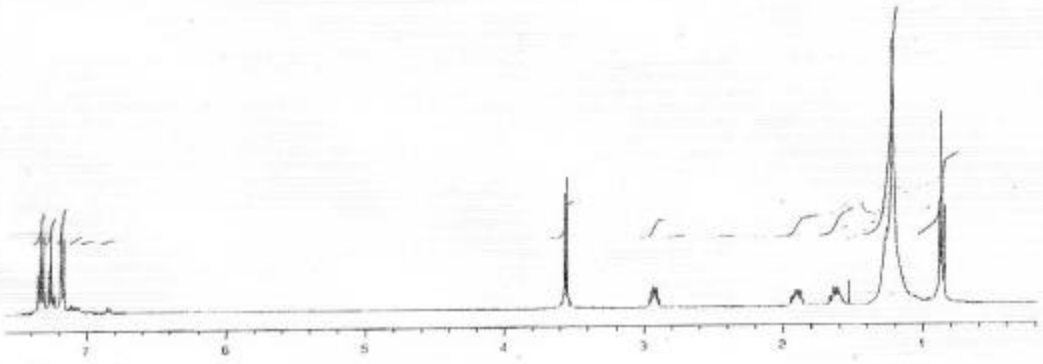




^{1}H NMR of **1-bromo-2-phenyldecane (9)**



^{13}C NMR of **1-bromo-2-phenyldecane (9)**