Supporting Information for:

t-Bu-Amphos/$RhCl_3$•$3H_2O$: a highly recyclable catalyst for the cross-coupling of aldehydes and aryl- and alkenylboronic acids in aqueous solvents

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General. All the experiments were carried out under nitrogen atmosphere using a dry box and Schlenk techniques unless noted. The coupling reactions were assembled in a dry box in screw-cap vials with a silicon/Teflon® septum or a round bottom flask sealed with a rubber septum. [Rh(acac)(coe)$_2$],[1] *t*-Bu-Amphos,[2] and TXPTS[3] were prepared as previously described. $RhCl_3 \bullet 3H_2O$ and [RhCl(cod)]$_2$ were purchased from Aldrich and stored in a nitrogen filled drybox. TPPTS was purchased from Strem chemical company. All aldehydes and boronic acids were purchased from Aldrich and were used without further purification. Toluene was freshly distilled from sodium under nitrogen prior to use. Water (deionized) and acetonitrile were deoxygenated by sparging with nitrogen prior to use.

General procedure for catalyst optimization studies. Under nitrogen, a vial was charged with $RhCl_3 \bullet 3H_2O$ (1.2 mg, 5 μmol), ligand (5 μmol), sodium hydroxide (40 mg, 1.0 mmol), phenylboronic acid (91 mg, 0.75 mmol). To this was added deoxygenated 1:1 H_2O:CH_3CN (1.5 mL). Benzaldehyde (51 μL, 0.5 mmol) was added via syringe. The reactions were stirred vigorously at 80 °C for one hour and then allowed to cool to room temperature. Ethyl acetate (0.5 mL) and the internal standard, mesitylene (50 μL), were added to the reaction mixture *via* syringe. Yields were calculated using GC response factors determined with authentic samples of benzhydrol.

General procedure for the addition of organoboronic acids to aldehydes in 1:1 acetonitrile/water. In a drybox, a round bottom flask was charged with $RhCl_3 \bullet 3H_2O$ (2.4 mg, 0.01 mmol), *t*-Bu-Amphos (2.7 mg, 0.01 mmol), sodium hydroxide (40 mg, 1.0 mmol), organoboronic acid (1.5 mmol). The flask was sealed and removed from the drybox. Deoxygenated 1:1 CH_3CN/H_2O (5 m L) and aldehyde (1.0 mmol) were added *via* syringe and the reaction was stirred at 80 °C for 2 h. After the reaction was allowed to cool to room temperature,

saturated sodium bicarbonate (20 mL) was added to the reaction mixture. The resulting mixture was extracted with ethyl acetate (3 × 25 mL). The combined ethyl acetate extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude material was flash chromatographed on a short silica gel column.

Benzhydrol (Table 1, entry 1). The addition of phenylboronic (183 mg, 1.50 mmol) acid to benzaldehyde (102 μL, 1.0 mmol) was accomplished by the above procedure in 1:1 CH_3CN/H_2O or neat water (5 mL). The crude material was eluted with 10 % ethyl acetate in hexanes to give the product as a white solid (150.5 mg, 82 %; 142.8 mg 78 %). ^{1}H and ^{13}C NMR spectra ($CDCl_3$) were identical to the commercially available material (Aldrich).

4-Cyanobenzhydrol (Table 1, entry 2; Table 2, entry 4).[4] The addition of phenylboronic acid (183 mg, 1.50 mmol) to 4-cyanobenzaldehyde (131.1 mg, 1.0 mmol) was conducted by above procedure. The crude material was eluted with 2.5 % ethyl acetate in methylene chloride to give a pale yellow oil which solidified to an off white solid (179.6 mg, 86 %). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.59 (d, J = 8.32 Hz, 2H), 7.49 (d, J = 8.32 Hz, 2H), 7.40-7.20 (m, 5H), 5.83 (d, J = 3.33 Hz, 1H), 2.59 (d, J = 3.33 Hz, 1H). ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 149.0, 142.9, 132.4, 129.0, 128.4, 127.1, 126.8, 118.9, 111.2, 75.7. The NMR data was identical to that previously reported.

Alternatively, 4-cyanobenzhydrol was prepared using benzaldehyde (102 μL, 1.00 mmol) and 4-cyanophenylboronic acid (220 mg, 1.50 mmol). The product was recovered as described above (48.1 mg, 23%).

4-Bromobenzhydrol (Table 1, entry 3).[5] The addition of phenylboronic acid (183 mg, 1.50 mmol) to 4-bromobenzaldehyde (185 mg, 1.0 mmol) was realized by the above procedure. The crude material was purified by flash chromatography eluting with 10 % ethyl acetate in hexanes.

The product was recovered as a colorless syrup (203.6 mg, 77 %), which solidified to a white solid on standing. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.88 Hz, 2H), 7.37-7.27 (m, 5H), 7.24 (d, *J* = 8.33 Hz, 2H), 5.76 (d, J = 2.78 Hz, 1H), 2.70 (brs, 1H). ^{13} C NMR (90.6 MHz, $CDCl_3$): δ 143.6, 143.0, 131.6, 128.7, 128.4, 127.9, 126.7, 121.5, 75.7. The NMR data was identical to that previously reported.

4-Fluorobenzhydrol (Table 1, entry 4; Table 2, entry 3).[6] The addition of phenylboronic acid (183 mg, 1.50 mmol) to 4-fluorobenzaldehde (107 μL, 1.0 mmol) was accomplished by the above procedure. The crude material was flash chromatographed using 15 % ethyl acetate in hexanes to give a pale yellow oil as the product (156.6 mg, 78 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39-7.20 (m, 7H), 7.05-6.99 (dd, *J* = 8.82 Hz, *J* = 8.82 Hz, 2H), 5.78 (s, 1H), 2.38 (brs, 1H). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 162.3 (d, $^{1}J_{C\text{-}F}$ = 245.67 Hz) 143.8, 139.7, 128.7, 128.4 (d, $^{3}J_{C\text{-}F}$ = 7.63 Hz), 127.8, 126.6, 115.4 (d, $^{2}J_{C\text{-}F}$ = 21.37 Hz), 75.7. The NMR data was identical to that previously reported.

Alternatively, 4-fluorobenzhydrol was prepared using benzaldehyde (102 μL, 1.00 mmol) and 4-fluorophenylboronic acid (210 mg, 1.50 mmol). The product was recovered as described above (112.2 mg, 55%).

4-Methoxybenzhydrol (Table 1, entry 5; Table 2, entry 1).[7] The addition of phenylboronic acid (183 mg, 1.50 mmol) to 4-methoxybenzaldehyde (122 μL, 1.0 mmol) was accomplished by the above procedure. The crude material was flash chromatographed eluting with 15 % ethyl acetate in hexanes. The product was recovered as a pale yellow oil which solidified to an off white solid on standing (126.7 mg, 59 %). ^{1}H NMR ($CDCl_3$, 360 MHz): δ 7.38-7.29 (m, 5H), 7.27 (d, *J* = 9.45 Hz, 2H), 6.85 (d, *J* = 8.59 Hz, 2H), 5.78 (d, *J* = 3.44 Hz, 1H), 3.77 (s, 3H), 2.25 (d, *J* = 3.44 Hz, 1H); ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 159.2, 144.2,

136.3, 128.5, 128.0, 127.5, 126.5, 114.0, 75.9, 55.4. The NMR data was identical to that previously reported. mp: 64-66 ºC.

Alternatively, 4-methoxybenzhydrol was synthesized from benzaldehyde (102 μL, 1.0 mmol) and 4-methoxyphenylboronic acid (227.9 mg, 1.500 mmol) to give 169.2 mg of the product (79%).

2-Methylbenzhydrol (Table 1, entry 7; Table 2, entry 6).[5] The addition of phenylboronic acid (183 mg, 1.50 mmol) to 2-methylbenzaldehyde (115 μL, 1.0 mmol) was carried out by the above procedure. The crude material was flash chromatographed using 10 % ethyl acetate in hexanes. The product was recovered as an off white solid (153.6 mg, 78 %). ^{1}H NMR ($CDCl_3$, 360 MHz): δ 7.57-7.46 (m, 1H), 7.39-7.04 (m, 8H), 5.98 (d, J = 3.66 Hz, 1H), 2.24 (s, 3H), 2.16 (d, J = 3.66 Hz, 1H). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 143.0, 141.6, 135.5, 130.7, 128.6, 127.6, 127.3, 126.4, 126.2, 73.5, 19.5. mp: 88-91 ºC. The NMR data was identical to that previously reported.

Alternatively, 2-methylbenzhydrol was synthesized from benzaldehyde (102 μL, 1.0 mmol) and 2-tolylboronic acid (204mg, 1.50 mmol) to give 170.4 mg of the product (86%).

1-Phenyl-1-nonanol (Table 1, entry 8).[8] The addition of phenylboronic acid (183 mg, 1.50 mmol) to nonanal (156 μL, 1.0 mmol) was accomplished by the above procedure. The crude material was eluted by 10 % ethyl acetate in hexanes to give the product as a pale oil (102.1 mg, 50 %). ^{1}H NMR ($CDCl_3$, 360 MHz): δ 7.33-7.12 (m, 5H), 4.55 (t, J = 6.61 Hz, 1H), 1.99 (brs, 1H), 1.78-1.53 (m, 2H), 1.43-1.06 (m, 10H), 0.79 (t, J = 6.61 Hz, 3H). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 145.1, 128.5, 127.6, 126.0, 74.7, 39.2, 31.9, 29.6, 29.3, 25.9, 22.8, 14.2. The NMR data was identical to that previously reported.

Cyclohexyl(phenyl)methanol (Table 1, entry 9).[4] The addition of phenylboronic acid (183 mg, 1.50 mmol) to cyclohexanecarboxaldehyde (120 μL, 1.0 mmol) was accomplished by the above procedure. The crude material was eluted with 10 % ethyl acetate to give a colorless oil as the product (99.3 mg, 52 %). ^{1}H NMR ($CDCl_3$, 360 MHz): δ 7.32-7.07 (m, 5H), 4.24 (d, J = 7.32 Hz, 1H), 1.99 (brs, 1H), 1.88 (d, J = 10.98, 1H), 1.74-1.61 (m, 1H), 1.60-1.41 (m, 3H), 1.28 (d, J = 10.99 Hz, 1H), 1.21-0.73 (m, 5 H). ^{13}C NMR ($CDCl_3$, 90.6 MHz): δ 143.8, 128.2, 127.4, 126.7, 79.4, 45.0, 29.4, 28.9, 26.5, 26.2, 26.1. The NMR data was identical to that previously reported.

4-Cyano-4'-methoxybenzhydrol (Table 2, entry 2). The addition of 4-methoxyphenylboronic acid (228.0 mg, 1.5 mmol) to 4-cyanobenzaldehyde (131.1 mg, 1.0 mmol) was accomplished by the above procedure. The crude material was flash chromatographed eluting with 25 % ethyl acetate in hexanes. The product was recovered as a pale yellow oil (215.2 mg, 90 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, J = 8.59 Hz, 2H), 7.48 (d, J = 8.59 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.79 (s, 1H), 3.78 (s, 3H), 1.9 (brs, 1H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 159.5, 149.5, 135.4, 132.3, 128.2, 127.0, 119.0, 114.3, 110.9, 75.1, 55.4.

4-Carboxybenzhydrol (Table 2, entry 5).[9] The addition of 4-carboxyphenylboronic acid (248.9 mg, 1.5 mmol) to benzaldehyde (102 μL, 1.0 mmol) was realized by the above procedure. 10 % aqueous HCl (20 mL) was added to the reaction mixture upon completion. The reaction was worked up by the above procedure. The crude material was eluted with 5 % MeOH in CH_2Cl_2 to give a white solid (63 mg, 28 %). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.89 (brs, 1H), 7.88 (d, J = 8.28 Hz, 2H), 7.50 (d, J = 8.28 Hz, 2H), 7.38 (d, J = 8.26, 2H), 7.30 (t, J = 7.24, 2H), 7.21 (d, J = 7.24 Hz, 1H), 6.04 (brs, 1H), 5.78 (s, 1H). ^{13}C NMR (DMSO-d_6, 125.8 MHz): δ

167.2, 150.6, 145.1, 129.2, 128.2, 126.9, 126.3, 126.2, 73.9. ^{1}H NMR data was identical to that previously reported.

***E*-1-Phenyl-2-nonen-1-ol (Table 2, entry 7).**[10] The addition of *E*-1-octen-1-ylboronic acid (234.6 mg, 1.5 mmol) to benzaldehyde (102 μL, 1.00 mmol) was accomplished by the above procedure. The crude material was eluted with 10 % ethyl acetate in hexanes to give the product as a clear oil (184.5 mg, 84%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39-7.31 (m, 4H), 7.30-7.23 (m, 1H), 5.75 (dt, *J* = 14.62 Hz, 6.88 Hz, 1H), 5.65 (dd, *J* = 14.62Hz, 6.88 Hz, 1H), 5.15 (d, 6.88 Hz, 1H), 2.04 (dt, *J* = 6.88 Hz, 2H), 1.99 (brs, 1H), 1.42-1.22 (m, 8H), 0.87 (t, *J* = 6.88 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 143.6, 132.9, 132.4, 128.5, 127.5, 126.3, 75.3, 32.3, 31.8, 29.1, 29.0, 22.7, 14.2. The NMR data was identical to that previously reported.

***E*-1-(4-Cyanophenyl)-2-nonen-1-ol (Table 2, entry 8).** The addition of *E*-1-octen-1-ylboronic acid (234.6 mg, 1.5 mmol) to 4-cyanobenzaldehyde (131.1 mg, 1.0 mmol) was accomplished by the above procedure. The crude product was flash chromatographed eluting with 25 % ethyl acetate in hexanes to give a pale yellow oil as the product (172.3 mg, 71 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 5.80 (dt, *J* = 15.47, 6.88 Hz, 1H), 5.57 (dd, *J* = 15.47 Hz, 6.88 Hz, 1H), 5.20 (d, *J* = 6.88 Hz, 1H), 2.16 (brs, 1H), 2.05 (dt, *J* = 6.88 Hz, 2H), 1.46-1.19 (m, 8H), 0.87 (t, *J* = 6.88 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 148.7, 134.4, 132.3, 131.5, 126.9, 119.0, 111.1, 74.7, 32.2, 31.7, 29.0, 28.9, 22.7, 14.1.

***E*-1-(2-methylphenyl)-2-nonen-1-ol (Table 2, entry 9).** The addition of *E*-1-octen-1-ylboronic acid (234.6 mg, 1.5 mmol) to 2-methylbenzaldehyde (116 μL, 1.0 mmol) was accomplished by the above procedure. The crude material was flash chromatographed using 10 % ethyl acetate in hexanes to give a pale yellow oil as the product (169.4 mg, 73 %). ^{1}H NMR

($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 6.89 Hz, 1H), 7.26-7.10 (m, 3H), 5.70 (dt, *J* = 15.75 Hz, 5.91 Hz, 1H), 5.61 (dd, *J* = 15.75, 6.89 Hz, 1H), 5.34 (d, *J* = 6.89 Hz, 1H), 2.31 (s, 3H), 2.03 (dt, *J* = 6.89 Hz, 2H), 1.87 (brs, 1H), 1.41-1.20 (m, 8 H), 0.87 (t, *J* = 6.89 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 141.4, 135.2, 133.1, 131.4, 130.5, 127.4, 126.3, 125.6, 72.1, 32.4, 31.8, 29.2, 29.0, 22.7, 19.3, 14.2.

General procedure for catalyst recycling trials. Under nitrogen, a vial was charged with $RhCl_3•3H_2O$ (1.4 mg, 6 μmol), *t*-Bu-Amphos (1.6 mg, 6 μmol), sodium hydroxide (12 mg, 0.3 mmol), phenylboronic acid (40.2mg, 0.33 mmol). To this mixture was added deoxygenated water (1.5 mL). Benzaldehyde (31 μL, 0.3 mmol) was added via syringe. The reaction was run at 80 °C for 1 h. After the reaction mixture was cooled to room temperature, deoxygenated ethyl acetate (1 mL) was added and stirred for one minute. The upper organic layer was separated *via* cannula and mesitylene (30 μL) was added to this layer as an internal standard. The benzhydrol yield was then determined by GC. The remaining aqueous layer was transferred *via* cannula to a vial that was charged with fresh reactants (phenylboronic acid (0.33 mmol), sodium hydroxide (0.33 mmol), and benzaldehyde (0.3 mmol)) for the next catalytic cycle. This process was repeated for a total of nine cycles. After the 6th cycle, the aqueous phase was allowed to stand overnight to allow precipitated salts to settle. The aqueous supernatant was removed with a syringe and added to a fresh batch of reactants. The recycling study was continued for three more cycles.

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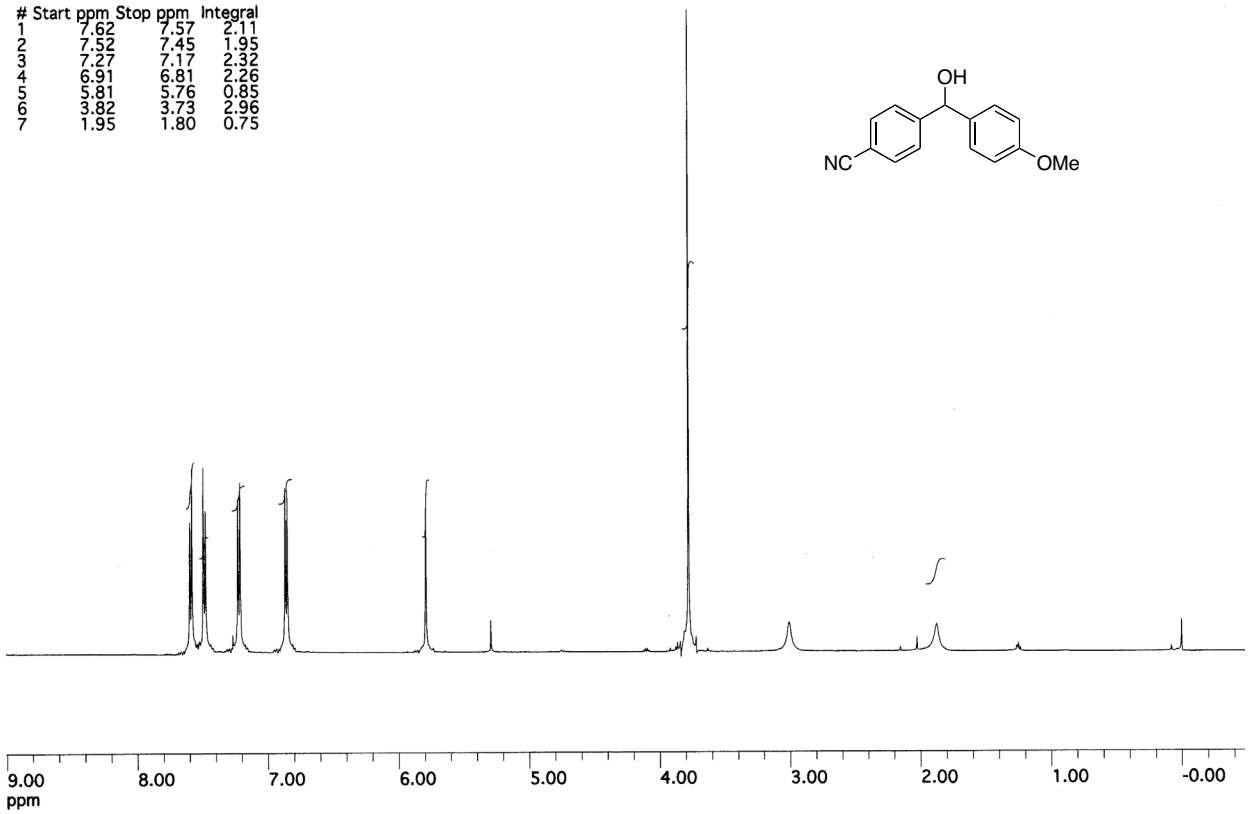
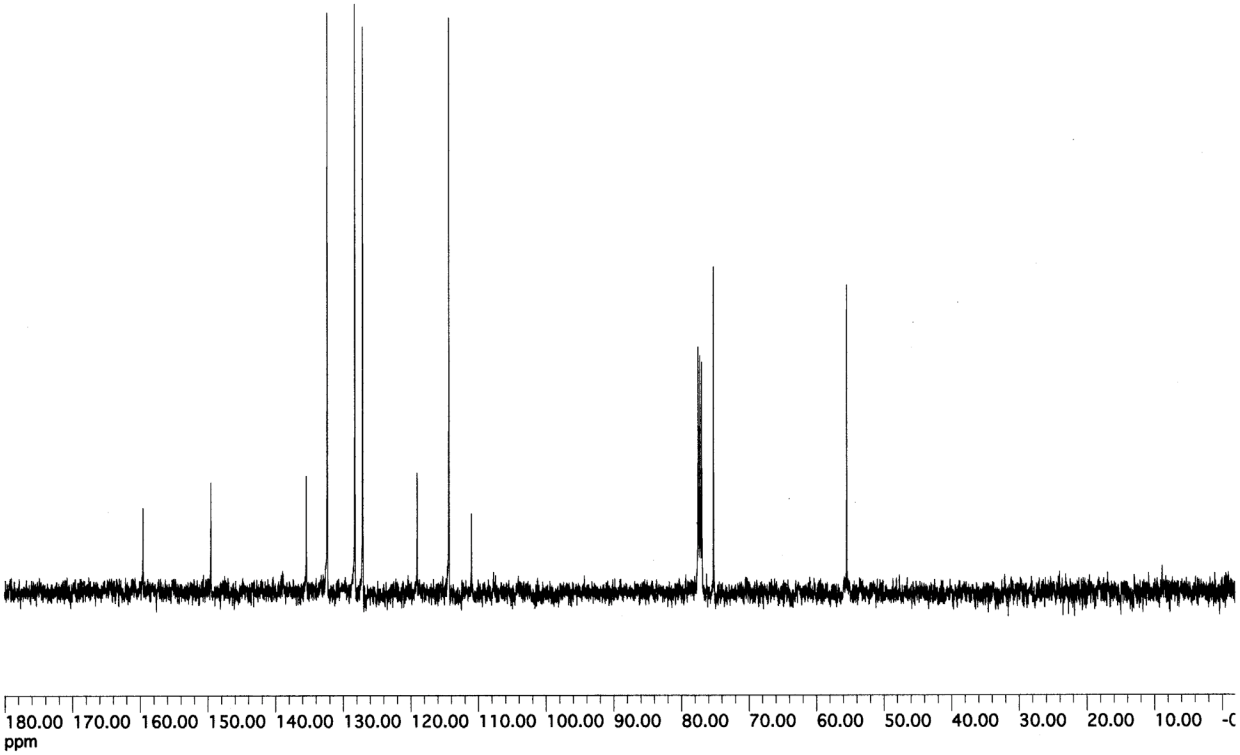
^{1}H NMR spectrum of 4-cyano-4'-methoxybenzydrol ($CDCl_3$, 500 MHz)

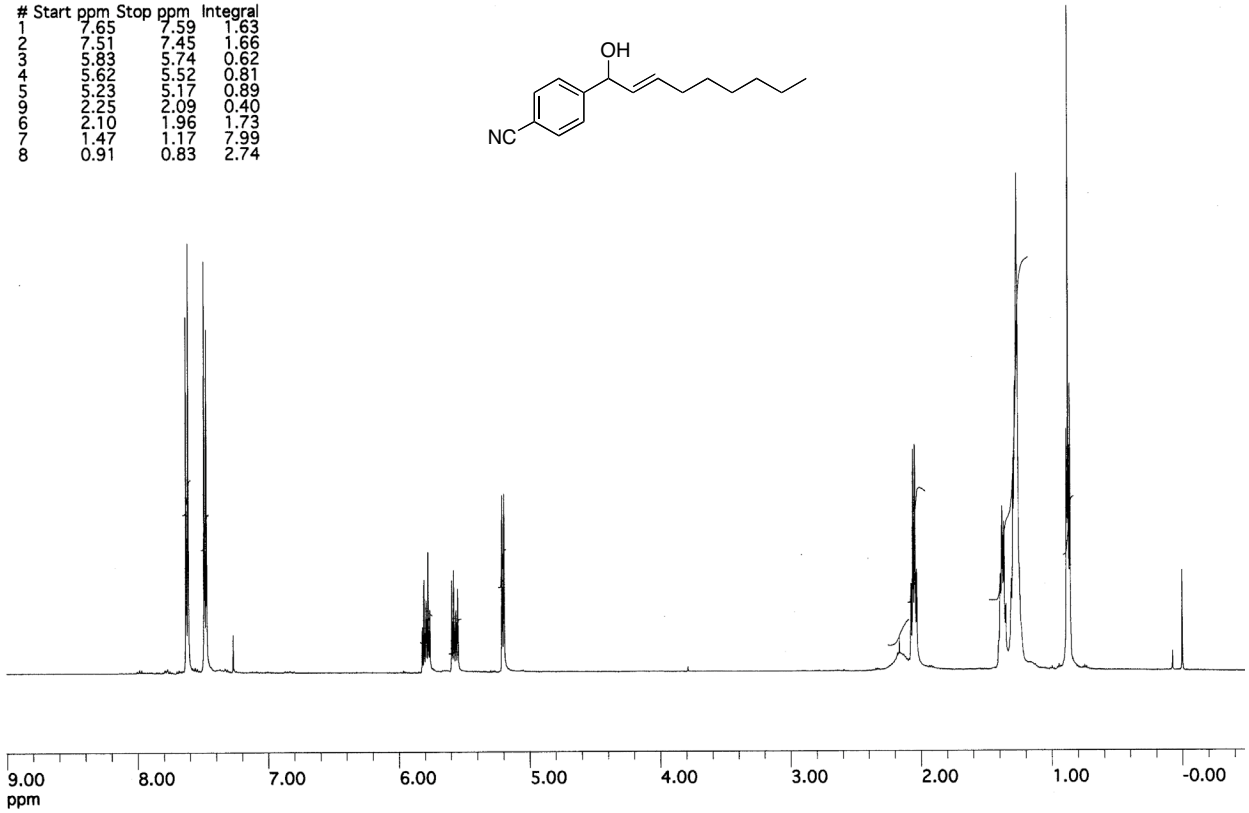


#	Start ppm	Stop ppm	Integral
1	7.62	7.57	2.11
2	7.52	7.45	1.95
3	7.27	7.17	2.32
4	6.91	6.81	2.26
5	5.81	5.76	0.85
6	3.82	3.73	2.96
7	1.95	1.80	0.75

^{13}C NMR spectrum of 4-cyano-4'-methoxybenzhydrol ($CDCl_3$, 125.8 MHz)

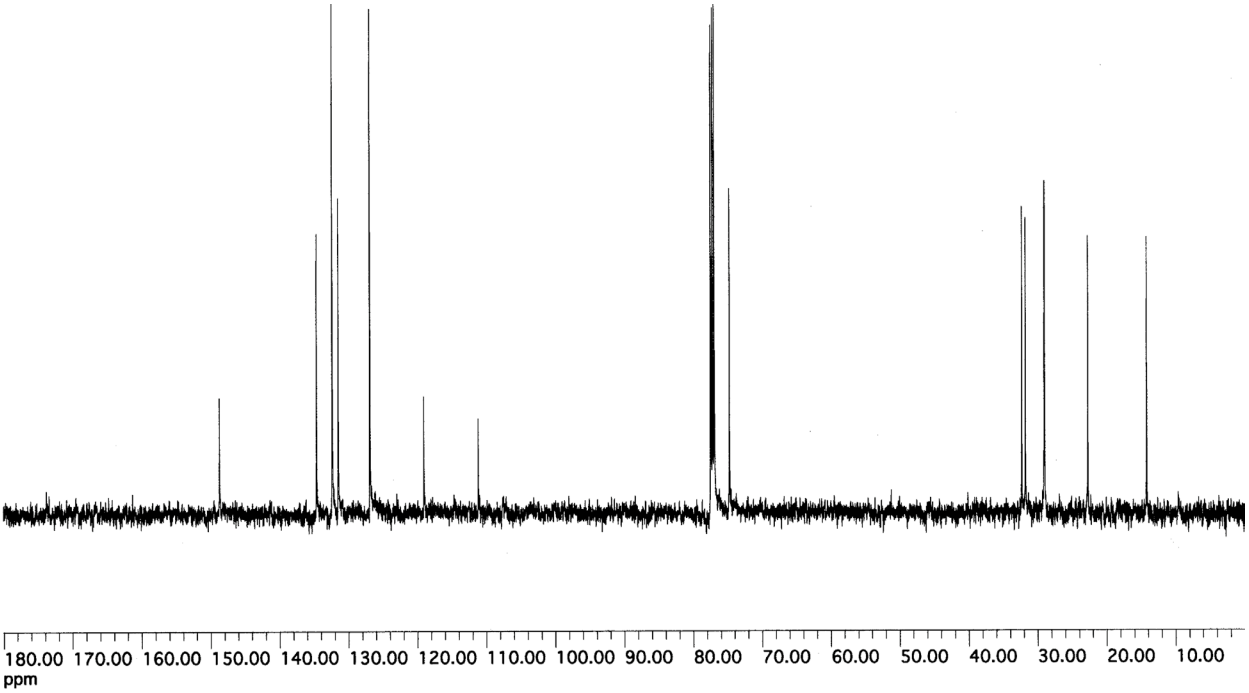


^{1}H NMR spectrum of *E*-1-(4-cyanophenyl)-2-nonen-1-ol ($CDCl_3$, 500 MHz)



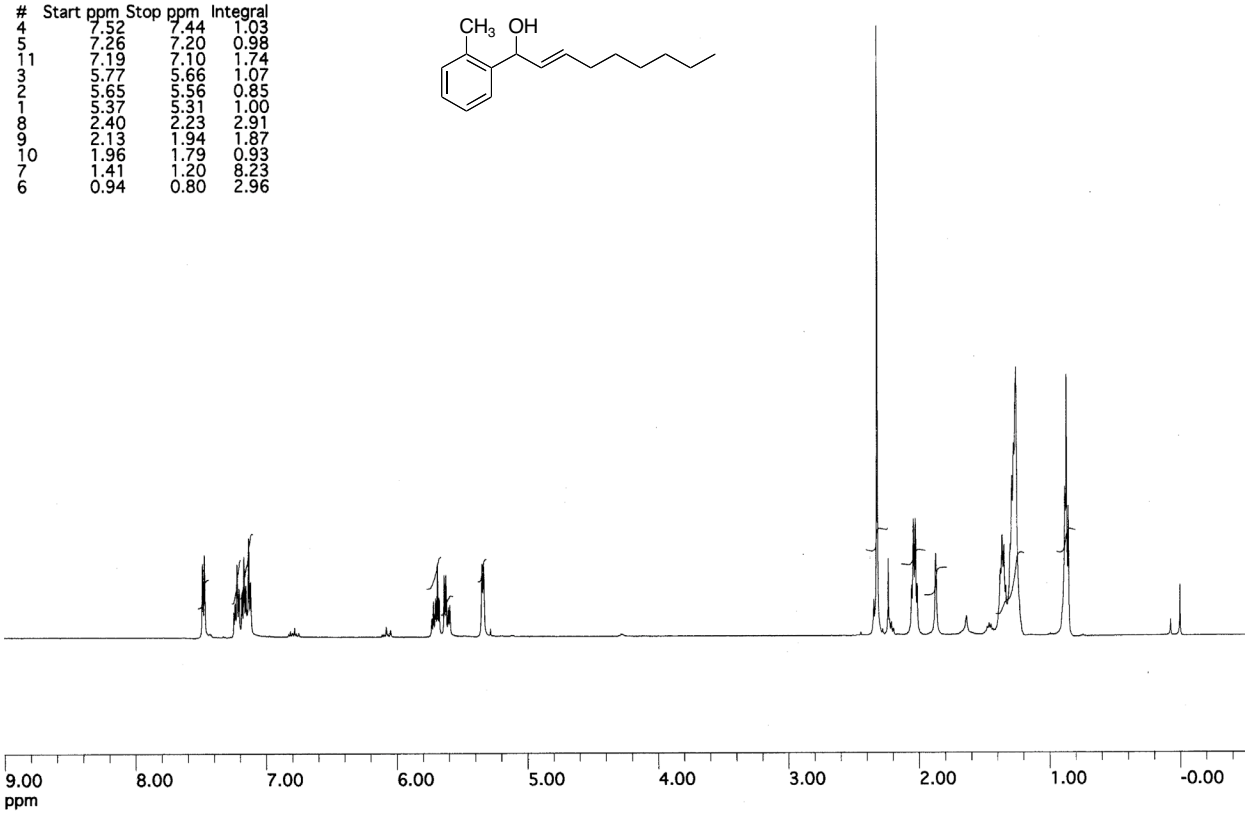
#	Start ppm	Stop ppm	Integral
1	7.65	7.59	1.63
2	7.51	7.45	1.66
3	5.83	5.74	0.62
4	5.62	5.52	0.81
5	5.23	5.17	0.89
9	2.25	2.09	0.40
6	2.10	1.96	1.73
7	1.47	1.17	7.99
8	0.91	0.83	2.74

^{13}C NMR spectrum of *E*-1-(4-cyanophenyl)-2-nonen-1-ol ($CDCl_3$, 125.8 MHz)



^{1}H NMR spectrum of *E*-1-(2-methylphenyl)-2-nonen-1-ol ($CDCl_3$, 500 MHz)

#	Start ppm	Stop ppm	Integral
4	7.52	7.44	1.03
5	7.26	7.20	0.98
11	7.19	7.10	1.74
3	5.77	5.66	1.07
2	5.65	5.56	0.85
1	5.37	5.31	1.00
8	2.40	2.23	2.91
9	2.13	1.94	1.87
10	1.96	1.79	0.93
7	1.41	1.20	8.23
6	0.94	0.80	2.96



^{13}C NMR spectrum of *E*-1-(2-methylphenyl)-2-nonen-1-ol ($CDCl_3$, 125.8 MHz)