

SUPPORTING INFORMATION

One-Pot Formation of Allylic Chlorides from Carbonyl Derivatives

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1. General Experimental Procedure:

All reagents and solvents were supplied from commercial sources mainly Sigma-Aldrich and Fluka and used as supplied unless otherwise indicated. Reactions requiring anhydrous conditions were conducted in glassware, which had been heated with a heat gun under dry N₂. All reactions were carried under dry N₂. All reactions were monitored by analytical thin-layer chromatography (TLC) performed using indicated solvent on E. Merck silica gel 60 F254 plates (0.25mm). TLC plates were visualized using UV light (254nm) and/or by staining in basic potassium permanganate KMnO₄ followed by heating.

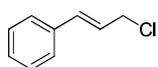
Solvents were removed by rotary evaporator below 50°C and the compounds further dried using low-pressure vacuum pumps. The purification of the compounds was achieved by column chromatography using Merck Flash Silica Gel 60 (230 – 400 mesh).

¹H and ¹³C NMR were recorded on a Bruker Advance 400 spectrophotometer at 400MHz. Chemical shifts (δ H) are quoted in ppm (parts per million) and referenced to CDCl₃ residual chloroform signal ¹H δ= 7.26, ¹³C δ= 77.0 or d6-DMSO residual dimethyl-sulphoxide signal ¹H δ= 2.54, ¹³C δ= 40.45.

2. General Procedure (A) for the synthesis of (3-chloroprop-1-enyl) substituted aromatic derivatives:

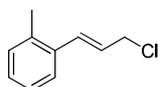
Benzaldehyde derivatives were diluted in dry THF (5 mL). Vinylmagnesium chloride (1 eq) was then added slowly at ambient temperature. The mixture was stirred and monitored by TLC. Following full consumption of the benzaldehyde derivative, the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. TiCl_4 (0.5 eq) was added and the reaction allowed to rise to ambient temperature, before warming to $80\text{ }^{\circ}\text{C}$. The reaction was stirred for several minutes at $80\text{ }^{\circ}\text{C}$, and then quenched with water (10 mL). AcOEt (10 mL) was added and the resulting phases separated. The organic layer was washed with water and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic phase was dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure followed by flash column chromatography (Silica, Eluent: Hexane/AcOEt 6/1) afforded (3-chloroprop-1-enyl) substituted aromatic derivatives.

(E)-(3-chloroprop-1-enyl)benzene (**11**):¹



Following the procedure A with benzaldehyde **7** (0.2 mL, 1.88 mmol), vinylmagnesium chloride 1.6 M (1.2 mL, 1.90 mmol) and titanium tetrachloride (0.1 mL, 0.95 mmol) gave the compound **11** (218 mg, 77%) as a pale yellow liquid: IR (ATR) 3083, 3027, 1644, 1579, 1488, 775 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.41 (m, 2H, Ar-H), 7.31-7.35 (m, 2H, Ar-H), 7.26-7.29 (m, 1H, Ar-H), 6.66 (d, $J = 15.6$ Hz, 1H, Ar-CH), 6.32 (dt, $J = 15.6, 7.2$ Hz, 1H, CH- CH_2Cl), 4.25 (dd, $J = 7.2, 1.2$ Hz, 2H, $\text{CH}_2\text{-Cl}$); ^{13}C NMR (100 MHz, CDCl_3) δ 135.5, 134.2, 128.6 (2C), 128.3, 126.7 (2C), 124.9, 45.4; MS (EI) m/z 152 (M); HRMS (EI) m/z calc for $\text{C}_9\text{H}_9\text{Cl}$ 152.0393, found: 152.0393.

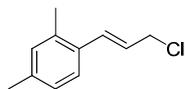
(E)-1-(3-chloroprop-1-enyl)-2-methylbenzene (**21**):



Following the procedure A with tolualdehyde **13** (0.2 mL, 1.66 mmol), vinylmagnesium chloride 1.6 M (1.06 mL, 1.70 mmol) and titanium tetrachloride (0.09 mL, 0.85 mmol) gave the compound **21** (184 mg, 67%) as a pale yellow liquid: IR (ATR) 2945, 1600, 1484, 749 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.46 (m, 1H, Ar-H), 7.14-7.20 (m, 3H, Ar-H), 6.88 (d, $J = 15.6$ Hz, 1H, Ar-CH), 6.21 (dt, $J = 15.6, 7.3$ Hz, 1H, CH- CH_2Cl), 4.27 (d, $J = 7.3$ Hz, 2H, $\text{CH}_2\text{-Cl}$), 2.36 (s, 3H, Ar- CH_3); ^{13}C NMR (100 MHz, DMSO) δ 135.4, 134.5, 131.3, 130.3, 128.0, 126.5, 126.1, 125.5, 45.9, 19.2; MS (EI) m/z 166 (M); HRMS (EI) m/z calc for $\text{C}_{10}\text{H}_{11}\text{Cl}$ 166.0549,

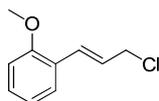
found: 166.0551.

(E)-1-(3-chloroprop-1-enyl)-2,4-dimethylbenzene (22):



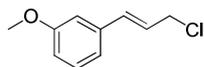
Following the procedure A with 2,4-dimethylbenzaldehyde **14** (0.2 mL, 1.49 mmol), vinylmagnesium chloride 1.6 M (0.94 mL, 1.50 mmol) and titanium tetrachloride (0.08 mL, 0.75 mmol) gave the compound **22** (195 mg, 73%) as a pale yellow liquid: IR (ATR) 3012, 2919, 1610, 1497, 630 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J=7.7$ Hz, 1H, Ar-*H*), 6.98-7.00 (m, 2H, Ar-*H*), 6.85 (d, $J=15.3$ Hz, 1H, Ar-*CH*), 6.18 (dt, $J=15.6, 7.0$ Hz, 1H, *CH-CH}_2\text{Cl}*), 4.26 (dd, $J=7.3, 1.0$ Hz, 2H, *CH}_2\text{-Cl}*), 2.32 (s, 3H, Ar-*CH}_3*), 2.31 (s, 3H, Ar-*CH}_3*); ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 135.7, 132.2, 132.0, 131.3, 127.0, 126.0, 125.4, 46.0, 21.2, 19.8; MS (EI) m/z 180 (M); HRMS (EI) m/z calc for $\text{C}_{11}\text{H}_{13}\text{Cl}$ 180.0706, found: 180.0709.

(E)-1-(3-chloroprop-1-enyl)-2-methoxybenzene (23):²



Following the procedure A with 2-methoxybenzaldehyde **15** (0.2 mL, 1.47 mmol), vinylmagnesium chloride 1.6 M (0.94 mL, 1.50 mmol) and titanium tetrachloride (0.08 mL, 0.75 mmol) gave the compound **23** (125 mg, 95% without purification) as a pale yellow liquid: IR (ATR) 2940, 1598, 1488, 1242, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J=7.7$ Hz, 1H, Ar-*H*), 7.23-7.27 (m, 1H, Ar-*H*), 6.97 (d, $J=15.8$ Hz, 1H, Ar-*CH*), 6.93 (t, $J=7.7$ Hz, 1H, Ar-*H*), 6.87 (d, $J=7.7$ Hz, 1H, Ar-*H*), 6.35 (dt, $J=15.8, 7.3$ Hz, 1H, *CH-CH}_2\text{Cl}*), 4.26 (d, $J=7.3$ Hz, 2H, *CH}_2\text{-Cl}*), 3.83 (s, 3H, O-*CH}_3*); ^{13}C NMR (100 MHz, CDCl_3) δ 157.1, 129.5, 129.3, 127.4, 125.7, 125.0, 120.8, 111.0, 55.6, 46.3; MS (EI) m/z 182 (M); HRMS (EI) m/z calc for $\text{C}_{10}\text{H}_{11}\text{ClO}$ 182.0498, found: 182.0497. Further purification (SiO_2) resulted in decomposition.

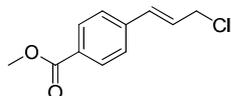
(E)-1-(3-chloroprop-1-enyl)-3-methoxybenzene (24):



Following the procedure A with 3-methoxybenzaldehyde **16** (0.2 mL, 1.47 mmol), vinylmagnesium chloride 1.6 M (0.94 mL, 1.50 mmol) and titanium tetrachloride (0.08 mL, 0.75 mmol) gave the compound **24** (127 mg, 59%) as a pale yellow liquid: IR (ATR) 1579, 1488, 776 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.25 (t, $J=8.0$ Hz, 1H, Ar-*H*), 6.99 (d, $J=7.7$ Hz, 1H, Ar-*H*), 6.93 (t, $J=1.8$ Hz, 1H, Ar-*H*), 6.83 (dd, $J=7.9, 2.4$ Hz, 1H, Ar-*H*), 6.63 (d, $J=15.6$ Hz, 1H, Ar-*CH*), 6.31 (dt, $J=15.6, 7.2$ Hz, 1H, *CH-CH}_2\text{Cl}*), 4.24 (dd, $J=7.2, 1.0$ Hz, 2H, *CH}_2\text{-Cl}*), 3.82 (s, 3H, O-*CH}_3*); ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 137.5, 134.2, 129.8, 125.4, 119.5, 114.1, 112.1, 55.4,

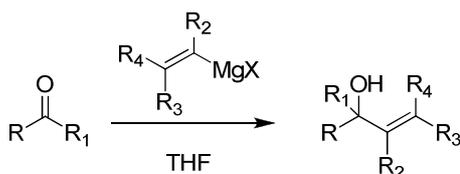
45.5; MS (EI) m/z 182 (M); HRMS (EI) m/z calc for $C_{10}H_{11}ClO$ 182.0498, found: 182.0497.

(E)-methyl 4-(3-chloroprop-1-enyl)benzoate (26):



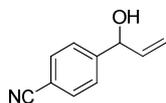
Following the procedure A with methyl 4-formylbenzoate **18** (200 mg, 1.22 mmol), vinylmagnesium chloride 1.6 M (0.77 mL, 1.23 mmol) and titanium tetrachloride (0.065 mL, 0.62 mmol) gave the compound **26** (194 mg, 76%) as a pale yellow solid: IR (ATR) 3043, 2956, 1716, 1431, 1104, 761 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J = 8.3$ Hz, 2H, Ar-*H*), 7.44 (d, $J = 8.3$ Hz, 2H, Ar-*H*), 6.69 (d, $J = 15.7$ Hz, 1H, Ar- CH_2), 6.43 (dt, $J = 15.7, 7.0$ Hz, 1H, $CH-CH_2Cl$), 4.25 (dd, $J = 7.0, 1.2$ Hz, 2H, CH_2Cl), 3.91 (s, 3H, O- CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 166.8, 140.5, 133.1, 130.1 (2C), 129.8, 127.6, 126.7 (2C), 52.2, 45.0; MS (CI) m/z 228 (M); HRMS (CI) m/z calc for $C_{11}H_{15}NO_2Cl$ 228.0791, found: 228.0799.

3. General Procedure (B) for the formation of allylic alcohols:

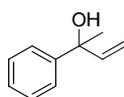


Benzaldehyde or ketone derivatives were diluted in dry THF (6 mL). The grignard reagent was added slowly at 0 °C. The mixture was stirred 30 min and allowed to warm to RT. The reaction was monitored by TLC. Following full consumption of the substrate, the mixture was quenched with a saturated solution of NH_4Cl (10 mL) and extracted with ether (3 x 10 mL). The combined organic phase was dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (Silica, Eluent: Hexane/AcOEt 4/1) afforded the alcohol derivatives.

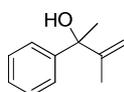
4-(1-hydroxyallyl)benzonitrile:³



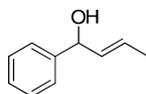
Following the procedure B with 4-formylbenzonitrile **17** (200 mg, 1.53 mmol), vinylmagnesium chloride 1.6 M (1.15 mL, 1.83 mmol) gave the compound (197 mg, 81%) as a pale yellow liquid: 1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, $J = 8.4, 1.7$ Hz, 2H, Ar-*H*), 7.49 (d, $J = 8.3$ Hz, 2H, Ar-*H*), 5.97 (ddd, $J = 16.2, 12.4, 3.8$ Hz, 1H, $CH-CH_2$), 5.37 (dt, $J = 17.1; 1.0$ Hz, 1H, CH_2), 5.23-5.26 (m, 2H, CH_2 and $CH-OH$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 139.4, 132.4 (2C), 127.0 (2C), 118.9, 116.7, 111.4, 74.8.

2-phenylbut-3-en-2-ol:³

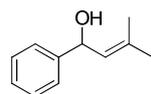
Following the procedure B with acetophenone (0.4 mL, 3.34 mmol), vinyl magnesium chloride 1.6 M (5 mL, 8.0 mmol) gave the compound (530 mg, 84%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.37 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.37 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 6.20 (dd, *J* = 17.2, 10.4 Hz, 1H, CH-CH₂), 5.32 (d, *J* = 17.2 Hz, 1H, CH₂), 5.17 (d, *J* = 10.8 Hz, 1H, CH₂), 1.08 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 144.9, 128.3 (2C), 127.0, 125.2 (2C), 112.4, 74.8, 29.4.

3-methyl-2-phenylbut-3-en-2-ol:⁴

Following the procedure B with acetophenone (1 mL, 8.35 mmol), isopropenylmagnesium bromide 0.5 M (30 mL, 15 mmol) gave the compound (1.2 g, 89%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.47 (m, 2H, Ar-*H*), 7.31-7.35 (m, 2H, Ar-*H*), 7.23-7.27 (m, 1H, Ar-*H*), 5.20-5.21 (m, 1H, CH₂), 4.96-4.98 (m, 1H, CH₂), 1.70 (s, 3H, CH₃-COH), 1.62-1.63 (m, 3H, CH₃-CCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 146.1, 128.3 (2C), 127.0, 125.4 (2C), 110.8, 77.1, 28.8, 19.2.

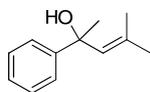
(*E*)-1-phenylbut-2-en-1-ol:⁵

Following the procedure B with crotonaldehyde (0.9 mL, 11 mmol), phenylmagnesium bromide 1 M (15 mL, 15 mmol) gave the compound (1.47 g, 90%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.38 (m, 4H, Ar-*H*), 7.24-7.29 (m, 1H, Ar-*H*), 5.66-5.80 (m, 2H, CH-CHCH₃ and CH-CH₃), 5.15 (dd, *J* = 6.3; 3.4 Hz, 1H, CH-OH), 1.93 (d, *J* = 3.6 Hz, 1H, OH), 1.72 (d, *J* = 5.9 Hz, 1H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 133.8, 129.7 (2C), 128.6, 127.6, 126.2 (2C), 75.3, 17.8.

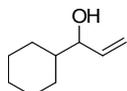
3-methyl-1-phenylbut-2-en-1-ol:⁶

Following the procedure B with benzaldehyde (0.6 mL, 5.64 mmol), 2-methyl-1-propenylmagnesium bromide 0.5 M (15 mL, 7.5 mmol) gave the compound (782 mg, 86%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.40 (m, 4H, Ar-*H*), 7.24-7.28 (m, 1H, Ar-*H*), 5.40 – 5.49 (m, 2H, CH-OH, CH-CHOH), 1.81 (s, 3H, CH₃), 1.76 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 135.4, 128.5 (2C), 127.7, 127.3, 125.8 (2C),

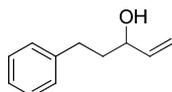
70.8, 25.9, 18.3.

4-methyl-2-phenylpent-3-en-2-ol:⁷

Following the procedure B with acetophenone (1 mL, 8.35 mmol), 2-methyl-1-propenylmagnesium bromide 0.5 M (30 mL, 15 mmol) gave the compound (1.37 g, 94%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.49 (m, 2H, Ar-H), 7.29-7.33 (m, 2H, Ar-H), 7.19-7.23 (m, 1H, Ar-H), 5.73 (s, 1H, CH), 1.74 (s, 3H, CH₃-COH), 1.60 (s, 3H, CH₃), 1.48 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 136.7, 132.4, 128.0 (2C), 126.3, 125.1 (2C), 74.0, 33.8, 26.8, 19.1.

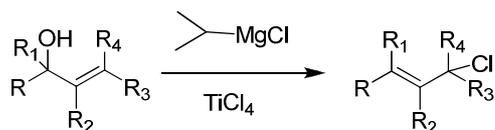
1-cyclohexylprop-2-en-1-ol:⁸

Following the procedure B with cyclohexanecarbaldehyde (0.54 mL, 4.5 mmol), vinylmagnesium chloride 1.6 M (3.4 mL, 5.4 mmol) gave the compound (530 mg, 84%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 5.86 (ddd, *J* = 17.3, 13.4, 3.9 Hz, 1H, CH-CH₂), 5.20 (dt, *J* = 17.3, 1.4 Hz, 1H, CH₂), 5.14 (dt, *J* = 10.4, 1.4 Hz, 1H, CH₂), 3.85 (m, CH-OH), 1.81-1.88 (m, 1H, CH-CHOH), 1.63-1.78 (m, 4H), 0.94-1.44 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 115.6, 77.9, 43.7, 28.9, 28.5, 26.7, 26.3, 26.2.

5-phenylpent-1-en-3-ol:⁹

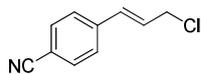
Following the procedure B with 3-phenylpropanal (0.5 mL, 3.7 mmol), vinylmagnesium chloride 1.6 M (2.7 mL, 4.3 mmol) gave the compound (538 mg, 90%) as a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.33 (m, 2H, Ar-H), 7.21-7.24 (m, 3H, Ar-H), 5.94 (ddd, *J* = 16.8, 12.4, 4.2 Hz, 1H, CH-CH₂), 5.28 (dt, *J* = 17.2, 1.4 Hz, 1H, CH₂), 5.17 (dt, *J* = 10.5, 1.2 Hz, 1H, CH₂), 4.16 (m, 1H, CH-OH), 2.68-2.82 (m, 2H, CH₂-Ar), 1.86-1.92 (m, 2H, CH₂-CH-OH); ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 141.2, 128.6 (2C), 128.5 (2C), 126.0, 115.0, 72.6, 38.7, 31.8.

4. General Procedure (C) for the rearrangement of allylic alcohols to allylic chlorides:



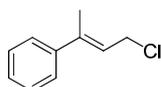
Alcohol derivatives were diluted in dry THF (5 mL). *iso*-Propyl magnesium chloride (1 eq) was added slowly at ambient temperature. The mixture was stirred for 10 min and then cooled to $-78\text{ }^{\circ}\text{C}$. TiCl_4 (0.5 eq) was added and the reaction was allowed to rise to ambient temperature before warming to $80\text{ }^{\circ}\text{C}$. The reaction was stirred for several hours at $80\text{ }^{\circ}\text{C}$, then quenched with water (10 mL) and cooled to ambient temperature. AcOEt (10 mL) was added. The organic layer was washed with water and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic phase was dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure followed by flash column chromatography (Silica, Eluent: Hexane/AcOEt 6/1) afforded (3-chloroprop-1-enyl) substituted aromatic derivatives.

(*E*)-4-(3-chloroprop-1-enyl)benzonitrile (**25**):

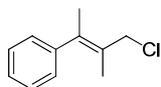


Following the procedure C with 4-(1-hydroxyallyl)benzonitrile (180 mg, 1.13 mmol), *iso*-propyl magnesium chloride 2 M (0.6 mL, 1.2 mmol) and titanium tetrachloride (0.06 mL, 0.57 mmol) gave the compound **25** (155 mg, 78%) as a pale yellow solid: IR (ATR) 2966, 2223, 1702, 836 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (dt, $J = 8.3, 1.7$ Hz, 2H, Ar-*H*), 7.47 (dt, $J = 8.3, 1.7$ Hz, 2H, Ar-*H*), 6.67 (d, $J = 15.7$ Hz, 1H, Ar-*CH*), 6.43 (dt, $J = 15.7, 6.9$ Hz, 1H, *CH-CH}_2\text{Cl}*), 4.25 (dd, $J = 6.9, 1.1$ Hz, 2H, CH_2Cl); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm) 140.4, 132.6, 132.2, 128.9, 127.3, 118.8, 111.7, 44.6; MS (CI) m/z 195 ($\text{M}+\text{NH}_4$); HRMS (CI) m/z calc for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{Cl}$ 195.0689, found: 195.0689.

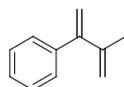
(*E*)-(4-chlorobut-2-en-2-yl)benzene (**36**):¹⁰



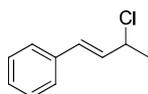
Following the procedure C with 2-phenylbut-3-en-2-ol (200 mg, 1.35 mmol), *iso*-propyl magnesium chloride 2 M (0.7 mL, 1.40 mmol) and titanium tetrachloride (0.07 mL, 0.67 mmol) gave the compound **36** (174 mg, 78%) as a pale yellow liquid: IR (ATR) 3038, 2960, 1492, 758, 695 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (m, 5H, Ar-*H*), 5.91 (tq, $J = 7.8, 1.5$ Hz, 1H, *CH-CH}_2\text{Cl}*), 4.19 (d, $J = 8.0$ Hz, 2H, $\text{CH}_2\text{-Cl}$), 2.06 (d, $J = 1.4$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 141.0, 128.4 (2C), 127.8, 126.0 (2C), 122.9, 41.2, 15.9; MS (EI) m/z 166 (M); HRMS (EI) m/z calc for $\text{C}_{10}\text{H}_{11}\text{Cl}$ 166.0549, found: 166.0550.

(E)-(4-chloro-3-methylbut-2-en-2-yl)benzene (37):

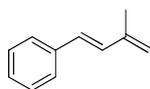
Following the procedure C with 3-methyl-2-phenylbut-3-en-2-ol (1 g, 6.17 mmol), *iso*-propyl magnesium chloride 2 M (3.1 mL, 6.2 mmol) and titanium tetrachloride (0.33 mL, 3.13 mmol) gave the compound **37** (900 mg, 81% without purification) as a yellow liquid: IR (thin film) 2953, 2924, 2855, 2357, 765, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.36 (m, 2H, *CH*-Ar), 7.19-7.28 (m, 2H, *CH*-Ar), 3.96 (s, 2H, $\text{CH}_2\text{-Cl}$), 2.02 (s, 3H, $\text{CH}_3\text{-Ar}$), 1.93 (s, 3H, $\text{CH}_3\text{-CH}_2\text{Cl}$); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 137.5, 128.3 (2C), 127.7 (2C), 127.4, 126.8, 48.8, 21.4, 16.7; MS (EI) m/z 180 (M); HRMS (EI) m/z calc for $\text{C}_{11}\text{H}_{13}\text{Cl}$ 180.0706, found: 180.0703.

(3-methylbuta-1,3-dien-2-yl)benzene:

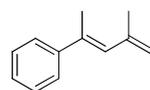
Obtained after purification of **37** on flash chromatography: colourless liquid diene (480 mg, 54%): IR (thin film) 3093, 3027, 2929, 2857, 897, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.33 (m, 5H, *CH*-Ar), 5.32 (s, 1H, $\text{CH}_2\text{-CAr}$), 5.14 (s, 1H, $\text{CH}_2\text{-CAr}$), 5.11 (s, 1H, $\text{CH}_2\text{-CCH}_3$), 4.87 (s, 1H, $\text{CH}_2\text{-CCH}_3$), 2.00 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 143.6, 141.5, 128.6 (2C), 127.9 (2C), 127.1, 116.9, 113.9, 21.2; MS (EI) m/z 144 (M); HRMS (EI) m/z calc for $\text{C}_{11}\text{H}_{12}$ 144.0939, found: 144.0935.

(E)-(3-chlorobut-1-enyl)benzene (38):

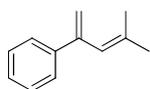
Following the procedure C with (E)-1-phenylbut-2-en-1-ol (200 mg, 1.34 mmol), *iso*-propyl magnesium chloride 2 M (0.7 mL, 1.40 mmol) and titanium tetrachloride (0.08 mL, 0.75 mmol) gave the compound **38** (210 mg, 95% without purification) as a pale yellow liquid: IR (thin film) 3026, 2970, 2926, 1448, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.40 (m, 5H, *CH*-Ar), 6.59 (d, $J = 16$ Hz, 1H, *CH*-Ar), 6.30 (dd, $J = 16, 8.4$ Hz, 1H, *CH-CHCl*), 4.70-4.78 (m, 1H, *CH-Cl*), 1.71 (d, $J = 6.8$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 135.9, 131.0, 130.9, 128.6 (2C), 128.1, 126.7 (2C), 58.3, 25.3; MS (EI) m/z 166 (M); HRMS (EI) m/z calc for $\text{C}_{10}\text{H}_{11}\text{Cl}$ 166.0549, found: 166.0546.

(E)-(3-methylbuta-1,3-dienyl)benzene (39):¹¹

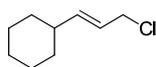
Following the procedure C with 3-methyl-1-phenylbut-2-en-1-ol (500 mg, 3.08 mmol), *iso*-propyl magnesium chloride 2 M (1.6 mL, 3.20 mmol) and titanium tetrachloride (0.17 mL, 1.61 mmol) gave the compound **39** (357 mg, 80%) as a colourless solid: IR (ATR) 2909, 1605, 1375, 1239, 753 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 7.4$ Hz, 2H, Ar-*H*), 7.33-7.37 (m, 2H, Ar-*H*), 7.23-7.27 (m, 1H, Ar-*H*), 6.91 (d, $J = 16.2$ Hz, 1H, Ar-*CH*), 6.57 (d, $J = 16.2$ Hz, 1H, Ar-*CH-CH*), 5.15 (s, 1H, C- CH_2), 5.12 (s, 1H, C- CH_2), 2.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 142.2, 137.6, 131.8, 128.8, 128.7 (2C), 127.5, 126.6 (2C), 117.4, 18.7.

(E)-(4-methylpenta-2,4-dien-2-yl)benzene (40a):¹²

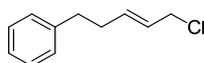
Following the procedure C with 4-methyl-2-phenylpent-3-en-2-ol (1 g, 5.58 mmol), *iso*-propyl magnesium chloride 2 M (2.8 mL, 5.60 mmol) and titanium tetrachloride (0.29 mL, 2.74 mmol) gave the compound **40a** (400 mg, 45%) as a colourless liquid: IR (thin film) 3080, 3021, 2967, 2919, 893, 756, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.47 (m, 2H, Ar-*H*), 7.34-7.38 (m, 2H, Ar-*H*), 7.28-7.30 (m, 1H, Ar-*H*), 6.24 (s, 1H, *CH-CCH}_3*), 5.13 (s, 1H, CH_2), 4.97 (s, 1H, CH_2), 2.26 (s, 3H, CH_3), 1.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 142.2, 136.2, 129.7, 128.2 (2C), 126.9, 125.9 (2C), 115.3, 23.8, 17.5; MS (EI) m/z 158 (M); HRMS (EI) m/z calc for $\text{C}_{12}\text{H}_{14}$ 158.1096, found: 158.1092.

(4-methylpenta-1,3-dien-2-yl)benzene (40b):¹³

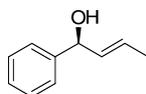
Following the procedure C with 4-methyl-2-phenylpent-3-en-2-ol (1 g, 5.58 mmol), *iso*-propyl magnesium chloride 2 M (2.8 mL, 5.60 mmol) and titanium tetrachloride (0.29 mL, 2.74 mmol) gave the compound **40b** (300 mg, 35%) as a colourless liquid: IR (thin film) 3080, 3025, 2969, 2929, 2911, 895, 773, 703 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.42 (m, 2H, Ar-*H*), 7.26-7.33 (m, 3H, Ar-*H*), 5.95 (s, 1H, *CH-CCH}_3*), 5.52 (s, 1H, CH_2), 5.07 (s, 1H, CH_2), 1.88 (s, 3H, CH_3), 1.72 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 141.3, 137.0, 128.1 (2C), 127.3, 126.5 (2C), 124.9, 114.3, 26.3, 19.6; MS (EI) m/z 158 (M); HRMS (EI) m/z calc for $\text{C}_{12}\text{H}_{14}$ 158.1096, found: 158.1092.

(E)-(3-chloroprop-1-enyl)cyclohexane (41):

Following the procedure C with 1-cyclohexylprop-2-en-1-ol (150 mg, 1.07 mmol), *iso*-propyl magnesium chloride 2 M (0.7 mL, 1.40 mmol) and titanium tetrachloride (0.07 mL, 0.66 mmol) gave the compound **41** (101 mg, 60%) as a colourless liquid: IR (ATR) 2923, 1448, 683 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (dd, $J = 15.6, 6.8$ Hz, 1H, *CH-CH*), 5.52-5.59 (m, 1H, *CH-CH}_2\text{Cl}*), 4.03 (d, $J = 7.2$ Hz, 2H, *CH}_2\text{-Cl}*), 1.94-2.02 (m, 1H, *CH*), 1.70-1.74 (m, 4H, *CH}_2*), 1.02-1.32 (m, 6H, *CH}_2*); ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 123.7, 46.0, 40.3, 32.7 (2C), 26.2, 26.1 (2C); MS (EI) m/z 158 (M); HRMS (EI) m/z calc for $\text{C}_9\text{H}_{15}\text{Cl}$ 158.0862, found: 158.0859.

(E)-(5-chloropent-3-enyl)benzene (42):¹⁴

Following the procedure C with 5-phenylpent-1-en-3-ol (160 mg, 0.99 mmol), *iso*-propyl magnesium chloride 2 M (0.5 mL, 1.00 mmol) and titanium tetrachloride (0.06 mL, 0.57 mmol) gave the compound **42** (98 mg, 50%) as a colourless liquid: IR (thin film) 3027, 2929, 2856, 1453, 966, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.27-7.31 (m, 2H, *Ar-H*), 7.17-7.22 (m, 3H, *Ar-H*), 5.78-5.85 (m, 1H, *CH-CH}_2\text{Cl}*), 5.61-5.70 (m, 1H, *CH-CHCH}_2\text{Cl}*), 4.03 (d, $J = 7.2$ Hz, 2H, *CH}_2\text{-Cl}*), 2.72 (t, $J = 7.2$ Hz, 2H, *CH}_2\text{-Ar}*), 2.36-2.42 (m, 2H, *CH}_2\text{-CH}_2\text{Ar}*); ^{13}C NMR (100 MHz, CDCl_3) δ 141.4, 135.0, 128.4 (2C), 128.3 (2C), 126.5, 125.9, 45.3, 35.2, 33.8; MS (EI) m/z 180 (M); HRMS (EI) m/z calc for $\text{C}_{11}\text{H}_{13}\text{Cl}$ 180.0706, found: 180.0701.

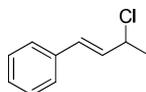
5. Chiral studies:**(E)-1-phenylbut-2-en-1-ol (45):**

Chiral alcohol **45** was prepared as previously reported.^{15,16}

Characterization as previously reported.

Chiral HPLC: CHIRALCEL OD-H, n-Hexane / Isopropanol = 95/5%, 1 ml / min, 26°C

Rt = 9.57 min (75% ee) ; Rt = 11.56 min

(E)-(3-chlorobut-1-enyl)benzene (38):

Characterization as previously reported.

Chiral HPLC: CHIRALCEL OJ-H, n-Hexane / Isopropanol = 99.5/0.5%, 1 ml / min, 26°C

Rt = 17.36 min (75% ee); Rt = 20.49 min

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