



Reduction of activated conjugated alkenes by the $\text{InCl}_3\text{--NaBH}_4$ reagent system

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Abstract—A combination of a catalytic amount of indium (III) chloride and sodium borohydride in acetonitrile reduces selectively the carbon–carbon double bonds in conjugated alkenes such as α,α -dicyano olefins, α,β -unsaturated nitriles, cyanoesters, cyanophosphonate and dicarboxylic esters. However, reduction of chalcones is little different. They are reduced to a mixture of saturated ketones and alcohols if the reaction mixture is quenched with H_2O , whereas quenching with MeOH leads to saturated alcohols only.

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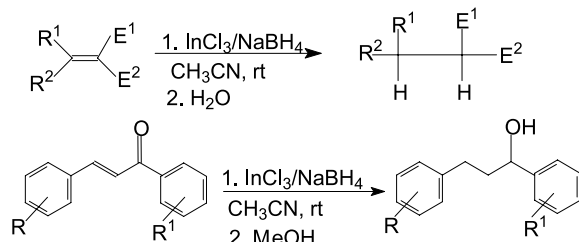
1. Introduction

Reduction by indium metal is receiving more and more attention in recent times because of its unique style of action.¹ Although metallic indium has been successfully used for the reduction of various functionalities such as aromatic nitro groups,^{2a} quinolines,^{2b} azides,^{2c} *vic*-aryl dibromides,^{2d} terminal alkynes^{2e} and conjugated olefins,^{2f} among others,² two major drawbacks of these processes are the use of a stoichiometric amount or more of the costly indium and its limited applicability to specific types of substrate. As these reactions are likely to proceed through single electron transfer process, search for other indium derivatives as better radical agents led to the discovery and use of a couple of indium hydrides.³ Recently, dichloroindium hydride (Cl_2InH) generated in situ from the combination of sodium borohydride and a catalytic amount of indium trichloride has been demonstrated to be a benign alternative to tributyltin hydride in the dehalogenation of alkyl halides and other radical cyclisations.^{3b}

As a part of our interest in indium-mediated reductions^{2d–f, j–h} we initiated an investigation to find applications for this simple reagent^{3d} and we have discovered that this system $\text{InCl}_3\text{--NaBH}_4$ shows much improved activity towards reduction of carbon–carbon double-bonds in conjugated alkenes compared to metallic indium.^{2f} A part of these results has been reported recently in a communication⁴ and we wish to present here further application of this reagent in chalcone system together with the experimental details of our earlier results (Scheme 1).

2. Results and discussion

The experimental procedure for this reduction is very simple. The conjugated alkene was stirred with a solution of a catalytic amount (10–15 mol%) of indium (III) chloride and sodium borohydride in acetonitrile at room temperature for the period of time required to complete the reduction (Thin Layer Chromatography). The reaction mixture was then quenched with water and extracted with ether. The usual work-up and purification produced the corresponding reduction product.



Scheme 1.

Keywords: indium chloride; sodium borohydride; reduction; conjugated alkene; chalcone.

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Several structurally diverse conjugated alkenes undergo selective reduction of their carbon–carbon double bonds by this procedure to provide the corresponding saturated products. The alkenes include α,α -dicyano olefins, α,β -unsaturated nitriles, cyanoesters, a cyanophosphonate, and dicarboxylic esters. The results are summarized in Table 1. As is evident from the results the conjugated monoester (entry 17) remains inert, whereas the diester (entry 16) is reduced easily. Apparently, this reagent system, $\text{InCl}_3\text{--NaBH}_4$ is quite different from metallic indium in its course of reduction as conjugated cyanoesters, diesters, nitriles

Table 1. The reduction of C=C bond in conjugated alkenes by $\text{InCl}_3/\text{NaBH}_4$

Entry	Alkene				Time (h)	Yield (%) ^a
	R ¹	R ²	E ¹	E ²		
1	Ph	H	CN	CN	3	85
2	<i>p</i> -(Cl)-C ₆ H ₄	H	CN	CN	3	83
3	Ph	Me	CN	CN	3.5	79
4	<i>p</i> -(Me)-C ₆ H ₄	Me	CN	CN	4	79
5	Cy-C ₆ H ₁₁		CN	CN	3.5	83
6	Me ₂ CH	Me	CN	CN	4	81
7	Ph	H	CN	H	12	69
8	<i>p</i> -(Me)-C ₆ H ₄	H	CN	H	12	57
9	H	CN	H	(O=)P(OMe) ₂	5	84
10	Ph	H	CN	CO ₂ Et	3	88
11	Ph	Me	CN	CO ₂ Et	4.5	82 (55:45) ^b
12		H	CN	CO ₂ Et	5	87
13	Me ₂ CH	Me	CN	CO ₂ Et	5	85 (60:40) ^b
14	<i>cy</i> -C ₆ H ₁₀		CN	CO ₂ Et	4.5	84
15	<i>cy</i> -C ₈ H ₁₄		CN	CO ₂ Et	4.5	81
16	Ph	H	CO ₂ Et	CO ₂ Et	6	87
17	Ph	H	CO ₂ Et	H	18	No reaction
18	Ph	H	H	COPh	0.5	96
19		H	H	COPh	0.75	88

^a Yields refer to those of pure isolated products characterized by spectral data (IR, ¹H NMR, ¹³C NMR).

^b The figure in parenthesis denotes the diastereomeric ratio of the product.

which are reduced readily by this procedure do not undergo reduction by indium metal.^{2f}

More significantly, the reduction of chalcone which was found to be problematic using indium metal^{2f,g} though successful using this reagent system, is very interesting. The reduction of unsubstituted chalcone by this procedure involves the reduction of double bond only to produce the corresponding saturated ketones, whereas the substituted chalcones underwent further reduction of the ketone functionality to the extent of 20–25% producing a mixture of saturated ketones and alcohols. This prompted us to look into details of this reduction and we discovered that chalcones, in general, are reduced directly to the corresponding saturated alcohols in one pot by $\text{InCl}_3/\text{NaBH}_4$ system in acetonitrile if quenched with methanol in place of water (Scheme 1). A wide range of structurally varied chalcones underwent clean and complete reduction to the corresponding saturated alcohols in high yields by this procedure. The results are reported in Table 2. Hetero-aromatic rings (entries 8–10) and ferrocene-substituted chalcones are also reduced without any difficulty. Very interestingly, the $\alpha,\beta,\gamma,\delta$ -unsaturated analogues (entries 12–14) underwent selective reduction at the α,β -carbon-carbon double bond producing the corresponding γ,δ -

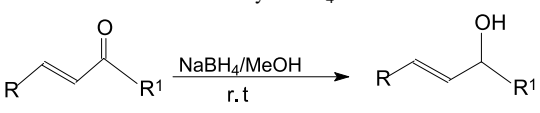
Table 2. Reduction of chalcones by $\text{InCl}_3/\text{NaBH}_4$


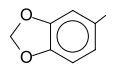
Entry	R	R ¹	Time (h)	Yield (%) ^a
1	Ph	Ph	1	94
2	Ph	<i>p</i> (Me)-C ₆ H ₄	2	93
3	<i>p</i> (Cl)-C ₆ H ₄	Ph	2	92
4	<i>p</i> (OMe)-C ₆ H ₄	<i>p</i> (Me)-C ₆ H ₄	2.5	91
5	<i>p</i> (O-allyl)-C ₆ H ₄	Ph	4	92
6	<i>m</i> (OBn)-C ₆ H ₄	Ph	1	95
7		Ph	2	94
8		<i>p</i> (Me)-C ₆ H ₄	2.5	91
9		Ph	1.5	91
10		Ph	2	89
11		Ph	3	89
12	Ph-CH=CH(t)	Ph	2	88
13	Ph-CH=CH(t)	<i>p</i> (Me)-C ₆ H ₄	2	85
14	Ph-CH=CH(t)	<i>p</i> (OBn)-C ₆ H ₄	2.5	81

^a Yields refer to those of pure isolated products properly characterized.

unsaturated alcohols. These reductions, when quenched with H₂O in place of MeOH led to the mixture of saturated ketones and alcohols, ketones being the major component. On the other hand, after the reaction, if the mixture was left to open atmosphere containing moisture and filtered through a short column of silica gel, mostly saturated ketones were isolated. These observations demonstrate that this reagent system, InCl_3 - NaBH_4 in CH_3CN , reduces chalcones to the corresponding saturated ketones in the first phase, which on addition of MeOH undergo further reduction by the hydride ion released by the relatively slow decomposition of remaining sodium borohydride with MeOH. However, quenching with H₂O leads to faster decomposition of NaBH_4 thus resulting in incomplete reduction of the C=O groups.

The one-step reduction of chalcones to the saturated alcohols by this reagent system is unique as other

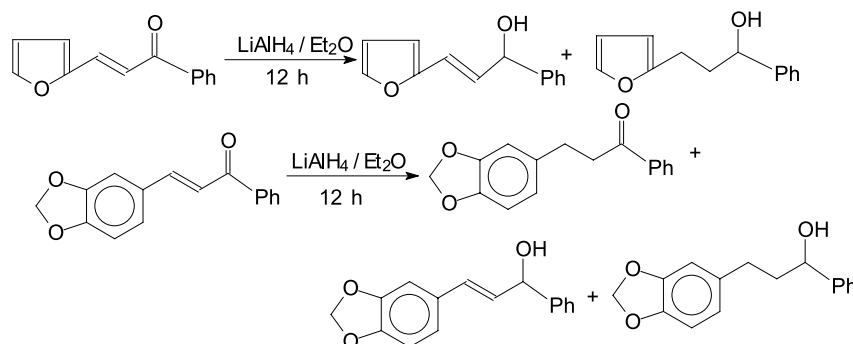
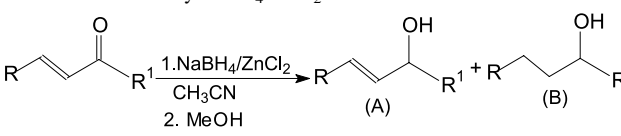
Table 3. Reduction of Chalcones by NaBH₄



Entry	R	R ¹	Time (min)	Yield (%)
1	<i>p</i> (Cl)-C ₆ H ₄	Ph	30	93
2		Ph	30	91
3	<i>m</i> (OBn)-C ₆ H ₄	Ph	30	94
4		Ph	30	92

conventional reducing agents failed to do this job cleanly. For comparison, a few representative chalcones were subjected to reduction by NaBH₄–MeOH and LiAlH₄–ether. Reduction by sodium borohydride furnished the corresponding allyl alcohol (Table 3) while lithium aluminium hydride produced a mixture of allyl alcohol, saturated alcohol and saturated ketone together with other unidentified products even after a reaction period of 12 h (Scheme 2). In another comparison experiment when indium (III) chloride has been replaced by zinc (II) chloride, a mixture of allyl alcohol and saturated alcohols were obtained (Table 4). Thus, a combination of indium (III) chloride and sodium borohydride in acetonitrile followed by quenching with methanol is very useful for the direct reduction of chalcones to the saturated alcohols.

In general, reductions by this procedure are clean, high yielding and quite fast. The reactions proceed at room temperature unlike using indium metal which requires a temperature of 90°C for a longer period.^{2f} The reaction conditions are mild enough to tolerate a sensitive furan ring.

To ascertain the role of indium (III) chloride a few reactions were carried out with the conjugated nitrile (listed in entry 7), cyanoester (entry 10), dicyano-olefin (entry 1) and chalcone (entry 18) under identical reaction conditions without the indium (III) chloride and no reduction was observed in each case.

**Scheme 2.****Table 4.** Reduction by NaBH₄/ZnCl₂


Entry	R	R ¹	Time (h)	Ratio of A/B (¹ H NMR)
1		Ph	2	72:28
2	<i>m</i> (OBn)-C ₆ H ₄	Ph	2	60:40

3. Conclusion

In conclusion, the combination of sodium borohydride and a catalytic amount of indium (III) chloride provides a highly chemoselective reduction of the carbon–carbon double-bonds in a wide range of activated conjugated alkenes such as α,α -dicyano olefins, α,β -unsaturated nitriles, cyanoesters, a cyanophosphonate, and dicarboxylic esters. On the other hand, the substituted chalcones are cleanly reduced to the corresponding saturated alcohols in one-step by this reagent which is difficult to achieve by other conventional reducing agents. Certainly, this reagent offers significant improvements with regard to convenience, cost, mildness and efficiency over the similar reduction by indium metal² and leaves great promise for other applications.

4. Experimental

4.1. General

Acetonitrile was distilled over anhydrous phosphorus pentoxide and stored over molecular sieves (4 Å). Sodium borohydride and indium (III) chloride (98%) was purchased from Aldrich. The conjugated alkenes and chalcones are prepared by standard methods. IR spectra were taken as thin films for oils and as KBr pellet for solid compounds. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions at 300 and 75 MHz respectively. Elemental Analyses were performed on a Perkin–Elmer autoAnalyzer 2400 II.

4.1.1. General procedure for the reduction of activated conjugated alkenes: representative one for the reduction of 1,1-dicyano-2-phenylethylene (entry 1, Table 1). To a stirred solution of anhydrous indium (III) chloride (30 mg, 0.135 mmol) and sodium borohydride (56 mg, 1.5 mmol) in dry acetonitrile (3 mL) was added a solution of 1,1-dicyano-2-phenylethylene (154 mg, 1 mmol) in acetonitrile (1 mL) at room temperature (28–30°C) under nitrogen. The reaction mixture was stirred for another 3 h as monitored by TLC and quenched with water (0.5 mL). The reaction mixture was extracted with ether (3×10 mL) and ether extract was washed with brine, dried (Na₂SO₄) and evaporated to leave the crude product which was purified by column chromatography over silica gel (hexane–ether 98:2) to provide the corresponding alkane (131 mg, 85%) as a white solid, mp 87–88°C (lit.,^{2f} mp 87°C) whose spectral data are in good agreement with those reported earlier.^{2f}

This procedure is followed for the reduction of all conjugated alkenes listed in Table 1. However, for the reduction of substituted chalcones the reaction mixture at the end of the reaction was quenched with methanol in place of water. All the products have been characterized by their spectroscopic (IR, ¹H NMR, ¹³C NMR) data and elemental analysis. The known compounds are in good agreement with the values reported for them.² Spectroscopic and analytical data of the products whose data are not available for comparison are presented below in order of their entries in Tables 1 and 2.

4.1.2. 2-(4'-Chlorophenyl)-1,1-dicyanoethane (entry 2). Pale yellow solid; mp 92°C. (lit.,^{2f} mp 92°C).

4.1.3. 1,1-Dicyano-2-phenylpropane (entry 3). Light yellow viscous oil.^{2f}

4.1.4. 1,1-Dicyano-2-(4'-methylphenyl)propane (entry 4). Light yellow viscous oil.^{2f}

4.1.5. 1,1-Dicyano-1-cyclohexylmethane (entry 5). Colourless liquid.^{2f}

4.1.6. 1,1-Dicyano-2,3-dimethylbutane (entry 6). Colourless oil; IR 2250 cm⁻¹; ¹H NMR δ 3.57 (d, *J*=5.49 Hz, 1H), 2.30–2.35 (m, 1H), 1.62–1.73 (m, 1H), 0.85–1.11 (m, 9H); ¹³C NMR δ 112.2 (2C), 39.8, 29.8, 25.9, 18.1, 17.1 (2C). Anal. calcd for C₈H₁₂N₂: C, 70.55; H, 8.88; N, 20.56. Found: C, 70.42; H, 8.72; N, 20.48.

4.1.7. 1-Cyano-2-phenylethane (entry 7). Colourless oil; IR 2248, 1602 cm⁻¹; ¹H NMR δ 7.22–7.47 (m, 5H), 2.95 (t, *J*=7.41 Hz, 2H), 2.61 (t, *J*=7.41 Hz, 2H); ¹³C NMR δ 138.5, 129.3 (2C), 128.7 (2C), 127.6, 119.6, 31.9, 19.7. Anal. calcd for C₉H₉N: C, 82.40; H, 6.91; N, 10.67. Found: C, 82.43; H, 6.88; N, 10.59.

4.1.8. 1-Cyano-2-(4'-methylphenyl)ethane (entry 8). Colourless oil; IR 2246, 1602 cm⁻¹; ¹H NMR δ 7.05–7.38 (m, 4H), 2.91 (t, *J*=7.44 Hz, 2H), 2.58 (t, *J*=7.44 Hz, 2H), 2.34 (s, 2H); ¹³C NMR δ 137.1, 135.4, 129.9 (2C), 128.5 (2C), 119.5, 31.6, 21.4, 19.8. Anal. calcd for C₁₀H₁₁N: C, 82.71; H, 7.63; N, 9.64. Found: C, 82.59; H, 7.66; N, 9.70.

4.1.9. Dimethyl 2-cyanoethylphosphonate (entry 9). Gummy liquid; IR 2247 cm⁻¹; ¹H NMR δ 3.68 (s, 3H), 3.64 (s, 3H), 2.46–2.56 (m, 2H), 1.92–2.03 (m, 2H); ¹³C NMR δ 118.5 (d, *J*_{CP}=16.87 Hz), 53.3 (d, *J*_{CP}=6.52 Hz, 2C), 21.7 (d, *J*_{CP}=145.27 Hz), 11.9 (d, *J*_{CP}=7.05 Hz). Anal. calcd for C₅H₁₀NO₂P: C, 40.82; H, 6.85; N, 9.52. Found: C, 40.77; H, 6.74; N, 9.39.

4.1.10. 1-Cyano-1-ethylcarboxy-2-phenylethane (entry 10). Gummy liquid; IR 2250, 1743 cm⁻¹; ¹H NMR δ 7.25–7.36 (m, 5H), 4.22 (q, *J*=7.14 Hz, 2H), 3.74 (d, *J*=5.88 Hz, 0.5H), 3.71 (d, *J*=5.88 Hz, 0.5H), 3.14–3.30 (m, 2H), 1.25 (t, *J*=7.14 Hz, 3H); ¹³C NMR δ 165.9, 135.7, 129.4 (2C), 129.2 (2C), 128.1, 116.6, 63.3, 40.0, 36.1, 14.3. Anal. calcd for C₁₂H₁₃NO₂: C, 70.91; H, 6.44; N, 6.89. Found: C, 70.82; H, 6.40; N, 6.81.

4.1.11. 1-Cyano-1-ethylcarboxy-2-phenylpropane (entry 11). Yellow liquid; IR 2248, 1743 cm⁻¹; ¹H NMR (a mixture of diastereoisomer 55:45) δ 7.27–7.41 (m, 5H), 4.17 (q, *J*=7.11 Hz, 1.1H), 4.15 (q, *J*=7.11 Hz, 0.9H), 3.70 (d, *J*=6.72 Hz, 0.45H), 3.65 (d, *J*=6.33 Hz, 0.55H), 3.47–3.55 (m, 1H), 1.51 (d, *J*=6.96 Hz, 0.55H), 1.50 (d, *J*=7.14 Hz, 0.45H), 1.20 (t, *J*=7.11 Hz, 1.65H), 1.18 (t, *J*=7.11 Hz, 1.35H); ¹³C NMR (major isomer) δ 165.8, 141.3, 129.1 (2C), 127.4 (2C), 125.9, 115.9, 63.1, 46.4, 40.8, 19.7, 14.3; minor isomer: δ 165.7, 140.8, 129.0 (2C), 127.5 (2C), 126.3, 115.9, 63.0, 46.1, 40.8, 19.7, 14.2. Anal. calcd for C₁₃H₁₅NO₂: C, 71.86; H, 6.95; N, 6.44. Found: C, 71.68; H, 6.86; N, 6.31.

4.1.12. 1-Cyano-1-ethylcarboxy-2-(2'-furyl)ethane (entry 12). Colourless liquid; IR 2251, 1743 cm⁻¹; ¹H NMR δ 7.35 (m, 1H), 6.31 (dd, *J*=3.09, 2.97 Hz, 1H), 6.24 (d, *J*=3.09 Hz, 1H), 4.26 (q, *J*=7.14 Hz, 2H), 3.83 (d, *J*=6.18 Hz, 0.5H), 3.80 (d, *J*=6.18 Hz, 0.5H), 3.24–3.36 (m, 2H), 1.29 (t, *J*=7.14 Hz, 3H); ¹³C NMR δ 165.1, 148.9, 142.5, 115.8, 110.6, 108.4, 63.0, 37.0, 28.5, 13.9. Anal. calcd for C₁₀H₁₁NO₃: C, 62.16; H, 5.73; N, 7.24. Found: C, 62.02; H, 5.75; N, 7.21.

4.1.13. 1-Cyano-1-ethylcarboxy-2,3-dimethylbutane (entry 13). Colourless oil; IR 2248, 1745 cm⁻¹; ¹H NMR (a mixture of diastereoisomers 6:4) δ 4.27 (2q, *J*=7.14 Hz, 2H), 3.48 (d, *J*=4.44 Hz, 0.6H), 3.43 (d, *J*=5.01 Hz, 0.4 Hz), 2.31–2.35 (m, 1H), 1.60–1.71 (m, 1H), 1.31 (t, *J*=7.14 Hz, 1.8H), 1.30 (t, *J*=7.14 Hz, 1.2H), 1.10 (d, *J*=6.78 Hz, 1.8H), 1.05 (d, *J*=6.66 Hz, 1.2H), 0.87–0.98 (m, 6H); ¹³C NMR (major isomer) δ 166.6, 115.7, 63.0, 44.3, 32.6, 27.6, 18.1, 17.7 (2C); (minor isomer) δ 166.3, 116.1, 62.9, 44.2, 32.8, 27.6, 18.3, 17.6 (2C). Anal. calcd for C₁₀H₁₇NO₂: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.38; H, 9.31; N, 7.53.

4.1.14. 1-Cyano-1-ethylcarboxy-1-cyclohexylmethane (entry 14). Colourless oil; IR 2251, 1743 cm⁻¹; ¹H NMR δ 4.11 (q, *J*=7.14 Hz, 2H), 3.30 (d, *J*=5.61 Hz, 1H), 1.41–2.11 (m, 5H), 0.96–1.24 (m, 9H); ¹³C NMR δ 166.1, 116.0, 62.7, 44.7, 39.0, 31.2, 28.2, 26.0, 25.9, 25.8, 14.3. Anal. calcd for C₁₁H₁₇NO₂: C, 67.66; H, 8.77; N, 7.17. Found: C, 67.45; H, 8.65; N, 7.05.

4.1.15. 1-Cyano-1-ethylcarboxy-1-cyclooctylmethane (entry 15). Colourless oil; IR 2249, 1743 cm⁻¹; ¹H NMR

δ 4.19 (q, $J=7.17$ Hz, 2H), 3.34 (d, $J=5.40$ Hz, 1H), 2.16–2.28 (m, 1H), 1.41–1.68 (m, 14H), 1.24 (t, $J=7.17$ Hz, 3H); ^{13}C NMR δ 166.4, 116.5, 62.8, 45.9, 38.3, 32.0, 29.2, 26.7 (2C), 26.6, 26.5, 24.0, 14.4. Anal. calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_2$: C, 69.92; H, 9.47; N, 6.27. Found: C, 69.78; H, 9.35; N, 6.19.

4.1.16. 1,1-Diethylcarboxy-2-phenylethane (entry 16). Colourless oil; IR 1749, 1604 cm^{-1} ; ^1H NMR δ 7.16–7.29 (m, 5H), 4.18 (q, $J=7.14$ Hz, 2H), 4.16 (q, $J=7.14$ Hz, 2H), 3.64 (t, $J=7.86$ Hz, 1H), 3.21 (d, $J=7.86$ Hz, 2H), 1.18 (t, $J=7.14$ Hz, 6H); ^{13}C NMR δ 169.2 (2C), 138.3, 129.2 (2C), 128.9 (2C), 127.1, 61.8 (2C), 54.2, 35.1, 14.4 (2C). Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.24. Found: C, 67.11; H, 7.15.

4.1.17. 1,3-Diphenylpropan-1-one (entry 18). Colourless solid; mp 73°C (lit.,⁵ mp 73°C).

4.1.18. 3-Naphthyl-1-phenylpropan-1-one (entry 19). Low melting solid; IR 1681, 1596 cm^{-1} ; ^1H NMR δ 8.19 (d, $J=8.61$ Hz, 1H), 8.08 (d, $J=8.1$ Hz, 2H), 7.99 (d, $J=7.56$ Hz, 1H), 7.86–7.89 (m, 1H), 7.53–7.70 (m, 7H), 3.61–3.70 (m, 2H), 3.50–3.58 (m, 2H); ^{13}C NMR δ 199.7, 137.8, 137.2, 134.3, 133.5, 132.1, 129.4, 129.0 (2C), 128.4 (2C), 127.4, 126.6, 126.5, 126.1, 126.0, 123.9, 40.1, 27.6. Anal. calcd for $\text{C}_{19}\text{H}_{16}\text{O}$: C, 87.66; H, 6.19. Found: C, 87.69; H, 6.16.

4.1.19. 1,3-Diphenylpropan-1-ol (entry 1, Table 2). Colourless oil; IR 3395, 1608 cm^{-1} ; ^1H NMR δ 7.24–7.47 (m, 10H), 4.72 (d, $J=5.58$ Hz, 0.5H), 4.70 (d, $J=5.79$ Hz, 0.5H), 2.71–2.81 (m, 2H), 2.04–2.22 (m, 2H); ^{13}C NMR δ 145.0, 142.3, 128.9 (4C), 128.8, 128.0, 126.4 (2C), 126.3 (2C), 74.2, 40.9, 35.5. Anal. calcd for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 84.86; H, 7.59. Found: C, 84.58; H, 7.47.

4.1.20. 1-(4'-Methylphenyl)-3-phenylpropan-1-ol (entry 2). Colourless oil; IR 3385, 1593 cm^{-1} ; ^1H NMR δ 7.02–7.19 (m, 9H), 4.51 (d, $J=5.7$ Hz, 0.5H), 4.49 (d, $J=5.7$ Hz, 0.5H), 2.52–2.61 (m, 2H), 2.23 (s, 3H), 1.87–2.04 (m, 2H); ^{13}C NMR δ 142.3, 142.0, 137.7, 129.6 (2C), 128.9 (2C), 128.8 (2C), 126.4 (2C), 126.3, 74.1, 40.8, 32.5, 21.6. Anal. calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: C, 84.91; H, 8.01. Found: C, 84.76; H, 8.08.

4.1.21. 3-(4'-Chlorophenyl)-1-phenylpropan-1-ol (entry 3). Colourless oil; IR 3381, 1596 cm^{-1} ; ^1H NMR δ 7.22–7.24 (m, 5H), 7.15 (d, $J=8.34$ Hz, 2H), 7.03 (d, $J=8.34$ Hz, 2H), 4.60 (d, $J=5.4$ Hz, 0.5H), 4.57 (d, $J=5.4$ Hz, 0.5H), 2.55–2.64 (m, 2H), 1.87–2.04 (m, 2H); ^{13}C NMR δ 144.8, 140.6, 132.5, 130.2 (2C), 129.0 (2C), 128.9 (2C), 128.1, 126.3 (2C), 74.1, 40.7, 31.8. Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{ClO}$: C, 73.01; H, 6.12. Found: C, 73.26; H, 6.05.

4.1.22. 1-(4'-Methylphenyl)-3-(4'-methoxyphenyl)propan-1-ol (entry 4). Colourless oil; IR 3376, 1601 cm^{-1} ; ^1H NMR δ 7.28 (d, $J=7.95$ Hz, 2H), 7.25 (d, $J=7.95$ Hz, 2H), 7.16 (d, $J=8.49$ Hz, 2H), 6.89 (d, $J=8.49$ Hz, 2H), 4.67 (d, $J=5.7$ Hz, 0.5H), 4.65 (d, $J=5.7$ Hz, 0.5H), 3.83 (s, 3H), 2.64–2.73 (m, 2H), 2.41 (s, 3H), 2.01–2.16 (m, 2H); ^{13}C NMR δ 158.2, 142.2, 137.6, 134.4, 129.8 (2C), 129.7 (2C), 126.4 (2C), 114.3 (2C), 74.0, 41.1, 31.6, 21.6. Anal. calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$: C, 79.65; H, 7.86. Found: C, 79.45; H, 8.75.

4.1.23. 3-(4'-Allyloxyphenyl)-1-phenylpropan-1-ol (entry 5). Colourless oil; IR 3377, 1642, 1597 cm^{-1} ; ^1H NMR δ 7.23–7.24 (m, 5H), 6.99 (d, $J=8.52$ Hz, 2H), 6.74 (d, $J=8.52$ Hz, 2H), 5.89–6.02 (m, 1H), 5.16–5.34 (m, 2H), 4.56 (d, $J=5.4$ Hz, 0.5H), 4.54 (d, $J=5.4$ Hz, 0.5H), 4.40 (d, $J=5.28$ Hz, 2H), 2.47–2.60 (m, 2H), 1.84–2.03 (m, 2H); ^{13}C NMR δ 157.2, 145.0, 134.4, 133.9, 129.7 (2C), 128.9 (2C), 128.0, 126.4 (2C), 117.9, 115.1 (2C), 74.2, 69.3, 41.0, 31.5. Anal. calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.56; H, 7.51. Found: C, 80.38; H, 7.46.

4.1.24. 3-(3'-Benzyloxyphenyl)-1-phenylpropan-1-ol (entry 6). Colourless oil; IR 3398, 1608 cm^{-1} ; ^1H NMR δ 7.15–7.40 (m, 11H), 6.75–6.79 (m, 3H), 4.98 (s, 2H), 4.59 (d, $J=5.4$ Hz, 0.5H), 4.56 (d, $J=5.4$ Hz, 0.5H), 2.58–2.70 (m, 2H), 1.91–2.09 (m, 2H); ^{13}C NMR δ 159.4, 145.0, 144.0, 137.6, 129.9, 129.0 (2C), 128.9 (2C), 128.4, 128.0, 127.9 (2C), 126.4 (2C), 121.6, 115.7, 112.6, 74.2, 70.3, 40.8, 32.5. Anal. calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2$: C, 82.98; H, 6.96. Found: C, 82.78; H, 6.84.

4.1.25. 3-(3',4'-Dioxymethylenphenyl)-1-phenylpropan-1-ol (entry 7). Colourless oil; IR 3381, 1602 cm^{-1} ; ^1H NMR δ 7.29–7.36 (m, 5H), 6.62–6.75 (m, 3H), 5.89 (s, 2H), 4.66 (d, $J=2.04$ Hz, 0.5H), 4.63 (d, $J=5.1$ Hz, 0.5H), 2.58–2.69 (m, 2H), 1.93–2.11 (m, 2H); ^{13}C NMR δ 147.9, 146.0, 145.0, 136.0, 128.9 (2C), 128.0, 126.4 (2C), 121.6, 109.4, 108.6, 101.1, 74.0, 41.1, 32.2. Anal. calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 74.98; H, 6.29. Found: C, 74.76; H, 6.18.

4.1.26. 1-(4'-Methylphenyl)-3-(2'-thiophenyl)propan-1-ol (entry 8). Colourless oil; IR 3378, 1596 cm^{-1} ; ^1H NMR δ 7.25 (d, $J=8.04$ Hz, 2H), 7.17 (d, $J=8.04$ Hz, 2H), 7.11–7.13 (m, 1H), 6.91–6.93 (m, 1H), 6.80–6.81 (m, 1H), 4.71 (d, $J=5.49$ Hz, 0.5H), 4.68 (d, $J=5.49$ Hz, 0.5H), 2.89–2.95 (m, 2H), 2.35 (s, 3H), 2.03–2.22 (m, 2H); ^{13}C NMR δ 145.1, 141.7, 137.8, 129.7 (2C), 127.1, 126.3 (2C), 124.7, 123.5, 73.8, 41.0, 26.7, 21.6. Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{SO}$: C, 73.37; H, 6.94. Found: C, 73.52; H, 6.84.

4.1.27. 3-(2'-Furyl)-1-phenylpropan-1-ol (entry 9). Colourless oil; IR 3377, 1598 cm^{-1} ; ^1H NMR δ 7.18–7.31 (m, 6H), 6.22–6.23 (m, 1H), 5.93–5.94 (m, 1H), 4.57 (t, $J=6.63$ Hz, 1H), 2.57–2.66 (m, 2H), 1.92–2.07 (m, 2H); ^{13}C NMR δ 156.0, 144.8, 141.4, 129.0 (2C), 128.0, 126.4 (2C), 110.6, 105.5, 74.0, 37.5, 24.8. Anal. calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20; H, 6.97. Found: 77.32; H, 7.01.

4.1.28. 3-(3'-N-Methylindolyl)-1-phenylpropan-1-ol (entry 10). Colourless oil; IR 3393, 1610 cm^{-1} ; ^1H NMR δ 7.05–7.51 (m, 9H), 6.83 (s, 1H), 4.76 (d, $J=5.58$ Hz, 0.5H), 4.73 (d, $J=5.61$ Hz, 0.5H), 3.72 (s, 3H), 2.70–2.93 (m, 2H), 2.05–2.26 (m, 2H); ^{13}C NMR δ 145.2, 137.5, 128.8 (2C), 128.2, 127.9, 126.5, 126.4 (2C), 121.9, 119.4, 119.0, 114.8, 109.5, 74.5, 39.8, 33.0, 21.8. Anal. calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$: C, 81.47; H, 7.21; N, 5.27. Found: C, 81.51; H, 7.16; N, 5.25.

4.1.29. 3-(2'-Ferrocenyl)-1-phenylpropan-1-ol (entry 11). Brown viscous oil; IR 3392, 1602 cm^{-1} ; ^1H NMR δ 7.25–7.36 (m, 5H), 4.69–4.71 (m, 1H), 4.19 (broad, 9H), 2.30–2.39 (m, 2H), 1.81–1.95 (m, 2H); ^{13}C NMR δ 145.0, 128.9 (2C), 128.0, 126.4 (2C), 88.1, 69.9 (5C), 69.2 (2C), 68.4

(2C), 40.3, 26.1. Anal. calcd for C₁₉H₂₀FeO: C, 71.26; H, 6.29. Found: C, 71.22; H, 6.28.

4.1.30. 1,5-Diphenyl-pent-4-en-1-ol (entry 12). Colourless viscous oil; IR 3363, 1651 cm⁻¹; ¹H NMR δ 7.23–7.37 (m, 10H); 6.42 (d, *J*=15.84 Hz, 1H), 6.25 (dt, *J*=15.84, 6.78 Hz, 1H), 4.74 (dd, *J*=7.38, 7.41 Hz, 1H), 2.24–2.29 (m, 2H), 1.84–2.04 (m, 2H); ¹³C NMR δ 145.0, 138.0, 130.8, 130.4, 128.8 (4C), 128.0, 127.4, 126.4 (4C), 74.4, 38.8, 29.7. Anal. calcd for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.63; H, 7.63.

4.1.31. 1-(4'-Methylphenyl)-5-phenylpent-4-en-1-ol (entry 13). Viscous oil; IR 3363, 1651 cm⁻¹; ¹H NMR δ 7.13–7.40 (m, 9H), 6.40 (d, *J*=15.81 Hz, 1H), 6.22 (dt, *J*=15.81, 6.81 Hz, 1H), 4.70 (dd, *J*=7.20, 7.32 Hz, 1H), 2.35 (s, 3H), 2.22–2.31 (m, 2H), 1.81–2.05 (m, 2H); ¹³C NMR δ 141.9, 138.0, 137.7, 130.7, 130.5, 129.7 (2C), 128.9 (2C), 127.3, 126.6 (4C), 74.3, 38.8, 29.7, 21.6. Anal. calcd for C₁₈H₂₀O: C, 85.67; H, 7.98. Found: C, 85.71; H, 7.91.

4.1.32. 1-(4'-Benzyloxyphenyl)-5-phenylpent-4-en-1-ol (entry 14). Colourless viscous oil; IR 3361, 1651 cm⁻¹; ¹H NMR δ 7.19–7.46 (m, 12H), 6.97 (d, *J*=8.67 Hz, 2H), 6.41 (d, *J*=15.84 Hz, 1H), 6.22 (dt, *J*=15.84, 6.69 Hz, 1H), 5.07 (s, 2H), 4.69 (dd, *J*=7.29, 7.20 Hz, 1H), 2.17–2.36 (m, 2H), 1.81–2.06 (m, 2H); ¹³C NMR δ 158.7, 138.0, 137.4, 130.7, 130.4, 128.9 (4C), 128.4, 127.9 (2C), 127.8 (2C), 127.6, 126.4 (2C), 115.0 (2C), 74.0, 70.4, 38.7, 29.8. Anal. calcd for C₂₄H₂₄O₂: C, 83.68; H, 7.02. Found: C, 83.57; H, 7.08.

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