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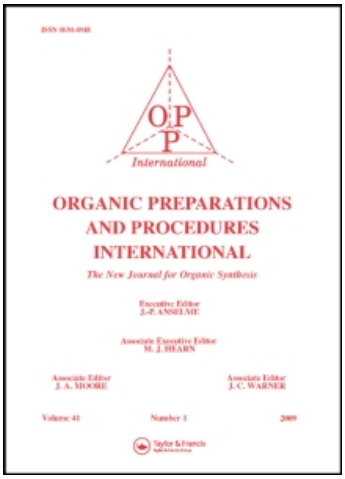

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Tetrahydronaphthalene Derivatives by Amberlyst® 15-Promoted Friedel-Crafts Cyclizations

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Tetrahydronaphthalene Derivatives by Amberlyst® 15-Promoted Friedel-Crafts Cyclizations

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A recent project required the preparation of a series of 1,1-disubstituted-1,2,3,4-tetrahydronaphthalene derivatives. These compounds are known to be both retinoic acid receptor (RAR) antagonists and retinoic X receptor (RXR) agonists. As RAR antagonists, these materials have been investigated for the treatment of dermatological diseases, such as psoriasis and eczema.[1] As RXR agonists, these agents have been co-administered with protein kinase A activators in efforts to control hyperproliferative diseases, such as leukemia and breast cancer.[2] Finally, studies are also underway to exploit these RXR agonists to ameliorate diabetes, atherosclerosis and hypercholesteremia.[3]

Amberlyst® 15 is a sulfonated polystyrene resin that has been used for a large number of transformations promoted by strong acids.[4] In the current work, we planned to use this resin in a Friedel-Crafts-type ring closure of 1,1-disubstituted-4-arylbutanols. Past reports have described the use of sulfuric acid[5] and polyphosphoric acid[6] for these cyclizations but extensive work-up and purification schemes were often required. Amberlyst® 15 offers the advantage that the reaction proceeds cleanly without the need for tedious isolation procedures. Reactions performed using this reagent require only filtration of the resin and removal of the solvent.

A series of substrates was prepared to assess the possibility of carrying out these cyclizations using Amberlyst® 15. Starting from 4-arylbutanoic acid derivatives **1–3**,[7] esterification with CH_3OH and H_2SO_4 in the presence of 3-Å molecular sieves[8] proceeded in 85–90% yield to give **4–6**. The trifluoromethyl-substituted ester **7** was prepared according to a literature procedure.[9] Treatment of 1 equivalent of each ester with 3 equivalents of (a) CH_3MgBr or (b) PhMgBr in ether gave the required tertiary alcohols **8a**–**11a** in 90–93% yields and **8b**–**11b** in 74–82% yields, respectively. The cyclizations to give **12a**–**15a** and **12b**–**14b** were carried out by reacting 0.25 g of each alcohol in PhH[10] with 0.25 g of Amberlyst® 15 for 0.5–8 h. Filtration and concentration of the crude reaction mixture

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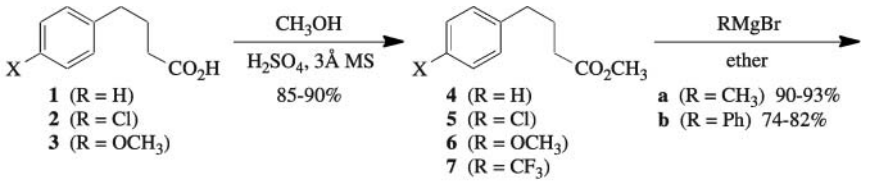

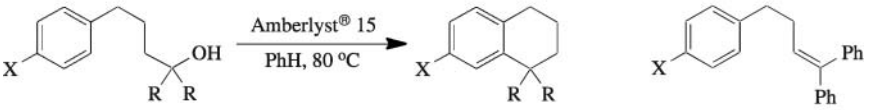

Reactant	X	R	Reflux Time (h)	Product	Yield (%)
8a	H	CH_3	0.5	**12a**	91
9a	Cl	CH_3	0.5	**13a**	90
10a	OCH_3	CH_3	0.5	**14a**	92
11a	CF_3	CH_3	3	**15a**	86
8b	H	Ph	8	**12b**	95
9b	Cl	Ph	8	**13b**	93
10b	OCH_3	Ph	8	**14b**	94
11b	CF_3	Ph	0.5	**15b**	0[a]

[a]This reaction gave 1,1-diphenyl-4-trifluoromethylphenyl-1-butene (**19b**) in 96% yield. Extended reaction times gave small amounts of the cyclized product, but it was inseparable from the alkene.

Scheme 1
Synthesis of 1,1,7-trisubstituted 1,2,3,4-tetrahydronaphthalenes.

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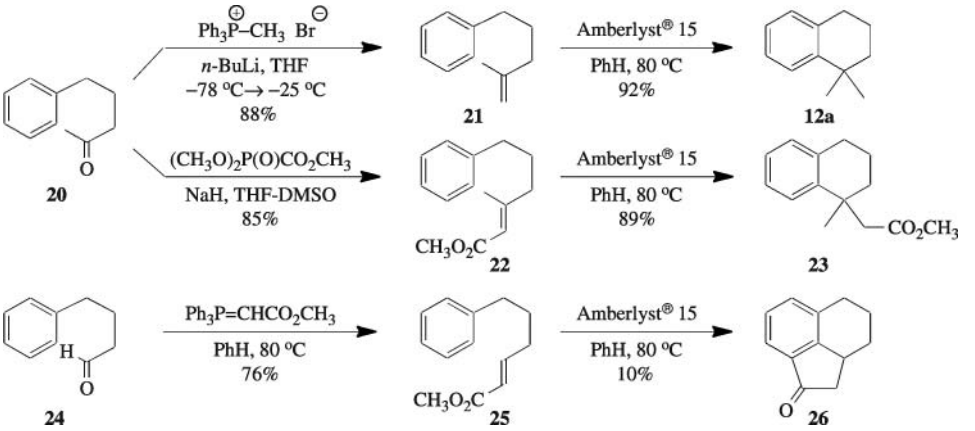
under vacuum gave the cyclized products in spectroscopically pure form. The synthesis and cyclization of our alcohol substrates are summarized in *Scheme 1*.

Reaction of the methyl-substituted tertiary alcohols generally proceeded faster than those substituted by phenyl. This presumably reflects the greater steric hindrance and lower reactivity of the more stabilized diphenyl-substituted carbocation intermediates. Although alkenes were not observed from the dimethyl precursors, exposure of diphenyl substrates **8b–10b** to Amberlyst® 15 in refluxing PhH for 0.5–1 h produced inseparable mixtures of 4-aryl-1,1-diphenylbutenes **16b–18b** (major) and 1,1-diphenyl-1,2,3,4-tetrahydronaphthalenes **12b–14b** (minor). Extending the reaction time to 8 h, however, resulted in clean conversion of these mixtures to the cyclized products[11] suggesting that ring closure occurs predominantly *via* alkenes **16b–18b** in the diphenyl series. Finally, substrate **11b** gave a nearly quantitative yield of alkene **19b**, with virtually none of the tetrahydronaphthalene **15b**, even after prolonged reaction.

The substituents on the aromatic ring were chosen to evaluate the ease of cyclization for electron-rich and electron-poor rings. To our surprise, the reaction proceeded smoothly for all of the alcohols studied except **11b** ($X = CF_3$, $R = Ph$), which failed to cyclize due to the hindered nature of the carbocation and the inductively deactivated aromatic ring at C4. In this case, the alkene dehydration product **19b** was isolated in 96% yield after 0.5 h at reflux. More forcing conditions (1.00 g of Amberlyst® 15, PhH, reflux, 72 h) produced an inseparable mixture of **19b** with small amounts of **15b** (< 5%) and several decomposition products.

In addition to the cyclization of alkenes **16b–18b**, produced as intermediates in the reaction of **8b**–**10b**, we explored the ring closure of several other selected alkenes (*Scheme 2*). Ketone **20**[12] was converted to 5-phenyl-2-methylpentene (**21**) by Wittig olefination and methyl (*E*)-3-methyl-6-phenyl-2-hexenoate (**22**) using the Wadsworth-Emmons procedure. Both of these substrates permitted reaction *via* a tertiary carbocation and gave excellent yields of **12a** and **23**, respectively. In an effort to define the limitations of the current procedure, aldehyde **24**[13] was converted to methyl (*E*)-6-phenyl-2-hexenoate (**25**) to evaluate a substrate that would require closure on a secondary carbocation. In this case, treatment with Amberlyst® 15 using our standard protocol for 72 h gave a complex product mixture containing recovered starting material and ketone **26** as the major components. This outcome likely arises from the greater difficulty in generating the less stabilized carbocation and suggests that cyclizations using this method may be limited to closures proceeding through tertiary carbocations.



Scheme 2
Cyclization of selected alkenes.

In conclusion, we report a convenient method for the preparation of 1,1-disubstituted-1,2,3,4-tetrahydronaphthalenes using Amberlyst® 15. Although a number of the compounds prepared have been previously reported, the current procedure gives comparably high yields and is operationally much simpler to perform in the laboratory. The procedure works well for systems proceeding through a tertiary carbocation, but is unsatisfactory for cyclizations involving less stabilized intermediates.

Experimental Section

All reactions were run in dry glassware under N_2. The saturated NaCl, saturated NH_4Cl and 5% $NaHCO_3$ used in work-up procedures refer to aqueous solutions. Reactions were monitored by thin layer chromatography (TLC) on silica gel GF plates (Analtech 21521). Preparative separations were performed by one of the following methods: (1) flash chromatography[14] (FC) on silica gel (grade 62, 60–200 mesh) containing UV-active phosphor (Sorbent Technologies UV-05) packed into quartz columns or (2) preparative thin layer chromatography (PTLC) on 20 cm × 20 cm silica gel GF plates (Analtech 02015). Band

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elution for all chromatographic separations was monitored using a hand-held UV lamp. Melting points were uncorrected. IR spectra were run as thin films on NaCl disks. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 MHz and 75 MHz, respectively, using $(CH_3)_4Si$ as the internal standard; coupling constants (J) are given in Hz. Mass spectra (EI/DP) were obtained at 70 eV.

General Procedure for the Conversion of Acids to Methyl Esters: Methyl 4-Phenyl-butanoate (4)

The procedure of Eisenbraun and co-workers was used.[8] To a solution of 6.00 g (36.6 mmol) of **1** in 100 mL of anhydrous CH_3OH was added 2 mL of concentrated H_2SO_4 and the mixture was heated under reflux such that the condensed CH_3OH passed through a Soxhlet cup containing 25–30 g of 3-Å molecular sieves. After 12 h, the reaction was cooled, concentrated, diluted with saturated NaCl solution and extracted with ether (3x). The combined ether layers were washed with saturated NaCl (1x), dried ($MgSO_4$) and concentrated to give a colorless oil, which was distilled *in vacuu* to afford 5.62 g (86%) of pure **4**, bp 87–88°C (1.5 mm Hg) [*lit.*[15] bp 123–124°C (13 mm Hg)]. IR: 1739 cm^{-1}; ^{1}H NMR: δ 7.28 (m, 2 H), 7.19 (m, 3 H), 3.66 (s, 3 H), 2.65 (t, J = 7.1 Hz, 2 H), 2.33 (t, J = 7.1 Hz, 2 H), 1.96 (quintet, J = 7.1 Hz, 2 H); ^{13}C NMR: δ 173.9, 141.3, 128.4, 128.3, 125.9, 51.5, 35.1, 33.3, 26.4.

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Methyl 4-(4-Chlorophenyl)butanoate (5)[16]

This compound (5.46 g, 85%) was isolated as a colorless oil from 6.00 g (30.2 mmol) of **2**,[7] bp 115–117°C (1.5 mm Hg). IR 1736 cm^{-1}; ^{1}H NMR: δ 7.24 (d, J = 8.2 Hz, 2 H), 7.10 (d, J = 8.2 Hz, 2 H), 3.66 (s, 3 H), 2.62 (t, J = 7.1 Hz, 2 H), 2.32 (t, J = 7.1 Hz, 2 H), 1.93 (quintet, J = 7.1 Hz, 2 H); ^{13}C NMR: δ 173.7, 139.7, 131.7, 129.8, 128.4, 51.5, 34.4, 33.2, 26.3.

Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.12. Found: C, 62.23; H, 6.15.

Methyl 4-(4-Methoxyphenyl)butanoate (6)

This compound (5.78 g, 90%) was isolated as a colorless oil from 6.00 g (30.9 mmol) of **3**, bp 120–122°C (1.5 mm Hg) [*lit.*[17] bp 105–110°C (0.25 mm Hg)]. IR: 2840, 1737 cm^{-1}; ^{1}H NMR: δ 7.09 (d, J = 8.2 Hz, 2 H), 6.83 (d, J = 8.2 Hz, 2 H), 3.78 (s, 3 H), 3.66 (s, 3 H), 2.59 (t, J = 7.1 Hz, 2 H), 2.31 (t, J = 7.1 Hz, 2 H), 1.92 (quintet, J = 7.1, 2 H); ^{13}C NMR: δ 174.0, 157.8, 133.4, 129.3, 113.7, 55.2, 51.4, 34.1, 33.3, 26.7.

General Procedure for Grignard Addition to the Esters: 2-Methyl-5-phenyl-2-pentanol (8a)

These reactions were carried out by reacting 1 eq of the ester with 3 eq of the Grignard reagent. Methylmagnesium bromide was prepared from 2.39 g (16.5 mmol) of CH_3I and 0.60 g (25.0 mmol) of Mg in 50 mL of anhydrous ether. To this reagent was slowly added a solution of 1.00 g (5.62 mmol) of **4** in 10 mL of dry ether. The reaction was warmed to reflux for 15 min, then cooled and quenched with 10 mL of saturated NH_4Cl. The mixture

was transferred to a separatory funnel and the aqueous phase was extracted with ether (3x). The combined ether layers were washed with saturated NaCl (1x), dried ($MgSO_4$) and concentrated under vacuum to afford 0.93 g (93%) of **8a** as a colorless oil. This oil was spectroscopically pure and used directly in the cyclization reaction. The spectral data matched those previously reported.[18]

2-Methyl-5-(4-chlorophenyl)-2-pentanol (9a)

This compound 0.90 g (90%) was isolated as a colorless oil from 1.00 g (4.71 mmol) of **5**. IR: 3375 cm^{-1}; ^1H NMR: δ 7.24 (d, $J = 8.2$ Hz, 2 H), 7.11 (d, $J = 8.2$ Hz, 2 H), 2.59 (t, $J = 7.1$ Hz, 2 H), 1.67 (m, 2 H), 1.51 (s, 1 H), 1.48 (m, 2 H), 1.19 (s, 6 H); ^{13}C NMR: δ 140.8, 131.4, 129.7, 128.3, 70.8, 43.2, 35.6, 29.2 (2 C), 26.1; MS: *m/z* 197, 199 (ca 3:1, M^+-CH_3).

Anal. Calcd for $C_{12}H_{17}ClO$: C, 67.76; H, 8.00. Found: C, 67.82; H, 8.01.

2-Methyl-5-(4-methoxyphenyl)-2-pentanol (10a)[19]

This compound 0.91 g (91%) was isolated as a colorless oil from 1.00 g (4.81 mmol) of **6**. IR: 3395, 2841 cm^{-1}; ^1H NMR: δ 7.10 (d, $J = 8.2$ Hz, 2 H), 6.82 (d, $J = 8.2$ Hz, 2 H), 3.78 (s, 3 H), 2.56 (t, $J = 7.1$ Hz, 2 H), 1.65 (m, 2 H), 1.51 (s, 1 H), 1.48 (m, 2 H), 1.19 (s, 6 H); ^{13}C NMR: δ 157.6, 134.5, 129.2, 113.7, 70.9, 55.2, 43.4, 35.4, 29.2 (2 C), 26.4; MS: *m/z* 193 (M^+-CH_3).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C: 75.07; H, 9.66.

2-Methyl-5-(4-trifluoromethylphenyl)-2-pentanol (11a)

This compound 0.90 g (90%) was isolated as a colorless oil from 1.00 g (4.07 mmol) of **7**.[9] IR: 3378 cm^{-1}; ^1H NMR: δ 7.53 (d, $J = 8.2$ Hz, 2 H), 7.29 (d, $J = 8.2$ Hz, 2 H), 2.67 (t, $J = 7.7$ Hz, 2 H), 1.72 (m, 2 H), 1.52 (s, 1 H), 1.50 (m, 2 H), 1.21 (s, 6 H); ^{13}C NMR: δ 146.5, 128.7, 128.1, 125.2 (q, $J = 3.7$ Hz), 124.3 (q, $J = 270.2$ Hz), 70.8, 43.2, 36.1, 29.2 (2 C), 25.9; MS: *m/z* 231 (M^+-CH_3).

Anal. Calcd for $C_{13}H_{17}F_3O$: C, 63.41; H, 6.91. Found: C, 63.54; H, 6.94.

1,1,4-Triphenylbutanol (8b)

These reactions were carried out by reacting 1 eq of the ester with 3 eq of phenylmagnesium bromide. This compound (1.36 g, 80%) was prepared from 1.00 g (5.62 mmol) of **4** and was purified by FC on a 30 cm $\times$ 2.5 cm column eluted with 10–15% ether in hexanes to give a white solid, mp 72–73°C (*lit.*[20] mp 72–73°C). IR: 3556, 3467 cm^{-1}; ^1H NMR: δ 7.50–7.10 (complex, 15 H), 2.63 (t, $J = 7.7$ Hz, 2 H), 2.30 (m, 2 H), 2.07 (s, 1 H), 1.63 (m, 2 H); ^{13}C NMR: δ 146.9, 142.1, 128.4, 128.2, 128.1, 126.8, 126.0, 125.7, 78.2, 41.3, 36.0, 25.4; MS: *m/z* 284 (M^+-H_2O).

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1,1-Diphenyl-4-(4-chlorophenyl)butanol (9b)

This compound (1.20 g, 76%) was prepared from 1.00 g (4.71 mmol) of **5** and was purified by FC on a 30 cm × 2.5 cm column eluted with 10–15% ether in hexanes to give a white solid, mp 77–79°C. IR: 3565, 3470 cm^{-1}; ^1H NMR: δ 7.40–7.17 (complex, 12 H), 7.04 (d, $J = 8.2$ Hz, 2 H), 2.59 (t, $J = 7.7$ Hz, 2 H), 2.27 (m, 2 H), 2.06 (s, 1 H), 1.60 (m, 2 H); ^{13}C NMR: δ 146.8, 140.5, 131.5, 129.7, 128.3, 128.1, 126.8, 125.9, 78.1, 41.1, 35.3, 25.2; MS: *m/z* 318, 320 (*ca* 3:1, M^+-H_2O).

Anal. Calcd for $C_{22}H_{21}ClO$: C, 78.45; H, 6.24, Found: C: 78.47; H, 6.24.

1,1-Diphenyl-4-(4-methoxyphenyl)butanol (10b)

This compound (1.31 g, 82%) was prepared from 1.00 g (4.81 mmol) of **6** and was purified by FC on a 30 cm × 2.5 cm column eluted with 10–15% ether in hexanes to give a white solid, mp 67–68°C. IR: 3556, 3480, 2839 cm^{-1}; ^1H NMR: δ 7.40–7.16 (complex, 10 H), 7.04 (d, $J = 8.2$ Hz, 2 H), 6.80 (d, $J = 8.2$ Hz, 2 H), 3.77 (s, 3 H), 2.57 (t, $J = 7.7$ Hz, 2 H), 2.28 (m, 2 H), 2.07 (s, 1 H), 1.59 (m, 2 H); ^{13}C NMR: δ 157.7, 147.0, 134.1, 129.3, 128.1, 126.8, 126.0, 113.7, 78.2, 55.2, 41.2, 35.0, 25.6; MS: *m/z* 314 (M^+-H_2O).

Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.13; H, 7.23. Found: C, 82.99; H, 7.20.

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1,1-Diphenyl-4-(4-trifluoromethylphenyl)butanol (11b)

This compound (1.12 g, 74%) was prepared from 1.00 g (4.07 mmol) of **7**[9] and purified by FC on a 30 cm × 2.5 cm column eluted with 10–15% ether in hexanes to give a white solid, mp 63–65°C. IR 3559, 3466, 1328 cm^{-1}; ^1H NMR: δ 7.49 (d, $J = 8.2$ Hz, 2 H), 7.39–7.17 (complex, 12 H), 2.67 (t, $J = 7.7$ Hz, 2 H), 2.29 (m, 2 H), 2.07 (s, 1 H), 1.63 (m, 2 H); ^{13}C NMR: δ 146.8, 146.2, 128.7, 128.4, 128.2, 126.9, 125.2 (q, $J = 3.7$ Hz), 78.1, 41.2, 35.8, 25.1 (the quartet of the CF_3 carbon and 1 aromatic carbon were obscured); MS: *m/z* 352 (M^+-H_2O).

Anal. Calcd for $C_{23}H_{21}F_3O$: C, 74.59; H, 5.68. Found: C; 74.66; H, 5.70.

General Procedure for the Cyclization with Amberlyst® 15: 1,1-Dimethyl-1,2,3,4-tetrahydronaphthalene (12a)

To a solution of 0.25 g (1.40 mmol) of **8a** in 5 mL of PhH was added 0.25 g of Amberlyst® 15 (dry, hydrogen form) and the mixture was heated under reflux for 0.5 h. The mixture was cooled, filtered through a thin layer of anhydrous $MgSO_4$ in a small fritted funnel, the $MgSO_4$ was washed with ether, and the solvent was removed under vacuum to afford 0.20 g (91%) of **12a** as a colorless oil. This compound was spectroscopically pure, and the data matched those previously reported.[18]

1,1-Dimethyl-7-chloro-1,2,3,4-tetrahydronaphthalene (13a)

This compound (0.21 g, 90%) was isolated as a colorless oil from 0.25 g (1.18 mmol) of **9a** after 0.5 h at reflux. IR: 1593, 1394, 1368 cm^{-1}; ^1H NMR: δ 7.27 (d, $J = 2.2$ Hz, 1 H), 7.02 (dd, $J = 8.2$, 2.2 Hz, 1 H), 6.96 (d, $J = 8.2$ Hz, 1 H), 2.70 (t, $J = 6.4$ Hz, 2 H),

1.78 (m, 2 H), 1.63 (m, 2 H), 1.26 (s, 6 H); ^{13}C NMR: δ 147.7, 134.5, 131.2, 130.4, 126.6, 125.4, 38.8, 34.1, 31.7, 30.1, 19.5 (2 C); MS: *m/z* 194, 196 (*ca* 3:1, M^+).

Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.04; H, 7.71. Found: C, 74.12; H, 7.75.

1,1-Dimethyl-7-methoxy-1,2,3,4-tetrahydronaphthalene (14a)[21]

This compound (0.21 g, 92%) was isolated as a colorless oil from 0.25 g (1.20 mmol) of **10a** after 0.5 h at reflux. IR: 2841, 1381, 1366 cm^{-1}; ^{1}H NMR: δ 6.97 (d, $J = 8.2$ Hz, 1 H), 6.87 (d, $J = 2.2$ Hz, 1 H), 6.65 (dd, $J = 8.2$, 2.2 Hz, 1 H), 3.78 (s, 3 H), 2.69 (t, $J = 6.0$ Hz, 2 H), 1.78 (m, 2 H), 1.64 (m, 2 H), 1.27 (s, 6 H); ^{13}C NMR: δ 157.7, 147.0, 129.8, 128.4, 112.1, 110.9, 55.2, 39.2, 34.1, 31.8, 29.9, 19.8 (2 C); MS: *m/z* 190 (M^+).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.11; H, 9.47. Found: C, 82.01; H, 9.44.

1,1-Dimethyl-7-trifluoromethyl-1,2,3,4-tetrahydronaphthalene (15a)

This compound (0.20 g, 86%) was isolated as a colorless oil from 0.25 g (1.02 mmol) of **11a** after 3 h at reflux. IR: 1619, 1389, 1360, 1332 cm^{-1}; ^{1}H NMR: δ 7.55 (s, 1 H), 7.29 (d, $J = 8.2$ Hz, 1 H), 7.12 (d, $J = 8.2$ Hz, 1 H), 2.79 (t, $J = 6.0$ Hz, 2 H), 1.82 (m, 2 H), 1.68 (m, 2 H), 1.29 (s, 6 H); ^{13}C NMR: δ 146.5, 140.2, 129.5, 128.2, 124.6 (q, $J = 270.6$ Hz), 123.4 (q, $J = 4.0$ Hz), 121.9 (q, $J = 3.7$ Hz), 38.9, 34.0, 31.7, 30.7, 19.3 (2 C); MS: *m/z* 228 (M^+).

Anal. Calcd for $C_{13}H_{15}F_3$: C, 68.42; H, 6.58. Found: C, 68.47; H, 6.60.

1,1-Diphenyl-1,2,3,4-tetrahydronaphthalene (12b)

This compound (0.22 g, 95%) was isolated as a white solid from 0.25 g (0.83 mmol) of **8b** after 8 h at reflux, mp 120–122°C (*lit.*[22] mp 125°C). The spectral data matched those previously reported.[22]

1,1-Diphenyl-7-chloro-1,2,3,4-tetrahydronaphthalene (13b)

This compound (0.22 g, 93%) was isolated as a white solid from 0.25 g (0.74 mmol) of **9b** after 8 h at reflux, mp 134–136°C. IR: 1594, 1499 cm^{-1}; ^{1}H NMR: δ 7.30–7.20 (complex, 7 H), 7.10–7.02 (complex, 5 H), 6.64 (d, $J = 1.6$ Hz, 1 H), 2.81 (t, $J = 6.6$ Hz, 2 H), 2.59 (m, 2 H), 1.63 (m, 2 H); ^{13}C NMR: δ 147.5, 144.8, 135.7, 130.9, 130.7, 130.6, 129.3, 127.9, 126.4, 126.2, 53.7, 38.0, 28.7, 18.8; MS: *m/z* 318, 320 (*ca* 3:1, M^+).

Anal. Calcd for $C_{22}H_{19}Cl$: C, 82.89; H, 5.97. Found: C, 82.87; H, 5.96.

1,1-Diphenyl-7-methoxy-1,2,3,4-tetrahydronaphthalene (14b)

This compound (0.22 g, 94%) was isolated as a white solid from 0.25 g (0.75 mmol) of **10b** after 12 h at reflux, mp 108–109°C. IR: 2833, 1609, 1493 cm^{-1}; ^{1}H NMR: δ 7.29–7.16 (complex, 7 H), 7.07 (d, $J = 7.1$ Hz, 4 H), 6.73 (dd, $J = 8.2$, 2.7 Hz, 1 H), 6.21 (d, $J = 2.7$ Hz, 1 H), 3.56 (s, 3 H), 2.79 (t, $J = 6.6$ Hz, 2 H), 2.59 (m, 2 H), 1.61 (m, 2 H); ^{13}C NMR: δ 156.9, 148.6, 143.9, 130.0, 129.5, 129.4, 127.7, 125.9, 116.7, 112.0, 55.0, 53.9, 38.2, 28.4, 19.1; MS: *m/z* 314 (M^+).

Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.78; H, 6.98.

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1,1-Diphenyl-4-trifluoromethylphenyl-1-butene (19b)

When this reaction was attempted on 0.25 g (0.68 mmol) of **11b**, 0.23 g (96%) of alkene **19b** was isolated as a white solid after 0.5 h of reflux, mp 66–68°C. Refluxing for 72 h gave a small amount of the tetrahydronaphthalene product, but it was inseparable from the alkene. The spectral data for **19b** were: IR: 1619, 1495, 1324 cm^{-1}; ^1H NMR: δ 7.50 (d, $J = 8.2$ Hz, 2 H), 7.36–7.17 (complex, 11 H), 7.04 (dd, $J = 7.7$, 1.6 Hz, 1 H), 6.07 (t, $J = 7.7$ Hz, 1 H), 2.79 (t, $J = 7.7$ Hz, 2 H), 2.44 (q, $J = 7.7$ Hz, 2 H); ^{13}C NMR: δ 145.7, 142.8, 142.4, 139.8, 129.7, 128.8, 128.3, 128.2, 128.1, 127.8, 127.1, 127.02, 127.00, 125.2 (q, $J = 3.7$ Hz), 124.4 (q, $J = 272.4$ Hz), 35.9, 31.2; MS: *m/z* 352 (M^+).

Anal. Calcd for $C_{23}H_{19}F_3$: C, 78.41; H, 5.40. Found: C, 78.29; H, 5.35.

2-Methyl-5-phenylpentene (21)

To a stirred slurry of 2.40 g (6.72 mmol) of triphenylphosphonium bromide in 40 mL of anhydrous THF at −78°C was slowly added 4.00 mL of 1.7 M *n*-butyllithium in hexanes (6.80 mmol) to give a bright yellow solution of the ylide. Stirring was continued for 15 min, and a solution of 0.81 g (5.00 mmol) of **20**[10] in 2 mL of dry THF was added dropwise. The reaction was stirred for 2 h with gradual warming to −25°C and the reaction was poured into 50 mL of saturated NH_4Cl solution and extracted with ether (3x). The combined ether layers were washed with saturated NaCl solution (1x), dried ($MgSO_4$) and concentrated under vacuum. The crude product was filtered through a plug of silica gel with pentane and concentrated to give 0.70 g (88%) of **21** as a colorless oil. The spectral data for this compound matched those reported previously.[23]

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1,1-Dimethyl-1,2,3,4-tetrahydronaphthalene (12a)

To a solution of 0.25 g (1.56 mmol) of **18** in 5 mL of PhH was added 0.25 g of Amberlyst® 15 and the mixture was heated under reflux for 0.5 h. Filtration of the mixture through a thin layer of $MgSO_4$ and concentration under vacuum afforded 0.23 g (92%) of **12a** as a colorless oil. This compound was spectroscopically pure and the data matched those reported previously.[18]

*Methyl (*E*)-3-Methyl-6-phenyl-2-hexenoate (22)*[24]

The general procedure of Balsevich[25] was used. Sodium hydride (0.28 g, 60% in mineral oil, 7.00 mmol) was washed with hexanes (3x) to remove the mineral oil and 8 mL of anhydrous THF was added. The resulting slurry was stirred and treated at 22°C with a solution of 1.28 g (7.02 mmol) of trimethyl phosphonoacetate in 2 mL of anhydrous DMSO added dropwise over 20 min. The mixture was stirred for 15 min to give a tan solution of the anion. To this anion was added a solution of 1.00 g (6.17 mmol) of **20**[12] in 3 mL of dry THF and the reaction was stirred for 24 h at 22°C. The crude reaction mixture was diluted with petroleum ether and washed with 5% $NaHCO_3$ solution (4x). The combined petroleum ether washes were dried ($MgSO_4$) and concentrated to give a tan oil, which was purified by FC on a 40 cm × 2 cm column eluted with 2% ether in hexane. The major band afforded 1.15 g (85%) of (*E*)-**22**. IR: 1718, 1648 cm^{-1}; ^1H NMR: δ 7.28 (t, $J = 7.7$ Hz, 2 H), 7.18

(overlapping d and t, $J \approx 7.7$ Hz, 3 H), 5.68 (s, 1 H), 3.68 (s, 3 H), 2.61 (t, $J = 7.7$ Hz, 2 H), 2.17 (t, $J = 7.1$ Hz, 2 H), 2.16 (s, 3 H), 1.80 (quintet, $J = 7.7$ Hz, 2 H); ^{13}C NMR: δ 167.2, 160.0, 141.7, 128.3 (2 C), 125.9, 115.3, 50.8, 40.3, 35.2, 29.7, 29.0; MS: *m/z* 218 (M^+).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 77.16; H, 8.30.

Methyl (±)-2-(1-Methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetate (23)[26]

To a solution of 0.25 g (1.15 mmol) of (*E*)-**22** in 5 mL of PhH was added 0.25 g of Amberlyst® 15 and the mixture was heated under reflux for 1 h. Filtration of the mixture through a thin layer of $MgSO_4$ and concentration under vacuum afforded 0.22 g (89%) of **23** as a colorless oil. (Note: A mixture of *E* and *Z* alkenes can also be used in the reaction.) This compound was spectroscopically pure and gave the following data: IR: 1736 cm^{-1}; ^{1}H NMR: δ 7.26 (d, $J = 7.1$ Hz, 1 H), 7.17–7.01 (complex, 3 H), 3.59 (s, 3 H), 2.77 (t, $J = 4.9$ Hz, 2 H), 2.68 (d, $J = 14.3$ Hz, 1 H), 2.60 (d, $J = 14.3$ Hz, 1 H), 2.06 (m, 1 H), 1.82 (m, 2 H), 1.64 (m, 1 H), 1.40 (s, 3 H); ^{13}C NMR: δ 172.1, 143.5, 136.4, 129.2, 126.4, 125.8, 125.7, 51.2, 47.1, 36.4, 35.7, 30.4, 29.5, 19.3; MS: *m/z* 203 ($M^+ - CH_3$).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 77.21; H, 8.29.

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Methyl (E)-6-phenyl-2-hexenoate (25)

A 100-mL PhH solution of 1.00 g (6.77 mmol) of **24**[13] and 6.74 g (20.2 mmol) of (methoxycarbonylmethylene)triphenylphosphorane[27] was heated under reflux for 12 h, then cooled and concentrated under vacuum. The residue was filtered through a 6 cm x 6 cm plug of silica gel in a sintered glass frit. FC of this material on a 30 cm × 2.5 cm column eluted with 5% ether in hexane gave two bands: band 1, 0.10 g (0.47 mmol, 7%) of (*Z*)-**25** contaminated with a small amount of the *E* isomer; band 2, 1.04 g (5.14 mmol, 76%) of (*E*)-**25**. The spectral data for (*E*)-**25** were: IR: 1725, 1656 cm^{-1}; ^{1}H NMR: δ 7.28 (t, $J = 7.7$ Hz, 2 H), 7.18 (overlapping t and d, $J \approx 7.7$ Hz, 3 H), 6.99 (dt, $J = 15.9$, 7.1 Hz, 1 H), 5.84 (d, $J = 15.9$ Hz, 1 H), 3.72 (s, 3 H), 2.64 (t, $J = 7.7$ Hz, 2 H), 2.23 (q, $J = 7.1$ Hz, 2 H), 1.79 (quintet, $J = 7.7$ Hz, 2 H); ^{13}C NMR: δ 167.0, 149.1, 141.6, 128.4, 128.3, 125.9, 121.2, 51.4, 35.1, 31.5, 29.6; MS: *m/z* 204 (M^+).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.47; H, 7.84. Found: C, 76.55; H, 7.87.

(±)-6,7,8,8a-Tetrahydroacenaphthalen-1(2H)-one (26)

To a solution of 0.25 g (1.23 mmol) of (*E*)-**25** in 5 mL of PhH was added 0.25 g of Amberlyst® 15 and the mixture was heated under reflux for 72 h. Filtration of the mixture through a thin layer of $MgSO_4$ and concentration under vacuum afforded the crude product as a colorless oil. The product was a complex mixture. Purification by PTLC using 5–10% ether in hexanes afforded two major bands: band 1: 71 mg (28%) of recovered starting material; band 2: 20 mg (10%) of **23**, mp 99–100°C (*lit.*[28] mp 100–101.5°C). IR: 1707 cm^{-1}; ^{1}H NMR: δ 7.52 (dd, $J = 8.2$, 1.6 Hz, 1 H), 7.28 (m, 2 H), 3.14 (apparent sextet, $J = 6.0$ Hz, 1 H), 3.04–2.72 (complex, 3 H), 2.32 (dd, J = 17.6, 6.0 Hz, 1 H), 2.24 (m, 1 H), 2.14 (m, 1 H), 1.95 (m, 1 H), 1.37 (m, 1 H); ^{13}C NMR: δ 205.7, 156.0, 135.6, 135.2, 133.1, 127.8, 120.5, 45.6, 36.5, 28.2, 25.9, 22.8; MS: *m/z* 172 (M^+).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.72; H, 6.98. Found: C, 83.59; H, 7.01.

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