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AMBERLYST-15 CATALYZED ADDITION OF PHENOLS TO α,β-UNSATURATED KETONES

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Abstract. Amberlyst-15 has been used to catalyze regioselective additions of phenols to α,β-unsaturated ketones in yields of 20-90%. The reaction is superior to the analogous reaction employing concentrated sulfuric acid in affording greater yields and purer products with a minimum of laboratory operations.

We have found that Amberlyst-15 is an effective catalyst for promoting regioselective addition from the para position of phenols to α,β-unsaturated ketones. The previously established route[2] employs concentrated sulfuric acid in toluene at -10°C for these additions; this procedure, however, is more difficult to carry out, gives lower yields and affords products requiring a more extensive purification regime. The use of Amberlyst-15, a heterogenous acid catalyst,[3] in toluene at 20-50°C was found to promote this same reaction in high yield with fewer laboratory operations. Since these compounds represent commercially useful flavor and fragrance chemicals as well as valuable precursors to oxygenated fused aromatic systems, a simple route for their synthesis was a desirable goal.

The reaction was carried out in toluene solution at 20-50°C and monitored by TLC until complete. Best conversions, with the fewest side reactions, were achieved using a 3:1 ratio of phenol to ketone and ca. 0.3 equivalents of the acidic resin. The concentration of the reagents was not critical but some dilution with toluene (15 mL/100 mmole of phenol) was advantageous, especially for solid

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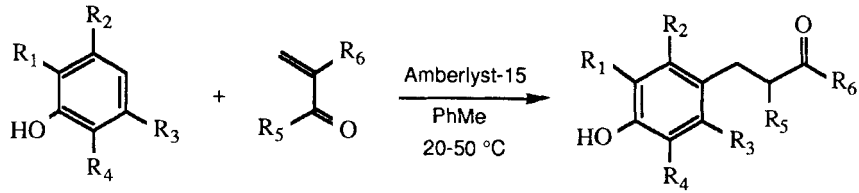

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Table. Phenol Additions to α,β-Unsaturated Ketones.

Entry	R_1	R_2	R_3	R_4	R_5	R_6	Yield (%)[a]
a	H	H	H	H	H	Me	58
b	Me	H	H	H	H	Me	65
c	H	Me	H	H	H	Me	63
d	n-Pr	H	H	H	H	Me	77
e	t-Bu	H	H	H	H	Me	42
f	Me	H	H	Me	H	Me	80
g	H	Me	Me	H	H	Me	57
h	Me	Me	H	H	H	Me	58
i	i-Pr	H	Me	H	H	Me	89
j	t-Bu	H	H	t-Bu	H	Me	21
k	$-(CH_2)_4-$		H	H	H	Me	69
l	OMe	H	H	H	H	Me	37
m	H	Me	H	H	Me	Me	56
n	H	H	H	H	H	Ph	72
o	Me	H	H	Me	H	Ph	84
p	i-Pr	H	Me	H	H	Ph	84
q	H	H	H	H	Me	Ph	56
r	Me	H	H	H	Me	Ph	59

[a] Yields refer to isolated purified products.

phenols. Finally, reactions were performed on scales ranging from 5-50 mmol based on the enone with little effect on the yield.

The results of our study are summarized in the Table. In the reaction, the acidic catalyst presumably protonates the carbonyl of the enone activating the β position to attack by the phenol in a Michael-type addition. The steric demands of the reaction, in fact, were found to parallel those of the Michael reaction with substitution at the enone terminus being the most critical factor.[4] Groups flanking the phenol reacting center were not as important though slightly lower yields are

observed for 3,5-disubstituted phenols. The reaction appears to work best for alkylated phenols unsubstituted in the para position. Phenols, such as p-cresol, were found to be unreactive toward ortho addition with both Amberlyst-15 and concentrated sulfuric acid. Our worst case was 2,6-di-*tert*-butylphenol (**1e**) which yielded only 21% of the desired adduct. We believe this derives from a perviously observed phenomenon[5] wherein the two *tert*-butyl groups force the lone pairs of the phenol oxygen out of conjugation with the ring thereby decreasing reactivity. Reactivity in the α,β-unsaturated ketones seems to follow the expected trend with the α-alkyl enones reacting more slowly than the unsubstituted cases.

Several control experiments were run on **1a**, **1b**, **1g**, **1i** and **1k** using the previously described procedure[2] with concentrated sulfuric acid. These reactions proved far more difficult to run, especially with solid phenols having minimal solubility in cold toluene. Additionally, the reactions generated a gummy solid which impeded stirring. Beyond these difficulties, it was found that yields were considerably diminished (15-30% less) under these conditions. Furthermore, the products obtained were contaminated by highly colored impurities and required a more extensive purification scheme which further decreased the yields. A final comparison experiment was performed using p-toluenesulfonic acid, a structurally related homogeneous catalyst. As expected, this catalyst provided yields comparable with those obtained using Amberlyst-15. Best results were achieved, however, when these reactions were run on a small scale where the crude product could be purified directly by chromatography. Larger scale reactions using p-toluenesulfonic acid gave products having colored impurities similar to those observed in reactions promoted by sulfuric acid.

An attempt was made to extend the scope of the addition process to other activated aromatic systems but these generally met with disappointing results. For example, anisole and veratrole were observed to react but yields were less than 10%; guaiacol (**1l**), a substrate incorporating a hydrogen-bonded phenol, gave only 37% of the addition product. Finally, other substrates such as 2-chlorophenol, 2-phenylphenol and 1-naphthol afforded mixtures of products and were not pursued further.

In summary, Amberlyst-15 is an effective and convenient catalyst for the addition of alkyl phenols to α,β-unsaturated ketones. Although the reaction is somewhat limited, it provides a readily available source of functionalized compounds which can serve as precursors to otherwise inaccessible fused-ring phenols. We are continuing to explore other variants to this reaction.

Experimental Section

General Considerations. Toluene and all of the phenols were used as received from the vendors. Amberlyst-15 was dried at 130°C prior to use. Methyl vinyl ketone was purified by drying over $CaCl_2$ and distilling at 45°C (120 mmHg). Isopropenyl methyl ketone,[6] phenyl vinyl ketone,[7] and isopropenyl phenyl ketone[7] were prepared and purified by literature methods or slight modifications thereof. All reactions were run under an atmosphere of dry nitrogen. Reactions were monitored by TLC on silica gel plates (Analtech No. 02521). Column chromatographic separations were performed on silica gel (Grace, grade 62, 60-200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. IR spectra were recorded using a PE-681 instrument and are referenced to polystyrene. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 300 MHz and 75 MHz, respectively, using a Varian VXR-XL-300 superconducting FT instrument; chemical shifts are reported in δ units relative to internal tetramethylsilane. Mass spectra were obtained at 70 eV using a VG TS-250 spectrometer; high resolution mass spectra were obtained using a VG ZAB-2SE. Elemental analyses ($\pm$ 0.4%) were performed by Galbraith Laboratories, Knoxville, TN.

General Procedure for Phenol Additions to α,β-Unsaturated Ketones. To a 10-mL toluene solution of 75 mmol of the phenol was added 1.6 g (7.5 meq H^+)[3] of Amberlyst-15. The slurry was stirred at 20-40°C while a 5-mL solution of 25 mmol of the unsaturated ketone was added during 1 h. The reaction was monitored by TLC until complete (2-8 h), then diluted with 25 mL of ether. The ether solution was washed with 50 mL of water, 50 mL of brine, dried by filtration through a plug of anhydrous $MgSO_4$ and concentrated under vacuum with rotary evaporation. The crude yellow-brown oil was vacuum distilled at 0.5 mmHg (short path or Kugelrohr apparatus) to yield a low boiling fraction (unreacted phenol) and a higher boiling fraction (addition product). For products having >14 carbons, removal of unreacted phenol was followed by chromatography on a 50 cm X 2 cm silica gel column eluted with gradually increasing concentrations of ether in hexane. Recrystallizations were carried out using ether-hexane mixtures. The following compounds were prepared:

4-(3-Oxobutyl)phenol (3a): 58.1%; bp. 140-146°C (0.5 mmHg); mp. 80-81°C (lit.[2] mp. 81-82°C); IR (thin film) 3390, 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ

7.10 (d, 2H, J = 8.1 Hz), 6.79 (d, 2H, J = 8.1 Hz), 6.75 (bs, 1H), 2.82 (A of ABm, 2H), 2.77 (B of ABm, 2H), 2.15 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 210.1, 154.2, 129.3, 129.2, 115.0, 45.4, 30.0, 28.9; MS, m/e (%) 164 (M^+, 58), 107 (100); exact mass calcd for $C_{10}H_{12}O_2$: 164.0837, found 164.0834.

2-Methyl-4-(3-oxobutyl)phenol (3b): 68.4%; bp. 153-160°C (0.5 mm Hg, Kugelrohr); mp. 38-40°C; IR (thin film) 3410, 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.93 (d. 1H, J = 2.1 Hz), 6.88 (dd, 1H, J = 8.1, 2.1 Hz), 6.85 (d, 1H, J = 8.1 Hz), 5.84 (bs, 1H), 2.81 (A of ABm, 2H), 2.78 (B of ABm, 2H), 2.23 (s, 3H), 2.16 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 209.6, 152.4, 132.5, 130.8, 126.5, 124.0, 114.9, 45.5, 30.0, 28.9, 15.8; MS, m/e (%) 178 (M^+, 29), 135 (14), 121 (100), 91 (10), 69 (16), 57 (16). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.40; H, 7.89.

3-Methyl-4-(3-oxobutyl)phenol (3c): 63.4%; bp. 150-160°C (0.5 mmHg, Kugelrohr); mp. 73-75°C; IR (thin film) 3400, 1705 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.92 (d, 1H, J = 8.4 Hz), 6.65 (m, 3H), 2.79 (A of ABm, 2H), 2.68 (B of ABm, 2H), 2.21 (s, 3H), 2.15 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 210.0, 154.2, 137.2, 130.5, 129.5, 117.2, 112.8, 44.2, 30.0, 26.2, 19.3; MS, m/e (%) 178 (M^+, 35), 135 (20), 121 (100), 108 (15), 91 (14), 77 (13). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.26; H, 8.04.

2-Propyl-4-(3-oxobutyl)phenol (3d): 76.6%, light yellow oil; IR (thin film) 3390, 1705 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.91 (d, 1H, J = 2.1 Hz), 6.84 (dd, 1H, J = 8.1, 2.1 Hz), 6.68 (d, 1H, J = 8.1 Hz), 6.26 (bs, 1H), 2.80 (A of ABm, 2H), 2.72 (B of ABm, 2H), 2.55 (t, 2H, J = 7.8 Hz), 2.13 (s, 3H), 1.62 (sextet, 2H, J = 7.8 Hz), 0.94 (t, 3H, J = 7.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 210.0, 152.1, 132.1, 129.9, 128.6, 126.3, 115.1, 45.4, 31.9, 29.9, 28.9, 22.8, 13.9; MS, m/e (%) 206 (M^+, 41), 177 (24), 149 (100), 91 (11); exact mass calcd for $C_{13}H_{18}O_2$: 206.1306, found 206.1302.

2-*tert*-Butyl-4-(3-oxobutyl)phenol (3e): 42.2%; mp. 87-88°C; IR ($CHCl_3$) 3430, 1709 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.06 (d, 1H, J = 2.1 Hz), 6.87 (dd, 1H, J = 8.1, 2.1 Hz), 6.60 (d, 1H, J = 8.1 Hz), 5.20 (s, 1H), 2.83 (A of ABm, 2H,), 2.73 (B of ABm, 2H), 2.16 (s, 3H), 1.40 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 209.0, 152.6, 136.1, 132.4, 127.0, 126.4, 116.5, 45.7, 34.5, 30.1, 29.5, 29.2; MS, m/e (%) 220 (M^+, 42), 205 (64), 163 (27), 147 (100), 91 (10), 57 (12). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 76.24; H, 9.14.

2,6-Dimethyl-4-(3-oxobutyl)phenol (3f): 85.9%; bp. 120-125°C (0.05 mmHg); mp. 58-59°C; IR ($CHCl_3$) 3460, 1705 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.79 (s, 2H), 4.81 (s, 1H), 2.75 (m, 4H), 2.22 (s, 6H), 2.14 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 208.7, 150.5, 132.3, 128.3, 123.0, 45.6, 30.0, 28.9, 15.9; MS, m/e (%) 192 (M^+, 85), 149 (61), 136 (31), 135 (100), 122 (26), 92 (24), 79 (14). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 75.29; H, 8.52.

3,5-Dimethyl-4-(3-oxobutyl)phenol (3g): 56.8%; bp. 165-185°C (0.5 mmHg, Kugelrohr); mp. 116-117°C; IR ($CHCl_3$) 3260, 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.53 (s, 2H), 5.81 (bs, 1H), 2.80 (A of ABm, 2H), 2.56 (B of ABm, 2H), 2.23 (s, 6H), 2.19 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 209.6, 153.6, 137.4, 129.3, 115.0, 43.1, 29.9, 22.9, 19.8; MS, m/e (%) 192 (M^+, 22), 159 (10), 136 (10), 135 (100), 134 (13). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 75.10; H, 8.38.

2,3-Dimethyl-4-(3-oxobutyl)phenol (3h): 57.9%; bp. 140-155°C (0.5 mmHg, Kugelrohr); mp. 91-92°C; IR (thin film) 3492, 3395, 1704 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.83 (d, 1H, J = 8.4 Hz), 6.58 (d, 1H, J = 8.4 Hz), 5.13 (bs, 1H), 2.85 (A of ABm, 2H), 2.66 (B of ABm, 2H), 2.20 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 209.0, 152.1, 135.9, 131.1, 126.7, 123.0, 112.3, 44.6, 30.0, 27.6, 15.5, 12.0; MS, m/e (%) 192 (M^+, 61), 159 (18), 149 (15), 136 (23), 135 (100), 134 (26), 122 (15), 91 (17). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.69; H, 8.16.

2-Isopropyl-5-methyl-4-(3-oxobutyl)phenol (3i): 88.5%; bp. 152-162°C (0.25 mmHg); mp. 85-86°C; IR ($CHCl_3$) 3420, 1708 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.91 (s, 1H), 6.57 (s, 1H), 5.03 (bs, 1H), 3.15 (septet, 1H, J = 7.5 Hz), 2.81 (A of ABm, 2H), 2.69 (B of ABm, 2H), 2.22 (s, 3H), 2.18 (s, 3H), 1.24 (d, 6H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 209.0, 151.0 134.1, 131.9, 131.0, 126.7, 117.2, 44.5, 30.0, 26.8, 26.7, 22.7, 18.7; MS, m/e (%) 220 (M^+, 42), 205 (33), 163 (100), 147 (46), 135 (10). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 76.05; H, 9.08.

2,6-Di-*tert*-butyl-4-(3-oxobutyl)phenol (3j): 21.0%; light yellow oil; IR (thin film) 3640, 1715 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.98 (s, 2H), 5.09 (s, 1H), 2.81 (A of ABm, 2H), 2.78 (B of ABm, 2H), 2.15 (s, 3H), 1.43 (s, 18H); ^{13}C-NMR ($CDCl_3$) δ 208.4, 152.0, 135.9, 131.4, 124.7, 45.7, 34.2, 30.2, 30.0, 29.7; MS, m/e (%) 276 (M^+, 66), 261 (100), 219 (25), 203 (27), 147 (16), 57 (24); exact mass calcd for $C_{18}H_{28}O_2$: 276.2089, found 276.2087.

4-(3-Oxobutyl)-5,6,7,8-tetrahydro-1-naphthol (3k): 69.4%; mp. 89-91°C; IR ($CHCl_3$) 3505, 3395, 1702 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.82 (d, 1H, J = 8.1 Hz), 6.58 (d, 1H, J = 8.1 Hz), 5.37 (bs, 1H), 2.78 (A of ABm, 2H), 2.68 (B of ABm, 2H), 2.66 (m, 4H), 2.17 (s, 3H), 1.80 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 209.1, 152.0, 136.4, 130.7, 126.1, 123.8, 111.7, 44.2, 30.0, 26.5, 26.0, 23.3, 22.8, 22.1; MS, m/e (%) 218 (M^+, 26), 200 (21), 185 (11), 161 (77), 160 (100), 145 (24), 61 (33), 57 (15). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 76.78: H, 8.44.

2-Methoxy-4-(3-oxobutyl)phenol (3l): 36.6%; bp. 140-148°C (0.5 mmHg, Kugelrohr); light green oil; IR (thin film) 3410, 2830, 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.82 (d, 1H, J = 7.8 Hz), 6.67 (s, 1H), 6.65 (d, 1H, J = 7.8 Hz), 5.76 (bs, 1H), 3.85 (s, 3H), 2.80 (A of ABm, 2H), 2.72 (B of ABm, 2H), 2.13 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 208.4, 146.4, 143.8, 132.8, 120.6, 114.3, 111.0, 55.7, 45.4, 30.0, 29.3; MS, m/e (%) 194 (M^+, 48), 138 (14), 137 (100), 119 (15), 91 (12); exact mass for $C_{11}H_{14}O_3$: 194.0789, found 194.0784.

5-Methyl-4-(2-methyl-3-oxobutyl)phenol (3m): 55.7%; bp. 125-140°C (0.5 mmHg, Kugelrohr); light yellow oil; IR (thin film) 3400, 1707 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.87 (d, 1H, J = 8.1 Hz), 6.65 (m, 3H), 2.84 (m, 2H), 2.48 (m, 1H), 2.22 (s, 3H), 2.07 (s, 3H) 1.07 (d, 3H, J = 7.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 214.4, 154.3, 137.3, 130.6, 129.2, 117.2, 112.7, 47.6, 35.4, 29.0, 19.4, 16.1; MS, m/e (%) 192 (M^+, 12), 121 (100), 91 (11), 77 (10); exact mass calcd for $C_{12}H_{16}O_2$: 192.1150, found 192.1150.

4-(3-Oxo-3-phenylpropyl)phenol (3n): 71.7%; mp. 119-120°C; IR (thin film) 3400, 1678 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.99 (dd, 2H, J = 7.5, 2.0 Hz), 7.58 (m, 1H), 7.48 (m, 2H), 7.12 (d, 2H, J = 8.1 Hz), 6.79 (d, 2H, J = 8.1 Hz), 5.12 (bs, 1H), 3.28 (A of ABt, 2H, J = 7.5 Hz), 3.00 (B of ABt, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 199.8, 153.9, 138.5, 133.2, 133.1, 129.5, 128.5, 128.0, 115.3, 40.7, 29.3; MS, m/e (%) 226 (M^+, 37), 107 (28), 105 (100), 91 (11), 77 (31). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.50; H, 6.40.

2,6-Dimethyl-4-(3-oxo-3-phenylpropyl)phenol (3o): 83.9%; light yellow oil; IR (thin film) 3490, 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.94 (d, 2H, J = 7.5 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.5 Hz), 6.83 (s, 2H), 5.18 (bs, 1H), 3.23 (A of ABt, 2H, J = 7.8 Hz), 2.91 (B of ABt, 2H, J = 7.8 Hz), 2.21 (s, 6H); ^{13}C-NMR ($CDCl_3$) δ 199.9, 150.5, 136.7, 133.0, 132.5, 128.4, 128.3, 40.8, 29.2, 15.9; MS, m/e (%) 254 (M^+, 52), 149 (27), 135 (100), 105 (42), 77 (30); exact mass calcd for $C_{17}H_{18}O_2$: 254.1306, found 254.1308.

2-Isopropyl-5-methyl-4-(3-oxo-3-phenylpropyl)phenol (3p): 83.6%; mp. 74-75°C; IR (thin film) 3420, 1678 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 7.98 (d, 2H, J= 7.5 Hz), 7.57 (m, 1H), 7.45 (m, 2H), 6.99 (s, 1H), 6.59 (s, 1H), 5.04 (bs, 1H), 3.21 (A of ABt, 2H, J = 7.5 Hz), 3.19 (septet, 1H, J = 7.5 Hz), 2.99 (B of ABt, 2H, J = 7.5 Hz), 2.25 (s, 3H), 1.24 (d, 6H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 200.1, 151.1, 136.8, 134.2, 133.1, 132.0, 131.3, 128.6, 128.0, 126.9, 117.2, 39.7, 27.3, 26.8, 22.7, 18.8; MS, m/e (%) 282 (M^+, 34), 163 (100), 147 (34), 135 (22), 105 (30), 77 (20). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80. Found: C, 80.97; H, 7.74.

4-(2-Methyl-3-oxo-3-phenylpropyl)phenol (3q): 55.8%; mp. 59-60°C; IR (thin film) 3400, 1678 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 7.90 (dd, 2H, J = 7.5, 2.1 Hz), 7.51 (m, 1H), 7.41 (m, 2H), 7.00 (d, 2H, J = 8.4 Hz), 6.84 (s, 1H), 6.75 (d, 2H, 8.4 Hz), 3.70 (sextet, 1H, J = 7.5 Hz), 3.06 (A of ABm, 1H,), 2.61 (B of ABm, 1H), 1.17 (d, 3H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 205,1, 154.3, 136.2, 133.1, 131.2, 130.0, 128.6, 128.3, 115.3, 43.0, 38.5, 17.2; MS, m/e (%) 240 (M^+, 71), 225 (12), 135 (24), 134 (34), 133 (15), 108 (16), 107 (100), 106 (14), 105 (98), 77 (65). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67. Found: C, 80.16; H, 6.87.

2-Methyl-4-(2-methyl-3-oxo-3-phenylpropyl)phenol (3r): 58.7 %; light yellow oil; IR (thin film) 3490, 3395, 1674 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 7.92 (m, 2H), 7.50 (m, 1H), 7.40 (m, 2H), 6.92 (d, 1H, J = 2.1 Hz), 6.84 (dd, 1H, J = 8.1, 2.1 Hz), 6.68 (d, 1H, J = 8.1 Hz), 6.28 (bs, 1H), 3.70 (sextet, 1H, J = 7.2 Hz), 3.04 (m, 1H), 2.57 (m, 1H), 2.20 (s, 3H), 1.17 (d, 3H, J = 7.2 Hz) ; ^{13}C-NMR ($CDCl_3$) δ 205.0, 152.5, 136.3, 133.0, 131.5, 131.3, 128.6, 128.3, 127.3, 123.9, 114.8, 43.0, 38.5, 17.2, 15.8; MS, m/e (%) 254 (M^+, 73), 239 (11), 149 (25), 134 (31), 121 (100), 105 (100), 91 (24), 77 (100); exact mass calcd for $C_{17}H_{18}O_2$: 254.1306, found 254.1301.

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