Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2008

Anti-Markovnikov hydroarylation of styrenes catalyzed by an *in situ* generated ruthenium complex

Remi Martinez, Jean-Pierre Genet, Sylvain Darses**

Laboratoire de Synthese Selective Organique (UMR 7573, CNRS), Ecole Nationale Superieure de Chimie de Paris, 11 rue P&M Curie, 75231 Paris cedex 05, France
sylvain-darses@enscp.fr, jean-pierre-genet@enscp.fr

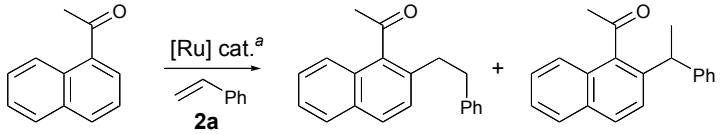
Supporting information

General Procedures

^{1}H NMR and ^{13}C NMR spectra were recorded on Avance 300 or Avance 400 instruments; chemical shifts (δ) are reported in ppm relative to Me_4Si; coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities. Mass spectra were determined on a Ribermag instrument. High-resolution mass spectra were performed on a Varian MAT311 at the Ecole Normale Superieure (Paris). Thin layer chromatography was carried out on silica-gel plates (Merck F_{254}), spots were detected with UV light and revealed with $KMnO_4$ solution. GC analyses were performed on a Hewlett-Packard instrument equipped with a J&W Scientific DB-1701 capillary column (30 m, ∅ = 0.25 μm), using an ionization flame detector and the following temperature program: 150°C during 1 min then 20°C/min up to 250°C.
Toluene was freshly distilled from Na/benzophenone. Tris-[di-3,5-(trifluoromethyl)phenyl]phosphine was prepared according to reported procedure.[1] Styrenes were distilled before use.

Ligand screening in the reaction of 1a with 2a

[1] S. Haji and C. Erkey, *Tetrahedron,* 2002, **58**, 3929.

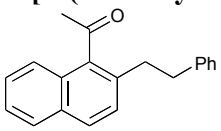


1a **3aa** **4aa**

Entry	Ligand	% Yield[b]	**3aa**/**4aa**[c]
1	PPh_3	97	63/37
2	$CyPPh_2$	79	76/24
3	Cy_2PPh	42	93/7
4	PCy_3	69	88/12
5	$MePPh_2$	17	60/40
6	Cy_2P(biphenyl)	0	-
7	P(*t*-Bu)$_3$	3	42/58
8	P(*o*-tolyl)$_3$	3	49/51
9	Binap[d]	8	93/7
10	P(4-MeOC_6H_4)$_3$	99	58/42
11	P(4-ClC_6H_4)$_3$	57	46/54
12	-[f]	100	48/52

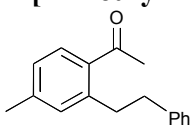
[a] Reactions conducted with 1 mmol of 1-acetylnaphthalene (**1a**), 2 equiv. of **2a**, 2.5 mol% of [Ru(*p*-cymene)Cl_2]$_2$, 30 mol% $NaHCO_2$ and 15 mol% of ligand, at 140°C in 1 mL of toluene. [b] Yield after 20h determined by GC using an internal standard. [c] Linear/branched ratio determined by GC/MS. [d] Use of 5 mol % ligand. [e] Reaction conducted with 5 mol % of $RuH_2(CO)(PPh_3)_3$.

1-[2-(2-Phenylethyl)naphthalen-1-yl]ethanone (3aa)



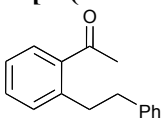
Reaction of 1-acetylnaphthalene **1a** (1 mmol, 153 µl) and styrene **2a** (4 mmol, 460 µl) afforded 252 mg of ketone **3aa** as a light yellow oil (yield 92%). R_f = 0.68 (cyclohexane/AcOEt 4:1). GC: rt = 10.01 min (branched 9.2 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.84–7.87 (m, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.59–7.63 (m, 1H), 7.45–7.53 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.16–7.31 (m, 5H), 2.98 (s, 4H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 208.1, 141.3, 138.9, 133.9, 131.9, 128.9 (2C), 128.6 (2C), 128.5 (2C), 128.3, 127.5, 126.9, 126.2, 125.7, 124.2, 38.0, 35.8, 33.3. MS (EI, 70eV, m/z): 274 ($M^{+\cdot}$, 11%), 259 (100%), 183 (35%), 153 (27%), 141 (18%), 115 (7%), 91 (21%). HRMS calculated for $C_{20}H_{19}O$ (M+H) 275.1436; found 275.1432.

1-[4-Methyl-2-(2-phenylethyl)phenyl]ethanone (3ba)



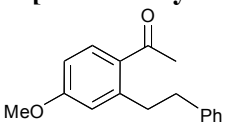
Reaction of 4-methylacetophenone **1a** (1 mmol, 134 mg) and styrene **2a** (2 mmol, 230 µl) afforded 237 mg of ketone **3ba** as a light yellow oil (yield 100%). R_f = 0.80 (cyclohexane/AcOEt 4:1). GC: rt = 6.0 min (branched 5.5 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.66 (d, *J* = 7.9 Hz, 1H), 7.09-7.32 (m, 7H), 3.16-3.22 (m, 2H), 2.88-2.93 (m, 2H), 2.56 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 201.1, 142.6, 142.2 (2C), 134.8, 132.4, 130.1, 128.7 (2C), 128.3 (2C), 126.7, 125.8, 38.3, 36.8, 29.5, 21.4. MS (EI, 70eV, m/z): 238 (7), 224 (17), 223 (100), 178 (14), 165 (10), 147 (91), 145 (29), 117 (3), 91 (100). HRMS calculated for $C_{17}H_{18}O$ 238.1358; found 238.1361.

1-[2-(2-Phenylethyl)phenyl]ethanone (3ca)[2] [19946-98-6]



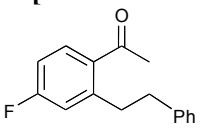
Reaction of acetophenone **1c** (1 mmol, 120 mg) and styrene **2a** (2 mmol, 230 µl) afforded 222 mg of ketone **3ca** as a light orange oil (yield 99%). R_f = 0.30 (cyclohexane/AcOEt 19:1). GC: rt = 5.5 min (branched 5.1 min, disubstituted 13.8 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.68 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.39 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.16-7.32 (m, 7H), 3.14-3.19 (m, 2H), 2.86-2.92 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 201.9, 142.0, 137.9, 131.6 (2C), 129.4, 128.7 (2C), 128.5, 128.4 (2C), 126.1, 125.9, 38.3, 36.5, 29.7. MS (EI, 70eV, m/z): 224 (7), 210 (11), 209 (68), 133 (63), 103 (29), 91 (100), 77 (23).

1-[4-Methoxy-2-(2-phenylethyl)phenyl]ethanone (3da)[3] [190669-12-6]

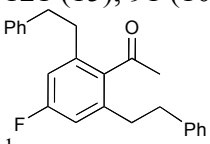


Reaction of 4-methoxyacetophenone **1d** (1 mmol, 150 mg) and styrene **2a** (4 mmol, 460 µl) afforded 180 mg of ketone **3da** as a light brown oil (yield 71%). R_f = 0.55 (cyclohexane/AcOEt 4:1). GC: rt = 7.1 min (branched 6.5 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.78 (d, *J* = 8.7 Hz, 1H), 7.29-7.32 (m, 4H), 7.21-7.25 (m, 1H), 6.79 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 3.81 (s, 3H) 3.23-3.28 (m, 2H), 2.89-2.95 (m, 2H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 199.5, 162.0, 145.7, 142.1, 132.8, 129.8, 128.7 (2C), 128.3 (2C), 125.8, 117.0, 111.0, 55.3, 37.9, 37.3, 29.2. MS (EI, 70eV, m/z): 254 (5), 240 (15), 239 (100), 163 (39), 161 (29), 105 (21), 91 (94), 77 (18).

1-[4-Fluoro-2-(2-phenylethyl)phenyl]ethanone (3ea)



Reaction of 4-fluoroacetophenone **1e** (1 mmol, 138 mg) and styrene **2a** (2 mmol, 230 µl) afforded 211 mg of ketone **3ea** as a light yellow oil (yield 87%, including 15% of disubstituted linear adduct). R_f = 0.20 (cyclohexane/AcOEt 19:1). GC: rt = 5.4 min (branched 5.0 min, disubstituted 13.5 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.74 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.17-7.34 (m, 5H), 6.93-7.01 (m, 2H), 3.19-3.24 (m, 2H), 2.89-2.94 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 200.1, 164.1 (d, *J* = 251 Hz), 146.0 (d, *J* = 8 Hz), 141.5, 132.1 (d, *J* = 9 Hz), 128.6 (2C), 128.4 (2C), 126.3, 126.0, 118.3 (d, *J* = 21 Hz), 112.9 (d, *J* = 21 Hz), 37.8, 36.5, 29.6. MS (EI, 70eV, m/z): 242 (4), 228 (12), 227 (68), 151 (20), 149 (23), 121 (15), 91 (100). HRMS calculated for $C_{16}H_{15}FO$ (M+H) 243.1185; found 243.1190.

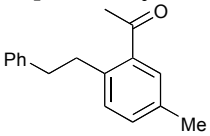


^{1}H RMN (300 MHz, $CDCl_3$, δ): 7.17-7.34 (10H, m), 6.83 (d, J_{H-F} = 9.3 Hz), 2.89-2.94 (4H, m), 2.81-2.84 (4H, m), 2.35 (3H, s). MS (EI, m/z): 346 ($M^{+\bullet}$, 1%), 328 (10%), 313 (9%), 253 (9%), 235 (15%), 196 (13%), 177 (10%), 105 (28%), 91 (100%). HRMS calculated for $C_{24}H_{24}FO$ (M+H) 347.1811; found 347.1812.

---

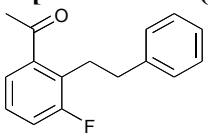
[2] F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.,* 1995, **68**, 62.
[3] P. W. R. Harris and P. D. Woodgate, *J. Organomet. Chem.,* 1997, **530**, 211-223.

1-[5-Methyl-2-(2-phenylethyl)phenyl]ethanone (3ga)



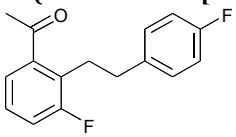
Reaction of 3-methylacetophenone **1g** (1 mmol, 134 mg) and styrene **2a** (3 mmol, 345 µl) afforded 237 mg of ketone **3ga** as a light yellow oil (yield 100%). R_f = 0.27 (cyclohexane/AcOEt 19:1). GC: rt = 6.0 min (branched 5.6 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.47 (s, 1H), 7.12-7.31 (m, 7H), 3.09-3.15 (m, 2H), 2.84-2.90 (m, 2H), 2.54 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 202.1, 142.1, 138.8, 137.8, 135.5, 132.2, 131.4, 129.8 128.7 (2C), 128.3 (2C), 125.8, 38.3, 36.0, 29.7, 21.0. MS (EI, 70eV, m/z): 238 (16), 224 (14), 223 (72), 178 (10), 165 (7), 147 (100), 145 (17), 117 (28), 91 (61). HRMS calculated for $C_{17}H_{18}O$ 238.1358; found 238.1362.

1-[3-Fluoro-2-(2-phenylethyl)phenyl]ethanone (3ha)



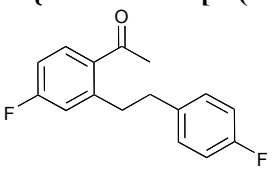
Reaction of 3-fluoroacetophenone **1h** (1 mmol, 138 mg) and styrene **2a** (2 mmol, 230 µl) afforded 220 mg of ketone **3ga** as a light yellow oil (yield 91%). R_f = 0.70 (cyclohexane/AcOEt 4:1). GC: rt = 5.3 min (branched 5.0 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.38 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.12-7.29 (m, 7H), 3.15-3.20 (m, 2H), 2.86-2.92 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 201.1, 161.8 (d, *J* = 244 Hz), 141.8, 140.4 (d, *J* = 4 Hz), 128.8 (d, *J* = 16 Hz), 128.8 (2C), 128.4 (2C), 127.2 (d, *J* = 9 Hz), 126.0, 124.5 (d, *J* = 3 Hz), 118.3 (d, *J* = 24 Hz), 36.8, 29.8, 28.0 (d, *J* = 4 Hz). MS (EI, 70eV, m/z): 242 (4), 227 (17), 151 (22), 149 (5), 91 (100). HRMS calculated for $C_{16}H_{15}FO$ 242.1107; found 242.1098.

1-{3-Fluoro-2-[2-(4-fluorophenyl)ethyl]phenyl}ethanone (3hb)



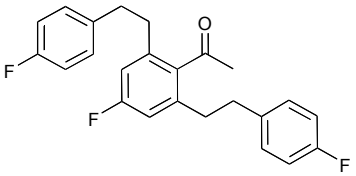
Reaction of 3-fluoroacetophenone **1h** (1 mmol, 138 mg) and 4-fluorostyrene **2b** (3 mmol, 366 mg) afforded 240 mg of ketone **3hb** as a light yellow oil (yield 92%). R_f = 0.21 (petrol/AcOEt 95:5). GC: rt = 5.3 min (branched 5.0 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.44 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.17-7.28 (m, 4H), 6.93-6.98 (m, 2H), 3.08-3.14 (m, 2H), 2.81-2.87 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 200.9, 161.7 (d, *J* = 244 Hz), 161.4 (d, *J* = 242 Hz), 140.1 (d, *J* = 4 Hz), 137.5 (d, *J* = 3 Hz), 130.0 (d, *J* = 8 Hz, 2C), 128.7 (d, *J* = 16 Hz), 127.2 (d, *J* = 9 Hz), 124.6 (d, *J* = 3 Hz), 118.4 (d, *J* = 24 Hz), 115.0 (d, *J* = 21 Hz, 2C), 35.8, 29.7, 28.1 (d, *J* = 3 Hz). MS (EI, 70eV, m/z): 260 (6), 245 (13), 151 (20), 149 (4), 110 (12), 109 (100), 103 (12), 83 (20). HRMS calculated for $C_{16}H_{14}F_2O$ 260.1013; found 260.1003.

1-{4-Fluoro-2-[2-(4-fluorophenyl)ethyl]phenyl}ethanone (3eb)



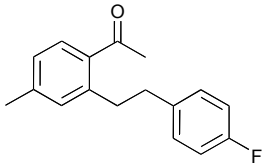
Reaction of 4-fluoroacetophenone **1e** (1 mmol, 138 mg) and 4-fluorostyrene **2b** (3 mmol, 366 mg) afforded 172 mg of ketone **3eb** as a light yellow oil (yield 99%, including 34% of

disubstituted linear adduct). R_f = 0.19 (petrol/AcOEt 95:5). GC: rt = 5.4 min (branched 5.0 min, disubstituted 13.7 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.73 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.16-7.21 (m, 2H), 6.88-6.98 (m, 4H), 3.13-3.18 (m, 2H), 2.82-2.87 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 199.8, 164.1 (d, *J* = 252 Hz), 161.5 (d, *J* = 242 Hz), 145.9 (d, *J* = 8 Hz), 137.2 (d, *J* = 3 Hz), 133.6 (d, *J* = 3 Hz), 132.3 (d, *J* = 9 Hz), 130.0 (2C, d, *J* = 8.0 Hz), 118.3 (d, *J* = 21 Hz), 115.0 (2C, d, *J* = 21 Hz), 112.9 (d, *J* = 22 Hz), 36.9, 36.6, 29.4. MS (EI, 70eV, m/z): 260 (3), 245 (32), 151 (12), 149 (9), 121 (8), 110 (12), 109 (100), 107 (12), 83 (22). HRMS calculated for $C_{16}H_{14}F_2O$ ($M+NH_4^+$) 278.1356; found 278.1356.



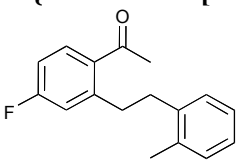
Rf = 0.21(petrol/AcOEt 95:5). ^{1}H RMN (300 MHz, $CDCl_3$, δ): 7.07-7.12 (4H, m), 6.88-6.98 (4H, m), 6.77 (2H, d, J_{H-F} = 8.5 Hz), 2.82-2.87 (4H, m), 2.73-2.79 (4H, m), 2.35 (3H, s). ^{13}C RMN (75 MHz, $CDCl_3$, δ): 207.2, 162.4 (d, *J* = 247 Hz), 161.4 (d, *J* = 242 Hz), 139.1 (d, *J* = 8 Hz), 138.5 (d, *J* = 2 Hz), 136.6 (d, *J* = 3 Hz), 129.8 (d, *J* = 8 Hz), 115.2 (d, *J* = 21 Hz), 114.0 (d, *J* = 22 Hz), 36.7, 35.4, 32.9. MS (CI, NH_3, m/z): 400 $[M+NH_4]^+$. HRMS calculated for $C_{24}H_{21}F_3O$ ($M+NH_4^+$) 400.1888; found 400.1899.

1-{4-Methyl-2-[2-(4-fluorophenyl)ethyl]phenyl}ethanone (3bb)



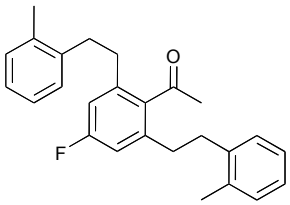
Reaction of 4-methylacetophenone **1b** (1 mmol, 134 mg) and 4-fluorostyrene **2b** (3 mmol, 366 mg) afforded 213 mg of ketone **3bb** as a light yellow oil (yield 83%). R_f = 0.27 (petrol/AcOEt 95:5). GC: rt = 5.9 min (branched 5.4 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.65 (d, *J* = 7.8 Hz, 1H), 7.19-7.24 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 6.94-7.00 (m, 2H), 3.10-3.15 (m, 2H), 2.81-2.87 (m, 2H), 2.55 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 201.0, 161.3 (d, *J* = 242 Hz), 142.4, 142.3, 137.8, 134.5, 132.5, 130.2, 130.0 (d, *J* = 8 Hz, 2C), 126.7, 114.9 (d, *J* = 21 Hz, 2C), 37.4, 36.9, 29.4, 21.4. MS (EI, 70eV, m/z): 256 (6), 242 (10), 147 (96), 145 (20), 117 (28), 109 (100), 103 (19), 91 (32), 83 (18). HRMS calculated for $C_{17}H_{17}FO$ 256.1263; found 256.1263.

1-{4-Fluoro-2-[2-(2-methylphenyl)ethyl]phenyl}ethanone (3ed)



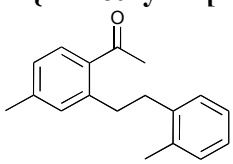
Reaction of 4-fluoroacetophenone **1e** (1 mmol, 138 mg) and 2-methylstyrene (**2d**) (3 mmol, 354 mg) afforded 234 mg of ketone **3ed** as a light yellow oil (yield 100%, including 9% of disubstituted linear adduct). R_f = 0.36 (petrol/AcOEt 95:5). GC: rt = 5.8 min (disubstituted 18.0 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.71 (dd, *J* = 8.5, 5.8 Hz, 1H), 7.12-7.15 (m, 4H), 6.91-6.99 (m, 2H), 3.12-3.17 (m, 2H), 2.86-2.92 (m, 2H), 2.49 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 200.1, 164.1 (d, *J* = 252 Hz), 146.0 (d, *J* = 8 Hz), 139.5, 136.1, 134.1, 131.8 (d, *J* = 9 Hz), 130.2, 129.3, 126.2, 126.0, 118.3 (d, *J* = 21 Hz), 112.8 (d, *J* = 21 Hz), 35.1, 34.9, 29.5, 19.2. MS (EI, 70eV, m/z): 256 (1), 241 (6), 238 (21), 151 (6), 106 (13), 105

(100), 103 (16), 79 (18), 77 (21). HRMS calculated for $C_{17}H_{17}FO$ (M+H) 257.1342; found 257.1345.

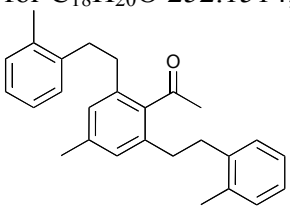


Rf = 0.41 (petrol/AcOEt 95:5). ^{1}H RMN (300 MHz, $CDCl_3$, δ): 7.12-7.18 (8H, m), 6.83 (2H, d, J_{H-F} = 9.5 Hz), 2.87-2.92 (4H, m), 2.72-2.78 (4H, m), 2.51 (3H, s), 2.32 (6H, s). ^{13}C RMN (75 MHz, $CDCl_3$, δ): 207.3, 162.5 (d, J = 246 Hz), 139.5 (d, J = 8 Hz), 139.1, 138.4, 135.9, 130.4, 129.0, 126.5, 126.2, 114.0 (d, J = 21 Hz), 35.1, 34.1, 33.1, 19.2. MS (CI, NH_3, m/z): 392 $[M+NH_4]^+$. HRMS calculated for $C_{26}H_{27}FO$ (M+H) 375.2124; found 375.2119.

1-{4-Methyl-2-[2-(4-methylphenyl)ethyl]phenyl}ethanone (3bd)

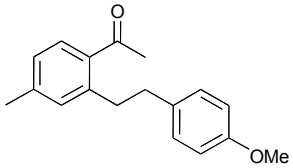


Reaction of 4-methylacetophenone **1b** (1 mmol, 134 mg) and 2-methylstyrene **2d** (3 mmol, 354 mg) afforded 206 mg of ketone **3bd** as a light yellow oil (yield 100%, including 18% of disubstituted linear adduct). R_f = 0.46 (petrol/AcOEt 95:5). GC: rt = 6.4 min (disubstituted 19.6 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.64 (d, J = 7.9 Hz, 1H), 7.09-7.25 (m, 6H), 3.13-3.18 (m, 2H), 2.89-2.95 (m, 2H), 2.55 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 201.2, 142.6, 142.1, 140.2, 136.1, 135.0, 132.5, 130.1, 129.9, 129.4, 126.7, 126.0, 125.9, 35.7, 35.2, 29.5, 21.4, 19.3. MS (EI, 70eV, m/z): 252 (2), 238 (4), 237 (23), 235 (5), 234 (26), 147 (48), 117 (14), 105 (100), 103 (22), 91 (17), 79 (16), 77 (24). HRMS calculated for $C_{18}H_{20}O$ 252.1514; found 252.1513.



Rf = 0.49(petrol/AcOEt 95:5). ^{1}H RMN (300 MHz, $CDCl_3$, δ): 7.09-7.25 (8H, m), 6.98 (2H, s), 2.89-2.95 (4H, m), 2.73-2.78 (4H, m), 2.44 (3H, s), 2.38 (3H, s), 2.37 (6H, s). ^{13}C RMN (75 MHz, $CDCl_3$, δ): 208.4, 139.8 (2 C), 139.6, 138.6, 136.7 (2 C), 136.0 (2 C), 130.3 (2 C), 129.0 (2 C), 128.1 (2 C), 126.3 (2 C), 126.2 (2 C), 35.7, 34.4, 33.2, 21.3, 19.2. MS (CI, NH_3, m/z): 388 $[M+NH_4]^+$. HRMS calculated for $C_{27}H_{30}O$ (M+H) 371.2375; found 371.2371.

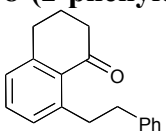
1-{4-Methyl-2-[2-(4-methoxyphenyl)ethyl]phenyl}ethanone (3bc)



Reaction of 4-methylacetophenone **1b** (1 mmol, 134 mg) and 2-methoxystyrene **2c** (3 mmol, 402 mg) afforded 229 mg of ketone **3bc** as a light yellow oil (yield 85%). R_f = 0.19 (petrol/AcOEt 95:5). GC: rt = 7.7 min (branched 7.0 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.63 (d, J = 8.0 Hz, 1H), 7.18 (dd, J = 6.6, 2.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 1H), 7.06 (s, 1H), 6.84 (dd, J = 6.6, 2.0 Hz, 2H), 3.80 (s, 3H), 3.09-3.14 (m, 2H), 2.78-2.83 (m, 2H), 2.54 (s,

3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 201.2, 157.8, 142.6, 142.1, 134.7, 134.3, 132.4, 130.0, 129.5 (2C), 126.6, 113.7 (2C), 55.3, 37.4, 36.9, 29.5, 21.4. MS (EI, 70eV, m/z): 268 (8), 122 (13), 121 (100), 91 (12), 78 (11), 77 (15). HRMS calculated for $C_{18}H_{20}O_2$ 268.1463; found 268.1469.

8-(2-phenylethyl)-3,4-dihydronaphthalen-1(2*H*)-one (3fa)



Reaction of α-tetralone **1f** (1 mmol, 146 mg) and styrene **2a** (4 mmol, 460 µl) afforded 171 mg of ketone **3fa** as a light yellow oil (yield 68%). R_f = 0.82 (cyclohexane /AcOEt 4:1). GC: rt = 7.5 min (branched 6.9 min). ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.10-7.39 (m, 8H), 3.35-3.40 (m, 2H), 2.90-3.01 (m, 4H), 2.67-2.72 (m, 2H), 2.07-2.16 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 200.0, 146.0, 145.0, 142.5, 132.4, 130.2, 128.7 (2C), 128.3 (2C), 128.1, 127.2, 125.8, 41.1, 38.0, 37.9, 31.2, 23.0. MS (EI, 70eV, m/z): 250 (35), 232 (12), 222 (19), 159 (100), 131 (32), 115 (24), 91 (78). HRMS calculated for $C_{18}H_{18}O$ 250.1358; found 250.1361.