Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2017

NEW JOURNAL OF CHEMISTRY

Hydrotalcite-Supported Palladium Nanoparticles as Catalyst for the Hydroarylation of Carbon-Carbon Multiple Bond

A. Di Nicola,[a] A. Arcadi[a]*, K. Gallucci,[b] V. Mucciante[a] and L. Rossi[a]*

EXPERIMENTAL

All commercially available reagents were used without further purification unless otherwise stated. Reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 pre-coated glass plates (0.25 mm thickness) and visualized using UV light, iodide, and vanillin reagent. Flash column chromatography was performed on a silica gel (230–400 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a 400 MHz nuclear magnetic resonance spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR).

Synthesis of Hydrotalcite HT (Mg/Al 2:1)

A solution containing 0.3 mol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.15 mol of $Al(NO_3)_3{\cdot}9H_2O$ in 125 mL of de-ionized water was used. This solution was slowly dropped over 250 mL of a Na_2CO_3 solution at pH 10 at 60 ◦C under vigorous stirring. The pH was kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was kept at 80 ◦C for 24 h, after which the solid was filtered and washed with 1 L of de-ionized water. The solid was dried in a stove at 110°C overnight. 4 g of the solid were suspended in a solution containing 1.38 g of Na_2CO_3 in 200 mL of de-ionized water at 100° C for 2h. Then, the solid was filtered off in vacuo, washed with 200 mL of de-ionized water and dried at 110°C.

Synthesis of Hydrotalcite HT (Mg/Al 3:1)

A solution containing 1.70 mol of NaOH and about 0.075 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.025 mol of $Al(NO_3)_3 \cdot 9H_2O$ with a molar ratio of 3:1 (Mg^{2+}/Al^{3+}) were dissolved in 90.0 ml deionized water (referred as Solution A). About 6.82 g NaOH and 5.65 g Na_2CO_3 were dissolved in 40.0 ml de-ionized water (referred as Solution B). At room temperature, Solution B was dropped to Solution A with vigorous stirring, maintaining the pH value of the mixture at ca. 10.0. The resultant slurry was filtered, washed with deionized water, and dried at 110° C in a stove.

Synthesis of HT/Pd

2.00 g of HT, were treated with 10.0 mL of *N*,*N*-dimethylformamide and 34.0 mg of $PdCl_2$, the amount required to ensure that final catalysts would include 1% of Pd by weight. Then, the suspension was stirred at room temperature for 24 h, the solvent was evaporated to dryness and the residual solid dried in a stove at 110° C for overnight. 1 g of the resulting solid, HT-Pd (II), was refluxed with 10 mL of cyclohexene at 83° C for 1 h. The mixture was then cooled and the catalyst thus formed (HT-Pd(0)) was filtered off and washed with cyclohexene and methanol.

Synthesis of arylethynyl, dialkylcarbinols 1a; 1e; 1f. This is exemplified by the reaction of ethynylcyclohexanol with methyl 4-iodobenzoate **2d**. To a stirred solution of methyl 4-iodobenzoate **2d** (0.63 g, 2.41 mmol), piperidine (0.29 mL, 2.41 mmol) in DMF (2 mL) were added ethynylcyclohexanol (0.30 g, 2.41 mmol), $Pd(OAc)_2(PPh_3)_2$ (0.046 g, 0.048 mmol), and CuI (0.019 g, 0.096 mmol). The mixture was gently purged with nitrogen. Then the mixture was stirred for 2 hr at 60 °C under a nitrogen atmosphere, AcOEt and water were added, and the organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography. Elution with a 90/10 n-hexane/AcOEt mixture gave compound **(1e)** (0.60 g).

1-(phenylethynyl)cyclohexan-1-ol (1a): white solid (yield 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19-2.08 (m, 11H); 7.20-7.36 (m, 5H). ^{13}C (100 MHz, $CDCl_3$): 23.4; 25.2; 40.0; 69.1; 84.3; 92.8; 122.9; 128.1; 128.2; 134.6; 135.8.

Methyl 4-((1-hydroxycyclohexyl)ethynyl)benzoate (1e): white solid (yield 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59-2.08 (m, 11H); 3.94 (s, 3H); 7.51 (d, J= 8.1Hz 2H); 7.99 (d, J= 8.1Hz, 2H). ^{13}C (100 MHz, $CDCl_3$): 23.3; 25.1; 39.9; 52.5; 69.1; 83.6; 95.8; 128.8; 129.1; 129.4; 131.6; 166.5.

Methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate (1f): white solid. (yield 90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65 (s, 6H); 3.94 (s, 3H); 7.49 (d, J=8.1Hz, 2H); 8.00 (d, J=8.1Hz, 2H). ^{13}C (100 MHz, $CDCl_3$): 31.3; 52.2; 66.6; 81.4; 127.4; 129.4; 131.5; 166.5.

Synthesis of 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (1g): To a stirred solution of 4-iodoanisole **(2a)** (0.664 g, 2.84 mmol) and piperidine (0.36 mL, 3.69 mmol) in THF (5 mL) were added 1-phenylprop-2-yn-1-ol (0.450 g, 3.04 mmol), $PdCl_2(PPh_3)_2$ (0.040 g, 0.057 mmol), and CuI (0.021 g, 0.114 mmol). The mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. Then, the mixture was extracted with treated with 1.0 M HCl and extracted with ethyl acetate. The organic layer was dried with Na_2SO_4 and concentred. The residue was purified by flash chromatography with petroleum ether/ethyl acetate 90/10 to give **(1g)** (0.621 g, 92% yield): brown oil. (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H); 5.65 (s, 1H); 6.82 (d, J=8.9Hz, 2H); 7.30-7.40 (m,5H); 7.58-7.61 (m, 2H). ^{13}C (100 MHz, $CDCl_3$): 55.2; 66.0; 86.5; 87.4;113.9; 114.4; 126.7; 128.3; 128.6; 133.2; 140.8; 159.7.

Synthesis of 3-phenylprop-2-yn-1-ol (1h): To a stirred solution of iodobenzene **(2b)** (1.00 g, 4.9 mmol), $PdCl_2(PPh_3)_2$, (0.034 g, 0.049 mmol), CuI (0.019 g, 0.098 mmol) and triethylamine (5 mL) was added 2-propin-3-ol (0.96 g, 5.39 mmol) and the mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. Then, the mixture was treated with 1.0 M HCl and extracted with ethyl acetate. The organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography with petroleum ether/ethyl acetate 75/25 to give 3-phenylprop-2-yn-1-ol **(1h):** 0.51 g. Oil (yield 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (bs, 1H); 4.49 (s, 2H); 7.25-7.32 (m, 3H), 7.42-7.44 (m, 2H). ^{13}C (100 MHz, $CDCl_3$): 51.5; 86.6; 87.2; 122.5; 128.3; 128.5; 131.6.

General procedure for the synthesis of compounds 3 and 4

To a stirred solution of aryl iodide **2** (2.54mmol), piperidine (3.57 mmol) in MeCN (2 mL) were added propargylic alcohol **1** (1.0 mmol), HT/Pd(0) (20 mg) and formic acid (2.77 mmol). The mixture was stirred at 80° C for the required time, than the mixture was filtered on celite with AcOEt and concentrated. The residue was purified by flash chromatography.

(*E*)-1-(2-(4-methoxyphenyl)-2-phenylvinyl)cyclohexan-1-ol (3a): yellow oil (yield 84%; 3a/4a = 92/8).^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (br, 1H); 1.39-1.57 (m, 10H); 3.69 (s, 3H); 6.02 (s, 1H); 6.70 (d, *J*=9.0 Hz, 2H); 7.03 (d, *J*=9.0 Hz, 2H); 7.16-7.18 (m, 2H); 7.22-7.32 (m, 3H). ^{13}C (100 MHz, $CDCl_3$): 22.0; 25.3; 39.4; 55.2; 72.5; 113.4;126.9; 127.3; 128.0; 128.3; 129.7; 130.9; 139.7; 140.2; 158.9. Characteristics signal of the minor regioisomer **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H); 6.07 (s, 1H). ^{13}C (100 MHz, $CDCl_3$): 113.8; 134.6; 135.7.

1-(2,2-diphenylvinyl)cyclohexan-1-ol (3b): yellow oil (yield 65%; 3b/4b = 98/2).^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (br, 1H); 1.36-1.60 (m, 10H); 6.10 (s, 1H); 7.10-7.20 (m, 7H); 7.23-7.33 (m, 3H).^{13}C (100 MHz, $CDCl_3$): 21.9; 25.4; 39.4; 72.6; 127.0; 127.1;127.5; ; 128.1; 128.4; 129.8; 136.4; 140.0; 140.2; 143.1

(*E*)-1-(2-(4-chlorophenyl)-2-phenylvinyl)cyclohexan-1-ol (3c): yellow oil (yield 65%; 3c/4c = 91/9).^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34-1.59 (m, 11H); 6.07 (s, 1H); 7.01-7.04 (m, 2H); 7.11-7.17 (m, 4H); 7.24-7.33 (m,3H). ^{13}C (100 MHz, $CDCl_3$): 21.9; 25.3; 39.3; 72.6; 127.0; 128.2; 128.2^{3};129.7; 131.2; 133.0; 136.8; 139.2; 139.5; 141.6. Characteristics signal of the minor regioisomer **4c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (s, 1H). ^{13}C (100 MHz, $CDCl_3$): 127.3; 127.6; 128.5

Methyl (*E*)-4-(2-(1-hydroxycyclohexyl)-1-phenylvinyl)benzoate (3d): yellow oil (yield 20%; 3d/4d = 92/8).^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26- 1.48 (m, 11H); 3.87 (s, 3H); 6.38 (s, 1H); 7.21-7.37 (m, 9H). ^{13}C (100 MHz, $CDCl_3$): 21.3; 25.2 40.0; 52.2; 69.1; 126.9; 127.7; 127.9; 128.2^{0}; 128.2^{1}; 128.6; 130.5; 138.5; 143.9; 150.6; 167.8. Characteristics signal of the minor regioisomer **4d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H). ^{13}C (100 MHz, $CDCl_3$): 23.4; 25.1; 37.8; 130.1; 131.6; 133.7.

Methyl (*E*)-4-(2-(1-hydroxycyclohexyl)-1-(4-methoxyphenyl)vinyl)benzoate (3e): yellow oil (yield 92%; 3e/4e = 99/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (br, 1H); 1.39-1.54 (m, 10H); 3.69 (s, 3H); 3.81 (s, 3H); 6.04 (s, 1H); 6.71 (d, *J*= 9.0Hz, 2H); 7.00 (d, *J*= 9.0Hz, 2H); 7.36-7.38 (m, 2H); 7.82-7.93 (m, 2H). ^{13}C (100 MHz, $CDCl_3$): 21.9; 25.3; 39.4; 52.1; 55.2; 72.5; 113.5; 128.1; 128.2; 128.4; 130.6; 134.3; 135.4^{2}; 138.9; 140.8; 159.0; 166.9. Characteristics signal of the minor regioisomer **4e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H); 3.87 (s, 3H). ^{13}C (100 MHz, $CDCl_3$): 130.1; 135.4^{0}.

Methyl (*E*)-4-(3-hydroxy-1-(4-methoxyphenyl)-3-methylbut-1-en-1-yl)benzoate (3f): yellow oil (yield 80%; 3f/4f = 85/15). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23(s, 6H); 1.32 (br,1H) 3.69 (s, 3H); 3.85 (s, 3H); 6.10 (s, 1H); 6.71 (d, J=9.0 Hz, 2H); 6.99 (d, J=9.0 Hz, 2H); 7.24 (d, J= 8.5 Hz, 2H); 7.95 (d, J= 8.5 Hz, 2H). ^{13}C (100 MHz, $CDCl_3$): 31.4; 52.1; 55.2; 71.7; 113.6; 128.1; 129.2; 129.4; 129.9; 134.8; 135.5; 138.3; 145.4; 159.1; 166.8.. Characteristics signal of the minor regioisomer **4f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (br,1H); 1.28 (s, 6H); 3.75 (s, 3H); 3.84 (s, 3H); 6.35 (s, 1H); 6.81(d, *J*=8.8 Hz, 2H); 7.17 (d, *J*=8.8 Hz, 2H); 7.33 (d, *J*= 8.1 Hz, 2H); 7.92 (d, *J*= 8.1 Hz, 2H). ^{13}C (100 MHz, $CDCl_3$): 31.1; 52.0; 74.2; 113.2; 128.3; 128.5; 128.8; 129.0; 144.0; 151.4; 158.6; 166.9.

(*E*)-3-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol (3h): pale yellow solid

.^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (bs, 1H); 3.82 (s, 3H); 4.16 (d, J= 6.9 Hz, 2H); 6.15 (t, J= 6.9 Hz, 1H); 6.85 (d, J= 8.9 Hz, 2H); 7.23-7.38 (m, 5H), 7.56 (d, J= 8.9 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$): 57.2, 60.3, 116.4, 124.1, 127.5, 128. 2, 128. 4, 129. 8, 139.6, 142.7, 159.3.

(Z)-3-(4-methoxyphenyl)-1,2-diphenylprop-2-en-1-ol (4g): yellow solid**;** ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 (br,1H); 3.77 (s, 3H); 6.19 (s, 1H); 6.86 (d, 8.7 Hz, 2H); 6.95 (s, 1H); 7.18- 7.21(m, 4H); 7.29-7.32 (m, 6H); 7.45 (d, 8.7 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$): 55.2, 71.3, 113.9, 126.2,127.0, 127.3, 128.1, 128.3, 128.4; 129.1, 130.1, 131.6, 139.7, 141.3, 142.4, 158.9.

(*Z*)-2-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol (4h): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (bs, 1 H), 3.87 (s, 3H); 4.71 (s, 2 H), 6.95-6.98 (m. 3 H), 7.43-7.57 (m, 7H); ^{13}C (100 MHz, $CDCl_3$): 55.4, 60.3, 114.1, 127.2, 127.8, 128.4, 128.9, 129.8, 137.2, 139.6, 159.4.

(*Z*)-3-(4-methoxyphenyl)-1,3-diphenylprop-2-en-1-one (5): yellow oil; (E/Z) mixture; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3,79 (s, 3 H), 3.86 (s, 3 H), 6.90 (d, H=8.7 Hz, 2H), 6.91 (d, H=8.7 Hz, 2H), 7.03 (s, 3 H), 7.13 (s, 1 H), 7.14-7.51 (m, 10H), /.91-7.94 (m, 2 H); ^{13}C (100 MHz, $CDCl_3$): 55.2, 55.4, 113.5, 113,9, 118.0, 121.9, 123.4, 128.0, 128.3, 128.4, 128.7, 128.8, 128.9,129.3, 129.7, 130.1, 131.2, 131.5, 132.5, 132.6, 133.7, 138.2, 138.6, 139.3, 154.9, 155.1, 159.9, 160.8, 192.4, 193.0.

Synthesis of (*E*)-(1-(*p*-tolyl)ethene-1,2-diyl)dibenzene (7): To a stirred solution of 4-iodotoluene **2f** (0.85 g, 3.90 mmol), piperidine (0.54 mL, 5.53 mmol) in MeCN (3 mL) were added 1,2-diphenylethyne **6** (0.29 g, 1.67 mmol), HT/Pd(0) (25 mg) and formic acid (0.20 g, 4.29 mmol). The mixture was stirred at 80° C for 24 h, than the mixture was filtered on celite with AcOEt and concentrated. The residue was purified by flash chromatography with petroleum ether to give (*E*)-(1-(*p*-tolyl)ethene-1,2-diyl)dibenzene **(7)**(0.38 g): brown solid (yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H); 6.93 (s, 1H); 7.00-7.40 (m, 14H). ^{13}C (100 MHz, $CDCl_3$): 21.1; 126.3; 127.4; 127.6; 128.0; 128.7; 129.0; 129.5; 130.4; 137.3; 140.6; 140.7; 142.5.

General procedure for the synthesis of exo-2-phenylbicyclo[2.2.1]heptanes 9a-d:

To a stirred solution of aryl iodide (**2**) (1.726 mmol) and norbornene (6.043 mmol) in MeCN (3.0 mL) were added HT/Pd(0) (25 mg). After 5.0 minutes piperidine (5.868 mmol) and formic acid (4.487 mmol) were added. The mixture was stirred at 80° C for 24 h, then water was added and the mixture was extracted with AcOEt. The organic layers were dried with Na_2SO_4 and concentred. The residue was purified by flash chromatography with petroleum ether.

2-phenylbicyclo[2.2.1]hept-2-ene (9a): oil. (yield 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16-1.76 (m, 8H); 2.33-2.39 (m, 2H); 2.72-2.75 (dd, J = 8.8 Hz and 5.7Hz, 1H); 7.14-7.27 (m, 5H). ^{13}C (100 MHz, $CDCl_3$): 28.9; 20.6; 36.1; 36.8; 39.1; 42.9; 47.3; 125.4; 127.1; 128.2; 147.7.

2-(4-methoxyphenyl)bicyclo[2.2.1]hept-2-ene (9b): oil. (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21-1.83 (m, 8H); 2.37-2.40 (m, 2H); 2.74-2.77 (m, 1H); 3.84 (s, 3H); 6.88-6.90 (m, 2H), 7.19-7.21 (m, 2H) . ^{13}C (100 MHz, $CDCl_3$): 28.9; 30.5; 35.9; 36.8; 39.1; 43.2; 46.5; 55.2; 113.5; 127.9; 139.8; 157.4.

2-(*p*-tolyl)bicyclo[2.2.1]hept-2-ene (9c): oil. (yield 79). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15-1.74 (m, 8H); 2.32 (s, 3H); 2.34 (br, 1H); 2.70 (dd, J = 8.8, 5.8 Hz, 1H); 7.04-7.12 (m, 4H). ^{13}C (100 MHz, $CDCl_3$): 21.6; 28.9; 30.6; 36.1; 36.8; 39.1; 43.0; 47.3; 126.1; 128.1; 137.7; 147.6.

2-(4-chlorophenyl)bicyclo[2.2.1]hept-2-ene (9d): oil. (yield 90). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16-1.78 (m, 8H); 2.31-2.34 (m, 2H); 2.69 (dd, J = 8.9, 5.5 Hz, 1H); 7.11-7.13 (m, 2H); 7.21-7.23 (m, 2 H). ^{13}C (100 MHz, $CDCl_3$): 28.8; 30.5; 36.0; 36.8; 39.2; 42.9; 46.7; 128.2; 128.4; 131.0; 146.1.

General procedure for the synthesis of 3,4-diphenyl ketones 11a-e:

To a stirred solution of aryl iodide (**2**) (1.234 mmol) and α,β-unsaturated ketone (**10**) (1.02 mmol) in *N*-methylpirrolydone (1.0 mL) were added HT/Pd(0) (20 mg). After 5 minutes diisopropylethilamine (5.1 mmol) was added. The mixture was stirred at 80° C for 24 h, then the mixture was treated with HCl (1 M) and extracted with AcOEt. The organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by flash chromatography with petroleum ether.

4-(4-methoxyphenyl)-4-phenylbutan-2-one (11a): Yellow solid. (Yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3 H); 3.12 (d, J= 7.6 Hz 2H); 3.71 (s, 3H); 4.52 (t, J= 7.6 Hz, 1 H); 6.80 (d, J= 8.7 Hz, 2H); 7.11-7.39 (m, 7 H). ^{13}C (100 MHz, $CDCl_3$): 30.5; 45.1; 49.7; 55.0; 113.8; 126.2; 127.5; 128.5; 135.8; 144.1; 158.0; 207.0.

4-phenyl-4-(*p*-tolyl)butan-2-one (11b): Colorless solid. (Yield 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3 H); 2.27 (s, 3 H); 3.15 (d, J= 7.6 Hz, 2H); 4.54 (t, J= 7.6 Hz, 1 H); 7.06-7.27 (m, 9 H). ^{13}C (100 MHz, $CDCl_3$): 20.9; 30.6; 45.7; 49.7; 126.3; 127.5; 127.6; 128.5; 129.2; 135.9; 140.8; 144.1; 207.0.

4-(4-fluorophenyl)-4-phenylbutan-2-one (11c): Pale yellow solid. (Yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3 H); 3.13 (d, J= 7.5 Hz, 2H); 4.56 (t, J= 7.5 Hz, 1 H); 7.00-7.27 (m, 9 H). ^{13}C (100 MHz, $CDCl_3$): 30.4; 45.0; 49.5; 115.2(d, J=22 Hz); 126.4; 127.5; 128.5; 129.1(d, J=7.9 Hz); 139.6 (d, J=2.8 Hz); 143.6, 161.3 (d, J =244 Hz) 206.4.

4,4-diphenylbutan-2-one (11d): Oil. (Yield 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3 H); 3.16 (d, J= 7.6 Hz, 2H); 4.58 (t, J= 7.6 Hz, 1 H); 7.13-7.38 (m, 10 H). ^{13}C (100 MHz, $CDCl_3$): 30.6; 46.0; 49.6; 126.4; 127.7; 128.5; 143.8; 206.7.

3-(4-methoxyphenyl)-1,3-diphenylpropan-1-one (11e): Pale yellow solid. (Yield 775). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16 (dd, J= 7.3, 1.0 Hz, 2H); 3.70 (s, 3 H); 4.77 (t, J= 7.3 Hz, 1 H); 6.79 (d, J=8.8, 2H); 7.15-7.52 (m, 10 H); 7.91 (d, J=8.8, 2H). ^{13}C (100 MHz, $CDCl_3$): 44.8; 45.1; 55.1; 113.9; 126.2; 127.7; 128.0; 128.5; 128.7; 136.2; 137.0; 144.5; 158.0; 198.0.

3-(4-methoxyphenyl)cyclohex-2-enone (11f): Oil. (Yield 53%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72-1.85 (m, 2 H); 2.02-2.14 (m, 2H); 2.33-2.58 (m, 4H); 2.91-2.99 (m, 1H); 3.78 (s, 3H); 6.86 (dd, J= 8.7 Hz, 2H); 7.13 (dd, J= 8.7 Hz, 2H). ^{13}C (100 MHz, $CDCl_3$): 25.4; 32.9; 41.0; 43.8; 49.1; 55.1; 113.9; 127.4; 136.5; 158.2; 211.0.