Electronic Supporting Information

Pd-catalyzed Synthesis of Benzofused Carbo- and Heterocycles through Carbene Migratory Insertion/Carbopalladation Cascades with Tosylhydrazones

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1.- Experimental procedures

1.1- General considerations:

Reactions performed by conventional heating were carried out in a RR98030 12 place Carousel Reaction Station[™] from Radleys Discovery Technologies, equipped with gas tight threaded caps with a valve, cooling reflux head system, and digital temperature controller. Lithium tert-butoxide was purchased from Acros Chemical Co., stored in a flask purged with nitrogen and weighted in the air. Dioxane, acetonitrile and CHCl₃ were dried using the procedures described in D. Perrin Purification of Laboratory Chemicals, Pergamon Press Ltd. 1980, 2nd Ed. 2-lodobenzyl bromide, 2-bromobenzyl bromide, 2-iodobenzyl alcohol and 2iodobenzaldehyde are commercially available from Aldrich Chemical Co. N-Tosylhydrazones were prepared from the corresponding carbonyl compounds and through previously described methodologies.¹ NMR spectra were recorded in CDCl₃, CD₂Cl₂ and C₆D₆ at 300 MHz and 600 MHz for ¹H and 75 MHz, 100 MHz and 150 MHz for ¹³C, with tetramethylsilane as internal standard for ¹H and the residual solvent signals as standard for ¹³C. The data is being reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quatriplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. Low resolution MS were measured in EI mode and the mass analyzer was quadrupole. HRMS were measured in EI mode, and the mass analyser of the HRMS was TOF. Melting points are uncorrected and were measured in a Gallenkamp apparatus.

¹ V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J.-L. Vasse and C. L. Winn, *J. Am. Chem. Soc.*, 2003, **125**, 10926

2.- General procedure for the synthesis of the starting materials

2.1- General procedure for the synthesis of 1 and 5

1-allyl-2-bromobenzene 1^2 and 1-allyl-2-iodobenzene 5^3 were synthesized following the processes described in the literature.

2.2- General procedure for the synthesis of 6a and 6b

1-lodo-2-(vinyloxy)benzene (6a)



To a solution of 2-iodophenol (4.5 mmol) and 1,2-dibromoethane (4.25 g, 22.59 mmol) in acetone (50 mL) was added K₂CO₃ (1.25 g, 9 mmol). The resulting mixture was stirred at room temperature for 14 h and then at reflux for 6 h. The reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by a silica gel column chromatography using hexane as eluent to give **A** (805 mg, 2.5 mmol, 55% yield) as a colorless solid.

To a solution of **A** (805 mg, 2.5 mmol) in DMSO (20 mL) was added KO*t*Bu (287 mg, 2.56 mmol). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with water, and extracted with AcOEt. The organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography using hexane as eluent to give **B** (6a) (409 mg, 1.66 mmol, 78% yield) as a yellow oil. NMR data were consistent with those reported in the literature.⁴

² J. Knight and P. J. Parsons, J. Chem. Soc., Perkin Trans. 1, 1989, 979-984.

³ S. García-Rubín, C. González-Rodríguez, C. García-Yebra, J. A. Varela, M. A. Esteruelas and C. Saá, *Angew. Chem. Int. Ed.*, 2014, **53**, 1841.

⁴ H. Bhandal, V. F. Patel, G. Pattenden and J. J. Russell, *J. Chem. Soc., Perkin Trans.* 1, 1990, 2691

¹H NMR (300 MHz, CDCl₃) δ 7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.34 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 6.61 (dd, *J* = 13.8, 6.1 Hz, 1H), 4.80 (dd, *J* = 13.7, 1.9 Hz, 1H), 4.54 (dd, *J* = 6.1, 1.9 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 155.79 (C), 148.07 (CH), 139.72 (CH), 129.58 (CH), 125.14 (CH), 117.31 (CH), 95.91 (CH), 87.43 (C). EI HRMS: calcd. For C₈H₇IO: 245.9542, found: 245.9541

1-lodo-4-methoxy-2-(vinyloxy)benzene (6b)



The title compound was prepared as a colorless oil in 82% isolated yield from 2lodo-5-methoxyphenol according to the procedure for **6a**.

¹H NMR (300 MHz, CDCl₃) δ 7.64 (d, *J* = 8.7 Hz, 1H), 6.70 – 6.51 (m, 2H), 6.46 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.80 (dd, *J* = 13.7, 1.9 Hz, 1H), 4.53 (dd, *J* = 6.1, 1.9 Hz, 1H), 4.53 (dd, *J* = 6.1, 1.9 Hz, 1H), 3.79 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 161.3 (C), 156. 7 (C) 148.0 (CH), 139.6 (CH), 111.0 (CH), 104.3 (CH), 96.4 (CH₂), 75.9 (C-l), 55.7 (CH₃). EI HRMS: calcd. For C₉H₉IO₂: 275.9647, found: 275.9650

2.3- General procedure for the synthesis of 8

lodochalcone 8 was prepared as previously described in the literature.⁵

3.- General procedure and charcerization data for indanes 3

Method A: employing 1-allyl-2-bromobenzene 1

A carousel reaction tube was charged under nitrogen atmosphere with the corresponding *N*-tosylhydrazone (1.1 equiv), 1-allyl-2-bromobenzene **(1)** (0.168 mmol), tris(dibenzylideneacetone)dipalladium(0) (3 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos) (12 mol %), lithium *tert*-butoxide (2.5 equiv), H₂O (5 equiv) and 1,4-dioxane (2 mL). The reaction mixture was stirred at 90 °C for 6 h. After cooling to room temperature, the reaction crude was dissolved in DCM and filtered through celite. The solvents were evaporated

⁵ A. Minatti, X. Zheng and S. L. Buchwald, *J. Org. Chem.*, 2007, **72**, 9253.

under reduced pressure and the residue was purified by flash chromatography on silica gel using hexane or a mixture of hexane / ethyl acetate as eluent.

Method B: employing 1-allyl-2-iodobenzene 5

A carousel reaction tube was charged under nitrogen atmosphere with the corresponding *N*-tosylhydrazone (2 equiv), 1-allyl-2-iodobenzene **5** (0.168 mmol), tris(dibenzylideneacetone)dipalladium(0) (3 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos) (12 mol %), lithium *tert*-butoxide (6 equiv), H₂O (5 equiv) and acetonitrile (1.8 mL). The reaction mixture was stirred at 110 °C for 1 h. After cooling to room temperature, the reaction crude was dissolved in DCM and filtered through celite. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using hexane or a mixture of hexane / ethyl acetate as eluent.

N,N-Dimethyl-4-(2-methylene-2,3-dihydro-1*H*-inden-1-yl)aniline (3a)

Following the general method A, from 1-allyl-2-bromobenzene **(1)** (0.168 mmol) and 4-(dimethylamino)benzaldehyde tosylhydrazone (46 mg, 0.184 mmol) were obtained 31.8 mg of **3a** (76 % isolated yield) as a yelow oil. R_f 0.18 (30:1 hexane : AcOEt).

Following the general method B, from 1-allyl-2-iodobenzene **(5)** (0.168 mmol) and 4-(dimethylamino)benzaldehyde tosylhydrazone (106.6 mg, 0.336 mmol) were obtained 40 mg of **3a** (96 % isolated yield) as a yellow oil. $R_f 0.18$ (30:1 hexane : AcOEt).



¹H NMR (300 MHz, CD_2Cl_2) δ 7.33 (d, J = 6.7 Hz, 1H), 7.28 – 7.14 (m, 2H), 7.10 – 6.97 (m, 3H), 6.81 – 6.68 (m, 2H), 5.18 (q, J = 2.0 Hz, 1H), 4.88 (m, 2H), 3.84 (s broad, 2H), 2.96 (s, 6H) ppm. ¹³C NMR (75 MHz, CD_2Cl_2) δ 155.5 (C), 150.1 (C), 147.3 (C), 142.2 (C), 133.1 (C), 129.6 (CH), 127.3, 127.2 (CH), 125.6 (CH), 124.8 (CH), 113.2 (CH), 109.3

(CH₂), 56.0 (CH), 41.1 (CH₃), 39.4 (CH₂) ppm. EI HRMS: calcd. For C₁₈H₁₉N: 249.1517, found: 249.1513

1-(4-Methoxyphenyl)-2-methylene-2,3-dihydro-1*H*-indene (3b)

Following the general method A, from 1-allyl-2-bromobenzene (1) (0.168 mmol) and *p*-anisaldehyde tosylhydrazone (56.2 mg, 0.184 mmol) were obtained 16 mg of **3b** (40 % isolated yield) as a colorless oil. $R_f 0.27$ (30:1 hexane : AcOEt).

Following the general method B, from 1-allyl-2-iodobenzene **(5)** (0.168 mmol) and *p*-anisaldehyde tosylhydrazone (102.2 mg, 0.336 mmol) were obtained 38 mg of **3b** (96 % isolated yield) as a colorless oil. $R_f 0.27$ (30:1 hexane : AcOEt).



¹H NMR (300 MHz, CD_2Cl_2) δ 7.34 (d, J = 7.0 Hz, 1H), 7.25 (t, J = 7.0 Hz, 1H), 7.19 (t, J = 7.0 Hz, 1H), 7.16 – 7.07 (m, 2H), 7.00 (d, J = 7.4 Hz, 1H), 6.96 – 6.84 (m, 2H),5.21 (q, J = 2.2 Hz, 1H), 4.93 (s broad, 1H), 4.87 (q, J = 2.2 Hz, 1H), 3.86 (s broad, 2H), 3.82 (s, 3H) ppm. ¹³C NMR (75 MHz, CD_2Cl_2) δ 158.3 (C), 154.6 (C), 146.3 (C), 141.6 (C), 136.8 (C), 129.5 (CH), 126.9 (CH), 126.7 (CH), 125.0 (CH), 124.3 (CH), 113.7 (CH), 109.1 (CH₂), 55.4 (CH), 55.2 (CH₃), 38.80 (CH₂) ppm. EI HRMS: calcd. For C₁₇H₁₆O: 236.1201, found: 236.1201

2-Methylene-1-phenyl-2,3-dihydro-1*H*-indene (3c)

Following the general method A, from 1-allyl-2-bromobenzene (1) (0.168 mmol) and benzaldehyde tosylhydrazone (50.6 mg, 0.184 mmol) were obtained 19.3 mg of **3c** (56 % isolated yield) as a colorless oil. $R_f 0.25$ (hexane).

Following the general method B, from 1-allyl-2-iodobenzene (5) (0.168 mmol) and benzaldehyde tosylhydrazone (92.1 mg, 0.336 mmol) were obtained 26.5 mg of

3c (77 % isolated yield) as a colorless oil. $R_f 0.25$ (hexane). Spectroscopic data were consistent with those reported in the literature.⁶



¹H NMR (300 MHz, CDCl₃) δ 7.37-7.18 (m, 8H), 7.03 (d, *J* = 7.3 Hz, 1H), 5.21 (q, *J* = 2.3 Hz, 1H), 4.96 (s broad, 1H), 4.88 (q, *J* = 2.3 Hz, 1H), 3.87 (s broad, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154. (C), 145.7 (C), 144.5 (C), 141.7 (C), 128.7 (CH), 128.5 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 125.3 (CH), 124.3 (CH), 109.7 (CH₂), 56.3 (CH), 39.0 (CH₂) ppm. EI MS: 206 (M⁺).

1-(4-Fluorophenyl)-2-methylene-2,3-dihydro-1*H*-indene (3d)

Following the general method A, from 1-allyl-2-bromobenzene **(1)** (0.168 mmol) and 4-fluorobenzaldehyde tosylhydrazone (54 mg, 0.184 mmol) were obtained 17.6 mg of **3d** (47 % isolated yield) as a colorless oil. R_f 0.32 (hexane).

Following the general method B, from 1-allyl-2-iodobenzene (5) (0.168 mmol) and 4-fluorobenzaldehyde tosylhydrazone (98.2 mg, 0.336 mmol) were obtained 30.1 mg of 3d (80 % isolated yield) as a colorless oil. $R_f 0.32$ (hexane).



¹H NMR (401 MHz, CD₂Cl₂) δ 7.34 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.04 (td, *J* = 8.8, 3.0 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 5.21 (s broad, 1H), 4.96 (s broad, 1H), 4.85 (s broad, 1H), 3.85 (s, 2H) ppm. ¹³C NMR (101 MHz, CD₂Cl₂) δ 161.6 (d, *J* = 243.5 Hz, C-F), 154.2 (C), 145.8 (C), 141.7 (C), 140.5 (d, *J* = 3.2 Hz, C), 130.1 (CH, d, *J* = 7.8 Hz), 127.1 (CH), 126.8 (CH), 124.9 (CH), 124.4 (CH), 115.1 (CH, d, *J* = 21.2 Hz),109.5 (CH₂), 55.4 (CH), 38.8 (CH₂) ppm. EI HRMS: calcd. For C₁₆H₁₃F: 224.1001, found: 224.1008

⁶ L. Ackermann, S. I. Kozhushkov and D. S. Yufit, *Chem. Eur. J.*, 2012, **18**, 12068.

2-Methylene-1-(p-tolyl)-2,3-dihydro-1H-indene (3e)

Following the general method A, from 1-allyl-2-bromobenzene (1) (0.168 mmol) and *p*-tolualdehyde tosylhydrazone (53 mg, 0.184 mmol) were obtained 12.9 mg of **3e** (35 % isolated yield) as a yellow oil. $R_f 0.25$ (hexane).

Following the general method B, from 1-allyl-2-iodobenzene **(5)** (0.168 mmol) and *p*-tolualdehyde tosylhydrazone (96.8 mg, 0.336 mmol) were obtained 33.2 mg of **3e** (90 % isolated yield) as a yellow oil. R_f 0.25 (hexane).



¹H NMR (300 MHz, CD_2Cl_2) δ 7.30 (d, J = 6.7 Hz, 1H), 7.25 – 7.10 (m, 5H), 7.03 (d, J = 7.9 Hz, 2H) , 6.96 (d, J = 7.3 Hz, 1H), 5.16 (s, broad 1H), 4.90-4.84 (m, 2H), 3.83 (s broad, 2H), 2.33 (s, 3H) ppm. ¹³C NMR (75 MHz, CD_2Cl_2) δ 155.0 (C), 146.8 (C), 142.3 (C), 136.6 (C), 129.7 (CH), 120.0 (CH), 127.5 (CH), 127.3 (CH), 125.6 (CH), 124.9 (CH), 109.8 (CH₂), 56.4 (CH), 39.4 (CH₂), 21.3 (CH₃) ppm. EI HRMS: calcd. For C₁₇H₁₆: 220.1252, found: 220.1261

1-(3-Chlorophenyl)-2-methylene-2,3-dihydro-1*H*-indene (3f)

Following the general method B, from 1-allyl-2-iodobenzene (5) (0.168 mmol) and 3-chlorobenzaldehyde tosylhydrazone (103.7 mg, 0.336 mmol) were obtained 33 mg of 3f (82 % isolated yield) as a colorless oil. $R_f 0.33$ (hexane).



¹H NMR (300 MHz, CD_2Cl_2) δ 7.31 (d, J = 7.5 Hz, 1H), 7.29 – 7.11 (m, 5H), 7.10 – 7.04 (m, 1H), 6.97 (d, J = 7.5 Hz, 1H), 5.21 (q, J = 2.2 Hz, 1H), 4.92 (s broad, 1H), 4.86 (q, J = 2.2 Hz, 1H), 3.83 (s broad) ppm. ¹³C NMR (75 MHz, CD_2Cl_2) δ 154.1 (C), 147.5 (C), 145.8 (C), 142.3 (C), 134.7 (C), 130.3 (CH), 129.1 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 127.1 (CH), 125.6 (CH), 125.0 (CH), 110.5 (CH₂), 56.4 (CH), 39.4 (CH₂) ppm. EI HRMS: calcd. For C₁₆H₁₃Cl: 240.0706, found: 240.0716

3-(2-Methylene-2,3-dihydro-1*H*-inden-1-yl)pyridine (3g)

Following the general method A, from 1-allyl-2-bromobenzene (1) (0.168 mmol) and 3-pyridinecarboxaldehyde tosylhydrazone (50.6 mg, 0.184 mmol) were obtained 30.2 mg of **3f** (87 % isolated yield) as a yellow oil. R_f 0.31(hexane).



¹H NMR (400 MHz, CDCl₃) δ 8.51 (s broad, 2H), 7.41 (d, J = 7.4 Hz, 1H), 7.35-7.15 (m, 4H), 6.94 (d, J = 7.4 Hz, 1H), 5.22 (s, 1H), 4.94 (s, 1H), 4.82 (s, 1H), 3.85 (s, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 153.3 (C), 150.1 (CH), 148.0 (CH), 144.9 (C), 141.8 (C), 140.1 (C), 136.3 (CH), 127.5 (CH), 127.2 (CH), 125.1 (CH), 124.6 (CH), 123.8 (CH), 110.6 (CH₂), 53.6 (CH), 39.0 (CH₂) ppm. HRMS: calcd. For C₁₆H₁₃Cl: 207.1048, found: 207.1050.

1-(*tert*-Butyl)-2-methylene-2,3-dihydro-1*H*-indene (3h)

Following the general method B, from 1-allyl-2-iodobenzene (5) (0.168 mmol) and trimethylacetaldehyde tosylhydrazone (85.4 mg, 0.336 mmol) were obtained 15 mg of 3g (48 % isolated yield) as a colorless oil. R_f 0.57 (hexane).



¹H NMR (300 MHz, CD_2Cl_2) δ 7.27-7.13 (m, 4H), 5.16 (m, 1H), 5.01 (m, 1H), 3.70 (d, J = 19.5 Hz, 1H), 3.38 (d, J = 19.5 Hz, 1H), 3.32 (s, 1H), 0.93 (s, 9H) ppm. ¹³C NMR (75 MHz, CD_2Cl_2) δ 152.1 (C), 144.9 (C), 143.8 (C), 127.11 (CHx2), 126.0 (CH), 124.6 (CH), 110.8 (CH₂), 61.8 (CH), 40.8 (CH₂), 35.7 (C), 27.7 (CH₃) ppm. HRMS: calcd. For C₁₆H₁₃Cl: 186.1409, found: 207.1412.

4-(2-Methylene-2,3-dihydro-1*H*-inden-1-yl)phenol (3i)

Following the general method B, from 1-allyl-2-iodobenzene **(5)** (0.168 mmol) and 4-acetoxybenzaldehyde tosylhydrazone (111.6 mg, 0.336 mmol) were obtained 23.5 mg of **3h** (63 % isolated yield) as a brown oil. $R_f 0.27$ (5:1 hexane : AcOEt).



¹H NMR (300 MHz, CD₂Cl₂) δ 7.33 (d, J = 7.2 Hz, 1H), 7.26-7.16 (m, 2H), 7.05 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 7.5 Hz, 1H), 6.81 (d, J = 8.6 Hz, 2H), 5.20 (m, 1H), 5.13 (broad, 1H), 4.90 (broad, 1H), 4.90-4.86 (m, 1H), 3.84 (s broad 2H) ppm. ¹³C NMR (75 MHz, CD₂Cl₂) δ 155.1 (C), 154.9 (C), 146.8 (C), 142.2 (C), 137.4 (C), 130.3 (CH), 127.5 (CH), 127.3 (CH), 125.5 (CH), 124.8 (CH), 115.7 (CH), 109.7 (CH₂), 56.0 (CH), 39.4 (CH₂) ppm. EI HRMS: calcd. For C₁₆H₁₄O: 222.1045, found: 222.1039

4-(2-Methylene-2,3-dihydro-1H-inden-1-yl)benzonitrile (3j)

Following the general method B, from 1-allyl-2-iodobenzene **(5)** (0.168 mmol) and 4-acetoxybenzaldehyde tosylhydrazone (100 mg, 0.336 mmol) were obtained 19.2 mg of **3j** (50 % isolated yield) as a colorless oil. R_f 0.30 (15:1 hexane : AcOEt).



¹H NMR (300 MHz, CD₂Cl₂) δ 7.60 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.21 (m, 1H), 7.16 (t, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.22 (q, *J* = 2.3 Hz, 1H), 4.82 (q, *J* = 2.3 Hz, 1H), 3.84 (s, 1H) ppm. ¹³C NMR (75 MHz, CD₂Cl₂) δ 153.8 (C), 150.7 (C), 145.3 (C), 142.4 (C), 132.9 (CH), 129.9 (CH), 128.0 (CH), 127.5 (CH), 125.5 (CH), 125.1 (CH), 119.5 (C), 110.9 (CH₂), 56.7 (CH), 39.4 (CH₂). For C₁₆H₁₄O: 231.1048, found: 231.1046.

2-Methylene-1-(2,4,6-trimethoxyphenyl)-2,3-dihydro-1*H*-indene (3k)

Following the general method B, from 1-allyl-2-iodobenzene **(5)** (0.168 mmol) and 2,4,6-trimethoxybenzaldehyde tosylhydrazone (122 mg, 0.336 mmol) were obtained 35 mg of **3i** (71 % isolated yield) as a colorless oil. R_f 0.31 (15:1 hexane: AcOEt).



¹H NMR (300 MHz, C₆D₆) δ 7.20 – 7.00 (m, 4H), 6.12 (broad, 2H), 5.96 (s broad, 1H), 5.12 (s broad, 2H), 3.96 (d, *J* = 20.2 Hz, 1H), 3.82 (d, *J* = 20.2 Hz, 1H), 3.38 (s, 1H), 3.4-2.9 (broad, 6H) ppm. ¹³C NMR (75 MHz, C₆D₆) δ 160.6 (C), 159.8 (C), 154.8 (C), 147.7 (C), 142.0 (C), 126.7 (CH), 126.3 (CH), 124.2 (CH), 124.0 (CH), 114.8 (s), 106.1 (CH₂), 92.1 (broad CH) 55.5 (CH₃), 54.9 (CH₃), 45.8 (CH), 39.7 (CH₂) ppm. For C₁₆H₁₄O: 296.1412, found: 296.1413.

4.- General procedure and characterization data for benzofurans 7

A carousel reaction tube was charged under nitrogen atmosphere with the corresponding 1-iodo-2-(vinyloxy)benzene **(6a)** or 1-iodo-4-methoxy-2-(vinyloxy)benzene **(6b)** (0.164 mmol), tris(dibenzylideneacetone)dipalladium(0) (3 mol %), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos) (12 mol %), lithium *tert*-butoxide (6 equiv), H₂O (5 equiv) and acetonitrile (1.8 mL). The N-tosylhydrazone (2 equiv) is added via syringe pump over a period of 1 h. The reaction mixture was stirred at 85 °C for 1 h. After cooling to room temperature, the reaction crude was dissolved in DCM and filtered through celite. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using hexane or a mixture of hexane / ethyl acetate as eluent.

N,N-Dimethyl-4-(2-methylbenzofuran-3-yl)aniline (7a)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and 4-(dimethylamino)benzaldehyde tosylhydrazone (104.1 mg, 0.328 mmol) were obtained 20.3 mg of **7a** (50 % isolated yield) as a yelow oil. R_f 0.21 (20:1 hexane : AcOEt).



¹H NMR (300 MHz, CDCl₃) δ 7.62 (m, 1H), 7.50-7.40 (m, 3H), 7.32-7.20 (m, 2H), 6.90 (d, 2H, ³*J* = 8.8 Hz), 3.05 (s, 6H), 2.57 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.0 (C), 150.5 (C), 149.5 (C), 129.7 (CH), 129.3 (C), 123.3 (CH), 122.4 (CH), 120.7 (C), 119.5 (CH), 116.8 (C), 112.8 (CH), 110.6 (CH), 40.6 (CH₃), 12.9 (CH₃) ppm. EI HRMS: calcd. For C₁₇H₁₇NO: 251.1310, found: 251.1311

3-(4-Methoxyphenyl)-2-methylbenzofuran (7b)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and *p*-anisaldehyde tosylhydrazone (99.8 mg, 0.328 mmol) were obtained 30 mg of **7b** (77 % isolated yield) as a colorless oil. $R_f 0.24$ (30:1 hexane : AcOEt).



¹H NMR (300 MHz, CD_2Cl_2) δ 7.53 (d, 1H, ³*J* = 6.7 Hz), 7.44 (m, 3H) 7.24 (m, 2H), 7.04 (d, 2H, ³*J* = 8.3 Hz), 3.86 (s, 3H), 2.52 (s, 3H). ¹³C NMR (75 MHz, CD_2Cl_2) δ 159.3 (C), 154.5 (C), 151.6 (C), 130.5 (CH), 129.5 (C), 125.5 (C), 124.0 (C), 123.1 (CH), 119.7 (CH), 116.9 (C), 114.7 (CH), 111.1 (CH), 55.9 (CH₃), 13.1 (CH₃). EI HRMS: calcd. For C₁₆H₁₄O₂: 238.0994, found: 238.0998

2-Methyl-3-phenylbenzofuran (7c)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and benzaldehyde tosylhydrazone (89.9 mg, 0.328 mmol) were obtained 20.4 mg of **7c** (60 % isolated yield) as a colorless oil. R_f 0.29 (hexane). NMR data were consistent with those reported in the literature.⁷

⁷ Kundu, D.; Samim, M.; Majee, A.; Hajra, A. Chem. Asian J. 2011, 6, 406



¹H NMR (300 MHz, CDCl₃) δ 7.74 (m, 1H) 7.70-7.55 (m, 5H), 7.50 (m, 1H), 7.39 (m, 2H), 2.69 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.1 (C), 151.4 (C), 133.0 (C), 129.1 (CH), 128.9 (CH), 127.1 (CH), 126.6 (C), 123.7 (CH), 122.7 (CH), 119.5 (CH), 117.0 (C), 110.9 (CH), 13.0 (CH₃) ppm.

3-(4-Fluorophenyl)-2-methylbenzofuran (7d)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and 4-fluorobenzaldehyde tosylhydrazone (95.8 mg, 0.328 mmol) were obtained 21 mg of **7d** (57 % isolated yield) as a colorless oil. $R_f 0.31$ (hexane).



¹H NMR (300 MHz, CDCl₃) δ 7.57-7.45 (m, 4H), 7.35-7.15 (m, 4H), 2.55 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 162.0 (C-F, d,²*J* = 246.2 Hz) 154.1 (C), 151.4 (C), 130.6 (CH, d, ${}^{4}J_{C-F}$ = 8.0 Hz), 128.9 (C), 128.8 (C), 123.8 (CH), 122.8 (CH), 119.2 (CH), 116.2 (C), 115.9 (CH, d, ${}^{3}J_{C-F}$ = 21.4 Hz), CH, 110.9 (CH), 12.9 (CH₃) ppm. EI HRMS: calcd. For C₁₅H₁₁FO: 226.0794, found: 226.0803

2-Methyl-3-(2,4,6-trimethoxyphenyl)benzofuran (7e)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and 2,4,6-trimethoxybenzaldehyde tosylhydrazone (119.5 mg, 0.328 mmol) were obtained 28.9 mg of **7e** (59 % isolated yield) as a yellow oil. R_f 0.12 (15:1 hexane : AcOEt).



¹H NMR (300 MHz, CDCl₃) δ 7.40 (m, 1H), 7.20-7.05 (m, 3H), 6.27 (s, 2H), 3.90 (s, 3H), 3.75 (s, 6H), 2.31 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 161.3 (C), 159.3 (C), 154.2 (C), 153.2 (C), 130.1 (C), 122.7 (CH), 122.0 (CH), 120.5 (CH), 110.7 (CH), 108.7 (C), 102.2 (C), 90.9 (CH), 55.9 (CH₃), 55.5 (CH₃), 13.5 (CH₃) ppm. EI HRMS: calcd. For C₁₈H₁₈O₄: 298.1205, found: 298.1207

2-Methyl-3-(p-tolyl)benzofuran (7f)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and *p*-tolualdehyde tosylhydrazone (94.5 mg, 0.328 mmol) were obtained 21 mg of **7f** (58 % isolated yield) as a colorless oil. $R_f 0.32$ (hexane).



¹H NMR (300 MHz, CDCl₃) δ 7.61 (m, 1H), 7.49 (m, 2H), 7.44 (d, ³*J* = 8.0 Hz, 2H), 7.34 (d, ³*J* = 8.0 Hz, 2H), 7.27 (m, 2H), 2.57 (s, 3H), 2.46 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.1 (C), 151.2 (C), 136.8 (C), 129.9 (C), 129.6 (CH), 129.0 (C), 128.9 (CH), 123.6 (CH), 122.7 (CH), 119.5 (CH), 116.9 (C), 110.9 (CH), 21.4 (CH₃), 13.0 (CH₃). EI HRMS: calcd. For C₁₆H₁₄O: 222.1045, found: 222.1047

3-(3-Chlorophenyl)-2-methylbenzofuran (7g)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and 3-chlorobenzaldehyde tosylhydrazone (101.2 mg, 0.328 mmol) were obtained 22.5 mg of **7g** (57 % isolated yield) as a colorless oil. $R_f 0.34$ (hexane).



¹H NMR (300 MHz, CDCl₃) δ 7.62-7.22 (M, 8H), 2.57 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.0 (C), 151.8 (C), 134.7 (C), 134.6 (C), 130.0 (CH), 128.9 (CH), 128.3 (C), 127.1 (CH), 123.8 (CH), 122.8 (CH), 119.1 (CH), 115.8 (C), 110.9 (CH), 12.9 (CH₃) ppm. EI HRMS: calcd. For C₁₅H₁₁ClO: 242.0498, found: 242.0500

2-Methyl-3-(4-(trifluoromethyl)phenyl)benzofuran (7h)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and 4-(trifluoromethyl)benzaldehyde tosylhydrazone (112.2 mg, 0.328 mmol) were obtained 30.7 mg of **7h** (68 % isolated yield) as a colorless oil. R_f 0.28 (hexane).



¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, 2H, 8.2 H), 7.68-7.65 (m, 2H), 7.61 (dd, 1H, ³*J* = 7. 0 Hz, ⁴*J* = 1.5 Hz), 7.54 (dd, 1H, ³*J* = 7. 30 Hz, ⁴*J* = 1.5 Hz), 7.40-7.27 (m, 2H), 2.61 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.0 (C), 152.1 (C), 136.7 (C), 129.1 (CH), 129.0 (q, C-CF₃, *J* = 32.5 Hz), 128.2 (C), 125.7 (q, CH, *J* = 3.5 Hz), 124.0 (CH), 122.9 (CH), 119.0 (CH), 115.9 (C), 111.0 (CH), 12.9 (CH₃) ppm. EI HRMS: calcd. For C₁₆H₁₁F₃O: 276.0762, found: 276.0752

4-(2-Methylbenzofuran-3-yl)benzonitrile (7i)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and 4-formylbenzonitrile tosylhydrazone (98.1 mg, 0.328 mmol) were obtained 27.9 mg of **7i** (73 % isolated yield) as a as a white solid. R_f 0.22 (15:1 hexane : AcOEt). m.p = 101.2 - 103.1 °C.



¹H NMR (300 MHz, CDCl₃) δ 7.81-7.79 (m, 2H), 7.66-7.63 (m, 2H), 7.57 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.36-7.25 (m, 2H), 2.58 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.1 (C), 152.5 (C), 138.0 (C), 132.6 (CH), 129.3 (CH), 127.7 (C), 124.5 (CH), 123.1 (CH), 118.9 (CH), 115.7 (C), 111.1 (CH), 110.5 (C), 13.0 (CH₃) ppm. EI HRMS: calcd. For C₁₆H₁₁NO: 233.0841, found: 233.0849

3-(Furan-2-yl)-2-methylbenzofuran (7j)

Following the general method, from 1-iodo-2-(vinyloxy)benzene **(6a)** (0.164 mmol) and furfural tosylhydrazone (86.7 mg, 0.328 mmol) were obtained 13 mg of **7j** (40 % isolated yield) as a colorless oil. $R_f 0.40$ (hexane).



¹H NMR (300 MHz, CDCl₃) δ 7.85-7.80 (m, 1H), 7.55 (s broad, 1H), 7.33-7.25 (m, 2H), 6.59-6.53 (m, 2H), 2.69 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 153.9 (C), 151.8 (C), 148.2 (C), 141.3 (CH), 126.8 (C), 123.8 (CH), 122.9 (CH), 120.2 (CH), 111.1 (CH), 110.6 (CH), 108.2 (C), 106.2 (CH), 13.8 (CH₃) ppm. For C₁₆H₁₄O: 198.0681, found: 198.0683.

6-Methoxy-2-methyl-3-phenylbenzofuran (7k)

Following the general method, from 1-iodo-4-methoxy-2-(vinyloxy)benzene **(6b)** (0.164 mmol) and benzaldehyde tosylhydrazone (89.9 mg, 0.328 mmol) were obtained 26.5 mg of **7k** (68 % isolated yield) as a colorless oil. R_f 0.19 (50:1 hexane : AcOEt). NMR data were consistent with those reported in the literature.⁸



¹H NMR (300 MHz, CDCl₃) δ 7.57 – 7.41 (m, 5H), 7.40 – 7.32 (m, 1H), 7.01 (d, *J* = 2.2 Hz, 1H) 6.86 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.87 (s, 3H), 2.52 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 157.5 (C), 154.9 (C), 150.2 (C), 133.0 (C), 128.8 (CH), 128.7 (CH), 126.9 (CH), 122.1 (C), 119.4 (CH), 116.6 (C), 111.1 (CH), 95.8 (CH), 55.8 (CH₃), 12.8 (CH₃) ppm.

4-(6-Methoxy-2-methylbenzofuran-3-yl)benzonitrile (7l)

Following the general method, from 1-iodo-4-methoxy-2-(vinyloxy)benzene **(6b)** (0.164 mmol) and 4-formylbenzonitrile tosylhydrazone (98.1 mg, 0.328 mmol)

⁸ A. R. Katritzky, Y. Ji, Y. Fang and I. Prakash, *J. Org. Chem.*, 2001, **66**, 5613

were obtained 22.8 mg of **7I** (53 % isolated yield) as a as a white solid. $R_f 0.22$ (10:1 hexane : AcOEt). m.p = 128.9 - 130.5 °C.



¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 2.1 Hz, 1H) ,6.89 (dd, *J* = 8.6, 2.2 Hz, 1H) 3.87 (s, 3H), 2.53 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 157.9 (C), 155.0 (C), 151.3 (C), 138.2 (C), 132.6 (CH), 129.2 (CH), 121.0 (C), 119.1 (CH), 119.0 (C), 115.5 (C), 111.7 (CH), 110.7 (C), 96.0 (CH), 55.8 (CH₃), 13.0 (CH₃) ppm. For C₁₆H₁₄O: 263.0946, found: 263.0944.

5.- General procedure and characterization data for benzylideneindenones 9

A carousel reaction tube was charged under nitrogen atmosphere with the corresponding *N*-tosylhydrazone (2 equiv), (*E*)-1-(2-iodophenyl)-3-phenylprop-2en-1-one **8** (0.170 mmol), tris(dibenzylideneacetone)dipalladium(0) (3 mol %), 2dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos) (12 mol %), K₂CO₃ (6 equiv), H₂O (5 equiv) and 1,4-dioxane (2 mL). The reaction mixture was stirred at 110 °C for 1 h. After cooling to room temperature, the reaction crude was dissolved in methylene chloride and filtered through celite. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ethyl acetate as eluent.

(E)-2-Benzylidene-3-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (9a)

Following the general method, from iodoketone **8** (0.170 mmol) and *p*-anisaldehyde tosylhydrazone (103.4 mg, 0.34 mmol) were obtained 38.8 mg of **9a** (70 % isolated yield) as a as a brown solid as a 5.8: 1 mixture of E/Z isomers. R_f 0.15 (10:1, hexane: AcOEt).



Spectroscopic data of major isomer *E*: ¹H NMR (300 MHz, CDCl₃) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.79 (s, 1H), 7.56, 7.56-7.51(m, 3H), 7.44-7.37 (m, 2H), 7.30-7.27 (m, 3H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 5.37 (s, 1H), 3.70 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 194.7 (C), 159.1 (C), 155.4 (C), 139.5 (C), 136.6 (C), 135.5 (CH), 135.4 (CH), 134.7 (C), 134.1 (C), 132.0 (CH), 130.2 (CH), 129.2 (CH), 128.9 (CH), 128.4 (CH), 126.5 (CH), 124.4 (CH), 114.7 (CH), 55.6 (CH₃), 48.4 (CH) ppm. EI HRMS: calcd. For C₂₃H₁₈O₂: 326.1307, found: 326.1312

(E)-2-Benzylidene-3-(p-tolyl)-2,3-dihydro-1H-inden-1-one (9b)

Following the general method, from iodoketone **8** (0.170 mmol) and *p*-tolualdehyde tosylhydrazone (98 mg, 0.34 mmol) were obtained 34 mg of **9b** (65 % isolated yield) as a as a brown solid as a 14: 1 mixture of *E*/*Z* isomers. R_f = 0.12 (20:1 hexane: AcOEt).



¹H NMR (600 MHz, CD₂Cl₂) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.55-7.53 (m, 3H), 7.40-7.38 (m, 3H), 7.29-7.28 (m, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.38 (s, 1H), 2.24 (s, 3H) ppm. ¹³C NMR (151 MHz, CD₂Cl₂) δ 194.7 (C), 155.3 (C), 139.4 (C), 139.1 (C), 137.2 (C), 136.6 (C), 135.5 (CH), 135.4 (CH), 134.7 (C), 132.0 (CH), 130.1 (CH), 128.9 (CH), 128.4 (CH), 128.0 (CH), 126.5 CH), 124.5 (CH), 48.8 (CH), 21.3 (CH₃) ppm. For C₁₆H₁₄O: 310.1358, found: 310.1367.

6.- Influence of the substitution of the double bond in the synthesis of indanes

The cascade reaction for the synthesis of indanes was attempted also with systems featuring a substituted double bond. In the case of (*E*)-1-(but-2-en-1-yl)-2-iodobenzene **A**, the cyclization under the optimized conditions proceeded with very high overall yield (83%), but unfortunately led to a mixture of isomers derived from the unselective β -hydride elimination in the final step.



However, aryliodides featuring other substituents on the double bond failed to provide the indene through the cascade reaction. This was the case for the ethoxycarbonyl substituted system **A**, and the trisubstituted alkene **B**. In both cases, the iodide was recovered after the reaction under standard conditions.



7.- Copies of the ¹H and ¹³C NMR spectra

1-lodo-2-(vinyloxy)benzene 6a







N,N-Dimethyl-4-(2-methylene-2,3-dihydro-1*H*-inden-1-yl)aniline 3a



S22

2-Methylene-1-phenyl-2,3-dihydro-1*H*-indene 3c





1-(4-Fluorophenyl)-2-methylene-2,3-dihydro-1*H*-indene 3d



2-Ethylene-1-(p-tolyl)-2,3-dihydro-1H-indene 3e



1-(3-Chlorophenyl)-2-methylene-2,3-dihydro-1*H*-indene 3f

3-(2-Methylene-2,3-dihydro-1*H*-inden-1-yl)pyridine 3g





S27



1-(tert-Butyl)-2-methylene-2,3-dihydro-1H-indene 3h





4-(2-Methylene-2,3-dihydro-1*H*-inden-1-yl)phenol 3i



4-(2-Methylene-2,3-dihydro-1*H*-inden-1-yl)benzonitrile 3j



2-Methylene-1-(2,4,6-trimethoxyphenyl)-2,3-dihydro-1*H*-indene 3k

N,N-Dimethyl-4-(2-methylbenzofuran-3-yl)aniline 7a.



3-(4-Methoxyphenyl)-2-methylbenzofuran 7b



2-Methyl-3-phenylbenzofuran 7c



3-(4-Fluorophenyl)-2-methylbenzofuran 7d





2-Methyl-3-(p-tolyl)benzofuran 3f



3-(3-Chlorophenyl)-2-methylbenzofuran 7g





2-Methyl-3-(4-(trifluoromethyl)phenyl)benzofuran 7h





S41

3-(Furan-2-yl)-2-methylbenzofuran 7j



5-Methoxy-2-methyl-3-phenylbenzofuran 7k



4-(5-Methoxy-2-methylbenzofuran-3-yl)benzonitrile 71



(*E*)-2-Benzylidene-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (5.8:1 mixture of E/Z isomers)



(*E*)-2-Benzylidene-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one 9b (14: 1 mixture of E/Z isomers)



S46