Supporting Information for: Pd-Catalyzed Intramolecular Coupling of Vinyl Halides and Ketone Enolates. Synthesis of Bridged Azabicyclic Compounds. Daniel Solé, Emma Peidró, and Josep Bonjoch.

Representative procedure for the intramolecular coupling using KO*t*-Bu as the base (Table 1, entry 1): To a solution of $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) in dry THF (5 mL) were added under Argon a solution of vinyl bromide **2a** (100 mg, 0.31 mmol) in dry THF (2 mL) and KO*t*-Bu (0.47 mmol, 0.47 mL of 1M solution in *t*-butyl alcohol). The solution was heated at reflux for 30 min. After cooling to room temperature, the mixture was diluted with ether and washed with saturated aqueous NH_4Cl. The aqueous layer was extracted with ether and the combined organic extracts were washed with brine, dried, and concentrated. The residue was purified by Flash chromatography (SiO_2, from CH_2Cl_2 to 98:2 CH_2Cl_2/MeOH) to give azabicyclic compound **1** (37 mg, 50%) and dimer **3** (4 mg, 5%).

Representative procedure for the intramolecular coupling using Cs_2CO_3 as the base in toluene (Table 2, Method B: entry 5): A solution of vinyl bromide **13** (100 mg, 0.34 mmol), Cs_2CO_3 (332 mg, 1.02 mmol), Et_3N (0.14 mL, 1.02 mmol), and $PdCl_2(PPh_3)_2$ (49 mg, 0.07 mmol) in dry toluene (10 mL) was stirred at 110 °C in a sealed tube for 24 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were dried and concentrated. The residue was purified by Flash chromatography (Al_2O_3, from hexane to 8:2 hexane/AcOEt) to give pyrrole **15** (33 mg, 45%).

2-Benzyl-4-methylene-2-azabicyclo[3.3.1]nonan-6-one (1): IR (film) 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.72 (dddd, *J* = 14.5, 10.5, 8, and 4.5 Hz, 1H, H-8), 1.97 (dt, *J* = 13 and 2.7 Hz, 1H, H-9), 2.24 (dm, *J* = 13 Hz, H-9), 2.25-2.33 (m, H-8), 2.45 (dd, *J* = 17.5 and 8.5 Hz, 1H, H-7), 2.59 (ddd, *J* = 17.5, 10.5, and 8.5 Hz, 1H, H-7), 3.08 (br s, H-1), 3.24 (br s, H-5), 3.34 (s, 2H, H-3), 3.70 (d, *J* = 13.5 Hz, 1H, NCH_2Ar), 3.77 (d, *J* = 13.5 Hz, 1H, NCH_2Ar), 4.84 (s, 1H, =CH), 4.91 (s, 1H, =CH), 7.22-7.36 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4 (C-8), 32.7 (C-9), 37.9 (C-7), 49.9 (C-1), 53.5 (C-5), 53.7 (C-3), 59.8 (NCH_2Ar), 112.6 ($=CH_2$), 127.1 (*p*-C), 128.5 and 128.7 (*o*-C and *m*-C), 139.0 (*ipso*-C), 141.0 (C-4), 210.5 (C-6). Anal. Calcd for $C_{16}H_{19}NO.H_2O$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.34; H, 7.69; N, 5.49.

Dimer 3: IR (film) 1712 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.40-2.62 (m, 16H), 3.10 (m, 2H), 3.19 (s, 2H), 3.50 (s, 2H), 3.71 (s, 2H), 3.80 (s, 2H), 5.45 (s, 1H), 5.58 (s, 1H), 7.20-7.45 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 27.6 (CH_2), 29.2 (CH_2), 38.7 (CH_2), 39.5(CH_2), 40.0 (CH_2), 54.0 (CH_2), 54.1 (CH_2), 55.4 (CH_2), 56.1 (CH_2), 56.4 (CH_2), 85.3 (C), 85.4 (C), 122.4 ($=CH_2$), 126.9 (CH), 127.2 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 130.0 (C), 139.2 (C), 140.0 (C), 210.9 (C), 211.3 (C); MS *m/z* 482 (M^+).

4-(*N*-Benzyl-*N*-propargylamino)cyclohexanone (4): IR (film) 1702 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.02 (dm, *J* = 13.2 Hz, 2H), 2.18 (dm, *J* = 13.2 Hz, 2H), 2.25 (t, *J* = 2.1 Hz, 1H), 2.35 (ddd, *J* = 14.7, 9.5, and 5.3 Hz, 2H, H-2ax), 2.55 (dt, *J* = 14.7 and 6 Hz, 2H, H-2eq), 3.09 (m, 1H, H-4), 3.37 (d, *J* = 2.1 Hz, 2H, NCH_2), 3.78 (s, 2H, NCH_2Ar), 7.22-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.2 (CH_2), 38.6 (CH_2), 38.7 (CH_2), 53.8 (CH_2), 56.4 (CH), 73.2 (C), 79.8 (CH), 127.2 (CH), 128.4 (CH), 128.7 (CH), 139.0 (C), 211.1 (C).

2-[a(*R*)-Methylbenzyl]-4-methylene-2-azabicyclo[3.3.1]nonan-6-one (7): IR (film) 1711 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, 1.5:1 mixture of diastereomers) δ 1.40 (d, *J* = 6.9 Hz, CH_3 minor), 1.41 (d, *J* = 6.6 Hz, CH_3 major), 1.43-1.82 (m, 1H, H-8), 1.86 (dt, *J* = 13.2 and 2.7 Hz, H-9 major), 1.99 (dt, *J* = 13 and 2.7 Hz, H-9 minor), 2.02-2.31 (m, 2H, H-8 and H-9), 2.32-2.45 (m, 1H, H-7), 2.58-2.80 (m, 1H, H-7), 3.06 (br s, H-1 major), 3.13 (d, *J* = 13.8 Hz, H-3 minor), 3.22 (br s, H-1 minor), 3.23 (br s, H-5 major), 3.27 (d, *J* = 13.8 Hz, H-3 minor), 3.33 (d, *J* = 14.1 Hz, H-3 major), 3.44 (br s, H-5 minor), 3.62 (d, *J* = 14.1 Hz, H-3 major), 3.74 (q, *J* = 6.9 Hz, NCHAr minor), 3.77 (q, *J* = 6.6 Hz, NCHAr major), 4.75 (s, $=CH_2$ minor), 4.85 (s, $=CH_2$ minor), 4.95 (s, $=CH_2$ major), 7.20-7.50 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz, 1.5:1 mixture of diastereomers) major: δ 21.4 (CH_3), 26.3 (C-8), 32.6 (C-9), 37.5 (C-7), 47.0 (C-1), 51.3 (C-3), 53.2 (C-5), 61.9 (NCHAr), 112.7 ($=CH_2$), 127.0 (CH), 127.2 (CH), 128.4 (CH), 141.3 (C-4), 144.8 (*ipso*-C), 210.8 (C-6); minor: 19.7 (CH_3), 27.3 (C-8), 32.2 (C-9), 37.2 (C-7), 47.2 (C-1), 51.0 (C-3), 52.6 (C-5), 62.0 (NCHAr), 112.1 ($=CH_2$), 126.9 (CH), 127.3 (CH), 128.3 (CH), 141.4 (C-4), 144.9 (*ipso*-C), 210.9 (C-6).

2-Benzyl-4-[(*Z*)-ethylidene]-2-azabicyclo[3.3.1]nonan-6-one (9): IR (film) 1712 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.52 (dd, *J* = 7 and 1.2 Hz, 3H, CH_3), 1.60-1.80 (m, 1H, H-8), 1.94 (dt, *J* = 12.8 and 3 Hz, 1H, H-9), 2.23 (ddd, *J* = 12.8, 6.6, and 3.4 Hz, 1H, H-9), 2.26-2.44 (m, 1H, H-8), 2.43 (dd, *J* = 17.2 and 8.2 Hz, 1H, H-7), 2.58 (ddd, *J* = 17.2, 10.6, and 8 Hz, 1H, H-7), 3.08 (br s, 1H, H-1), 3.13 (br s, 1H, H-5), 3.23 (d, *J* = 14.6 Hz, 1H, H-3), 3.61 (d, *J* = 14.6 Hz, 1H, H-3), 3.79 (s, 2H, NCH_2Ar), 5.43 (qm, *J* = 7 Hz, 1H, =CH), 7.20-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.0 (CH_3), 25.5 (C-8), 32.8 (C-9), 38.0 (C-7), 48.4 (C-3), 50.2 (C-1), 54.4 (C-5), 59.9 (NCH_2Ar), 122.3 (=CH), 127.5 (CH), 128.3 (CH), 128.6 (CH), 131.5 (C-4), 139.0 (*ipso*-C), 211.2 (C-6).

2-Benzyl-4-ethyl-2-azabicyclo[3.3.1]non-3-en-6-one (10): IR (film) 1711 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.95 (t, *J* = 7.4 Hz, 3H, CH_3), 1.60-2.50 (m, 5H), 2.64 (ddd, *J* = 15.4, 13.8, and 7.6 Hz, 1H), 2.91 (s, 1H), 3.16-3.32 (m, 2H), 3.64 (s, 1H), 4.20 (d, *J* = 15.4 Hz, 1H, NCH_2Ar), 4.29 (d, *J* = 15.4 Hz, 1H, NCH_2Ar), 6.13 (s.

1H), 7.20-7.52 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5 (CH_3), 26.7 (CH_2), 28.8 (CH_2), 34.3 (CH_2), 34.7 (CH_2), 48.6 (CH), 48.7 (CH), 57.7 (CH_2), 105.7 (C), 127.3 (CH), 127.5 (CH), 128.4 (CH), 132.6 (CH), 139.2 (C), 211.3 (C).

2-Benzyl-2-azabicyclo[4.3.1]dec-4-en-7-one (12): IR (film) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.78 (dddd, *J* = 14, 12.6, 5.1, and 2.4 Hz, 1H, H-9), 2.03 (dddd, *J* = 14.7, 6.1, 2.7, and 1.3 Hz, 1H, H-10), 2.14-2.28 (m, 2H, H-8 and H-9), 2.59 (dtd, *J* = 14.7, 3.6, and 1.3 Hz, 1H, H-10), 3.04 (br s, 1H, H-1), 3.05 (dd, *J* = 16.5 and 8.1 Hz, 1H, H-3), 3.16 (br t, *J* = 6.1 Hz, 1H, H-6), 3.31 (ddd, *J* = 15.3, 12.6, and 6.9 Hz, 1H, H-8), 3.49 (br d, *J* = 16.5 Hz, 1H, H-3), 3.55 (d, *J* = 14.5 Hz, 1H, NCH_2Ar), 3.96 (d, *J* = 14.5 Hz, 1H, NCH_2Ar), 5.61 (dddd, *J* = 10.8, 6.1, 2.4, and 1.3 Hz, 1H, H-5), 5.77 (dddd, *J* = 10.8, 8.1, 2.7, and 1.3 Hz, 1H, H-4), 7.20-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.9 (C-9), 31.9 (C-10), 34.8 (C-8), 48.2 (C-3), 51.3 (C-6), 55.3 (C-1), 59.9 (NCH_2Ar), 126.8 (*p*-C), 128.0 (CH), 128.4 (CH), 129.5 (C-5), 132.2 (C-4), 140.0 (*ipso*-C), 211.7 (C-7).

3-Acetyl-1-benzyl-4-methyl-3-pyrroline (14): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 3H), 2.23 (s, 3H), 3.59 (br s, 2H), 3.75 (br s, 2H), 3.79 (s, 2H), 7.20-7.40 (5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.6 (CH_3), 30.1 (CH_3), 59.8 (CH_2), 60.5 (CH_2), 66.1 (CH_2), 127.0 (CH), 128.3 (CH), 128.5 (CH), 133.3 (C), 138.3 (C), 150.0 (C), 195.6 (C).

3-Acetyl-1-benzyl-4-methylpyrrole (15): IR (film) 1653 cm^{-1}; ^{1} H NMR ($CDCl_3$, 200 MHz) δ 2.27 (s, 3H), 2.35 (s, 3H), 4.99 (s, 2H), 6.41 (s, 1H), 7.10-7.43 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4 (CH_3), 27.9 (CH_3), 53.7 (CH_2), 121.4 (CH), 121.7 (C), 124.1 (C), 127.2 (CH), 127.6 (CH), 128.0 (CH), 128.9 (CH), 136.5 (C), 193.9 (C).

3-Acetyl-1-benzyl-2,4,5,6,7,7a-hexahydro-1*H*-indole (17) : ^{1} H NMR ($CDCl_3$, 200 MHz) δ 1.24-1.48 (m, 2H), 1.60-2.25 (m, 6H), 2.20 (s, 3H), 3.31-3.52 (m, 2H), 3.54 (d, *J* = 13 Hz, 1H, NCH_2Ar), 3.87 (dd, *J* = 8.5 and 1.4 Hz, 1H), 4.01 (d, *J* = 13 Hz, 1H, NCH_2Ar), 7,20-7,50 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 23.4 (CH_2), 25.7 (CH_2), 27.4 (CH_2), 29.8 (CH_2), 30.5 (CH_3), 58.2 (CH_2), 59.7 (CH_2), 71.5 (CH), 127.1 (CH), 128.3 (CH), 128.8 (CH), 135.2 (C), 136.8 (C), 150.5 (C), 194.0 (C).

3-Acetyl-1-benzyl-4,5,6,7-tetrahydro-1*H*-indole (18) : IR (film) 1654 cm^{-1}; ^{1} H NMR ($CDCl_3$, 200 MHz) δ 1.66-1.80 (m, 4H), 2.35 (s, 3H), 2.32-2.43 (m, 2H), 2.80 (tm, *J* = 5 Hz, 2H), 4.99 (s, 2H), 7.02-7.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.7 (CH_2), 22.7 (CH_2), 23.1 (CH_2), 23.5 (CH_2), 27.7 (CH_3), 50.5 (CH_2), 119.5 (C), 122.6 (C), 126.3 (CH), 126.6 (CH), 127.8 (CH), 128.9 (CH), 130.4 (C), 136.8 (C), 193.8 (C).