Supporting Information: The Potassium Hydride Mediated Trimerization of Imines

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Experimental Section

1.1 General

Syntheses of the imine starting materials were performed under standard conditions. Fulvene syntheses were conducted in oven (95 °C) and vacuum dried glassware under an inert atmosphere of dry argon 5.0 via standard Schlenk or glove box techniques. NMR spectra were recorded on a Bruker ARX 250 (250 MHz) spectrometer or on a Varian Inova 300 or 400 (300 or 400 MHz). Chemical shifts are reported in ppm from TMS with the solvent resonance resulting from incomplete deuteration as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant. Melting points were determined in sealed capillaries with a Stuart SMP3 melting point apparatus. Elemental analysis was performed with a Vario elementar EL *III* elemental analyzer. GC-MS analyses were performed on a Thermo Focus GC with DSQ-MS unit equipped with a HP-5-MS column (30m x 0.32mm x 0.25µm). GC analyses were performed with an Agilent 6890 N Network GC-System equipped with a HP-5 column (30m x 0.32mm x 0.25µm). Non-halogenated solvents were distilled from sodium benzophenone ketyl and halogenated solvents from P_2O_5. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. All chemicals were purchased from commercial vendors and used without further purification.

1.2 Synthesis of Imines

N-Aryl imines were synthesized according to Taguchi *et al.*[1] – a solution of 0.1 mol amine, 0.1 mol ketone and 40 g of molecular sieves (4 Å) in 20 mL of diethyl ether was stirred for 24 hours. The molecular sieves were filtered off and washed with ether. The combined filtrates

[1] K. Taguchi, F. H. Westheimer, *J. Org. Chem.* **1971**, 1570-1572.

were evaporated to dryness and the residue was purified *via* vacuum distillation (liquid residue) or recrystallization.

N-(1-phenylethylidene)aniline **1a**: yielded as a pale yellow solid (14.66 g, 75 %). M.p. 37 °C. Found: C, 86.0; H, 6.9; N, 7.3. Calc. for $C_{14}H_{13}N$ (195.26): C, 86.1; H, 6.7; N, 7.2%. δ_H (299.83 MHz, C_6D_6, 298 K, TMS) 7.97-7.94 (m, 2H, C_6H_5), 7.21-7.14 (m, 5H, C_6H_5), 6.69-6.91 (t, 1H, C_6H_5, J = 7.2), 6.78-6.74 (m, 2H, C_6H_5) and 1.82 (s, 3H, CH_3); δ_C (75.39 MHz, C_6D_6, 298 K, TMS) 164.34 (C=N), 152.45, 139.69 (C_q, C_6H_5), 130.40, 129.14, 128.31, 127.54, 123.20, 119.58 ($C_{o,m,p}$, C_6H_5) and 16.63 (CH_3).

3-methyl-*N*-(1-phenylethylidene)aniline **1b**: yielded as a pale yellow solid (11.00 g, 53%). M.p. 34 °C. Found: C, 85.8; H, 7.4; N, 6.8. Calc. for $C_{15}H_{15}N$ (209.29): C, 86.1; H, 7.2; N, 6.7%. δ_H (299.83 MHz, C_6D_6, 298 K, TMS) 7.99-7.96 (m, 2H, aryl C*H*); 7.18-7.12 (m, 4H, aryl C*H*); 6.80-6.78 (d, 1H, aryl C*H*, J = 7.5), 6.63-6.60 (d, 2H, aryl C*H*, J = 8.7), 2.14 (s, 3H, CH_3) and 1.86 (s, 3H, CH_3); δ_C (75.39 MHz, C_6D_6, 298 K, TMS) 164.10 (C=N), 152.54, 139.80, 139.67 (aryl C_q), 130.34, 129.04, 128.31, 127.52, 123.98, 120.22, 116.64 (aryl *C*H), 21.37 (CH_3) and 16.68 (CH_3).

4-methoxy-*N*-(1-phenylethylidene)aniline **1c**: yielded as a pale yellow solid (19.40 g, 86%). M.p. 86 °C. Found: C, 79.5; H, 6.7; N, 6.1. Calc. for $C_{15}H_{15}NO$ (225.29): C, 80.0; H, 6.7; N; 6.2%. δ_H (399.80 MHz, [d_6]DMSO, 298 K, TMS) 8.00-7.97 (m, 2H, C_6H_5), 7.48-7.45 (m, 3H, C_6H_5), 6.95-6.93 (d, 2H, $C_6H_4OCH_3$, J = 8.4), 6.76-6.74 (d, 2H, $C_6H_4OCH_3$, J = 8.4), 3.75 (s, 3H, OCH_3) and 2.21 (s, 3H, CH_3); δ_C (100.53 MHz, [d_6]DMSO, 298 K, TMS) 165.59 (C=N), 156.15, 144.94, 139.87, 131.02, 128.94, 127.70, 121.40, 114.86 (aryl C_q, aryl *C*H), 55.82 (OCH_3) and 17.64 (CH_3).

4-methoxy-*N*-(1-(*p*-tolyl)ethylidene)aniline **1d**: yielded as a pale yellow solid (10.68 g; 45%). M.p. 83 °C. Found: C, 80.2; H, 7.4; N, 5.9. Calc. for $C_{16}H_{17}NO$ (239.31): C, 80.3; H, 7.2; N, 5.85%. δ_H (299.83 MHz, $CDCl_3$, 298 K, TMS) 7.91-7.89 (d, 2H, aryl C*H*, J = 8.1), 7.29-7.26 (d, 2H, aryl C*H*, J = 8.1), 6.95-6.92 (d, 2H, aryl C*H*, J = 9.0), 6.80-6.77 (d, 2H, aryl C*H*, J = 9.0), 3.84 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3) and 2.26 (s, 3H, CH_3); δ_C (75.39 MHz, $CDCl_3$, 298 K, TMS): 165.79 (C=N), 156.11, 145.22, 140.79, 137.33, 129.30, 127.36, 121.08, 114.47 (aryl C_q, aryl *C*H), 55.73 (OCH_3), 21.64 (*p*-CH_3) and 17.49 (CH_3).

N-(1-(naphthalen-2-yl)ethylidene)aniline **1e**: yielded as a pale yellow solid (10.07 g, 60%). M.p. 140 °C. Found: C, 88.0; H, 6.1; N, 5.8. Calc. for $C_{18}H_{15}N$ (245.32): C, 88.1; H, 6.2; N, 5.7%. δ_H (299.83 MHz, [d_6]DMSO, 298 K, TMS) 8.51 (s, 1H, 2-naphtyl), 8.23-8.20 (dd, 1H, 2-naphtyl, *J* = 1.8), 8.09-8.06 (m, 1H, 2-naphtyl), 8.00-7.97 (m, 2H, 2-naphtyl), 7.61-7.58 (m, 2H, 2-naphtyl), 7.42-7.36 (t, 2H, H_m, C_6H_5), 7.13-7.08 (t, 1H, H_p, C_6H_5), 6.86-6.83 (d, 2H, H_o, C_6H_5) and 2.33 (s, 3H, CH_3); δ_C (75.39 MHz, [d_6]DMSO, 298 K, TMS): 164.83 (C=N), 151.36, 136.21, 133.90, 132.54 (aryl C_q), 128.97, 127.90, 127.68, 127.52, 127.36, 126.51, 123.94, 123.12, 119.30 (aryl *C*H) and 17.09 (CH_3).

2-methyl-*N*-(1-phenylethylidene)aniline **1f**: yielded as a pale yellow solid (15.60 g, 75%). M.p. 61 °C. Found: C, 85.7; H, 7.5; N, 6.7. Calc. for $C_{15}H_{15}N$ (209.29): C, 86.1; H, 7.2; N, 6.7%. δ_H (399.83 MHz, [d_6]DMSO, 298 K, TMS) 7.99-7.96 (m, 2H, C_6H_5), 7.48-7.43 (m, 3H, C_6H_5), 7.20-7.18 (d, 1H, aryl C*H*, *J* = 7.6), 7.16-7.12 (t, 1H, aryl C*H*, *J* = 7.6), 6.97-6.93 (t, 1H, aryl C*H*, *J* = 7.6), 6.60-6.59 (d, aryl C*H*, 1H, *J* = 7.6), 2.09 (s, 3H, CH_3) and 1.98 (s, 3H, CH_3); δ_C (100.53 MHz, [d_6]DMSO, 298 K, TMS) 165.31 (C=N), 150.67, 139.50, 131.19, 130.83, 129.02, 127.74, 127.20, 127.05, 123.72, 118.89 (aryl *C*H, aryl C_q), 18.10 (CH_3) and 17.87 (CH_3).

N-(1-(*p*-tolyl)ethylidene)aniline **1g**: yielded as a pale yellow solid (14.51 g, 70%). M.p. 62 °C. Found: C, 85.7; H, 7.5; N, 6.8. Calc. for $C_{15}H_{15}N$ (209.29): C, 86.1; H, 7.2; N, 6.7%. δ_H (299.83 MHz, C_6D_6, 298 K, TMS) 7.94-7.91 (d, 2H, aryl C*H*, *J* = 8.1), 7.21-7.14 (m, 4H, aryl C*H*), 7.02-6.99 (d, 2H, aryl C*H*, *J* = 8.1), 6.96-6.91 (t, 1H, aryl C*H*, *J* = 7.2), 6.78-6.75 (d, 2H, aryl C*H*, *J* = 7.2), 2.09 (s, 3H, CH_3) and 1.86 (s, 3H, CH_3); δ_C (75.39 MHz, C_6D_6, 298 K, TMS) 164.00 (C=N), 152.41, 140.30, 137.00 (aryl C_q), 128.96, 128.92, 127.44, 122.92, 119.53 (aryl *C*H) and 21.00, 16.47 (CH_3).

3-chloro-2-methyl-*N*-(1-phenylethylidene)aniline **1h**: yielded as pale yellow solid (17.80 g, 73%). M.p. 80 °C. Found: C, 73.8, H, 5.9; N, 5.7. Calc. for $C_{15}H_{17}ClN$ (243.73): C, 73.9; H, 5.8; N, 5.75%. δ_H (299.83 MHz, [d_6]DMSO, 298 K, TMS) 8.03-8.01 (d, 2H, C_6H_5, *J* = 7.6), 7.53-7.49 (m, 3H, C_6H_5), 7.19-7.16 (m, 2H, aryl C*H*), 6.65-6.63 (d, 1H, aryl C*H*, *J* = 7.6), 2.15 (s, 3H, CH_3) and 2.07 (s, 3H, CH_3); δ_C (100.53 MHz, [d_6]DMSO, 298 K, TMS) 166.18 (C=N), 151.86, 138.83, 134.35, 125.11 (aryl C_q), 131.17, 128.77, 127.70, 127.55, 123.89, 117.74 (aryl *C*H), 17.79 (CH_3) and 14.72 (CH_3).

3,5-dimethyl-*N*-(1-phenylethylidene)aniline **1f**: yielded as an orange liquid (14.40 g, 65%). Found: C, 85.6, H, 7.5; N, 6.6. Calc. for $C_{16}H_{17}N$ (223.31): C, 86.05; H, 7.7; N, 6.3%. δ_H (299.83 MHz, [d_6]DMSO, 298 K, TMS) 7.98-7.95 (m, 2H, C_6H_5), 7.48-7.46 (m, 3H, C_6H_5), 6.69 (s, 1H, H_p, $C_6H_3(CH_3)_2$), 6.38 (s, 2H, H_o, $C_6H_3(CH_3)_2$), 2.26 (s, 6H, $C_6H_3(CH_3)_2$) and 2.17 (s, 3H, CH_3); δ_C (75.39 MHz, [d_6]DMSO, 298 K, TMS) 164.40 (C=N), 151.37, 138.98, 137.95, 130.34, 128.23, 127.00, 124.49, 116.74 (aryl C_q, aryl *C*H), 20.92 (2 x CH_3, $C_6H_3(CH_3)_2$) and 16.97 (CH_3).

1.3 Synthesis of Fulvenes

General procedure: In a pressure tube 20.0 mmol of the imine **1** were dissolved in about 10.0 mL of THF. Then 0.57 g (14.0 mmol) of potassium hydride were added, immediately the color changed from orange to green and a second color change to dark red, accompanied by hydrogen evolution, took place. The dark brown solution was heated under slight reflux for three to four days. Then it was cooled to room temperature and water (about 5 mL) was added. The solution was extracted with diethyl ether (10 mL), the organic phase was dried over Na_2SO_4 and evaporated to dryness by rotary evaporation. The dark red product was purified via column chromatography (*n*-hexane/ ethyl acetate) or recrystallized.

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-phenyl-amine **2a**: yielded as red crystalline product (1.18 g, 45%). M.p. 160-170 °C. Found: C, 90.3; H, 5.7; N, 3.6. Calc. for $C_{30}H_{23}N$ (397.51): C, 90.6; H, 5.8; N, 3.5%. δ_H (299.83 MHz, C_6D_6, 298 K, TMS) 7.34-7.27 (m, 5H), 7.15-7.14 (d, 1H, J = 1.5), 7.13-7.12 (d, 1H, J = 2.1), 6.92-6.67 (m, 9H), 6.43-6.39 (m, 4H), 6.29-6.24 (t, 1H, J = 7.5) and 5.90-5.87 (d, 2H, J = 7.5); δ_C (63,89 MHz, $CDCl_3$, 298 K, TMS) 154.51, 141.83, 140.68, 139.21, 138.75, 136.85, 136.46, 124.25 (C_q fulvene, aryl C_q), 133.08, 130.85, 130.80, 130.73, 130.39, 130.21, 127.17, 122.86 ($C_{o,m}$, aryl *C*H), 132.06, 129.02, 128.59, 127.87, 125.27 and 121.95 (C_p, aryl *C*H, *C*H fulvene).

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-*m*-tolyl-amine **2b**: at -20 °C a red crystalline material (1.52 g, 57%) was obtained. M.p. 181-185 °C. Found: C, 90.4; H, 6.05; N, 3.35. Calc. for $C_{31}H_{25}N$ (411.54): C, 90.5; H, 6.1; N, 3.4%. δ_H (299.83 MHz, C_6D_6, 298 K, TMS) 7.62-7.60 (d, 4H, J = 8.1), 7.45-7.44 (d, 1H, J = 1.5), 7.43-7.42 (d, 1H, J = 2.1), 7.20-6.94 (m, 11H), 6.73-6.72 (d, 1H, J = 1.8), 6.67-6.62 (t, 1H, J = 7.8), 6.43-6.40 (d, 1H, J = 7.5), 6.08-6.06 (d, 1H, J = 7.8), 5.99 (s, 1H) and 1.79 (s, 3H, CH_3); δ_C (75.39 MHz, C_6D_6, 298 K, TMS) 151.32,

140.36, 139.27, 138.50, 138.13, 137.21, 135.60, 135.01, 123.71 (aryl C_q, C_q fulvene), 131.34, 129.74, 128.77, 128.60, 126.27, 125.29, 125.36, 123.80, 121.72, 120.51, 117.99 (aryl *C*H, *C*H fulvene) and 20.86 (CH_3).

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-*p*-methoxy-phenyl-amine **2c**: yielded as red crystalline product (0.77 g, 37%). M.p. 199 °C. Found: C, 87.4; H, 5.9; N, 3.2. Calc. for $C_{31}H_{25}NO$ (427.54): C, 87.1; H, 5.9; N, 3.3%. δ_H (399.83 MHz, $CDCl_3$, 298 K, TMS) 7.63-7.58 (m, 6H), 7.52 (s, 1H), 7.48-7.17 (m, 9H), 7.19-7.15 (t, 1H, *J* = 7.2), 6.92 (s, 1H), 6.62-6.60 (d, 2H, *J* = 8.4), 6.47-6.44 (d, 2H, *J* = 8.4), 6.42 (s, 1H) and 3.71 (s, 3H, OCH_3); δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 156.11, 153.88, 138.90, 136.99, 136.44, 134.81, 134.09, 132.93 123.23 (aryl C_q, C_q fulvene), 131.18, 128.89, 128.68, 128.39, 128.10, 125.14, 123.23, 114.11 ($C_{o,m}$, aryl *C*H), 129.92, 126.49, 126.45, 125.69, 120.01 (C_p, aryl *C*H, *C*H fulvene) and 55.33 (O*C*H_3).

[(2,4-di-*p*-tolyl-cyclopenta-2,4-dienylidene)-*p*-tolyl-methyl]-*p*-methoxy-phenyl-amine **2d**: In a pressure tube 3.59 g (15.00 mmol) of the imine **1d** were dissolved in about 10 mL of THF. Then 0.42 g (10.50 mmol) of potassium hydride were added, immediately the color changed from orange to green and a second color-change to dark red, accompanied by hydrogen evolution, took place. The dark brown solution was heated under slight reflux for three days, then cooled to room temperature and water (about 5 mL) was added. The solution was extracted with diethyl ether (10 mL) and the organic phase was dried with Na_2SO_4. At -20 °C a red crystalline material **2d** (0.67 g, 29%) was obtained. M.p. 185 °C. Found: C, 86.5; H, 6.75; N, 2.85. Calc. for $C_{34}H_{31}NO$ (469.62): C, 87.0; H, 6.65; N, 3.0%. δ_H (399.83 MHz, $CDCl_3$, 298 K, TMS) 7.47-7.41 (m, 7H), 7.16-7.07 (m, 6H), 6.81 (s, 1H), 6.59-6.57 (d, 2H, *J* = 8.4), 6.44-6.21 (d, 2H, *J* = 8.4), 6.33 (s, 1H), 3.68 (s, 3H, OCH_3), 2.39 (s, 3H, CH_3) and 2.31 (s, 6H, 2x CH_3); δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 155.89, 153.71, 139.95, 136.21, 135.90, 135.04, 134.26, 133.86, 133.20, 131.86, 120.82 (aryl C_q, C_q fulvene), 131.12, 129.47, 129.00, 128.73, 128.46, 124.99, 123.27, 113.97 (aryl $C_{o,m}$), 126.13, 119.16 (*C*H fulvene), 55.25 (O*C*H_3) 21.44 (*C*H_3), 21.11(*C*H_3) and 21.08 (*C*H_3).

[(2,4-di-naphtalen-2-yl-cyclopenta-2,4-dienylidene)-naphtalen-2-yl-methyl]-phenyl-amine **2e**: yielded as a red solid (0.50 g, 21%). M.p. 202 °C. Found: C, 92.0; H, 5.4; N, 2.4. Calc. for $C_{42}H_{29}N$ (547.59): C, 92.1; H, 5.3; N, 2.6%. δ_H (399.83 MHz, C_6D_6, 298 K, TMS) 8.20 (s, 3H),

7.83-7.7.78 (t, 2H, *J* = 9.2), 7.68-7.43 (m, 11H), 7.27-7.16 (m, 7H), 7.01 (m, 1H), 6.57-6.49 (m, 3H) and 6.16-6.15 (d, 2H, *J* = 7.2). δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 152.61, 139.88, 137.46, 135.94, 134.87, 134.06, 134.03, 133.91, 133.89, 132.72, 132.51, 132.22, 132.15, 123.11 (aryl C_q, C_q fulvene), 128.88, 128.84, 128.30, 127.94, 127.88, 127.85, 127.78, 127.65, 127.52, 127.45, 126.71, 126.62, 126.22, 125.91, 125.53, 124.96, 124.44, 123.45, 122.86 and 121.05 (aryl C*H*, C*H* fulvene).

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-*o*-tolyl-amine **2f**: yielded as a red solid (0.85 g, 31%). M.p. 165 °C. Found: C, 90.3; H, 6.0; N, 3.6. Calc. for $C_{31}H_{25}N$ (411.54): C, 90.5; H, 6.1; N, 3.4%. δ_H (399.83 MHz, C_6D_6, 298 K, TMS) 7.58-7.54 (m, 6H), 7.44-7.42 (m, 1H), 7.39-7.36 (m, 2H), 7.32-7.28 (m, 4H), 7.24-7.22 (m, 2H), 7.18-7.12 (m, 1H), 6.99-6.97 (d, 1H, *J* = 6.4), 6.91-6.90 (d, 1H, *J* = 1.6), 6.81-6.79 (m, 2H), 6.46-6.45 (m, 1H, *J* = 1.6), 6.37-6.35 (d, 1H, *J* = 6.4) and 1.75 (s, 3H, CH_3); δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 153.48, 139.02, 138.40, 137.41, 137.08, 135.19, 134.79, 129.22, 122.52 (aryl C_q, C_q fulvene), 131.21, 130.62, 130.30, 129.16, 129.08, 128.66, 128.42, 127.00, 126.90, 126.39, 126.12, 125.46, 123.74, 122.16, 120.05 (aryl *C*H, *C*H fulvene) and 17.37 (CH_3).

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-*p*-tolyl-amine **2g**: yielded as a red solid (1.52 g, 57%). M.p. 167 °C. Found: C, 90.2; H, 6.0; N, 3.3. Calc. for $C_{31}H_{25}N$ (411.54): C, 90.5; H, 6.1; N, 3.4%; δ_H (399.83 MHz, $CDCl_3$, 298 K, TMS) 7.55-7.52 (m, 6H), 7.48-7.43 (m, 2H), 7.39-7.24 (m, 6H), 7.21-7.10 (m, 2H), 6.86 (s, 1H), 6.81-6.79 (d, 2H, *J* = 7.6), 6.36 (s, 1H), 6.29-6.27 (d, 2H, *J* = 7.6) and 2.17 (s, 3H, CH_3); δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 153.14, 138.76, 137.17, 136.86, 136.72, 134.84, 134.21, 133.14, 121.52 (aryl C_q, C_q fulvene), 131.06, 129.94, 129.38, 128.84, 128.35, 128.12, 126.63, 126.51, 125.72, 125.12, 121.12, 119.94 (aryl *C*H, *C*H fulvene) and 20.66 (CH_3).

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-2-chloro-3-methyl-amine **2h**: yielded as a red solid (1.30 g, 44%). M.p. 205 °C. Found: C, 83.5; H, 5.0; N, 3.0. Calc. for $C_{31}H_{24}ClN$ (445.98): C, 83.5; H, 5.4; N, 3.1%. δ_H (399.83 MHz, C_6D_6, 298 K, TMS) 7.63-7.61 (d, 2H, *J* = 8.0), 7.49-7.47 (d, 2H, *J* = 8.0), 7.41-7.38 (d, 2H, *J* = 7.2), 7.22-7.20 (m, 2H), 7.10-7.6.91 (m, 9H), 6.77 (s, 1H), 6.72-6.70 (d, 1H, *J* = 7.6), 6.31-6.28 (m, 2H) and 1.68 (s, 3H, CH_3); δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 152.34, 139.73, 138.57, 137.86, 136.56, 134.79, 134.78, 134.64, 127.25, 123.19 (aryl C_q, C_q fulvene), 130.93, 130.14, 128.84, 128.42, 128.25, 127.31,

126.83, 126.23, 126.06, 125.23, 124.30, 120.64, 119.72 (aryl *C*H, *C*H fulvene) and 13.65 (CH_3).

[(2,4-diphenyl-cyclopenta-2,4-dienylidene)-phenyl-methyl]-3,5-dimethyl-amine **2i**:
yielded as red solid (1.40 g, 49%). M.p. 214 °C. Found: C, 89.9; H, 6.4; N 3.5. Calc. for $C_{32}H_{27}N$ (425.56): C, 90.3; H, 6.4; N, 3.3%. δ_H (399.83 MHz, C_6D_6, 298 K, TMS) 7.68-7.63 (m, 4H), 7.49-7.48 (d, 2H, *J* = 6.8), 7.29 (s, 1H), 7.20-7.13 (m, 4H), 7.03-7.02 (m, 6H), 6.77 (s, 1H), 6.29 (s, 1H), 5.93 (s, 2H) and 1.83 (s, 6H, 2x CH_3); δ_C (100.53 MHz, $CDCl_3$, 298 K, TMS) 153.09, 139.45, 138.79, 138.36, 136.87, 136.72, 135.02, 134.21, 121.51 (aryl C_q, C_q fulvene), 130.99, 129.88, 128.87, 128.72, 128.36, 128.06, 126.69, 126.47, 125.73, 125.12, 120.01, 118.84 (aryl *C*H, *C*H fulvene) and 21.14 (2x CH_3).

1.4 Base optimization experiments

Table 1: Variation of imine - potassium hydride ratio.

No.	Ratio imine : KH	Conv.[a] [%]	Main product[b]
1	1.0 : 0.3	98.3	fulvene
2	1.0 : 0.7	99.9	fulvene
3	1.0 : 1.0	34.0	imine
4	1.0 : 3.0	70.9	amine

50 °C, 72h; [a] determined after workup *via* GC; [b] determined after workup *via* GC-MS

Table 2: Base Screening.

No.	Base (0.7 eq.)	Conv.[a] [%]
1	KH	99.9
2	KOH	22.0
3	KO*t*Bu	90.0
4	LiH	51.0
5	LiO*t*Bu	0
6	$KOSiMe_3$	0
7	$NaNH_2$	70.0
8	K_2CO_3	0

50 °C, 72h; [a] determined after workup *via* GC

1.5 Kinetic experiments

In a Schlenk tube 4.0 g (20.48 mmol) of **1a** were dissolved in 25 mL THF, then 0.58 g KH (14.34 mmol) were added carefully. Thereby the color of the orange solution changed to green and later red with hydrogen being evolved. The Schlenk tube was stirred at 50 °C and periodically samples (0.6 mL) were taken. Water (1 mL), dodecane (93.15 µL) and 2 mL of diethyl ether were added to 500 µL of the sample. The organic phase was extracted and analyzed via GC-(MS).

GC-MS analyses of kinetic-samples:

Aniline: MS (70 eV, EI); m/z (%): 93(M^+, 100), 66(54).

Imine: MS (70 eV, EI); m/z (%): 195(M^+, 40), 180(85), 118(20), 77(100).

By-Product: MS (70 eV, EI); m/z (%): 299(M^+, 7), 284(11), 206(7), 194(23), 180(34), 129(6), 105(43), 91(19), 77(100).
Hydrolysis of (1,3-diphenyl-butylidene)-phenyl-amine to aniline and 1,3-diphenyl-butan-1-one [224(M^+, 10)] was observed after some days.

Intermediate: MS (70 eV, EI); m/z (%): 297(M^+, 6), 284(4), 194(6), 180(4), 207(7), 184(7), 194(6), 180(4), 117(19), 91(100), 77(28), 65(10), 51(39).

Fulvene: MS (70 eV, EI); m/z (%): 397(M^+, 47), 319(7), 294(9), 215(14), 180(29), 153(11), 77(10).

Isolation of (1,3-diphenyl-butylidene)-phenyl-amine ("by-product") 4a:

In a pressure tube 4.0 g (20.48 mmol) of **1a** were dissolved in 10 mL THF, then 0.58 g KH (14.34 mmol) were added carefully. Thereby the color of the orange solution changed to green and later red with hydrogen being evolved. The Schlenk tube was stirred at 50 °C for 3 days. Then water (10 mL) was added. The organic phase was extracted, dried with Na_2SO_4 and reduced to dryness *in vacuo*. Pentane was added to the residue and red fulvene precipitated. The remaining solution was filtered, reduced to dryness *in vacuo*, and distilled in high vacuum yielding (1,3-diphenyl-butylidene)-phenyl-amine as an orange viscous liquid (0.67 g, 22%). Found: C, 88.0; H, 7.2; N 4.7. Calc. for $C_{22}H_{21}N$ (299.41): C, 88.25; H, 7.1; N, 4.7%. δ_H (250.13 MHz, C_6D_6, 298 K, TMS) 8.03-7.99 (m, 2H, C_6H_5), 7.32-7.10 (m, 9H, C_6H_5), 6.89-6.85 (m, 2H, C_6H_5), 6.67-6.64 (m, 2H), 3.13-3.02 (m, 1H, C*H*), 2.95-2.92 (m, 2H, CH_2) and 1.10-1.07 (d, 3H, CH_3, J = 7.0); δ_C (62.90 MHz, $CDCl_3$, 298 K, TMS) 166.80 (C=N), 151.25, 145.12,

138.69 (C_q, C_6H_5), 129.57, 128.35, 127.97, 127.88, 127.50, 126.46, 125.92, 122.33, 118.87 ($C_{o,m,p}$, C_6H_5), 38.14 (CH_2), 37.68 (CH) and 20.61 (CH_3).

Synthesis of (1,3-diphenyl-but-3-enylidene)-phenyl-amine ("intermediate product") 3a:

To a solution of 4.00 g (18.00 mmol) of dypnone and 1.97 mL (21.60 mmol) aniline in 15 mL of benzene, 10.0 g molecular sieves (5 Å) and catalytic amounts of *p*-toluene sulfonic acid were added. The solution was refluxed for 5 days. The solution was filtered off the molecular sieves, and washed with diethyl ether. The organic phase was evaporated to dryness via rotary evaporation. Then the aniline and dypnone were removed by vacuum distillation. The remaining orange-brown solid was recrystallized from ether/hexane yielding 1.20 g (22%) of (1,3-diphenyl-but-3-enylidene)-phenyl-amine as orange needles.

Found: C, 88.45; H, 6.4; N 4.3. Calc. for $C_{22}H_{19}N$ (297.39): C, 88.85; H, 6.4; N, 4.7%. δ_H (250.13 MHz, C_6D_6, 298 K, TMS) 8.26-8.22 (m, 2H, C_6H_5), 7.33-7.12 (m, 11H, C_6H_5), 7.03-6.97 (m, 2H), 6.43 (s, 1H, CH) and 1.76 (s, 3H, CH_3); δ_C (62.90 MHz, $CDCl_3$, 298 K, TMS) 165.32 (C=N), 151.55, 141.04, 141.01, 138.88 (C_q, C_6H_5, C-CH_3), 130.08, 128.09, 127.97, 127.92, 127.86, 127.40, 125.41, 123.35, 122.65, 120.40 ($C_{o,m,p}$, C_6H_5, CH) and 18.26 (CH_3).

1.6 X-Ray Crystallographic Data

1.6.1 Molecular Structure of 2a

X-ray crystal structure analysis of **2a**, STOE-IDPS II equipped with an Oxford Cryostream low temperature unit, graphite monochromatized $Mo_{K\alpha}$-radiation, λ=0.71069 Å, structure solution and refinements were accomplished with SHELXL-97 (G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Analysis* Release 97-2, Institut für Anorganische Chemie der Universität, Göttingen, Germany, **1998**), WinGX (L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837-838) und SIR97 (A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115-119), crystal size 0.56 x 0.41 x 0.35 mm, red prisms, symmetry space group $P2_1/n$, monoclinic, a = 11.4870(8), b = 10.7950(8), c = 17.4210(13) Å, $ß$= 101.575(5)°, V = 2116.3(2) $Å^3$, Z = 4, $\rho_{ber.}$ = 1.248 g/cm^3, 3993 measured reflections, 2986 independent reflections, R = 0.0330 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0746, 373 parameters. CCDC-782978 contains the supplementary crystallographic data for this publication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre,

12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

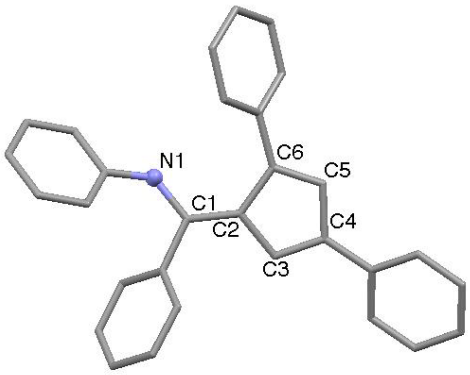

Figure 1: Molecular structure of **2a**; selected bond lengths [Å] and angles [°] for **2a**: C1-N1, 1.3662(15); C1-C2, 1.3751 (16); C2-C3, 1.4483(17); C3-C4, 1.3563(17); C4-C5, 1.4496(17); C5-C6, 1.3587(17); C6-C2, 1.4676(17); N1-C1-C2, 122.19(11); N1-C1-C25, 116.17(10); C1-N1-C19, 128.98(11).

1.6.2 Molecular Structure of 2c

X-ray crystal structure analysis of **2c**, crystal size 0.39 x 0.26 x 0.13 mm, red prisms, symmetry space group $P2_1/n$, monoclinic, a = 10.0630(8), b = 15.9800(13), c = 13.9950(12) Å, $ß$=93.129(7)°, V = 2247.1(3) Å^3, Z = 4, $\rho_{ber.}$ = 1.264 g/cm^3, 4256 measured reflections, 2494 independent reflections, R = 0.0534 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0880, 303 parameters. CCDC-782980 contains the supplementary crystallographic data for this publication.

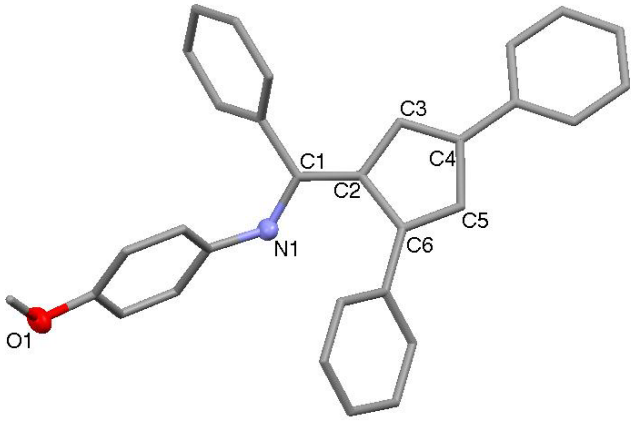

Figure 2: Molecular structure of **2c**; selected bond lengths [Å] and angles [°] for **2c**: C1-N1, 1.362(3); C1-C2 1.378(3); C2-C3, 1.444(3); C3-C4, 1.360(3); C4-C5, 1.451(3); C5-C6, 1.362(3); C6-C2, 1.461(3); N1-C1-C2, 121.5(2); N1-C1-C26, 116.89(19); C1-N1-C19, 127.1(2).

1.6.2 Molecular Structure of 5a

X-ray crystal structure analysis of **5a**, crystal size 0.48 x 0.08 x 0.08 mm, yellow needles, symmetry space group P-1, triclinic, a = 9.2950(11), b = 11.2290(15), c = 13.2300(16) Å, *ß*= 90.466(10)°, V = 1349.2(3) Å^3 , Z = 2, $\rho_{ber.}$ = 1.250 g/cm^3, 5098 measured reflections, 1784 independent reflections, R = 0.0561 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0989, 334 parameters. CCDC-782979 contains the supplementary crystallographic data for this publication.

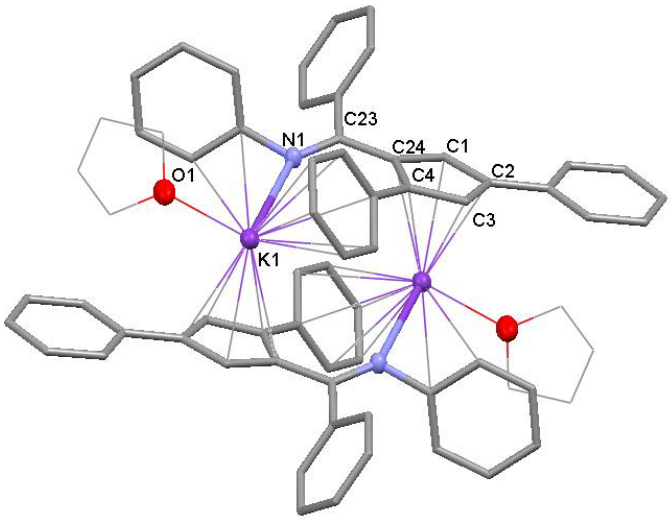

Figure 3: Molecular structure of **6a**; selected bond lengths [Å] and angles [°]: C1-C2, 1.404(5); C1-C24, 1.416(6); C2-C3, 1.409(6); C3-C4, 1.386(6); C4-C24, 1.425(6); C17-K1, 3.208(4); C22-K1, 3.229; C23-N1, 1.304(5); C23-C24, 1.458(6); N1-K1, 2.814(4); N1-C22-K1, 60.4(2); N1-C23-C24, 120.1(4); N1-C23-C25, 122.5(4); C23-N1-C22, 121.4(4).