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C-C Bond Formation via C-H Bond Activation: Catalytic Arylation and Alkenylation of Alkane Segments

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Supporting Information

I. Results for arylation reaction under various stoichiometric and catalytic conditions

Table 1. Screening of various solvents and phenyl donors for stoichiometric arylation of substrate **8**.

Phenyl donor	DMF	AcOH	MeOH	DMA	NMP	THF
PhSi(OH)Me ₂	48 %	15 %	12 %	< 1	NR	NR
PhSi(OH) ₂ Me	42 %	21 %	13 %	8 %	NR	NR
PhSi(OH) ₃	-	< 1	-	-	NR	NR
Ph ₂ Si(OH)Me	52 %	18 %	9 %	11 %	NR	NR
PhSi(OMe) ₃	56 %	16 %	6 %	< 1	NR	NR
PhSiF ₃	< 1	< 1	-	-	NR	NR
Bu ₃ SnPh	-	-	-	-	NR	NR
PhB(OH) ₂	-	-	-	-	NR	NR

* Yields were determined from the integration of methylene peaks (at 3.44 ppm) in the crude NMR spectra taken in the presence of trichloroethylene as the internal standard.

Table 2. Screening of various oxidants for catalytic arylation of substrate **8**.

Oxidant	with PhSi(OH)Me ₂	with Ph ₂ Si(OH)Me
Cu(OAc)₂	44	56
CuCl₂	<1	-
CuCl₂ + NaOAc	48	55
K₂S₂O₈ + NaOAc	<1	<1
MnO₂ + NaOAc	<1	9
BQ + NaOAc	18	7
TCBQ + NaOAc	7	5
EtONO + NaOAc	-	-

* Yields were determined from the integration of methylene peaks (at 3.44 ppm) in the crude NMR spectra taken in the presence of trichloroethylene as the internal standard.

Table 3. Catalytic arylation of substrate **1**.

Silanol	Pd(OAc) ₂	Yield (%)	TON	Ph-Ph	PhOAc
PhSi(OH)Me₂	5 %	18	3	6	6
	2.5 %	22	9	4	6
	1 %	8	8	8	7
Ph₂Si(OH)Me	5 %	43	9	< 1	< 1
	2.5 %	37	15	< 1	< 1
	1 %	16	16	< 1	< 1

Table 4. Catalytic arylation of substrate **8**.

Silanol	Pd(OAc) ₂	Yield (%)	TON	Ph-Ph	PhOAc
PhSi(OH)Me₂	5 %	45 (51 with BQ)	9 (10)	5 (11)	4 (6)
	4 %	46 (55 with BQ)	12 (14)	5 (11)	2 (5)
	2.5 %	38 (46 with BQ)	15 (18)	4 (8)	3 (5)
	1 %	19	19	6	8
Ph₂Si(OH)Me	5 %	69 (76 with BQ)	14 (15)	< 1	< 1
	4 %	68 (78 with BQ)	17 (19)	< 1	< 1
	2.5 %	62 (67 with BQ)	25 (27)	< 1	< 1
	1 %	28	28	< 1	< 1

Table 5. Stoichiometric arylation reactions tested on substrate **15**.

Silanol	Solvent	Yield (%)
PhSi(OH)Me₂	DMF	27
	AcOH	32
Ph₂Si(OH)Me	DMF	35
	AcOH	44
none	DMF	31
	AcOH	42

Table 6. Catalytic arylation reactions tested on substrate **15**.

Silanol	$\text{Pd}(\text{OAc})_2$	Ph-Ph	PhOAc
PhSi(OH)Me₂	5 %	41	18
	4 %	38	15
Ph₂Si(OH)Me	5 %	31	< 1
	4 %	22	< 1

II. Experimental procedures and characterization data

The procedures below are representative for the preparation of Schiff base substrates and catalytic arylation and alkenylation reactions.

Synthesis of (2-*tert*-butylphenyl)-(2-thiomethyl-benzylidene)-amine **5**

2-*tert*-Butyl-aniline (2.24 g, 15 mmol) was combined with 2-thiomethylbenzaldehyde (2.28 g, 15 mmol) in 80 ml of toluene. The reaction mixture was heated to reflux and the water was azeotropically removed. Upon completion the reaction was cooled to room temperature and concentrated to an oil. The reaction was quantitative and Schiff base **5** could be chromatographed (5 % NEt₃ / 20 % ethyl acetate / 75 % hexanes) to give 4.17 grams (98 % yield).

¹H NMR data (400MHz, CDCl₃)

C(CH ₃) ₃	1.46, 9H, s
SCH ₃	2.50, 3H, s
H-1	6.86, 1H, dd, J ₁ = 1.5, J ₂ = 7.6 Hz
H-2, H-3, H-7	7.15-7.36, 3H, m
H-4, H-5, H-6	7.36-7.46, 3H, m
H-8	8.11, 1H, dd, J ₁ = 1.3, J ₂ = 7.8 Hz
N=CH	8.82, 1H, s

¹³C NMR data (100MHz, CDCl₃)

SCH ₃	16.9
C(CH ₃) ₃	30.5
C(CH ₃) ₃	35.6
N=CH	156.0
aromatic C's	119.7 (C-H)
	125.6 (C-H)
	125.6 (C-H)
	125.9 (C-H)
	127.1 (C-H)
	127.4 (C-H)
	128.7 (C-H)
	131.1 (C-H)
	134.5 (quat. C)
	140.2 (quat. C)
	143.0 (quat. C)
	151.7 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 3059.4, 2955.0, 1617.7, 1586.0, 1482.4, 1436.9 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₈H₂₂NS m/z 284.1473, observed m/z 284.1454.

Catalytic arylation of (2-*tert*-butylphenyl)-(2-thiomethyl-benzylidene)-amine **5 with phenyldimethyl silanol**

In a flame dried 25-ml round bottom flask, Pd(OAc)₂ (2.7 mg, 0.012 mmol, 4 %) and Cu(OAc)₂ (109 mg, 0.6 mmol, 2 eq) were dissolved in 5 ml dry DMF and purged with argon. Phenyldimethyl silanol¹ (91 mg, 0.6 mmol, 2 eq) was dissolved in 5 ml dry DMF and added dropwise to this solution. Schiff base **5** (85 mg, 0.3 mmol) and benzoquinone (1.3 mg, 0.012 mmol, 4 %) which were dissolved in 5 ml dry DMF were added next and the reaction mixture was heated to 100 °C. The reaction propagation was monitored by TLC and upon completion (after about 10 hours), the crude mixture was treated with Na₂S and filtered through a pad of Celite. DMF was evaporated and the residue was purified by flash column chromatography (5 % NEt₃ / 15 % ethyl acetate / 80 % hexanes) to give 56 mg of product **6** (52 % yield) along with 33 mg of recovered starting Schiff base **5** (39 %).

Catalytic arylation of (2-*tert*-butylphenyl)-(2-thiomethyl-benzylidene)-amine **5 with diphenylmethyl silanol**

In a flame dried 25-ml round bottom flask, Pd(OAc)₂ (2.7 mg, 0.012 mmol, 4 %) and Cu(OAc)₂ (109 mg, 0.6 mmol, 2 eq) were dissolved in 5 ml dry DMF and purged with argon. Diphenylmethyl silanol¹ (129 mg, 0.6 mmol, 2 eq) was dissolved in 5 ml dry DMF and added dropwise to this solution. Schiff base **5** (85 mg, 0.3 mmol) and benzoquinone (1.3 mg, 0.012 mmol, 4 %) which were dissolved in 5 ml dry DMF were added next and

the reaction mixture was heated to 100 °C. The reaction propagation was monitored by TLC and upon completion (after about 10 hours), the crude mixture was treated with Na₂S and filtered through a pad of Celite. DMF was evaporated and the residue was purified by flash column chromatography (5 % NEt₃ / 15 % ethyl acetate / 80 % hexanes) to give 79 mg of product **6** (73 % yield) along with 14 mg of recovered starting Schiff base **5** (16 %).

¹H NMR data (400MHz, CDCl₃)

C(CH ₃) ₂	1.40, 6H, s
SCH ₃	2.53, 3H, s
CH ₂	3.35, 2H, s
H-1 and two of phenyl H's	6.87-6.94, 3H, m
H-2, H-7 and three of phenyl H's	7.08-7.12, 5H, m
H-3, H-4	7.24-7.34, 2H, m
H-5, H-6	7.38-7.45, 2H, m
H-8	8.17, 1H, dd, J ₁ = 1.3, J ₂ = 7.8 Hz
N=CH	8.91, 1H, s

¹³C NMR data (100MHz, CDCl₃)

SCH ₃	17.5
C(CH ₃) ₂	29.2
CH ₂	40.2
CH ₂	46.1
N=CH	156.4
aromatic C's	120.1 (C-H)
	125.8 (C-H)
	125.8 (C-H)
	126.1 (C-H)
	126.1 (C-H)
	126.1 (C-H)
	127.5 (C-H)
	127.9 (C-H)
	128.1 (2 C-H's)
	129.1 (C-H)
	130.9 (2 C-H's)
	132.8 (C-H)
	134.4 (quat. C)
	138.9 (quat. C)
	140.6 (quat. C)
	142.3 (quat. C)
	151.9 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 3060.2, 3032.6, 2956.4, 1618.2, 1581.2, 1433.7 cm⁻¹.

HRMS (FAB⁺) calculated for C₂₄H₂₆NS m/z 360.1786, observed m/z 360.1800.

Catalytic alkenylation of (2-*tert*-butylphenyl)-(2-thiomethyl-benzylidene)-amine 5 with styrenyl dimethyl silanol

In a flame dried 25-ml round bottom flask, Pd(OAc)₂ (2.7 mg, 0.012 mmol, 4 %) and Cu(OAc)₂ (109 mg, 0.6 mmol, 2 eq) were dissolved in 5 ml dry DMF and purged with argon. Styrenyldimethyl silanol² (107 mg, 0.6 mmol, 2 eq) was dissolved in 5 ml dry DMF and added dropwise to this solution. Schiff base **5** (85 mg, 0.3 mmol) and benzoquinone (1.3 mg, 0.012 mmol, 4 %) which were dissolved in 5 ml dry DMF were added next and the reaction mixture was heated to 100 °C. The reaction propagation was monitored by TLC and upon completion (after about 10 hours), the crude mixture was treated with Na₂S and filtered through a pad of Celite. DMF was evaporated and the residue was purified by flash column chromatography (5 % NEt₃ / 10 % ethyl acetate / 85 % hexanes) to give 74 mg of product **7** (64 % yield) along with 19 mg of recovered starting Schiff base **5** (22 %).

¹ H NMR data (400MHz, CDCl ₃)		¹³ C NMR data (100MHz, CDCl ₃)	
C(CH ₃) ₂	1.38, 6H, s	SCH ₃	17.3
SCH ₃	2.52, 3H, s	C(CH ₃) ₂	29.4
CH ₂	2.71, 2H, d, J=7.5 Hz	C(CH ₃) ₂	38.7
CH ₂ CH=CH	5.94, 1H, dt, J ₁ = 7.5, J ₂ = 16.2 Hz	CH ₂	43.0
CH=CHPh	6.36, 1H, d, J= 16.2 Hz	CH ₂ CH=CH	128.3
H-1	6.88, 1H, dd, J ₁ = 1.6, J ₂ = 7.5 Hz	CH=CHPh	128.8
two of phenyl H's	7.02-7.07, 2H, m	N=CH	156.3
H-2, H-7 and three of phenyl H's	7.16-7.32, 5H, m	aromatic C's	120.0 (C-H)
H-3, H-4	7.39-7.45, 2H, m		125.7 (C-H)
H-5, H-6	7.49-7.55, 2H, m		125.8 (C-H)
H-8	8.15, 1H, d, J=8.7 Hz		126.0 (C-H)
N=CH	8.78, 1H, s		126.7 (2 C-H's)
			127.5 (C-H)
			127.7 (C-H)
			128.4 (C-H)
			129.0 (C-H)
			130.5 (2 C-H's)
			132.5 (C-H)
			134.4 (quat. C)
			135.0 (quat. C)
			140.4 (quat. C)
			142.5 (quat. C)
			151.8 (quat. C)

IR (NaCl plate) ν_{max} 3059.7, 3039.5, 2956.8, 2842.1, 1621.4, 1594.2, 1583.3, 1476.1 cm^{-1} .

HRMS (FAB⁺) calculated for $\text{C}_{26}\text{H}_{28}\text{NS}$ m/z 386.1942, observed m/z 386.1925.

¹H NMR data (400MHz, CDCl₃)

$\text{C}(\text{CH}_3)_3$	1.49, 9H, s
OCH_3	3.86, 6H, s
H-1	6.83, 1H, dd, $J_1 = 1.3$, $J_2 = 7.6$ Hz
H-2	7.11, 1H, ddd, $J_1 = 1.4$, $J_2 = 7.6$, $J_3 = 7.6$ Hz
H-3	7.21, 1H, ddd, $J_1 = 1.3$, $J_2 = 7.4$, $J_3 = 7.4$ Hz
H-4	7.36, 1H, dd, $J_1 = 1.2$, $J_2 = 7.8$ Hz
H-5	6.58, 2H, d, $J = 8.4$ Hz
H-6	7.30, 1H, t, $J = 8.4$ Hz
$\text{N}=\text{CH}$	8.75, 1H, s

¹³C NMR data (100MHz, CDCl₃)

$\text{C}(\text{CH}_3)_3$	29.9
$\text{C}(\text{CH}_3)_3$	35.5
OCH_3	55.9
$\text{N}=\text{CH}$	154.6
aromatic C's	103.9 (2 C-H's)
	113.9 (quat. C)
	119.9 (C-H)
	124.8 (C-H)
	125.6 (C-H)
	126.9 (C-H)
	131.9 (C-H)
	142.6 (quat. C)
	153.7 (quat. C)
	160.3 (2 quat. C's)

IR (NaCl plate) ν_{max} 3056.0, 2956.3, 1619.7, 1593.9, 1474.1, 1433.9, 1255.7, 1112.9 cm^{-1} .

HRMS (FAB⁺) calculated for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}$ m/z 298.1807, observed m/z 298.1829.

¹ H NMR data (400MHz, CDCl ₃)		¹³ C NMR data (100MHz, CDCl ₃)	
C(CH ₃) ₂	1.43, 6H, s	C(CH ₃) ₂	28.8
CH ₂	3.38, 2H, s	C(CH ₃) ₂	40.2
OCH ₃	3.90, 6H, s	CH ₂	45.9
H-1 and two of phenyl H's	6.84-6.93, 3H, m	OCH ₃	56.2
H-2 and three of phenyl H's	7.04-7.13, 4H, m	N=CH	154.9
H-3	7.24, 1H, ddd, J ₁ = 1.3, J ₂ = 7.6, J ₃ = 7.6 Hz	aromatic C's	104.4 (2 C-H's)
H-4	7.47, 1H, dd, J ₁ = 1.4, J ₂ = 7.6 Hz		113.7 (quat. C)
H-5	6.66, 2H, d, J= 8.4 Hz		120.1 (C-H)
H-6	7.36, 1H, t, J= 8.4 Hz		125.2(C-H)
N=CH	8.88, 1H, s		125.7 (C-H)
			126.3 (C-H)
			127.4 (C-H)
			128.1 (2 C-H's)
			130.8 (2 C-H's)
			133.4 (C-H)
			139.0 (quat. C)
			141.0 (quat. C)
			153.9 (quat. C)
			160.9 (2 quat. C's)

IR (NaCl plate) ν_{max} 3042.6, 2955.1, 1622.4, 1588.6, 1472.3 cm⁻¹.

HRMS (FAB⁺) calculated for C₂₅H₂₈O₂N m/z 374.2120, observed m/z 374.2122.

¹H NMR data (400MHz, CDCl₃)

C(CH ₃) ₃	1.46, 9H, s
H-1	7.89, 1H, ddd, J ₁ = 1.0, J ₂ = 1.0, J ₃ = 7.9 Hz
H-2	7.79, 1H, ddd, J ₁ = 1.8, J ₂ = 7.7, J ₃ = 7.7 Hz
H-3	7.38, 1H, ddd, J ₁ = 1.3, J ₂ = 4.8, J ₃ = 7.5 Hz
H-4	8.62, 1H, ddd, J ₁ = 0.8, J ₂ = 1.7, J ₃ = 4.7 Hz

¹³C NMR data (100MHz, CDCl₃)

C(CH ₃) ₃	27.5
C(CH ₃) ₃	44.2
C=O	207.0
aromatic C's	123.6 (C-H)
	125.8 (C-H)
	136.6 (C-H)
	147.8 (C-H)
	154.8 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 2968.6, 2932.3, 2869.6, 1686.3, 1481.8, 1296.3, 1202.9 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₀H₁₄ON m/z 164.1075, observed m/z 164.1053.

¹H NMR data (400MHz, CDCl₃)

C(CH ₃) ₂	1.40, 6H, s
CH ₂	3.44, 2H, s
H-1	7.88, 1H, ddd, J ₁ = 1.0, J ₂ = 1.0, J ₃ = 7.9 Hz
H-2	7.81, 1H, ddd, J ₁ = 1.8, J ₂ = 7.5, J ₃ = 7.5 Hz
H-3	7.42, 1H, ddd, J ₁ = 1.4, J ₂ = 4.7, J ₃ = 7.5 Hz
H-4	8.69, 1H, ddd, J ₁ = 0.9, J ₂ = 1.7, J ₃ = 4.7 Hz
phenyl H's	6.99-7.01, 2H, m
	7.15-7.20, 3H, m

¹³C NMR data (100MHz, CDCl₃)

C(CH ₃) ₂	25.8
CH ₂	46.0
C(CH ₃) ₂	49.2
C=O	206.2
aromatic C's	124.2 (C-H)
	126.3 (C-H)
	126.5 (C-H)
	128.2 (2 C-H's)
	130.7 (2 C-H's)
	137.2 (C-H)
	139.0 (quat. C)
	148.2 (C-H)
	155.5 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 30056.8, 3026.3, 2965.1, 2923.8, 1683.0, 1453.3, 1218.0 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₆H₁₈ON m/z 240.1388, observed m/z 240.1379.

¹ H NMR data (400MHz, CDCl ₃)		¹³ C NMR data (100MHz, CDCl ₃)	
C(CH ₃) ₂	1.38, 6H, s	C(CH ₃) ₂	26.3
CH ₂	2.79, 2H, d, J= 7.4 Hz	CH ₂	43.2
H-1	7.88, 1H, ddd, J ₁ = 1.0, J ₂ = 1.0, J ₃ = 7.9 Hz	C(CH ₃) ₂	47.7
H-2	7.80, 1H, ddd, J ₁ = 1.8, J ₂ = 7.6, J ₃ = 7.6 Hz	C=O	206.8
H-3	7.41, 1H, ddd, J ₁ = 1.4, J ₂ = 4.7, J ₃ = 7.6 Hz	CH ₂ CH=CH	128.1
H-4	8.66, 1H, ddd, J ₁ = 0.9, J ₂ = 1.7, J ₃ = 4.7 Hz	CH=CHPh	128.5
CH ₂ CH=CH	5.92, 1H, dt, J ₁ = 7.4, J ₂ = 16.2 Hz	aromatic C's	124.2 (C-H)
CH=CHPh	6.34, 1H, d, J=16.2 Hz		126.4 (C-H)
phenyl H's	7.05-7.09, 2H, m		126.4 (2 C-H's)
	7.17-7.24, 3H, m		128.1 (C-H)
			130.5 (2 C-H's)
			135.1 (quat. C)
			137.1 (C-H)
			148.1 (C-H)
			155.3 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 3027.7, 2964.2, 1683.5, 1459.6, 1294.1, 1205.7 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₈H₂₀ON m/z 266.1545, observed m/z 266.1548.

¹H NMR data (400MHz, CDCl₃)

CH(CH ₃) ₂	1.24, 6H, d, J= 6.9 Hz
SCH ₃	2.50, 3H, s
CH(CH ₃) ₂	3.57, 1H, sep, J= 6.9 Hz
H-1	6.91-6.96, 1H, m
H-2, H-3, H-4, H-5, H-6, H-7	7.13-7.45, 6H, m
H-8	8.06, 1H, dd, J ₁ = 1.4, J ₂ = 7.7 Hz
N=CH	8.84, 1H, s

¹³C NMR data (100MHz, CDCl₃)

SCH ₃	16.8
CH(CH ₃) ₂	23.2
CH(CH ₃) ₂	28.1
N=CH	157.5
aromatic C's	118.0 (C-H)
	125.3 (C-H)
	125.4 (C-H)
	126.1 (C-H)
	126.5 (C-H)
	127.1 (C-H)
	129.2 (C-H)
	131.1 (C-H)
	134.3 (quat. C)
	140.3 (quat. C)
	142.3 (quat. C)
	150.1 (quat. C)

IR (NaCl plate) ν_{max} 3061.3, 2959.9, 1619.9, 1587.1, 1484.4, 1436.5 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₇H₂₀NS m/z 270.1316, observed m/z 270.1316.

¹H NMR data (400MHz, CDCl₃)

C(CH ₃) ₂	1.32, 6H, s
CO ₂ CH ₃	2.00, 3H, s
SCH ₃	2.67, 3H, s
H-1	6.93-6.98, 1H, m
H-2, H-3, H-4, H-5, H-6, H-7, H-8	7.08-7.58, 7H, m
N=CH	8.18, 1H, s

¹³C NMR data (100MHz, CDCl₃)

C(CH ₃) ₂	18.6
SCH ₃	19.5
CO ₂ CH ₃	24.2
C(CH ₃) ₂	55.1
N=CH	165.8
OC(=O)CH ₃	177.0
aromatic C's	119.7 (C-H)
	125.4 (C-H)
	126.3 (C-H)
	126.9 (C-H)
	127.9 (C-H)
	131.0 (C-H)
	133.0 (quat. C)
	133.8 (quat. C)
	134.1 (C-H)
	135.6 (C-H)
	143.8 (quat. C)
	149.6 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 2956.8, 1685.6, 1603.1, 1524.5, 1251.8 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₉H₂₁O₂NS¹⁰⁴Pd m/z 431.0334, observed m/z 431.0327.

2-*tert*-Butyl-5-methoxy-phenylamine **17** was prepared via the following route. For further information on the experimental details see ref. 7.

¹H NMR data (400MHz, CDCl₃)

C(CH ₃) ₃	1.39, 9H, s
OCH ₃	3.75, 3H, s
NH ₂	3.84, 2H, br s
H-1	6.22, 1H, d, J= 2.7 Hz
H-2	6.30, 1H, dd, J ₁ = 8.7, J ₂ = 2.7 Hz
H-3	7.13, 1H, d, J= 8.7 Hz

¹³C NMR data (100MHz, CDCl₃)

C(CH ₃) ₂	30.0
C(CH ₃) ₃	33.8
OCH ₃	55.2
aromatic C's	103.4 (C-H)
	103.5 (C-H)
	126.7 (quat. C)
	127.6 (C-H)
	145.9 (quat. C)
	158.7 (quat. C)

IR (NaCl plate) ν_{max} 3495.0, 3385.2, 2956.8, 1613.3, 1508.6, 1212.0, 1169.6 cm⁻¹.

HRMS (FAB⁺) calculated for C₁₁H₁₈ON m/z 180.1388, observed m/z 180.1386.

Synthesis of (2-*tert*-butyl-5-methoxy-phenyl)-(2-thiomethyl-benzylidene)-amine **11**

2-*tert*-Butyl-5-methoxy-phenylamine **17** (2.69 g, 15 mmol) was combined with 2-thiomethylbenzaldehyde (2.28 g, 15 mmol) in 80 ml of toluene. The reaction mixture was heated to reflux and the water was azeotropically removed. Upon completion the reaction was cooled to room temperature and concentrated to an oil. The reaction was quantitative and Schiff base **11** could be chromatographed (5 % NEt_3 / 20 % ethyl acetate / 75 % hexanes) to give 4.61 grams (98 % yield).

^1H NMR data (400MHz, CDCl_3)		^{13}C NMR data (100MHz, CDCl_3)	
$\text{C}(\text{CH}_3)_3$	1.43, 9H, s	SCH_3	17.0
SCH_3	2.50, 3H, s	$\text{C}(\text{CH}_3)_3$	30.8
OCH_3	3.82, 3H, s	$\text{C}(\text{CH}_3)_3$	35.1
H-1	6.44, 1H, d, $J = 2.8$ Hz	OCH_3	55.4
H-2	6.71, 1H, dd, $J_1 = 2.8$, $J_2 = 8.7$ Hz	$\text{N}=\text{CH}$	156.5
H-3, H-6	7.27-7.31, 2H, m	aromatic C's	106.1 (C-H)
H-4, H-5	7.35-7.44, 2H, m		109.8 (C-H)
H-7	8.10, 1H, dd, $J_1 = 1.4$, $J_2 = 7.8$ Hz		125.8 (C-H)
$\text{N}=\text{CH}$	8.82, 1H, s		126.9 (C-H)
			127.5 (C-H)
			128.9 (C-H)
			131.4 (C-H)
			134.6 (quat. C)
			135.6 (quat. C)
			140.5 (quat. C)
			152.8 (quat. C)
			158.5 (quat. C)

IR (NaCl plate) ν_{max} 2955.9, 1621.4, 1591.2, 1480.4, 1432.5, 1259.7 cm^{-1} .

HRMS (FAB⁺) calculated for $\text{C}_{19}\text{H}_{24}\text{ONS}$ m/z 314.1579, observed m/z 314.1563.

Catalytic alkenylation of (2-*tert*-butyl-5-methoxy-phenyl)-(2-thiomethyl-benzylidene)-amine **11 with styrenyldimethyl silanol**

In a flame dried 250-ml round bottom flask, $\text{Pd}(\text{OAc})_2$ (27 mg, 0.12 mmol, 4 %) and $\text{Cu}(\text{OAc})_2$ (1.09 g, 6 mmol, 2 eq) were dissolved in 50 ml dry DMF and purged with argon. Styrenyl dimethyl silanol³ (1.07 g, 6 mmol, 2 eq) was dissolved in 50 ml dry DMF and added dropwise to this solution. Schiff base **11** (940 mg, 3 mmol) and benzoquinone (13 mg, 0.12 mmol, 4 %) which were dissolved in 50 ml dry DMF were added next and the reaction mixture was heated to 100 °C. The reaction propagation was monitored by TLC and upon completion (after about 15 hours), the crude mixture was treated with Na_2S and filtered through a pad of Celite. DMF was evaporated and the residue was purified by flash column chromatography (5 % NEt_3 / 15 % ethyl acetate / 80 % hexanes) to give 561 mg of product **12** (45 % yield) along with 395 mg of recovered starting Schiff base **11** (42 %). 82 mg of alkene **12** (66 % yield) could be obtained when the reaction was carried out by using 94 mg (0.3 mmol) of Schiff base **11**.

¹ H NMR data (400MHz, CDCl ₃)		¹³ C NMR data (100MHz, CDCl ₃)	
C(CH ₃) ₂	1.36, 6H, s	SCH ₃	17.3
SCH ₃	2.51, 3H, s	C(CH ₃) ₂	29.6
CH ₂	2.70, 2H, d, J=7.5 Hz	C(CH ₃) ₂	38.4
OCH ₃	3.84, 3H, s	CH ₂	42.8
CH ₂ CH=CH	5.93, 1H, dt, J ₁ = 7.5, J ₂ = 16.3 Hz	OCH ₃	55.5
CH=CHPh	6.36, 1H, d, J= 16.3 Hz	CH ₂ CH=CH	127.8
H-1	6.45, 1H, d, J= 2.7 Hz	CH=CHPh	128.4
H-2	6.73, 1H, dd, J ₁ = 2.7, J ₂ = 8.7 Hz	N=CH	156.9
two of phenyl H's		aromatic C's	106.2 (C-H)
	7.03-7.07, 2H, m		109.9 (C-H)
H-3 and three of phenyl H's			125.8 (C-H)
	7.18-7.31, 4H, m		126.9 (2 C-H's)
H-6	7.39-7.44, 1H, m		127.0 (C-H)
H-4, H-5	7.50-7.55, 2H, m		127.6 (C-H)
H-7	8.10, 1H, dd, J ₁ = 1.5, J ₂ = 7.8 Hz		128.6 (C-H)
N=CH	8.78, 1H, s		129.0 (C-H)
			130.9 (2 C-H's)
			131.6 (C-H)
			134.7 (quat. C)
			135.2 (quat. C)
			135.6 (quat. C)
			140.7 (quat. C)
			153.1 (quat. C)
			158.5 (quat. C)

IR (NaCl plate) $\nu_{\max}$ 2952.8, 2837.6, 1621.3, 1595.2, 1583.1, 1474.3, 1257.0 cm⁻¹.

HRMS (FAB⁺) calculated for C₂₇H₃₀ONS m/z 416.2048, observed m/z 416.2053.

Synthesis of (2-thiomethyl-benzylidene)-(3-ethoxy-8,8-dimethyl-5-phenyl-5,6,7,8-tetrahydro-napthalen-1-yl)-amine 13

Alkene **12** (500 mg, 1.2 mmol) was dissolved in dry 100 ml of CH₂Cl₂ and cooled to -78 °C. A 25 ml CH₂Cl₂ solution containing methanesulfonic acid (5.77 g, 3.89 ml, 60 mmol, 50 eq.) was added dropwise. The solution was allowed to come to 0 °C and react. Monitored the reaction by ¹H-NMR. Upon completion the reaction mixture was diluted with CH₂Cl₂ and quenched with NEt₃. The organic solution was washed with water, dried over MgSO₄, filtered and evaporated. Product **13** was isolated by flash column chromatography (5 % NEt₃ / 15 % ethyl acetate / 80 % hexanes) in 52 % yield (259 mg).

¹ H NMR data (400MHz, CDCl ₃)		¹³ C NMR data (100MHz, CDCl ₃)	
C(CH ₃) ₂	1.35, 3H, s 1.43, 3H, s	SCH ₃	17.4
H-8	1.52-1.57, 1H, m 1.68-1.72, 1H, m	CH ₂	24.9
H-9	1.64-1.68, 1H, m 1.91-1.97, 1H, m	C(CH ₃) ₂	26.9 and 31.2
SCH ₃	2.51, 3H, s	C(CH ₃) ₂	34.4
OCH ₃	3.82, 3H, s	CH ₂	39.6
CHPh	4.24, 1H, dd, J ₁ = 4.5, J ₂ = 7.1 Hz	CHPh	44.9
H-1	6.39, 1H, d, J= 2.6 Hz	OCH ₃	55.6
H-2	6.62, 1H, d, J= 2.6 Hz	N=CH	156.8
H-5 and three of phenyl H's	7.33-7.46, 4H, m	aromatic C's	103.9 (C-H)
H-3, H-4 and two of phenyl H's	7.50-7.58, 4H, m		109.8 (C-H)
H-6	8.10, 1H, dd, J ₁ = 1.5, J ₂ = 7.8 Hz		125.7 (C-H)
N=CH	8.80, 1H, s		125.9 (C-H)
			127.1 (C-H)
			128.6 (2 C-H's)
			129.0 (C-H)
			129.4 (2 C-H's)
			131.8 (C-H)
			134.7 (quat. C)
			135.5 (quat. C)
			140.7 (quat. C)
			142.6 (quat. C)
			143.4 (quat. C)
			153.4 (quat. C)
			157.3 (quat. C)

IR (NaCl plate) ν_{max} 3058.4, 2955.5, 1620.6, 1593.7, 1473.8, 1434.2 cm⁻¹.

HRMS (FAB⁺) calculated for C₂₇H₃₀ONS *m/z* 416.2048, observed *m/z* 416.2032.

Catalytic arylation of (2-thiomethyl-benzylidene)-(3-ethoxy-8,8-dimethyl-5-phenyl-5,6,7,8-tetrahydro-napthalen-1-yl)-amine **13 with diphenylmethyl silanol**

In a flame dried 25-ml round bottom flask, Pd(OAc)_2 (5.4 mg, 0.024 mmol, 8 %) and Cu(OAc)_2 (109 mg, 0.6 mmol, 2 eq) were dissolved in 5 ml dry DMF and purged with argon. Diphenylmethyl silanol¹ (129 mg, 0.6 mmol, 2 eq) was dissolved in 5 ml dry DMF and added dropwise to this solution. Schiff base **13** (125 mg, 0.3 mmol) and benzoquinone (2.6 mg, 0.024 mmol, 8 %) which were dissolved in 5 ml dry DMF were added next and the reaction mixture was heated to 100 °C. The reaction propagation was monitored by TLC and upon completion (after about 22 hours), the crude mixture was treated with Na_2S and filtered through a pad of Celite. DMF was evaporated and the residue was purified by flash column chromatography (5 % NEt_3 / 15 % ethyl acetate / 80 % hexanes) to give 66 mg of product **14** (45 % yield) along with 54 mg of recovered starting Schiff base **13** (43 %).

Catalytic arylation of substrate **13** yields 4:1 diastereomeric mixture of **14**. In the following tables for ^1H NMR and ^{13}C NMR data, values marked as H' or C' correspond to the minor isomer.

¹ H NMR data (400MHz, CDCl ₃)		¹³ C NMR data (100MHz, CDCl ₃)	
CH ₃	1.32, 3H, s	SCH ₃	18.6
CH' ₃	1.47, 0.75H, s	SC'H ₃	18.3
H-8, H-9 and H'-8, H'-9	1.46-1.83, 5H, m	CH ₂	25.1
SCH ₃	2.56, 3H, s	C'H ₂	24.4
SC'H ₃	2.55, 0.75H, s	CH ₃	26.1
CH ₂ Ph	3.36, 1H, d, J= 17 Hz	C'H ₃	32.8
	3.54, 1H, d, J= 17 Hz	CH ₂	39.2
CH' ₂ Ph	3.21, 0.25H, d, J= 17 Hz	C'H ₂	39.7
	3.40, 0.25H, d, J= 17 Hz	C(CH ₃)(CH ₂ Ph)	40.3
OCH ₃	3.84, 3H, s	CHPh	45.9
OCH' ₃	3.85, 0.75H, s	C'HPh	43.4
CHPh	4.28, 1H, dd, J ₁ = 4.4, J ₂ = 7.2 Hz	CH ₂ Ph	47.4
CH'Ph	4.35, 0.25H, dd, J ₁ = 3.9, J ₂ = 7.1 Hz	C'H ₂ Ph	49.0
H-1	6.41, 1H, d, J= 2.6 Hz	OCH ₃	55.6
H'-1	6.43, 0.25H, d, J= 2.6 Hz	OC'H ₃	56.0
H-2	6.63, 1H, d, J= 2.6 Hz	N=CH	158.7
H'-2	6.64, 0.25H, d, J= 2.6 Hz	N=C'H	156.9
aromatics	6.92-6.93, 2.5H, m	aromatic C's	103.8 (C'-H)
	7.00-7.03, 3.75H, m		104.1 (C-H)
	7.24-7.48, 5H, m		109.7 (C-H)
	7.54-7.60, 5H, m		110.2 (C'-H)
H-6 and H'-6	8.14, 1.25H, dd, J ₁ = 1.2, J ₂ = 7.8 Hz		125.6 (C-H)
N=CH	8.91, 1H, s		125.9 (C-H)
N=CH'	8.94, 0.25H, s		126.4 (C'-H)
			127.3 (C-H)
			127.9 (C-H)
			128.3 (2 C'-H's)
			128.8 (2 C-H's)
			129.3 (2 C-H's)
			129.9 (2 C'-H's)
			130.2 (C-H)
			131.0 (2 C-H's)
			131.8 (2 C-H's)
			132.7 (2 C'-H's)
			133.7 (C-H)
			134.7 (quat. C)
			135.3 (quat. C)
			138.9 (quat. C)
			140.5 (quat. C)
			142.6 (quat. C)
			143.1 (quat. C)
			153.8 (quat. C)
			157.7 (quat. C)

IR (NaCl plate) ν_{max} 3058.5, 2954.9, 1619.8, 1589.1, 1478.4, 1313.7 cm^{-1} .

HRMS (FAB^+) calculated for $\text{C}_{33}\text{H}_{34}\text{ONS}$ m/z 492.2361, observed m/z 492.2394.

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