SUPPORTING INFORMATION

An Anionic O $\rightarrow$ α and β -Vinyl Carbamoyl Translocation of 2-(O-Carbamoyl) Stilbenes

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General Methods. Melting points are uncorrected. IR spectra were recorded neat or as thin films using BOMEM FT-IR spectrometer. ^1H 300 MHz and ^{13}C 75.43 MHz NMR spectra were obtained on a Bruker Avance-300, 400 or 500 spectrometer. THF was freshly distilled from sodium benzophenone ketyl under nitrogen and CH_2Cl_2 and HN^iPr_2 were freshly distilled from CaH_2 under nitrogen. *n*-Butyllithium and *s*-butyllithium were purchased from Aldrich as solutions in hexanes, stored in resealable containers, and titrated periodically against *sec*-butanol using 1,10-phenanthroline as indicator.¹ All experiments were carried out under argon in dried glassware, using syringe-septum cap techniques. The $-78\text{ }^\circ\text{C}$ and $0\text{ }^\circ\text{C}$ external bath temperatures designated are approximate as achieved by a dry ice-acetone or ice baths, respectively. Flash column chromatography was carried out using Merck Kieselgel 60 silica gel (particle size: 32-63).

General Procedure A. Suzuki Reactions

A round bottom flask equipped with a reflux condenser was charged with aromatic bromide/iodide, borolane, degassed 2M Na_2CO_3 (5 equiv, degassed) and degassed DME (10 mL/g halide). $\text{Pd}(\text{PPh}_3)_4$ (3 mol%), was added and the reaction mixture was heated at reflux for the indicated time, cooled and extracted with EtOAc (3 x 20 mL) and the organic phase was washed with brine, dried (Na_2SO_4), subjected to filtration, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography then recrystallized from hexanes.

General Procedure B. Migration Reactions

A stock solution of LDA (0.7 M) was prepared by adding a solution of *n*-BuLi (9.8 mmol) in hexanes, dropwise to a solution of diisopropylamine (10 mmol) in THF (10mL) at $-10\text{ }^\circ\text{C}$ and allowed to stir for 30 min. The required amount of LDA was added dropwise *via* syringe to a solution of stilbene (1 mmol) in THF (7 mL) precooled to temperatures between $-78\text{ }^\circ\text{C}$ and rt. The reaction was stirred for the indicated time then quenched with a cooled satd NH_4Cl solution. The mixture was extracted with EtOAc (3

x 20mL). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel) and / or by recrystallization from hexanes.

2-iodo-6-(trimethylsilyl)phenyl diethylcarbamate (15). A solution of O-phenyl N,N-diethylcarbamate (5 g, 25.9 mmol) and TMEDA (4.35 mL, 28.9 mmol) in THF (100 mL) was cooled to -78°C and treated with *s*-BuLi (19.79 mL, 1.46 M, 28.9 mmol). After stirring for 45 min, TMSCl (3.67 mL, 28.9 mmol) was slowly added and the solution was warmed to -30°C over 1h. The solution was re-cooled to -85°C and treated with *s*-BuLi (19.79 mL, 1.46 M, 28.9 mmol) and stirred for 45 min. To the solution was slowly added, (maintaining -85°C internal temperature) *via* cannular, a solution of iodine (8.52g, 33.67) in THF (60 mL). The solution was slowly warmed to 0°C over 3h and then quenched with satd NH_4Cl solution (150 mL). The THF was evaporated *in vacuo* and the residue was extracted with EtOAc (3x 50 mL). The combined organic extracts were washed with $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL), brine (50 mL) then dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 :19) to give **15** (7.79 g, 19.9 mmol, 77%) as an orange oil; IR (film) ν_{max} 2972, 2934, 2897, 2876, 1723, 1587, 1387, 1268, 1198, 1144 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.84 (dd, $J = 7.80, 1.47$, 1H), 7.44 (dd, $J = 7.26, 1.50$, 1H), 6.94 (t, $J = 7.51$, 1H), 3.50 (m, 4H), 1.38 (t, $J = 7.14$, 3H), 1.25 (t, $J = 7.11$, 3H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 153.0, 141.0, 135.3, 135.2, 127.2, 93.4, 42.3, 42.1, 14.7, 13.5, -0.5; EI MS (m/z) 376 ($\text{M}^+ - 15$, 3), 266 (2), 264 (27), 177 (37), 148 (29), 101 (29), 100 (100), 72 (100); EI HRMS (calcd for $\text{C}_{14}\text{H}_{22}\text{INO}_2\text{Si}$) 391.0464, found 391.0456.

Procedure 1

2-(trimethylsilyl)-6-(2-(trimethylsilyl)ethynyl)phenyl diethylcarbamate (12). To a solution of **15** (0.25g, 0.64mmol) in acetonitrile (4mL) was added Et₃N (0.5 mL, 3.6mmol), Pd(PPh₃)₂Cl₂ (13mg, 0.03mmol), Copper (II) iodide (5.7mg, 0.03mmol) and (trimethylsilyl)acetylene (0.18mL, 1.27mmol). The solution was stirred for 6h at rt and then concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 : 9.75) to give **12** (0.187g, 0.52 mmol, 81%) as a colorless oil.

Procedure 2.

To a solution of **11** (25g, 0.11mol) in THF (125mL) at -78 °C was added slowly LDA (0.126mmol, 0.83M) [preformed by addition of nBuLi (52.1mL, 2.32M, 0.121mol) to DIPA (17.7mL, 0.126mmol) in THF (100mL) at -78 °C]. To the colorless suspension was slowly added diethyl chlorophosphate (19.1mL, 0.132mol) and the solution was slowly warmed to 0°C over 3h. The solution was then slowly cannulated into a solution of LDA [preformed by addition of nBuLi (189.7mL, 2.32M, 0.44mol) to DIPA (61.5mL, 0.44mmol) in THF (250 mL) at -78 °C] and TMSCl (55.9mL, 0.44mmol). The mixture was warmed to 0 °C over 6h then quenched with satd. NH₄Cl (300 mL). The THF was evaporated *in vacuo* and the residue was extracted with EtOAc (3x 100 mL). The combined organic extracts were washed with brine (150 mL) then dried (Na₂SO₄) and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 : 9.75) to give **12** (36.7 g, 0.1 mmol, 91%) as a colorless oil;

IR (film) ν_{max} 2966, 2154, 1726, 1400, 1272, 1176, 1150, 837, 760 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, *J* = 7.56, 1.6, 1H), 7.40 (dd, *J* = 7.40, 1.6, 1H), 7.14 (t, *J* = 7.18, 1H), 3.65-3.10 (m, 4H), 1.35 (t, *J* = 7.15, 3H), 1.23 (t, *J* = 7.15, 3H), 0.31 (s, 9H), 0.24 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 157.5, 153.6, 135.4, 135.0, 133.4, 125.1, 118.1, 101.1, 98.8, 42.6, 42.3, 14.8, 13.8, 0.29 -0.5; EI MS (*m/z*) 362 (M+1, 13), 361 (M+, 16),

360 (2), 348 (13), 347 (100), 346 (26), 345 (4), 196(4), 100 (24); ES HRMS (M+1) (calcd for C₁₉H₃₁NO₂Si₂) 362.1971, found 362.1975.

(E)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-6-(trimethylsilyl)phenyl diethylcarbamate (13). To a solution of **12** (15.6g, 47.1mmol) in MeOH (150mL) was added K₂CO₃ (13.4g, 94.3mmol). The solution was stirred for 1h, filtered through a pad of celite then concentrated *in vacuo*. The resulting residue was passed through a short column (silica gel, EtOAc-Hexanes 1:9) and the resulting solution was dried (Na₂SO₄) then concentrated *in vacuo* and to give the terminal acetylene **12a** (15g, 45.3mmol, 96%) as a colorless oil. In a separate flame dried flask under an argon atmosphere was added 2,5-Dimethyl-2,4-hexadiene (15.5mL, 108.7mmol) and THF (20 mL) and cooled to 0 °C, and BH₃.THF solution (55.2mL, 1M) was added whilst maintaining the reaction temperature below 5°C. The resulting solution was aged, with stirring, for 3h at 0°C and then treated with a solution of **12a** (15g, 45.3mmol) in THF (20mL) whilst maintaining the reaction temperature below 5°C. The reaction mixture was stirred at 0°C for 2h, warmed to rt over 1h then slowly quenched with H₂O (25mL) and stirred for 30 min at rt, and then treated with formaldehyde (4.4mL, 54.4mmol, 37wt%) in a single addition. The resulting exothermic reaction was compensated by application of an ambient-temperature bath. The reaction was stirred for 24h at rt concentrated *in vacuo* to which was added H₂O (100 mL) and then extracted with EtOAc (3 x 80mL). After separation of layers, the organic phase was dried (Na₂SO₄), transferred into a flask containing diethanolamine (5.7g, 54.4mmol), and the combined mixture was evaporated *in vacuo* (25 torr, then 0.5torr, heating bath at 50 then to 80 °C). The resulting solid residue was recrystallized from ethyl acetate/ethanol to give a colorless solid which was added to a flask charged with a solution of 50% citric acid (43g, 226mmol), hexanes (300mL) and pinacol (6.4g, 54.3mmol) then stirred vigorously for 24h. The layers were separated and the organic phase washed with brine (100mL), dried (Na₂SO₄) and concentrated *in vacuo* to give **13** as colorless oil (15.3g, 36.7mmol, 78%); bp 178 °C (0.001mm); IR (film) $\nu_{\max}$ 2980,

2154, 1718, 1621, 1396, 1267, 1138, 842 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, J = 7.64, 1.48, 1H), 7.42-7.38 (m, 2H), 7.20 (t, J = 7.48, 1H), 6.10 (d, J = 18.24, 1H), 3.80-3.34 (m, 4H), 1.33 (t, J = 7.12, 3H), 1.26 (s, 12H), 1.22 (t, J = 7.12, 3H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 154.2, 143.9, 135.7 (2), 133.33, 131.0, 128.1, 125.7, 83.4, 42.1, 41.9, 25.1, 14.5, 13.5, -0.42; EI MS (m/z) 417 (M^+ , 0.2), 402 (24), 317 (8), 302 (11), 101 (42), 100 (99), 83 (88), 72(100); EI HRMS (calcd for $\text{C}_{22}\text{H}_{36}\text{BNO}_4\text{Si}$) 417.2506, found 417.2503.

(E)-2-styryl-6-(trimethylsilyl)phenyl diethylcarbamate (17a). Following **General Procedure A** using the following materials [bromobenzene (2.4 g, 6.13 mmol), **13** (1.4 g, 6.13 mmol), Na_2CO_3 (15.3 mL, 2M, 30.6mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.212 g, 0.183mmol) in DME (24 mL); reflux for 2 h], followed by flash column chromatography (10% EtOAc/hexanes) and recrystallization afforded **17a** as colorless crystals; mp 103° C (hexanes) IR (KBr disk) ν_{max} 3037, 2962, 1712, 1394, 1260, 1151, 838; ^1H NMR (300 MHz, CDCl_3) δ 7.84 (dd, J = 7.62, 1.55, 1H), 7.62- 7.26 (m, 7H), 7.20 (d, J = 8.19, 2H) 4.00-3.40 (m, 4H), 1.41 (t, J = 7.05, 3H), 1.16 (t, J = 7.05, 3H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.8, 154.2, 138.2, 134.8, 133.7, 131.3, 130.9, 129.4, 128.4, 128.1, 127.0, 126.1, 123.2, 42.3, 42.2, 14.6, 13.4, -0.8; EI MS (m/z) 367 (M^+ , 14), 352 (30) 252 (9), 219 (6), 178 (9), 100 (100), 72 (43); EI HRMS (calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_2\text{Si}$) 367.1967, found 367.1982. Anal. Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_2\text{Si}$: C, 71.89; H, 7.95; N, 3.81; Found: C, 71.92; H, 8.02; N, 3.90.

(E)-2-styrylphenyl diethylcarbamate (17b). To a solution of **17a** (1.8g, 4.9 mmol) in THF (20mL) was added TBAF (4.9 mL, 4.9 mmol, 1M). The solution was stirred for 12h, concentrated in *vacuo* and the residue. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 : 9) to give **17b** (1.33 g, 4.5 mmol, 91%) as a colorless oil: IR (film) $\nu_{\max}$ 3049, 2978, 2940, 1719, 1470, 1419, 1272, 1202, 1157, 1087, 952, 754 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (dd, $J = 7.84, 1.24$, 1H), 7.48 (d, $J = 7.56$, 2H), 7.37-7.19 (m, 6H), 7.14 (dd, $J = 7.84, 1.00$, 1H), 7.05 (d, $J = 16.4$, 1H) 3.65-3.38 (m, 4H), 1.45-1.15 (m, 6H), ; ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, 149.3, 137.7, 130.5, 128.9, 128.6, 127.9, 126.8, 126.5, 125.8, 123.3, 122.7; ES MS (m/z) 297 ($M+2$, 22), 296 ($M+1$, 100), 223 (89); ES HRMS ($M + 1$) (calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2$) 296.1645, found 296.1640.

(E)-N,N-diethyl-2-hydroxy-3-styrylbenzamide (16). Following **General Procedure B** using the following materials [**17b**, (700mg, 2.37 mmol), LDA (6.77 mL, 4.74 mmol) at 0 °C, 2h], followed by recrystallization from hexanes afforded **16** as colorless crystals; mp 101 °C (hexanes); IR (film) $\nu_{\max}$ 3500-300 (br), 2978, 1591, 1572, 1489, 1451, 1285, 1240, 1119, 1087 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 10.27 (s, 1H), 7.6 (d, $J = 7.72$, 1H), 7.56 (d, $J = 7.64$, 2H), 7.52 (d, $J = 16.6$, 1H), 7.37 (t, $J = 7.48$, 2H), 7.30-7.15 (m, 3H) 6.87 (t, $J = 7.68$, 1H), 3.55 (q, $J = 7.12$, 4H), 1.29 (t, $J = 7.12$, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 156.3, 137.9, 129.6, 128.9, 128.7, 127.6, 126.9, 126.7, 126.5, 123.14, 118.7, 118.5, 42.3, 13.52; EI MS (m/z) 296 ($M+1$, 26), 295 (M^+ , 100), 222 (8), 194 (21), 165 (14); ES HRMS ($M + 1$) (calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2$) 296.1645, found 296.1646.

(Z)-N,N-diethyl-2-(2-hydroxy-3-(trimethylsilyl)phenyl)-3-phenylacrylamide (18)

Following **General Procedure B** using the following materials [**17a**, (250mg, 0.7 mmol), LDA (3 mL 2.1 mmol) at -20 °C, 3h]. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 :9) followed by recrystallization from hexanes to afford **18** as colorless crystals (0.237 g, 94%); mp 118° C (hexanes); IR (KBr disk) ν_{max} 3055, 2980, 2952, 2757, 2705, 2645, 1580, 1400, 1243, 843; ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$) δ 10.66 (s, 1H), 7.52-7.49 (m, 2H), 7.43-7.31 (m, 5H), 6.94 (t, $J=7.37$, 1H), 6.74 (s, 1H), 3.70 (m, 1H), 3.40 (m, 1H), 3.20 (m, 2H), 1.14 (t, $J = 7.14$, 3H), 0.81 (t, $J = 7.17$, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 171.8, 161.4, 136.2, 136.0, 135.7, 133.7, 132.0, 129.2, 129.2, 128.9, 127.1, 125.3, 120.1, 43.5, 39.8, 13.5, 11.886, -0.9; EI MS (m/z) 367 (M^+ , 9), 352 (5), 295 (19), 294 (66), 252 (30), 251 (100), 191 (30), 189 (11), 176 (15); EI HRMS (calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_2\text{Si}$) 367.1967, found 296.1980. Anal. Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_2\text{Si}$: C, 71.89; H, 7.95; N, 3.81; O, 8.71; Si, 7.64. Found: C, 71.92; H, 8.06; N, 3.92.

(E)-2-(2,4-dimethoxystyryl)-6-(trimethylsilyl)phenyl diethylcarbamate (20e)

Following **General Procedure A** using the following materials [1-Bromo-2,4-dimethoxybenzene (2.34 g, 10.78 mmol), **13** (3 g, 7.19 mmol), Na_2CO_3 (17.9 mL, 2M, 35.9 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.166 g, 0.144 mmol) in DME (24 mL); reflux for 6 h], the residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 :9) followed by recrystallization from hexanes gave **20e** (2.52g, 5.89mmol, 82%) as colorless

crystals; mp 94-95 °C (hexanes); IR (KBr disk) ν_{max} 2972, 1719, 1604, 1502, 1400, 1266, 1208, 1157, 1023, 824; ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, $J = 7.7$, 1H), 7.41 (d, $J = 8.4$, 1H), 7.34-7.29 (m, 2H), 7.20 (t, $J = 7.55$, 1H), 6.94 (d, $J = 15.6$, 1H), 6.49-6.45 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.7-3.25 (m, 4H), 1.32 (m, 3H), 1.17 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.5, 158.1, 153.9, 153.6, 133.6, 132.7, 131.5, 127.7, 127.3, 125.5, 125.3, 120.9, 119.7, 104.9, 98.4, 55.3 (2), 41.9, 41.6, 14.4, 13.3; EI MS (m/z) 428 (M+1, 4), 427 (M+, 13), 164 (7), 101 (23), 100 (100); Anal. Calcd for $\text{C}_{24}\text{H}_{33}\text{NO}_4\text{Si}$: C, 67.41; H, 7.78; N, 3.28. Found: C, 67.96; H, 8.00; N, 3.26.

(Z)-3-(2,4-dimethoxyphenyl)-N,N-diethyl-2-(2-hydroxy-3(trimethylsilyl)phenyl)

acrylamide (21e). Following **General Procedure B** using the following materials [**20e**, (0.5g, 1.17 mmol), LDA (6.9 mL, 4.68 mmol) at 0 °C, 6h]. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1:9) followed by recrystallization from hexanes afforded **21e** as colorless crystals (0.344 g, 69%); mp 173-176 °C (hexanes); IR (KBr) ν_{max} 2959, 1585, 1470, 1400, 1214, 1125, 1042, 837; ^1H NMR (500 MHz, CDCl_3) δ 10.6 (s, 1H), 7.42 (d, $J = 8.5$, 1H), 7.36 (d, $J = 7.7$, 1H), 7.31 (s, 1H), 6.90 (m, 1H), 6.84 (s, 1H), 6.50-6.42 (m, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 3.80-3.10 (m, 4H), 1.10 (t, $J = 7.0$, 3H), 0.81 (t, $J = 7.1$, 3H), 0.3 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.1, 161.4, 161.1, 158.4, 135.3, 132.7, 131.5, 129.8, 129.1, 127.3, 125.2, 119.3, 117.6, 104.4, 98.2, 55.6, 55.4, 43.1, 39.5, 13.5, 12.1, -0.8; EI MS (m/z) 427 (M+, 1), 355 (39), 354 (81), 296 (24), 163 (97), 137 (47), 74 (19), 72 (100); Anal. Calcd for $\text{C}_{24}\text{H}_{33}\text{NO}_4\text{Si}$: C, 67.41; H, 7.78; N, 3.28. Found: C, 67.84; H, 7.39; N, 2.99.

(E)-tert-butyl 4-(2-(diethylcarbamoyloxy)-3-(trimethylsilyl)styryl)benzoate (20i).

Following **General Procedure A** using the following materials [*tert*-butyl 4-iodobenzoate (4.24 g, 13.9 mmol), **13** (5 g, 11.9 mmol), Na₂CO₃ (29.7 mL, 2M, 59.5 mmol), Pd(PPh₃)₄ (0.277 g, 0.239 mmol) in DME (42 mL); reflux for 2 h], the residue was purified by column chromatography (silica gel, EtOAc - hexanes 1 :9) followed by recrystallization from hexanes gave **20i** (4.0g, 8.56mmol, 72%) as colorless crystals;

mp 107-110 °C (hexanes); IR (KBr disk) ν_{max} 2978, 1713, 1604, 1393, 1304, 1157, 1112, 959, 844; ¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 8.2, 2H), 7.71 (d, *J* = 7.6, 1H), 7.48 (d, *J* = 8.2, 2H), 7.44 (d, *J* = 6.1, 1H), 7.28-7.04 (m, 3H), 3.88-3.35 (m, 4H), 1.65 (s, 9H) 1.37 (t, *J* = 7.0, 3H), 1.19 (t, *J* = 7.0, 3H), 0.3 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 165.5, 154.1, 153.9, 141.6, 134.9, 133.2, 130.9, 130.1, 129.8, 129.6, 127.8, 126.2, 125.7 125.2, 80.9, 42.0, 41.7, 28.3, 14.5, 13.3, -0.6; EI MS (*m/z*) 468(M+ 1, 1), 467 (M+, 4), 452 (10), 396 (15), 394 (11), 295 (22), 294 (100), 101 (67); Anal. Calcd for C₂₇H₃₇NO₄Si: C, 69.34; H, 7.97; N, 2.99. Found: C, 69.80; H, 8.06; N, 2.84.

(Z)-tert-butyl 4-(3-(diethylamino)-2-(2-hydroxy-3-(trimethylsilyl)phenyl)-3-oxoprop-1-enyl)benzoate (21i). Following **General Procedure B** using the following materials [**20i**, (0.5g, 1.07 mmol), LDA (4.6 mL, 3.21 mmol) at -30°C, 5h]. The residue was purified by column chromatography (silica gel, EtOAc-hexanes 1:4) followed by

recrystallization from hexanes afforded **21i** as colorless crystals (0.374 g, 75%); mp 123-125 °C (hexanes); IR (KBr disk) $\nu_{\max}$ 3400-3010, 2979, 1719, 1591, 1387, 1298, 1240, 1170, 1119, 844; ^1H NMR (400 MHz, CDCl_3) δ 10.26 (s, 1H), 7.95 (d, $J = 8.3$, 2H), 7.47 (d, $J = 8.2$, 2H), 7.38 (dd, $J = 7.2$, 1.6, 1H), 7.21 (dd, $J = 7.4$, 1.5, 1H), 6.91 (t, 7.4, 1H), 6.51 (s, 1H), 3.75-3.05 (m, 4H), 1.62 (s, 9H), 1.18 (t, $J = 7.2$, 3H), 0.78 (t, $J = 7.2$, 3H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 165.6, 161.1, 139.6, 137.2, 136.2, 132.5, 132.0, 131.1, 129.9, 128.3, 128.1, 124.4, 119.7, 81.55, 43.4, 39.9, 28.5, 13.8, 12.2, -0.6; EI MS (m/z) 469 ($M+2$, 1), 467 (M^+ , 4), 452 (4), 395 (17), 394 (56), 338 (41), 295 (84), 73 (100); Anal. Calcd for $\text{C}_{27}\text{H}_{37}\text{NO}_4\text{Si}$: C, 69.34; H, 7.97; N, 2.99. Found: C, 69.49; H, 8.30; N, 2.94.

2-(trimethylsilyl)-6-vinylphenyl diethylcarbamate (23). To a solution of **15** (5.25g, 13.4 mmol), in degassed toluene (60 mL) was added tributyl(vinyl)tin (4.7mL, 16.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (773 mg, 0.67 mmol). The solution was refluxed for 2h, cooled and then concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1:39) to give **23** (1.75 g, 6.03 mmol, 45%) as a colorless oil; IR (film) $\nu_{\max}$; 2978, 1726, 1457, 1387, 1266, 1195, 1144, 959, 844; ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 7.6$, 1H), 7.38 (m, 1H), 7.19 (t, $J = 7.5$, 1H), 6.67 (dd, $J = 17.5$, 11.0, 1H), 5.72 (d, $J = 17.5$, 1H), 5.29 (d, $J = 11.0$, 1H), 3.75-3.20 (m, 4H), 1.30 (t, $J = 7.1$, 3H), 1.19 (t, $J = 7.1$, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.2, 153.7, 134.9, 133.2, 131.4, 131.2, 128.0, 125.8, 116.2, 42.2, 41.8, 14.6, 13.5, -0.4; ES MS (m/z) 293 ($M+2$, 41), 292 ($M+1$, 100), 288 (9), 266 (15); ES HRMS (calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{Si}$) 314.1546, found 314.1538.

3-(diisopropylamino)-N,N-diethyl-2-(2-hydroxy-3-(trimethylsilyl)phenyl)propanamide (24). Following **General Procedure B** using the following materials [**23**, (2.5g, 8.59 mmol), LDA (61.3 mL, 42.9 mmol) at -10°C, 2h]. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1:9) afforded **24** as a colorless oil (2.82 g, 7.21 mmol, 84%); IR (film) $\nu_{\max}$: 2966, 1643, 1611, 1457, 1457, 1425, 1246, 1163, 856, 748; ^1H NMR (300 MHz, CDCl_3) δ 7.22 (d, $J = 7.1$, 1H), 6.97 (d, $J = 7.5$, 1H), 6.76 (t, $J = 7.4$, 1H), 4.23-4.15 (m, 1H), 3.73-3.60 (m, 1H), 3.22-2.91 (m, 7H), 1.14 (t, $J = 7.1$, 4H), 1.06-0.82 (m, 18H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.4, 162.1, 133.8, 128.9, 127.9, 126.4, 119.5, 50.6, 49.6, 44.8, 41.9, 39.9, 20.5, 19.3, 14.4, 12.7, -0.7; ES MS (m/z) 394 ($M+2$, 68), 393 ($M+1$, 100); ES HRMS (calcd for $M+1$ $\text{C}_{22}\text{H}_{41}\text{N}_2\text{O}_2\text{Si}$) 393.2931, found 393.2926.

(E)-2-(1,2-diphenylvinyl)-6-(trimethylsilyl)phenyldiethylcarbamate (26a). Following **General Procedure A** using the following materials [**15** (2.40 g, 5.12 mmol), **25a** (1.3 g, 4.26 mmol), Na_2CO_3 (10.65 mL, 2M, 21.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.148g, 0.128 mmol) in DME (25 mL); reflux for 5 h], the residue was purified by column chromatography (silica gel, EtOAc - hexanes 2.5 :97.5) followed by recrystallization from hexanes to give **26a** (1.74g, 3.94 mmol, 72%) as colorless crystals; mp 144°C (hexanes); IR (KBr disk) $\nu_{\max}$ 3411, 3052, 2960, 2950, 1712, 1401, 1268, 1181, 1147, 965, 840; ^1H NMR (300 MHz, CDCl_3) δ 7.39 (dd, $J = 7.2$, 1.73, 1H), 7.33-7.04 (m, 12H), 6.78 (s, 1H), 3.41 (m,

1H), 3.16 (m, 3H), 1.04 (t, $J = 7.2$, 3H), 0.93 (t, $J = 7.07$, 3H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 153.9, 141.2, 138.7, 138.1, 137.7, 134.0, 133.4, 132.6, 130.8, 130.6, 129.6, 128.5, 128.1, 127.6, 127.0, 125.1, 41.4, 41.3, 13.7, 12.8, -1.0; EI MS (m/z) 443 (M^+ , 39), 429 (26), 428 (55), 252 (14), 100 (100), 73 (35), 72 (49); EI HRMS (calcd for $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{Si}$) 443.2280, found 443.2290. Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{Si}$: C, 75.80; H, 7.50; N, 3.16. Found: C, 75.95; H, 7.71; N, 3.22.

(Z)-N,N-diethyl-3-(2-hydroxy-3-(trimethylsilyl)phenyl)-2,3-diphenylacrylamide

(30a). Following **General Procedure B** using the following materials [**26a**, (0.250 g, 0.54 mmol), LDA (4.03 mL, 2.82 mmol) at rt, 2h]. The residue was purified by column chromatography (silica gel, EtOAc - hexanes 1:9) followed by recrystallization from hexanes to afford **30a** as colorless crystals 0.229 g, 92% (0.229 g, 0.51 mmol, 92%); mp 141°C (hexanes); IR (KBr disk) ν_{max} 3150, 3050, 2949, 2894, 1713, 1596, 1438, 1357, 1245, 1216, 844; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 8.10 (s, 1H), 7.37, (dd, $J=7.53$, 1.69, 1H), 7.32-7.27 (m, 3H), 7.25-7.20 (m, 5H), 7.19-7.14 (m, 3H), 6.94 (t, $J=7.37$, 1H), 3.83-3.72 (m, 1H), 3.57-3.45 (m, 1H), 3.40-3.30 (m, 1H), 3.01-2.90 (m, 1H), 0.87 (t, $J=7.13$, 3H), 0.65 (t, $J=7.07$, 3H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 171.6, 158.6, 140.4, 138.4, 137.1, 136.5, 134.8, 130.9, 130.0, 129.5, 128.6, 128.3, 127.9, 127.5, 120.7, 42.9, 38.2, 13.1, 11.1, -1.1; EI MS (m/z) 443 (M^+ , 11), 428 (13), 373 (14), 371 (100), 370 (52), 356 (22), 355 (56), 343 (46), 328 (27) 327 (69), 252 (17) 73 (66); EI HRMS (calcd for $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{Si}$) 443.2280, found 443.2290. Anal. Calcd for $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{Si}$: C, 75.80; H, 7.50; N, 3.16. Found: C, 75.92; H, 7.56; N, 3.23.

X-ray crystallographic data for compound 18

X-ray Crystallographic Analysis. Single crystals **18** was obtained and characterized by X-ray diffraction analysis. The crystal was obtained from hexane and mounted on glass fiber for data collection. Data was collected on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo K α radiation, operating at 50 kV and 30 mA ambient temperature. The data collection range over the 2θ ranges was 3.18 – 57.12°. No significant decay was observed for the sample. Data was processed on a PC using Bruker SHELXTL software package (version 5.10) and are corrected for Lorentz and polarization effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

Molecular structure of compound 18

Table 1. Crystal data and structure refinement.

Empirical formula	C ₂₂ H ₂₉ N O ₂ Si	
Formula weight	367.55	
Temperature	302(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.892(2) Å	α = 85.305(5)°.
	b = 9.613(2) Å	β = 81.768(4)°.
	c = 13.018(3) Å	γ = 89.900(5)°.
Volume	1097.6(5) Å ³	
Z	2	
Density (calculated)	1.112 Mg/m ³	
Absorption coefficient	0.121 mm ⁻¹	
F(000)	396	
Crystal size	0.5 x 0.5 x 0.2 mm ³	
Theta range for data collection	1.59 to 28.26°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 10, -16 ≤ l ≤ 17	
Reflections collected	7965	
Independent reflections	5037 [R(int) = 0.0203]	
Completeness to theta = 28.26°	92.5 %	
Absorption correction	Bruker SADABS	
Max. and min. transmission	1.0000 and 0.7894	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5037 / 0 / 235	
Goodness-of-fit on F ²	0.807	
Final R indices [I > 2σ(I)]	R1 = 0.0455, wR2 = 0.0947	
R indices (all data)	R1 = 0.1093, wR2 = 0.1090	
Largest diff. peak and hole	0.377 and -0.163 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized $U^{\dagger\dagger}$ tensor.

	x	y	z	U(eq)
N(1)	761(2)	1717(2)	11071(1)	51(1)
Si(1)	1905(1)	2526(1)	5612(1)	66(1)
O(1)	1314(2)	3366(1)	7813(1)	58(1)
O(2)	185(2)	3216(1)	9760(1)	60(1)
C(1)	2353(2)	2319(2)	7755(2)	48(1)
C(2)	2757(2)	1794(2)	6776(1)	53(1)
C(3)	3810(2)	719(2)	6720(2)	63(1)
C(4)	4455(2)	186(2)	7566(2)	66(1)
C(5)	4067(2)	748(2)	8507(2)	57(1)
C(6)	3021(2)	1824(2)	8629(1)	45(1)
C(7)	2743(2)	2487(2)	9636(1)	43(1)
C(8)	3883(2)	3106(2)	9988(1)	48(1)
C(9)	3841(2)	3888(2)	10919(1)	46(1)
C(10)	5088(2)	3881(2)	11443(2)	60(1)
C(11)	5109(3)	4658(2)	12289(2)	71(1)
C(12)	3884(3)	5454(2)	12615(2)	75(1)
C(13)	2647(3)	5481(2)	12105(2)	71(1)
C(14)	2622(2)	4714(2)	11257(2)	59(1)
C(15)	1144(2)	2497(2)	10171(2)	47(1)
C(16)	1798(2)	789(2)	11554(2)	58(1)
C(17)	1724(3)	-687(2)	11246(2)	94(1)
C(18)	-818(2)	1716(2)	11596(2)	69(1)
C(19)	-1035(3)	2650(3)	12469(2)	106(1)
C(20)	2121(3)	4454(2)	5436(2)	102(1)
C(21)	2924(3)	1788(3)	4432(2)	95(1)
C(22)	-133(3)	2015(3)	5764(2)	96(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$].

N(1)-C(15)	1.339(2)
N(1)-C(16)	1.454(2)
N(1)-C(18)	1.471(2)
Si(1)-C(20)	1.855(2)
Si(1)-C(22)	1.857(2)
Si(1)-C(21)	1.861(2)
Si(1)-C(2)	1.875(2)
O(1)-C(1)	1.364(2)
O(2)-C(15)	1.249(2)
C(1)-C(6)	1.407(2)
C(1)-C(2)	1.408(2)
C(2)-C(3)	1.393(2)
C(3)-C(4)	1.376(3)
C(4)-C(5)	1.378(2)
C(5)-C(6)	1.393(2)
C(6)-C(7)	1.494(2)
C(7)-C(8)	1.331(2)
C(7)-C(15)	1.491(2)
C(8)-C(9)	1.473(2)
C(9)-C(10)	1.382(3)
C(9)-C(14)	1.384(2)
C(10)-C(11)	1.384(3)
C(11)-C(12)	1.367(3)
C(12)-C(13)	1.364(3)
C(13)-C(14)	1.379(3)
C(16)-C(17)	1.509(3)
C(18)-C(19)	1.496(3)
C(15)-N(1)-C(16)	124.06(17)
C(15)-N(1)-C(18)	119.56(16)
C(16)-N(1)-C(18)	116.30(17)
C(20)-Si(1)-C(22)	110.50(12)
C(20)-Si(1)-C(21)	108.16(11)
C(22)-Si(1)-C(21)	108.92(11)

C(20)-Si(1)-C(2)	110.95(10)
C(22)-Si(1)-C(2)	109.65(10)
C(21)-Si(1)-C(2)	108.60(10)
O(1)-C(1)-C(6)	121.25(17)
O(1)-C(1)-C(2)	116.90(17)
C(6)-C(1)-C(2)	121.82(18)
C(3)-C(2)-C(1)	116.85(18)
C(3)-C(2)-Si(1)	122.29(15)
C(1)-C(2)-Si(1)	120.86(15)
C(4)-C(3)-C(2)	122.74(19)
C(3)-C(4)-C(5)	118.98(19)
C(4)-C(5)-C(6)	121.86(19)
C(5)-C(6)-C(1)	117.70(17)
C(5)-C(6)-C(7)	119.83(17)
C(1)-C(6)-C(7)	122.27(16)
C(8)-C(7)-C(15)	122.86(17)
C(8)-C(7)-C(6)	119.97(17)
C(15)-C(7)-C(6)	117.06(15)
C(7)-C(8)-C(9)	128.69(18)
C(10)-C(9)-C(14)	117.95(18)
C(10)-C(9)-C(8)	119.76(19)
C(14)-C(9)-C(8)	122.16(18)
C(9)-C(10)-C(11)	121.1(2)
C(12)-C(11)-C(10)	119.8(2)
C(13)-C(12)-C(11)	120.0(2)
C(12)-C(13)-C(14)	120.4(2)
C(13)-C(14)-C(9)	120.7(2)
O(2)-C(15)-N(1)	121.38(19)
O(2)-C(15)-C(7)	119.20(18)
N(1)-C(15)-C(7)	119.41(16)
N(1)-C(16)-C(17)	112.77(17)
N(1)-C(18)-C(19)	112.65(18)

Symmetry transformations used to generate equivalent atoms.

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	43(1)	62(1)	49(1)	-7(1)	-6(1)	-3(1)
Si(1)	84(1)	73(1)	45(1)	-12(1)	-16(1)	14(1)
O(1)	65(1)	54(1)	57(1)	-6(1)	-18(1)	20(1)
O(2)	50(1)	73(1)	60(1)	-7(1)	-16(1)	13(1)
C(1)	48(1)	47(1)	49(1)	-7(1)	-8(1)	0(1)
C(2)	55(1)	56(1)	48(1)	-8(1)	-9(1)	4(1)
C(3)	67(2)	73(1)	50(1)	-18(1)	-8(1)	12(1)
C(4)	67(2)	75(1)	60(1)	-17(1)	-11(1)	25(1)
C(5)	52(1)	66(1)	54(1)	-8(1)	-13(1)	12(1)
C(6)	45(1)	48(1)	45(1)	-5(1)	-9(1)	-1(1)
C(7)	40(1)	47(1)	43(1)	-4(1)	-10(1)	1(1)
C(8)	43(1)	52(1)	48(1)	-4(1)	-6(1)	1(1)
C(9)	48(1)	44(1)	47(1)	1(1)	-10(1)	-6(1)
C(10)	60(2)	62(1)	61(1)	-5(1)	-19(1)	-3(1)
C(11)	85(2)	75(2)	61(2)	-6(1)	-30(1)	-10(1)
C(12)	101(2)	72(2)	51(1)	-13(1)	-9(1)	-16(2)
C(13)	74(2)	67(1)	74(2)	-24(1)	-2(1)	-4(1)
C(14)	57(2)	58(1)	66(1)	-15(1)	-13(1)	-3(1)
C(15)	45(1)	50(1)	48(1)	-14(1)	-11(1)	1(1)
C(16)	59(2)	61(1)	52(1)	1(1)	-11(1)	-6(1)
C(17)	98(2)	64(2)	120(2)	-8(2)	-17(2)	-6(1)
C(18)	53(2)	89(2)	63(2)	-10(1)	2(1)	-6(1)
C(19)	88(2)	127(2)	102(2)	-48(2)	12(2)	3(2)
C(20)	165(3)	77(2)	64(2)	4(1)	-25(2)	11(2)
C(21)	125(2)	111(2)	52(1)	-22(1)	-14(1)	30(2)
C(22)	86(2)	127(2)	83(2)	-21(2)	-31(2)	13(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$).

	x	y	z	U(eq)
H(3A)	4090	347	6084	75
H(4A)	5143	-543	7504	79
H(5A)	4515	400	9077	68
H(8A)	4834	3036	9593	57
H(10A)	5927	3346	11222	72
H(11A)	5954	4639	12636	86
H(12A)	3895	5977	13184	90
H(13A)	1814	6021	12330	86
H(14A)	1777	4752	10910	71
H(16A)	1555	782	12305	69
H(16B)	2827	1146	11356	69
H(17A)	2428	-1255	11585	140
H(17B)	1986	-690	10505	140
H(17C)	713	-1054	11454	140
H(18A)	-1113	771	11868	83
H(18B)	-1480	2016	11091	83
H(19A)	-2080	2613	12785	159
H(19B)	-766	3591	12202	159
H(19C)	-400	2346	12979	159
H(20A)	1677	4804	4837	152
H(20B)	3181	4700	5336	152
H(20C)	1617	4854	6043	152
H(21A)	2498	2154	3830	142
H(21B)	2818	789	4505	142
H(21C)	3981	2039	4352	142
H(22A)	-566	2391	5167	144
H(22B)	-663	2374	6380	144
H(22C)	-223	1016	5823	144

ⁱ Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, 9, 165. (b) Gau, M.; House, H. O. *Org. Syn.* Collective Volume VI, 121.