Supporting Information

Direct Electrophilic Silylation of Terminal Alkynes

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NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) instrument. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Quantitative GC/MS analyses were carried out using calibration of the MSD versus *n*-pentadecane as an internal standard. Investigation of the reaction kinetics was performed by sampling aliquots from competitive experiments for quantitative GC/MS analysis directly from the reaction mixtures.

All manipulations with anhydrous zinc halides were conducted under an argon atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous solvents were stored in argon atmosphere over calcium hydride. Starting materials, terminal alkynes **1b**,¹ **1h**,² **1j**,³ **1k**,⁴ **1l**,⁵ were prepared according to the known procedures and their physical and spectral properties matched to those reported in literature. Preparation of compounds **4a-d** is described below. All other materials were commercially available.

Products **3a,c,e,m** are commercially available compounds. All properties of the obtained substances were identical to those for authentic samples purchased from commercial sources. Products **3b**,⁶ **d**,⁷ **f**,⁸ **h**,⁹ **i**,¹⁰ **5a**,¹¹ **5c**¹² are known compounds, which possessed all the same properties described in the literature.

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Syntheses of Aminosilanes 4:

4a: Oven-dried two-neck round bottomed flask equipped with reflux condenser and septum was loaded with palladium-black (50 mg), dry diethylamine (7.8 mL, 75 mmol), and dimethylphenylsilane (4.8 mL, 25 mmol). The mixture was refluxed for 24 hrs, then transferred via cannula into pre-dried 25 mL round bottomed flask and fractioned in vacuum. (Dimethylphenylsilyl)diethylamine was obtained as colorless oil, bp 88°C at 10 mm Hg. Yield 4.22 g (20.4 mmol), 82%. Spectral data recorded for this material were identical to those reported in literature.¹³

4b: Step 1. (Preparation of dimethyl(4-trifluoromethylphenyl)silane). 1-Bromo-4-trifluoromethylbenzene (2.5 mL, 4.08 g, 18 mmol) was added dropwise over 5 min to magnesium turnings (1.3 g, 54 mmol) stirred in anhydrous THF (45 mL) at 0°C. Chlorodimethylsilane (3 mL, 2.56 g, 27 mmol) was added, and the mixture was stirred at 0°C for 1 hr. Then, the mixture was diluted with hexane, washed with water and filtered through a short column of Silica gel. Hexane was distilled off under ambient pressure and the residual oil was distilled in vacuum (bp 100°C at 10 mm Hg) to give 3.07 g (15 mmol, 84%) of dimethyl(4-trifluoromethylphenyl)silane, identical to the material reported in literature.¹⁴ **Step 2.** (Preparation of **4b**). Oven dried two-neck round bottomed flask equipped with reflux condenser and septum was loaded with palladium-black (21 mg), dry diethylamine (3.7 mL, 36 mmol), and dimethyl(4-trifluoromethylphenyl)silane (2.44 g, 12 mmol). The mixture was stirred at reflux for 24 hr under argon atmosphere. Then the reaction mixture was siphoned through cannula into oven-dried 10 mL round bottomed flask and fractioned in vacuum. [Dimethyl(4-trifluoromethylphenyl)silyl]-diethylamine was obtained as colorless oil, bp 130°C at 4.5 mm Hg. Yield 2.07 g (7.5 mmol, 63%).

4c: Chlorotriethylsilane (3.0 mL, 18 mmol) was added to dry diethylamine (15 mL, 150 mmol) under argon atmosphere. The mixture was stirred for 5 min at room temperature, and then hexane (50 mL) was added. Formed precipitate was removed by filtration under argon atmosphere, the filtrate was concentrated under ambient pressure and the residue was fractioned in vacuum. (Triethylsilyl)diethylamine was obtained as colorless oil, bp 45°C at 3 mm Hg. Yield 2.59 g (13.9 mmol, 77%). Spectral data for this material were identical to those reported in literature.¹⁵

4d: To a stirred solution of diethylamine (1.7 mL, 16.5 mmol) in anhydrous ether (4.1 mL) *n*-butyllithium (2.5 M in hexanes, 6.6 mL, 16.5 mmol) was added dropwise at 0°C under argon atmosphere. The temperature was ramped to 20°C and a solution of TBSCl (2.26 g, 15 mmol) in dry ether (4.4 mL) was added dropwise. The mixture was stirred

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overnight, then filtered under argon and concentrated under ambient pressure. The residue was distilled in vacuum. Yield 1.69 g (9.0 mmol, 60%). Spectral data measured for this material were identical to those reported in literature.¹⁶

Typical Procedures for the Lewis Acid-Mediated Silylation of Terminal Alkynes.

Method A: An oven-dried 3 mL Wheaton microreactor was loaded with anhydrous zinc chloride (225 mg, 1.65 mmol) and dry 1,4-dioxane (1.0 mL). [Dimethyl(4-trifluoromethylphenyl)silyl]diethylamine (**4b**) (392 μ L, 1.2 mmol) and phenylacetylene (**1a**) (110 μ L, 1.0 mmol) were added and the reaction mixture was stirred at 100°C for 1 hr. Then, the mixture was quenched with cold diluted HCl and extracted with pentane. Combined organic phases were washed (water, brine), dried (MgSO₄), and concentrated in vacuum. Preparative column chromatography on Silica gel gave dimethylphenylethynyl(4-trifluoromethyl-phenyl)silane (**5b**) as a colorless oil. Yield 0.292 g (0.96 mmol, 96%).

¹H NMR (500.13 MHz, CDCl₃) δ 7.83 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.54-7.52 (m, 2H), 7.37-7.32 (m, 3H), 0.54 (s, 6H); ¹³C NMR (125.76 MHz) δ 142.5, 134.5 (+, 2C), 132.5 (+, 2C), 131.8 (q, ² J_{CF} = 32.2 Hz), 129.4 (+), 128.7 (+, 2C), 124.9 (+, q, ³ J_{CF} = 3.0 Hz, 2C), 124.6 (q, ¹ J_{CF} = 272.3 Hz), 123.0, 107.9, 91.3, -0.6 (+, 2C); GC/MS m/z 304 (M^+ , 22), 289 (M^+ -Me, 100).

Method B: An oven-dried three-neck round bottomed flask equipped with thermometer, addition funnel and reflux condenser, was loaded with dry 1,4-dioxane (80 mL) and anhydrous zinc chloride (22.44 g, 165 mmol). Exothermic reaction occurred, leading to the formation of amorphous light precipitate. N-Trimethylsilyldiethylamine (**2a**) (14.5 g, 100 mmol) was added dropwise to maintain the temperature of the reaction mixture below 40°C. Then, propargyl (2*E*)-but-2-enoate (**1k**) (12.41 g, 100 mmol) in dry 1,4-dioxane (20 mL) was added. Simultaneously the temperature of the reaction mixture was ramped to reach the boiling point. The mixture was refluxed for 2 hr, then cooled down and poured into mixture of crushed ice (200 g) and conc. HCl (40 mL). Organic phase was separated, washed with water and distilled in vacuum. Yield of **3k** 14.72 g (75 mmol, 75%).

3k: bp 87-88 °C (3 mm Hg); n_D^{20} 1.4605; d_4^{20} 1.019; ¹H NMR (80.02 MHz, CDCl₃) δ 7.05 (dq, J = 15.2 Hz, 6.4 Hz, 1H), 5.80 (dq, J = 15.2, 1.6 Hz, 1H), 4.73 (s, 2H), 1.90 (dd, J = 6.4 Hz, 1.6 Hz, 3H), 0.18 (s, 9H); Found, %: C 61.10, H 8.16, Si 14.14; Calculated for C₁₀H₁₆O₂Si, %: C 61.18, H 8.21, Si 14.31.

3j: ¹H NMR (80.02 MHz, CDCl₃) δ 4.82 (s, 2H), 0.09 (s, 9H);

3l: mp 52-53 °C; ¹H NMR (80.02 MHz, CDCl₃) δ 6.93 (s, 2H), 4.81 (s, 4H), 0.19 (s, 18H); Found, %: C 57.03, H 7.10, Si 16.32; Calculated for C₁₆H₂₄O₄Si₂, %: C 57.10, H 7.19, Si 16.69.

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Competitive kinetic experiments

Relative rates of the Lewis acid-mediated silylation reactions in series of p-substituted arylacetylenes were determined by competitive reactions in pairs **3a/3d**, **3c/3d**, **3e/3d**, **3m/3d**. Three equivalents of each terminal alkyne were employed in each competitive reaction to ensure pseudo-first order of the reaction kinetics.

In a typical experiment an oven-dried 3 mL Wheaton microreactor was loaded with anhydrous zinc chloride (138 mg, 1.02 mmol) and dry 1,4-dioxane (1 mL). N-Trimethylsilyldiethylamine (**2a**) (23 μ L, 0.12 mmol), phenylacetylene (**3a**) (33 μ L, 0.3 mmol), 4-ethynyltoluene (**3d**) (38 μ L, 0.3 mmol), and *n*-pentadecane (internal standard) were added, and the reaction mixture was stirred at 100°C for 1 hr. The relative ratios of the formed silylalkynes were determined by quantitative GC/MS analysis of the aliquots taken directly from the reaction mixtures.

Attempt on silylation of phenylacetylene under Carreira's conditions

A 1 mL oven-dried Wheaton microreactor was loaded with zinc triflate (33 mg, 0.1 mmol), (-)-N-methylephedrine (20 mg, 0.11 mmol). Toluene (0.5 mL), triethylamine (104 μ L, 0.75 mmol), chlorotrimethylsilane (82 μ L, 0.65 mmol), phenylacetylene (**1a**) (55 μ L, 0.5 mmol),¹⁷ and *n*-pentadecane (internal standard) were added, and the mixture was stirred overnight at 60°C. Analysis of the crude reaction mixture showed the formation ~10% (quantitative GC/MS) of compound **3a**. Analogous experiment in the absence of N-methylephedrine did not provide the formation of any **3a** at all.

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Current Data Parameters

NAME	cb0096
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20030404
Time	11.28
INSTRUM	spect
PROBHD	5 mm BBO BB-1
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	64
DW	83.200 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
P1	5.00 usec
SFO1	500.1327507 MHz
NUC1	1H
PL1	3.00 dB

F2 - Processing parameters

SI	16384
SF	500.1300130 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	10.100 ppm
F1	5051.31 Hz
F2P	-0.100 ppm
F2	-50.01 Hz
PPMCM	0.51000 ppm/cm
HZCM	255.06631 Hz/cm

Current Data Parameters

NAME	cb0096
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20030404
Time	11.39
INSTRUM	spect
PROBHD	5 mm BBO BB-1
PULPROG	zgpg3
TD	32768
SOLVENT	CDCl3
NS	256
DS	2
SWH	30303.031 Hz
FIDRES	0.924775 Hz
AQ	0.5407220 sec
RG	8192
DW	16.500 usec
DE	6.00 usec
TE	300.0 K
d11	0.03000000 sec
d12	0.00020000 sec
PL13	22.00 dB
D1	2.00000000 sec
CPDPRG2	waltz16
PCPD2	80.00 usec
SFO2	500.1320000 MHz
NUC2	13C
PL2	3.00 dB
PL12	22.00 dB
P1	3.80 usec
SFO1	125.7715724 MHz
NUC1	13C
PL1	3.00 dB

F2 - Processing parameters

SI	32768
SF	125.7577390 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	161.000 ppm
F1	22762.15 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCM	9.55000 ppm/cm
HZCM	1200.98633 Hz/cm