Supplementary Material (ESI) for Chemical Communications

$BiPh_3$ – A convenient synthon for heavy alkaline earth metal amides

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Supporting Information:

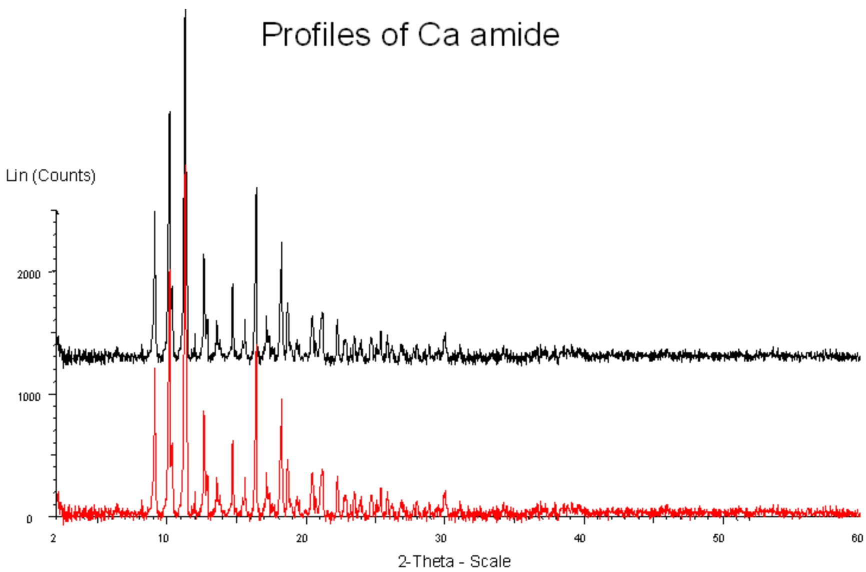
XRD Powder Profiles:

Powder X-ray Crystallography:

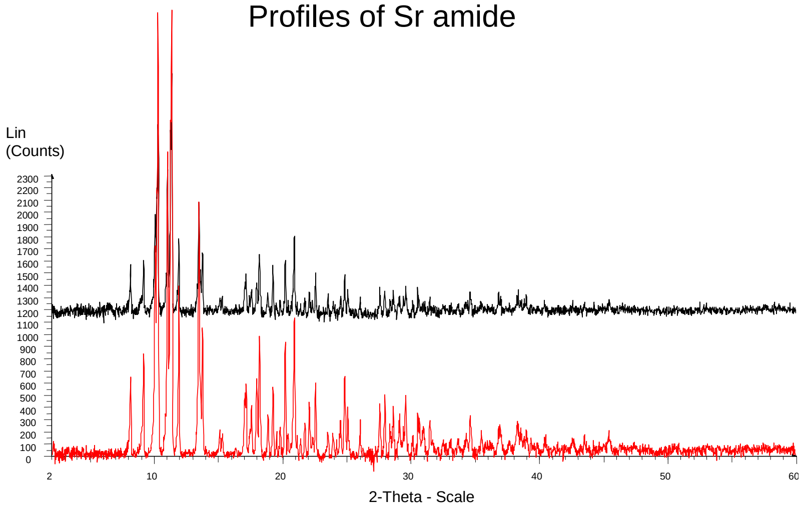
Powder patterns for the compounds were collected on a Bruker AXS D8 Advance automated diffractometer using Cu Kα radiation (λ = 1.54 Å). The finely ground sample was prepared in a capillary tube in the drybox and sealed with high vacuum silicone grease. The step size was 0.02° in 2θ, and the sample was collected under vacuum.

Compound	Powder Pattern Profiles that were compared	
$Ca\{N(SiMe_3)_2\}_2(THF)_2$, **1**	Salt Metathesis	Redox Transmetallation/ Ligand Exchange
$Sr\{N(SiMe_3)_2\}_2(THF)_2$, **2**	Salt Metathesis	Redox Transmetallation/ Ligand Exchange
$Ba\{N(SiMe_3)_2\}_2(THF)_2$, **3**	Direct Metallation via $NH_{3(l)}$ activation	Redox Transmetallation/ Ligand Exchange

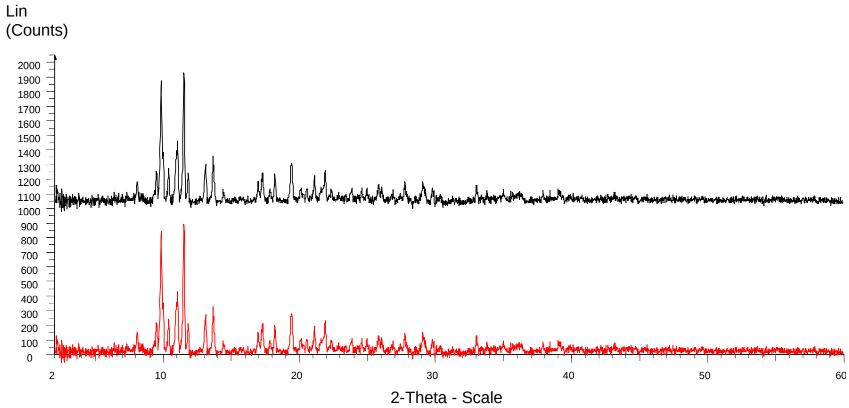
(1) Profile in red via Redox Transmetallation/ Ligand Exchange
(2) Profile in black either Salt Metathesis or Direct Metallation

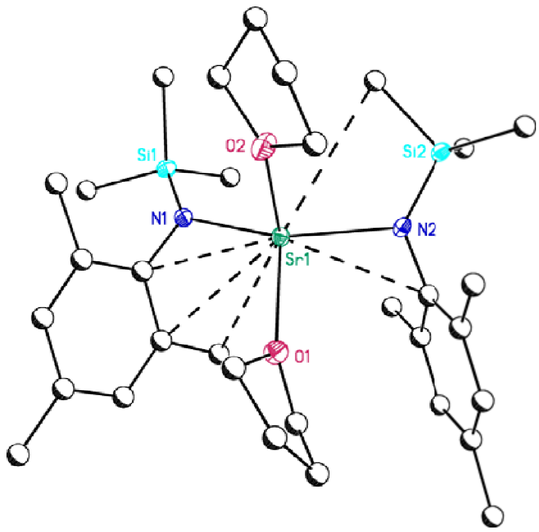


Profiles of Sr amide



Profiles of Ba amide





Graphical representation of compound **5**.

[1]H NMR (500 MHz, D_8-thf, 25 °C):

1: Ca{N($SiMe_3)_2\}_2$, δ 0.011 (s, 18H, $SiMe_3$);

2: Sr{N($SiMe_3)_2\}_2$, δ 0.012 (s, 18H, $SiMe_3$);

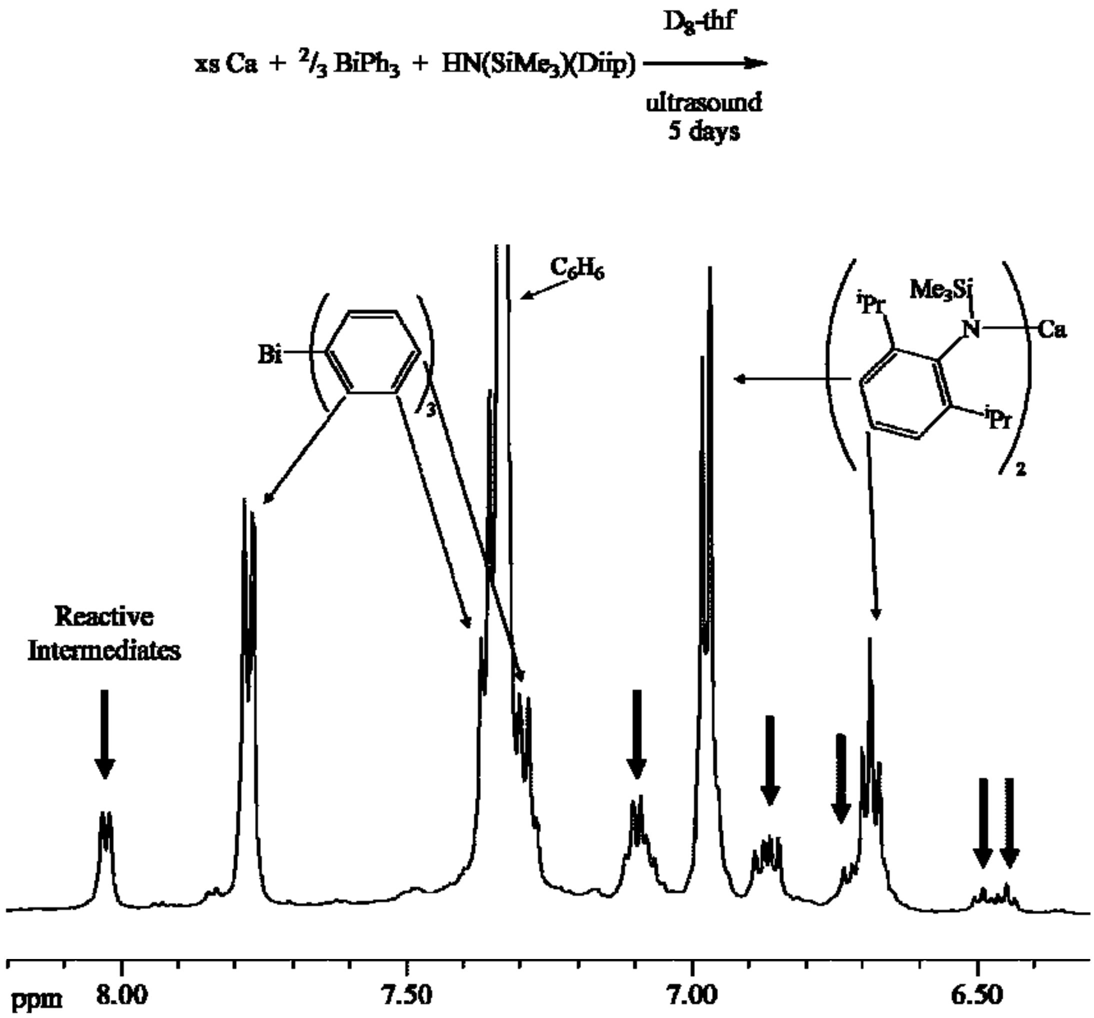
3: Ba{N($SiMe_3)_2\}_2$, δ 0.017 (s, 18H, $SiMe_3$).

[1]H NMR (500 MHz, D_8-thf, 25 °C):

7: Ca{N($SiMe_3$)(Dipp)}$_2$, δ 0.190 (s, 18H, $SiMe_3$), 1.234 (s, 24H, CH_3), 3.906 (m, 4H, CH), 6.705 (t, 2H, *p*-Ar-H), 6.989 (d, 4H, *m*-Ar-H), 7.337 (s, 12H, C_6H_6);

8: Sr{N($SiMe_3$)(Dipp)}$_2$, δ 0.195 (s, 18H, $SiMe_3$), 1.224 (s, 24H, CH_3), 3.893 (m, 4H, CH), 6.671 (t, 2H, *p*-Ar-H), 7.005 (d, 4H, *m*-Ar-H), 7.337 (s, 12H, C_6H_6);

9: Ba{N($SiMe_3$)(Dipp)}$_2$, δ 0.220 (s, 18H, $SiMe_3$), 1.212 (s, 24H, CH_3), 3.821 (m, 4H, CH), 6.664 (t, 2H, *p*-Ar-H), 7.032 (d, 4H, *m*-Ar-H), 7.337 (s, 12H, C_6H_6).


D8-thf
xs Ca + 2/3 BiPh3 + HN(SiMe3)(Diip)
ultrasound
5 days
C6H6
Bi
3
iPr
Me3Si
N
Ca
iPr
2
Reactive
Intermediates
ppm
8.00
7.50
7.00
6.50

[Sr{N(SiMe$_3$)(Mes)}$_2$.thf$_2$] 5

Bond Lengths (Å)

Sr(1)-N(2)	2.4276(16)	N(1)-Si(1)	1.6846(16)
Sr(1)-N(1)	2.4350(16)	N(2)-C(13)	1.396(2)
Sr(1)-O(1)	2.5025(14)	N(2)-Si(2)	1.6805(17)
Sr(1)-O(2)	2.5082(15)	Si(1)-C(10)	1.871(2)
Sr(1)-C(1)	2.8842(18)	Si(1)-C(11)	1.873(2)
Sr(1)-C(13)	3.1053(18)	Si(1)-C(12)	1.874(2)
Sr(1)-C(2)	3.2838(19)	Si(2)-C(22)	1.871(2)
Sr(1)-Si(2)	3.6530(7)	Si(2)-C(24)	1.878(2)
N(1)-C(1)	1.395(2)	Si(2)-C(23)	1.881(2)

Bond Angles (°)

N(2)-Sr(1)-N(1)	122.85(5)	N(1)-Sr(1)-C(2)	47.75(5)
N(2)-Sr(1)-O(1)	105.03(5)	O(1)-Sr(1)-C(2)	71.30(5)
N(1)-Sr(1)-O(1)	116.73(5)	O(2)-Sr(1)-C(2)	125.89(5)
N(2)-Sr(1)-O(2)	106.91(5)	C(1)-Sr(1)-C(2)	25.54(5)
N(1)-Sr(1)-O(2)	106.68(5)	C(13)-Sr(1)-C(2)	109.58(5)
O(1)-Sr(1)-O(2)	94.59(5)	C(1)-N(1)-Si(1)	127.36(13)
N(2)-Sr(1)-C(1)	142.34(5)	C(1)-N(1)-Sr(1)	93.74(11)
N(1)-Sr(1)-C(1)	28.86(5)	Si(1)-N(1)-Sr(1)	138.86(9)
O(1)-Sr(1)-C(1)	88.19(5)	C(13)-N(2)-Si(2)	129.93(13)
O(2)-Sr(1)-C(1)	106.95(5)	C(13)-N(2)-Sr(1)	105.41(11)
N(2)-Sr(1)-C(13)	25.68(5)	Si(2)-N(2)-Sr(1)	124.55(8)
N(1)-Sr(1)-C(13)	128.59(5)	N(1)-Si(1)-C(10)	111.99(10)
O(1)-Sr(1)-C(13)	81.62(5)	N(1)-Si(1)-C(11)	111.80(10)
O(2)-Sr(1)-C(13)	119.86(5)	C(10)-Si(1)-C(11)	107.54(12)
C(1)-Sr(1)-C(13)	132.63(5)	N(1)-Si(1)-C(12)	111.51(10)
N(2)-Sr(1)-C(2)	127.15(5)	C(10)-Si(1)-C(12)	107.85(12)

C(11)-Si(1)-C(12)	105.83(12)	C(22)-Si(2)-C(23)	105.31(12)
N(2)-Si(2)-C(22)	115.34(10)	C(24)-Si(2)-C(23)	106.90(12)
N(2)-Si(2)-C(24)	105.77(11)	C(4)-C(5)-C(6)	122.57(18)
C(22)-Si(2)-C(24)	107.44(13)	C(5)-C(6)-C(1)	120.31(17)
N(2)-Si(2)-C(23)	115.55(10)	N(2)-C(13)-Sr(1)	48.91(9)

Ba{N(MesSiMe$_3$)}$_2$.thf$_3$ 6

Bond Lengths (Å)

Ba(1)-N(2)	2.5716(17)	C(2)-C(7)	1.504(3)
Ba(1)-N(1)	2.6381(17)	C(3)-C(4)	1.384(4)
Ba(1)-O(1)	2.7539(16)	C(4)-C(5)	1.389(4)
Ba(1)-O(3)	2.7575(16)	C(4)-C(8)	1.512(3)
Ba(1)-O(2)	2.7728(15)	C(5)-C(6)	1.391(3)
Ba(1)-C(1)	3.205(2)	C(6)-C(9)	1.503(3)
N(1)-C(1)	1.387(3)	C(13)-C(14)	1.422(3)
N(1)-Si(1)	1.6754(19)	C(13)-C(18)	1.426(3)
N(2)-C(13)	1.398(3)	C(14)-C(15)	1.394(3)
N(2)-Si(2)	1.6869(18)	C(14)-C(19)	1.505(3)
Si(1)-C(10)	1.874(3)	C(15)-C(16)	1.388(3)
Si(1)-C(11)	1.877(3)	C(16)-C(17)	1.388(3)
Si(1)-C(12)	1.886(3)	C(16)-C(20)	1.512(3)
Si(2)-C(22)	1.866(3)	C(17)-C(18)	1.392(3)
Si(2)-C(23)	1.871(3)	C(18)-C(21)	1.511(3)
Si(2)-C(24)	1.873(3)	C(25)-C(26)	1.469(4)
O(1)-C(28)	1.443(3)	C(26)-C(27)	1.516(4)
O(1)-C(25)	1.444(3)	C(27)-C(28)	1.513(3)
O(2)-C(32)	1.443(3)	C(29)-C(30)	1.512(4)
O(2)-C(29)	1.446(3)	C(30)-C(31)	1.520(4)
O(3)-C(36)	1.438(3)	C(31)-C(32)	1.479(4)
O(3)-C(33)	1.442(3)	C(33)-C(34)	1.511(3)
C(1)-C(2)	1.421(3)	C(34)-C(35)	1.518(4)
C(1)-C(6)	1.425(3)	C(35)-C(36)	1.495(4)
C(2)-C(3)	1.399(3)		

Bond Angles (°)

N(2)-Ba(1)-N(1)	123.19(6)	C(29)-O(2)-Ba(1)	130.57(13)
N(2)-Ba(1)-O(1)	101.93(5)	C(36)-O(3)-C(33)	109.02(18)
N(1)-Ba(1)-O(1)	102.28(5)	C(36)-O(3)-Ba(1)	129.04(14)
N(2)-Ba(1)-O(3)	91.54(5)	C(33)-O(3)-Ba(1)	121.93(13)
N(1)-Ba(1)-O(3)	92.36(5)	N(1)-C(1)-C(2)	120.5(2)
O(1)-Ba(1)-O(3)	149.73(5)	N(1)-C(1)-C(6)	122.7(2)
N(2)-Ba(1)-O(2)	116.58(5)	C(2)-C(1)-C(6)	116.6(2)
N(1)-Ba(1)-O(2)	119.51(5)	N(1)-C(1)-Ba(1)	53.93(10)
O(1)-Ba(1)-O(2)	72.59(5)	C(2)-C(1)-Ba(1)	97.77(13)
O(3)-Ba(1)-O(2)	77.14(5)	C(6)-C(1)-Ba(1)	113.97(14)
N(2)-Ba(1)-C(1)	141.91(5)	C(3)-C(2)-C(1)	120.5(2)
N(1)-Ba(1)-C(1)	25.14(5)	C(3)-C(2)-C(7)	119.6(2)
O(1)-Ba(1)-C(1)	106.05(5)	C(1)-C(2)-C(7)	119.8(2)
O(3)-Ba(1)-C(1)	76.94(5)	C(4)-C(3)-C(2)	122.6(2)
O(2)-Ba(1)-C(1)	96.34(5)	C(3)-C(4)-C(5)	117.0(2)
C(1)-N(1)-Si(1)	131.46(15)	C(3)-C(4)-C(8)	121.9(2)
C(1)-N(1)-Ba(1)	100.93(12)	C(5)-C(4)-C(8)	121.1(2)
Si(1)-N(1)-Ba(1)	127.56(9)	C(4)-C(5)-C(6)	122.7(2)
C(13)-N(2)-Si(2)	124.74(14)	C(5)-C(6)-C(1)	120.5(2)
C(13)-N(2)-Ba(1)	100.38(12)	C(5)-C(6)-C(9)	119.9(2)
Si(2)-N(2)-Ba(1)	134.88(9)	C(1)-C(6)-C(9)	119.5(2)
N(1)-Si(1)-C(10)	107.20(11)	N(2)-C(13)-C(14)	121.91(19)
N(1)-Si(1)-C(11)	112.79(11)	N(2)-C(13)-C(18)	121.14(19)
C(10)-Si(1)-C(11)	109.56(13)	C(14)-C(13)-C(18)	116.80(19)
N(1)-Si(1)-C(12)	116.65(11)	C(15)-C(14)-C(13)	120.3(2)
C(10)-Si(1)-C(12)	104.85(12)	C(15)-C(14)-C(19)	119.1(2)
C(11)-Si(1)-C(12)	105.40(12)	C(13)-C(14)-C(19)	120.6(2)
N(2)-Si(2)-C(22)	107.85(11)	C(16)-C(15)-C(14)	122.7(2)
N(2)-Si(2)-C(23)	115.19(11)	C(15)-C(16)-C(17)	117.2(2)
C(22)-Si(2)-C(23)	107.40(15)	C(15)-C(16)-C(20)	121.3(2)
N(2)-Si(2)-C(24)	113.92(11)	C(17)-C(16)-C(20)	121.5(2)
C(22)-Si(2)-C(24)	107.47(14)	C(16)-C(17)-C(18)	122.5(2)
C(23)-Si(2)-C(24)	104.61(15)	C(17)-C(18)-C(13)	120.5(2)
C(28)-O(1)-C(25)	109.70(19)	C(17)-C(18)-C(21)	119.3(2)
C(28)-O(1)-Ba(1)	121.90(13)	C(13)-C(18)-C(21)	120.19(19)
C(25)-O(1)-Ba(1)	127.62(16)	O(1)-C(25)-C(26)	107.6(3)
C(32)-O(2)-C(29)	109.30(18)	C(25)-C(26)-C(27)	105.6(2)
C(32)-O(2)-Ba(1)	120.05(14)	C(28)-C(27)-C(26)	103.3(2)

O(1)-C(28)-C(27)	105.7(2)	O(3)-C(33)-C(34)	105.6(2)
O(2)-C(29)-C(30)	105.6(2)	C(33)-C(34)-C(35)	101.5(2)
C(29)-C(30)-C(31)	103.1(2)	C(36)-C(35)-C(34)	104.0(2)
C(32)-C(31)-C(30)	102.1(2)	O(3)-C(36)-C(35)	107.0(2)
O(2)-C(32)-C(31)	105.8(2)		

Relative costs of making $Ae(HMDS)_2$

Method 1

xs Ae + $^{2}/_{3}$ $BiPh_3$ + 2 $HN(SiMe_3)_2$
20 mmol $^{20}/_{3}$ mmol 20 mmol

Method 2

AeI_2 + 2 $KN(SiMe_3)_2$
10 mmol 20mmol

These calculations are based on US prices, using the cheapest reagent prices we were quoted on 26th May 2008. In method 1 a twofold excess of metal is calculated as this is the maximum (relative) quantity used. All calculations are based on reactions on a 10mmol scale, excluding solvents.

Ca $(HMDS)_2$

Method 1

Calcium Turnings 99.5%
Acros - USA
AC20138-5000 500g $150.50

Triphenylbismuth 98.0%
Shangai FWD Chemicals
K6245 1Kg $285.00

1,1,1,3,3,3-Hexamethyldisilazane [HMDS(H)] 98+ %
Alfa Aesar
A15139 2.5L $191.00

2 fold excess Ca (20mmol)	0.8018g	$0.24
$BiPh_3$ ($^{20}/_{3}$ mmol)	2.9352g	$0.84
$HN(SiMe_3)_2$ (20 mmol)	4.1702ml	$0.32
Total Cost		$1.40

Method 2

Calcium Iodide Anhydrous Beads, -10 mesh, 99.95%
Aldrich
516244 100g $145.00

Calcium Iodide Ultra dry, 99.99%, -10 mesh beads ampouled under Argon

Aldrich
43674 100g $274.00

Potassium Hexamethyldisilazide [K(HMDS)] 95 %
Aldrich
324671 100g $242.00

Anhydrous CaI_2

CaI_2 (10mmol)	2.9389g	$4.26	
$KN(SiMe_3)_2$ (20 mmol)	3.9896g	$9.65	
Total Cost			$13.92

Ultra dry CaI_2

CaI_2 (10mmol)	2.9389g	$8.05	
$KN(SiMe_3)_2$ (20 mmol)	3.9896g	$9.65	
Total Cost			$17.71

% Cost Method 1/ Method 2

Anhydrous CaI_2	10.06%
Ultra dry, under Argon	7.91%

$Sr(HMDS)_2$

Method 1

Strontium Granules 99% under Argon with thin layer Oil
Alfa Aesar
35789` 100g $200.00

Triphenylbismuth 98.0%
Shangai FWD Chemicals
K6245 1Kg $285.00

1,1,1,3,3,3-Hexamethyldisilazane [HMDS(H)] 98+ %
Alfa Aesar
A15139 2.5L $191.00

2 fold excess Sr (20mmol)	1.7524g	$3.50		
$BiPh_3$ ($^{20}/_3$ mmol)	2.9352g	$0.84		
$HN(SiMe_3)_2$ (20 mmol)	4.1702ml		$0.32	
Total Cost				$4.66

Method 2

Strontium Iodide Anhydrous Powder, 99.99%
Aldrich
466336 10g $195.50

Potassium Hexamethyldisilazide [K(HMDS)] 95 %
Aldrich
324671 100g $242.00

SrI_2 (10mmol)	3.4143g	$66.75	
$KN(SiMe_3)_2$ (20 mmol)	3.9896g	$9.65	
Total Cost			$76.40

% Cost Method 1/ Method 2 6.10%

$Ba(HMDS)_2$

Method 1

Barium Rods 99+%
Aldrich
237094 100g $108.50

Triphenylbismuth 98.0%
Shangai FWD Chemicals
K6245 1Kg $285.00

1,1,1,3,3,3-Hexamethyldisilazane [HMDS(H)] 98+ %
Alfa Aesar
A15139 2.5L $191.00

2 fold excess Ba (20mmol)	2.7466g	$2.98	
$BiPh_3$ ($^{20}/_3$ mmol)	2.9352g	$0.84	
$HN(SiMe_3)_2$ (20 mmol)	4.1702ml	$0.32	
Total Cost			$4.14

Method 2

Barium Iodide Anhydrous Beads, -10 mesh, 99.995%
Aldrich
413615 25g $371.00

Barium Iodide Ultra dry, 99.999%, -10 mesh beads ampouled under Argon
Aldrich
35679 25g $561.00

Potassium Hexamethyldisilazide [K(HMDS)] 95 %
Aldrich
324671 100g $242.00

Anhydrous BaI_2

BaI_2 (10mmol)	3.9114g	$58.05	
$KN(SiMe_3)_2$ (20 mmol)	3.9896g	$9.65	
Total Cost			$67.70

Ultra dry BaI_2

SrI_2 (10mmol)	3.9114g	$87.77	
$KN(SiMe_3)_2$ (20 mmol)	3.9896g	$9.65	
Total Cost			$97.43

% Cost Method 1/ Method 2

Anhydrous BaI_2	6.12%
Ultra dry, under Argon	4.25%

Metal	Method	Comment	Cost ($)	Relative cost	%
Calcium	1		1.40		-
Calcium	2a	Anhydrous	13.92	Method 1/ Method2a	10.06
Calcium	2b	Ultra Dry	17.71	Method 1/ Method 2b	7.91
Strontium	1		4.66		-
Strontium	2		76.40	Method 1/ Method 2	6.10
Barium	1		2.98		
Barium	2a	Anhydrous	67.70	Method 1/ Method2a	6.12
Barium	2b	Ultra Dry	97.43	Method 1/ Method 2b	4.25