Supporting Information

Conversion of a (sp^3)C-F Bond of Alkyl Fluorides to (sp^3)C-X (X=Cl, C, H, O, S, N) Bonds Using Organoaluminum Reagents

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General

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts are given in parts per million (d) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass analyses (EI) were run using a JEOL JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. Elemental analyses were performed on a Perkin Elmer 240C apparatus.

Experimental Procedures and Analytical Data of Products.

Hexadec-7-ene (**15**) [1a] CAS Registry Number: 18899-19-9, 35507-09-6, 74533-92-9

Into a hexane solution of di-iso-propyl-oct-1-enyl-aluminum formed by the reaction of 1-octyne (257.8 mg, 2.34 mmol) with DIBAL (1.9 mL, 2.4 mmol, 0.97 in hexane) was added 1-fluoroocatane (133.2 mg, 1.00 mmol) at 25 °C under nitrogen. After stirring for 6 h, the reaction mixture was quenched with 1N HCl at 0 °C. The mixture was warmed to 25 °C and a saturated $NaHCO_3$ solution (50 mL) was added. The product was extracted with ether (50 mL) extract with ether (15 ml). The organic layer was dried over $MgSO_4$, and evaporated to give a crude product (90 % GC yield [*E*/*Z*=91/9]). Purification by Silica gel column chromatography with hexane as the eluent afforded with 168 mg (75%) of **15**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37-5.40 (m, 2H), 1.94-1.99 (m, 4H), 1.26-1.37

(m, 20H), 0.86-0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.2, 32.7, 32.1, 31.9, 30.4, 30.3, 29.84, 29.79, 29.6, 29.5, 29.3, 29.0, 28.9, 22.8, 14.3.

Hexadec-7-yne (**16**)[1b] CAS Registry Number: 74685-28-2

Into a hexane solution of diethyl(1-octynyl)aluminum formed by the reaction of 1-octyne (245.0 mg, 2.2 mmol) with *n*-BuLi (2.4 mmol, 1.59 M in hexane) at -40 °C for 1 h followed by treatment with Et_2AlCl (2.3 ml, 2.1 mmol, 0.92M in hexane) at 25 °C and stirring for 2 h at 40 °C was added 1-fluoroocatane (133.2 mg, 1.00 mmol) at 25 °C under nitrogen. After stirring for 6 h, the reaction mixture was quenched with 1N HCl at 0 °C. The mixture was warmed to 25 °C and a saturated $NaHCO_3$ solution (50 mL) was added. The product was extracted with ether (50 mL) extract with ether (15 mL). The organic layer was dried over $MgSO_4$, and evaporated to give a crude product (94 % GC yield). Purification by Silica gel column chromatography with hexane as the eluent afforded with 328 mg (67%) of **16**. ^{1}H NMR (400 MHz,$CDCl_3$): 2.10-2.19 (m, 4H), 1.28-1.49 (m, 20H), 0.81-0.95 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 80.2, 32.0, 31.5, 29.6, 29.4, 29.34, 29.30, 29.0, 28.7, 22.84, 22.75, 18.9, 14.26, 14.22.

Octyloxy-benzene (**18**)[1c] CAS Registry Number: 1818-07-1

A hexane solution of ^{i}Bu$_2$Al-OPh was prepared by the reaction of phenol 746.3 mg (8.0 mmol) and DIBAH, 6.3 ml, 6.0 mmol, 0.97 M in hexane) at 70 °C for 2 h under nitrogen. To the mixture was added 1-fluoroocatane (266.2 mg, 2.01 mmol) at 25 °C. After stirring for 100 h at 25 °C, water was added at 0 °C. A similar work up to that mentioned above afforded the corresponding product **18** in 78% GC yield. ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.25-7.29 (m, 2H), 6.88-6.97 (m, 3H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.74-1.82 (m, 2H), 1.28-1.49 (m, 10H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 129.2, 120.3, 114.4, 67.9, 31.9, 29.5, 29.44, 29.38, 26.2, 22.8, 14.3.

(^{i}Bu$_2$Al-XPh, X= S, Se, Te)

^{i}Bu$_2$Al-SPh (**7**), ^{i}Bu$_2$Al-SePh (**8**), and ^{i}Bu$_2$Al-TePh (**9**) were prepared from corresponding diphenyldichalcogenide (PhX-XPh, X= S, Se, Te) and DIBAH following a reported procedure.

Octylsulfanyl-benzene (**19**)[1d] CAS Registry Number: 13910-16-2

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.53 (m, 5H), 2.91 (t, *J*=7.4 Hz, 2H), 1.61-1.68 (m, 2H), 1.27-1.43 (m, 10H), 0.88 (t, *J*=6.8 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 128.7, 128.6, 125.4, 33.7, 31.9, 29.3, 29.27, 29.25, 29.0, 22.8, 14.3.

Octylselanyl-benzene (**20**) [1e] CAS Registry Number: 72474-75-0

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46-7.51 (m, 2H), 7.21-7.27 (m, 3H), 2.90 (t, *J*=7.4 Hz, 2H), 1.66-1.75 (m, 2H), 1.26-1.49 (m, 10H), 0.87 (t, *J*=6.8Hz, 3H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 132.2, 130.6, 128.8, 126.4, 31.93, 30.3, 29.9, 29.3, 29.2, 28.1, 22.8, 14.27.

Octyltellanyl-benzene (**21**) [1f] CAS Registry Number: 13846-40-7

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.69-7.72 (m, 2H), 7.16-7.28 (m, 3H), 2.89 (t, *J*=8.0 Hz, 2H), 1.75-1.83 (m, 2H), 1.24-1.54 (m, 10H); 0.87 (t, *J* =7.0 Hz, 3H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 138.0, 128.9, 127.2, 111.7, 32.1, 31.9, 29.3, 29.0, 22.8, 14.3, 9.0.

Diethyloctyl amine (**22**) [1h] CAS Registry Number: 4088-37-3

^{1}H NMR (400 MHz, CDCl$_3$): δ 2.45 (q, *J*=7.2 Hz, 4H), 2.37-2.42 (m, 2H), 1.41-1.45 (m, 2H), 1.27-1.31 (m, 10H), 1.02 (t, *J*= 7.0 Hz, 6H) 0.88 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 53.0, 46.9, 32.0, 29.7, 29.4, 27.9, 27.0, 22.8, 14.3, 11.8.

α-d_1-β-Phenylethyl fluoride (**23**)

This compound was prepared following a reported procedure.[2]

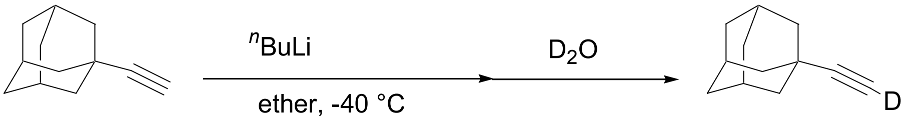
^{1}H NMR (400 MHz,CDCl$_3$): δ 3.03 (dd, $^{2}J_{\mathrm{F,H}}$=23.0 and $^{2}J_{\mathrm{H,H}}$=6.8 Hz, benzylic H), 4.62 (dd, $^{2}J_{\mathrm{F,H}}$=47.0 and $^{2}J_{\mathrm{H,H}}$=7.2 Hz , 1H, CDH), 7.24-7.36 (m, 5H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.3, 128.8, 128.5, 128.4, 126.5, 83.7 (t, $^{1}J_{\mathrm{CD}}$=23.2 Hz, $^{1}J_{\mathrm{F\text{-}C}}$=167 Hz), 36.9.

1-Ethynyladamantane (**27-1**) CAS Registry Number: 40430-66-8

This compound was prepared following a reported procedure. [1g]

^{1}H NMR (400 MHz, CDCl$_3$): δ 2.10 (s, 1H), 1.96 (s, 3H), 1.89 (s, 6H), 1.68-1.72 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 93.0, 66.6, 42.8, 36.4, 29.4, 28.0.

1-Deuterio-2-adamantane-ethyne (**27-4**)

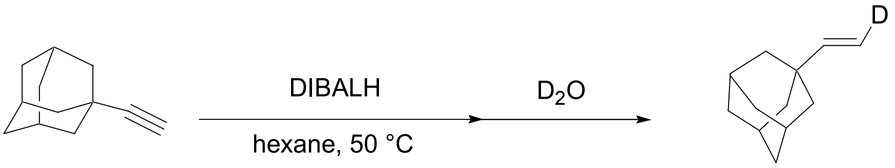


27-1 **27-4**

To dry ether solution (25 mL) of 1-ethynyladamantane (19.0 mmol, 3.02 g) was added *n*-butyllithium (23.0 mmol, 14.5mL, 1.6 M, in hexane) at -40 °C over a 30 min period. After stirring for 1 h at -40 °C, deuterium oxide (2 mL) was cautiously added. The product was extracted with ether (170 mL), dried over $MgSO_4$, and evaporated to give 2.86g (17.8 mmol) of **27-4**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (s, 3H), 1.89 (s, 6H), 1.68-1.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 93.0 (t, $^1J_{CD}$=7.3 Hz), 66.3 (t, $^1J_{CD}$=37.6 Hz), 42.8, 36.4, 36.2, 29.4, 28.0.

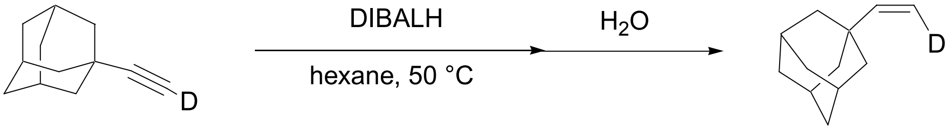
(*E*)-2-Adamantan-ethen -*1-d₁* (**27-2**)



27-1 **27-2**

To dry ether solution (25 mL) of 1-ethynyladamantane (9.9 mmol, 1.62 g) was added DIBALH (11.3 mmol, 11.5 mL, 0.95 M, in hexane) at 25 °C. After stirring for 4 h at 50 °C, deuterium oxide (2 mL) was cautiously added. The product was extracted with ether (170 mL), dried over $MgSO_4$, evaporated. Purification by silica gel column chromatography (1% Et_2O in hexane) afforded 8.65 mmol (1.41 g) of **27-2**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.70 (d, *J*=17.6 Hz, 1H), 4.84 (d, *J*=17.6 Hz, 1H), 1.99 (s, 3H), 1.54-1.74 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz); δ 149.7, 108.6 (t, $^1J_{CD}$=95.4 Hz), 42.1, 37.0, 35.6, 28.6.

(*Z*)- 2-Adamantan-ethen -*1-d₁* (**27-5**)

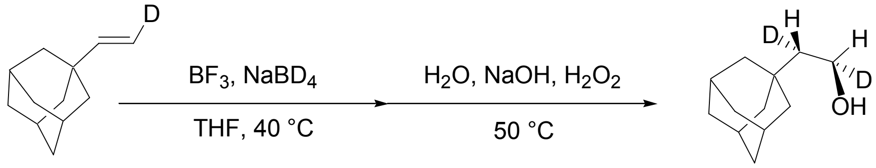


27-4 **27-5**

To dry ether solution (25 mL) of 1-deuterio-2-adamantane-ethyne (10.0 mmol, 1.63 g) was added DIBALH (11.3 mmol, 11.5 mL, 0.95 M, in hexane) at 25 °C. After stirring for 4 h at 50 °C, water (2 mL) was cautiously added. The product was extracted with ether (170 mL), dried over $MgSO_4$, evaporated. Purification by silica gel column chromatography (1% Et_2O in hexane) afforded 9.32 mmol

(1.52 g) of **27-5**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.69 (d, *J*=10.6 Hz, 1H), 4.83 (d, *J*=10.6 Hz, 1H), 1.99 (s, 3H), 1.58-1.96 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 108.6 (t, $^1J_{CD}$=93.4 Hz), 42.0, 37.0 35.6, 28.6.

erythro-2-Adamantan-1-yl-ethanol-*1,2-d₂* (**27-3**)

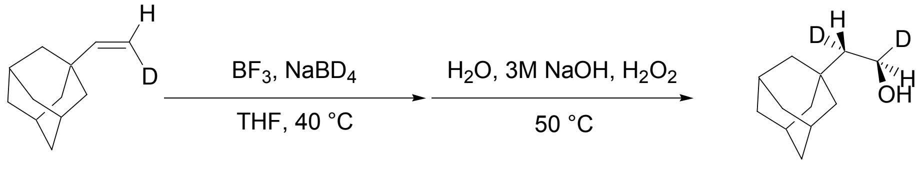


27-2

27-3 erythro

To THF suspension (8 mL) of $NaBD_4$ (8.85 mmol, 370.2 g) and (*E*)-2-adamantan-ethene-*1-d₁* (7.9 mmol, 1.29 g) was added boron trifluoride etherate (11.9 mmol, 1.5 mL) at 25 °C over 20 min. The resulting suspension was heated to 40 ºC and stirred for 3 h. The reaction mixture was then cooled to 0 °C, and water (2.5 mL) was added drop wise cautiously, followed by 3 M NaOH (3.0 mL), and then 30% hydrogen peroxide (3.0 mL; drop wise). The resulting reaction mixture heated to 50 ºC for 2 h. NaCl was then added to the reaction mixture and the organic layer was extracted with ether, washed with brine (3 x 20 mL), and dried over $MgSO_4$. The solvent was removed, and the product was purified by purified using neutral silica gel column (40% Et_2O in hexane) and obtained pure, white solid alcohol as 6.03 mmol (1.1 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.67 (d, *J*=9.2 Hz, 1H), 1.89-1.99 (brs 3H), 1.65-1.69 (m, 6H), 1.50-1.54 (brs, 6H), 1.35 (d, *J*=9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 58.1 (t, $^1J_{CD}$ = 85.2 Hz), 46.6 (t, $^1J_{CD}$ = 75.2 Hz), 42.7, 37.1, 31.8, 28.7; *m/z* (relative intensity, %) 182 (1), 164 (0.2), 152 (11), 136 (11), 135 (100), 107 (8), 93 (12), 81 (3), 79 (10), 67 (4); HRMS calcd for $C_{12}H_{18}D_2O$ 182.1638, found 182.1644.

threo-2-Adamantan-1-yl-ethanol-*1,2-d₂* (**27-6**)

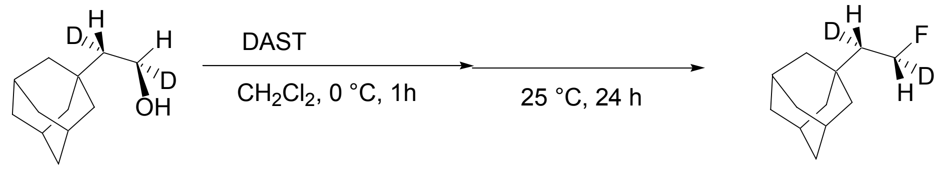


27-5

27- 6 threo

The (*Z*)-2-adamantan-ethene-*1-d*$_1$ was treated in the manner described above for (*E*)-2-adamantan-ethene-*1-d*$_1$ using as alkene to give 1.81 g (9.9 mmol) of the corresponding alcohol as colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.69 (d, J = 5.4 Hz, 1H), 1.94 (brs 3H), 1.62-1.77 (m, 6H), 1.50-1.54 (brs, 6H) 1.35 (d, J=5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 58.1 (t, $^1J_{CD}$=85.2 Hz), 46.6 (t, $^1J_{CD}$=75.2 Hz), 42.7, 37.1, 31.8, 28.7; *m/z* (relative intensity, %) 182 (1), 164 (0.2), 152 (11), 136 (11), 135 (100), 107 (8), 93 (12), 81 (3), 79 (10), 67 (4); HRMS calcd for $C_{12}H_{18}D_2O$ 182.1638, found 182.1647.

threo-1-(2-Fluoro-ethyl)-adamantane-*1,2-d*$_2$ (**27b**)

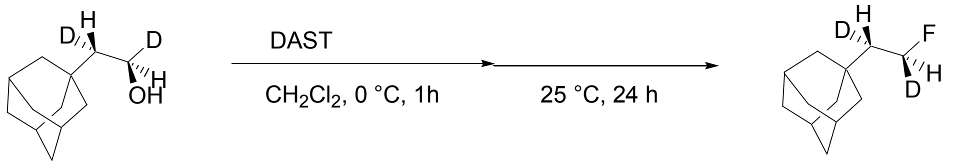


27-3 erythro

27b threo (J = 6.6 Hz)

To dry CH_2Cl_2 solution (15 mL) of alcohol **27-3** (5.4 mmol, 1.0 g) was added DAST, diethyl aminosulphur trifluoride (8.25 mmol, 1.33g, 0.98 mL) by syringe under argon at 0 °C. The mixture was stirred at 0 °C for 1 h followed by stirring for 24 h at 25 °C and then quenched with cold water. Extracted by CH_2Cl_2 and washed organic layer with $NaHCO_3$ solution and dried over $MgSO_4$. A crude yellow product was obtained and purified by silica gel column chromatography with hexane as an eluent to give the corresponding fluoride as colorless liquid 0.623 g (3.38 mmol). ^{1}H{^{2}H}NMR ($CDCl_3$, 750 MHz): δ 4.5 (dd, $^1J_{F\text{-}H}$=47.3 Hz, $J_{H\text{-}H}$=6.6 Hz, 1H), 1.95 (brs 3H), 1.72-1.62 (m, 6H), 1.50-1.54 (m, 6H), 1.47 (dd, $^1J_{F\text{-}H}$ = 26.3 Hz, $J_{H\text{-}H}$=6.6 Hz, 1H); ^{13}C ($CDCl_3$, 100 MHz): δ 80.6 (dt, $^1J_{CD}$=22.7 Hz, $^1J_{F\text{-}C}$=160.9 Hz), 43.83 (dt, $^1J_{CD}$= 18.7 Hz, $^2J_{F\text{-}C}$= 22.7 Hz), 42.7, 37.1, 31.7, 28.7; *m/z* (relative intensity, %) 184 (4), 136 (11), 135 (100), 107 (7), 93 (10), 81 (3) 79 (10), 67 (4); HRMS calcd for $C_{12}H_{17}D_2F$ 184.1594, found 184.1590.

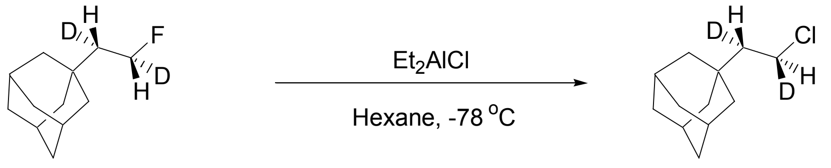
erythro-1-(2-Fluoro-ethyl)-adamantane-*1,2-d₂* (**27a**)



27- 6 threo **27a** erythro (*J* = 6.6 Hz)

The *threo*-2-adamantan-1-yl-ethanol-*1,2-d₂* was treated in the manner described above for *erythro*-2-adamantan-1-yl-ethanol-*1,2-d₂* using as alcohol to give 0.98 g (5.32 mmol) of the corresponding fluoride as colorless liquid. $^1H\{^2H\}$ NMR ($CDCl_3$, 750 MHz): δ 4.5 (dd, $^1J_{F\text{-}H}$=47.3 Hz, $J_{H\text{-}H}$=6.6 Hz, 1H), 1.95 (brs 3H), 1.72-1.62 (m, 6H), 1.50-1.54 (m, 6H), 1.47 (dd, $^1J_{F\text{-}H}$ = 26.3 Hz, $J_{H\text{-}H}$=6.6 Hz, 1H); ^{13}C ($CDCl_3$,100 MHz): δ 80.6 (dt, $^1J_{CD}$ = 22.7 Hz, $^1J_{F\text{-}C}$ = 160.9 Hz), 43.8 (dt, $^1J_{CD}$ = 18.8 Hz, $^2J_{F\text{-}C}$ = 22.7 Hz), 43.5, 37.1, 31.7, 28.7. *m/z* (relative intensity, %) 184 (4), 136 (11), 135 (100), 107 (7), 93 (10), 81 (3), 79 (9), 67(4); HRMS calcd for $C_{12}H_{17}D_2F$ 184.1594, found 184.1580.

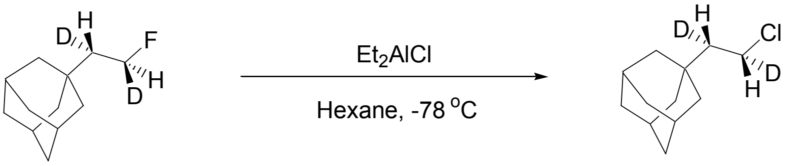
erythro-1-(2-Chloro-ethyl)-adamantane-*1,2-d₂* (**D3-51**)



threo **27b** *erythro* **D3-51**

To a hexane solution (1 mL) of Et_2AlCl (0.46 mmol, 0.46 M) was added 50.6 mg (0.27 mmol) *threo*-1-(2-Fluoro-ethyl)-adamantane-*1,2-d₂* under nitrogen at -78 °C. The reaction mixture was stirred for 4h. Then reaction mixture was then cooled in an ice bath, and water (1 mL) was added drop wise and extracted with ether (5 mL x 3), organic layer was dried over $MgSO_4$. The solvents were removed, and the product was obtained by silica gel column chromatography with hexane as an eluent to give 19.0 mg (0.1 mmol) of the corresponding chloride (**D3-51**).$^1H\{^2H\}$ NMR ($CDCl_3$, 750 MHz): δ 3.52 (d, $J_{H\text{-}H}$ =11.3 Hz, 1H), 1.95 (brs, 3H), 1.71-1.61 (m, 4H), 1.58 (3.52 (d, $J_{H\text{-}H}$=11.3 Hz, 1H), 1.51 (brs, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 47.0 (t, $^1J_{CD}$=19.5 Hz), 42.3, 40.4 (t, $^1J_{CD}$=22.5 Hz), 37.1, 32.9, 28.6; MS (EI) *m/z* (relative intensity, %) 200 (M^+, 2), 164 (0.2), 136 (11), 135 (100), 107 (6), 93 (8), 79 (8), 67 (3); HRMS calcd for $C_{12}H_{17}D_2Cl$ 200.1299, found 200.1308.

threo-1-(2-Chloro-ethyl)-adamantane-*1,2-d*$_2$ (**D3-50**)



erythro **27a** *threo* **D3-50**

The *erythro* diastereomer was treated in the manner described above for the *threo* isomer. ^{1}H{^{2}H} ($CDCl_3$, 750 MHz): δ 3.52 (d, $J_{H\text{-}H}$=11.3 Hz, 1H), 1.95 (brs, 3H), 1.71-1.61 (m, 4H), 1.58 (3.52 (d, $J_{H\text{-}H}$=11.3 Hz, 1H), 1.51 (brs, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 47.0 (t, $^{1}J_{CD}$=19.5 Hz), 42.3, 40.4 (t, $^{1}J_{CD}$=22.5 Hz), 37.1, 32.9, 28.7; *m/z* (relative intensity, %) 200 (M^+, 1.4), 164 (0.1),136 (11), 135 (100), 107 (6), 93 (8), 79 (8), 67 (3); HRMS calcd for $C_{12}H_{17}D_2Cl$ 200.1299, found 200.1295.

Registry No of known products

The following compounds are known and their spectral data (^{1}H NMR, ^{13}C NMR) were consistent with those previously reported.

Hexadec-7-ene (**15**) [1a] CAS Registry Number: 18899-19-9, 35507-09-6, 74533-92-9
Hexadec-7-yne (**16**) [1b] CAS Registry Number: 74685-28-2
Octyloxy-benzene (**18**) [1c] CAS Registry Number: 1818-07-1
Octylsulfanyl-benzene (**19**) [1d] CAS Registry Number: 13910-16-2
Octylselanyl-benzene (**20**) [1e] CAS Registry Number: 72474-75-0
Octyltellanyl-benzene (**21**) [1f] CAS Registry Number: 13846-40-7
Diethyloctyl amine (**22**) [1h] CAS Registry Number: 4088-37-3
1-Ethynyladamantane (**27-1**) CAS Registry Number: 40430-66-8

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