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Supporting Information

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A Novel Tandem Semipinacol rearrangement/ Alkylation of α-Epoxy Alcohols: Efficient and Stereoselective Approach to Multifunctional 1,3-Diols

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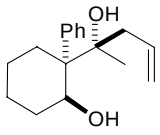
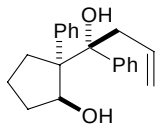
General: All anhydrous solvents ($Cl(CH_2)_2Cl$, Et_2O, CH_2Cl_2 and THF) were dried by standard techniques and freshly distilled before use. Allylboronic acid, allenylboronic acid and Samarium(II) diiodide (SmI_2) were prepared according to the literature respectively. All reactions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates. The distillation range of light petroleum is 60-80 ^oC. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution (unless otherwise noted) on an Avance DRX-200Hz or Varian Mercury-plus 300BB instruments Spectral data are reported in ppm relative to tetramethylsilane (TMS) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI or EI Technique.

Spectroscopic, crystallographic and analytical data of the products



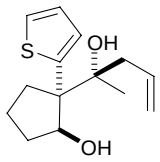
product **2a**

^{1}H NMR (200MHz, $CDCl_3$): δ =7.34-7.25 (m, 5H), 6.02-5.81 (m, 1H), 5.13-5.00 (m, 3H), 2.81-2.71 (m, 1H), 2.48-2.18 (m, 3H), 1.63-1.26 (m, 6H), 0.83 ppm (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$): δ =140.9, 134.8, 127.7 (4C), 126.1, 118.6, 77.9, 70.5, 51.0, 40.5, 29.5, 22.6, 22.4, 21.5, 19.5 ppm; HRMS (ESI) Calcd for $C_{17}H_{24}O_2Na$ [M^++Na]: 283.1669, found: 283.1669.



product **2b**

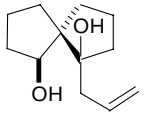
^{1}H NMR (200MHz, $CDCl_3$): δ =7.55-6.39 (m, 10H), 5.46-5.35 (m, 1H), 5.27-5.07 (m, 3H), 3.26 (dd, *J*=13.6, 4.6 Hz, 1H), 2.98 (dd, *J*=13.8, 8.6 Hz, 1H), 2.85-2.69 (m, 1H), 1.91-1.21 ppm (m, 5H); ^{13}C NMR (50MHz, $CDCl_3$): δ =142.4, 139.9, 134.0, 127.5 (4C), 127.3 (4C), 126.7, 126.6, 120.2, 79.9, 78.9, 62.1, 41.9, 33.3, 26.4, 18.7 ppm; HRMS (ESI) Calcd for $C_{21}H_{24}O_2Na$ [M^++Na]: 331.1669, found: 331.1670.



product **2c**

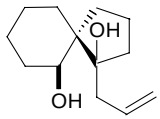
^{1}H NMR (200MHz, $CDCl_3$): δ =7.25-7.17 (m, 1H), 6.97-6.93 (m, 2H), 6.02-5.85 (m, 1H),

5.16-5.05 (m, 2H), 4.84 (brs, 1H), 2.82-2.51 (m, 2H), 2.25-1.25 (m, 6H), 1.01 ppm (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$): δ =147.6, 134.4, 126.4, 125.7, 123.7, 118.6, 80.8, 76.3, 60.7, 42.7, 33.9, 29.9, 25.0, 19.9 ppm; HRMS (ESI) Calcd for $C_{14}H_{24}O_2SN$ [M^++NH_4]: 270.1522, found: 270.1523.



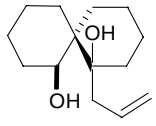
product **2d**

^{1}H NMR (300MHz, $CDCl_3$): δ =6.02-5.94 (m, 1H), 5.18-5.10 (m, 2H), 4.05 (s, 1H), 2.60-2.49 (m, 1H), 2.36-2.19 (m, 2H), 1.97-1.06 ppm (m, 11H); ^{13}C NMR (75MHz, $CDCl_3$): δ =134.6, 118.1, 81.7, 79.2, 58.3, 40.2, 33.8, 33.7, 32.2, 28.0, 19.6, 17.4 ppm; HRMS **(**ESI**)** Calcd for $C_{24}H_{41}O_2$ [$2M^+$+H]: 393.2999, found: 393.3010.



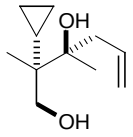
product **2e**/**2e′**

major product **2e**: ^{1}H NMR (300MHz, $CDCl_3$): δ =6.06-5.94 (m, 1H), 5.18-5.10 (m, 2H), 3.89 (s, 1H), 2.55 (dd, *J*=13.1, 6.3 Hz, 1H), 2.22 (dd, *J*=13.8, 8.1 Hz, 1H), 2.02-1.07 ppm (m, 14H); ^{13}C NMR (75MHz, $CDCl_3$): δ =135.0, 118.2, 83.4, 71.8, 48.6, 39.2, 32.2, 30.8, 29.0, 23.7, 21.4, 19.3, 17.5 ppm; minor product **2e′**: ^{13}C NMR (75MHz, $CDCl_3$): δ =135.2, 118.0, 84.6, 71.2, 50.4, 42.6, 37.6, 34.1, 30.6, 27.8, 22.0, 20.6, 19.3 ppm; HRMS (ESI) Calcd for $C_{13}H_{22}O_2Na$ [M^++Na]: 233.1512, found: 233.1511.



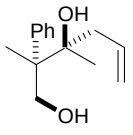
product **2f**

^{1}H NMR (200MHz, $CDCl_3$): δ =6.01-5.86 (m, 1H), 5.30-5.10 (m, 2H), 3.86 (brs, 1H), 2.68-2.47 (m, 2H), 2.25-0.85 ppm (m, 16H); ^{13}C NMR (50MHz, $CDCl_3$): δ =134.6, 117.8, 77.1, 72.9, 42.5, 37.2, 31.0, 29.0, 27.8, 22.4, 20.7, 20.4, 19.9, 19.4 ppm; HRMS (ESI) Calcd for $C_{14}H_{24}O_2Na$ [M^++Na]: 247.1669, found: 247.1665.



product **2g′**

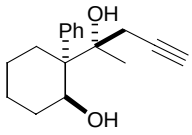
^{1}H NMR (200MHz, $CDCl_3$): δ =6.01-5.93 (m, 1H), 5.23-5.11 (m, 2H), 3.64, 3.62 (ABq, *J*=10.5 Hz, 2H), 2.46-2.33 (m, 2H), 1.29 (s, 3H), 1.06-0.98 (m, 1H), 0.54 (s, 3H), 0.44-0.35 ppm (m, 4H); ^{13}C NMR (50MHz, $CDCl_3$): δ =134.2, 119.2, 78.7, 70.0, 42.4, 41.6, 22.4, 13.1, 12.1, 1.8, -0.9 ppm; HRMS (ESI) Calcd for $C_{22}H_{41}O_4$ [$2M^+$+H]: 369.2999, found: 369.3003.



product **2h′**

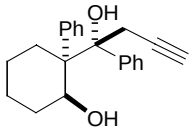
^{1}H NMR (300MHz, CD_3COCD_3): δ =7.55-7.51 (m, 2H), 7.31-7.26 (m, 2H), 7.21-7.16 (m, 1H), 5.96-5.82 (m, 1H), 4.98-4.86 (m, 2H), 4.28, 3.94 (ABq, *J*=10.5 Hz, 2H), 2.46 (dd, *J*=13.5, 4.5 Hz, 1H), 1.92 (dd, *J*=14.1, 8.7 Hz, 1H), 1.52 (s, 3H), 1.08 ppm (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ =142.5, 134.1, 128.4 (2C), 128.0 (2C), 126.6, 118.9, 76.6, 68.3, 49.6, 41.7, 22.9, 18.8 ppm; HRMS (ESI) Calcd for $C_{14}H_{24}O_2N$ [M^++NH_4]: 238.1802, found:

238.1803.



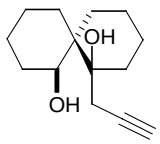
product **3a**

^{1}H NMR (300MHz, $CDCl_3$): δ=7.32-7.22 (m, 5H), 5.04 (brs, 1H), 2.96 (d, *J*=16.5 Hz, 1H), 2.49-2.05 (m, 3H), 2.04 (t, *J*=2.4 Hz, 1H), 1.74-1.26 (m, 6H), 1.03 ppm (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ=140.3, 128.0 (4c), 126.4, 81.5, 77.4, 71.2, 70.5, 50.6, 29.4, 27.9, 23.0, 22.6, 21.4, 19.3 ppm; HRMS (ESI) Calcd for $C_{17}H_{22}O_2Na$ [M^++Na]: 281.1512, found: 281.1509.



product **3b**

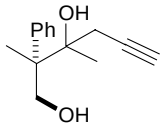
^{1}H NMR (300MHz, $CDCl_3$): δ=7.57-6.24 (m, 10H), 5.16 (brs, 1H), 3.29 (dd, *J*=16.2, 2.7 Hz, 1H), 3.11 (dd, *J*=16.2, 2.7 Hz, 1H), 2.59-2.48 (m, 1H), 1.78 (t, *J*=2.7 Hz, 1H), 1.86-1.09 ppm (m, 7H); ^{13}C NMR (75MHz, $CDCl_3$): δ=140.8, 139.1, 131.2 (2C), 127.9 (2C), 127.6 (2C), 127.3 (2C), 126.8, 126.6, 82.3, 80.9, 71.5, 70.8, 51.6, 29.8, 27.5, 22.6, 21.0, 19.1 ppm; HRMS (ESI) Calcd for $C_{22}H_{28}O_2N$ [M^++NH_4]: 338.2115, found: 338.2119.



product **3c**

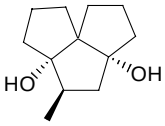
^{1}H NMR (300MHz, CD_3COCD_3): δ=3.74 (brs, 1H), 2.78 (dd, *J*=16.5 Hz, 2.4Hz, 1H), 2.66 (dd, *J*=16.5, 2.4 Hz, 1H), 2.32 (t, *J*=2.4 Hz, 1H), 2.07-1.83 (m, 4H), 1.68-1.28 ppm (m, 12H);

^{13}C NMR (75MHz, CD_3COCD_3): δ=82.2, 75.9, 72.6, 71.1, 42.3, 30.8, 29.0, 28.0, 24.9, 22.8, 21.2, 20.6, 20.1, 19.6 ppm; HRMS (ESI) Calcd for $C_{14}H_{22}O_2Na$ [M^++Na]: 245.1512, found: 245.1510.



product **3d**/**3d′**

^{1}H NMR (300MHz, $CDCl_3$, **3d**/**3d′** mixed): δ=7.49-7.23 (m, 10H), 4.28 (dd, *J*=11.1, 5.4 Hz, 1H), 4.19 (dd, *J*=11.1, 6.6 Hz, 1H), 4.11 (dd, *J*=11.1, 4.2 Hz, 1H), 4.00 (dd, *J*=11.4, 4.8 Hz, 1H), 2.67 (dd, *J*=16.2, 1.8 Hz, 1H), 2.53-2.44 (m, 5H), 2.21 (dd, *J*=18.9, 1.8 Hz, 1H), 2.17 (dd, *J*=18.9, 1.8 Hz, 1H), 2.07 (t, *J*=1.8 Hz, 1H), 2.03 (t, *J*=1.8 Hz, 1H), 1.53 (s, 3H), 1.51 (s, 3H), 1.35 (s, 3H), 1.29 ppm (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ=142 (2C), 128.3 (4C), 128.1 (4C), 126.9 (2C), 80.8, 77.2, 76.0, 75.8, 71.9, 71.8, 68.2 (2C), 49.1 (2C), 29.4, 29.1, 23.4, 23.2, 19.1, 18.5 ppm;



product **5**

^{1}H NMR (300MHz, $CDCl_3$): δ=2.02-1.48 (m, 12H), 1.32-1.24 (m, 3H), 1.00 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (75MHz, $CDCl_3$): δ=91.0, 86.4, 64.0, 46.2, 44.8, 40.6, 36.7, 35.9, 35.2, 24.9, 24.6, 13.6 ppm; HRMS (EI) Calcd for $C_{12}H_{20}O_2$ [M^+]: 196.1463, found: 196.1467.

The ^{1}H NMR NOE experiment of the acetonide or benzylidene acetal of the major products and the minor products (the key spatial correlations were demonstrated in Figures 1–6)

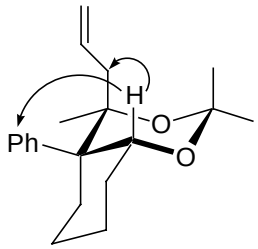


Figure 1. the acetonide of **2a**

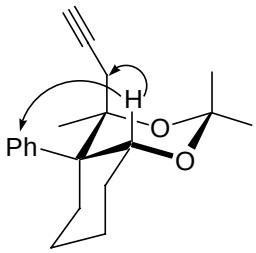


Figure 2. the acetonide of **3a**

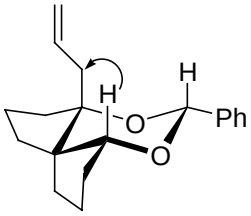


Figure 3. the benzylidene acetal of **2d**

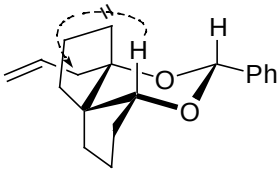


Figure 4. the benzylidene acetal of **2d′**

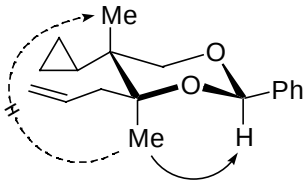


Figure 5. the benzylidene acetal of **2g′**

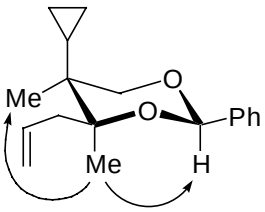


Figure 6. the benzylidene acetal of **2g**

2. The crystal structure of product **2f**

Table 1. Crystal data and structure refinement for **2f**.

Identification code	**2f**
Empirical formula	C14 H24 O2
Formula weight	224.33
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 7.205(1) A alpha = 90 deg.

	b = 20.662(3) A beta = 107.57(1) deg.
	c = 9.241(2) A gamma = 90 deg.
Volume, Z	1311.5(4) A^3, 4
Density (calculated)	1.136 Mg/m^3
Absorption coefficient	0.073 mm^-1
F(000)	496
Crystal size	0.58 x 0.56 x 0.46 mm
Theta range for data collection	1.97 to 25.25 deg.
Limiting indices	0<=h<=8, 0<=k<=24, -11<=l<=10
Reflections collected	2754
Independent reflections	2374 [R(int) = 0.0121]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2374 / 0 / 162
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0899
R indices (all data)	R1 = 0.0553, wR2 = 0.0953
Extinction coefficient	0.057(4)
Largest diff. peak and hole	0.206 and -0.122 e.A^-3