

Supporting Information
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An entry to carbapenem antibiotics scaffold via asymmetric Kinugasa reaction

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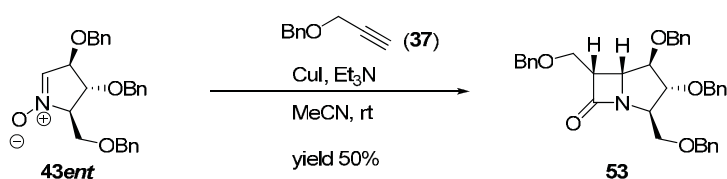
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SUPPORTING INFORMATIONS

General: ^1H and ^{13}C NMR spectra were recorded on a Varian-NMR-vnmrs 600 spectrometer using deuterated solvents and TMS as an internal standard. Chemical shifts are reported as δ values in ppm and coupling constants are in Hertz. Infrared spectra were recorded on a FT-IR-1600 Perkin-Elmer spectrophotometer. The optical rotations were measured on JASCO P-2000 digital polarimeter. High-resolution mass spectra were recorded on ESI-TOF Mariner Spectrometer (Perspective Biosystem). Thin layer chromatography was performed on aluminium sheet Silica Gel 60 F254 (20x20x0.2) from Merck. Column chromatography was carried out using Merck silica gel (230-400 mesh). HPLC chromatography was carried out on Hitachi Chromatograph with DAD detector equipped with LiChrospher[®] Si60 analytical column (250x4.6, 5 μm).



(2R,3R,4R,5R,6S)-3,4-di(benzyloxy)-2,6-di(benzyloxymethyl)-1-azabicyclo[3.2.0]heptan-7-one (**53**)

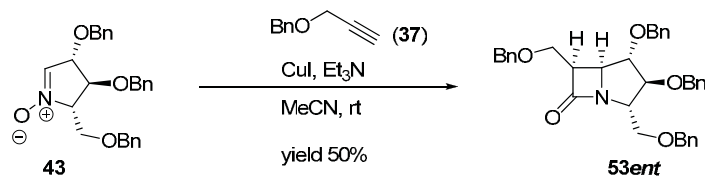
Colorless oil; $[\alpha]_{\text{D}} -39$ (c 1, CH_2Cl_2); R_f 0.51 (hexanes-EtOAc, 2:1)

IR (film) ν : 3031, 2863, 1770, 1098 cm^{-1} ;

^1H NMR (600 MHz, C_6D_6) δ : 3.30 (dd, J 9.4, 5.5 Hz, 1H, CHH-OBn), 3.38 (dd, J 9.3, 7.9 Hz, 1H, CHH-OBn), 3.52 (dd, J 9.8, 5.1 Hz, 1H, H-1'a), 3.56 (ddd, J 15.0, 10.4, 5.2 Hz, 1H, H-6), 3.65 (dd, J 5.4, 3.4 Hz, 1H, H-5), 3.67 (d, J 9.9 Hz, 1H, H-1'b), 4.10-4.15 (m, 2H, H-4, CHHOBn), 4.18-4.30 (m, 6 H, CH_2 -Ph), 4.33-4.37 (m, 3H, H-2, H-3, CHHOBn), 6.99-7.23 (Ar, 20H)

^{13}C NMR (150 MHz, C_6D_6) δ : 53.2, 60.6, 62.0, 65.3, 68.6, 71.2, 71.8, 72.7, 72.8, 82.8, 88.4, 127.3 (x2), 127.4(x2), 127.5, 127.6(x2), 127.7, 127.8, 127.9, 128.2(x2), 128.3, 137.8, 138.0, 138.4, 175.4;

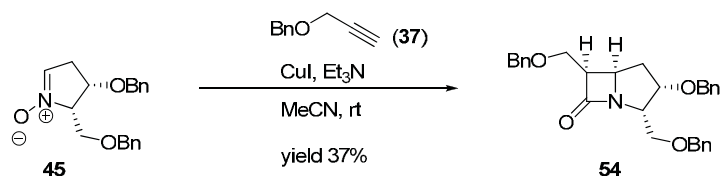
HRMS(ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{36}\text{H}_{37}\text{NO}_5\text{Na}$ 586.2564 found 586.2590



(2S,3S,4S,5S,6R)-3,4-di(benzyloxy)-2,6-di(benzyloxymethyl)-1-azabicyclo[3.2.0]heptan-7-one (53ent)

Colorless oil; $[\alpha]_{\text{D}} +38.5$ (c 1, CH_2Cl_2); R_f 0.51 (hexanes-EtOAc, 2:1)

HRMS(ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{36}\text{H}_{37}\text{NO}_5\text{Na}$ 586.2564; found 586.2566



(2S,3S,5R,6R)-3-(benzyloxy)-2,6-di(benzyloxymethyl)-1-azabicyclo[3.2.0]heptan-7-one (54)

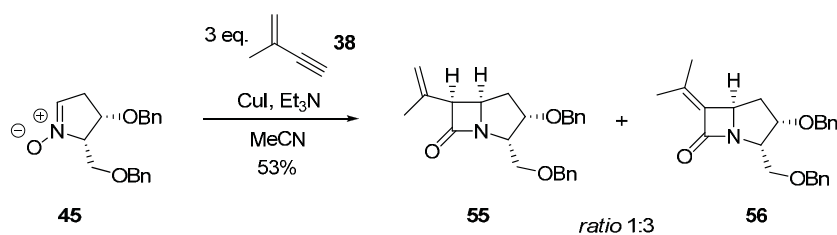
Colorless oil; $[\alpha]_{\text{D}} +33$ (c 1, CH_2Cl_2); R_f 0.41 (hexanes-EtOAc, 2:1)

IR (film) ν : 2972, 2867, 1763, 1094 cm^{-1} ;

^1H NMR (600 MHz, CDCl_3) δ : 1.85-1.87 (m, 1H, H-4a), 2.12 (ddd, J 4.6, 7.0, 11.5 Hz, 1H, H-4b), 3.57-3.72 (m, 5H, CHHOBn , H-1'a, H-1'b, CHHOBn , H-6), 3.99-4.03 (m, 2H, H-2, H-5), 4.29-4.3 (m, 1H, H-3), 4.41-4.57 (m, 6H, $3\times\text{CH}_2\text{Ph}$), 7.23-7.35 (Ar, 15 H);

^{13}C NMR (150 MHz, CDCl_3) δ : 31.4, 51.4, 54.3, 60.6, 64.8, 67.8, 72.4, 73.3, 73.5, 83.1, 127.5, 128.6, 137.6, 137.9, 138.3, 177.6;

HRMS(ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{29}\text{H}_{31}\text{NO}_4\text{Na}$: 480.3251 Found: 480.3248.



(2S,3S,5R,6S)-3-(benzyloxy)-2-(benzyloxymethyl)-6-(prop-1-en-2-yl)-1-azabicyclo[3.2.0]heptan-7-one (55)

Colorless oil; $[\alpha]_D^{+56}$ (*c* 1, CH₂Cl₂); *R_f* 0.65 (hexanes-EtOAc, 2:1)

IR (film) ν : 2917, 2861, 1761, 1093 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.54 (ddd, *J* 5.4, 8.0, 13.3 Hz, 1H, H-4a), 1.66 (s, 3H, Me), 2.12 (ddd, *J* 3.0, 5.8, 13.3 Hz, 1H, H-4b), 3.63 (dd, *J* 6.4, 9.8 Hz, 1H, CH₂OBn), 3.67 (dd, *J* 6.7, 9.8 Hz, 1H, CH₂OBn), 3.97-4.02 (m, 2H, H-3, H-5), 4.05-4.07 (m, 1H, H-5), 4.30-4.33 (m, 1H, H-2), 4.46-4.60 (m, 4H, CH₂Ph), 4.95-4.98 (m, 1H, C=CHH), 5.07-5.09 (m, 1H, C=CHH), 7.24-7.35 (Ar, 10H)

¹³C NMR (150 MHz, CDCl₃) δ : 22.1, 32.2, 55.4, 56.4, 61.1, 68.0, 72.3, 73.2, 83.5, 114.0, 127.4, 127.5, 127.7(x2), 128.3, 128.4, 136.8, 137.9, 138.2, 177.9;

HRMS(ESI) *m/z* [M+Na⁺] calcd for C₂₄H₂₇NO₃Na: 400.1883; found 400.1891

(2*S*,3*S*,5*R*)-3-(benzyloxy)-2-(benzyloxymethyl)-6-(propan-2-ylidene)-1-azabicyclo[3.2.0]heptan-7-one (56)

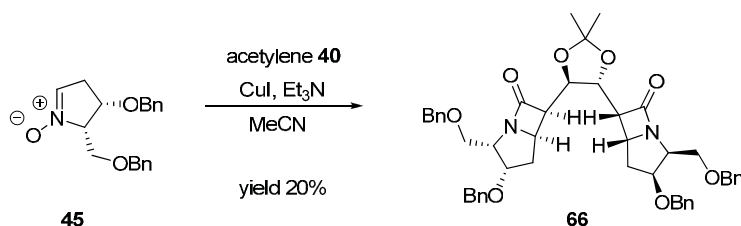
Colorless oil; $[\alpha]_D^{+47}$ (*c* 1, CH₂Cl₂); *R_f* 0.65 (hexanes-EtOAc, 2:1)

IR (film) ν : 2932, 2861, 1745, 1096 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.73 (s, 3H, Me), 1.78-1.79 (m, 1H, CH₂), 2.02 (s, 3H, Me), 2.26 (ddd, *J* 13.0, 6.8, 5.1 Hz, 1H), 3.68 (dd, *J* 9.8, 5.7 Hz, 1H, CHHOBn), 3.72 (dd, *J* 9.8, 6.2 Hz, 1H, CHHOBn), 4.05-4.06 (m, 1H, H-3), 4.29-4.34 (m, 2H, H-2, H-4), 4.49-4.61 (m, 4H, CH₂Ph), 7.24-7.37 (Ar, 10H);

¹³C NMR (150 MHz, CDCl₃) δ : 20.2, 20.7, 34.8, 58.7, 60.5, 68.3, 72.4, 73.3, 83.4, 126.9, 127.4, 127.6, 127.7, 128.3, 128.4, 128.5, 136.0, 138.0, 138.4, 139.3, 173.8;

HRMS(ESI) *m/z* [M+Na⁺] calcd for C₂₄H₂₇NO₃Na: 400.1889; found 400.1892.



(2*S*,2'*S*,3*S*,3'*S*,5*R*,5'*R*,6*R*,6'*R*)-6,6'-((4''*R*,5''*R*)-2'',2''-dimethyl-1'',3''-dioxolane-4'',5''-diyl)bis(3-(benzyloxy)-2-(benzyloxymethyl)-1-azabicyclo[3.2.0]heptan-7-one (66)

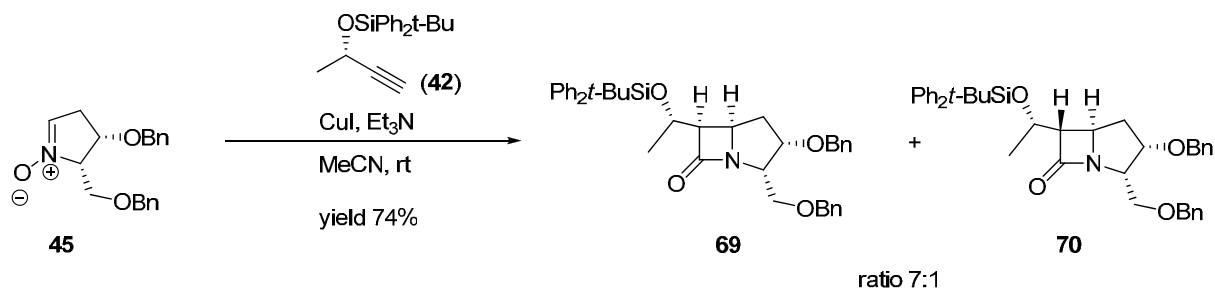
Colorless oil; $[\alpha]_D^{+19}$ (*c* 1, CH₂Cl₂); *R_f* = 0.31 (hexanes-EtOAc, 2:1)

IR (film) ν : 1104, 1771, 2856, 2931 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.35 (s, 6H, Me), 2.12- 2.24 (m, 4H, H-4a, H-4b), 3.61 (dd, *J* 9.7, 6.1 Hz, 2H, CHHOBn), 3.65 (dd, *J* 9.7, 6.2 Hz, 2H, CHHOBn), 3.61-3.07 (m, 2H, H-6), 4.02-4.08 (m, 2H, H-2, H-5), 4.24-4.25 (m, 2H, H-6'), 4.44-4.59 (m, 10H, 4xCH₂Ph, H-3), 7.23 -7.34 (Ar, 20H, 4xPh);

^{13}C NMR (150 MHz, CDCl_3) δ : 26.9, 32.0, 52.7, 54.3, 60.9, 67.9, 72.3, 73.2, 75.0, 83.3, 109.8, 127.5, 127.5, 127.6, 127.7, 128.3, 128.4, 138.0, 138.3, 176.2;

HRMS(ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{47}\text{H}_{52}\text{N}_2\text{O}_8\text{Na}$: 795.3621; found 795.3625



(2S,3S,5R,6R)-3-(benzyloxy)-2-(benzyloxymethyl)-6-((S)-1'-(tert-butylidiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (69)

Colorless oil; $[\alpha]_D^{25} +1.7$ (c 1, CH_2Cl_2); R_f 0.7 (hexanes-EtOAc, 2:1)

IR (film) ν : 2931, 2857, 1761, 1111 cm^{-1} ;

^1H NMR (600 MHz, CDCl_3) δ : 1.29 (d, J 6.1 Hz, 3H, CH₃), 1.43 (ddd J 13.4, 8.5, 5.2 Hz, 1H, H-4a), 1.78 (dq, J 13.4, 9.0, 5.9, 3.1 Hz, 1H, H-4b), 3.21 (dd, J 9.0, 5.3 Hz, 1H, H-6), 3.57 (dd, J 9.2, 5.5 Hz, 1H, CHHOBn), 3.64 (dd J 9.4, 7.2 Hz, 1H, CHHOBn), 3.78-3.85 (m, 2H, H-3, H-5), 3.89-3.91 (m, 1H, H-2), 4.00-4.12 (m, 3H, CH₂Ph, H-1'), 4.24-4.32 (m, 2H, CH₂Ph), 6.95-7.26 (Ar, 10H), 7.63-7.75 (Ar, 10H)

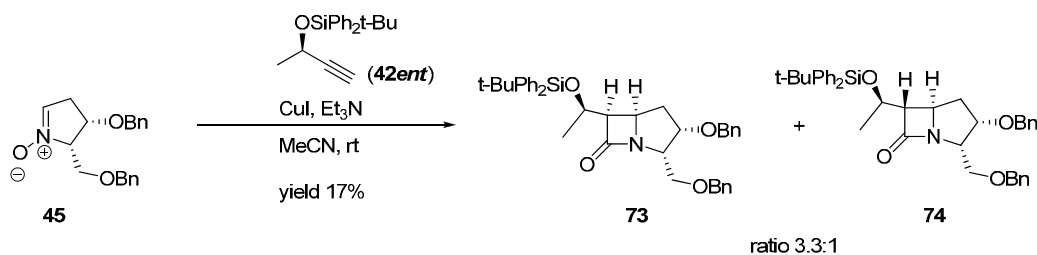
^{13}C NMR (150 MHz, CDCl_3) δ : 19.0, 22.2, 26.7, 32.4, 55.1, 58.4, 60.8, 66.6, 68.2, 71.8, 72.9, 83.6, 129.4, 129.7, 133.6, 134.1, 134.9, 135.8, 135.9, 136.0, 138.5, 138.8, 176.6;

HR MS(ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{39}\text{H}_{45}\text{NO}_4\text{SiNa}$: 642.3016; found: 642.3042.

(2S,3S,5R,6S)-3-(benzyloxy)-2-(benzyloxymethyl)-6-((S)-1'-(tert-butylidiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (70)

Compound 70 was not isolated from diastereomers' mixture. Selected diagnostic signals from crude proton NMR spectra: ^1H NMR (600 MHz, CDCl_3) δ : 2.87 (dd, J 2.02, 4.6 Hz, 1H);

HR MS(ESI) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{39}\text{H}_{45}\text{NO}_4\text{SiNa}$: 642.3016; found: 642.3040.



(2S,3S,5R,6R)-3-(benzyloxy)-2-(benzyloxymethyl)-6-((R)-1'-(tert-butylidiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (73)

Colorless oil; $[\alpha]_D^{25} +49$ (*c* 1, CH₂Cl₂); *R_f* 0.7 (hexanes-EtOAc, 2:1)

IR (film) ν : 2932, 2863, 1744, 1111 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.01 (d, *J* 6.2 Hz, 3H, CH₃), 1.08 (s, 9H, *t*Bu), 1.65 (ddd, *J* 13.5, 8.5, 5.3 Hz, 1H, H-4a), 2.06 (ddd, *J* 13.4, 6.0, 3.0 Hz, 1H, H-4b), 3.47 (dd, *J* 8.3, 5.7 Hz, 1H, H-6), 3.61 (dd, *J* 9.4, 6.0 Hz, 1H, CHHOBn), 3.67 (dd, *J* 9.5, 7.1 Hz, 1H, CHH-OBn), 3.86-3.87 (m, 1H, H-5), 3.97-3.99 (m, 1H, H-2), 4.06-4.07 (m, 1H, H-1'), 4.26 (dd, *J* 8.0, 5.0 Hz, 1H, H-3), 4.45-4.59 (m, 4H, CH₂Ph), 7.25-7.73 (Ar, 10H);

¹³C NMR (150 MHz, CDCl₃) δ : 19.2, 22.5, 26.6, 27.0, 32.6, 54.0, 57.5, 60.6, 66.7, 68.0, 72.3, 73.3, 83.3, 127.3, 127.4, 127.5(x2), 127.6, 127.7(x2), 128.3, 128.4, 129.5, 129.6, 129.7, 133.3, 134.6, 134.7, 135.2, 135.9, 136.2, 137.9, 138.3, 178.3;

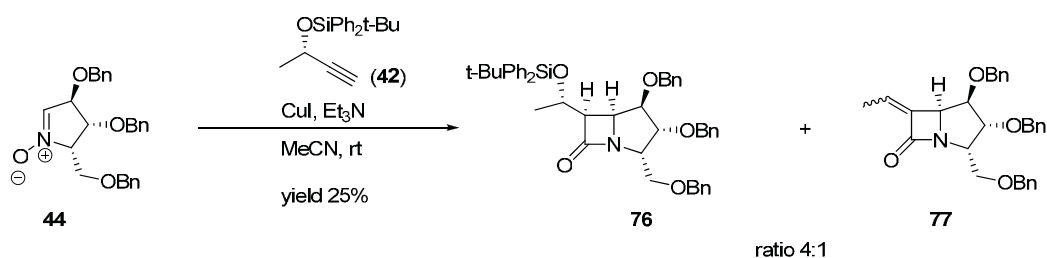
HR MS(ESI) *m/z* [M+Na]⁺ calcd for C₃₉H₄₅NO₄SiNa: 642.3016; found: 642.3010

(2S,3S,5R,6S)-3-(benzyloxy)-2-(benzyloxymethyl)-6-((R)-1'-(tert-butylidiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (74)

Compound was not isolated in pure form

¹H NMR (600 MHz, CDCl₃) δ : 1.03 (s, 9H, *t*-Bu), 1.15 (d, *J* 6.2 Hz, 3H, CH₃), 1.54-1.57 (m, 1H, H-4a), 2.22 (ddd, *J* 13.2, 6.0, 3.2 Hz, 1H, H-4b), 2.84 (dd, *J* 2.0, 6.7 Hz, 1H, H-6), 3.55 (dd, *J* 9.7, 6.1 Hz, 1H, CHHOBn), 3.62 (dd, *J* 9.6, 6.8 Hz, 1H, CHHOBn), 3.68-3.72 (m, 1H, H-5), 4.02-4.03 (m, 1H, H-2), 4.16-4.18 (m, 1H, H-1'), 4.32-4.35 (m, 1H, H-2), 4.47-4.68 (m, 4H, CH₂Ph), 7.25-7.67 (Ar, 20H)

HR MS(ESI) *m/z* [M+Na]⁺ calcd for C₃₉H₄₅NO₄SiNa: 642.3010; found: 642.3011



(2S,3R,4R,5S,6R)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((S)-1'-(tert-butylidiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (76)

Colorless oil; $[\alpha]_D^{25} -54$ (*c* 1, CH₂Cl₂); *R_f* 0.72 (hexanes/EtOAc, 2:1);

IR (film) ν : 2931, 2858, 1767, 1111 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.10 (s, 9H, *t*-Bu), 1.26 (d, *J* 6.6 Hz, 3H, CH₃), 3.48 (dd, *J* 8.7, 5.6 Hz, 1H, H-6), 3.51-3.52 (m, 1H, H-4), 3.60-3.62 (m, 2H, CH₂OBn), 3.74 (dd, 1H, *J* 5.5, 2.9 Hz, H-5), 3.81-

3.84 (m, 1H, H-2), 4.05-4.08 (m, 1H, H-3), 4.41-4.52 (m, 6H, CH₂-Ph), 4.71 (dq, *J* 8.8, 6.1 Hz, 1H, H-1'), 7.19-7.77 (Ar, 25H)

¹³C NMR (150 MHz, CDCl₃) δ: 19.2, 22.7, 25.1, 57.1, 58.9, 60.3, 66.1, 70.3, 72.9, 73.2, 77.1, 80.3, 86.1, (Ar 126.7, 127.5, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4, 129.6, 129.7, 129.8, 133.1, 133.4, 133.6, 133.7, 134.2, 134.8, 135.2, 135.7, 136.0, 137.3, 137.8, 138.2), 177.9

HR MS (ESI) *m/z* [M+Na⁺] calcd for C₄₆H₅₁NO₅NaSi 748.3428 found 748.3451

(2S,3R,4R,5S,Z)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-ethylidene-1-azabicyclo[3.2.0]heptan-7-one (77)

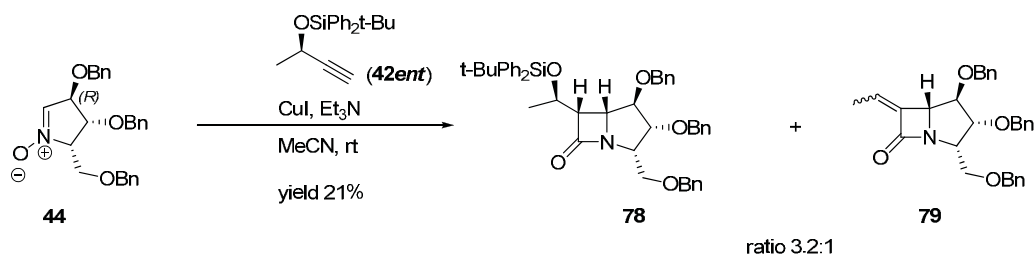
Colorless oil; [α]_D -54 (c 1, CH₂Cl₂); *R*_f 0.57 (hexanes-EtOAc, 2:1);

IR (film) *v*: 2925, 2855, 1760, 1646 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ: 2.02 (d, *J* 7.1 Hz, 3H, CH₃), 3.64 (dd, *J* 9.4, 6.6 Hz, 1H, CHHOBn), 3.69 (dd, *J* 9.4, 5.0 Hz, 1H, CHHOBn), 4.08-4.09 (m, 1H, H-2), 4.11-4.13 (m, 1H, H-4), 4.22 (dd, *J* 5.2, 3.8 Hz, 1H, H-3), 4.29 (d, *J* 4.5 Hz, 1H, H-5), 4.47-4.58 (m, 6H, CH₂-Ph), 5.71 (q, *J* 7 Hz, 1H, H-1'), 7.20-7.33 (Ar, 15H)

¹³C NMR (150 MHz, CDCl₃) δ: 15.2, 26.8, 59.4, 62.3, 68.0, 72.1, 73.1, 73.3, 80.7, 86.8, 127.2, 127.4, 127.6, 127.7, 127.8, 128.3, 128.4, 128.5, 129.9, 134.7, 135.7, 136.7, 137.7, 137.8, 138.2, 173.3

HR MS (ESI) *m/z* [M+Na⁺] calcd for C₃₀H₃₁NO₄Na 492.2151 found 492.2145.



(2S,3R,4R,5R,6S)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((R)-1'-(tert-butylidiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (78)

Colorless oil; [α]_D -5 (c 1, CH₂Cl₂); *R*_f 0.8 (hexanes/EtOAc, 2:1);

IR (film) *v*: 2930, 2856, 1751, 1112 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ: 1.05 (s, 9H, *t*-Bu), 1.32 (d, *J* 6.0 Hz, 3H, Me), 3.53 (ddd, *J* 8.6, 6.0, 3.0 Hz, 1H, H-2), 3.62 (dd, *J* 10.1, 6.1 Hz, 1H, H-6), 3.84-3.88 (m, 4H, H-3, H-4, H-5, OCHHPh), 3.97-4.02 (m, 2H, CHHOBn, OCHHPh), 4.10-4.22 (m, 4H, H-1', OCHHPh, CH₂OBn), 4.43-4.55 (m, 2H, OCH₂Ph), 7.00-7.8 (Ar, 25H);

^{13}C NMR (150 MHz, CDCl_3), δ : 19.0, 26.5, 26.6, 26.9, 60.4, 62.1, 64.7, 65.0, 67.3, 70.3, 71.8, 73.4, 80.4, 83.6, (Ar 127.0, 127.3, 127.4, 127.5(x2), 127.6(x2), 127.7, 127.8, 128.2, 128.3, 128.4, 129.6, 129.8, 134.0, 134.7, 135.2, 135.6, 135.7, 135.9, 137.2, 137.6, 138.1), 177.1;

HR MS (ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{46}\text{H}_{51}\text{NO}_5\text{NaSi}$ 748.3428 found 748.3454

(2S,3R,4R,5R,Z)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-ethylidene-1-azabicyclo[3.2.0]heptan-7-one (79)

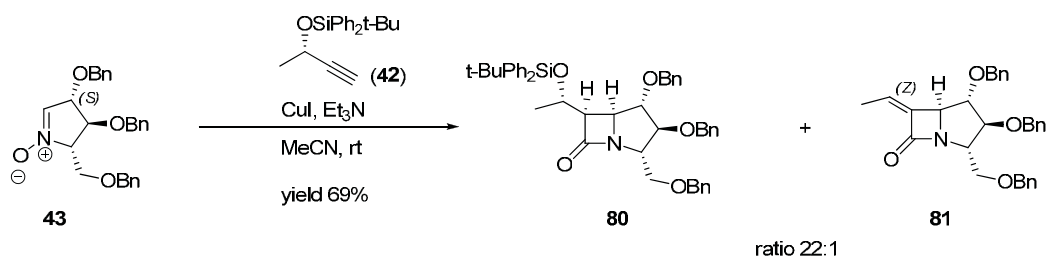
Colorless oil; $[\alpha]_D^{25} +4$ (c 1, CH_2Cl_2); R_f 0.69 (hexanes-EtOAc, 2:1)

IR (film) ν : 2918, 2852, 1753, 1570 cm^{-1}

^1H NMR (600 MHz, CDCl_3), δ : 1.96 (d, J 7.2 Hz, 3H, CH_3), 3.69 (ddd, J 8.9, 4.9, 4.2 Hz, 1H, H-2), 3.95-3.96 (m, 1H, H-4), 4.03 (br s, 1H, H-5), 4.12-4.20 (m, 3H, H-3, CH_2OBn), 4.47-4.62 (m, 6H, CH_2Ph), 5.56 (q, J 7.2 Hz, 1H, $\text{HC}=\text{C}$), 7.15-7.50 (Ar, 15H);

^{13}C NMR (150 MHz, CDCl_3), δ : 14.7, 26.8, 64.7, 64.8(x2), 71.4, 72.0, 73.3, 76.3, 82.5, 84.9, 127.0, 127.4, 127.5, 127.6(x2), 127.7, 127.9, 128.0, 128.2, 128.3, 128.5, 135.7, 135.9, 137.5, 137.9, 138.3, 139.6, 173.2;

HRMS(ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for 492.2146 found 492.2145



2S,3S,4S,5S,6R)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((S)-1'-(tert-butyl)diphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (80)

Colorless oil; $[\alpha]_D^{25} +39$ (c 1, CH_2Cl_2); R_f 0.73 (hexanes/EtOAc, 2:1);

IR (film) ν : 2930, 2857, 1769, 1111 cm^{-1}

^1H NMR (600 MHz CDCl_3) δ : 1.10 (s, 9H, *t*-Bu), 1.37 (d, J 6.3 Hz, 3H, CH_3), 3.32 (dd, J 6.1, 9.4 Hz, 1H, CHHOBn), 3.39-3.44 (m, 2H, CHHOBn , H-6), 3.86 (dd, J 6.0, 2.1 Hz, 1H, H-5), 3.91- 4.26 (m, 8H, 3x CHHPh , H-3, H-4), 4.39-4.44 (m, 1H, H-2), 4.48 (dq, J 9.4, 6.0 Hz, 1H, H1'), 7.05-7.75 (Ar, 25H)

^{13}C NMR (150 MHz, C_6D_6), δ : 22.4, 26.3, 26.7, 26.8, 61.1, 62.2, 62.5, 67.4, 68.3, 70.5, 71.8, 72.7, 83.2, 86.2, (Ar 127.31, 127.32, 127.35, 127.4(x2), 127.5(x3), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 129.4, 129.6, 129.7, 133.9, 134.2, 134.8, 135.7, 135.8, 137.7, 138.2, 138.3), 176.7

HR MS (ESI) m/z $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{46}\text{H}_{51}\text{NO}_5\text{NaSi}$ 748.3428 found 748.3444.

(2S,3S,4S,5S,Z)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-ethylidene-1-azabicyclo[3.2.0]heptan-7-one (81)

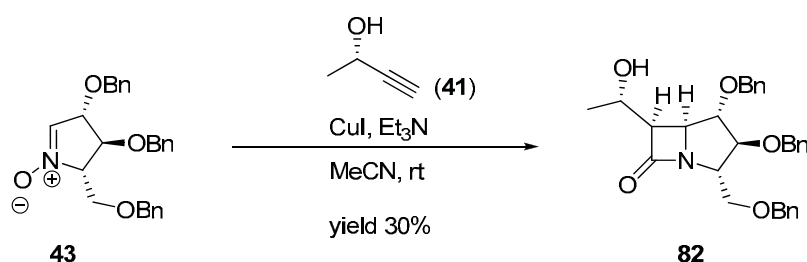
Colorless oil; $[\alpha]_D^{25} +53$ (c 1, CH₂Cl₂); R_f 0.54 (hexanes/EtOAc, 2:1);

IR (film) : 2925, 2858, 1756, 1095 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.69 (d, J 7.1 Hz, 3H, CH₃), 3.49 (dd, J 12.4, 8.7 Hz, 1H, CHH-OBn), 3.54 (dd, J 9.7, 6.1 Hz, 1H, CHH-OBn), 3.93-3.96 (m, 1H, H-4), 4.24-4.26 (m, 1H, H-5), 4.28-4.31 (m, 3H, H-2, H-3), 4.39-4.60 (m, 6H, CH₂-Ph), 6.18 (dq, J 1.6 Hz, 1H, HC=C), 7.25-7.32 (Ar, 15H)

¹³C NMR (150 MHz, CDCl₃) δ : 14.1, 63.1, 64.9, 68.4, 71.3, 72.2, 73.1, 84.3, 87.5, 125.2, 127.4(x2), 127.5(x2), 127.6(x2), 127.7(x2), 127.8, 127.9, 128.2, 128.3(x2), 128.4(x2), 135.7, 135.8, 137.4, 138.0, 128.5, 141.2, 173.1;

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₀H₃₃NO₅ Na 492.2146 found 492.2145.

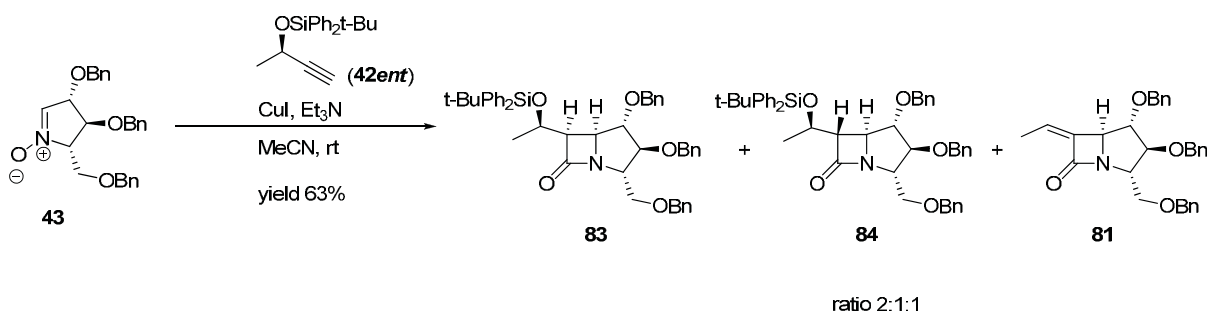


(2S,3S,4S,5S,6R)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((S)-1'-hydroxyethyl)-1-azabicyclo[3.2.0]heptan-7-one (82)

Compound **86** was not isolated in pure form

¹H NMR (600 MHz, CDCl₃) δ : 1.31 (d, J 6.2 Hz, 3H, CH₃), 3.42 (dd, J 10.2, 5.9 Hz, 1H, H-6), 3.45-3.52 (m, 2H, CH₂OBn), 3.83 (dd J 5.7, 3.2 Hz, 1H, H-5), 4.06-4.12 (m, 1H, H-1'), 4.20-4.24 (m, 1H, H-2), 4.27-4.30 (m, 2H, H-3, H-4), 4.40-4.62 (m, 6H, 3xCH₂Ph), 7.22-7.35 (Ar, 15H)

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₀H₃₃NO₅ Na 510.2251 found 510.2251



(2S,3S,4S,5S,6R)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((R)-1'-(tert-butyl-diphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (83)

Colorless oil; $[\alpha]_D^{+31}$ (c 1, CH₂Cl₂); R_f 0.73 (hexanes/EtOAc, 2:1)

IR (film) ν : 2930, 2857, 1753, 1111 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 0.92 (d, J 5.9 Hz, 3H, Me), 1.05 (s, 9H, *t*-Bu), 3.43-3.49 (m, 2H, CH₂OBn), 3.56 (dd, J 8.8, 5.9 Hz, 1H, H-6), 3.65 (dd, J 5.7, 4.5 Hz, 1H, H-5), 4.03 (dd, J 4.4, 3.4 Hz, 1H, H-4), 4.15 (ddd, J 8.7, 5.7, 3.1 Hz, 1H, H-2), 4.23-4.29 (m, 2H, H-1', H-3), 4.30-4.52 (m, 6H, CH₂Ph), 7.20-7.45 (m, 25H);

¹³C NMR (150 MHz, CDCl₃) δ : 18.9, 19.3, 22.3, 26.5, 26.8, 59.2, 59.8, 61.3, 66.9, 68.9, 71.7, 72.0, 73.0, 82.9, 88.0, 127.3, 127.4, 127.5, 127.6(x2), 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 129.4, 129.5, 129.6, 129.7, 133.7, 134.7, 134.9, 135.2, 135.9, 136.0, 137.4, 137.5, 176.4

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₀H₃₃NO₅ NaSi 748.3434 found 748.3450.

(2S,3S,4S,5S,6S)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((R)-1'-(*tert*-butyldiphenylsilyloxy)ethyl)-1-azabicyclo[3.2.0]heptan-7-one (84)

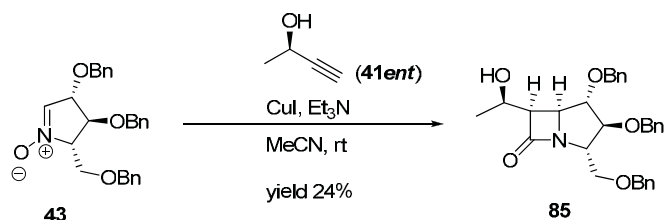
Colorless oil; $[\alpha]_D^{+45.5}$ (c 1, CH₂Cl₂); R_f 0.67 (hexanes/EtOAc, 2:1)

IR (film) ν : 2930, 2857, 1769, 1111 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.02 (s, 9H, *t*Bu), 1.07 (d, J 6.3 Hz, 3H, CH₃), 3.15 (dd, J 5.5, 2.5 Hz, 1H, H-6), 3.47-3.48 (m, 2H, CH₂OBn), 3.74-3.85 (m, 1H, H-5), 3.93-3.94 (m, 1H, H-4), 4.19-4.24 (m, 2H, H-2, H-1'), 4.31-4.32 (m, 1H, H-3), 4.47-4.62 (m, 6H, CH₂Ph), 7.15-7.67 (Ar, 25H);

¹³C NMR (150 MHz, CDCl₃) δ : 19.3, 22.2, 26.8, 26.9, 58.8, 62.4, 64.7, 67.0, 68.7, 71.8, 72.2, 73.1, 86.0, 87.9, 127.3, 127.4, 127.5, 127.6(x2), 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.5, 129.8, 134.4, 135.8, 135.9, 136.0, 137.4, 137.6, 138.0, 176.5

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₀H₃₃NO₅ NaSi 748.3434; found 748.3433



(2S,3S,4S,5S,6R)-3,4-di-(benzyloxy)-2-(benzyloxymethyl)-6-((R)-1'-hydroxyethyl)-1-azabicyclo[3.2.0]heptan-7-one (85)

Colorless oil; $[\alpha]_D^{+29}$ (c 1, CH₂Cl₂); R_f 0.35 (hexanes/EtOAc, 2:1);

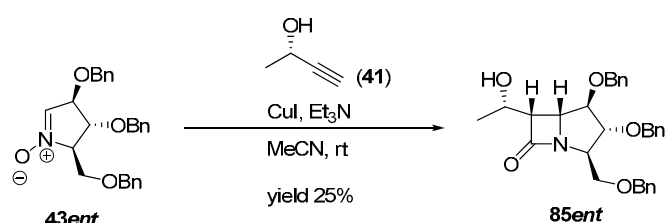
IR (film) ν : 2928, 2865, 1760, 1098 cm⁻¹;

¹H NMR (600 MHz, CDCl₃) δ : 1.11 (d, J 6.2 Hz, 3H, CH₃), 3.37 (dd, J 8.9, 5.7 Hz, 1H, H-6), 3.44-3.51

(m, 2H, CH₂OBn), 3.75 (dd, *J* 5.7, 3.5, Hz, 1H, H-5), 4.06-4.12 (m, 2H, H-4, H-1'), 4.23-4.26 (m, 1H, H-2), 4.28-4.29 (m, 1H, H-3), 4.41-4.62 (m, 6H, CH₂-Ph), 7.22-7.37 (m, 15H);

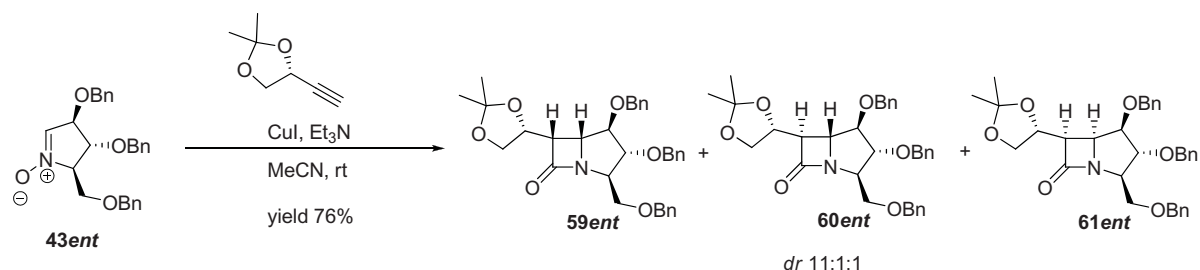
¹³C NMR (150 MHz, CDCl₃) δ: 20.9, 58.5, 60.0, 61.7, 65.0, 68.2, 71.7, 81.8, 88.1, 127.5, 127.6, 127.7, 127.8(x2), 127.9(x2), 128.0, 128.1, 128.2, 128.3(x2), 128.4, 128.5, 128.6, 137.2, 137.9, 178.5;

HR MS (ESI) *m/z* [M+Na⁺] calcd for C₃₀H₃₃NO₅Na 510.2251; found 510.2268.



Colorless oil; [α]_D -29 (c 1, CH₂Cl₂);

HR MS (ESI) *m/z* [M+Na⁺] calcd for C₃₀H₃₃NO₅Na 510.2251; found 510.2257.



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((*R*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)-1-azabicyclo[3.2.0]heptan-7-one (59ent)

Colorless oil; [α]_D -10.0 (c 1, CH₂Cl₂); *R_f* 0.30 (hexanes/EtOAc 2:1);

IR (film) *v*: 2934, 2867, 1769, 1098 cm⁻¹;

HR MS (ESI) *m/z* [M+Na⁺] calcd for C₃₃H₃₇NO₆Na 566.2530 found 566.2513

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((*R*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)-1-azabicyclo[3.2.0]heptan-7-one (60ent)

[α]_D -24.0 (c 1, CH₂Cl₂); *R_f*=0.41 (hexanes-EtOAc, 2:1)

IR (film) *v*: 2924, 2858, 1767, 1092 cm⁻¹

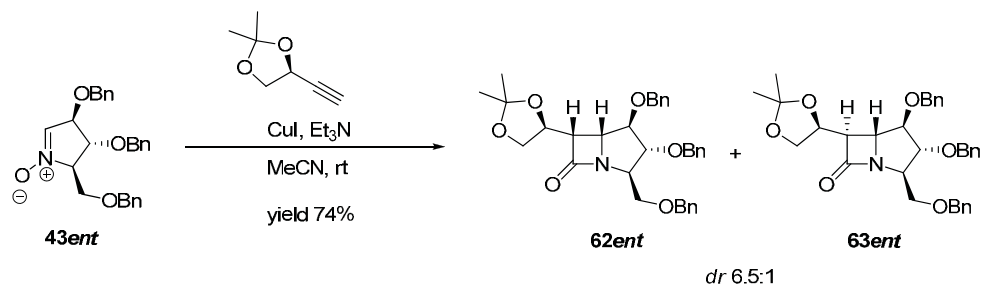
HR MS (ESI) *m/z* [M+Na⁺] calcd for C₃₃H₃₇NO₆Na 566.2513 found 566.2533

(2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((*R*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)-1-azabicyclo[3.2.0]heptan-7-one (61ent)

Colorless oil; $[\alpha]_D -20.0$ (*c* 1.00, CH₂Cl₂); $R_f = 0.60$ (hexanes-EtOAc, 2:1)

IR (film) ν : 2925, 2859, 1767, 1096 cm⁻¹

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₃H₃₇NO₆Na 566.2513 found 566.2515



(2*R*,3*R*,4*R*,5*R*,6*S*)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((*S*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)-1-azabicyclo[3.2.0]heptan-7-one (62ent)

Colorless oil; $[\alpha]_D -62$ (*c* 1, CH₂Cl₂); R_f 0.71 (hexanes/EtOAc 2:1);

IR (film) ν : 2934, 2868, 1767, 1098 cm⁻¹;

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₃H₃₇NO₆Na 566.2513 found 566.2503

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4-di(benzyloxy)-2-(benzyloxymethyl)-6-((*S*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)-1-azabicyclo[3.2.0]heptan-7-one (63ent)

Colorless oil; $[\alpha]_D -78$ (*c* 1, CH₂Cl₂); R_f 0.55 (hexanes-EtOAc, 2:1)

IR (film) ν : 2931, 2867, 1768, 1096 cm⁻¹

HR MS (ESI) m/z [M+Na⁺] calcd for C₃₃H₃₇NO₆Na 566.2513 found 566.2523.