Supporting Information for

Synthesis and Stereochemical Analysis of Planar Chiral Nine-membered Aza-orthocyclophyne

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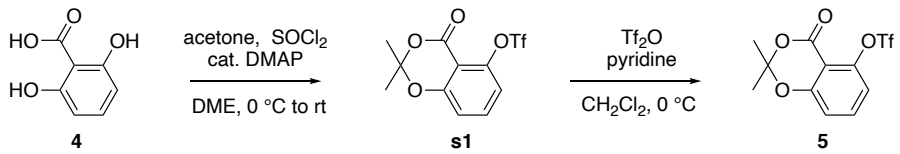
1. General Experimental:

All reactions were carried out in heat-gun-dried glassware under an argon atmosphere unless otherwise noted. Dry 1,2-dimethoxyethane (DME), CH_2Cl_2, THF, MeOH, DMF and CH_3CN were purchased from Kanto Chemical Co., Inc. and used without purification. ^1H NMR spectra were recorded on Varian Mercury spectrometer (300 MHz), JEOL JNM-ECZ400S (400 MHz) or JEOL JNM-ECA600 (600 MHz). ^{13}C NMR spectra were recorded on Varian Mercury spectrometer (75 MHz), JEOL JNM-ECZ400S (100 MHz) or JEOL JNM-ECA600 (150 MHz) at ambient temperature using $CDCl_3$ as a solvent. Chemical shifts (δ) in parts per million were referenced to the solvent residual peak as an internal standard: $CHCl_3$ for ^1H NMR (δ 7.26) and $CDCl_3$ for ^{13}C NMR (δ 77.1). The peak multiplicities were given as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Single crystal X-ray structural analysis was carried out on a XtaLAB Synergy R/DW diffractometer with Rigaku HyPix-6000 area detector using multi-layer mirror monochromated Cu-K_α radiation at 100 K. Infrared spectra (IR) were recorded on a Fourier transfer infrared spectrophotometer (Perkin Elmer SpectrumOne) as neat liquid on NaCl plates and as crystals used a diffuse reflector. Melting points (mp) were measured on a Yanaco Micro Melting Point Apparatus. High performance liquid chromatography (HPLC) was performed on a JASCO CD-2095 detectors equipped with a JASCO PU-2089 using Daicel CHIRALCEL IB column (0.46 cm × 25 cm). HRMS analyses were recorded on a JEOL JMS-700 at the Analytical Center in IMCE, Kyushu University. Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F_{254} (Merck 5715) plates and developed plates were visualized by UV (254 nm) and by heating on a hot plate after staining with a 4% solution of phosphomolybdic acid in ethanol or a 2.5% solution of *p*-anisaldehyde in ethanol. Silica gel column chromatography were performed using Kanto 60N (spherical neutral, particle size 100-210 μm).

2. Detailed Reaction Procedures and Analytical Data

triflate **5**



To a solution of 2,6-dihydroxylbenzoic acid is need to be revised to be "2,6-dihydroxylbenzoic acid" (**4**) (5.00 g, 32.4 mmol) in DME (25 mL) were added DMAP (198 mg, 1.62 mmol), acetone (3.10 mL, 42.1 mmol), and $SOCl_2$ (3.06 mL, 42.1 mmol) at ambient temperture. After stirred at that temperture for 6 h, the reaction was quenched with sat. aq. $NaHCO_3$ and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to afford crude **s1**. To a solution of the afforded crude **s1** in CH_2Cl_2 (30 mL) were added pyridine (9.40 mL, 117 mmol) and Tf_2O (6.40 mL, 38.9 mmol) at 0 °C. After stirred at that temperture for 1 h, the reaction was quenched with sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2 (20 mL) / hexane (80 mL) to afford 7.82 g (74%) of **5** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (dd, J = 8.4, 8.4 Hz, 1H), 7.06 (dd, J = 8.4, 1.2 Hz, 1H), 7.00 (dd, J = 8.4, 1.2 Hz, 1H), 1.76 (s, 6H).

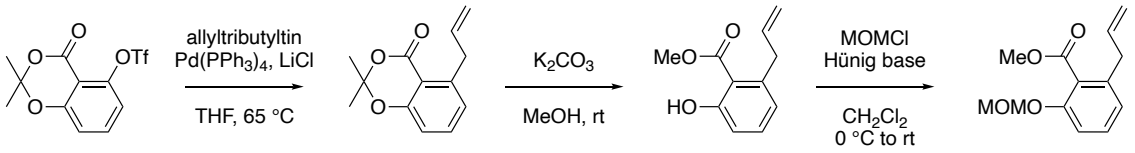
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 157.2, 148.7, 136.3, 118.9 (q, $J_{C\text{-}F}$ = 319 Hz), 117.9, 116.7, 108.4, 107.0, 25.6.

IR (reflection, cm^{-1}): 1745, 1621, 1435, 1204, 1023, 814, 751, 686, 592.

Mp: 109.5-110.0 °C.

HRMS (EI, positive): Exact mass calcd. for $C_{11}H_9F_3O_6S$ $[M]^+$ requires m/z: 326.0072, found m/z: 326.0073.

methyl ester **7**



5 **s2** **s3** **7**

To a solution of **5** (5.00 g, 15.3 mmol) in THF (150 mL) were added LiCl (4.00 g, 93.3 mmol), **5** (5.00 g, 15.3 mmol) $Pd(PPh_3)_4$ (354 mg, 0.306 mmol), and allyltributyltin at ambient temperature. After stirred at 65 °C for 48 h, the reaction mixture was cooled to ambient temperature then filtered through a pad of Celite, filtered, and the filtrate was concentrated under reduced pressure to afford crude **s2**. To a solution of the afforded **s2** in MeOH (50 mL) was added K_2CO_3 (7.43 g, 76.5 mmol) at ambient temperature. After stirred for 3 days at that temperature, the mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to afford crude **s3** To a solution of the afforded crude **s3** in CH_2Cl_2 (65 mL) were added Hünig base (8.12 mL, 61.2 mmol) and MOMCl (1.38 mL, 18.4 mmol) at 0 °C. After stirred at ambient temperature for 10 h, the reaction was quenched with H_2O, and extracted with AcOEt. The combined organic phases were washed brine, dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 3:1 to 0:1) to afford 3.34 g (93% in 3 steps) of **7** as a colorless oil.

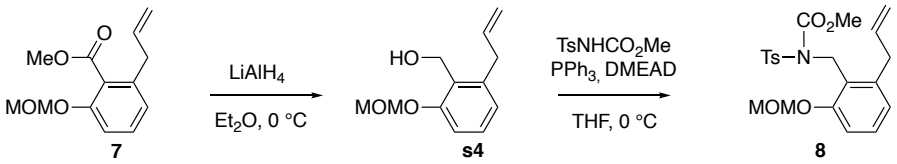
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.94-5.84 (m, 1H), 5.17 (s, 2H), 5.07-5.03 (m, 2H), 3.88 (s, 3H), 3.45 (s, 3H), 3.35 (d, *J* =6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 154.0, 138.6, 136.3, 130.5, 124.6, 122.9, 116.4, 112.8, 94.7, 56.2, 52.2, 37.7.

IR (reflection, cm^{-1}): 2653, 1733, 1585, 1466, 1256, 1029, 922, 755.

HRMS (EI, positive): Exact mass calcd. for $C_{13}H_{16}O_4$ $[M]^+$ requires *m/z*: 236.1049, found *m/z*: 236.1048.

N-tosylcarbamate **8**



To a solution of $LiAlH_4$ (836 mg, 22.0 mmol) in Et_2O (70 mL) was added a solution of **7** (2.60 g, 11.0 mmol) of Et_2O (40 mL) in 0 °C. After stirred at that temperature for 3 h, the reaction was quenched with 0 °C then H_2O (836 μL), 15% NaOH (836μL), and H_2O (2.51 mL). The white precipitate was filtrated through a pad of Celite and the filtrate was concentrated under reduced pressure to afford crude **s4**. To a solution of the afforded crude **s4** in THF (200 mL) was added methyl *N*-tosylcarbamate (2.53 g, 11.0 mmol), PPh_3 (3.76 g, 14.3 mmol), and DMEAD (3.36 g, 14.3 mmol) at 0 °C. After stirred at that temperature for 3 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 1:1) to afford 3.30 g (72%) of **8** as white crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23-7.17 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.91 (dd *J* = 7.5, 0.9 Hz, 1H), 6.82 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.89-5.93 (m, 1H), 5.07-4.89 (m, 4H), 4.68 (s, 2H), 3.78 (s, 3H), 3.71 (ddt, *J* = 5.7, 1.5 Hz, 2H), 3.04 (s, 3H), 2.34 (s, 3H).

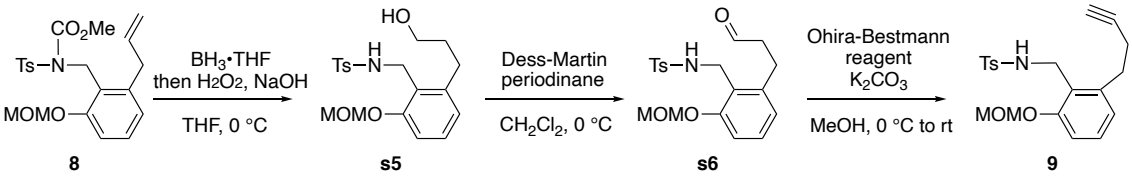
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 153.8, 143.9, 141.2, 137.6, 136.5, 129.1, 128.7, 128.6, 123.6, 122.57, 115.7, 111.9, 94.4, 55.7, 53.7, 43.6, 37.5, 21.6.

IR (reflection, cm^{-1}): 2956, 1738, 1587, 1434, 1362, 1157, 775, 678, 581, 548.

Mp: 73.0-74.0 °C.

HRMS (EI, positive): Exact mass calcd. for $C_{21}H_{25}NO_6S$ $[M]^+$ requires *m*/*z*: 419.1403, found *m*/*z*: 419.1403.

alkyne **9**



To a solution of **8** (3.30 g, 7.88 mmol) in THF (100 mL) was added BH_3·THF (0.94 M in THF, 4.20 mL, 3.94 mmol) at 0 °C. After stirred at that temperature for 3 h, 3 M NaOH (7.90 mL, 23.6 mmol) and aq. H_2O_2 (34%, 16.5 mL) was added to themixture and stirred for 15 min at that temperature. The reaction was quenched with sat. aq. $Na_2S_2O_3$, and extracted with AcOEt. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to afforde crude **s5**. To a solution of the afforded crude **s5** in CH_2Cl_2 (65mL) was added Dess-Martin periodinane (4.00 g, 9.44 mmol) at 0 °C. After stirred at that temperature for 3.5 h, the reaction was quenched with sat. aq. $Na_2S_2O_3$ and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and the filtrated was concentrated under reduced pressure to afforde crude **s6**. To a solution of dimethyl (1-azo-2-oxopropyl)phosphonate (2.27 g, 11.8 mmol) in MeOH (20 mL) was added K_2CO_3 (3.26 g, 23.6 mmol) at 0 °C. After stirred at that temperature for 40 min, a solution of the afforded **s6** in MeOH (45 mL) was added. After stirred at ambient temperature for 5 h, the reaction was quenched with sat. aq. NH_4Cl and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 5:1 to 3:1) to afford 2.17 g (74%) of **9** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.13 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.87 (dd, *J* = 7.5, 0.6 Hz, 1H), 6.82 (dd, *J* = 7.5, 0.6 Hz, 1H), 5.03 (s, 2H), 4.96 (t, *J* = 6.3 Hz, 1H), 4.12 (d, *J* = 6.3 Hz, 2H), 3.35 (s, 3H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.40-2.34 (m, 5H), 1.95 (t, *J* = 2.4 Hz, 1H).

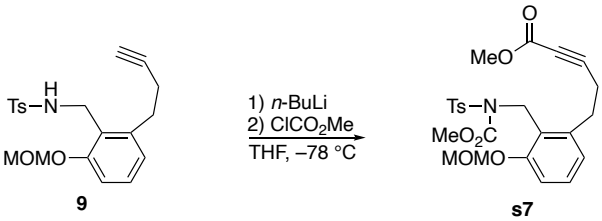
^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8, 143.3, 140.6, 136.9, 129.6, 129.2, 127.2, 123.4, 123.4, 112.5, 94.8, 83.5, 69.5, 56.4, 39.0, 31.4, 21.6, 20.4.

IR (reflection, cm^{-1}): 3279, 2904, 1583, 1325, 1161, 1013, 820, 795, 679.

Mp: 79.4-80.2 °C.

HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calcd. for $C_{20}H_{24}NO_4S$ $[M+H]^+$ requires *m*/*z*: 374.1426, found *m*/*z*: 374.1425.

methyl ester **s7**



9 **s7**

To a solution of **9** (2.17 g, 5.82 mmol) in THF (60 mL) was added *n*-BuLi (1.40 M in hexane, 9.55 mL, 13.4 mmol) at –78 °C. After stirred at that temperature for 35 min, methyl chloroformate (2.24 mL, 5.70 mmol) was added to the mixture. After stirred at ambient temperature for 2 h, the reaction was quenched with sat. aq. NH_4Cl and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 1:1) to afford 1.75 g (61%) of **s7** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.97 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.89 (dd, *J* = 7.8, 0.6 Hz, 1H), 5.18 (s, 2H), 4.76 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 3.24 (t, *J* = 7.5 Hz, 2H), 3.09 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.38 (s, 3H).

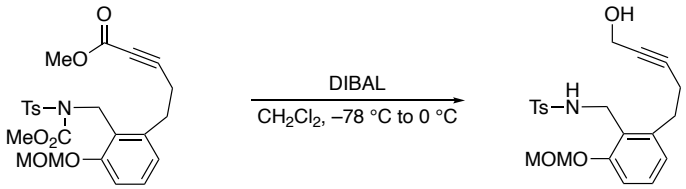
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 154.5, 154.1, 144.4, 141.3, 136.8, 129.6, 129.2 128.9, 123.6, 122.9, 112.7, 94.7, 88.9, 74.2, 56.1, 54.2, 53.1, 43.8, 31.1, 22.0, 21.4.

IR (reflection, cm^{-1}): 2953, 2233, 1700, 1267, 757, 690, 654, 573.

Mp: 97.8-99.0 °C.

HRMS (EI, positive): Exact mass calcd. for $C_{24}H_{27}NO_8S$ $[M]^+$ requires *m*/*z*: 489.1457, found *m*/*z*: 489.1455.

alcohol **10**



s7 **10**

To a solution of **s7** (587 mg, 1.20 mmol) in CH_2Cl_2 (25 mL) was added DIBAL (1.02 M in hexane, 6.0 mL, 6.15 mmol) at –78 °C. After stirred at that temperature at 0 °C for 1 h, the reaction was quenched with $Na_2SO_4 \cdot 10H_2O$. The slurry was diluted with hexane and Na_2SO_4 and stirred at ambient temperature. After the organic phase turned clear, the mixture was filtered through a pad of Celite and the filtrate was concentrted under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 1:2) to afford 413 mg (85%) of **10** as colorless crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (dd, *J* = 8.4, 8.4 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.17 (t, *J* = 6.0 Hz, 1H), 5.04 (s, 2H), 4.21-4.17 (m, 4H), 3.36 (s, 3H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 3.17 (s, 3H).

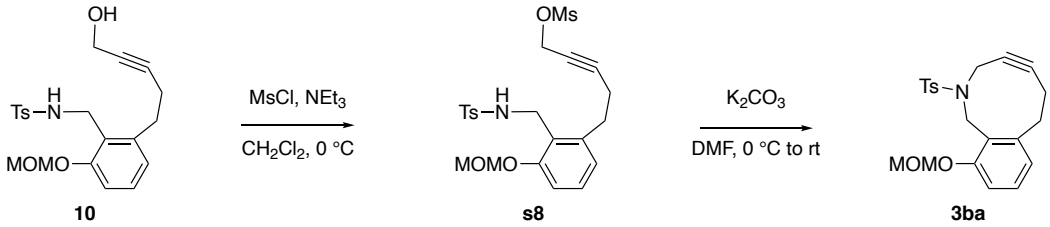
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 143.4, 140.9, 136.6, 129.6, 129.3, 127.3, 123.4, 123.2, 112.4, 94.7, 85.3, 80.4, 56.3, 51.2, 38.6, 21.6, 20.9.

IR (reflection, cm^{-1}): 3303, 2906, 1584, 1464, 1348, 1157, 1007, 821, 672, 545.

Mp: 84.9-85.4 °C.

HRMS (EI, positive): Exact mass calcd. for $C_{21}H_{25}NO_5S$ $[M]^+$ requires *m*/*z*: 403.1453, found *m*/*z*: 403.1453.

1^6-methylmetylether-3-aza[7]orthobenzenophyne **3ba**



10 **s8** **3ba**

To a solution of **10** (413 mg, 1.02 mmol) and NEt_3 (0.5 mL, 3.57 mmol) in dry CH_2Cl_2 (20 mL) was added MsCl (0.18 mL, 2.35 mmol) at 0 °C. After stirred at that temperature for 1 h, the reaction mixture was quenched with sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford crude **s8**. To a solution of the afford crude **s8** in DMF (100 mL) was added K_2CO_3 (1.41 g, 10.2 mmol) in at 0 °C. After stirred at that temperature at that temperature for 17 h, the reaction was quenched with H_2O and extracted with AcOEt. The combine organic phases were washed with brine, dried over Na_2SO_4, filtered and the filtrate was oncentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 3:1) to afford 226 mg (58%) of **3ba** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J = 7.8, 2H), 7.35 (d, J =7.8 Hz, 2H), 7.21 (dd, J = 7.5, 7.5 Hz, 1H), 7.04 (dd, J = 7.5, 0.9 Hz, 1H), 6.80 (dd, J = 7.5, 0.9 Hz, 1H), 5.19 (d, J = 8.0 Hz, 2H), 4.97 (d, J = 12.6 Hz, 1H), 4.17-4.07 (m, 2H), 3.76 (ddd, J = 17.4, 3.3, 3.3 Hz, 1H), 3.49 (s, 3H), 2.89-2.83 (m, 2H), 2.46 (s, 3H), 2.41-2.23 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.0, 143.2, 141.3, 136.2, 129.8, 129.0, 127.3, 123.4, 111.9, 95.2, 93.7, 84.1, 56.1, 43.7, 37.6, 32.9, 29.6, 22.7, 21.5.

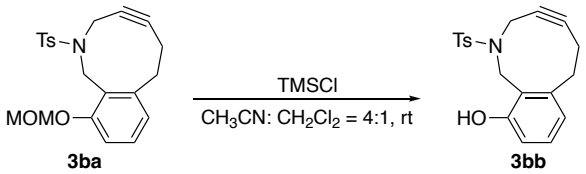
IR (reflection, cm^{-1}): 2965, 1597, 1459, 1338, 792, 655, 578, 548.

Mp: 156.2-157.0 °C.

HRMS (EI, positive): Exact mass calcd. for $C_{21}H_{23}NO_4S$ $[M]^+$ requires m/z: 385.1348, found m/z: 385.1347.

Analytical HPLC: column: CHIRALPAK IB (0.46 cm × 25 cm), eluent: hexane/IPA = 30:70, flow rate: 0.5 mL/min, detection: UV 270 nm, temperature: –20 °C, retention time: t_1 = 20.1 min, t_2 = 29.2 min.

1^6-hydroxy-3-aza[7]orthobenzenophyne **3bb**



3ba **3bb**

To a solution of **3ba** (14.0 mg, 0.0364 mmol) in MeCN (2 mL) / CH_2Cl_2 (0.5 mL) was added TMSCl (55.0 μL, 0.432 mmol) at ambient temperature. After stirred at that temperature for 7 days, the reaction was quenched with H_2O and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 1:1) to afford 8.2 mg (67%) of **3bb** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.17 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.87 (dd, *J* = 7.5 1.2 Hz, 1H), 6.69 (dd, *J* = 7.5, 1.2 Hz, 1H), 4.76 (d, *J* = 14.4 Hz, 1H), 4.18-3.96 (m, 3H), 2.82 (dd, *J* = 8.4, 3.6 Hz, 2H), 2.49 (s, 3H), 2.40-2.38 (m, 2H).

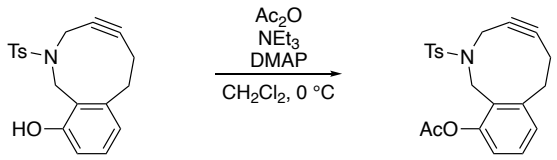
^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7, 144.3, 139.4, 132.9, 129.8, 129.7, 127.4, 122.0, 120.8, 115.5, 94.9, 81.6, 44.2, 38.7, 32.8, 22.1, 21.3.

IR (reflection, cm^{-1}): 3418, 2944, 2240, 1595, 1281, 656.

Mp: 152.0-153.0 °C.

HRMS (EI, positive): Exact mass calcd. for $C_{19}H_{19}NO_3S$ $[M]^+$ requires *m/z*: 341.1086, found *m/z*: 341.1087.

1^6-acetoxy-3-aza[7]orthobenzenophyne **3bc**



3bb **3bc**

To a solution of **3bb** (40.0 mg, 0.117 mmol) in CH_2Cl_2 (1 mL) were added NEt_3 (82.0 μL, 0.585 mmol), DMAP (14.3 mg, 0.117 mmol), and Ac_2O (55.3 μL, 0.585 mmol) at 0 °C. After stirred at that temperature for 30 min, the reaction was quenched with H_2O and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 3:1) to afford 18.8 mg (42%) of **3bc** as a colorless crystal.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.08 (dd, *J* = 17.6, 2.8 Hz, 1H), 3.95-3.86 (m, 2H), 2.85-2.81 (m, 2H), 2.49 (s, 3H), 2.47 (s, 3H), 2.40-2.22 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0, 151.3, 143.7, 141.4, 135.0, 130.0, 129.0, 128.3, 128.1, 127.4, 122.2, 94.7, 83.8, 43.9, 38.1, 32.8, 29.8, 22.6, 21.7, 21.4.

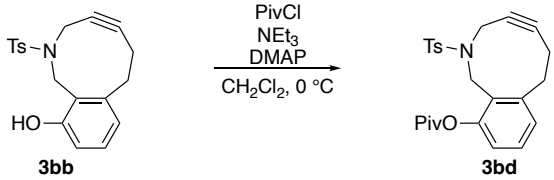
IR (reflection, cm^{-1}): 2948, 1758, 1595, 1199, 882, 725, 657, 578.

Mp: 210.0-211.0 °C.

HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calcd. for $C_{21}H_{22}NO_4S$ $[M+H]^+$ requires *m*/*z*: 384.1270, found *m*/*z*: 383.1267.

Analytical HPLC: column: CHIRALPAK IB (0.46 cm × 25 cm), eluent: hexane/IPA = 30:70, flow rate: 0.5 mL/min, detection: UV 270 nm, temperature: –20 °C, retention time: t_1 = 21.2 min, t_2 = 31.2 min.

1^6-pivaloyl-3-aza[7]orthobenzenophyne **3bd**



3bb **3bd**

To a solution of **3bb** (30.0 mg, 0.0880 mmol) in CH_2Cl_2 (1 mL) were added NEt_3 (37.0 μL, 0.264 mmol), DMAP (10.8 mg, 0.088 mmol), and pivaloyl chloride (32.5 μL, 0.264 mmol) at 0 °C. After stirred at that temperature for 3.5 h, the reaction was quenched with H_2O and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography (hexane/AcOEt = 10:1 to 3:1) to afford 25.5 mg (68%) of **3bd** as a colorless crystal.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.28 (dd, J = 8.1, 8.1 Hz, 1H), 7.01 (dd, J = 8.1, 1.2 Hz, 1H), 6.87 (dd, J = 8.1, 1.2 Hz, 1H), 4.80 (d, J =12.0 Hz, 1H), 4.13 (ddd, J = 18.6, 1.8, 1.8 Hz, 1H), 3.92-3.82 (m, 2H), 2.85-2.66 (m, 2H), 2.47 (s, 3H), 2.20-2.17 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 151.9, 143.7, 142.0, 134.1, 129.7, 129.1, 127.9, 127.8, 127.4, 121.5, 94.8, 84.3, 44.0, 39.5, 38.0, 33.0, 27.4, 22.6, 21.7.

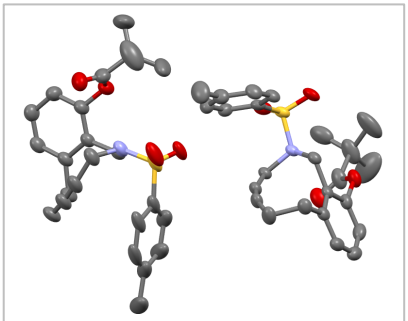
IR (reflection, cm^{-1}): 2966, 1746, 1119, 897, 818, 724, 661, 583.

Mp: 133.5-134.0 °C.

HRMS (FAB, matrix: 3-nitrobenzyl alcohol, positive): Exact mass calcd. for $C_{24}H_{28}NO_4S$ $[M+H]^+$ requires m/z: 426.1739, found m/z: 426.1738.

Analytical HPLC: column: CHIRALPAK IB (0.46 cm × 25 cm), eluent: hexane/IPA = 30:70, flow rate: 0.5 mL/min, detection: UV 270 nm, temperature: –20 °C) retention time: t_1 = 15.2 min, t_2 = 19.3 min.

Single crystal X-ray structural analysis: The structure was solved by the direct methods and expanded using Fourier techniques. All the non-hydrogen atoms were anisotropically refined. The hydrogen atoms were refined using the riding model. Structural solution and refinement were performed by SHELXL, using Olex2 software package as a front-end application. CCDC 2156588 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


ellipsoid set at 50% of probability level

Selected crystallographic data: triclinic, P–1, a = 11.50586(17) Å, b = 12.5371(2) Å, c = 17.1225(2) Å, α = 83.5826(14)°, β = 79.8978(12)°, γ = 69.6621(16)°, V = 2276.59(7) Å^3, Z = 2, R_1 = 0.0623, wR_2 = 0.1725.