- Supporting Information-

Catalytic Enantioselective Nitroso Diels-Alder Reaction

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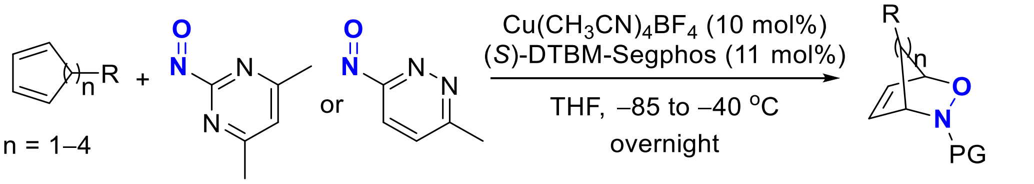
1. General.

Chemicals. Anhydrous THF, Et_2O, toluene and CH_2Cl_2 were dried with Glass Contour solvent purification system. Dry acetonitrile, EtOH, MeOH, and *n*-hexane were purchased from WAKO chemicals and used as received. All other chemicals were purchased from their commercial sources and used as it received.

Analytics.

NMR spectra were recorded on a JEOL JNM LA-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts were reported in ppm on the δ scale relative to solvent residual signal $CDCl_3$ (δ = 7.26 ^{1}H NMR and for 77.2 for ^{13}C NMR), DMSO (δ = 2.50 ^{1}H NMR and for 39.5 for ^{13}C NMR), α,α,α-trifluorotoluene (δ = −63.72 for ^{19}F NMR) as an internal reference. Multiplicities are indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), spt (septate), td (triplet of doublet), or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). High performance liquid chromatography (HPLC) was performed on Agilent Technologies 1220 Inifinity LC instruments using Daicel Chiralpak AD-H, OD-H, OJ-H and AS-H 4.6 mm × 25 cm column or Shimadzu HPLC instrument using IA-3, IB-3, IC-3 4.6 mm × 25 cm column. Optical rotations were measured on an ATAGO CO., LTD AP-300 polarimeter. Low temperature reactions were performed on UC reactor from Techno Signa. Column chromatography was conducted with silica gel 60 N (KANTO CHEMICAL, spherical, neutral, 40-50 or 63-210 μm). For thin-layer chromatography (TLC) analysis Merck precoated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), I_2, $KMnO_4$, and cerium molybdate.

2. Enantioselective nitroso Diels-Alder reaction with symmetrical dienes 2a–h.

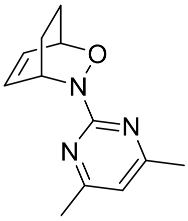


2a–**h** **1c**, pyM-NO **1j**, pyD-NO **3**, PG = pyM or pyD

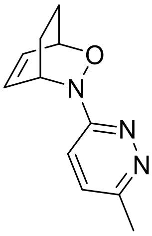
General procedure 1:

$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a –85 °C bath. The nitroso compound **1c**,**j** (0.1 mmol) was then added and the wall of the test tube was rinsed with THF (0.5 mL). The mixture was further stirred for 10 min before the diene **2a–h** (0.12 mmol) was added. Then the reaction mixture was warmed to –40 °C over ~2 h and stirred at –40 °C overnight. It was then allowed to warm to 0 °C before directly loaded into a column packed with silica gel and purified using EtOAc/*n*-hexane (1:1 to 3:1), Acetone/*n*-hexane (1:4 to 1:3) as eluent to afford the nitroso Diels-Alder adducts **3**.

All the racemic samples were prepared by mixing the nitroso compounds **1c**,**j** (0.1 mmol) with the dienes **2a–h** (0.12 mmol) in CH_2Cl_2 at 0 °C.

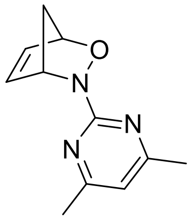


3ac: According to GP 1. 21 mg, 97%. $[\alpha]_D^{24}$ –73.3 (*c* = 1.5, $CHCl_3$, 1.6:98.4 e.r.). ^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.44 - 6.58 (m, 2 H), 6.41 (s, 1 H), 5.43 – 5.46 (m, 1 H), 4.84 – 4.87 m, 1 H), 2.10 - 2.40 (m, 8 H), 1.47 - 1.62 (m, 1 H), 1.37 - 1.47 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 165.4, 132.3, 132.0, 112.4, 112.4, 70.7, 50.4, 24.2, 24.0, 23.9, 21.1 ppm. HRMS (ESI): Calculated for $C_{12}H_{15}N_3Na_1O_1$ ($[M + Na]^+$) is 240.1121, found 240.1113. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 16.5 min, t_R(major) = 17.4 min.

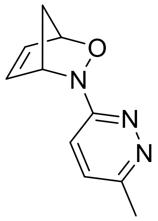


3aj: According to GP 1. 20.3 mg, 99%. $[\alpha]_D^{28}$ –164.3 (*c* = 1.4, $CHCl_3$, 99.3:0.7 e.r.).

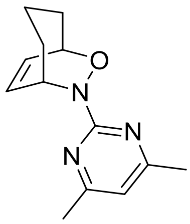
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.12 (d, *J* = 8.9 Hz, 1 H), 7.05 (d, *J* = 8.9 Hz, 1 H), 6.53 - 6.36 (m, 2 H), 5.51 (dd, *J* = 2.5, 5.3 Hz, 1 H), 4.74 - 4.61 (m, 1 H), 2.56 (s, 3 H), 2.32 - 2.17 (m, 2 H), 1.69 - 1.54 (m, 1 H), 1.51 - 1.35 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.9, 154.2, 133.3, 131.0, 128.2, 117.4, 70.1, 51.8, 24.5, 21.6, 20.3. HRMS (ESI): Calculated for $C_{11}H_{14}N_3O_1$ ($[M + H]^+$) is 204.1131, found 204.1124. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 21.8 min, t_R(minor) = 24.0 min.



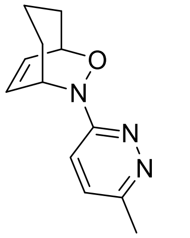
3bc: According to GP 1. 19 mg, 93%. $[\alpha]_D^{24}$ −154.6 (*c* = 1.5, $CHCl_3$, 2.3:97.7 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.48 (s, 1 H), 6.36 (dt, *J*=5.6, 1.9 Hz, 1 H), 6.28 (dt, *J*=5.5, 1.9 Hz, 1 H), 5.47 - 5.57 (m, 1 H), 5.24 - 5.36 (m, 1 H), 2.35 (s, 6 H), 2.15 (dt, *J*=8.5, 1.8 Hz, 1 H), 1.80 (d, *J*=8.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.6, 166.2, 135.3, 133.4, 113.4, 83.7, 65.8, 48.0, 24.2 ppm. HRMS (ESI): Calculated for $C_{11}H_{13}N_3Na_1O_1$ ($[M + Na]^+$) is 226.0951, found 226.0942. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 17.1 min, t_R(major) = 22.2 min.



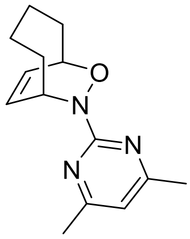
3bj: According to GP 1. 18 mg, 95%. $[\alpha]_D^{24}$ −6.7 (*c* = 0.60, $CHCl_3$, 95.0:5.0 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.14 (d, *J*=8.9 Hz, 1 H), 7.00 (d, *J*=8.9 Hz, 1 H), 6.29 (t, *J*=1.9 Hz, 1 H), 5.70 (t, *J*=1.6 Hz, 1 H), 5.15 - 5.28 (m, 1 H), 2.18 (dt, *J*=8.5, 1.9 Hz, 1 H), 1.89 (d, *J*=8.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.5, 154.7, 136.6, 132.9, 128.2, 118.1, 83.0, 66.6, 48.6, 21.6. HRMS (FAB): Calculated for $C_{10}H_{12}N_3O_1$ ($[M + H]^+$) is 190.0980, found 190.0975. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 26.7 min, t_R(minor) = 30.3 min.



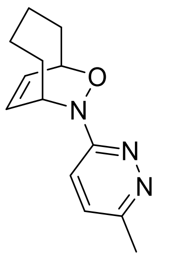
3cc: According to GP 1. 22 mg, 96%. $[\alpha]_D^{24}$ −50.8 (*c* = 1.2, $CHCl_3$, 2.6:97.4 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.38 (s, 1 H), 6.31 (ddd, *J*=9.1, 6.9, 0.9 Hz, 1 H), 6.15 (ddd, *J*=9.2, 6.2, 1.4 Hz, 1 H), 5.44 - 5.58 (m, 1 H), 4.91 (t, *J*=5.2 Hz, 1 H), 2.33 (s, 6 H), 1.86 - 2.06 (m, 3 H), 1.71 - 1.84 (m, 1 H), 1.53 - 1.65 (m, 1 H), 1.36 - 1.52 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.5, 164.3, 130.0, 127.9, 111.5, 74.8, 54.8, 31.1, 28.0, 24.3, 18.9 ppm. HRMS (ESI): Calculated for $C_{13}H_{17}N_3Na_1O_1$ ($[M + Na]^+$) is 254.1264, found 254.1259. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 12.2 min, t_R(major) = 16.4 min.



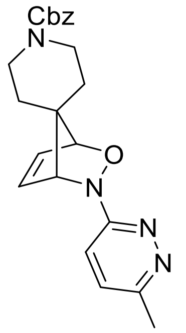
3cj: According to GP 1. 21 mg, 97%. $[\alpha]_D^{25}$ −138.0 (*c* = 1.0, $CHCl_3$, 98.1:1.9 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.21 - 7.10 (m, 2 H), 6.33 – 6.35 (m, 1 H), 5.99 – 6.03 (m, 1 H), 5.68 - 5.53 (m, 1 H), 4.75 – 4.78 (m, 1 H), 2.56 (s, 3 H), 2.15 - 1.87 (m, 3 H), 1.85 - 1.70 (m, 2 H), 1.68 - 1.56 (m, 1 H), 1.53 - 1.36 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.2, 153.6, 132.0, 128.4, 126.0, 116.7, 74.3, 56.3, 31.8, 27.2, 21.5, 18.9. HRMS (FAB): Calculated for $C_{12}H_{16}N_3O_1$ ($[M + H]^+$) is 218.1293, found 218.1292. HLPC analysis: Daicel Chiralpak IB-3, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 29.7 min, t_R(minor) = 39.1 min.



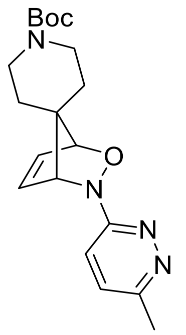
3dc: According to GP 1. 22 mg, 90%. $[\alpha]_D^{25}$ +90.0 (*c* = 1.0, $CHCl_3$, 2.0:98.0 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 6.44 (s, 1 H), 6.30 (dd, *J*=9.8, 6.6 Hz, 1 H), 5.71 (dd, *J*=10.1, 4.4 Hz, 1 H), 5.19 – 5.22 (m, 1 H), 5.01 - 5.11 (m, 1 H), 2.34 (s, 6 H), 2.09 - 2.32 (m, 3 H), 1.79 - 1.87 (m, 1 H), 1.56 - 1.78 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.7, 166.3, 132.1, 126.8, 112.4, 74.5, 55.1, 34.4, 32.1, 26.4, 24.3, 22.6, 22.6 ppm. HRMS (ESI): Calculated for $C_{14}H_{19}N_3Na_1O_1$ ($[M + Na]^+$) is 268.1434, found 268.1430. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 7.5 min, t_R(major) = 10.2 min.



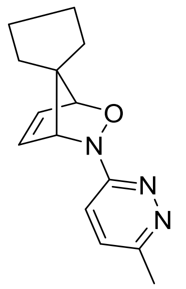
3dj: According to GP 1. 21 mg, 91%. $[\alpha]_D^{24}$ +95.0 (*c* = 1.0, $CHCl_3$, 99.9:0.1 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.25 (d, *J* = 9.2 Hz, 1 H), 7.16 (d, *J* = 9.2 Hz, 1 H), 6.39 (dd, *J* = 6.8, 10.2 Hz, 1 H), 5.67 (dd, *J* = 4.6, 10.1 Hz, 1 H), 5.52 - 5.37 (m, 1 H), 4.85 (t, *J* = 4.1 Hz, 1 H), 2.57 (s, 3 H), 2.25 – 2.32 (m, 1 H), 2.17 - 2.00 (m, 2 H), 1.89 (tt, *J* = 4.5, 9.1 Hz, 1 H), 1.80 - 1.56 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 163.7, 153.7, 133.1, 128.6, 125.5, 116.1, 74.1, 54.3, 35.0, 31.8, 26.3, 22.0. HRMS (FAB): Calculated for $C_{13}H_{18}N_3O_1$ ($[M + H]^+$) is 231.1450, found 231.1446. HLPC analysis: Daicel Chiralpak IB-3, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 26.4 min, t_R(minor) = 28.9 min.



3ej: According to GP 1. 37 mg, 94%. $[\alpha]_D^{25}$ − 82.7 (c = 1.5, $CHCl_3$, 99.4:0.6 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.43 - 7.28 (m, 5 H), 7.11 (d, J = 8.9 Hz, 1 H), 6.93 (d, J = 8.9 Hz, 1 H), 6.29 - 6.14 (m, 2 H), 5.32 (s, 1 H), 5.14 (s, 2 H), 4.73 (s, 1 H), 3.70 - 3.57 (m, 1 H), 3.57 - 3.43 (m, 2 H), 3.41 - 3.29 (m, 1 H), 2.57 (s, 3 H), 2.04 (br. s., 1 H), 1.91 (br. s., 1 H), 1.64 (br. s., 1 H), 1.61 - 1.48 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 154.6, 136.9, 135.9, 131.0, 128.6, 128.2, 128.1, 128.0, 117.6, 86.4, 70.0, 67.2, 60.8, 42.4, 41.7, 29.3, 29.2, 21.6. HRMS (FAB): Calculated for $C_{22}H_{25}N_4O_3$ ($[M + H]^+$) is 393.1927, found 393.1933. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 34.9 min, t_R(minor) = 37.8 min.

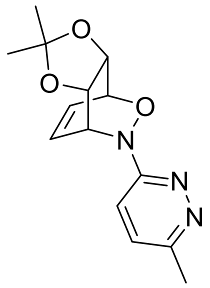


3fj: According to GP 1. 33 mg, 92%. $[\alpha]_D^{25}$ − 93.3 (c = 1.5, $CHCl_3$, 99.0:1.0 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.10 (d, J=8.9 Hz, 1 H), 6.92 (d, J=8.9 Hz, 1 H), 6.11 - 6.26 (m, 2 H), 5.29 (s, 1 H), 4.71 (s, 1 H), 3.47 - 3.60 (m, 1 H), 3.34 - 3.45 (m, 2 H), 3.21 - 3.32 (m, 1 H), 2.56 (s, 3 H), 1.96 - 2.07 (m, 1 H), 1.85 – 1.91 (m, 1 H), 1.48 - 1.67 (m, 2 H), 1.45 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.3, 154.9, 154.5, 135.9, 131.0, 128.2, 128.1, 117.6, 86.4, 79.7, 70.1, 61.0, 29.3, 28.6, 28.6, 21.6 ppm. HRMS (FAB): Calculated for $C_{19}H_{27}N_4O_3$ ($[M + H]^+$) is 359.2083, found 359.2070. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 11.1 min, t_R(minor) = 13.0 min.



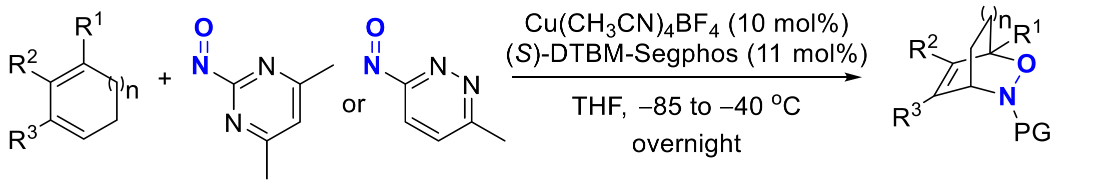
3gj: According to GP 1. 23 mg, 95%. $[\alpha]_D^{25}$ − 216.7 (c = 1.7, $CHCl_3$, 98.7:1.3 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.10 (d, J=8.9 Hz, 1 H), 6.94 (d, J=8.9 Hz, 1 H), 6.10 - 6.29 (m, 2 H), 5.10 (s, 1 H), 4.47 - 4.62 (m, 1 H), 2.56 (s, 3 H), 1.81 - 1.89 (m, 2 H), 1.49 - 1.75 (m, 5 H), 1.37 - 1.49 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.4, 154.3, 137.7, 133.4, 128.1, 117.6, 88.1, 73.0, 68.6, 31.9, 31.4, 26.6, 26.3, 21.6 ppm. HRMS (FAB): Calculated for

$C_{14}H_{18}N_3O_1$ ([M + H]$^+$) is 244.1450, found 244.1451. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 15.7 min, t_R(minor) = 18.7 min.



3hj: According to GP 1. With 5 mol% catalyst loading and 0.2 mmol of **1j**. 54.5 mg, 99%. $[\alpha]_D^{25}$ − 130.8 (*c* = 1.3 $CHCl_3$, 0.1:99.9 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.16 (d, *J*=8.9 Hz, 1 H), 7.09 (d, *J*=9.2 Hz, 1 H), 6.21 - 6.41 (m, 2 H), 5.82 – 5.84 (m, 1 H), 4.83 – 4.86 (m, 1 H), 4.70 (dd, *J*=6.9, 4.1 Hz, 1 H), 4.56 - 4.66 (m, 1 H), 2.58 (s, 3 H), 1.34 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 163.7, 155.0, 132.0, 128.7, 128.4, 128.4, 117.9, 110.9, 73.8, 73.3, 73.2, 70.4, 54.8, 25.8, 25.5, 21.6 ppm. HRMS (FAB): Calculated for $C_{14}H_{18}N_3O_3$ ([M + H]$^+$) is 276.1348, found 276.1346. HLPC analysis: Daicel Chiralpak IB-3, hexane/*i*-PrOH = 93/7, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 19.3 min, t_R(major) = 35.6 min.

3. Enantioselective nitroso Diels-Alder reaction with unsymmetrical dienes 2i–p.

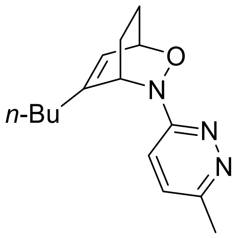


2i–p **1c**, pyM-NO **1j**, pyD-NO **3**, PG = pyM or pyD

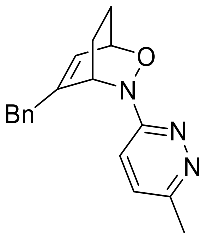
General procedure 2:

$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a –85 °C bath. Nitroso compound **1c**,**j** (0.1 mmol) was then added and the wall of the test tube was rinsed with THF (0.5 mL). The mixture was further stirred for 10 min before the diene **2i–p** (0.12 mmol) was added. Then the reaction mixture was warmed to –40 °C over ~2 h and stirred at –40 °C overnight. It was then allowed to warm to 0 °C before directly loaded into a column packed with silica gel and purified using EtOAc/*n*-hexane (1:1 to 3:1), Acetone/*n*-hexane (1:4 to 1:3), or EtOAc/*n*-hexane/NEt_3 (10:40/1 to 10:20:1) as eluent to afford the nitroso Diels-Alder adducts **3**.

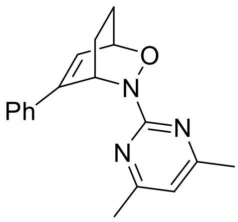
All the racemic samples were prepared by mixing the nitroso compounds **1c**,**j** (0.1 mmol) with the dienes **2i‒p** (0.12 mmol) in CH_2Cl_2 at ‒20 to 0°C.



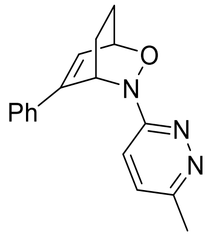
3ij: According to GP 2. 25.5 mg, 98%. $[\alpha]_D^{25}$ ‒ 74.3 (*c* = 1.4 $CHCl_3$, 0.4:99.6 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.09 - 7.13 (m, 1 H), 7.04 - 7.09 (m, 1 H), 5.93 - 6.07 (m, 1 H), 5.28 - 5.42 (m, 1 H), 4.70 – 4.72 (m, 1 H), 2.56 (s, 3 H), 2.00 - 2.30 (m, 4 H), 1.48 - 1.65 (m, 1 H), 1.13 - 1.42 (m, 5 H), 0.80 (t, *J*=7.3 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.0, 153.9, 146.8, 128.1, 122.1, 116.9, 71.0, 55.9, 34.5, 28.8, 25.5, 22.3, 21.6, 20.8, 14.0 ppm. HRMS (FAB): Calculated for $C_{15}H_{22}N_3O_1$ ($[M + H]^+$) is 260.1763, found 260.1764. HLPC analysis: Daicel Chiralpak IB-3, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 18.1 min, t_R(major) = 25.3 min.



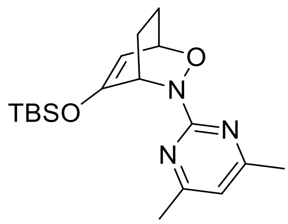
3jj: According to GP 2. 29 mg, 99%. $[\alpha]_D^{25}$ ‒ 68.0 (*c* = 1.1 $CHCl_3$, 0.3:99.7 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.01 - 7.30 (m, 8 H), 5.87 - 5.98 (m, 1 H), 5.30 - 5.43 (m, 1 H), 4.62 - 4.76 (m, 1 H), 3.35 - 3.49 (m, 2 H), 2.61 (s, 3 H), 2.07 - 2.28 (m, 2 H), 1.28 - 1.48 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.0, 154.2, 145.9, 137.7, 129.4, 128.5, 128.5, 128.1, 126.4, 123.4, 117.3, 71.2, 55.4, 41.6, 25.5, 21.6, 20.8 ppm. HRMS (FAB): Calculated for $C_{18}H_{20}N_3O_1$ ($[M + H]^+$) is 294.1606, found 294.1610. HLPC analysis: Daicel Chiralpak IB-3, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 21.8 min, t_R(major) = 28.7 min.



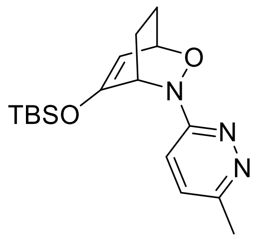
3kc: According to GP 2. 26 mg, 89%. $[\alpha]_D^{26}$ +208.3 (*c* = 1.2, $CHCl_3$, 96.6:3.4 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.66 - 7.74 (m, 2 H), 7.30 - 7.37 (m, 2 H), 7.23 - 7.30 (m, 1 H), 6.75 (dd, *J*=6.0, 2.3 Hz, 1 H), 6.39 (s, 1 H), 5.96 (q, *J*=2.6 Hz, 1 H), 5.05 – 5.08 (m, 1 H), 2.29 - 2.45 (m, 9 H), 1.60 - 1.75 (m, 1 H), 1.44 - 1.57 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 143.7, 136.1, 128.5, 128.1, 125.8, 123.7, 112.6, 71.1, 52.3, 24.4, 24.1, 21.6 ppm. HRMS (ESI): Calculated for $C_{18}H_{19}N_3Na_1O_1$ ($[M + Na]^+$) is 316.1420, found 316.1433. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 18.9 min, t_R(minor) = 23.0 min.



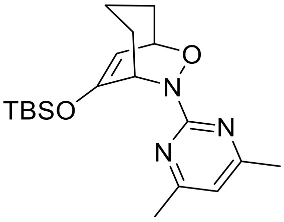
3kj: According to GP 2. 27.5 mg, 99%. $[\alpha]_D^{25}$ + 140.0 (c = 1.5 $CHCl_3$, 0.1:99.9 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.51 - 7.70 (m, 2 H), 7.29 - 7.37 (m, 2 H), 7.20 - 7.28 (m, 1 H), 7.02 - 7.15 (m, 2 H), 6.67 (dd, J=6.2, 2.3 Hz, 1 H), 5.98 (q, J=2.7 Hz, 1 H), 4.91 – 4.93 (m, 1 H), 2.52 (s, 3 H), 2.27 - 2.47 (m, 2 H), 1.57 - 1.84 (m, 2 H), 1.42 - 1.57 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.3, 154.0, 144.0, 135.9, 128.8, 128.3, 128.2, 125.8, 122.9, 116.5, 70.5, 54.5, 24.7, 21.5, 21.1 ppm. HRMS (FAB): Calculated for $C_{17}H_{18}N_3O_1$ ($[M + H]^+$) is 280.1450, found 280.1458. HLPC analysis: Daicel Chiralpak IB-3, hexane/i-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 31.1 min, t_R(major) = 43.5 min.



3lc: According to GP 2. 32 mg, 92%. $[\alpha]_D^{26}$ +30.0 (c = 1.0, $CHCl_3$, 1.9:98.1 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 6.43 (s, 1 H), 5.20 - 5.32 (m, 2 H), 4.96 – 4.99 (m, 1 H), 2.33 (s, 6 H), 2.11 - 2.29 (m, 2 H), 1.71 - 1.83 (m, 1 H), 1.38 - 1.49 (m, 1 H), 0.85 (s, 10 H), 0.09 (s, 3 H), -0.11 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 154.6, 112.5, 102.0, 72.8, 56.3, 25.9, 25.6, 25.6, 24.2, 21.6, 18.0, -4.3, -5.3 ppm. HRMS (ESI): Calculated for $C_{18}H_{29}N_3Na_1O_2Si_1$ ($[M + Na]^+$) is 370.1921, found 370.1936. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 7.0 min, t_R(major) = 7.7 min.

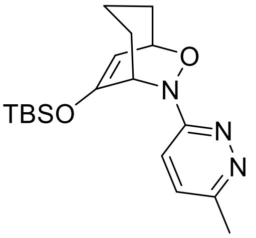


3lj: According to GP 2. 30 mg, 90%. $[\alpha]_D^{26}$ − 22.2 (c = 0.9 $CHCl_3$, 99.9:0.1 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.12 (s, 2 H), 5.27 (q, J=2.8 Hz, 1 H), 5.17 (dd, J=6.6, 2.7 Hz, 1 H), 4.77 - 4.88 (m, 1 H), 2.57 (s, 3 H), 2.08 - 2.29 (m, 2 H), 1.65 - 1.85 (m, 2 H), 1.38 - 1.48 (m, 2 H), 1.24 - 1.34 (m, 2 H), 0.81 (s, 9 H), 0.02 (s, 3 H), -0.15 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.0, 154.7, 154.0, 127.9, 116.6, 100.9, 72.4, 58.3, 26.3, 25.6, 21.5, 20.8, 18.1, -4.5, -5.2 ppm. HRMS (FAB): Calculated for $C_{17}H_{28}N_3O_2Si_1$ ($[M + H]^+$) is 334.1951, found 334.1945. HLPC analysis: Daicel Chiralpak IA-3, hexane/i-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 12.5 min, t_R(minor) = 15.9 min.



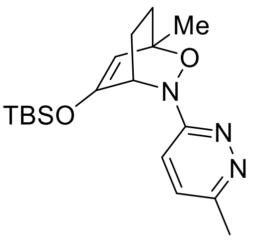
3mc: According to GP 2. 30 mg, 83%. 97.8:2.2 e.r.

^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.39 (s, 1 H), 5.28 – 5.29 (m, 1 H), 4.98 – 5.01 (m, 1 H), 4.89 (dd, *J*=6.9, 2.5 Hz, 1 H), 2.33 (s, 6 H), 2.00 - 2.11 (m, 1 H), 1.88 - 1.98 (m, 1 H), 1.76 - 1.88 (m, 1 H), 1.67 - 1.76 (m, 1 H), 1.55 - 1.65 (m, 1 H), 1.41 – 1.52 (m, 1 H), 0.88 (s, 9 H), 0.11 (s, 3 H), -0.02 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 164.7, 153.6, 111.8, 97.9, 74.9, 60.7, 32.4, 26.5, 25.6, 24.3, 18.9, 18.0, -4.5, -4.9 ppm. HRMS (ESI): Calculated for $C_{19}H_{31}N_3Na_1O_2Si_1$ ($[M + Na]^+$) is 384.2078, found 374.2083. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 20.6 min, t_R(minor) = 21.9 min.



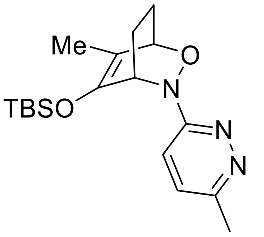
3mj: According to GP 2. 32 mg, 92%. $[\alpha]_D^{25}$ + 57.1 (*c* = 1.4 $CHCl_3$, 99.9:0.1 e.r.).

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.18 (d, *J*=8.9 Hz, 1 H), 7.12 (d, *J*=9.2 Hz, 1 H), 5.35 (dd, *J*=7.3, 2.1 Hz, 1 H), 4.86 - 4.93 (m, 1 H), 4.80 (dd, *J*=7.1, 2.5 Hz, 1 H), 2.56 (s, 3 H), 2.06 - 2.22 (m, 1 H), 1.82 - 1.95 (m, 2 H), 1.68 - 1.78 (m, 1 H), 1.57 - 1.67 (m, 1 H), 1.41 - 1.55 (m, 1 H), 0.83 (s, 9 H), 0.03 (s, 3 H), -0.08 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.1, 154.1, 153.4, 128.1, 116.1, 96.5, 74.9, 62.6, 33.2, 26.0, 25.6, 21.5, 18.8, 18.1, -4.5, -4.9 ppm. HRMS (FAB): Calculated for $C_{18}H_{30}N_3O_2Si_1$ ($[M + H]^+$) is 348.2107, found 248.2103. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 15.2 min, t_R(minor) = 21.9 min.

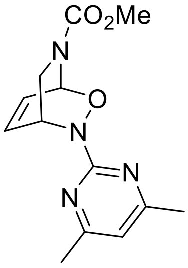


3nj: According to GP 2. 31 mg, 89%. $[\alpha]_D^{25}$ + 30.0 (*c* = 1.0 $CHCl_3$, 99.8:0.2 e.r.).

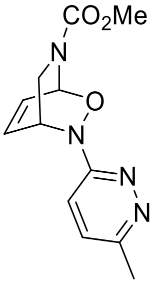
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.07 - 7.14 (m, 2 H), 5.29 (s, 1 H), 5.24 (q, *J*=3.1 Hz, 1 H), 4.94 (d, *J*=2.5 Hz, 1 H), 2.57 (s, 3 H), 2.20 - 2.32 (m, 1 H), 1.99 – 1.92 (m, 1 H), 1.74 - 1.85 (m, 2 H), 1.48 - 1.52 (m, 3 H), 0.81 (s, 9 H), 0.02 (s, 3 H), -0.16 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.1, 154.7, 153.9, 127.9, 116.6, 105.0, 78.0, 58.4, 32.7, 25.6, 23.7, 22.0, 21.5, 18.1, -4.4, -5.1 ppm. HRMS (FAB): Calculated for $C_{18}H_{30}N_3O_2Si_1$ ($[M + H]^+$) is 348.2107, found 248.2103. HLPC analysis: Daicel Chiralpak IA-3, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 9.3 min, t_R(minor) = 12.6 min.



3oj: According to GP 2. 31 mg, 89%. $[\alpha]_D^{25}$ − 55.0 (*c* = 1.2 $CHCl_3$, 98.5:1.5 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.02 - 7.17 (m, 2 H), 5.22 (t, *J*=3.0 Hz, 1 H), 4.63 (dd, *J*=3.7, 1.4 Hz, 1 H), 2.57 (s, 3 H), 2.14 - 2.28 (m, 1 H), 2.00 - 2.14 (m, 1 H), 1.60 - 1.74 (m, 4 H), 1.44 - 1.52 (m, 1 H), 0.89 (s, 9 H), 0.14 (s, 3 H), 0.05 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.3, 153.9, 147.3, 128.2, 116.4, 113.3, 57.6, 25.7, 25.3, 21.6, 21.6, 18.3, 12.1, -4.0, -4.2 ppm. HRMS (FAB): Calculated for $C_{18}H_{30}N_3O_2Si_1$ ($[M + H]^+$) is 348.2107, found 248.2103. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 14.6 min, t_R(minor) = 30.7 min.

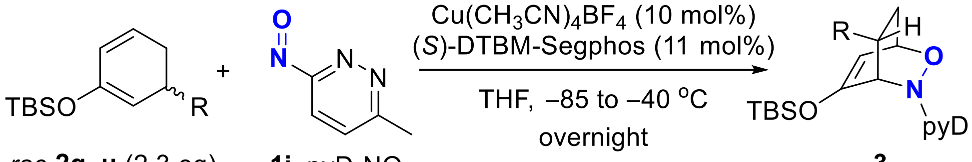


Mixture of product (>10:1 ratio).
3pc: According to GP 2. 23 mg, 83%. $[\alpha]_D^{24}$ −53.3 (*c* = 1.1 $CHCl_3$, 99.4:0.6 e.r.).
^1H NMR (CD_3CN,400MHz): δ = 6.57 - 6.71 (m, 2 H), 6.46 - 6.56 (m, 1 H), 6.05 - 6.19 (m, 1 H), 5.52 (br. s., 1 H), 3.62 - 3.88 (m, 4 H), 3.16 - 3.32 (m, 1 H), 2.30 (s, 6 H) ppm. ^{13}C NMR (CD_3CN, 101 MHz): δ = 168.8, 166.2, 131.6, 131.4, 131.0, 114.5, 77.3, 76.8, 53.3, 52.4, 45.5, 24.1 ppm. HRMS (ESI): Calculated for $C_{13}H_{16}N_4Na_1O_2$ ($[M + Na]^+$) is 299.1115, found 299.1122. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 35.6 min, t_R(minor) = 40.6 min.



Mixture of product (2:1 ratio).
3pj: According to GP 2.12 mg, 46%. $[\alpha]_D^{25}$ − 83.5 (*c* = 0.8 $CHCl_3$, 97.8:2.2 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.15 - 7.22 (m, 1 H), 7.04 - 7.14 (m, 1 H), 6.44 - 6.64 (m, 2 H), 6.03 - 6.28 (m, 1 H), 5.61 - 5.79 (m, 1 H), 3.98 – 3.94 (m, 1 H), 3.72 - 3.83 (m, 3 H), 3.23 - 3.39 (m, 1 H), 2.60 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = d = 163.3, 155.3, 130.6, 130.3, 129.8, 128.6, 117.7, 76.0, 75.5, 53.0, 51.9, 51.8, 44.4, 21.6 ppm. HRMS (FAB): Calculated for $C_{12}H_{15}N_4O_3$ ($[M + H]^+$) is 263.1144, found 263.1134. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 39.2 min, t_R(minor) = 45.4 min.

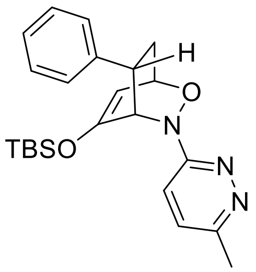
4. Enantioselective nitroso Diels-Alder reaction with racemic 2,6-disubstituted 1,3-cyclohexadienes 2q–u.



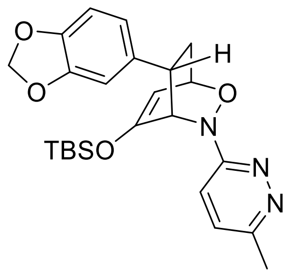
General procedure 3:

$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a −85 °C bath. The nitroso compound **1j** (12.3 mg, 0.1 mmol) was then added and the wall of the test tube was rinsed with THF (0.5 mL). The mixture was further stirred for 10 min before the diene **2q–u** (0.23 mmol) was added. Then the reaction mixture was warmed to −40 °C over ~2 h and stirred at −40 °C overnight. It was then allowed to warm to 0 °C before directly loaded into a column packed with silica gel and purified using EtOAc/*n*-hexane/NEt_3 (10:50/1 to 10:25:1) as eluent to afford the nitroso Diels-Alder adducts **3**.

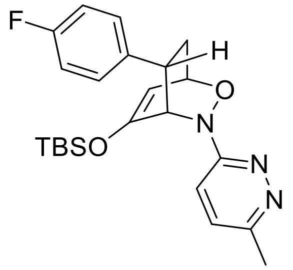
All the racemic samples were prepared by mixing the nitroso compound **1j** (0.1 mmol) with the diene **2q–u** (0.12 mmol) in CH_2Cl_2 at −20 to 0°C.



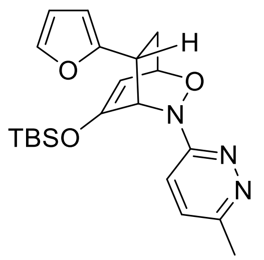
3qj: According to GP 3. 40 mg, 98%. $[\alpha]_D^{26}$ + 31.0 (*c* = 2.0 $CHCl_3$, 99.6:0.4 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.25 - 7.33 (m, 4 H), 7.11 - 7.24 (m, 3 H), 5.33 (t, *J*=2.7 Hz, 1 H), 5.25 (dd, *J*=6.6, 2.7 Hz, 1 H), 4.91 - 5.00 (m, 1 H), 3.66 – 3.70 (m, 1 H), 2.65 – 3.72 (m, 1 H), 2.58 (s, 3 H), 1.66 – 1.71 (m, 1 H), 0.69 (s, 9 H), -0.07 (s, 3 H), -0.21 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = d = 164.8, 154.3, 153.1, 142.7, 128.5, 128.0, 128.0, 127.9, 126.8, 116.8, 100.4, 72.2, 63.7, 38.2, 35.3, 25.3, 21.5, 17.9, -4.8, -5.3 ppm. HRMS (ESI): Calculated for $C_{23}H_{32}N_3O_2Si_1$ ($[M + H]^+$) is 410.2258, found 410.2254. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 24.7 min, t_R(minor) = 28.7 min.



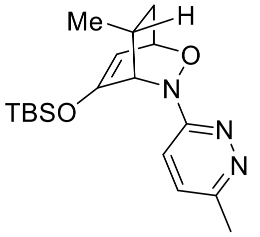
3rj: According to GP 3. 42 mg, 93%. $[\alpha]_D^{25}$ + 22.2 (*c* = 1.8 $CHCl_3$, 99.7:0.3 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.11 - 7.18 (m, 2 H), 6.69 - 6.78 (m, 3 H), 5.85 - 5.94 (m, 2 H), 5.20 - 5.27 (m, 2 H), 4.89 - 4.96 (m, 1 H), 3.56 – 3.70 (m, 1 H), 2.61 – 2.68 (m, 1 H), 2.57 (s, 3 H), 1.56 – 1.60 (m, 1 H), 0.71 (s, 9 H), -0.05 (s, 3 H), -0.19 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.8, 154.2, 153.1, 147.8, 146.3, 136.8, 127.9, 121.2, 116.8, 108.3, 108.2, 108.1, 101.0, 100.3, 72.1, 63.8, 38.0, 35.7, 25.6, 25.3, 21.5, 17.9, -4.9, -5.3 ppm. HRMS (FAB): Calculated for $C_{24}H_{32}N_3O_4Si_1$ ($[M + H]^+$) is 454.2162, found 454.2169. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 59.2 min, t_R(minor) = 67.4 min.



3sj: According to GP 3. 39 mg, 91%. $[\alpha]_D^{25}$ + 11.1 (*c* = 1.8 $CHCl_3$, 99.3:0.7 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.20 - 7.26 (m, 2 H), 7.16 (d, *J*=1.4 Hz, 2 H), 6.92 - 7.01 (m, 2 H), 5.22 - 5.31 (m, 2 H), 4.93 – 4.95 (m, 1 H), 3.61 - 3.70 (m, 1 H), 2.64 – 2.70 (m, 1 H), 2.58 (s, 3 H), 1.60 – 1.74 (m, 1 H), 0.69 (s, 9 H), -0.07 (s, 3 H), -0.21 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.7, 163.1, 160.6, 154.3, 153.0, 138.5, 138.4, 129.5, 129.4, 127.9, 116.8, 115.3, 115.1, 100.5, 72.1, 63.6, 37.5, 35.4, 25.3, 21.5, 17.8, -4.8, -5.3 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = −116.51 ppm. HRMS (ESI): Calculated for $C_{23}H_{31}F_1N_3O_2Si_1$ ($[M + H]^+$) is 428.2164, found 428.2168. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 27.2 min, t_R(minor) = 31.8 min.



3tj: According to GP 3. 37 mg, 93%. $[\alpha]_D^{25}$ − 17.5 (*c* = 0.8 $CHCl_3$, 99.5:0.5 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.31 (d, J=1.1 Hz, 1 H), 7.15 (s, 2 H), 6.27 (dd, J=3.2, 2.1 Hz, 1 H), 6.04 - 6.11 (m, 1 H), 5.51 (t, J=2.9 Hz, 1 H), 5.15 (dd, J=6.8, 2.6 Hz, 1 H), 4.89 – 4.91 (m, 1 H), 3.69 - 3.77 (m, 1 H), 2.56 - 2.63 (m, 4 H), 1.64 – 1.68 (m, 1 H), 0.73 (s, 9 H), -0.09 (s, 3 H), -0.18 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.7, 155.9, 154.3, 153.0, 141.6, 127.9, 116.8, 110.2, 105.5, 100.1, 71.9, 61.5, 32.7, 32.3, 25.4, 21.5, 17.9, -4.9, -5.2 ppm. HRMS (FAB): Calculated for $C_{21}H_{30}N_3O_3Si_1$ ($[M + H]^+$) is 400.2056, found 400.2042. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 27.7 min, t_R(minor) = 32.1 min.

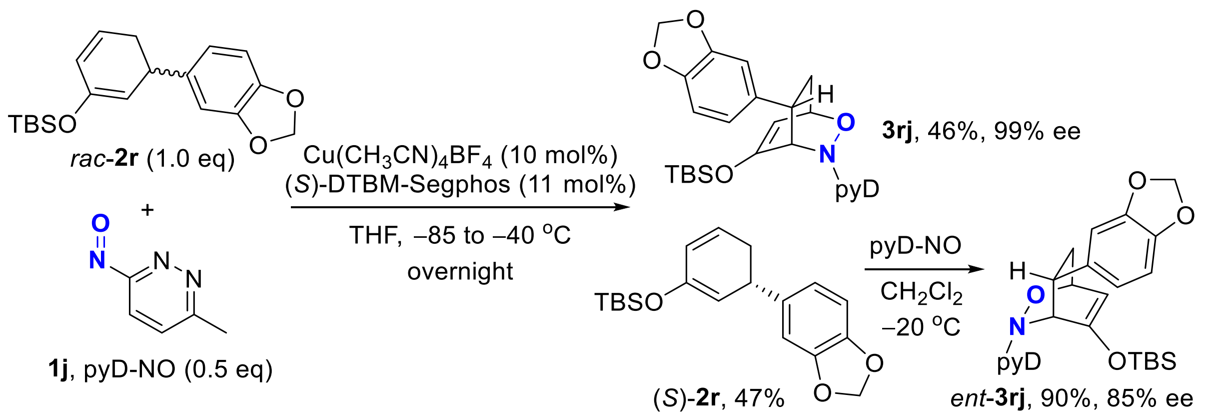


Mixture of products (4:1 ratio).

3uj: According to GP 3. 24 mg, 69%. $[\alpha]_D^{25}$ − 36.4 (*c* = 1.1 $CHCl_3$, 99.9:0.1 e.r.).

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.12 (s, 2 H), 5.04 - 5.13 (m, 2 H), 4.73 - 4.80 (m, 1 H), 2.57 (s, 3 H), 2.40 - 2.50 (m, 1 H), 2.31 - 2.40 (m, 1 H), 1.00 (d, *J*=7.1 Hz, 3 H), 0.90 - 0.97 (m, 1 H), 0.80 (s, 9 H), 0.01 (s, 3 H), -0.15 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.9, 154.0, 153.4, 127.9, 116.6, 99.5, 72.1, 63.8, 35.2, 27.1, 25.5, 25.5, 21.5, 20.5, 18.0, -4.6, -5.2 ppm. HRMS (FAB): Calculated for $C_{18}H_{30}N_3O_2Si_1$ ($[M + H]^+$) is 348.2107, found 248.2107. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 12.6 min, t_R(minor) = 14.9 min

5. Kinetic resolution of racemic diene 2r *via* enantioselective NDA reaction.



$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a −85 °C bath. Nitroso compound **1j** (12.3 mg, 0.1 mmol) was then added and the wall of the test tube was rinsed with THF (0.5 mL). The mixture was further stirred for 10 min before the diene **2r** (0.20 mmol) was added. Then the reaction mixture was warmed to −40 °C over ~2 h and stirred at −40 °C overnight. It was then allowed to warm to 0 °C before directly loaded into a column packed with silica gel and purified using EtOAc/*n*-hexane/NEt_3 (10:40/1 to 10:20:1) as eluent to afford the nitroso Diels-Alder adduct **3rj** (41.7 mg, 46% yield, 99% ee) and the yield of the unreacted diene (*S*)-**2r** was 32 mg (47%).

To a CH_2Cl_2 solution (2 mL) of the diene (*S*)-**2r** (32 mg, 0.094 mmol) at −20 °C, the nitroso compound **1j** (12.3 mg, 0.1 mmol) was added and the mixture was stirred at that temperature for 16 h before purified by column chromatography using EtOAc/*n*-hexane/NEt_3 (10:40/1 to 10:20:1) to yield *ent*-**3rj** (38.4 mg, 90% yield, 85% ee).

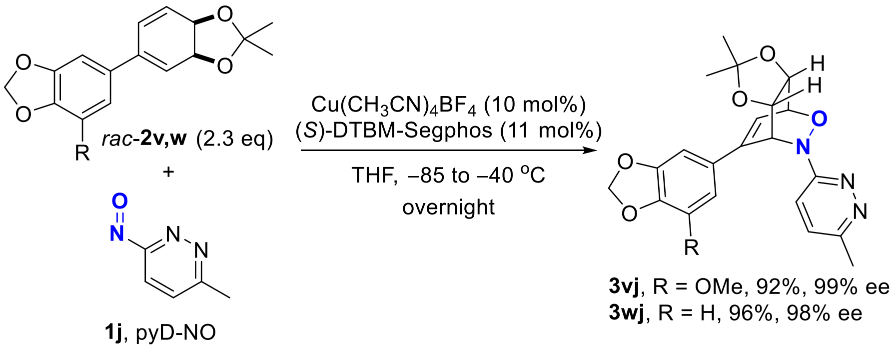
Calculation of the selectivity factor (s):

$$\text{conversion } c = \frac{ees}{ees + eep} = 0.4619$$

ees = ee of the recovered substrate
eep = ee of the product

$$\text{selectivity factor (s)} = \frac{\ln[(1\text{-}c)(1\text{-}ees)]}{\ln[(1\text{-}c)(1\text{+}ees)]} = \frac{\ln[(1\text{-}0.462)(1\text{-}0.85)]}{\ln[(1\text{-}0.462)(1\text{+}0.85)]} = \frac{\ln 0.0807}{\ln 0.9953} = \frac{-2.517}{-0.0047} = 534$$

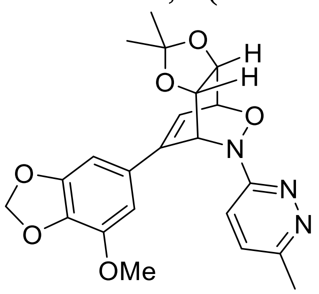
6. Enantioselective NDA reaction of *rac*-2v,w.



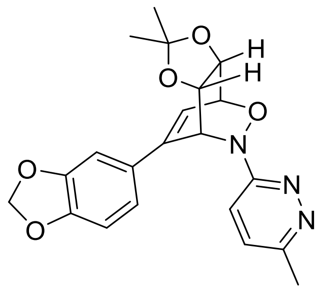
General procedure 4:

$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a −85 °C bath. The nitroso compound **1j** (12.3 mg, 0.1 mmol) was then added and the wall of the test tube was rinsed with THF (0.5 mL). The mixture was further stirred for 10 min before the dienes **2v,w** (0.23 mmol) was added. Then the reaction mixture was warmed to −40 °C over ~2 h and stirred at −40 °C overnight. It was then allowed to warm to −20 °C before directly loaded into a column packed with silica gel and purified using EtOAc/*n*-hexane/NEt_3 (10:40/1 to 10:20:1) as eluent to afford the nitroso Diels-Alder adducts **3**.

All the racemic samples were prepared by mixing the nitroso compounds **1j** (0.1 mmol) with the dienes **2v**,**w** (0.12 mmol) in CH_2Cl_2 at −20 to 0°C.

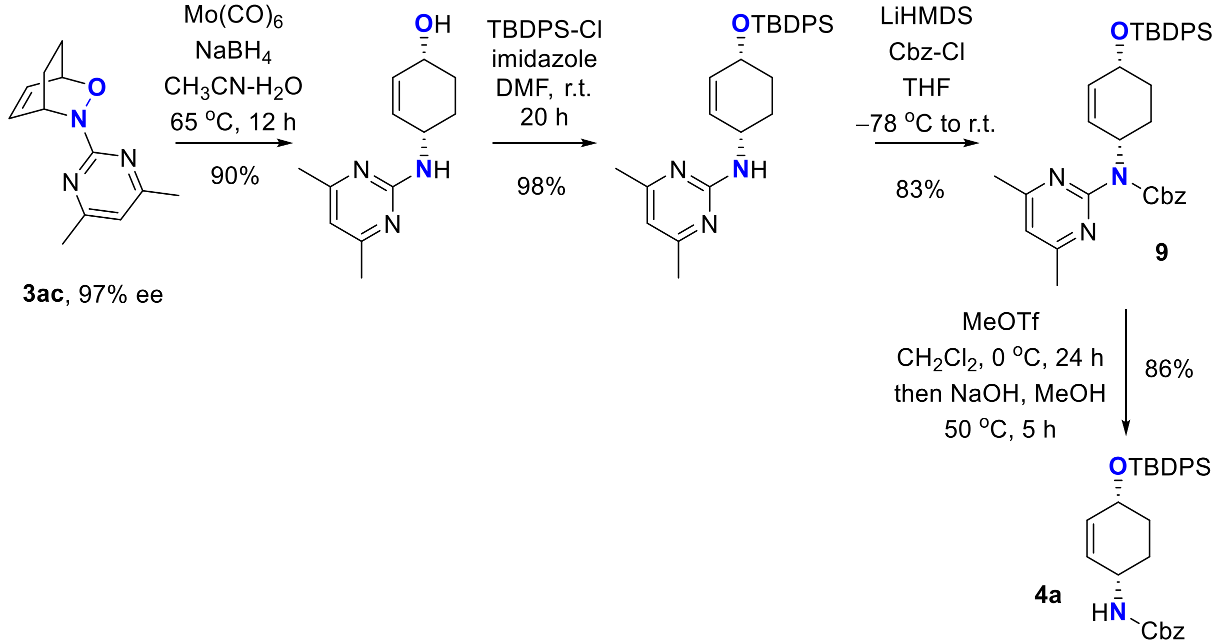


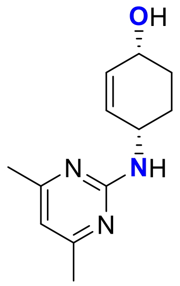
3vj: According to GP 4. 39 mg, 92%. $[\alpha]_D^{25}$ + 195.0 (*c* = 1.0 $CHCl_3$, 0.6:99.4 e.r.).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.10 - 7.17 (m, 2 H), 6.91 (d, *J*=1.4 Hz, 1 H), 6.67 (d, *J*=1.4 Hz, 1 H), 6.36 (dd, *J*=6.2, 2.1 Hz, 1 H), 6.16 (dd, *J*=4.4, 2.5 Hz, 1 H), 5.92 (dd, *J*=7.1, 1.4 Hz, 2 H), 5.03 (dd, *J*=6.2, 4.4 Hz, 1 H), 4.85 (dd, *J*=7.1, 4.4 Hz, 1 H), 4.57 - 4.76 (m, 1 H), 3.94 (s, 3 H), 2.55 (s, 3 H), 1.34 (s, 3 H), 1.27 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 163.5, 154.9, 149.1, 143.8, 142.6, 135.7, 132.1, 128.4, 119.5, 116.9, 111.1, 106.0, 101.7, 99.9, 73.6, 73.5, 70.7, 58.3, 56.6, 26.0, 25.5, 21.6 ppm. HRMS (FAB): Calculated for $C_{22}H_{24}N_3O_6$ ([M + H]$^+$) is 426.1659, found 426.1667. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(minor) = 13.5 min, t_R(major) = 22.6 min.



3wj: According to GP 4. 38 mg, 96%. $[\alpha]_D^{25}$ + 170.59 (c = 1.7 $CHCl_3$, 1.2:98.8 e.r.).
^1H NMR ($CDCl_3$, 400MHz): δ = 7.06 - 7.19 (m, 3 H), 7.00 (d, J=1.8 Hz, 1 H), 6.77 (d, J=8.0 Hz, 1 H), 6.37 (dd, J=6.1, 2.2 Hz, 1 H), 6.18 (dd, J=4.4, 2.5 Hz, 1 H), 5.91 (dd, J=6.1, 1.5 Hz, 2 H), 5.02 (dd, J=6.2, 4.4 Hz, 1 H), 4.84 (dd, J=6.9, 4.4 Hz, 1 H), 4.68 (dd, J=6.9, 3.9 Hz, 1 H), 2.54 (s, 3 H), 1.34 (s, 3 H), 1.24 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 163.3, 154.7, 148.1, 148.1, 142.4, 131.4, 128.4, 120.2, 118.8, 117.0, 111.1, 108.6, 106.0, 101.2, 73.6, 70.7, 57.8, 26.0, 25.5, 21.5 ppm. HRMS (ESI): Calculated for $C_{21}H_{22}N_3O_5$ ($[M + H]^+$) is 396.1554, found 396.1547. HLPC analysis: Daicel Chiralpak AD-H, hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 18.4 min, t_R(major) = 34.7 min.

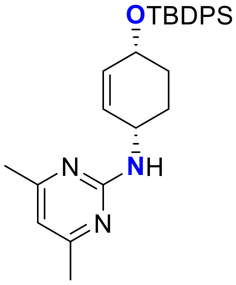
7. Synthesis of benzyl ((1S,4R)-4-((tert-butyldiphenylsilyl)oxy)cyclohex-2-en-1-yl)carbamate 4a.



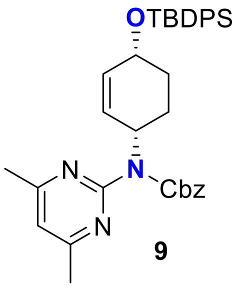


$Mo(CO)_6$ (177 mg, 0.67 mmol) followed by $NaBH_4$ (30 mg, 0.79 mmol) were added to a solution (CH_3CN-H_2O, 9:1, 10 mL) of **3ac** (145 mg, 0.67 mmol) and the mixture was heated to 65 °C and stirred at that temperature for 12 h. It was then evaporated and the crude residue

was purified by column chromatography using acetone/*n*-hexane (1:1) as eluent to obtain (1R,4S)-4-((4,6-dimethylpyrimidin-2-yl)amino)cyclohex-2-en-1-ol (133 mg, 90%).
$[\alpha]_D^{25}$ –55.0 (c = 1.6 $CHCl_3$).
^1H NMR ($CDCl_3$, 400MHz): δ = 6.28 (s, 1 H), 5.85 - 5.97 (m, 1 H), 5.74 - 5.85 (m, 1 H), 5.15 (d, J=8.5 Hz, 1 H), 4.52 – 4.56 (m, 1 H), 4.10 - 4.25 (m, 1 H), 3.22 (br. s., 1 H), 2.25 (s, 6 H), 1.66 - 1.96 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.6, 161.6, 132.3, 131.7, 131.7, 109.9, 64.7, 46.1, 29.3, 25.4, 24.0 ppm. HRMS (ESI): Calculated for $C_{12}H_{37}N_3Na_1O_1$ ($[M + Na]^+$) is 242.1264, found 242.1260.



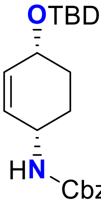
Imidazole (125 mg, 1.82 mmol) and TBDPS-Cl (204 μL, 217 mg, 0.788 mmol) were added to a solution (DMF, 2 mL) of (1R,4S)-4-((4,6-dimethylpyrimidin-2-yl)amino)cyclohex-2-en-1-ol (133 mg, 0.61 mmol) and the mixture was allowed to stir at room temperature for 20 h. Saturated $NaHCO_3$ (5 mL) was then added and the mixture was extracted in EtOAc. Combined organic layer was washed with water, dried over Na_2SO_4, evaporated and then purified by column chromatography using EtOAc/*n*-hexane (3/1) as eluent to yield N-((1S,4R)-4-((tert-butyldiphenylsilyl)oxy)cyclohex-2-en-1-yl)-4,6-dimethylpyrimidin-2-amine (273 mg, 98%).
$[\alpha]_D^{25}$ −5.88 (c = 1.7, $CHCl_3$). ^1H NMR ($CDCl_3$, 400MHz): δ = 7.62 - 7.76 (m, 4 H), 7.33 - 7.52 (m, 6 H), 6.30 (s, 1 H), 5.72 (s, 2 H), 5.06 (d, *J*=8.7 Hz, 1 H), 4.43 - 4.60 (m, 1 H), 4.12 - 4.27 (m, 1 H), 2.27 (s, 6 H), 1.62 - 1.90 (m, 4 H), 1.08 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.6, 161.8, 136.0, 135.9, 134.5, 133.1, 130.3, 129.7, 127.7, 109.8, 66.6, 45.8, 29.3, 27.1, 25.8, 24.1, 19.3 ppm. HRMS (FAB): Calculated for $C_{28}H_{36}N_3O_1Si_1$ ($[M + H]^+$) is 458.2628, found 458.2626.



9

To a solution (THF, 6 mL) of N-((1S,4R)-4-((tert-butyldiphenylsilyl)oxy)cyclohex-2-en-1-yl)-4,6-dimethylpyrimidin-2-amine (273 mg, 0.596 mmol) at −78 °C, LiHMDS (0.89 mL, 1 M in THF) was added dropwise and the mixture was allowed to stir at −78 °C for 10 min. Then Cbz-Cl (0.17 mL, 203 mg, 1.19 mmol) was added and the mixture was allowed to warm to room temperature. The reaction was quenched with saturated $NaHCO_3$ solution (5 mL), extracted in CH_2Cl_2, dried over Na_2SO_4, and purified by column chromatography using EtOAc/*n*-hexane (3/1) as eluent to yield **9** (293 mg, 83%).
$[\alpha]_D^{25}$ +8.57 (c = 2.7, $CHCl_3$). ^1H NMR ($CDCl_3$, 400MHz): δ = 7.80 - 8.07 (m, 4 H), 7.53 - 7.78 (m, 12 H), 6.10 (dd, J=10.2, 2.4 Hz, 1 H), 5.85 – 5.89 (m, 1 H), 5.41 - 5.62 (m, 2 H), 5.13 - 5.33 (m, 1 H), 4.39 (d, J=3.4 Hz, 1 H), 2.82 (s, 6 H), 2.61 - 2.76 (m, 1 H), 2.11 - 2.29 (m, 2 H), 1.80 - 1.94 (m, 1 H), 1.33 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 168.4, 159.0, 155.0, 136.7, 135.9, 135.9, 134.6, 134.4, 131.0, 130.7, 129.7, 129.6, 128.4, 127.8, 127.7, 127.6, 118.3,

77.5, 77.2, 76.8, 67.4, 64.5, 54.8, 30.3, 27.0, 24.0, 23.4, 19.3 ppm. HRMS (FAB): Calculated for $C_{36}H_{42}N_3O_3Si_1$ ([M + H]$^+$) is 592.2995, found 592.2988.

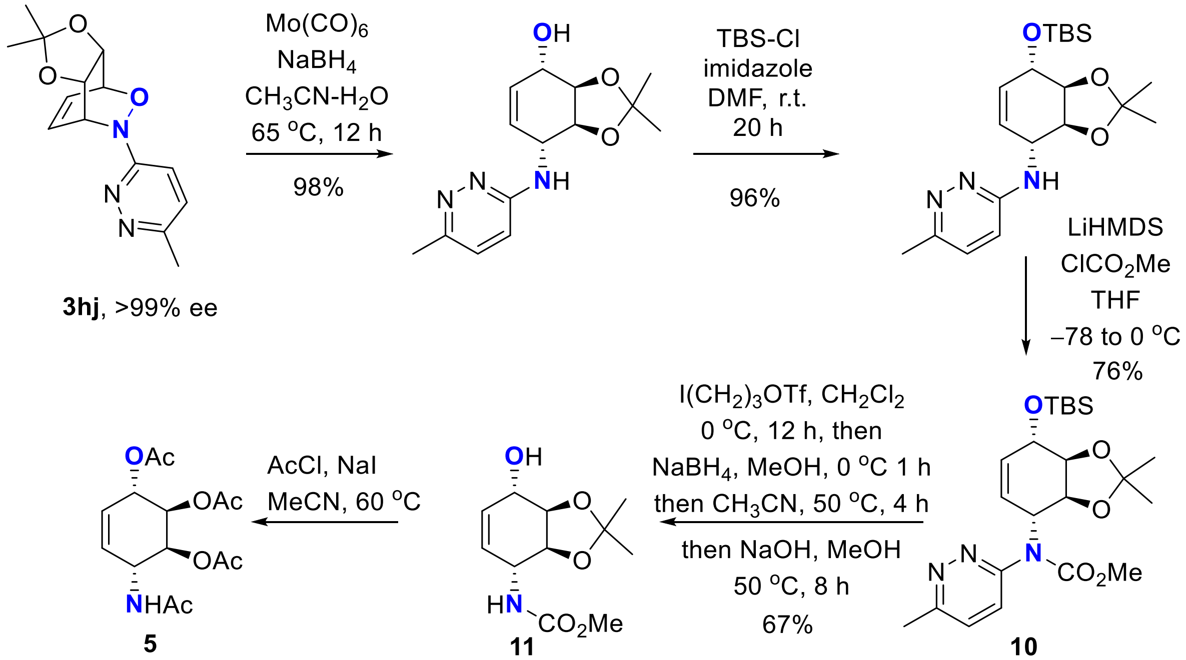


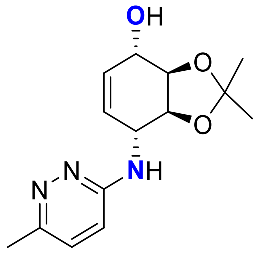
4a

MeOTf (13.1 mL, 19.7 mg, 0.12 mmol) was added to a solution (CH_2Cl_2, 2 mL) of **9** (59.2 mg, 0.10 mmol) at 0 °C and the reaction mixture was stirred at that temperature for 20 h. Then the solvent was evaporated and added MeOH (1 mL) and NaOH (0.8 mL, 2 M solution in water) and the mixture was then heated to 50 °C and stirred at that temperature for 5 h. Then MeOH was evaporated and the organics were extracted in CH_2Cl_2, dried over Na_2SO_4, concentrated, and purified by column chromatography using EtOAc/*n*-hexane (4/1) as eluent to yield **4a** (42 mg, 86%).

$[\alpha]_D^{25}$ −5.0 (*c* = 2.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.62 - 7.74 (m, 4 H), 7.29 - 7.49 (m, 11 H), 5.72 (d, *J*=9.8 Hz, 1 H), 5.60 (dd, *J*=10.1, 2.7 Hz, 1 H), 5.03 - 5.20 (m, 2 H), 4.78 (d, *J*=8.5 Hz, 1 H), 4.17 (br. s., 1 H), 4.04 - 4.14 (m, 1 H), 1.62 - 1.84 (m, 4 H), 1.07 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 155.8, 136.7, 136.0, 135.9, 134.3, 134.3, 133.9, 129.8, 129.2, 128.7, 128.3, 127.7, 77.5, 77.2, 76.8, 66.8, 66.4, 46.2, 29.0, 27.1, 26.1, 19.3 ppm. HRMS (ESI): Calculated for $C_{30}H_{36}N_1O_3Si_1$ ([M + H]$^+$) is 486.2464, found 486.2479.

8. Formal synthesis tetraacetylated conduramine A-1 (5).

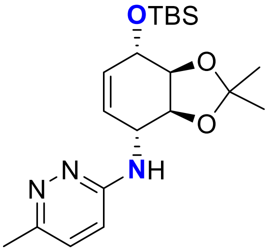




Mo(CO)$_6$ (116 mg, 0.44 mmol) followed by $NaBH_4$ (17 mg, 0.45 mmol) were added to a solution (CH_3CN-H_2O, 9:1, 6 mL) of **3hj** (110 mg, 0.4 mmol) and the mixture was heated to

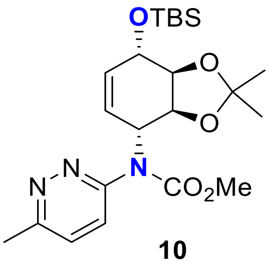
65 °C and stirred at that temperature for 12 h. Then the mixture was evaporated and the crude residue was purified by column chromatography using acetone/*n*-hexane (1:1) as eluent to obtain (3aR,4S,7R,7aS)-2,2-dimethyl-7-((6-methylpyridazin-3-yl)amino)-3a,4,7,7a-tetrahydrobenzo[d][1,3]dioxol-4-ol (109 mg, 98%).

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.08 (d, *J*=8.9 Hz, 1 H), 6.73 (d, *J*=8.7 Hz, 1 H), 5.95 - 6.09 (m, 1 H), 5.83 – 5.86 (m, 1 H), 5.69 (br. s., 1 H), 4.21 - 4.42 (m, 4 H), 2.51 (s, 3 H), 1.46 (s, 3 H), 1.35 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 157.5, 151.6, 131.3, 129.3, 128.9, 114.8, 109.2, 79.5, 68.8, 52.5, 27.3, 25.0, 21.3 ppm. HRMS (FAB): Calculated for $C_{14}H_{20}N_3O_3$ ($[M + H]^+$) is 278.1505, found 278.1499.



Imidazole (41 mg, 0.60 mmol) and TBS-Cl (38 mg, 0.25 mmol) were added to a solution (DMF, 1 mL) of (3aR,4S,7R,7aS)-2,2-dimethyl-7-((6-methylpyridazin-3-yl)amino)-3a,4,7,7a-tetrahydrobenzo [d][1,3]dioxol-4-ol (55 mg, 0.20 mmol) and the mixture was allowed to stir at room temperature for 20 h. Saturated $NaHCO_3$ (2 mL) was then added and the mixture was extracted in EtOAc. Combined organic layer was washed with water, dried over Na_2SO_4, evaporated and then purified by column chromatography using EtOAc/*n*-hexane (3/1) as eluent to yield N-((3aS,4R,7S,7aS)-7-((tert-butyldimethylsilyl)oxy)-2,2-dimethyl-3a,4,7,7a-tetrahydrobenzo[d][1,3]dioxol-4-yl)-6-methylpyridazin-3-amine (75 mg, 96%).

$[\alpha]_D^{24}$ −17.65 (*c* = 1.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.00 (d, *J*=9.2 Hz, 1 H), 6.58 (d, *J*=9.2 Hz, 1 H), 5.87 - 6.02 (m, 2 H), 5.09 (d, *J*=8.5 Hz, 1 H), 4.56 - 4.69 (m, 1 H), 4.35 (dd, *J*=6.8, 4.5 Hz, 1 H), 4.17 - 4.29 (m, 2 H), 2.50 (s, 3 H), 1.40 (s, 3 H), 1.30 (s, 3 H), 0.92 (s, 10 H), 0.07 - 0.18 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 157.1, 151.7, 132.5, 130.5, 128.3, 114.8, 108.7, 79.5, 69.1, 50.1, 26.9, 26.0, 24.7, 21.5, 18.2, -4.6, -4.6 ppm. m/z = HRMS (ESI): Calculated for $C_{20}H_{34}N_3O_3Si_1$ ($[M + H]^+$) is 392.2369, found 392.2363.

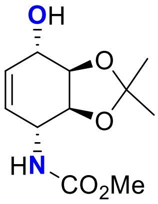


10

LiHMDS (0.24 mL, 1 M in THF) was added dropwise to a stirred THF solution (1 mL) N-((3aS,4R,7S,7aS)-7-((tert-butyldimethylsilyl)oxy)-2,2-dimethyl-3a,4,7,7a-tetrahydrobenzo[d][1,3]dioxol-4-yl)-6-methylpyridazin-3-amine (65 mg, 0.17 mmol) at −78 °C and the mixture was allowed to stir at −78 °C for another 10 min. Then $ClCO_2Me$ (14 μL, 17 mg, 0.18 mmol) was added and the mixture was then allowed to warm to 0 °C and stirred at 0 °C for 10 h. The reaction was quenched with saturated $NaHCO_3$ solution (5 mL), extracted in EtOAc, dried over Na_2SO_4, and purified by column chromatography using EtOAc/*n*-hexane (3/1) as eluent to yield **10** (57 mg, 76%).

$[\alpha]_D^{25}$ −6.45 (*c* = 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.61 (d, *J*=8.9 Hz, 1 H), 7.30 (d, *J*=8.9 Hz, 1 H), 5.78 – 5.82 (m, 1 H), 5.60 - 5.67 (m, 1 H), 5.04 (dd, *J*=6.0, 2.7 Hz, 1 H), 4.50 - 4.58 (m, 1 H), 4.18 – 4.21 (m, 1 H), 4.08 (dd, *J*=7.3, 5.3 Hz, 1 H), 3.76 (s, 3 H), 2.67 (s, 3 H), 1.37 (s, 3 H), 1.29 (s, 3 H), 0.90 (m, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H) ppm. ^{13}C NMR

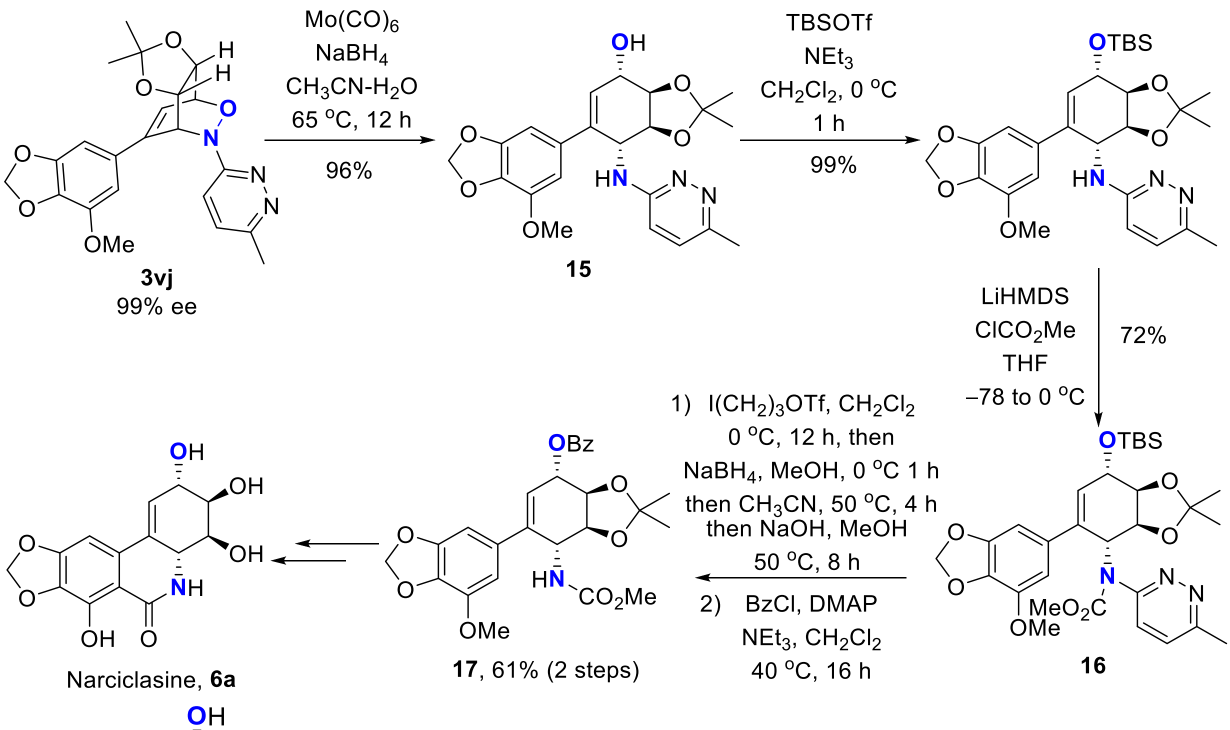
($CDCl_3$, 101 MHz): δ = 158.1, 156.3, 155.3, 131.5, 128.0, 127.9, 125.9, 108.7, 80.5, 71.7, 59.6, 53.4, 27.6, 26.0, 25.6, 21.9, 18.3, -4.4, -4.8 ppm. HRMS (ESI): Calculated for $C_{22}H_{35}N_3Na_1O_5Si_1$ ([M + Na]$^+$) is 472.2238, found 472.2231.

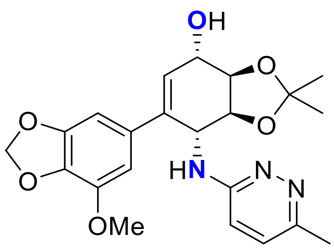


11

$I(CH_2)_3OTf$ (35 mg, 0.11 mmol) was added to a stirred solution (CH_2Cl_2, 1 mL) of **10** (33 mg, 0.073 mmol) at 0 °C and the reaction mixture stirred at 0 °C for 12 h. $NaBH_4$ (13 mg, 0.35 mmol) and MeOH (1 mL) were then added and it was stirred at 0 °C for another 1 h before warm to r.t. The solvent was evaporated. CH_3CN was added and the mixture was heated to 50 °C for 4 h. Then NaOH (0.7 mL, 2 M in water) and MeOH (1 mL) were added and the heating continued for another 8 h. Then the organic solvents were evaporated and the residue was extracted in CH_2Cl_2, dried over Na_2SO_4, purified by column chromatography using 1:1 acetone/*n*-hexane as eluent to yield 11 (12 mg, 67%).
$[\alpha]_D^{24}$ −58.0 (*c* = 1.0, $CHCl_3$). NMR spectra matches with those in literature.

9. Formal synthesis of narciclasine 6a.

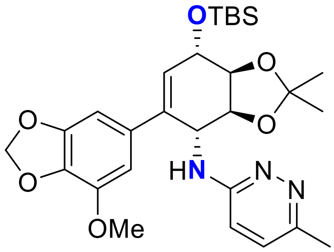




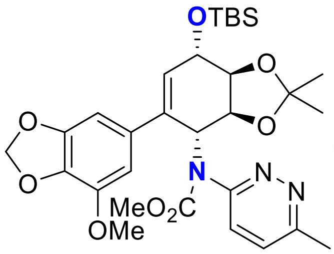
15

$Mo(CO)_6$ (29 mg, 0.11 mmol) followed by $NaBH_4$ (5.7 mg, 0.15 mmol) were added to a solution (CH_3CN-H_2O, 9:1, 3 mL) of **3vj** (43 mg, 0.1 mmol) and the mixture was heated to 65 °C and stirred at that temperature for 12 h. Then the mixture was evaporated and the crude

residue was purified by column chromatography using acetone/*n*-hexane (1:1) as eluent to obtain **15** (41 mg, 96%).
$[\alpha]_D^{25}$ −200.0 (c = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 400MHz): δ = 6.95 - 7.07 (m, 1 H), 6.54 - 6.68 (m, 3 H), 6.27 - 6.45 (m, 1 H), 6.06 (d, J=8.7 Hz, 1 H), 5.88 - 5.95 (m, 2 H), 5.05 - 5.20 (m, 1 H), 4.62 - 4.85 (m, 2 H), 4.39 - 4.62 (m, 2 H), 3.65 - 3.82 (m, 3 H), 2.50 (s, 3 H), 1.28 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 156.9, 151.3, 151.2, 149.0, 143.6, 143.0, 142.7, 135.3, 135.1, 128.9, 126.1, 114.8, 108.2, 106.0, 101.6, 100.2, 77.4, 76.8, 65.7, 56.6, 51.5, 26.7, 24.6, 21.3 ppm. HRMS (ESI): Calculated for $C_{22}H_{36}N_3O_6$ ($[M + H]^+$) is 428.1816, found 428.1822.



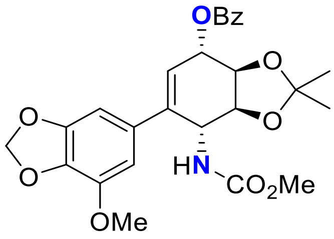
NEt_3 (21 μl, 15 mg, 0.15 mmol) followed by TBSOTf (17.2 μl, 20 mg, 0.075 mmol) were added to a stirred CH_2Cl_2 solution (1 mL) of **15** at 0 °C stirred for 30 min. The ice bath was then removed and the mixture was stirred for 30 min before directly transferred to a column packed with SiO_2 and purified using 1:1 EtOAc/*n*-hexane as eluent to yield **15-TBS** (27 mg, 99%).
$[\alpha]_D^{26}$ −125.0 (c = 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$, 400MHz): δ = 6.99 (d, J=8.9 Hz, 1 H), 6.75 (d, J=1.6 Hz, 1 H), 6.69 (d, J=1.6 Hz, 1 H), 6.44 (d, J=8.9 Hz, 1 H), 6.32 (d, J=6.2 Hz, 1 H), 5.93 (q, J=1.5 Hz, 2 H), 5.56 (dd, J=10.1, 1.8 Hz, 1 H), 5.45 (d, J=10.1 Hz, 1 H), 4.73 (dd, J=6.9, 2.1 Hz, 1 H), 4.34 - 4.49 (m, 2 H), 3.83 (s, 3 H), 2.52 (s, 3 H), 1.25 - 1.35 (m, 6 H), 0.95 (s, 9 H), 0.19 (s, 3 H), 0.16 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 156.3, 151.5, 149.1, 143.9, 143.7, 135.4, 135.0, 128.4, 125.0, 115.0, 108.2, 106.2, 101.6, 100.2, 77.6, 76.8, 67.1, 56.8, 49.9, 26.5, 26.1, 24.5, 21.5, 18.3, -4.3, -4.7 ppm. HRMS (ESI): Calculated for $C_{28}H_{40}N_3O_6Si_1$ ($[M + H]^+$) is 542.2681, found 542.2680.



16

LiHMDS (75 μL, 1 M in THF) was added dropwise to a stirred THF solution (1 mL) **15-TBS** (27 mg, 0.05 mmol) at −78 °C and the mixture was allowed to stir at −78 °C for another 10 min. Then $ClCO_2Me$ (5.8 μL, 7.1 mg, 0.075 mmol) was added and the mixture was then allowed to warm to 0 °C and stirred at 0 °C for 10 h. The reaction was quenched with saturated $NaHCO_3$ solution (1 mL), extracted in EtOAc, dried over Na_2SO_4, and purified by column chromatography using EtOAc/*n*-hexane (2/1) as eluent to yield **16** (22 mg, 72%).
$[\alpha]_D^{26}$ −28.57 (c = 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$, 400MHz): δ = 7.24 (br. s., 1 H), 7.13 (d, J=9.2 Hz, 1 H), 6.47 (br. s., 1 H), 6.39 (s, 1 H), 5.90 (dd, J=4.9, 1.5 Hz, 2 H), 5.77 - 5.85 (m, 1 H), 5.65 (t, J=2.5 Hz, 1 H), 4.86 - 5.02 (m, 1 H), 4.28 - 4.33 (m, 1 H), 4.22 - 4.27 (m, 1 H), 3.67 (s, 3 H), 3.63 (s, 3 H), 2.64 (s, 3 H), 1.36 (d, J=8.0 Hz, 6 H), 0.92 (s, 9 H), 0.14 (s, 3 H), 0.12 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 157.3, 155.0, 148.5, 143.2, 134.5, 133.6, 130.6, 127.5, 125.1, 108.5, 106.5, 101.5, 101.5, 77.7, 76.8, 71.2, 59.4, 56.4, 53.4, 28.0, 26.1,

21.8, 18.4, -4.3, -4.6 ppm. HRMS (FAB): Calculated for $C_{30}H_{41}N_3O_8Si_1$ ($[M + H]^+$) is 600.2741, found 600.2731.

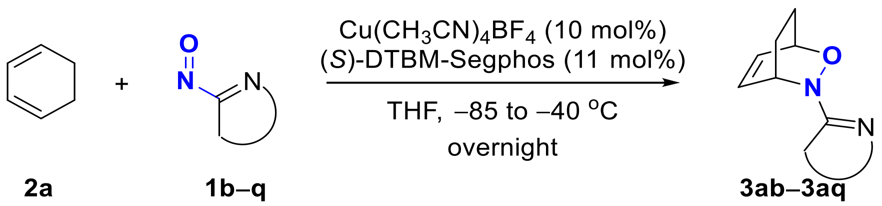


17, 61% (2 steps)

$I(CH_2)_3OTf$ (19 mg, 0.06 mmol) was added to a stirred solution (CH_2Cl_2, 1 mL) of **16** (30 mg, 0.05 mmol) at 0 °C and the reaction mixture stirred at 0 °C for 12 h. $NaBH_4$ (9.5 mg, 0.25 mmol) and MeOH (1 mL) were then added and it was stirred at 0 °C for another 1 h before warm to r.t. The solvent was evaporated. CH_3CN was added and the mixture was heated to 50 °C for 4 h. Then NaOH (0.6 mL, 2 M in water) and MeOH (1 mL) were added and the heating continued for another 8 h. Then the organic solvents were evaporated and the residue was extracted in CH_2Cl_2, dried over Na_2SO_4, and filtered through a small pad of SiO_2 using 1:1 acetone/*n*-hexane as eluent. The filtrate was then concentrated and the residue was dissolved in CH_2Cl_2. DMAP (1.2 mg, 0.01 mmol), NEt_3 (21 µL, 15 mg, 0.15 mmol) and PhCOCl (14 mg, 11.6 mL) were then added and the mixture was heated to 40 °C for 16 h. After cooling down to room temperature, $NaHCO_3$ solution (1mL) was added and the organics were extracted in CH_2Cl_2, dried over Na_2SO_4, concentrated and purified using EtOAc/*n*-hexane (1/1) as eluent to yield **17** (15.2 mg, 61% 2 steps).

$[\alpha]_D^{26}$ −11.5 (*c* = 1.0, $CHCl_3$). ^1H NMR (C_6D_6, 400MHz): δ = 8.09 (d, *J*=6.9 Hz, 2 H), 7.04 - 7.15 (m, 3 H), 6.90 - 6.94 (m, 1 H), 6.78 - 6.83 (m, 1 H), 6.28 (d, *J*=6.6 Hz, 1 H), 5.86 (dd, *J*=6.5, 1.5 Hz, 1 H), 5.36 - 5.47 (m, 2 H), 5.26 (q, *J*=1.3 Hz, 2 H), 4.55 (d, *J*=5.7 Hz, 1 H), 4.36 (d, *J*=6.9 Hz, 1 H), 3.49 (s, 3 H), 3.39 (s, 3 H), 1.30 (s, 4 H), 1.13 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.3, 156.5, 150.3, 145.9, 144.7, 136.9, 134.0, 133.7, 130.6, 130.3, 129.2, 121.6, 109.0, 107.4, 101.8, 100.8, 78.3, 75.3, 69.4, 56.6, 52.4, 50.8, 26.9, 24.8 ppm. HRMS (FAB): Calculated for $C_{26}H_{27}N_1O_9$ ($[M]^{\cdot+}$) is 497.1686, found 497.1678.

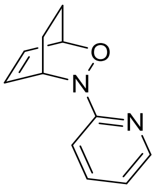
10. Effect of steric and electronic properties of nitroso compounds on nitroso Diels-Alder reaction.



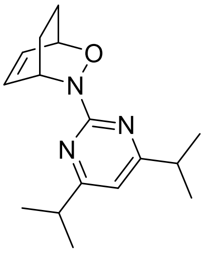
General procedure 5:

$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a −85 °C bath. Nitroso compound **1b−q** (0.1 mmol) was then added and the wall of the test tube was rinsed with THF (0.5 mL). The mixture was further stirred for 10 min before **2a** (11.5 µL, 0.12 mmol) was added. Then the reaction mixture was warmed to −40 °C over ~2 h and stirred at −40 °C overnight. The mixture was then allowed to warm to 0 °C before it was directly

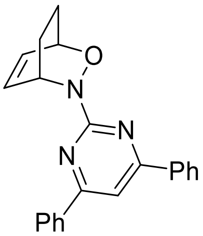
loaded into a column packed with silica gel and purified using EtOAc/*n*-hexane (1:1 to 3:1) to afford the nitroso Diels-Alder adducts **3**.
All the racemic samples were prepared by mixing the nitroso compounds **1b─q** (0.1 mmol) with the dienes **2a** (11.5 μL, 0.12 mmol) in CH_2Cl_2 at 0 °C.



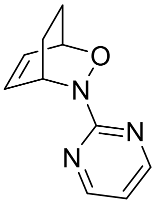
3ab: According to GP 5. 18.7 mg, 99%, 97:3 e.r.
NMR spectra matches with those reported in the literature.



3ad: According to GP 5. 20 mg, 77%. 54.6:45.6 e.r.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.48 - 6.54 (m, 2 H), 6.46 (s, 1 H), 5.41 - 5.53 (m, 1 H), 4.82 – 4.85 (m, 1 H), 2.87 (spt, *J*=6.9 Hz, 2 H), 2.18 - 2.34 (m, 2 H), 1.53 - 1.63 (m, 1 H), 1.37 - 1.46 (m, 1 H), 1.22 (dd, *J*=6.9, 1.4 Hz, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 176.5, 165.7, 132.8, 132.0, 106.5, 70.5, 50.4, 36.1, 24.2, 22.3, 21.8, 21.0 ppm. m/z = 273. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 16.5 min, t_R(major) = 17.4 min.

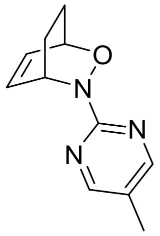


3ae: According to GP 5. 31 mg, 91%. 67.6:32.4 e.r.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.08 - 8.16 (m, 4 H), 7.55 (s, 1 H), 7.45 - 7.53 (m, 6 H), 6.62 – 6.66 (m, 1 H), 6.56 – 6.60 (m, 1 H), 5.64 - 5.75 (m, 1 H), 4.85 - 4.97 (m, 1 H), 2.28 - 2.46 (m, 2 H), 1.62 - 1.72 (m, 1 H), 1.44 - 1.56 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 166.4, 165.7, 137.9, 132.7, 132.2, 130.6, 128.8, 127.4, 105.6, 70.9, 50.5, 24.2, 21.1 ppm. m/z = 341. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 275 nm, retention time; t_R(major) = 20.1 min, t_R(minor) = 41.2 min.



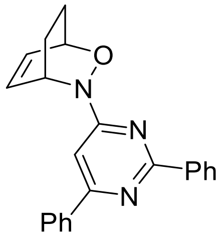
3af: According to GP 5. 17 mg, 90%. 91.9:8.1 e.r.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.41 (d, *J*=4.8 Hz, 2 H), 6.68 (t, *J*=4.7 Hz, 1 H), 6.41 - 6.59 (m, 2 H), 5.37 – 5.40 (m, 1 H), 4.85 – 4.88 (m, 1 H), 2.15 - 2.40 (m, 2 H), 1.56 – 1.63 (m, 1 H), 1.35 - 1.52 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.7, 157.9, 132.2, 132.1, 113.3, 71.0, 50.9, 24.0, 20.8 ppm. m/z = 189. HLPC analysis: Daicel Chiralpak OD-H, hexane/*i*-PrOH

= 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 26.8 min, t_R(minor) = 44.1 min.



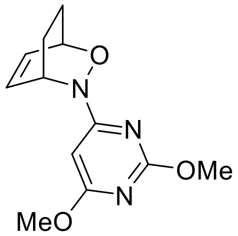
3ag: According to GP 5. 19 mg, 94%. 3.1:96.9 e.r.

^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.25 (s, 2 H), 6.50 – 6.54 (m, 1 H), 6.43 – 6.47 (m, 1 H), 5.29 - 5.36 (m, 1 H), 4.71 - 4.93 (m, 1 H), 2.19 - 2.38 (m, 2 H), 2.15 (s, 3 H), 1.53 - 1.64 (m, 1 H), 1.32 - 1.48 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.8, 157.9, 132.2, 132.1, 132.0, 132.0, 122.4, 70.7, 51.4, 24.1, 20.8, 14.9 ppm. m/z = 203. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 10.2 min, t_R(major) = 12.0 min.



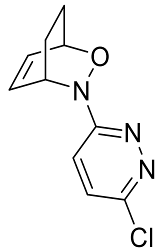
3ah: According to GP 5. 34 mg, 99%. Racemic.

^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.47 - 8.65 (m, 2 H), 8.12 - 8.27 (m, 2 H), 7.38 - 7.58 (m, 6 H), 7.17 (s, 1 H), 6.44 - 6.59 (m, 2 H), 5.66 – 5.69 (m, 1 H), 4.72 - 4.92 (m, 1 H), 2.24 - 2.40 (m, 2 H), 1.61 - 1.74 (m, 1 H), 1.43 - 1.55 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 169.5, 164.3, 163.1, 138.4, 138.1, 132.6, 131.3, 130.4, 130.4, 128.8, 128.4, 128.4, 127.4, 127.4, 127.3, 100.7, 70.9, 51.2, 24.3, 20.6 ppm. m/z = 341. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R = 18.5 min, t_R = 26.7 min.

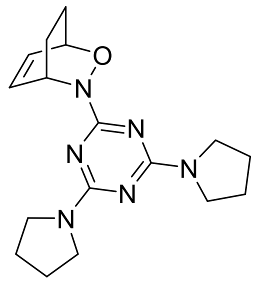


3ai: According to GP 5. 24 mg, 96%. 40.9:59.1 e.r.

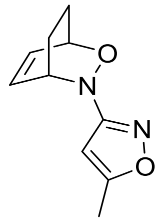
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.45 – 6.49 (m, 1 H), 6.37 – 6.39 (m, 1 H), 5.82 (s, 1 H), 5.23 - 5.35 (m, 1 H), 4.71 – 4.73 (m, 1 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 2.10 - 2.29 (m, 2 H), 1.47 - 1.61 (m, 1 H), 1.34 - 1.45 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 172.7, 171.1, 164.4, 131.7, 131.0, 84.8, 70.6, 54.5, 53.9, 53.8, 51.4, 51.4, 24.2, 20.4 ppm. m/z = 249. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 275 nm, retention time; t_R(minor) = 56.0 min, t_R(major) = 69.1 min.



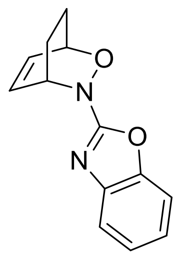
3ak: According to GP 5. 19 mg, 85%. 98.9:1.1 e.r.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.27 (d, *J*=9.2 Hz, 1 H), 7.11 (d, *J*=9.2 Hz, 1 H), 6.36 - 6.62 (m, 2 H), 5.49 – 5.53 (m, 1 H), 4.73 – 4.75 (m, 1 H), 2.14 - 2.36 (m, 2 H), 1.59 - 1.71 (m, 1 H), 1.33 - 1.54 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 165.4, 149.8, 133.3, 131.2, 129.1, 119.6, 70.6, 70.6, 51.7, 24.3, 20.2, 20.2 ppm. m/z = 223. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 21.1 min, t_R(minor) = 25.0 min.



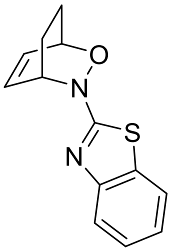
3am: According to GP 5. 28 mg, 85%. 65.4:34.6 e.r.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.43 - 6.57 (m, 2 H), 5.29 - 5.42 (m, 1 H), 4.61 - 4.79 (m, 1 H), 3.50 (br. s., 8 H), 2.21 - 2.34 (m, 1 H), 2.10 - 2.20 (m, 1 H), 1.77 - 1.93 (m, 8 H), 1.50 (tt, *J*=12.0, 3.0 Hz, 1 H), 1.29 - 1.42 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 169.6, 163.6, 132.5, 131.7, 70.6, 49.3, 46.0, 25.3, 24.0, 21.0 ppm. m/z = 328. HLPC analysis: Daicel Chiralpak OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 13.3 min, t_R(minor) = 20.5 min.



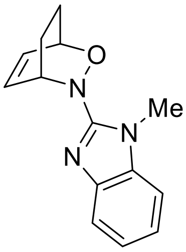
3an: According to GP 5. 18 mg, 94%. 61.9:38.1 e.r.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.46 - 6.54 (m, 2 H), 5.70 (d, *J*=0.7 Hz, 1 H), 4.58 - 4.65 (m, 2 H), 2.29 (s, 3 H), 2.16 - 2.26 (m, 2 H), 1.48 - 1.59 (m, 1 H), 1.35 - 1.43 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 170.8, 169.4, 132.4, 131.4, 95.8, 69.5, 69.5, 53.3, 24.0, 24.0, 20.6, 12.7 ppm. m/z = 192. HLPC analysis: Daicel Chiralpak AS-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 15.4 min, t_R(minor) = 22.6 min.



3ao: According to GP 5. 22 mg, 96%. Racemic.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.42 - 7.59 (m, 1 H), 7.31 - 7.42 (m, 1 H), 7.06 - 7.30 (m, 2 H), 6.52 - 6.70 (m, 2 H), 4.92 - 5.12 (m, 1 H), 4.75 - 4.92 (m, 1 H), 2.16 - 2.46 (m, 2 H), 1.53 - 1.73 (m, 1 H), 1.36 - 1.53 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 164.3, 149.4, 141.7, 132.2, 132.1, 132.0, 124.3, 122.6, 118.2, 109.7, 70.9, 52.9, 23.6, 20.2 ppm. m/z = 228. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R = 25.8 min, t_R = 28.9 min.



3ap: According to GP 5. 21 mg, 86%. Racemic.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.48 - 7.62 (m, 1 H), 7.10 - 7.25 (m, 3 H), 6.77 – 6.81 (m, 1 H), 6.14 – 6.18 (m, 1 H), 4.65 - 4.77 (m, 1 H), 4.02 - 4.13 (m, 1 H), 2.14 - 2.41 (m, 2 H), 1.48 - 1.61 (m, 1 H), 1.37 - 1.47 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 147.8, 133.6, 129.1, 128.2, 127.0, 126.9, 123.3, 119.7, 111.1, 69.8, 55.9, 23.3, 22.1 ppm. m/z = 244. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R = 13.9 min, t_R = 16.7 min.

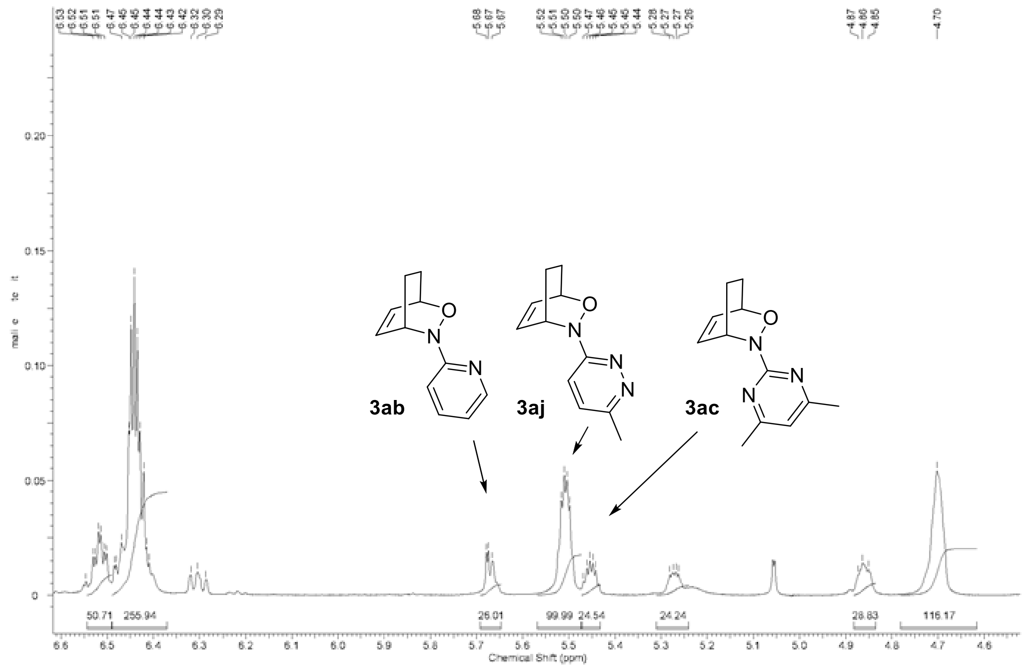


3aq: According to GP 5. 23 mg, 95%. Racemic.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.52 - 7.62 (m, 1 H), 7.12 - 7.21 (m, 3 H), 6.86 (dd, *J*=7.6, 6.4 Hz, 1 H), 6.47 - 6.55 (m, 1 H), 4.86 - 4.97 (m, 1 H), 4.54 - 4.68 (m, 1 H), 3.72 (s, 3 H), 2.18 - 2.35 (m, 2 H), 1.56 - 1.70 (m, 1 H), 1.39 - 1.54 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 156.9, 141.0, 136.0, 134.6, 130.9, 121.7, 121.5, 118.6, 108.5, 70.0, 51.8, 31.1, 24.2, 20.9 ppm. m/z = 241. HLPC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R = 18.1 min, t_R = 19.7 min.

11. Competition experiment.

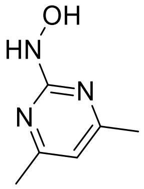
$Cu(CH_3CN)_4BF_4$ (3.1 mg, 0.010 mmol) and (S)-DTBM-Segphos (13.0 mg, 0.011 mmol) were taken in an oven dried 16 × 150 mm test tube equipped with a magnetic stir bar and a rubber septum. The test tube was evacuated and carefully purged with nitrogen. THF (1 mL) was added to it and the mixture was stirred for 1 h. After that the catalyst solution was placed on a −85 °C bath. Nitroso compounds **1b,c,j** (0.1 mmol each) was added (as mixture at one time) and the wall of the test tube was rinsed with THF (1 mL). The mixture was further stirred for 10 min before the dienes **2a** (10 μL, 0.1 mmol) was added. Then the reaction mixture was warmed to −40 °C over ~2 h and stirred at −40 °C overnight. The mixture was then allowed to warm to 0 °C before water was added. The organic mixture was extracted in EtOAc, dried over Na2SO4, evaporated and the ratio of the product was determined by ^{1}H NMR.

Ratio of **3ab:3ac:3aj** = 17:17:66

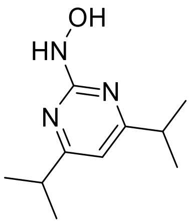


12. Synthesis of nitroso compounds.

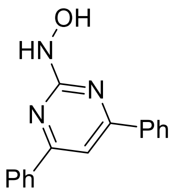
The nitroso compounds **1c–n** were prepared by the oxidation of the corresponding aryl hydroxyl amines following the modified literature procedure by Moskalenko and coworkers.[S1a] *Synthesis of aryl hydroxyl amines.*[S1b] Aryl chloride (10 mmol) and $NH_2OH.HCl$ (2.38 g, 40 mmol) was taken in a to a two necked round bottom flask equipped with a reflux condenser. It was then added EtOH (20 mL) and NEt_3 (5.62 mL, 40 mmol) and the mixture was refluxed at 90 °C. The reaction was monitored by TLC. After complete consumption, ethanol was evaporated and water (5 mL) was added. The organics were extracted in EtOAc, dried over Na_2SO_4, concentrated and purified by column chromatography.



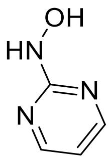
1.00 g, 72%. ^{1}H NMR (DMSO-d$_6$, 400MHz): δ = 9.16 (s, 1 H), 8.57 (s, 1 H), 6.49 (s, 1 H), 2.23 (s, 6 H) ppm. ^{13}C NMR (DMSO-d$_6$, 101MHz): δ = 166.8, 165.6, 110.9, 23.4 ppm. m/z = 139. [S1b]



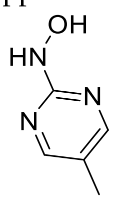
1.56 g, 80%. ^{1}H NMR (CDCl$_3$, 400MHz): δ = 9.80 (br. s., 1 H), 7.55 (br. s., 1 H), 6.53 (s, 1 H), 2.93 (spt, *J*=6.9 Hz, 2 H), 1.26 (d, *J*=6.9 Hz, 12 H) ppm. ^{13}C NMR (CDCl$_3$, 101 MHz): δ = 177.3, 165.9, 107.0, 35.9, 21.9 ppm. m/z = 195.



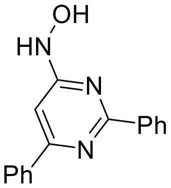
2.02 g, 77%. ^{1}H NMR (CDCl$_3$, 400MHz): δ = 8.03 - 8.17 (m, 4 H), 7.62 - 7.67 (m, 1 H), 7.45 - 7.60 (m, 7 H), 6.92 - 7.15 (m, 1 H) ppm. m/z = 263. [S1b]



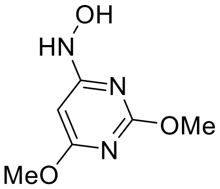
0.50 g, 45%. ^{1}H NMR (DMSO-d$_6$, 400MHz): δ = 9.38 (s, 1 H), 8.61 (s, 1 H), 8.36 (d, *J*=4.6 Hz, 2 H), 6.71 ppm (t, *J*=4.7 Hz, 1 H). ^{13}C NMR (DMSO-d$_6$, 101MHz): δ = 165.6, 157.8, 112.1 ppm. m/z = 111. [S1b]



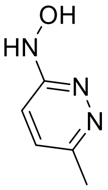
0.81 g, 65%. ^{1}H NMR (DMSO-d$_6$, 400MHz): δ = 9.10 (s, 1 H), 8.51 (s, 1 H), 8.16 - 8.28 (m, 2 H), 2.10 (s, 3 H) ppm. ^{13}C NMR (DMSO-d$_6$, 101MHz): δ = 164.5, 157.5, 120.6, 14.2 ppm. m/z = 125.



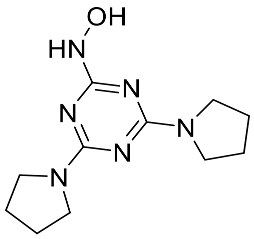
1.92 g, 73%. ^{1}H NMR (DMSO-d$_6$, 400MHz): δ = 10.01 (s, 1 H), 9.20 (s, 1 H), 8.34 - 8.53 (m, 2 H), 8.22 (dd, *J*=7.6, 1.8 Hz, 2 H), 7.41 - 7.65 (m, 6 H), 7.16 (s, 1 H) ppm. ^{13}C NMR (DMSO-d$_6$, 101MHz): δ = 167.8, 162.5, 162.4, 137.9, 137.4, 130.4, 130.4, 128.9, 128.4, 127.8, 126.7, 95.4, 40.1, 39.9, 39.7, 39.3, 39.1, 38.9 ppm. m/z = 263. [S1b]



1.12 g, 66%. ^{1}H NMR (DMSO-d$_6$, 400MHz): δ = 9.51 (s, 1 H), 8.88 (s, 1 H), 5.66 (s, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H) ppm. ^{13}C NMR (DMSO-d$_6$, 101MHz): δ = 171.7, 169.7, 164.2, 78.2, 53.9, 53.3 ppm. m/z = 171.



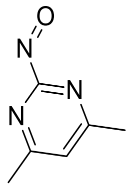
0.96 g, 77%. ^{1}H NMR (CDCl$_3$, 400MHz): δ = 7.15 (d, *J*=9.6 Hz, 1 H), 6.91 (d, *J*=9.6 Hz, 1 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (CDCl$_3$, 101 MHz): δ = 161.2, 145.5, 134.9, 130.2, 20.7 ppm. m/z = 125.



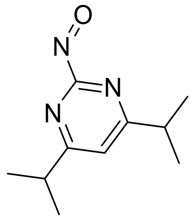
1.65 g, 66%. ^{1}H NMR (DMSO-d$_6$, 400MHz): δ = 8.91 (s, 1 H), 8.24 (br. s., 1 H), 3.41 (br. s., 8 H), 1.83 ppm (t, *J*=6.6 Hz, 8 H) ppm. ^{13}C NMR (DMSO-d$_6$, 101MHz): δ = 169.0, 163.0, 45.6, 24.7 ppm. m/z = 250.

Synthesis of nitroso compounds.[S1a] To a round bottom flash charged with MnO_2 (3.5 g) was added dry CH_2Cl_2 (50 mL) and the black suspension was stirred for 20 min at room temperature before 0.5 mL MeOH was added. It was then cooled to −10 °C and corresponding hydroxyl amine (2 mmol) was added in two equal portion (as solid). The mixture was then stirred at −10 °C for 30 min and then at r.t. for 30 min. It was then filtered over a small pad of celite and thoroughly washed with CH_2Cl_2. Then the solution was evaporated on a rotary evaporator (bath temperature <20 °C). Then the solid residue was washed with dry ether (3 mL) to obtain the nitroso compounds **1c–n**.

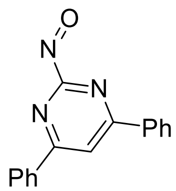
1b,n,**o**,**q** were prepared similar to method described by Rampal[S1c] and Miller.[S1d] **1p** was prepared according to the report by Almeida.[S1e]



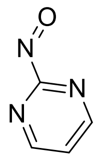
1c. 260 mg, 95%. Mixture of monomer and dimer (1:10 ratio).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.35 (s, 1 H)*, 7.05 (s, 1 H), 2.69 (s, 6 H)*, 2.39 (s, 6 H) ppm. * = minor. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 169.6, 159.8, 121.1, 23.8 ppm. m/z = 137. IR (ATR): 1602.3, 1525.3, 1430.6, 1396.0, 1372.2, 1290.5, 819.1. [S1a]



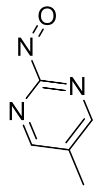
1d. 378 mg, 98%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.98 (s, 1 H), 2.91 (spt, *J*=6.8 Hz, 2 H), 1.08 (d, *J*=6.9 Hz, 12 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 178.8, 160.2, 116.4, 35.8, 21.6 ppm. m/z = 193. IR (ATR): 1595.6, 1523.2, 1471.7, 1399.3, 1390.4, 1372.8, 1328.5, 1296.6, 1282.1, 793.7.



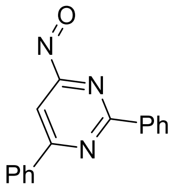
1e. 511 mg, 98%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.62 (s, 1 H), 8.16 (d, *J*=7.6 Hz, 4 H), 7.56 (t, *J*=7.3 Hz, 2 H), 7.42 (t, *J*=7.7 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 166.7, 160.1, 134.1, 132.5, 129.1, 127.6, 113.5 ppm. m/z = 261. IR (ATR): 1591.5, 1576.7, 1510.0, 1439.1, 1397.7, 1366.1, 1323.8, 1306.1, 1267.2, 1239.4, 786.1, 687.0. [S1a]



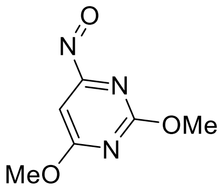
1f. 209 mg, 96%. Mixture of monomer and dimer (1:3 ratio)
^{1}H NMR ($CDCl_3$, 400MHz): δ = d = 9.10 (d, *J*=4.6 Hz, 2 H)*, 8.70 (d, *J*=4.8 Hz, 2 H), 7.65 (t, *J*=4.8 Hz, 1 H)*, 7.41 (t, *J*=4.8 Hz, 1 H) ppm. * = minor. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 159.4, 159.2, 122.6 ppm. m/z = 109. IR (ATR): 1576.3, 1444.3, 1377.3, 1238.5, 998.4, 978.1, 785.4, 717.3. [S1a]



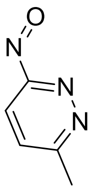
1g. 229 mg, 93%. Mixture of monomer and dimer (1:6 ratio)
^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.86 (s, 2 H) *, 8.47 (s, 2 H), 2.48 (s, 3 H) *, 2.37 (s, 3 H) ppm. * = minor. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 158.9, 158.5, 132.9, 15.6 ppm. m/z = 123. IR (ATR): 1572.5, 1395.2, 1290.4, 1253.1, 982.2, 787.5, 775.8, 651.0.



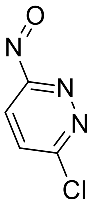
1h. 506 mg, 97%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.30 (dd, *J*=7.7, 1.9 Hz, 2 H), 8.21 (s, 1 H), 7.99 (d, *J*=7.3 Hz, 2 H), 7.54 - 7.68 (m, 3 H), 7.34 (t, *J*=7.4 Hz, 1 H), 7.19 (t, *J*=7.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 168.6, 163.9, 163.4, 135.8, 135.6, 132.4, 131.9, 129.4, 128.7, 128.4, 127.8, 106.8 ppm. m/z = 261. IR (ATR): 1589.0, 1571.1, 1532.2, 1493.6, 1413.2, 1369.0, 1339.4, 1287.8, 1177.4, 776.6, 759.3, 690.4. [S1a]



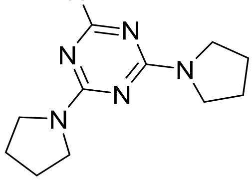
1i. 318 mg, 94%. Mixture of monomer and dimer (1:3 ratio)
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.85 (s, 1 H), 6.79 (s., 1 H)*, 4.10 (s., 6 H)*, 4.03 (s, 3 H), 3.63 (s, 3 H) ppm. * = minor. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 173.5, 164.0, 163.3, 95.1, 55.5, 55.3 ppm. m/z = 169. IR (ATR): 1609.6, 1567.5, 1490.0, 1470.0, 1411.0, 1357.5, 1206.7, 1100.5, 1055.3, 831.8.



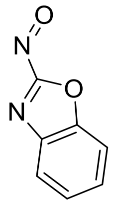
1j. 234 mg, 95%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.99 (d, *J*=8.9 Hz, 1 H), 7.61 (d, *J*=8.9 Hz, 1 H), 7.13 (d, *J*=9.7 Hz, 1 H)*, 6.87 (d, *J*=9.6 Hz, 1 H)*, 2.68 (s, 3 H), 2.30 (s, 3 H)* ppm. * = minor. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 20.6,* 22.2, 123.6, 129.3, 130.1*, 130.6, 134.8*, 158.5, 161.2*, 162.8, 165.2* ppm. * = minor. m/z = 123. IR (ATR): 1654.5, 1550.5, 1395.8, 1247.2, 1097.9, 947.7, 834.2, 807.6.



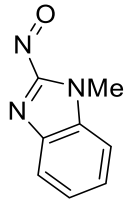
1k. 260 mg, 91%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.11 (d, *J*=7.8 Hz, 6 H), 7.84 (d, *J*=8.1 Hz, 6 H), 7.74 (d, *J*=9.2 Hz, 8 H), 6.63 (d, *J*=8.5 Hz, 7 H) ppm. m/z = 143. IR (ATR): 1651.1, 1551.8, 1410.6, 1384.5, 1245.9, 1137.8, 1082.3, 946.2, 862.4, 843.7, 764.1.



1m. 468 mg, 94%. ^{1}H NMR ($CDCl_3$, 400MHz): δ = 3.34 - 3.61 (m, 8 H), 1.75 - 2.05 (m, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 166.6, 163.1, 46.5, 46.4, 25.3, 25.2 ppm. m/z = 249. IR (ATR): 2970.6, 2873.9, 1591.1, 1514.7, 1478.3, 1457.5, 1345.0, 727.9.

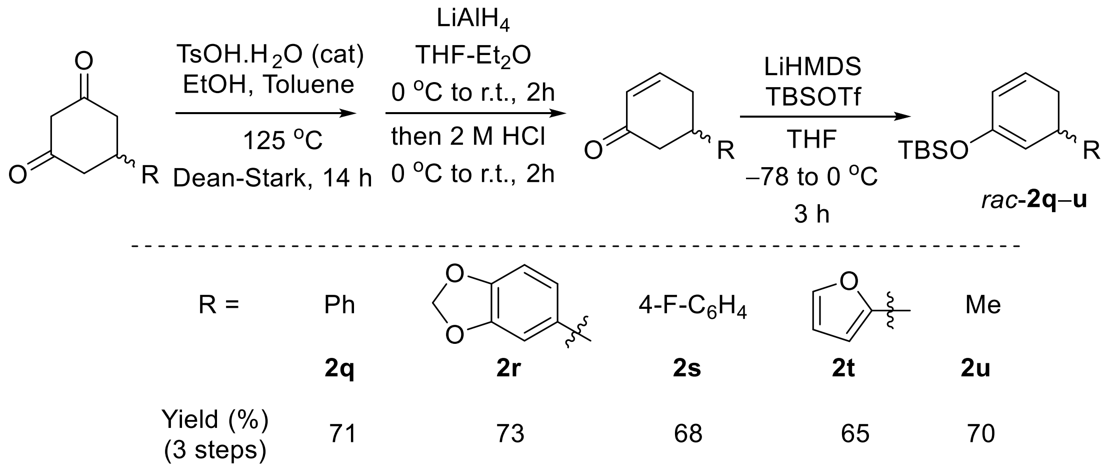


1o. 298 mg, 20% (10 mmol scale). [1]H NMR ($CDCl_3$, 400MHz): δ = 8.12 - 8.27 (m, 1 H), 7.66 - 7.77 (m, 1 H), 7.51 - 7.65 (m, 2 H) ppm. [13]C NMR ($CDCl_3$, 101 MHz): δ = 168.1, 146.6, 140.6, 132.5, 127.5, 125.3, 112.9, 77.5, 76.8 ppm. m/z = 149. IR (ATR): 1452.0, 1431.5, 1419.6, 1274.2, 1218.3, 1117.3, 1100.4, 943.0, 832.6, 765.3, 751.2.



1q. 354 mg, 22% (10 mmol scale). [1]H NMR ($CDCl_3$, 400MHz): δ = 8.01 (d, *J*=8.5 Hz, 1 H), 7.58 - 7.71 (m, 2 H), 7.48 (ddd, *J*=8.4, 5.3, 3.1 Hz, 1 H), 4.62 (s, 3 H) ppm. [13]C NMR ($CDCl_3$, 101 MHz): δ = 165.3, 140.5, 134.1, 129.2, 126.8, 125.7, 111.8, 31.2 ppm. m/z = 161. IR (ATR): 1572.0, 1509.2, 1410.4, 1269.1, 1238.0, 1161.4, 1117.0, 1079.5, 884.4, 856.5, 777.5, 745.5.

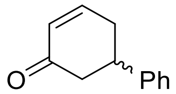
13. Synthesis of the dienes 2q-u.



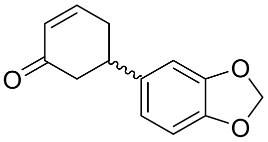
General procedure 6:

To a two-necked round bottom flask equipped with Dean-Stark apparatus and a magnetic stir bar was charged with the 5-substituted cyclohexane-1,3-dione (5 mmol), TsOH.H_2O (19 mg, 0.1 mmol), EtOH (2.5 mL) and toluene (10 mL) and the mixture was heated to 125 °C for 14 h. After cooling down to room temperature 1 mL NaOH solution (2 M in H_2O) was added and the organic phase was separated. The aqueous layer was extracted with EtOAc. Combined layer were washed with brine solution and then dried over Na_2SO_4, filtered, concentrated and the residue was used for next step without purification.

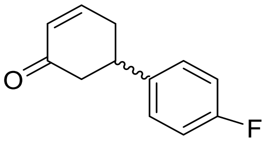
The residue was dissolved in THF (10 mL) and was added drop wise to a stirred suspension of $LiAlH_4$ (190 mg, 5 mmol) in Et_2O (10 mL) at 0 °C. After 20 min the ice bath was removed and the mixture was allowed to stir at r.t. for another 2 h. It was cooled to 0 °C again and 12 mL aq. HCl (2 M) was carefully added. Then the ice bath was removed and the mixture was stirred for another 1 h. The organic layer was then separated and the aq. layer was extracted with ether. Combined layer was washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4, concentrated, and purified by column chromatography using EtOAc/*n*-hexane (1/4) as eluent to yield 5-substituted cyclohex-2-en-1-ones.



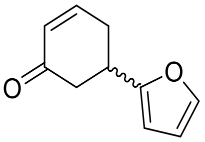
According to GP 6 on 10 mmol scale. 1.25 g, 79%.
NMR spectra in accord with the literature.[S2]



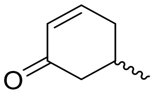
According to GP 6 on 10 mmol scale. 1.65 g, 76%.
NMR spectra in accord with the literature.[S3]



According to GP 6. 815 mg, 86%.
NMR spectra in accord with the literature.[S4]

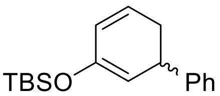


According to GP 6. 649 mg, 80%.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.34 (dd, *J*=1.8, 0.9 Hz, 1 H), 7.00 (ddd, *J*=10.1, 5.3, 3.0 Hz, 1 H), 6.30 (dd, *J*=3.2, 1.8 Hz, 1 H), 5.99 - 6.17 (m, 2 H), 3.33 - 3.55 (m, 1 H), 2.69 - 2.83 (m, 2 H), 2.53 - 2.68 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 198.3, 156.4, 148.7, 141.7, 130.0, 110.3, 104.8, 42.4, 34.3, 30.8 ppm. m/z = 162.

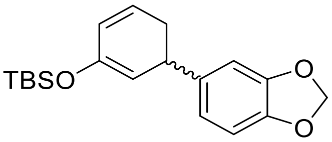


According to GP 6. 402 mg, 73%.
NMR spectra in accord with the literature.[S5]

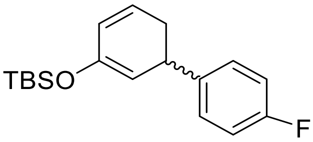
General procedure 7:
LiHMDS (3 mL, 1 M in THF) was added dropwise to a THF solution (3 mL) of 5-substituted cyclohex-2-en-1-one (2 mmol) at −78 °C and the mixture was stirred at that temperature for another 1 h before TBSOTf (0.69 mL, 794 mg, 3 mmol) was added. The mixture was the slowly warm to 0 °C for 3 h and quenched with 3 mL saturated $NaHCO_3$ solution. The organic layer was extracted with ether, dried over Na_2SO_4, concentrated, and purified by column chromatography using Et_2O/NEt_3/-pentane (1/2/50) as eluent to yield the dienes **2q-u**.



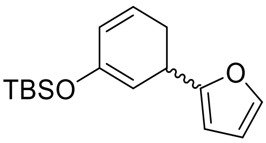
2q, According to GP 7. 516 mg, 90%.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.27 - 7.34 (m, 4 H), 7.18 - 7.25 (m, 1 H), 5.75 - 5.87 (m, 2 H), 4.89 - 4.99 (m, 1 H), 3.67 – 3.71 (m, 1 H), 2.40 - 2.54 (m, 1 H), 2.17 - 2.31 (m, 1 H), 0.95 (s, 9 H), 0.18 – 0.17 (2 s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 128.5, 127.7, 127.7, 126.5, 126.4, 106.8, 40.3, 32.5, 25.9, -4.3 ppm. m/z = 286.



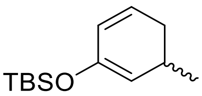
2r, According to GP 7. 635 mg, 96%.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.83 (s, 1 H), 6.74 (s, 2 H), 5.93 (q, *J*=1.4 Hz, 2 H), 5.72 - 5.87 (m, 2 H), 4.81 - 4.94 (m, 1 H), 3.59 - 3.65 (m, 1 H), 2.38 - 2.51 (m, 1 H), 2.17 - 2.28 (m, 1 H), 0.96 (s, 10 H), 0.18 (2 s, 7 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 149.1, 147.6, 146.0, 140.3, 127.7, 126.4, 120.4, 108.2, 106.9, 100.9, 39.9, 32.7, 25.8, 18.2, -4.3 ppm. m/z = 330.



2s, According to GP 7. 482 mg, 79%.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.46 - 7.60 (m, 2 H), 7.17 - 7.34 (m, 2 H), 5.90 - 6.19 (m, 2 H), 5.20 (d, *J*=4.1 Hz, 1 H), 3.92 - 4.04 (m, 1 H), 2.68 - 2.86 (m, 1 H), 2.44 - 2.59 (m, 1 H), 1.24 (s, 9 H), 0.46 (2 s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 161.6 (d, *J*=244.4 Hz), 149.3, 141.8 (d, *J*=2.0 Hz), 129.0 (d, *J*=9.1 Hz), 127.6, 126.5, 115.2 (d, *J*=21.2 Hz), 106.6, 39.4, 32.5, 26.1, 25.8, 18.3, -4.3 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = −117.1 ppm. m/z = 304.

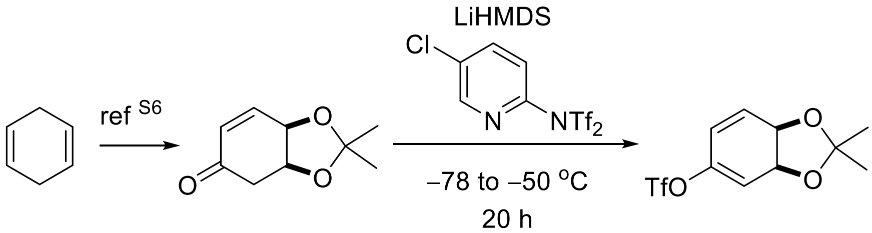


2t, According to GP 7. 448 mg, 81%.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.30 - 7.37 (m, 1 H), 6.26 - 6.36 (m, 1 H), 6.00 - 6.12 (m, 1 H), 5.81 - 5.94 (m, 1 H), 5.72 - 5.81 (m, 1 H), 5.00 (dd, *J*=4.1, 2.1 Hz, 1 H), 3.68 - 3.83 (m, 1 H), 2.31 - 2.58 (m, 2 H), 0.97 (s, 10 H), 0.19 (2 s Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 158.3, 149.4, 141.2, 127.8, 126.4, 110.1, 104.5, 103.4, 33.1, 28.5, 25.8, 18.2, -4.3 ppm. m/z = 276.

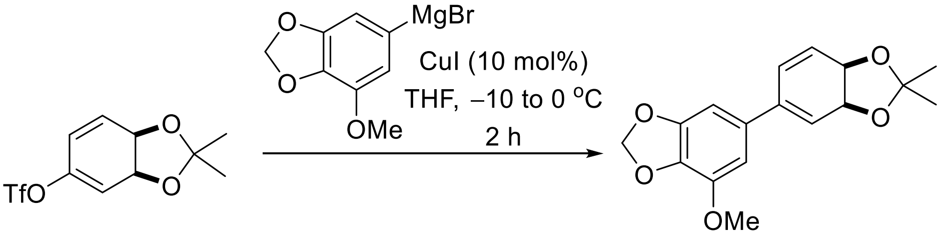


2u, According to GP 7. 431 mg, 96%.
^{1}H NMR ($CDCl_3$, 400MHz): δ = 5.75 - 5.86 (m, 1 H), 5.63 - 5.72 (m, 1 H), 4.77 (dd, *J*=3.8, 1.9 Hz, 1 H), 2.40 - 2.56 (m, 1 H), 2.18 - 2.21 (m, 1 H), 1.77 - 1.92 (m, 1 H), 1.00 (d, *J*=6.9 Hz, 3 H), 0.93 (s, 9 H), 0.14 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 148.0, 128.0, 126.1, 109.7, 31.3, 28.3, 26.1, 25.9, 20.9, 18.2, -4.4 ppm. m/z = 224.

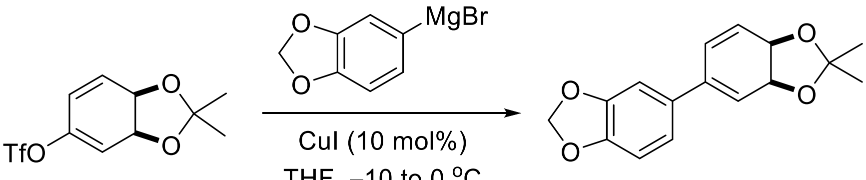
14. Synthesis of the dienes 2v,w.



12 *rac*-**13**, 39% *rac*-**14**, 51%



rac-**14** *rac*-**2v**, R = OMe, 70%



rac-**14** *rac*-**2w**, R = H, 65%

rac-**13** was prepared in 5 steps from 1,4-cyclohexadine according to the literature procedure.[S6]

rac-**14**. LiHMDS (1.5 mL, 1 M in THF) was added dropwise to a THF solution (3 mL) of *rac*-**15** (168 mg, 1 mmol) at −78 °C. The mixture was stirred at that temperature for 75 min before Cl-PyNTf$_2$ (698 mg, 1.5 mmol) was added. The mixture was stirred at −78 °C for another 10 h before warm to −50 °C and stirred for 10 h. Then the reaction was quenched with saturated NH_4Cl, extracted in CH_2Cl_2, dried over Na_2SO_4, purified by column chromatography using EtOAc/*n*-hexane (10/1) as eluent to yield *rac*-**14** (153 mg, 51%).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.11 (ddd, *J*=10.2, 3.7, 0.9 Hz, 1 H), 5.91 - 6.00 (m, 1 H), 5.83 - 5.90 (m, 1 H), 4.89 (dd, *J*=8.9, 4.4 Hz, 1 H), 4.72 - 4.70 (m, 1 H), 1.41 (2 s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 145.7, 130.4, 121.3, 120.2, 118.6 (q, *J*=322 Hz), 106.3, 70.9, 69.7, 26.7, 24.8 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz): δ = −73.3 ppm. m/z = 300.

rac-**2v.** (7-methoxybenzo[d][1,3]dioxol-5-yl)magnesium bromide (0.75 mmol, 0.5 M in THF) was added dropwise over 20 min to a suspension of *rac*-**14** (0.5 mmol) and CuI (9.5 mg, 0.05 mmol) in THF (1 mL) at −10 °C. The mixture was stirred for 2 h maintaining temperature below 0 °C before quenched with saturated NH_4Cl, extracted in CH_2Cl_2, dried over Na_2SO_4, purified by column chromatography using EtOAc/*n*-hexane (10/1) as eluent to yield *rac*-**2v** (106 mg, 70%).
^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.57 - 6.63 (m, 2 H), 6.28 - 6.31 (m, 1 H), 5.95 - 6.05 (m, 4 H), 4.77 - 4.82 (m, 1 H), 4.70 - 4.76 (m, 1 H), 3.91 (s, 3 H), 1.43 (2 s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 149.1, 143.6, 135.5, 135.3, 134.7, 127.0, 125.9, 120.2, 106.0, 105.3, 101.7, 100.6, 71.1, 70.5, 56.8, 26.9, 25.0 ppm. m/z = 302.

rac-**2w.** benzo[d][1,3]dioxol-5-ylmagnesium bromide (0.75 mmol, 0.5 M in THF) was added dropwise over 20 min to a suspension of *rac*-**14** (0.5 mmol) and CuI (9.5 mg, 0.05 mmol) in

THF (1 mL) at −10 °C. The mixture was stirred for 2 h maintaining temperature below 0 °C before quenched with saturated NH_4Cl, extracted in CH_2Cl_2, dried over Na_2SO_4, purified by column chromatography using EtOAc/*n*-hexane (10/1) as eluent to yield *rac*-**2w** (89 mg, 65%). ^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.87 - 6.94 (m, 2 H), 6.77 - 6.83 (m, 1 H), 6.30 - 6.34 (m, 1 H), 5.92 - 6.08 (m, 4 H), 4.80 (dd, *J*=8.7, 4.1 Hz, 1 H), 4.70 – 4.73 (m, 1 H), 1.43 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 148.0, 147.6, 135.3, 134.0, 126.9, 125.9, 119.9, 119.8, 108.4, 106.7, 105.3, 101.3, 71.2, 70.5, 27.0, 25.1 ppm. m/z = 272.

15. References

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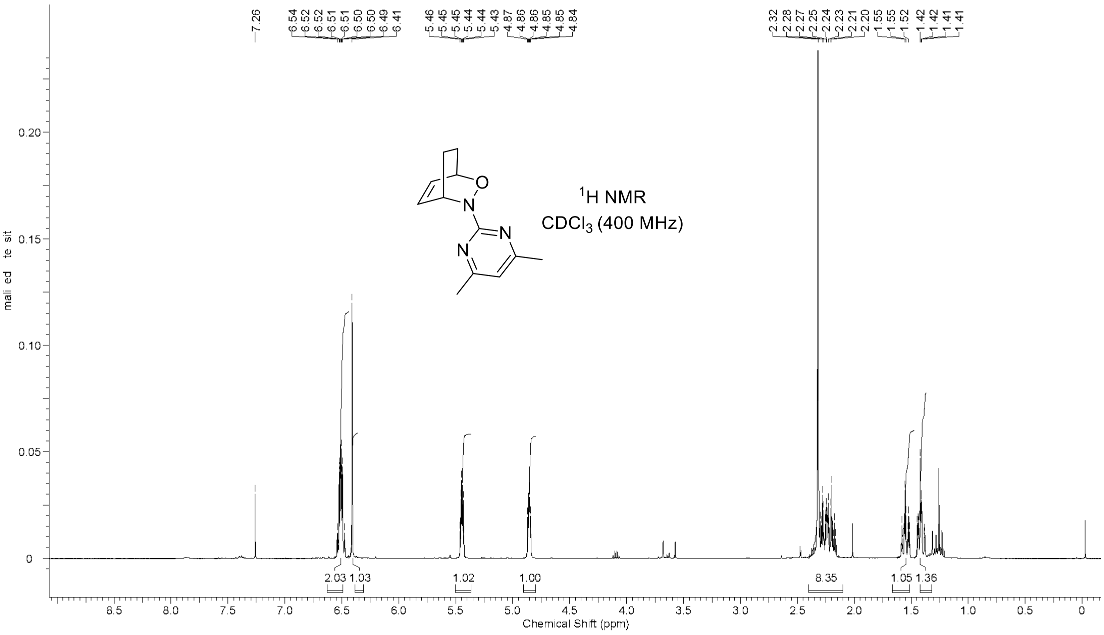
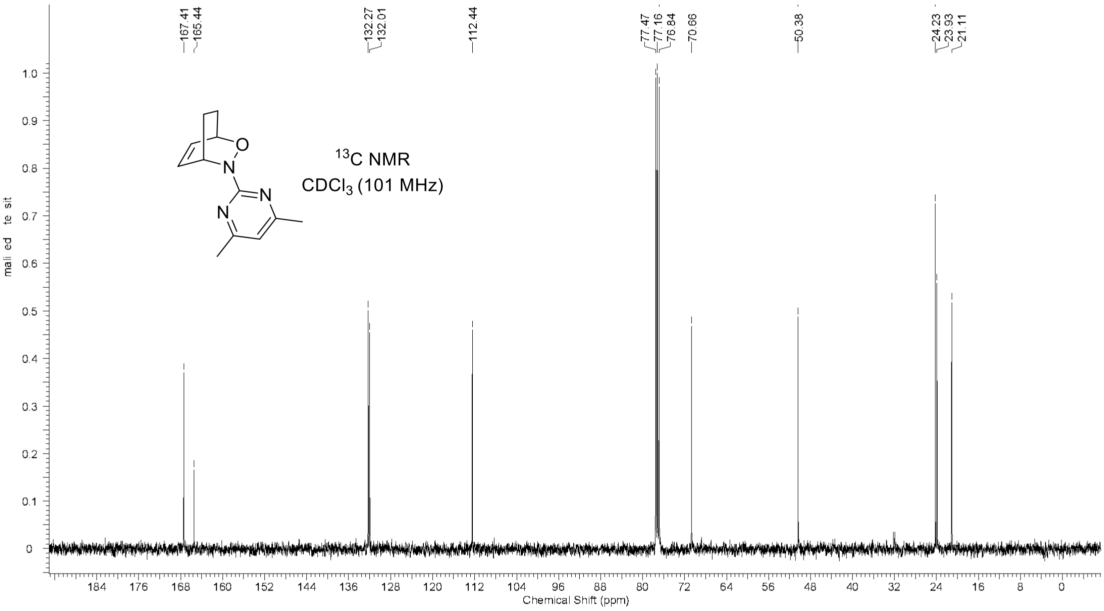
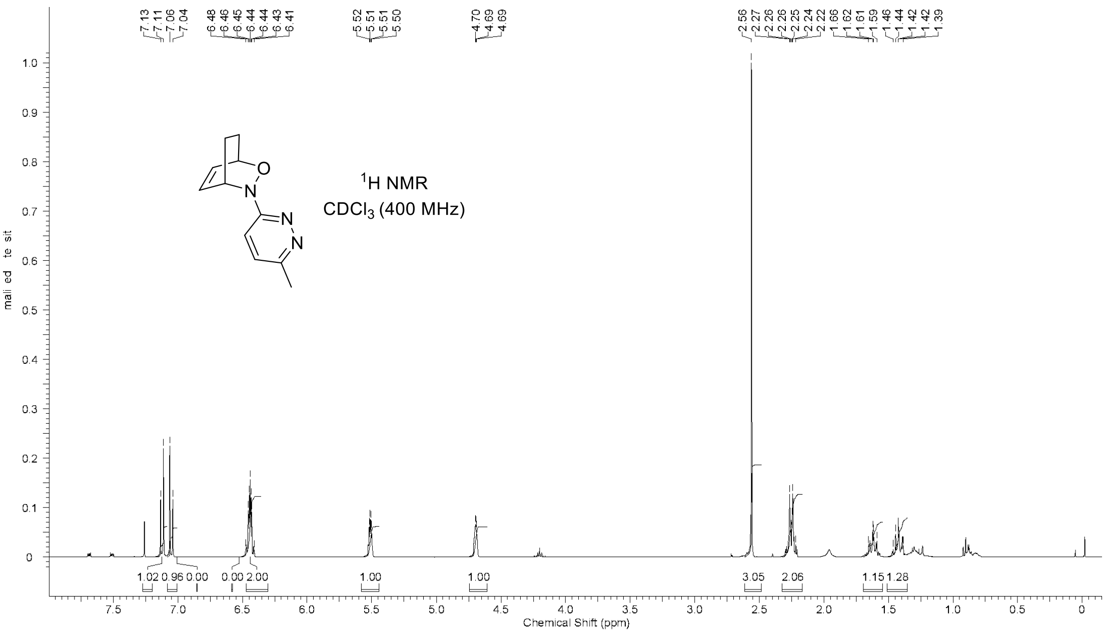
(S2) Kryshtal, G. V.; Kulganek, V. V.; Kucherov, V. F.; Yanovskaya, L. A. *Synthesis* **1979**, *1979*, 107.
(S3) Poe, S. L.; Morken, J. P. *Angew. Chem. Int. Ed.* **2011**, *50*, 4189.
(S4) Carlone, A.; Marigo, M.; North, C.; Landa, A.; Jorgensen, K. A. *Chem. Commun.* **2006**, 4928.
(S5) Fleming, I.; Maiti, P.; Ramarao, C. *Org. Biomol. Chem.* **2003**, *1*, 3989.
(S6) Krow, G. R.; Carmosin, R.; Mancuso, A. *Org. Prep. Proced. Int.* **1977**, *9*, 285.

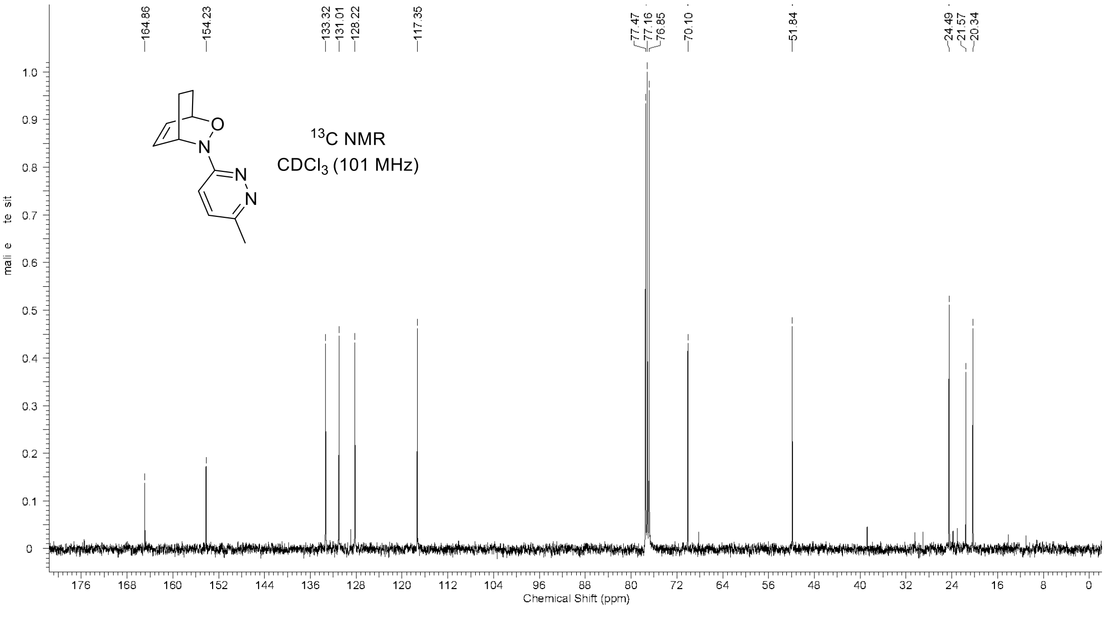
16. Copies of ^{1}H and ^{13}C NMR spectra



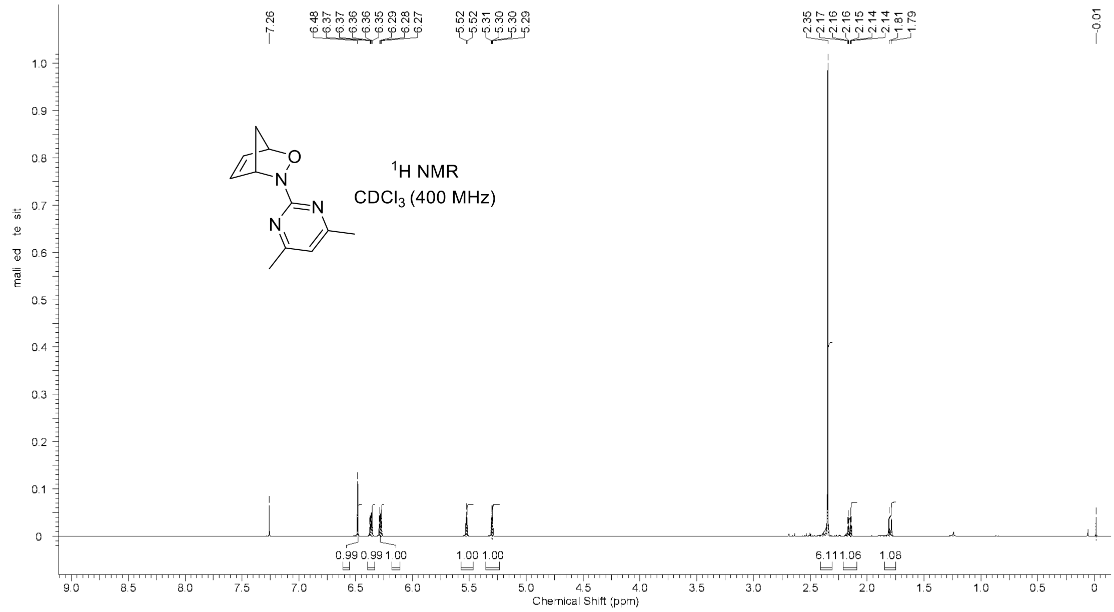




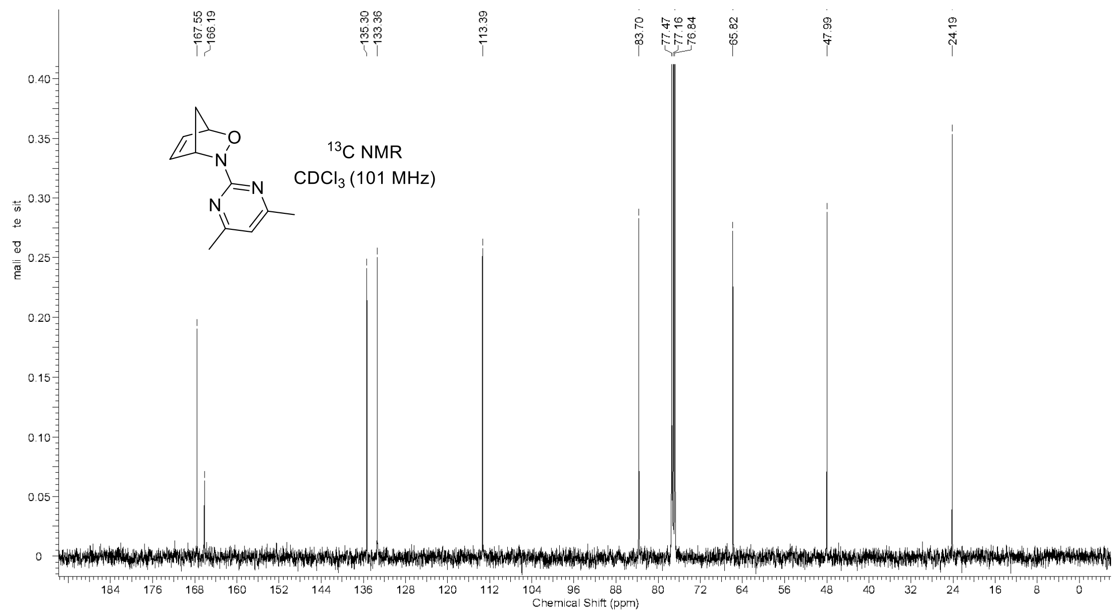
7.13
7.11
7.06
7.04
6.48
6.46
6.45
6.44
6.44
6.44
6.43
6.41
5.52
5.51
5.51
5.50
4.70
4.69
4.69
2.56
2.27
2.26
2.26
2.25
2.24
2.24
2.22
1.66
1.62
1.61
1.59
1.46
1.44
1.42
1.42
1.39
^{1}H NMR
$CDCl_3$ (400 MHz)
1.02
0.96
0.00
0.00
2.00
1.00
1.00
3.05
2.06
1.15
1.28
Chemical Shift (ppm)



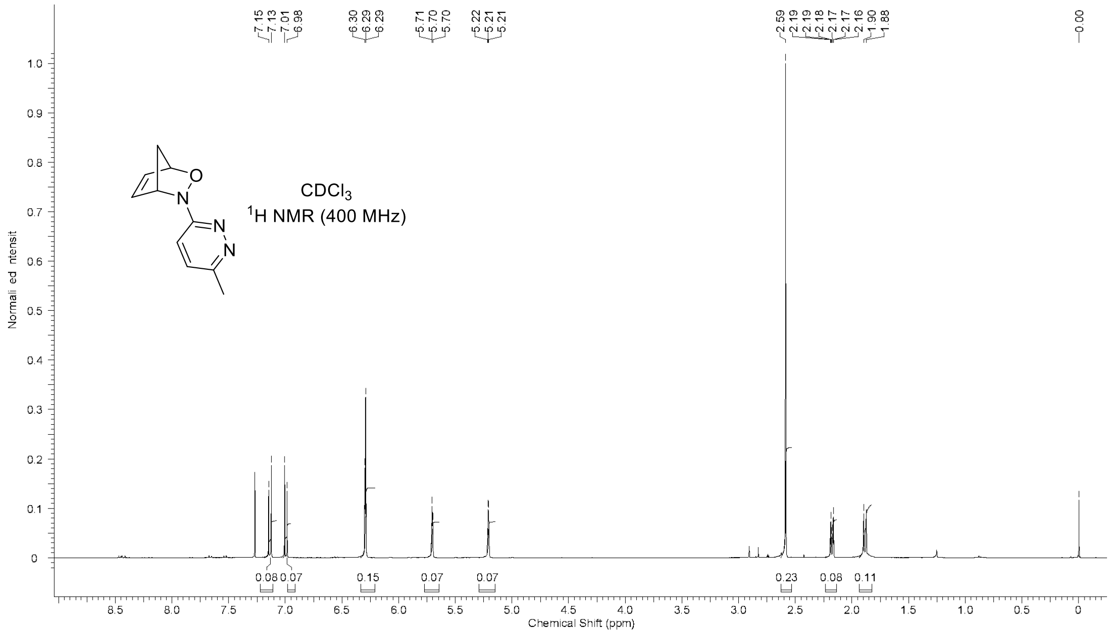
164.86
154.23
133.32
131.01
128.22
117.35
77.47
77.16
76.85
70.10
51.84
24.49
21.57
20.34
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)

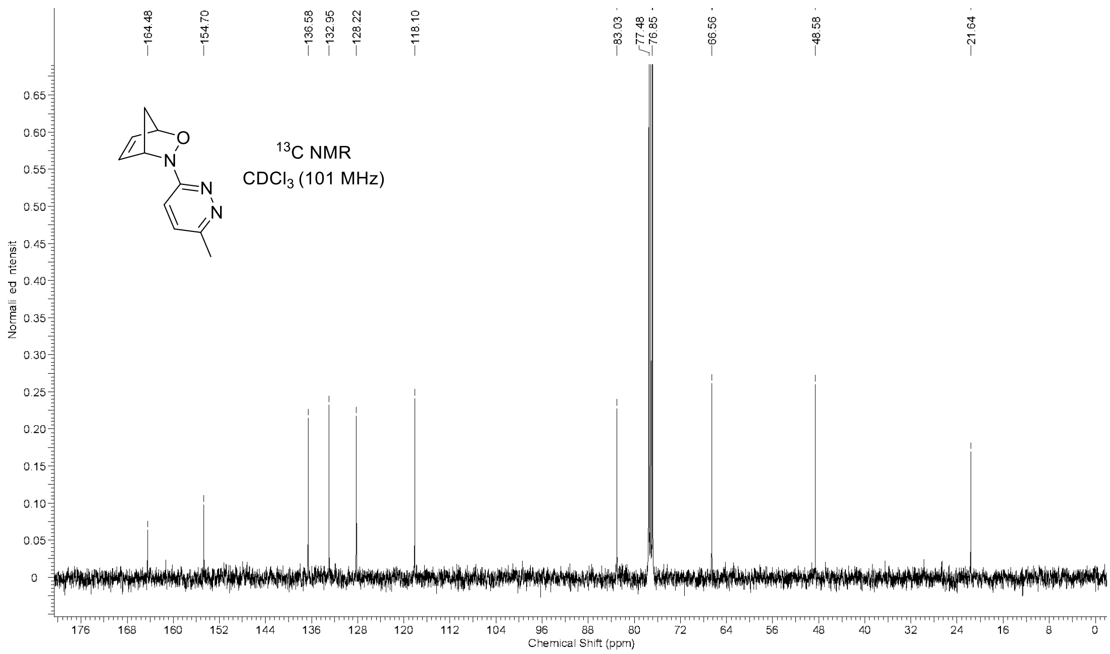


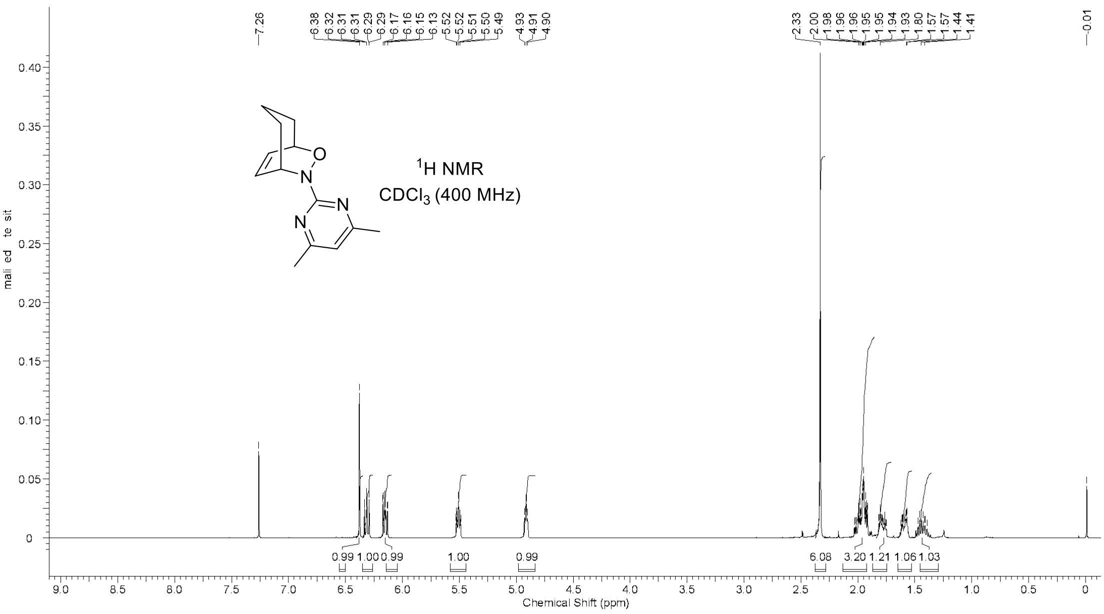
^{1}H NMR
CDCl$_3$ (400 MHz)
7.26
6.48 6.37 6.37 6.36 6.36 6.35 6.29 6.28 6.27
5.52 5.52 5.31 5.30 5.30 5.29
2.35 2.17 2.16 2.16 2.15 2.14 2.14 1.81 1.79
-0.01
0.99 0.99 1.00 1.00 1.00 6.11 1.06 1.08
Chemical Shift (ppm)



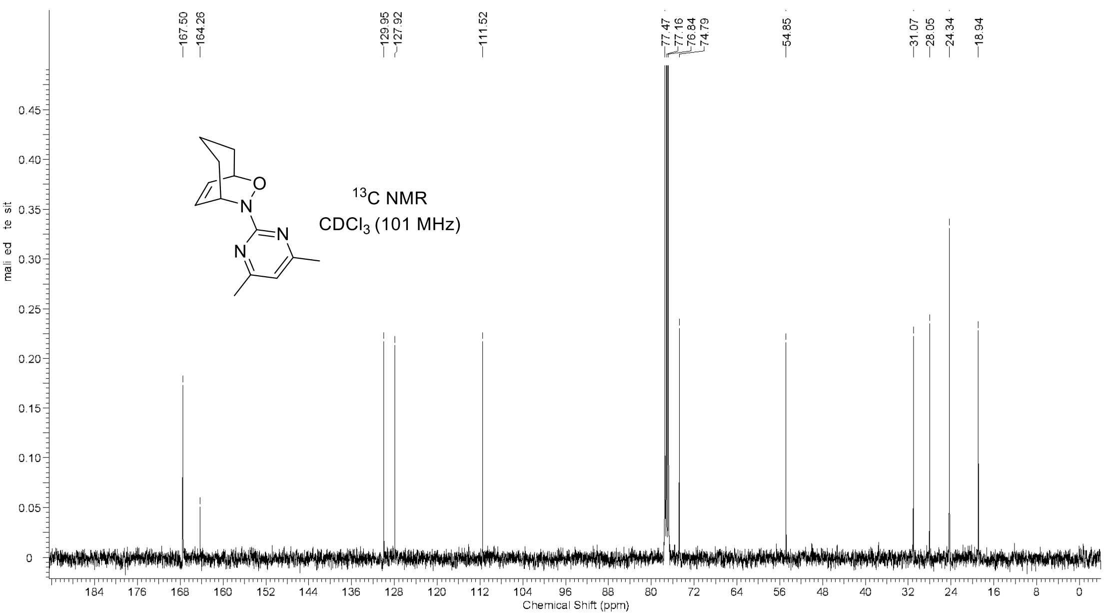
^{13}C NMR
CDCl$_3$ (101 MHz)
167.55 166.19
135.30 133.36
113.39
83.70 77.47 77.16 76.84
65.82
47.99
24.19
Chemical Shift (ppm)


CDCl3
1H NMR (400 MHz)
Chemical Shift (ppm)

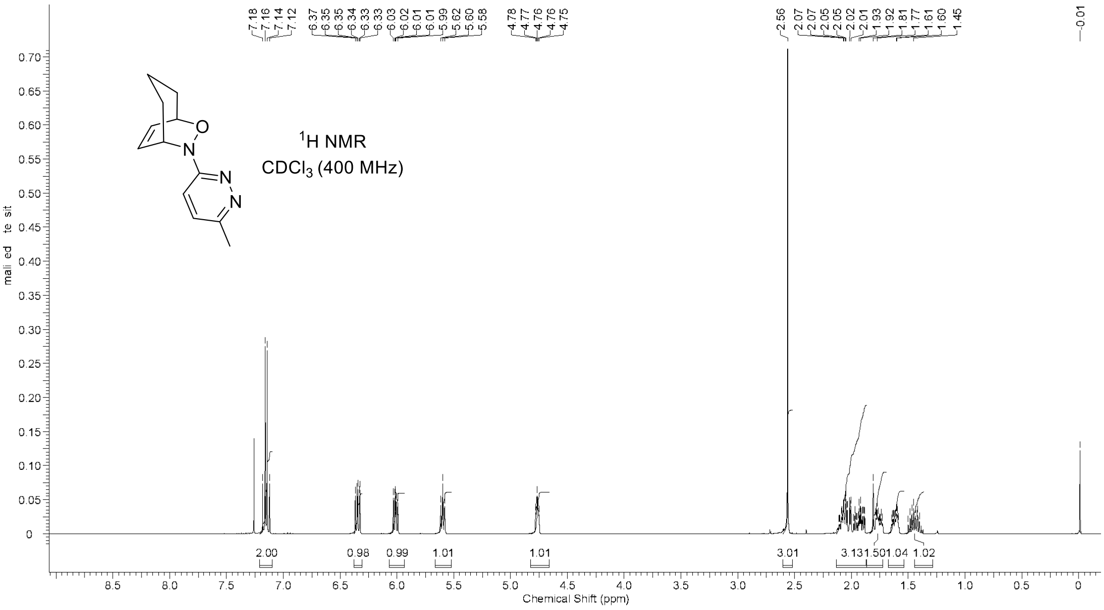

13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



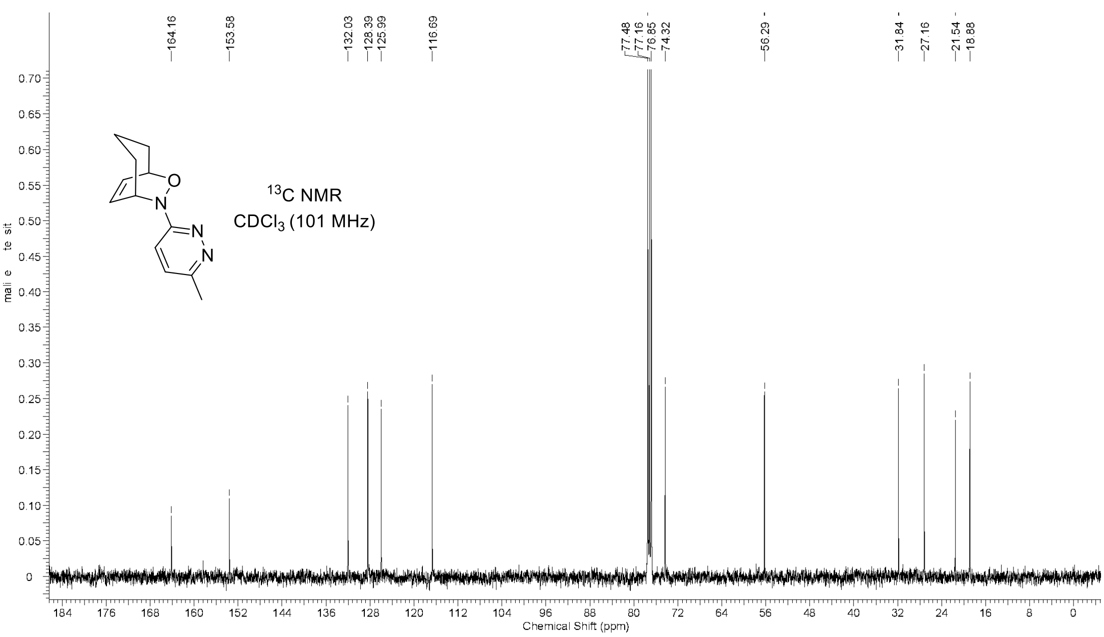
1H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



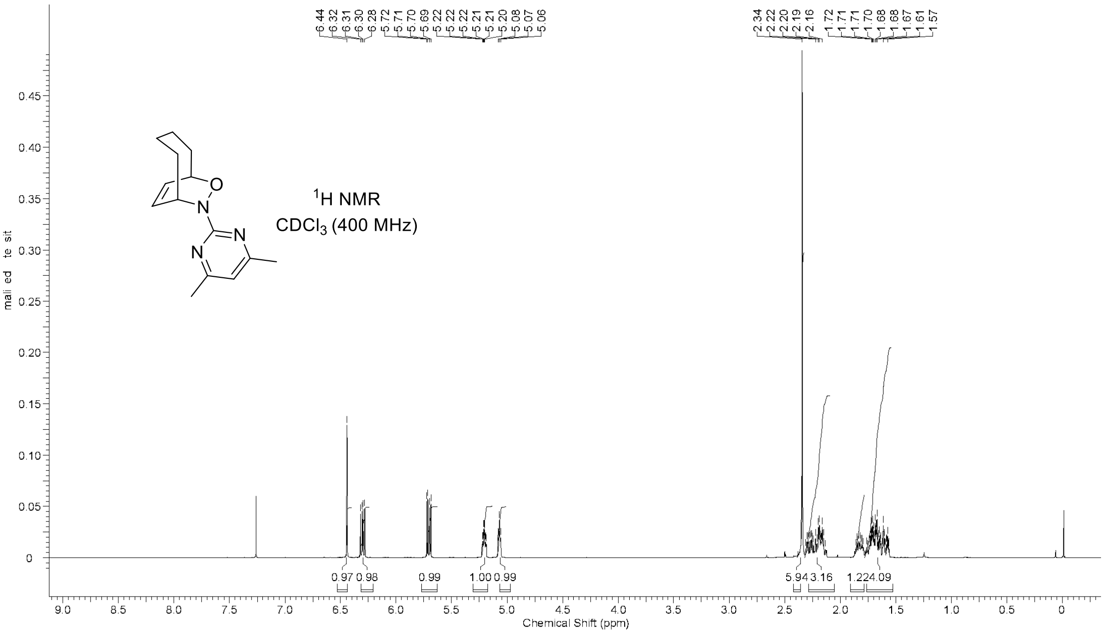
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



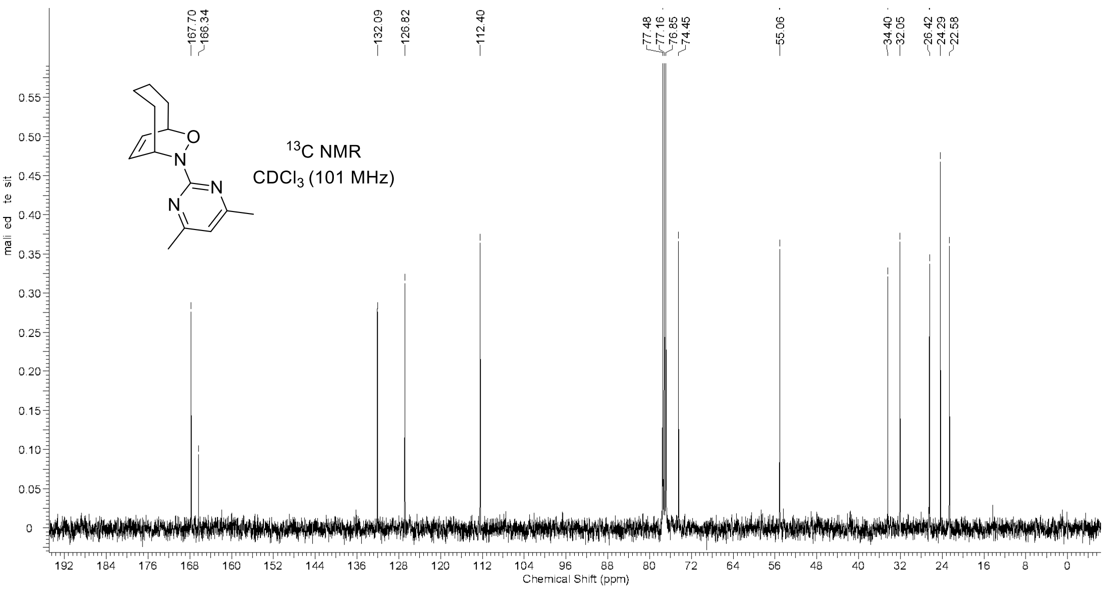
^{1}H NMR
$CDCl_3$ (400 MHz)
Chemical Shift (ppm)



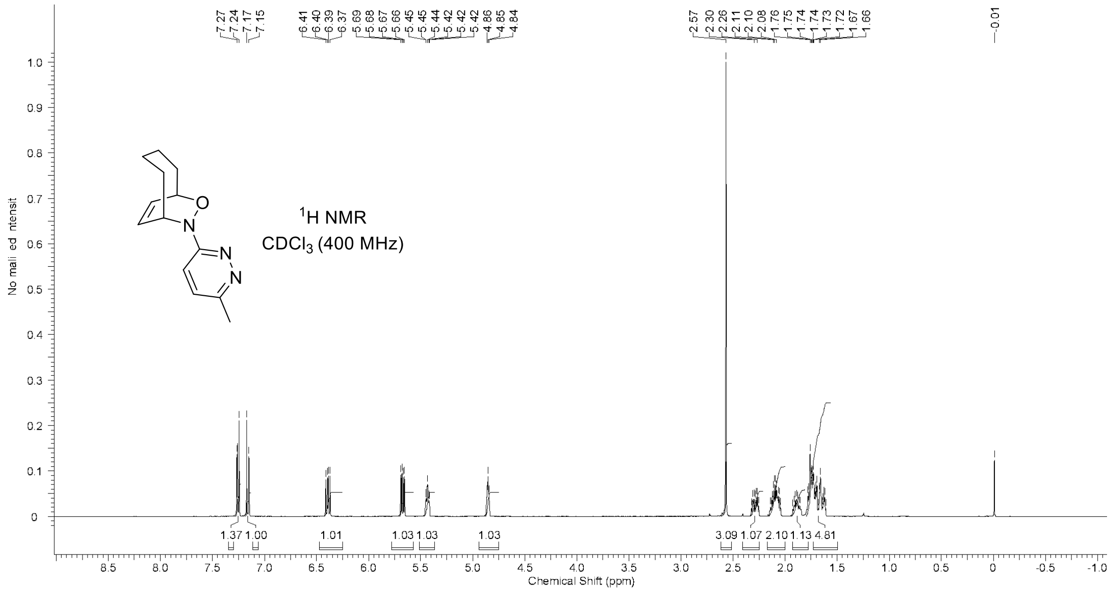
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)

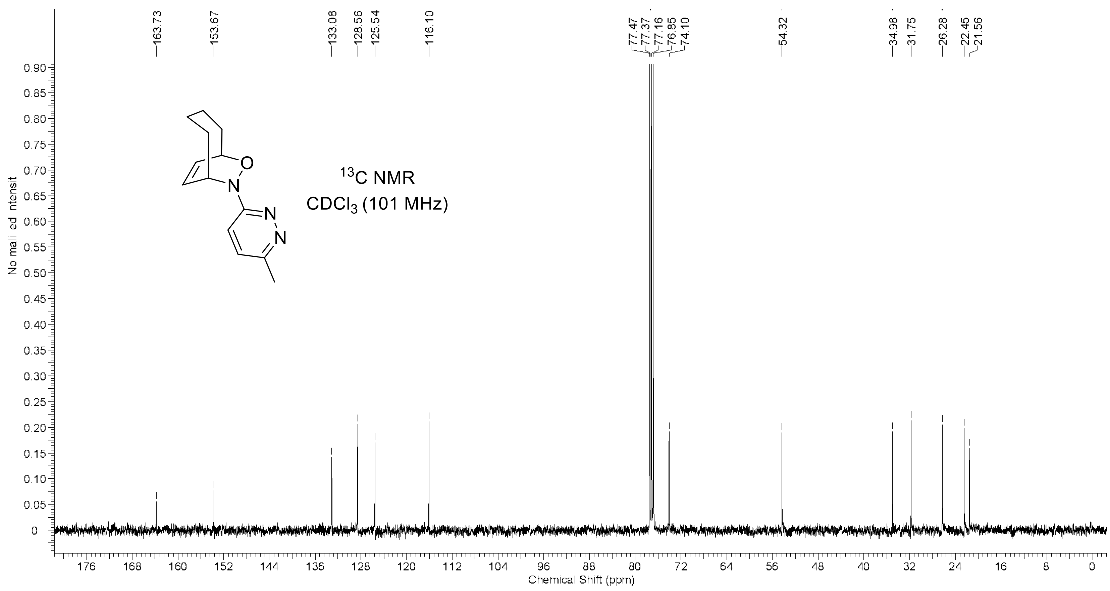


6.44 6.32 6.31 6.30 6.28 5.72 5.71 5.70 5.69 5.22 5.22 5.21 5.21 5.20 5.08 5.07 5.06
2.34 2.22 2.20 2.19 2.16 1.72 1.71 1.71 1.70 1.68 1.68 1.67 1.61 1.57
N
O
N
N
¹H NMR
CDCl₃ (400 MHz)
0.97 0.98 0.99 1.00 0.99 5.94 3.16 1.22 4.09
Chemical Shift (ppm)



167.70 166.34 132.09 126.82 112.40 77.48 77.16 76.85 74.45 55.06 34.40 32.05 26.42 24.29 22.58
N
O
N
N
¹³C NMR
CDCl₃ (101 MHz)
Chemical Shift (ppm)


^{1}H NMR
$CDCl_3$ (400 MHz)
Chemical Shift (ppm)


^{13}C NMR
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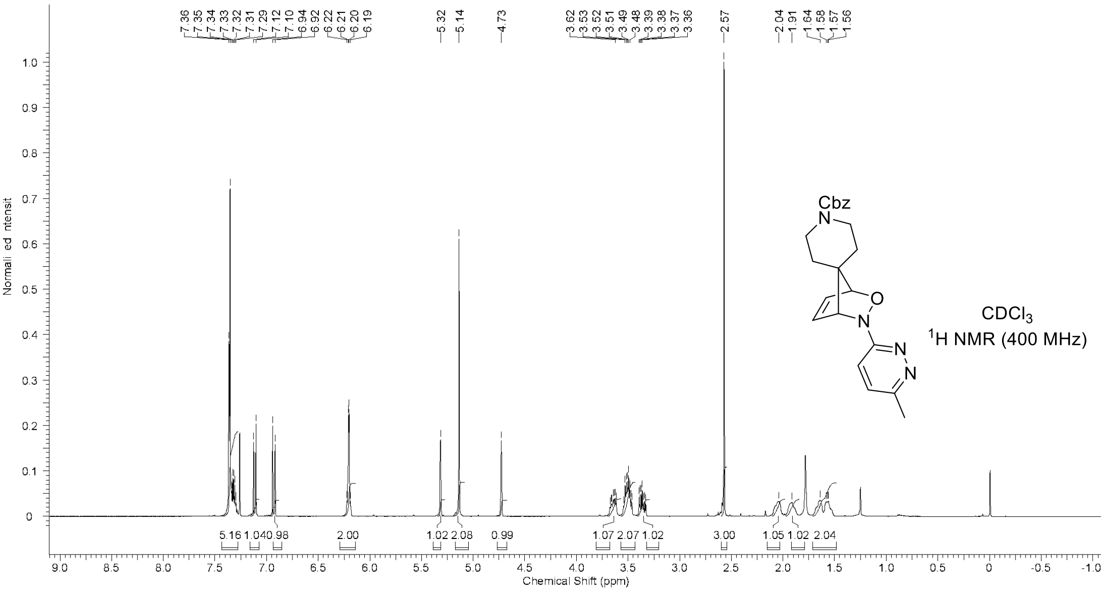
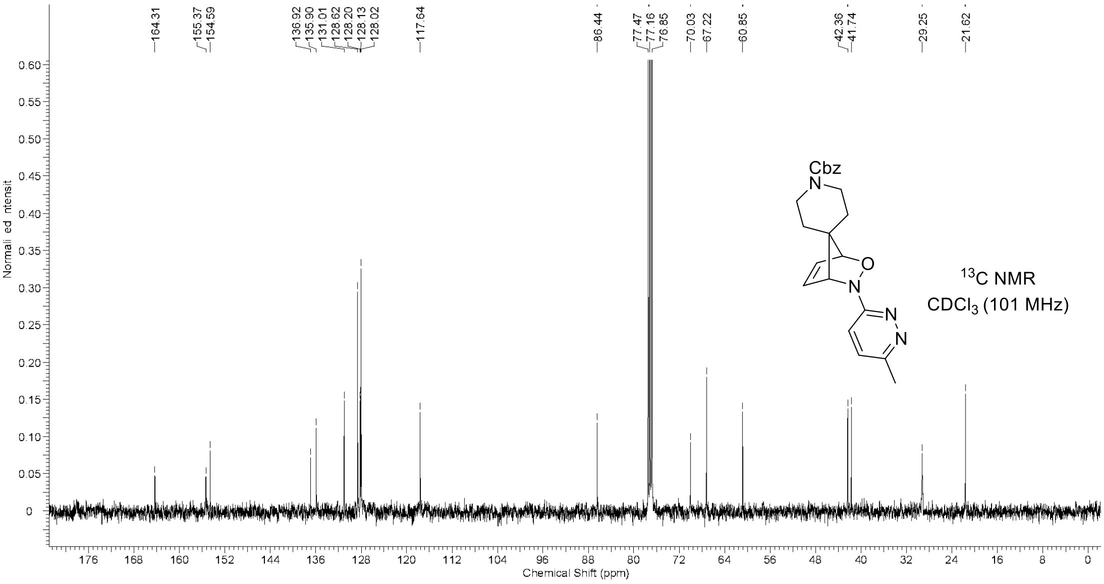
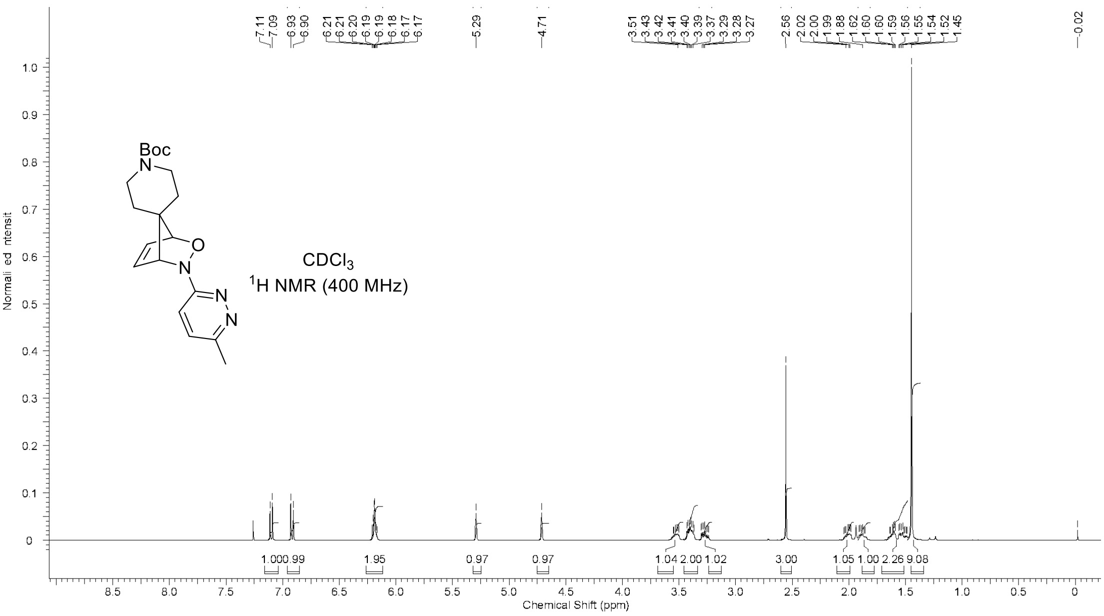
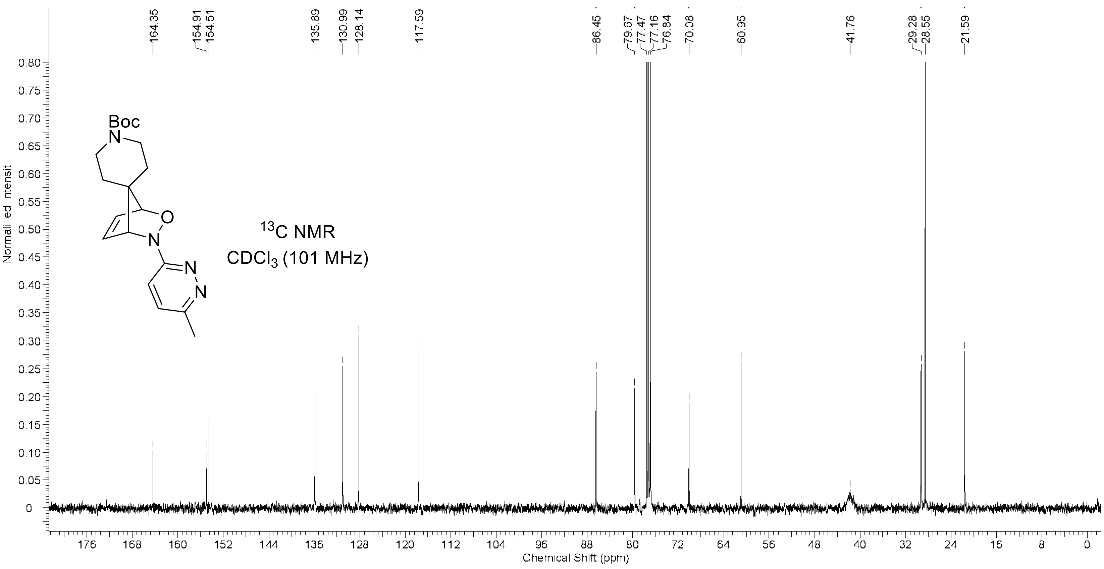
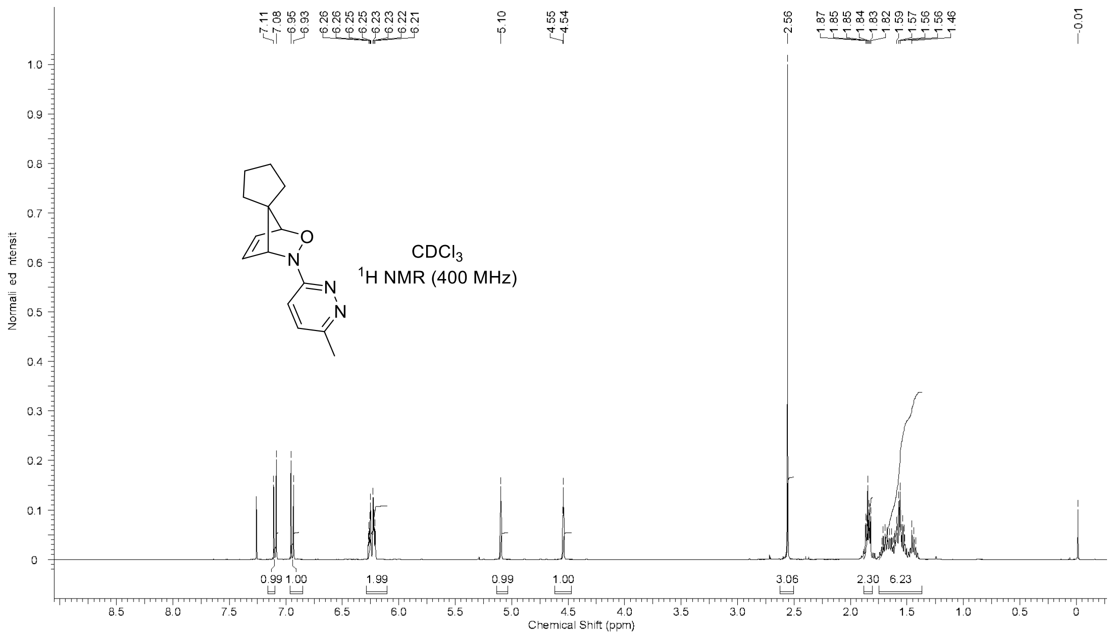
Chemical Shift (ppm)


CDCl$_3$
^{1}H NMR (400 MHz)
Cbz
Chemical Shift (ppm)
Normalized Intensity

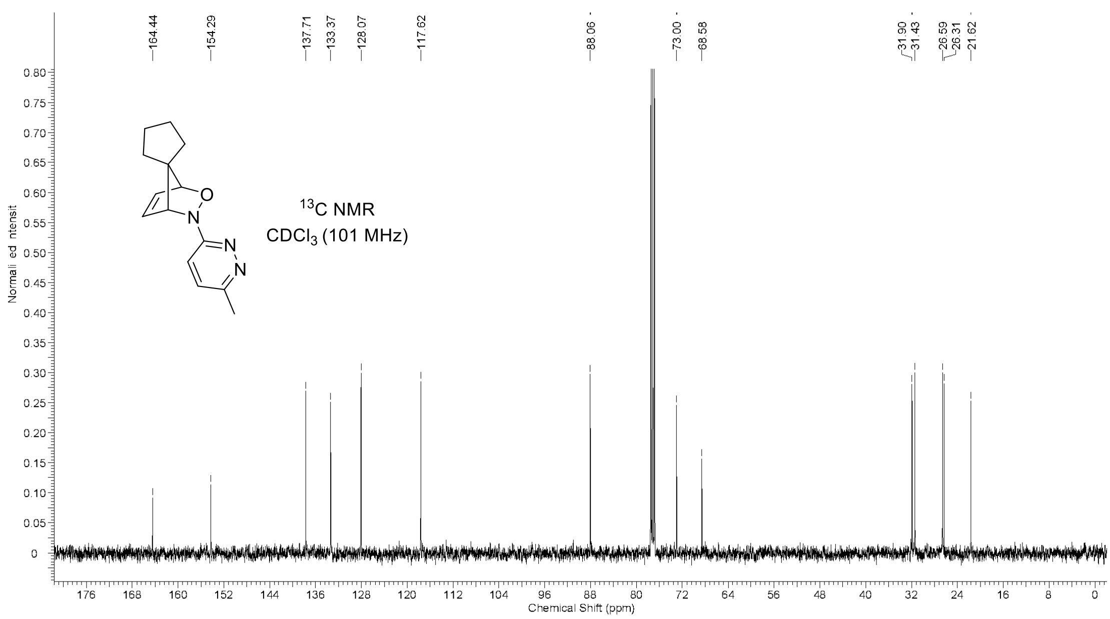

^{13}C NMR
CDCl$_3$ (101 MHz)
Cbz
Chemical Shift (ppm)
Normalized Intensity


CDCl3
1H NMR (400 MHz)
Boc
N
O
N
Chemical Shift (ppm)

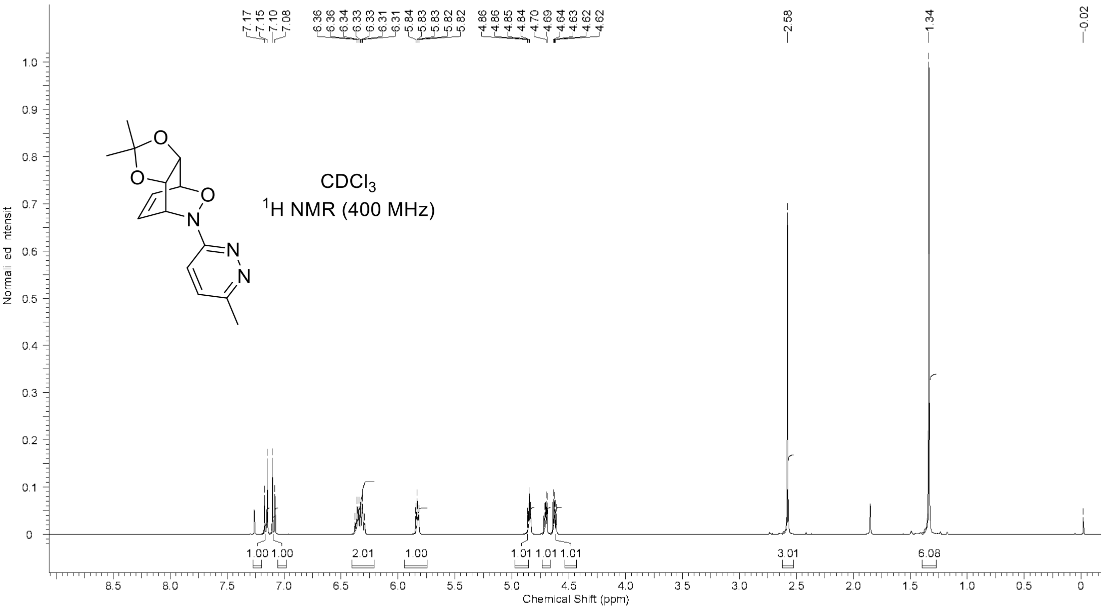

13C NMR
CDCl3 (101 MHz)
Boc
N
O
N
Chemical Shift (ppm)

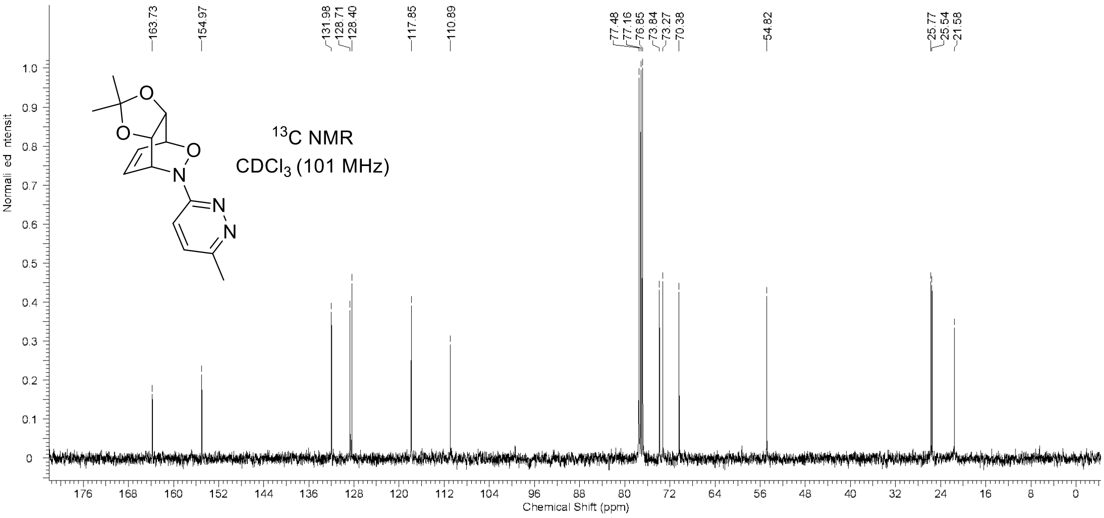


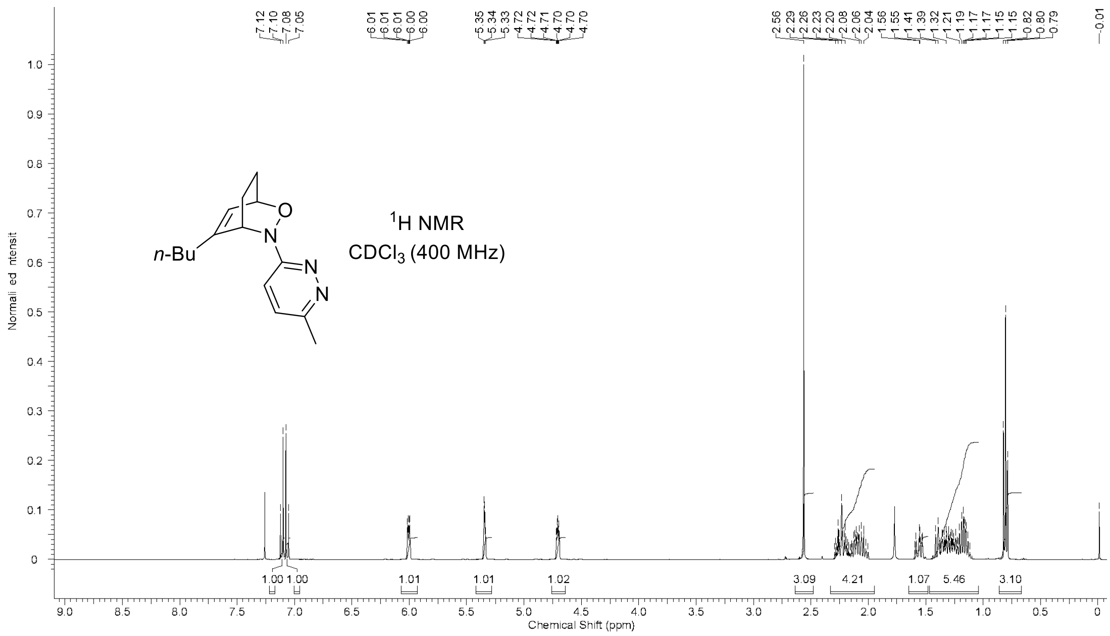
CDCl3
1H NMR (400 MHz)
Chemical Shift (ppm)

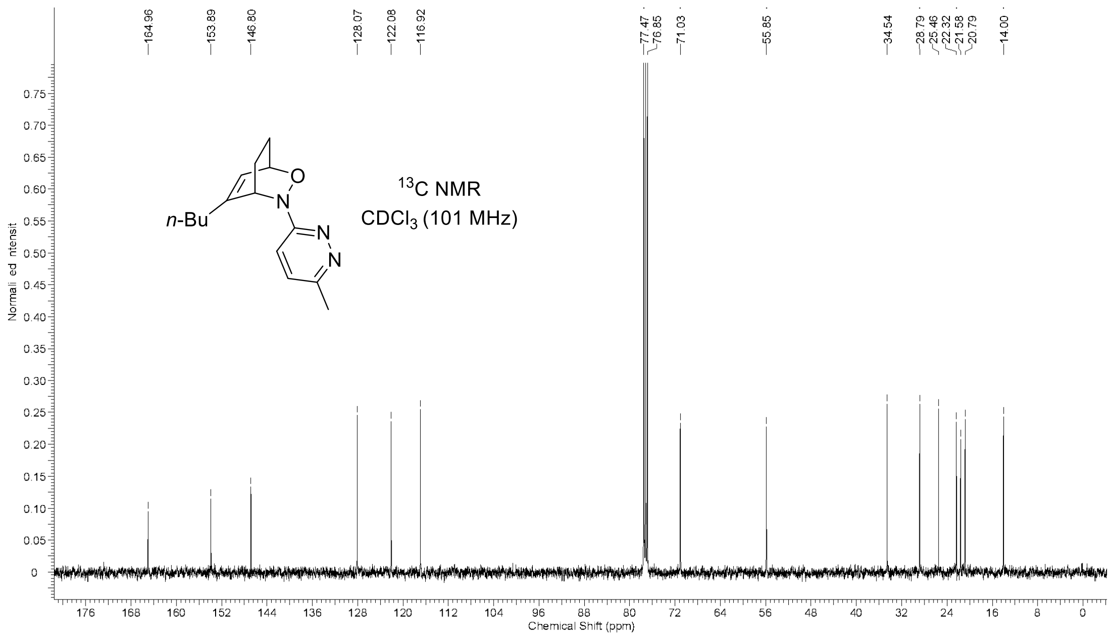


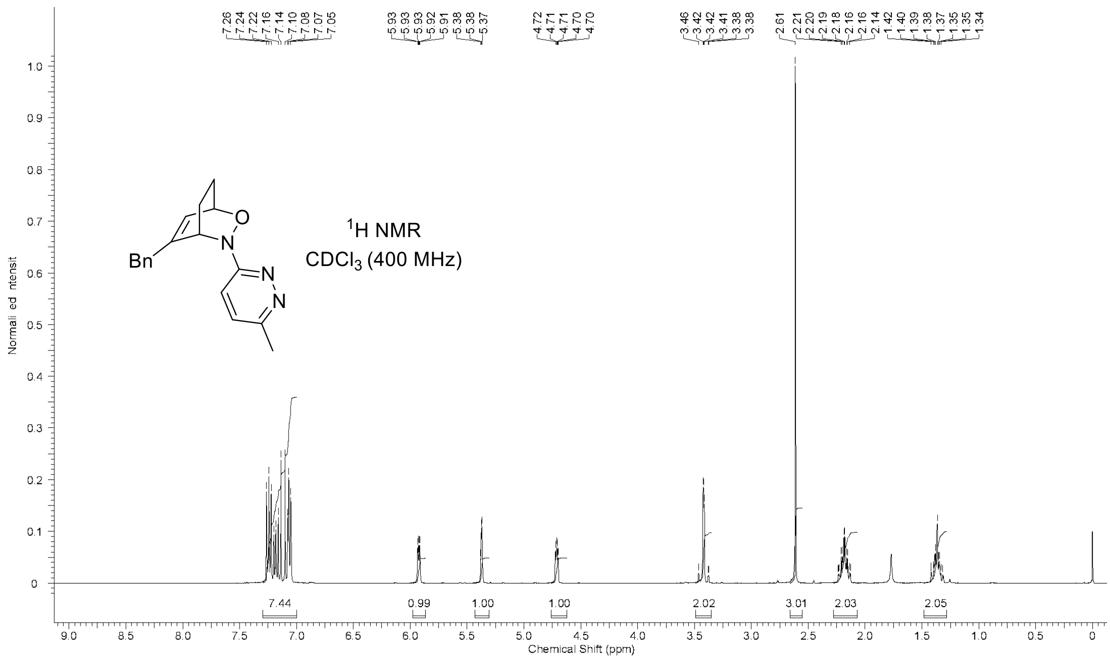
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)


7.17
7.15
7.10
7.08
6.36
6.36
6.34
6.33
6.33
6.31
6.31
5.84
5.83
5.83
5.82
5.82
4.86
4.86
4.85
4.84
4.70
4.69
4.64
4.63
4.62
4.62
2.58
1.34
-0.02
CDCl3
1H NMR (400 MHz)
N
O
N
N
O
O
Normalized Intensity
1.00
1.00
2.01
1.00
1.01
1.01
1.01
3.01
6.08
Chemical Shift (ppm)

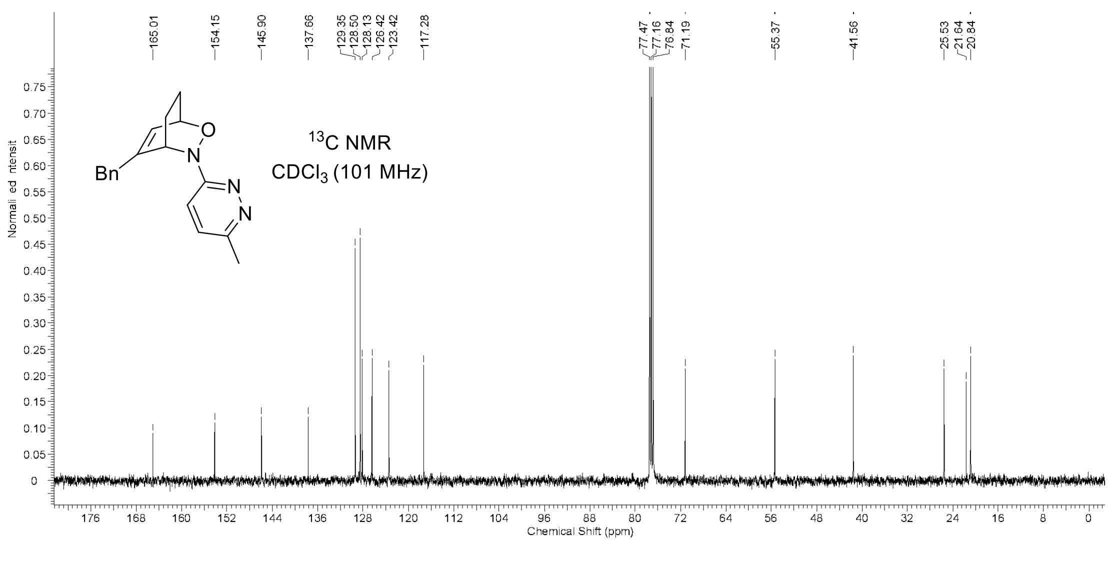

163.73
154.97
131.98
128.71
128.40
117.85
110.89
77.48
77.16
76.85
73.84
73.27
70.38
54.82
25.77
25.54
21.58
13C NMR
CDCl3 (101 MHz)
O
O
O
N
N
N
Normalized Intensity
Chemical Shift (ppm)


n-Bu
O
N
N
N
1H NMR
CDCl3 (400 MHz)
Normalized Intensity
Chemical Shift (ppm)

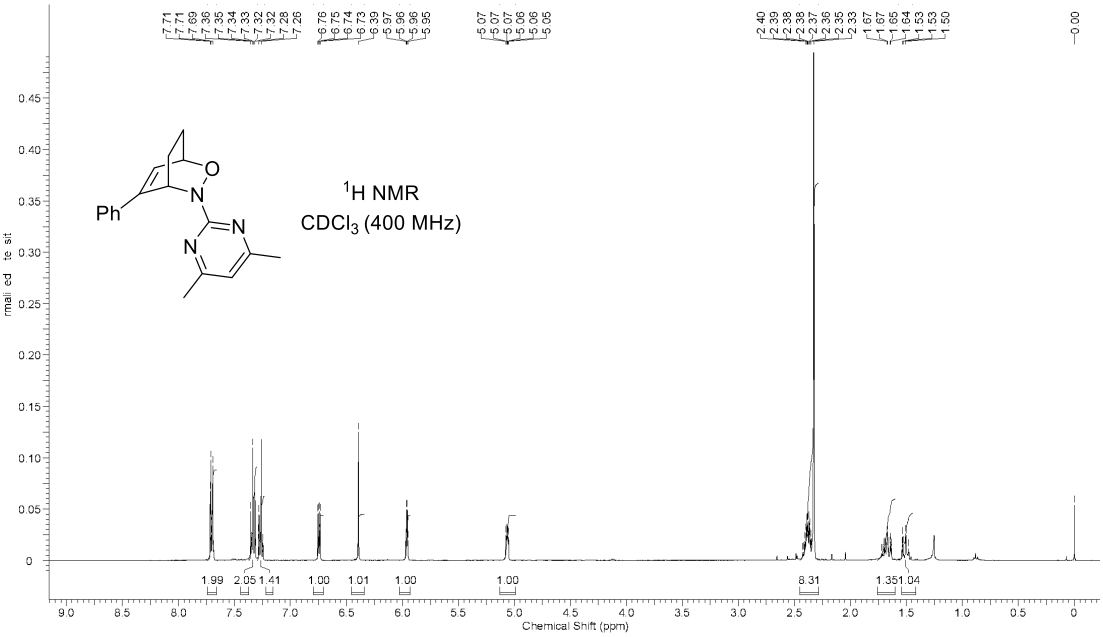

n-Bu
O
N
N
N
13C NMR
CDCl3 (101 MHz)
Normalized Intensity
Chemical Shift (ppm)



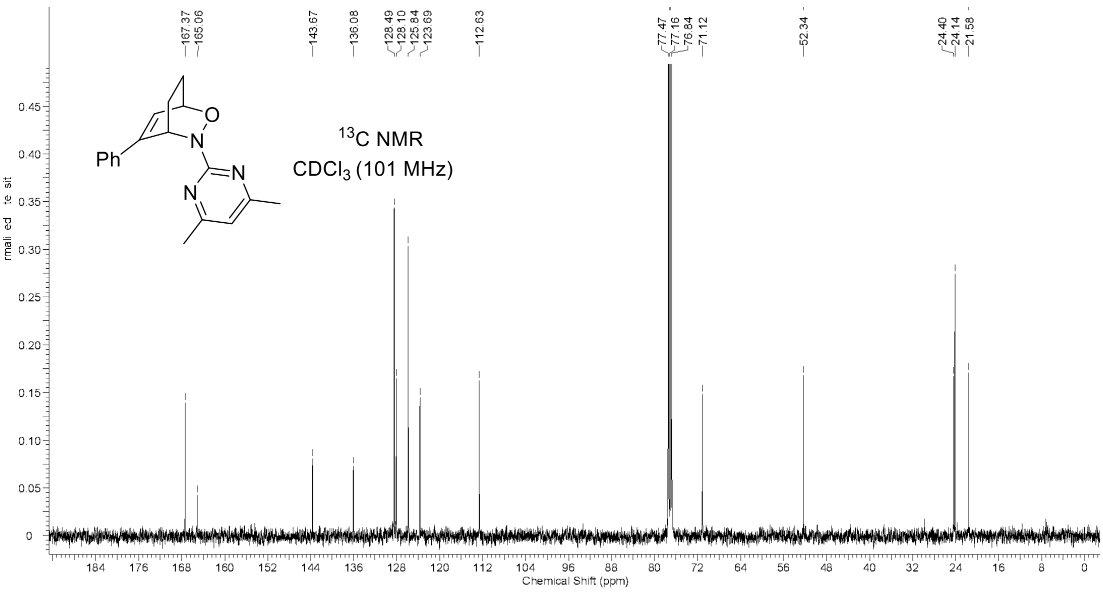
7.26 7.24 7.22 7.16 7.14 7.10 7.08 7.07 7.05
5.93 5.93 5.93 5.92 5.91 5.38 5.38 5.37
4.72 4.71 4.71 4.70 4.70
3.46 3.42 3.42 3.41 3.38 3.38
2.61 2.21 2.20 2.19 2.18 2.16 2.16 2.14 1.42 1.40 1.39 1.38 1.37 1.35 1.35 1.34
Bn
N
O
N
N
^{1}H NMR
$CDCl_3$ (400 MHz)
Normalized Intensity
7.44 0.99 1.00 1.00 2.02 3.01 2.03 2.05
Chemical Shift (ppm)



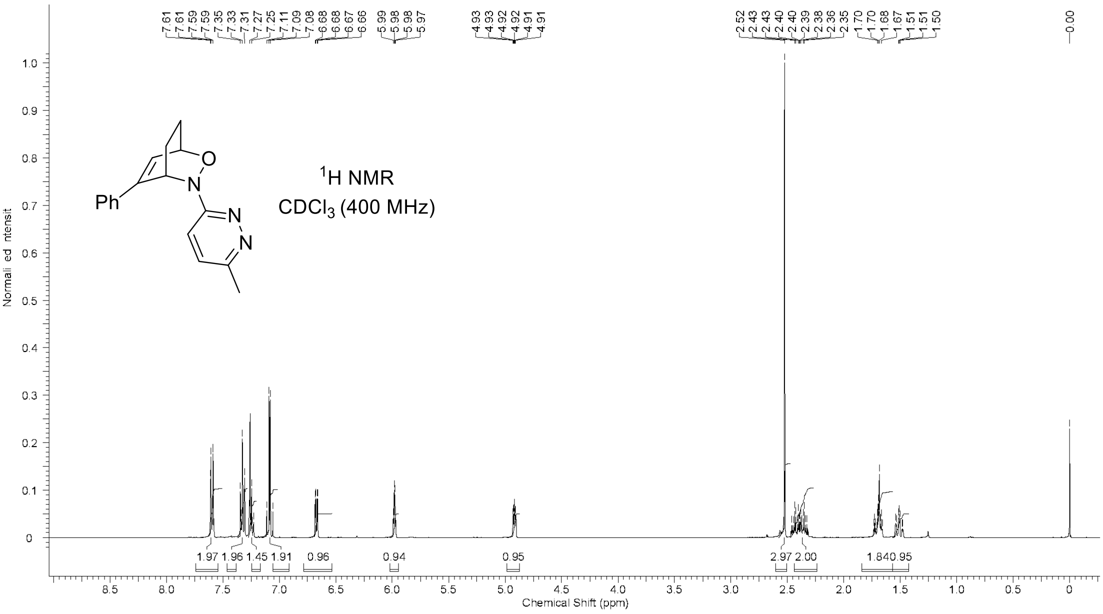
165.01 154.15 145.90 137.66 129.35 128.50 128.13 126.42 123.42 117.28
77.47 77.16 76.84 71.19 55.37 41.56 25.53 21.64 20.84
Bn
N
O
N
N
^{13}C NMR
$CDCl_3$ (101 MHz)
Normalized Intensity
Chemical Shift (ppm)

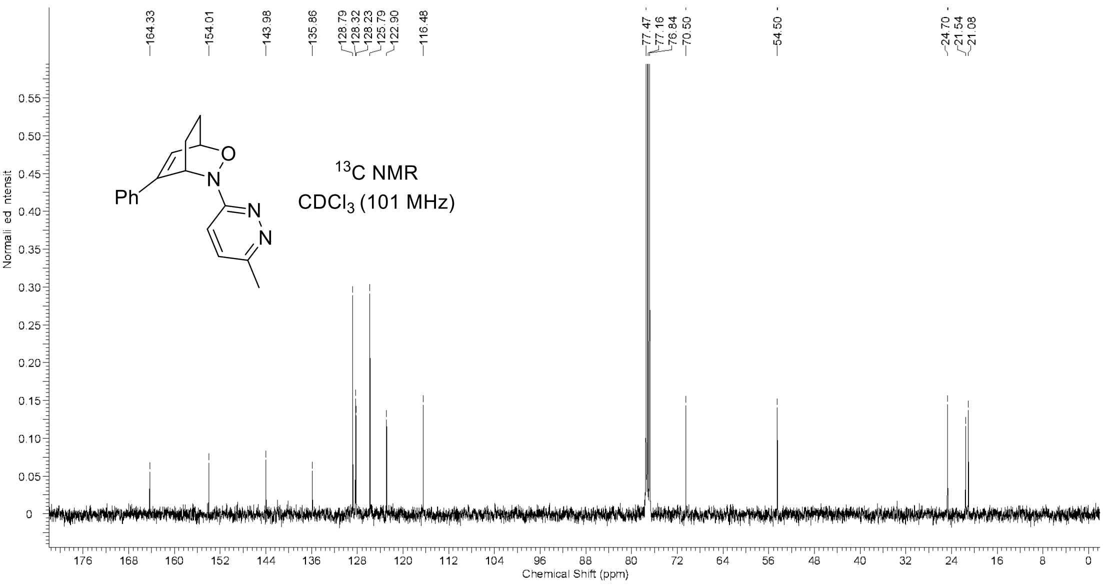


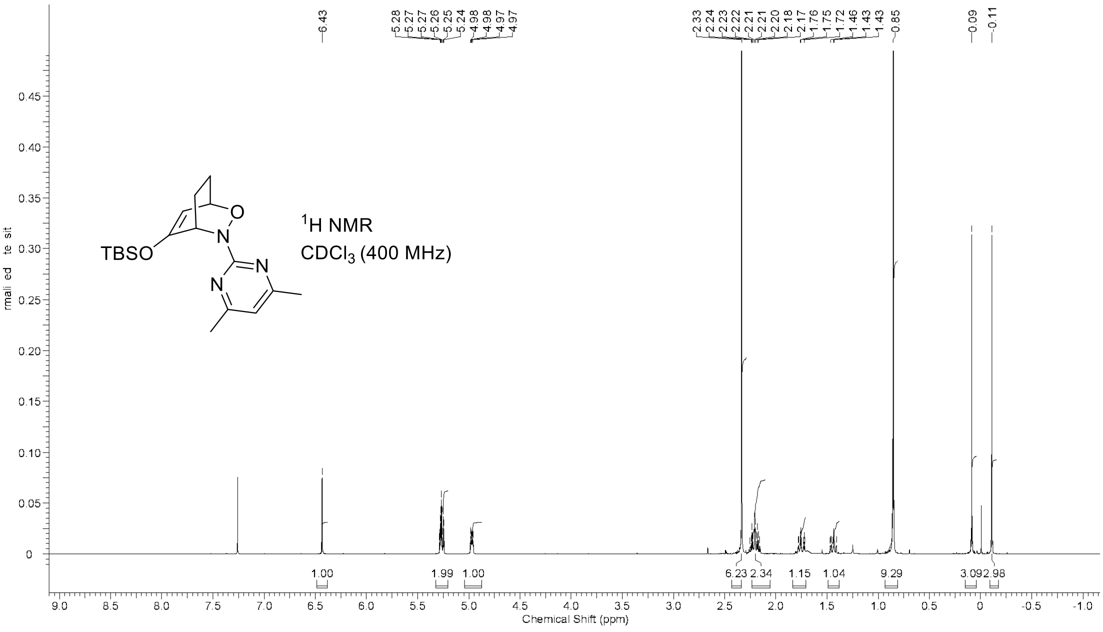
1H NMR
CDCl3 (400 MHz)
Ph
Chemical Shift (ppm)



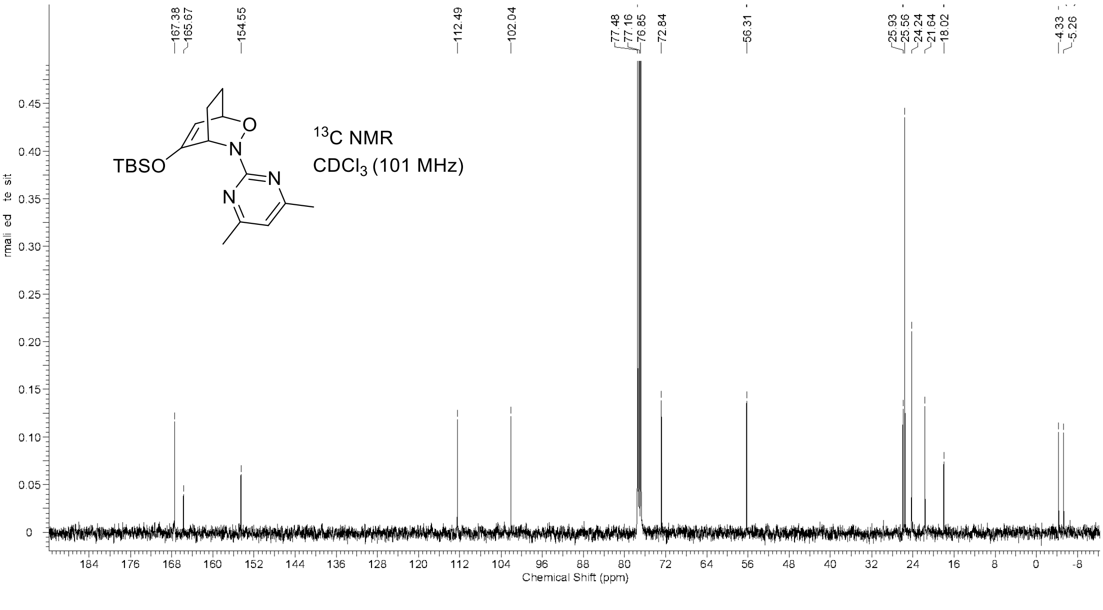
13C NMR
CDCl3 (101 MHz)
Ph
Chemical Shift (ppm)


1H NMR
CDCl3 (400 MHz)
Ph
Chemical Shift (ppm)

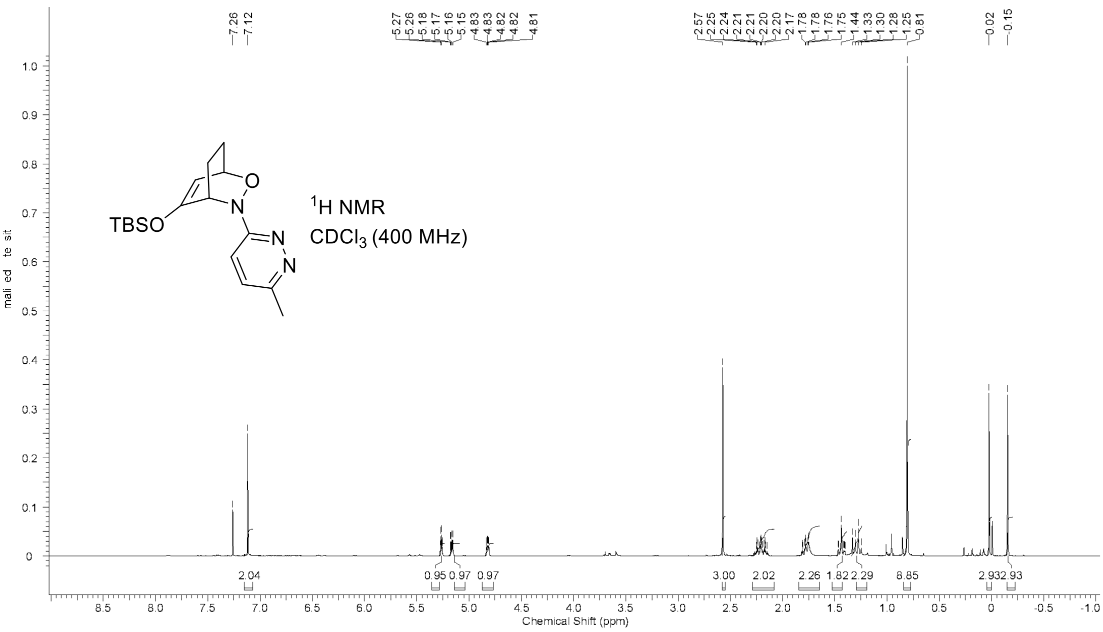

13C NMR
CDCl3 (101 MHz)
Ph
Chemical Shift (ppm)



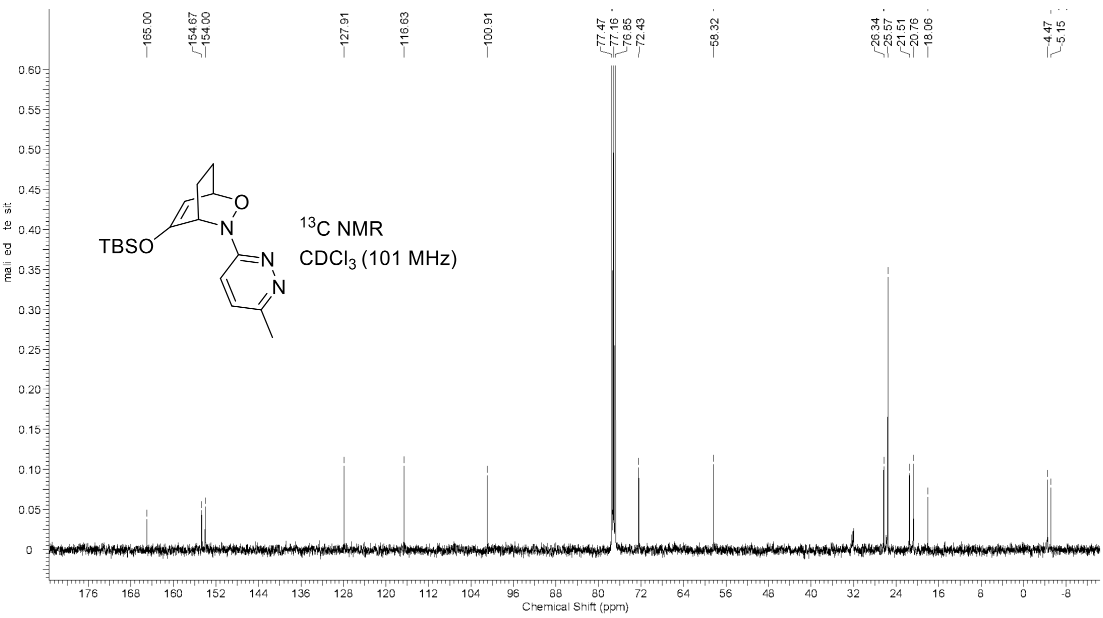
TBSO
N
O
N
N
¹H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



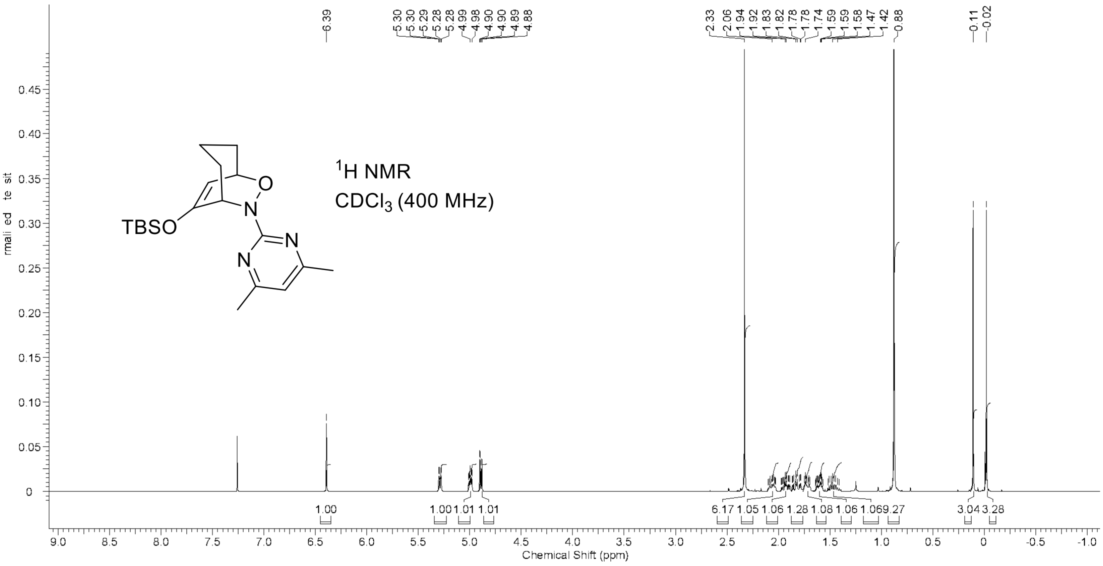
TBSO
N
O
N
N
¹³C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



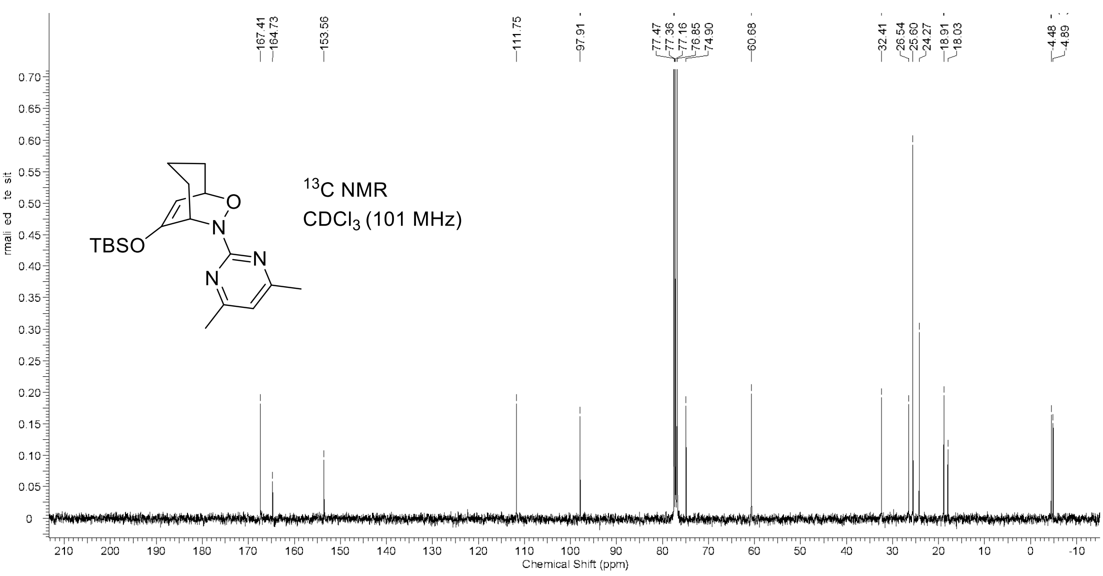
TBSO
N
O
N
N
^{1}H NMR
$CDCl_3$ (400 MHz)
Chemical Shift (ppm)



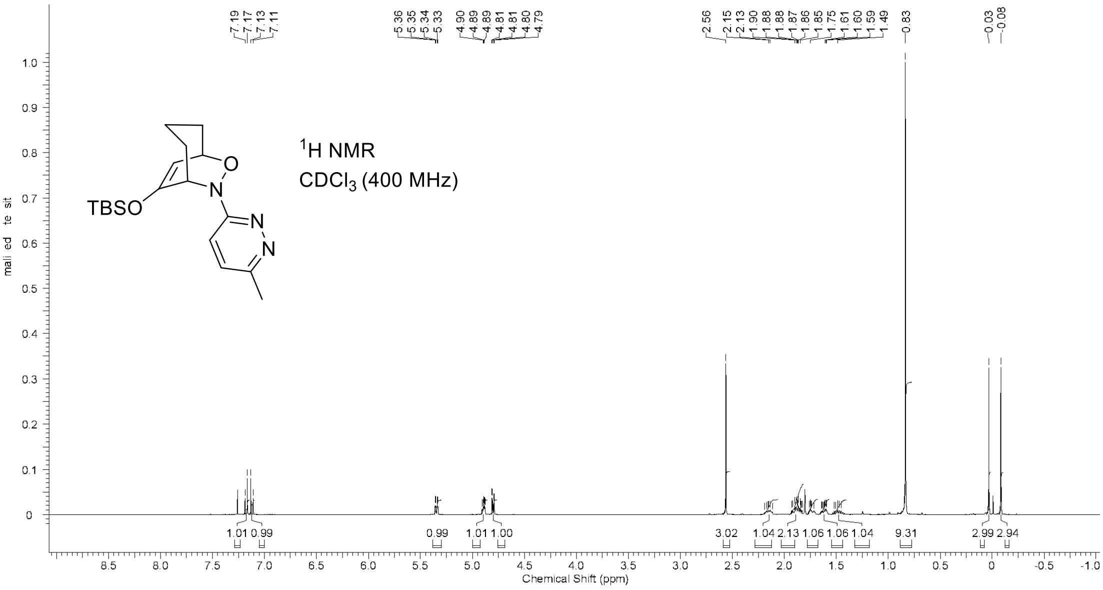
TBSO
N
O
N
N
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)



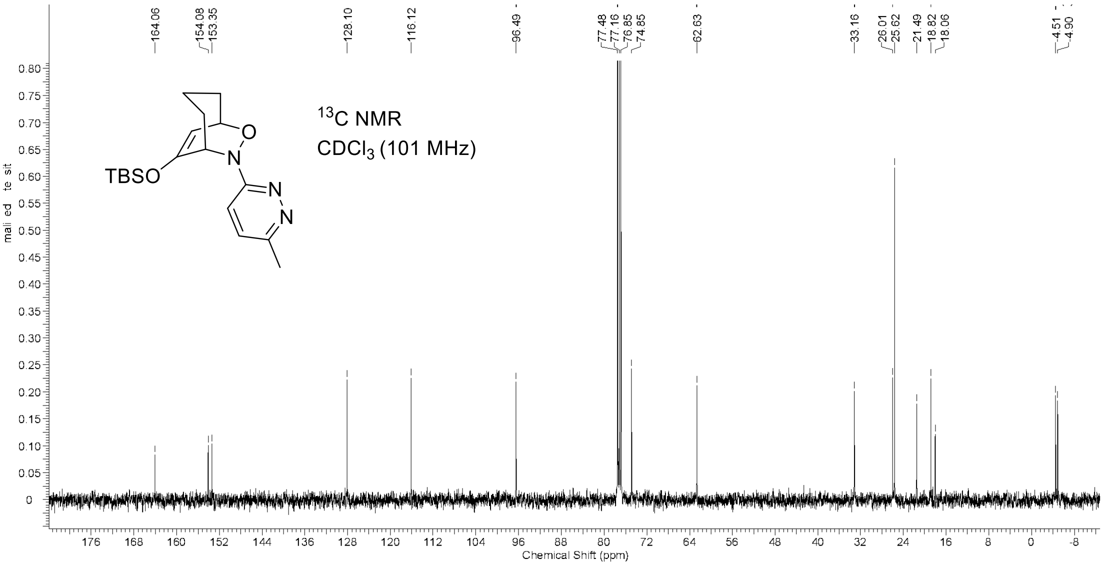
1H NMR
CDCl3 (400 MHz)
TBSO
N
O
N
N
Chemical Shift (ppm)



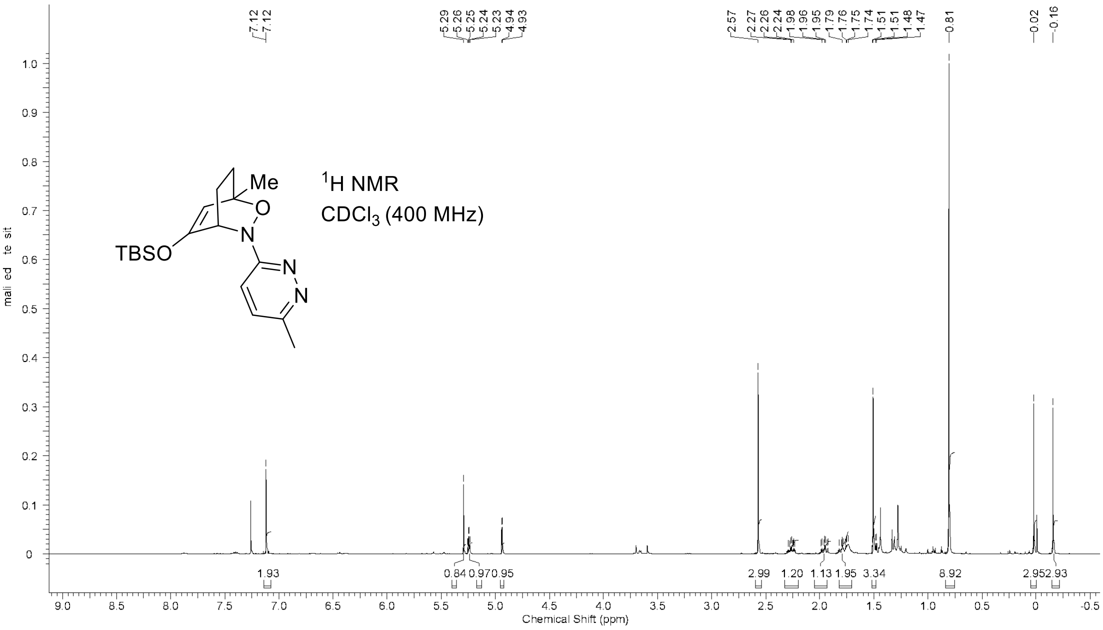
13C NMR
CDCl3 (101 MHz)
TBSO
N
O
N
N
Chemical Shift (ppm)



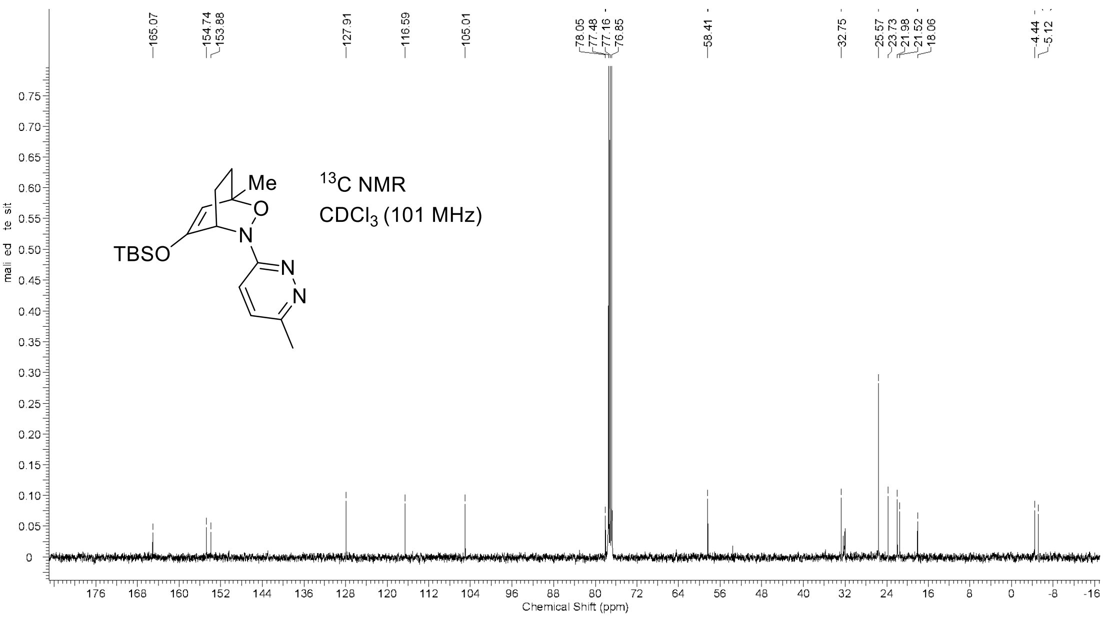
7.19
7.17
7.13
7.11
5.36
5.35
5.34
5.33
4.90
4.89
4.89
4.81
4.81
4.80
4.79
2.56
2.15
2.13
1.90
1.88
1.88
1.87
1.86
1.85
1.75
1.61
1.60
1.59
1.49
0.83
0.03
-0.08
^{1}H NMR
$CDCl_3$ (400 MHz)
TBSO
O
N
N
N
1.01
0.99
0.99
1.01
1.00
3.02
1.04
2.13
1.06
1.06
1.04
9.31
2.99
2.94
Chemical Shift (ppm)



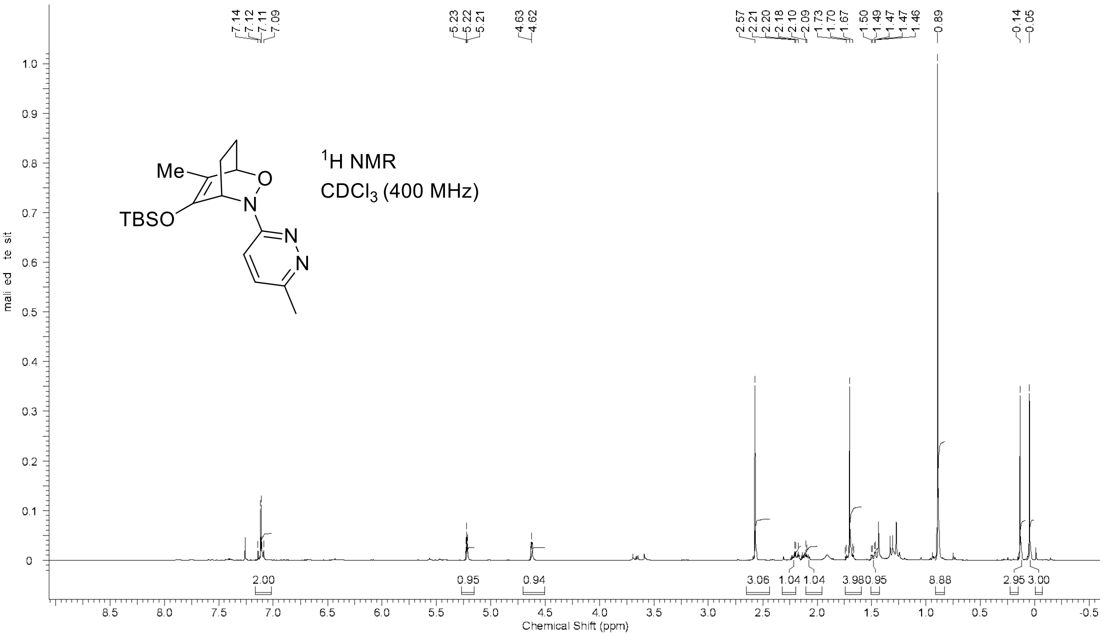
164.06
154.08
153.35
128.10
116.12
96.49
77.48
77.16
76.85
74.85
62.63
33.16
26.01
25.62
21.49
18.82
18.06
-4.51
-4.90
^{13}C NMR
$CDCl_3$ (101 MHz)
TBSO
O
N
N
N
Chemical Shift (ppm)



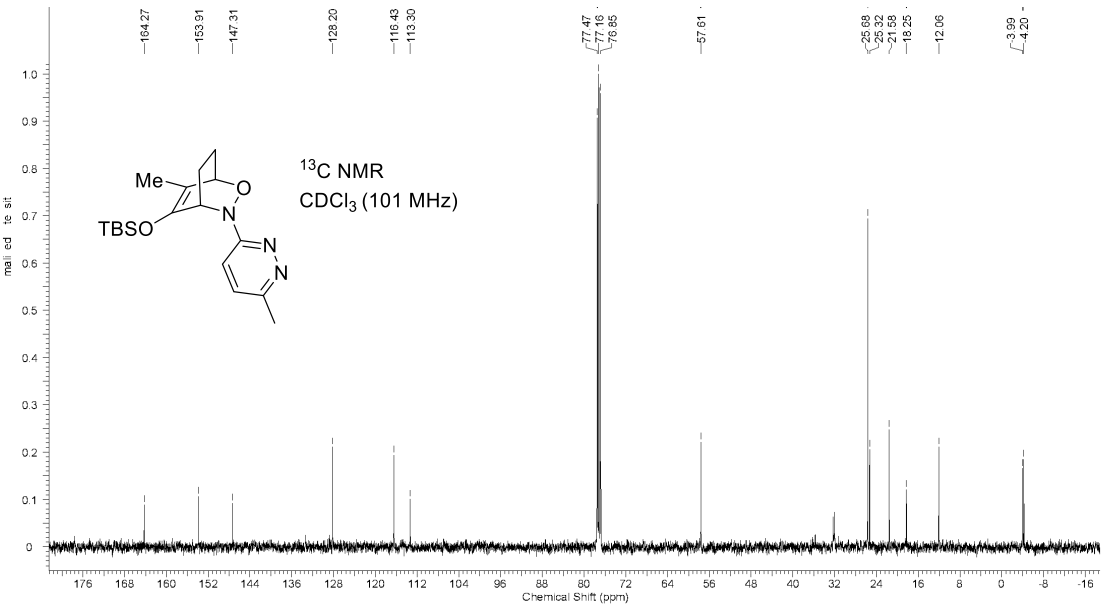
7.12
7.12
5.29
5.26
5.25
5.24
5.23
4.94
4.93
2.57
2.27
2.26
2.24
1.98
1.96
1.95
1.79
1.76
1.75
1.74
1.51
1.51
1.48
1.47
0.81
0.02
-0.16
Me
O
N
TBSO
N
N
^{1}H NMR
$CDCl_3$ (400 MHz)
1.93
0.84
0.97
0.95
2.99
1.20
1.13
1.95
3.34
8.92
2.95
2.93
Chemical Shift (ppm)



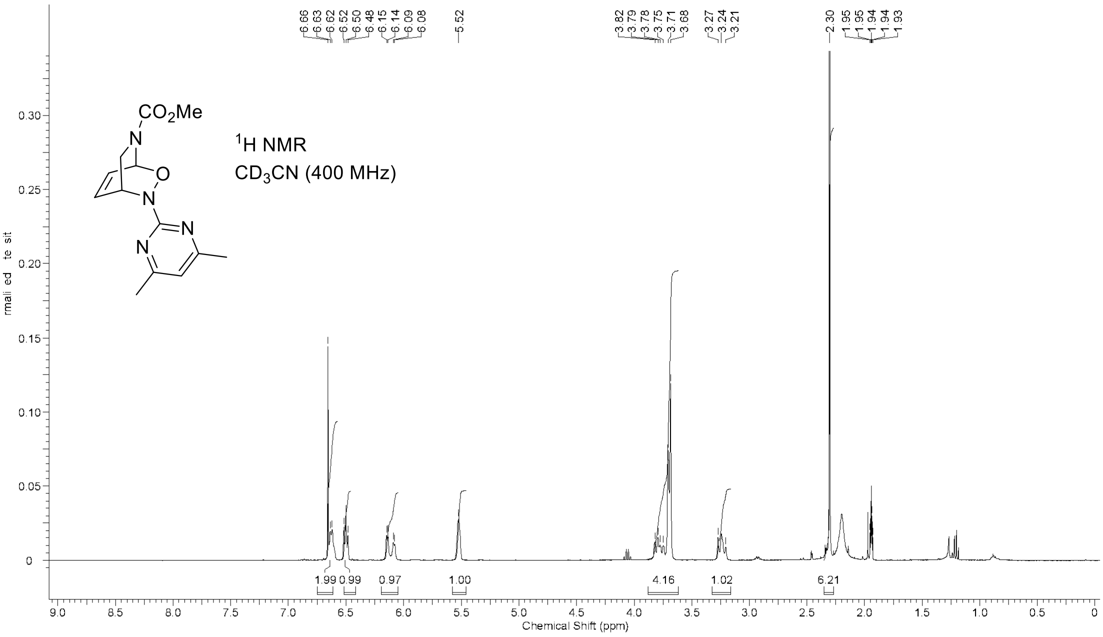
165.07
154.74
153.88
127.91
116.59
105.01
78.05
77.48
77.16
76.85
58.41
32.75
25.57
23.73
21.98
21.52
18.06
-4.44
-5.12
Me
O
N
TBSO
N
N
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)



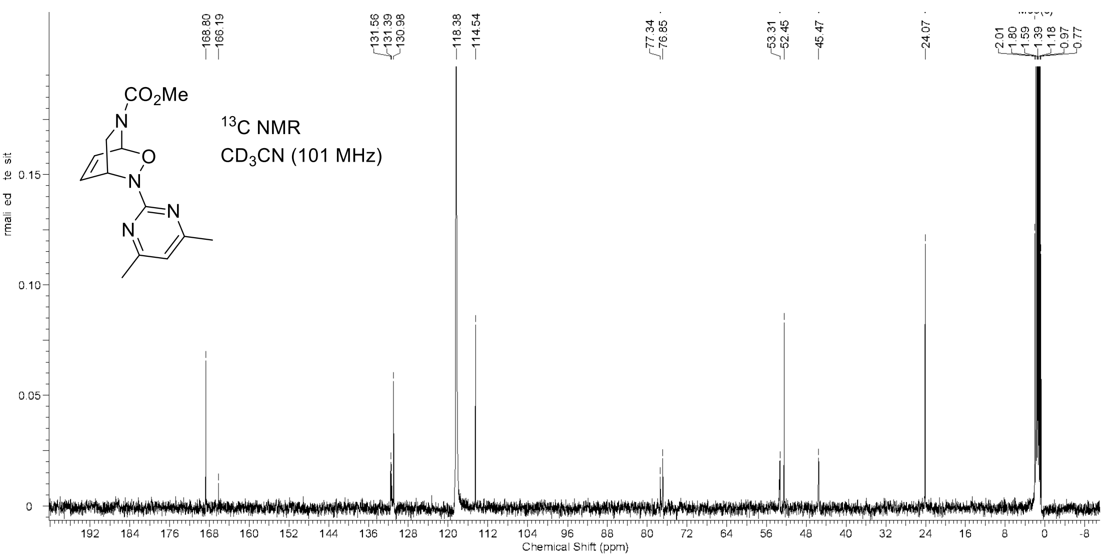
^{1}H NMR
CDCl$_3$ (400 MHz)
Me
TBSO
O
N
N
N
7.14
7.12
7.11
7.09
5.23
5.22
5.21
4.63
4.62
2.57
2.21
2.20
2.18
2.10
2.09
1.73
1.70
1.67
1.50
1.49
1.47
1.47
1.46
0.89
0.14
0.05
2.00
0.95
0.94
3.06
1.04
1.04
3.98
0.95
8.88
2.95
3.00
Chemical Shift (ppm)



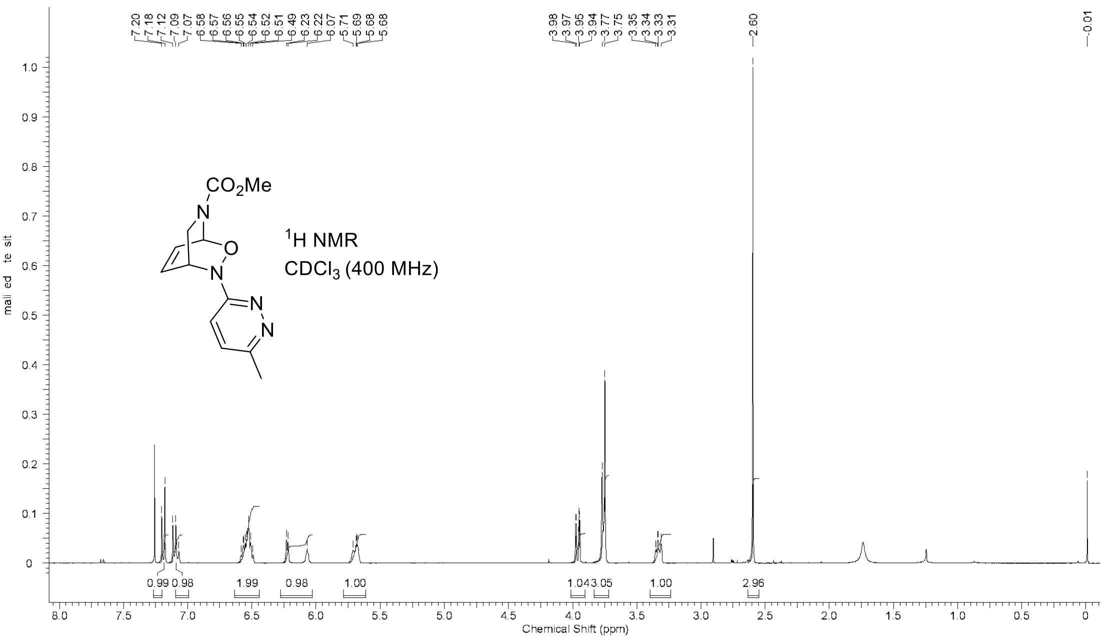
^{13}C NMR
CDCl$_3$ (101 MHz)
Me
TBSO
O
N
N
N
164.27
153.91
147.31
128.20
116.43
113.30
77.47
77.16
76.85
57.61
25.68
25.32
21.58
18.25
12.06
-3.99
-4.20
Chemical Shift (ppm)



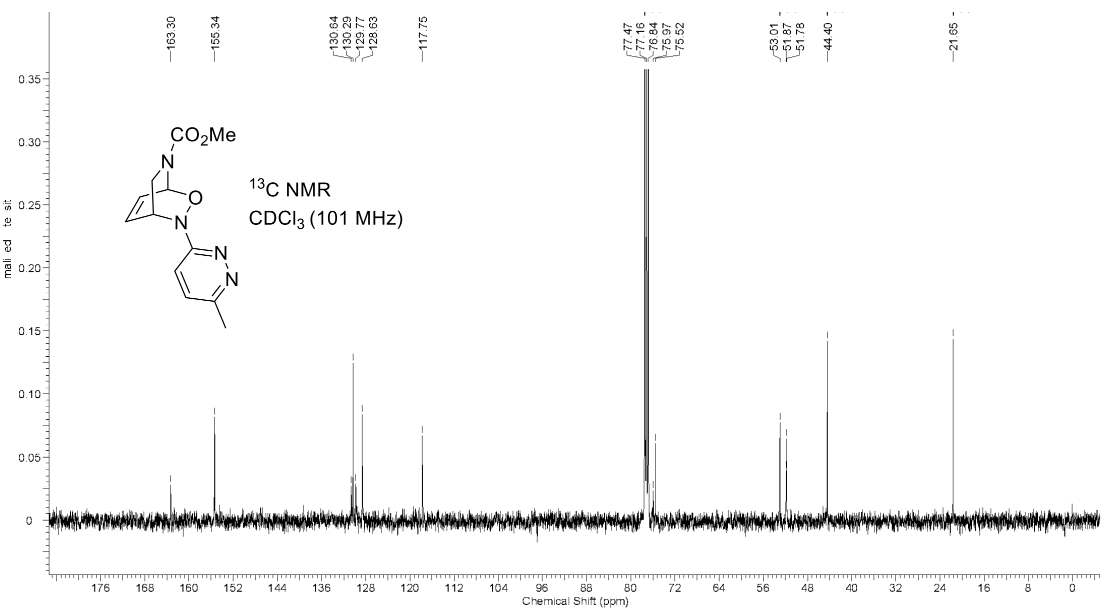
CO2Me
N
O
N
N
N
1H NMR
CD3CN (400 MHz)
Chemical Shift (ppm)



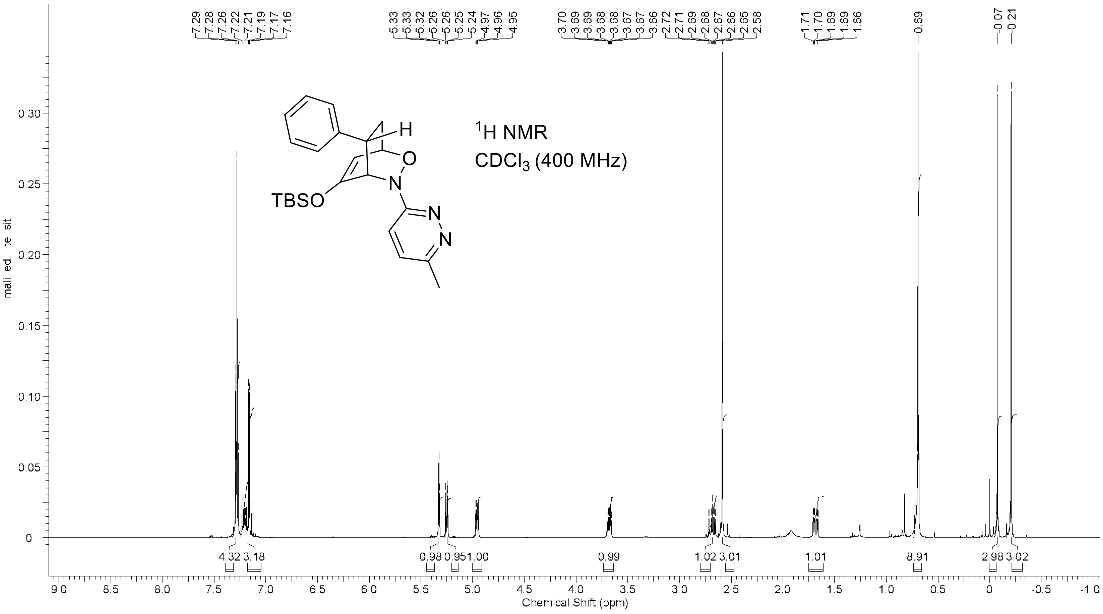
CO2Me
N
O
N
N
N
13C NMR
CD3CN (101 MHz)
Chemical Shift (ppm)



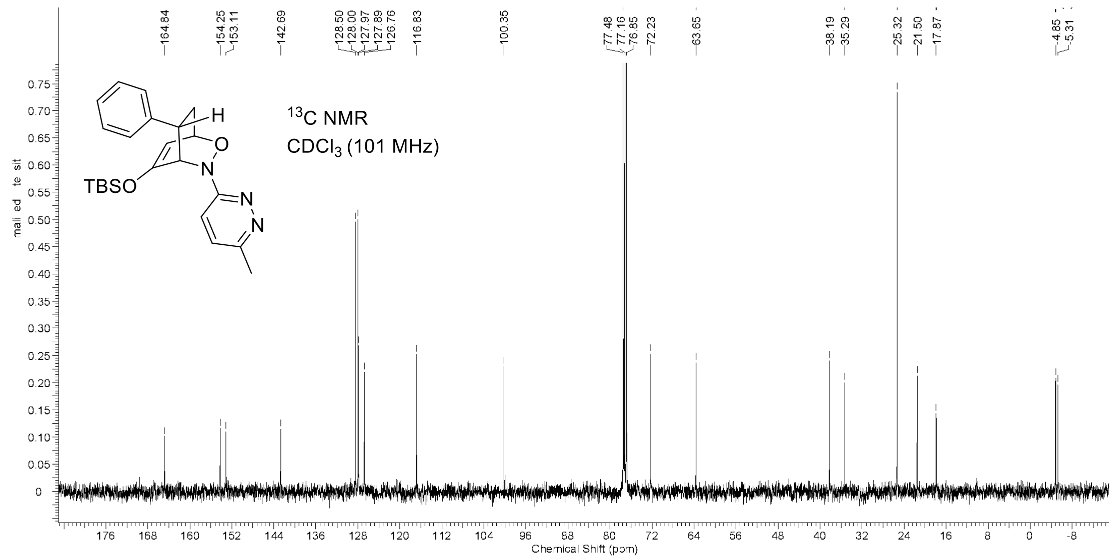
CO2Me
N
O
N
N
N
1H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



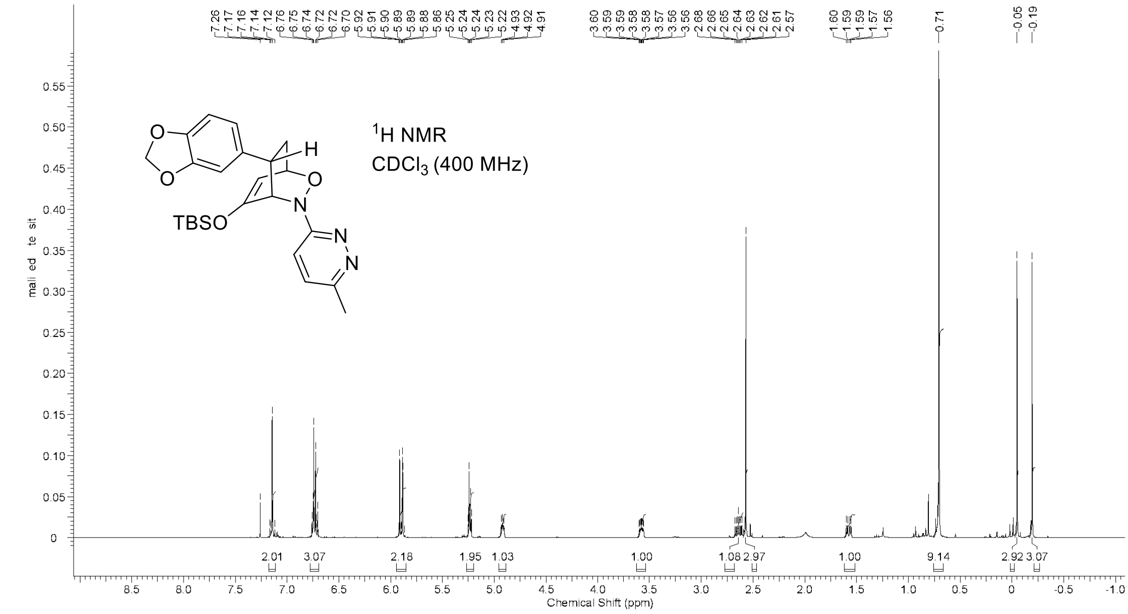
CO2Me
N
O
N
N
N
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)

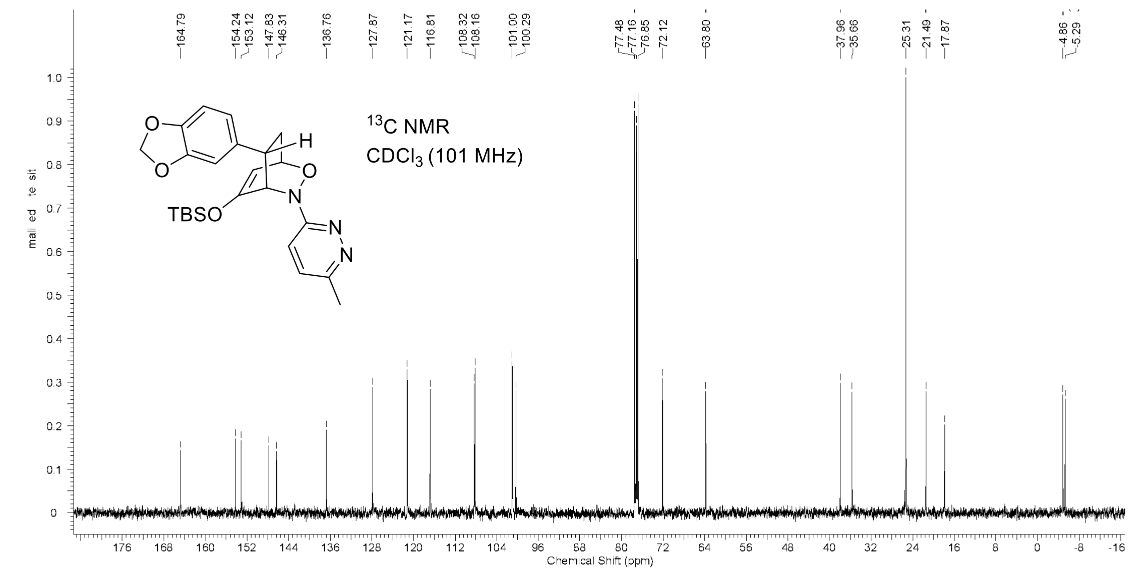


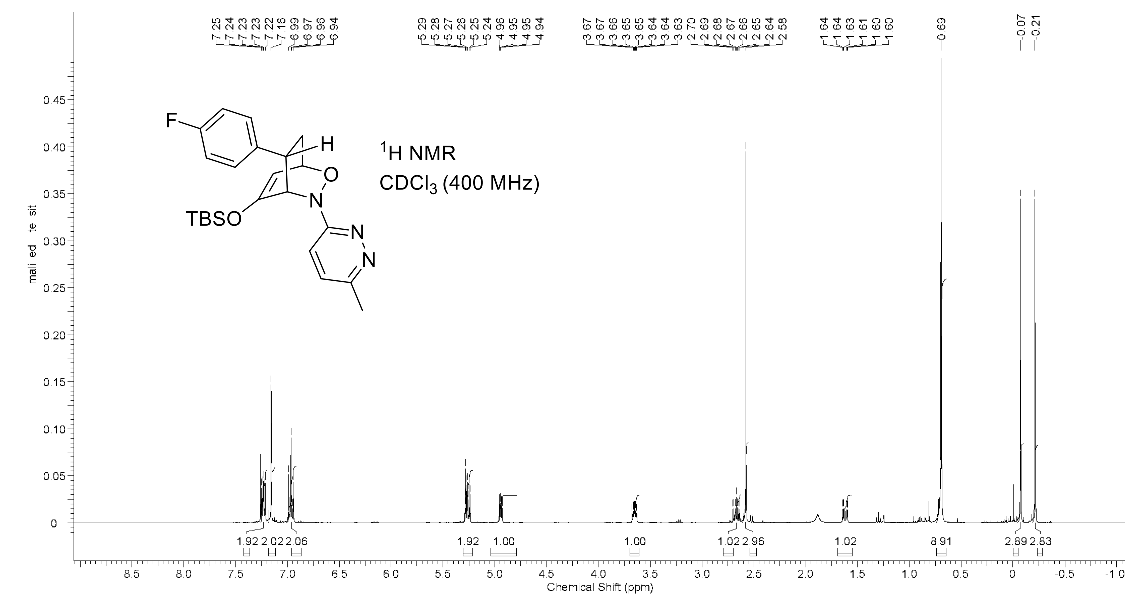
7.29 7.28 7.26 7.22 7.21 7.19 7.17 7.16
5.33 5.33 5.32 5.26 5.26 5.25 5.24 4.97 4.96 4.95
3.70 3.69 3.69 3.68 3.68 3.67 3.67 3.66
2.72 2.71 2.69 2.68 2.67 2.66 2.65 2.58
1.71 1.70 1.69 1.69 1.66
0.69
-0.07 -0.21
H
O
N
TBSO
N
N
^{1}H NMR
$CDCl_3$ (400 MHz)
4.32 3.18 0.98 0.95 1.00 0.99 1.02 3.01 1.01 8.91 2.98 3.02
Chemical Shift (ppm)

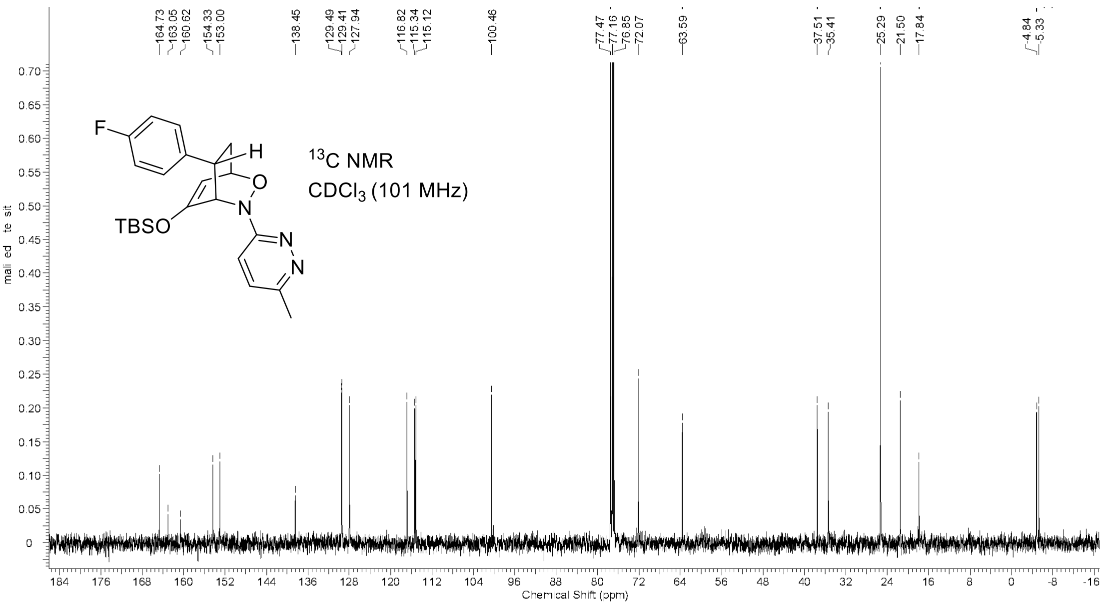


164.84
154.25 153.11
142.69
128.50 128.00 127.97 127.89 126.76
116.83
100.35
77.48 77.16 76.85 72.23
63.65
38.19 35.29
25.32 21.50 17.87
-4.85 -5.31
H
O
N
TBSO
N
N
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)

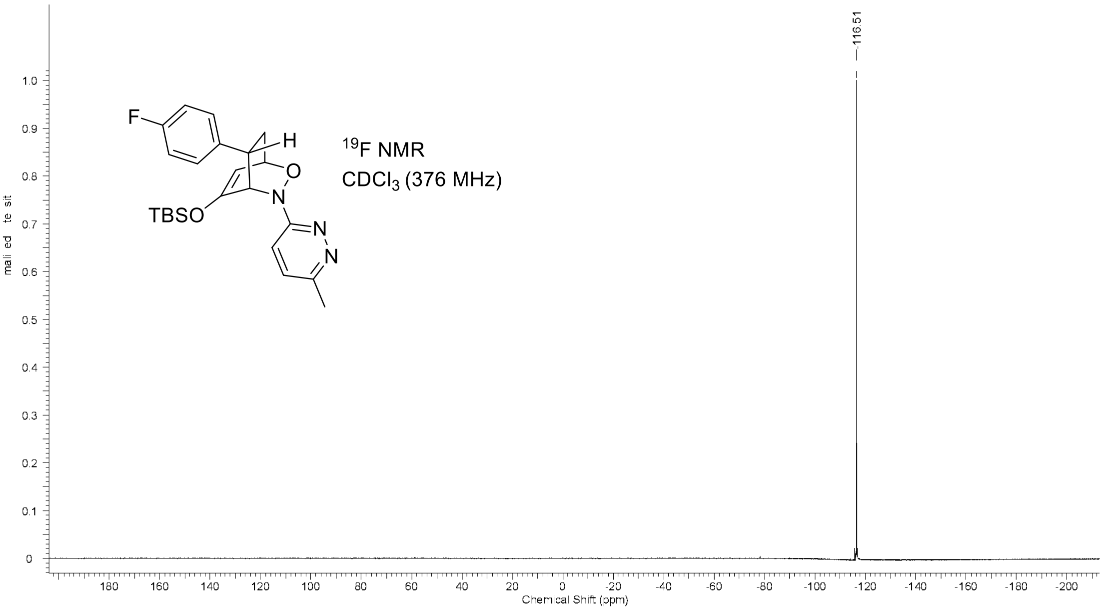

1H NMR
CDCl3 (400 MHz)
TBSO
Chemical Shift (ppm)


13C NMR
CDCl3 (101 MHz)
TBSO
Chemical Shift (ppm)

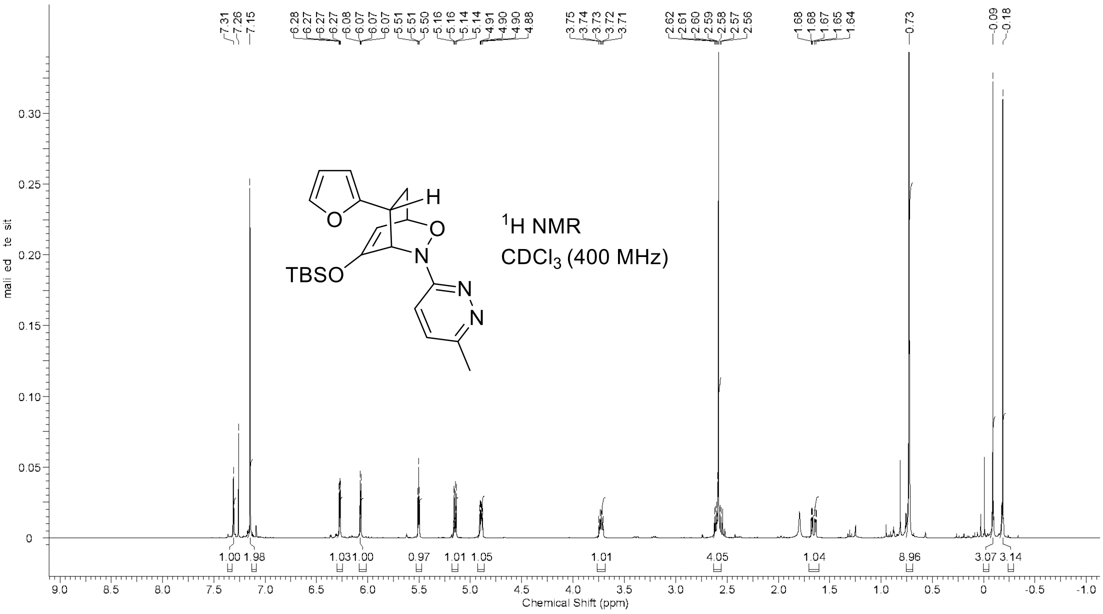

1H NMR
CDCl3 (400 MHz)
F
TBSO
Chemical Shift (ppm)



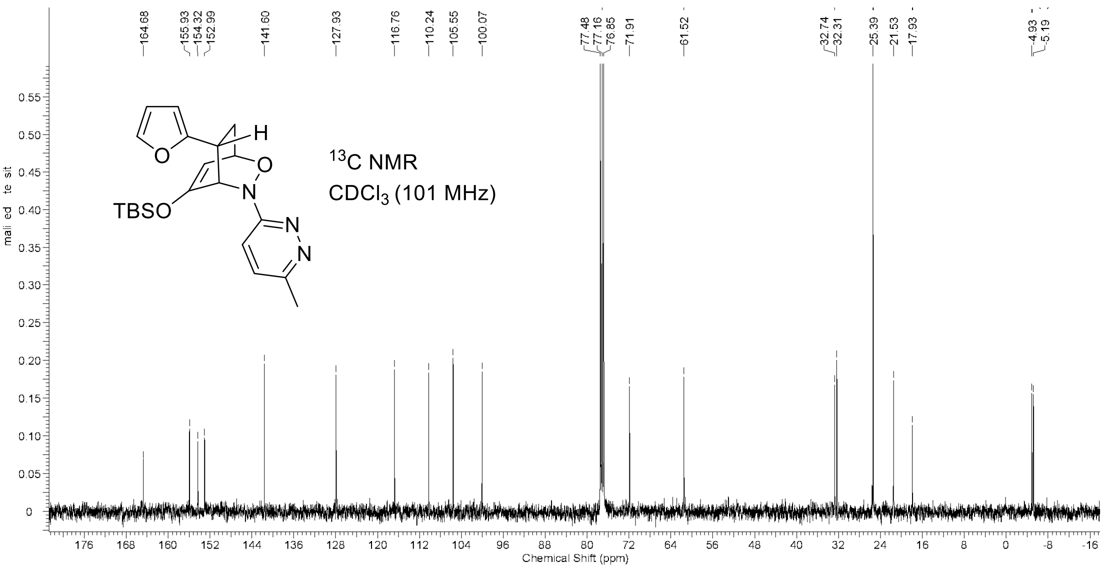
13C NMR
CDCl3 (101 MHz)
TBSO
Chemical Shift (ppm)



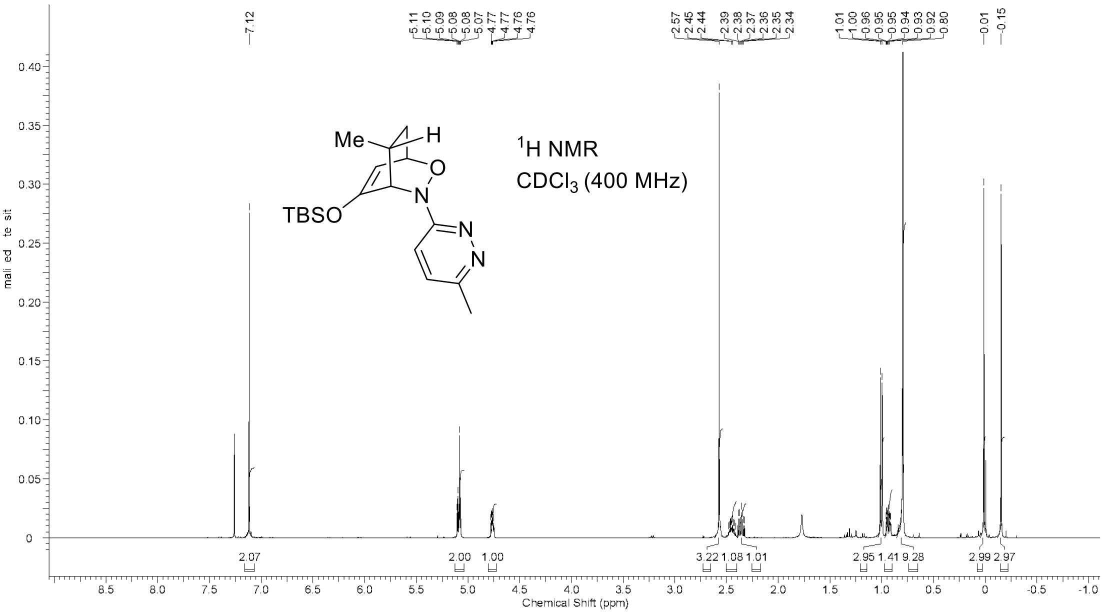
19F NMR
CDCl3 (376 MHz)
TBSO
-116.51
Chemical Shift (ppm)

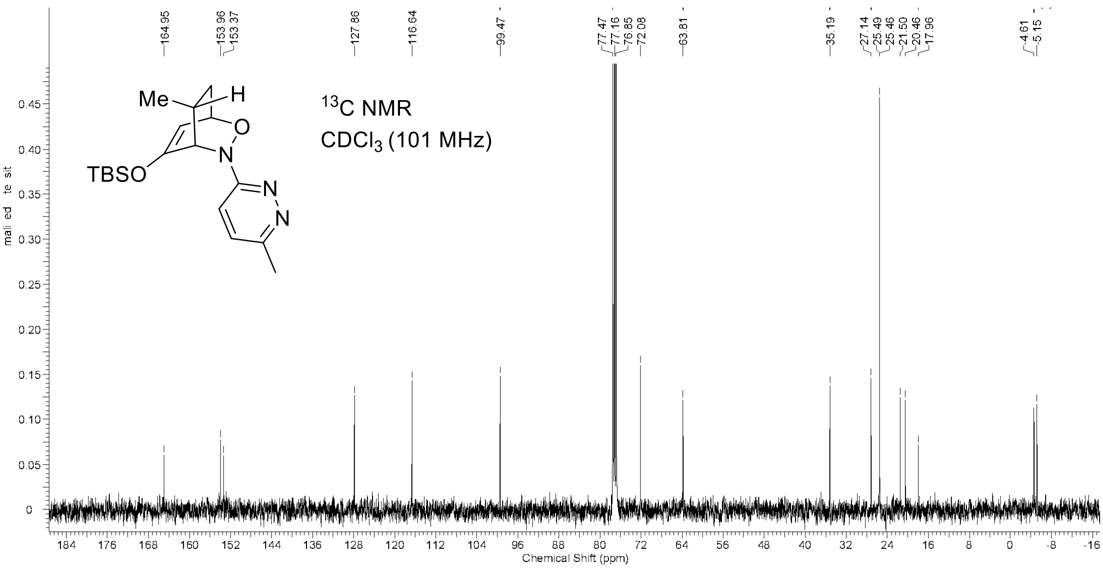


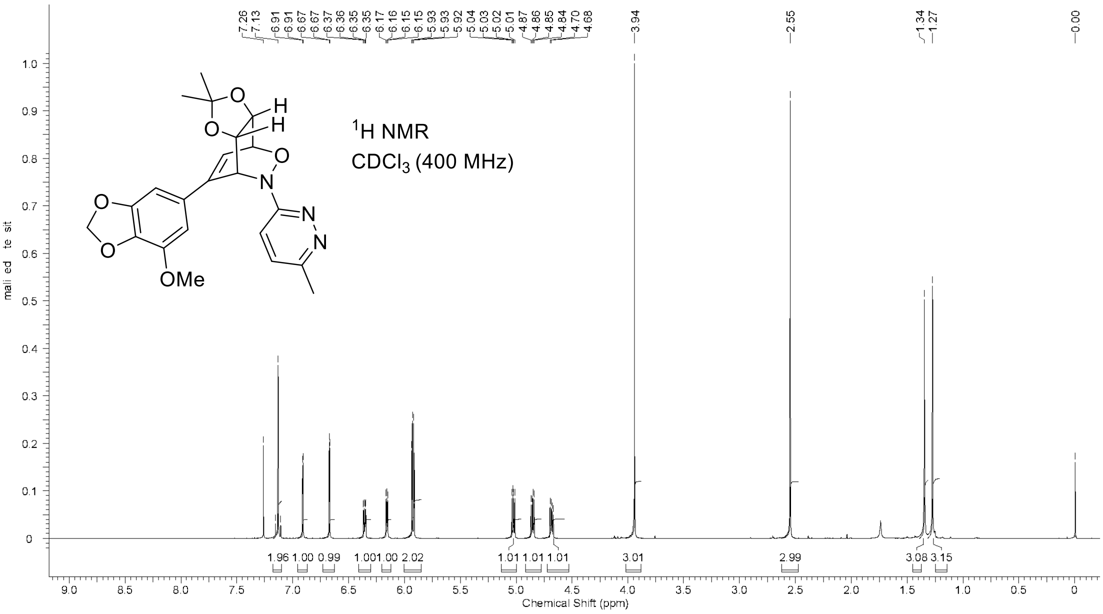
1H NMR
CDCl3 (400 MHz)
TBSO
Chemical Shift (ppm)



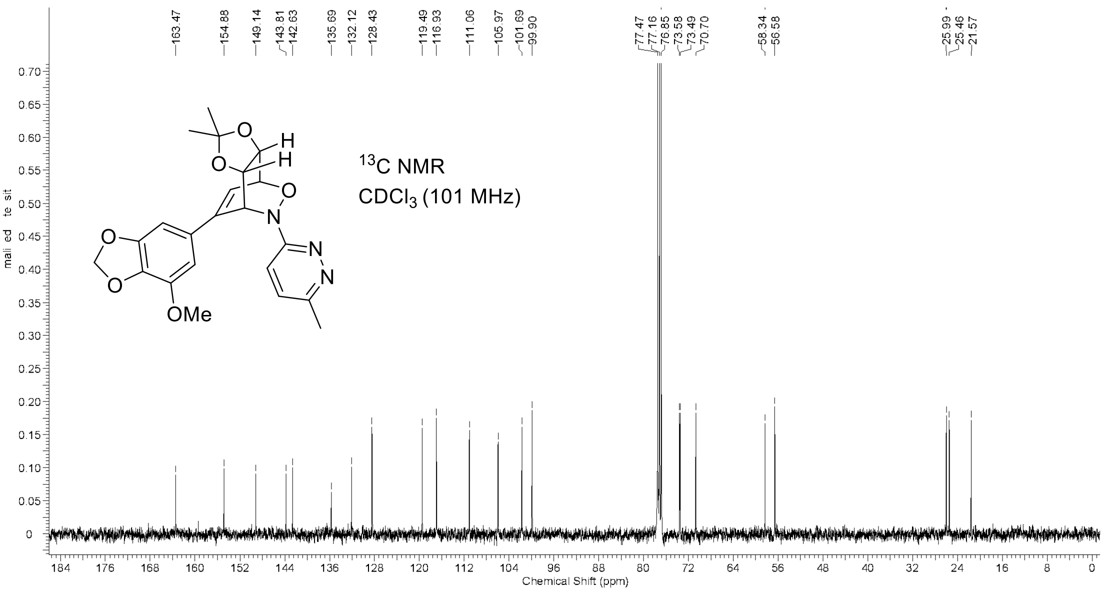
13C NMR
CDCl3 (101 MHz)
TBSO
Chemical Shift (ppm)


Me
H
O
N
TBSO
N
N
^{1}H NMR
CDCl$_3$ (400 MHz)
Chemical Shift (ppm)

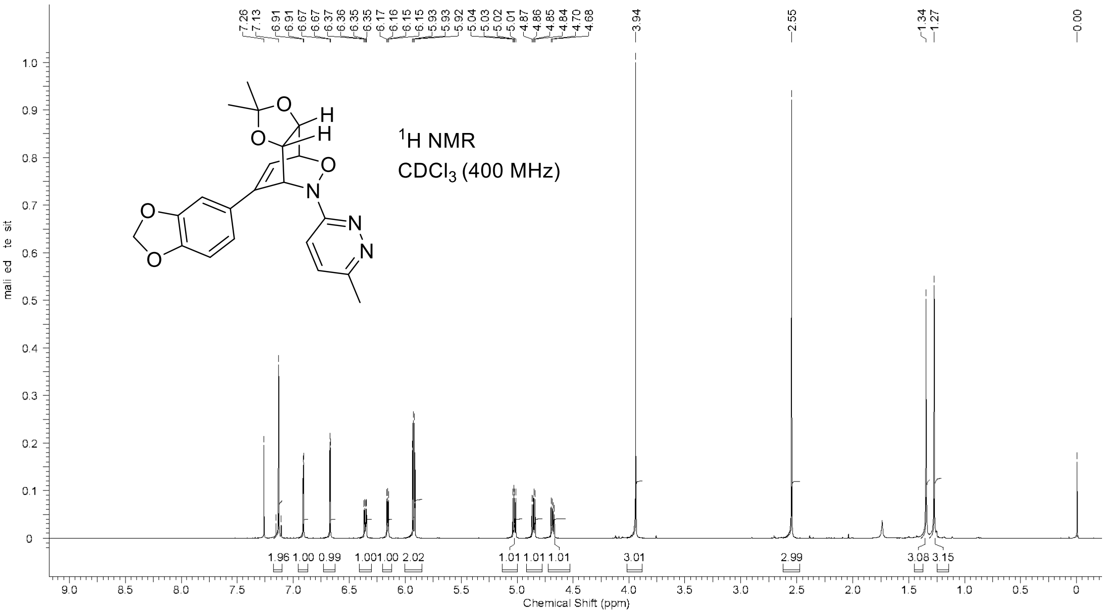

Me
H
O
N
TBSO
N
N
^{13}C NMR
CDCl$_3$ (101 MHz)
Chemical Shift (ppm)



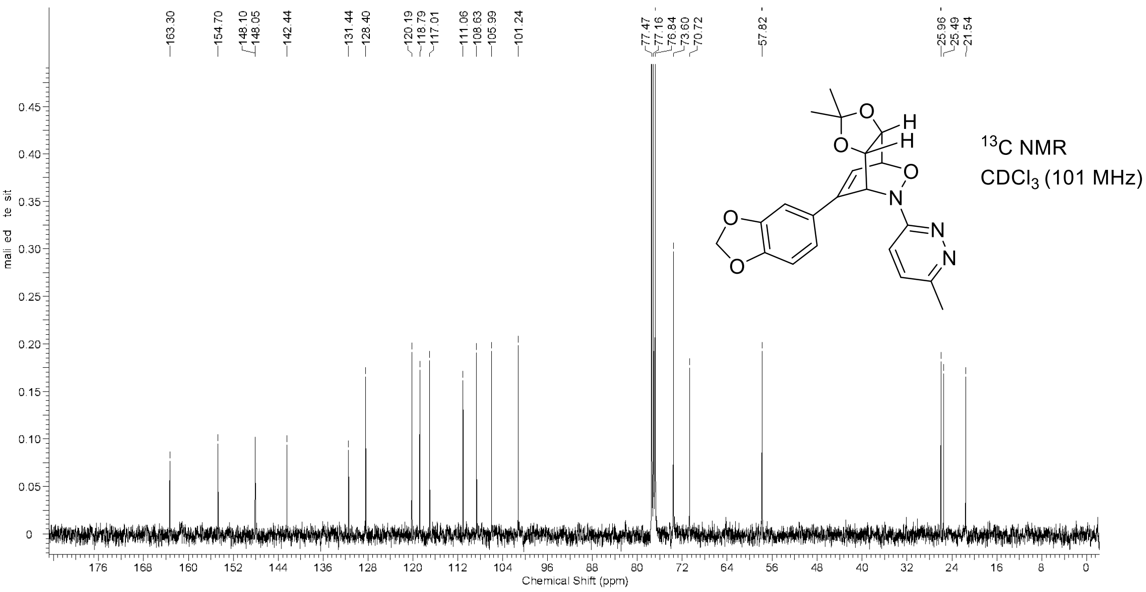
7.26 7.13 6.91 6.91 6.67 6.67 6.37 6.36 6.35 6.35 6.17 6.16 6.15 6.15 5.93 5.93 5.92 5.04 5.03 5.02 5.01 4.87 4.86 4.85 4.84 4.70 4.68
3.94
2.55
1.34 1.27
0.00
H
H
O
O
O
O
N
N
N
O
O
OMe
1H NMR
CDCl3 (400 MHz)
1.96 1.00 0.99 1.00 1.00 2.02 1.01 1.01 1.01 3.01 2.99 3.08 3.15
Chemical Shift (ppm)



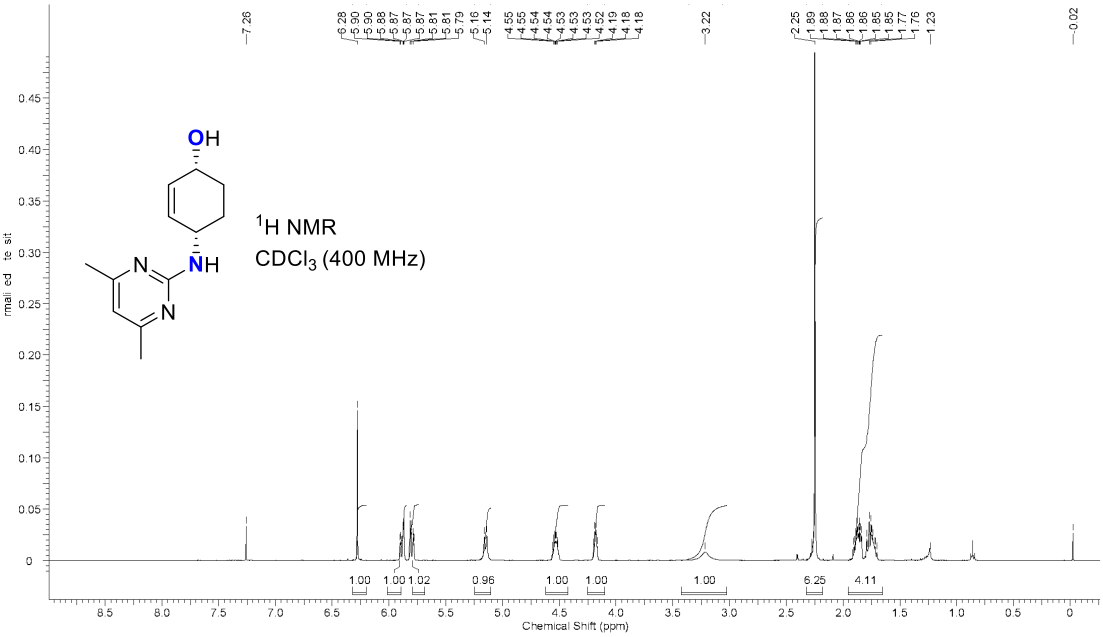
163.47 154.88 149.14 143.81 142.63 135.69 132.12 128.43 119.49 116.93 111.06 105.97 101.69 99.90
77.47 77.16 76.85 73.58 73.49 70.70 58.34 56.58 25.99 25.46 21.57
H
H
O
O
O
O
N
N
N
O
O
OMe
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



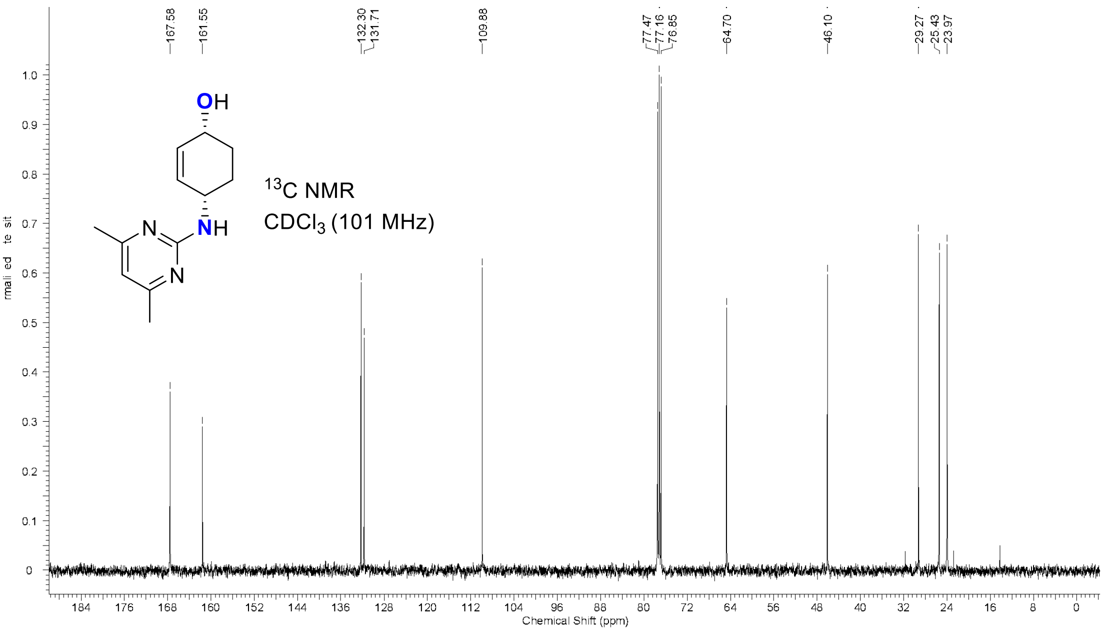
7.26
7.13
6.91
6.91
6.67
6.67
6.37
6.36
6.35
6.35
6.17
6.16
6.15
6.15
5.93
5.93
5.92
5.04
5.03
5.02
5.01
4.87
4.86
4.85
4.84
4.70
4.68
3.94
2.55
1.34
1.27
0.00
^{1}H NMR
$CDCl_3$ (400 MHz)
1.96 1.00 0.99 1.00 1.00 2.02 1.01 1.01 1.01 3.01 2.99 3.08 3.15
Chemical Shift (ppm)



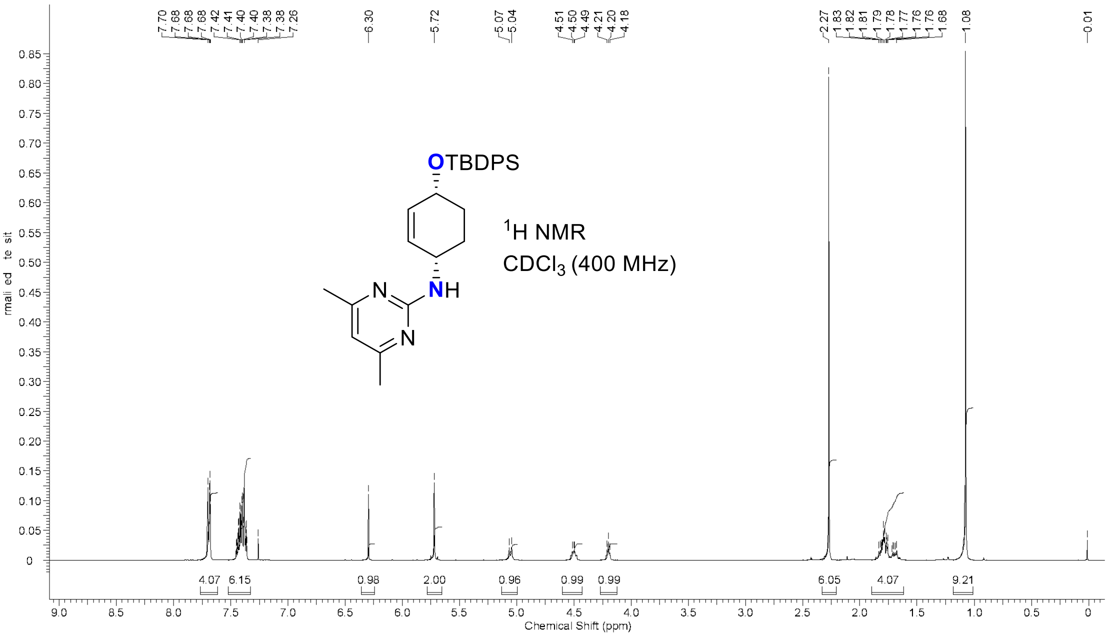
163.30
154.70
148.10
148.05
142.44
131.44
128.40
120.19
118.79
117.01
111.06
108.63
105.99
101.24
77.47
77.16
76.84
73.60
70.72
57.82
25.96
25.49
21.54
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)



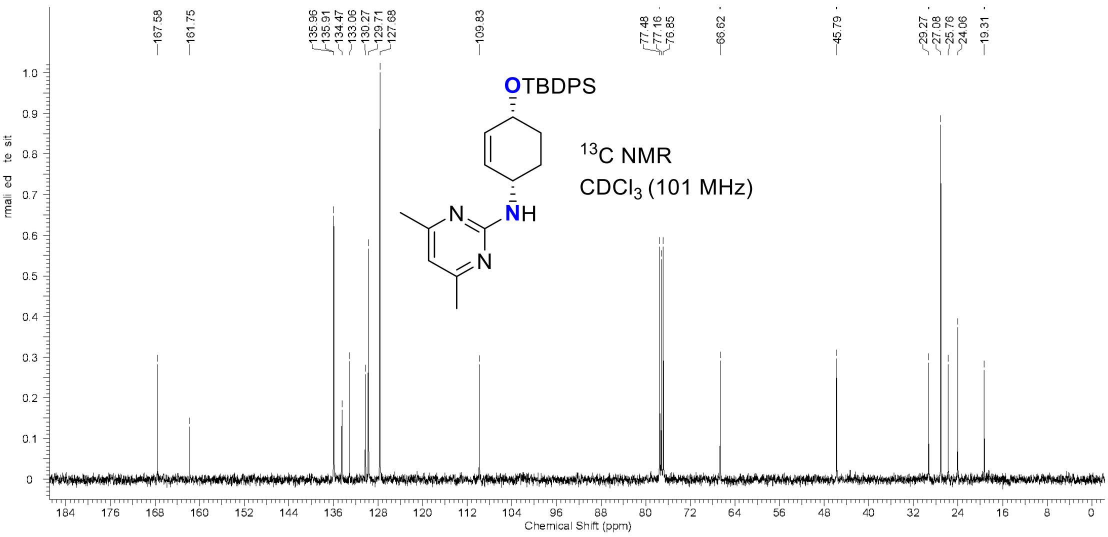
^{1}H NMR
$CDCl_3$ (400 MHz)
Chemical Shift (ppm)



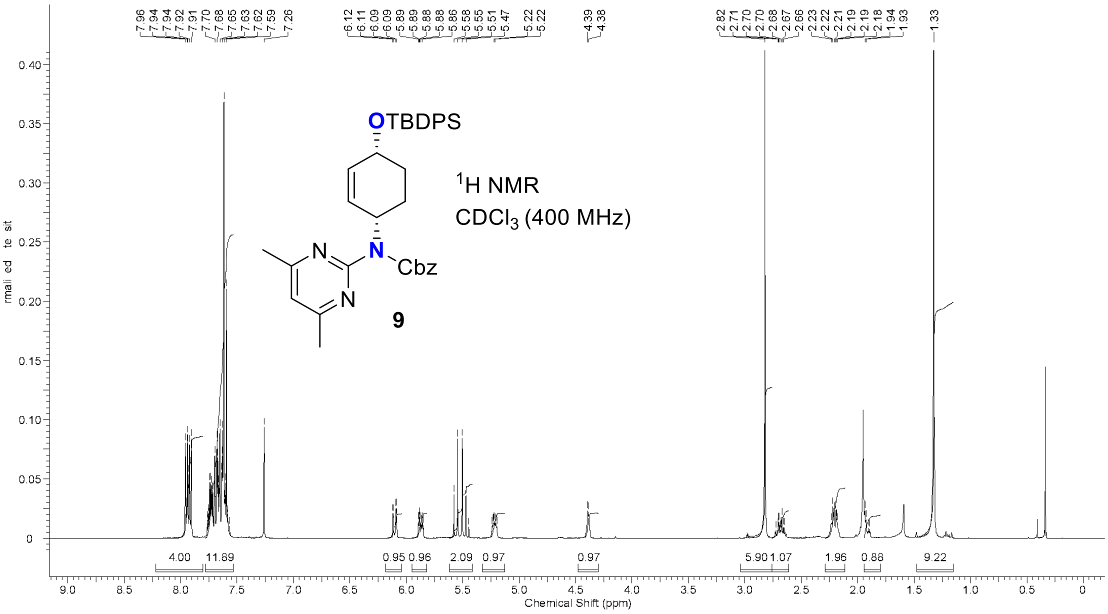
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)



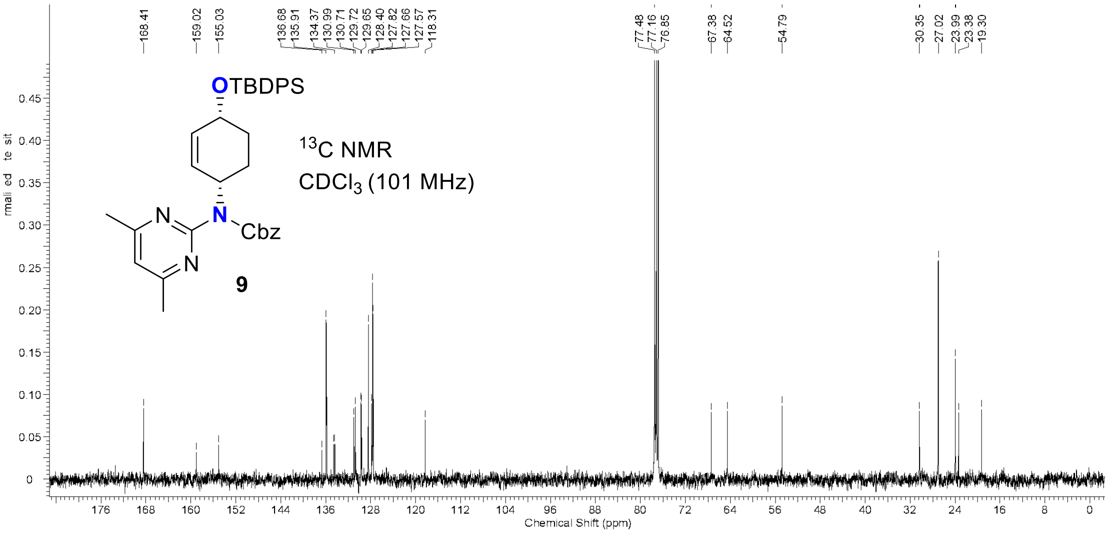
7.70 7.68 7.68 7.68 7.42 7.41 7.40 7.40 7.38 7.38 7.26
6.30
5.72
5.07 5.04
4.51 4.50 4.49 4.21 4.20 4.18
2.27 1.83 1.82 1.81 1.79 1.78 1.77 1.76 1.68
1.08
0.01
OTBDPS
NH
N
N
^{1}H NMR
$CDCl_3$ (400 MHz)
4.07 6.15 0.98 2.00 0.96 0.99 0.99 6.05 4.07 9.21
Chemical Shift (ppm)



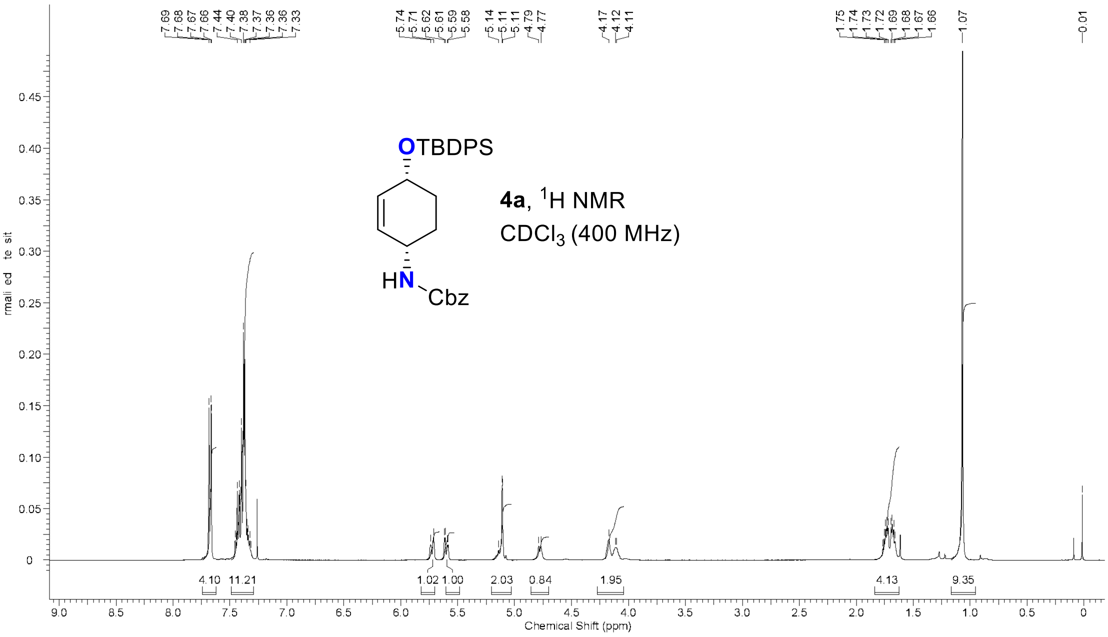
167.58
161.75
135.96 135.91 134.47 133.06 130.27 129.71 127.68
109.83
77.48 77.16 76.85
66.62
45.79
29.27 27.08 25.76 24.06 19.31
OTBDPS
NH
N
N
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)

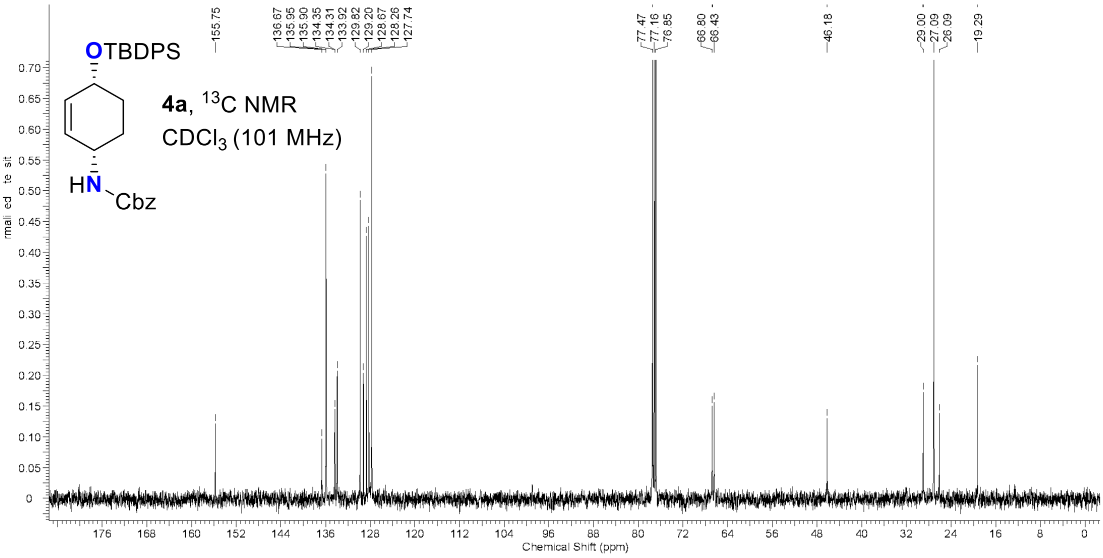


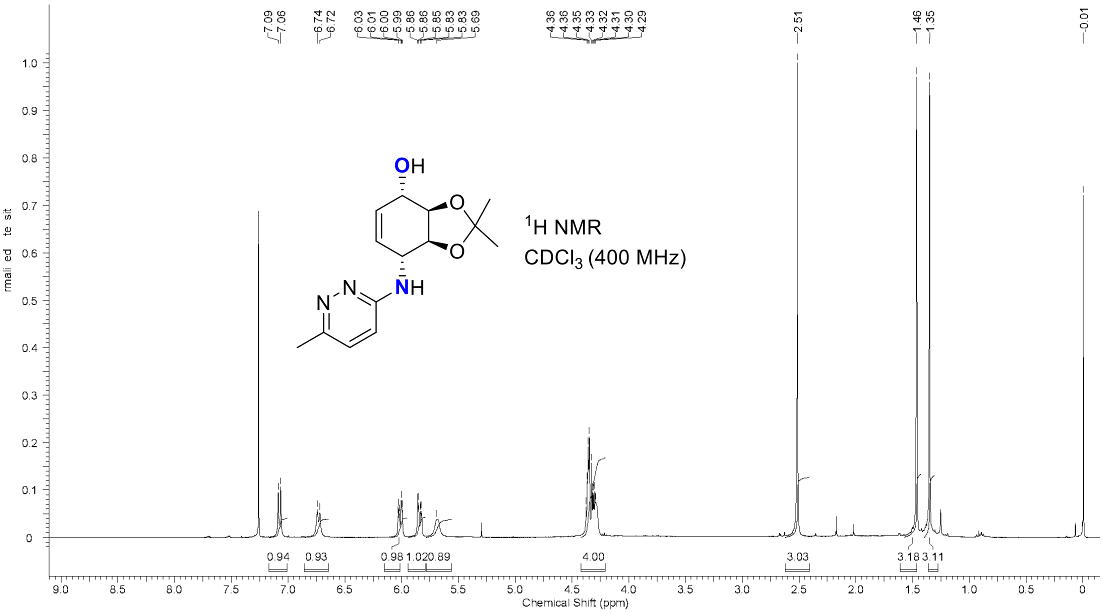
OTBDPS
N
Cbz
9
^{1}H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



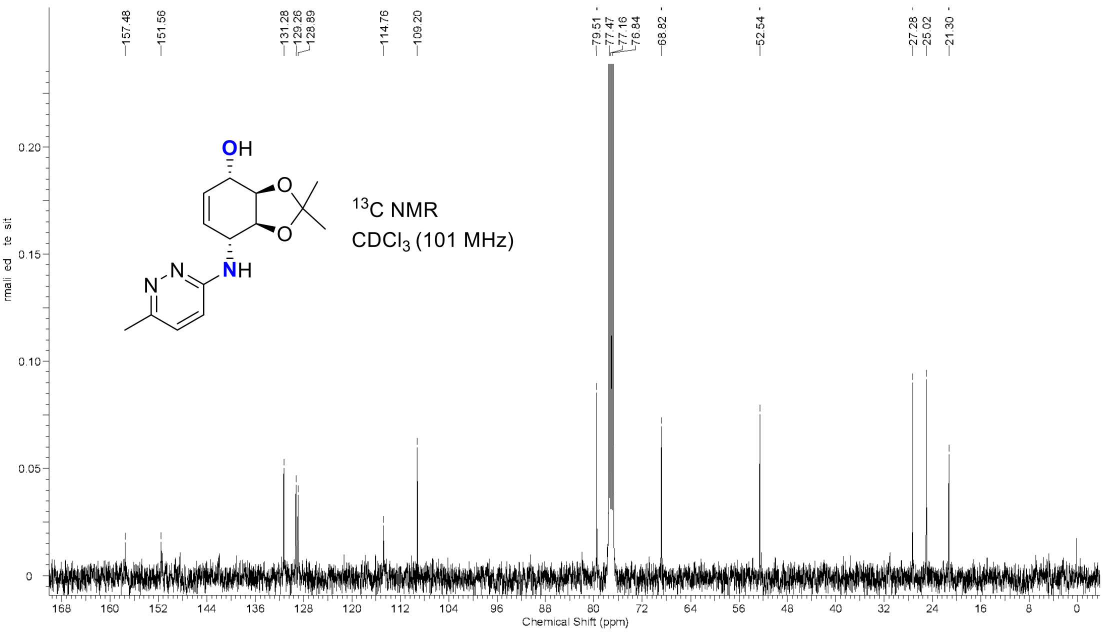
OTBDPS
N
Cbz
9
^{13}C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)


OTBDPS
HN
Cbz
4a, ¹H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)

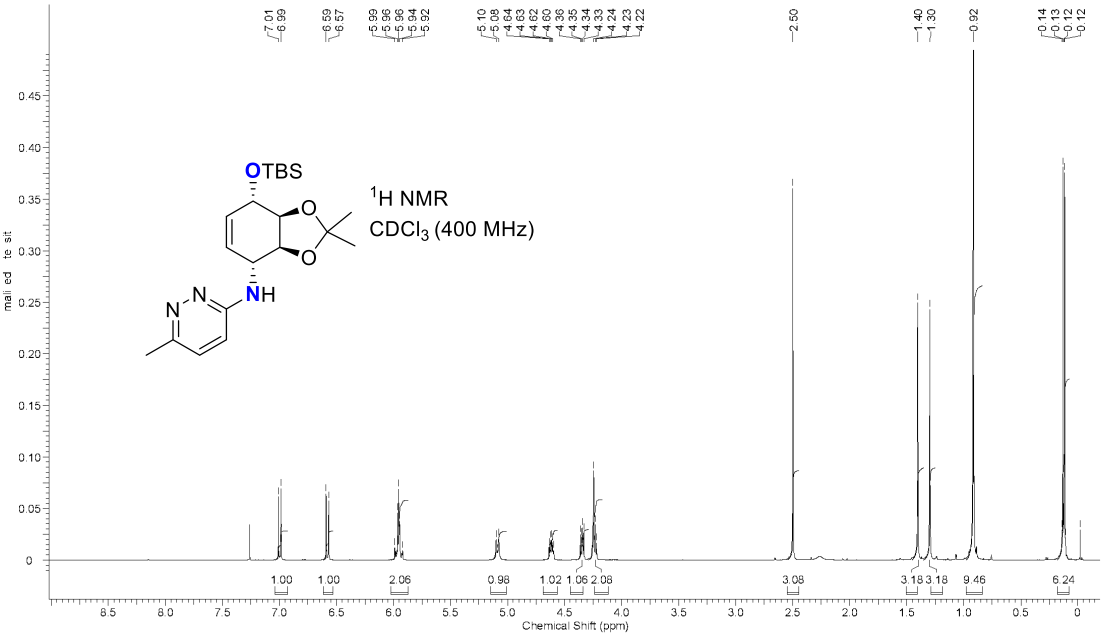

OTBDPS
HN
Cbz
4a, ¹³C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



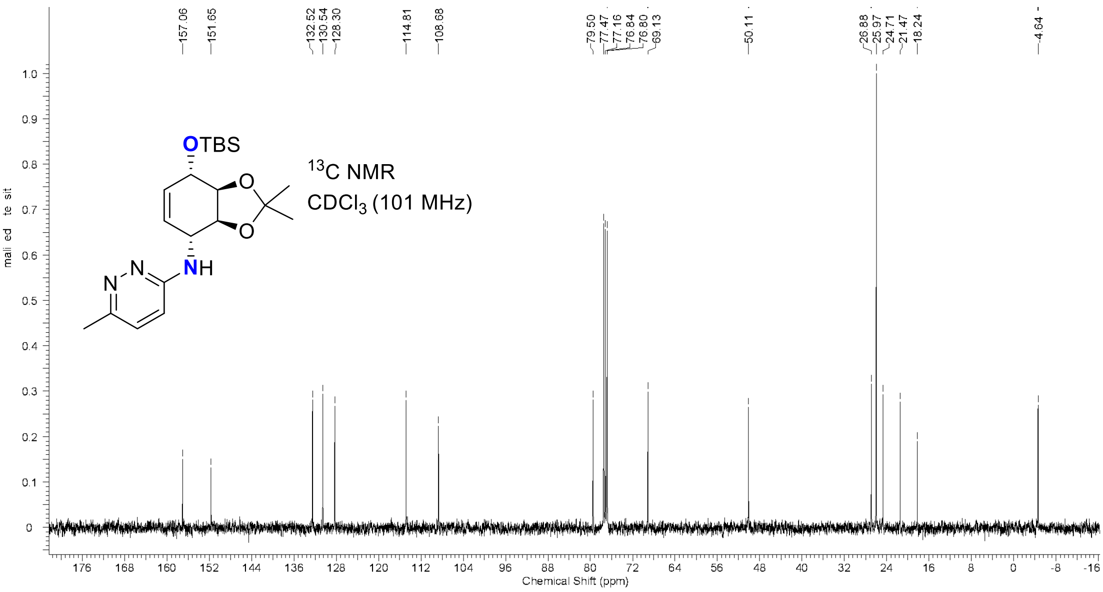
OH
NH
N
N
O
O
^{1}H NMR
$CDCl_3$ (400 MHz)
7.09
7.06
6.74
6.72
6.03
6.01
6.00
5.99
5.86
5.86
5.85
5.83
5.83
5.69
4.36
4.36
4.35
4.33
4.32
4.31
4.30
4.29
2.51
1.46
1.35
-0.01
0.94
0.93
0.98
1.02
0.89
4.00
3.03
3.18
3.11
Chemical Shift (ppm)



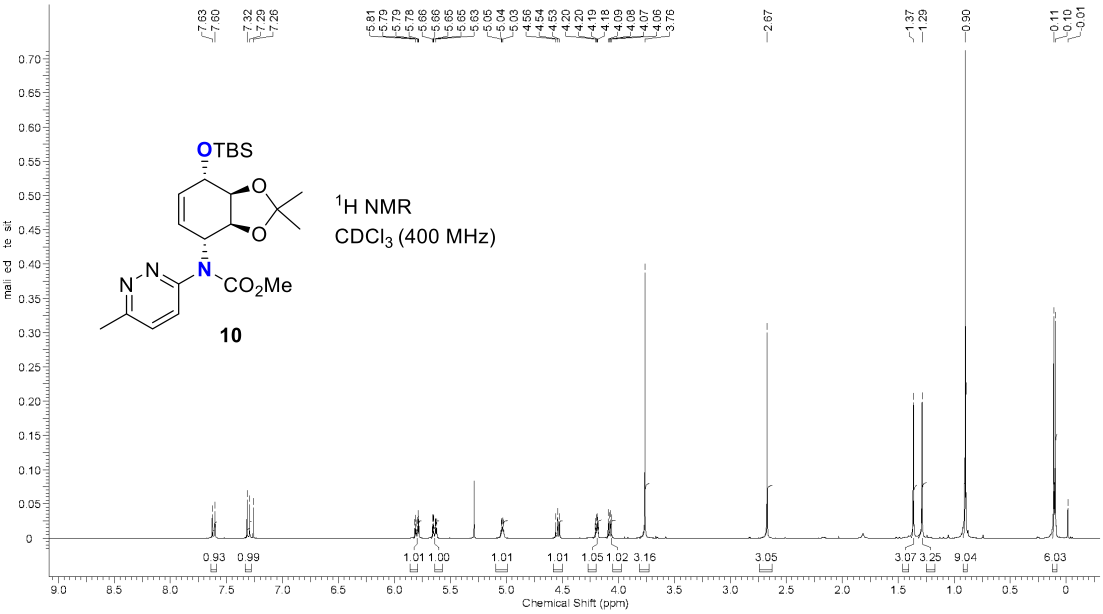
OH
NH
N
N
O
O
^{13}C NMR
$CDCl_3$ (101 MHz)
157.48
151.56
131.28
129.26
128.89
114.76
109.20
79.51
77.47
77.16
76.84
68.82
52.54
27.28
25.02
21.30
Chemical Shift (ppm)

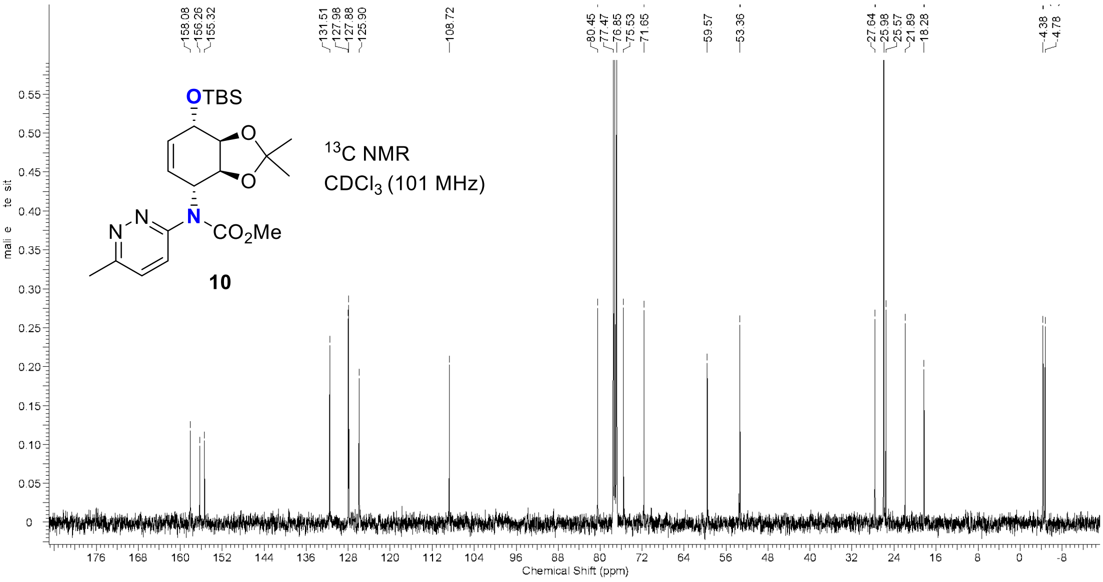


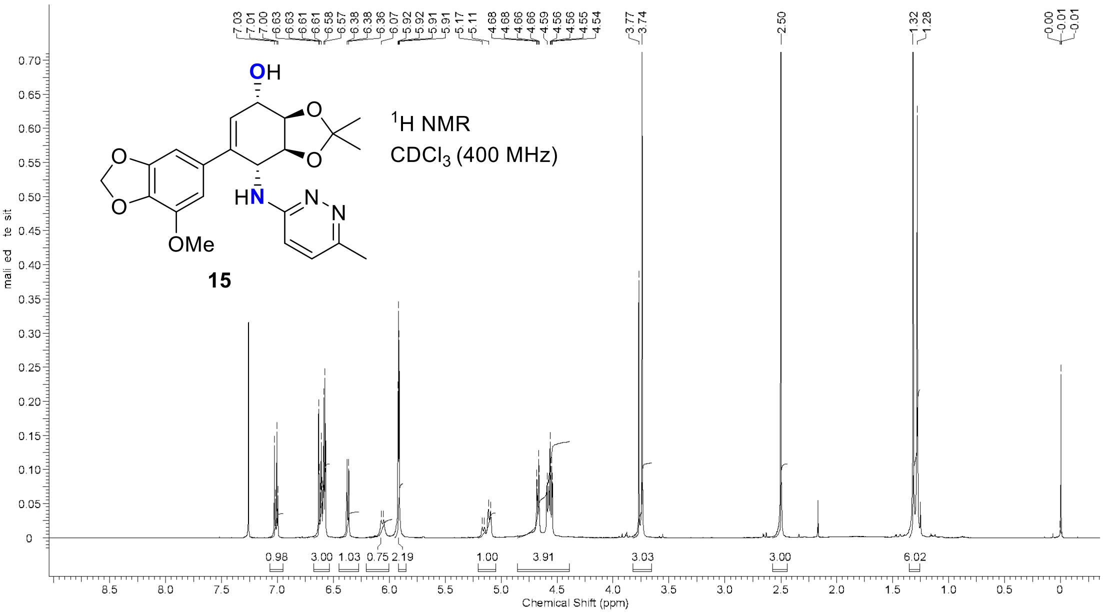
OTBS
NH
N
N
O
O
1H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



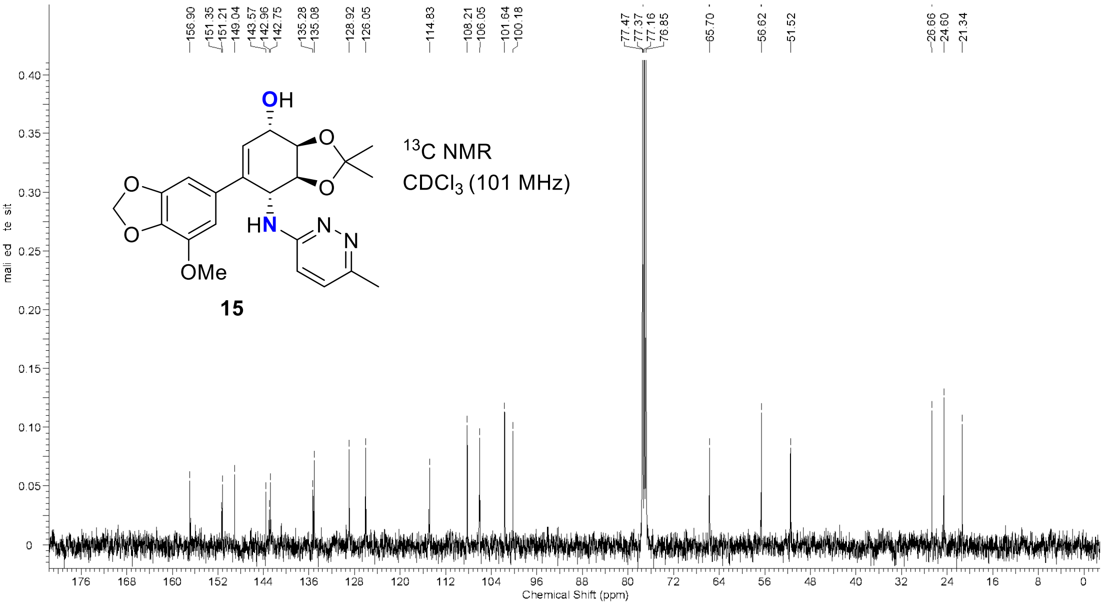
OTBS
NH
N
N
O
O
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)


OTBS
N
CO2Me
N
N
10
1H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)

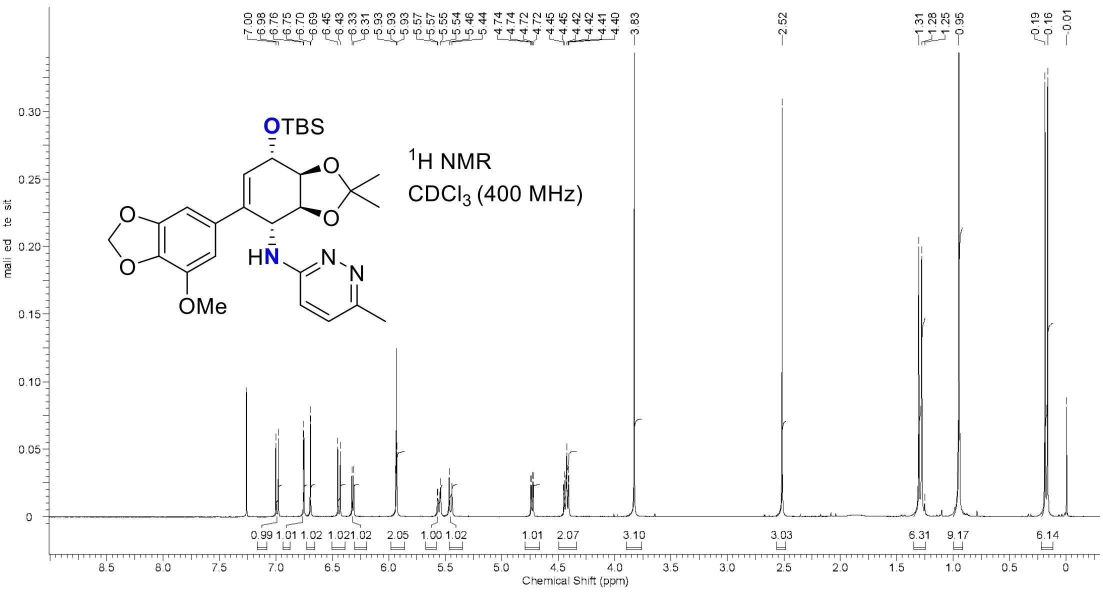

OTBS
N
CO2Me
N
N
10
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)

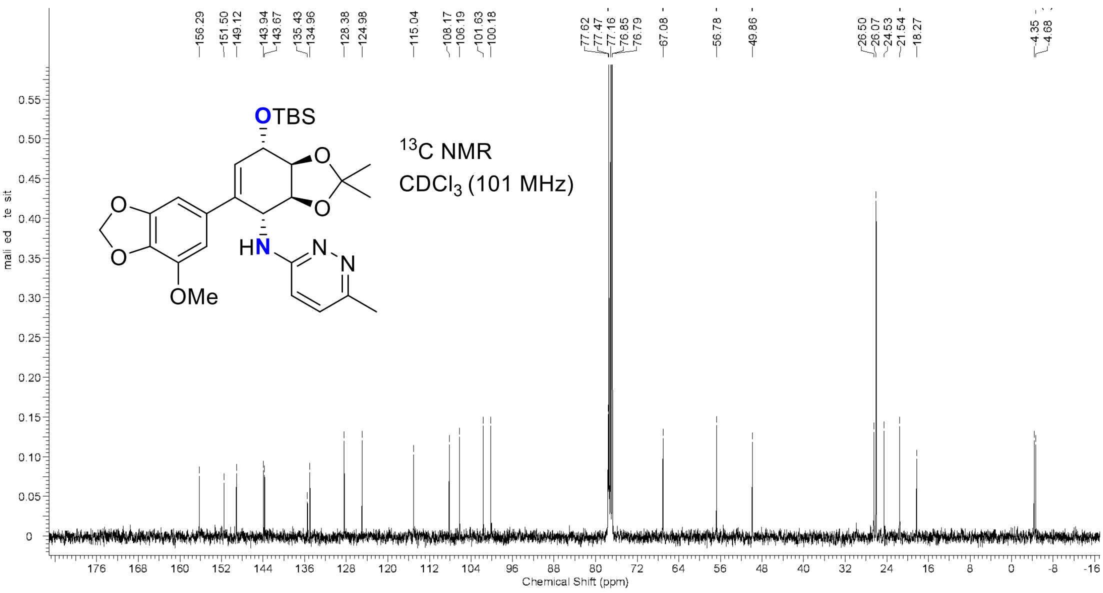


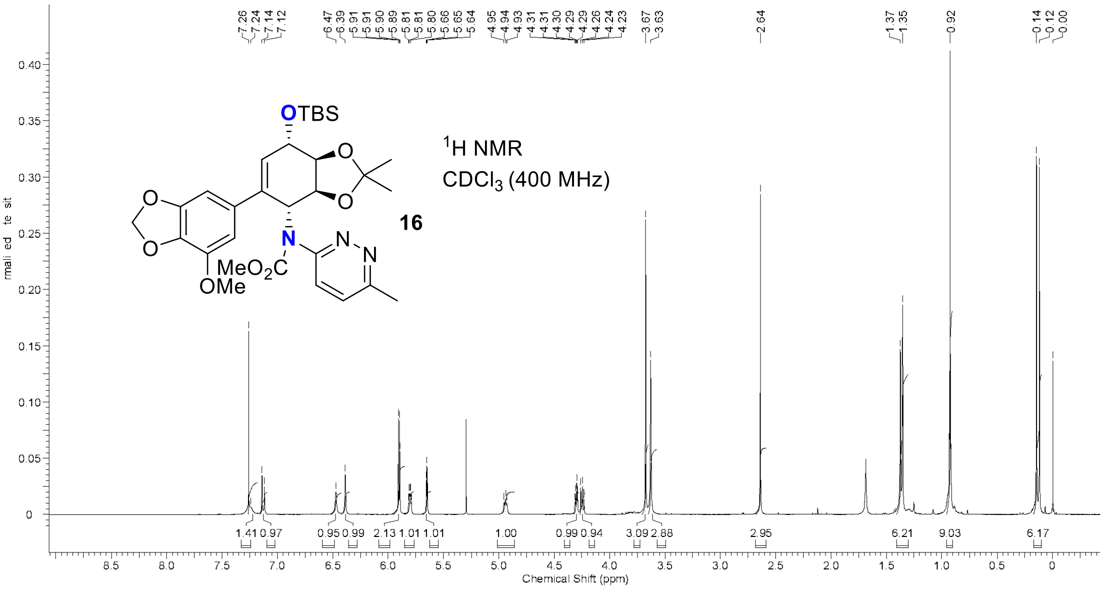
^1H NMR
$CDCl_3$ (400 MHz)
15
OH
HN
OMe
Chemical Shift (ppm)



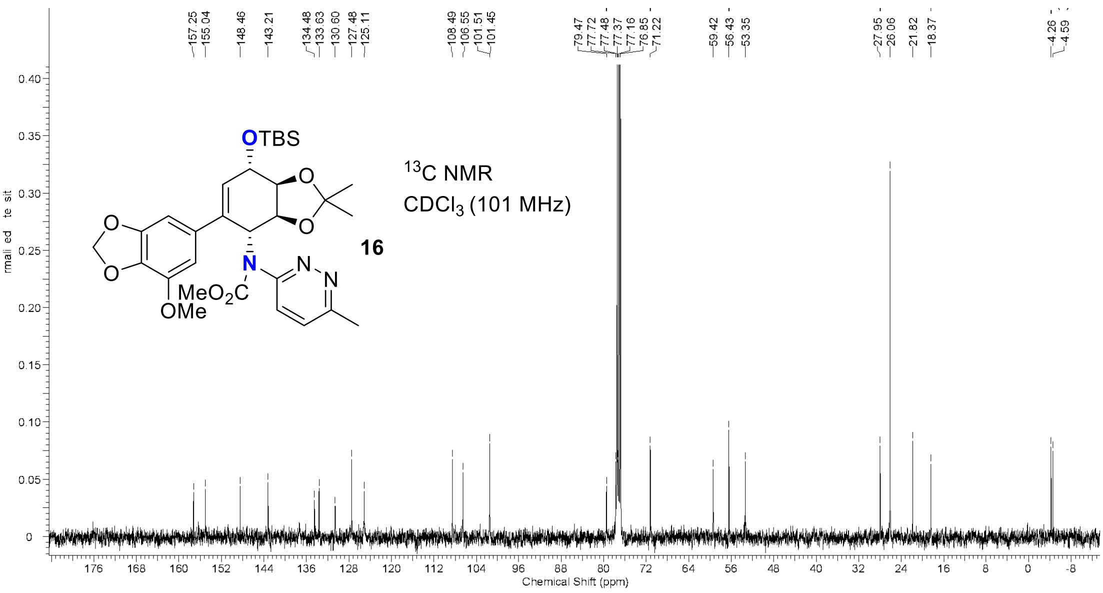
^{13}C NMR
$CDCl_3$ (101 MHz)
15
OH
HN
OMe
Chemical Shift (ppm)


OTBS
HN
^{1}H NMR
CDCl$_3$ (400 MHz)
OMe
Chemical Shift (ppm)

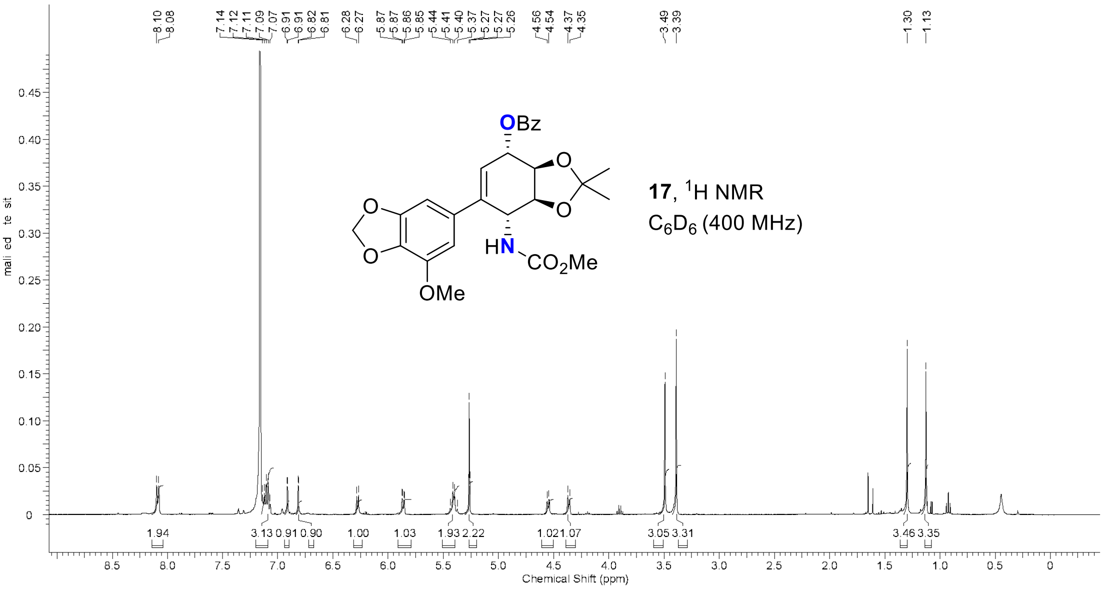

OTBS
HN
^{13}C NMR
CDCl$_3$ (101 MHz)
OMe
Chemical Shift (ppm)

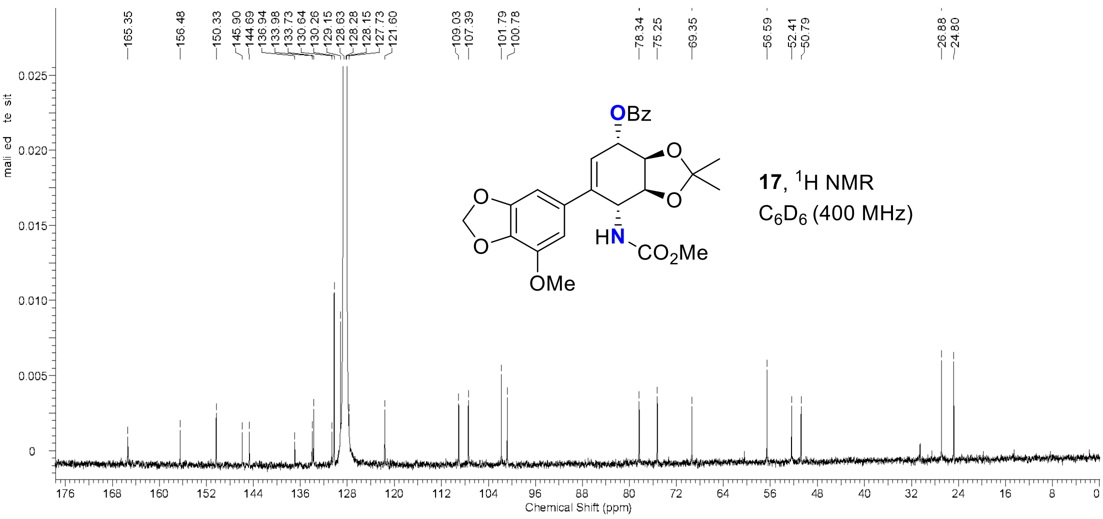


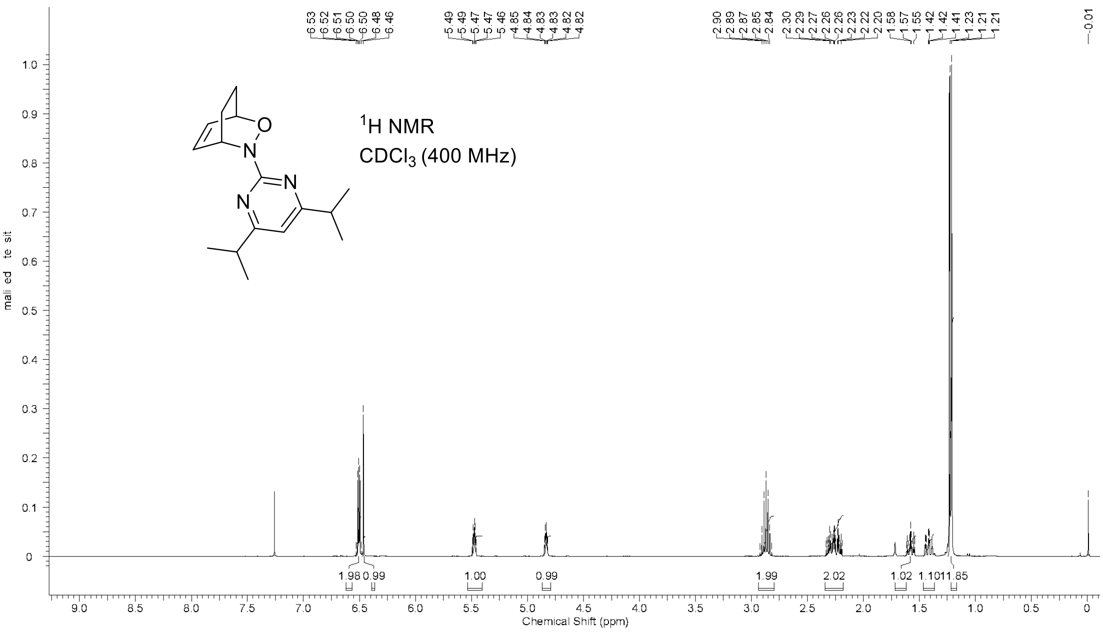
^{1}H NMR
CDCl$_3$ (400 MHz)
16
Chemical Shift (ppm)

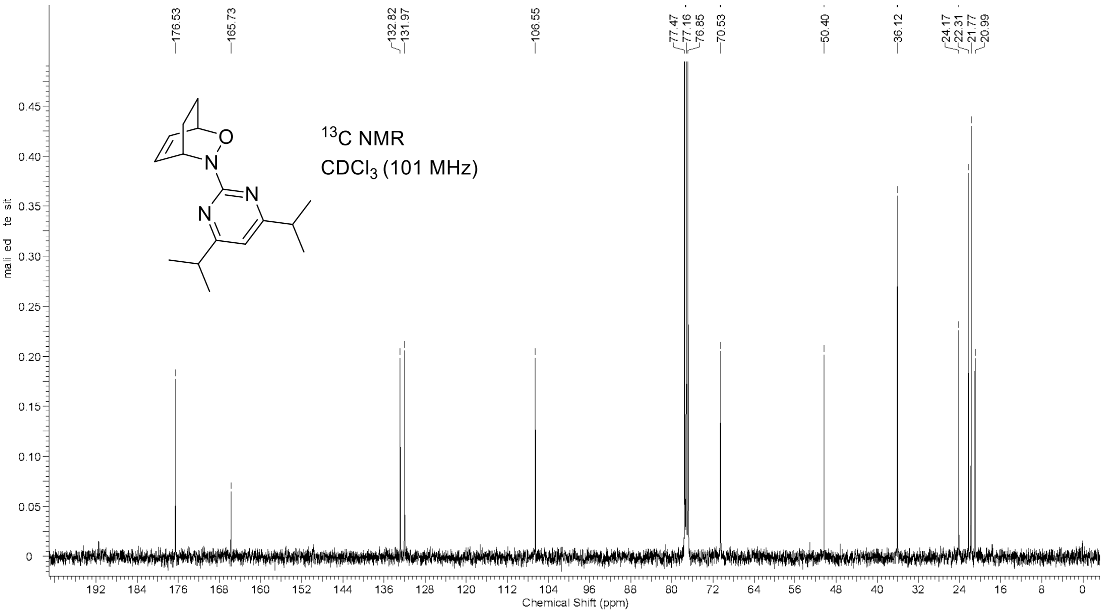


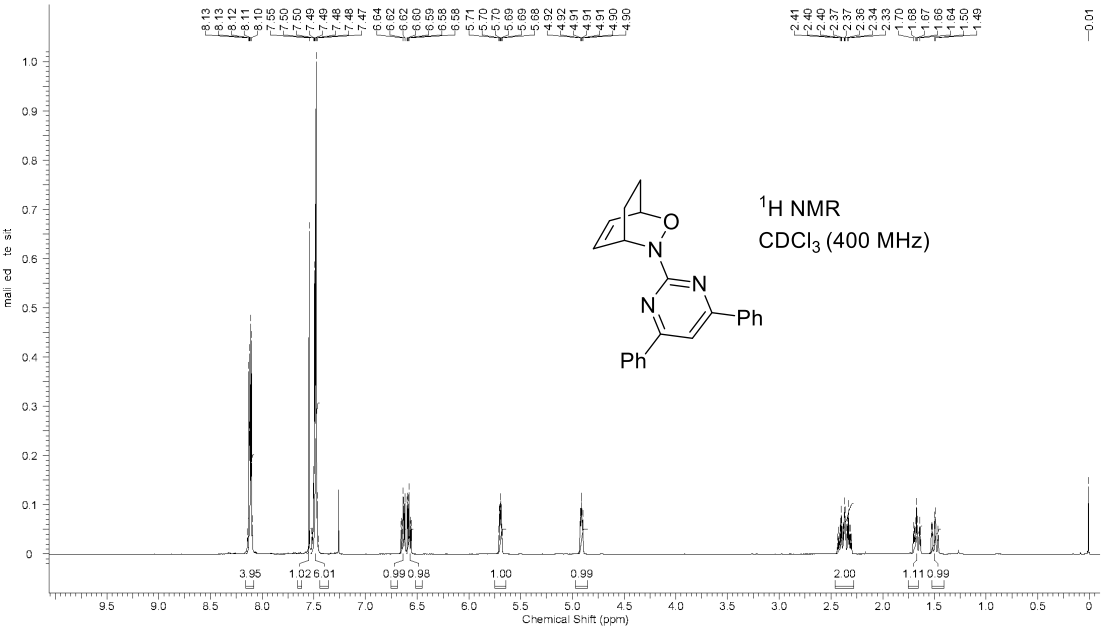
^{13}C NMR
CDCl$_3$ (101 MHz)
16
Chemical Shift (ppm)

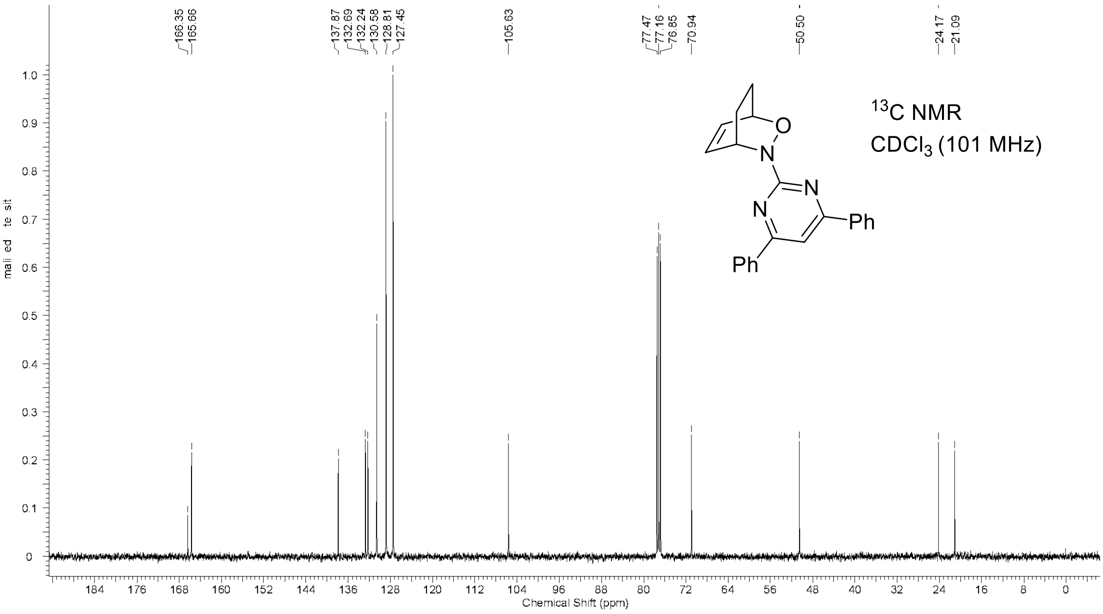

OBz
HN
CO2Me
OMe
17, 1H NMR
C6D6 (400 MHz)
Chemical Shift (ppm)

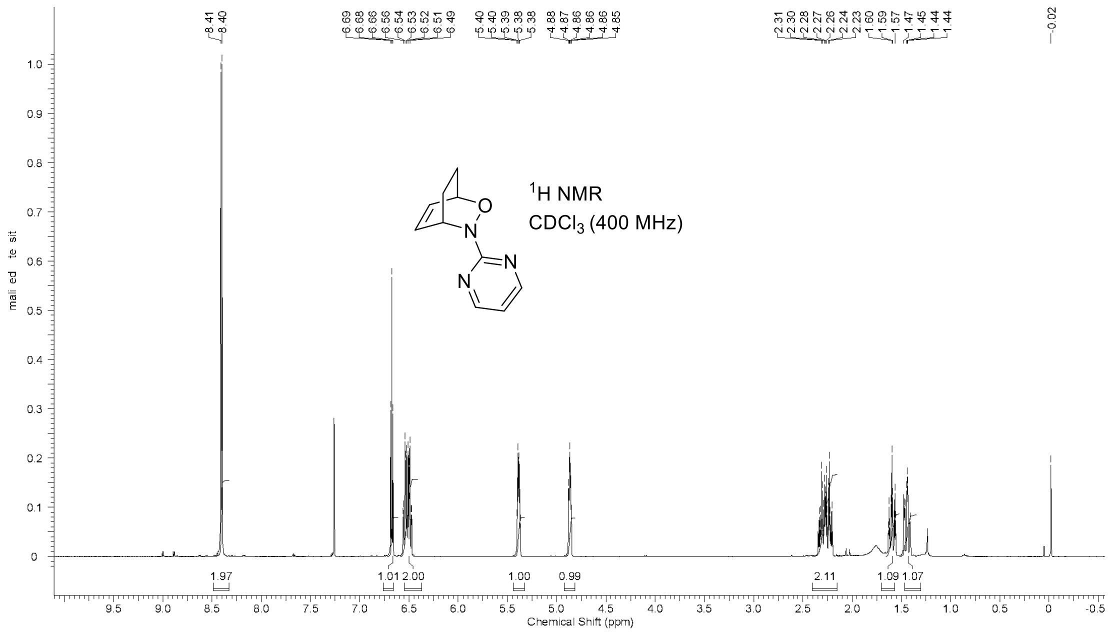

OBz
HN
CO2Me
OMe
17, 1H NMR
C6D6 (400 MHz)
Chemical Shift (ppm)



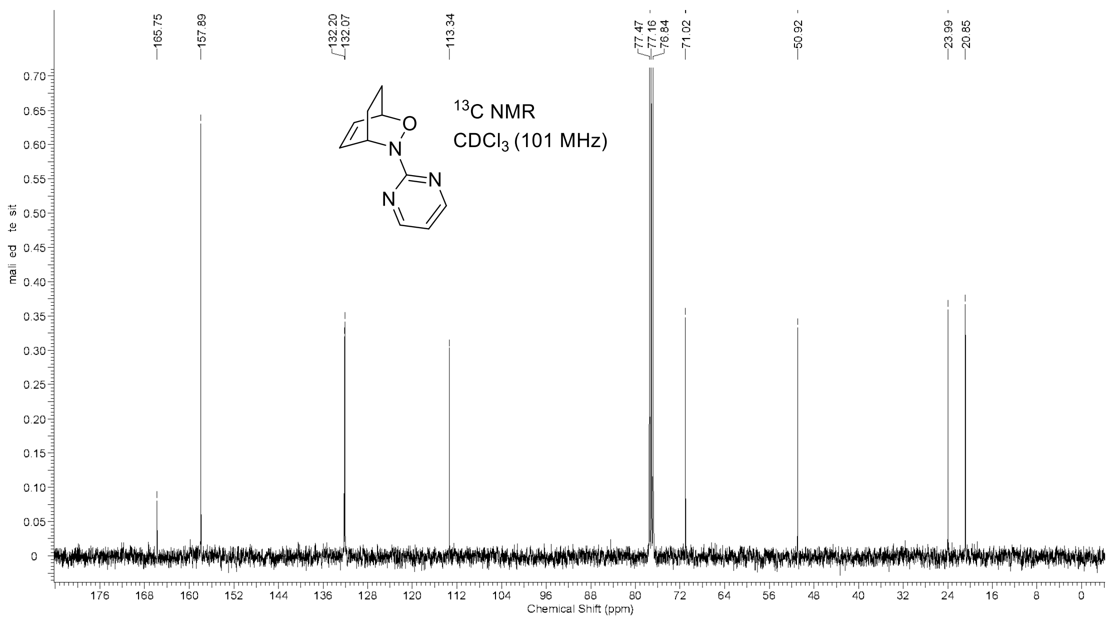



1H NMR
CDCl3 (400 MHz)
Ph
Ph
Chemical Shift (ppm)

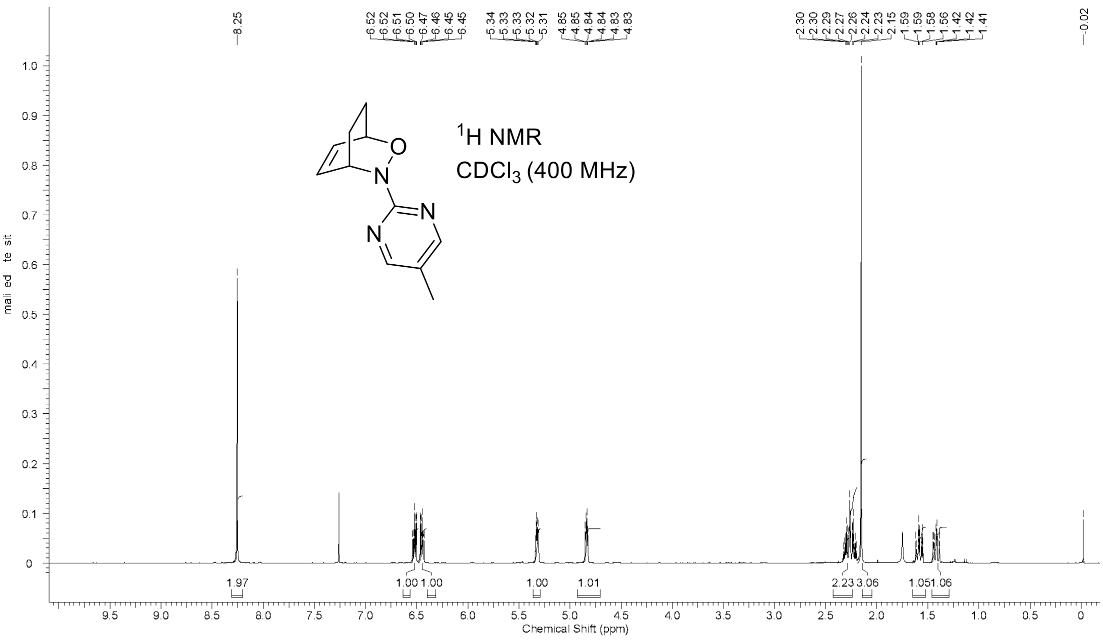

13C NMR
CDCl3 (101 MHz)
Ph
Ph
Chemical Shift (ppm)



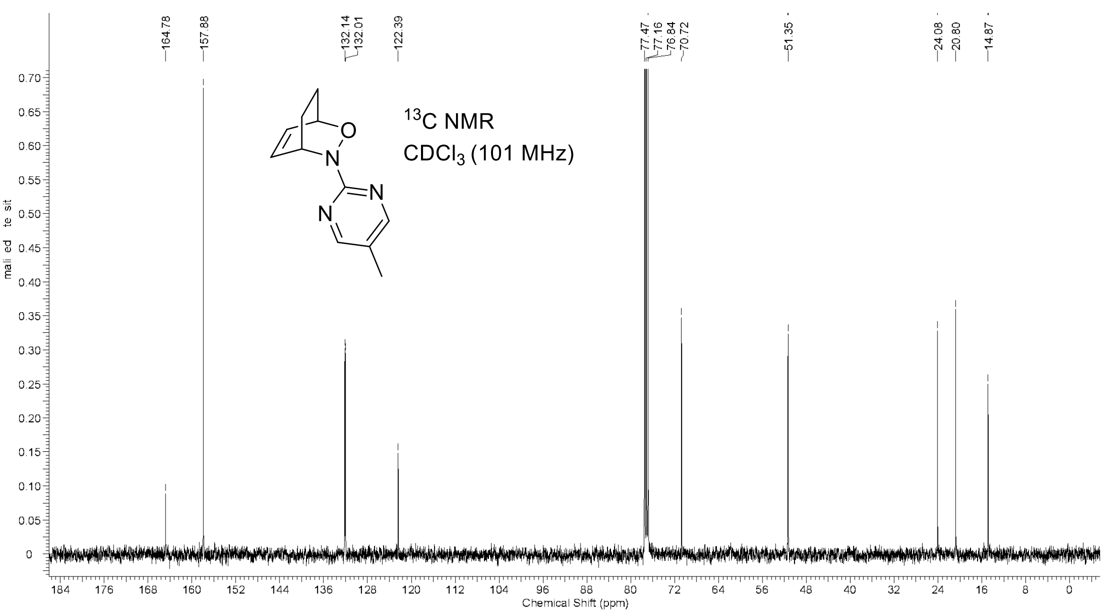
^{1}H NMR
CDCl$_3$ (400 MHz)
Chemical Shift (ppm)



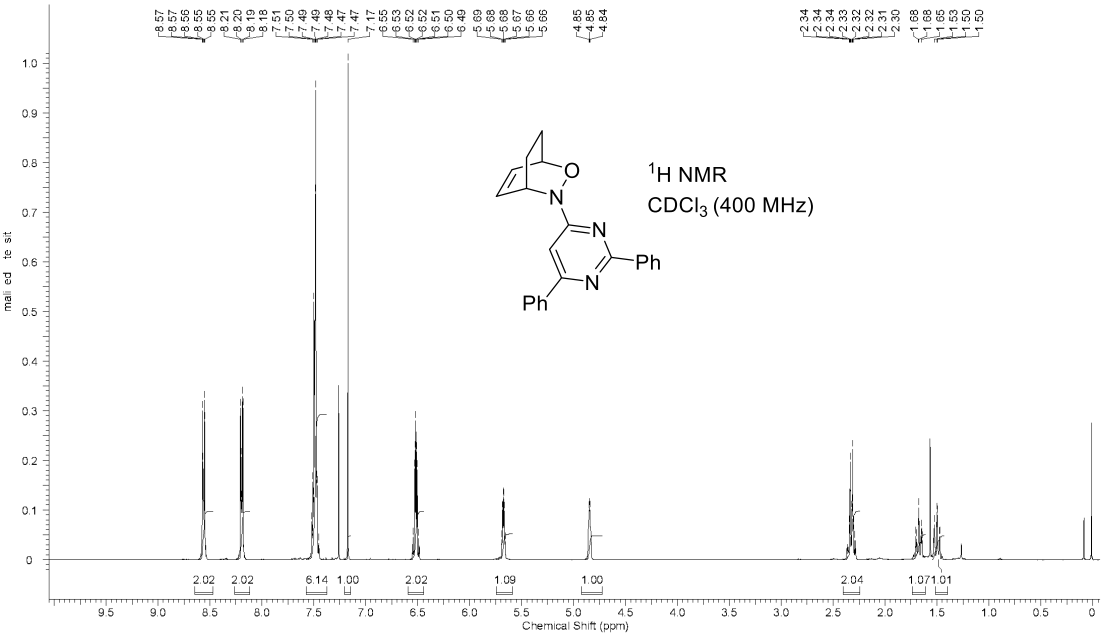
^{13}C NMR
CDCl$_3$ (101 MHz)
Chemical Shift (ppm)



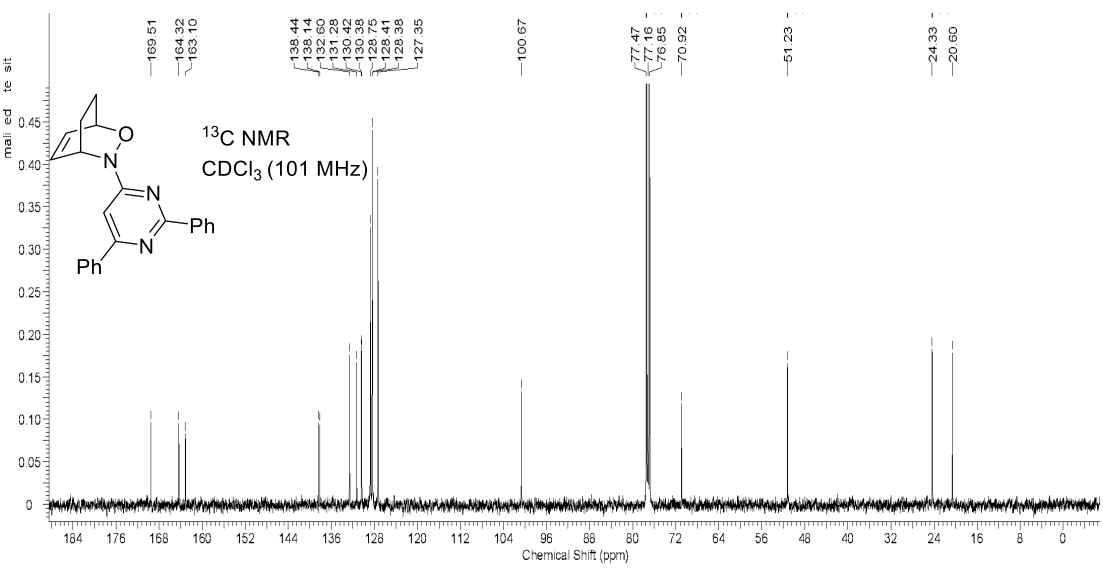
^{1}H NMR
$CDCl_3$ (400 MHz)
Chemical Shift (ppm)



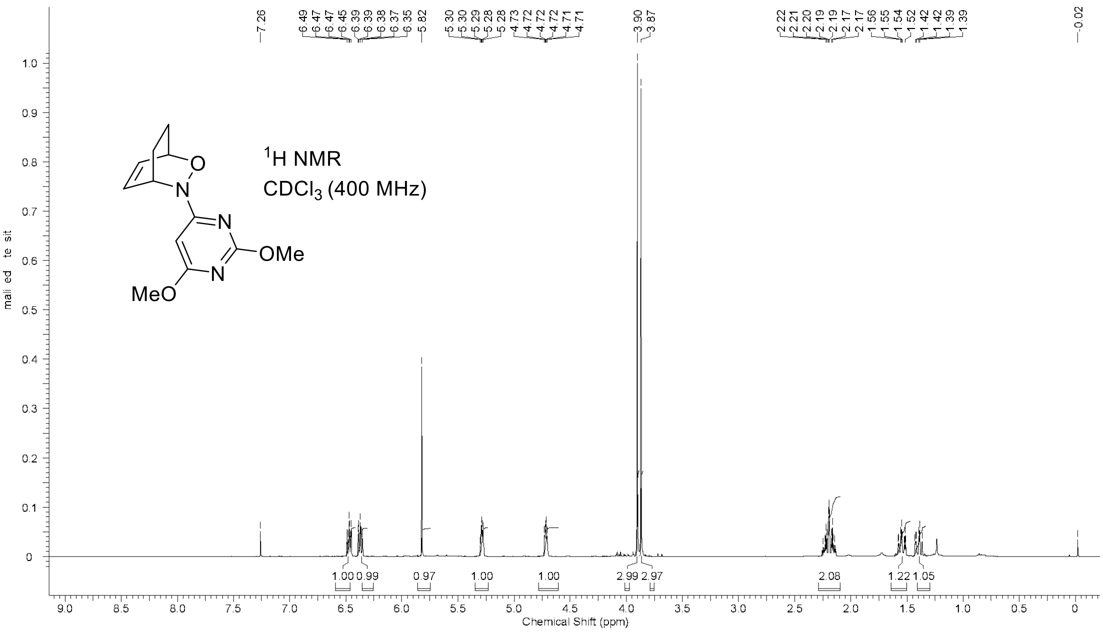
^{13}C NMR
$CDCl_3$ (101 MHz)
Chemical Shift (ppm)



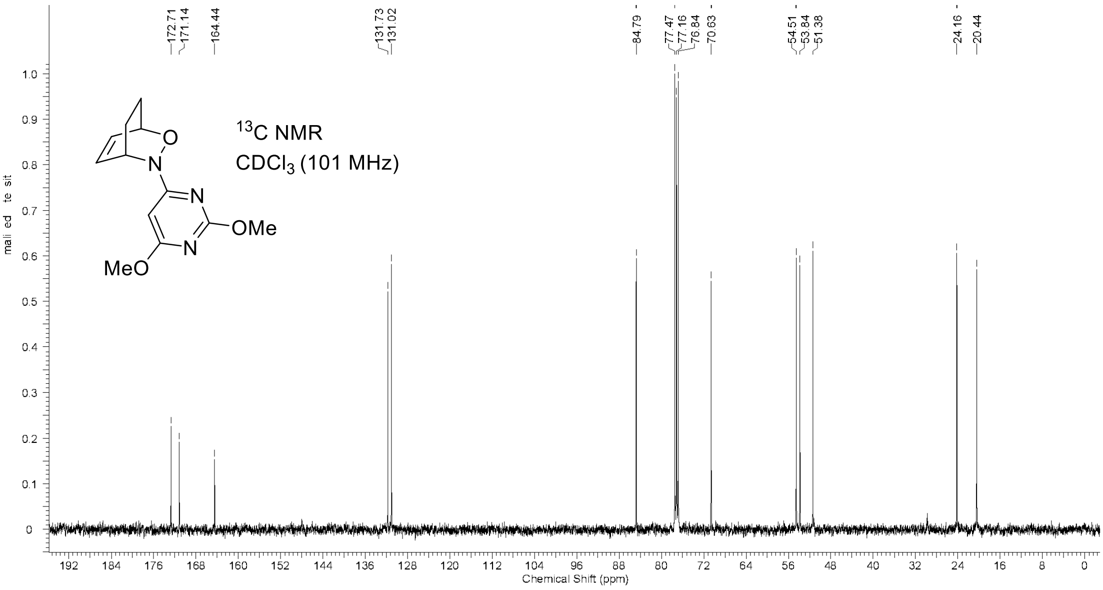
^{1}H NMR
$CDCl_3$ (400 MHz)
Ph
Ph
N
N
N
O
Chemical Shift (ppm)



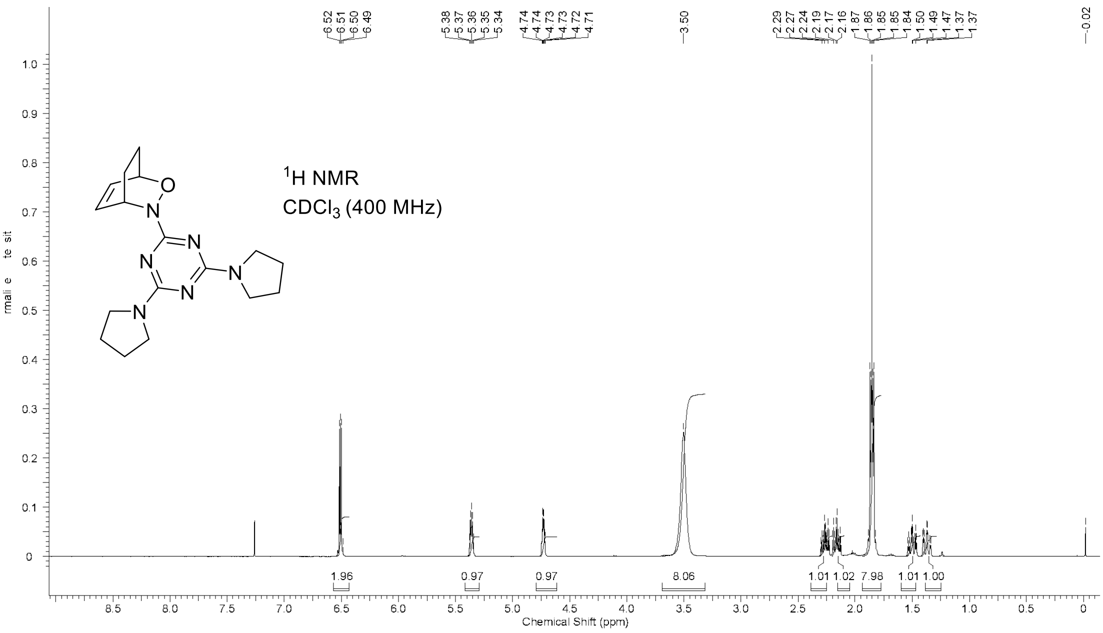
^{13}C NMR
$CDCl_3$ (101 MHz)
Ph
Ph
N
N
N
O
Chemical Shift (ppm)



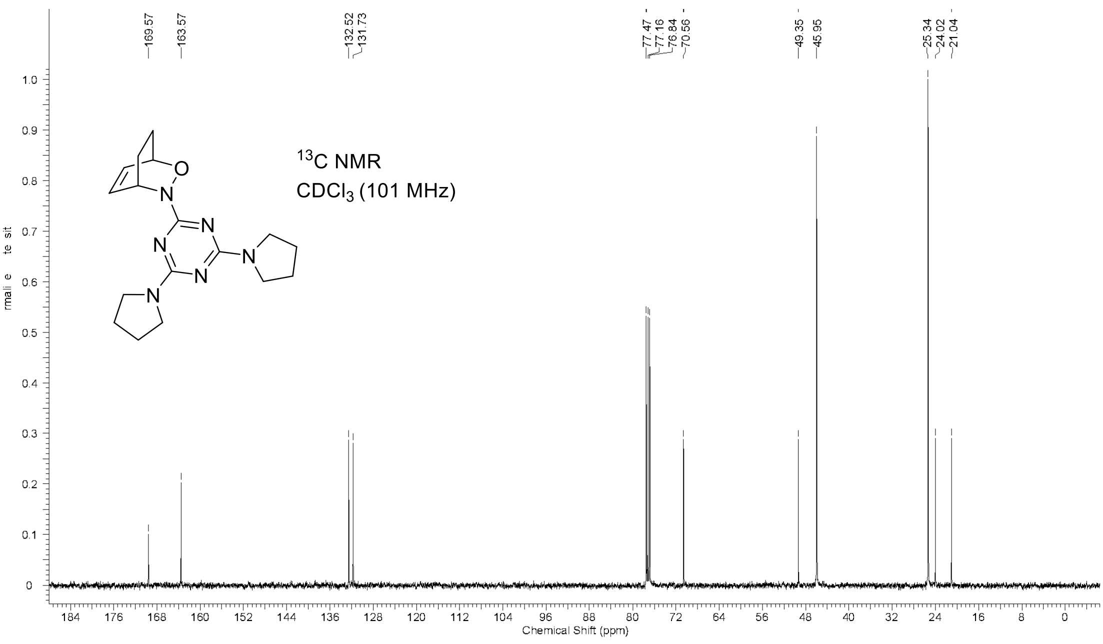
^{1}H NMR
CDCl$_3$ (400 MHz)
OMe
MeO
Chemical Shift (ppm)



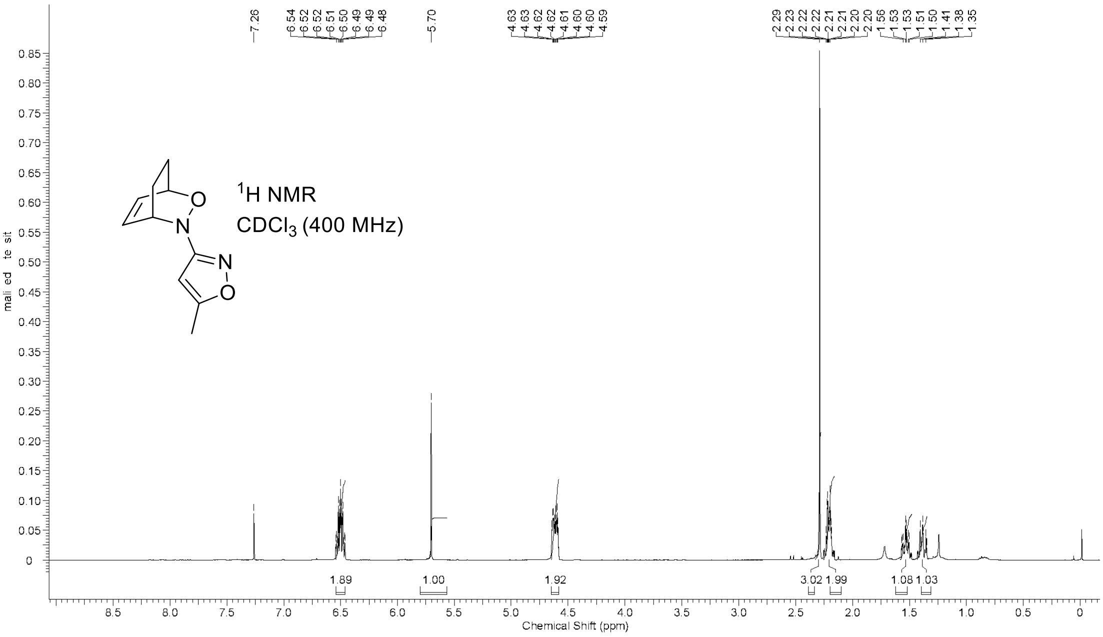
^{13}C NMR
CDCl$_3$ (101 MHz)
OMe
MeO
Chemical Shift (ppm)



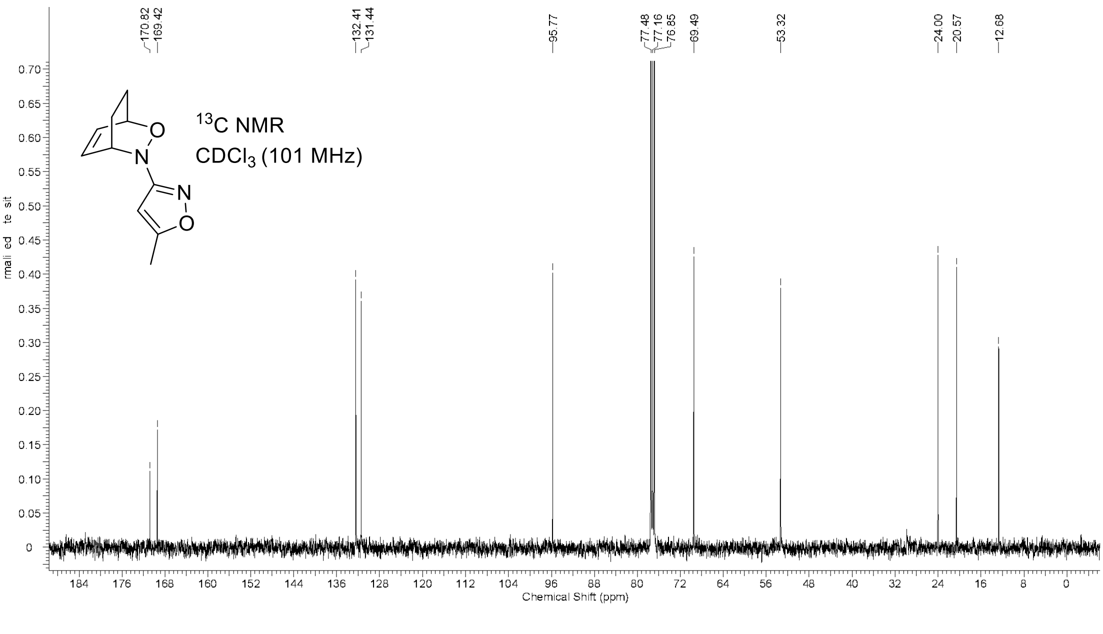
^{1}H NMR
CDCl$_3$ (400 MHz)
1.96
0.97
0.97
8.06
1.01
1.02
7.98
1.01
1.00
Chemical Shift (ppm)



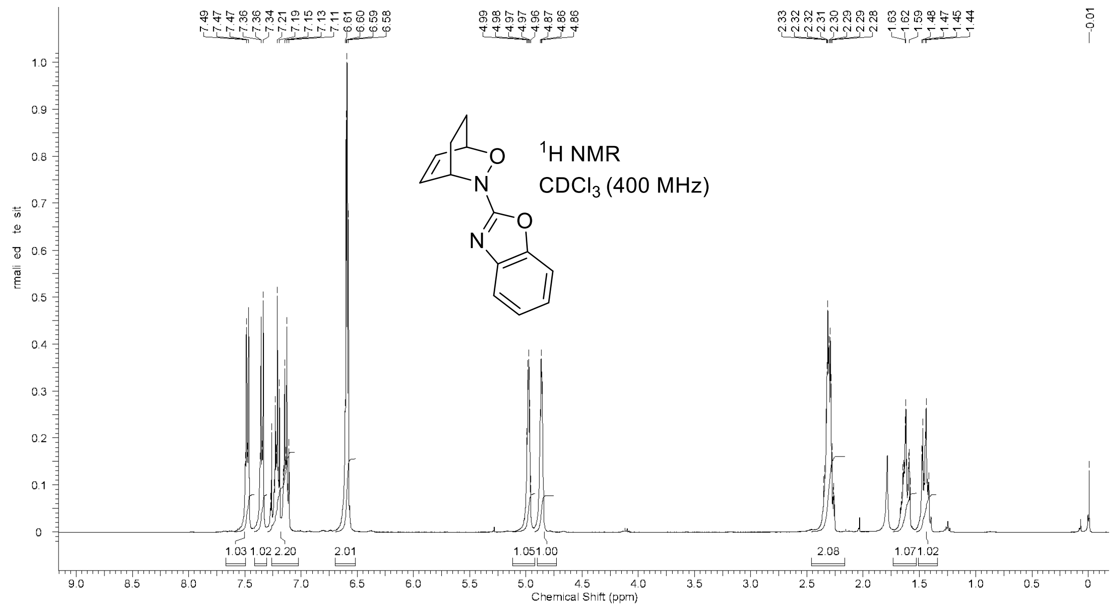
^{13}C NMR
CDCl$_3$ (101 MHz)
169.57
163.57
132.52
131.73
77.47
77.16
76.84
70.56
49.35
45.95
25.34
24.02
21.04
Chemical Shift (ppm)



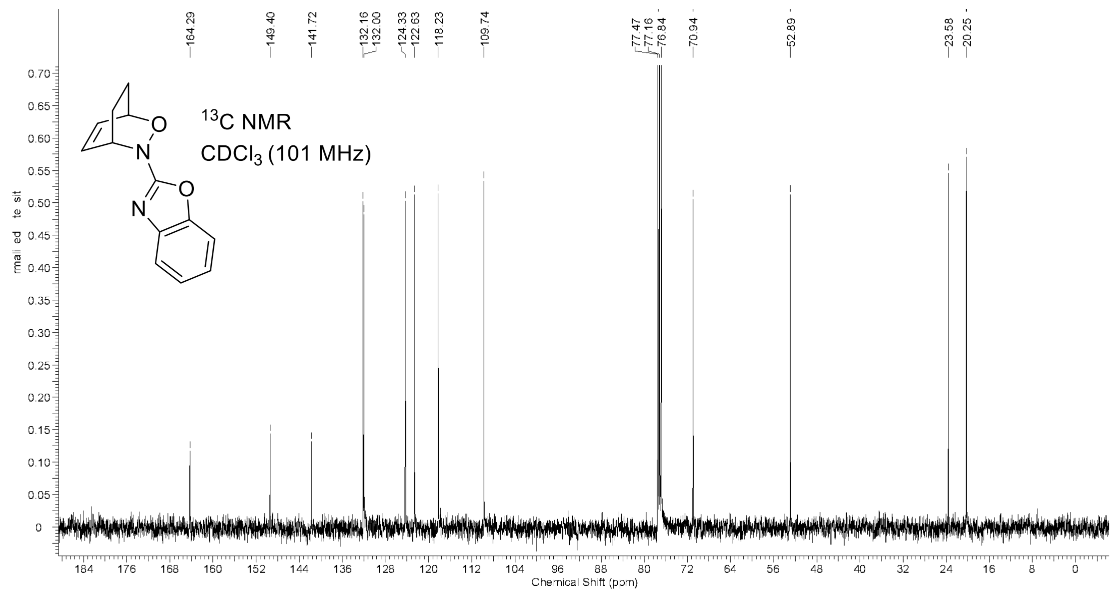
1H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



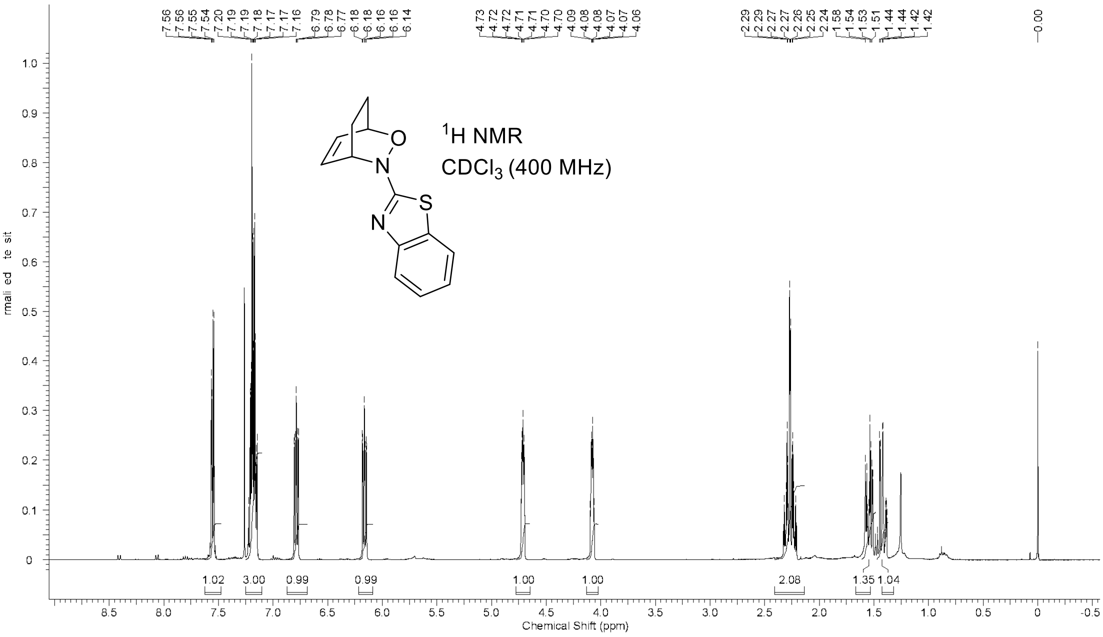
13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



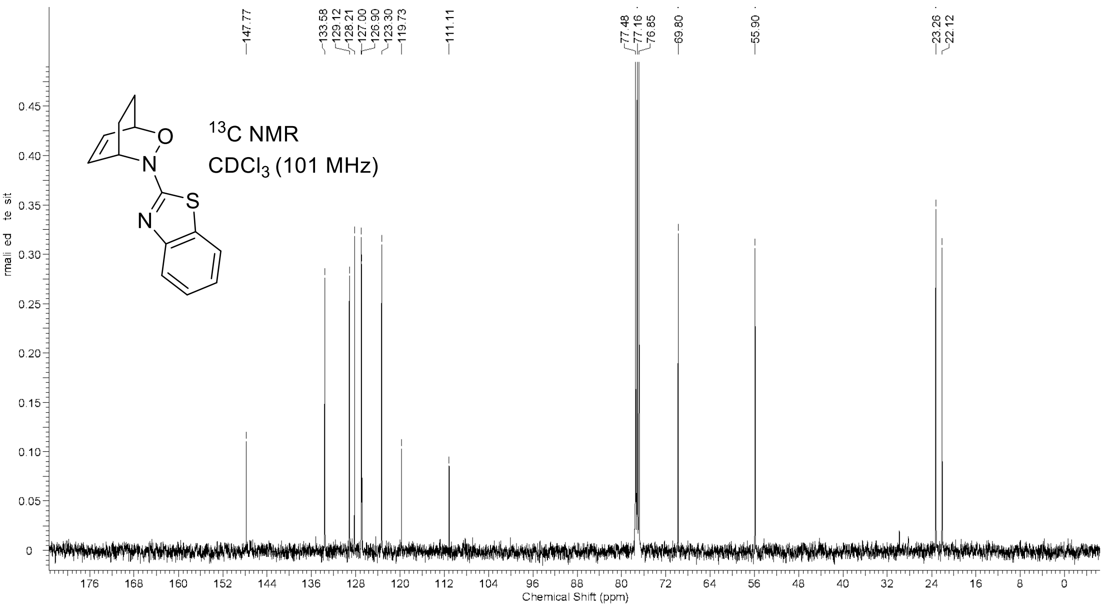
7.49
7.47
7.47
7.36
7.36
7.34
7.21
7.19
7.15
7.13
7.11
6.61
6.60
6.59
6.58
4.99
4.98
4.97
4.97
4.96
4.87
4.86
4.86
2.33
2.32
2.32
2.31
2.30
2.29
2.29
2.28
1.63
1.62
1.59
1.48
1.47
1.45
1.44
-0.01
^{1}H NMR
$CDCl_3$ (400 MHz)
O
N
O
N
1.03
1.02
2.20
2.01
1.05
1.00
2.08
1.07
1.02
Chemical Shift (ppm)



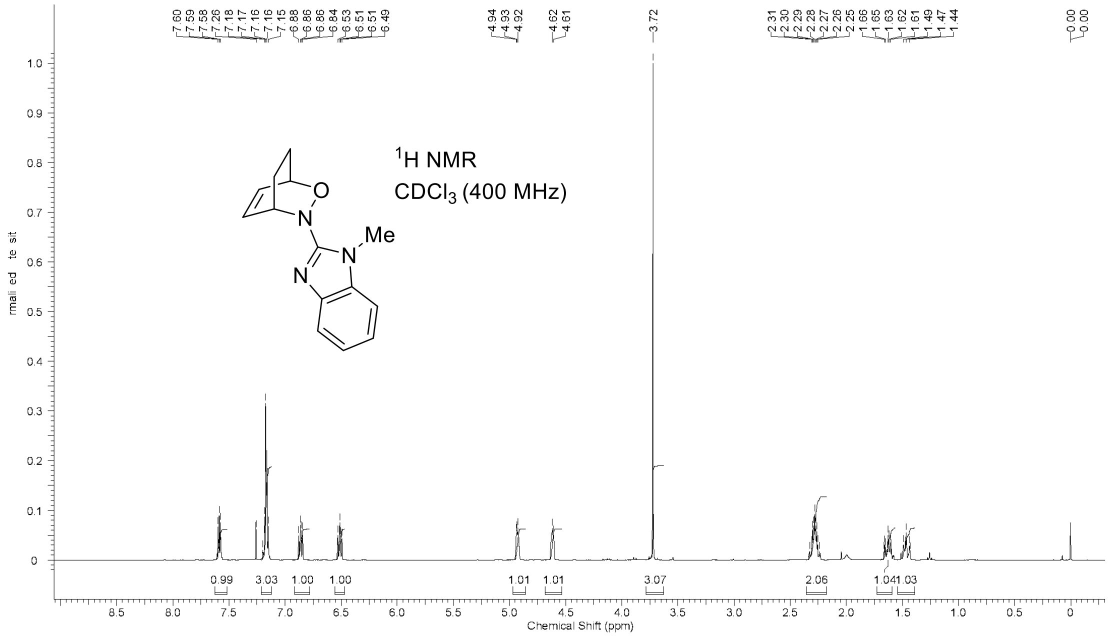
164.29
149.40
141.72
132.16
132.00
124.33
122.63
118.23
109.74
77.47
77.16
76.84
70.94
52.89
23.58
20.25
^{13}C NMR
$CDCl_3$ (101 MHz)
O
N
O
N
Chemical Shift (ppm)



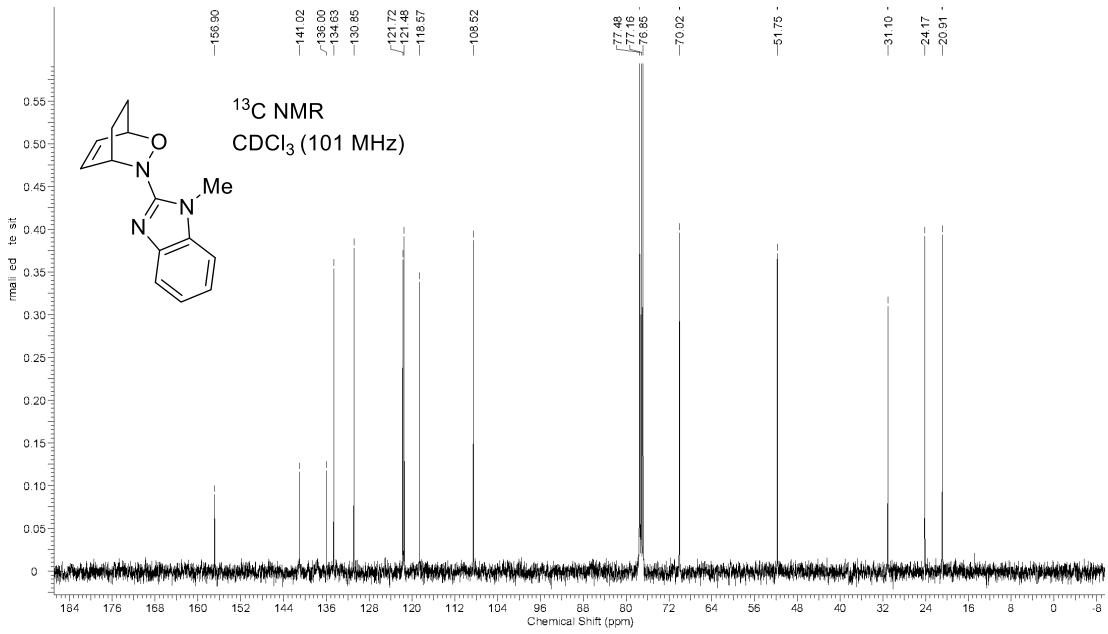
1H NMR
CDCl3 (400 MHz)
Chemical Shift (ppm)



13C NMR
CDCl3 (101 MHz)
Chemical Shift (ppm)



1H NMR
CDCl3 (400 MHz)
Me
N
O
Chemical Shift (ppm)

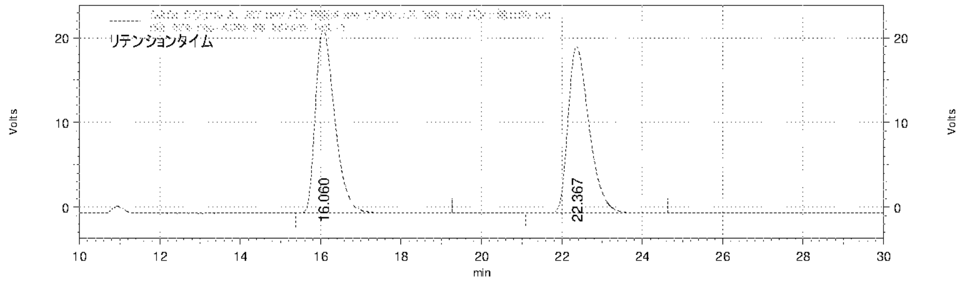


13C NMR
CDCl3 (101 MHz)
Me
N
O
Chemical Shift (ppm)

17. Copies HPLC chromatogram

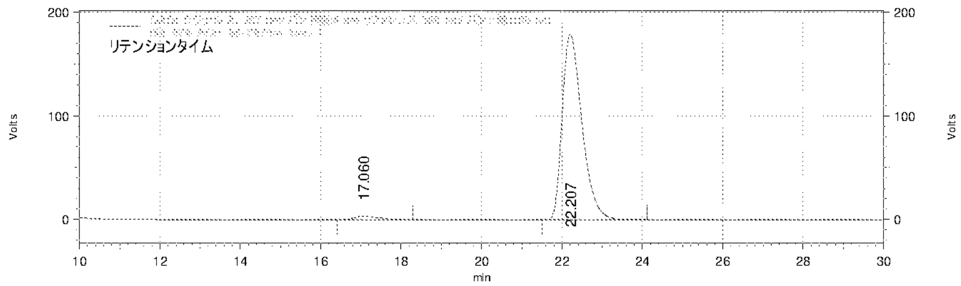
3ac

Daicel Chiralpak AD-H, hexane/***i***-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 16.5 min, t_R(major) = 17.4 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
16.060	50.282
22.367	49.718
合計	100.000

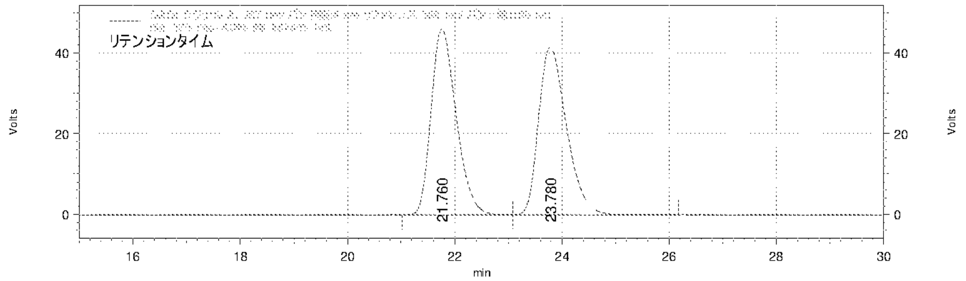


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
17.060	2.378
22.207	97.622
合計	100.000

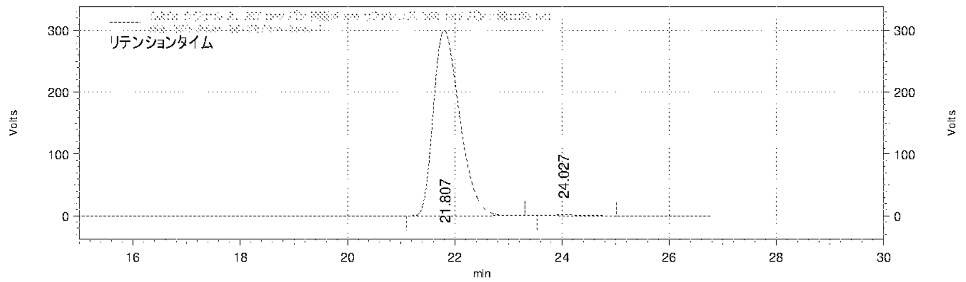
3aj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 21.8 min, t_R(minor) = 24.0 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
21.760	49.930
23.780	50.070
合計	100.000

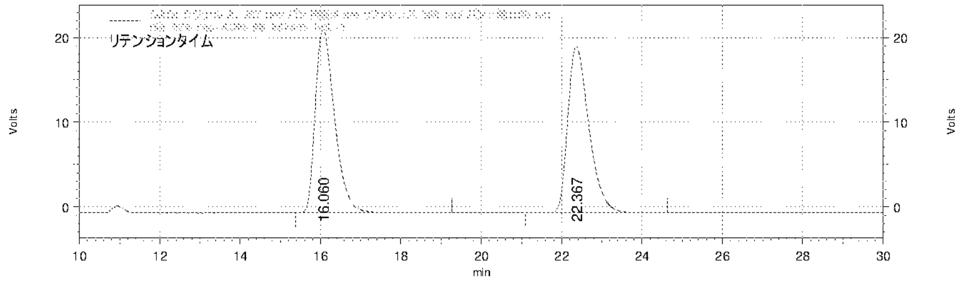


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
21.807	99.343
24.027	0.657
合計	100.000

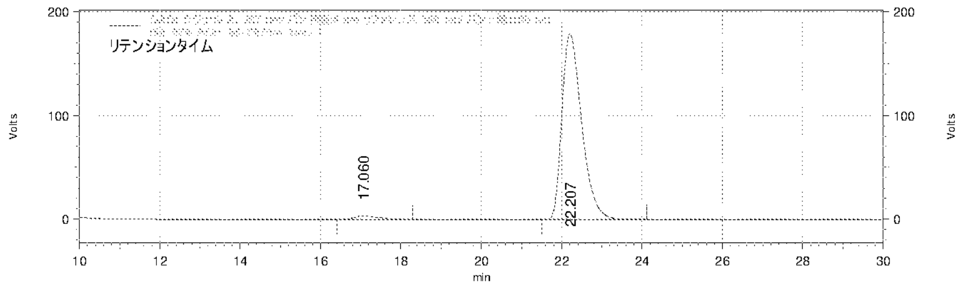
3bc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 17.1 min, t_R(major) = 22.2 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
16.060	50.282
22.367	49.718
合計	100.000

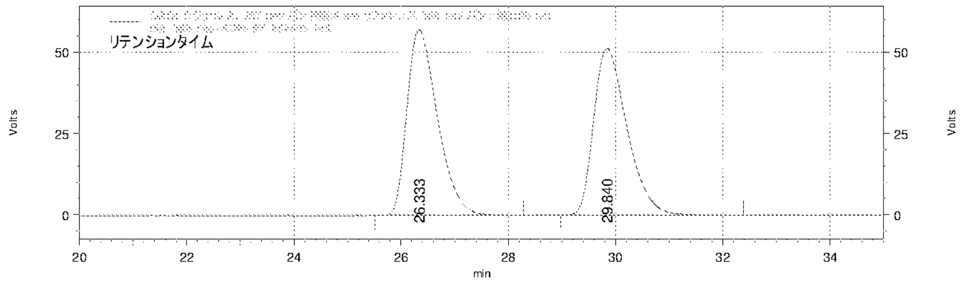


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
17.060	2.378
22.207	97.622
合計	100.000

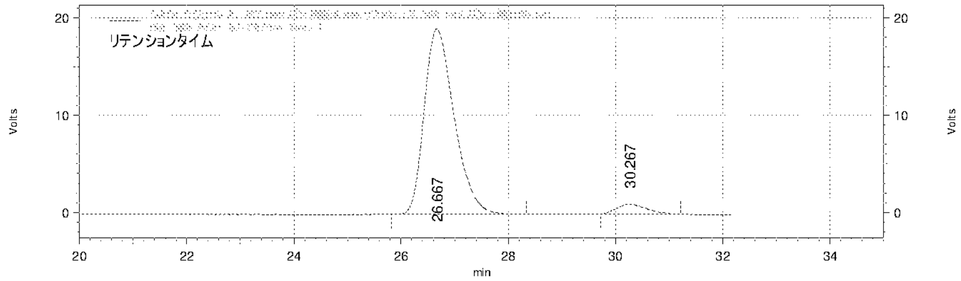
3bj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 26.7 min, t_R(minor) = 30.3 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
26.333	50.531
29.840	49.469
合計	100.000

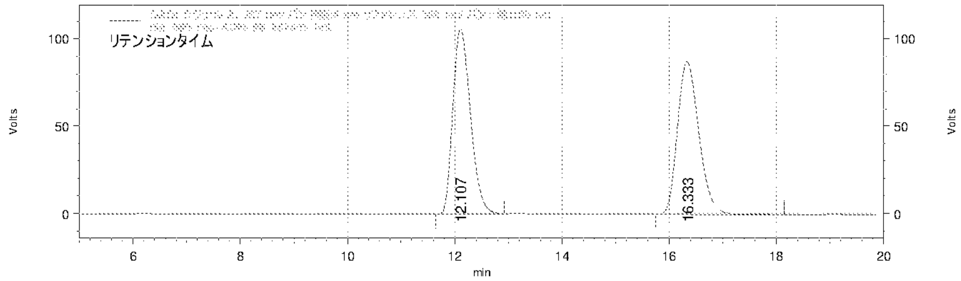


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
26.667	94.965
30.267	5.035
合計	100.000

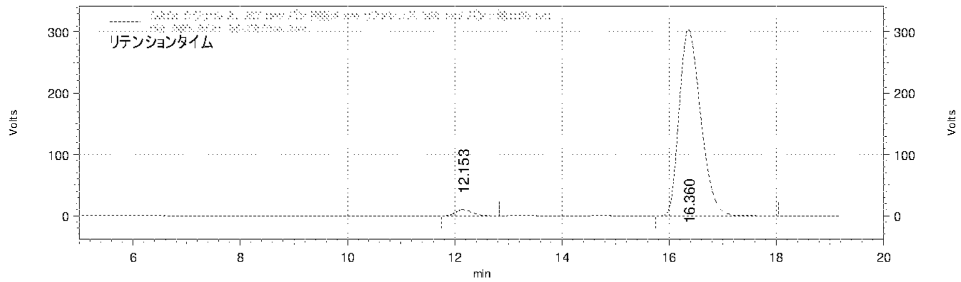
3cc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 12.2 min, t_R(major) = 16.4 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
12.107	49.887
16.333	50.113
合計	100.000

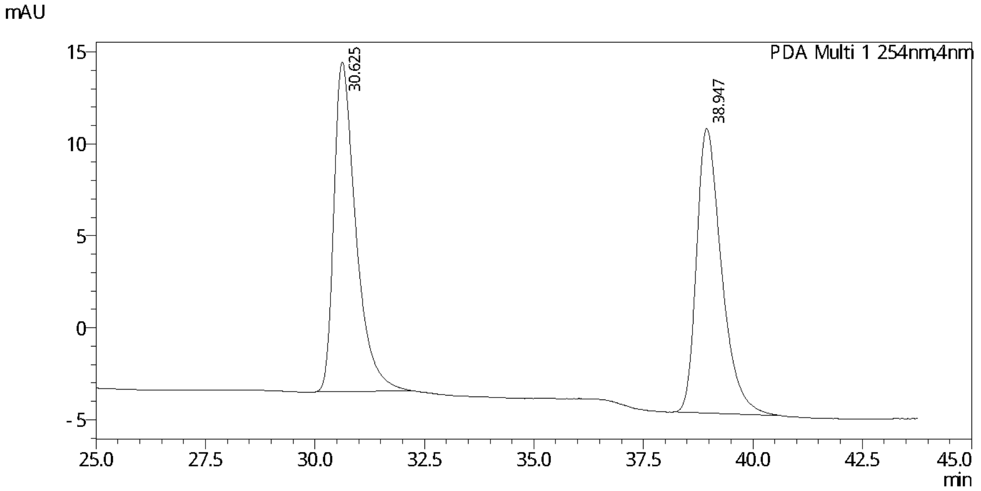


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
12.153	2.550
16.360	97.450
合計	100.000

3cj

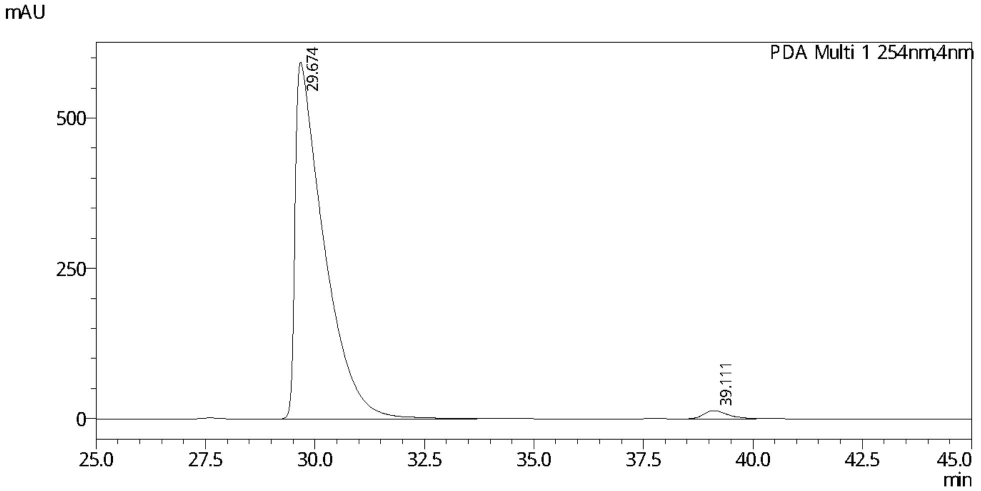
Daicel Chiralpak IB-3, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 29.7 min, t_R(minor) = 39.1 min.



<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	高さ	面積%
1	30.625	17910	50.433
2	38.947	15472	49.567
Total		33382	100.000

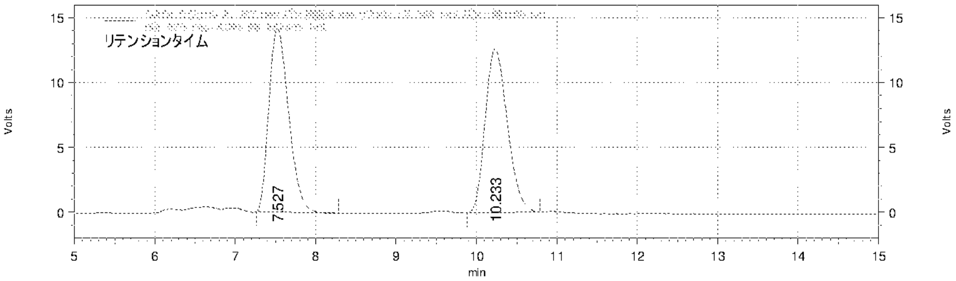


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	29.674	27212735	593773	98.064
2	39.111	537315	13746	1.936
Total		27750050	607519	100.000

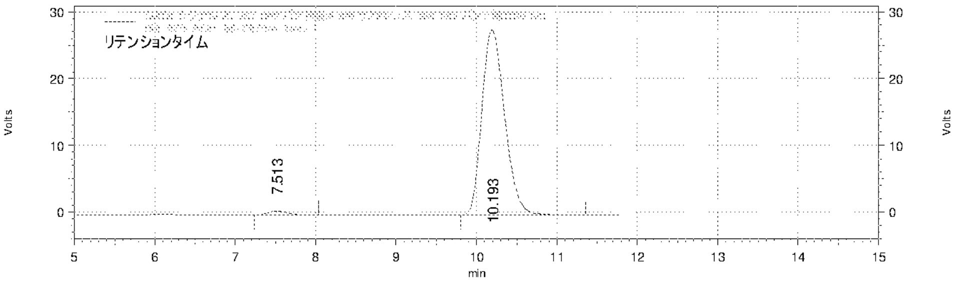
3dc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 7.5 min, t_R(major) = 10.2 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
7.527	49.949
10.233	50.051
合計	100.000

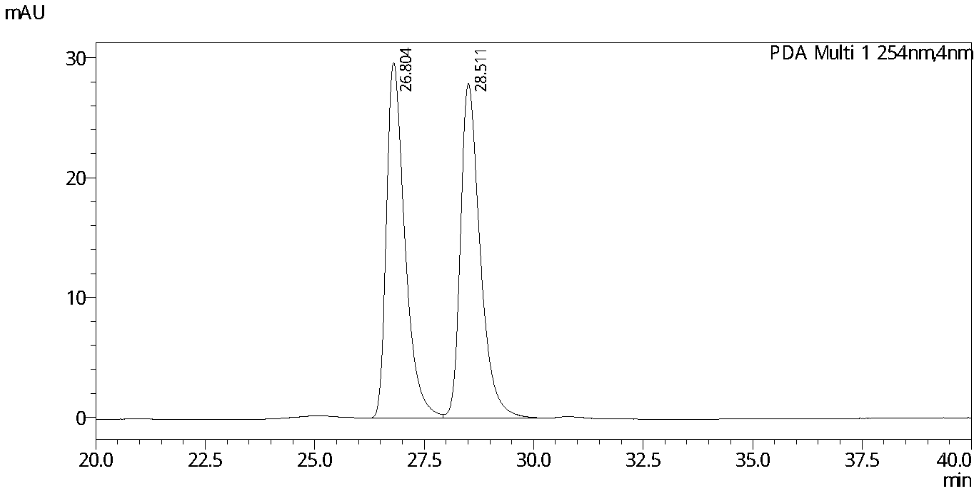


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
7.513	1.991
10.193	98.009
合計	100.000

3dj

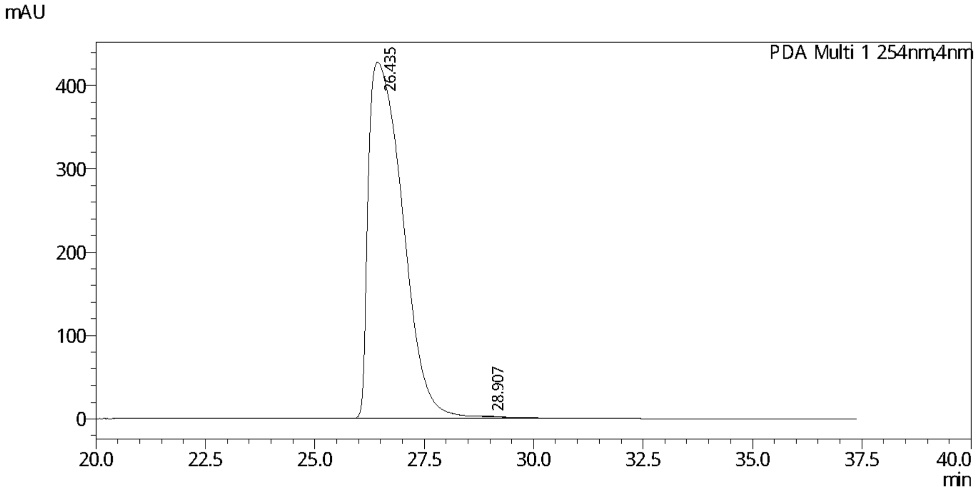
Daicel Chiralpak IB-3, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 26.4 min, t_R(minor) = 28.9 min.



<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	26.804	872611	29693	49.965
2	28.511	873831	27942	50.035
Total		1746442	57635	100.000



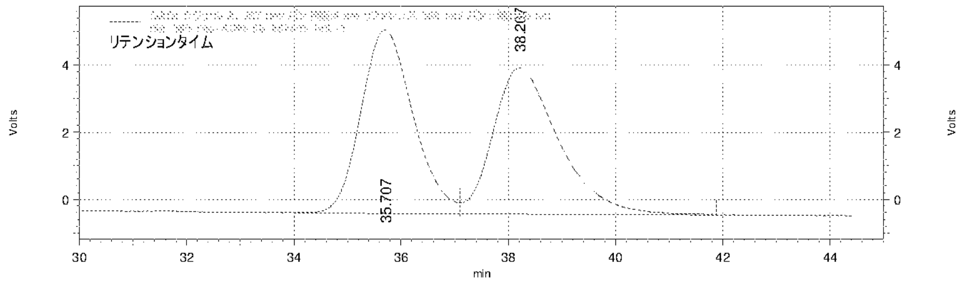
<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	26.435	23462447	427765	99.919
2	28.907	18906	804	0.081
Total		23481353	428569	100.000

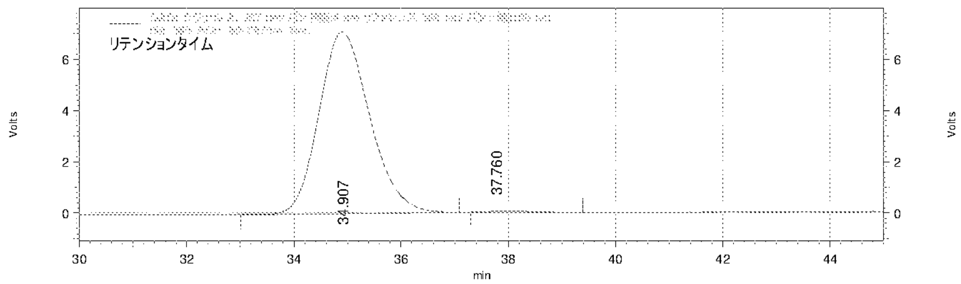
3ej

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 34.9 min, t_R(minor) = 37.8 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
35.707	49.942
38.207	50.058
合計	100.000

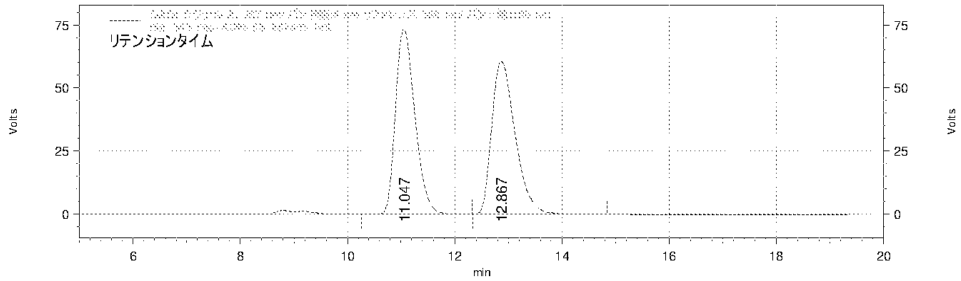


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
34.907	99.444
37.760	0.556
合計	100.000

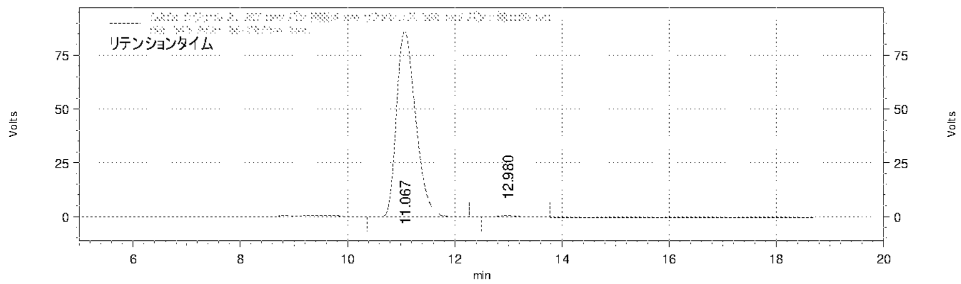
3fj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 11.1 min, t_R(minor) = 13.0 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
11.047	50.103
12.867	49.897
合計	100.000

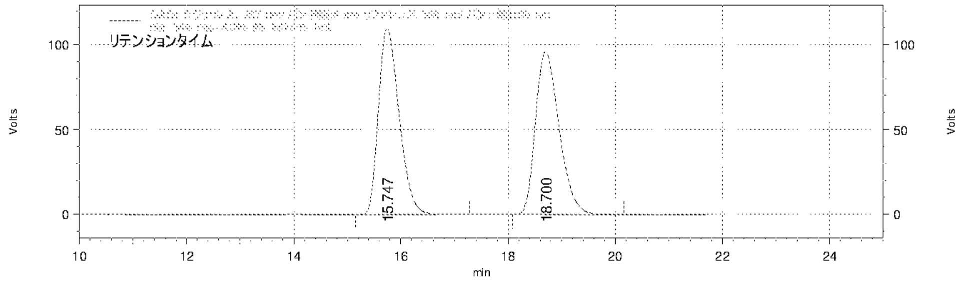


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
11.067	99.035
12.980	0.965
合計	100.000

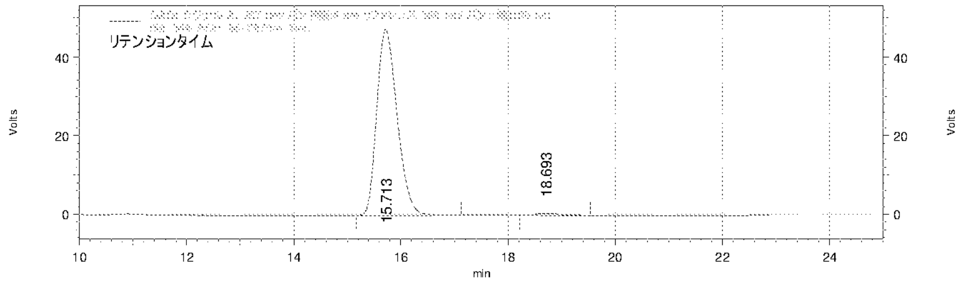
3gj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 15.7 min, t_R(minor) = 18.7 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
15.747	50.032
18.700	49.968
合計	100.000

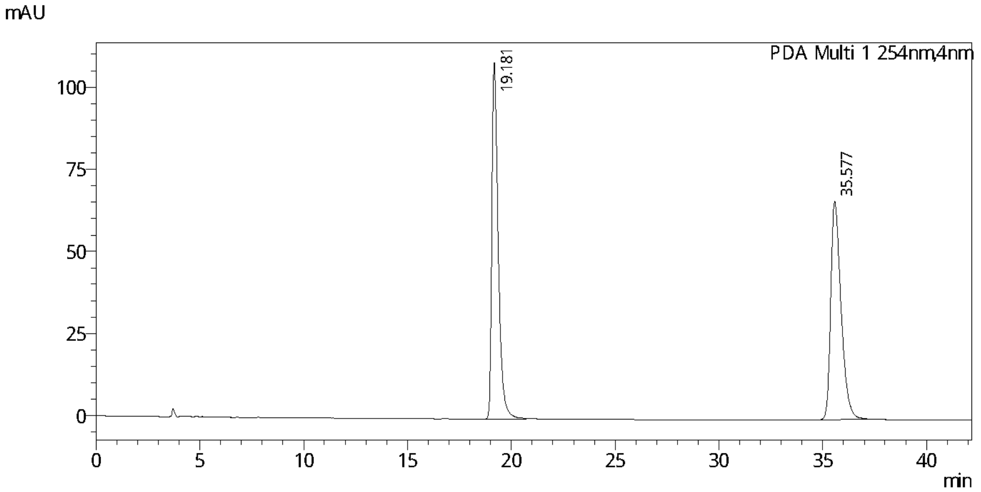


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
15.713	98.658
18.693	1.342
合計	100.000

3hj

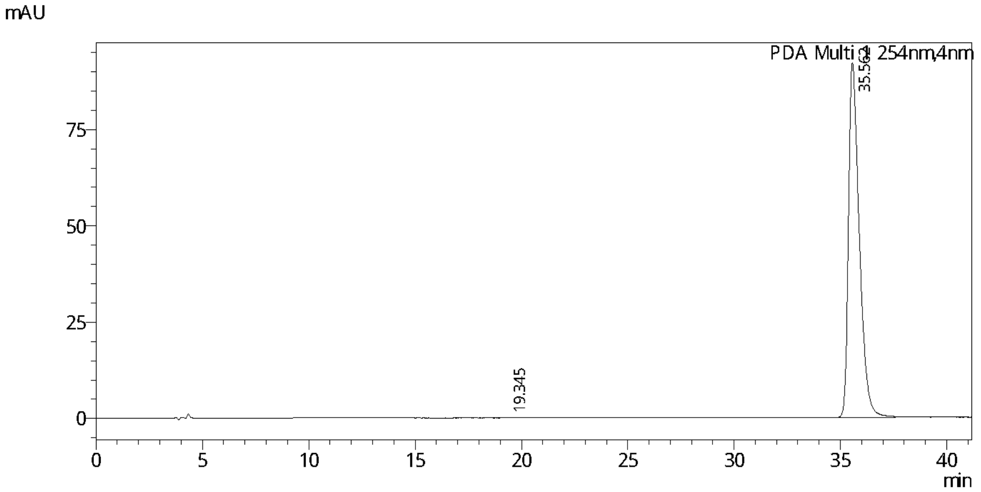
Daicel Chiralpak IB-3, hexane/*i*-PrOH = 93/7, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 19.3 min, t_R(major) = 35.6 min.



<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	19.181	2310640	108502	50.122
2	35.577	2299430	66476	49.878
Total		4610070	174978	100.000



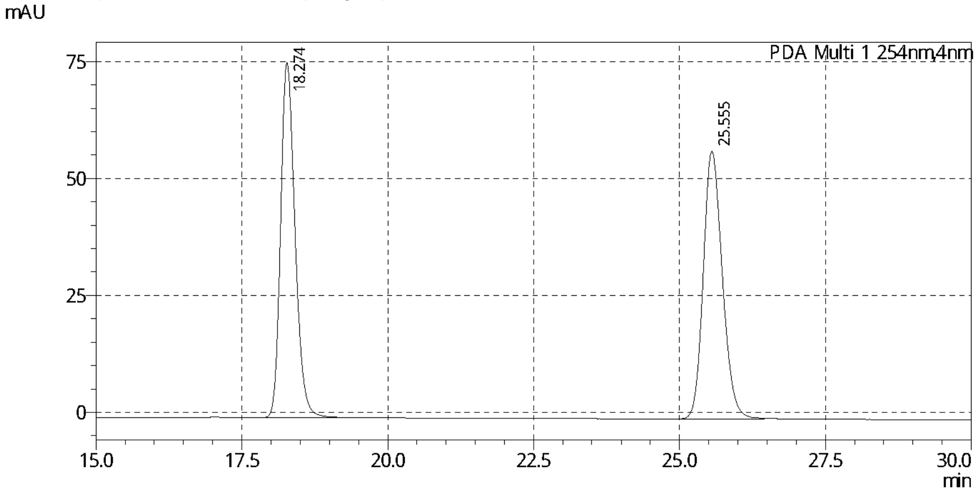
<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	19.345	3242	171	0.099
2	35.562	3267939	92141	99.901
Total		3271181	92312	100.000

3ij

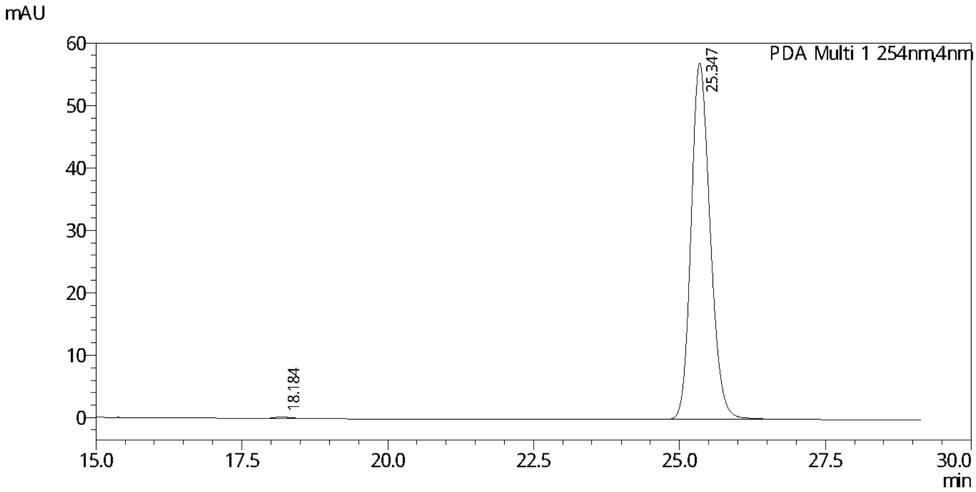
Daicel Chiralpak IB-3, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 18.1 min, t_R(major) = 25.3 min.



<ピークレポート>

PDA Ch1 254nm

ﾋﾟｰｸ#	保持時間	面積	高さ	面積%
1	18.274	1304782	75965	50.104
2	25.555	1299368	57218	49.896
Total		2604150	133183	100.000



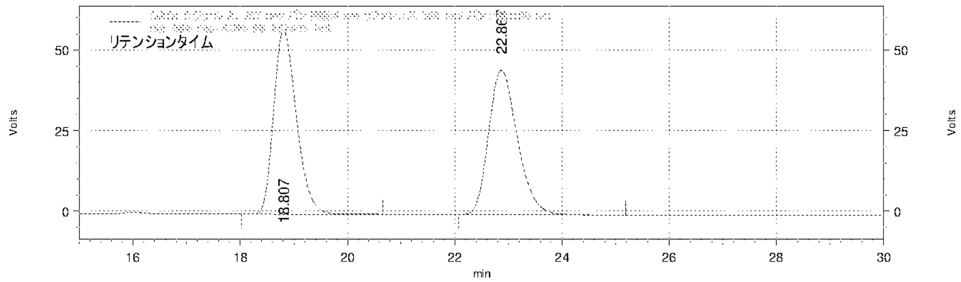
<ピークレポート>

PDA Ch1 254nm

ﾋﾟｰｸ#	保持時間	面積	高さ	面積%
1	18.184	4830	300	0.371
2	25.347	1297362	57091	99.629
Total		1302192	57390	100.000

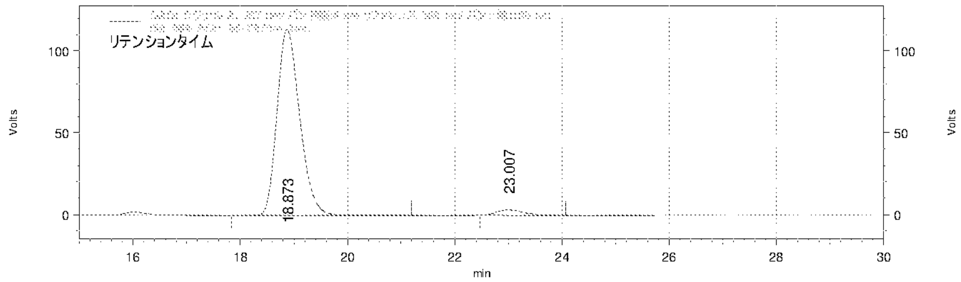
3jj

Daicel Chiralpak IB-3, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 21.8 min, t_R(major) = 28.7 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.807	50.142
22.867	49.858
合計	100.000

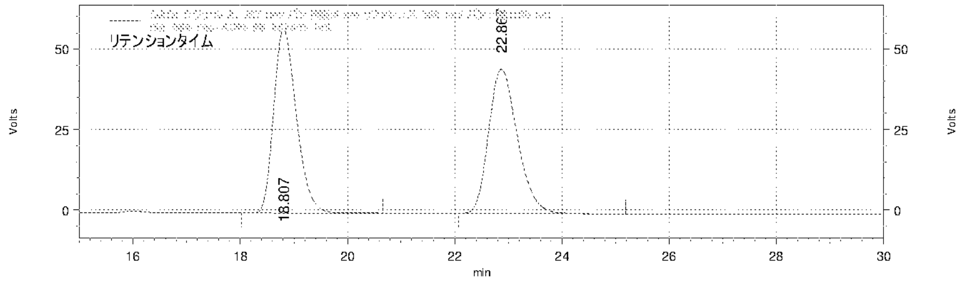


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.873	96.560
23.007	3.440
合計	100.000

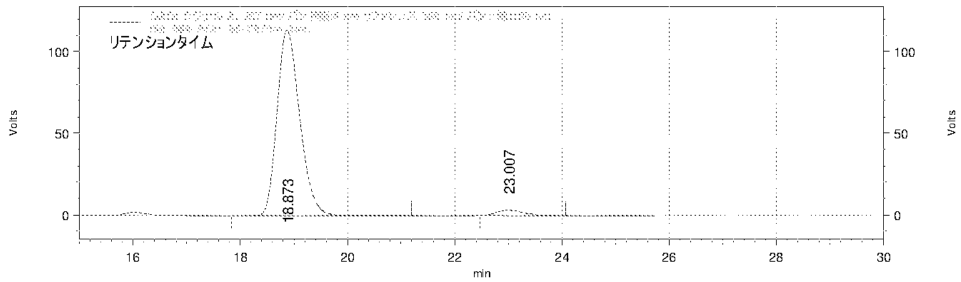
3kc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 18.9 min, t_R(minor) = 23.0 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.807	50.142
22.867	49.858
合計	100.000

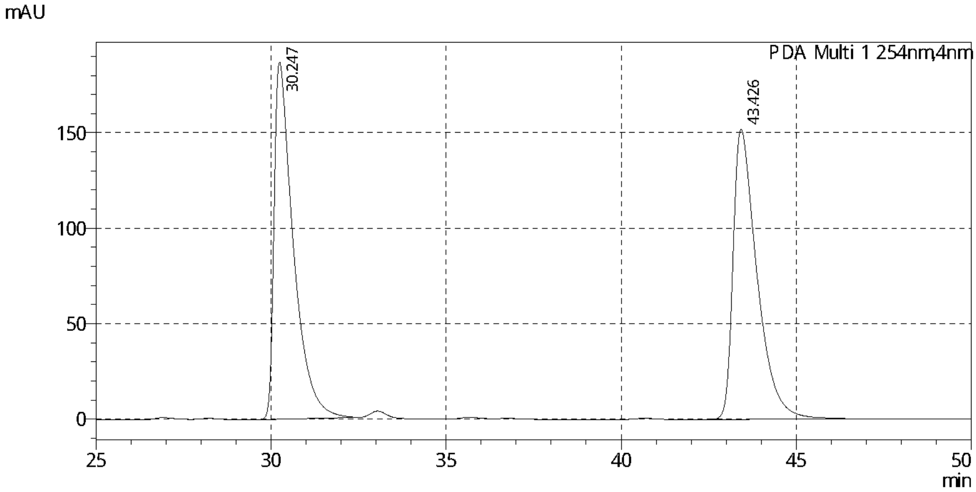


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.873	96.560
23.007	3.440
合計	100.000

3kj

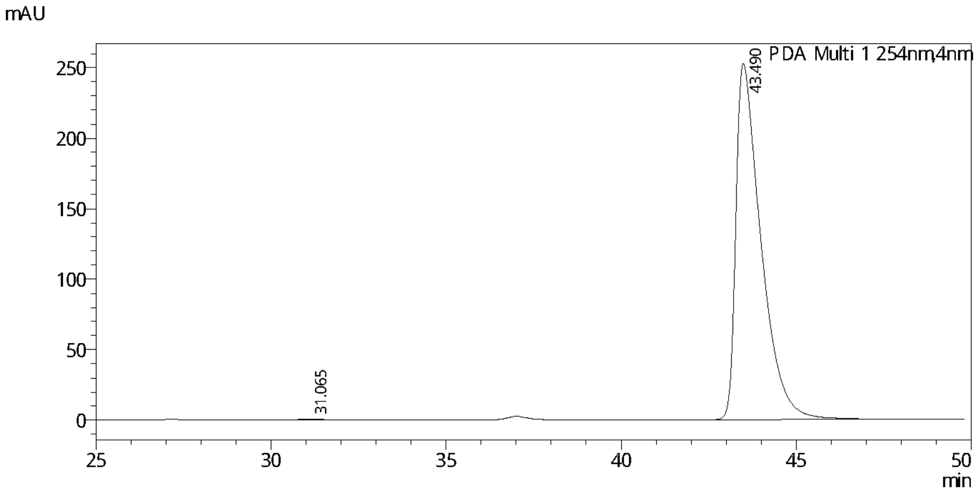
Daicel Chiralpak IB-3, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 31.1 min, t_R(major) = 43.5 min.



<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	30.247	7144850	186978	49.727
2	43.426	7223297	152007	50.273
Total		14368147	338985	100.000



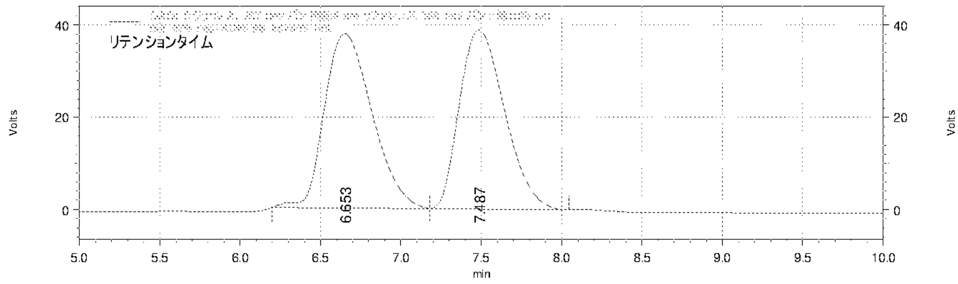
<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	31.065	13765	400	0.109
2	43.490	12571889	252645	99.891
Total		12585654	253044	100.000

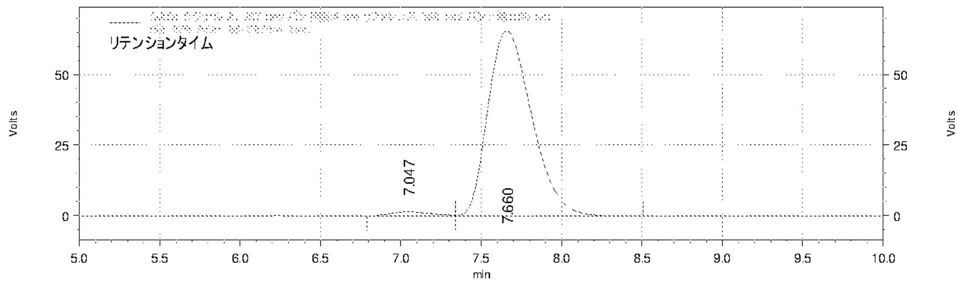
3lc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 7.0 min, t_R(major) = 7.7 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
6.653	50.558
7.487	49.442
合計	100.000

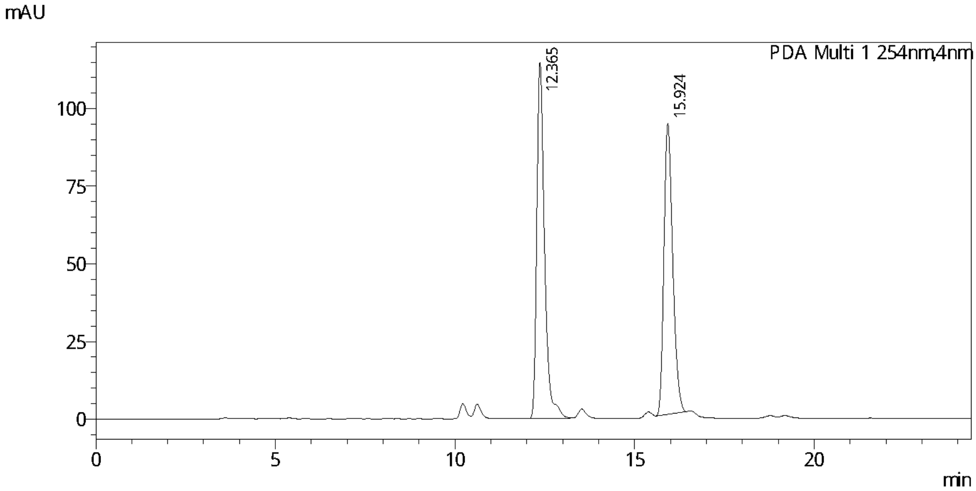


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
7.047	1.926
7.660	98.074
合計	100.000

3lj

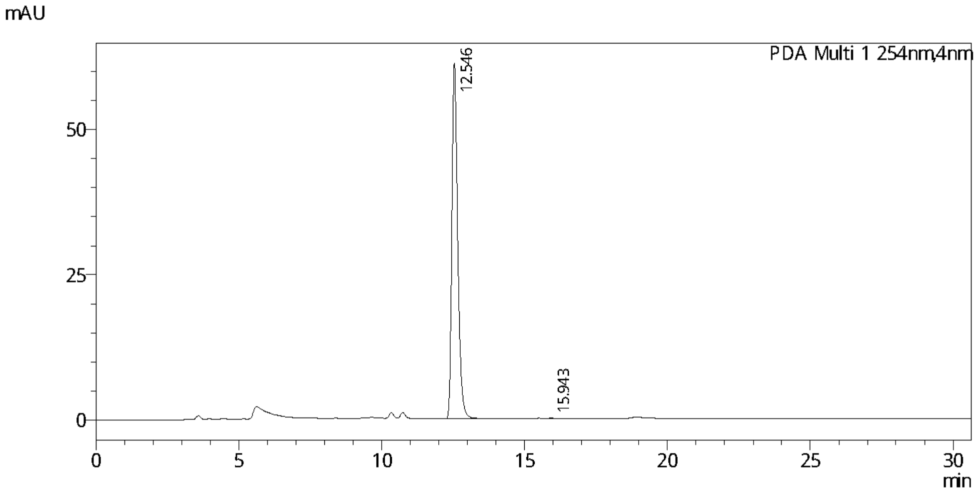
Daicel Chiralpak IA-3, hexane/*i*-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 12.5 min, t_R(minor) = 15.9 min.



<ピークレポート>

PDA Ch1 254nm

ﾋﾟｰｸ#	保持時間	面積	高さ	面積%
1	12.365	1720929	114770	51.877
2	15.924	1596372	93682	48.123
Total		3317301	208452	100.000



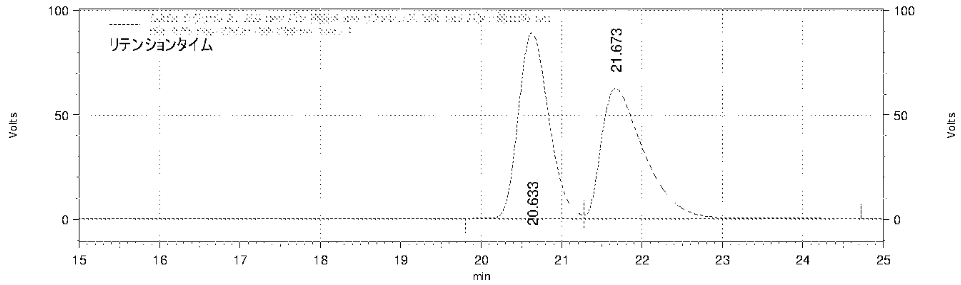
<ピークレポート>

PDA Ch1 254nm

ﾋﾟｰｸ#	保持時間	面積	高さ	面積%
1	12.546	869495	61222	99.868
2	15.943	1147	90	0.132
Total		870642	61312	100.000

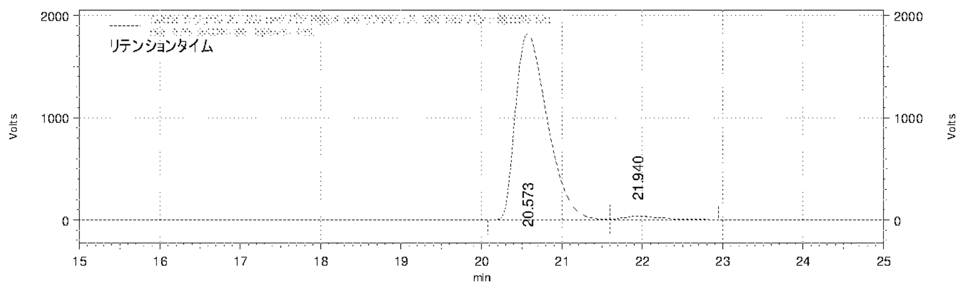
3mc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 20.6 min, t_R(minor) = 21.9 min.



DAD: シグナル A, 259 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
20.633	50.472
21.673	49.528
合計	100.000

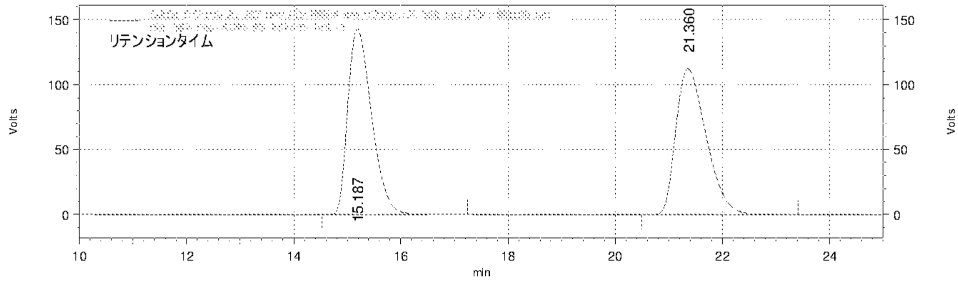


DAD: シグナル A, 259 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
20.573	97.834
21.940	2.166
合計	100.000

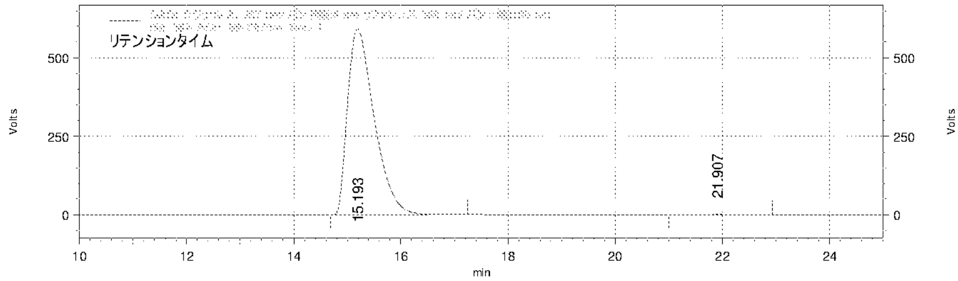
3mj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 15.2 min, t_R(minor) = 21.9 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
15.187	50.134
21.360	49.866
合計	100.000

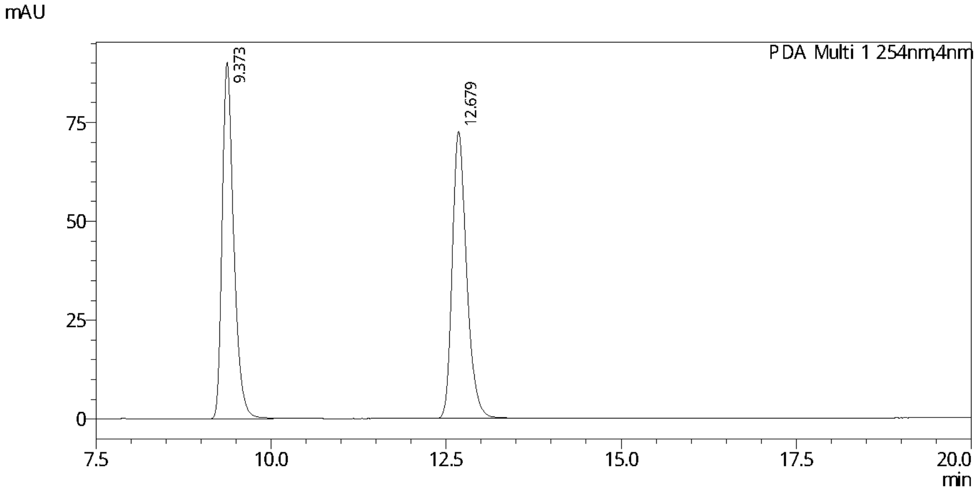


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
15.193	99.884
21.907	0.116
合計	100.000

3nj

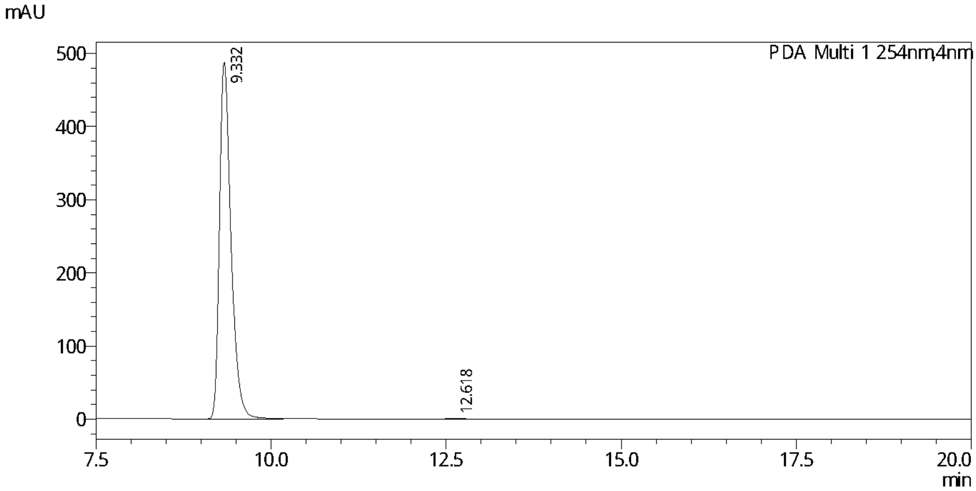
Daicel Chiralpak IA-3, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 9.3 min, t_R(minor) = 12.6 min.



<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	9.373	1034366	90236	49.917
2	12.679	1037789	72675	50.083
Total		2072155	162910	100.000



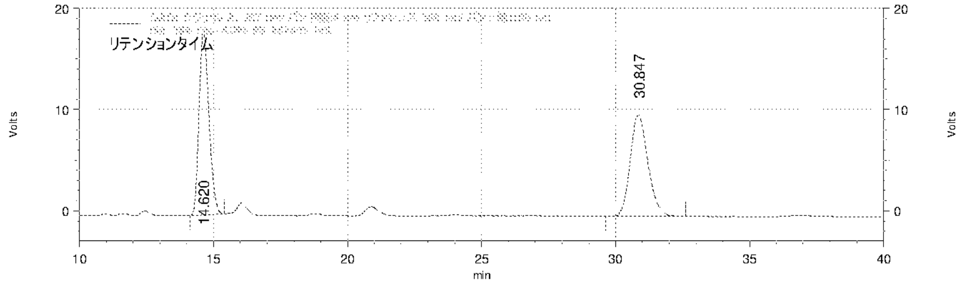
<ピークレポート>

PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%
1	9.332	5587117	487794	99.776
2	12.618	12532	905	0.224
Total		5599649	488699	100.000

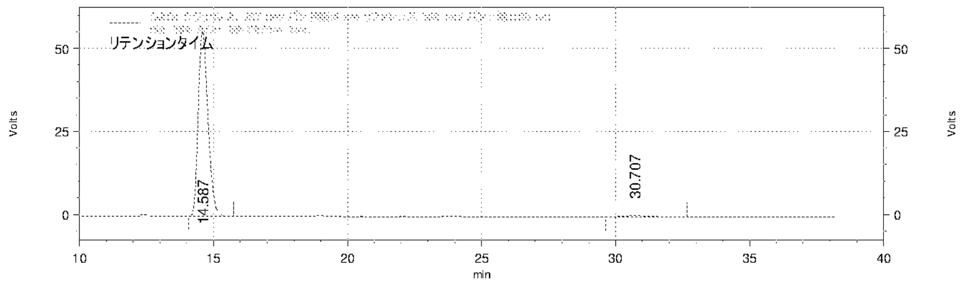
3oj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 14.6 min, t_R(minor) = 30.7 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
14.620	50.237
30.847	49.763
合計	100.000

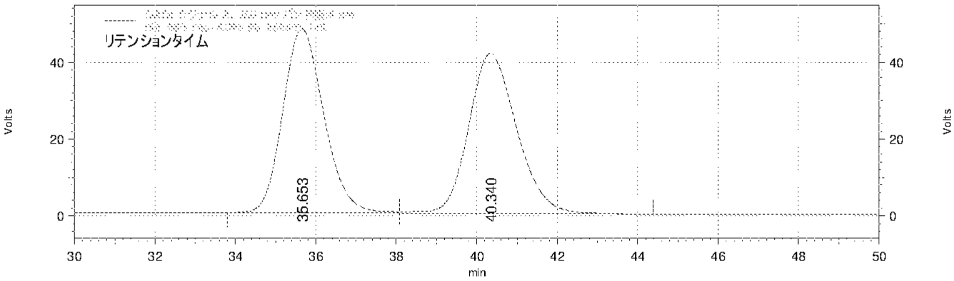


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
14.587	98.490
30.707	1.510
合計	100.000

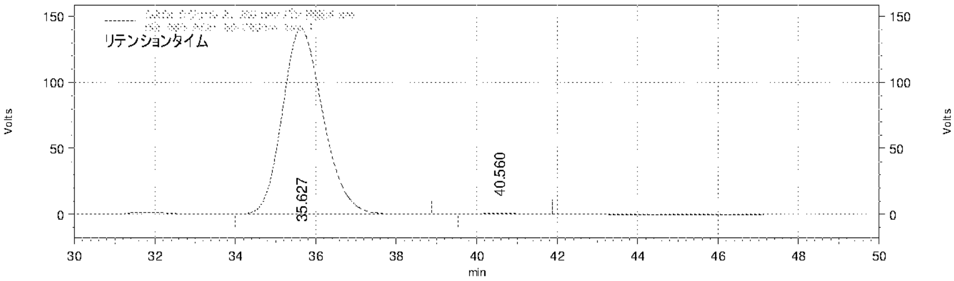
3pc

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 35.6 min, t_R(minor) = 40.6 min.



DAD: シグナル A, 250 nm/ バンド幅:4 nm 結果

リテンションタイム	面積%
35.653	49.557
40.340	50.443
合計	100.000

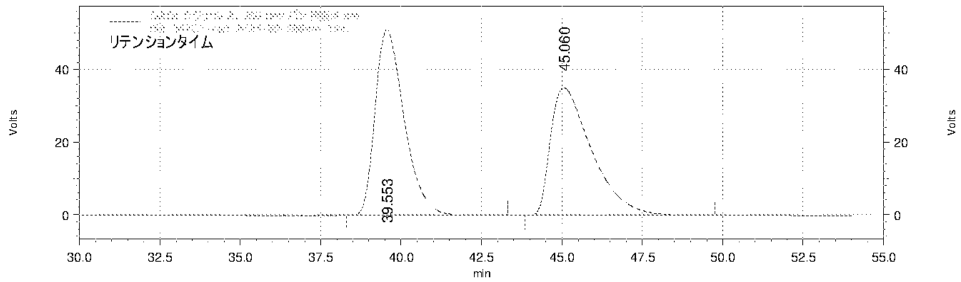


DAD: シグナル A, 260 nm/ バンド幅:4 nm 結果

リテンションタイム	面積%
35.627	99.425
40.560	0.575
合計	100.000

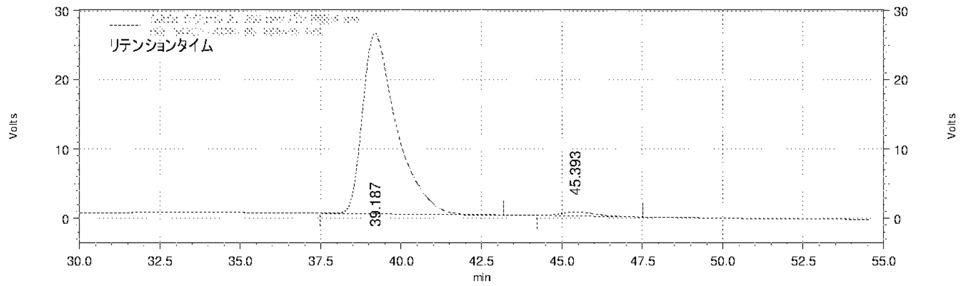
3pj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 39.2 min, t_R(minor) = 45.4 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm 結果

リテンションタイム	面積%
39.553	50.785
45.060	49.215
合計	100.000

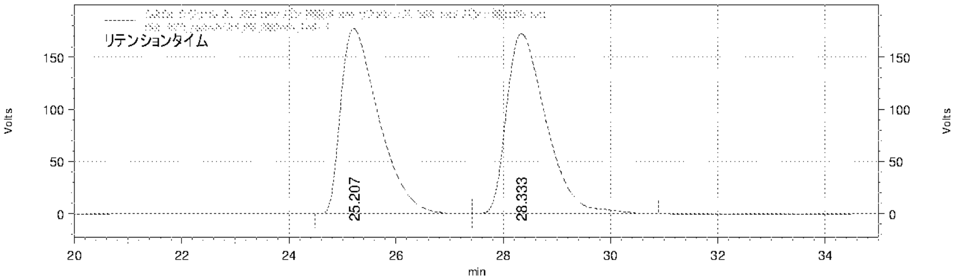


DAD: シグナル A, 260 nm/ バンド幅:4 nm 結果

リテンションタイム	面積%
39.187	97.760
45.393	2.240
合計	100.000

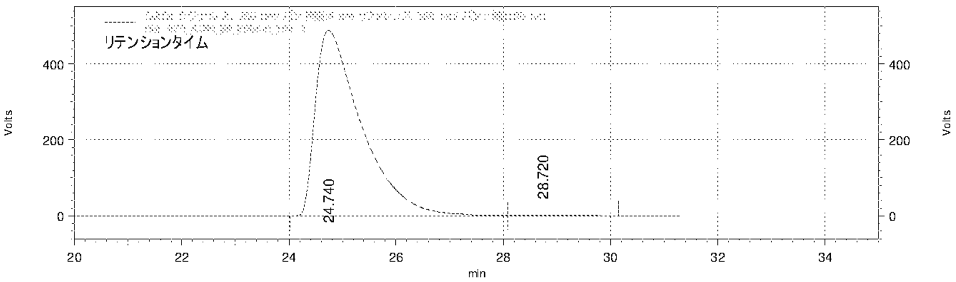
3qj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 24.7 min, t_R(minor) = 28.7 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
25.207	49.651
28.333	50.349
合計	100.000

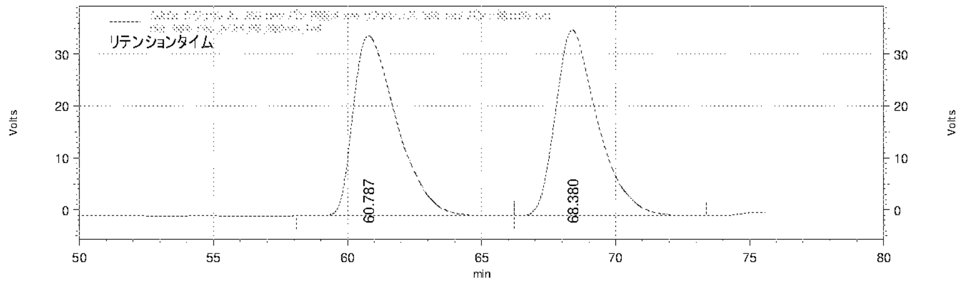


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
24.740	99.641
28.720	0.359
合計	100.000

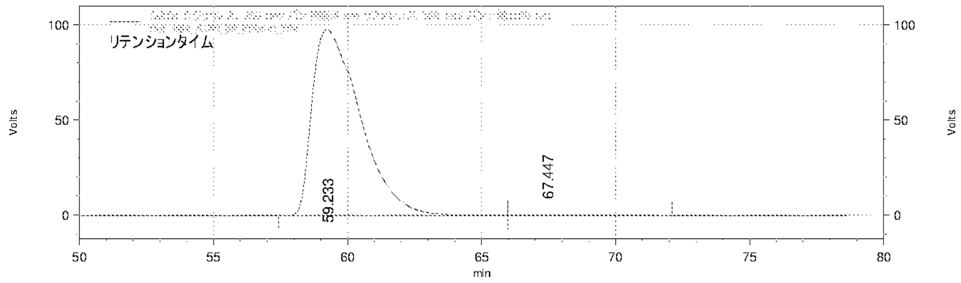
3rj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 59.2 min, t_R(minor) = 67.4 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
60.787	50.050
68.380	49.950
合計	100.000

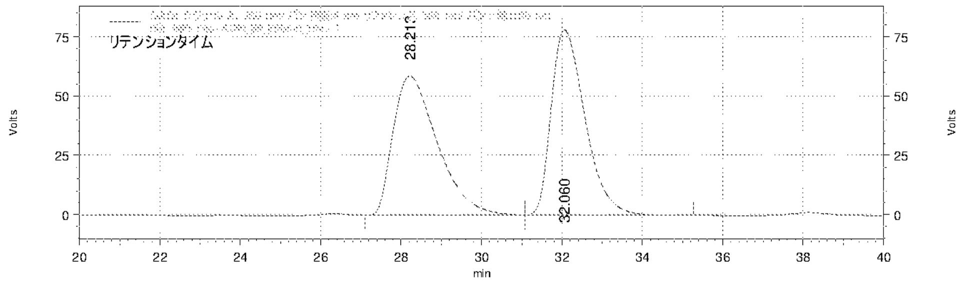


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
59.233	99.659
67.447	0.341
合計	100.000

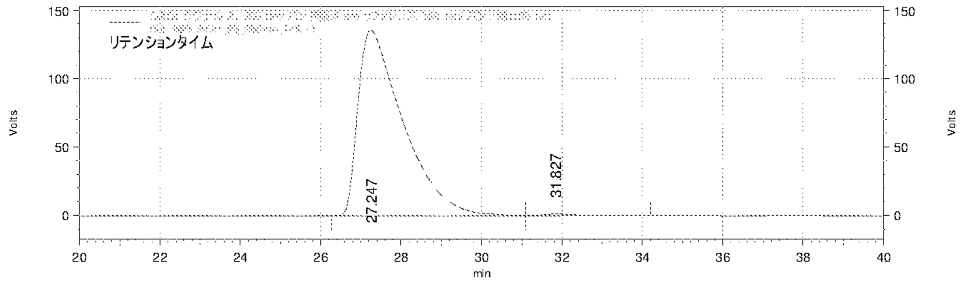
3sj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 27.2 min, t_R(minor) = 31.8 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
28.213	49.572
32.060	50.428
合計	100.000

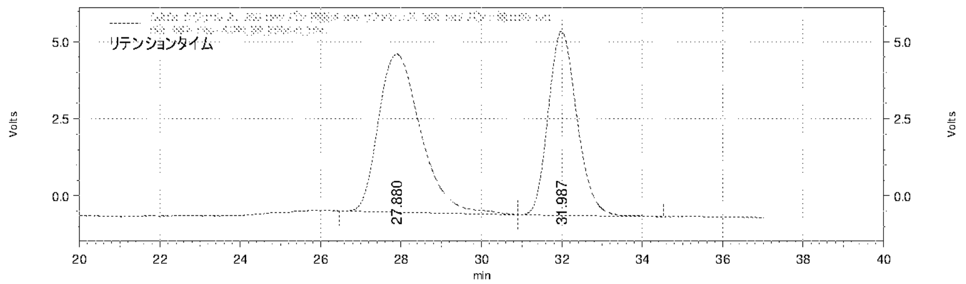


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
27.247	99.320
31.827	0.680
合計	100.000

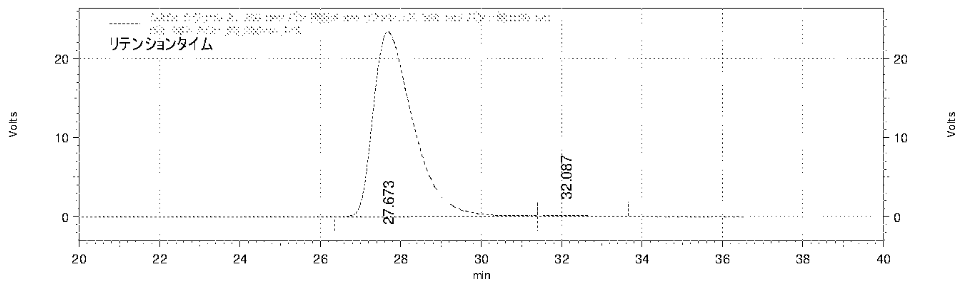
3tj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 27.7 min, t_R(minor) = 32.1 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
27.880	55.852
31.987	44.148
合計	100.000

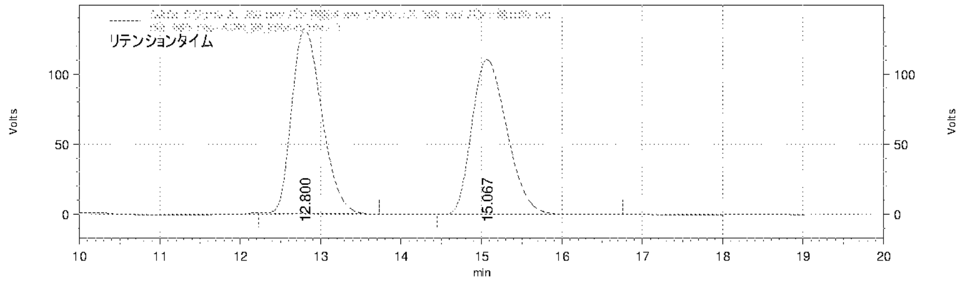


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
27.673	99.490
32.087	0.510
合計	100.000

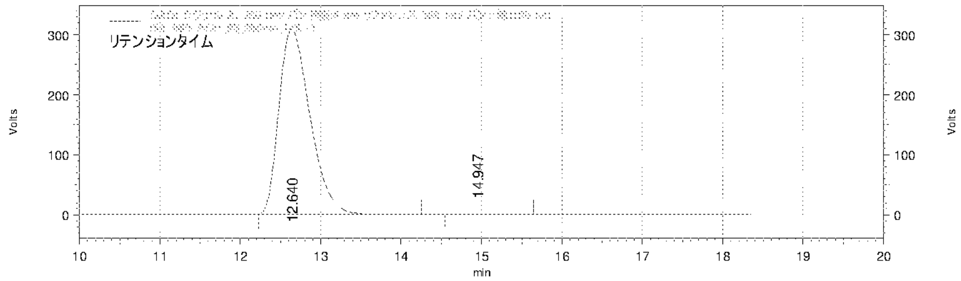
3uj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(major) = 12.6 min, t_R(minor) = 14.9 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
12.800	50.364
15.067	49.636
合計	100.000

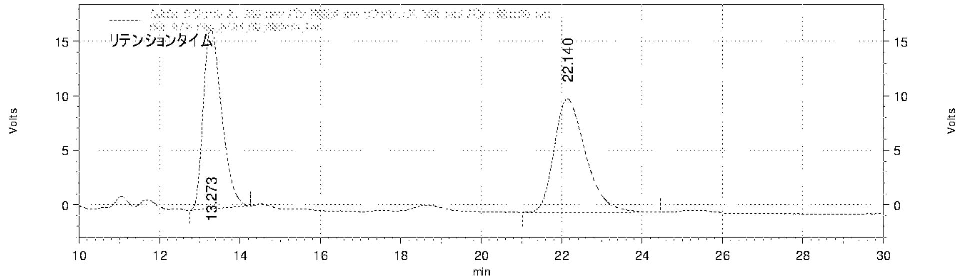


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
12.640	99.867
14.947	0.133
合計	100.000

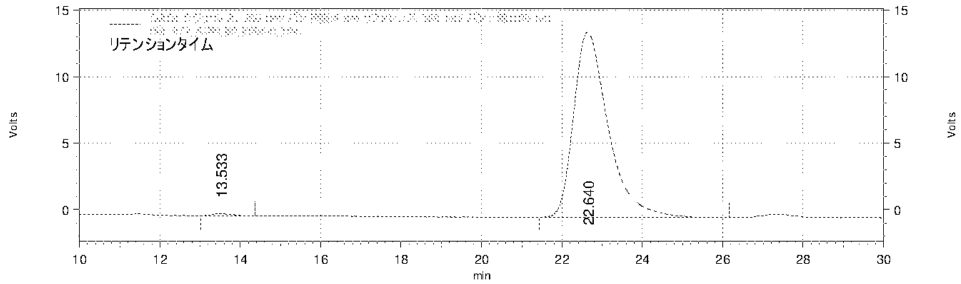
3vj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R(minor) = 13.5 min, t_R(major) = 22.6 min.



DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
13.273	48.034
22.140	51.966
合計	100.000

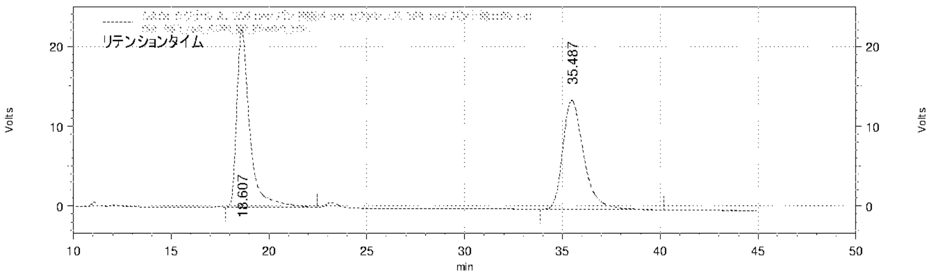


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
13.533	0.647
22.640	99.353
合計	100.000

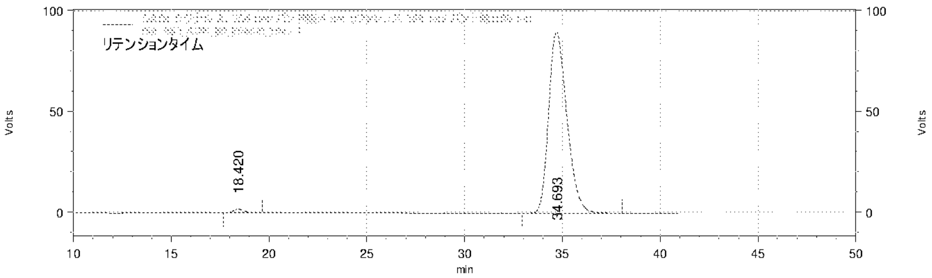
3wj

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(minor) = 18.4 min, t_R(major) = 34.7 min.



DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.607	50.095
35.487	49.905
合計	100.000

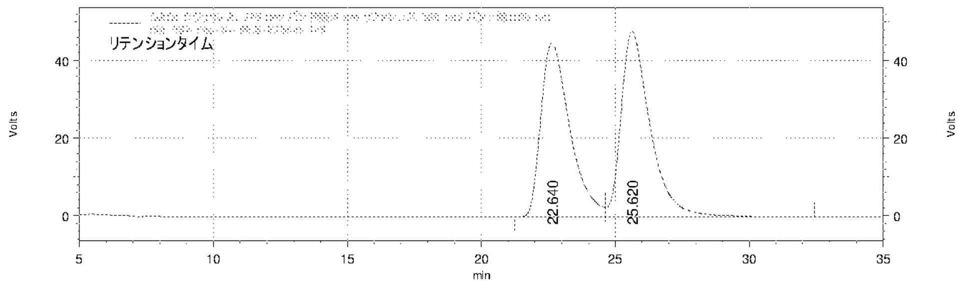


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.420	1.230
34.693	98.770
合計	100.000

3ad

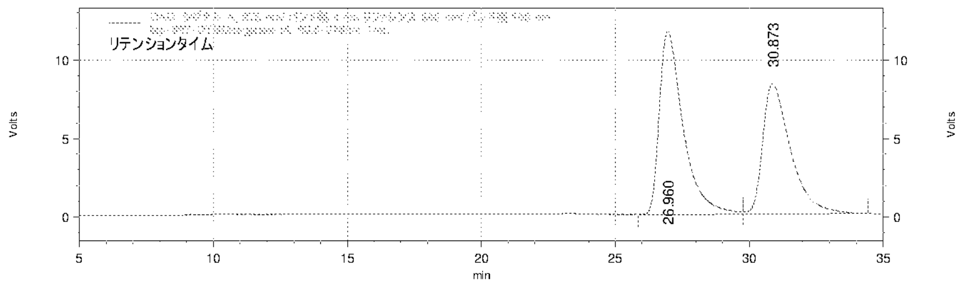
Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 16.5 min, t_R(major) = 17.4 min.



DAD: シグナル A, 275 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
22.640	48.186
25.620	51.814

合計	
	100.000



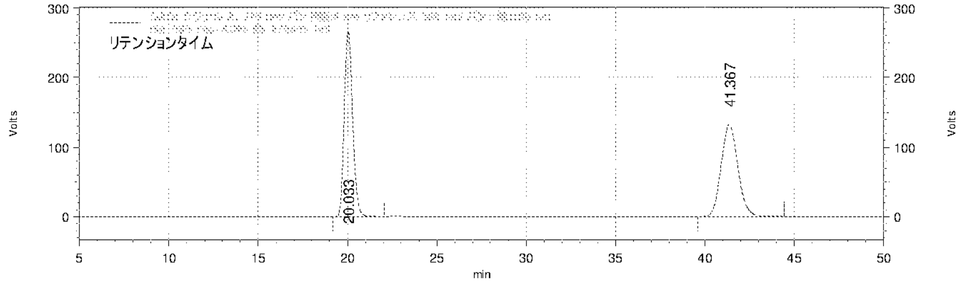
DAD: シグナル A, 275 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
26.960	54.599
30.873	45.401

合計	
	100.000

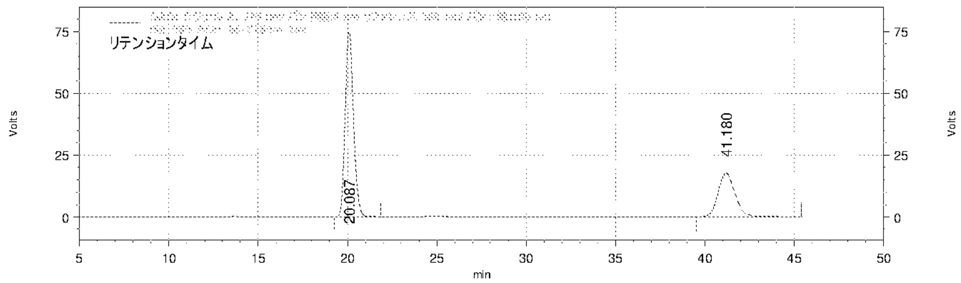
3ae

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 275 nm, retention time; t_R(major) = 20.1 min, t_R(minor) = 41.2 min.



DAD: シグナル A, 275 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
20.033	50.117
41.367	49.883
合計	100.000

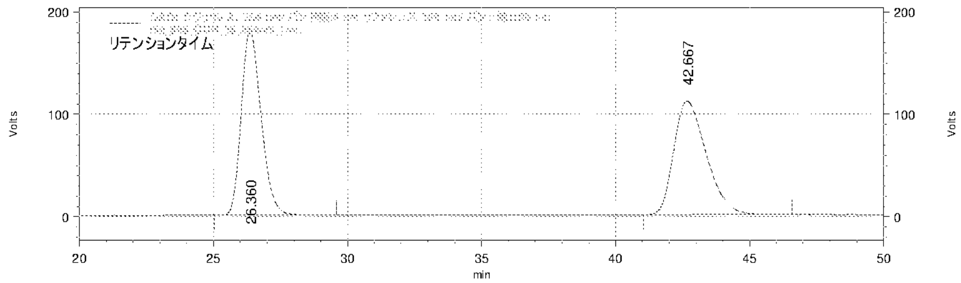


DAD: シグナル A, 275 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
20.087	67.634
41.180	32.366
合計	100.000

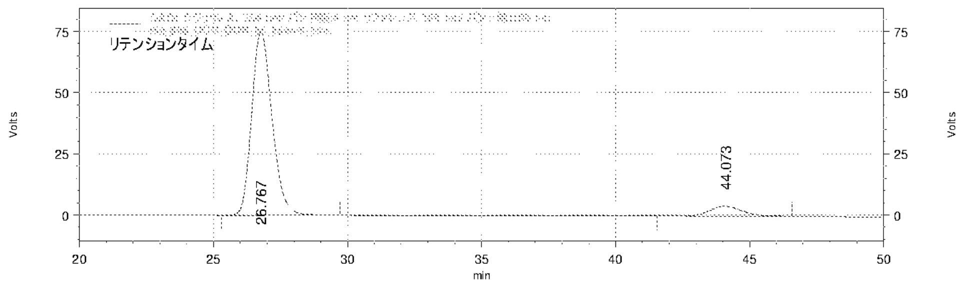
3af

Daicel Chiralpak OD-H, hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 26.8 min, t_R(minor) = 44.1 min.



DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
26.360	49.933
42.667	50.067
合計	100.000

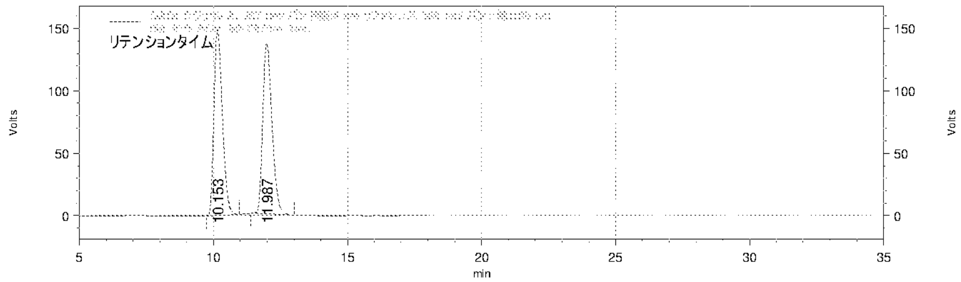


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
26.767	91.916
44.073	8.084
合計	100.000

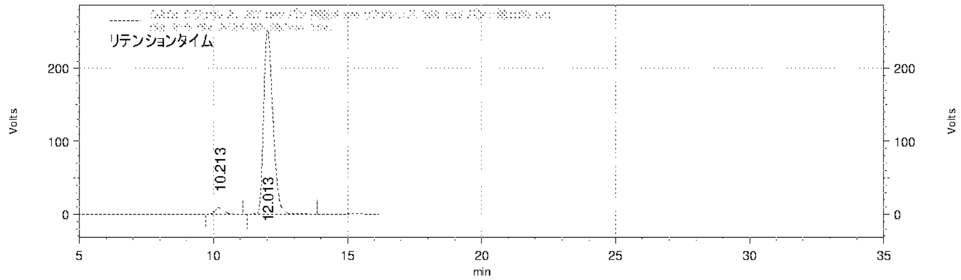
3ag

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(minor) = 10.2 min, t_R(major) = 12.0 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
10.153	49.716
11.987	50.284
合計	100.000

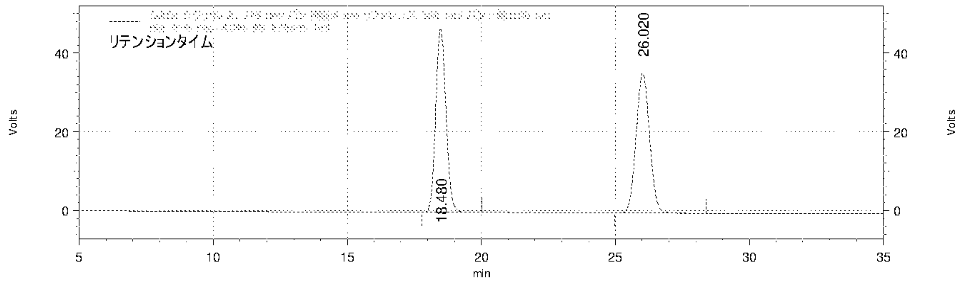


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
10.213	3.058
12.013	96.942
合計	100.000

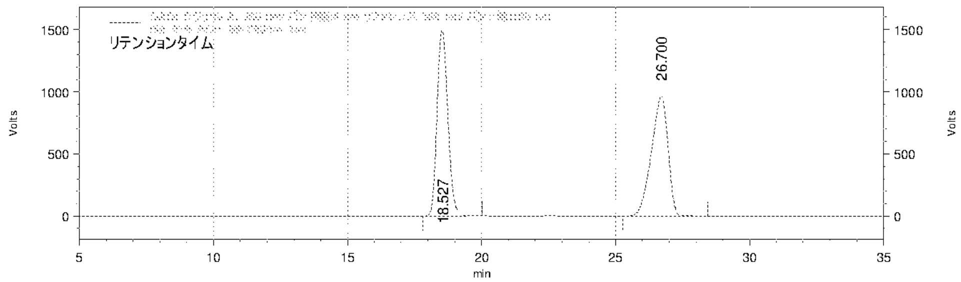
3ah

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 260 nm, retention time; t_R = 18.5 min, t_R = 26.7 min.



DAD: シグナル A, 275 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.480	49.931
26.020	50.069
合計	100.000

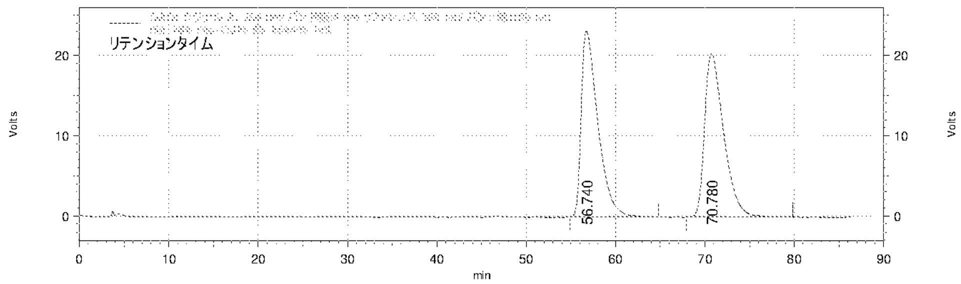


DAD: シグナル A, 260 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.527	50.126
26.700	49.874
合計	100.000

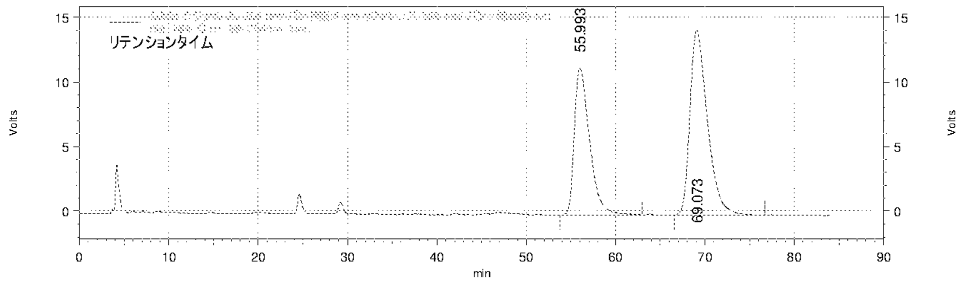
3ai

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 275 nm, retention time; t_R(minor) = 56.0 min, t_R(major) = 69.1 min.



DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
56.740	49.833
70.780	50.167
合計	100.000

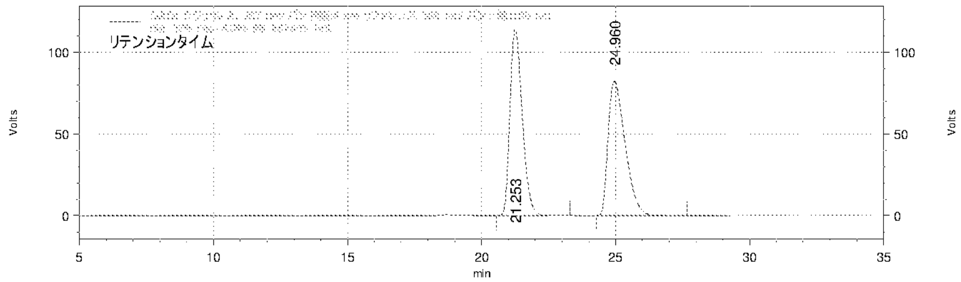


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
55.993	40.909
69.073	59.091
合計	100.000

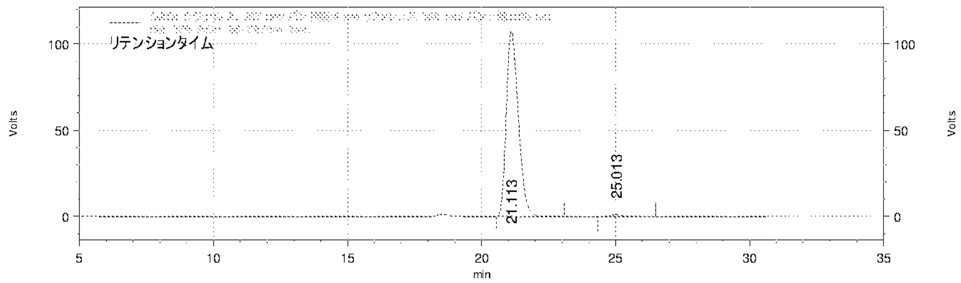
3ak

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 267 nm, retention time; t_R(major) = 21.1 min, t_R(minor) = 25.0 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果
リテンションタイム

リテンションタイム	面積%
21.253	50.156
24.960	49.844
合計	100.000

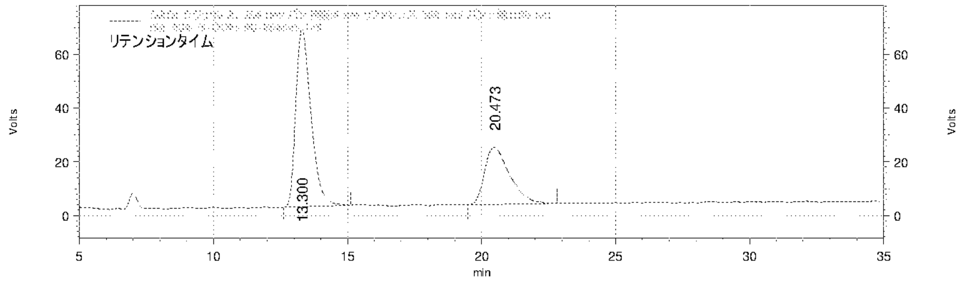


DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果
リテンションタイム

リテンションタイム	面積%
21.113	98.907
25.013	1.093
合計	100.000

3am

Daicel Chiralpak OD-H, hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 13.3 min, t_R(minor) = 20.5 min.

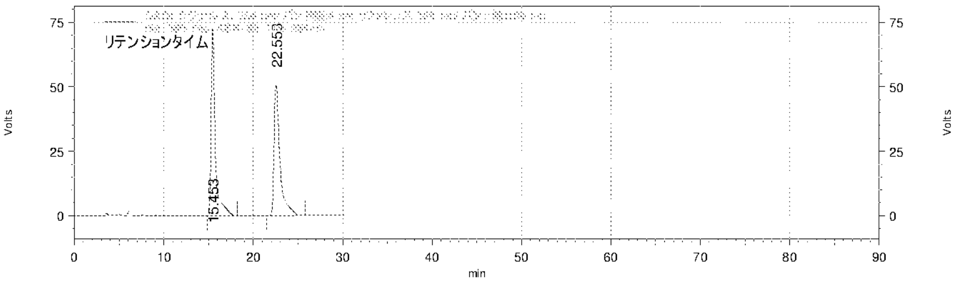


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
13.300	65.408
20.473	34.592
合計	100.000

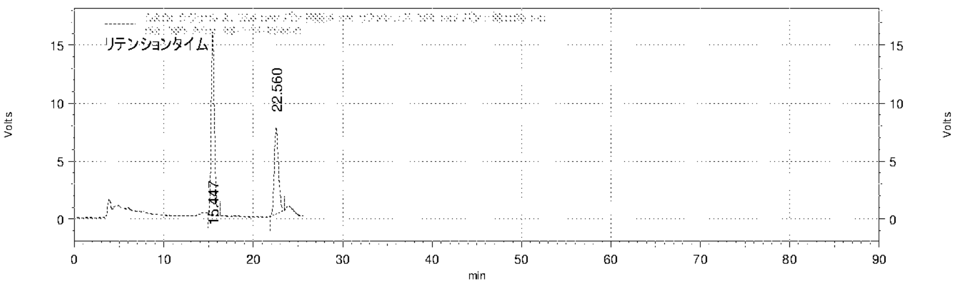
3an

Daicel Chiralpak AS-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R(major) = 15.4 min, t_R(minor) = 22.6 min.



DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
15.453	49.892
22.553	50.108
合計	100.000

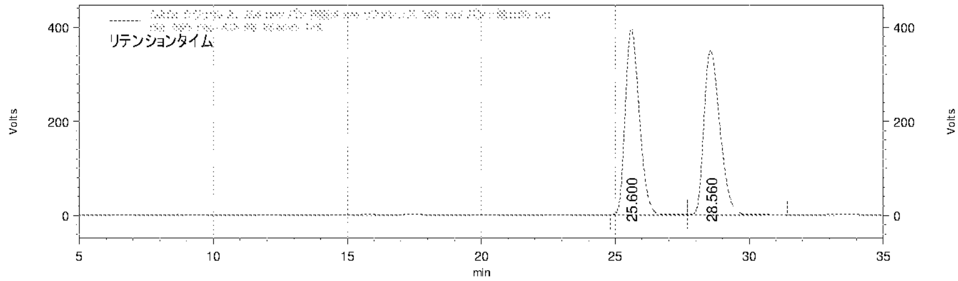


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
15.447	61.942
22.560	38.058
合計	100.000

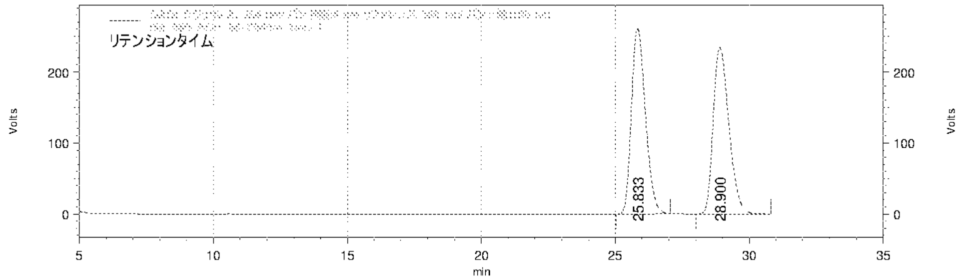
3ao

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R = 25.8 min, t_R = 28.9 min.



DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
25.600	50.009
28.560	49.991
合計	100.000

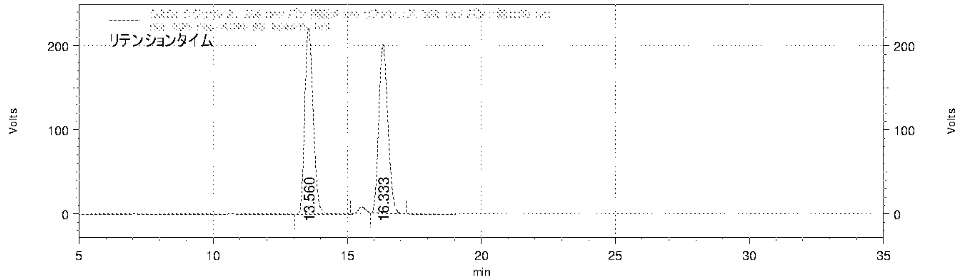


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
25.833	49.867
28.900	50.133
合計	100.000

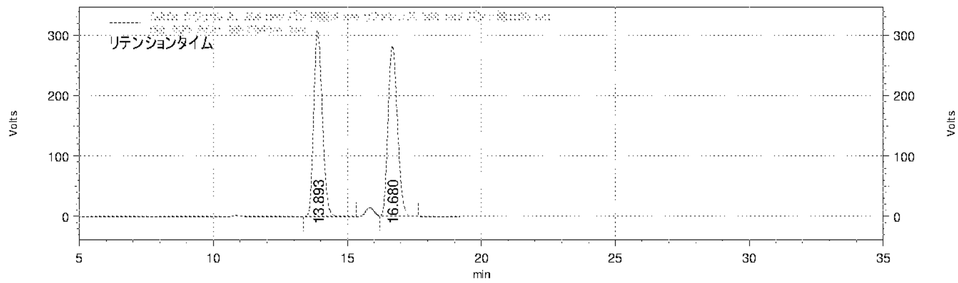
3ap

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R = 13.9 min, t_R = 16.7 min.



DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
13.560	50.406
16.333	49.594
合計	100.000

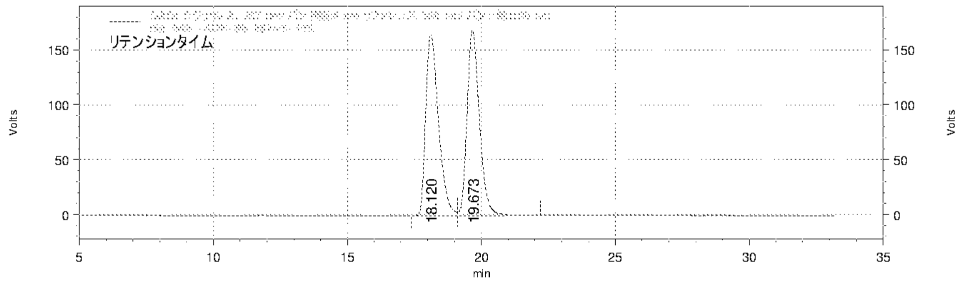


DAD: シグナル A, 254 nm/ バンド幅:4 nm リファレンス 360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
13.893	50.296
16.680	49.704
合計	100.000

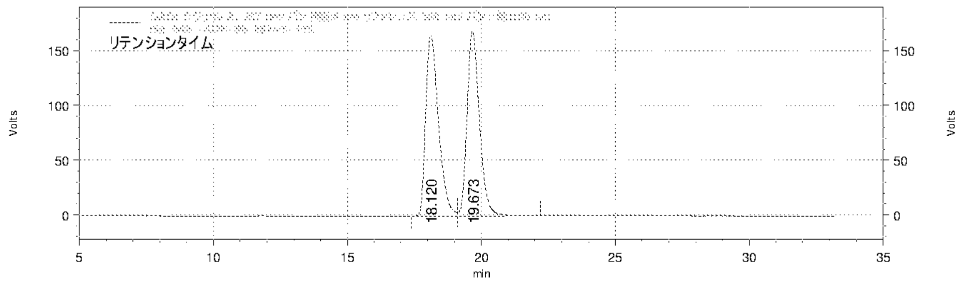
3aq

Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time; t_R = 18.1 min, t_R = 19.7 min.



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.120	50.061
19.673	49.939
合計	100.000



DAD: シグナル A, 267 nm/ バンド幅:4 nm リファレンス
360 nm/ バンド幅:100 nm 結果

リテンションタイム	面積%
18.120	50.061
19.673	49.939
合計	100.000