Oxathiaborolium-Catalyzed Enantioselective [2+2] Cycloadditions

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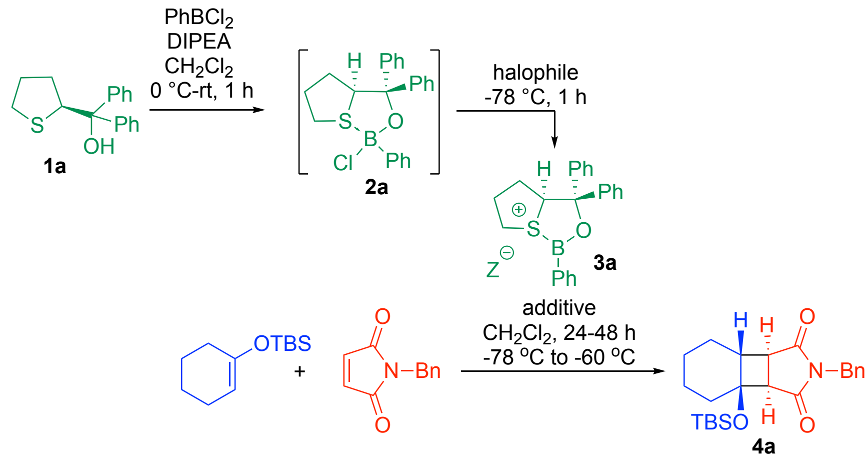
Table S1 Screening various halophiles and additives for the [2+2] cycloaddition reaction[a]



entry	halophile	additive (30 mol%)	**4a** yield[c] (*exo*:*endo*)[d]	**4a** ee[e]
1[e]	$SnCl_4$	-	62% (20:1)	96%
2[e]	$AlCl_3$	-	0	NA
3[e]	BCl_3	-	0	NA
4	$SnCl_4$	2,6-DTBP	50% (20:1)	96%
5	$SnCl_4$	TBDMSCl	54% (20:1)	96%
6	$SnCl_4$	TMSCl	50% (20:1)	96%
7	$SnCl_4$	TBSOTf	62% (20:1)	96%
8	$SnCl_4$	4 Å MS	0	NA

[a]Reactions were carried out in Schlenk tubes under nitrogen with catalyst **3** prepared using a 1:1:2:1.9 **1a**:$PhBCl_2$:DIPEA:$SnCl_4$ reagent ratio. [b]Isolated yield. [c]*Exo*/*endo* ratio was determined by NMR spectroscopy. [d]*Ee* determined by chiral HPLC. [e]A 1:1:1:0.9 **1a**:$PhBCl_2$:DIPEA:halophile ratio was used. (NA: not available).

General information

Unless stated otherwise, the reactions were performed in flame-dried glassware under a positive pressure of nitrogen. The progress of all the reactions were monitored by TLC using TLC glass plates precoated with silica gel 60 F_{254} (Merck). The visualization of TLC was done with UV, $KMnO_4$ stain, ammonium molybdate stain. Column chromatography was performed on silica gel Geduran® Si 60 (230-400 mesh) (Merck). ^{1}H and ^{13}C NMR spectra were recorded in Bruker AV-400 MHz, AVIII-400 MHz, AV-500 MHz or AVIII-500 MHz spectrometers and chemical shifts were measured in δ (ppm) with residual solvent peaks as internal standards ($CDCl_3$, δ 7.26 ppm in ^{1}H NMR, δ 77.0 ppm in ^{13}C NMR). Abbreviations in the NMR data are m = multiplet, s = singlet, d = doublet, t = triplet, br = broad, dd = doublet of doublet, dm = doublet of multiplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, p = pentet, h =heptet. Enantioselectivity of cycloaddition products were determined by Agilent HPLC using Daicel chiral columns (Chiralpak AD-H, Chiralpak IA, Chiralcel OJ, Chiralcel OD-H). Specific rotation was recorded in Jassco 2020 polarimeter. Melting point was determined by Buchi M-565 instrument. Cold-Spray Ionization Mass spectra were recorded in JMS-T100LP AccuTOF LC-plus 4G mass spectrometer.

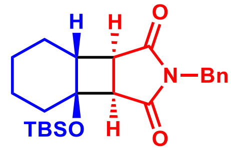
N-benzylmaleimide,[1] *N*-phenylmaleimides,[2] and silyl enol ethers[3] were prepared as reported previously. Dichloromethane used for cycloaddition reactions was freshly filtered from Innovative technology solvent drying system.

Representative procedures for oxathiaborolium 3a catalyzed asymmetric [2+2] cycloaddition

THTOH **1a** (27 mg, 0.1 mmol) was weighed into a flame dried Schlenk tube under nitrogen atmosphere. After evacuation of the air and refilling with nitrogen (three cycles), DCM (0.5 mL) was added. To this solution was added DIPEA (35 µL, 0.2 mmol) at room temperature. The solution was cooled in an ice bath and a DCM (0.5 mL) solution of $PhBCl_2$ (13 µL, 0.1 mmol) was added dropwise. The resulting precursor **2a** solution was stirred for 1 hour in the ice bath and then cooled down to -78 °C. Halophile $SnCl_4$ (1M solution in heptane, 190 µL, 0.19 mmol) was added and the catalyst solution was stirred for 1 hour at -78 °C. The catalyst temperature was gradually raised to -60 °C in 40 min. Then, To the catalyst solution was added Maleimide (0.5 mmol) in DCM (0.5 mL) followed by dropwise addition of DCM (0.5 mL) solution of silyl enol ether (1.5 mmol) along the wall of the Schlenk tube for 10 min. After stirring for 24-48 h at -60 °C (TLC check), the reaction mixture was quenched with methanol (200 µL), diluted with DCM, filtered via SiO_2 gel plug (washed with DCM ~ 25 mL). The filtrate was concentrated under vacuum to give the crude product, which was purified by column chromatography to afford the desired product.

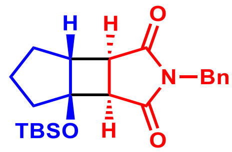
Characterization date of [2+2] cycloaddition adducts

(3a*R*,3b*S*,7a*R*,7b*R*)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)octahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4a**)



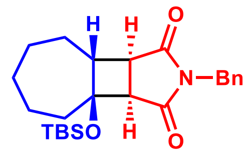
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (317 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4a** (123 mg, 62%, white solid). mp: 113-115 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 6.9 Hz, 2H), 7.29-7.22 (m, 3H), 4.66-4.59 (m, 2H), 3.18 (dd, *J* = 5.08, 1.0 Hz, 1H), 2.72 (t, *J* = 6.1 Hz, 1H), 2.45-2.43 (m, 1H), 2.01-1.96 (m, 1H), 1.80-1.61 (m, 4H), 1.55-1.49 (m, 2H), 1.46-1.38 (m, 1H), 0.80 (s, 9H), 0.12 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.4, 174.7, 136.2, 128.9, 128.7, 127.9, 73.1, 50.8, 48.5, 42.5, 36.8, 36.6, 25.8, 23.9, 19.7, 19.4, 18.0, -2.5, -2.6. IR (KBr film, $\bar{\upsilon}$): 2944, 2851, 1762, 1696, 1455, 1430, 1391, 1358, 1337, 1297, 1255, 1178, 1147, 1078, 882, 838, 779, 699 cm^{-1}. HRMS -ESI^{+} (m/z): $[M+Na]^{+}$ calcd. for $[C_{23}H_{33}NNaO_3Si]^{+}$ 422.2122, found 422.2218. *ee* = 96% [determined by HPLC, Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 6.7 min, $t_{r(major)}$ = 8.6 min]. $[\alpha]_D^{23}$ = -3.7° (*c* 0.5 $CHCl_3$).

(3a*R*,3b*S*,6a*R*,6b*R*)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)hexahydrocyclopenta-[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H,3aH)-dione (**4b**)



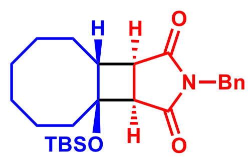
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (296 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4b** (102 mg, 53%, white solid). mp: 83-85 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.40 (m, 2H), 7.31-7.25 (m, 3H), 4.70-4.61 (m, 2H), 3.08 (d, *J* = 6.2 Hz, 1H), 2.61-259 (m, 1H), 2.44 (dd, *J* = 6.3, 2.9 Hz, 1H), 2.01-1.78 (m, 4H), 1.69-1.67 (m, 2H), 0.80 (s, 9H), 0.04 (s, 3H), -0.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.6, 175.1, 136.2, 129.1, 128.7, 127.9, 84.5, 50.1, 49.4, 42.8, 40.9, 38.4, 31.6, 25.7, 24.1, 17.9, -2.6, -2.9. IR (KBr film, $\bar{\upsilon}$): 2953, 2932, 2855, 1771, 1704, 1496, 1471, 1429, 1391, 1346, 1288, 1258, 1223, 1164, 1101, 892, 838, 776, 742, 699 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^{+}$ $[C_{22}H_{31}NNaO_3Si]^{+}$ 408.1965, found 408.1972. *ee* = 84% [determined by HPLC Chiralpak IA column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 9.2 min, $t_{r(major)}$ = 11.7 min]. $[\alpha]_D^{31}$ = +21.3° (*c* 1.0 $CHCl_3$).

(3aR,3bS,8aR,8bR)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)octahydrocyclohepta-[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H,3aH)-dione (**4c**)



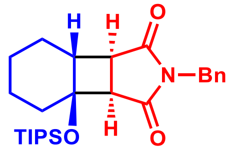
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyl(cyclohept-1-en-1-yloxy)dimethylsilane (338 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4c** (107 mg, 52%, white solid). mp: 92-94 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.36 (m, 2H), 7.27-7.21 (m, 3H), 4.61 (q, J = 14 Hz, 2H), 3.24 (d, J = 6.2 Hz, 1H), 2.75 -2.73 (m, 1H), 2.64-2.61 (m, 1H), 1.94-1.89 (m, 1H), 1.84-1.77 (m, 2H), 1.75-1.69 (m, 3H), 1.64-1.53 (m, 1H), 1.40-1.33 (m, 2H), 0.80 (s, 9H), 0.07 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.9, 175.1, 136.3, 129.1, 128.7, 127.9, 80.5, 52.7, 48.1, 42.7, 41.3, 35.8, 31.7, 30.2, 26.2, 25.7, 24.5, 18.1, -2.0, -2.4. IR (KBr film, ῡ): 2926, 2855, 1771, 1703, 1558, 1540, 1521, 1472, 1428, 1390, 1343, 1256, 1166, 1107, 936, 835, 773, 699 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_3Si]^+$ 436.2278, found 436.2286. *ee* = 90% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 8.9 min, $t_{r(major)}$ = 12.0 min]. $[\alpha]_D^{23}$ = +11.9° (c 1.0 $CHCl_3$).

(3aR,3bS,9aR,9bR)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)decahydro-1H-cycloocta[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4d**)



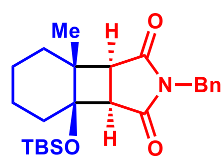
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), (E)-tert-butyl(cyclooct-1-en-1-yloxy)dimethylsilane (359 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4d** (96 mg, 45%, white solid). mp: 80-82 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.36 (m, 2H), 7.29-7.24 (m, 3H), 4.63 (q, J = 14.5 Hz, 2H), 3.04-3.02 (m, 1H), 2.49-2.46 (m, 1H), 2.42-2.38 (m, 1H), 1.93-1.90 (m, 2H), 1.86-1.77 (m, 2H), 1.74-1.59 (m, 3H), 1.53-1.46 (m, 3H), 1.42-1.32 (m, 1H), 1.27-1.23 (m, 2H), 0.85 (s, 9H), 0.14 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.4, 174.9, 136.2, 129.04, 128.7, 127.9, 79.8, 52.9, 51.5, 42.7, 39.3, 38.6, 29.9, 26.4, 25.5, 25.3, 23.8, 18.9, -1.3, -1.5. IR (KBr film, ῡ): 2923, 2855, 1763, 1697, 1495, 1455, 1425, 1388, 1336, 1292, 1254, 1224, 1166, 1106, 1074, 991, 896, 834, 772 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^+$ $[C_{25}H_{37}NNaO_3Si]^+$ 450.2435, found 450.2437. *ee* = 91% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 25 °C, 220 nm, $t_{r(minor)}$ = 6.9 min, $t_{r(major)}$ = 9.6 min]. $[\alpha]_D^{23}$ = +3.0° (c 1.0 $CHCl_3$).

(3a*R*,3b*S*,7a*R*,7b*R*)-2-Benzyl-3b-((triisopropylsilyl)oxy)octahydro-1H-benzo[3,4]- cyclobuta-[1,2-c]pyrrole-1,3(2H)-dione (**4e**)



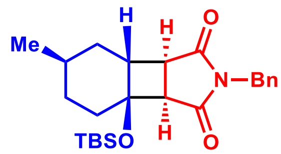
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), (cyclohex-1-en-1-yloxy)triisopropylsilane (380 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 48 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4e** (79 mg, 36%, colourless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40-7.38 (m, 2H), 7.30-7.24 (m, 3H), 4.66-4.60 (m, 2H), 3.27-3.25 (m, 2H), 2.53-2.50 (m, 2H), 1.93-1.88 (m, 1H), 1.86-1.75 (m, 3H), 1.67-1.60 (m, 2H), 1.56-1.48 (m, 2H), 1.11-1.03 (m, 3H), 1.01 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.7, 174.9, 136.3, 134.3, 128.9, 128.7, 127.9, 73.7, 50.2, 48.7, 42.6, 36.4, 35.7, 23.8, 19.2, 18.4, 18.1, 13.6. IR (KBr film, ῡ): 2941, 2865, 1770, 1708, 1498, 1456, 1433, 1391, 1345, 1292, 1249, 1162, 1137, 1108, 1081, 999, 881, 832, 726 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^+$ $[C_{26}H_{39}NNaO_3Si]^+$ 464.2591, found 464.2599. *ee* = 95% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 5.4 min, $t_{r(major)}$ = 6.7 min]. $[\alpha]_D^{23}$ = -17.1° (*c* 0.5 $CHCl_3$).

(3a*R*,3b*R*,7a*R*,7b*S*)-2-Benzyl-3b-(tert-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4f**)



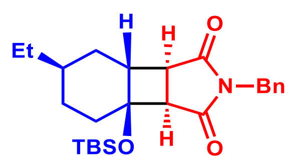
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyldimethyl((2-methylcyclohex-1-en-1-yl)oxy)silane (339 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 48 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4f** (109 mg, 53%, colourless gummy liquid). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-7.39 (m, 2H), 7.28-7.23 (m, 3H), 4.66-4.58 (m, 2H), 3.28 (d, *J* = 6.7 Hz), 2.84 (d, *J* = 6.8 Hz, 1H), 1.84-1.80 (m, 2H), 1.75-1.73 (m, 1H), 1.63-1.57 (m, 5H), 0.92 (s, 3H), 0.79 (s, 9H), 0.15 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.3, 175.7, 136.2, 134.3, 129.4, 128.6, 127.9, 48.2, 46.9, 42.6, 42.4, 33.9, 33.7, 26.2, 19.4, 18.6, 18.5, 17.3, -1.6, -1.9. IR (KBr film, ῡ): 2929, 2855, 1769, 1704, 1498, 1471, 1462, 1430, 1390, 1345, 1255, 1163, 1141, 1112, 961, 898, 837, 776, 698 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_3Si]^+$ 436.2278, found 436.2278. *ee* = 79% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 6.2 min, $t_{r(major)}$ = 8.1 min]. $[\alpha]_D^{28}$ = -25.1° (*c* 0.5 $CHCl_3$).

(3aR,3bS,6R,7aR,7bR)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)-6-methyloctahydro -1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4g**)



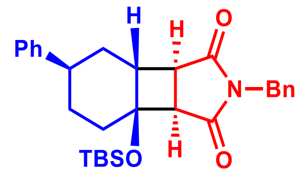
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyldimethyl((4-methylcyclohex-1-en-1-yl)oxy)silane (339 mg, 1.497 mmol), and catalyst **3a** (20 mol in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4g** (111 mg, 54%, white solid). mp: 126-128 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J = 6.6 Hz, 2H), 7.31 – 7.23 (m, 3H), 4.63 (s, 2H), 3.13 (d, J = 6.0 Hz, 1H), 2.72 (t, J = 6.4 Hz, 1H), 2.46 (t, J = 6.0 Hz, 1H), 2.13 (dt, J = 13.3, 4.0 Hz, 1H), 1.80-1.76 (m, 1H), 1.71-1.64 (m, 1H), 1.55-1.52 (m, 2H), 1.34-1.26 (m, 1H), 1.14-1.08 (m, 1H), 0.95 (d, J = 6.2 Hz, 3H), 0.81 (s, 9H), 0.14 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 179.4, 174.6, 136.2, 128.9, 128.8, 127.9, 77.48, 71.8, 51.7, 50.1, 42.4, 37.9, 36.4, 32.9, 29.1, 27.3, 25.9, 22.7, 18.1, -2.5, -2.6. IR (KBr film, ʋ̄): 2925, 2855, 1769, 1704, 1557, 1539, 1453, 1421, 1391, 1361, 1327, 1255, 1170, 1073, 872, 837, 669 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_3Si]^+$ 436.2278, found 436.2269. *ee* = 96% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 5.8 min, $t_{r(major)}$ = 7.2 min]. $[\alpha]_D^{23}$ = -8.5° (c 0.5 $CHCl_3$).

(3aR,3bS,6R,7aR,7bR)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)-6-ethyloctahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4h**)



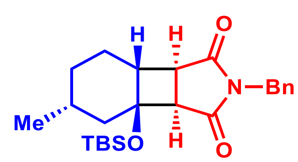
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyl((4-ethylcyclohex-1-en-1-yl)oxy)dimethylsilane (360 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 48 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4h** (75 mg, 35%, white solid). mp: 103-105 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J = 6.7 Hz, 2H), 7.34-7.26 (m, 3H), 4.66 (s, 2H), 3.17 (d, J = 6.0 Hz, 1H), 2.75 (t, J = 6.4 Hz, 1H), 2.49 (d, J = 5.6 Hz, 1H), 2.20-2.08 (m, 1H), 1.85 (d, J = 11.3 Hz, 1H), 1.72 (s, 2H), 1.38-1.26 (m, 4H), 1.21-1.05 (m, 1H), 0.92 (t, J = 7.3 Hz, 3H), 0.83 (s, 9H), 0.15 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.49, 174.64, 136.27, 128.93, 128.78, 127.95, 77.55, 77.23, 76.91, 72.43, 51.51, 49.82, 42.49, 37.66, 36.47, 33.83, 30.74, 30.08, 26.72, 25.94, 18.14, 11.57, -2.55, -2.59. IR (KBr film, ʋ̄): 2927, 2855, 1771, 1707, 1498, 1461, 1431, 1390, 1344, 1315, 1297, 1256, 1220, 1167, 1086, 971, 938, 876, 841, 780, 701 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^+$ $[C_{25}H_{37}NNaO_3Si]^+$ 450.2435, found: 450.2428. *ee* = 88% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 5.1 min, $t_{r(major)}$ = 6.1 min]. $[\alpha]_D^{29}$ = -3.5° (c 0.5 $CHCl_3$).

(3a*R*,3b*S*,6*R*,7a*R*,7b*R*)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)-6-phenyloctahydro -1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4i**)



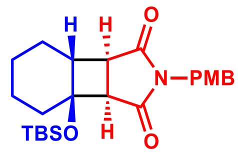
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyldimethyl((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane (432 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4i** (75 mg, 35%, colourless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 6.7 Hz, 2H), 7.36-7.28 (m, 5H), 7.24-7.21 (m, 3H), 4.72-4.64 (m, 2H), 3.23 (d, *J* = 6.0 Hz, 1H), 2.91 (t, *J* = 6.5 Hz, 1H), 2.76-2.69 (m, 1H), 2.62 (t, *J* = 6.2 Hz, 1H), 2.36 (d, *J* = 14.4 Hz, 1H), 2.07-2.00 (m, 1H), 1.93-1.80 (m, 3H), 1.74-1.64 (m, 1H), 0.88 (s, 9H), 0.22 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.1, 174.4, 146.3, 136.2, 128.9, 128.8, 128.00, 126.9, 126.6, 71.5, 51.9, 50.2, 42.5, 39.2, 38.8, 36.3, 32.6, 28.0, 26.0, 18.2, -2.5, -2.6. IR (KBr film, ῡ): 2927, 2853, 1775, 1705, 1635, 1560, 1540, 1506, 1475, 1456, 1388, 1339, 1259, 1164, 1133, 1078, 872, 837, 775, 699 cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{29}H_{37}NNaO_3Si]^+$ 498.2435, found 498.2433. *ee* = 87% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 7.4 min, $t_{r(major)}$ = 13.9 min]. $[\alpha]_D^{29}$ = +22.6° (*c* 0.5 $CHCl_3$).

(3aR,3bS,5R,7aR,7bR)-2-Benzyl-3b-((tert-butyldimethylsilyl)oxy)-5-methyloctahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4j**)



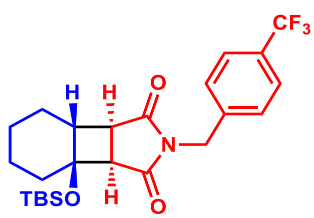
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), tert-butyldimethyl((5-methylcyclohex-1-en-1-yl)oxy)silane (339 mg, 1.497 mmol), and catalyst **3a** (20 mol in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4j** (100 mg, 49%, white solid). mp: 111-113 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.36 (m, 2H), 7.30-7.24 (m, 3H), 4.62 (s, 2H), 3.06 (d, *J* = 6 Hz, 1 Hz, 1H), 2.70-2.66 (m, 1H), 2.38 (t, *J* = 6.6 Hz, 1H), 2.11 (dq, *J* = 14.6 Hz, 2.1 Hz 1H), 1.78-1.61 (m, 3H), 1.50-1.40 (m, 1H), 1.25 (dd, *J* = 14.7 Hz, 12.5 Hz, 1H), 1.02-1.00 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.81 (s, 9H), 0.16 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.3, 174.4, 136.2, 128.8, 128.7, 127.9, 72.5, 52.6, 49.5, 47.7, 42.4, 35.9, 30.5, 27.3, 26.0, 24.6, 26.0, 22.2, 18.1, -2.7, -2.8. IR (KBr film, ῡ): 2927, 2855, 1770, 1707, 1496, 1456, 1430, 1390, 1341, 1293, 1255, 1170, 1140, 1102, 1073, 1004, 953, 872, 837, 775, 726, 699 cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_3Si]^+$ 436.2278, found 436.2276. *ee* = 91% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 5.4 min, $t_{r(major)}$ = 6.2 min]. $[\alpha]_D^{28}$ = -8.5° (*c* 0.5 $CHCl_3$).

(3aR,3bS,7aR,7bR)-3b-((Tert-butyldimethylsilyl)oxy)-2-(4-methoxybenzyl)octahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4k**)



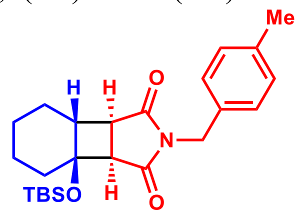
The experiment was performed using 1-(4-methoxybenzyl)-1H-pyrrole-2,5-dione (108 mg, 0.499 mmol), tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (317 mg, 1.497 mmol), and catalyst **3a** (20 mol%) in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4k** (133 mg, 62%, white solid). mp: 131-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 4.59-4.53 (m, 2H), 3.75 (s, 4H), 3.15 (d, J = 6.2 Hz, 1H), 2.70 (t, J = 6.1 Hz, 1H), 2.42-2.39 (m, 1H), 1.99-1.94 (m, 1H), 1.78-1.59 (m, 4H), 1.54-1.48 (m, 2H), 1.45-1.37 (m, 1H), 0.80 (s, 9H), 0.11 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.5, 174.8, 159.3, 130.4, 128.6, 114.0, 73.1, 55.3, 50.7, 48.4, 41.9, 36.7, 36.6, 25.8, 24.0, 19.7, 19.4, 18.0, -2.5, -2.6. IR (KBr film, ῡ): 2928, 2854, 1775, 1704, 1669, 1652, 1635, 1558, 1540, 1515, 1475, 1456, 1394, 1248, 1176, 1086, 1034, 872, 839, 778 cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_4Si]^+$ 452.2228, found 452.2229. *ee* = 96% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 8.7 min, $t_{r(major)}$ = 11.6 min]. $[\alpha]_D^{23}$ = -2.9° (c 0.5 $CHCl_3$).

(3aR,3bS,7aR,7bR)-3b-((Tert-butyldimethylsilyl)oxy)-2-(4-(trifluoromethyl)benzyl)octahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4l**)



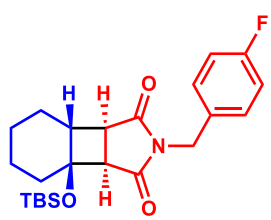
The experiment was performed using 1-(4-(trifluoromethyl)benzyl)-1H-pyrrole-2,5-dione (127 mg, 0.499 mmol), tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (317 mg, 1.497 mmol), and catalyst **3a** in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4l** (156 mg, 67%, colourless liquid). ^{1}H NMR (500 MHz, **$CDCl_3$**): δ 7.53 (d, J= 8.3 Hz, 2H), 7.48 (d, J= 8.3 Hz, 2H), 4.66 (q, J= 14.2 Hz 2H), 3.19 (d, J = 6.2 Hz, 1H), 2.75 (t, J = 6.2 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.85 – 1.59 (m, 4H), 1.54-1.49 (m, 2H), 1.45-1.37 (m, 1H), 0.76 (s, 9H), 0.10 (s, 3H), 0.01 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 179.3, 174.6, 140.1, 130.2 (q, $^2J_{C-F}$ = 32.3 Hz), 129.3, 125.7, 125.6, 124.1 (q, J_{C-F} = 270.3 Hz)73.2, 50.8, 48.7, 42.0, 36.7, 36.5, 25.8, 23.9, 19.7, 19.3, 18.0, -2.6; IR (KBr film, ῡ): 2931, 2857, 1772, 1708, 1620, 1471, 1422, 1391, 1324, 1294, 1253, 1163, 1128, 1112, 1066, 1019, 837, 776. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{32}F_3NNaO_3Si]^+$ 490.1996, found 490.1986. *ee* = 95% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 6.2 min, $t_{r(major)}$ = 7.6 min]. $[\alpha]_D^{23}$ = -7.4° (c 0.5 $CHCl_3$).

(3aR,3bS,7aR,7bR)-3b-((Tert-butyldimethylsilyl)oxy)-2-(4-methylbenzyl)octahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4m**)



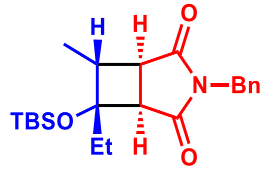
The experiment was performed using 1-(4-methylbenzyl)-1H-pyrrole-2,5-dione (100 mg, 0.499 mmol tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (317 mg, 1.497 mmol), and catalyst **3a** in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4m** (115 mg, 56%, white solid). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 4.59 (s, 2H), 3.17 (d, J= 6.3 Hz, 1H), 2.72 (t, J = 6.1 Hz, 1H), 2.46-2.43 (m, 1H), 2.30 (s, 1H), 2.01 – 1.96 (m, 1H), 1.79-1.61 (m, 4H), 1.56-1.50 (m, 2H), 1.46-1.38 (m, 1H), 0.81 (s, 9H), 0.13 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.4, 174.7, 137.5, 133.3, 129.4, 128.9, 73.1, 50.8, 48.5, 42.3, 36.8, 36.6, 25.9, 24.0, 21.3, 19.7, 19.4, 18.1, -2.5, -2.6; IR (KBr film, ῡ): 2928, 2855, 1773, 1706, 1516, 1428, 1389, 1341, 1307, 1289, 1252, 1170, 1107, 1085, 979, 886, 837, 775 cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_3Si]^+$ 436.2278, found 436.2275. *ee* = 95% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 6.9 min, $t_{r(major)}$ = 8.9 min]. $[\alpha]_D^{23}$ = -3.5° (c 0.5 $CHCl_3$).

(3aR,3bS,7aR,7bR)-3b-((Tert-butyldimethylsilyl)oxy)-2-(4-fluorobenzyl)octahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4n**)



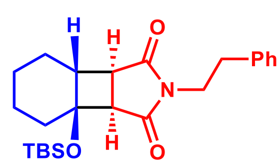
The experiment was performed using 1-(4-fluorobenzyl)-1H-pyrrole-2,5-dione (102 mg, 0.499 mmol), tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (317 mg, 1.497 mmol), and catalyst **3b** in DCM (2.0 mL, 0.25M) for 24 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4n** (135 mg, 65%, white solid). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.34 (m, 2H), 6.94 (t, J = 8.7 Hz, 2H), 4.61 – 4.54 (m, 2H), 3.17 (d, J = 6.2 Hz, 1H), 2.72 (t, J = 6.1 Hz, 1H), 2.41 – 2.38 (m, 1H), 1.99 – 1.94 (m, 1H), 1.79-1.60 (m, 4H), 1.54 – 1.48 (m, 2H), 1.45-1.37 (m, 1H), 0.78 (s, 9H), 0.10 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.4, 174.7, 163.5, 161.5, 132.1 (d, J= 2.9 Hz), 130.8 (d, J= 8.6 Hz), 115.6, 115.4, 73.1, 50.8, 48.6, 41.7, 36.7, 36.5, 25.8, 23.9, 19.7, 19.3, 18.0, -2.5, -2.6; IR (KBr film, ῡ): 2937, 2853, 1759, 1693, 1512, 1443, 1394, 1354, 1340, 1295, 1250, 1230, 1177, 1135, 1086, 888, 870, 839, 819, 780 cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{23}H_{32}FNNaO_3Si]^+$ 440.2028, found 440.2027. *ee* = 95% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 6.2 min, $t_{r(major)}$ = 7.6 min]. $[\alpha]_D^{23}$ = -6.6° (c 0.5 $CHCl_3$).

(6*S*,7*R*)-3-Benzyl-6-((tert-butyldimethylsilyl)oxy)-6-ethyl-7-methyl-3-azabicyclo-[3.2.0]heptane-2,4-dione (**4o**)



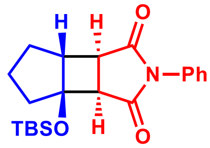
The experiment was performed using *N*-benzylmaleimide (93 mg, 0.499 mmol), (*Z*)-tert-butyldimethyl(pent-2-en-3-yloxy)silane (299 mg, 1.497 mmol), and catalyst **3a** in DCM (2.0 mL, 0.25M) for 48 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4o** (43 mg, 22%, colourless liquid). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42-7.40 (m, 2H), 7.30-7.24 (m, 3H), 4.67-4.60 (m, 2H), 3.17 (d, *J* = 5.9 Hz, 1H), 2.97-2.93 (m, 1H), 2.88-2.82 (m, 1H), 1.86-1.70 (m, 2H), 1.03 (t, *J* = 7.5 Hz , 3H), 0.95 (d, *J* = 7.5 Hz, 3H), 0.15 (s, 9H), 0.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 178.0, 175.6, 136.3, 129.4, 128.7, 128.0, 78.7, 49.0, 42.7, 39.8, 37.6, 34.3, 26.2, 18.7, 11.6, 8.8, -1.5, -1.8. IR (KBr film, ῡ): 2929, 2856, 1772, 1708, 1498, 1462, 1429, 1389, 1343, 1290, 1254, 1165, 1151, 1132, 1060, 1022, 894, 836, 776, cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{22}H_{33}NNaO_3Si]^+$ 410.2122, found 410.2119. *ee* = 96% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(major)}$ = 7.6 min, $t_{r(minor)}$ = 9.9 min]. $[\alpha]_D^{23}$ = -28.4° (*c* 0.5 $CHCl_3$).

(3aR,3bS,7aR,7bR)-3b-((Tert-butyldimethylsilyl)oxy)-2-phenethyloctahydro-1H-benzo[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H)-dione (**4p**)



The experiment was performed using 1-phenethyl-1H-pyrrole-2,5-dione (100 mg, 0.499 mmol), tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (317 mg, 1.497 mmol), and catalyst **3a** in DCM (2.0 mL, 0.25M) for 48 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4p** (74 mg, 36%, white solid). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.21 (m, 5H), 3.75-3.69 (m, 2H), 3.18-3.16 (m, 2H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.70 (t, *J*= 6.1 Hz, 1H), 2.44-2.41 (m, 1H), 2.00 – 1.95 (m, 1H), 1.81 – 1.67 (m, 3H), 1.57-1.53 (m, 2H), 1.47-1.40 (m, 1H), 0.85 (s, 9H), 0.15 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.7, 175.1, 138.2, 129.1, 128.7, 126.8, 73.3, 50.5, 48.6, 40.1, 36.64, 36.63, 34.0, 25.9, 24.0, 19.7, 19.3, 18.1, -2.5; IR (KBr film, ῡ): 2927, 2853, 1761, 1695, 1461, 1435, 1397, 1361, 1346, 1293, 1255, 1172, 1145, 1082, 977, 878, 838, 773, 700 cm^{-1}. HRMS-ESI$^+$ (m/z): calcd. for $[M+Na]^+$ $[C_{24}H_{35}NNaO_3\ Si]^+$ 436.2278, found 436.2287. *ee* = 95% [determined by HPLC Chiralpak AD-H column, 3% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 7.4 min, $t_{r(major)}$ = 9.2 min]. $[\alpha]_D^{23}$ = -7.3° (*c* 0.5 $CHCl_3$)

(3aR,3bS,6aR,6bR)-3b-((tert-butyldimethylsilyl)oxy)-2-phenylhexahydrocyclopenta[3,4]cyclobuta[1,2-c]pyrrole-1,3(2H,3aH)-dione (**4q**)



The experiment was performed using 1-phenyl-1H-pyrrole-2,5-dione (86 mg, 0.499 mmol), tert-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (297 mg, 1.497 mmol), and catalyst **3a** in DCM (2.0 mL, 0.25M) for 48 h. The crude mixture was purified by column chromatography (94:6 Hexane:EtOAc) to afford the desired product **4q** (50 mg, 27%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.23 (d, *J* = 6.3 Hz, 1H), 2.75 (d, *J*= 3.9 Hz, 1H), 2.61 (dd, *J* = 6.4, 2.6 Hz, 1H), 2.07 – 1.85 (m, 4H), 1.77 – 1.74 (m, 2H), 0.84 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9, 174.5, 132.5, 129.2, 128.5, 126.6, 84.8, 50.1, 49.9, 40.9, 38.5, 31.7, 25.8, 24.12, 18.04, -2.5; IR (KBr film, ῡ): 2924, 2854, 1771, 1708, 1652, 1557, 1539, 1497, 1471, 1456, 1385, 1247, 1226, 1194, 1171, 1098, 912, 895, 836, 796, 772, 738, 699 cm^{-1}. HRMS-ESI^{+} (m/z): calcd. for $[M+Na]^{+}$ $[C_{21}H_{29}NNaO_3Si]^{+}$ 408.1965, found 408.1972. *ee* = 89% [determined by HPLC Chiralpak ADH column, 20% IPA/Hex, 1.0 mL/min, 220 nm, $t_{r(minor)}$ = 6.5 min, $t_{r(major)}$ = 6.9 min]. $[\alpha]_D^{23}$ = +13.2° (*c* 0.5 $CHCl_3$).

References

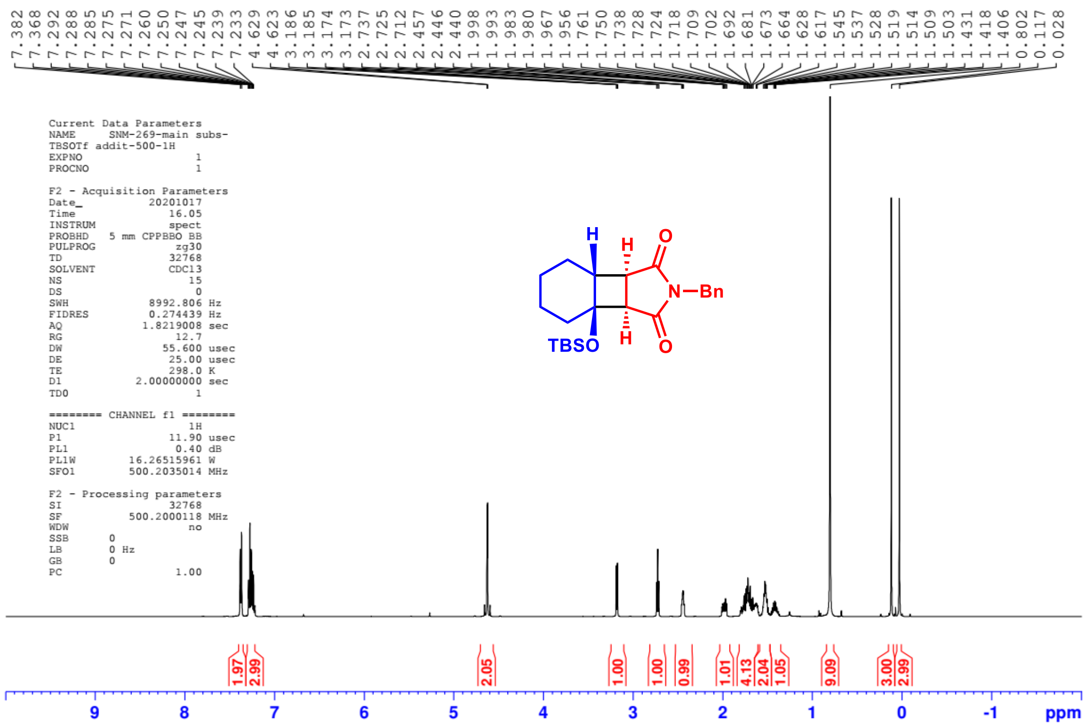
(1) Mandal, R.; Emayavaramban, B.; Sundararaju, B. *Org. Lett*. **2018**, *20*, 2835.

(2) Cava, M. P.; Deana, A. A.; Muth, K.; Mitchell, M. J. *Org. Syn.* **1973***,* Coll. Vol. 5, 944.

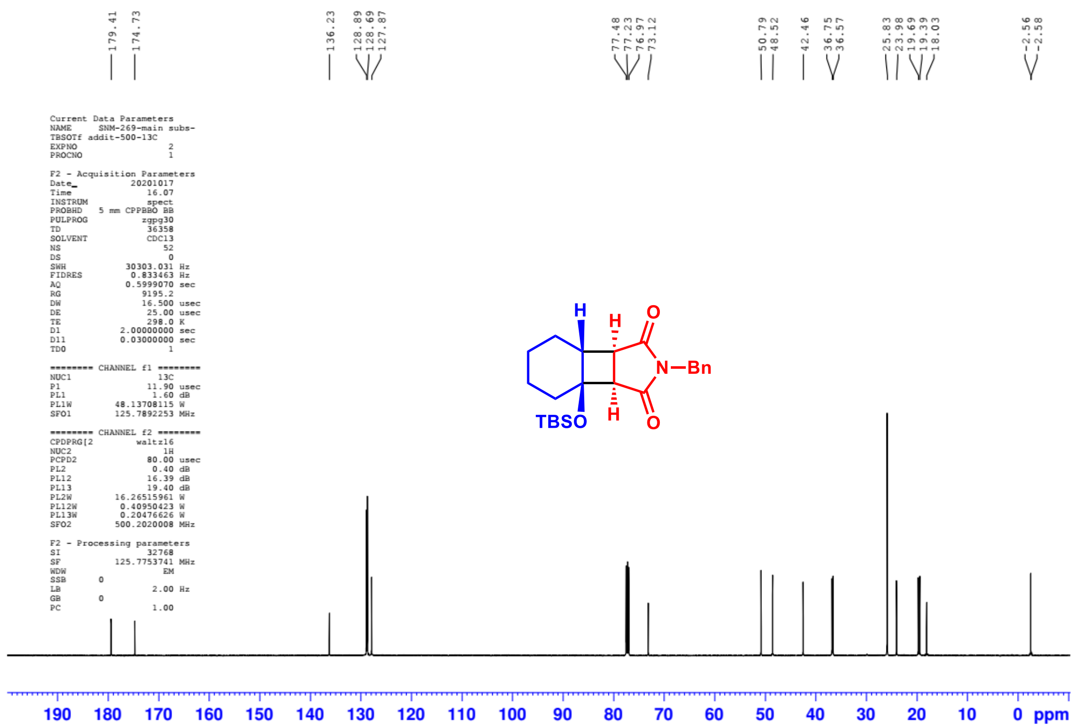
(3) Khan, I.; Reed-Berendt, B. G.; Melen, R. L.; Morrill, L. C. *Angew. Chem., Int. Ed.* **2018**, *57*, 12356.

^{1}H, ^{13}C NMR, HPLC spectra of [2+2] cycloaddition adducts 4a-4p

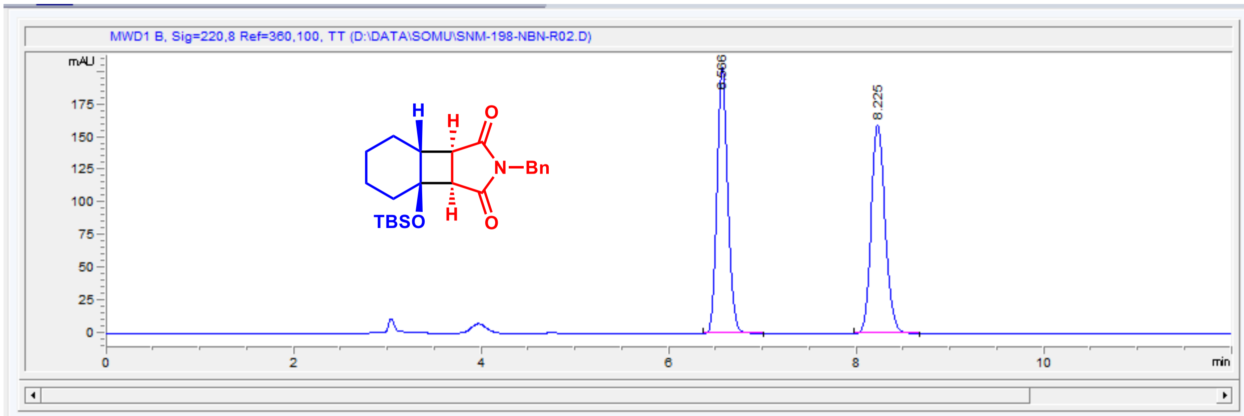
^{1}H NMR spectrum of 4a



^{13}C NMR spectrum of 4a



Racemic HPLC chromatogram of 4a



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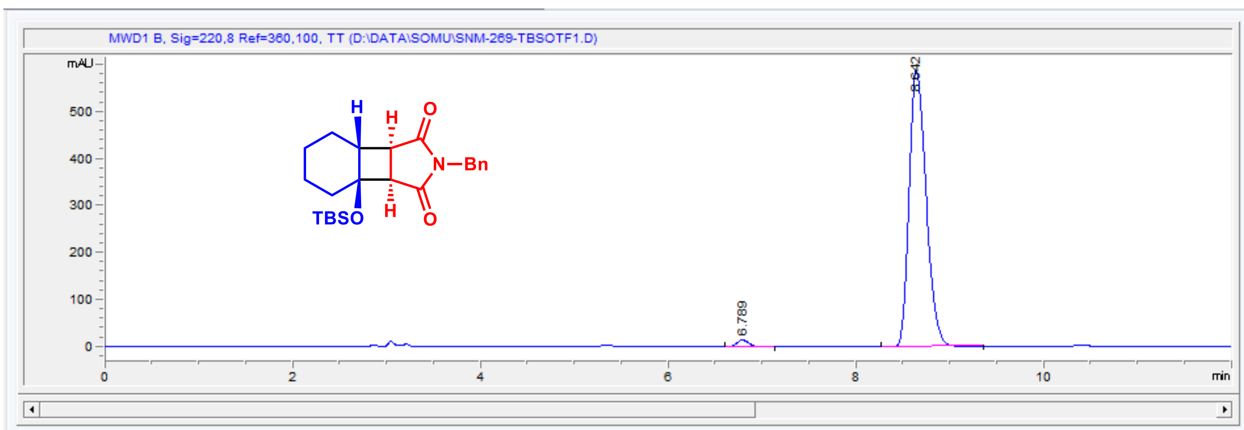
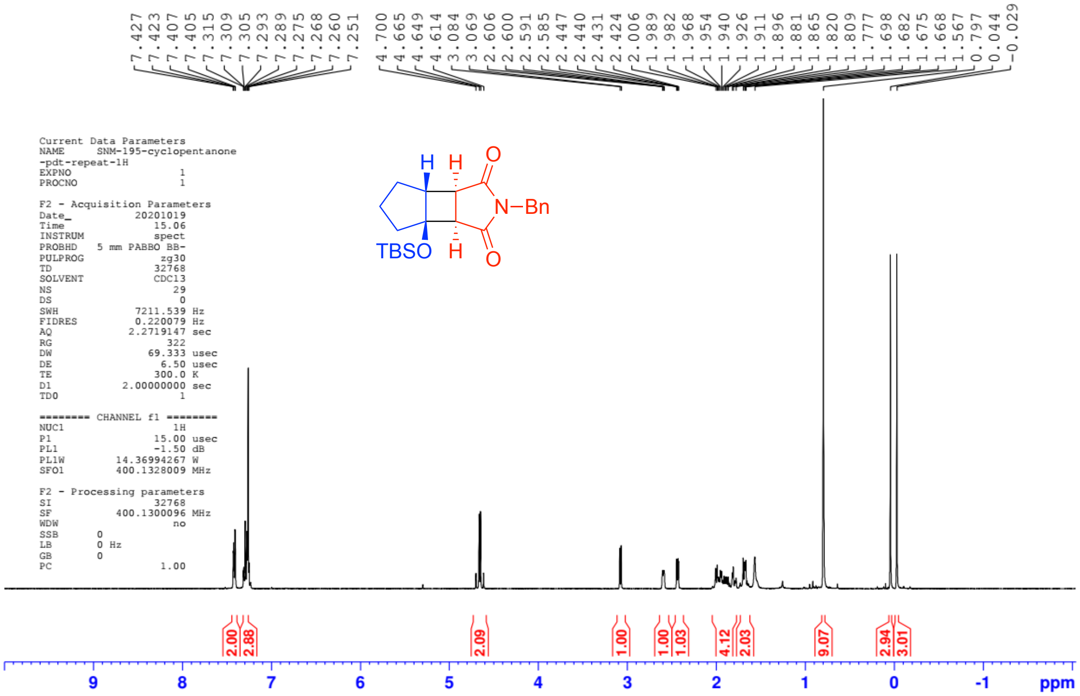
Chiral HPLC chromatogram of 4a

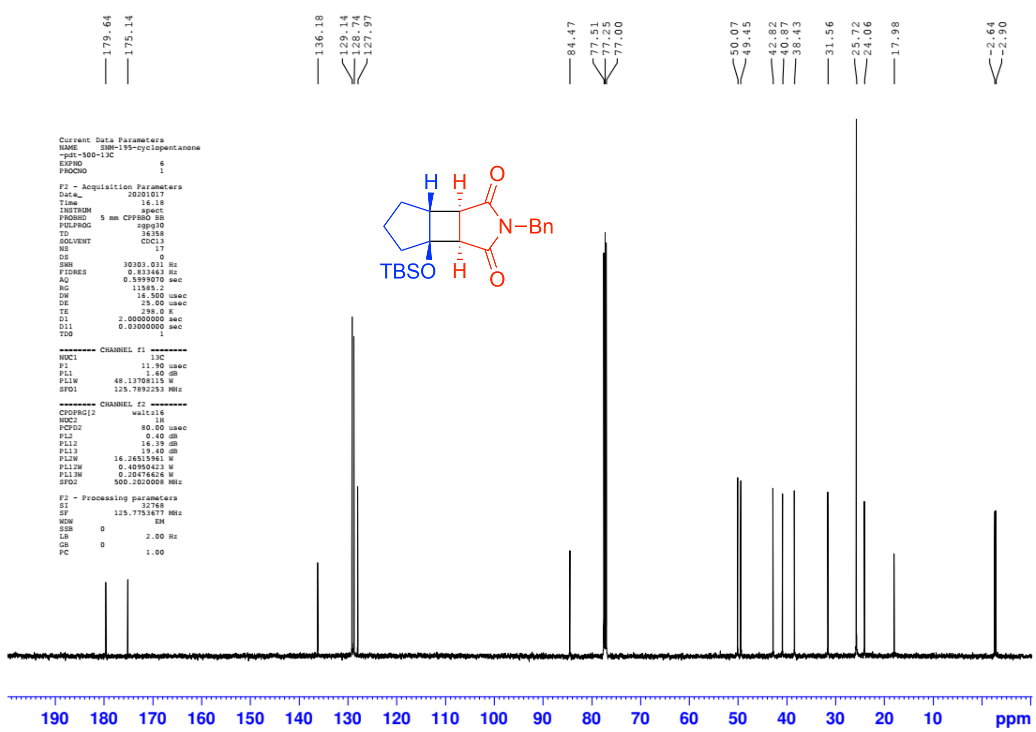


#	Time	Area	Height	Width	Area%	Symmetry
1	6.789	136.5	14.9	0.1409	1.803	0.849
2	8.642	7429.8	588.6	0.1973	98.197	0.695

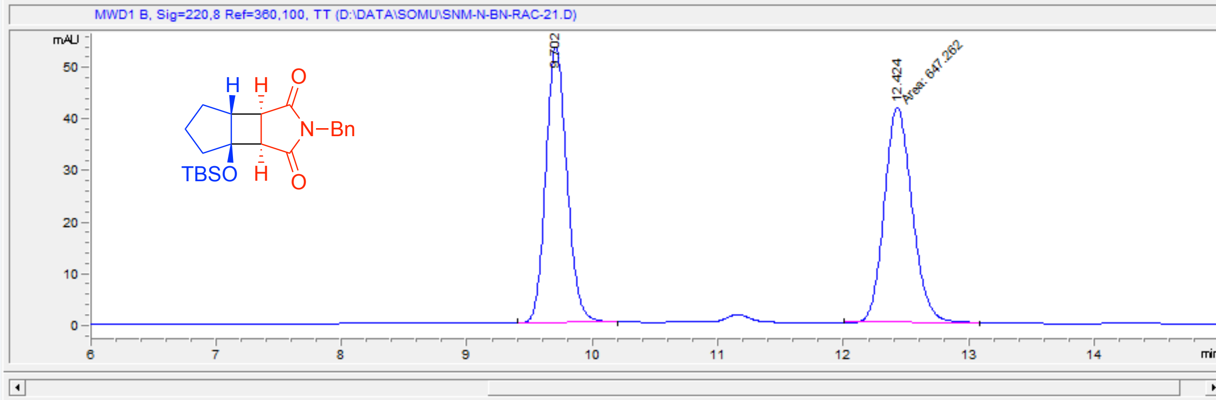
[1]H NMR spectrum of 4b



[13]C NMR spectrum a of 4b

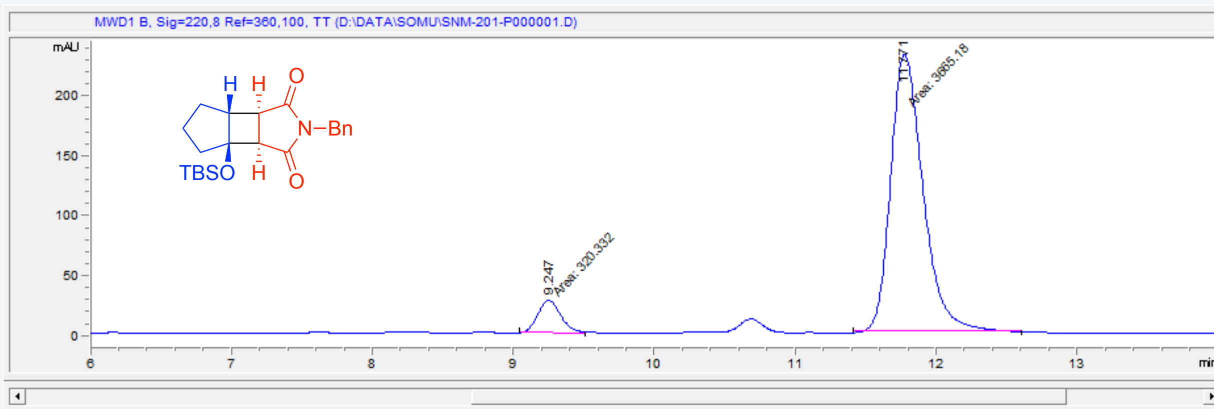


Racemic HPLC chromatogram of 4b



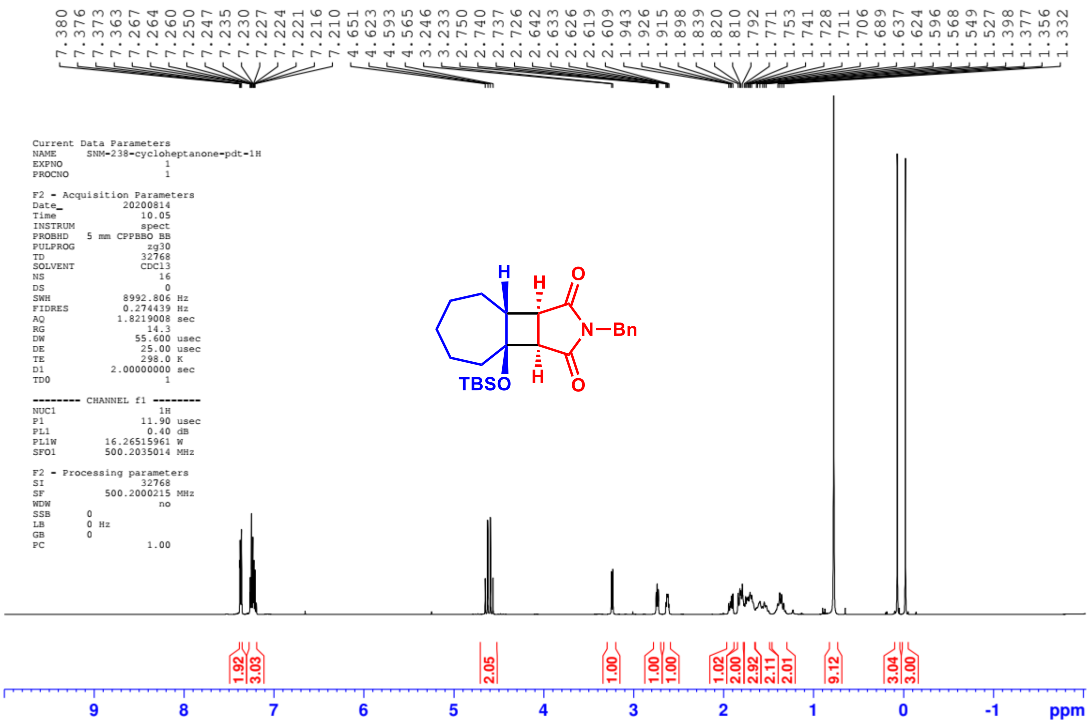
#	Time	Area	Height	Width	Area%	Symmetry
1	9.702	627.8	53.6	0.1807	49.239	0.834
2	12.424	647.3	41.8	0.2583	50.761	0.837

Chiral HPLC chromatogram of 4b

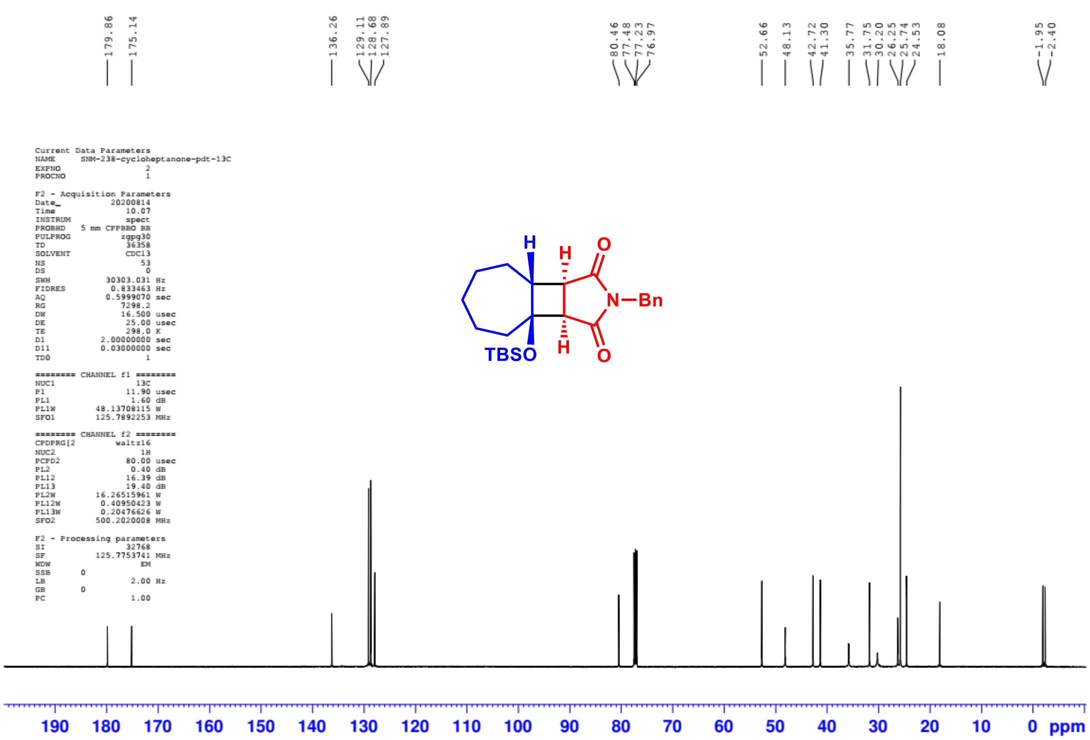


#	Time	Area	Height	Width	Area%	Symmetry
1	9.247	320.3	27.6	0.1936	8.037	0.818
2	11.771	3665.2	230.8	0.2646	91.963	0.718

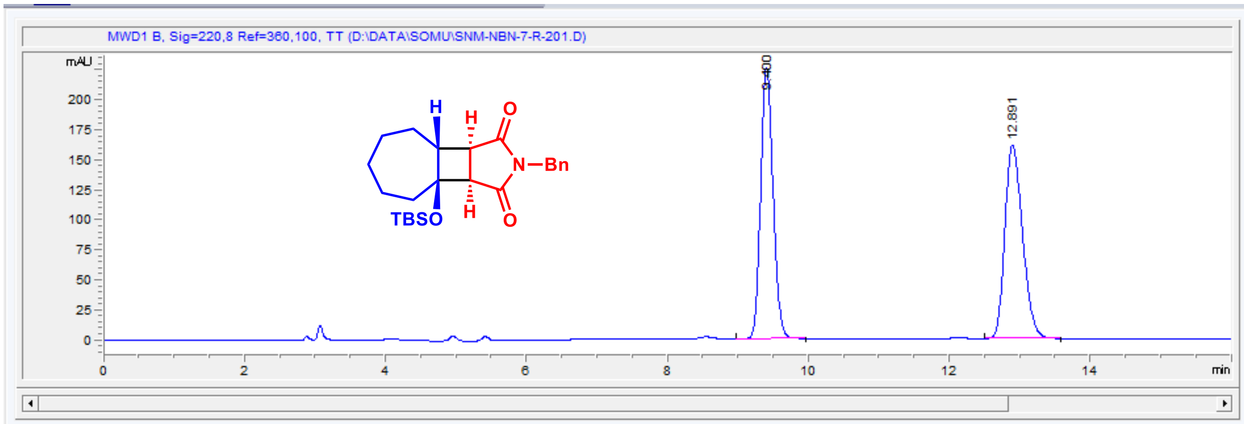
[1]H NMR spectrum of 4c



[13]C NMR spectrum of 4c

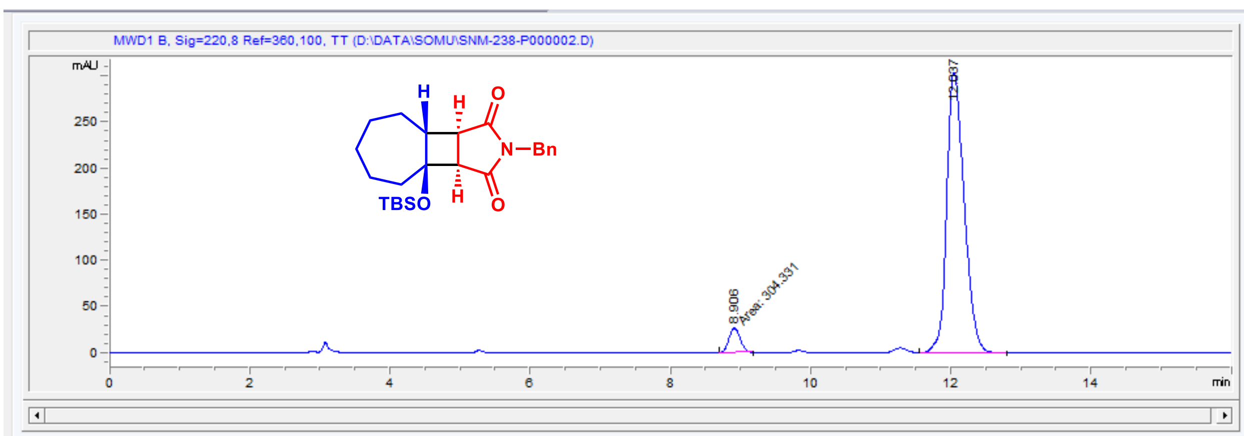


Racemic HPLC chromatogram of 4c



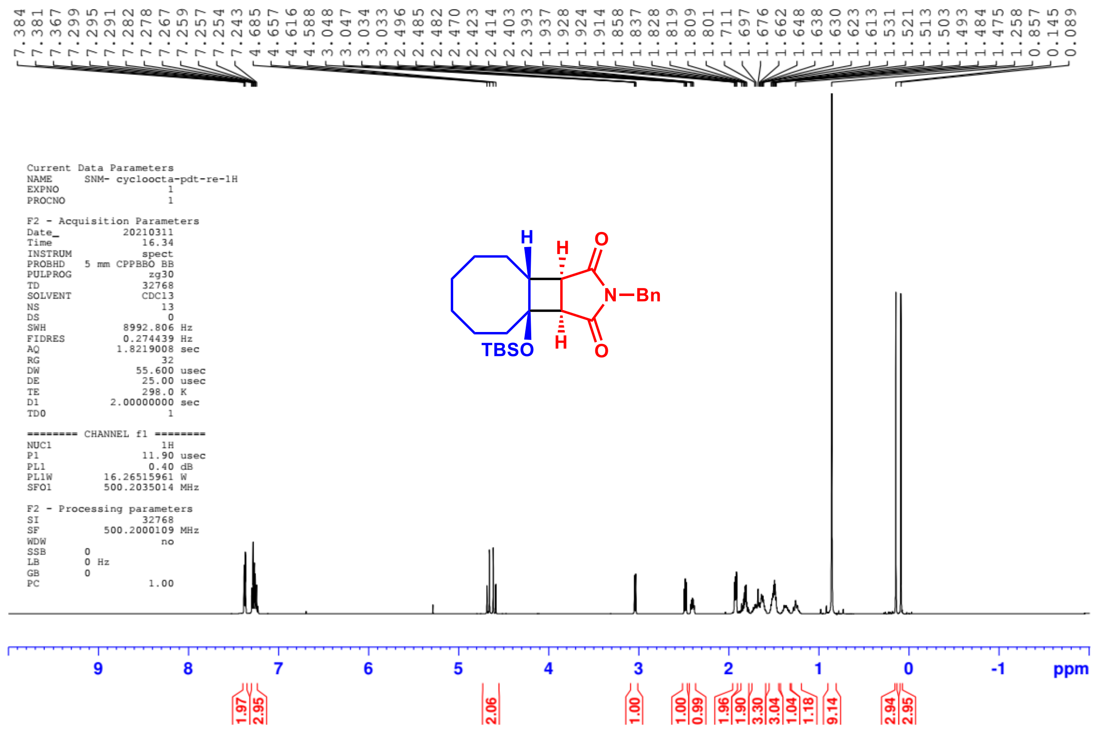
#	Time	Area	Height	Width	Area%	Symmetry
1	9.4	2769.3	225.3	0.1914	49.731	0.846
2	12.891	2799.2	161.2	0.2706	50.269	0.72

Chiral HPLC chromatogram of 4c

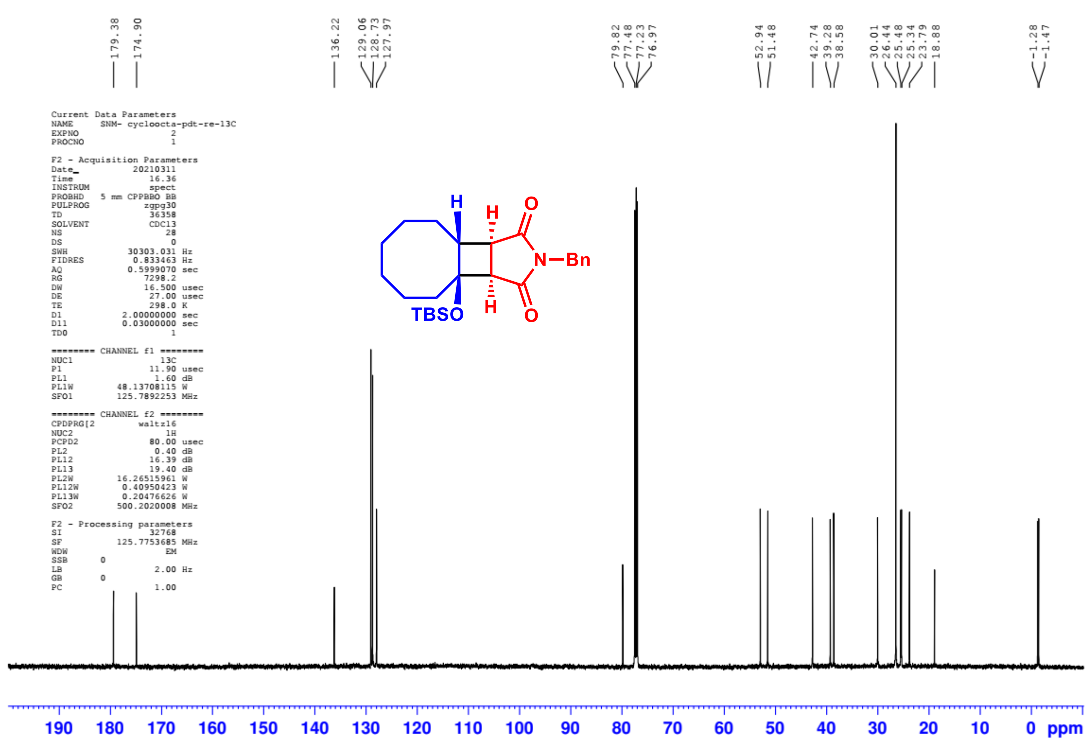


#	Time	Area	Height	Width	Area%	Symmetry
1	8.906	304.3	26.8	0.1889	5.459	0.945
2	12.037	5270.8	304	0.2683	94.541	0.672

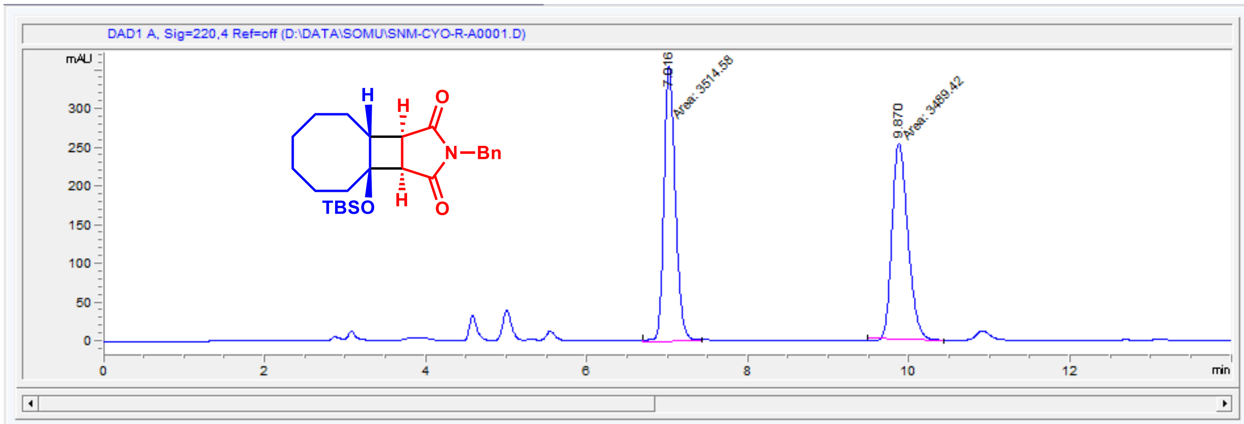
^{1}H NMR spectrum of 4d



^{13}C NMR spectrum a of 4d

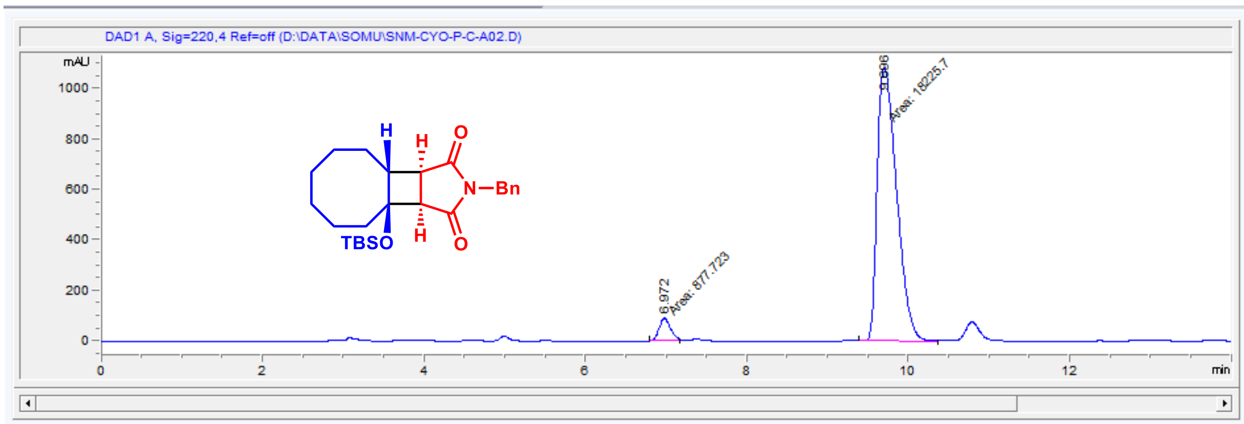


Racemic HPLC chromatogram of 4d



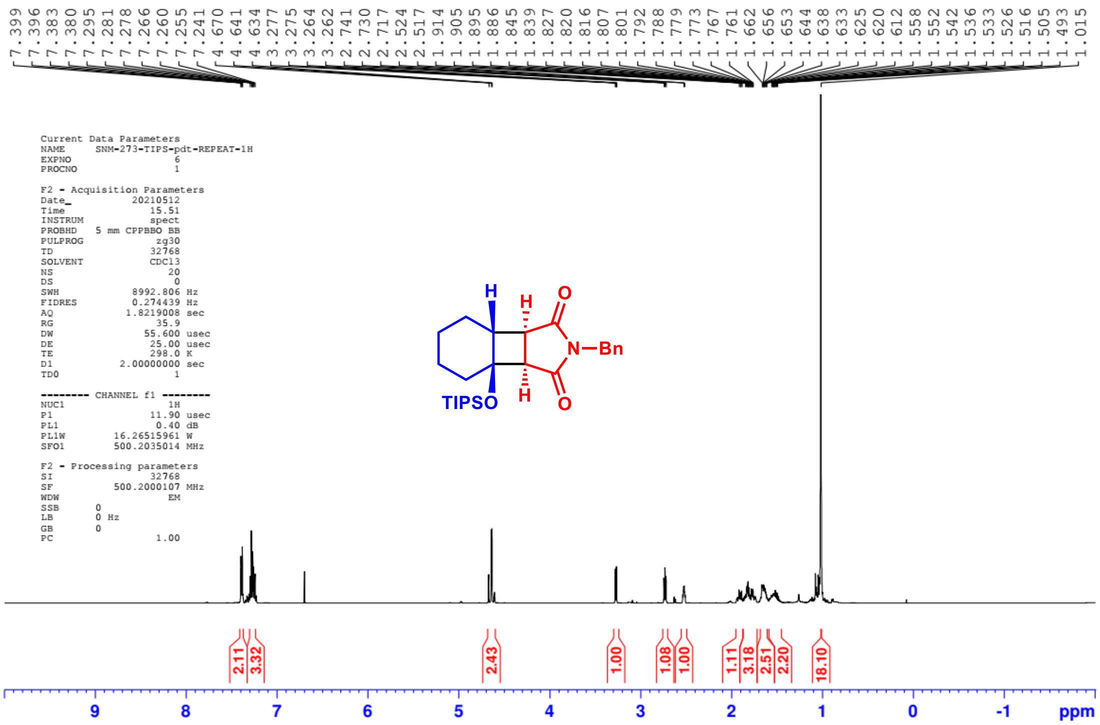
#	Time	Area	Height	Width	Area%	Symmetry
1	7.016	3514.6	357.1	0.1641	50.180	0.785
2	9.87	3489.4	253.4	0.2295	49.820	0.74

Chiral HPLC chromatogram of 4d

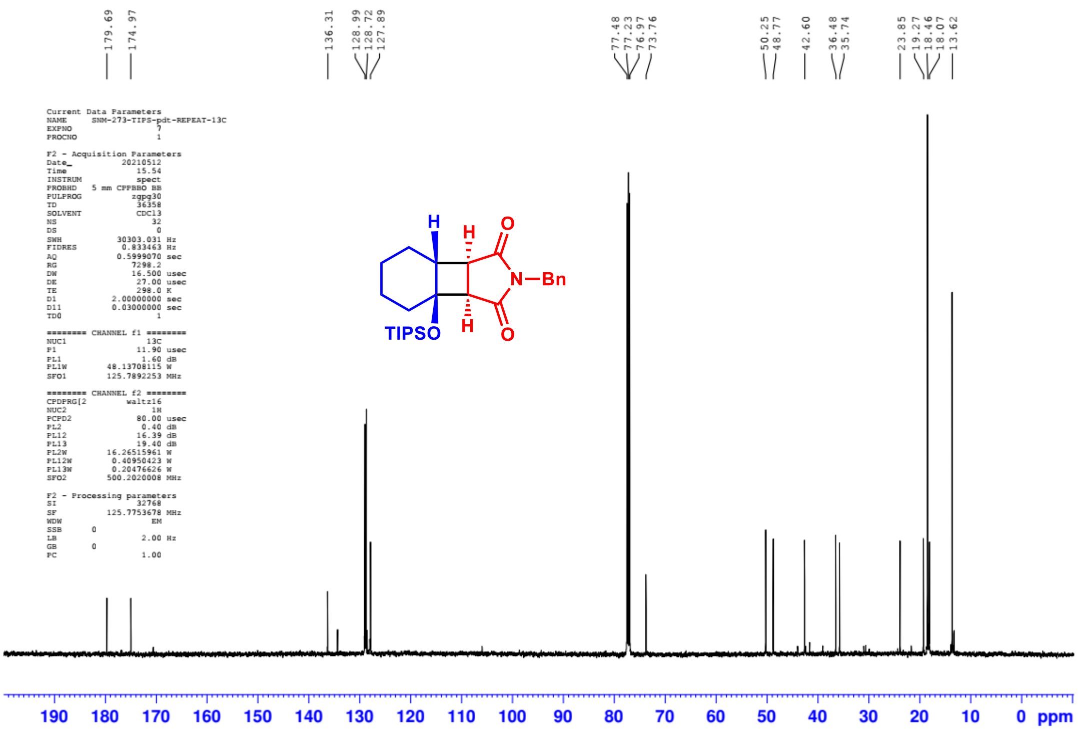


#	Time	Area	Height	Width	Area%	Symmetry
1	6.972	877.7	89	0.1644	4.595	0.782
2	9.696	18225.7	1081.8	0.2808	95.405	0.537

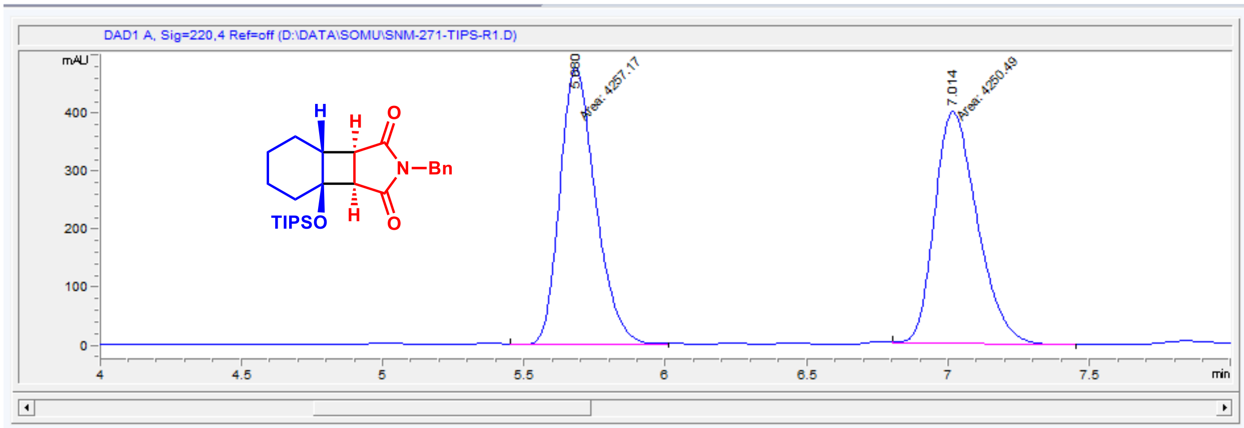
^{1}H NMR spectrum of 4e



^{13}C NMR spectrum of 4e

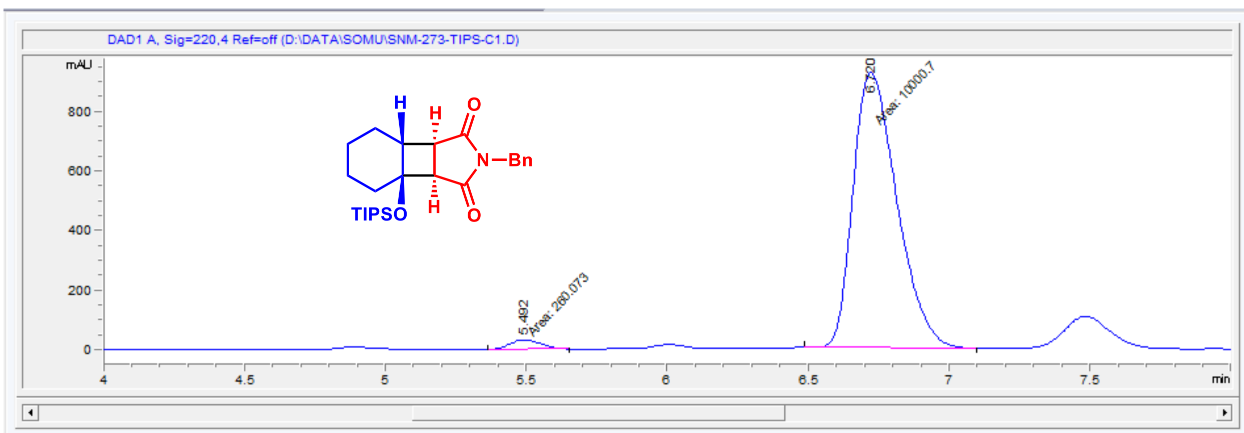


Racemic HPLC chromatogram of 4e



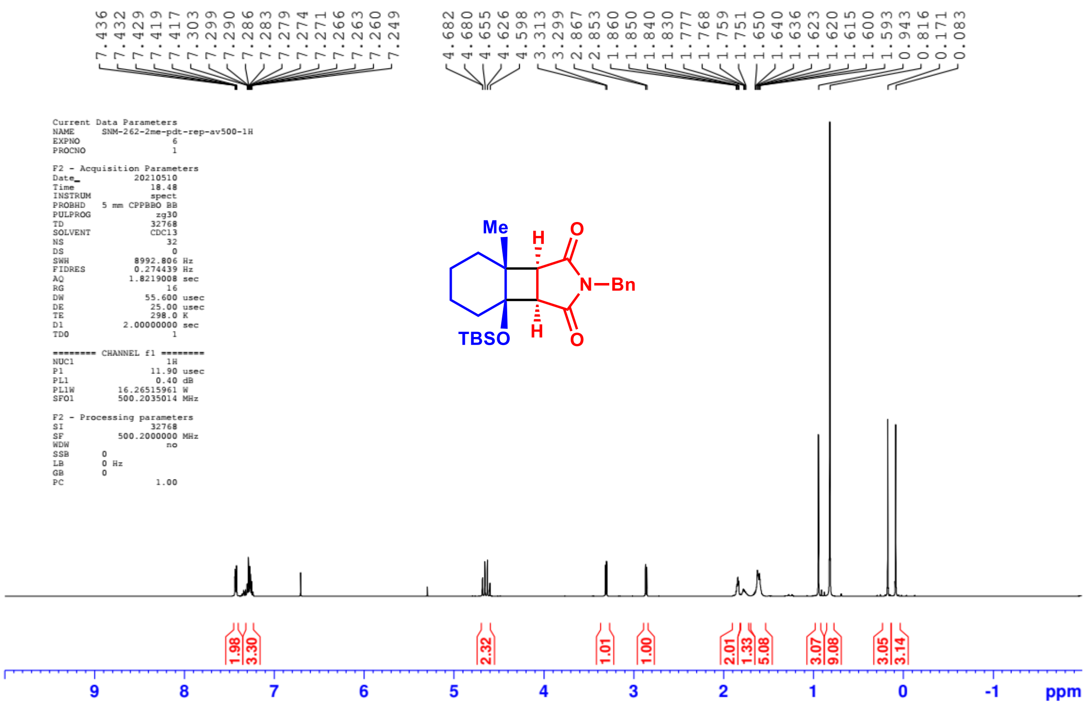
#	Time	Area	Height	Width	Area%	Symmetry
1	5.68	4257.2	479.8	0.1479	50.039	0.755
2	7.014	4250.5	402.1	0.1762	49.961	0.718

Chiral HPLC chromatogram of 4e

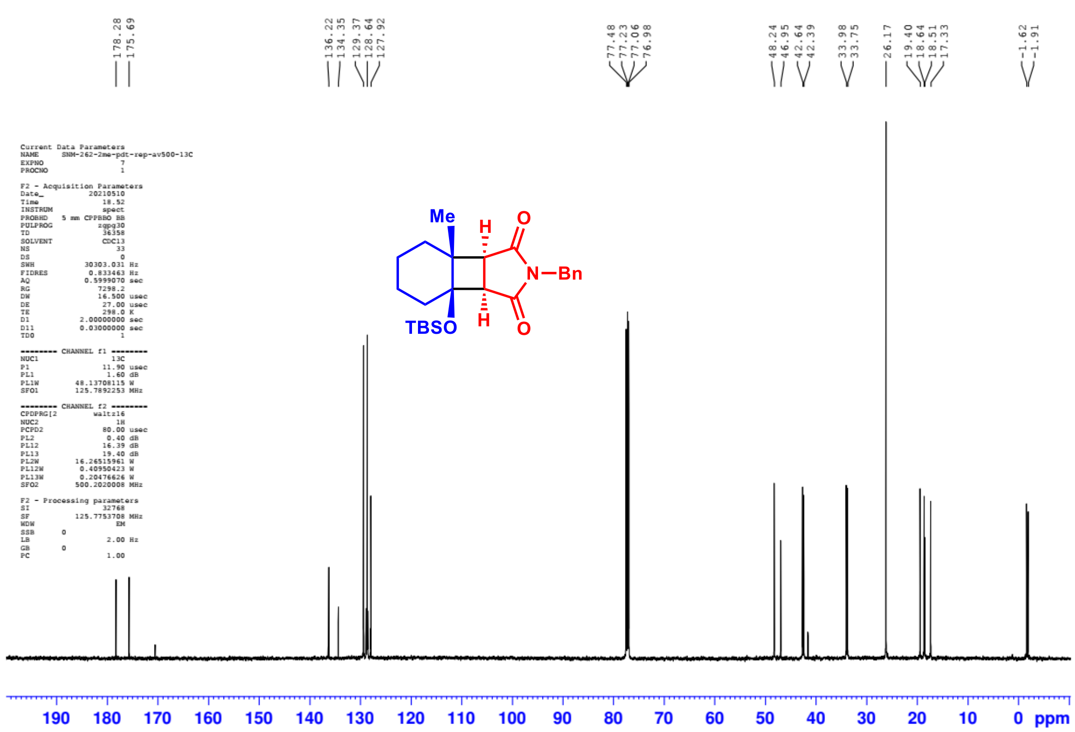


#	Time	Area	Height	Width	Area%	Symmetry
1	5.492	260.1	33.2	0.1306	2.535	0.963
2	6.72	10000.7	927	0.1798	97.465	0.654

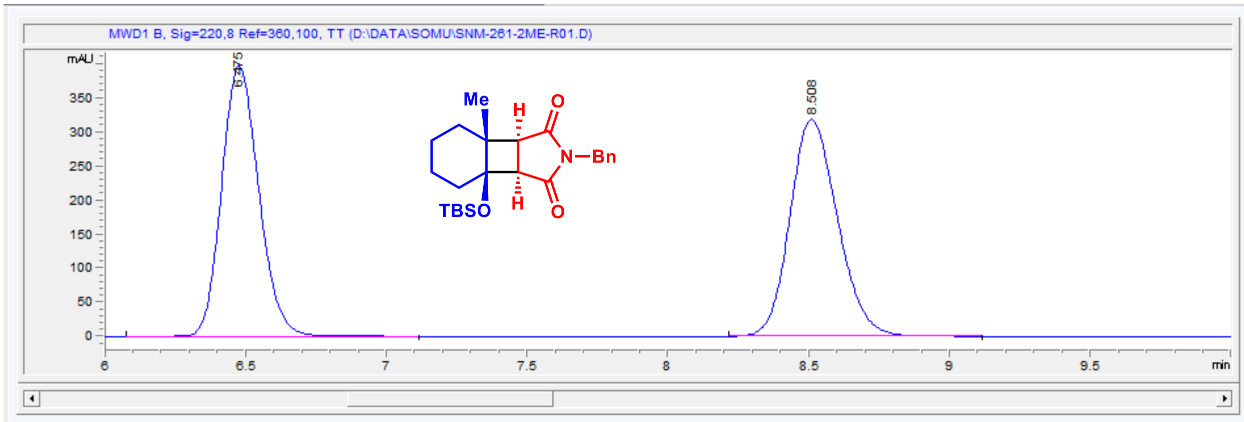
[1]H NMR spectrum of 4f



[13]C NMR spectrum of 4f

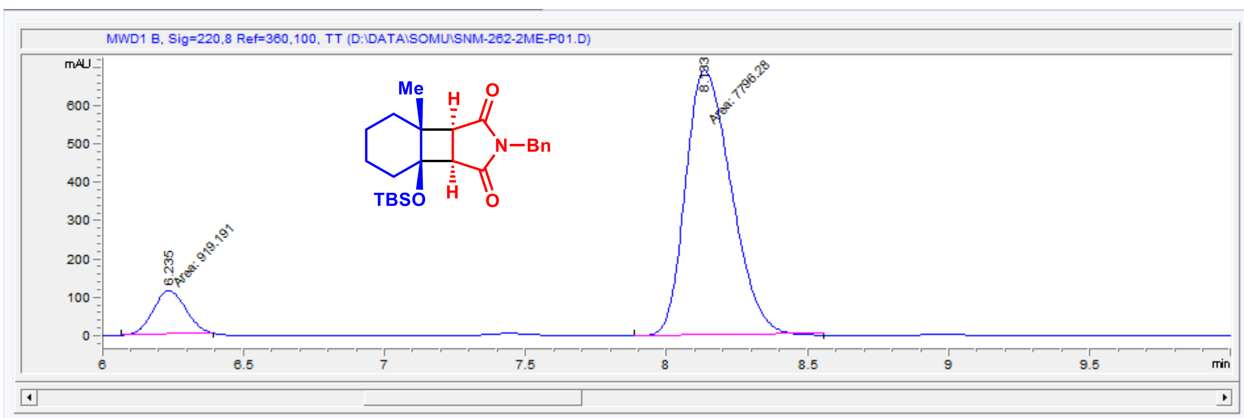


Racemic HPLC chromatogram of 4f



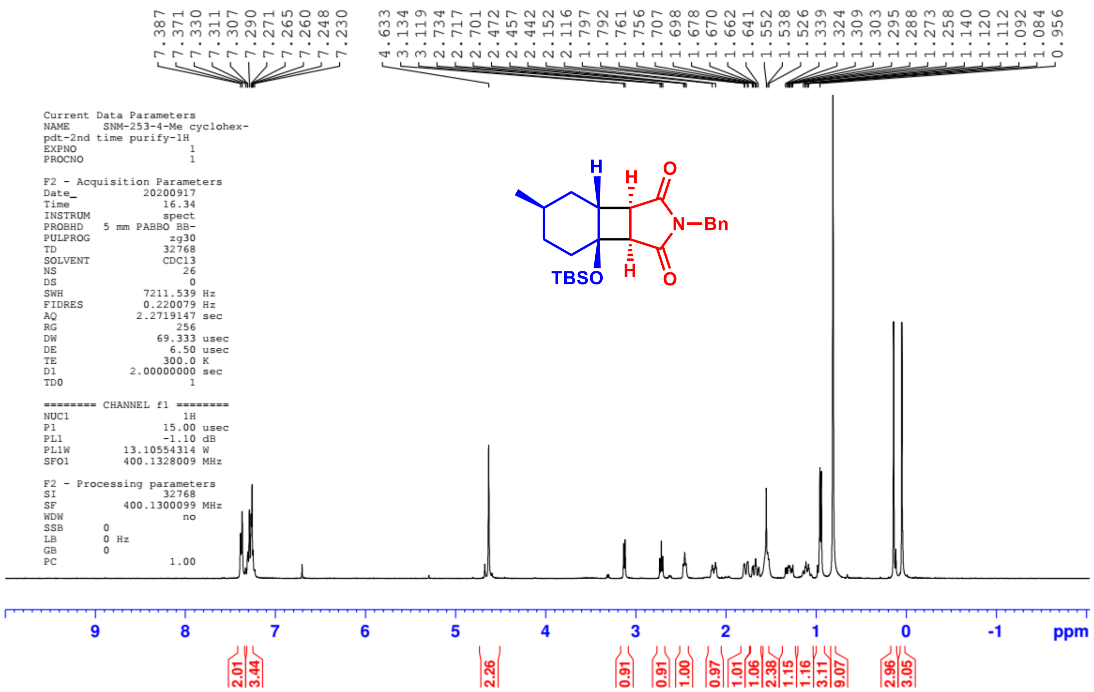
#	Time	Area	Height	Width	Area%	Symmetry
1	6.475	3695	398	0.1423	49.583	0.823
2	8.508	3757.2	319.1	0.1814	50.417	0.788

Chiral HPLC chromatogram of 4f

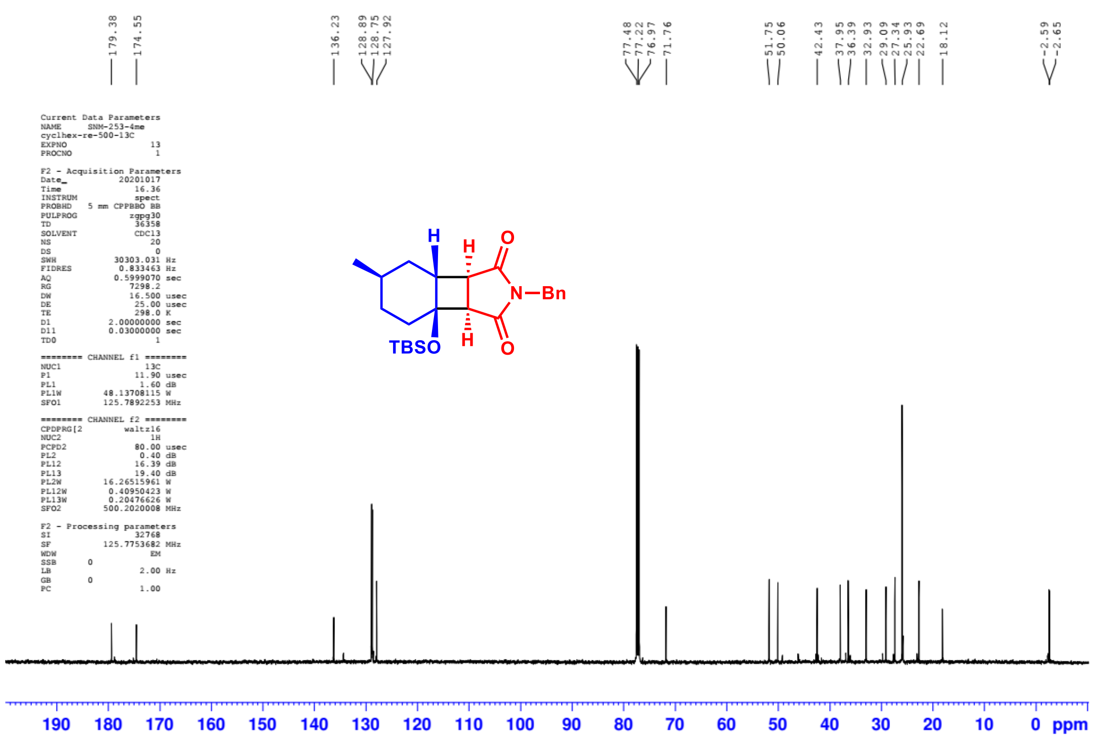


#	Time	Area	Height	Width	Area%	Symmetry
1	6.235	919.2	113.7	0.1347	10.547	0.912
2	8.133	7796.3	692.2	0.1877	89.453	0.708

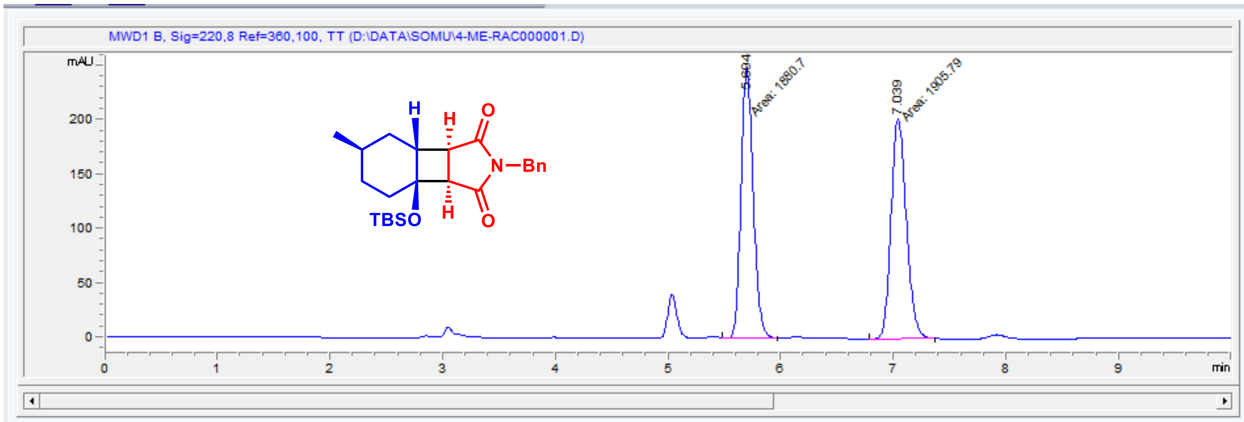
1H NMR spectrum of 4g



13C NMR spectrum of 4g

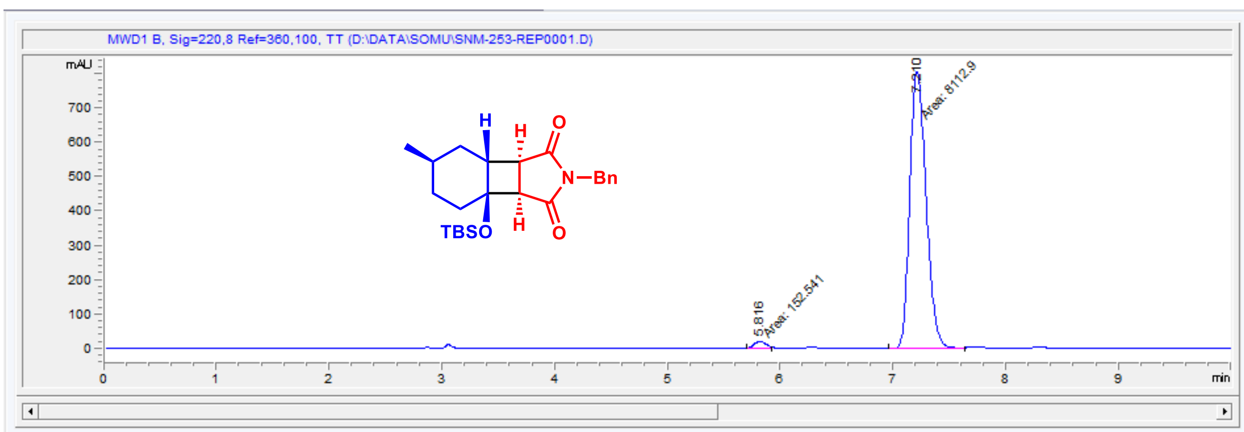


Racemic HPLC chromatogram of 4g



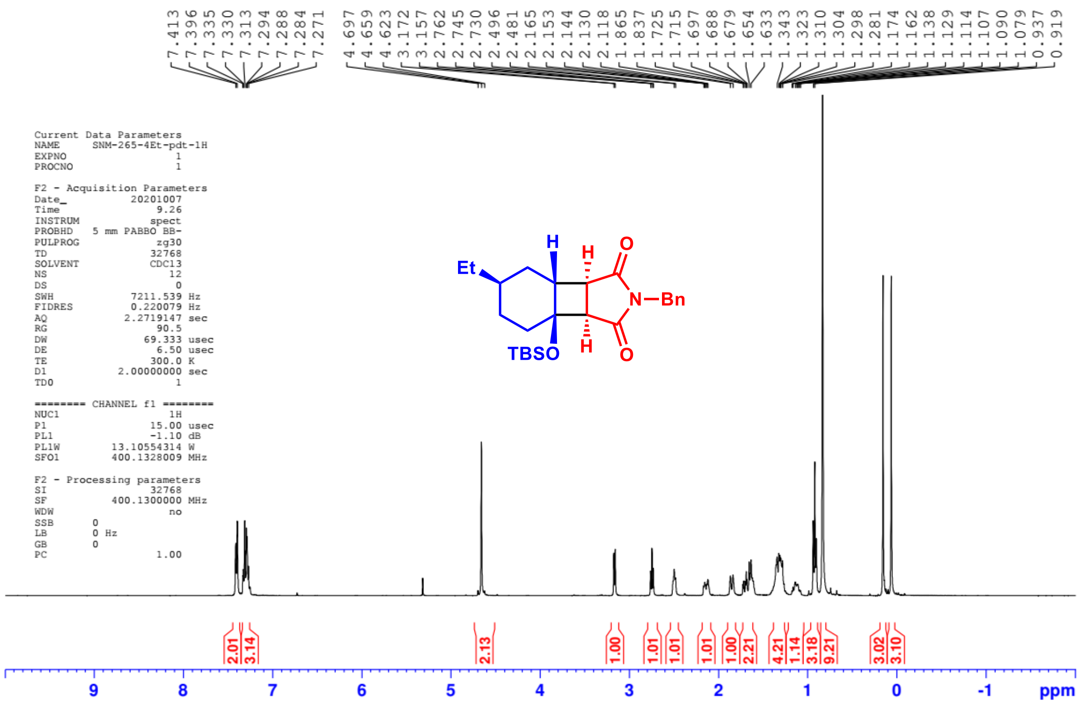
#	Time	Area	Height	Width	Area%	Symmetry
1	5.694	1880.7	249.1	0.1258	49.669	0.833
2	7.039	1905.8	202.7	0.1567	50.331	0.826

Chiral HPLC chromatogram of 4g

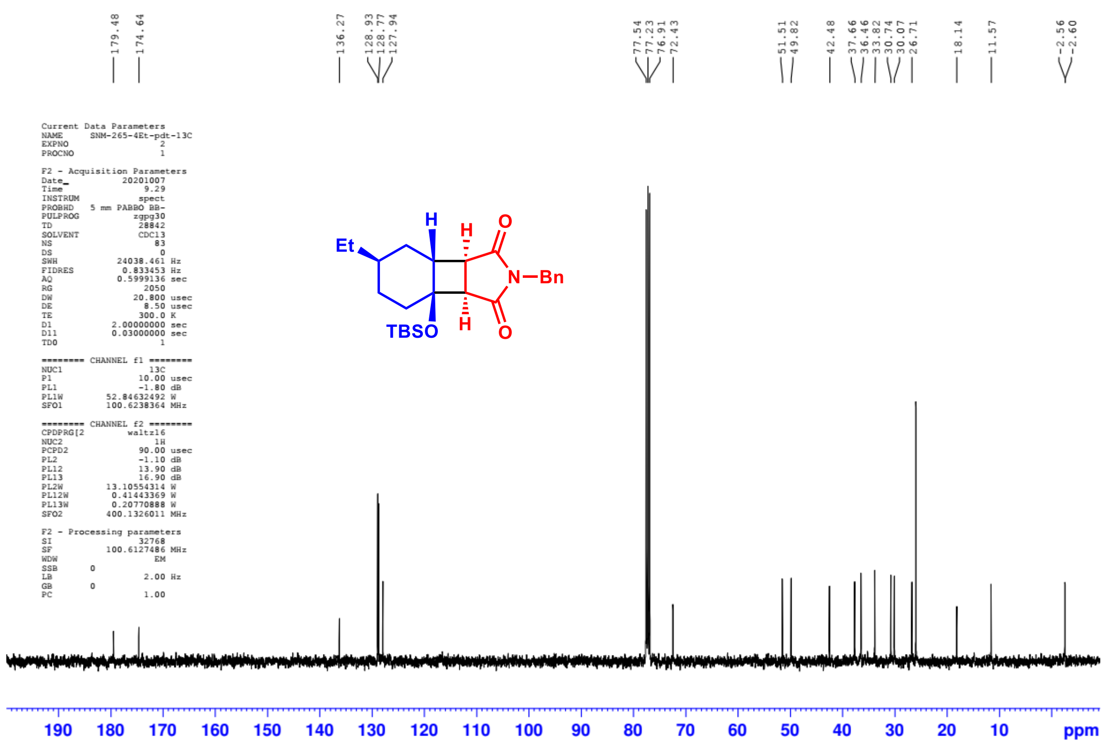


#	Time	Area	Height	Width	Area%	Symmetry
1	5.816	152.5	20.7	0.123	1.846	0.808
2	7.21	8112.9	807.4	0.1675	98.154	0.755

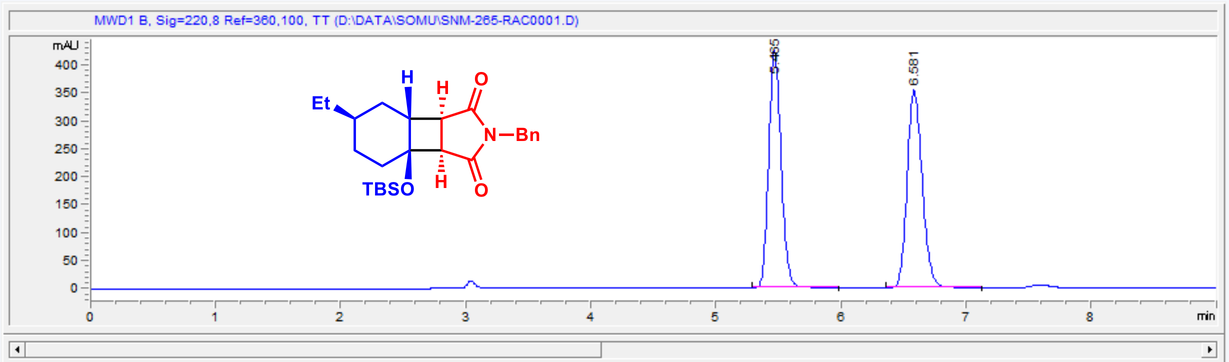
^{1}H NMR spectrum of 4h



^{13}C NMR spectrum of 4h

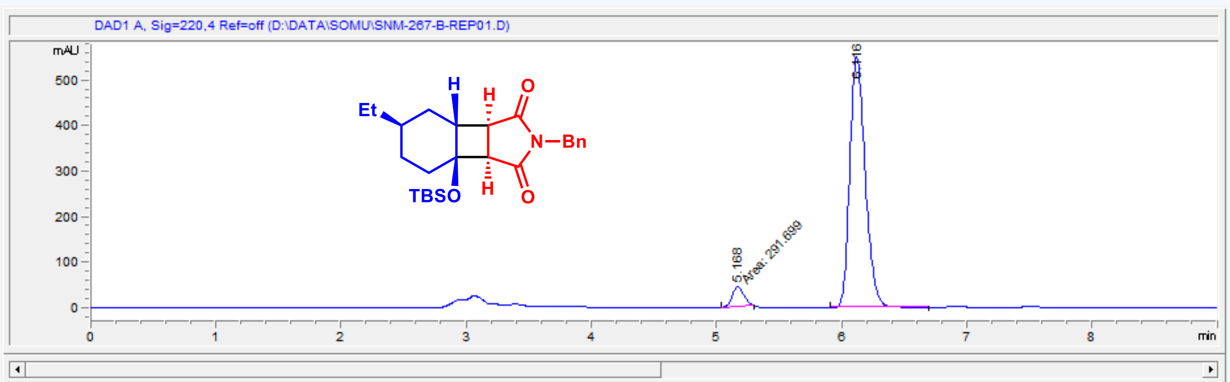


Racemic HPLC chromatogram of 4h



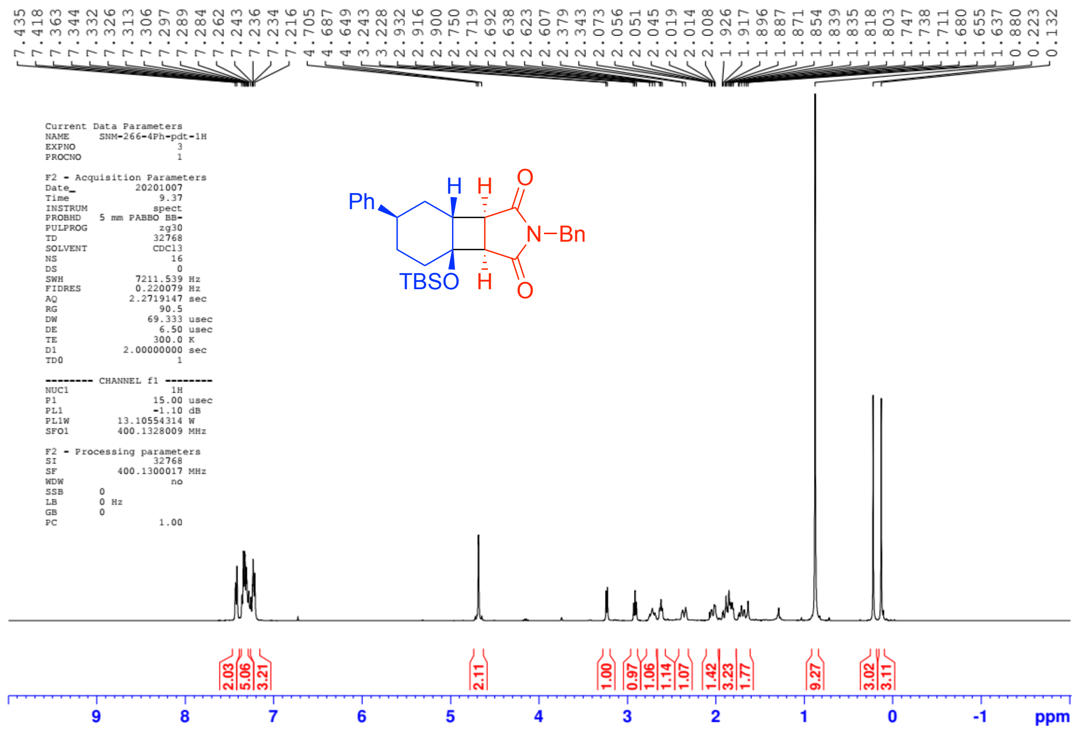
#	Time	Area	Height	Width	Area%	Symmetry
1	5.465	2920.4	423.9	0.1064	49.642	0.829
2	6.581	2962.6	353.3	0.1298	50.358	0.806

Chiral HPLC chromatogram of 4h

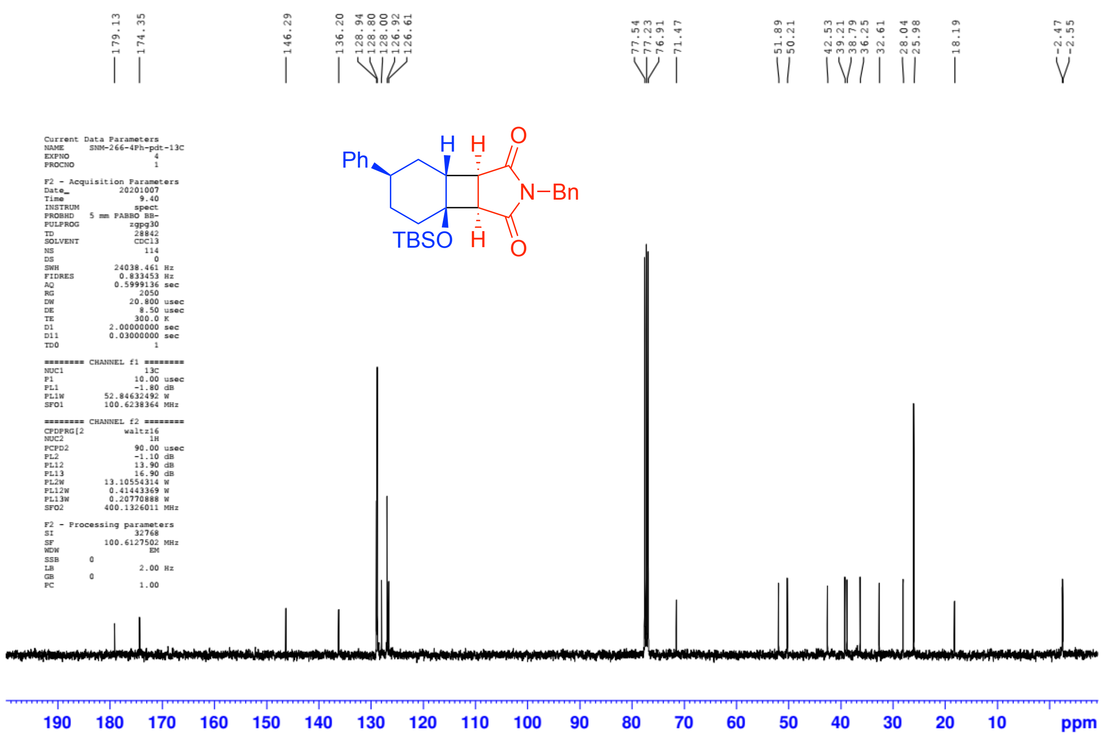


#	Time	Area	Height	Width	Area%	Symmetry
1	5.168	291.7	44.4	0.1094	5.835	0.882
2	6.116	4707.1	552.2	0.1315	94.165	0.727

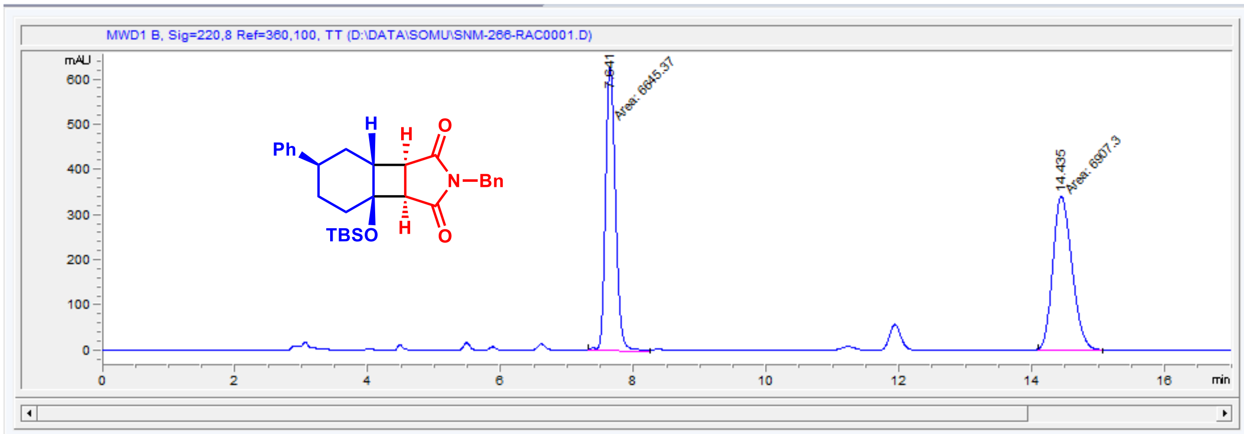
[1]H NMR spectrum of 4i



[13]C NMR spectrum of 4i

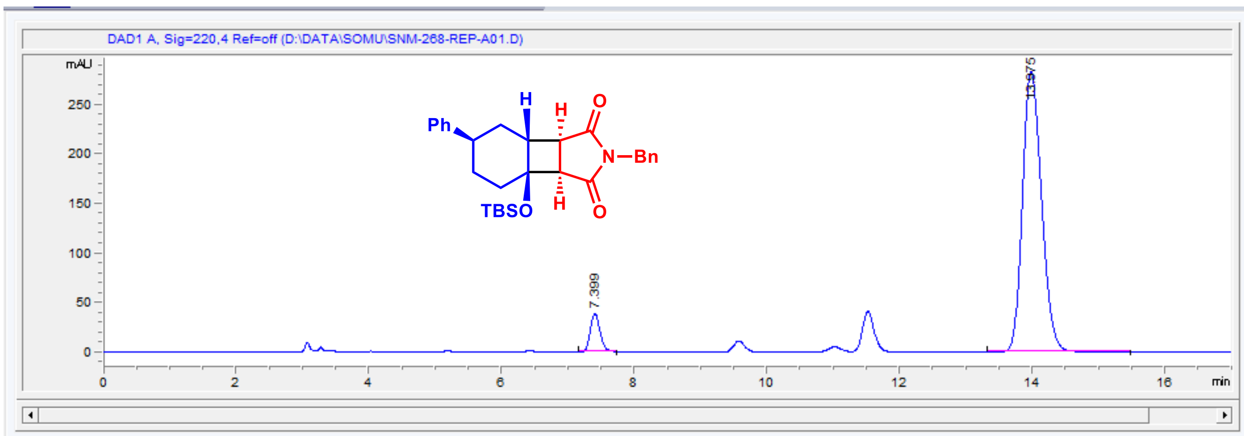


Racemic HPLC chromatogram of 4i



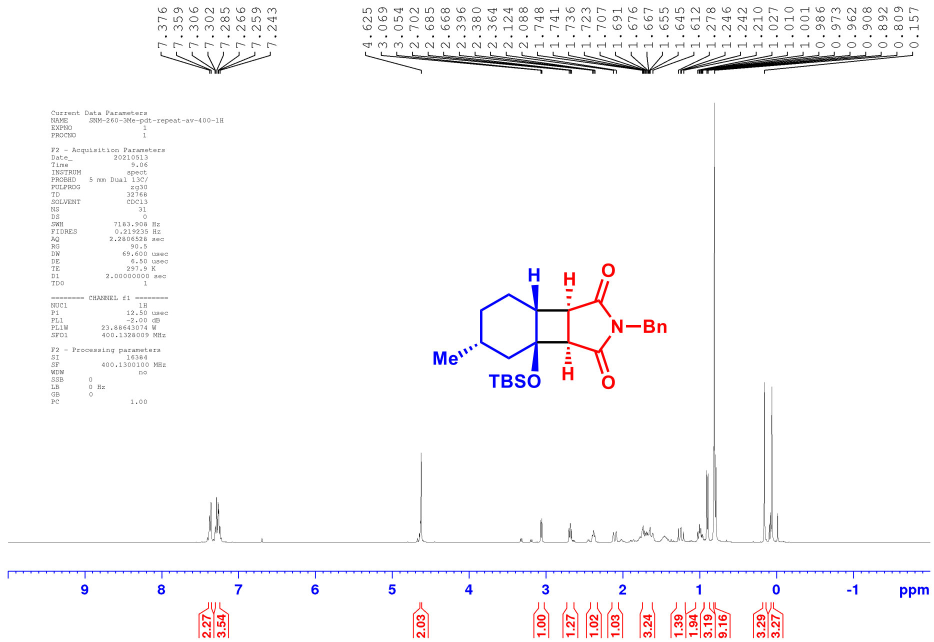
#	Time	Area	Height	Width	Area%	Symmetry
1	7.641	6645.4	628.1	0.1763	49.034	0.799
2	14.435	6907.3	340.7	0.3379	50.966	0.766

Chiral HPLC chromatogram of 4i

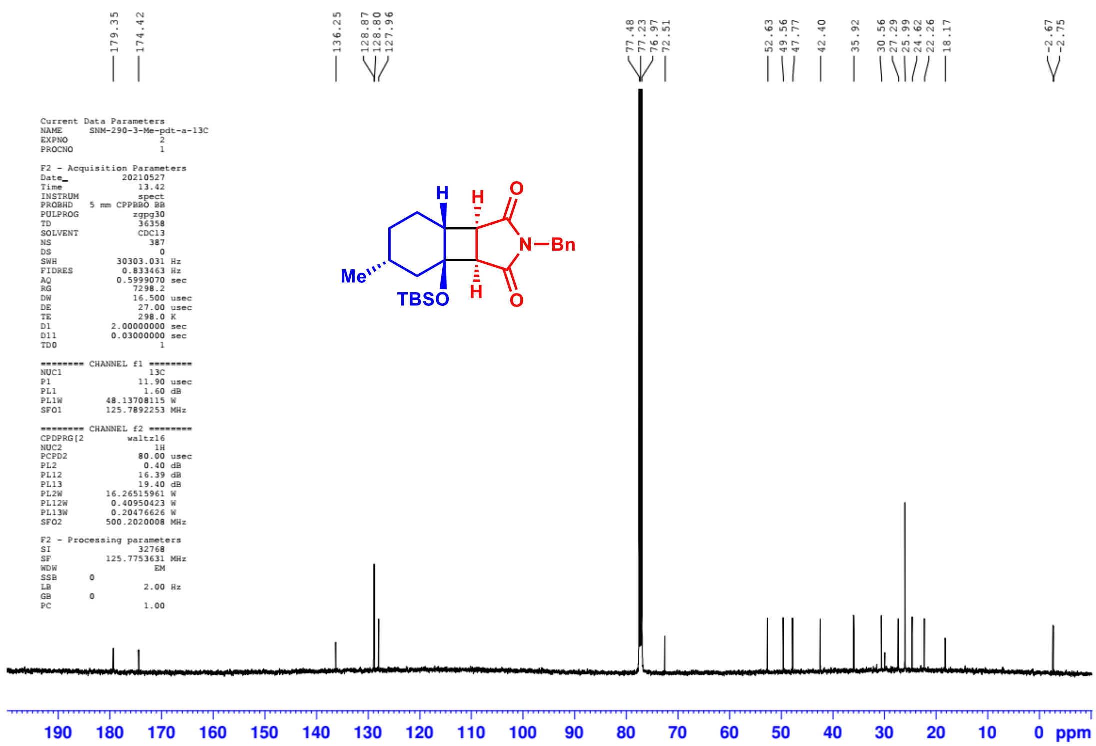


#	Time	Area	Height	Width	Area%	Symmetry
1	7.399	384	38.7	0.1538	6.337	0.801
2	13.975	5675.2	283.4	0.3116	93.663	0.764

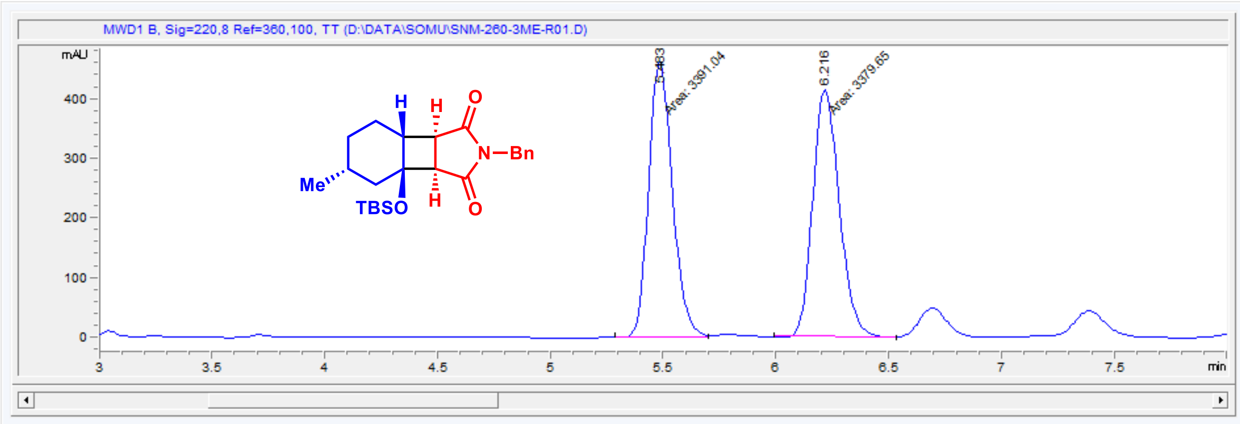
^{1}H NMR spectrum of 4j



^{13}C NMR spectrum of 4j

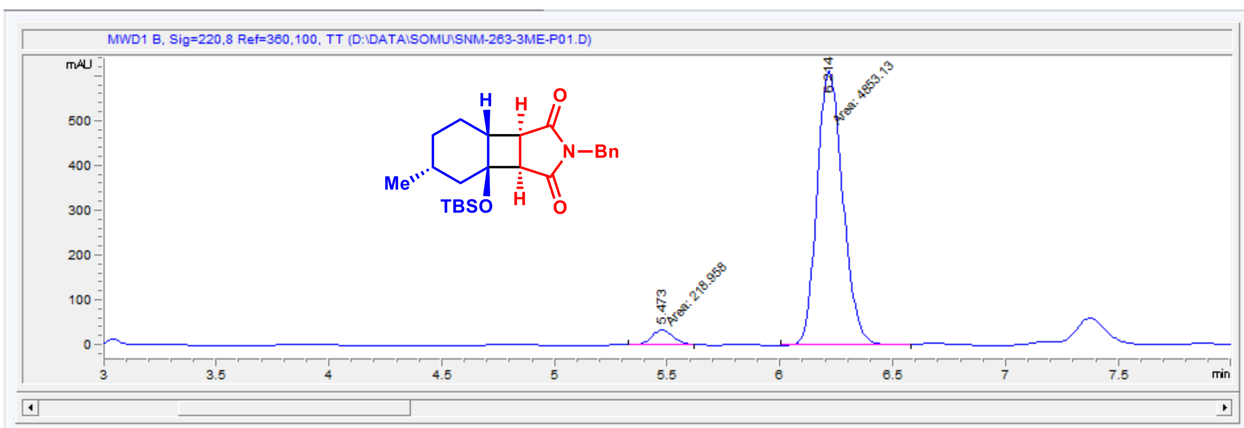


Racemic HPLC chromatogram of 4j



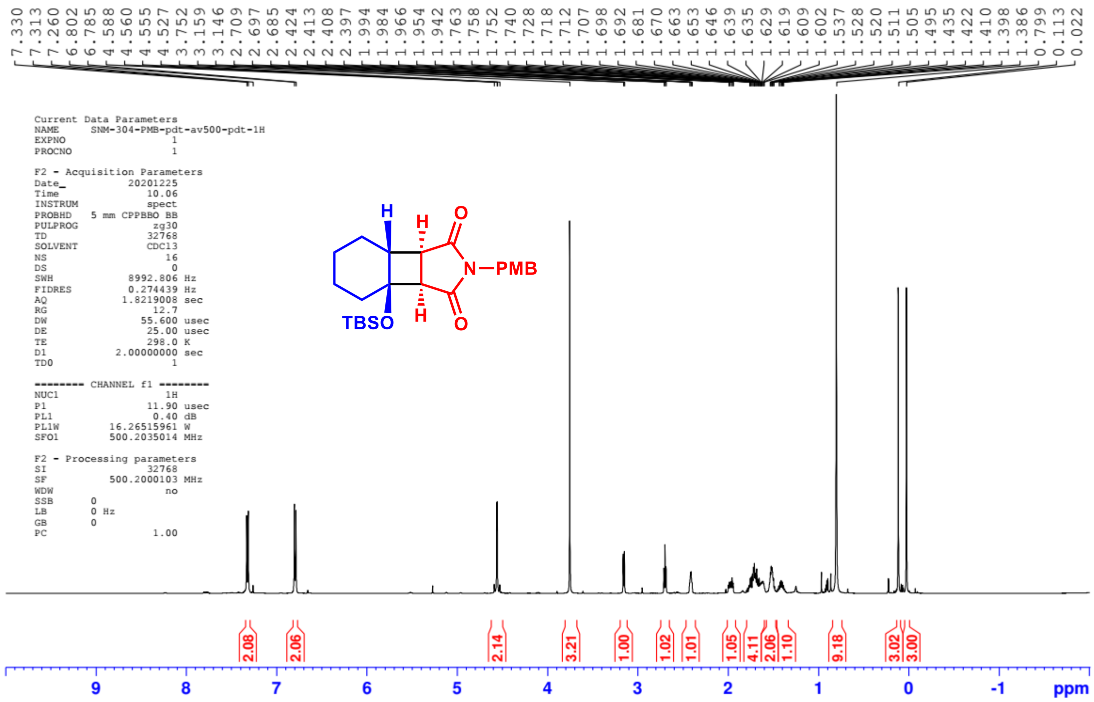
#	Time	Area	Height	Width	Area%	Symmetry
1	5.483	3391	463	0.1221	50.084	0.822
2	6.216	3379.6	413.6	0.1362	49.916	0.811

Chiral HPLC chromatogram of 4j

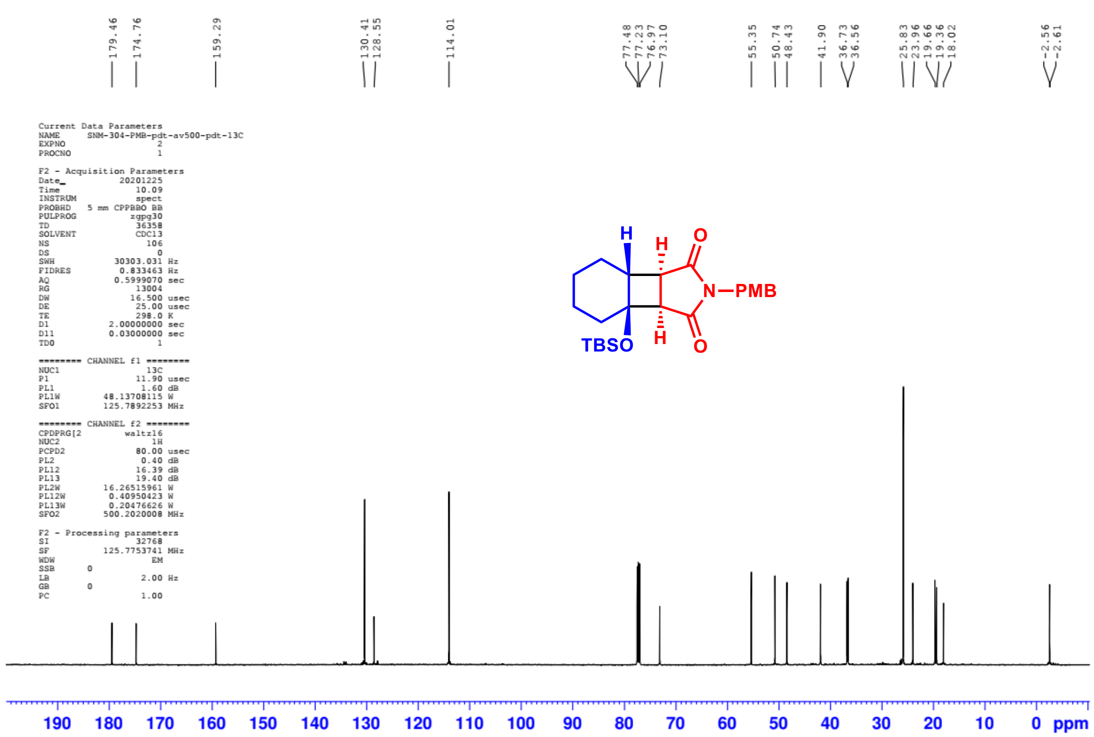


#	Time	Area	Height	Width	Area%	Symmetry
1	5.473	219	33.3	0.1096	4.317	0.869
2	6.214	4853.1	611.7	0.1322	95.683	0.816

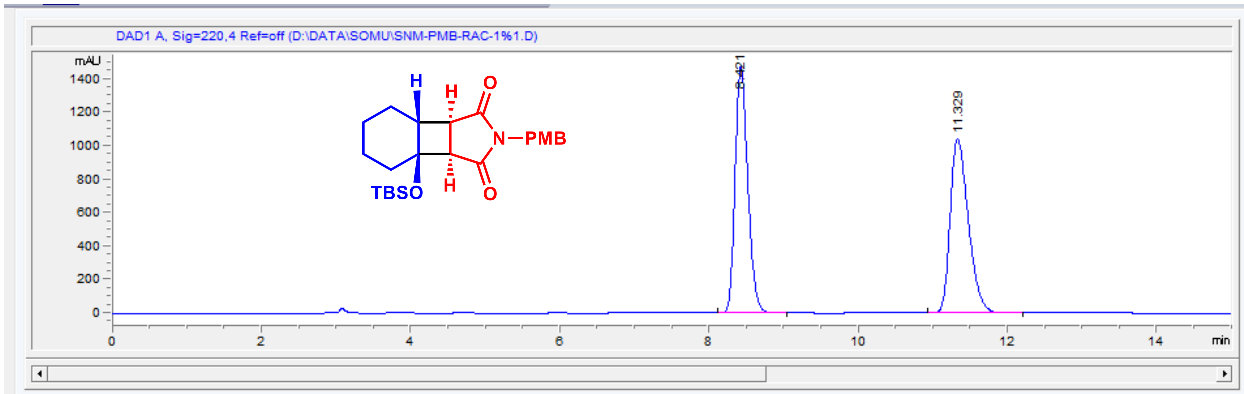
^{1}H NMR spectrum of 4k



^{13}C NMR spectrum of 4k

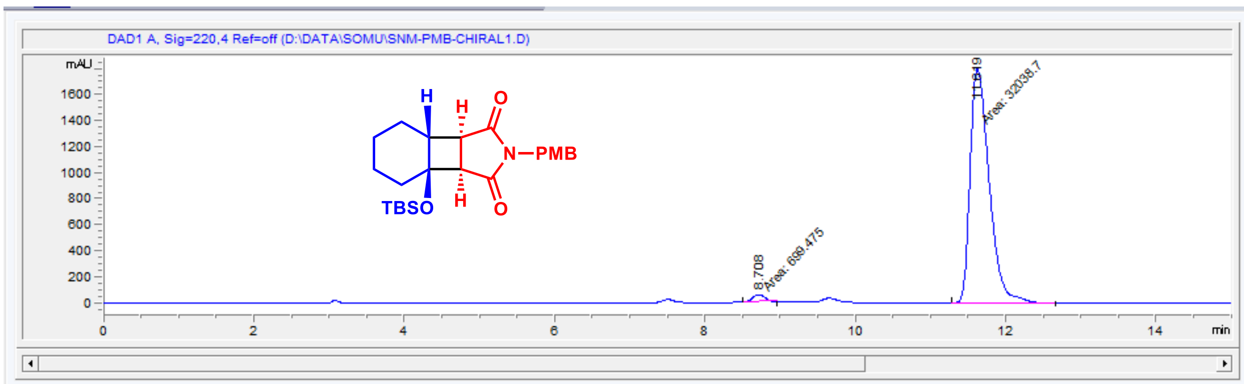


Racemic HPLC chromatogram of 4k



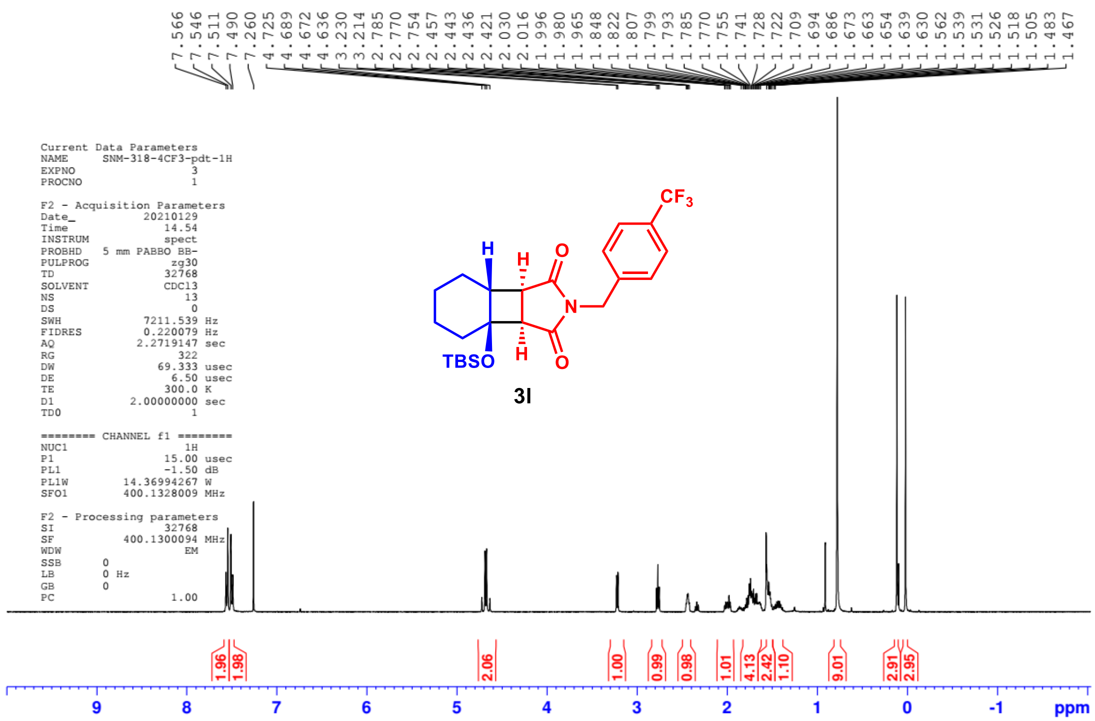
#	Time	Area	Height	Width	Area%	Symmetry
1	8.421	17423.6	1474.7	0.1818	49.787	0.762
2	11.329	17573	1041.4	0.2609	50.213	0.66

Chiral HPLC chromatogram of 4k

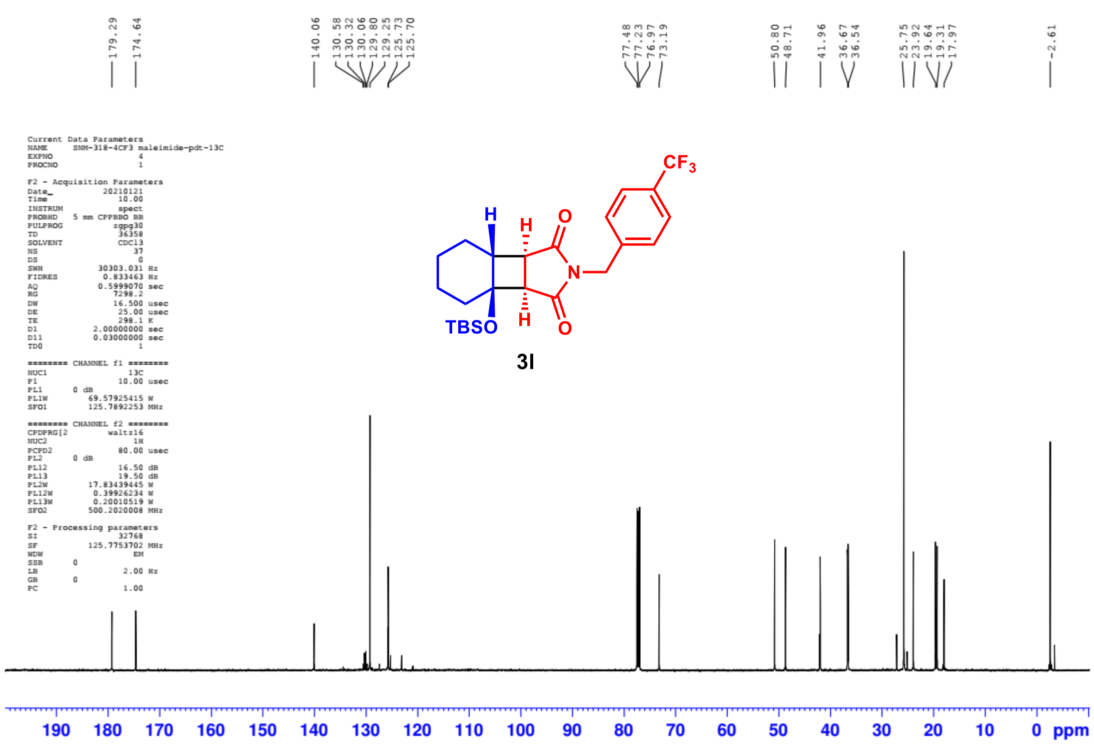


#	Time	Area	Height	Width	Area%	Symmetry
1	8.708	699.5	58.7	0.1985	2.137	1.021
2	11.619	32038.7	1804.2	0.296	97.863	0.595

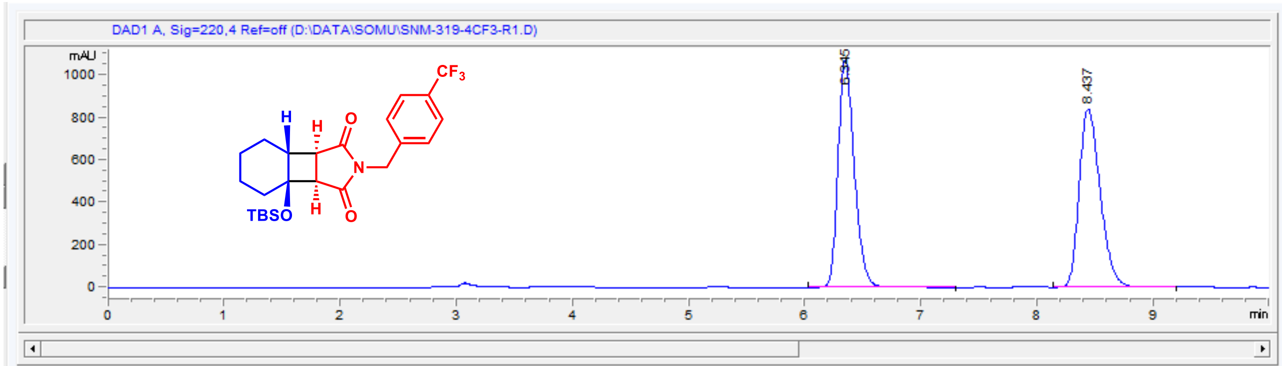
[1]H NMR spectrum of 4l



[13]C NMR spectrum of 4l

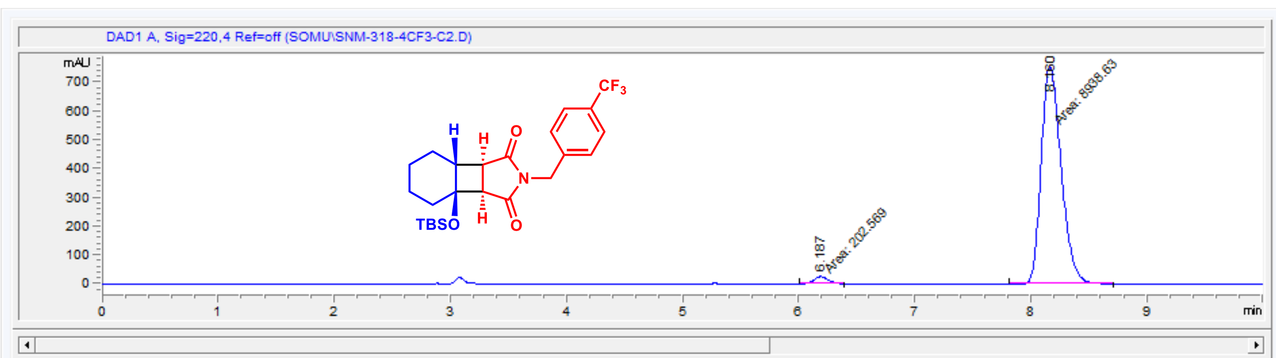


Racemic HPLC chromatogram of 4l



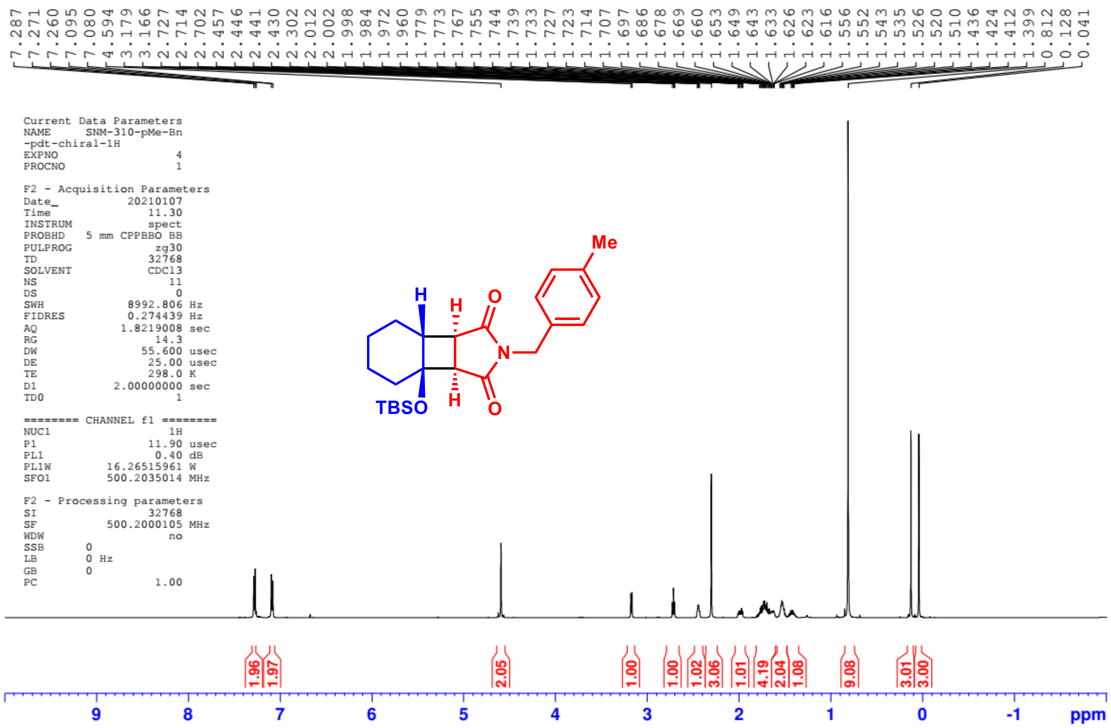
#	Time	Area	Height	Width	Area%	Symmetry
1	6.345	10400.2	1071.5	0.1492	49.587	0.726
2	8.437	10573.3	841	0.1967	50.413	0.7

Chiral HPLC chromatogram of 4l

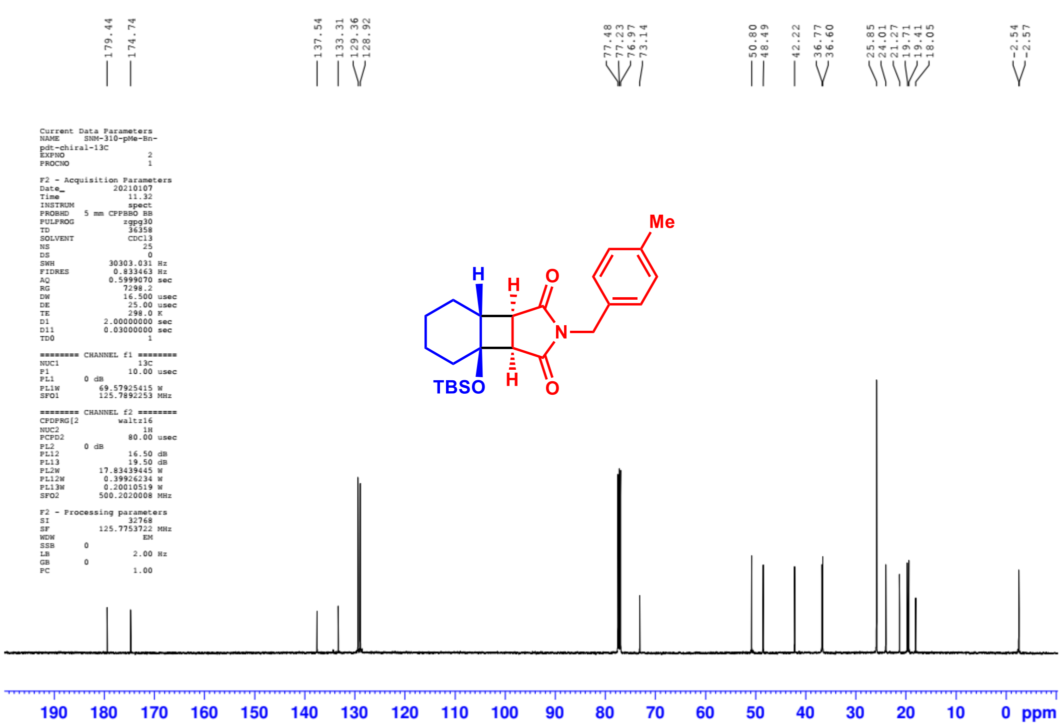


#	Time	Area	Height	Width	Area%	Symmetry
1	6.187	202.6	24.5	0.1378	2.216	0.96
2	8.16	8938.6	753	0.1978	97.784	0.729

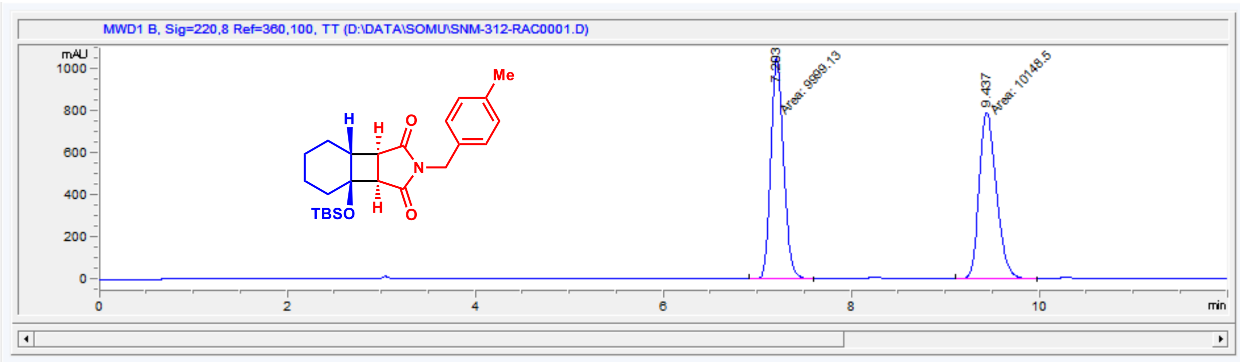
[1]H NMR spectrum of 4m



[13]C NMR spectrum of 4m

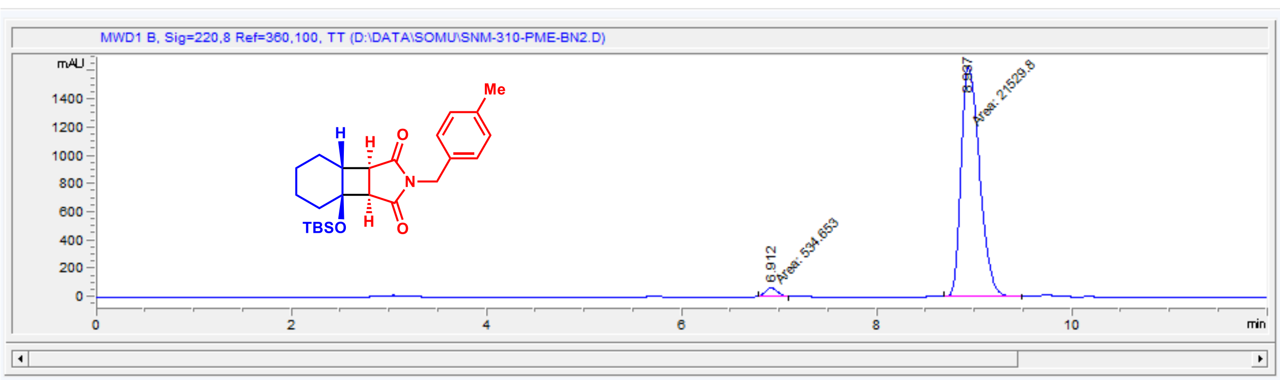


Racemic HPLC chromatogram of 4m



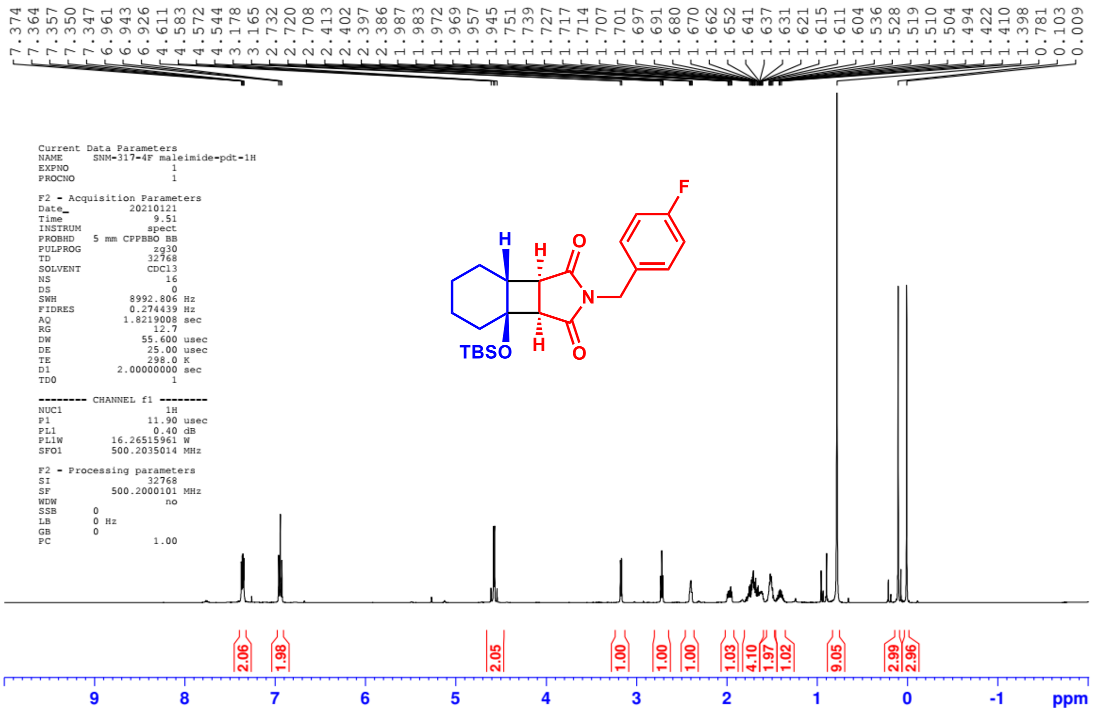
#	Time	Area	Height	Width	Area%	Symmetry
1	7.203	9999.1	1051.7	0.1585	49.629	0.82
2	9.437	10148.5	793.5	0.2132	50.371	0.744

Chiral HPLC chromatogram of 4m

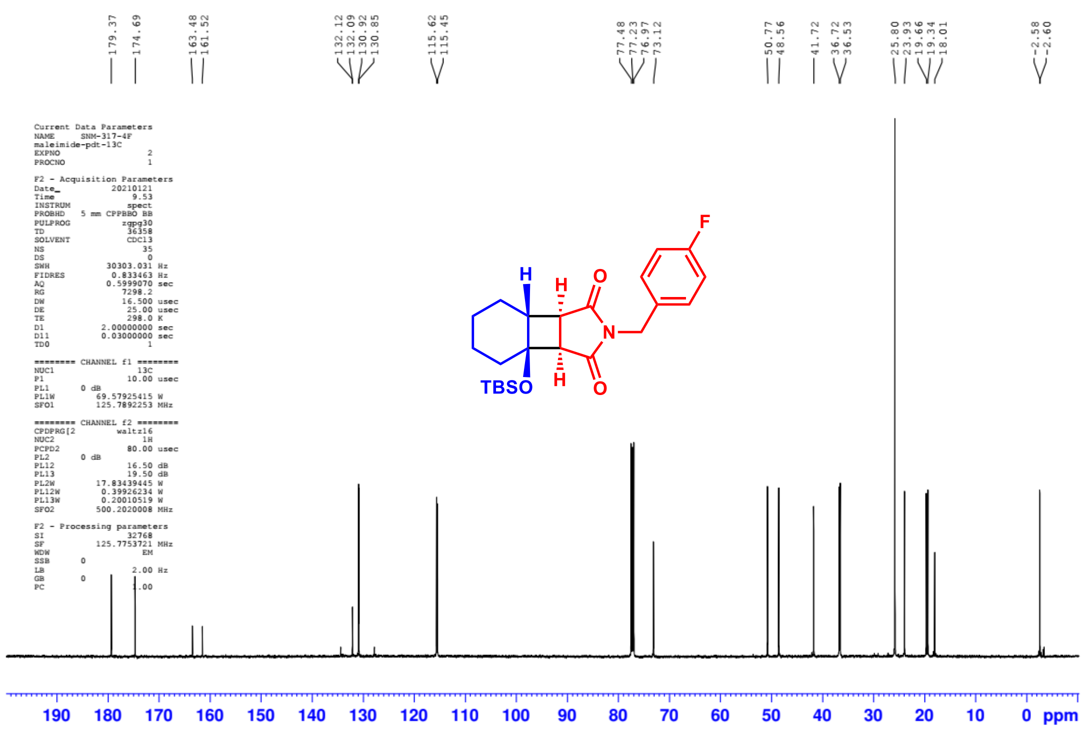


#	Time	Area	Height	Width	Area%	Symmetry
1	6.912	534.7	62.7	0.1421	2.423	0.852
2	8.937	21529.8	1622	0.2212	97.577	0.642

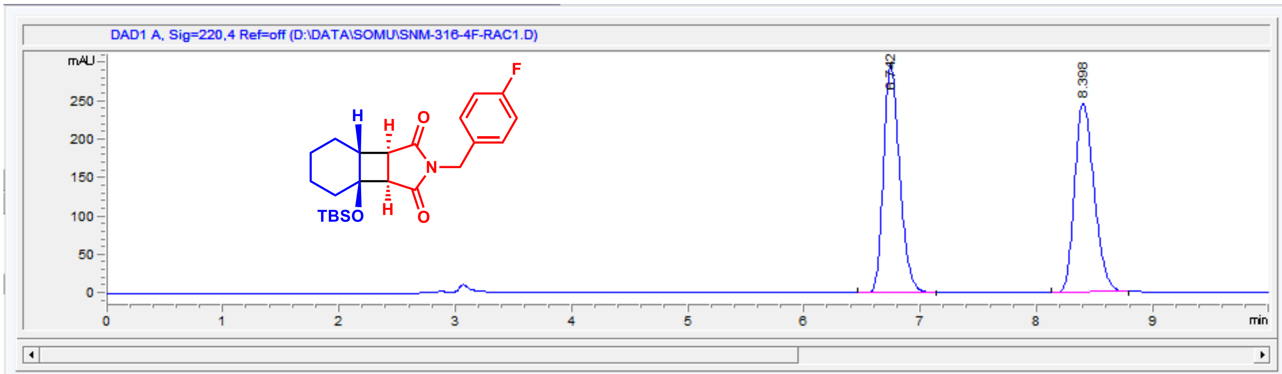
[1]H NMR spectrum of 4n



[13]C NMR spectrum of 4n

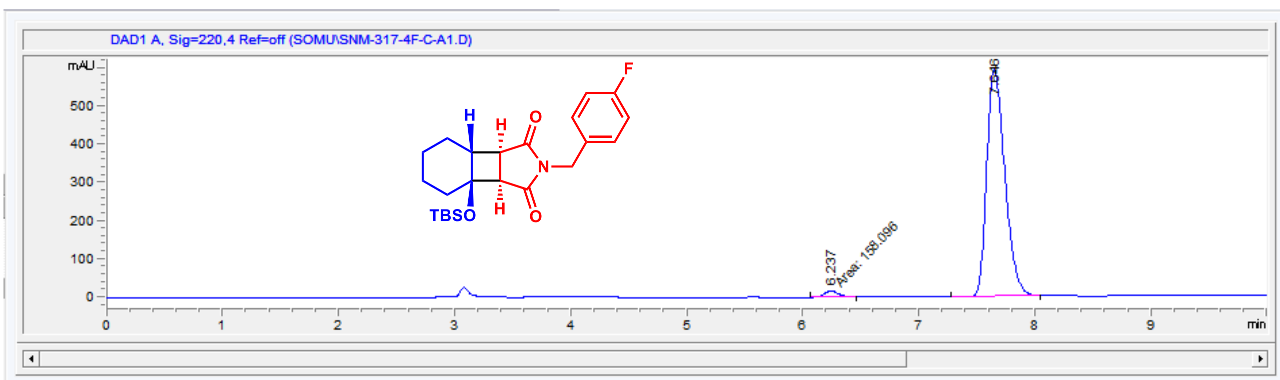


Racemic HPLC chromatogram of 4n



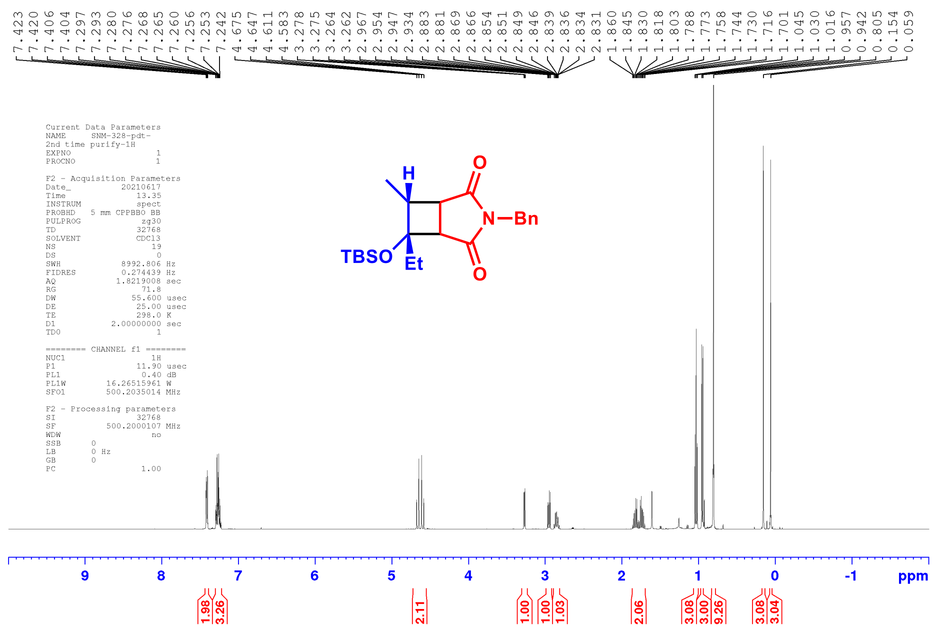
#	Time	Area	Height	Width	Area%	Symmetry
1	6.742	2882.1	297	0.1492	49.916	0.745
2	8.398	2891.8	246.6	0.1828	50.084	0.744

Chiral HPLC chromatogram of 4n

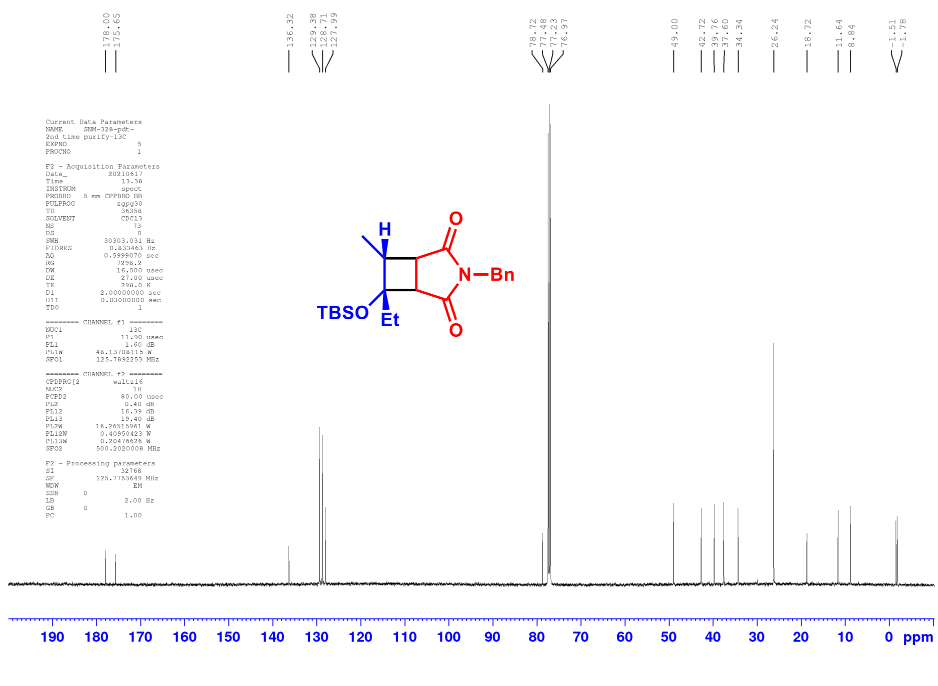


#	Time	Area	Height	Width	Area%	Symmetry
1	6.237	158.1	16.9	0.1558	2.382	0.796
2	7.646	6477.8	593.2	0.1694	97.618	0.675

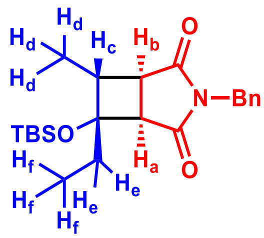
^{1}H NMR spectrum of 4o

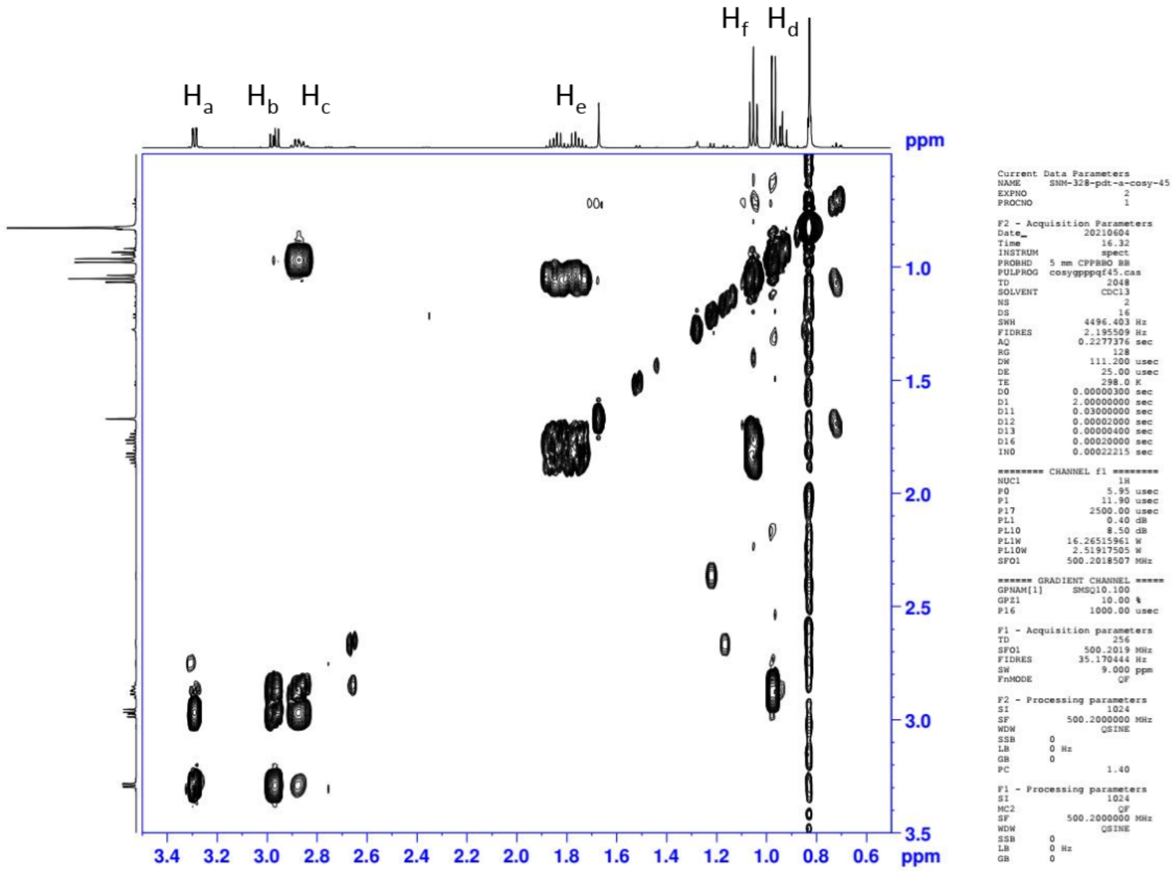


^{13}C NMR spectrum of 4o

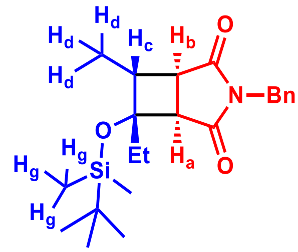


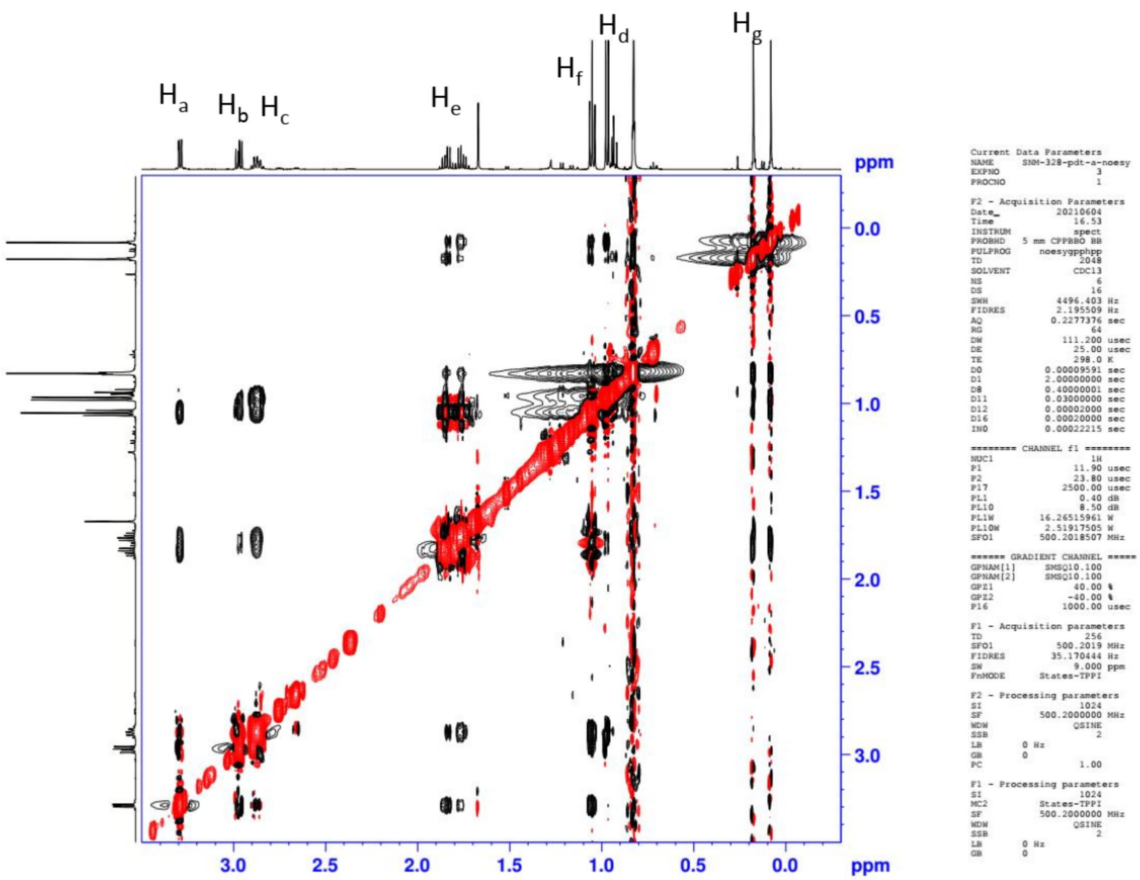
COSY spectrum of 4o:



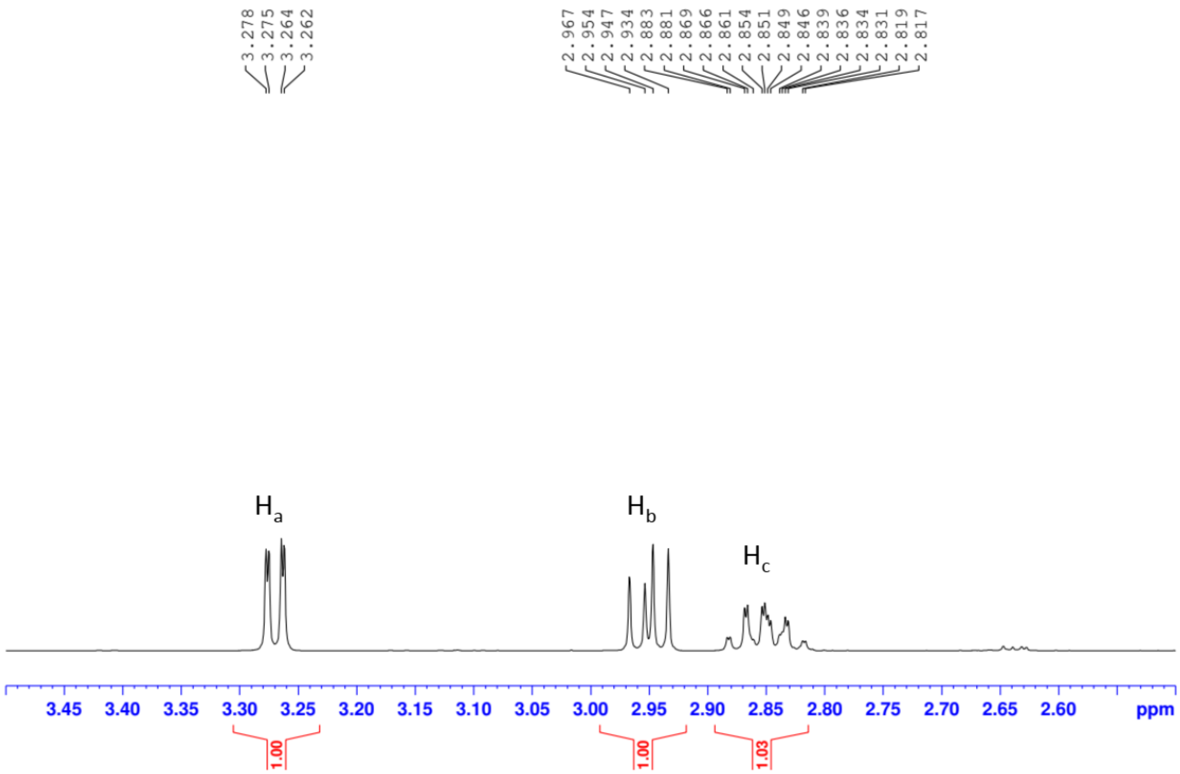


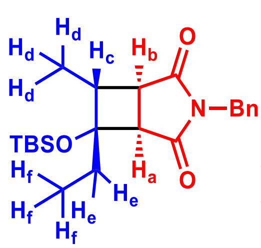
NOESY spectrum of 4o:





Expanded ^{1}H NMR spectrum of **4o** for the comparision of cupling constant of H_b with H_a and H_c





$^{3}J_{Hb\text{-}Ha}$ = 6.5 Hz
$^{3}J_{Hb\text{-}Hc}$ = 9.9 Hz

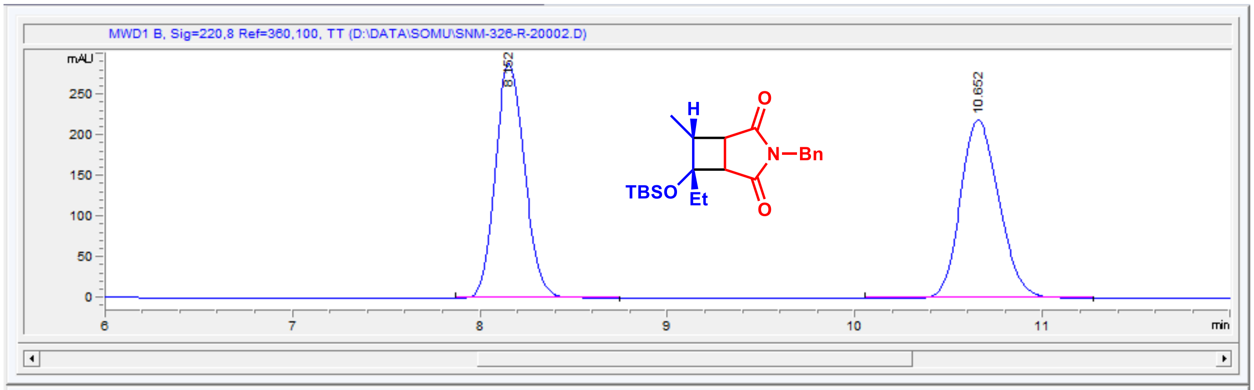
On the bases of:

(a) NOE effect between H_d and H_g

(b) NOE effect between H_c and H_e, H_f

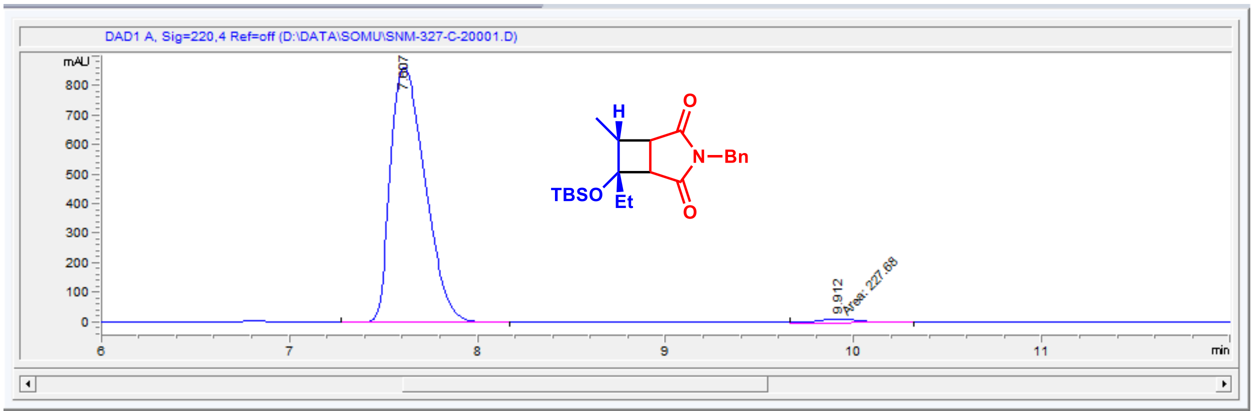
(c) Comparing the coupling constant between H_b and H_a, also Coupling constant between H_b and H_a the stereochemistry **4o** was assigned accordingly

Racemic HPLC chromatogram of 4o



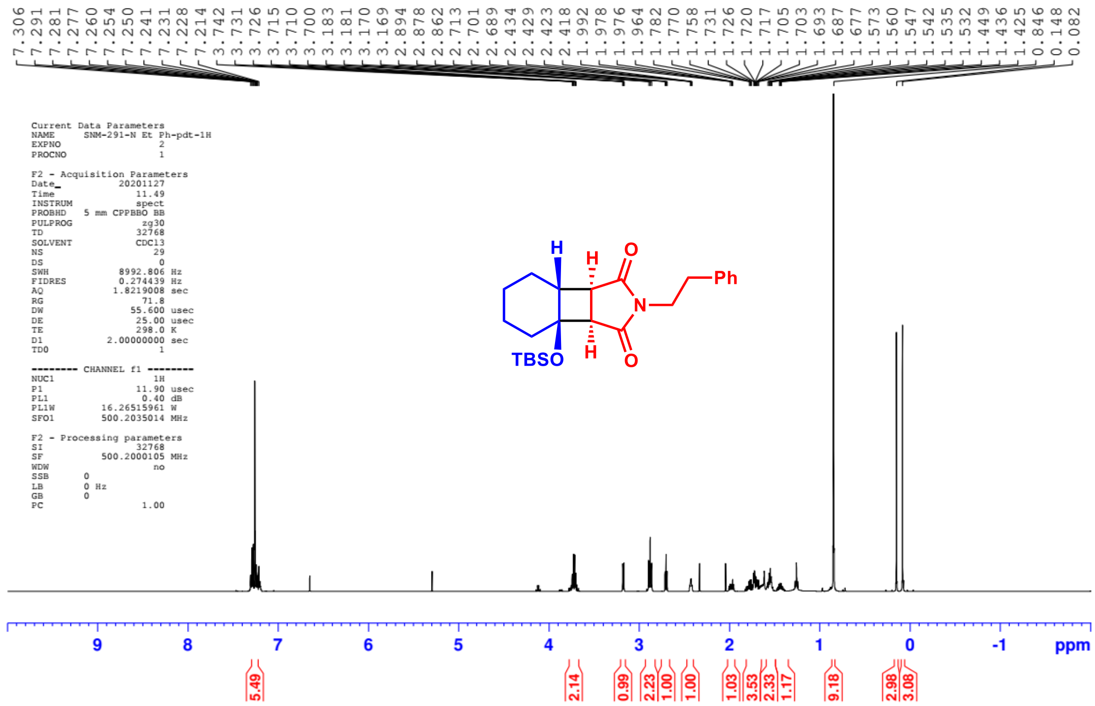
#	Time	Area	Height	Width	Area%	Symmetry
1	8.152	3128	288.9	0.1703	49.953	0.834
2	10.652	3133.9	219.6	0.2245	50.047	0.804

Chiral HPLC chromatogram of 4o

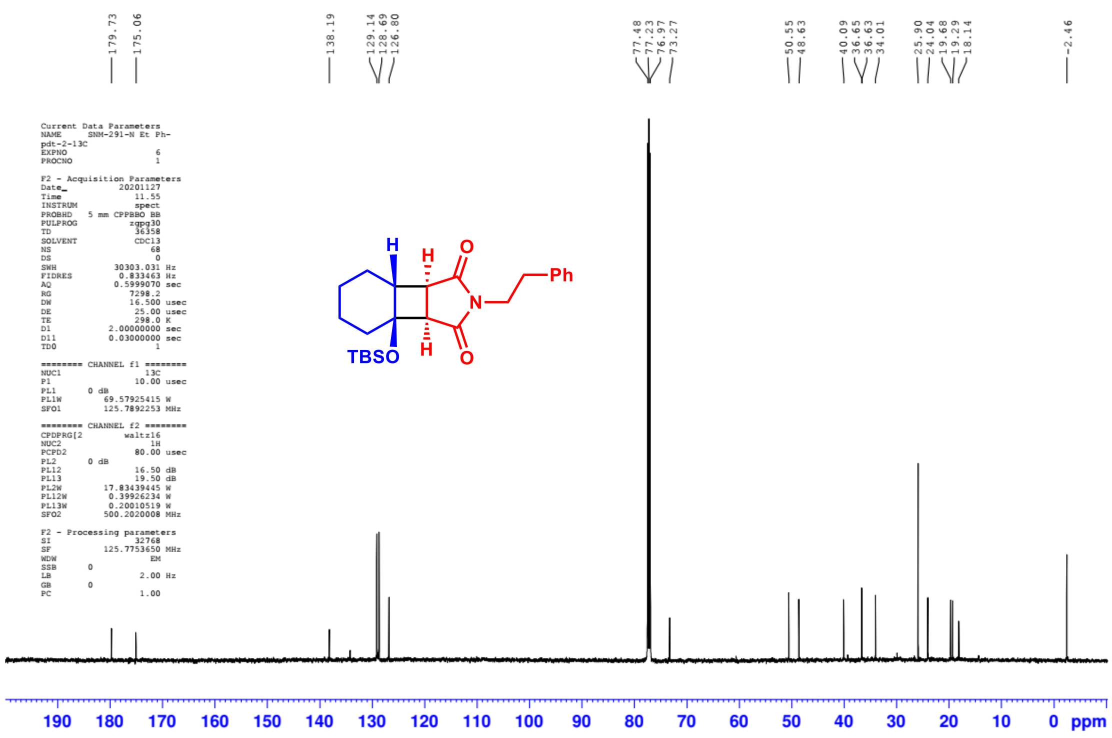


#	Time	Area	Height	Width	Area%	Symmetry
1	7.607	11027.4	862.8	0.2031	97.977	0.604
2	9.912	227.7	14.2	0.2665	2.023	1.047

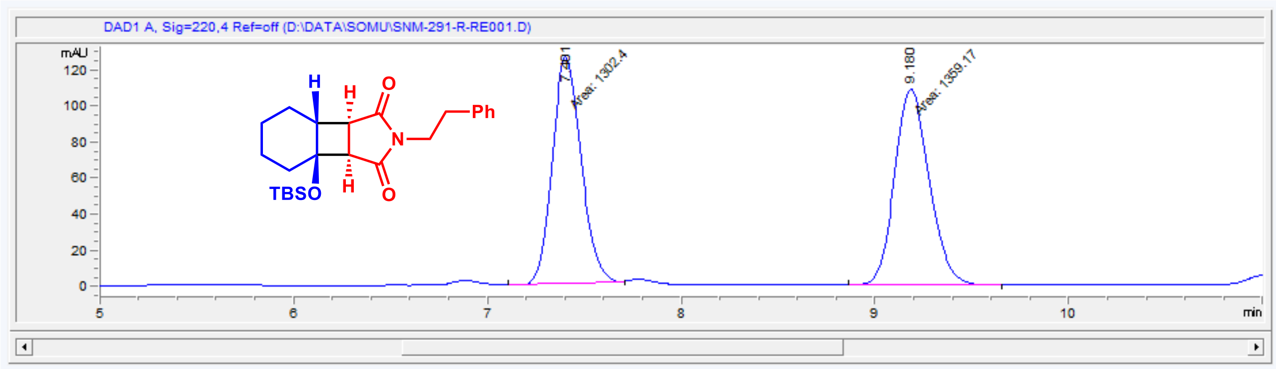
^{1}H NMR spectrum of 4p



^{13}C NMR spectrum of 4p

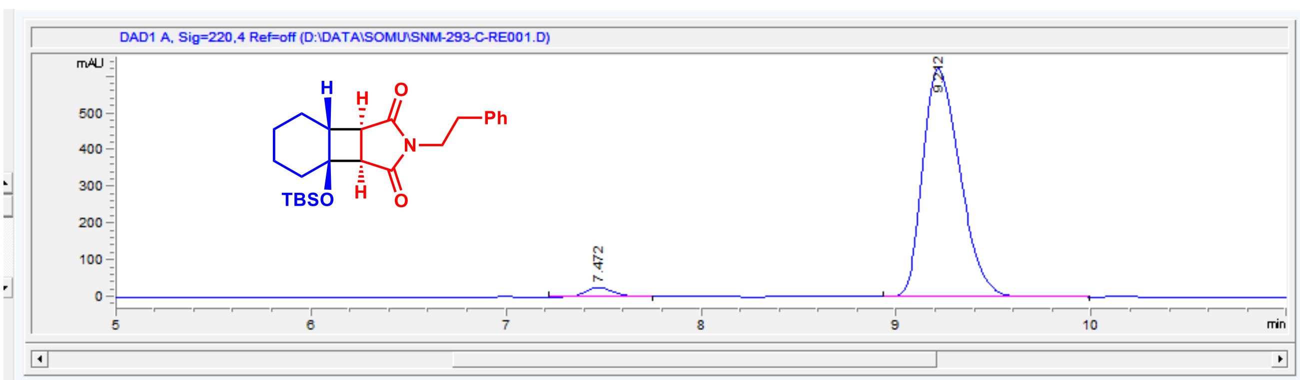


Racemic HPLC chromatogram of 4p



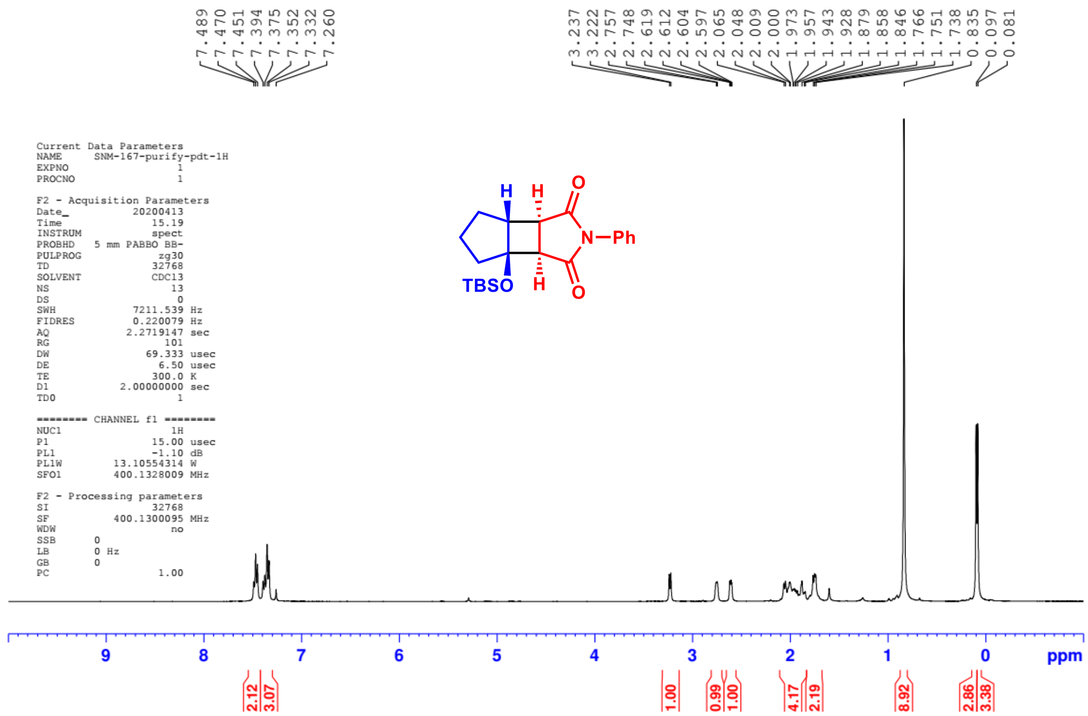
#	Time	Area	Height	Width	Area%	Symmetry
1	7.401	1302.4	125.7	0.1727	48.933	0.834
2	9.18	1359.2	108.8	0.2082	51.067	0.826

Chiral HPLC chromatogram of 4p

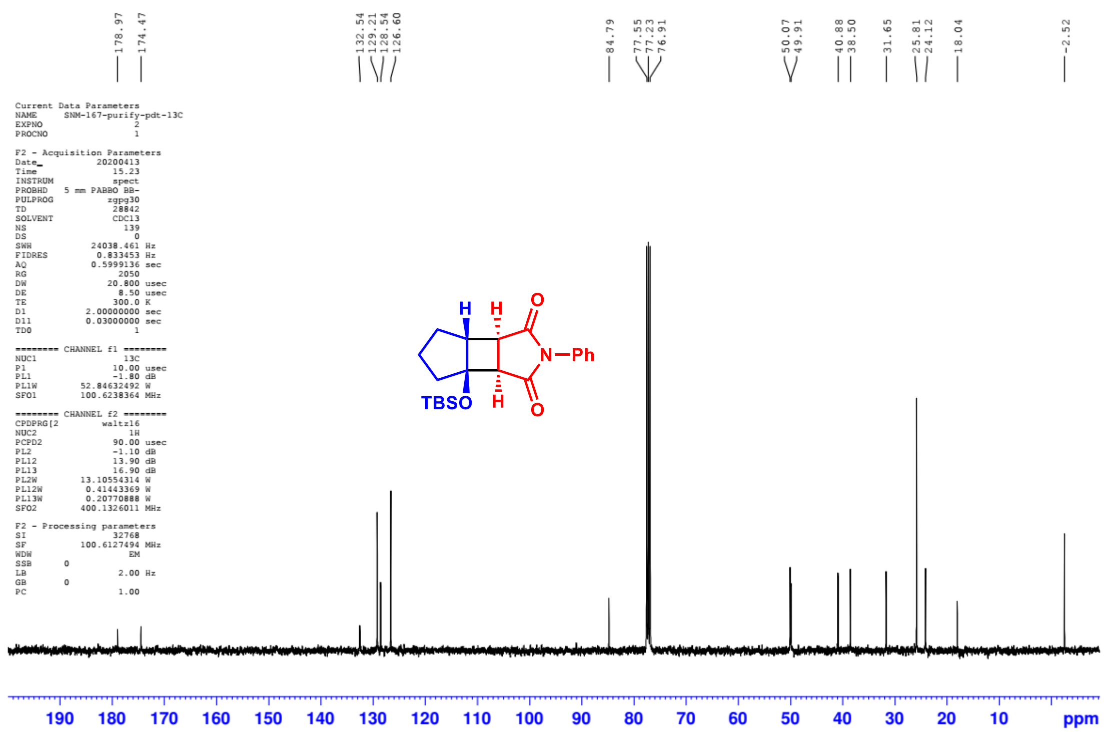


#	Time	Area	Height	Width	Area%	Symmetry
1	7.472	254.1	26.1	0.1497	3.000	0.831
2	9.212	8216	624.2	0.2056	97.000	0.679

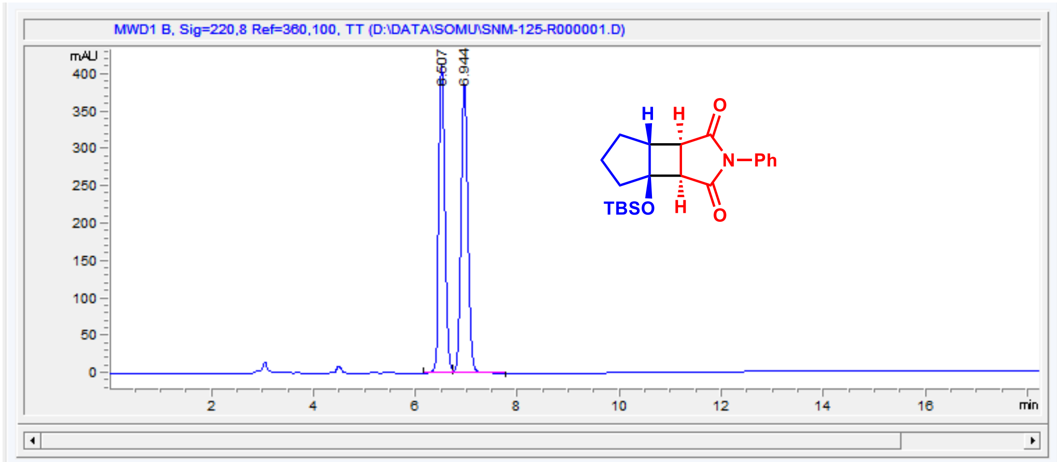
[1]H NMR spectrum of 4q



^{13}C NMR spectrum of 4q

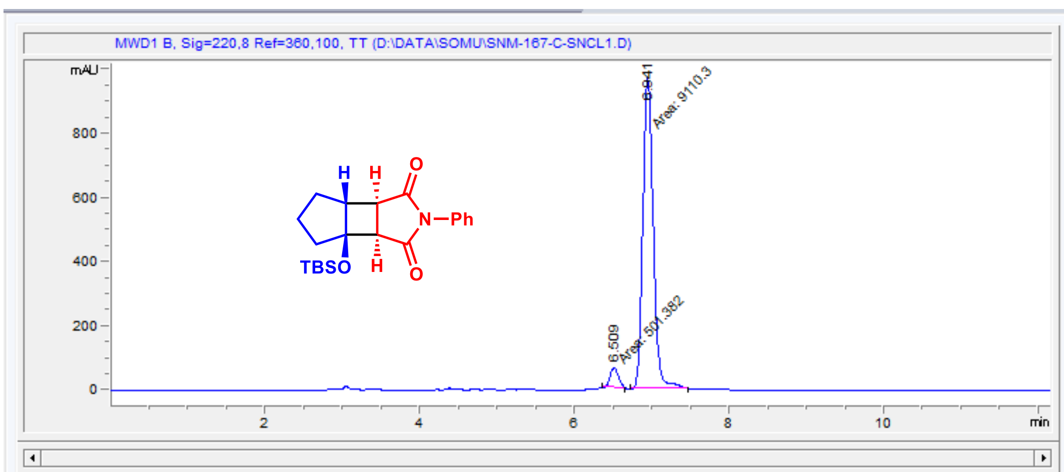


Racemic HPLC chromatogram of 4q



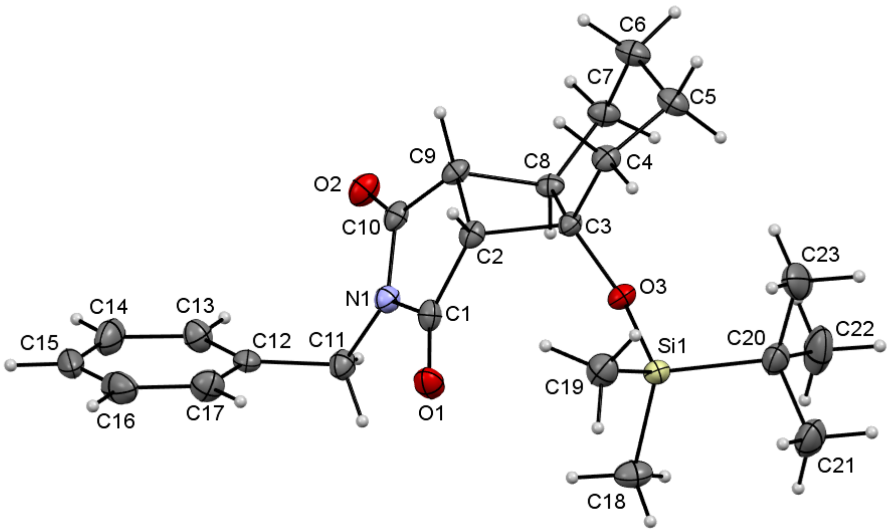
#	Time	Area	Height	Width	Area%	Symmetry
1	6.507	3553.4	413.9	0.1322	49.951	0.908
2	6.944	3560.3	387.5	0.1412	50.049	0.874

Chiral HPLC chromatogram of 4q



#	Time	Area	Height	Width	Area%	Symmetry
1	6.509	501.4	63.7	0.1311	5.216	0.87
2	6.941	9110.3	968.9	0.1567	94.784	0.834

X-ray structure of 4a and its data



X-ray crystal structure of **4a** (Deposition number: CCDC 2083039)

Table S2. Crystal data and structure refinement for i17962.

Identification code	i17962	
Empirical formula	C23 H33 N O3 Si	
Formula weight	399.59	
Temperature	100.0(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.3096(2) Å	α= 90°.
	b = 12.9213(4) Å	β= 90°.
	c = 26.6212(8) Å	γ = 90°.
Volume	2170.38(12) $Å^3$	
Z	4	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	1.132 mm^{-1}	
F(000)	864	
Crystal size	0.245 x 0.173 x 0.117 mm^3	
Theta range for data collection	3.802 to 66.583°.	
Index ranges	-7<=h<=7, -15<=k<=15, -31<=l<=31	
Reflections collected	46023	
Independent reflections	3844 [R(int) = 0.1278]	
Completeness to theta = 66.583°	100.0 %	

Absorption correction	Numerical
Max. and min. transmission	1 and 0.8054
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3844 / 0 / 258
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0824
R indices (all data)	R1 = 0.0357, wR2 = 0.0840
Absolute structure parameter	0.029(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.213 and -0.264 e.Å^{-3}

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for i17962. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	3757(1)	5661(1)	3662(1)	17(1)
O(1)	5425(3)	6004(1)	2369(1)	26(1)
O(2)	10483(3)	8530(1)	2368(1)	25(1)
O(3)	5374(3)	6661(1)	3591(1)	18(1)
N(1)	8238(3)	7136(2)	2311(1)	18(1)
C(1)	6234(4)	6830(2)	2471(1)	19(1)
C(2)	5267(4)	7706(2)	2766(1)	17(1)
C(3)	5302(4)	7638(2)	3356(1)	16(1)
C(4)	3557(4)	8332(2)	3571(1)	19(1)
C(5)	4269(4)	8888(2)	4049(1)	24(1)
C(6)	6149(4)	9584(2)	3931(1)	25(1)
C(7)	8045(4)	8937(2)	3769(1)	21(1)
C(8)	7480(4)	8167(2)	3357(1)	17(1)
C(9)	7069(4)	8517(2)	2799(1)	18(1)
C(10)	8792(4)	8128(2)	2467(1)	19(1)
C(11)	9693(4)	6458(2)	2035(1)	22(1)
C(12)	9836(4)	6694(2)	1480(1)	19(1)
C(13)	11664(4)	7119(2)	1284(1)	24(1)
C(14)	11855(5)	7284(2)	770(1)	34(1)
C(15)	10244(5)	7021(2)	453(1)	32(1)
C(16)	8394(5)	6605(2)	648(1)	35(1)
C(17)	8187(4)	6452(2)	1160(1)	27(1)
C(18)	5332(5)	4503(2)	3479(1)	29(1)
C(19)	1381(5)	5761(2)	3254(1)	27(1)
C(20)	2958(5)	5573(2)	4348(1)	27(1)
C(21)	1830(5)	4536(2)	4429(1)	37(1)
C(22)	4948(6)	5620(3)	4681(1)	46(1)
C(23)	1433(6)	6442(2)	4495(1)	43(1)

Table S4. Bond lengths [Å] and angles [°] for i17962.

Si(1)-O(3)	1.6571(17)
Si(1)-C(19)	1.855(3)
Si(1)-C(18)	1.861(3)
Si(1)-C(20)	1.897(3)
O(1)-C(1)	1.213(3)
O(2)-C(10)	1.216(3)
O(3)-C(3)	1.409(3)
N(1)-C(10)	1.391(3)
N(1)-C(1)	1.392(3)
N(1)-C(11)	1.467(3)
C(1)-C(2)	1.507(3)
C(2)-C(9)	1.548(3)
C(2)-C(3)	1.571(3)
C(2)-H(2)	1.0000
C(3)-C(4)	1.531(3)
C(3)-C(8)	1.535(3)
C(4)-C(5)	1.529(3)
C(4)-H(4A)	0.9900
C(4)-H(4AB)	0.9900
C(5)-C(6)	1.522(4)
C(5)-H(5A)	0.9900
C(5)-H(5AB)	0.9900
C(6)-C(7)	1.522(3)
C(6)-H(6A)	0.9900
C(6)-H(6AB)	0.9900
C(7)-C(8)	1.524(3)
C(7)-H(7A)	0.9900
C(7)-H(7AB)	0.9900
C(8)-C(9)	1.573(3)
C(8)-H(8)	1.0000
C(9)-C(10)	1.489(3)
C(9)-H(9)	1.0000
C(11)-C(12)	1.510(3)
C(11)-H(11A)	0.9900

C(11)-H(11B)	0.9900
C(12)-C(13)	1.380(4)
C(12)-C(17)	1.381(4)
C(13)-C(14)	1.389(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.364(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.386(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.383(4)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(23)	1.529(4)
C(20)-C(21)	1.533(4)
C(20)-C(22)	1.538(4)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
O(3)-Si(1)-C(19)	112.15(11)
O(3)-Si(1)-C(18)	105.58(11)
C(19)-Si(1)-C(18)	109.54(13)
O(3)-Si(1)-C(20)	108.63(10)
C(19)-Si(1)-C(20)	110.59(13)

C(18)-Si(1)-C(20)	110.23(12)
C(3)-O(3)-Si(1)	136.77(16)
C(10)-N(1)-C(1)	113.5(2)
C(10)-N(1)-C(11)	122.9(2)
C(1)-N(1)-C(11)	123.5(2)
O(1)-C(1)-N(1)	124.3(2)
O(1)-C(1)-C(2)	127.3(2)
N(1)-C(1)-C(2)	108.3(2)
C(1)-C(2)-C(9)	103.9(2)
C(1)-C(2)-C(3)	118.21(19)
C(9)-C(2)-C(3)	88.35(17)
C(1)-C(2)-H(2)	114.3
C(9)-C(2)-H(2)	114.3
C(3)-C(2)-H(2)	114.3
O(3)-C(3)-C(4)	112.41(19)
O(3)-C(3)-C(8)	111.65(19)
C(4)-C(3)-C(8)	112.47(19)
O(3)-C(3)-C(2)	119.68(19)
C(4)-C(3)-C(2)	109.26(19)
C(8)-C(3)-C(2)	89.39(18)
C(5)-C(4)-C(3)	112.0(2)
C(5)-C(4)-H(4A)	109.2
C(3)-C(4)-H(4A)	109.2
C(5)-C(4)-H(4AB)	109.2
C(3)-C(4)-H(4AB)	109.2
H(4A)-C(4)-H(4AB)	107.9
C(6)-C(5)-C(4)	109.6(2)
C(6)-C(5)-H(5A)	109.8
C(4)-C(5)-H(5A)	109.8
C(6)-C(5)-H(5AB)	109.8
C(4)-C(5)-H(5AB)	109.8
H(5A)-C(5)-H(5AB)	108.2
C(5)-C(6)-C(7)	110.2(2)
C(5)-C(6)-H(6A)	109.6
C(7)-C(6)-H(6A)	109.6
C(5)-C(6)-H(6AB)	109.6

C(7)-C(6)-H(6AB)	109.6
H(6A)-C(6)-H(6AB)	108.1
C(6)-C(7)-C(8)	112.3(2)
C(6)-C(7)-H(7A)	109.2
C(8)-C(7)-H(7A)	109.2
C(6)-C(7)-H(7AB)	109.2
C(8)-C(7)-H(7AB)	109.2
H(7A)-C(7)-H(7AB)	107.9
C(7)-C(8)-C(3)	120.1(2)
C(7)-C(8)-C(9)	122.0(2)
C(3)-C(8)-C(9)	88.77(17)
C(7)-C(8)-H(8)	108.1
C(3)-C(8)-H(8)	108.1
C(9)-C(8)-H(8)	108.1
C(10)-C(9)-C(2)	105.9(2)
C(10)-C(9)-C(8)	110.1(2)
C(2)-C(9)-C(8)	88.86(17)
C(10)-C(9)-H(9)	116.2
C(2)-C(9)-H(9)	116.2
C(8)-C(9)-H(9)	116.2
O(2)-C(10)-N(1)	123.3(2)
O(2)-C(10)-C(9)	128.7(2)
N(1)-C(10)-C(9)	107.8(2)
N(1)-C(11)-C(12)	114.0(2)
N(1)-C(11)-H(11A)	108.8
C(12)-C(11)-H(11A)	108.8
N(1)-C(11)-H(11B)	108.8
C(12)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.6
C(13)-C(12)-C(17)	119.1(2)
C(13)-C(12)-C(11)	120.1(2)
C(17)-C(12)-C(11)	120.8(2)
C(12)-C(13)-C(14)	120.5(3)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	120.4(3)

C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	119.5(2)
C(14)-C(15)-H(15)	120.3
C(16)-C(15)-H(15)	120.3
C(17)-C(16)-C(15)	120.3(3)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(12)-C(17)-C(16)	120.3(3)
C(12)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
Si(1)-C(18)-H(18A)	109.5
Si(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
Si(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(23)-C(20)-C(21)	108.2(2)
C(23)-C(20)-C(22)	109.7(3)
C(21)-C(20)-C(22)	109.4(2)
C(23)-C(20)-Si(1)	111.74(18)
C(21)-C(20)-Si(1)	108.19(17)
C(22)-C(20)-Si(1)	109.59(19)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5

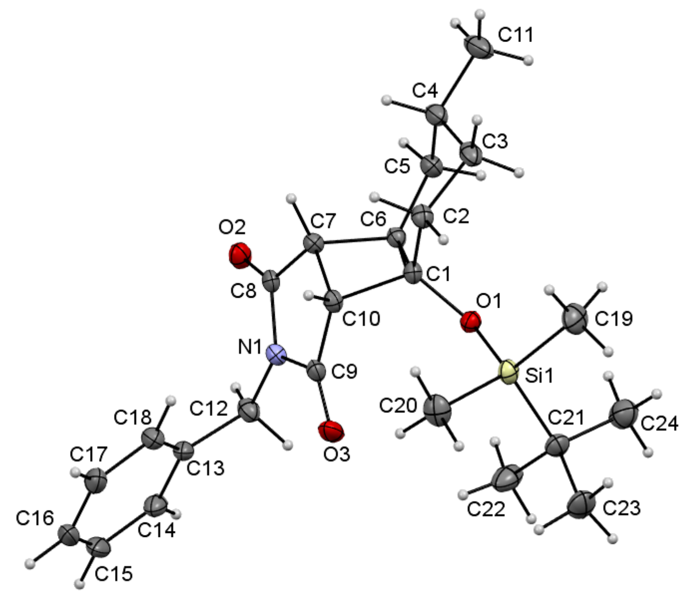
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3)for i17962. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	19(1)	14(1)	18(1)	1(1)	0(1)	-1(1)
O(1)	28(1)	26(1)	24(1)	-4(1)	2(1)	-7(1)
O(2)	19(1)	27(1)	29(1)	6(1)	2(1)	-3(1)
O(3)	19(1)	15(1)	21(1)	3(1)	0(1)	0(1)
N(1)	17(1)	19(1)	19(1)	1(1)	2(1)	0(1)
C(1)	19(1)	24(1)	15(1)	2(1)	-1(1)	0(1)
C(2)	14(1)	19(1)	18(1)	3(1)	0(1)	1(1)
C(3)	17(1)	15(1)	16(1)	2(1)	0(1)	1(1)
C(4)	15(1)	19(1)	22(1)	1(1)	1(1)	2(1)
C(5)	24(2)	22(1)	24(1)	-6(1)	1(1)	3(1)
C(6)	26(1)	19(1)	29(1)	-6(1)	-1(1)	3(1)
C(7)	18(1)	19(1)	26(1)	-3(1)	-1(1)	-1(1)
C(8)	15(1)	15(1)	20(1)	0(1)	-2(1)	3(1)
C(9)	16(1)	16(1)	22(1)	4(1)	-2(1)	0(1)
C(10)	17(1)	21(1)	18(1)	6(1)	-2(1)	2(1)
C(11)	21(1)	24(1)	20(1)	2(1)	4(1)	2(1)
C(12)	22(1)	14(1)	19(1)	-1(1)	2(1)	4(1)
C(13)	21(1)	29(1)	23(1)	-2(1)	2(1)	-1(1)
C(14)	37(2)	33(2)	31(1)	8(1)	14(1)	3(1)
C(15)	52(2)	25(1)	18(1)	1(1)	4(1)	11(1)
C(16)	48(2)	29(2)	29(1)	-5(1)	-17(1)	3(1)
C(17)	26(2)	27(2)	29(1)	0(1)	-3(1)	-6(1)
C(18)	28(2)	20(1)	40(2)	-1(1)	1(1)	4(1)
C(19)	27(2)	29(1)	27(1)	2(1)	-5(1)	-4(1)
C(20)	34(2)	26(1)	21(1)	4(1)	2(1)	-6(1)
C(21)	47(2)	35(2)	30(1)	9(1)	4(1)	-11(2)
C(22)	59(2)	58(2)	22(1)	9(2)	-10(1)	-22(2)
C(23)	61(2)	36(2)	32(2)	-2(1)	26(2)	-5(2)

X-ray structure of 4g and its data



X-ray crystal structure of **4g** (Deposition number: CCDC 2083040)

Table S6. Crystal data and structure refinement for i18031.

Identification code	i18031	
Empirical formula	C24 H35 N O3 Si	
Formula weight	413.62	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.5874(3) Å	α= 90°.
	b = 6.3337(2) Å	β= 92.1940(10)°.
	c = 15.8579(4) Å	γ = 90°.
Volume	1162.98(6) $Å^3$	
Z	2	
Density (calculated)	1.181 Mg/m^3	
Absorption coefficient	0.125 mm^{-1}	
F(000)	448	
Crystal size	0.264 x 0.183 x 0.120 mm^3	
Theta range for data collection	2.571 to 27.102°.	
Index ranges	-14<=h<=14, -8<=k<=8, -20<=l<=20	
Reflections collected	34193	

Independent reflections	5088 [R(int) = 0.0398]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Numerical
Max. and min. transmission	1 and 0.975
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5088 / 1 / 268
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0657
R indices (all data)	R1 = 0.0308, wR2 = 0.0686
Absolute structure parameter	0.03(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.204 and -0.147 e.$Å^{-3}$

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for i18031. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	6815(1)	2393(1)	8562(1)	19(1)
O(1)	6008(1)	4296(2)	8129(1)	17(1)
O(2)	4948(1)	9253(2)	5483(1)	22(1)
O(3)	7769(1)	4920(3)	6554(1)	27(1)
N(1)	6536(1)	7303(3)	5917(1)	17(1)
C(1)	5221(1)	4253(3)	7429(1)	15(1)
C(2)	4317(2)	2496(3)	7484(1)	19(1)
C(3)	3317(2)	3113(3)	8034(1)	23(1)
C(4)	2688(2)	5036(3)	7648(1)	23(1)
C(5)	3511(2)	6910(3)	7646(1)	20(1)
C(6)	4654(2)	6421(3)	7257(1)	15(1)
C(7)	4750(2)	5979(3)	6283(1)	16(1)
C(8)	5356(2)	7709(3)	5829(1)	16(1)
C(9)	6794(2)	5448(3)	6360(1)	18(1)
C(10)	5679(2)	4297(3)	6509(1)	16(1)
C(11)	1601(2)	5561(4)	8122(1)	33(1)
C(12)	7429(2)	8738(3)	5644(1)	21(1)
C(13)	8082(2)	7995(3)	4885(1)	19(1)
C(14)	8960(2)	9304(4)	4606(1)	25(1)
C(15)	9628(2)	8683(4)	3944(1)	32(1)
C(16)	9433(2)	6743(4)	3557(1)	31(1)
C(17)	8563(2)	5443(4)	3827(1)	28(1)
C(18)	7882(2)	6079(3)	4488(1)	21(1)
C(19)	5962(2)	725(4)	9287(1)	31(1)
C(20)	7432(2)	747(3)	7717(1)	29(1)
C(21)	7992(2)	3819(3)	9190(1)	22(1)
C(22)	8519(2)	5531(4)	8647(1)	35(1)
C(23)	8943(2)	2257(4)	9472(1)	34(1)
C(24)	7491(2)	4853(4)	9971(1)	33(1)

Table S8. Bond lengths [Å] and angles [°] for i18031.

Si(1)-O(1)	1.6585(13)
Si(1)-C(20)	1.862(2)
Si(1)-C(19)	1.871(2)
Si(1)-C(21)	1.888(2)
O(1)-C(1)	1.410(2)
O(2)-C(8)	1.208(2)
O(3)-C(9)	1.207(2)
N(1)-C(8)	1.393(2)
N(1)-C(9)	1.395(2)
N(1)-C(12)	1.456(2)
C(1)-C(2)	1.533(2)
C(1)-C(6)	1.542(2)
C(1)-C(10)	1.572(2)
C(2)-C(3)	1.528(2)
C(2)-H(2A)	0.9900
C(2)-H(2AB)	0.9900
C(3)-C(4)	1.534(3)
C(3)-H(3A)	0.9900
C(3)-H(3AB)	0.9900
C(4)-C(5)	1.523(3)
C(4)-C(11)	1.529(3)
C(4)-H(4)	1.0000
C(5)-C(6)	1.514(2)
C(5)-H(5A)	0.9900
C(5)-H(5AB)	0.9900
C(6)-C(7)	1.579(2)
C(6)-H(6)	1.0000
C(7)-C(8)	1.501(2)
C(7)-C(10)	1.547(2)
C(7)-H(7)	1.0000
C(9)-C(10)	1.510(2)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800

C(11)-H(11C)	0.9800
C(12)-C(13)	1.520(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(18)	1.383(3)
C(13)-C(14)	1.398(3)
C(14)-C(15)	1.385(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.387(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.382(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.396(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.527(3)
C(21)-C(24)	1.534(3)
C(21)-C(23)	1.534(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
O(1)-Si(1)-C(20)	109.55(8)
O(1)-Si(1)-C(19)	111.25(9)

C(20)-Si(1)-C(19)	110.65(10)
O(1)-Si(1)-C(21)	104.80(8)
C(20)-Si(1)-C(21)	110.99(9)
C(19)-Si(1)-C(21)	109.47(9)
C(1)-O(1)-Si(1)	130.53(11)
C(8)-N(1)-C(9)	113.38(14)
C(8)-N(1)-C(12)	124.08(16)
C(9)-N(1)-C(12)	122.34(15)
O(1)-C(1)-C(2)	113.09(14)
O(1)-C(1)-C(6)	112.33(14)
C(2)-C(1)-C(6)	111.72(14)
O(1)-C(1)-C(10)	119.91(14)
C(2)-C(1)-C(10)	108.74(14)
C(6)-C(1)-C(10)	88.70(12)
C(3)-C(2)-C(1)	112.41(15)
C(3)-C(2)-H(2A)	109.1
C(1)-C(2)-H(2A)	109.1
C(3)-C(2)-H(2AB)	109.1
C(1)-C(2)-H(2AB)	109.1
H(2A)-C(2)-H(2AB)	107.9
C(2)-C(3)-C(4)	109.55(15)
C(2)-C(3)-H(3A)	109.8
C(4)-C(3)-H(3A)	109.8
C(2)-C(3)-H(3AB)	109.8
C(4)-C(3)-H(3AB)	109.8
H(3A)-C(3)-H(3AB)	108.2
C(5)-C(4)-C(11)	111.08(17)
C(5)-C(4)-C(3)	109.37(15)
C(11)-C(4)-C(3)	111.38(17)
C(5)-C(4)-H(4)	108.3
C(11)-C(4)-H(4)	108.3
C(3)-C(4)-H(4)	108.3
C(6)-C(5)-C(4)	113.54(15)
C(6)-C(5)-H(5A)	108.9
C(4)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5AB)	108.9

C(4)-C(5)-H(5AB)	108.9
H(5A)-C(5)-H(5AB)	107.7
C(5)-C(6)-C(1)	118.89(14)
C(5)-C(6)-C(7)	122.01(14)
C(1)-C(6)-C(7)	88.23(12)
C(5)-C(6)-H(6)	108.6
C(1)-C(6)-H(6)	108.6
C(7)-C(6)-H(6)	108.6
C(8)-C(7)-C(10)	106.23(14)
C(8)-C(7)-C(6)	113.05(14)
C(10)-C(7)-C(6)	88.25(12)
C(8)-C(7)-H(7)	115.3
C(10)-C(7)-H(7)	115.3
C(6)-C(7)-H(7)	115.3
O(2)-C(8)-N(1)	124.14(16)
O(2)-C(8)-C(7)	128.74(16)
N(1)-C(8)-C(7)	107.01(14)
O(3)-C(9)-N(1)	122.84(17)
O(3)-C(9)-C(10)	128.66(18)
N(1)-C(9)-C(10)	108.48(15)
C(9)-C(10)-C(7)	102.93(14)
C(9)-C(10)-C(1)	118.40(14)
C(7)-C(10)-C(1)	88.31(13)
C(9)-C(10)-H(10)	114.5
C(7)-C(10)-H(10)	114.5
C(1)-C(10)-H(10)	114.5
C(4)-C(11)-H(11A)	109.5
C(4)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(4)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(1)-C(12)-C(13)	115.03(15)
N(1)-C(12)-H(12A)	108.5
C(13)-C(12)-H(12A)	108.5
N(1)-C(12)-H(12B)	108.5

C(13)-C(12)-H(12B)	108.5
H(12A)-C(12)-H(12B)	107.5
C(18)-C(13)-C(14)	119.19(17)
C(18)-C(13)-C(12)	123.54(16)
C(14)-C(13)-C(12)	117.22(17)
C(15)-C(14)-C(13)	120.4(2)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	120.03(19)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	119.93(19)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	120.0(2)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(13)-C(18)-C(17)	120.36(18)
C(13)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(24)	108.90(18)
C(22)-C(21)-C(23)	108.86(17)
C(24)-C(21)-C(23)	109.26(16)
C(22)-C(21)-Si(1)	109.80(13)

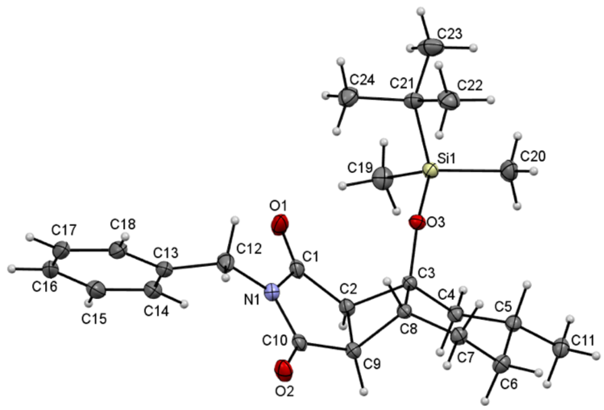
C(24)-C(21)-Si(1)	110.03(13)
C(23)-C(21)-Si(1)	109.96(15)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3)for i18031. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	22(1)	17(1)	16(1)	3(1)	2(1)	2(1)
O(1)	18(1)	19(1)	16(1)	2(1)	-1(1)	0(1)
O(2)	25(1)	23(1)	19(1)	5(1)	3(1)	6(1)
O(3)	17(1)	40(1)	26(1)	10(1)	5(1)	8(1)
N(1)	16(1)	20(1)	15(1)	1(1)	3(1)	-1(1)
C(1)	18(1)	17(1)	12(1)	-1(1)	1(1)	0(1)
C(2)	21(1)	17(1)	17(1)	0(1)	2(1)	-2(1)
C(3)	23(1)	27(1)	19(1)	-2(1)	5(1)	-9(1)
C(4)	18(1)	31(1)	19(1)	-4(1)	4(1)	-5(1)
C(5)	18(1)	25(1)	18(1)	-1(1)	3(1)	1(1)
C(6)	16(1)	16(1)	14(1)	0(1)	2(1)	-1(1)
C(7)	14(1)	18(1)	15(1)	0(1)	2(1)	0(1)
C(8)	18(1)	20(1)	11(1)	-1(1)	2(1)	1(1)
C(9)	18(1)	23(1)	13(1)	1(1)	3(1)	3(1)
C(10)	18(1)	17(1)	14(1)	-1(1)	3(1)	1(1)
C(11)	21(1)	44(1)	33(1)	-7(1)	10(1)	-5(1)
C(12)	21(1)	23(1)	19(1)	-1(1)	5(1)	-5(1)
C(13)	13(1)	28(1)	15(1)	2(1)	0(1)	-2(1)
C(14)	19(1)	35(1)	20(1)	5(1)	-2(1)	-8(1)
C(15)	15(1)	56(1)	24(1)	12(1)	2(1)	-7(1)
C(16)	18(1)	60(2)	16(1)	5(1)	4(1)	8(1)
C(17)	24(1)	43(1)	18(1)	-5(1)	-1(1)	5(1)
C(18)	18(1)	28(1)	19(1)	-1(1)	2(1)	-2(1)
C(19)	35(1)	30(1)	26(1)	11(1)	2(1)	-5(1)
C(20)	37(1)	22(1)	27(1)	-1(1)	4(1)	7(1)
C(21)	20(1)	25(1)	21(1)	3(1)	-1(1)	5(1)
C(22)	27(1)	40(1)	36(1)	12(1)	-8(1)	-12(1)
C(23)	30(1)	43(1)	28(1)	3(1)	-4(1)	16(1)
C(24)	31(1)	37(1)	31(1)	-8(1)	-2(1)	4(1)

X-ray structure of 4j and its data



X-ray crystal structure of **4j** (Deposition number: CCDC 2089102)

Table S10. Crystal data and structure refinement for i18225.

Identification code	i18225	
Empirical formula	C24 H35 N O3 Si	
Formula weight	413.62	
Temperature	100.0(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.43550(10) Å	α= 90°.
	b = 11.0753(2) Å	β= 90°.
	c = 32.5101(4) Å	γ = 90°.
Volume	2317.16(6) Å^3	
Z	4	
Density (calculated)	1.186 Mg/m^3	
Absorption coefficient	1.076 mm^{-1}	
F(000)	896	
Crystal size	0.232 x 0.077 x 0.051 mm^3	
Theta range for data collection	2.718 to 70.235°.	
Index ranges	-7<=h<=7, -13<=k<=13, -39<=l<=39	
Reflections collected	56117	
Independent reflections	4416 [R(int) = 0.0468]	
Completeness to theta = 67.679°	100.0 %	

Absorption correction	Numerical
Max. and min. transmission	1 and 0.9093
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4416 / 0 / 268
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0241, wR2 = 0.0615
R indices (all data)	R1 = 0.0262, wR2 = 0.0626
Absolute structure parameter	0.032(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.188 and -0.185 e.Å^{-3}

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for i18225. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	2419(1)	5889(1)	6783(1)	15(1)
O(1)	4018(2)	4944(1)	5734(1)	28(1)
O(2)	8660(2)	7648(1)	5216(1)	23(1)
O(3)	4160(2)	6673(1)	6519(1)	15(1)
N(1)	6602(2)	6093(1)	5448(1)	17(1)
C(1)	4724(3)	5927(2)	5654(1)	19(1)
C(2)	3804(3)	7145(2)	5751(1)	16(1)
C(3)	4034(3)	7562(2)	6210(1)	14(1)
C(4)	2467(3)	8562(1)	6306(1)	15(1)
C(5)	3329(3)	9507(2)	6606(1)	16(1)
C(6)	5180(3)	10128(2)	6399(1)	19(1)
C(7)	6920(3)	9225(2)	6315(1)	17(1)
C(8)	6193(3)	8078(2)	6102(1)	14(1)
C(9)	5562(3)	8032(2)	5633(1)	15(1)
C(10)	7124(3)	7305(2)	5397(1)	16(1)
C(11)	1678(3)	10421(2)	6734(1)	20(1)
C(12)	7986(3)	5101(2)	5342(1)	23(1)
C(13)	7416(3)	4393(1)	4960(1)	21(1)
C(14)	5485(3)	4470(2)	4770(1)	22(1)
C(15)	5004(4)	3708(2)	4443(1)	27(1)
C(16)	6447(4)	2879(2)	4302(1)	31(1)
C(17)	8391(4)	2815(2)	4483(1)	31(1)
C(18)	8875(3)	3566(2)	4811(1)	25(1)
C(19)	343(3)	5289(2)	6440(1)	24(1)
C(20)	1262(3)	6839(2)	7199(1)	24(1)
C(21)	3994(3)	4627(2)	7019(1)	19(1)
C(22)	5840(3)	5174(2)	7253(1)	26(1)
C(23)	2651(4)	3898(2)	7321(1)	31(1)
C(24)	4819(3)	3775(2)	6685(1)	24(1)

Table S12. Bond lengths [Å] and angles [°] for i18225.

Si(1)-O(3)	1.6566(12)
Si(1)-C(19)	1.862(2)
Si(1)-C(20)	1.8690(18)
Si(1)-C(21)	1.8897(18)
O(1)-C(1)	1.207(2)
O(2)-C(10)	1.211(2)
O(3)-C(3)	1.4084(19)
N(1)-C(1)	1.393(2)
N(1)-C(10)	1.394(2)
N(1)-C(12)	1.455(2)
C(1)-C(2)	1.508(2)
C(2)-C(9)	1.546(2)
C(2)-C(3)	1.571(2)
C(2)-H(2)	1.0000
C(3)-C(4)	1.530(2)
C(3)-C(8)	1.543(2)
C(4)-C(5)	1.534(2)
C(4)-H(4A)	0.9900
C(4)-H(4AB)	0.9900
C(5)-C(11)	1.526(2)
C(5)-C(6)	1.530(2)
C(5)-H(5)	1.0000
C(6)-C(7)	1.526(2)
C(6)-H(6A)	0.9900
C(6)-H(6AB)	0.9900
C(7)-C(8)	1.521(2)
C(7)-H(7A)	0.9900
C(7)-H(7AB)	0.9900
C(8)-C(9)	1.577(2)
C(8)-H(8)	1.0000
C(9)-C(10)	1.500(2)
C(9)-H(9)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800

C(11)-H(11C)	0.9800
C(12)-C(13)	1.516(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.389(3)
C(13)-C(18)	1.398(3)
C(14)-C(15)	1.392(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.384(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.384(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.388(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(24)	1.534(2)
C(21)-C(22)	1.537(3)
C(21)-C(23)	1.538(2)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
O(3)-Si(1)-C(19)	111.28(8)
O(3)-Si(1)-C(20)	110.42(8)

C(19)-Si(1)-C(20)	110.39(9)
O(3)-Si(1)-C(21)	103.58(7)
C(19)-Si(1)-C(21)	111.38(8)
C(20)-Si(1)-C(21)	109.60(8)
C(3)-O(3)-Si(1)	134.11(11)
C(1)-N(1)-C(10)	113.21(14)
C(1)-N(1)-C(12)	122.98(15)
C(10)-N(1)-C(12)	123.45(15)
O(1)-C(1)-N(1)	123.30(17)
O(1)-C(1)-C(2)	127.86(16)
N(1)-C(1)-C(2)	108.84(14)
C(1)-C(2)-C(9)	103.27(14)
C(1)-C(2)-C(3)	115.15(14)
C(9)-C(2)-C(3)	88.80(12)
C(1)-C(2)-H(2)	115.4
C(9)-C(2)-H(2)	115.4
C(3)-C(2)-H(2)	115.4
O(3)-C(3)-C(4)	113.61(13)
O(3)-C(3)-C(8)	111.74(13)
C(4)-C(3)-C(8)	111.83(13)
O(3)-C(3)-C(2)	118.52(13)
C(4)-C(3)-C(2)	110.05(13)
C(8)-C(3)-C(2)	88.62(12)
C(3)-C(4)-C(5)	112.58(14)
C(3)-C(4)-H(4A)	109.1
C(5)-C(4)-H(4A)	109.1
C(3)-C(4)-H(4AB)	109.1
C(5)-C(4)-H(4AB)	109.1
H(4A)-C(4)-H(4AB)	107.8
C(11)-C(5)-C(6)	111.36(14)
C(11)-C(5)-C(4)	111.99(14)
C(6)-C(5)-C(4)	107.99(14)
C(11)-C(5)-H(5)	108.5
C(6)-C(5)-H(5)	108.5
C(4)-C(5)-H(5)	108.5
C(7)-C(6)-C(5)	110.82(14)

C(7)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6A)	109.5
C(7)-C(6)-H(6AB)	109.5
C(5)-C(6)-H(6AB)	109.5
H(6A)-C(6)-H(6AB)	108.1
C(8)-C(7)-C(6)	113.81(14)
C(8)-C(7)-H(7A)	108.8
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7AB)	108.8
C(6)-C(7)-H(7AB)	108.8
H(7A)-C(7)-H(7AB)	107.7
C(7)-C(8)-C(3)	118.79(14)
C(7)-C(8)-C(9)	123.09(14)
C(3)-C(8)-C(9)	88.73(12)
C(7)-C(8)-H(8)	108.1
C(3)-C(8)-H(8)	108.1
C(9)-C(8)-H(8)	108.1
C(10)-C(9)-C(2)	106.03(13)
C(10)-C(9)-C(8)	109.89(13)
C(2)-C(9)-C(8)	88.29(12)
C(10)-C(9)-H(9)	116.3
C(2)-C(9)-H(9)	116.3
C(8)-C(9)-H(9)	116.3
O(2)-C(10)-N(1)	123.85(16)
O(2)-C(10)-C(9)	128.87(16)
N(1)-C(10)-C(9)	107.07(14)
C(5)-C(11)-H(11A)	109.5
C(5)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(5)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(1)-C(12)-C(13)	115.92(15)
N(1)-C(12)-H(12A)	108.3
C(13)-C(12)-H(12A)	108.3
N(1)-C(12)-H(12B)	108.3

C(13)-C(12)-H(12B)	108.3
H(12A)-C(12)-H(12B)	107.4
C(14)-C(13)-C(18)	119.18(16)
C(14)-C(13)-C(12)	123.25(16)
C(18)-C(13)-C(12)	117.43(18)
C(13)-C(14)-C(15)	120.01(18)
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0
C(16)-C(15)-C(14)	120.4(2)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(15)-C(16)-C(17)	119.94(18)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	119.90(18)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(17)-C(18)-C(13)	120.5(2)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(24)-C(21)-C(22)	109.05(15)
C(24)-C(21)-C(23)	108.93(15)
C(22)-C(21)-C(23)	108.95(15)
C(24)-C(21)-Si(1)	110.63(12)

C(22)-C(21)-Si(1)	108.95(12)
C(23)-C(21)-Si(1)	110.30(13)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters ($Å^2$x 10^3)for i18225. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	15(1)	15(1)	15(1)	0(1)	3(1)	-1(1)
O(1)	42(1)	17(1)	25(1)	-6(1)	13(1)	-9(1)
O(2)	23(1)	27(1)	20(1)	-3(1)	9(1)	-5(1)
O(3)	17(1)	14(1)	15(1)	2(1)	3(1)	0(1)
N(1)	21(1)	15(1)	14(1)	-2(1)	1(1)	1(1)
C(1)	24(1)	20(1)	12(1)	-4(1)	1(1)	-2(1)
C(2)	16(1)	17(1)	13(1)	-2(1)	1(1)	-2(1)
C(3)	16(1)	14(1)	11(1)	0(1)	0(1)	-1(1)
C(4)	15(1)	16(1)	14(1)	-1(1)	0(1)	2(1)
C(5)	18(1)	16(1)	16(1)	-2(1)	-1(1)	2(1)
C(6)	22(1)	16(1)	21(1)	-2(1)	0(1)	-1(1)
C(7)	16(1)	17(1)	17(1)	-1(1)	0(1)	-3(1)
C(8)	14(1)	14(1)	12(1)	0(1)	0(1)	2(1)
C(9)	18(1)	15(1)	12(1)	0(1)	-1(1)	0(1)
C(10)	20(1)	19(1)	10(1)	-1(1)	-2(1)	-2(1)
C(11)	21(1)	19(1)	20(1)	-4(1)	-1(1)	3(1)
C(12)	27(1)	22(1)	19(1)	-3(1)	0(1)	8(1)
C(13)	32(1)	14(1)	15(1)	2(1)	5(1)	2(1)
C(14)	32(1)	18(1)	16(1)	1(1)	3(1)	3(1)
C(15)	44(1)	22(1)	17(1)	3(1)	-1(1)	-4(1)
C(16)	62(2)	15(1)	15(1)	-2(1)	7(1)	-4(1)
C(17)	55(1)	16(1)	23(1)	1(1)	14(1)	7(1)
C(18)	36(1)	17(1)	22(1)	3(1)	8(1)	6(1)
C(19)	19(1)	27(1)	25(1)	-2(1)	-2(1)	-1(1)
C(20)	28(1)	22(1)	23(1)	-4(1)	9(1)	0(1)
C(21)	20(1)	17(1)	19(1)	4(1)	1(1)	-1(1)
C(22)	30(1)	27(1)	22(1)	3(1)	-6(1)	1(1)
C(23)	34(1)	26(1)	33(1)	12(1)	7(1)	1(1)
C(24)	26(1)	20(1)	26(1)	-1(1)	-2(1)	4(1)