Supporting Information

Gold(I)-Catalyzed Highly Stereoselective Synthesis of Polycyclic Indolines: Construction of Four Contiguous Stereocenters

Jin-Ming Yang,[†] Peng-Hua Li,[‡] Yin Wei,[†] Xiang-Ying Tang[†] and Min Shi[†‡*]*

[†]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032 China.

[‡]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei-Long Road, Shanghai 200237 China. siocxiangying@sioc.ac.cn; mshi@mail.sioc.ac.cn. Fax (+86)-21-64166128

CONTENTS

(A) General Remarks.

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded by using a Agilent or Bruker AM-400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. ^{1}H NMR and ^{13}C NMR chemical shift were referenced to 0.00 ppm (TMS) and 77.0 ppm ($CDCl_3$), respectively; coupling constants *J* are given in Hz. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, HRMS was measured on a HP-5989 instrument. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Flash column chromatography was performed by using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed by using Waters 1525 series with chiral columns (Chiralpak AD-H and OD-H columns, ϕ 4.6 x 250 mm, Daicel Chemical Ind., Ltd). Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}

(B) Gold Catalysts, Reaction Procedure for the Preparation of Substrates and Analytical Data of Substrates 1a-1u.

Figure S1 was the structures of the gold catalysts.

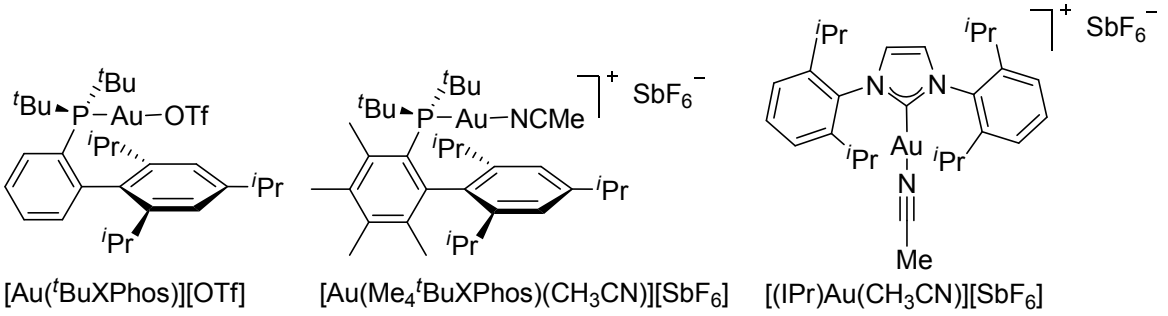
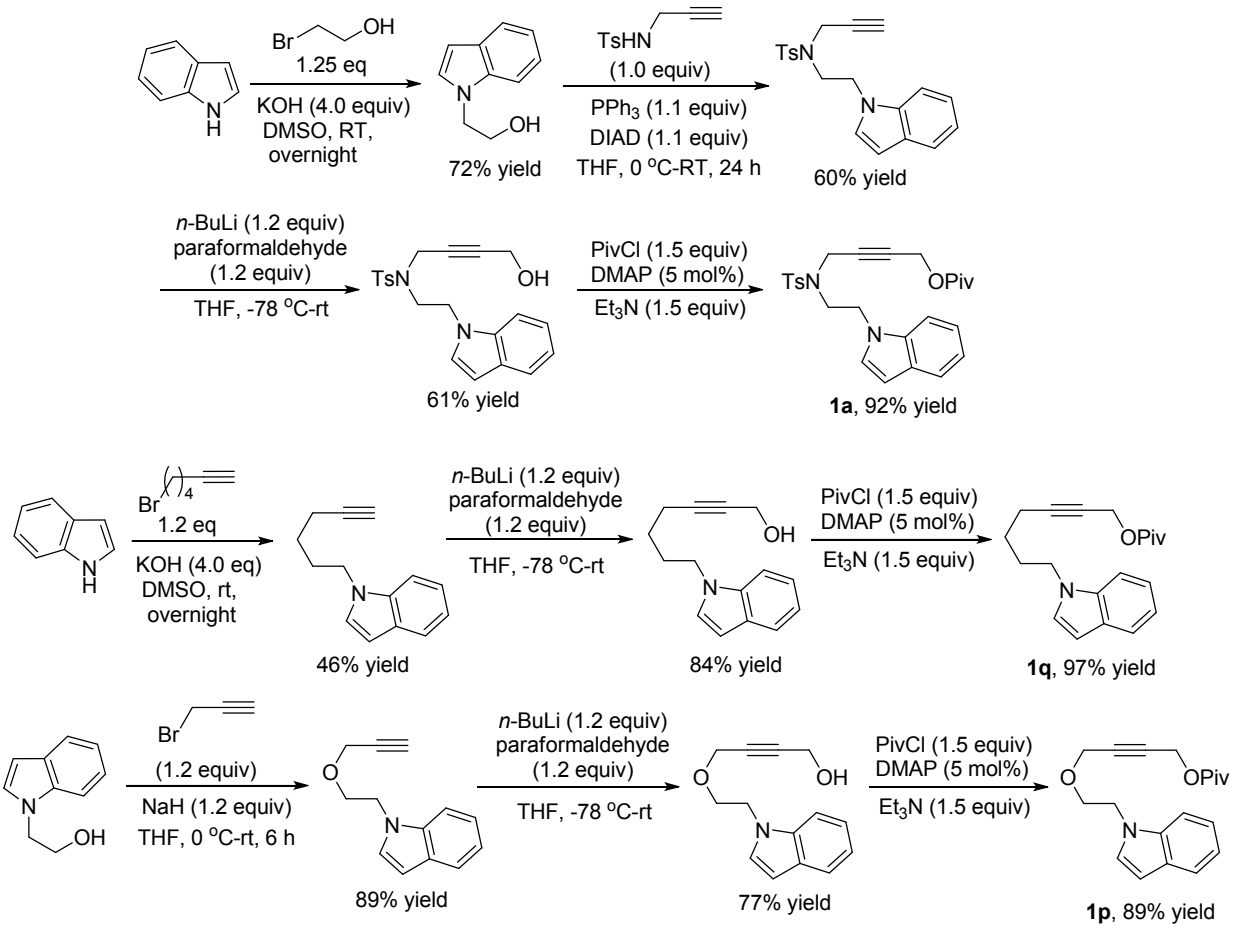
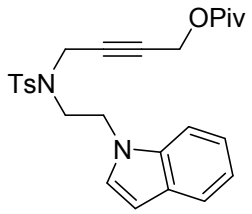


Figure S1

Substrates[1] (Scheme S1) and gold catalysts[2] were synthesized according to the previous literature.

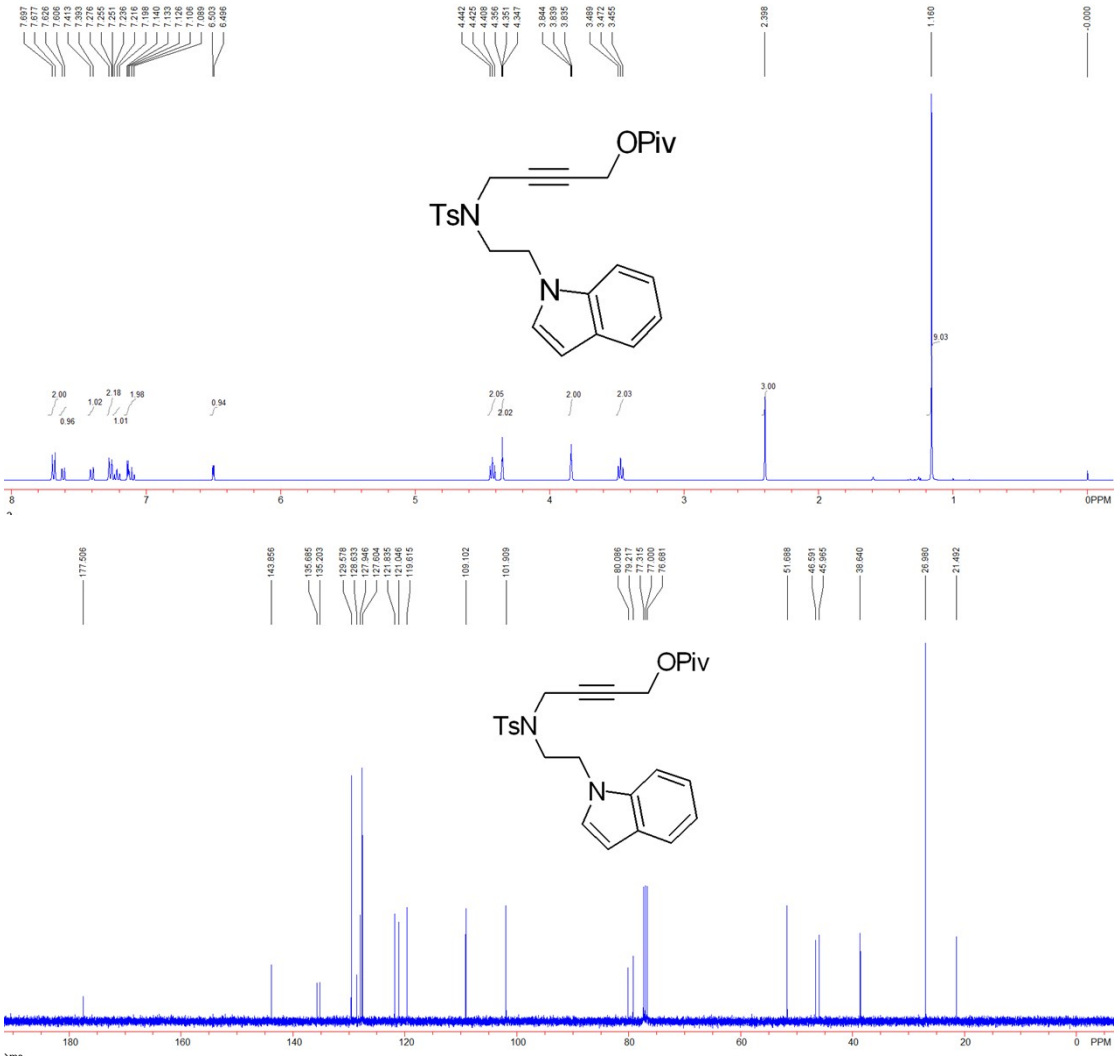


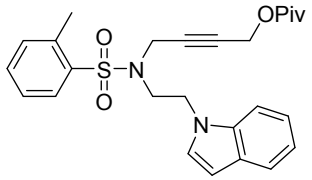
Scheme S1



4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

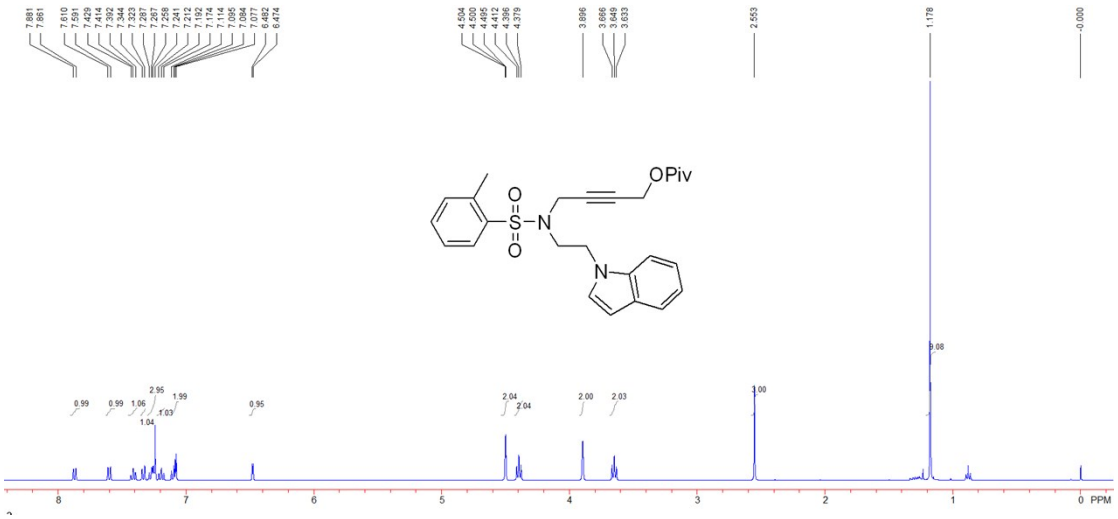
Compound **1a**: a white solid. m.p. 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 3.47 (t, J = 6.8 Hz, 2H), 3.84 (t, J = 2.0 Hz, 2H), 4.35 (t, J = 2.0 Hz, 2H), 4.43 (t, J = 6.8 Hz, 2H), 6.50 (d, J = 3.2 Hz, 1H), 7.09-7.14 (m, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.0, 38.6, 46.0, 46.6, 51.7, 79.2, 80.1, 101.9, 109.1, 119.6, 121.0, 121.8, 127.6, 127.9, 128.6, 129.6, 135.2, 135.7, 143.9, 177.5. IR (neat) ν 2974, 2872, 1733, 1479, 1463, 1348, 1279, 1158, 1140, 1090, 921, 813, 742, 726, 658 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{30}N_2O_4S$+H] requires 467.1999, found 467.1998 [M^++H].

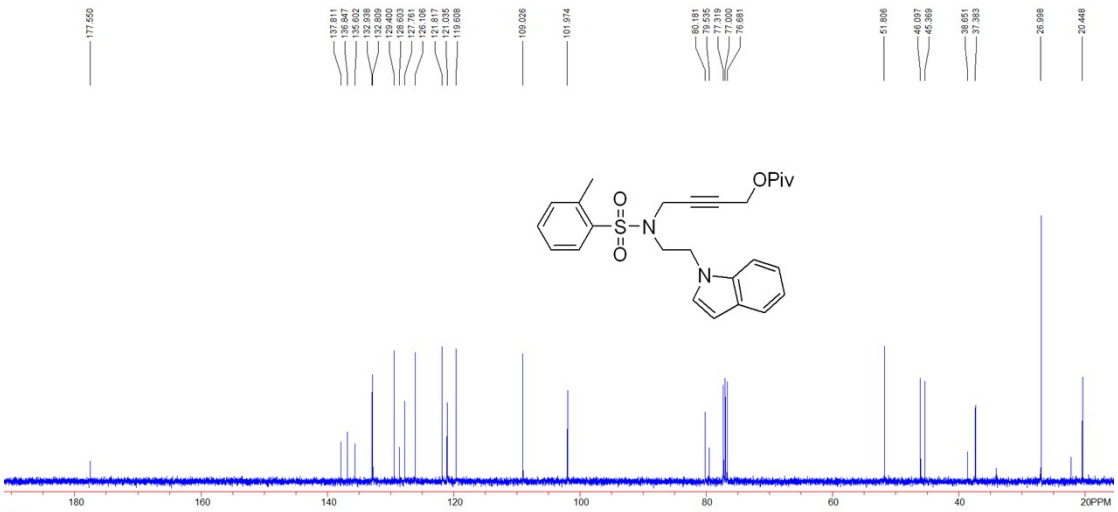


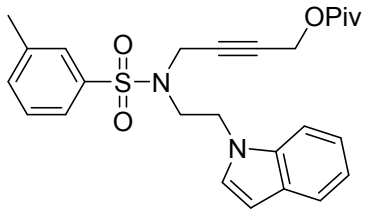


4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-2-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1b**: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18 (s, 9H), 2.55 (s, 3H), 3.65 (t, J = 6.8 Hz, 2H), 3.90 (s, 2H), 4.40 (t, J = 6.8 Hz, 2H), 4.50 (t, J = 2.0 Hz, 2H), 6.48 (d, J = 3.2 Hz, 1H), 7.08-7.11 (m, 2H), 7.19 (t, J = 8.0 Hz, 1H), 7.24-7.29 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 27.0, 37.4, 38.7, 45.4, 46.1, 51.8, 79.5, 80.2, 102.0, 109.0, 119.6, 121.0, 121.8, 126.1, 127.8, 128.6, 129.4, 132.8, 132.9, 135.6, 136.8, 137.8, 177.6. IR (neat) ν 2971, 1732, 1463, 1325, 1278, 1157, 1132, 919, 761, 736, 682 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{30}N_2O_4S$+H] requires 467.1999, found 467.1997 [M^++H].

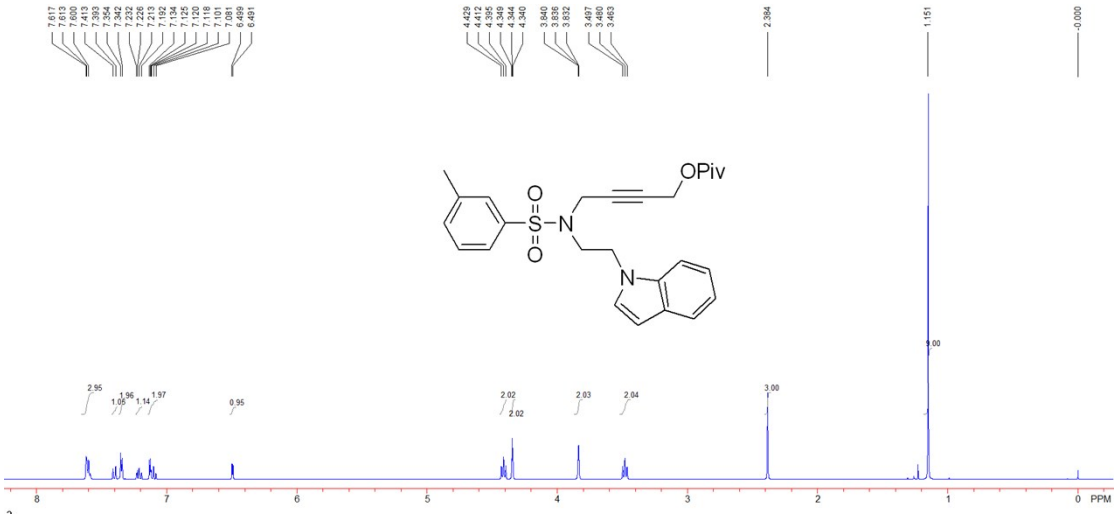


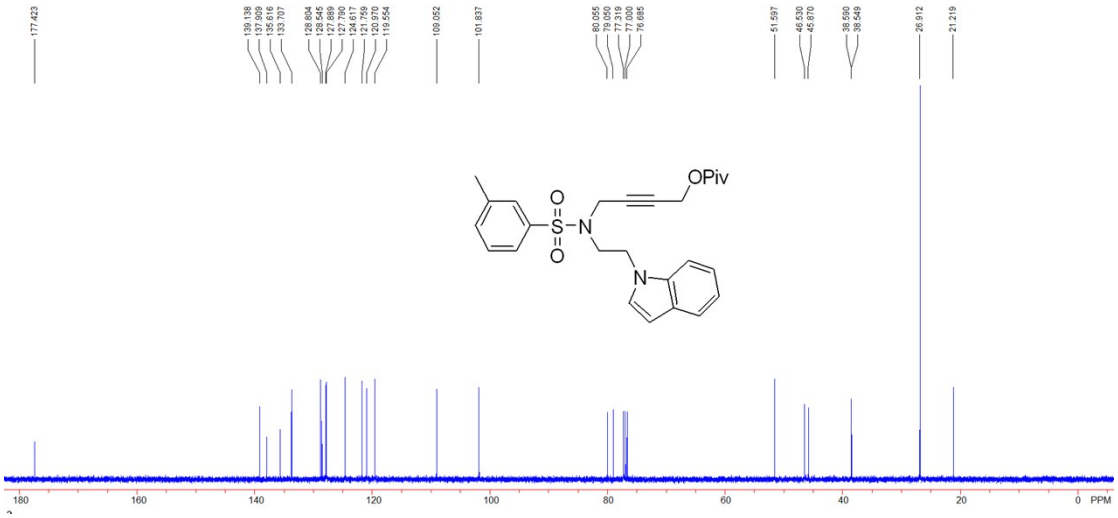


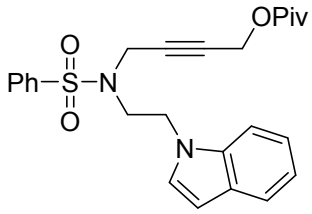


4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-3-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1c**: a white solid. m.p. 90-92 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.15 (s, 9H), 2.38 (s, 3H), 3.48 (t, J = 6.8 Hz, 2H), 3.84 (t, J = 1.6 Hz, 2H), 4.34 (t, J = 1.6 Hz, 2H), 4.41 (t, J = 6.8 Hz, 2H), 6.50 (d, J = 3.2 Hz, 1H), 7.08-7.13 (m, 2H), 7.19-7.23 (m, 1H), 7.35 (d, J = 4.8 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.59-7.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 26.9, 38.5, 38.6, 45.9, 46.5, 51.6, 79.1, 80.1, 101.8, 109.1, 119.6, 121.0, 121.8, 124.6, 127.8, 127.9, 128.5, 128.8, 133.7, 135.4, 137.9, 139.1, 177.4. IR (neat) ν 2971, 1732, 1479, 1463, 1347, 1278, 1137, 1106, 1086, 1029, 965, 919, 873, 765, 740, 725, 688 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{30}N_2O_4S$+H] requires 467.1999, found 467.1998 [M^{+}+H].

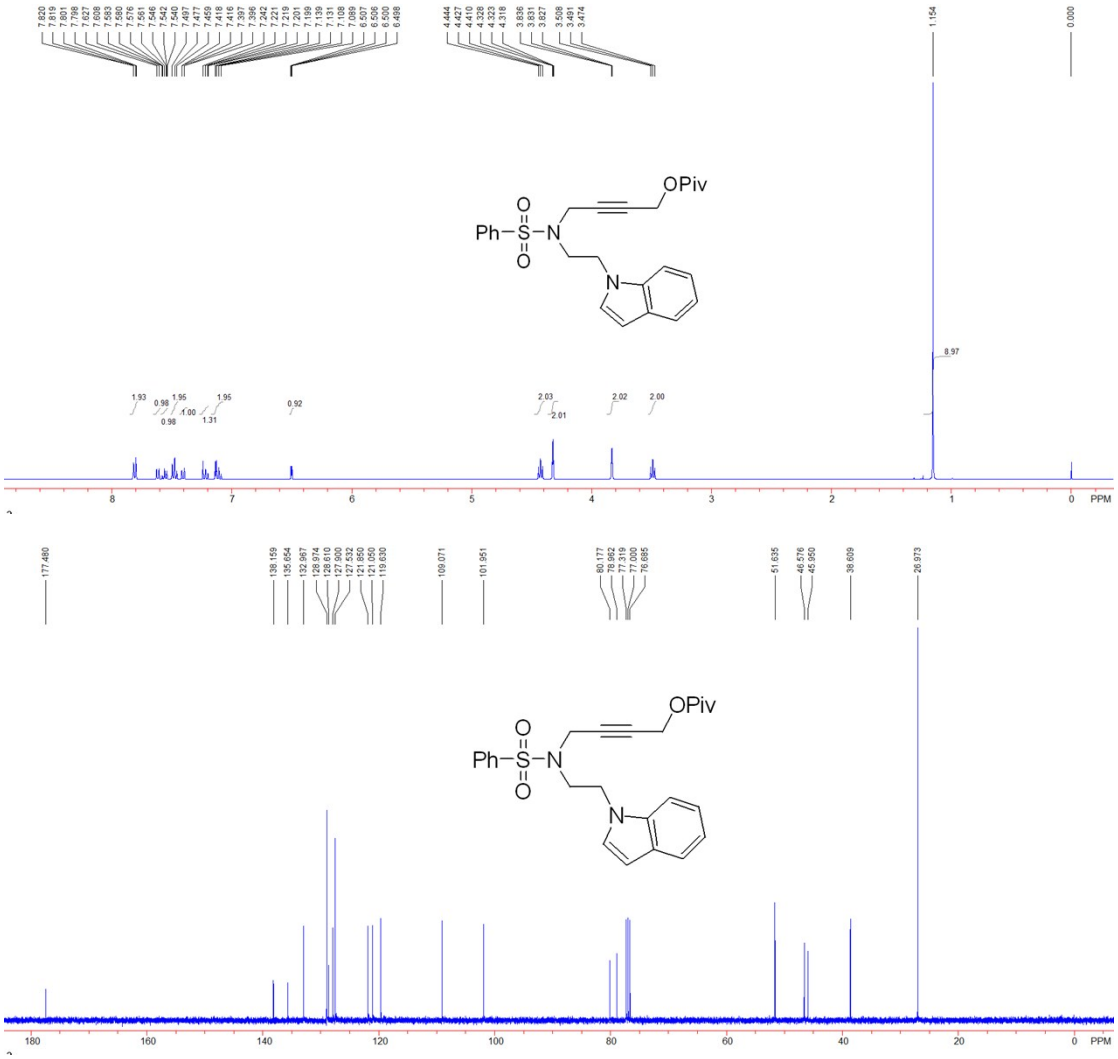


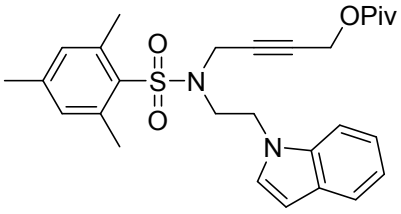




4-(*N*-(2-(1*H*-indol-1-yl)ethyl)phenylsulfonamido)but-2-yn-1-yl pivalate

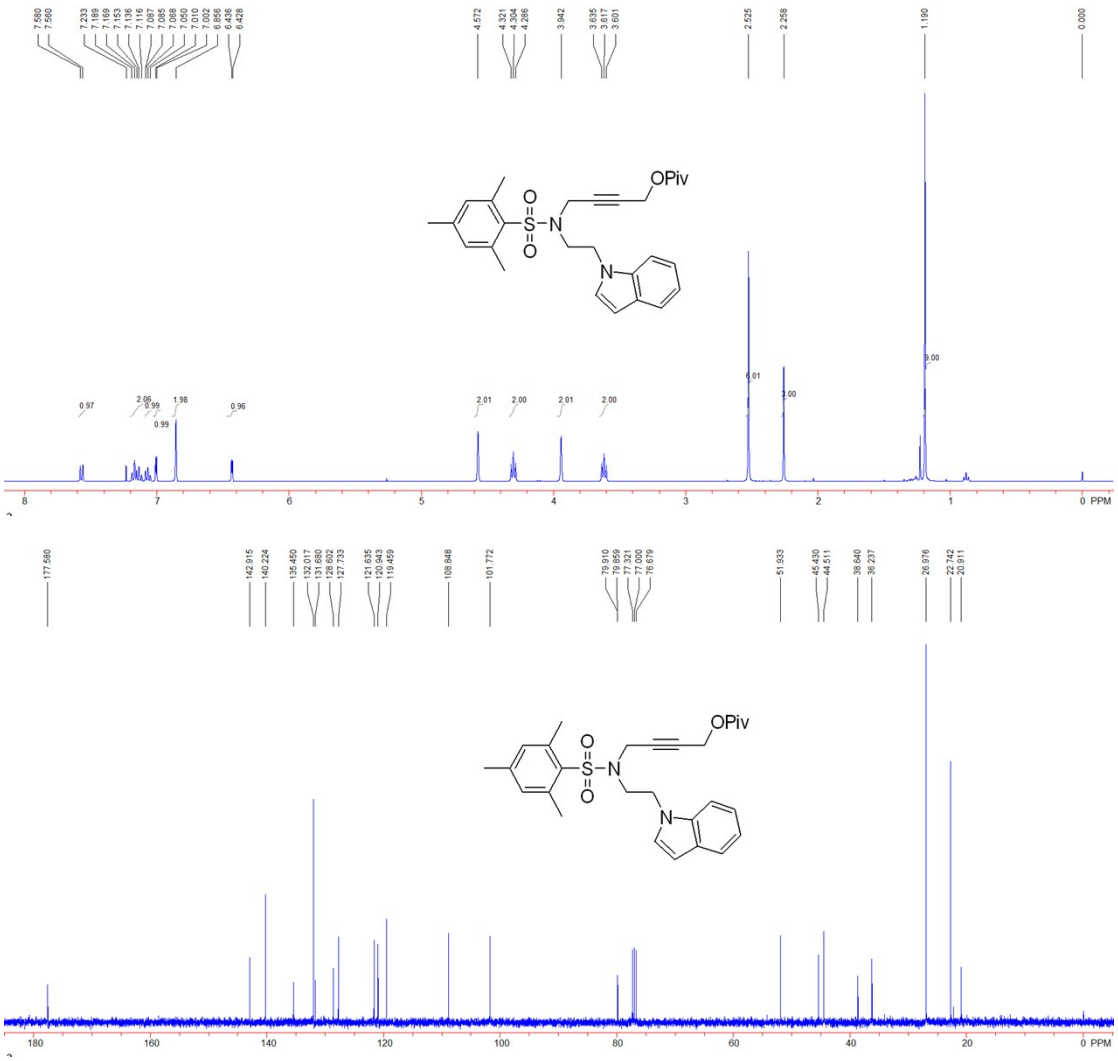
Compound **1d**: a white solid. m.p. 125-127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.15 (s, 9H), 3.49 (t, J = 6.8 Hz, 2H), 3.83 (t, J = 2.0 Hz, 2H), 4.32 (t, J = 2.0 Hz, 2H), 4.43 (t, J = 6.8 Hz, 2H), 6.50 (dd, J = 2.8, 0.8 Hz, 1H), 7.09-7.14 (m, 2H), 7.20-7.24 (m, 1H), 7.41 (dd, J = 8.0, 0.8 Hz, 1H), 7.46-7.50 (m, 2H), 7.54-7.58 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.80-7.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 38.6, 46.0, 46.6, 51.6, 79.0, 80.2, 102.0, 109.1, 119.6, 121.1, 121.9, 127.5, 127.9, 128.6, 129.0, 133.0, 135.7, 138.2, 177.5. IR (neat) ν 2974, 2938, 2872, 1732, 1512, 1463, 1446, 1348, 1279, 1138, 1107, 1090, 917, 764, 736, 690 cm^{-1}. HRMS (ESI) calcd for [$C_{25}H_{28}N_2O_4S$+H] requires 453.1843, found 453.1841 [M^++H].

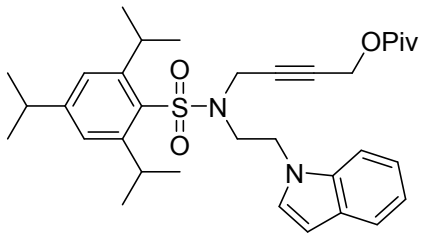




4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-2,4,6-trimethylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1e**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.19 (s, 9H), 2.26 (s, 3H), 2.53 (s, 6H), 3.62 (t, J = 7.2 Hz, 2H), 3.94 (s, 2H), 4.30 (t, J = 7.2 Hz, 2H), 4.57 (s, 2H), 6.43 (d, J = 3.2 Hz, 1H), 6.86 (s, 2H), 7.01 (d, J = 3.2 Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 7.12-7.19 (m, 2H), 7.57 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 22.7, 27.0, 36.2, 35.6, 44.5, 45.4, 51.9, 79.86, 79.91, 101.8, 108.8, 119.5, 120.9, 121.6, 127.7, 128.6, 131.7, 132.0, 135.5, 140.2, 142.9, 177.6. IR (neat) ν 2974, 2934, 2868, 1733, 1601, 1463, 1318, 1278, 1138, 1107, 1034, 854, 763, 739, 712 cm^{-1}. HRMS (ESI) calcd for [$C_{28}H_{34}N_2O_4S$+H] requires 495.2312, found 495.2315 [M^++H].

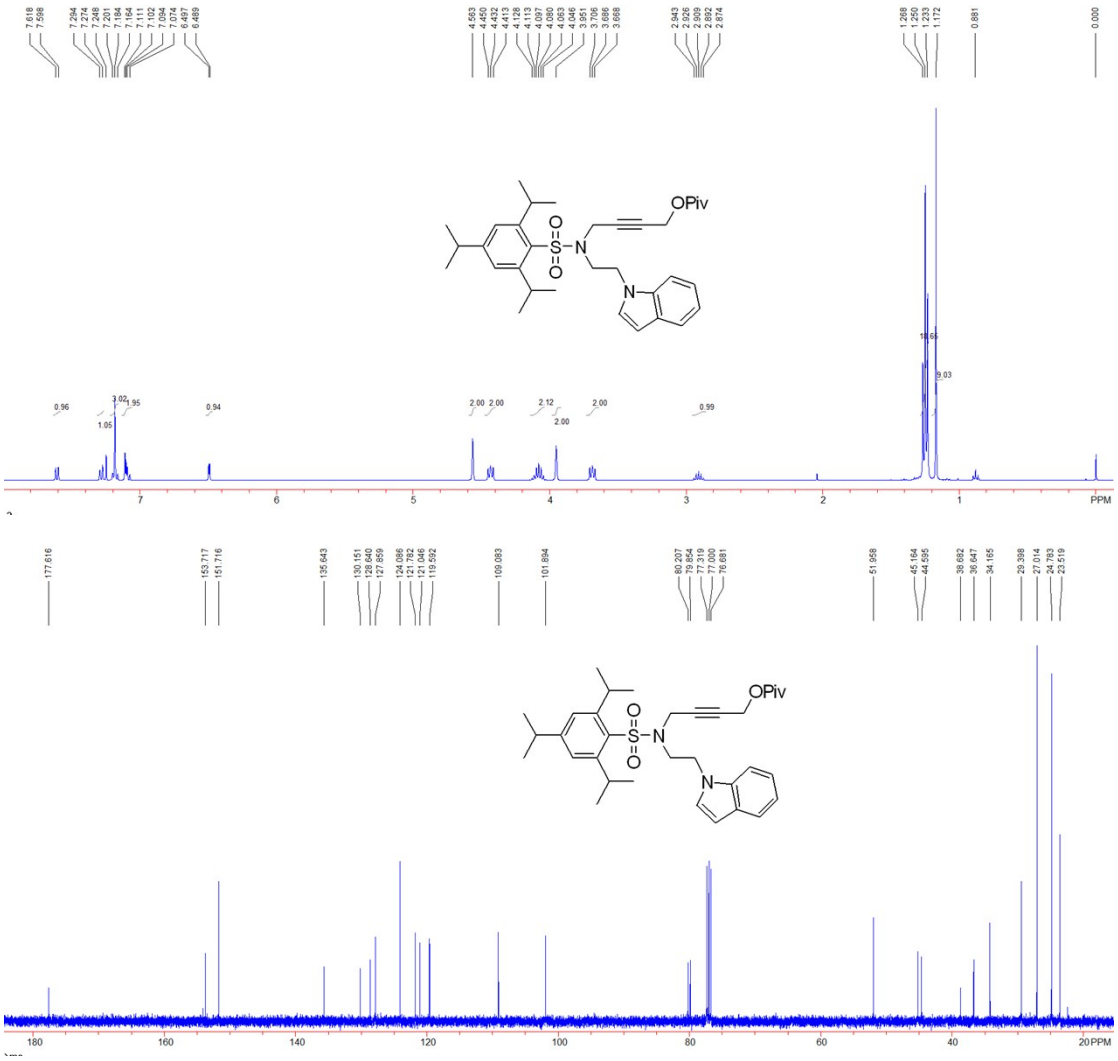


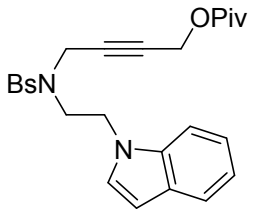


4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-2,4,6-triisopropylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1f**: a white solid. m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.17 (s, 9H), 1.25 (t, J = 7.2 Hz, 18H), 2.87-2.94 (m, 1H), 3.69 (t, J = 8.0 Hz, 2H), 3.95 (s, 2H), 4.05-4.13 (m, 2H), 4.43 (t, J = 7.2 Hz, 2H), 4.56 (s, 2H), 6.49 (d, J = 3.2 Hz, 1H), 7.07-7.11 (m, 2H), 7.16-7.20 (m, 3H), 7.28 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 24.8, 27.0, 29.4, 34.2, 36.6, 38.7, 44.6, 45.2, 52.0, 79.9, 80.2, 101.9, 109.1, 119.6, 121.0, 121.8, 124.1, 127.9, 128.6, 130.2, 135.6, 151.7, 153.7, 177.6. IR (neat) ν 2956, 2930, 2872, 1735, 1599, 1463, 1364, 1317, 1278, 1140, 884, 740, 725 cm^{-1}. HRMS (ESI) calcd for [$C_{34}H_{46}N_2O_4S$+H]

requires 579.3251, found 579.3249 [M^++H].

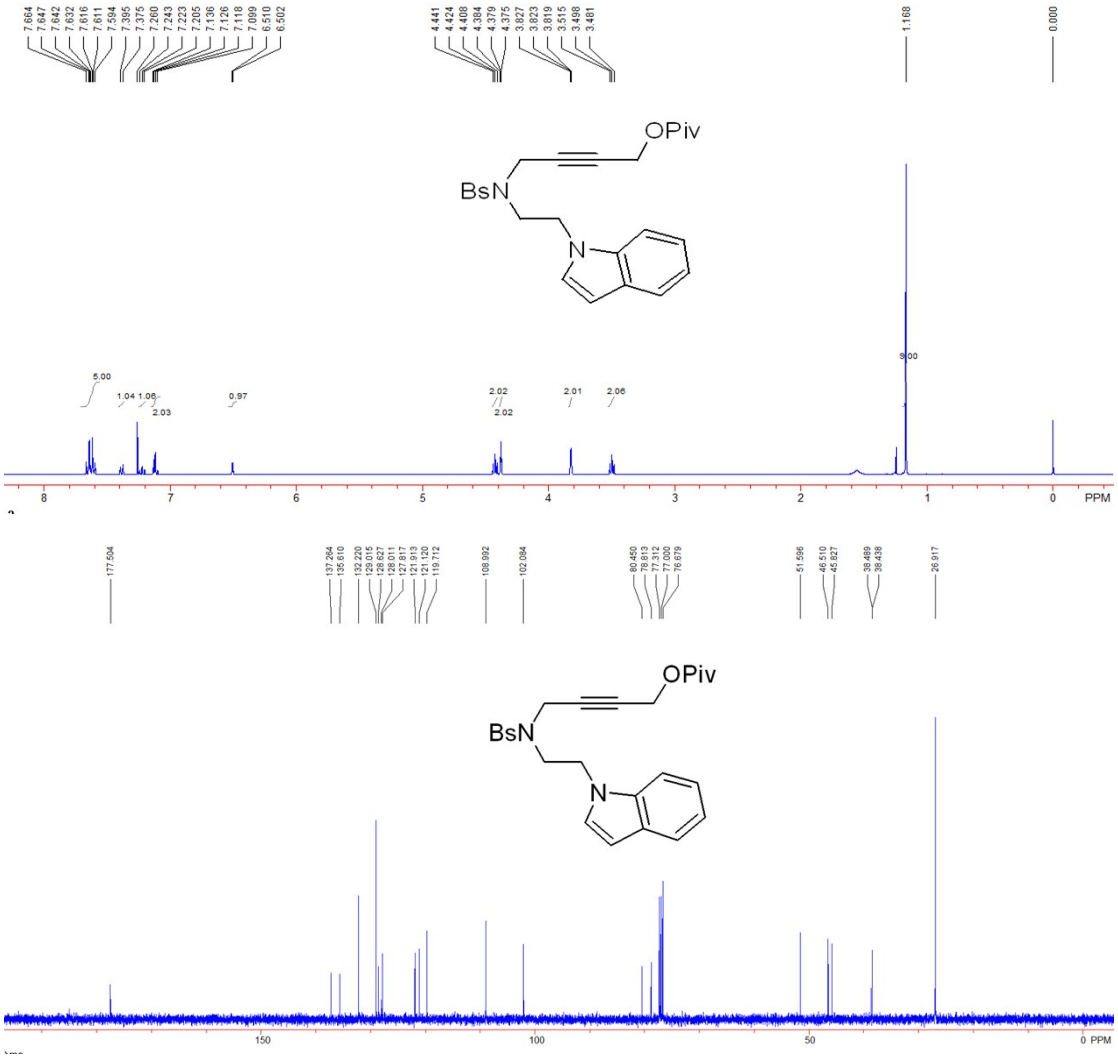


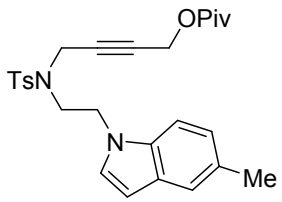


4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-4-bromophenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1g**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.17 (s, 9H), 3.50 (t, J = 6.8 Hz, 2H), 3.82 (t, J = 1.6 Hz, 2H), 4.38 (t, J = 1.6 Hz, 2H), 4.42 (t, J = 6.8 Hz, 2H), 6.50 (d, J = 3.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.59-7.66 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 38.4, 38.5, 45.8, 46.5, 51.6, 78.8, 80.4, 102.1, 109.0, 119.7, 121.1, 121.9, 127.8, 128.0, 128.6, 129.0, 132.2, 135.6, 137.3, 177.5. IR (neat) ν 2971, 1733, 1574, 1463, 1352, 1278, 1160, 1140, 1088, 1010, 919, 824, 764, 744 cm^{-1}. HRMS (ESI) calcd for

[$C_{25}H_{27}BrN_2O_4S$+H] requires 531.0948, found 531.0945 [M^++H].

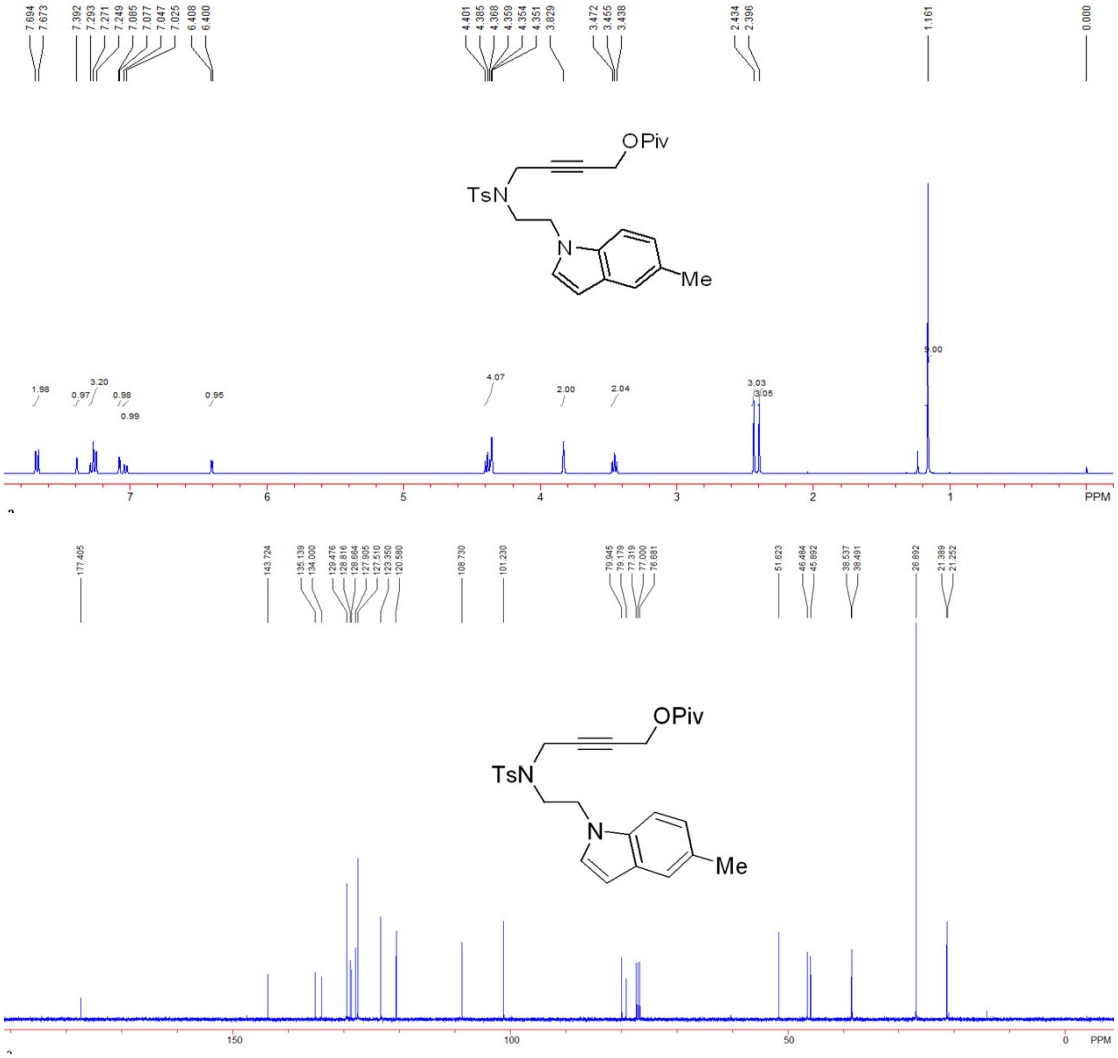


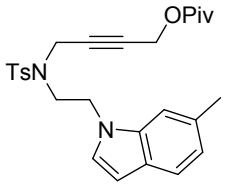


4-((4-methyl-*N*-(2-(5-methyl-1*H*-indol-1-yl)ethyl)phenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1h**: a white solid. m.p. 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 2.43 (s, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.83 (s, 2H), 4.35 (t, J = 2.0 Hz, 2H), 4.39 (t, J = 6.8 Hz, 2H), 6.40 (d, J = 3.2 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 7.08 (d, J = 3.2 Hz, 1H), 7.25-7.29 (m, 3H), 7.39 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.4, 26.9, 38.49, 38.54, 45.9, 46.5, 51.6, 79.2, 79.9, 101.2, 108.7, 120.6, 123.4, 127.5, 127.9, 128.7, 128.8, 129.5, 134.0, 135.1, 143.7, 177.4. IR (neat) ν 2974, 2934, 2872, 1732, 1598, 1486, 1347, 1278, 1158, 1137,

1090, 1030, 996, 873, 813, 793, 760, 719, 656 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_4S$+H] requires 481.2156, found 481.2153 [M^++H].

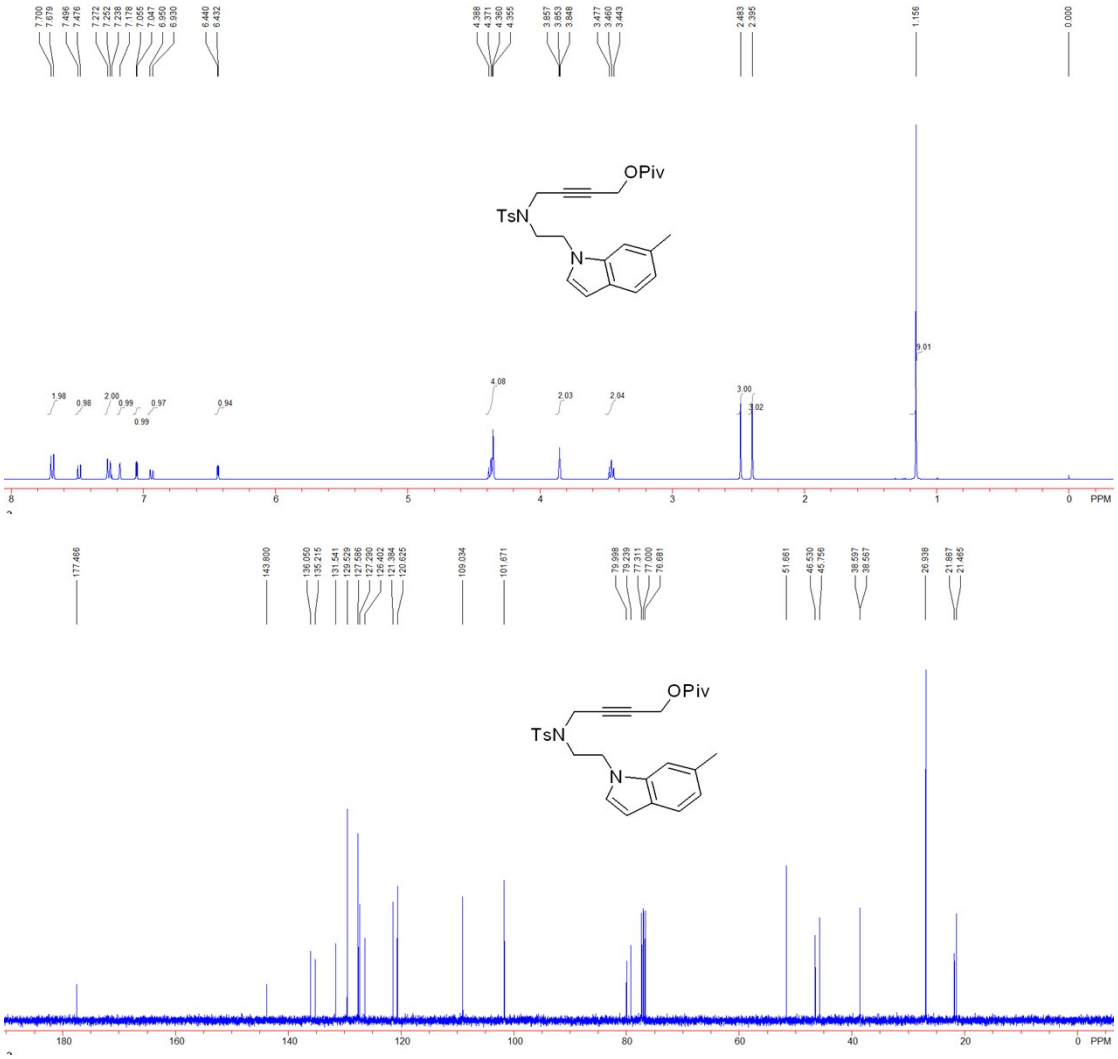


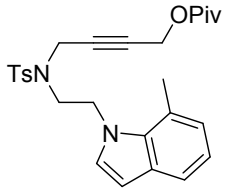


4-((4-methyl-*N*-(2-(6-methyl-1*H*-indol-1-yl)ethyl)phenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1i**: a white solid. m.p. 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 2.48 (s, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.85 (t, J = 2.0 Hz, 2H), 4.36-4.39 (m, 4H), 6.44 (d, J = 3.2 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 3.2 Hz, 1H), 7.24 (s, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.9, 26.9, 38.57, 38.60, 45.8, 46.5, 51.7, 79.2, 80.0, 101.7, 109.0, 120.6, 121.4, 126.4, 127.3, 127.6,

129.5, 131.5, 135.2, 136.1, 143.8, 177.5. IR (neat) ν 2974, 2927, 2868, 1732, 1594, 1464, 1346, 1278, 1138, 1105, 1089, 1030, 917, 802, 720, 656 cm^{-1}. HRMS (ESI) calcd for $[C_{27}H_{32}N_2O_4S+H]$ requires 481.2156, found 481.2154 $[M^+ + H]$.

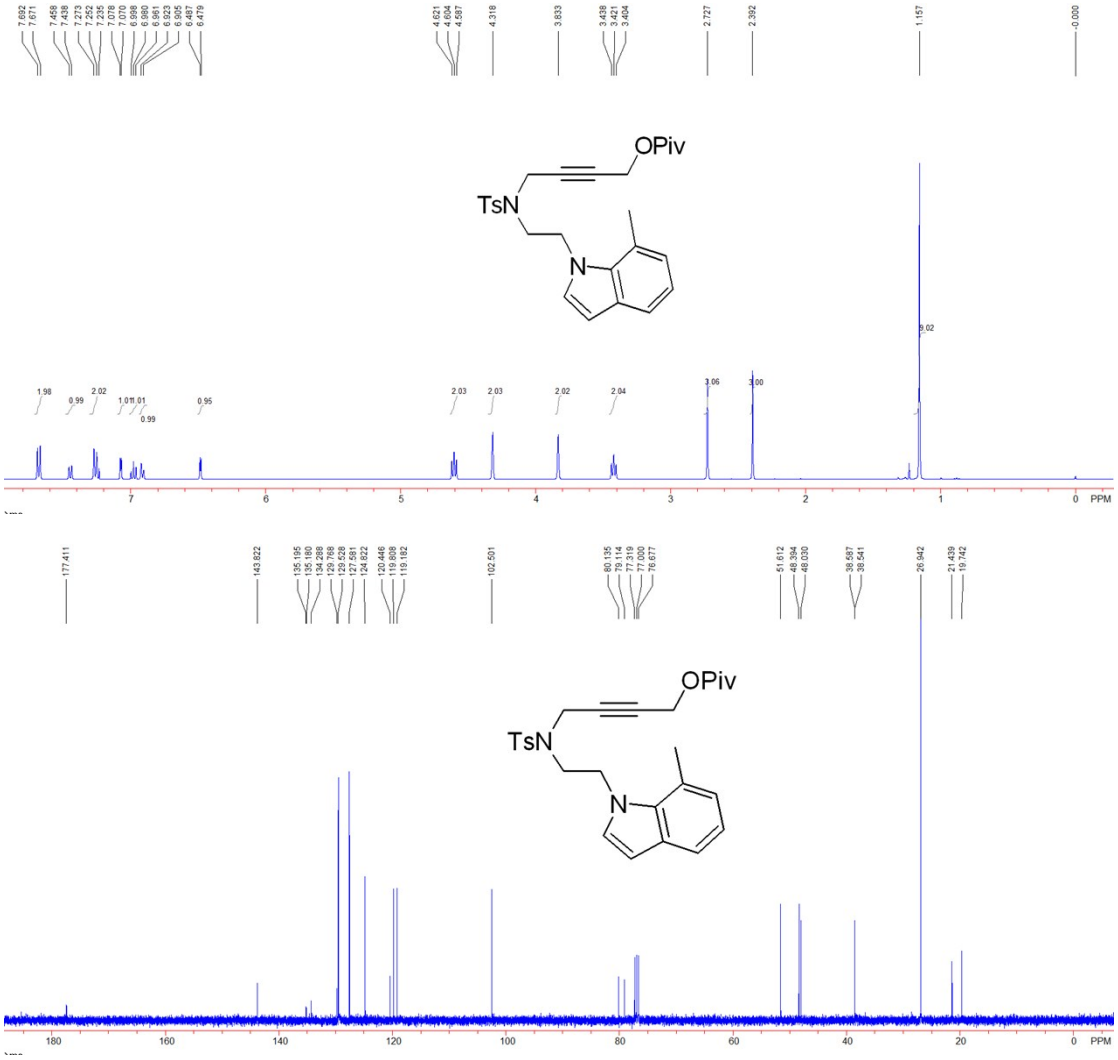


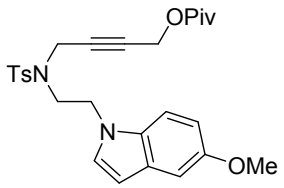


4-((4-methyl-*N*-(2-(7-methyl-1*H*-indol-1-yl)ethyl)phenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1j**: a light yellow solid. m.p. 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.39 (s, 3H), 2.73 (s, 3H), 3.42 (t, J = 6.8 Hz, 2H), 3.83 (s, 2H), 4.32 (s, 2H), 4.60 (t, J = 6.8 Hz, 2H), 6.48 (d, J = 3.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 3.2 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 19.7, 21.4, 26.9, 38.5, 38.6, 48.0, 48.4, 51.6, 79.1, 80.1, 102.5, 119.2, 119.8, 120.4, 124.8, 127.6, 129.5, 129.8, 134.3, 135.18, 135.20, 143.8, 177.4. IR (neat) ν 2974, 2868, 1733, 1457, 1347, 1309, 1279, 1157, 1139, 1096, 1034, 917, 784, 725, 660 cm^{-1}. HRMS (ESI) calcd for $[C_{27}H_{32}N_2O_4S+H]$ requires 481.2156, found 481.2154 $[M^+ +H]$.

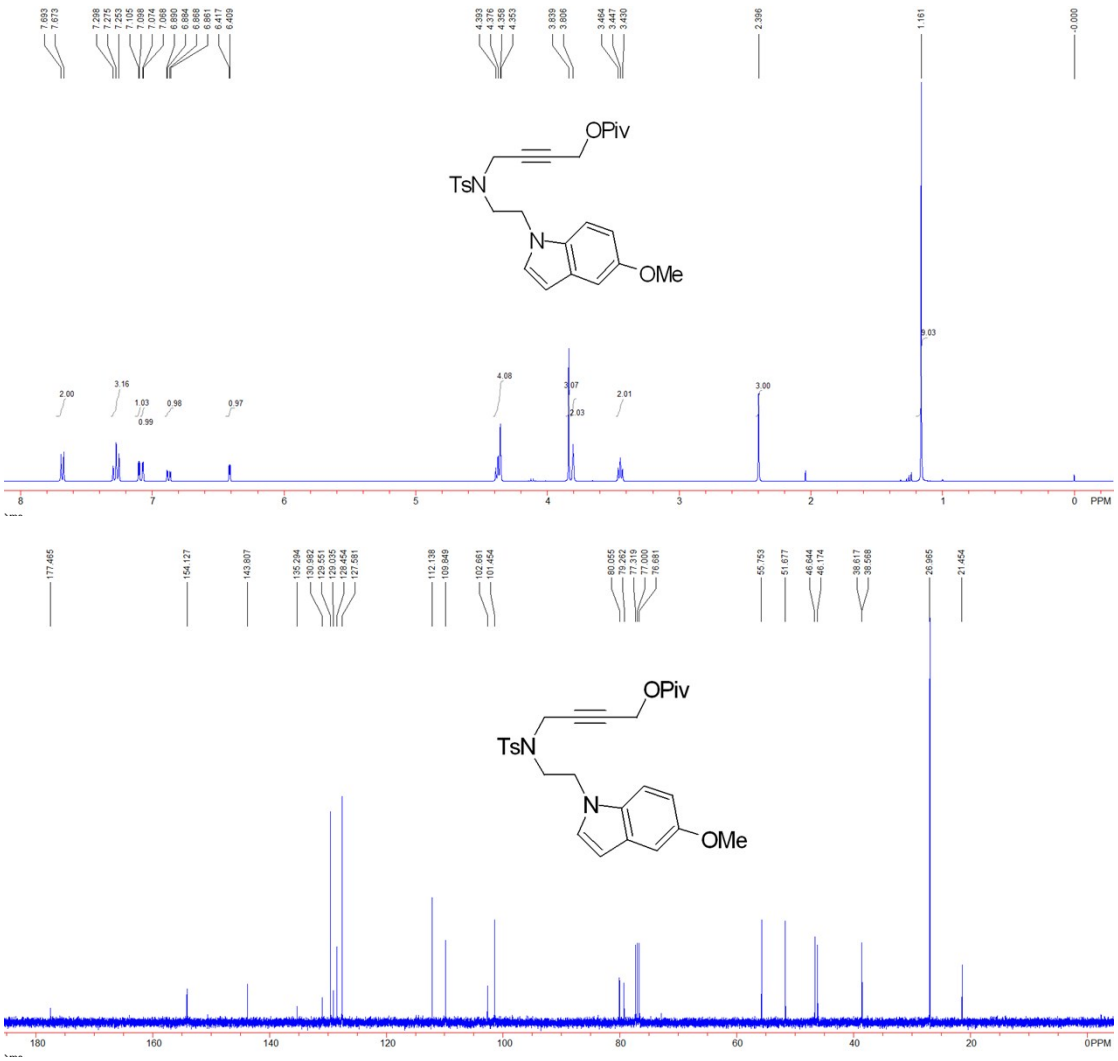


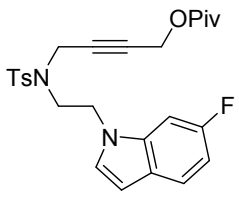


4-((*N*-(2-(5-methoxy-1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1k**: a light yellow solid. m.p. 94-96 °C. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 3.45 (t, J = 6.8 Hz, 2H), 3.81 (s, 2H), 3.84 (s, 3H), 4.35-4.39 (m, 4H), 6.41 (d, J = 3.2 Hz, 1H), 6.88 (dd, J = 8.8, 2.4 Hz, 1H), 7.07 (d, J = 2.4 Hz, 1H), 7.10 (d, J = 2.8 Hz, 1H), 7.25-

7.30 (m, 3H), 7.68 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.0, 38.57, 38.62, 46.2, 46.6, 51.7, 55.8, 79.3, 80.1, 101.5, 102.7, 109.8, 112.1, 127.6, 128.5, 129.0, 129.6, 131.0, 135.3, 143.8, 154.1, 177.5. IR (neat) ν 2971, 1732, 1621, 1596, 1487, 1446, 1346, 1279, 1239, 1139, 1090, 1033, 915, 801, 722, 657 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_5S$+H] requires 497.2105, found 497.2104 [M^++H].

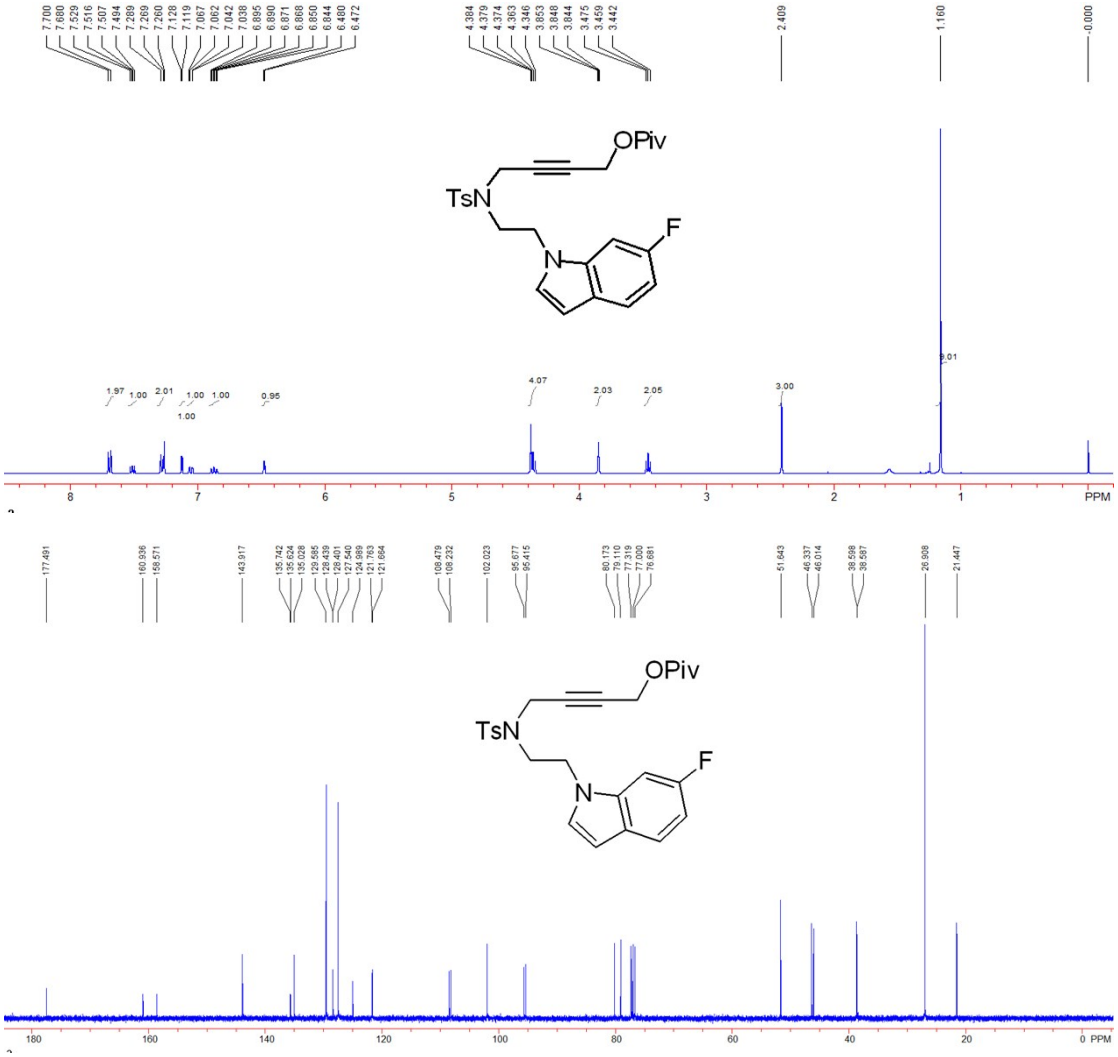


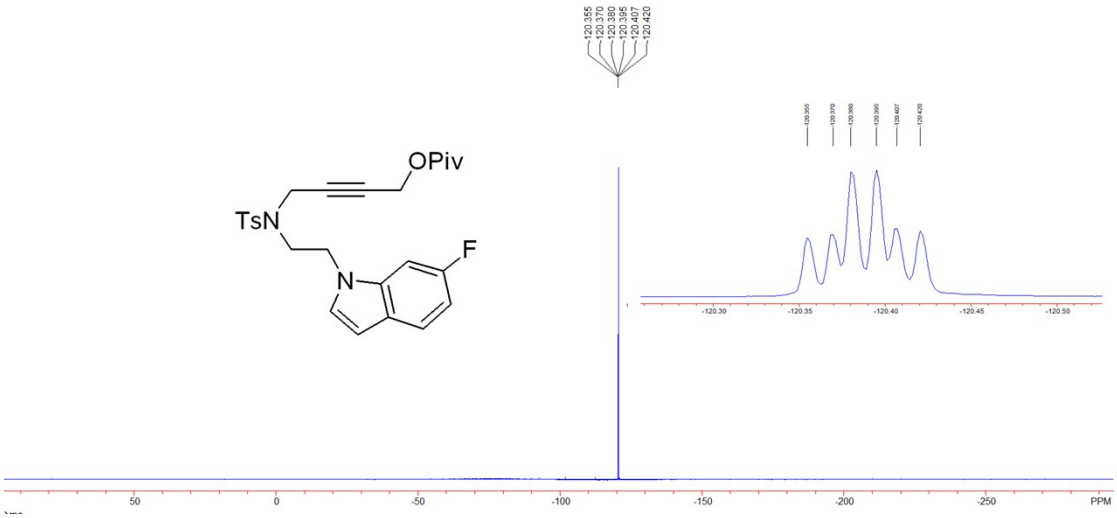


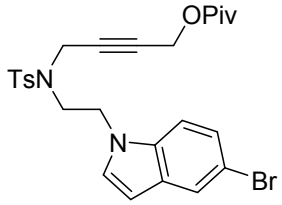
4-((*N*-(2-(6-fluoro-1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1l**: a light yellow solid. m.p. 91-93 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.41 (s, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.85 (t, J = 2.0 Hz, 2H), 4.36 (t, J = 6.8 Hz, 2H), 4.38 (t, J =

2.0 Hz, 2H), 6.48 (d, J = 3.2 Hz, 1H), 6.87 (td, J = 9.6, 2.0 Hz, 1H), 7.05 (dd, J = 9.6, 2.0 Hz, 1H), 7.12 (d, J = 3.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.51 (dd, J = 8.8, 5.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 26.9, 38.59, 38.60, 46.0, 46.3, 51.6, 79.1, 80.2, 95.6 (d, J = 26.2 Hz), 102.0, 108.4 (d, J = 24.7 Hz), 121.7 (d, J = 9.9 Hz), 125.0, 127.5, 128.4 (d, J = 3.8 Hz), 129.6, 135.0, 135.7 (d, J = 11.8 Hz), 143.9, 159.8 (d, J = 236.5 Hz), 177.5. ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -120.420 ~ -120.355 (m). IR (neat) ν 2974, 2934, 2875, 1732, 1619, 1464, 1330, 1279, 1139, 1099, 947, 802, 720, 656 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{29}FN_2O_4S$+NH_4] requires 502.2170, found 502.2169 [M^++NH_4].

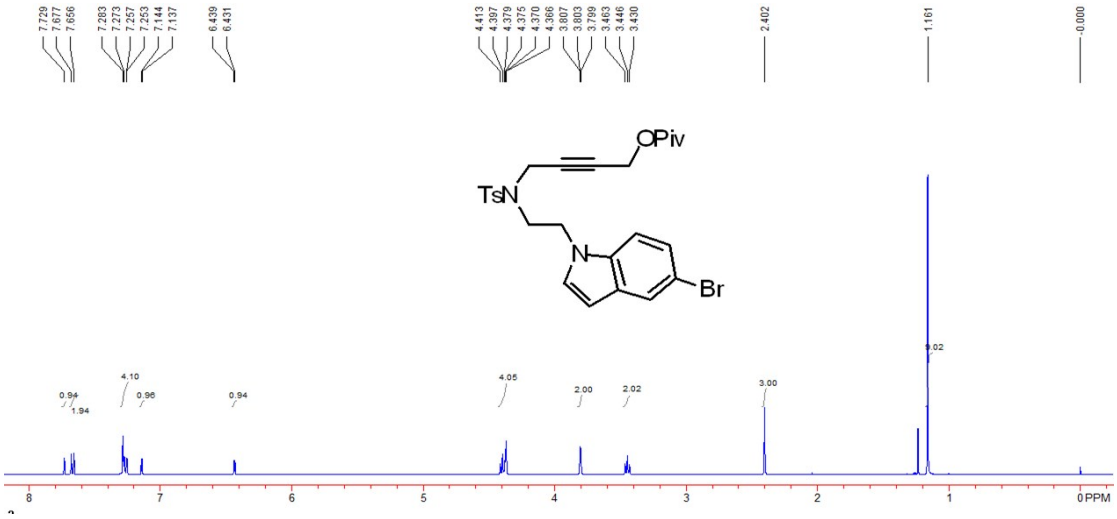


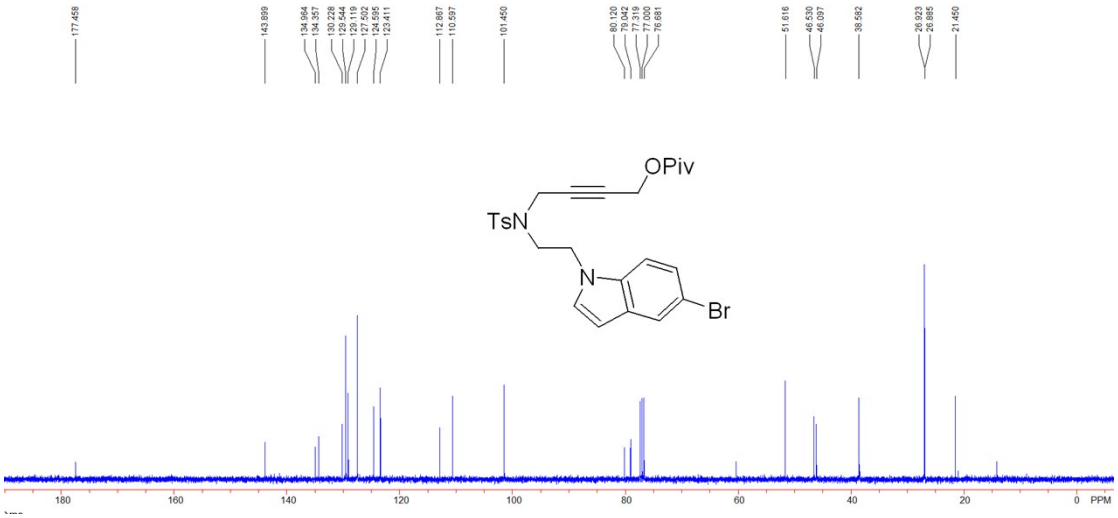


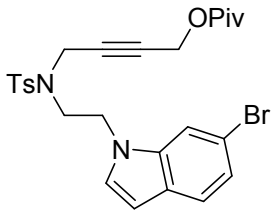


4-((*N*-(2-(5-bromo-1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1m**: a light yellow solid. m.p. 90-92 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 3.45 (t, J = 6.4 Hz, 2H), 3.80 (t, J = 1.6 Hz, 2H), 4.37 (t, J = 1.6 Hz, 2H), 4.40 (t, J = 6.4 Hz, 2H), 6.44 (d, J = 3.2 Hz, 1H), 7.14 (d, J = 2.8 Hz, 1H), 7.25-7.28 (m, 4H), 7.67 (d, J = 8.4 Hz, 2H), 7.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.88, 26.92, 38.6, 46.1, 46.5, 51.6, 79.0, 80.1, 101.5, 110.6, 112.9, 123.4, 124.6, 127.5, 129.1, 129.5, 130.2, 134.4, 135.0, 143.9, 177.5. IR (neat) ν 2971, 2930, 2868, 1732, 1469, 1347, 1279, 1158, 1139, 1090, 871, 793, 720, 660 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{29}BrN_2O_4S$+H] requires 545.1104, found 545.1101 [M^++H].

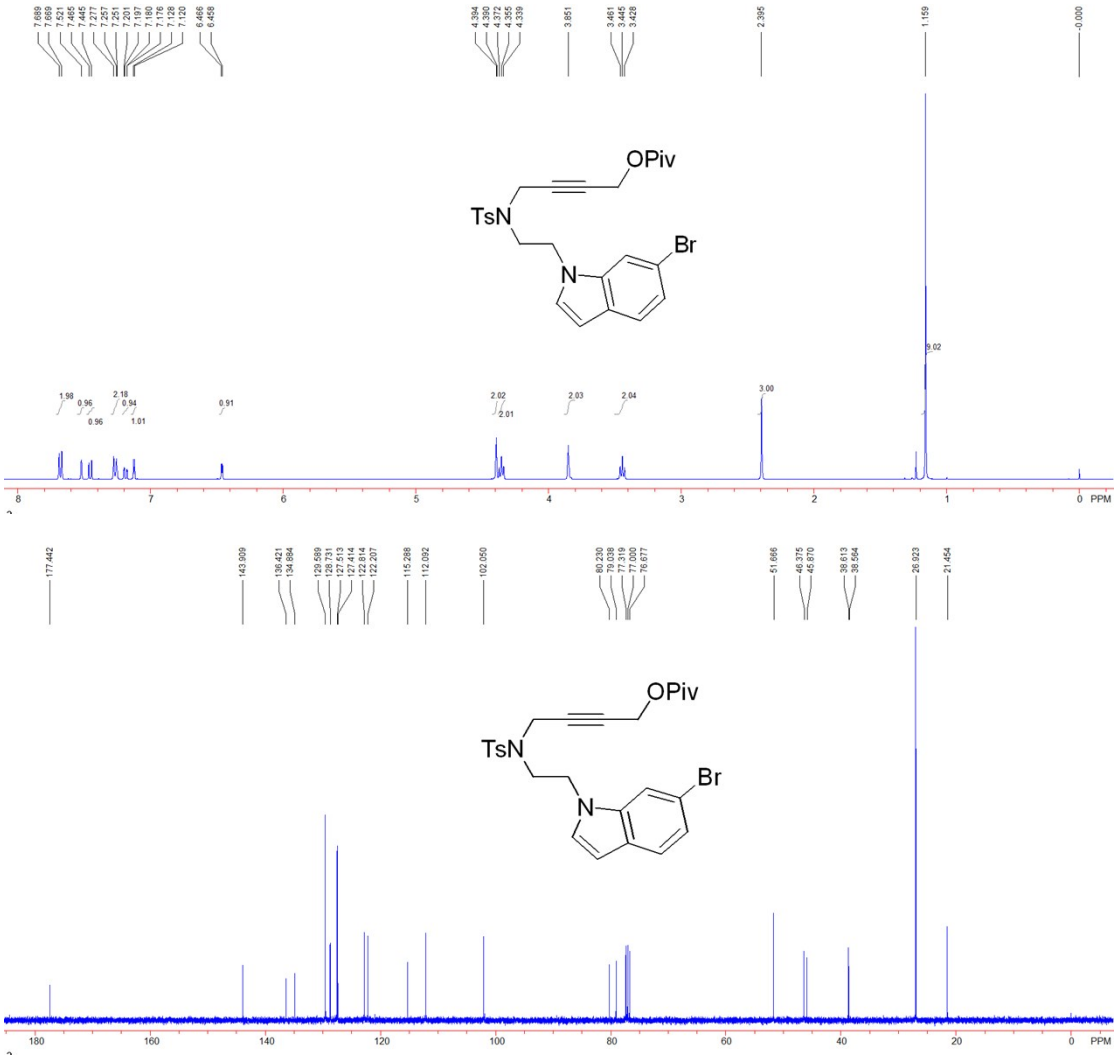


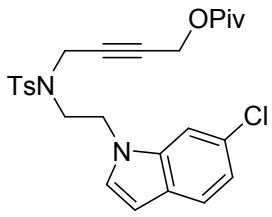




4-((*N*-(2-(6-bromo-1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1n**: a white solid. m.p. 100-102 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 3.45 (t, J = 6.8 Hz, 2H), 3.85 (s, 2H), 4.36 (t, J = 6.8 Hz, 2H), 4.39 (t, J = 1.6 Hz, 2H), 6.46 (d, J = 3.2 Hz, 1H), 7.12 (d, J = 3.2 Hz, 1H), 7.19 (dd, J = 8.4, 1.6 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.52 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.9, 38.56, 38.61, 45.9, 46.4, 51.7, 79.0, 80.2, 102.1, 112.1, 115.3, 122.2, 122.8, 127.4, 127.5, 128.7, 129.6, 134.9, 136.4, 143.9, 177.4. IR (neat) ν 2971, 1732, 1598, 1462, 1348, 1278, 1157, 1137, 1091, 891, 804, 724, 660 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{29}BrN_2O_4S$+ NH_4] requires 562.1370 found 562.1367 [M^++ NH_4].

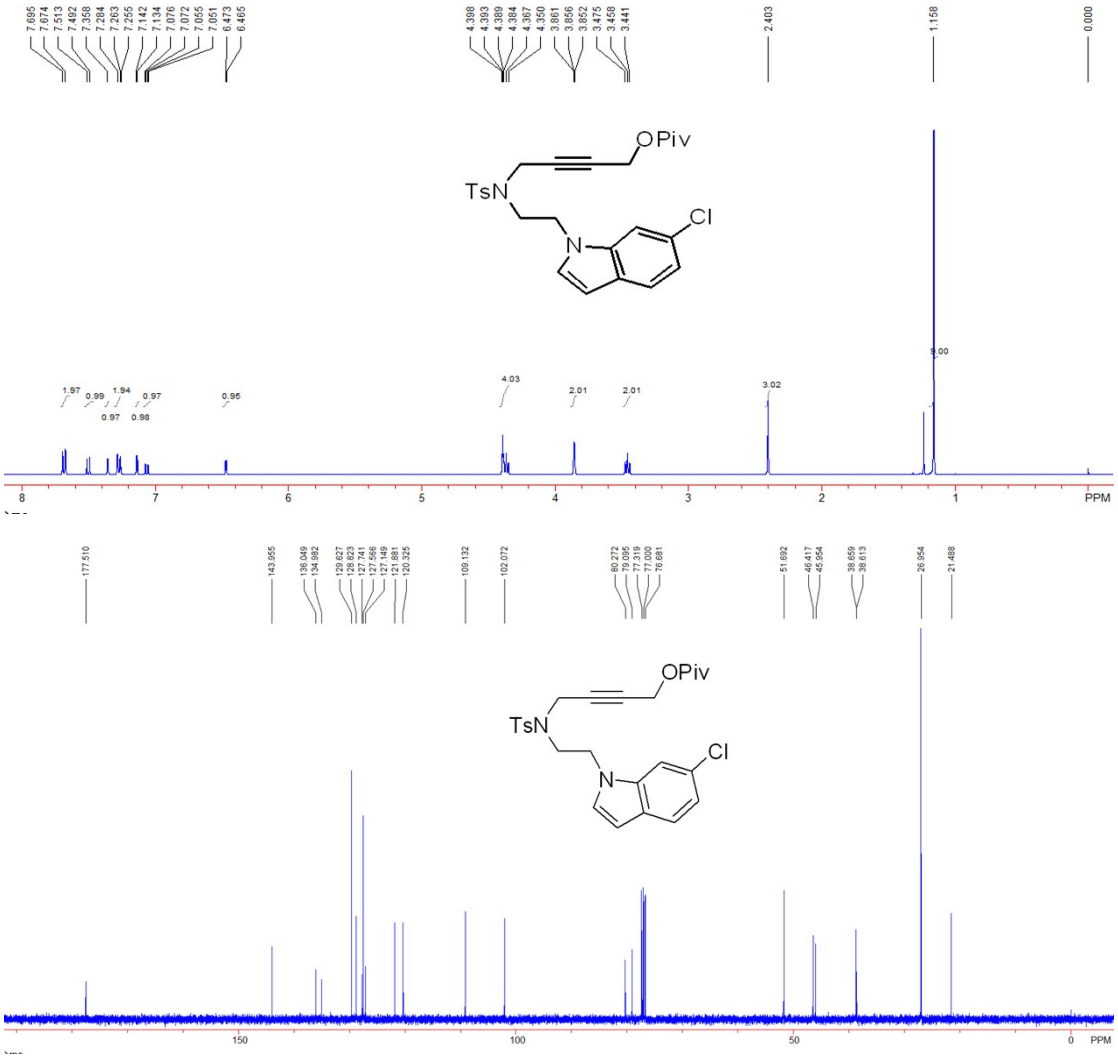


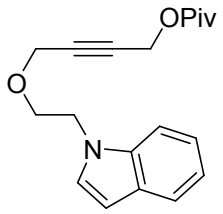


4-((*N*-(2-(6-chloro-1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl pivalate

Compound **1o**: a yellow solid. m.p. 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.40 (s, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.86 (t, J = 2.0 Hz, 2H), 4.37 (t, J = 6.8 Hz, 2H), 4.39 (t, J = 2.0 Hz, 2H), 6.47 (d, J = 3.2 Hz, 1H), 7.06 (dd, J = 8.4, 1.6 Hz, 1H), 7.14 (d, J = 3.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.36 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.0, 38.61, 38.66, 46.0, 46.4, 51.7, 79.1, 80.3, 102.1, 109.1, 120.3, 121.9, 127.1, 127.6, 127.7, 128.8, 129.6, 135.0, 136.0, 144.0, 177.5. IR (neat) ν 2974, 2930, 2864, 1732, 1596, 1464, 1348, 1279, 1157, 1138, 1093, 901, 804, 719, 655 cm^{-1}. HRMS (ESI) calcd for

$[C_{26}H_{29}ClN_2O_4S+NH_4]$ requires 518.1875 found 518.1873 $[M^+ + NH_4]$.

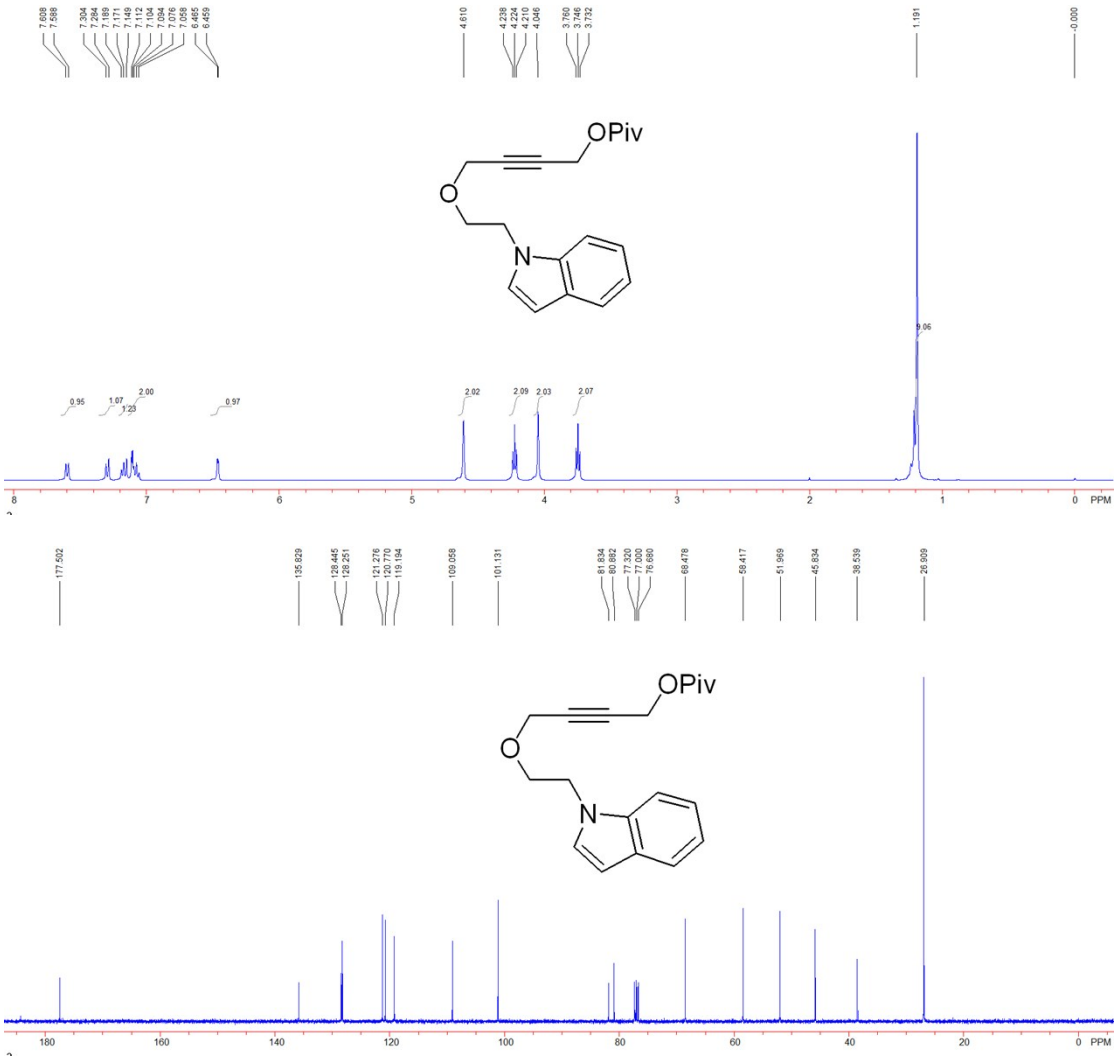


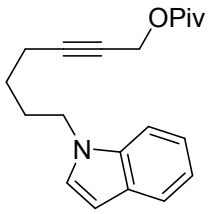


4-(2-(1*H*-indol-1-yl)ethoxy)but-2-yn-1-yl pivalate

Compound **1p**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.19 (s, 9H), 3.75 (t, J = 6.4 Hz, 2H), 4.05 (s, 2H), 4.22 (t, J = 6.4 Hz, 2H), 4.61 (s, 2H), 6.46 (d, J = 2.4 Hz, 1H), 7.06-7.11 (m, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 38.5, 45.8, 52.0, 58.4, 68.5, 80.9, 81.8, 101.1, 109.1, 119.2, 120.8, 121.3, 128.3, 128.4, 135.8, 177.5. IR (neat) ν 2967, 2864, 1732, 1480, 1463, 1352, 1315, 1278, 1135, 1096, 1032, 966, 764, 739 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{23}NO_3+H]$ requires 314.1751 found 314.1752

[M^++H].

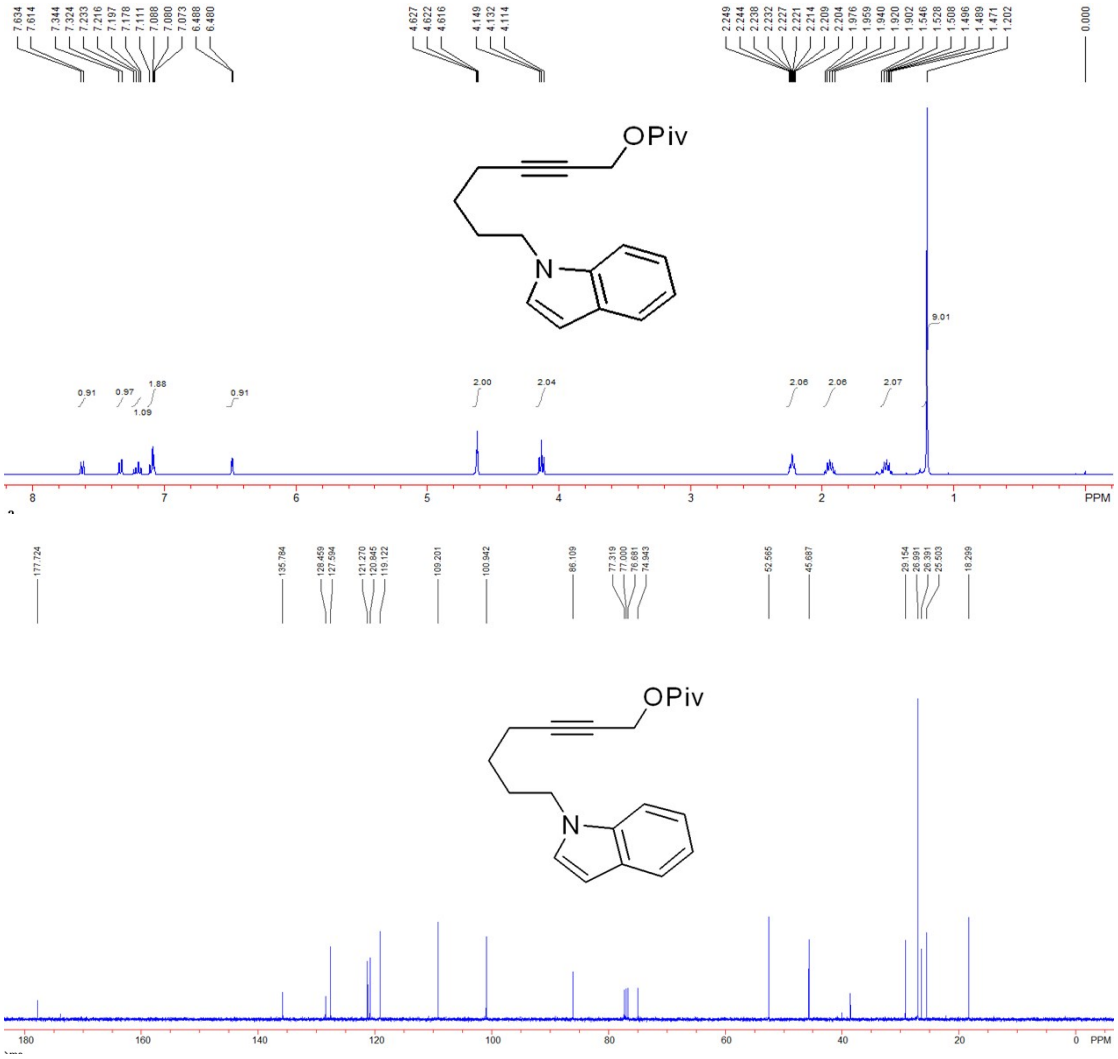


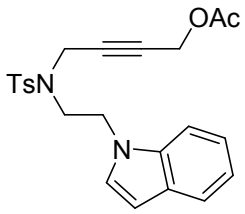


7-(1*H*-indol-1-yl)hept-2-yn-1-yl pivalate

Compound **1q**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (s, 9H), 1.47-1.55 (m, 2H), 1.90-1.98 (m, 2H), 2.20-2.25 (m, 2H), 4.13 (t, J = 7.2 Hz, 2H), 4.62 (t, J = 2.0 Hz, 2H), 6.48 (d, J = 3.2 Hz, 1H), 7.07-7.11 (m, 2H), 7.18-7.23 (m, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 25.5, 26.4, 27.0, 29.2, 45.7, 52.6, 74.9, 86.1, 100.9, 109.2, 119.1, 120.8, 121.3, 127.6, 128.5, 135.8, 177.7. IR (neat) ν 2934, 2872, 1731, 1479, 1463, 1315, 1279, 1137, 1032, 961, 763, 738, 716 cm^{-1}. HRMS (ESI) calcd for [$C_{20}H_{25}NO_2$+H] requires

312.1958 found 312.1960 [M^++H].

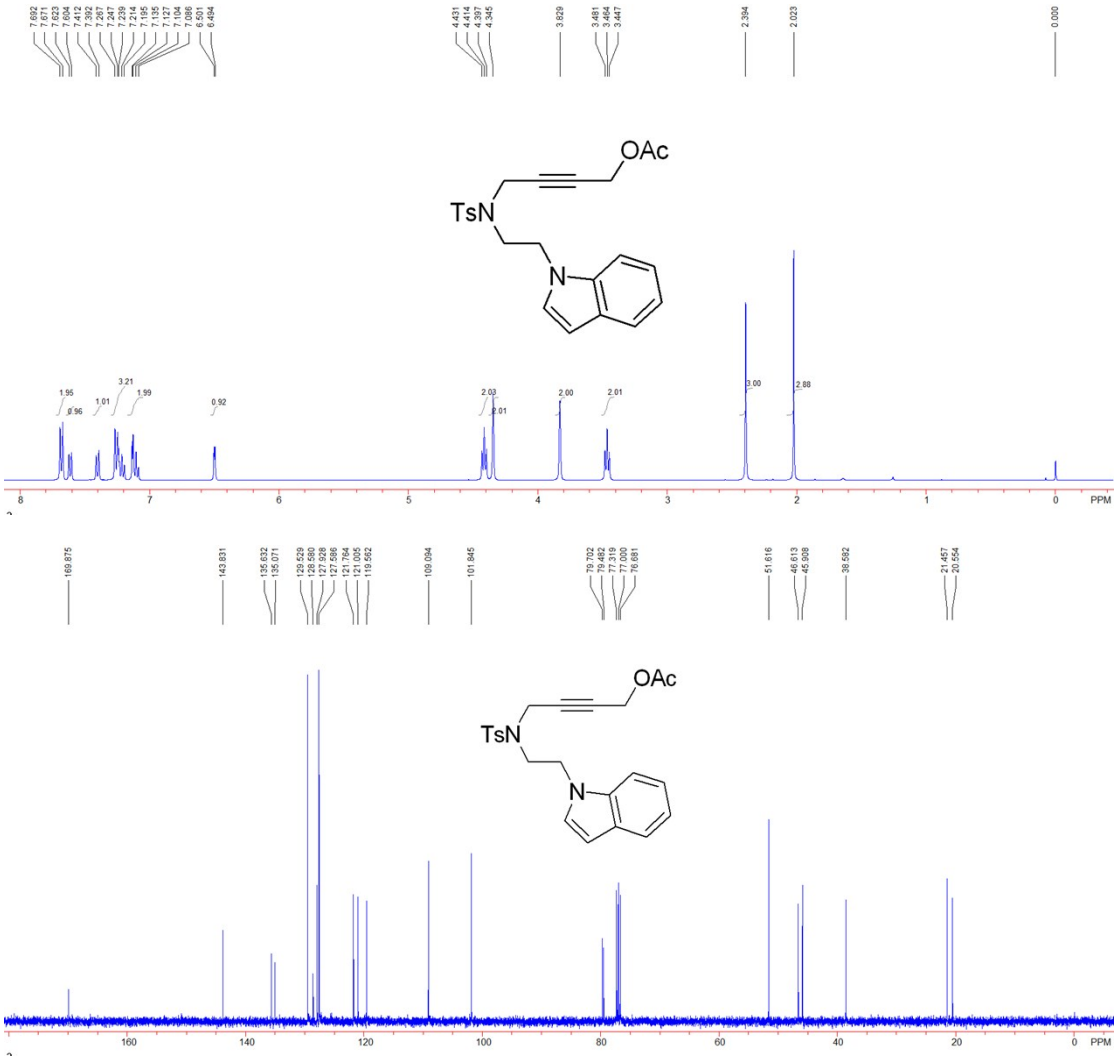


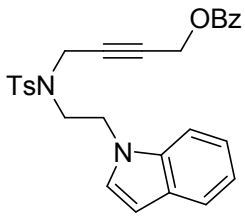


4-((*N*-(2-(1*H*-indol-1-yl)ethyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl acetate

Compound **1r**: a white solid. m.p. 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.02 (s, 3H), 2.39 (s, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.83 (s, 2H), 4.35 (s, 2H), 4.41 (t, J = 6.8 Hz, 2H), 6.50 (d, J = 2.8 Hz, 1H), 7.09-7.14 (m, 2H), 7.20-7.27 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.5, 38.6, 45.9, 46.6, 51.6, 79.5, 79.7, 101.8, 109.1, 119.6, 121.0, 121.8, 127.6, 127.9, 128.6, 129.5, 135.1, 135.6, 143.8, 169.9. IR (neat) ν 3051, 2927, 2872, 1740, 1596, 1512, 1464, 1346, 1221, 1158, 1087, 1025, 921, 813, 742,

725, 657 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{24}N_2O_4S+H]$ requires 425.1530, found 425.1528 $[M^+ +H]$.

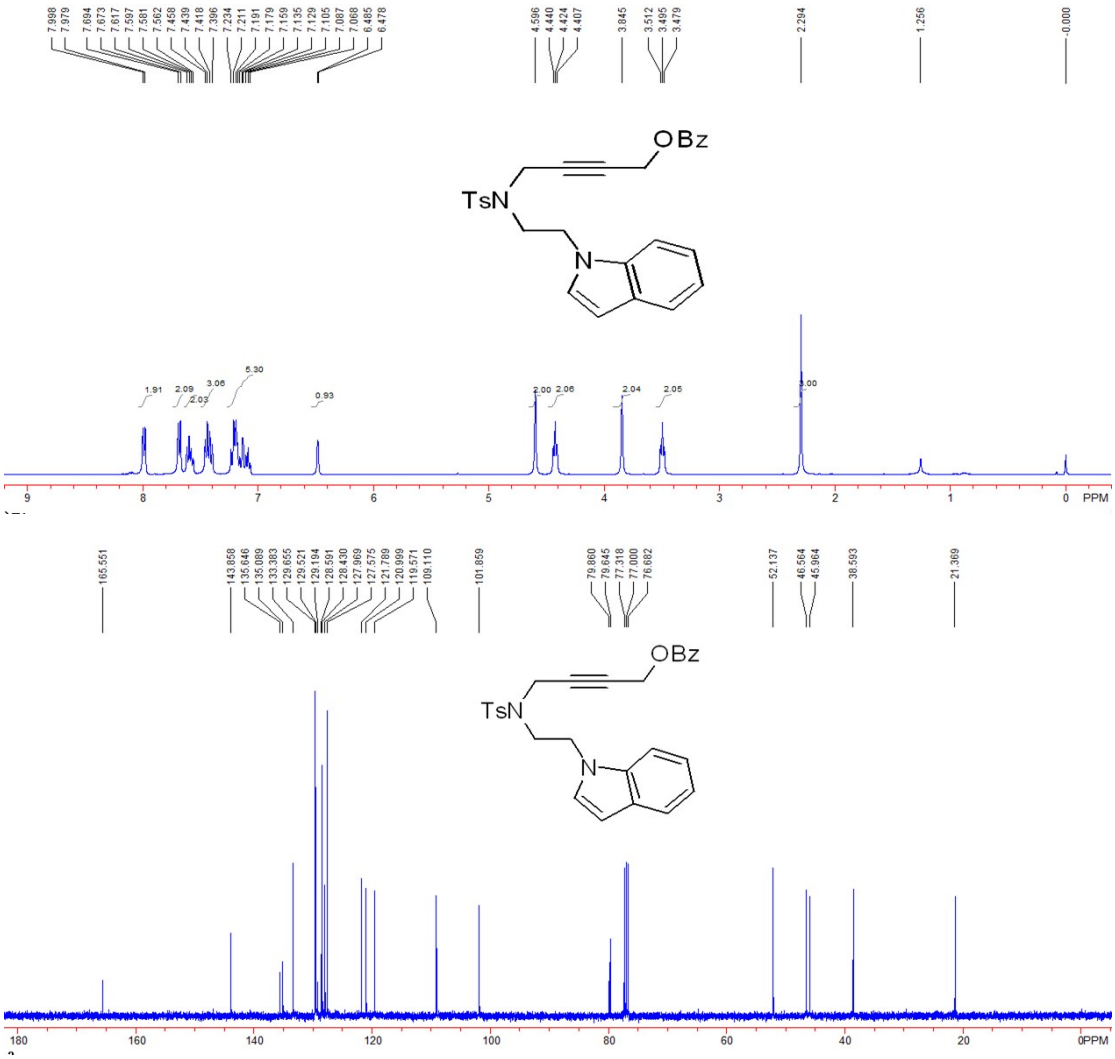


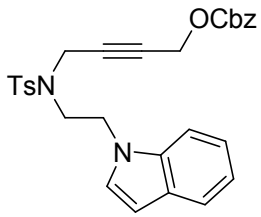


4-(*N*-(2-(1*H*-indol-1-yl)ethyl)-4-methylphenylsulfonamido)but-2-ynyl benzoate

Compound **1s**: a white solid. m.p. 150-152 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.29 (s, 3H), 3.50 (t, J = 6.8 Hz, 2H), 3.85 (s, 2H), 4.42 (t, J = 6.8 Hz, 2H), 4.60 (s, 2H), 6.48 (d, J = 2.8 Hz, 1H), 7.07-7.23 (m, 5H), 7.40-7.46 (m, 3H), 7.56-7.62 (m, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 38.6, 46.0, 46.6, 52.1, 79.6, 79.9, 101.9, 109.1, 119.6, 121.0, 121.8, 127.6, 128.0, 128.4, 128.6, 129.2, 129.5, 129.7, 133.4, 135.1, 135.6, 143.9, 165.6. IR

(neat) ν 3059, 2923, 2850, 1722, 1598, 1513, 1451, 1329, 1265, 1157, 1091, 1065, 921, 811, 740, 710, 657, 657 cm^{-1}. HRMS (ESI) calcd for $[C_{28}H_{26}N_2O_4S+H]$ requires 487.1686, found 487.1683 $[M^+ +H]$.

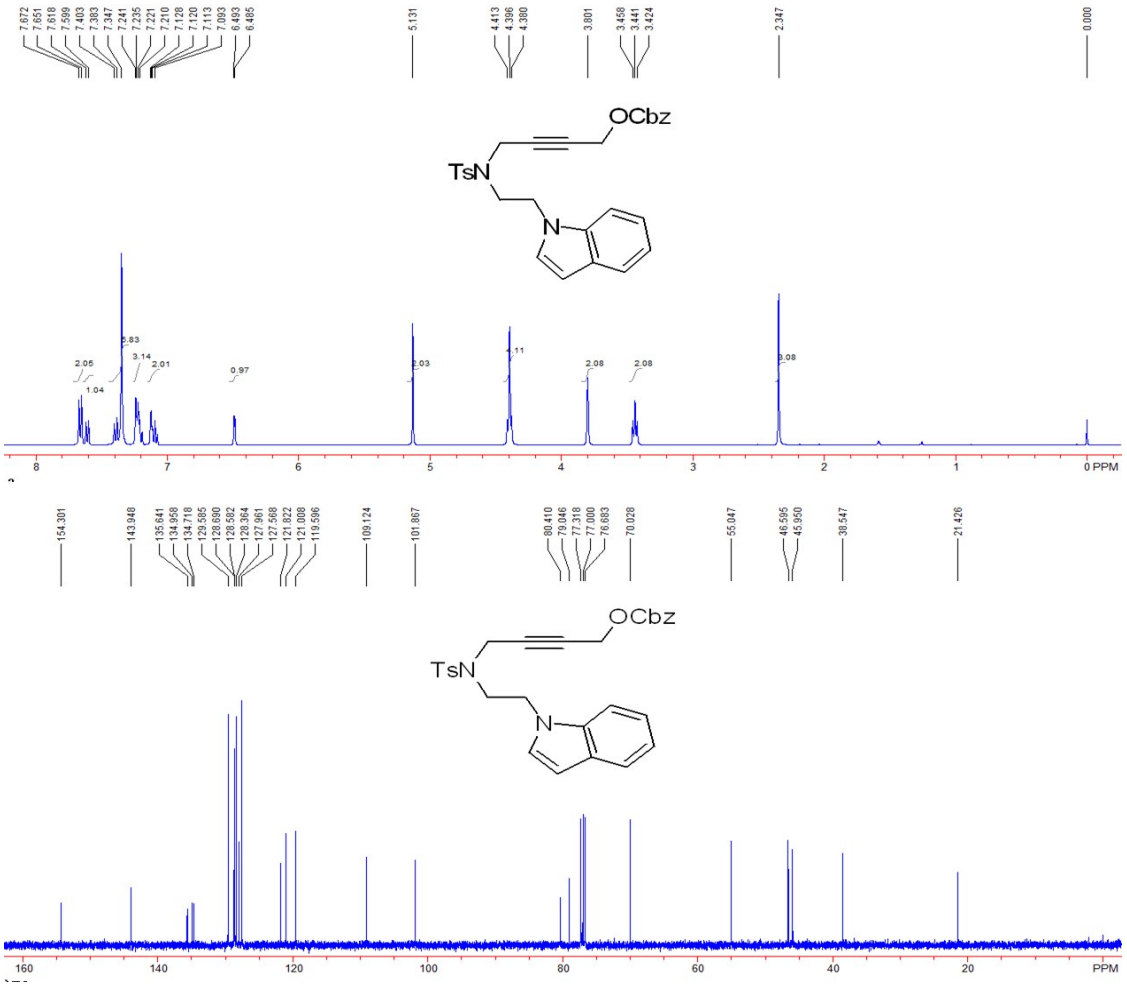


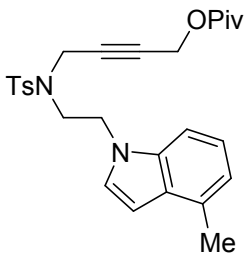


4-(*N*-(2-(1*H*-indol-1-yl)ethyl)-4-methylphenylsulfonamido)but-2-ynyl benzyl carbonate

Compound **1t**: a white solid. m.p. 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.35 (s, 3H), 3.44 (t, J = 6.8 Hz, 2H), 3.80 (s, 2H), 4.40 (t, J = 6.8 Hz, 4H), 5.13 (s, 2H), 6.49 (d, J = 3.2 Hz, 1H), 7.09-7.13 (m, 2H), 7.21-7.24 (m, 3H), 7.35-7.40 (m, 6H), 7.61 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 38.5, 46.0, 46.6, 55.0, 70.0, 79.0, 80.4, 101.9, 109.1,

119.6, 121.0, 121.8, 127.6, 128.0, 128.4, 128.6, 128.7, 129.6, 134.7, 135.0, 135.6, 143.9, 154.3. IR (neat) ν 3029, 2949, 2872, 1749, 1596, 1510, 1462, 1347, 1250, 1158, 1085, 933, 742, 727, 698, 658 cm^{-1}. HRMS (ESI) calcd for [$C_{29}H_{28}N_2O_5S$+H] requires 517.1792, found 517.1788 [M^++H].

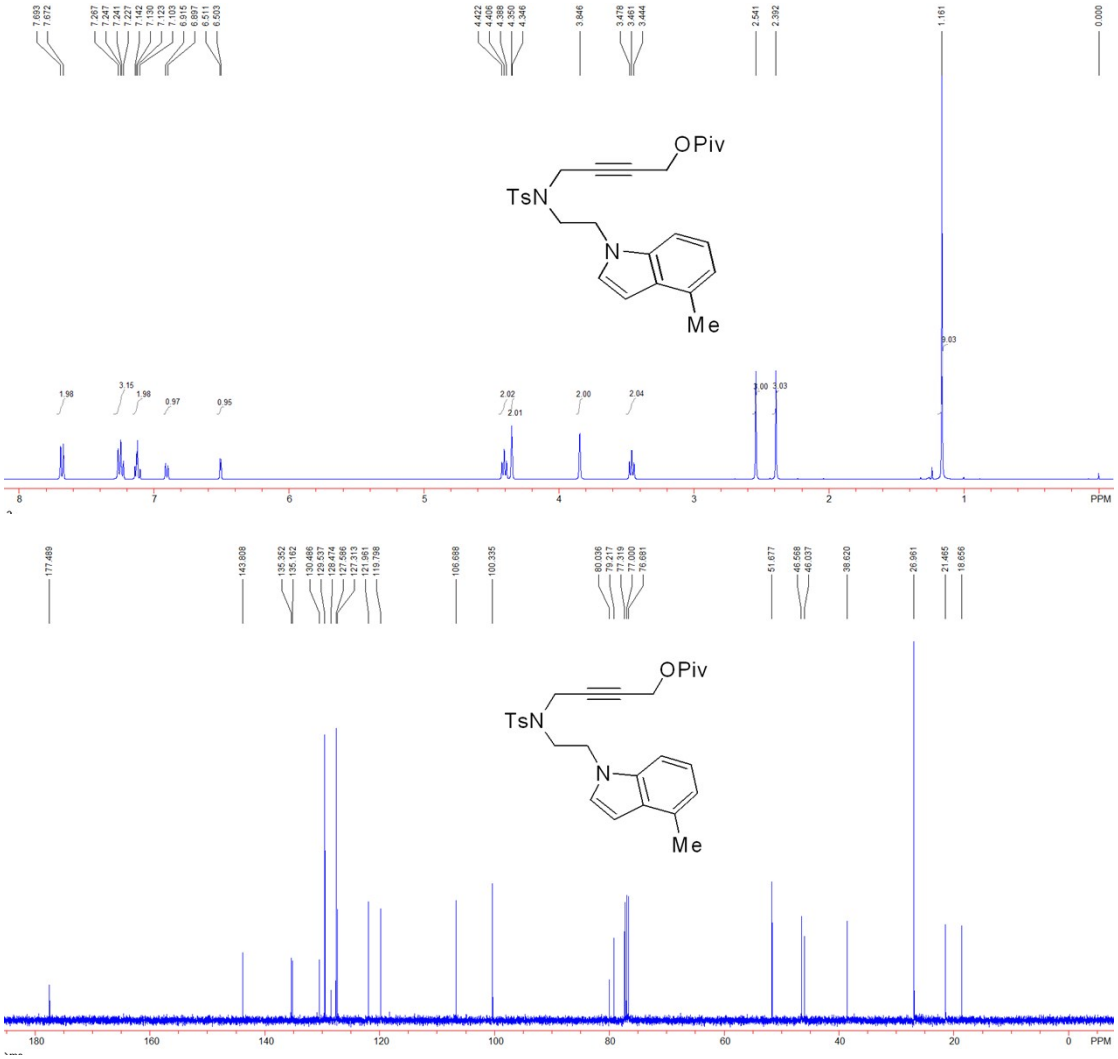




4-((4-methyl-*N*-(2-(4-methyl-1*H*-indol-1-yl)ethyl)phenyl)sulfonamido)but-2-yn-1-yl pivalate

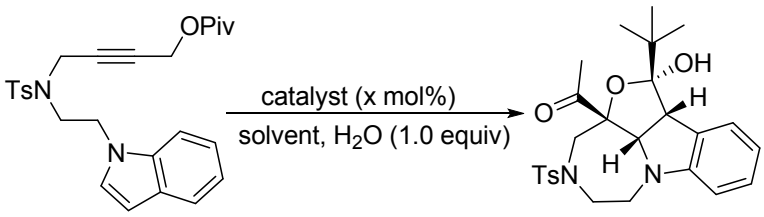
Compound **1u**: a white solid. m.p. 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.16 (s, 9H), 2.39 (s, 3H), 2.54 (s, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.85 (s, 2H), 4.35(t, J = 1.6 Hz, 2H), 4.41 (t, J = 6.8 Hz, 2H), 6.51 (d, J = 3.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 7.10-7.14 (m, 2H), 7.23-7.27 (m, 3H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 21.5, 27.0, 38.6, 46.0, 46.6, 51.7,

79.2, 80.0, 100.3, 106.7, 119.8, 122.0, 127.3, 127.6, 128.5, 129.5, 130.5, 135.2, 135.4, 143.8, 177.5. IR (neat) ν 2974, 2923, 2868, 1733, 1493, 1458, 1347, 1302, 1279, 1158, 1139, 1099, 1034, 814, 750, 726, 657 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_4S$+H] requires 481.2156, found 481.2154 [M^++H].



(C) Screening of the Asymmetric Reaction Conditions.

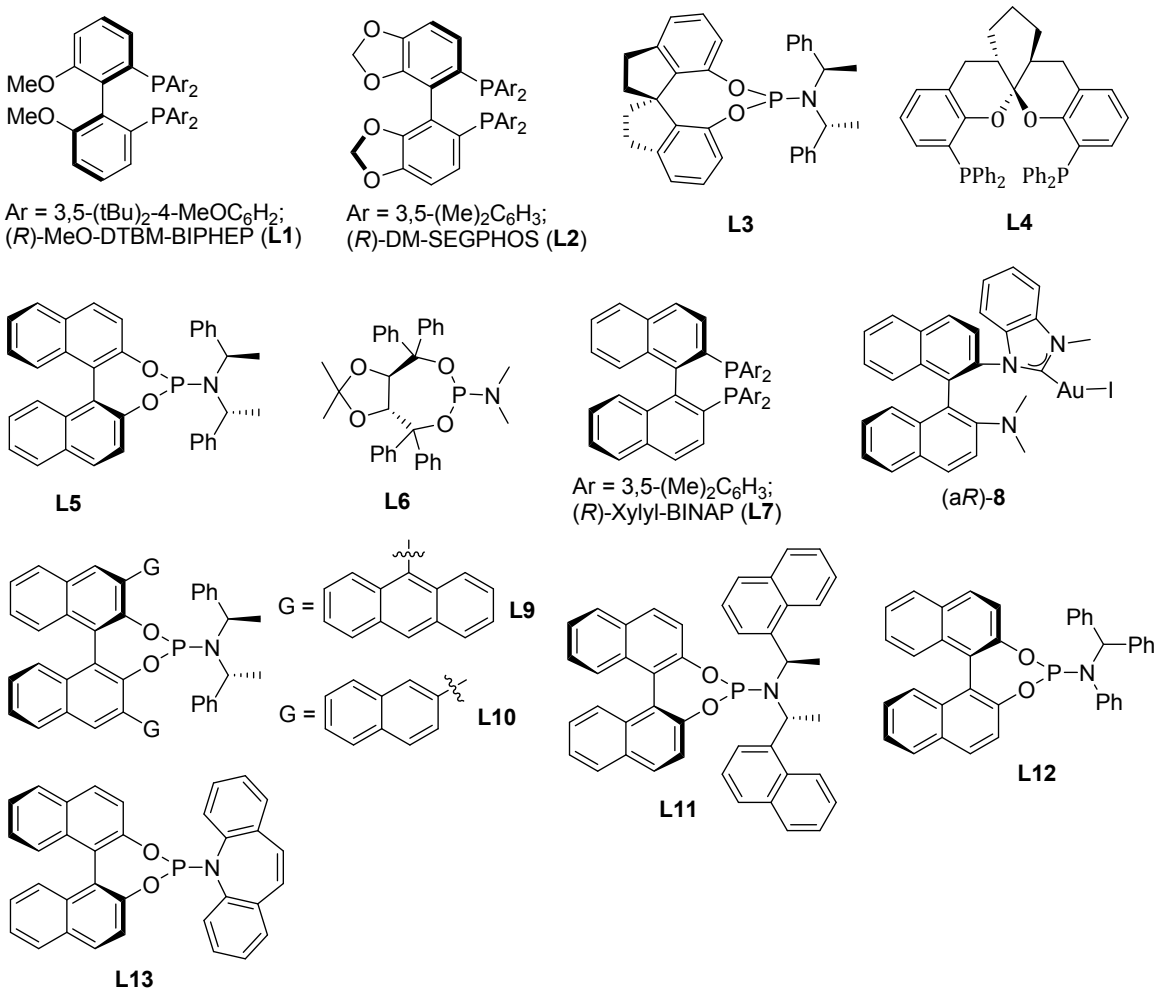
Table S1: Optimization of the asymmetric reaction conditions.



1a **3a**

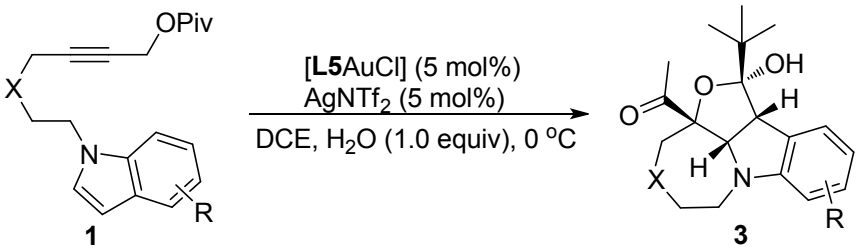
entry[a]	catalyst (x mol%)	solvent	T (^{o}C)	time	yield (%)[b]	ee (%)[c]
1	[**L1**AuCl] (5)/$AgSbF_6$ (5)	DCE	RT	1 h	74	0
2	[**L2**Au_2Cl_2] (5)/AgOPNB (5)	DCE	RT	2 d	trace	-[d]
3	[**L2**Au_2Cl_2] (5)/$AgSbF_6$ (5)	DCE	RT	2 h	72	0
4	[**L3**Au(CH_3CN)][SbF_6] (5)	DCE	RT	3 h	85	40
5	[**L4**$Au_2(CH_3CN)_2$][$(SbF_6)_2$] (5)	DCE	RT	3 d	67	15
6	[**L5**Au(CH_3CN)][SbF_6] (5)	DCE	RT	1 h	86	71
7	[**L5**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	3.5 h	79	71
8	[**L5**AuCl] (5)/$AgNTf_2$ (5)	Toluene	RT	4 h	23	47
9	[**L5**Au(CH_3CN)][SbF_6] (5)	DCM	RT	1 h	87	67
10	[**L5**Au(CH_3CN)][SbF_6] (5)	$CHCl_3$	RT	5 h	85	50
11	[**L5**AuCl] (5)/$AgBF_4$ (5)	DCE	RT	45 min	65	31
12	[**L5**AuCl] (5)/$AgSbF_6$ (5)	DCE	RT	4 h	77	14
13	[**L5**AuCl] (5)/AgOTf (5)	DCE	RT	4 h	trace	-[d]
14	[**L5**AuCl] (5)/AgOONB (5)	DCE	RT	4 d	trace	-[d]
15	[**L6**Au(CH_3CN)][SbF_6] (5)	DCE	RT	6 h	55	-7
16	[**L7**Au_2Cl_2] (5)/$AgSbF_6$ (10)	DCE	RT	5 h	67	2
17	(a*R*)-**8** (5)/$AgSbF_6$ (5)	DCE	RT	30 min	79	0
18	[**L9**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	4 h	78	-17
19	[**L10**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	22 h	77	43
20	[**L11**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	2 h	84	52
21	[**L12**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	18 h	69	-46
22	[**L13**AuCl] (5)/$AgNTf_2$ (5)	DCE	RT	1.5 h	72	27
23	[**L5**AuCl] (5)/$AgNTf_2$ (5)	DCE	0	16 h	72	77

[a] All reactions were carried out using **1a** (0.1 mmol) in the presence of catalyst (x mol%) in various solvents (1.0 mL) unless otherwise specified. [b] Yield of isolated product. [c] Determined by HPLC on a chiral stationary phase. [d] Not determined.
OPNB = *p*-nitrobenzoate, OONB = *o*-nitrobenzoate



Scheme S2: Catalyst ligands for **Table S1**

Table S2: Substrate scope of the asymmetric reaction.



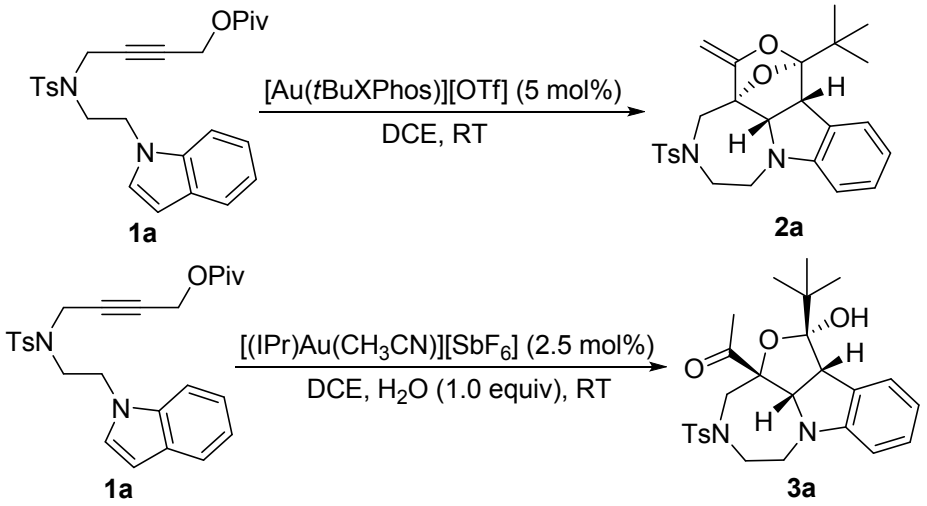
entry[a]	**1**	X	R	time [days]	**3**	yield [%][b]	ee [%][c]
1	**1b**	2-$MeC_6H_4SO_2N$	H	3	**3b**	30	74
2	**1o**	TsN	6-Cl	3		_[d]	_[d]
3	**1p**	O	H	3	**3p**	30	72
4	**1q**	CH_2	H	3	**3q**	25	60

[a] Reaction conditions: **1** (0.1 mmol), [**L5**AuCl] (5 mol%), $AgNTf_2$ (5 mol%), H_2O (1.0 equiv), anhydrous DCE (1.0 mL). [b] Yields are those of the isolated yields. [c] Determined by HPLC on a chiral stationary phase. [d] Complex mixtures, not determined. DCE = 1,2-dichloroethane.

(D) General Procedure for Gold-Catalyzed Cyclization of Propargylic Esters with Indole Derivatives, the Control Experiments and Analytical Data of Products 2a-2r, 3a-3s, 4q and 4u.

Under argon atmosphere, dry 1,2-dichloroethane (DCE) (1.0 mL) was added to a mixture of propargylic ester **1a** (47.5 mg, 0.10 mmol) and [Au(*t*BuXPhos)][OTf] (3.9 mg, 0.005 mmol). The reaction system was stirred for 2 h at RT until **1a** was completely consumed by TLC monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 5/1) to give the product **2a** (45 mg, 95% yield) as a white solid (Scheme S3).

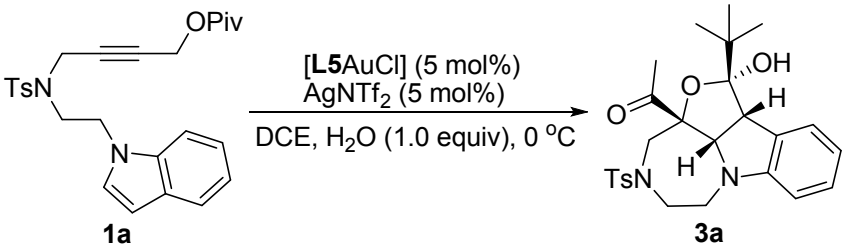
Under argon atmosphere, dry 1,2-dichloroethane (DCE) (1.0 mL) was added to a mixture of propargylic ester **1a** (47 mg, 0.10 mmol), [(IPr)Au(CH_3CN)][SbF_6] (2.2 mg, 0.0025 mmol) and H_2O (1.8 μL, 0.10 mmol). The reaction system was stirred for 5 h at RT until **1a** was completely consumed by TLC monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 5/1) to give the product **3a** (42 mg, 86% yield) as a white solid (Scheme S3).



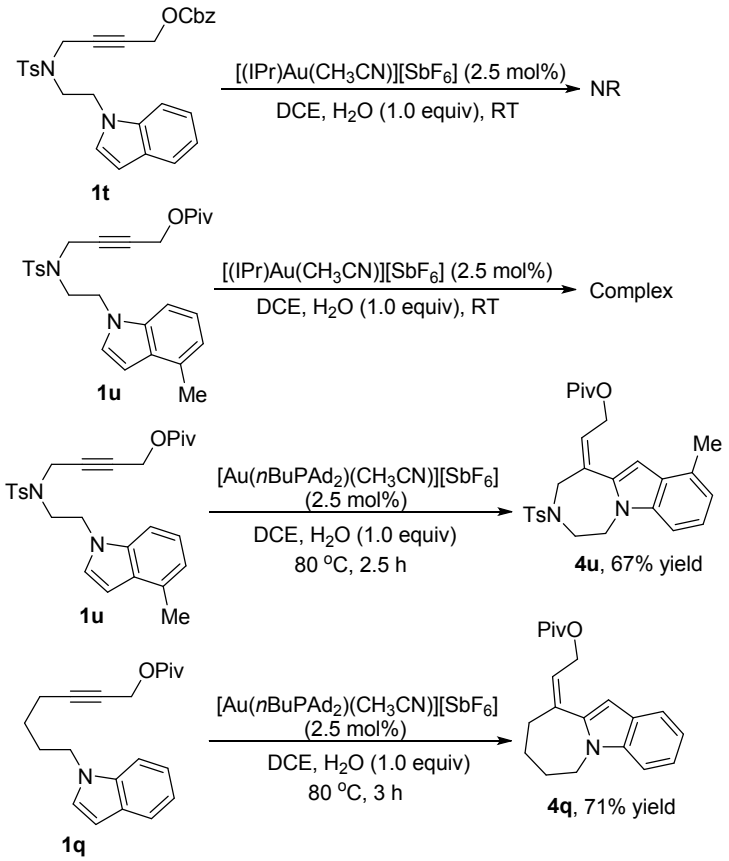
Scheme S3

L5AuCl (3.9 mg, 0.005 mmol) was added to a suspension of $AgNTf_2$ (2.0 mg, 0.005 mmol) in dry 1,2-dichloroethane (DCE) (1.0 mL) at 0 °C. The suspension was left for 5 min at this temperature. Then propargylic ester **1a** (46.7 mg, 0.10 mmol) and H_2O (1.8 μL, 0.10 mmol) were added. The reaction system was stirred for 16 h at 0 °C until **1a** was completely consumed by TLC

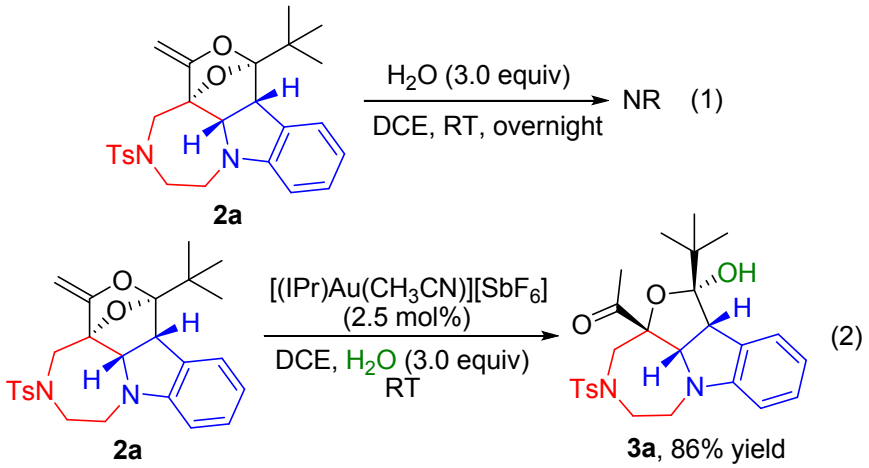
monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 5/1) to give the product **3a** (35 mg, 72% yield, 77% ee) as a white solid (Scheme S4).



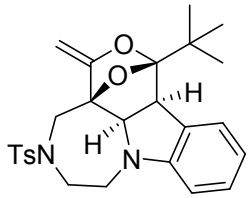
Scheme S4



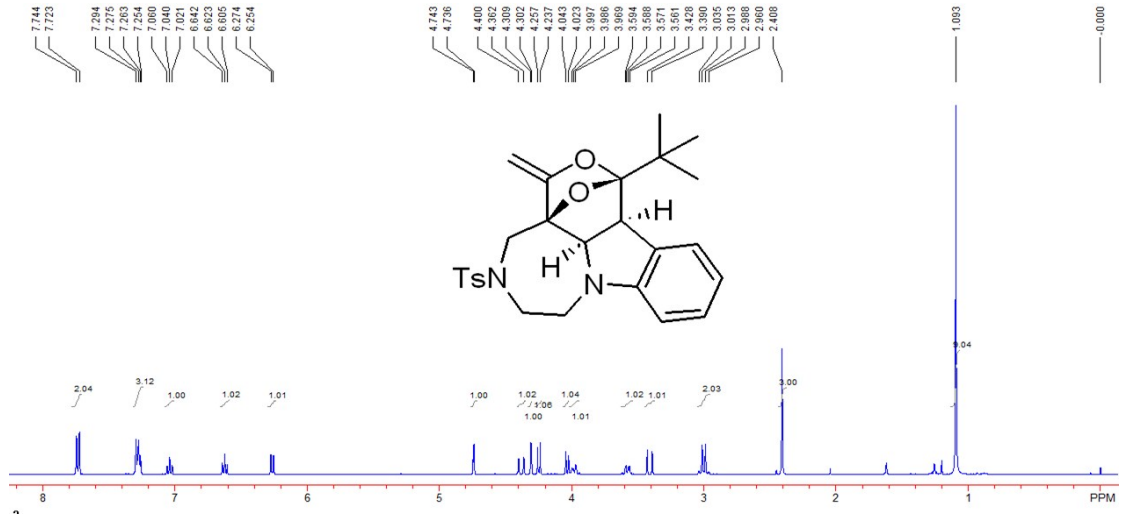
Scheme S5



Scheme S6: The control experiments



Compound **2a**: a white solid. 45 mg, 95% yield. m.p. 195-197 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (s, 9H), 2.41 (s, 3H), 2.96-3.04 (m, 2H), 3.41 (d, J = 15.2 Hz, 1H), 3.56-3.59 (m, 1H), 3.94-4.00 (m, 1H), 4.03 (d, J = 8.0 Hz, 1H), 4.25 (d, J = 8.0 Hz, 1H), 4.31 (d, J = 2.8 Hz, 1H), 4.38 (d, J = 15.2 Hz, 1H), 4.74 (d, J = 2.8 Hz, 1H), 6.26 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 7.25-7.29 (m, 3H), 7.73 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.6, 34.8, 49.2, 51.5, 53.9, 56.0, 75.5, 79.0, 88.4, 106.7, 117.1, 117.4, 125.6, 127.2, 127.6, 128.5, 129.8, 135.5, 143.8, 153.1, 157.7. IR (neat) ν 2960, 2927, 1691, 1603, 1487, 1394, 1334, 1242, 1159, 1124, 1089, 990, 923, 851, 733, 665 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{30}N_2O_4S$+H] requires 467.1999, found 467.2011 [M^++H].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6.254
4.743
4.736
4.400
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4.302
4.257
4.237
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4.023
3.997
3.986
3.969
3.594
3.588
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3.561
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3.390
3.035
3.013
2.988
2.960
2.408
1.093
0.000
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H
N
O
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3.12
1.00
1.02
1.01
1.00
1.02
1.00
1.04
1.01
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1.01
2.03
3.00
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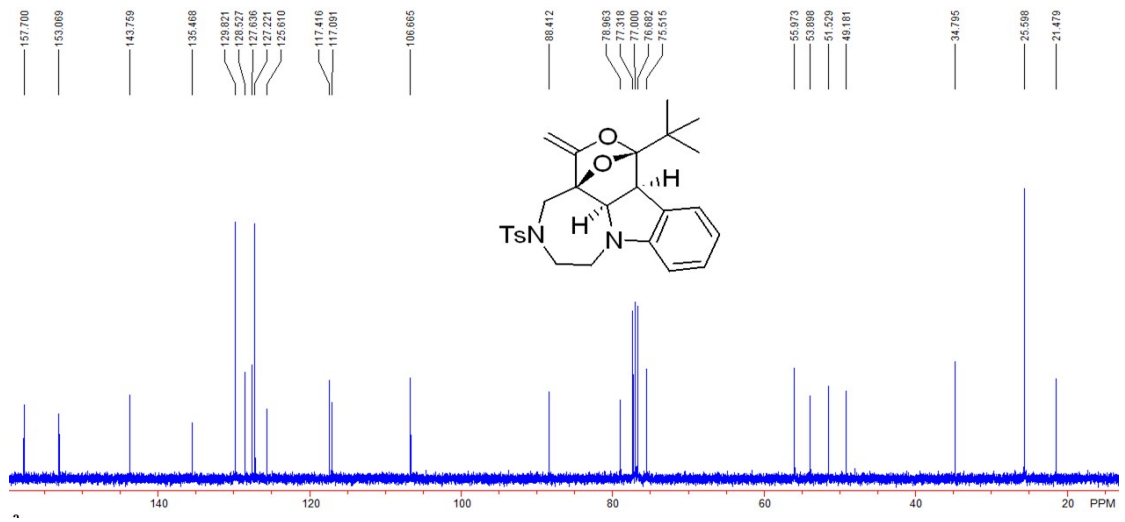
7
6
5
4
3
2
1
PPM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76.682
75.515
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51.529
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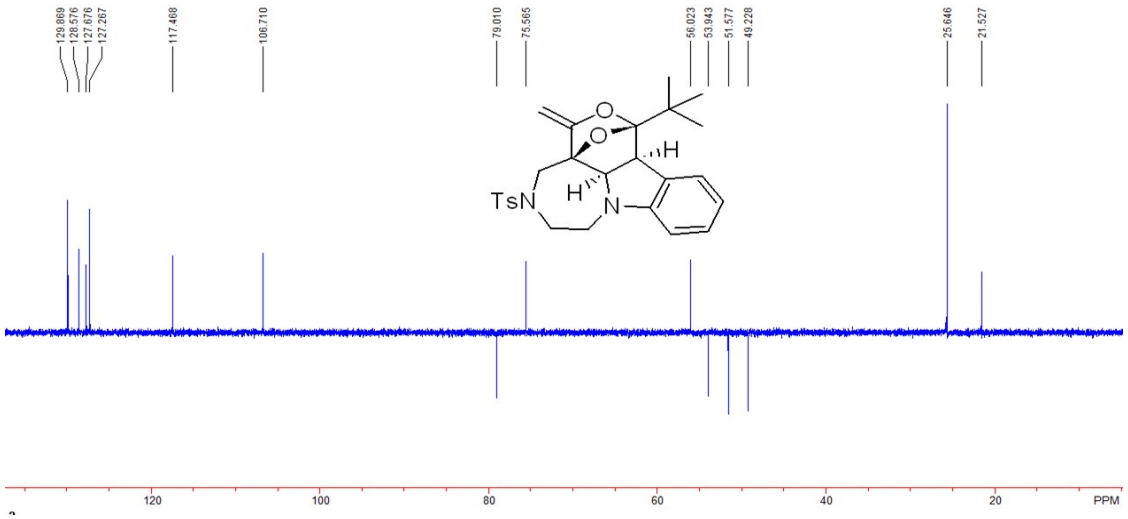
20
PPM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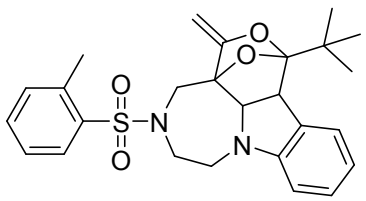
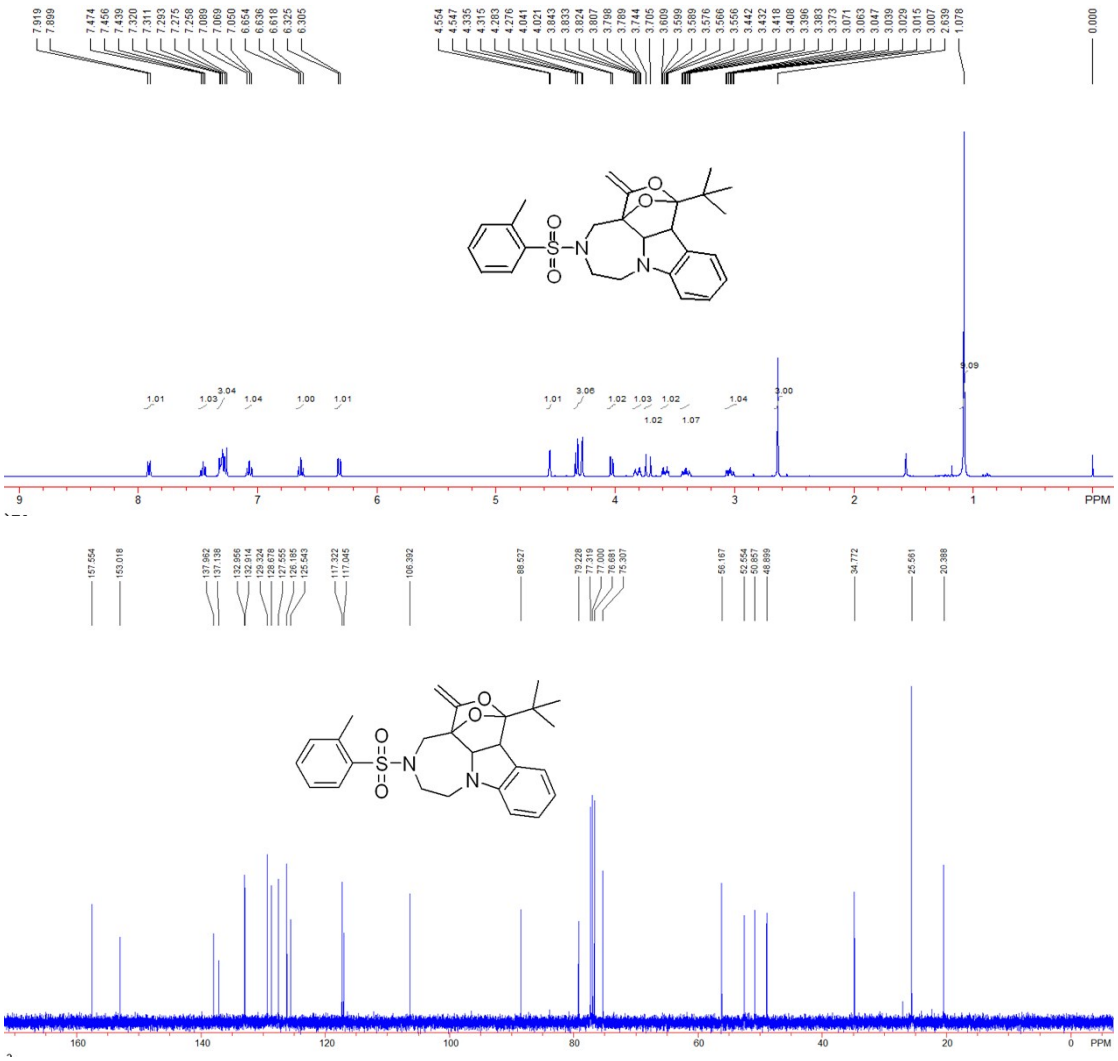
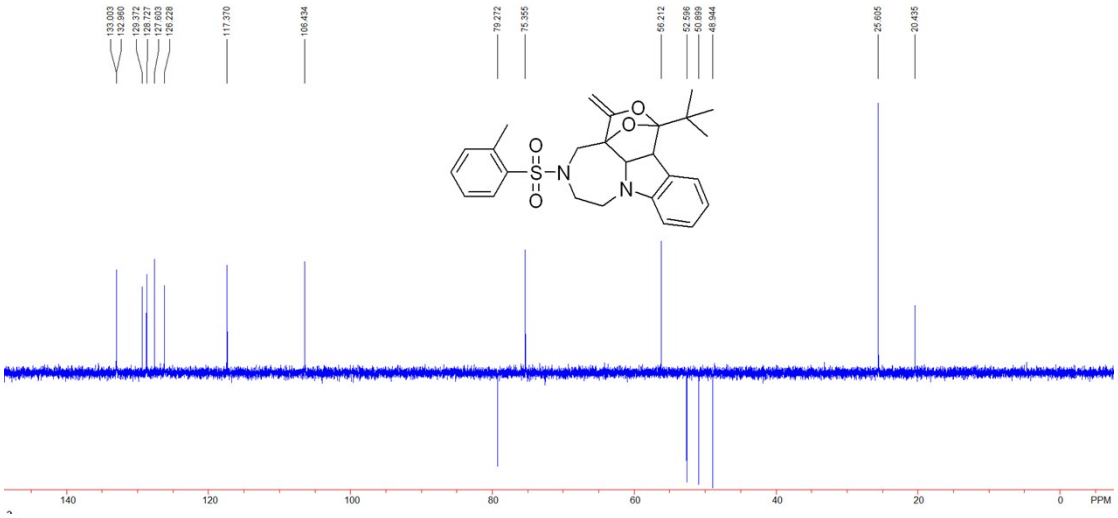
60
40
20
PPM

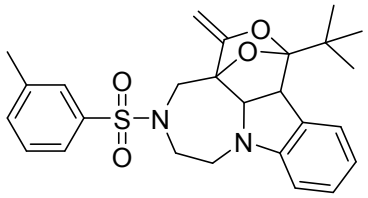

O
S
N
O
O
N

1-(*tert*-butyl)-3-methylene-5-(o-tolylsulfonyl)-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2b**: a white solid. 45 mg, 80% yield. m.p. 171-173 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.08 (s, 9H), 2.64 (s, 3H), 3.00-3.07 (m, 1H), 3.37-3.43 (m, 1H), 3.58 (dt, J = 13.2, 4.0 Hz, 1H), 3.72 (d, J = 15.6 Hz, 1H), 3.82 (dt, J = 14.4, 4.0 Hz, 1H), 4.03 (d, J = 7.6 Hz, 1H), 4.28-4.33 (m, 3H), 4.56 (d, J = 2.8 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 6.64 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.28-7.32 (m, 3H), 7.46 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 25.5, 34.85, 48.9, 50.9, 52.6, 56.2, 75.3, 79.2, 88.5, 106.4, 117.0, 117.3, 125.5, 126.2, 127.6, 128.7, 129.3, 132.9, 133.0, 137.1, 138.0, 153.0, 157.6. IR (neat) ν 2964, 2923, 1688, 1604, 1487, 1328, 1240, 1158, 1125, 989, 950, 906, 851, 730 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{30}N_2O_4S$+H] requires 467.1999, found 467.2001 [M^++H].

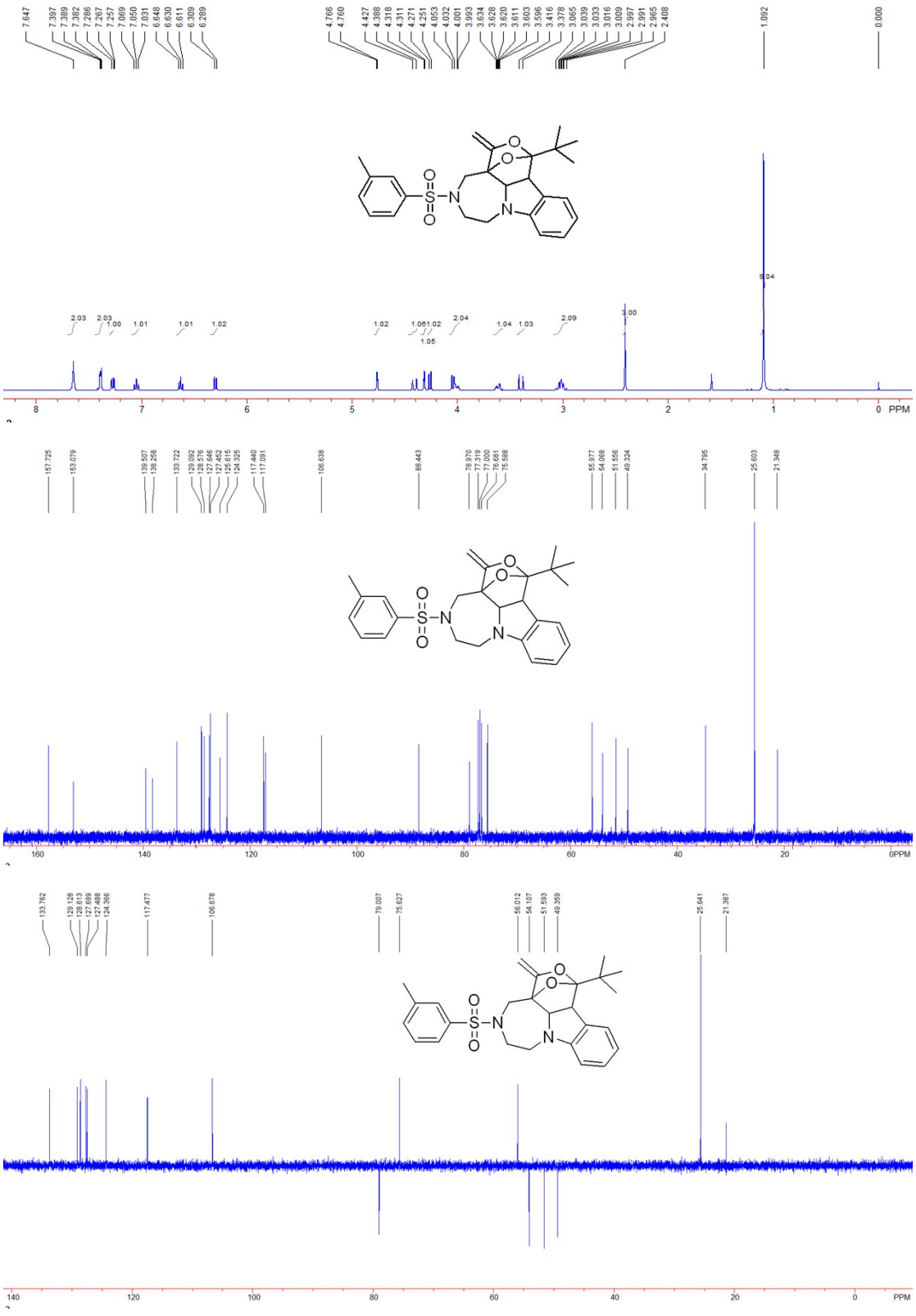






1-(*tert*-butyl)-3-methylene-5-(m-tolylsulfonyl)-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2c**: a white solid. 47 mg, 96% yield. m.p. 91-94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (s, 9H), 2.41 (s, 3H), 2.97-3.07 (m, 2H), 3.40 (d, J = 15.2 Hz, 1H), 3.57-3.63 (m, 1H), 3.99-4.05 (m, 2H), 4.26 (d, J = 8.0 Hz, 1H), 4.31 (d, J = 2.8 Hz, 1H), 4.40 (d, J = 15.6 Hz, 1H), 4.76 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 8.0 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.38-7.40 (m, 2H), 7.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 25.6, 34.8, 49.3, 51.6, 54.1, 56.0, 75.6, 79.0, 88.4, 106.6, 117.1, 117.4, 124.3, 125.6, 127.5, 127.6, 128.6, 129.1, 133.7, 138.3, 139.5, 153.1, 157.7. IR (neat) ν 2960, 2923, 1693, 160, 1482, 1393, 1334, 1243, 1154, 1124, 989, 920, 850, 730, 687, 657 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{30}N_2O_4S$+H] requires 467.1999, found 467.2003 [M^++H].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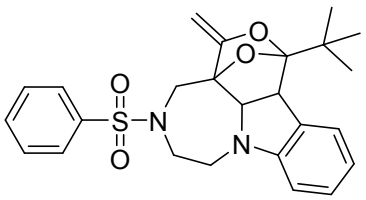
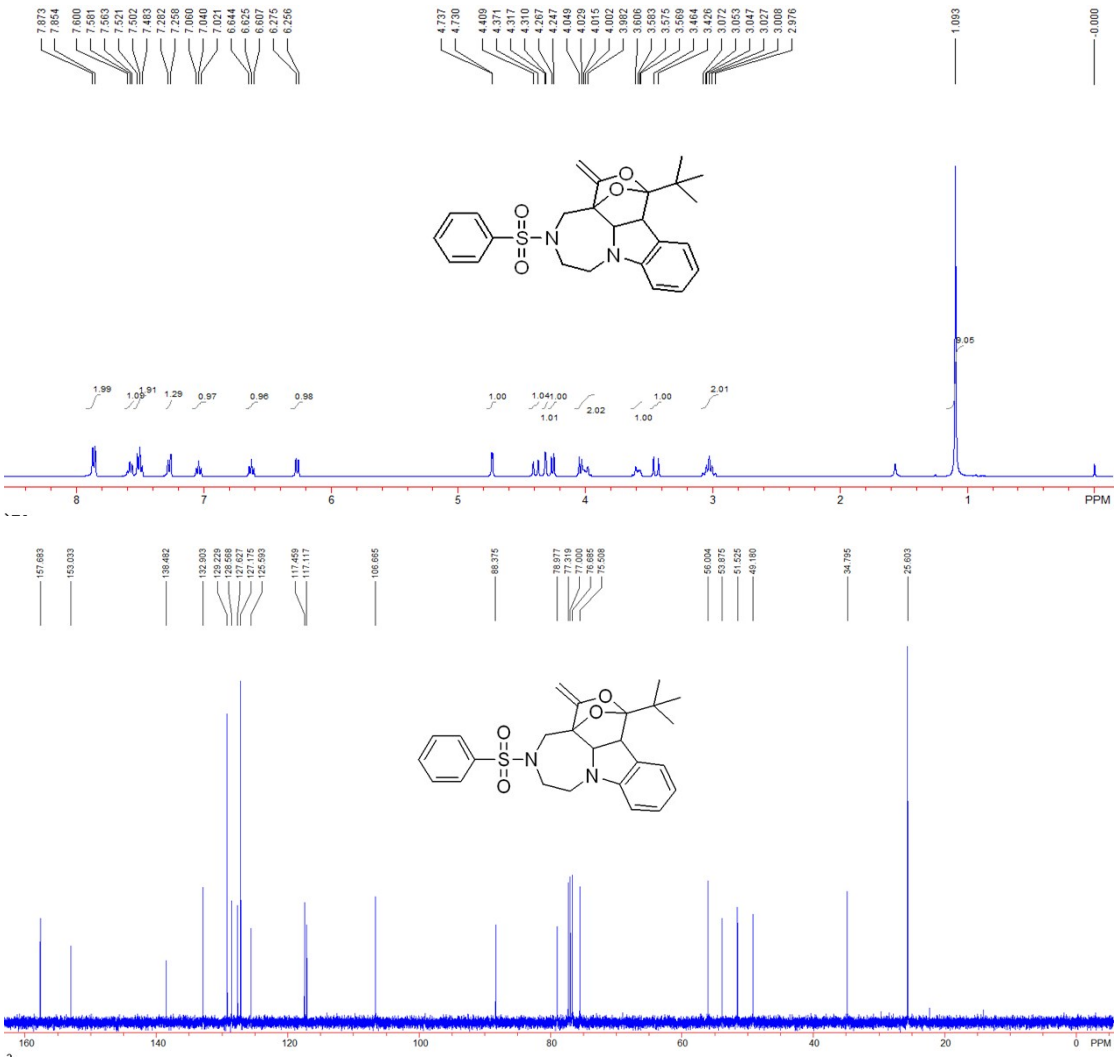
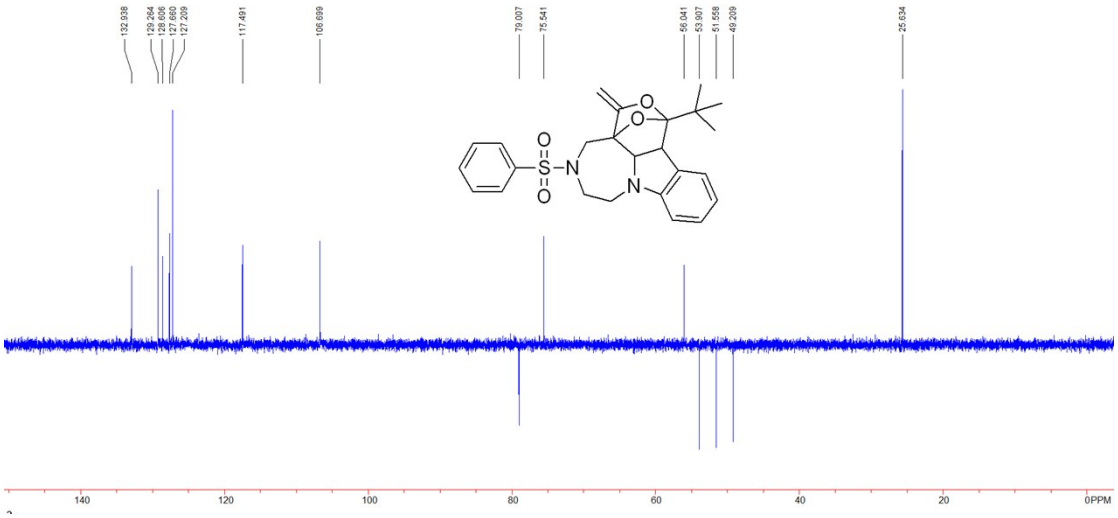
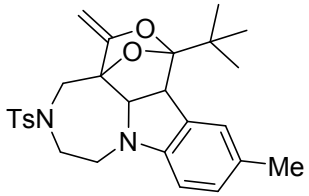


1-(*tert*-butyl)-3-methylene-5-(phenylsulfonyl)-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2d**: a white solid. 40 mg, 85% yield. m.p. 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (s, 9H), 2.98-3.07 (m, 2H), 3.44 (d, J = 14.8 Hz, 1H), 3.57-3.61 (m, 1H), 3.98-4.05 (m, 2H), 4.25 (d, J = 8.0 Hz, 1H), 4.31 (d, J = 2.4 Hz, 1H), 4.39 (d, J = 14.8 Hz, 1H), 4.74 (d, J = 2.4 Hz, 1H), 6.27 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 34.8, 49.2, 51.5, 53.9, 56.0, 75.5, 79.0, 88.4, 106.7, 117.1, 117.5, 125.6, 127.2, 127.6, 128.6, 129.2, 132.9, 138.5, 153.0, 157.7. IR (neat) ν 2960, 2919, 2831, 1687, 1607, 1486, 1448, 1396, 1334, 1241, 1166, 1125, 989, 926, 846, 739, 696 cm^{-1}. HRMS (ESI) calcd for [$C_{25}H_{28}N_2O_4S$+H] requires 453.1843, found 453.1846 [M^++H].

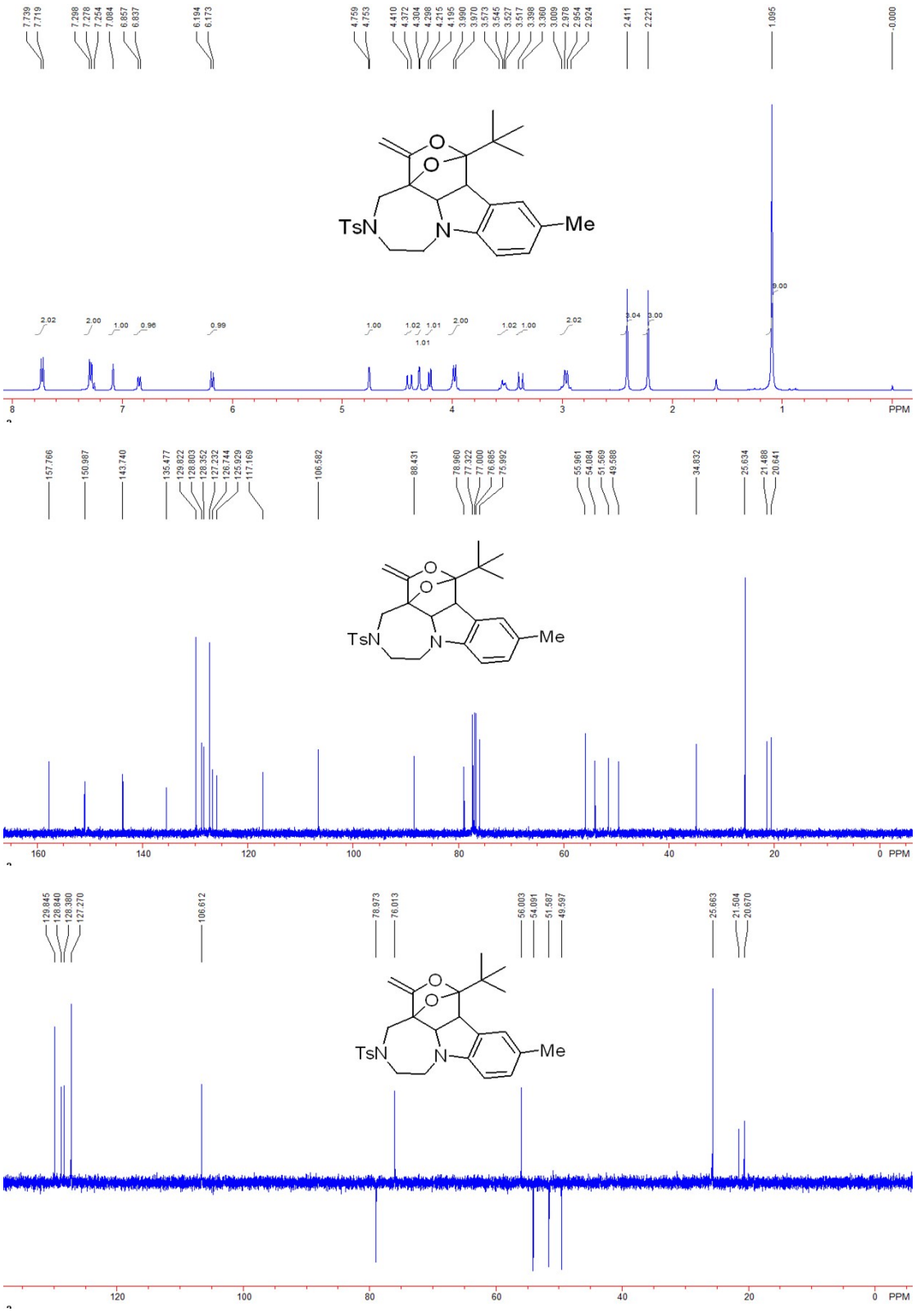






1-(*tert*-butyl)-10-methyl-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2h**: a white solid. 44 mg, 88% yield. m.p. 182-184 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (s, 9H), 2.22 (s, 3H), 2.41 (s, 3H), 2.92-3.01 (m, 2H), 3.38 (d, J = 15.2 Hz, 1H), 3.52-3.57 (m, 1H), 3.98 (d, J = 8.0 Hz, 2H), 4.21 (d, J = 8.0 Hz, 1H), 4.30 (d, J = 2.4 Hz, 1H), 4.39 (d, J = 15.2 Hz, 1H), 4.76 (d, J = 2.4 Hz, 1H), 6.18 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.6, 21.5, 25.6, 34.8, 49.6, 51.6, 54.1, 56.0, 76.0, 79.0, 88.4, 106.6, 117.2, 125.9, 126.7, 127.2, 128.4, 128.8, 129.8, 135.5, 143.7, 151.0, 157.8. IR (neat) ν 2967, 2923, 2864, 1691, 1618, 1594, 1497, 1400, 1334, 1243, 1160, 1124, 1054, 989, 907, 801, 730, 663 cm^{-1}; HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_4S$+H] requires 481.2156, found 481.2156 [M^++H].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Me
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2.00
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0.96
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2.00
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3.00
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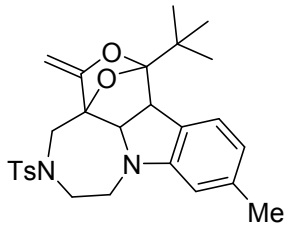
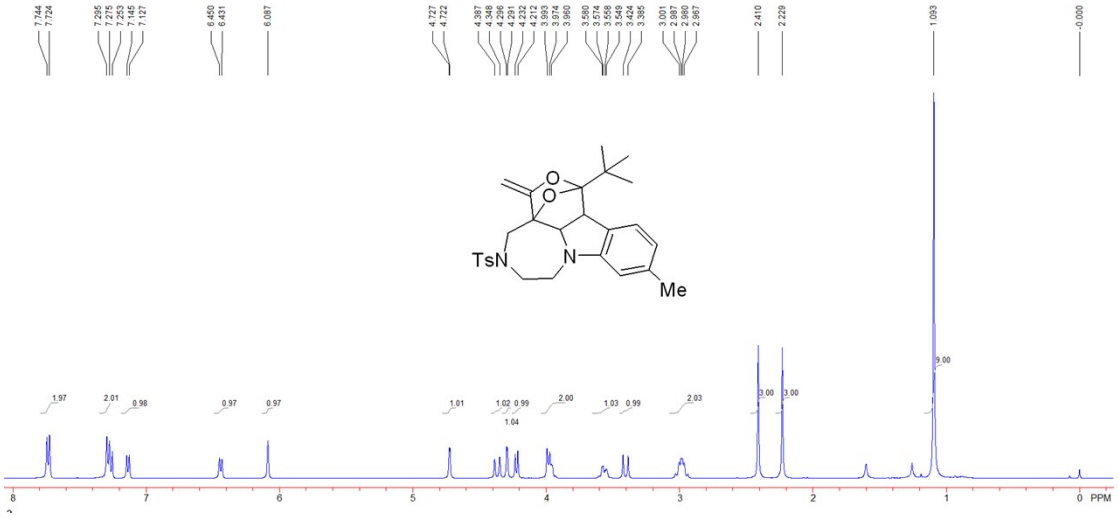
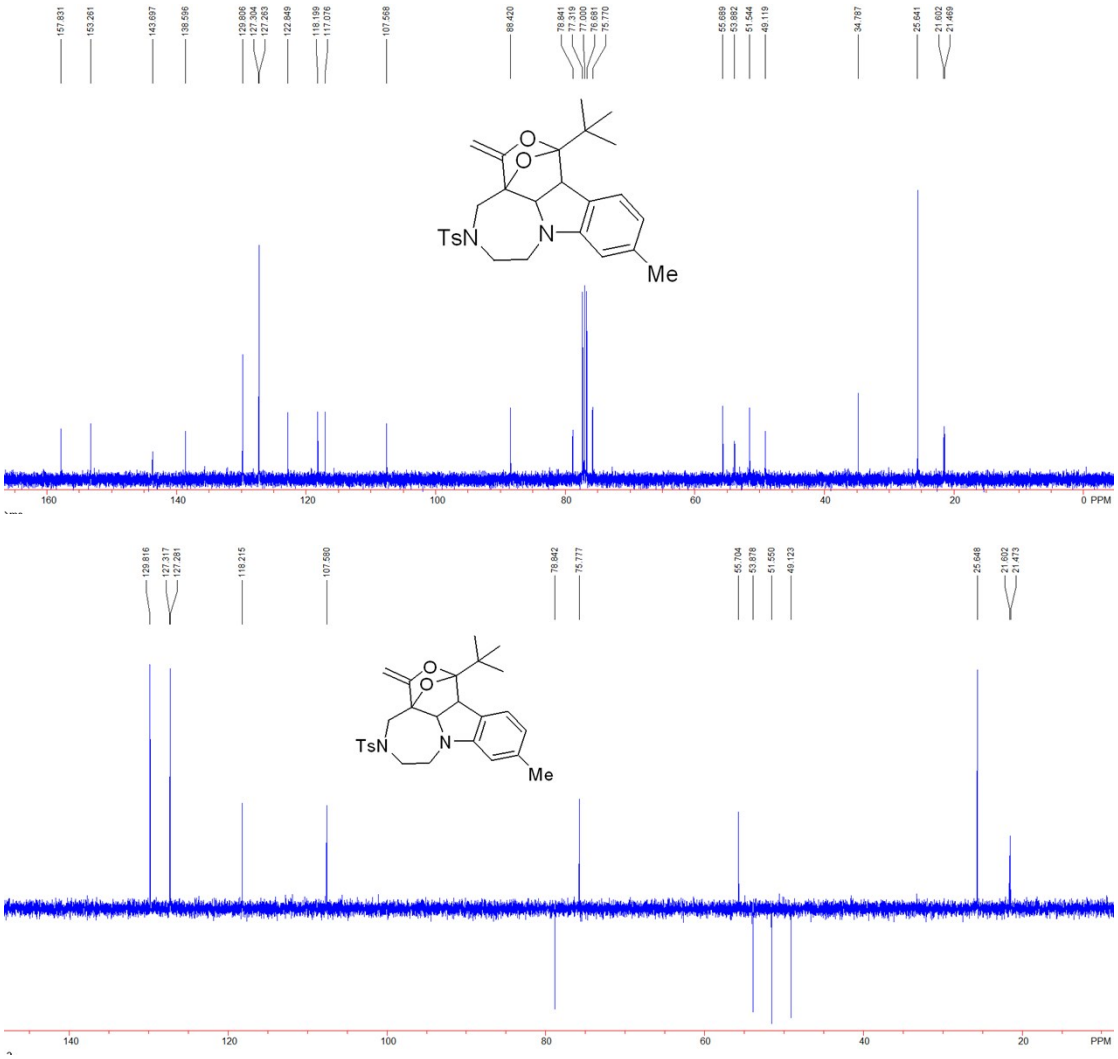
54.091
51.587
49.597
25.663
21.504
20.670

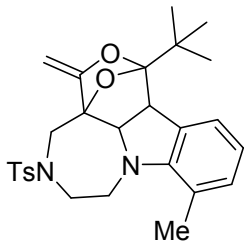


1-(*tert*-butyl)-9-methyl-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2i**: a white solid. 40 mg, 83% yield. m.p. 210-212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (s, 9H), 2.23 (s, 3H), 2.41 (s, 3H), 2.94-3.03 (m, 2H), 3.40 (d, J = 15.6 Hz, 1H), 3.55-3.60 (m, 1H), 3.93-3.99 (m, 2H), 4.22 (d, J = 8.0 Hz, 1H), 4.29 (d, J = 2.0 Hz, 1H), 4.37 (d, J = 15.6 Hz, 1H), 4.72 (d, J = 2.0 Hz, 1H), 6.09 (s, 1H), 6.44 (d, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 21.6, 25.6, 34.8, 49.1, 51.5, 53.9, 55.7, 75.8, 78.8, 88.4, 107.6, 117.1, 118.2, 122.8, 127.26, 127.30, 129.8, 138.6, 143.7, 153.3, 157.8. IR (neat) ν 2982, 2960, 2919, 1689, 1607, 1497, 1437, 1365, 1334, 1298, 1252, 1159, 1124, 1008, 946, 904, 853, 819, 733, 663 cm^{-1}; HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_4S$+H] requires 481.2156, found 481.2158 [M^++H].



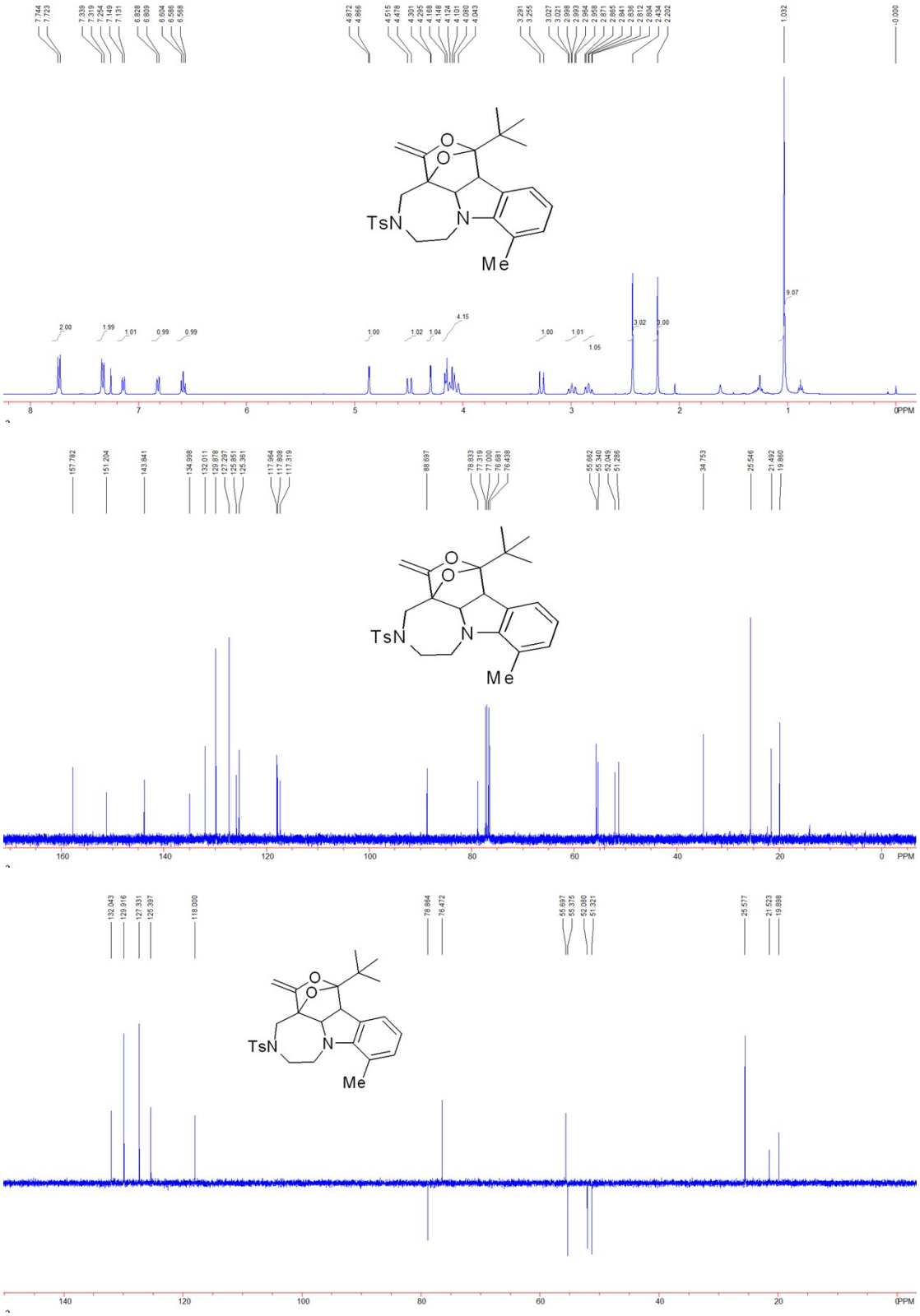


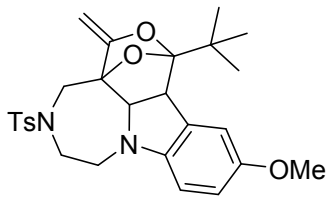


1-(*tert*-butyl)-8-methyl-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2j**: a white solid. 35 mg, 73% yield. m.p. 198-199 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.03 (s, 9H), 2.20 (s, 3H), 2.43 (s, 3H), 2.84 (td, J = 12.0, 2.0 Hz, 1H), 2.99 (td, J = 12.0, 2.0 Hz, 1H), 3.27 (d, J = 14.4 Hz, 1H), 4.04-4.17 (m, 4H), 4.30 (d, J = 2.4 Hz, 1H), 4.50 (d, J = 14.8 Hz, 1H), 4.87 (d, J = 2.4 Hz, 1H), 6.59 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.9, 21.5, 25.5, 34.8, 51.3, 52.0, 55.3, 55.7, 76.4, 78.8, 88.7, 117.3, 117.8, 117.9, 125.4, 125.9, 127.3,

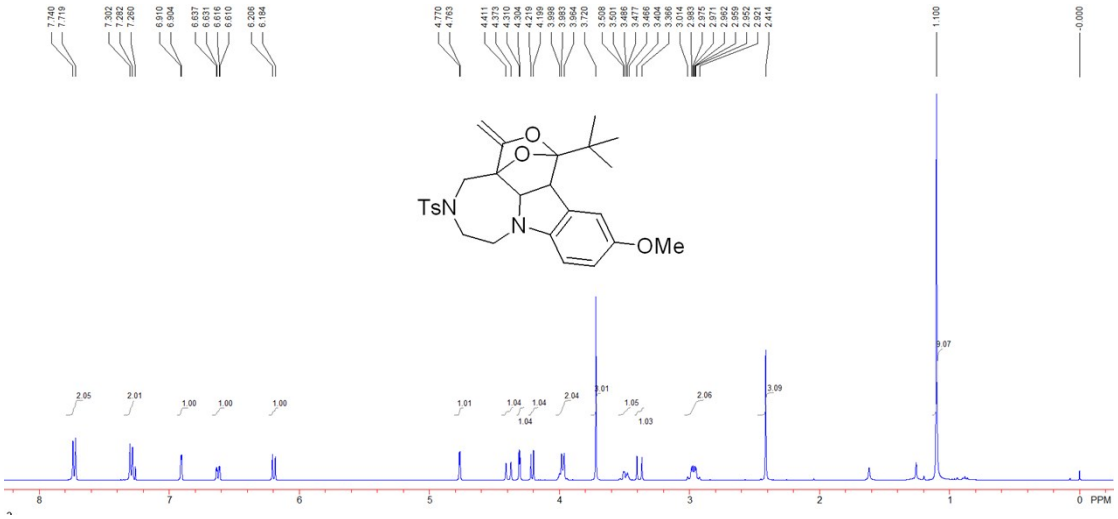
129.9, 132.0, 135.0, 143.8, 151.2, 157.8. IR (neat) ν 2960, 2919, 2868, 1689, 1594, 1471, 1426, 1363, 1334, 1160, 1120, 985, 908, 829, 734, 665 cm^{-1}; HRMS (ESI) calcd for $[C_{27}H_{32}N_2O_4S+H]$ requires 481.2156, found 481.2157 $[M^+ + H]$.

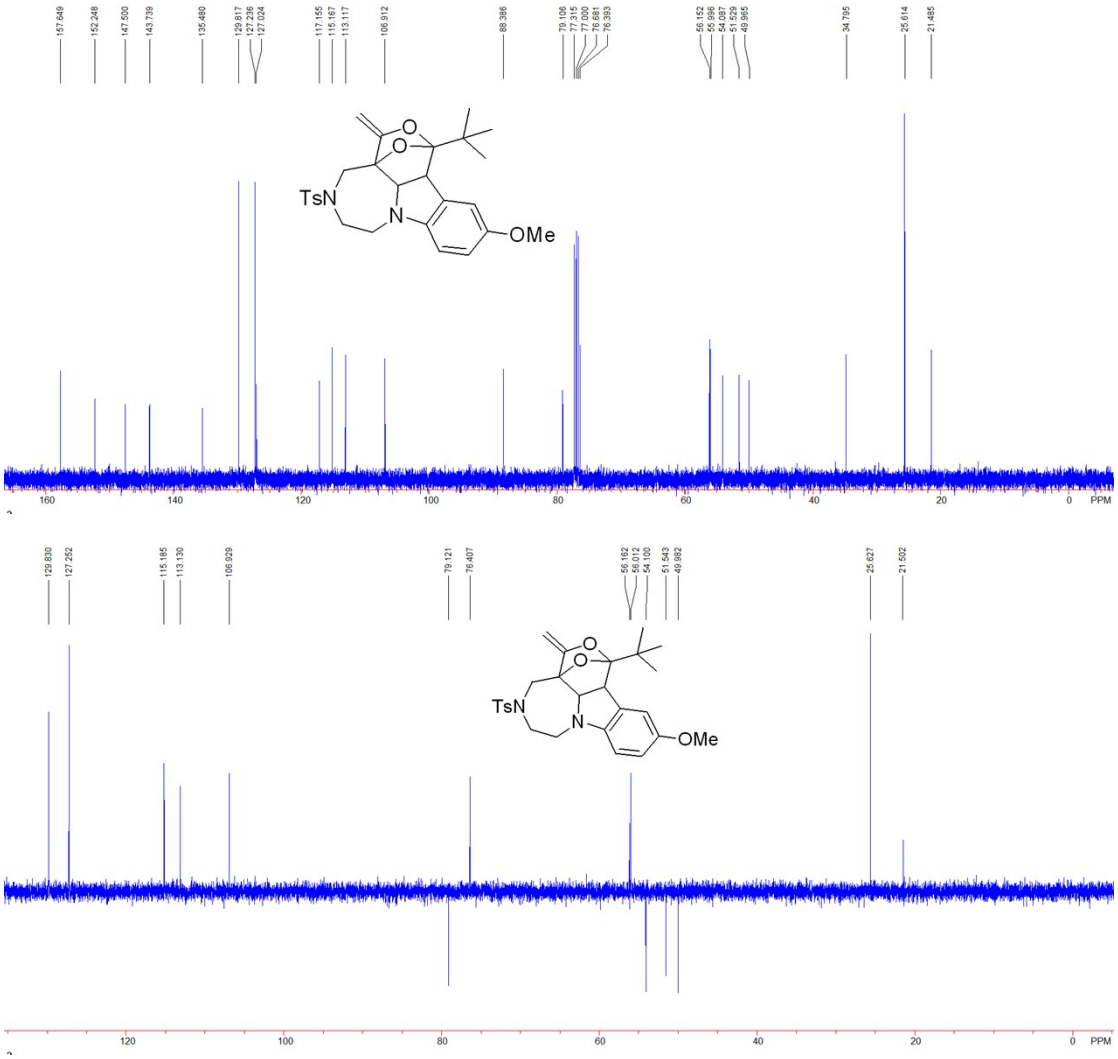


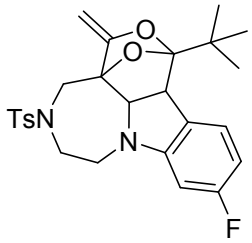


1-(*tert*-butyl)-10-methoxy-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2k**: a white solid. 39 mg, 78% yield. m.p. 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.10 (s, 9H), 2.41 (s, 3H), 2.92-3.01 (m, 2H), 3.39 (d, J = 15.2 Hz, 1H), 3.47-3.51 (m, 1H), 3.72 (s, 3H), 3.96-4.00 (m, 2H), 4.21 (d, J = 8.0 Hz, 1H), 4.31 (d, J = 2.4 Hz, 1H), 4.39 (d, J = 15.2 Hz, 1H), 4.77 (d, J = 2.8 Hz, 1H), 6.20 (d, J = 8.8 Hz, 1H), 6.62 (dd, J = 8.4, 2.4 Hz, 1H), 6.91 (d, J = 2.4 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.6, 34.8, 50.0, 51.5, 54.1, 56.0, 56.2, 76.4, 79.1, 88.4, 106.9, 113.1, 115.2, 117.2, 127.0, 127.2, 129.8, 135.5, 143.74, 147.5, 152.2, 157.6. IR (neat) ν 2963, 2919, 2824, 1685, 1590, 1492, 1334, 1288, 1234, 1161, 1124, 1037, 989, 908, 842, 812, 731, 661 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_5S$+H] requires 497.2105, found 497.2108 [M$^+$+H].



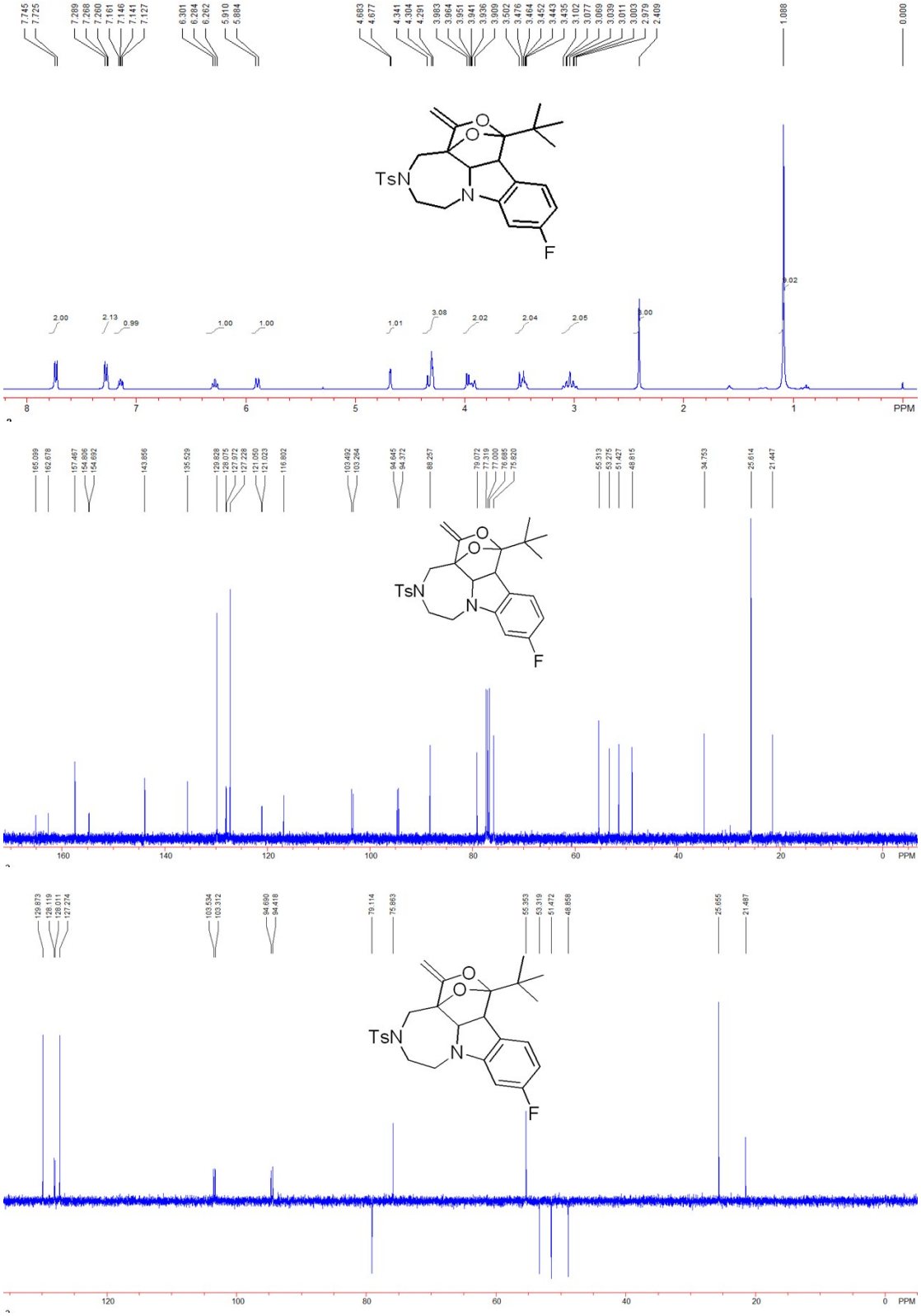


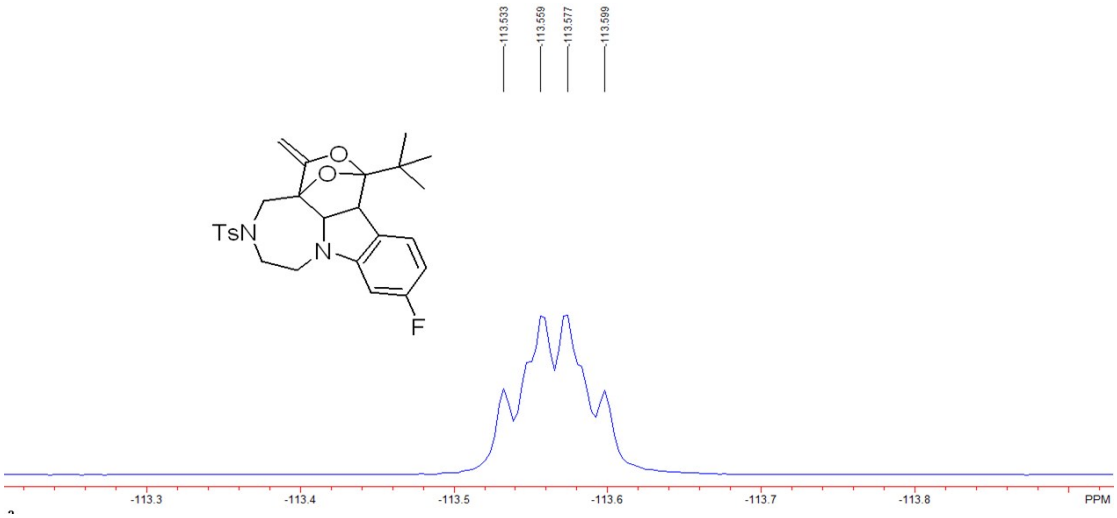


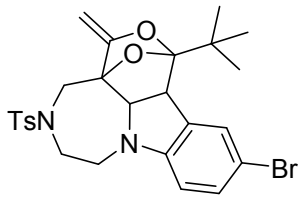
1-(*tert*-butyl)-9-fluoro-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2l**: a white solid. 37 mg, 76% yield. m.p. 178-180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (s, 9H), 2.41 (s, 3H), 2.98-3.10 (m, 2H), 3.44-3.50 (m, 2H), 3.91-3.98 (m, 2H), 4.29-4.34 (m, 3H), 4.68 (d, J = 2.4 Hz, 1H), 5.90 (d, J = 9.2 Hz, 1H), 6.28 (t, J = 8.0 Hz, 1H), 7.15 (dd, J = 7.6, 6.0 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 25.6, 34.8, 48.8, 51.4, 53.2, 55.3, 75.8, 79.1, 88.3, 94.5 (d, J = 27.3 Hz), 103.4 (d, J = 22.8 Hz), 116.8 (d, J = 0.9 Hz), 121.0 (d, J = 2.7 Hz), 127.2, 128.0 (d, J = 10.3 Hz), 129.8, 15.5, 143.9,

154.7 (d, J = 11.4 Hz), 157.5, 163.9 (d, J = 242.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -113.599 ~ -113.533 (m). IR (neat) ν 2974, 2897, 2842, 1691, 1616, 1598, 1495, 143, 1303, 1158, 1120, 1003, 910, 816, 734, 666 cm^{-1}; HRMS (ESI) calcd for [$C_{26}H_{29}FN_2O_4S$+H] requires 485.1905, found 485.1909 [M^++H].

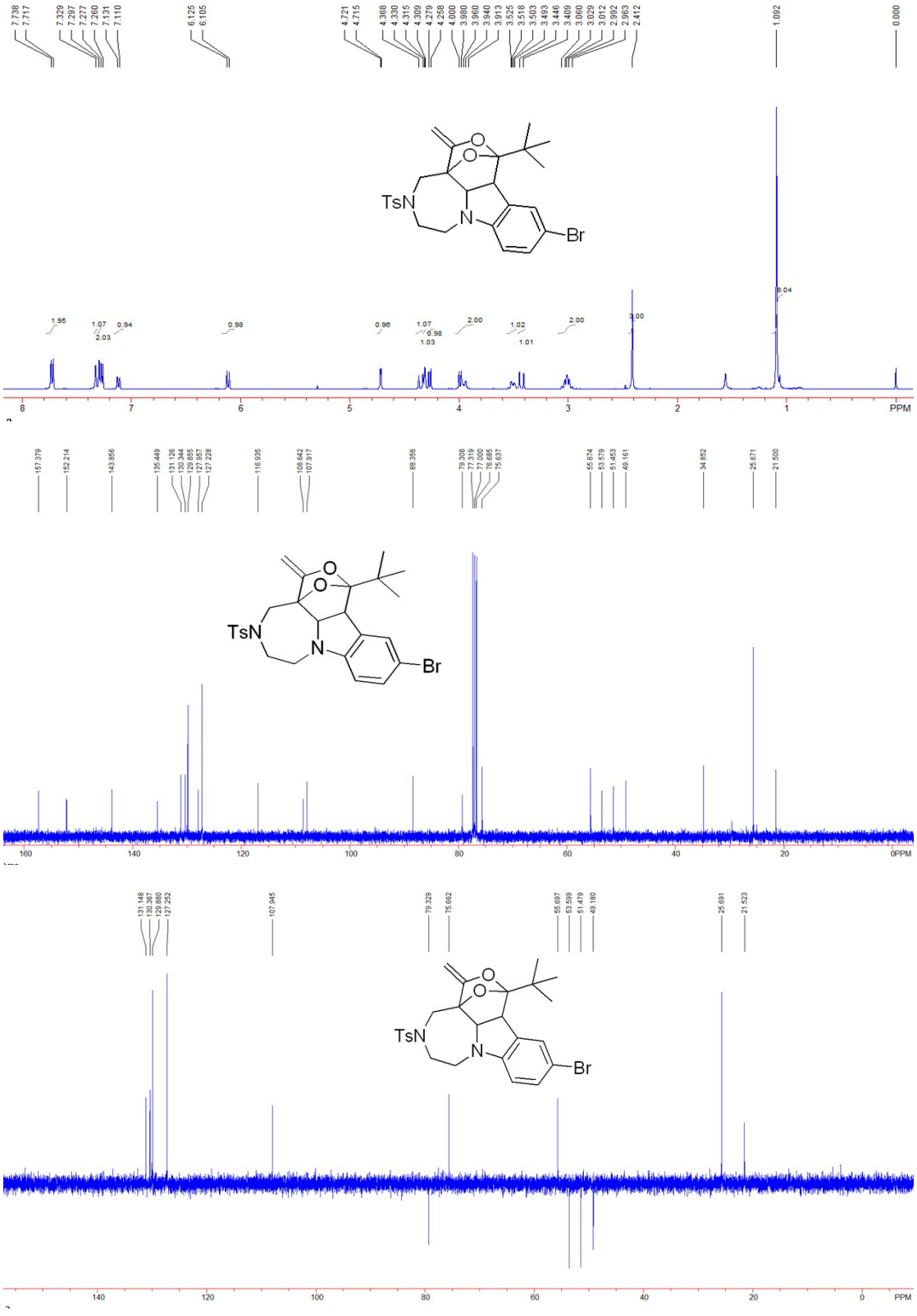






10-bromo-1-(*tert*-butyl)-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2m**: a white solid. 41 mg, 72% yield. m.p. 210-212 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (s, 9H), 2.41 (s, 3H), 2.96-3.06 (m, 2H), 3.42 (d, J = 15.6 Hz, 1H), 3.49-3.53 (m, 1H), 3.91-4.00 (m, 2H), 4.27 (d, J = 8.0 Hz, 1H), 4.31 (d, J = 2.4 Hz, 1H), 4.35 (d, J = 15.2 Hz, 1H), 4.72 (d, J = 2.4 Hz, 1H), 6.12 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.33 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.7, 34.9, 49.2, 51.5, 53.6, 55.7, 75.6, 79.3, 88.4, 107.9, 108.6, 116.9, 127.2, 128.0, 129.9, 130.3, 131.1, 135.4, 143.9, 152.2, 157.3. IR (neat) ν 2972, 2923, 1698, 1593, 1482, 1443, 1316, 1282, 1244, 1151, 1125, 1115, 1090, 1073, 1015, 990, 921, 849, 843, 831, 812, 803, 735, 661 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{29}BrN_2O_4S$+H] requires 545.1104, found 545.1106 [M^++H].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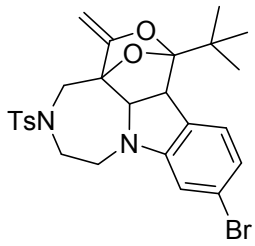
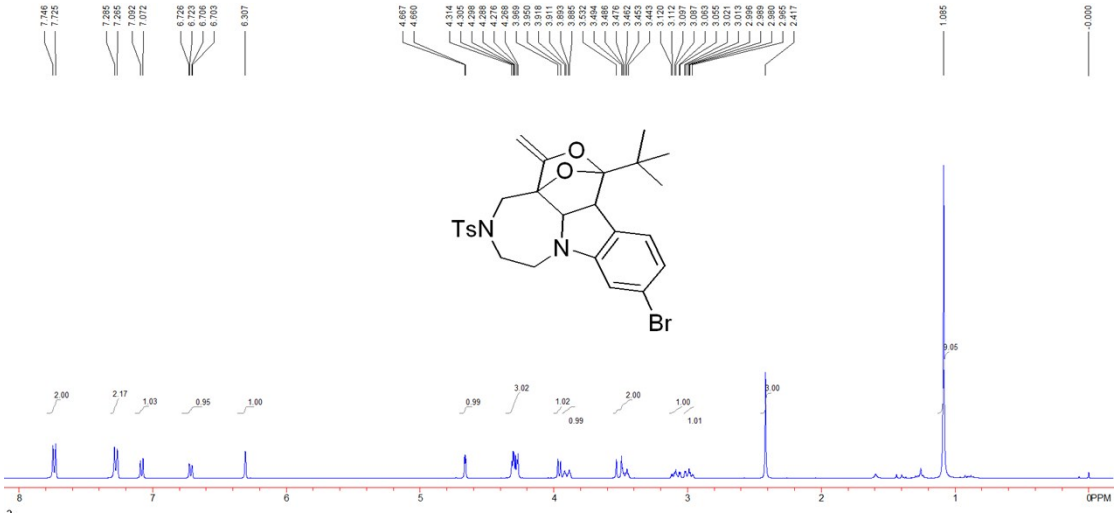
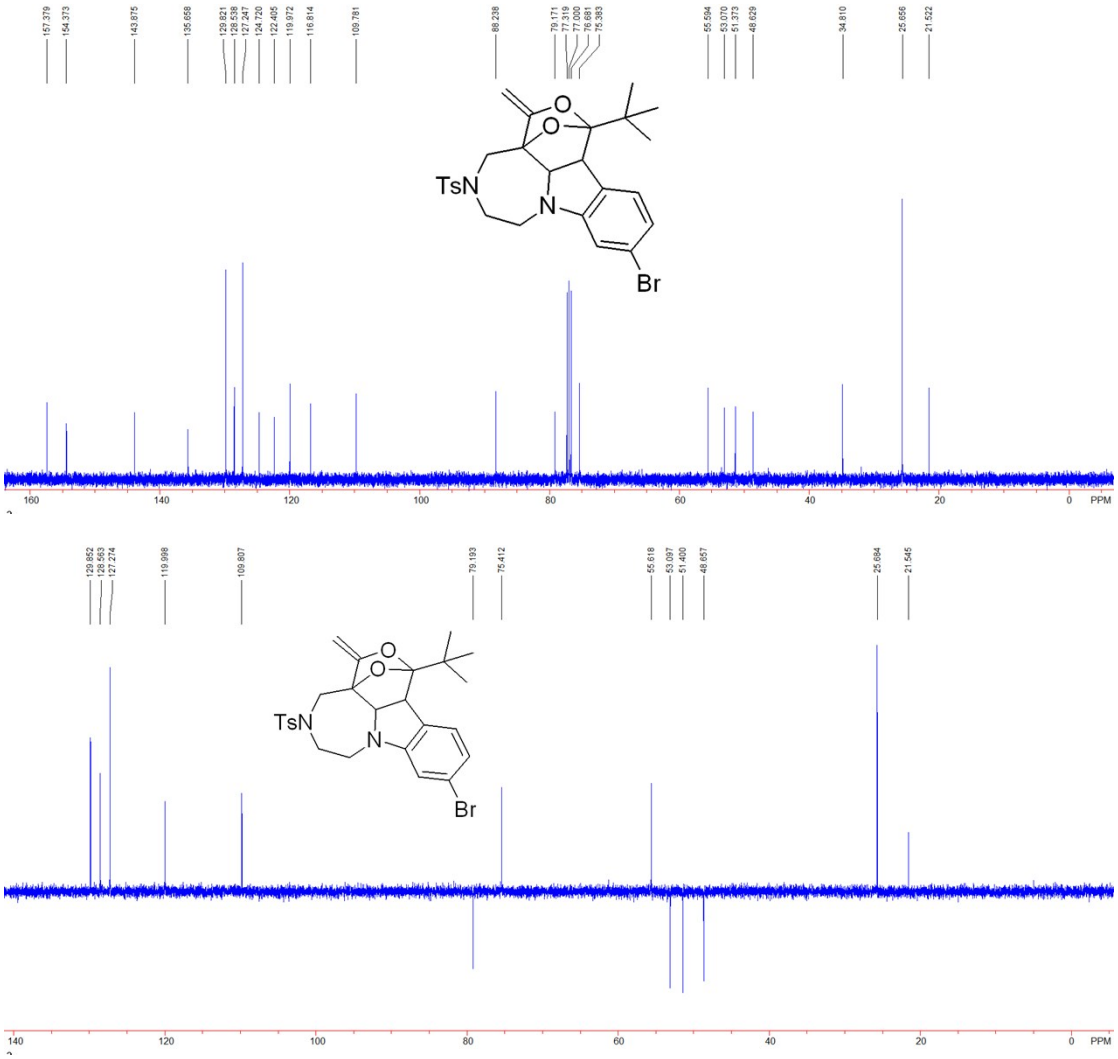
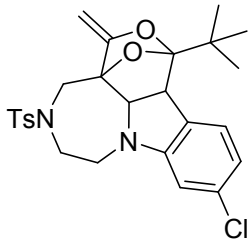


9-bromo-1-(*tert*-butyl)-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

Compound **2n**: a white solid. 41 mg, 70% yield. m.p. 183-185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (s, 9H), 2.42 (s, 3H), 2.96-3.02 (m, 1H), 3.06-3.12 (m, 1H), 3.44-3.53 (m, 2H), 3.90 (dt, J = 13.2, 3.2 Hz, 1H), 3.96 (d, J = 8.0 Hz, 1H), 4.27-4.31 (m, 3H), 4.66 (d, J = 2.8 Hz, 1H), 6.31 (s, 1H), 6.71 (dd, J = 8.0, 1.2 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 25.7, 34.8, 48.6, 51.4, 53.1, 55.6, 75.4, 79.2, 88.2, 109.8, 116.8, 120.0, 122.4, 124.7, 127.2, 128.5, 129.8, 135.7, 143.9, 154.4, 157.4. IR (neat) ν 2974, 2927, 1689, 1597, 1484, 1431, 1367, 1334, 1237, 1158, 1124, 993, 948, 904, 853, 816, 732, 661 cm^{-1}; HRMS (ESI) calcd for [$C_{26}H_{29}BrN_2O_4S$+H] requires 545.1104, found 545.1105 [M^++H].



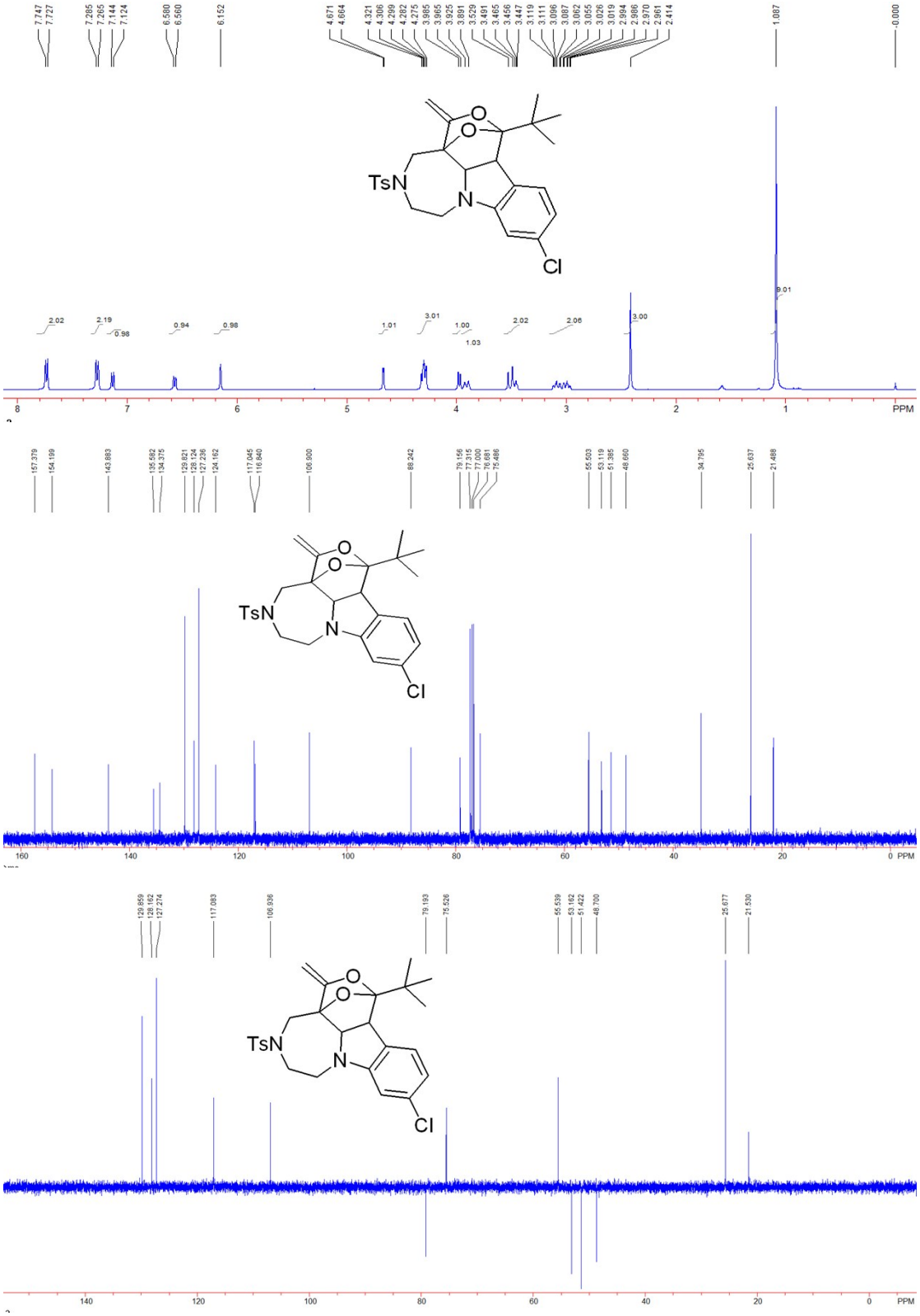


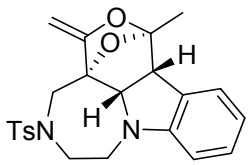


1-(*tert*-butyl)-9-chloro-3-methylene-5-tosyl-3a[1],4,5,6,7,11b-hexahydro-1*H*,3*H*-2,12-dioxa-5,7a-diaza-1,3a-methanocyclohepta[*jk*]fluorine

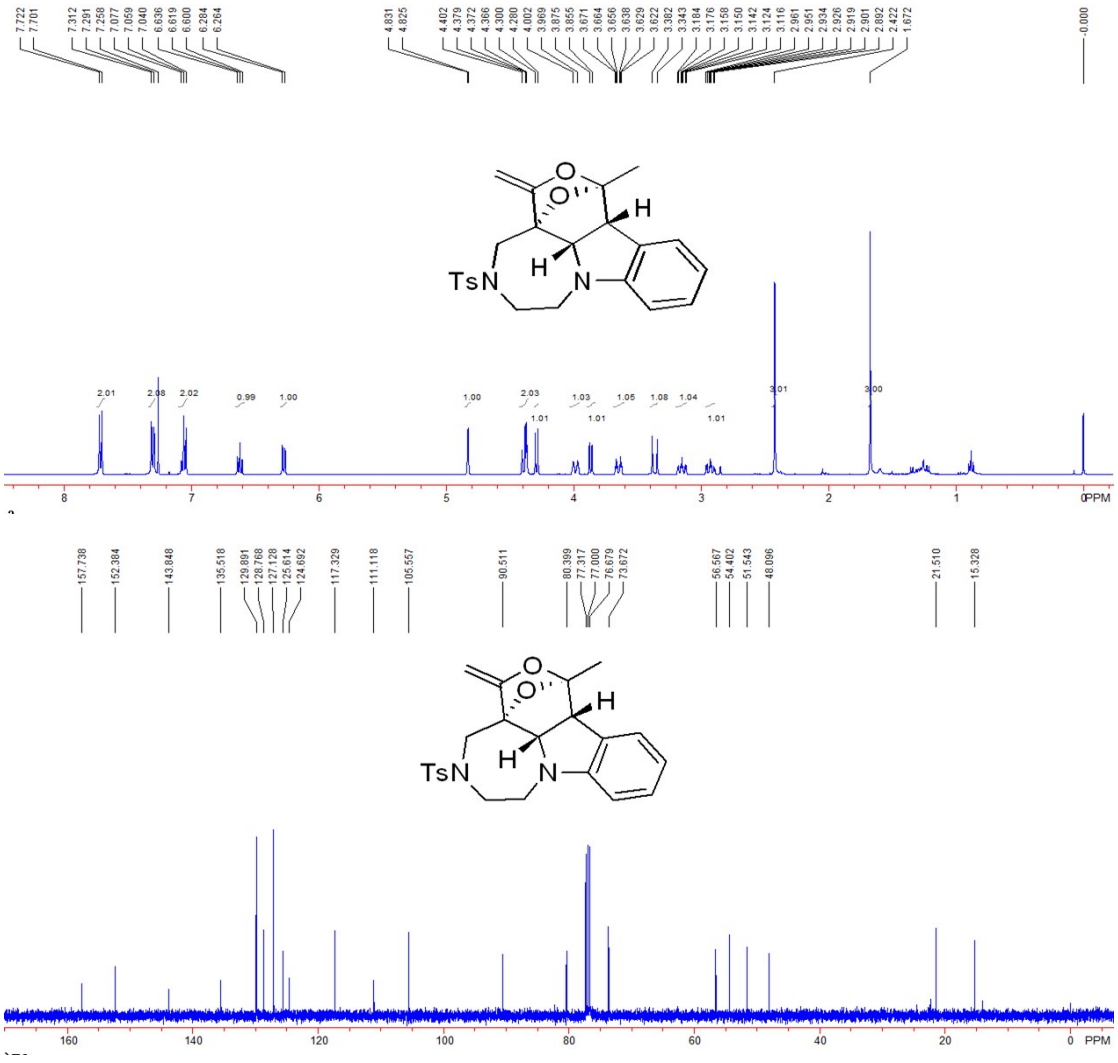
Compound **2o**: a white solid. 39 mg, 74% yield. m.p. 196-198 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (s, 9H), 2.41 (s, 3H), 2.96-3.12 (m, 2H), 3.45-3.53 (m, 2H), 3.91 (d, J = 13.6 Hz, 1H), 3.98 (d, J = 8.0 Hz, 1H), 4.28-4.32 (m, 3H), 4.67 (d, J = 2.8 Hz, 1H), 6.15 (s, 1H), 6.57 (d, J = 8.0, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 25.6, 34.8, 48.7, 51.4, 53.1, 55.5, 75.5, 79.2, 88.2, 106.9, 116.8, 117.0, 124.2, 127.2, 128.1, 129.8, 134.4, 135.6, 143.9, 154.2, 157.4. IR (neat) ν 2971, 2930, 2890, 2842,

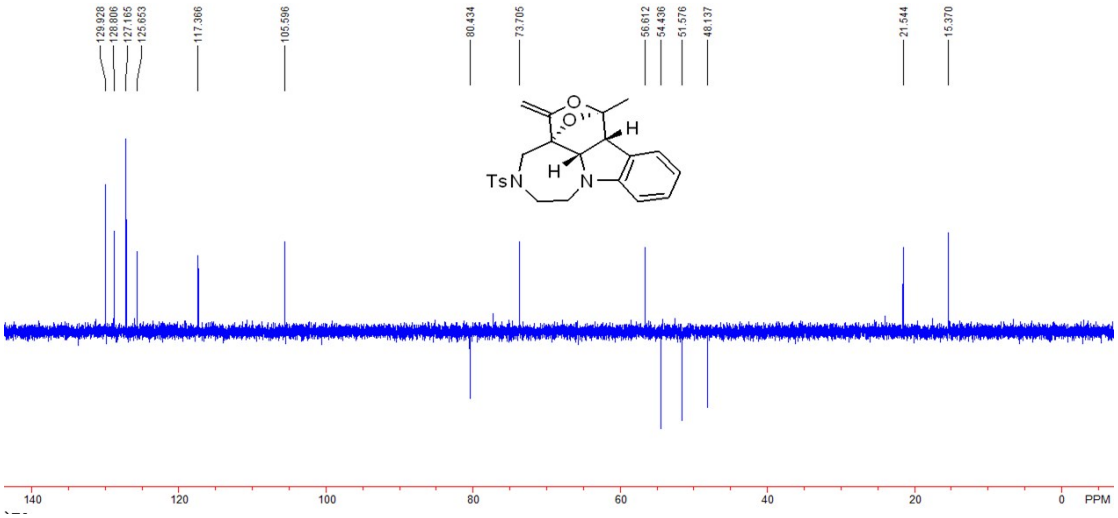
1689, 1601, 1482, 1440, 1363, 1334, 1299, 1244, 1162, 1122, 1088, 1019, 993, 888, 849, 819, 729, 659 cm^{-1}; HRMS (ESI) calcd for [$C_{26}H_{29}ClN_2O_4S$+H] requires 501.1609, found 501.1613 [M^++H].

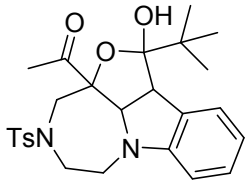




Compound **2r**: a white solid. 37 mg, 79% yield. m.p. 155-157 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.67 (s, 3H), 2.42 (s, 3H), 2.89-2.96 (m, 1H), 3.12-3.18 (m, 1H), 3.36 (d, J = 15.2 Hz, 1H), 3.65 (dt, J = 13.2, 3.2 Hz, 1H), 3.87 (d, J = 8.0 Hz, 1H), 3.99 (d, J = 13.2 Hz, 1H), 4.29 (d, J = 8.0 Hz, 1H), 4.37-4.40 (m, 2H), 4.83 (d, J = 2.8 Hz, 1H), 6.27 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 7.04-7.08 (m, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 21.5, 48.1, 51.5, 54.4, 56.6, 73.7, 80.4, 90.5, 105.6, 111.1, 117.3, 124.7, 125.6, 127.1, 128.8, 129.9, 135.5, 143.9, 152.4, 157.7. IR (neat) ν 2923, 2846, 1607, 1490, 1401, 1329, 1244, 1159, 1129, 1089, 986, 952, 911, 834, 814, 730, 703, 676 cm^{-1}. HRMS (ESI) calcd for [$C_{23}H_{24}N_2O_4S$+H] requires 425.1530, found 425.1527 [M^++H].



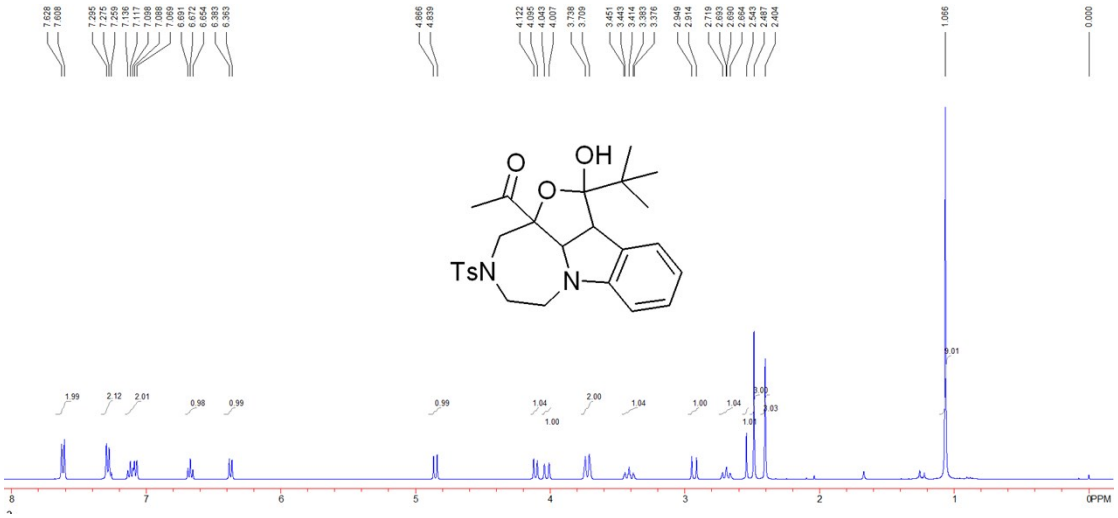


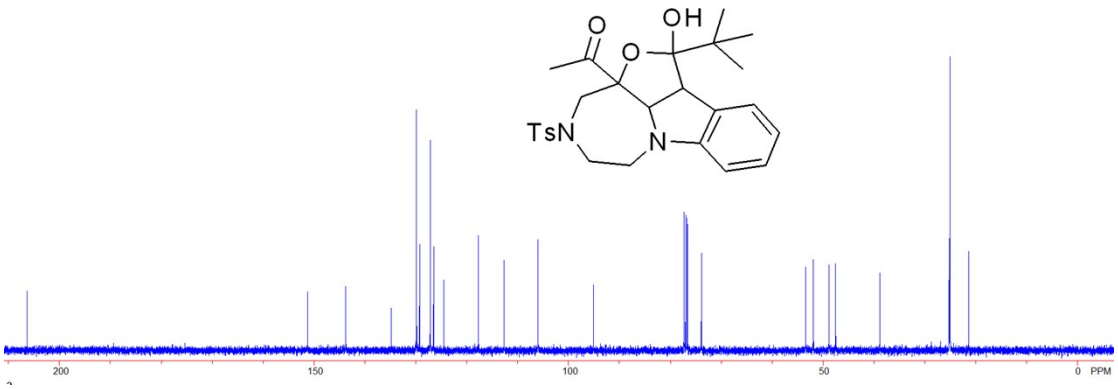


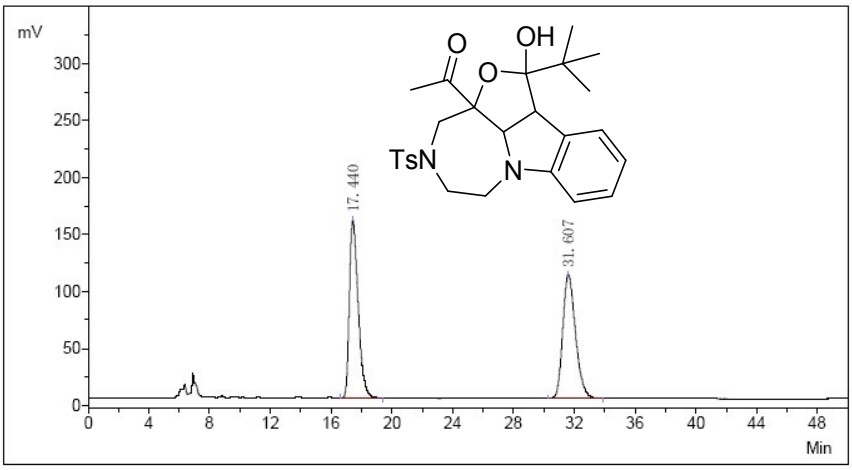
1-(1-(*tert*-butyl)-1-hydroxy-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3a**: a white solid. 42 mg, 86% yield. m.p. 228-230 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 2.40 (s, 3H), 2.49 (s, 3H), 2.54 (s, 1H), 2.69 (dd, J = 11.6, 10.4 Hz, 1H), 2.93 (d, J = 14.0 Hz, 1H), 3.38-3.45 (m, 1H), 3.72 (d, J = 11.6 Hz, 2H), 4.03 (d, J = 14.0 Hz, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.85 (d, J = 10.8 Hz, 1H), 6.37 (d, J = 8.0 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 7.07-7.14 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.1, 25.3, 38.9, 47.6, 48.8, 51.9, 53.4, 73.9, 95.1, 106.0, 112.7, 117.7, 124.5, 126.5, 127.2, 129.2, 129.9, 134.8, 143.8, 151.3, 206.4. IR (neat) ν 3538, 2974, 2905, 1718, 1605, 1489, 1334, 1208, 1163, 1107, 1070, 1037, 1006, 909, 813, 736, 720, 666 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{32}N_2O_5S$-H_2O+H] requires 467.1999, found 467.1998 [M^+-H_2O+H].

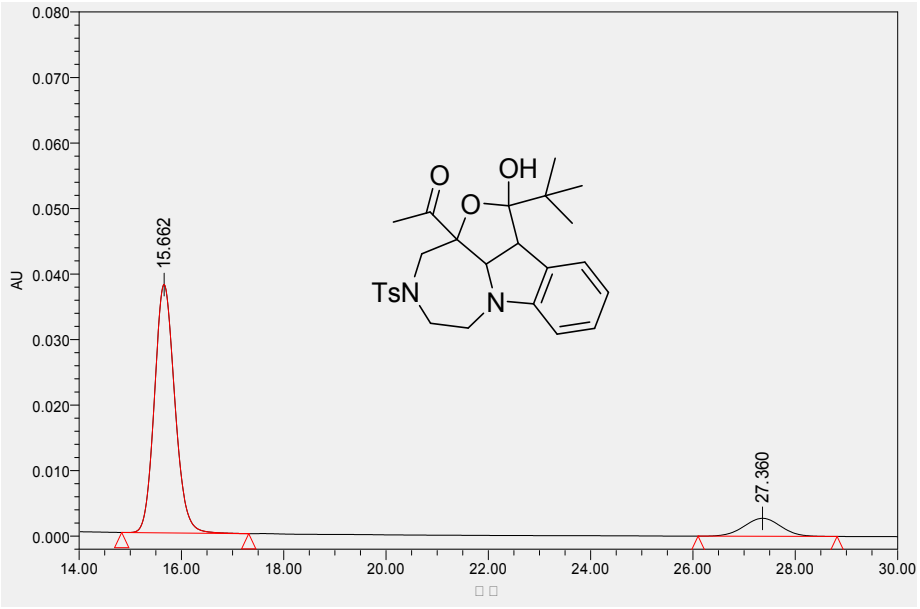
3a: a white solid. 35 mg, 72% yield. m.p. 212-214 °C. $[\alpha]^{20}_D$ = +9.2 (c 0.50, CH_2Cl_2) (77% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 15.7 min, t_{minor} = 27.4 min.







No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	17.440	156533.3	6268951.7	49.6071
2	2	Unknown	31.607	109030.6	6368242.8	50.3929
Total				265563.9	12637194.5	100.0000



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1	15.662	1049944	88.33	37938
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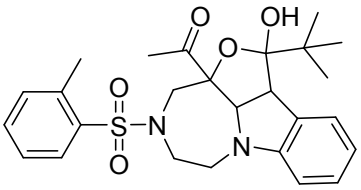
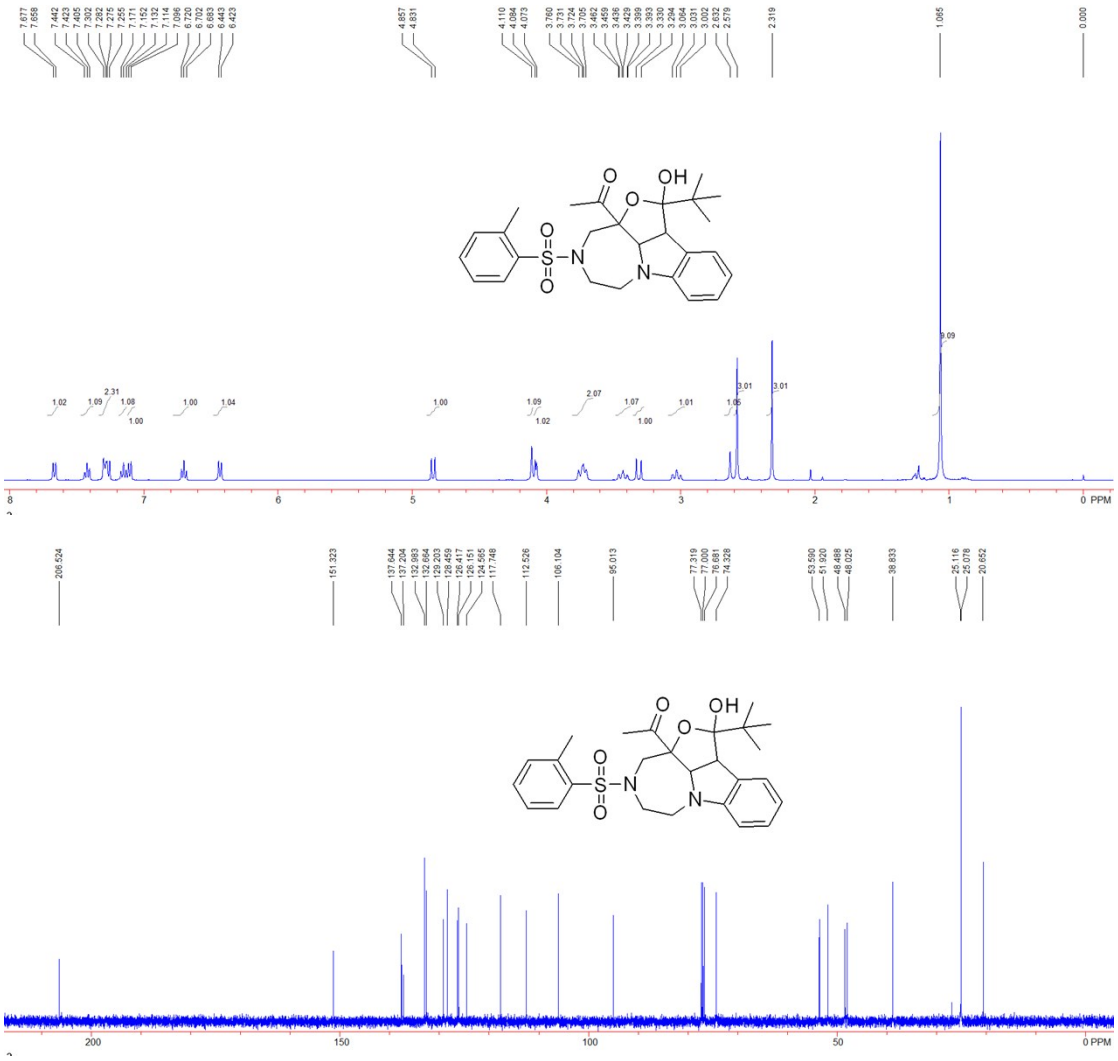


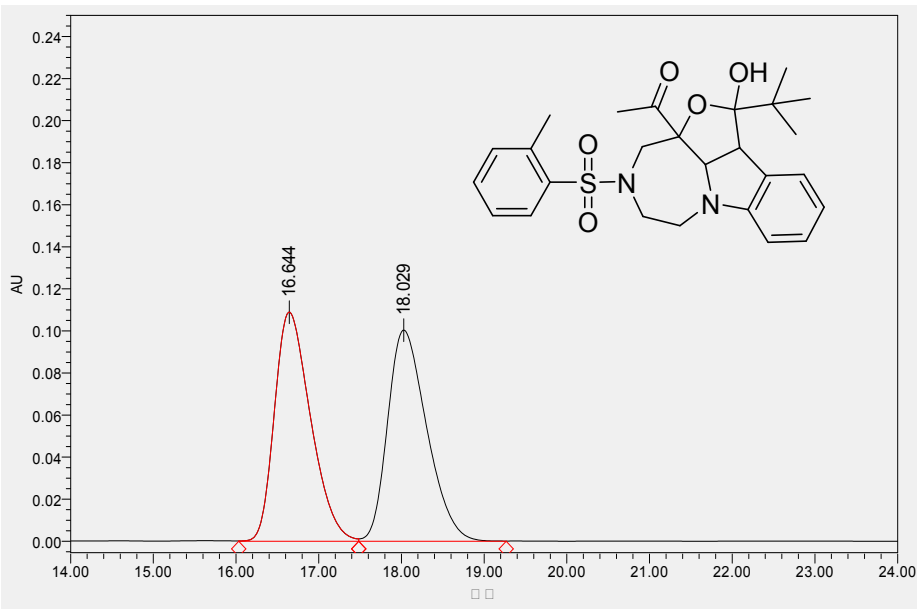
1-(1-(*tert*-butyl)-1-hydroxy-4-(*o*-tolylsulfonyl)-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3b**: a white solid. 82 mg, 82% yield. m.p. 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 2.32 (s, 3H), 2.58 (s, 3H), 2.63 (s, 1H), 3.03 (t, J = 11.6 Hz, 1H), 3.31 (d, J = 14.4 Hz, 1H) 3.39-3.46 (m, 1H), 3.71-3.76 (m, 2H), 4.08 (d, J = 4.4 Hz, 1H), 4.11 (s, 1H), 4.84 (d, J = 10.4 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.26-7.30 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 25.08, 25.12, 38.8, 48.0, 48.5, 51.9, 53.6, 74.3, 95.0, 106.1, 112.5, 117.7, 124.6, 126.2, 126.4, 128.5, 129.2, 132.7, 133.0, 137.2, 137.6, 151.3, 206.5. IR (neat) ν 3531, 2960, 2905, 1715, 1601, 1484, 1365, 1324, 1206, 1157, 1130, 1043, 1005, 949, 906, 804, 736, 723 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{32}N_2O_5S$+H] requires 485.2105, found 485.2101 [M^++H].

3b: a white solid. 14 mg, 30% yield. m.p. 84-86 °C. $[\alpha]^{20}_{D}$ = -15.1 (c 0.15, CH_2Cl_2) (74% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 50/50, 0.5 mL/min, 254 nm, t_{major} = 18.2 min,

t_{minor} = 16.9 min.





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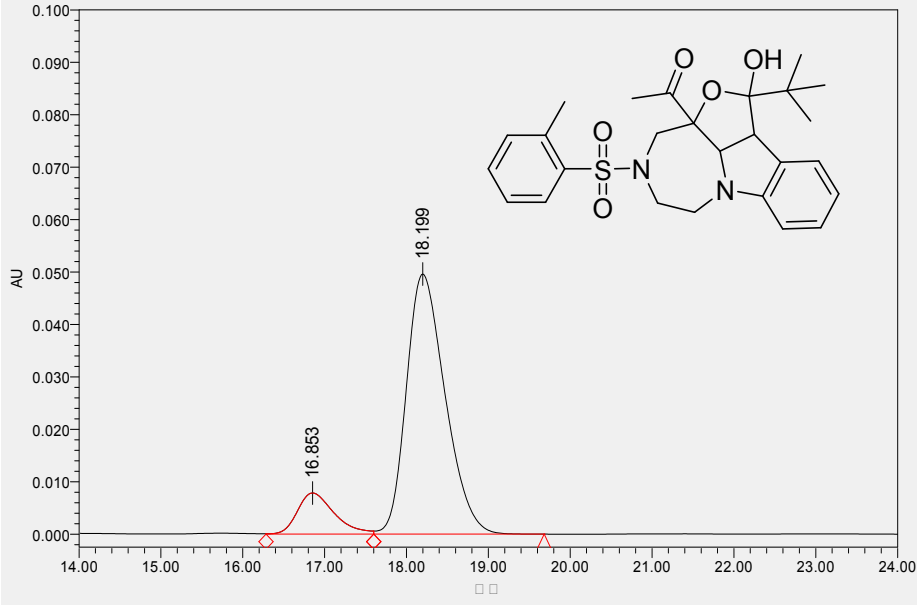
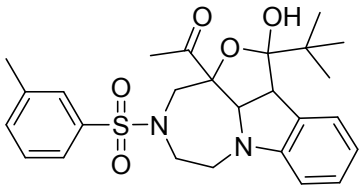
1	16.644	3314552	50.07	109017

2	18.029	3305328	49.93	100449



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	16.853	244157	13.01	7837
2	18.199	1632014	86.99	49608

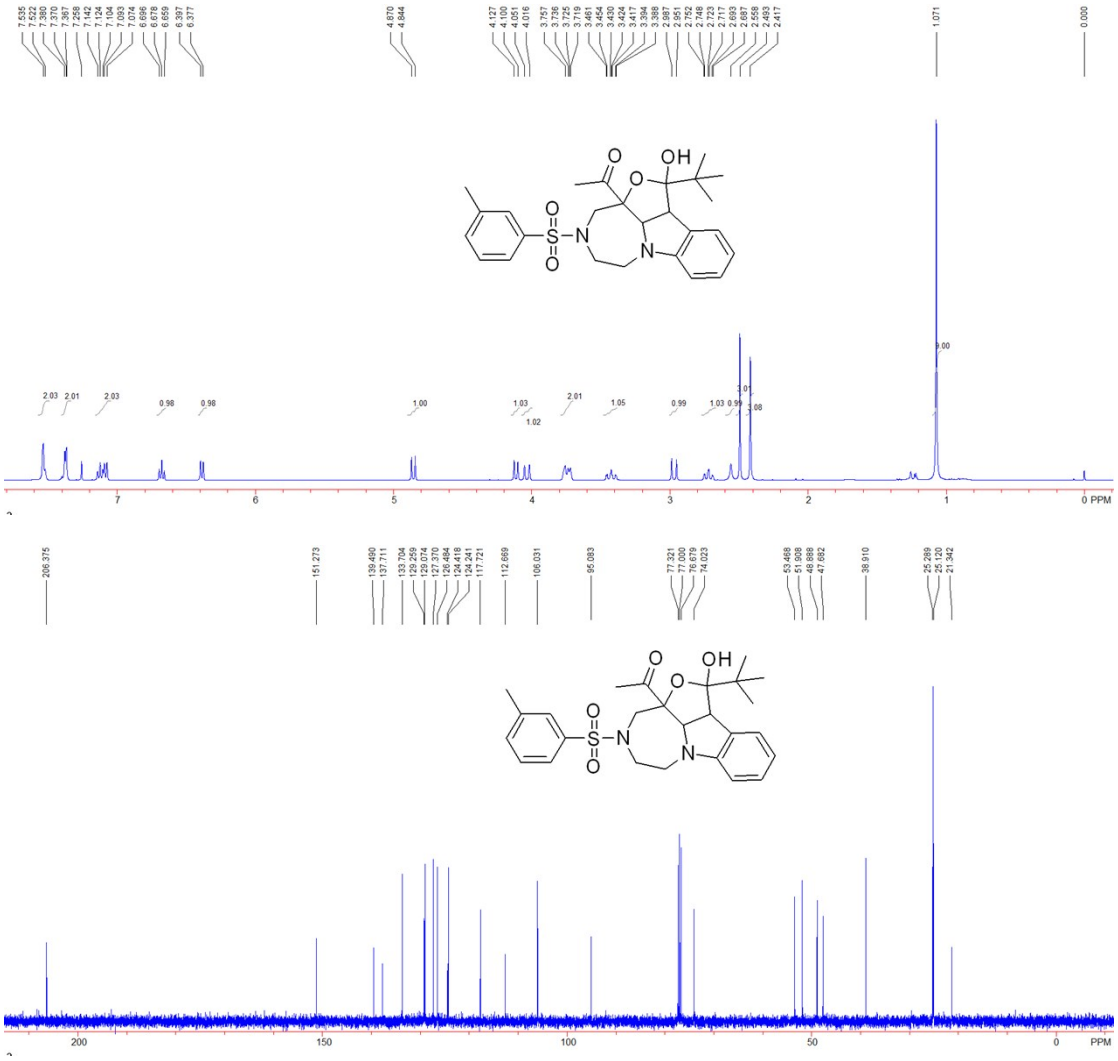


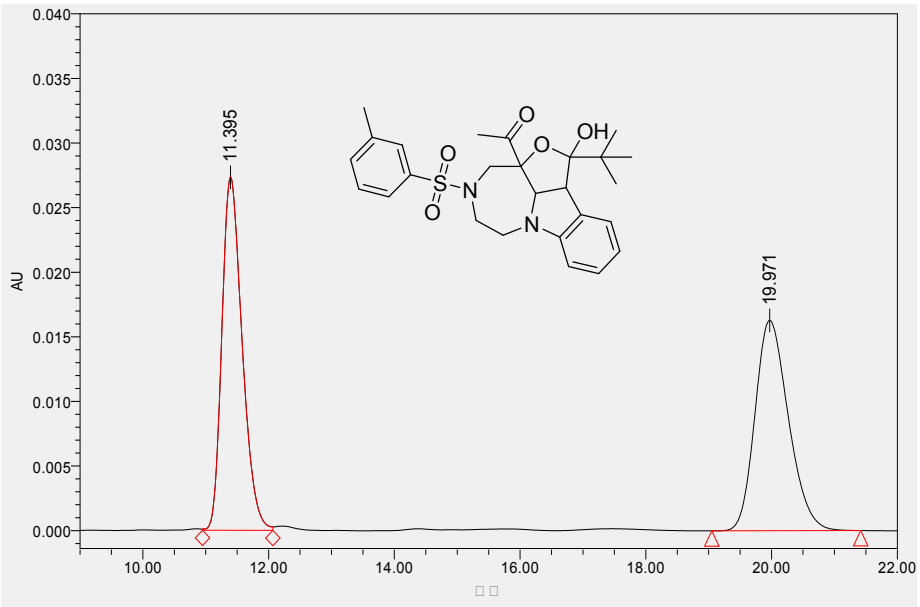
1-(1-(*tert*-butyl)-1-hydroxy-4-(*m*-tolylsulfonyl)-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3c**: a white solid. 46 mg, 87% yield. m.p. 208-210 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 2.42 (s, 3H), 2.49 (s, 3H), 2.56 (s, 1H), 2.72 (td, J = 12.0, 2.0 Hz, 1H), 2.97 (d, J = 14.4 Hz, 1H) 3.42 (td, J = 12.0, 2.4 Hz, 1H), 3.72-3.76 (m, 2H), 4.03 (d, J = 14.0 Hz, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.86 (d, J = 10.4 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 6.68 (t, J = 7.6 Hz, 1H), 7.07-7.14 (m, 2H), 7.37-7.38 (m, 2H), 7.52-7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 25.1, 25.3, 38.9, 47.7, 48.9, 51.9, 53.4, 74.0, 95.1, 106.0, 112.7, 117.7, 124.2, 124.4, 126.5, 127.4, 129.1, 129.3, 133.7, 137.7, 139.5, 151.3, 206.4. IR (neat) ν 3531, 2956, 2916, 1718, 1607, 1489, 1338, 1211, 1154, 1047, 1027, 1007, 910, 738, 689 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{32}N_2O_5S$-H_2O+H] requires 467.1999, found 467.1999 [M^+-H_2O+H].

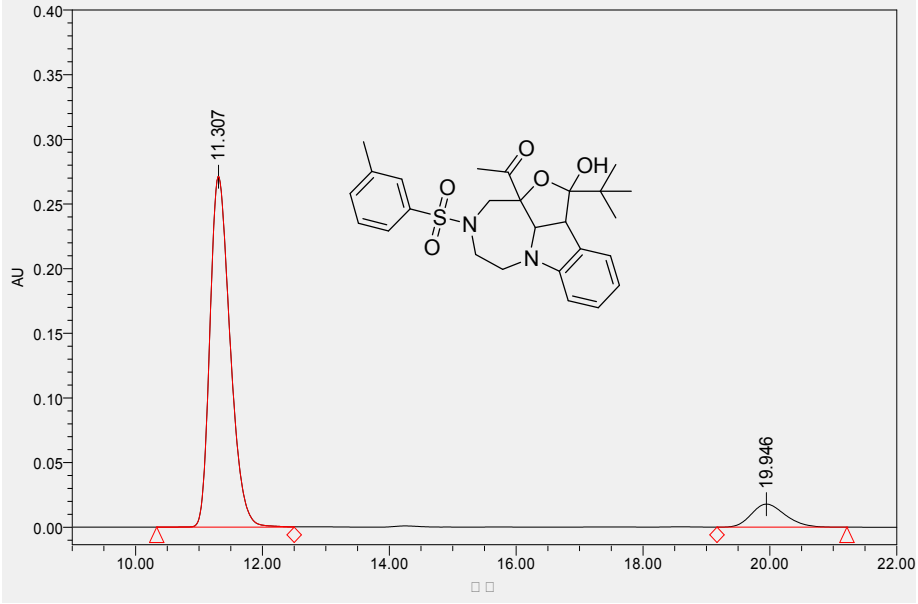
3c: a white solid. 29 mg, 60% yield. m.p. 110-113 °C. $[\alpha]^{20}_D$ = +4.9 (c 0.50, CH_2Cl_2) (80% ee).

HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 50/50, 0.5 mL/min, 254 nm, t_{major} = 11.3 min, t_{minor} = 19.9 min.

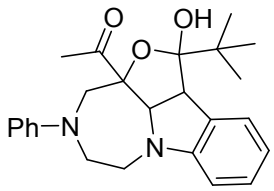




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	11.395	613049	50.45	27351
2	19.971	602118	49.55	16290



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	11.307	5995822	90.05	271583
2	19.946	662201	9.95	17834

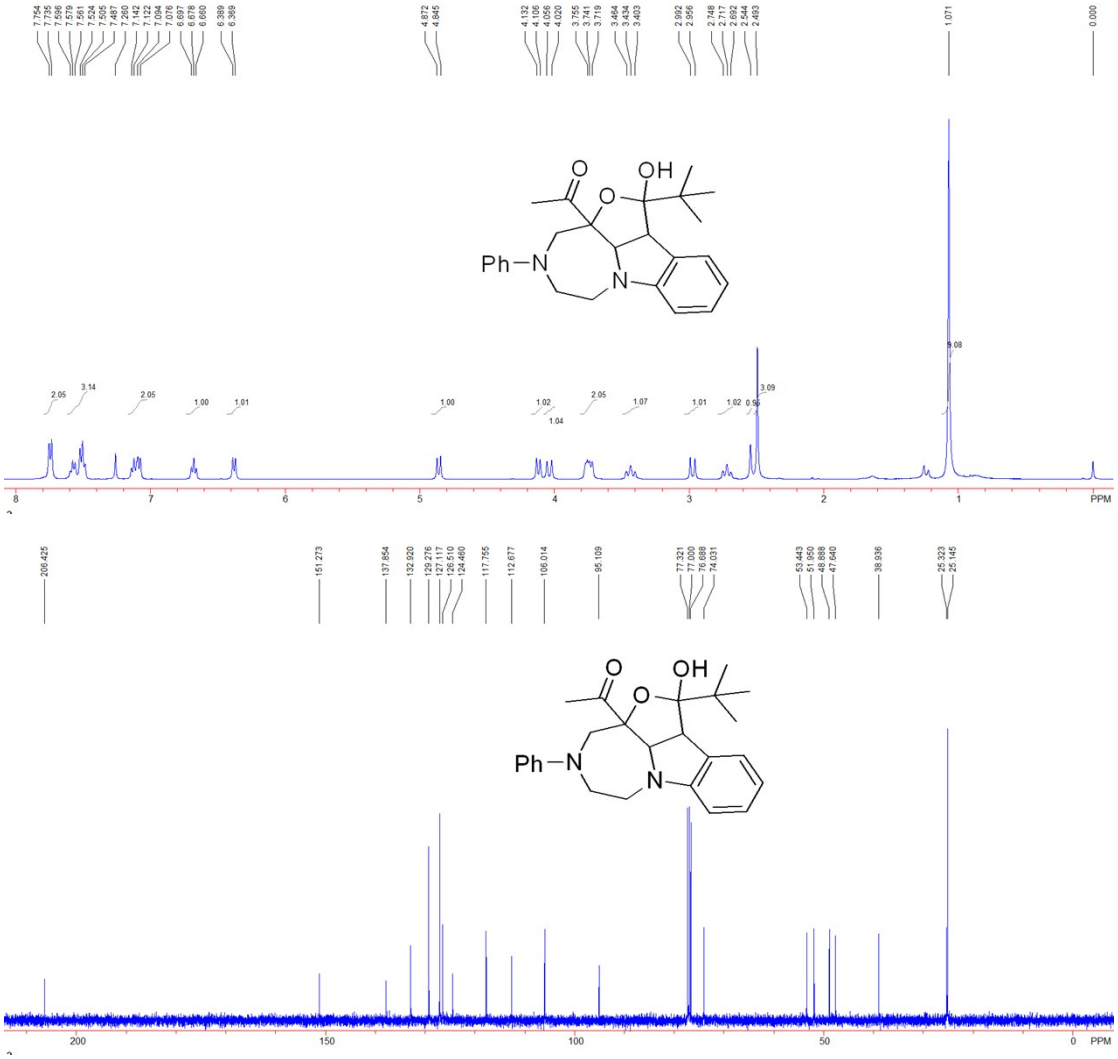


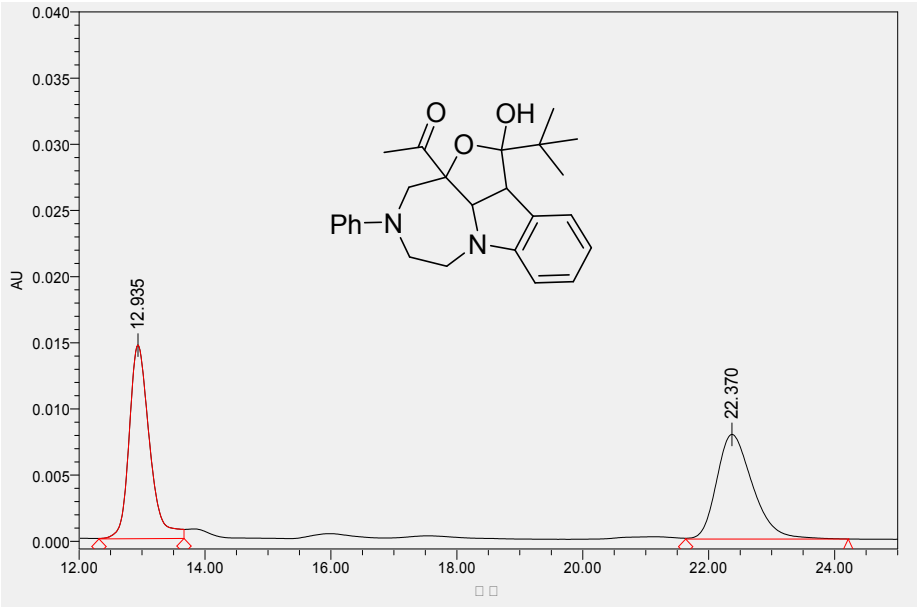
1-(1-(*tert*-butyl)-1-hydroxy-4-phenyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3d**: a white solid. 36 mg, 71% yield. m.p. 270-272 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 2.49 (s, 3H), 2.54 (s, 1H), 2.72 (t, J = 12.4 Hz, 1H), 2.97 (d, J = 14.4 Hz, 1H) 3.43 (t, J = 12.4 Hz, 1H), 3.72-3.76 (m, 2H), 4.04 (d, J = 14.4 Hz, 1H), 4.12 (d, J = 10.4 Hz, 1H), 4.86 (d, J = 10.8 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 6.68 (t, J = 7.2 Hz, 1H), 7.08-7.14 (m, 2H), 7.49-7.60 (m, 3H), 7.75 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 25.3, 38.9, 47.6, 48.9, 52.0, 53.4, 74.0, 95.1, 106.0, 112.7, 117.8, 124.5, 126.5, 127.1, 129.3, 132.9, 137.9, 151.3, 206.4. IR (neat) ν 3516, 2974, 2908, 1717, 1605, 1497, 1448, 1332, 1166, 1070, 1007, 910, 747, 736, 723 cm^{-1}. HRMS (ESI) calcd for [$C_{25}H_{30}N_2O_5S$-H_2O+H] requires 453.1843, found 453.1841

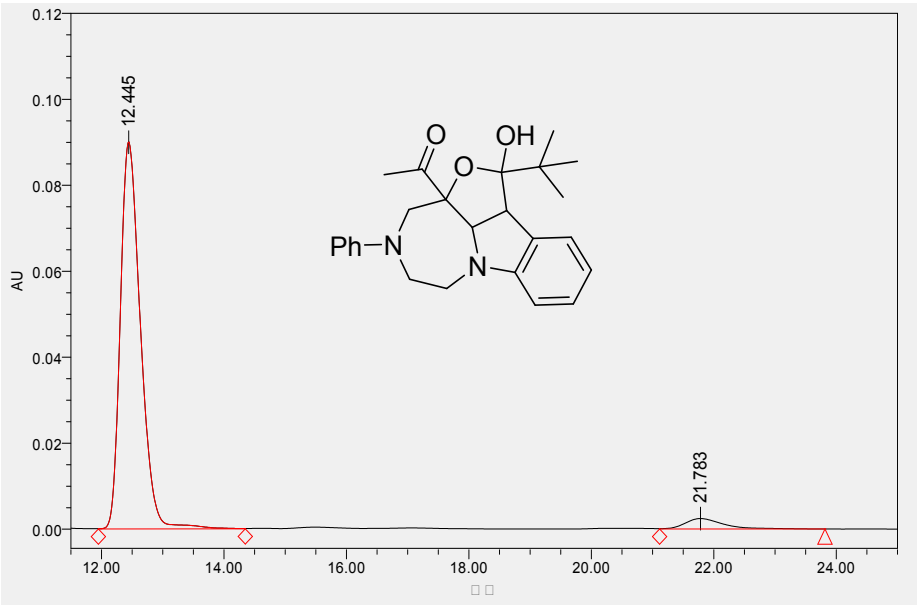
[M^+-H_2O+H].

3d: a white solid. 20 mg, 43% yield. m.p. 172-174 °C. $[\alpha]^{20}_D$ = +5.4 (c 0.50, CH_2Cl_2) (90% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 12.4 min, t_{minor} = 21.8 min.

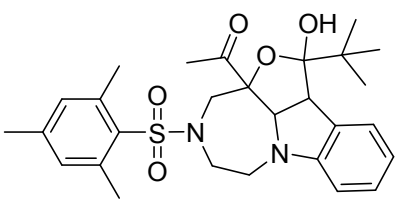




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.935	329534	51.26	14637
2	22.370	313301	48.74	7911



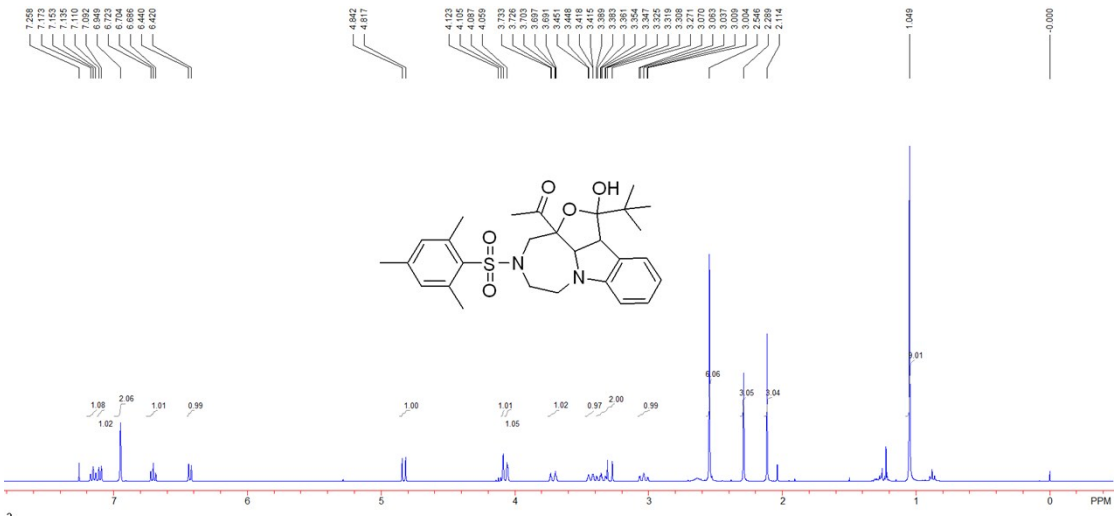
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.445	2055772	95.09	90068
2	21.783	106241	4.91	2426

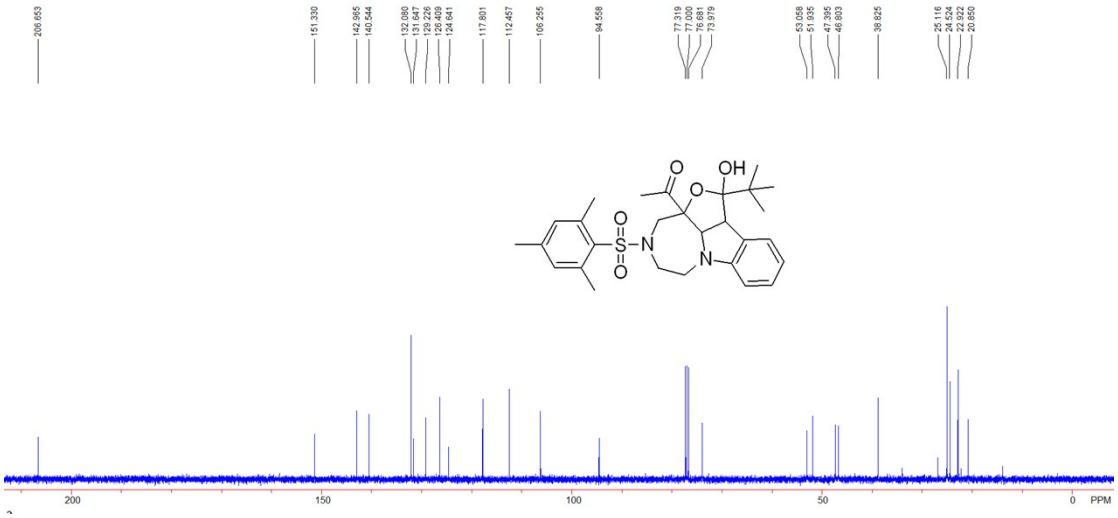


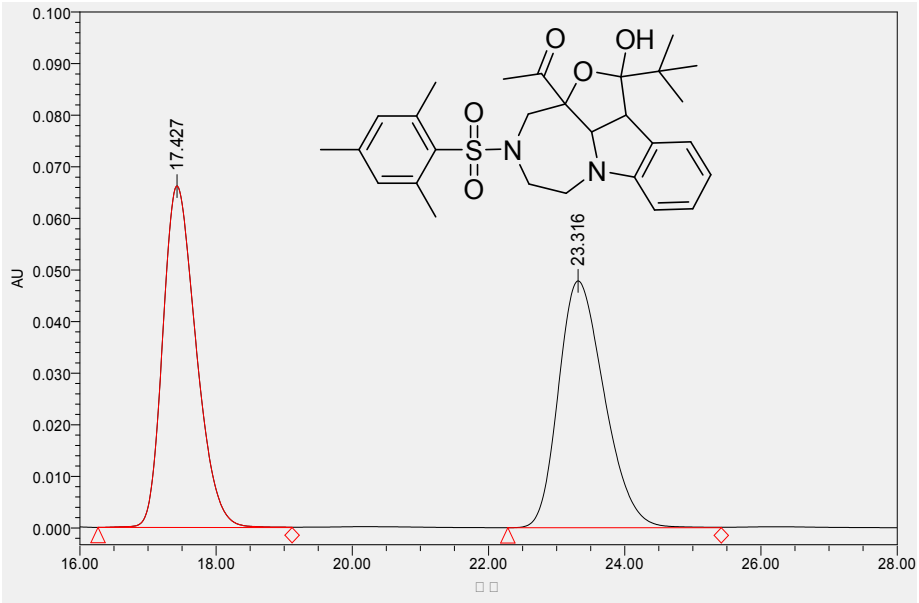
1-(1-(*tert*-butyl)-1-hydroxy-4-(mesitylsulfonyl)-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3e**: a white solid. 68 mg, 89% yield. m.p. 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.05 (s, 9H), 2.11 (s, 3H), 2.29 (s, 3H), 2.55 (s, 6H), 3.04 (td, J = 13.2, 2.0 Hz, 1H), 3.27-3.39 (m, 2H), 3.43 (dd, J = 13.2, 1.2 Hz, 1H) 3.72 (dt, J = 14.4, 2.4 Hz, 1H), 4.06 (s, 1H), 4.09 (s, 1H), 4.83 (d, J = 10.0 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 6.95 (s, 2H), 7.10 (d, J = 7.2 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 22.9, 24.5, 25.1, 38.8, 46.8, 47.4, 51.9, 53.1, 74.0, 94.6, 106.3, 112.5, 117.8, 124.6, 126.4, 129.2, 131.6, 132.1, 140.5, 143.0, 151.3, 206.7. IR (neat) ν 3527, 2952, 2912, 1718, 1601, 1488, 1364, 1320, 1206, 1152, 1047, 1003, 901, 853, 731, 673 cm^{-1}. HRMS (ESI) calcd for [$C_{28}H_{36}N_2O_5S$-H_2O+H] requires 495.2312, found 495.2312 [M^+-H_2O+H].

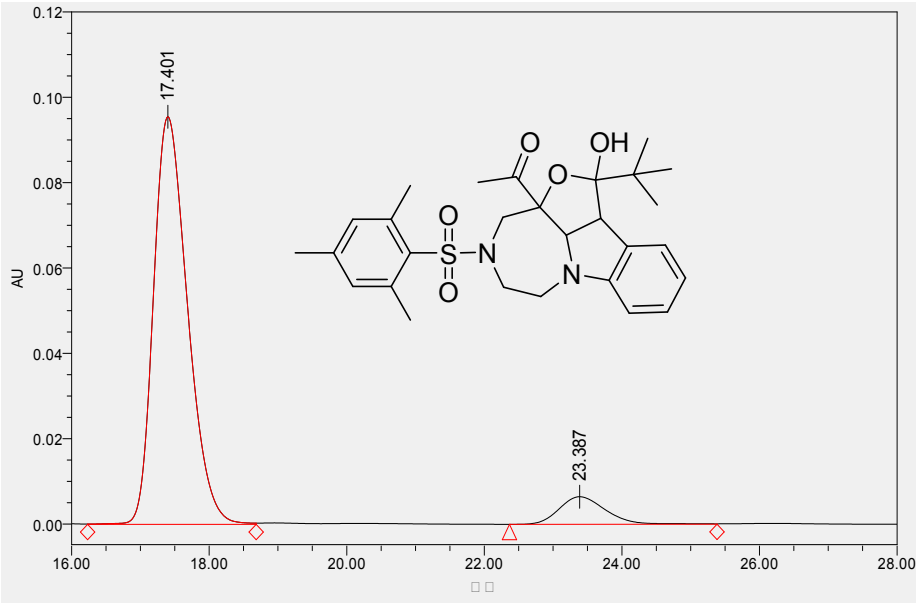
3e: a white solid. 26 mg, 51% yield. m.p. 77-79 °C. $[\alpha]^{20}_D$ = -18.5 (c 0.40, CH_2Cl_2) (83% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 50/50, 0.5 mL/min, 254 nm, t_{major} = 17.4 min, t_{minor} = 23.4 min.



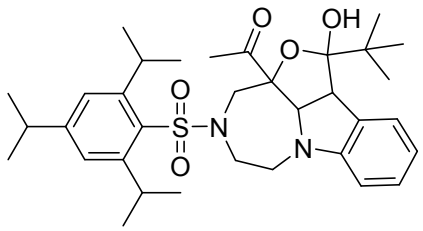




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	17.427	2247216	50.13	66213
2	23.316	2235624	49.87	47837



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	17.401	3275024	91.47	95529
2	23.387	305224	8.53	6470

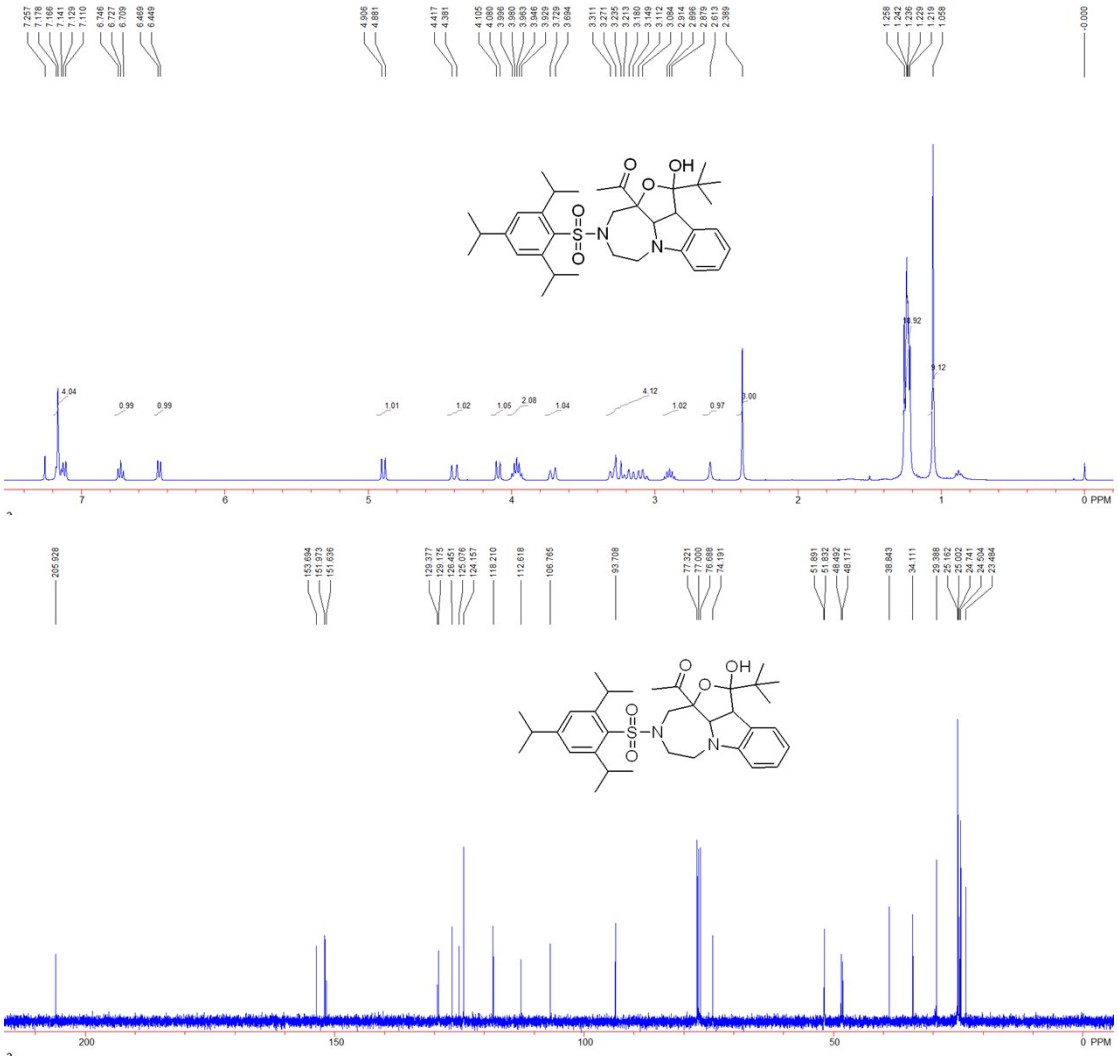


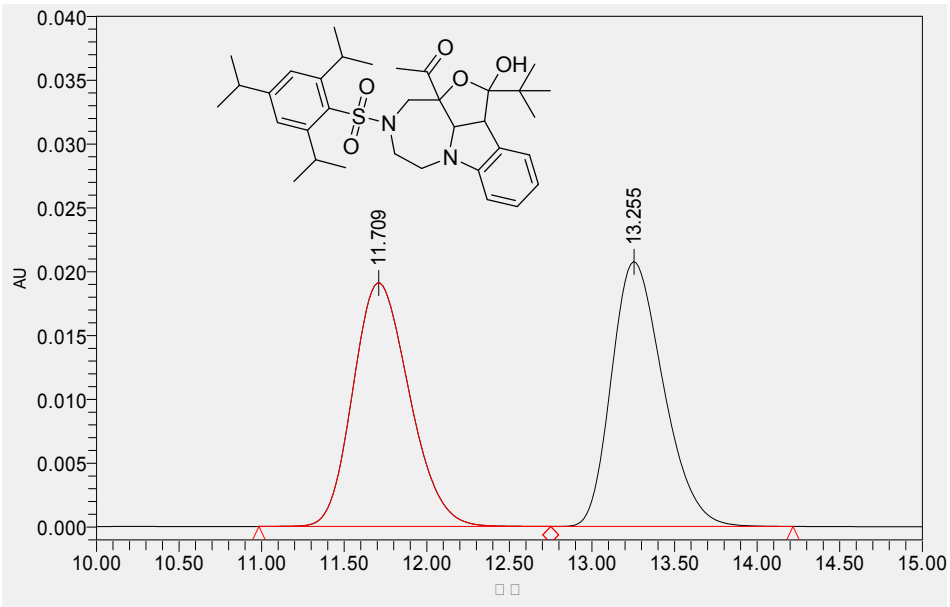
1-(1-(*tert*-butyl)-1-hydroxy-4-((2,4,6-triisopropylphenyl)sulfonyl)-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3f**: a white solid. 48 mg, 76% yield. m.p. 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 1.22-1.26 (m, 18H), 2.39 (s, 3H), 2.61 (s, 1H), 2.88-3.08 (m, 1H), 3.11-3.31 (m, 4H), 3.71 (d, J = 14.0 Hz, 1H), 3.93-4.00 (m, 2H), 4.09 (d, J = 10.0 Hz, 1H) 4.40 (d, J = 14.4 Hz, 1H), 4.89 (d, J = 10.0 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 6.73 (t, J = 7.6 Hz, 1H), 7.11-7.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.48, 24.5, 24.7, 25.0, 25.2, 29.4, 34.1, 38.8, 48.2, 48.5, 51.8, 52.0, 74.2, 93.7, 106.8, 112.6, 118.2, 124.2, 125.1, 126.5, 129.2, 129.4, 151.6, 152.0, 153.7, 205.9. IR (neat) ν 3531, 2958, 2872, 1720, 1601, 1485, 1463, 1363, 1307, 1208, 1151, 1038, 1004, 899, 743, 722, 674 cm^{-1}. HRMS (ESI) calcd for [$C_{34}H_{48}N_2O_5S$-H_2O+H] requires 579.3251, found 579.3248 [M^+-H_2O+H].

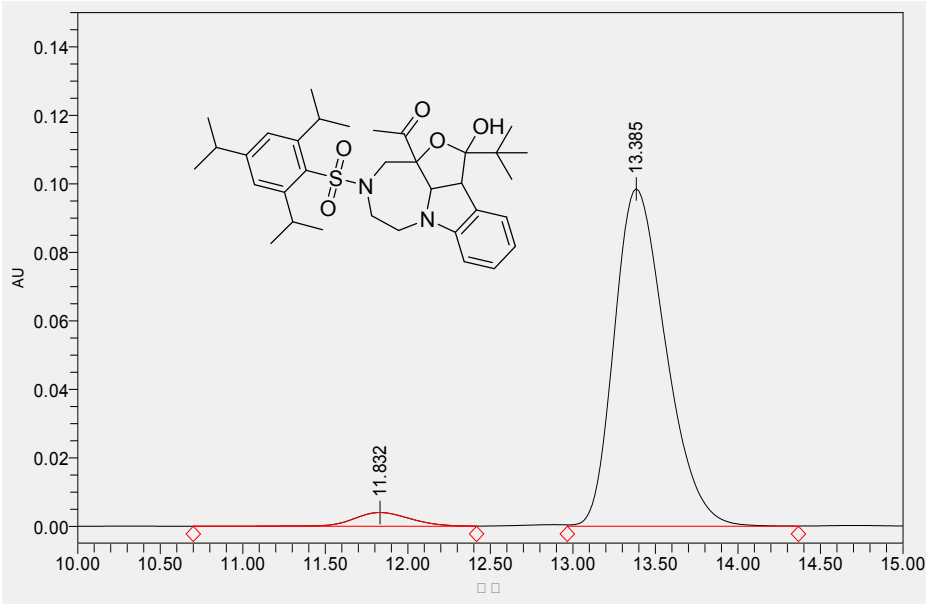
3f: a white solid. 23 mg, 40% yield. m.p. 94-96 °C. $[\alpha]^{20}_D$ = +3.6 (c 0.50, CH_2Cl_2) (91% ee). HPLC

conditions: Chiralpak AD-H, hexane/^{i}PrOH = 90/10, 0.5 mL/min, 254 nm, t_{major} = 13.4 min, t_{minor} = 11.8 min.

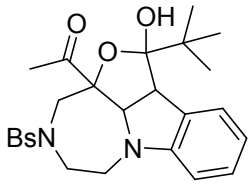




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	11.709	453546	50.06	19096
2	13.255	452536	49.94	20752



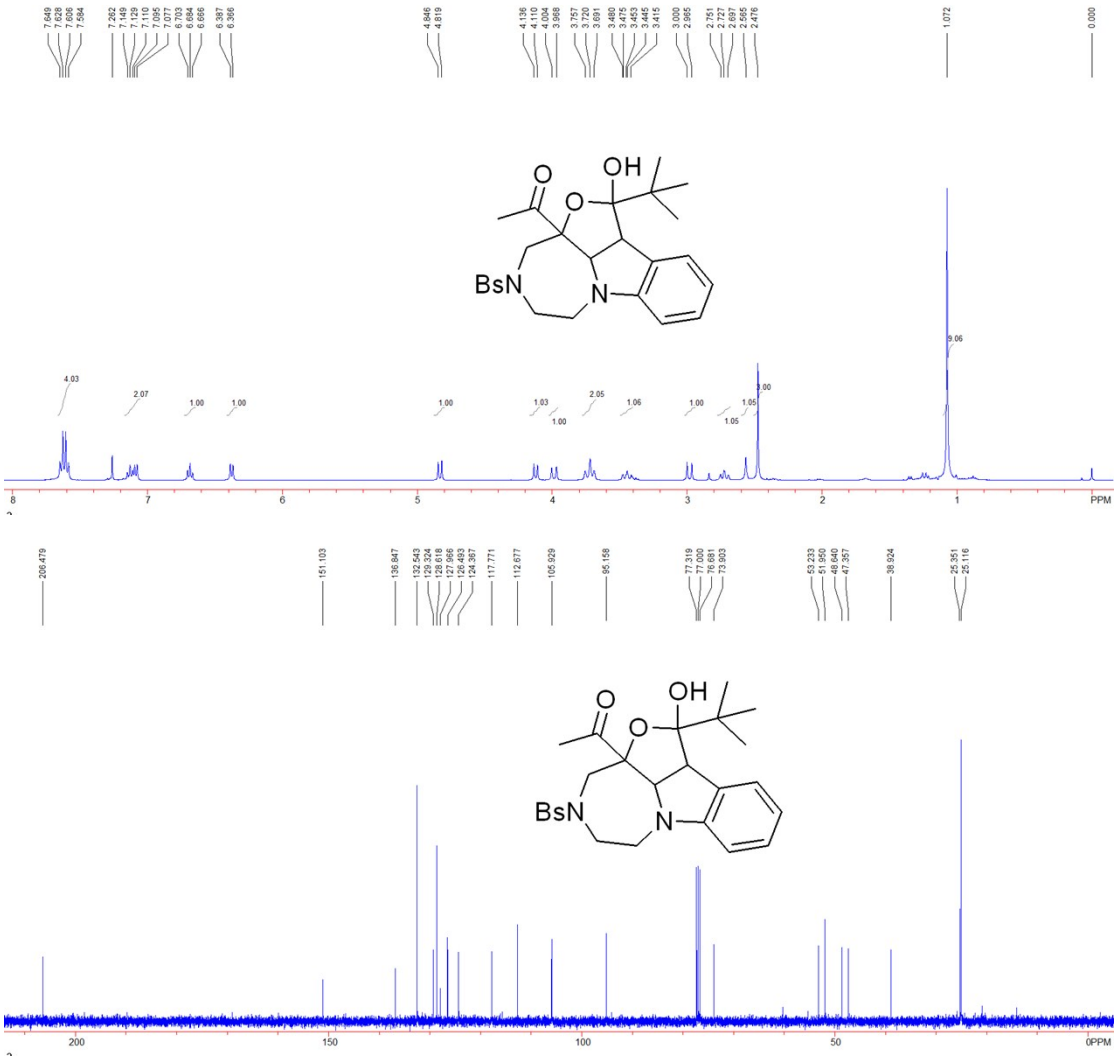
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	11.832	98116	4.38	4035
2	13.385	2142382	95.62	98568

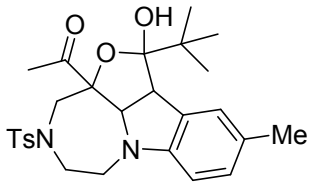


1-(4-((4-bromophenyl)sulfonyl)-1-(*tert*-butyl)-1-hydroxy-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3g**: a white solid. 47 mg, 86% yield. m.p. 237-239 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 2.48 (s, 3H), 2.57 (s, 1H), 2.73 (t, J = 12.0 Hz, 1H), 2.98 (d, J = 14.0 Hz, 1H), 3.42-3.48 (m, 1H), 3.72 (t, J = 11.6 Hz, 2H), 3.99 (d, J = 14.4 Hz, 1H), 4.12 (d, J = 10.4 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 6.68 (t, J = 7.6 Hz, 1H), 7.08-7.15 (m, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 25.4, 38.9, 47.4, 48.6, 52.0, 53.2, 73.9, 95.2, 105.9, 112.7, 117.8, 124.4, 126.5, 128.0, 128.6, 129.3, 132.5, 136.8, 151.1, 206.5. IR (neat) ν 3524, 2960, 2908, 2872, 1718, 1599, 1574, 1489, 1358, 1340, 1206, 1163, 1069, 1007, 910, 751, 734, 661 cm^{-1}. HRMS (ESI) calcd for [$C_{25}H_{29}BrN_2O_5S$-H_2O+H] requires

531.0948, found 531.0946 [M^+-H_2O+H].



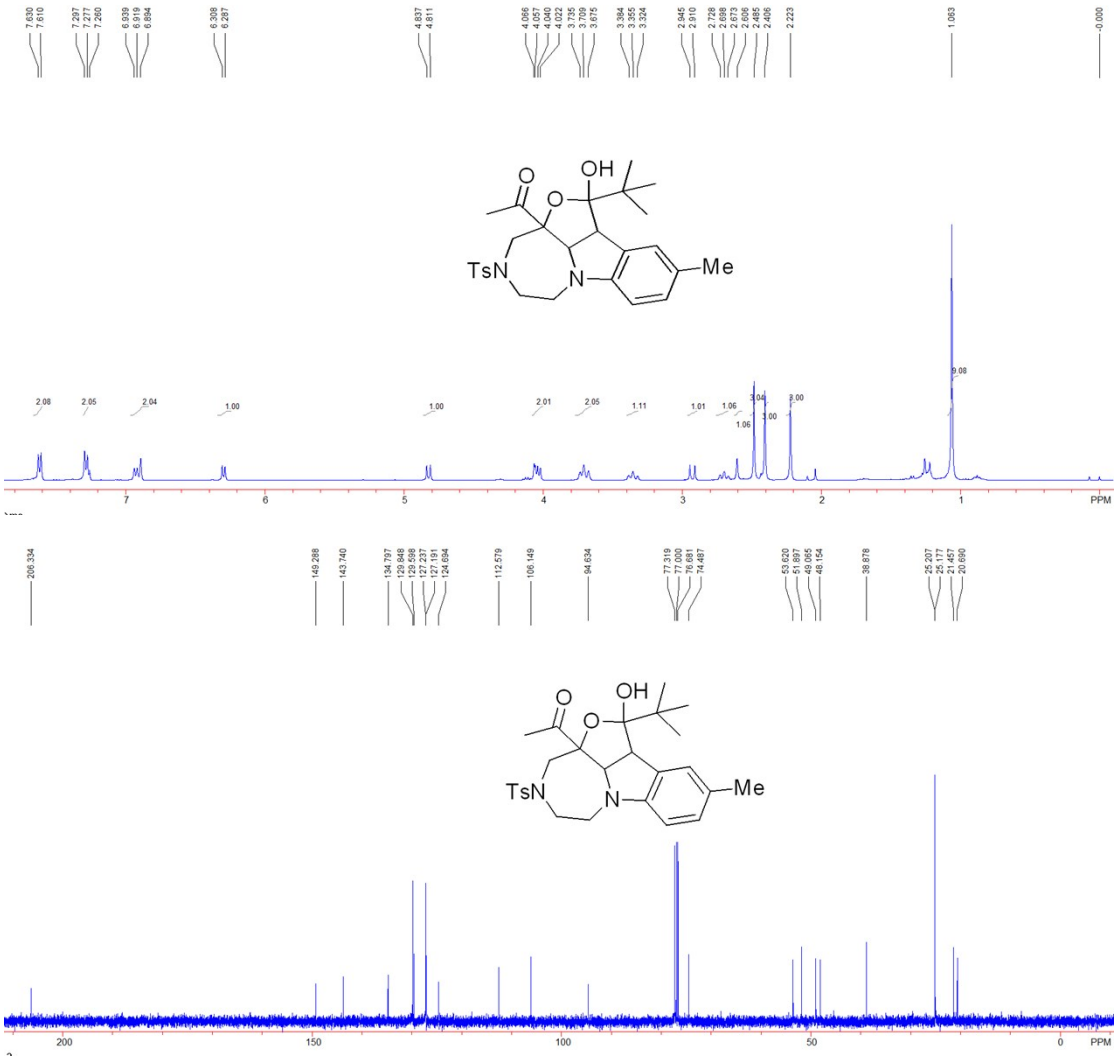


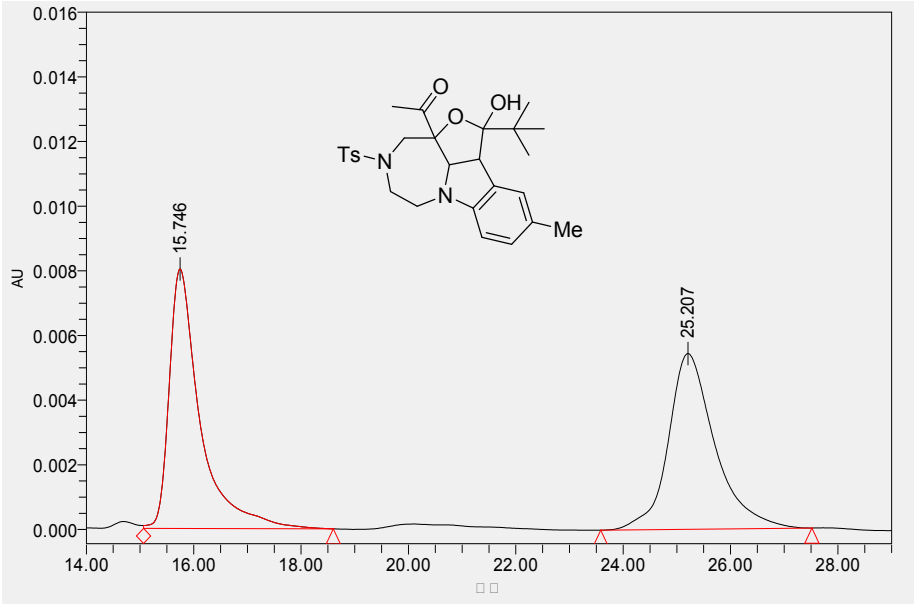
1-(1-(*tert*-butyl)-1-hydroxy-9-methyl-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3h**: a light red solid. 33 mg, 66% yield. m.p. 260-262 ^oC (dec). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.22 (s, 3H), 2.41 (s, 3H), 2.49 (s, 3H), 2.61 (s, 1H), 2.70 (t, J = 12.0 Hz, 1H), 2.93 (d, J = 14.0 Hz, 1H), 3.36 (t, J = 14.0 Hz, 1H), 3.71 (t, J = 10.4 Hz, 2H), 4.02-4.07 (m, 2H), 4.82 (d, J = 10.4 Hz, 1H), 6.30 (d, J = 8.4 Hz, 1H), 6.89-6.94 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.5, 25.18, 25.21, 38.9, 48.2, 49.1,

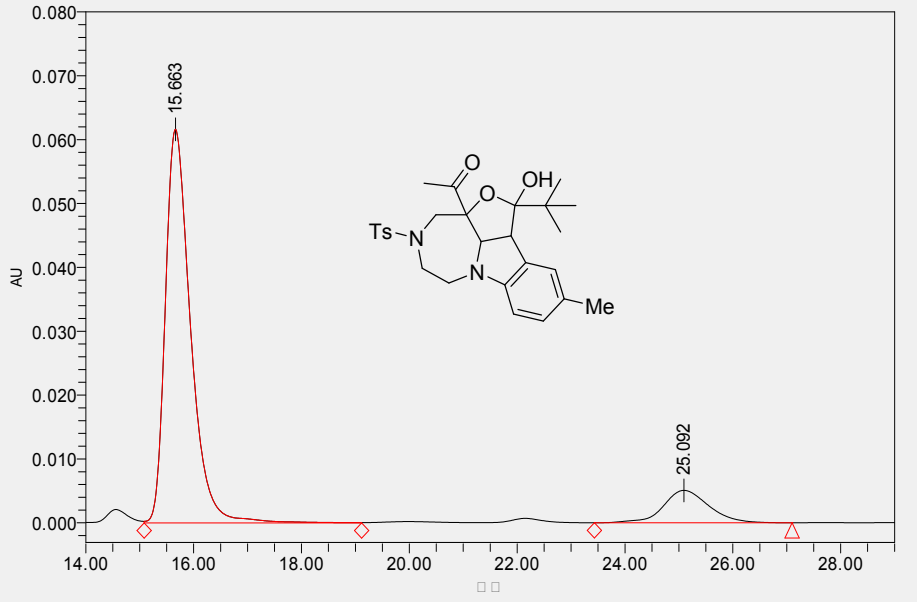
51.9, 53.6, 74.5, 94.6, 106.1, 112.6, 124.7, 127.19, 127.24, 129.6, 129.8, 134.8, 143.7, 149.3, 206.3. IR (neat) ν 3553, 3513, 2956, 2919, 2868, 1714, 1612, 1498, 1446, 1336, 1212, 1163, 1052, 1006, 992, 908, 811, 755, 738, 722, 660 cm^{-1}. HRMS (ESI) calcd for $[C_{27}H_{34}N_2O_5S+H]$ requires 499.2261, found 499.2260 $[M^+ + H]$.

3h: a white solid. 24 mg, 50% yield. m.p. 230-232 °C. $[\alpha]^{20}_D$ = +14.4 (c 0.50, CH_2Cl_2) (74% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 15.7 min, t_{minor} = 25.1 min.

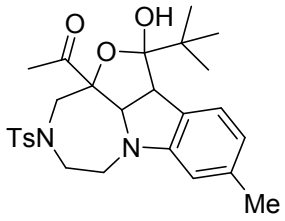




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	15.746	321569	49.50	8029
2	25.207	328006	50.50	5438



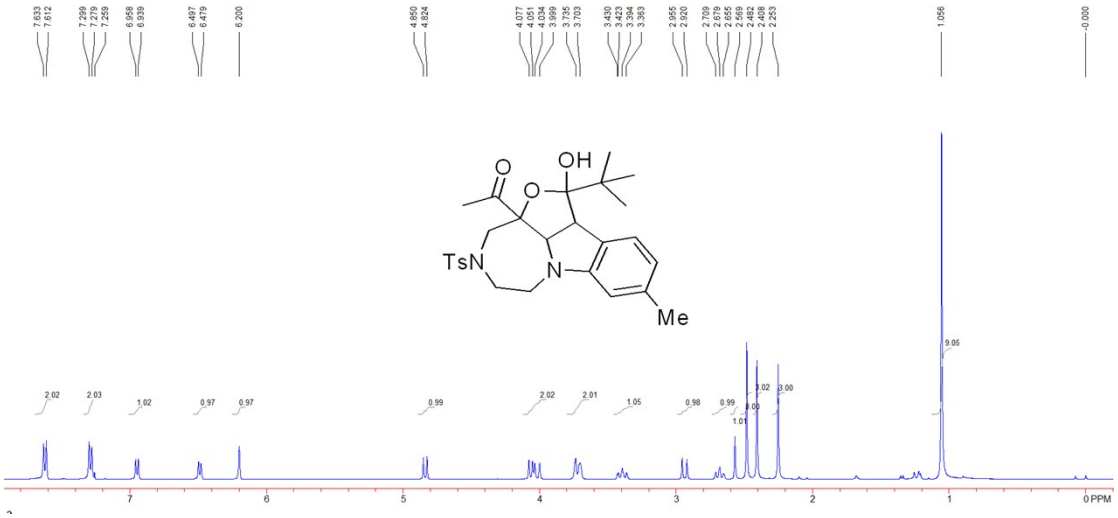
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	15.663	1998720	86.92	61647
2	25.092	300644	13.08	5080

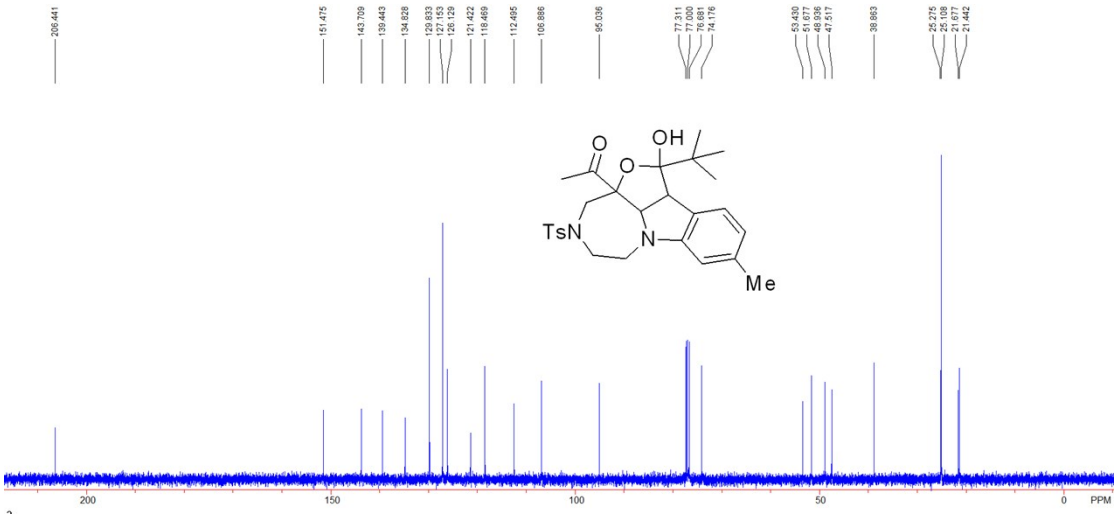


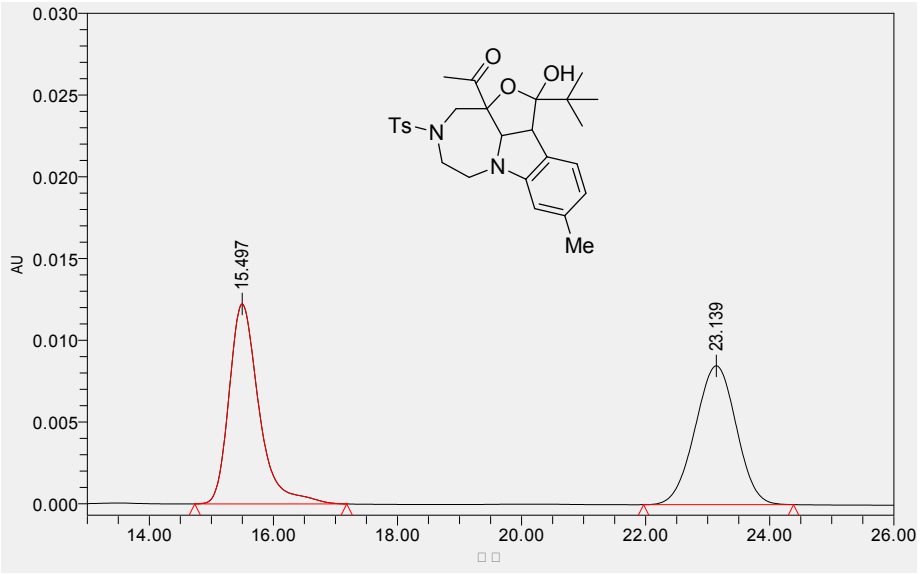
1-(1-(*tert*-butyl)-1-hydroxy-8-methyl-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3i**: a white solid. 44 mg, 77% yield. m.p. 279-281 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.25 (s, 3H), 2.41 (s, 3H), 2.48 (s, 3H), 2.57 (s, 1H), 2.68 (t, J = 12.4 Hz, 1H), 2.94 (d, J = 14.0 Hz, 1H), 3.36-3.43 (m, 1H), 3.70-3.74 (m, 2H), 4.00-4.08 (m, 2H), 4.84 (d, J = 10.4 Hz, 1H), 6.20 (s, 1H), 6.49 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.7, 25.1, 25.3, 38.9, 47.5, 48.9, 51.7, 53.4, 84.2, 95.0, 106.9, 112.5, 118.5, 121.4, 126.1, 127.2, 129.8, 134.8, 139.4, 143.7, 151.5, 206.4. IR (neat) ν 3531, 2960, 2908, 1719, 1615, 1498, 1433, 1352, 1337, 1164, 1105, 1071, 1047, 1012, 904, 815, 752, 723 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{34}N_2O_5S$+H] requires 499.2261, found 499.2258 [M^++H].

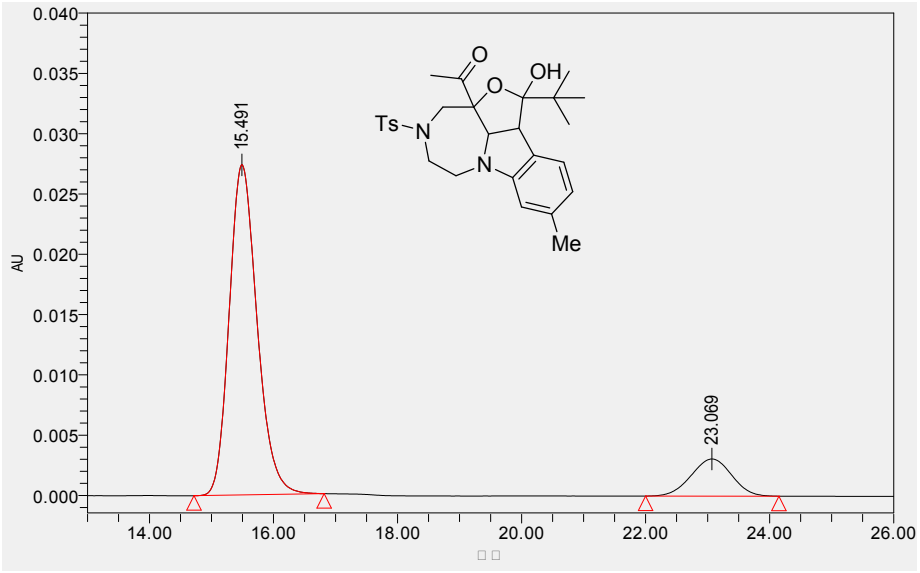
3i: a white solid. 23 mg, 46% yield. m.p. 218-220 °C. $[\alpha]^{20}_D$ = -16.7 (c 0.50, CH_2Cl_2) (72% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 15.5 min, t_{minor} = 23.1 min.



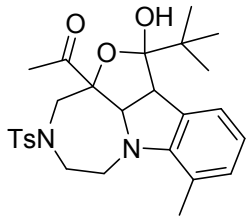




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	15.497	409636	51.11	12238
2	23.139	391793	48.89	8495



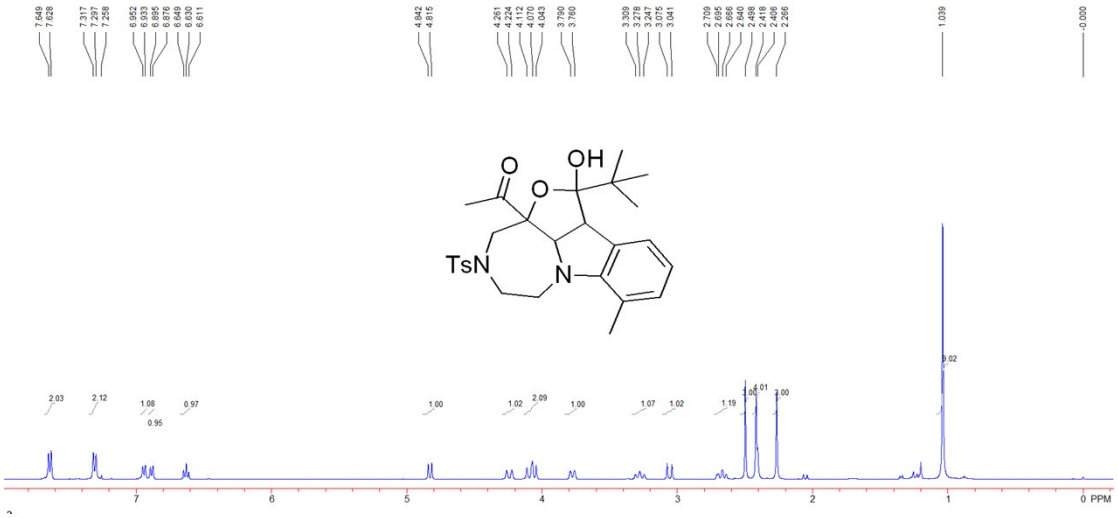
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	15.491	854335	85.91	27399
2	23.069	140068	14.09	3080

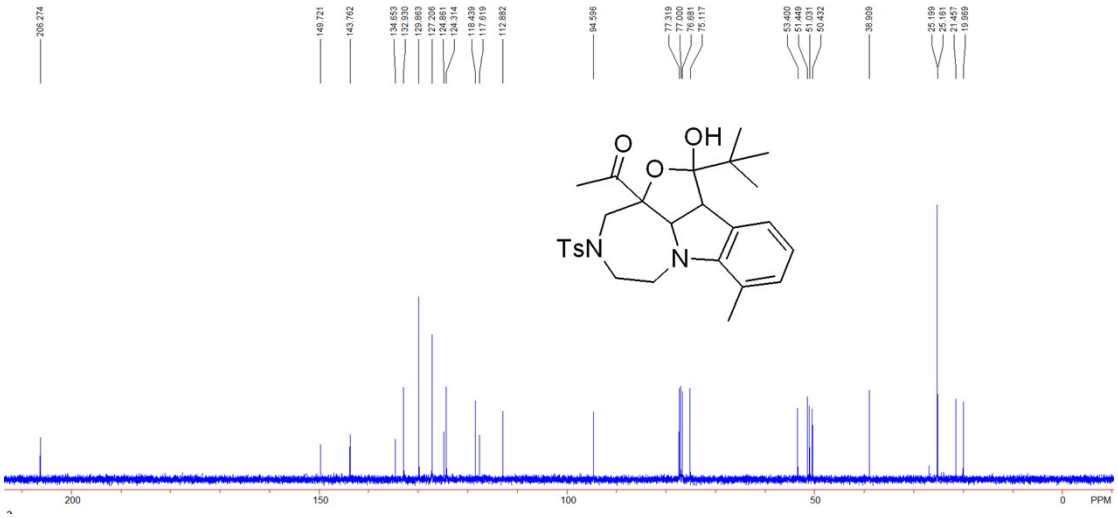


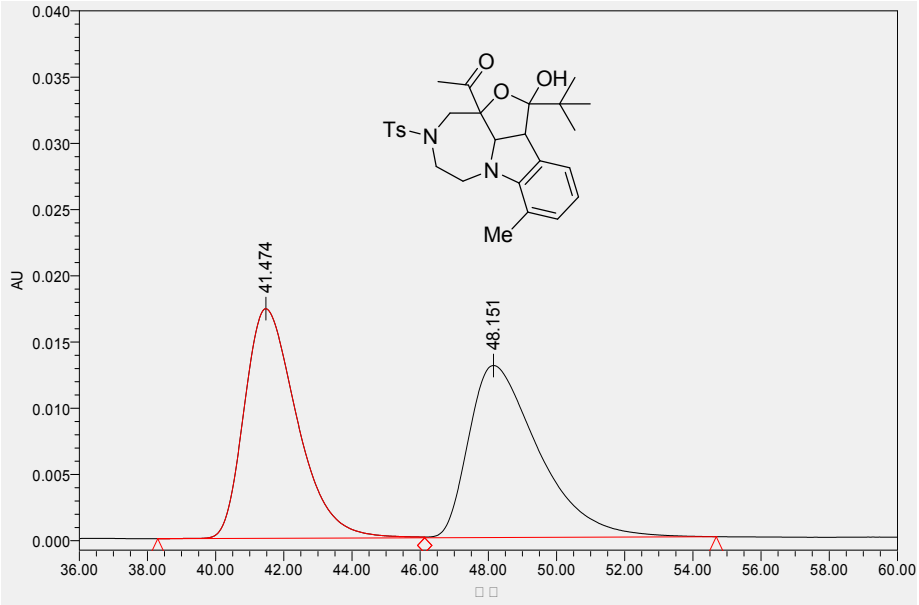
1-(1-(*tert*-butyl)-1-hydroxy-7-methyl-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3j**: a white solid. 44 mg, 85% yield. m.p. 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.04 (s, 9H), 2.27 (s, 3H), 2.41-2.42 (m, 4H), 2.50 (s, 3H), 2.64-2.71 (m, 1H), 3.06 (d, J = 13.6 Hz, 1H), 3.28 (t, J = 12.4 Hz, 1H), 3.78 (d, J = 12.0 Hz, 1H), 4.04-4.11 (m, 2H), 4.24 (d, J = 14.8 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.649 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.5, 25.16, 25.20, 38.9, 50.4, 51.0, 51.4, 53.4, 75.1, 94.6, 112.9, 117.6, 118.4, 124.3, 124.9, 127.2, 129.9, 132.9, 134.7, 143.8, 149.7, 206.3. IR (neat) ν 3535, 2960, 2912, 2872, 1718, 1596, 1470, 1422, 1354, 1336, 1307, 1208, 1161, 1108, 1091, 1054, 1006, 949, 907, 813, 740, 666 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{34}N_2O_5S$+H] requires 499.2261, found 499.2260 [M^++H].

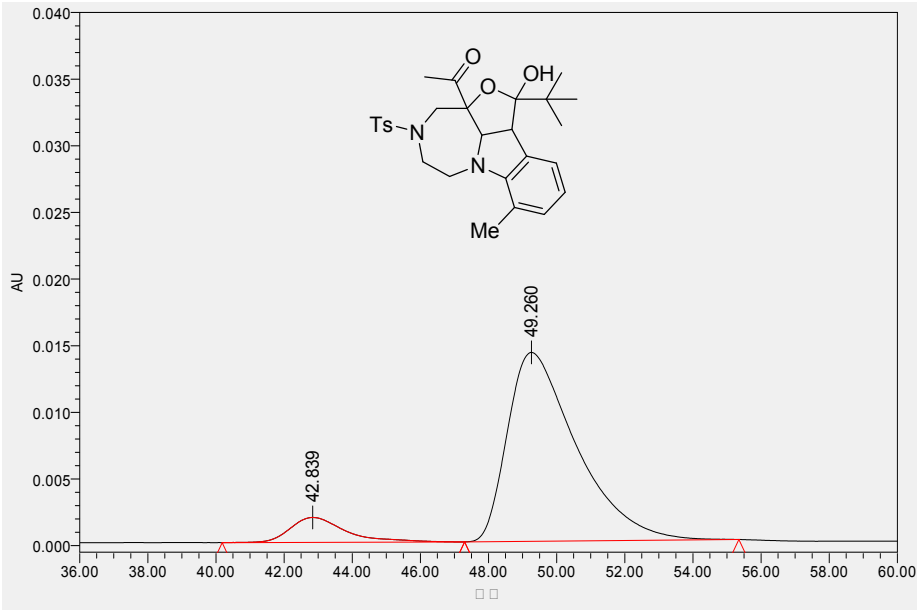
3j: a light yellow solid. 44 mg, 88% yield. m.p. 122-124 °C. $[\alpha]^{20}_{D}$ = +11.0 (c 0.50, CH_2Cl_2) (81% ee). HPLC conditions: Chiralcel OD-H, hexane/^{i}PrOH = 90/10, 0.3 mL/min, 254 nm, t_{major} = 49.3 min, t_{minor} = 42.8 min.



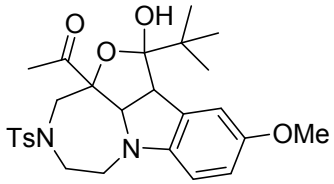




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	41.474	1862546	50.17	17337
2	48.151	1849750	49.83	12984



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	42.839	211302	9.57	1866
2	49.260	1996408	90.43	14179

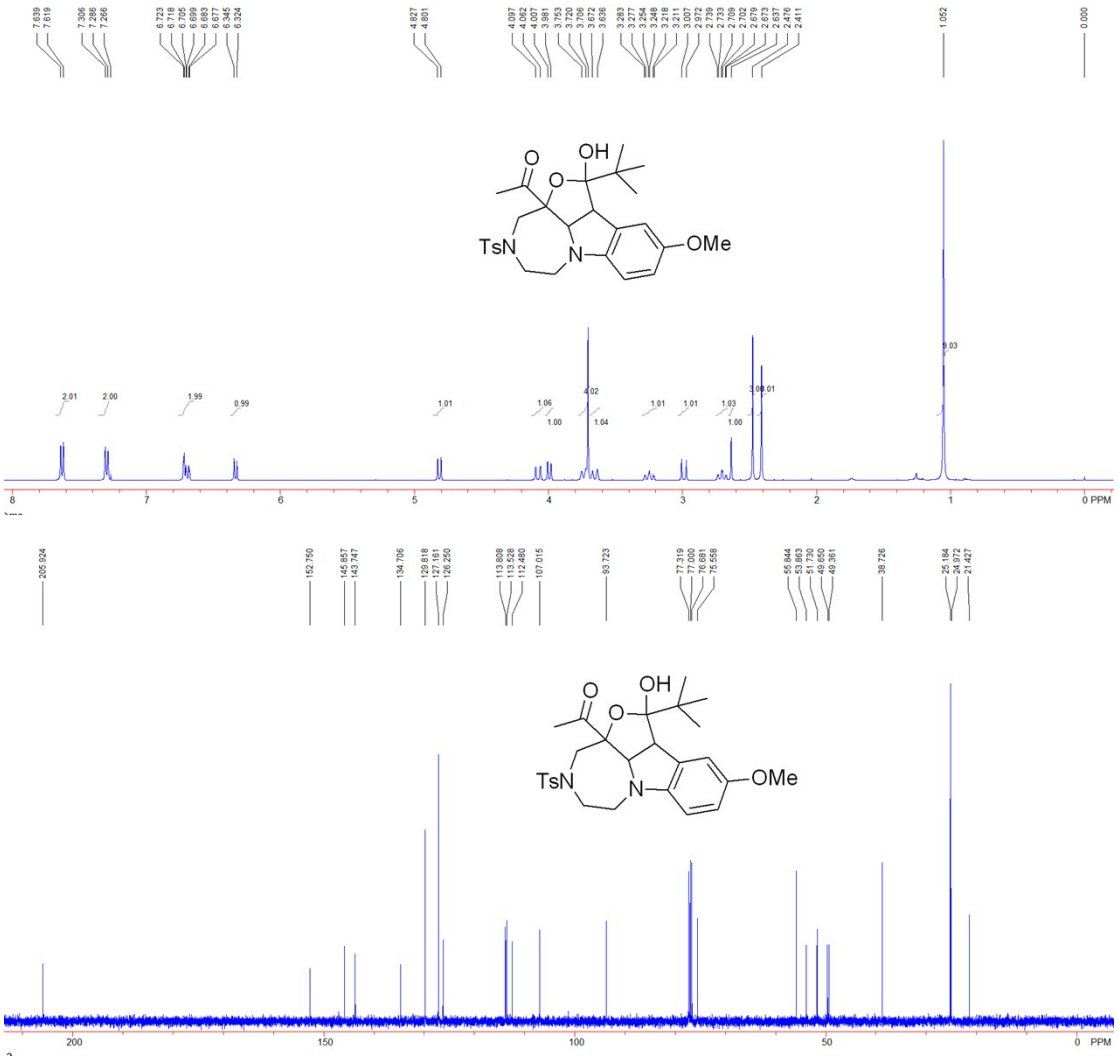


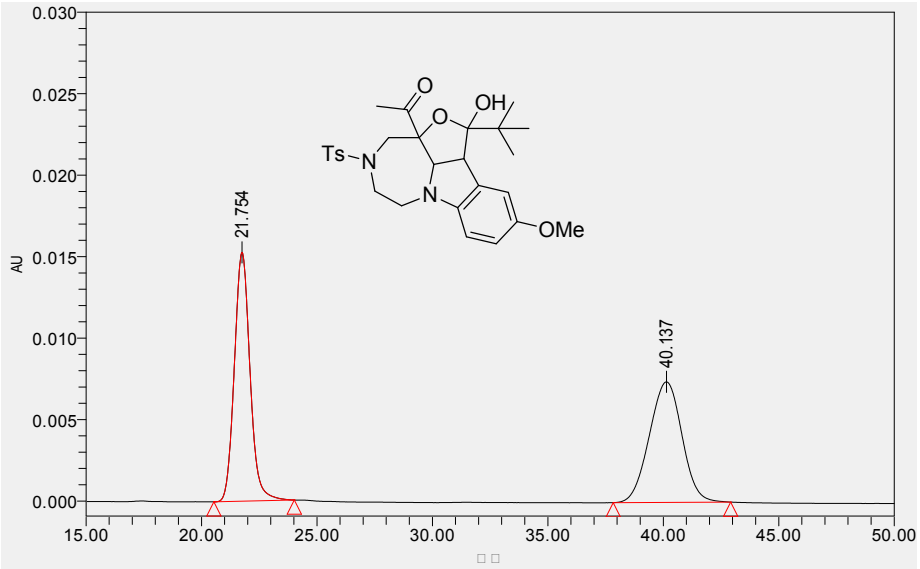
1-(1-(*tert*-butyl)-1-hydroxy-9-methoxy-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3k**: a light red solid. 45 mg, 79% yield. m.p. 239-241 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.05 (s, 9H), 2.41 (s, 3H), 2.48 (s, 3H), 2.64 (s, 1H), 2.71 (td, J = 12.0, 2.4 Hz, 1H), 2.99 (d, J = 14.0 Hz, 1H), 3.21-3.28 (m, 1H), 3.65 (d, J = 14.4 Hz, 1H), 3.71-3.75 (m, 4H), 3.99 (d, J = 10.4 Hz, 1H), 4.08 (d, J = 14.0 Hz, 1H), 4.81 (d, J = 10.4 Hz, 1H), 6.33 (d, J = 8.4 Hz, 1H), 6.68-6.72 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 25.0, 25.2, 38.7, 49.4, 49.7, 51.7, 53.9, 55.8, 75.6, 93.7, 107.0, 112.5, 113.5, 113.8, 126.3, 127.2, 129.8, 134.7, 143.7, 145.9, 152.8, 205.9. IR (neat) ν 3516, 2960, 1718, 1594, 1492, 1337, 1306, 1239, 1207, 1161, 1037, 1006, 907, 736, 721 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{34}N_2O_6S$+H] requires 515.2210, found 515.2205 [M^++H].

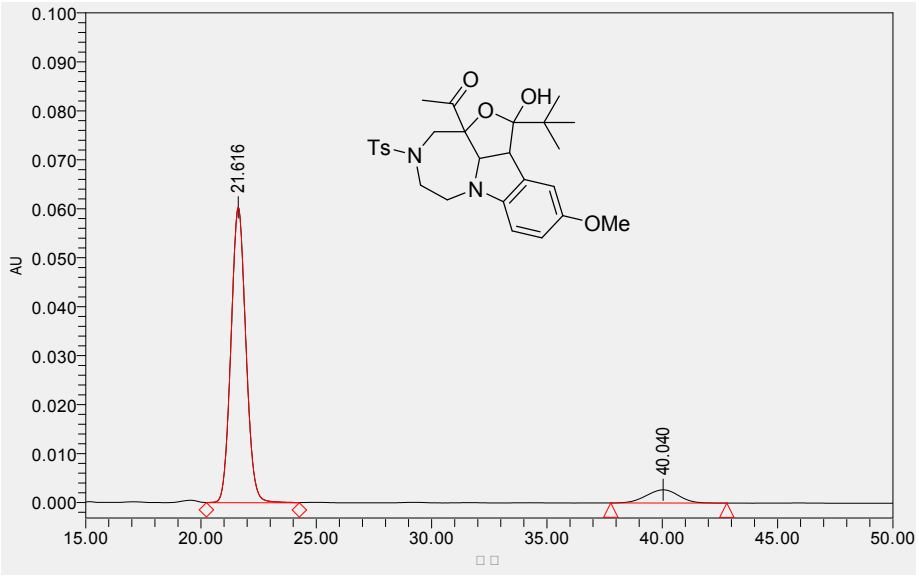
3k: a white solid. 32 mg, 62% yield. m.p. 111-113 °C. $[\alpha]^{20}_D$ = +8.3 (c 0.050, CH_2Cl_2) (82% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 21.6 min,

t_{minor} = 40.0 min.

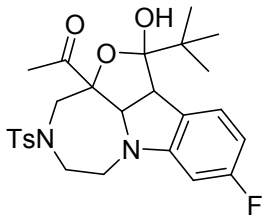




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	21.754	721313	49.82	15277
2	40.137	726610	50.18	7398



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	21.616	2712533	91.10	60330
2	40.040	264898	8.90	2701

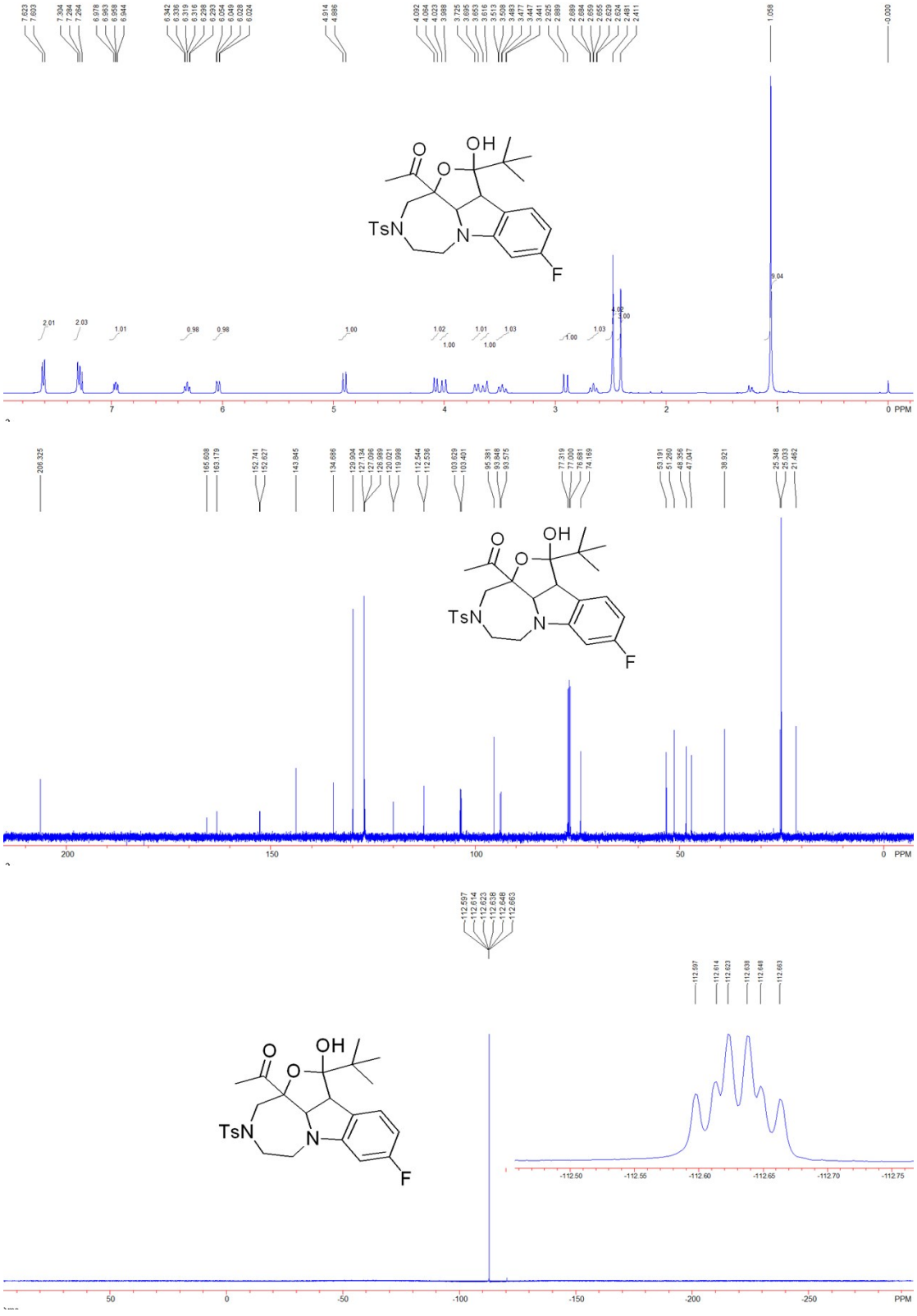


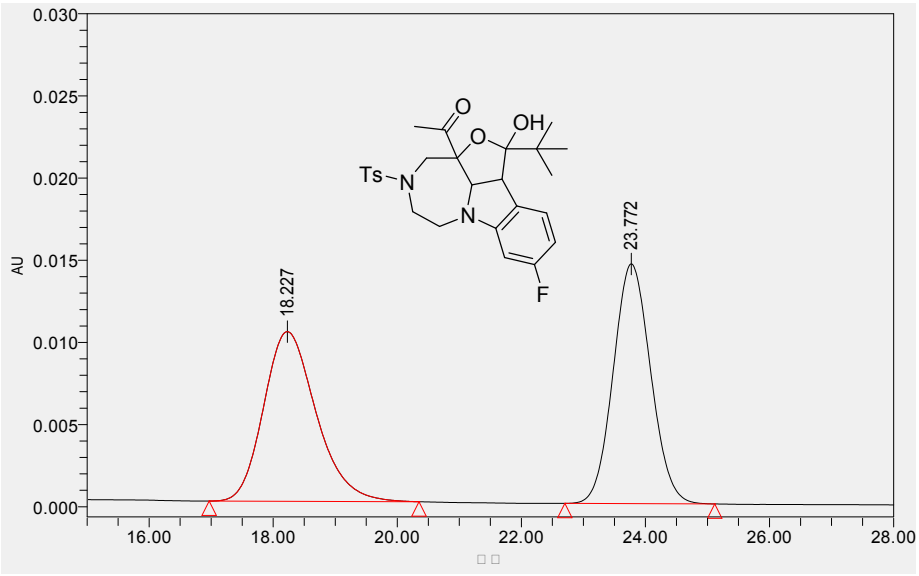
1-(1-(*tert*-butyl)-8-fluoro-1-hydroxy-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3l**: a white solid. 40 mg, 77% yield. m.p. 260-262 °C ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.41 (s, 3H), 2.48 (s, 4H), 2.66 (td, J = 12.0, 2.0 Hz, 1H), 2.91 (d, J = 14.4 Hz, 1H), 3.44-3.51 (m, 1H), 3.63 (d, J = 14.4 Hz, 1H), 3.71 (d, J = 12.0 Hz, 1H), 4.01 (d, J = 14.0 Hz, 1H), 4.08 (d, J = 11.2 Hz, 1H), 4.90 (d, J = 11.2 Hz, 1H), 6.04 (dd, J = 10.0, 2.0 Hz, 1H), 6.32 (td, J = 9.2, 2.0 Hz, 1H), 6.96 (dd, J = 8.0, 6.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.0, 25.3, 38.9, 47.0, 48.4, 51.3, 53.2, 74.2, 93.7 (d, J = 27.3 Hz), 95.4, 103.5 (d, J = 22.8 Hz), 112.5 (d, J = 0.8 Hz), 120.0 (d, J = 2.3 Hz), 127.0 (d, J = 10.7 Hz), 127.1, 129.9, 134.7, 143.8, 152.7 (d, J = 11.4 Hz), 164.4 (d, J = 242.9 Hz), 206.3. ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -112.663 ~ -112.597 (m). IR (neat) ν 3535, 2956, 2912, 1717, 1616, 1495, 1336, 1162, 1071, 1047, 1008, 907, 814, 753, 729, 662 cm^{-1}. HRMS (ESI) calcd for

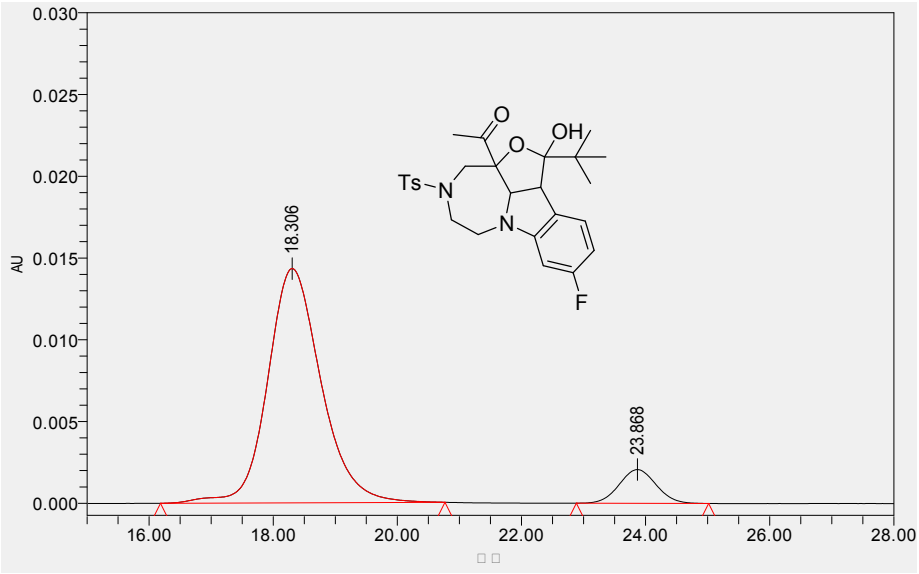
[$C_{26}H_{31}FN_2O_5S$-H_2O+H] requires 485.1905, found 485.1902 [M^+-H_2O+H].

3l: a white solid. 36 mg, 72% yield. m.p. 227-229 ^oC. $[\alpha]^{20}_D$ = -0.7 (c 1.0, CH_2Cl_2) (82% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 18.3 min, t_{minor} = 23.9 min.

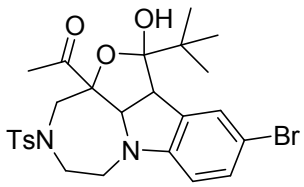




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	18.227	607616	49.78	10331
2	23.772	612932	50.22	14593



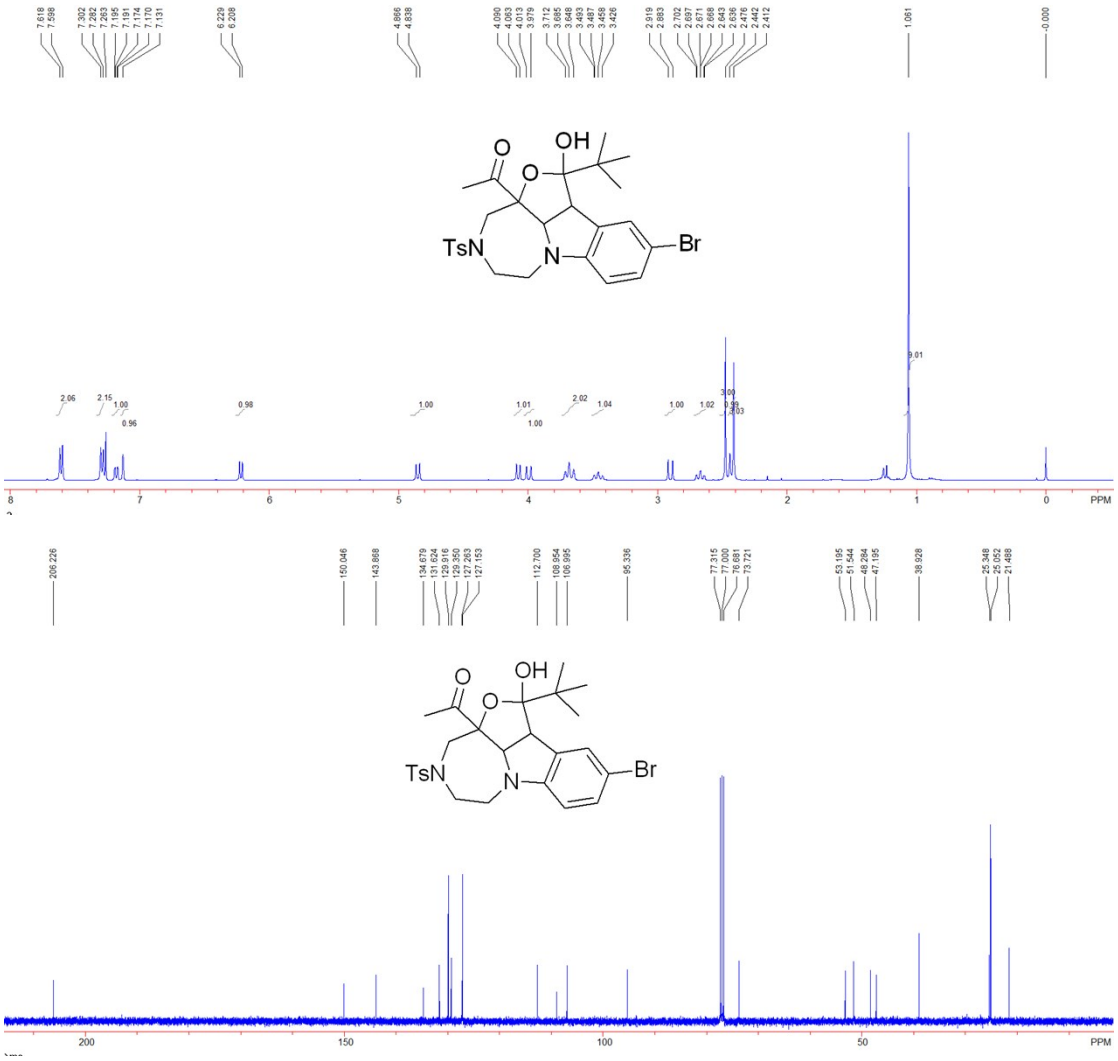
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	18.306	858100	90.95	14331
2	23.868	85350	9.05	2063

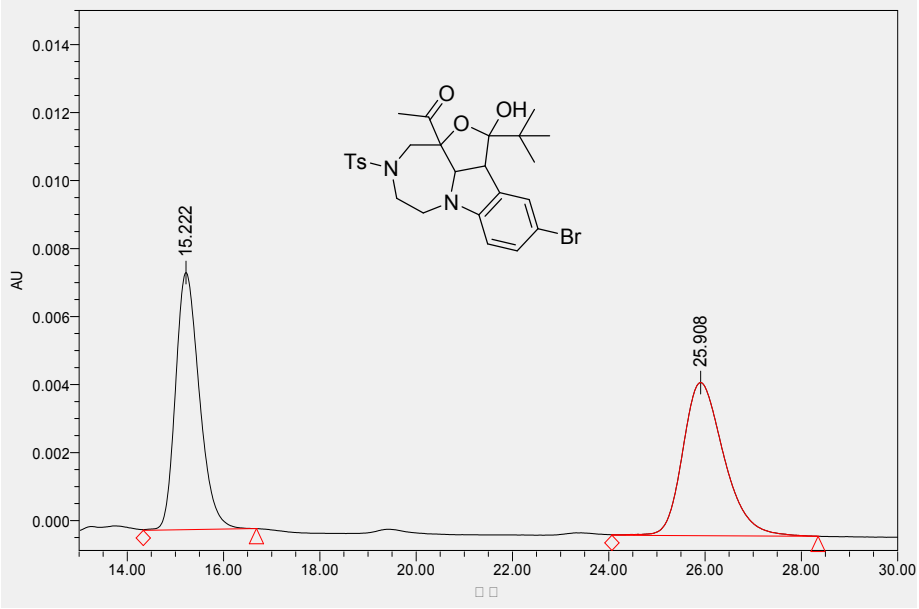


1-(9-bromo-1-(*tert*-butyl)-1-hydroxy-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

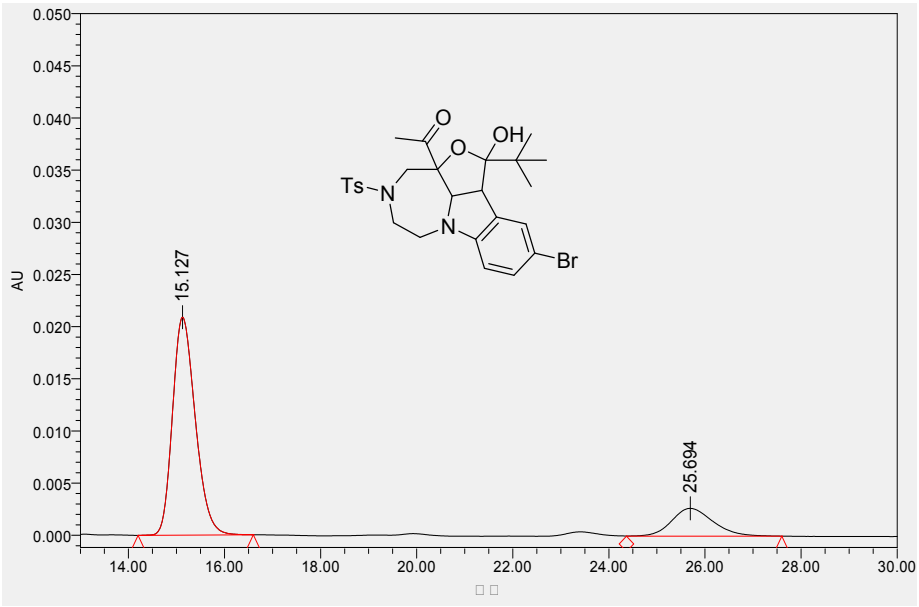
Compound **3m**: a white solid. 42 mg, 72% yield. m.p. 258-260 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.41 (s, 3H), 2.44 (s, 1H), 2.48 (s, 3H), 2.67 (td, J = 12.4, 2.0 Hz, 1H), 2.90 (d, J = 14.4 Hz, 1H), 3.43-3.49 (m, 1H), 3.69 (t, J = 14.8 Hz, 2H), 4.00 (d, J = 13.6 Hz, 1H), 4.08 (d, J = 10.8 Hz, 1H), 4.85 (d, J = 11.2 Hz, 1H), 6.22 (d, J = 8.4 Hz, 1H), 7.13 (s, 1H), 7.18 (dd, J = 8.4, 1.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.1, 25.3, 38.9, 47.2, 48.3, 51.5, 53.2, 73.7, 95.3, 107.0, 109.0, 112.7, 127.2, 127.3, 129.4, 129.9, 131.6, 134.7, 143.9, 150.0, 206.2. IR (neat) ν 3531, 2960, 2923, 1717, 1596, 1491, 1366, 1335, 1213, 1161, 1068, 1049, 1007, 909, 815, 741, 670 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{31}BrN_2O_5S$-H_2O+H] requires 545.1104, found 545.1101 [M^+-H_2O+H].

3m: a white solid. 37 mg, 66% yield. m.p. 225 °C (dec.). $[\alpha]^{20}_D$ = +16.6 (c 1.0, CH_2Cl_2) (62% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 50/50, 0.5 mL/min, 254 nm, t_{major} = 15.1 min, t_{minor} = 25.7 min.

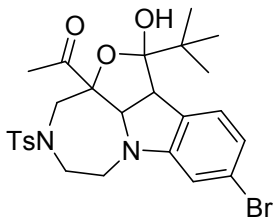




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	15.222	260142	49.22	7567
2	25.908	268412	50.78	4506



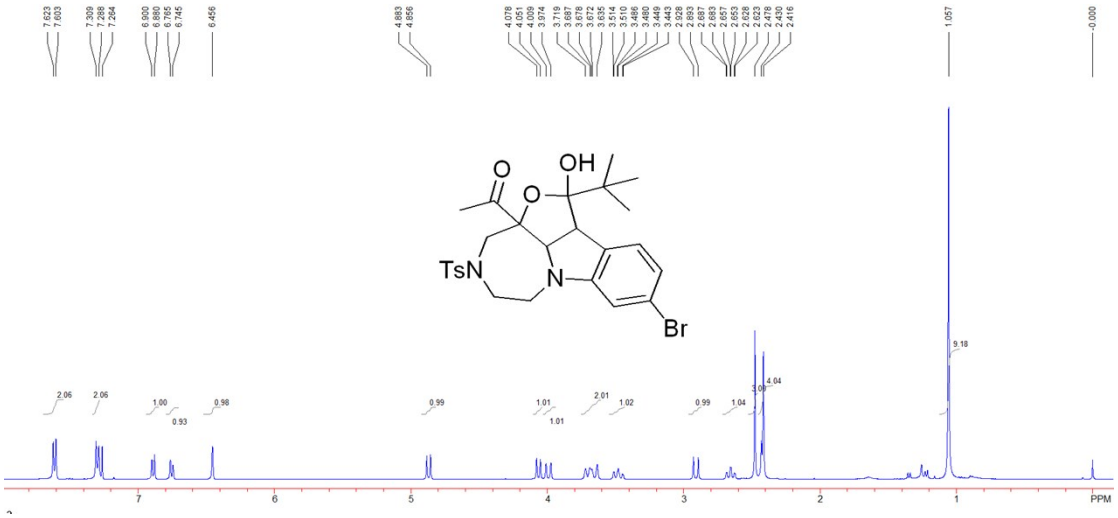
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	15.127	688212	81.07	20902
2	25.694	160716	18.93	2666

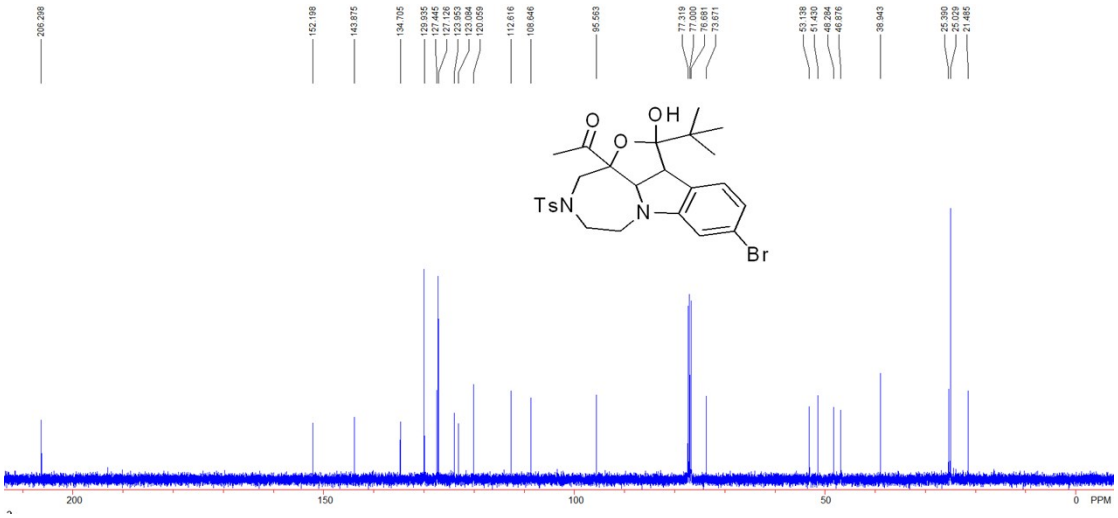


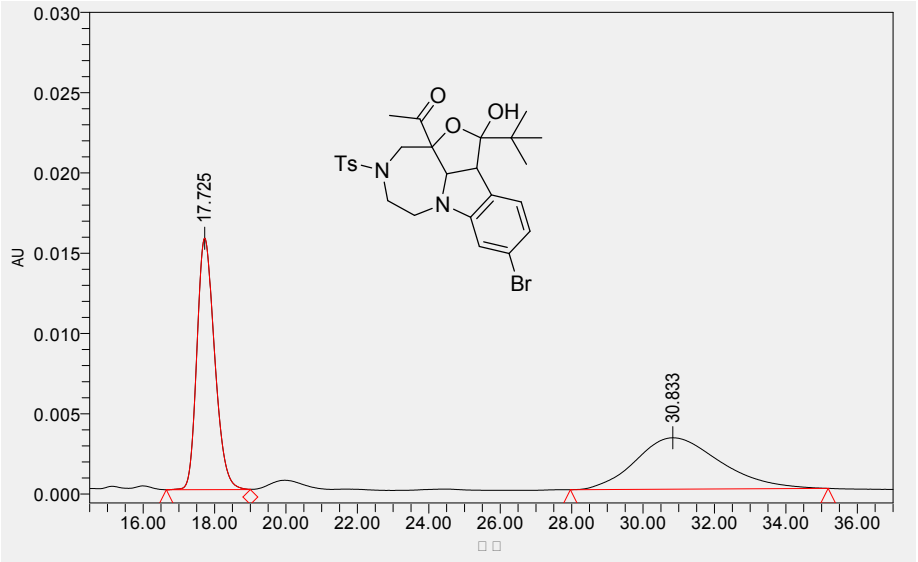
1-(8-bromo-1-(*tert*-butyl)-1-hydroxy-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3n**: a white solid. 36 mg, 64% yield. m.p. 276-278 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.42 (s, 3H), 2.43 (s, 1H), 2.48 (s, 3H), 2.66 (td, J = 12.0, 1.6 Hz, 1H), 2.91 (d, J = 14.0 Hz, 1H), 3.44-3.51 (m, 1H), 3.64-3.72 (m, 2H), 3.99 (d, J = 14.0 Hz, 1H), 4.06 (d, J = 10.8 Hz, 1H), 4.87 (d, J = 10.8 Hz, 1H), 6.46 (s, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.0, 25.4, 38.9, 46.9, 48.3, 51.4, 53.1, 73.7, 95.6, 108.6, 112.6, 120.1, 123.1, 124.0, 127.1, 127.4, 129.9, 134.7, 143.9, 152.2, 206.3. IR (neat) ν 3538, 2956, 2916, 1718, 1600, 1489, 1367, 1337, 1210, 1162, 1106, 1067, 1048, 1007, 909, 814, 743 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{31}BrN_2O_5S$-H_2O+H] requires 545.1104, found 545.1101 [M^+-H_2O+H].

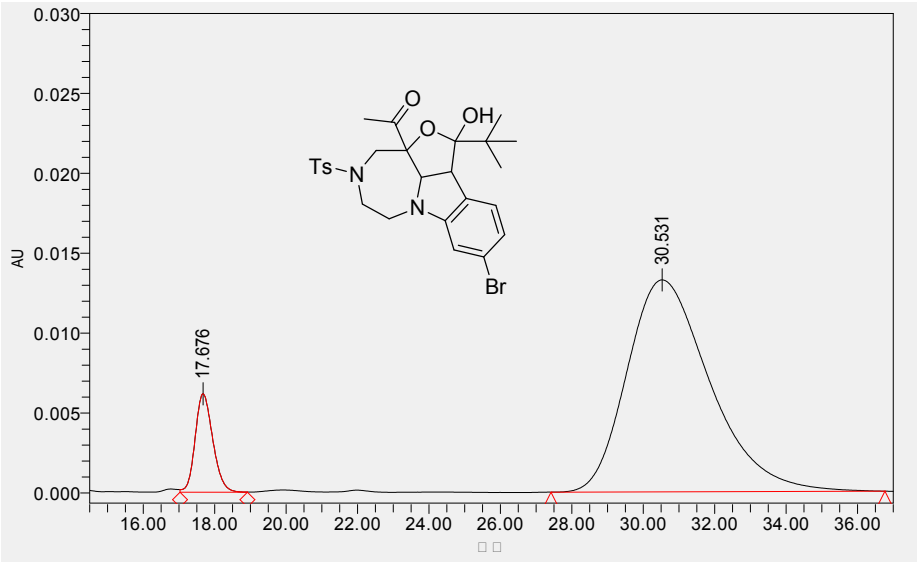
3n: a white solid. 48 mg, 85% yield. m.p. 220 °C (dec.). $[\alpha]^{20}_{D}$ = -68.3 (c 0.50, CH_2Cl_2) (82% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 60/40, 0.5 mL/min, 230 nm, t_{major} = 30.5 min, t_{minor} = 17.7 min.



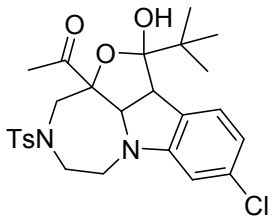




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	17.725	539739	50.57	15669
2	30.833	527558	49.43	3200

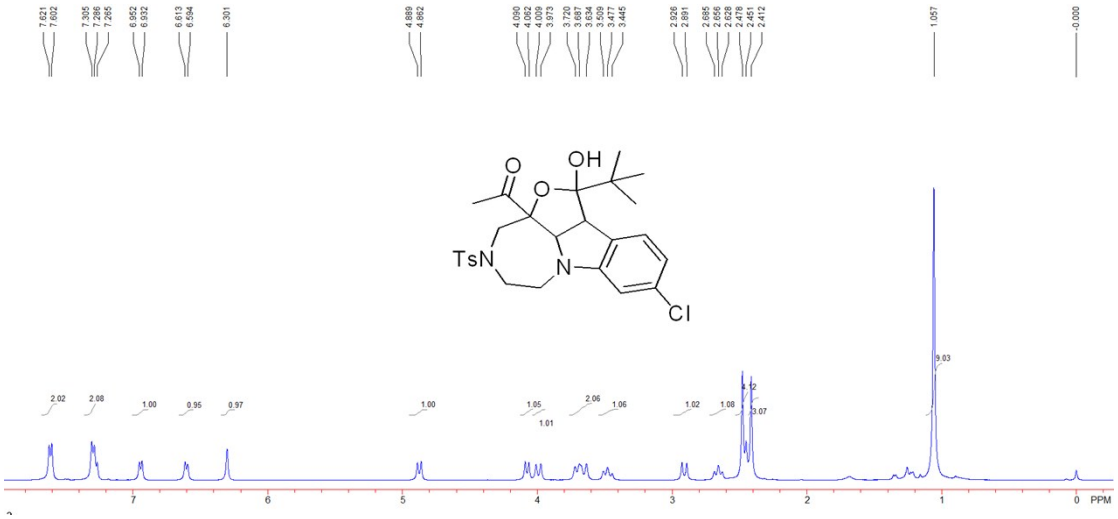


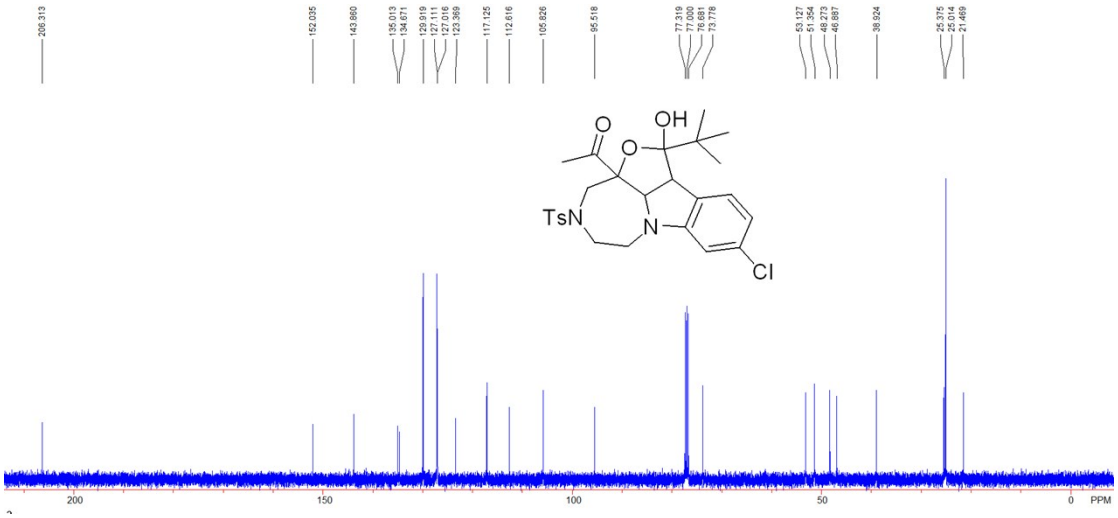
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	17.676	211577	9.00	6158
2	30.531	2139449	91.00	13263

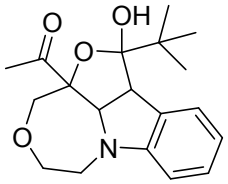


1-(1-(*tert*-butyl)-8-chloro-1-hydroxy-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3o**: a white solid. 43 mg, 83% yield. m.p. 270-272 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.41 (s, 3H), 2.45 (s, 1H), 2.48 (s, 3H), 2.66 (t, J = 11.2 Hz, 1H), 2.91 (d, J = 14.0 Hz, 1H), 3.48 (t, J = 12.8 Hz, 1H), 3.63-3.72 (m, 2H), 3.99 (d, J = 14.4 Hz, 1H), 4.08 (d, J = 11.2 Hz, 1H), 4.88 (d, J = 11.2 Hz, 1H), 6.30 (s, 1H), 6.60 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.0, 25.4, 38.9, 46.9, 48.3, 51.4, 53.1, 73.8, 95.5, 105.8, 112.6, 117.1, 123.4, 127.0, 127.1, 129.9, 134.7, 135.0, 143.9, 152.0, 206.3. IR (neat) ν 3494, 2956, 2872, 1718, 1604, 1494, 1366, 1350, 1320, 1217, 1156, 1111, 1089, 1073, 1050, 1007, 954, 912, 886, 814, 742, 671, 656 cm^{-1}. HRMS (ESI) calcd for [$C_{26}H_{31}ClN_2O_5S$-H_2O+H] requires 501.1609, found 501.1607 [M^+-H_2O+H].



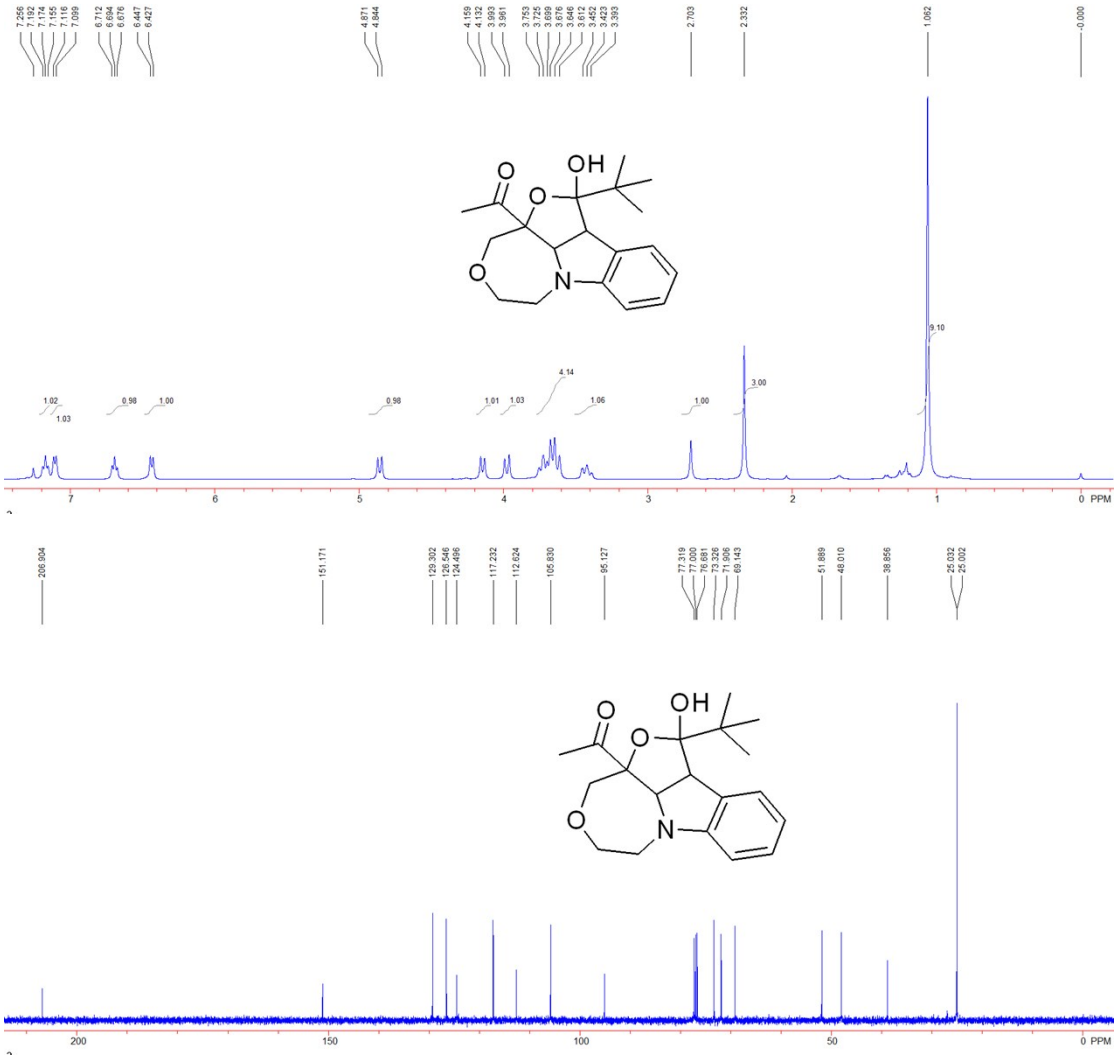


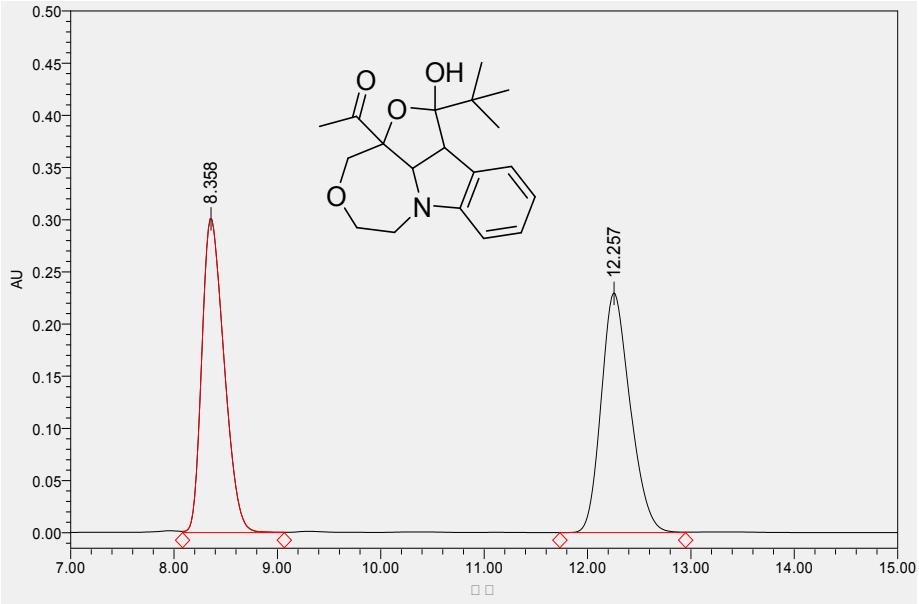


1-(1-(*tert*-butyl)-1-hydroxy-2a[1],5,6,10b-tetrahydro-1*H*-2,4-dioxa-6a-azabenzo[*a*]cyclopenta[*cd*]azulen-2a(3*H*)-yl)ethan-1-one

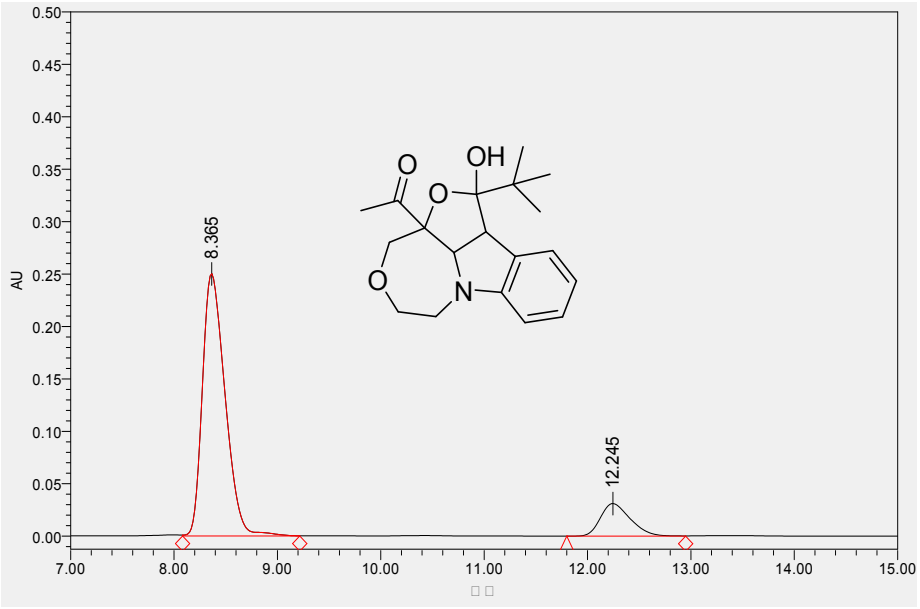
Compound **3p**: a white solid. 47 mg, 86% yield. m.p. 154-156 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (s, 9H), 2.33 (s, 3H), 2.70 (s, 1H), 3.42 (t, J = 12.0 Hz, 1H), 3.61-3.75 (m, 4H), 3.98 (d, J = 12.8 Hz, 1H), 4.15 (d, J = 10.8 Hz, 1H), 4.86 (d, J = 10.8 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 6.69 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.00, 25.03, 38.9, 48.0, 51.9, 69.1, 71.9, 73.3, 95.1, 105.8, 112.6, 127.2, 124.5, 126.5, 129.3, 151.2, 206.9. IR (neat) ν 3535, 2952, 2868, 1720, 1603, 1589, 1464, 1361, 1210, 1123, 1098, 1084, 1070, 1011, 981, 882, 742, 692 cm^{-1}. HRMS (ESI) calcd for [$C_{19}H_{25}NO_4$+H] requires 332.1856, found 332.1857 [M^++H].

3p: a light yellow solid. 10 mg, 30% yield. m.p. 104-106 ^{o}C. $[\alpha]^{20}_{D}$ = -46.2 (c 0.15, CH_2Cl_2) (72% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 50/50, 0.5 mL/min, 254 nm, t_{major} = 8.4 min, t_{minor} = 12.2 min.

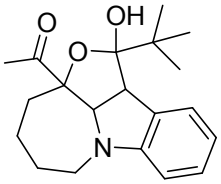




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.358	4507983	50.13	302049
2	12.257	4484251	49.87	229858



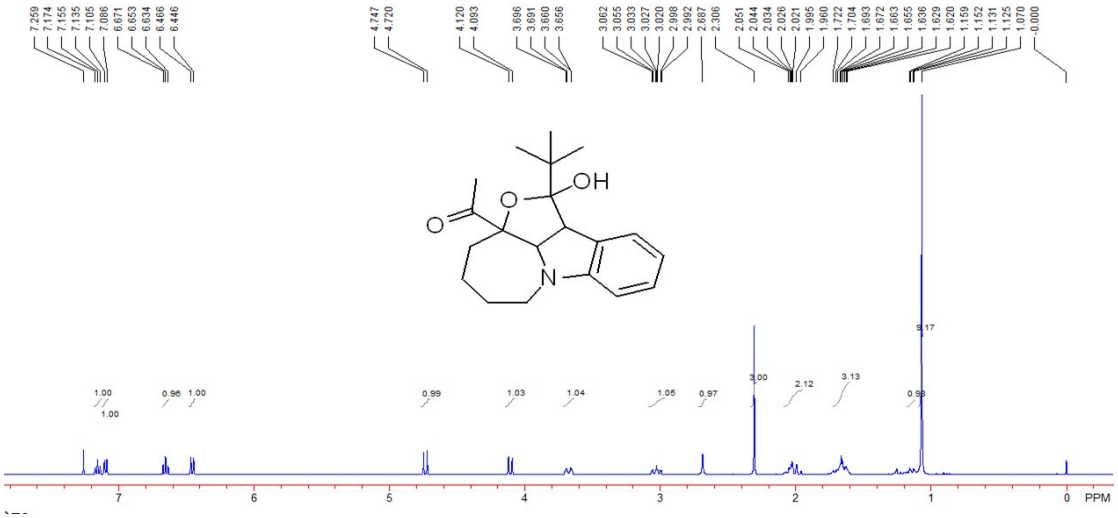
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.365	3816850	85.98	250262
2	12.245	622365	14.02	31076

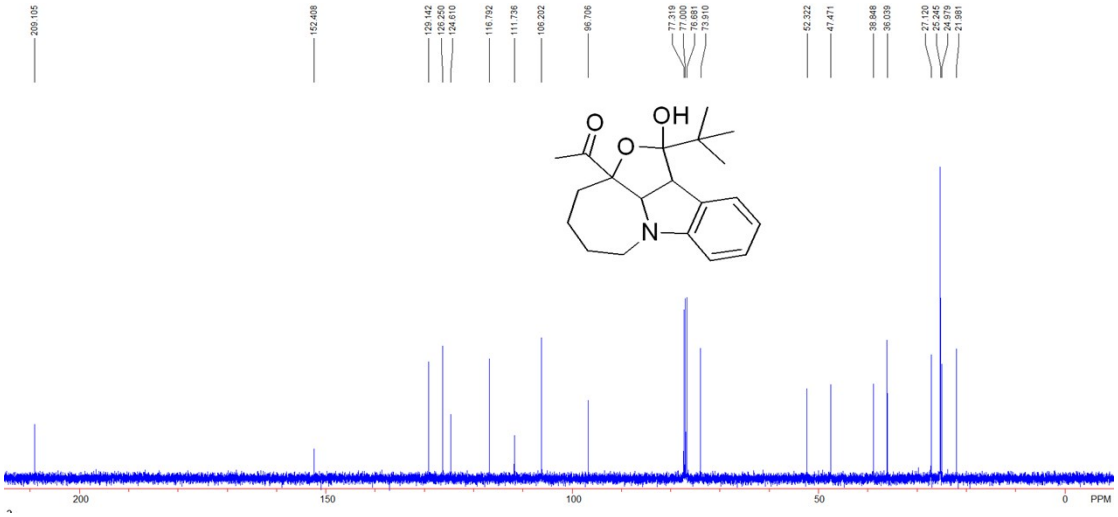


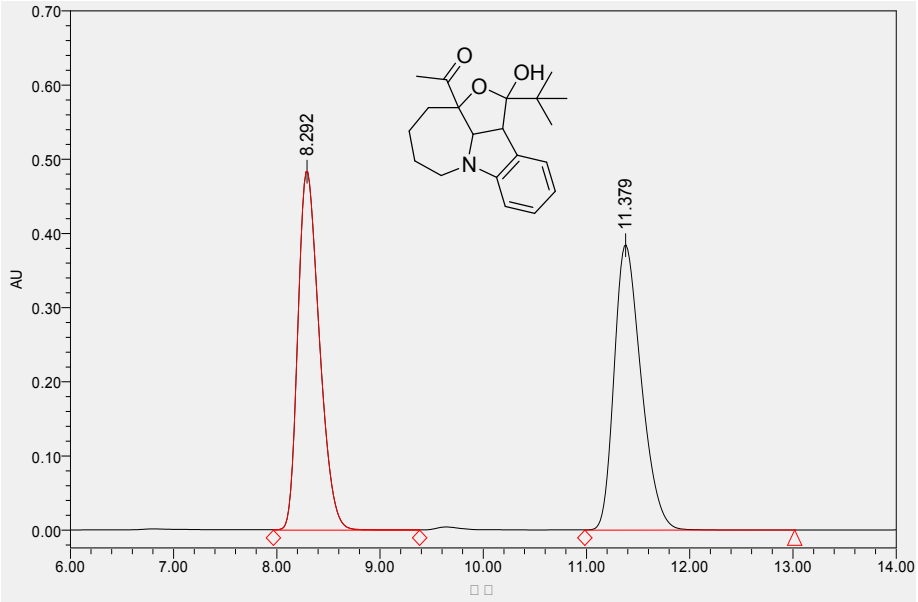
1-(1-(*tert*-butyl)-1-hydroxy-2a[1],3,4,5,6,10b-hexahydro-2-oxa-6a-azabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3q**: a white solid. 29 mg, 46% yield. m.p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (s, 9H), 1.13-1.16 (m, 1H), 1.62-1.72 (m, 3H), 1.96-2.05 (m, 2H), 2.31 (s, 3H), 2.69 (s, 1H), 2.99-3.06 (m, 1H), 3.66-3.70 (m, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 25.0, 25.2, 27.1, 36.0, 38.8, 47.5, 52.3, 73.9, 96.7, 106.2, 111.7, 116.8, 124.6, 126.3, 129.1, 152.4, 209.1. IR (neat) ν 3549, 2956, 2929, 2864, 1714, 1604, 1491, 1361, 1275, 1261, 1158, 1072, 1045, 1009, 868, 749 cm^{-1}. HRMS (ESI) calcd for [$C_{20}H_{27}NO_3$+H] requires 330.2064, found 330.2063 [M^++H].

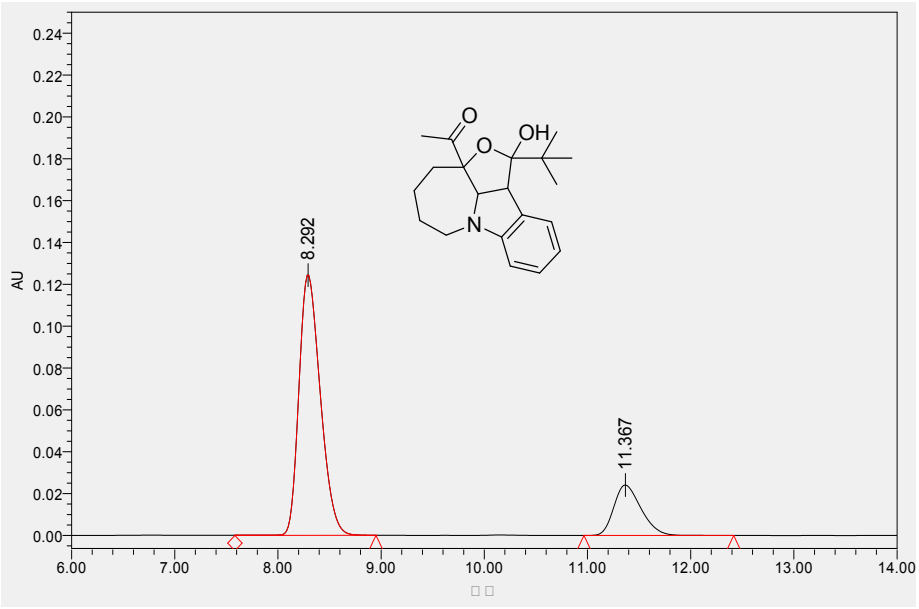
3q: a light yellow solid. 8 mg, 25% yield. m.p. 104-106 °C. $[\alpha]^{20}_D$ = -12.2 (c 0.20, CH_2Cl_2) (60% ee). HPLC conditions: Chiralpak AD-H, hexane/^{i}PrOH = 50/50, 0.5 mL/min, 254 nm, t_{major} = 8.3 min, t_{minor} = 11.4 min.



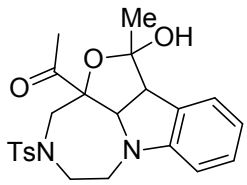




	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.292	7000127	50.04	485582
2	11.379	6990037	49.96	384780

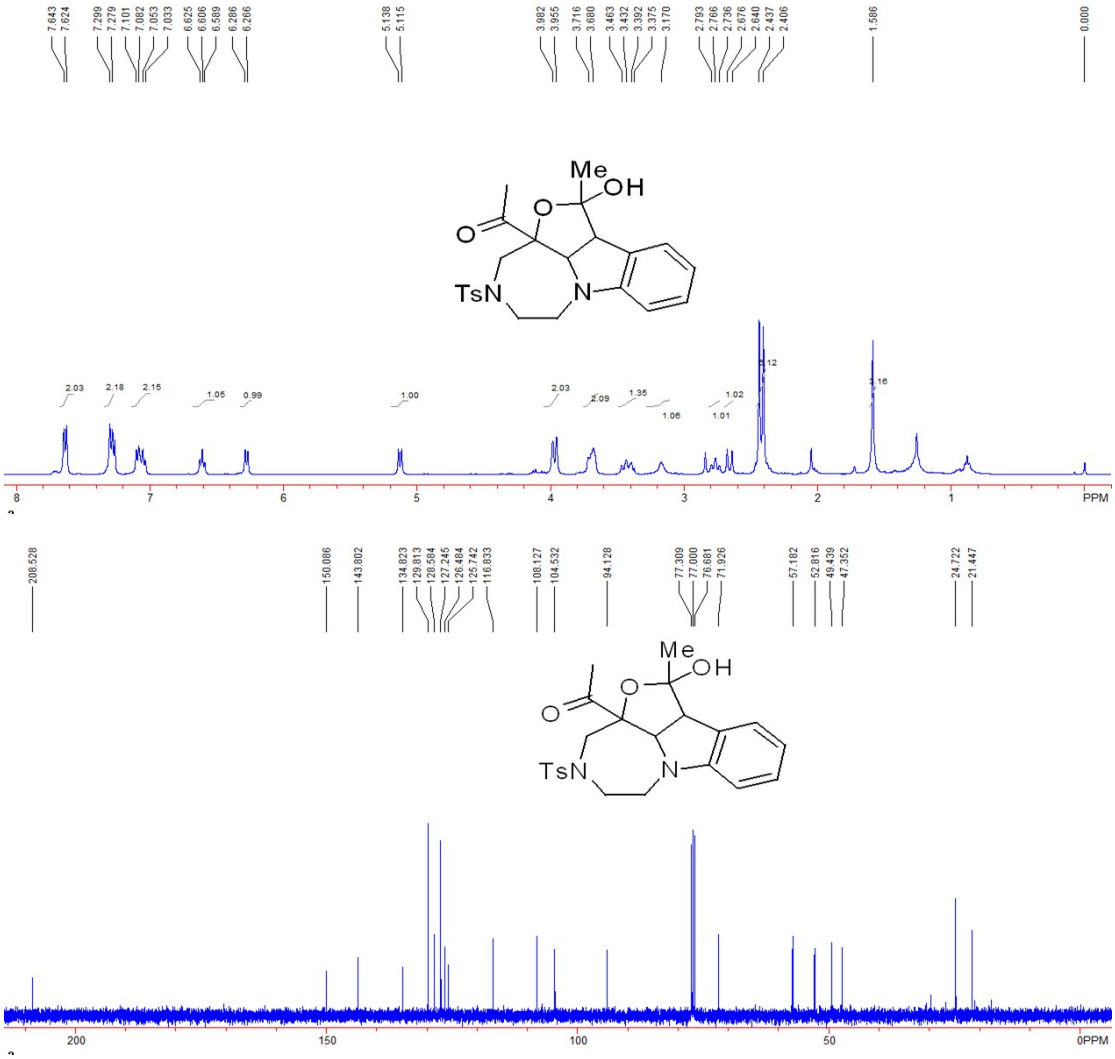


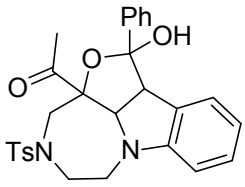
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.292	1794404	80.21	124901
2	11.367	442731	19.79	24129



1-(1-hydroxy-1-methyl-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3r**: a white solid. 44 mg, ca. 94% yield (containing small amount of impurities, can't be purified). m.p. 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.59 (s, 3H), 2.41 (s, 3H), 2.44 (s, 3H), 2.66 (d, J = 14.4 Hz, 1H), 2.77 (t, J = 10.8 Hz, 1H), 3.17 (s, broad, 1H), 3.38-3.46 (m, 1H), 3.68-3.72 (m, 2H), 3.97 (d, J = 10.8 Hz, 2H), 5.13 (d, J = 9.2 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 6.61 (t, J = 7.6 Hz, 1H), 7.03-7.10 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 24.7, 47.4, 49.4, 52.8, 57.2, 71.9, 94.1, 104.5, 108.1, 116.8, 125.7, 126.5, 127.2, 128.6, 129.8, 134.8, 143.8, 150.1, 208.5. IR (neat) ν 3491, 2927, 1713, 1601, 1490, 1355, 1338, 1213, 1158, 1094, 1025, 1001, 909, 737, 719, 653 cm^{-1}. HRMS (ESI) calcd for [$C_{23}H_{26}N_2O_5S$+H] requires 443.1635, found 443.1631 [M^++H].

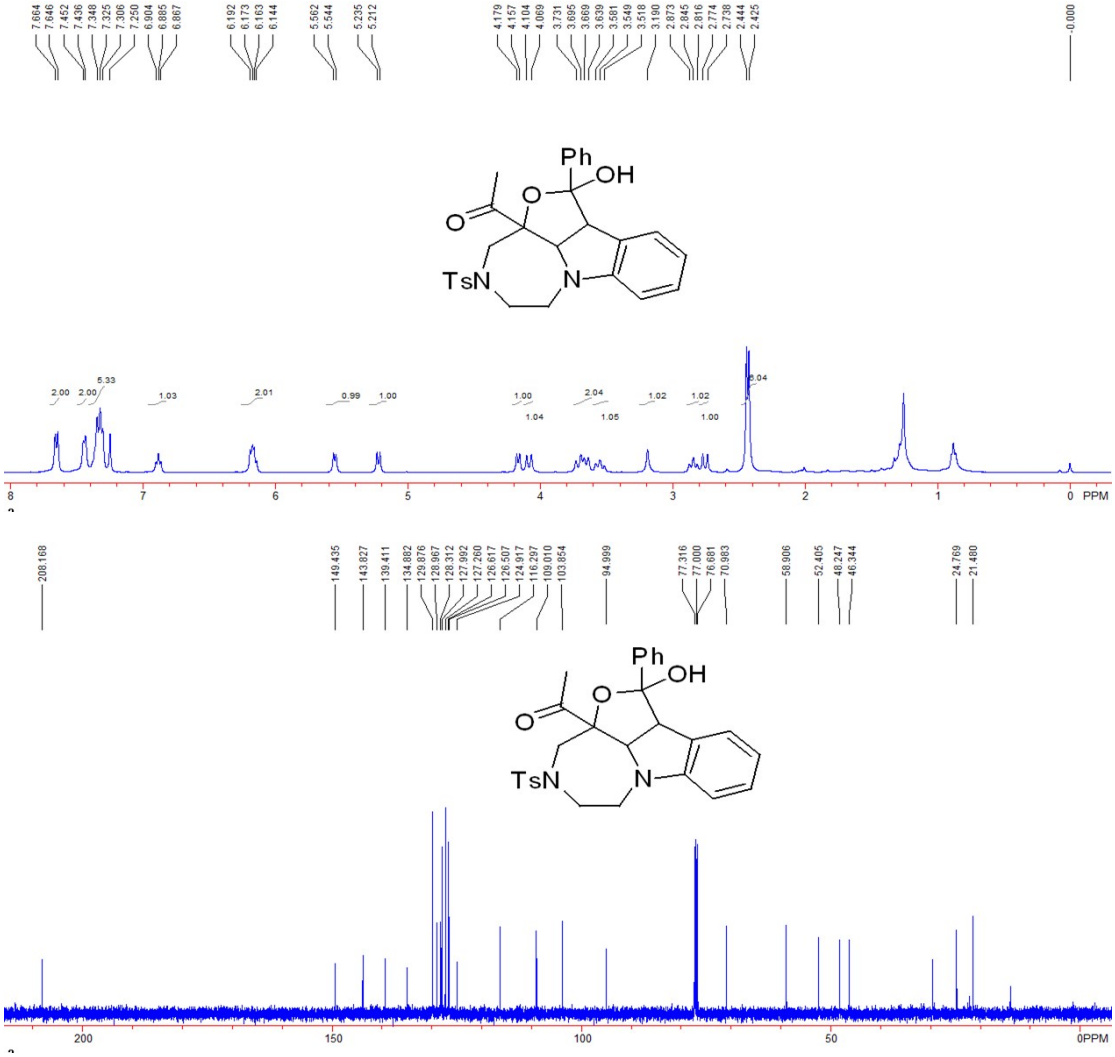


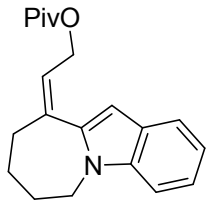


1-(1-hydroxy-1-phenyl-4-tosyl-2a[1],3,4,5,6,10b-hexahydro-2-oxa-4,6a-diazabenzo[*a*]cyclopenta[*cd*]azulen-2a(1*H*)-yl)ethan-1-one

Compound **3s**: a white solid. 36 mg, ca.70% yield (containing small amount of impurities, can't be purified). m.p. 125-127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.43 (s, 3H), 2.44 (s, 3H), 2.76 (d, J = 14.4 Hz, 1H), 2.85 (t, J = 11.2 Hz, 1H), 3.19 (s, broad, 1H), 3.55 (t, J = 12.4 Hz, 1H), 3.64-3.73 (m, 2H), 4.09 (d, J = 14.4 Hz, 1H), 4.17 (d, J = 8.8 Hz, 1H), 5.22 (d, J = 8.8 Hz, 1H), 5.55 (d, J = 7.2 Hz, 1H), 6.14-6.19 (m, 2H), 6.89 (t, J = 7.2 Hz, 1H), 7.31-7.35 (m, 5H), 7.44 (d, J = 6.4 Hz, 2H), 7.66 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 24.8, 46.3, 48.2, 52.4, 58.9, 71.0,

95.0, 103.9, 109.0, 116.3, 124.9, 126.5, 126.6, 127.3, 128.0, 128.3, 129.0, 129.9, 134.9, 139.4, 143.8, 149.4, 208.2. IR (neat) ν 3472, 2923, 2853, 1714, 1601, 1489, 1339, 1213, 1160, 1091, 1068, 1025, 1003, 908, 767, 737, 701, 688, 657 cm^{-1}. HRMS (ESI) calcd for [$C_{28}H_{28}N_2O_5S$+H] requires 505.1792, found 505.1788 [M^++H].

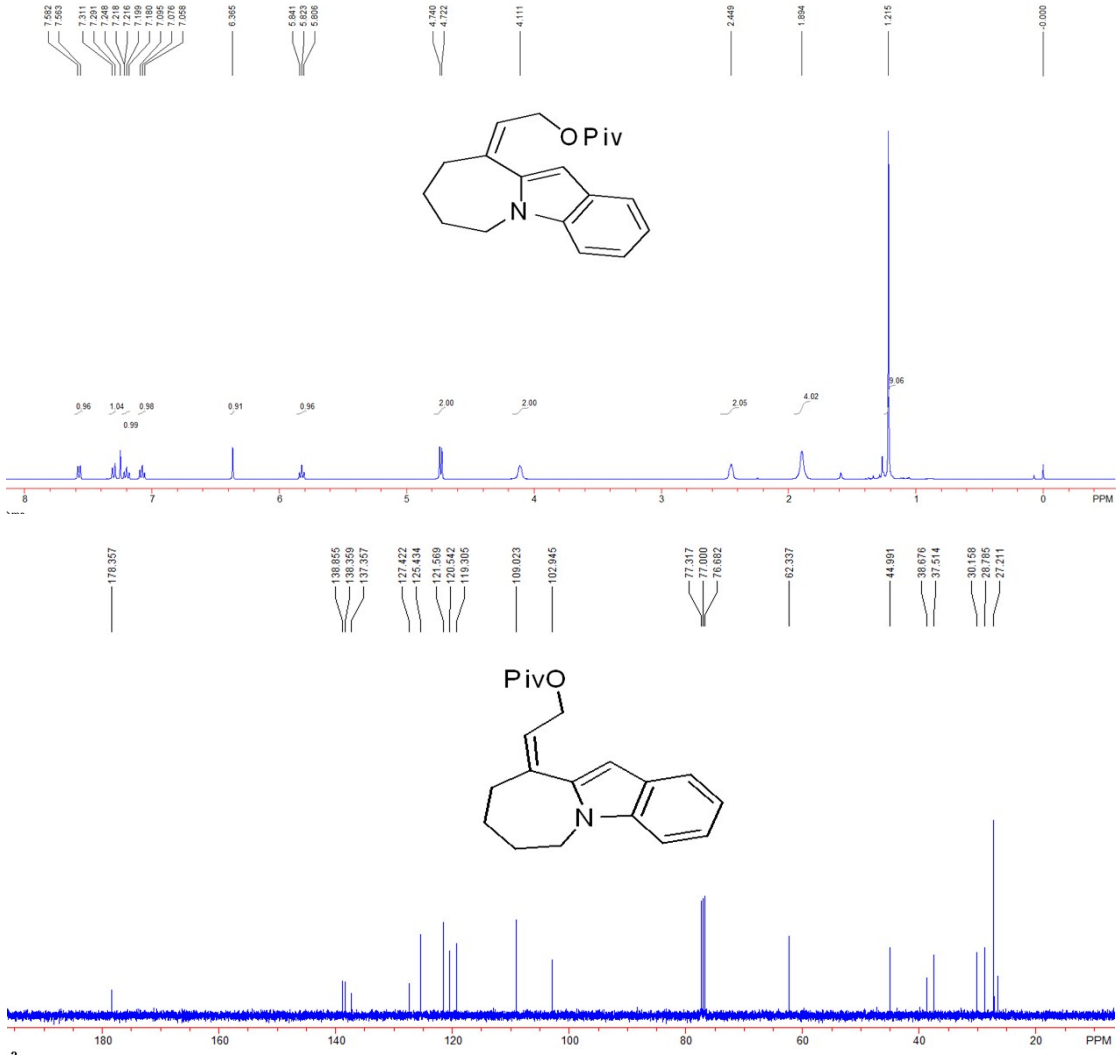


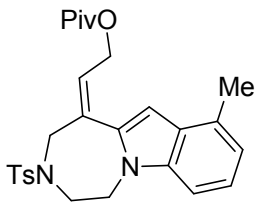


(*Z*)-2-(8,9-dihydro-6*H*-azepino[1,2-*a*]indol-10(7*H*)-ylidene)ethyl pivalate

Compound **4q**: colorless oil. 22 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (s, 9H), 1.89 (s, 4H), 2.45 (s, 2H), 4.11 (s, 2H), 4.73 (d, J = 7.2 Hz, 2H), 5.82 (t, J = 7.2 Hz, 1H), 6.37 (s, 1H),7.07 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz,

1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 28.8, 30.2, 37.5, 38.7, 45.0, 62.3, 102.9, 109.0, 119.3, 120.5, 121.6, 125.4, 127.4, 137.4, 138.4, 138.9, 178.4. IR (neat) ν 2971, 2930, 2872, 1725, 1480, 1460, 1396, 1358, 1280, 1149, 1030, 966, 749, 735 cm^{-1}. HRMS (ESI) calcd for [$C_{20}H_{25}NO_2$+H] requires 312.1958, found 312.1960 [M$^+$+H].

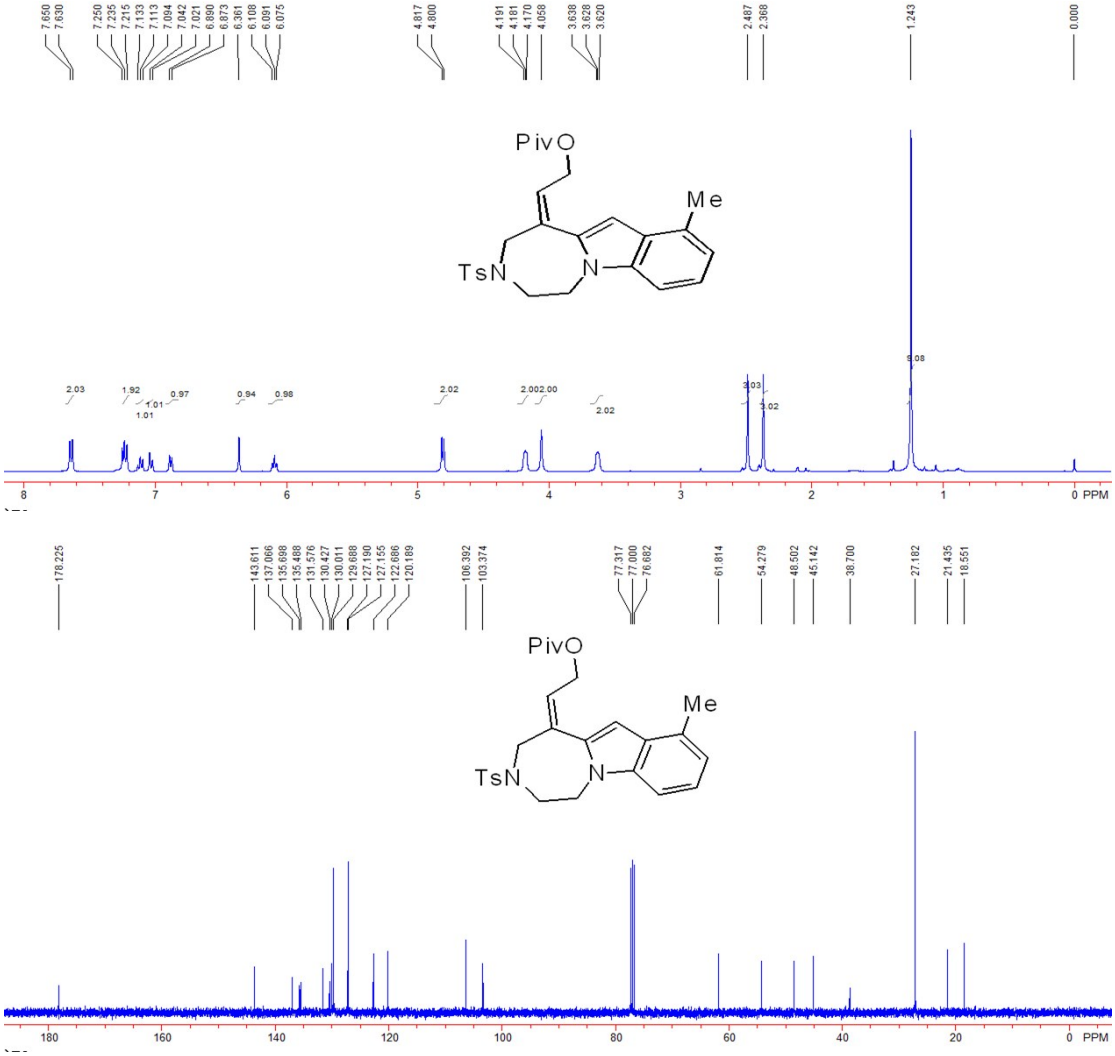




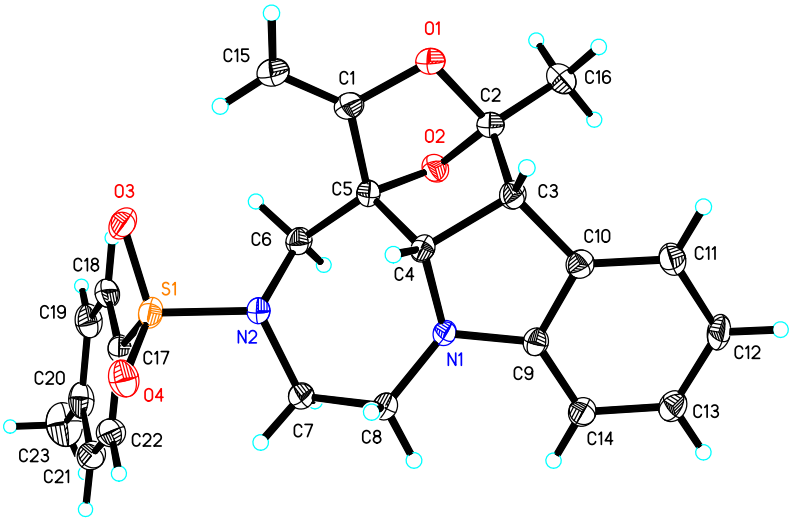
(*Z*)-2-(10-methyl-3-tosyl-2,3,4,5-tetrahydro-1*H*-[1,4]diazepino[1,7-*a*]indol-1-ylidene)ethyl pivalate

Compound **4u**: a white solid. 37 mg, 67% yield. m.p. 84-86 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24 (s, 9H), 2.37 (s, 3H), 2.49 (s, 3H), 3.63 (t, J = 4.0 Hz, 2H), 4.06 (s, 2H), 4.18 (t, J = 4.0 Hz, 2H), 4.81 (d, J = 6.8 Hz, 2H), 6.09 (t, J = 6.8 Hz, 1H), 6.36 (s, 1H), 6.88 (d, J = 6.8 Hz, 1H), 7.03 (d,

J = 8.4 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 21.4, 27.2, 38.7, 45.1, 48.5, 54.3, 61.8, 103.4, 106.4, 120.2, 122.7, 127.16, 127.19, 129.7, 130.0, 130.4, 131.6, 135.5, 135.7, 137.1, 143.6, 178.2. IR (neat) ν 2967, 2938, 2864, 1725, 1596, 1480, 1451, 1321, 1279, 1156, 1085, 906, 768, 710, 665 cm^{-1}. HRMS (ESI) calcd for [$C_{27}H_{32}N_2O_4S$+H] requires 481.2156, found 481.2153 [M^++H].

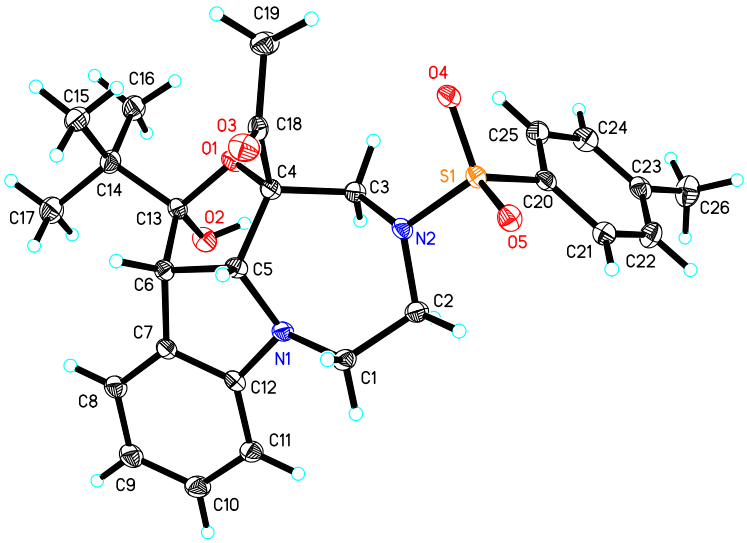


(E) X-ray Crystal Data of Compound 2r.



The crystal data of **2r** have been deposited in CCDC with number 1058692. Empirical Formula: $C_{23}H_{24}N_2O_4S$; Formula Weight: 424.50; Crystal Color, Habit: colorless, Crystal Dimensions: 0.211 x 0.145 x 0.068 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 9.5226(8)Å, b = 36.221(3)Å, c = 24.769(2)Å, α = 90°, β = 99.375(2)°, γ = 90°, V = 8429.2(12)$Å^3$; Space group: 21/c; Z = 16; D_{calc}= 1.338 g/cm^3; F_{000} = 3584, Final R indices [I>2sigma(I)] R1 = 0.0541, wR2 = 0.1001.

(F) X-ray Crystal Data of Compound 3a.



The crystal data of **3a** have been deposited in CCDC with number 1035121. Empirical Formula: $C_{26}H_{32}N_2O_5S$; Formula Weight: 484.59; Crystal Color, Habit: colorless, Crystal Dimensions: 0.20 x 0.15 x 0.05 mm; Crystal System: Monoclinic; Lattice Parameters: a = 9.814(4)Å, b = 10.840(4)Å, c = 23.074(9)Å, α = 90°, β = 95.566(6)°, γ = 90°, V = 2443.3(16)Å^3; Space group: P 1 21/n 1; Z = 4; D_{calc}= 1.317 g/cm^3; F_{000} = 1032, Final R indices [I>2sigma(I)] R1 = 0.0766, wR2 = 0.1627.

(G) References.

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