Supporting Information

Rhodium-Catalyzed Enantio- and Diastereoselective Intramolecular [2 + 2 + 2] Cycloaddition of Unsymmetrical Dienynes

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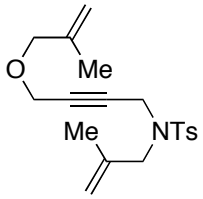
I. General

Anhydrous CH_2Cl_2 (No. 27099-7) and anhydrous $(CH_2Cl)_2$ (No. 28450-5) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. Ligands, (*R*)-H_8-BINAP and (*R*)-Segphos, were obtained from Takasago International Corporation. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of Unsymmetrical Dienynes

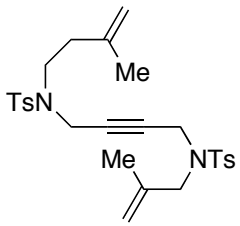
4-Methyl-*N*-(2-methylallyl)-*N*-[4-(2-methylallyloxy)but-2-ynyl]benzenesulfonamide (1a). 4-Methyl-*N*-(2-methylallyl)-benzenesulfonamide[1] (0.530 g, 2.35 mmol) and triphenylphosphine (0.561 g, 2.14 mmol) were dissolved in THF (20 mL). To this were added 4-(2-methylallyloxy)but-2-yn-1-ol[2] (0.300 g, 2.14 mmol) dropwise and then diisopropyl azadicarboxylate (0.433 g, 2.14 mmol) in a portion at 0 °C. The resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 15:1), which furnished **1a** (0.724 g, 2.08 mmol, 97% yield) as a colorless oil.



IR (neat) 2977, 2917, 2853, 1422, 1348, 1163, 1097, 904, 659 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 4.96 (s, 2H), 4.90 (s, 2H), 4.09 (s, 2H),

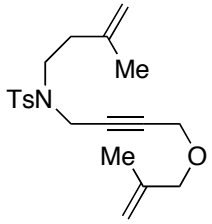
3.83 (t, J = 1.8 Hz, 2H), 3.74 (t, J = 1.8 Hz, 2H), 3.72 (s, 2H), 2.42 (s, 3H), 1.77 (s, 3H), 1.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 141.3, 139.2, 136.1, 129.3, 127.8, 115.4, 112.9, 81.6, 78.7, 73.3, 56.8, 52.5, 35.8, 21.5, 19.7, 19.4; HRMS (ESI) calcd for $C_{19}H_{25}NO_3SNa$ $[M+Na]^+$ 370.1453, found 370.1428.

4-Methyl-*N*-(3-methylbut-3-enyl)-*N*-{4-[(2-methylprop-3-enyl)(toluene-4-sulfonyl)amino] but-2-ynyl}benzenesulfonamide (1b). To a CH_3CN (10 mL) solution of 4-methyl-*N*-(3-methylbut-3-enyl)benzenesulfonamide[3] (0.255 g, 1.07 mmol) was added K_2CO_3 (0.148 g, 1.07 mmol). The resulting mixture was stirred at room temperature for 30 min. *N*-(4-Chlorobut-2-ynyl)-4-methyl-*N*-(2-methylprop-2-enyl)benzenesulfonamide[4] (0.300 g, 0.97 mmol) was added, and the resulting mixture was stirred at 80 °C for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1), which furnished **1b** (0.450 g, 0.874 mmol, 90% yield) as a colorless solid.



Mp 87.1–87.3 °C; IR (neat) 2974, 2920, 2868, 1443, 1348, 1161, 1096, 905, 661 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.90 (s, 1H), 4.78 (s, 1H), 4.72 (s, 1H), 4.66 (s, 1H), 3.87 (s, 2H), 3.82 (s, 2H), 3.52 (s, 2H), 3.12 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 2.12 (t, J = 7.5 Hz, 2H), 1.71 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.6, 143.5, 141.9, 139.0, 135.9, 135.8, 129.4, 129.3, 127.6, 127.4, 115.2, 112.3, 78.2, 78.1, 52.3, 44.4, 36.0, 35.6, 35.3, 22.0, 21.42, 21.40, 19.5; HRMS (FAB) calcd for $C_{27}H_{35}N_2O_4S_2$ $[M+H]^+$ 515.2038, found 515.2068.

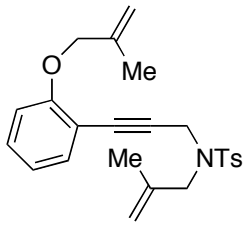
4-Methyl-*N*-[4-(2-methylallyloxy)but-2-ynyl]-*N*-(3-methylbut-3-enyl)benzenesulfonamide (1c). This compound (0.584 g, 1.62 mmol, 76% yield) was prepared from 4-(2-methylallyloxy)-2-butyn-1-ol[2] (0.300 g, 2.14 mmol) and 4-methyl-*N*-(3-methylbut-3-enyl)benzenesulfonamide[3] (0.562 g, 2.35 mmol) by the procedure described for **1b**.



Colorless oil; IR (neat) 3075, 2973, 2920, 1453, 1347, 1162, 1098, 901, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.90 (s, 2H), 4.80 (s, 1H),

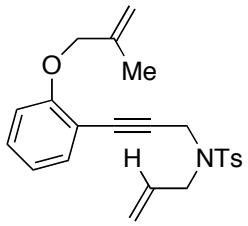
4.74 (s, 1H), 4.19 (t, J = 1.8 Hz, 2H), 3.88 (t, J = 1.8 Hz, 2H), 3.75 (s, 2H), 3.31 (t, J = 7.5 Hz, 2H), 2.41 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 1.76 (s, 3H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 142.1, 141.2, 135.9, 129.4, 127.7, 112.9, 112.4, 81.6, 78.9, 73.4, 56.8, 44.6, 36.5, 35.9, 22.1, 21.5, 19.4; HRMS (ESI) calcd for $C_{20}H_{27}NO_3SNa$ $[M+Na]^+$ 384.1609, found 384.1624.

4-Methyl-*N*-(2-methylallyl)-*N*-{3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl}benzenesulfonamide (1d). To a solution of 1-iodo-2-(2-methylallyloxy)benzene[5] (0.344 g, 1.26 mmol) in i-Pr_2NH (20 mL) were added $PdCl_2(PPh_3)_2$ (16 mg, 0.023 mmol) and CuI (8.7 mg, 0.046 mmol). 4-Methyl-*N*-(2-methylallyl)-*N*-prop-2-ynylbenzenesulfonamide[6] (0.300 g, 1.14 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished **1d** (0.353 g, 0.862 mmol, 76% yield) as a yellow solid.



Mp 55.6–56.0 °C; IR (neat) 3079, 2974, 2918, 1597, 1492, 1444, 1348, 1163, 903, 754, 658 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, J = 8.4 Hz, 2H), 7.23 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.92 (dd, J = 7.5, 1.8 Hz, 1H), 6.81 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 6.78 (dd, J = 7.5, 1.8 Hz, 1H), 5.10–5.03 (m, 2H), 5.03–4.94 (m, 2H), 4.41 (s, 2H), 4.30 (s, 2H), 3.81 (s, 2H), 2.27 (s, 3H), 1.80 (s, 3H), 1.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 143.2, 140.3, 139.3, 136.1, 133.4, 129.6, 129.4, 127.8, 120.2, 115.5, 112.8, 112.0, 85.6, 82.2, 72.0, 52.5, 36.7, 21.3, 19.8, 19.3; HRMS (ESI) calcd for $C_{24}H_{27}NO_3SNa$ $[M+Na]^+$ 432.1609, found 432.1607.

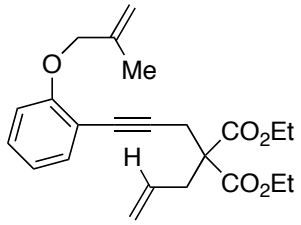
***N*-Allyl-4-methyl-*N*-{3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl}benzenesulfonamide (1e).** This compound (0.725 g, 1.83 mmol, 57% yield) was prepared from 1-iodo-2-(2-methylallyloxy)benzene[5] (0.959 g, 3.50 mmol) and *N*-allyl-4-methyl-*N*-prop-2-ynylbenzenesulfonamide[7] (0.800 g, 3.20 mmol) by the procedure described for **1d**.



Yellow solid: mp 32.2–32.5 °C; IR (neat) 2980, 2919, 2865, 1491, 1445, 1348, 1162, 897, 754, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (d, J = 8.4 Hz, 2H), 7.24 (ddd, J = 7.5, 7.5, 1.8 Hz,

1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.81 (ddd, *J* = 7.5, 7.5, 1.8 Hz, 1H), 6.78 (dd, *J* = 7.5, 1.8 Hz, 1H), 5.79 (ddt, *J* = 17.1, 10.2, 6.3 Hz, 1H), 5.34 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.24 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.11–5.02 (m, 1H), 5.02–4.91 (m, 1H), 4.42 (s, 2H), 4.35 (s, 2H), 3.90 (d, *J* = 6.3 Hz, 2H), 2.28 (s, 3H), 1.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 143.3, 140.3, 136.0, 133.4, 132.1, 129.6, 129.4, 127.8, 120.3, 120.0, 112.8, 112.0, 85.6, 82.2, 77.2, 72.0, 49.1, 37.0, 21.4, 19.3; HRMS (FAB) calcd for $C_{23}H_{26}NO_3S$ $[M+H]^+$ 396.1633, found 396.1635.

2-Allyl-2-{3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl}malonic acid diethyl ester (1f). This (1.09 g, 2.83 mmol, 62% yield) was prepared from 1-iodo-2-(2-methylallyloxy)benzene[5] (1.50 g, 5.47 mmol) and 2-allyl-2-prop-2-ynyl-malonic acid diethyl ester[8] (1.10 g, 4.56 mmol) by the procedure described for **1d**.

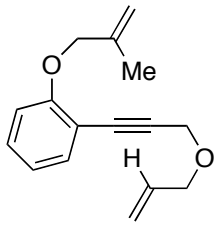


Yellow oil: IR (neat) 3078, 2980, 2935, 1735, 1492, 1445, 1289, 1215, 909, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.21 (ddd, *J* = 7.5, 7.5, 1.8 Hz, 1H), 6.86 (ddd, *J* = 7.5, 7.5, 1.8 Hz, 1H), 6.82 (dd, *J* = 7.5, 1.8 Hz, 1H), 5.70 (ddt, *J* = 17.4, 10.2, 7.5 Hz, 1H), 5.21 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.13 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.14–5.07 (m, 1H), 5.01–4.94 (m, 1H), 4.47 (s, 2H), 4.21 (q, *J* = 6.9 Hz, 4H), 3.07 (s, 2H), 2.75 (d, *J* = 12.3, Hz, 2H), 1.84 (s, 3H), 1.25 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.9, 159.2, 140.6, 133.6, 132.1, 129.1, 120.4, 119.6, 113.0, 112.7, 112.2, 88.3, 79.7, 72.0, 61.5, 57.1, 36.5, 23.8, 19.3, 14.1; HRMS (ESI) calcd for $C_{23}H_{28}O_5Na$ $[M+Na]^+$ 407.1834, found 407.1828.

1-(3-Allyloxyprop-1-ynyl)-2-(2-methylallyloxy)benzene (1g). To a solution of 1-iodo-2-(2-methylallyloxy)benzene[5] (2.00 g, 7.3 mmol) in *i*-Pr_2NH (40 mL) were added $PdCl_2(PPh_3)_2$ (103 mg, 0.147 mmol) and CuI (55.7 mg, 0.292 mmol). Propargyl alchol (0.409 g, 7.30 mmol) was added dropwise and the resulting mixture was stirred at 60 °C for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished 3-[2-(2-methylallyloxy)phenyl]prop-2-yn-1-ol (1.02 g, 5.05 mmol, 69% yield) as a colorless oil.

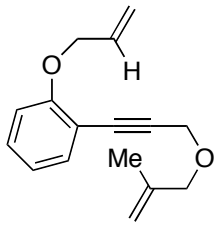
To a THF (20 mL) solution of 3-[2-(2-methylallyloxy)phenyl]prop-2-yn-1-ol (0.400 g, 2.00 mmol) was added NaH (0.576 g, 2.40 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 30 min. 3-Bromopropene (0.363 g, 3.00 mmol) was added, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc

= 50:1), which furnished **1g** (0.208 g, 0.858 mmol, 43% yield) as a yellow oil.



IR (neat) 3078, 2977, 2916, 2852, 1491, 1445, 1262, 1086, 1013, 907, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41 (dd, J = 7.5, 1.8 Hz, 1H), 7.26 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 6.89 (ddd, J = 7.5, 7.5, 1.8 Hz, 1H), 6.85 (dd, J = 7.5, 1.8 Hz, 1H), 5.95 (ddt, J = 15.9, 11.1, 5.7 Hz, 1H), 5.34 (dd, J = 15.9, 1.5 Hz, 1H), 5.22 (dd, J = 11.1, 1.5 Hz, 1H), 5.18–5.13 (m, 1H), 5.02–4.96 (m, 1H), 4.49 (s, 2H), 4.43 (s, 2H), 4.16 (d, J = 5.7 Hz, 2H), 1.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.3, 140.5, 134.2, 133.6, 129.6, 120.5, 117.7, 112.6, 112.4, 112.2, 89.1, 82.7, 72.1, 70.4, 58.1, 19.3; HRMS (ESI) calcd for $C_{16}H_{18}O_2Na$ $[M+Na]^+$ 265.1205, found 265.1203.

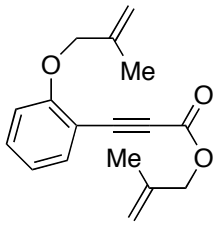
1-Allyloxy-2-[3-(2-methylallyloxy)prop-1-ynyl]benzene (1h). This compound (0.452 g, 1.87 mmol, 68% yield) was prepared from 1-allyloxy-2-iodobenzene[9] (0.853 g, 3.28 mmol) and 2-methyl-3-prop-2-ynyloxypropene[10] (0.300 g, 2.73 mmol) by the procedure described for **1d**.



Yellow oil; IR (neat) 3077, 2917, 2850, 2364, 1491, 1445, 1264, 1085, 997, 927, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42 (dd, J = 7.5, 1.2 Hz, 1H), 7.26 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 6.90 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 6.88 (dd, J = 7.5, 1.2 Hz, 1H), 6.07 (ddt, J = 17.1, 10.2, 5.1 Hz, 1H), 5.47 (ddt, J = 17.1, 4.8, 1.8 Hz, 1H), 5.29 (ddt, J = 10.2, 4.8, 1.8 Hz, 1H), 5.08–5.00 (m, 1H), 4.97–4.88 (m, 1H), 4.61 (dt, J = 4.8, 1.8 Hz, 2H), 4.41 (s, 2H), 4.08 (s, 2H), 1.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 141.6, 133.6, 133.0, 129.6, 120.6, 117.4, 112.9, 112.5, 112.3, 89.3, 82.5, 73.4, 69.2, 57.9, 19.6; HRMS (ESI) calcd for $C_{16}H_{18}O_2Na$ $[M+Na]^+$ 265.1205, found 265.1203.

[2-(2-Methylallyloxy)phenyl]propynoic acid 2-methylallyl ester (1i). To a CH_3CN (20 mL) solution of 3-(2-hydroxyphenyl)propynoic acid[11] (0.400 g, 2.47 mmol) was added K_2CO_3 (0.683 g, 4.94 mmol), and the resulting mixture was stirred at room temperature for 30 min. 3-Bromo-2-methylpropene (0.367 g, 2.72 mmol) was added, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The

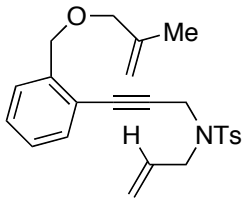
residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished **1i** (0.523 g, 1.93 mmol, 78% yield) as a yellow oil.



IR (neat) 2919, 2326, 2220, 1709, 1491, 1446, 1301, 1175, 1011, 904, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54 (dd, J = 7.5, 1.5 Hz, 1H), 7.38 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 6.94 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 6.88 (dd, J = 7.5, 1.5 Hz, 1H), 5.26–5.17 (m, 1H), 5.09–5.04 (m, 1H), 5.04–4.95 (m, 2H), 4.65 (s, 2H), 4.51 (s, 2H), 1.86 (s, 3H), 1.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.8, 154.0, 140.0, 139.1, 134.7, 132.2, 120.6, 113.7, 112.6, 112.2, 109.3, 84.5, 83.6, 72.0, 69.0, 19.4, 19.2; HRMS (FAB) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ 271.1334, found 271.1340.

***N*-Allyl-4-methyl-*N*-{3-[2-(2-methylallyloxymethyl)phenyl]prop-2-ynyl}benzenesulfonamide (1j).** To a EtOH (40 mL) solution of $NaBH_4$ (0.310 g, 8.18 mmol) was added dropwise *N*-allyl-*N*-[3-(2-formylphenyl)prop-2-ynyl]-4-methylbenzenesulfonamide[12] (2.22 g, 6.29 mmol) at 0 °C, and the resulting mixture was stirred at 0 °C for 2 h. The reaction was quenched with water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1), which furnished *N*-allyl-*N*-[3-(2-hydroxymethylphenyl)prop-2-ynyl]-4-methylbenzenesulfonamide (2.03 g, 5.70 mmol, 91% yield) as a colorless oil.

To a THF (20 mL) solution of *N*-allyl-*N*-[3-(2-hydroxymethylphenyl)prop-2-ynyl]-4-methylbenzenesulfonamide (1.00 g, 2.81 mmol) was added NaH (0.0812 g, 3.38 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min. 3-Bromo-2-methylpropene (0.456 g, 3.38 mmol) was added at 0 °C, and the resulting mixture was stirred at room temperature for 16 h. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by preparative TLC (hexane/EtOAc = 10:1), which furnished *N*-allyl-4-methyl-*N*-{3-[2-(2-methylallyloxymethyl)phenyl]prop-2-ynyl}benzenesulfonamide (50.2 mg, 0.0127 mmol, 5% yield, unoptimized) as a colorless oil.



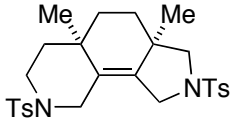
IR (neat) 2918, 2853, 2367, 1349, 1164, 1092, 897, 760, 663 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 5.80 (ddt, J = 16.5, 9.9, 6.3 Hz,

1H), 5.33 (d, *J* = 16.5 Hz, 1H), 5.27 (d, *J* = 9.9 Hz, 1H), 5.00 (s, 1H), 4.92 (s, 1H), 4.37 (s, 2H), 4.35 (s, 2H), 3.91 (s, 2H), 3.89 (d, *J* = 6.3 Hz, 2H), 2.28 (s, 3H), 1.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.6, 142.0, 140.2, 136.0, 132.1, 129.5, 128.6, 127.7, 127.2, 126.9, 120.5, 119.9, 112.3, 86.3, 83.4, 74.5, 69.7, 49.3, 36.8, 21.4, 19.5; HRMS (ESI) calcd for $C_{24}H_{27}NO_3SNa$ $[M+Na]^+$ 432.1609, found 432.1601.

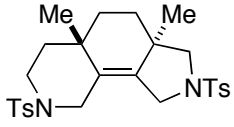
III. Intramolecular [2 + 2 + 2] Cycloaddition of Unsymmetrical Dienynes

General Procedure (Table 1, entry 1). Under an Ar atmosphere, a CH_2Cl_2 (1.0 mL) solution of (*R*)-H_8-BINAP (6.3 mg, 0.010 mmol) was added to a CH_2Cl_2 (1.0 mL) solution of $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) at room temperature, and the solution was stirred at room temperature for 5 min. H_2 (1 atm) was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting solution was concentrated to dryness and the residue was dissolved in $(CH_2Cl)_2$ (0.5 mL). To this solution was added a $(CH_2Cl)_2$ (1.5 mL) solution of **1b** (102.9 mg, 0.200 mmol). The solution was stirred at 80 °C for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc = 2:1), which furnished the mixture of **2b** and **3b** [102.9 mg, 0.200 mmol, >99% yield, **2b**/**3b** = 1:2.4, 4% ee (**2b**), 99% ee (**3b**)] as a colorless oil.

3a,5a-Dimethyl-2,8-bis-(toluene-4-sulfonyl)-2,3,3a,4,5,5a,6,7,8,9-decahydro-1*H*-pyrrolo[3, 4-*h*]isoquinoline [2b/3b = 1:2.4, Table 1, entry 1, >99% yield, 4% ee (2b), 99% ee (3b)].



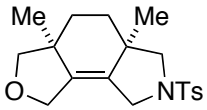
2b



3b

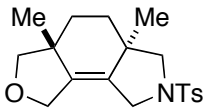
$[\alpha]^{25}_D$ +12.1° [acetone, *c* 1.430, a mixture of **2b** (4% ee) and **3b** (99% ee)]; IR (neat) 3398, 2926, 2864, 2368, 2367, 1344, 1160, 1093, 942, 815, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) **2b**: δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.42–7.21 (m, 4H), 4.05 (d, *J* = 14.1 Hz, 1H), 3.91 (d, *J* = 14.1 Hz, 2H), 3.62–3.53 (m, 1H), 3.44 (d, *J* = 8.7 Hz, 1H), 2.93 (d, *J* = 12.9 Hz, 1H), 2.74–2.56 (m, 1H), 2.49 (d, *J* = 8.7 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 1.66–1.31 (m, 4H), 1.20–1.10 (m, 2H), 1.07 (s, 3H), 0.94 (s, 3H); **3b**: δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.42–7.21 (m, 4H), 3.94 (d, *J* = 12.9 Hz, 2H), 3.81 (d, *J* = 12.9 Hz, 1H), 3.76–3.65 (m, 1H), 3.40 (d, *J* = 9.3 Hz, 1H), 2.95 (d, *J* = 12.6 Hz, 1H), 2.81 (d, *J* = 9.3 Hz, 1H), 2.74–2.56 (m, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 1.66–1.31 (m, 6H), 0.83 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.5, 143.44, 134.40, 137.0, 135.4, 134.3, 133.6, 129.8, 129.6, 128.8, 127.7, 127.5, 127.4, 127.3, 61.2, 61.0, 60.3, 48.6, 47.8, 44.8, 44.0, 42.4, 42.3, 41.5, 41.3, 39.3, 37.5, 34.8, 34.6, 33.1, 32.9, 29.8, 28.4, 25.1, 24.3, 23.6, 22.9, 21.5, 21.4, 21.0, 14.1; HRMS (FAB) calcd for $C_{27}H_{35}N_2O_4S_2$ $[M+H]^+$ 515.2038, found 515.2045; CHIRALPAK AD, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 110.6 min (minor *cis*-isomer), 125.4 min (minor *trans*-isomer), 159.7 min (major *cis*-isomer), and 240.0 min (major *trans*-isomer).

(+)-3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1*H*-2-oxa-7-aza-*as*-indacene [(+)-2a, eq 1, 81% yield, 38% ee].



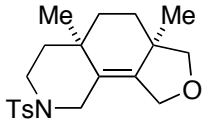
Colorless oil; $[\alpha]^{25}_{D}$ +10.8° (acetone, *c* 3.140, 38% ee); IR (neat) 3390, 2962, 2925, 2866, 2326, 1453, 1345, 1166, 1093, 1053, 817, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.27 (d, J = 13.2 Hz, 1H), 4.06 (d, J = 13.2 Hz, 1H), 3.84 (d, J = 13.2 Hz, 1H), 3.83 (d, J = 7.8 Hz, 1H), 3.62 (d, J = 13.2 Hz, 1H), 3.32 (d, J = 9.3 Hz, 1H), 3.12 (d, J = 7.8 Hz, 1H), 2.70 (d, J = 9.3 Hz, 1H), 2.43 (s, 3H), 1.73–1.42 (m, 2H), 1.33–1.05 (m, 2H), 1.10 (s, 3H), 1.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.5, 137.5, 133.8, 130.3, 129.6, 127.4, 79.8, 67.5, 59.0, 47.9, 41.2, 40.3, 30.1, 29.6, 26.0, 23.7, 21.5; HRMS (ESI) calcd for $C_{19}H_{25}NO_3SNa$ $[M+Na]^+$ 370.1453, found 370.1433; CHIRALPAK AD-H, hexane:2-PrOH = 95:5, 1.0 mL/min, retention times: 27.6 min (major isomer) and 32.8 min (minor isomer).

(+)-3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1*H*-2-oxa-7-aza-*as*-indacene [(+)-3a, eq 1, 17% yield, 93% ee].



Colorless oil; $[\alpha]^{25}_{D}$ +7.9° (acetone, *c* 0.965, 93% ee); IR (neat) 3390, 2966, 2933, 2862, 2366, 1456, 1343, 1161, 1094, 1041, 817, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.30 (d, J = 12.3 Hz, 1H), 4.06 (d, J = 12.3 Hz, 1H), 3.89 (d, J = 12.6 Hz, 1H), 3.77 (d, J = 7.5 Hz, 1H), 3.64 (d, J = 12.6 Hz, 1H), 3.47 (d, J = 9.0 Hz, 1H), 3.25 (d, J = 7.5 Hz, 1H), 2.84 (d, J = 9.0 Hz, 1H), 2.43 (s, 3H), 1.73–1.42 (m, 4H), 1.04 (s, 3H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.4, 135.4, 134.7, 129.6, 129.4, 127.3, 80.3, 66.5, 61.2, 47.7, 42.2, 41.7, 29.5, 28.2, 24.7, 24.2, 21.5; HRMS (ESI) calcd for $C_{19}H_{25}NO_3SNa$ $[M+Na]^+$ 370.1453, found 370.1441; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 27.5 min (minor isomer) and 32.0 min (major isomer).

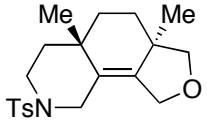
(+)-Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-*h*]isoquinoline [(+)-2c, Table 1, entry 2, 24% yield, 45% ee].



Colorless solid; mp 139.1–139.3 °C; $[\alpha]^{25}_{D}$ +67.1° (acetone, *c* 0.830, 45% ee); IR (neat) 3390, 2925, 2853, 2366, 2327, 1349, 1156, 1092, 1053, 923, 678 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.49 (d, J = 13.2 Hz, 1H), 4.41 (dd, J = 13.2, 1.2 Hz, 1H), 3.90 (dd, J = 12.6, 1.2 Hz, 1H), 3.77 (d, J = 7.8 Hz, 1H), 3.73–3.62 (m, 1H), 3.27 (d,

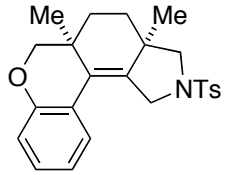
J = 7.8 Hz, 1H), 2.99 (d, *J* = 12.6 Hz, 1H), 2.73 (dt, *J* = 12.6, 3.3 Hz, 1H), 2.44 (s, 3H), 1.89–1.70 (m, 2H), 1.65–1.41 (m, 2H), 1.29–1.18 (m, 2H), 1.09 (s, 3H), 0.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.5, 141.1, 133.6, 129.6, 127.6, 126.5, 81.0, 67.9, 44.3, 42.6, 42.1, 37.9, 35.0, 33.2, 28.7, 25.2, 22.9, 21.5; HRMS (ESI) calcd for $C_{20}H_{27}NO_3SNa$ $[M+Na]^+$ 384.1609, found 384.1596; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 37.9 min (minor isomer) and 41.1 min (major isomer).

(3a*R*,5a*S*)-(+)-3a,5a-Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-*h*]isoquinoline [(3a*R*,5a*S*)-(+)-3c, Table 1, entry 2, 75% yield, >99% ee].



Colorless solid; mp 131.2–131.5 °C; $[\alpha]^{25}_D$ +51.5° (acetone, *c* 2.100, >99% ee); IR (neat) 3394, 2966, 2928, 2857, 2368, 2327, 1456, 1349, 1156, 1092, 1031, 676 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.50 (dd, *J* = 12.6, 1.2 Hz, 1H), 4.24 (d, *J* = 12.6 Hz, 1H), 3.91 (dd, *J* = 12.6, 1.2 Hz, 1H), 3.76 (d, *J* = 7.5 Hz, 1H), 3.80–3.67 (m, 1H), 3.24 (d, *J* = 7.5 Hz, 1H), 3.09 (d, *J* = 12.6 Hz, 1H), 2.69 (dt, *J* = 12.6, 3.9 Hz, 1H), 2.44 (s, 3H), 1.67–1.30 (m, 6H), 1.09 (s, 3H), 0.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.4, 139.2, 133.9, 129.6, 127.6, 125.3, 80.8, 67.1, 45.0, 42.4, 41.9, 39.4, 35.1, 33.3, 27.2, 23.8, 22.9, 21.5; HRMS (ESI) calcd for $C_{20}H_{27}NO_3SNa$ $[M+Na]^+$ 384.1609, found 384.1609; CHIRALPAK AD-H, hexane/2-PrOH = 90:10, 1.0 mL/min, retention times: 14.1 min (minor isomer) and 23.8 min (major isomer). The absolute configuration was determined by X-ray crystallographic analysis (CCDC 673294).

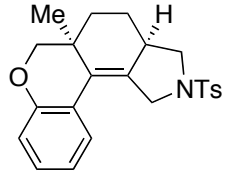
(+)-3a,5a-Dimethyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-azacyclopenta[*c*]phenanthrene [(+)-2d, Table 1, entry 3, 98% yield, 94% ee].



Colorless solid; mp 136.0–136.2 °C; $[\alpha]^{25}_D$ +2.5° (acetone, *c* 0.680, 94% ee); IR (neat) 3394, 2925, 2864, 2369, 2331, 1485, 1341, 1233, 1164, 1094, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.15 (ddd, *J* = 7.8, 6.3, 1.2 Hz, 1H), 6.90 (dd, *J* = 6.3, 1.2 Hz, 2H), 6.77 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.48 (d, *J* = 14.4 Hz, 1H), 3.94 (d, *J* = 14.4 Hz, 1H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.77 (d, *J* = 10.2 Hz, 1H), 3.45 (d, *J* = 9.3 Hz, 1H), 2.65 (d, *J* = 9.3 Hz, 1H), 2.40 (s, 3H), 1.79 (ddd, *J* = 12.3, 3.9, 3.9 Hz, 1H), 1.66 (ddd, *J* = 12.3, 3.9, 3.9 Hz, 1H), 1.47 (ddd, *J* = 12.3, 3.9, 3.9 Hz, 1H), 1.25 (ddd, *J* = 12.3, 3.9, 3.9 Hz, 1H), 1.17 (s, 3H), 1.08 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.0, 143.4, 133.8, 133.5, 129.7, 129.6, 128.8, 128.3, 127.4, 120.9, 119.9, 115.9, 75.5, 60.1, 50.2, 42.7, 31.5, 30.3, 30.0, 25.3, 24.4, 21.5; HRMS (FAB) calcd for $C_{24}H_{28}NO_3S$ $[M+H]^+$ 410.1790, found 410.1750; CHIRALPAK AD-H,

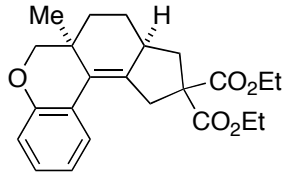
hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 15.7 min (major isomer) and 19.1 min (minor isomer).

(3a*R*,5a*S*)-(+)-5a-Methyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-aza-cyclopenta[*c*]phenanthrene [(3a*R*,5a*S*)-(+)-2e, Table 1, entry 5, 89% yield, 99% ee].



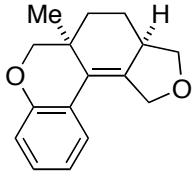
Orange solid; mp 172.1–172.5 °C; $[\alpha]^{25}_{D}$ +23.3° (acetone, *c* 2.470, 99% ee); IR (neat) 3062, 2927, 2865, 2370, 2318, 1484, 1449, 1343, 1233, 1161, 1094, 758, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.16 (ddd, *J* = 8.1, 6.3, 1.2 Hz, 1H), 7.03–6.84 (m, 2H), 6.78 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.41 (dd, *J* = 14.4, 1.2 Hz, 1H), 3.94 (dd, *J* = 14.4, 1.2 Hz, 1H), 3.85 (d, *J* = 10.2 Hz, 1H), 3.82 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 8.4 Hz, 1H), 2.83–2.66 (m, 1H), 2.55 (dd, *J* = 16.2, 8.4 Hz, 1H), 2.40 (s, 3H), 1.92–1.79 (m, 1H), 1.67–1.50 (m, 2H), 1.13–0.95 (m, 1H), 1.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.0, 143.4, 133.4, 130.2, 130.1, 129.7, 128.7, 128.0, 127.5, 121.0, 120.0, 116.0, 75.6, 60.3, 52.5, 51.1, 40.4, 32.6, 31.7, 24.9, 23.4; HRMS (ESI) calcd for $C_{23}H_{25}NO_3SNa$ $[M+Na]^+$ 418.1453, found 418.1450; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 20.2 min (major isomer) and 26.8 min (minor isomer). The absolute configuration was determined by X-ray crystallographic analysis (CCDC 673295).

(+)-5a-Methyl-3,3a,4,5,5a,6-hexahydro-1*H*-7-oxacyclopenta[*c*]phenanthrene-2,2-dicarboxylic acid diethyl ester [(+)-2f, Table 1, entry 7, 87% yield, 97% ee].



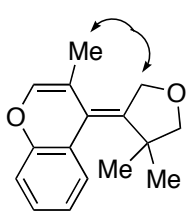
Colorless oil; $[\alpha]^{25}_{D}$ +81.9° (acetone, *c* 3.665, 97% ee); IR (neat) 3413, 2928, 2368, 2327, 1731, 1254, 1232, 1176, 1065, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29 (dd, *J* = 8.1, 1.5Hz, 1H), 7.11 (ddd, *J* = 8.1, 1.5, 1.5 Hz, 1H), 6.88 (ddd, *J* = 8.1, 1.5, 1.5 Hz, 1H), 6.78 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 10.2 Hz, 1H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.50 (d, *J* = 17.7 Hz, 1H), 3.67 (dd, *J* = 17.7, 1.8 Hz, 1H), 2.70–2.46 (m, 2H), 1.92 (ddt, *J* = 9.0, 4.5, 4.5 Hz, 1H), 1.80–1.68 (m, 1H), 1.66–1.57 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.24–1.13 (m, 1H), 1.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3, 171.7, 153.1, 134.9, 129.0, 128.7, 127.9, 122.2, 119.5, 115.8, 76.3, 61.6, 61.5, 58.9, 41.2, 39.7, 38.9, 33.3, 32.1, 25.7, 25.1, 14.0, 13.9; HRMS (ESI) calcd for $C_{23}H_{28}O_5Na$ $[M+Na]^+$ 407.1834, found 407.1834; CHIRALPAK AD-H, hexane/2-PrOH = 98:2, 1.0 mL/min, retention times: 7.3 min (minor isomer) and 8.0 min (major isomer).

(+)-5a-Methyl-3,3a,4,5,5a,6-hexahydro-1*H*-2,7-dioxa-cyclopenta[*c*]phenanthrene [(+)-2g, Table 1, entry 9, 95% yield, 93% ee].

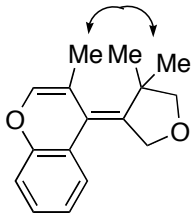


Colorless oil; $[\alpha]^{25}_{D}$ +72.4° (acetone, *c* 2.265, 93% ee); IR (neat) 3357, 2927, 2862, 2365, 2331, 1484, 1449, 1231, 1042, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.08 (m, 1H), 6.96–6.74 (m, 3H), 4.82 (d, *J* = 13.5 Hz, 1H), 4.45 (d, *J* = 13.5 Hz, 1H), 4.20 (dd, *J* = 16.2, 8.1 Hz, 1H), 4.06 (d, *J* = 10.2 Hz, 1H), 3.88 (d, *J* = 10.2 Hz, 1H), 3.19 (dd, *J* = 16.2, 8.1 Hz, 1H), 2.88–2.67 (m, 1H), 1.97–1.85 (m, 1H), 1.74–1.65 (m, 2H), 1.18–1.03 (m, 1H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.0, 134.8, 128.3, 128.1, 127.9, 121.7, 119.9, 116.1, 75.9, 72.9, 70.1, 41.7, 33.3, 31.9, 25.3, 22.9; HRMS (FAB) calcd for $C_{16}H_{19}O_2$ $[M+H]^+$ 243.1385, found 265.1404; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 6.5 min (minor isomer) and 8.5 min (major isomer).

4-(4,4-Dimethyldihydrofuran-3-ylidene)-3-methyl-4*H*-chromene [4, Table 1, entry 10, 70% yield (*E*/*Z* = 1:3.3)].



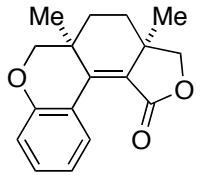
minor-*E*



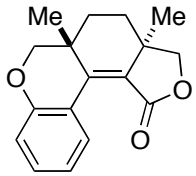
major-*Z*

Colorless oil; IR (neat) 3360, 2961, 2368, 2327, 1475, 1452, 1229, 1124, 1080, 959, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ 7.24–7.14 (m, 1H), 7.14–6.97 (m, 3H), 6.67 (d, *J* = 1.2 Hz, 1H), 4.63 (s, 2H), 3.51 (s, 2H), 2.07 (d, *J* = 1.2 Hz, 3H), 1.36 (s, 6H); *Z*-isomer: δ 7.43 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.24–7.14 (m, 1H), 7.14–6.97 (m, 2H), 6.60 (d, *J* = 1.2 Hz, 1H), 4.67 (s, 2H), 3.47 (s, 2H), 1.90 (d, *J* = 0.2 Hz, 3H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.4, 141.0, 140.5, 140.1, 139.9, 128.6, 127.5, 127.0, 126.5, 126.4, 124.3, 122.5, 122.0, 120.94, 120.90, 116.5, 115.6, 115.5, 115.3, 83.1, 83.0, 77.4, 73.52, 73.49, 65.4, 42.9, 42.5, 24.9, 23.6, 19.0, 16.8; HRMS (FAB) calcd for $C_{16}H_{19}O_2$ $[M+H]^+$ 243.1385, found 243.1421. The double bond geometry was determined by NOE experiments shown the above structures.

3a,5a-Dimethyl-3,3a,4,5,5a,6-hexahydro-2,7-dioxa-cyclopenta[*c*]phenanthren-1-one [2i/3i = 14:1, Table 1, entry 11, 57% yield, 96% ee (2i), >99% ee (3i)].



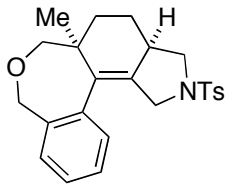
2i



3i

Yellow solid; mp 155.7–156.1 °C; $[\alpha]^{25}_{D}$ –170.9° [acetone, *c* 0.895, a mixture of **2i** (96% ee) and **3i** (>99% ee)] IR (neat) 3398, 2954, 2370, 2327, 1769, 1489, 1265, 1222, 1058, 1025, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) **2i**: δ 7.72 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.07 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1H), 6.92 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1H), 6.83 (dd, *J* = 7.5, 1.5 Hz, 1H), 4.20 (d, *J* = 9.3 Hz, 1H), 4.11 (d, *J* = 10.2 Hz, 1H), 3.97 (d, *J* = 9.3 Hz, 1H), 3.78 (d, *J* = 10.2 Hz, 1H), 1.61 (d, *J* = 4.5 Hz, 1H), 1.56 (d, *J* = 4.5 Hz, 1H), 1.51 (s, 3H), 1.26 (d, *J* = 5.4 Hz, 1H), 1.20 (s, 3H), 1.03 (d, *J* = 5.4 Hz, 1H); **3i**: δ 7.07 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1H), 6.92 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1H), 6.83 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.31 (d, *J* = 10.2 Hz, 1H), 4.26 (d, *J* = 10.2 Hz, 1H), 4.09 (d, *J* = 10.2 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H), 1.61 (d, *J* = 4.5 Hz, 1H), 1.58 (s, 3H), 1.56 (d, *J* = 4.5 Hz, 1H), 1.26 (d, *J* = 5.4 Hz, 1H), 1.14 (s, 3H), 1.03 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 129.0, 126.1, 126.0, 121.4, 117.6, 71.4, 66.8, 30.2, 29.9, 28.8, 24.1, 24.0, 18.0, 16.5, 14.9; HRMS (ESI) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ 293.1154, found 293.1148; CHIRALPAK AD-H, hexane/2-PrOH = 95:5, 1.0 mL/min, retention times: 11.6 min (major *cis*-isomer), 13.8 min (minor *cis*-isomer), 14.3 min (minor *trans*-isomer), and 17.9 min (major *trans*-isomer).

(+)-5,7,7a,8,9,10-hexahydro-10,11-(*N*-(4-methylphenylsulfonyl)methaniminomethano)-7 a-methyl-Dibenz[c,e]oxepin [(+)-2j, Table 1, entry 12, 81% yield, 98% ee].



Yellow solid; mp 118.2–118.4 °C; $[\alpha]^{25}_{D}$ +12.7° (acetone, *c* 1.035, 98% ee); IR (neat) 3360, 2925, 2853, 2370, 2326, 1770, 1457, 1340, 1160, 1095, 811, 762, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.30–7.18 (m, 4H), 7.15–7.10 (m, 1H), 7.02–6.97 (m, 1H), 4.47 (d, *J* = 13.2 Hz, 1H), 4.11 (d, *J* = 13.2 Hz, 1H), 4.05 (d, *J* = 14.4 Hz, 1H), 3.86–3.73 (m, 1H), 3.68 (d, *J* = 11.7 Hz, 1H), 3.61 (d, *J* = 11.7 Hz, 1H), 3.40 (d, *J* = 14.4 Hz, 1H), 2.73–2.60 (m, 2H), 2.43 (s, 3H), 1.92–1.81 (m, 1H), 1.59–1.48 (m, 2H), 1.37–1.20 (m, 1H), 0.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.3, 139.7, 138.6, 136.2, 134.3, 133.8, 129.8, 129.6, 127.83, 127.78, 127.43, 127.37, 84.6, 74.7, 54.0, 50.6, 40.1, 37.3, 35.0, 25.5, 22.8, 21.5; HRMS (ESI) calcd for $C_{24}H_{27}NO_3SNa$ $[M+Na]^+$ 432.1609, found 432.1612; CHIRALPAK AD-H, hexane/2-PrOH = 90:10, 1.0 mL/min, retention times: 20.8 min (major isomer) and 27.3 min (minor isomer).

IV. References

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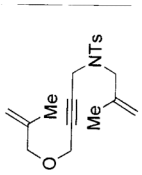
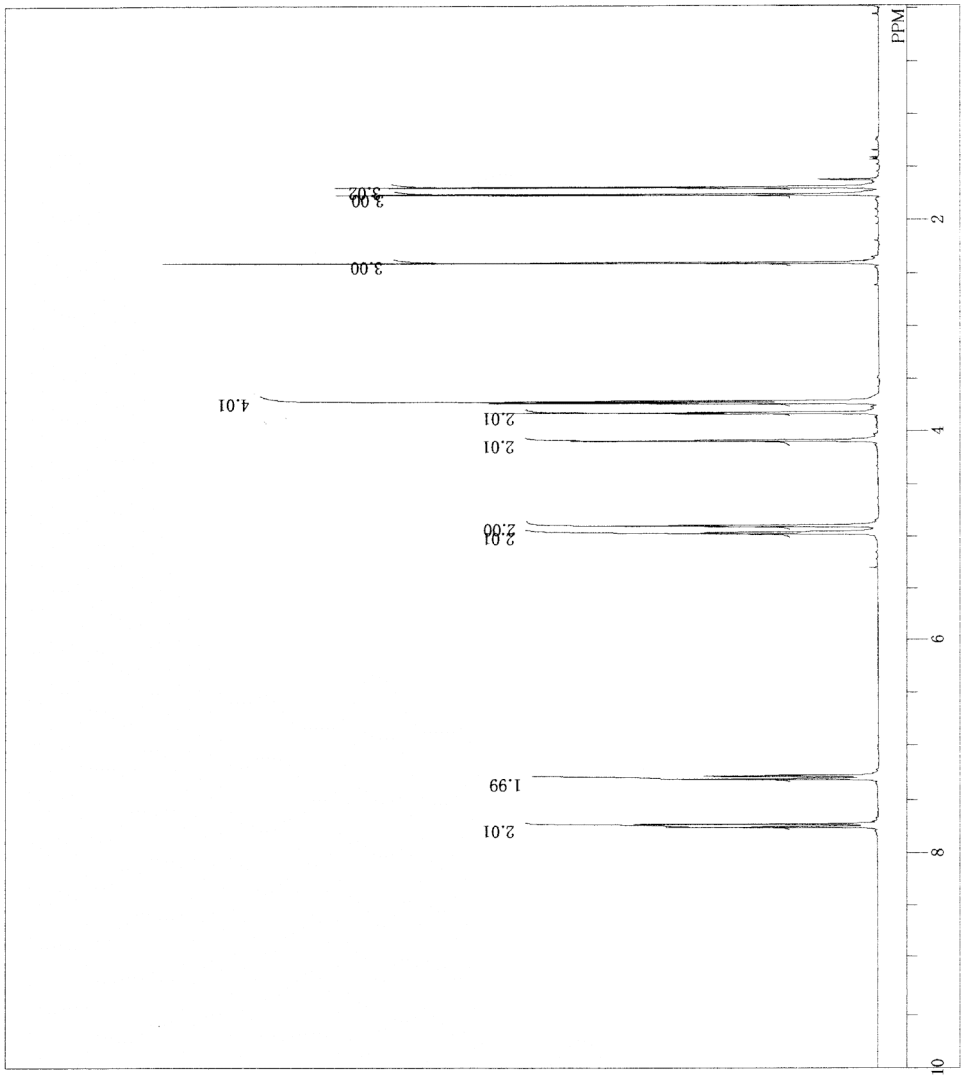
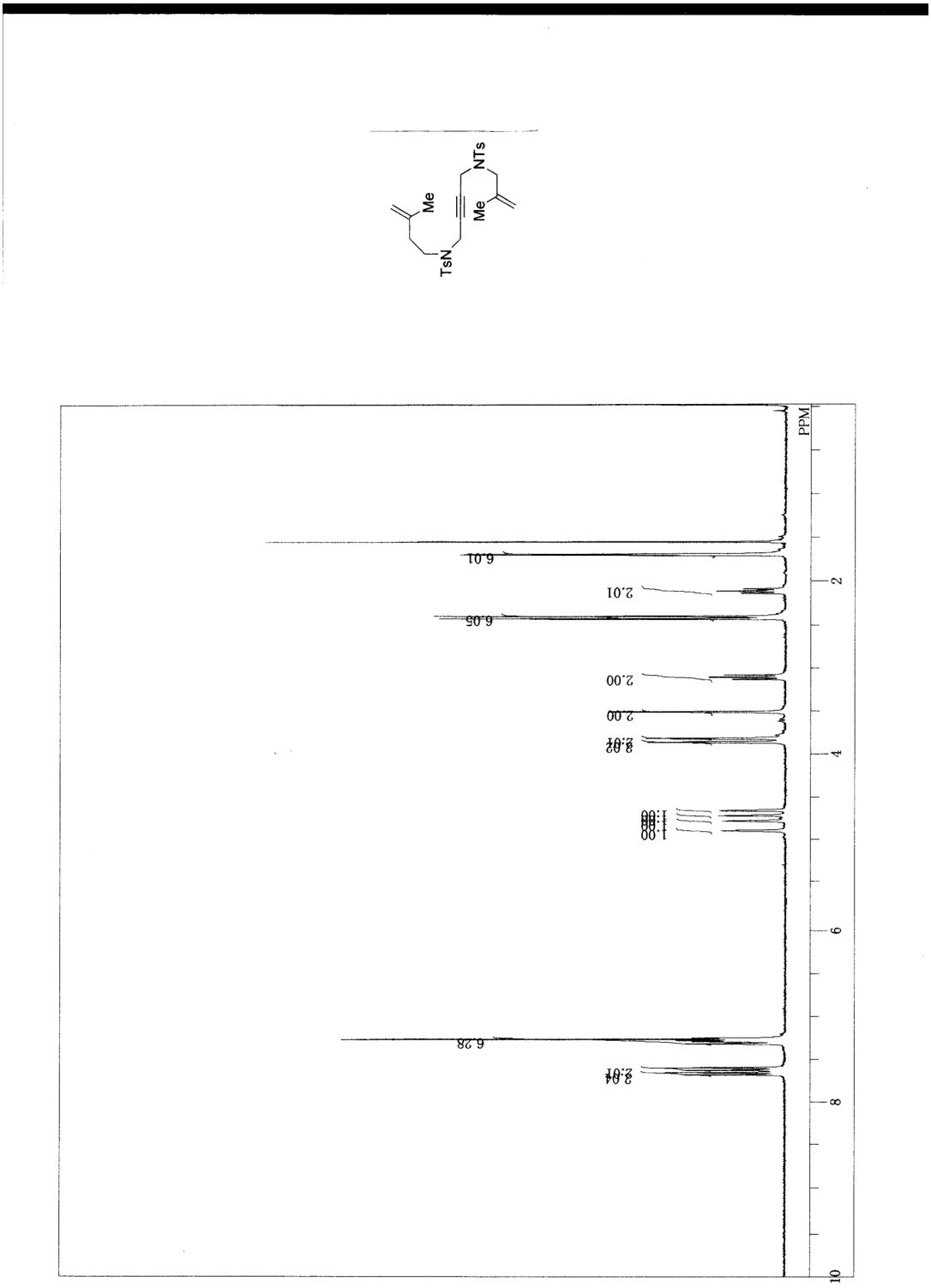
4-Methyl-*N*-(2-methylallyl)-*N*-[4-(2-methylallyloxy)but-2-ynyl]benzenesulfonamide (1a)

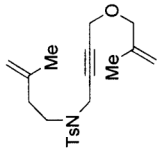


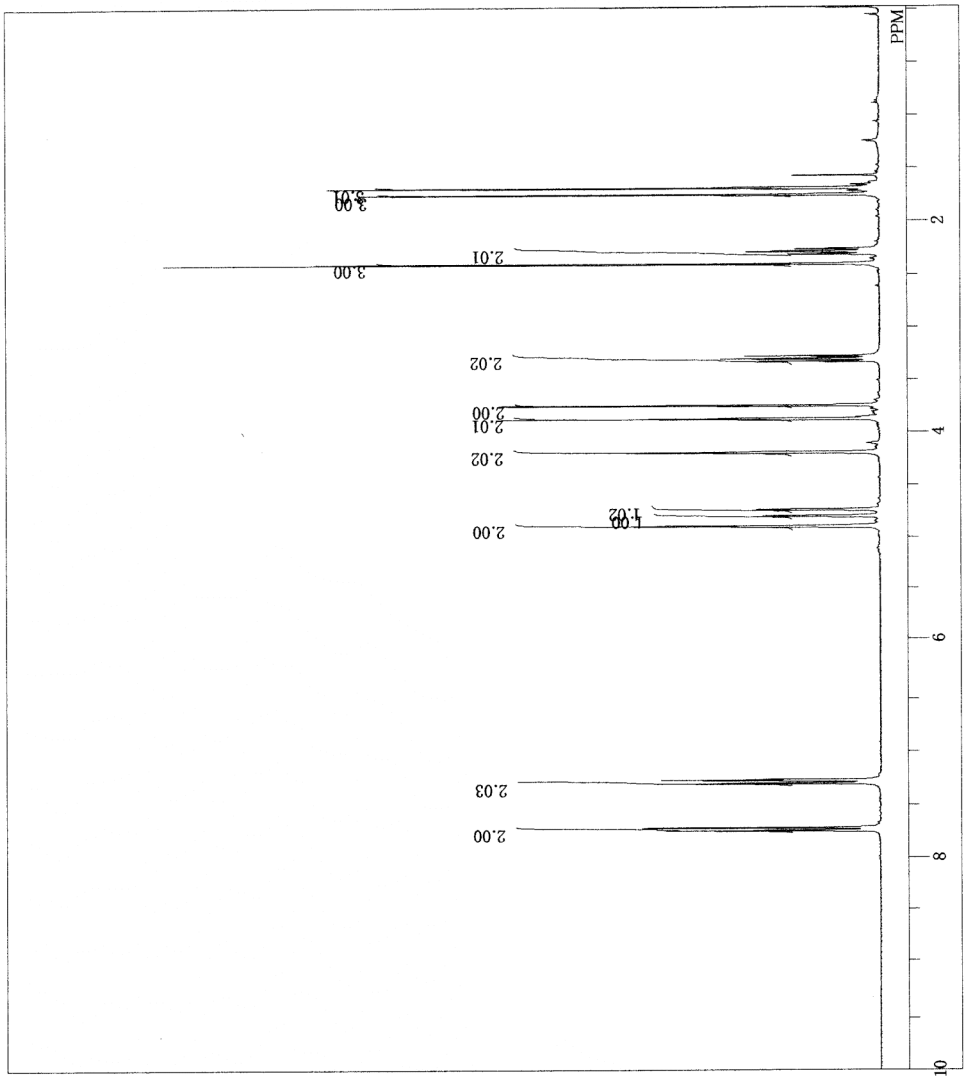


4-Methyl-*N*-(3-methylbut-3-enyl)-*N*-{4-[(2-methylprop-3-enyl)(toluene-4-sulfonyl)amino] but-2-ynyl}benzenesulfonamide (1b)

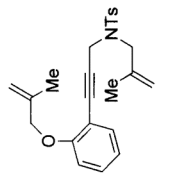


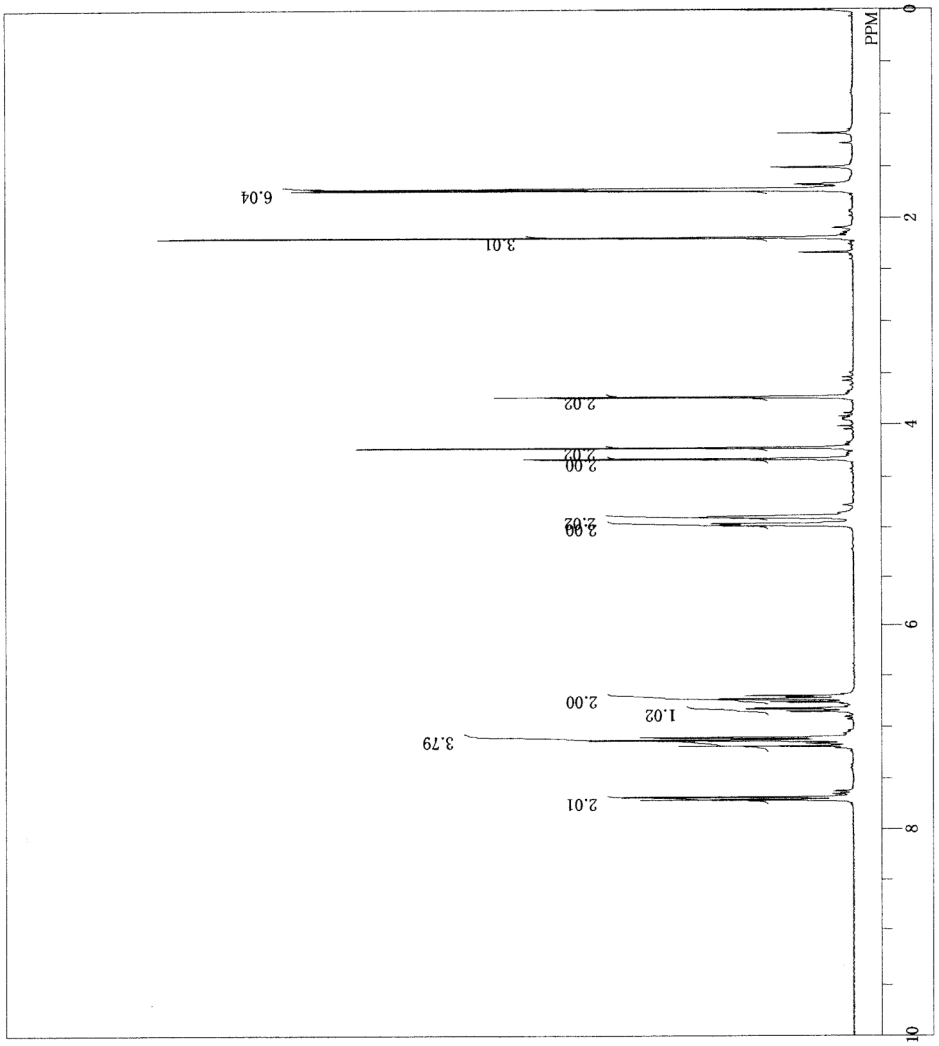
4-Methyl-*N*-[4-(2-methylallyloxy)but-2-ynyl]-*N*-(3-methylbut-3-enyl)benzenesulfonamide (1c)



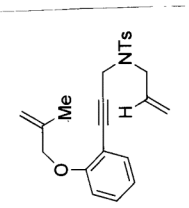


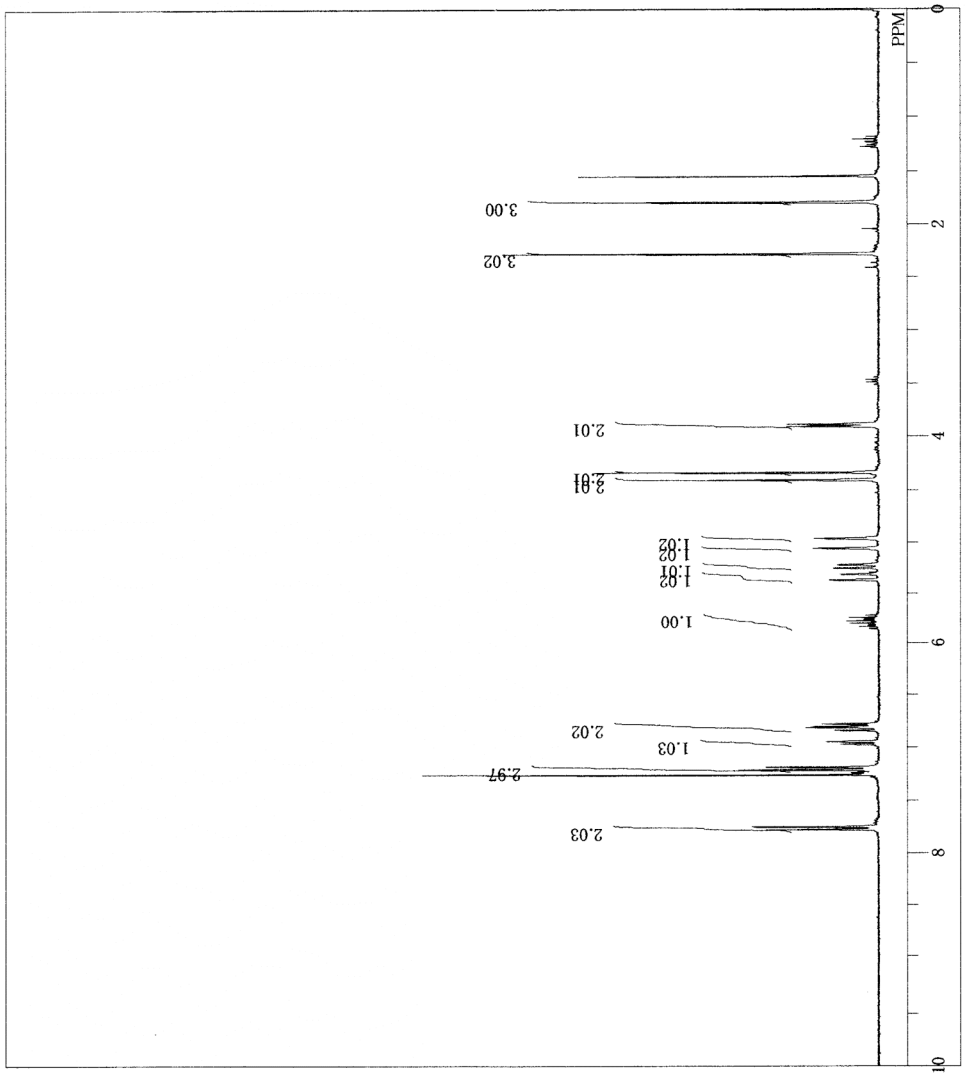
4-Methyl-*N*-(2-methylallyl)-*N*-{3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl}benzenesulfonamide (1d)



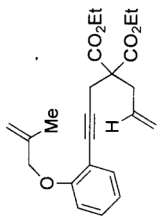


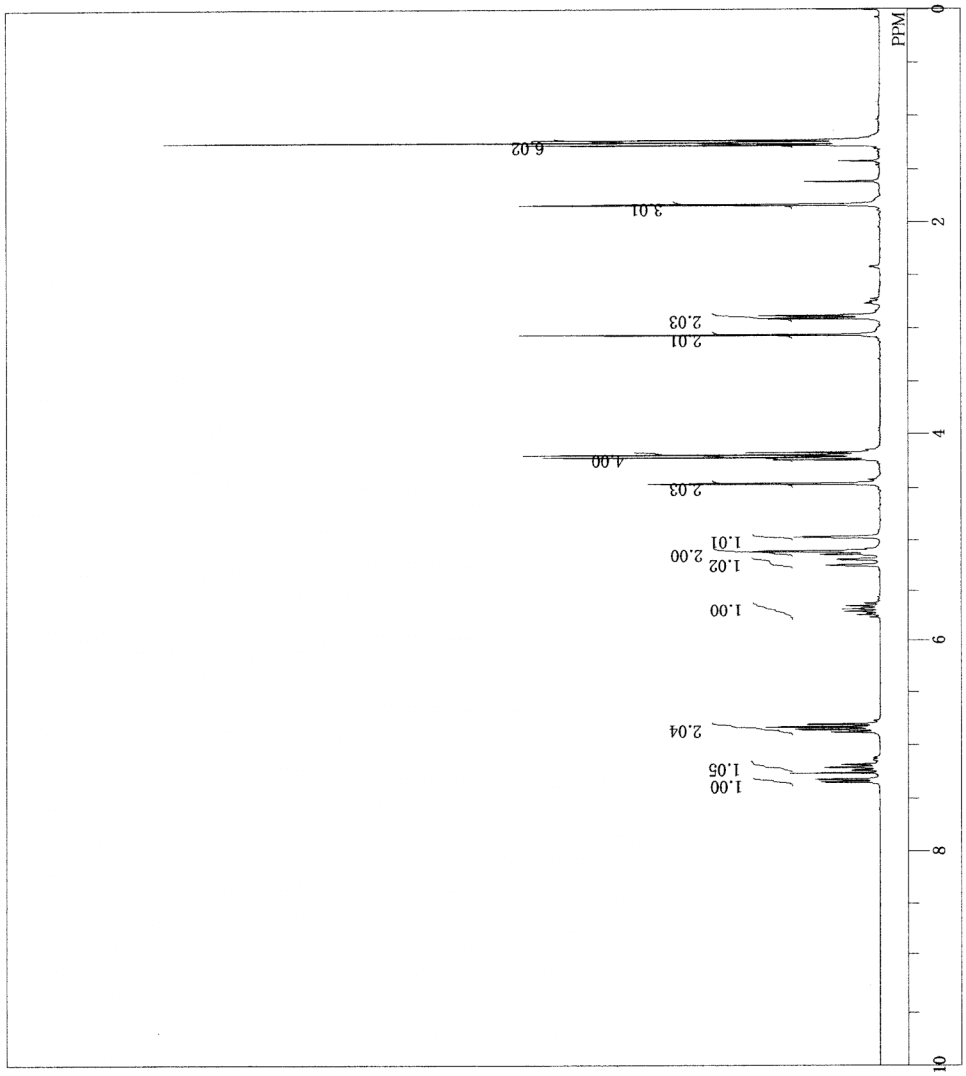
N-Allyl-4-methyl-*N*-{3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl}benzenesulfonamide (1e)



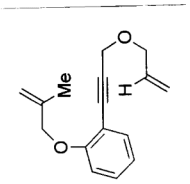


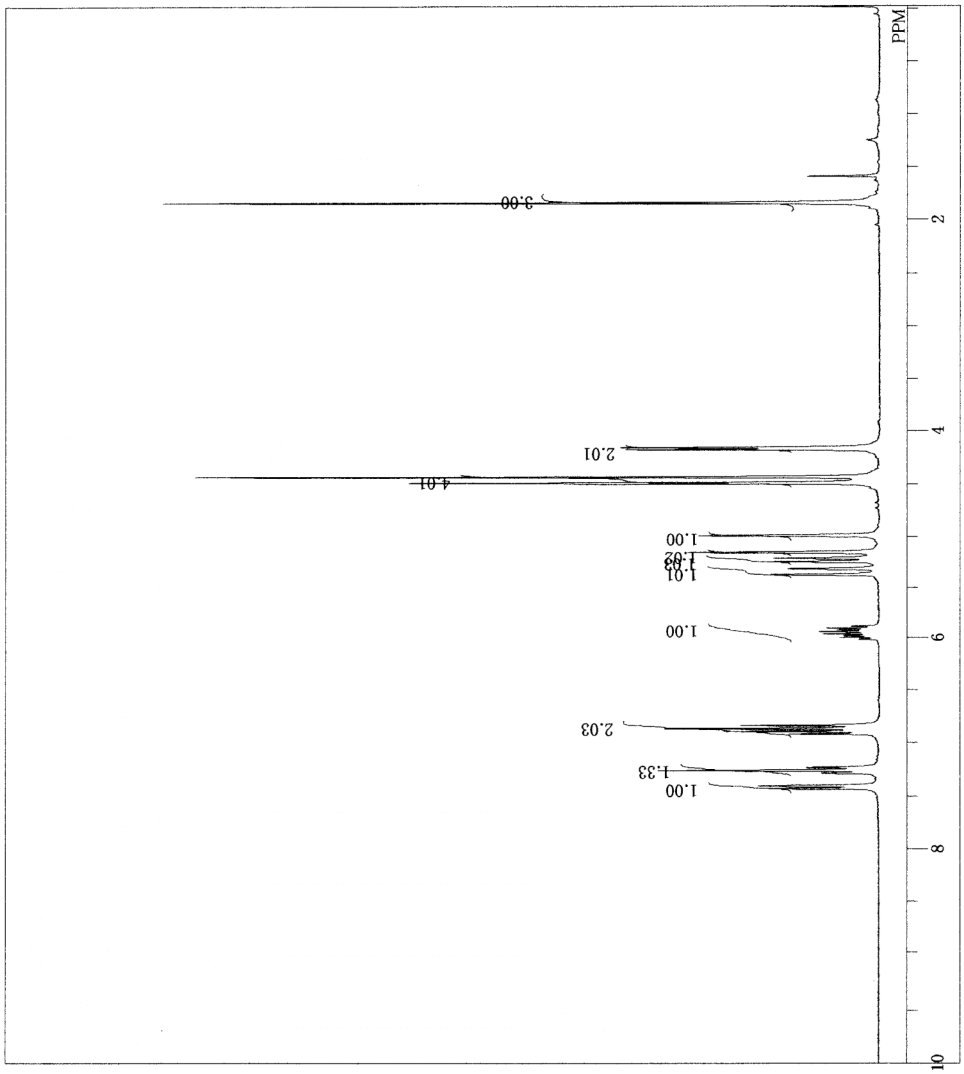
2-Allyl-2-{3-[2-(2-methylallyloxy)phenyl]prop-2-ynyl}malonic acid diethyl ester (1f)



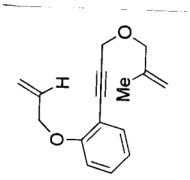


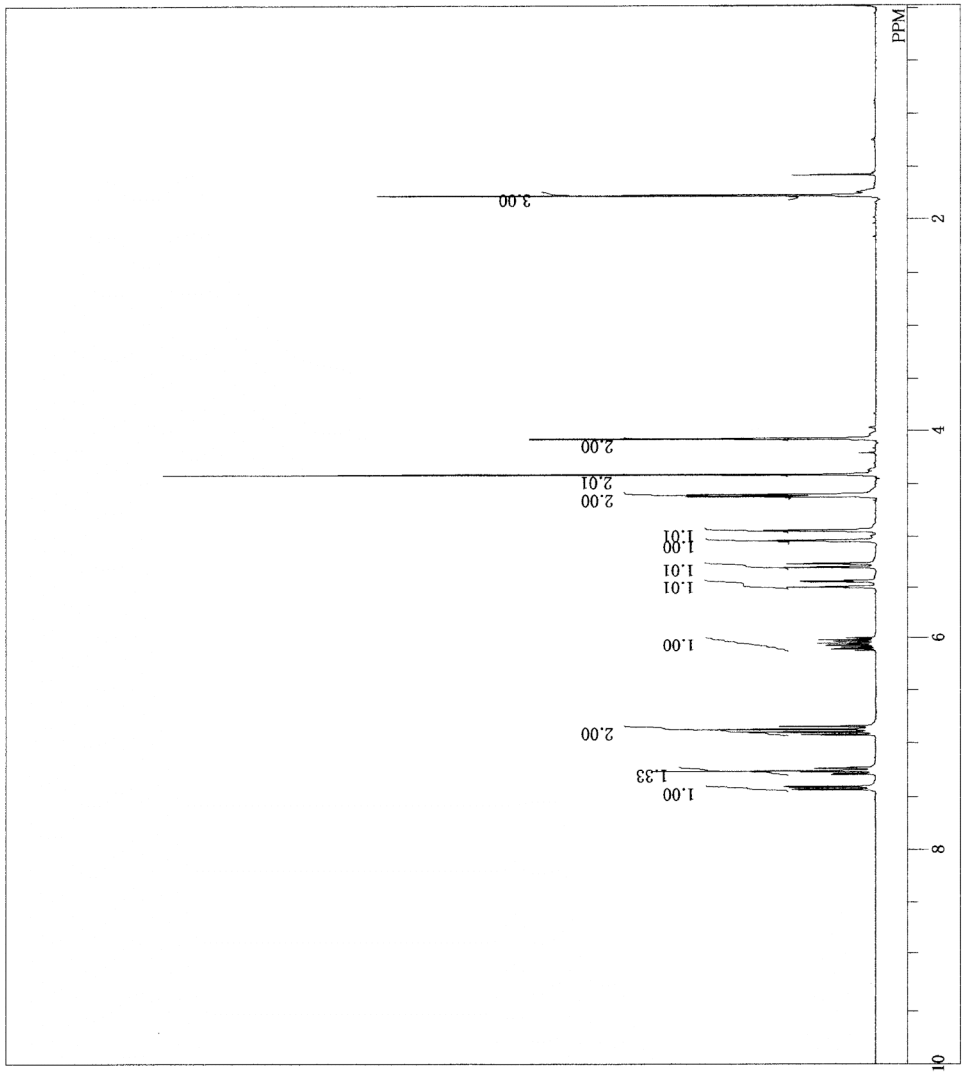
1-(3-Allyloxyprop-1-ynyl)-2-(2-methylallyloxy)benzene (1g)



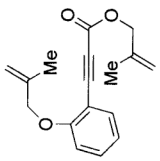


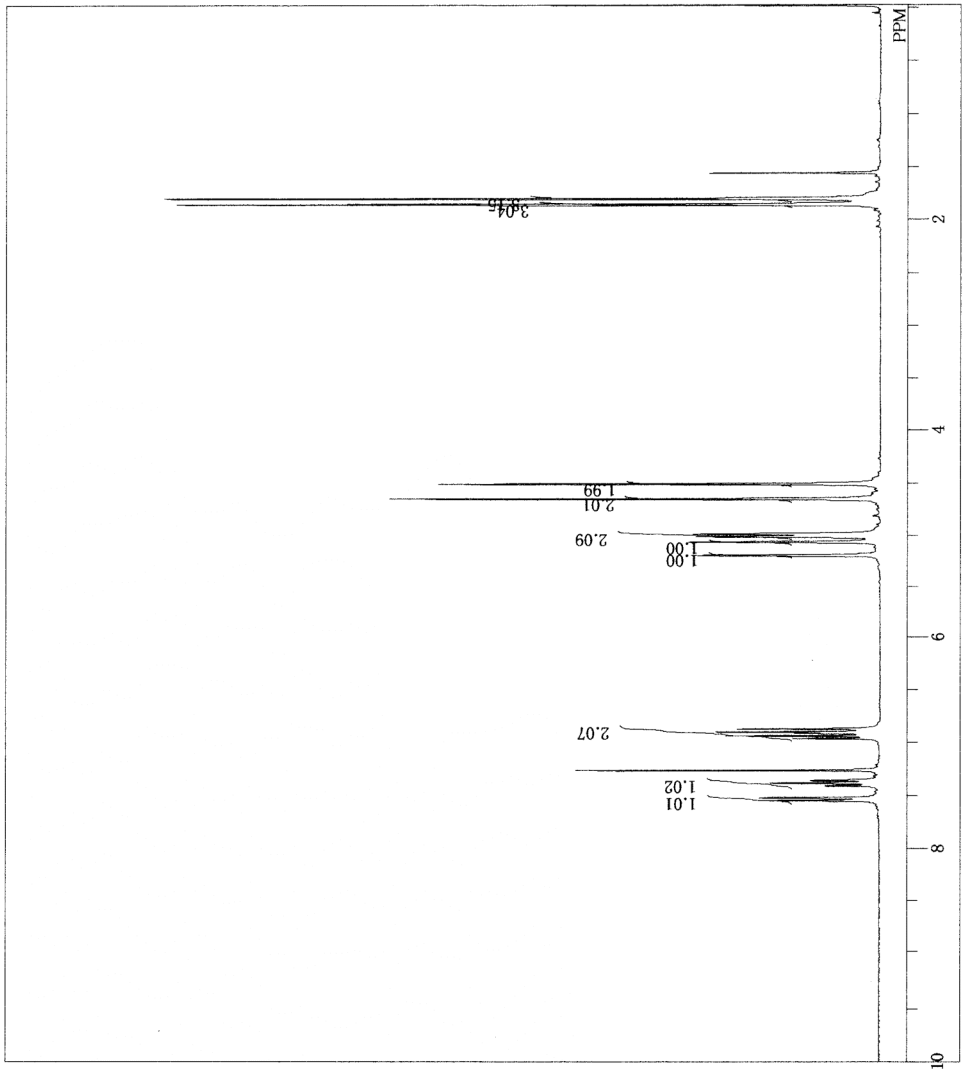
1-Allyloxy-2-[3-(2-methylallyloxy)prop-1-ynyl]benzene (1h)



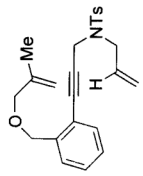


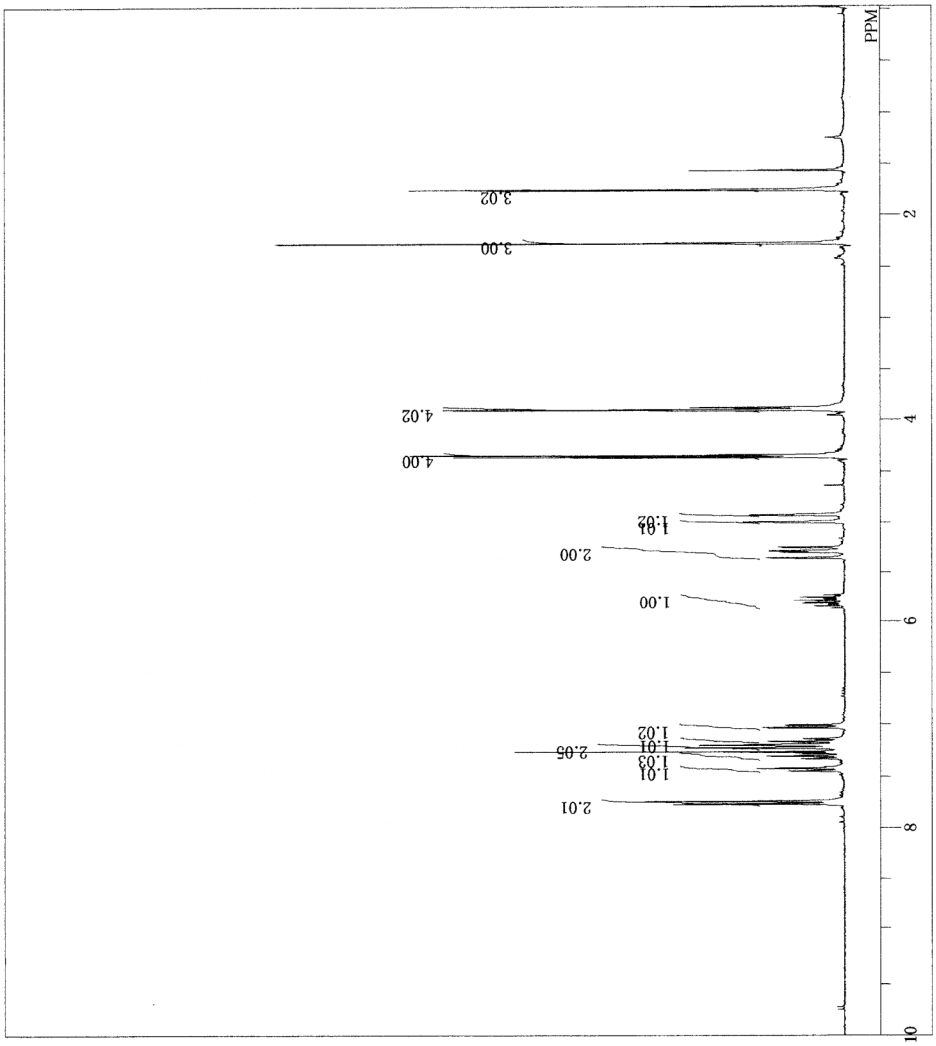
[2-(2-Methylallyloxy)phenyl]propynoic acid 2-methylallyl ester (1i)



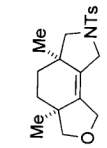


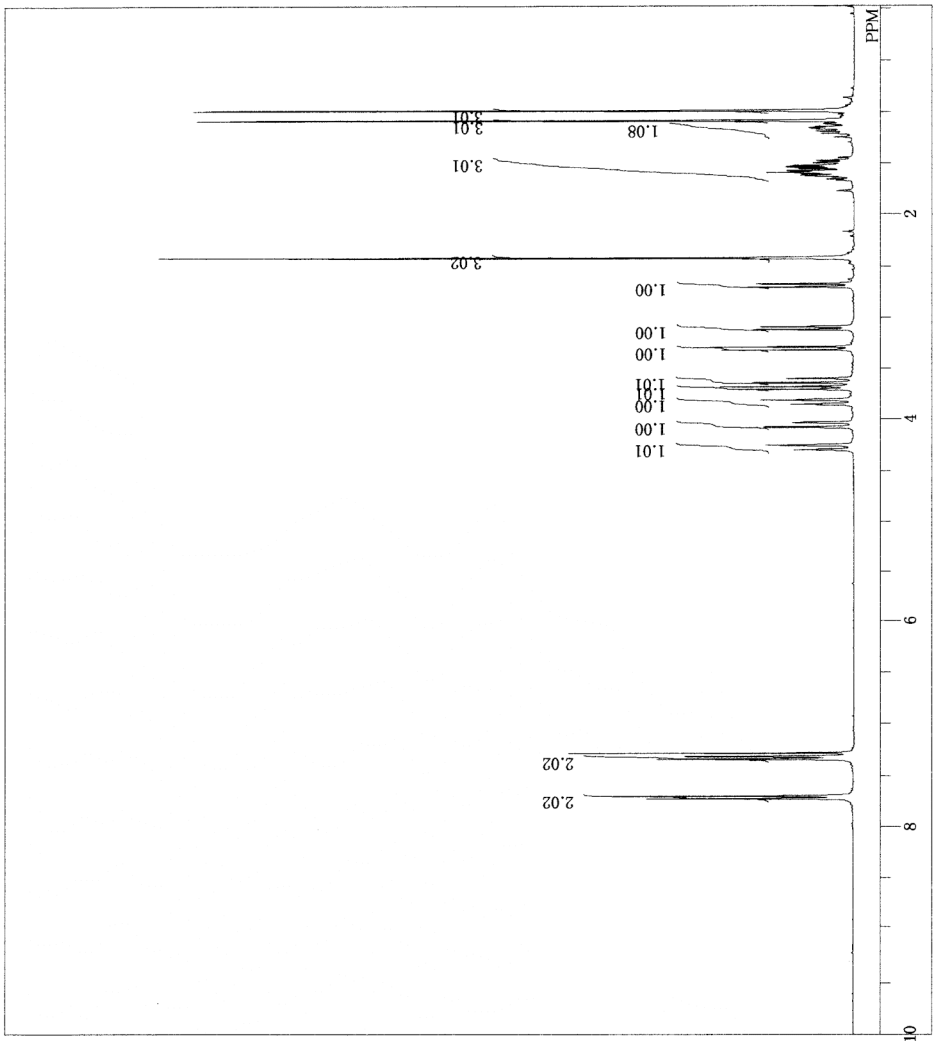
_N_-Allyl-4-methyl-_N_-{3-[2-(2-methylallyloxymethyl)phenyl]prop-2-ynyl}benzenesulfonamide (1j)



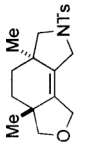


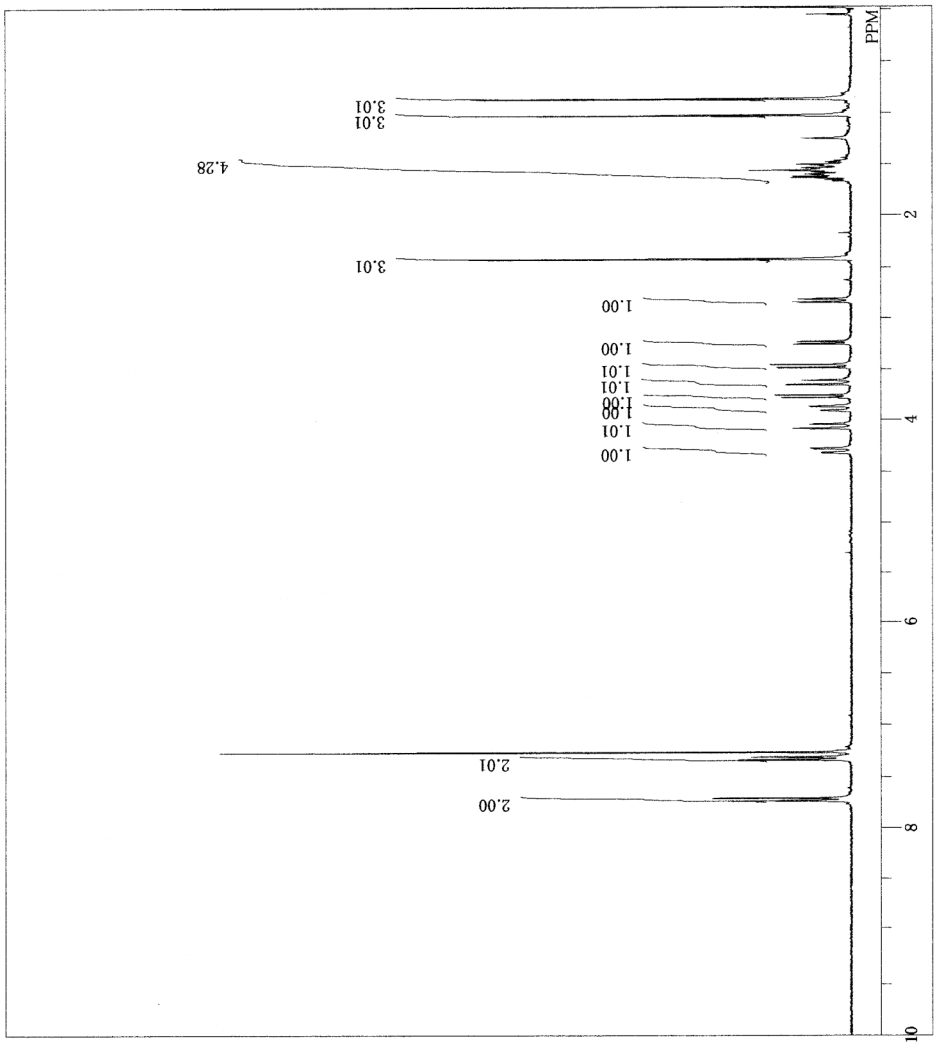
3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1*H*-2-oxa-7-aza-*as*-indacene (2a)



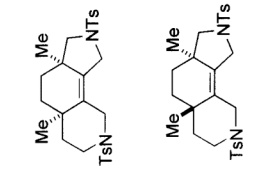


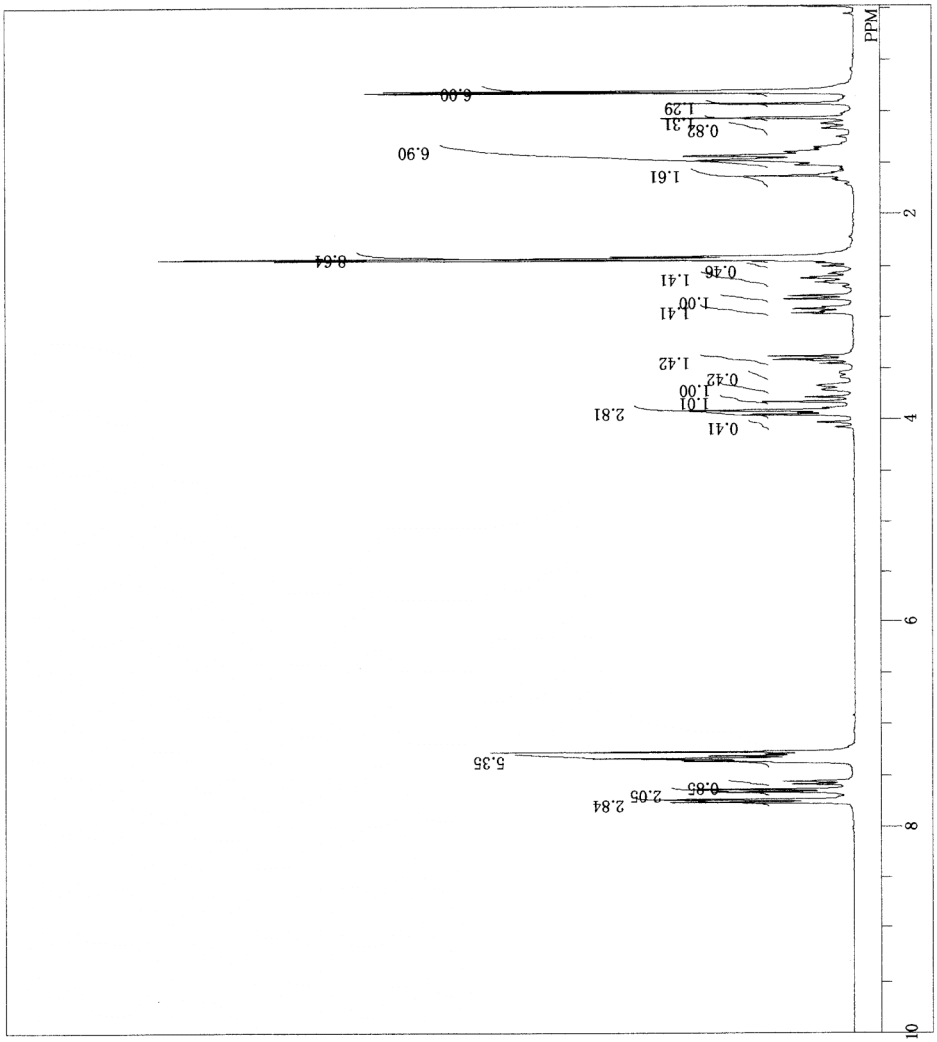
3a,5a-Dimethyl-7-(toluene-4-sulfonyl)-3,3a,4,5,5a,6,7,8-octahydro-1*H*-2-oxa-7-aza-*as*-indacene (3a)



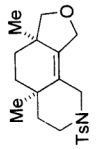


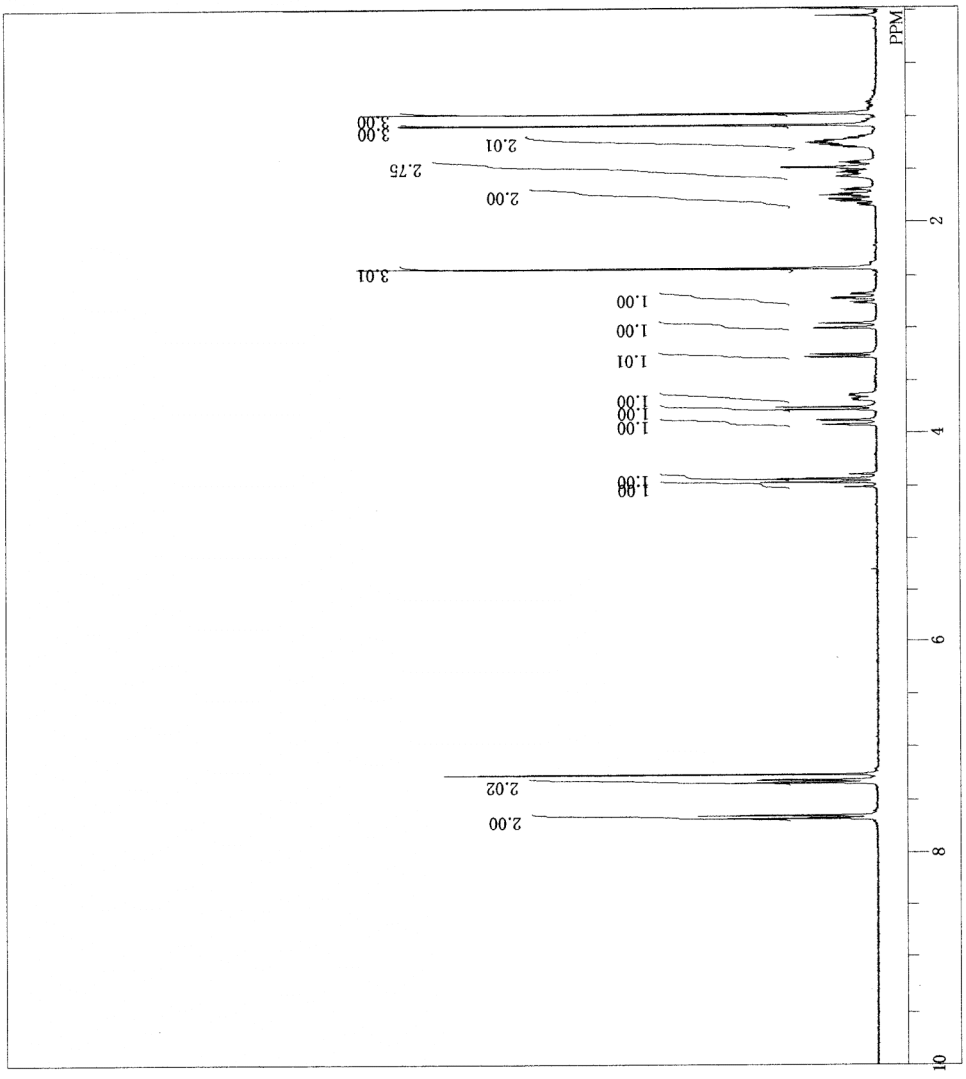
3a,5a-Dimethyl-2,8-bis-(toluene-4-sulfonyl)-2,3,3a,4,5,5a,6,7,8,9-decahydro-1*H*-pyrrolo[3,4-*h*]isoquinoline (2b/3b)



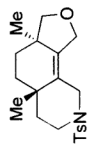


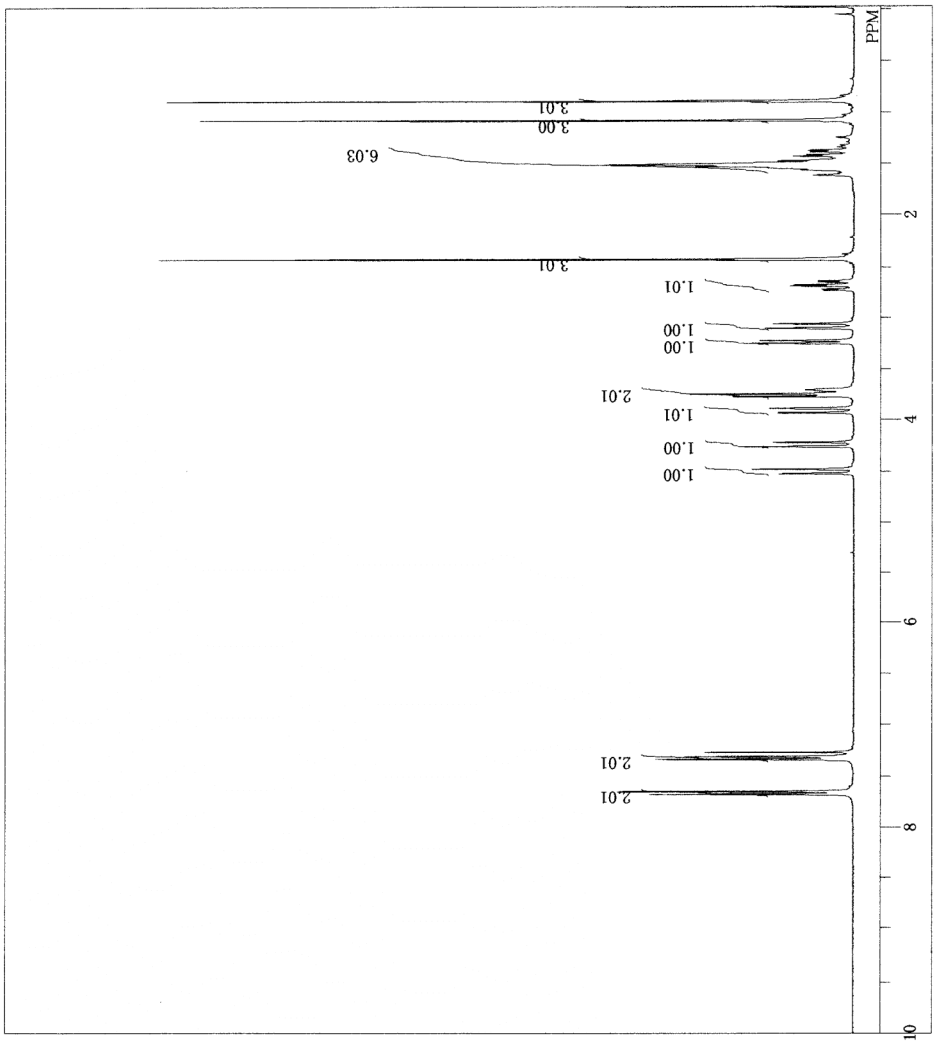
Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-*h*]isoquinoline (2c)



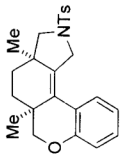


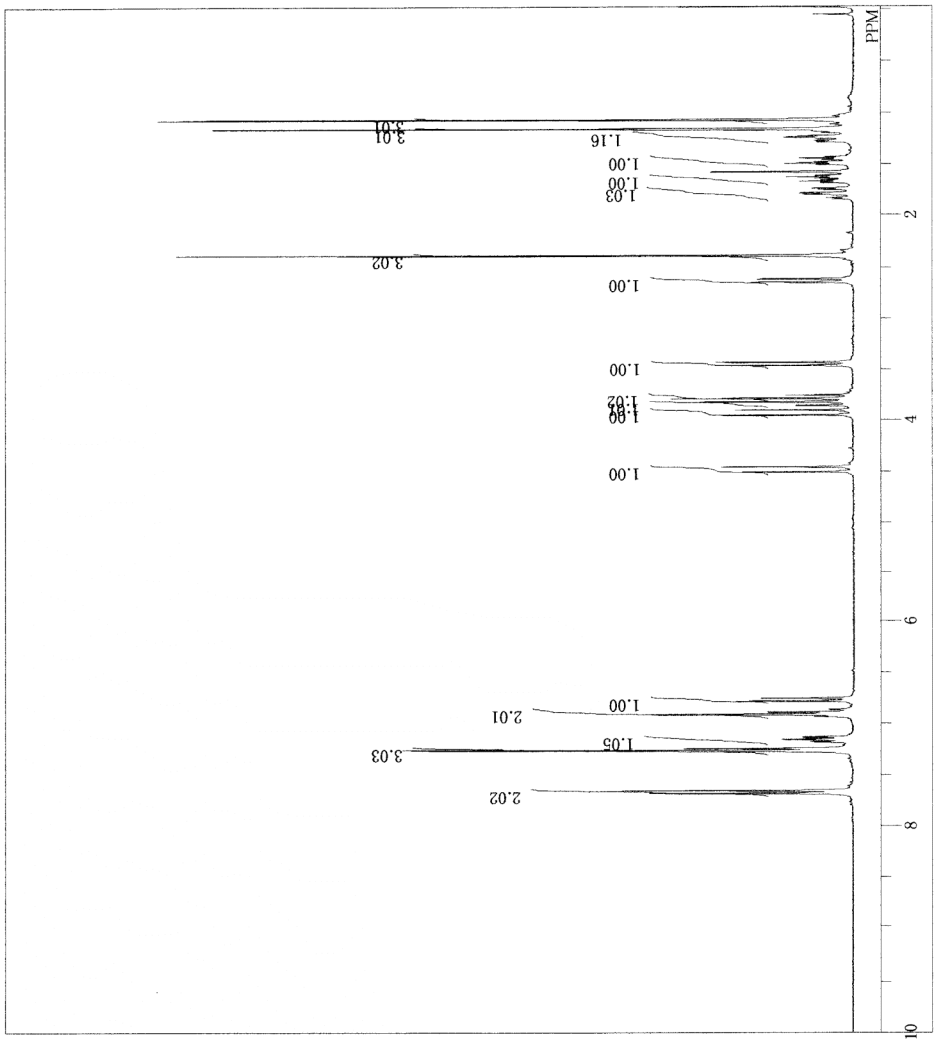
3a,5a-Dimethyl-8-(toluene-4-sulfonyl)-1,3,3a,4,5,5a,6,7,8,9-decahydro-furo[3,4-*h*]isoquinoline (3c)



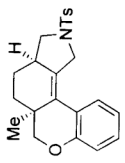


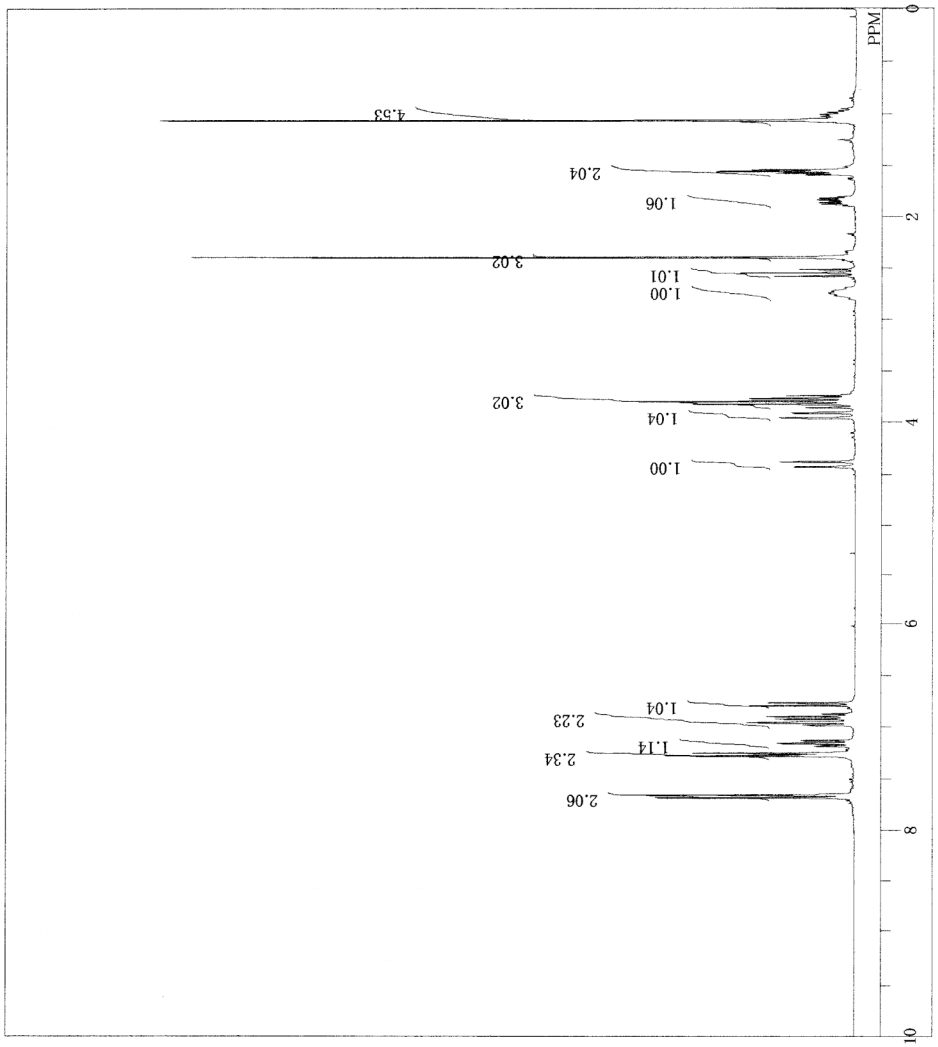
3a,5a-Dimethyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-azacyclopenta[*c*]phenanthrene (2d)



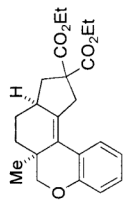


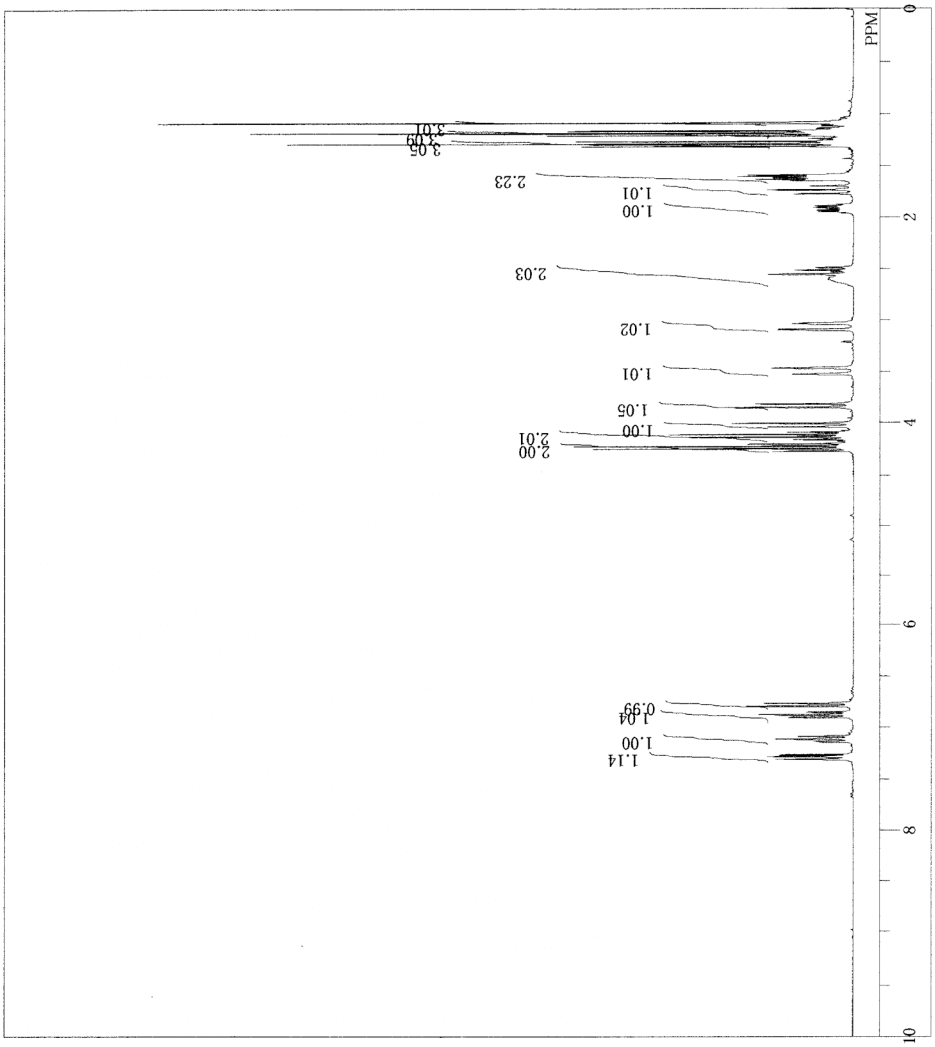
5a-Methyl-2-(toluene-4-sulfonyl)-1,2,3,3a,4,5,5a,6-octahydro-7-oxa-2-aza-cyclopenta[*c*]phenanthrene (2e)



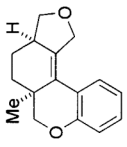


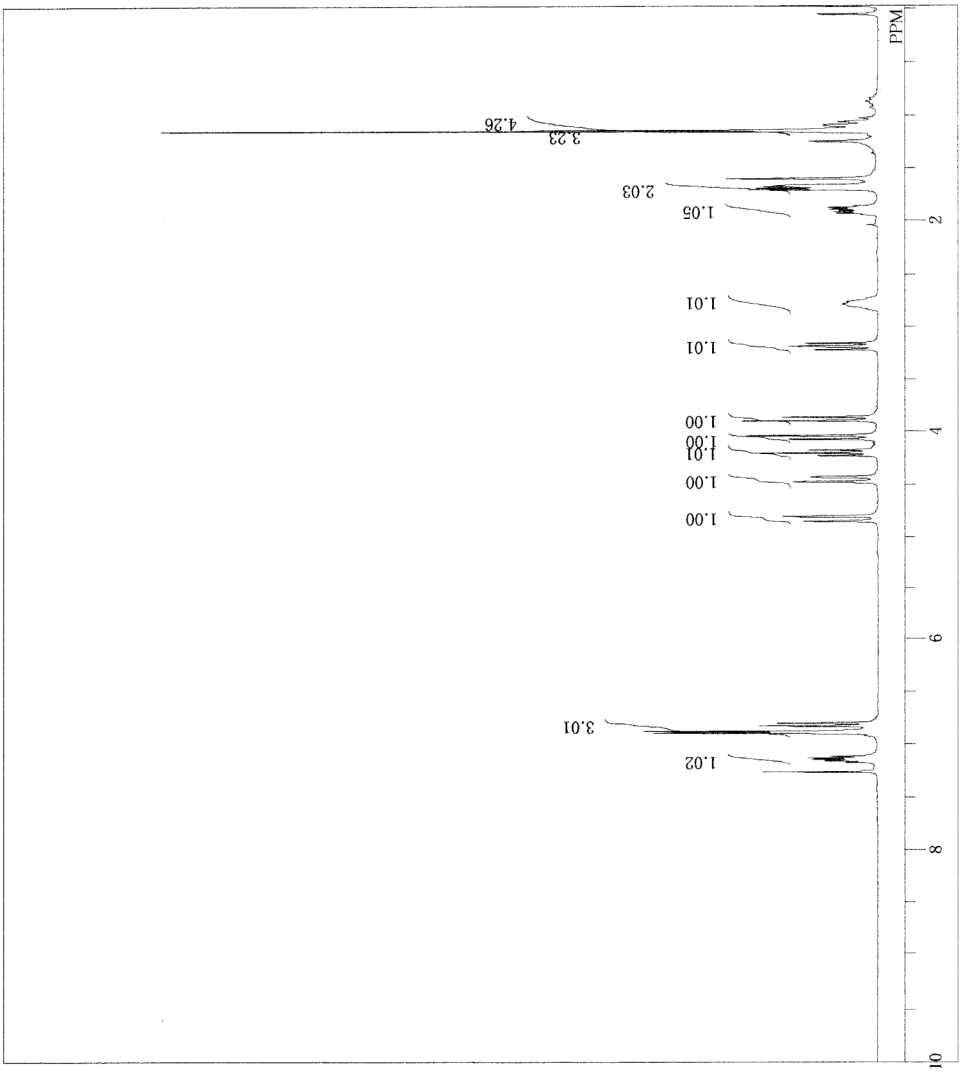
5a-Methyl-3,3a,4,5,5a,6-hexahydro-1*H*-7-oxacyclopenta[*c*]phenanthrene-2,2-dicarboxylic acid diethyl ester (2f)



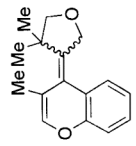


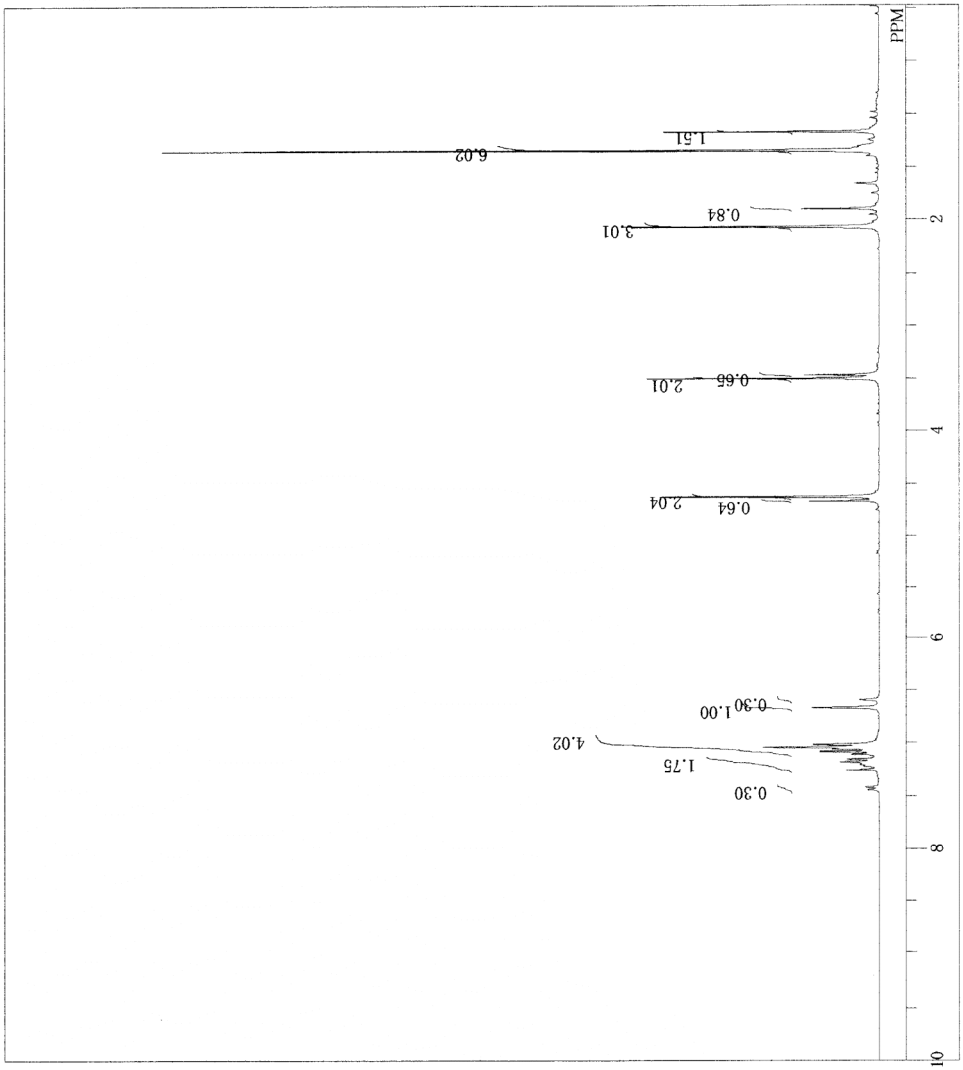
5a-Methyl-3,3a,4,5,5a,6-hexahydro-1*H*-2,7-dioxa-cyclopenta[*c*]phenanthrene (2g)



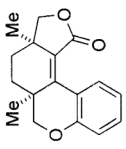


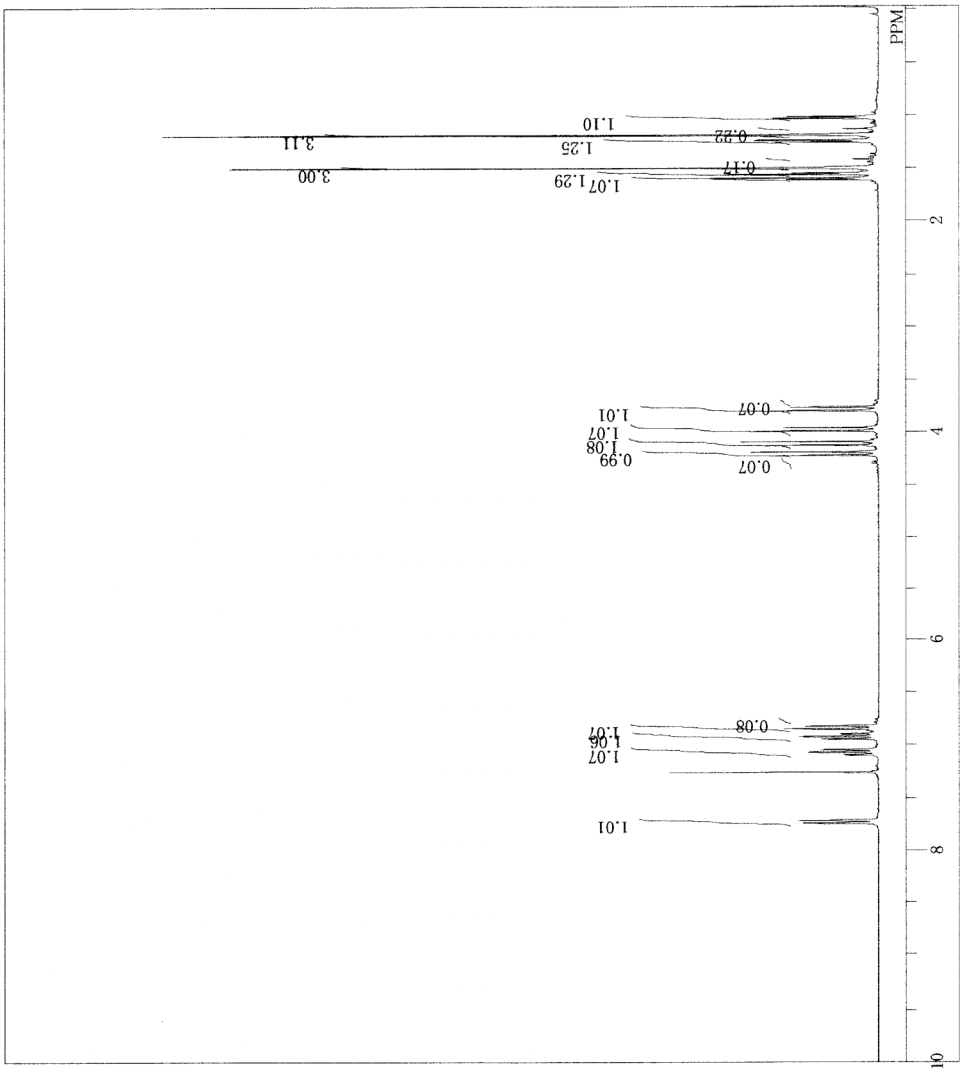
4-(4,4-Dimethyldihydrofuran-3-ylidene)-3-methyl-4*H*-chromene (4)





3a,5a-Dimethyl-3,3a,4,5,5a,6-hexahydro-2,7-dioxa-cyclopenta[*c*]phenanthren-1-one (2i/3i)





5,7,7a,8,9,10-hexahydro-10,11-(N-(4-methylphenylsulfonyl)methaniminomethano)-7a-methyl-Dibenz[c,e]oxepin (2j)