Electronic supporting information (ESI) for

SKELETAL REARRANGEMENTS AND THE STRUCTURE OF PRODUCTS OF HALOSULFONAMIDATION OF CARYOPHYLLENE

Mikhail Yu. Moskalik, Ivan A. Garagan, Valentina S. Myasnikova, Tatyana N. Borodina

Bagrat A. Shainyan*

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation;

E-mail: bagrat@irioch.irk.ru

Table of contents

1. General information

2. Preparation of products 3, 4, 5

2.1 Procedures for the synthesis of compounds 3

2.2 Procedures for the synthesis of compounds 4, 5

1. General Information

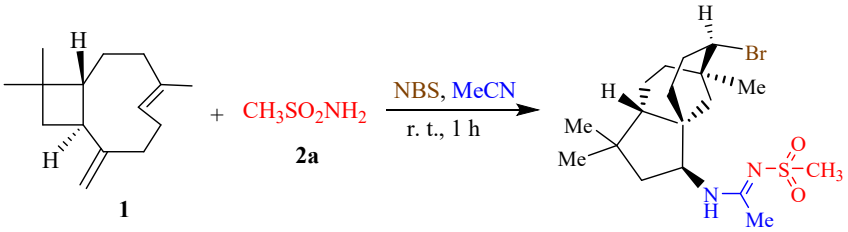
Experimental. All reactions were carried out under air in dry solvents unless otherwise stated. Reactions were stirred using Teflon-coated magnetic stirrers. Organic solutions were concentrated using a rotary evaporator with a membrane vacuum pump. Analytical TLC analysis was performed on 0.2 mm thick silica gel 60 F254 coated aluminum plates visualized with a 254 nm UV lamp or with aqueous NaIO4 solutions. Purification of products was accomplished by flash column chromatography on silica gel 60 Å 230 mesh. Reagents and solvents were purchased from commercial sources and used without further purification.

Analytical. Melting points were determined on a MeltEMP apparatus and are uncorrected. NMR spectra were recorded on a on Bruker DPX 400 nuclear magnetic resonance spectrometer at working frequencies 400 (^{1}H), 100 (^{13}C), 376 (^{19}F) Hz. The NMR spectra were calibrated using residual undeuterated solvent as internal references ($CHCl_3$ peak [7.27 (^{1}H) and 77.1 (^{13}C) ppm] and CD_3CN peak [1.95 (^{1}H), 1.3 and 118.0 (^{13}C) ppm]). Data for 1H NMR are recorded as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, coupling constants in Hz, integration). IR spectra were taken on a Bruker Vertex 70 spectrophotometer in KBr or film. High-resolution mass spectra (HRMS) were measured on an Agilent 1200 HPLC chromatograph with Agilent 6210 mass spectrometer (HR-TOF-MS, ESI^+ ionization in acetonitrile with 0.1% HFBA). Elemental compositions were determined by accurate mass measurement with standard deviation. Crystal data were collected on a Bruker D8 Venture diffractometer with MoKα radiation (λ = 0.71073) using the φ and ω scans. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

2. Preparation of products 3, 4, 5

2.1 Procedures for the synthesis of compounds 3

The reaction of *β*-caryophyllene 1 with methanesulfonamide 2a and NBS in MeCN

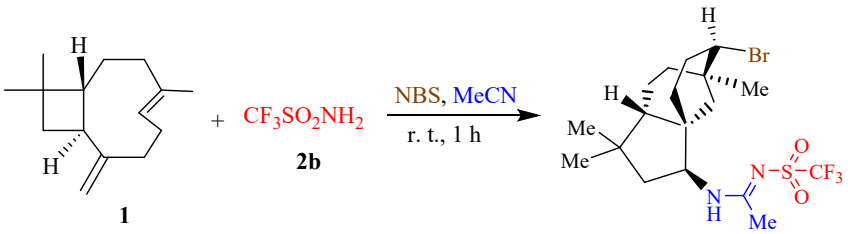


3a (63%)

1 g (10.5 mmol) of methanesulfonamide **2a** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 2.1 ml (10.5 mmol) of *β*-caryophyllene and, after a few minutes, 2 g (11.1 mmol) of NBS. The mixture was stirred for 1 h, the solvent was removed under reduced pressure. The residue was dissolved in 50 ml of $CHCl_3$ and washed with water (3×100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3a** was isolated. Yield of product **3a** 3.08 g (63%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-(methylsulfonyl)acetimidamide, 3a. White solid. M.p. 179.3°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20–5.13 (m, 1H), 5.10 (s, 1H), 3.33 (d, J = 10.3 Hz, 1H), 3.23 (d, J = 10.3 Hz, 1H), 3.04 (s, 3H), 2.78 (d, J = 13.9 Hz, 1H), 2.41 (d, J = 3.0 Hz, 3H), 2.35–2.27 (m, 2H), 2.25–2.16 (m, 1H), 2.13 (m, 1H), 2.00 (dd, J = 13.9, 3.2 Hz, 1H), 1.95–1.79 (m, 2H), 1.75–1.67 (m, 1H), 1.66–1.62 (m, 1H), 1.51 (m, 2H), 1.47–1.41 (m, 1H), 1.03 (s, 3H), 1.02 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 63.2, 56.8, 45.0, 43.9, 43.4, 38.6, 36.7, 36.6, 35.5, 35.4, 35.3, 35.1, 31.2, 30.6, 22.6, 20.8, 20.4. IR, ν, cm^{-1}: 3244, 2949, 2864, 1711, 1631, 1555, 1369, 1270, 1176, 1130, 1040, 968, 790, 611, 555. Anal. calcd (%) for $C_{18}H_{31}BrN_2O_2S$: C, 51.55; H, 7.45; Br, 19.05; N, 6.68; S, 7.64; found: C, 51.32; H, 7.36; Br, 19.40; N, 6.68; S, 7.75.

The reaction of *β*-caryophyllene 1 with triflamide 2b and NBS in MeCN



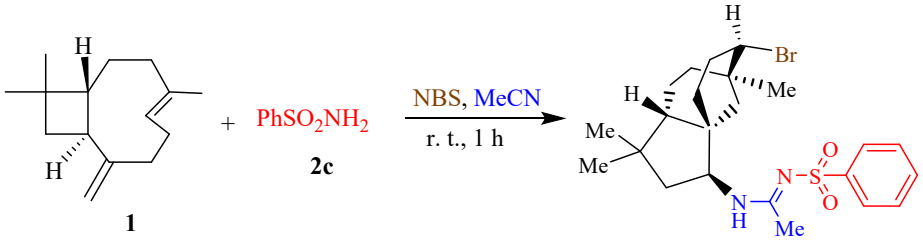
3b (79%)

1 g (6.7 mmol) of triflamide **2b** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.5 ml (6.7 mmol) of *β*-caryophyllene **1**. After a few minutes, 1.3 g (7.3 mmol) of NBS was added. The mixture was stirred for 1 h. Then the solvent was removed under

reduced pressure. The residue was dissolved in 50 ml of $CHCl_3$ and washed with water (3×100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3b** was isolated. Yield of product **3b** 2.77 g (79%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-((trifluoromethyl)sulfonyl)acetimidamide, 3b. White solid. M.p. 172.0°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ 6.14 (d, J = 8.7 Hz, 1H), 4.33–4.27 (m, 1H), 4.12–4.10 (m, 1H), 2.53 (s, 3H), 2.29 (ddd, J = 12.4, 8.7, 4.9 Hz, 1H), 2.03–1.97 (m, 1H), 1.96 (m, 1H), 1.76–1.69 (m, 2H), 1.64–1.59 (m, 3H), 1.51–1.44 (m, 2H), 1.40–1.33 (m, 2H), 1.31–1.24 (m, 1H), 1.06 (s, 6H), 1.01 (m, 1H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.3, 121.2, 118.0, 66.3, 61.0, 51.9, 44.9, 44.3, 38.2, 36.3, 35.9, 33.5, 32.2, 30.6, 28.5, 28.4, 24.4, 22.7, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$), δ: -78.94. IR, ν, cm^{-1}: 3301, 2960, 2839, 2198, 1700, 1511, 1416, 1298, 1224, 1190, 1012, 903, 725, 646, 556. Anal. calcd (%) for $C_{18}H_{28}BrF_3N_2O_2S$: C, 45.67; H, 5.96; Br, 16.88; F, 12.04; N, 5.92; S, 6.77; found: C, 45.41; H, 6.00; Br, 16.58; F, 11.99; N, 5.95; S, 6.92.

The reaction of *β*-caryophyllene 1 with benzenesulfonamide 2c and NBS in MeCN



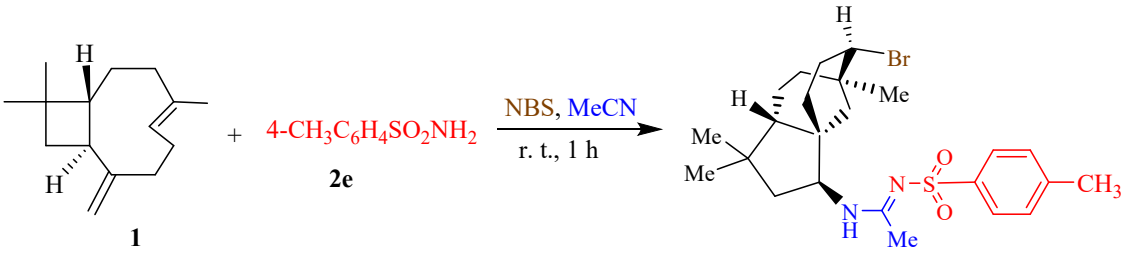
3c (66%)

1 g (6.3 mmol) of benzenesulfonamide **2c** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.45 ml (6.3 mmol) of *β*-caryophyllene **1** and, after a few minutes, 1.3 g (7 mmol) of NBS. The mixture was stirred for 1 h, the solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with water (3×100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent removed under reduced pressure, the residue dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3c** was isolated. Yield of product **3c** 2.23 g (66%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-(phenylsulfonyl)acetimidamide, 3c. White solid. M.p. 197.2°C. ^{1}H NMR(400 MHz, CD_3CN) δ: 7.90–7.81 (m, 2H), 7.55–7.43 (m, 3H), 6.71 (m, 1H), 4.31–4.13 (m, 2H), 2.32 (s, 3H), 2.30–2.21 (m, 1H), 1.87 (dd, J = 15.2, 3.3 Hz, 1H), 1.67 (d, J = 13.4 Hz, 1H), 1.58–1.53 (m, 2H), 1.53–1.49 (m, 1H), 1.48–1.35 (m, 2H), 1.35–1.23 (m, 3H), 1.04 (s, 3H), 0.98 (m, 1H), 0.95 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ: 167.1, 132.4, 129.7, 127.0, 69.1, 61.0, 52.6, 45.6, 45.4,

38.6, 37.7, 36.8, 34.1, 32.7, 30.6, 29.4, 29.2, 24.8, 21.0, 21.0. IR, ν, cm^{-1}: 3335, 3161, 2837, 2229, 1741, 1700, 1430, 1351, 1286, 1132, 917, 706, 553. Anal. calcd (%) for $C_{23}H_{33}BrN_2O_2S$: C, 57.37; H, 6.91; Br, 16.60; N, 5.82; S, 6.66; found: C, 57.60; H, 6.97; Br, 16.52; N, 5.93; S, 6.87

The reaction of *β*-caryophyllene 1 with tosylamide 2e and NBS in MeCN

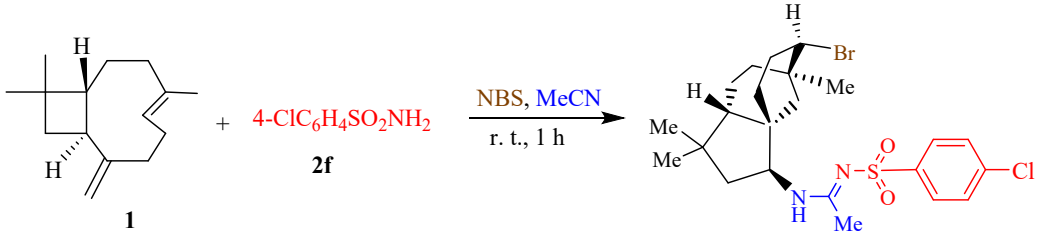


3e (74%)

1 g (4.9 mmol) of tosylamide **2e** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.3 ml (5.8 mmol) of *β*-caryophyllene **1**. After a few minutes, 0.9 g (6 mmol) of NBS was added and the mixture was stirred for 1 h. Then the solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with water (3×100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3e** was isolated. Yield of product **3e** 2.35 g (74%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-tosylacetimidamide, 3e. White solid. M.p. 196.9°C. ^{1}H NMR(400 MHz, CD_3CN) δ 7.81–7.74 (m, 2H), 7.31 (d, J = 7.7 Hz, 2H), 6.77–6.63 (m, 1H), 4.32–4.08 (m, 2H), 2.42 (m, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 2.26 (m, 1H), 1.64 (d, J = 13.4 Hz, 1H), 1.57 (d, J = 9.3 Hz, 2H), 1.52–1.42 (m, 2H), 1.42–1.33 (m, 2H), 1.31–1.27 (m, 2H), 1.04 (s, 3H), 0.98 (m, 1H), 0.95 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ: 166.9, 143.0, 130.2, 127.1, 126.7, 69.1, 60.8, 52.6, 45.5, 45.3, 37.7, 36.8, 34.1, 32.6, 30.6, 29.4, 29.2, 24.8, 21.4, 21.0, 20.9. IR, ν, cm^{-1}: 3296, 3115, 2901, 2263, 1732, 1698, 1470, 1402, 1311, 1119, 904, 703. Anal. calcd (%) for $C_{24}H_{35}BrN_2O_2S$: C, 58.17; H, 7.12; Br, 16.13; N, 5.65; S, 6.47; found: C, 58.02; H, 7.20; Br, 15.89; N, 5.75; S, 6.57.

The reaction of *β*-caryophyllene 1 with *p*-chlorobenzenesulfonamide 2f and NBS in MeCN

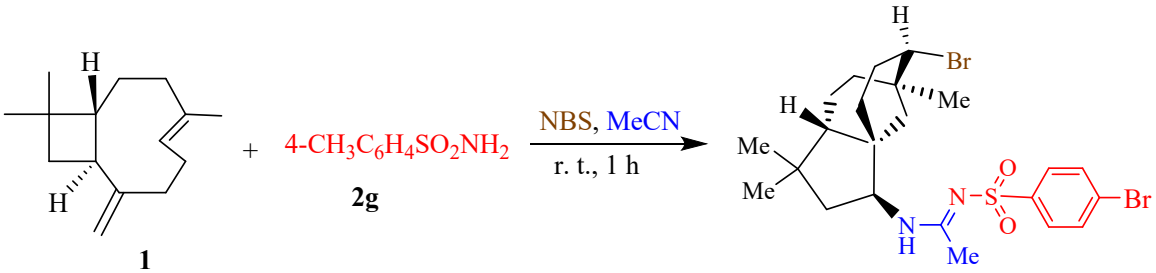


3f (68%)

1 g (5.2 mmol) of *p*-chlorobenzenesulfonamide **2f** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.07 ml (4.6 mmol) of *β*-caryophyllene **1** and, after a few minutes, 1 g (5.7 mmol) of NBS. The mixture was stirred for 1 h, the solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with water (3ᔓ100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, hexane-ether 1:9. From the hexane-ether 1:9 fraction, product **3f** was isolated. Yield of product **3f** 1.97 g (68%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-(4-chlorophenylsulfonyl)acetimidamide, 3f. White solid. M.p. 200.3°C. ^{1}H NMR(400 MHz, CD_3CN) δ: 7.84 (d, J = 6.7 Hz, 2H), 7.51–7.48 (m, 2H), 6.79 (m, 1H), 4.25–4.13 (m, 2H), 2.35 (s, 3H), 2.29–2.23 (m, 1H), 1.60–1.55 (m, 4H), 1.53 (m, 1H), 1.51–1.48 (m, 1H), 1.46 (m, 1H), 1.44–1.40 (m, 1H), 1.38 (m, 1H), 1.34–1.24 (m, 2H), 1.04 (s, 3H), 0.99 (m, 1H), 0.91 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ: 166.9, 129.9, 128.8, 69.2, 61.0, 52.6, 45.5, 45.3, 38.5, 37.6, 36.7, 34.0, 32.6, 30.6, 29.48, 29.2, 24.8, 21.0, 21.0. IR, ν, cm^{-1}: 3274, 3161, 2890, 2203, 1722, 1668, 1451, 1393, 1365, 1084, 916, 694. Anal. calcd (%) for $C_{23}H_{32}BrClN_2O_2S$: C, 53.54; H, 6.25; Br, 15.49; Cl, 6.87; N, 5.43; S, 6.21; found: C, 53.32; H, 6.29; Br, 15.31; Cl, 6.71; N, 5.35; S, 6.28.

The reaction of *β*-caryophyllene 1 with *p*-bromobenzenesulfonamide 2g and NBS in MeCN



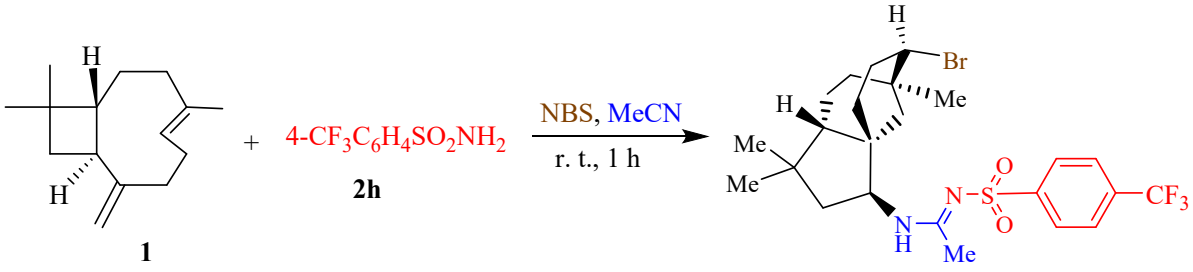
3g (79%)

1 g (4.2 mmol) of *p*-bromobenzenesulfonamide **2g** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1 ml (4.4 mmol) of *β*-caryophyllene **1**. After a few minutes, 0.78 g (4.4 mmol) of NBS was added and the mixture was stirred for 1 h. Then the solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with water (3ᔓ100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent removed at a reduced pressure, the residue dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3g** was isolated. Yield of product **3g** 2.03 g (79%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-((4-bromophenyl)sulfonyl)acetimidamide, 3g. White solid. M.p. 194.6°C. ^{1}H NMR(400 MHz,

$CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.7 Hz, 1H), 6.21 (d, J = 8.8 Hz, 1H), 4.30–4.09 (m, 1H), 4.06 (m, 1H), 2.42 (s, 3H), 2.36 (m, 1H), 2.20–2.12 (m, 1H), 1.88–1.81 (m, 1H), 1.57 (m, 3H), 1.50–1.42 (m, 2H), 1.41–1.34 (m, 1H), 1.29–1.17 (m, 3H), 1.10–1.01 (m, 1H), 0.98 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.7, 142.6, 131.9, 128.1, 126.3, 67.3, 60.3, 52.03, 45.1, 44.5, 38.0, 36.82, 36.0, 33.5, 32.3, 30.6, 28.5, 28.4, 24.6, 21.6, 20.3. IR, ν, cm^{-1}: 3239, 3117, 2856, 2168, 1750, 1691, 1433, 1327, 1241, 1129, 903, 701. Anal. calcd (%) for: $C_{23}H_{32}Br_2N_2O_2S$: C, 49.30; H, 5.76; Br, 28.52; N, 5.00; S, 5.72; found: C, 49.18; H, 5.77; Br, 28.20; N, 4.96; S, 5.81.

The reaction of *β*-caryophyllene 1 with *p*-trifluoromethylbenzenesulfonamide 2h and NBS in MeCN

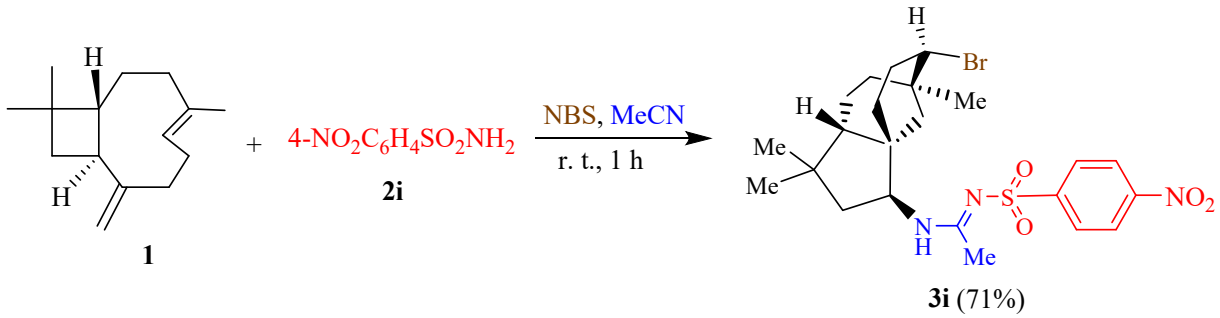


3h (83%)

1 g (4.4 mmol) of *p*-trifluoromethylbenzenesulfonamide **2h** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1 ml (4.4 mmol) of *β*-caryophyllene **1**. After a few minutes, 0.86 g (4.8 mmol) of NBS was added, the mixture was stirred for 1 h, the solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with water (3ß100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3h** was isolated. Yield of product **3h** 2.20 g (83%).

N-(6-Bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-((4-(trifluoromethyl)phenyl)sulfonyl)acetimidamide, 3h. White solid. M.p. 207.7°C. ^{1}H NMR (400 MHz, CD_3CN) δ 8.04 (d, J = 8.1 Hz, 2H), 7.80 (d, 2H), 6.85 (s, 1H), 4.18 (m, 2H), 2.37 (s, 3H), 2.30–2.24 (m, 1H), 1.85 (m 1H), 1.56 (m, 2H), 1.50 (m 3H), 1.41–1.38 (m, 2H), 1.30–1.24 (m, 2H), 1.07 (m 1H), 1.04 (s, 3H), 0.91 (m 1H), 0.87 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ: 167.4, 142.3, 140.7, 133.6, 128.1, 127.1, 127.0, 123.8, 120.2, 69.3, 61.5, 53.0, 45.9, 45.7, 38.9, 38.0, 37.0, 34.4, 32.8, 30.8, 29.8, 29.5, 25.0, 21.3, 21.2. ^{19}F NMR (376 MHz, CD_3CN) δ: -62.67. IR, ν, cm^{-1}: 2930, 2862, 1653, 1550, 1436, 1323, 1285, 1159, 1093, 871, 792, 754, 711, 624. Anal. calcd (%) for $C_{24}H_{32}BrF_3N_2O_2S$: C, 52.46; H, 5.87; Br, 14.54; F, 10.37; N, 5.10; S, 5.83; found: C, 52.75; H, 5.93; Br, 14.32; F, 10.29; N, 5.08; S, 5.75.

The reaction of *β*-caryophyllene 1 with nosylamide 2i and NBS in MeCN

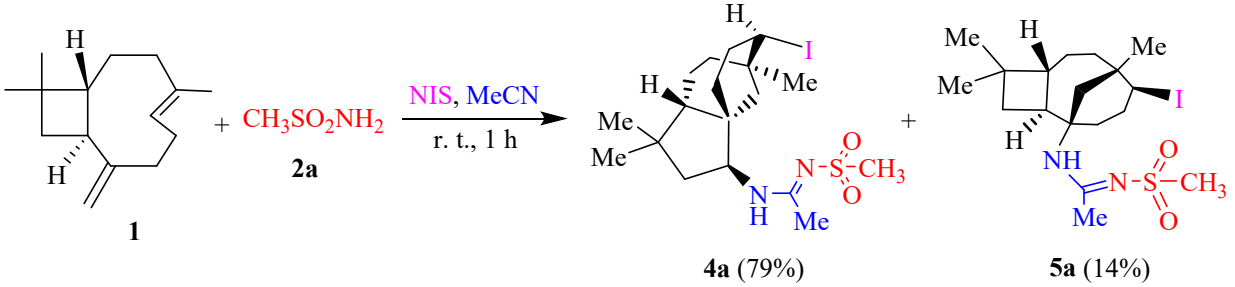


1 g (4.9 mmol) of nosylamide **2i** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 2.93 ml (12.8 mmol) of *β*-caryophyllene **1**. After a few minutes, 2.28 g (12.8 mmol) of NBS was added and the mixture was stirred for 1 h. The solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with water (3×100 ml) to remove succinimide. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **3i** was isolated. Yield of product **3i** 2.01 g (71%).

N-(6-bromo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-((4-nitrophenyl)sulfonyl)acetimidamide, 3i. White solid. M.p. 194.6°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.33–8.26 (m, 2H), 8.17–8.05 (m, 2H), 6.07 (d, J = 8.5 Hz, 1H), 4.14 (m, 1H), 4.06 (m, 1H), 2.51 (s, 3H), 2.25–2.12 (m, 1H), 1.87 (ddt, J = 15.5, 4.5, 2.4 Hz, 1H), 1.63 (dd, J = 11.6, 5.9 Hz, 1H), 1.56–1.43 (m, 3H), 1.43–1.36 (m, 1H), 1.28 (m, 1H), 1.25–1.13 (m, 2H), 1.02 (d, J = 2.4 Hz, 1H), 1.00 (s, 3H), 0.95–0.88 (m, 1H), 0.85 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.8, 149.4, 149.0, 127.7, 124.0, 67.2, 60.5, 52.0, 45.2, 44.4, 38.1, 36.9, 35.9, 33.3, 32.2, 30.5, 28.4, 28.4, 24.6, 21.9, 20.2. IR, ν, cm^{-1}: 3263, 3098, 2792, 2315, 1728, 1656, 1402, 1363, 1236, 1059, 900, 697, 541. Anal. calcd (%) for $C_{23}H_{32}BrN_3O_4S$: C, 52.47; H, 6.13; Br, 15.18; N, 7.98; S, 6.09; found: C, 52.68; H, 6.11; Br, 15.27; N, 8.05; S, 6.23.

2.2 Procedures for the synthesis of compounds 4, 5

The reaction of *β*-caryophyllene 1 with methanesulfonamide 2a and NIS in MeCN



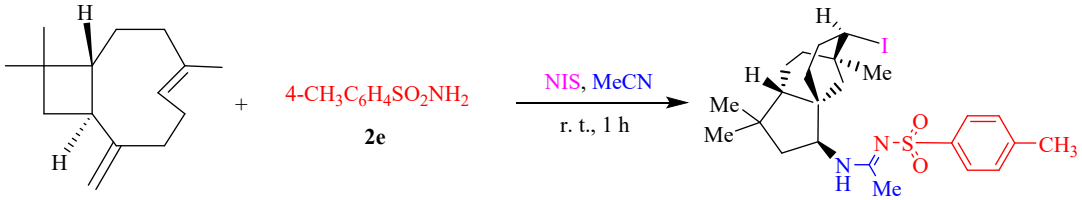
1 g (10.5 mmol) of methanesulfonamide **2a** was dissolved in 50 ml (0.954 mol) of MeCN. Then, 2.4 ml (10.5 mmol) of *β*-caryophyllene **1** was added, and after a few minutes, 2.4 g (10.5

mmol) of NIS. The mixture was stirred for 1 h, the solvent was removed under reduced pressure, the residue dissolved in 50 ml of $CHCl_3$ and washed with a saturated solution of $Na_2S_2O_3$ to remove NIS. The extract was dried over $CaCl_2$, the solvent removed under reduced pressure, the residue dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether fraction 1:5 two solid products **4a** and **5a** were isolated in a mixture with oil. The precipitate was washed with ether 3 times to remove the oil impurity. The yield of product **4a** was 3.90 g (79%), and of product **5a** 0.7 g (14%).

N-(6-Iodo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-(methylsulfonyl)acetimidamide, 4a. White solid. M.p. 164.5°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ: 5.43 (d, J = 8.4 Hz, 1H), 4.38 (s, 1H), 4.18 (ddd, J = 12.3, 8.2, 5.9 Hz, 1H), 3.05 (s, 3H), 2.48 (s, 3H), 2.17 (s, 1H), 2.09 (dt, J = 12.7, 3.8 Hz, 1H), 2.06–1.96 (m, 1H), 1.81 (d, J = 13.4 Hz, 1H), 1.77–1.67 (m, 2H), 1.66–1.57 (m, 2H), 1.49–1.41 (m, 2H), 1.37–1.31 (m, 2H), 1.30–1.23 (m, 1H), 1.05 (d, J = 2.2 Hz, 6H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.0, 60.2, 53.3, 45.5, 44.6, 43.1, 42.2, 38.8, 38.6, 38.2, 36.0, 35.9, 31.5, 30.6, 29.8, 24.6, 21.6, 20.4. IR, ν, cm^{-1}: 3272, 3077, 2918, 1696, 1578, 1501, 1404, 1309, 1250, 1141, 1019, 901, 785, 616. Anal. calcd (%) for $C_{18}H_{31}IN_2O_2S$: C, 46.35; H, 6.70; I, 27.21; N, 6.01; S, 6.87; found: C, 46.19; H, 6.62; I, 27.26; N, 6.19; S, 7.02.

N-(9-Iodo-4,4,8-trimethyltricyclo[6.3.1.02,5]dodecan-1-yl)-N'-(methylsulfonyl)acetimidamide, 5a. White solid. M.p. 193.1°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 4.48 (s, 1H), 2.95 (s, 3H), 2.51 (m, 1H), 2.38 (s, 3H), 2.29 (m, 1H), 2.23–2.10 (m, 1H), 1.96–1.88 (m, 1H), 1.79 (m, 5H), 1.61 (m, 1H), 1.54–1.46 (m, 1H), 1.23 (m, 2H), 1.01 (s, 3H), 0.96 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.6, 57.5, 46.8, 45.1, 43.3, 42.0, 41.0, 39.1, 35.3, 34.4, 33.8, 32.8, 32.2, 30.5, 28.3, 22.0, 21.9, 20.8. IR, ν, cm^{-1}: 3291, 3102, 2898, 1703, 1569, 1457, 1398, 1317, 1269, 1152, 1005, 906, 793, 708, 599. Anal. calcd (%) for $C_{18}H_{31}IN_2O_2S$: C, 46.35; H, 6.70; I, 27.21; N, 6.01; S, 6.87; found: C, 46.06; H, 6.75; I, 26.97; N, 6.14; S, 7.00.

The reaction of *β*-caryophyllene 1 with tosylamide 2e and NIS in MeCN

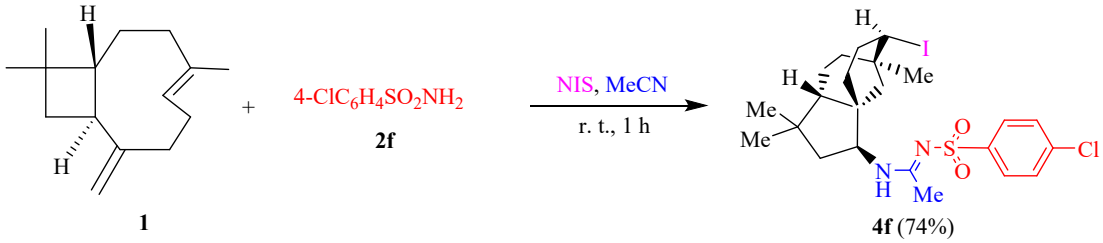


1 **2e** **4e** (74%)

1 g (5.8 mmol) of tosylamide **2e** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.3 ml (5.8 mmol) of *β*-caryophyllene **1**, and, after a few minutes, 1.3 g (5.8 mmol) of NIS. After stirring for 1 h, the precipitate of product **4e** was formed. The mixture was filtered, the precipitate was washed with ether. The yield of product **4e** 2.34 g (74%).

N-(6-Iodo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-tosylacetimidamide, 4e. White solid. M.p. 259.5°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.7 Hz, 2H), 5.48 (s, 1H), 5.41–5.28 (m, 1H), 4.35 (dt, J = 12.3, 7.5 Hz, 1H), 2.43 (s, 3H), 2.41(s, 3H), 2.27 (m, J = 1H), 1.81 (m, 1H), 1.76–1.68 (m, 3H), 1.52–1.35 (m, 2H), 1.34–1.27 (m, 3H), 1.13–1.06 (m, 2H), 1.03 (m, J = 1H), 0.92 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.2, 134.6, 132.0, 129.0, 126.5, 60.5, 56.4, 56.0, 48.4, 47.4, 38.5, 36.9, 33.0, 32.7, 29.9, 28.0, 27.8, 26.7, 22.6, 21.9, 21.5, 21.2. IR, ν, cm^{-1}: 3307, 3127, 2939, 2860, 1554, 1443, 1645, 1273, 1145, 1090, 1032, 905, 813, 757, 702, 613, 555. HRMS (ESI): *m/z* calcd for $C_{24}H_{36}IN_2O_2S^+$: 543.15423; found: 543.15497.

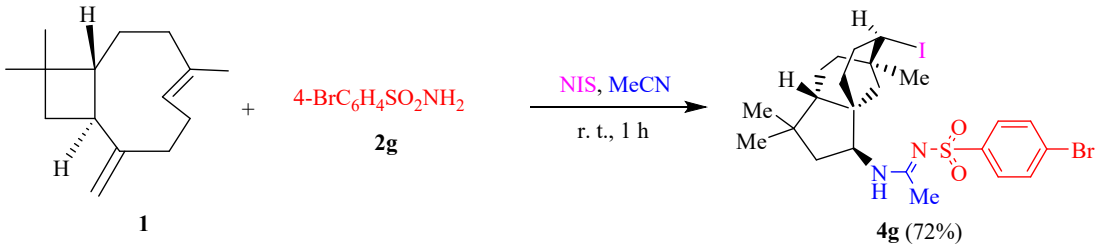
The reaction of *β*-caryophyllene 1 with *p*-chlorobenzenesulfonamide 2f and NIS in MeCN



1 g (5.2 mmol) of *p*-chlorobenzenesulfonamide **2f** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.2 ml (5.2 mmol) of *β*-caryophyllene **1**. Then, after a few minutes, 1.2 g (5.2 mmol) of NIS was added to this solution. The mixture was stirred for 1 h. Then the solvent was removed under reduced pressure. The resulting reaction mixture was dissolved in 50 ml of $CHCl_3$ and washed with a saturated solution of sodium thiosulfate $Na_2S_2O_3$ to remove NIS. The extract was dried over $CaCl_2$. Then the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, solid product **4f** mixed with oil was isolated. The precipitate was washed with ether 3 times to remove the oil impurity. Yield of product **4f** 2.23 g (75%).

N-(6-iodo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-tosylacetimidamide, 4f. White solid. M.p. 173°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.89 (d, J = 7.3 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 5.88 (d, J = 8.4 Hz, 1H), 4.31 (s, 1H), 4.18 (ddd, J = 13.7, 8.5, 5.8 Hz, 1H), 2.47 (s, 3H), 2.14 (s, 1H), 2.06–1.97 (m, 1H), 1.90 (dd, J = 15.2, 3.9 Hz, 1H), 1.71 (m, 1H), 1.64–1.52 (m, 2H), 1.46 (m, 3H), 1.34–1.21 (m, 3H), 1.06 (d, J = 12.2 Hz, 1H), 1.00 (s, 6H), 0.90 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 165.4, 142.0, 137.8, 128.9, 128.0, 60.1, 53.5, 53.1, 45.2, 44.7, 38.5, 38.0, 35.9, 35.8, 31.5, 30.6, 30.5, 29.8, 24.6, 21.7, 20.2. IR, ν, cm^{-1}: 3906, 3856, 3746, 3309, 3130, 2953, 2866, 2346, 2252, 1547, 1445, 1269, 1145, 1099, 1011, 910, 723, 618. HRMS (ESI): m/z calcd for: $C_{23}H_{33}ClIN_2O_2S^+$: 563.09961; found: 563.09999.

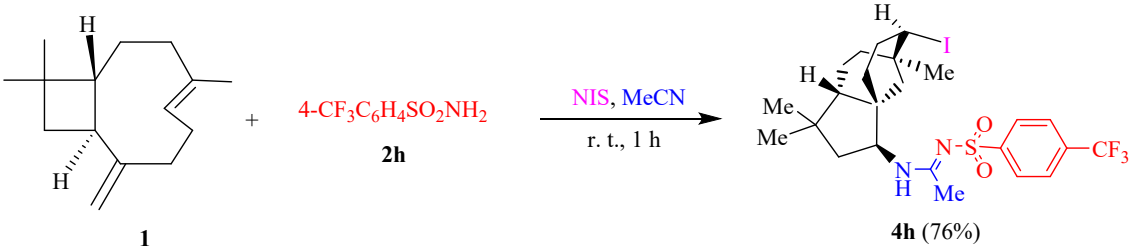
The reaction of *β*-caryophyllene 1 with *p*-bromobenzenesulfonamide 2g and NIS in MeCN



1 g (4.2 mmol) of *p*-bromobenzenesulfonamide **2g** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1 ml (4.2 mmol) of *β*-caryophyllene **1** and, after a few minutes, 0.95 g (4.2 mmol) of NIS. After stirring for 1 h, the precipitate of product **4g** was formed. The precipitate was filtered off and washed with ether to give 1.85 g (72%) of **4g**.

N'-((4-bromophenyl)sulfonyl)-N-(6-iodo-1,1,7-trimethyldecahydro-3a,7-methano-cyclopenta[8]annulen-3-yl)acetimidamide, 4g. White solid. M.p. 185.5°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.83 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 5.68 (s, 1H), 4.32 (s, 1H), 4.19 (tt, J = 8.8, 5.8 Hz, 1H), 2.49 (s, 3H), 2.14 (m, 1H), 2.10–1.98 (m, 1H), 1.92 (m, 1H), 1.61 (m, 2H), 1.55–1.50 (m, 1H), 1.43 (m, 2H), 1.37–1.33 (m, 1H), 1.30 (m, 1H), 1.26 (m, 2H), 1.06 (m, 1H), 1.01 (s, 3H), 0.90 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.4, 142.5, 131.9, 128.2, 126.3, 60.1, 53.4, 53.2, 46.2, 44.6, 38.5, 38.1, 35.9, 35.9, 31.6, 30.6, 30.5, 29.8, 24.7, 21.9, 20.3. IR, ν, cm^{-1}: 3307, 3130, 2952, 2866, 2346, 1959, 1655, 1554, 1465, 1387, 1268, 1145, 1090, 1007, 755, 667, 617, 569. HRMS (ESI): *m/z* calcd for: $C_{23}H_{33}BrIN_2O_2S^+$: 607.04909; found: 607.04940.

The reaction of *β*-caryophyllene 1 with *p*-triphosphorbenzenesulfonamide 2h and NIS in MeCN

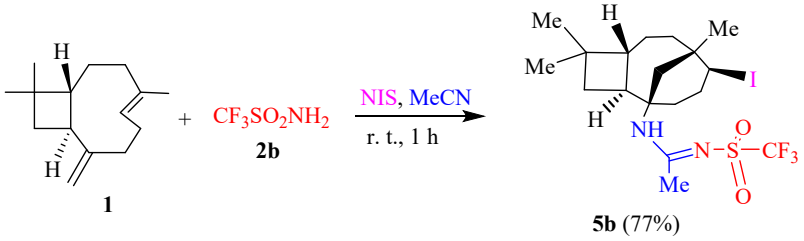


1 g (4.4 mmol) of *p*-trifluorobenzenesulfonamide **2h** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution 1 ml (4.4 mmol) of *β*-caryophyllene **1** was added. After a few minutes, 1 g (4.4 mmol) of NIS was added, the mixture was stirred for 1 h. The formed precipitate of **4h** wass filtered and washed with ether. The yield of product **4h** 1.80 g (76%).

N-(6-Iodo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-((4-(trifluoromethyl)phenyl)sulfonyl)acetimidamide, 4h. White solid. M.p. 193.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 5.54 (d, J = 8.6 Hz, 1H), 4.31 (s, 1H), 4.18 (ddd, J = 13.8, 8.7, 5.9 Hz, 1H), 2.54 (s, 3H), 2.09–2.02 (m, 1H), 1.99–1.91

(m, 1H), 1.78–1.61 (m, 2H), 1.55 (d, J = 6.8 Hz, 1H), 1.44–1.38 (m, 2H), 1.30 (d, J = 4.1 Hz, 1H), 1.27 (d, J = 4.3 Hz, 1H), 1.18 (m, 1H), 1.08 (d, 1H), 1.02 (s, 3H), 0.98 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.5, 149.6, 147.2, 127.1, 125.8, 60.3, 53.4, 53.2, 45.3, 44.7, 38.6, 38.1, 35.8, 35.7, 31.5, 30.6, 30.5, 29.9, 24.7, 22.0, 20.2. IR, ν, cm^{-1}: 3307, 3133, 2954, 1656, 1551, 1445, 1403, 1326, 1280, 1136, 1094, 1012, 910, 842, 792, 724, 620. Anal. calcd (%) for $C_{24}H_{32}F_3IN_2O_2S$: C, 48.33; H, 5.41; F, 9.56; I, 21.28; N, 4.70; S, 5.37; found: C, 48.61; H, 5.47; F, 9.32; I, 21.04; N, 4.55; S, 5.39.

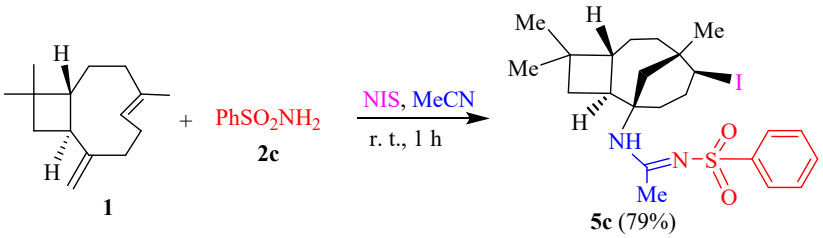
The reaction of *β*-caryophyllene 1 with triflamide 2b and NIS in MeCN



1 g (6.7 mmol) of triflamide **2b** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution 1.53 ml (6.7 mmol) of *β*-caryophyllene **1** was added. After a few minutes, 1.5 g (6.7 mmol) of NIS was added and the mixture was stirred for 1 h. The formed precipitate of **5b** was filtered and washed with ether. The yield of product **5b** 2.70 g (77%).

N-(9-Iodo-4,4,8-trimethyltricyclo[6.3.1.02,5]dodecan-1-yl)-N'-(trifluoromethylsulfonyl)-acetimidamide, 5b. White solid. M.p. 189.5°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ: 5.87 (s, 1H), 4.58–4.44 (m, 1H), 2.69–2.56 (m, 1H), 2.48 (s, 3H), 2.44–2.30 (m, 2H), 2.20 (m, 1H), 1.85 (m, 3H), 1.77–1.69 (m, 2H), 1.58–1.44 (m, 1H), 1.36–1.18 (m, 1H), 1.07 (d, J = 1.8 Hz, 1H), 1.05 (s, 3H), 0.99 (s, 3H), 0.98 (s, 3H), 0.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 59.3, 45.4, 44.6, 42.4, 41.1, 39.1, 39.1, 35.2, 34.4, 33.9, 32.9, 32.2, 30.4, 23.0, 22.0, 20.7. ^{19}F NMR (376 MHz,) δ -79.06. IR, ν, cm^{-1}: 3317, 2929, 2866, 1653, 1558, 1447, 1318, 1189, 1142, 1039, 909, 789, 732, 663, 602, 540, 484. Anal. calcd (%) for $C_{18}H_{28}F_3IN_2O_2S$: C, 41.55; H, 5.42; F, 10.95; I, 24.39; N, 5.38; S, 6.16; found: C, 41.43; H, 5.49; F, 10.72; I, 24.21; N, 5.34; S, 6.39.

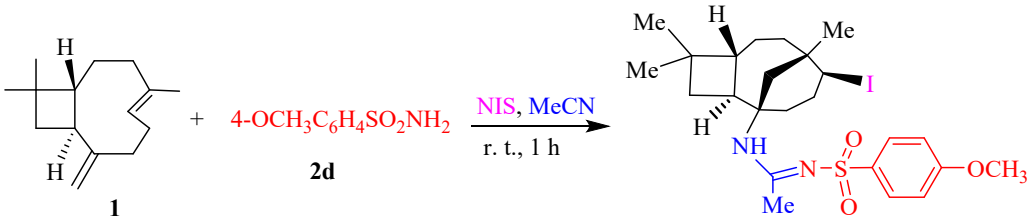
The reaction of *β*-caryophyllene 1 with benzenesulfonamide 2c and NIS in MeCN



1 g (6.3 mmol) of benzenesulfonamide **2c** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution 1.45 ml (6.3 mmol) of *β*-caryophyllene **1** was added. After a few minutes, 1.4 g (6.3 mmol) of NIS was added and the mixture was stirred for 1 h. The formed precipitate of **5c** was filtered and washed with ether. The yield of product **5c** 2.66 g (79%).

N-(9-Iodo-4,4,8-trimethyltricyclo[6.3.1.02,5]dodecan-1-yl)-N'-(phenylsulfonyl)acetimidamide, 5c. White solid. M.p. 178.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93–7.82 (m, 2H), 7.51–7.45 (m, 3H), 5.27 (s, 1H), 4.46 (t, J = 4.5 Hz, 1H), 2.51–2.43 (m, 1H), 2.37–2.28 (m, 1H), 2.28–2.16 (m, 1H), 2.15–2.08 (m, 1H), 1.81 (m, 2H), 1.77–1.69 (m, 2H), 1.68 (s, 1H), 1.49–1.38 (m, 2H), 1.24–1.12 (m, 3H), 0.98 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.8, 143.5, 131.6, 128.6, 126.4, 57.8, 54.8, 46.4, 45.1, 42.2, 41.1, 39.1, 39.0, 35.2, 34.3, 34.0, 33.4, 32.2, 30.4, 22.1, 20.8. IR, ν, cm^{-1}: 3311, 3119, 2930, 2859, 1959, 1655, 1554, 1446, 3181, 1270, 1145, 1090, 3903, 741, 690, 640, 587, 522. HRMS (ESI): *m/z* calcd for $C_{23}H_{33}IN_2O_2S^+$: 529.13858; found: 529.13890.

The reaction of *β*-caryophyllene 1 with *p*-methoxybenzenesulfonamide 2d and NIS in MeCN

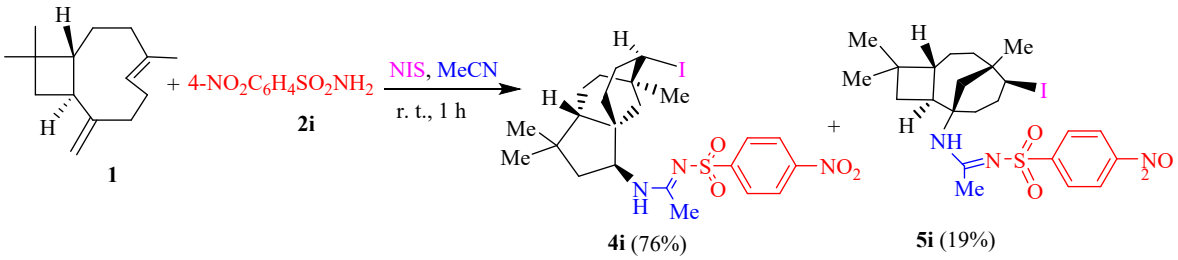


5d (80%)

1 g (5.3 mmol) of *p*-methoxybenzenesulfonamide **2d** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 1.2 ml (5.3 mmol) of *β*-caryophyllene **1**. After a few minutes, 1.2 g (5.3 mmol) of NIS was added, the mixture was stirred for 1 h, the solvent was removed under reduced pressure. The residue was dissolved in 50 ml of $CHCl_3$ and washed with a saturated solution of $Na_2S_2O_3$ to remove NIS. The extract was dried over $CaCl_2$, the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and separated by column chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, hexane-ether 1:9. From the hexane-ether 1:3.5 fraction, a solid product **5d** mixed with oil was isolated. The precipitate was washed with ether 3 times to remove the oil impurity. Yield of product **5d** 2.40 g (80%).

N-(9-Iodo-4,4,8-trimethyltricyclo[6.3.1.02,5]dodecan-1-yl)-N'-(phenylsulfonyl)acetimidamide, 5d. White solid. M.p. 112.5°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.81 (d, J = 8.8 Hz, 2H), 7.01–6.89 (d, 2H), 5.39 (s, 1H), 4.46 (m, 1H), 3.86 (s, 3H), 2.57–2.47 (m, 1H), 2.38 (s, 3H), 2.31 (m, 1H), 2.21 (m, 1H), 2.11 (m, 1H), 1.84–1.69 (m, 4H), 1.51–1.35 (m, 2H), 1.23–1.12 (m, 2H), 0.98 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0, 161.8, 135.5, 128.0, 113.6, 57.6, 55.5, 46.5, 44.8, 42.0, 41.6, 39.2, 38.6, 35.0, 34.1, 33.9, 33.4, 32.1, 30.2, 22.0, 21.1, 20.7. IR, ν, cm^{-1}: 3312, 3120, 2951, 2862, 2251, 1549, 1503, 1448, 1381, 1261, 1145, 1090, 1032, 911, 805, 737, 630, 565. HRMS (ESI): *m/z* calcd $C_{24}H_{36}IN_2O_3S^+$: 559.14913; found: 559.14935.

The reaction of *β*-caryophyllene 1 with nosylamide 2i and NIS in MeCN

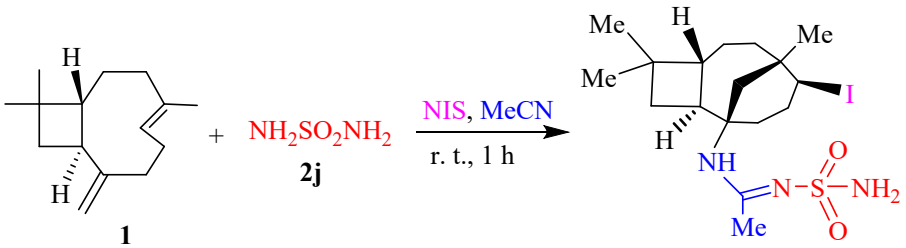


1 g (4.9 mmol) of nosylamide **2i** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution 1.1 ml (4.9 mmol) of *β*-caryophyllene **1** was added. After a few minutes, 1.1 g (4.9 mmol) of NIS was added and the mixture was stirred for 1 h. The solvent was removed under reduced pressure, the residue was dissolved in 50 ml of $CHCl_3$ and washed with a saturated solution of $Na_2S_2O_3$ to remove NIS. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and separated by flash chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, two solid products **4i** and **5i** were isolated in a mixture with oil. The precipitate was washed with ether 3 times to remove the oil impurity. Yield of product **4i** 2.16 g (76%) and of product **5i** (19%).

N-(6-Iodo-1,1,7-trimethyldecahydro-3a,7-methanocyclopenta[8]annulen-3-yl)-N'-((4-nitrophenyl)sulfonyl)acetimidamide, 4i. White solid. M.p. 167.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33–8.29 (d, J = 8.8 Hz, 2H), 8.19–8.12 (d, J = 8.8 Hz, 2H), 5.61 (d, J = 9.0 Hz, 1H), 4.32 (d, J = 3.1 Hz, 1H), 4.22–4.10 (m, 1H), 2.55 (s, 3H), 2.10–2.02 (m, 1H), 1.98–1.87 (m, 1H), 1.67 (m, 1H), 1.64–1.54 (m, 2H), 1.53–1.44 (m, 1H), 1.45–1.35 (m, 2H), 1.32 (m, 1H), 1.27 (m, 1H), 1.26–1.13 (m, 1H), 1.03 (s, 3H), 0.92 (d, J = 3.8 Hz, 1H), 0.89–0.81 (s, 6H), 0.84–0.76 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.8, 149.3, 149.0, 127.8, 127.5, 124.2, 124.0, 123.8, 60.3, 53.8, 53.0, 45.0, 44.7, 38.7, 38.0, 35.8, 35.7, 31.3, 30.4, 30.4, 29.8, 24.6, 21.8, 20.1. IR, ν, cm^{-1}: 3313, 3130, 2954, 2867, 2254, 1795, 1530, 1445, 1354, 1281, 1141, 1099, 1033, 911, 855, 733, 686, 620, 569. HRMS (ESI): m/z calcd for $C_{23}H_{33}IN_3O_4S^+$: 574.12366; found: 574.12329.

N-(9-Iodo-4,4,8-trimethyltricyclo[6.3.1.02,5]dodecan-1-yl)-N'-((4-nitrophenyl)sulfonyl)-acetimidamide, 5i. White solid. M.p. 185.5°C. ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.35–8.26 (m, 2H), 8.11–8.02 (m, 2H), 5.30 (s, 1H), 4.42 (t, J = 4.3 Hz, 1H), 2.47 (s, 3H), 2.31 (m, 2H), 2.23–2.13 (m, 1H), 2.13–2.04 (m, 1H), 1.87–1.74 (m, 2H), 1.73–1.66 (m, 2H), 1.62 (m, 1H), 1.44 (m, 2H), 1.21–1.12 (m, 2H), 0.98 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.2, 149.5, 149.0, 127.6, 124.0, 58.2, 46.2, 45.1, 42.1, 40.8, 39.1, 39.0, 35.2, 34.5, 33.7, 32.7, 32.1, 30.4, 22.6, 21.9, 20.7. IR, ν, cm^{-1}: 3322, 3107, 2932, 2862, 2255, 1657, 1535, 1449, 1349, 1282, 1150, 1094, 911, 855, 733, 662, 610, 540, 163. HRMS (ESI): *m/z* calcd for $C_{23}H_{33}IN_3O_4S^+$: 574.12366; found: 574.12363.

The reaction of *β*-caryophyllene 1 with sulfamide 2j and NIS in MeCN



5j (80%)

1 g (10.4 mmol) of sulfamide **2j** was dissolved in 50 ml (0.954 mol) of MeCN. To this solution was added 2.37 ml (10.4 mmol) of *β*-caryophyllene **1**. After a few minutes, 2.34 g (10.4 mmol) of NIS were added and the mixture was stirred for 1 h. Then the solvent was removed under reduced pressure, the residue was dissolved in 50 ml of $CHCl_3$ and washed with saturated solution of $Na_2S_2O_3$ to remove NIS. The extract was dried over $CaCl_2$, the solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and separated by flash chromatography on silica gel by successive elution with hexane, hexane-ether 1:2, 1:3.5, 1:5, 1:7, 1:9. From the hexane-ether 1:9 fraction, product **5j** was isolated as an oil. Yield of product **5j** 3.93 g (80%).

N-(9-Iodo-4,4,8-trimethyltricyclo[6.3.1.02,5]dodecan-1-yl)-N'-sulfamoylacetimidamide, 5j. Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.31 (s, 1H), 4.59 (s, 2H), 4.49 (m, 1H), 2.58–2.48 (m, 1H), 2.39 (s, 3H), 2.36–2.30 (m, 1H), 2.19–2.14 (m, 1H), 2.03–1.96 (m, 1H), 1.84 (m, 3H), 1.71 (m, 1H), 1.56 (m, 1H), 1.47 (m, 1H), 1.22 (m, 2H), 1.04 (s, 1H), 1.02 (s, 3H), 0.98 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1, 57.4, 47.4, 44.8, 41.9, 40.9, 39.1, 39.0, 35.1, 34.2, 33.7, 32.7, 32.1, 30.3, 21.9, 20.9, 20.7. IR, ν, cm^{-1}: 3323, 3125, 2945, 2862, 2252, 1775, 1712, 1558, 1449, 1381, 1294, 1141, 1036, 908, 728, 646, 550, 406. Anal. calcd (%) for: $C_{17}H_{30}IN_3O_2S$: C, 43.68; H, 6.47; I, 27.15; N, 8.99; S, 6.86; found: C, 43.92; H, 6.55; I, 26.97; N, 9.03; S, 6.59.

X-ray study and refinement

Crystal data were collected on a Bruker D8 Venture diffractometer with MoKa radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set 1 . Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set. **CCDC 2430945 (3b), CCDC 2430948 (3h), CCDC 2430944 (4h), CCDC 2430947 (5a), CCDC 2430946 (5b)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures

Crystal Structure Determination

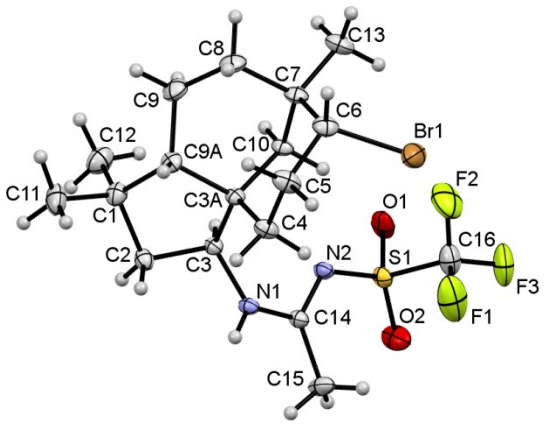
Data were collected on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer with CuK_α radiation (λ = 1.54178 Å) using the φ and ω scans technique. Using Olex2 [31], the structure was solved with the ShelXS [32] structure solution program using Direct Methods and refined with the XL [32] refinement package using Least Squares minimisation. Data were corrected for absorption effects using the multi-scan method (SADABS) [33]. All non-hydrogen atoms were refined anisotropically using SHELX [32]. The coordinates of the hydrogen atoms were calculated from geometrical positions and refined using a riding model.

References

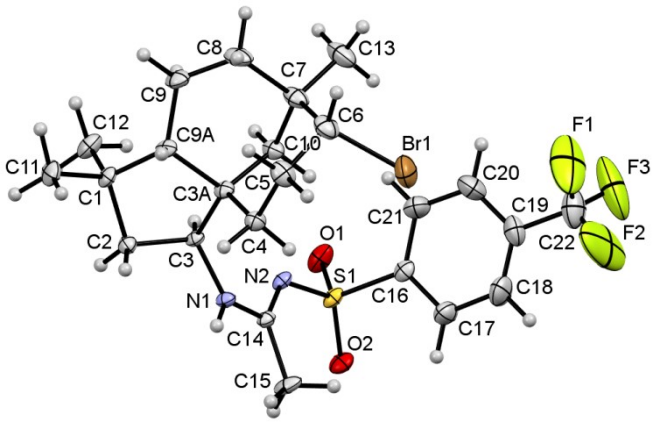
31. Dolomanov O.V., Bourhis L.J., Gildea R.J, Howard, J.A.K. & Puschmann, H. *A Complete Structure Solution, Refinement and Analysis Program*, J. Appl. Crystallogr., **2009**, 42, 339. https://doi.org/10.1107/S0021889808042726

32. Sheldrick G.M. *A short history of SHELX*, Acta Crystallographica Section A: Foundations and Advances, **2008**, A64, 112. https://doi.org/10.1107/S0108767307043930

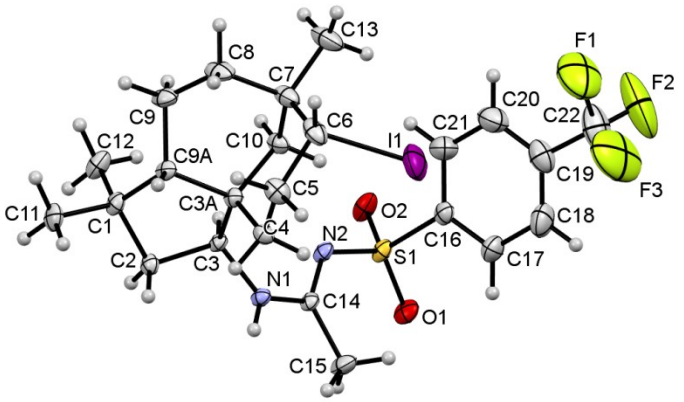
33. Bruker. Program name. Bruker AXS Inc., Madison, Wisconsin, USA, **2001**. / Bruker. Program name. Bruker AXS Inc., Madison, Wisconsin, USA, **2012**.



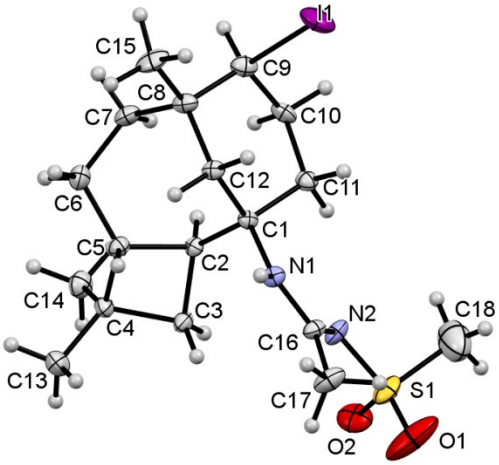
3b



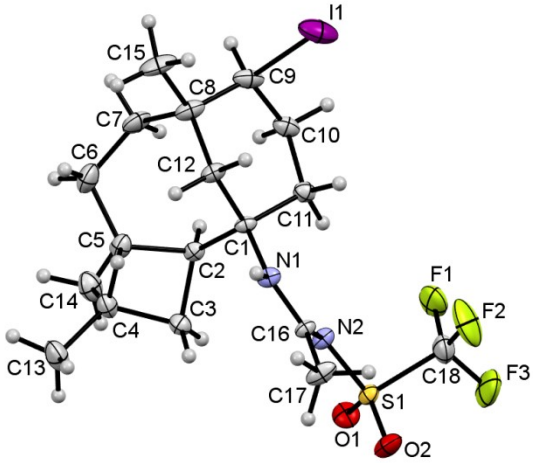
3h



4h



5a



5b

Table S1. Bond lengths, bond angles and torsion angles for compound 3b

Bond *l*, Å						Angle ϕ, ˚					Torsion angle θ, ˚				
Br1	C6	1.981(5)	O1	S1	N2	108.55(17)	Br1	C6	C5	C4	-77.1(4)
S1	O1	1.431(3)	O1	S1	C16	102.8(2)	S1	N2	C14	N1	-179.4(3)
S1	O2	1.415(3)	O2	S1	O1	116.6(2)	S1	N2	C14	C15	0.9(5)
S1	N2	1.564(3)	O2	S1	N2	118.09(16)	O1	S1	N2	C14	160.2(3)
S1	C16	1.819(5)	O2	S1	C16	104.8(2)	O1	S1	C16	F1	171.5(4)
F1	C16	1.304(6)	N2	S1	C16	103.93(18)	O1	S1	C16	F2	50.7(4)
F2	C16	1.321(6)	C14	N2	S1	123.9(2)	O1	S1	C16	F3	-68.2(4)
F3	C16	1.316(5)	C14	N1	C3	126.8(3)	O2	S1	N2	C14	24.5(4)
N2	C14	1.342(5)	F1	C16	S1	111.7(3)	O2	S1	C16	F1	-66.1(4)
N1	C14	1.310(4)	F1	C16	F2	108.1(5)	O2	S1	C16	F2	173.1(3)
N1	C3	1.467(4)	F1	C16	F3	108.1(5)	O2	S1	C16	F3	54.1(4)
C14	C15	1.496(5)	F2	C16	S1	111.1(4)	N2	S1	C16	F1	58.4(4)
C3	C3A	1.562(4)	F3	C16	S1	110.3(3)	N2	S1	C16	F2	-62.4(4)
C3	C2	1.528(5)	F3	C16	F2	107.4(4)	N2	S1	C16	F3	178.7(3)
C3A	C10	1.536(5)	N2	C14	C15	127.0(3)	N1	C3	C3A	C10	94.5(3)
C3A	C4	1.530(5)	N1	C14	N2	116.8(3)	N1	C3	C3A	C4	-27.0(4)
C3A	C9A	1.573(5)	N1	C14	C15	116.2(3)	N1	C3	C3A	C9A	-147.3(3)
C10	C7	1.545(4)	N1	C3	C3A	116.6(3)	N1	C3	C2	C1	168.0(3)
C7	C13	1.525(6)	N1	C3	C2	109.3(3)	C16	S1	N2	C14	-91.0(3)
C7	C6	1.545(6)	C2	C3	C3A	104.6(3)	C14	N1	C3	C3A	-91.5(4)
C7	C8	1.561(6)	C3	C3A	C9A	102.8(3)	C14	N1	C3	C2	150.3(3)
C6	C5	1.517(6)	C10	C3A	C3	113.3(3)	C3	N1	C14	N2	6.4(5)
C5	C4	1.533(5)	C10	C3A	C9A	109.6(3)	C3	N1	C14	C15	-173.9(3)
C9A	C1	1.553(6)	C4	C3A	C3	111.3(3)	C3	C3A	C10	C7	173.4(3)
C9A	C9	1.531(6)	C4	C3A	C10	107.6(3)	C3	C3A	C4	C5	-178.4(3)
C1	C2	1.524(6)	C4	C3A	C9A	112.2(3)	C3	C3A	C9A	C1	1.9(4)
C1	C11	1.533(6)	C3A	C10	C7	111.0(3)	C3	C3A	C9A	C9	-126.2(3)

C1	C12	1.536(6)	C10	C7	C8	110.1(3)	C3A	C3	C2	C1	42.4(4)
C9	C8	1.518(6)	C13	C7	C10	109.9(3)	C3A	C10	C7	C13	-176.1(3)
			C13	C7	C6	112.1(3)	C3A	C10	C7	C6	60.7(4)
			C13	C7	C8	109.4(3)	C3A	C10	C7	C8	-55.6(4)
			C6	C7	C10	108.8(3)	C3A	C9A	C1	C2	23.2(4)
			C6	C7	C8	106.4(3)	C3A	C9A	C1	C11	142.3(4)
			C7	C6	Br1	111.7(3)	C3A	C9A	C1	C12	-94.3(4)
			C5	C6	Br1	109.2(3)	C3A	C9A	C9	C8	-51.0(5)
			C5	C6	C7	113.2(4)	C10	C3A	C4	C5	56.8(4)
			C6	C5	C4	113.6(3)	C10	C3A	C9A	C1	122.7(3)
			C3A	C4	C5	112.5(3)	C10	C3A	C9A	C9	-5.4(4)
			C1	C9A	C3A	108.2(3)	C10	C7	C6	Br1	71.5(3)
			C9	C9A	C3A	112.5(3)	C10	C7	C6	C5	-52.1(4)
			C9	C9A	C1	114.9(4)	C10	C7	C8	C9	-1.9(5)
			C2	C1	C9A	102.3(3)	C7	C6	C5	C4	47.9(5)
			C2	C1	C11	111.5(4)	C13	C7	C6	Br1	-50.3(4)
			C2	C1	C12	108.9(3)	C13	C7	C6	C5	-173.9(3)
			C11	C1	C9A	111.1(3)	C13	C7	C8	C9	119.0(4)
			C11	C1	C12	108.7(4)	C6	C7	C8	C9	-119.6(4)
			C12	C1	C9A	114.2(4)	C6	C5	C4	C3A	-50.6(5)
			C1	C2	C3	104.0(3)	C4	C3A	C10	C7	-63.1(4)
			C8	C9	C9A	111.5(4)	C4	C3A	C9A	C1	-117.8(3)
			C9	C8	C7	112.7(3)	C4	C3A	C9A	C9	114.1(4)
							C9A	C3A	C10	C7	59.2(4)
							C9A	C3A	C4	C5	-63.9(4)
							C9A	C1	C2	C3	-40.0(4)
							C9A	C9	C8	C7	55.1(5)
							C1	C9A	C9	C8	-175.5(3)
							C2	C3	C3A	C10	-144.7(3)
							C2	C3	C3A	C4	93.8(3)
							C2	C3	C3A	C9A	-26.5(3)
							C11	C1	C2	C3	-158.8(3)
							C12	C1	C2	C3	81.3(4)
							C9	C9A	C1	C2	149.9(3)
							C9	C9A	C1	C11	-91.0(4)
							C9	C9A	C1	C12	32.4(5)
							C8	C7	C6	Br1	-169.8(2)
							C8	C7	C6	C5	66.5(4)

Table S2. Bond lengths, bond angles and torsion angles for compound **3h**

Bond *l*, Å			Angle ϕ, ˚				Torsion angle θ, ˚				
Br1	C6	1.987(7)	F3	C22	C19	113.7(8)	Br1	C6	C5	C4	-74.6(5)
Br1A	C106	1.975(7)	F1	C22	F3	102.9(12)	Br1A	C106	C105	C104	-75.4(6)
C22	F3	1.254(12)	F1	C22	C19	114.8(8)	C22	C19	C20	C21	-179.4(7)
C22	F1	1.225(12)	F2	C22	F3	104.0(12)	S1	C16	C17	C18	-178.7(5)
C22	F2	1.183(14)	F2	C22	F1	103.5(12)	S1	N2	C14	N1	176.5(3)
C22	C19	1.484(10)	F2	C22	C19	116.3(10)	S1	N2	C14	C15	-4.7(7)
S1	O2	1.431(3)	O2	S1	O1	116.6(2)	S101	C116	C121	C120	179.0(7)
S1	O1	1.436(4)	O2	S1	C16	106.7(2)	S101	C116	C117	C118	-179.5(8)
S1	C16	1.765(5)	O2	S1	N2	115.6(2)	F3	C22	C19	C18	110.0(12)
S1	N2	1.598(3)	O1	S1	C16	106.3(2)	F3	C22	C19	C20	-70.8(13)
S101	O102	1.434(3)	O1	S1	N2	106.60(19)	C13	C7	C8	C9	120.3(6)
S101	O101	1.433(3)	N2	S1	C16	103.94(19)	C13	C7	C6	Br1	-53.7(5)
S101	N102	1.591(3)	O102	S101	O101	116.3(2)	C13	C7	C6	C5	-175.7(5)
S101	C116	1.760(5)	O102	S101	N102	116.42(19)	F1	C22	C19	C18	-131.8(12)
C13	C7	1.534(8)	O102	S101	C116	106.5(2)	F1	C22	C19	C20	47.3(14)

C18	C19	1.322(10)	O101	S101	N102	107.04(19)	F2	C22	C19	C18	-10.8(16)
C18	C17	1.386(9)	O101	S101	C116	106.5(2)	F2	C22	C19	C20	168.3(14)
C19	C20	1.409(11)	N102	S101	C116	102.7(2)	O2	S1	C16	C21	162.3(5)
C20	C21	1.363(10)	C19	C18	C17	121.8(6)	O2	S1	C16	C17	-19.6(5)
C21	C16	1.382(8)	C18	C19	C22	120.5(7)	O2	S1	N2	C14	26.0(4)
C16	C17	1.378(7)	C18	C19	C20	119.1(6)	O1	S1	C16	C21	37.2(5)
N2	C14	1.306(5)	C20	C19	C22	120.4(7)	O1	S1	C16	C17	-144.7(4)
C14	N1	1.318(5)	C21	C20	C19	121.0(6)	O1	S1	N2	C14	157.4(4)
C14	C15	1.499(6)	C20	C21	C16	118.4(6)	O102	S101	N102	C114	11.1(5)
N1	C3	1.460(5)	C21	C16	S1	119.6(4)	O102	S101	C116	C121	-29.0(6)
C3	C3A	1.540(6)	C21	C16	C17	120.9(5)	O102	S101	C116	C117	151.1(6)
C3	C2	1.525(6)	C17	C16	S1	119.4(4)	O101	S101	N102	C114	143.2(4)
C3A	C10	1.526(6)	C14	N2	S1	123.1(3)	O101	S101	C116	C121	-153.8(5)
C3A	C4	1.530(6)	N2	C14	N1	118.4(3)	O101	S101	C116	C117	26.3(6)
C3A	C9A	1.575(6)	N2	C14	C15	127.4(4)	C18	C19	C20	C21	-0.3(12)
C10	C7	1.529(7)	N1	C14	C15	114.2(4)	C19	C18	C17	C16	-0.1(11)
C7	C8	1.577(8)	C14	N1	C3	125.9(3)	C19	C20	C21	C16	-0.3(12)
C7	C6	1.532(9)	N1	C3	C3A	115.4(3)	C20	C21	C16	S1	178.9(6)
C8	C9	1.484(9)	N1	C3	C2	110.8(3)	C20	C21	C16	C17	0.8(10)
C6	C5	1.538(8)	C2	C3	C3A	104.4(3)	C21	C16	C17	C18	-0.6(9)
C5	C4	1.518(7)	C3	C3A	C9A	103.1(3)	C16	S1	N2	C14	-90.5(4)
C2	C1	1.531(6)	C10	C3A	C3	112.2(3)	N2	S1	C16	C21	-75.1(5)
C1	C9A	1.538(7)	C10	C3A	C4	108.2(4)	N2	S1	C16	C17	103.0(5)
C1	C11	1.528(6)	C10	C3A	C9A	110.6(3)	N2	C14	N1	C3	2.0(6)
C1	C12	1.540(7)	C4	C3A	C3	111.2(3)	C14	N1	C3	C3A	-99.3(4)
C9A	C9	1.526(6)	C4	C3A	C9A	111.6(3)	C14	N1	C3	C2	142.4(4)
C113	C107	1.531(8)	C3A	C10	C7	110.2(4)	N1	C3	C3A	C10	91.5(4)
C107	C110	1.531(7)	C13	C7	C8	108.6(5)	N1	C3	C3A	C4	-29.8(5)
C107	C106	1.532(10)	C10	C7	C13	109.4(4)	N1	C3	C3A	C9A	-149.5(3)
C107	C108	1.556(9)	C10	C7	C8	110.0(5)	N1	C3	C2	C1	168.4(3)
C110	C13A	1.531(6)	C6	C7	C13	112.2(6)	C3	C3A	C10	C7	174.1(4)
C13A	C103	1.531(6)	C6	C7	C10	109.0(4)	C3	C3A	C4	C5	-178.2(4)
C13A	C104	1.550(6)	C6	C7	C8	107.7(4)	C3	C3A	C9A	C1	2.5(4)
C13A	C19A	1.560(6)	C9	C8	C7	113.0(4)	C3	C3A	C9A	C9	-126.7(4)
C103	N101	1.453(5)	C7	C6	Br1	112.5(4)	C3	C2	C1	C9A	-40.6(4)
C103	C102	1.533(6)	C7	C6	C5	112.9(5)	C3	C2	C1	C11	-159.7(4)
N101	C114	1.317(5)	C5	C6	Br1	107.6(4)	C3	C2	C1	C12	80.0(4)
C114	N102	1.317(5)	C4	C5	C6	111.6(4)	C3A	C3	C2	C1	43.5(4)
C114	C115	1.495(6)	C5	C4	C3A	112.5(4)	C3A	C10	C7	C13	-175.8(5)
C116	C121	1.340(8)	C16	C17	C18	118.7(6)	C3A	C10	C7	C8	-56.6(5)
C116	C117	1.364(9)	C3	C2	C1	103.5(3)	C3A	C10	C7	C6	61.2(6)
C121	C120	1.392(12)	C2	C1	C9A	102.1(3)	C3A	C9A	C9	C8	-49.5(5)
C120	C119	1.358(14)	C2	C1	C12	109.7(4)	C10	C3A	C4	C5	58.1(5)
C119	C118	1.367(13)	C9A	C1	C12	113.5(4)	C10	C3A	C9A	C1	122.5(4)
C119	C122	1.456(14)	C11	C1	C2	111.5(4)	C10	C3A	C9A	C9	-6.6(5)
C106	C105	1.523(9)	C11	C1	C9A	111.5(4)	C10	C7	C8	C9	0.6(6)
C105	C104	1.511(7)	C11	C1	C12	108.5(4)	C10	C7	C6	Br1	67.7(5)
C108	C109	1.509(9)	C1	C9A	C3A	108.0(3)	C10	C7	C6	C5	-54.4(6)
C109	C19A	1.528(6)	C9	C9A	C3A	111.8(4)	C7	C8	C9	C9A	52.9(6)
C19A	C101	1.547(7)	C9	C9A	C1	116.3(4)	C7	C6	C5	C4	50.1(7)
C101	C102	1.519(6)	C8	C9	C9A	113.0(4)	C8	C7	C6	Br1	-173.0(3)
C101	C112	1.534(6)	C113	C107	C108	109.1(5)	C8	C7	C6	C5	64.9(5)
C101	C111	1.546(7)	C110	C107	C113	109.7(4)	C6	C7	C8	C9	-118.0(5)
C117	C118	1.371(11)	C110	C107	C108	109.8(5)	C6	C5	C4	C3A	-51.9(6)
C122	F101	1.258(16)	C106	C107	C113	112.5(6)	C4	C3A	C10	C7	-62.8(5)
C122	F103	1.217(15)	C106	C107	C110	108.9(4)	C4	C3A	C9A	C1	-117.0(4)
C122	F102	1.266(17)	C106	C107	C108	106.8(5)	C4	C3A	C9A	C9	113.9(4)
			C107	C110	C13A	110.9(4)	C17	C18	C19	C22	179.6(7)
			C110	C13A	C103	113.4(3)	C17	C18	C19	C20	0.5(12)

C110	C13A	C104	107.2(4)	C15	C14	N1	C3	-176.9(4)
C110	C13A	C19A	110.7(3)	C2	C3	C3A	C10	-146.6(4)
C103	C13A	C104	111.0(3)	C2	C3	C3A	C4	92.0(4)
C103	C13A	C19A	103.9(3)	C2	C3	C3A	C9A	-27.7(4)
C104	C13A	C19A	110.6(3)	C2	C1	C9A	C3A	23.3(4)
N101	C103	C13A	116.5(3)	C2	C1	C9A	C9	149.8(4)
N101	C103	C102	110.7(3)	C1	C9A	C9	C8	-174.2(4)
C102	C103	C13A	104.3(3)	C9A	C3A	C10	C7	59.7(5)
C114	N101	C103	126.0(3)	C9A	C3A	C4	C5	-63.7(5)
N101	C114	C115	114.2(4)	C11	C1	C9A	C3A	142.4(4)
N102	C114	N101	118.7(3)	C11	C1	C9A	C9	-91.0(5)
N102	C114	C115	127.2(4)	C12	C1	C9A	C3A	-94.7(4)
C114	N102	S101	124.5(3)	C12	C1	C9A	C9	31.9(5)
C121	C116	S101	119.2(5)	C113	C107	C110	C13A	-175.4(5)
C121	C116	C117	120.1(6)	C113	C107	C106	Br1A	-52.3(6)
C117	C116	S101	120.7(4)	C113	C107	C106	C105	-175.3(5)
C116	C121	C120	120.0(7)	C113	C107	C108	C109	119.5(6)
C119	C120	C121	120.4(8)	C107	C110	C13A	C103	174.5(4)
C120	C119	C118	118.9(7)	C107	C110	C13A	C104	-62.6(5)
C120	C119	C122	120.9(10)	C107	C110	C13A	C19A	58.2(5)
C118	C119	C122	120.1(10)	C107	C106	C105	C104	49.9(7)
C107	C106	Br1A	112.4(4)	C107	C108	C109	C19A	54.4(6)
C107	C106	C105	113.1(5)	C110	C107	C106	Br1A	69.5(5)
C105	C106	Br1A	108.3(5)	C110	C107	C106	C105	-53.5(6)
C104	C105	C106	112.7(5)	C110	C107	C108	C109	-0.7(7)
C105	C104	C13A	112.3(4)	C110	C13A	C103	N101	90.1(4)
C109	C108	C107	113.4(4)	C110	C13A	C103	C102	-147.6(4)
C108	C109	C19A	111.2(5)	C110	C13A	C104	C105	57.4(5)
C109	C19A	C13A	112.0(4)	C110	C13A	C19A	C109	-3.8(5)
C109	C19A	C101	115.8(4)	C110	C13A	C19A	C101	124.3(4)
C101	C19A	C13A	107.3(3)	C13A	C103	N101	C114	-99.7(5)
C19A	C101	C111	114.1(4)	C13A	C103	C102	C101	43.0(4)
C102	C101	C19A	102.6(3)	C13A	C19A	C101	C102	23.7(4)
C102	C101	C112	111.6(4)	C13A	C19A	C101	C112	143.2(4)
C102	C101	C111	109.8(4)	C13A	C19A	C101	C111	-95.0(4)
C112	C101	C19A	111.4(4)	C103	C13A	C104	C105	-178.2(4)
C112	C101	C111	107.4(4)	C103	C13A	C19A	C109	-125.9(4)
C101	C102	C103	103.0(3)	C103	C13A	C19A	C101	2.2(4)
C116	C117	C118	120.1(7)	C103	N101	C114	N102	5.1(6)
C119	C118	C117	120.5(8)	C103	N101	C114	C115	-175.0(4)
F101	C122	C119	114.7(11)	N101	C103	C102	C101	169.1(3)
F101	C122	F103	109.8(14)	N101	C114	N102	S101	176.5(3)
F101	C122	F102	90.0(12)	N102	S101	C116	C121	93.8(6)
F103	C122	C119	119.4(11)	N102	S101	C116	C117	-86.0(6)
F103	C122	F102	107.3(14)	C116	S101	N102	C114	-104.8(4)
F102	C122	C119	111.7(13)	C116	C121	C120	C119	0.8(15)
				C116	C117	C118	C119	0.2(16)
				C121	C116	C117	C118	0.7(13)
				C121	C120	C119	C118	0.0(15)
				C121	C120	C119	C122	-178.1(10)
				C120	C119	C118	C117	-0.5(15)
				C120	C119	C122	F101	-118.7(14)
				C120	C119	C122	F103	108.0(16)
				C120	C119	C122	F102	-18.1(18)
				C106	C107	C110	C13A	61.1(6)
				C106	C107	C108	C109	-118.7(5)
				C106	C105	C104	C13A	-51.9(7)
				C104	C13A	C103	N101	-30.7(5)
				C104	C13A	C103	C102	91.7(4)

C104	C13A	C19A	C109	114.9(4)
C104	C13A	C19A	C101	-117.0(4)
C108	C107	C110	C13A	-55.6(6)
C108	C107	C106	Br1A	-171.9(3)
C108	C107	C106	C105	65.1(6)
C108	C109	C19A	C13A	-51.5(6)
C108	C109	C19A	C101	-174.9(4)
C109	C19A	C101	C102	149.6(4)
C109	C19A	C101	C112	-90.9(5)
C109	C19A	C101	C111	30.9(5)
C19A	C13A	C103	N101	-149.6(3)
C19A	C13A	C103	C102	-27.3(4)
C19A	C13A	C104	C105	-63.4(5)
C19A	C101	C102	C103	-40.5(4)
C102	C103	N101	C114	141.4(4)
C115	C114	N102	S101	-3.3(7)
C117	C116	C121	C120	-1.1(13)
C118	C119	C122	F101	63.2(16)
C118	C119	C122	F103	-70.1(18)
C118	C119	C122	F102	163.8(14)
C112	C101	C102	C103	-159.9(4)
C111	C101	C102	C103	81.1(5)
C122	C119	C118	C117	177.6(10)

Table S3. Bond lengths, bond angles and torsion angles for compound **4h**

Bond *l*, Å			Angle ϕ, ˚			Torsion angle θ, ˚				
I1	C6	2.208(6)	O1	S1	N2	116.0(2)	I1	C6	C5	C4	-75.9(5)
S1	O1	1.436(3)	O1	S1	O2	116.6(2)	I1	C6	C7	C8	-173.2(3)
S1	N2	1.599(4)	O1	S1	C16	106.4(2)	I1	C6	C7	C13	-54.8(5)
S1	O2	1.437(3)	N2	S1	C16	103.7(2)	I1	C6	C7	C10	69.0(5)
S1	C16	1.779(5)	O2	S1	N2	106.72(19)	S1	N2	C14	N1	178.3(3)
N1	C3	1.462(5)	O2	S1	C16	106.2(3)	S1	N2	C14	C15	-1.8(7)
N1	C14	1.322(5)	C14	N1	C3	126.1(3)	S1	C16	C17	C18	177.7(5)
N2	C14	1.319(6)	C14	N2	S1	123.5(3)	S1	C16	C21	C20	-178.4(6)
C3A	C4	1.539(6)	C4	C3A	C3	111.0(3)	O1	S1	N2	C14	20.9(5)
C3A	C3	1.540(6)	C4	C3A	C9A	110.9(3)	O1	S1	C16	C17	-18.8(5)
C3A	C9A	1.574(6)	C3	C3A	C9A	103.1(3)	O1	S1	C16	C21	160.1(4)
C3A	C10	1.525(6)	C10	C3A	C4	108.4(4)	N2	S1	C16	C17	104.1(4)
C2	C3	1.526(6)	C10	C3A	C3	113.0(3)	N2	S1	C16	C21	-77.1(5)
C2	C1	1.524(6)	C10	C3A	C9A	110.4(3)	O2	S1	N2	C14	152.8(4)
C6	C5	1.531(8)	C1	C2	C3	103.5(3)	O2	S1	C16	C17	-143.6(4)
C6	C7	1.535(10)	C5	C6	I1	106.9(4)	O2	S1	C16	C21	35.2(5)
C5	C4	1.523(7)	C5	C6	C7	113.5(5)	C3A	C9A	C9	C8	-50.1(5)
C14	C15	1.507(6)	C7	C6	I1	113.0(4)	C2	C1	C9A	C3A	22.8(4)
C16	C17	1.360(8)	C4	C5	C6	112.0(4)	C2	C1	C9A	C9	149.7(4)
C16	C21	1.377(8)	C5	C4	C3A	112.2(4)	C6	C5	C4	C3A	-51.4(6)
C17	C18	1.377(10)	N1	C3	C3A	115.4(3)	C6	C7	C10	C3A	59.8(6)
C18	C19	1.355(12)	N1	C3	C2	111.0(3)	C5	C6	C7	C8	64.9(6)
C19	C22	1.470(12)	C2	C3	C3A	104.7(3)	C5	C6	C7	C13	-176.7(5)
C19	C20	1.373(12)	N1	C14	C15	114.2(4)	C5	C6	C7	C10	-53.0(6)
C22	F1	1.360(16)	N2	C14	N1	118.8(3)	C4	C3A	C3	N1	-31.2(5)
C22	F2	1.223(14)	N2	C14	C15	127.0(4)	C4	C3A	C3	C2	91.1(4)
C22	F3	1.192(16)	C17	C16	S1	120.0(4)	C4	C3A	C9A	C1	-116.1(4)
C20	C21	1.380(12)	C17	C16	C21	120.0(6)	C4	C3A	C9A	C9	114.7(4)
C1	C11	1.532(6)	C21	C16	S1	120.0(4)	C4	C3A	C10	C7	-62.0(5)
C1	C9A	1.552(7)	C16	C17	C18	120.6(6)	C3	N1	C14	N2	2.3(6)
C1	C12	1.542(7)	C19	C18	C17	119.6(7)	C3	N1	C14	C15	-177.6(4)

C9A	C9	1.529(6)	C18	C19	C22	117.2(9)	C3	C3A	C4	C5	-178.1(4)
C9	C8	1.505(10)	C18	C19	C20	120.5(7)	C3	C3A	C9A	C1	2.8(4)
C8	C7	1.574(9)	C20	C19	C22	122.2(10)	C3	C3A	C9A	C9	-126.4(4)
C7	C13	1.540(8)	F1	C22	C19	111.7(10)	C3	C3A	C10	C7	174.5(4)
C7	C10	1.520(7)	F2	C22	C19	116.9(9)	C3	C2	C1	C11	-159.8(4)
			F2	C22	F1	100.4(14)	C3	C2	C1	C9A	-40.1(4)
			F3	C22	C19	117.1(12)	C3	C2	C1	C12	80.5(5)
			F3	C22	F1	93.5(10)	C14	N1	C3	C3A	-98.8(5)
			F3	C22	F2	113.2(13)	C14	N1	C3	C2	142.4(4)
			C19	C20	C21	119.9(7)	C16	S1	N2	C14	-95.4(4)
			C16	C21	C20	119.4(7)	C16	C17	C18	C19	1.6(11)
			C2	C1	C11	112.1(4)	C17	C16	C21	C20	0.4(10)
			C2	C1	C9A	102.3(3)	C17	C18	C19	C22	-178.9(7)
			C2	C1	C12	109.3(4)	C17	C18	C19	C20	-1.4(12)
			C11	C1	C9A	111.6(4)	C18	C19	C22	F1	-148.2(11)
			C11	C1	C12	108.0(4)	C18	C19	C22	F2	97.0(16)
			C12	C1	C9A	113.5(4)	C18	C19	C22	F3	-42.1(16)
			C1	C9A	C3A	107.7(3)	C18	C19	C20	C21	0.7(12)
			C9	C9A	C3A	112.2(4)	C19	C20	C21	C16	-0.2(12)
			C9	C9A	C1	116.4(4)	C22	C19	C20	C21	178.1(8)
			C8	C9	C9A	111.2(5)	C20	C19	C22	F1	34.3(14)
			C9	C8	C7	113.6(4)	C20	C19	C22	F2	-80.5(17)
			C6	C7	C8	105.8(5)	C20	C19	C22	F3	140.4(14)
			C6	C7	C13	113.2(6)	C21	C16	C17	C18	-1.1(9)
			C13	C7	C8	108.3(5)	C1	C2	C3	N1	168.5(3)
			C10	C7	C6	109.4(4)	C1	C2	C3	C3A	43.3(4)
			C10	C7	C8	109.5(5)	C1	C9A	C9	C8	-174.7(4)
			C10	C7	C13	110.5(5)	C11	C1	C9A	C3A	142.9(4)
			C7	C10	C3A	111.1(4)	C11	C1	C9A	C9	-90.3(5)
							C9A	C3A	C4	C5	-64.1(5)
							C9A	C3A	C3	N1	-150.0(3)
							C9A	C3A	C3	C2	-27.7(4)
							C9A	C3A	C10	C7	59.6(5)
							C9A	C9	C8	C7	54.3(6)
							C9	C8	C7	C6	-119.1(5)
							C9	C8	C7	C13	119.2(6)
							C9	C8	C7	C10	-1.4(7)
							C8	C7	C10	C3A	-55.7(6)
							C7	C6	C5	C4	49.4(7)
							C13	C7	C10	C3A	-174.9(6)
							C10	C3A	C4	C5	57.3(5)
							C10	C3A	C3	N1	90.9(4)
							C10	C3A	C3	C2	-146.8(4)
							C10	C3A	C9A	C1	123.8(4)
							C10	C3A	C9A	C9	-5.5(5)
							C12	C1	C9A	C3A	-94.8(4)
							C12	C1	C9A	C9	32.0(5)

Table S4. Bond lengths, bond angles and torsion angles for compound **5a**

Bond *l*, Å			Angle ϕ, ˚				Torsion angle θ, ˚				
I1	C9	2.200(6)	N2	S1	C18	101.8(5)	I1	C9	C8	C7	164.8(4)
I101	C109	2.215(7)	O2	S1	N2	107.5(4)	I1	C9	C8	C12	-71.7(6)
S1	N2	1.593(6)	O2	S1	C18	105.4(6)	I1	C9	C8	C15	47.7(7)
S1	O2	1.419(6)	O1	S1	N2	116.7(4)	I1	C9	C10	C11	74.6(6)
S1	O1	1.386(8)	O1	S1	O2	115.2(6)	I101	C109	C110	C111	73.7(7)
S1	C18	1.724(16)	O1	S1	C18	108.8(7)	S1	N2	C16	N1	178.2(5)

S101	N102	1.595(6)	N102	S101	C118	100.6(5)	S1	N2	C16	C17	-1.8(11)
S101	O102	1.426(6)	O102	S101	N102	107.8(4)	S101	N102	C116	N101	177.6(6)
S101	O101	1.392(7)	O102	S101	C118	105.1(5)	S101	N102	C116	C117	-3.0(13)
S101	C118	1.741(12)	O101	S101	N102	116.1(4)	O102	S101	N102	C116	128.4(7)
N2	C16	1.316(9)	O101	S101	O102	116.2(6)	C9	C8	C12	C1	-57.4(7)
N102	C116	1.312(8)	O101	S101	C118	109.4(6)	C9	C10	C11	C1	51.3(8)
C9	C8	1.520(11)	C16	N2	S1	125.5(5)	C102	C105	C106	C107	-10.9(9)
C9	C10	1.507(10)	C116	N102	S101	126.0(5)	C102	C101	N101	C116	71.3(9)
C102	C105	1.537(9)	C8	C9	I1	112.2(4)	C102	C101	C111	C110	69.1(7)
C102	C101	1.539(9)	C10	C9	I1	108.3(5)	O101	S101	N102	C116	-4.0(10)
C102	C103	1.534(10)	C10	C9	C8	112.7(6)	C112	C101	N101	C116	-170.6(7)
C112	C101	1.535(9)	C105	C102	C101	116.8(5)	C112	C101	C111	C110	-51.1(7)
C112	C108	1.536(10)	C103	C102	C105	87.6(5)	C112	C108	C109	I101	-69.7(6)
C13	C4	1.509(11)	C103	C102	C101	126.7(5)	C112	C108	C109	C110	51.7(7)
C4	C3	1.559(9)	C101	C112	C108	115.6(5)	C13	C4	C3	C2	-139.5(6)
C4	C5	1.551(9)	C13	C4	C3	116.3(6)	C13	C4	C5	C2	139.8(6)
C4	C14	1.540(10)	C13	C4	C5	116.0(6)	C13	C4	C5	C6	-96.5(8)
C3	C2	1.537(9)	C13	C4	C14	109.9(6)	C4	C3	C2	C1	143.6(6)
C2	C1	1.543(8)	C5	C4	C3	86.4(5)	C4	C3	C2	C5	22.4(5)
C2	C5	1.533(9)	C14	C4	C3	112.1(6)	C4	C5	C6	C7	-122.2(7)
C1	N1	1.473(9)	C14	C4	C5	114.5(6)	C3	C4	C5	C2	22.2(5)
C1	C11	1.530(9)	C2	C3	C4	88.2(5)	C3	C4	C5	C6	145.9(7)
C1	C12	1.522(9)	C3	C2	C1	126.9(5)	C3	C2	C1	N1	-18.7(9)
N1	C16	1.330(8)	C5	C2	C3	87.8(5)	C3	C2	C1	C11	106.8(8)
C16	C17	1.505(10)	C5	C2	C1	115.9(5)	C3	C2	C1	C12	-133.8(7)
C5	C6	1.538(10)	N1	C1	C2	110.6(6)	C3	C2	C5	C4	-22.5(5)
C6	C7	1.525(11)	N1	C1	C11	111.8(5)	C3	C2	C5	C6	-151.7(6)
C7	C8	1.566(10)	N1	C1	C12	104.8(5)	C2	C1	N1	C16	69.8(8)
C8	C12	1.543(10)	C11	C1	C2	112.1(5)	C2	C1	C11	C10	68.1(7)
C8	C15	1.526(10)	C12	C1	C2	109.7(5)	C2	C1	C12	C8	-64.4(7)
C10	C11	1.520(10)	C12	C1	C11	107.4(6)	C2	C5	C6	C7	-12.6(9)
C114	C104	1.516(10)	C16	N1	C1	128.9(5)	C1	C2	C5	C4	-153.0(6)
C104	C105	1.564(10)	N2	C16	N1	117.9(6)	C1	C2	C5	C6	77.8(7)
C104	C113	1.522(11)	N2	C16	C17	126.6(6)	C1	N1	C16	N2	1.7(10)
C104	C103	1.548(10)	N1	C16	C17	115.6(6)	C1	N1	C16	C17	-178.2(7)
C105	C106	1.522(11)	C2	C5	C4	88.6(5)	N1	C1	C11	C10	-166.9(5)
C101	N101	1.470(8)	C2	C5	C6	118.0(6)	N1	C1	C12	C8	176.7(6)
C101	C111	1.543(10)	C6	C5	C4	124.6(6)	O2	S1	N2	C16	126.9(7)
N101	C116	1.329(8)	C7	C6	C5	112.7(6)	O1	S1	N2	C16	-4.3(10)
C116	C117	1.506(10)	C6	C7	C8	117.8(6)	C5	C4	C3	C2	-22.1(5)
C106	C107	1.531(13)	C9	C8	C7	107.0(6)	C5	C2	C1	N1	89.5(7)
C107	C108	1.558(10)	C9	C8	C12	108.8(6)	C5	C2	C1	C11	-145.0(6)
C108	C109	1.524(11)	C9	C8	C15	113.4(7)	C5	C2	C1	C12	-25.6(8)
C108	C115	1.523(10)	C12	C8	C7	113.9(6)	C5	C6	C7	C8	-60.8(9)
C109	C110	1.511(10)	C15	C8	C7	106.5(6)	C6	C7	C8	C9	152.1(7)
C110	C111	1.531(11)	C15	C8	C12	107.4(6)	C6	C7	C8	C12	31.8(9)
			C9	C10	C11	114.7(6)	C6	C7	C8	C15	-86.4(8)
			C10	C11	C1	112.9(6)	C7	C8	C12	C1	61.9(8)
			C1	C12	C8	115.0(5)	C8	C9	C10	C11	-50.1(8)
			C114	C104	C105	113.4(7)	C10	C9	C8	C7	-72.7(7)
			C114	C104	C113	110.1(6)	C10	C9	C8	C12	50.8(7)
			C114	C104	C103	111.4(6)	C10	C9	C8	C15	170.2(6)
			C113	C104	C105	117.6(7)	C11	C1	N1	C16	-55.9(9)
			C113	C104	C103	116.4(7)	C11	C1	C12	C8	57.7(7)
			C103	C104	C105	86.2(5)	C12	C1	N1	C16	-172.0(6)
			C102	C105	C104	88.3(5)	C12	C1	C11	C10	-52.5(7)
			C106	C105	C102	118.3(7)	C15	C8	C12	C1	179.5(6)
			C106	C105	C104	125.9(6)	C14	C4	C3	C2	92.9(6)
			C102	C101	C111	112.6(5)	C14	C4	C5	C2	-90.5(6)

C112	C101	C102	109.2(5)	C14	C4	C5	C6	33.2(10)
C112	C101	C111	107.4(6)	C114	C104	C105	C102	-89.5(7)
N101	C101	C102	111.9(6)	C114	C104	C105	C106	34.8(11)
N101	C101	C112	104.7(5)	C114	C104	C103	C102	91.4(7)
N101	C101	C111	110.7(5)	C104	C105	C106	C107	-121.2(8)
C116	N101	C101	127.3(5)	C105	C102	C101	C112	-24.9(8)
N102	C116	N101	118.4(6)	C105	C102	C101	N101	90.5(7)
N102	C116	C117	126.8(6)	C105	C102	C101	C111	-144.1(6)
N101	C116	C117	114.8(6)	C105	C102	C103	C104	22.6(5)
C102	C103	C104	88.9(5)	C105	C104	C103	C102	-22.3(5)
C105	C106	C107	112.9(7)	C105	C106	C107	C108	-62.8(9)
C106	C107	C108	116.7(7)	C101	C102	C105	C104	-153.0(6)
C112	C108	C107	114.3(6)	C101	C102	C105	C106	76.5(8)
C109	C108	C112	107.9(6)	C101	C102	C103	C104	144.9(7)
C109	C108	C107	106.7(6)	C101	C112	C108	C107	60.1(8)
C115	C108	C112	107.2(6)	C101	C112	C108	C109	-58.4(8)
C115	C108	C107	107.7(6)	C101	C112	C108	C115	179.4(6)
C115	C108	C109	113.2(7)	C101	N101	C116	N102	-1.4(11)
C108	C109	I101	111.9(4)	C101	N101	C116	C117	179.1(7)
C110	C109	I101	107.3(5)	N101	C101	C111	C110	-164.8(5)
C110	C109	C108	113.2(6)	C118	S101	N102	C116	-121.9(8)
C109	C110	C111	114.9(6)	C113	C104	C105	C102	140.1(7)
C110	C111	C101	112.7(5)	C113	C104	C105	C106	-95.6(9)
				C113	C104	C103	C102	-141.3(7)
				C103	C102	C105	C104	-22.4(5)
				C103	C102	C105	C106	-153.0(6)
				C103	C102	C101	C112	-133.6(7)
				C103	C102	C101	N101	-18.2(9)
				C103	C102	C101	C111	107.3(8)
				C103	C104	C105	C102	22.2(5)
				C103	C104	C105	C106	146.5(8)
				C106	C107	C108	C112	33.9(9)
				C106	C107	C108	C109	153.1(7)
				C106	C107	C108	C115	-85.1(9)
				C107	C108	C109	I101	167.0(5)
				C107	C108	C109	C110	-71.6(7)
				C108	C112	C101	C102	-64.2(8)
				C108	C112	C101	N101	175.8(6)
				C108	C112	C101	C111	58.1(7)
				C108	C109	C110	C111	-50.3(8)
				C109	C110	C111	C101	50.0(8)
				C111	C101	N101	C116	-55.2(9)
				C115	C108	C109	I101	48.7(7)
				C115	C108	C109	C110	170.1(6)
				C18	S1	N2	C16	-122.6(8)

Table S5. Bond lengths, bond angles and torsion angles for compound **5b**

Bond *l*, Å			Angle ϕ, ˚				Torsion angle θ, ˚				
I1	C9	2.199(5)	O1	S1	O2	116.9(2)	I1	C9	C10	C11	77.0(4)
S1	O1	1.423(3)	O1	S1	N2	108.98(18)	S1	N2	C16	N1	177.1(3)
S1	O2	1.424(3)	O1	S1	C18	104.2(3)	S1	N2	C16	C17	-5.0(6)
S1	N2	1.559(3)	O2	S1	N2	118.31(19)	O1	S1	N2	C16	144.1(3)
S1	C18	1.816(5)	O2	S1	C18	104.9(2)	O1	S1	C18	F1	55.0(5)
F1	C18	1.312(6)	N2	S1	C18	101.2(2)	O1	S1	C18	F2	175.0(4)
F2	C18	1.296(7)	C16	N2	S1	126.5(2)	O1	S1	C18	F3	-65.5(5)
F3	C18	1.305(7)	C16	N1	C1	127.6(3)	O2	S1	N2	C16	7.4(4)

N2	C16	1.323(5)	F1	C18	S1	111.6(3)	O2	S1	C18	F1	178.3(4)
N1	C16	1.310(5)	F2	C18	S1	110.9(4)	O2	S1	C18	F2	-61.7(5)
N1	C1	1.492(4)	F2	C18	F1	107.6(5)	O2	S1	C18	F3	57.9(5)
C16	C17	1.505(5)	F2	C18	F3	107.9(5)	N2	S1	C18	F1	-58.1(5)
C1	C2	1.535(5)	F3	C18	S1	110.4(4)	N2	S1	C18	F2	61.8(4)
C1	C12	1.539(6)	F3	C18	F1	108.2(5)	N2	S1	C18	F3	-178.6(4)
C1	C11	1.533(5)	N2	C16	C17	125.9(3)	N1	C1	C2	C5	91.5(4)
C2	C5	1.539(6)	N1	C16	N2	118.6(3)	N1	C1	C2	C3	-18.6(5)
C2	C3	1.543(5)	N1	C16	C17	115.5(3)	N1	C1	C12	C8	175.6(3)
C5	C4	1.549(6)	N1	C1	C2	111.3(3)	N1	C1	C11	C10	-165.3(3)
C5	C6	1.532(7)	N1	C1	C12	104.3(3)	C18	S1	N2	C16	-106.4(4)
C4	C14	1.520(6)	N1	C1	C11	110.1(3)	C16	N1	C1	C2	69.9(5)
C4	C3	1.542(6)	C2	C1	C12	109.2(3)	C16	N1	C1	C12	-172.5(3)
C4	C13	1.527(5)	C11	C1	C2	113.4(3)	C16	N1	C1	C11	-56.7(5)
C12	C8	1.530(5)	C11	C1	C12	108.2(3)	C1	N1	C16	N2	-2.4(6)
C8	C9	1.526(7)	C1	C2	C5	117.8(3)	C1	N1	C16	C17	179.5(3)
C8	C7	1.566(7)	C1	C2	C3	127.8(3)	C1	C2	C5	C4	-154.9(3)
C8	C15	1.544(7)	C5	C2	C3	87.4(3)	C1	C2	C5	C6	74.6(5)
C9	C10	1.512(7)	C2	C5	C4	88.0(3)	C1	C2	C3	C4	146.7(4)
C10	C11	1.531(5)	C6	C5	C2	118.5(3)	C1	C12	C8	C9	-57.7(5)
C7	C6	1.520(7)	C6	C5	C4	125.9(4)	C1	C12	C8	C7	60.8(5)
			C14	C4	C5	114.1(4)	C1	C12	C8	C15	179.0(4)
			C14	C4	C3	112.2(4)	C2	C1	C12	C8	-65.4(4)
			C14	C4	C13	109.6(4)	C2	C1	C11	C10	69.4(4)
			C3	C4	C5	87.0(3)	C2	C5	C4	C14	-90.1(4)
			C13	C4	C5	115.8(4)	C2	C5	C4	C3	22.9(3)
			C13	C4	C3	116.7(3)	C2	C5	C4	C13	141.3(4)
			C8	C12	C1	114.7(3)	C2	C5	C6	C7	-9.6(7)
			C12	C8	C7	114.6(4)	C5	C2	C3	C4	23.0(3)
			C12	C8	C15	107.1(4)	C5	C4	C3	C2	-22.9(3)
			C9	C8	C12	108.5(4)	C4	C5	C6	C7	-119.8(5)
			C9	C8	C7	106.2(4)	C14	C4	C3	C2	92.0(4)
			C9	C8	C15	113.9(4)	C12	C1	C2	C5	-23.1(4)
			C15	C8	C7	106.8(5)	C12	C1	C2	C3	-133.2(4)
			C8	C9	I1	113.1(3)	C12	C1	C11	C10	-51.9(4)
			C10	C9	I1	108.2(3)	C12	C8	C9	I1	-72.7(4)
			C10	C9	C8	113.5(3)	C12	C8	C9	C10	51.1(5)
			C9	C10	C11	114.8(4)	C12	C8	C7	C6	33.9(6)
			C10	C11	C1	112.4(3)	C8	C9	C10	C11	-49.4(5)
			C6	C7	C8	116.7(4)	C8	C7	C6	C5	-63.3(7)
			C7	C6	C5	112.5(4)	C9	C8	C7	C6	153.6(4)
			C4	C3	C2	88.1(3)	C9	C10	C11	C1	49.7(5)
							C11	C1	C2	C5	-143.8(3)
							C11	C1	C2	C3	106.1(4)
							C11	C1	C12	C8	58.4(5)
							C7	C8	C9	I1	163.7(3)
							C7	C8	C9	C10	-72.6(4)
							C6	C5	C4	C14	34.3(6)
							C6	C5	C4	C3	147.3(4)
							C6	C5	C4	C13	-94.3(5)
							C3	C2	C5	C4	-22.9(3)
							C3	C2	C5	C6	-153.4(4)
							C13	C4	C3	C2	-140.4(5)
							C15	C8	C9	I1	46.5(5)
							C15	C8	C9	C10	170.3(4)
							C15	C8	C7	C6	-84.6(5)

Figure S1. ^{1}H NMR spectrum of compound **3a**

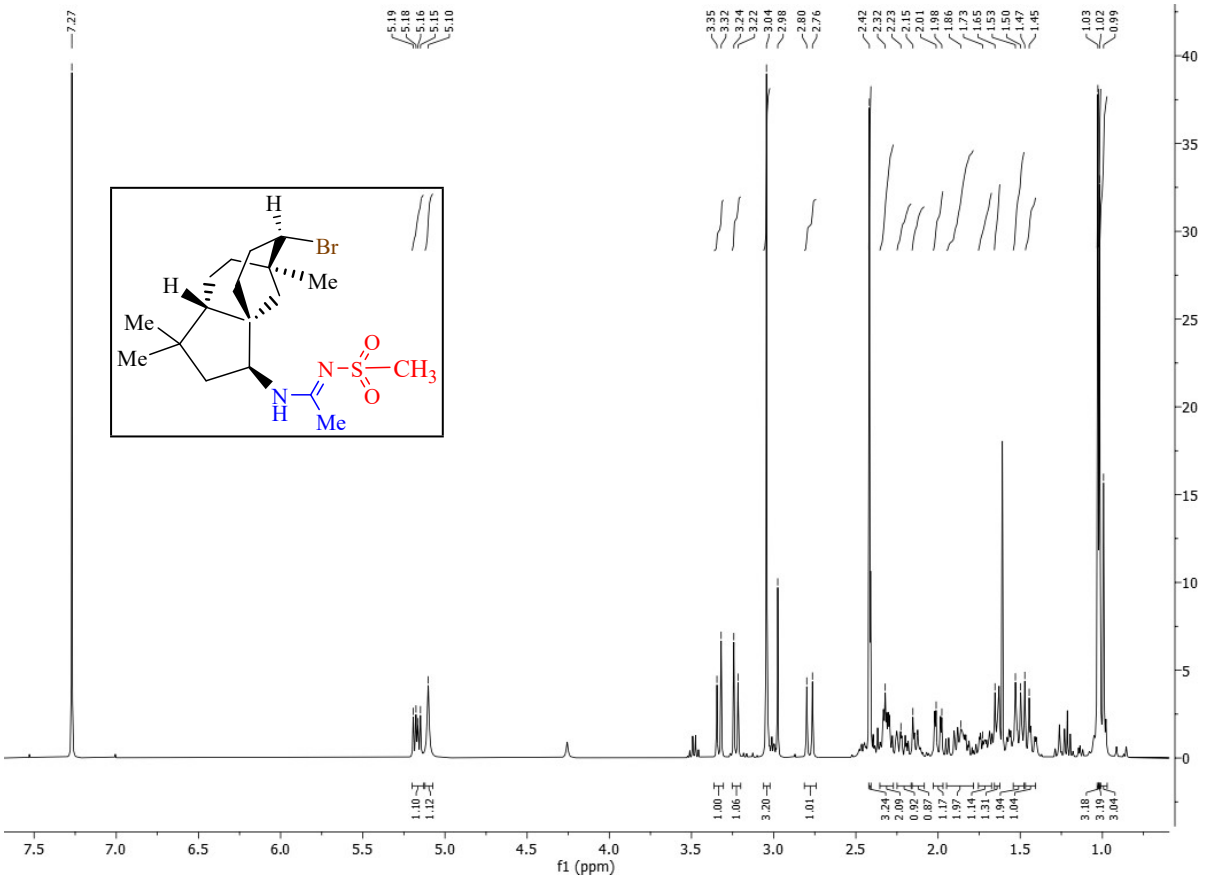


Figure S2. ^{13}C NMR spectrum of compound **3a**

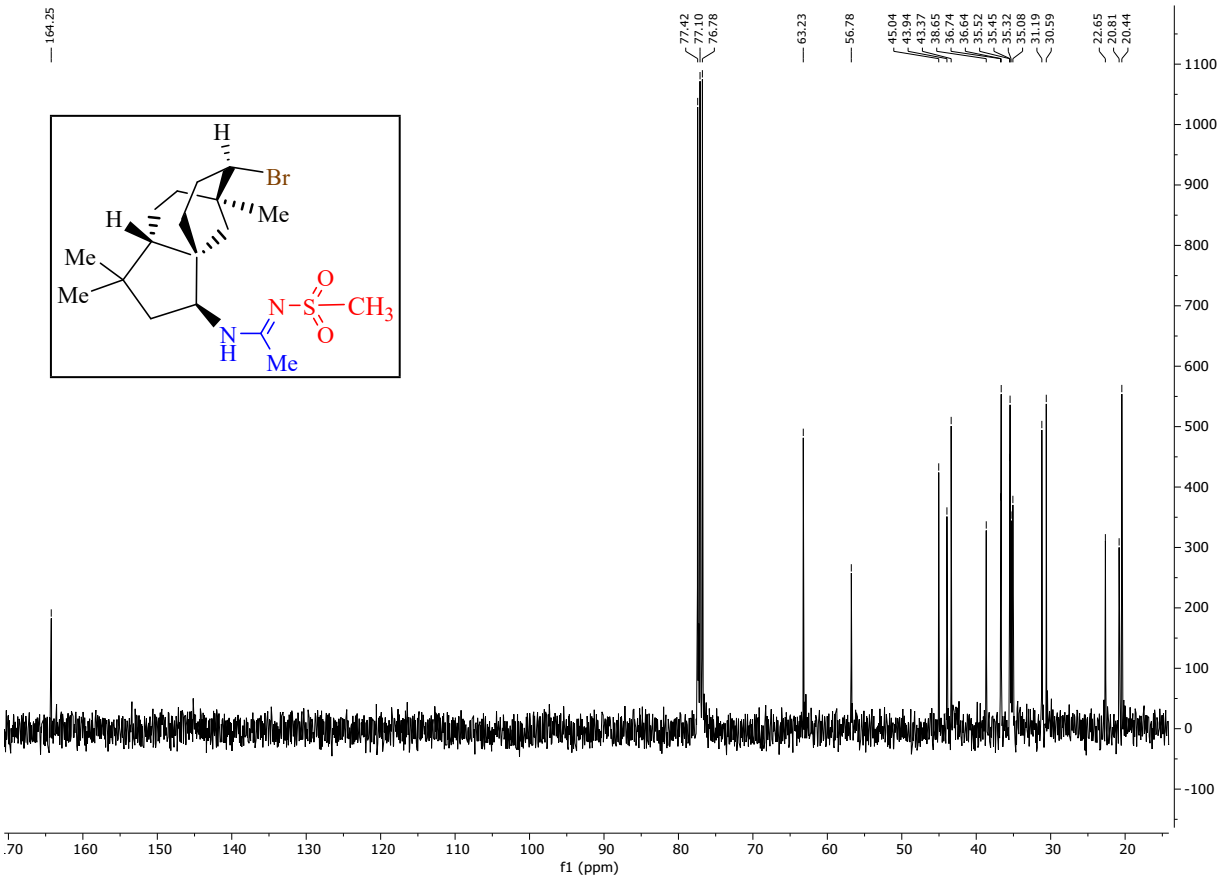


Figure S3. ^{1}H NMR spectrum of compound **3b**

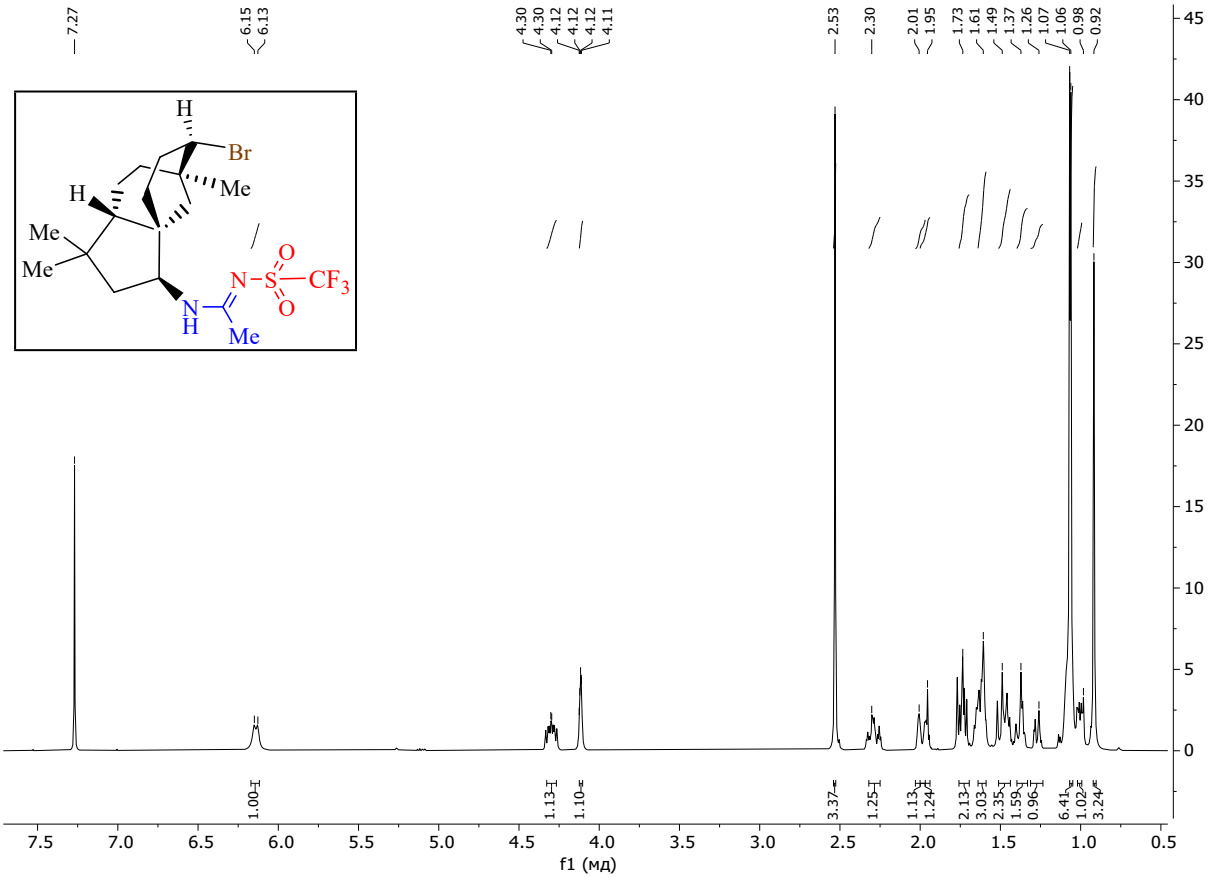


Figure S4. ^{13}C NMR spectrum of compound **3b**

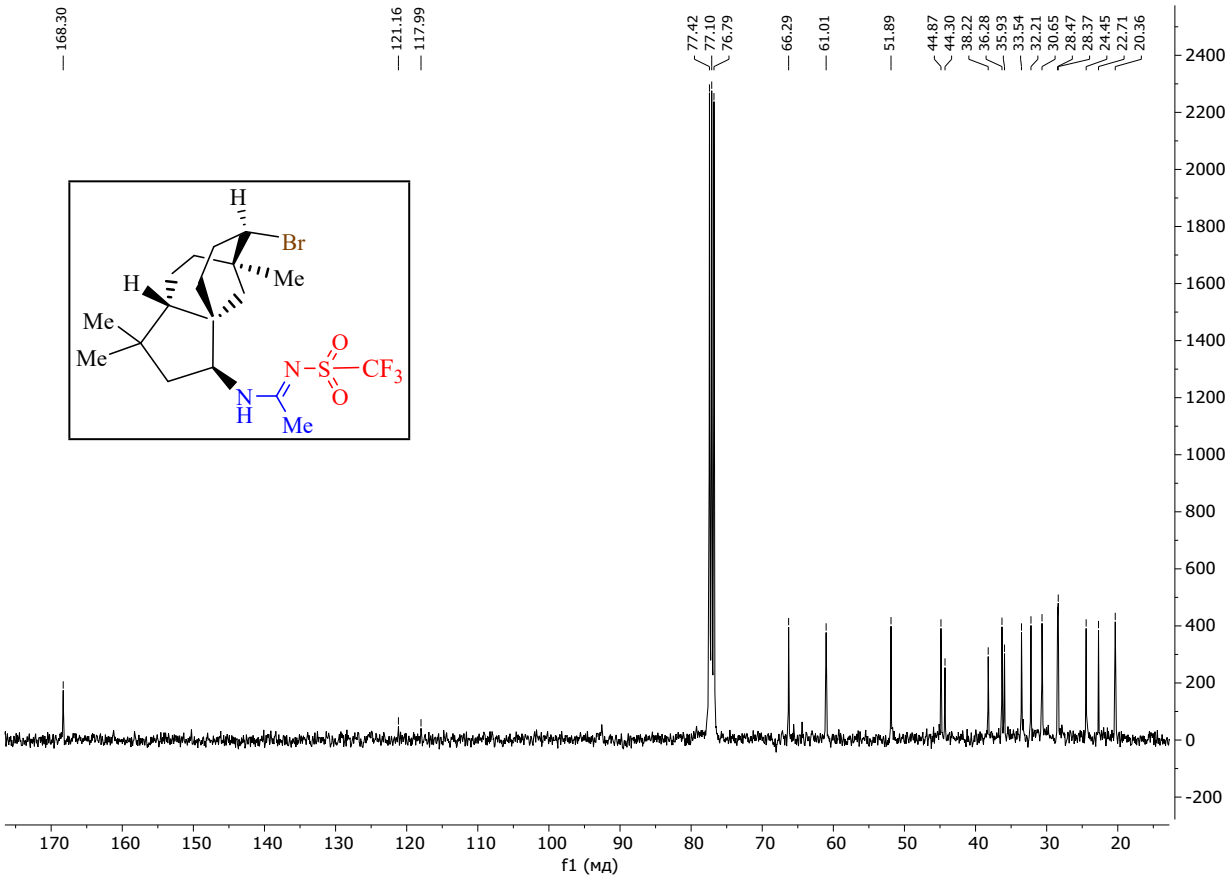


Figure S5. ^{19}F NMR spectrum of compound **3b**

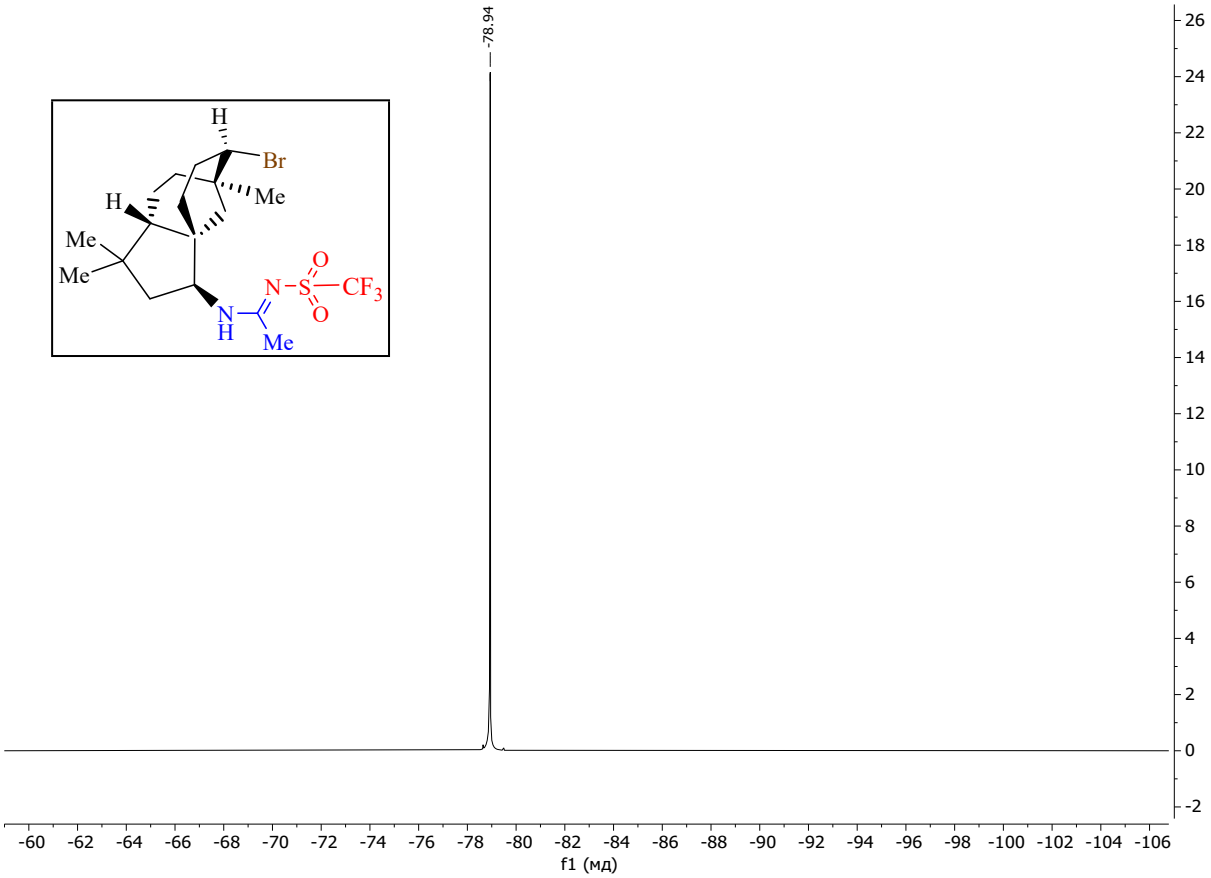


Figure S6. ^{1}H NMR spectrum of compound **3c**

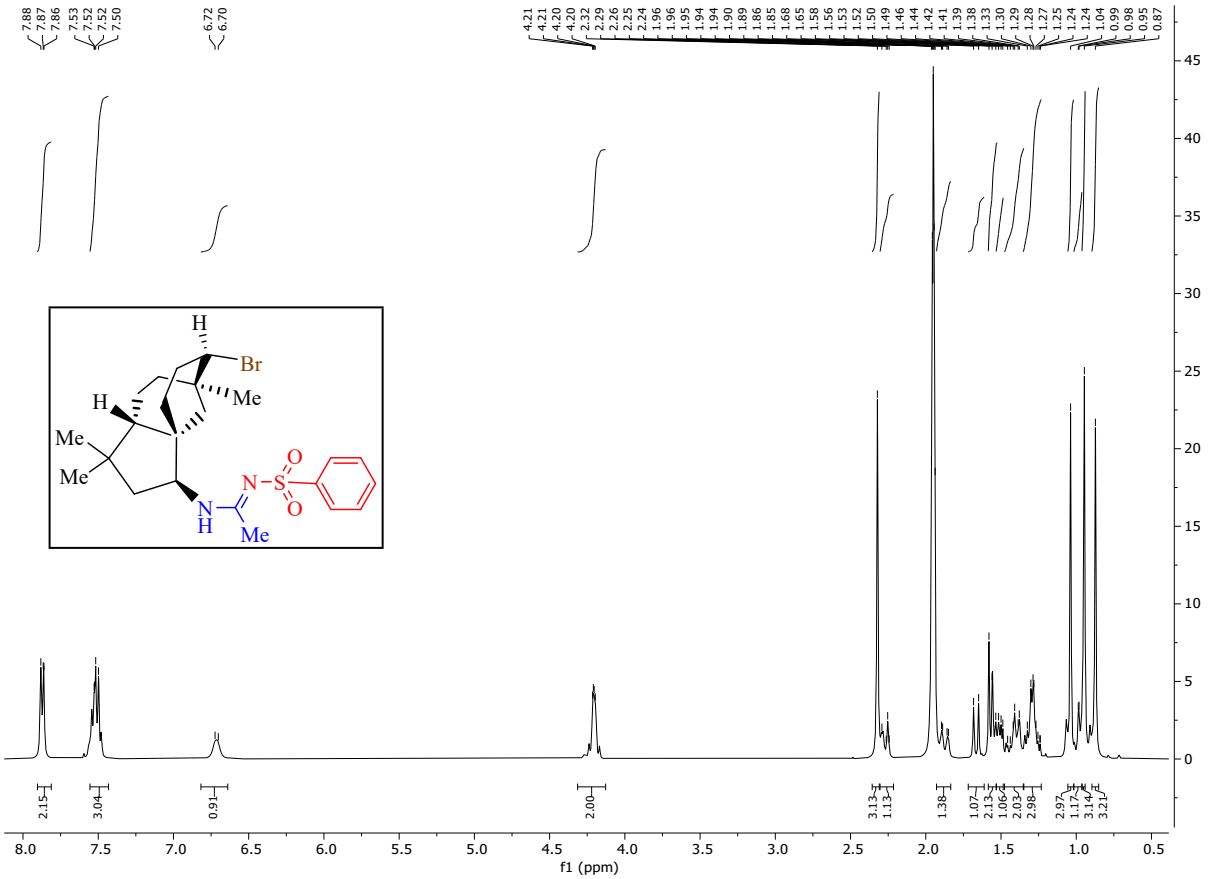


Figure S7. ^{13}C NMR spectrum of compound **3c**

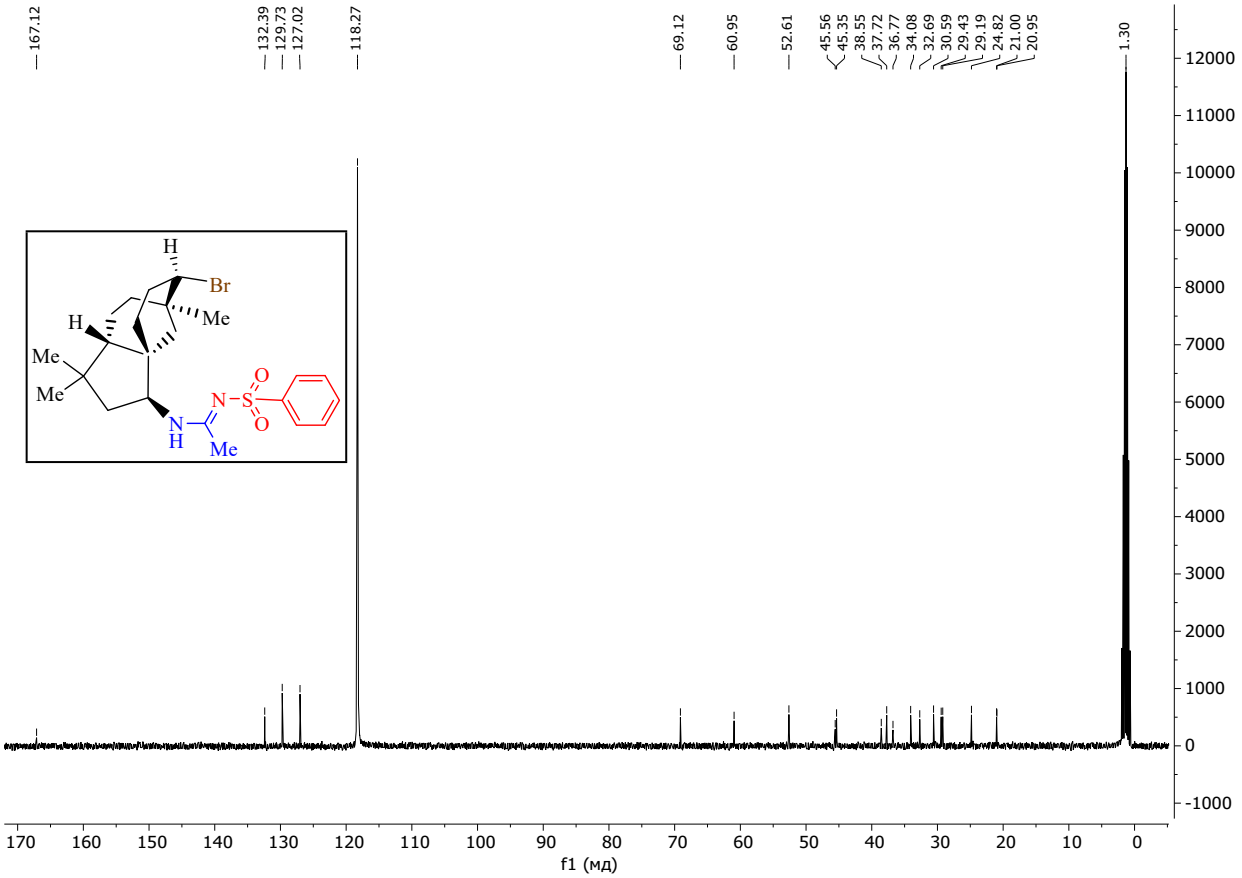


Figure S8. ^{1}H NMR spectrum of compound **3e**

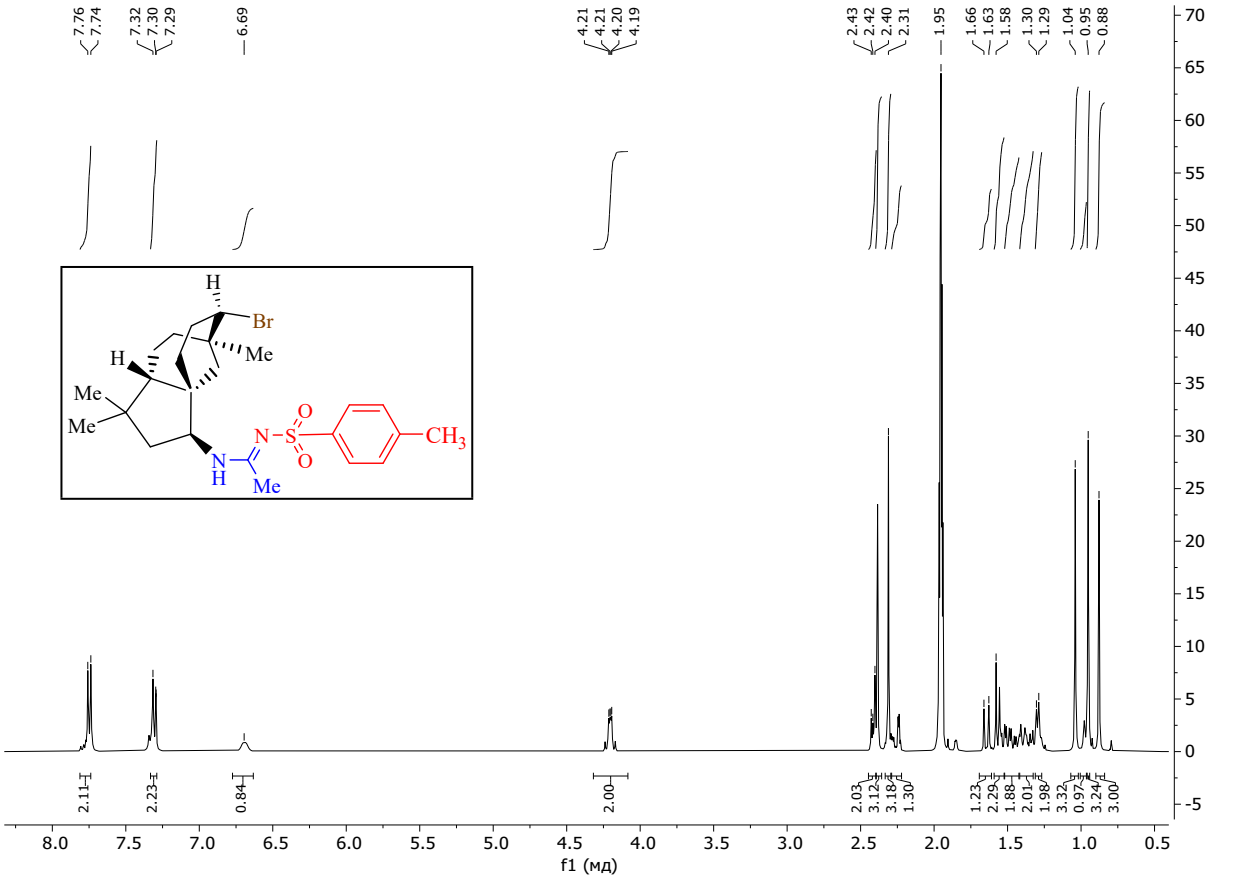


Figure S9. ^{13}C NMR spectrum of compound **3e**

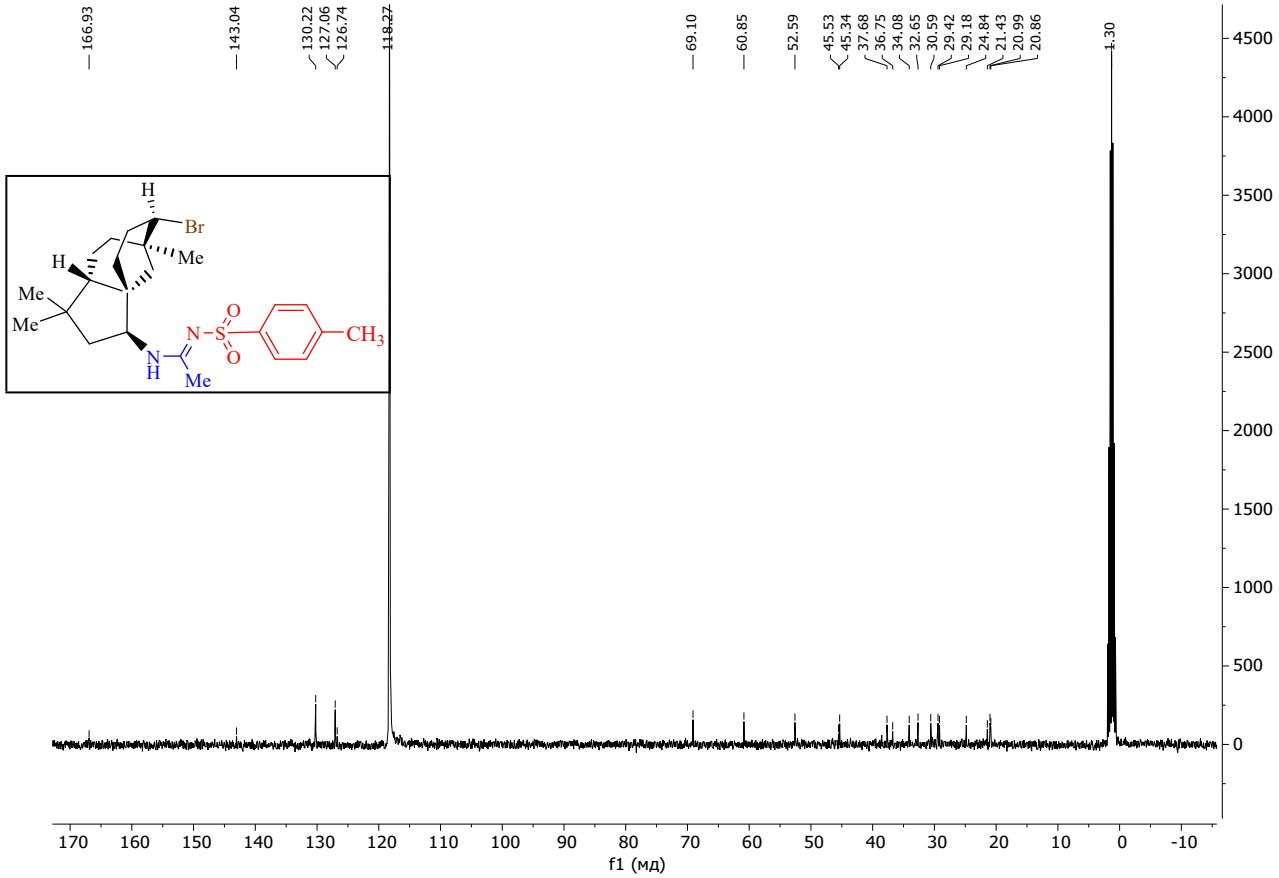


Figure S10. ^{1}H NMR spectrum of compound **3f**

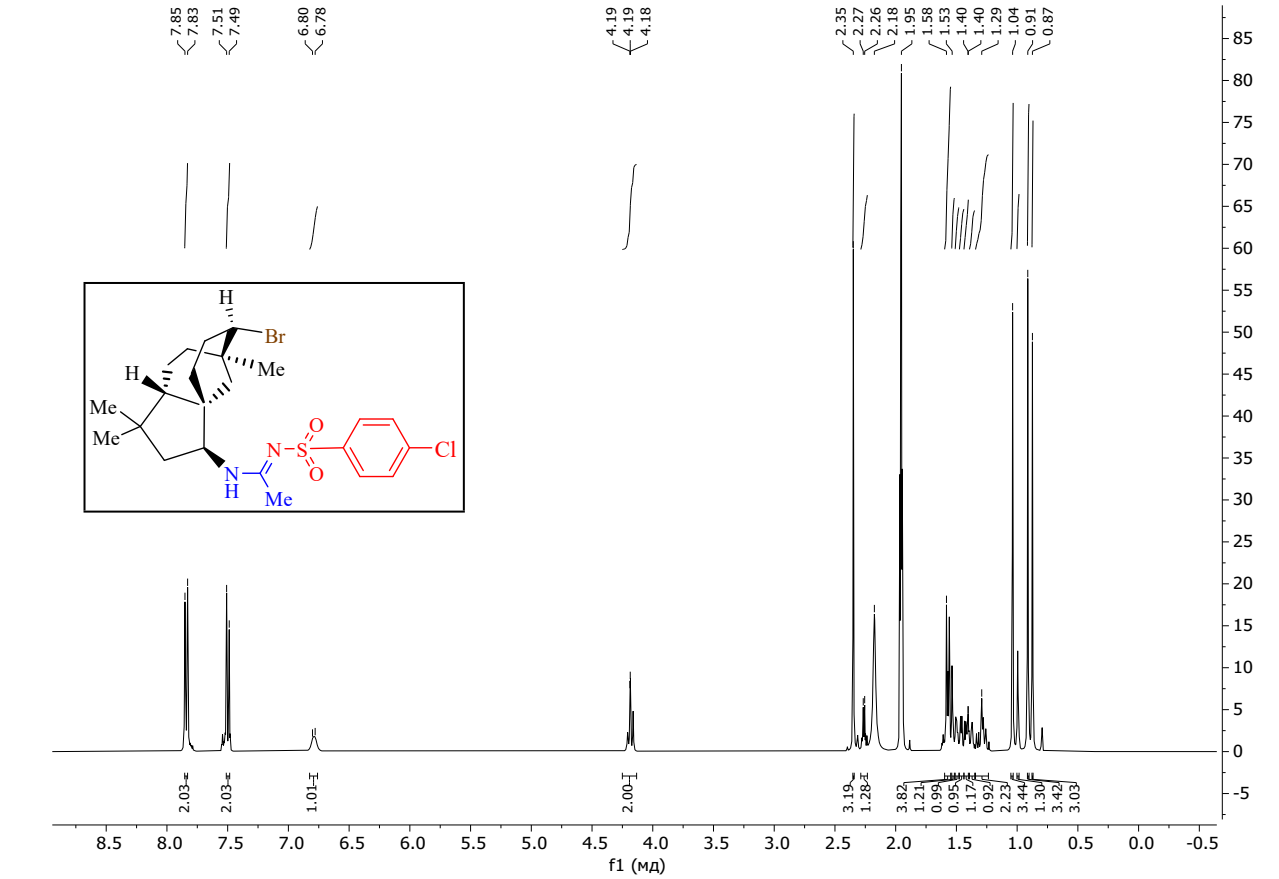


Figure S11. ^{13}C NMR spectrum of compound **3f**

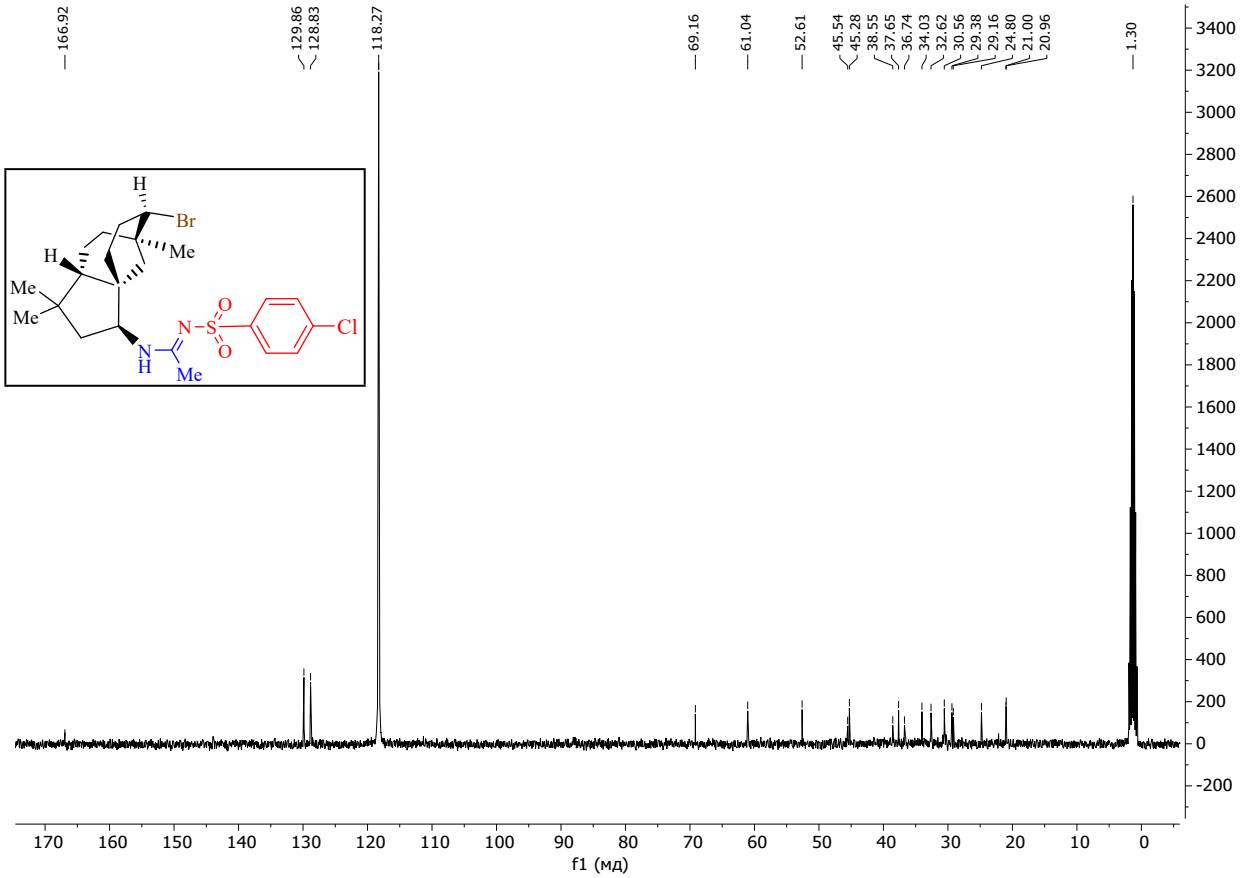


Figure S12. ^{1}H NMR spectrum of compound **3g**

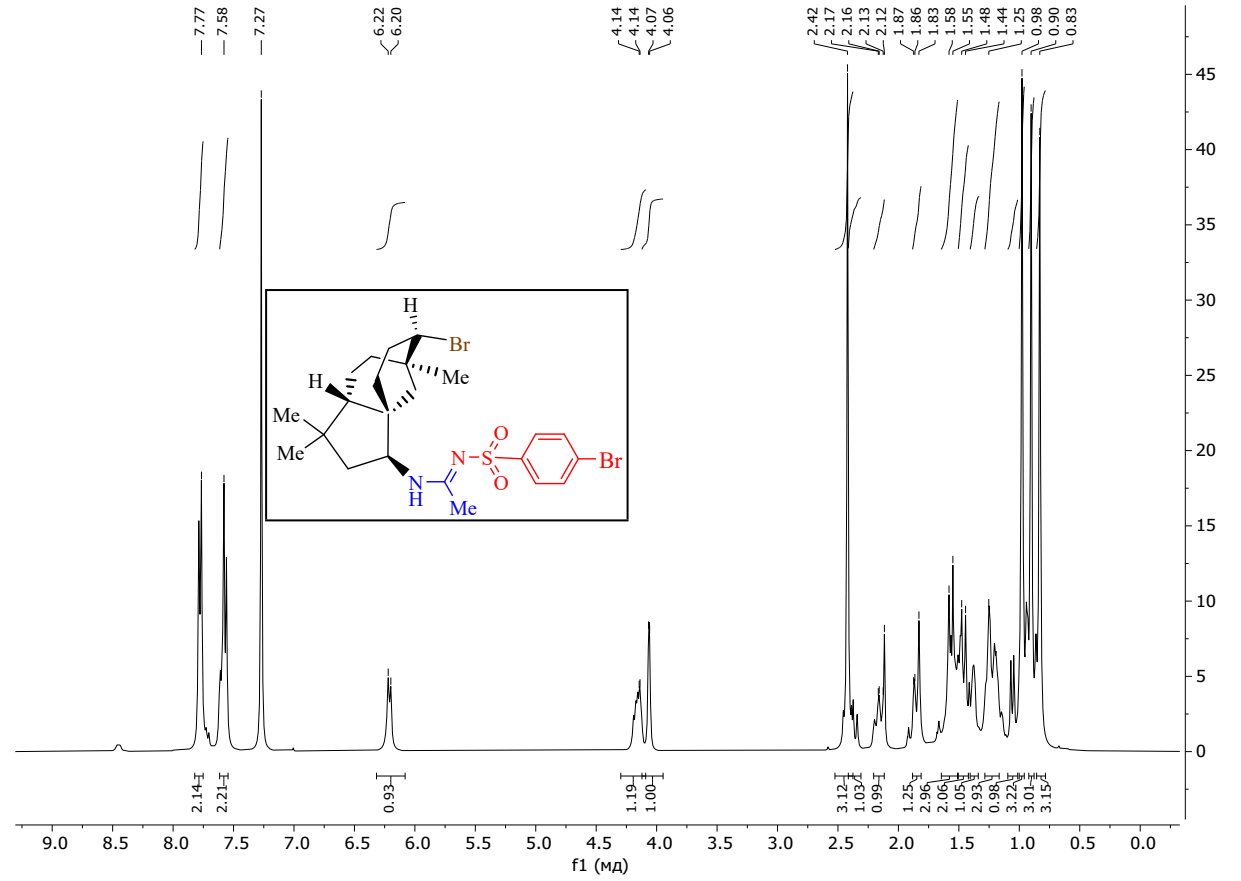


Figure S13. ^{13}C NMR spectrum of compound **3g**

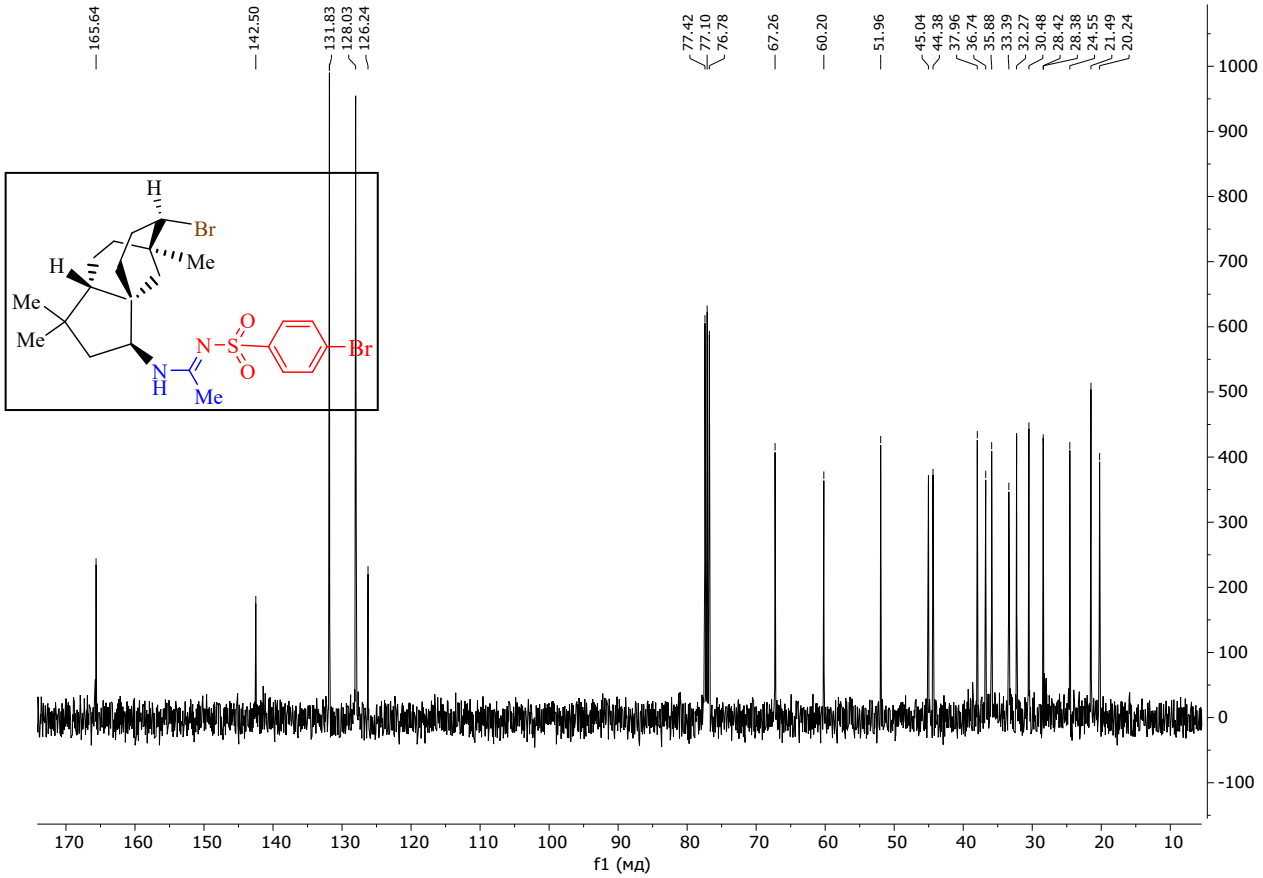


Figure S14. ^{1}H NMR spectrum of compound **3h**

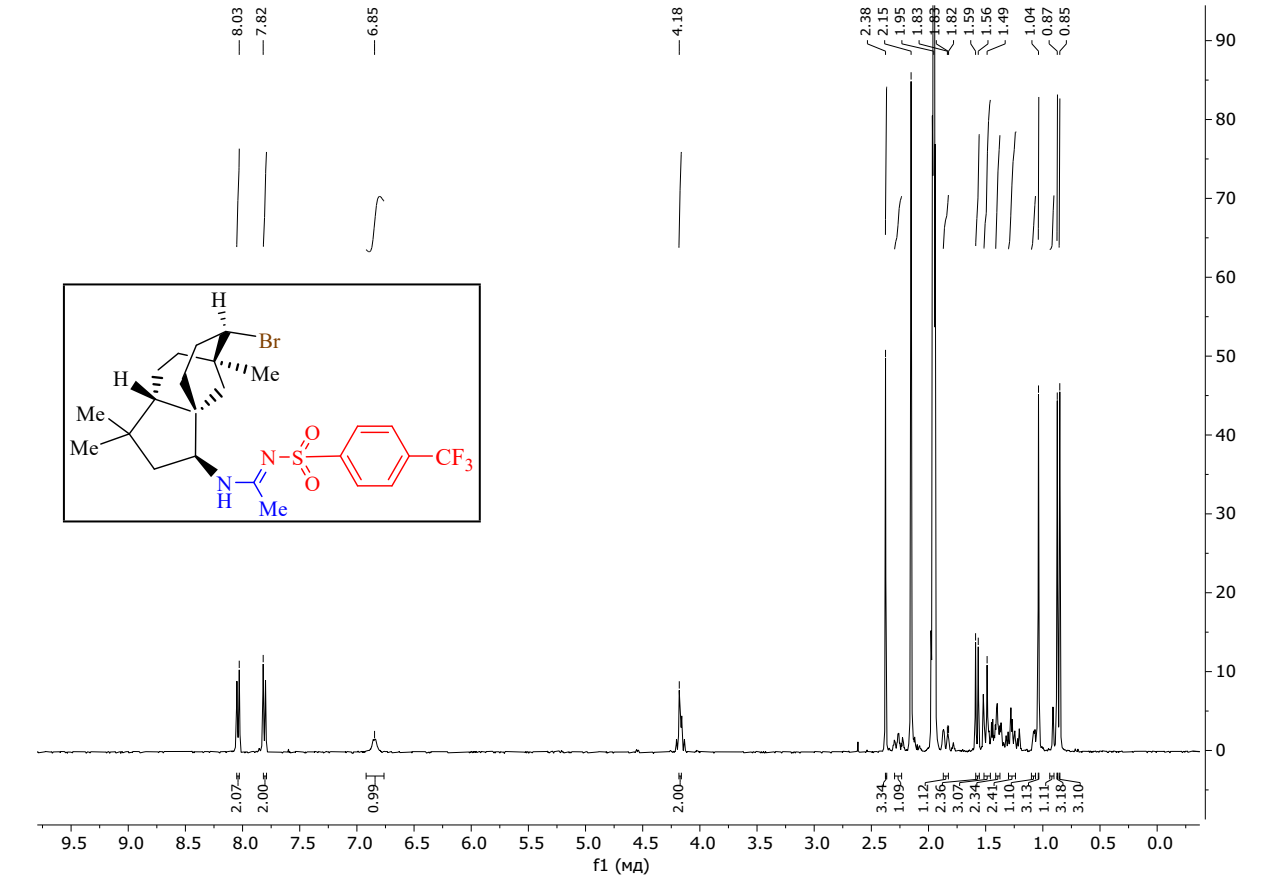


Figure S15. ^{13}C NMR spectrum of compound **3h**

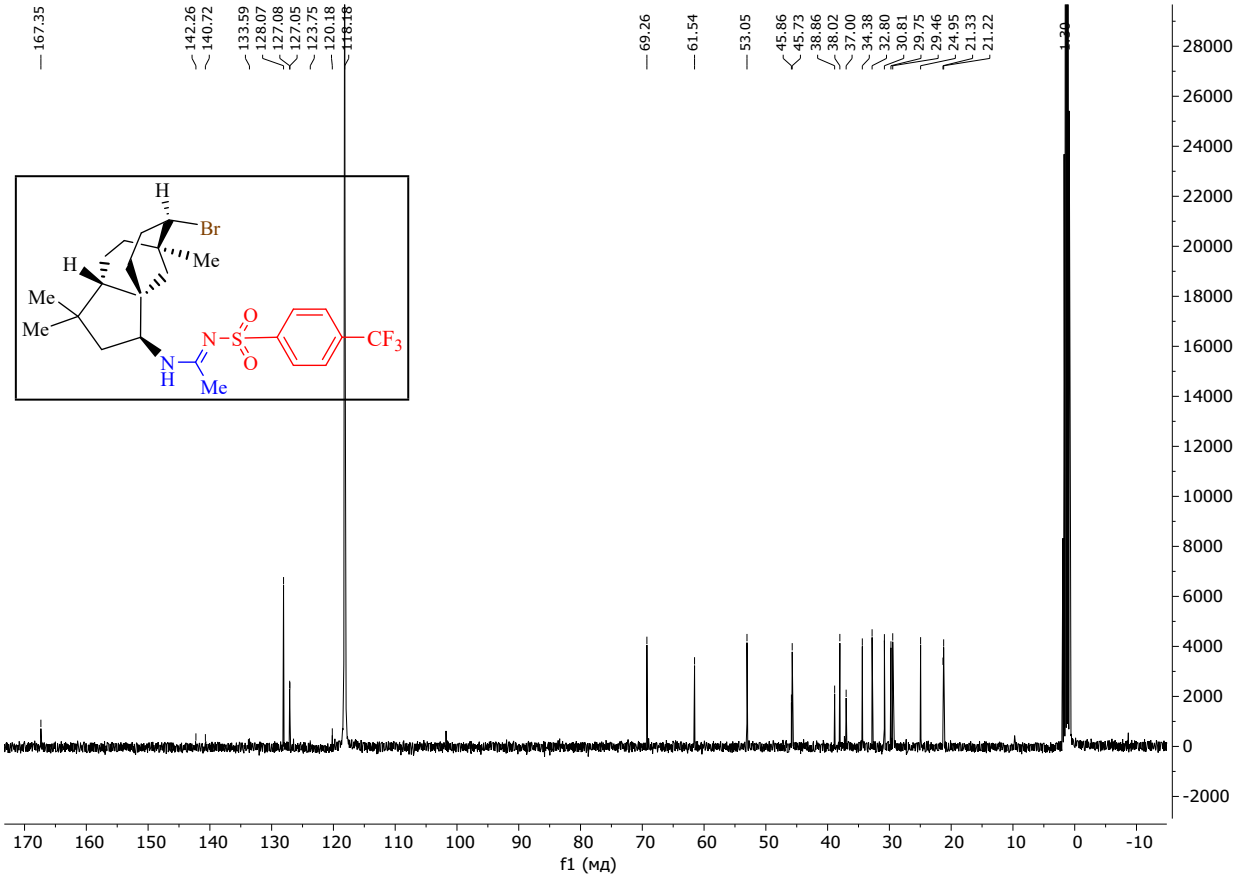


Figure S16. ^{19}F NMR spectrum of compound **3h**

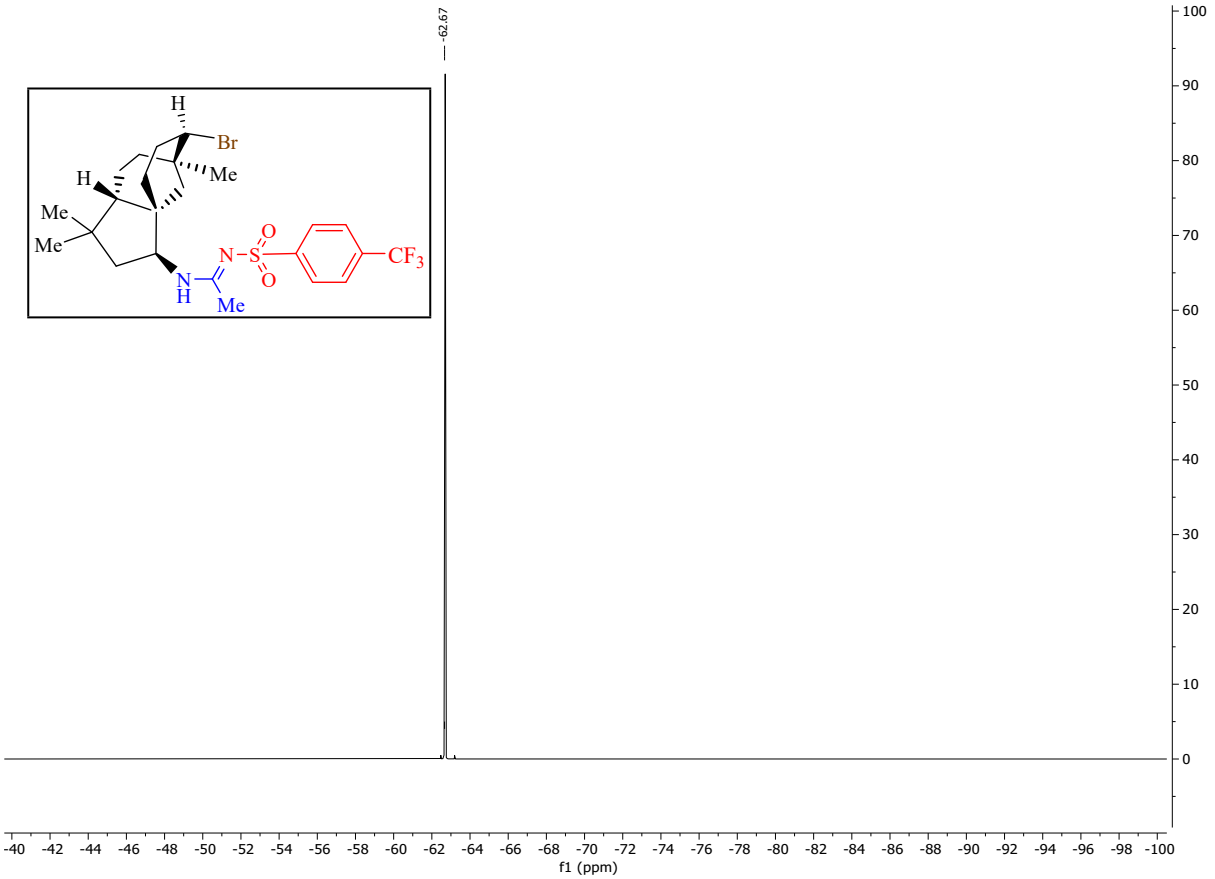


Figure S17. ^{1}H NMR spectrum of compound **3i**

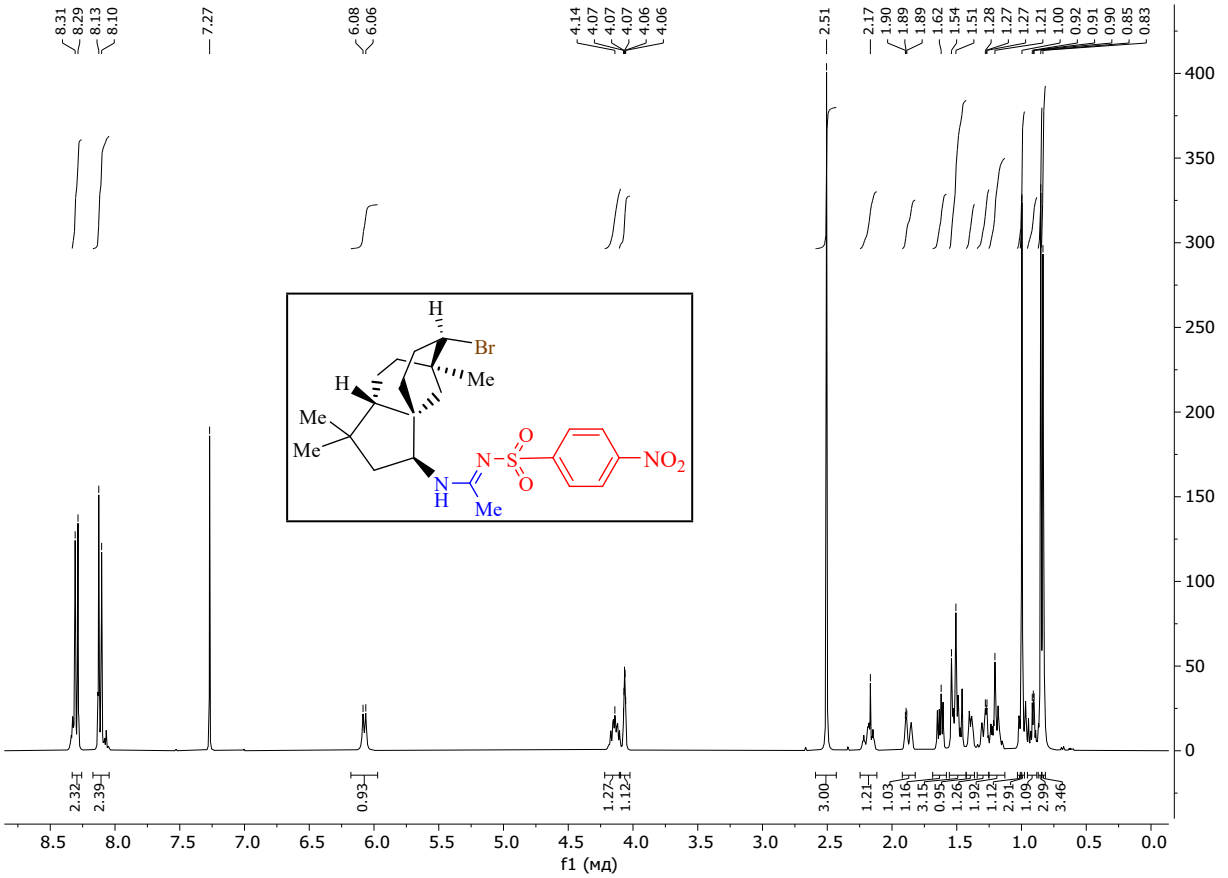


Figure S18. ^{13}C NMR spectrum of compound **3i**

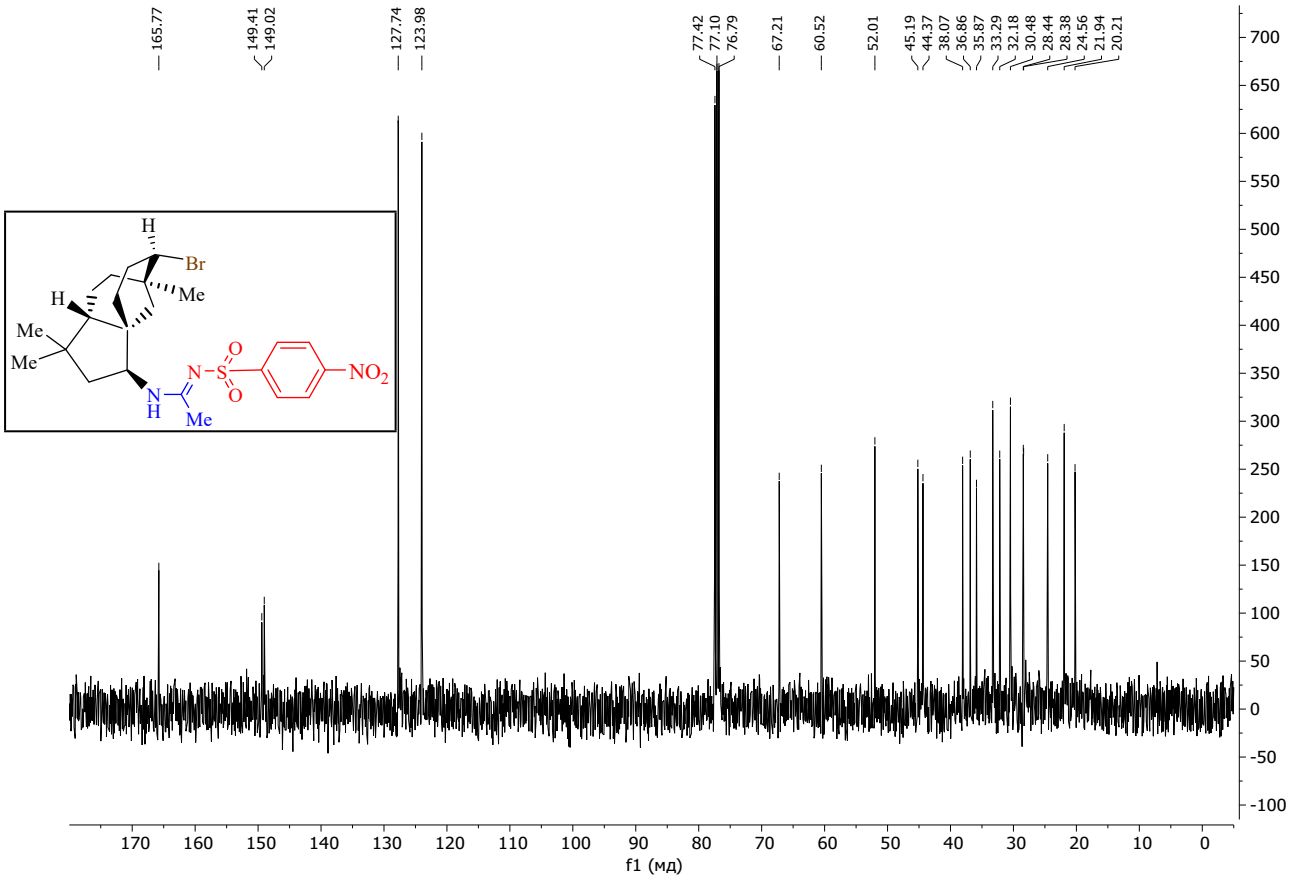


Figure S19. ^{1}H NMR spectrum of compound **4a**

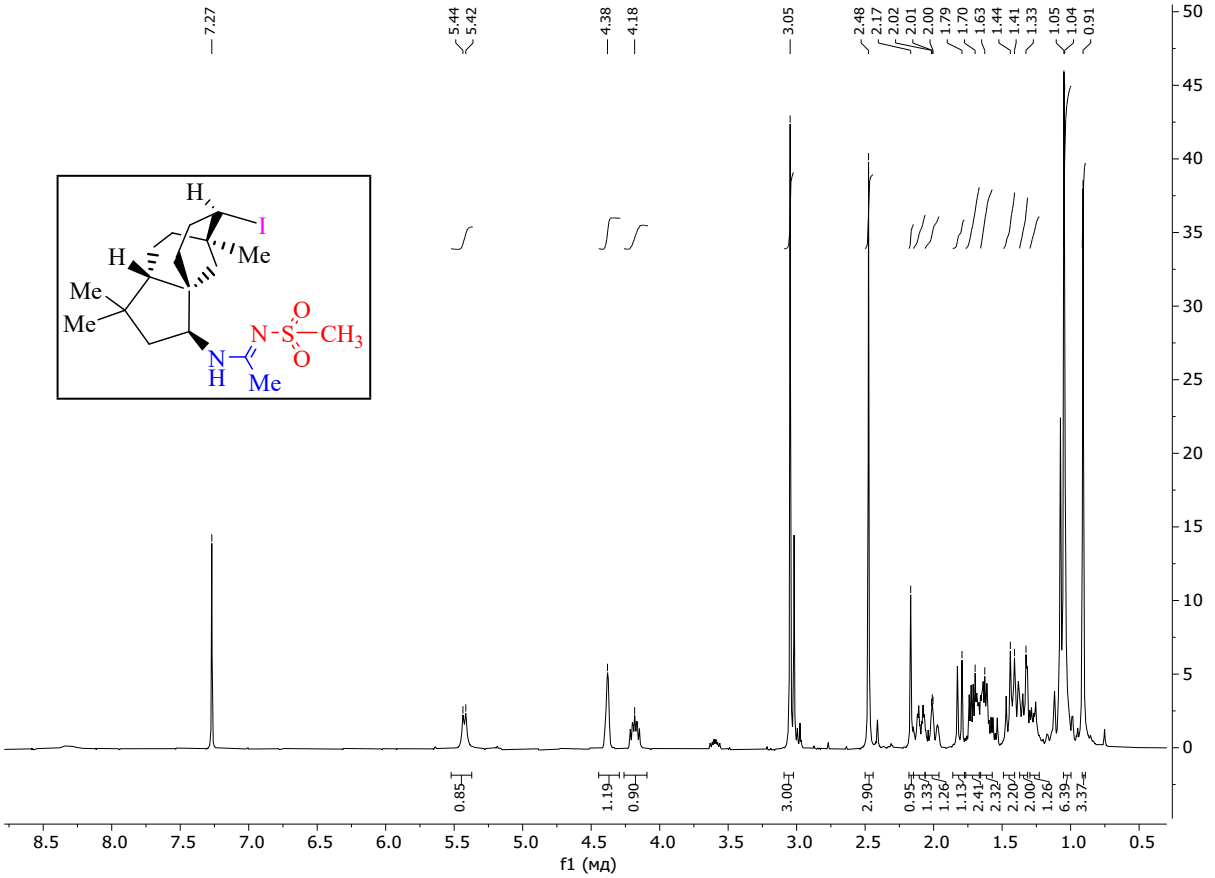


Figure S20. ^{13}C NMR spectrum of compound **4a**

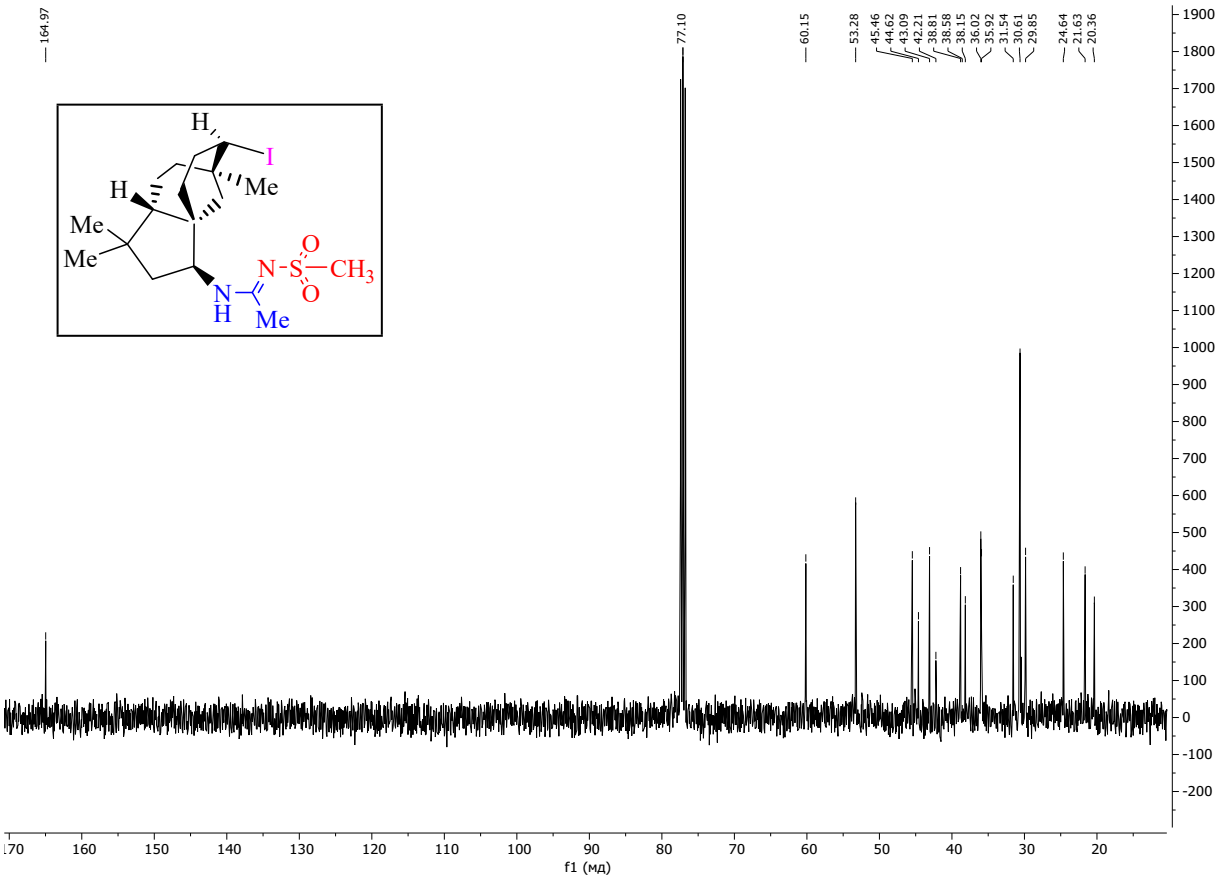


Figure S21. ^{1}H NMR spectrum of compound **5a**

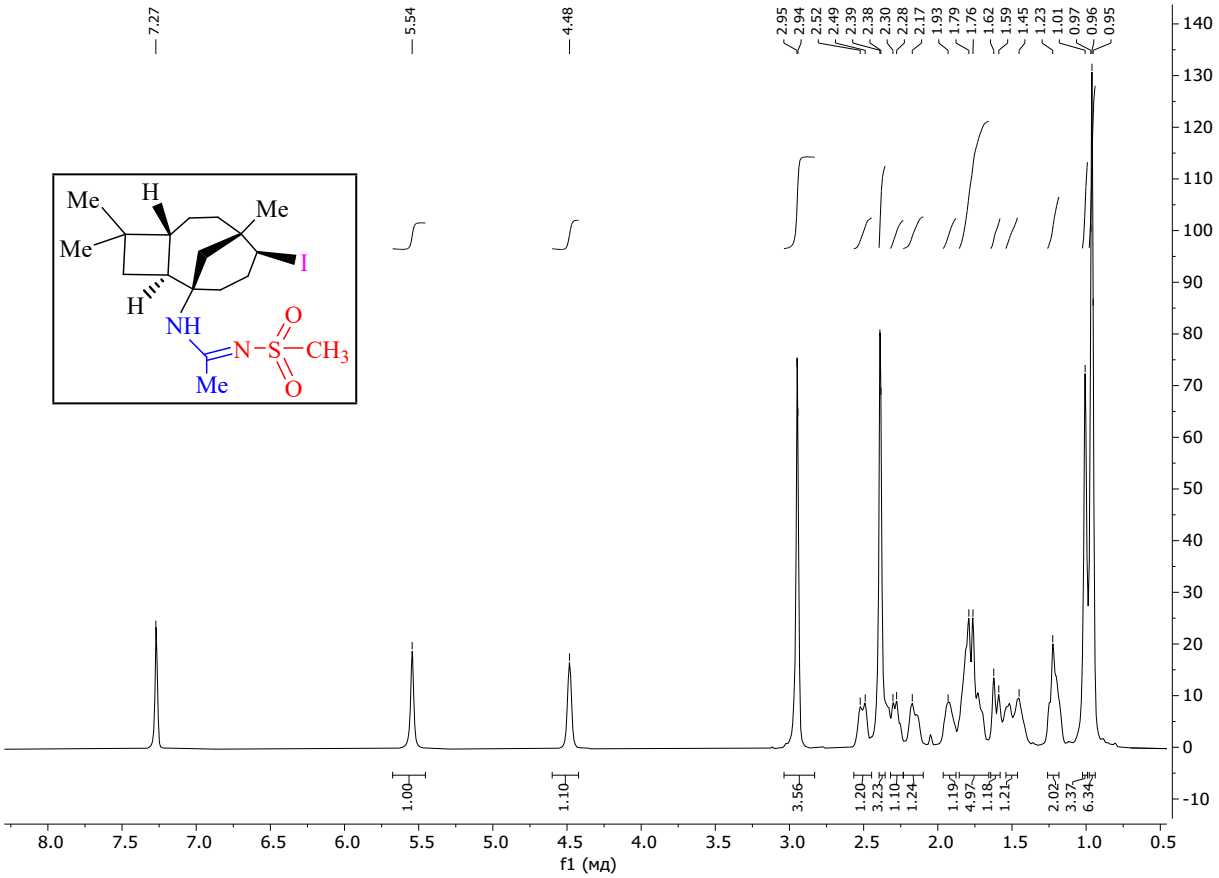


Figure S22. ^{13}C NMR spectrum of compound **5a**

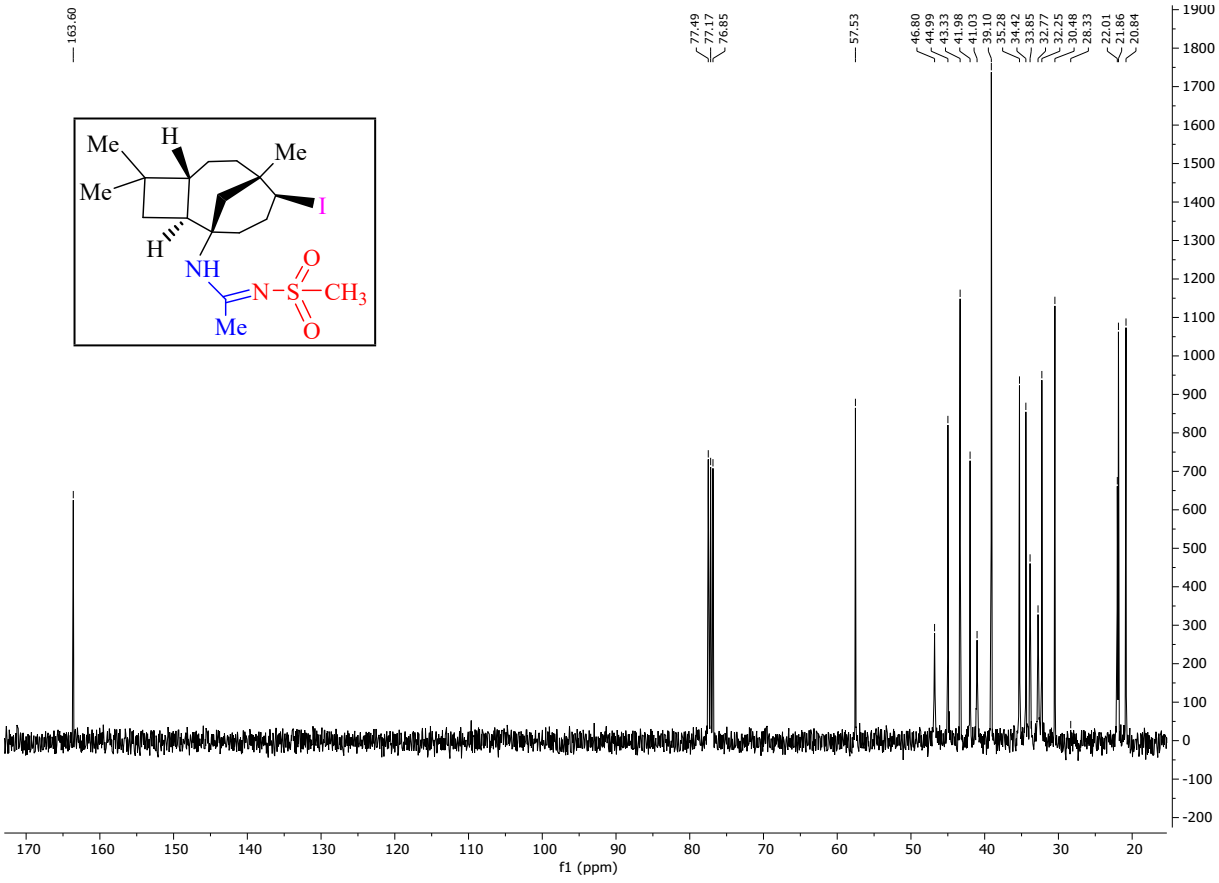


Figure S23. ^{1}H NMR spectrum of compound **4e**

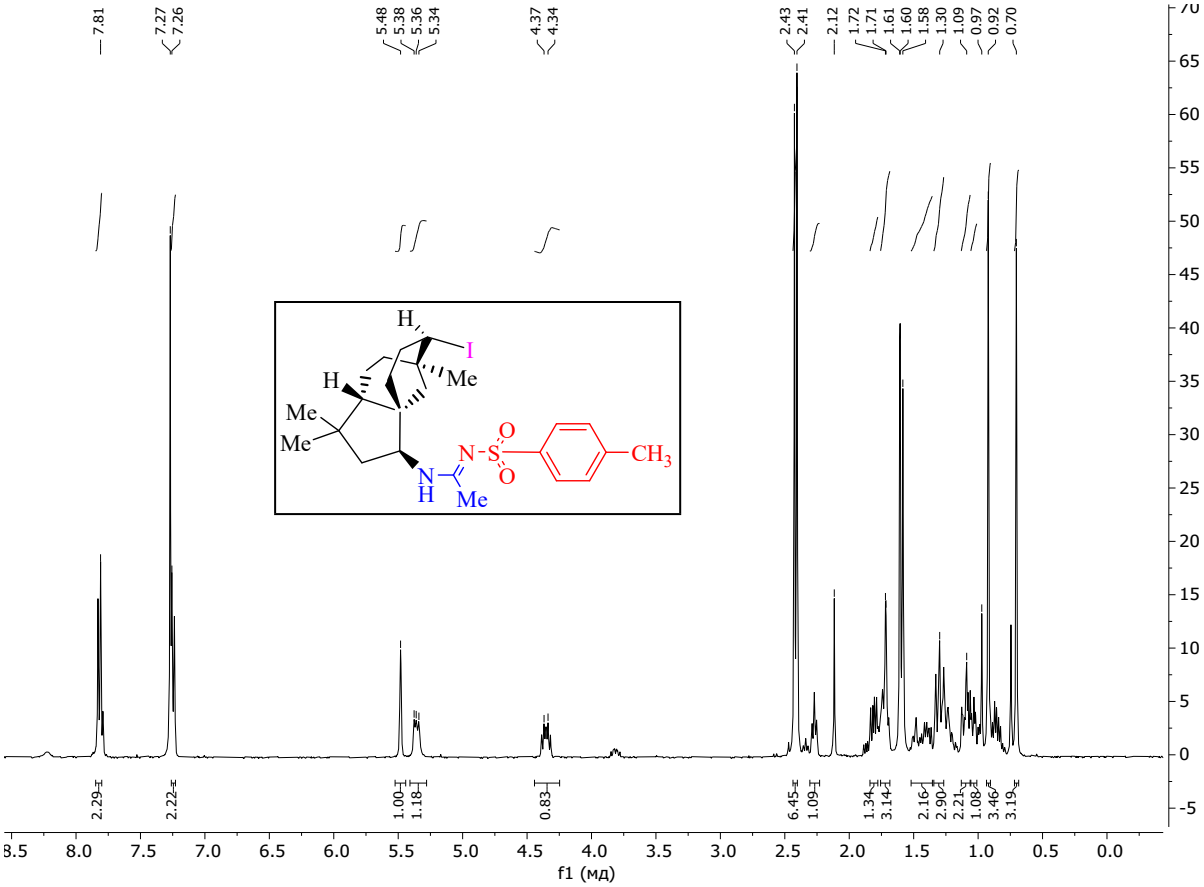


Figure S24. ^{13}C NMR spectrum of compound **4e**

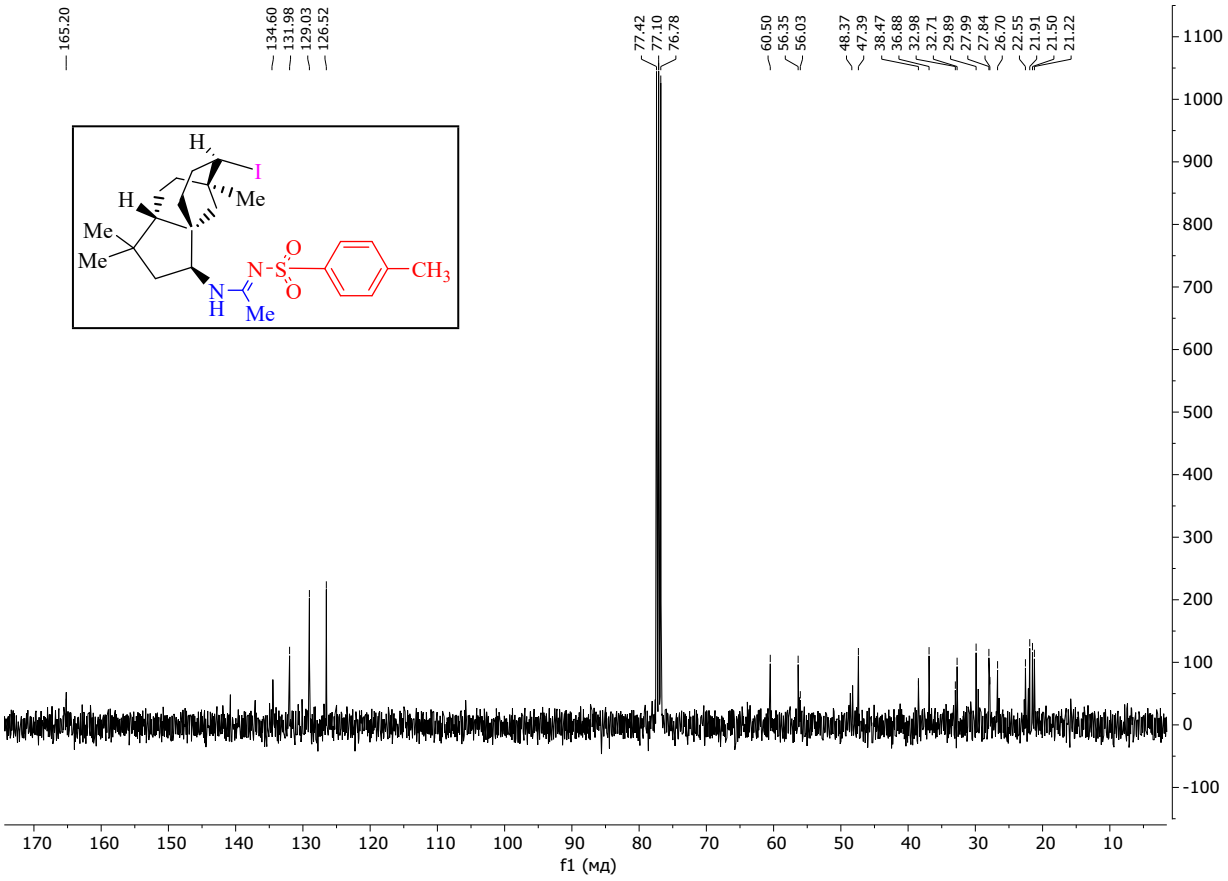


Figure S25. ^{1}H NMR spectrum of compound **4f**

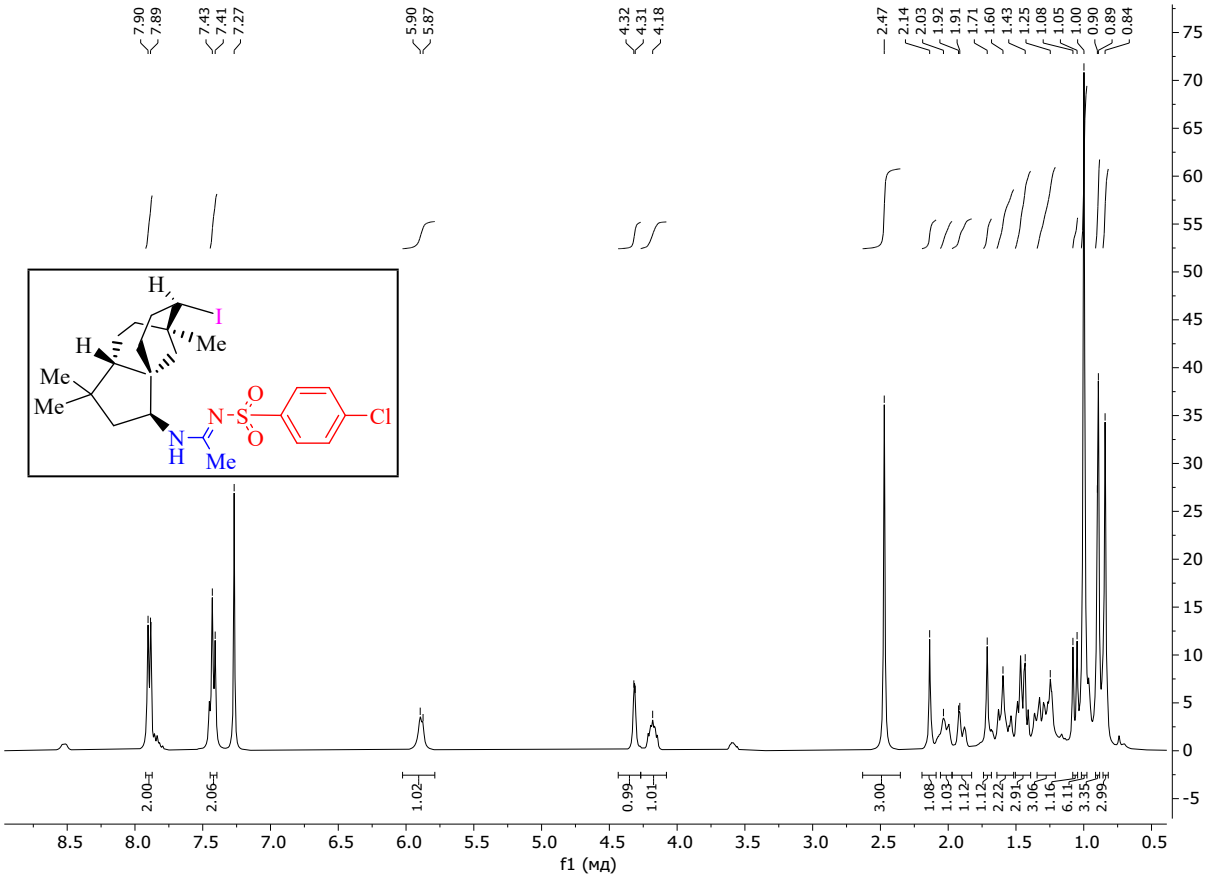


Figure S26. ^{13}C NMR spectrum of compound **4f**

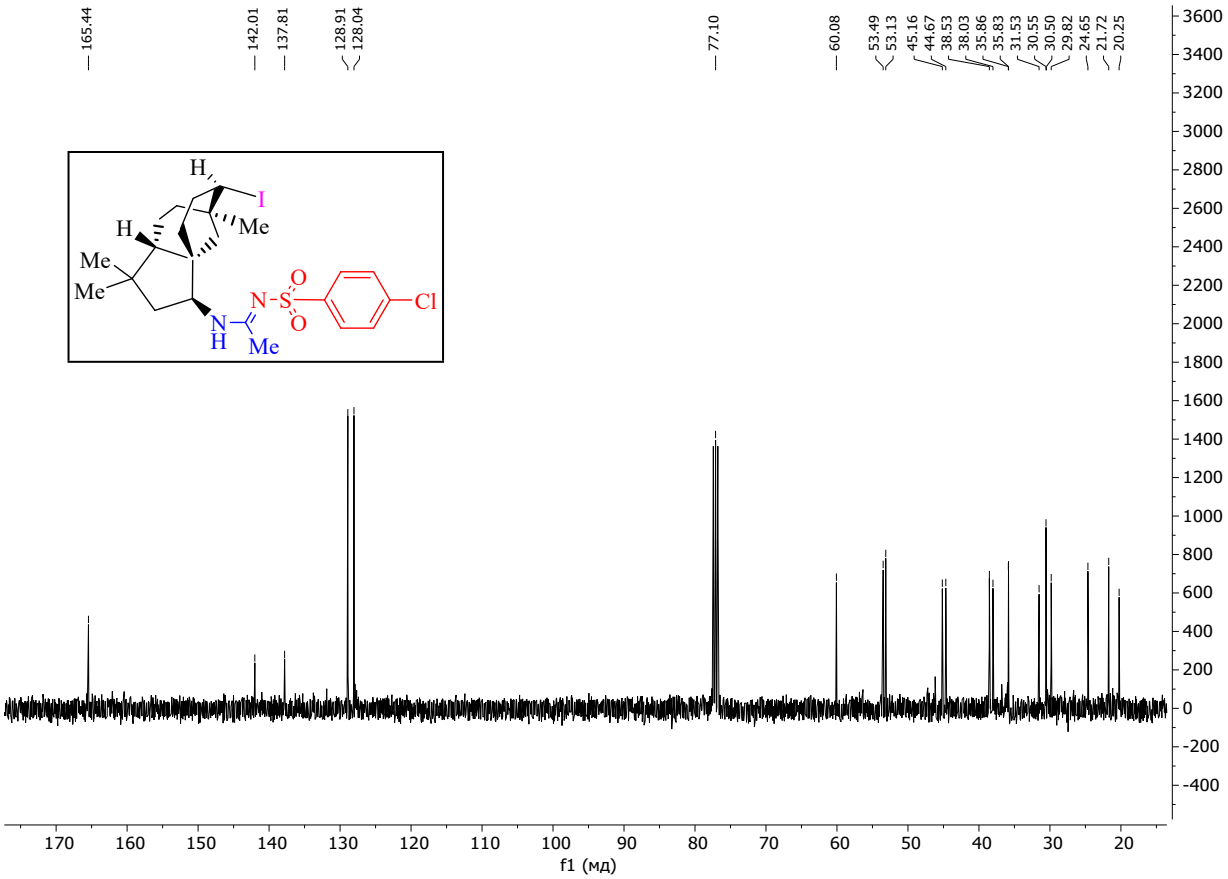


Figure S27. ^{1}H NMR spectrum of compound **4g**

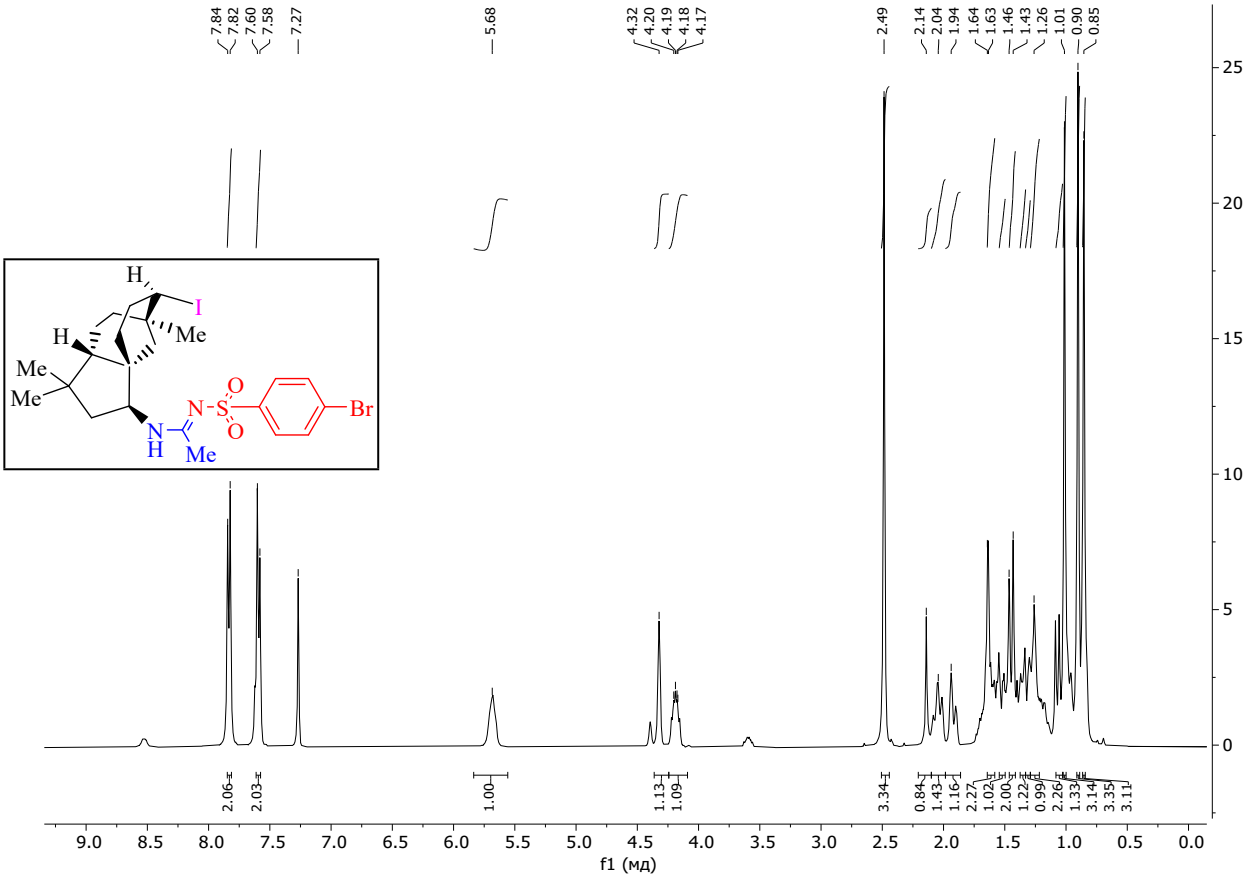


Figure S28. ^{13}C NMR spectrum of compound **4g**

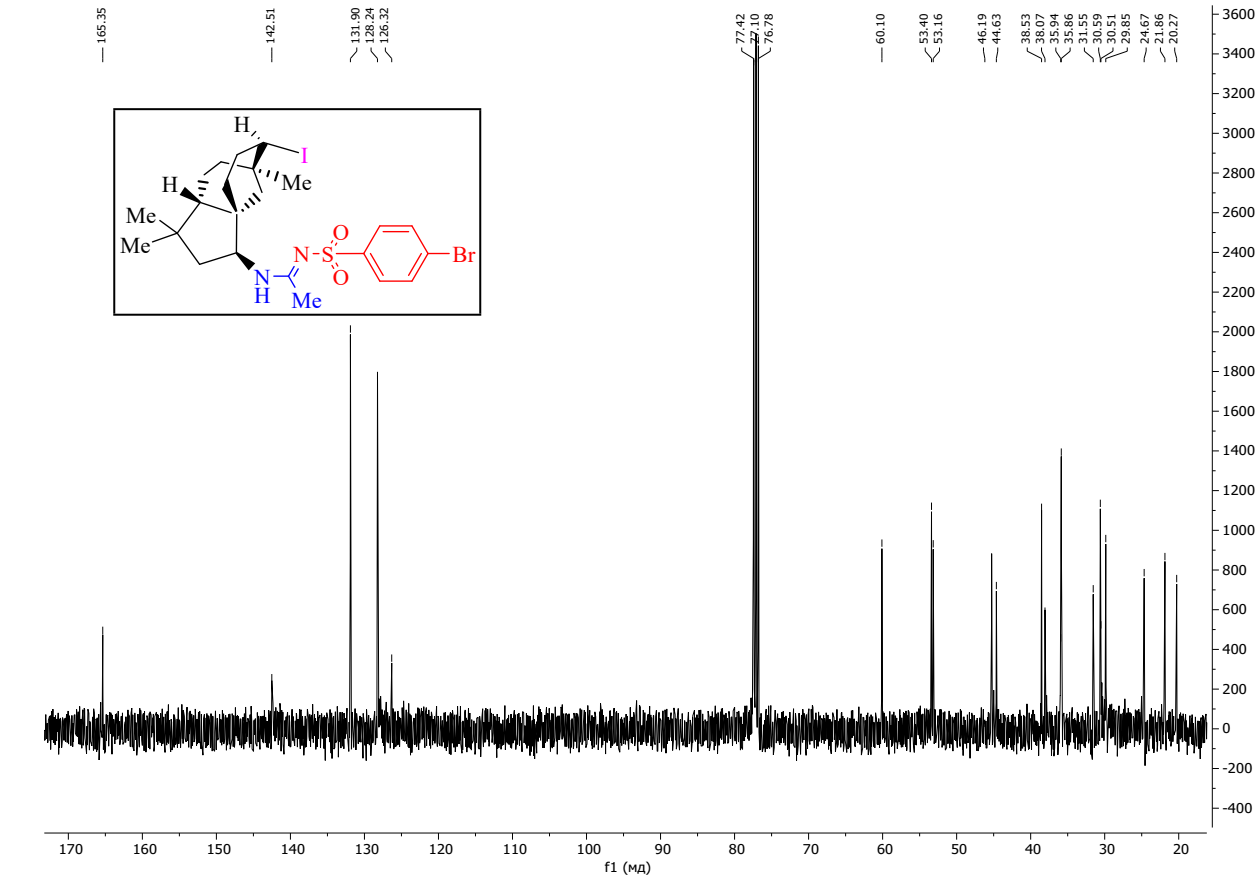


Figure S29. ^{1}H NMR spectrum of compound **4h**

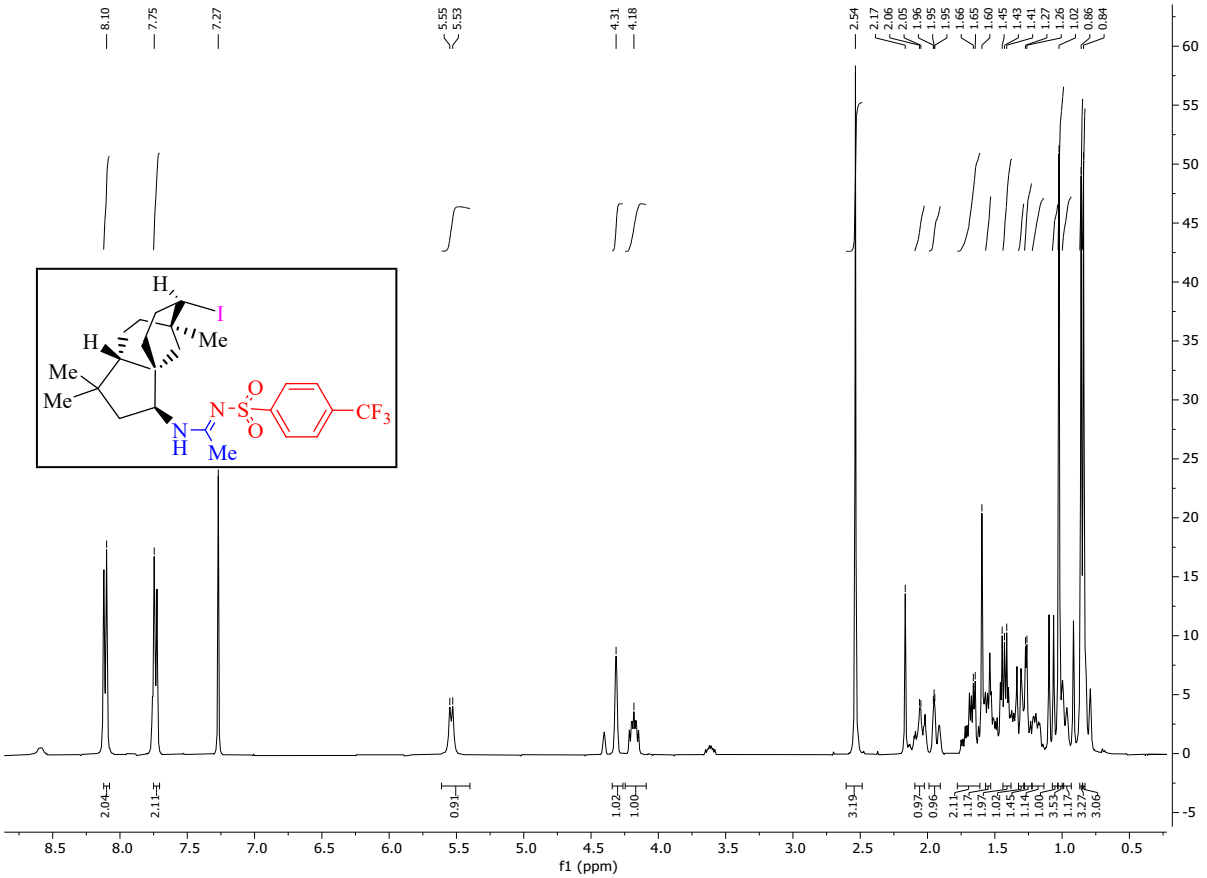


Figure S30. ^{13}C NMR spectrum of compound **4h**

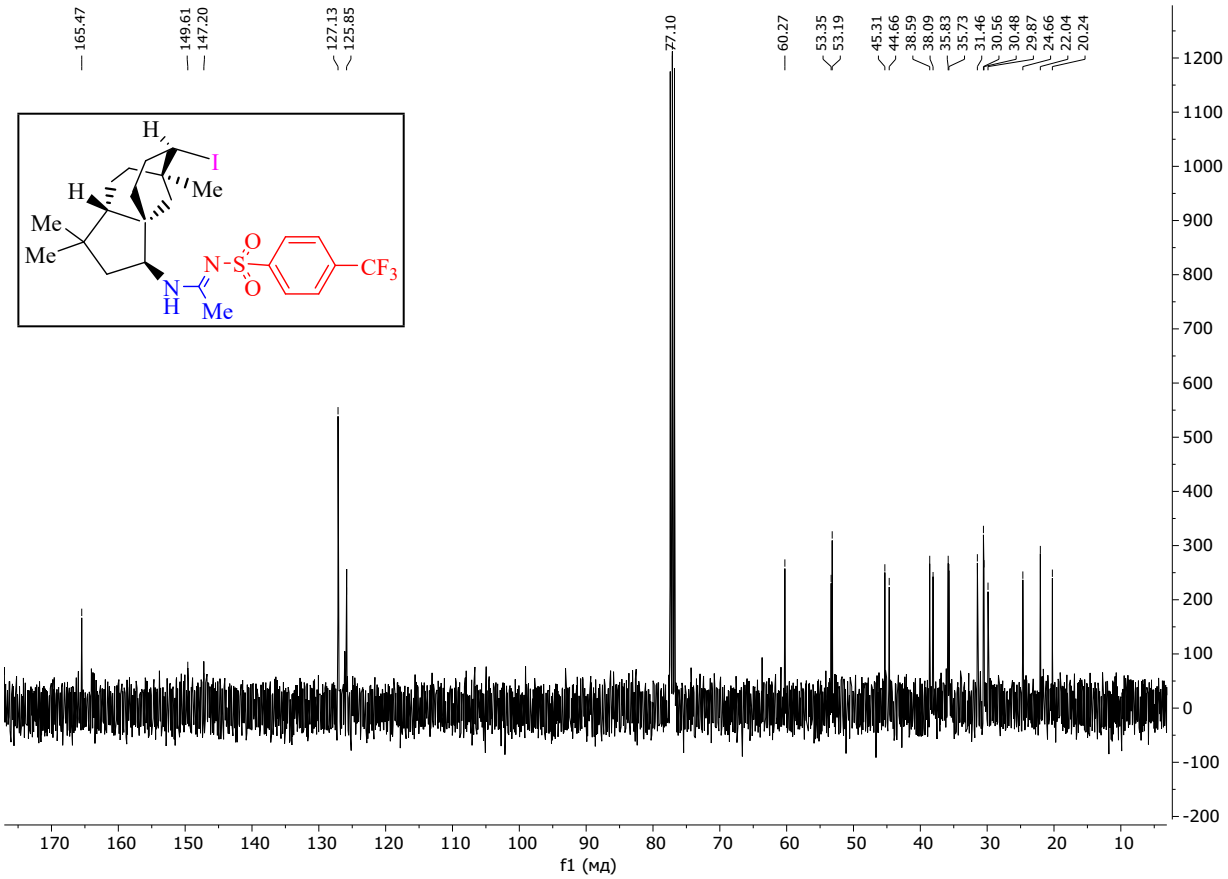


Figure S31. ^{19}F NMR spectrum of compound **4h**

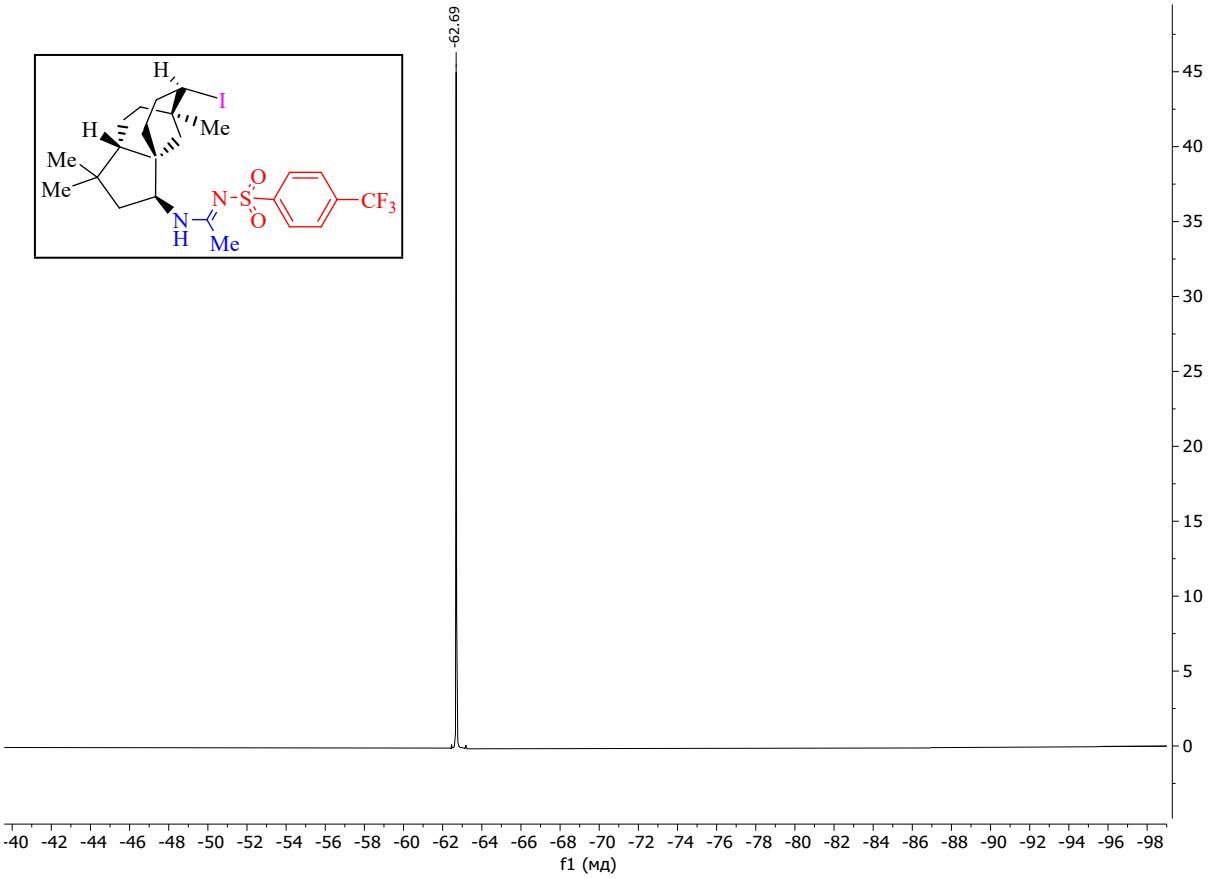


Figure S32. ^{1}H NMR spectrum of compound **4i**

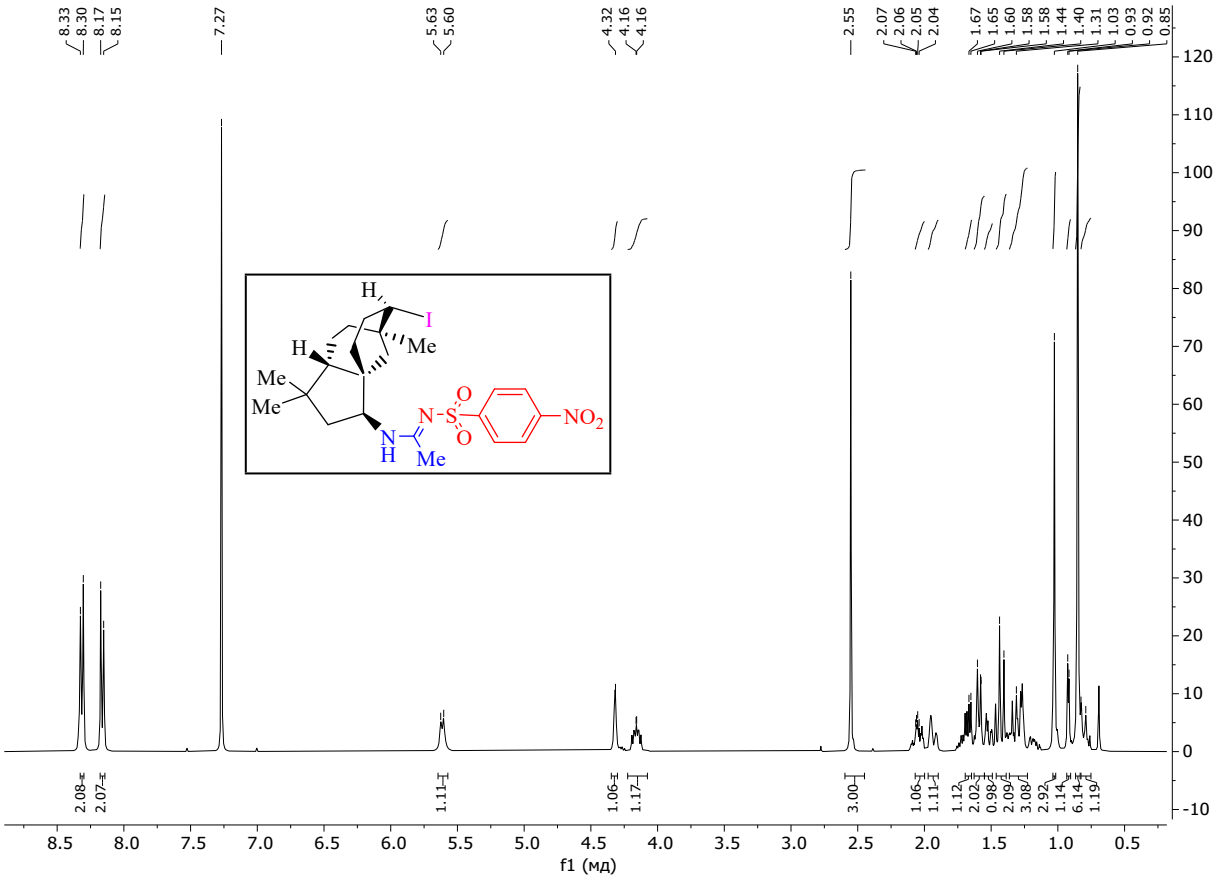


Figure S33. ^{13}C NMR spectrum of compound **4i**

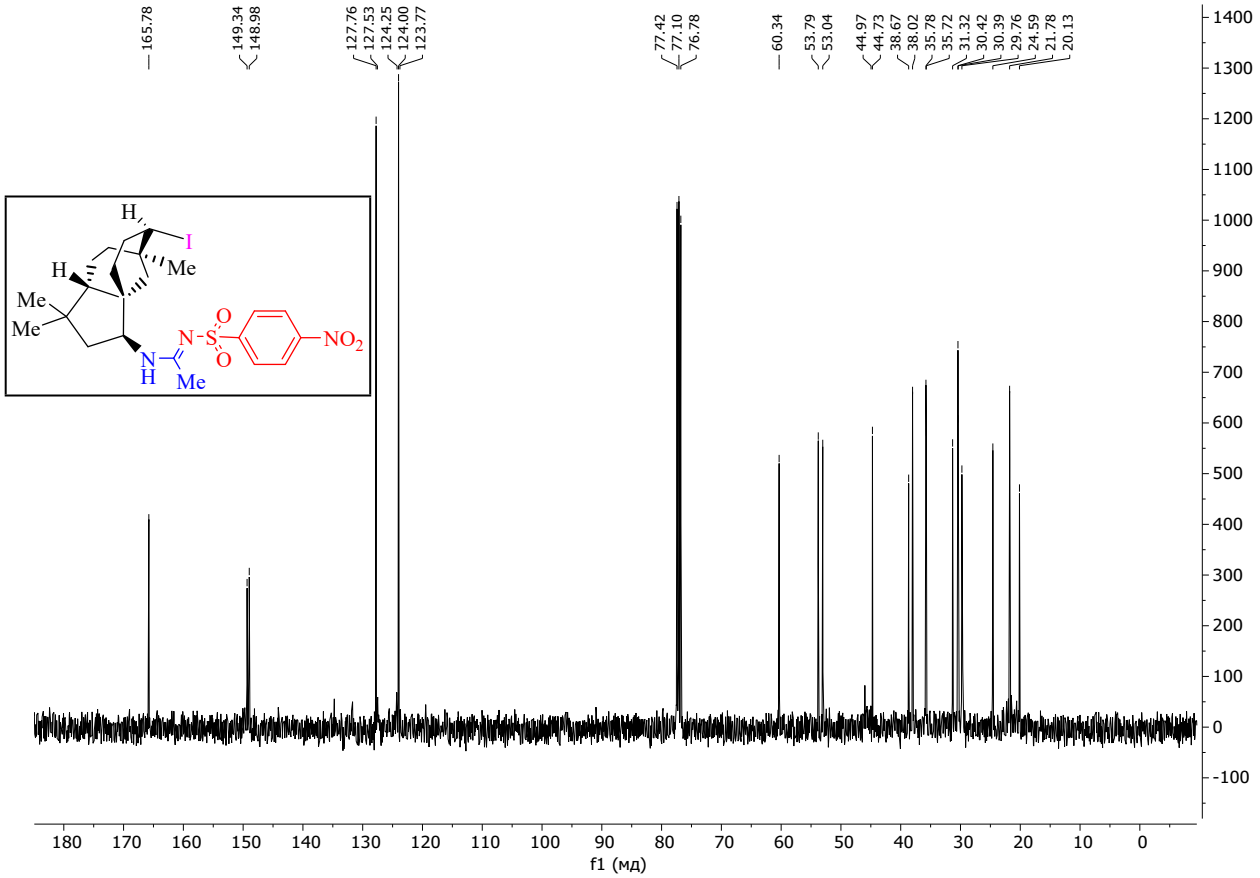


Figure S34. ^{1}H NMR spectrum of compound **5i**

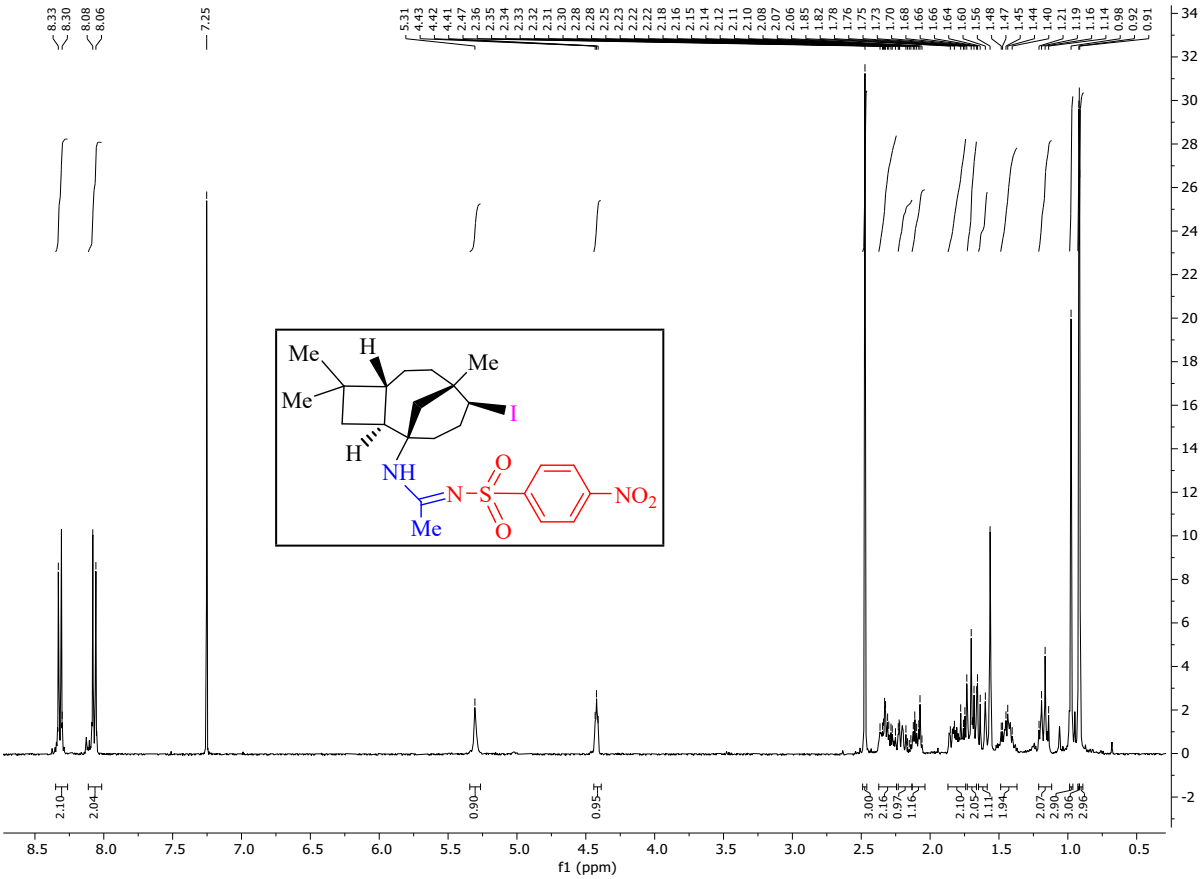


Figure S35. ^{13}C NMR spectrum of compound **5i**

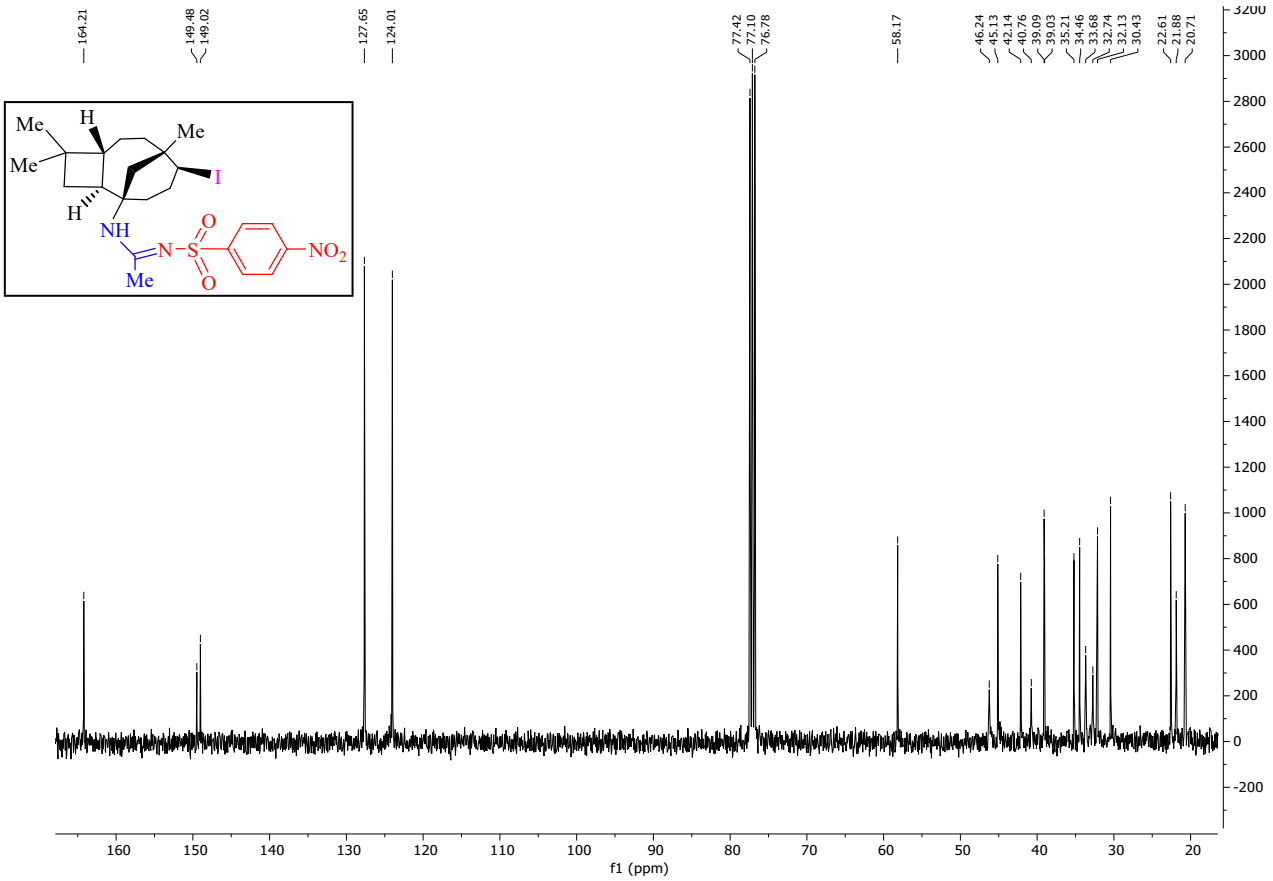


Figure S36. ^{1}H NMR spectrum of compound **5b**

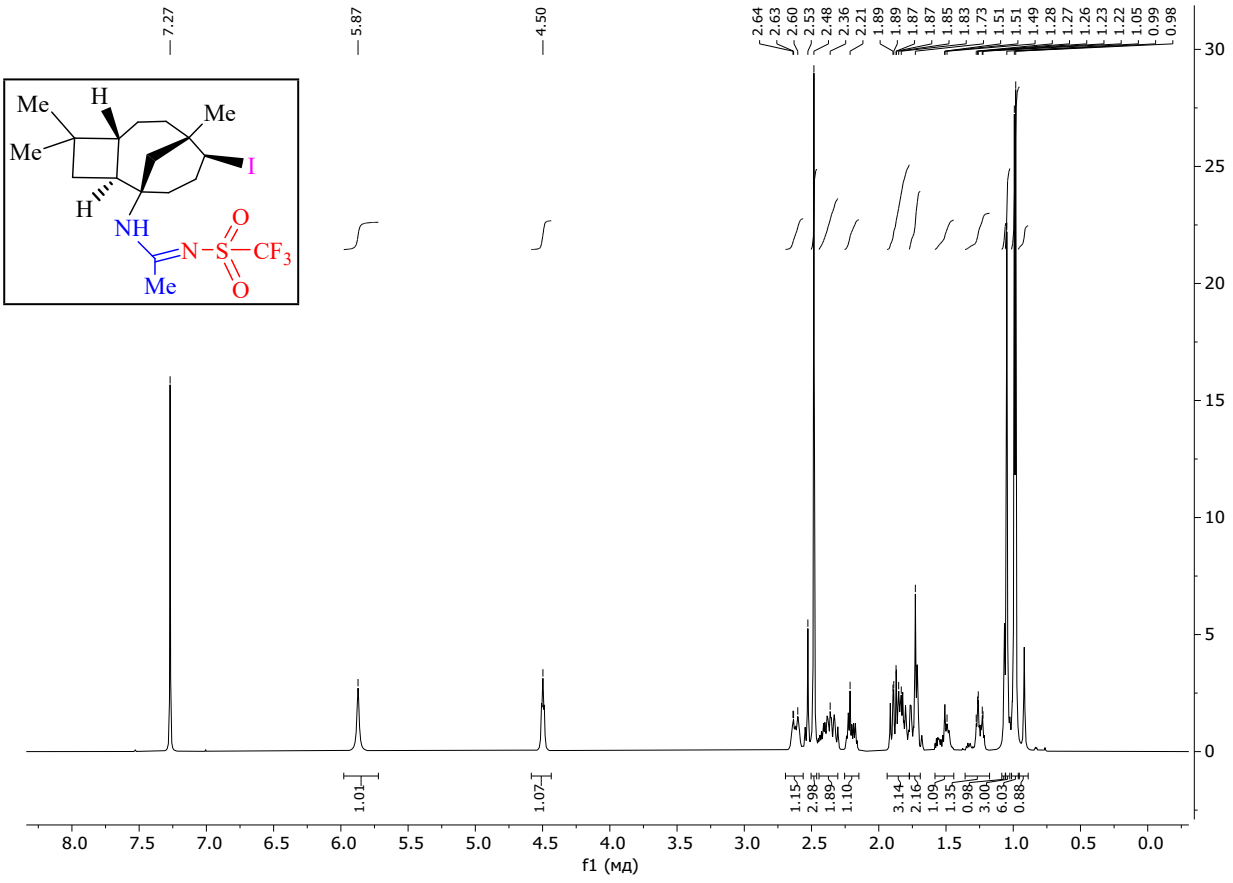


Figure S37. ^{13}C NMR spectrum of compound **5b**

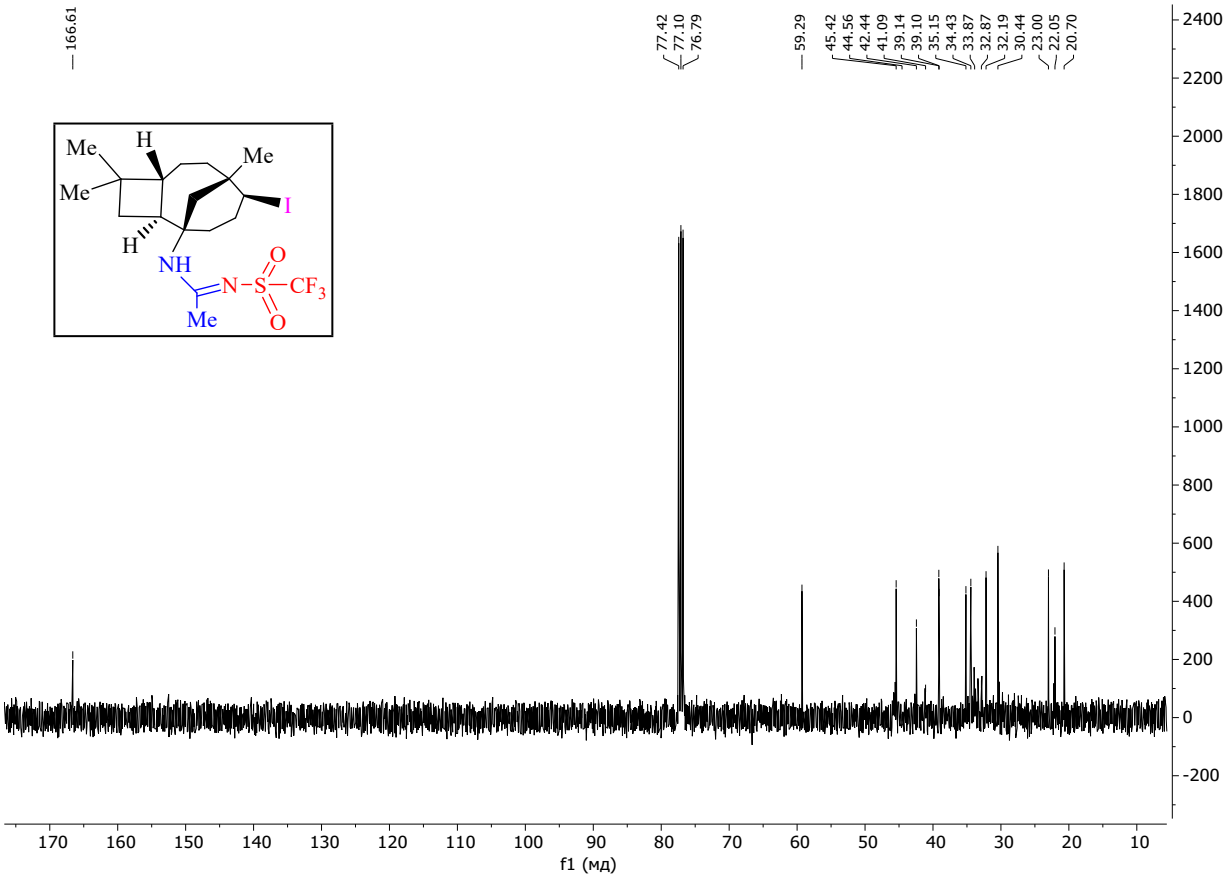


Figure S38. ^{19}F NMR spectrum of compound **5b**

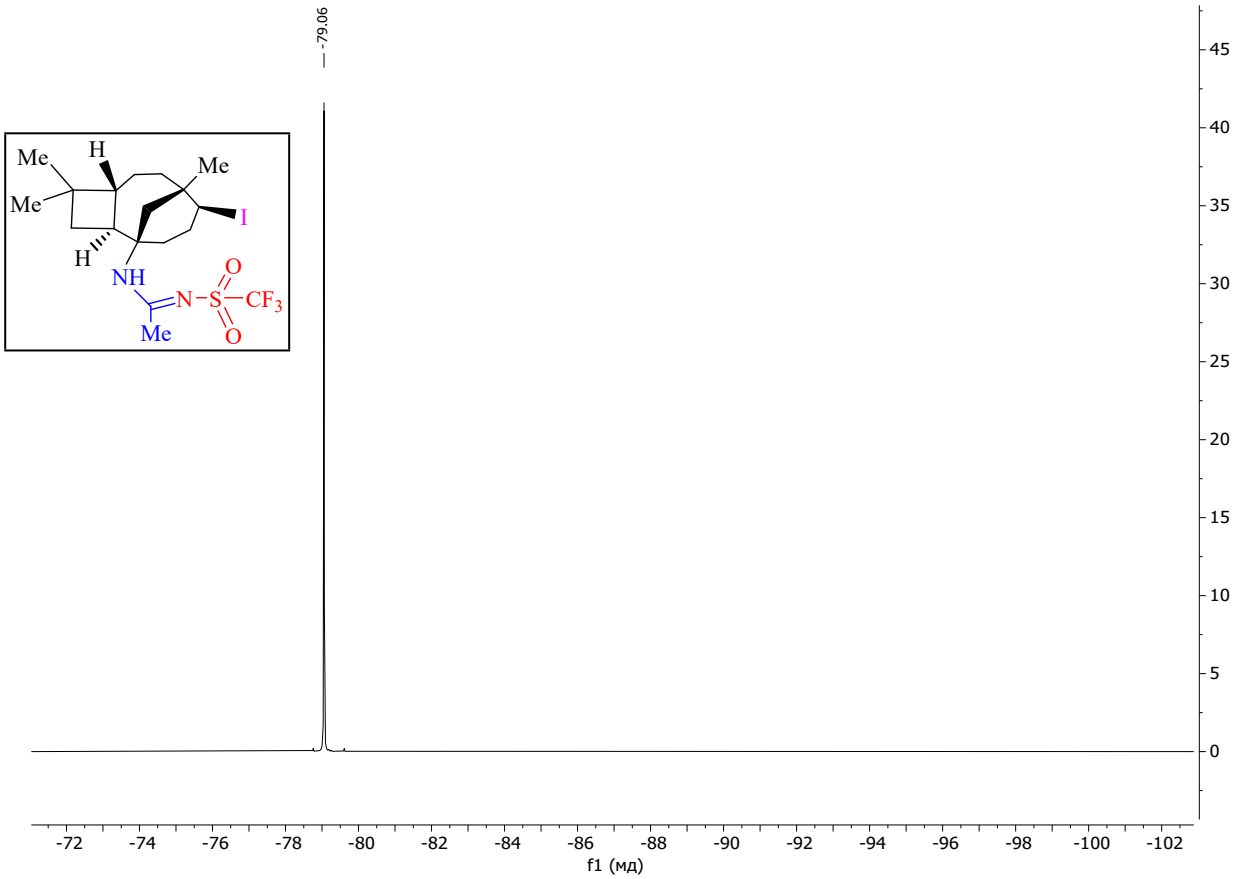


Figure S39. ^{1}H NMR spectrum of compound **5c**

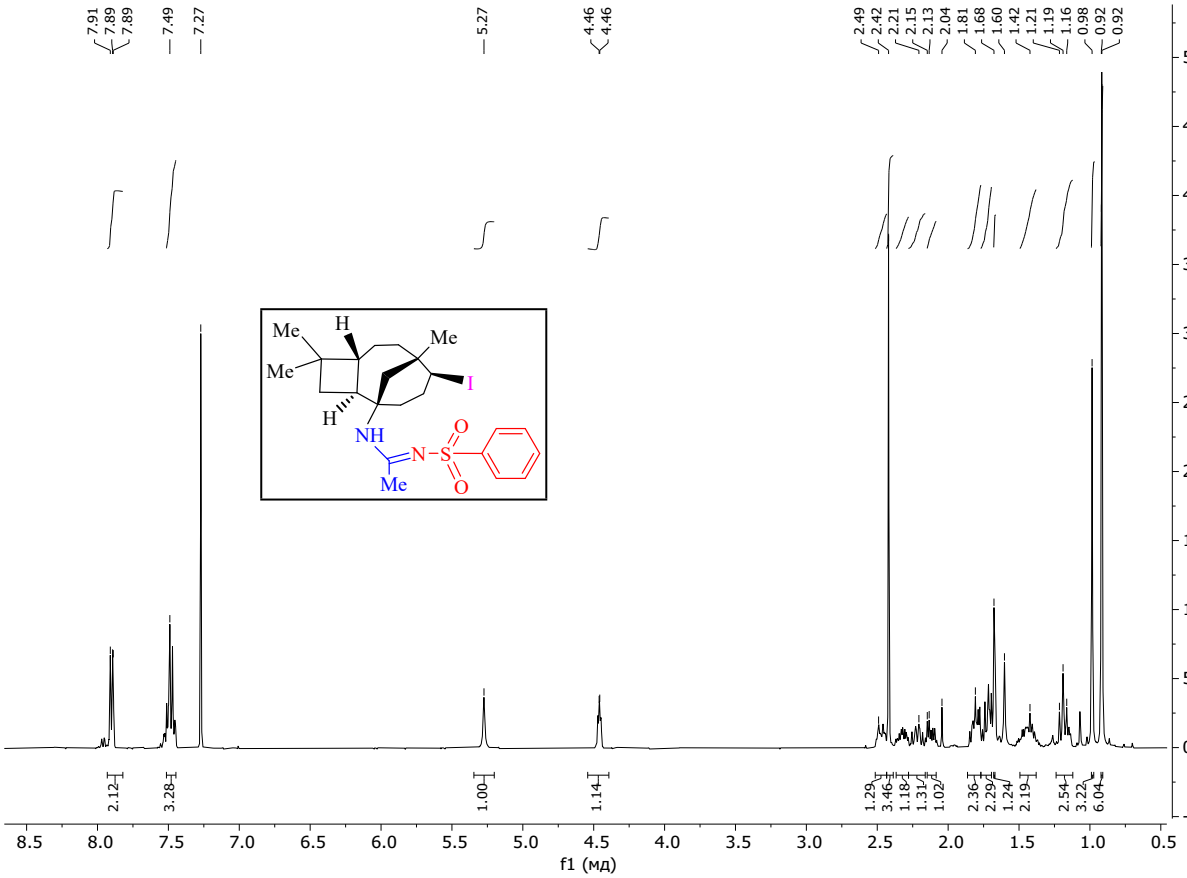


Figure S40. ^{13}C NMR spectrum of compound **5c**

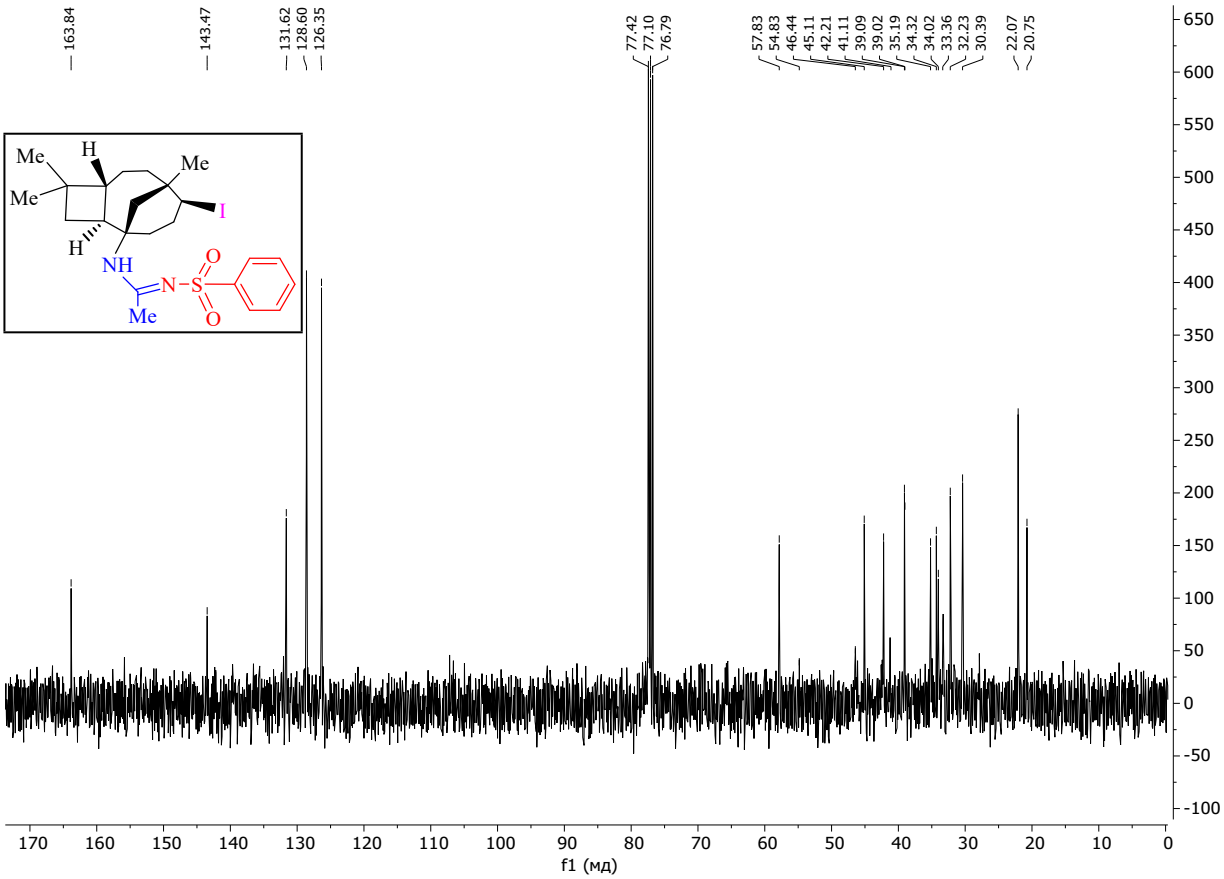


Figure S41. ^{1}H NMR spectrum of compound **5d**

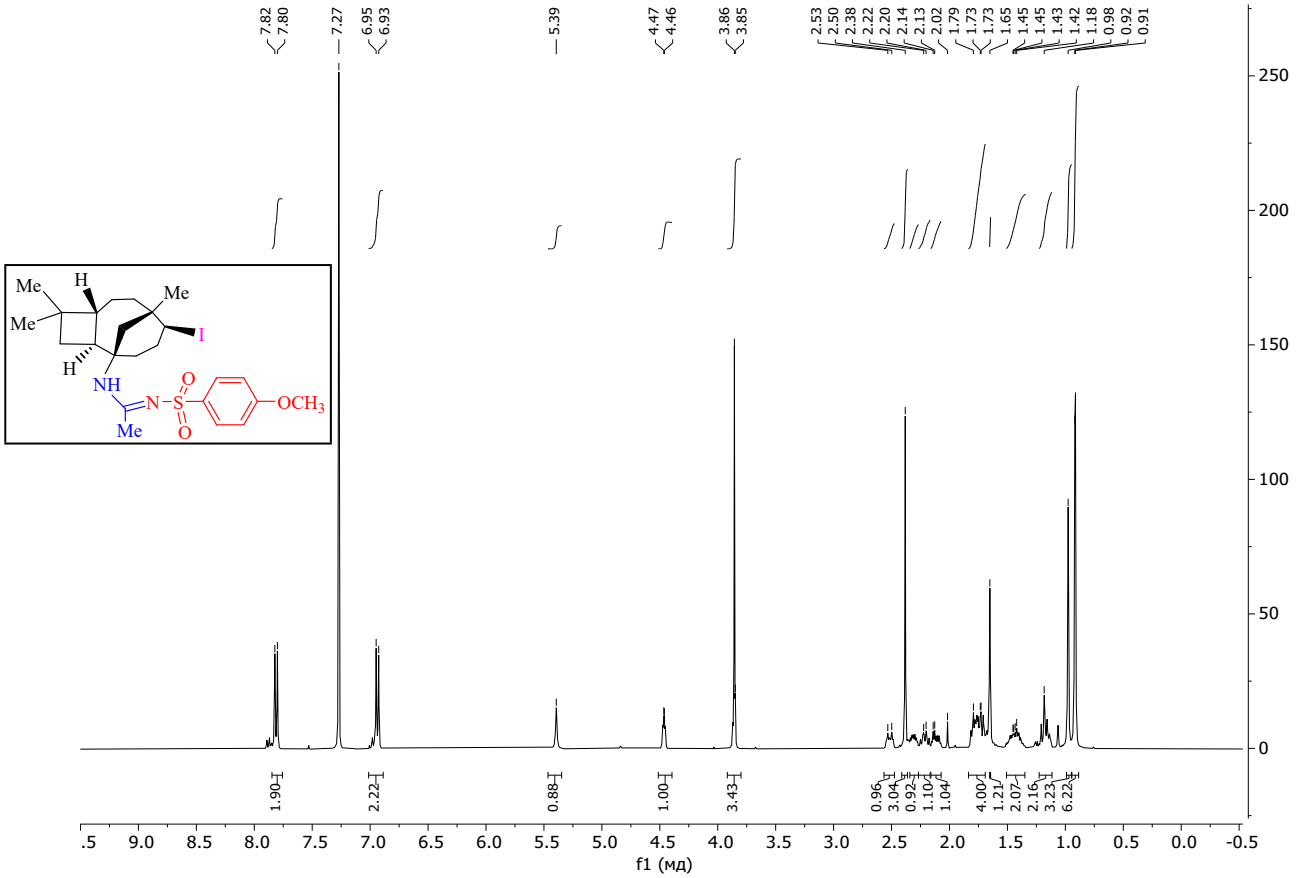


Figure S42. ^{13}C NMR spectrum of compound **5d**

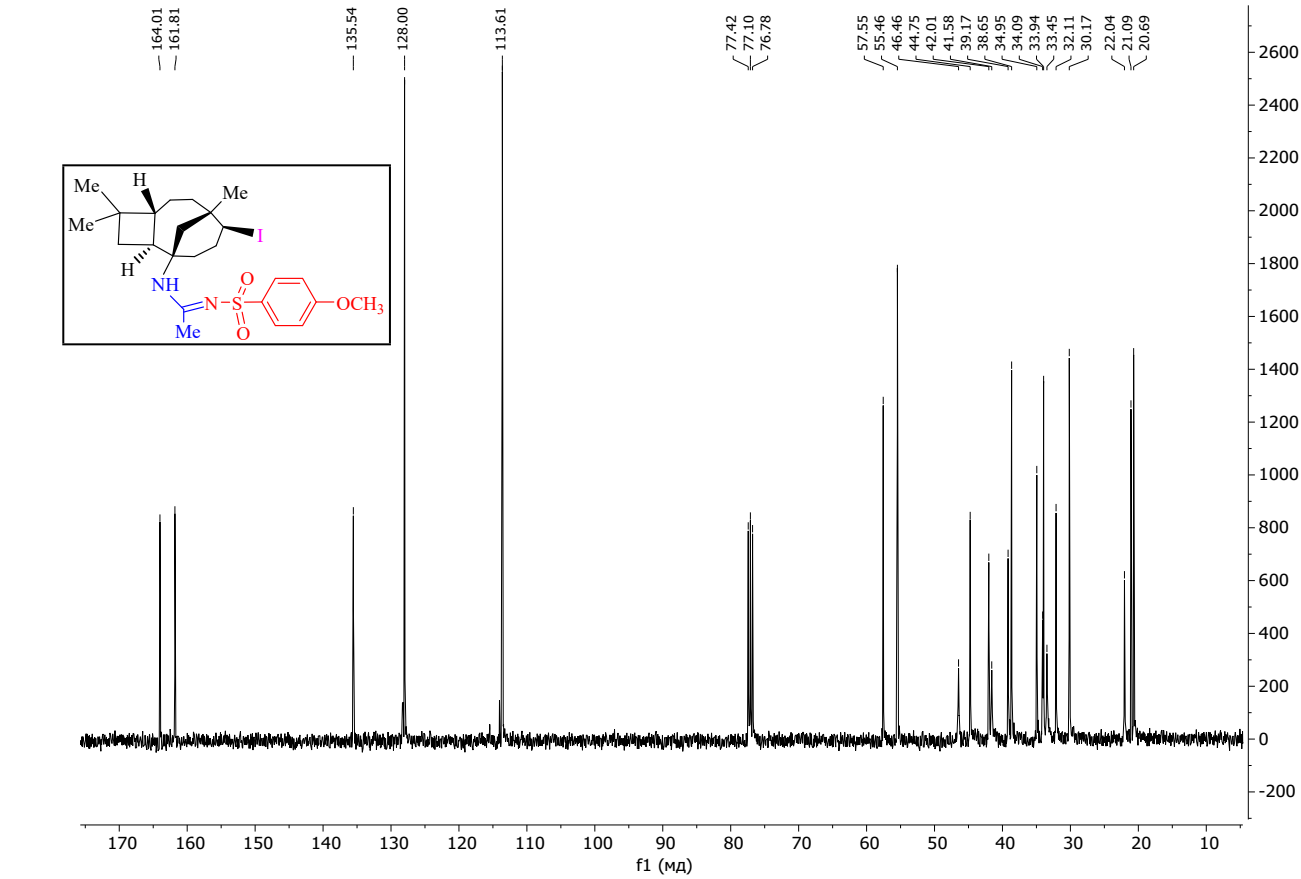


Figure S43. ^{1}H NMR spectrum of compound **5j**

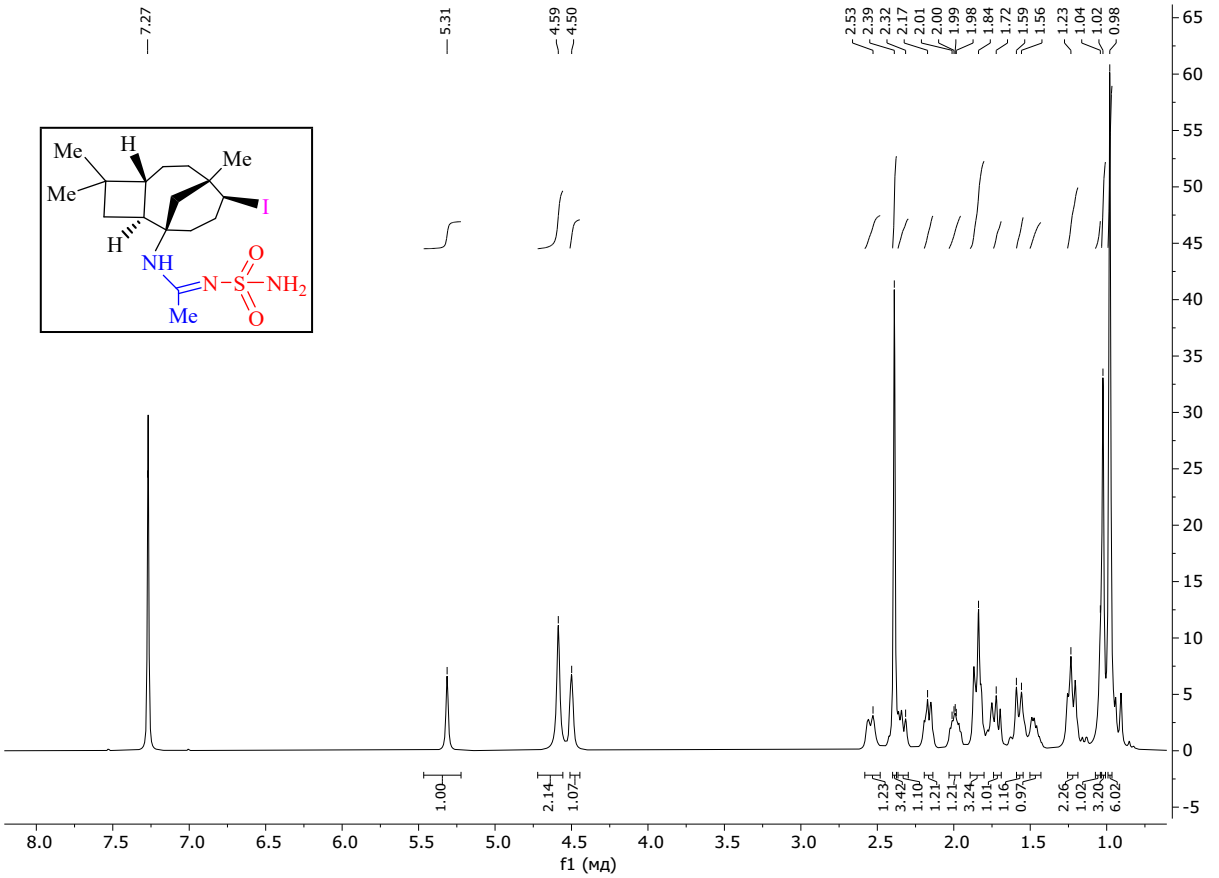


Figure S44. ^{13}C NMR spectrum of compound **5j**

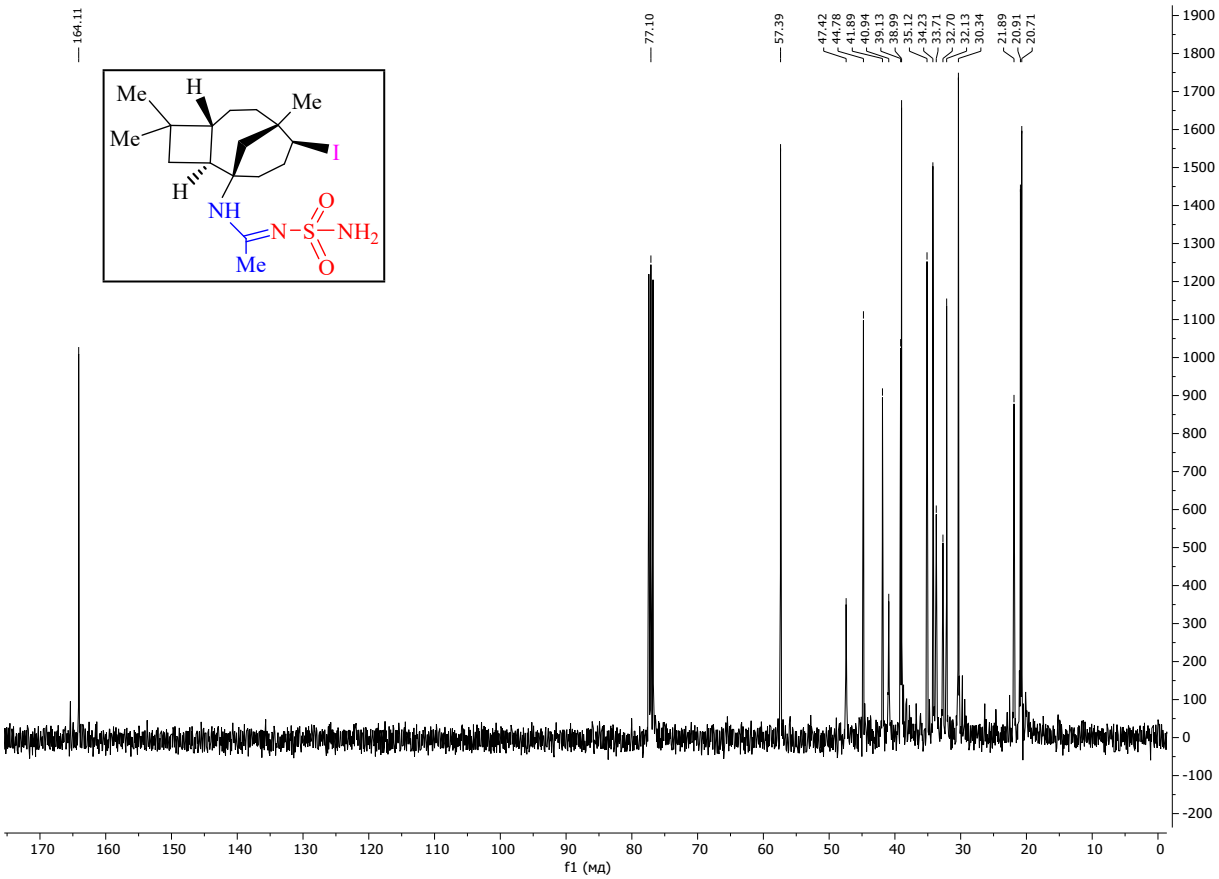


Figure S45. HRMS (ESI) of compound **4e**

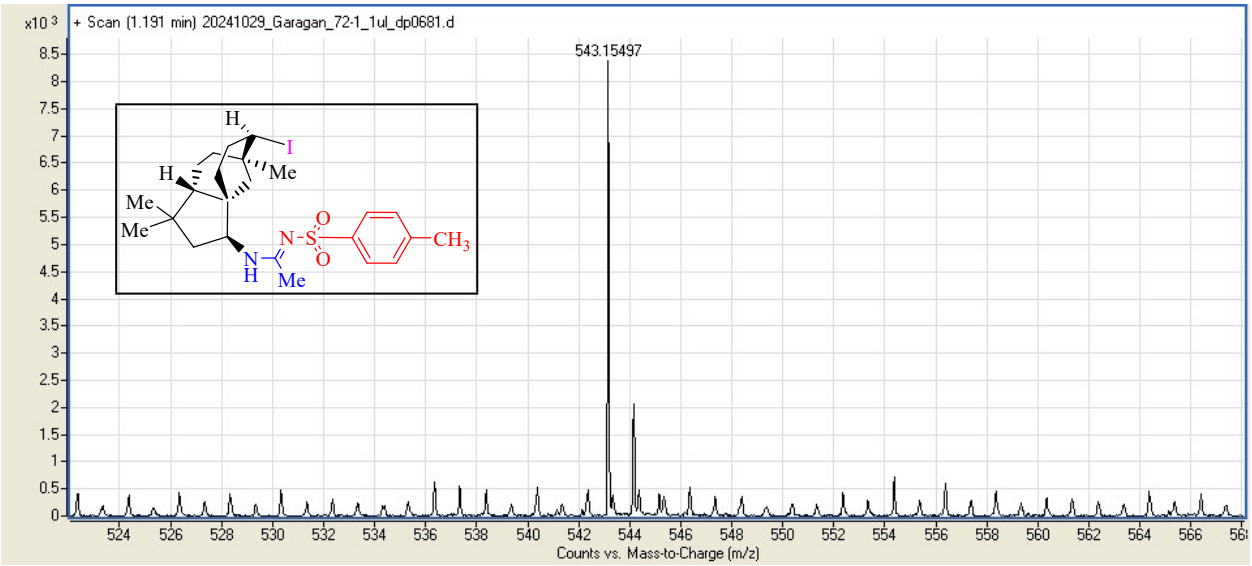


Figure S46. HRMS (ESI) of compound **4f**

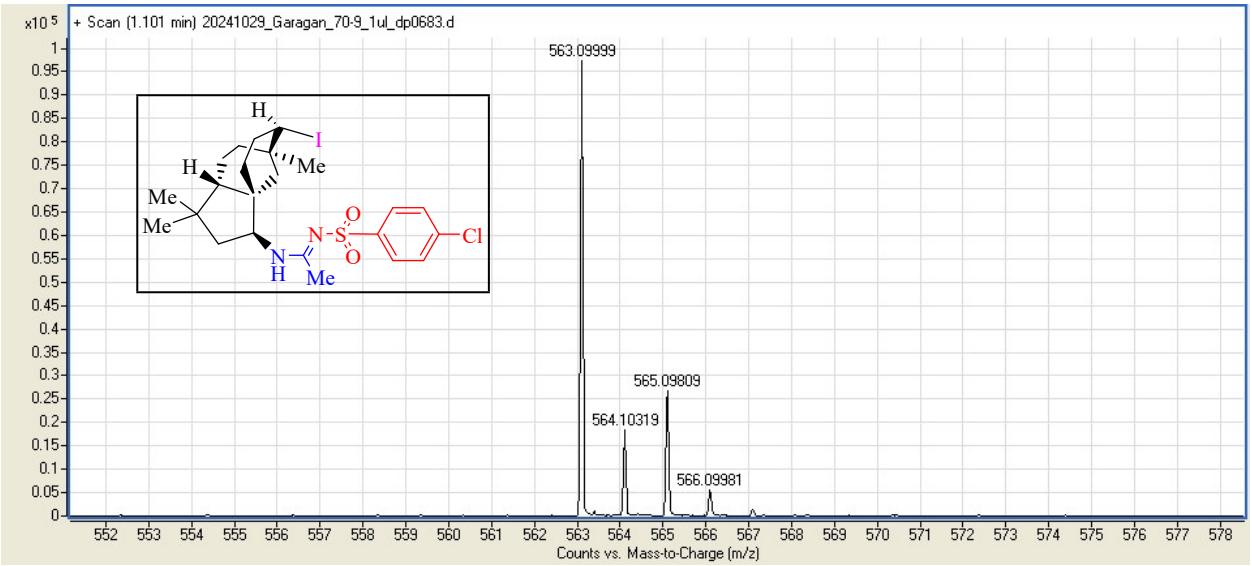


Figure S47. HRMS (ESI) of compound **4g**

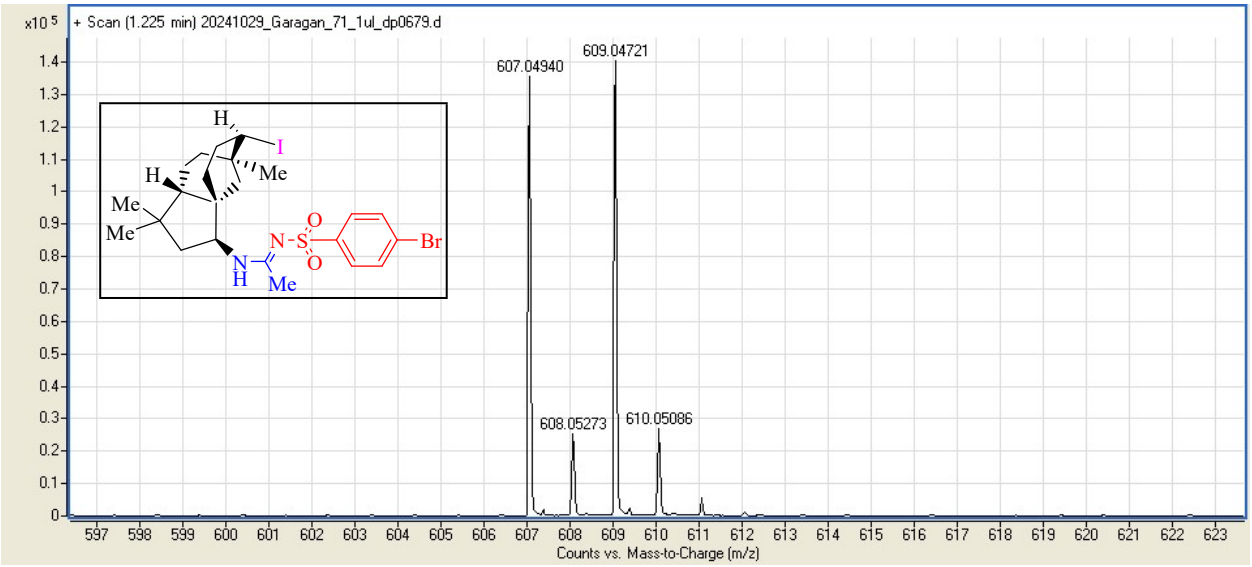


Figure S48. HRMS (ESI) of compound **4i**

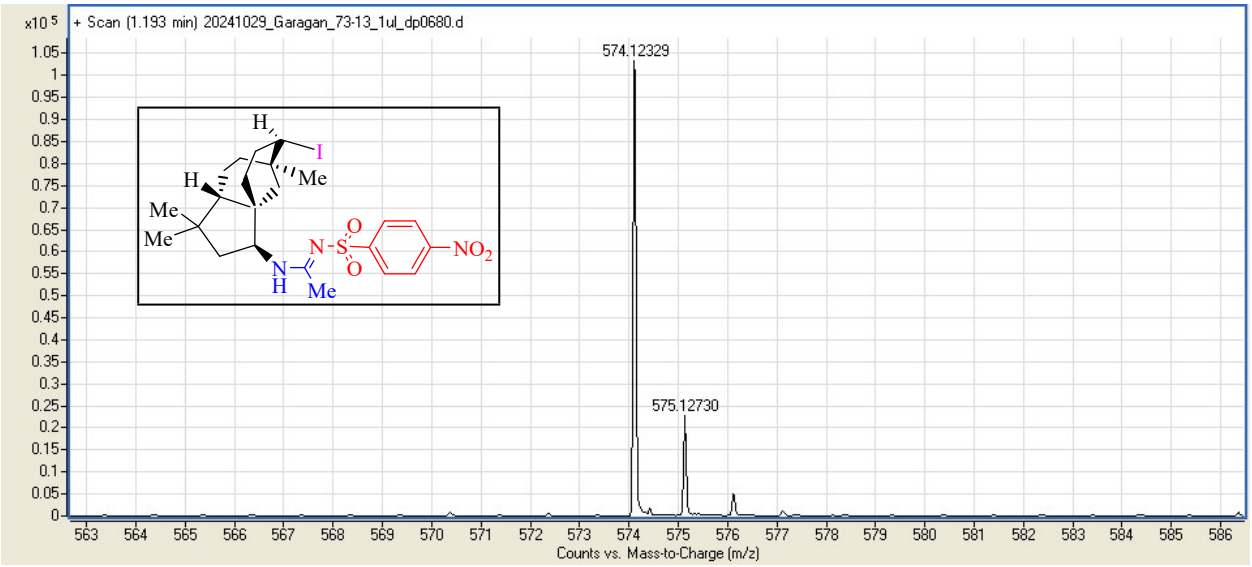


Figure S49. HRMS (ESI) of compound **5c**

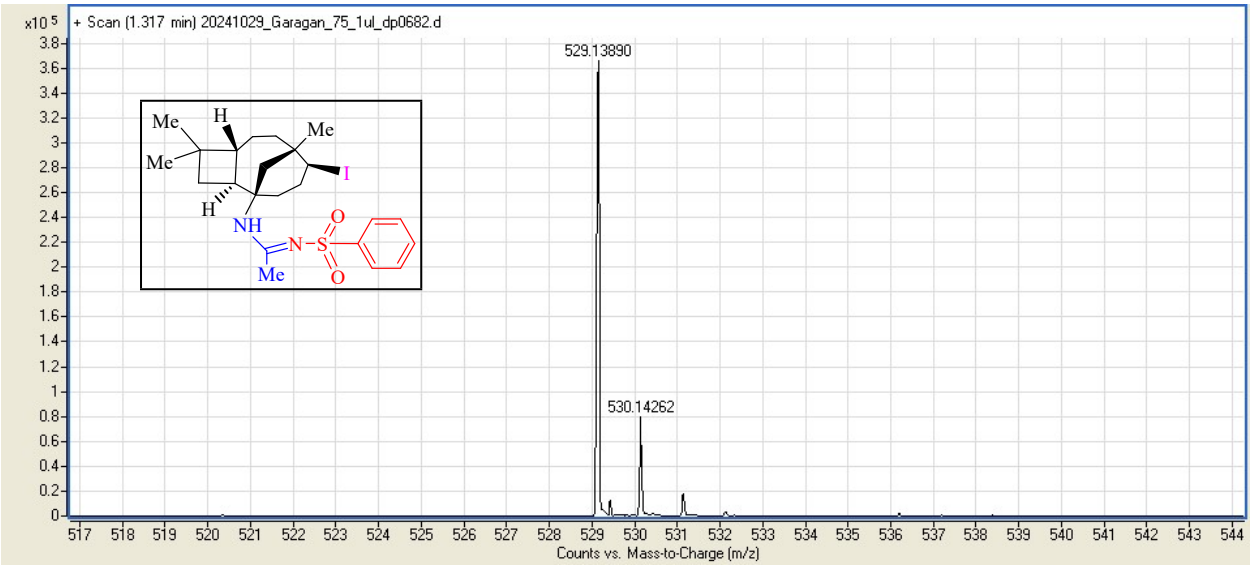


Figure S50. HRMS (ESI) of compound **5d**

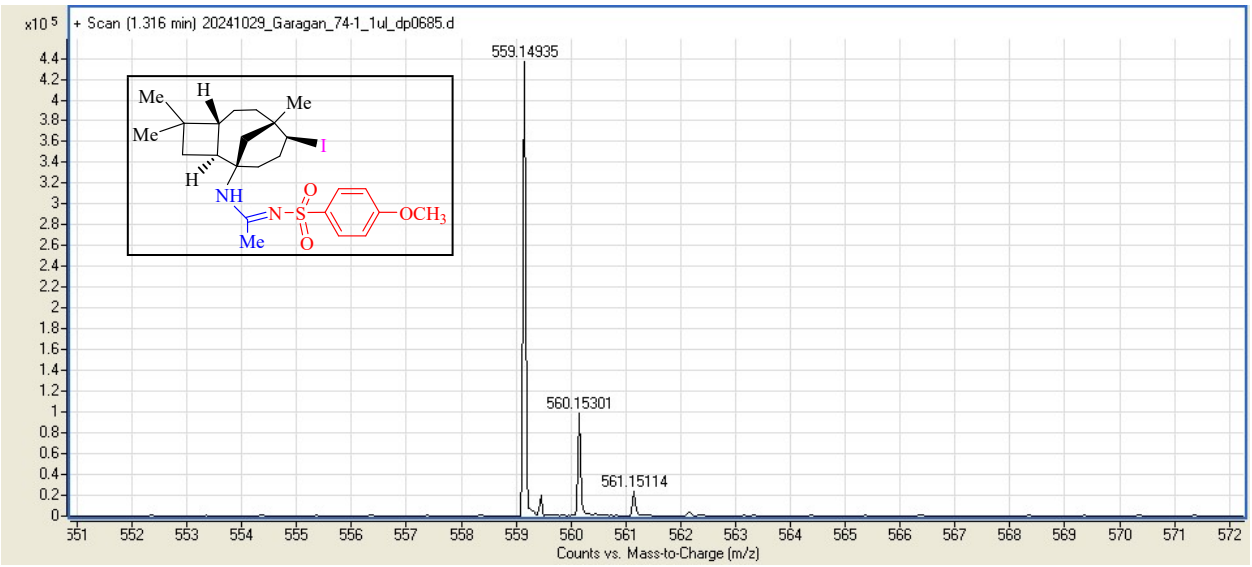
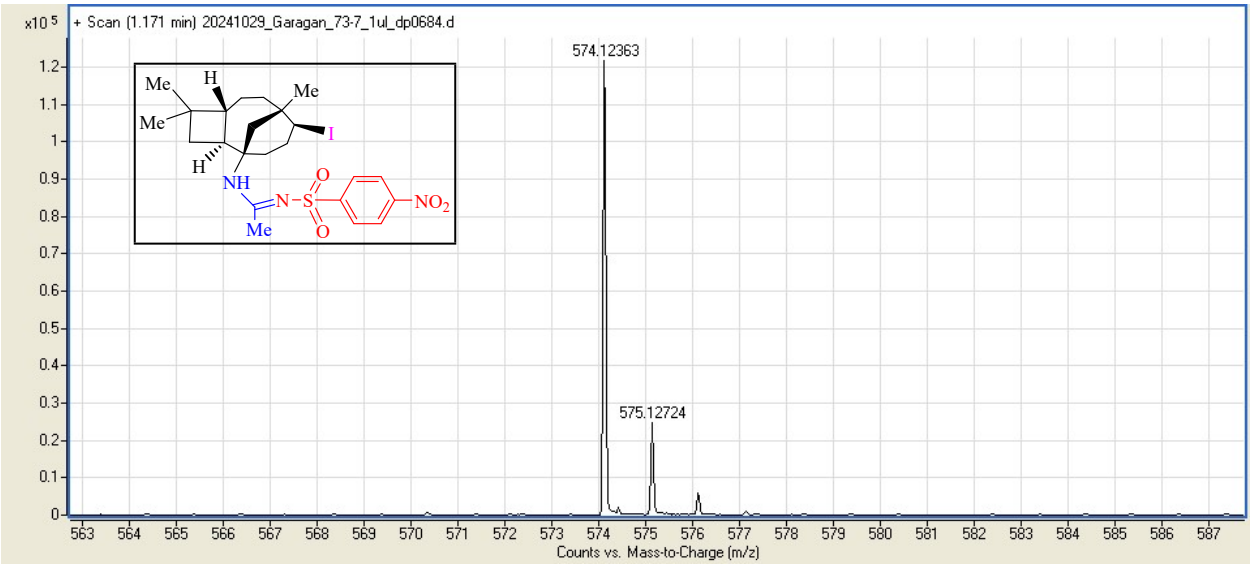


Figure S51. HRMS (ESI) of compound **5i**


x10 5
+ Scan (1.171 min) 20241029_Garagan_73-7_1ul_dp0684.d
574.12363
575.12724
Me
H
Me
Me
I
H
NH
N
S
O
O
NO2
Me
Counts vs. Mass-to-Charge (m/z)