Supplementary information

Halosulfonamidation of Camphene: Chemo and Stereoselectivity, Rearrangement, Solvent Interception, Heterocyclization

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Materials and Methods

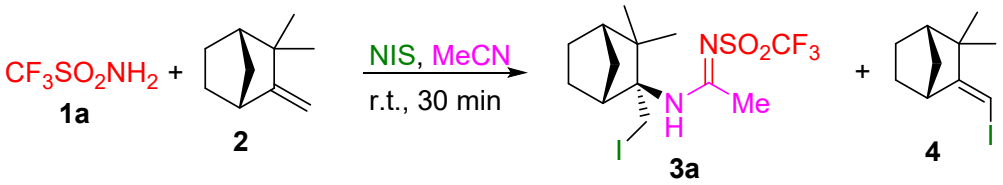
Experimental. All reactions were carried out under argon atmosphere in dry solvents unless otherwise noted. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using thermostat-controlled heating blocks. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical TLC analysis was carried out on aluminum plates coated with silica gel 60 F_{254}, 0.2 mm thickness, visualized by 254 nm UV lamp or aqueous $NaIO_4$ 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 were used without further purification. Camphene was used as a racemic mixture of enantiomers.

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 ^{1}H 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 MoKa radiation (λ = 0.71073) using the φ and ω scans.

Preparation of camphene amidation products 3-17

Procedures for the Synthesis of all products

1. Addition of triflamide 1a to camphene 2 in the presence of NIS in MeCN.



To 1 g (6.7 mmol) of triflamide **1a** dissolved in 50 ml of acetonitrile was added 0.92 g (6.7 mmol) of camphene **2**, then 1.66 g (1.1 equiv., 7.0 mmol) of NIS. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The residue was purified on a silica gel column (80 g, eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.19 g (11%) of product **4** and 2.18 g (72%) of product **3a.**

N-(1-(Iodomomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((trifluoromethyl)sulfonyl)acetamidine ***(3a)*****.**

White solid. M.p. 160°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (s, 1H), 4.85 – 4.66 (d, *J* = 9.7 Hz, 1H), 3.41 (d, *J* = 9.7 Hz, 1H), 2.54 (s, 3H), 2.37 – 2.29 (m, 1H), 2.10 – 2.05 (m, 1H), 1.94 – 1.88 (m, 1H), 1.68 – 1.54 (m, 1H), 1.50-1.42 (m, 1H), 1.49 – 1.42 (m, 1H), 1.32 – 1.24 (m, 2H), 1.22 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 119.4 (q, CF_3, *J* = 319.8 Hz), 69.7, 51.8, 51.1, 46.7, 33.6, 27.2, 23.0, 22.8, 21.9, 21.3, 11.2.

^{19}F NMR (376 MHz, CD_3CN): δ -79.04. IR: 3308, 2964, 1630, 1547, 1316, 1208, 1202, 1126, 1054, 775, 652, 601 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{13}H_{21}IF_3N_2O_2S^+$: 453,03205 $(M+H)^+$; found: 453,03218.

Anal. calcd (%) for $C_{13}H_{20}F_3IN_2O_2S$: C, 34.52; H, 4.46; N, 6.19; I, 28.06; found: C, 34.50; H, 4.48; N, 6.16; I, 28.21.

3-(Iodomethylene)-2,2-dimethylbicyclo[2.2.1]heptane[1] ***(4)***. Colorless liquid.

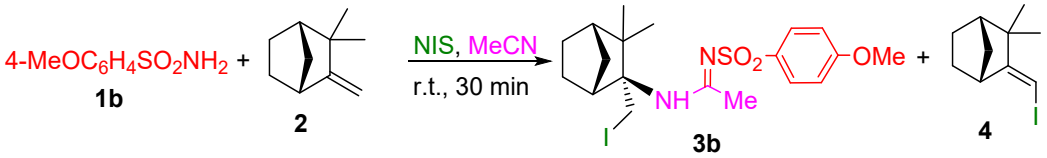
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (s, 1H), 3.02 (m, 1H), 2.20 (m, 1H), 1.81 - 1.77 (m, 1H), 1.75 - 1.61 (m, 2H), 1.53 - 1.40 (m, 1H), 1.33 - 1.24 (m, 2H), 1.08 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 64.6, 49.7, 49.3, 45.4, 36.6, 28.9, 27.0, 25.8, 23.5.

IR: 3051, 2969, 2868, 1627, 1462, 1304, 1234, 1130, 1105, 948, 765, 645 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{10}H_{16}I^+$: 263,02967 $(M+H)^+$; found: 263.02957.

2. Addition of 4-methoxyphenylsulfonamide 1b to camphene 2 in the presence of NIS in MeCN.



*N'-((4-Methoxyphenyl)sulfonyl)-N-(2-(iodomethyl)-3,3-dimethylbicyclo[2.2.1]-heptan-2-yl)acetamidine **(3b).*** The reaction was carried out as mentioned above: 1 g (5.3 mmol) of 4-methoxyphenylsulfonamide **1b**, 0.74 g (5.3 mmol) of **2**, 1.30 g (5.8 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.13 g (9%) of product **4** and product **3b** as white solid (2.24 g, 84%).

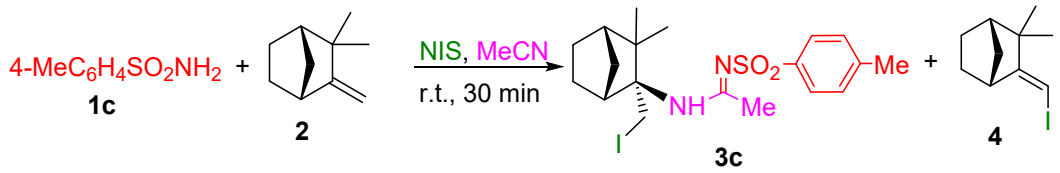
White solid. M.p. 199°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.26 (s, 1H), 4.77 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 3H), 3.29 (d, *J* = 10.0 Hz, 1H), 2.42 (s, 3H), 2.25 – 2.17 (m, 1H), 2.00 – 1.95 (m, 1H), 1.93 – 1.86 (m, 1H), 1.59 – 1.47 (m, 2H), 1.45 – 1.33 (m, 2H), 1.28 – 1.20 (m, 1H), 1.18 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 162.1, 135.4, 128.4, 113.8, 68.1, 55.5, 51.8, 50.9, 46.4, 33.6, 27.5, 22.8, 21.9, 21.66, 21.62, 13.5.

Anal. calcd (%) for $C_{19}H_{27}IN_2O_3S$: C, 46.54; H, 5.55; I, 25.88; N, 5.71; S, 6.54; found: C, 46.68; H, 5.62; I, 25.39; N, 5.75; S, 6.50.

3. Addition of tosylamide 1c to camphene 2 in the presence of NIS in MeCN.



N-(2-(Iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-tosylacetamidine ***(3c).*** The reaction was carried out as mentioned above: 1 g (5.8 mmol) of tosylamide **1c**, 0.79 g (5.8 mmol) of **2**, 1.45 g (6.4 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4, ether) to afford 0.17 g (11%) of product **4** and of product **3c** as white solid **(**1.98 g, 72%).

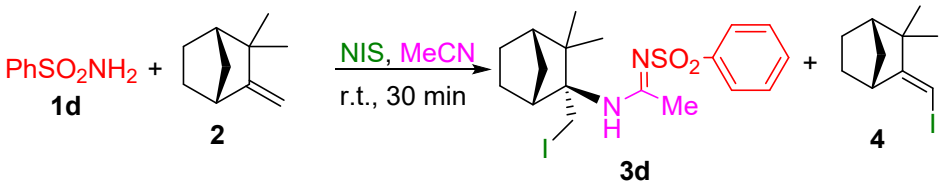
White solid. M.p. 197°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 5.08 (s, 1H), 4.75 (d, *J* = 10.3 Hz, 1H), 3.30 (d, *J* = 10.3 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 2.24 – 2.12 (m, 2H), 2.03 – 1.99 (m, 1H), 1.94 – 1.84 (m, 1H), 1.57 – 1.48 (m, 2H), 1.45 – 1.35 (m, 2H), 1.19 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 142.2, 140.4, 129.2, 126.4, 68.1, 51.8, 50.8, 46.5, 33.6, 27.5, 22.8, 21.9, 21.8, 21.6, 21.5, 13.4.

Anal. calcd (%) for $C_{19}H_{27}IN_2O_2S$: C, 48.10; H, 5.74; N, 5.91; S, 6.76; I, 26.75; found: C, 48.02; H, 5.62; N, 5.99; S, 6.88; I, 26.39.

4. Addition of phenylsulfonamide 1d to camphene in the presence of NIS in MeCN.



N-(2-(Iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-phenylsulfonylacetamidine ***(3d).*** The reaction was carried out as mentioned above: 1 g (6.4 mmol) of phenylsulfonamide **1d**, 0.87 g (6.4 mmol) of **2**, 1.58 g (7.0 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane -

ether 1:4) to afford 0.13 g (8%) of product **4** and product 3**d** as white solid (2.58 g, 88%).

White solid. M.p. 172°C.

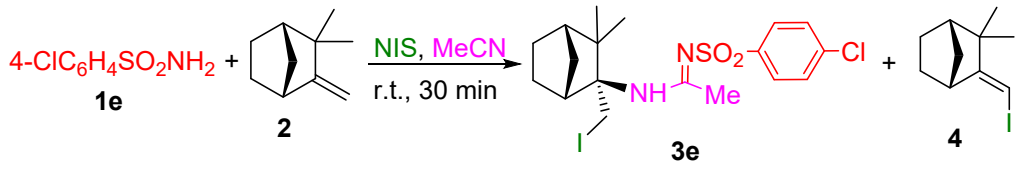
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.50 (tr, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 5.21 (s, 1H), 4.74 (d, *J* = 10.4 Hz, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 2.46 (s, 3H), 2.27 – 2.16 (m, 1H), 2.04 – 1.97 (s, 1H), 1.92 – 1.85 (m, 1H), 1.64 – 1.59 (m, 1H), 1.58 – 1.49 (m, 2H), 1.43 – 1.30 (m, 2H), 1.19 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 143.2, 131.7, 128.69, 125.92, 68.2, 51.8, 51.0, 46.5, 33.6, 27.5, 22.8, 21.9, 21.8, 21.5, 13.2.

IR: 3312, 2958, 1544, 1445, 1274, 1141, 1086, 771, 689, 587 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{18}H_{26}IN_2O_2S^+$: 461,0760 $(M+H)^+$; found: 461.07603.

5. Addition of 4-chlorophenylsulfonamide 1e to camphene 2 in the presence of NIS in MeCN.



N'-((4-Chlorophenyl)sulfonyl)-N-(2-(iodomethyl)bicyclo[2.2.1]heptan-2-yl)acetamidine ***(3e)*****.** The reaction was carried out as mentioned above: 1 g (5.2 mmol) of 4-chlorophenylsulfonamide **1e**, 0.71 g (5.2 mmol) of **2**, 1.30 g (5.7 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.16 g (12 %) of product **4** and product **3e** as white solid (1.80 g, 70%).

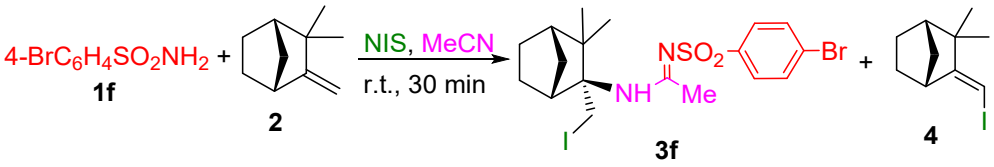
White solid. M.p. 211°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 5.11 (br. s, 1H), 4.66 (d, *J* = 10.6 Hz, 1H), 3.30 (d, *J* = 10.6 Hz, 1H), 2.46 (s, 3H), 2.25 – 2.16 (m, 1H), 2.05 –1.97 (m, 1H), 1.93 – 1.86 (m, 1H), 1.57 – 1.47 (m, 2H), 1.46 – 1.32 (m, 2H), 1.25 – 1.21 (m, 1H), 1.19 (s, H-9, 3H), 0.94 (s, H-10, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 141.7, 138.0, 128.9, 127.9, 68.3, 51.7, 51.0, 46.5, 33.6, 27.5, 22.8, 22.1, 21.8, 21.6, 13.2.

Anal. calcd (%) for $C_{18}H_{24}ClIN_2O_2S$: C, 43.69; H, 4.89; N, 5.66; S, 6.48; found: C, 43.80; H, 4.95; N, 5.72; S, 6.43.

6. Addition of 4-bromophenylsulfonamide 1f to camphene 2 in the presence of NIS in MeCN.



N'-((4-Bromophenyl)sulfonyl)-N-(2-(iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)acetamidine ***(3f).*** The reaction was carried out as mentioned above: 1 g (4.2 mmol) of 4-bromophenylsulfonamide **1f**, 0.58 g (4.2 mmol) of **2**, 1.05 g (4.6 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.16 g (14 %) of product **4** and 1.69 g (74%) of product **3f** as white solid.

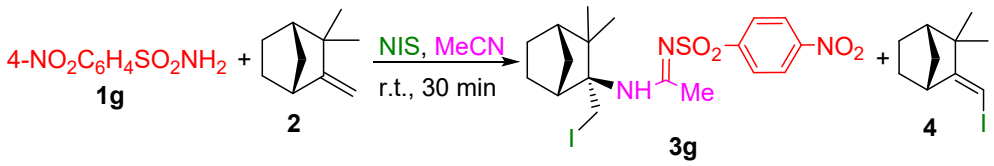
White solid. M.p. 218°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 5.13 (s, 1H), 4.66 (d, *J* = 10.4 Hz, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 2.46 (s, 3H), 2.25 – 2.17 (m, 1H), 2.03 – 1.99 (m, 1H), 1.68 –1.07 (m, 4H), 1.26 – 1.19 (m, 1H), 1.18 (s, 3H), 1.05 – 0.84 (m, 1H), 0.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 142.3, 131.9, 128.1, 126.5, 68.3, 51.7, 51.0, 46.5, 33.6, 27.5, 22.8, 22.1, 21.8, 21.6, 13.0.

Anal. calcd (%) for $C_{18}H_{24}BrIN_2O_2S$: C, 40.09; H, 4.49; N, 5.19; S, 5.95; found: C, 39.99; H, 4.42; N, 5.26; S, 6.01.

7. Addition of 4-nitrobenzenesulfonamide 1g to camphene 2 in the presence of NIS in MeCN.



N-(2-(Iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-nitrophenyl)sulfonyl)acetamidine ***(3g).*** The reaction was carried out as mentioned above: 1 g (5.0 mmol) of 4-nitrobenzenesulfonamide **1g**, 0.67 g (5.0 mmol) of **2**, 1.23 g (5.5 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.18 g (14 %) of product **4** and 1.60 g (64%) *of* product **3g** as white solid.

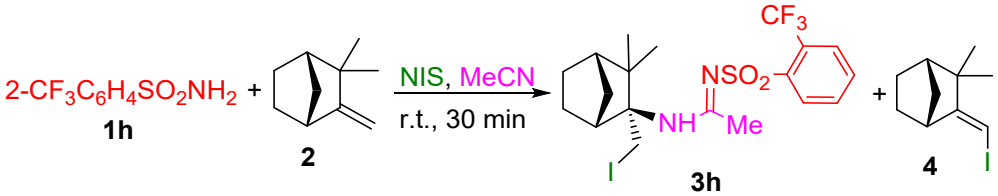
White solid. M.p. 190°C.

^{1}H NMR (δ, ppm, $CDCl_3$) δ= 8.35 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.6 Hz, 2H), 5.21 (br. s, 1H), 4.55 (d, *J* = 10.9 Hz, 1H), 3.29 (d, *J* = 10.9 Hz, 1H), 2.51 (s, 3H), 2.27 – 2.17 (m, 1H), 2.04 - 2.00 (m, 1H), 1.95 – 1.86 (m, 1H), 1.60 – 1.51 (m, 2H), 1.45 – 1.38 (m, 1H), 1.19 (s, 3H), 1.15 – 0.94 (m, 2H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 149.5, 145.5, 127.7, 124.1, 68.6, 51.7, 50.7, 46.5, 29.7, 27.5, 22.8, 22.4, 21.9, 21.7, 12.5.

Anal. calcd (%) for $C_{18}H_{24}IN_3O_4S$: C, 42.78; H, 4.79; N, 8.31; S, 6.34; I, 25.11; found: C, 42.54; H, 4.85; N, 8.37; S, 6.22; I, 24.90.

8. Addition of 2-(trifluoromethyl)benzenesulfonamide 1h to camphene 2 in the presence of NIS in MeCN.



N-(2-(Iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(2-(trifluoromethyl)phenylsulfonyl)acetimidamide ***(3h).*** The reaction was carried out as above: 1 g (4.4 mmol) of 2-(trifluoromethyl)benzenesulfonamide **1h**, 0.60 g (4.4 mmol) of **2**, 1.00 g (4.4 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane – ether 3:1, hexane – ether 1:4, hexane – ether 1:6) to afford 1.43 g (61%) of product **3h** and 0.1 g (8%) of product **4.**

White solid. M.p. 159°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.7, 1H), 7.65 (m, 2H), 5.44 (s, 1H), 4.57 (d, *J* = 10.5 Hz, 1H), 3.20 (d, *J* = 10.5 Hz, 1H), 2.51 (s, 3H), 2.21 (s, 1H), 1.95 (m, *J* = 2.7 Hz, 1H), 1.88 (d, *J* = 10.6 Hz, 1H), 1.48 (m, 2H), 1.34 (m, 2H), 1.17 (m, 1H), 1.12 (s, 3H), 0.78 (s, 3H).

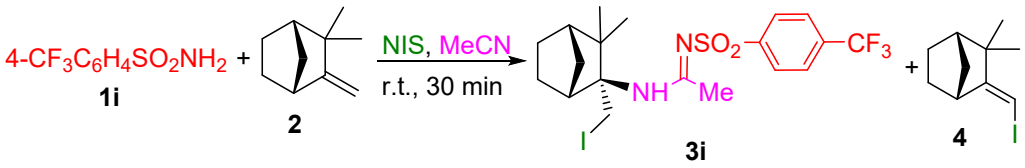
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.81, 141.95, 132.16, 131.84, 130.61, 127.76 (q, *J* = 6.2 Hz), 123.00 (q, *J* = 274.4 Hz), 68.28, 51.85, 50.99, 46.37, 33.62, 27.27, 22.83, 22.17, 21.87, 21.18, 12.85.

^{19}F NMR (376 MHz, $CDCl_3$): -56.69.

IR: 3997, 3373, 3267, 3113, 2962, 2612, 2381, 2310, 1651, 1551, 1440, 1309, 1141, 1038, 921, 776, 727, 655, 595 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{24}F_3IN_2O_2S$: C, 43.19; H, 4.58; F, 10.79; I, 24.02; N, 5.30; S, 6.07; found: C, 42.95; H, 4.63; F, 10.70; I, 23.43; N, 5.21; S, 6.37.

9. Addition of 4-(trifluoromethyl)benzenesulfonamide 1i to camphene 2 in the presence of NIS in MeCN.



N-(2-(Iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(4-(trifluoromethyl)phenylsulfonyl)acetimidamide ***(3i).*** The reaction was carried out as above: 1 g (4.4 mmol) of 4-(trifluoromethyl)benzenesulfonamide **1i**, 0.60 g (4.4 mmol) of **2**, 1.00 g (4.4 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane – ether 3:1, hexane – ether 1:4) to afford 0.14 g (12%) of product **4** and 1.59 g (68%) of product **3i** as white solid.

White solid. M.p. 159°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.78 – 7.72 (m, 2H), 5.32 (s, 1H), 4.63 (d, *J* = 10.6 Hz, 1H), 3.29 (d, *J* = 10.5 Hz, 1H), 2.48 (s, 3H), 2.22 (s, 1H), 2.00 (s, 1H), 1.53 (s, 1H), 1.39 (d, *J* = 9.1 Hz, 1H), 1.27 (s, 1H), 1.18 (s, 2H), 0.92 (s, 3H).

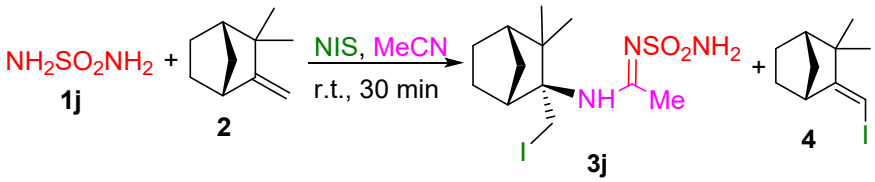
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.38, 146.65, 133.58 (q, *J* = 32.9 Hz), 126.98, 125.94, 125.90, 123.44 (q, *J* = 273.4 Hz), 68.51, 51.76, 50.94, 46.55, 33.66, 27.51, 22.82, 22.16, 21.89, 21.64, 12.82.

^{19}F NMR (376 MHz, $CDCl_3$): -62.69.

IR: 3567, 3322, 3119, 2946, 1547, 1404, 1323, 1144, 894, 843, 724, 658, 606, 542, 427 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{24}F_3IN_2O_2S$: C, 43.19; H, 4.58; F, 10.79; I, 24.02; N, 5.30; S, 6.07; found: C, 43.40; H, 4.59; F, 10.51; I, 23.78; N, 5.15; S, 6.30.

10. Addition of sulfamide 1j to camphene 2 in the presence of NIS in MeCN.



N-(2-(Iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-sulfamoylacetimidamide ***(3j).*** The reaction was carried out as above: 1 g (10.4 mmol) of sulfamide **1j**, 0.60 g (4.4 mmol) of **2**, 1.00 g (4.4 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane – ether 3:1, hexane – ether 1:10) to afford to afford 0.51 g (18%) of product **4** and 2.54 g (63%) of product **3k** as white solid.

White solid. M.p. 124°C.

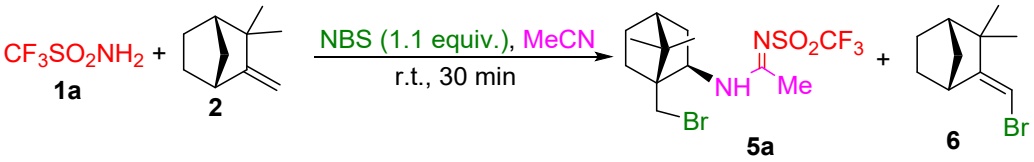
^{1}H NMR (400 MHz, CD_3CN) δ 6.10 (s, 1H), 5.13 (d, *J* = 10.6 Hz, 1H), 5.10 (s, 2H), 3.51 (d, *J* = 10.4 Hz, 1H), 2.30 (s, 3H), 2.26 (m, 1H), 1.97 (m, *J* = 16.2 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.46 – 1.38 (m, 2H), 1.23 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 166.00, 68.56, 52.77, 51.20, 47.27, 34.33, 27.89, 23.39, 22.66, 21.93, 20.11, 15.61.

IR: 3329, 3119, 2946, 1708, 1546, 1409, 1365, 1299, 1213, 1138, 1035, 980, 896, 759, 643 cm^{-1}.

Anal. calcd (%) for $C_{12}H_{22}IN_3O_2S$: C, 36.10; H, 5.55; I, 31.78; N, 10.52; S, 8.03; found: C, 35.94; H, 5.42; I, 32.00; N, 10.64; S, 8.12.

11. Addition of triflamide 1a to camphene 2 in the presence of NBS in MeCN.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((trifluoromethyl)sulfonyl)acetamidine ***(5a)*** and *3-(bromomethylene)-2,2-dimethylbicyclo[2.2.1]heptane* ***(6)*****.** To 2 g of triflamide **1a** (1 equiv., 13.4 mmol) dissolved in 50 ml of acetonitrile was added 1.83 g (1 equiv., 13.4 mmol) of camphene **2**, then 2.63 g (1.1 equiv., 14.8 mmol) of NBS. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The residue was purified on a silica gel column (80 g, eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.4 g (14%) of product **6** and 4.18 g (77%) of product **5a.**

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((trifluoromethyl)sulfonyl)acetamidine ***(5a)*****.**

White solid. M.p. 154°C.

^{1}H NMR (400 MHz, CD_3CN): δ 7.34 (s, 1H), 4.02 (dt, *J* = 8.1, 5.5 Hz, 1H), 3.76 (d, *J* = 10.9 Hz, 1H), 3.54 (d, *J* = 10.9 Hz, 1H), 2.44 (s, 3H), 1.93 – 1.88 (m, 2H), 1.82 – 1.76 (m, 2H), 1.76 – 1.71 (m, 1H), 1.62 – 1.49 (m, 1H), 1.29 – 1.20 (m, 1H), 1.04 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN): δ 169.4, 119.14 (q, CF_3, *J* = 320 Hz), 59.8, 53.3, 49.9, 47.4, 39.2, 35.5, 35.2, 27.0, 21.8, 20.78, 20.74.

^{19}F NMR (376 MHz, CD_3CN): δ - 80.2.

IR: 3433, 3354, 2959, 2935, 1634, 1574, 1542, 1439, 1328, 1220, 1191, 1146, 1060, 778, 651, 594 cm^{-1}.

Anal. calcd (%) for $C_{13}H_{20}BrF_3N_2O_2S$: C, 38.53; H, 4.97; N, 6.91; S, 7.91; found: C, 38.45; H, 4.92; N, 6.90; S, 7.83.

3-(Bromomethylene)-2,2-dimethylbicyclo[2.2.1]heptane[1,2] ***(6).*** Colorless liquid.

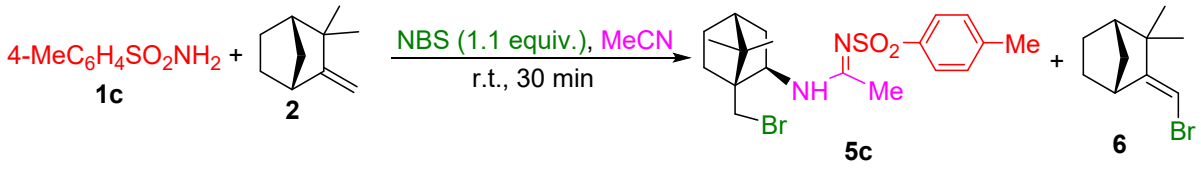
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62 (s, 1H), 3.15 (d, *J* = 3.5 Hz, 1H), 2.08 – 2.02 (m, 1H), 1.79 – 1.65 (m, 3H), 1.49 – 1.40 (m, 1H), 1.33 – 1.28 (m, 1H), 1.27 – 1.24 (m, 1H), 1.08 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 94.1, 49.1, 45.1, 44.3, 36.8, 28.9, 27.0, 25.8, 23.5.

IR: 3067, 2959, 2883, 1641, 1461, 1307, 1241, 950, 887, 770, 696 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{10}H_{16}Br^+$: 215,04354 $(M+H)^+$; found: 215.04340.

12. Addition of tosylamide 1c to camphene 2 in the presence of NBS in MeCN.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-tosylacetamidine ***(5c).*** The reaction was carried out as mentioned above: 1.5 g (8.8 mmol) of tosylamide **1c**, 1.19 g of **2**, 1.72 g (9.7 mmol) of NBS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g, eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 0.28 g (15%) of product **6** and compound **5c** as white solid (2.74 g, 73%).

White solid. M.p. 156°C.

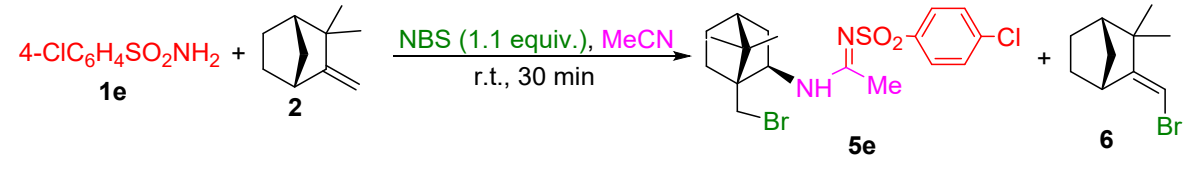
^{1}H NMR (400 MHz, CD_3CN): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.32 (*J* = 8.3 Hz, 2H), 6.52 (s, 1H), 4.03 (dt, *J* = 8.1, 5.0 Hz, 1H), 3.71 (d, *J* = 10.7 Hz, 1H), 3.49 (d, *J* = 10.7 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 1.90 – 1.82 (m, 2H), 1.80 – 1.74 (m, 2H), 1.56 – 1.48 (m, 1H), 1.29 – 1.24 (m, 1H), 1.24 – 1.19 (m, 1H), 1.01 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN): δ 166.6, 143.2, 142.4, 130.1, 127.0, 58.4, 53.3, 49.8, 47.4, 39.5, 35.5, 35.4, 27.0, 21.4, 20.9, 20.84, 20.81.

IR: 3352, 2955, 1538, 1281, 1145, 1088, 809, 764, 665, 604 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{27}BrN_2O_2S$: C, 53.39; H, 6.37; N, 6.55; S, 7.50 Br, 18.70; found: C, 53.44; H, 6.40; N, 6.48; S, 7.52 Br, 18.89.

13. Addition of 4-chlorophenylsulfonamide 1e to camphene 2 in the presence of NBS in MeCN.



N-(1-(Chloromethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-chlorophenyl)-sulfonyl)acetamidine ***(5e).*** The reaction was carried out as mentioned above: 1.5 g (7.8 mmol) of 4-chlorophenylsulfonamide **1e**, 1.06 g (7.8 mmol) of **2**, 1.53 g (8.2 mmol) of NBS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether

3:1, hexane - ether 1:4) to afford 0.32 g (19%) of product **6** and product **5e** as white solid (2.45 g, 70%).

White solid. M.p. 162°C.

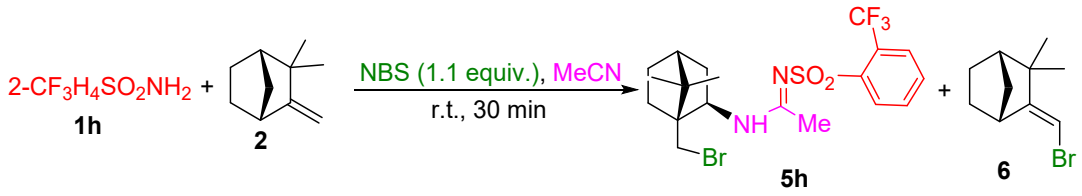
^{1}H NMR (400 MHz, CD_3CN): δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 4.03 (dt, *J* = 8.2, 5.0 Hz, 1H), 3.70 (d, *J* = 10.7 Hz, 1H), 3.50 (d, *J* = 10.3 Hz, 1H), 3.49 (d, *J* = 10.7 Hz, 1H), 3.39 (d, *J* = 10.7 Hz, 1H), 2.32 (s, 3H), 2.10 (s, 3H), 1.89 – 1.82 (m, 3H), 1.81 – 1.67 (m, 5H), 1.06 (s, 3H), 1.01 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN): δ 166.8, 143.9, 138.0, 130.1, 129.8, 128.8, 128.6, 58.5, 53.3, 49.8, 47.4, 39.4, 35.49, 35.47, 27.04, 20.9, 20.8, 20.7, 20.6, 20.4.

IR: 3374, 2954, 1534, 1293, 1274, 1146, 1086, 1011, 778, 635, 602 cm^{-1}.

Anal. calcd (%) for $C_{18}H_{24}BrClN_2O_2S$: C, 48.28; H, 5.40; N, 6.26; S, 7.16; found: C, 48,77; H, 5.35; N, 6.12; S, 7.40.

14. Addition of 2-(trifluoromethyl)benzenesulfonamide 1h to camphene 2 in the presence of NBS in MeCN.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(2-(trifluoromethyl-phenyl)sulfonyl)acetimidamide ***(5h).*** The reaction was carried out as above: (1 g (4.4 mmol) of 2-(trifluoromethyl)benzenesulfonamide **1h,** 0.60 g (4.4 mmol) of **2**, 0.79 g (4.4 mmol) of NBS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane – ether 3:1, hexane – ether 1:4) to afford 0.13 g (14%) of product **6** and of product **5h** as white solid (1.60 g, 75%).

White solid. M.p. 149°C.

^{1}H NMR (400 MHz, CD_3CN) δ 8.26 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.76 (m, 2H), 6.65 (s, 1H), 4.05 – 3.90 (m, 1H), 3.70 (d, *J* = 10.8 Hz, 1H), 3.48 (d, *J* = 10.7 Hz, 1H), 2.34 (s, 3H), 1.84 (m, 1H), 1.81-1.65 (m, 3H), 1.44 (m, 1H), 1.01 (s, 3H), 0.92 (s, 3H).

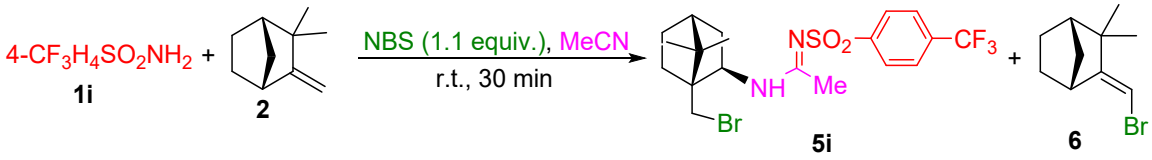
^{13}C NMR (100 MHz, CD_3CN) δ 166.51, 143.26, 133.55, 132.99, 130.99, 129.06 (q, *J* = 6.3 Hz), 127.58 (q, *J* = 32.9 Hz), 124.31 (q, *J* = 273.7 Hz), 58.64, 53.24, 49.83, 47.43, 39.46, 35.43, 35.37, 27.05, 21.19, 20.89, 20.78.

^{19}F NMR (376 MHz, CD_3CN): -57.18.

IR: 3341, 3109, 2961, 1601, 1543, 1440, 1310, 1149, 1034, 964, 870, 762, 653 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{24}BrF_3N_2O_2S$: C, 47.41; H, 5.03; Br, 16.60; F, 11.84; N, 5.82; S, 6.66; found: C, 47.55; H, 5.01; Br, 16.59; F, 11.38; N, 5.72; S, 6.60.

15. Addition of 4-(trifluoromethyl)benzenesulfonamide 1i to camphene 2 in the presence of NBS in MeCN.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(4-(trifluoromethylphenyl)sulfonyl)acetimidamide ***(5i).*** The reaction was carried out as above: 1 g (4.4 mmol) of 4-(trifluoromethyl)benzenesulfonamide **1i,** 0.60 g (4.4 mmol) of **2**, 0.79 g (4.4 mmol) of NBS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane – ether 3:1, hexane – ether 1:4) to afford 0.16 g (17%) of product **6** and of product **5i** as white solid (1.65 g, 77%).

White solid. M.p. 151°C.

^{1}H NMR (400 MHz, CD_3CN) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 6.68 (s, 1H), 4.04 (q, *J* = 5.0 Hz, 1H), 3.70 (d, *J* = 10.7 Hz, 1H), 3.49 (d, *J* = 10.7 Hz, 1H), 2.35 (s, 3H), 1.87 (m, 2H), 1.76 (m, 3H), 1.51 (m, 1H), 1.21 (m, 1H), 1.01 (s, 3H), 0.93 (s, 3H).

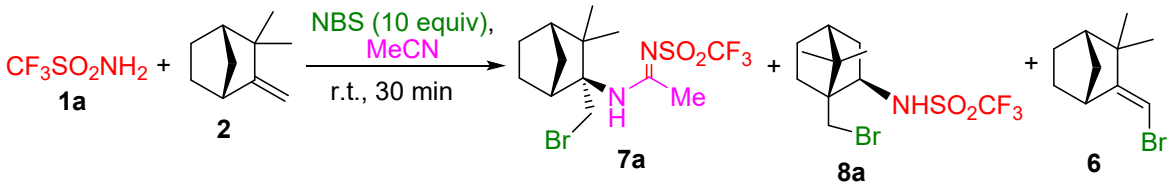
^{13}C NMR (100 MHz, CD_3CN) δ 167.01, 127.84, 127.72, 126.86 (q, *J* = 3.9 Hz), 124.81 (q, *J* = 272 Hz), 58.67, 53.36, 49.87, 47.47, 39.41, 35.47, 27.03, 21.10, 20.86, 20.78.

^{19}F NMR (376 MHz, CD_3CN): -63.19.

IR: 3345, 3104, 2961, 1716, 1596, 1543, 1404, 1324, 1136, 1063, 963, 843, 760, 654, 427 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{24}BrF_3N_2O_2S$: C, 47.41; H, 5.03; Br, 16.60; F, 11.84; N, 5.82; S, 6.66; found: C, 47.12; H, 4.97; Br, 16.50; F, 11.71; N, 5.84; S, 6.67.

16. Addition of triflamide 1a to camphene 2 in the presence of NBS in MeCN.



N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(trifluoromethylsulfonyl)acetimidamide ***(7a)*** *and N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-trifluoromethanesulfonamide* ***(8a).*** To 0.45 g of triflamide **1a** (3.0 mmol) dissolved in 180 ml of acetonitrile was added 4.08 g (30.0 mmol) of camphene **2**, then 5.34 g (30.0 mmol) of NBS. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The residue was purified on a silica gel column (80 g, eluents: hexane - ether 3:1, hexane - ether 1:2, hexane - ether 1:4) to afford bromosubstituted camphene, 0.23 g (21%) of product **8a** and 0.87 g (71%) of product **7a.** The amidines formed, except triflamide, were washed twice with ether (2*5 mL) to give analytically pure samples. The monoadducts, except triflamide, were also washed twice with ether (2*5 mL) to obtain analytically pure samples.

N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(trifluoromethylsulfonyl)acetimidamide ***(7a)***. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (s, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 3.56 (d, *J* = 10.4 Hz, 1H), 2.53 (s, 3H), 2.36 (m, 1H), 1.95 (m, 2H), 1.61 (m, 3H), 1.52 – 1.47 (m, 1H), 1.35 – 1.25 (m, 1H), 1.19 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.02, 119.46 (q, *J* = 319.4 Hz), 70.27, 51.25, 49.42, 47.47, 34.19, 33.94, 26.79, 23.17, 22.93, 22.02, 20.91.

^{19}F NMR (376 MHz, $CDCl_3$): -79.11.

IR: 3347, 3118, 2960, 1778, 1713, 1557, 1445, 1322, 1190, 1136, 1057, 939, 879, 777, 648, 598, 482 cm^{-1}.

Anal. calcd (%) for $C_{13}H_{20}BrF_3N_2O_2S$: C, 38.53; H, 4.97; Br, 19.72; F, 14.06; N, 6.91; S, 7.91; found: C, 38.14; H, 5.06; Br, 19.62; F, 13.98; N, 6.99; S, 8.00.

*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-trifluoromethanesulfonamide (**8a**).* White solid. M.p 120°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02 (d, *J* = 9.4 Hz, 1H), 3.78 (dt, *J* = 8.9, 4.8 Hz, 1H), 3.51 (d, *J* = 10.7, 1H), 3.42 (d, *J* = 10.7, 1H), 2.04 – 1.90 (m, 3H), 1.88 – 1.76 (m, 2H), 1.61 – 1.54 (m, 1H), 1.28 – 1.18 (m, 1H), 1.01 (s, 3H), 0.96 (s, 3H), 1.14 – 0.77 (m, 1H).

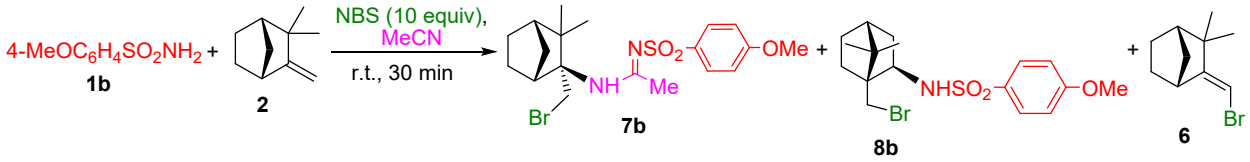
^{13}C NMR (100 MHz, $CDCl_3$): δ 60.7, 52.8, 48.8, 46.51, 39.58, 34.34, 32.32, 26.23, 20.74, 20.61.

^{19}F NMR (376 MHz, CD_3CN): δ - 77.0.

IR: 3321, 2963, 1440, 1383, 1231, 1192, 1149, 1069, 953, 686, 609 cm^{-1}.

Anal. calcd (%) for $C_{11}H_{17}BrF_3NO_2S$: C, 36.27; H, 4.70; N, 3.85; S, 8.80; found: C, 36.50; H, 4.65; N, 3.92; S, 8.89.

17. Addition of 4-methoxyphenylsulfonamide 1b to camphene 2 in the presence of NBS in MeCN.



*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-methoxyphenyl)-sulfonyl)acetimidamide **(7b)** and N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-methoxyphenylsulfonamide (8**b**)*. The reaction was carried out as above: 0.56 g (3.0 mmol) of 4-methoxyphenylsulfonamide **1b**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8b** as white solid (0,29 g, 24%) and **7b** as white solid (0.80 g, 60%).

*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-methoxyphenyl)-sulfonyl)acetimidamide **(7b).***

White solid. M.p. 180°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.77 (d, J = 8.8 Hz, 2H), 7.12 – 6.85 (d, *J* = 8.9 Hz, 2H), 5.24 (br. s, 1H), 4.88 (d, *J* = 10.6 Hz, 1H), 3.86 (s, 3H), 3.44 (d, *J* = 10.5

Hz, 1H), 2.41 (s, 3H), 2.29 – 2.20 (m, 1H), 1.87 (m, 2H), 1.53 (m, 3H), 1.44 – 1.33 (m, 1H), 1.19 (m, 1H), 1.15 (s, 3H), 0.91 (s, 3H).

^{13}C (100 MHz, CDCl3) δ 164.91, 162.16, 135.48, 128.39, 113.80, 68.71, 55.58, 51.29, 49.36, 47.27, 35.51, 33.94, 27.06, 23.29, 22.03, 21.67, 21.12.

IR: 3320, 2919, 1602, 1340, 1201, 1069, 797, 761, 663, 601 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{19}H_{28}BrN_2O_3S^+$: 443,10040 (M+H)+; found: 443.10078.

*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-methoxyphenylsulfonamide (8**b**).*

White solid. M.p. 153°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.78 (m, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 4.81 (br. d, *J* = 9.2 Hz, 1H), 3.88 (s, 3H), 3.49 (d, *J* = 10.5 Hz, 1H), 3.35 (d, *J* = 10.5 Hz, 1H), 3.26 – 3.14 (m, 1H), 1.92 – 1.79 (m, 2H), 1.76 – 1.64 (m, 2H), 1.64 – 1.54 (m, 1H), 1.45 – 1.32 (m, 1H), 1.14 – 1.05 (m, 1H), 1.01 (s, 3H), 0.88 (s, 3H).

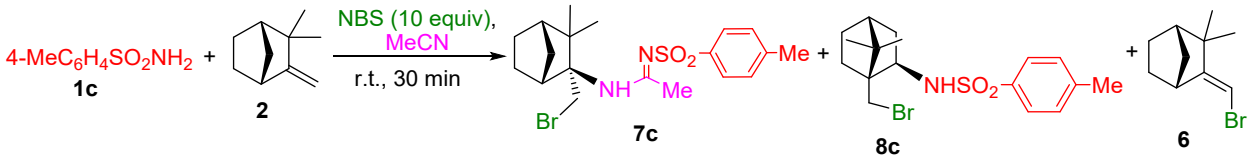
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 131.60, 129.70, 114.21, 59.05, 55.65, 52.78, 48.83, 46.85, 38.83, 34.46, 33.95, 26.38, 20.84, 20.60.

IR: 3258, 2842, 1774, 1702, 1597, 1557, 1500, 1335, 1260, 1156, 1098, 1024, 909, 834, 672, 567 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{17}H_{25}BrNO_3S^+$: 402.07385 (M+H)$^+$; found: 402.07404.

Anal. calcd (%) for $C_{17}H_{24}BrNO_3S$: C, 50.75; H, 6.01; N, 3.48; Br, 19.86; found: C, 50.68; H, 6.14; N, 3.45; Br, 19.94.

18. Addition of tosylamide 1c to camphene 2 in the presence of NBS in MeCN.



*N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-tosylacetimidamide **(7c)*** *and N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-methylbenzene-sulfonamide **(8c).*** The reaction was carried out as above: 0.51 g (3.0 mmol) of tosylamide **1c**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction

mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8c** as white solid (0.22 g, 19%) and **7c** as white solid (0,87 g, 68%).

N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-tosylacetimidamide **(7c).** White crystals. M.p. 140°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.23 (m, 2H), 5.38 (s, 1H), 4.88 (d, *J* = 13.5 Hz, 1H), 3.43 (d, *J* = 10.5 Hz, 1H), 2.43 (s, 1H), 2.40 (s, 6H), 2.30 – 2.19 (m, 1H), 1.85 (d, *J* = 3.4 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.40 (m, 1H), 1.20 (m, 1H), 1.15 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.15, 142.22, 140.46, 129.25, 126.37, 68.74, 51.25, 49.28, 47.27, 35.50, 33.94, 27.04, 23.26, 22.02, 21.67, 21.54, 21.09.

IR: 3980, 3295, 3122, 2955, 2410, 2305, 1546, 1418, 1272, 1140, 1088, 1037, 987, 896, 815, 709, 630, 556 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{27}BrN_2O_2S$: C, 53.39; H, 6.37; Br, 18.70; N, 6.55; S, 7.50; found: C, 53.08; H, 6.32; Br, 18.67; N, 6.64; S, 7.59.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-methylbenzene-sulfonamide ***(8c).***

White solid. M.p. 154°C.

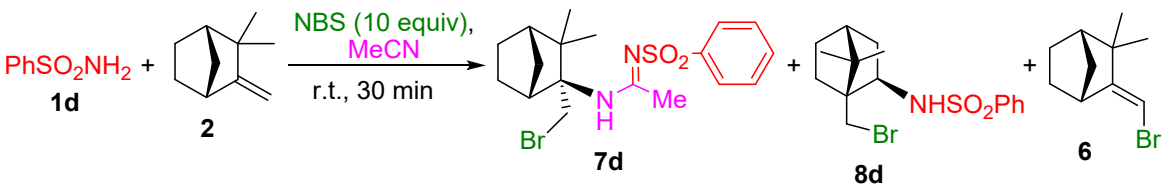
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.72 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.53 (d, *J* = 6.4 Hz, 1H), 3.47 (d, *J* = 10.2 Hz, 1H), 3.38 (d, *J* = 10.1 Hz, 1H), 3.27 – 3.15 (m, 1H), 2.44 (m, 3H), 2.09 – 1.91 (m, 1H), 1.85 (d, *J* = 4.4 Hz, 1H), 1.69 (m, 1H), 1.65 – 1.59 (m, 1H), 1.56 (m, 1H), 1.39 (m, 1H), 1.13 (m, 1H), 1.03 (s, 3H), 0.89 (s, 3H).

^{13}C (100 MHz, $CDCl_3$) δ 143.59, 136.91, 129.72, 127.64, 59.18, 52.83, 48.90, 46.89, 38.69, 34.42, 33.84, 26.41, 21.65, 20.86, 20.64.

IR: 3285, 2904, 2850, 1435, 1260, 1174, 1104, 805, 769, 668, 600 cm^{-1}.

Anal. calcd (%) for $C_{17}H_{24}BrNO_2S$: C, 52.85; H, 6.26; Br, 20.68; N, 3.63; S, 8.30; found: C, 53.14; H, 6.31; Br, 20.24, N, 3.59; S, 8.12.

19. Addition of phenylsulfonamide 1d to camphene 2 in the presence of NBS in MeCN.



N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(phenylsulfonyl)acetimidamide ***7(d)*** *and N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)phenylsulfonamide (**8d**)*[3]. The reaction was carried out as above: 0.47 g (3.0 mmol) of phenylsulfonamide **1d**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product and **8d** as white solid (0.30 g, 27%) and **7d** as white solid (0.73 g, 59%).

*N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(phenylsulfonyl)acetimidamide (**7d**).*

White solid. M.p. 173°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9, 2H), 7.68 – 7.42 (m, 3H), 4.85 (d, *J* = 10.7 Hz, 1H), 3.43 (d, *J* = 10.9 Hz, 1H), 2.43 (s, 3H), 2.25 (m, 1H), 1.87 (m, *J* = 11.3, 7.5 Hz, 2H), 1.58 – 1.46 (m, 2H), 1.46 – 1.35 (m, 2H), 1.19 (m, 1H), 1.14 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.15, 143.30, 131.75, 128.68, 126.35, 68.81, 51.27, 49.34, 47.27, 35.38, 33.93, 27.03, 23.27, 22.01, 21.81, 21.04.

IR: 3368, 2950, 1662, 1359, 1210, 1043, 829, 770, 709, 654, 591 cm^{-1}.

Anal. calcd (%) for $C_{18}H_{25}BrN_2O_2S$: C, 52.30; H, 6.10; Br, 19.33; N, 6.78; S, 7.76; found C, 52.48; H, 6.12; Br, 18.99; N, 6.71; S, 7.80.

*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)phenylsulfonamide (**8d**)*[3].

White solid. M.p. 147 °C.

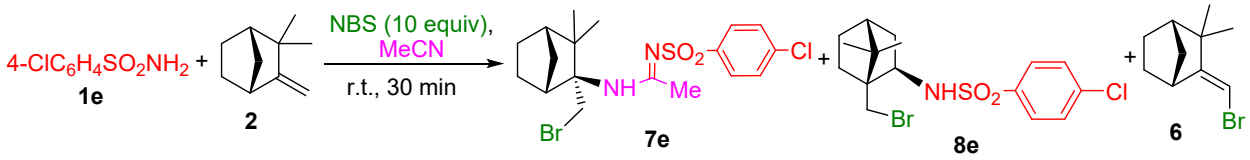
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.59 (tr, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 4.67 (d, *J* = 6.4 Hz, NH, 1H), 3.47 (d, *J* = 10.5 Hz, 1H), 3.34 (d, *J* = 10.5 Hz, 1H), 3.28 – 3.19 (m, 1H), 1.91 - 1.81 (m, 2H), 1.77 – 1.54 (m, 4H), 1.45 – 1.36 (m, 1H), 1.02 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 132.7, 129.0, 127.5, 59.1, 52.8, 48.8, 46.8, 38.9, 34.4, 33.7, 26.3, 20.8, 20.6.

IR: 3289, 2957, 1715, 1460, 1322, 1160, 1095, 1027, 926, 757, 690, 645, 592 cm^{-1}.

Anal. calcd (%) for $C_{16}H_{22}BrNO_2S$: C, 51.62; H, 5.96; N, 3.76; S, 8.61; Br, 21.46; found: C, 51.99; H, 6.00; N; 3.61; S, 8.45; Br, 21.02.

20. Addition of 4-chlorophenylsulfonamide 1e to camphene 2 in the presence of NBS in MeCN.



N-(2-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-chlorophenyl)sulfonyl)acetimidamide ***(7e)*** and *N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-chlorobenzenesulfonamide* ***(8e).*** The reaction was carried out as above: 0.57 g (3.0 mmol) of 4-chlorophenylsulfonamide **1e**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8e** as white solid (0.24 g, 20%) and **7e** as white solid (0.91 g, 62%).

N-(2-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-chlorophenyl)sulfonyl)acetimidamide ***(7e).*** White solid. M.p. 185°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 5.26 (s, 1H), 4.78 (d, *J* = 10.7 Hz, 1H), 3.46 (dd, *J* = 17.6, 8.9 Hz, 1H), 2.44 (s, 3H), 2.26 (m, 1H), 1.88 (m, 2H), 1.51 (m, 2H), 1.46 – 1.35 (m, 2H), 1.22 (m, 1H), 1.15 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.22, 141.89, 138.07, 128.97, 127.91, 96.22, 68.93, 51.25, 49.38, 47.29, 35.21, 33.94, 27.05, 23.26, 22.00, 21.17.

IR: 3347, 2896, 1644, 1351, 1199, 1074, 802, 765, 660, 598 cm^{-1}.

Anal. calcd (%) for $C_{18}H_{24}BrClN_2O_2S$: C, 48.28; H, 5.40; Br, 17.84; Cl, 7.92; N, 6.26; S, 7.16; found: C, 48.59; H, 5.54; Br, 17.60; Cl, 7.63; N, 6.25; S, 7.28.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-chlorobenzene-sulfonamide ***(8e).*** White solid. M.p. 152°C.

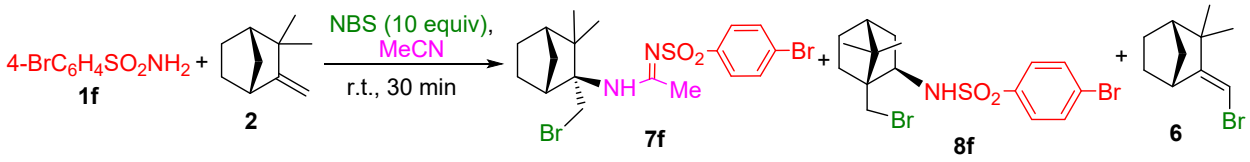
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.75 (m, 2H), 7.71 – 7.47 (m, 2H), 4.61 (d, *J* = 6.6 Hz, 1H), 3.44 (d, *J* = 10.5 Hz, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 3.30 – 3.18 (m, 1H), 2.07 – 1.84 (m, 2H), 1.69 (m, 2H), 1.50 – 1.34 (m, 1H), 1.22 – 1.04 (m, 2H), 1.03 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.95, 139.35, 138.44, 129.41, 129.11, 59.18, 52.88, 48.94, 46.89, 38.99, 34.50, 33.73, 26.38, 20.78, 20.64.

IR: 3293, 2901, 2752, 1511, 1310, 1170, 1103, 769, 702, 669, 635, 597 cm^{-1}.

Anal. calcd (%) for $C_{16}H_{21}BrClNO_2S$: C, 47.25; H, 5.20; Br, 19.64; Cl, 8.72; N, 3.44; S, 7.88; found: C, 47.11; H, 5.39; Br, 19.86; Cl, 9.00; N, 3.47; S, 7.59.

21. Addition of 4-bromophenylsulfonamide 1f to camphene 2 in the presence of NBS in MeCN.



N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-bromophenyl)sulfonyl)acetamidine ***(7f)*** and *N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-bromobenzenesulfonamide* ***(8f).*** The reaction was carried out as above: 0.71 g (3.0 mmol) of 4-bromophenylsulfonamide **1f**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8f** as white solid (0.30 g, 22%) and **7f** (0.90 g, 61%).

N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-bromophenyl)sulfonyl)acetamidine ***(7f)****.* White solid. M.p. 194°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 5.11 (s, 1H), 4.77 (d, *J* = 10.8 Hz, 1H), 3.45 (d, *J* = 10.9 Hz, 1H), 2.45 (s, 3H), 2.26 (br. m, 1H), 1.91 – 1.84 (m, 2H), 1.53 – 1.34 (m, 3H), 1.28 – 1.21 (m, 2H), 1.16 (s, 3H), 0.90 (s, 3H).

^{3}C NMR (100 MHz, $CDCl_3$): δ 165.2, 142.4, 131.9, 128.0, 126.5, 68.9, 51.2, 49.4, 47.2, 35.2, 33.9, 27.0, 23.2, 22.0, 22.0, 21.1.

IR: 3285, 2955, 1773, 1700, 1575, 1471, 1433, 1390, 1349, 1329, 1168, 1068, 1009, 915, 819, 741, 644, 621 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{18}H_{25}Br_2N_2O_2S$: 491,0003; (M+H); found: 491,0006.

Anal. calcd (%) for $C_{18}H_{24}Br_2N_2O_2S$: C, 43.92; H, 4.91; N, 5.69; Br, 32.46; found: C, 43.83; H, 5.00; N, 5.63; Br, 32.32.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-bromobenzene-sulfonamide ***(8f).*** White solid. M.p. 160°C.

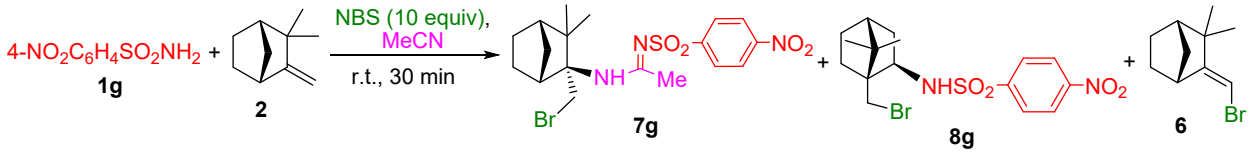
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.71 (d, *J* = 10.4 Hz, 2H), 7.71 – 7.60 (d, *J* = 10.4 Hz, 2H,), 4.74 (d, *J* = 6.7 Hz, 1H), 3.46 (d, *J* = 10.6 Hz, 1H), 1.89 (m, 1H), 1.77 – 1.66 (m, 2H), 1.21 – 1.10 (m, 1H), 1.02 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.95, 139.35, 138.44, 129.41, 129.11, 77.42, 77.10, 76.78, 59.18, 52.88, 48.94, 46.89, 38.99, 34.50, 33.73, 26.38, 20.78, 20.64.

IR: 3263, 2817, 2756, 1402, 1326, 1191, 1114, 800, 765, 669, 599 cm^{-1}.

Anal. calcd (%) for $C_{16}H_{21}Br_2NO_2S$: C, 42.59; H, 4.69; Br, 35.42; N, 3.10; S, 7.11; found: C, 42.17; H, 4.74; Br, 35.02; N, 3.09; S, 7.18.

22. Addition of 4-nitrobenzenesulfonamide 1g to camphene in the presence of NBS in MeCN.



N-(2-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-nitrophenyl)-sulfonyl)acetimidamide ***(7g)*** and *N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-nitrophenylsulfonamide* ***(8g).*** The reaction was carried out as above: 0.61 g (3.0 mmol) of 4-nitrobenzenesulfonamide **1g**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, eluents: hexane – ether 1:4) to afford of product **8g** as white solid (0.33 g, 26%) and **7g** as white solid (0.81 g, 59%).

N-(2-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-nitrophenyl)-sulfonyl)acetimidamide ***(7g).*** White solid. M.p. 198°C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.76 – 8.29 (m, 2H), 8.29 – 8.11 (m, 2H), 7.45 (br.s, 1H), 4.98 (d, *J* = 10.7 Hz,1H), 3.66 (d, *J* = 10.7 Hz,1H), 2.49 (s, 3H), 2.26 – 1.97 (m, 2H), 1.77 – 1.59 (m, 1H), 1.52 – 1.32 (m, 2H), 1.32 – 1.22 (m, 1H), 1.19 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) 166.97, 150.55, 128.51, 124.98, 69.64, 51.99, 49.39, 48.19, 36.63, 34.63, 27.40, 23.71, 22.64, 21.33, 21.08.

IR: 3332, 2911, 1610, 1265, 1207, 1123, 902, 836, 712, 658, 601 cm^{-1}.

Anal. calcd (%) for $C_{18}H_{24}BrN_3O_4S$: C, 47.17; H, 5.28; Br, 17.43; N, 9.17; S, 6.99; found: C, 46.98; H, 5.24; Br, 17.68; N, 9.01; S, 7.16.

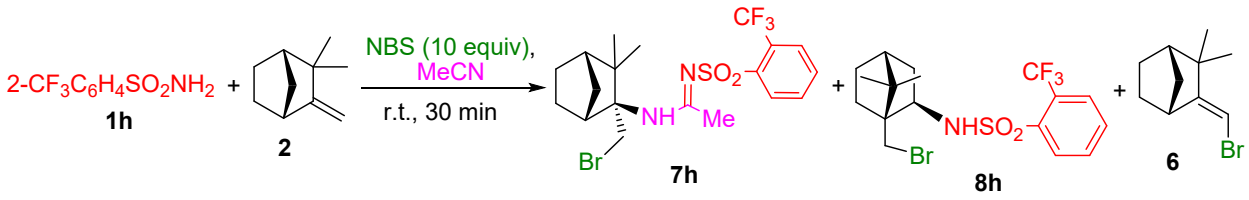
*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-nitrophenylsulfonamide (**8g**).* White solid. M.p. 171 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.7 Hz, 2H), 4.91 (d, *J* = 7.0 Hz, 1H), 3.42 (d, *J* = 10.7 Hz, 1H), 3.33 (d, *J* = 10.7 Hz, 1H), 3.29 (dt, *J* = 7.9, 4.0 Hz, 1H), 1.96 – 1.85 (m, 2H), 1.80 – 1.63 (m, 3H), 1.49 – 1.34 (m, 1H), 1.21 – 1.10 (m, 1H), 1.03 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 145.7, 128.9, 124.3, 59.2, 52.9, 49.0, 46.8, 39.4, 34.5, 33.6, 26.3, 20.69, 20.66.

Anal. calcd (%) for $C_{16}H_{21}BrN_2O_4S$: C, 46.05; H, 5.07; N, 6.71; S, 7.68; Br, 19.15; found: C, 46.14; H, 5.09; N, 6.63; S, 7.73; Br, 19.45.

23. Addition of 2-(trifluoromethyl)benzenesulfonamide 1h to camphene 2 in the presence of NBS in MeCN.



*N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((2-(trifluoromethyl)-phenyl)sulfonyl)acetimidamide **(7h)*** and *N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-2-(trifluoromethyl)benzenesulfonamide **(8h).*** The reaction was carried out as above: 0.67 g (3.0 mmol) of 2-(trifluoromethyl)benzenesulfonamide **1h**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed

in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, : hexane – ether 1:4) to afford of product **8h** as white solid (0.47 g, 24%) and **7h** as white solid (0.81 g, 57%).

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((2-(trifluoromethyl)-phenyl)sulfonyl)acetimidamide ***(7h).*** White solid. M.p. 145°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.69 (m, 2H), 5.38 (br. s, 1H), 4.66 (d, *J* = 10.7 Hz, 1H), 3.35 (d, *J* = 10.7 Hz, 1H), 2.51 (s, 3H), 2.26 (m, 1H), 1.83 (m, 2H), 1.50 (m, 1H), 1.22 – 1.15 (m, 1H), 1.10 (s, 3H), 0.89 (m, 1H), 0.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.82, 141.96, 132.16, 131.85, 130.53, 130.50, 127.81 (q, ^{3}J = 6.2 Hz), 127.43, (q, ^{2}J = 33.2 Hz), 123.02 (q, ^{1}J = 274.2 Hz), 68.87, 51.33, 49.40, 47.16, 35.12, 33.90, 29.77, 26.82, 23.26, 22.20, 21.99, 20.73.

IR: 3393, 2915, 1563, 1277, 1140, 1066, 796, 751, 603 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{19}H_{25}BrF_3N_2O_2S^+$: 481.0772 $(M+H)^+$; found: 481.0772.

Anal. calcd (%) for $C_{19}H_{24}BrF_3N_2O_2S$: C, 47.41; H, 5.03; Br, 16.60; F, 11.84; N, 5.82; S, 6.66; found: C, 47.58; H, 5.18; Br, 16.22; F, 11.53; N, 5.80; S, 6.60.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-2-(trifluoromethyl)benzenesulfonamide ***(8h).*** White solid. M.p. 137°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (m, 1H), 7.87 (m, 1H), 7.71 (m, 2H), 4.97 – 4.73 (d, *J* = 7.2 Hz, 1H), 3.42 (d, *J* = 10.4 Hz, 1H), 3.41 (m, 1H), 3.32 (d, *J* = 10.5 Hz, 1H), 1.85 (m, 1H), 1.68 (m, 3H), 1.62 – 1.55 (m, 1H), 1.42 (m, 1H), 1.14 – 1.05 (m, 1H), 0.97 (s, 3H), 0.88 (s, 3H).

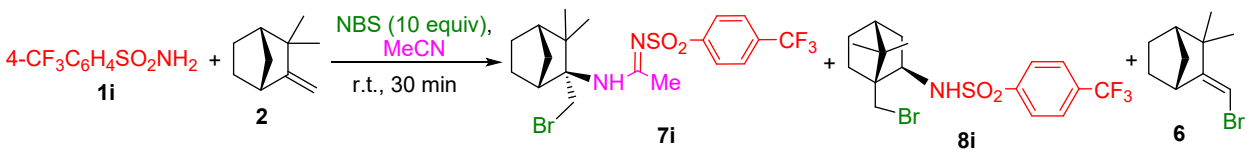
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.20, 132.73, 132.39, 131.90, 128.57 (q, $^{3}J_{C-F}$ = 6.4 Hz), 127.62 (q, $^{2}J_{C-F}$ = 32.7 Hz), 123.22 (q, $^{1}J_{C-F}$ = 273.8 Hz), 59.15, 52.71, 48.76, 46.71, 39.50, 34.43, 33.29, 26.26.

^{19}F NMR (376 MHz, CDCl3) δ -57.68.

IR: 3396, 2900, 1617, 1200, 1136, 1020, 899, 743, 620, 599 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{17}H_{22}BrF_3NO_2S^+$: 440.0507 $(M+H)^+$; found: 440.0508.

24. Addition of 4-(trifluoromethyl)benzenesulfonamide 1i to camphene 2 in the presence of NBS in MeCN.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-(trifluoromethyl)-phenyl)sulfonyl)acetimidamide ***(7i)*** and *N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-(trifluoromethyl)benzenesulfonamide* ***(8i).*** The reaction was carried out as above: 0.68 g (3.0 mmol) of 4-(trifluoromethyl)benzenesulfonamide **1i**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8i** as white solid (0.33 g, 25%) and **7i** as white solid (0.90 g, 63%).

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-((4-(trifluoromethyl)-phenyl)sulfonyl)acetimidamide ***(7i).*** White solid. M.p. 146°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 5.76 (br. s, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 3.42 (d, *J* = 10.8 Hz, 1H), 2.44 (s, 3H), 2.26 (m, 1H), 1.98 – 1.76 (m, 2H), 1.58 – 1.45 (m, 2H), 1.38 (m, 1H), 1.23 – 1.17 (m, 1H), 1.12 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.78, 146.66, 133.51 (q, $^{2}J_{C\text{-}F}$ = 32.9 Hz), 126.83, 125.88 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.48 (q, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 69.06, 51.11, 49.09, 47.31, 35.17, 33.95, 26.99, 23.17, 21.98, 21.84, 21.12.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67.

IR: 3404, 2810, 1499, 1297, 1143, 1102, 797, 711, 651, 588 cm^{-1}.

Anal. calcd (%) for $C_{19}H_{24}BrF_3N_2O_2S$: C, 47.41; H, 5.03; Br, 16.60; F, 11.84; N, 5.82; S, 6.66; found: C, 46.99; H, 5.08; Br, 16.36; F, 11.71; N, 5.92; S, 6.79.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-4-(trifluoromethyl)-benzenesulfonamide ***(8i).*** White solid. M.p. 140°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 7.93 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 5.16 (d, *J* = 7.0 Hz, 1H), 3.46 (d, *J* = 10.6 Hz, 1H), 3.35 (d, *J* = 10.6 Hz, 1H), 3.34 (m, 1H), 1.87 (d, *J* = 3.6 Hz, 2H), 1.80 – 1.62 (m, 3H), 1.41 (m, 1H), 1.11 (m, 1H), 1.01 (s, 3H), 0.88 (s, 3H).

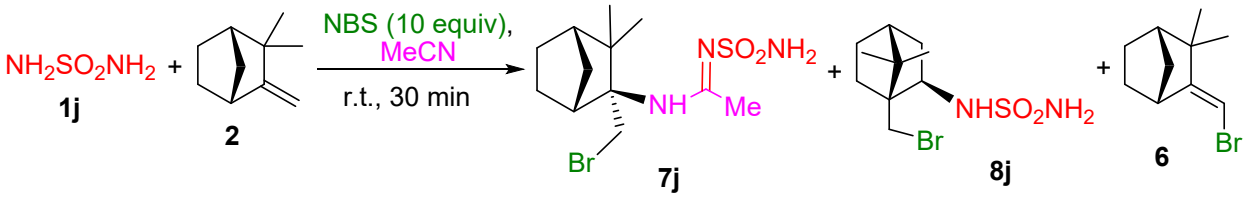
^{13}C NMR (101 MHz, CDCl3) δ 143.74, 134.38 (q, *J* = 32.6 Hz), 128.09, 126.24 (q, *J* = 3.8 Hz), 123.54 (q, *J* = 273.4 Hz) 59.10, 52.90, 48.88, 46.82, 39.29, 34.57, 33.65, 26.31, 20.71, 20.60.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.80.

IR: 3310, 2897, 1540, 1302, 1104, 1009, 800, 762, 667, 600, 568 cm^{-1}.

Anal. calcd (%) for $C_{17}HBrF_3NO_2S$: C, 46.37; H, 4.81; Br, 18.15; F, 12.94; N, 3.18; S, 7.28; found: C, 46.71; H, 4.90; Br, 17.91; F, 12.77; N, 3.10; S, 7.56.

25. Addition of sulfamide 1j to camphene 2 in the presence of NIS in MeCN.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-sulfamoylacetimidamide ***(7j)*** and *N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)sulfamide* ***(8j).*** The reaction was carried out as above: 0.29 g (3.0 mmol) of sulfamide **1j**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8j** (0.19 g, 20%) and **7j** as white solid (0.55 g, 52%).

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-sulfamoylacetimidamide ***(7j).*** White solid. M.p. 113°C.

^{1}H NMR (400 MHz, acetone-d_6) δ 6.79 (br. s, 1H), 5.80 (br. s, 2H), 5.37 (d, J = 10.5 Hz, 1H), 3.69 (d, J = 10.5 Hz, 1H), 2.83 (m, 1H), 2.39 (s, 3H), 2.37 (m, 1H), 1.89 (m, 1H), 1.74 – 1.68 (m, 1H), 1.44 – 1.38 (m, 1H), 1.34 (m, 2H), 1.30 (s, 3H), 1.16 (s, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 166.37, 69.48, 53.03, 50.38, 48.83, 38.26, 35.38, 28.34, 24.65, 23.48, 22.16, 20.64.

IR: 3341, 3006, 1520, 1270, 1136, 1072, 800, 756, 661, 589 cm^{-1}.

Anal. calcd (%) for $C_{12}H_{22}BrN_3O_2S$: C, 40.91; H, 6.29; Br, 22.68; N, 11.93; S, 9.10; found: C, 40.57; H, 6.32; Br, 22.52; N, 12.04; S, 9.30.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)sulfamide ***(8j).*** White solid**.** M.p. 107°C.

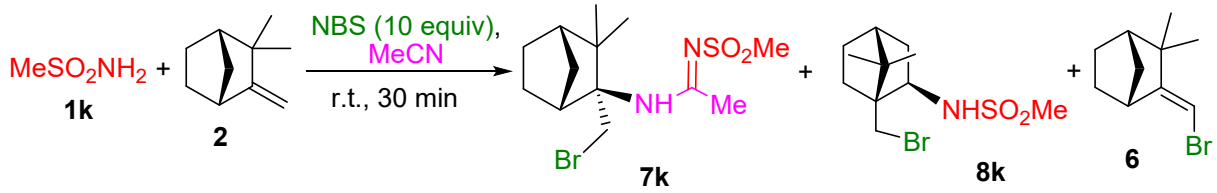
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (s, 2H), 4.66 (d, *J* = 8.8 Hz, 1H), 3.62 (d, *J* = 10.3 Hz, 1H), 3.57 (m, 1H), 3.43 (d, *J* = 10.3 Hz, 1H), 1.99 (m, 3H), 1.77 (s, 2H), 1.57 (m, 1H), 1.21 (m, 1H), 1.00 (m, 3H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 59.39, 52.74, 48.97, 46.85, 39.88, 35.10, 34.62, 26.41, 20.79, 20.60.

IR: 3301, 3073, 2962, 1652, 1538, 1471, 1418, 1371, 1310, 1237, 1164, 1081, 1032, 944, 758, 641, 549 cm^{-1}.

Anal. calcd (%) for $C_{10}H_{19}BrN_2O_2S$: C, 38.59; H, 6.15; Br, 25.67; N, 9.00; S, 10.30; found: C, 38.40; H, 6.07; Br, 25.55; N, 8.89; S, 10.09.

26. Addition of methanesulfonamide 1k to camphene 2 in the presence of NBS in acetonitrile



N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(methylsulfonyl)-acetamidine ***(7k)*** and *N-(1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)methanesulfonamide* ***(8k)***. The reaction was carried out as above: 0.29 g (3.0 mmol) of methanesulfonamide **1k**, 4.08 g (30.0 mmol) of **2**, 5.34 g (30.0 mmol) of NBS, 180 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was further purified after extraction on a silica gel column (80 g, eluents: hexane – ether 1:2, hexane – ether 1:4) to afford of product **8k** (0.28 g, 30%) and **7k** as white solid (0.46 g, 42%).

N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(methylsulfonyl)-acetamidine ***(7k).*** White solid. M.p. 144°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (s, 1H), 4.96 (d, *J* = 10.7 Hz, 1H), 3.56 (d, *J* = 10.7 Hz, 1H), 3.00 (s, 3H), 2.46 (s, 3H), 2.32 – 2.26 (m, 1H), 1.96 – 1.88 (m, 2H), 1.62 – 1.55 (m, 3H), 1.53 – 1.38 (m, 2H), 1.24 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 68.6, 49.5, 51.3, 47.2, 43.0, 35.1, 33.9, 27.1, 23.3, 22.0, 21.9, 21.3.

IR: 3308, 2964, 1571, 1544, 1446, 1273, 1141, 1087, 977, 757, 691, 639, 586 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{13}H_{24}BrN_2O_2S^+$: 351,07419 $(M+H)^+$; found: 351,07428.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)methanesulfonamide ***(8k).*** White solid. M.p. 105°C.

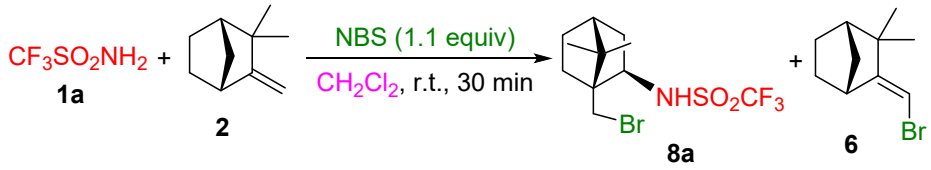
^1H NMR (400 MHz, $CDCl_3$): δ 4.68 (d, *J* 8.7 Hz, 1H), 3.58 (d, *J* = 10.3 Hz, 1H), 3.51 (dt, *J* = 8.6, 4.3 Hz, 1H), 3.41 (d, *J* = 10.3 Hz, 1H), 3.05 (s, 3H), 2.00 (m, 3H), 1.80 – 1.71 (m, 2H), 1.55 (t, *J* = 9.4 Hz, 1H), 1.20 (t, *J* = 8.9 Hz, 1H), 1.01 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 59.13, 52.66, 48.94, 46.88, 41.28, 40.84, 34.68, 34.45, 26.36, 20.79, 20.65.

IR: 3342, 2957, 2719, 1703, 1635, 1595, 1539, 1266, 1143, 1086, 1029, 805, 462, 604, 566 cm^{-1}.

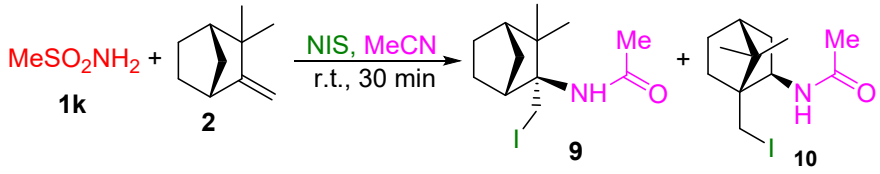
HRMS (ESI): *m/z* calcd for $C_{11}H_{21}BrNO_2S^+$: 310.04764 (M+H); found: 310.04779.

27. Addition of triflamide 1a to camphene 2 in the presence of NBS in CH_2Cl_2.



N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-trifluoromethanesulfonamide ***(8a).*** The reaction was carried out as mentioned above: 1 g (6.7 mmol)) of triflamide **1a**, 0.91 g (6.7 mmol) of camphene **2**, 1.31 g (7.4 mmol) of NBS were dissolved in 40 ml of CH_2Cl_2. The mixture was stirred on a magnetic stirrer for 30 min. The solvent was removed in a vacuum, the resulting residue was washed with 50 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The residue was purified on a silica gel column (80 g, eluents: hexane - ether 3:1, hexane - ether 1:2) to afford 0.37 g (14%) of product **6** and 1.56 g (77%) of product **8a**.

28. Addition of methanesulfonamide 1k to camphene 2 in the presence of NIS in MeCN.



N-(2-(iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)acetamide ***(9)*** *and N-(1-(iodomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)acetamide* ***(10).***

The reaction was carried out as mentioned above: 1 g (10.5 mmol) of methanesulfonamide **1k**, 1.43 g (10.5 mmol) of **2**, 2.61 g (11.6 mmol) of NIS, 40 ml of MeCN. The mixture was stirred for 30 min. Next, acetonitrile was removed in a vacuum, the resulting residue was dissolved in 15 ml of chloroform. The formed succinimide was extracted three times from the chloroform in a separating funnel by adding 100 mL of water and shaking vigorously. The chloroform was removed in a vacuum. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 1.42 g (42%) of product **9** and 0.68 g (20%) of product **10**.

N-(2-(iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)acetamide ***(9).*** White solid. M.p. 159°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27 (s, 1H), 4.82 (d, *J* = 10.5 Hz, 1H), 3.45 (d, *J* = 10.3 Hz, 1H), 2.17 –2.10 (m, 1H), 2.04 – 2.00 (m, 1H), 2.00 (s, 3H), 1.94 – 1.88 (m, 1H), 1.65 – 1.53 (m, 2H), 1.48 – 1.34 (m, 2H), 1.24 -1.18 (m, 1H), 1.16 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 65.9, 51.8, 50.7, 45.8, 33.5, 27.3, 24.0, 22.4, 22.3, 21.7, 15.1.

HRMS (ESI): *m/z* calcd for $C_{12}H_{21}ONI^{+}$: $(M+H)^{+}$ 322,06679; found: 322,06663.

N-(1-(Iodomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)acetamide ***(10).*** White solid. M.p. 165°C.

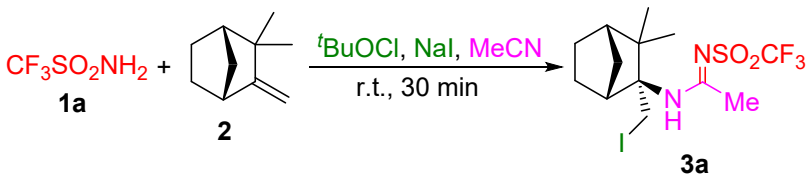
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (s, NH, 1H), 4.07 (dt, *J* = 8.9, 4.8 Hz, 1H), 3.19 (d, *J* = 9.9 Hz, 1H), 3.12 (d, *J* = 9.9 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.99 (s, 3H), 1.98 – 1.90 (m, 1H), 1.79 – 1.70 (m, 1H), 1.69 – 1.59 (m, 2H), 1.35 – 1.12 (m, 2H), 0.99 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 55.4, 51.4, 48.3, 47.0, 39.4, 36.4, 26.3, 23.8, 20.8, 20.6, 6.6.

HRMS (ESI): *m/z* calcd for $C_{12}H_{21}ONI$ 322,06679; found 322,06656.

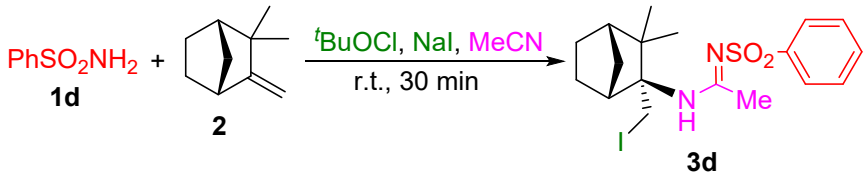
Anal. calcd (%) for $C_{12}H_{20}INO$: C, 44.87; H, 6.28; N, 4.36; I, 39.51; found: C, 44.69; H, 6.26; N, 4.31; I, 39.45.

29. Addition of triflamide 1a to camphene 2 in the presence of *t*-BuOCl+NaI in MeCN.



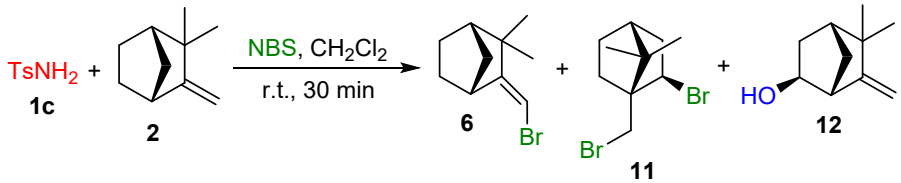
*Reaction with triflamide **1a**.* 1 g (6.7 mmol) of triflamide **1a**, 0.92 g (6.7 mmol) of camphene **2**, and 2.51 g (16.8 mmol) of NaI were dissolved in 40 mL of MeCN. The mixture was cooled to –30 °C and 1.92 ml (16.8 mmol) of *t*-BuOCl was added dropwise and stirred on a magnetic stirrer for 2 hours at –30 °C. Next, MeCN was removed in a vacuum, the residue was dissolved in 50 ml of ether, washed with 10 ml of an aqueous solution of sodium thiosulfate, the extract was dried under $CaCl_2$, and the solvent was removed in a vacuum. The residue was purified on a silica gel column (eluents: hexane – ether 3:1, hexane – ether 1:4) (1.30 g, 43%) of product **3a**.

30. Addition of phenylsulfonamide 1d to camphene 2 in the presence of *t*-BuOCl+NaI in MeCN.



*Reaction with phenylsulfonamide **1d**.* The reaction was carried out as mentioned above (1 g (6.4 mmol) of phenylsulfonamide **1d,** 0.92 g (6.4 mmol) of **2**, 2.4 g (16.0 mmol) of NaI, 1.85 mL (16.0 mmol) *t*-BuOCl, 40 ml of MeCN). The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, hexane - ether 1:4) to afford 1.40 g (45%) of product **3d.**

31. Addition of tosylamide 1c to camphene 2 in the presence of NBS in CH_2Cl_2.



*2-Bromo-1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptane **(11)** and 5,5-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol[3] **(12)**.* The reaction was carried out as mentioned above: 1 g (5.8 mmol) of tosylamide **1c**, 0.79 g (5.8 mmol) of camphene **2**, 1.13 g (6.4 mmol) of NBS, 40 ml of CH_2Cl_2. The reaction mixture was purified on a silica gel column (80 g; eluents: hexane - ether 3:1, 2:1, 1:1) to afford 0.34 g (27%) of product **6,** 0.24 g (14%) of product **11** and 0.18 g (21%) of product **12.**

2-Bromo-1-(bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptane[4] ***(11).*** White solid. M.p. 56°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (dd, *J* = 8.5, 4.6 Hz, 1H), 3.78 (d, *J* = 9.9 Hz, 1H), 3.49 (d, *J* = 9.8 Hz, 1H), 2.53 – 2.37(m, 1H), 2.24 – 2.13 (m, 1H), 2.05 – 1.89 (m, 2H), 1.87 – 1.75 (m, 1H), 1.67 - 1.50 (m, 1H), 1.22 (s, 3H), 1.03 (m, 1H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 56.7, 53.1, 49.4, 48.4, 42.1, 37.2, 34.5, 26.4, 21.0, 20.4.

IR: 2989, 2958, 2884, 1731, 1458, 1305, 1231, 1103, 951, 831, 758, 649, 573 cm^{-1}.

Anal. calcd (%) for $C_{10}H_{16}Br_2$: C, 40.57; H, 5.45; Br, 53.98; found: C, 40.97; H, 5.49; Br, 53.88.

5,5-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol[5] ***(12).*** White solid. M.p. 176°C.

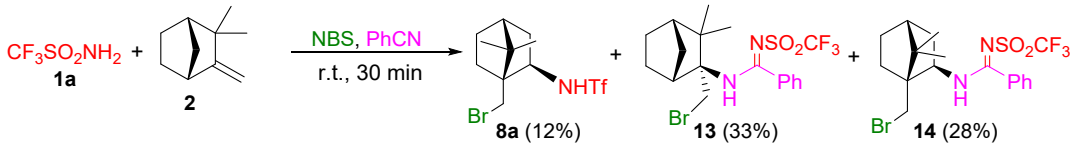
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.89 (s, 1H), 4.67 (s, 1H), 3.84 (d, *J* = 6.1 Hz, 1H), 2.65 (m, 1H), 2.23 (ddd, *J* = 13.5, 6.9, 2.7 Hz, 1H), 1.94 (m, 1H), 1.77 (d, *J* = 10.1 Hz, 1H), 1.68 (*J* = 10.2 Hz, 1H), 1.55 (br. s, 1H), 1.20 (dt, *J* = 14.0, 2.8 Hz, 1H), 1.06 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.18, 103.17, 74.07, 55.97, 47.72, 41.00, 36.92, 33.50, 29.34, 25.47.

IR: 2923, 2363, 1733, 1653, 1559, 1457, 1220, 1158, 1094, 772 cm^{-1}.

Anal. calcd (%) for $C_{10}H_{16}O$: C, 78.90; H, 10.59; found: C: 78.63, H, 10.44.

32. Addition of triflamide 1a to camphene 2 in the presence of NBS in PhCN.



To 0.3 g (2.0 mmol) of triflamide **1a** dissolved in 15 ml of benzonitrile was added 0.27 g (2.0 mmol) of camphene **2**, then 0.43 g (1.2 equiv., 2.4 mmol) of NBS. The mixture was stirred for 30 min. Next, benzonitrile was removed in a vacuum distillation, the resulting residue was washed with 25 ml of diethyl ether, and after cooling, the succinimide was filtered off, and the solvent was distilled in a vacuum. The residue was purified on a silica gel column (80 g, eluents: hexane - ether 1:2, hexane - ether 1:4) to afford 0.09 g (12%) of product **8**, 0.31 g (33%) of product **13** and 0.26 g (28%) of product **14.**

N-(2-(Bromomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-*N*′-(triflyl)benzimidamide (**13**).

White powder. M.p. 177°C

^{1}H NMR (400 MHz, CD_3CN): δ 7.60–7.55 (m, 5H, Ph), 7.16 (br.s, 1H, NH), 4.97 (d, J = 11.2 Hz, 1H, C*H*^{A}HBr), 3.82 (d, J = 11.2 Гц, 1H, CH*H*^{B}Br), 2.43–2.42 (m, 1H), 1.85–1.81 (m, 1H), 1.65–1.62 (m, 2H), 1.50–1.48 (m, 1H), 1.32 (s, 3H, CH_3), 1.12 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CD_3CN): δ 169.02 (C=N), 132.60 (C^u), 129.37 (C^p), 129.33 (C^m), 128.58 (C^o), 60.74 (CNH), 52.26 (*C*HCH_2), 51.98 (*C*HCH_2), 49.40 (*C*$(CH_3)_2$), 35.78 (*C*$H(CH_3)$), 34.84 (CH_2), 27.19 (CH_2), 23.64 (CH_2), 22.81 (CH_3), 21.14 (CH_3).

^{19}F NMR (376 MHz, CD_3CN): δ –80.63

IR: 3319 (NH), 3064, 2962 (Ph), 2264, 1959, 1588, 1537 (C=N), 1446, 1337 (SO_2), 1198 (CF_3), 1122, 1080, 1031, 966, 928, 870, 779, 721, 670, 609, 596, 505 cm^{-1}.

N-(1-(Bromomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-*N*′-(triflyl)benzimidamide (**14**).

White powder. M.p. 181°C.

^{1}H NMR (400 MHz, CD_3CN): δ 7.59 – 7.47 (m, 5H, Ph), 7.40 (br.s, 1H, NH), 4.17 – 4.14 (m, 1H, CHN), 3.77 (d, *J* = 10.9 Hz, 1H, C*H*^{A}HBr), 3.56 (d, *J* = 10.9 Hz, 1H, CH*H*^{B}Br), 1.84 (m, 2H), 1.64 (m, 1H), 1.33 – 1.29 (m, 3H), 1.16 – 1.13 (m, 1H), 1.04 (s, 3H, CH_3), 0.97 (s, 3H, CH_3).

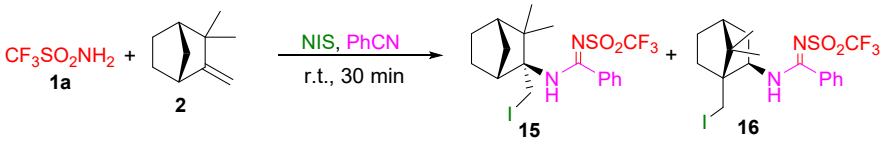
^{13}C NMR (100 MHz, CD_3CN): δ 168.83 (C=N), 132.88 (C^u), 129.31 (C^p), 129.10 (C^m), 128.49 (C^o), 60.70 (CHNH), 53.59 (*C*CH_2), 48.60 (*C*$(CH_3)_2$), 47.50 (CH), 39.43 (CH_2Br), 35.55 (CH_2), 35.42 (CH_2), 27.07 (CH_2), 20.78 (CH_3), 20.63 (CH_3).

^{19}F NMR (376 MHz, CD_3CN): δ –80.57.

IR: 3336 (NH), 2959, 2925, 2853 (Ph), 1588, 1532 (C=N), 1446, 1394 (SO_2), 1339, 1200 (CF_3), 1123, 1080, 1031, 928, 872, 779, 732, 698, 662, 598, 502 cm^{-1}.

Anal. calcd (%) for $C_{18}H_{22}BrF_3N_2O_2S$: C 46.26; H 4.75; Br 17.10; F 12.20; N 5.99; S 6.86. found: C 46.72; H 4.89; Br 16.87; F 12.05; N 6.04; S 6.93

33. Addition of triflamide 1a to camphene 2 in the presence of NIS in PhCN.



(63%)

The interaction of triflamide (**1a**) with camphene (**2**) in the NIS + PhCN system was carried out similarly to the interaction in the NBS + PhCN system, triflamide (0.30 g, 2 mmol), camphene (0.27 g, 2 mmol), 15 ml of benzonitrile, 0.54 g (1.2 eq, 2.4 mmol) of

NIS were used in the reaction. The residue (~0.75 g) was placed on a silica gel column (0.063-0.2 mm, Acros Organics) and eluted with ether-hexane (2:1), ether-hexane (4:1) to give 0.65 g (63%) of a mixture of 2 isomers: N-(2-(iodomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(triflyl)benzimidamide (**15**) and N-(1-(iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-N'-(triflyl)benzimidamide (**16**) as a white powder.

N-(2-(iodomethyl)-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)-*N'*-(triflyl)benzimidamide **(15).**

White powder. M.p. 192°C

^{1}H NMR (400 MHz, CD_3CN): δ 7.63–7.60 (m, 5H, Ph), 7.17 (br.s, 1H, NH), 4.86 (d, J = 11.0 Hz, 1H, CHH^AI), 3.36 (d, J = 11.0 Hz, 1H, CHH^BI), 2.39–2.38 (m, 1H), 1.77–1.75 (m, 1H), 1.69–1.66 (m, 2H), 1.62–1.58 (m, 2H), 1.46–1.42 (m, 2H), 1.35 (s, 3H, CH_3), 1.16 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CD_3CN): 168.89 (C=N), 134.49 (C^u), 132.52 (C^p), 129.34 (C^m), 128.58 (C^o), 118.53 (q, J = 319.2 Hz, CF_3), 70.98 (CNH), 52.91 (CH), 49.29 (*C*$(CH_3)_2$), 47.90 (CH), 34.56 (CH_2), 27.64 (CH_3), 23.23 (CH_2), 22.68 (CH_2), 21.60 (CH_3), 9.12 (CH_2I).

^{19}F NMR (376 MHz, CD_3CN): –80.46.

IR: 3317 (NH), 2963, 2888 (Ph), 1586, 1542 (C=N), 1492, 1465, 1446, 1413, 1380 (SO_2), 1338, 1262, 1200 (CF_3), 1154, 1121, 1090, 1031, 988, 957, 928, 895, 881, 864, 840, 808, 777, 717, 633, 609, 555, 503 cm^{-1}.

N-(1-(iodomethyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl)-*N'*-(triflyl)benzimidamide **(16).**

White powder. M.p. 188°C

^{1}H NMR (400 MHz, CD_3CN): δ 7.65–7.62 (m, 5H, Ph), 7.38 (br.s, 1H, NH), 4.04–4.02 (m, 1H, CHN), 3.67 (d, J = 10.5 Hz, 1H, CHH^AI), 3. 44 (d, J = 10.5 Гц, 1H, CHH^AI), 2.11 (m, 2H), 1.66–1.63 (m, 1H) 1.48–1.43 (m, 1H), 1.27–1.22 (m. 1H), 1.01 (s, 3H, CH_3), 0.94 (s, 3H, CH_3).

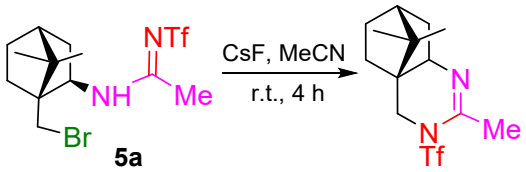
^{13}C NMR (100 MHz, CD_3CN): 169.11 (C=N), 134.47 (C^u), 132.77 (C^p), 129.28 (C^m), 128.48 (C^o), 118.36 (q, J = 318.8 Hz, CF_3), 61.92 (CHNH), 52.47 (*C*CH_2I), 50.96 (*C*H$(CH_2)_2$), 49.26 (CH_2), 37.38 (*C*$H_2(CH_3)_2$), 34.53 (CH_2), 23.20 (CH_2), 20.74 (CH_3), 20.61 (CH_3), 12.70 (CH_2I).

^{19}F NMR (376 MHz, CD_3CN): –80.40.

IR: 3315 (NH), 2961, 2886 (Ph), 1586, 1538 (C=N), 1492, 1471, 1446, 1413, 1390 (SO_2), 1338, 1262, 1191 (CF_3), 1154, 1121, 1080, 1031, 984, 957, 928, 895, 881, 864, 840, 808, 777, 735, 717, 669, 609, 570, 507 cm^{-1}.

Anal. calcd (%) for $C_{18}H_{22}F_3IN_2O_2S$: C 42.03; H 4.31; F 11.08; I 24.67; N 5.45; S 6.23, found: C 42.25; H 4.34; F 11.00; I 24.42; N 5.60; S 6.35.

34. Heterocyclization of amidine 5a in the presence CsF im MeCN.



5a **17**

*2,9,9-Trimethyl-3-(trifluoromethylsulfonyl)-3,5,6,7,8,8a-hexahydro-4H-4a,7-methanoquinazoline **(17).*** 100 mg (0.25 mmol) of **5a** was dissolved in 5 ml of MeCN and CsF (113 mg, 0.75 mmol) was added. The mixture was stirred for 30 min. Next, acetonitrile was removed in vacuum to afford 64 mg (80%) of product **17**.

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (d, *J* = 13.0 Hz, 1H), 3.62 (d, *J* = 12.8 Hz, 1H) 3.25 (ddd, *J* = 9.1, 5.6, 2.5 Hz 1H), 2.30 (d, *J* = 2.4 Hz, 3H), 1.92 (m, 2H), 1.80 (m, 2H), 1.68 – 1.60 (m, 1H), 1.22 (m, 2H), 0.94 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.98, 119.95 (q, *J* = 323.5 Hz), 62.47, 47.71, 46.85, 46.52, 46.12, 37.93, 33.52, 26.64, 24.31, 20.93, 19.49.

^{19}F NMR (376 MHz, $CDCl_3$): δ -75.18.

IR: 3980, 3350, 3113, 2961, 1539, 1444, 1373, 1323, 1188, 1057, 939, 880, 837, 777, 602, 505 cm^{-1}.

HRMS (ESI): *m/z* calcd for $C_{13}H_{20}F_3N_2O_2S^+$: 325.1198 ($M+H^+$); found: 325.1204.

1. L. Garamszegi, M. Schlosser, Halogen/Metal vs. Hydrogen/Metal Exchange: General or Specific Site Selectivity as Exemplified in the Camphene Series. *Chem. Ber*. 1997, **130**, 77-82.

2. J. D. Roberts, E. R. Trumbull, The Reaction of N-Bromosuccinimide with Camphene and α-Pinene. *J. Am. Chem. Soc.*, 1949, **71**, 1630-1632.

3. I. A. Garagan, M. Y. Moskalik, I. V. Sterkhova, A. S. Ganin, *Molbank,* 2023, M1645.

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5. N. Darby, N. Lamb, T. Money, Synthesis and absolute configuration of nojigiku alcohol, *Can. J. Chem.,* 1979, ***57***, 742-746.

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[1]. **CCDC 2164790 (3a), CCDC 2159125 (5a), CCDC 2177719 (7k), CCDC CCDC 2177406 (8k), , CCDC 2306786 (8a)** 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

X-Ray single crystal structure analysis

The single crystals of **3a** were obtained by re-crystallization from acetonitrile solution. In order to investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of the single crystal of compound **3a** was carried out. The molecular structure is depicted in Figure S1. Crystal data, data collection and structure refinement details are summarized in Table S1. Principal bond distances, bond angles and torsion angles are presented in Table S2.

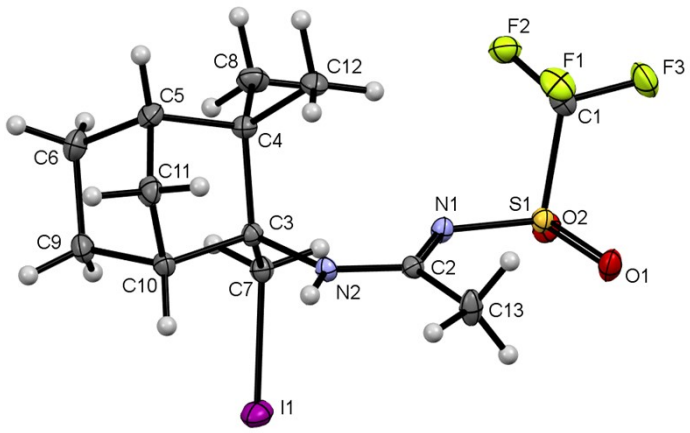


Figure S1. Molecular structure of compound **3a** (ORTEP, 20% probability ellipsoids).

Table S1. Crystal data, details of intensity measurements, and structure refinement for compound **3a**

Empirical formula	$C_{13}H_{20}IF_3N_2O_2S$
Formula weight / g·mol^{-1}	452.27
Crystal system	monoclinic
Space group	C 2/c
a / Å	32.242(4)
b / Å	7.985(1)
c / Å	13.549(2)
α, β, γ / °	90, 98.260(4), 90
Volume / Å^3	3451.9(7)
Z	8
Density (calculated) / g·cm^{-3}	1.741
Absorptions coefficient / mm^{-1}	2.012
Radiation (*λ* / Å)	MoKα (0.71073)
Temperature / K	293(2)
2*Θ* range / °	5.01 – 60.60
Crystal size / mm	0.10 × 0.38 × 0.50
Crystal habit	colorless plate
F(000)	1792
Index ranges	-45 ≤ h ≤ 45, -11 ≤ k ≤ 11, -18 ≤ l ≤ 19
Reflections collected	72361
Independent reflections	5163
Max. and min. transmission	0.5407 / 0.7460
Number of ref. parameters	202
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0351 / 0.0794
R_1 / wR_2 (all data)	0.0891 / 0.0884
Goodness-of-fit on F^2	1.056
Largest diff. peak and hole / e·Å^{-3}	1.384 / -1.232

Weight scheme	$w=1/[\sigma^2(F_o^2) + (0.0411\ P)^2 + 1.4451\ P]$ where $P=(F_o^2 + 2F_c^2)/3$

Table S2. Bond lengths, bond and torsion angles in compound **3a**

Bond	*l*, Å	Angle	φ, °	Torsion angle	θ, °
I1-C7	2.170(2)	O1-S1-O2	117.2(1)	O1-S1-N1-C2	9.5(3)
S1-O1	1.432(2)	O1-S1-N1	118.7 (1)	O2-S1-N1-C2	146.4(2)
S1-O2	1.432(2)	O2-S1-N1	108.4(1)	C1-S1-N1-C2	-104.1(2)
S1-N1	1.572(2)	O1-S1-C1	104.4(1)	O1-S1-C1-F1	-58.8(2)
S1-C1	1.835(3)	O2-S1-C1	104.3(1)	O2-S1-C1-F1	177.7(2)
F1-C1	1.315(3)	N1-S1-C1	101.6(1)	N1-S1-C1-F1	65.1(2)
F2-C1	1.323(3)	C2-N1-S1	126.4(2)	O1-S1-C1-F2	-180.0(2)
N1-C2	1.329(3)	C2-N2-C3	129.4(2)	O2-S1-C1-F2	56.5(2)
N2-C2	1.311(3)	F1-C1-F2	108.7(2)	N1-S1-C1-F2	-56.1(2)
N2-C3	1.488(3)	F1-C1-S1	110.4(2)	O1-S1-C1-F3	60.2(2)
C2-C13	1.507(3)	N2-C2-N1	118.5(2)	O2-S1-C1-F3	-63.3(2)
C3-C7	1.523(3)	N2-C2-C13	116.2(2)	N1-S1-C1-F3	-175.9(2)
C3-C10	1.559(3)	N1-C2-C13	125.3(2)	C3-N2-C2-N1	-0.7(3)
C3-C4	1.618(3)	N2-C3-C7	109.6(2)	C3-N2-C2-C13	179.1(2)
C4-C5	1.557(4)	C3-C7-I1	112.8(2)	N2-C3-C7-I1	60.7(2)
C5-C6	1.538(4)	C7-C3-C10	113.9(2)	S1-N1-C2-C13	-0.2(4)
C6-C9	1.543(4)	C7-C3-C4	112.7(2)	C2-N2-C3-C7	51.4(3)

Molecules of compound **3a** crystallize in monoclinic space group C 2/c. There are one molecule in the asymmetric unit. The geometry of triflimidamide fragment is near to geometry of that in other similar structures [2-4]. In molecule of compound **3a** formally double bond N1-C4 (1.329(3)Å) is longer than the ordinary bond C4-N2 (1.311(3)Å). This is the result of very strong conjugation in the triad NH-C=NTf due to strong electron-withdrawing effect of the triflyl group, as in the earlier studied by us compounds.[2-4]

In the crystal molecules of **3a** connected by intermolecular hydrogen bonds NH···O=S by lengths 2.180 Å (Figure S2).

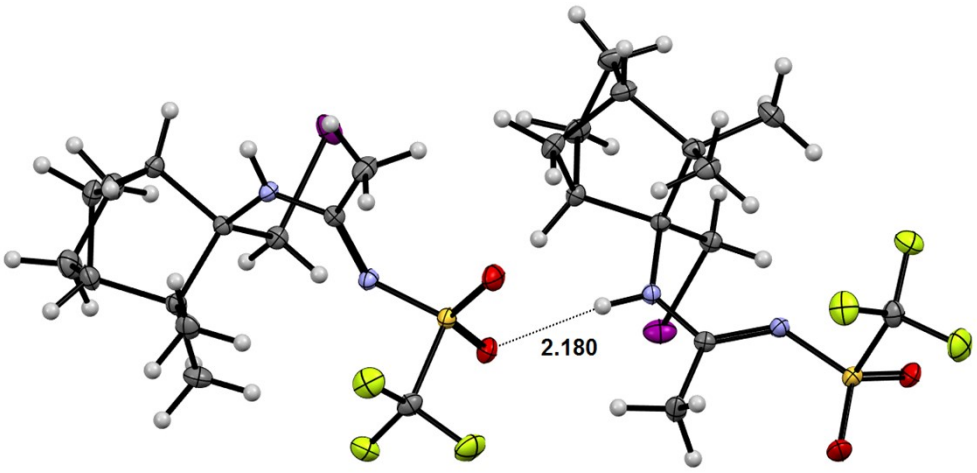


Figure S2. Hydrogen bonds NH···O=S in the crystal of **3a**

The single crystals of **5a** were obtained by re-crystallization from acetonitrile solution. In order to investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of the single crystal of compound **5a** was carried out. The molecular structure is depicted in Figure S3. Crystal data, data collection and structure refinement details are summarized in Table S3. Principal bond distances, bond angles and torsion angles are presented in Table S4.

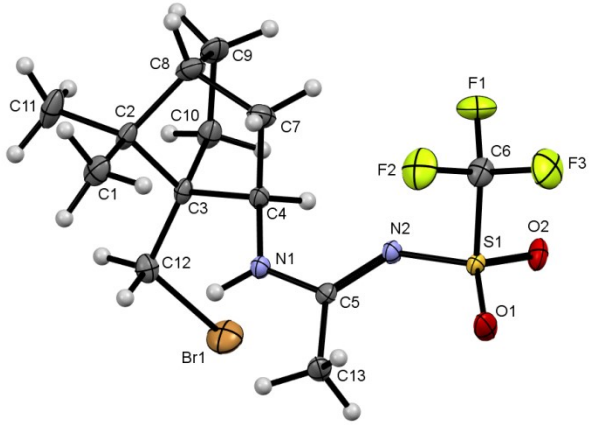


Figure S3. Molecular structure of compound **5a** (ORTEP, 20% probability ellipsoids).

Table S3. Crystal data, details of intensity measurements, and structure refinement for compound **5a**

Empirical formula	$C_{13}H_{20}BrF_3N_2O_2S$
Formula weight / g·mol^{-1}	405.28
Crystal system	monoclinic
Space group	P 2_1/c
a / Å	10.233(4)

b / Å	12.379(4)
c / Å	13.802(4)
α, β, γ / °	90, 105.009(13), 90
Volume / Å^3	1688.8(10)
Z	4
Density (calculated) / g·cm^{-3}	1.594
Absorptions coefficient / mm^{-1}	2.594
Radiation (*λ* / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	4.49 – 60.64
Crystal size / mm	0.12 × 0.32 × 0.40
Crystal habit	colorless plate
F(000)	824
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	60138
Independent reflections	5035
Max. and min. transmission	0.4649 / 0.7460
Number of ref. parameters	202
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0929 / 0.2417
R_1 / wR_2 (all data)	0.1864 / 0.2728
Goodness-of-fit on F^2	1.058
Largest diff. peak and hole / e·Å^{-3}	1.185 / -0.819
Weight scheme	$w=1/[\sigma^2(F_o^2) + (0.1339\ P)^2 + 1.6510\ P]$ where $P=(F_o^2 + 2F_c^2)/3$

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

Bond	*l*, Å	Angle	φ, °	Torsion angle	θ, °
Br1-C12	1.969(6)	O1-S1-O2	117.7(3)	O1-S1-N2-C5	1.9(6)
S1-O1	1.421(4)	O1-S1-N2	119.1(2)	O2-S1-N2-C5	141.2(4)
S1-O2	1.425(4)	O2-S1-N2	109.3(2)	C6-S1-N2-C5	-109.9(5)
S1-N2	1.576(4)	O1-S1-C6	103.7(3)	C11-C2-C3-C12	-60.8(6)
S1-C6	1.832(6)	O2-S1-C6	104.2(3)	C1-C2-C3-C12	63.7(6)
F1-C6	1.327(8)	N2-S1-C6	99.8(3)	C8-C2-C3-C12	-178.5(4)

F2-C6	1.325(7)	C5-N1-C4	122.7(4)	C11-C2-C3-C10	63.0(6)
F3-C6	1.306(7)	C5-N2-S1	126.2(3)	C1-C2-C3-C10	-172.5(5)
N1-C5	1.316(6)	N1-C4-C3	114.8(4)	C8-C2-C3-C10	-54.6(4)
N1-C4	1.470(6)	N1-C4-C7	114.1(4)	C11-C2-C3-C4	170.5(5)
N2-C5	1.323(6)	N1-C5-N2	116.0(4)	C1-C2-C3-C4	-65.0(6)
C1-C2	1.541(7)	N1-C5-C13	117.0(4)	C2-C3-C4-N1	93.4(5)
C2-C3	1.561(7)	N2-C5-C13	127.0(4)	C10-C3-C4-N1	-161.0(4)
C3-C4	1.556(6)	F1-C6-S1	110.9(4)	S1-N2-C5-N1	172.0(4)
C3-C10	1.549(7)	F2-C6-S1	110.7(5)	C10-C3-C12-Br1	66.8(5)
C2-C8	1.553(8)	C4-C7-C8	103.6(4)	C4-C3-C12-Br1	-54.9(5)
C8-C9	1.536(9)	C3-C12-Br1	112.3(3)	C2-C3-C12-Br1	-176.3(3)

Molecules of compound **5a** crystallize in monoclinic space group $P2_1/c$. The geometry of triflimidamide fragment is near to geometry of that in other similar structures.[2-4] In molecule of compound **3a** formally double bond N1-C4 (1.323(2)Å) is longer than the ordinary bond C4-N2 (1.316(2)Å). This is the result of very strong conjugation in the triad NH-C=NTf due to strong electron-withdrawing effect of the triflyl group, as in the earlier studied by us compounds.[2-4]

In the crystal molecules of **5a** connected by intermolecular hydrogen bonds NH···O=S by lengths 2.215 Å (Figure S4).

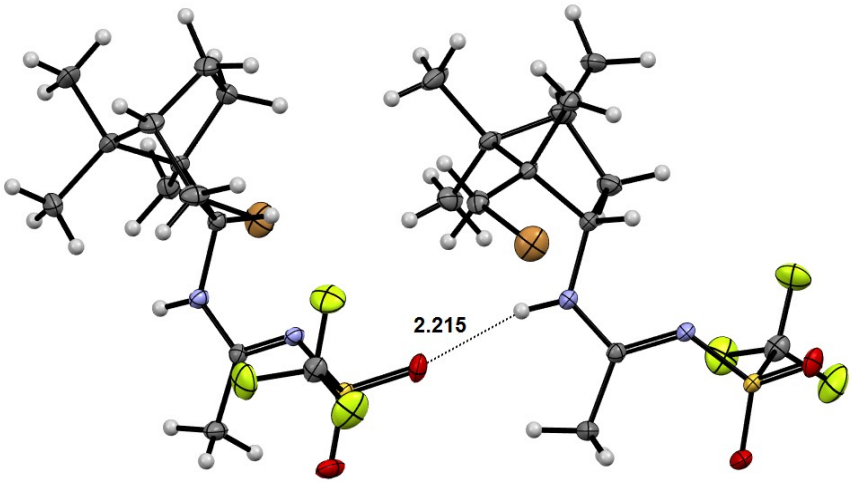


Figure S4. Hydrogen bonds NH···O=S in the crystal of **5a**

The single crystals of **7k** were obtained by re-crystallization from diethyl ether. In order to investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of the single crystal of compound **7k** was carried out. The molecular structure is depicted in Figure S5. Crystal data, data collection and structure refinement details are summarized in Table S5. Principal bond distances, bond angles and torsion angles are presented in Table S6.

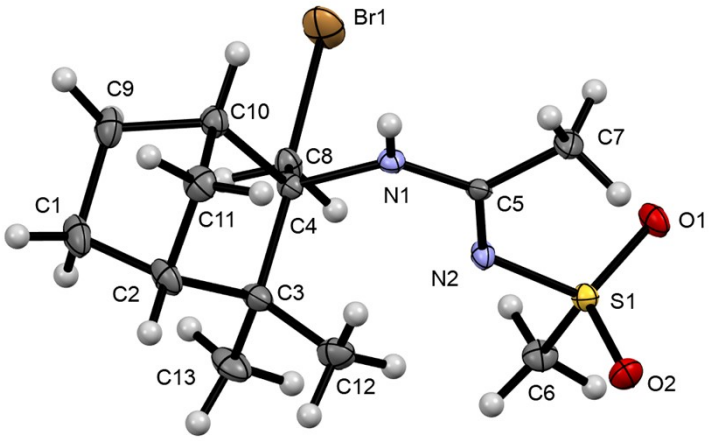


Figure S5. Molecular structure of compound **7k** (ORTEP, 20% probability ellipsoids).

Table S5. Crystal data, details of intensity measurements, and structure refinement for compound **7k**

Empirical formula	$C_{13}H_{22}BrN_2O_2S$
Formula weight / g·mol^{-1}	350.29
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	8.417(7)
b / Å	16.197(13)
c / Å	12.549(12)
α, β, γ / °	90, 107.97(3), 90
Volume / Å^3	1627(2)
Z	4
Density (calculated) / g·cm^{-3}	1.430
Absorptions coefficient / mm^{-1}	2.655
Radiation (*λ* / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	5.03 – 60.41

Crystal size / mm	0.04 × 0.24 × 0.35
Crystal habit	colorless plate
F(000)	724
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 22, -17 ≤ l ≤ 14
Reflections collected	24712
Independent reflections	4684
Max. and min. transmission	0.7460 / 0.5861
Number of ref. parameters	180
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0839 / 0.1712
R_1 / wR_2 (all data)	0.2170 / 0.2111
Goodness-of-fit on F^2	1.010
Largest diff. peak and hole / e·Å^{-3}	1.278 / -0.650
Weight scheme	$w=1/[\sigma^2(F_o^2) + (0.0889\ P)^2 + 0.9183P]$, where $P=(F_o^2 + 2F_c^2)/3$

Table S6. Selected bond lengths, bond and torsion angles in compound **7k**

Bond	*l*, Å	Angle	φ, °	Torsion angle	θ, °
Br1-C8	1.966(6)	O2-S1-O1	115.6(2)	O2-S1-N2-C5	78.5(4)
S1-O2	1.447(4)	O2-S1-N2	111.2(2)	O1-S1-N2-C5	-53.5(5)
S1-O1	1.450(4)	O1-S1-N2	113.1(2)	C6-S1-N2-C5	-168.1(4)
S1-N2	1.603(4)	O2-S1-C6	107.8(3)	C9-C1-C2-C11	35.1(6)
S1-C6	1.760(5)	O1-S1-C6	108.2(3)	C9-C1-C2-C3	-72.4(6)
N1-C5	1.324(6)	N2-S1-C6	99.6(2)	C11-C2-C3-C12	82.3(5)
N1-C4	1.503(6)	C5-N1-C4	127.7(4)	C1-C2-C3-C13	-53.4(6)
N2-C5	1.317(6)	C5-N2-S1	123.3(3)	S1-N2-C5-N1	-177.1(3)
C1-C2	1.546(8)	C2-C1-C9	103.8(4)	S1-N2-C5-C7	2.4(7)
C1-C9	1.556(9)	C11-C2-C1	101.0(5)	C4-N1-C5-N2	-5.9(7)
C2-C3	1.561(8)	C11-C2-C3	101.8(4)	C4-N1-C5-C7	174.6(4)
C3-C4	1.609(7)	C1-C2-C3	111.3(5)	N1-C4-C8-Br1	-56.9(5)
C4-C8	1.528(7)	N1-C4-C8	108.5(4)	C3-C4-C8-Br1	177.7(3)
C5-C7	1.514(7)	N2-C5-N1	120.0(4)	N1-C4-C10-C11	-83.0(4)

Molecules of compound **7k** crystallize in monoclinic space group $P2_1/n$. There are four molecules in the unit cell and one molecule in the asymmetric unit. In the crystal

molecules of **7k** connected by intermolecular hydrogen bonds NH···O=S by lengths 2.098 Å (Figure S6).

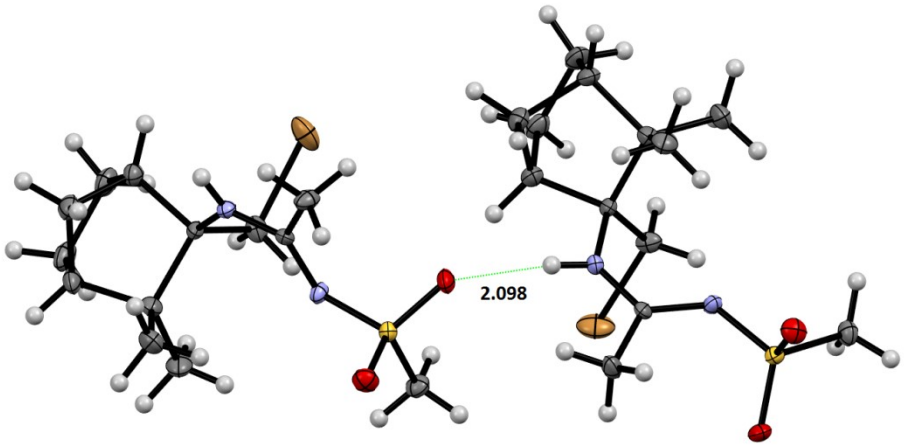


Figure S6. Hydrogen bonds NH···O=S in the crystal of **7k**

The single crystals of **8a** were obtained by re-crystallization from chloroform solution. In order to investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of the single crystal of compound **8a** was carried out. The molecular structure is depicted in Figure S7. Crystal data, data collection and structure refinement details are summarized in Table S7.

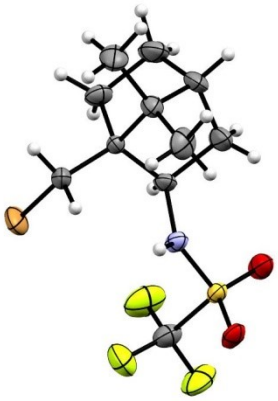


Figure S7. Molecular structure of compound **8a**

Table S7. Crystal data, details of intensity measurements, and structure refinement for compound **8a**

CCDC number	2306786
Empirical formula	$C_{11}H_{17}BrF_3NO_2S$
Formula weight	364.22
Temperature, K	150(2)

CCDC number	2306786
Crystal system	triclinic
Space group	P-1
a, Å	7.6458(8)
b, Å	8.4634(10)
c, Å	11.3756(8)
α, °	75.804(8)
β, °	81.317(7)
γ, °	85.101(9)
Volume, $Å^3$	704.55(13)
Z	2
ρ_{calc}, g/cm^3	1.717
μ, mm^{-1}	3.096
F(000)	368.0
Crystal size, mm^3	0.2 × 0.17 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection, °	4.97 to 51.994
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected	6375
Independent reflections	2717 [R_{int} = 0.0437, R_{sigma} = 0.0598]
Data/restraints/parameters	2717/0/174
Goodness-of-fit on F^2	0.974
Final R indexes [I≥2σ (I)]	R_1 = 0.0426, wR_2 = 0.0971

The single crystals of **8k** were obtained by re-crystallization from diethyl ether-hexane solution. In order to investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of the single crystal of compound **8k** was carried out. The molecular structure is depicted in Figure S8. Crystal data, data collection and structure refinement details are summarized in

Table S8. Principal bond distances, bond angles and torsion angles are presented in Table S9.

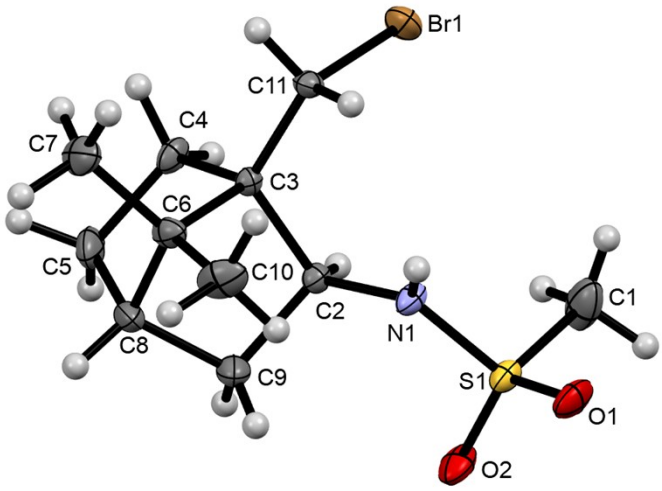


Figure S8. Molecular structure of compound **8k** (ORTEP, 20% probability ellipsoids).

Table S8. Crystal data, details of intensity measurements, and structure refinement for compound **8k**

Empirical formula	$C_{11}H_{20}BrNO_2S$
Formula weight / g·mol^{-1}	310.25
Crystal system	triclinic
Space group	P-1
a / Å	7.546(4)
b / Å	8.634(4)
c / Å	10.975(5)
α, β, γ / °	75.459(14), 80.375(16), 83.214(15)
Volume / Å^3	680.2(5)
Z	2
Density (calculated) / g·cm^{-3}	1.515
Absorptions coefficient / mm^{-1}	3.163
Radiation (*λ* / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	3.68 – 60.36
Crystal size / mm	0.05 × 0.35 × 0.42
Crystal habit	yellow plate
F(000)	320

Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	20988
Independent reflections	3982
Max. and min. transmission	0.7460 / 0.3260
Number of ref. parameters	148
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0775 / 0.1720
R_1 / wR_2 (all data)	0.1647 / 0.1989
Goodness-of-fit on F^2	1.034
Largest diff. peak and hole / e·Å^{-3}	0.526 / -0.870
Weight scheme	$w=1/[\sigma^2(F_o^2) + (0.0742\ P)^2 + 1.1921P]$, where $P=(F_o^2 + 2F_c^2)/3$

Table S9. Selected bond lengths, bond and torsion angles in compound **8k**

Bond	*l*, Å	Angle	φ, °	Torsion angle	θ, °
Br1-C11	1.966(5)	O2-S1-O1	118.1(3)	O2-S1-N1-C2	-39.1(5)
S1-O2	1.428(4)	O2-S1-N1	108.1(2)	O1-S1-N1-C2	-167.2(4)
S1-O1	1.441(4)	O1-S1-N1	106.9(2)	C1-S1-N1-C2	78.5(5)
S1-N1	1.613(4)	O2-S1-C1	108.8(4)	S1-N1-C2-C3	-165.5(3)
S1-C1	1.759(7)	O1-S1-C1	106.5(4)	S1-N1-C2-C9	79.0(5)
N1-C2	1.463(6)	N1-S1-C1	108.2(3)	N1-C2-C3-C11	39.4(6)
C2-C3	1.554(6)	C2-N1-S1	121.4(3)	C9-C2-C3-C11	161.2(4)
C2-C9	1.557(7)	N1-C2-C3	113.8(4)	N1-C2-C3-C4	165.3(4)
C3-C11	1.512(6)	N1-C2-C9	112.8(4)	C9-C2-C3-C4	-73.0(5)
C3-C4	1.557(6)	C3-C2-C9	101.9(4)	N1-C2-C3-C6	-88.6(5)
C3-C6	1.575(7)	C11-C3-C2	117.5(4)	C9-C2-C3-C6	33.2(5)
C4-C5	1.550(8)	C11-C3-C4	112.7(4)	C11-C3-C4-C5	-157.8(4)
C5-C8	1.531(10)	C2-C3-C4	104.7(4)	C2-C3-C4-C5	73.5(5)
C6-C7	1.534(8)	C3-C11-Br1	112.4(3)	C4-C3-C11-Br1	-62.8(5)

Molecules of compound **8k** crystallize in triclinic space group P-1. There are two molecules in the unit cell and one molecule in the asymmetric unit. In the crystal molecules of **8k** connected by intermolecular hydrogen bonds NH···O=S by lengths 2.333 Å (Figure S9).

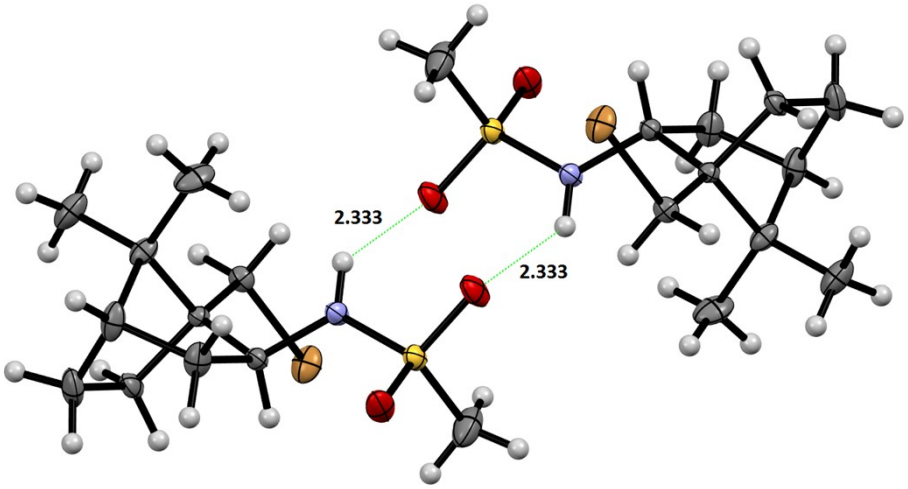


Figure S9. Hydrogen bonds NH···O=S in the crystal of **8k**

References:

1. G.M. Sheldrick, Acta Crystallogr, **2008,** D64, 112.
2. Shainyan B. A., Meshcheryakov V. I., Sterkhova I. V., Tetrahedron **2015**, 71, 7906.
3. Moskalik M. Yu., Shainyan B. A., Ushakov I. A., Sterkhova I. V., Astakhova V. V., Tetrahedron **2020**, 76,131018.
4. Moskalik M. Yu., Garagan I. A., Astakhova V. V., Sterkhova I. V., Shainyan B. A., Tetrahedron 88 (2021) 132145.

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

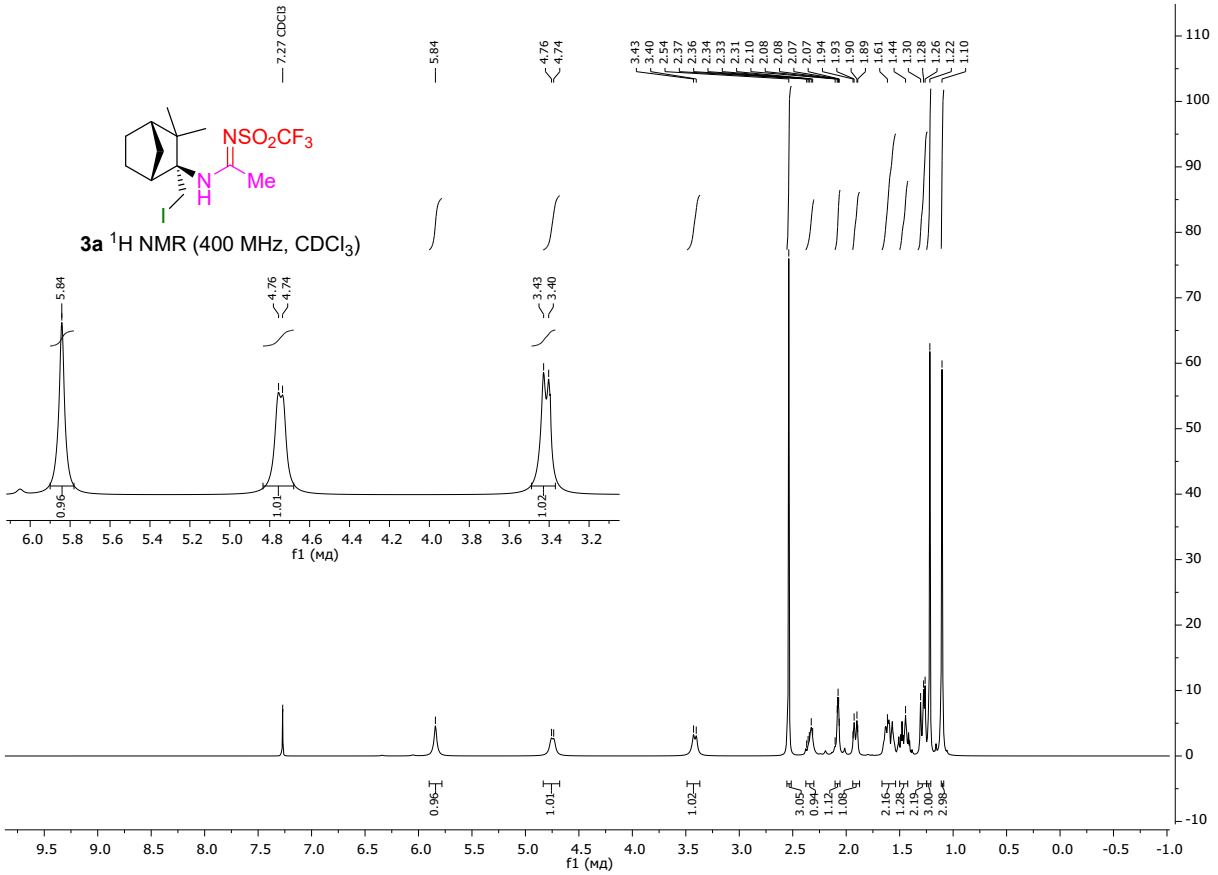


Figure S11. ^{13}C NMR spectrum of compound **3a**

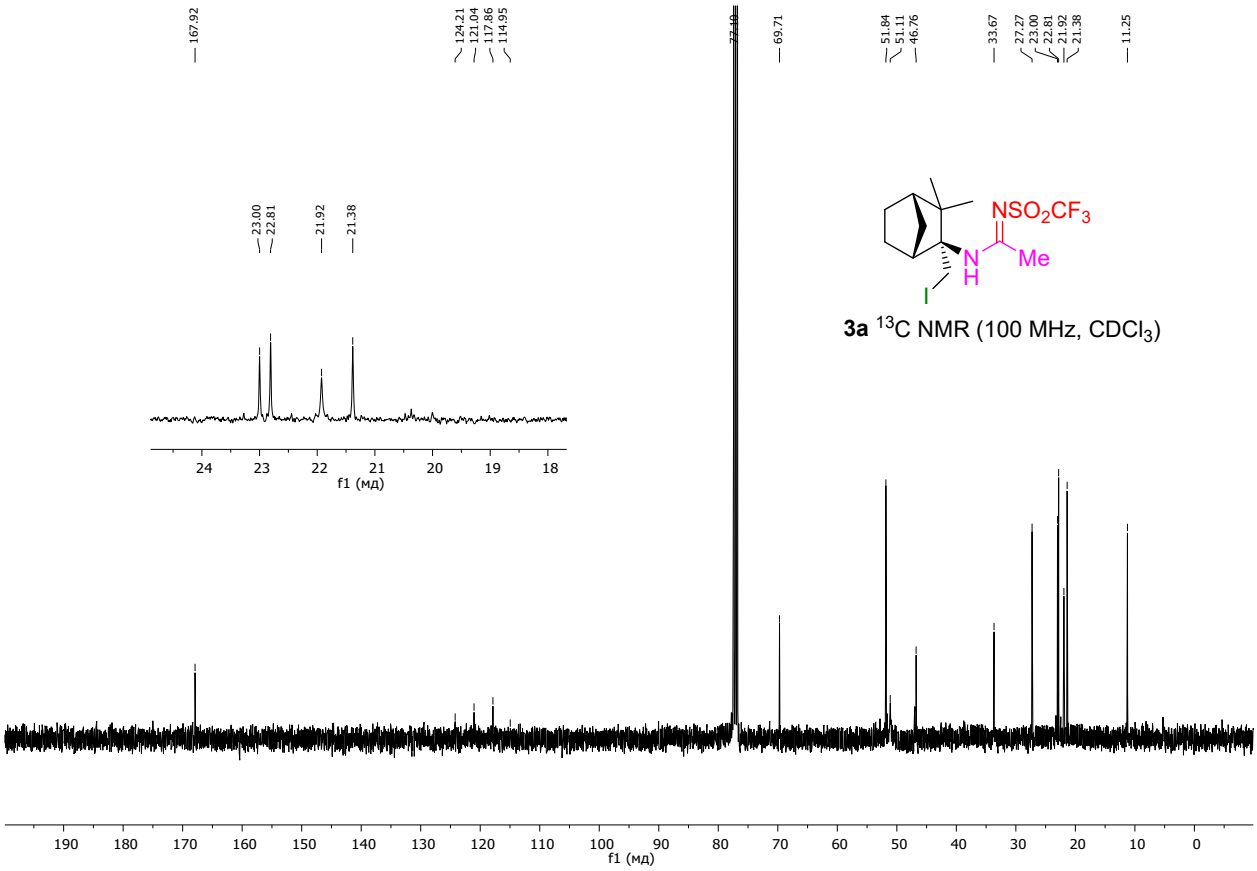
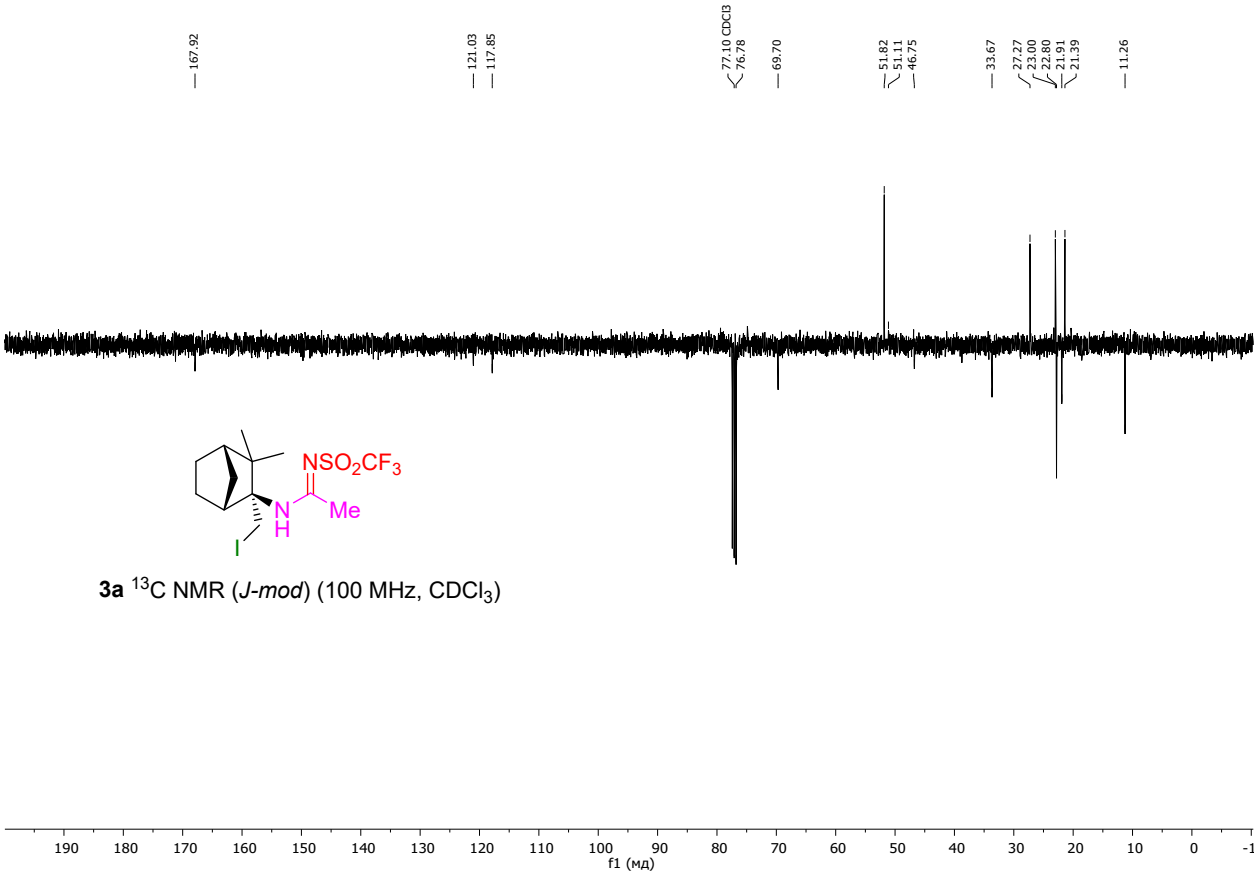


Figure S12. ^{13}C NMR (*J-mod*) spectrum of compound **3a**



3a ^{13}C NMR (*J-mod*) (100 MHz, $CDCl_3$)

Figure S13. ^{19}F NMR spectrum of compound 3a

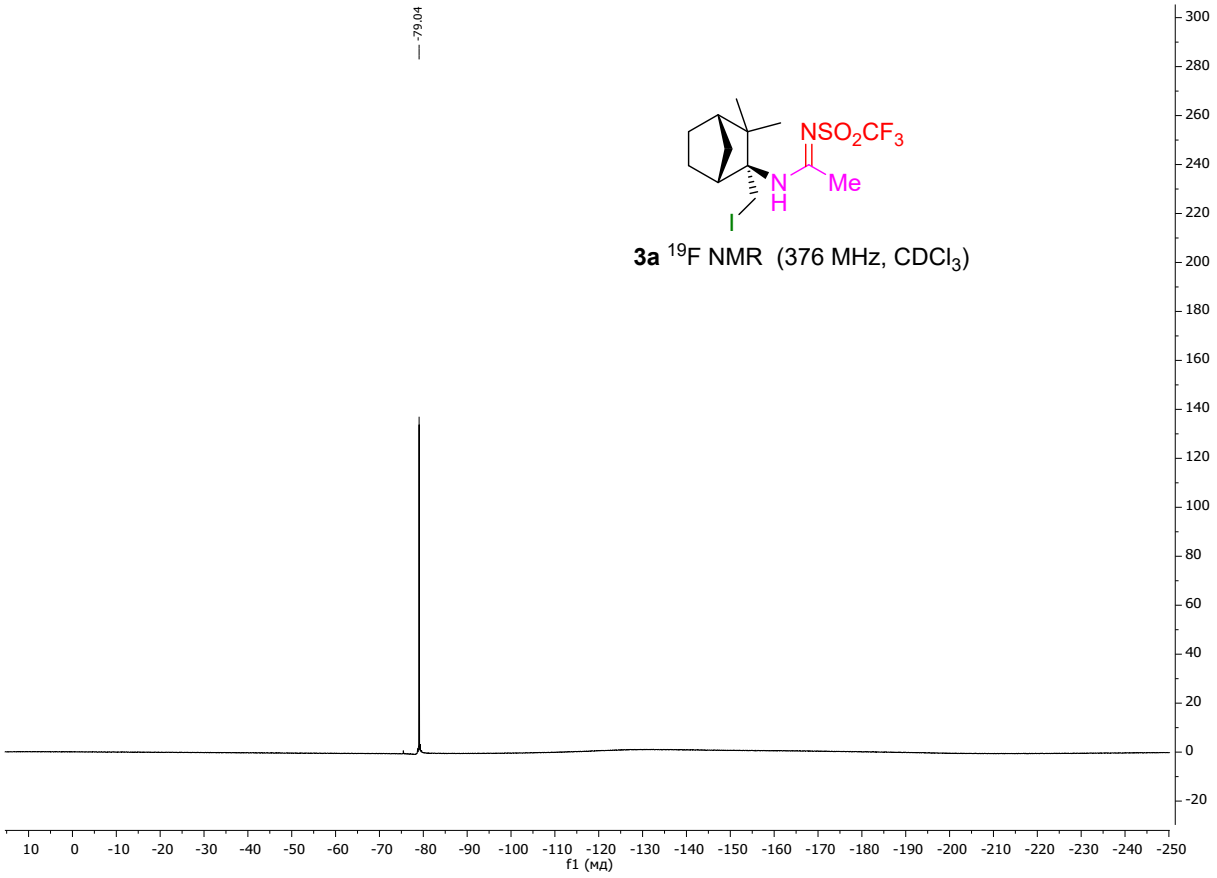


Figure S14. ^{1}H NMR spectrum of compound **3b**

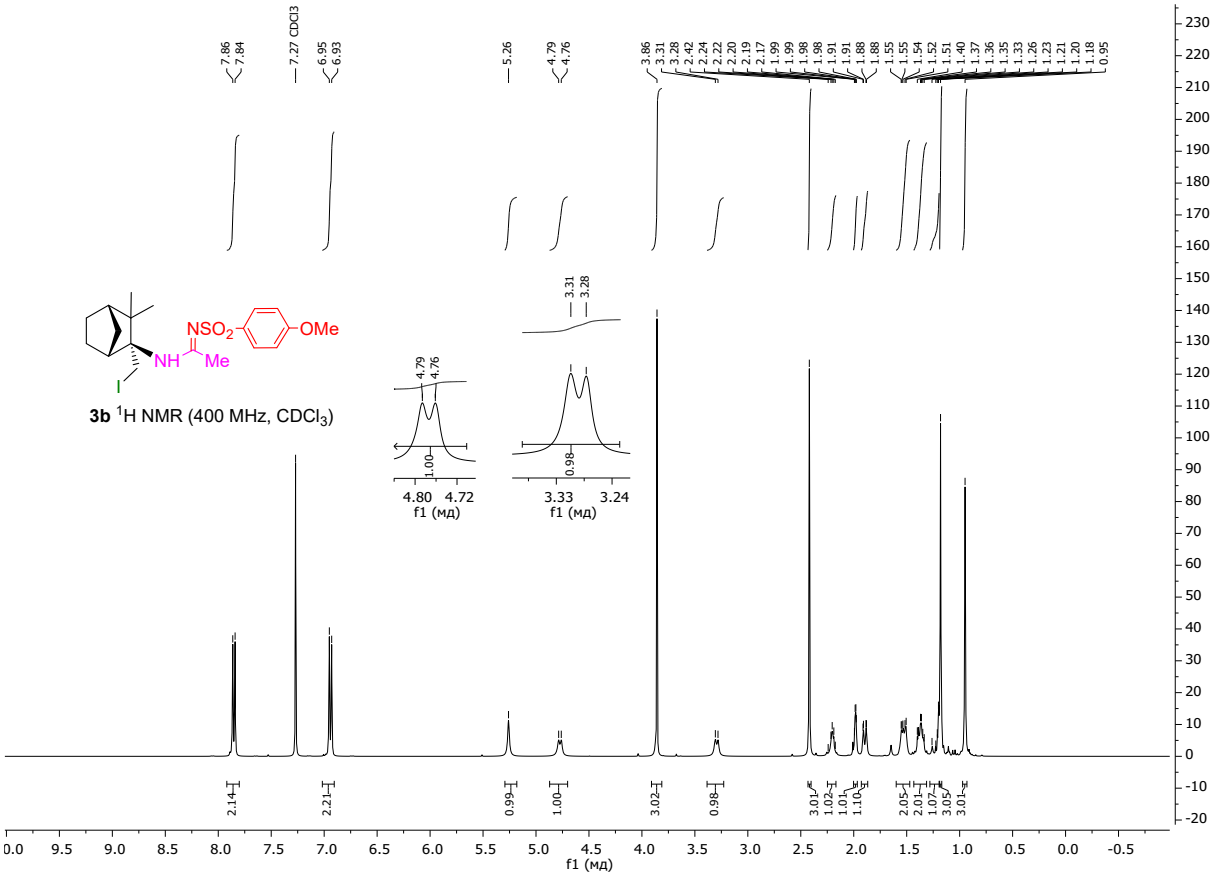


Figure S15. ^{13}C NMR spectrum of compound **3b**

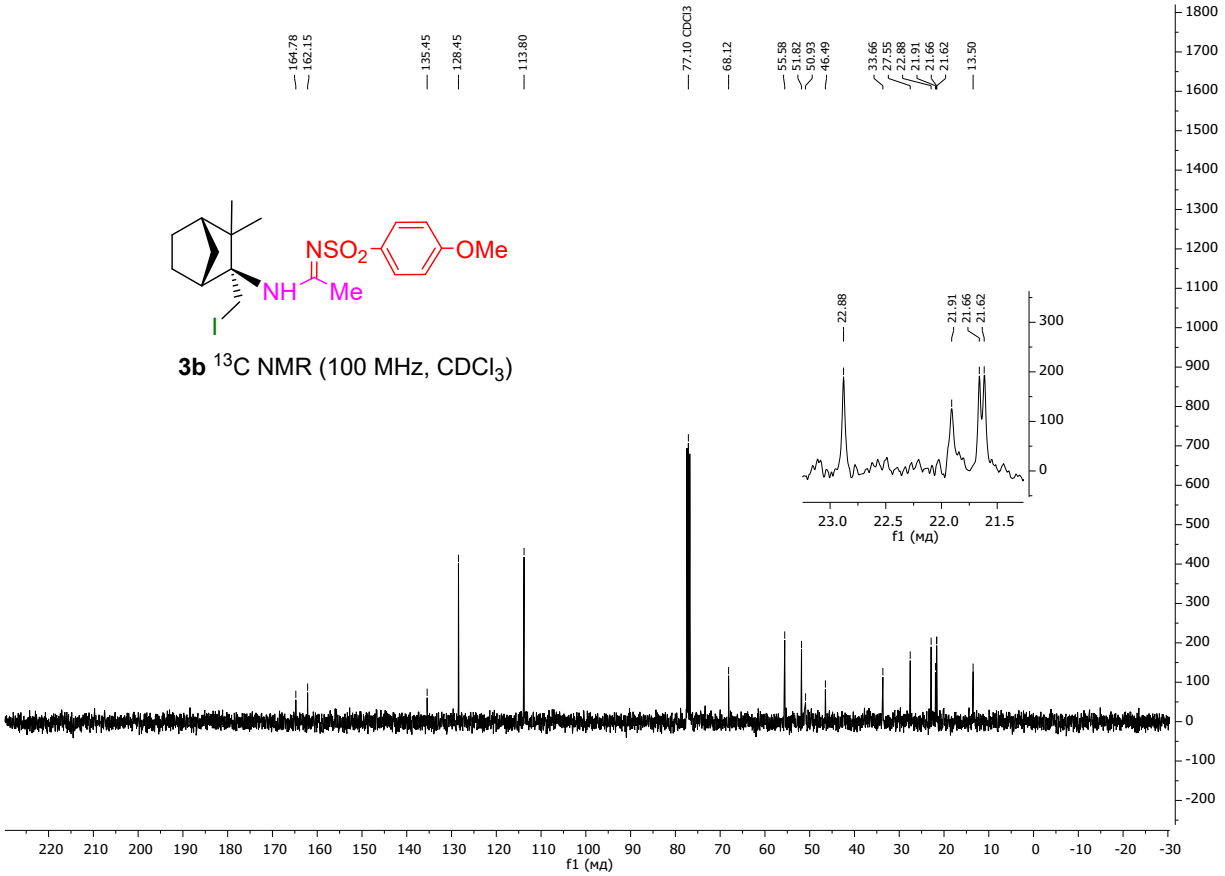


Figure S16. ^{1}H NMR spectrum of compound **3c**

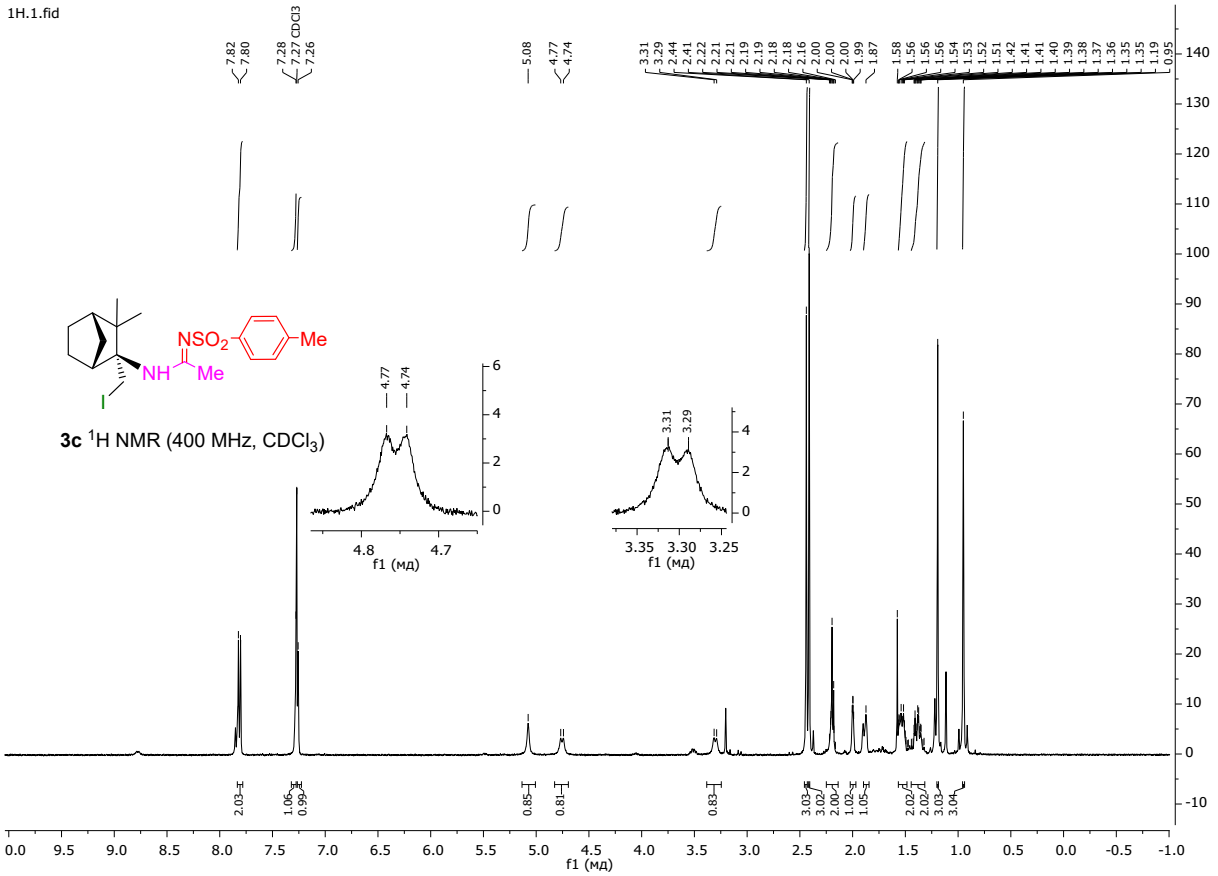


Figure S17. ^{13}C NMR spectrum of compound **3c**

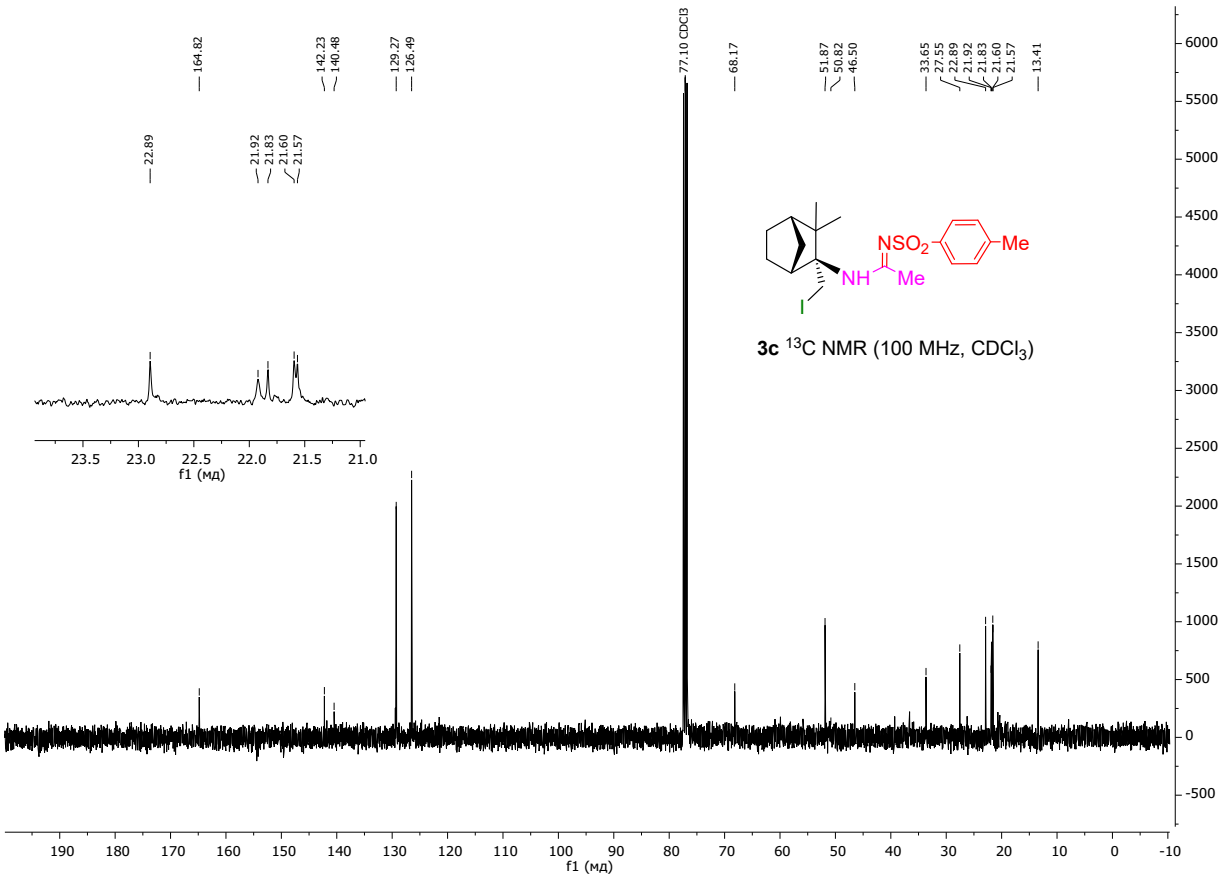


Figure S18. ^{1}H NMR spectrum of compound **3d**

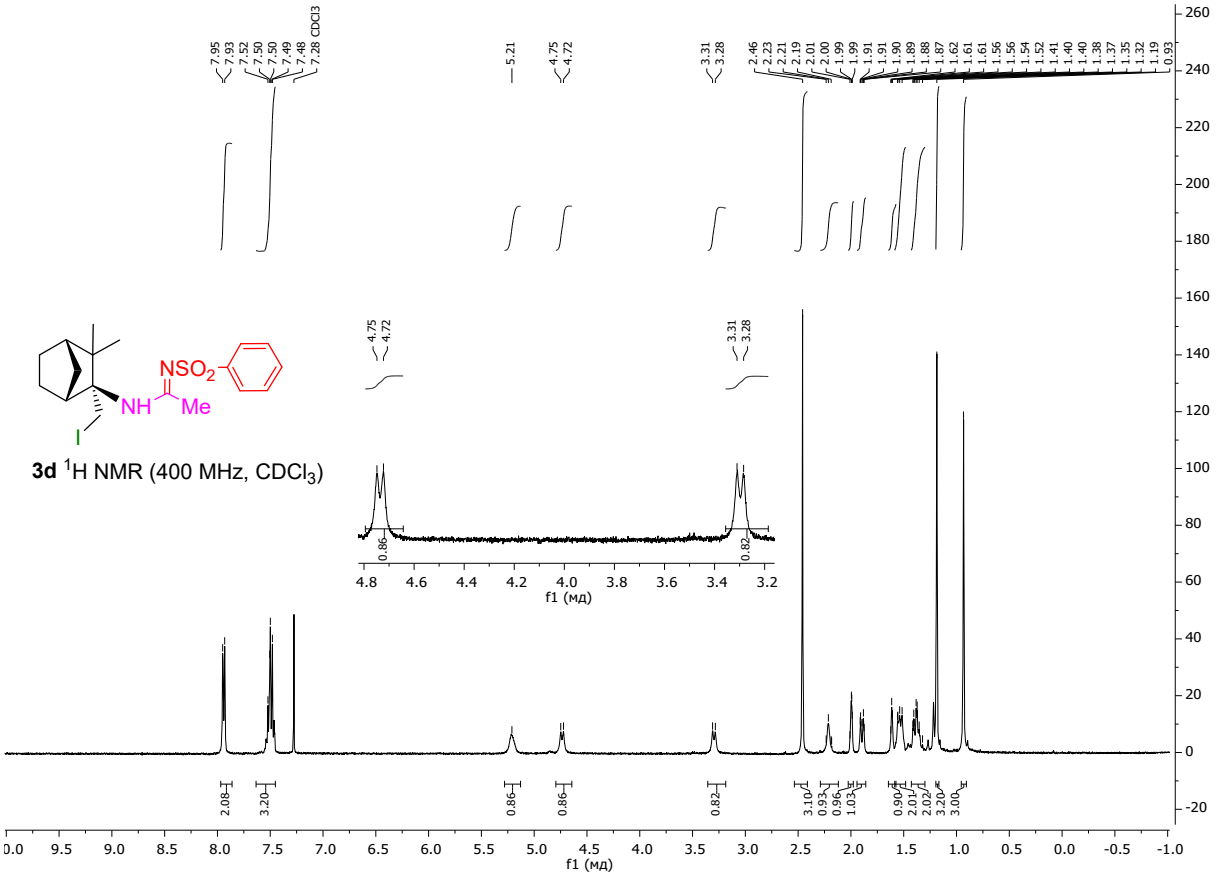


Figure S19. ^{13}C NMR spectrum of compound **3d**

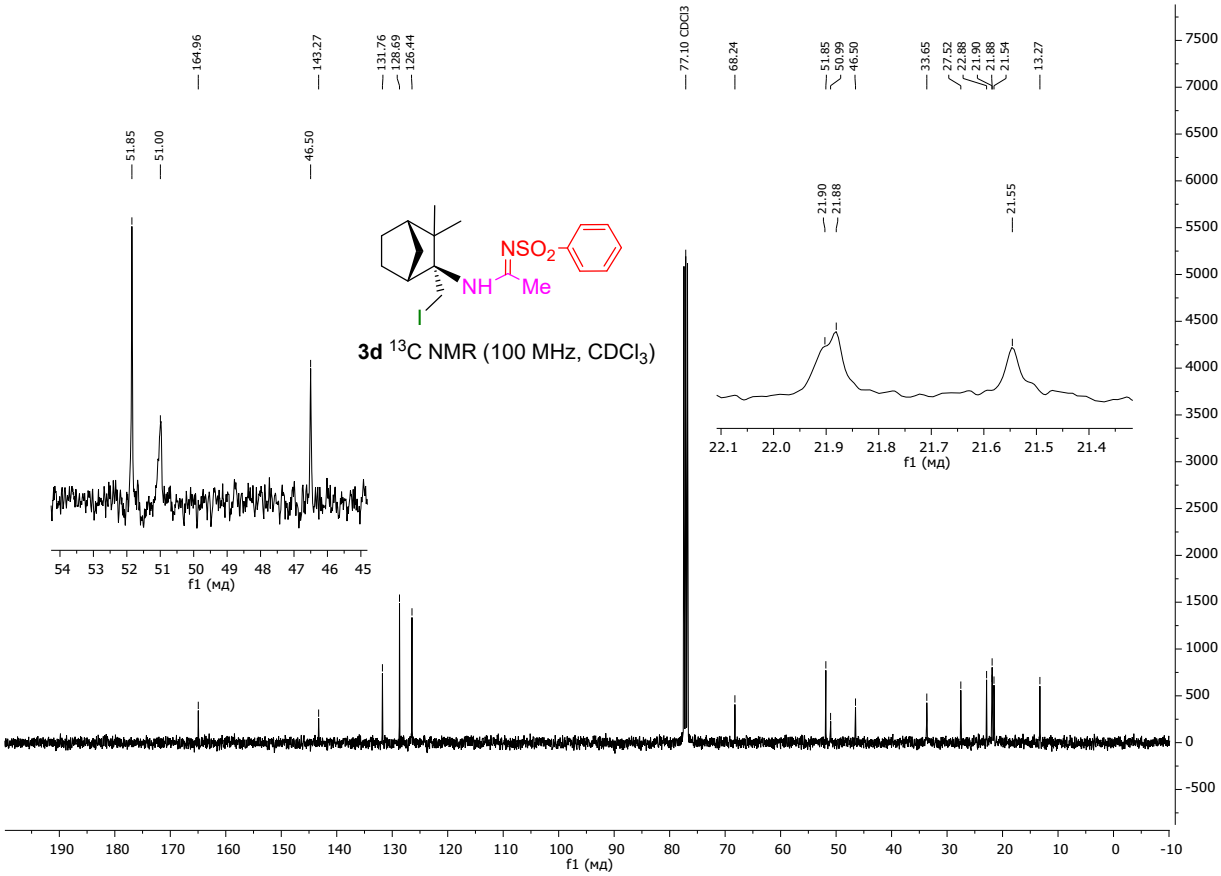


Figure S20. ^{1}H NMR spectrum of compound **3e**

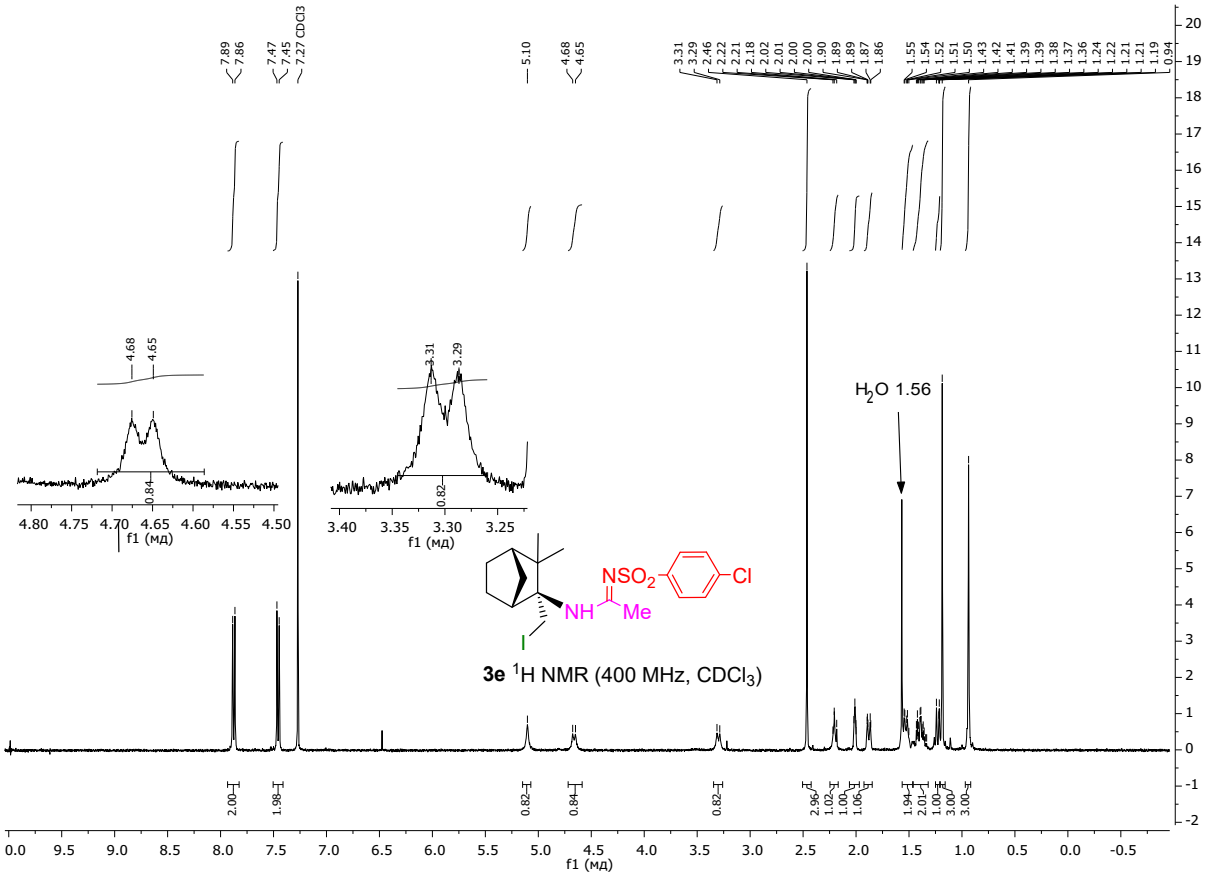


Figure S21. ^{13}C NMR spectrum of compound **3e**

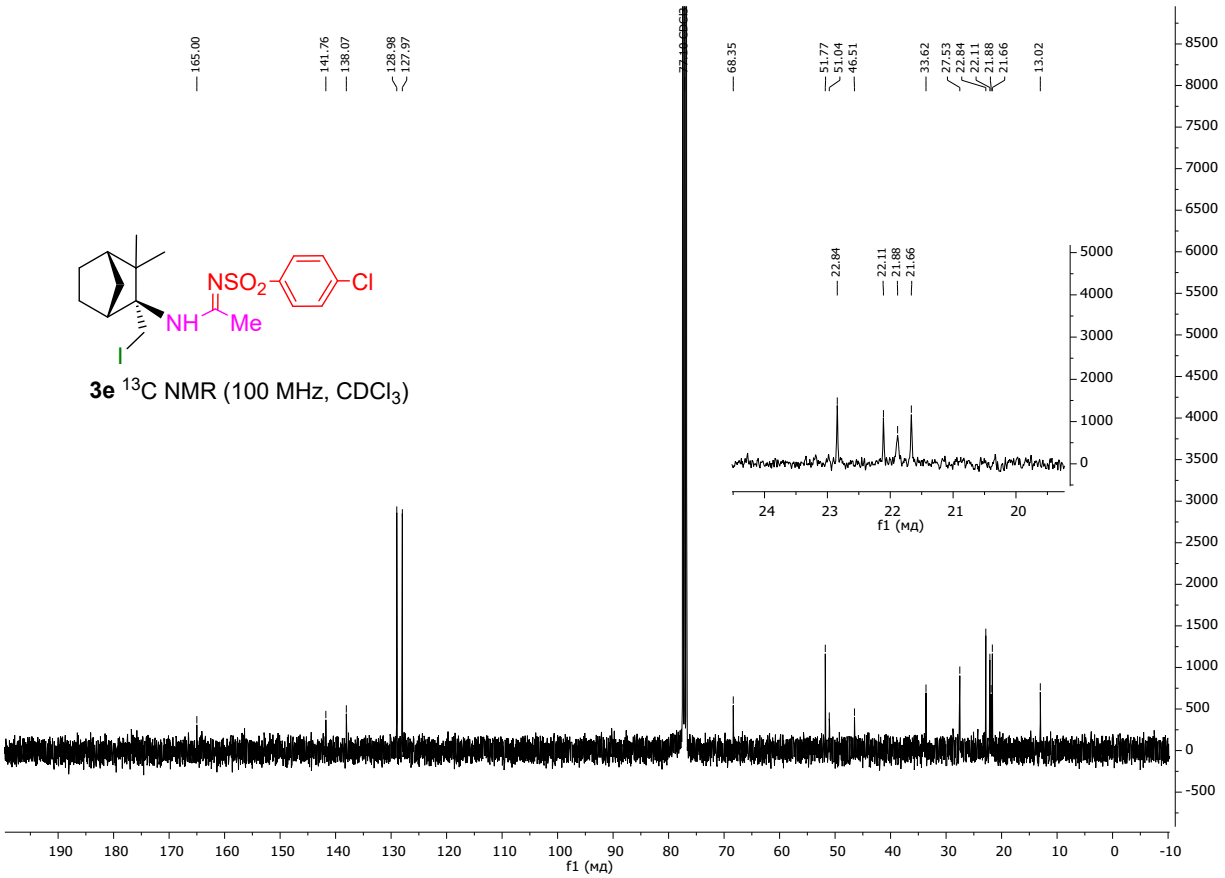


Figure S22. ^{1}H NMR spectrum of compound **3f**

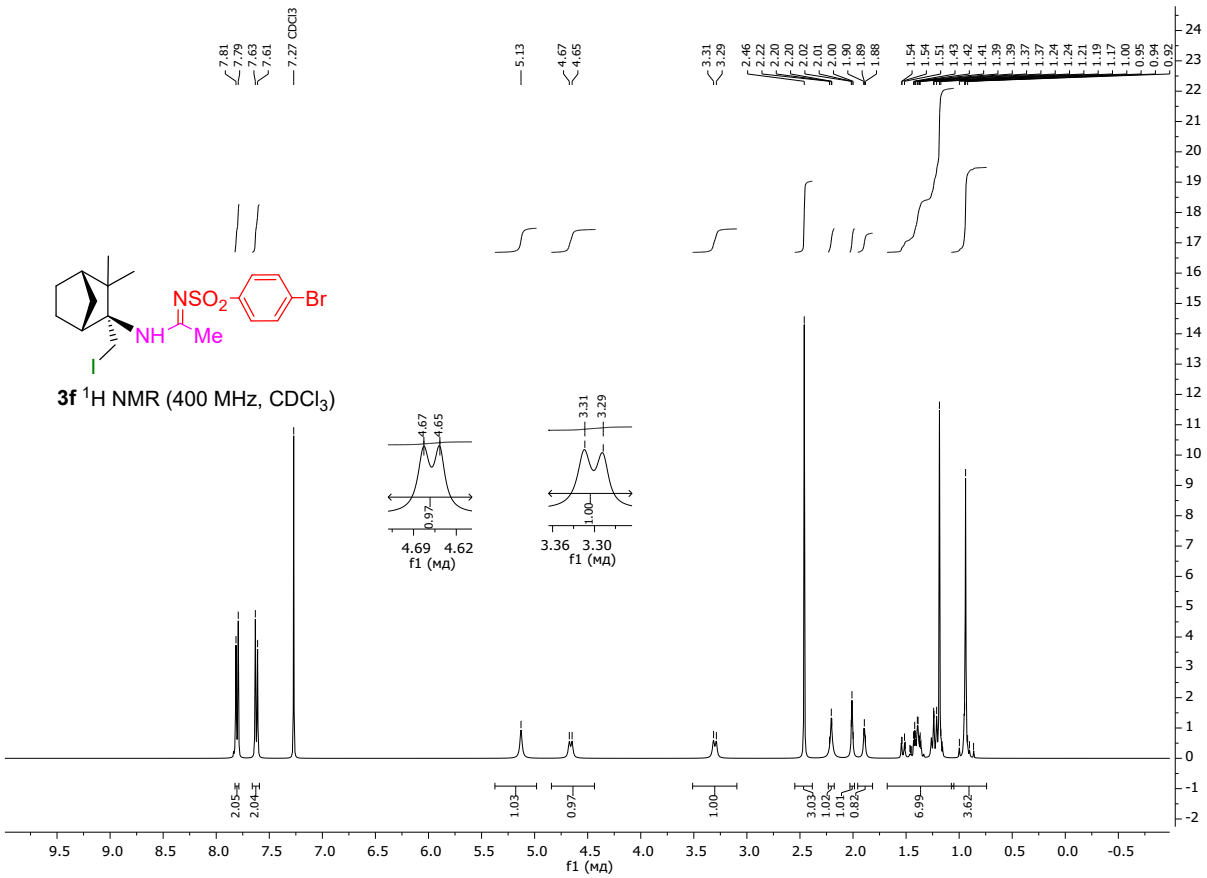


Figure S23. ^{13}C NMR spectrum of compound **3f**

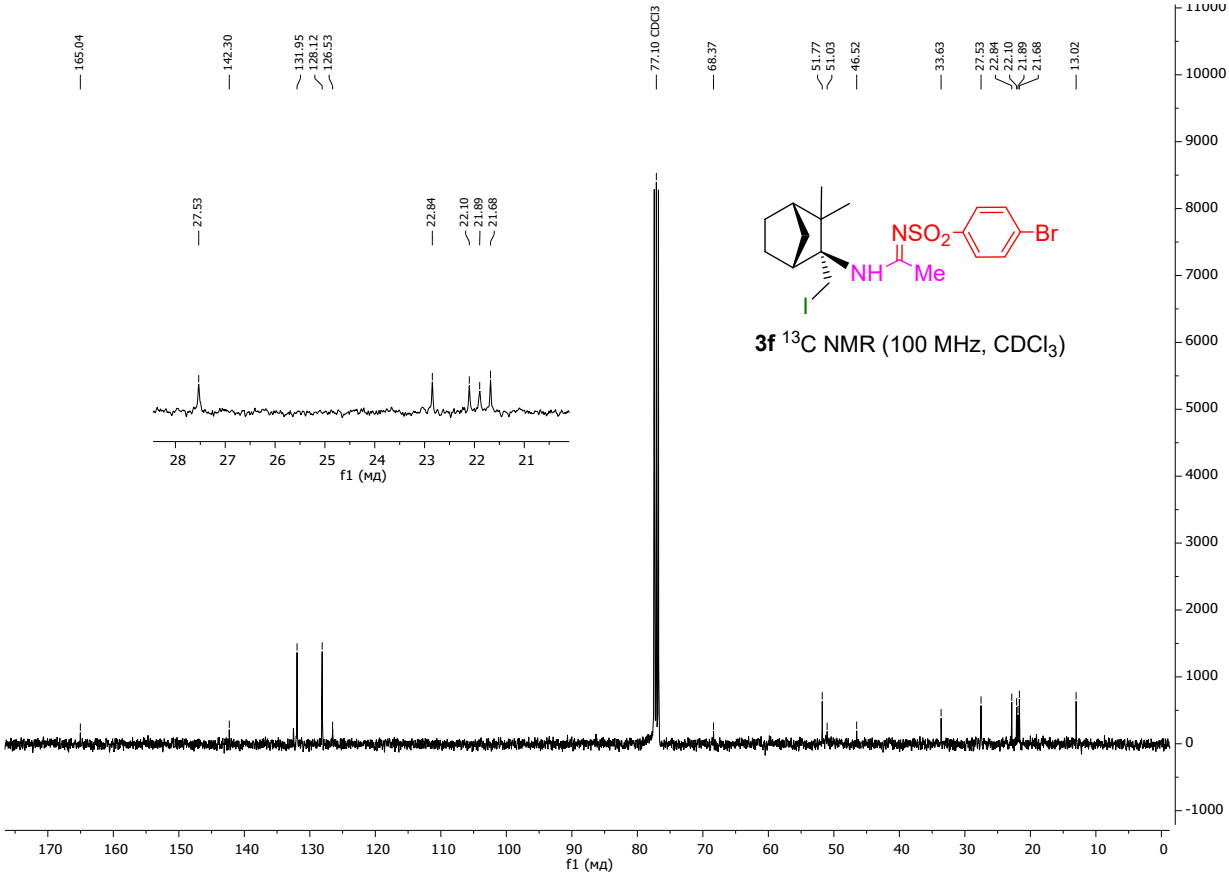


Figure S24. ^{1}H NMR spectrum of compound **3g**

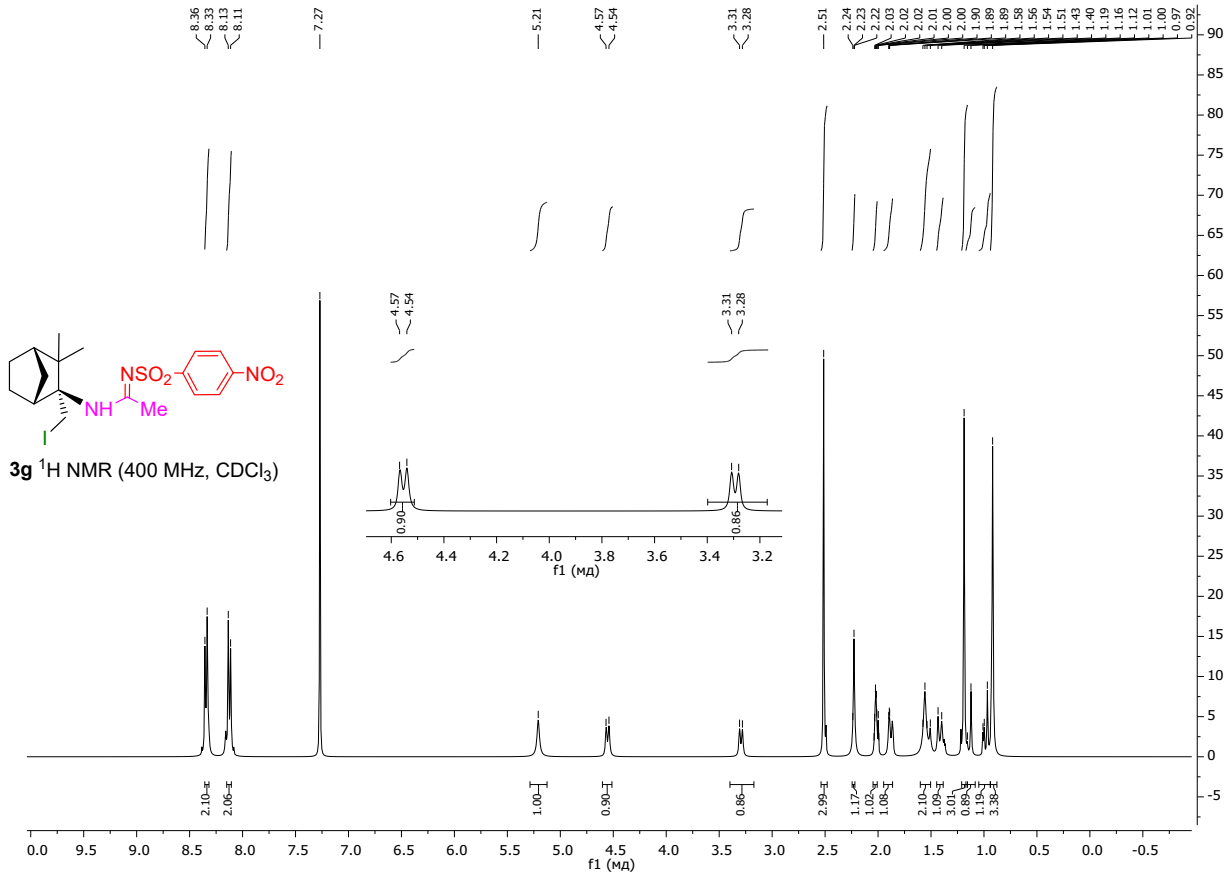


Figure S25. ^{13}C NMR spectrum of compound **3g**

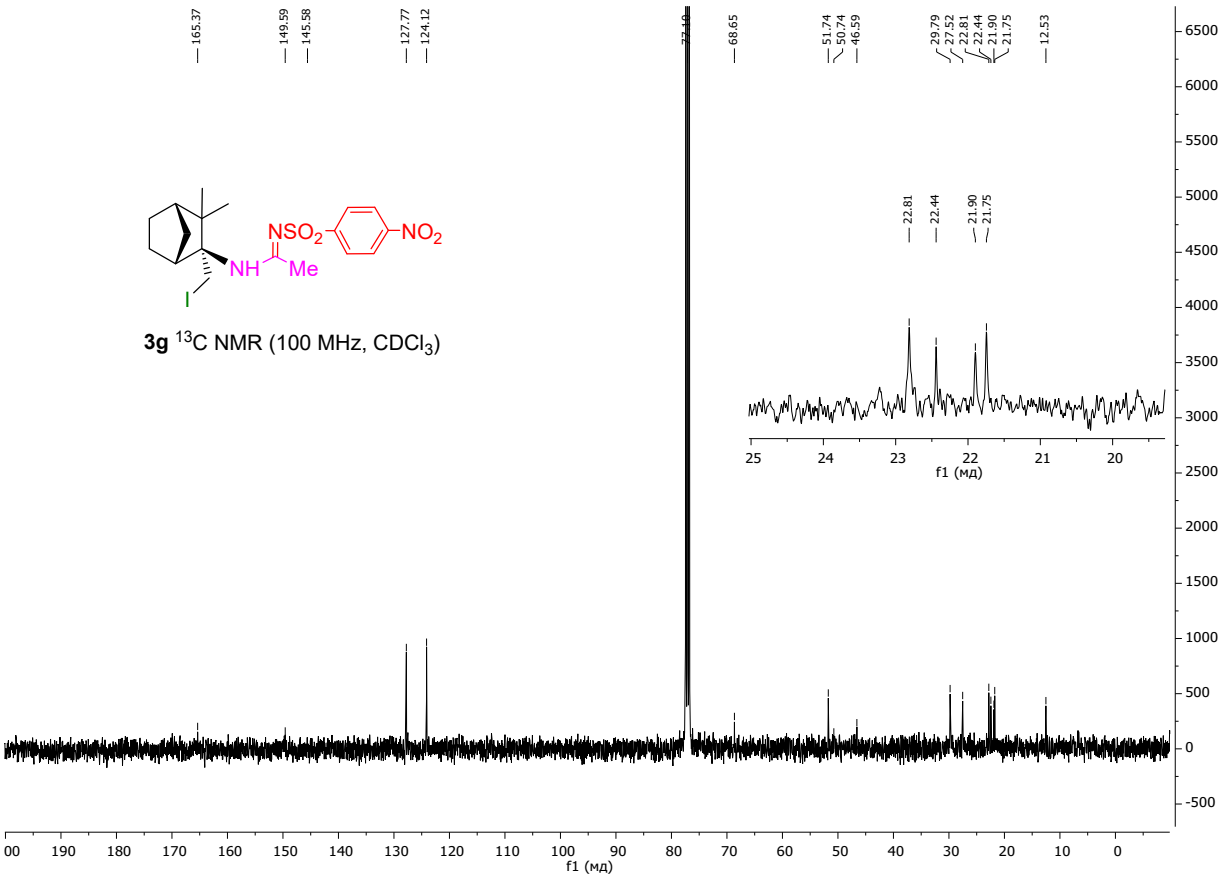


Figure S26. ^{1}H NMR spectrum of compound **3h**

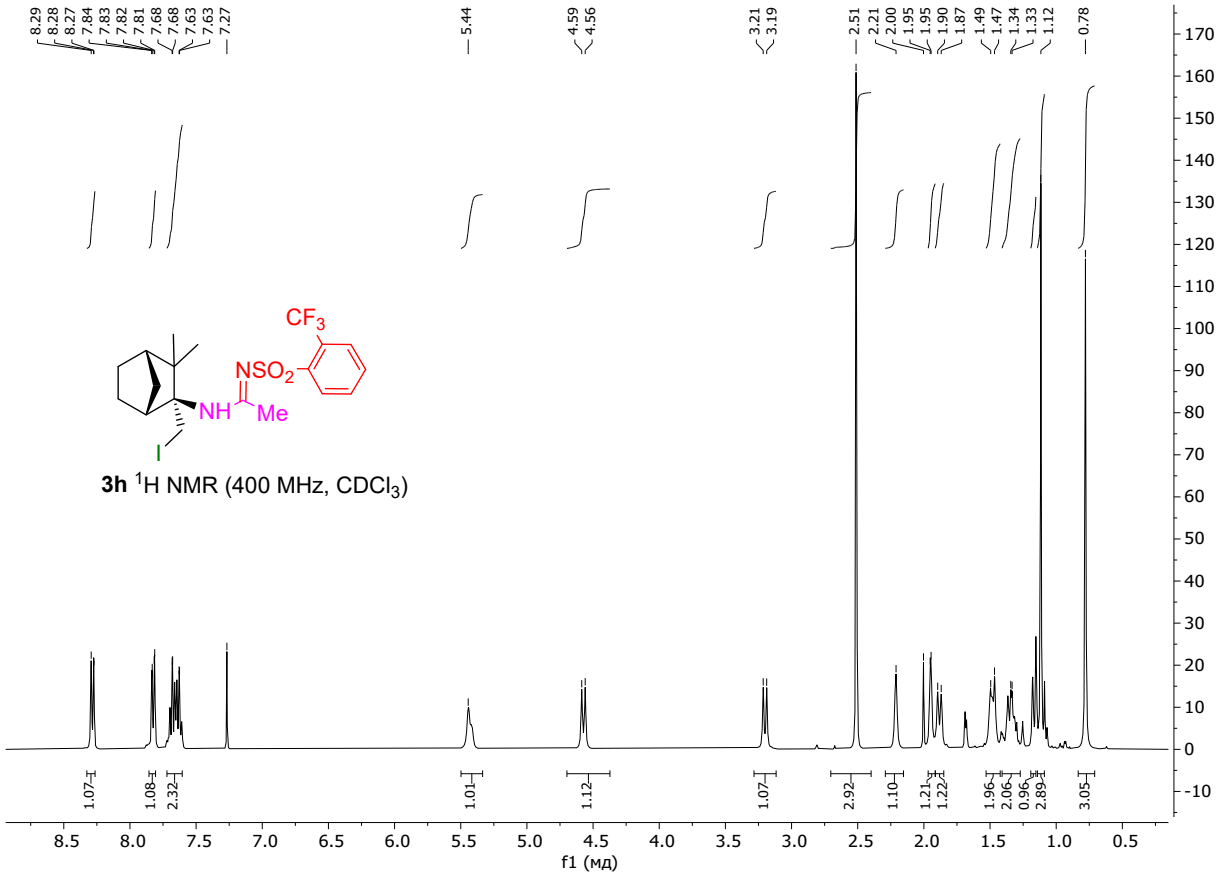


Figure S27. ^{13}C NMR spectrum of compound **3h**

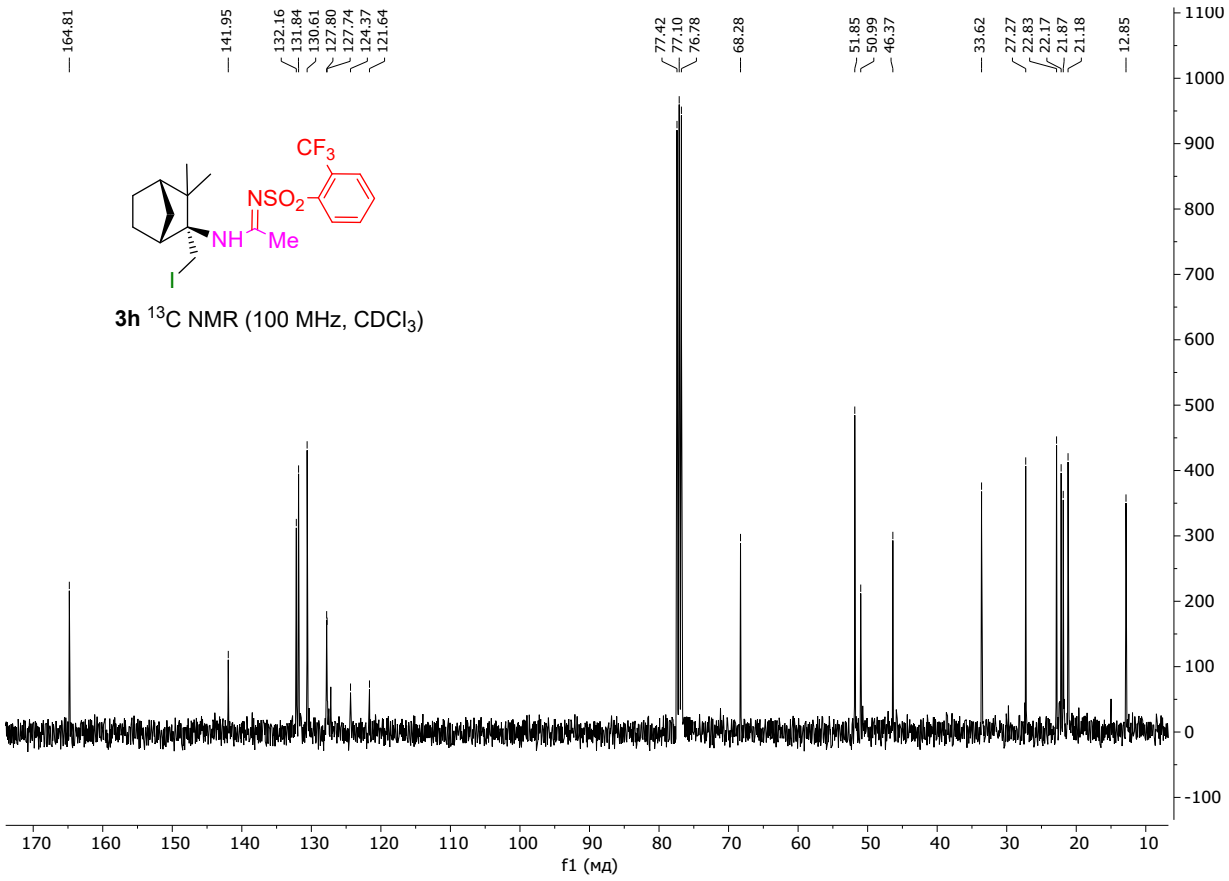


Figure S28. ^{19}F NMR spectrum of compound **3h**

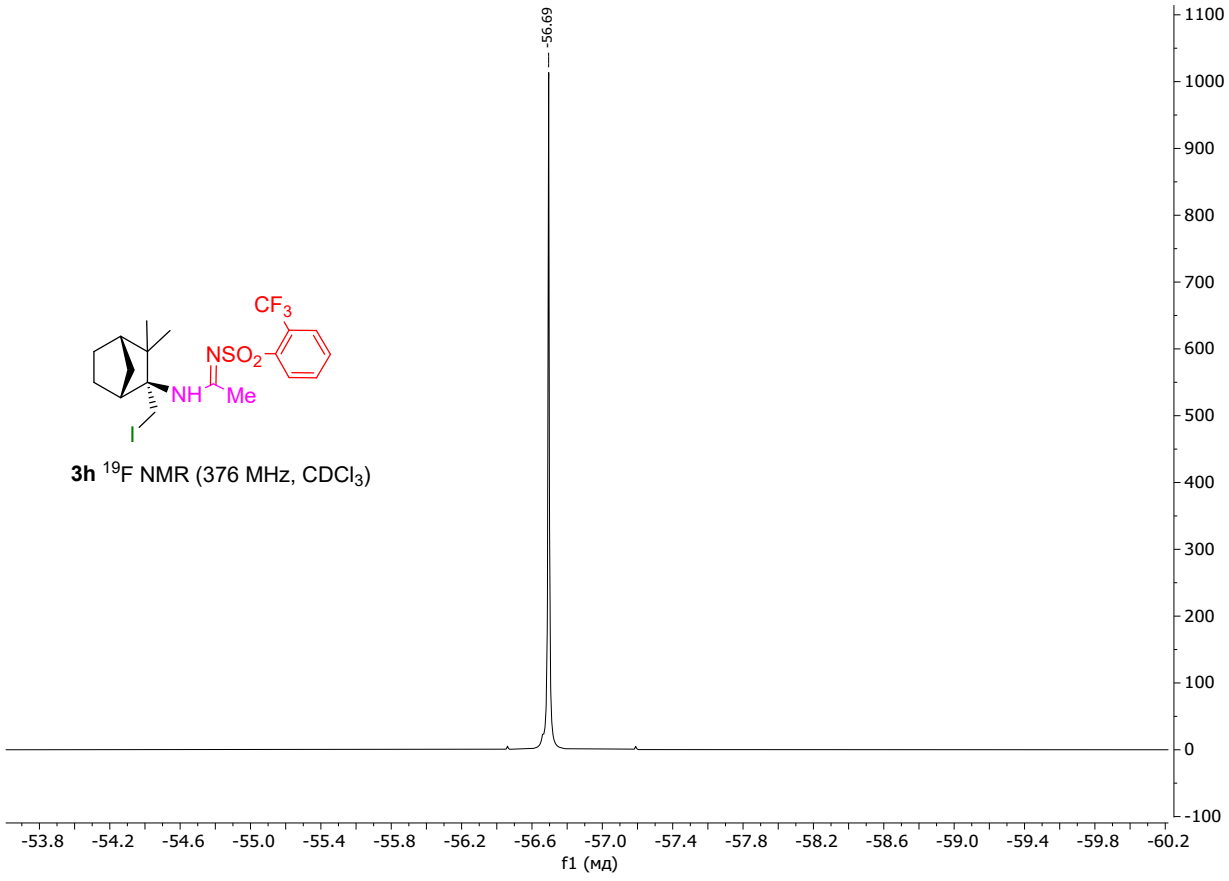


Figure S29. ^{1}H NMR spectrum of compound **3i**

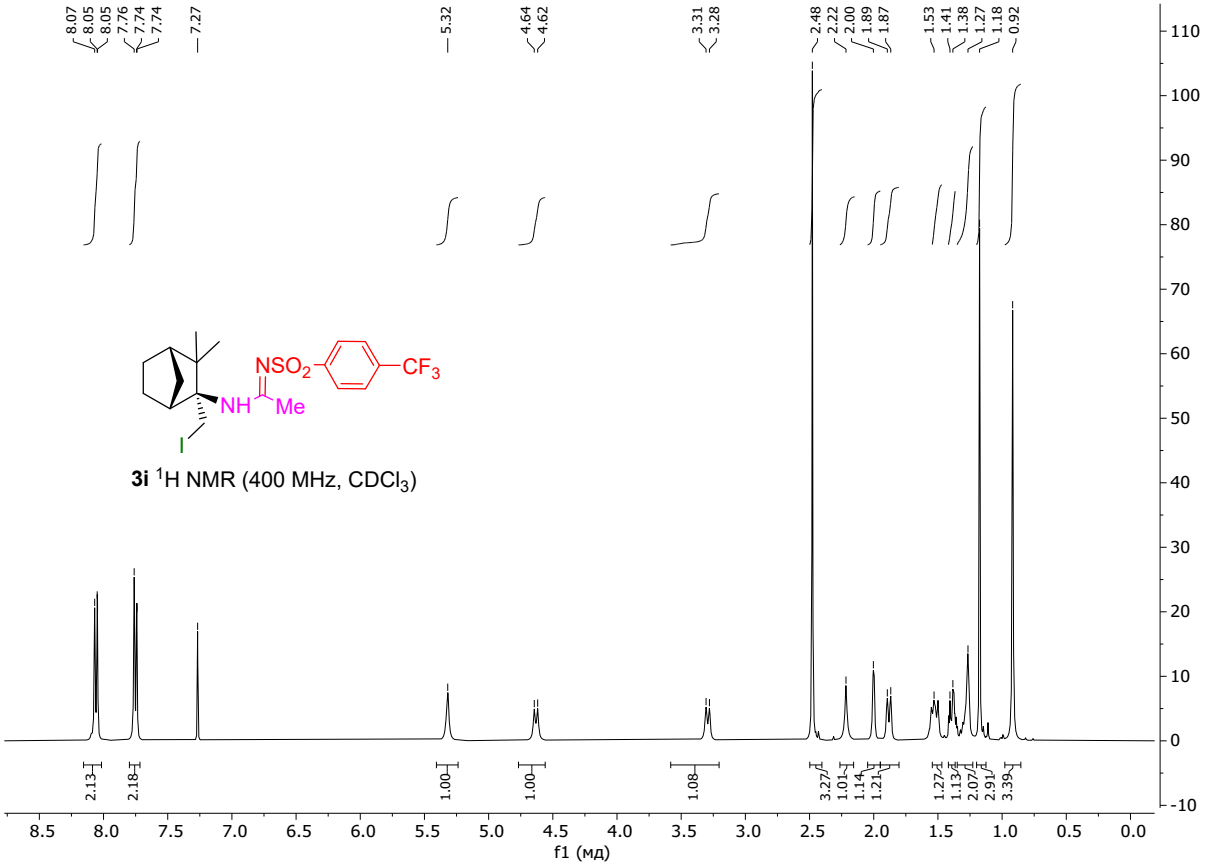


Figure S30. ^{13}C NMR spectrum of compound **3i**

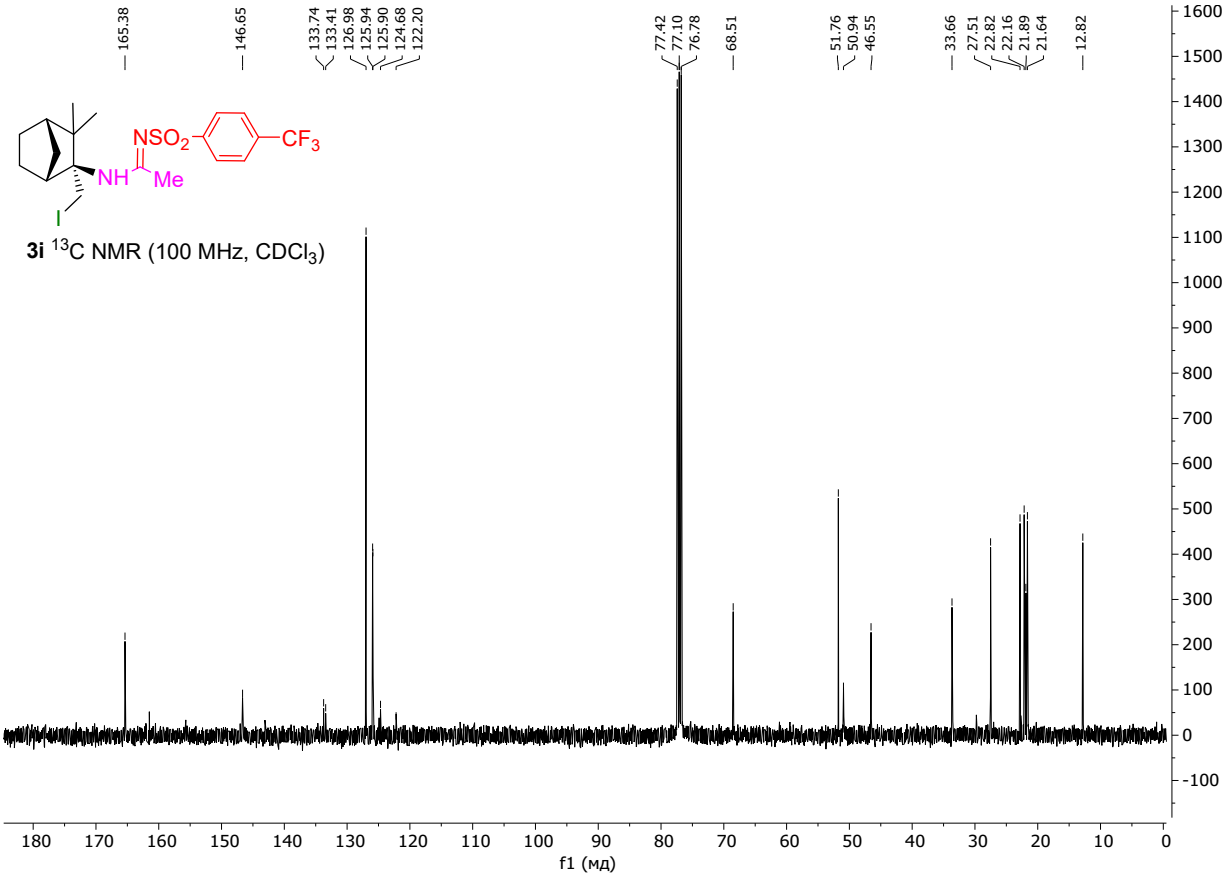


Figure S31. ^{19}F NMR spectrum of compound **3i**

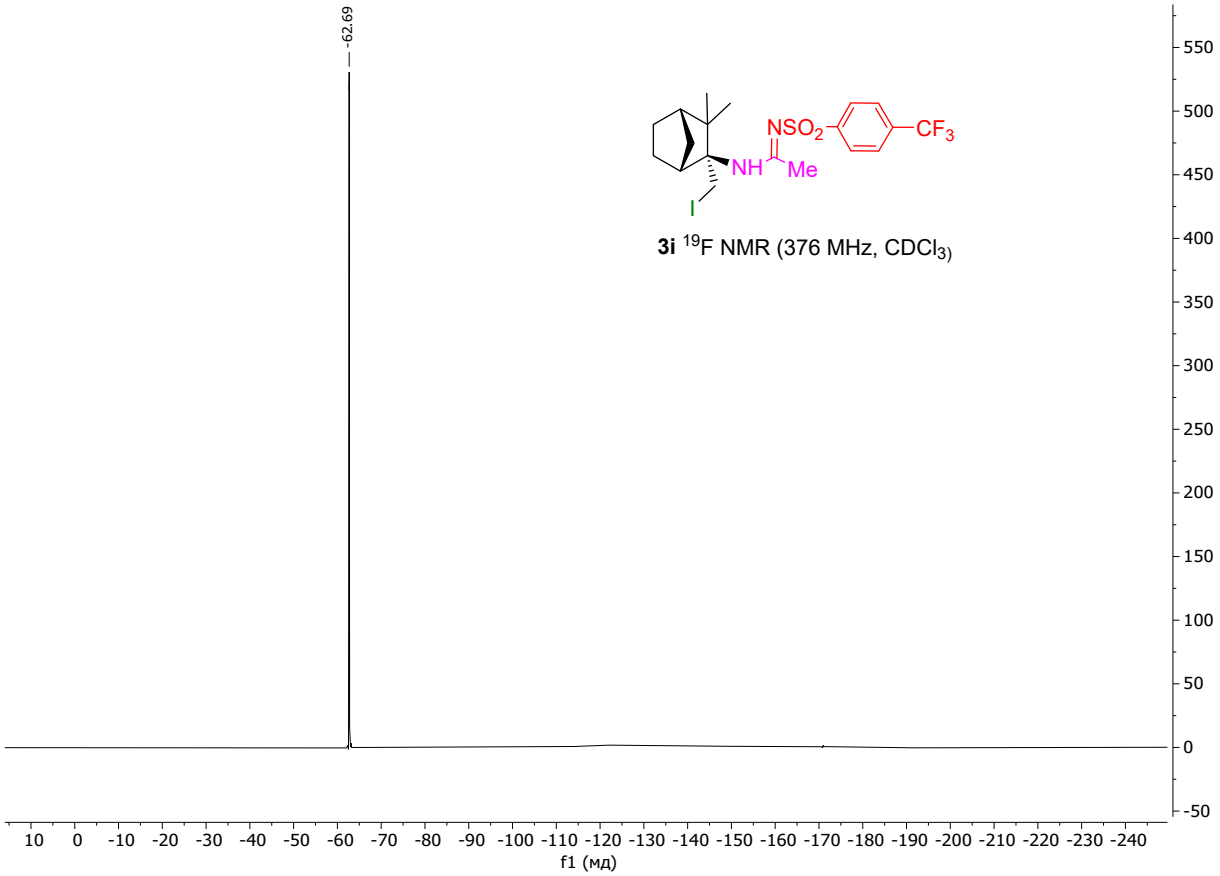


Figure S32. ^{1}H NMR spectrum of compound **3j**

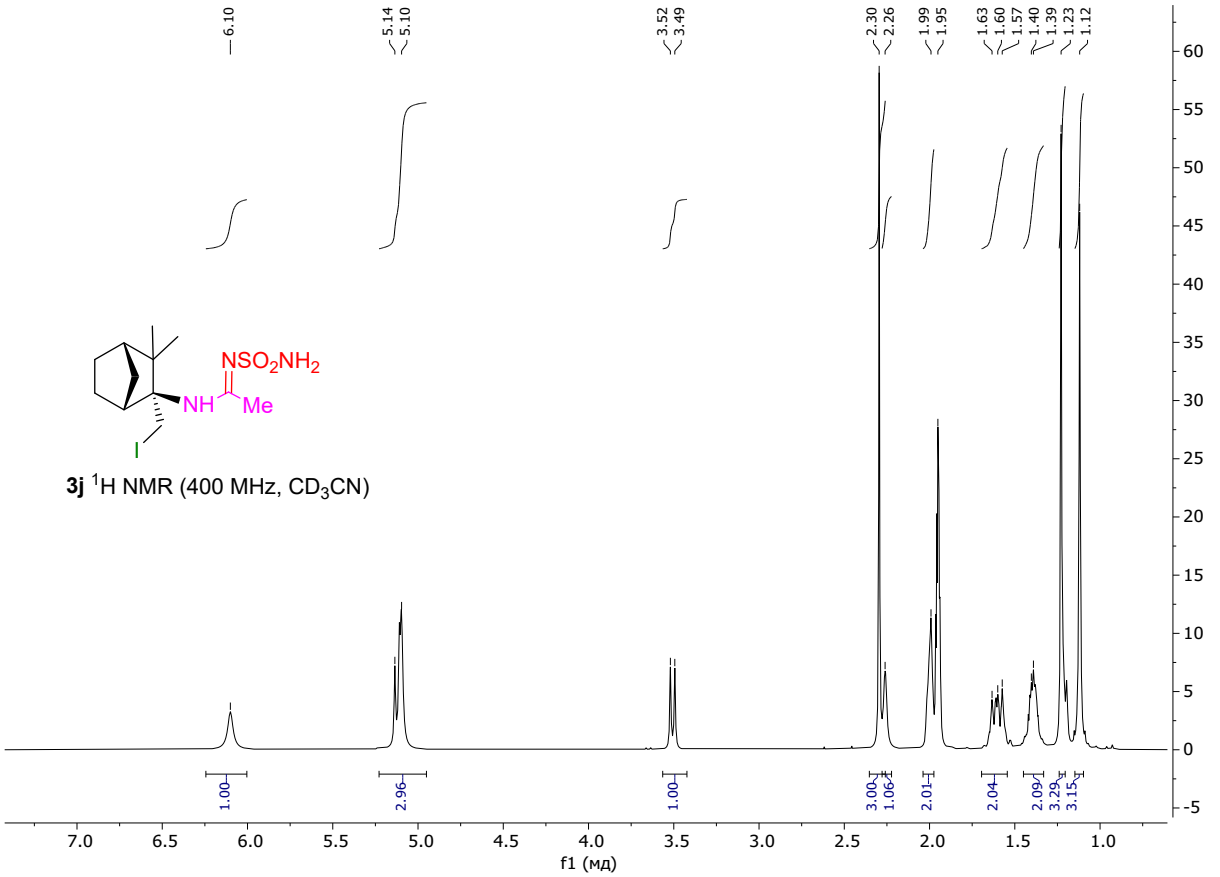


Figure S33. ^{13}C NMR spectrum of compound **3j**

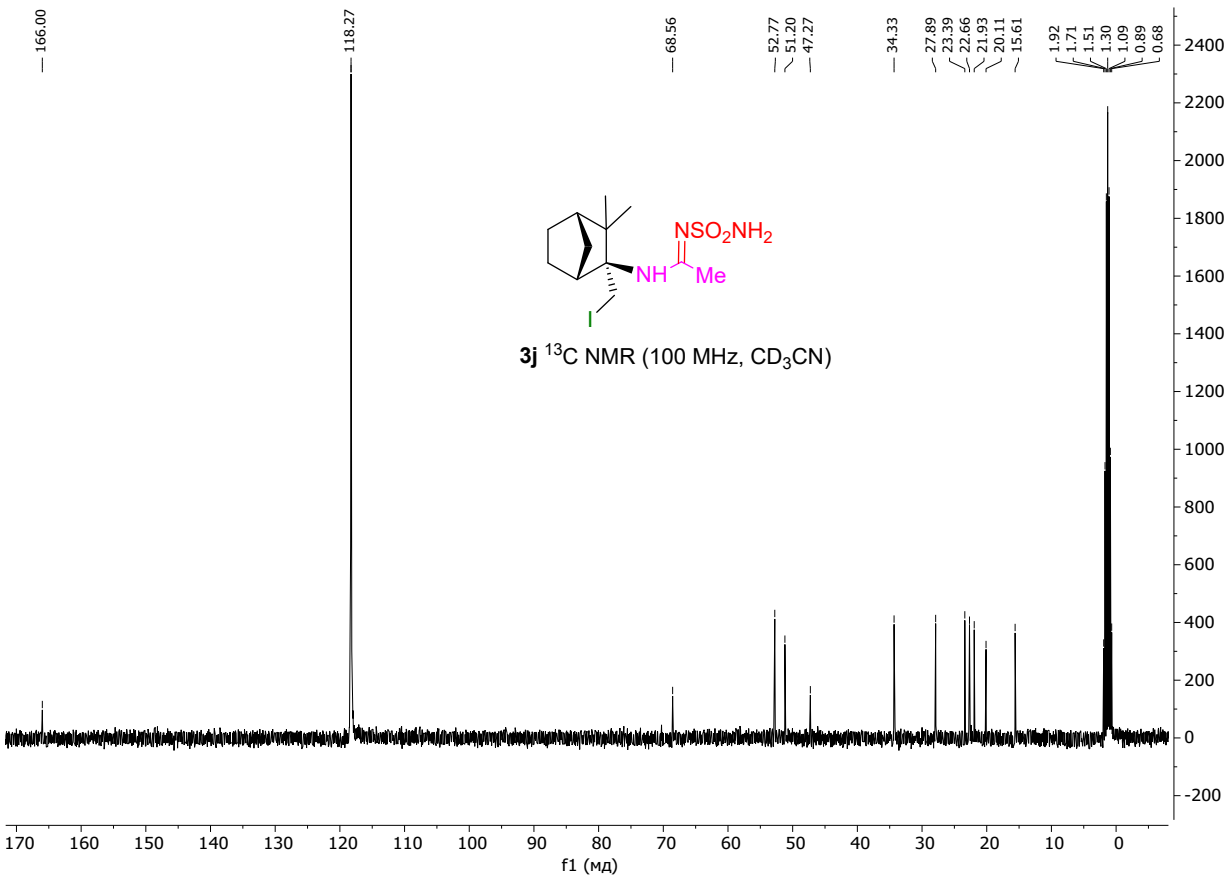
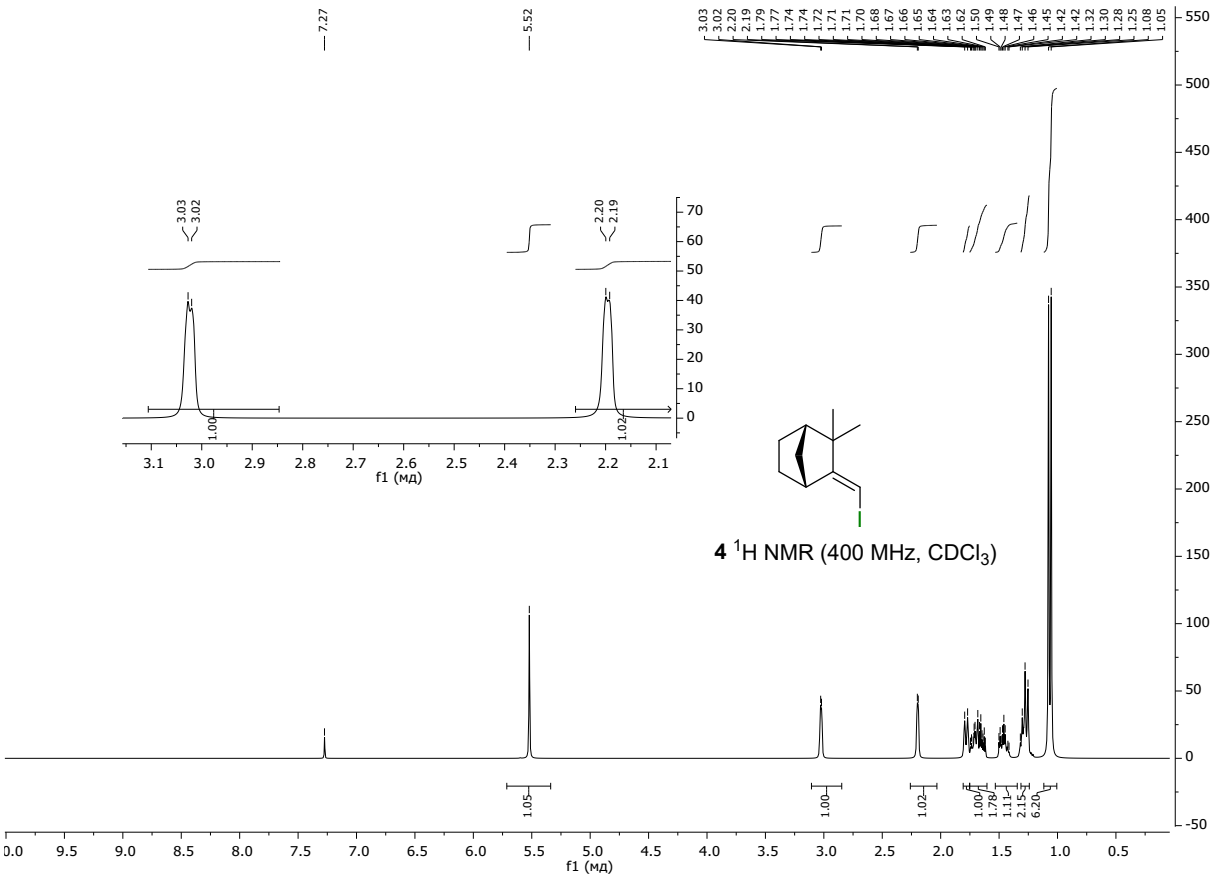


Figure S34. ^{1}H NMR spectrum of compound **4**



4 ^{1}H NMR (400 MHz, $CDCl_3$)

Figure S35. ^{13}C NMR spectrum of compound **4**

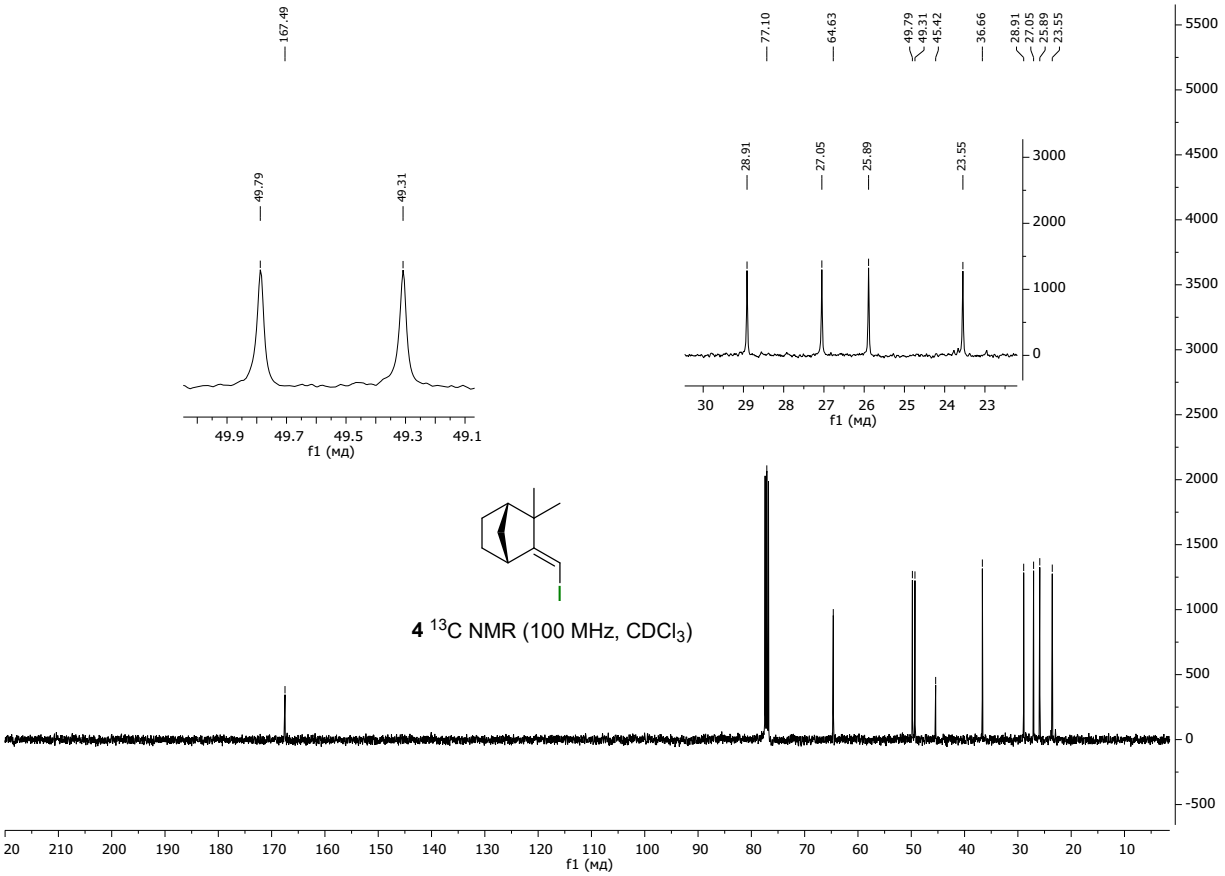
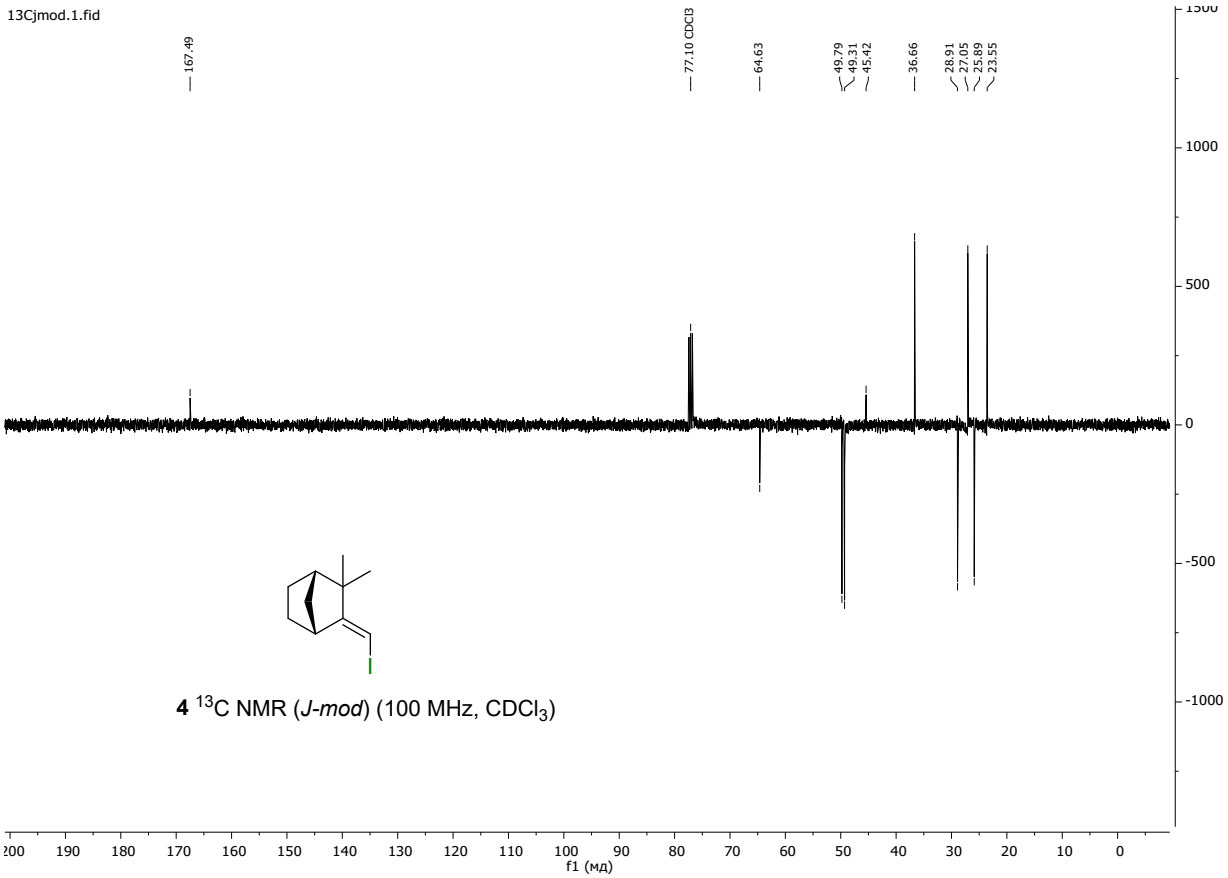
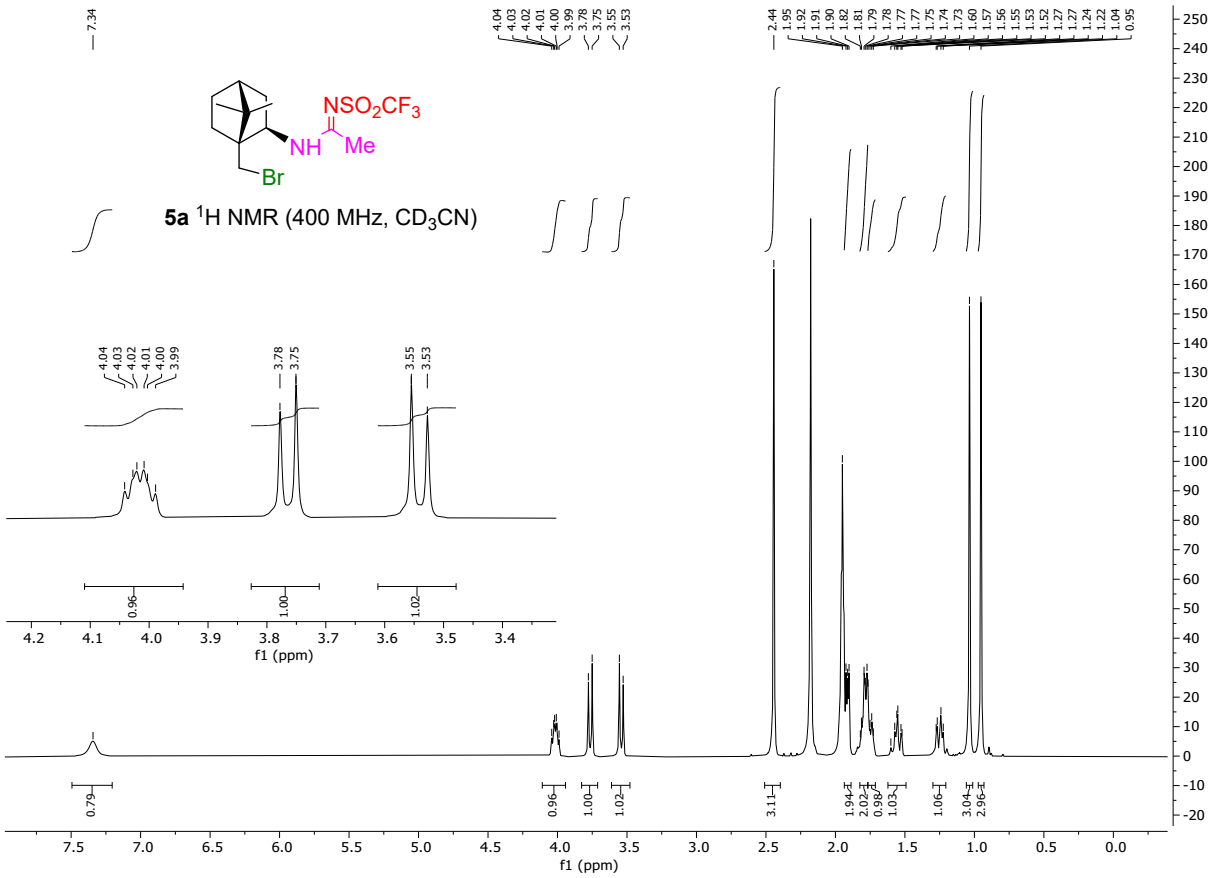


Figure S36. ^{13}C NMR *(J-mod)* spectrum of compound **4**



4 ^{13}C NMR (*J-mod*) (100 MHz, $CDCl_3$)

Figure S37. ^{1}H NMR spectrum of compound **5a**



5a ^{1}H NMR (400 MHz, CD_3CN)

Figure S38. ^{13}C NMR spectrum of compound **5a**

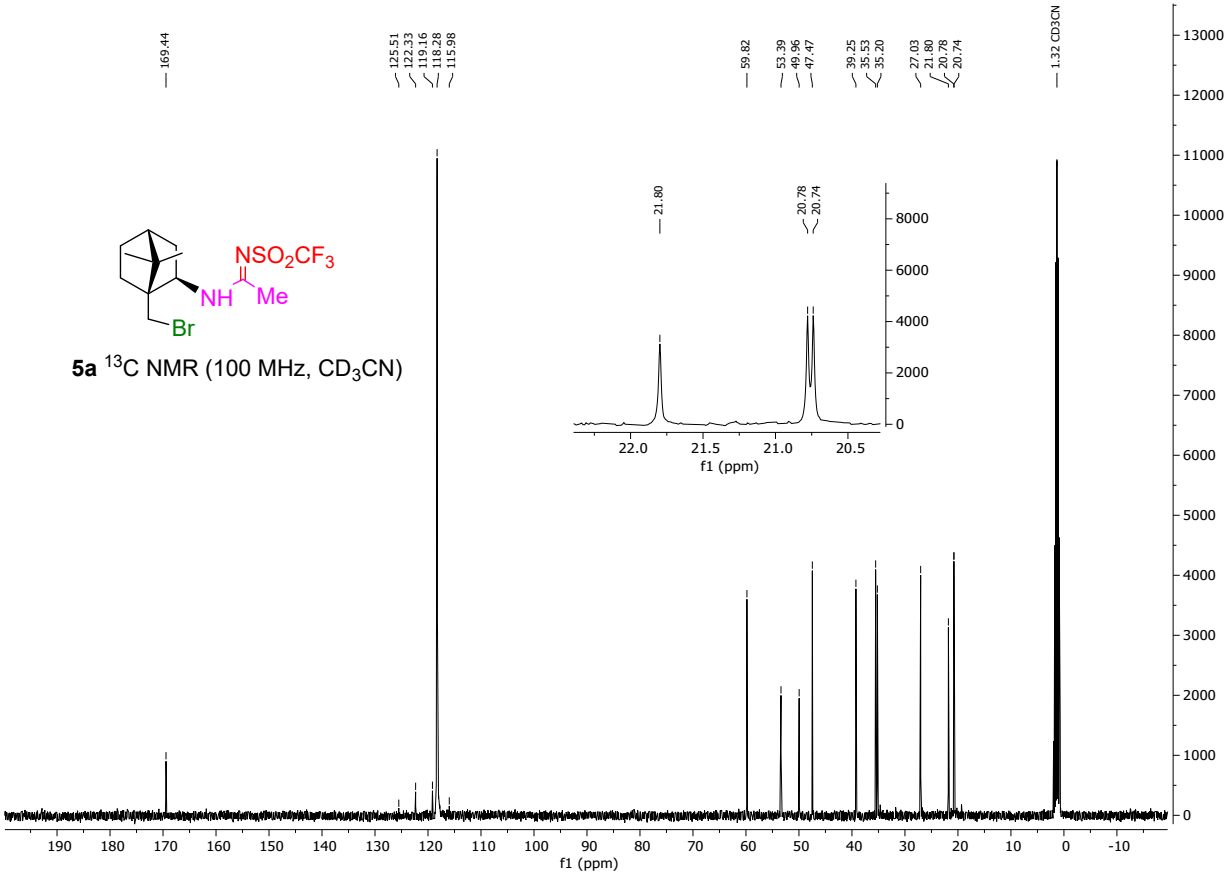


Figure S39. ^{13}C NMR *(J-mod)* spectrum of compound **5a**

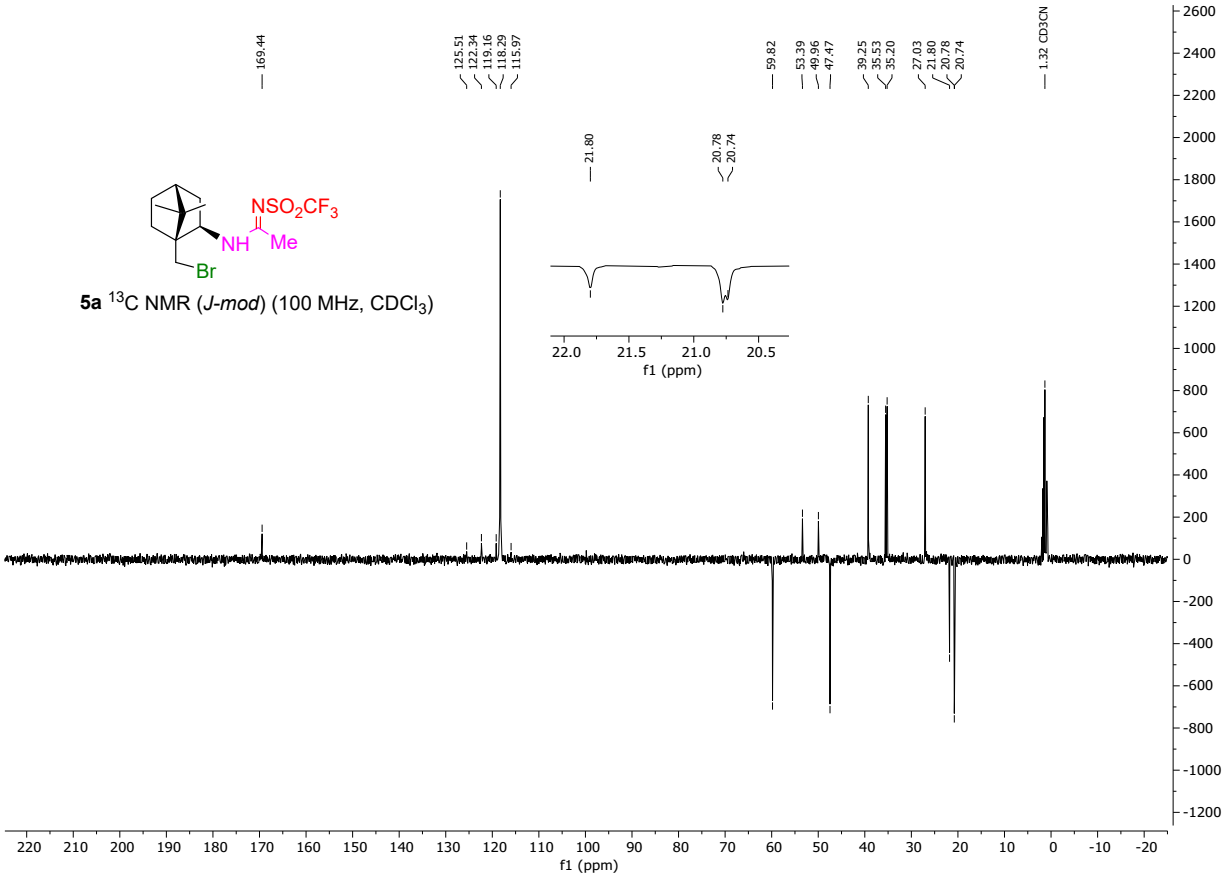


Figure S40. ^{19}F NMR spectrum of compound **5a**

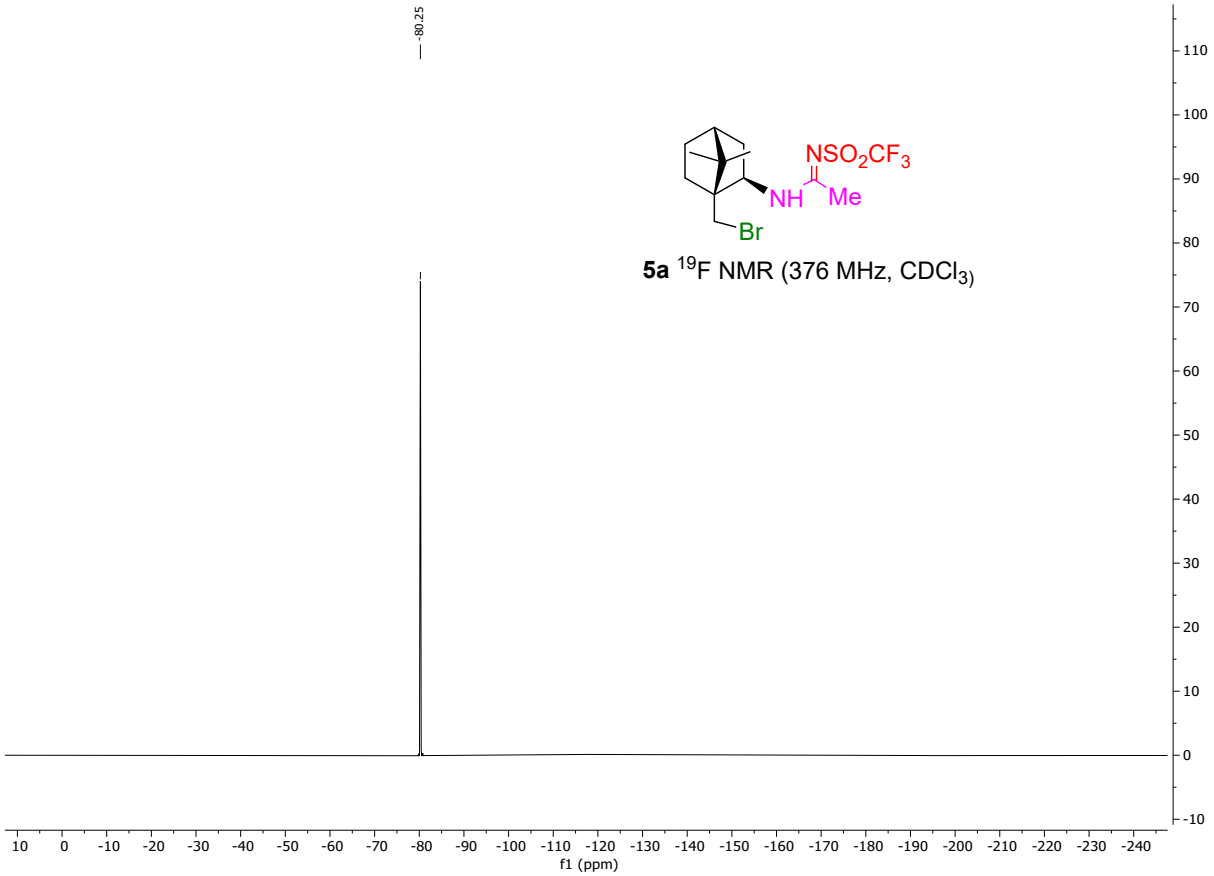


Figure S41. ^{1}H NMR spectrum of compound **5c**

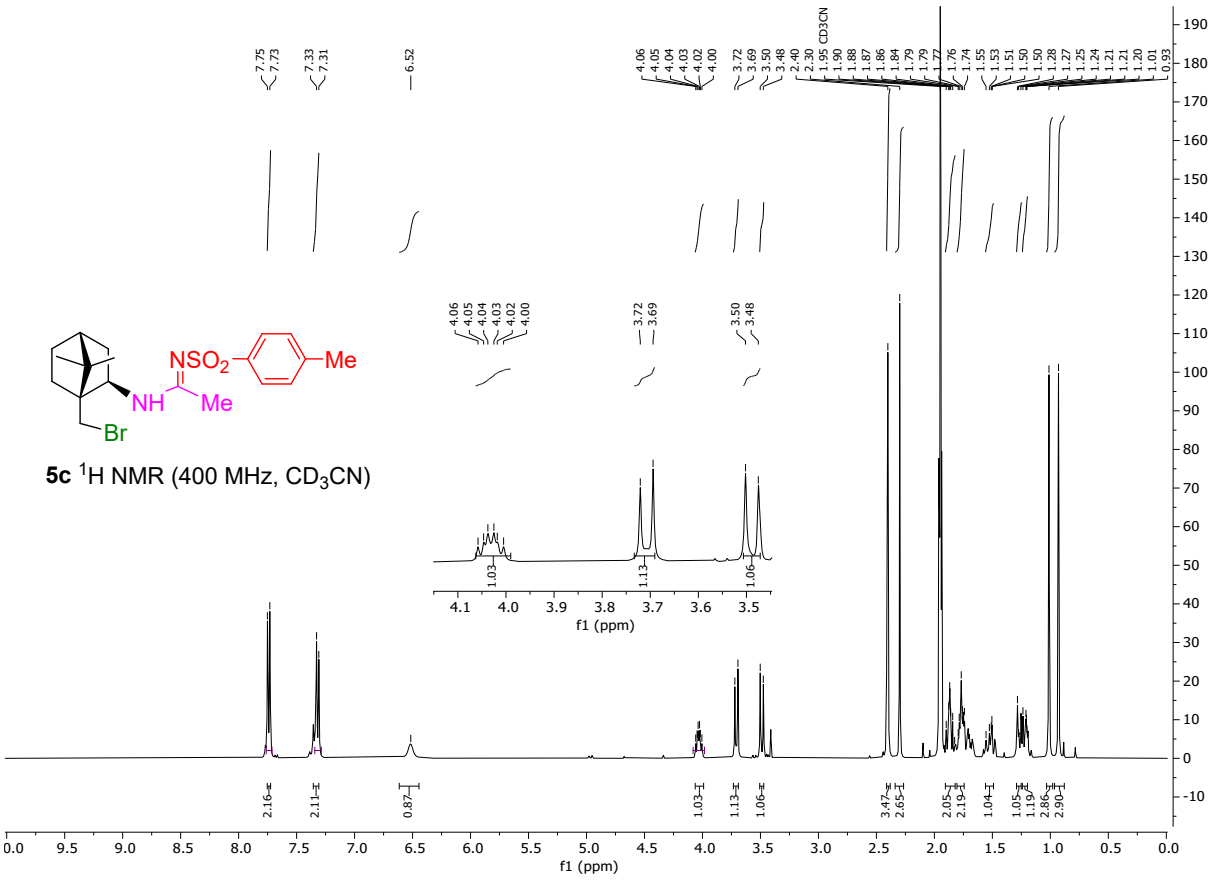


Figure S42. ^{13}C NMR spectrum of compound **5c**

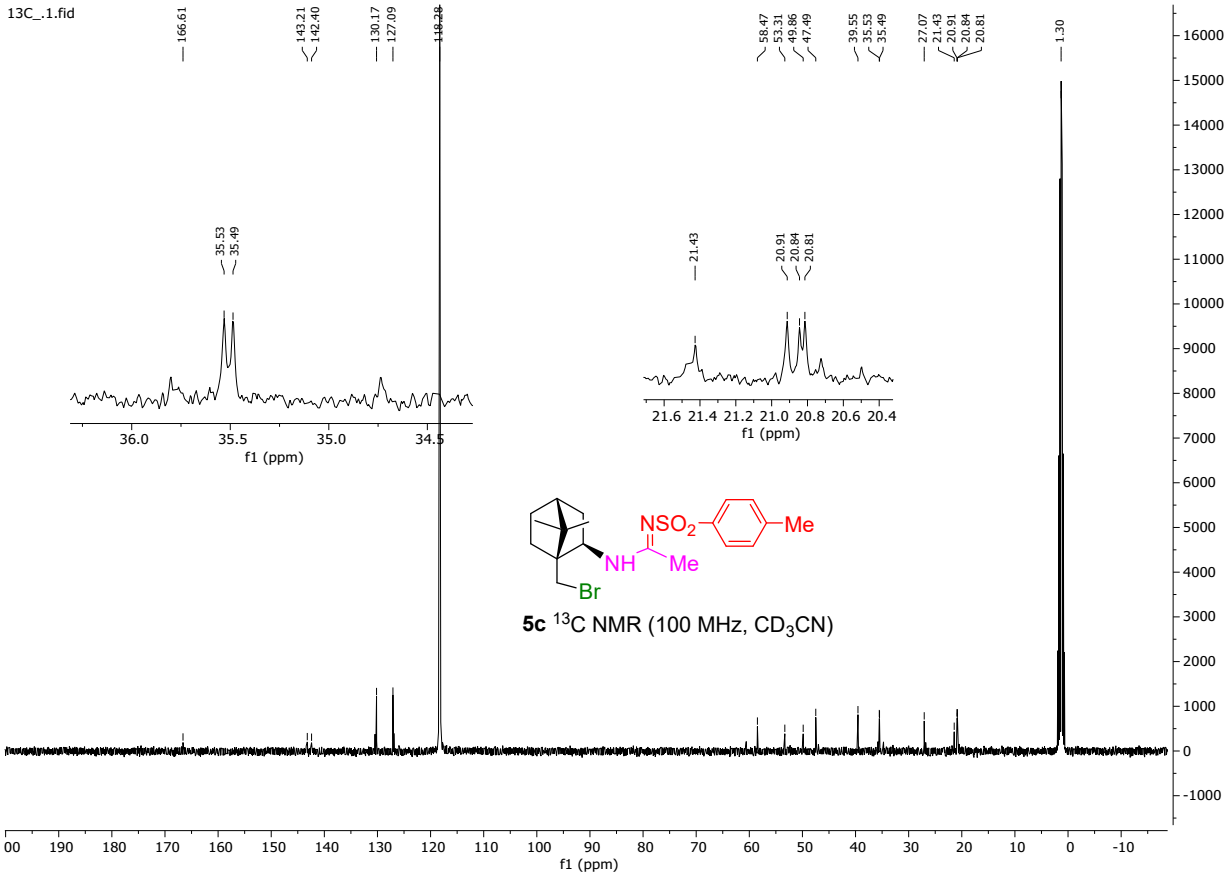


Figure S43. ^{1}H NMR spectrum of compound **5e**

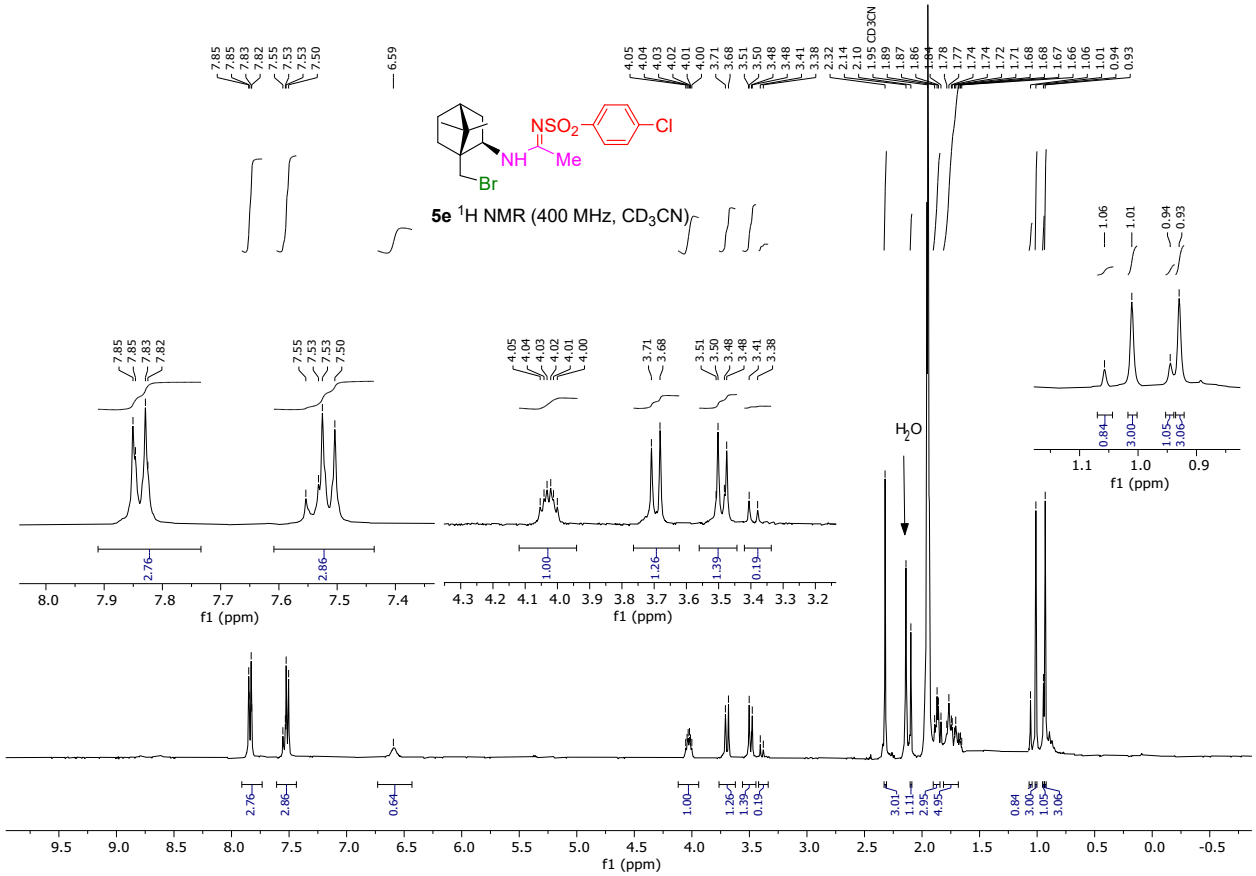


Figure S44. ^{13}C NMR spectrum of compound **5e**

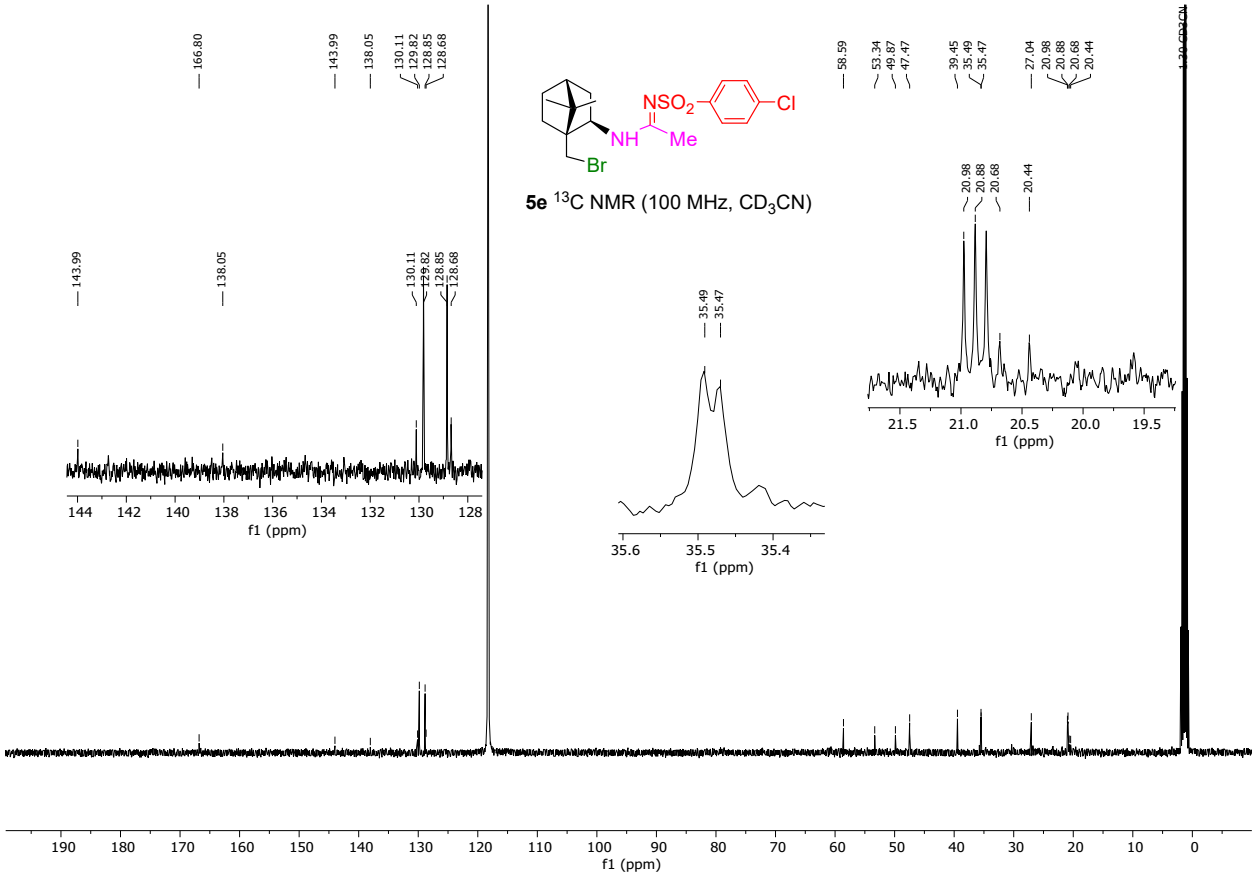


Figure S45. ^{1}H NMR spectrum of compound **5h**

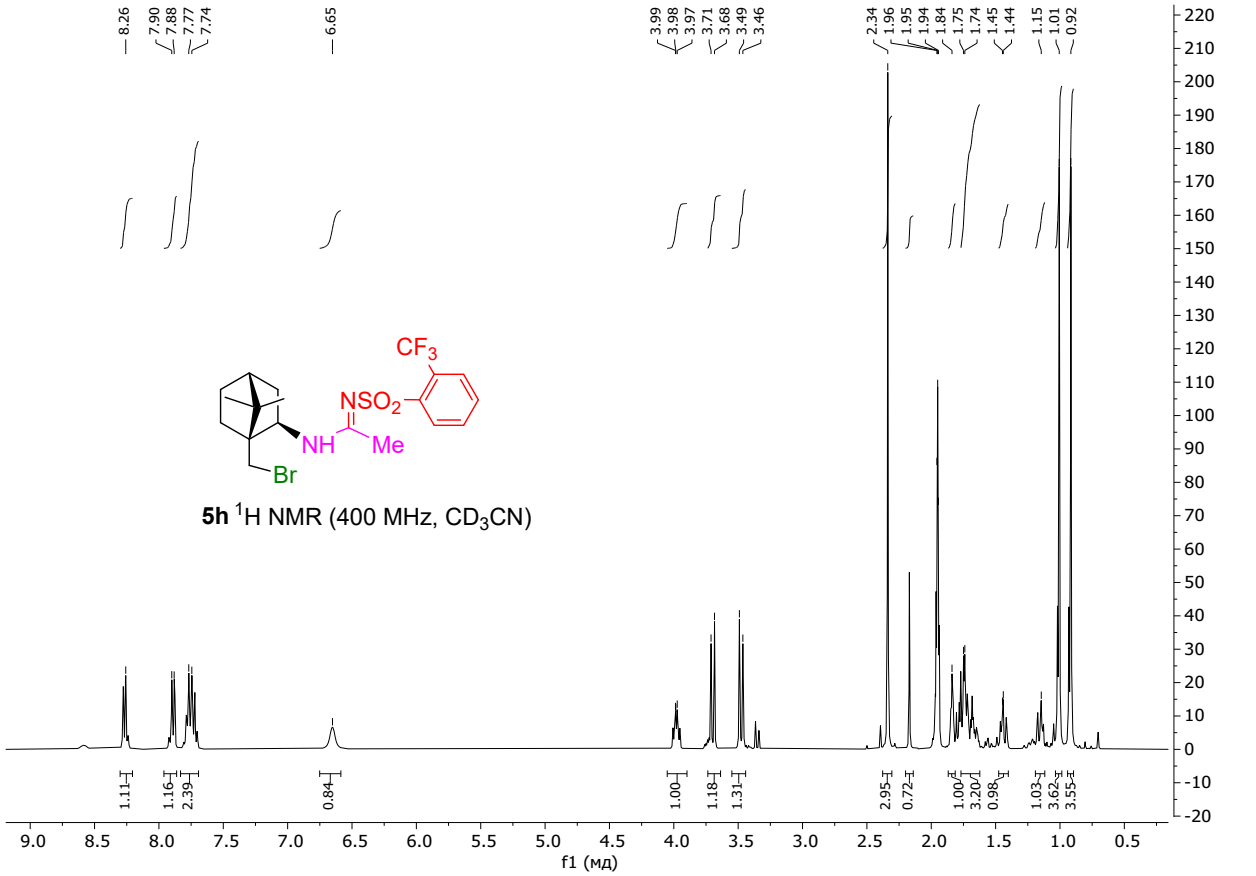


Figure S46. ^{13}C NMR spectrum of compound **5h**

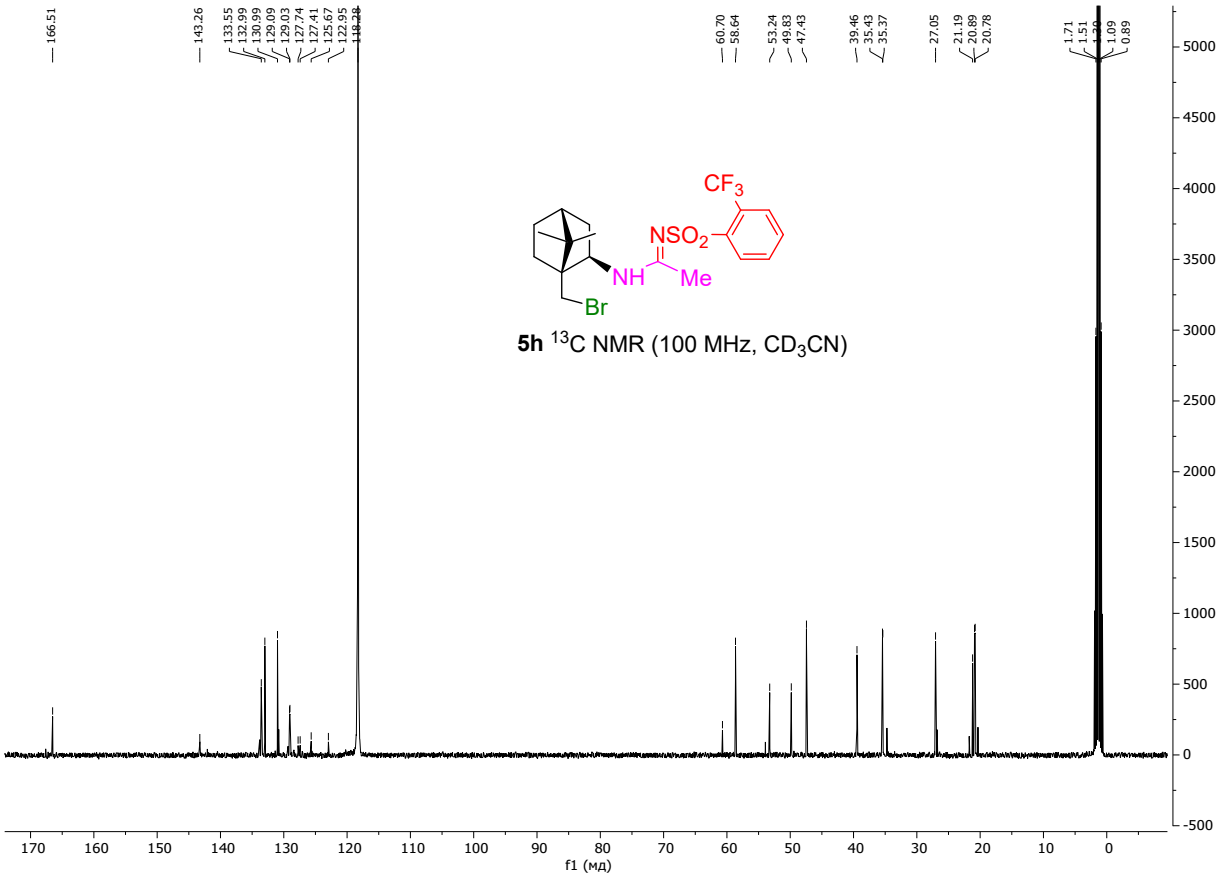


Figure S47. ^{19}F NMR spectrum of compound **5h**

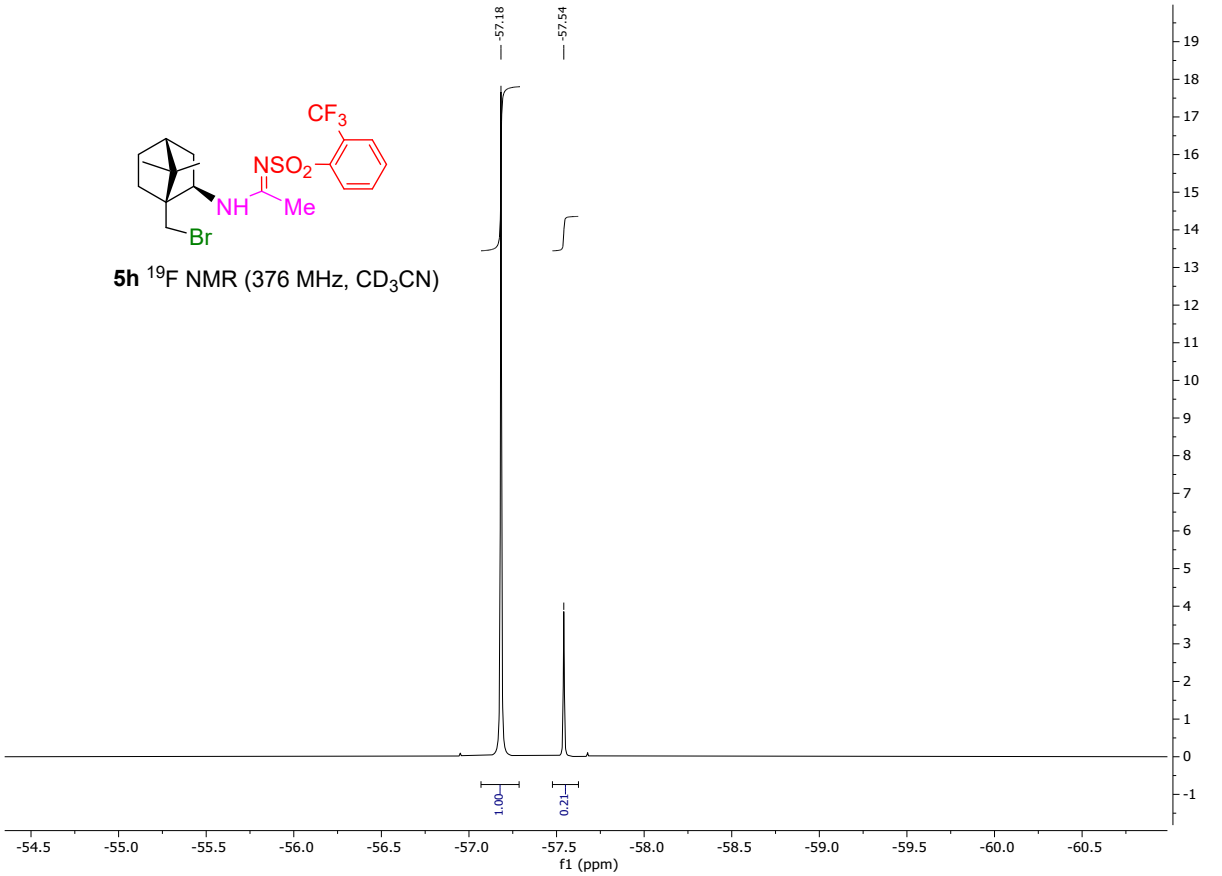
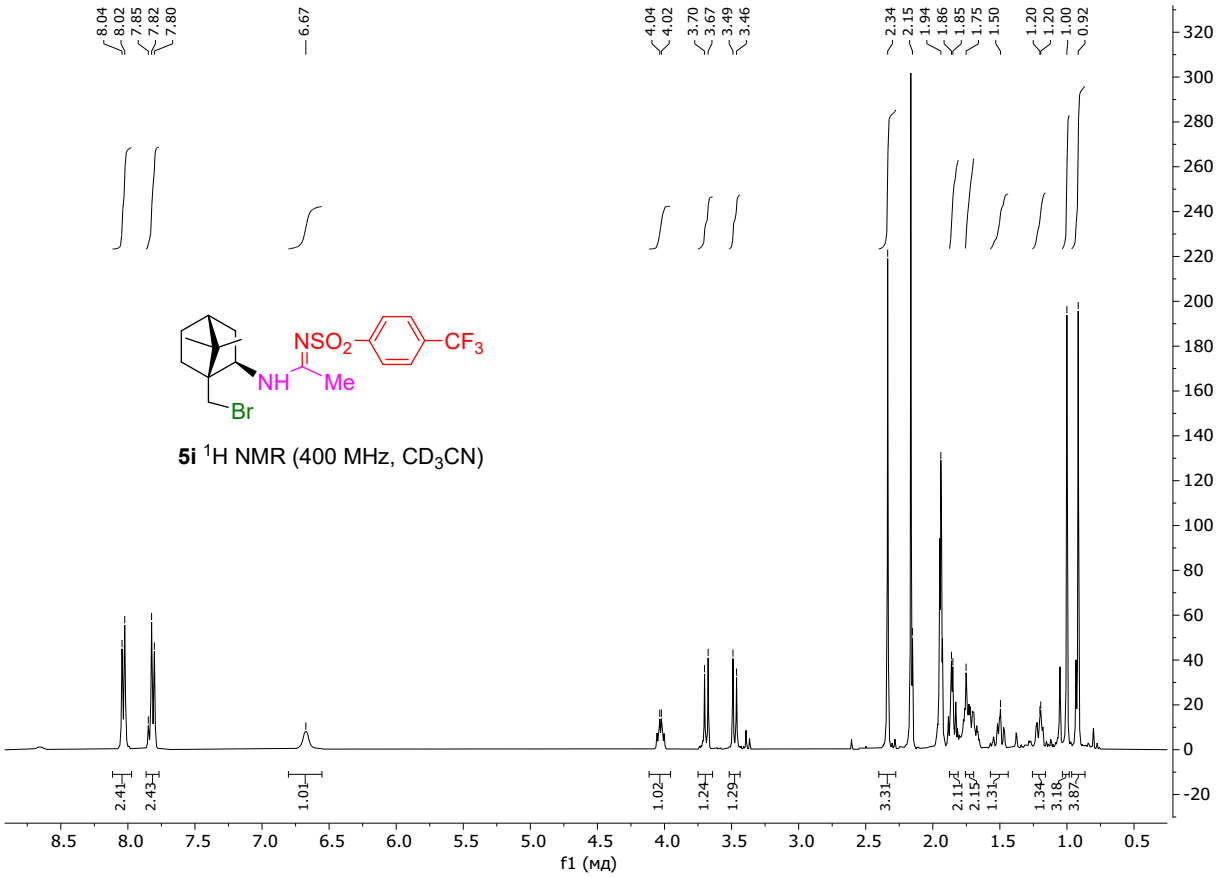
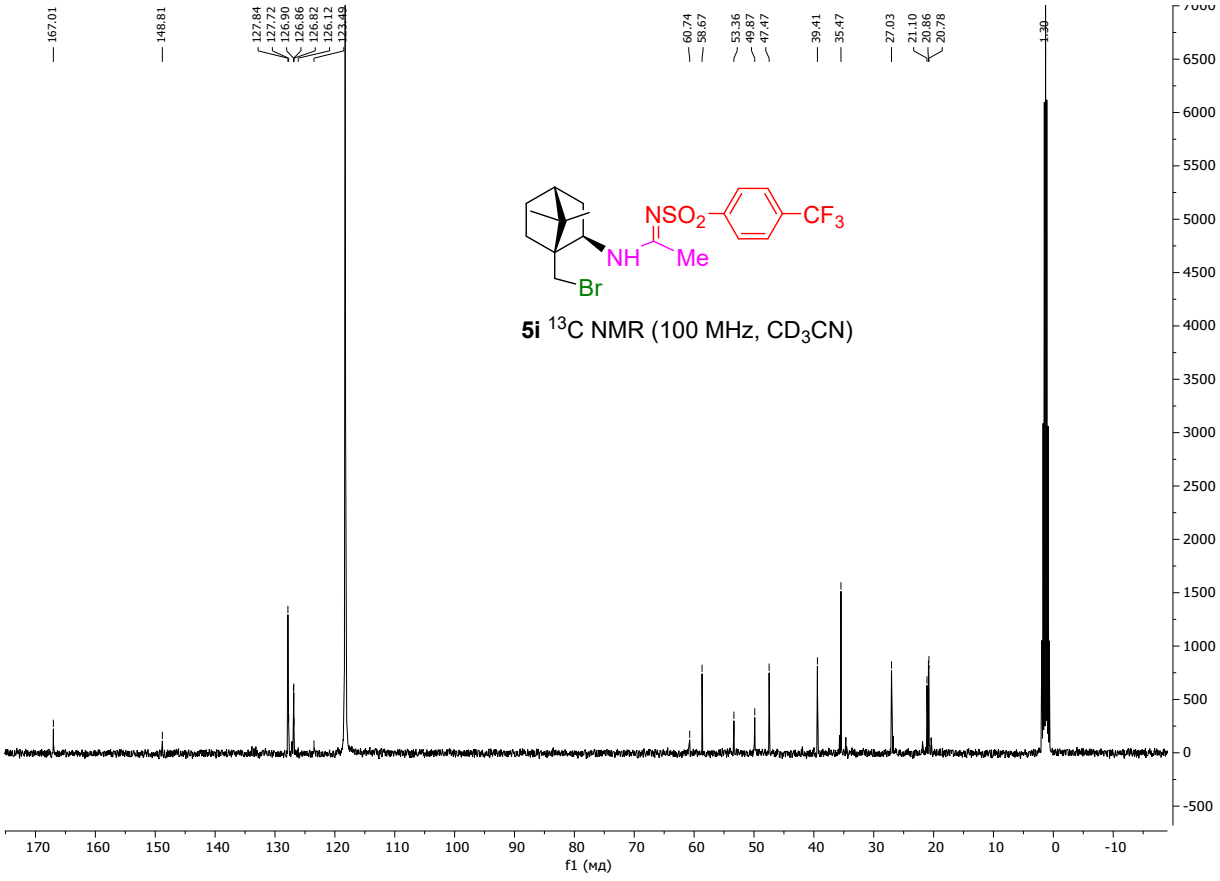


Figure S48. ^{1}H NMR spectrum of compound **5i**



5i ^{1}H NMR (400 MHz, CD_3CN)

Figure S49. ^{13}C NMR spectrum of compound **5i**



5i ^{13}C NMR (100 MHz, CD_3CN)

Figure S50. ^{19}F NMR spectrum of compound **5i**

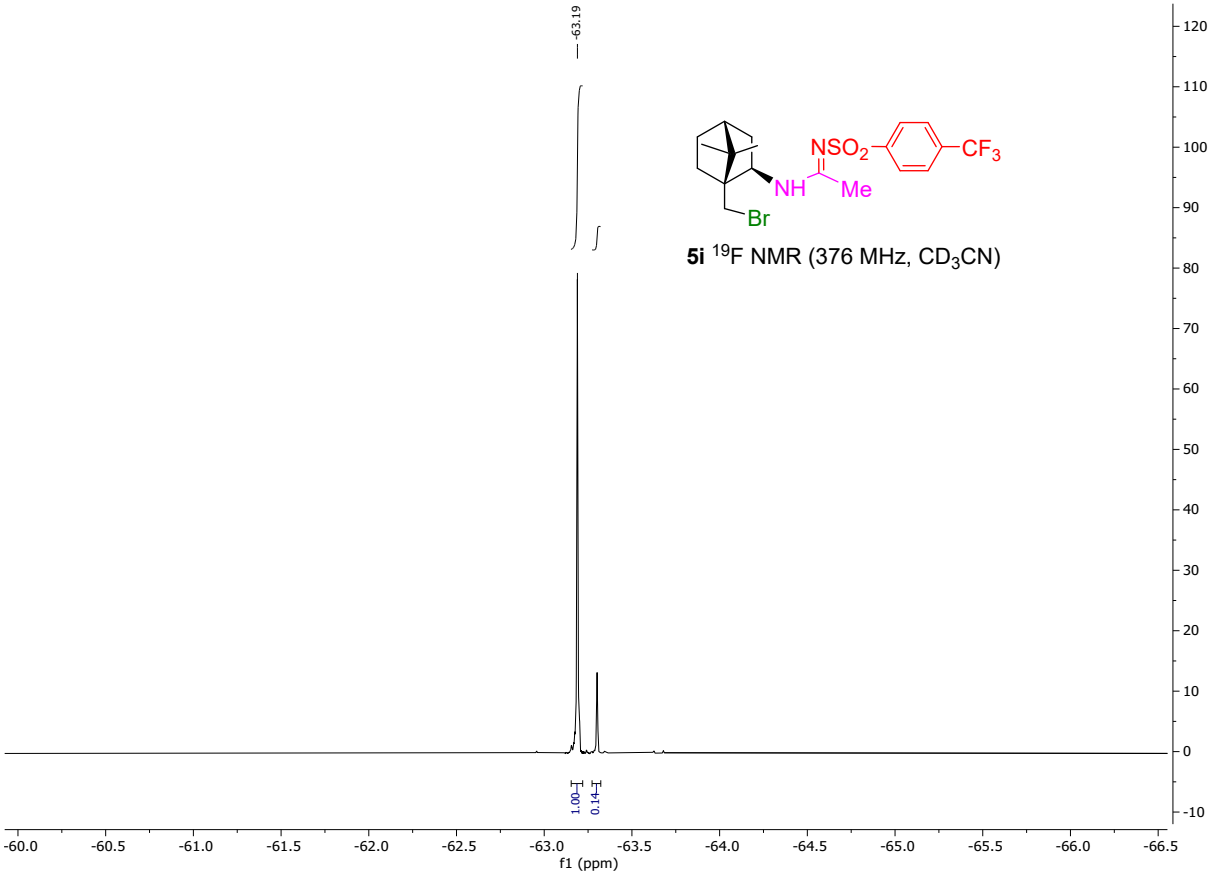


Figure S51. ^{1}H NMR spectrum of compound **6**

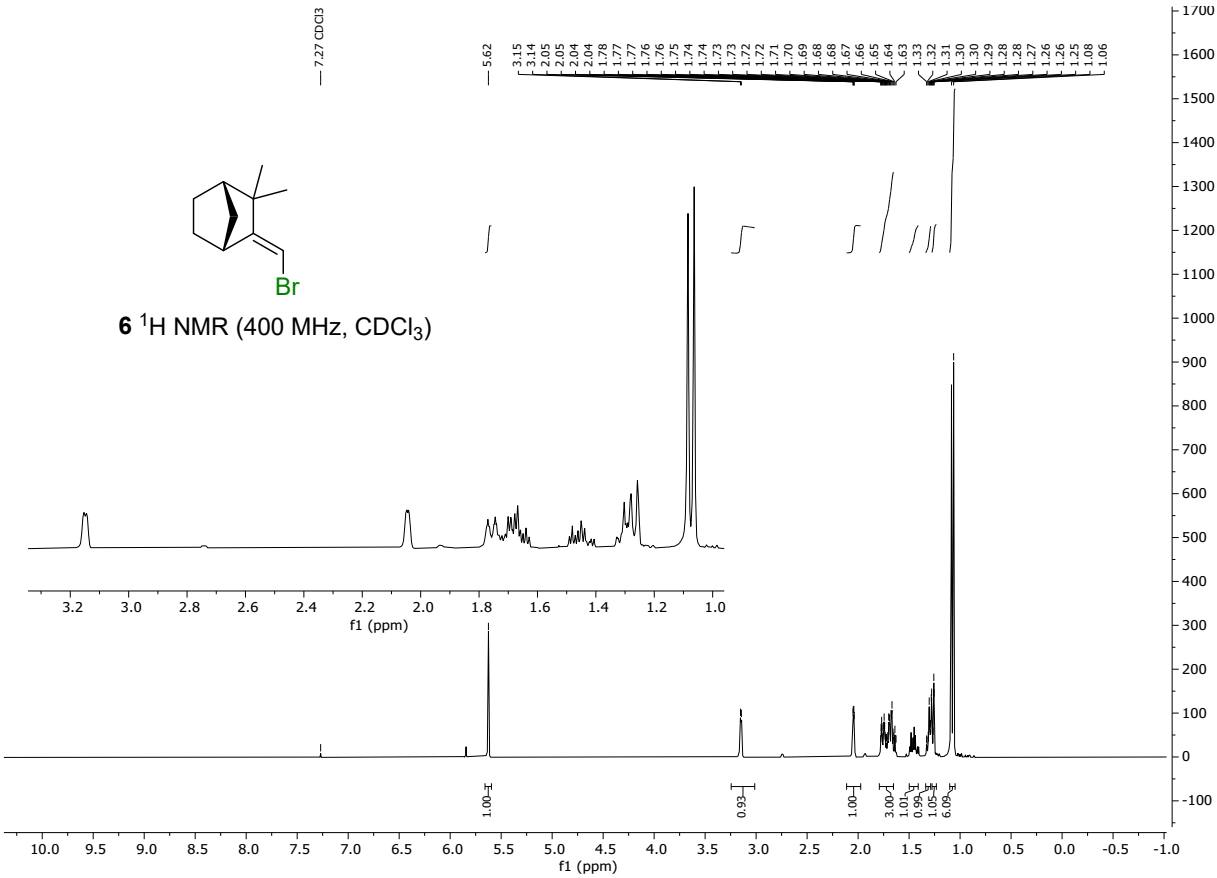
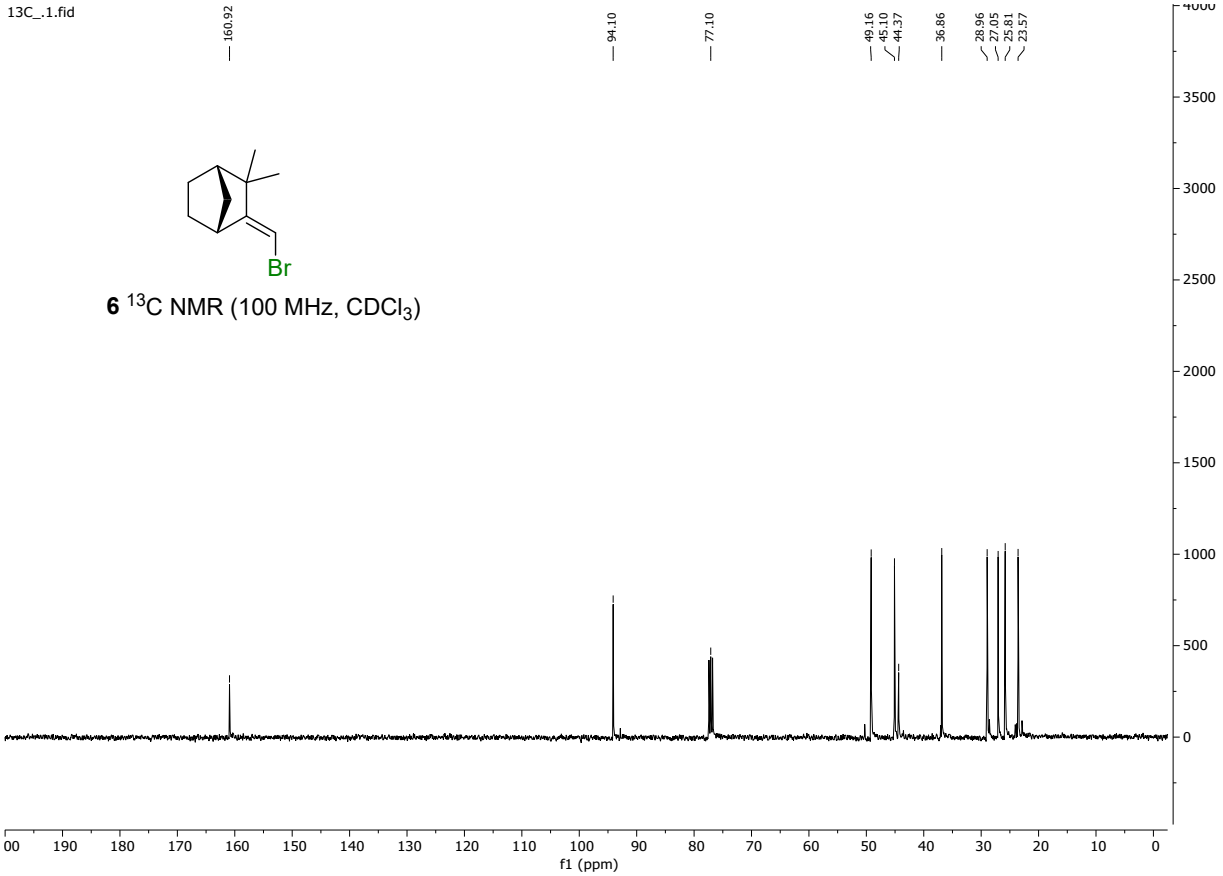
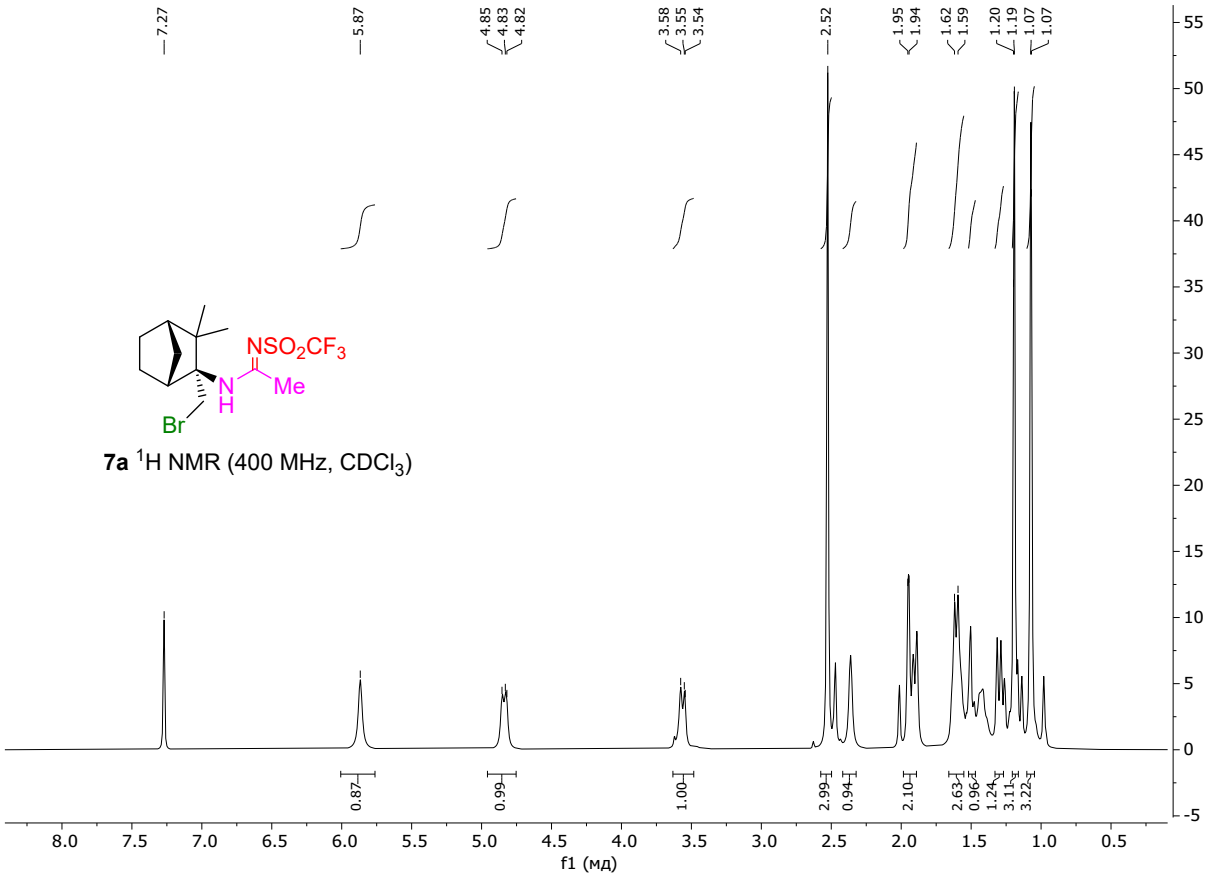


Figure S52. ^{13}C NMR spectrum of compound **6**



6 ^{13}C NMR (100 MHz, $CDCl_3$)

Figure S53. ^{1}H NMR spectrum of compound **7a**



7a ^{1}H NMR (400 MHz, $CDCl_3$)

Figure S54. ^{13}C NMR spectrum of compound **7a**

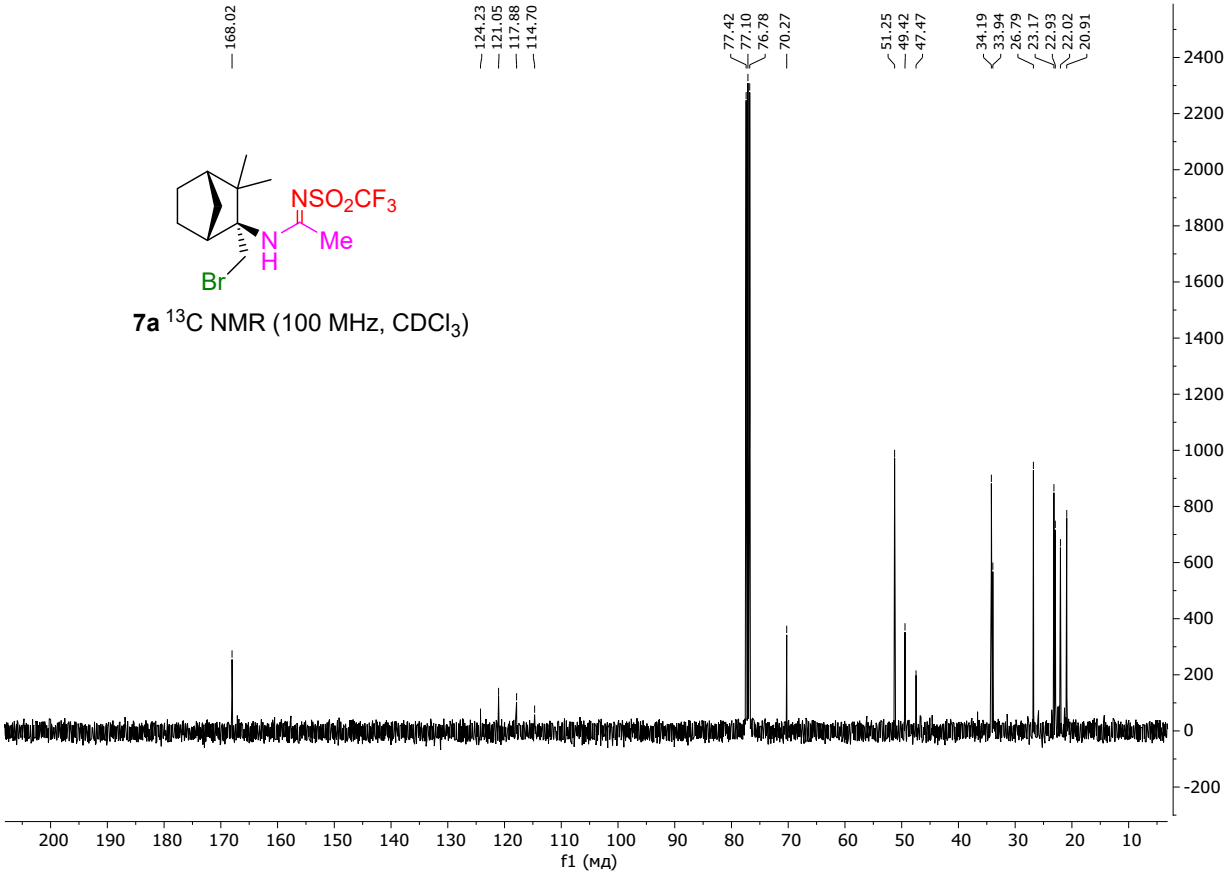


Figure S55. ^{19}F NMR spectrum of compound **7a**

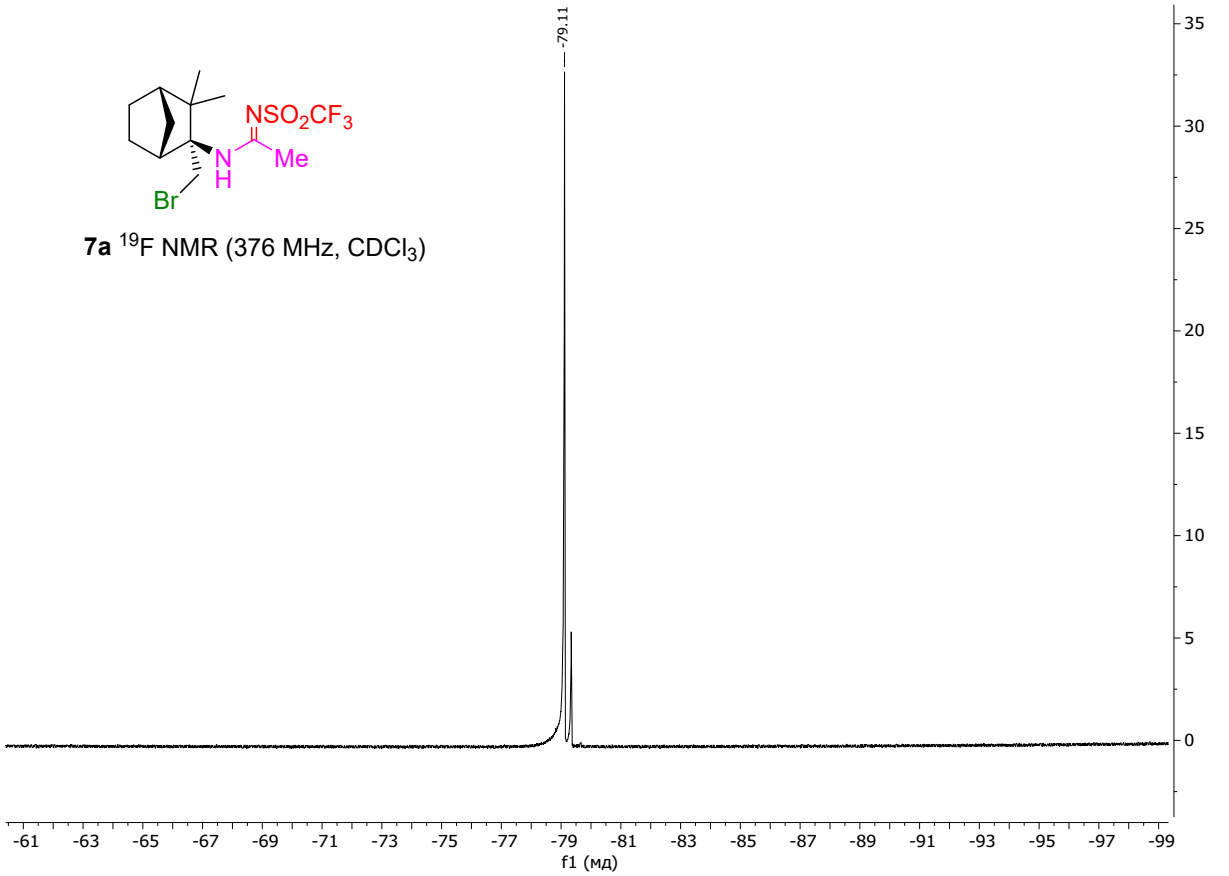


Figure S56. ^{1}H NMR spectrum of compound **7b**

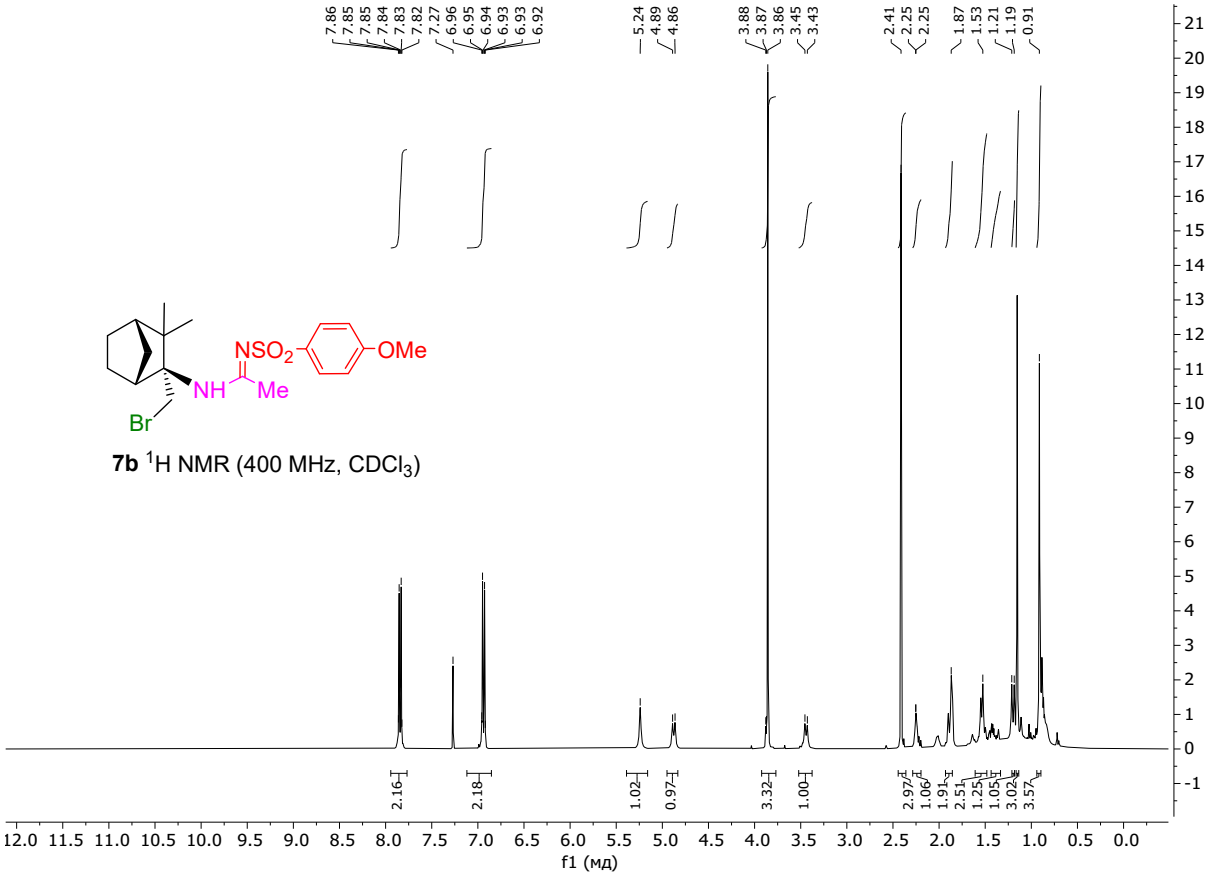


Figure S57. ^{13}C NMR spectrum of compound **7b**

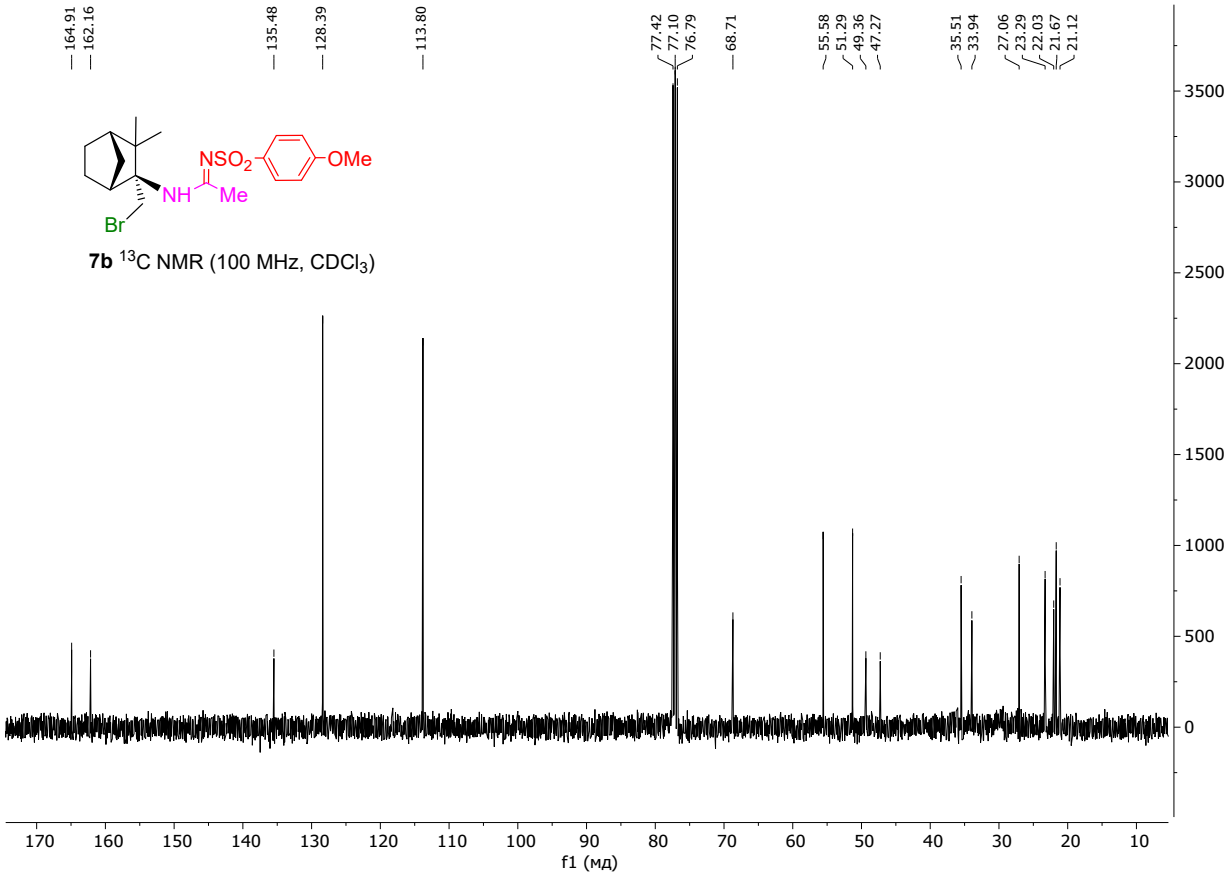


Figure S58. ^{1}H NMR spectrum of compound **7c**

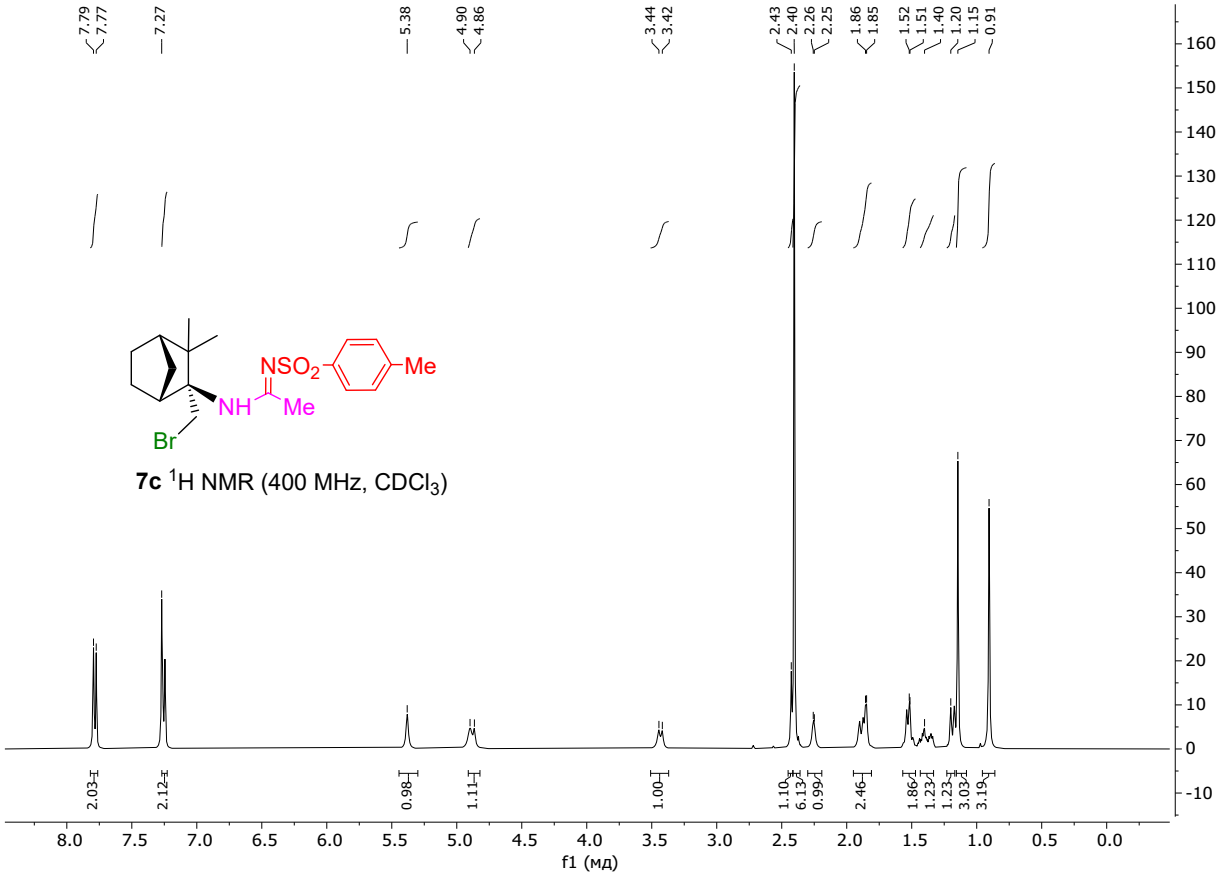


Figure S59. ^{13}C NMR spectrum of compound **7c**

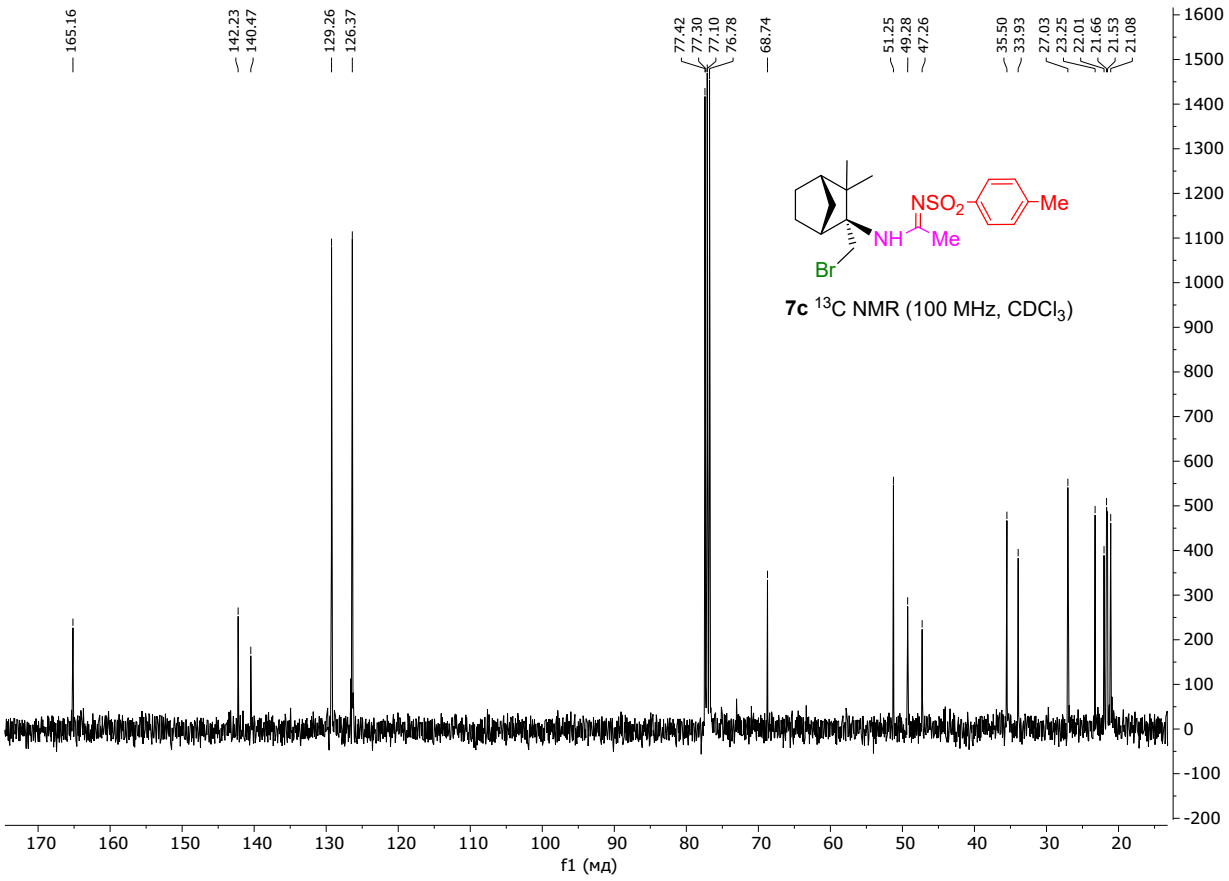


Figure S60. ^{1}H NMR spectrum of compound **7d**

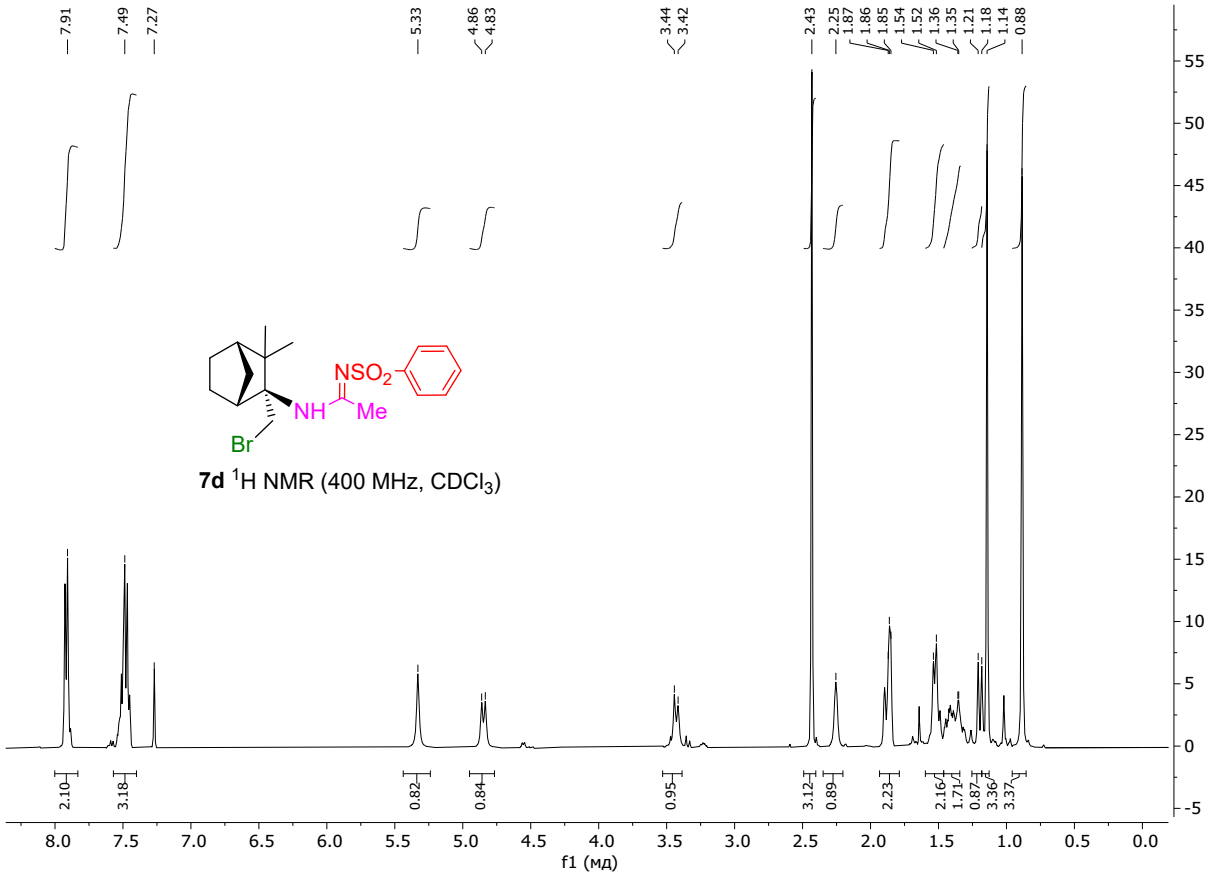


Figure S61. ^{13}C NMR spectrum of compound **7d**

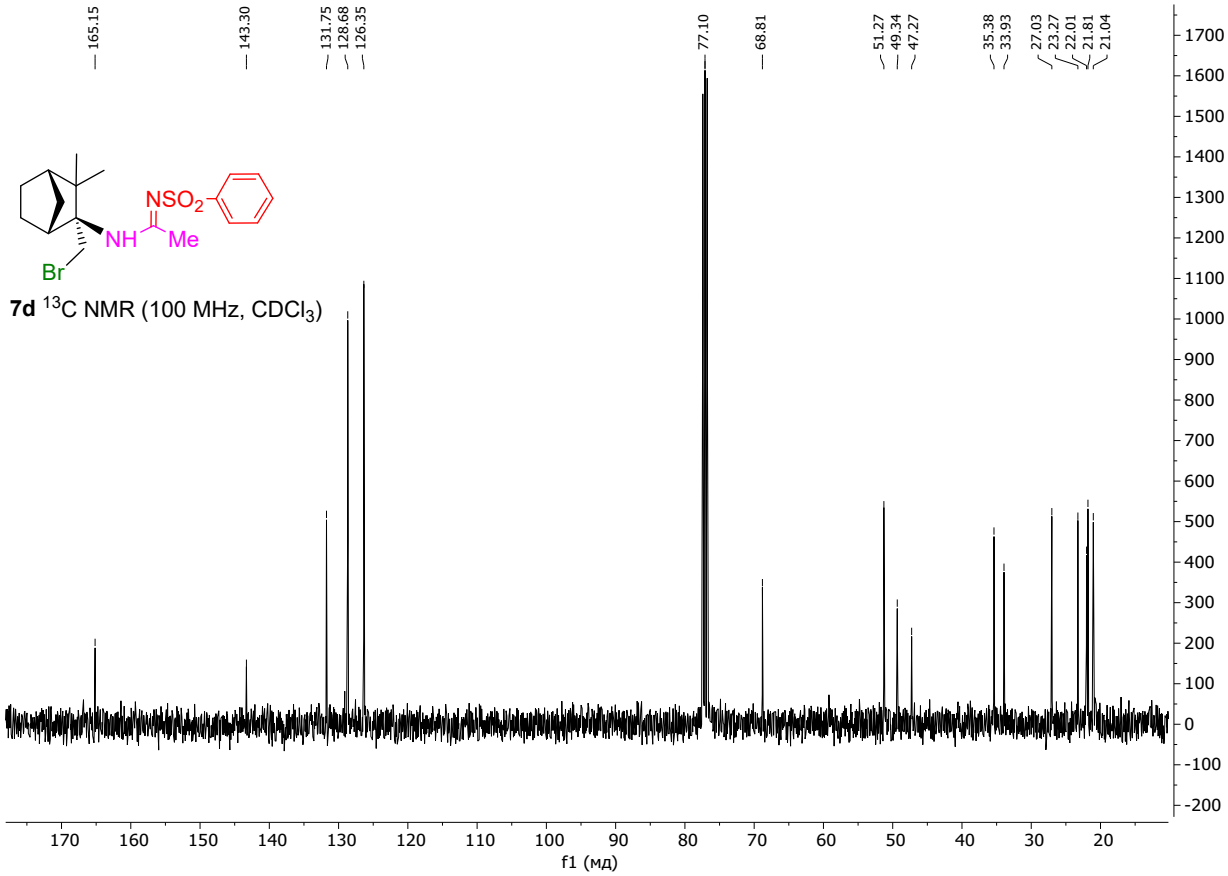


Figure S62. ^{1}H NMR spectrum of compound **7e**

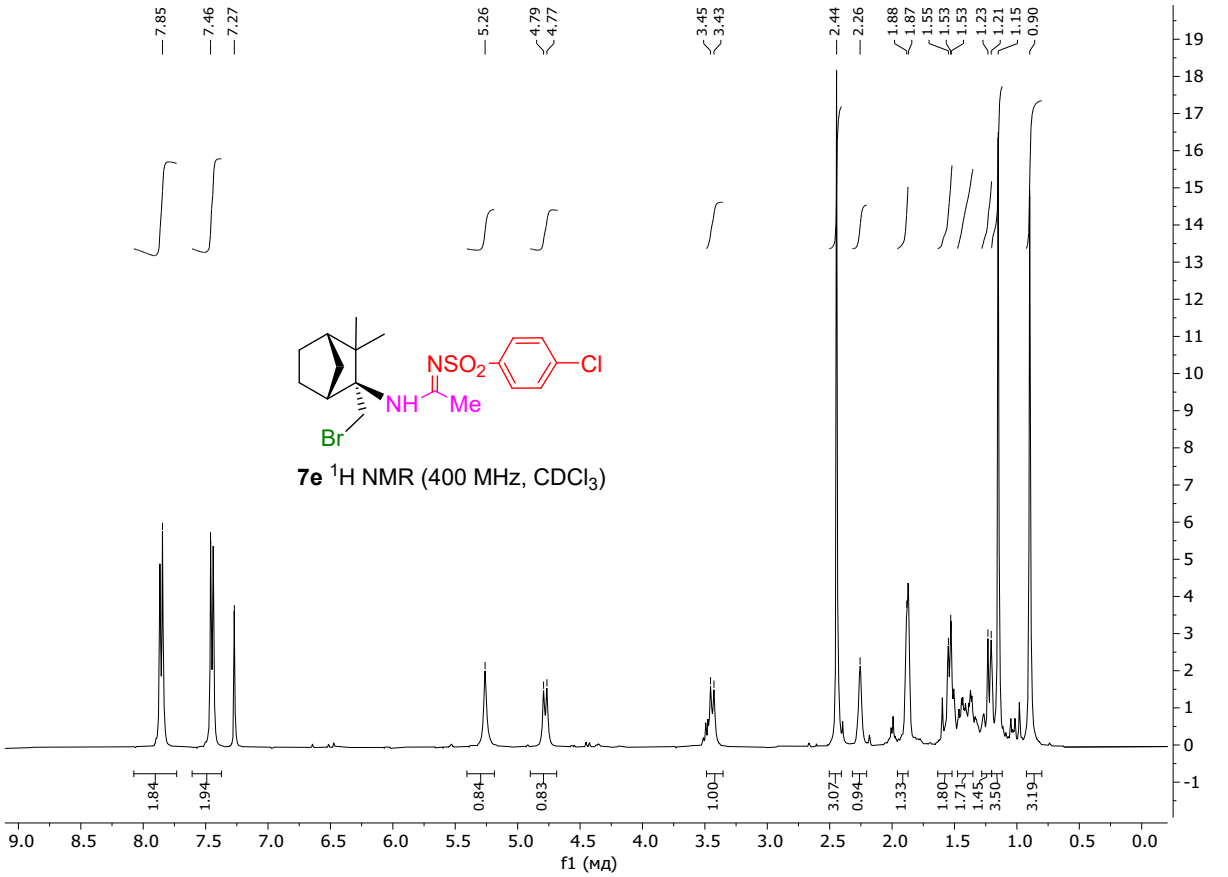


Figure S63. ^{13}C NMR spectrum of compound **7e**

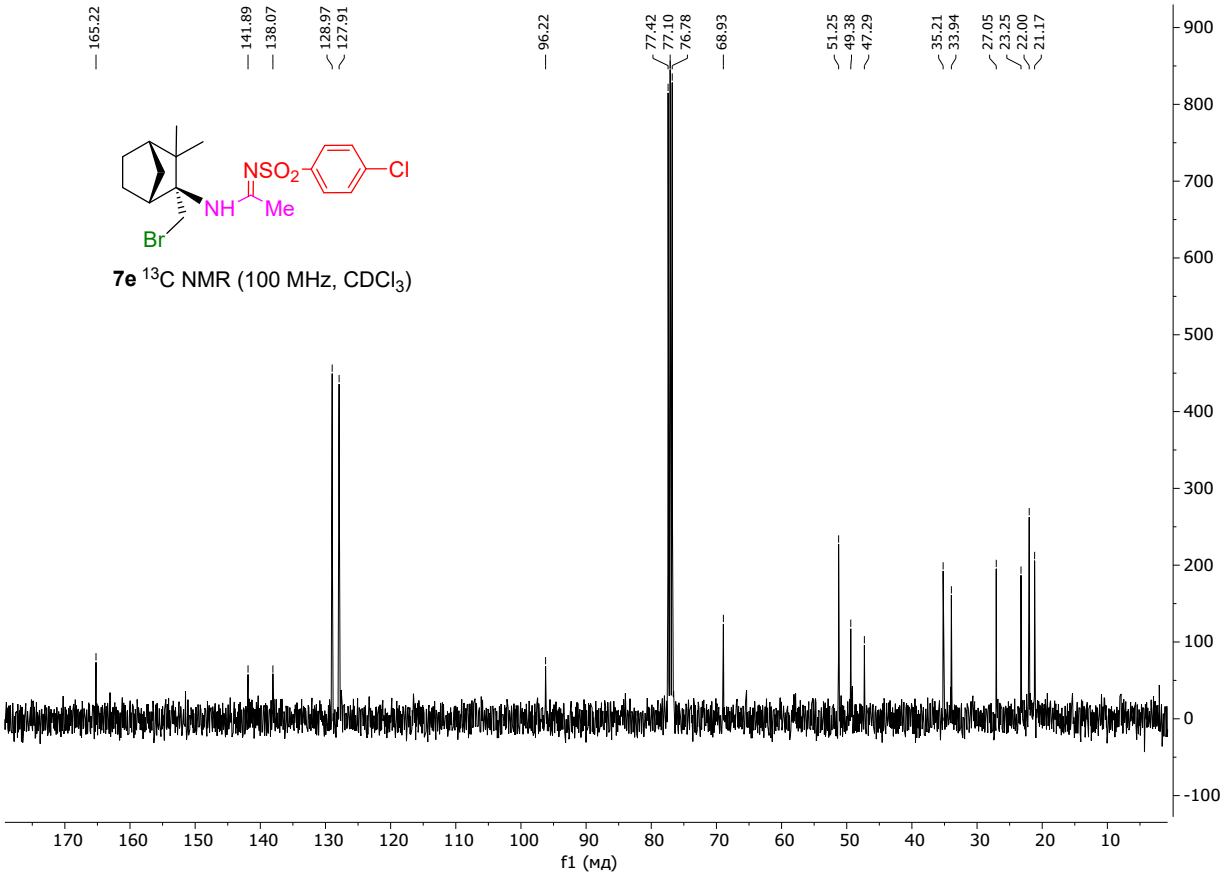


Figure S64. ^{1}H NMR spectrum of compound **7f**

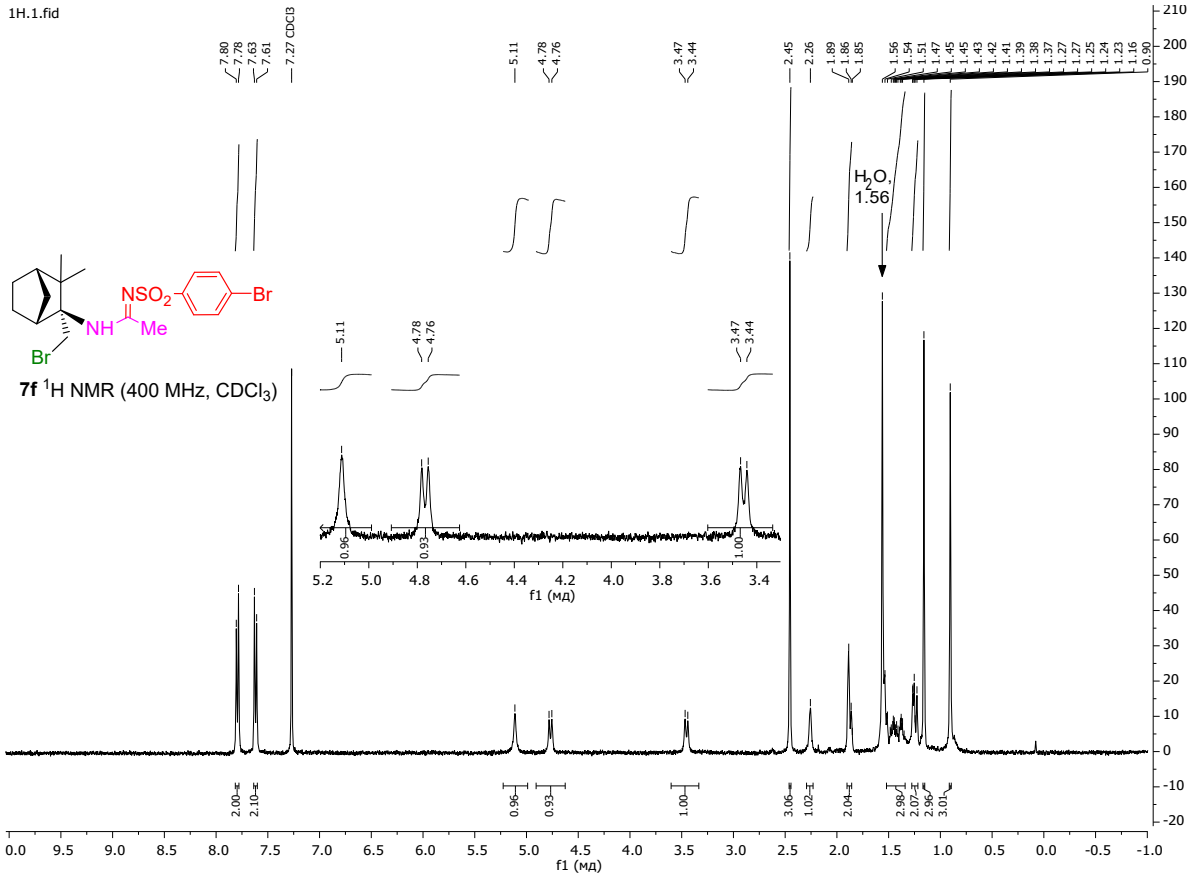


Figure S65. ^{13}C NMR spectrum of compound **7f**

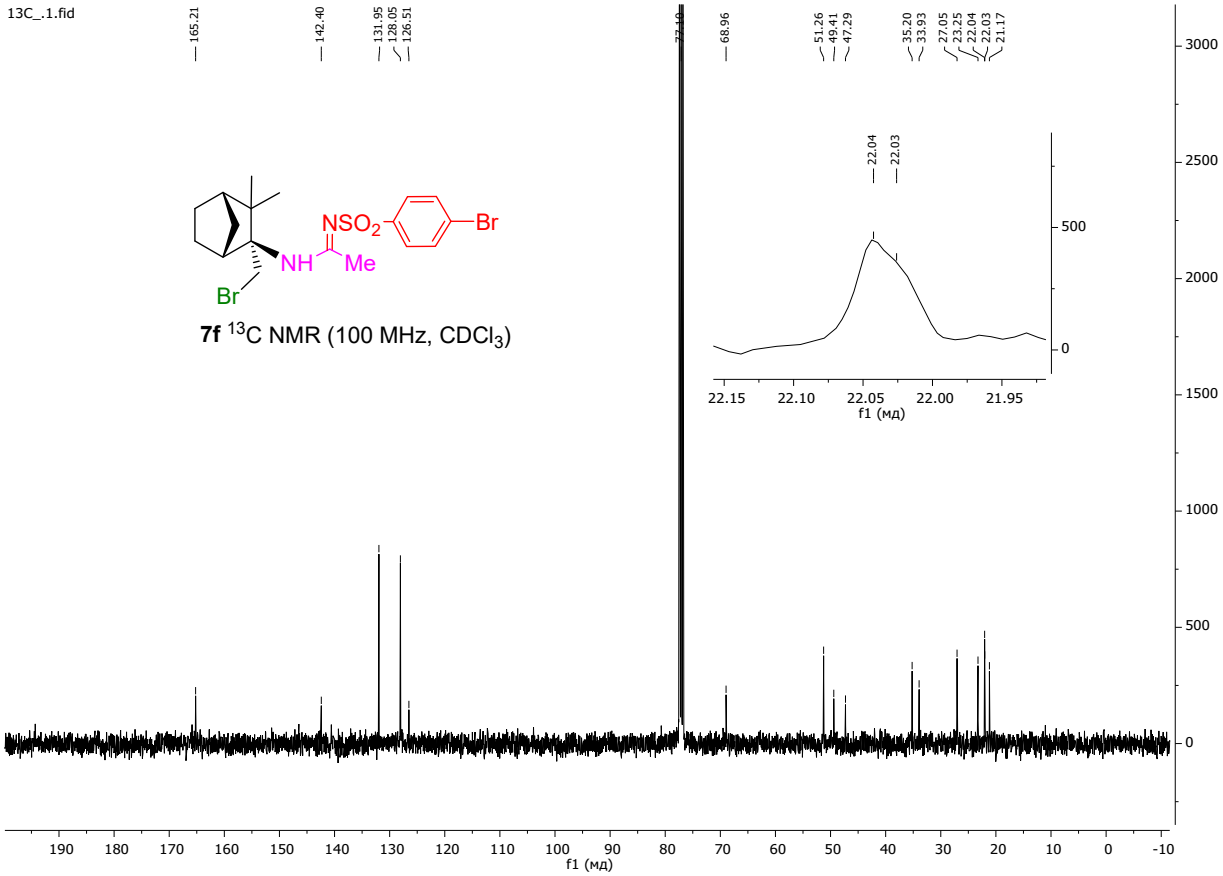


Figure S66. ^{1}H NMR spectrum of compound **7g**

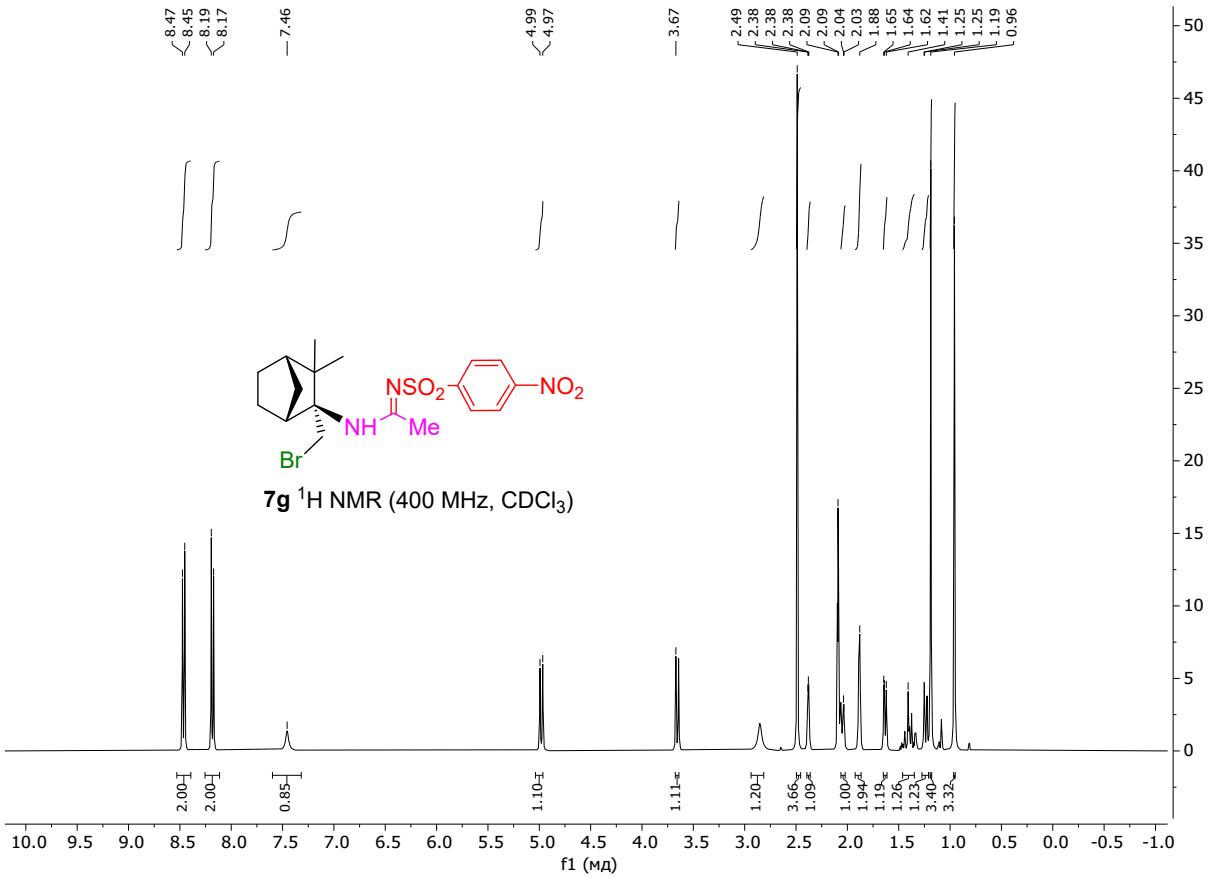


Figure S67. ^{13}C NMR spectrum of compound **7g**

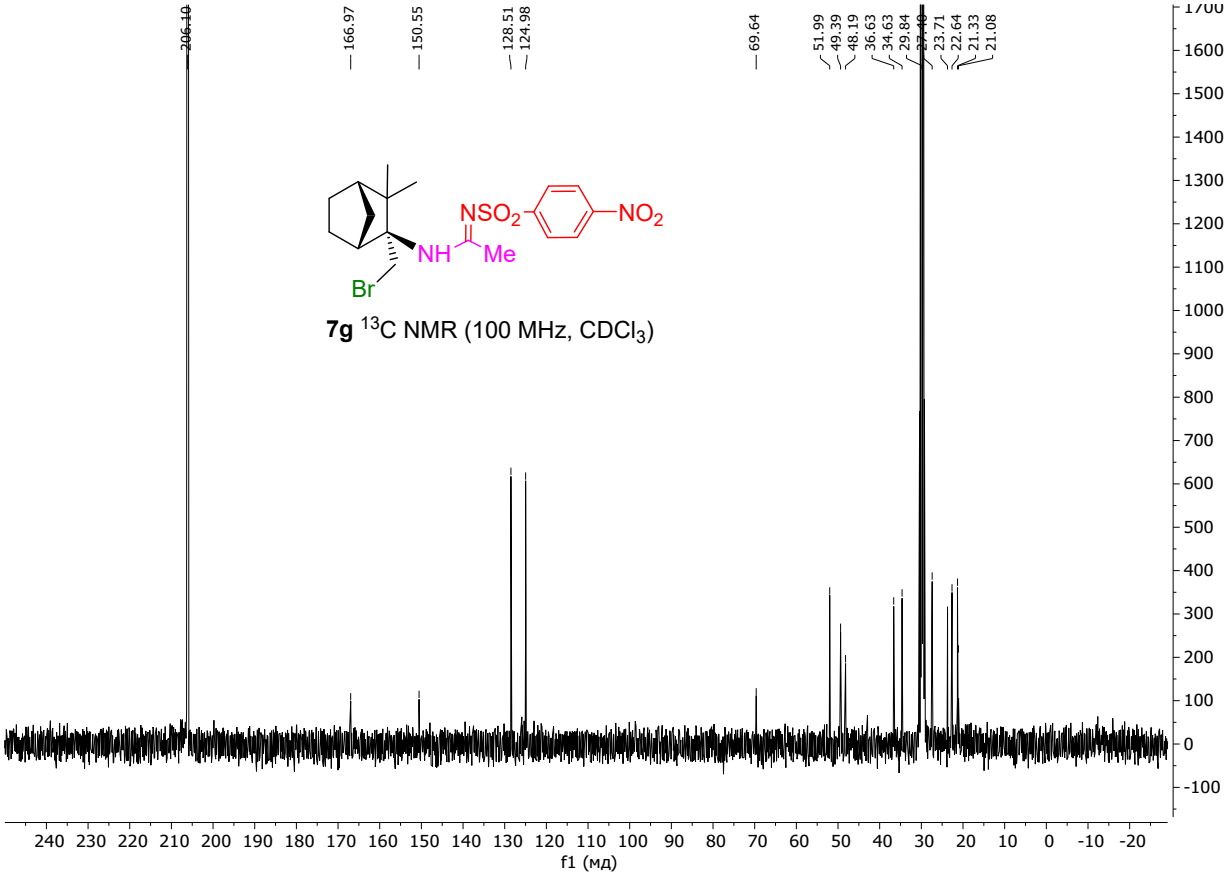
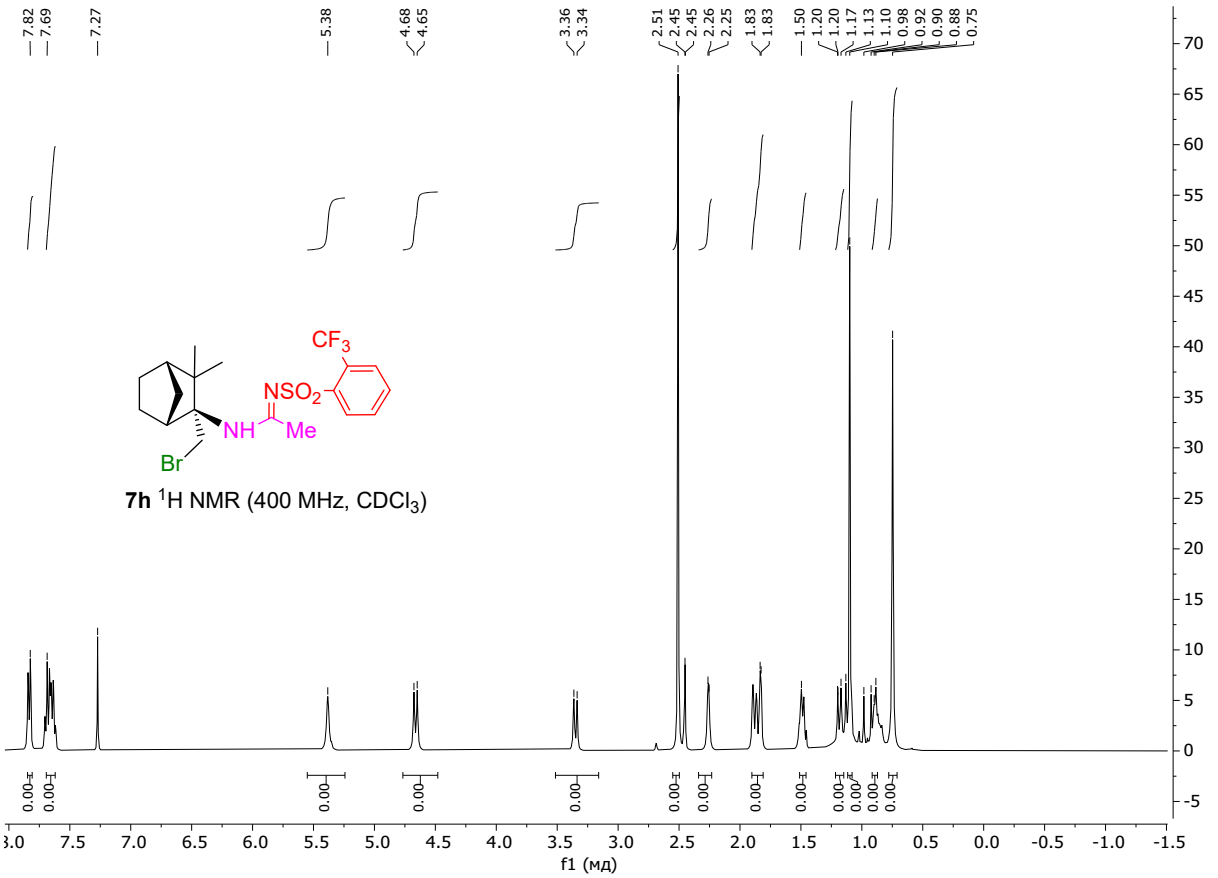
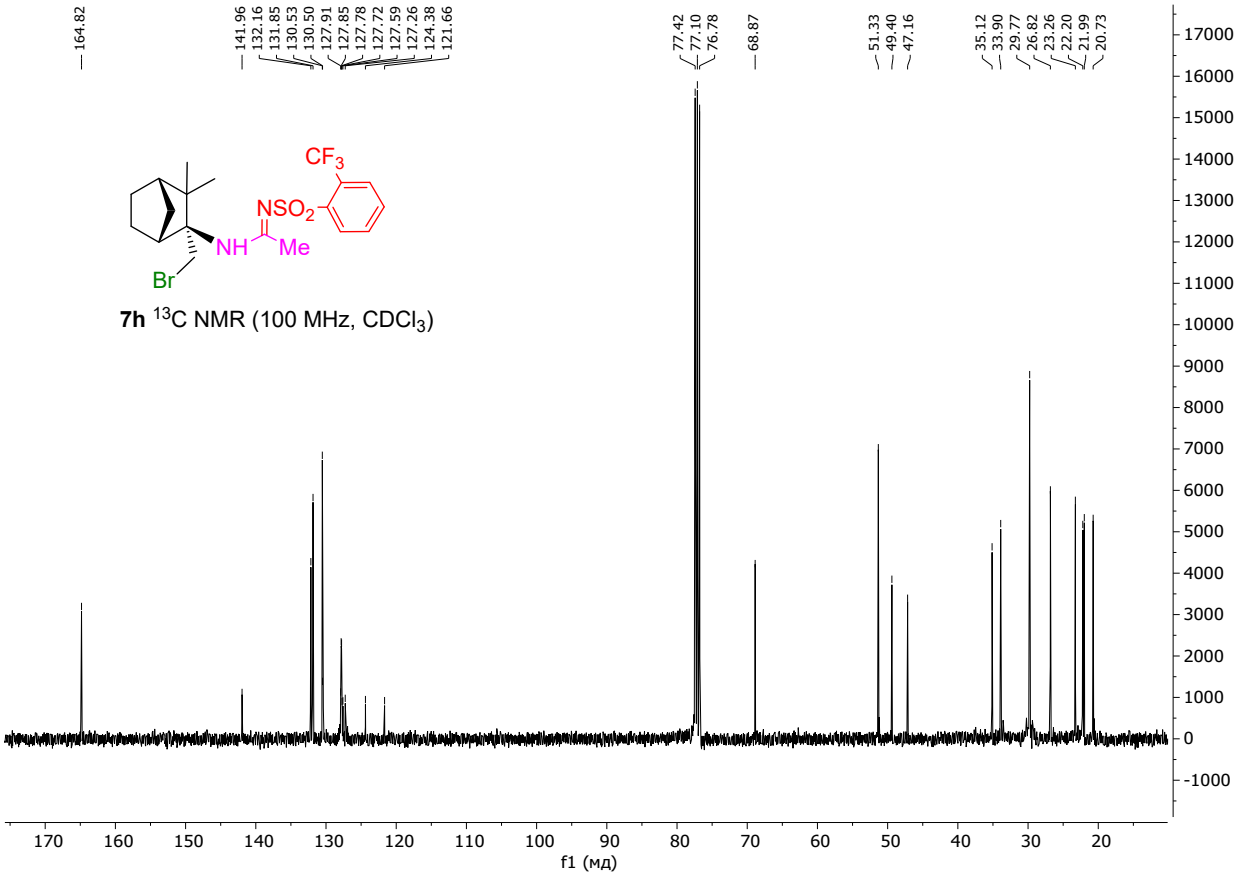


Figure S68. ^{1}H NMR spectrum of compound **7h**



7h ^{1}H NMR (400 MHz, $CDCl_3$)

Figure S69. ^{13}C NMR spectrum of compound **7h**



7h ^{13}C NMR (100 MHz, $CDCl_3$)

Figure S70. ^{19}F NMR spectrum of compound **7h**

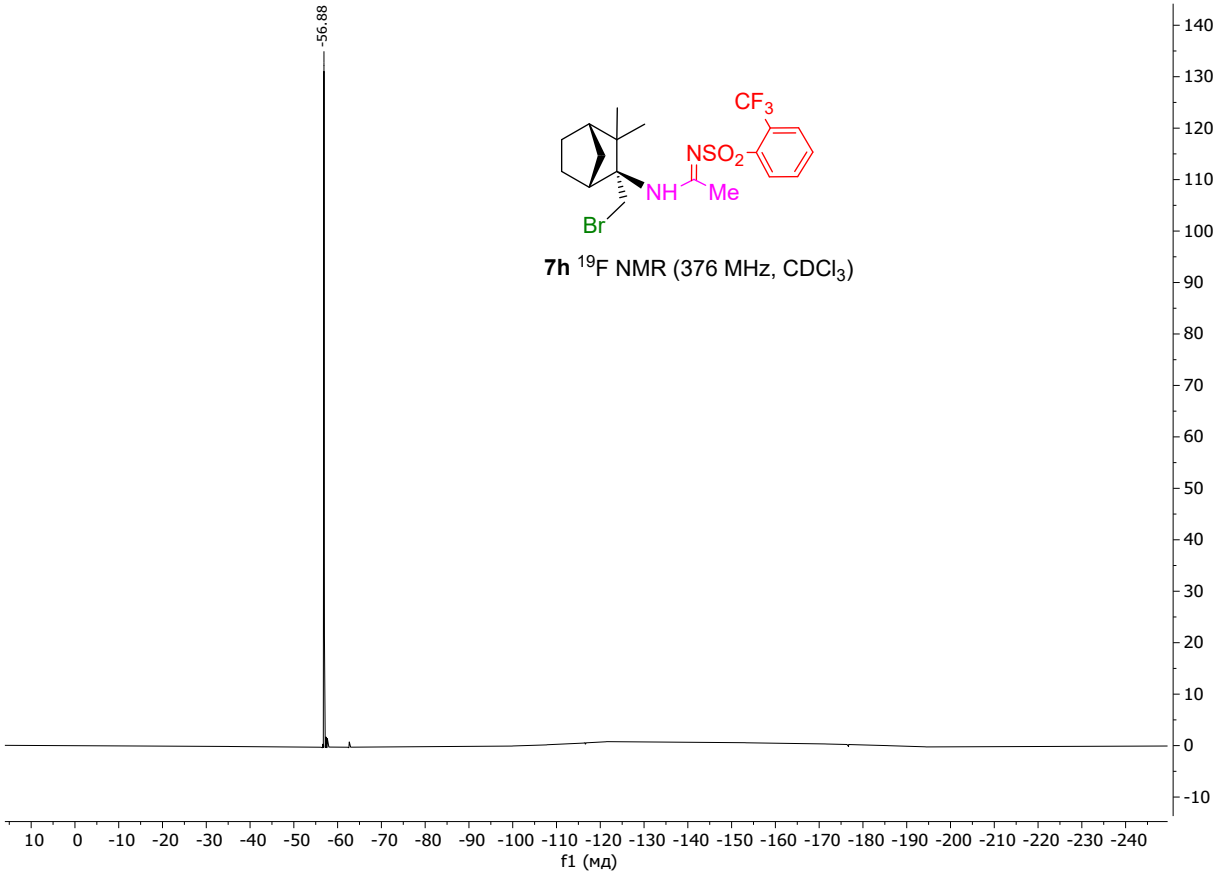


Figure S71. ^{1}H NMR spectrum of compound **7i**

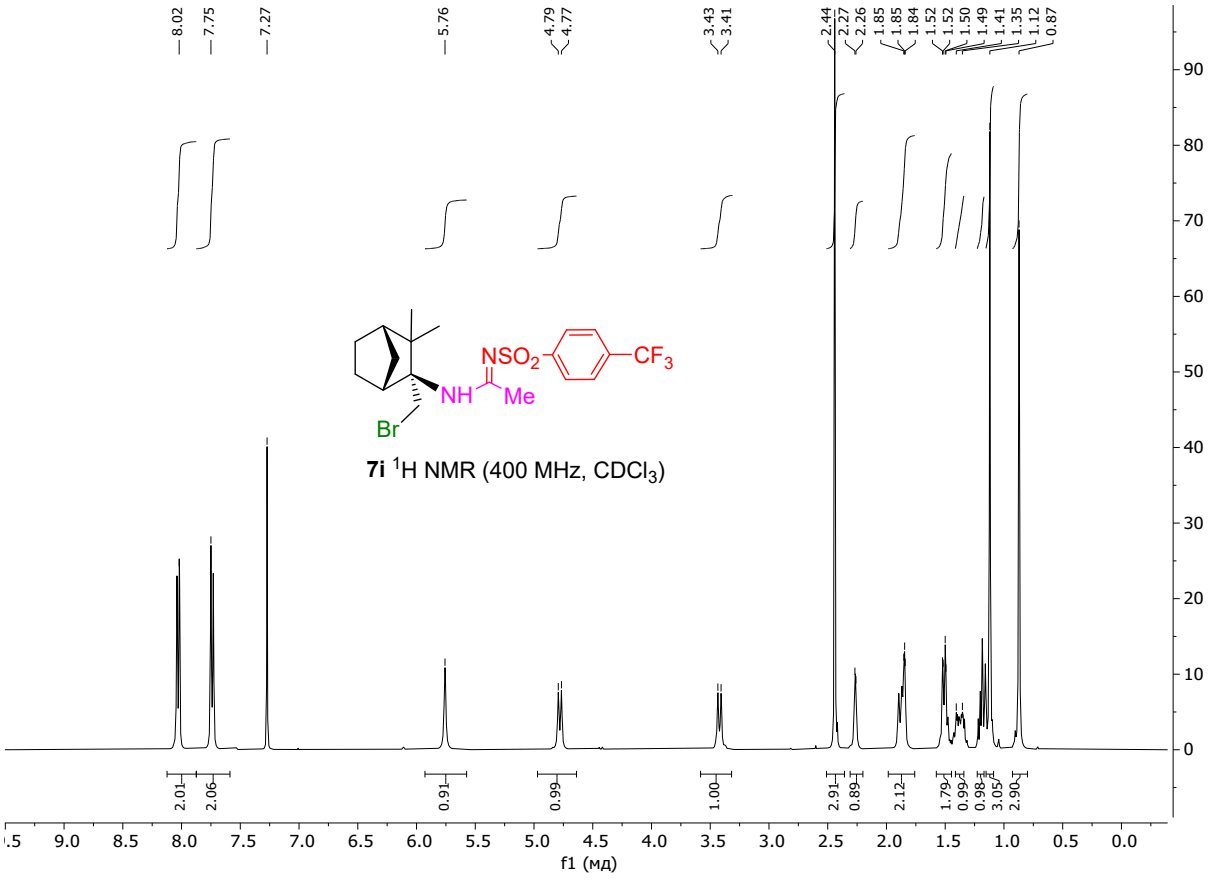


Figure S72. ^{13}C NMR spectrum of compound **7i**

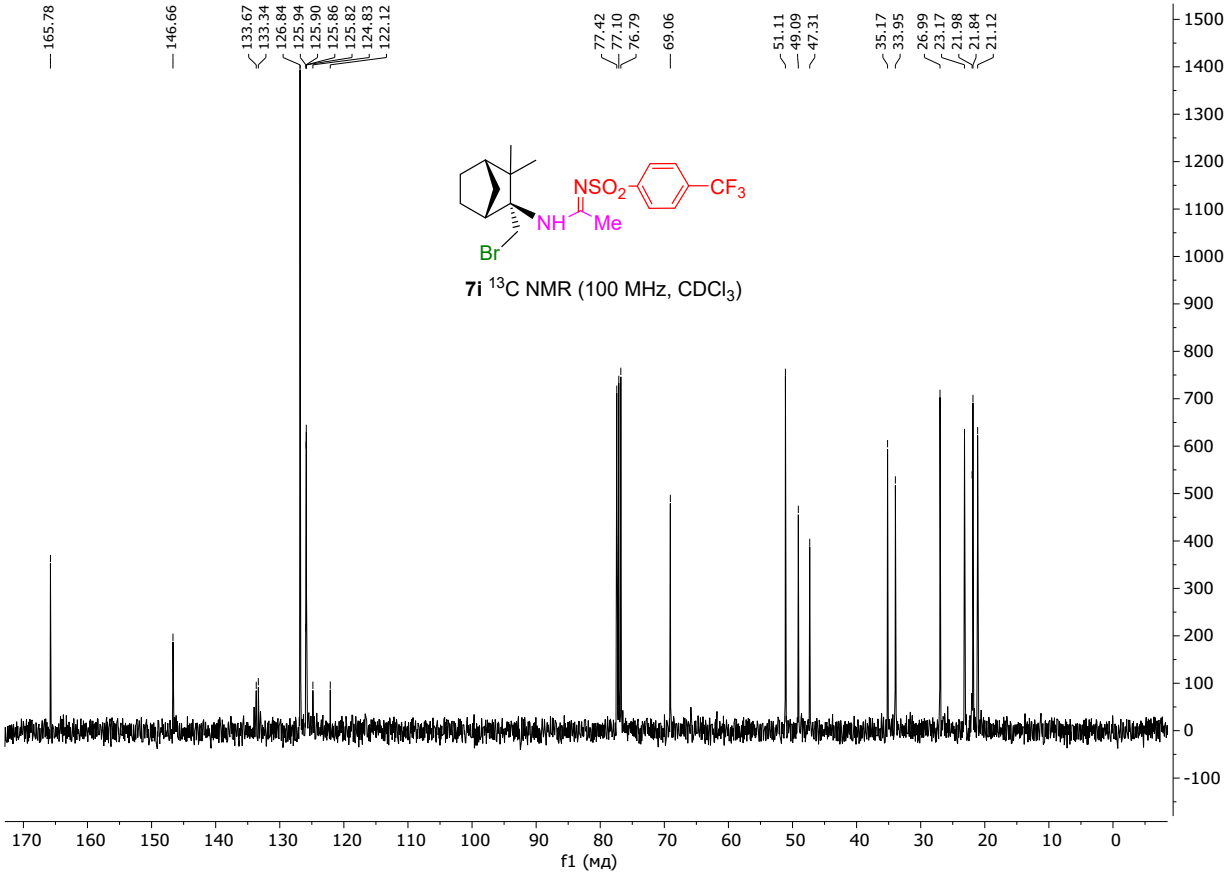


Figure S73. ^{19}F NMR spectrum of compound **7i**

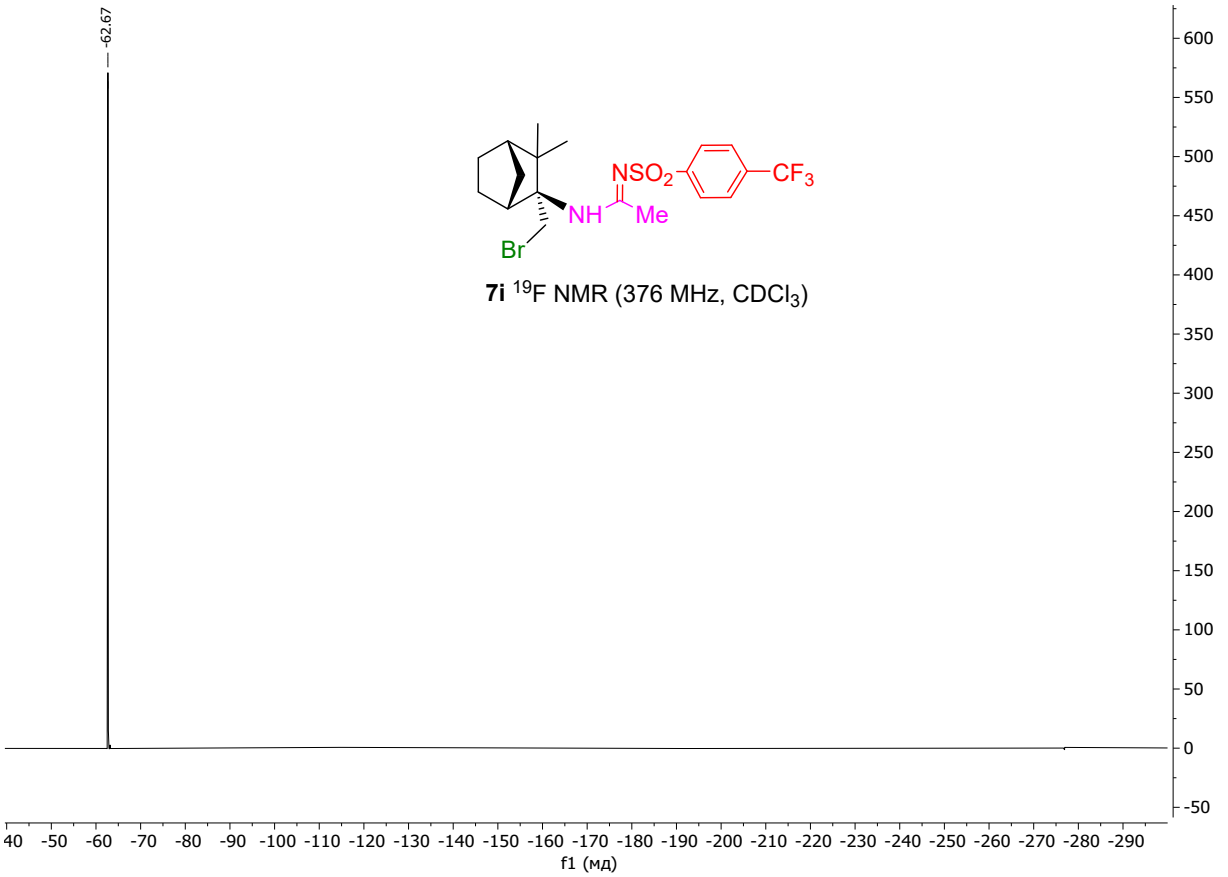


Figure S74. ^{1}H NMR spectrum of compound **7j**

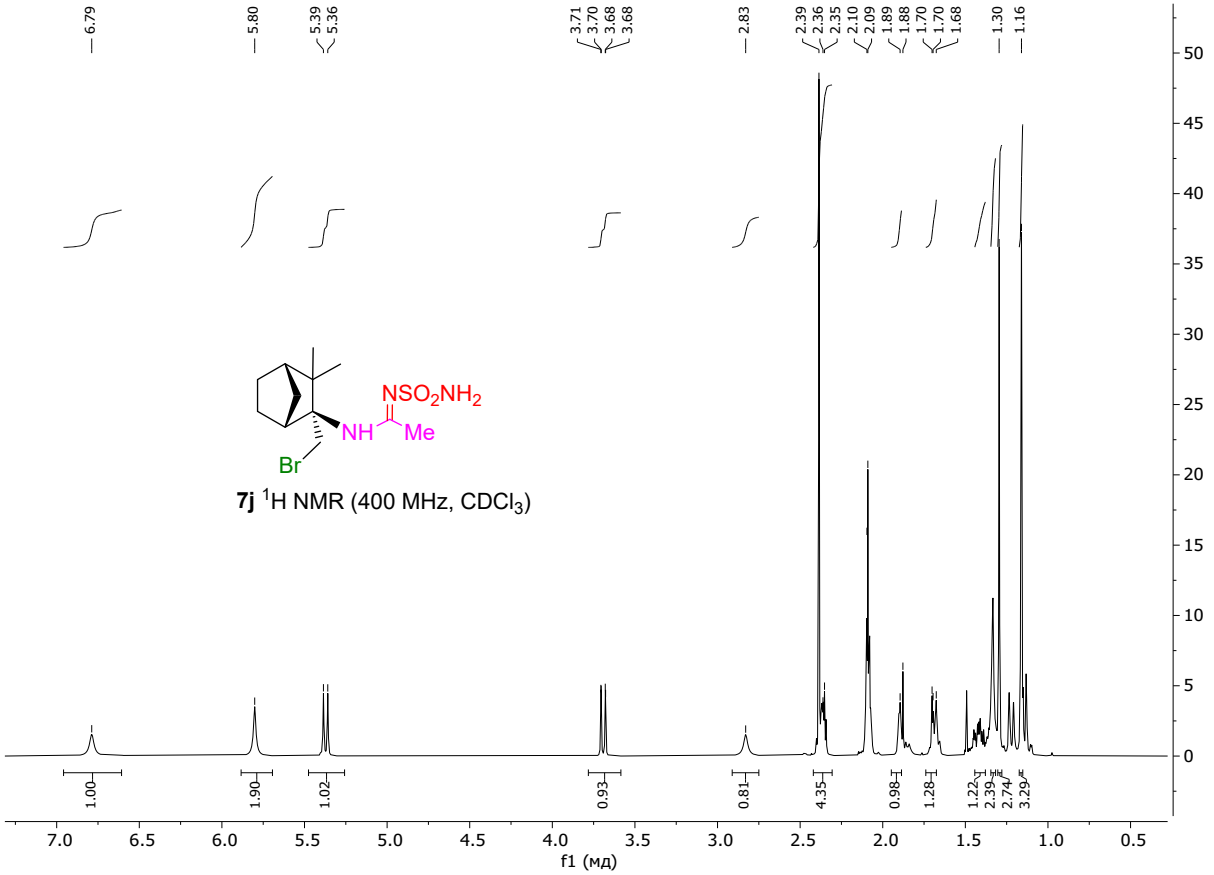


Figure S75. ^{13}C NMR spectrum of compound **7j**

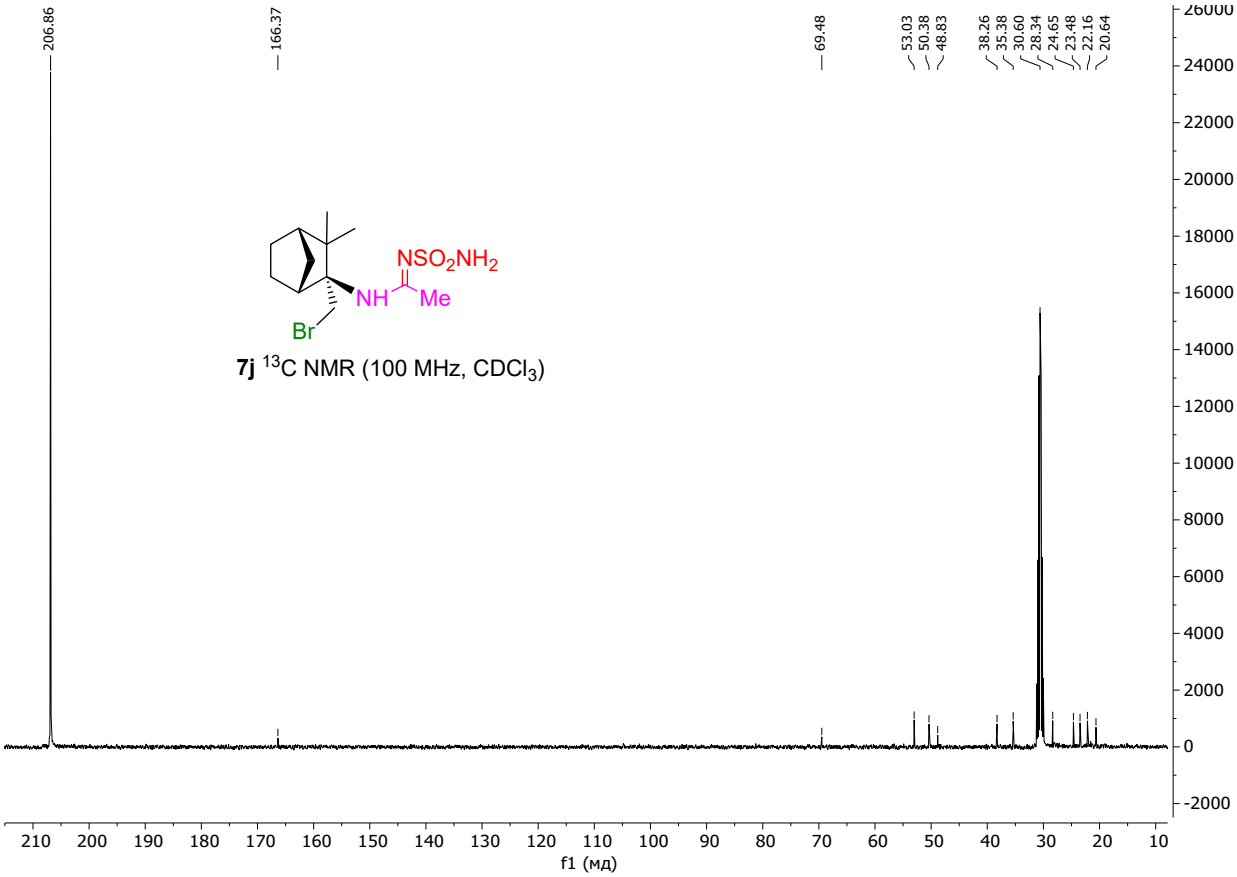


Figure S76. ^{1}H NMR spectrum of compound **7k**

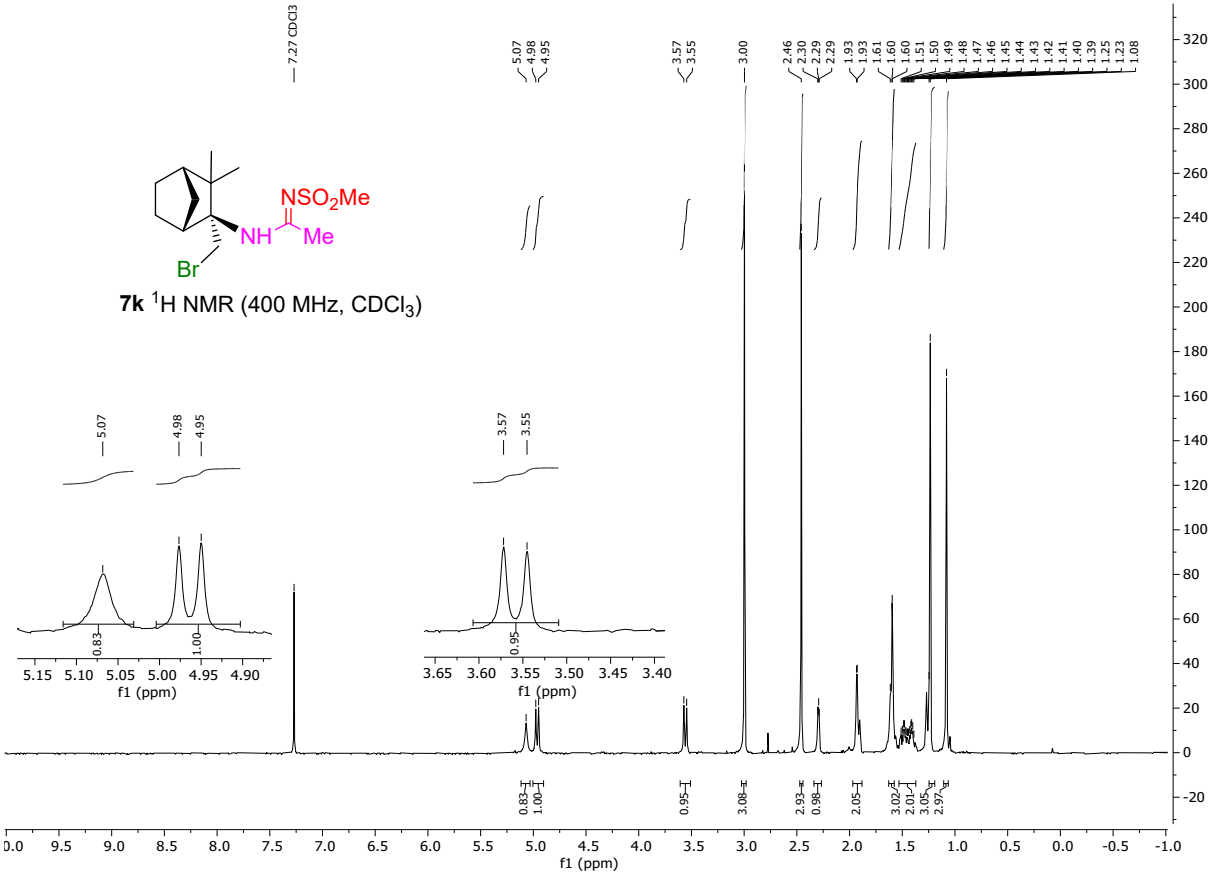


Figure S77. ^{13}C NMR spectrum of compound **7k**

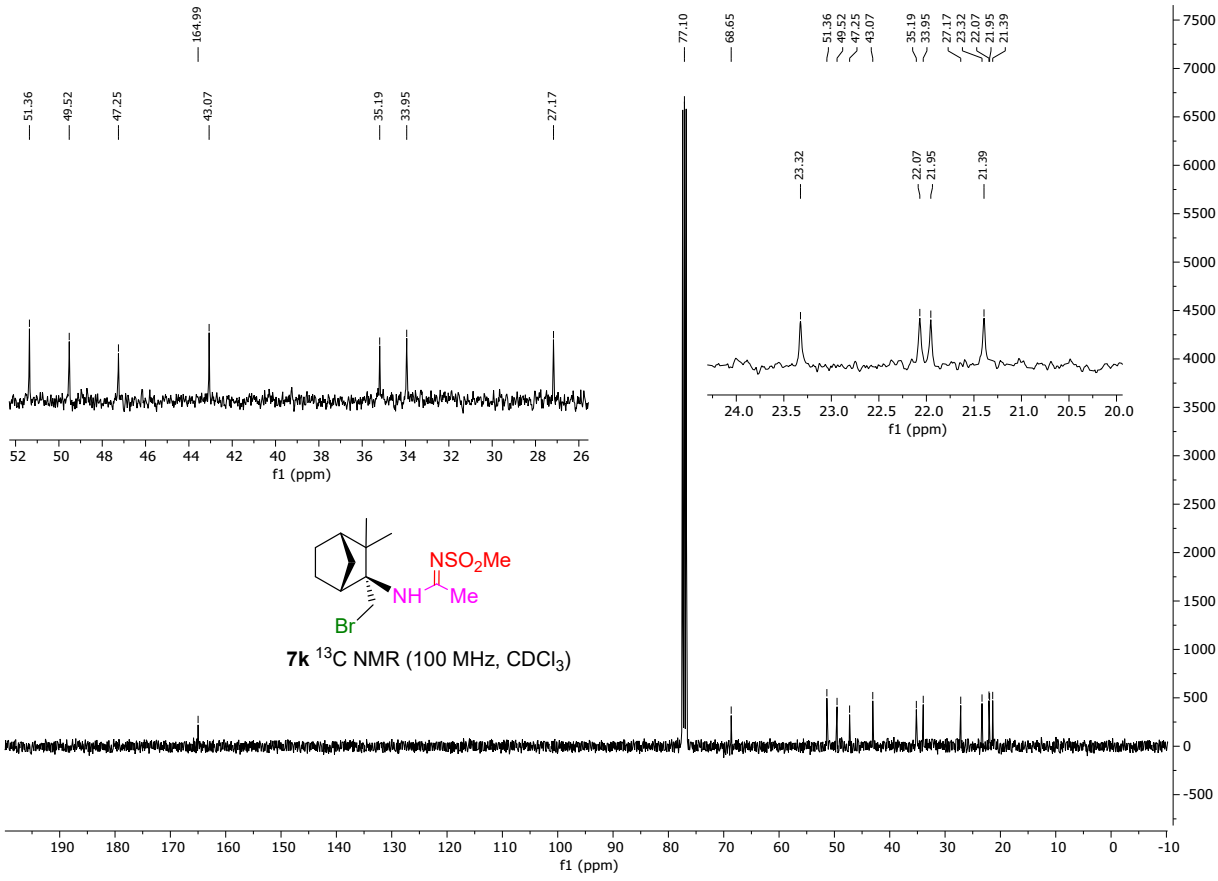


Figure S78. ^{1}H NMR spectrum of compound **8a**

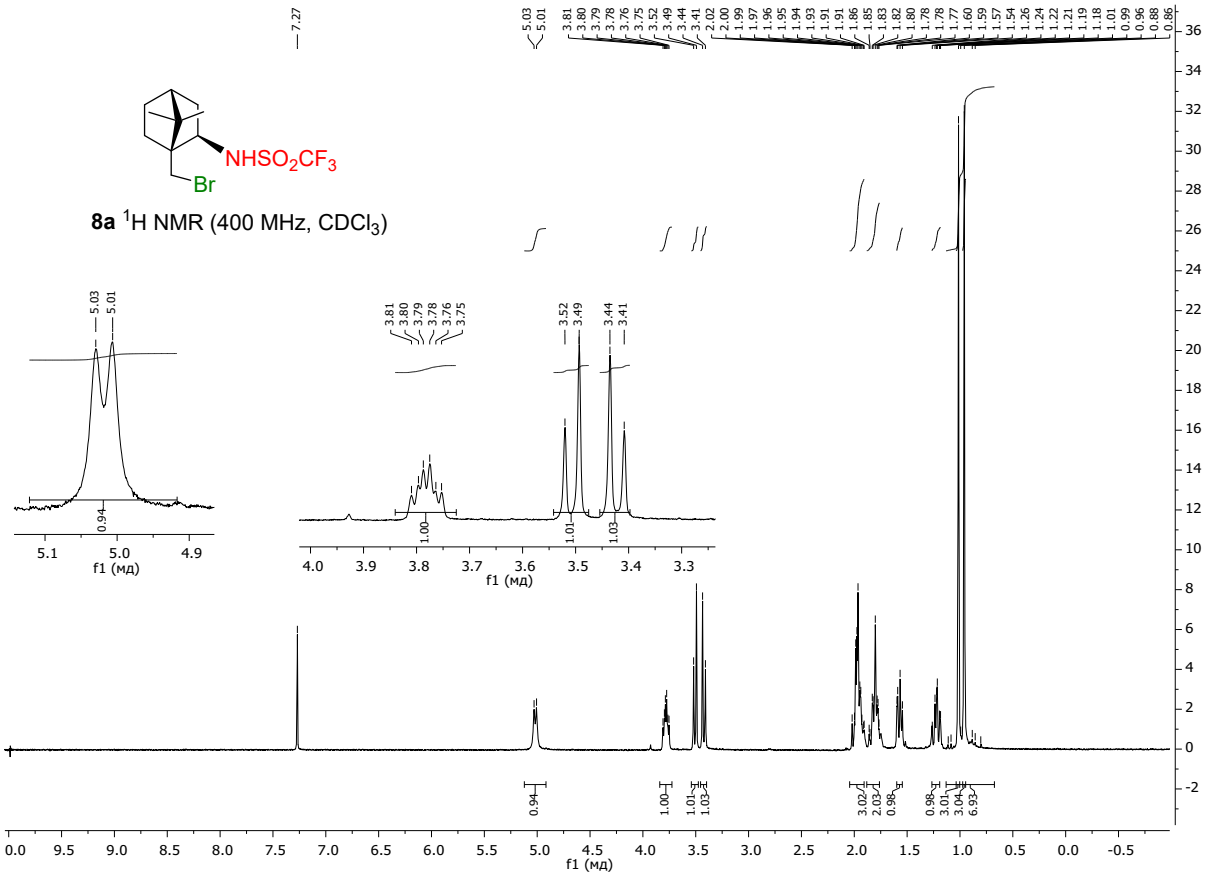
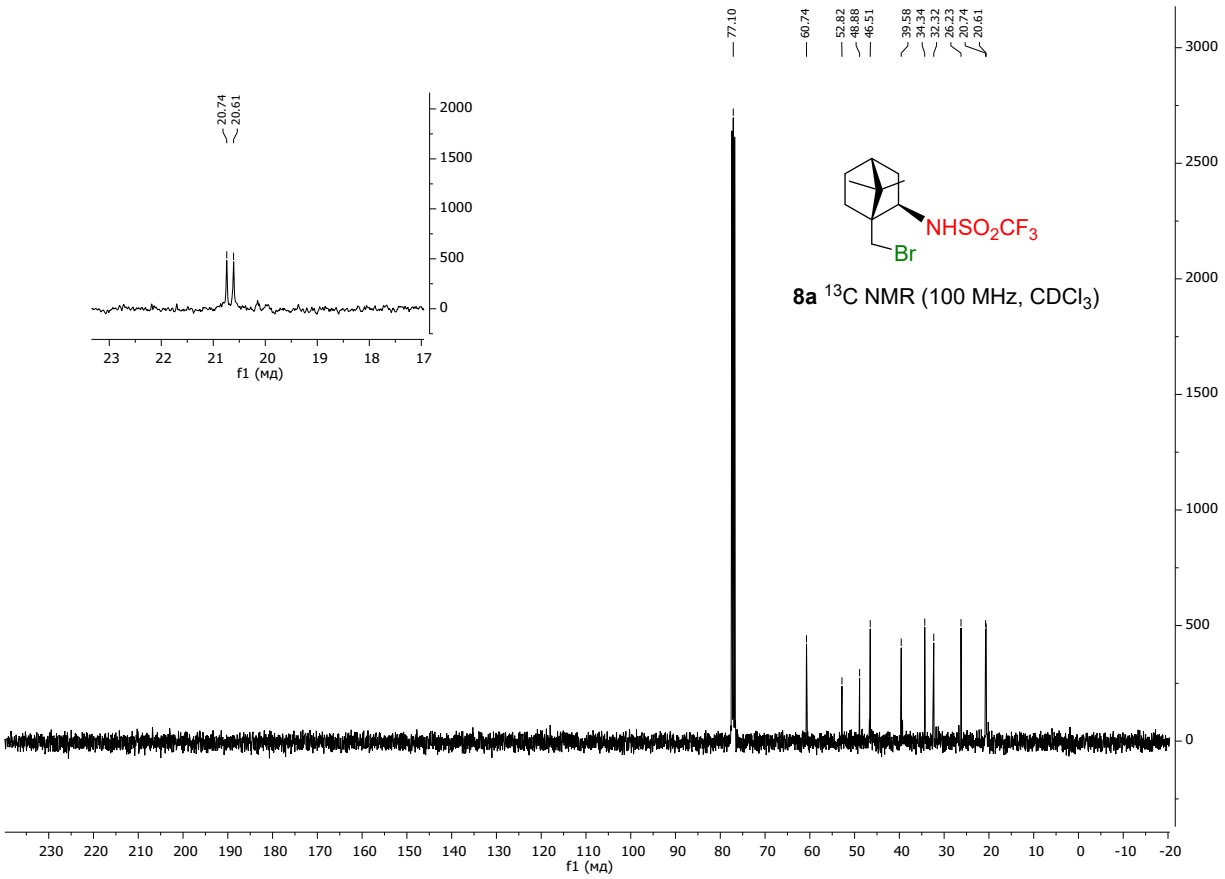


Figure S79. ^{13}C NMR spectrum of compound **8a**



8a ^{13}C NMR (100 MHz, $CDCl_3$)

Figure S80. ^{19}F NMR spectrum of compound **8a**

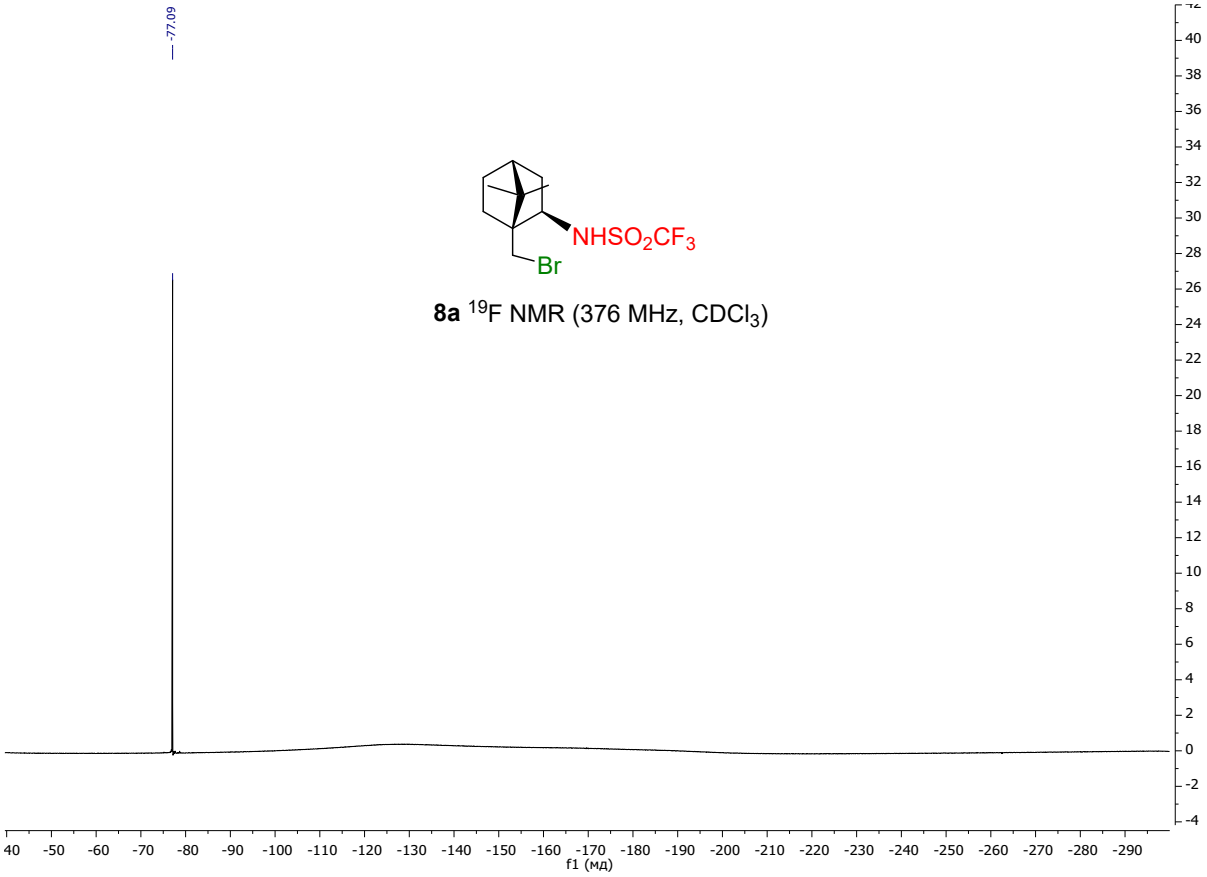


Figure S81. ^{1}H NMR spectrum of compound **8b**

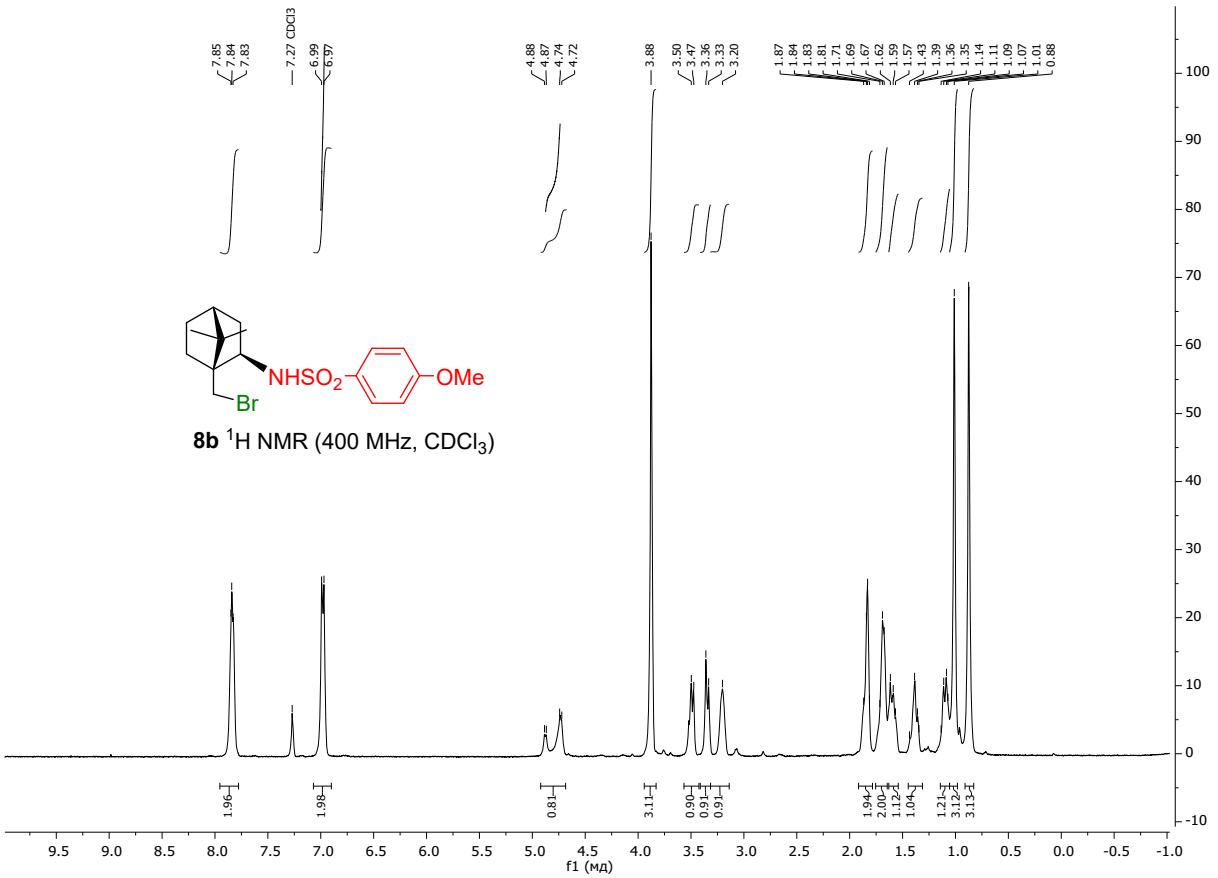


Figure S82. ^{13}C NMR spectrum of compound **8b**

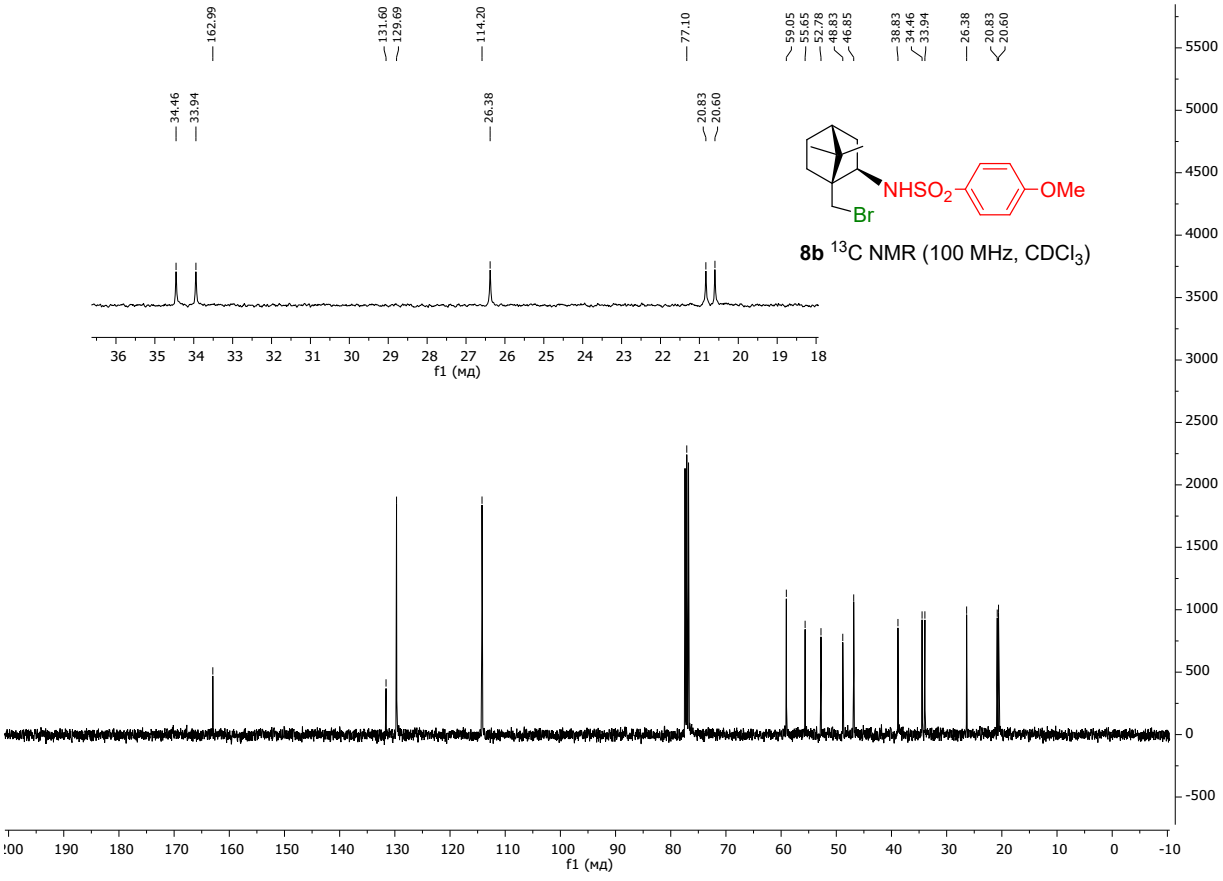


Figure S83. ^{1}H NMR spectrum of compound **8c**

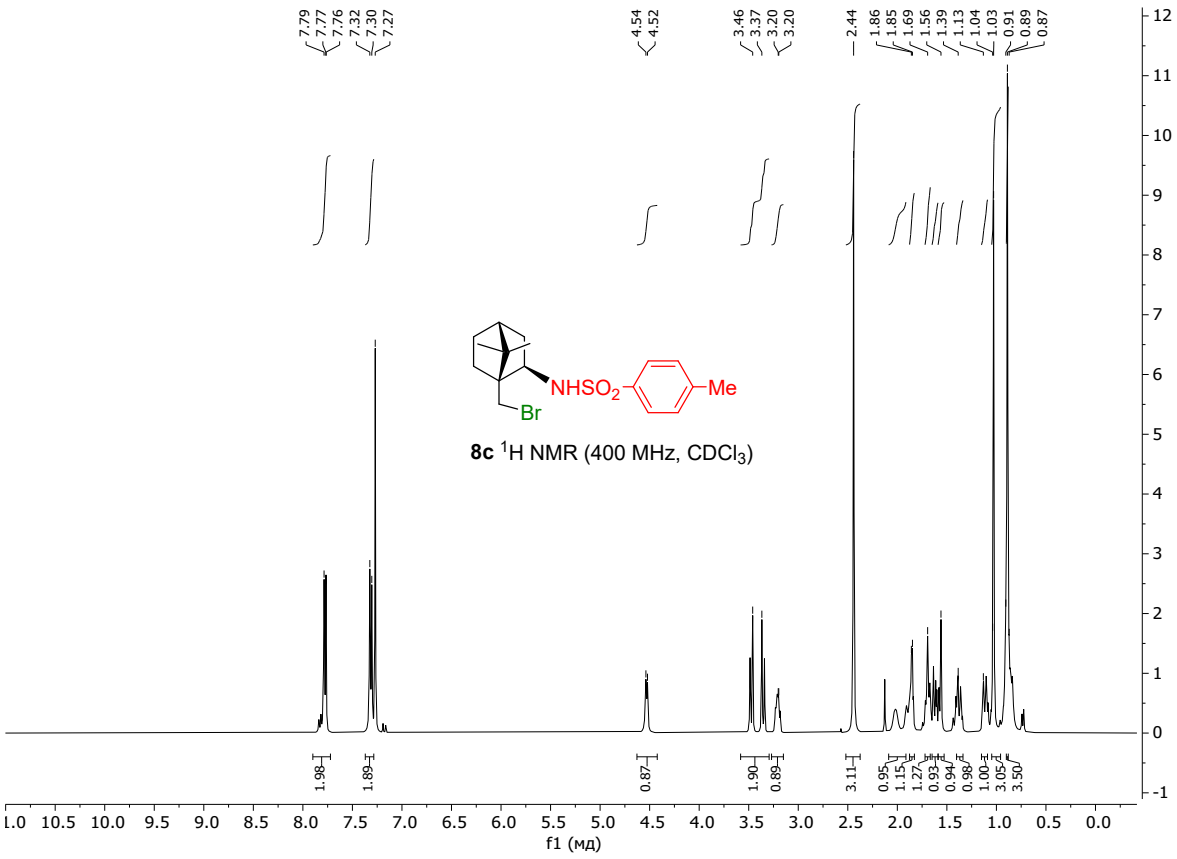


Figure S84. ^{13}C NMR spectrum of compound **8c**

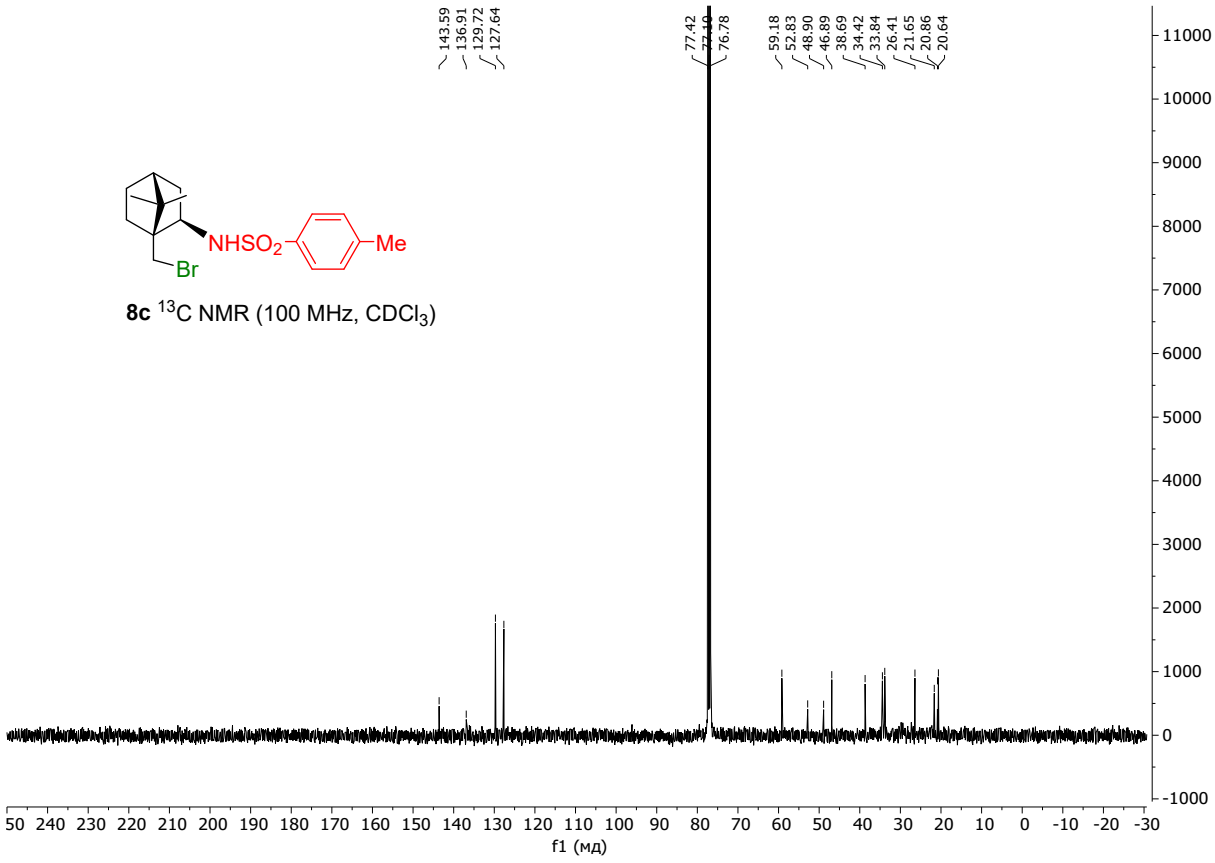


Figure S85. ^{1}H NMR spectrum of compound **8d**

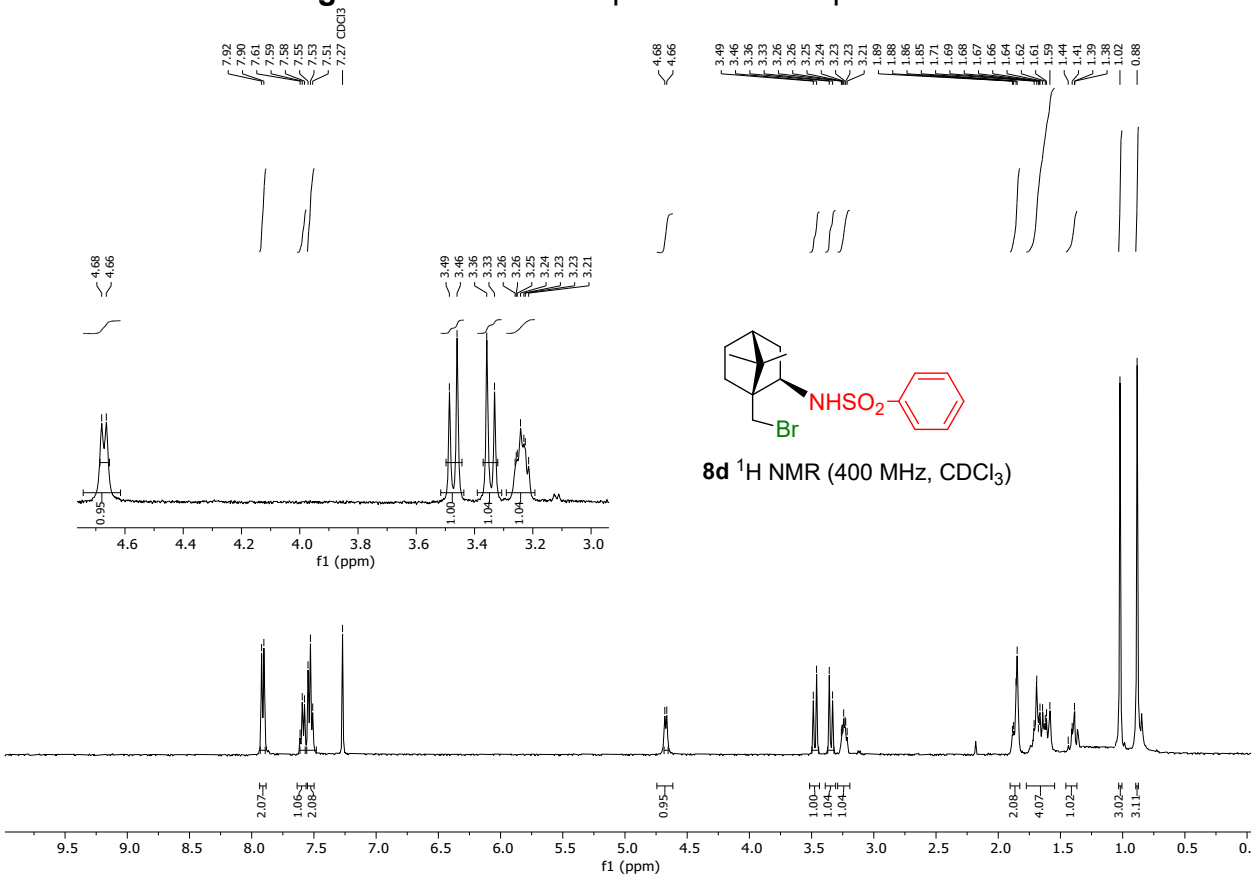


Figure S86. ^{13}C NMR spectrum of compound **8d**

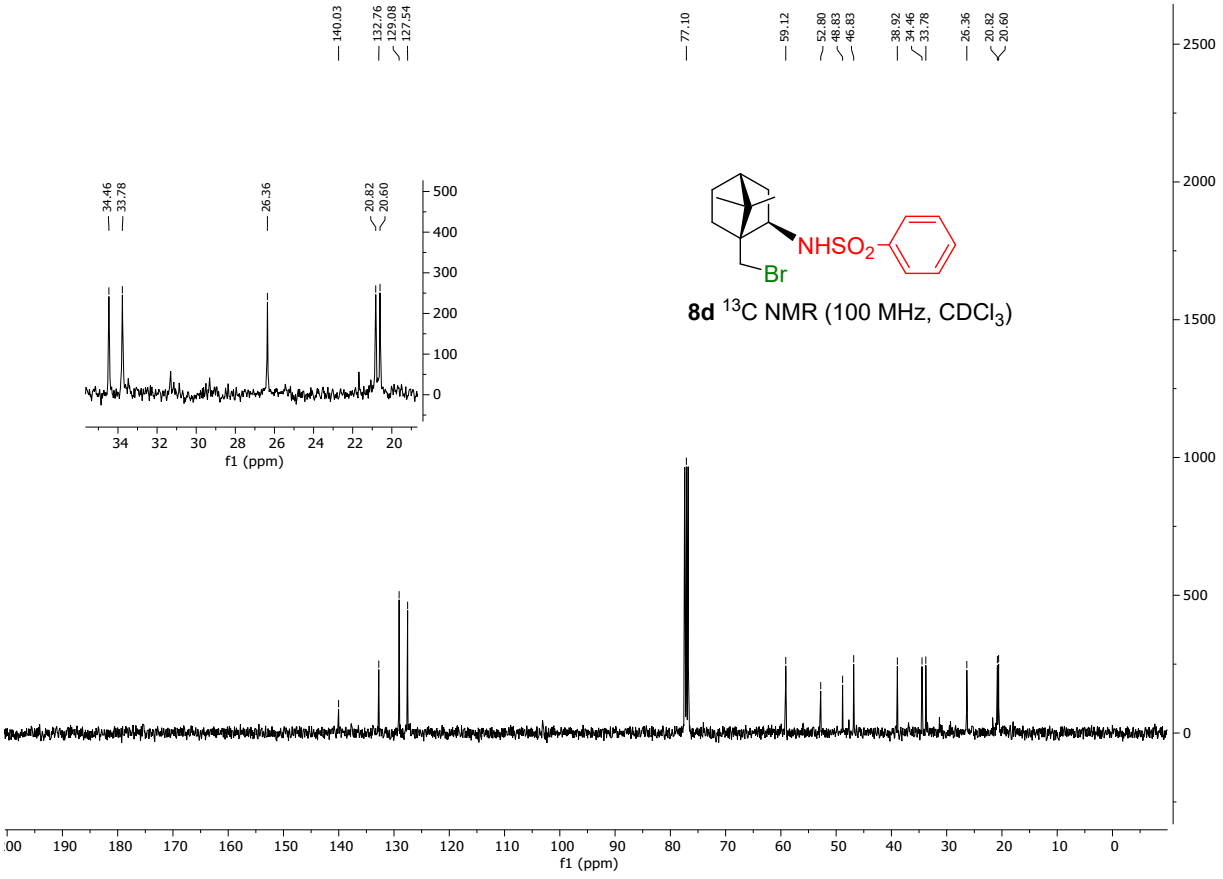


Figure S87. ^{1}H NMR spectrum of compound **8e**

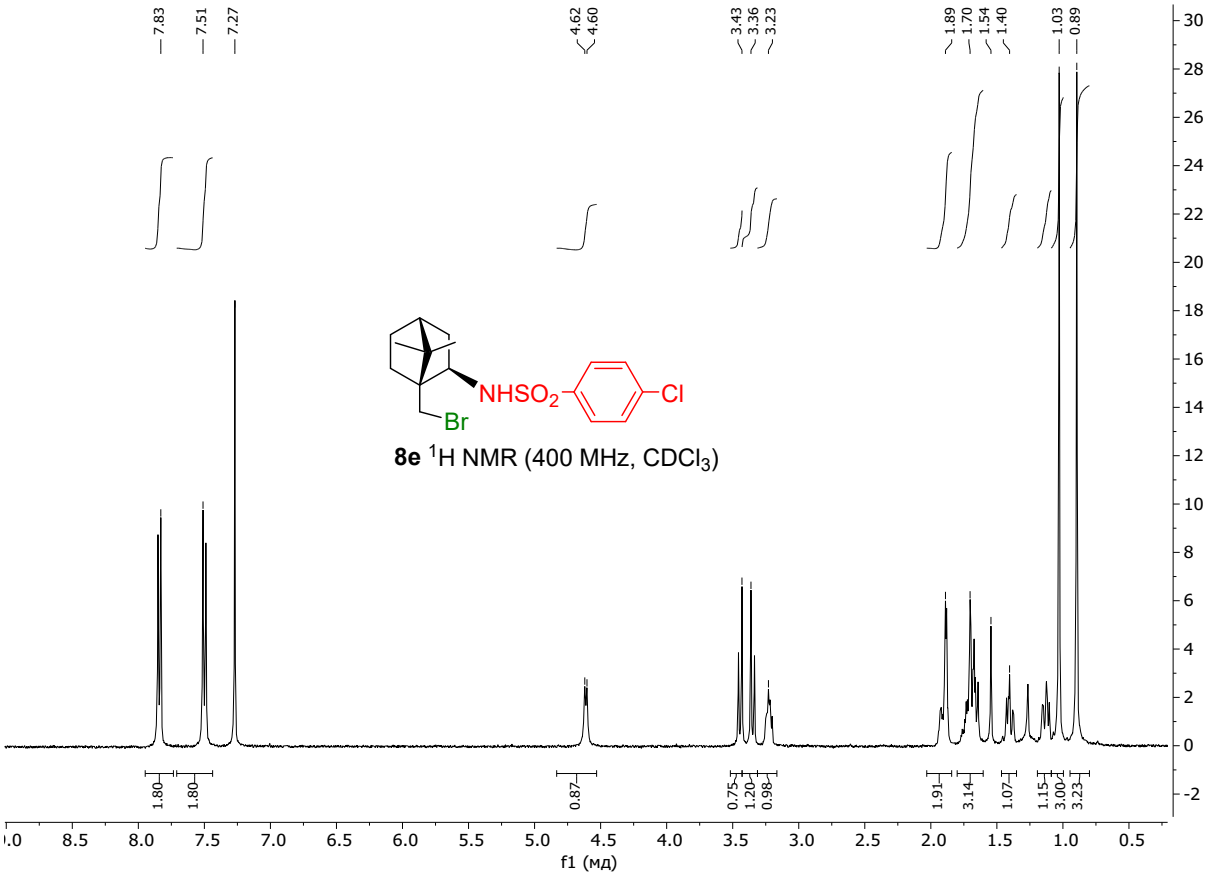


Figure S88. ^{13}C NMR spectrum of compound **8e**

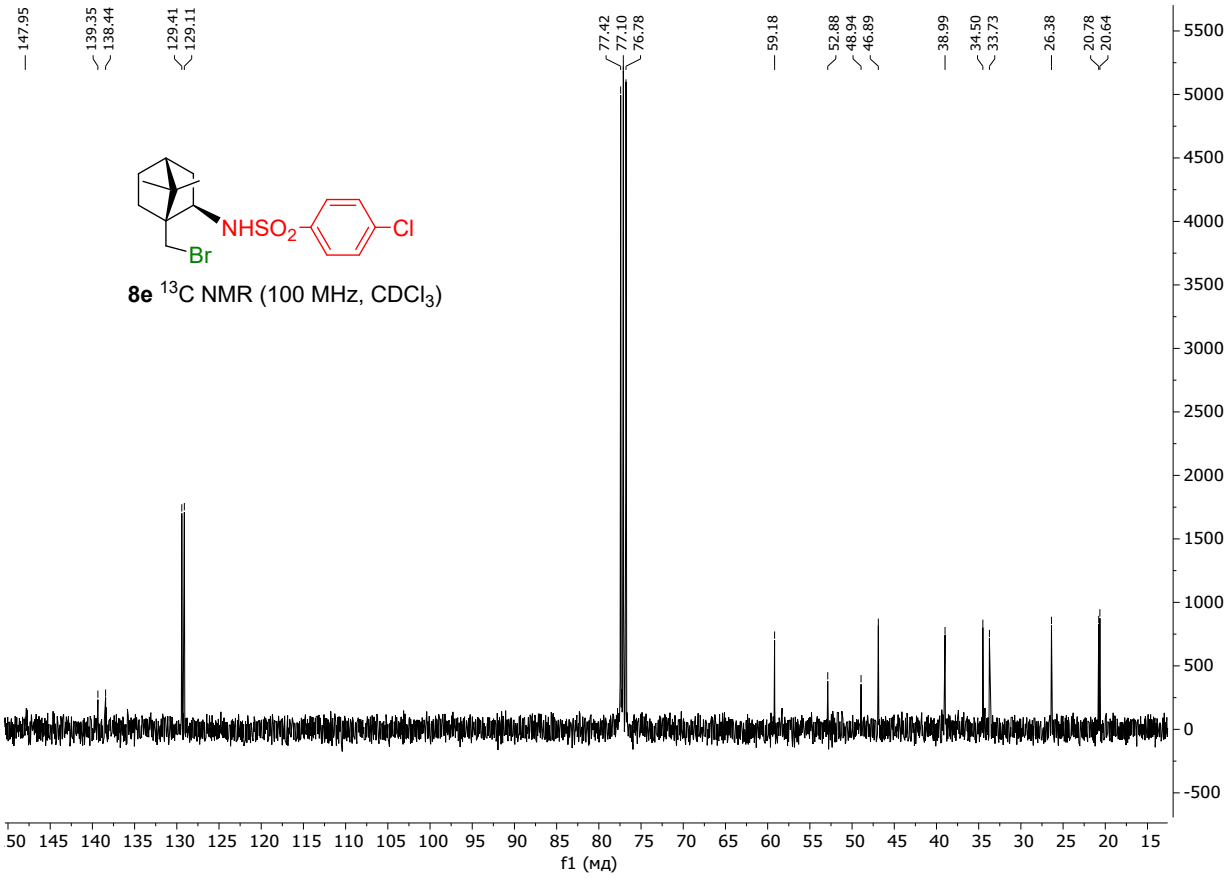


Figure S89. ^{1}H NMR spectrum of compound **8f**

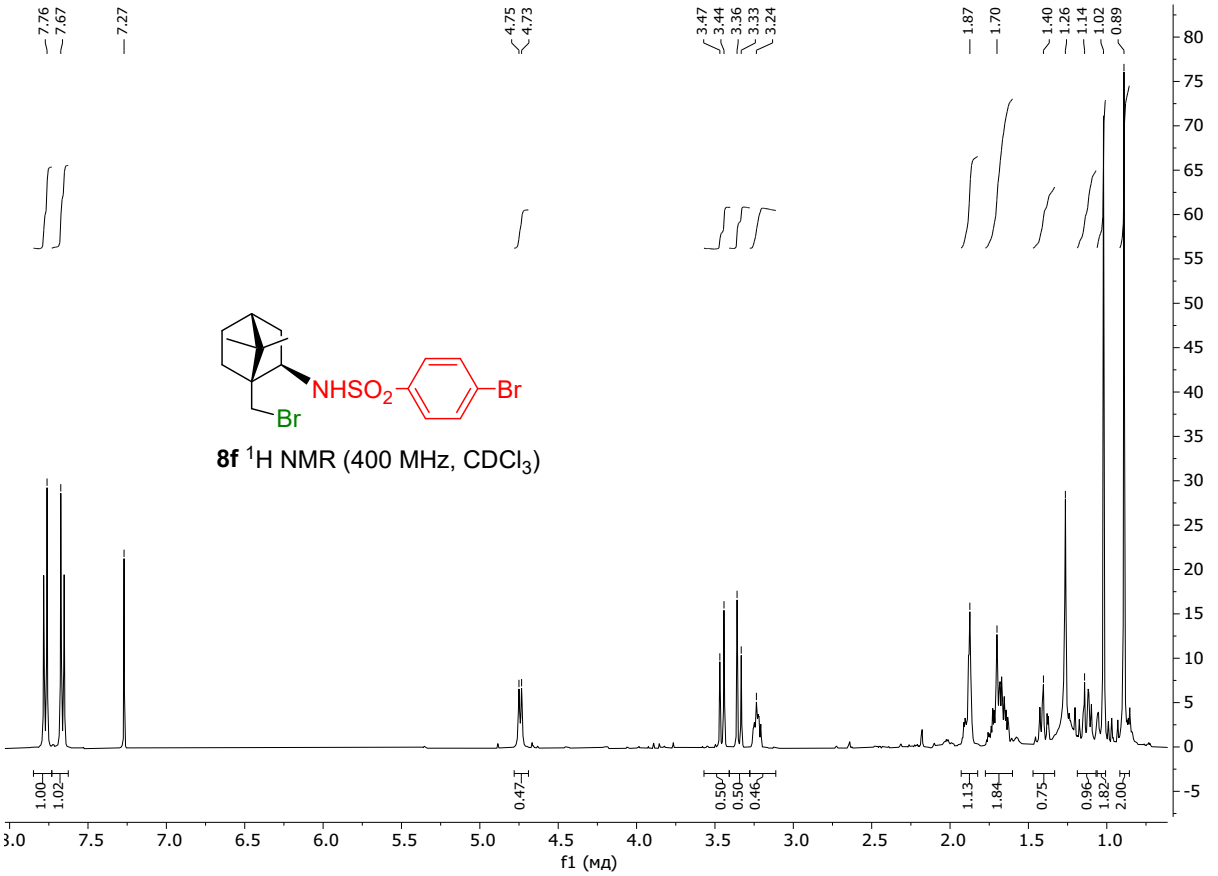


Figure S90. ^{13}C NMR spectrum of compound **8f**

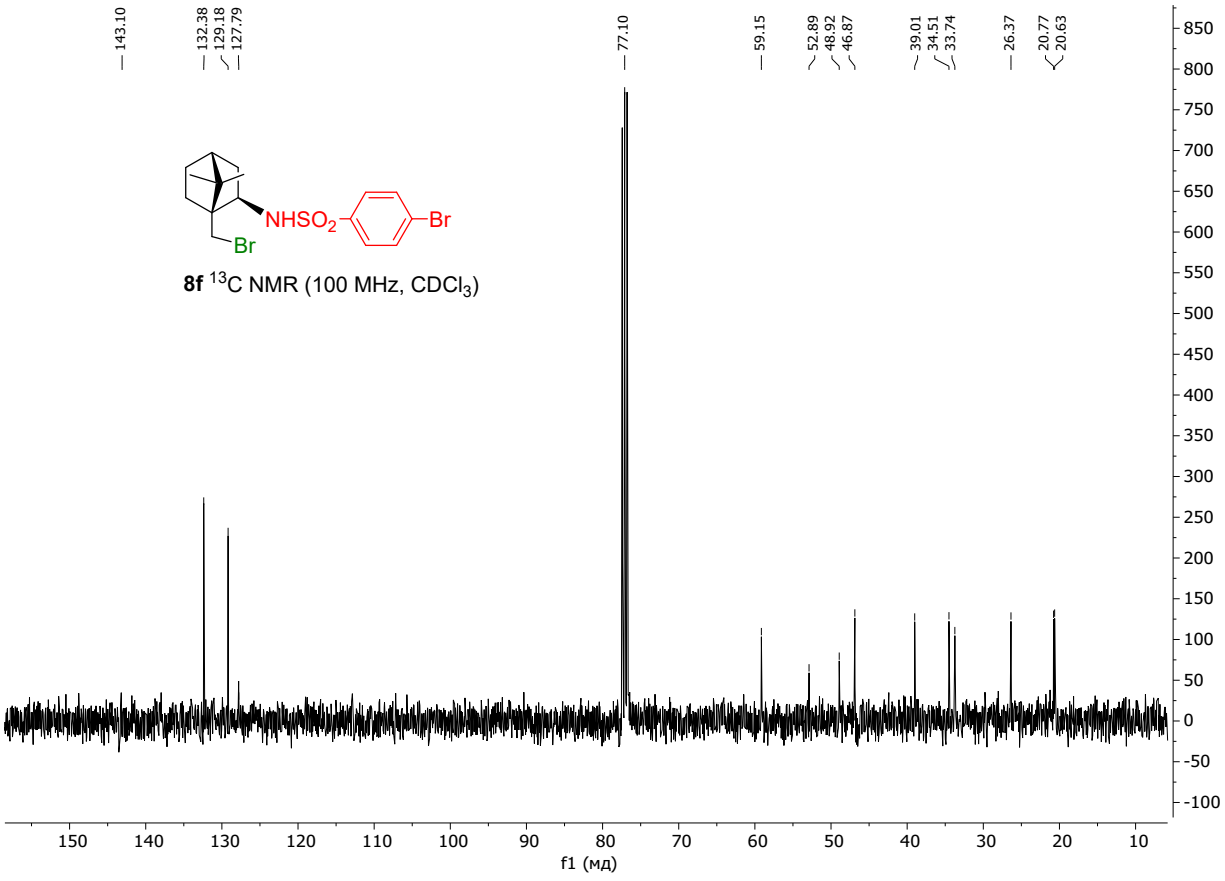


Figure S91. ^{1}H NMR spectrum of compound **8g**

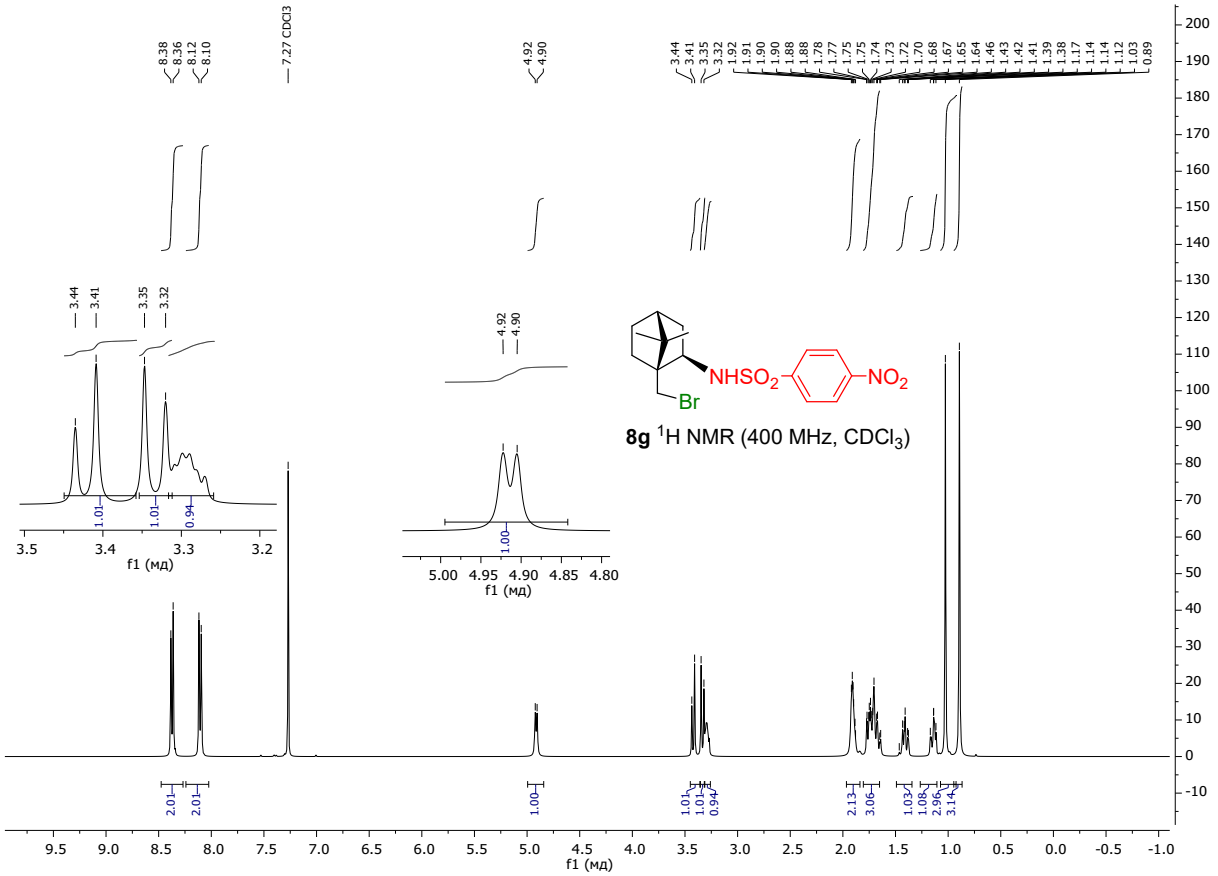
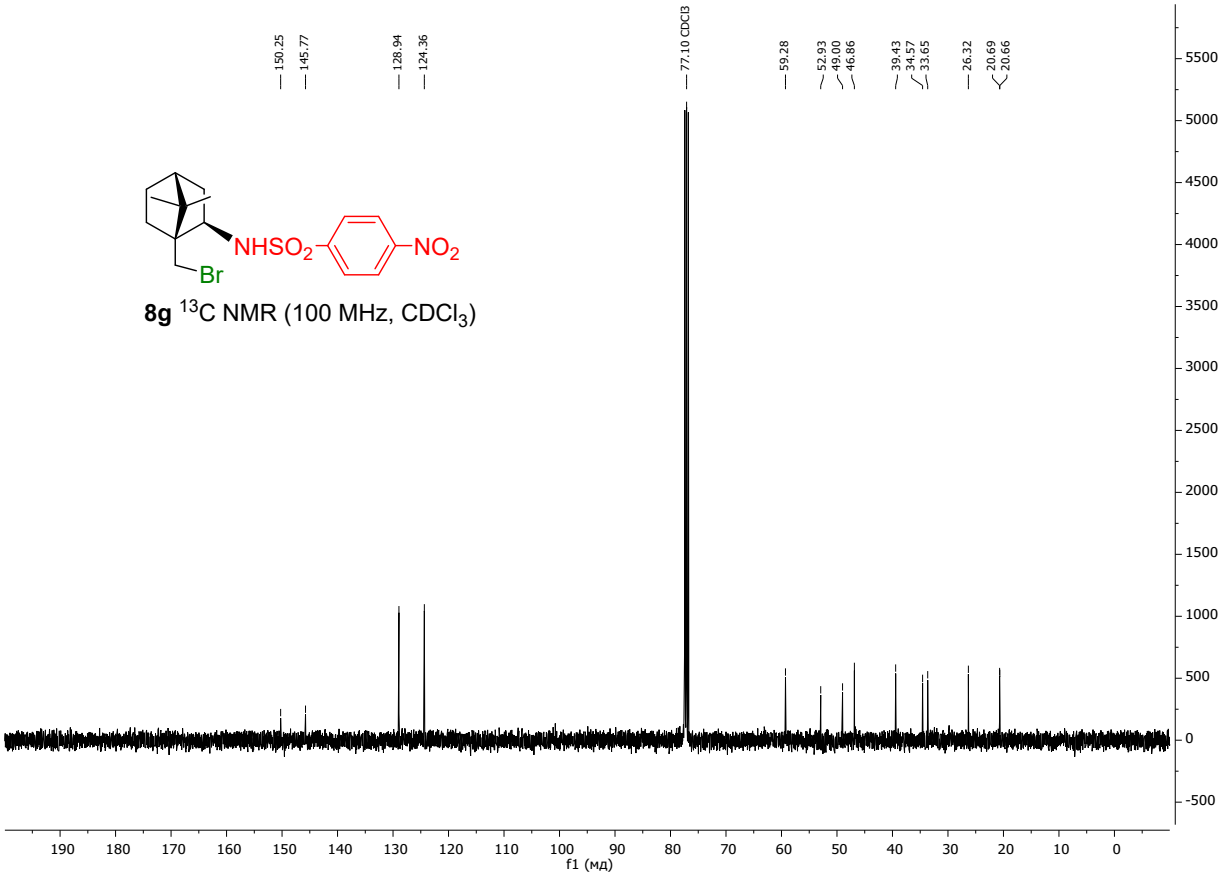
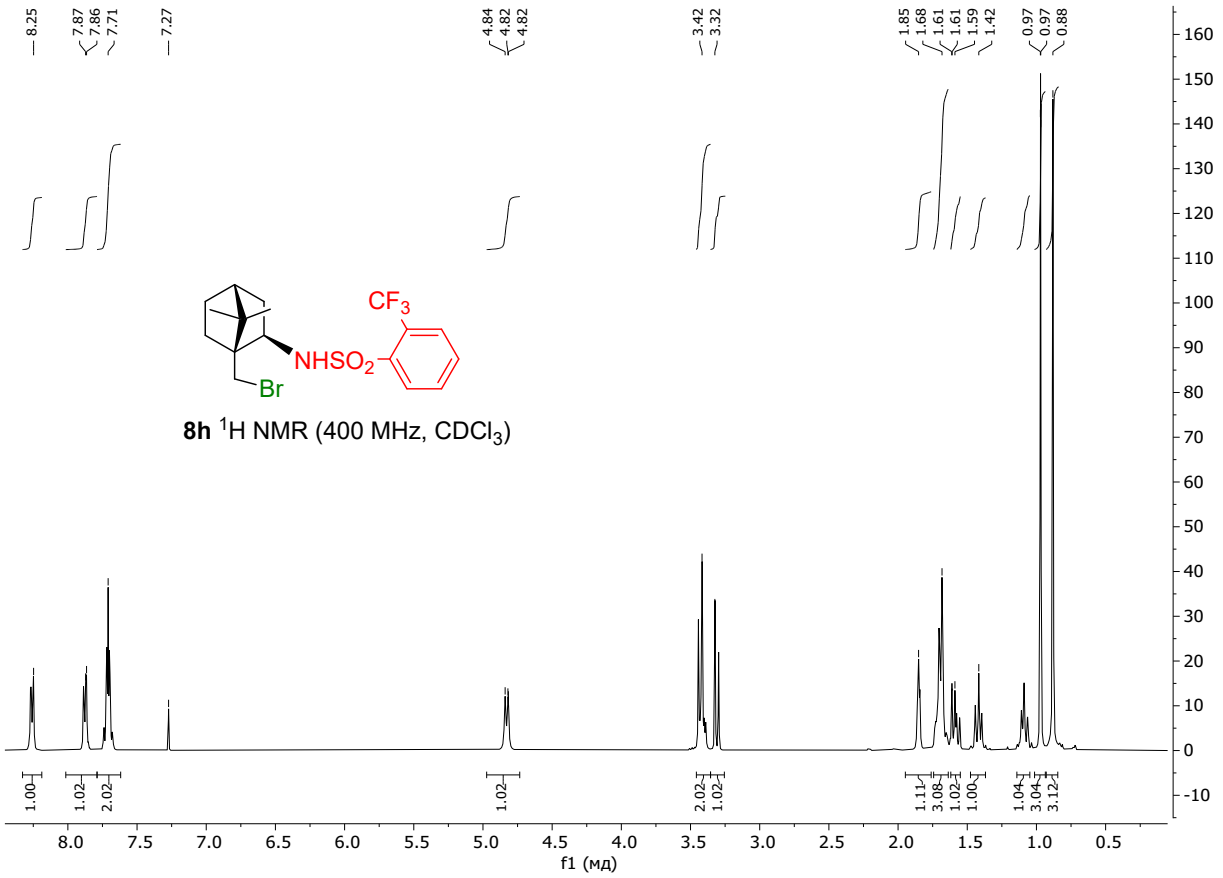


Figure S92. ^{13}C NMR spectrum of compound **8g**



8g ^{13}C NMR (100 MHz, $CDCl_3$)

Figure S93. ^{1}H NMR spectrum of compound **8h**



8h ^{1}H NMR (400 MHz, $CDCl_3$)

Figure S94. ^{13}C NMR spectrum of compound **8h**

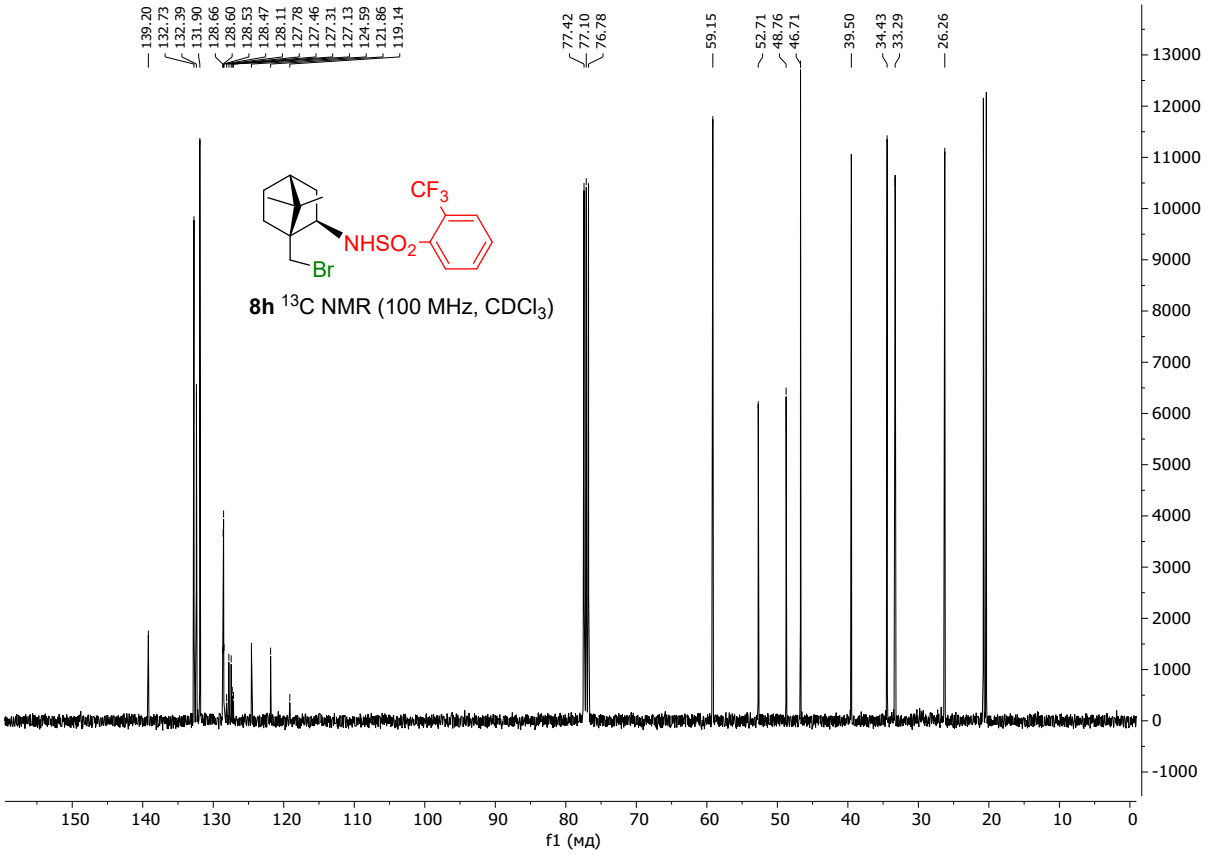


Figure S95. ^{19}F NMR spectrum of compound **8h**

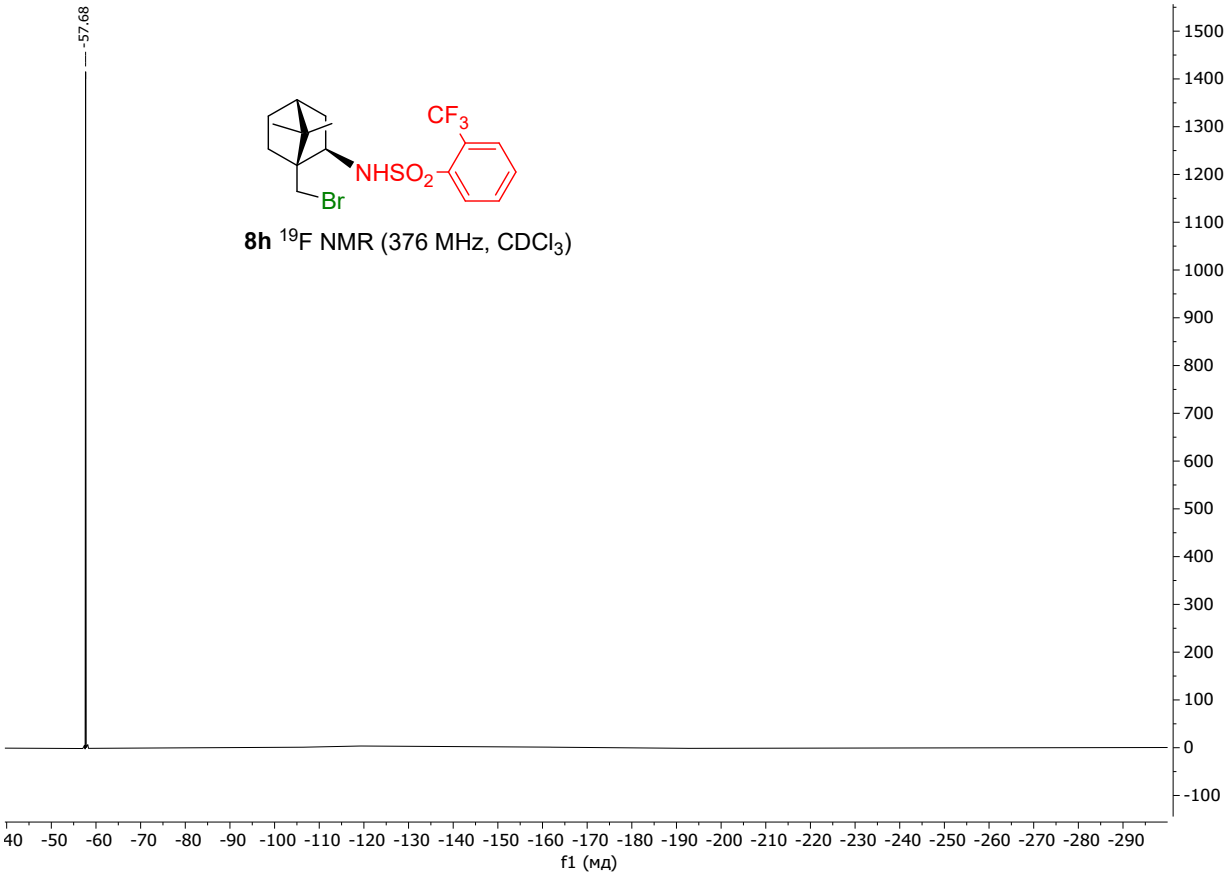


Figure S96. ^{1}H NMR spectrum of compound **8i**

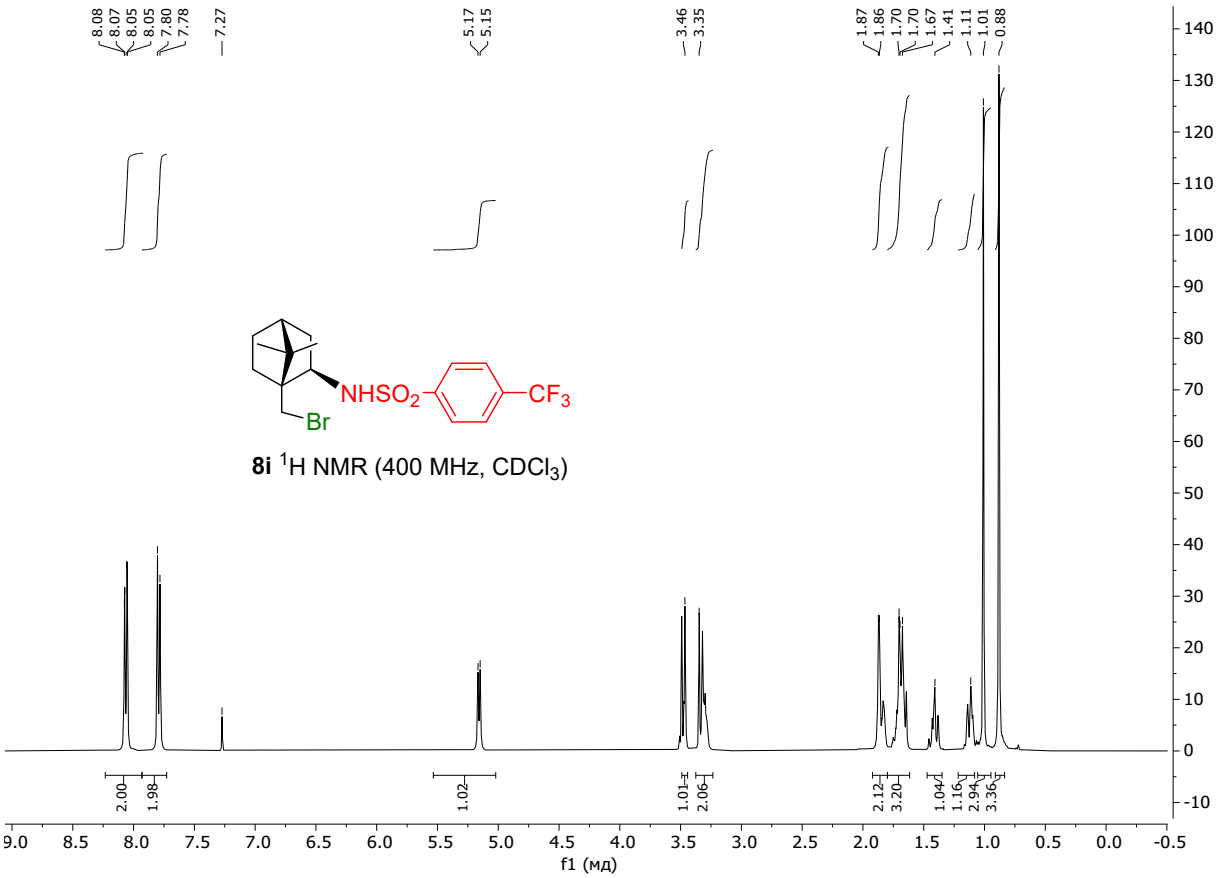


Figure S97. ^{13}C NMR spectrum of compound **8i**

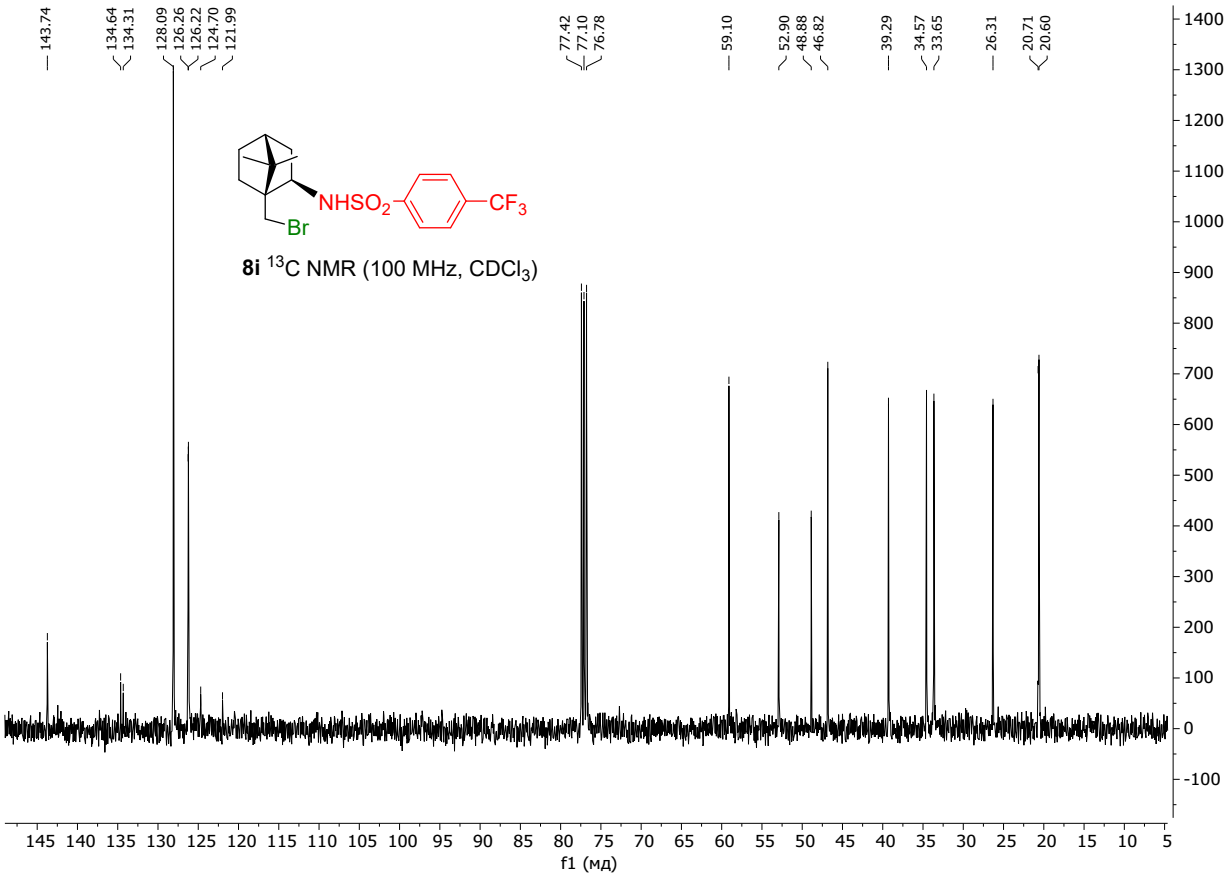
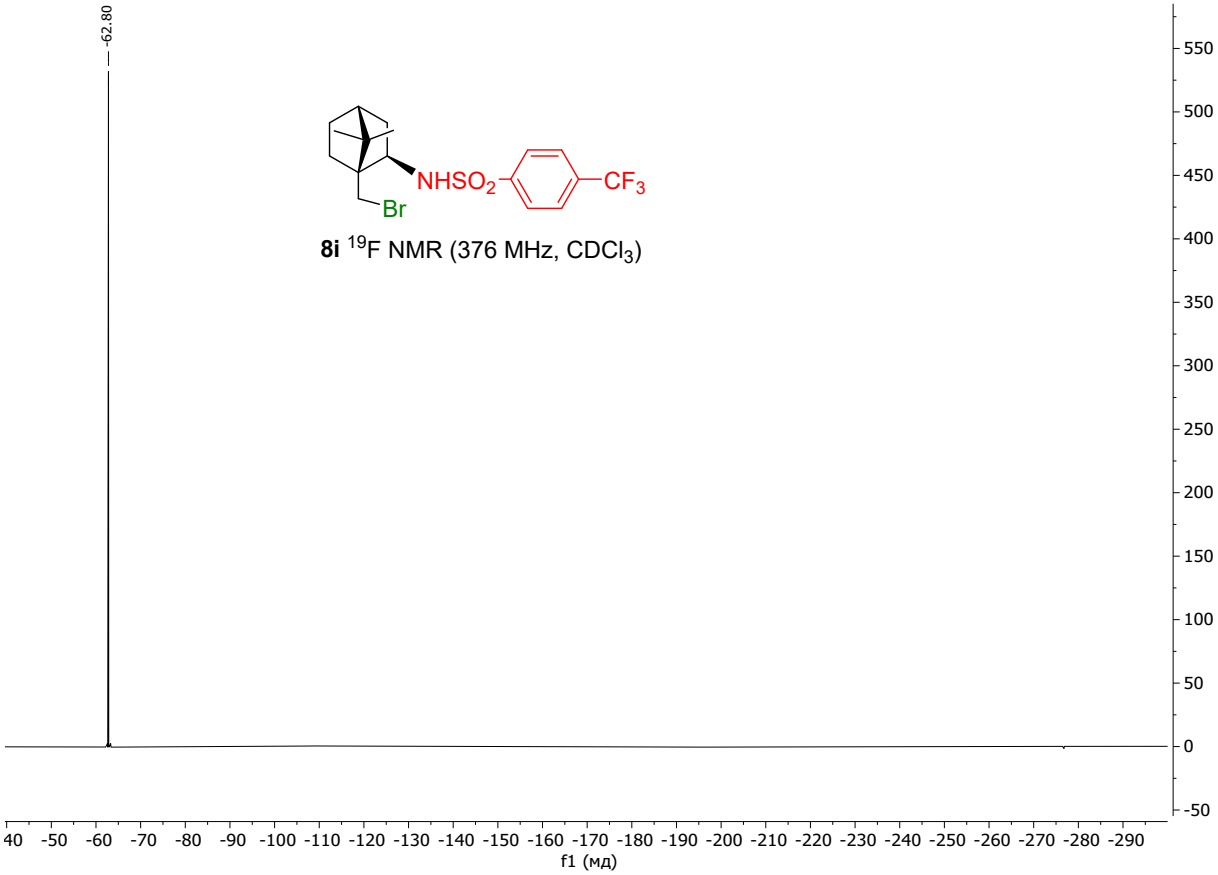
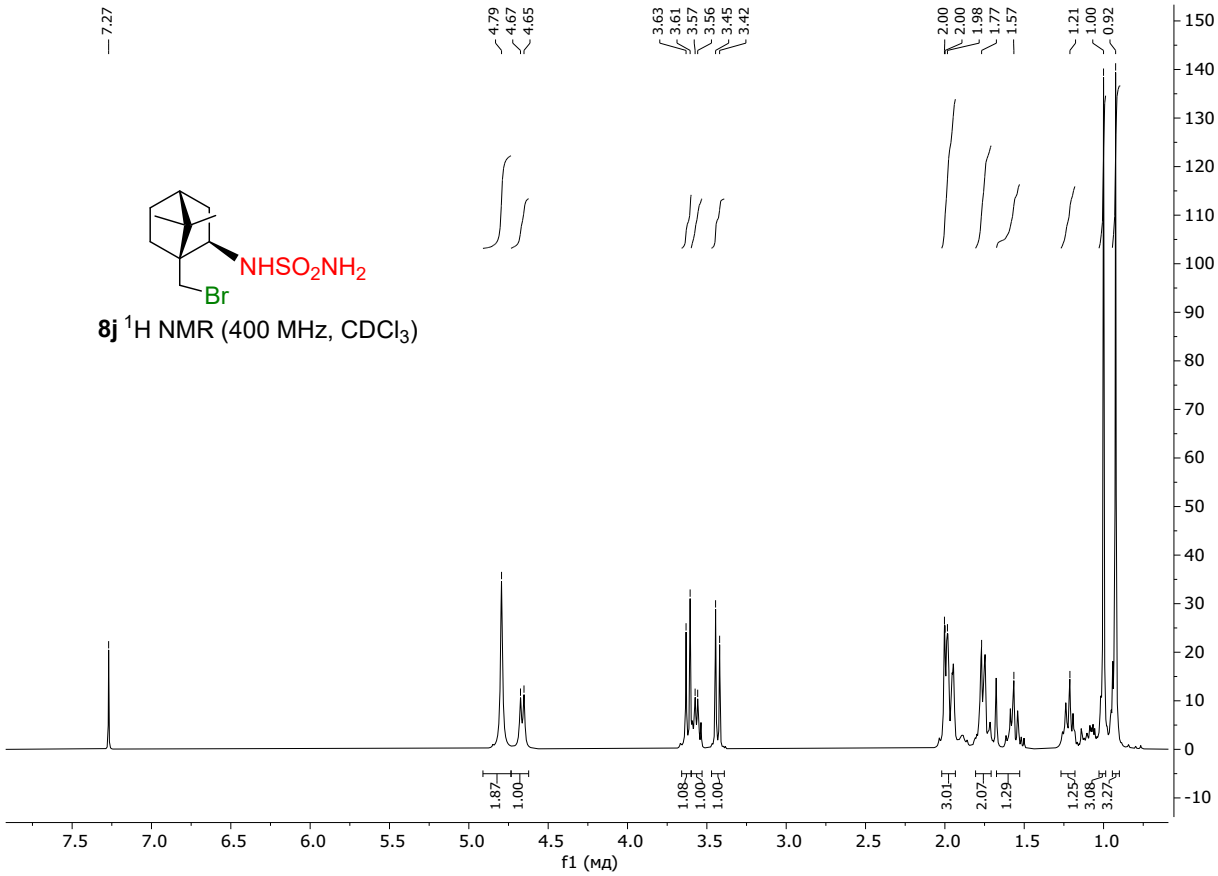


Figure S98. ^{19}F NMR spectrum of compound **8i**



8i ^{19}F NMR (376 MHz, $CDCl_3$)

Figure S99. ^{1}H NMR spectrum of compound **8j**



8j ^{1}H NMR (400 MHz, $CDCl_3$)

Figure S100. ^{13}C NMR spectrum of compound **8j**

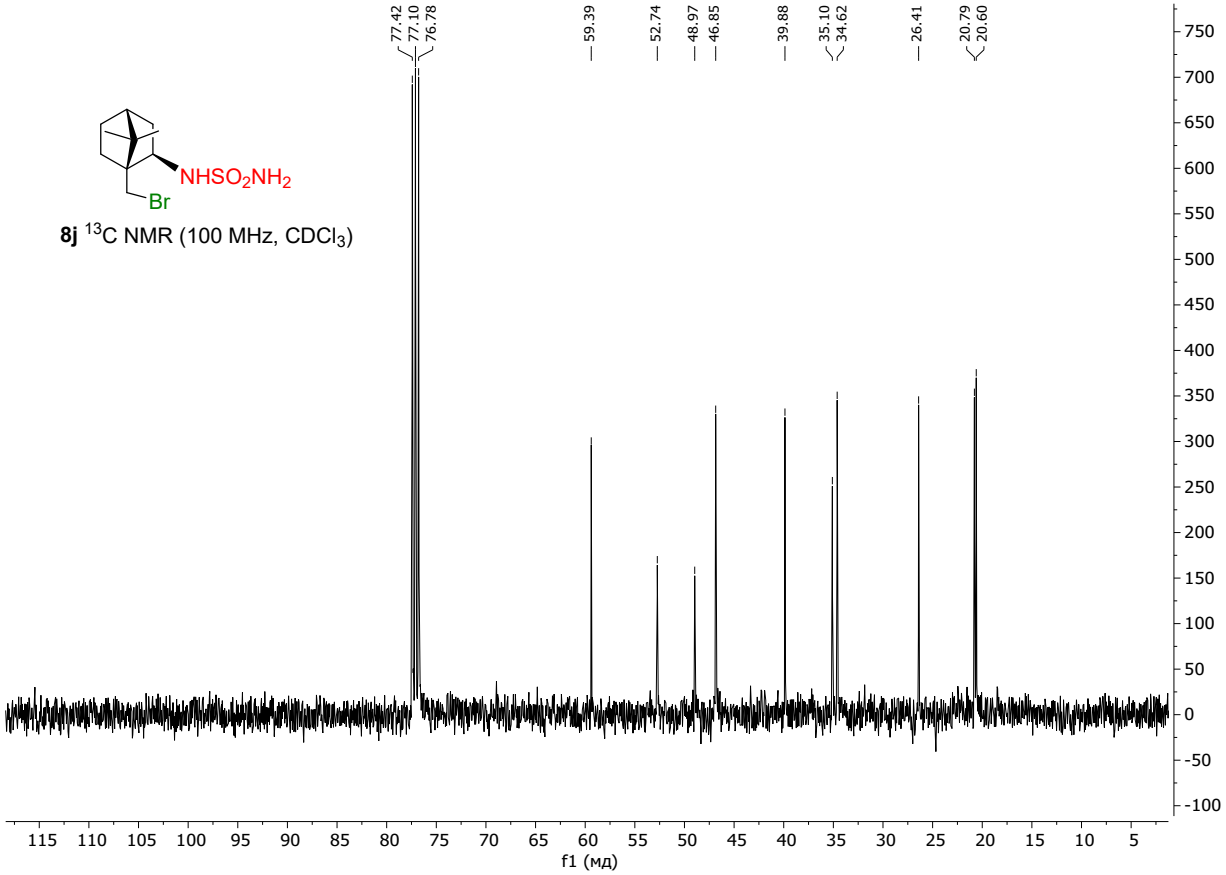


Figure S101. ^{1}H NMR spectrum of compound **8k**

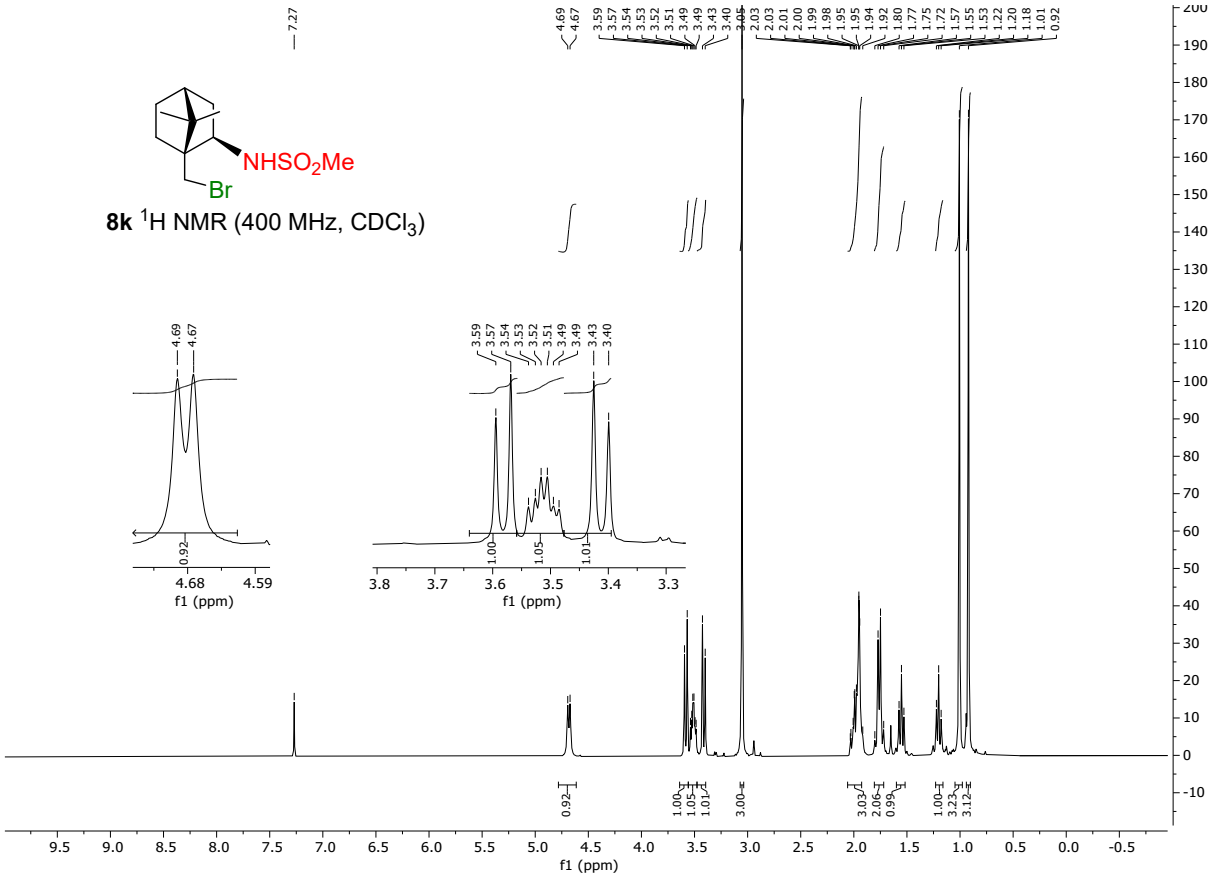


Figure S102. ^{13}C NMR spectrum of compound **8k**

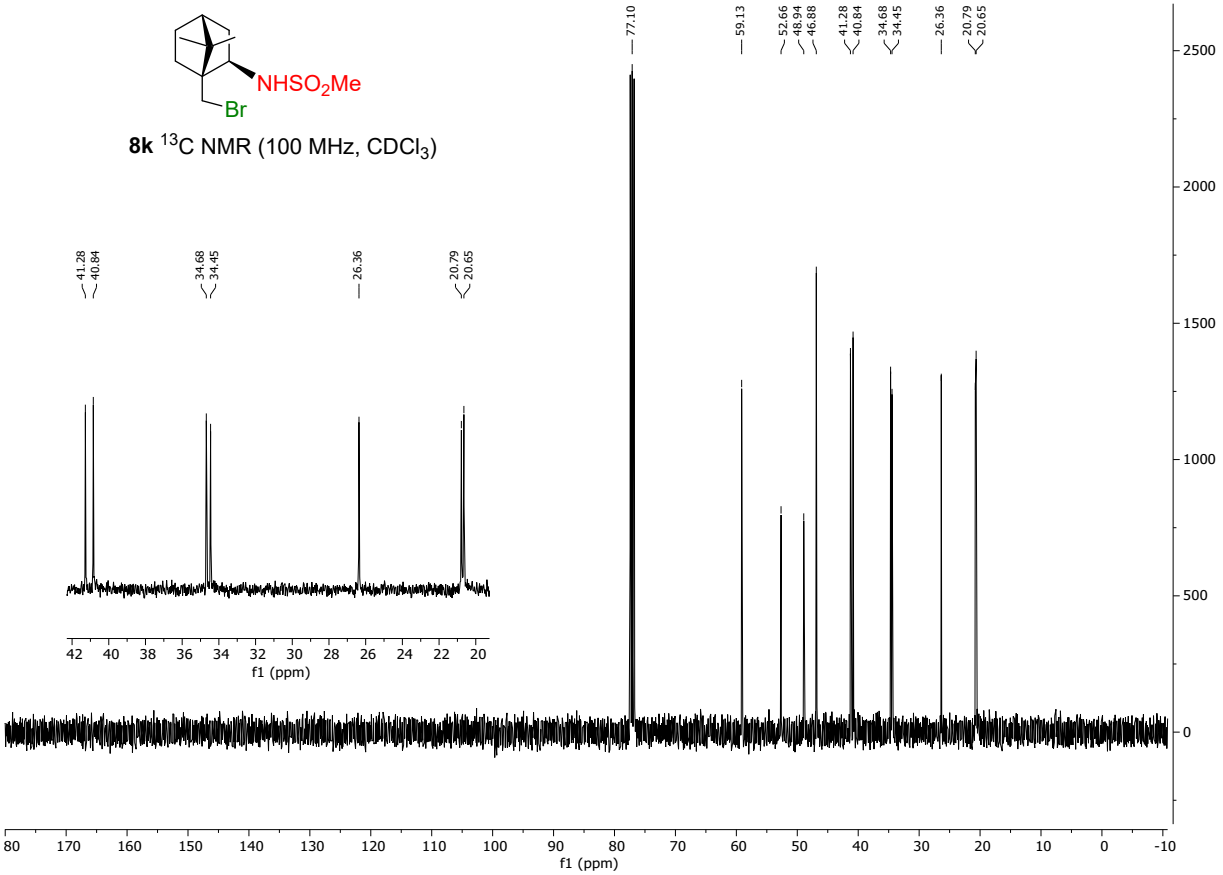
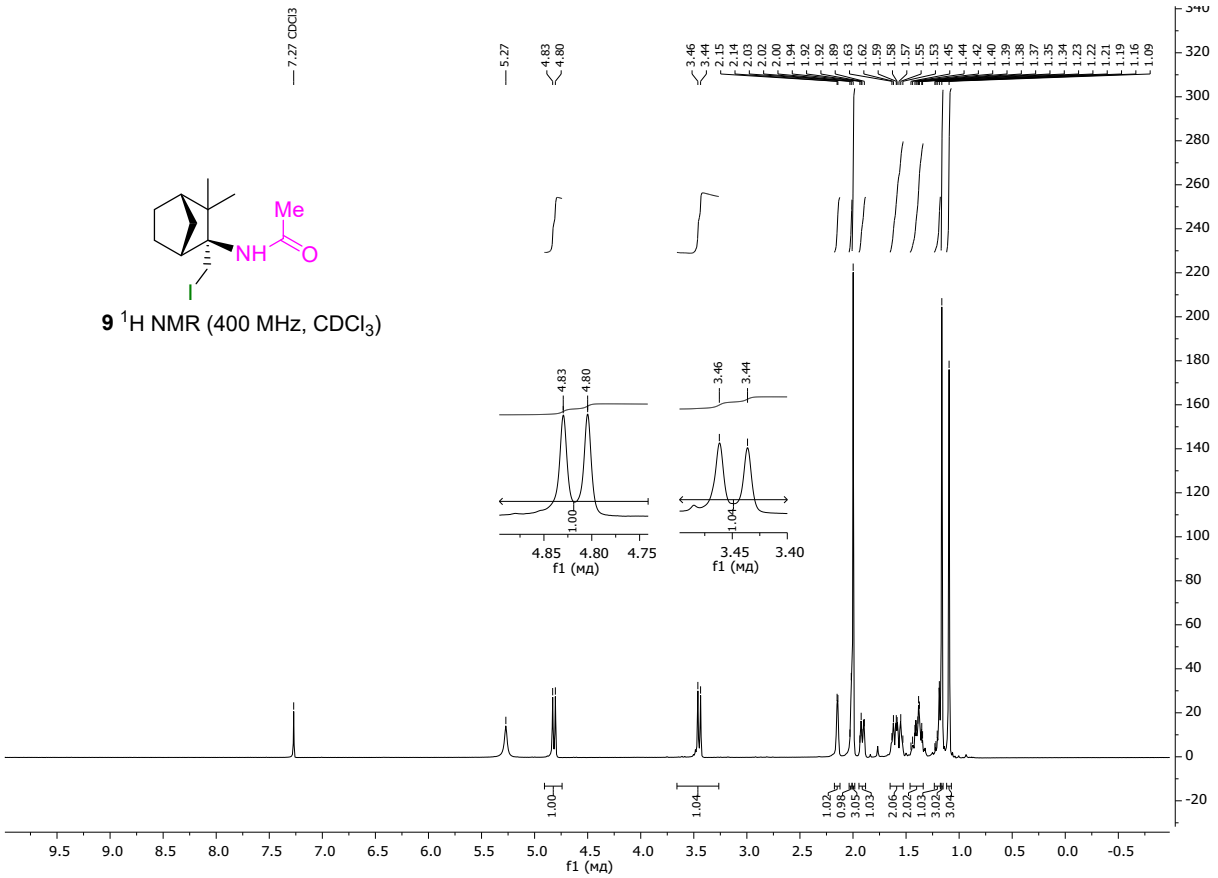


Figure S103. ^{1}H NMR spectrum of compound **9**



igure S104. ^{13}C NMR spectrum of compound **9**

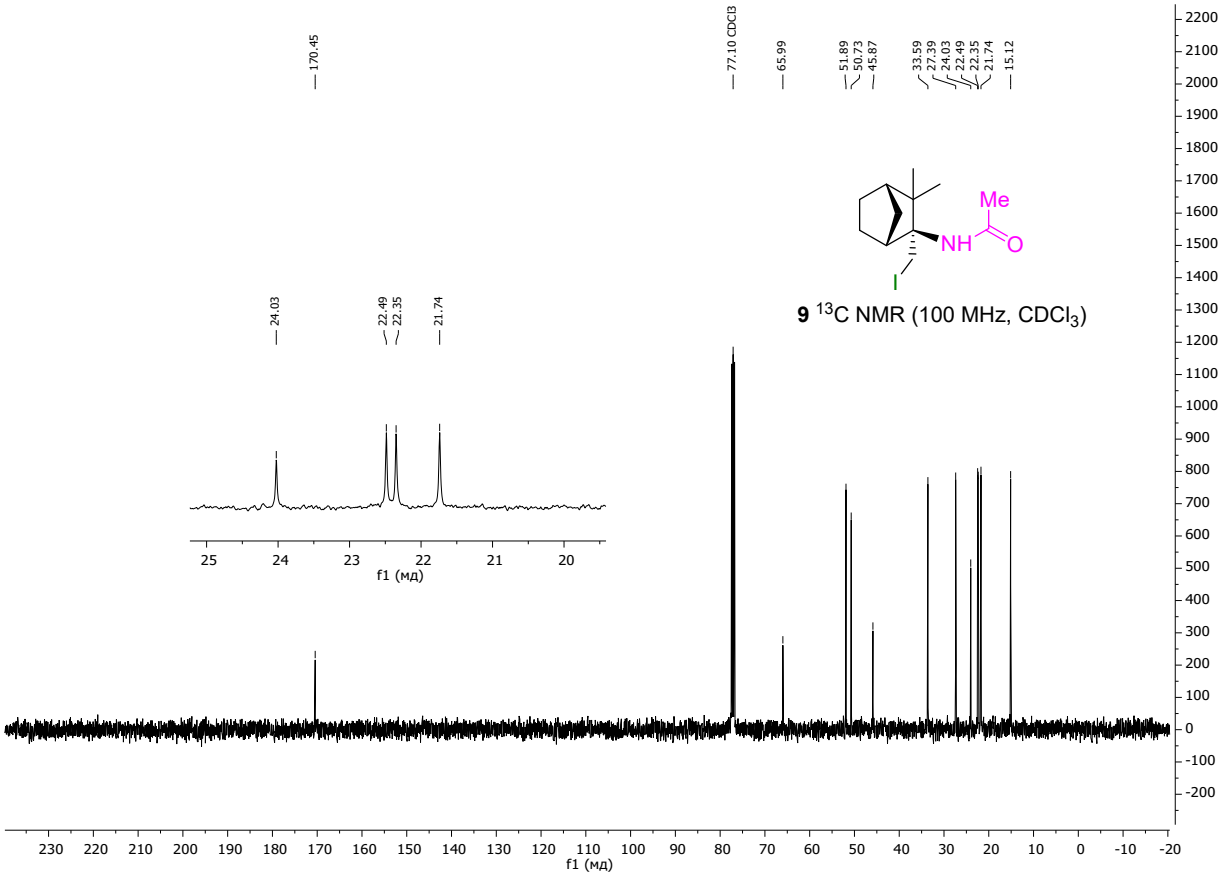


Figure S105. ^{1}H NMR spectrum of compound **10**

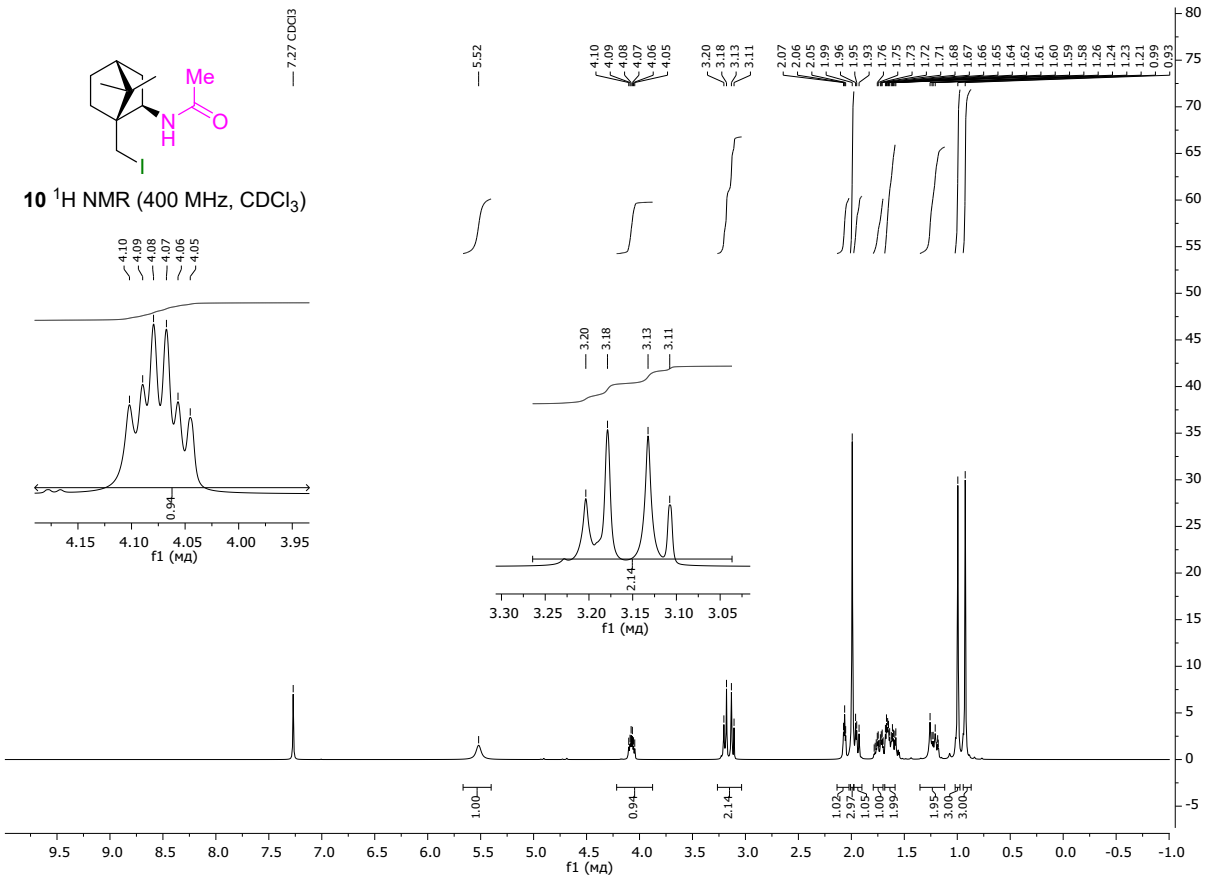


Figure S106. ^{13}C NMR spectrum of compound **10**

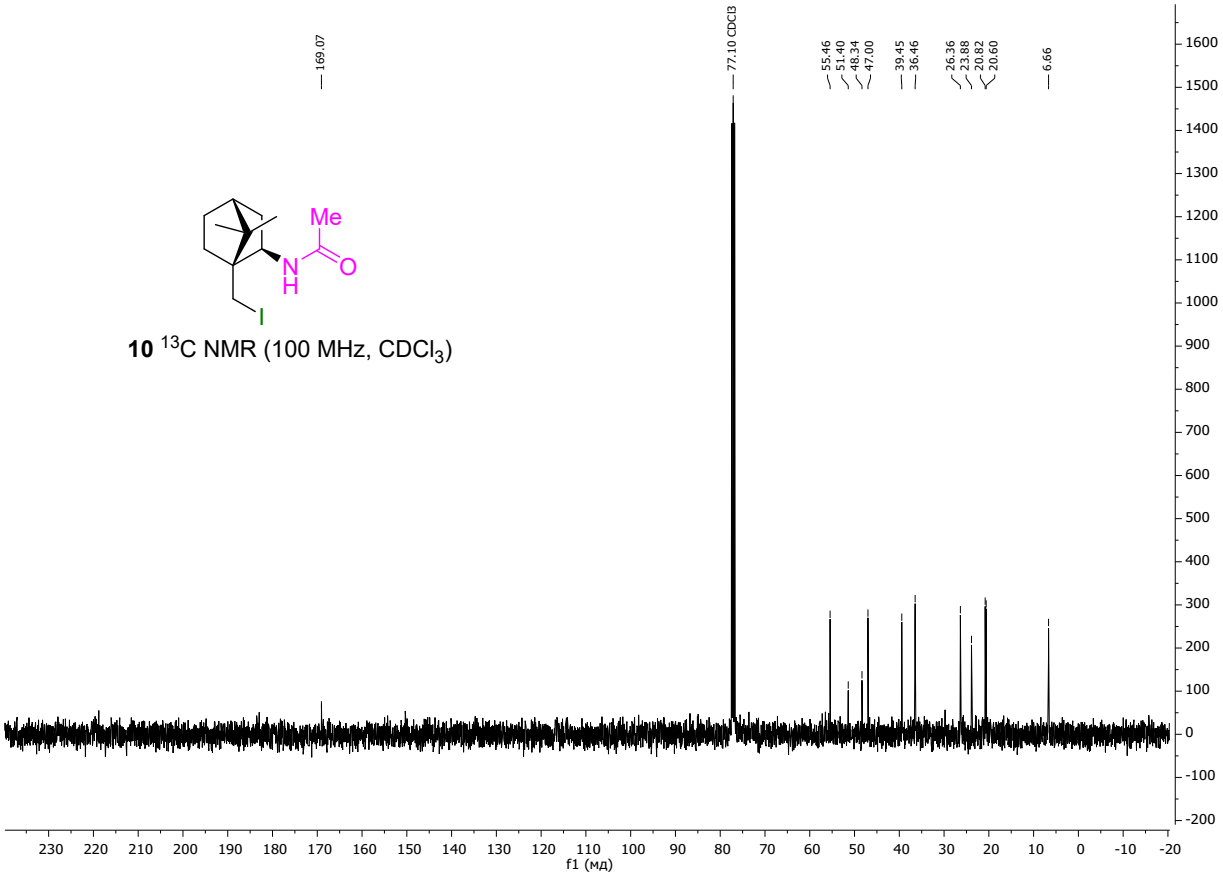


Figure S107. ^{1}H NMR spectrum of compound **11**

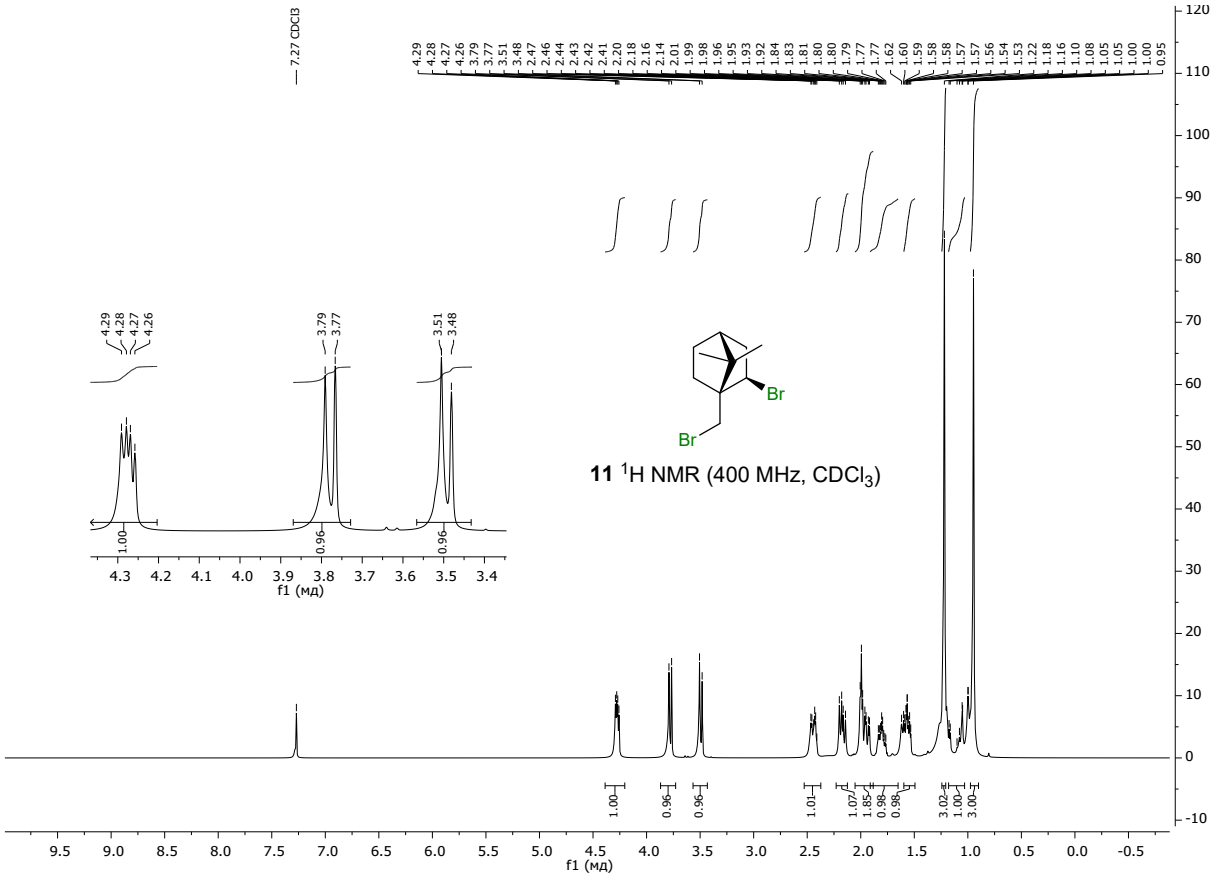


Figure S108. ^{13}C NMR spectrum of compound **11**

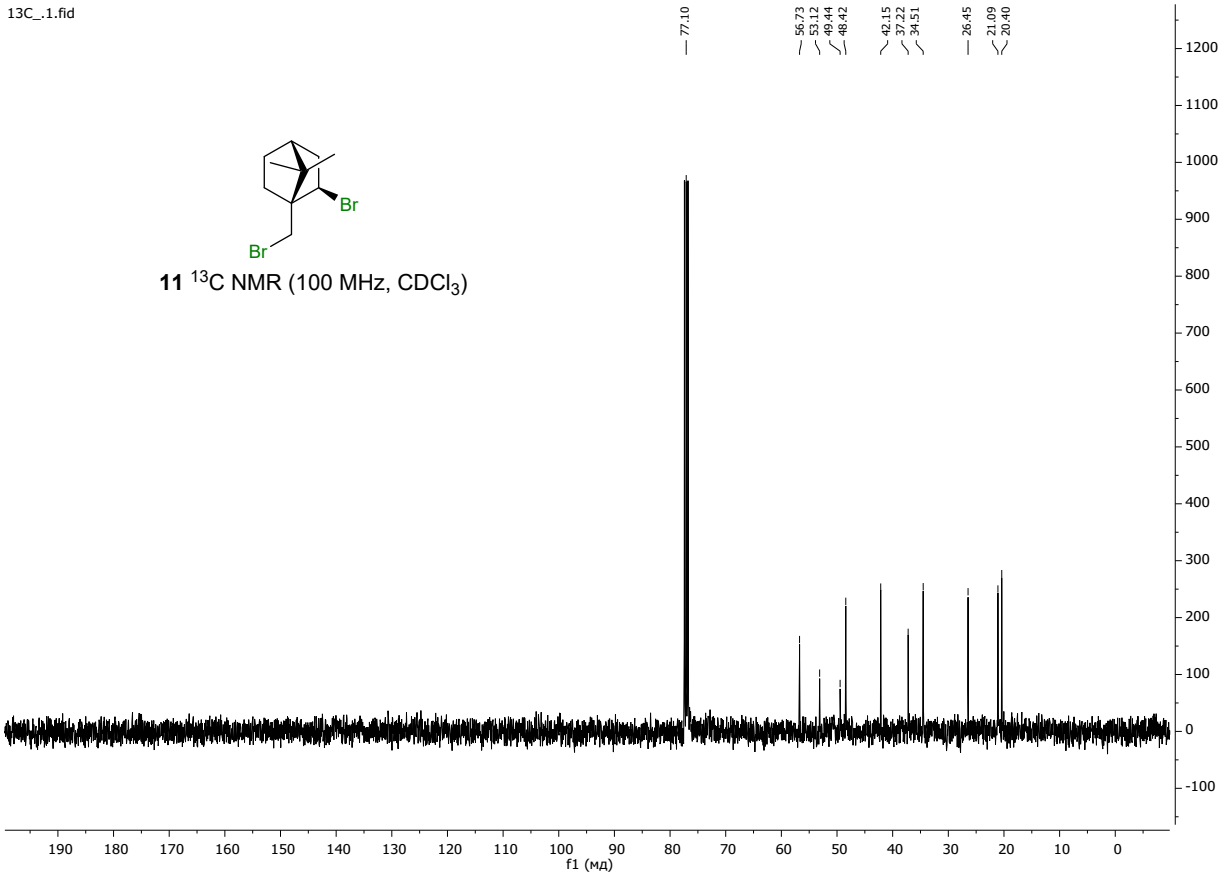


Figure S109. ^{1}H NMR spectrum of compound **12**

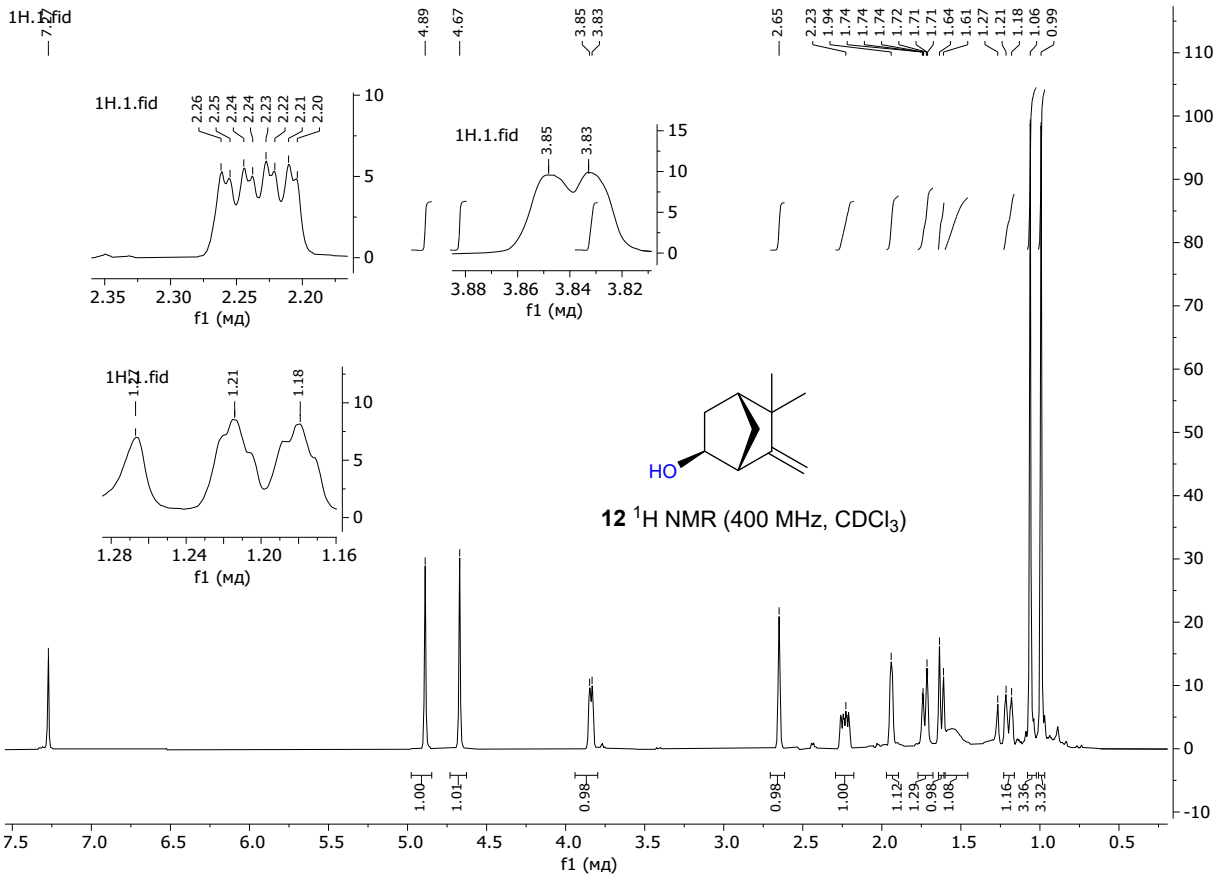


Figure S110. ^{13}C NMR spectrum of compound **12**

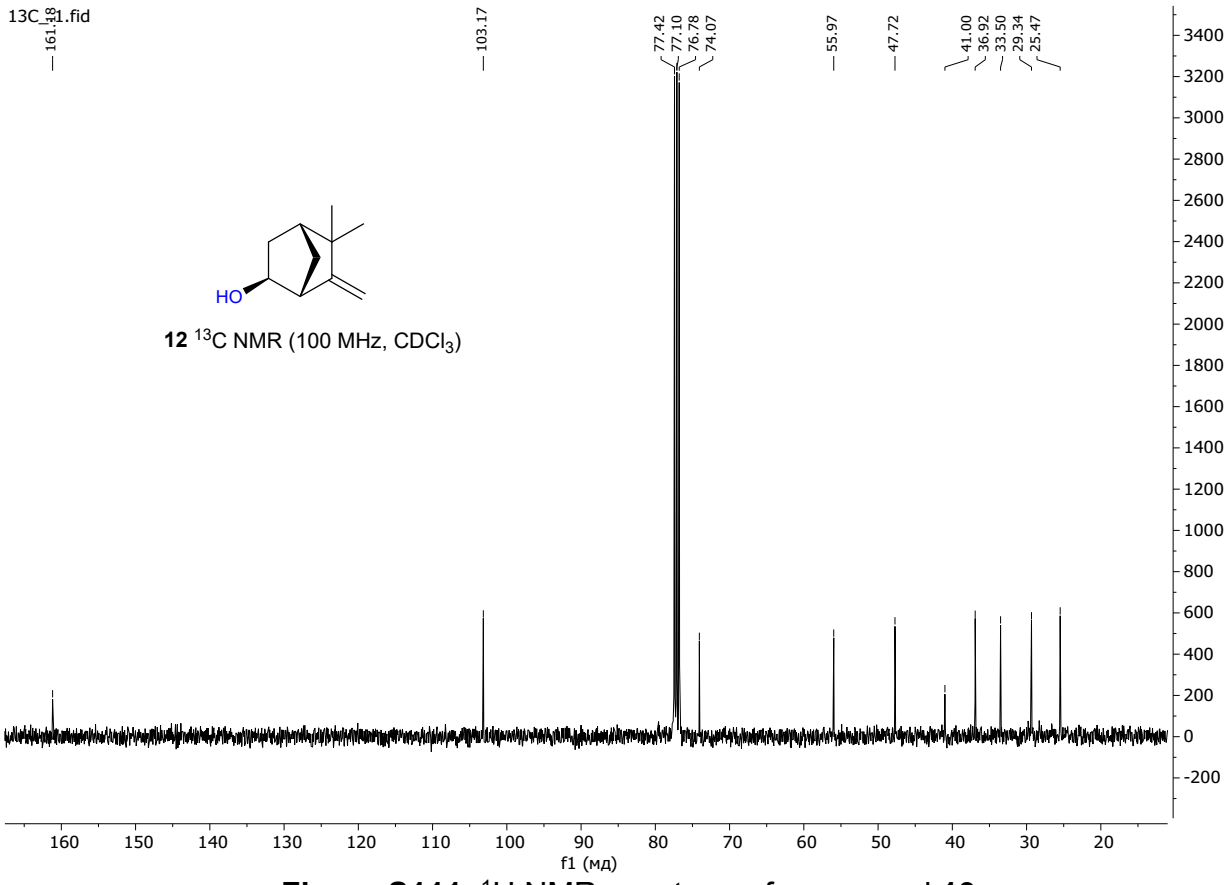


Figure S111. ^{1}H NMR spectrum of compound **13**

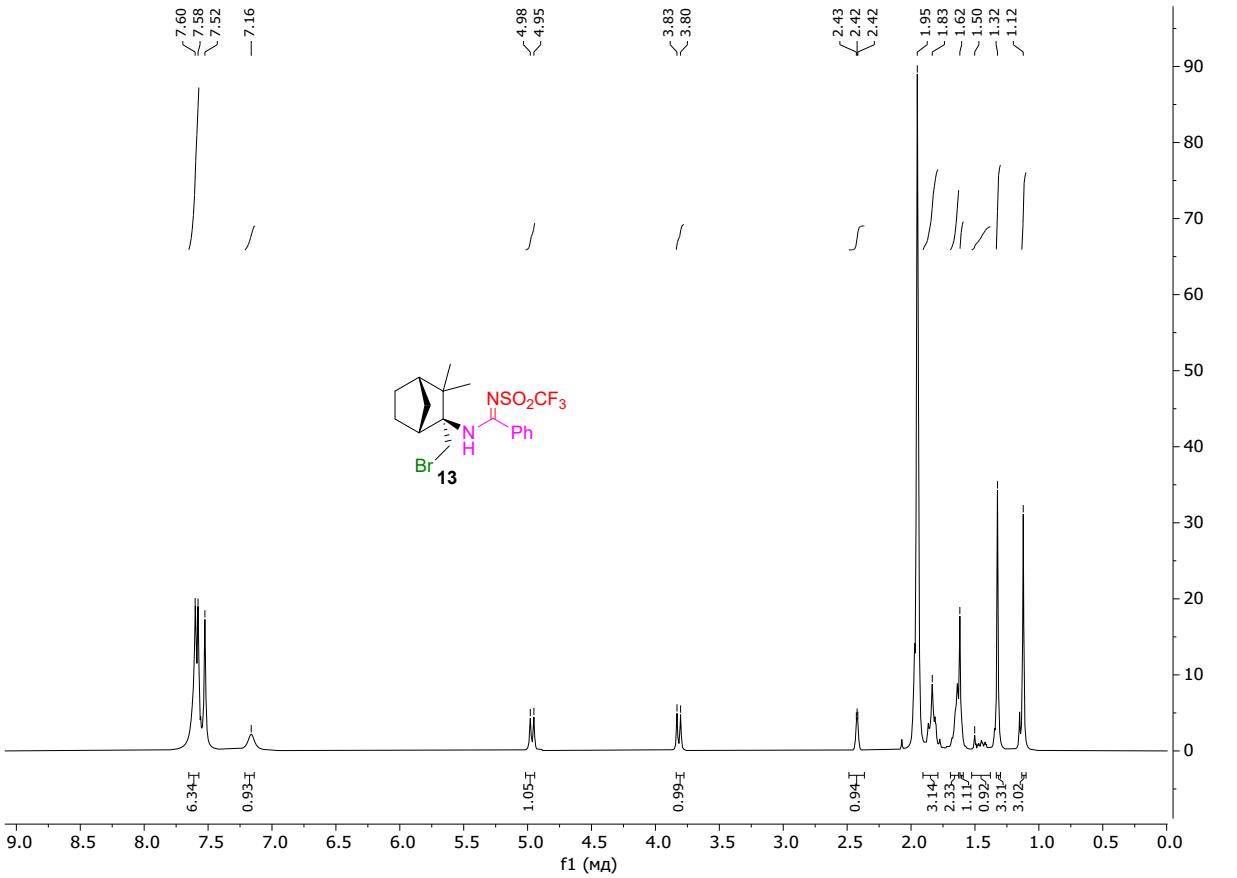


Figure S112. ^{13}C NMR spectrum of compound **13**

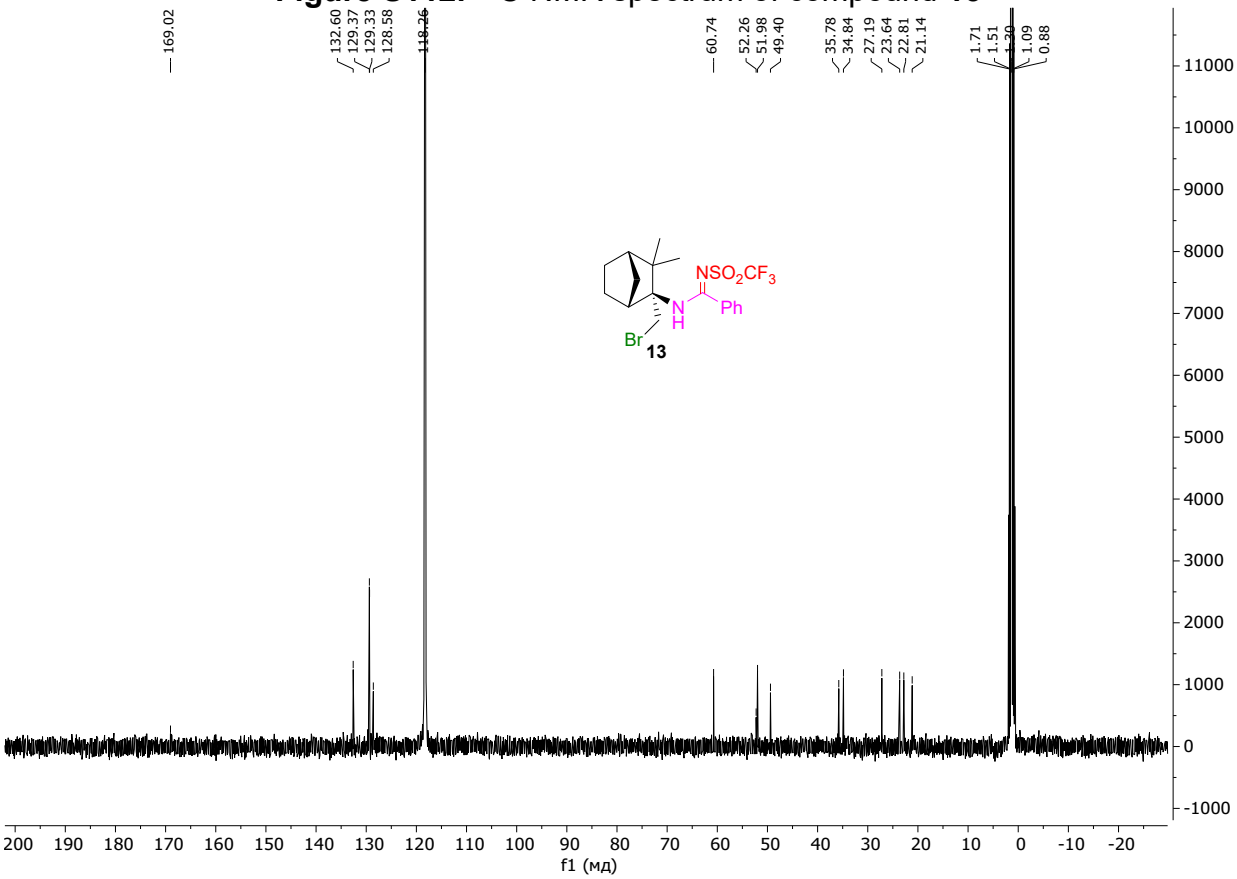


Figure S113. ^{19}F NMR spectrum of compound **13**

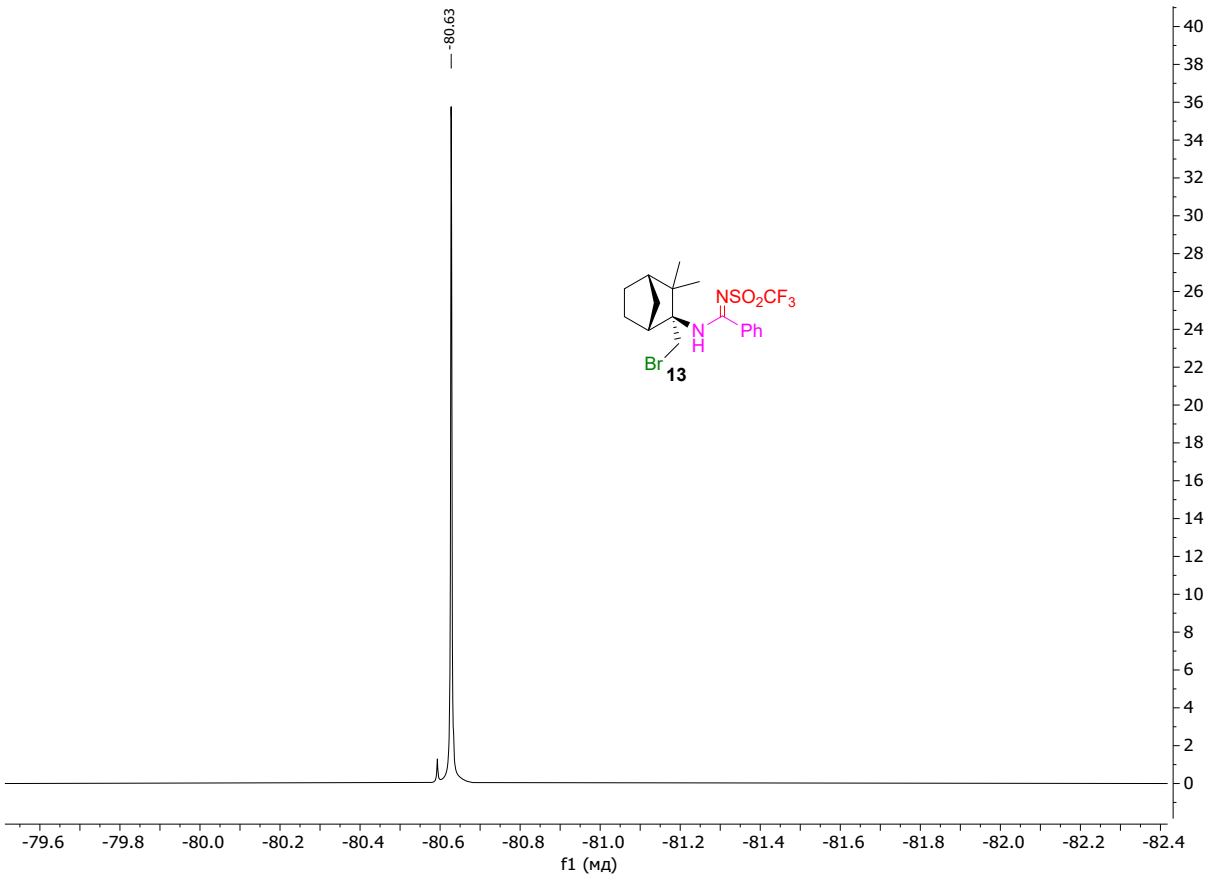


Figure S114. ^{1}H NMR spectrum of compound **14**

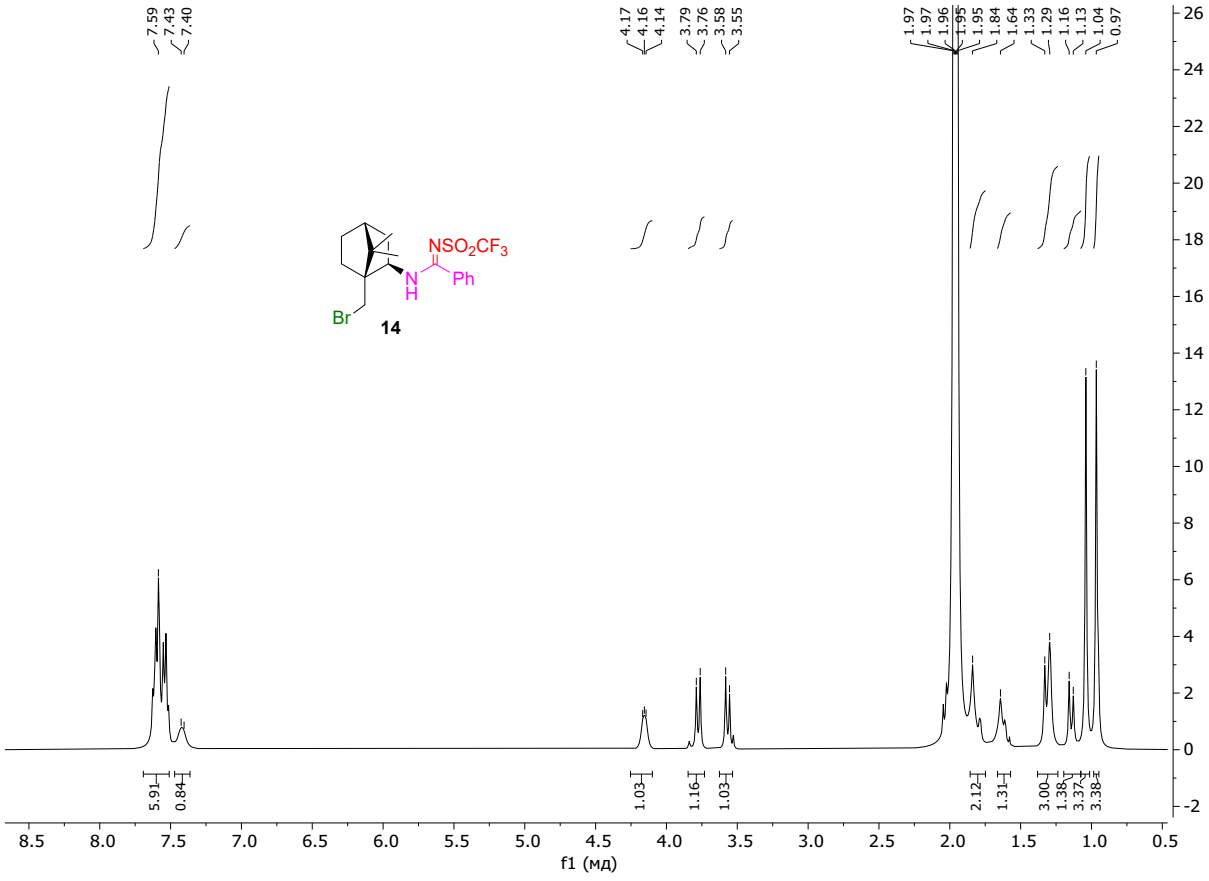


Figure S115. ^{13}C NMR spectrum of compound **14**

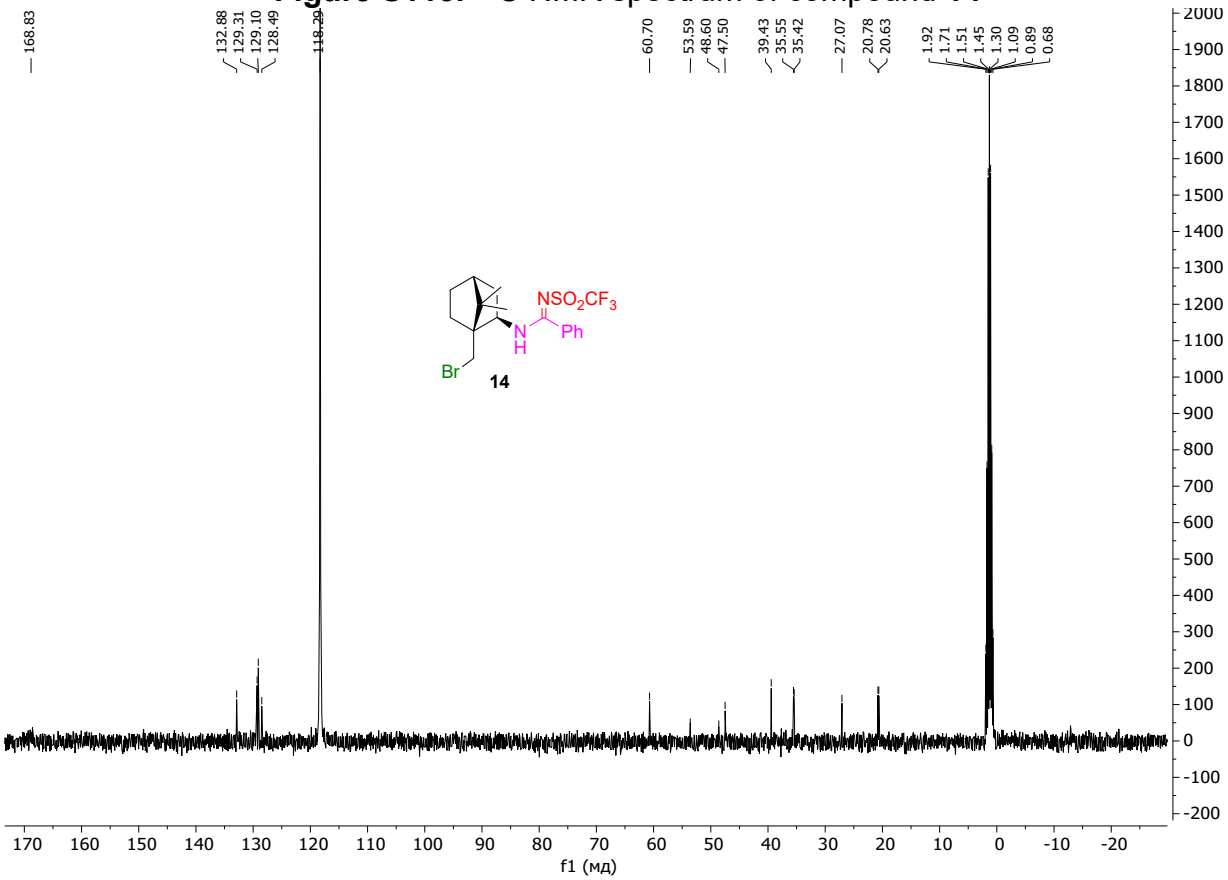


Figure S116. ^{19}F NMR spectrum of compound **14**

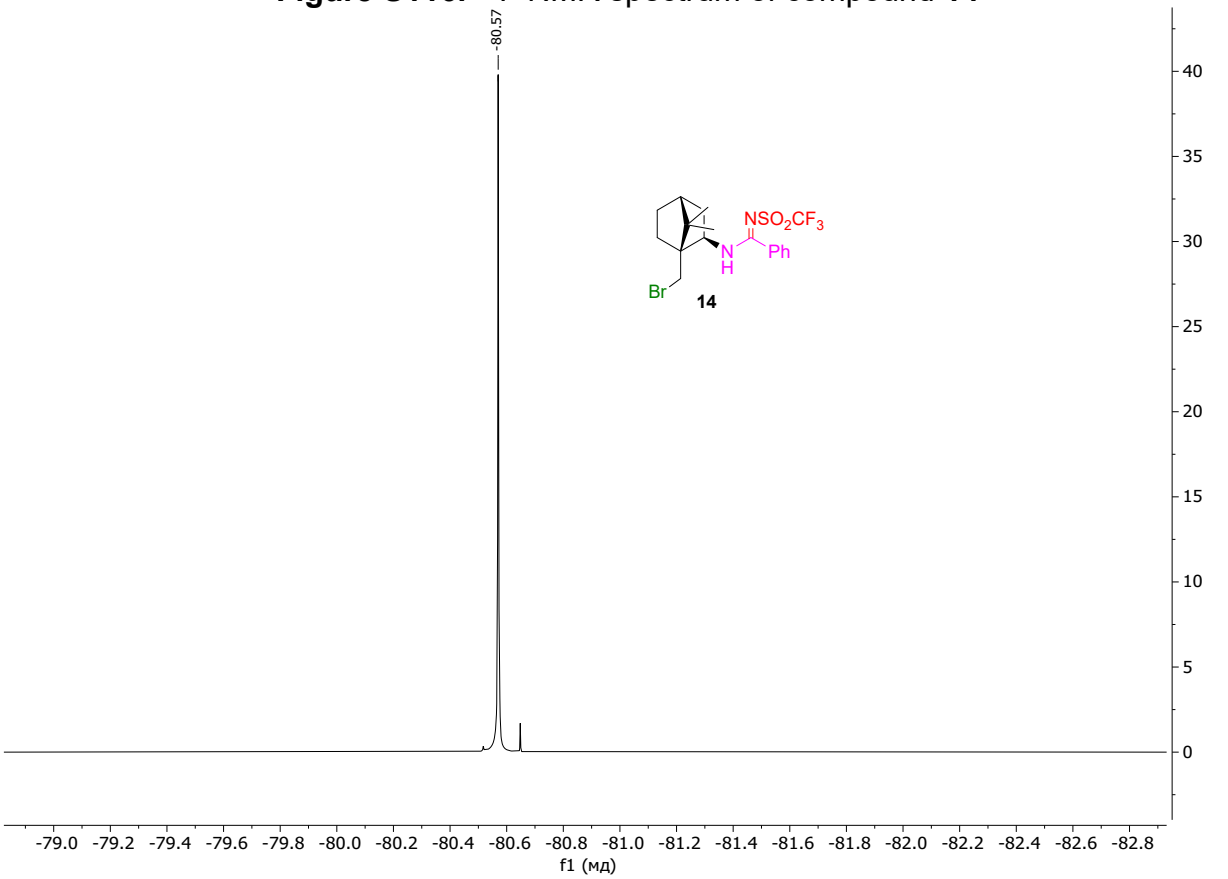


Figure S117. ^{1}H NMR spectrum of compound **15**

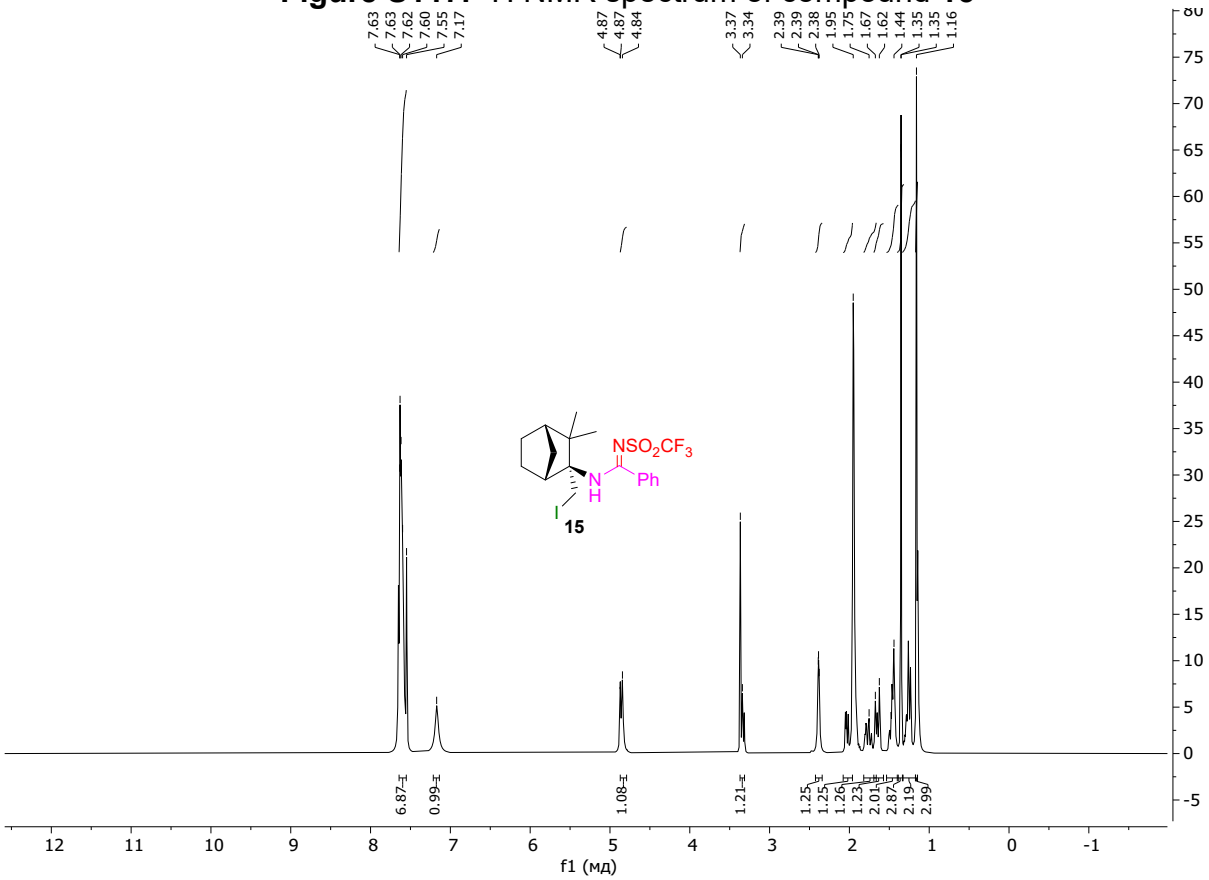


Figure S118. ^{13}C NMR spectrum of compound **15**

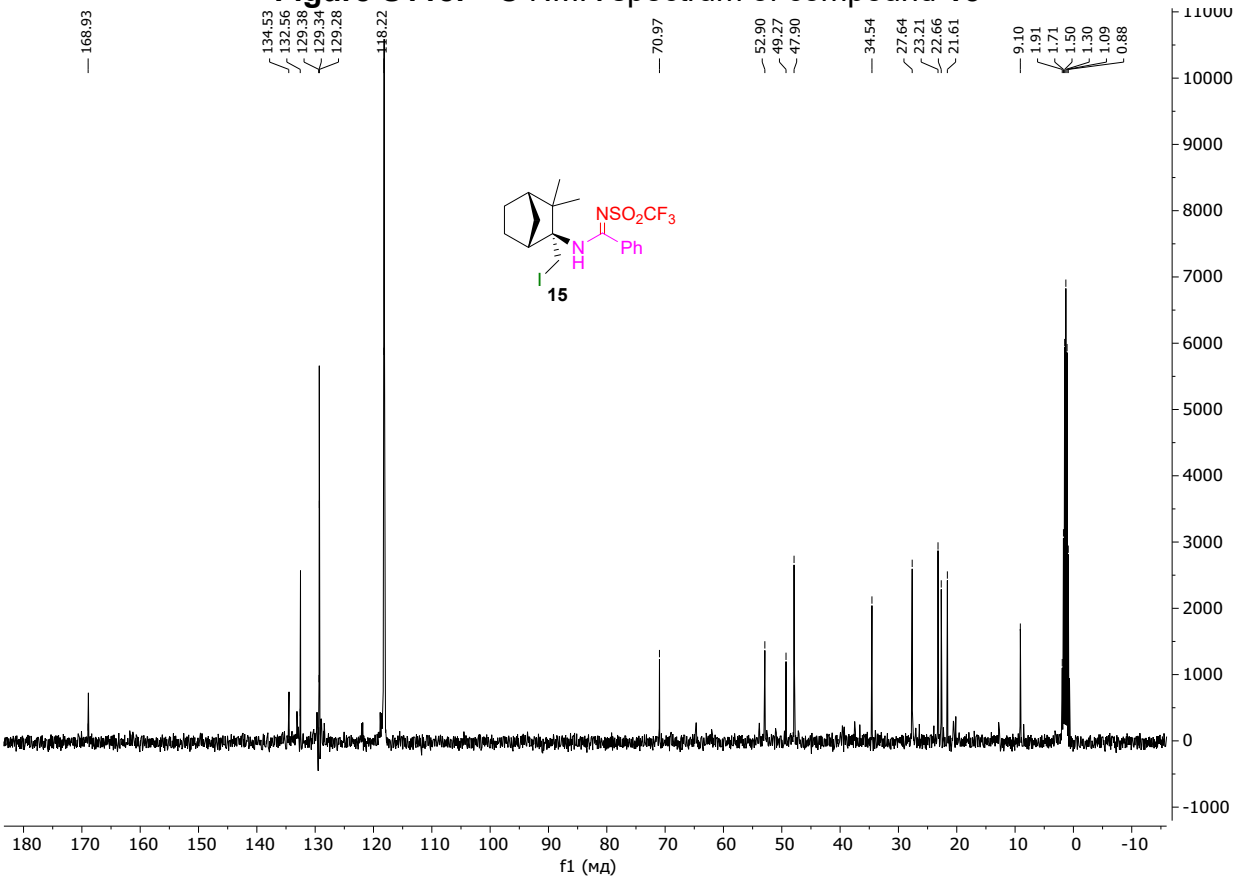


Figure S119. ^{19}F NMR spectrum of compound **15**

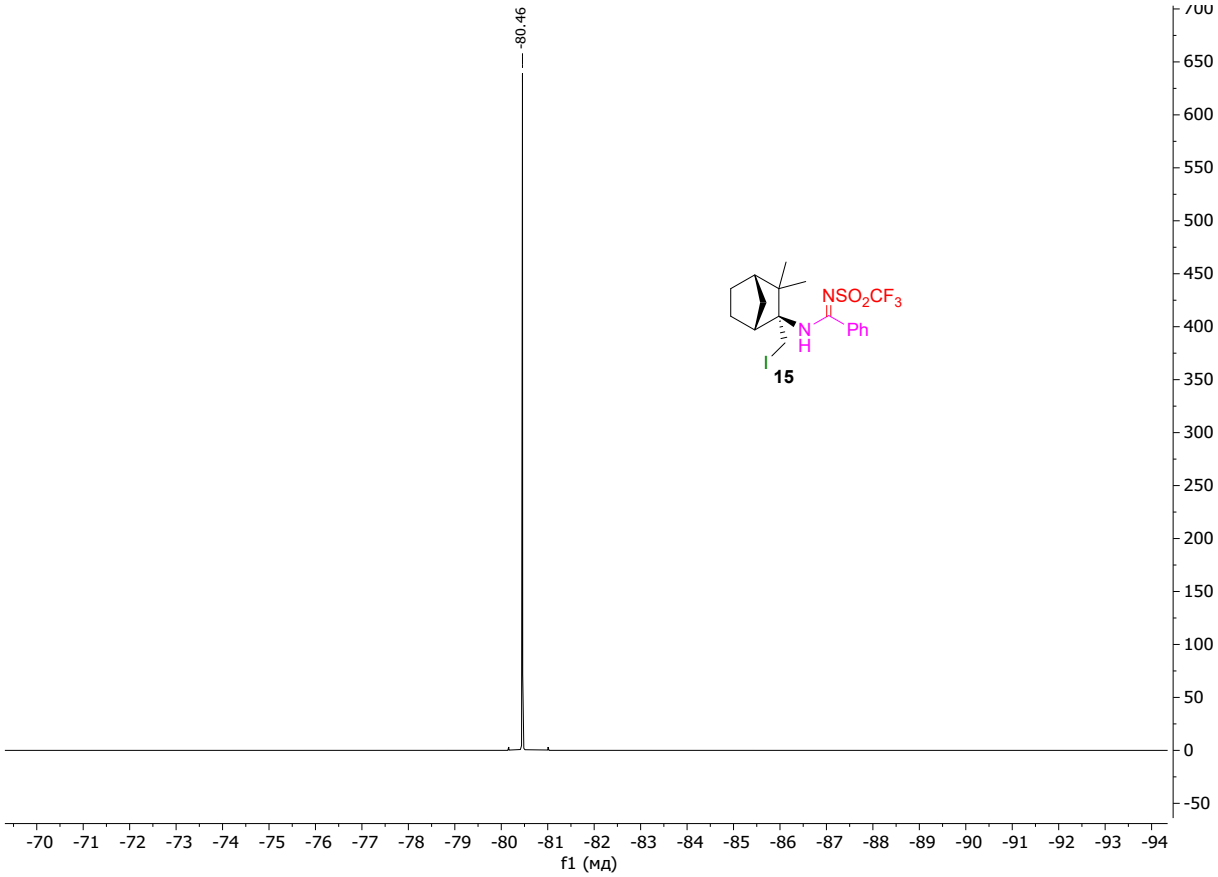


Figure S120. ^{1}H NMR spectrum of compound **16**

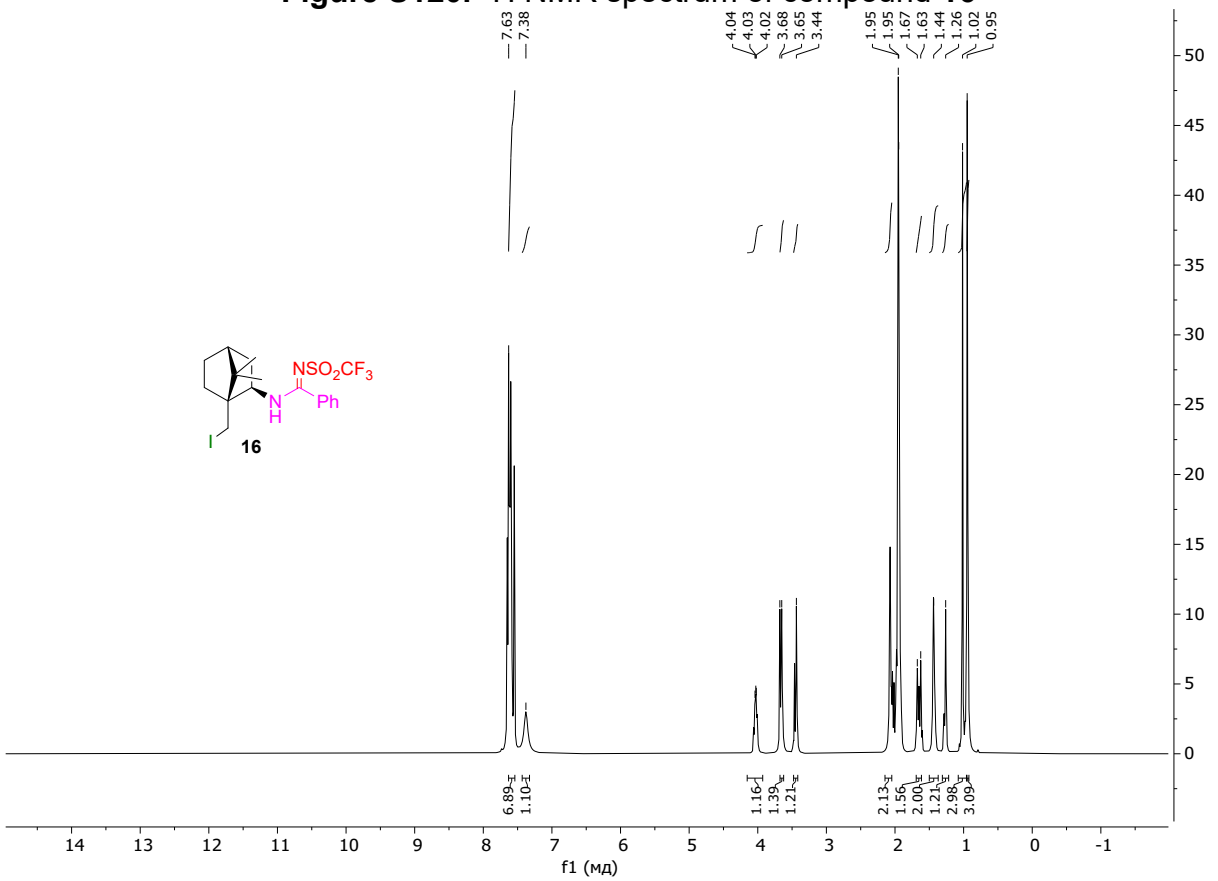


Figure S121. ^{13}C NMR spectrum of compound **16**

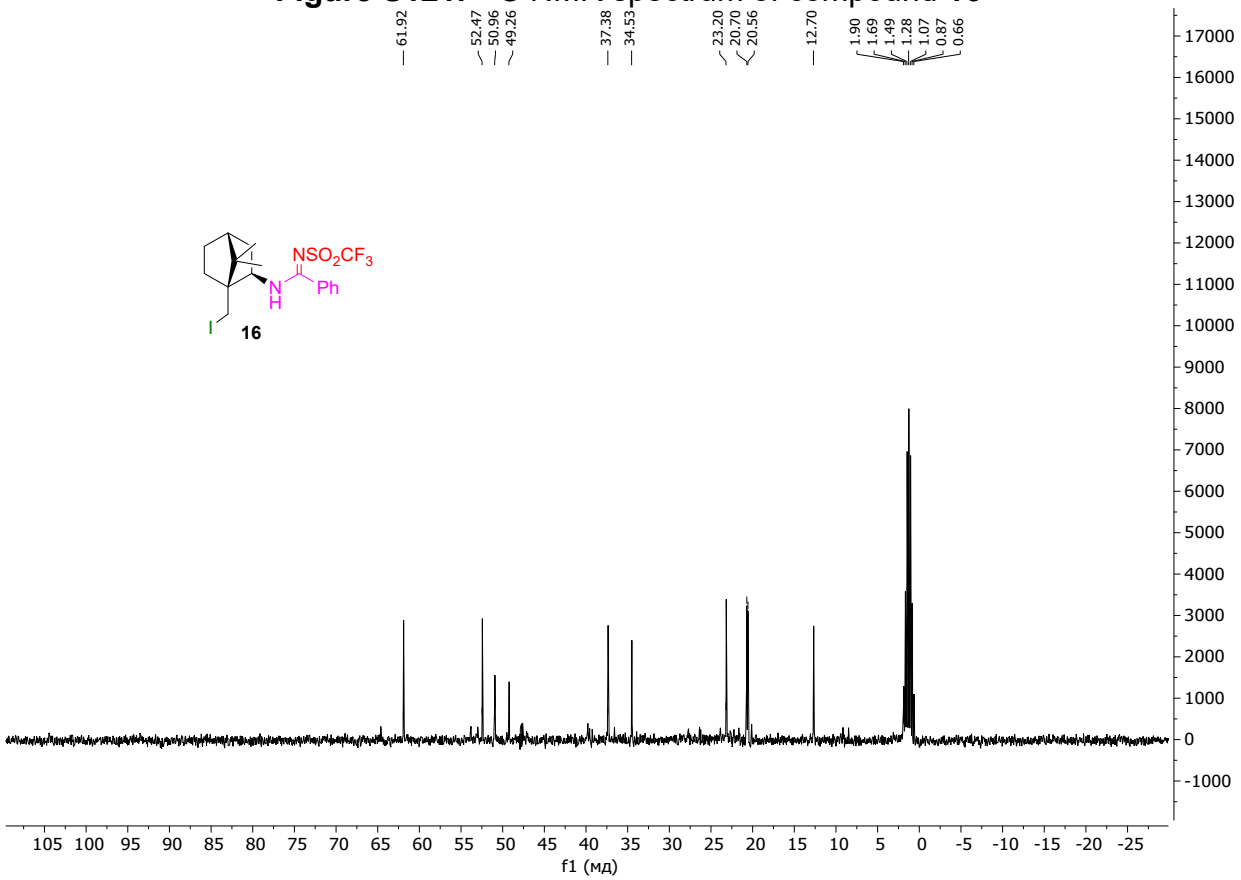


Figure S122. ^{19}F NMR spectrum of compound **11**

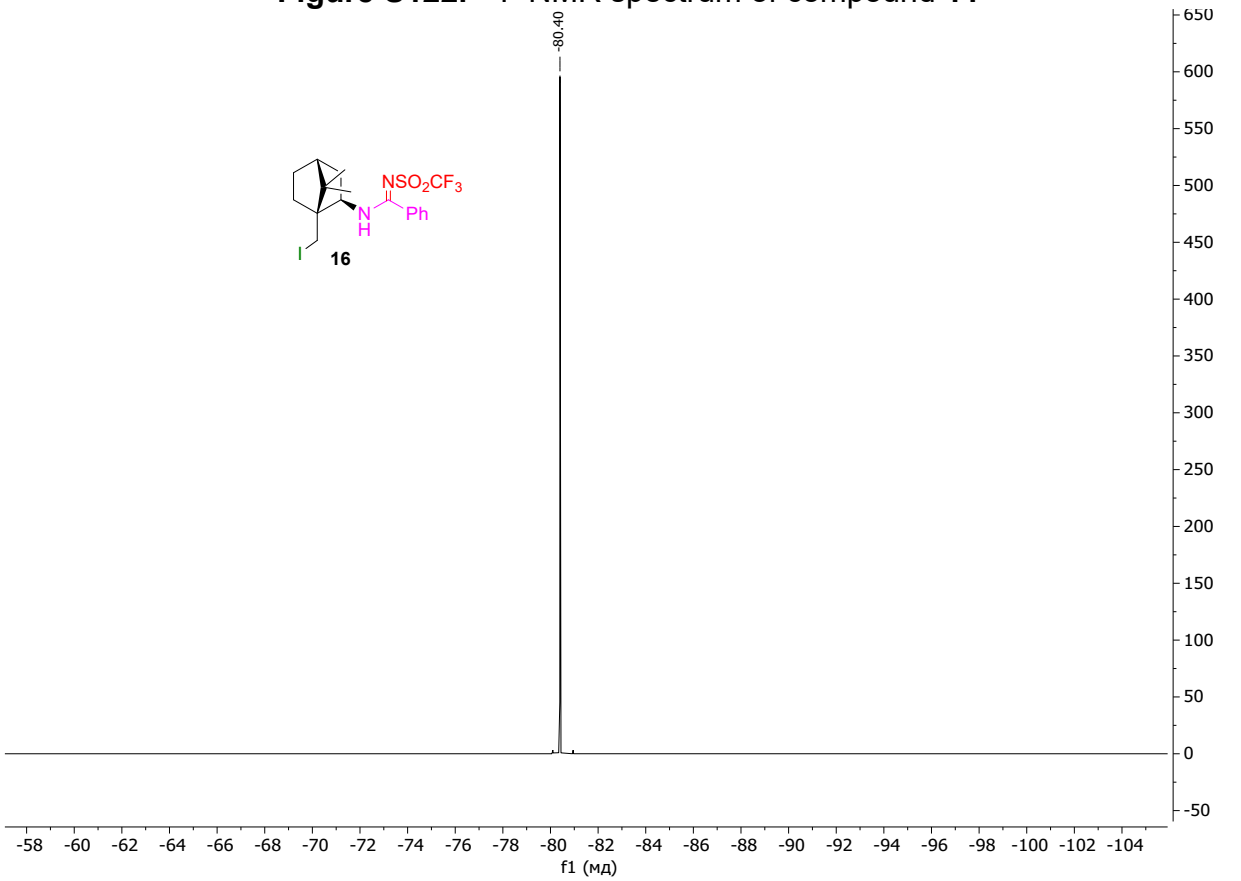


Figure S123. ^{1}H NMR spectrum of compound **13**

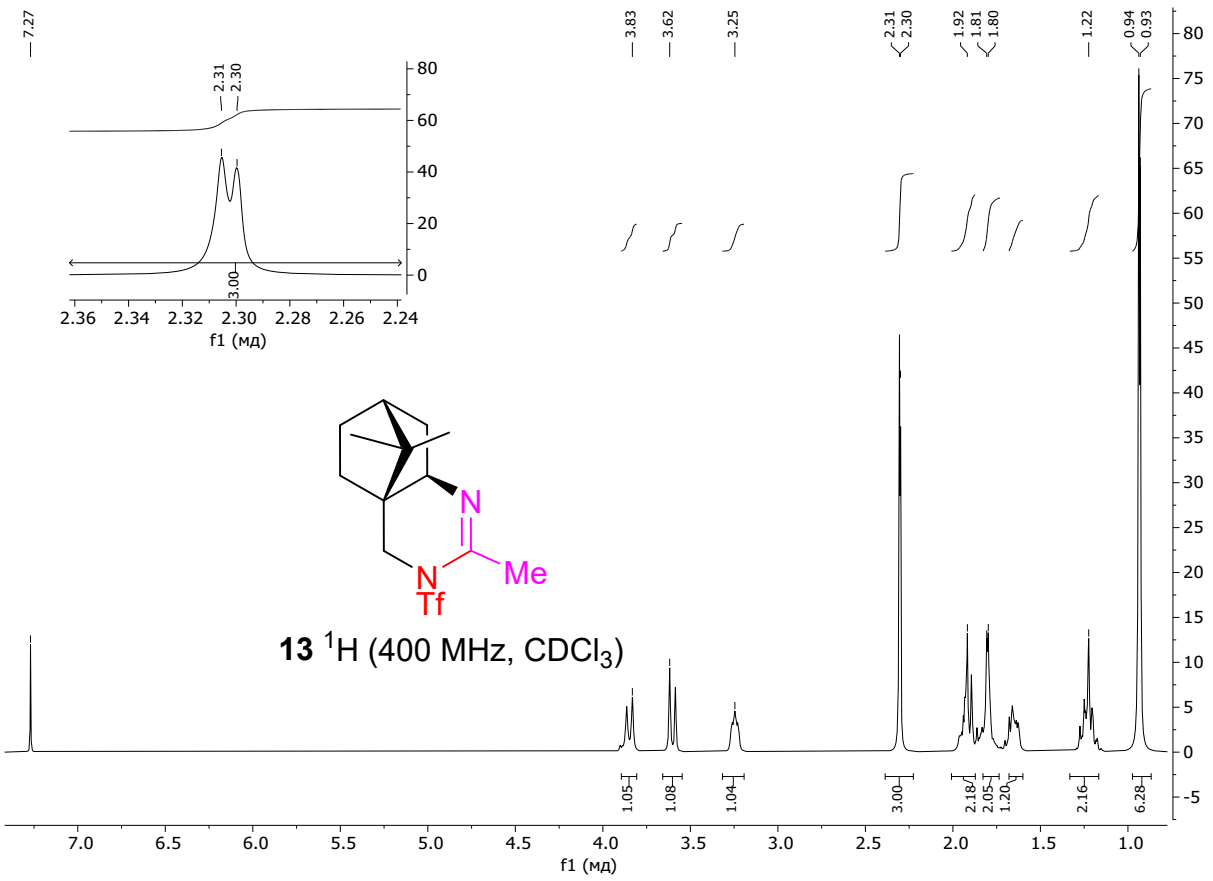


Figure S124. ^{13}C NMR spectrum of compound **13**

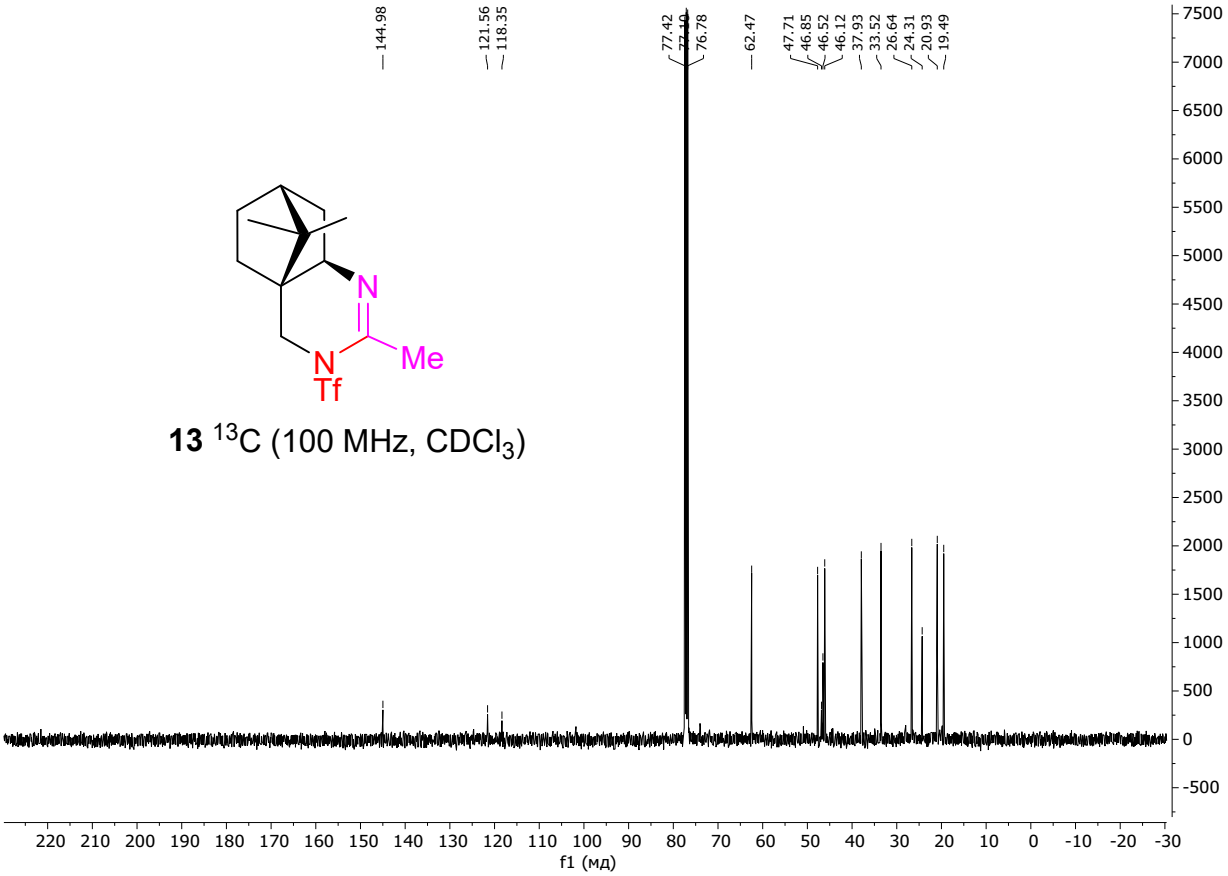
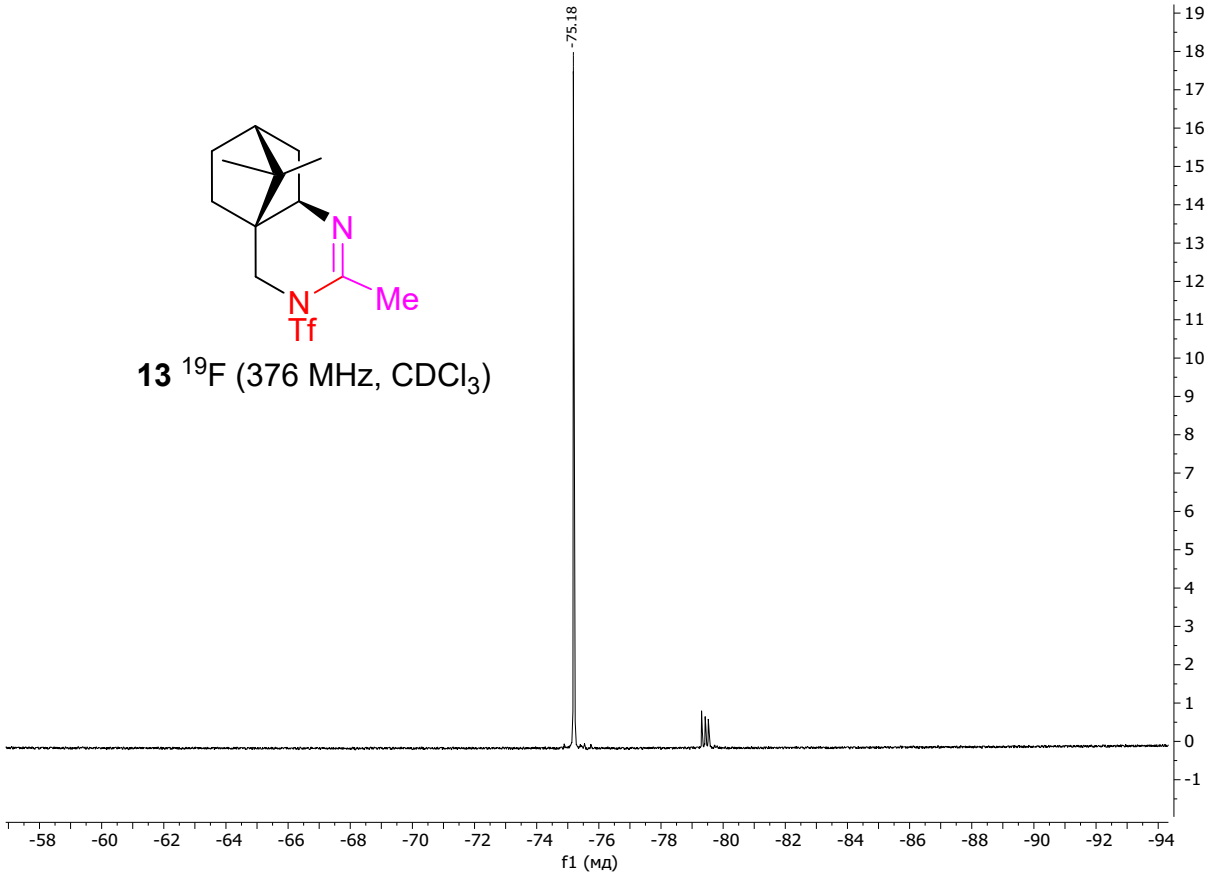


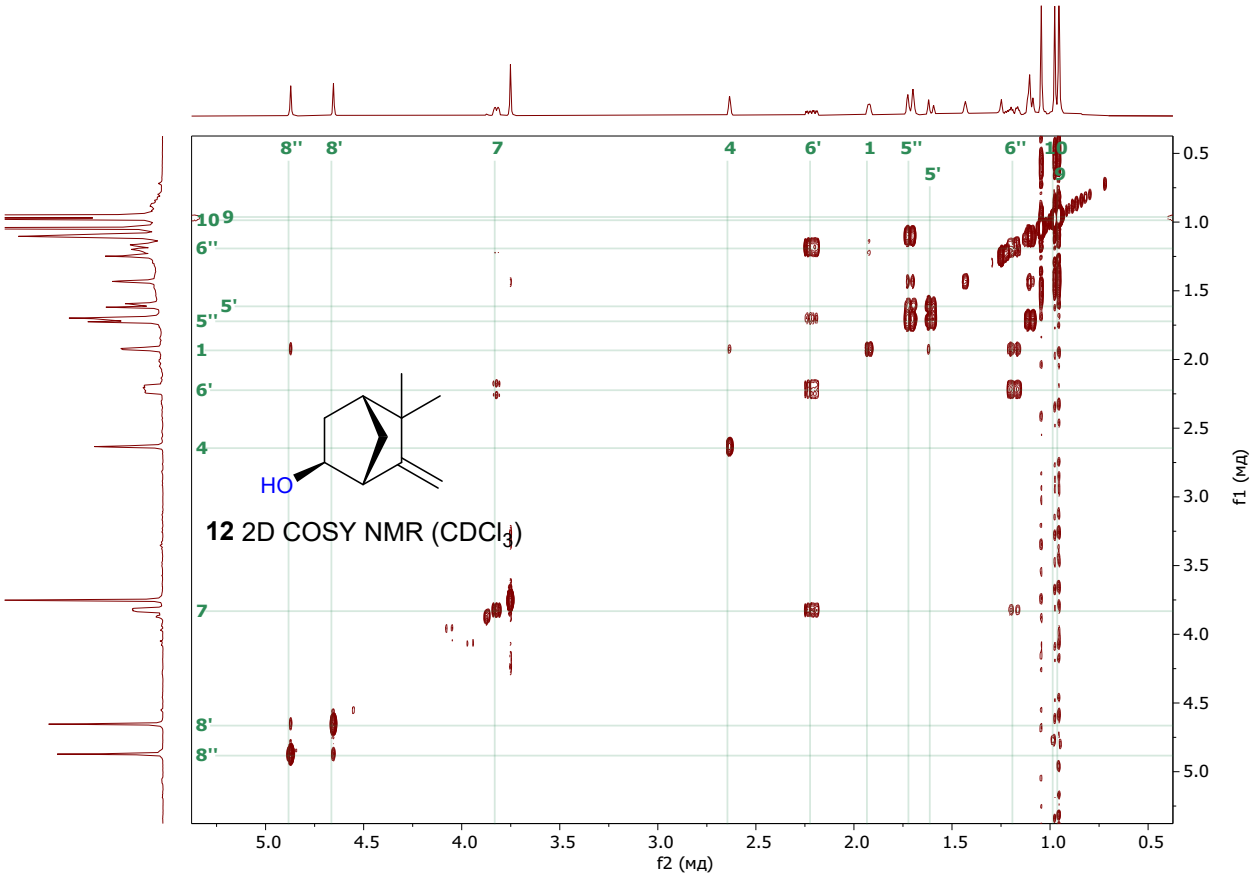
Figure S125. ^{19}F NMR spectrum of compound **13**



13 ^{19}F (376 MHz, $CDCl_3$)

2D-NMR spectra of compounds

Figure S126. 2D COSY spectrum of compound **12**



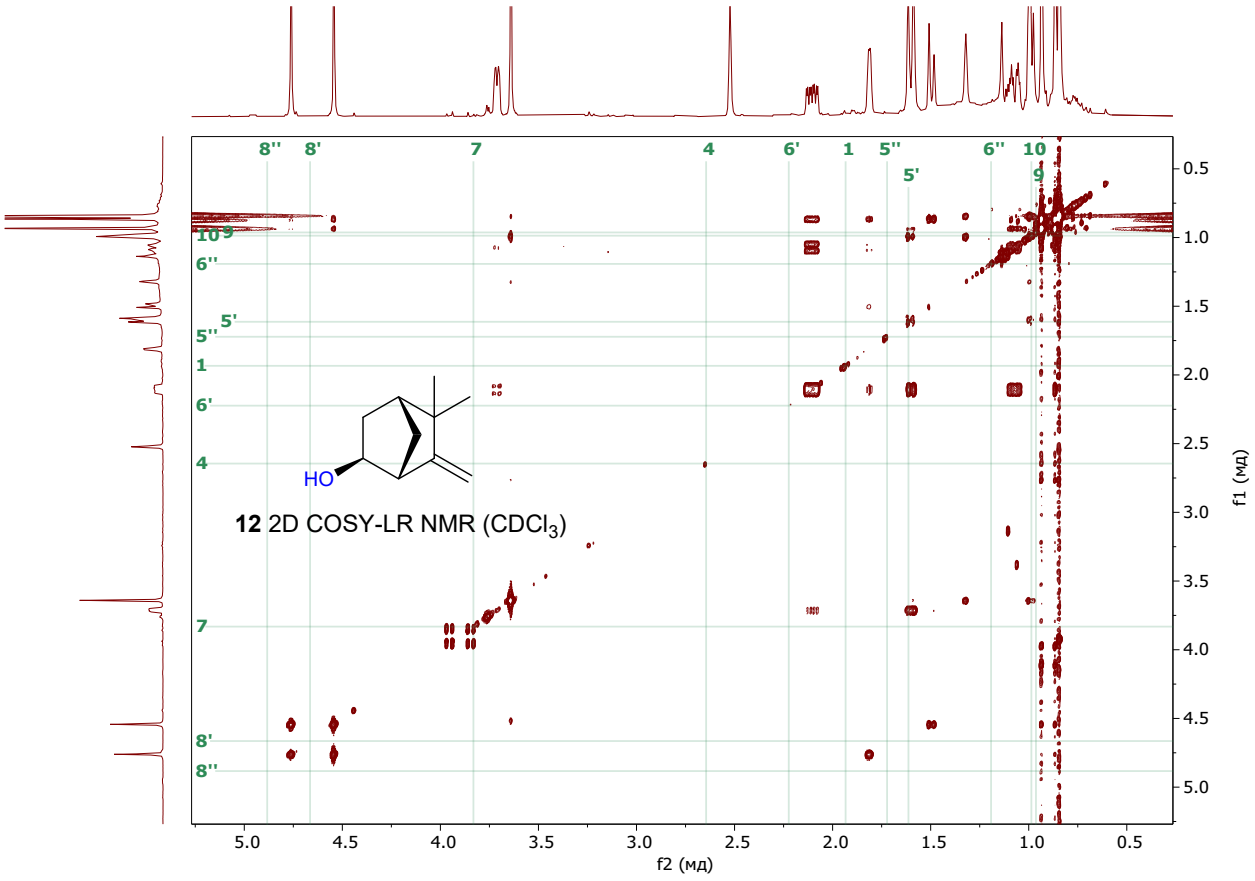


Figure S127. 2D NOESY spectrum of compound **12**

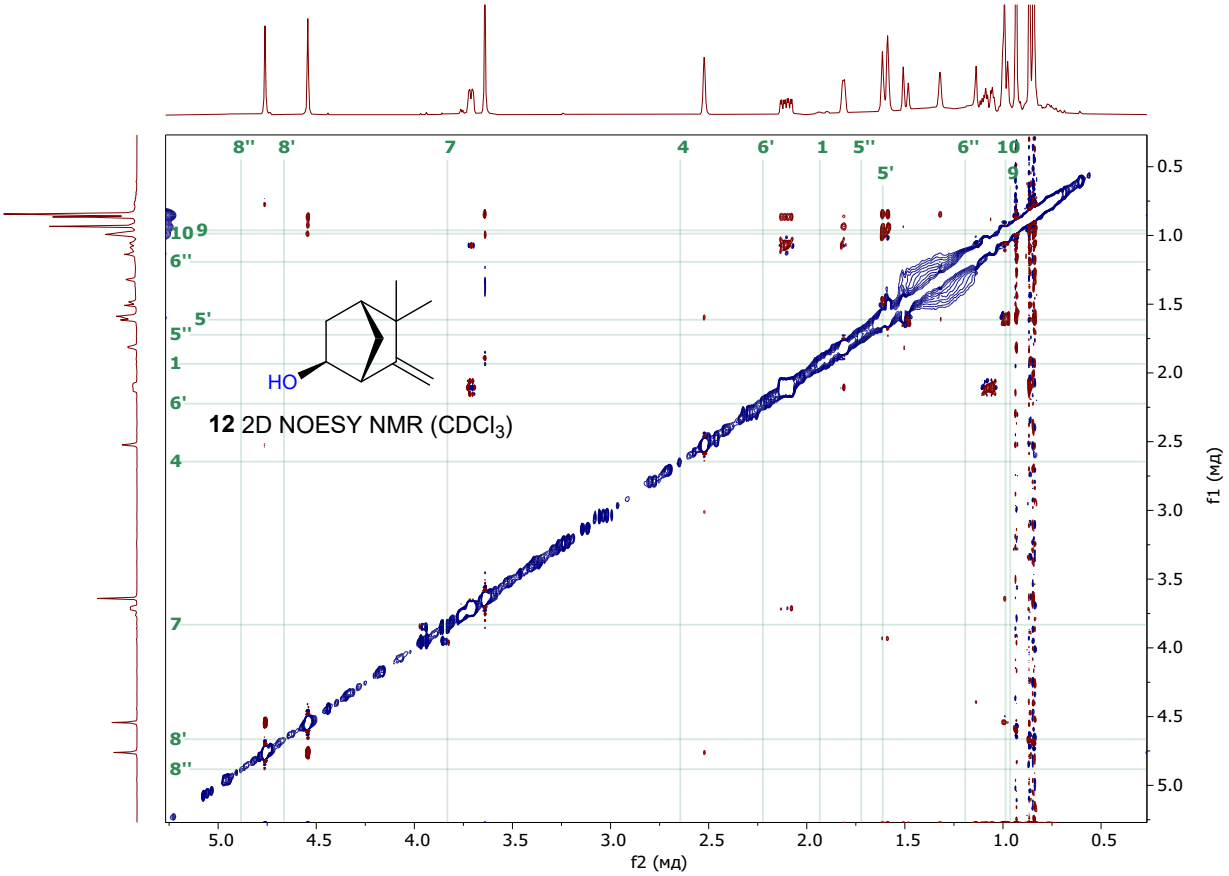


Figure S128. 2D ^{1}H-^{13}C HSQC spectrum of compound **12**

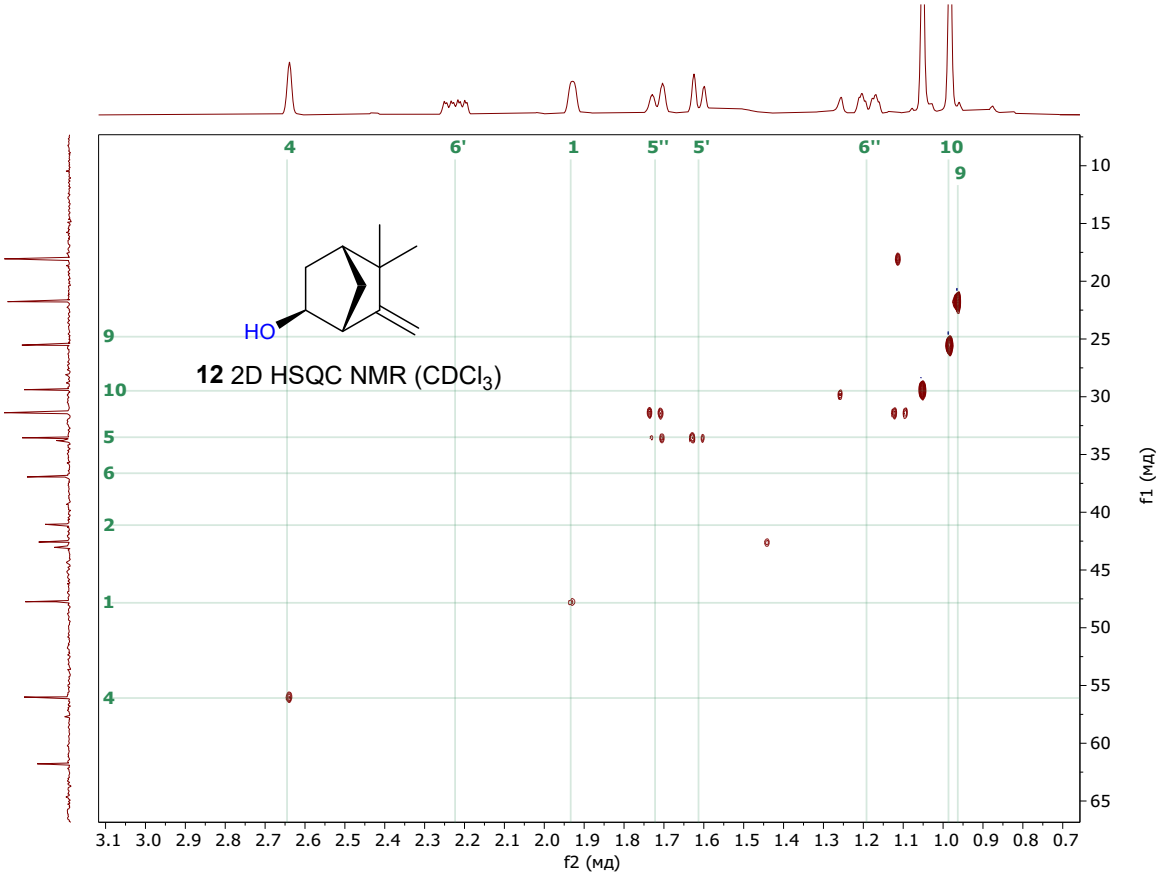
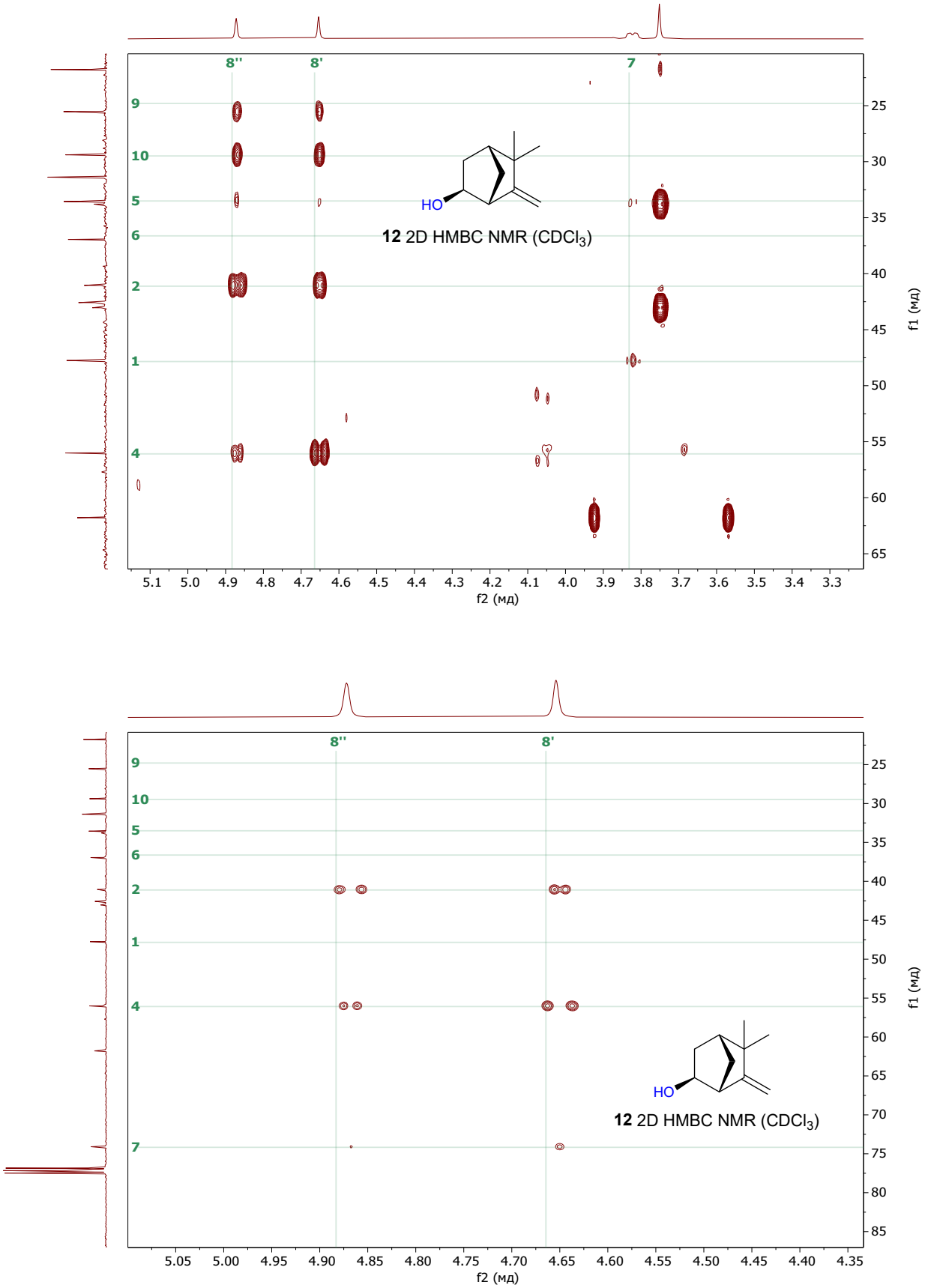
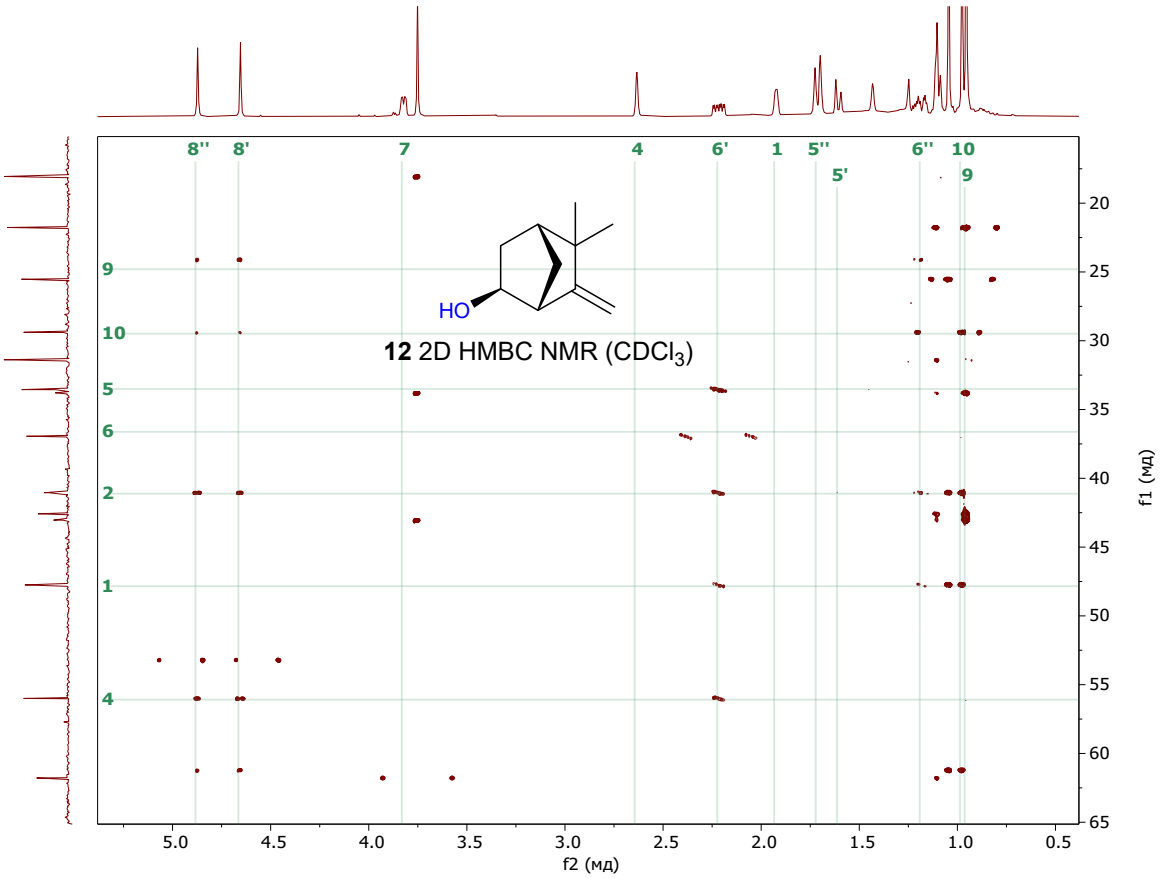


Figure S129. 2D ^{1}H-^{13}C HMBC spectrum of compound **12**





HRMS (ESI) data

Figure S130. HRMS (ESI) of compound **3a**

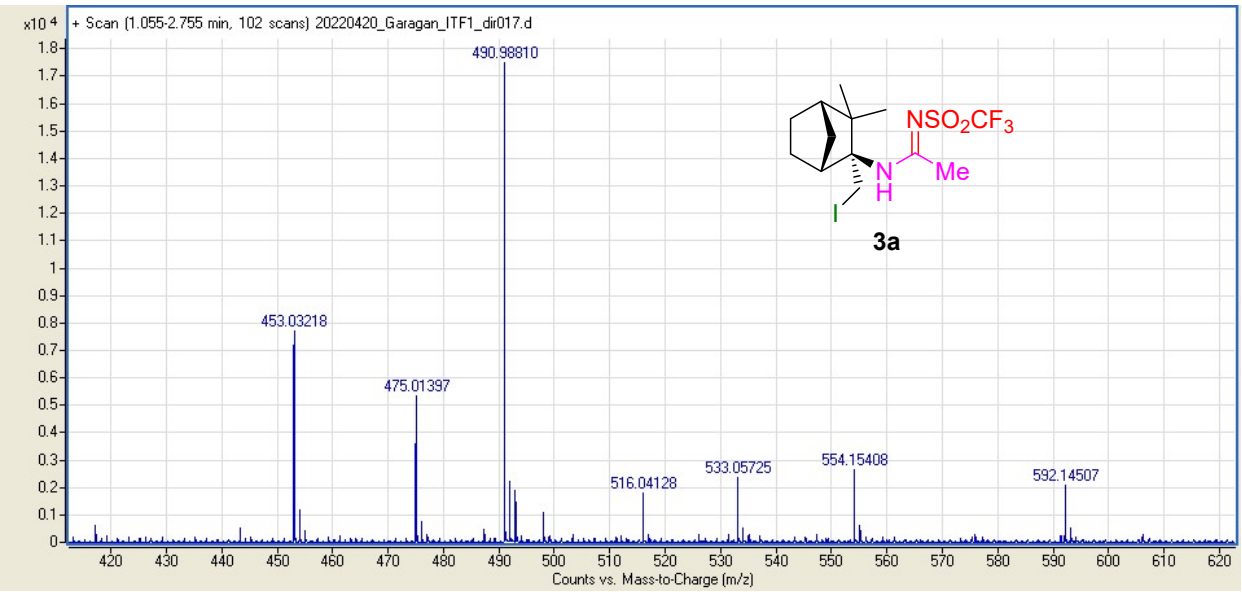


Figure S131. HRMS (ESI) of compound **3d**

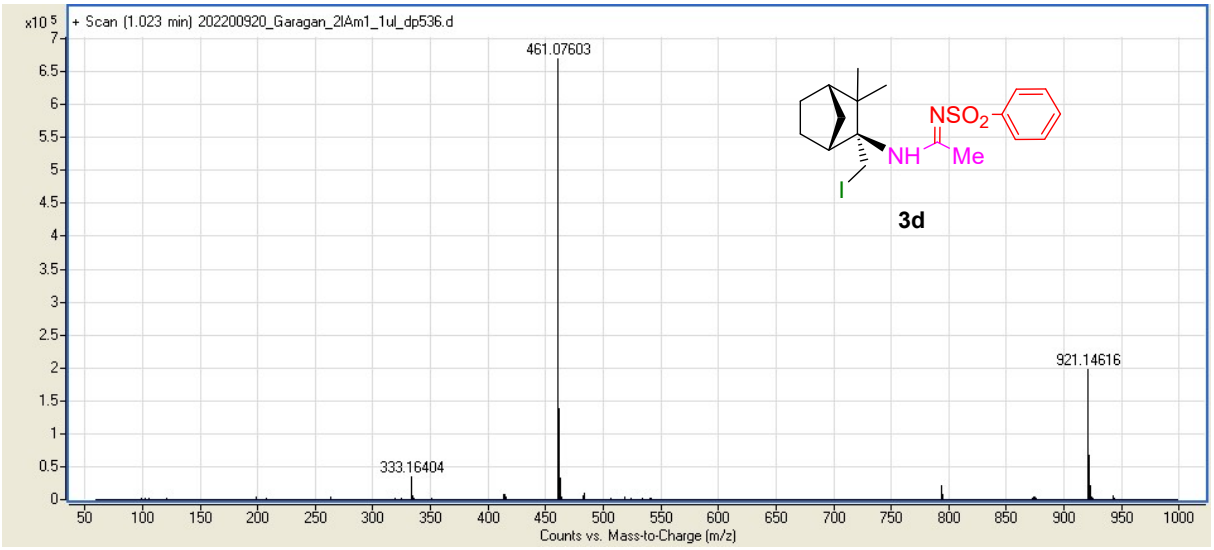


Figure S132. HRMS (ESI) of compound **4**

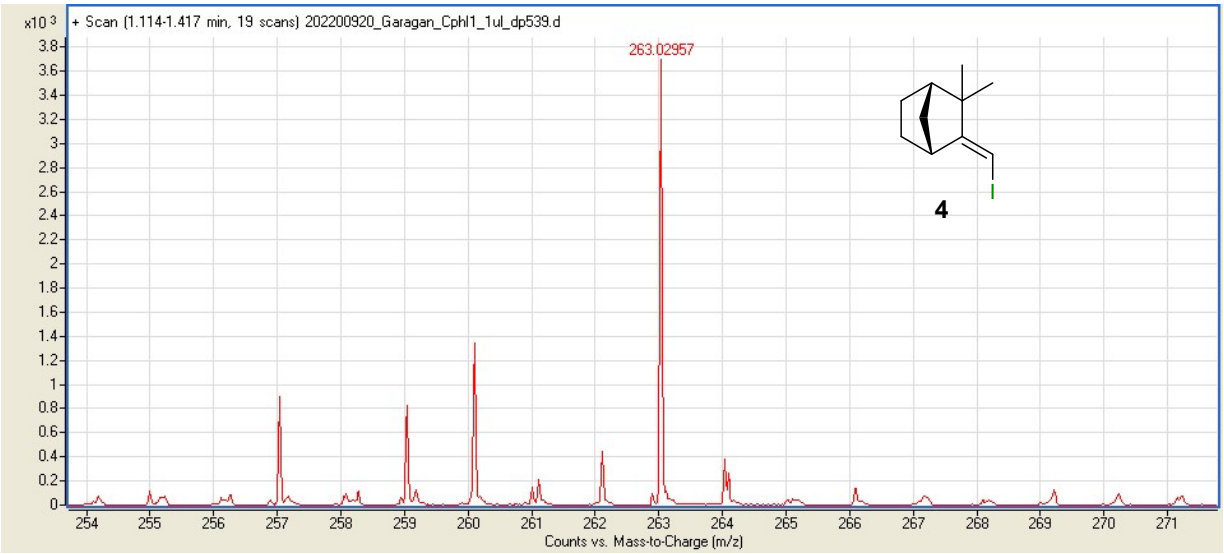


Figure S133. HRMS (ESI) of compound **6**

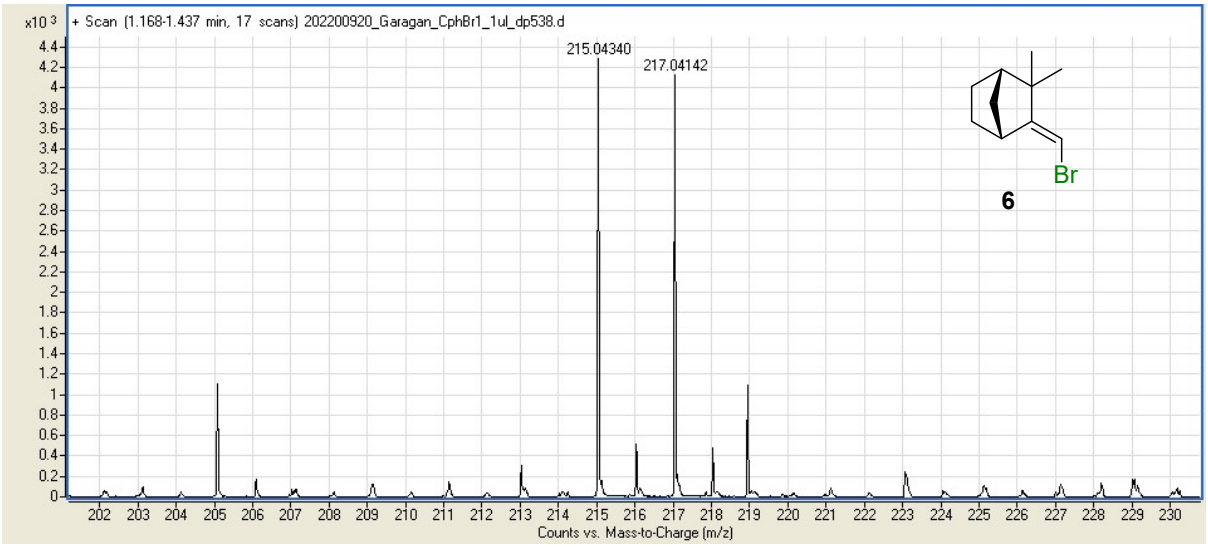


Figure S134. HRMS (ESI) of compound **7a**

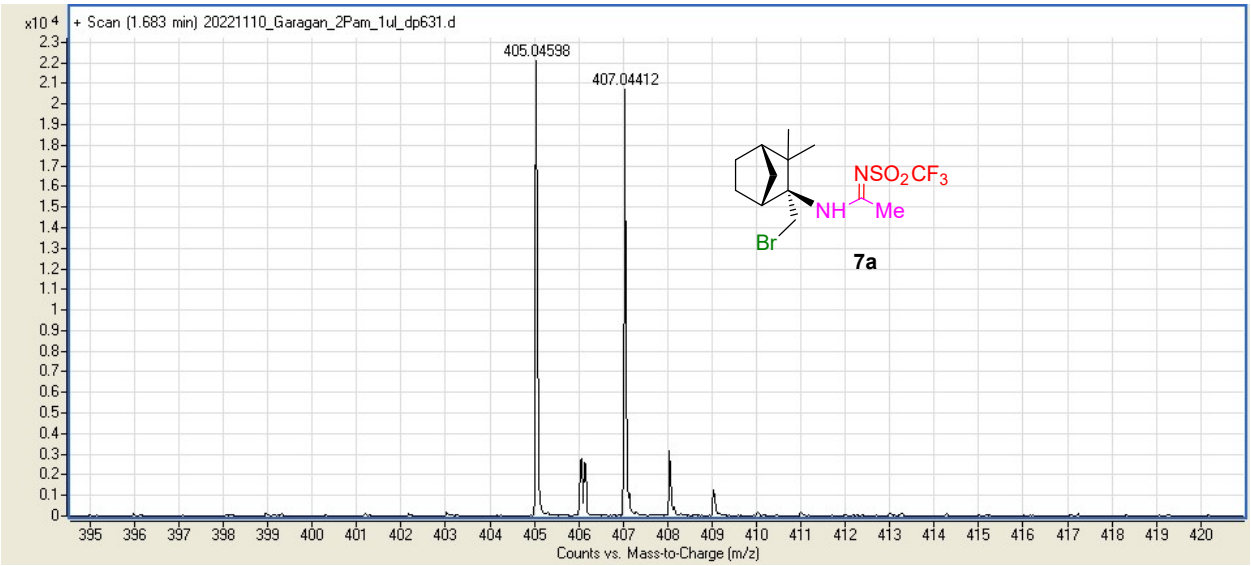


Figure S135. HRMS (ESI) of compound **7b**

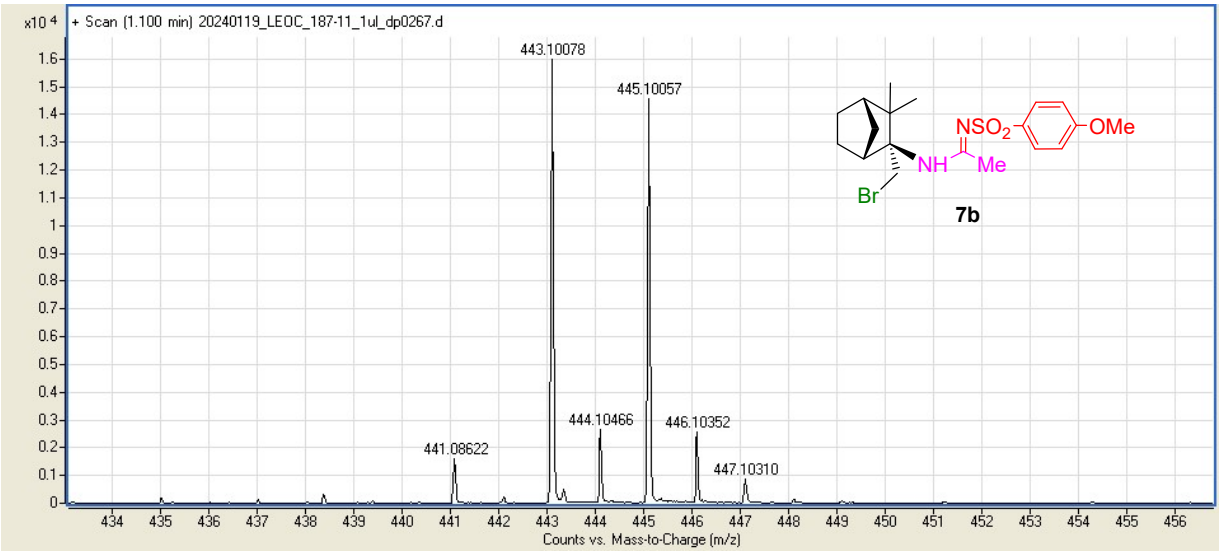


Figure S136. HRMS (ESI) of compound **7f**

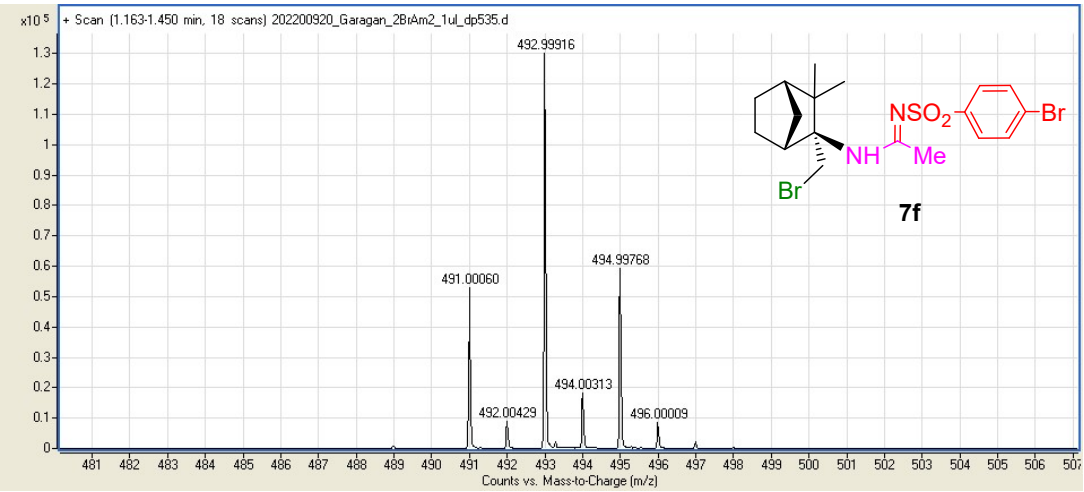


Figure S137. HRMS (ESI) of compound **7g**

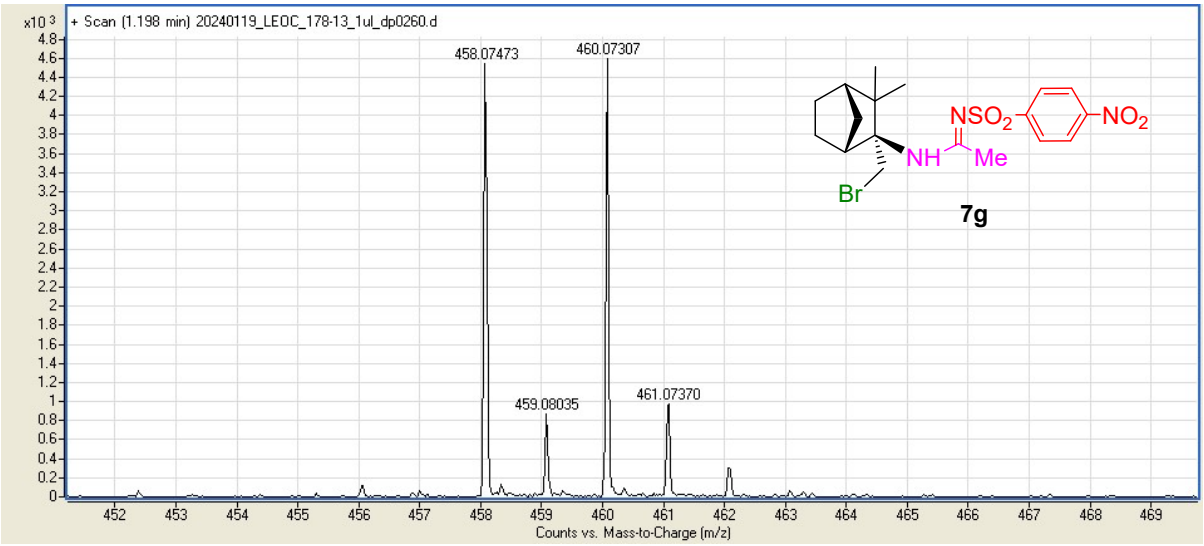


Figure S138. HRMS (ESI) of compound **7h**

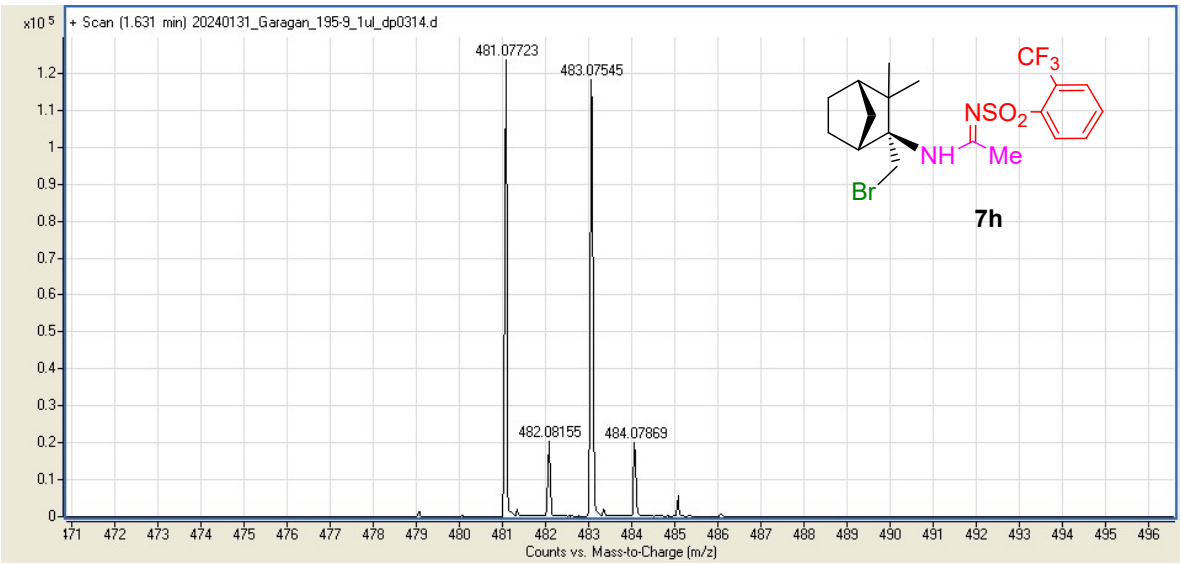


Figure S139. HRMS (ESI) of compound **7k**

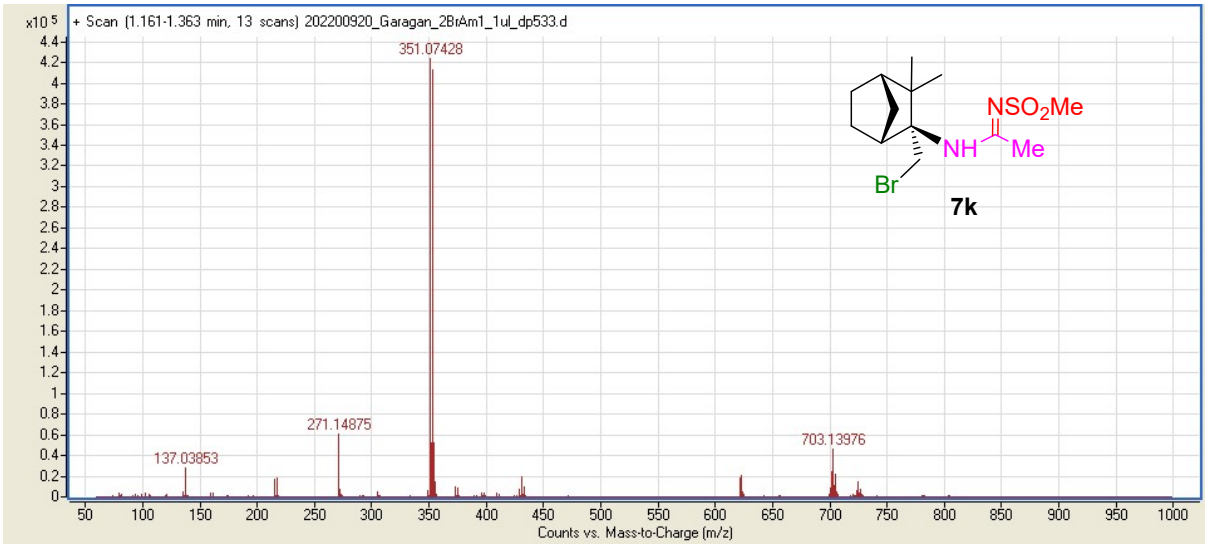


Figure S140. HRMS (ESI) of compound **8b**

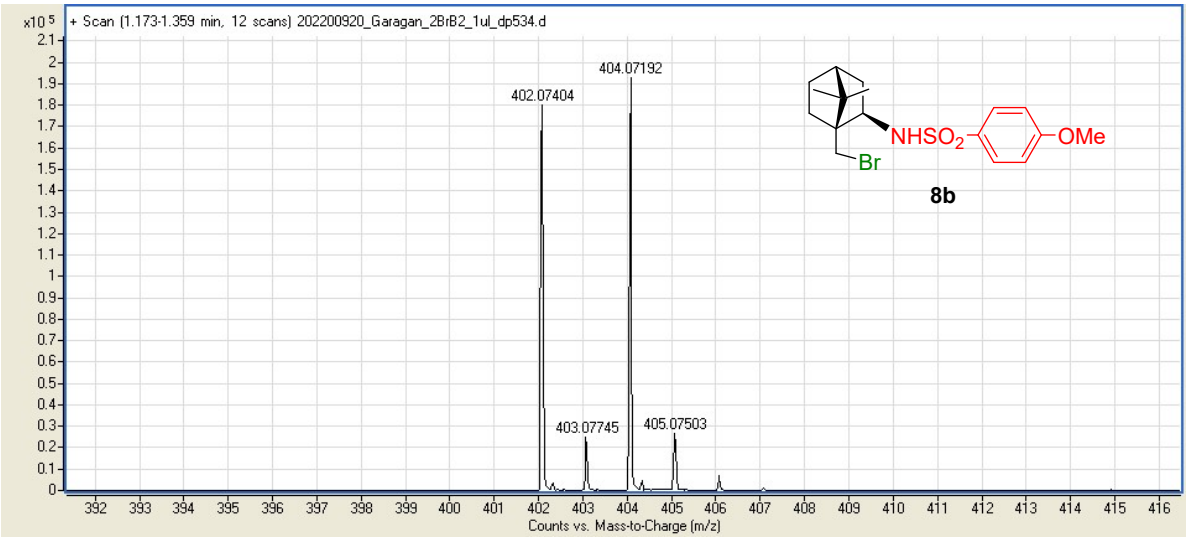


Figure S141. HRMS (ESI) of compound **8h**

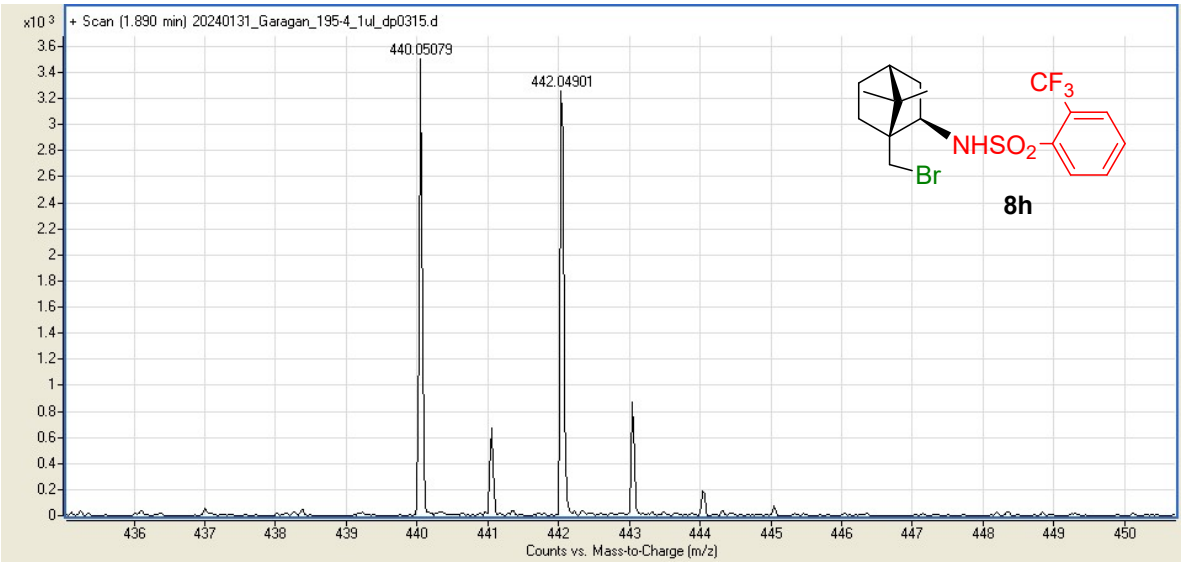


Figure S142. HRMS (ESI) of compound **8k**

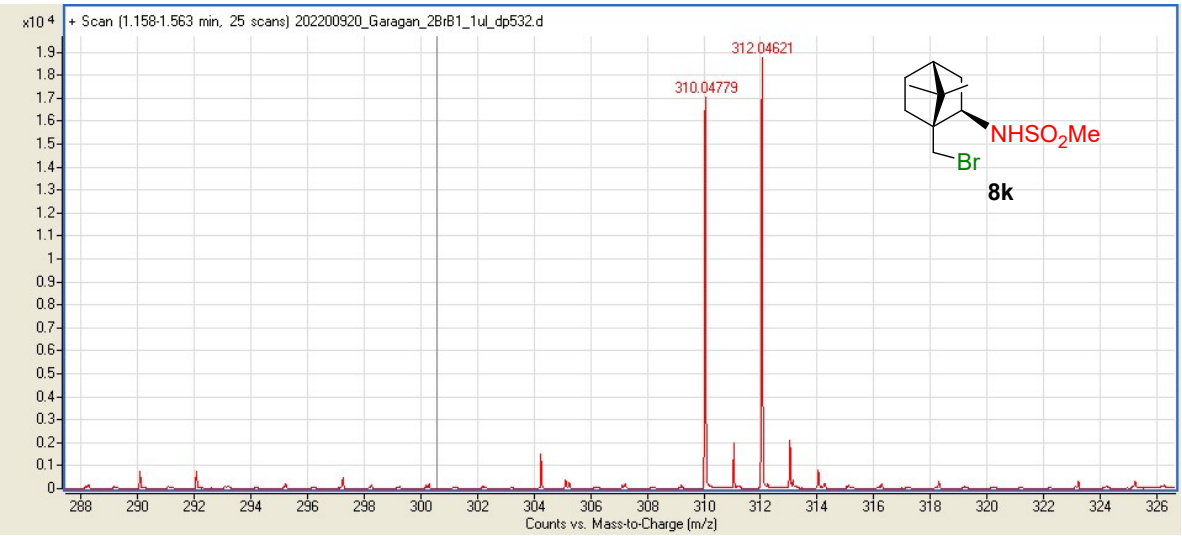


Figure S143. HRMS (ESI) of compound **9**

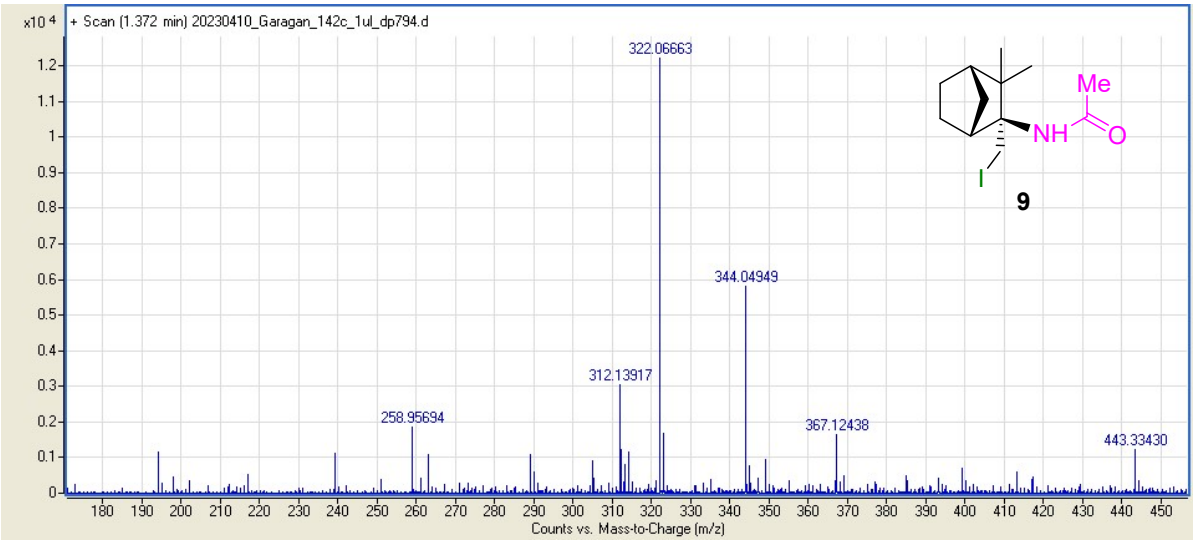


Figure S144. HRMS (ESI) of compound **10**

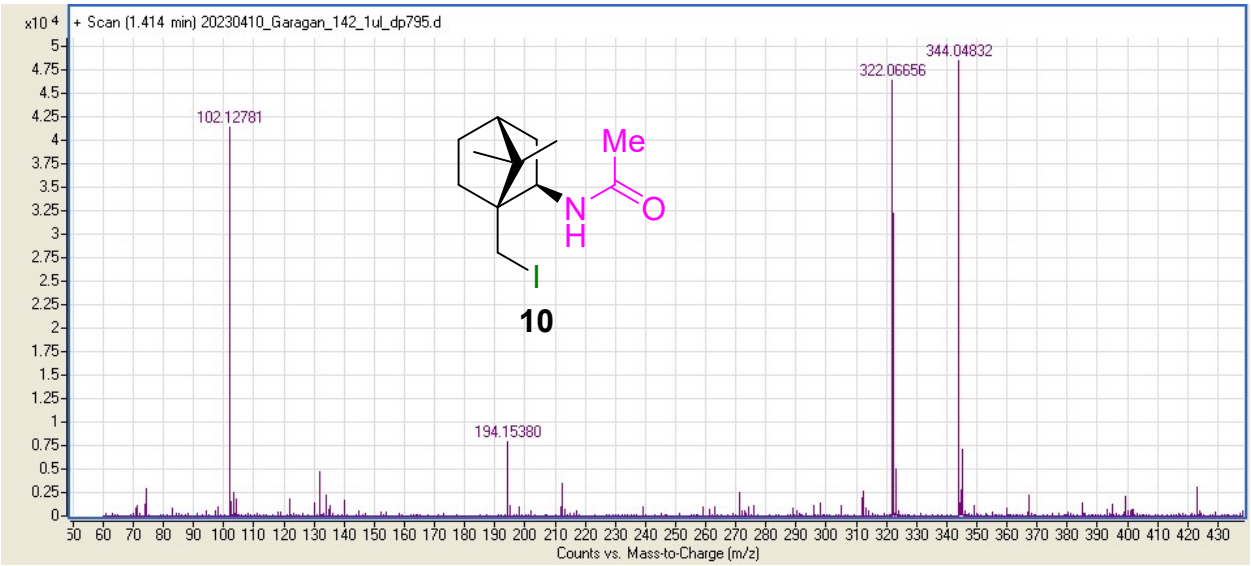


Figure S145. HRMS (ESI) of compound **17**