Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Metal-free stereoselective annulation of quinolines with trifluoroacetylacetylenes and water: an access to fluorinated oxazinoquinolines

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General methods. NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C) and AV-400 spectrometers (40.5 MHz for ^{15}N and 376.5 MHz for ^{19}F) in $CDCl_3$ and CD_3CN. The internal standards were HMDS (for ^{1}H nuclei δ 0.05 ppm) or the residual solvent signals (for ^{13}C nuclei δ 77.16 ppm), CH_3NO_2 (for ^{15}N nuclei δ 0.0 ppm) and $CFCl_3$ (for ^{19}F nuclei δ 0.00 ppm) or C_6F_6 (for ^{19}F nuclei δ -162.90 ppm). IR spectra were recorded on a two-beam Bruker Vertex 70 spectrometer. Elemental analysis was carried out on a FLASH EA 1112 Series analyzer. Melting points were determined on a Kofler hot stage apparatus. Commercial samples of quinolines **1a-g** and isoquinoline **4** were used. 1,8-Naphthyridine **6** was prepared according to method (M. Balkenhohl, R. Greiner, I. S. Makarov, B. Heinz, K. Karaghiosoff, H. Zipse, P. Knochel, *Chem. - A Eur. J.*, **2017**, *23*, 13046-13050). Samples of aryl(trifluoroacetyl)acetylenes **2a-i** were obtained according to method (V. M. Muzalevskiy, A. Yu. Rulev, A. R. Romanov, E. V. Kondrashov, I. A. Ushakov, V. A. Chertkov, V. G. Nenajdenko. *J. Org. Chem.* **2017**, *82*, 7200–7214). Monitoring of the reaction course was carried out by IR spectroscopy following the disappearance of the absorption band of the C≡C bond in starting acetylene **2** at 2174-2202 cm^{-1} or using ^{19}F NMR. The products **3a-o**, **5** and **7** were separated and purified by column chromatography. Column and thin-layer chromatography were carried out on silica gel (0.06-0.2 mm) with chloroform/benzene/ethanol (20:4:1) mixture as eluent or silica gel which was treated with NEt_3 (about 3-5 weight %) with CH_2Cl_2, and mixtures of CH_2Cl_2 and MeOH (300:1, 150:1, 100:1, 40:1) as eluent. Solvents effect (on the example of reaction between quinoline **1a**, phenyltrifluoroacetylacetylene **2a** and water) effected on the reaction times and yield of oxazinoquinoline **3a** is demonstrated in the Table S1.

Table S1 Solvent effect on the reaction times and yield of oxazinoquinoline **3a**[a]

Entry	Solvent	Time (h)	Yield of **3a** (%)[b]
1	MeCN	20	91
2	DMF	84	74
3	DMSO	84	86
4	THF	84	60
5	1,2-DCE	84	86
6	Et_2O	84	88
7	PhMe	84	88
8	CH_2Cl_2	84	83
9	NEt_3[c]	84	9
10	EtOAc	84	87

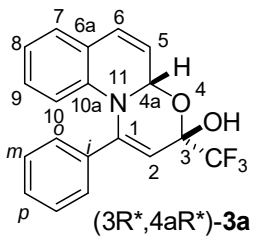
[a] Conditions: quinoline **1a** (0.475 mmol) and phenyltrifluoroacetylacetylene **2a** (0.5 mmol), H_2O (0.5 mmol), Solvent (3 mL), temperature -18 …+25 °C. [b] ^{19}F NMR yield. [c] Conversion 66%.

Reaction of quinolines, trifluoroacetylacetylenes and water (general procedure for pure isomers, procedure I): Solution of quinoline **1** (0.475 mmol, 0.95 equiv.) in MeCN (1.5 mL) and solution of acetylene **2** (0.5 mmol, 1 equiv.) and H_2O (0.009 g, 0.5 mmol, 1 equiv.) in MeCN (1.5 mL) were cooled in the fridge (-18 °C) and then mixed in 4 mL vial with a screw cap. The reaction mixture

was left at room temperature for appropriate time (TLC or ^{19}F NMR control). The solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel which was treated with NEt_3 (about 3-5 weight %) to prevent acid catalyzed isomerization. CH_2Cl_2, and mixtures of CH_2Cl_2 and MeOH (300:1, 150:1, 100:1, 40:1) were consistently used as eluents. Solvents were evaporated in vacuo, the rest amount of the solvents and NEt_3 were removed by co-evaporation with MeCN (1 mL, 2-3 times) to give pure (3*R**,4a*R**)-isomers of **3**. The residue thus obtained solidifies at standing during several hours at room temperature. Alternatively compounds **3** can be crystallized by evaporation of solutions in Et_2O-Hexane (1:3-1:5). Diastereomer ratio of 1,3-oxazinoquinolines **3** appeared to be capable of changing in the presence of acids. To avoid isomerization NMR spectra were measured from solution in CD_3CN with traces of NEt_3 intentionally added.

Reaction of quinolines, trifluoroacetylacetylenes and water (general procedure for synthesis of the mixture of isomers, procedure II): To the mixture of acetylene **2** (0.5 mmol) and H_2O (0.009 g, 0.5 mmol) in 1.5 mL MeCN at -5~0 °C with stirring the solution of quinoline **1** (0.5 mmol) in 1.5 mL MeCN was added slowly (during 0.5 h) by drops. After that reaction mixture was warmed to the room temperature and stirred appropriate time. The solvent was removed under reduced pressure. The reaction mixture was passed through a column (chloroform/benzene/ethanol (20:4:1) mixture as an eluent) to give a mixture of (3*R**,4a*R**)- and (3*S**,4a*R**)-diastereomers of 1,3-oxazinoquinoline **3**. Formation of (3*S**,4a*R**)-diastereomer is a result of acid catalyzed isomerization of (3*R**,4a*R**)-diastereomer on silica gel.

(3*R,4a*R**)-1-Phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]-quinolin-3-ol (3a).** Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 20 h. White needles, m.p. 155-157 °C (hexane), yield 0.148 g (90%).



(3R*,4aR*)-**3a**

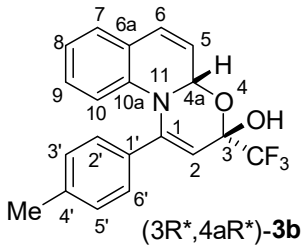
^1H NMR (400.1 MHz, CD_3CN): δ 7.56-7.54 (m, 2H, H_o from Ph), 7.39-7.47 (m, 3H, $H_{m,p}$ from Ph), 7.24 (dd, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.90 (td, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1H, H-9), 6.85 (td, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, H-8), 6.29 (d, ^3J = 7.9 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.01 (s, 1H, H-2), 5.63 (d, $^3J_{4a,5}$ = 4.9 Hz, 1H, H-4a), 5.34 (s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.4 (C-1), 137.1 (C-10a), 134.6 (C_i from Ph), 130.5 (C-6), 130.1 (C_p from Ph), 129.2 (C_m from Ph), 129.0 (C-9), 128.0 (C-7), 126.6 (C_o from Ph), 122.4 (q, $^1J_{CF}$ = 286.1 Hz, CF_3), 121.4 (C-6a), 120.8 (C-8), 117.6 (C-10), 117.5 (C-5), 110.4 (C-2), 92.3 (q, $^2J_{CF}$ = 33.0 Hz, C-3), 78.3 (C-4a) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.2 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M-OH]^+$ Calcd for $C_{19}H_{13}F_3NO^+$: 328.0944; found: 328.0945; m/z $[M+H]^+$ Calcd for $C_{19}H_{15}F_3NO_2^+$: 346.1049; found: 346.1048.

(3*R,4a*R**)-1-(4-methylphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3b)**



(3R*,4aR*)-**3b**

Pure (3*R**,4a*R**)-**3b** obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2b** (0.106 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 15 h. Light-brown needles, m.p. 133-135 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.27, yield 0.154 g (90%).

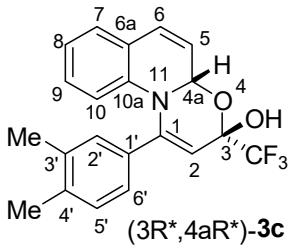
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.43 (d, ^3J = 8.2 Hz, 2H, H-2',6'), 7.24 (dd, ^3J = 7.1 Hz, ^4J = 1.9 Hz, 1H, H-7), 7.22 (d, ^3J = 8.2 Hz, 2H, H-3',5'), 6.99 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.89 (td, ^3J = 7.4 Hz, ^4J = 2.0 Hz, 1H, H-9), 6.85 (td, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H, H-8), 6.33 (d, ^3J = 7.6 Hz, 1H, H-10), 6.11 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.97 (s, 1H, H-2), 5.65 (d, ^3J = 4.8 Hz, 1H, H-4a), 5.46 (br s, 1H, OH), 2.35 (s, 3H, Me) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 148.6 (C-1), 141.2, 138.3, 132.8, 130.7, 130.4, 129.4, 128.8, 127.2, 123.6 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 122.5, 121.4, 119.3, 118.0, 111.9 (C-2), 93.0 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.4 (C-4a), 21.3 (Me) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.3 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{20}H_{15}F_3NO^+$: 342.1100; found: 342.1106; m/z $[M+H]^+$ Calcd for $C_{20}H_{17}F_3NO_2^+$: 360.1206; found: 360.1205.

(3*R,4a*R**)-1-(3,4-dimethylphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol**



(3R*,4aR*)-**3c**

(3c). Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2c** (0.113 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 24 h. Light-brown needles, m.p. 94-96 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.30, yield 0.171 g (97%).

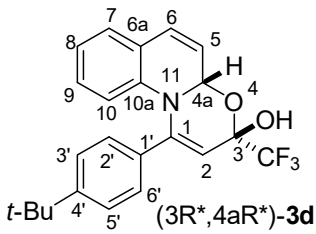
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.35 (s, 1H, H-2'), 7.22-7.24 (m, 2H, H-7, H-6'), 7.16 (d, ^3J = 7.9 Hz, 1H, H-5'), 6.99 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.89 (td, ^3J = 7.4 Hz, ^4J = 1.7 Hz, 1H, H-9), 6.84 (td, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H, H-8), 6.35 (d, ^3J = 7.9 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.9 Hz, 1H, H-5), 5.95 (s, 1H, H-2), 5.62 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.45 (br s, 1H, OH), 2.27 (s, 3H, Me), 2.24 (s, 3H, Me) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 148.7 (C-1), 139.8, 138.6, 138.4, 133.3, 131.1, 130.4, 129.4, 128.7, 128.2, 124.8, 123.6 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 122.5, 121.4, 119.3, 118.0, 111.8 (C-2), 93.0 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.4 (C-4a), 19.7 (Me), 19.6 (Me) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.3 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{21}H_{17}F_3NO^+$: 356.1257; found: 356.1260; m/z $[M+H]^+$ Calcd for $C_{21}H_{19}F_3NO_2^+$: 374.1362; found: 374.1362.

(3*R,4a*R**)-1-(4-(*tert*-Butyl)phenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3d).** Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2d** (0.127 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 24 h. Light-brown needles, m.p. 105-107 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.27, yield 0.187 g (98%).



(3R*,4aR*)-**3d**

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.43-7.48 (m, 4H, H-2',3',5',6'), 7.24 (dd, ^3J = 7.2 Hz, ^4J = 1.7 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.89 (td, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1H, H-9), 6.85 (td, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1H, H-8), 6.32 (d, ^3J = 7.9 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.98 (s, 1H, H-2), 5.63 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.44 (s, 1H, OH), 1.31 (s, 9H, 3Me from *t*-Bu) ppm.

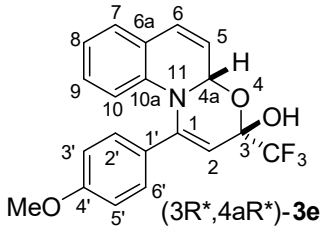
^{13}C NMR (100.6 MHz, CD_3CN): δ 154.3, 148.4 (C-1), 138.4, 132.8, 130.4, 129.5, 128.8, 127.0 ($C_{2',6'}$ and $C_{3',5'}$ from Ar), 123.6 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 122.5, 121.5, 119.3, 118.0, 112.2 (C-2), 93.0 (q, $^2J_{CF}$ = 33.2 Hz, C-3), 78.4 (C-4a), 35.3 (C from *t*-Bu), 31.4 (3Me from *t*-Bu) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -81.9 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{23}H_{21}F_3NO^+$: 384.1570; found: 384.1573; m/z $[M+H]^+$ Calcd for $C_{23}H_{23}F_3NO_2^+$: 402.1675; found: 402.1676.

$C_{23}H_{22}F_3NO_2$ (401.43): calcd C, 68.82; H, 5.52; N, 3.49; F, 14.20. Found: C, 68.47; H, 5.53; N, 3.15; F, 13.99.

(3*R,4a*R**)-1-(4-Methoxyphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3e).** Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2e** (0.114 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 48 h. Light-brown needles, m.p. 95-97 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.43, yield 0.168 g (94%).



(3R*,4aR*)-**3e**

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.47 (d, ^3J = 8.9 Hz, 2H, H-2',6'), 7.24 (dd, ^3J = 7.3 Hz, ^4J = 1.6 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.93 (d, ^3J = 8.9 Hz, 2H, H-3',5'), 6.90 (td, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H, H-9), 6.85 (td, ^3J = 7.3 Hz, ^4J = 1.1 Hz, 1H, H-8), 6.36 (d, ^3J = 8.0 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.94 (s, 1H, H-2), 5.64 (d, $^3J_{4a,5}$ = 3.4 Hz, 1H, H-4a), 5.55 (br s, 1H, OH), 3.79 (s, 3H, OMe) ppm.

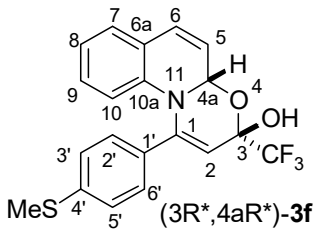
^{13}C NMR (100.6 MHz, CD_3CN): δ 162.0 (C-4'), 148.2 (C-1), 138.4, 130.4, 129.5, 128.7, 127.9, 123.6 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 122.5, 121.4, 119.3, 118.2, 118.1, 115.3, 110.9 (C-2), 93.0 (q, $^2J_{CF}$ = 32.4 Hz, C-3), 78.3 (C-4a), 55.9 (OMe) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{20}H_{15}F_3NO_2^+$: 358.1049; found: 358.1053; m/z $[M+H]^+$ Calcd for $C_{20}H_{17}F_3NO_3^+$: 376.1155; found: 376.1153.

$C_{20}H_{16}F_3NO_3$ (375.34): calcd C, 64.00; H, 4.30; N, 3.73; F, 15.18. Found: C, 64.07; H, 4.39; N, 3.62; F, 14.78.

(3*R,4a*R**)-1-[4-(Methylthio)phenyl]-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3f).** Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2f** (0.122 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 24 h. Light-brown needles, m.p. 98-100 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.20, yield 0.185 g (99%).



(3R*,4aR*)-**3f**

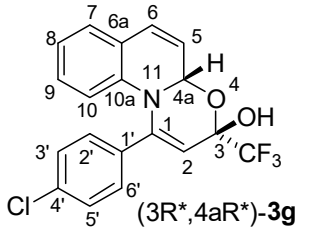
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.44 (d, ^3J = 8.5 Hz, 2H, H-2',6'), 7.21-7.25 (m, 3H, H-7, H-3',5'), 6.99 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.90 (td, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1H, H-9), 6.85 (td, ^3J = 7.2 Hz, ^4J = 1.1 Hz, 1H, H-8), 6.34 (d, ^3J = 7.9 Hz, 1H, H-10), 6.11 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.9 Hz, 1H, H-5), 6.01 (s, 1H, H-2), 5.64 (d, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-4a), 5.60 (br s, 1H, OH), 2.45 (s, 3H, MeS) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 148.0 (C-1), 142.3, 138.2, 131.8, 130.4, 129.5, 128.8, 127.7, 126.8, 123.6 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 122.5, 121.5, 119.3, 118.0, 112.0 (C-2), 93.0 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.4(C-4a), 15.0 (SMe) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.2 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M-OH]^+$ Calcd for $C_{20}H_{15}F_3NOS^+$: 374.0821; found: 374.0823; m/z $[M+H]^+$ Calcd for $C_{20}H_{17}F_3NO_2S^+$: 392.0927; found: 392.0926.

(3*R,4a*R**)-1-(4-Chlorophenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3g).** Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2g** (0.116 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 24 h. Light-brown needles, m.p. 91-93 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.70, yield 0.175 g (97%).



(3R*,4aR*)-**3g**

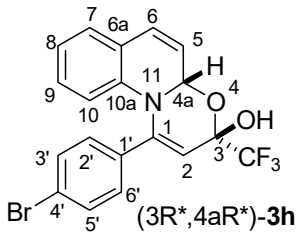
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.52 (d, ^3J = 8.6 Hz, 2H, H-2',6'), 7.40 (d, ^3J = 8.6 Hz, 2H, H-3',5'), 7.24 (dd, ^3J = 7.3 Hz, ^4J = 1.7 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.91 (td, ^3J = 7.4 Hz, ^4J = 2.0 Hz, 1H, H-9), 6.86 (td, ^3J = 7.2 Hz, ^4J = 1.1 Hz, 1H, H-8), 6.29 (d, ^3J = 8.0 Hz, 1H, H-10), 6.11 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.06 (s, 1H, H-2), 5.64 (d, ^3J = 4.7 Hz, 1H, H-4a), 5.60 (br s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 147.4 (C-1), 138.0, 136.1, 134.3, 130.4, 130.1, 129.6, 128.92, 128.86, 123.5 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 122.5, 121.7, 119.3, 118.0, 113.3 (C-2), 92.9 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.4 (C-4a) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -81.9 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{19}H_{12}ClF_3NO^+$: 362.0554; found: 362.0558; m/z $[M+H]^+$ Calcd for $C_{19}H_{14}ClF_3NO_2^+$: 380.066; found: 380.0661.

(3*R,4a*R**)-1-(4-Bromophenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3h).**



(3R*,4aR*)-**3h**

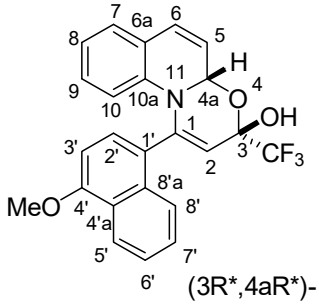
Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2h** (0.138 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 6 h. Light-brown needles, m.p. 128-130 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.73, yield 0.201 g (99%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.55 (d, ^3J = 8.7 Hz, 2H, H-3',5'), 7.45 (d, ^3J = 8.7 Hz, 2H, H-2',6'), 7.24 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.91 (td, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1H, H-9), 6.86 (td, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, H-8), 6.29 (d, ^3J = 8.1 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.06 (s, 1H, H-2), 5.63 (d, $^3J_{4a,5}$ = 4.7 Hz, 1H, H-4a), 5.56 (s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 147.5(C-1), 138.0, 134.8, 133.1, 130.5, 129.6, 129.2, 128.9, 124.5, 123.5 (q, $^1J_{CF}$ = 288.0 Hz, CF_3), 122.6, 121.7, 119.3, 118.0, 113.3 (C-2), 93.0 (q, $^2J_{CF}$ = 33.3 Hz, C-3), 78.4 (C-4a) ppm. ^{19}F NMR (376.3 MHz, CD_3CN): δ -81.9 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{19}H_{12}BrF_3NO^+$: 406.0049; found: 406.0055; m/z $[M+H]^+$ Calcd for $C_{19}H_{14}BrF_3NO_2^+$: 424.0155; found: 424.0153.

(3*R,4a*R**)-1-(4-Methoxynaphthalen-1-yl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3i).**



(3R*,4aR*)-**3i**

Obtained from quinoline **1a** (0.061 g, 0.475 mmol), acetylene **2i** (0.139 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 184 h. Light-brown needles, m.p. 120-122 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.50, yield 0.168 g (83%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 8.31-8.28 (m, 2H, H-5', H-8'), 7.49-7.60 (m, 3H, H-2', H-6' and H-7'), 7.18 (dd, ^3J = 7.3 Hz, ^4J = 1.6 Hz, 1H, H-7), 6.99 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.89 (d, $^3J_{2',3'}$ = 8.1 Hz, 1H, H-2'), 6.73 (td, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1H, H-9), 6.68 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, H-8), 6.42 (d, ^3J = 8.1 Hz, 1H, H-10), 6.15 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.7 Hz, 1H, H-5), 5.90 (d, $^3J_{4a,5}$ = 4.5 Hz, 1H, H-4a), 5.86 (s, 1H, H-2), 5.63 (s, 1H, OH), 3.98 (s, 3H, MeO) ppm.

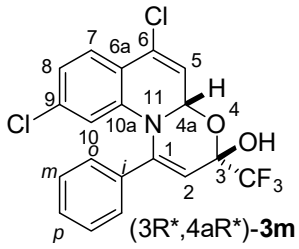
^{13}C NMR (100.6 MHz, CD_3CN): δ 157.5, 147.1 (C-1), 137.8, 132.4, 130.2, 129.6, 128.9, 128.5, 126.7, 125.6, 124.6, 123.8 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 123.3, 122.0, 121.4, 119.2, 116.4, 114.5 (C-2), 104.8, 93.1 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.7 (C-4a), 56.4 (OMe) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -81.7 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{24}H_{17}F_3NO_2^+$: 408.1206; found: 408.1209; m/z $[M+H]^+$ Calcd for $C_{24}H_{19}F_3NO_3^+$: 426.1312; found: 426.1312.

$C_{24}H_{18}F_3NO_3$ (425.40): calcd C, 67.76; H, 4.26; N, 3.29; F, 13.40. Found C, 67.77; H, 4.51; N, 3.68; F, 13.23.

(3*R,4a*R**)-6,9-Dichloro-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol**



(3m). Obtained from quinoline **1e** (0.094 g, 0.475 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 80 h. Yellow crystals, m.p. 135-137 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.63, yield 0.095 g (48%).

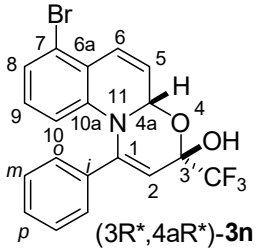
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.64 (d, ^3J = 8.4 Hz, 1H, H-7), 7.56-7.59 (m, 2H, H_o from Ph), 7.42-7.48 (m, 3H, $H_{m,p}$ from Ph), 6.96 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 1H, H-8), 6.37 (d, $^3J_{4a,5}$ = 5.4 Hz, 1H, H-5), 6.32 (d, ^4J = 2.0 Hz, 1H, H-10), 6.10 (s, 1H, H-2), 5.70 (d, $^3J_{4a,5}$ = 5.4 Hz, 1H, H-4a), 5.92 (br. s., 1H, OH) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 147.6 (C-1), 139.9, 135.9, 134.6, 133.6, 131.3, 130.2, 127.7, 127.3, 123.3 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 121.6, 117.9, 117.8, 114.1 (C-2), 93.1 (q, $^2J_{CF}$ = 33.2 Hz, C-3), 78.8 (C-4a) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -81.9 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{19}H_{11}Cl_2F_3NO^+$: 396.0164; found: 396.0161; m/z $[M+H]^+$ Calcd for $C_{19}H_{13}Cl_2F_3NO_2^+$: 414.027; found: 414.025.

(3*R,4a*R**)-6-Bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3n).**



Obtained from quinoline **1f** (0.099 g, 0.475 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 40 h. Light-brown needles, m.p. 109-111 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.71, yield 0.175 g (87%).

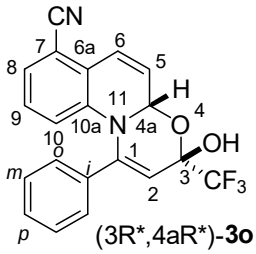
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.52-7.57 (m, 2H, H_o from Ph), 7.34-7.48 (m, 4H, H-6, $H_{m,p}$ from Ph), 7.11 (dd, ^3J = 8.0 Hz, ^4J = 0.7 Hz, 1H, H-8), 6.78 (t, ^3J = 8.1 Hz, 1H, H-9), 6.33 (d, ^3J = 8.4 Hz, 1H, H-10), 6.24 (dd, $^3J_{5,6}$ = 10.1 Hz, $^3J_{4a,5}$ = 4.9 Hz, 1H, H-5), 6.07 (s, 1H, H-2), 5.64 (d, ^3J = 4.9 Hz, 1H, H-4a), 5.47 (br., s, OH) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 148.2 (C-1), 139.8, 135.2, 131.0, 130.3, 130.1, 128.7, 127.2, 125.5, 123.5 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 123.0, 121.4, 117.9, 113.7 (C-2), 93.1 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.0 (C-4a) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{19}H_{12}BrF_3NO^+$: 406.0049; found: 406.0057; m/z $[M+H]^+$ Calcd for $C_{19}H_{14}BrF_3NO_2^+$: 424.0155; found: 424.0155.

(3*R,4a*R**)-3-Hydroxy-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinoline-6-carbonitrile (3o).** Obtained from quinoline **1g** (0.073 g, 0.475 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 45 h. Light-brown needles, m.p. 108-110 °C (MeCN), R_F(CH_2Cl_2-MeOH 100:1) = 0.30, yield 0.149 g (85%).



(3R*,4aR*)-**3o**

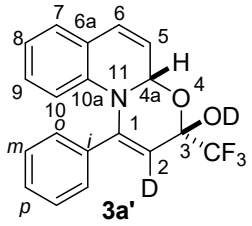
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.51-7.56 (m, 2H, H_o from Ph), 7.38-7.47 (m, 3H, $H_{m,p}$ from Ph), 7.31 (d, $^3J_{5,6}$ = 9.9 Hz, 1H, H-6), 7.21 (dd, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1H, H-8), 6.99 (t, ^3J = 8.0 Hz, 1H, H-9), 6.59 (d, ^3J = 8.5 Hz, 1H, H-10), 6.37 (dd, $^3J_{5,6}$ = 9.9 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.11 (s, 1H, H-2), 5.64 (d, $^3J_{4a,5}$ = 4.9 Hz, 1H, H-4a), 4.19 (br., s, OH) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 147.8 (C-1), 138.6, 134.8, 131.1, 130.2, 129.7, 127.2, 126.4, 125.6, 124.1, 123.4 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 123.2, 122.3, 117.8, 113.8 (C-2), 110.8 (CN), 93.1 (q, $^2J_{CF}$ = 33.2 Hz, C-3), 77.8 (C-4a) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M-OH]^+$ Calcd for $C_{20}H_{12}F_3N_2O^+$: 353.0896; found: 353.0899; m/z $[M+H]^+$ Calcd for $C_{20}H_{14}F_3N_2O_2^+$: 371.1002; found: 371.1004.

(3*R,4a*R**)-1-Phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]-quinolin-3-ol-*d*$_2$ (3a').** Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol) by modified procedure I: D_2O (0.010 g, 0.5 mmol, 1 equiv.) was used instead of H_2O. Reaction mixture was kept for 24 h. Crude product was obtained by evaporation of MeCN in vacuo to give 0.170 g (~100%) of **3a'** as light-brown needles.



3a'

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.55-7.63 (m, 2H, Ph), 7.38-7.47 (m, 3H, Ph), 7.23-7.30 (m, 1H), 6.82-7.07 (m, 3H), 6.28-6.39 (m, 1H), 6.07-6.19 (m, 1H), 5.61-5.73 (m, 1H) ppm. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.48-7.56 (m, 2H, H_o from Ph), 7.35-7.43 (m, 3H, $H_{m,p}$ from Ph), 7.18 (d, ^3J = 7.0 Hz, 1H, H-7), 6.96 (d, $^3J_{5,6}$ = 9.5 Hz, 1H, H-6), 6.91 (t, ^3J = 7.9 Hz, 1H, H-9), 6.85 (t, ^3J = 7.2 Hz, 1H, H-8), 6.35 (d, ^3J = 7.7 Hz, 1H, H-10), 6.06 (m, 1H, H-5), 5.70 (m, 1H, H-4a) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.1, 137.1, 134.5, 130.4, 130.0, 129.1, 128.9, 127.9, 126.4, 122.3 (q, $^1J_{CF}$ = 286.0 Hz, CF_3), 120.7, 117.5, 110.52-110.56 (m, C-D), 92.1 (q, $^2J_{CF}$ = 32.8 Hz), 78.2 ppm. ^{13}C NMR (100.6 MHz, CD_3CN): δ 148.4 (C-1), 138.3, 135.6, 130.9, 130.4, 130.0, 129.6, 128.9, 127.5, 125.0, 123.6 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 119.4, 118.1, 112.69-112.90 (m, $^1J_{CD}$, C-2), 92.9 (q, $^2J_{CF}$ = 32.4 Hz, C-3), 78.4 (C-4a) ppm.

^{19}F NMR (376.3 MHz, $CDCl_3$): δ -83.6 (CF_3) ppm; ^{19}F NMR (376.3 MHz, CD_3CN): δ -81.9 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OD]^+$ Calcd for $C_{19}H_{12}DF_3NO^+$: 329.1007; found: 329.1003; m/z $[M\text{-}D+H]^+$ Calcd for $C_{19}H_{14}DF_3NO_2^+$: 347.1112; found: 347.1107. Exchange of D on H in hydroxyl has takes place during the experiment.

1-Phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]-quinolin-3-ol (3a), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.** Obtained from quinoline **1a** (0.065 g, 0.5 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 20 h. White needles, m.p. 119-121 °C (hexane), yield 0.118 g (68%). Initial quinoline **1a** was recovered (0.010 g, conversion was 85%). IR (microlayer): 3401 (OH), 1649, 1635, 1602 (C=C), 1188, 1181, 1088 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 80:20 (^{1}H NMR).

(3*R**,4a*R**)-**3a**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.51 (m, 2H, H$_o$ from Ph), 7.37 (m, 2H, H$_m$ from Ph), 7.36 (m, 1H, H$_p$ from Ph), 7.15 (d, $^3J_{7,8}$ = 7.1 Hz, 1H, H-7), 6.92 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.88 (m, 1H, H-9), 6.83 (m, 1H, H-8), 6.31 (d, $^3J_{9,10}$ = 8.2 Hz, 1H, H-10), 6.02 (dd, $^3J_{4a,5}$ = 4.4 Hz, $^3J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.95 (s, 1H, H-2), 5.76 (d, $^3J_{4a,5}$ = 4.4 Hz, 1H, H-4a), 3.14 (s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.4 (C-1), 137.1 (C-10a), 134.6 (C$_i$ from Ph), 130.5 (C-6), 130.1 (C$_p$ from Ph), 129.2 (C$_m$ from Ph), 129.0 (C-9), 128.0 (C-7), 126.6 (C$_o$ from Ph), 122.4 (q, $^1J_{CF}$ = 286.1 Hz, CF_3), 121.4 (C-6a), 120.8 (C-8), 117.6 (C-10), 117.5 (C-5), 110.4 (C-2), 92.3 (q, $^2J_{CF}$ = 33.0 Hz, C-3), 78.3 (C-4a) ppm.

^{15}N NMR (40.5 MHz, $CDCl_3$): δ -283.7 (N-11) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.8 (CF_3) ppm.

(3*S**,4a*R**)-**3a** as a minor isomer in a mixture with the (3*R**,4a*R**)-**3a** isomer (ratio is 50:50): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.51 (m, 2H, H$_o$ from Ph), 7.37 (m, 2H, H$_m$ from Ph), 7.36 (m, 1H, H$_p$ from Ph), 7.15 (d, $^3J_{7,8}$ = 7.1 Hz, 1H, H-7), 6.92 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.88 (m, 1H, H-9), 6.83 (m, 1H, H-8), 6.31 (d, $^3J_{9,10}$ = 8.2 Hz, 1H, H-10), 6.07 (dd, $^3J_{4a,5}$ = 4.7 Hz, $^3J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.98 (s, 1H, H-2), 5.61 (d, $^3J_{5a,6}$ = 4.7 Hz, 1H, H-4a), 3.14 (s, 1H, OH) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.6 (CF_3) ppm. The signals in ^{13}C NMR spectrum are not detected due to overlap with signals of other isomer.

$C_{19}H_{14}F_3NO_2$ (345.32): calcd C, 66.09; H, 4.09; N, 4.06; F, 16.51. Found C, 66.43; H, 4.06; N, 3.99; F, 16.76.

1-(4-(*tert*-Butyl)phenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3d), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-**

diastereomers. Obtained from quinoline **1a** (0.039 g, 0.3 mmol), acetylene **2d** (0.076 g, 0.3 mmol) and H_2O (0.005 g, 0.3 mmol) in 2 mL MeCN by procedure II keeping the reaction mixture for 24 h. Light-brown needles, m.p. 74-77 °C, yield 0.109 g (91%). IR (microlayer): 3399 (OH), 1649, 1633, 1602 (C=C), 1259, 1180, 1153, 1099 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 70:30 (^{1}H NMR).

(3*R**,4a*R**)-**3d**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.41 (m, 2H, H-2',6'), 7.33 (m, 2H, H-3',5'), 7.12 (d, $^3J_{7,8}$ = 7.2 Hz, 1H, H-7), 6.88 (d, $^3J_{5,6}$ = 9.6 Hz, 1H, H-6), 6.86 (m, 1H, H-9), 6.79 (m, 1H, H-8), 6.35 (d, $^3J_{9,10}$ = 8.0 Hz, 1H, H-10), 5.98 (dd, $^3J_{4a,5}$ = 4.6 Hz, $^3J_{5,6}$ = 9.6 Hz, 1H, H-5), 5.92 (s, 1H, H-2), 5.62 (d, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-4a), 3.44 (br. s, 1H, OH), 1.28 (s, 9H, 3Me from *t*-Bu) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.5 (C-4'), 148.3 (C-1), 137.4 (C-10a), 131.8 (C-1'), 130.5 (C-6), 129.0 (C-9), 128.0 (C-7), 126.3 (C-2',6'), 126.1 (C-3',5'), 122.6 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 121.5 (C-6a), 120.7 (C-8), 117.7 (C-10, C-5), 110.0 (C-2), 92.4 (q, $^2J_{CF}$ = 33.4 Hz, C-3), 78.4 (C-4a), 34.9 (C from *t*-Bu), 31.3 (3Me from *t*-Bu) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.7 (CF_3) ppm.

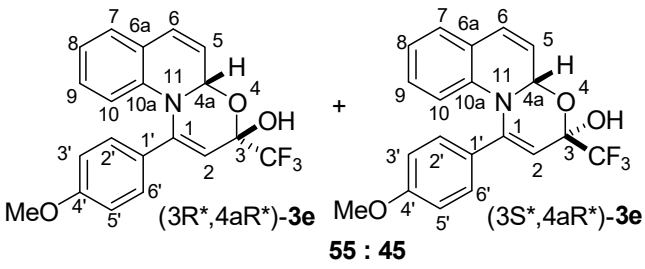
(3*S**,4a*R**)-**3d**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.41 (m, 2H, H-2',6'), 7.33 (m, 2H, H-3',5'), 7.12 (d, $^3J_{7,8}$ = 7.2 Hz, 1H, H-7), 6.89 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.86 (m, 1H, H-9), 6.79 (m, 1H, H-8), 6.35 (d, $^3J_{9,10}$ = 8.0 Hz, 1H, H-10), 6.05 (dd, $^3J_{4a,5}$ = 4.6 Hz, $^3J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.90 (s, 1H, H-2), 5.58 (d, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-4a), 3.44 (br. s, 1H, OH), 1.28 (s, 9H, 3Me from *t*-Bu) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.4 (C-4'), 148.8 (C-1), 137.4 (C-10), 131.7 (C-1'), 130.3 (C-6), 129.0 (C-9), 128.0 (C-7), 126.2 (C-2',6'), 126.1 (C-3',5'), 122.3 (q, $^1J_{CF}$ = 285.9 Hz, CF_3), 121.3 (C-6a), 120.5 (C-8), 117.6 (C-5), 117.5 (C-10), 111.5 (C-4), 94.8 (q, $^2J_{CF}$ = 31.8 Hz, C-3), 79.3 (C-4a), 34.9 (C from *t*-Bu), 31.3 (3Me from *t*-Bu) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.8 (CF_3) ppm.

$C_{23}H_{22}F_3NO_2$ (401.43): calcd C, 68.82; H, 5.52; N, 3.49; F, 14.20. Found: C, 68.47; H, 5.53; N, 3.15; F, 13.99.

1-(4-Methoxyphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3e), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.**



Obtained from quinoline **1a** (0.065 g, 0.5 mmol), acetylene **2e** (0.114 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 48 h. Light-yellow gum, yield 0.160 g (85%). Initial quinoline **1a** was recovered (0.009 g, conversion was 86%). IR (microlayer): br. 3393 (OH), 1633, 1605 (C=C), 1256, 1176, 1091 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 55:45 (^{1}H NMR).

(3*R**,4a*R**)-**3e**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.42 (m, 2H, H-3',5'), 7.13 (d, $^{3}J_{7,8}$ = 6.8 Hz, 1H, H-7), 6.86 (m, 1H, H-9), 6.82 (m, 2H, H-2',6'), 6.89 (d, $^{3}J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.79 (m, 1H, H-8), 6.35 (d, $^{3}J_{9,10}$ = 8.1 Hz, 1H, H-10), 5.98 (dd, $^{3}J_{4a,5}$ = 4.7 Hz, $^{3}J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.84 (s, 1H, H-2), 5.63 (d, $^{3}J_{4a,5}$ = 4.7 Hz, 1H, H-4a), 3.77 (s, 3H, OMe), 3.44 (br. s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 161.2 (C-4'), 148.1 (C-1), 137.4 (C-10a), 130.5 (C-6), 128.9 (C-9), 128.5 (C-7), 128.0 (C-2',6'), 127.1 (C-1'), 122.6 (q, $^{1}J_{CF}$ = 284.3 Hz, CF_3), 121.6 (C-6a), 120.7 (C-8), 117.7 (C-5, C-10), 114.6 (C-3',5'), 108.9 (C-2), 92.5 (q, $^{2}J_{CF}$ = 33.4 Hz, C-3), 78.3 (C-4a), 55.4 (OMe) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.6 (CF_3) ppm.

(3*S**,4a*R**)-**3e**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.42 (m, 2H, H-3',5'), 7.13 (d, $^{3}J_{7,8}$ = 6.8 Hz, 1H, H-7), 6.88 (m, 1H, H-9), 6.82 (m, 2H, H-2',6'), 6.89 (d, $^{3}J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.78 (m, 1H, H-8), 6.35 (d, $^{3}J_{9,10}$ = 8.1 Hz, 1H, H-10), 6.05 (dd, $^{3}J_{4a,5}$ = 4.7 Hz, $^{3}J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.83 (s, 1H, H-2), 5.58 (d, $^{3}J_{4a,5}$ = 4.7 Hz, 1H, H-4a), 3.77 (s, 3H, OMe), 3.44 (br. s, 1H, OH) ppm.

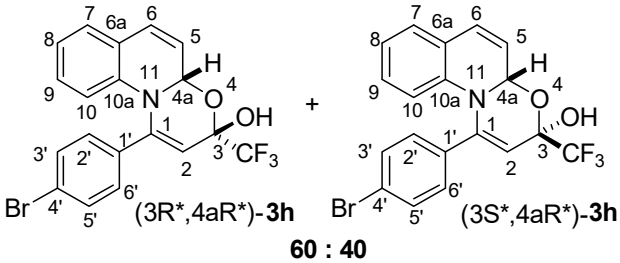
^{13}C NMR (100.6 MHz, $CDCl_3$): δ 161.1 (C-4'), 148.5 (C-1), 137.4 (C-10a), 130.3 (C-6), 128.9 (C-9), 128.5 (C-7), 128.0 (C-2',6'), 127.1 (C-1'), 122.3 (q, $^{1}J_{CF}$ = 285.1 Hz, CF_3), 121.4 (C-6a), 120.6 (C-8), 117.5 (C-5, C-10), 114.6 (C-3',5'), 110.3 (C-2), 94.8 (q, $^{2}J_{CF}$ = 32.2 Hz, C-3), 79.2 (C-4a), 55.4 (OMe) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.8 (CF_3) ppm.

$C_{20}H_{16}F_3NO_3$ (375.34): calcd C, 64.00; H, 4.30; N, 3.73; F, 15.18. Found: C, 64.07; H, 4.39; N, 3.62; F, 14.78.

1-(4-Bromophenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3h), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.** Obtained from quinoline **1a** (0.065 g, 0.5 mmol), acetylene **2h** (0.139 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 6 h. Light-yellow gum, yield 0.178 g (84%). Initial quinoline **1a** was recovered (0.009 g, conversion was 86%). IR (microlayer): 3395 (OH), 1639, 1597 (C=C), 1260, 1184, 1092 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 60:40 (^{1}H NMR).

(3*R**,4a*R**)-**3h**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.48 (m, 2H, H-3',5'), 7.38 (m, 2H, H-2',6'), 7.16 (d, $^{3}J_{7,8}$ = 7.4 Hz, 1H, H-7), 6.92 (d, $^{3}J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.91 (m, 1H, H-9), 6.85 (m, 1H, H-8), 6.27 (d, $^{3}J_{9,10}$ = 7.8 Hz, 1H, H-10), 6.01 (dd, $^{3}J_{4a,5}$ = 4.7 Hz, $^{3}J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.95 (s, 1H, H-2), 5.63 (d, $^{3}J_{4a,5}$ = 4.7 Hz, 1H, H-4a), 3.33 (br. s, 1H, OH) ppm.



^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.6 (C-1), 137.0 (C-10a), 133.7 (C-1'), 132.5 (C-3',5'), 130.4 (C-6), 129.1 (C-9), 128.5 (C-7), 128.1 (C-2',6'), 124.4 (C-4'), 122.6 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 121.6 (C-6a), 120.9 (C-8), 117.6 (C-5), 117.5 (C-10), 111.0 (C-2), 92.5 (q, $^2J_{CF}$ = 33.4 Hz, C-3), 78.3 (C-4a) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.7 (CF_3) ppm.

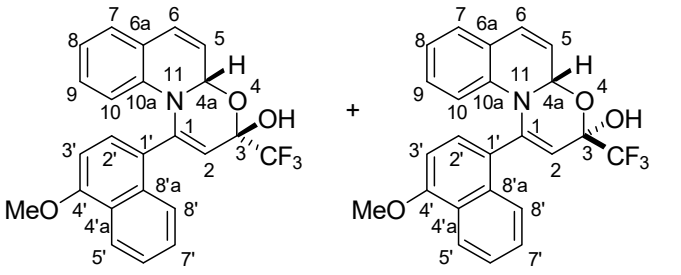
(3*S**,4a*R**)-**3h**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.48 (m, 2H, H-3',5'), 7.38 (m, 2H, H-2',6'), 7.16 (d, $^3J_{7,8}$ = 7.4 Hz, 1H, H-7), 6.92 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.91 (m, 1H, H-9), 6.83 (m, 1H, H-8), 6.26 (d, $^3J_{9,10}$ = 7.8 Hz, 1H, H-10), 6.06 (dd, $^3J_{4a,5}$ = 4.6 Hz, $^3J_{5,6}$ = 9.7 Hz, 1H, H-5), 5.93 (s, 1H, H-2), 5.57 (d, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-4a), 3.33 (br. s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.4 (C-1), 137.0 (C-10a), 133.7 (C-1'), 132.5 (C-3',5'), 130.6 (C-6), 129.1 (C-9), 128.5 (C-7), 128.1 (C-2',6'), 124.3 (C-4'), 122.3 (q, $^1J_{CF}$ = 285.5 Hz, CF_3), 121.6 (C-8), 121.5 (C-6a), 117.5 (C-5), 117.4 (C-10), 112.8 (C-2), 94.8 (q, $^2J_{CF}$ = 32.0 Hz, C-3), 79.1 (C-4a) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.3 (CF_3) ppm.

$C_{19}H_{13}BrF_3NO_2$ (424.21): calcd C, 53.79; H, 3.09; Br, 18.84; N, 3.30; F, 13.44. Found C, 53.74; H, 3.25; Br, 19.22; F, 13.18; N, 3.05.

1-(4-Methoxynaphthalen-1-yl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol, (3i)



mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.** Obtained from quinoline **1a** (0.065 g, 0.5 mmol), acetylene **2i** (0.139 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 184 h. Light-beige needles, m.p. 114-117 °C (hexane), yield 0.163 g (77%). Initial quinoline **1a** was recovered (0.013 g, conversion was 80%). IR (microlayer): 3398 (OH), 1643, 1630 (C=C), 1245, 1183, 1100 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 80:20 (^{1}H NMR).

(3*R**,4a*R**)-**3i**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.32 (m, 2H, H-5', H-8'), 7.48 (m, 3H, H-2', H-6' and H-7'), 7.09 (m, 1H, H-7), 6.90 (d, $^3J_{5,6}$ = 9.6 Hz, 1H, H-6), 6.72 (m, 1H, H-3'), 6.71 (m, 2H, H-8, H-9), 6.43 (m, 1H, H-10), 6.03 (dd, $^3J_{4a,5}$ = 4.7 Hz, $^3J_{5,6}$ = 9.6 Hz, 1H, H-5), 5.87 (s, 1H, H-2), 5.87 (d, $^3J_{4a,5}$ = 4.7 Hz, 1H, H-4a), 4.74 (br. s, 1H, OH), 3.97 (s, 3H, OMe) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 156.8 (C-4'), 146.5 (C-1), 137.0 (C-10a), 131.9 (C-8'a), 130.4 (C-6), 129.2 (C-9), 128.1 (C-7), 127.8 (C-8'), 127.6 (C-1'), 126.3 (C-7'), 125.7 (C-6'), 124.8 (C-4'a), 124.1 (C-2'), 122.8 (q, $^1J_{CF}$ = 284.3 Hz, CF_3; C-5'), 121.1 (C-6a), 120.6 (C-8), 117.6 (C-5), 116.3 (C-10), 113.1 (C-2), 103.6 (C-3'), 92.5 (q, $^2J_{CF}$ = 33.0 Hz, C-3), 78.6 (C-4a), 55.7 (OMe) ppm.

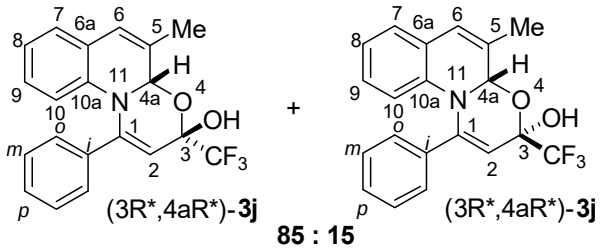
^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.3 (CF_3) ppm.

(3*S**,4a*R**)-**3i** as a minor isomer in a mixture with the (3*R**,4a*R**)-**3i** isomer and quinoline **1a** (ratio is 15:55:30): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.32 (m, 2H, H-5', H-8'), 7.48 (m, 3H, H-2', H-6' and H-7'), 7.09 (m, 1H, H-7), 6.92 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.72 (m, 1H, $H_{3'}$ from Napht), 6.71 (m, 2H, H-8, H-9), 6.43 (m, 1H, H-10), 6.11 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-5), 5.81 (s, 1H, H-2), 5.80 (d, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-4a), 4.74 (br. s, 1H, OH), 3.97 (s, 3H, OMe) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 156.8 (C-4'), 145.0 (C-1), 137.0 (C-10a), 131.9 (C-8'a), 130.3 (C-6), 129.2 (C-9), 128.1 (C-7), 127.8 (C-8'), 127.6 (C-1'), 126.3 (C-7'), 125.7 (C-6'), 124.8 (C-4'a), 124.1 (C-2'), 122.8 (C-5'), 122.6 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 121.1 (C-6a), 120.5 (C-8), 117.3 (C-5), 116.2 (C-10), 114.2 (C-2), 103.6 (C-3'), 94.7 (q, $^2J_{CF}$ = 32.4 Hz, C-3), 79.7 (C-4a), 55.7 (OMe) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.5 ppm.

$C_{24}H_{18}F_3NO_3$ (425.40): calcd C, 67.76; H, 4.26; N, 3.29; F, 13.40. Found C, 67.77; H, 4.51; N, 3.68; F, 13.23.



5-Methyl-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3j), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.** Obtained from quinoline **1b** (0.072 g, 0.5 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 24 h. White needles, m.p. 104-106 °C (hexane), yield 0.134 g (75%). Initial quinoline **1b** was recovered (0.015 g, conversion was 79%). IR (microlayer): 3372 (OH), 1632, 1601 (C=C), 1258, 1178, 1084 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 85:15 (^{1}H NMR).

(3*R**,4a*R**)-**3j**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.50 (m, 2H, H_o from Ph), 7.36 (m, 2H, H_m from Ph), 7.36 (m, 1H, H_p from Ph), 7.08 (d, $^3J_{7,8}$ = 7.0 Hz, 1H, H-7), 6.80 (m, 2H, H-8, H-9), 6.64 (s, 1H, H-6), 6.27 (d, $^3J_{9,10}$ = 8.0 Hz, 1H, H-10), 5.94 (s, 1H, H-2), 5.47 (s, 1H, H-4a), 3.19 (s, 1H, OH), 2.10 (s, 3H, Me) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.6 (C-1), 136.0 (C-10a), 134.9 (C_i from Ph), 130.1 (C_p from Ph), 129.2 (C_m from Ph), 127.9 (C-9), 127.1 (C-7), 126.9 (C-5), 126.7 (C_o from Ph), 126.1 (C-6), 122.6 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 122.2 (C-6a), 120.9 (C-8), 117.3 (C-10), 110.2 (C-2), 92.5 (q, $^2J_{CF}$ = 33.4 Hz, C-3), 82.4 (C-4a), 19.7 (Me) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.7 (CF_3) ppm.

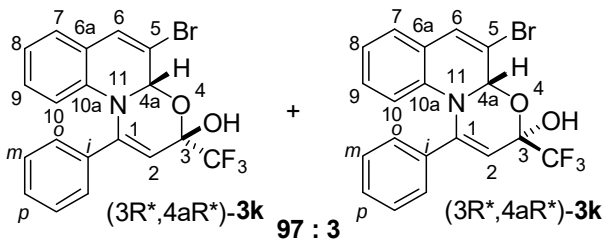
(3*S**,4a*R**)-**3j**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 5.91 (s, 1H, H-2), 5.43 (s, 1H, H-4a), 2.14 (s, 3H, Me) ppm.

Other ^{1}H and ^{13}C signals were not detected due to low concentration of this isomer.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.0 (CF_3) ppm.

$C_{20}H_{16}F_3NO_2$ (359.34): calcd C, 66.85; H, 4.49; N, 3.90; F, 15.86. Found C, 66.72; H, 4.29; N, 4.02; F, 15.61.

5-Bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3k), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.**



Obtained from quinoline **1c** (0.104 g, 0.5 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 144 h. Light-yellow needles, m.p. 64-67 °C, yield 0.145 g (68%). Initial quinoline **1c** was recovered (0.007 g, conversion was 93%). IR (microlayer): 3366 (OH), 1636, 1602 (C=C), 1258, 1180, 1097 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 97:3 (^{1}H NMR).

(3*R**,4a*R**)-**3k**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.51 (m, 2H, H_o from Ph), 7.37 (m, 2H, H_m from Ph), 7.36 (m, 1H, H_p from Ph), 7.22 (s, 1H, H-6), 7.10 (d, $^3J_{7,8}$ = 7.4 Hz, 1H, H-7), 6.90 (m, 1H, H-9), 6.83 (m, 1H, H-8), 6.32 (d, $^3J_{9,10}$ = 8.1 Hz, 1H, H-10), 6.00 (s, 1H, H-2), 5.72 (s, 1H, H-4a), 3.85 (br. s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.7 (C-2), 136.0 (C-11a), 134.3 (C_i from Ph), 132.3 (C-6), 130.3 (C_p from Ph), 129.3 (C_m from Ph), 128.5 (C-9), 127.5 (C-7), 126.6 (C_o from Ph), 122.4 (q, $^1J_{CF}$ = 284.7 Hz, CF_3), 121.4 (C-6a), 121.3 (C-8), 117.7 (C-10), 111.4 (C-5), 111.1 (C-2), 92.8 (q, $^2J_{CF}$ = 33.3 Hz, C-3), 83.1 (C-4a) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.6 (CF_3) ppm.

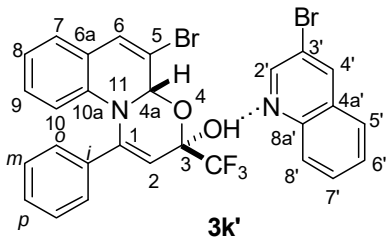
(3*S**,4a*R**)-**3k**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 5.95 (s, 1H, H-2), 5.68 (s, 1H, H-4a) ppm.

Other ^{1}H and ^{13}C signals were not detected due to low concentration of this isomer.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -78.7 (CF_3) ppm.

$C_{19}H_{13}BrF_3NO_2$ (424.21): calcd C, 53.79; H, 3.09; N, 3.30; Br, 18.84; F, 13.44. Found C, 53.98; H, 3.11; N, 3.68; Br, 18.90; F, 13.27.

Associate of 5-bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol and 3-bromoquinoline (3k') (composition 1:1). Isolated as an admixture in the synthesis of the mixture of (3*R**,4a*R**)-**3k** and (3*S**,4a*R**)-**3k.**



Colorless needles, m.p. 146-148 °C (ethanol), yield 0.040 g (13%). IR (microlayer): 1637, 1601 (C=C), 1258, 1177, 1125 (C-F) cm^{-1}; (diluted solution with CCl_4, d = 1 cm): 3568 (OH) cm^{-1}.

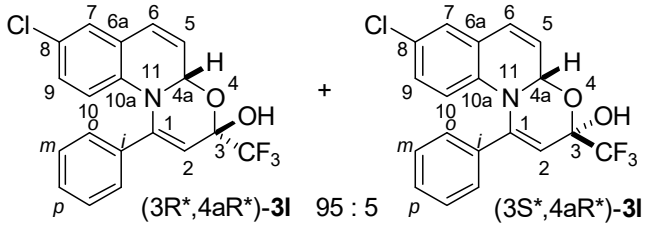
^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.91 (s, 1H, H-2'), 8.31 (s, 1H, H-4'), 8.10 (d, $^3J_{7,8}$ = 8.6 Hz, 1H, H-8'), 7.70 (m, 2H, H-5', H-7'), 7.54 (m, 1H, H-6'), 7.51 (m, 2H, H_o from

Ph), 7.37 (m, 2H, H_m from Ph), 7.36 (m, 1H, H_p from Ph), 7.22 (s, 1H, H-6), 7.10 (d, $^3J_{7,8}$ = 7.4 Hz, 1H, H-7), 6.90 (m, 1H, H-9), 6.83 (m, 1H, H-8), 6.32 (d, $^3J_{9,10}$ = 8.1 Hz, 1H, H-10), 6.00 (s, 1H, H-2), 5.72 (s, 1H, H-4a), 4.63 (br. s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.4 (C-2'), 147.7 (C-1), 146.2 (C-8a'), 137.7 (C-4'), 136.0 (C-10a), 134.3 (C_i from Ph), 132.3 (C-6), 130.3 (C_p from Ph), 130.0 (C-8'), 129.4 (C-7'), 129.3 (C_m from Ph; C-5'; C-4a'), 128.5 (C-9), 127.5 (C-7), 127.1 (C-6'), 126.6 (C_o from Ph), 122.4 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 121.4 (C-6a), 121.3 (C-8), 117.7 (C-10), 117.3 (C-3'), 111.4 (C-5), 111.1 (C-2), 92.8 (q, $^2J_{CF}$ = 33.3 Hz, C-3), 83.1 (C-4a) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.5 (CF_3) ppm.

$C_{28}H_{19}Br_2F_3N_2O_2$ (633.27): calcd C, 53.19; H, 3.03; N, 4.43; F, 9.01; Br, 25.28. Found C, 53.53; H, 3.20; N, 4.49; F, 10.00; Br, 24.89.

8-Chloro-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-a]quinolin-3-ol (3l), mixture of (3*R,4a*R**)- and (3*S**,4a*R**)-diastereomers.** 

Obtained from quinoline **1d** (0.082 g, 0.5 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure II keeping the reaction mixture for 24 h. White needles, m.p. 127-129 °C (hexane), yield 0.130 g (68%). Initial quinoline **1d** was recovered (0.015 g, conversion was 82%). IR (microlayer): 3392 (OH), 1638 (C=C), 1259, 1185, 1090 (C-F) cm^{-1}. (3*R**,4a*R**):(3*S**,4a*R**)-isomers ratio is 95:5 (^{1}H NMR).

(3*R**,4a*R**)-**3l**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.49 (m, 2H, H_o from Ph), 7.37 (m, 3H, $H_{m,p}$ from Ph), 7.14 (d, $^4J_{7,9}$ = 1.5 Hz, 1H, H-7), 6.85 (d, $^3J_{5,6}$ = 9.4 Hz, 1H, H-6), 6.83 (dd, $^3J_{9,10}$ = 8.8 Hz, 1H, H-9), 6.24 (d, $^3J_{9,10}$ = 8.8 Hz, 1H, H-10), 6.07 (dd, $^3J_{5,6}$ = 9.4 Hz, $^3J_{4a,5}$ = 3.8 Hz, 1H, H-5), 5.96 (s, 1H, H-2), 5.64 (d, $^3J_{4a,5}$ = 3.8 Hz, 1H, H-4a), 3.22 (s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.2 (C-1), 135.7 (C-10a), 134.3 (C_i from Ph), 130.4 (C-6), 129.6 (C_p from Ph), 129.4 (C_m from Ph), 128.7 (C-9), 127.5 (C-7), 126.6 (C_o from Ph), 125.9 (C-8), 122.9 (C-6a), 122.4 (q, $^1J_{CF}$ = 284.3 Hz, CF_3), 119.0 (C-5), 118.8 (C-10), 110.7 (C-2), 92.4 (q, $^2J_{CF}$ = 34.1 Hz, C-3), 78.1 (C-4a) ppm.

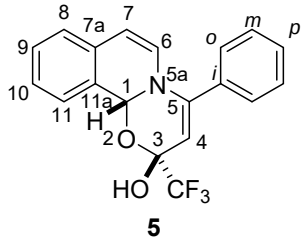
^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.8 (CF_3) ppm.

(3*S**,4a*R**)-**3l**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 6.12 (dd, $^3J_{4a,5}$ = 4.4 Hz, $^3J_{5,6}$ = 9.6 Hz, 1H, H-5), 5.88 (s, 1H, H-2), 5.59 (d, $^3J_{4a,5}$ = 4.4 Hz, 1H, H-4a) ppm.

Other ^{1}H and ^{13}C signals were not detected due to low concentration of this isomer.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -79.6 (CF_3) ppm.

$C_{19}H_{13}ClF_3NO_2$ (379.76): calcd C, 60.09; H, 3.45; N, 3.69; Cl, 9.34; F, 15.01. Found C, 59.91; H, 3.50; N, 3.30; Cl, 9.63; F, 15.13.



5

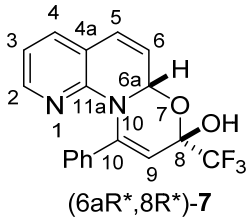
(2*R,11b*R*)-4-Phenyl-2-(trifluoromethyl)-2*H*,11b*H*-[1,3]oxazino-[2,3-*a*]isoquinolin-2-ol (5).** Analogously procedure II, from isoquinoline (**4**) (0.039 g, 0.3 mmol), acetylene **2a** (0.059 g, 0.3 mmol), and H_2O (0.005 g, 0.3 mmol) in 2 mL MeCN (-5~0 °C to 20-24 °C, 4 h) 1,3-oxazinoisoquinoline **5** (0.065 g, 63%) was obtained as an yellow oil. Initial isoquinoline **4** was recovered (0.010 g, conversion was 74%). IR (microlayer): br. 3344 (OH), 1634, 1603 (C=C), 1257, 1179, 1073 (C-F) cm^{-1}.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.50-7.40 (m, 7H, H-9, H-11, $H_{o,m,p}$ from Ph), 7.27 (m, 1H, H-10), 7.15 (d, $^3J_{8,9}$ = 7.2 Hz, 1H, H-8), 6.35 (d, $^3J_{6,7}$ = 7.6 Hz, 1H, H-6), 5.71 (d, $^3J_{6,7}$ = 7.6 Hz, 1H, H-7), 5.58 (s, 1H, H-11b), 3.58 (br. s, 1H, OH) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.6 (C-4), 133.6 (C_i from Ph), 131.6 (C-7a), 130.3 (C_p from Ph), 129.7 (C-6), 129.0 (C_o from Ph), 128.9 (C-9), 128.7 (C_m from Ph), 127.5 (C-11), 126.9 (C-10), 125.3 (C-11a), 124.9 (C-8), 122.6 (q, $^1J_{CF}$ = 285.7 Hz, CF_3), 103.8 (C-3), 101.8 (C-7), 92.6 (q, $^2J_{CF}$ = 33.4 Hz, C-2), 79.4 (C-11b) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -82.0 (CF_3) ppm.

$C_{19}H_{14}F_3NO_2$ (345.32): calcd C, 66.09; H, 4.09; N, 4.06; F, 16.51. Found C, 65.97; H, 3.98; N, 3.68; F, 16.16.

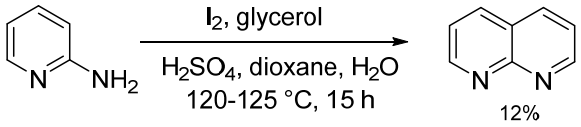


(6aR*,8R*)-**7**

(6a*R*,8*R)-10-phenyl-8-(trifluoromethyl)-6a*H*,8*H*-[1,3]oxazino[3,2-*a*][1,8]naphthyridin-8-ol (7)** obtained from 1,8-naphthyridine (**6**) (0.062 g, 0.475 mmol), acetylene **2a** (0.099 g, 0.5 mmol) and H_2O (0.009 g, 0.5 mmol) by procedure I keeping the reaction mixture for 36 h. Pale brown crystals, m.p. 145-147 °C (hexane), yield 0.149 g (91%). ^{1}H NMR (400.1 MHz, CD_3CN): δ 7.73 (dd, ^3J = 5.0 Hz, ^4J = 1.8 Hz, 1H), 7.55 (dd, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 1H), 7.49-7.45 (m, 2H, H_o from Ph), 7.37-7.32 (m, 3H, $H_{m,p}$ from Ph), 7.00 (d, ^3J = 9.7 Hz, 1H), 6.82 (dd, ^3J = 7.4 Hz, ^3J = 4.9 Hz, 1H), 6.16 (dd, ^3J = 9.7 Hz, ^3J = 4.7 Hz, 1H), 5.96 (s, 1H), 5.81 (d, ^3J = 4.8 Hz, 1H), 5.48 (s, 1H, OH) ppm. ^{19}F NMR (376.50 Hz, CD_3CN): δ -82.2 (CF_3) ppm. ^{13}C NMR (100.6 Hz, CD_3CN): δ 150.4, 148.6, 147.9, 137.2, 135.9, 129.8, 129.3, 126.7, 123.5 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 120.5, 117.8, 116.9, 111.9, 92.9 (q, $^2J_{CF}$ = 33.2 Hz, C-CF_3), 78.8 ppm.

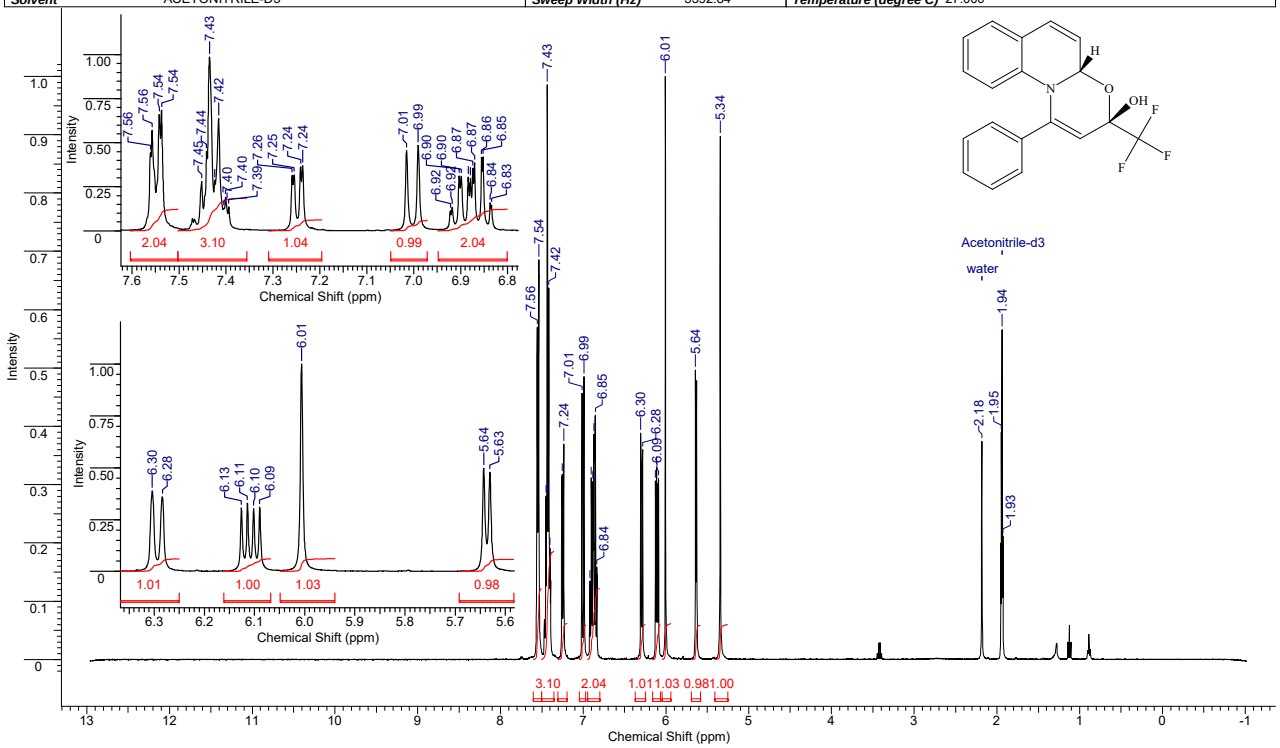
HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{18}H_{12}F_3N_2O^+$: 329.0896; found: 329.0899; m/z $[M+H]^+$ Calcd for $C_{18}H_{14}F_3N_2O_2^+$: 347.1002; found: 347.1002.

Synthesis of 1,8-naphthyridine 6



Round bottom 250 mL three-neck flask was charged with dioxane (30 mL), water (30 mL), 2-aminopyridine (5.00 g, 53 mmol) and glycerol (15.5 mL, 212 mmol) at stirring to give clear solution. After cooling on ice bath, conc. H_2SO_4 (55 mL) were added dropwise at 0-5 °C (about 2.5-3 h). Then, iodine (4.04 g, 15.9 mmol) were added and the reaction mixture was heated at reflux for 15 h (internal temperature 120-125 °C). After cooling to room temperature, the reaction mixture was carefully basified by 50% aq. NaOH solution (200-250 mL). The obtained brown-black syrup-like solution was filtered through a celite pad and extracted with CH_2Cl_2 (6 times by 70-80 mL until no spot of the product were observed on TLC run of new extracted portion). Light brown extract was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2-MeOH 30:1 as an eluent) to give 0.820 g (12%) of 1,8-naphthyridine as a pale brown solid, m.p. 97-99 °C (lit. data: 97-98 °C, E. M. Hawes, D. G. Wibberley, *J. Chem. Soc. [Section] C: Organic*, **1967**, 1564-1568). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 9.04–9.01 (m, 2H), 8.09 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 2H), 7.38 (dd, ^3J = 8.1 Hz, ^4J = 4.2 Hz, 2H). ^{13}C NMR (100.6 Hz, $CDCl_3$): δ 155.9, 153.4, 136.9, 122.6, 121.9 ppm. NMR data are in agreement with those in the literature (N. R. Rivera, Y. Hsiao, J. A. Cowen, C. McWilliams, J. Armstrong, N. Yasuda, D. L. Hughes, *Synth. Commun.*, **2001**, *31*, 1573-1579).

FW	345.3152	Formula	$C_{19}H_{14}F_3NO_2$				
Acquisition Time (sec)	2.9295	Comment	Imported from UXNMR.			Date	24 Jun 2017 22:42:08
File Name	D:\BN\output\2017\06.èþ í ú\170624 (1)\BM-1114-K2_001001r			Frequency (MHz)	400.13	Nucleus	1H
Number of Transients	16	Original Points Count	16384	Points Count	65536	Pulse Sequence	zg30
Solvent	ACETONITRILE-D3			Sweep Width (Hz)	5592.84	Temperature (degree C)	27.000



^{1}H NMR spectrum of (3*R**,4a*R**)-**3a** (400.1 MHz, CD_3CN)

FW	345.3152	Formula	$C_{19}H_{14}F_3NO_2$				
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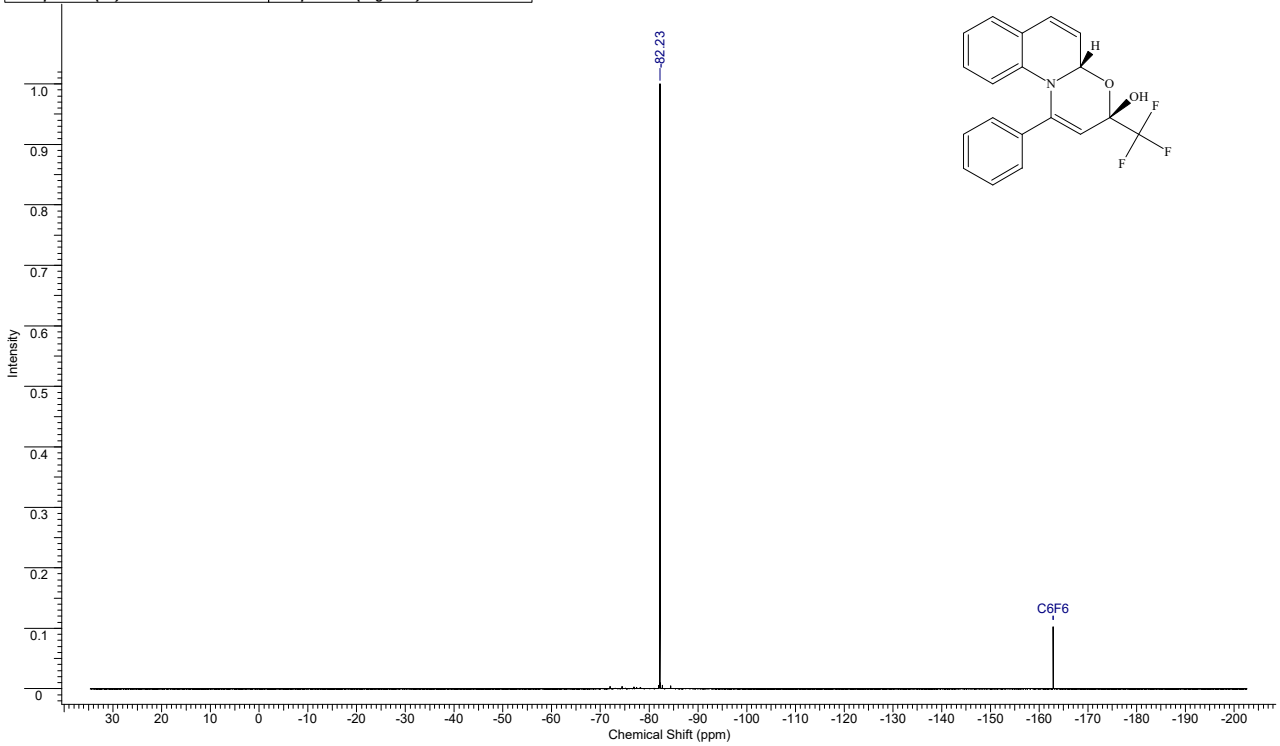
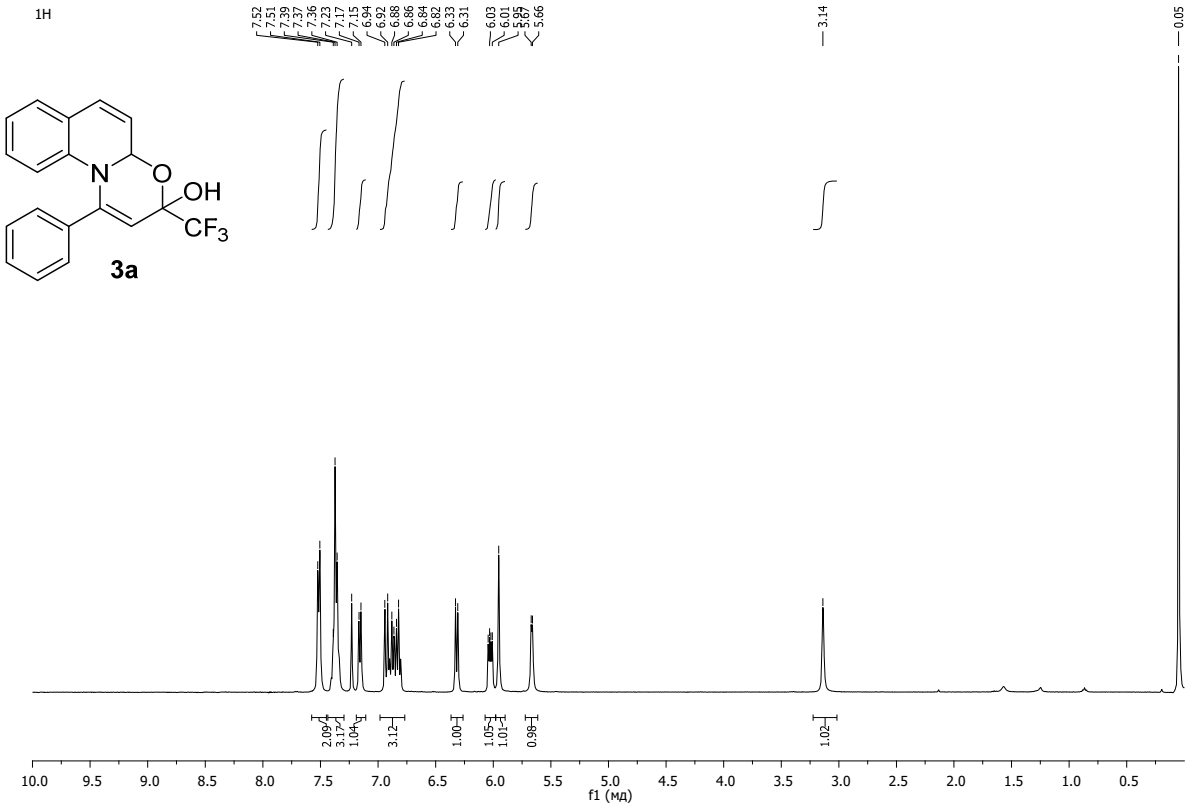
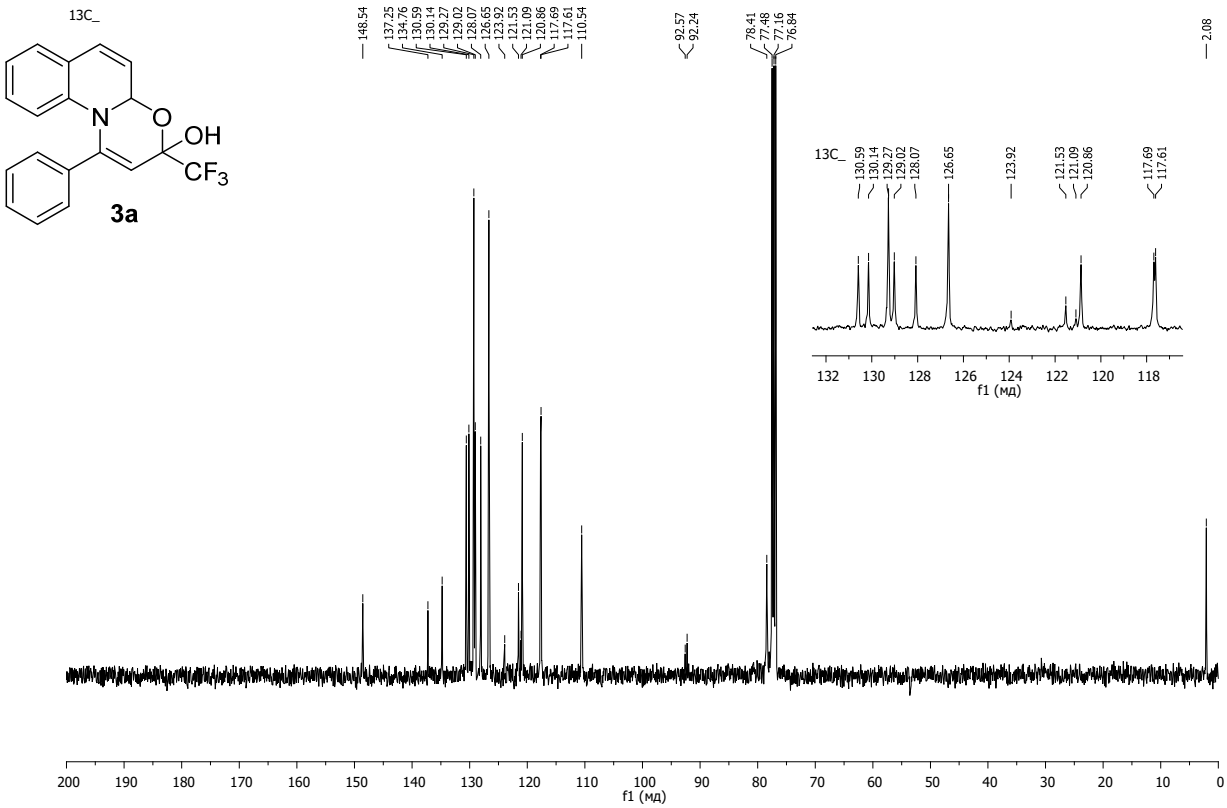
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	133929
Points Count	262144	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



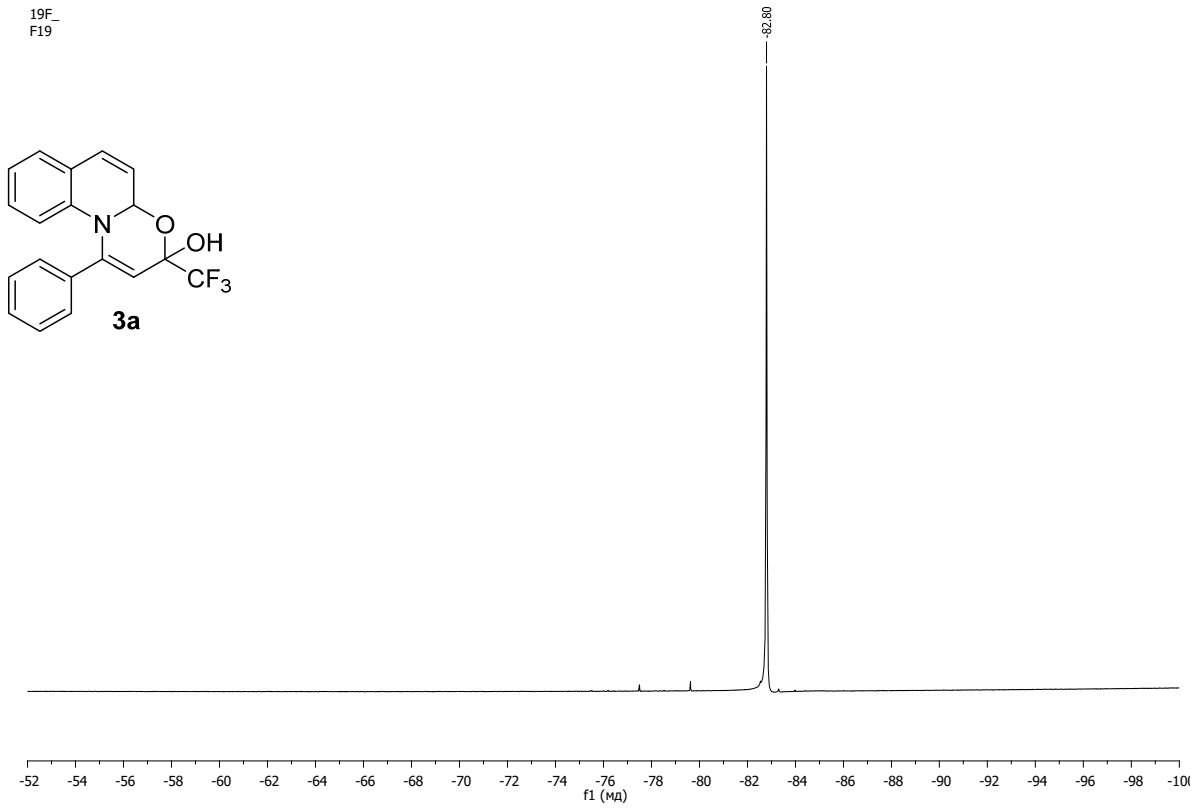
^{19}F NMR spectrum of (3*R**,4a*R**)-**3a** (376.3 MHz, CD_3CN)



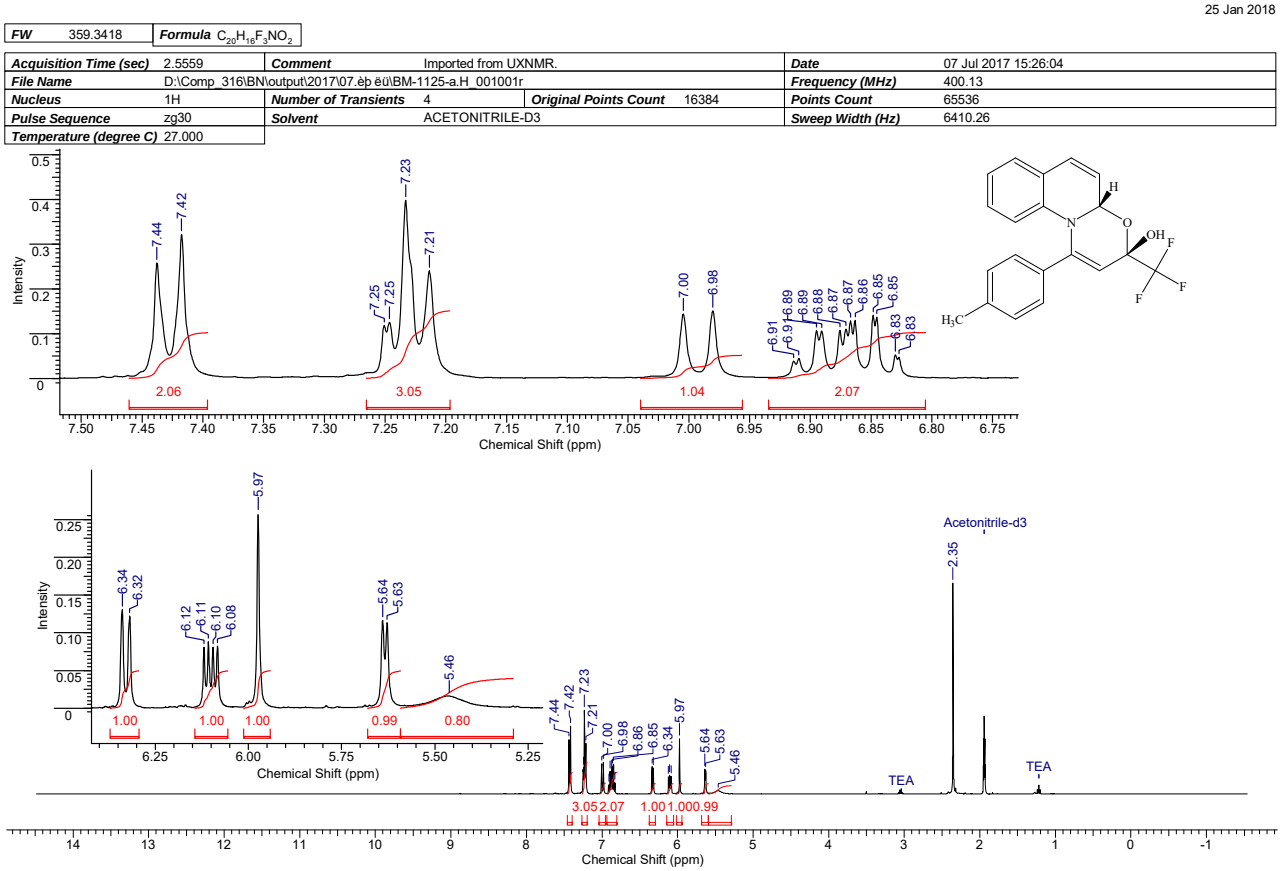
^{1}H NMR spectrum of (3*R**,4a*R**)-**3a** (400.1 MHz, $CDCl_3$)



^{13}C NMR spectrum of (3*R**,4a*R**)-**3a** (100.6 MHz, $CDCl_3$)



^{19}F NMR spectrum of (3*R**,4a*R**)-**3a** (376.5 MHz, $CDCl_3$)



^{1}H NMR spectrum of (3*R**,4a*R**)-**3b**(400.1 MHz, CD_3CN)

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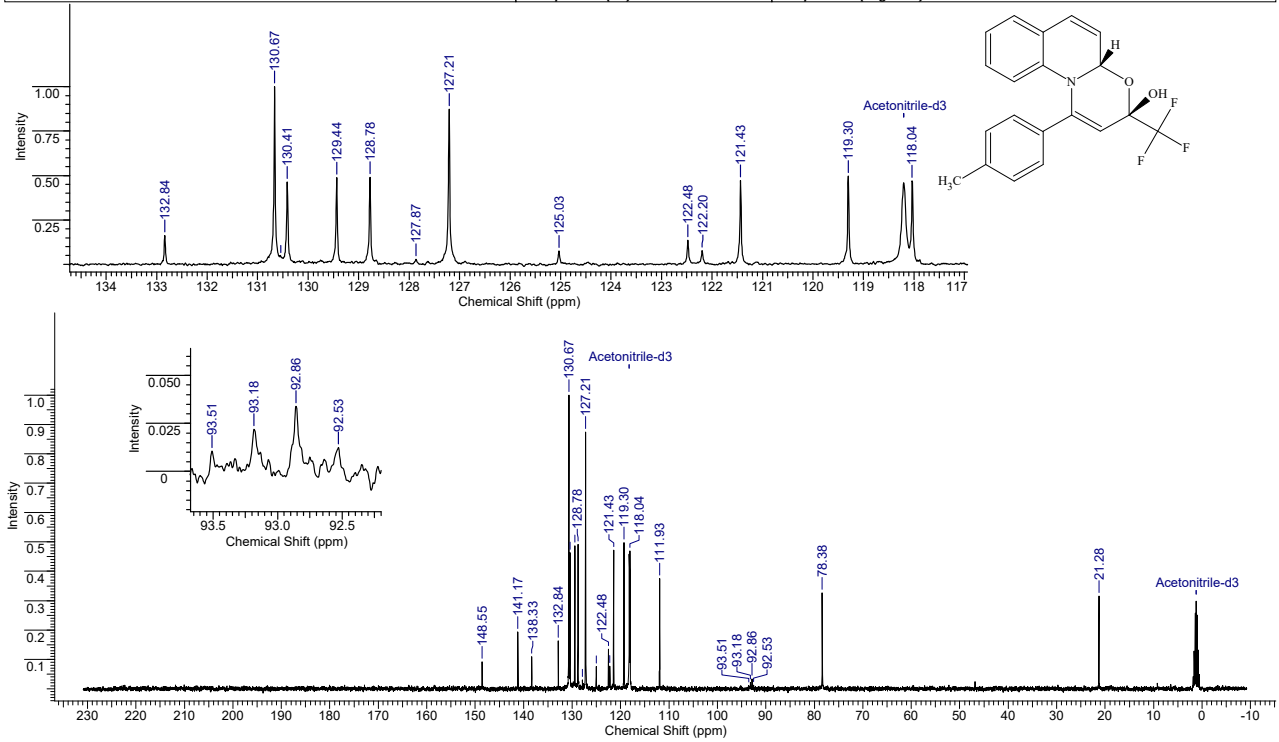
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	29 Jun 2017 11:51:02
File Name	D:\BN\output\2017\06.èþ í ú\BM-1125.C_002001r			Frequency (MHz)	100.61	Nucleus	13C
Number of Transients	64	Original Points Count	12076	Points Count	65536	Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D			Sweep Width (Hz)	24154.59	Temperature (degree C)	27.000

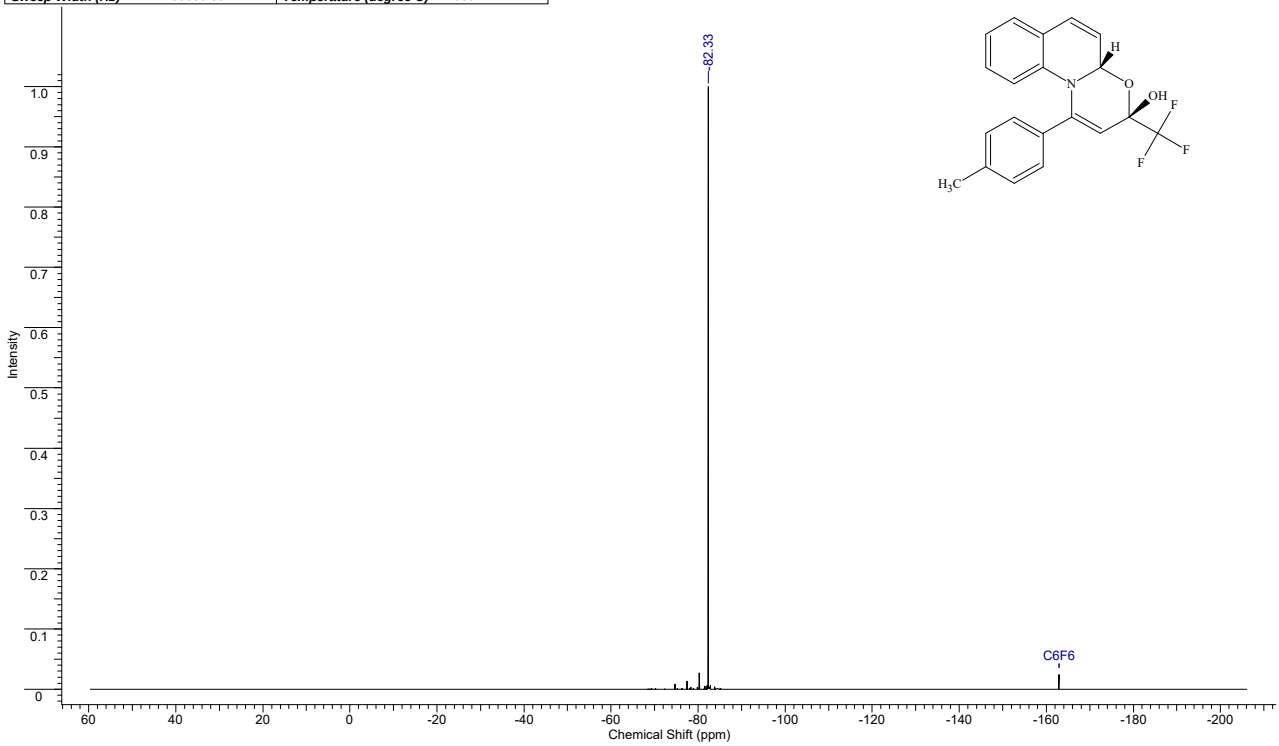


^{13}C NMR spectrum of (3*R**,4a*R**)-**3b** (100.6 MHz, CD_3CN)

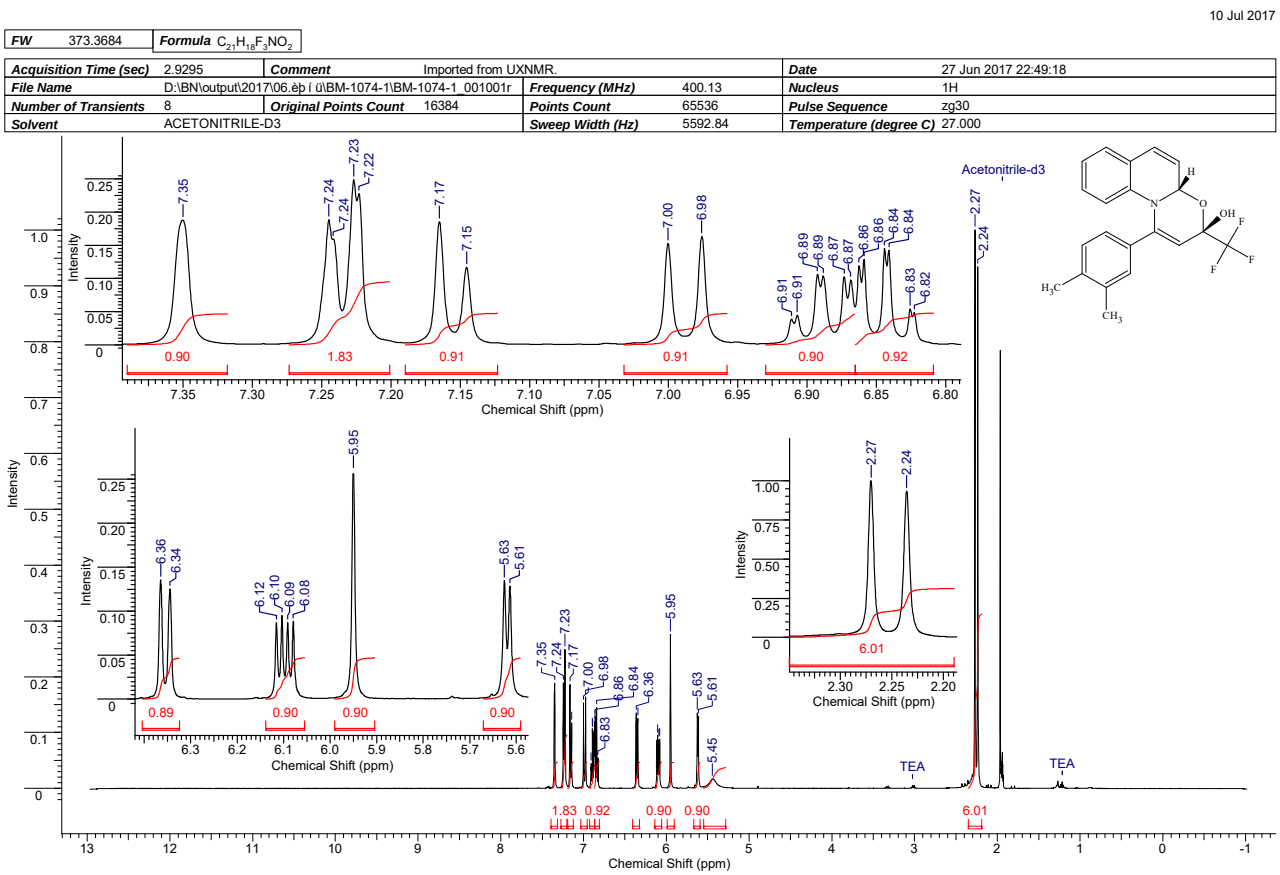
10 Jul 2017

FW	359.3418	Formula	$C_{20}H_{16}F_3NO_2$

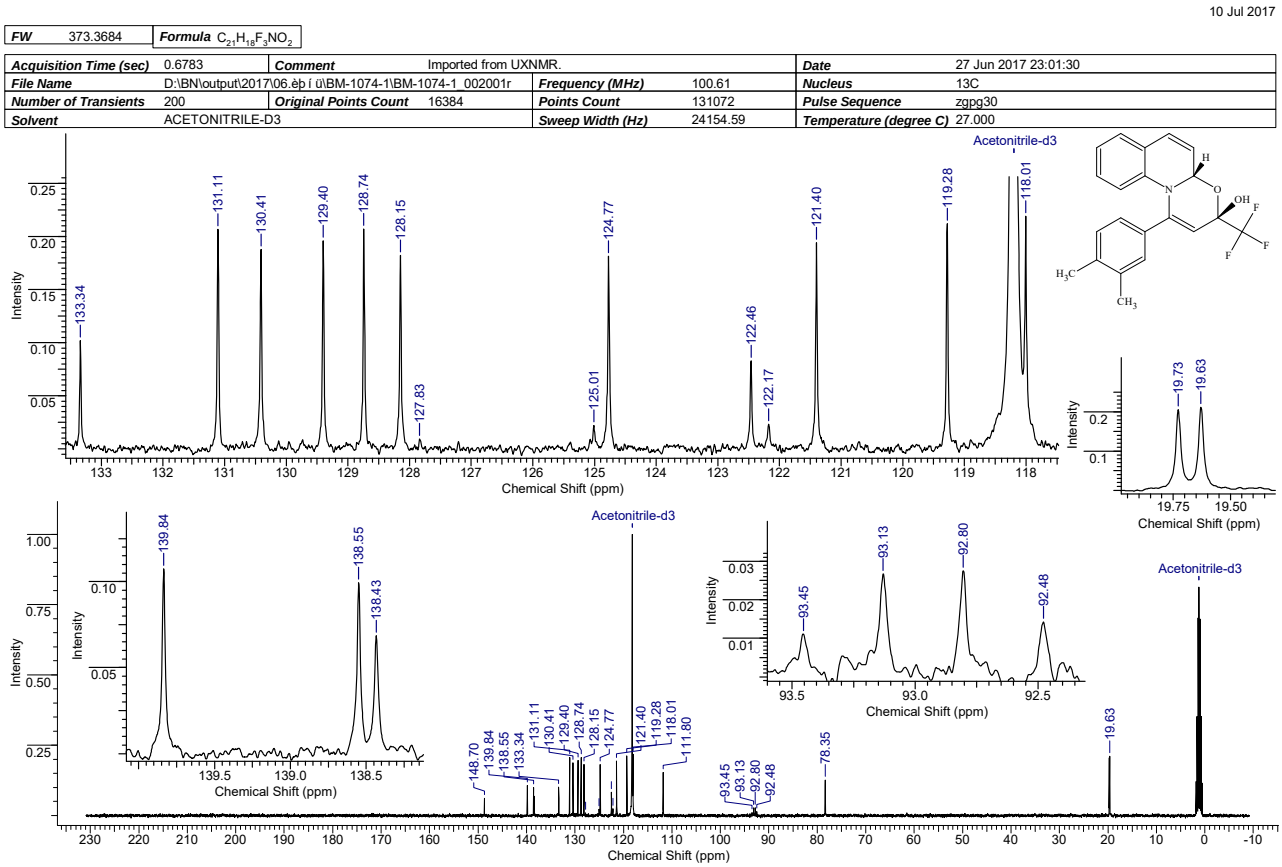
Acquisition Time (sec)	2.6214	Date	Jun 29 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1125-F_20170629_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	8	Original Points Count	262144
Points Count	262144	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	100000.00	Temperature (degree C)	22.000				



^{19}F NMR spectrum of (3*R**,4a*R**)-**3b** (376.3 MHz, CD_3CN)

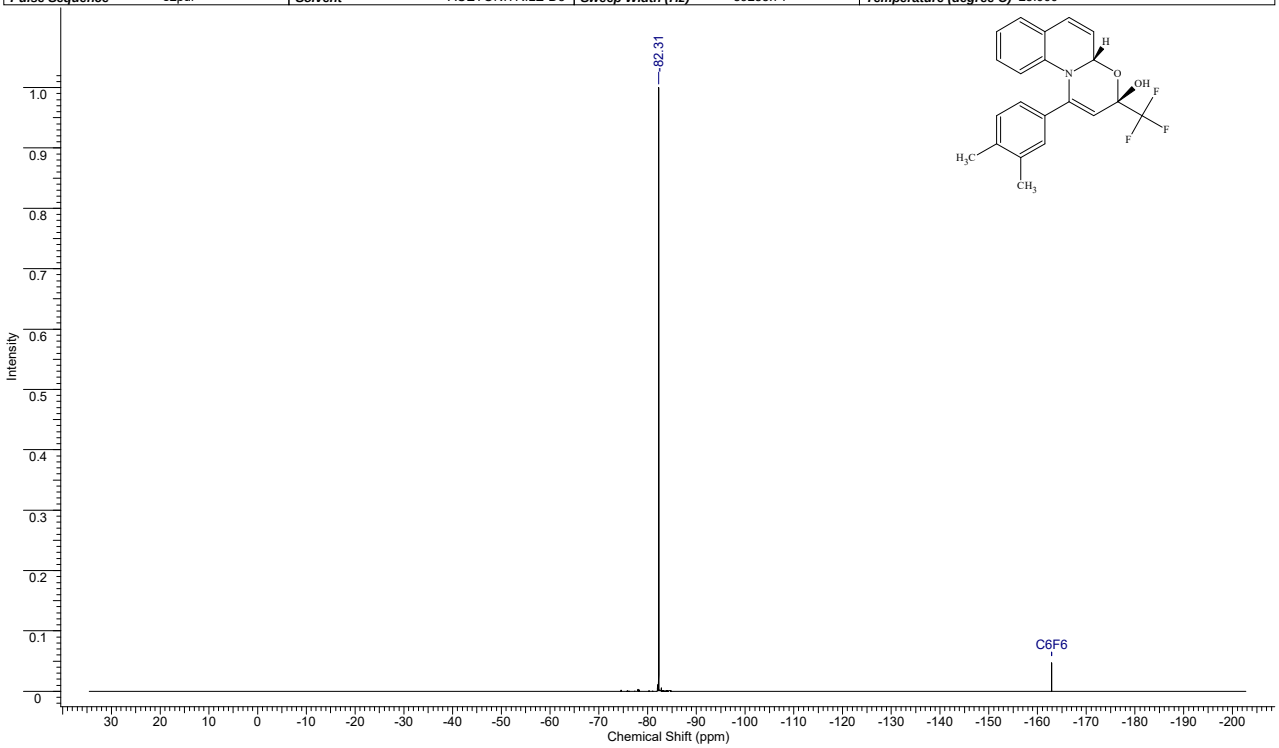


^{1}H NMR spectrum of (3*R**,4a*R**)-**3c** (400.1 MHz, CD_3CN)



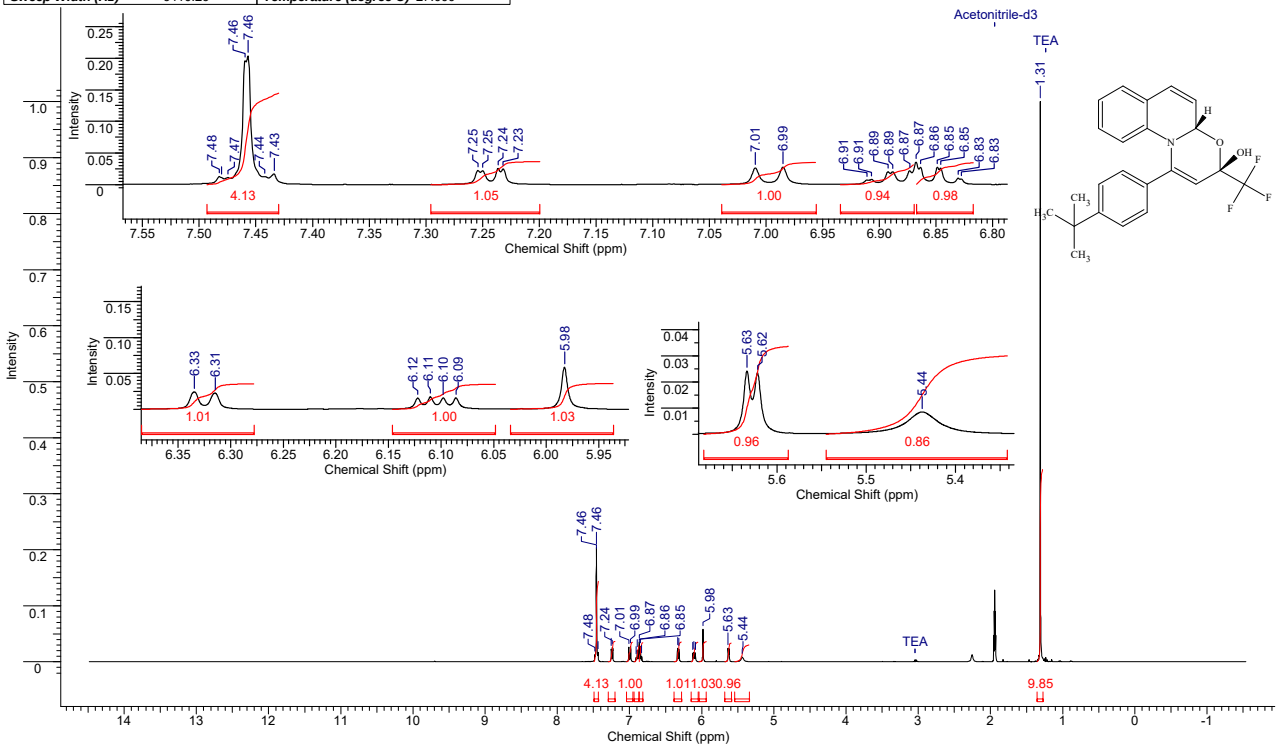
^{13}C NMR spectrum of (3*R**,4a*R**)-**3c** (100.6 MHz, CD_3CN)

FW	373.3684	Formula	$C_{21}H_{18}F_3NO_2$				
Acquisition Time (sec)	1.5000	Comment	STANDARD FLUORINE PARAMETERS			Date	Jun 28 2017
File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1074-1_20170628_01\FLUORINE_01					Frequency (MHz)	376.31
Nucleus	19F	Number of Transients	16	Original Points Count	133929	Points Count	262144
Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3	Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000



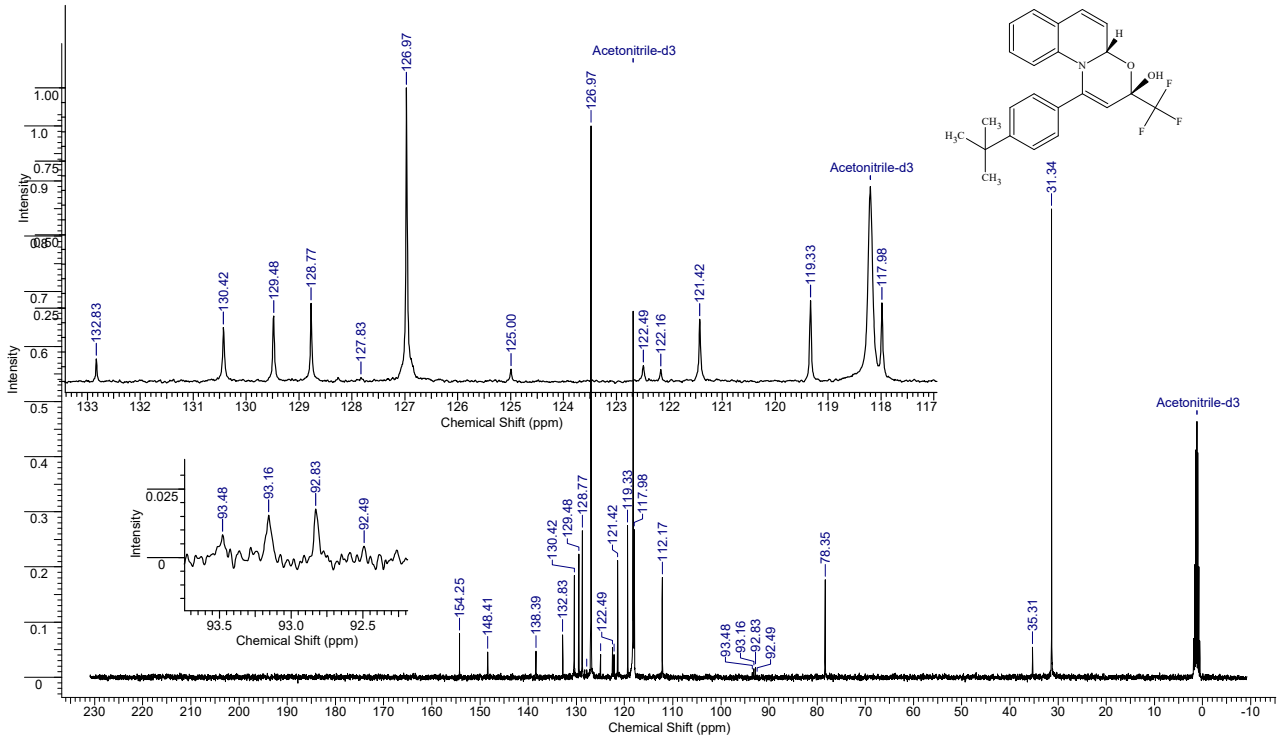
^{19}F NMR spectrum of (3*R**,4a*R**)-**3c** (376.3 MHz, CD_3CN)

FW	401.4215	Formula	$C_{23}H_{22}F_3NO_2$						
Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	29 Jun 2017 12:19:14		
File Name	D:\BN\output\2017\06.èþ í ü\BM-1118.H_001001r			Frequency (MHz)	400.13	Nucleus	1H	Number of Transients	7
Original Points Count	16384	Points Count	65536	Pulse Sequence	zg30	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	6410.26	Temperature (degree C)	27.000						



^{1}H NMR spectrum of (3*R**,4a*R**)-**3d** (400.1 MHz, CD_3CN)

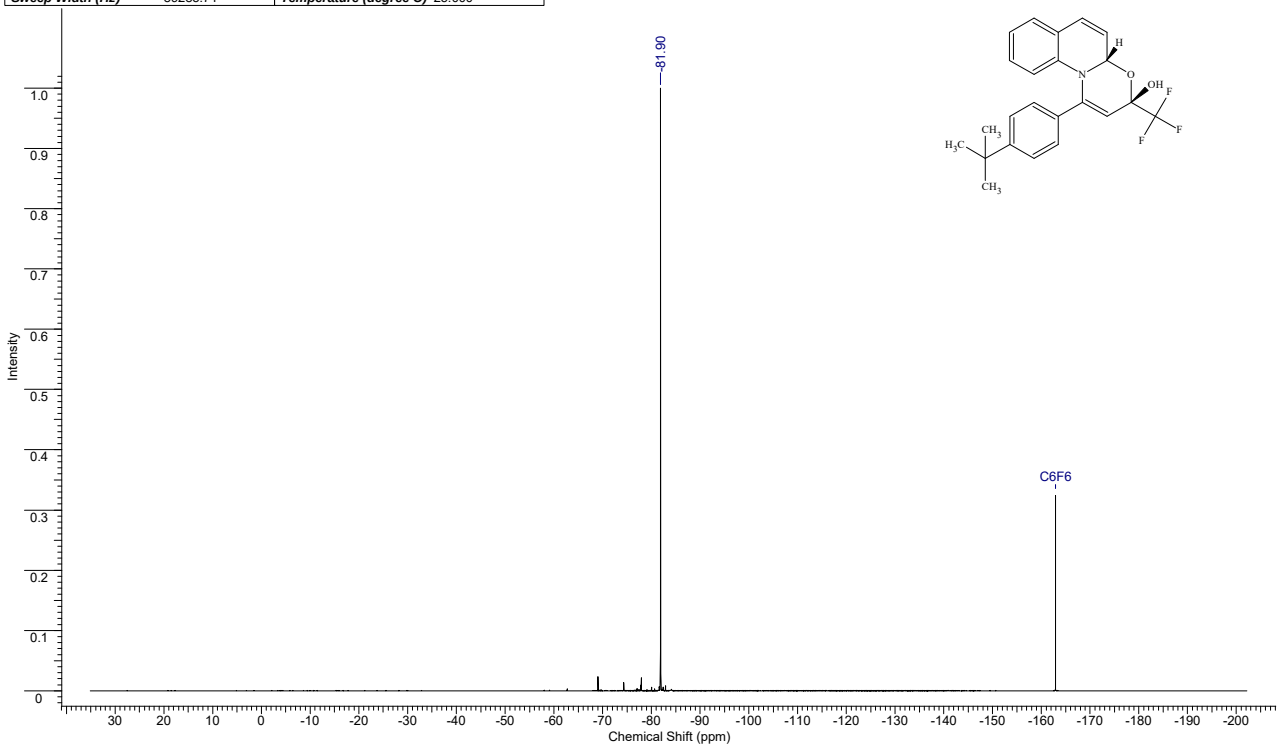
FW	401.4215	Formula	$C_{23}H_{22}F_3NO_2$				
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	29 Jun 2017 12:31:04
File Name	D:\BN\output\2017\06.èþ í ú\BM-1118.C_002001r			Frequency (MHz)	100.61	Nucleus	13C
Number of Transients	409	Original Points Count	12076	Points Count	65536	Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D			Sweep Width (Hz)	24154.59	Temperature (degree C)	27.000



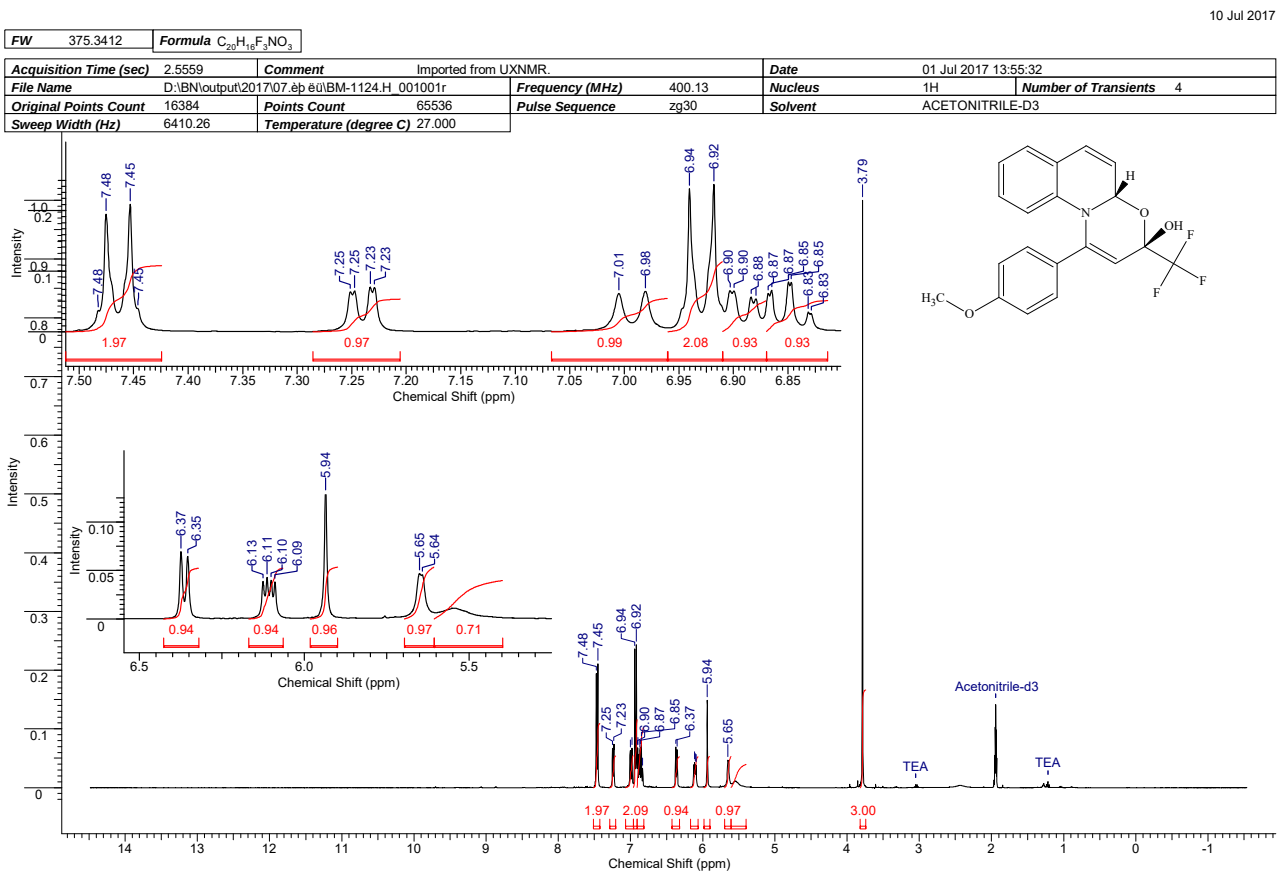
^{13}C NMR spectrum of (3*R**,4a*R**)-**3d** (100.6 MHz, CD_3CN)

10 Jul 2017

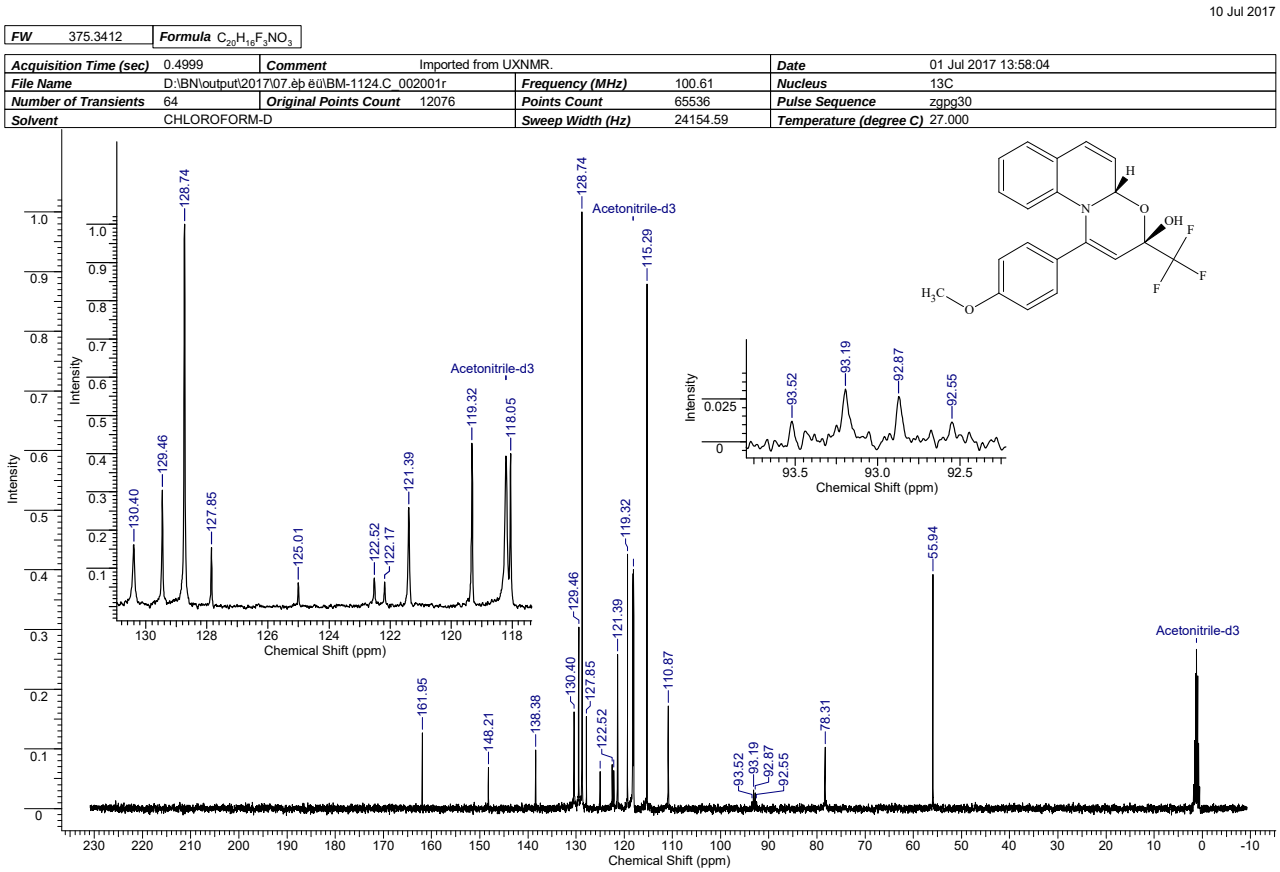
FW	401.4215	Formula	$C_{23}H_{22}F_3NO_2$				
Acquisition Time (sec)	1.0000	Date	Jun 30 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1118_20170630_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	89286
Points Count	131072	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



^{19}F NMR spectrum of (3*R**,4a*R**)-**3d** (376.3 MHz, CD_3CN)

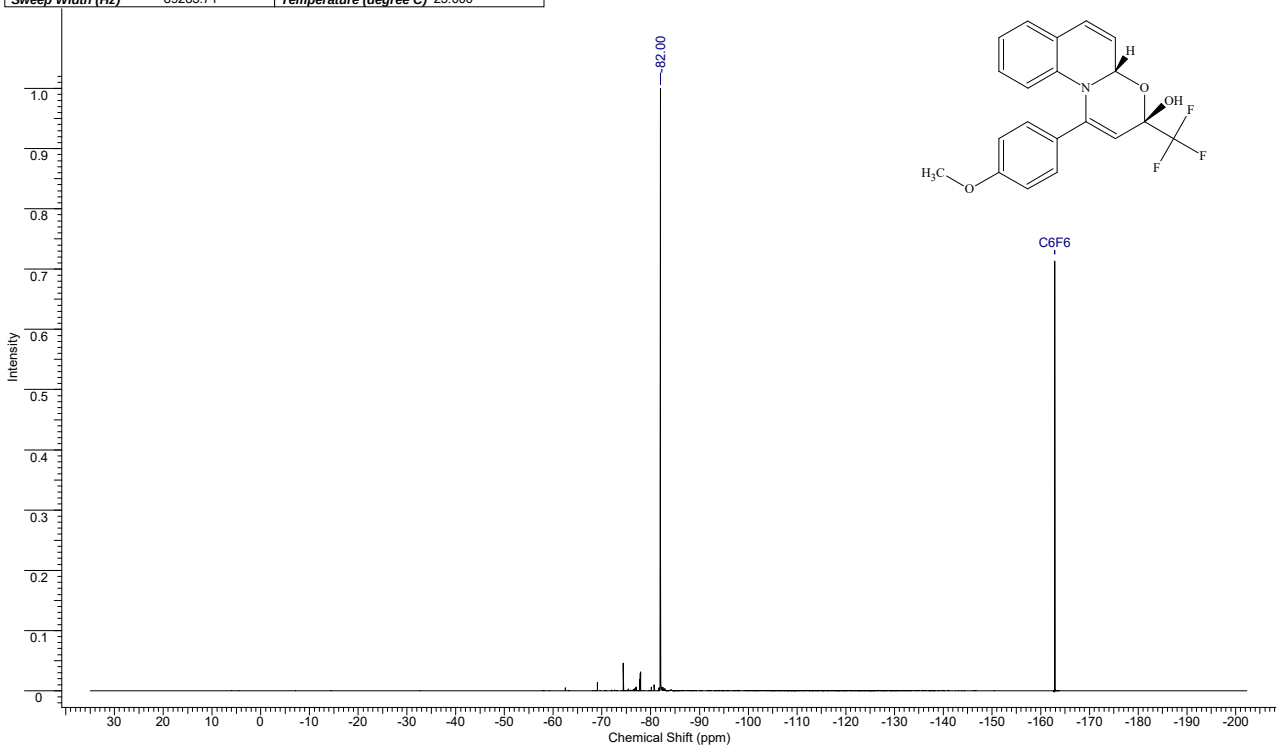


^{1}H NMR spectrum of (3*R**,4a*R**)-**3e** (400.1 MHz, CD_3CN)



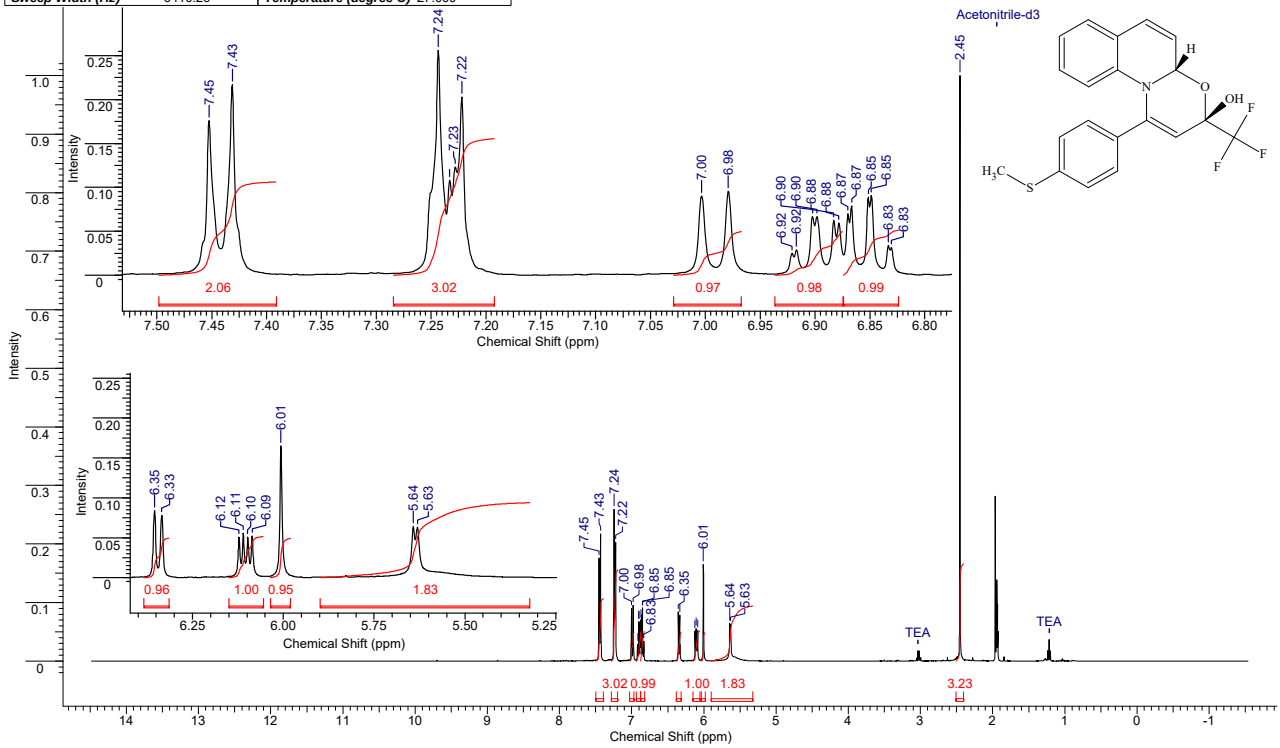
^{13}C NMR spectrum of (3*R**,4a*R**)-**3e** (100.6 MHz, CD_3CN)

FW	375.3412	Formula	$C_{20}H_{16}F_3NO_3$				
Acquisition Time (sec)	1.5000	Date	Jul 3 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1124_20170703_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	133929
Points Count	262144	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



^{19}F NMR spectrum of (3*R**,4a*R**)-**3e** (376.3 MHz, CD_3CN)

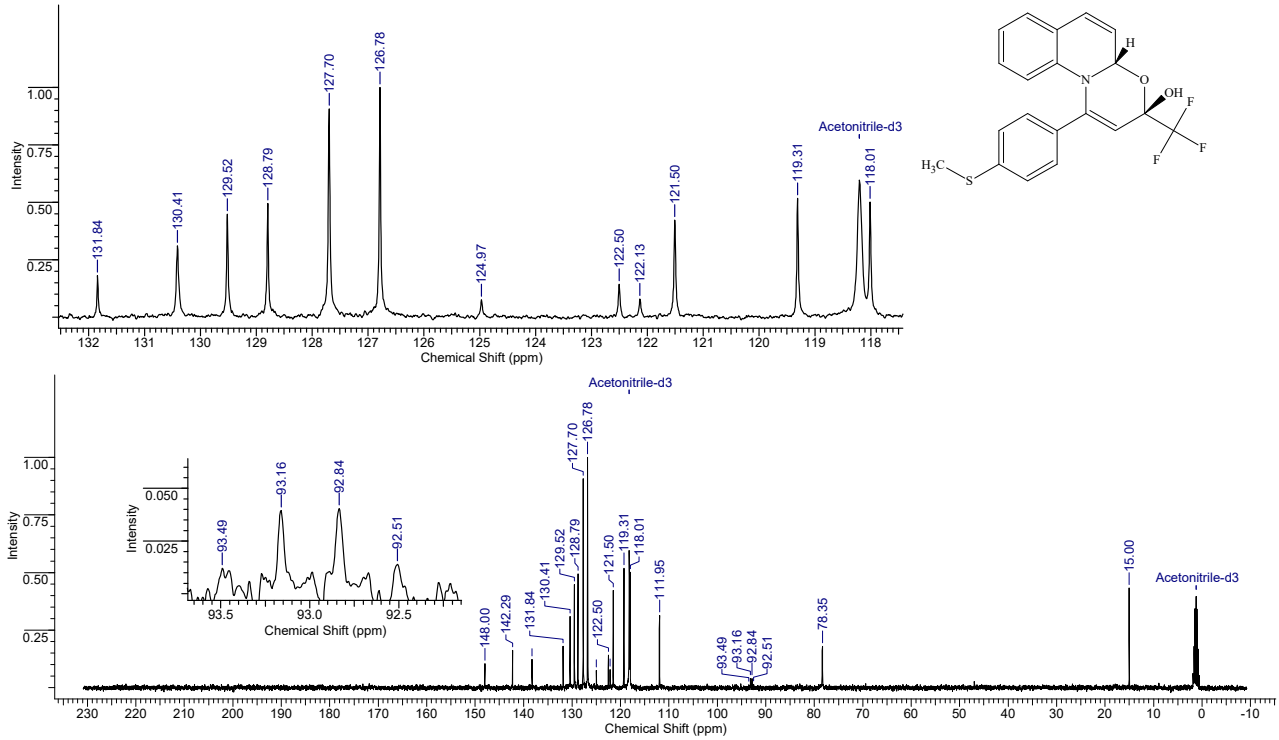
FW	391.4078	Formula	$C_{20}H_{16}F_3NO_2S$						
Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	29 Jun 2017 11:53:50		
File Name	D:\BN\output\2017\06.èþ í ú\BM-1126.H_001001r			Frequency (MHz)	400.13	Nucleus	1H	Number of Transients	4
Original Points Count	16384	Points Count	65536	Pulse Sequence	zg30	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	6410.26	Temperature (degree C)	27.000						



^{1}H NMR spectrum of (3*R**,4a*R**)-**3f** (400.1 MHz, CD_3CN)

10 Jul 2017

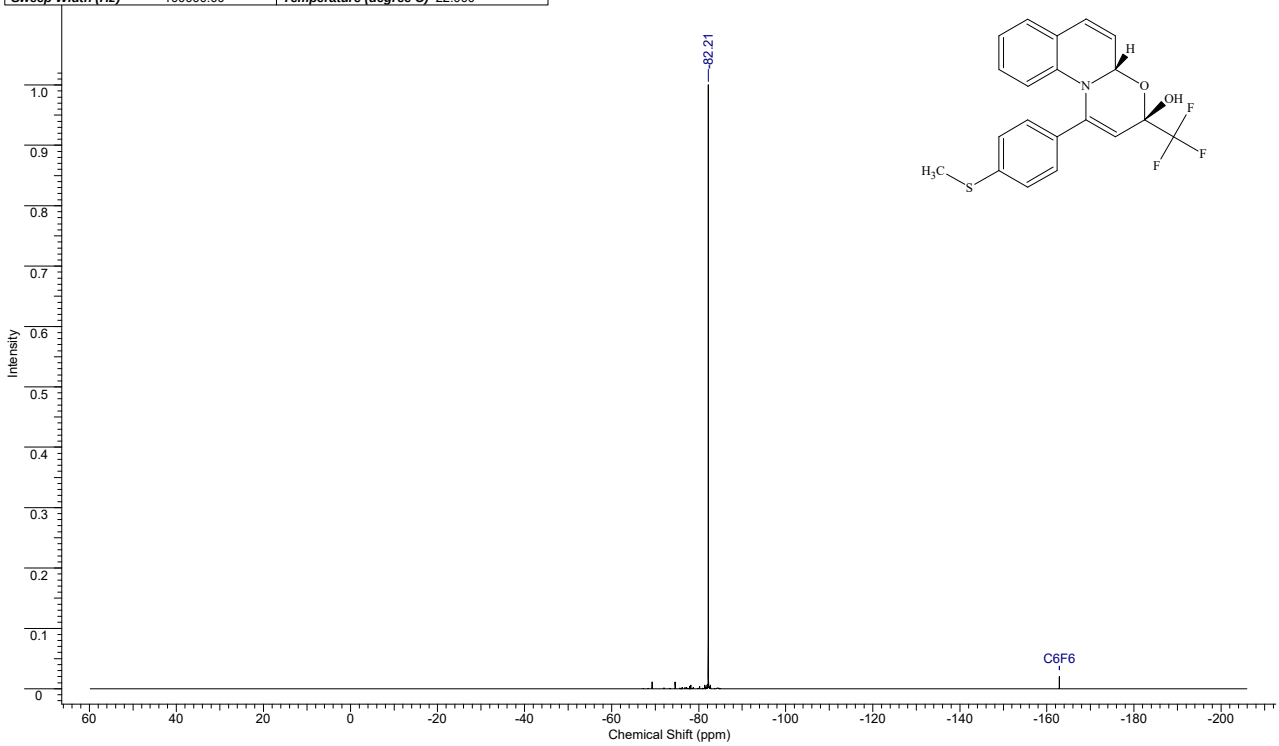
FW	391.4078	Formula	$C_{20}H_{16}F_3NO_2S$				
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	29 Jun 2017 11:55:58
File Name	D:\BN\output\2017\06.èþ í ú\BM-1126.C_002001r			Frequency (MHz)	100.61	Nucleus	13C
Number of Transients	45	Original Points Count	12076	Points Count	65536	Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D			Sweep Width (Hz)	24154.59	Temperature (degree C)	27.000



^{13}C NMR spectrum of (3*R**,4a*R**)-**3f** (100.6 MHz, CD_3CN)

10 Jul 2017

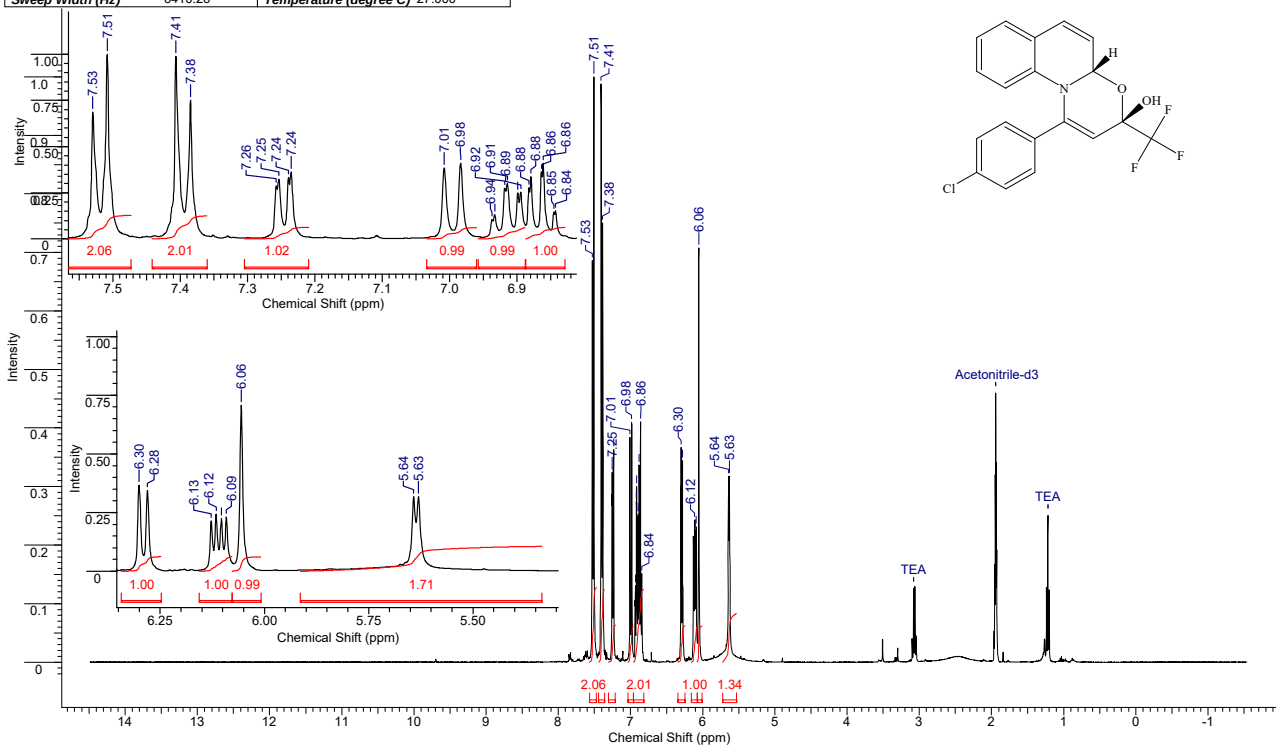
FW	391.4078	Formula	$C_{20}H_{16}F_3NO_2S$				
Acquisition Time (sec)	2.6214	Date	Jun 29 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1126-F_20170629_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	8	Original Points Count	262144
Points Count	262144	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	100000.00	Temperature (degree C)	22.000				



^{19}F NMR spectrum of (3*R**,4a*R**)-**3f** (376.3 MHz, CD_3CN)

FW	379.7600	**Formula**	$C_{19}H_{13}ClF_3NO_2$

Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.			**Date**	01 Jul 2017 13:43:36
File Name	D:\BN\output\2017\07.èþ ëü\BM-1123.H_001001r			**Frequency (MHz)**	400.13	**Nucleus**	1H	**Number of Transients**	4
Original Points Count	16384	**Points Count**	65536	**Pulse Sequence**	zg30	**Solvent**	ACETONITRILE-D3		
Sweep Width (Hz)	6410.26	**Temperature (degree C)**	27.000						

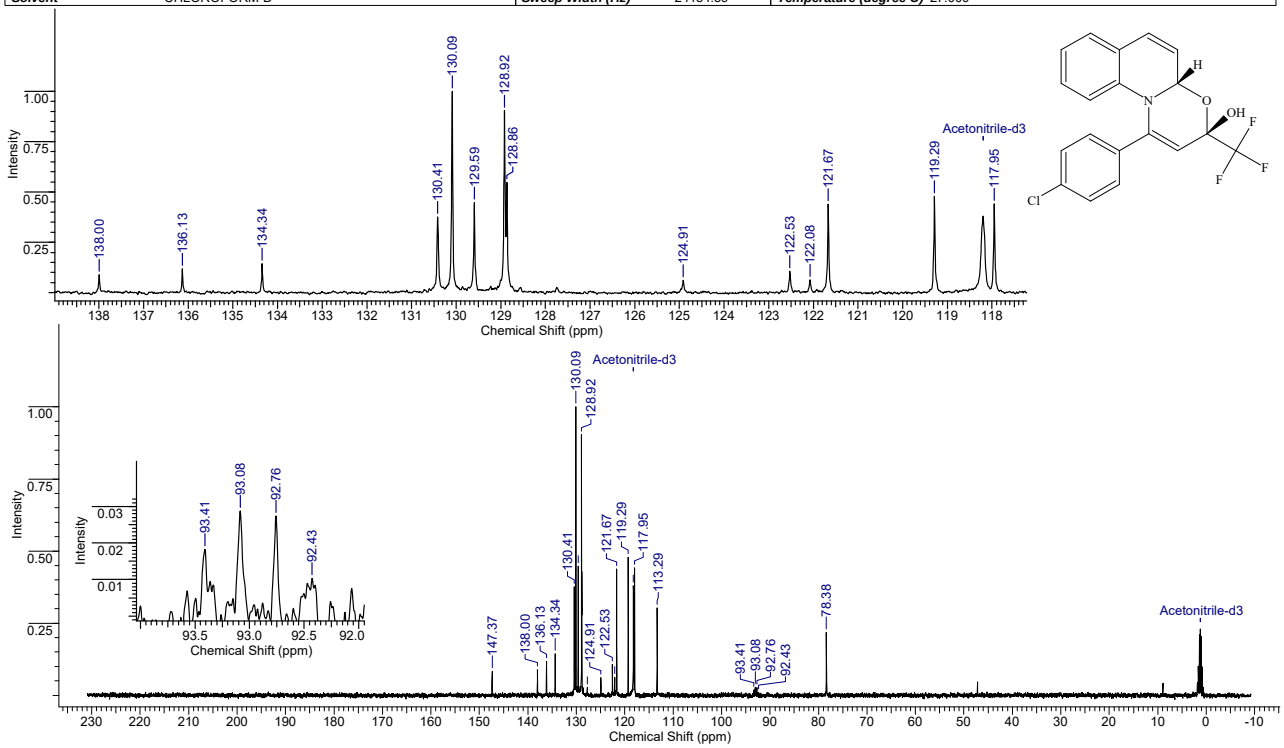


^{1}H NMR spectrum of (3*R**,4a*R**)-**3g** (400.1 MHz, CD_3CN)

10 Jul 2017

FW	379.7600	**Formula**	$C_{19}H_{13}ClF_3NO_2$

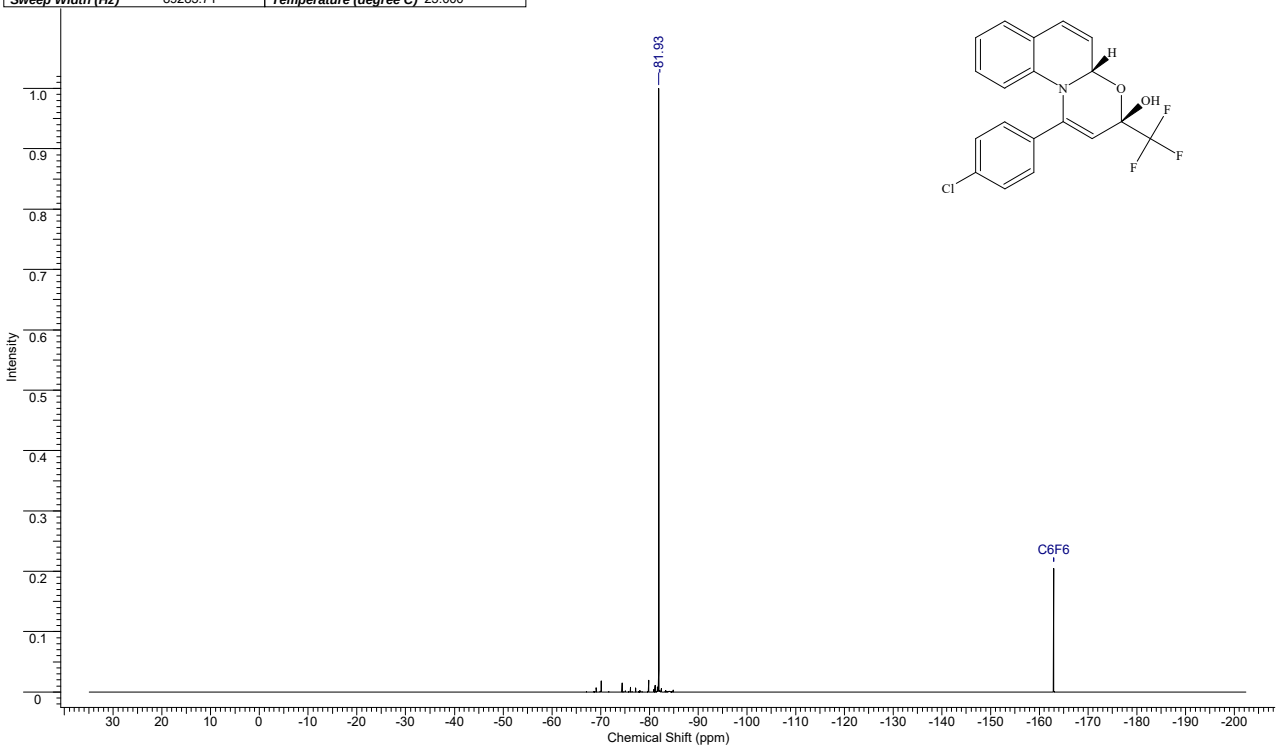
Acquisition Time (sec)	0.4999	**Comment**	Imported from UXNMR.			**Date**	01 Jul 2017 13:47:44
File Name	D:\BN\output\2017\07.èþ ëü\BM-1123.C_002001r			**Frequency (MHz)**	100.61	**Nucleus**	13C
Number of Transients	64	**Original Points Count**	12076	**Points Count**	65536	**Pulse Sequence**	zgpg30
Solvent	CHLOROFORM-D			**Sweep Width (Hz)**	24154.59	**Temperature (degree C)**	27.000



^{13}C NMR spectrum of (3*R**,4a*R**)-**3g** (100.6 MHz, CD_3CN)

10 Jul 2017

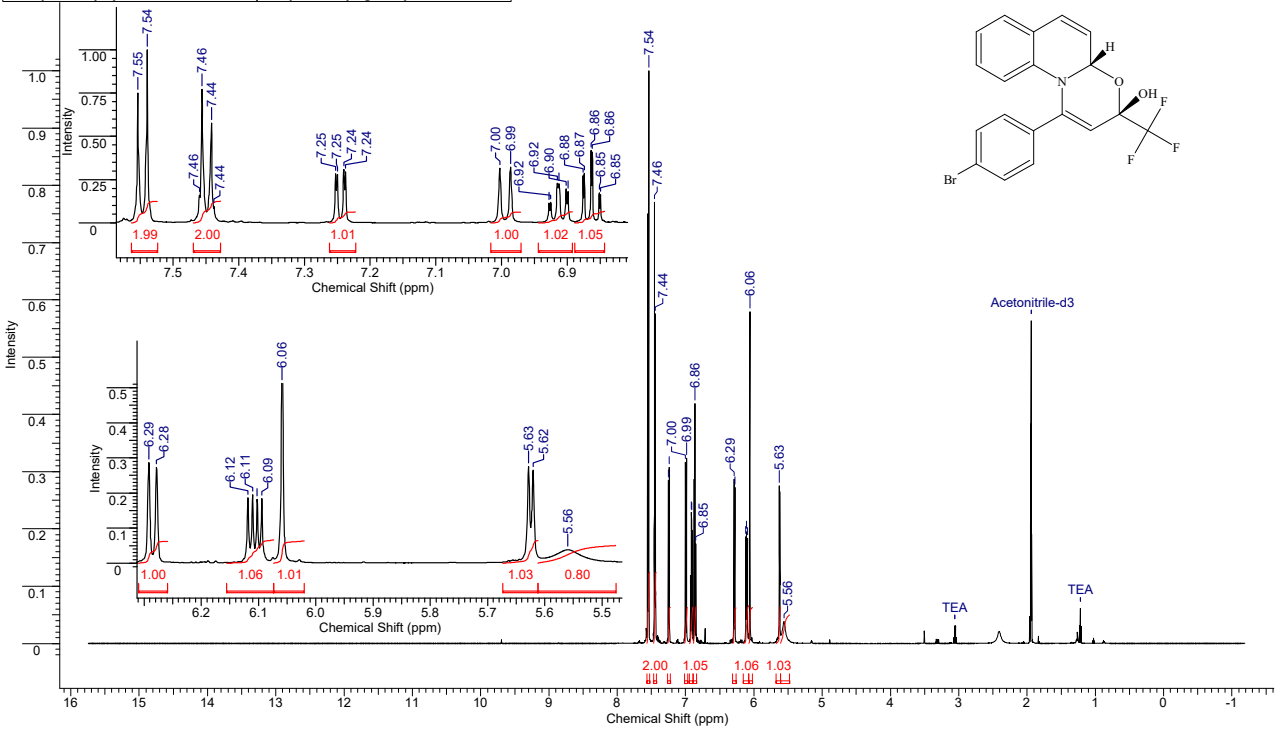
FW	379.7600	**Formula**	$C_{19}H_{13}ClF_3NO_2$		
Acquisition Time (sec)	1.0000	**Date**	Jun 30 2017	**File Name**	D:\BN\output\F19\F_2017\2017.06.30\BM-1123_20170630_01\FLUORINE_01
Frequency (MHz)	376.31	**Nucleus**	19F	**Number of Transients**	16
Points Count	131072	**Pulse Sequence**	s2pul	**Original Points Count**	89286
Sweep Width (Hz)	89285.71	**Temperature (degree C)**	25.000	**Solvent**	ACETONITRILE-D3



^{19}F NMR spectrum of (3*R**,4a*R**)-**3g** (376.3 MHz, CD_3CN)

8 Jul 2017

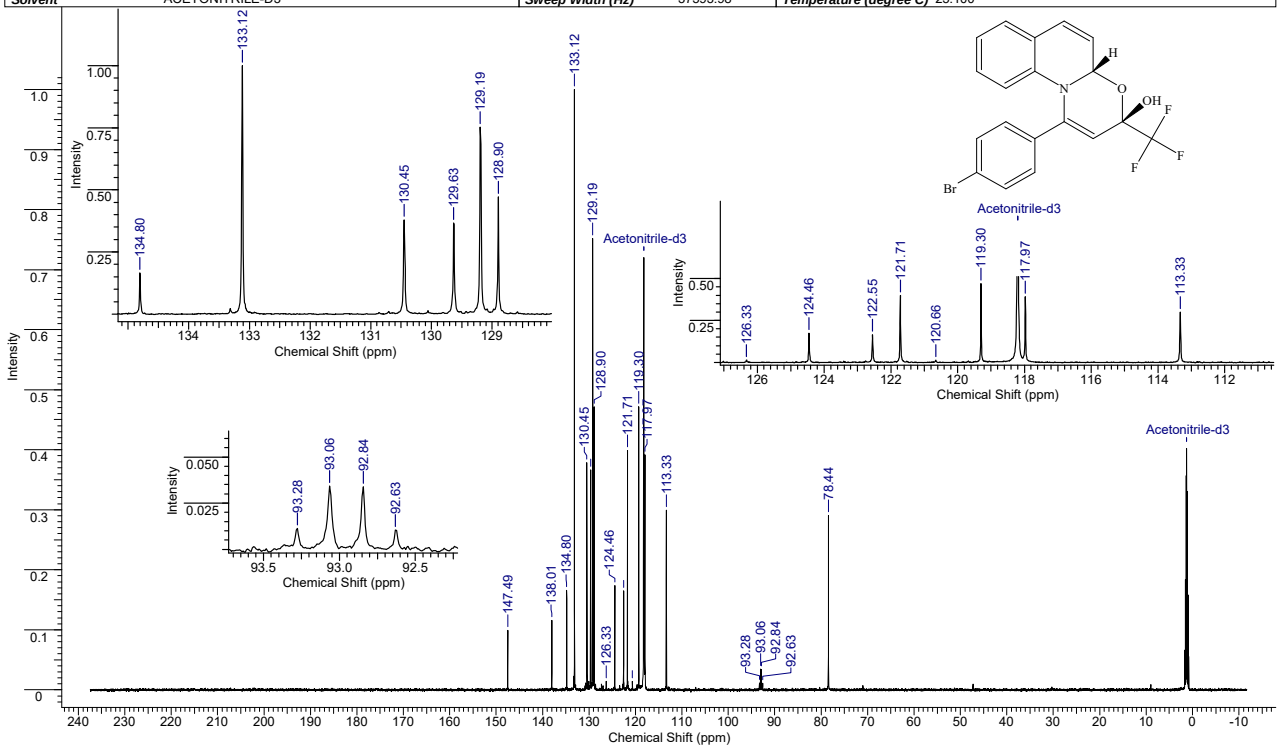
FW	424.2113	**Formula**	$C_{19}H_{13}BrF_3NO_2$		
Acquisition Time (sec)	3.5479	**Date**	03 Jul 2017 11:28:52	**File Name**	D:\BN\output\2017\07.èþ ëü\BM-1127 (1)\BM-1127_001001r
Frequency (MHz)	600.13	**Nucleus**	1H	**Number of Transients**	8
Points Count	131072	**Pulse Sequence**	zg30	**Original Points Count**	36056
Sweep Width (Hz)	10162.60	**Temperature (degree C)**	20.400	**Solvent**	ACETONITRILE-D3



^{1}H NMR spectrum of (3*R**,4a*R**)-**3h** (400.1 MHz, CD_3CN)

8 Jul 2017

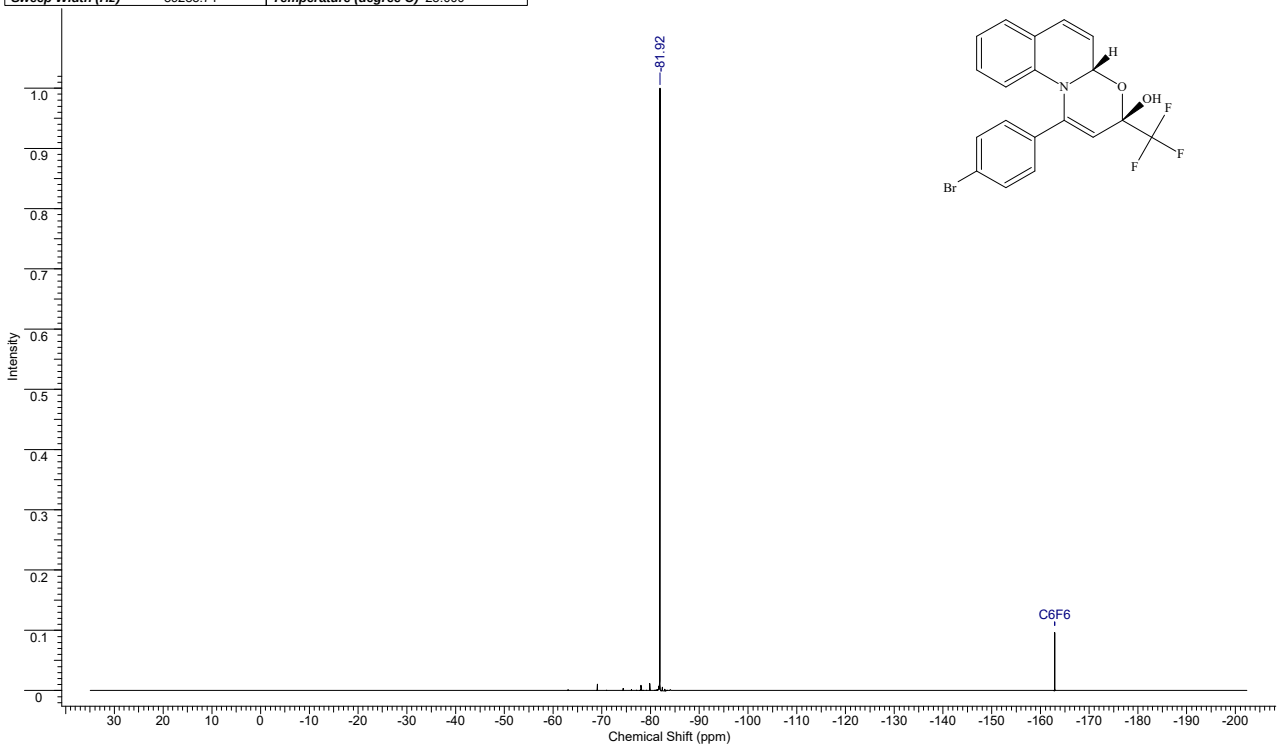
FW	424.2113	Formula	$C_{19}H_{13}BrF_3NO_2$				
Acquisition Time (sec)	0.4783	Date	03 Jul 2017 11:24:26				
File Name	D:\BN\output\2017\07.èþ ëü\BM-1127 (1)\BM-1127_002001r			Frequency (MHz)	150.90	Nucleus	13C
Number of Transients	350	Original Points Count	17983	Points Count	32768	Pulse Sequence	zgpg30
Solvent	ACETONITRILE-D3			Sweep Width (Hz)	37593.98	Temperature (degree C)	25.100



^{13}C NMR spectrum of (3*R**,4a*R**)-**3h** (100.6 MHz, CD_3CN)

8 Jul 2017

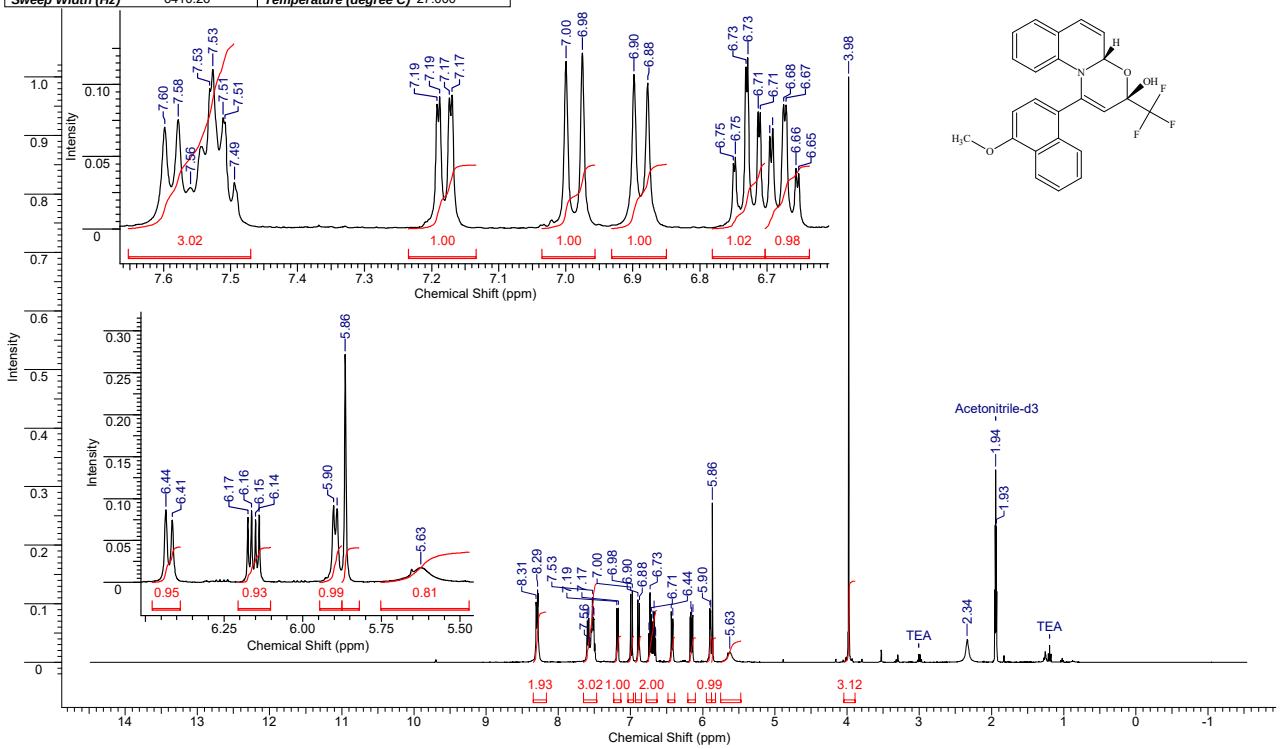
FW	424.2113	Formula	$C_{19}H_{13}BrF_3NO_2$				
Acquisition Time (sec)	0.7340	Date	Jul 4 2017	File Name	D:\BN\output\F19\F_2017\2017.07.04\bm1127-f_20170704_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	1000	Original Points Count	65536
Points Count	65536	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



^{19}F NMR spectrum of (3*R**,4a*R**)-**3h** (376.3 MHz, CD_3CN)

10 Jul 2017

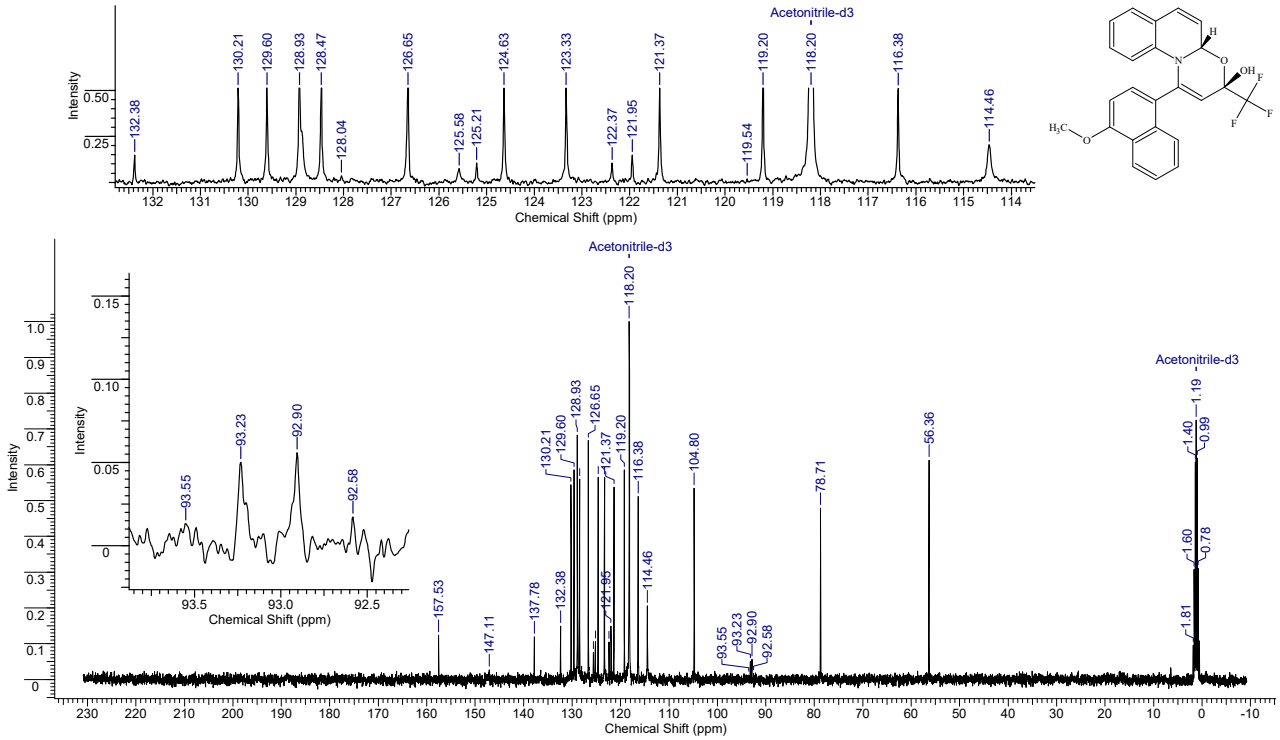
FW	425.3999	Formula	$C_{24}H_{18}F_3NO_3$				
Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	01 Jul 2017 13:50:12
File Name	D:\BN\output\2017\07.èþ ëü\BM-1119.H_001001r			Frequency (MHz)	400.13	Nucleus	1H
Original Points Count	16384	Points Count	65536	Pulse Sequence	zg30	Solvent	ACETONITRILE-D3
Sweep Width (Hz)	6410.26	Temperature (degree C)	27.000				



^{1}H NMR spectrum of (3*R**,4a*R**)-**3i** (400.1 MHz, CD_3CN)

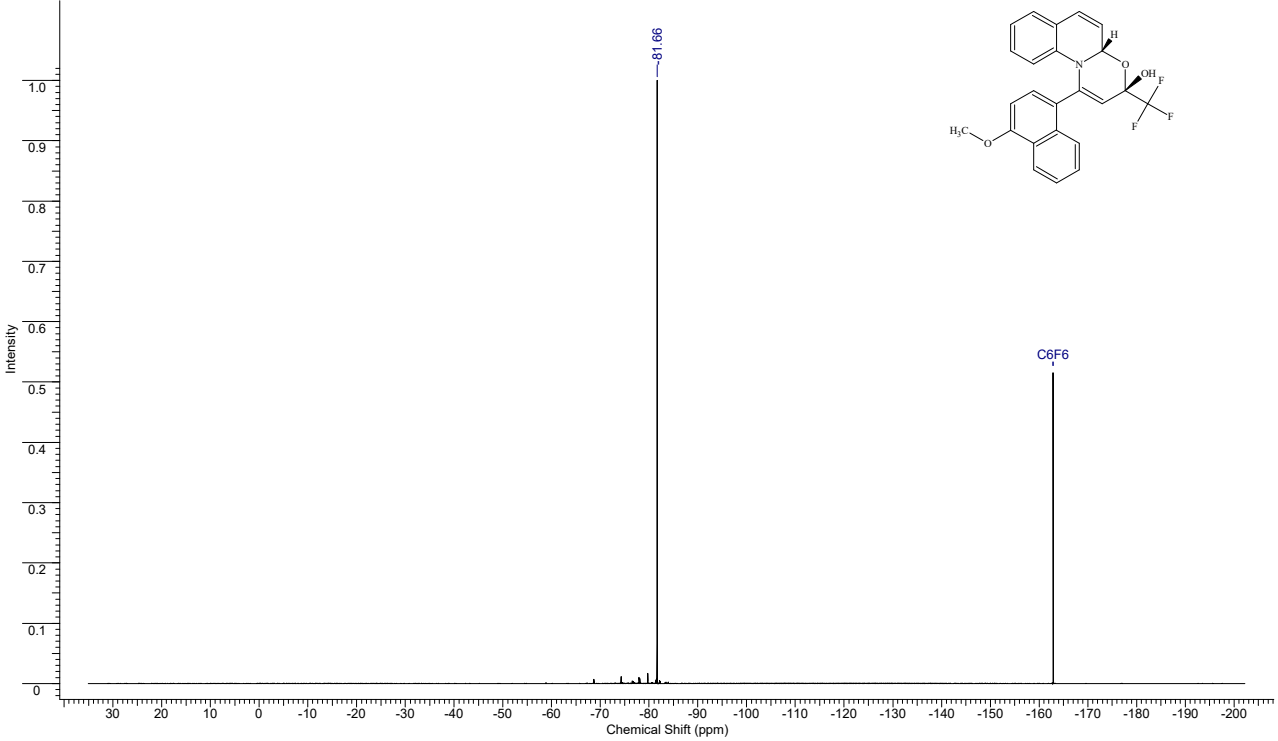
8 Sep 2017

FW	425.3999	Formula	$C_{24}H_{18}F_3NO_3$				
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	01 Jul 2017 13:53:14
File Name	D:\BN\output\2017\07.èþ ëü\BM-1119.C_002001r			Frequency (MHz)	100.61	Nucleus	13C
Number of Transients	82	Original Points Count	12076	Points Count	65536	Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D			Sweep Width (Hz)	24154.59	Temperature (degree C)	27.000

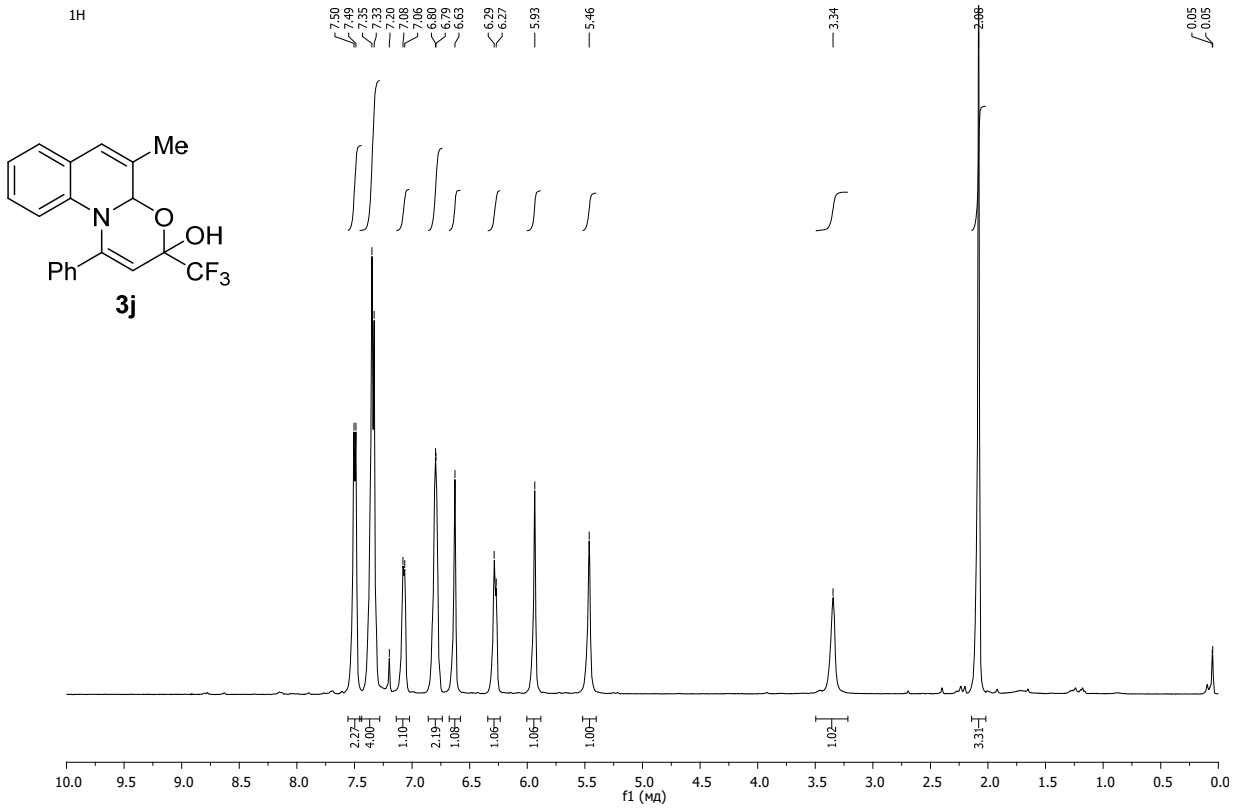


^{13}C NMR spectrum of (3*R**,4a*R**)-**3i** (100.6 MHz, CD_3CN)

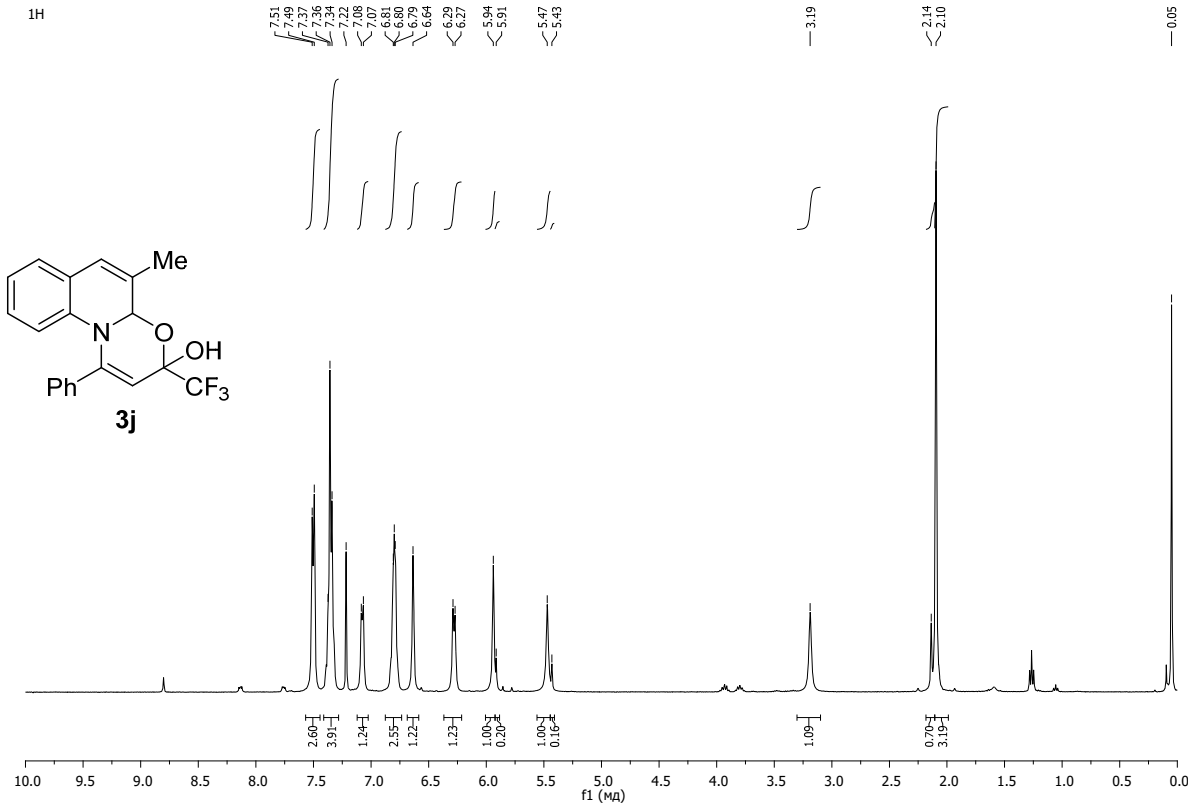
FW	425.3999	Formula	$C_{24}H_{18}F_3NO_3$				
Acquisition Time (sec)	1.5000	Date	Jul 3 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1119_20170703_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	133929
Points Count	262144	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



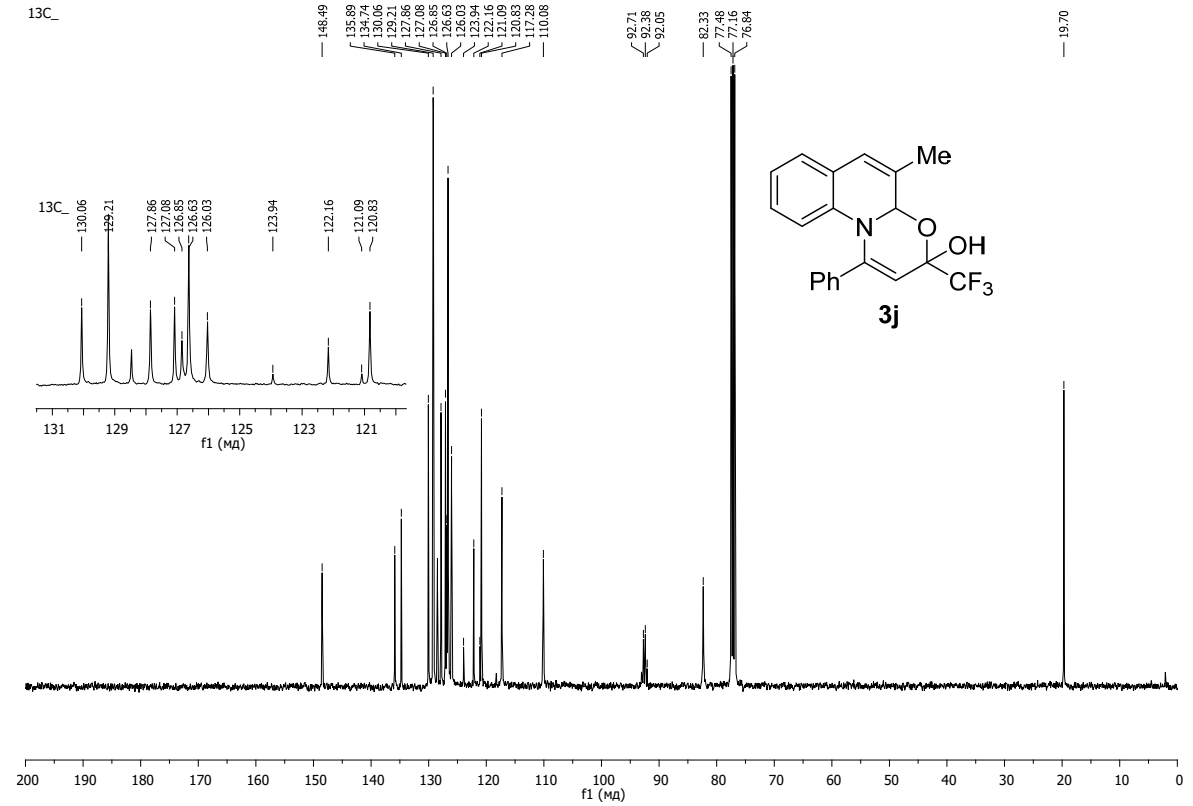
^{19}F NMR spectrum of (3*R**,4a*R**)-**3i** (376.3 MHz, CD_3CN)



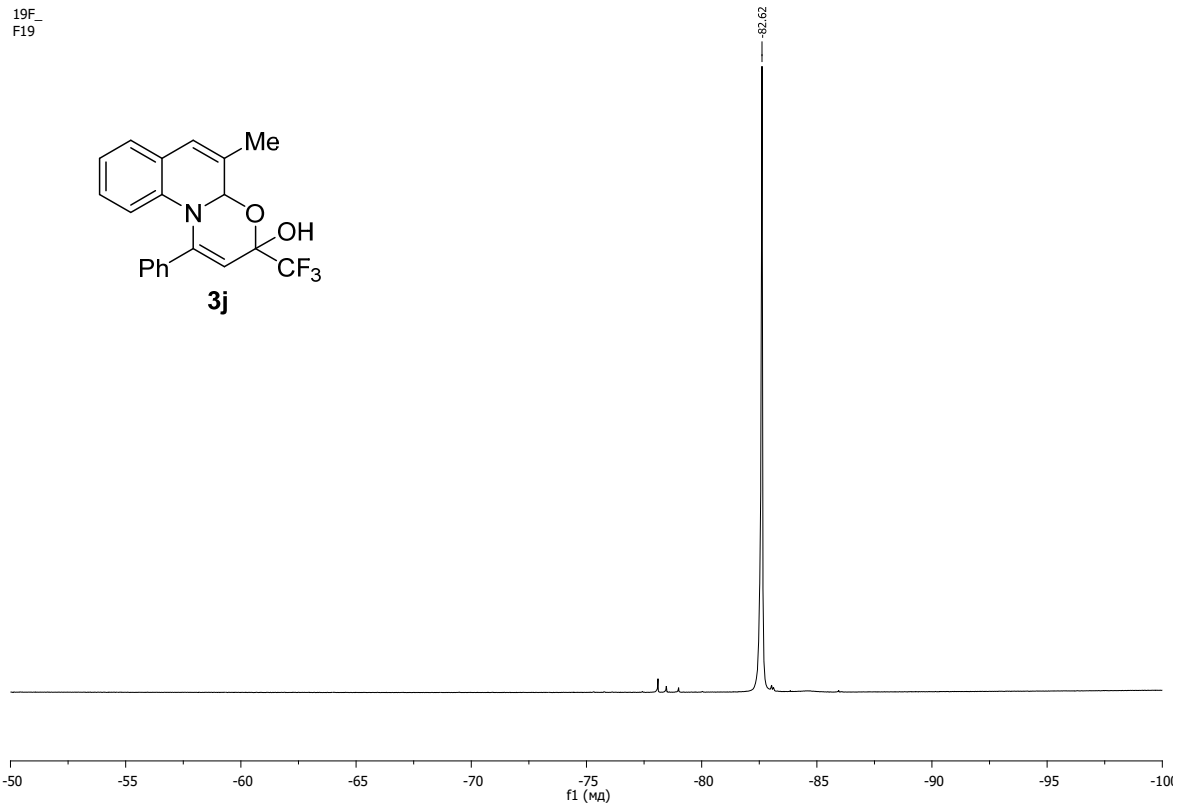
^{1}H NMR spectrum of (3*R**,4a*R**)-**3j** (400.1 MHz, $CDCl_3$)



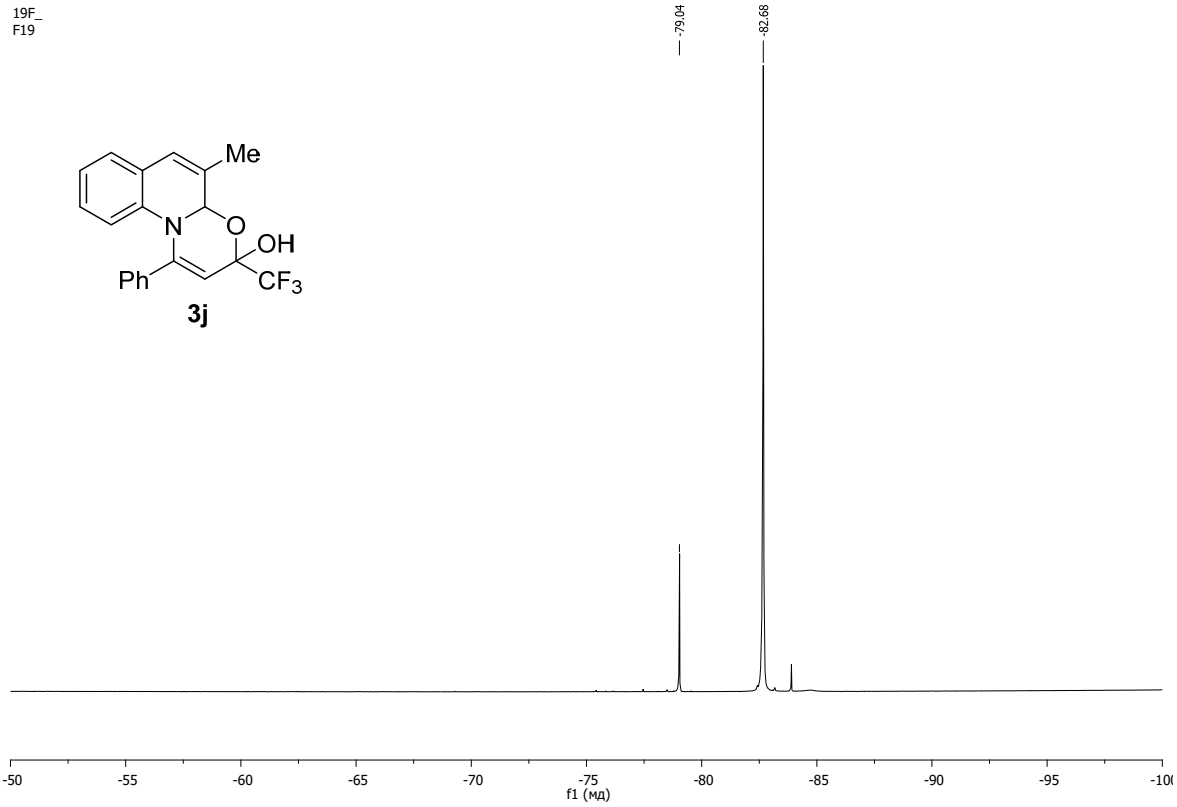
^{1}H NMR spectrum of **3j** (400.1 MHz, $CDCl_3$)



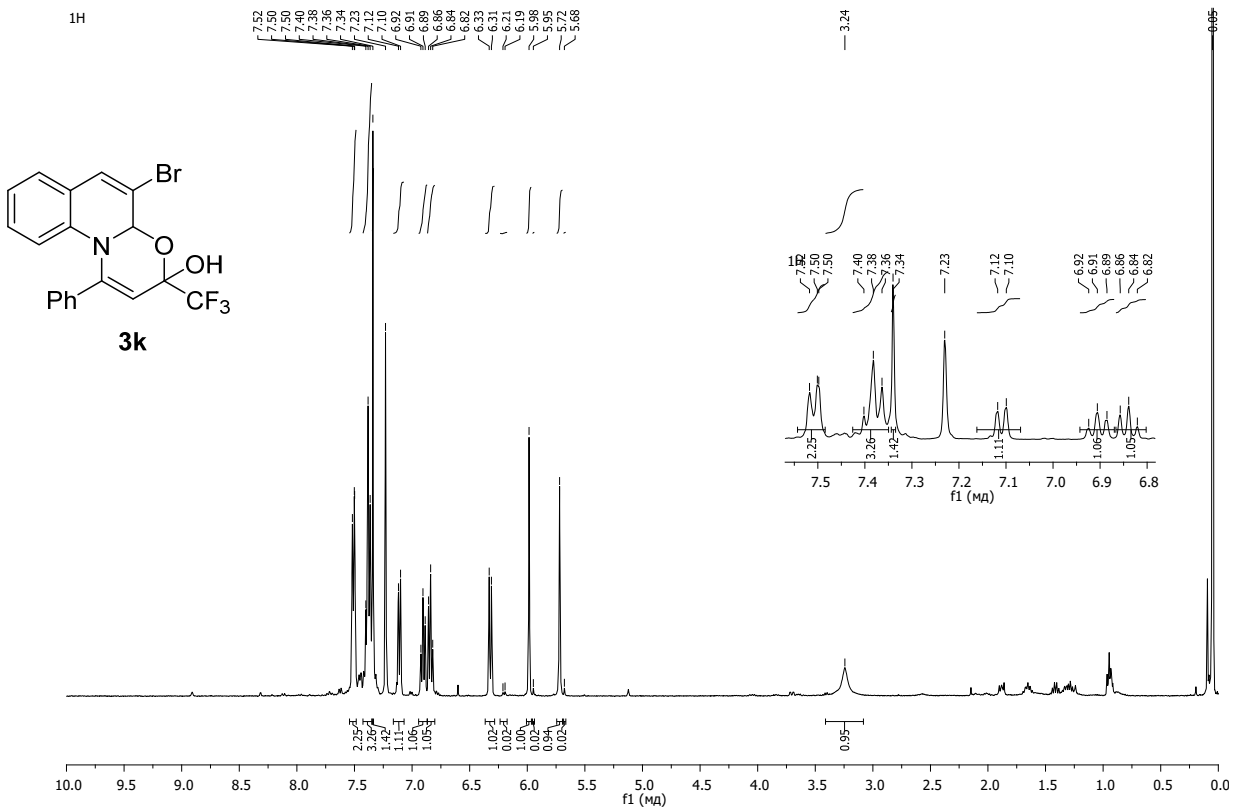
^{13}C NMR spectrum of (3*R**,4a*R**)-**3j** (100.6 MHz, $CDCl_3$)



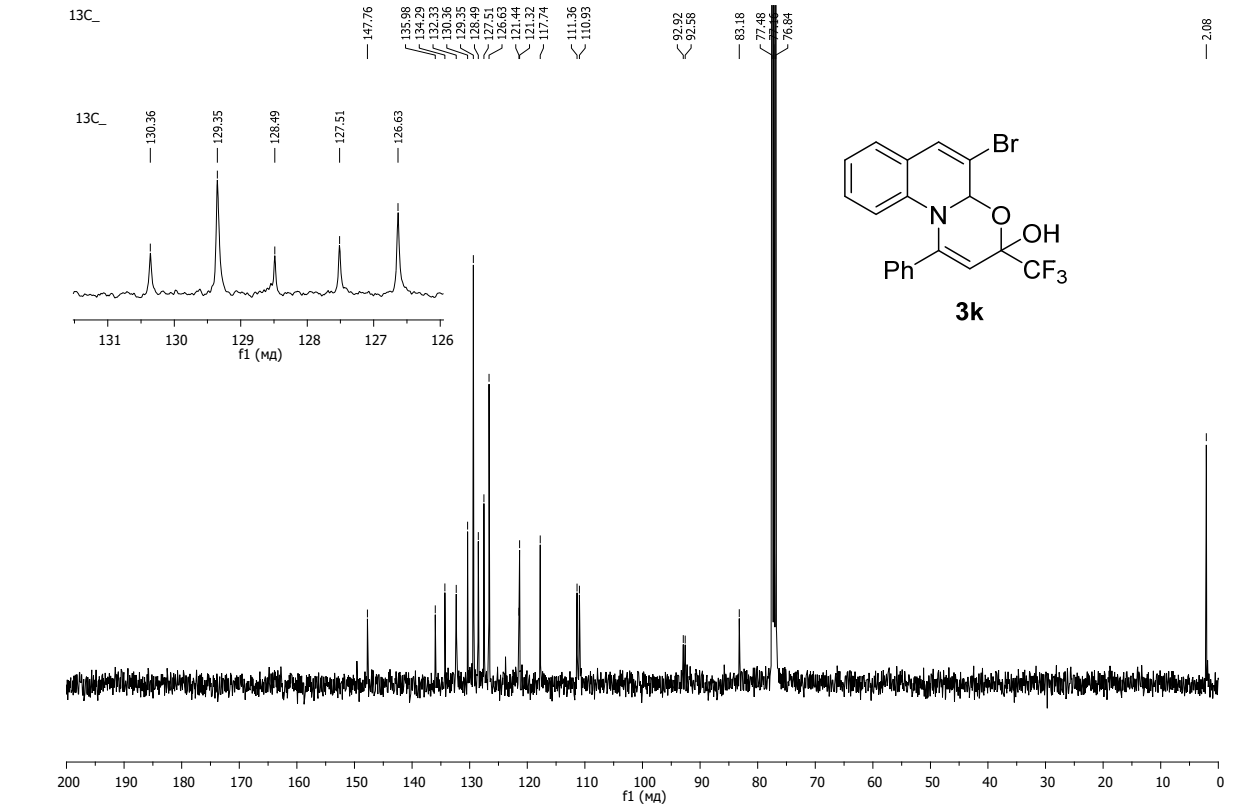
^{19}F NMR spectrum of (3*R**,4a*R**)-**3j** (376.5 MHz, $CDCl_3$)



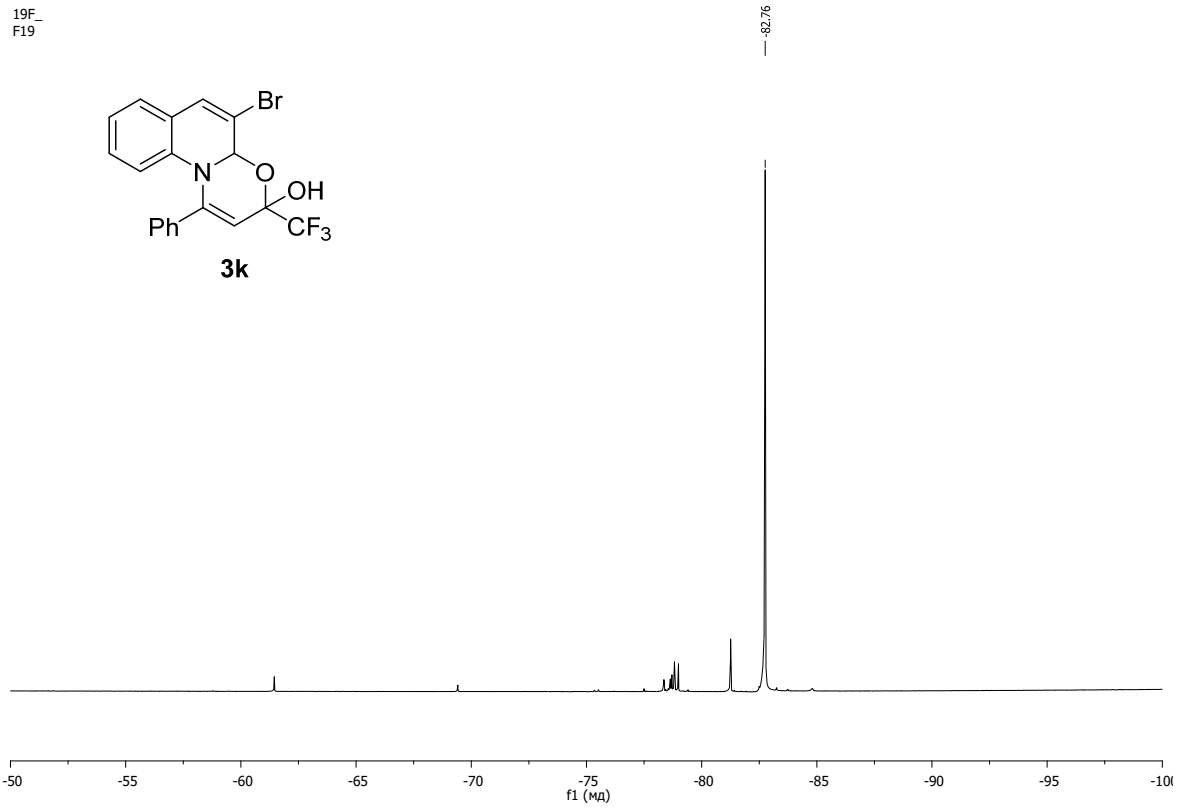
^{19}F NMR spectrum of **3j** (376.5 MHz, $CDCl_3$)



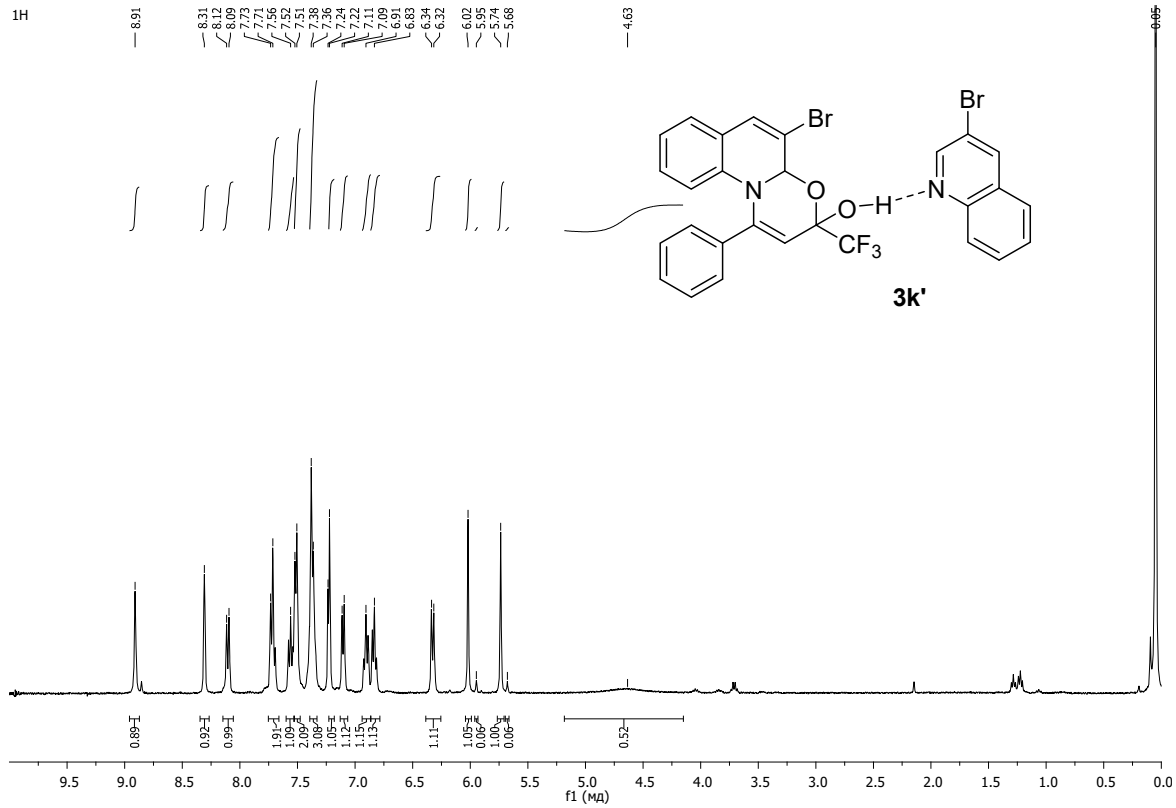
^{1}H NMR spectrum of (3*R**,4a*R**)-**3k** (400.1 MHz, $CDCl_3$)



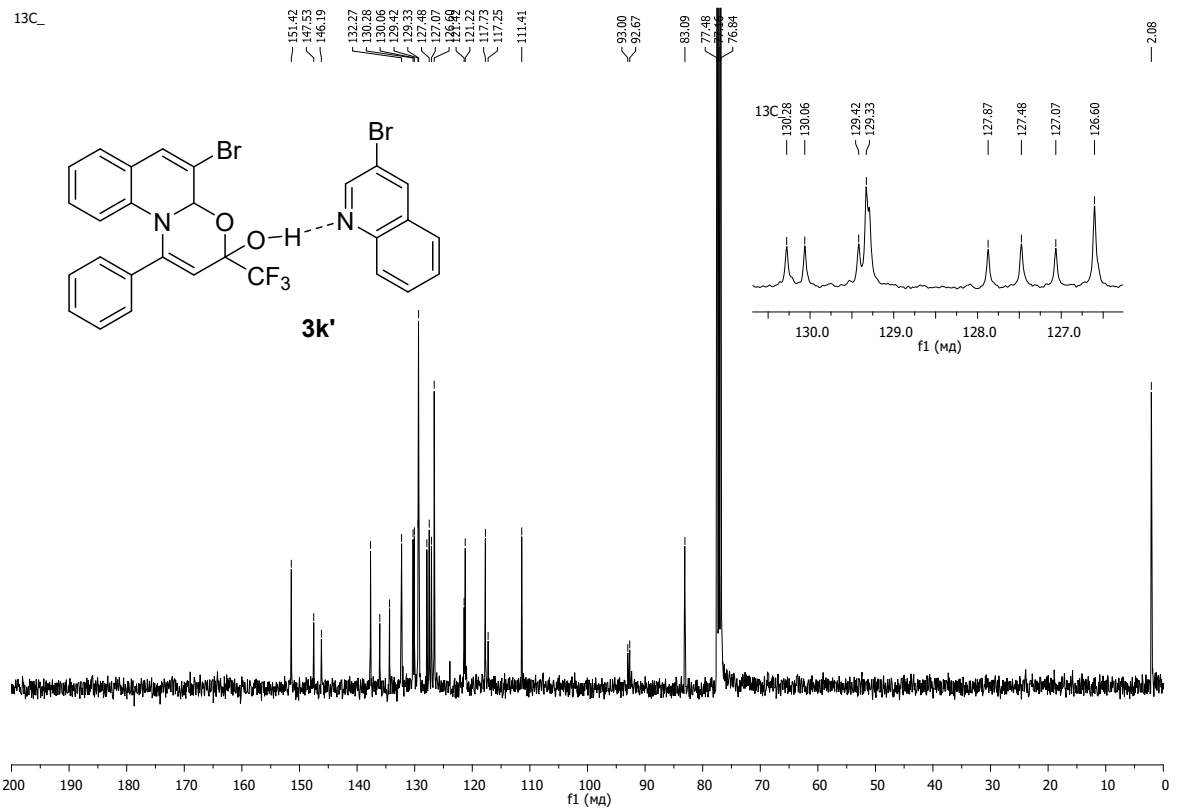
^{13}C NMR spectrum of (3*R**,4a*R**)-**3k** (100.6 MHz, $CDCl_3$)



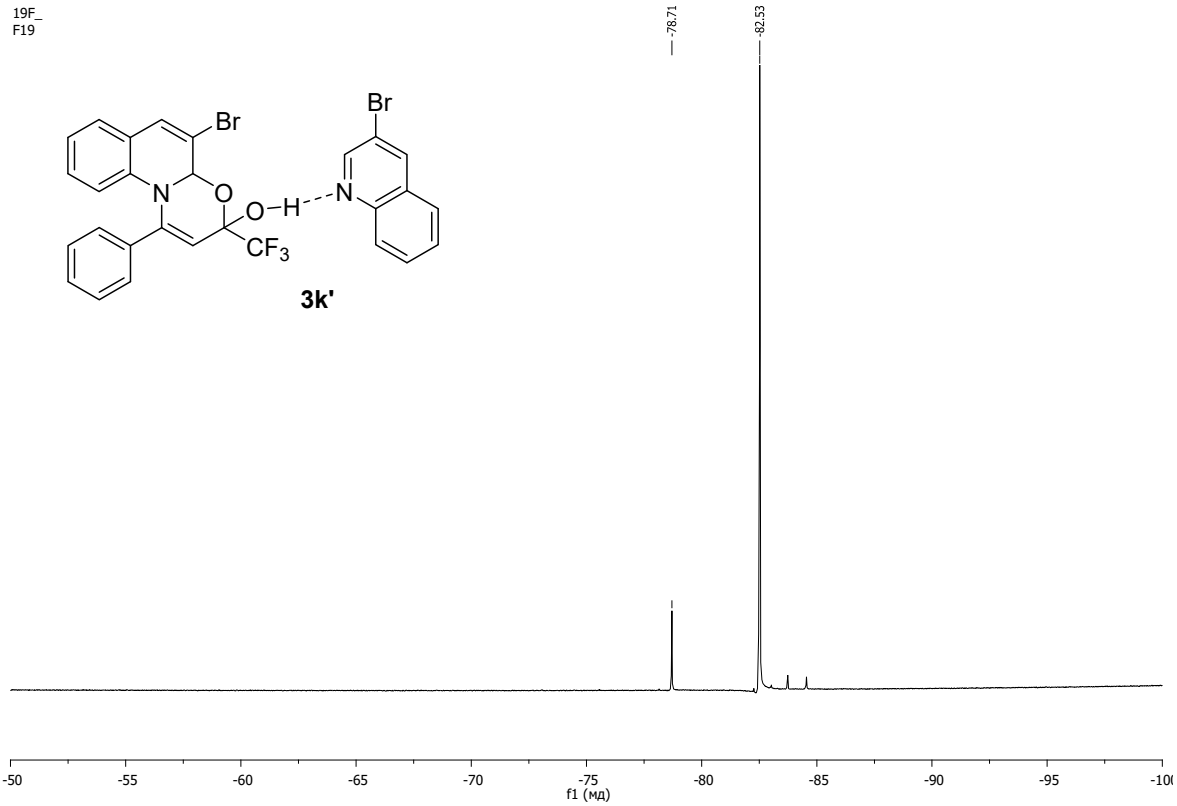
^{19}F NMR spectrum of (3*R**,4a*R**)-**3k** (376.5 MHz, $CDCl_3$)



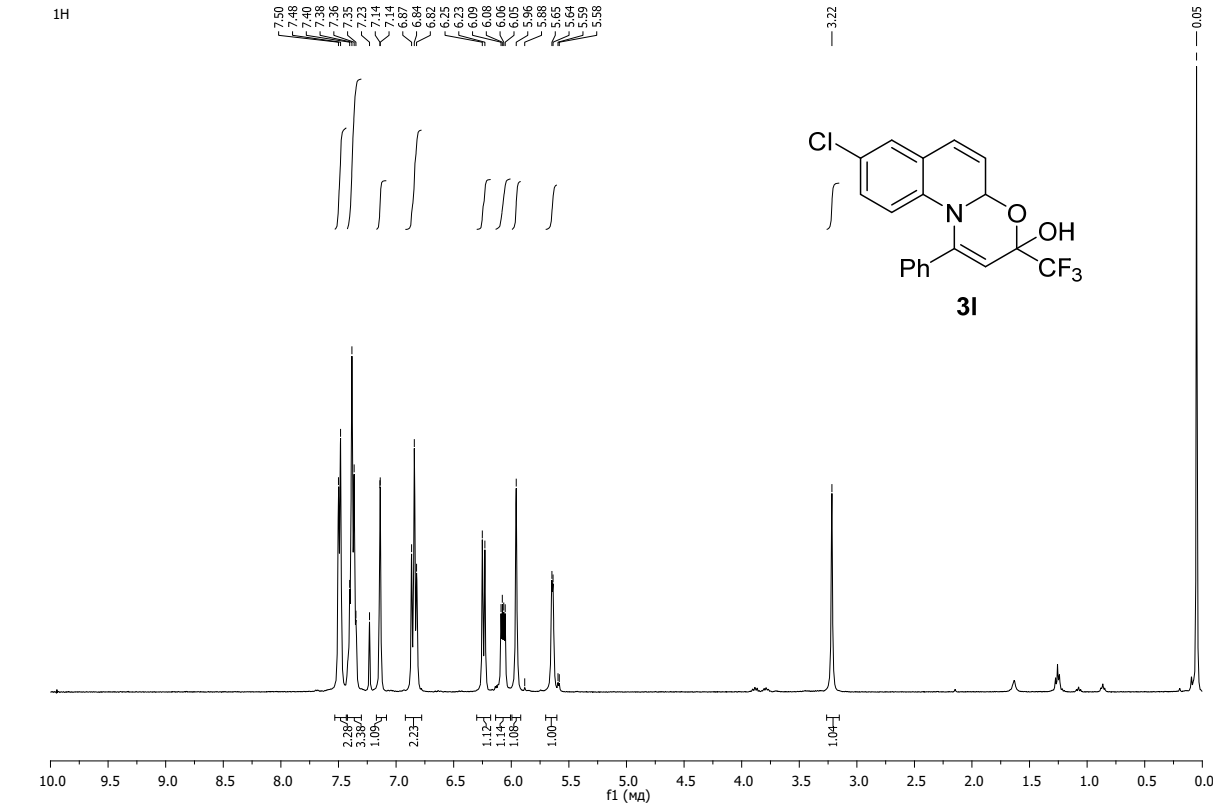
^{1}H NMR spectrum of (3*R**,4a*R**)-**3k'** (400.1 MHz, $CDCl_3$)



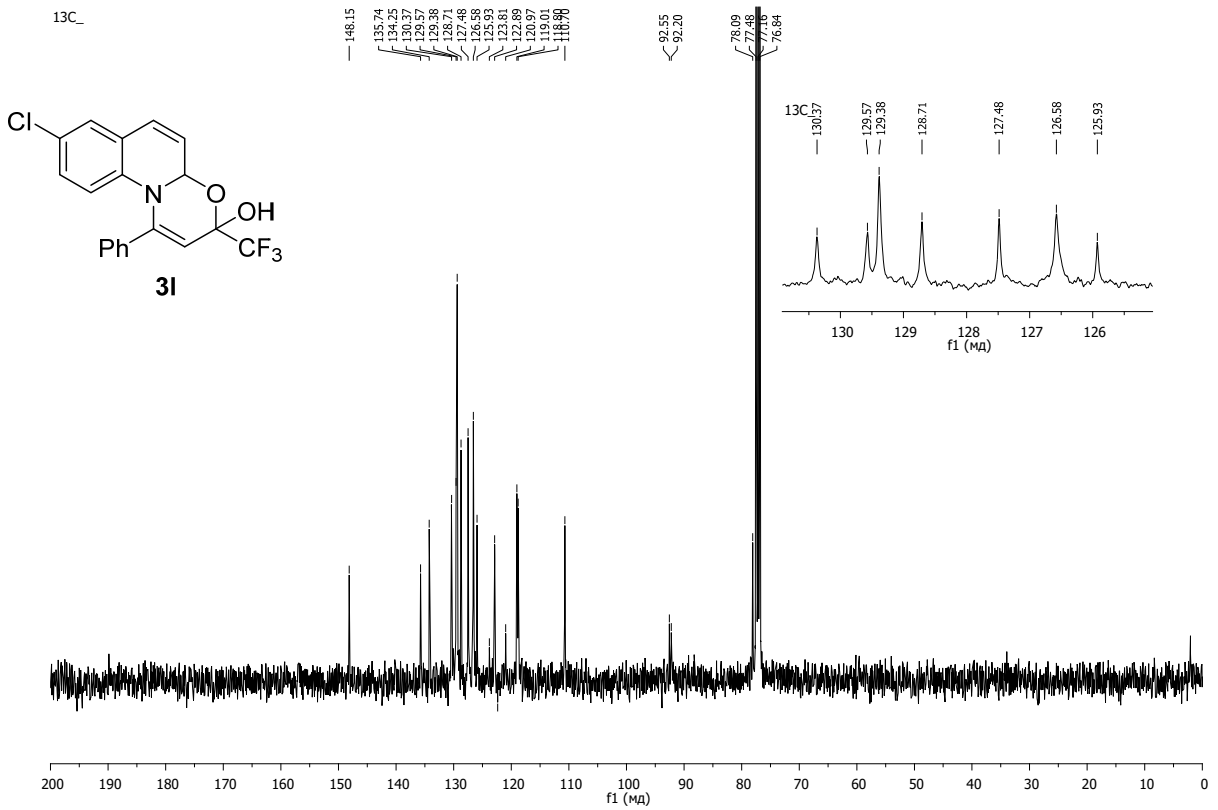
^{13}C NMR spectrum of (3*R**,4a*R**)-**3k'** (100.6 MHz, $CDCl_3$)



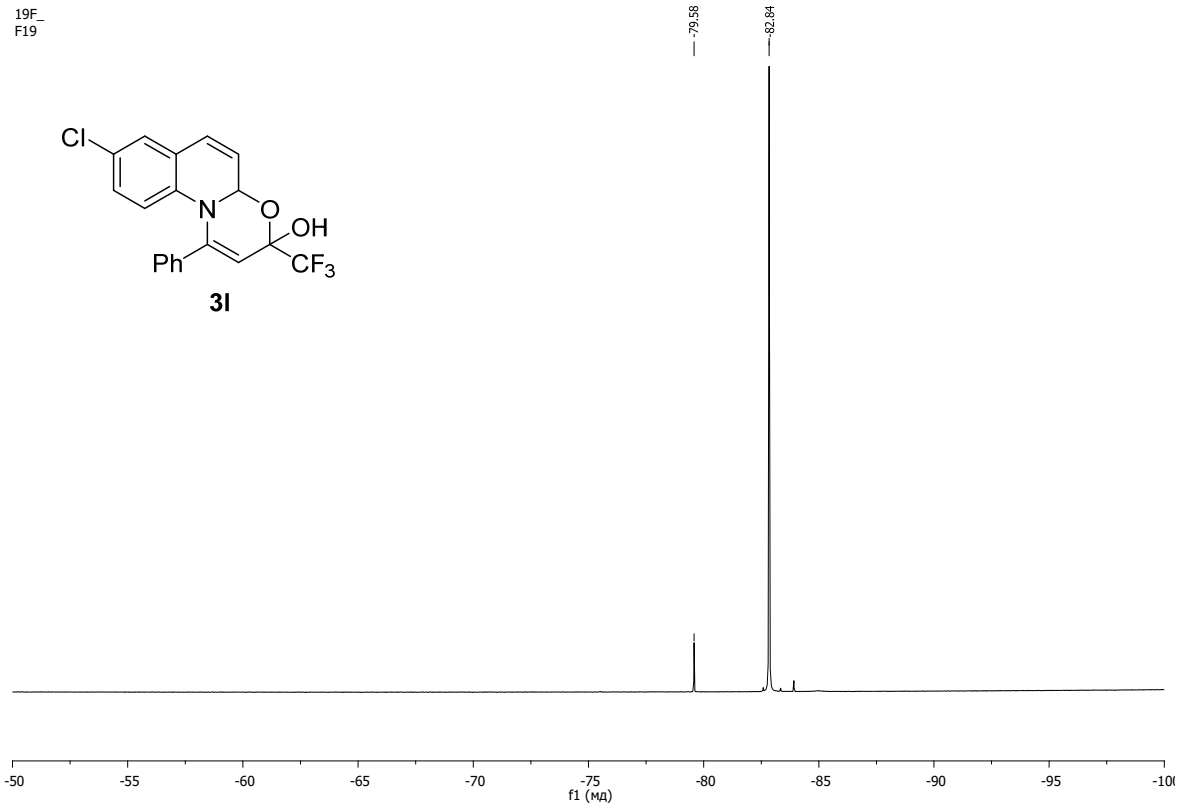
^{19}F NMR spectrum of **3k'** (376.5 MHz, $CDCl_3$)



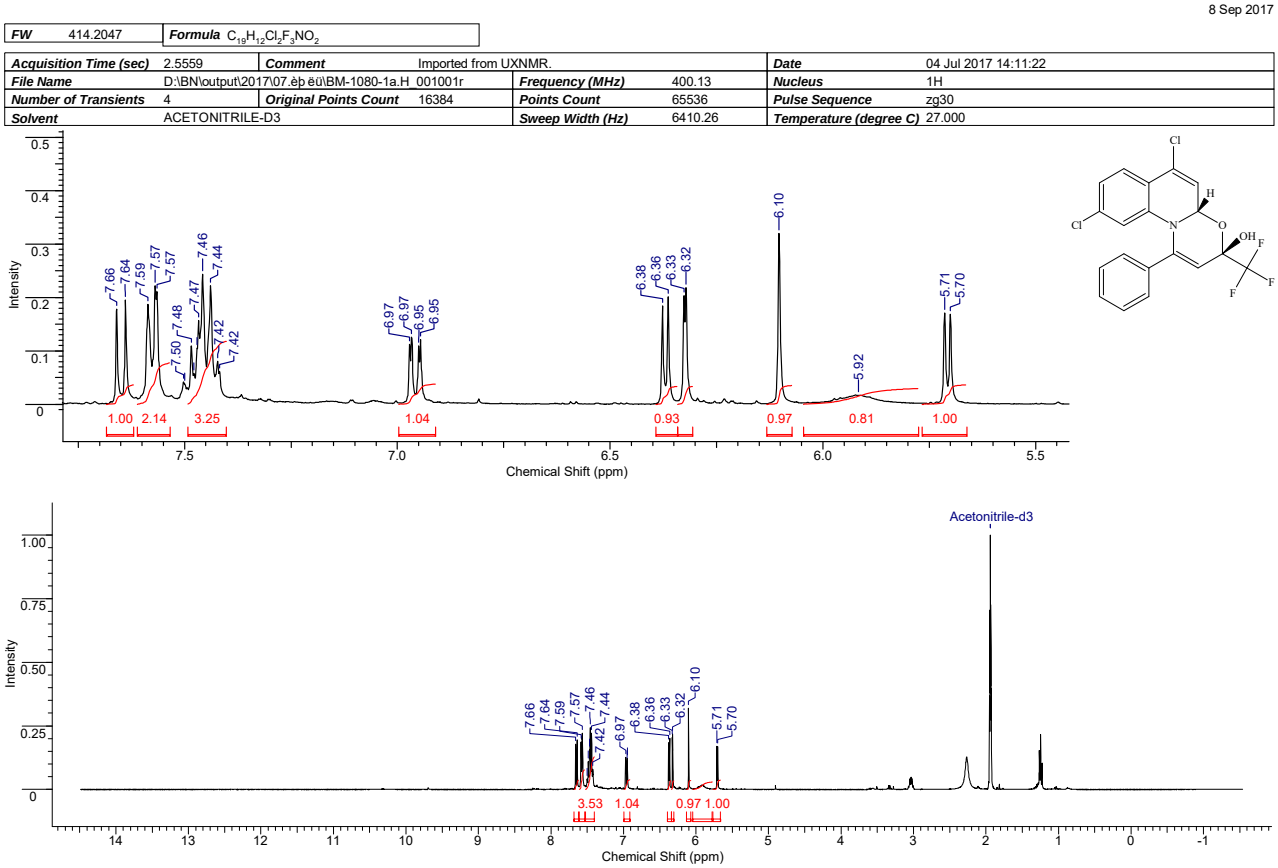
^{1}H NMR spectrum of (3*R**,4a*R**)-**3l** in (400.1 MHz, $CDCl_3$)



^{13}C NMR spectrum of (3*R**,4a*R**)-**3l** (100.6 MHz, $CDCl_3$)

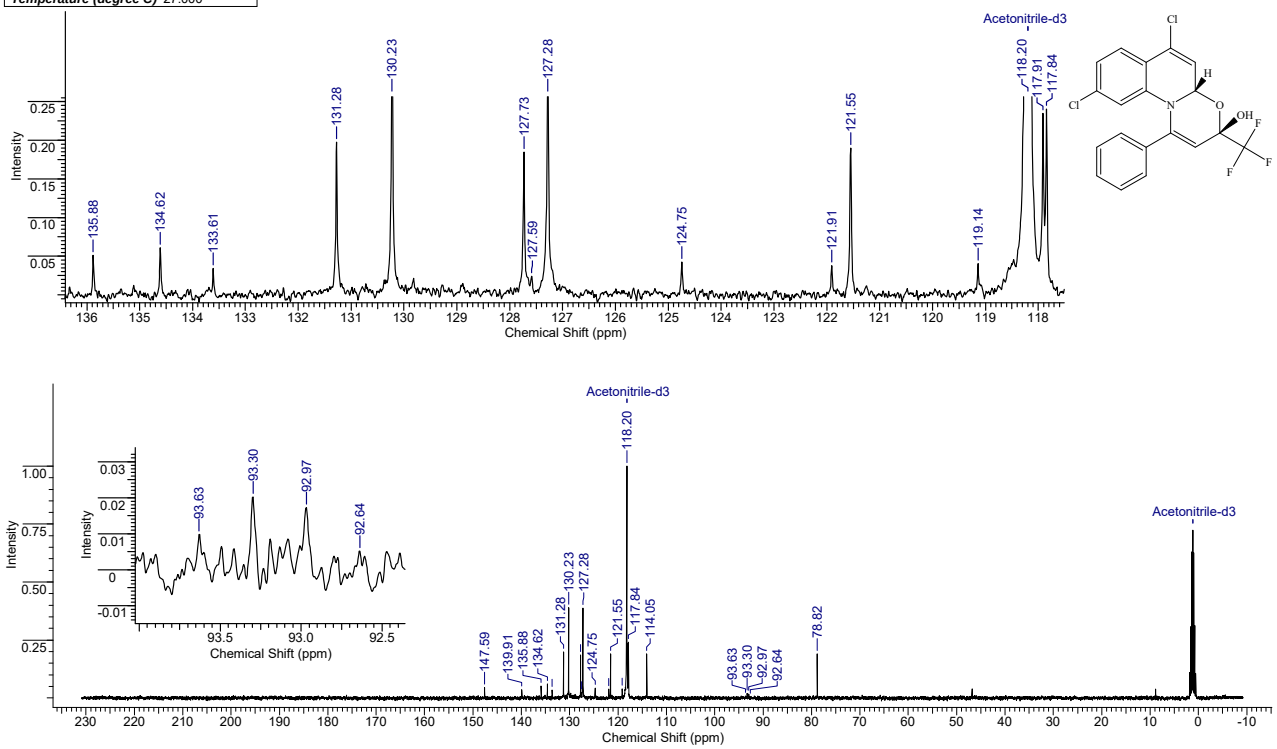


^{19}F NMR spectrum of **3l** (376.5 MHz, $CDCl_3$)



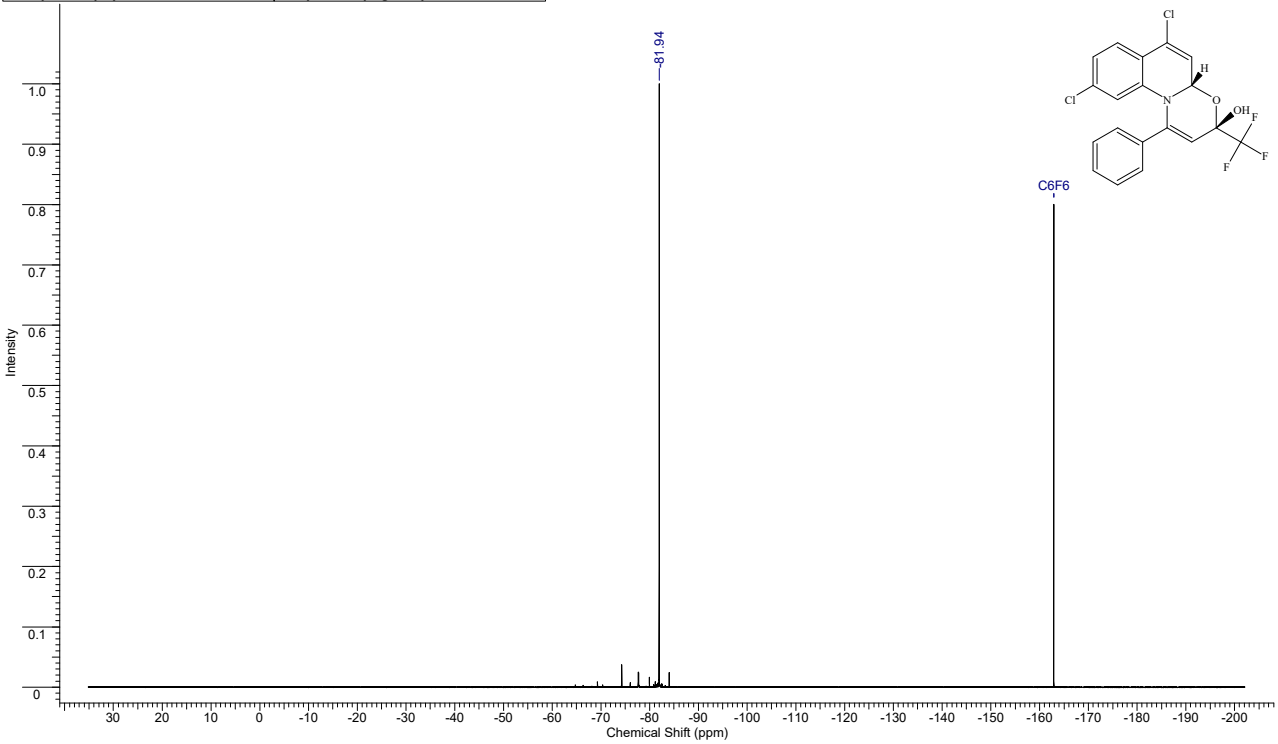
^{1}H NMR spectrum of (3*R**,4a*R**)-**3m** (400.1 MHz, CD_3CN)

FW	414.2047	Formula	$C_{19}H_{12}Cl_2F_3NO_2$						
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	03 Jul 2017 15:49:42		
File Name	D:\BN\output\2017\07.èþ ëü\BM-1080-1a.C_002001r			Frequency (MHz)	100.61	Nucleus	13C	Number of Transients	401
Original Points Count	12076	Points Count	65536	Pulse Sequence	zgpg30	Solvent	DMSO-D6	Sweep Width (Hz)	24154.59
Temperature (degree C)	27.000								



^{13}C NMR spectrum of (3*R**,4a*R**)-**3m** (100.6 MHz, CD_3CN)

FW	414.2047	Formula	$C_{19}H_{12}Cl_2F_3NO_2$				
Acquisition Time (sec)	1.5000	Date	Jul 3 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1080-1a_20170703_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	133929
Points Count	262144	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				

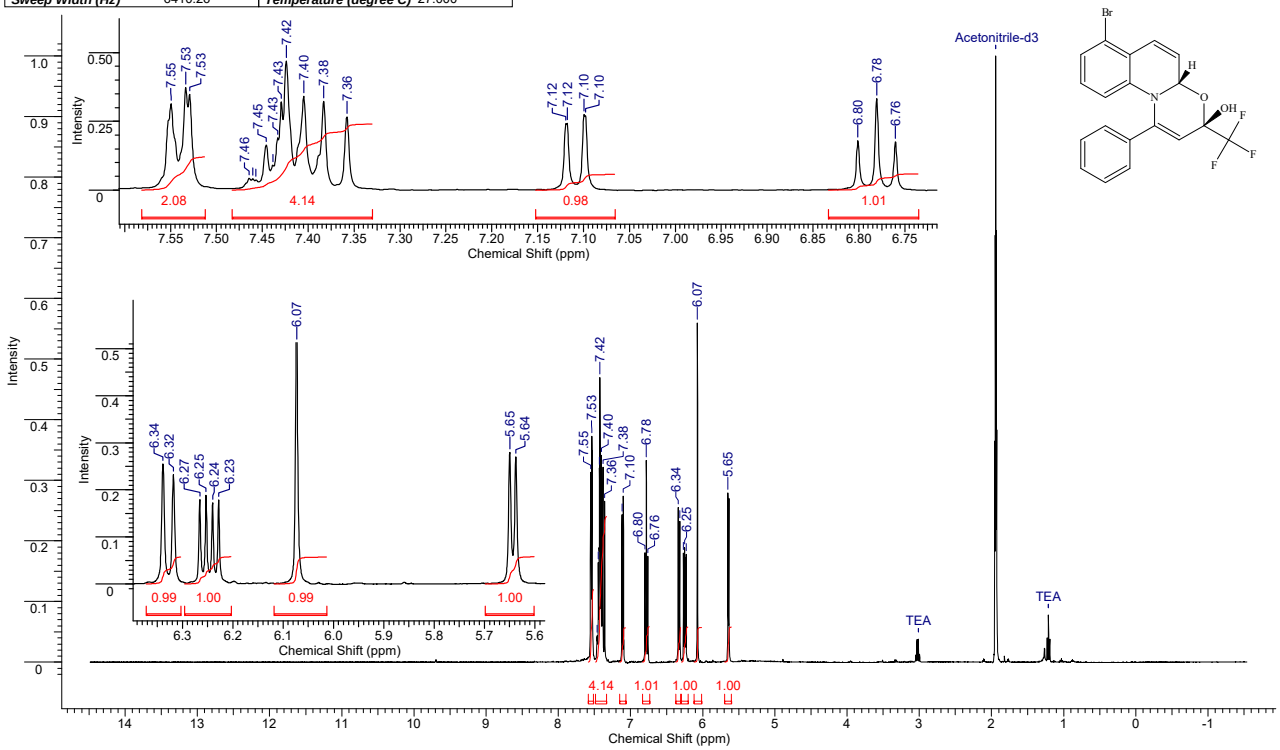


^{19}F NMR spectrum of (3*R**,4a*R**)-**3m** (376.3 MHz, CD_3CN)

11 Jul 2017

FW	424.2113	**Formula**	$C_{19}H_{13}BrF_3NO_2$

Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.			**Date**	07 Jul 2017 15:29:14
File Name	D:\BN\output\2017\07.èþ ëü\BM-1087-a.H_001001r			**Frequency (MHz)**	400.13	**Nucleus**	1H
Original Points Count	16384	**Points Count**	65536	**Pulse Sequence**	zg30	**Solvent**	ACETONITRILE-D3
Sweep Width (Hz)	6410.26	**Temperature (degree C)**	27.000				

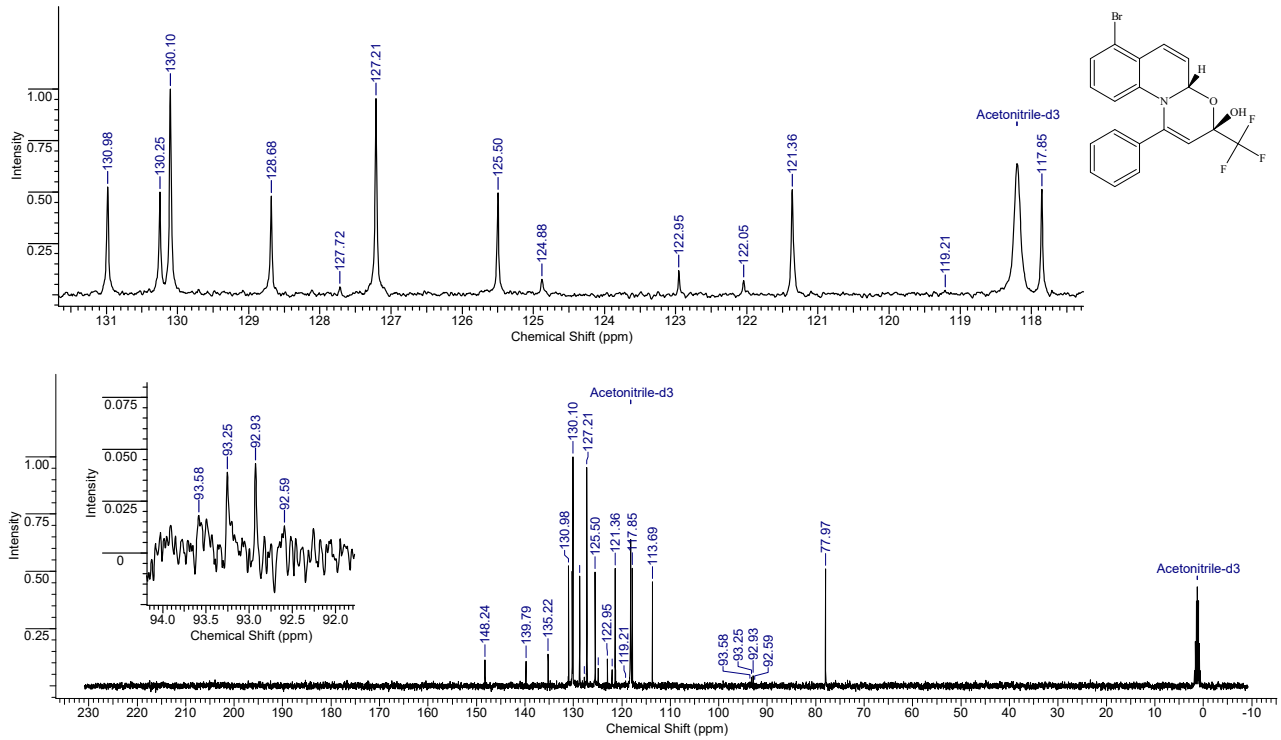


^{1}H NMR spectrum of (3*R**,4a*R**)-**3n** (400.1 MHz, CD_3CN)

11 Jul 2017

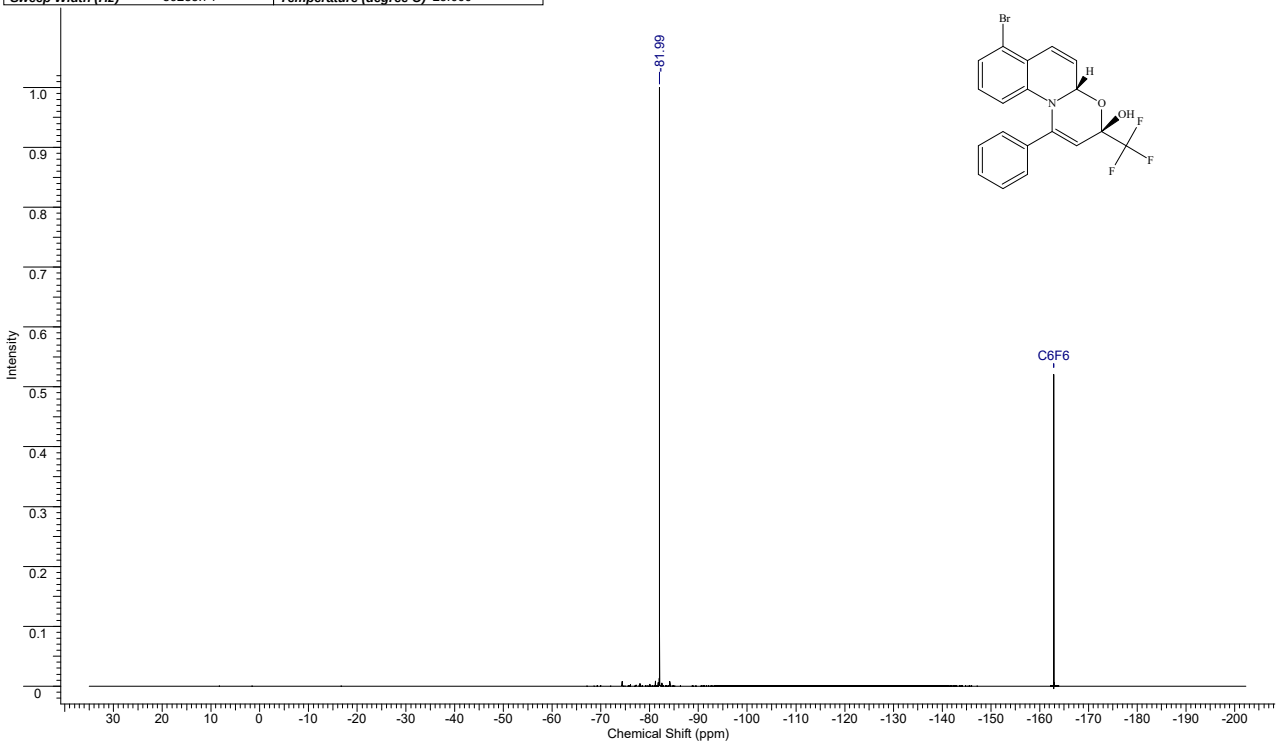
FW	424.2113	**Formula**	$C_{19}H_{13}BrF_3NO_2$

Acquisition Time (sec)	0.4999	**Comment**	Imported from UXNMR.			**Date**	30 Jun 2017 15:54:04
File Name	D:\BN\output\2017\06.èþ í ü\BM-1087.C_002001r			**Frequency (MHz)**	100.61	**Nucleus**	13C
Number of Transients	35	**Original Points Count**	12076	**Points Count**	65536	**Pulse Sequence**	zgpg30
Solvent	CHLOROFORM-D			**Sweep Width (Hz)**	24154.59	**Temperature (degree C)**	27.000



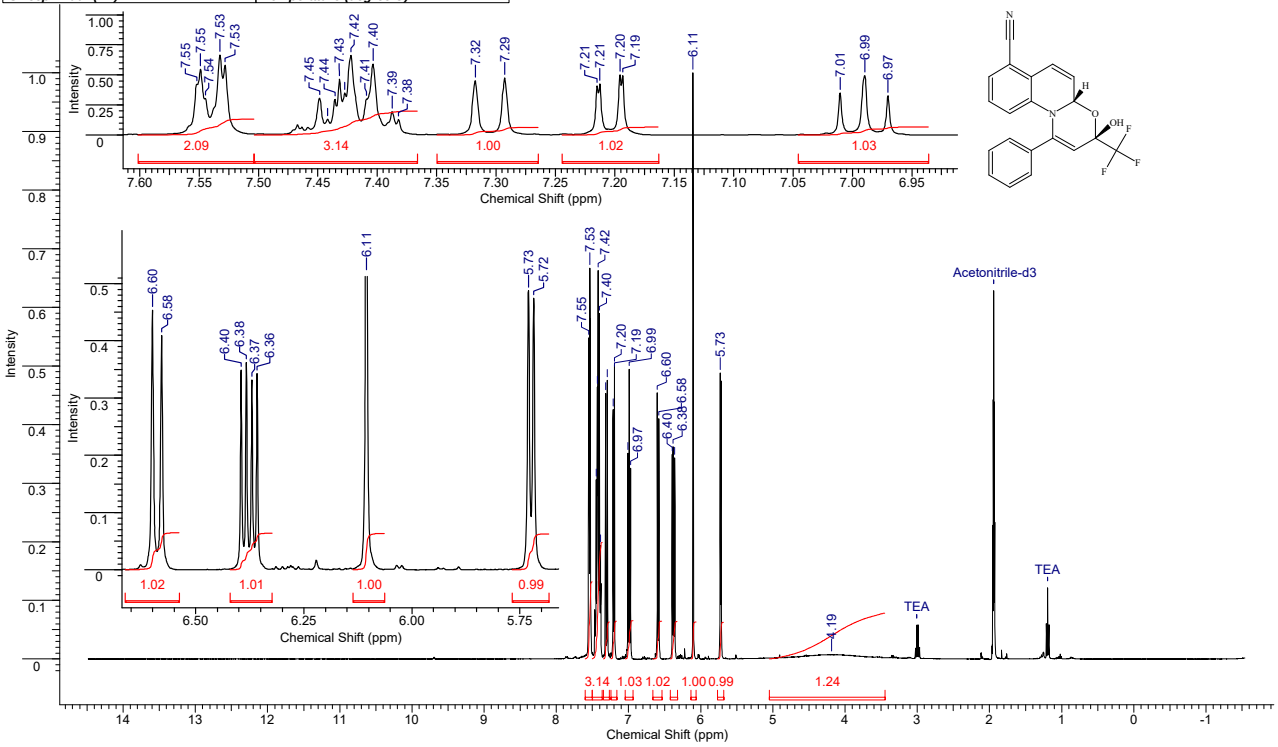
^{13}C NMR spectrum of (3*R**,4a*R**)-**3n** (100.6 MHz, CD_3CN)

FW	424.2113	Formula	$C_{19}H_{13}BrF_3NO_2$				
Acquisition Time (sec)	1.0000	Date	Jun 30 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1087_20170630_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	89286
Points Count	131072	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



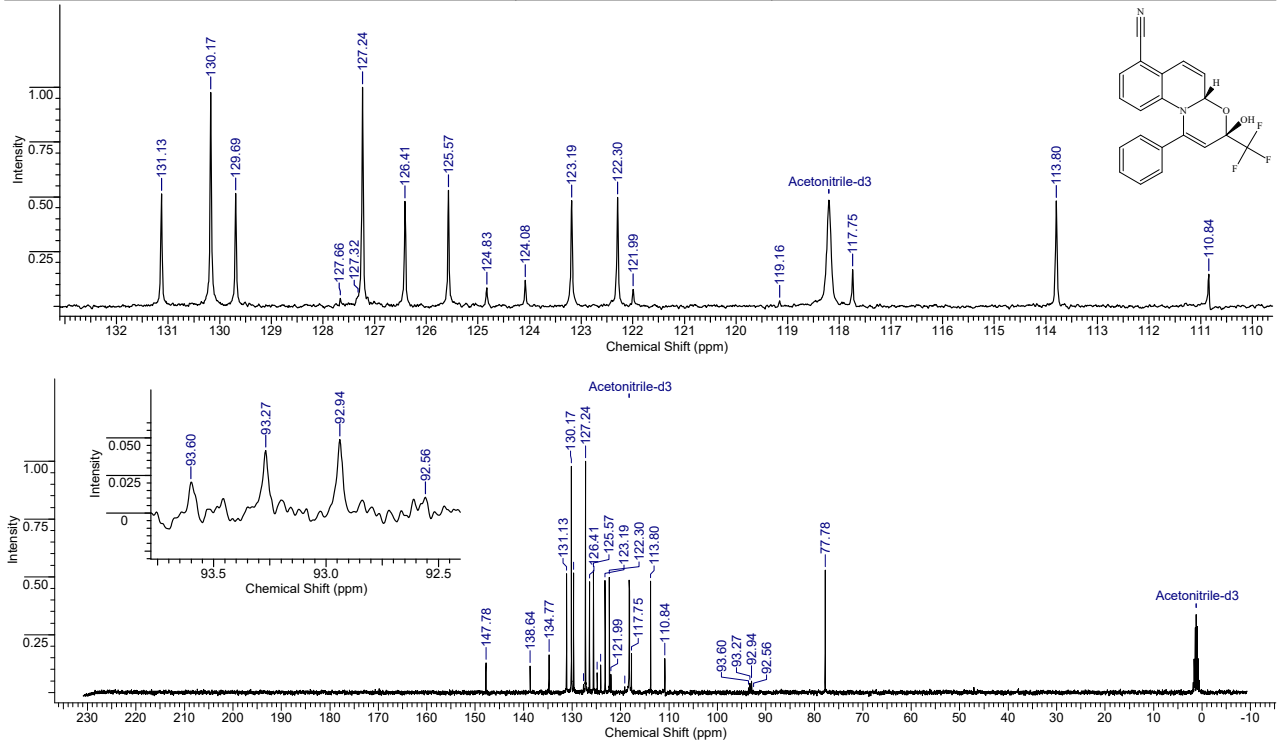
^{19}F NMR spectrum of (3*R**,4a*R**)-**3n** (376.3 MHz, CD_3CN)

FW	370.3247	Formula	$C_{20}H_{13}F_3N_2O_2$						
Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	30 Jun 2017 15:45:52		
File Name	D:\BN\output\2017\06.èþ í ú\BM-1086.H_001001r			Frequency (MHz)	400.13	Nucleus	1H	Number of Transients	4
Original Points Count	16384	Points Count	65536	Pulse Sequence	zg30	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	6410.26	Temperature (degree C)	27.000						



^{1}H NMR spectrum of (3*R**,4a*R**)-**3o** (400.1 MHz, CD_3CN)

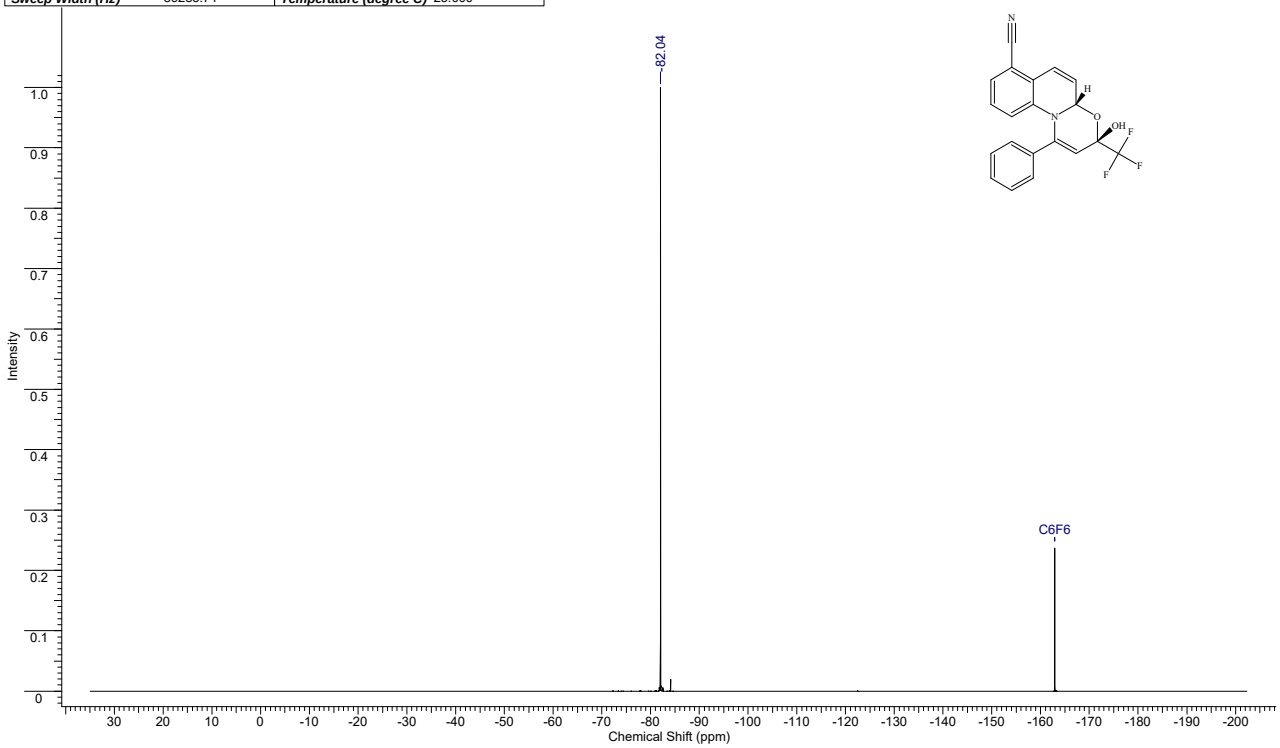
FW	370.3247	Formula	$C_{20}H_{13}F_3N_2O_2$				
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	30 Jun 2017 15:50:00
File Name	D:\BN\output\2017\06.èþ í ú\BM-1086.C_002001r			Frequency (MHz)	100.61	Nucleus	13C
Number of Transients	64	Original Points Count	12076	Points Count	65536	Pulse Sequence	zgpg30
Solvent	CHLOROFORM-D			Sweep Width (Hz)	24154.59	Temperature (degree C)	27.000



^{13}C NMR spectrum of (3*R**,4a*R**)-**3o** (100.6 MHz, CD_3CN)

11 Jul 2017

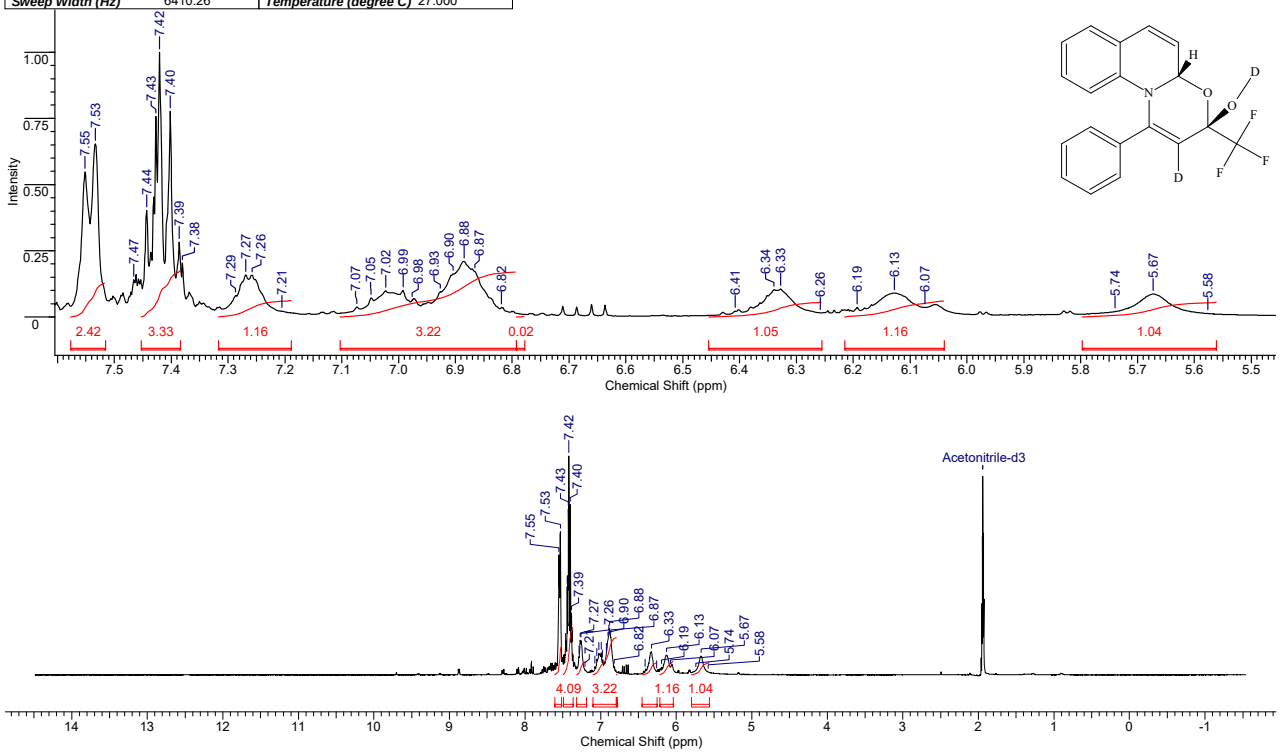
FW	370.3247	Formula	$C_{20}H_{13}F_3N_2O_2$				
Acquisition Time (sec)	1.0000	Date	Jun 30 2017	File Name	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1086_20170630_01\FLUORINE_01		
Frequency (MHz)	376.31	Nucleus	19F	Number of Transients	16	Original Points Count	89286
Points Count	131072	Pulse Sequence	s2pul	Solvent	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	Temperature (degree C)	25.000				



^{19}F NMR spectrum of (3*R**,4a*R**)-**3o** (376.3 MHz, CD_3CN)

12 Jul 2017

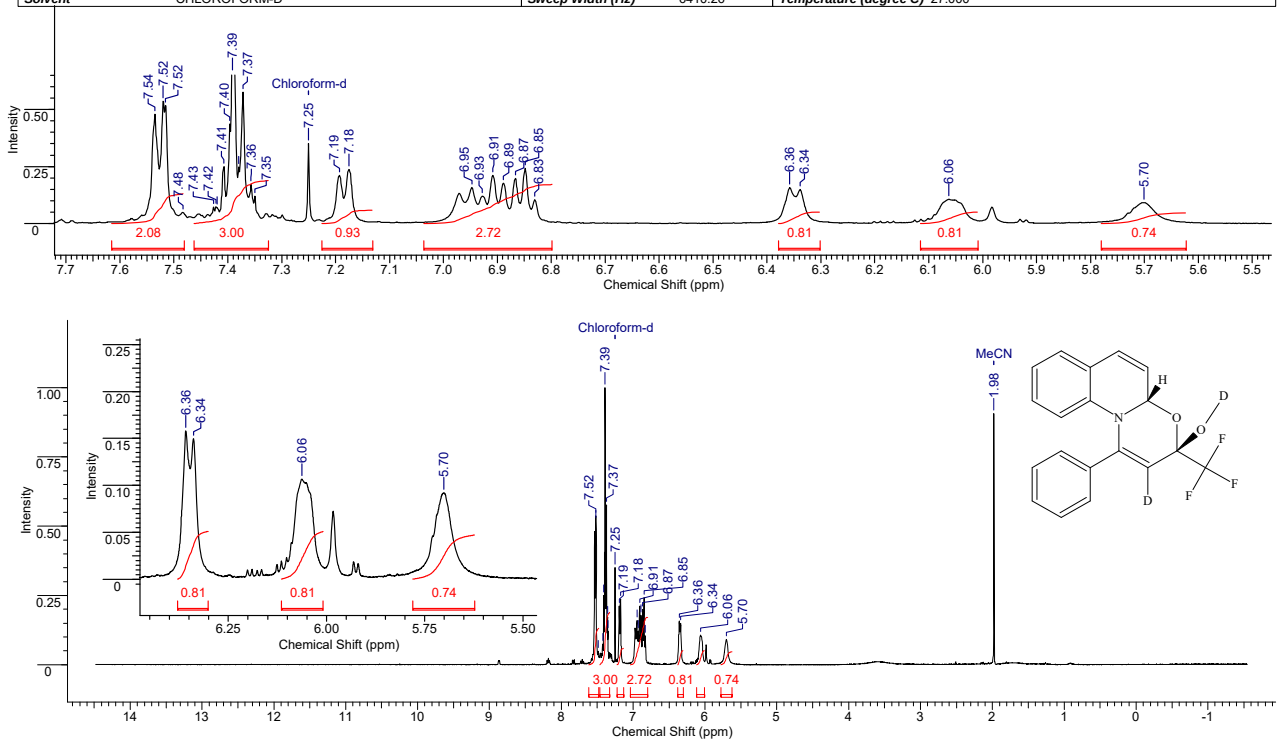
FW	347.3193	**Formula**	$C_{19}H_{12}D_2F_3NO_2$				
Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.			**Date**	01 Jul 2017 14:00:30
File Name	D:\BN\output\2017\07.èþ ëü\BM-1109-2.H_001001r			**Frequency (MHz)**	400.13	**Nucleus**	1H
Number of Transients	4	**Original Points Count**	16384	**Points Count**	65536	**Pulse Sequence**	zg30
Solvent	ACETONITRILE-D3	**Sweep Width (Hz)**	6410.26	**Temperature (degree C)**	27.000		



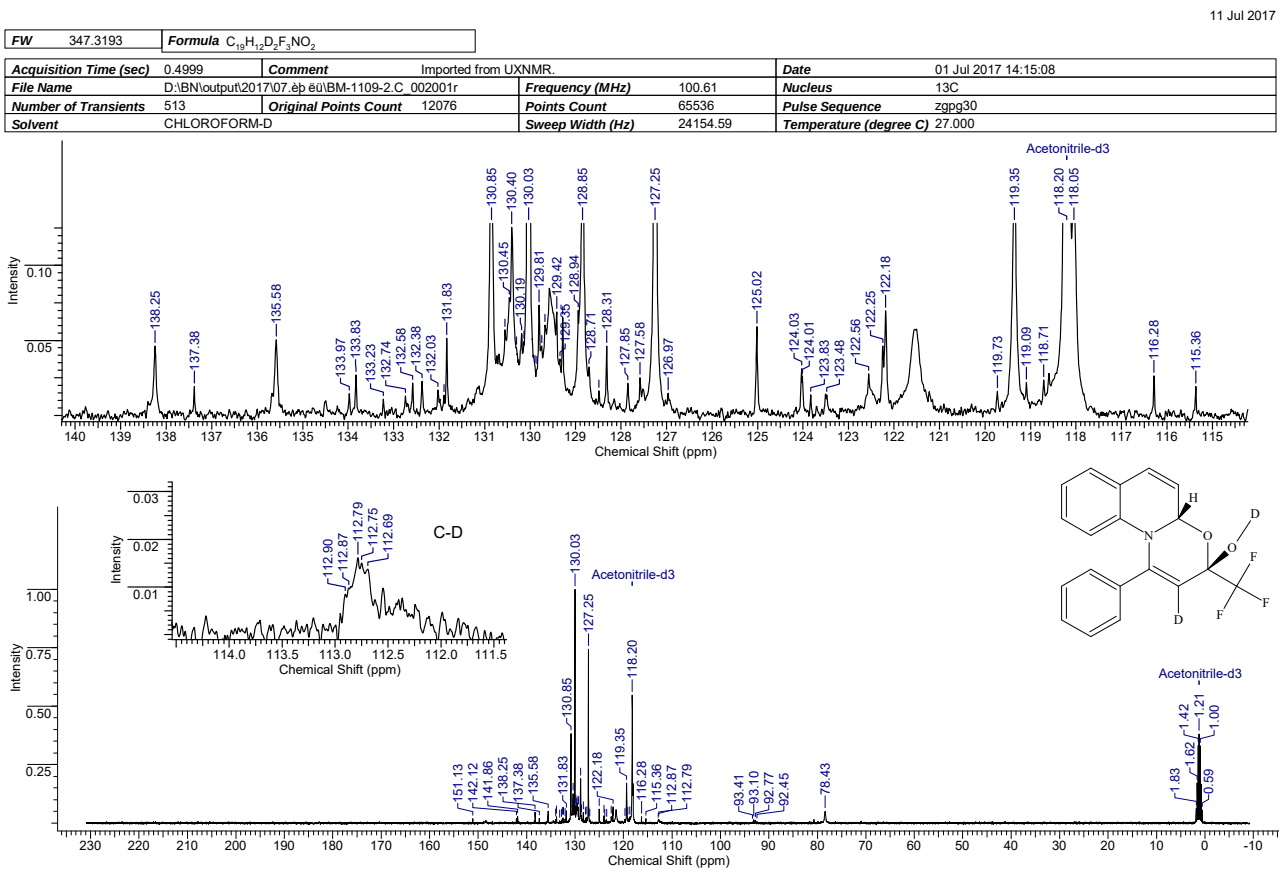
^{1}H NMR spectrum of (3*R**,4a*R**)-**3'** (400.1 MHz, CD_3CN)

11 Jul 2017

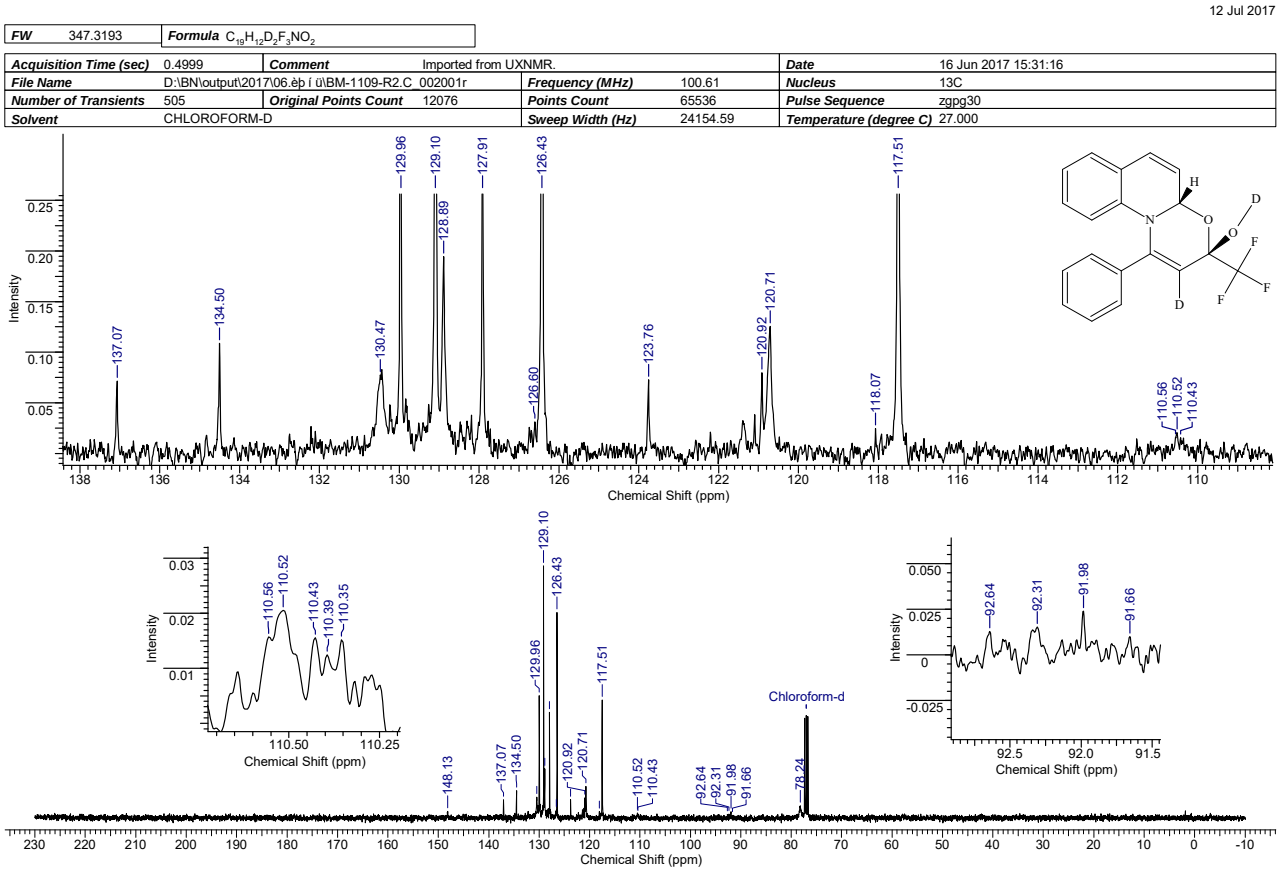
FW	347.3193	**Formula**	$C_{19}H_{12}D_2F_3NO_2$				
Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.			**Date**	16 Jun 2017 15:14:54
File Name	D:\BN\output\2017\06.èþ í ü\BM-1109-R2.H_001001r			**Frequency (MHz)**	400.13	**Nucleus**	1H
Number of Transients	4	**Original Points Count**	16384	**Points Count**	65536	**Pulse Sequence**	zg30
Solvent	CHLOROFORM-D			**Sweep Width (Hz)**	6410.26	**Temperature (degree C)**	27.000



^{1}H NMR spectrum of (3*R**,4a*R**)-**3'** (400.1 MHz, $CDCl_3$)

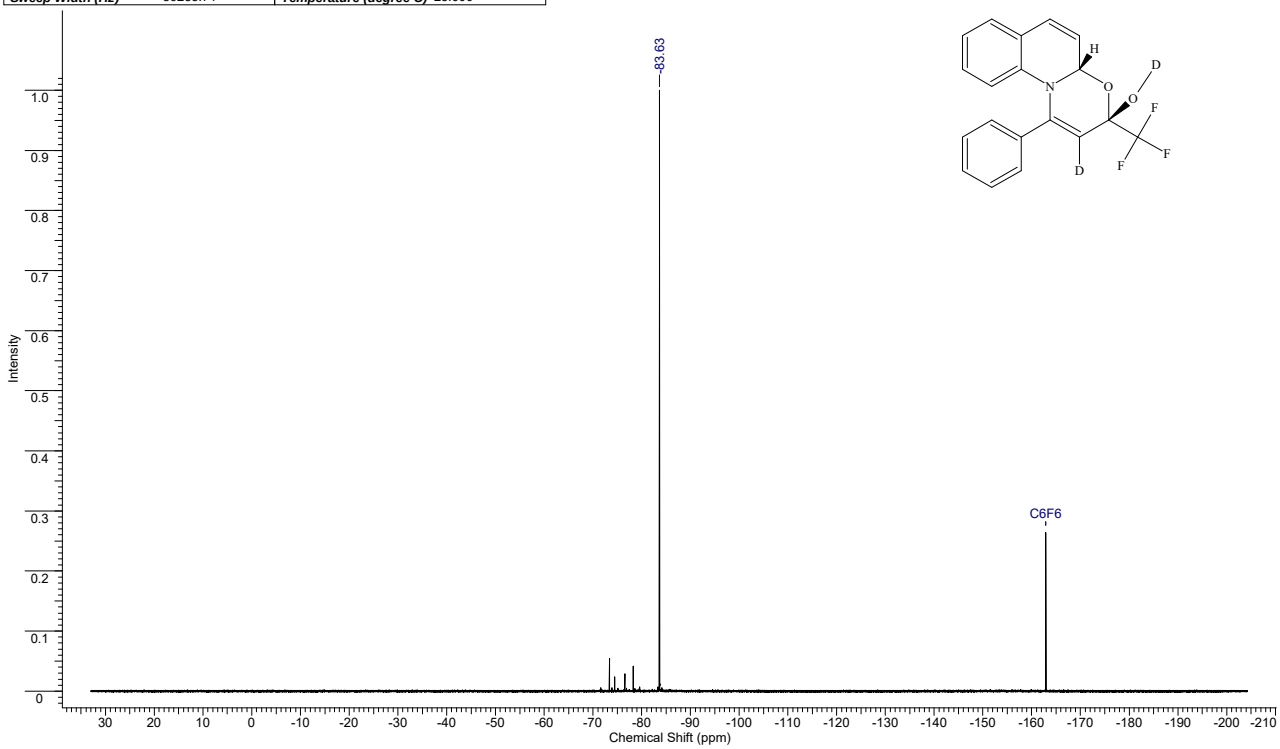


^{13}C NMR spectrum of (3*R**,4a*R**)-**3'** (100.6 MHz, CD_3CN)

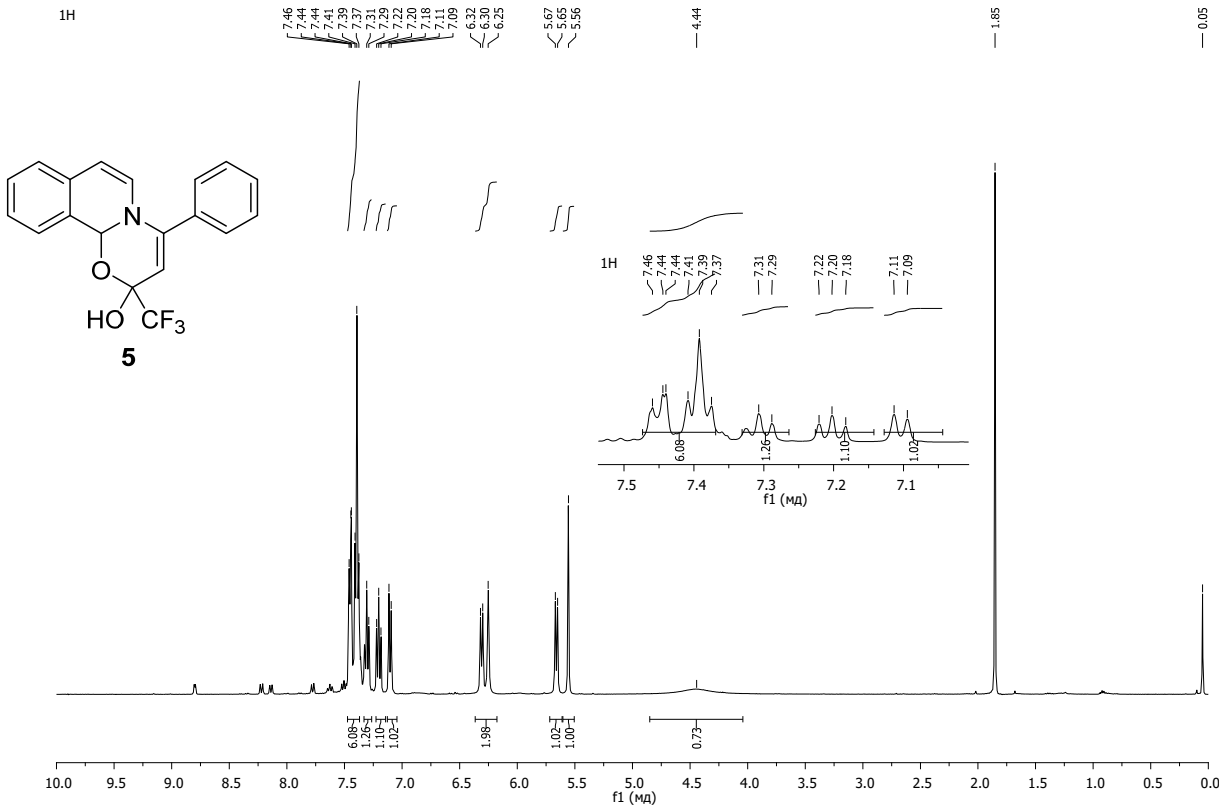


^{13}C NMR spectrum of (3*R**,4a*R**)-**3'** (100.6 MHz, $CDCl_3$)

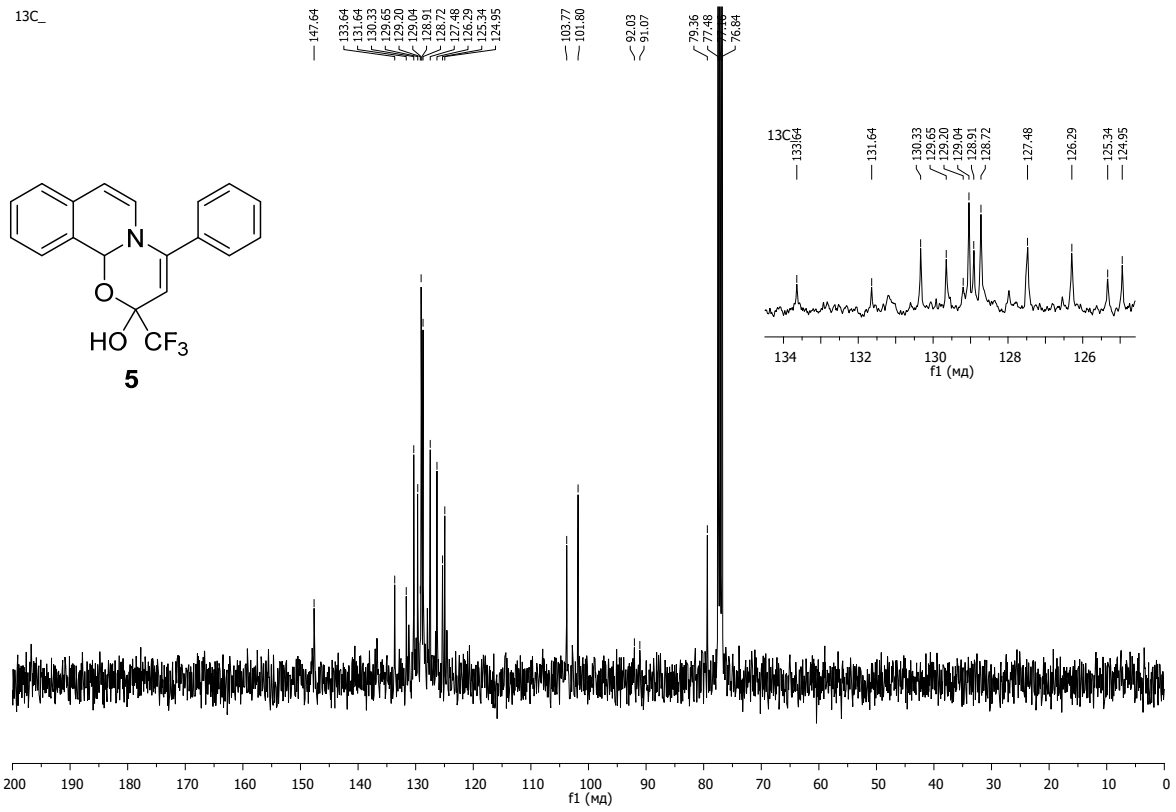
FW	347.3193	**Formula**	$C_{19}H_{12}D_2F_3NO_2$		
Acquisition Time (sec)	1.5000	**Date**	Jun 14 2017	**File Name**	D:\BN\Docs (BN)\vasiliy\SPEC_BM_F\2017.07.06_F\BM-1109-R_20170614_01\FLUORINE_01
Frequency (MHz)	376.31	**Nucleus**	19F	**Number of Transients**	16
Points Count	262144	**Pulse Sequence**	s2pul	**Solvent**	CHLOROFORM-D
Sweep Width (Hz)	89285.71	**Temperature (degree C)**	25.000		



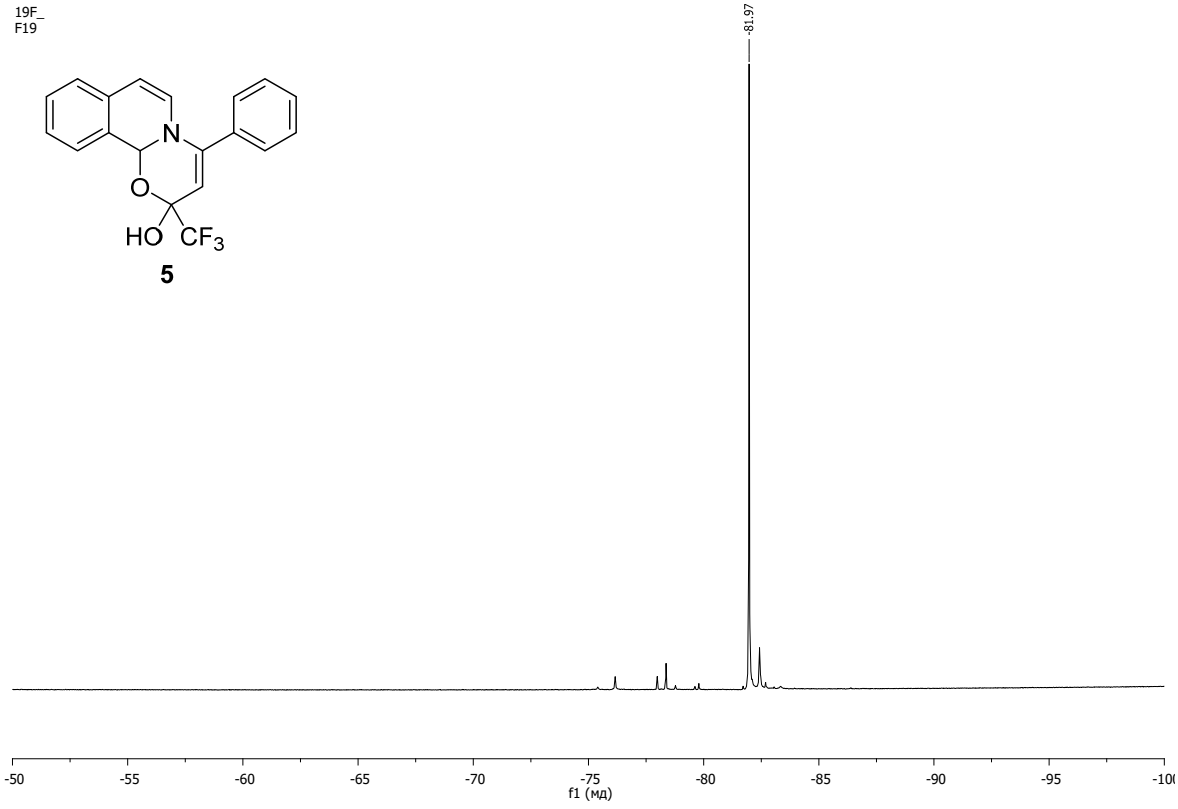
^{19}F NMR spectrum of (3*R**,4a*R**)-**3'** (376.3 MHz, CD_3CN)



^{1}H NMR spectrum of **5** (the signal at 1.85 ppm is from MeCN) (400.1 MHz, $CDCl_3$)



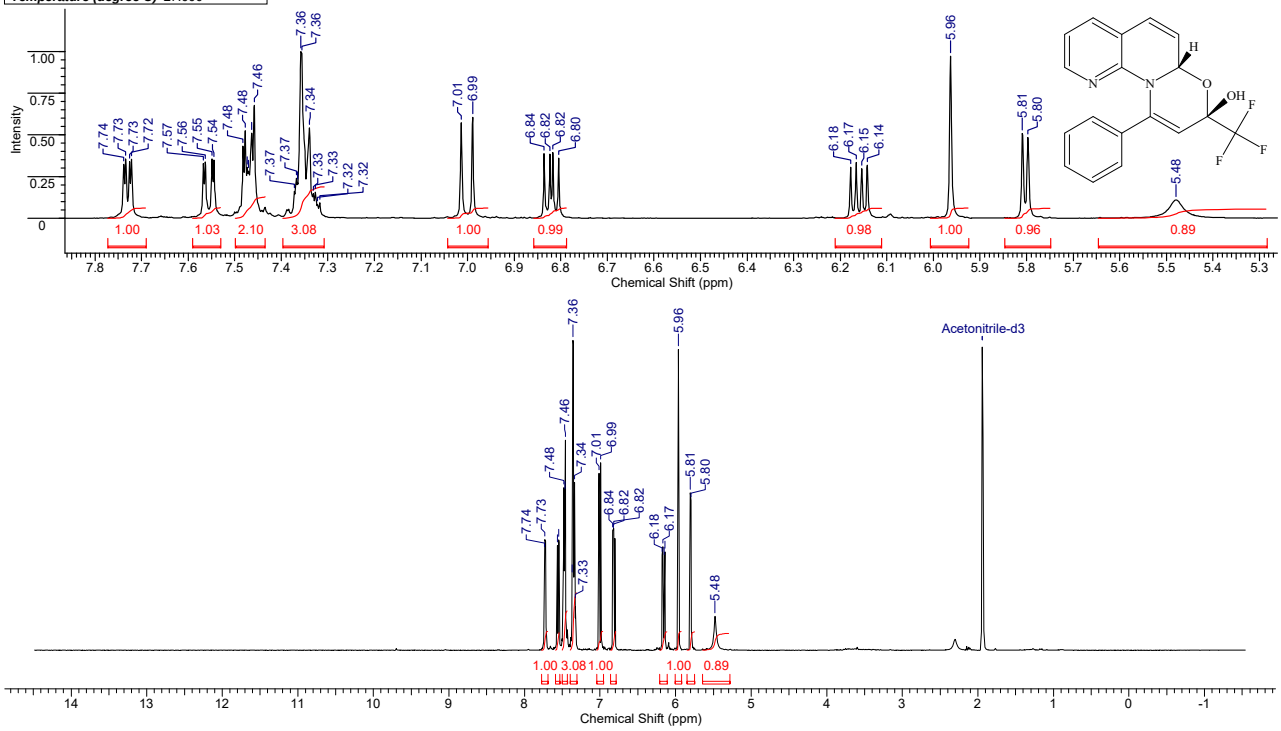
^{13}C NMR spectrum of **5** (100.6 MHz, $CDCl_3$)



^{19}F NMR spectrum of **5** (376.5 MHz, $CDCl_3$)

24 Jan 2018

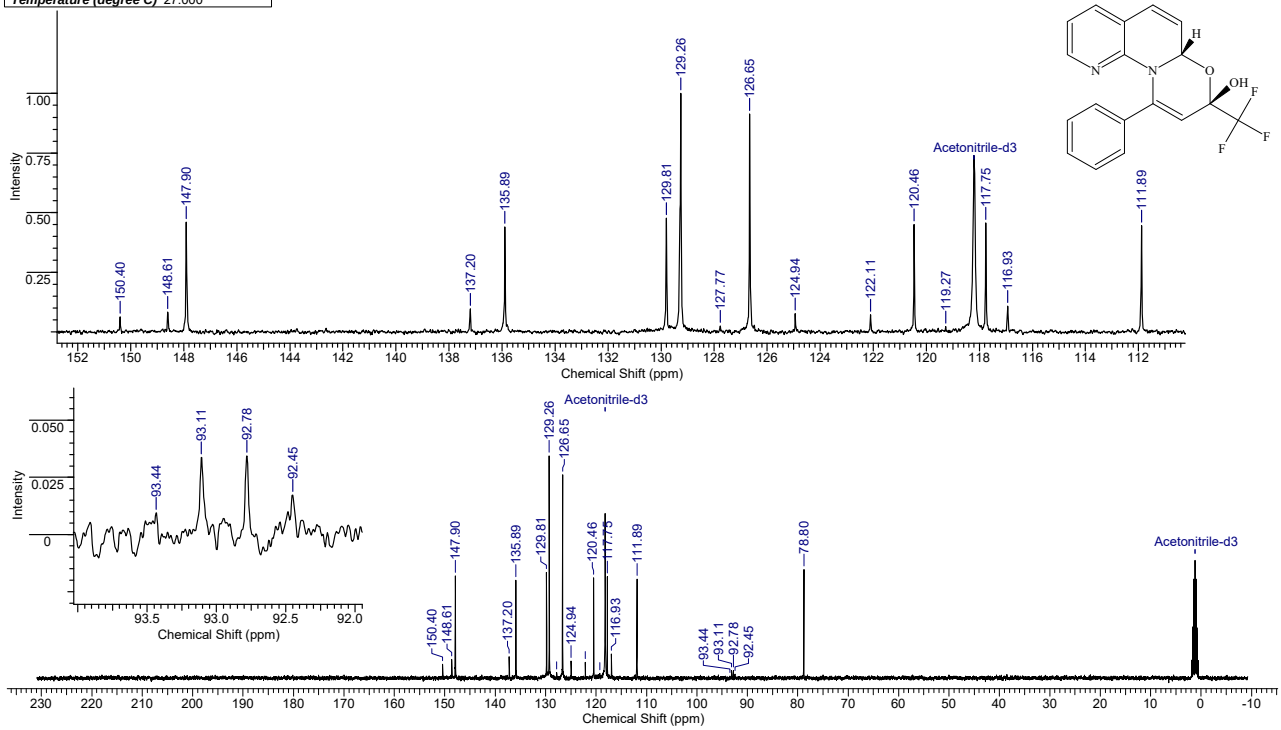
FW	346.3033	**Formula**	$C_{18}H_{13}F_3N_2O_2$		
Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.	**Date**	22 Jan 2018 15:42:48
File Name	D:\Comp_316\BN\output\2018\22.01.2018\BM-1286-R2.H_001001r			**Frequency (MHz)**	400.13
Nucleus	1H	**Number of Transients**	4	**Original Points Count**	16384	**Points Count**	65536
Pulse Sequence	zg30	**Solvent**	ACETONITRILE-D3	**Sweep Width (Hz)**	6410.26
Temperature (degree C)	27.000				



^{1}H NMR spectrum of **7** (400.1 MHz, CD_3CN)

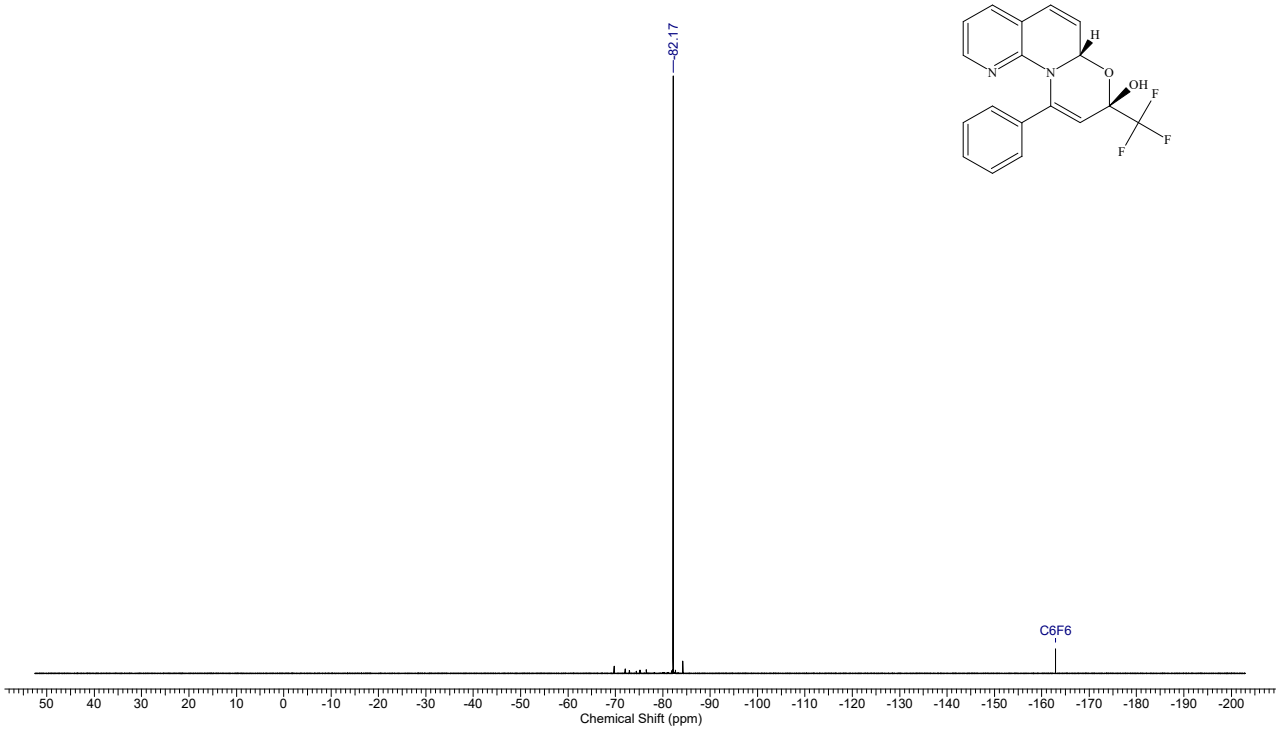
25 Jan 2018

FW	346.3033	**Formula**	$C_{18}H_{13}F_3N_2O_2$		
Acquisition Time (sec)	0.4999	**Comment**	Imported from UXNMR.	**Date**	22 Jan 2018 15:48:18
File Name	D:\Comp_316\BN\output\2018\22.01.2018\BM-1286-R2.C_002001r			**Frequency (MHz)**	100.61
Nucleus	13C	**Number of Transients**	147	**Original Points Count**	12076	**Points Count**	65536
Pulse Sequence	zgpg30	**Solvent**	DEUTERIUM OXIDE	**Sweep Width (Hz)**	24154.59
Temperature (degree C)	27.000				



^{13}C NMR spectrum of **7** (100.6 MHz, CD_3CN)

FW	346.3033	***Formula***	$C_{18}H_{13}F_3N_2O_2$		
Acquisition Time (sec)	2.4117	***Date***	Jan 22 2018	***File Name***	D:\Comp_316\BN\output\F19\F_2018\2018.01.22\BM-1286-R-F_20180122_01\FLUORINE_01
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	8
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D
Sweep Width (Hz)	96153.84	***Temperature (degree C)***	5.000		



^{19}F NMR spectrum of **7** (376.3 MHz, CD_3CN)

Monitoring of the reaction mixture by ^{19}F NMR spectrum

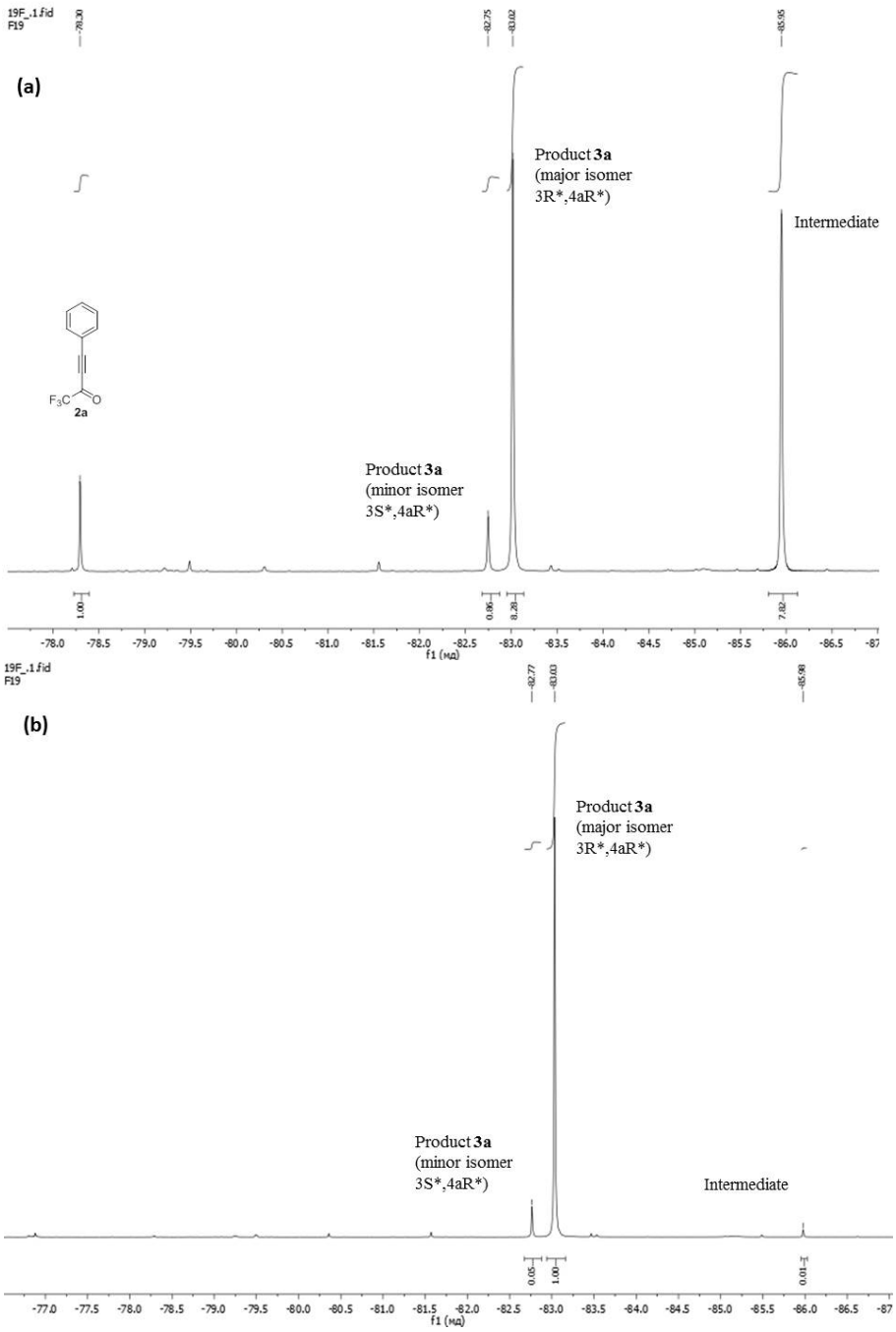


Fig. 1. The ^{19}F NMR spectrum of mixture of quinoline **1a** phenyltrifluoroacetylacetylene **2a** with after 4 hours (**a**) and after 40 hours (**b**).

X-ray diffraction structural analysis data

The X-ray diffraction structural analysis was carried out on a Bruker D8 Venture monocrystal diffractometer with a Photon 100 detector using ω-2θ scanning. The reflection intensities were integrated using the Bruker SAINT monitoring program. X-ray absorption by the crystal was taken into account by analysis of the intensities of equivalent reflections. After averaging the intensities of equivalent reflections, only independent reflections were used. The search for a model was carried out using the SHELXS program (G. M. Sheldrick, *Acta Crystallogr*., *Sect. A*: *Found. Crystallogr*. **2008**, *A64*, 112) and direct methods, which gave the coordinates of all the non-hydrogen atoms. The structures obtained were refined by method of least squares using the SHELXL program.

The determination of the unit cell and the data collection for 1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (**3a**) (Fig. 2) was performed at 100.0(2) K using the ω–φ scan technique. A specimen of $C_{19}H_{14}NO_2F_3$, approximate dimensions 0.210 mm x 0.330 mm x 0.470 mm, pale, yellow, irregular crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with *C2/c* space group yielded a total of 21815 reflections to a maximum θ angle of 26.14° (0.81 Å resolution), of which 3200 were independent (average redundancy 6.817, completeness = 99.4%, Rint = 2.54%, Rsig = 1.53%) and 2855 (89.22%) were greater than 2σ(F2). The final cell constants of **a** = 19.9333(7) Å, **b** = 9.8491(3) Å, **c** = 16.6571(6) Å, β=98.9990(10)°, Z= 8, volume = 3229.95(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 9996 reflections above 20 σ(I) with 4.952° < 2θ < 52.27°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.912. The H atoms were determined from a difference Fourier synthesis. The unit cell is presented by 2 enantiomers: (3*R*,4a*R*)- and (3*S*,4a*S*)-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (**3a**).

The final anisotropic full-matrix least-squares refinement on F2 with 229 variables converged at R1 = 3.34%, for the observed data and wR2 = 9.00% for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.34 $e^-/Å^3$ and the largest hole was -0.240 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.420 g/cm^3 and F(000), 1424 e^-. CCDC 1545030.

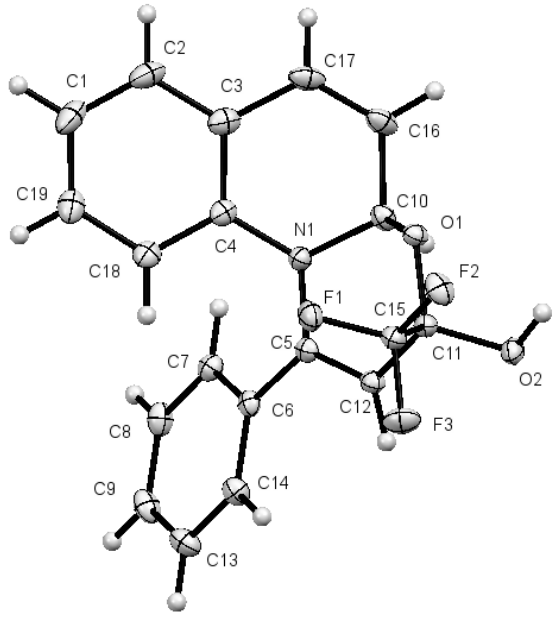


Figure 2. X-ray structure of 1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3a). Thermal ellipsoids set at 50% probability.

Table S2. Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C15	1.3341(14)	C4	C18	1.3992(18)
F2	C15	1.3452(14)	C5	C6	1.4824(16)
F3	C15	1.3422(14)	C5	C12	1.3398(18)
O1	C10	1.4758(15)	C6	C7	1.3989(18)
O1	C11	1.4217(15)	C6	C14	1.3967(18)
O2	C11	1.3961(15)	C7	C8	1.3889(18)
N1	C4	1.4097(16)	C8	C9	1.385(2)
N1	C5	1.4146(16)	C9	C13	1.388(2)
N1	C10	1.4383(15)	C10	C16	1.4881(17)
C1	C2	1.386(2)	C11	C12	1.5068(16)
C1	C19	1.389(2)	C11	C15	1.5429(18)
C2	C3	1.3952(19)	C13	C14	1.3895(18)
C3	C4	1.4091(18)	C16	C17	1.330(2)
C3	C17	1.4537(19)	C18	C19	1.3912(19)

Table S3. Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

C11	O1	C10	111.43(9)	N1	C10	O1	108.50(9)
C4	N1	C5	123.03(10)	N1	C10	C16	113.67(11)
C4	N1	C10	120.56(10)	O1	C11	C12	113.57(10)
C5	N1	C10	111.27(10)	O1	C11	C15	103.48(9)
C2	C1	C19	119.64(13)	O2	C11	O1	112.08(9)
C1	C2	C3	120.75(13)	O2	C11	C12	108.62(10)
C2	C3	C4	119.29(13)	O2	C11	C15	109.41(10)
C2	C3	C17	121.89(12)	C12	C11	C15	109.53(10)
C4	C3	C17	118.69(12)	C5	C12	C11	122.45(11)
C3	C4	N1	117.88(11)	C9	C13	C14	120.32(12)
C18	C4	N1	122.43(11)	C13	C14	C6	120.38(12)
C18	C4	C3	119.68(12)	F1	C15	F2	107.35(10)
N1	C5	C6	117.99(11)	F1	C15	F3	107.30(10)
C12	C5	N1	117.11(11)	F1	C15	C11	111.94(10)
C12	C5	C6	124.33(11)	F2	C15	C11	111.60(10)
C7	C6	C5	120.29(11)	F3	C15	F2	106.95(10)
C14	C6	C5	120.65(11)	F3	C15	C11	111.43(10)
C14	C6	C7	118.98(11)	C17	C16	C10	121.19(12)
C8	C7	C6	120.14(12)	C16	C17	C3	121.63(12)
C9	C8	C7	120.61(12)	C19	C18	C4	119.63(12)
C8	C9	C13	119.57(12)	C1	C19	C18	120.78(13)
O1	C10	C16	108.12(10)				

Table S4. Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C10	C16	C17	-106.99(14)	C5	N1	C10	C16	175.54(10)
O1	C11	C12	C5	-15.32(16)	C5	C6	C7	C8	176.73(11)
O1	C11	C15	F1	61.72(12)	C5	C6	C14	C13	-176.90(11)
O1	C11	C15	F2	-58.63(12)	C6	C5	C12	C11	-175.68(11)
O1	C11	C15	F3	-178.12(9)	C6	C7	C8	C9	0.49(19)
O2	C11	C12	C5	-140.75(12)	C7	C6	C14	C13	0.00(18)
O2	C11	C15	F1	-178.66(9)	C7	C8	C9	C13	-0.6(2)
O2	C11	C15	F2	60.99(13)	C8	C9	C13	C14	0.4(2)
O2	C11	C15	F3	-58.49(13)	C9	C13	C14	C6	-0.1(2)
N1	C4	C18	C19	-175.01(11)	C10	O1	C11	O2	101.39(11)
N1	C5	C6	C7	19.79(16)	C10	O1	C11	C12	-22.17(13)
N1	C5	C6	C14	-163.35(11)	C10	O1	C11	C15	-140.83(9)
N1	C5	C12	C11	13.24(17)	C10	N1	C4	C3	27.92(16)
N1	C10	C16	C17	13.54(18)	C10	N1	C4	C18	-152.58(12)
C1	C2	C3	C4	2.3(2)	C10	N1	C5	C6	-144.80(11)
C1	C2	C3	C17	-173.53(13)	C10	N1	C5	C12	26.86(15)
C2	C1	C19	C18	-2.7(2)	C10	C16	C17	C3	2.9(2)
C2	C3	C4	N1	174.08(11)	C11	O1	C10	N1	61.23(12)
C2	C3	C4	C18	-5.43(18)	C11	O1	C10	C16	-175.06(10)
C2	C3	C17	C16	170.74(13)	C12	C5	C6	C7	-151.22(13)

C3	C4	C18	C19	4.48(18)	C12	C5	C6	C14	25.64(18)
C4	N1	C5	C6	60.56(15)	C12	C11	C15	F1	-59.71(13)
C4	N1	C5	C12	-127.78(12)	C12	C11	C15	F2	179.94(10)
C4	N1	C10	O1	91.21(13)	C12	C11	C15	F3	60.46(13)
C4	N1	C10	C16	-29.10(16)	C14	C6	C7	C8	-0.19(18)
C4	C3	C17	C16	-5.14(19)	C15	C11	C12	C5	99.81(14)
C4	C18	C19	C1	-0.39(19)	C17	C3	C4	N1	-9.93(17)
C5	N1	C4	C3	-179.69(11)	C17	C3	C4	C18	170.56(12)
C5	N1	C4	C18	-0.19(18)	C19	C1	C2	C3	1.8(2)
C5	N1	C10	O1	-64.14(12)					

The determination of the unit cell and the data collection for 5-bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-dihydro-[1,3]oxazino[3,2-*a*]quinolin-3-ol (**3k'**) (Fig. 3) was performed at 296.15(2) K using the ω–φ scan technique. A specimen of $\underline{C_{19}H_{13}N_1O_2F_3Br_1}\cdot C_9H_6N_1Br_1$, approximate dimensions 0.228 mm x 0.315 mm x 0.513 mm, lustrous, light, block-like crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with *P2₁/n* space group yielded a total of 52763 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 5518 were independent (average redundancy 9.562, completeness = 99.7%, Rint = 5.89%, Rsig = 3.76%) and 3696 (66.98%) were greater than 2σ(F2). The final cell constants of **a** = 10.054(5) Å, **b** = 15.229(9) Å, **c** = 17.101(10) Å, β=95.46(2)º, Z= 4, volume = 2606.(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9890 reflections above 20 σ(I) with 4.541° < 2θ < 47.61°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.543. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2940 and 0.5330. The structure was solved and refined using the Bruker SHELXTL Software Package (G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*: *Found. Crystallogr*. **2008**, *A64*, 112). The H atoms were determined from a difference Fourier synthesis. The unit cell is presented by 2 enantiomers: (3*R*,4a*R*)- and (3*S*,4a*S*)-5-bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-dihydro-[1,3]oxazino[3,2-*a*]quinolin-3-ol (**3k'**).

The final anisotropic full-matrix least-squares refinement on F2 with 337 variables converged at R1 = 4.45%, for the observed data and wR2 = 8.89% for all data. The goodness-of-fit was 1.021. The largest peak in the final difference electron density synthesis was 0.56 $e^-/Å^3$ and the largest hole was -0.460 $e^-/Å^3$ with an RMS deviation of 0.076 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.611 g/cm^3 and F(000), 1256 e^-. CCDC 1545031.

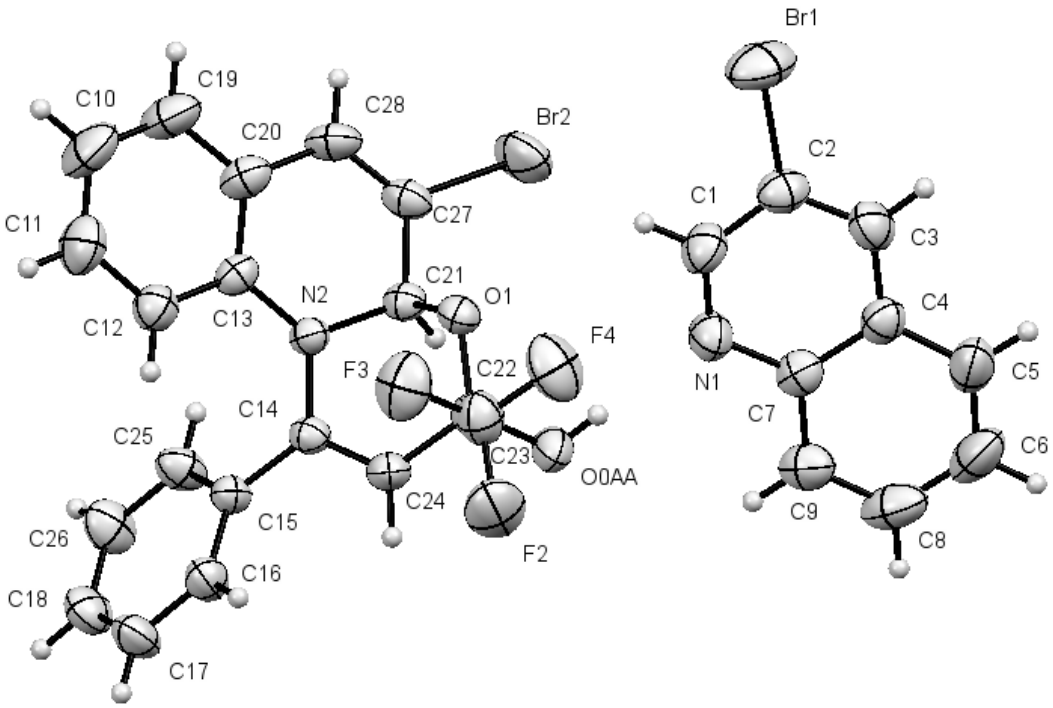


Figure 3. X-ray structure of 5-bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-dihydro-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3k'). Thermal ellipsoids set at 50% probability.

Table S5. Bond Lengths for 3k'.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C2	1.893(3)	C8	C9	1.360(5)
Br2	C27	1.892(3)	C10	C11	1.375(5)
O1	C21	1.455(3)	C10	C19	1.366(5)
O1	C22	1.419(3)	C11	C12	1.390(5)
F2	C23	1.342(4)	C12	C13	1.394(4)
F3	C23	1.328(4)	C13	C20	1.402(4)
F4	C23	1.335(4)	C14	C15	1.480(4)
O0AA	C22	1.387(3)	C14	C24	1.339(4)
N1	C1	1.313(4)	C15	C16	1.389(4)
N1	C7	1.372(4)	C15	C25	1.384(4)
N2	C13	1.413(3)	C16	C17	1.379(4)
N2	C14	1.425(3)	C17	C18	1.364(5)
N2	C21	1.439(3)	C18	C26	1.367(5)
C1	C2	1.394(5)	C19	C20	1.399(5)
C2	C3	1.352(5)	C20	C28	1.449(4)
C3	C4	1.423(4)	C21	C27	1.490(4)
C4	C5	1.412(5)	C22	C23	1.535(4)
C4	C7	1.411(4)	C22	C24	1.504(4)
C5	C6	1.354(5)	C25	C26	1.385(4)
C6	C8	1.398(6)	C27	C28	1.322(4)
C7	C9	1.411(4)			

Table S6. Bond Angles for 3k'.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	O1	C21	110.2(2)	C25	C15	C16	118.1(3)
C1	N1	C7	118.1(3)	C17	C16	C15	120.5(3)
C13	N2	C14	122.4(2)	C18	C17	C16	120.6(3)
C13	N2	C21	120.5(2)	C17	C18	C26	120.0(3)
C14	N2	C21	110.7(2)	C10	C19	C20	120.9(3)
N1	C1	C2	123.2(3)	C13	C20	C28	119.0(3)
C1	C2	Br1	117.7(2)	C19	C20	C13	119.4(3)
C3	C2	Br1	122.1(3)	C19	C20	C28	121.5(3)
C3	C2	C1	120.3(3)	O1	C21	C27	108.5(2)
C2	C3	C4	118.9(3)	N2	C21	O1	110.2(2)
C5	C4	C3	123.9(3)	N2	C21	C27	112.2(2)
C7	C4	C3	117.2(3)	O1	C22	C23	104.3(2)
C7	C4	C5	118.8(3)	O1	C22	C24	112.4(2)
C6	C5	C4	120.6(4)	O0AA	C22	O1	112.5(2)
C5	C6	C8	120.3(4)	O0AA	C22	C23	109.9(3)
N1	C7	C4	122.2(3)	O0AA	C22	C24	107.5(2)
N1	C7	C9	118.4(3)	C24	C22	C23	110.2(2)
C9	C7	C4	119.4(3)	F2	C23	C22	110.2(3)
C9	C8	C6	121.1(4)	F3	C23	F2	107.8(3)
C8	C9	C7	119.8(4)	F3	C23	F4	107.3(3)
C19	C10	C11	119.8(3)	F3	C23	C22	112.4(3)
C10	C11	C12	120.9(3)	F4	C23	F2	107.1(3)
C11	C12	C13	119.9(3)	F4	C23	C22	111.8(3)
C12	C13	N2	122.5(3)	C14	C24	C22	124.1(3)
C12	C13	C20	119.0(3)	C15	C25	C26	120.9(3)
C20	C13	N2	118.5(3)	C18	C26	C25	120.0(3)
N2	C14	C15	118.6(2)	C21	C27	Br2	114.6(2)
C24	C14	N2	117.6(2)	C28	C27	Br2	122.6(2)
C24	C14	C15	123.2(3)	C28	C27	C21	122.8(3)
C16	C15	C14	121.2(3)	C27	C28	C20	120.5(3)
C25	C15	C14	120.7(2)				

Table S7. Torsion Angles for 3k'.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C2	C3	C4	179.8(2)	C11	C10	C19	C20	0.9(6)
Br2	C27	C28	C20	179.6(2)	C11	C12	C13	N2	-174.4(3)
O1	C21	C27	Br2	75.4(2)	C11	C12	C13	C20	3.9(5)
O1	C21	C27	C28	-105.4(3)	C12	C13	C20	C19	-3.9(5)
O1	C22	C23	F2	-178.8(2)	C12	C13	C20	C28	174.6(3)
O1	C22	C23	F3	60.9(3)	C13	N2	C14	C15	61.6(3)
O1	C22	C23	F4	-59.9(3)	C13	N2	C14	C24	-127.4(3)
O1	C22	C24	C14	-2.5(4)	C13	N2	C21	O1	91.3(3)
O0AA	C22	C23	F2	-58.0(3)	C13	N2	C21	C27	-29.8(3)
O0AA	C22	C23	F3	-178.3(3)	C13	C20	C28	C27	-5.9(5)

O0AA	C22	C23	F4	60.9(3)	C14	N2	C13	C12	-6.4(4)
O0AA	C22	C24	C14	-126.9(3)	C14	N2	C13	C20	175.3(3)
N1	C1	C2	Br1	179.2(3)	C14	N2	C21	O1	-61.2(3)
N1	C1	C2	C3	-2.2(5)	C14	N2	C21	C27	177.7(2)
N1	C7	C9	C8	-178.0(3)	C14	C15	C16	C17	-176.4(3)
N2	C13	C20	C19	174.4(3)	C14	C15	C25	C26	177.1(3)
N2	C13	C20	C28	-7.0(4)	C15	C14	C24	C22	177.5(3)
N2	C14	C15	C16	-155.6(3)	C15	C16	C17	C18	-0.8(5)
N2	C14	C15	C25	26.9(4)	C15	C25	C26	C18	-0.6(5)
N2	C14	C24	C22	7.0(4)	C16	C15	C25	C26	-0.5(5)
N2	C21	C27	Br2	-162.51(19)	C16	C17	C18	C26	-0.3(5)
N2	C21	C27	C28	16.6(4)	C17	C18	C26	C25	1.0(5)
C1	N1	C7	C4	2.0(5)	C19	C10	C11	C12	-1.0(6)
C1	N1	C7	C9	-178.8(3)	C19	C20	C28	C27	172.6(3)
C1	C2	C3	C4	1.2(5)	C21	O1	C22	O0AA	89.0(3)
C2	C3	C4	C5	-180.0(3)	C21	O1	C22	C23	-152.0(2)
C2	C3	C4	C7	1.1(5)	C21	O1	C22	C24	-32.6(3)
C3	C4	C5	C6	-178.7(4)	C21	N2	C13	C12	-155.6(3)
C3	C4	C7	N1	-2.8(4)	C21	N2	C13	C20	26.1(4)
C3	C4	C7	C9	178.0(3)	C21	N2	C14	C15	-146.5(2)
C4	C5	C6	C8	0.4(6)	C21	N2	C14	C24	24.5(3)
C4	C7	C9	C8	1.2(5)	C21	C27	C28	C20	0.5(5)
C5	C4	C7	N1	178.2(3)	C22	O1	C21	N2	66.0(3)
C5	C4	C7	C9	-1.0(5)	C22	O1	C21	C27	-170.7(2)
C5	C6	C8	C9	-0.2(6)	C23	C22	C24	C14	113.4(3)
C6	C8	C9	C7	-0.6(5)	C24	C14	C15	C16	34.0(4)
C7	N1	C1	C2	0.5(5)	C24	C14	C15	C25	-143.6(3)
C7	C4	C5	C6	0.2(5)	C24	C22	C23	F2	60.3(3)
C10	C11	C12	C13	-1.4(5)	C24	C22	C23	F3	-60.0(3)
C10	C19	C20	C13	1.6(5)	C24	C22	C23	F4	179.2(3)
C10	C19	C20	C28	-176.9(4)	C25	C15	C16	C17	1.2(4)