A Povarov-Type Reaction to Access Tetrahydroquinolines from *N*-Benzylhydroxylamines and Alkenes in HFIP

Supporting Information

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1. General Remarks

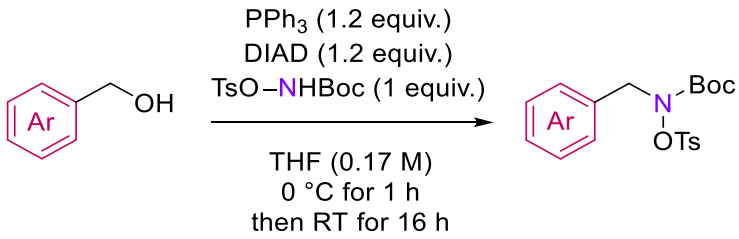
Materials: All commercial materials were purchased from Sigma-Aldrich, TCI and FluoroChem, and were used as received, without further purification. HFIP (CAS: 920-66-1) was purchased from FluoroChem. The other starting starting materials were prepared according to known protocols.

Reactions wert monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F_{254} with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm and/or by staining using potassium permanganate. Flash column chromatography (FC) was performed using silica gel 60 (230-400 mesh, Merck and co.). Yields refer to chromatographically and spectroscopically pure compounds. When stated, NMR yields were calculated by using mesitylene as an external standard.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{31}P NMR spectra were recorded using a Bruker UltraShield 400 or 500 at 300K. ^{1}H NMR chemical shifts are reported in ppm using residual solvent peak as reference ($CDCl_3$: δ = 7.26 ppm; CD_2Cl_2: 5.32 ppm; MeOD: 3.31 ppm). Data for ^{1}H NMR are presented as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant J (Hz) and integration; ^{13}C NMR spectra were recorded at 100, 126 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference ($CDCl_3$: δ = 77.16 ppm; CD_2Cl_2: 53.84 ppm; MeOD: 49.00 ppm). Multiplicity was defined by recorded a ^{13}C NMR spectra using the attached proton test (APT). ^{19}F NMR spectra were recorded at 471 MHz at ambient temperature. ^{31}P NMR spectra were recorded at 162 MHz at ambient temperature. High-resolution mass spectrometry (HRMS) analysis was performed on instruments GCT 1er Waters (EI and IC), MicroTOF-Q Bruker (ESI) and a GC Thermo Scientific Trace 1300 GC unit coupled to an APPI MasCom source mounted on a Thermo Scientific Exactive Plus EMR mass unit (Orbitrap FT-HRMS analyzer).

2. Synthesis of Hydroxylamine Reagents

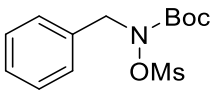
2.1 General procedure (A) for the Mitsunobu reaction to synthesize hydroxylamine reagents



To a stirring solution of triphenylphosphine (1.2 equiv.) and TsO–NHBoc (1.0 equiv.) in anhydrous THF (0.17 M) at 0 °C were added the corresponding benzylic alcohol (1.0 equiv.) and DIAD (1.2 equiv.). After stirring at 0 °C for 1 h, the reaction was allowed to warm to RT and was stirred for another 16 h. Upon completion, all volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (FC) over silica gel to furnish target hydroxylamine reagents **2a-2l**.

2.2 Characterization data of new hydroxylamine reagents 2a-2l

***tert-butyl benzyl((methylsulfonyl)oxy)carbamate* 2a**

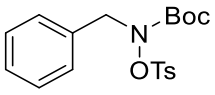


Chemical Formula: $C_{13}H_{19}NO_5S$
Exact Mass: 301.0984

General Procedure **A** was followed with MsO–NHBoc (1.10 g, 5.2 mmol, 1.0 equiv.), benzyl alcohol (560 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2a** (1.26 g, 4.2 mmol, 80% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.21 (m, 5H), 4.76 (brs, 2H), 3.02 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.3 (C), 134.7 (C), 129.0 (CH), 128.6 (CH), 128.3 (CH), 84.5 (C), 56.9 (CH_2), 36.9 (CH_3), 28.0 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{13}H_{19}NO_5SNa$ $[M+Na]^+$ 324.0876, found 324.0879.

***tert-butyl benzyl(tosyloxy)carbamate* 2b**

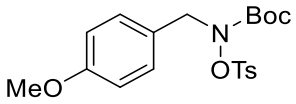


Chemical Formula: $C_{19}H_{23}NO_5S$
Exact Mass: 377.1297

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), benzyl alcohol (560 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2b** (1.48 g, 4.4 mmol, 85% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.34–7.28 (m, 5H), 4.79 (brs, 2H), 2.48 (s, 3H), 1.21 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.2 (C), 145.8 (C), 134.8 (C), 131.2 (C), 129.7 (CH), 129.6 (CH), 128.9 (CH), 128.5 (CH), 128.1 (CH), 83.5 (C), 56.3 (CH_2), 27.6 (CH_3), 21.8 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{19}H_{23}NO_5SNa$ $[M+Na]^+$ 400.1189, found 400.1185.

***tert-butyl (4-methoxybenzyl)(tosyloxy)carbamate* 2c**

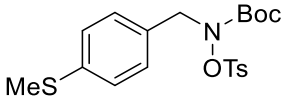


Chemical Formula: $C_{20}H_{25}NO_6S$
Exact Mass: 407.1403

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 4-methoxybenzyl alcohol (720 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 80/20) afforded **2c** (1.62 g, 4.0 mmol, 77% yield) as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 4.72 (brs, 2H), 3.81 (s, 3H), 2.48 (s, 3H), 1.21 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.5 (C), 155.3 (C), 145.7 (C), 131.3 (C), 130.6 (CH), 129.7 (CH), 129.5 (CH), 126.9 (C), 113.8 (CH), 83.4 (C), 55.8 (CH_2), 55.2 (CH_3), 27.6 (CH_3), 21.7 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{20}H_{25}NO_6SNa$ $[M+Na]^+$ 430.1295, found 430.1289.

***tert-butyl (4-(methylthio)benzyl)(tosyloxy)carbamate* 2d**



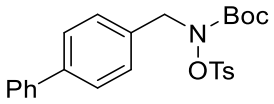
Chemical Formula: $C_{20}H_{25}NO_5S_2$
Exact Mass: 423.1174

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 4-methylthiobenzyl alcohol (800 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2d** (1.60 g, 3.8 mmol, 73% yield) as a bright brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.26–7.19 (m, 4H), 4.75 (brs, 2H), 2.49 (s, 3H), 2.48 (s, 3H), 1.21 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):**

δ 155.2 (C), 145.8 (C), 138.5 (C), 131.5 (C), 131.2 (C), 129.7 (CH), 129.6 (CH), 129.5 (CH), 126.5 (CH), 83.6 (C), 55.8 (CH_2), 27.6 (CH_3), 21.7 (CH_3), 15.7 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{20}H_{25}NO_5S_2K$ $[M+K]^+$ 462.0806, found 462.0799.

***tert-butyl ([1,1'-biphenyl]-4-ylmethyl)(tosyloxy)carbamate* 2e**

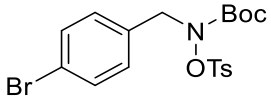


Chemical Formula: $C_{25}H_{27}NO_5S$
Exact Mass: 453.1610

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 4-phenylbenzyl alcohol (960 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2e** (2.10 g, 4.6 mmol, 88% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.3 Hz, 2H), 7.59–7.53 (m, 4H), 7.44 (ddd, J = 7.8, 6.5, 1.2 Hz, 2H), 7.39–7.34 (m, 5H), 4.82 (brs, 2H), 2.45 (s, 3H), 1.21 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.4 (C), 145.9 (C), 141.1 (C), 140.8 (C), 134.0 (C), 131.4 (C), 129.9 (CH), 129.7 (CH), 129.6 (CH), 128.9 (CH), 127.5 (C), 127.4 (CH), 127.2 (CH), 83.7 (C), 56.1 (CH_2), 27.7 (CH_3), 21.8 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{25}H_{27}NO_5SNa$ $[M+Na]^+$ 476.1502, found 476.1501.

***tert-butyl (4-bromobenzyl)(tosyloxy)carbamate* 2f**

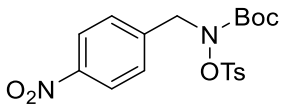


Chemical Formula: $C_{19}H_{22}BrNO_5S$
Exact Mass: 455.0402

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 4-bromobenzyl alcohol (970 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2f** (1.77 g, 3.9 mmol, 75% yield) as a bright purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 4.65 (brs, 2H), 2.38 (s, 3H), 1.11 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.1 (C), 145.9 (C), 133.8 (C), 131.7 (CH), 131.1 (C), 130.8 (CH), 129.7 (CH), 129.6 (CH), 122.3 (C), 83.8 (C), 55.7 (CH_2), 27.6 (CH_3), 21.8 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{19}H_{22}NO_5BrSNa$ $[M+Na]^+$ 478.0294, found 478.0299.

***tert-butyl (4-nitrobenzyl)(tosyloxy)carbamate* 2g**

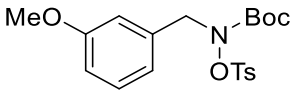


Chemical Formula: $C_{20}H_{25}NO_5S_2$
Exact Mass: 423.1174

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 4-nitrobenzyl alcohol (795 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2g** (2.00 g, 4.8 mmol, 92% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.87 (s, 2H), 2.45 (s, 3H), 1.17 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.0 (C), 147.7 (C), 146.3 (C), 142.3 (C), 130.9 (C), 129.8 (2CH), 129.7 (CH), 123.8 (CH), 84.3 (C), 55.6 (CH_2), 27.6 (CH_3), 21.8 (CH_3).

***tert-butyl (3-methoxybenzyl)(tosyloxy)carbamate* 2h**

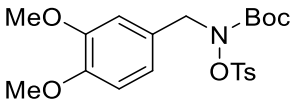


Chemical Formula: $C_{20}H_{25}NO_6S$
Exact Mass: 407.1403

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 3-methoxybenzyl alcohol (720 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.25 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.25 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2h** (1.75 g, 4.3 mmol, 83% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.26–7.21 (m, 1H), 6.91–6.87 (m, 1H), 6.86–6.83 (m, 2H), 4.77 (brs, 2H), 3.80 (s, 3H), 2.48 (s, 3H), 1.23 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.7 (C), 155.2 (C), 145.7 (C), 136.3 (C), 131.3 (C), 129.7 (CH), 129.6 (CH), 129.5 (CH), 121.2 (CH), 114.1 (CH), 113.9 (CH), 83.5 (C), 56.2 (CH_2), 55.2 (CH_3), 27.6 (CH_3), 21.7 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{20}H_{25}NO_6SNa$ $[M+Na]^+$ 430.1295, found 430.1310.

***tert-butyl (3,4-dimethoxybenzyl)(tosyloxy)carbamate* 2i**

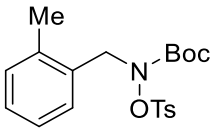


Chemical Formula: $C_{21}H_{27}NO_7S$
Exact Mass: 437.1508

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 3,4-dimethoxybenzyl alcohol (870 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2i** (1.61 g, 3.7 mmol, 71% yield) as a dark brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.83–6.71 (m, 3H), 4.67 (brs, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.39 (s, 3H), 1.12 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.4 (C), 148.9 (C), 148.8 (C), 145.7 (C), 131.2 (C), 129.7 (CH), 129.5 (CH), 127.2 (CH), 122.0 (CH), 112.1 (CH), 110.8 (CH), 83.4 (C), 56.1 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 27.6 (CH_3), 21.7 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{21}H_{28}NO_7S$ $[M+H]^+$ 438.1581, found 438.1586.

***tert-butyl (2-methylbenzyl)(tosyloxy)carbamate* 2j**

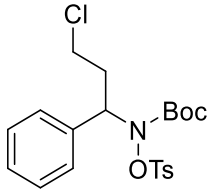


Chemical Formula: $C_{20}H_{25}NO_5S$
Exact Mass: 391.1453

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 2-methylbenzyl alcohol (635 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2j** (1.83 g, 4.7 mmol, 90% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.13–7.03 (m, 4H), 4.78 (brs, 2H), 2.38 (s, 3H), 2.25 (s, 3H), 1.14 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.3 (C), 145.7 (C), 136.6 (C), 133.3 (C), 131.2 (C), 130.5 (CH), 129.7 (CH), 129.6 (CH), 128.4 (CH), 127.8 (CH), 126.0 (CH), 83.5 (C), 53.4 (CH_2), 27.6 (CH_3), 21.7 (CH_3), 19.4 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{20}H_{26}NO_5S$ $[M+H]^+$ 392.1526, found 392.1524.

***tert-butyl (3-chloro-1-phenylpropyl)(tosyloxy)carbamate* 2k**



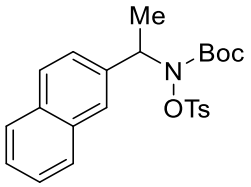
Chemical Formula: $C_{21}H_{26}ClNO_5S$
Exact Mass: 439.1220

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 3-chloro-1-phenylpropan-1-ol (880 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.25 mmol, 1.2 equiv.), and

DIAD (1.22 mL, 6.25 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2k** (1.49 g, 3.4 mmol, 65% yield) as a dark brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.28–7.21 (m, 7H), 5.20 (brs, 1H), 3.74-3.63 (m, 1H), 3.48-3.39 (m, 1H), 2.74-2.65 (m, 1H), 2.36 (s, 3H), 2.35–2.25 (m, 1H), 1.10 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.9 (C), 145.8 (C), 136.7 (C), 131.5 (C), 129.6 (CH), 129.5 (CH), 128.5 (2CH), 128.4 (CH), 84.0 (C), 42.1 (CH_2), 35.0 (CH_2), 27.5 (CH_3), 21.7 (CH_3), one CH unobserved. **HRMS (ESI):** *m/z* calcd. for $C_{21}H_{26}NO_5ClSNa$ $[M+Na]^+$ 462.1112, found 462.1102.

***tert-butyl (1-(naphthalen-2-yl)ethyl)(tosyloxy)carbamate* 2l**



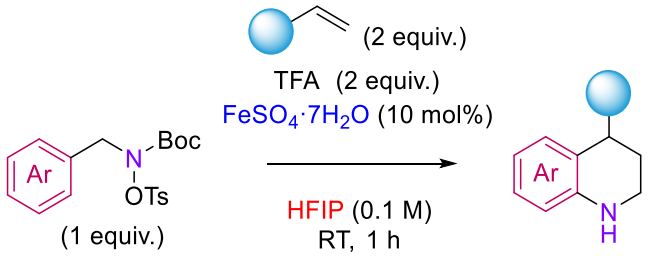
Chemical Formula: $C_{24}H_{27}NO_5S$
Exact Mass: 441.1610

General Procedure **A** was followed with TsO–NHBoc (1.50 g, 5.2 mmol, 1.0 equiv.), 1-(naphthalen-2-yl)ethan-1-ol (895 mg, 5.2 mmol, 1.0 equiv.), PPh_3 (1.63 g, 6.2 mmol, 1.2 equiv.), and DIAD (1.22 mL, 6.2 mmol, 1.2 equiv.) in THF (30 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **2l** (1.19 g, 2.7 mmol, 52% yield) as a bright purple solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91–7.84 (m, 3H), 7.82–7.69 (m, 3H), 7.53–7.50 (m, 2H), 7.47 (dd, J = 8.5, 1.8 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 5.25 (q, J = 7.0 Hz, 1H), 2.37 (s, 3H), 1.64 (d, J = 7.0 Hz, 3H), 1.15 (s, 9H). **^{13}C NMR (100 MHz, DMSO-d_6):** δ 160.5 (C), 151.1 (C), 142.0 (C), 137.9 (C), 137.7 (C), 136.2 (C), 135.0 (CH), 134.3 (CH), 133.1 (CH), 133.0 (CH), 132.6 (CH), 131.4 (CH), 131.4 (CH), 131.2 (CH), 130.7 (CH), 88.6 (C), 68.1 (CH), 32.4 (CH_3), 26.3 (CH_3), 22.5 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{24}H_{27}NO_5SNa$ $[M+Na]^+$ 464.1502, found 464.1486.

3. Synthesis of Tetrahydroquinolines

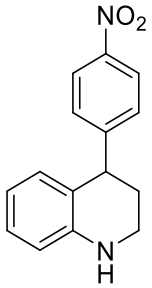
3.1 General procedure (B) for the synthesis of tetrahydroquinolines



A 5 ml vial equipped with a Teflon-coated magnetic stir bar was charged with $FeSO_4·7H_2O$ (10 mol%) under air and HFIP (0.1 M) was added. The mixture was purged by argon bubbling through the solution for 5 min. Then, hydroxylamine reagent (1 equiv.), alkene (2 equiv.) and TFA (2 equiv.) were sequentially added. The reaction mixture was stirred at RT for 1 h while maintaining the bubbling of argon though the solution. Upon completion, the reaction mixture was quenched with a solution of sat. $NaHCO_3$ (10 mL) and then extracted with DCM (10 mL × 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (FC) over silica gel to furnish the target products **3-25**.

3.2 Characterization data of tetrahydroquinolines 3-25

***4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 3**



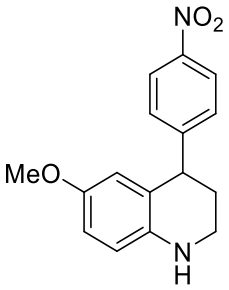
Chemical Formula: $C_{15}H_{14}N_2O_2$
Exact Mass: 254.1055

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2b** (75.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4·7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **3** (31.0 mg, 0.12 mmol, 60% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 6.99–6.94 (m, 1H), 6.60 (d, J = 7.4 Hz, 1H), 6.52–6.47 (m, 2H), 4.19 (t, J = 6.0 Hz, 1H), 3.93 (brs, 1H), 3.24 (ddd, J = 10.9, 6.9, 3.6 Hz, 1H), 3.11 (ddd, J = 11.7, 8.5, 3.4 Hz, 1H), 2.22–2.14 (m, 1H),

1.99–1.91 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.5 (C), 146.5 (C), 144.9 (C), 130.3 (CH), 129.5 (CH), 128.0 (CH), 123.6 (CH), 121.5 (C), 117.3 (CH), 114.5 (CH), 42.8 (CH), 38.8 (CH_2), 30.9 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{15}H_{15}N_2O_2$ $[M+H]^+$ 255.1134, found 255.1177.

***6-methoxy-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 5**

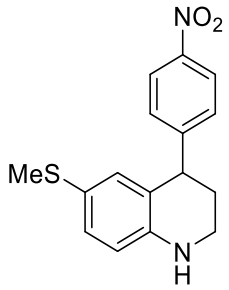


Chemical Formula: $C_{16}H_{16}N_2O_3$
Exact Mass: 284.1161

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2c** (81.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **5** (38.0 mg, 0.13 mmol, 67% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 6.61 (dd, J = 8.7, 2.8 Hz, 1H), 6.49 (d, J = 8.7 Hz, 1H), 6.19 (d, J = 2.8 Hz, 1H), 4.18 (t, J = 6.2 Hz, 1H), 3.69 (s, 1H), 3.55 (s, 3H), 3.24–3.18 (m, 1H), 3.13–3.07 (m, 1H), 2.23-2.15 (m, 1H), 1.98-1.90 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.4 (C), 151.9 (C), 146.5 (C), 139.1 (C), 129.5 (CH), 123.7 (CH), 122.8 (C), 115.9 (CH), 115.4 (CH), 114.4 (CH), 55.7 (CH_3), 43.1 (CH), 39.3 (CH_2), 31.4 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1234, found 285.1229.

***6-(methylthio)-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 6**



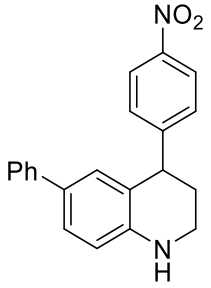
Chemical Formula: $C_{16}H_{16}N_2O_2S$
Exact Mass: 300.0932

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2d** (85.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica

gel (pentane/EtOAc: 100/0 to 85/15) afforded **6** (35.0 mg, 0.12 mmol, 58% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.02 (dd, J = 8.4, 2.1 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 4.17 (t, J = 5.9 Hz, 1H), 3.96 (s, 1H), 3.29-3.20 (m, 1H), 3.12 (ddd, J = 11.8, 8.7, 3.4 Hz, 1H), 2.25 (s, 3H), 2.20–2.14 (m, 1H), 2.00-1.90 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.9 (C), 146.6 (C), 143.7 (C), 132.2 (CH), 130.2 (CH), 129.5 (CH), 124.1 (C), 123.7 (CH), 122.1 (C), 115.2 (CH), 42.7 (CH), 38.7 (CH_2), 30.7 (CH_2), 19.1 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{16}H_{17}N_2O_2S$ $[M+H]^+$ 301.1005, found 301.0996.

***4-(4-nitrophenyl)-6-phenyl-1,2,3,4-tetrahydroquinoline* 7**

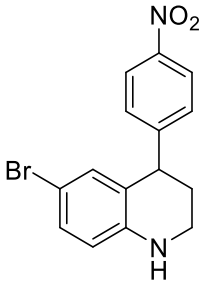


Chemical Formula: $C_{21}H_{18}N_2O_2$
Exact Mass: 330.1368

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2e** (91.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **7** (45.0 mg, 0.136 mmol, 68% yield) as a yellow oil.

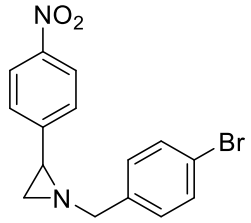
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 2H), 7.43–7.39 (m, 2H), 7.36–7.30 (m, 5H), 7.24–7.19 (m, 1H), 6.97–6.95 (m, 1H), 6.66 (d, J = 8.3 Hz, 1H), 4.34 (t, J = 5.9 Hz, 1H), 4.14 (brs, 1H), 3.36 (ddd, J = 10.6, 6.8, 3.5 Hz, 1H), 3.22 (ddd, J = 11.8, 8.7, 3.4 Hz, 1H), 2.34–2.27 (m, 1H), 2.12–2.03 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.3 (C), 146.7 (C), 144.5 (C), 141.1 (C), 130.4 (C), 129.6 (CH), 128.9 (CH), 128.7 (CH), 126.9 (CH), 126.3 (CH), 126.2 (CH), 123.8 (CH), 121.8 (C), 115.0 (CH), 43.0 (CH), 38.9 (CH_2), 31.0 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 331.1441, found 331.1443.

***6-bromo-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 8**



Chemical Formula: $C_{15}H_{13}BrN_2O_2$
Exact Mass: 332.0160

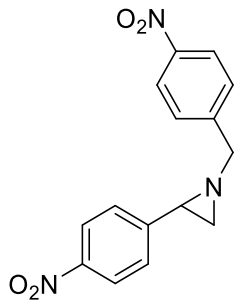
General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2f** (91.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **8** in mixture with aziridine **8'** (ratio 10:1, 33.0 mg, 0.10 mmol, 50% global yield, 46% corrected yield for **8**) as a yellow oil.



Chemical Formula: $C_{15}H_{13}BrN_2O_2$
Exact Mass: 332.0160

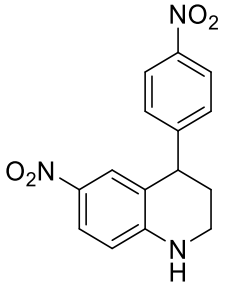
8: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.05 (dd, J = 8.6, 2.2 Hz, 1H), 6.72 (d, J = 2.2 Hz, 1H), 6.39 (d, J = 8.6 Hz, 1H), 4.15 (t, J = 5.9 Hz, 1H), 3.97 (s, 1H), 3.24 (ddd, J = 10.7, 6.6, 3.6 Hz, 1H), 3.10 (ddd, J = 11.9, 8.7, 3.4 Hz, 1H), 2.19–2.10 (m, 1H), 2.00-1.90 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.4 (C), 146.7 (C), 143.8 (C), 132.5 (CH), 130.8 (CH), 129.4 (CH), 123.8 (CH), 123.4 (C), 116.0 (CH), 108.5 (C), 42.6 (CH), 38.6 (CH_2), 30.4 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{15}H_{14}N_2O_2Br$ $[M+H]^+$ 333.0233, found 333.0226.

***1-(4-nitrobenzyl)-2-(4-nitrophenyl)aziridine* 9'**



Chemical Formula: $C_{15}H_{13}N_3O_4$
Exact Mass: 299.0906

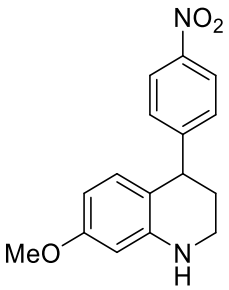
General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2g** (85.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 40/60) afforded **9'** in mixture with 1,2,3,4-tetrahydroquinoline **9** (ratio 5:1, 24.0 mg, 0.08 mmol, 40% global yield, 7% corrected yield for **9**) as a yellow oil.



Chemical Formula: $C_{15}H_{13}N_3O_4$
Exact Mass: 299.0906

9': ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (m, 4H), 7.53 (d, J = 8.9 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 3.84 (d, J = 14.8 Hz, 1H), 3.71 (d, J = 14.8 Hz, 1H), 2.61 (dd, J = 6.5, 3.2 Hz, 1H), 2.06 (d, J = 3.2 Hz, 1H), 2.01 (d, J = 6.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.6 (2C), 146.3 (2C), 128.4 (CH), 126.9 (CH), 123.9 (CH), 123.8 (CH), 63.7 (CH_2), 40.9 (CH), 39.5 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{15}H_{14}N_3O_4$ $[M+H]^+$ 300.0979, found 300.0962.

***7-methoxy-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 10**

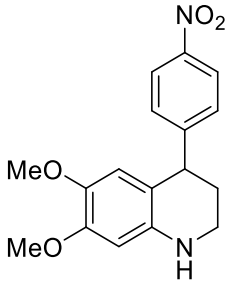


Chemical Formula: $C_{16}H_{16}N_2O_3$
Exact Mass: 284.1161

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2h** (81.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **10** (29.0 mg, 0.10 mmol, 50% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.51 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.11 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.05 (d, *J* = 2.5 Hz, 1H), 4.14 (t, *J* = 6.0 Hz, 1H), 3.68 (s, 3H), 3.26–3.20 (m, 1H), 3.14–3.08 (m, 1H), 2.21–2.15 (m, 1H), 1.98–1.92 (m, 1H), NH unobserved. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.6 (C), 154.7 (C), 146.5 (C), 145.8 (C), 131.1 (CH), 129.4 (CH), 123.6 (CH), 114.4 (C), 103.6 (CH), 99.3 (CH), 55.1 (CH_3), 42.2 (CH), 38.8 (CH_2), 31.1 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1234, found 285.1231.

***6,7-dimethoxy-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 11**

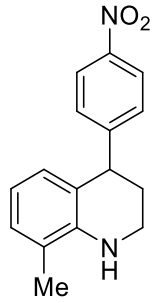


Chemical Formula: $C_{17}H_{18}N_2O_4$
Exact Mass: 314.1267

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2i** (87.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **11** (34.0 mg, 0.11 mmol, 54% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.15 (s, 1H), 6.12 (s, 1H), 4.14 (t, *J* = 5.9 Hz, 1H), 3.77 (s, 3H), 3.68 (brs, 1H), 3.57 (s, 3H), 3.18 (ddd, *J* = 10.2, 6.7, 3.4 Hz, 1H), 3.07 (ddd, *J* = 11.7, 8.9, 3.1 Hz, 1H), 2.25-2.15 (m, 1H), 1.95-1.85 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.9 (C), 149.2 (C), 146.5 (C), 141.7 (C), 139.2 (C), 129.4 (CH), 123.6 (CH), 114.0 (CH), 112.6 (C), 99.4 (CH), 56.6 (CH_3), 55.8 (CH_3), 42.3 (CH), 38.9 (CH_2), 31.6 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{17}H_{19}N_2O_4$ $[M+H]^+$ 315.1339, found 315.1333.

***8-methyl-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 12**

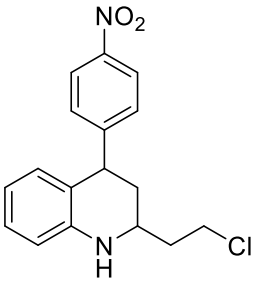


Chemical Formula: $C_{16}H_{16}N_2O_2$
Exact Mass: 268.1212

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2j** (78.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **12** (34.0 mg, 0.13 mmol, 63% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 6.91–6.87 (m, 1H), 6.53–6.43 (m, 2H), 4.22 (t, J = 6.0 Hz, 1H), 3.76 (s, 1H), 3.31 (ddd, J = 10.7, 6.7, 3.6 Hz, 1H), 3.18 (ddd, J = 11.8, 8.7, 3.3 Hz, 1H), 2.24-2.14 (m, 1H), 2.07 (s, 3H), 2.01-1.91 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.7 (C), 146.4 (C), 142.9 (C), 129.5 (CH), 129.0 (CH), 128.2 (CH), 123.6 (CH), 121.5 (C), 121.0 (C), 116.6 (CH), 43.0 (CH), 39.0 (CH_2), 30.8 (CH_2), 17.4 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1285, found 269.1285.

***2-(2-chloroethyl)-4-(4-nitrophenyl)-1,2,3,4-tetrahydroquinoline* 13**



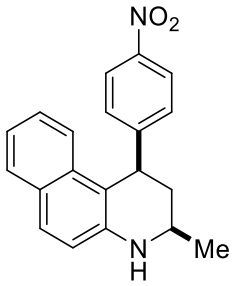
Chemical Formula: $C_{17}H_{17}ClN_2O_2$
Exact Mass: 316.0979

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2k** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **13** (35.0 mg, 0.11 mmol, 55% yield, *cis/trans* 5:1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, major): δ 8.11 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 6.98–6.93 (m, 1H), 6.50 (ddd, J = 14.0, 7.7, 1.0 Hz, 2H), 6.42 (d, J = 7.7 Hz, 1H), 4.25 (dd, J = 12.1,

5.5 Hz, 1H), 3.92 (s, 1H), 3.71–3.51 (m, 3H), 2.14 (ddd, *J* = 12.8, 5.6, 2.4 Hz, 1H), 1.97–1.92 (m, 2H), 1.83–1.74 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$, major):** δ 153.6 (C), 146.8 (C), 144.9 (C), 129.5 (2CH), 127.8 (CH), 124.0 (CH), 123.3 (C), 118.2 (CH), 115.0 (CH), 49.6 (CH), 44.1 (CH), 41.3 (CH_2), 38.9 (CH_2), 38.7 (CH_2). **HRMS (ESI):** *m/z* calcd. for $C_{17}H_{18}N_2O_2Cl$ $[M+H]^+$ 317.1051, found 317.1070.

***3-methyl-1-(4-nitrophenyl)-1,2,3,4-tetrahydrobenzo[f]quinoline* 14**

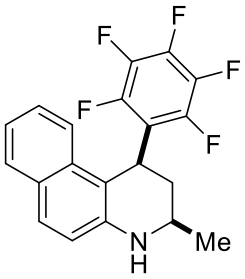


Chemical Formula: $C_{20}H_{18}N_2O_2$
Exact Mass: 318.1368

General Procedure **B** was followed with 4-nitrostyrene (59.8 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **14** (40.0 mg, 0.12 mmol, 62% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.59–7.56 (m, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.06-6.96 (m, 3H), 6.80 (d, *J* = 8.7 Hz, 1H), 4.65 (dd, *J* = 10.0, 7.9 Hz, 1H), 3.88 (s, 1H), 3.36 (dtt, *J* = 12.6, 6.3, 3.2 Hz, 1H), 2.40 (ddd, *J* = 13.3, 7.8, 2.5 Hz, 1H), 1.69-1.59 (m, 1H), 1.12 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.3 (C), 146.1 (C), 144.9 (C), 132.7 (C), 128.9 (CH), 128.8 (C), 128.6 (CH), 128.1 (CH), 126.2 (CH), 124.1 (CH), 123.4 (CH), 121.8 (CH), 118.6 (CH), 112.5 (C), 47.1 (CH), 43.9 (CH_2), 41.2 (CH), 22.0 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{20}H_{19}N_2O_2$ $[M+H]^+$ 319.1441, found 319.1444.

***3-methyl-1-(perfluorophenyl)-1,2,3,4-tetrahydrobenzo[f]quinoline* 15**

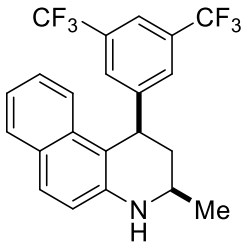


Chemical Formula: $C_{20}H_{14}F_5N$
Exact Mass: 363.1046

General Procedure **B** was followed with 2,3,4,5,6-pentafluorostyrene (77.6 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **15** (43.0 mg, 0.12 mmol, 59% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.16–7.04 (m, 3H), 6.78 (d, J = 8.7 Hz, 1H), 4.93 (dd, J = 10.5, 8.4 Hz, 1H), 3.57 (brs, 1H), 3.32 (dtt, J = 12.4, 6.1, 3.1 Hz, 1H), 2.38 (ddd, J = 12.9, 8.1, 2.1 Hz, 1H), 1.77 (q, J = 11.3 Hz, 1H), 1.22 (d, J = 6.2 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.6 (dm, J = 245 Hz, C), 144.2 (C), 139.6 (dm, J = 251 Hz, C), 137.6 (dm, J = 249 Hz, C), 132.3 (C), 128.9 (CH), 128.7 (C), 128.6 (CH), 126.4 (CH), 121.9 (CH), 121.2 (CH), 120.9 (m, C), 118.5 (CH), 111.9 (C), 47.3 (CH), 40.3 (CH_2), 30.9 (CH), 21.6 (CH_2). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -157.7 (t, J = 21.0 Hz), -162.2 (brs). **HRMS (ESI):** *m/z* calcd. for $C_{20}H_{15}NF_5$ $[M+H]^+$ 364.1119, found 364.1113.

***1-(3,5-bis(trifluoromethyl)phenyl)-3-methyl-1,2,3,4-tetrahydrobenzo[f]quinoline* 16**

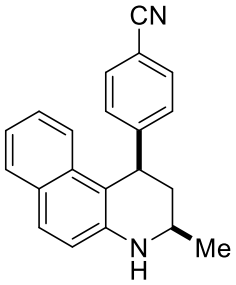


Chemical Formula: $C_{22}H_{17}F_6N$
Exact Mass: 409.1265

General Procedure **B** was followed with 3,5-bis(trifluoromethyl)styrene (96.0 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.2 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **16** (50.0 mg, 0.12 mmol, 61% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.57 (m, 2H), 7.55 (d, J = 8.8 Hz, 1H), 7.43 (s, 2H), 7.08–7.02 (m, 2H), 6.98–6.94 (m, 1H), 6.83 (d, J = 8.8 Hz, 1H), 4.69 (dd, J = 10.0, 7.9 Hz, 1H), 3.95 (brs, 1H), 3.42–3.36 (m, 1H), 2.44 (ddd, J = 13.4, 7.8, 2.5 Hz, 1H), 1.71–1.64 (m, 1H), 1.14 (d, J = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.8 (C), 144.9 (C), 132.5 (C), 131.8 (q, J = 33.0 Hz, C), 129.2 (CH), 128.9 (C), 128.7 (CH), 127.4 (m, CH), 126.3 (CH), 123.4 (q, J = 271.0 Hz, C), 123.2 (CH), 121.9 (CH), 120.0 (m, CH), 118.6 (CH), 11.8 (C), 47.1 (CH), 44.2 (CH_2), 41.1 (CH), 22.0 (CH_3). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.7. **HRMS (ESI):** *m/z* calcd. for $C_{22}H_{18}NF_6$ $[M+H]^+$ 410.1338, found 410.1332.

***3-methyl-1,2,3,4-tetrahydrobenzo[f]quinolin-1-yl)benzonitrile* 17**

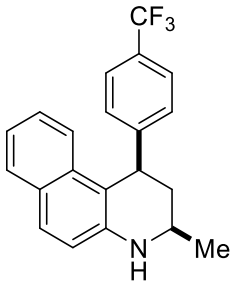


Chemical Formula: $C_{21}H_{18}N_2$
Exact Mass: 298.1470

General Procedure **B** was followed with 4-cyanostyrene (51.6 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 80/20) afforded **17** (45.0 mg, 0.150 mmol, 75% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.55 (m, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 7.06-6.96 (m, 3H), 6.80 (d, J = 8.8 Hz, 1H), 4.60 (dd, J = 10.0, 7.8 Hz, 1H), 3.89 (s, 1H), 3.41–3.32 (m, 1H), 2.40 (ddd, J = 13.3, 7.8, 2.5 Hz, 1H), 1.69–1.61 (m, 1H), 1.12 (d, J = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.0 (C), 144.9 (C), 132.7 (C), 132.6 (CH), 128.8 (CH), 128.7 (C), 128.6 (CH), 128.1 (CH), 126.1 (CH), 123.5 (CH), 121.8 (CH), 119.1 (C), 118.5 (CH), 112.5 (C), 109.6 (C), 47.1 (CH), 43.9 (CH_2), 41.4 (CH), 22.0 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1543, found 299.1537.

***3-methyl-1-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydrobenzo[f]quinoline* 18**

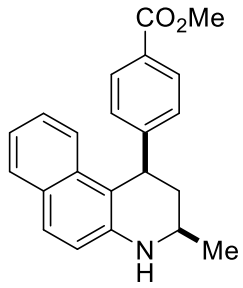


Chemical Formula: $C_{21}H_{18}F_3N$
Exact Mass: 341.1391

General Procedure **B** was followed with 4-trifluoromethylstyrene (69.0 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **18** (53.0 mg, 0.154 mmol, 77% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.54 (m, 1H), 7.53–7.49 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.12–6.98 (m, 5H), 6.80 (d, *J* = 8.7 Hz, 1H), 4.60 (dd, *J* = 9.9, 7.9 Hz, 1H), 3.83 (s, 1H), 3.40–3.31 (m, 1H), 2.39 (ddd, *J* = 13.3, 7.8, 2.6 Hz, 1H), 1.72–1.63 (m, 1H), 1.11 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.4 (C), 144.8 (C), 132.9 (C), 128.8 (C), 128.7 (CH), 128.5 (CH), 128.0 (q, *J* = 32 Hz, C), 127.6 (CH), 126.0 (CH), 125.7 (q, *J* = 3.2 Hz, CH), 124.4 (q, *J* = 270 Hz, C), 123.8 (CH), 121.7 (CH), 118.5 (CH), 113.2 (C), 47.1 (CH), 44.2 (CH_2), 41.1 (CH), 22.1 (CH_3). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.2. **HRMS (ESI):** *m/z* calcd. for $C_{21}H_{19}NF_3$ $[M+H]^+$ 342.1464, found 342.1466.

***methyl 4-(3-methyl-1,2,3,4-tetrahydrobenzo[f]quinolin-1-yl)benzoate* 19**

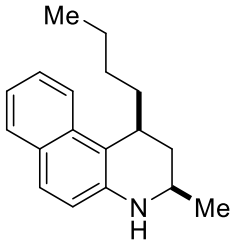


Chemical Formula: $C_{22}H_{21}NO_2$
Exact Mass: 331.1572

General Procedure **B** was followed with methyl 4-vinylbenzoate (65.0 mg, 0.40 mmol. 2 equiv.), hydroxylamine **2l** (88.0 mg, 0.2 mmol, 1 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 80/20) afforded **19** (53.0 mg, 0.160 mmol, 80% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.66–7.62 (m, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.18–7.05 (m, 5H), 6.88 (d, *J* = 8.8 Hz, 1H), 4.68 (dd, *J* = 10.0, 7.8 Hz, 1H), 3.92 (s, 1H), 3.86 (s, 3H), 3.50–3.41 (m, 1H), 2.49 (ddd, *J* = 13.3, 7.7, 2.5 Hz, 1H), 1.82–1.74 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.4 (C), 154.1 (C), 145.0 (C), 133.2 (C), 130.3 (CH), 129.0 (C), 128.8 (CH), 128.6 (CH), 127.9 (C), 127.6 (CH), 126.1 (CH), 124.0 (CH), 121.9 (CH), 118.7 (CH), 113.6 (C), 52.2 (CH_3), 47.4 (CH), 44.3 (CH_2), 41.6 (CH), 22.3 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{22}H_{22}NO_2$ $[M+H]^+$ 332.1645, found 332.1650.

***1-butyl-3-methyl-1,2,3,4-tetrahydrobenzo[f]quinoline* 22**

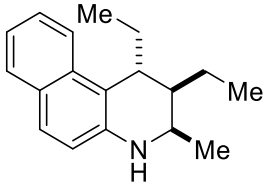


Chemical Formula: $C_{18}H_{23}N$
Exact Mass: 253.1830

General Procedure **B** was followed with 1-hexene (34.0 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **22** (35.0 mg, 0.14 mmol, 69% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.6 Hz, 1H), 7.61 (dd, J = 8.1, 1.3 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.33 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.14 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 6.74 (d, J = 8.6 Hz, 1H), 3.72 (brs, 1H), 3.38 (q, J = 8.6 Hz, 1H), 3.18-3.08 (m, 1H), 2.30 (ddd, J = 13.3, 8.5, 3.4 Hz, 1H), 1.95–1.84 (m, 1H), 1.59–1.51 (m, 1H), 1.40–1.23 (m, 5H), 1.21 (d, J = 6.3 Hz, 3H), 0.82 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.8 (C), 132.7 (C), 129.0 (C), 128.7 (CH), 127.0 (CH), 125.8 (CH), 122.5 (CH), 121.6 (CH), 118.6 (C), 118.5 (CH), 47.6 (CH), 39.5 (CH_2), 37.5 (CH_2), 32.3 (CH), 29.5 (CH_2), 22.9 (CH_2), 22.7 (CH_3), 14.2 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{18}H_{24}N$ $[M+H]^+$ 254.1903, found 254.1899.

***1,2-diethyl-3-methyl-1,2,3,4-tetrahydrobenzo[f]quinoline* 23**



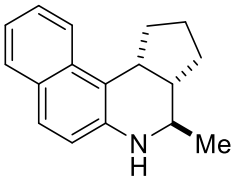
Chemical Formula: $C_{18}H_{23}N$
Exact Mass: 253.1830

General Procedure **B** was followed with *trans*-3-hexene (34.0 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **23** (36.0 mg, 0.14 mmol, 70% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.6 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.38 (d, J = 8.7 Hz, 1H), 7.31 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 8.7 Hz, 1H), 3.80-3.50 (m, 2H), 3.05 (d, J = 10.0 Hz, 1H), 1.88 (dtt, J = 15.1, 7.5, 3.8 Hz, 1H), 1.53–

1.36 (m, 3H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.88-0.77 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.8 (C), 133.8 (C), 128.8 (CH), 128.3 (C), 127.3 (CH), 126.2 (CH), 121.5 (CH), 121.2 (CH), 117.8 (CH), 114.7 (C), 44.8 (CH), 39.3 (CH), 38.1 (CH), 29.5 (CH_2), 19.1 (CH_3), 18.5 (CH_2), 12.5 (CH_3), 12.2 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{18}H_{24}N$ $[M+H]^+$ 254.1903, found 254.1889.

***4-methyl-2,3,3a,4,5,11c-hexahydro-1H-benzo[f]cyclopenta[c]quinoline* 24 and 24'**



Chemical Formula: $C_{17}H_{19}N$
Exact Mass: 237.1517
major

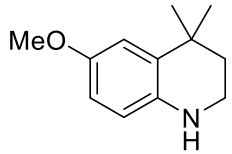
Chemical Formula: $C_{17}H_{19}N$
Exact Mass: 237.1517
minor

General Procedure **B** was followed with cyclopentene (28.0 mg, 0.40 mmol, 2.0 equiv.), hydroxylamine **2l** (88.0 mg, 0.20 mmol, 1 equiv.), TFA (32.0 µL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL). Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **24** (30.0 mg, 0.13 mmol, 63% yield) as a colorless oil and **24'** (14.0 mg, 0.06 mmol, 29% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, major): δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.32 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.14–7.07 (m, 1H), 6.71 (d, *J* = 8.7 Hz, 1H), 3.84 (brs, 1H), 3.35-3.27 (m, 1H), 3.00-2.92 (m, 1H), 2.57–2.49 (m, 1H), 1.97–1.82 (m, 2H), 1.70–1.60 (m, 3H), 1.40–1.32 (m, 1H), 1.17 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$, major):** δ 140.9 (C), 133.8 (C), 128.5 (CH), 128.0 (C), 127.2 (CH), 126.1 (CH), 122.3 (CH), 121.4 (CH), 117.8 (CH), 115.9 (C), 47.3 (CH), 42.6 (CH), 39.1 (CH), 34.2 (CH_2), 28.2 (CH_2), 22.8 (CH_2), 20.4 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{17}H_{20}N$ $[M+H]^+$ 238.1590, found 238.1601.

^{1}H NMR (400 MHz, $CDCl_3$, minor): δ 7.76–7.72 (m, 1H), 7.62–7.58 (m, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.33 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.15 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 1H), 3.79–3.70 (m, 1H), 3.47 (brs, 1H), 3.34–3.26 (m, 1H), 2.45–2.34 (m, 2H), 1.66–1.38 (m, 5H), 1.18 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$, minor):** δ 143.0 (C), 133.1 (C), 129.0 (C), 128.6 (CH), 126.6 (CH), 125.8 (CH), 123.1 (CH), 121.8 (CH), 119.9 (C), 118.3 (CH), 49.4 (CH), 46.5 (CH), 37.2 (CH), 35.9 (CH_2), 25.4 (CH_2), 25.3 (CH_2), 20.0 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{17}H_{20}N$ $[M+H]^+$ 238.1590, found 238.1601.

***6-methoxy-4,4-dimethyl-1,2,3,4-tetrahydroquinoline* 25**

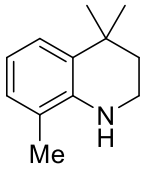


Chemical Formula: $C_{12}H_{17}NO$
Exact Mass: 191.1310

The modified general procedure **B** was followed with hydroxylamine **2c** (81.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL) without the addition of alkene and purging with Ar. Purification by FC over silica gel (pentane/EtOAc: 100/0 to 85/15) afforded **25** (37.0 mg, 0.19 mmol, 95% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (d, J = 2.9 Hz, 1H), 6.52 (dd, J = 8.6, 2.9 Hz, 1H), 6.38 (d, J = 8.6 Hz, 1H), 3.67 (s, 3H), 3.32 (brs, 1H), 3.18 (s, 2H), 1.67 (dd, J = 6.4, 5.0 Hz, 2H), 1.22 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.9 (C), 137.8 (C), 132.1 (C), 115.4 (CH), 112.9 (CH), 112.2 (CH), 55.9 (CH_3), 38.8 (CH_2), 37.7 (CH_2), 32.1 (C), 31.4 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383 found 192.1389.

***4,4,8-trimethyl-1,2,3,4-tetrahydroquinoline* 26**

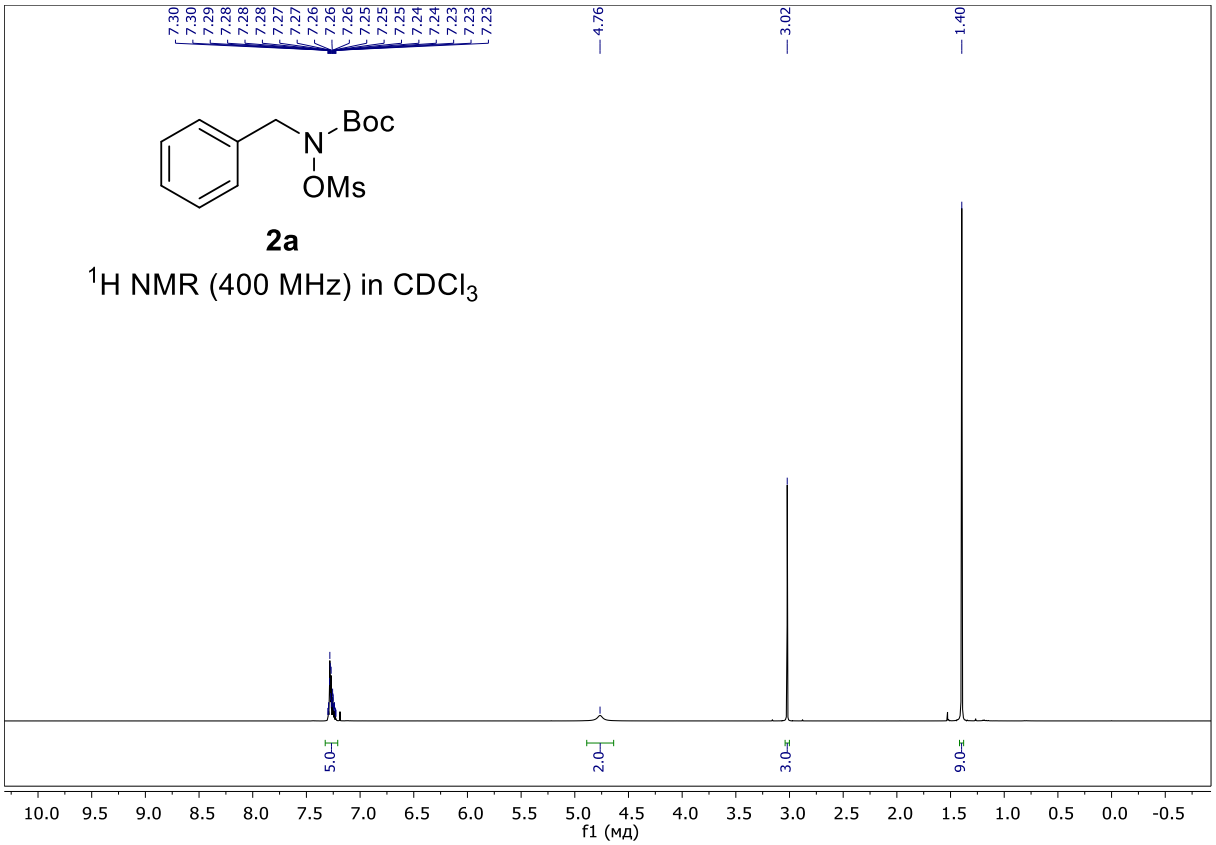


Chemical Formula: $C_{12}H_{17}N$
Exact Mass: 175.1361

The modified general procedure **B** was followed with hydroxylamine **2j** (78.0 mg, 0.20 mmol, 1.0 equiv.), TFA (32.0 μL, 0.40 mmol, 2.0 equiv.) and $FeSO_4 \cdot 7H_2O$ (5.5 mg, 0.02 mmol, 0.1 equiv.) in HFIP (2 mL) without the addition of alkene and purging with Ar. Purification by FC over silica gel (pentane/EtOAc: 100/0 to 90/10) afforded **26** (28.0 mg, 0.16 mmol, 80% yield) as a colorless oil.

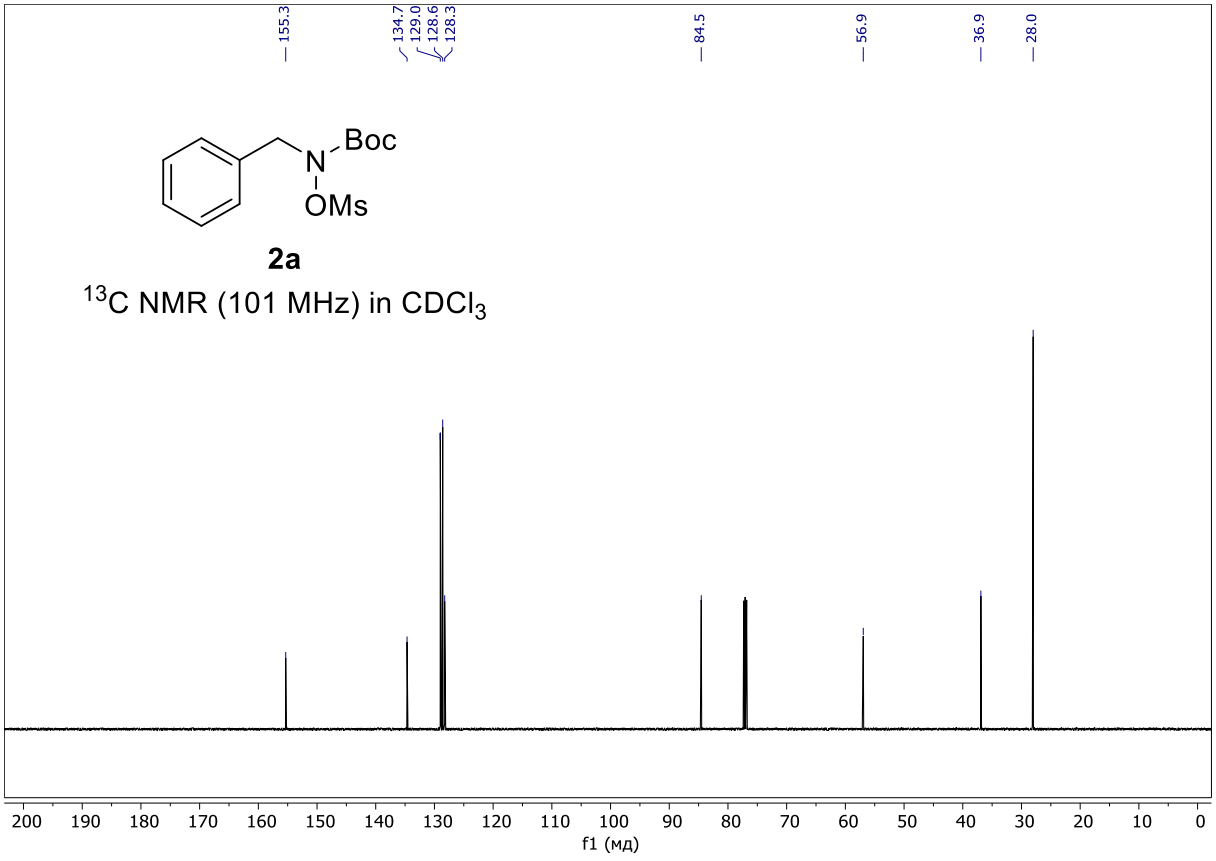
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.08–7.04 (m, 1H), 6.82 (ddd, J = 7.3, 1.4, 0.7 Hz, 1H), 6.53 (t, J = 7.5 Hz, 1H), 3.77 (s, 1H), 3.38–3.34 (m, 2H), 2.05 (s, 3H), 1.74–1.71 (m, 2H), 1.28 (s, 6H). **^{13}C NMR (100 MHz, CD_2Cl_2):** δ 142.3 (C), 130.1 (C), 128.0 (CH), 124.7 (CH), 121.4 (C), 116.6 (CH), 39.0 (CH_2), 37.8 (CH_2), 32.2 (C), 31.5 (CH_3), 17.8 (CH_3). **HRMS (ESI):** *m/z* calcd. for $C_{12}H_{18}N$ $[M+H]^+$ 176.1439 found 176.2060.

4. Spectra of Compounds



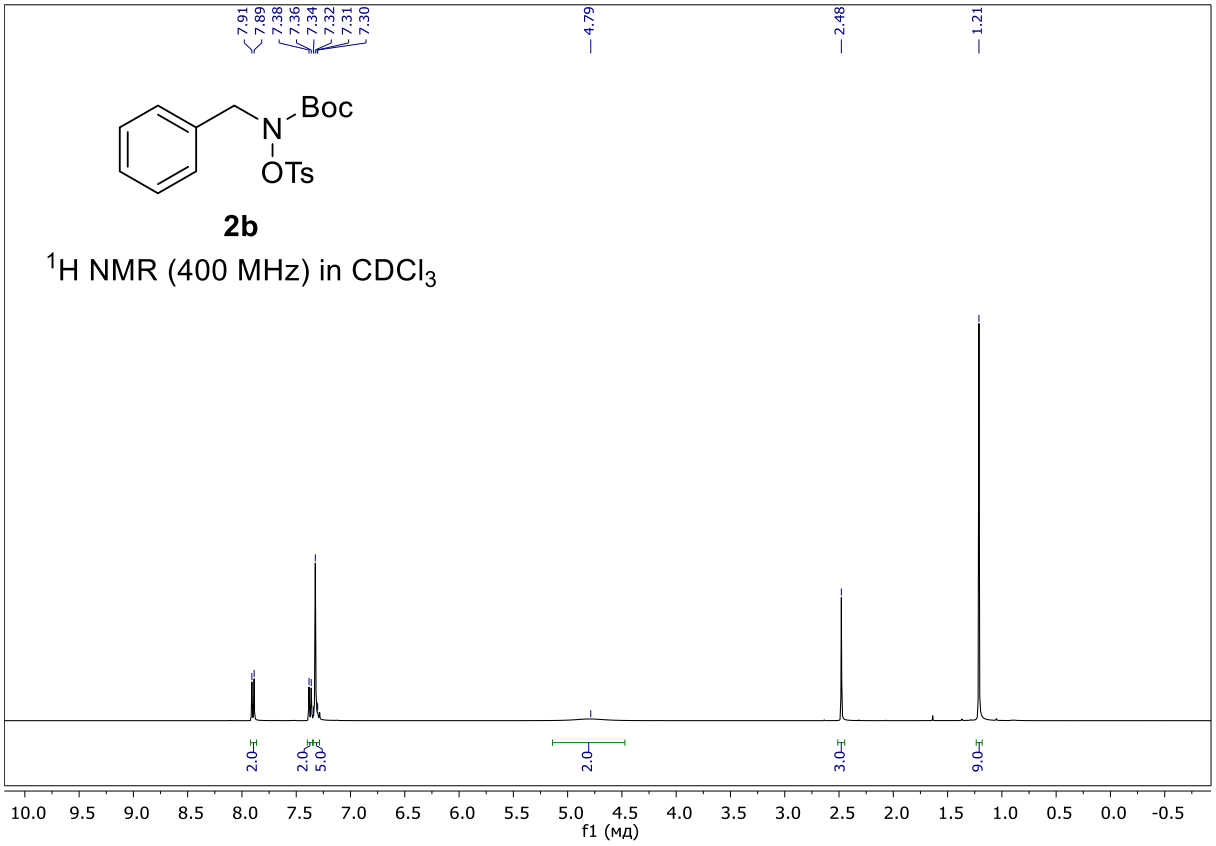
2a

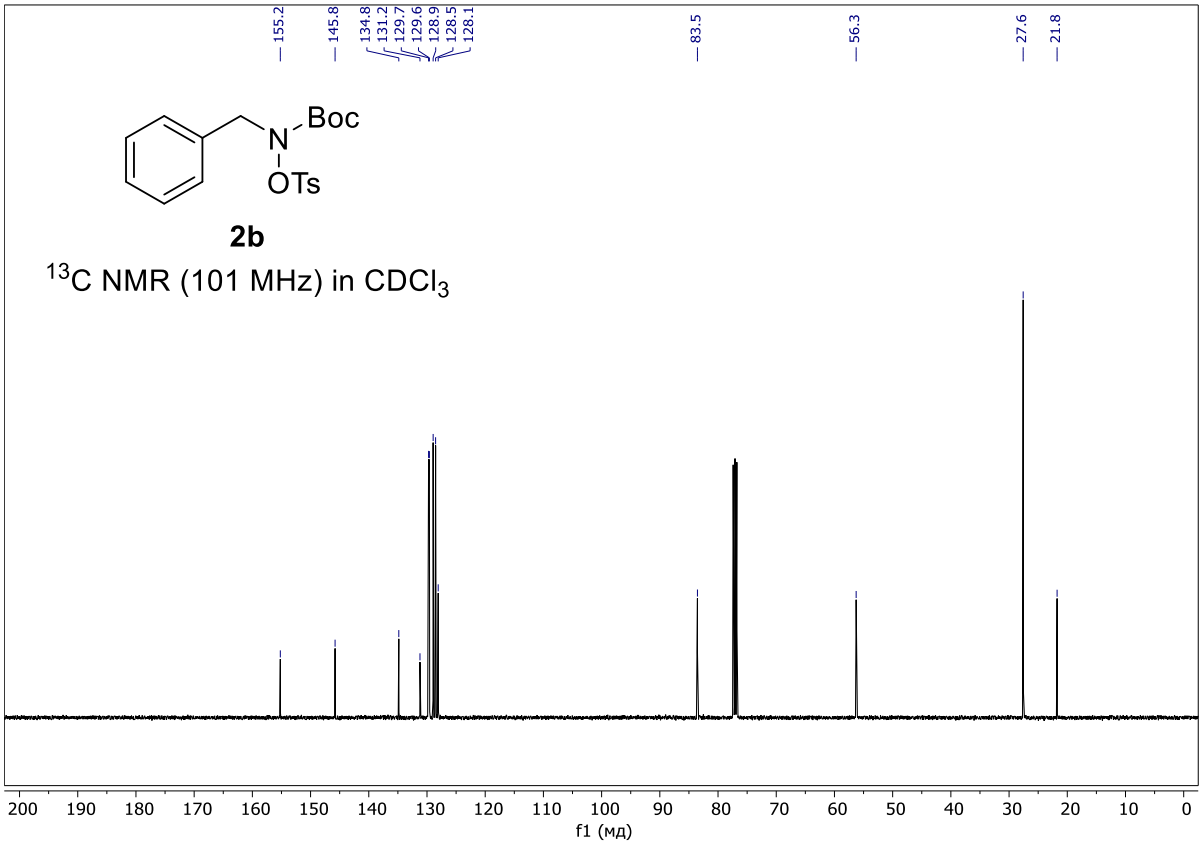
^{1}H NMR (400 MHz) in $CDCl_3$

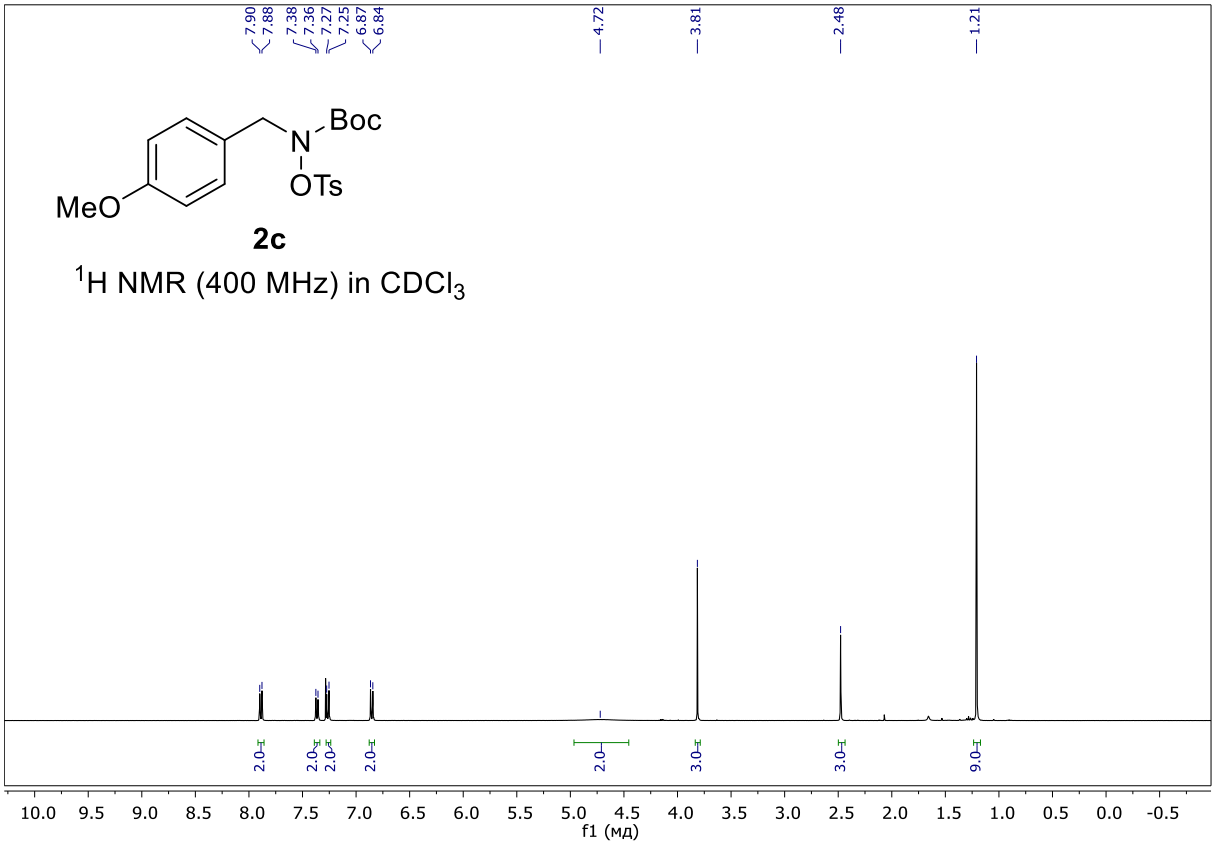


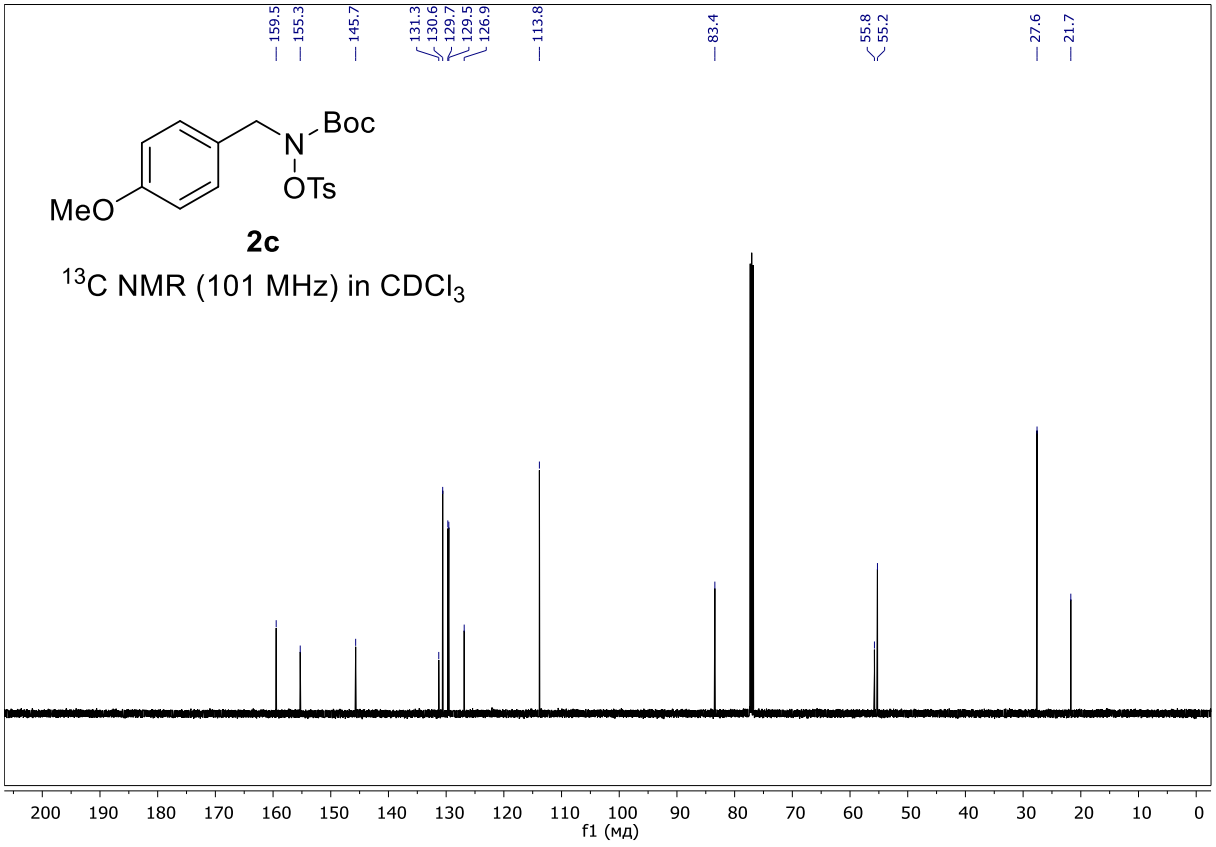
2a

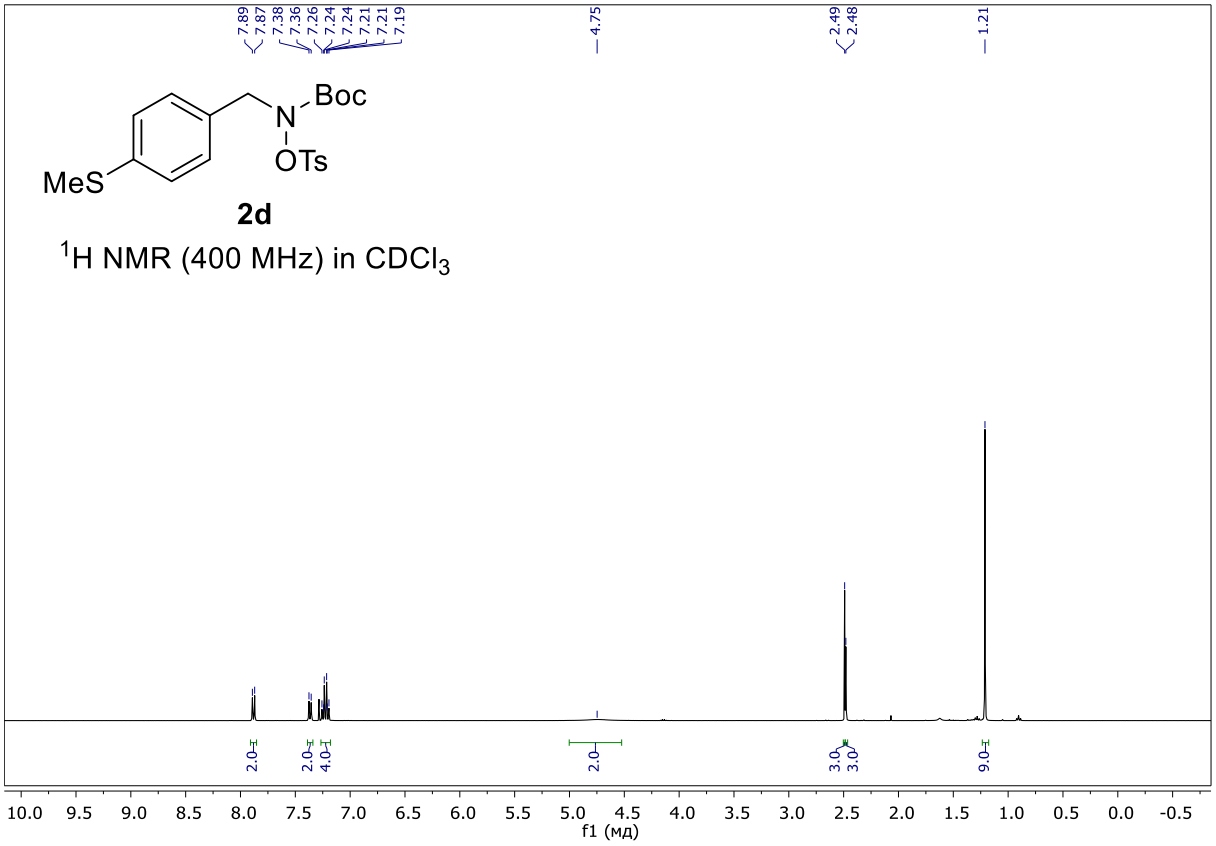
^{13}C NMR (101 MHz) in $CDCl_3$


7.91
7.89
7.38
7.36
7.34
7.32
7.31
7.30
4.79
2.48
1.21
Boc
N
OTs
2b
1H NMR (400 MHz) in CDCl3
2.0
2.0
5.0
2.0
3.0
9.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (мд)


155.2
145.8
134.8
131.2
129.7
129.6
128.9
128.5
128.1
83.5
56.3
27.6
21.8
Boc
N
OTs
2b
13C NMR (101 MHz) in CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

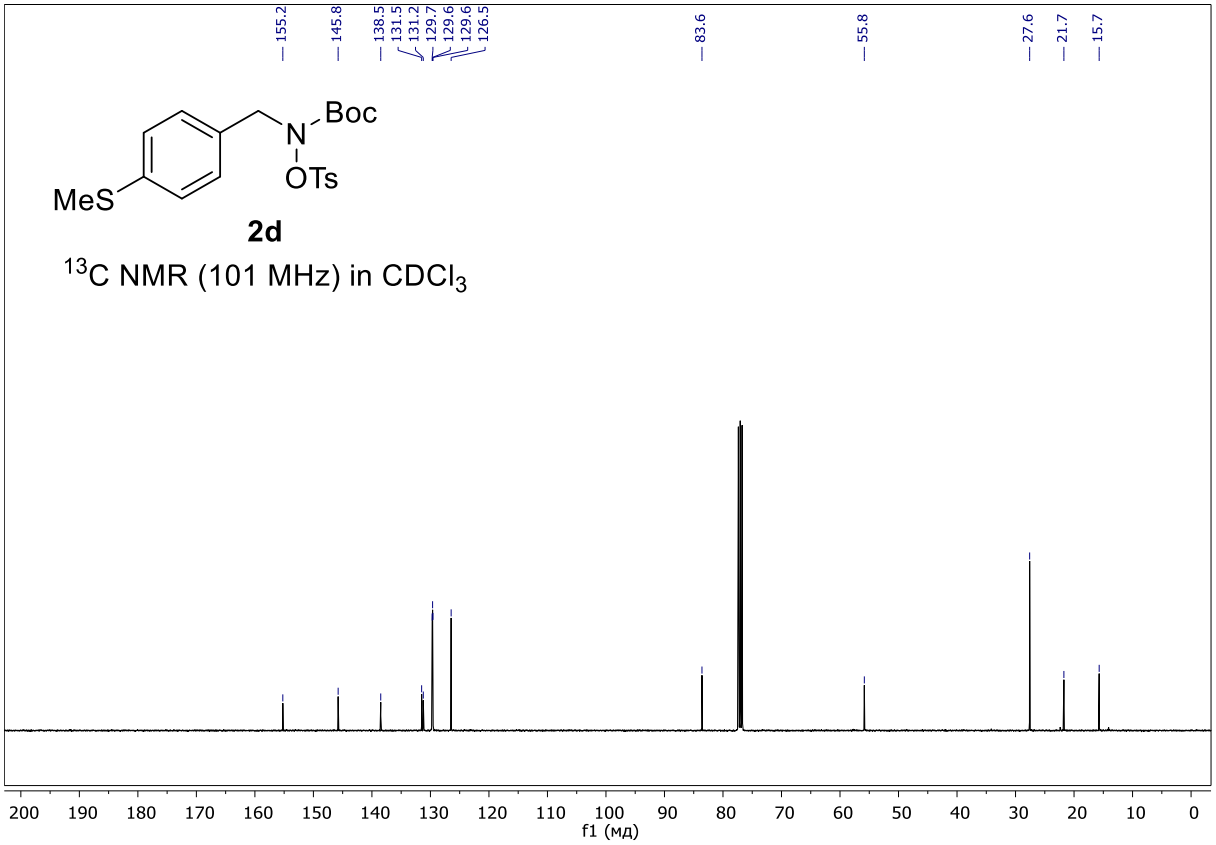

7.90
7.88
7.38
7.36
7.27
7.25
6.87
6.84
4.72
3.81
2.48
1.21
Boc
N
OTs
MeO
2c
1H NMR (400 MHz) in CDCl3
2.0
2.0
2.0
2.0
2.0
3.0
3.0
9.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (мд)


159.5
155.3
145.7
131.3
130.6
129.7
129.5
126.9
113.8
83.4
55.8
55.2
27.6
21.7
Boc
N
OTs
MeO
2c
13C NMR (101 MHz) in CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)



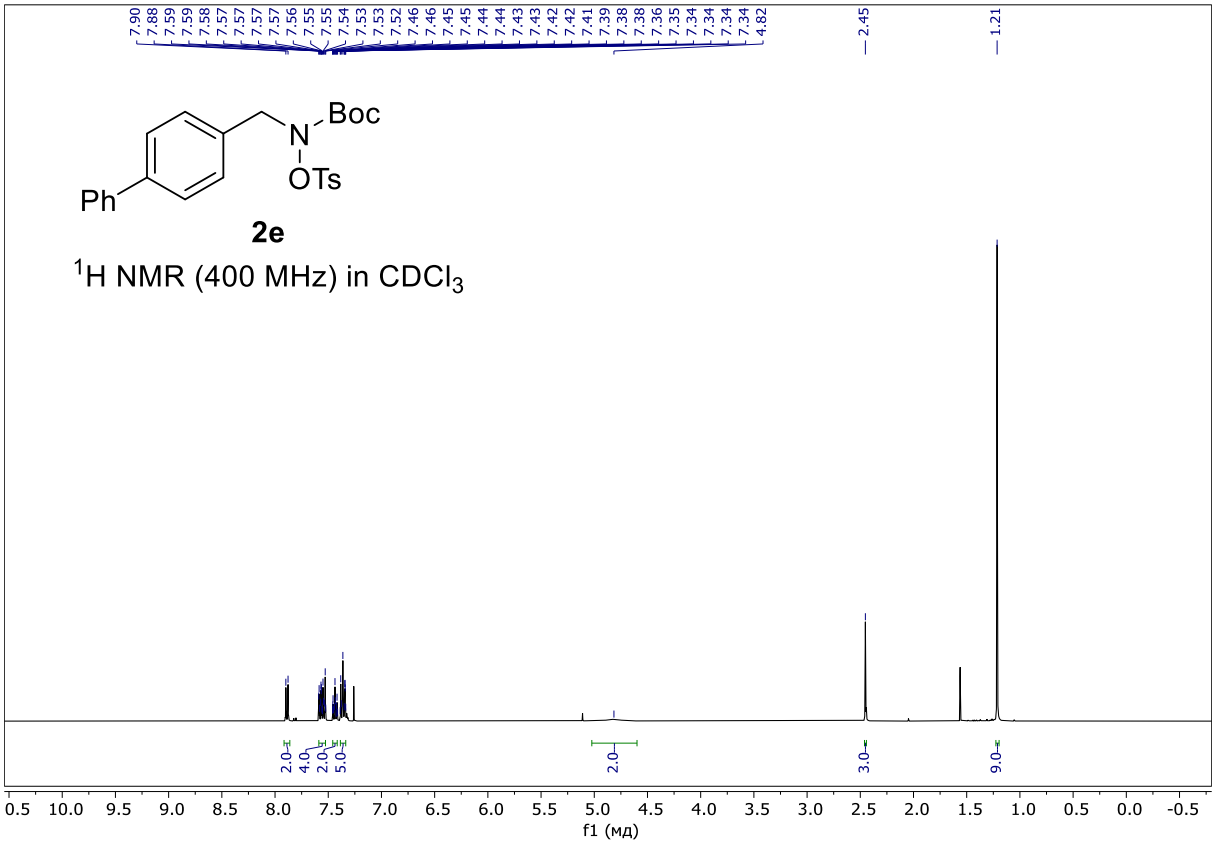
2d

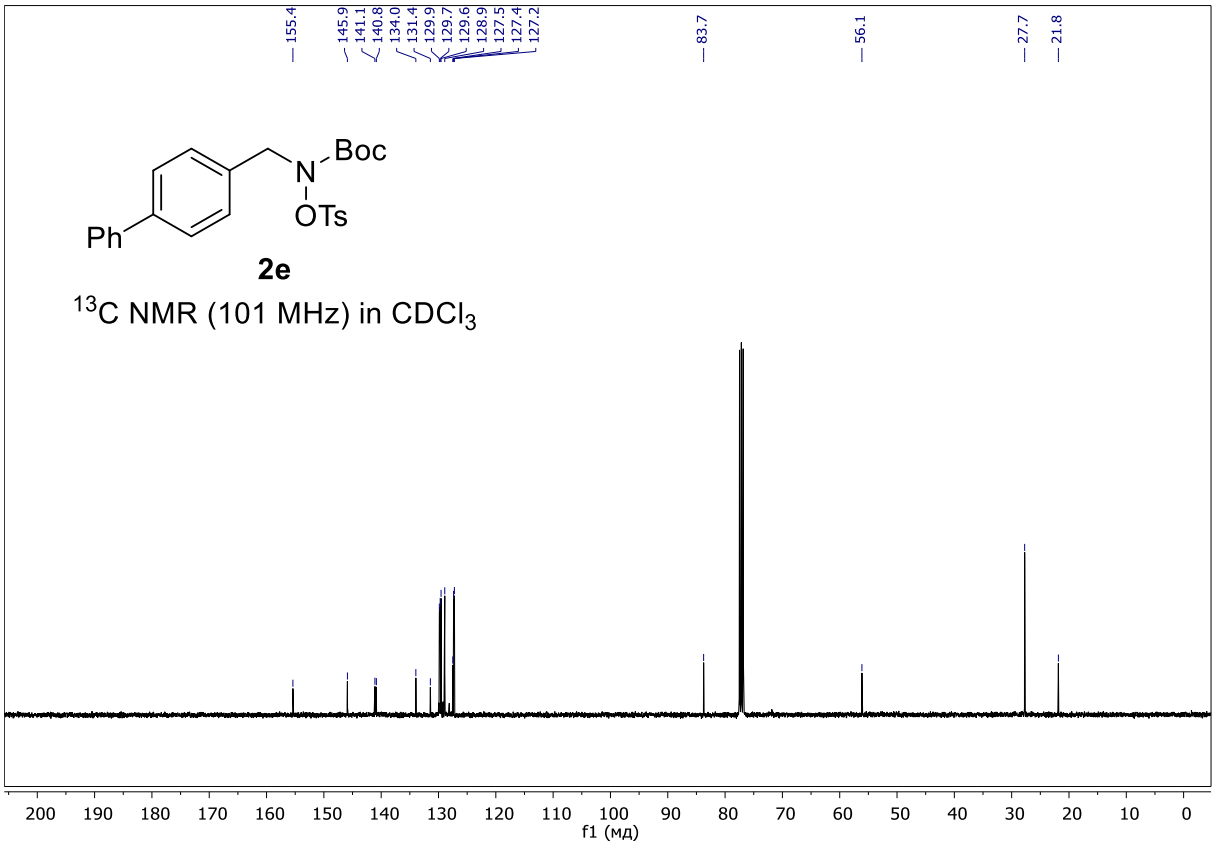
^{1}H NMR (400 MHz) in $CDCl_3$

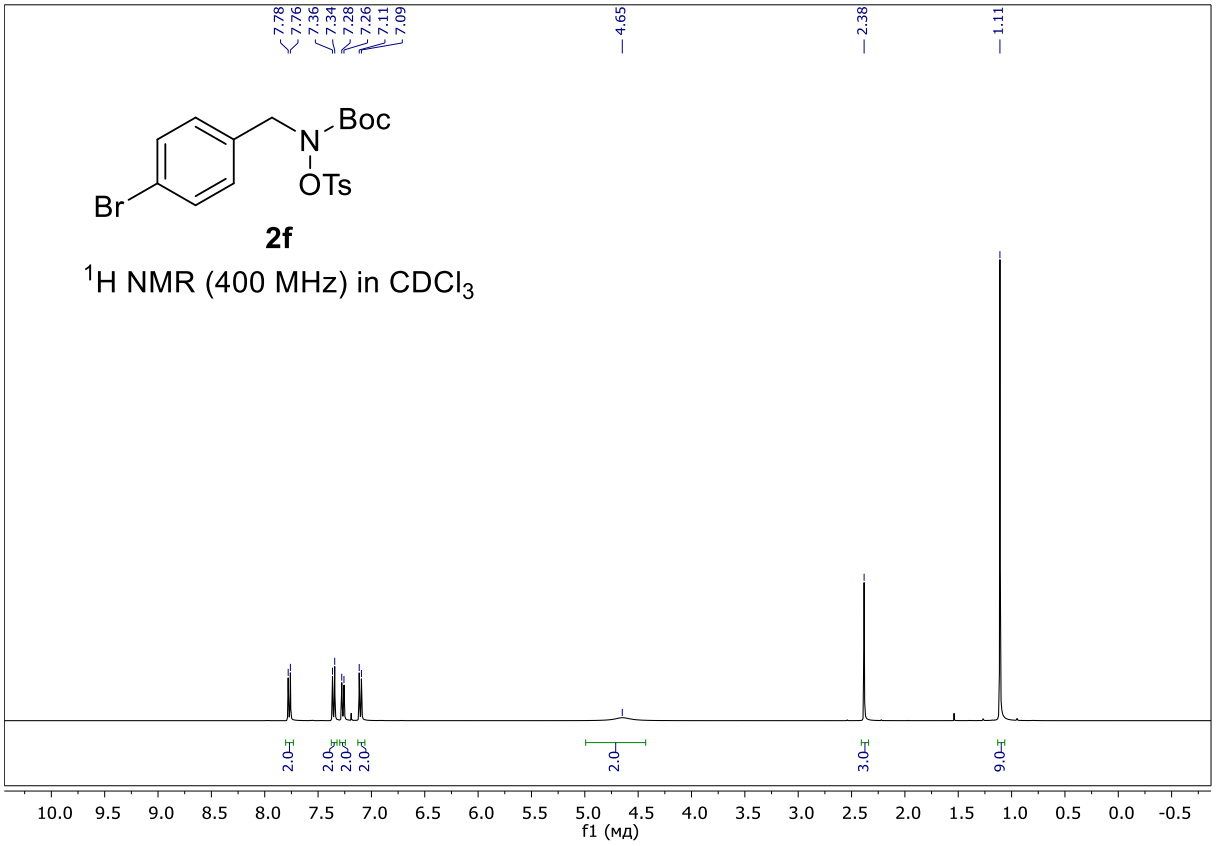


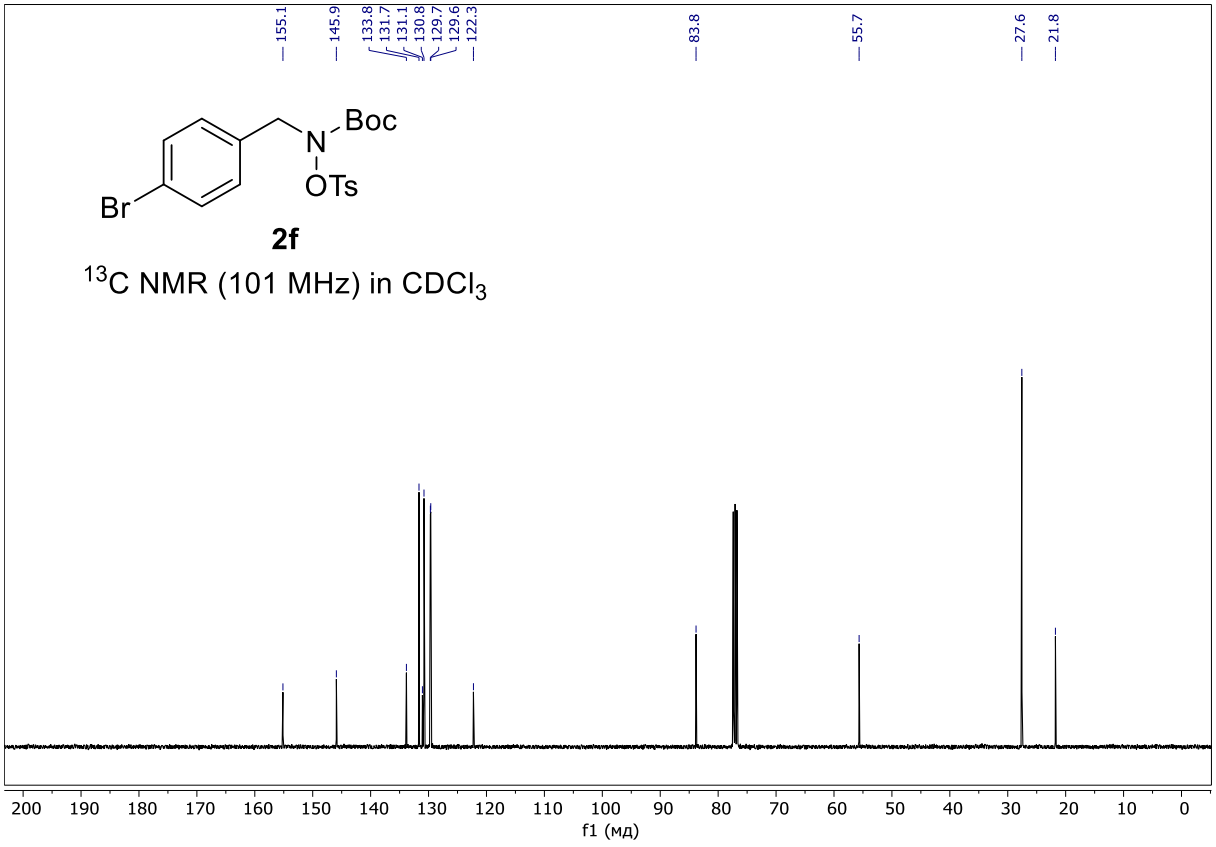
2d

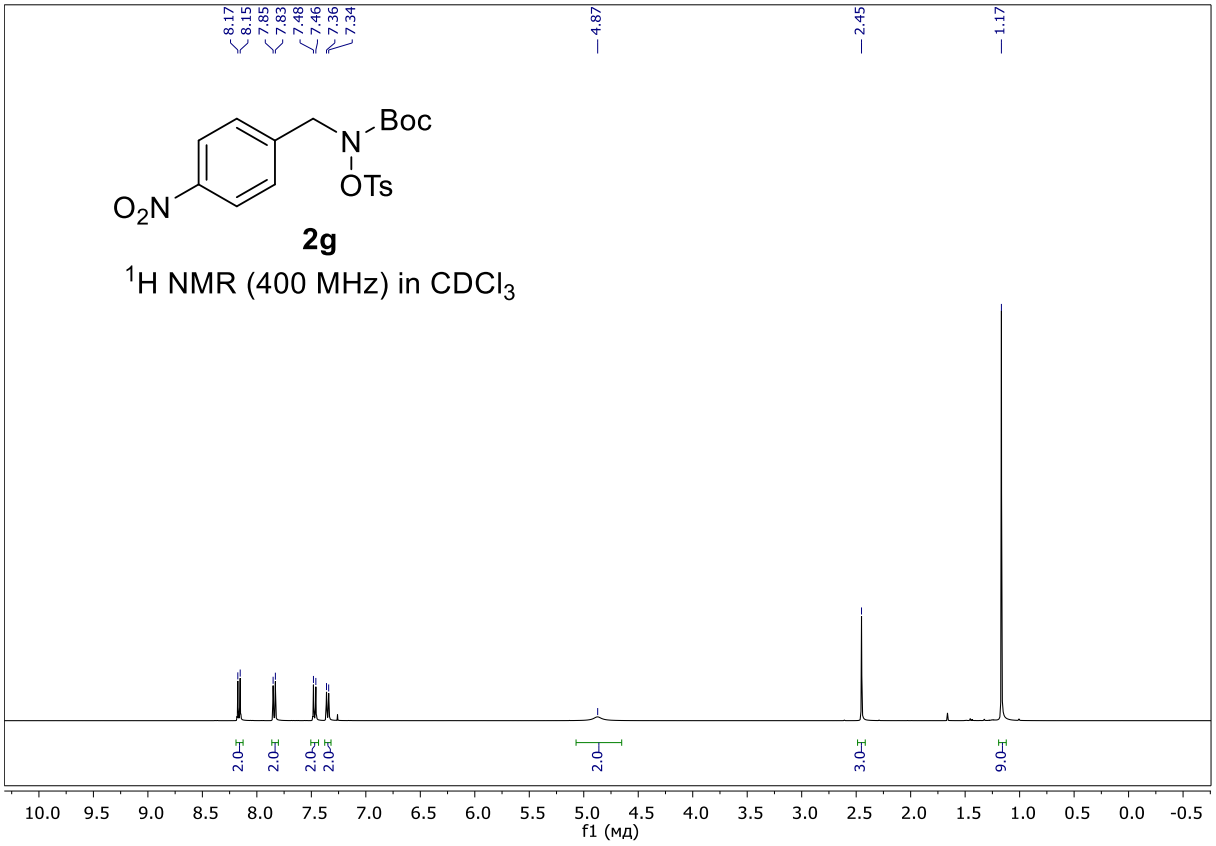
^{13}C NMR (101 MHz) in $CDCl_3$

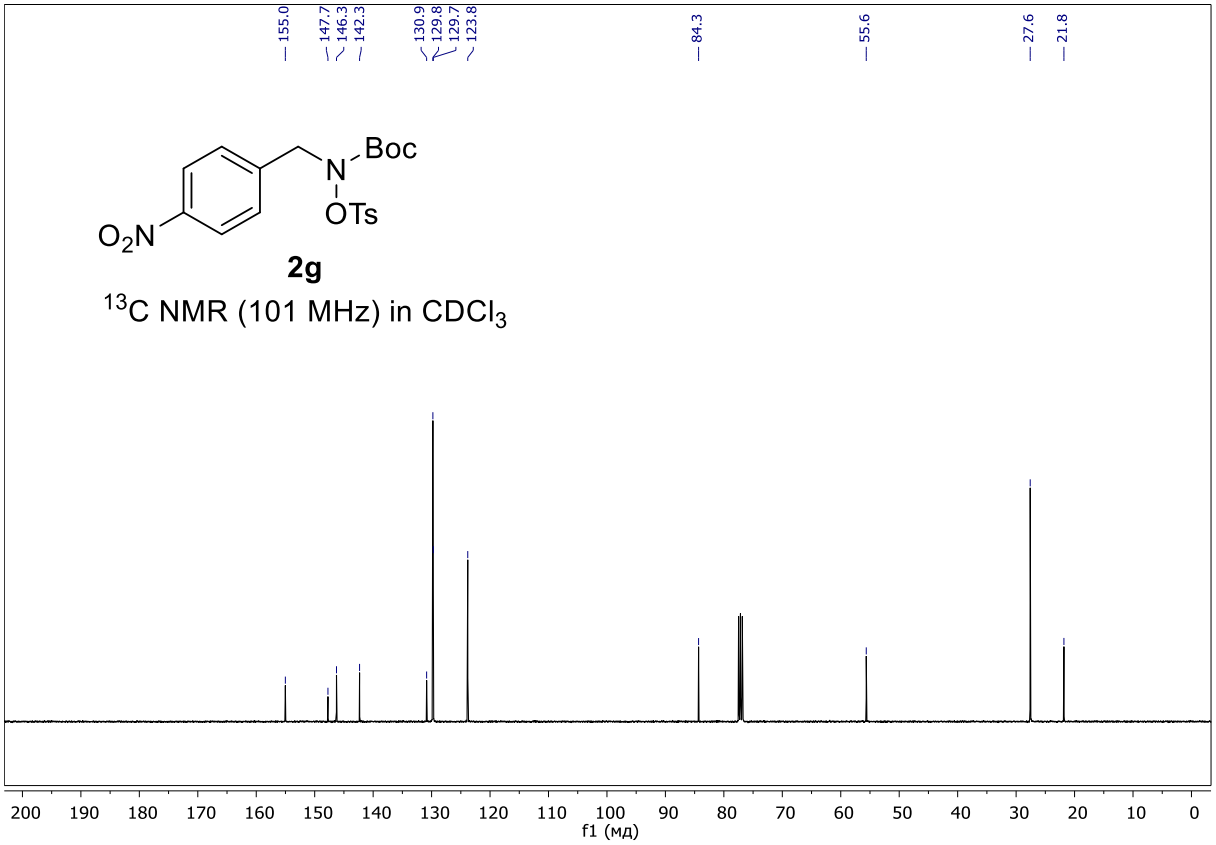

Boc
N
OTs
Ph
2e
1H NMR (400 MHz) in CDCl3
f1 (мд)

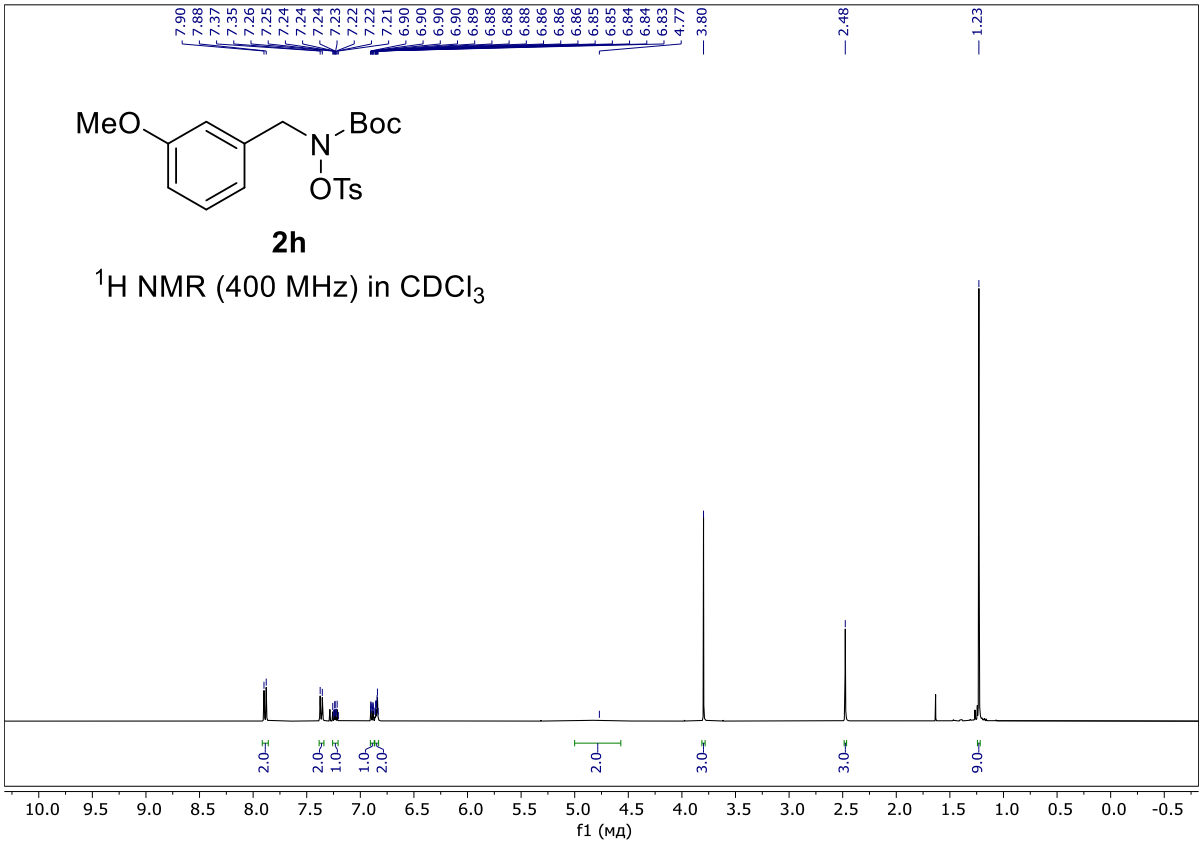

Boc
N
OTs
Ph
2e
13C NMR (101 MHz) in CDCl3
f1 (мд)

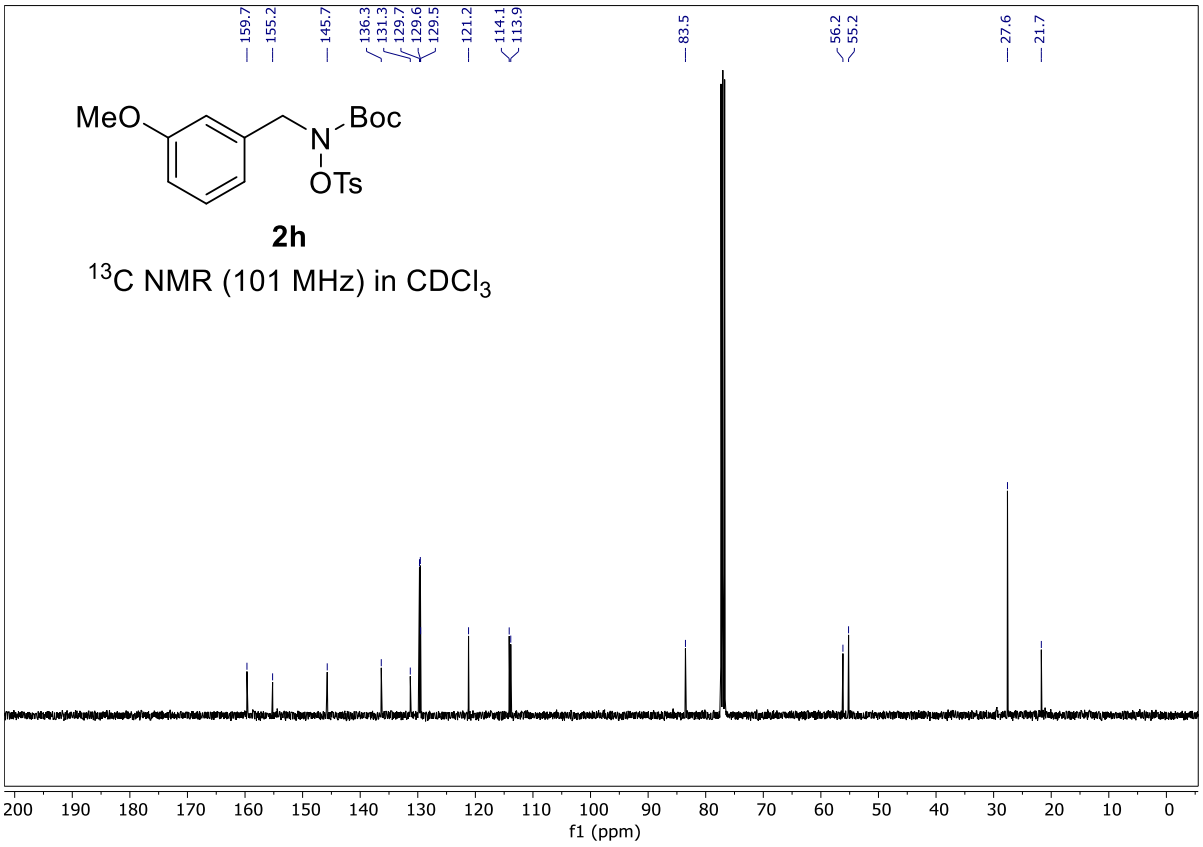

7.78
7.76
7.36
7.34
7.28
7.26
7.11
7.09
4.65
2.38
1.11
Boc
N
OTs
Br
2f
1H NMR (400 MHz) in CDCl3
2.0
2.0
2.0
2.0
2.0
3.0
9.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (мд)

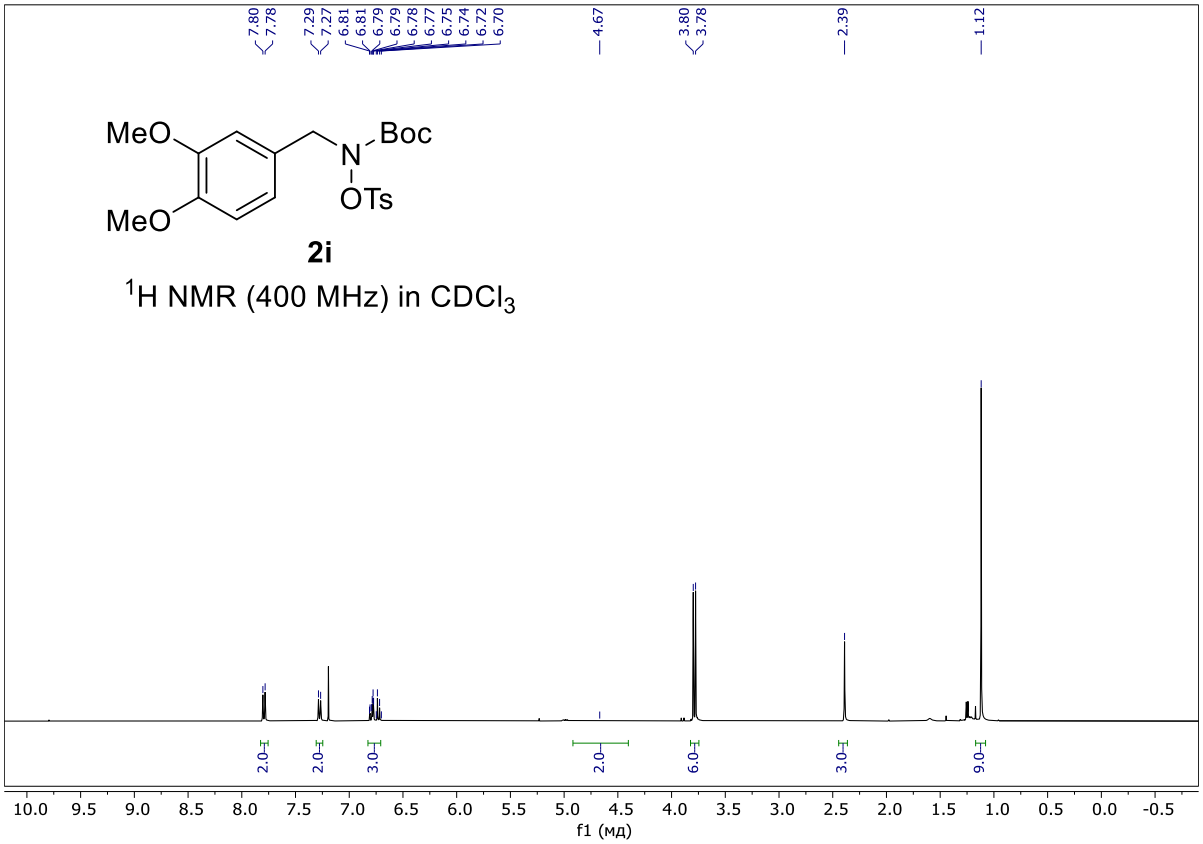

155.1
145.9
133.8
131.7
131.1
130.8
129.7
129.6
122.3
83.8
55.7
27.6
21.8
Boc
N
OTs
Br
2f
13C NMR (101 MHz) in CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

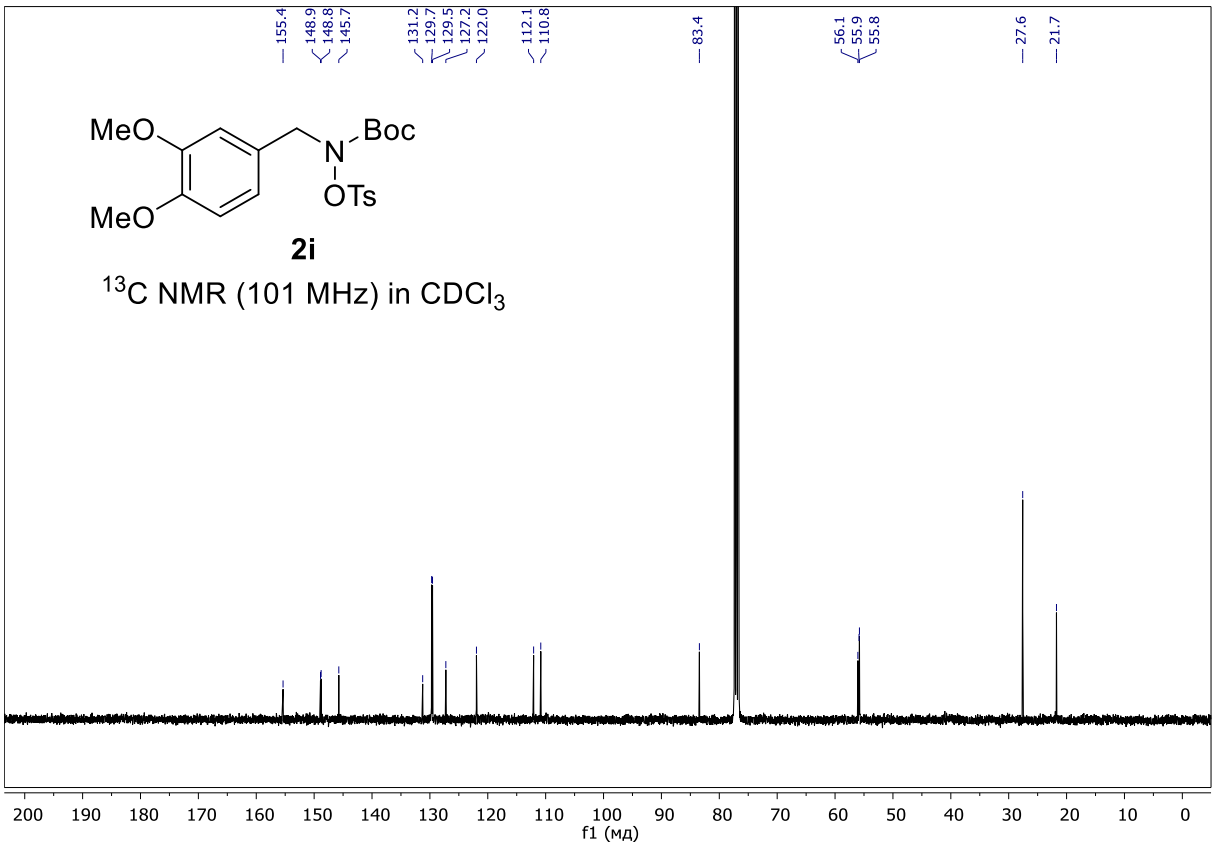

8.17
8.15
7.85
7.83
7.48
7.46
7.36
7.34
4.87
2.45
1.17
Boc
N
OTs
O2N
2g
1H NMR (400 MHz) in CDCl3
2.0
2.0
2.0
2.0
2.0
3.0
9.0
f1 (мд)

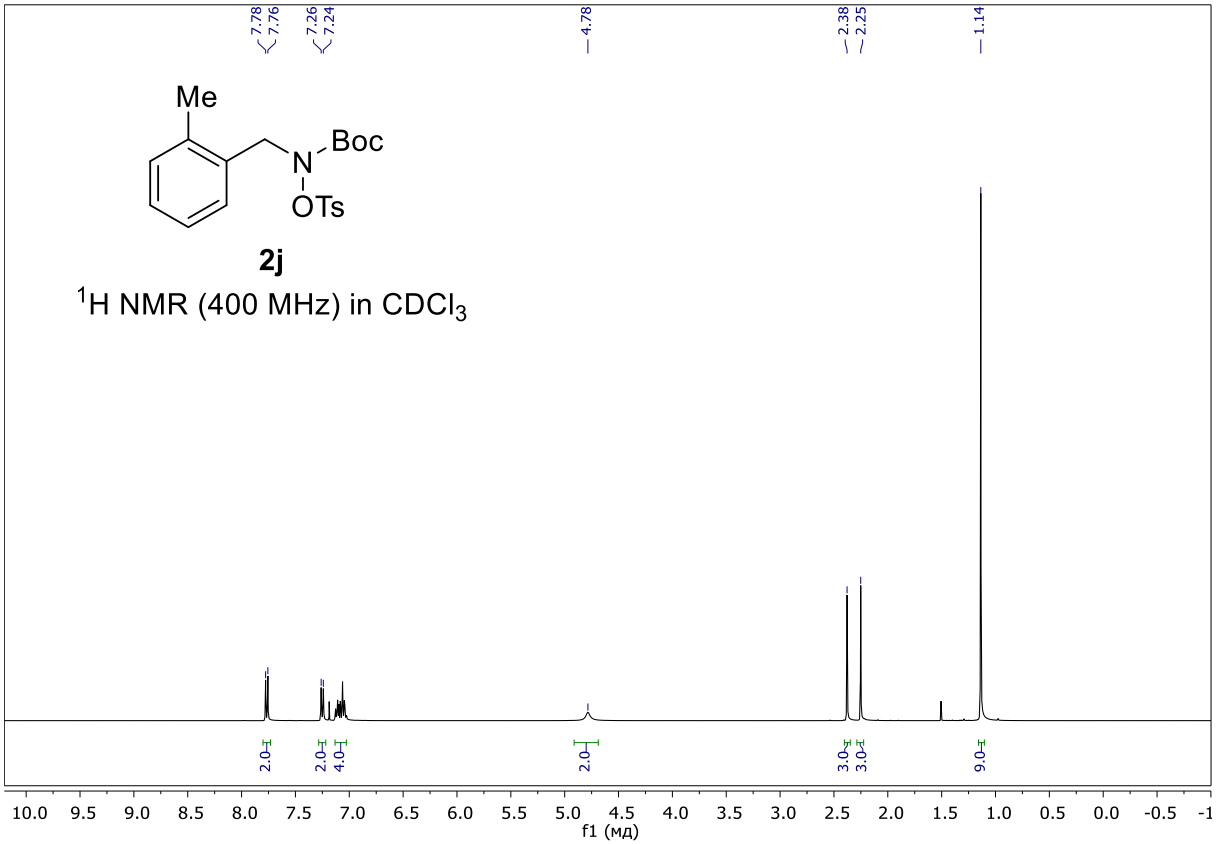

155.0
147.7
146.3
142.3
130.9
129.8
129.7
123.8
84.3
55.6
27.6
21.8
Boc
N
OTs
O2N
2g
13C NMR (101 MHz) in CDCl3
f1 (мд)


MeO
N
Boc
OTs
2h
1H NMR (400 MHz) in CDCl3
f1 (мд)


MeO
N
Boc
OTs
2h
13C NMR (101 MHz) in CDCl3
f1 (ppm)

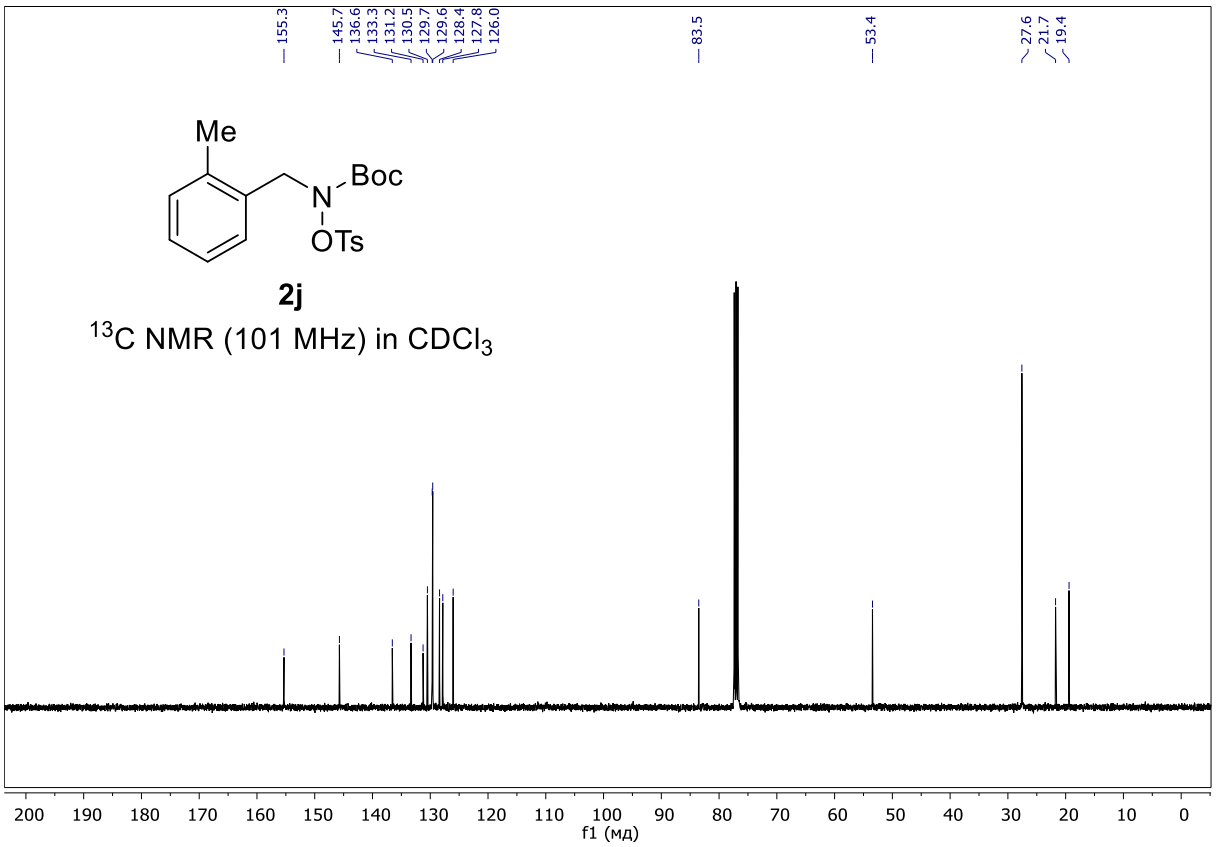

7.80
7.78
7.29
7.27
6.81
6.81
6.79
6.79
6.78
6.77
6.75
6.74
6.72
6.70
4.67
3.80
3.78
2.39
1.12
MeO
MeO
N
Boc
OTs
2i
1H NMR (400 MHz) in CDCl3
2.0
2.0
3.0
2.0
6.0
3.0
9.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (мд)


155.4
148.9
148.8
145.7
131.2
129.7
129.5
127.2
122.0
112.1
110.8
83.4
56.1
55.9
55.8
27.6
21.7
MeO
MeO
N
Boc
OTs
2i
13C NMR (101 MHz) in CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)



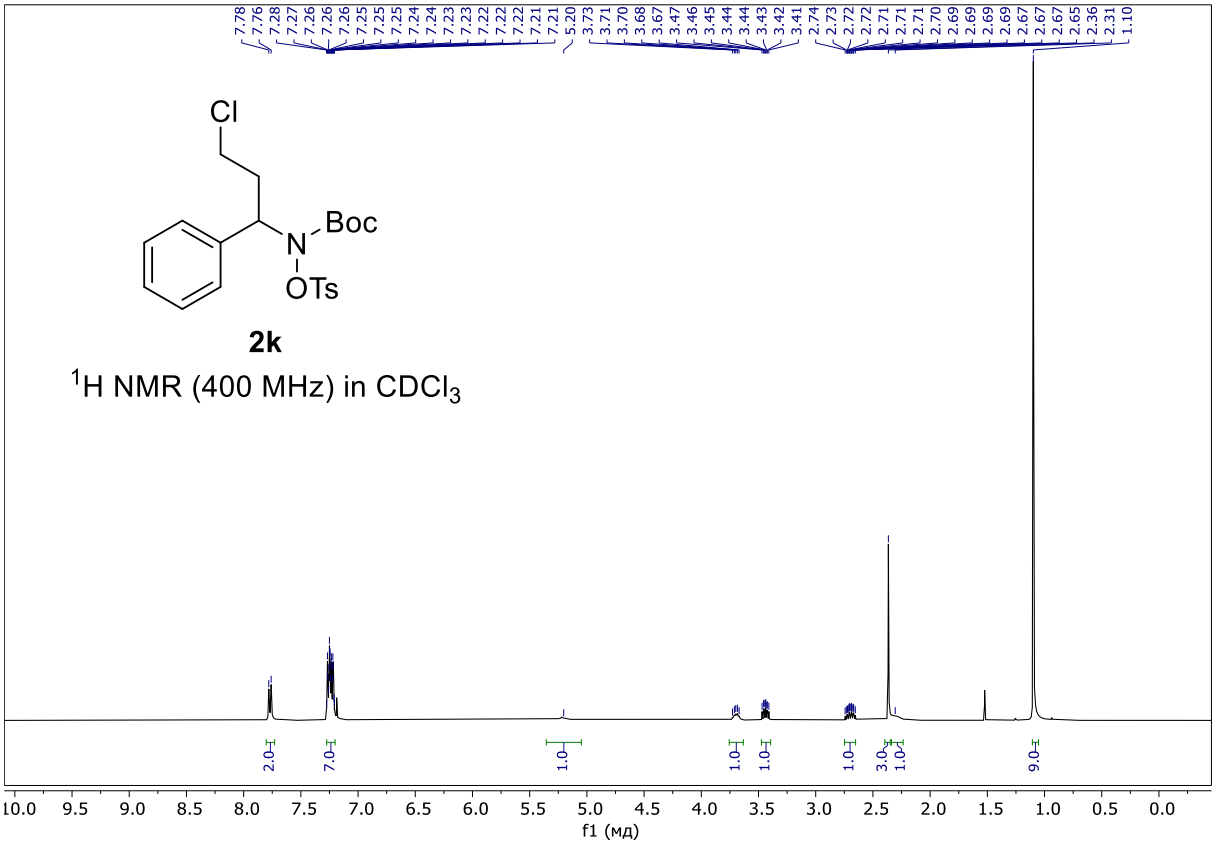
2j

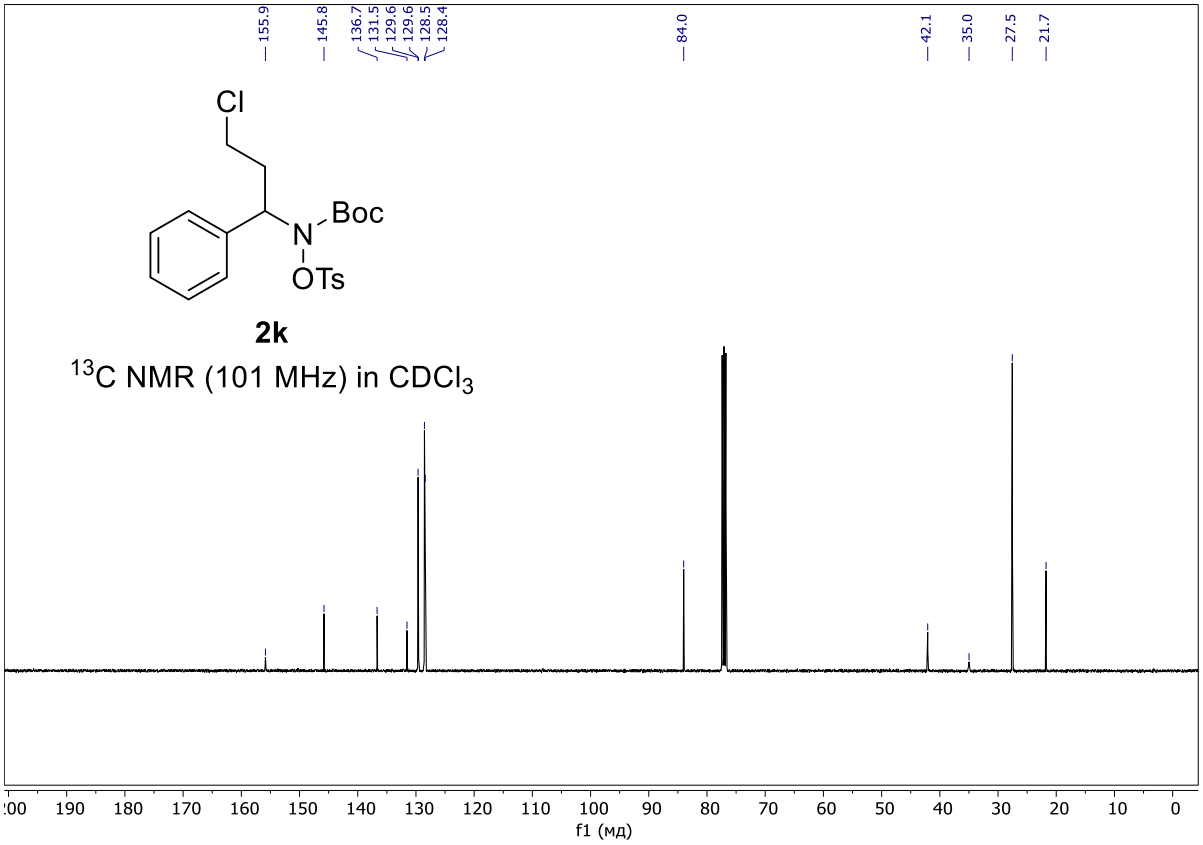
^{1}H NMR (400 MHz) in $CDCl_3$

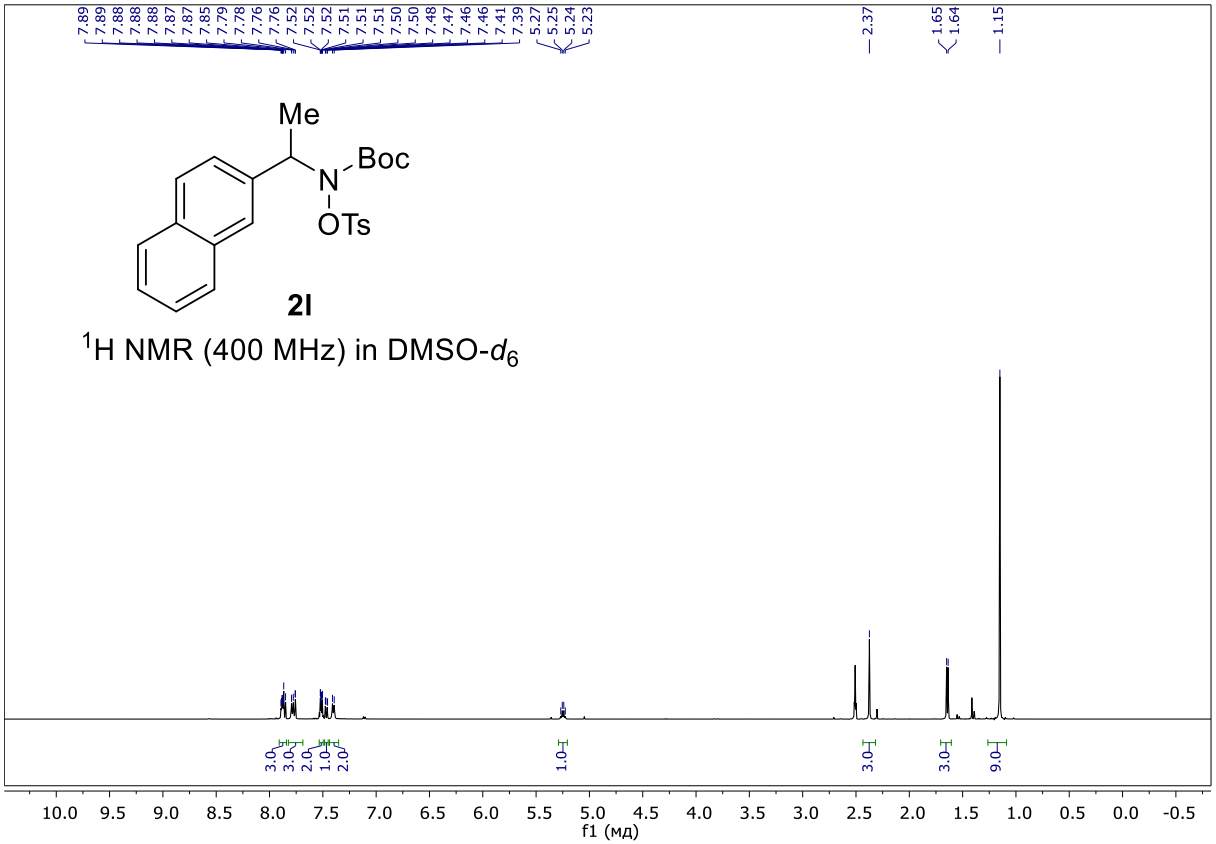


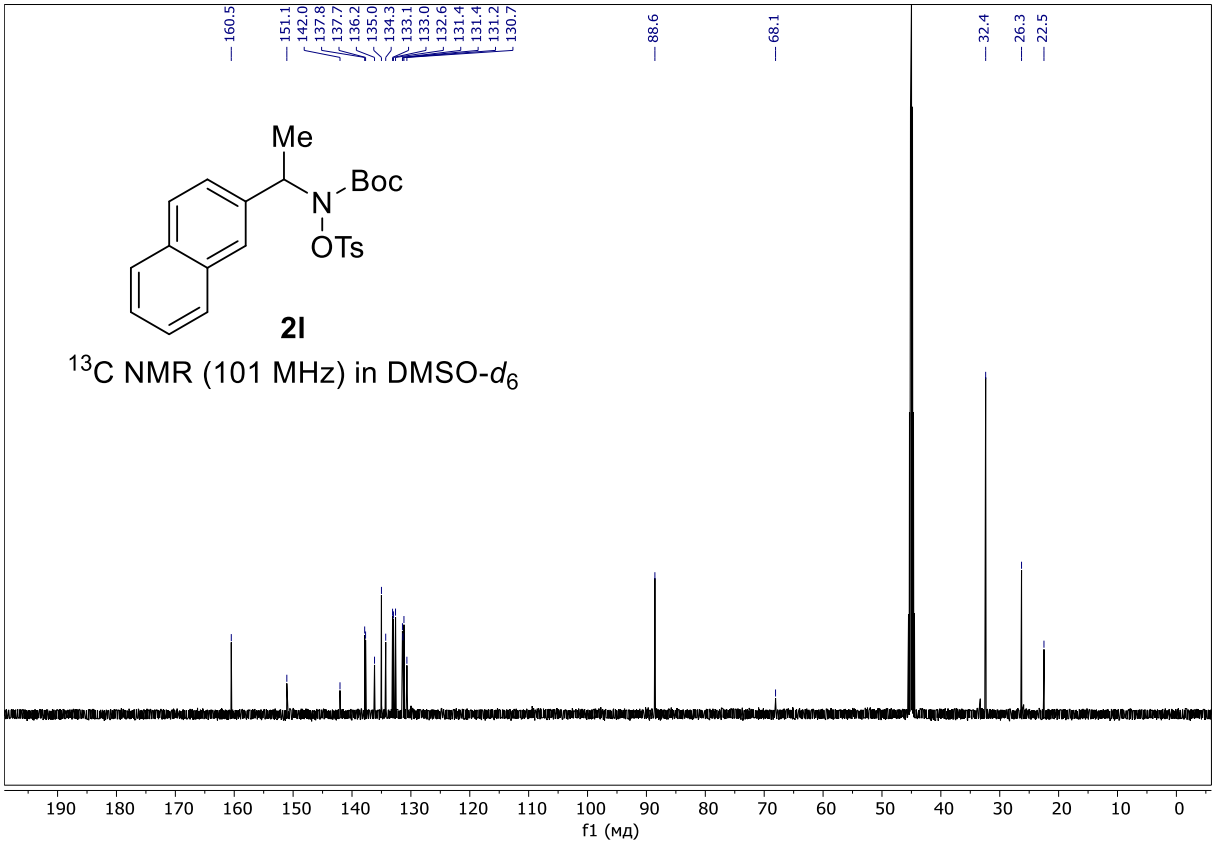
2j

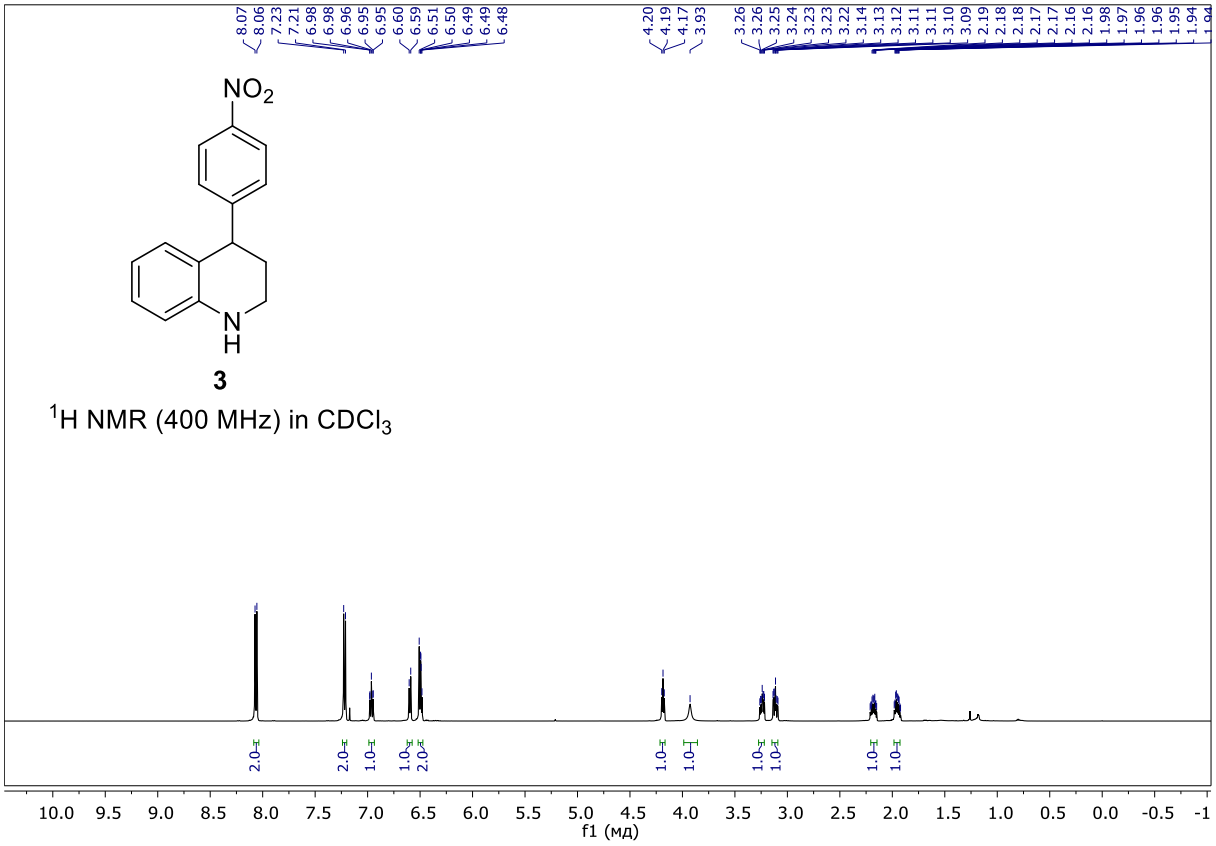
^{13}C NMR (101 MHz) in $CDCl_3$

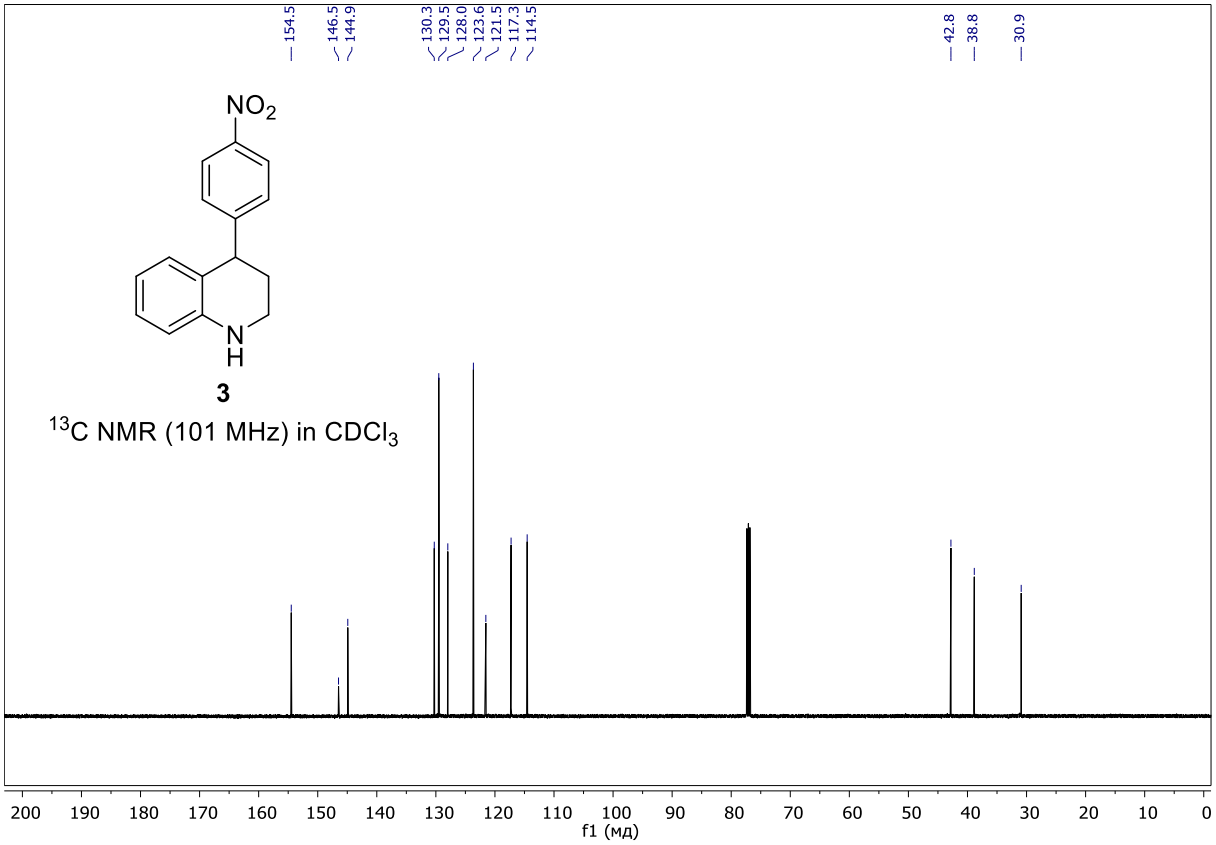

Cl
Boc
N
OTs
2k
1H NMR (400 MHz) in CDCl3
f1 (мд)

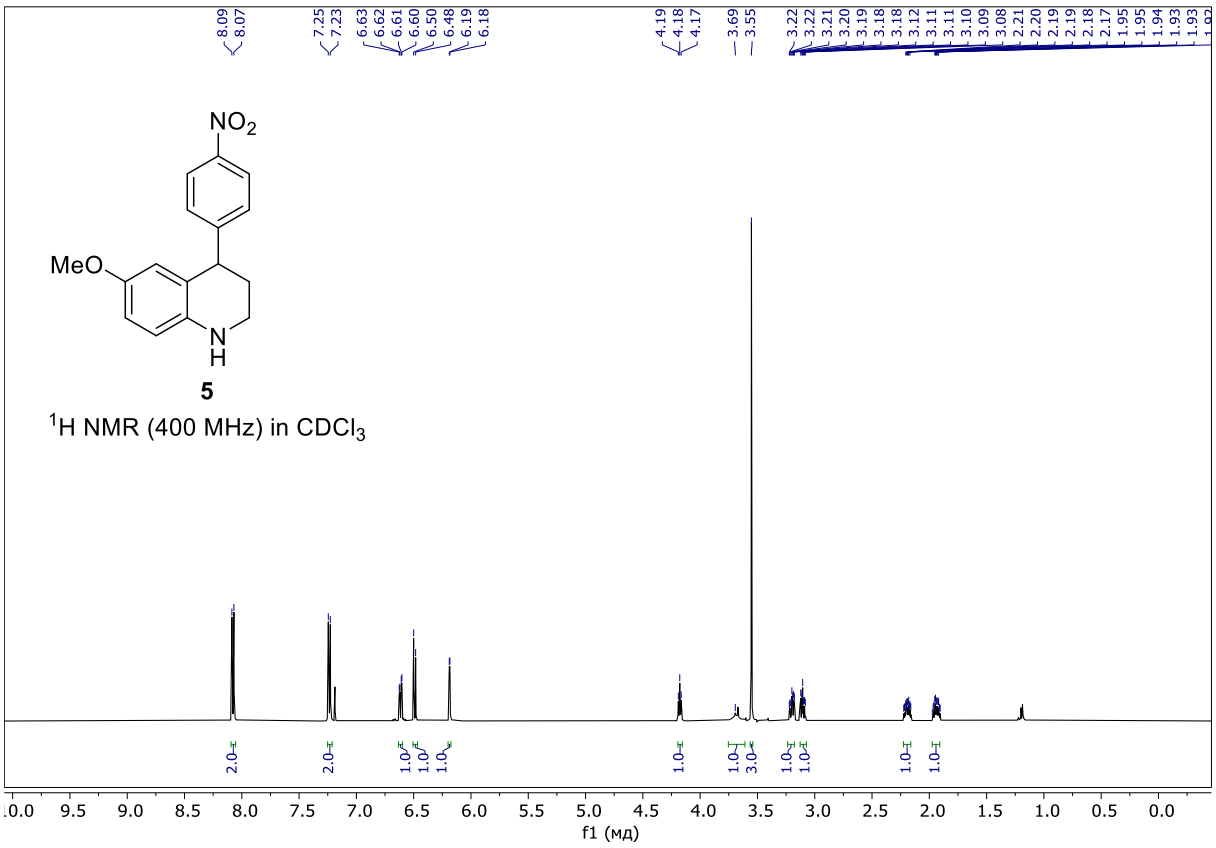

Cl
Boc
N
OTs
2k
13C NMR (101 MHz) in CDCl3
f1 (мд)

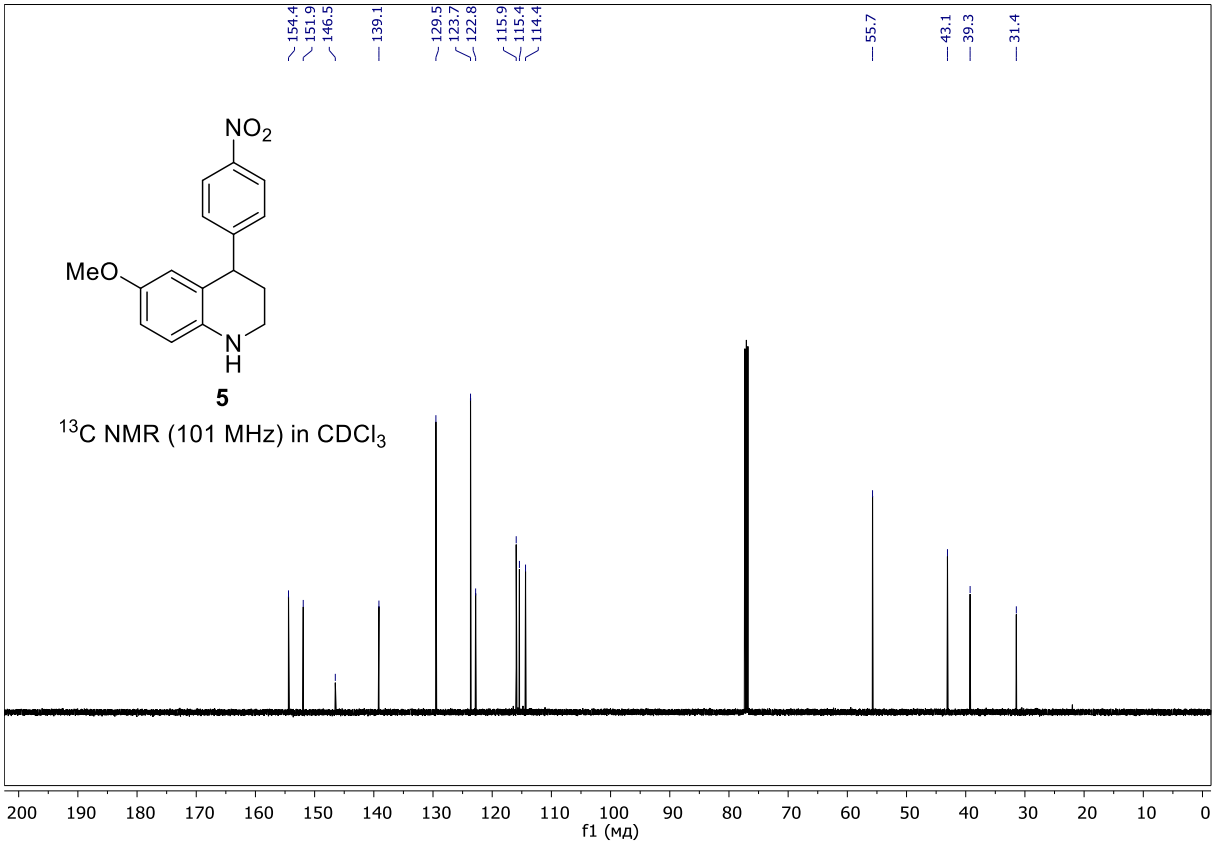

Me
Boc
N
OTs
2l
^{1}H NMR (400 MHz) in DMSO-d_6
f1 (мд)

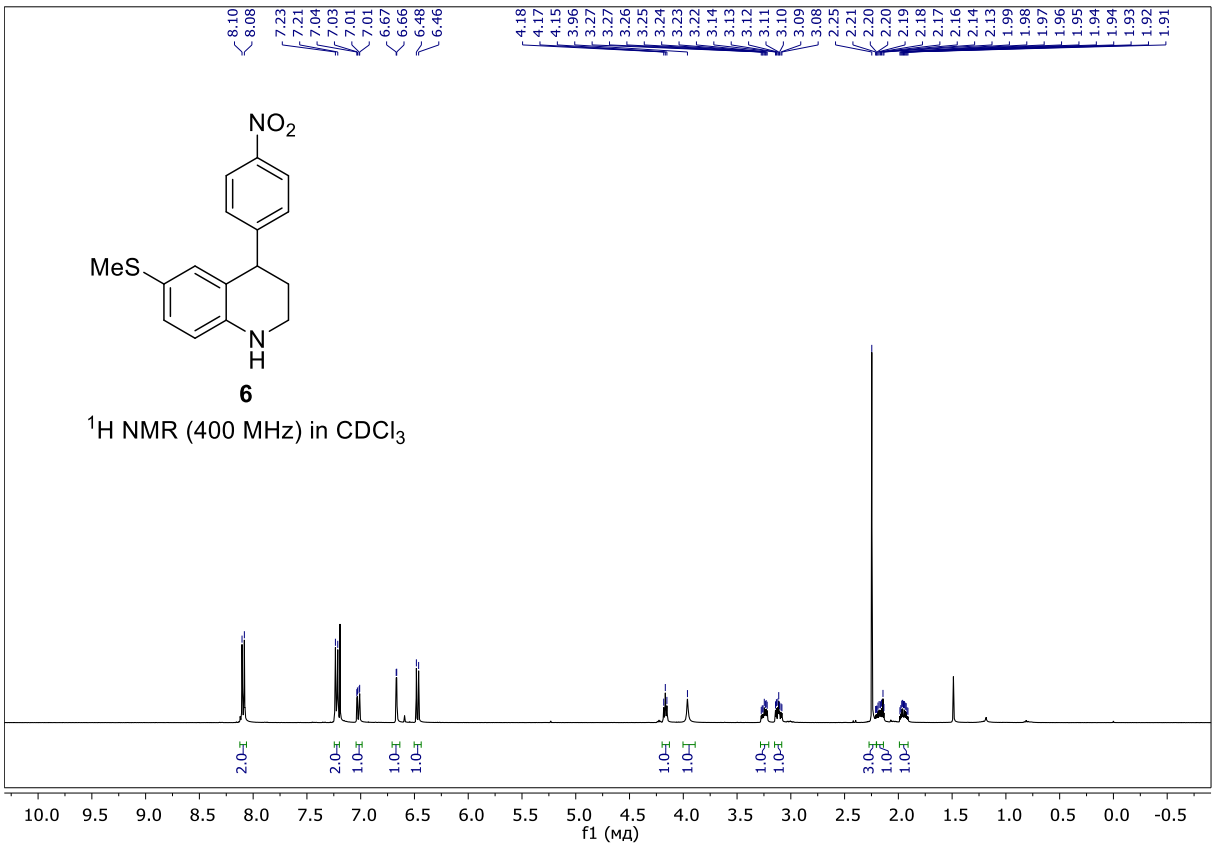

Me
Boc
N
OTs
2l
^{13}C NMR (101 MHz) in DMSO-d_6
f1 (мд)

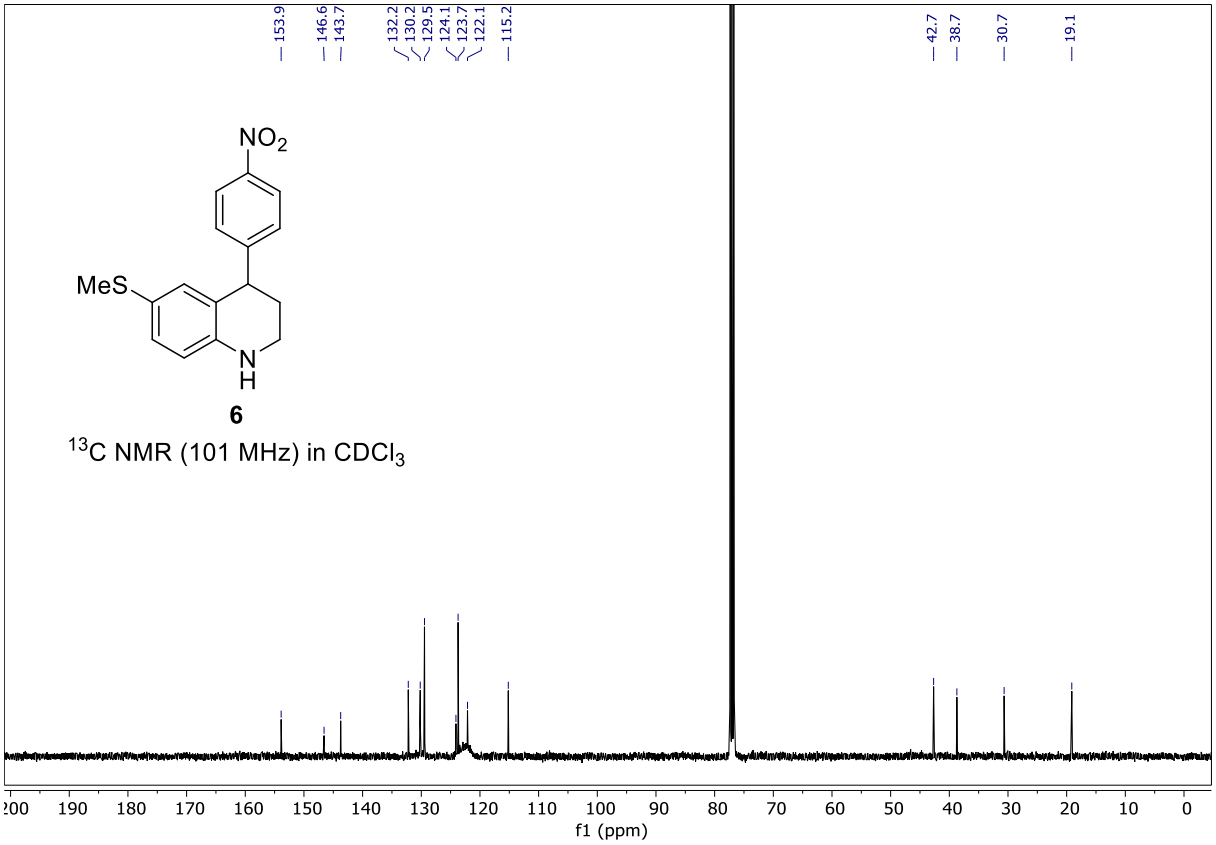

NO2
N
H
3
1H NMR (400 MHz) in CDCl3
f1 (мд)

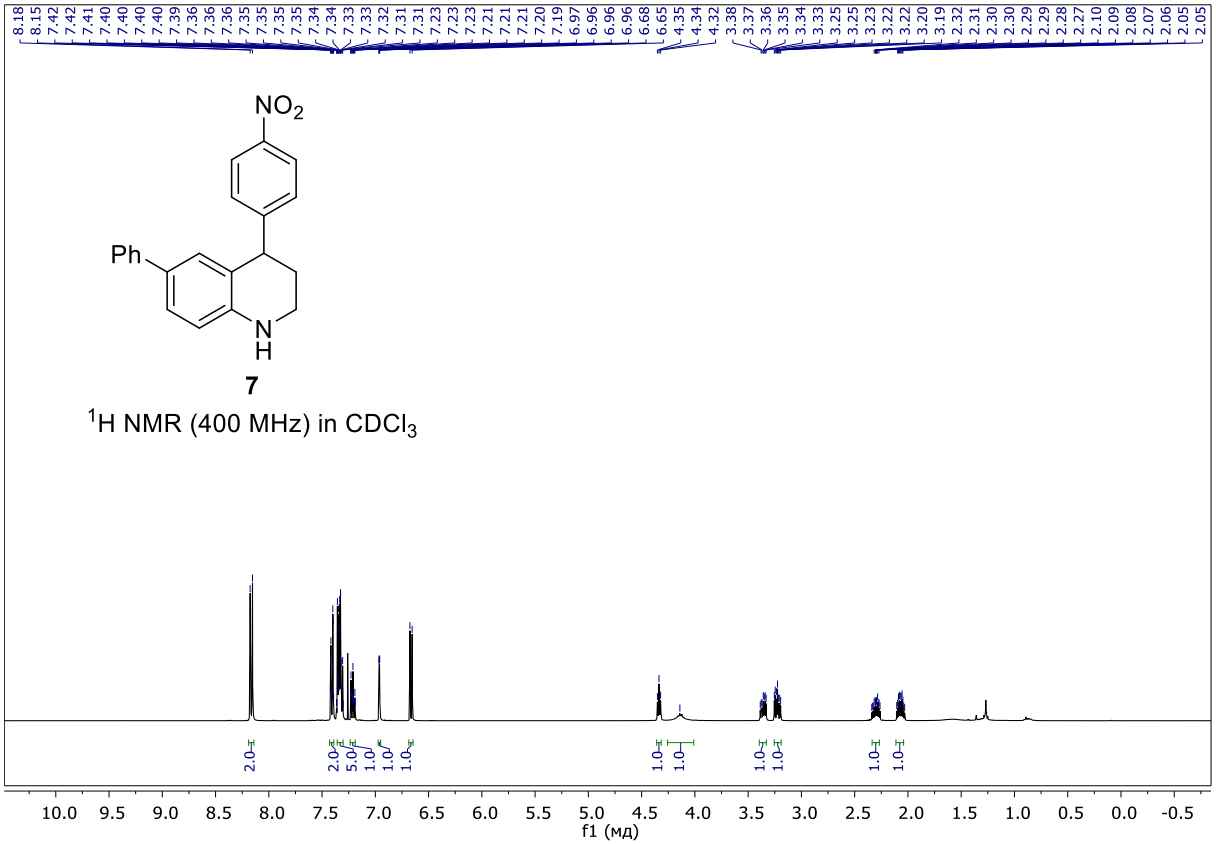

NO2
N
H
3
13C NMR (101 MHz) in CDCl3
f1 (мд)

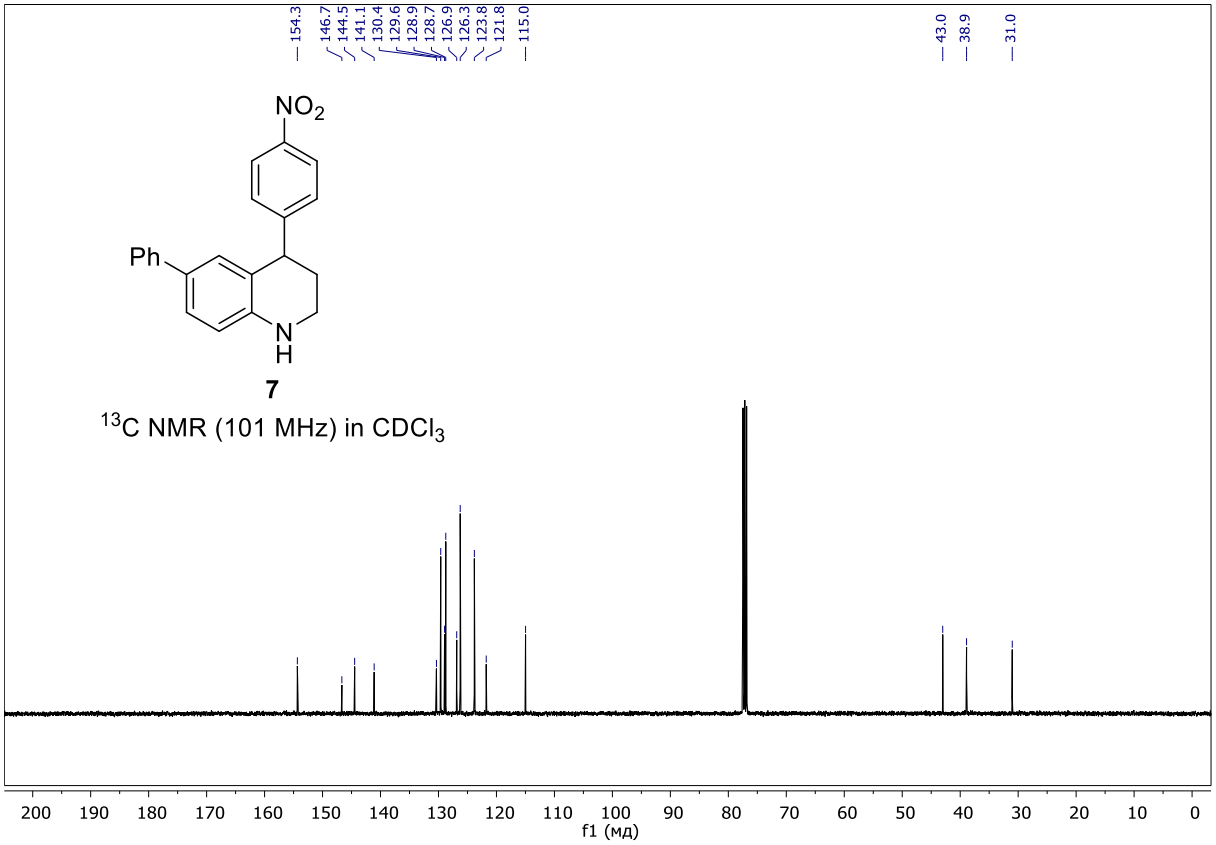

NO2
MeO
N
H
5
1H NMR (400 MHz) in CDCl3
f1 (мд)

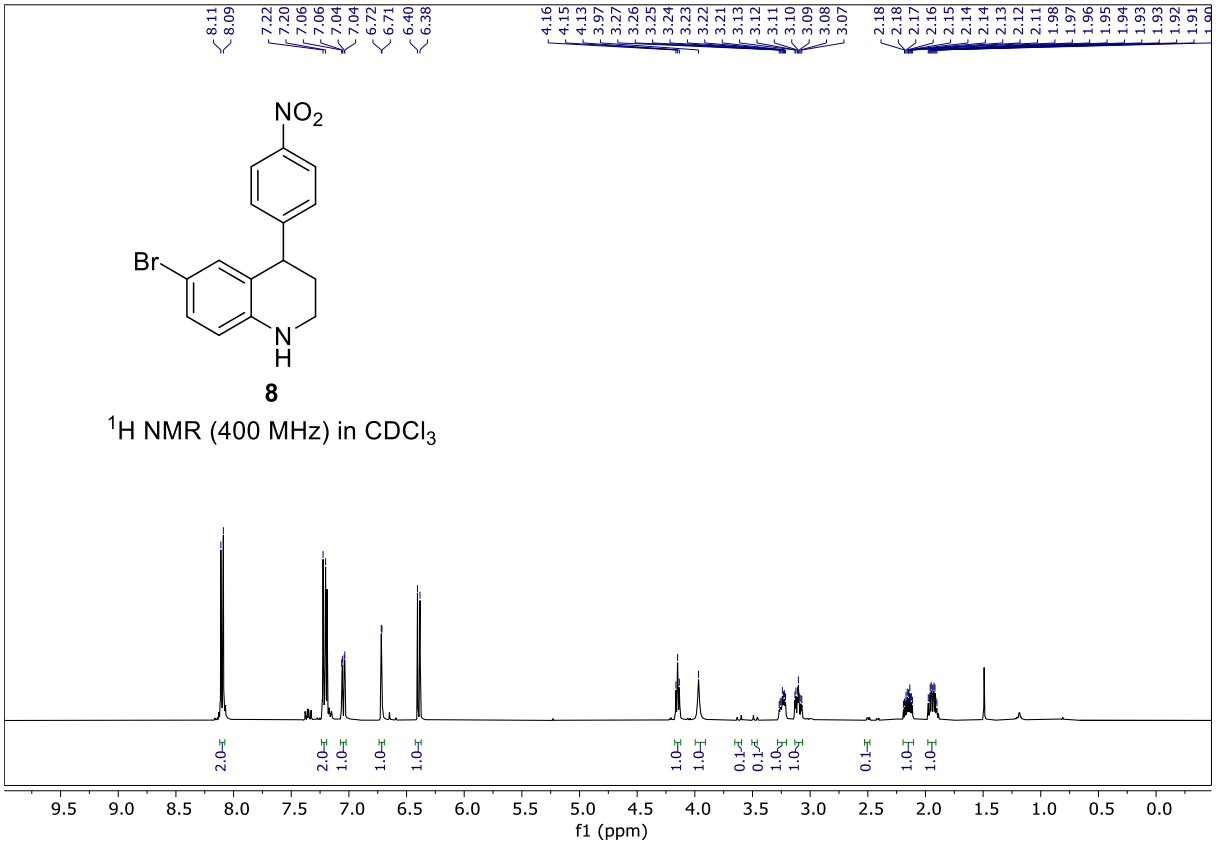

NO2
MeO
N
H
5
13C NMR (101 MHz) in CDCl3
f1 (мд)

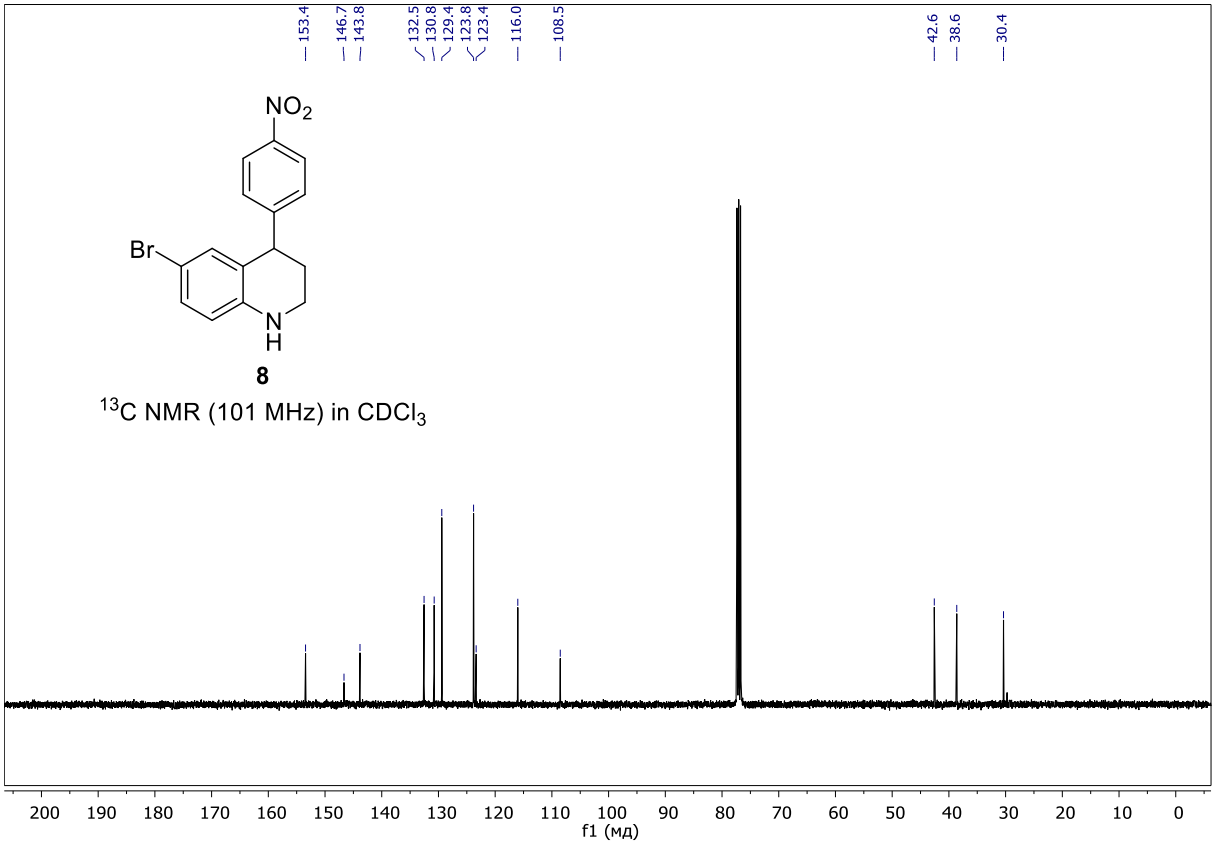

NO2
MeS
N
H
6
1H NMR (400 MHz) in CDCl3
f1 (мд)

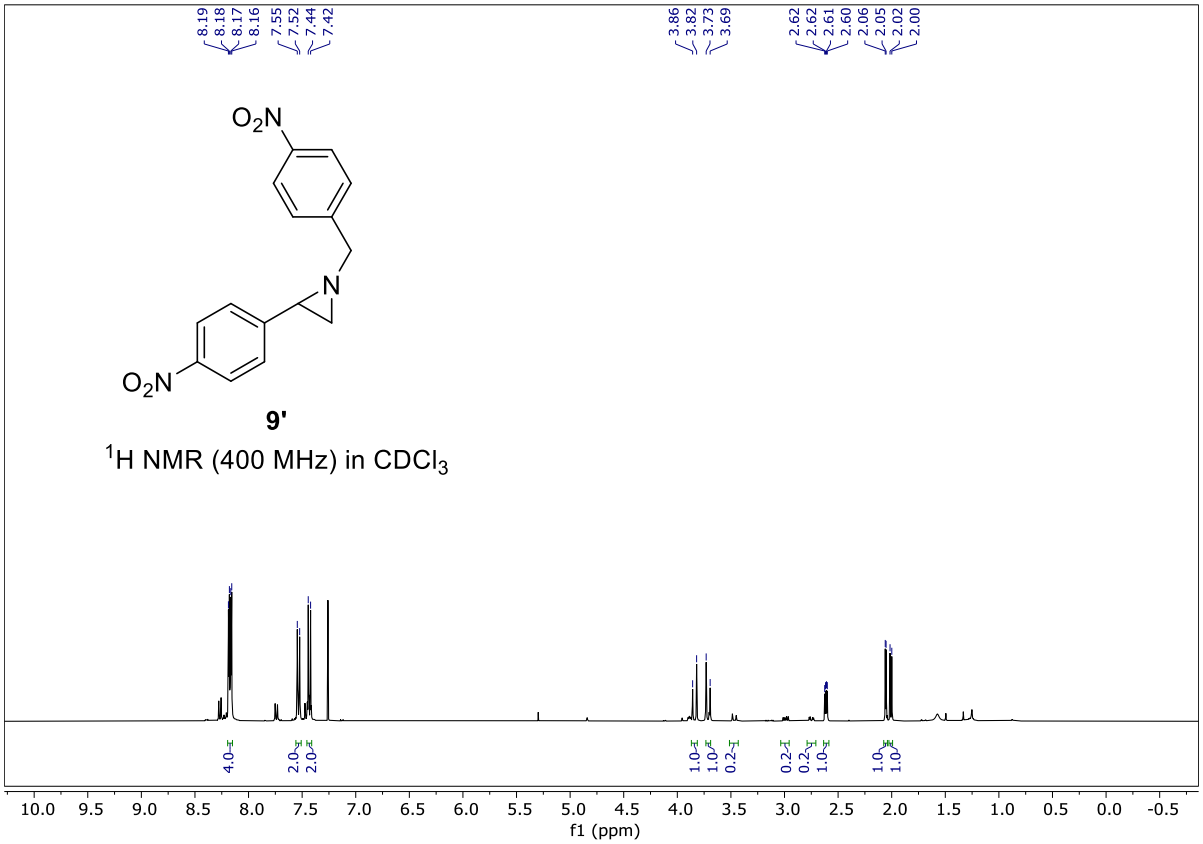

NO2
MeS
N
H
6
13C NMR (101 MHz) in CDCl3
f1 (ppm)


NO2
Ph
N
H
7
1H NMR (400 MHz) in CDCl3
f1 (мд)


NO2
Ph
N
H
7
13C NMR (101 MHz) in CDCl3
f1 (мд)

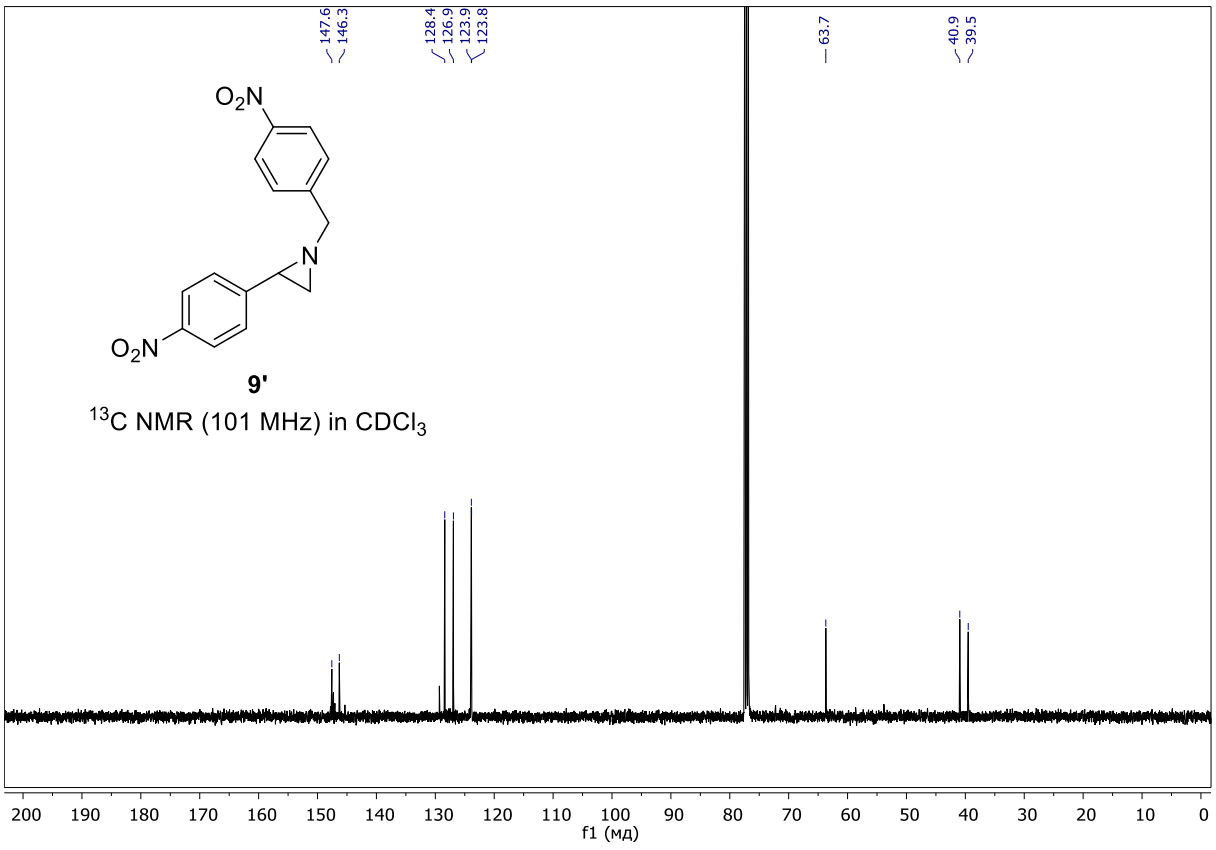

NO2
Br
N
H
8
1H NMR (400 MHz) in CDCl3
f1 (ppm)


NO2
Br
N
H
8
13C NMR (101 MHz) in CDCl3
f1 (мд)



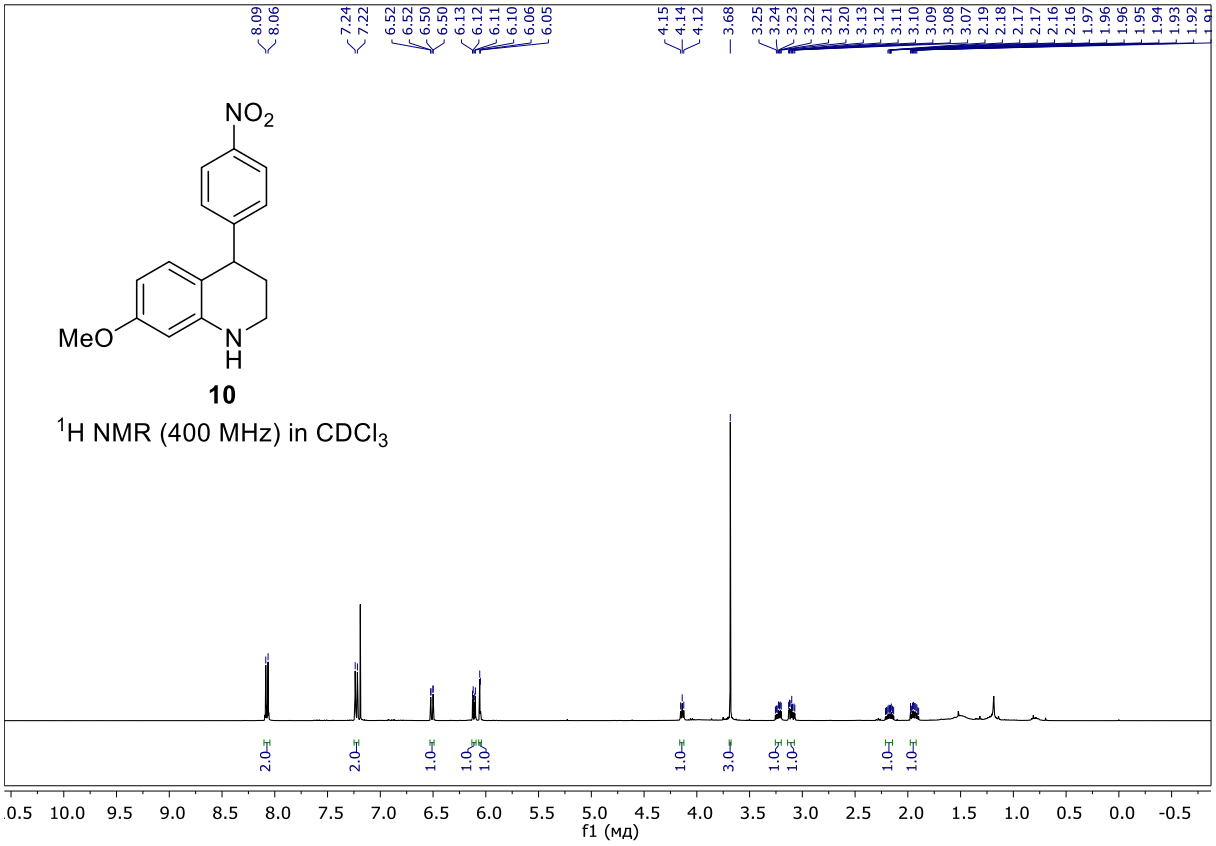
9'

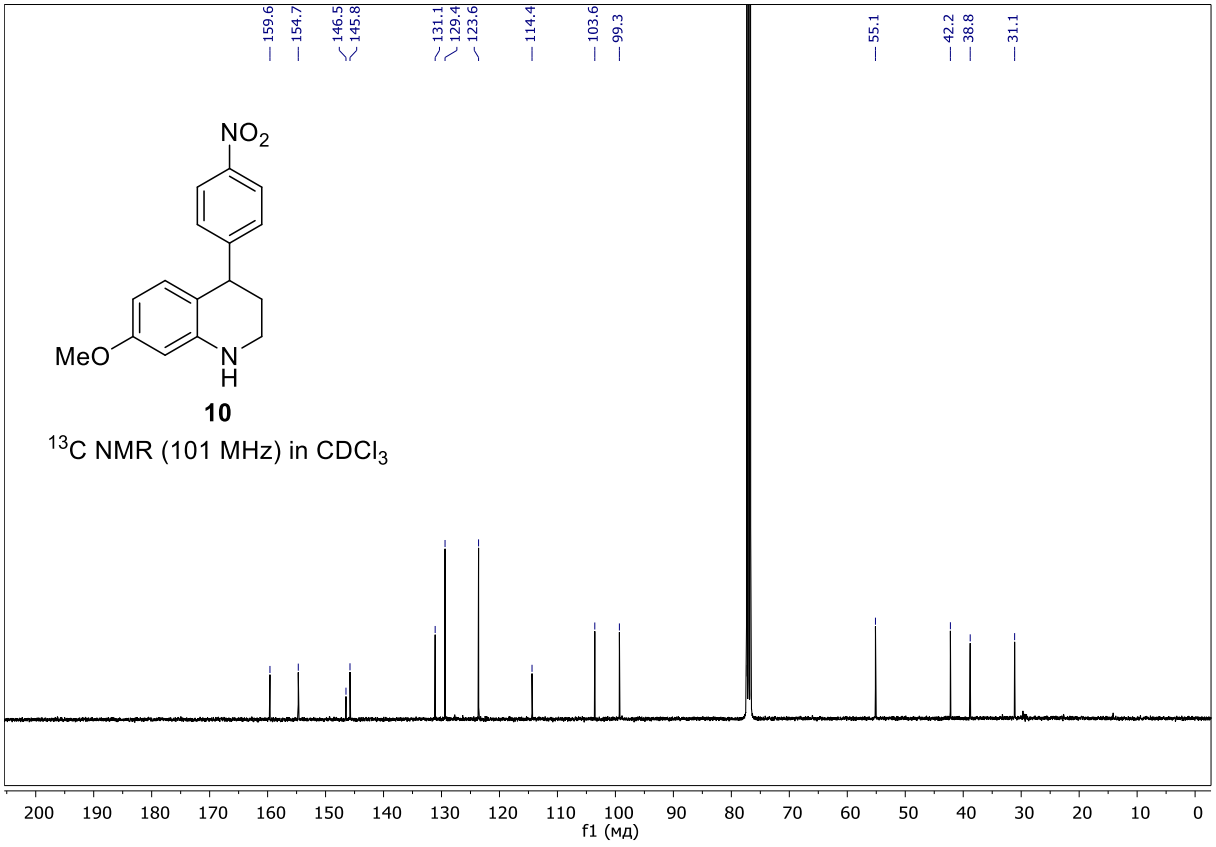
^{1}H NMR (400 MHz) in $CDCl_3$

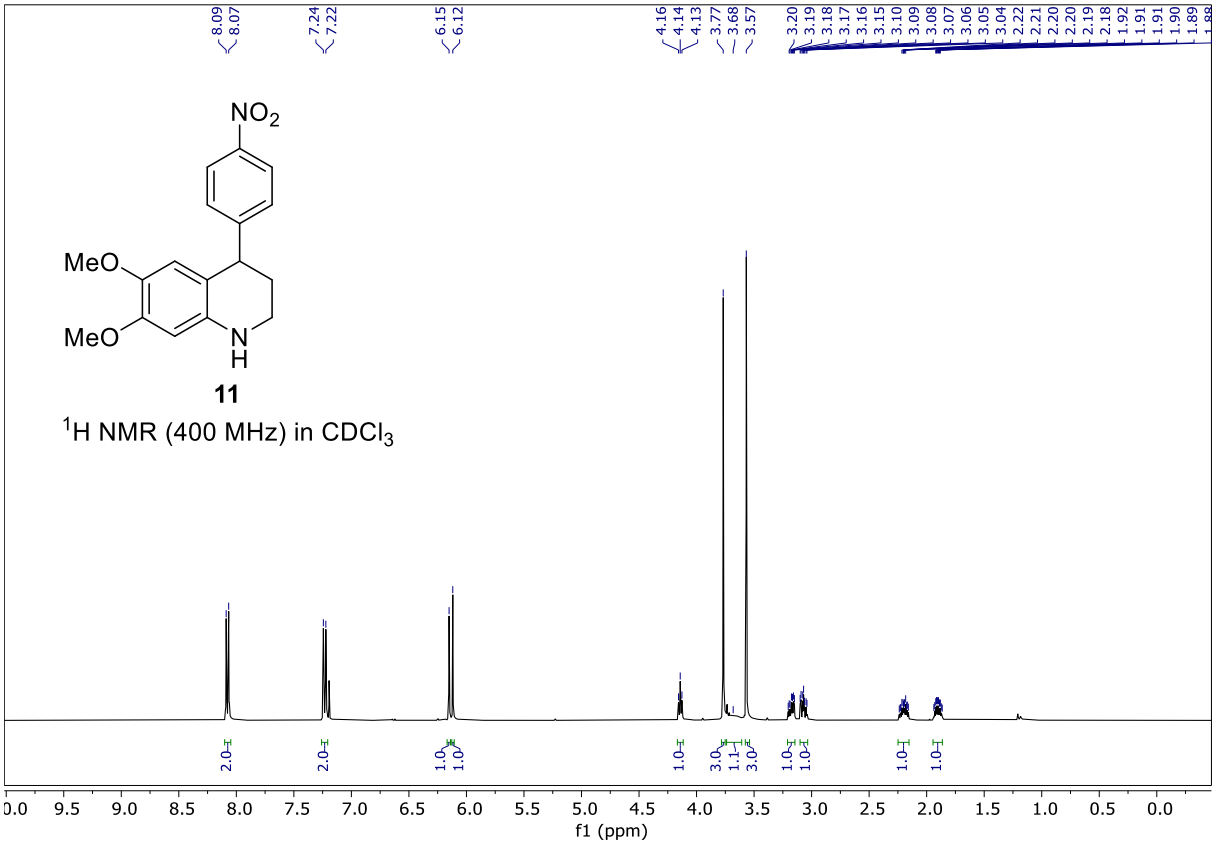


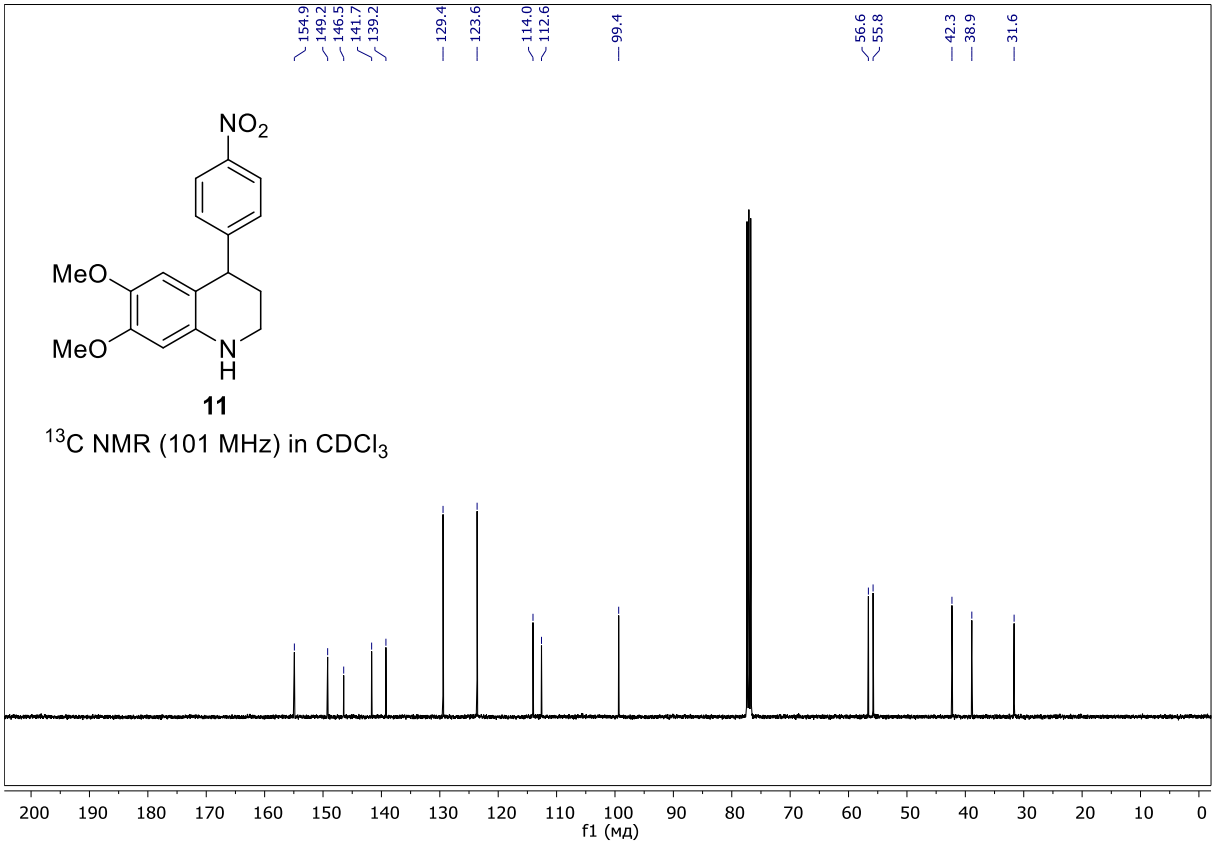
9'

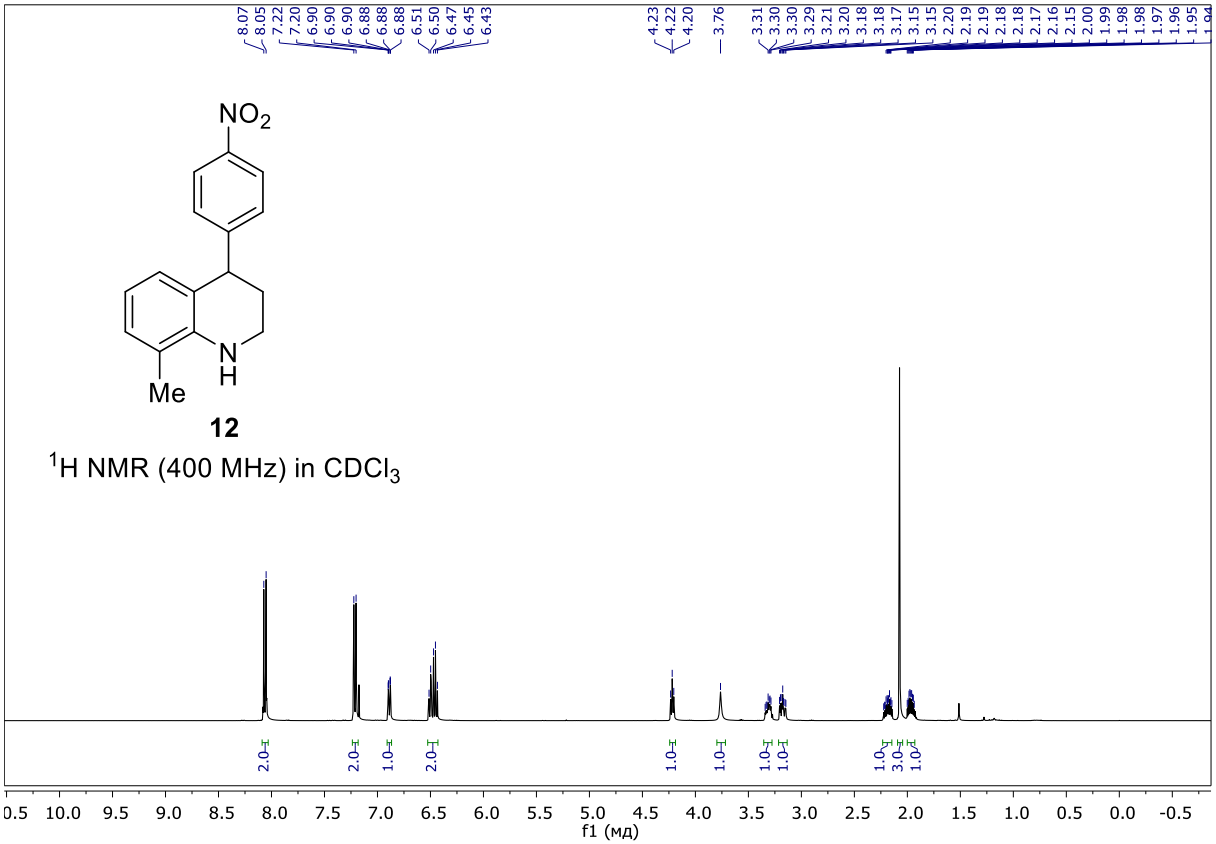
^{13}C NMR (101 MHz) in $CDCl_3$

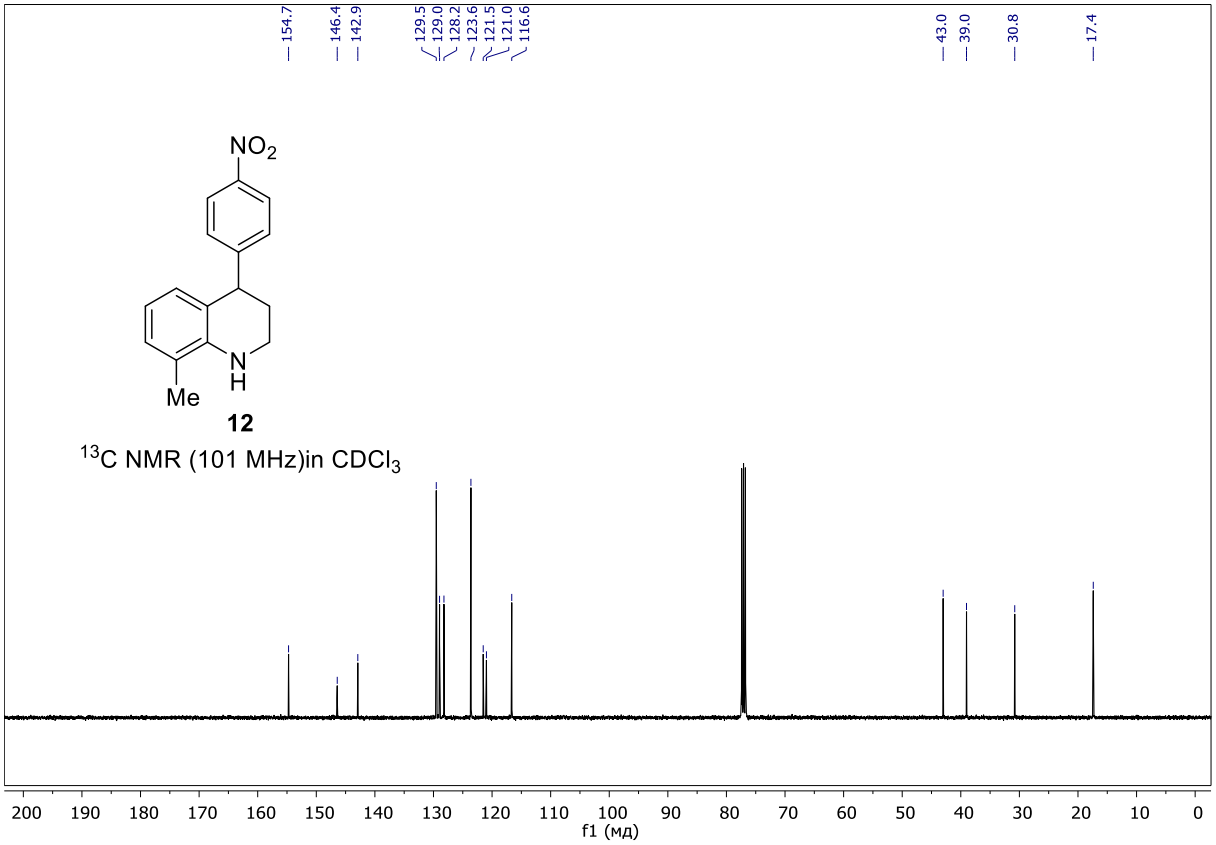

NO2
MeO
N
H
10
1H NMR (400 MHz) in CDCl3
f1 (мд)

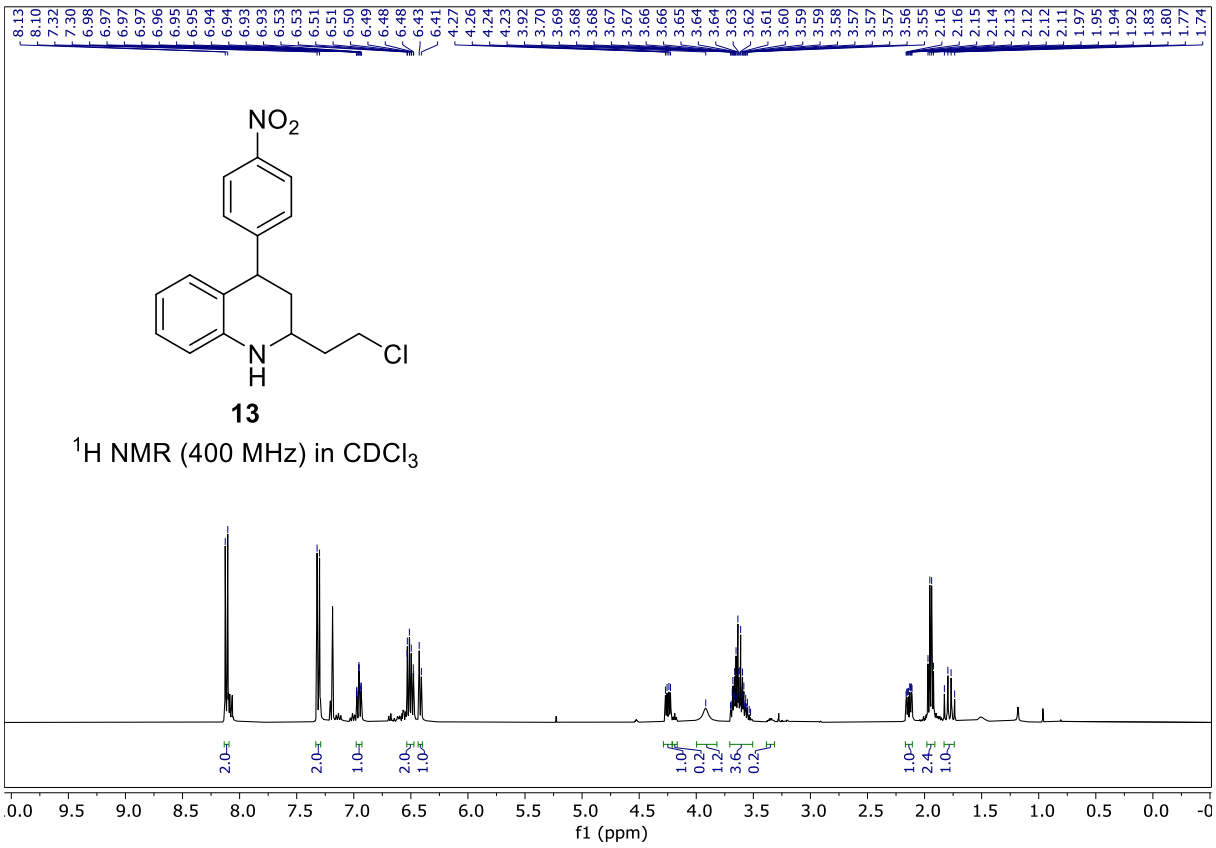

NO2
MeO
N
H
10
13C NMR (101 MHz) in CDCl3
f1 (мд)

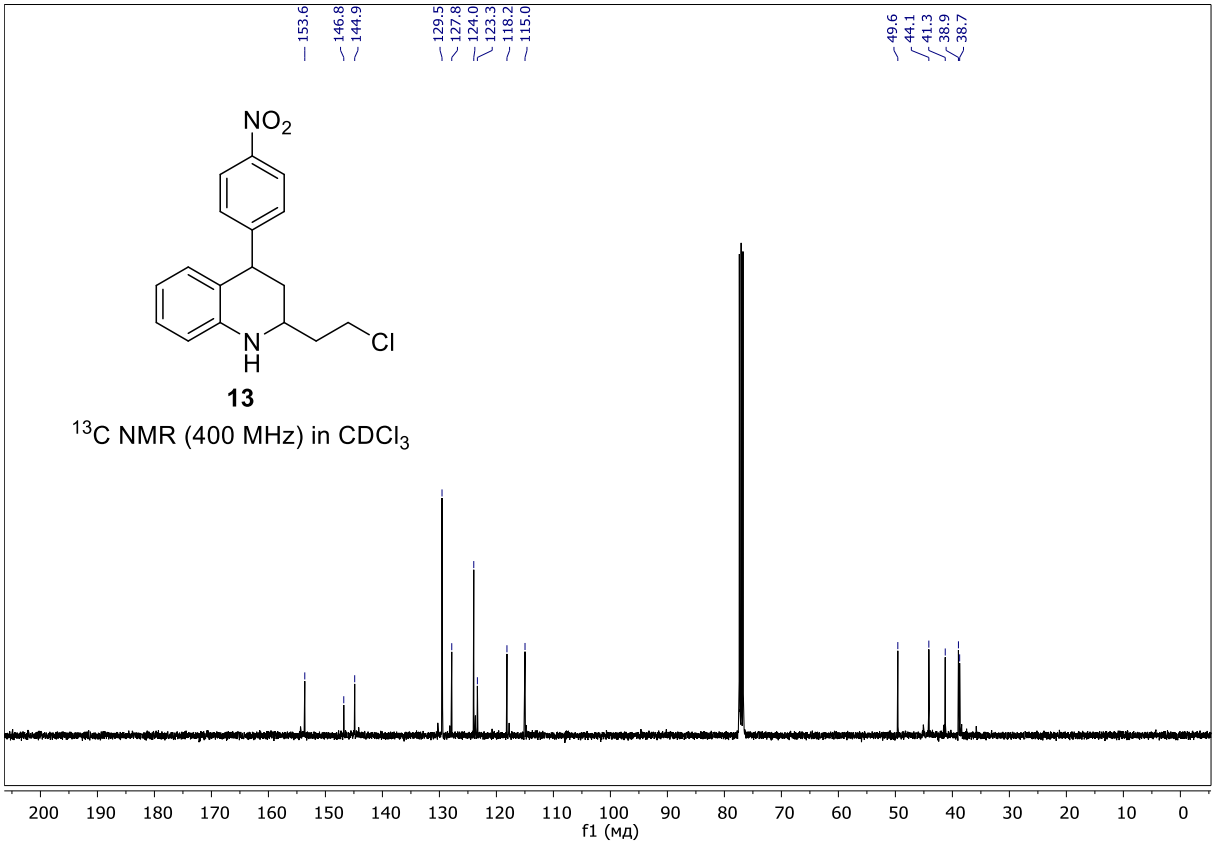

NO2
MeO
MeO
N
H
11
1H NMR (400 MHz) in CDCl3
f1 (ppm)

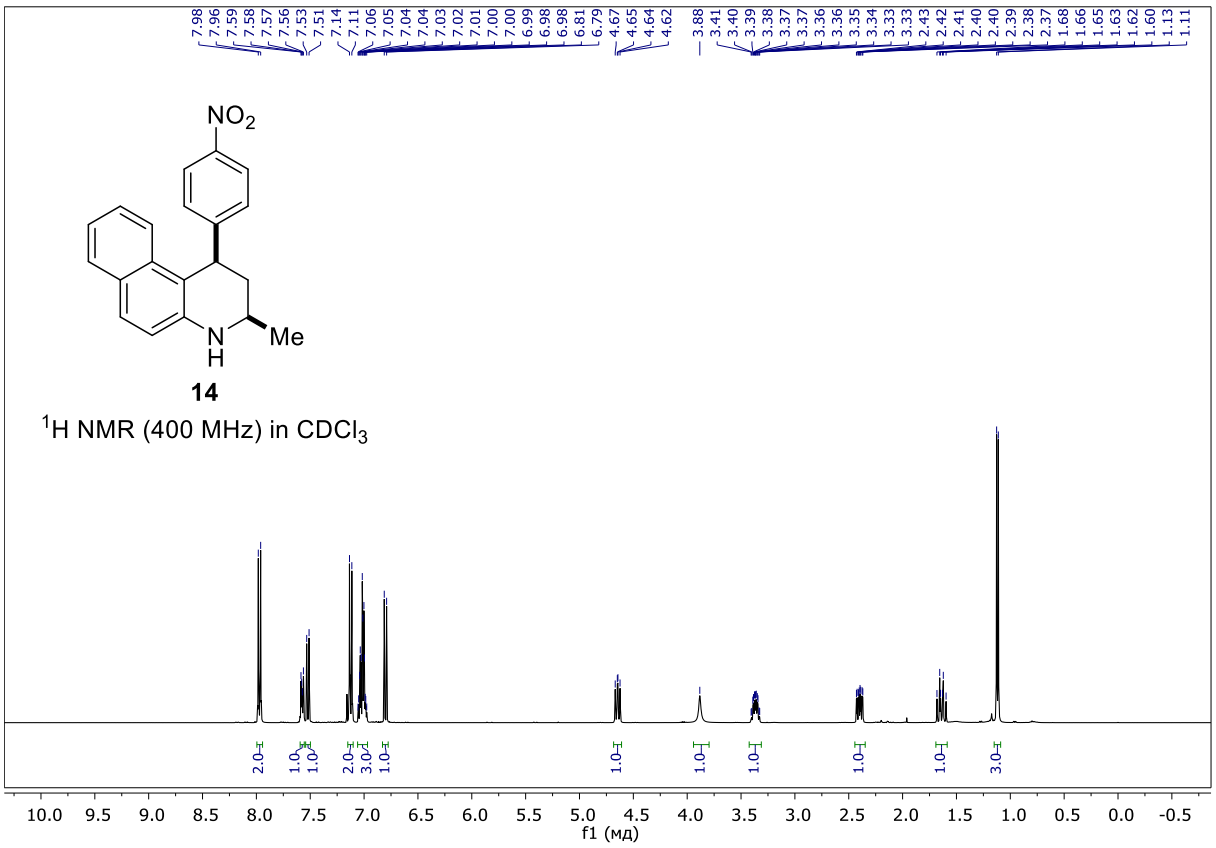

NO2
MeO
MeO
N
H
11
13C NMR (101 MHz) in CDCl3
f1 (мд)


NO2
N
H
Me
12
1H NMR (400 MHz) in CDCl3
f1 (мд)


NO2
N
H
Me
12
13C NMR (101 MHz)in CDCl3
f1 (мд)

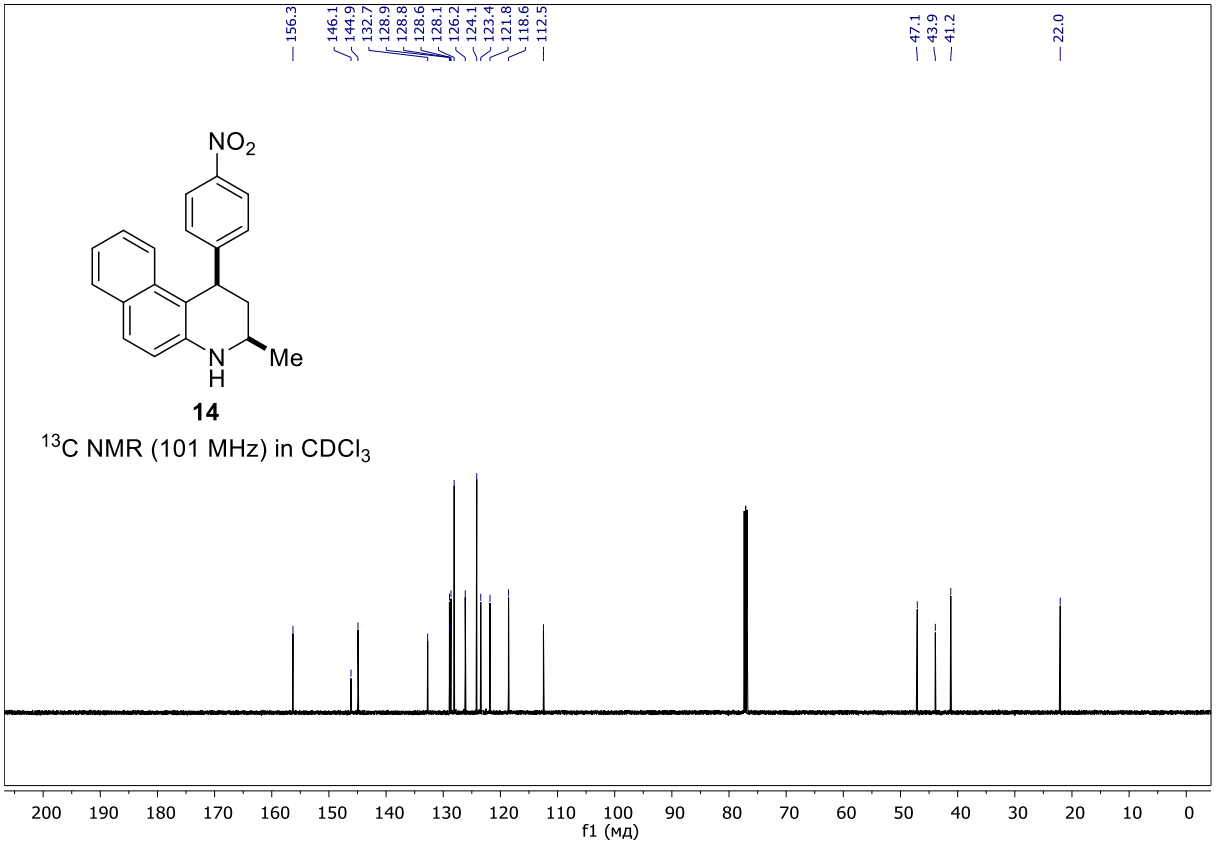

NO2
N
H
Cl
13
1H NMR (400 MHz) in CDCl3
f1 (ppm)


NO2
N
H
Cl
13
13C NMR (400 MHz) in CDCl3
f1 (мд)



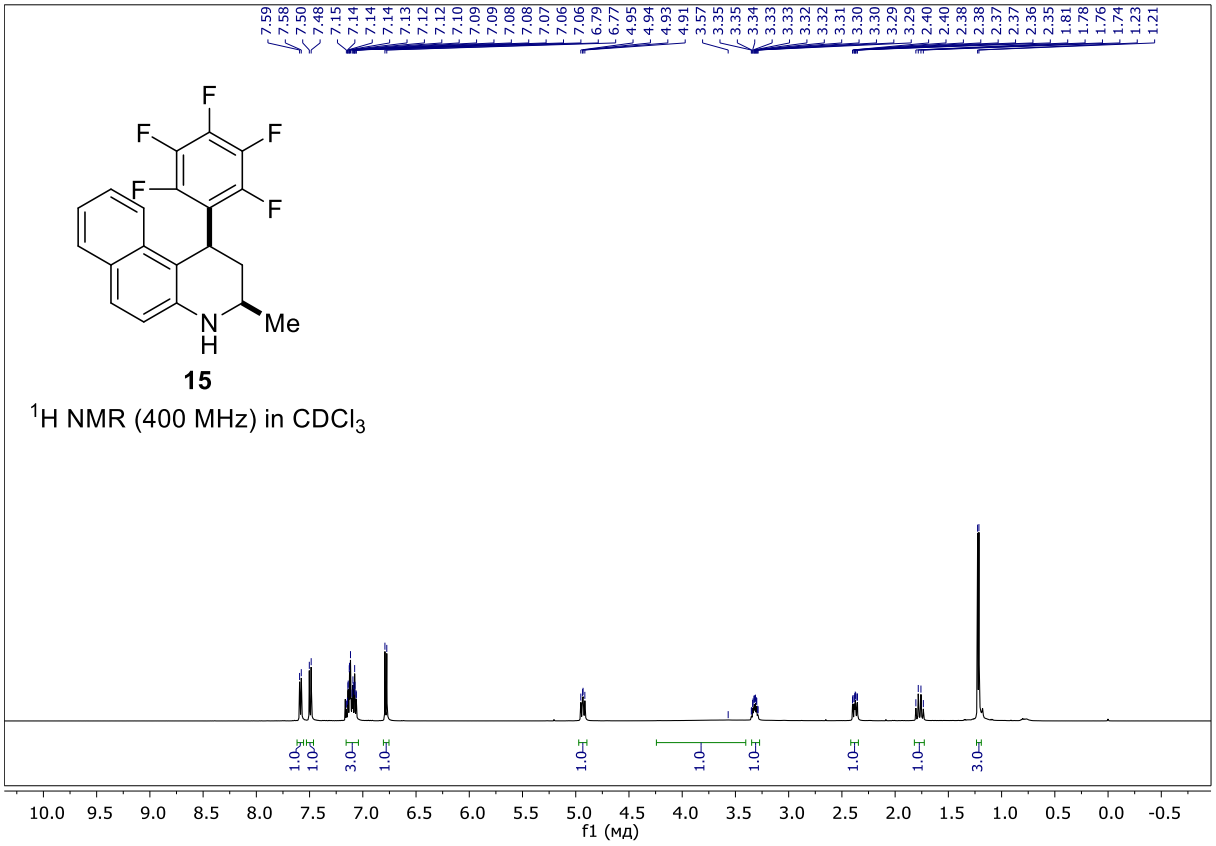
14

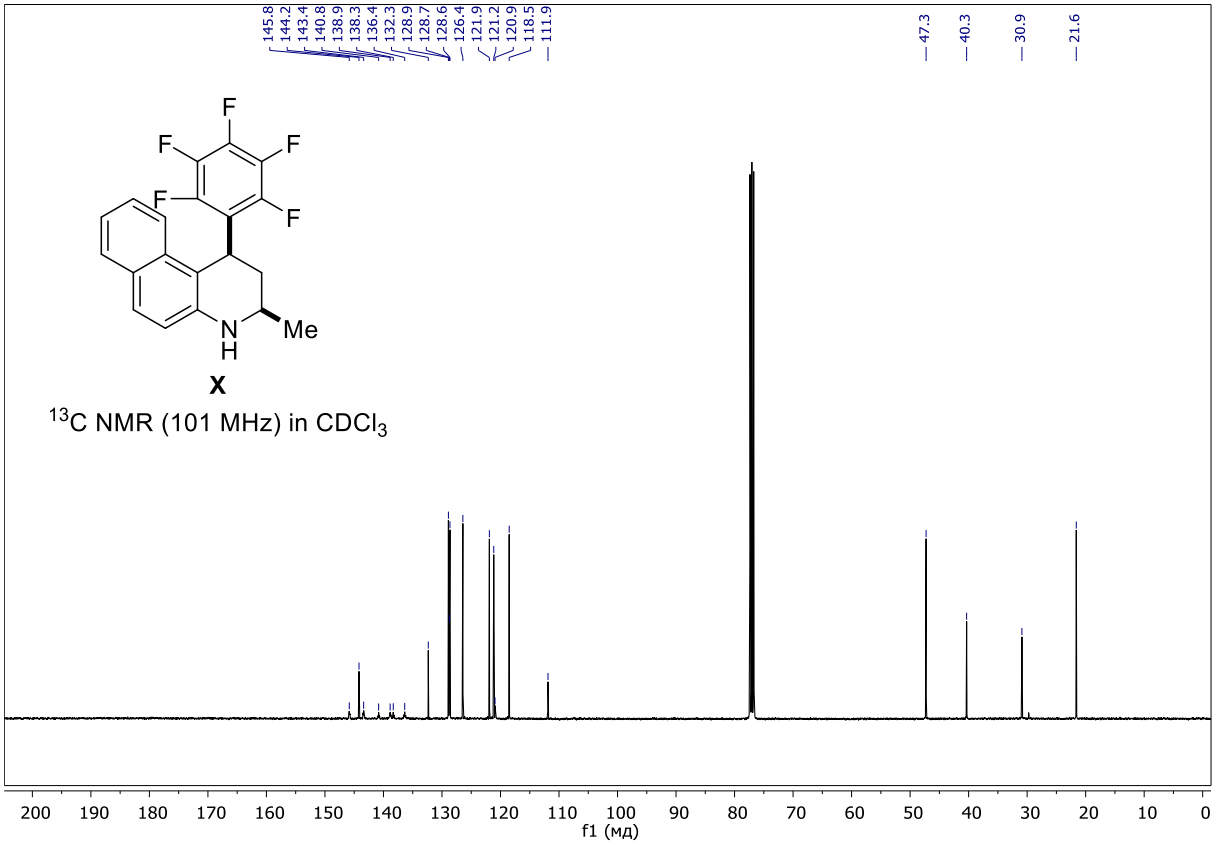
^{1}H NMR (400 MHz) in $CDCl_3$

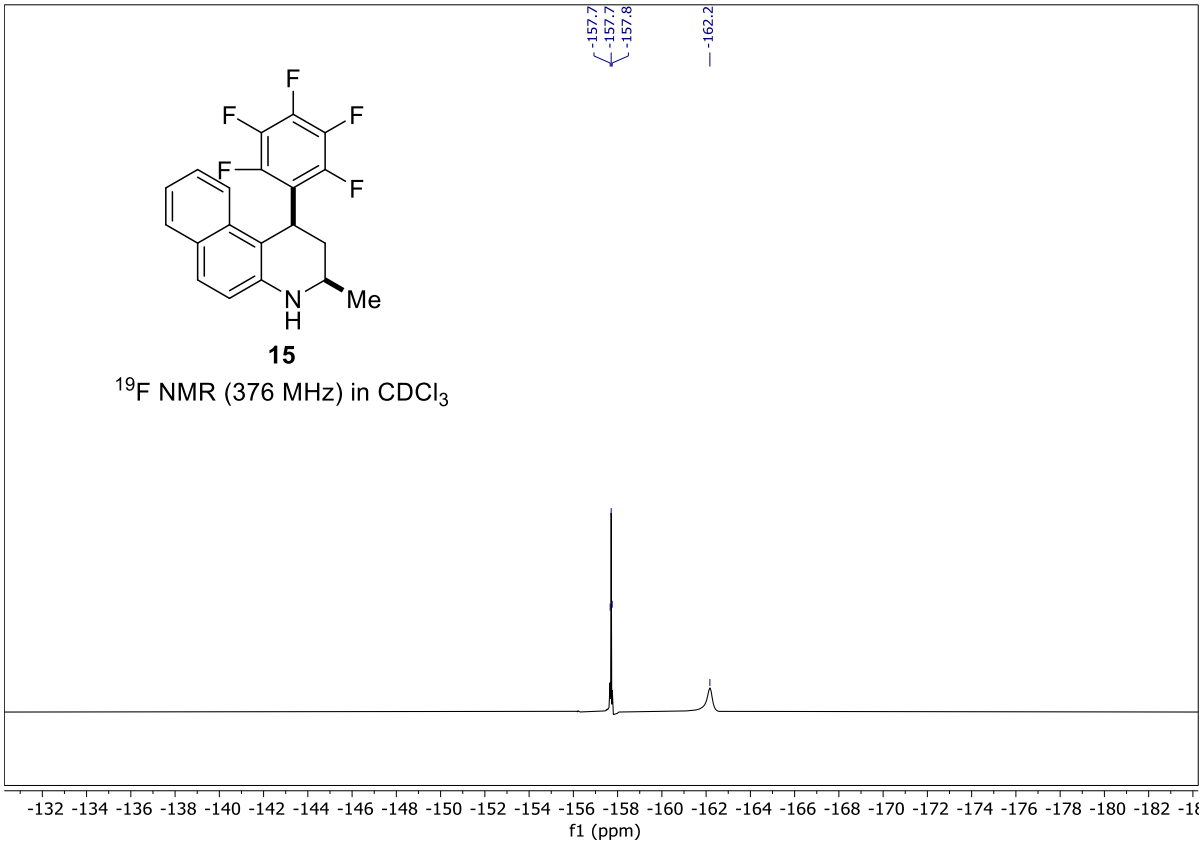


14

^{13}C NMR (101 MHz) in $CDCl_3$

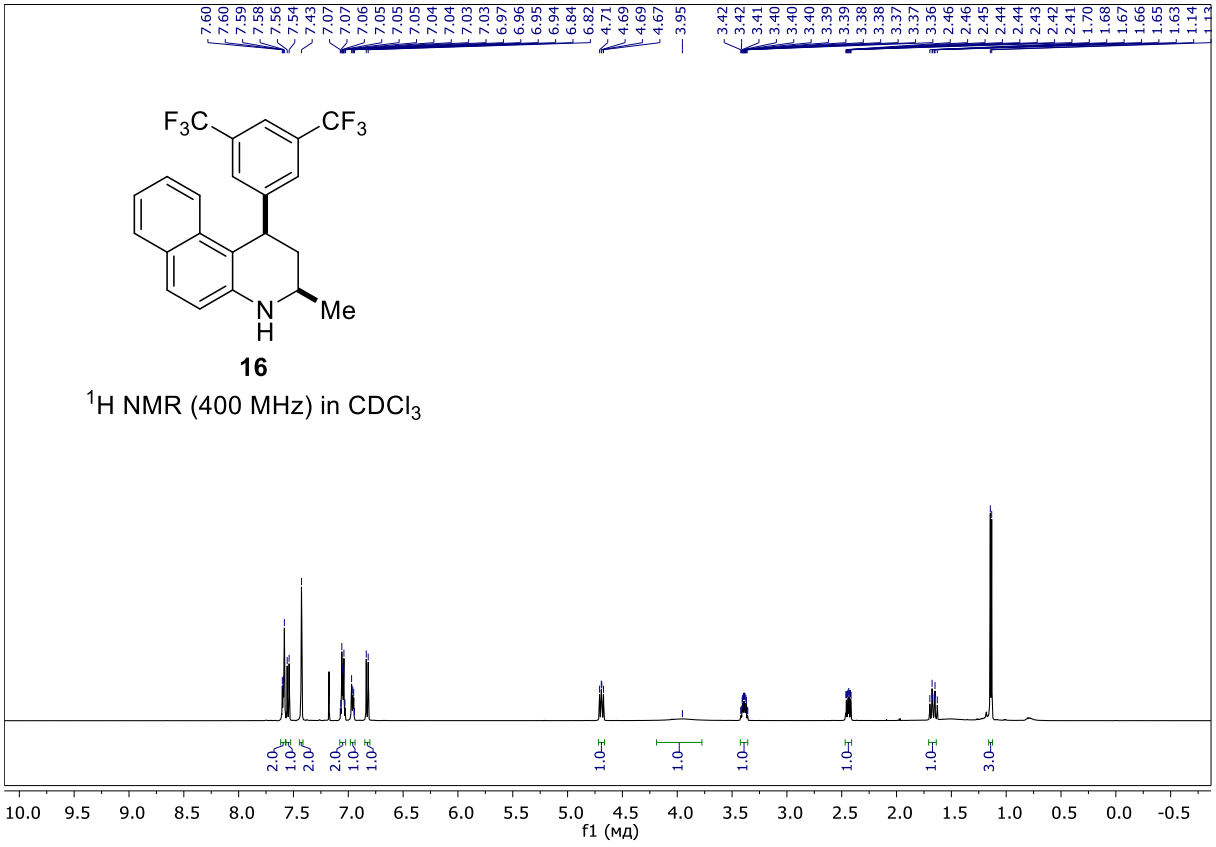

F
F
F
F
F
N
H
Me
15
1H NMR (400 MHz) in CDCl3
f1 (мд)


F
F
F
F
F
N
H
Me
X
13C NMR (101 MHz) in CDCl3
f1 (мд)



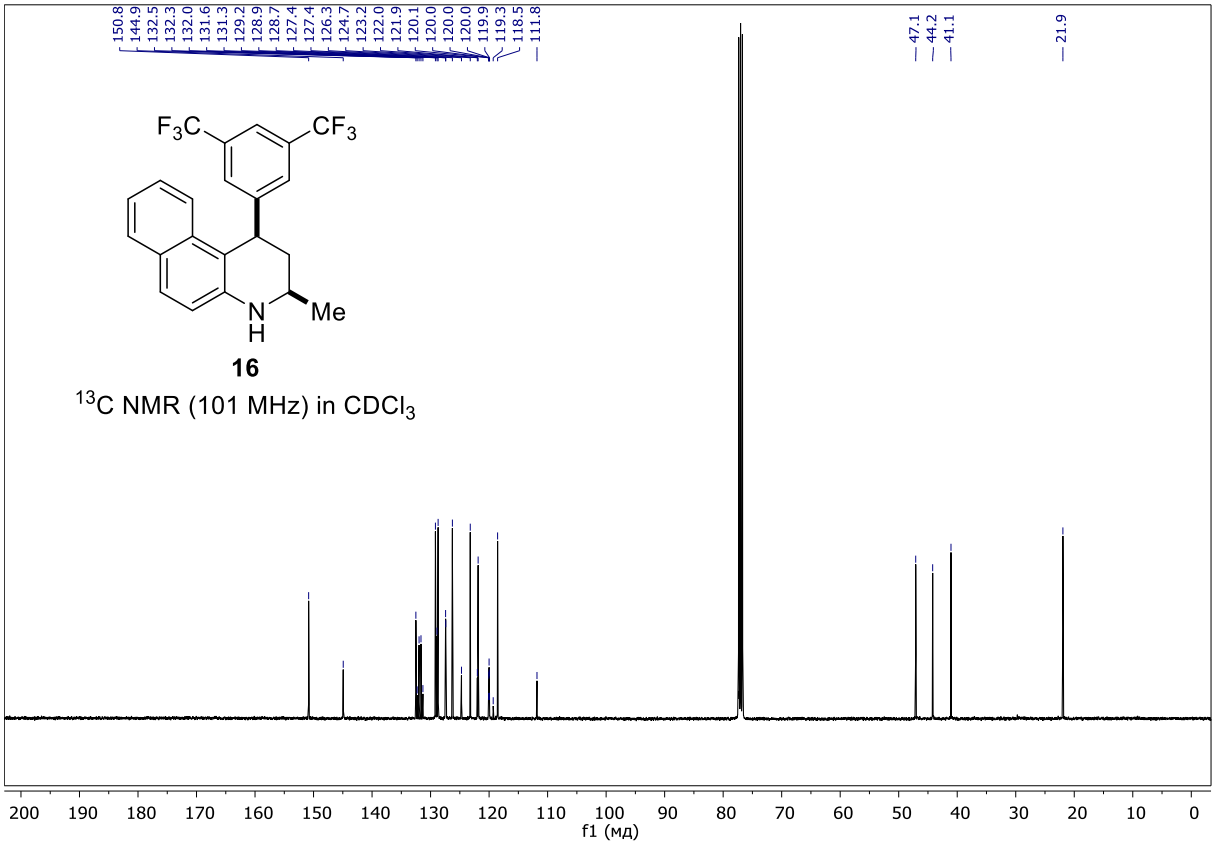
15

^{19}F NMR (376 MHz) in $CDCl_3$



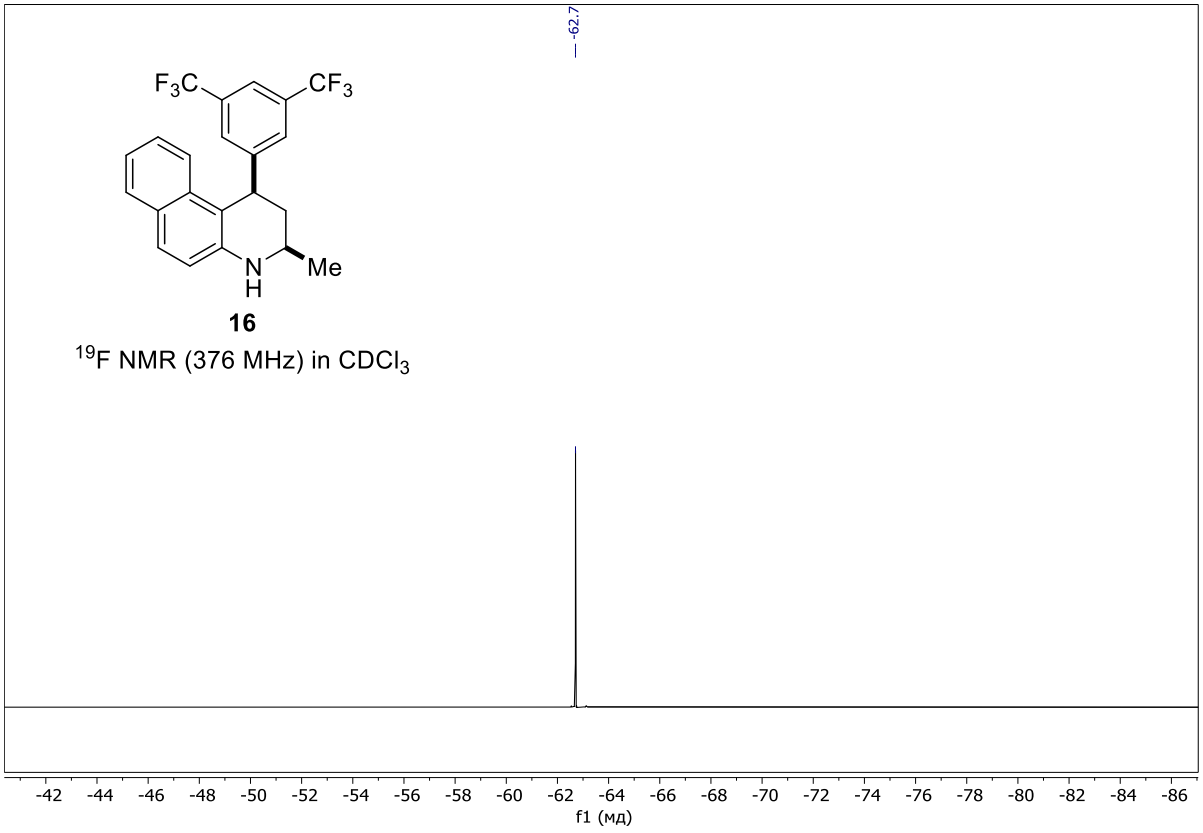
16

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



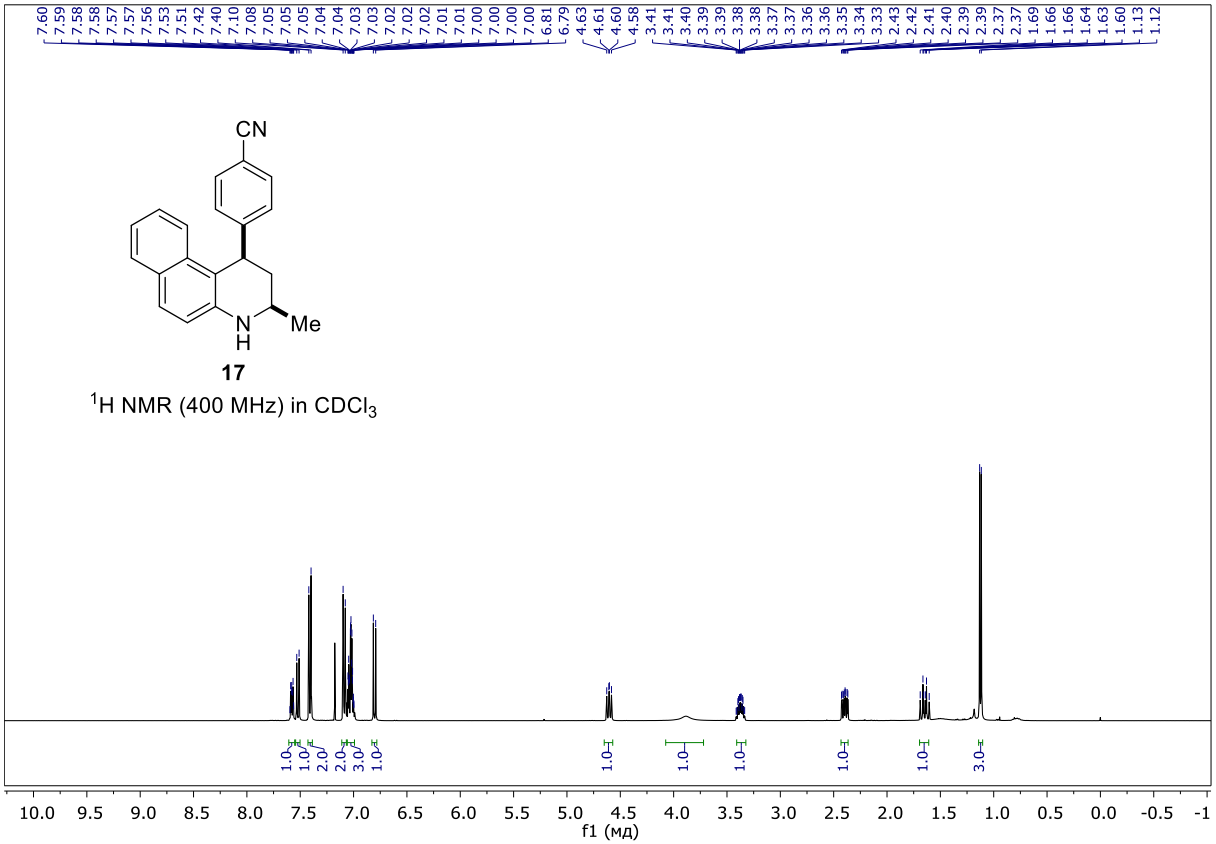
16

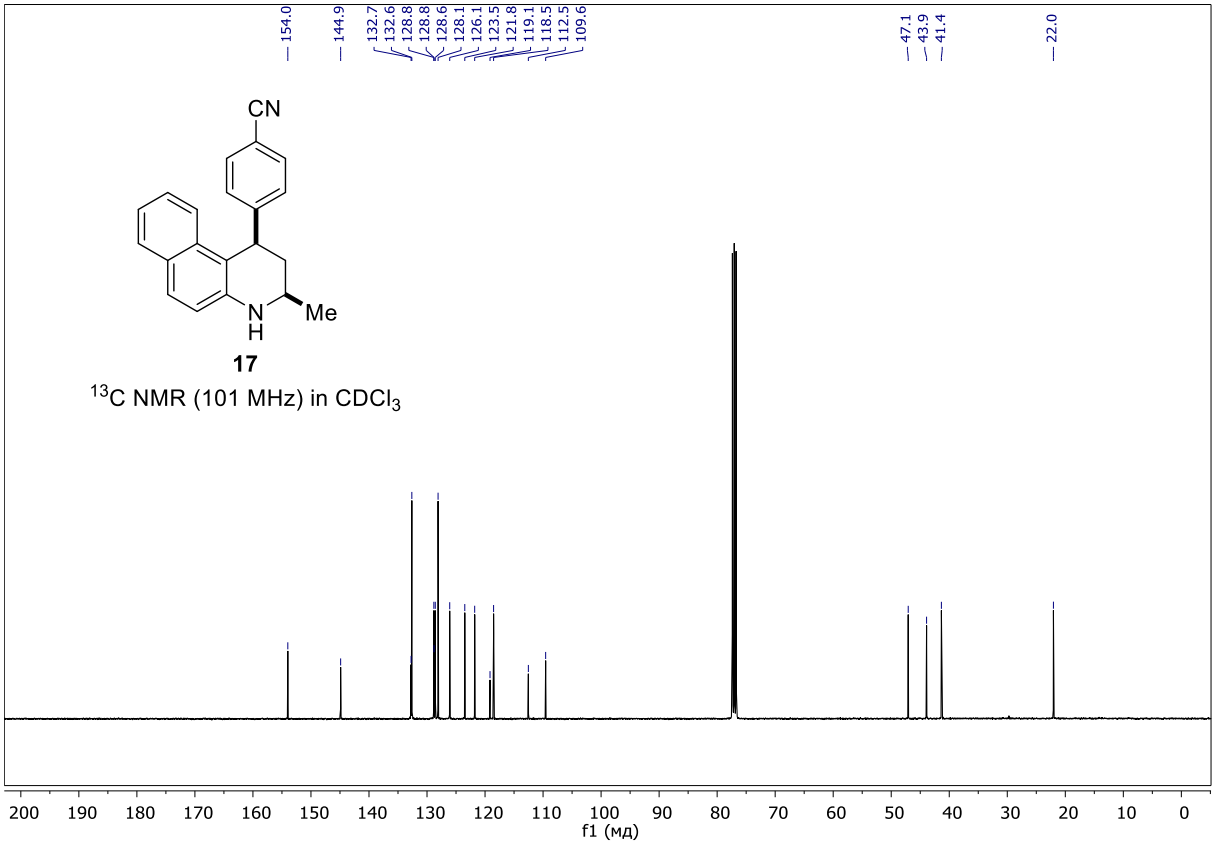
^{13}C NMR (101 MHz) in $CDCl_3$

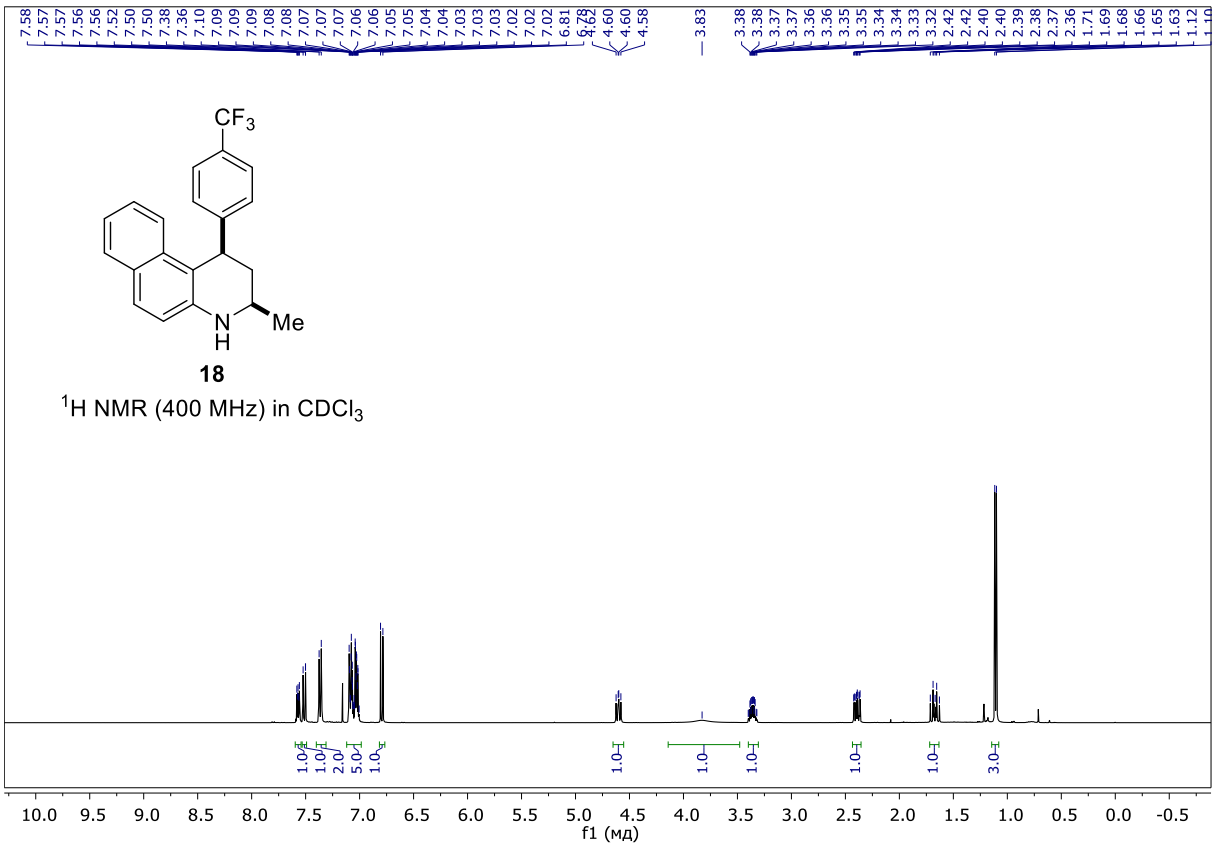


16

^{19}F NMR (376 MHz) in $CDCl_3$

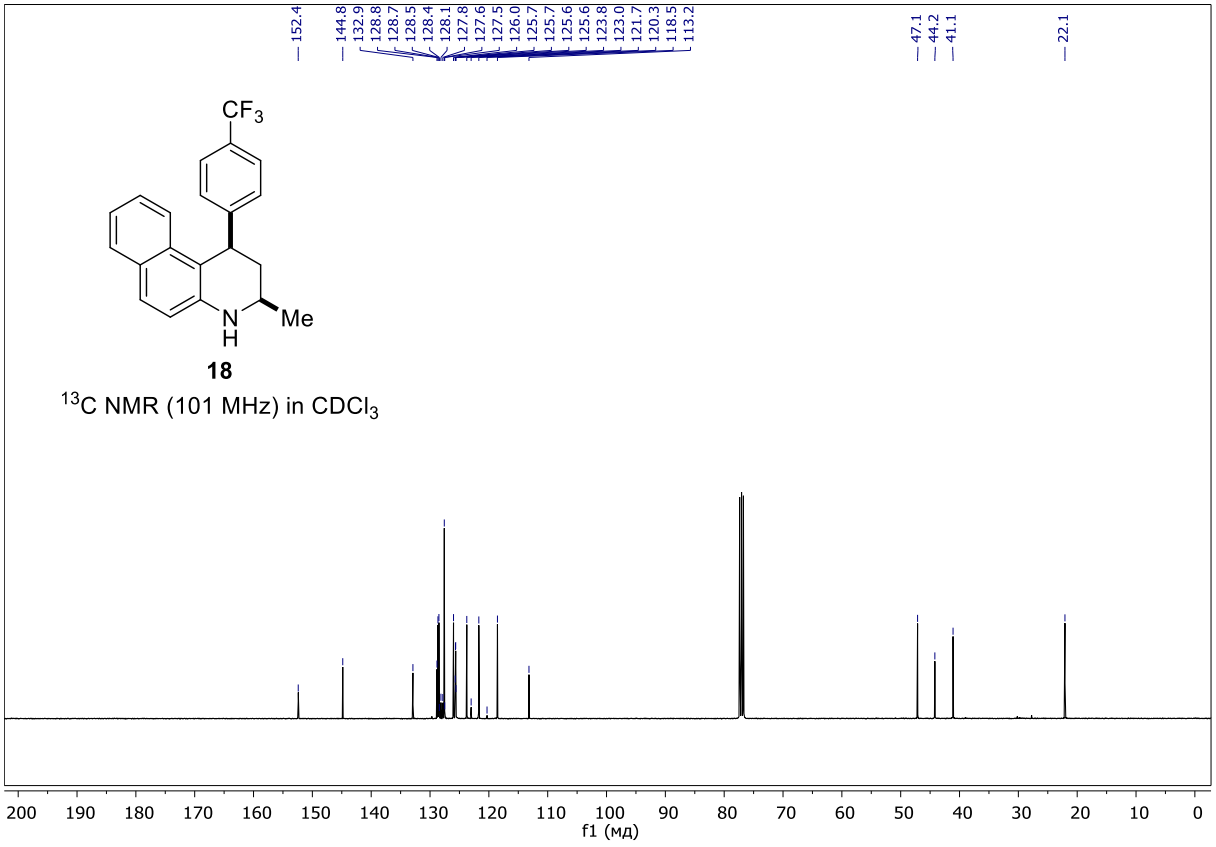

CN
N
H
Me
17
1H NMR (400 MHz) in CDCl3
f1 (мд)


CN
N
H
Me
17
13C NMR (101 MHz) in CDCl3
f1 (мд)



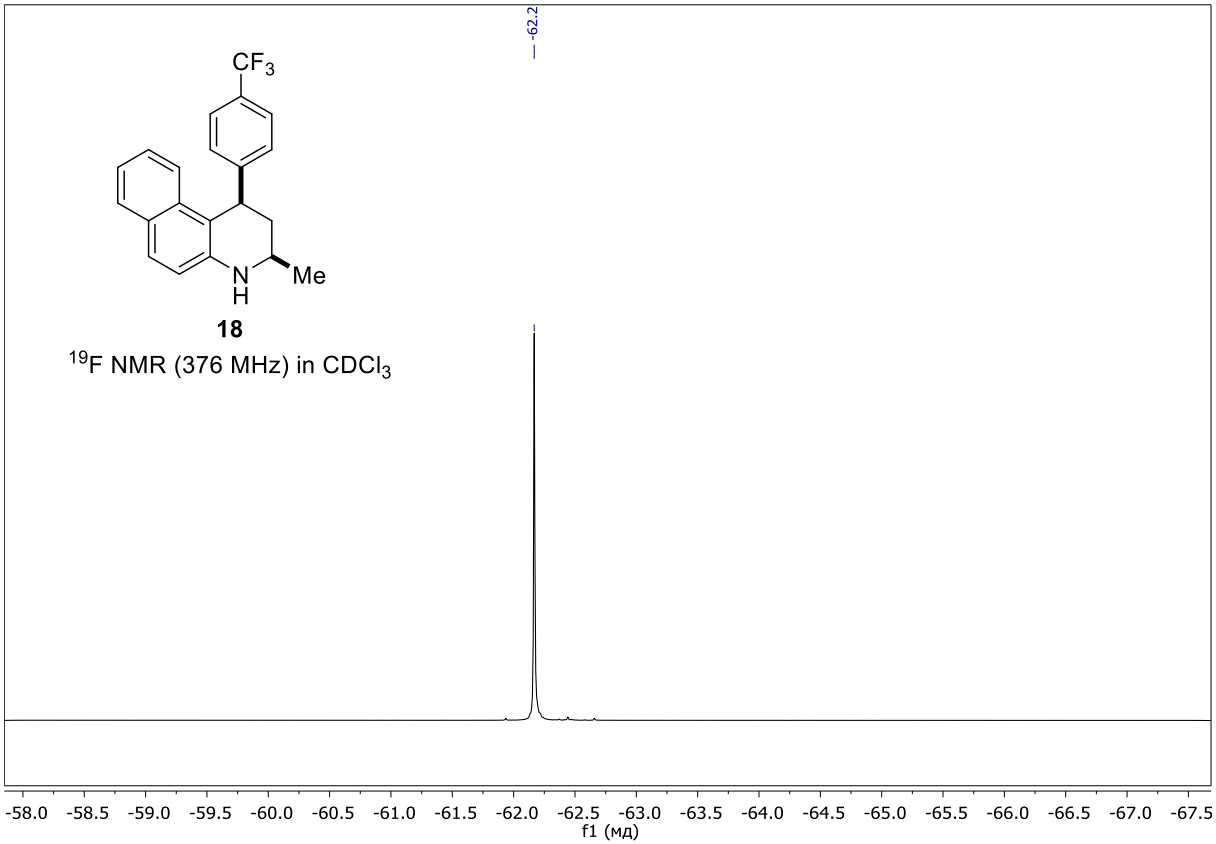
18

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



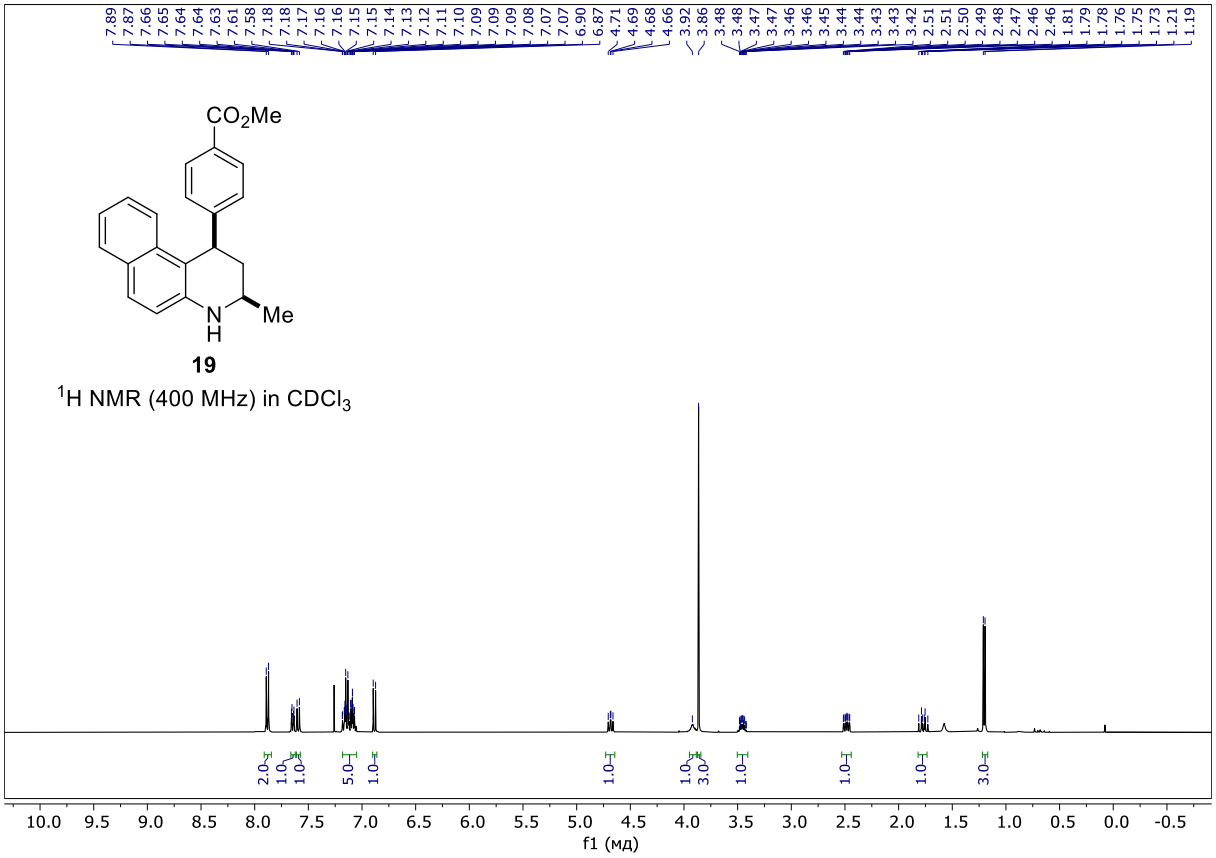
18

^{13}C NMR (101 MHz) in $CDCl_3$



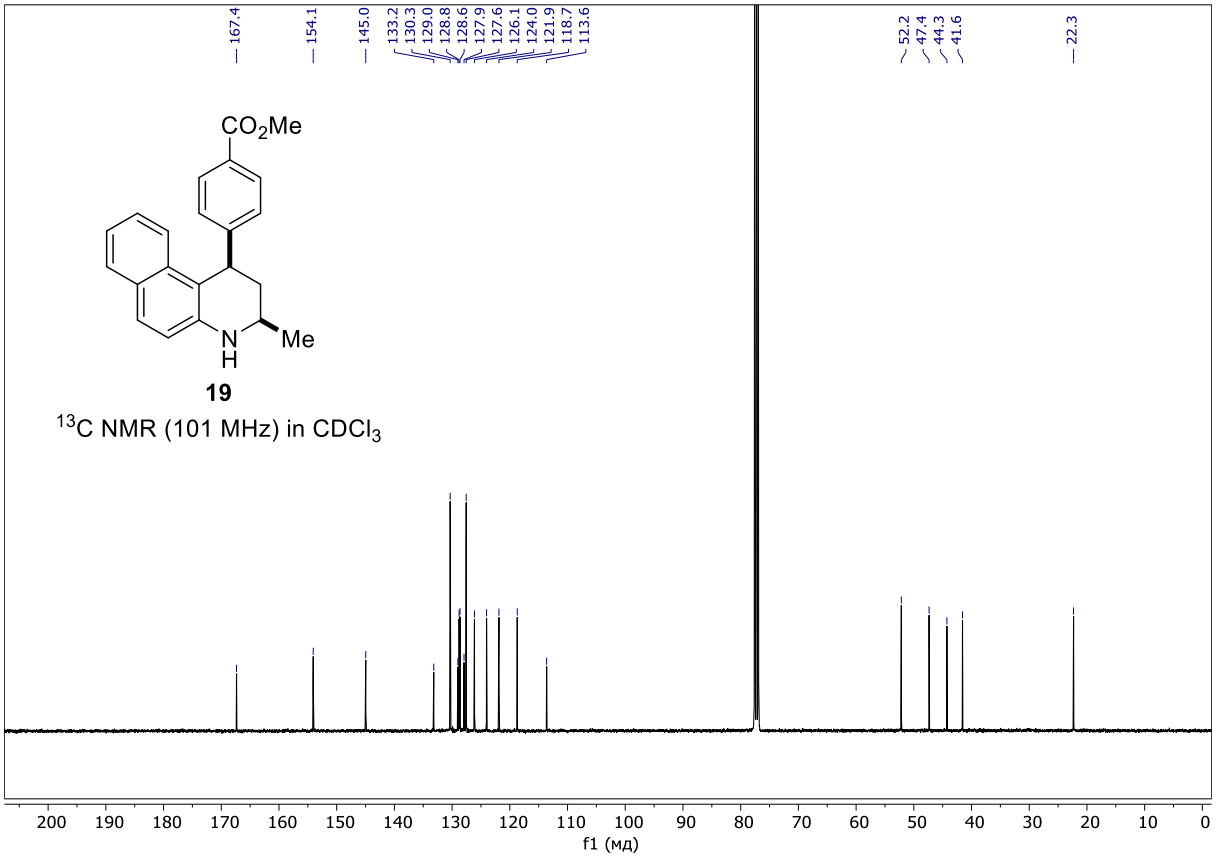
18

^{19}F NMR (376 MHz) in $CDCl_3$



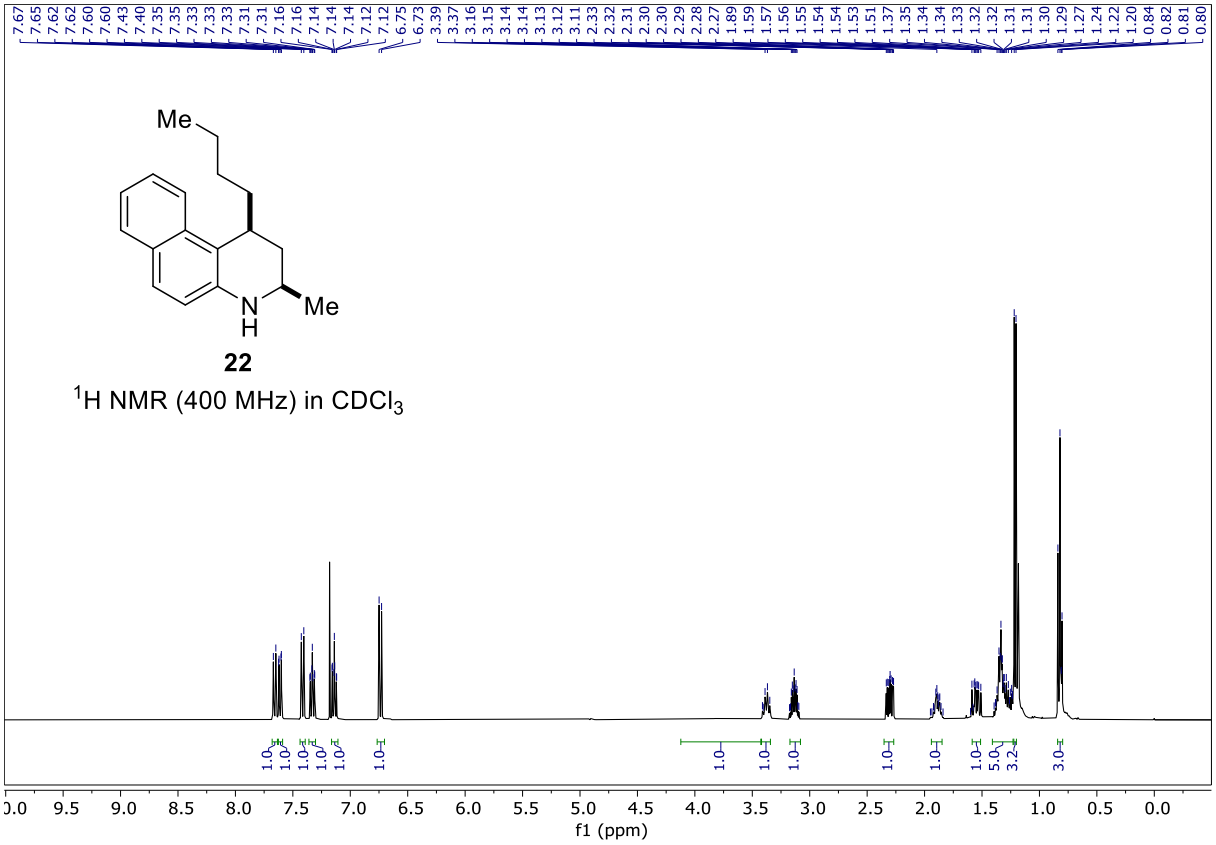
19

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



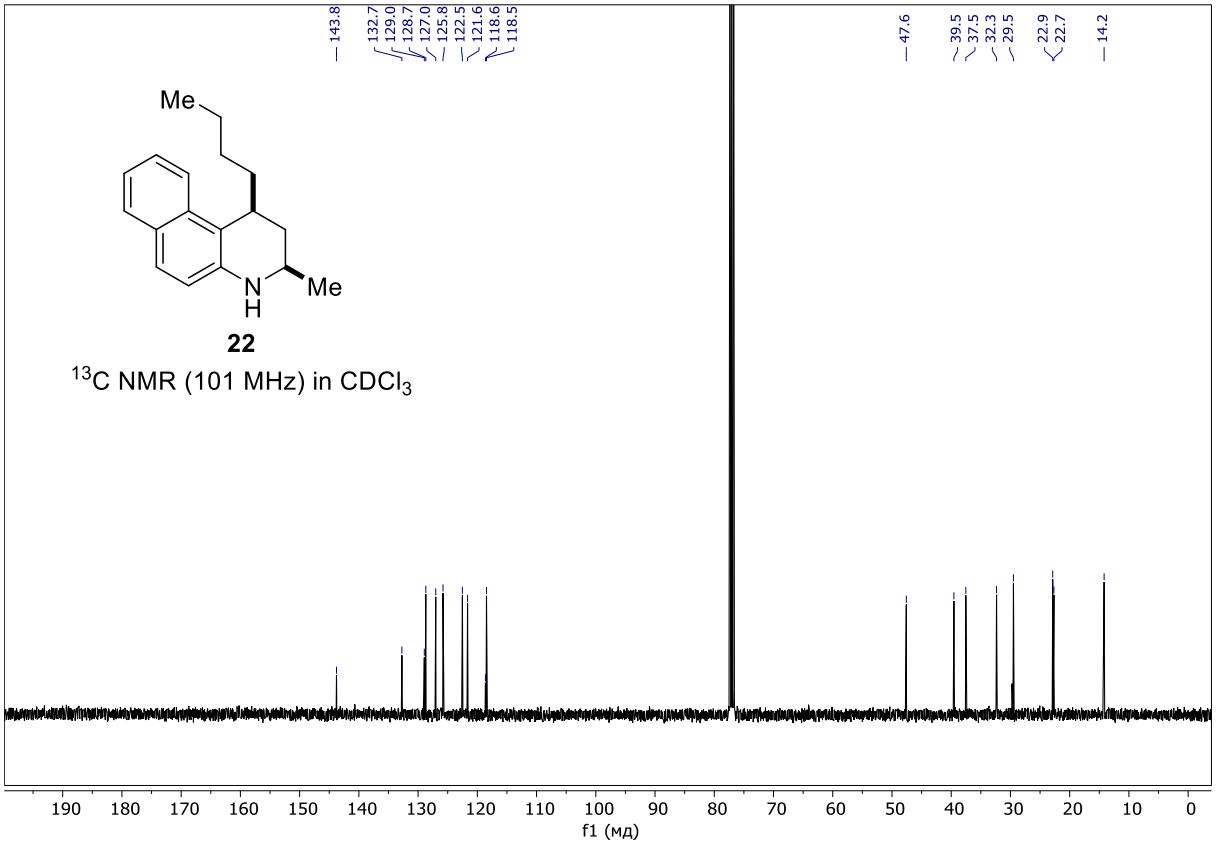
19

^{13}C NMR (101 MHz) in $CDCl_3$



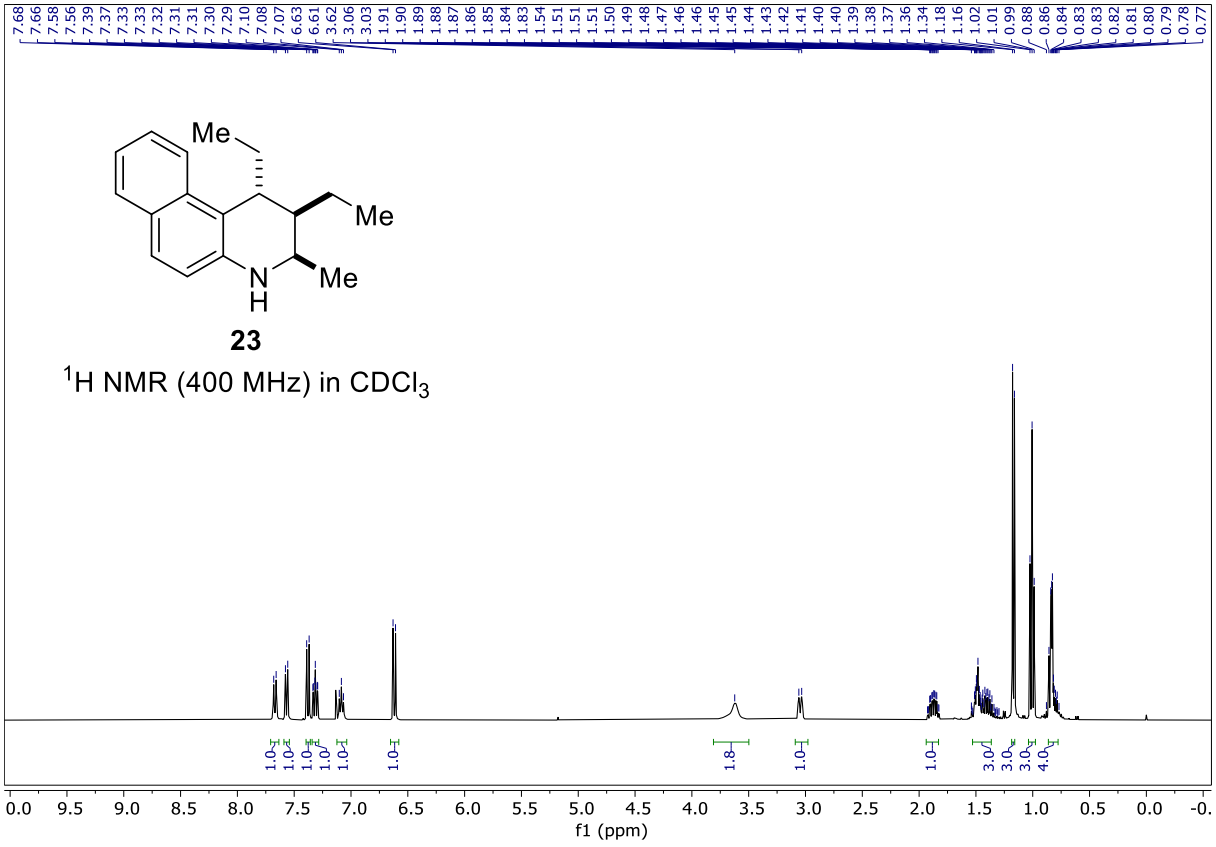
22

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



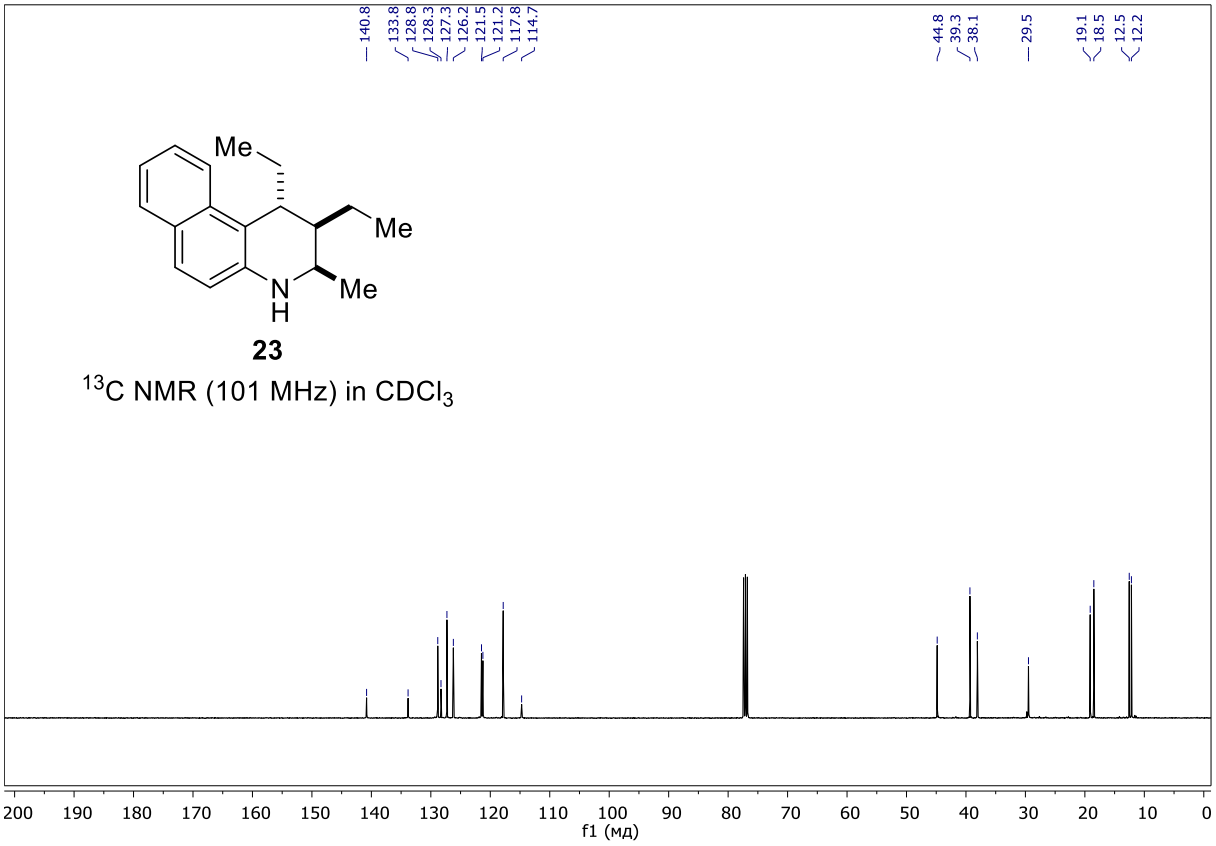
22

^{13}C NMR (101 MHz) in $CDCl_3$



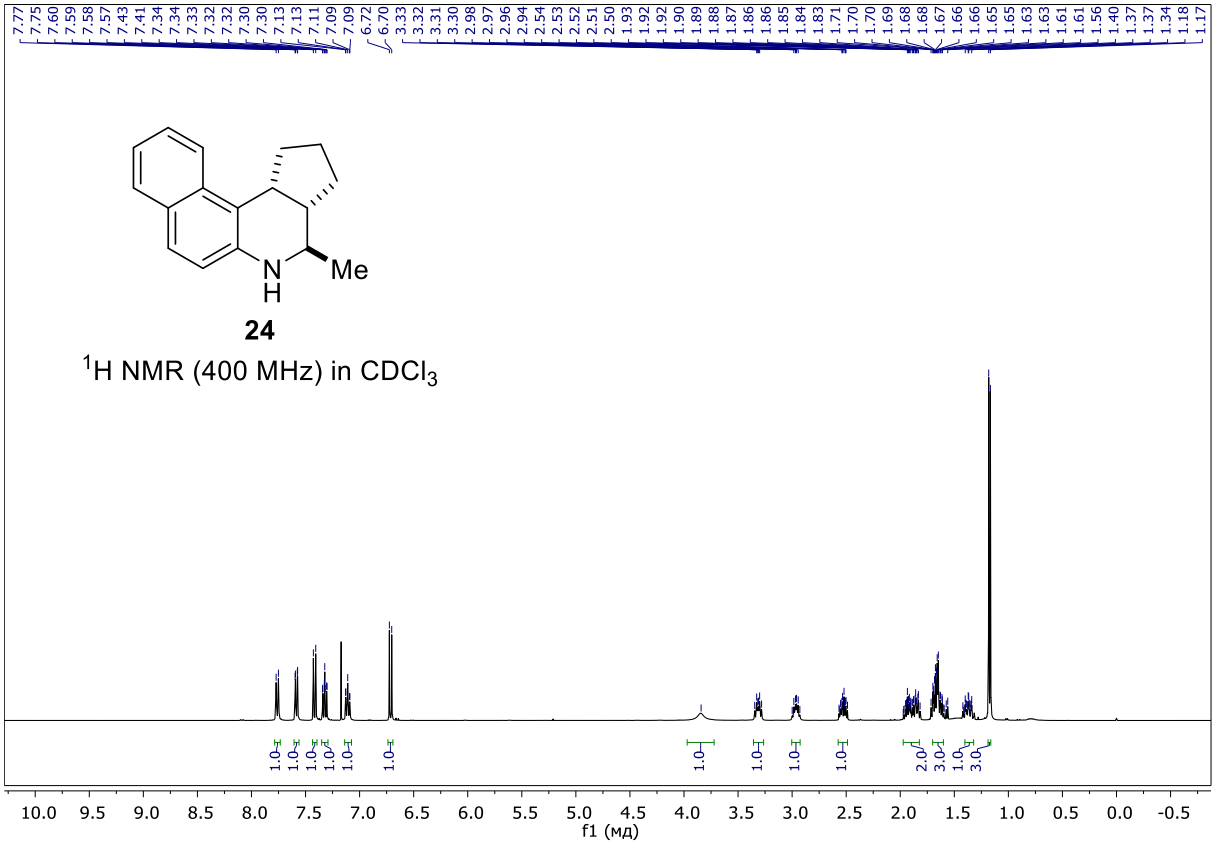
23

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



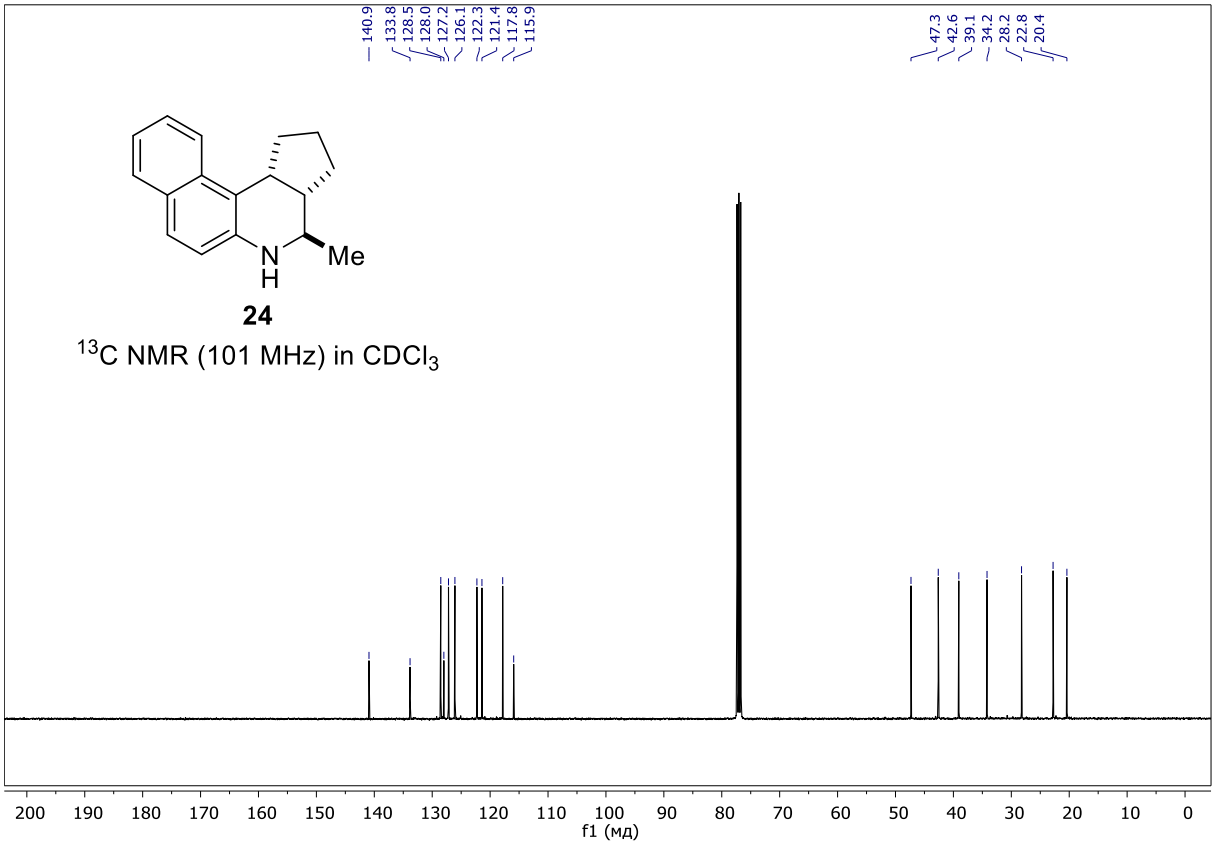
23

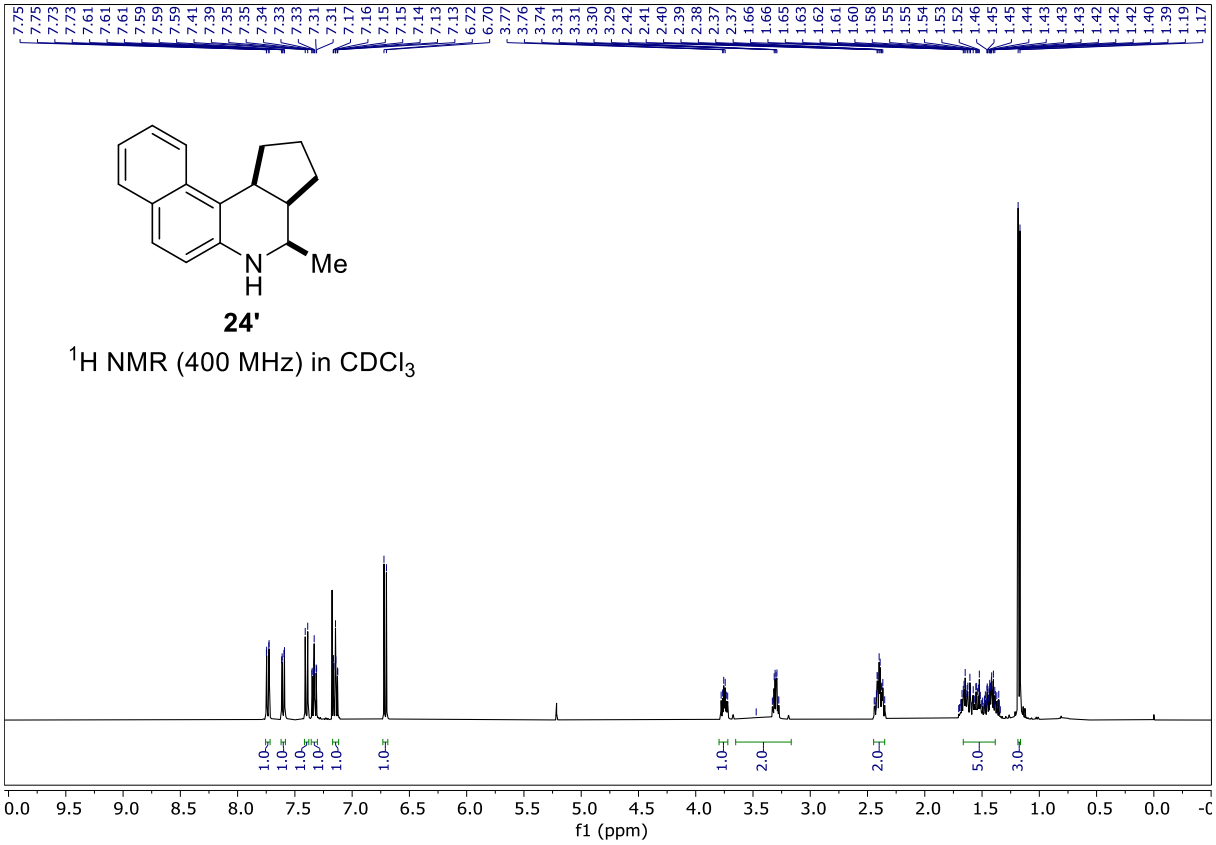
^{13}C NMR (101 MHz) in $CDCl_3$

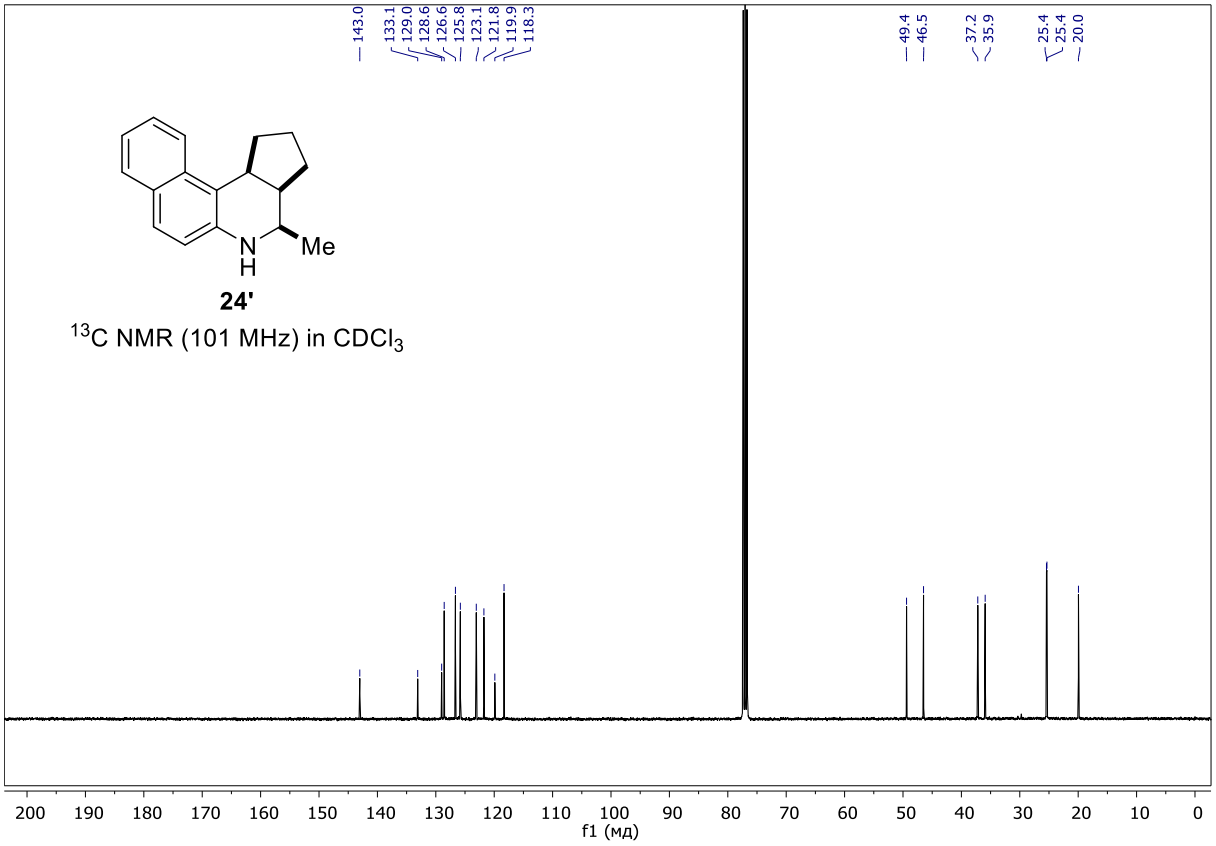


24

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

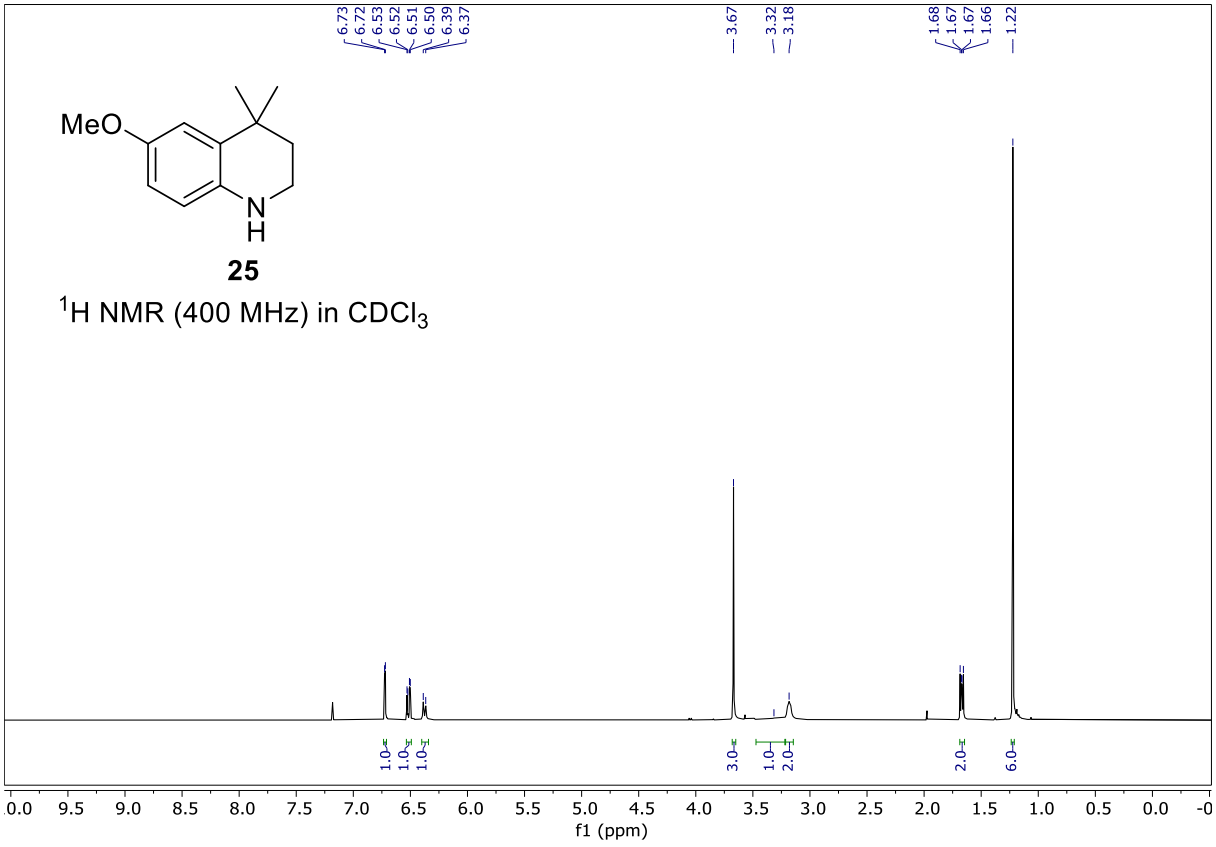

140.9
133.8
128.5
128.0
127.2
126.1
122.3
121.4
117.8
115.9
47.3
42.6
39.1
34.2
28.2
22.8
20.4
N
H
Me
24
13C NMR (101 MHz) in CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)


N
H
Me
24'
1H NMR (400 MHz) in CDCl3
1.0
1.0
1.0
1.0
1.0
1.0
2.0
2.0
5.0
3.0
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



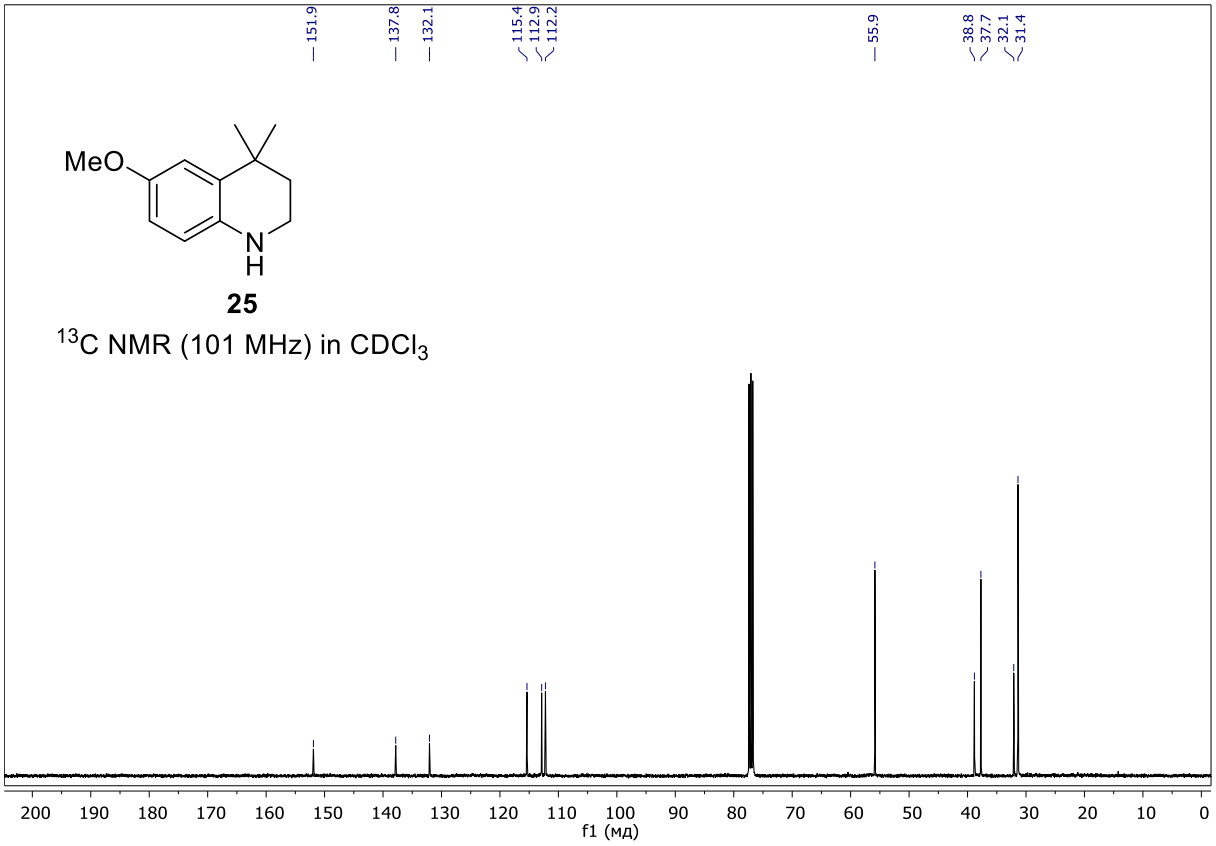
24'

^{13}C NMR (101 MHz) in $CDCl_3$



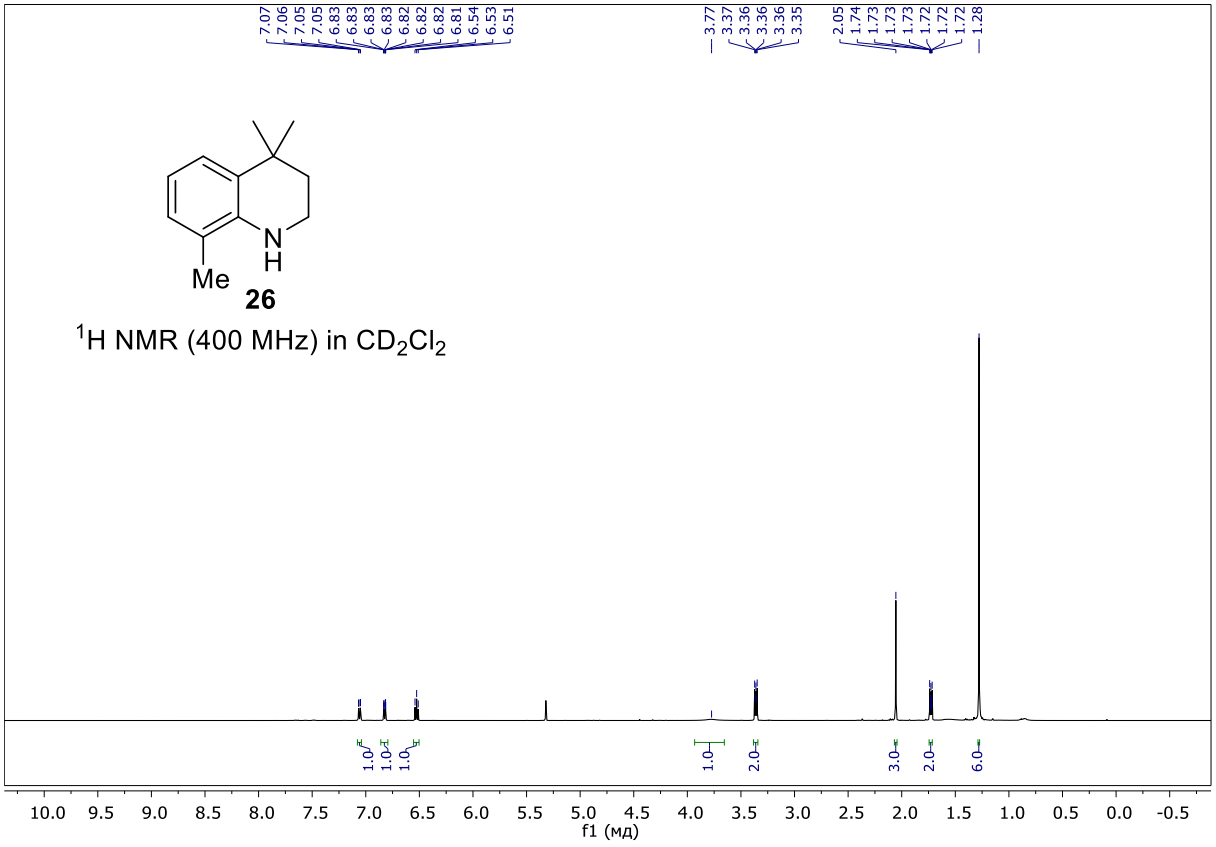
25

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



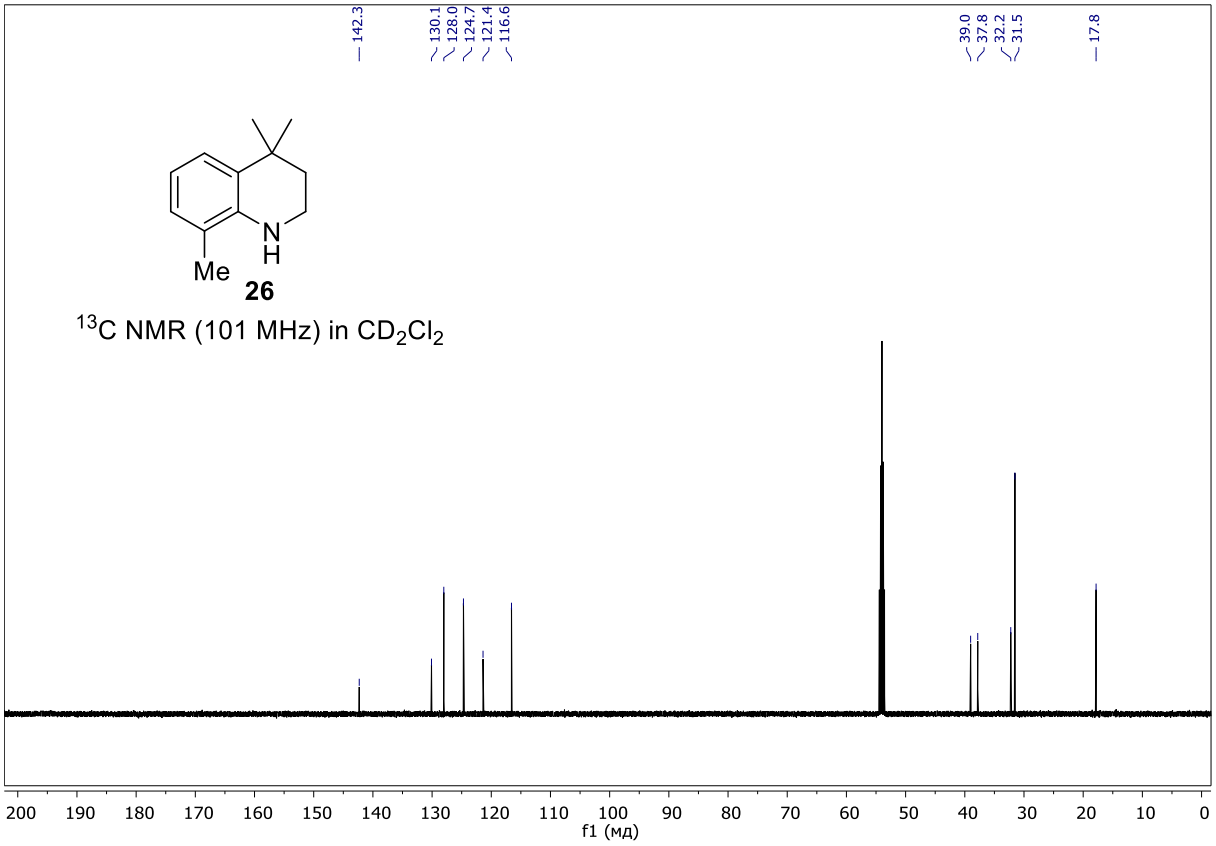
25

^{13}C NMR (101 MHz) in $CDCl_3$

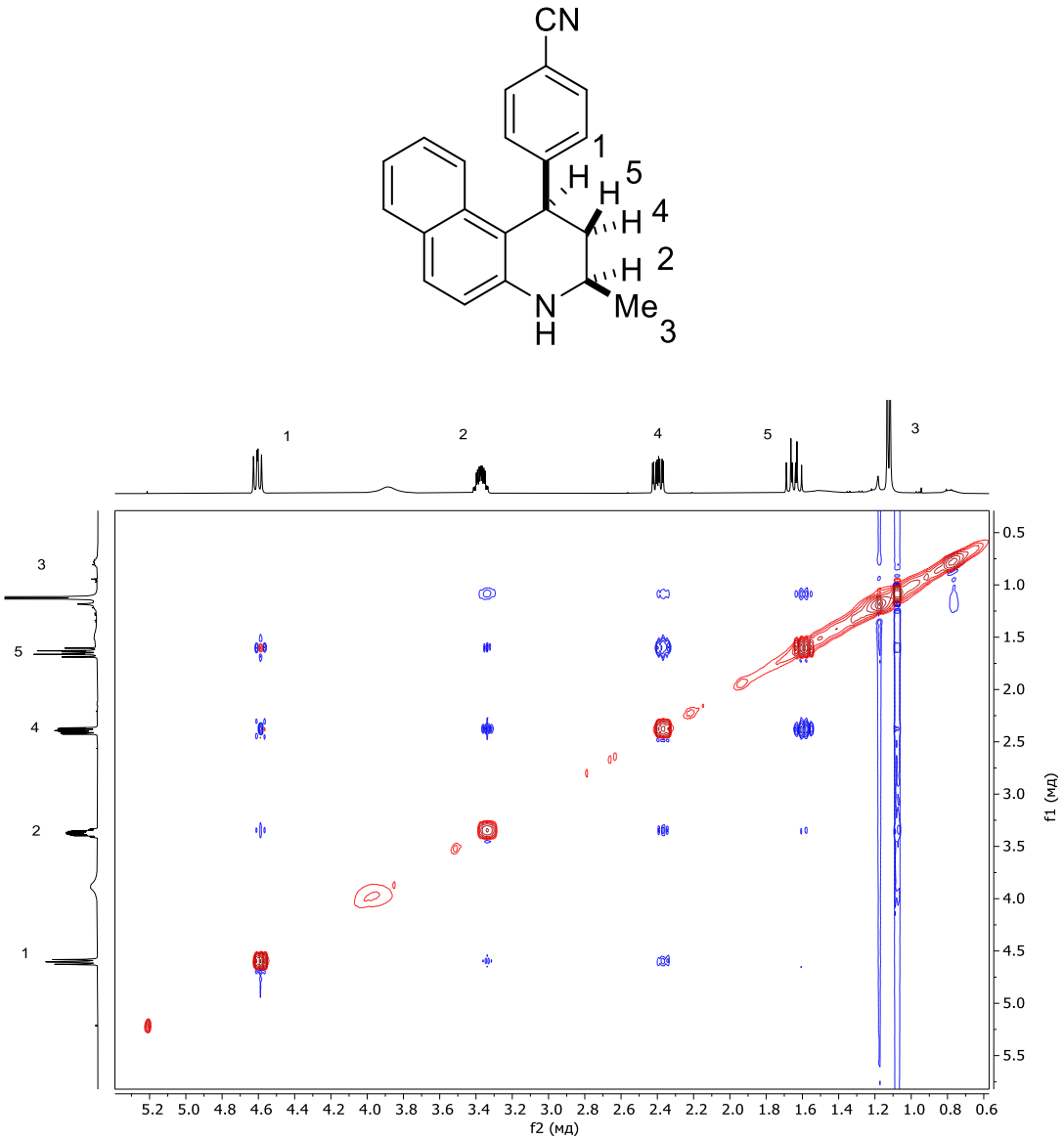


26

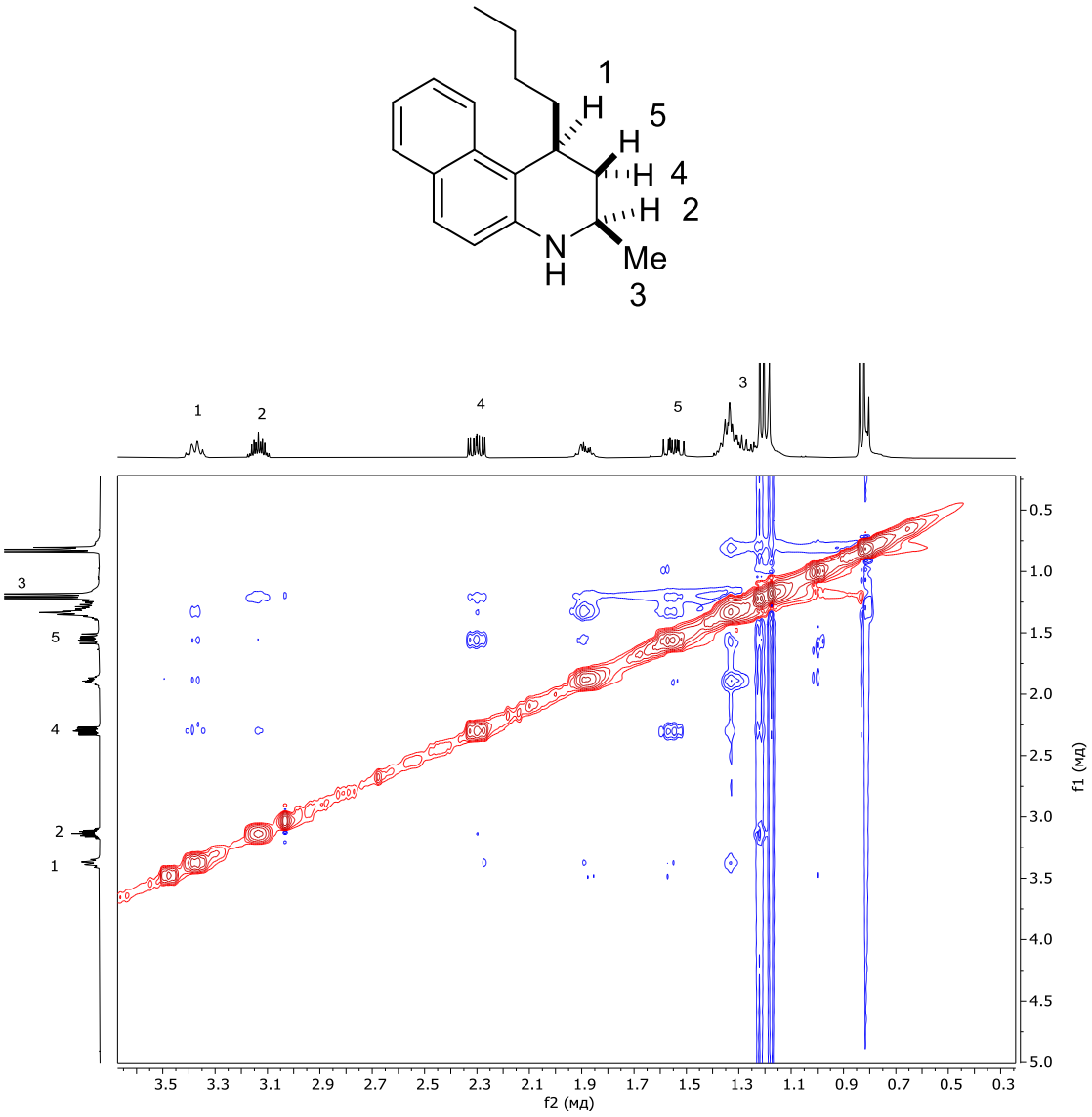
^{1}H NMR (400 MHz) in CD_2Cl_2


142.3
130.1
128.0
124.7
121.4
116.6
39.0
37.8
32.2
31.5
17.8
N
H
Me
26
13C NMR (101 MHz) in CD2Cl2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

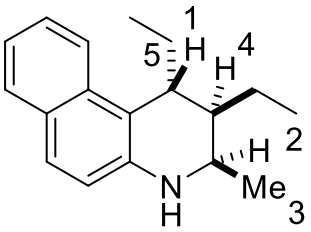
5. NOESY Spectra

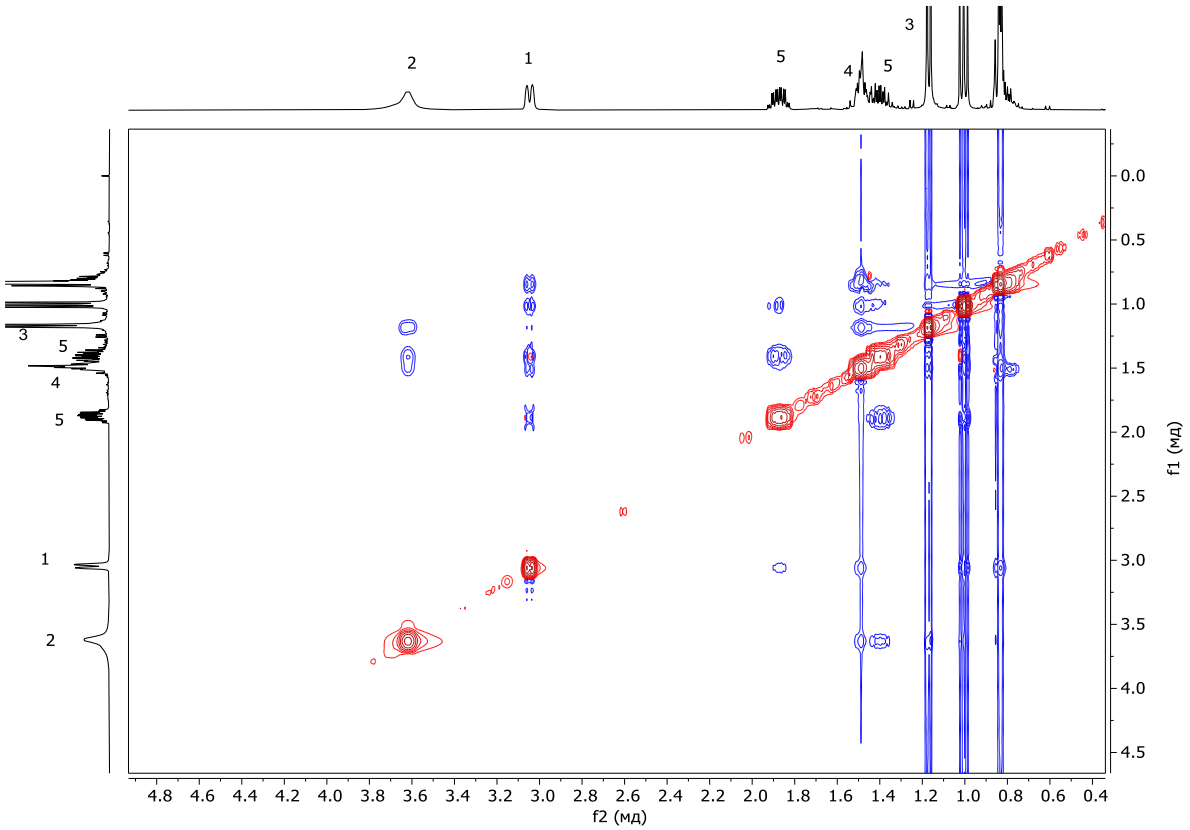


Analysis: proton 1 correlates with proton 2 but does not correlate with protons of the methyl group 3. Proton 4 correlates with both proton 1 and proton 2. These observations confirm a *cis* relative configuration.

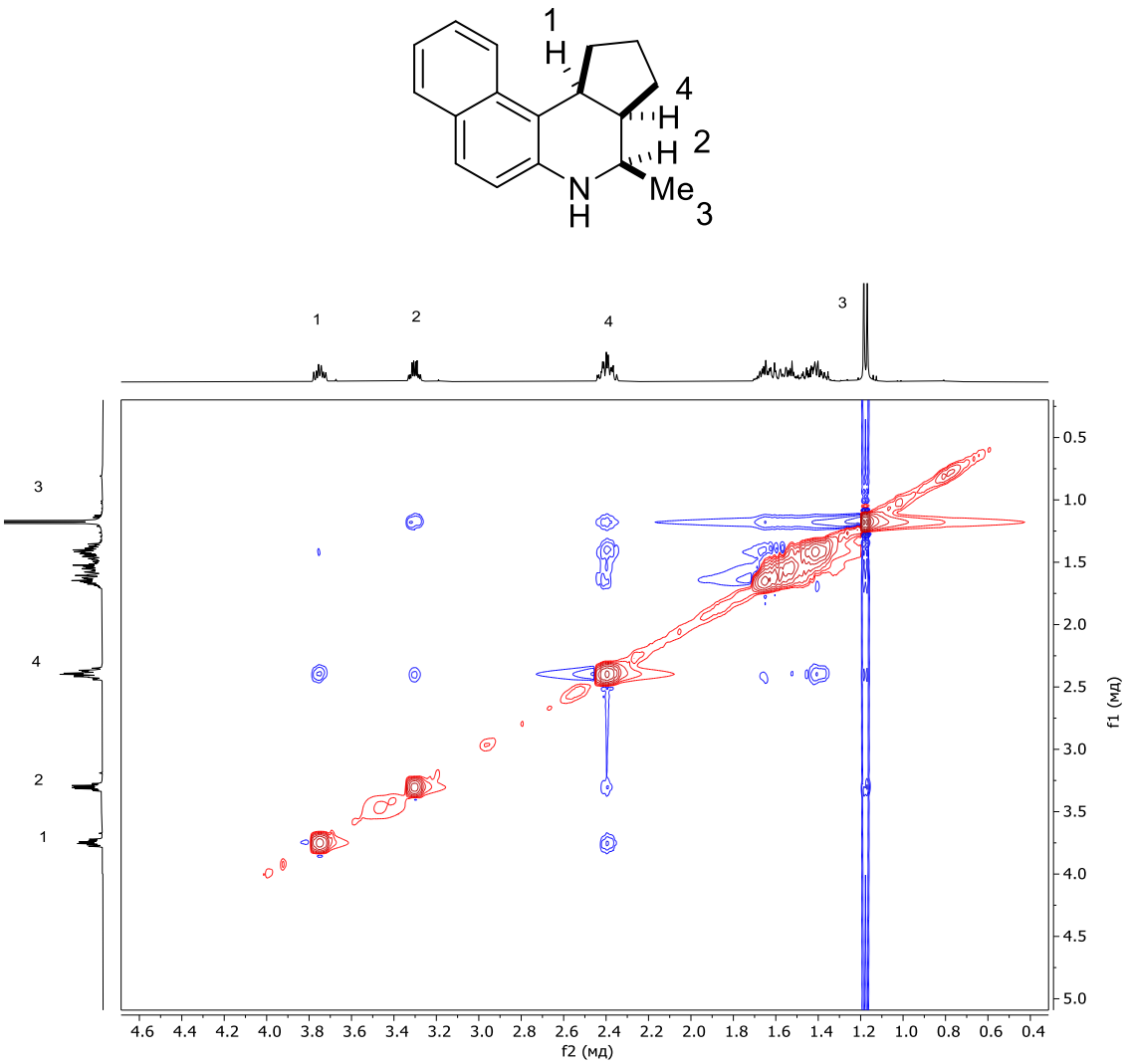


Analysis: Proton 1 correlates with proton 4. Protons 1 and 2 do not correlate with each other. Proton 4 correlates with proton 2. These observations suggest the relative configuration shown on the scheme above.

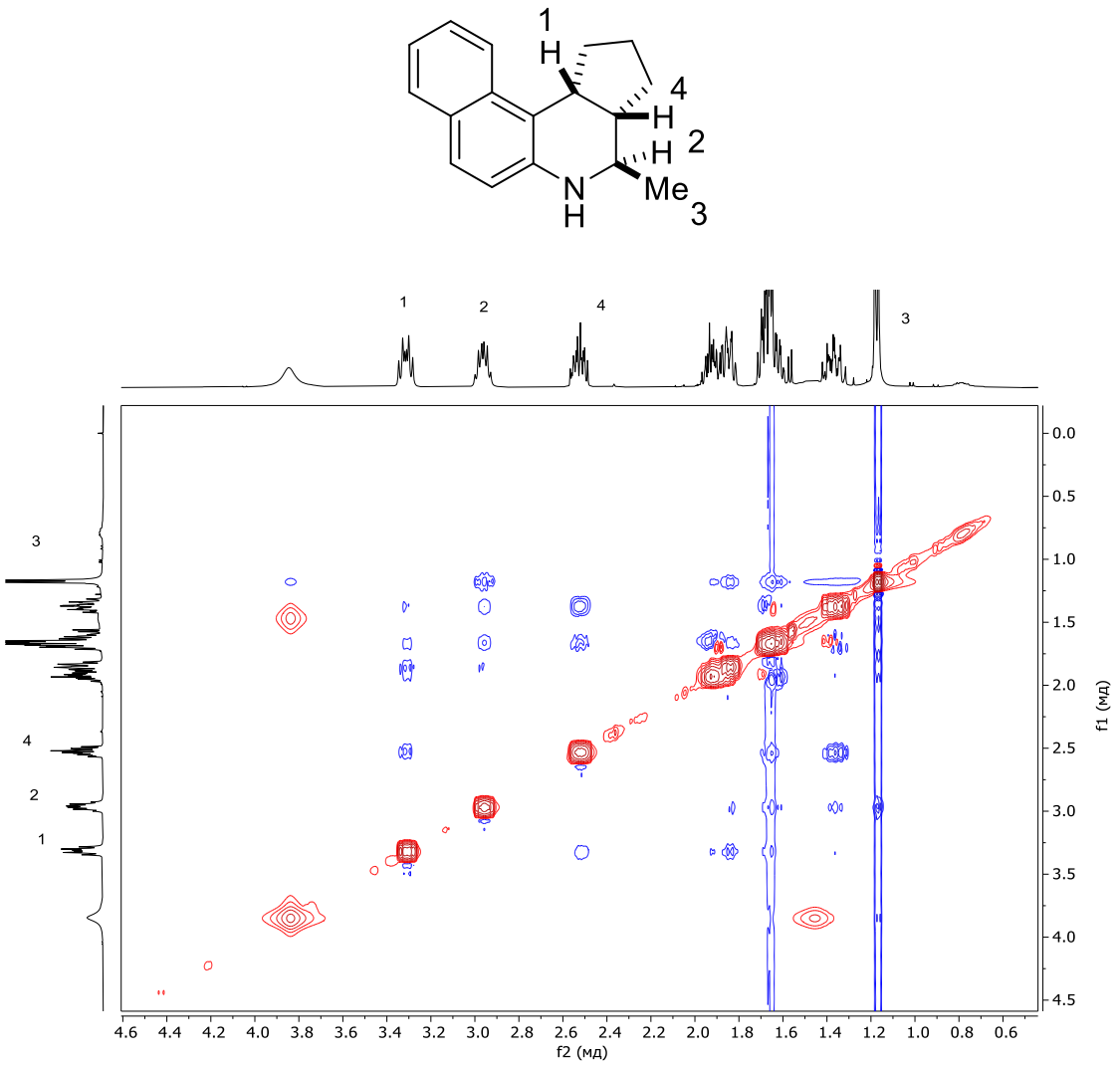




Analysis: Proton 1 does not correlate with proton 2. Protons 1 and 2 correlates with protons 5. These observations confirm the relative configuration shown on the scheme above.



Analysis: Proton 1 correlates with proton 4. Proton 4 correlates with both proton 1 and proton 2. These observations suggest the relative configuration shown on the scheme above.



Analysis: Proton 1 correlates with proton 4. Protons 1 and 4 do not correlate with proton 2. These observations suggest the relative configuration shown on the scheme above.