5-(Methylthio)tetrazoles as Versatile Synthons in the Stereoselective Synthesis of Polycyclic Pyrazolines via Photoinduced Intramolecular Nitrile Imine–Alkene 1,3-Dipolar Cycloaddition

Supporting Information

Daniel Pla,*[†] Derek S. Tan,*[†,‡] and David Y. Gin[†,‡,§]

[†]Molecular Pharmacology and Chemistry Program and [‡]Tri-Institutional Research Program,
Memorial Sloan–Kettering Cancer Center, 1275 York Avenue, Box 422,
New York, New York 10065, United States

[§]Deceased March 22, 2011

TABLE OF CONTENTS

A. General Experimental Procedures, Materials and Instrumentation.

Materials. CH_2Cl_2, THF, Et_2O, MeCN and toluene were purified by passage through two packed columns of neutral alumina under an argon atmosphere. Methanol was distilled from magnesium at 760 Torr. All other chemicals were obtained from commercial vendors and were used without further purification unless noted otherwise.

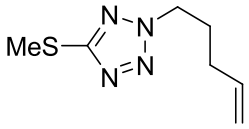
Instrumentation. Automated flash chromatography was performed with an Isco Combiflash medium-pressure liquid chromatograph with Redisep silica or alumina gel columns (47-60 μm). Photochemical irradiation was performed in sealed quartz tubes with a Luzchem® Photochemical reactor or with a Pen-Ray lamp. Microwave-assisted reactions were run in a Biotage microwave. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 500 MHz spectrometer and a Bruker 600 MHz spectrometer. Chemical shifts are reported in ppm referenced to the appropriate residual solvent peaks (CD_3OD, d_6-DMSO, C_6D_6 or $CDCl_3$) and coupling constants are reported in Hz. The multiplicity of signals is indicated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, bs = broad singlet, bd = broad doublet, m = multiplet. Infrared (FTIR) spectra were obtained using a Bruker Tensor 27. Vibration frequencies are expressed in cm^{-1}. High-resolution mass spectrometry (HRMS) was performed on a Waters LCT Premier XE high-resolution mass spectrometer. Melting points were determined in open glass capillaries with an Stanford Research Systems OptiMelt automated melting point system and are uncorrected. Optical rotations were determined on a JASCO P-1020 polarimeter at 589 nm using a PTC-103T temperature controller. UV spectra were recorded on an Agilent Cary 100 UV-Visible Spectrophotometer using the Cary WinUV software.

General Experimental Procedures. Reactions were performed in flame-dried borosilicate or quartz sealed-tubes or modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe. Organic solutions were concentrated by rotary evaporation below 30 ºC. Thin-layer chromatography was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm) and visualized under UV light (254 and 360 nm), or stained with I_2, Ceric Ammonium Molybdate in conc. H_2SO_4 or with a $KMnO_4$ solution (contains K_2CO_3, NaOH). Column chromatography was run using silica gel 60.

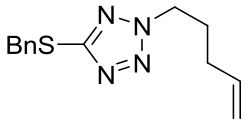
A) General Procedure for the Alkylation of Tetrazoles using Mitsunobu Conditions. Diisopropyl azodicarboxylate (292 μL, 1.50 mmol) was added to a stirred solution of 5-methylthio-1*H*-tetrazole (116.2 mg, 1.00 mmol, 1.0 equiv), PPh_3 (393.1 mg, 1.50 mmol) and the alcohol **5** (1.1 or 1.3 equiv) in THF (10 mL) at r.t. under Ar. The resulting mixture was heated to 80 ºC for 16 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc gave **3** in moderate to good yields (39-90%).[1]

B) General Procedure for the Carboamination Reaction. A solution of tetrazole derivative **3** (1.0 mmol) in MeCN (3 mL) was purged with Ar. The reaction mixture was irradiated under 254 nm at r.t. for 5 h, unless otherwise stated. The organic solution was concentrated to give a crude material, which was purified by silica gel chromatography to give **2** (yield 19−96%).[2]

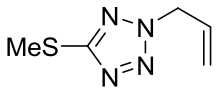
B. Synthesis of 2-Alkylated Tetrazole Derivatives 2, 5, 11, 13, 15.



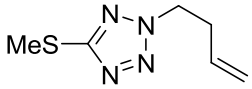
5-(Methylthio)-2-(pent-4-enyl)-2*H*-tetrazole (**2a**). Following the general procedure **A** and starting from pent-4-en-1-ol (733 mg, 8.50 mmol, 1.3 equiv), elution with hexane/EtOAc (100:0 to 80:20) gave **2a** (1.006 g, 84%) as a colorless oil. **TLC** R_f 0.57 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.77 (dd, *J* = 17.0, 10.3 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.59 (t, *J* = 6.9 Hz, 2H), 2.65 (s, 3H), 2.15 – 2.04 (m, 4H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.8, 136.1, 116.4, 52.5, 30.2, 28.2, 14.4. **FTIR** (neat film) 3078, 2933, 1642, 1438, 1416, 1401, 1364, 1286 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{13}N_4S$ (M+H) 185.0861, found 185.0860.



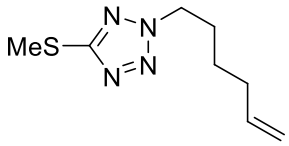
5-(Benzylthio)-2-(pent-4-enyl)-2*H*-tetrazole (**5**). Diisopropyl azodicarboxylate (0.831 mL, 4.22 mmol) was added to a stirred solution of 5-benzylthio-1*H*-tetrazole (541 mg, 2.81 mmol), PPh_3 (1.107 g, 4.22 mmol) and pent-4-en-1-ol (315 mg, 3.66 mmol) in THF (30 mL) at r.t. under Ar. The resulting mixture was heated to 80 ºC for 16 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc (100:0 to 90:10) gave **5** (536 mg, 73%) as a colorless oil. **TLC** R_f 0.67 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 5.79 (ddd, *J* = 16.9, 6.4, 3.8 Hz, 1H), 5.12 – 5.03 (m, 2H), 4.58 (t, *J* = 6.7 Hz, 2H), 4.44 (s, 2H), 2.13 – 2.07 (s, 4H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 163.4, 136.6, 136.1, 129.0, 128.5, 127.6, 116.4, 52.5, 36.5, 30.2, 28.2. **FTIR** (neat film) 3065, 2936, 1642, 1453, 1400, 1287 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{16}N_4NaS$ (M+Na) 283.0993, found 283.1003.



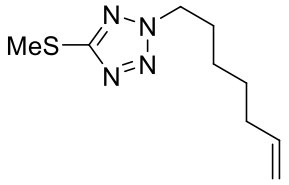
2-Allyl-5-(methylthio)-2*H*-tetrazole (**2b**). Following the general procedure **A** and starting from allyl alcohol (429 mg, 7.38 mmol, 1.3 equiv), elution with hexane/EtOAc (90:10 to 80:20) gave **2b** (498 mg, 56%) as a colorless oil. **TLC** R_f 0.54 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.58 – 5.39 (m, 1H), 4.88 – 4.70 (m, 2H), 4.46 – 4.30 (m, 2H), 2.25 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 166.0, 130.4, 120.3, 55.3, 14.3. **FTIR** (neat film) 2989, 2933, 1647, 1416, 1398, 1353, 1277, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_5H_9N_4S$ (M+H) 157.0548, found 157.0546.



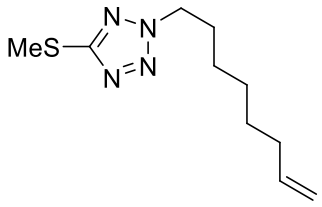
2-(But-3-enyl)-5-(methylthio)-2*H*-tetrazole (**2c**). Following the general procedure **A** and starting from but-3-en-1-ol (529 mg, 7.34 mmol, 1.3 equiv), elution with hexane/EtOAc (90:10 to 80:20) gave **2c** (739 mg, 77%) as a colorless oil. **TLC** R_f 0.56 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.42 – 5.19 (m, 1H), 4.79 – 4.69 (m, 2H), 3.91 – 3.82 (m, 2H), 2.28 (s, 3H), 2.19 – 2.12 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.7, 133.3, 118.3, 52.5, 33.5, 14.3. **FTIR** (neat film) 2981, 2933, 1643, 1416, 1401, 1361, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_6H_{11}N_4S$ (M+H) 171.0704, found 171.0705.



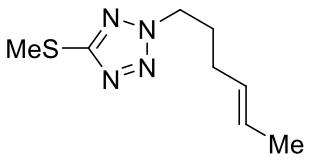
2-(Hex-5-enyl)-5-(methylthio)-2*H*-tetrazole (**2d**). Following the general procedure **A** and starting from hex-5-en-1-ol (254 mg, 2.54 mmol, 1.3 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2d** (305 mg, 79%) as a colorless oil. **TLC** R_f 0.58 (75:25 hexane/EtOAc). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.01 (bd, *J* = 17.0 Hz, 1H), 4.98 (bd, *J* = 10.2 Hz, 1H), 4.56 (t, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 2.13 – 2.07 (m, 2H), 2.05 – 1.92 (m, 2H), 1.53 – 1.33 (m, 2H). **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.7, 137.6, 115.3, 53.1, 32.8, 28.5, 25.5, 14.4. **FTIR** (neat film) 2932, 2861, 1641, 1437, 1400, 1362, 1055, 914 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1020.



2-(Hept-6-enyl)-5-(methylthio)-2*H*-tetrazole (**2e**). Following the general procedure **A** and starting from hept-6-en-1-ol (703 mg, 6.16 mmol, 1.3 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2e** (771 mg, 77%) as a colorless oil. **TLC** R_f 0.68 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.62 (ddt, *J* = 18.2, 9.4, 6.7 Hz, 1H), 4.98 – 4.90 (m, 2H), 3.89 – 3.81 (m, 2H), 2.29 (s, 3H), 1.78 – 1.69 (m, 2H), 1.51 – 1.37 (m, 2H), 1.09 – 0.94 (m, 2H), 0.88 – 0.76 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.6, 138.9, 115.2, 53.2, 33.9, 29.3, 28.6, 26.1, 14.3. **FTIR** (neat film) 2932, 2859, 1640, 1437, 1400, 1362, 1290, 1178, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_4S$ (M+H) 213.1174, found 213.1175.

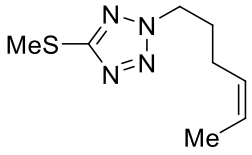


5-(Methylthio)-2-(oct-7-enyl)-2*H*-tetrazole (**2f**). Following the general procedure **A** and starting from oct-7-en-1-ol (1.015 g, 7.92 mmol, 1.3 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2f** (1.067 g, 77%) as a colorless oil. **TLC** R_f 0.69 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.70 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1H), 5.10 – 4.89 (m, 2H), 3.92 – 3.82 (m, 2H), 2.30 (s, 3H), 1.84 (dd, *J* = 14.4, 7.1 Hz, 2H), 1.49 – 1.42 (m, 2H), 1.11 – 1.04 (m, 2H), 0.97 – 0.89 (m, 2H), 0.88 – 0.80 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.7, 139.2, 115.0, 53.3, 34.2, 29.5, 29.1, 28.8, 26.5, 14.3. **FTIR** (neat film) 2931, 2858, 1640, 1438, 1400, 1361, 1284, 1054 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{19}N_4S$ (M+H) 227.1330, found 227.1324.

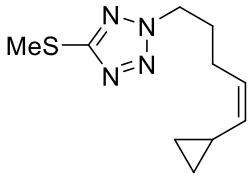


(*E*)-2-(Hex-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2g**). Following the general procedure **A** and starting from (*E*)-hex-4-en-1-ol (562.8 mg, 5.62 mmol, 1.3 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2g** (640.3 g, 75%) as a colorless oil. **TLC** R_f 0.63 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.21 (dqt, *J* = 12.8, 6.4, 1.2 Hz, 1H),

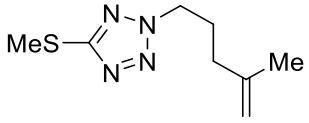
5.09 – 4.98 (m, 1H), 3.89 (t, *J* = 6.9 Hz, 2H), 2.29 (s, 3H), 1.65 – 1.59 (m, 2H), 1.58 – 1.52 (m, 2H), 1.49 (dd, *J* = 6.4, 1.4 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.2, 129.1, 126.7, 52.2, 29.2, 28.8, 17.9, 13.9. **FTIR** (neat film) 2934, 1400, 1285, 1179, 1055, 968 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1013.



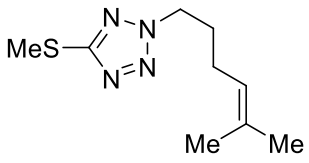
(*Z*)-2-(Hex-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2h**). Following the general procedure **A** and starting from (*Z*)-hex-4-en-1-ol (281 mg, 2.80 mmol, 1.3 equiv), elution with hexane/EtOAc (100:0 to 90:10) gave **2h** (344 mg, 81%) as a colorless oil. **TLC** R_f 0.65 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.54 (dq, *J* = 10.8, 6.8 Hz, 1H), 5.41 – 5.29 (m, 1H), 4.55 (t, *J* = 6.8 Hz, 2H), 2.67 (s, 3H), 2.16 – 1.90 (m, 4H), 1.58 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.8, 127.8, 126.0, 52.7, 28.9, 23.5, 14.5, 12.8. **FTIR** (neat film) 3014, 2933, 1437, 1400, 1365, 1287 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1016.



(*Z*)-2-(5-Cyclopropylpent-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2i**). Following the general procedure **A** and starting from (*Z*)-5-cyclopropylpent-4-en-1-ol[3] (732 mg, 5.80 mmol, 1.1 equiv), elution with hexane/EtOAc (90:10 to 80:20) gave **2i** (849 mg, 72%) as a colorless oil. **TLC** R_f 0.64 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.03 (dt, *J* = 10.7, 7.4 Hz, 1H), 4.65 (ddt, *J* = 10.7, 10.0, 1.3 Hz, 1H), 4.00 – 3.88 (m, 2H), 2.28 (s, 3H), 1.86 (dd, *J* = 7.3, 7.3 Hz, 2H), 1.67 – 1.59 (m, 2H), 1.21 (dd, *J* = 6.9, 2.8 Hz, 1H), 0.54 – 0.47 (m, 2H), 0.19 – 0.13 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.5, 136.3, 125.8, 52.8, 29.5, 24.8, 14.3, 10.2, 7.5. **FTIR** (neat film) 3005, 2933, 1653, 1400, 1287, 1180, 1054 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{17}N_4S$ (M+H) 225.1174, found 225.1164.

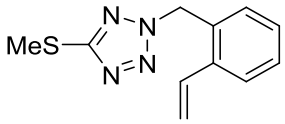


2-(4-Methylpent-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2j**). Following the general procedure **A** and starting from 4-methylpent-4-en-1-ol[4] (478.4 mg, 4.78 mmol, 1.1 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2j** (657.3 mg, 76%) as a colorless oil. **TLC** R_f 0.66 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 4.68 (d, *J* = 0.8 Hz, 1H), 4.56 (d, *J* = 0.8 Hz, 1H), 3.88 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H), 1.67 – 1.56 (m, 4H), 1.41 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 165.3, 143.4, 111.4, 52.3, 34.1, 26.9, 22.1, 13.9. **FTIR** (neat film) 3075, 2933, 1649, 1400, 1375, 1288, 1179, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1012.

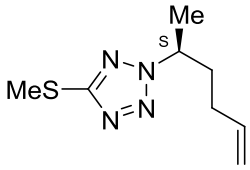


2-(5-Methylhex-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2k**). Following the general procedure **A** and starting from 5-methylhex-4-en-1-ol[5] (668.3 mg, 1.3 equiv), elution

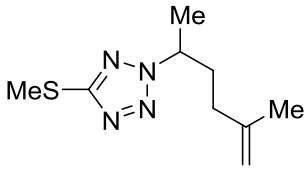
with hexane/EtOAc (95:5 to 85:15) gave **2k** (738.8 mg, 77%) as a colorless oil. **TLC** R_f 0.76 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 4.85 (tdd, *J* = 7.2, 2.7, 1.4 Hz, 1H), 3.91 (t, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 1.71 – 1.65 (m, 1H), 1.59 (dt, *J* = 14.0, 7.1 Hz, 2H), 1.56 (d, *J* = 0.9 Hz, 3H), 1.37 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 165.6, 133.5, 123.0, 52.7, 29.5, 26.1, 25.2, 18.0, 14.3. **FTIR** (neat film) 2932, 1673, 1438, 1400, 1376, 1287, 1178, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_4S$ (M+H) 213.1174, found 213.1169.



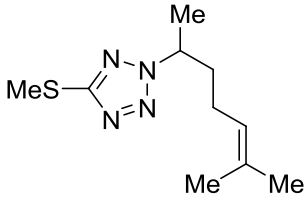
5-(Methylthio)-2-(2-vinylbenzyl)-2*H*-tetrazole (**2l**). Following the general procedure **A** and starting from (2-vinylphenyl)methanol[4b, 6] (592 mg, 4.41 mmol, 1.1 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2l** (602 mg, 65%, 98% estimated purity by NMR) as a colorless oil. **TLC** R_f 0.75 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.21 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.90 (m, 3H), 6.90 – 6.85 (m, 1H), 5.38 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.22 – 4.93 (m, 3H), 2.21 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 166.1, 138.1, 134.0, 131.1, 130.7, 130.6, 129.8, 127.1, 118.1, 54.4, 14.2. **FTIR** (neat film) 2932, 1697, 1491, 1415, 1399, 1355, 1054 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{13}N_4S$ (M+H) 233.0861, found 233.0862.



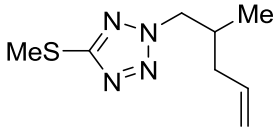
(*S*)-2-(Hex-5-en-2-yl)-5-(methylthio)-2*H*-tetrazole (**2m**). Following the general procedure **A** and starting from (*R*)-5-methylhex-5-en-2-ol (280 mg, 2.80 mmol, 1.3 equiv), elution with hexane/EtOAc (100: 0 to 90:10) gave **2m** (355 mg, 83%) as a colorless oil. **TLC** R_f 0.69 (75:25 hexane/EtOAc). $[\alpha]_D^{20}$ +60.0° (c 0.42, $CHCl_3$). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 12.0, 10.3, 6.5 Hz, 1H), 5.04 – 4.96 (m, 2H), 4.92 (dd, *J* = 6.8, 1.5 Hz, 1H), 2.67 (s, 3H), 2.22 – 2.13 (m, 1H), 2.00 – 1.65 (m, 3H), 1.60 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.5, 136.3, 116.0, 60.3, 35.1, 29.8, 20.5, 14.5. **FTIR** (neat film) 3078, 2984, 2934, 1642, 1409, 1371, 1296 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1023.



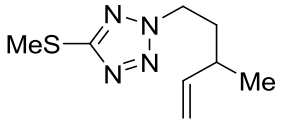
2-(5-Methylhex-5-en-2-yl)-5-(methylthio)-2*H*-tetrazole (**2n**). Following the general procedure **A** and starting from 5-methylhex-5-en-2-ol[4b, 7] (463 mg, 4.06 mmol, 1.3 equiv), elution with hexane/EtOAc (100:0 to 90:10) gave **2n** as a colorless oil (479 mg, 72%). **TLC** R_f 0.71 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 4.93 (dq, *J* = 13.1, 6.7 Hz, 1H), 4.74 (s, 1H), 4.65 (s, 1H), 2.68 (s, 3H), 2.26 – 2.16 (m, 1H), 2.03 – 1.92 (m, 2H), 1.90 – 1.82 (m, 1H), 1.69 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.5, 143.6, 111.1, 60.6, 33.9, 33.7, 22.3, 20.5, 14.5. **FTIR** (neat film) 3074, 2934, 1650, 1449, 1408, 1370, 1295 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_4S$ (M+H) 213.1174, found 213.1173.



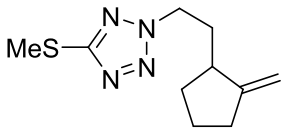
2-(6-Methylhept-5-en-2-yl)-5-(methylthio)-2*H*-tetrazole (**2o**). Following the general procedure **A** and starting from 6-methylhept-5-en-2-ol (359 mg, 2.80 mmol, 1.3 equiv), elution with hexane/EtOAc (100:0 to 90:10) gave **2o** (428 mg, 88%) as a colorless oil. **TLC** R_f 0.68 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.01 (ddd, *J* = 4.7, 4.2, 1.3 Hz, 1H), 4.95 – 4.89 (m, 1H), 2.70 (s, 3H), 2.18 – 2.04 (m, 1H), 1.98 – 1.67 (m, 3H), 1.69 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.54 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.4, 133.3, 122.1, 60.5, 36.1, 25.7, 24.3, 20.6, 17.6, 14.5. **FTIR** (neat film) 2982, 2932, 1436, 1409, 1371, 1296 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{19}N_4S$ (M+H) 227.1330, found 227.1321.



2-(2-Methylpent-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2p**). Following the general procedure **A** and starting from 2-methylpent-4-en-1-ol[8] (476.0 mg, 4.75 mmol, 1.1 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2XX** (669.4 mg, 78%) as a colorless oil. **TLC** R_f 0.69 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.41 (ddt, *J* = 17.2, 10.2, 7.2 Hz, 1H), 4.97 – 4.78 (m, 2H), 3.90 (ddd, *J* = 13.4, 6.2, 0.6 Hz, 1H), 3.76 (ddd, *J* = 13.4, 7.7, 0.7 Hz, 1H), 2.28 (s, 3H), 1.97 – 1.81 (m, 1H), 1.75 – 1.60 (m, 1H), 1.60 – 1.45 (m, 1H), 0.53 (d, *J* = 6.8 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 165.3, 135.2, 117.3, 57.8, 38.1, 33.4, 16.8, 13.9. **FTIR** (neat film) 3078, 2966, 2932, 1641, 1400, 1282, 1173, 918 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1010.

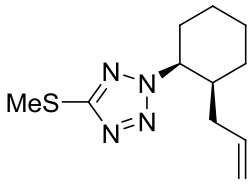


2-(3-Methylpent-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2q**). Following the general procedure **A** and starting from 3-methylpent-4-en-1-ol[8a, 9] (478.2 g, 4.77 mmol, 1.1 equiv), elution with hexane/EtOAc (95:5 to 85:15) gave **2XX** (645.6 mg, 75%) as a colorless oil. **TLC** R_f 0.69 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.26 (ddd, *J* = 17.2, 10.3, 8.0 Hz, 1H), 4.83 – 4.79 (m, 2H), 4.06 – 3.88 (m, 2H), 2.30 (s, 3H), 1.77 – 1.66 (m, 1H), 1.60 – 1.49 (m, 1H), 1.48 – 1.35 (m, 1H), 0.67 (d, *J* = 6.7 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.2, 142.2, 114.5, 51.2, 35.3, 35.3, 20.0, 14.0. **FTIR** (neat film) 3077, 2959, 1641, 1401, 1175, 1055, 917 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_4S$ (M+H) 199.1017, found 199.1014.

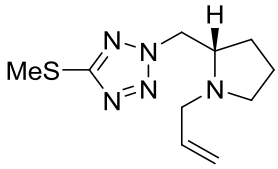


2-(2-(2-Methylenecyclopentyl)ethyl)-5-(methylthio)-2*H*-tetrazole (**2r**). Following the general procedure **A** and starting from 2-(2-methylenecyclopentyl)ethanol[10,11] (158 mg, 1.25 mmol, 1.1 equiv), elution with hexane/EtOAc (90:10 to 80:20) gave **2r** (197 mg, 77%) as a colorless oil. **TLC** R_f 0.67 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 4.93 (d, *J* = 1.9 Hz, 1H), 4.82 (d, *J* = 1.9 Hz, 1H), 4.67 – 4.54 (m, 2H), 2.67 (s, 3H), 2.40 – 2.24 (m, 4H), 2.00 – 1.87 (m, 2H), 1.79 – 1.69 (m, 1H), 1.65 – 1.51 (m, 1H), 1.36 – 1.26 (m, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.8, 154.7, 105.6, 52.0, 40.9, 33.6, 32.7, 32.3, 24.1, 14.5.

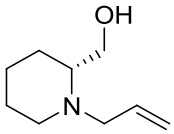
FTIR (neat film) 2953, 1652, 1400, 1363, 1285 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{17}N_4S$ (M+H) 225.1174, found 225.1175.



2-(2-Allylcyclohexyl)-5-(methylthio)-2*H*-tetrazole (**2s**). Following the general procedure **A** and starting from *trans*-2-allylcyclohexanol[4b, 12] (656 mg, 4.68 mmol, 1.1 equiv), elution with hexane/EtOAc (100:0 to 90:10) gave **2s** (710 mg, 70%) as a colorless oil. **TLC** R_f 0.72 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.43 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 4.79 (d, *J* = 17.0 Hz, 1H), 4.59 (bs, 1H), 2.29 (s, 3H), 1.87 – 1.61 (m, 6H), 1.52 – 1.35 (m, 2H), 1.29 – 1.18 (m, 1H), 1.13 – 0.95 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 164.9, 136.4, 117.1, 64.4, 40.1, 35.0, 29.2, 27.2, 23.7, 22.5, 14.4. **FTIR** (neat film) 3078, 2935, 2861, 1643, 1451, 1410, 1379, 1297 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{19}N_4S$ (M+H) 239.1330, found 239.1328.

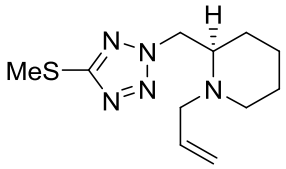


(*S*)-2-((1-Allylpyrrolidin-2-yl)methyl)-5-(methylthio)-2*H*-tetrazole (**2t**). Following the general procedure **A** and starting from (*S*)-(1-allylpyrrolidin-2-yl)methanol[4b, 13] (897 mg, 7.06 mmol, 1.1 equiv), elution with hexane/EtOAc (70:30 to 60:40) gave **2t** (1.092 g, 71%) as a colorless oil. **TLC** R_f 0.31 (75:25 hexane/EtOAc). $[\alpha]_D^{18}$ -26.4º (c 0.55, $CHCl_3$). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.82 – 5.67 (m, 1H), 5.09 – 5.02 (m, 1H), 4.98 – 4.88 (m, 2H), 4.14 (ddd, *J* = 13.4, 4.4, 1.5 Hz, 1H), 4.01 (ddd, *J* = 13.4, 7.8, 1.5 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.80 (td, *J* = 7.2, 3.8 Hz, 1H), 2.75 – 2.64 (m, 1H), 2.29 (s, 3H), 1.92 (td, *J* = 9.3, 6.7 Hz, 1H), 1.55 – 1.49 (m, 1H), 1.45 – 1.32 (m, 2H), 1.28 – 1.20 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.5, 136.8, 117.0, 72.2, 58.1, 57.1, 54.5, 29.5, 23.4, 14.3. **FTIR** (neat film) 2980, 2804, 1644, 1400, 1376, 1264, 1097 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{18}N_5S$ (M+H) 240.1283, found 240.1285.

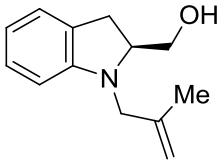


(*R*)-(1-Allylpiperidin-2-yl)methanol. $LiAlH_4$ (517 mg, 13.6 mmol) was added to a 0 ºC cooled solution of (*R*)-methyl 1-allylpiperidine-2-carboxylate[14,15] (1.915 g, 10.5 mmol) in THF (100 mL). The suspension was allowed to warm to r.t. and stirred for 1 h. Then, H_2O (0.5 mL) was added dropwise, followed by 15% aq. NaOH (0.5 mL), and H_2O (1.5 mL). The resulting mixture was stirred for 15 min. The resulting suspension was filtered through a pad of Celite, and the pad was washed with methanol. The combined organic fractions were concentrated under reduced pressure to give the entitled compound (1.513 g, 93%) as a yellowish oil. **TLC** R_f 0.16 (95:5 CH_2Cl_2/MeOH). $[\alpha]_D^{18}$ +21.2º (c 0.54, $CHCl_3$). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.86 (dddd, *J* = 17.6, 10.2, 7.6, 5.5 Hz, 1H), 5.19 – 5.11 (m, 2H), 3.77 (dd, *J* = 10.8, 4.2 Hz, 1H), 3.49 – 3.37 (m, 2H), 2.99 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.96 – 2.90 (m, 1H), 2.61 (bs, 1H), 2.39 – 2.32 (m, 1H), 2.27 – 2.18 (m, 1H), 1.75 – 1.66 (m, 1H), 1.66 – 1.51 (m, 3H), 1.46 – 1.36 (m, 1H), 1.35 – 1.25 (m, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 135.2, 117.4, 62.3, 60.2,

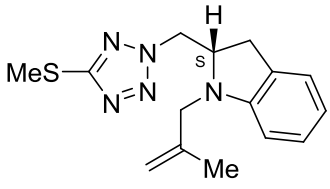
56.4, 51.2, 27.6, 24.5, 23.5. **FTIR** (neat film) 3374, 2934, 1643, 1444, 1062 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{18}NO$ (M+H) 156.1388, found 156.1381.



(*R*)-1-Allyl-2-((5-(methylthio)-2*H*-tetrazol-2-yl)methyl)piperidine (**2u**). Following the general procedure **A** and starting from (*R*)-(1-allylpiperidin-2-yl)methanol (942 mg, 6.07 mmol, 1.1 equiv), elution with hexane/EtOAc (70:30 to 60:40) gave **3u** (542 mg, 39%, 96% estimated purity by NMR)[16] as a colorless oil. **TLC** R_f 0.41 (75:25 hexane/EtOAc). $[\alpha]_D^{18}$ +29.9º (c 0.59, $CHCl_3$). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.62 (ddd, *J* = 12.6, 10.4, 6.3 Hz, 1H), 4.99 – 4.88 (m, 2H), 4.69 – 4.57 (m, 1H), 2.93 – 2.73 (m, 4H), 2.38 (dd, *J* = 12.3, 6.7 Hz, 1H), 2.31 (s, 3H), 2.30 – 2.26 (m, 1H), 2.10 – 1.97 (m, 1H), 1.88 – 1.79 (m, 1H), 1.57 – 1.47 (m, 1H), 1.45 – 1.35 (m, 1H), 1.35 – 1.24 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.1, 136.5, 117.5, 65.2, 62.1, 58.4, 56.0, 33.9, 29.5, 22.9, 14.4. **FTIR** (neat film) 2932, 2805, 1643, 1403, 1345, 1290, 1094, 1054 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{20}N_5S$ (M+H) 254.1439, found 254.1438.

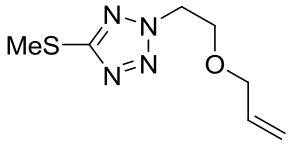


(*S*)-(1-(2-Methylallyl)indolin-2-yl)methanol. 3-Bromo-2-methylprop-1-ene (1.075 g, 7.97 mmol) was added to a solution of (*S*)-indolin-2-ylmethanol[4b,17] (792.3 mg, 5.31 mmol) and Et_3N (1.48 mL, 10.62 mmol) in THF (20 mL) at r.t. The reaction mixture was heated to 40 ºC and stirred for 6 h. Then, solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography and elution with hexane/EtOAc (80:20 to 70:30) gave the entitled compound (780.5 mg, 72%) as a yellowish oil. **TLC** R_f 0.36 (75:25 hexane/EtOAc). $[\alpha]_D^{18}$ -38.3º (c 0.12, $CHCl_3$). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 7.12 – 6.98 (m, 2H), 6.69 (td, *J* = 7.4, 0.9 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.10 – 4.95 (m, 1H), 4.95 – 4.85 (m, 1H), 3.83 (dt, *J* = 11.6, 3.5 Hz, 1H), 3.75 (tt, *J* = 9.5, 3.5 Hz, 1H), 3.69 – 3.60 (m, 3H), 3.14 (dd, *J* = 15.9, 9.5 Hz, 1H), 3.04 (dd, *J* = 15.9, 9.5 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.78 (d, *J* = 0.5 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 153.1, 143.1, 128.5, 127.4, 124.2, 118.2, 111.1, 107.7, 67.0, 63.0, 55.5, 31.3, 20.5. **FTIR** (neat film) 3387, 3050, 2914, 1654, 1606, 1487, 1266, 1024 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{18}NO$ (M+H) 204.1388, found 204.1379.

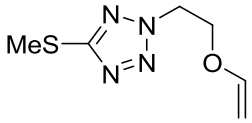


(*S*)-1-(2-Methylallyl)-2-((5-(methylthio)-2*H*-tetrazol-2-yl)-methyl)indoline (**2v**). Following the general procedure **A** and starting from (*S*)-(1-(2-methylallyl)indolin-2-yl)methanol (602 mg, 2.96 mmol, 1.1 equiv), elution with hexane/EtOAc (85:15 to 75:25) gave **2v** (614 mg, 76%, 95% estimated purity by NMR)[16] as a pinkish oil. **TLC** R_f 0.61 (75:25 hexane/EtOAc). $[\alpha]_D^{19}$ -23.4º (c 0.66, $CHCl_3$). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.01 (dd, *J* = 7.7, 7.5 Hz, 1H), 6.85 (dd, *J* = 7.3, 0.7 Hz, 1H), 6.68 (dd, *J* = 7.5, 7.3 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 4.82 (bs, 1H), 4.74 (bs, 1H), 4.23 – 4.12 (m, 1H), 3.97 (ddd, *J* = 13.5, 8.0, 2.8 Hz,

1H), 3.75 – 3.65 (m, 1H), 3.23 – 3.19 (m, 2H), 2.68 (dd, *J* = 16.1, 9.3 Hz, 1H), 2.62 (dd, *J* = 16.1, 7.2 Hz, 1H), 2.27 (s, 3H), 1.46 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.9, 152.3, 142.5, 128.7, 127.6, 125.0, 119.0, 112.5, 108.1, 63.9, 56.0, 55.0, 34.0, 20.6, 14.3. **FTIR** (neat film) 3074, 3051, 2932, 1656, 1607, 1486, 1399, 1054, 747 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{15}H_{20}N_5S$ (M+H) 302.1439, found 302.1440.

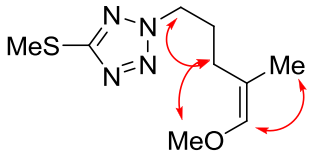


2-(2-(Allyloxy)ethyl)-5-(methylthio)-2*H*-tetrazole (**2w**). Following the general procedure **A** and starting from 2-(allyloxy)ethanol (800 mg, 7.83 mmol, 1.3 equiv), elution with hexane/EtOAc (80:20 to 70:30) gave **2w** as a colorless oil (979 mg, 81%). **TLC** R_f 0.42 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.55 (ddt, *J* = 21.8, 10.6, 5.4 Hz, 1H), 5.05 – 4.84 (m, 2H), 4.02 (dd, *J* = 7.4, 3.7 Hz, 2H), 3.54 – 3.44 (m, 2H), 3.33 (dd, *J* = 7.4, 3.3 Hz, 2H), 2.24 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.8, 134.8, 117.2, 72.1, 67.3, 53.1, 14.3. **FTIR** (neat film) 2933, 2870, 1721, 1402, 1348, 1284, 1109 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{13}N_4OS$ (M+H) 201.0810, found 201.0814.

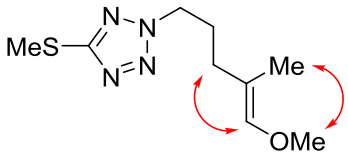


5-(Methylthio)-2-(2-(vinyloxy)ethyl)-2*H*-tetrazole (**2x**). Following the general procedure **A** and starting from 2-(vinyloxy)ethanol (513 mg, 5.82 mmol, 1.3 equiv), elution with hexane/EtOAc (90:10 to 80:20) gave **2x** (648 mg, 78%) as a colorless oil. **TLC** R_f 0.40 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 6.06 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.92 – 3.87 (m, 1H), 3.80 (dd, *J* = 6.8, 2.3 Hz, 1H), 3.52 – 3.37 (m, 2H), 2.22 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 166.0, 151.3, 87.7, 64.8, 52.2, 14.3. **FTIR** (neat film) 2934, 2884, 1622, 1402, 1322, 1200, 961 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_6H_{11}N_4OS$ (M+H) 187.0654, found 187.0645.

(*Z*)-2-(5-Methoxy-4-methylpent-4-enyl)-5-(methylthio)-2*H*-tetrazole (**2y**) and **(*E*)-2-(5-Methoxy-4-methylpent-4-enyl)-5-(methylthio)-2*H*-tetrazole** (**2z**). Following the general procedure **A** and starting from (*Z/E*)-5-methoxy-4-methylpent-4-en-1-ol[4b, 18] (305 mg, 2.33 mmol, 37:63 *Z/E*-mixture, 1.3 equiv), elution with hexane/EtOAc (90:10 to 60:40) gave **2y** (132 mg, 86%) and **2z** (219 mg, 85%) as colorless oils.

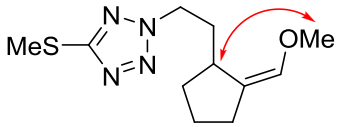


2y: **TLC** R_f 0.53 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.80 (bs, 1H), 4.51 (t, *J* = 7.4 Hz, 2H), 3.50 (s, 3H), 2.66 (s, 3H), 2.20 – 2.02 (m, 4H), 1.53 (d, *J* = 1.3 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.6, 142.9, 111.3, 59.2, 53.0, 26.8, 25.6, 17.0, 14.5. **FTIR** (neat film) 2932, 1684, 1400, 1220, 1139 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{16}N_4NaOS$ ($M+Na^+$) 251.0943, found 251.0933.

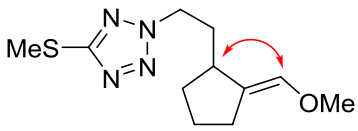


2z: **TLC** R_f 0.47 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.78 (d, *J* = 1.2 Hz, 1H), 4.52 (t, *J* = 7.0 Hz, 2H), 3.55 (s, 3H), 2.67 (s, 3H), 2.06 (p, *J* = 7.2 Hz, 2H), 1.91 (t, *J* = 7.2 Hz, 2H), 1.58 (d, *J* = 1.2 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.8, 143.2, 110.9, 59.3, 52.5, 30.4, 27.1, 14.4, 12.4. **FTIR** (neat film) 2933, 1685, 1400, 1204, 1125 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{16}N_4NaOS$ ($M+Na^+$) 251.0943, found 251.0945.

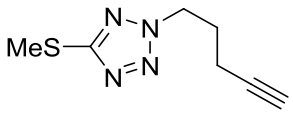
(*Z*)-2-(2-(2-(Methoxymethylene)cyclopentyl)ethyl)-5-(methylthio)-2*H*-tetrazole (**2aa**) and **(*E*)-2-(2-(2-(Methoxymethylene)cyclopentyl)ethyl)-5-(methylthio)-2*H*-tetrazole** (**2bb**). Following the general procedure **A** and starting from (*Z/E*)-2-(2-(methoxymethylene)cyclopentyl)ethanol[19,20] (312 mg, 1.99 mmol, 50:50 *Z/E*-mixture, 1.1 equiv), elution with hexane/EtOAc (100:0 to 80:20) gave **2aa** (216 mg, 94%) and **2bb** (199 mg, 86%) as colorless oils.



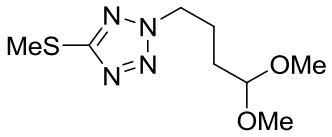
2aa: **TLC** R_f 0.65 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.92 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.64 – 4.46 (m, 2H), 3.51 (s, 3H), 2.80 – 2.70 (m, 1H), 2.66 (s, 3H), 2.32 – 2.22 (m, 1H), 2.21 – 2.11 (m, 2H), 2.03 – 1.92 (m, 1H), 1.88 (dt, *J* = 13.4, 7.4 Hz, 1H), 1.76 – 1.60 (m, 1H), 1.56 – 1.45 (m, 1H), 1.42 – 1.31 (m, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.5, 140.1, 122.1, 59.3, 52.5, 36.8, 33.9, 32.6, 28.8, 25.0, 14.5. **FTIR** (neat film) 2934, 1723, 1400, 1362, 1284 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{18}N_4ONaS$ (M+Na) 277.1099, found 277.1093.



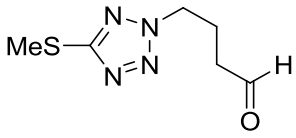
2bb: **TLC** R_f 0.53 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.88 (dd, *J* = 4.2, 2.2 Hz, 1H), 4.70 – 4.50 (m, 2H), 3.57 (s, 3H), 2.67 (s, 3H), 2.41 – 2.29 (m, 2H), 2.29 – 2.19 (m, 1H), 2.18 – 2.04 (m, 1H), 1.98 – 1.81 (m, 2H), 1.80 – 1.68 (m, 1H), 1.67 – 1.51 (m, 1H), 1.39 – 1.24 (m, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 164.8, 140.2, 122.5, 59.6, 51.9, 38.2, 34.1, 32.8, 26.6, 24.0, 14.4. **FTIR** (neat film) 2935, 1723, 1401, 1362, 1119 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{18}N_4ONaS$ (M+Na) 277.1099, found 277.1101.



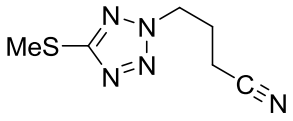
5-(Methylthio)-2-(pent-4-ynyl)-2*H*-tetrazole (**2cc**). Following the general procedure **A** and starting from pent-4-yn-1-ol (235 mg, 2.80 mmol, 1.3 equiv), elution with hexane/EtOAc (90:10 to 80:20) gave **2cc** (331 mg, 84%) as a colorless oil. **TLC** R_f 0.54 (75:25 hexane/EtOAc). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 4.69 (t, *J* = 6.7 Hz, 2H), 2.66 (s, 3H), 2.33 – 2.26 (m, 2H), 2.21 (p, *J* = 6.7 Hz, 2H), 2.02 (t, *J* = 2.5 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 165.0, 81.7, 70.0, 51.9, 27.8, 15.7, 14.4. **FTIR** (neat film) 3291, 2934, 2119, 1435, 1401, 1287, 1056 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{11}N_4S$ (M+H) 183.0704, found 183.0709.



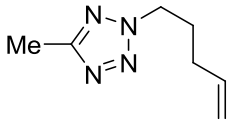
2-(4,4-Dimethoxybutyl)-5-(methylthio)-2*H*-tetrazole. Following the general procedure **A** and starting from 4,4-dimethoxybutan-1-ol[21] (644.5 mg, 4.80 mmol, 1.1 equiv), elution with hexane/EtOAc (35:65 to 45:55) gave **2-(4,4-dimethoxybutyl)-5-(methylthio)-2*H*-tetrazole** (828.8 mg, 82%) as a colorless oil. **TLC** R_f 0.60 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 4.00 (t, *J* = 5.5 Hz, 1H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.99 (s, 6H), 2.27 (s, 3H), 1.70 – 1.64 (m, 2H), 1.31 (ddd, *J* = 9.7, 7.7, 5.6 Hz, 2H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 165.3, 103.7, 52.7, 52.5, 29.3, 24.5, 21.6, 13.9. **FTIR** (neat film) 2936, 2832, 1801, 1739, 1400, 1265, 1127, 1095 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{16}N_4O_2SNa$ (M+Na) 255.0892, found 255.0886.



4-(5-(Methylthio)-2*H*-tetrazol-2-yl)butanal (**2dd**). $LiBF_4$ (308.5 mg, 3.29 mmol) was added to a solution of 2-(4,4-dimethoxybutyl)-5-(methylthio)-2*H*-tetrazole (254.8 mg, 1.10 mmol) in MeCN - H_2O (10 mL, 98:2%), and the mixture was stirred for 21 h at r.t. Solvents were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and washed with H_2O and brine. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography, and elution with hexane/EtOAc (50:50 to 40:60) gave **2dd** (175.1 mg, 86%, 98% estimated purity by NMR) as a colorless oil. **TLC** R_f 0.50 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 8.95 (d, *J* = 7.6 Hz, 1H), 3.82 – 3.76 (m, 2H), 2.28 (s, 3H), 1.61 – 1.54 (m, 2H), 1.49 – 1.41 (m, 2H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 199.0, 165.8, 52.1, 40.1, 21.8, 14.3. **FTIR** (neat film) 2935, 1722, 1401, 1320, 1056 cm^{-1}. **HRMS** (API) *m/z*: Calcd for $C_6H_{11}N_4OS$ (M+H) 187.0654, found 187.0647.

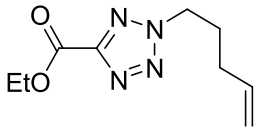


4-(5-(Methylthio)-2*H*-tetrazol-2-yl)butanenitrile (**2ee**). Following the general procedure **A** and starting from 4-hydroxybutanenitrile[8a, 22] (488.2 mg, 5.74 mmol, 1.3 equiv), elution with CH_2Cl_2/MeCN (95:5 to 90:10) gave **2XX** (582.1 mg, 72%) as a colorless oil. **TLC** R_f 0.54 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 3.67 – 3.59 (m, 2H), 2.26 (s, 3H), 1.24 – 1.12 (m, 4H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 166.1, 118.2, 51.1, 25.1, 14.3, 14.2. **FTIR** (neat film) 2934, 2249, 1770, 1401, 1286, 1180, 1155, 1016 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_6H_{10}N_5S$ (M+H) 184.0657, found 184.0651.

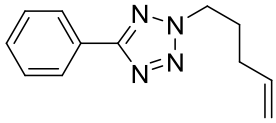


5-Methyl-2-(pent-4-enyl)-2*H*-tetrazole (**11**). Diisopropyl azodicarboxylate (1.77 mL, 9.01 mmol) was added to a stirred solution of 5-methyl-1*H*-tetrazole (504.9 mg, 6.01 mmol), PPh_3 (2.36 g, 9.01 mmol) and pent-4-en-1-ol (0.795 mL, 7.81 mmol) in THF (50 mL) at r.t. under Ar. The resulting mixture was heated to 80 ºC for 16 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc (80:20 to 70:30) gave **11** (601.2 mg, 66%) as a colorless oil. **TLC** R_f

0.40 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.44 (ddt, *J* = 16.9, 10.4, 6.5 Hz, 1H), 4.93 – 4.79 (m, 2H), 3.94 (t, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 1.68 – 1.57 (m, 4H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 163.4, 137.0, 116.4, 52.0, 30.7, 28.7, 11.1. **FTIR** (neat film) 3080, 2978, 2942, 1642, 1504, 1446, 1360, 1192, 1033, 918 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{13}N_4$ (M+H) 153.1140, found 153.1141.

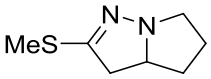


Ethyl 2-(pent-4-enyl)-2*H*-tetrazole-5-carboxylate (**13**)**.** Diisopropyl azodicarboxylate (0.470 mL, 2.39 mmol) was added to a stirred suspension of ethyl 1*H*-tetrazole-5-carboxylate (226.3 mg, 1.59 mmol), PPh_3 (626.5 mg, 2.39 mmol) and pent-4-en-1-ol (0.211 mL, 2.07 mmol) in THF (20 mL) at r.t. under Ar. The resulting mixture was heated to 80 ºC for 16 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc (95:5 to 70:30) gave **13** (152.1 mg , 45%) as a colorless oil. **TLC** R_f 0.44 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.36 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.92 – 4.74 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (t, *J* = 7.0 Hz, 2H), 1.54 (td, *J* = 7.5, 1.1 Hz, 2H), 1.48 (qd, *J* = 7.5, 1.1 Hz, 2H), 0.98 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 158.6, 158.2, 136.2, 116.2, 62.0, 52.5, 30.2, 28.0, 14.0. **FTIR** (neat film) 3079, 2982, 2939, 1736, 1641, 1507, 1448, 1277, 1182, 1156 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{15}N_4O_2$ (M+H) 211.1195, found 211.1194.

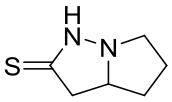


2-(Pent-4-enyl)-5-phenyl-2*H*-tetrazole (**15**).[23] Diisopropyl azodicarboxylate (0.624 mL, 3.17 mmol) was added to a stirred solution of 5-phenyl-1*H*-tetrazole (308.9 mg, 2.11 mmol), PPh_3 (831.5 mg, 3.17 mmol) and pent-4-en-1-ol (236.7 mg, 2.75 mmol) in THF (40 mL) at r.t. under Ar. The resulting mixture was heated to 80 ºC for 16 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc (95:5 to 80:20) gave **15** (412.0 mg, 91%) as a colorless oil. **TLC** R_f 0.76 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 8.42 (d, *J* = 7.8 Hz, 2H), 7.18 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.43 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 4.89 – 4.83 (m, 2H), 3.95 (t, *J* = 6.7 Hz, 2H), 1.68 – 1.56 (m, 4H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.6, 136.6, 130.3, 129.2, 128.6, 127.2, 116.1, 52.0, 30.4, 28.3. **FTIR** (neat film) 3076, 2979, 2950, 1642, 1530, 1466, 1450, 1358, 1045, 918 cm^{-1}. **MS** (ESI) *m/z*: 215 (M+H, 14), 237 (M+Na, 100). The spectroscopic data matches the product reported in literature.[23]

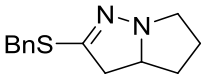
C. Synthesis of Fused Pyrazoline, and Pyrazole Derivatives 3, 4, 6 – 8, 14 and 16.



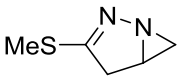
2-(Methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole (**3a**). Following the general procedure **B** and starting from **2a** (604.6 mg, 3.28 mmol), elution with CH_2Cl_2/THF (80:20 to 65:35) gave **3a** as a yellowish oil (328 mg, 64%). **TLC** R_f 0.28 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.71 – 3.61 (m, 1H), 3.44 – 3.47 (m, 1H), 2.94 (ddd, *J* = 12.1, 9.0, 7.2 Hz, 1H), 2.63 (dd, *J* = 16.2, 9.2 Hz, 1H), 2.25 (s, 3H), 2.22 (d, *J* = 16.2 Hz, 1H), 1.49 – 1.36 (m, 1H), 1.31 (dd, *J* = 12.4, 7.6 Hz, 1H), 1.26 – 1.16 (m, 1H), 1.08 – 0.96 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 150.9, 65.2, 55.6, 44.3, 31.8, 24.8, 14.1. **FTIR** (neat film) 2959, 2872, 1609, 1449, 1128, 1058 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{13}N_2S$ (M+H) 157.0799, found 157.0796.



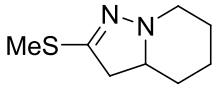
Tetrahydro-1*H*-pyrrolo[1,2-*b*]pyrazole-2(3*H*)-thione (**4a**). Following the general procedure **B**, starting from **2a** (53.7 mg, 0.29 mmol), irradiation at r.t. for 16 h, and elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **4a** as a yellowish oil (12.8 mg, 31%, 83% estimated purity by NMR). **TLC** R_f 0.50 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 4.20 – 4.11 (m, 1H), 3.28 (dd, *J* = 18.1, 9.8 Hz, 1H), 3.21 – 3.07 (m, 2H), 2.95 (dd, *J* = 18.1, 5.4 Hz, 1H), 2.08 (ddd, *J* = 15.9, 12.9, 8.0 Hz, 1H), 1.99 – 1.90 (m, 1H), 1.89 – 1.78 (m, 1H), 1.79 – 1.69 (m, 1H), 1.70 – 1.60 (m, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 190.5, 63.6, 57.0, 50.1, 32.0, 23.7. **FTIR** (neat film) 3417, 2957, 1512, 1447, 1268, 1121 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_6H_{11}N_2S$ (M+H) 143.0643, found 143.0645.



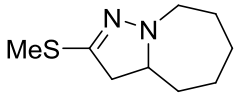
2-(Benzylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole (**6**). Following the general procedure **B** and starting from **5** (54.9 mg, 0.21 mmol), elution with CH_2Cl_2/THF (85:15 to 75:25) gave **6** as a yellowish oil (31.9 mg, 65%, 98% estimated purity by NMR). **TLC** R_f 0.54 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.29 (d, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.25 (d, *J* = 13.3 Hz, 1H), 4.19 (d, *J* = 13.3 Hz, 1H), 3.71 – 3.65 (m, 1H), 3.42 (m, 1H), 2.94 (ddd, *J* = 12.1, 9.2, 6.8 Hz, 1H), 2.58 (dd, *J* = 16.1, 9.3 Hz, 1H), 2.15 (dd, *J* = 16.1, 1.7 Hz, 1H), 1.43 – 1.33 (m, 1H), 1.31 – 1.16 (m, 2H), 0.99 – 0.91 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 149.9, 138.7, 129.8, 129.0, 127.7, 65.1, 55.6, 44.4, 36.0, 31.8, 24.7. **FTIR** (neat film) 2957, 2868, 1683, 1602, 1561, 1495, 1453, 1267, 1070 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{17}N_2S$ (M+H) 233.1112, found 233.1107.



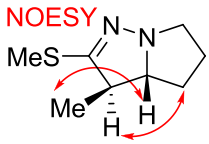
3-(Methylthio)-1,2-diazabicyclo[3.1.0]hex-2-ene (**3b**). Following the general procedure **B** and starting from **2b** (46.6 mg, 0.30 mmol), elution with CH_2Cl_2/TBME (30:70 to 20:80) gave **3b** as a yellowish oil (26.0 mg, 68%). **TLC** R_f 0.20 (50:50 CH_2Cl_2/TBME). **^{1}H-NMR** (600 MHz, C_6D_6) δ 2.42 (dd, *J* = 17.3, 7.6 Hz, 1H), 2.36 (dd, *J* = 17.3, 2.2 Hz, 1H), 2.16 (s, 3H), 2.13 – 2.08 (m, 1H), 1.78 (dd, *J* = 6.0, 1.8 Hz, 1H), 0.80 – 0.76 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 166.9, 41.4, 40.9, 39.3, 14.2. **FTIR** (neat film) 2918, 2849, 1549, 1428, 1290, 1134, 1103 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_5H_9N_2S$ (M+H) 129.0486, found 129.0487.



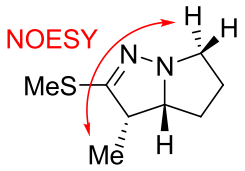
2-(Methylthio)-3,3a,4,5,6,7-hexahydropyrazolo[1,5-*a*]pyridine (**3d**). Following the general procedure **B** and starting from **2d** (56.6 mg, 0.29 mmol), elution with CH_2Cl_2/THF (90:10 to 80:20) gave **3d** as a yellowish oil (27.1 mg, 56%). **TLC** R_f 0.69 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.94 – 3.85 (m, 1H), 2.65 – 2.52 (m, 2H), 2.30 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.27 (s, 3H), 2.11 (dd, *J* = 14.6, 11.3 Hz, 1H), 1.60 – 1.51 (m, 1H), 1.49 – 1.40 (m, 1H), 1.31 (tdd, *J* = 11.3, 9.4, 3.8 Hz, 2H), 1.27 – 1.18 (m, 1H), 1.03 – 0.88 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 150.0, 67.1, 53.3, 43.2, 28.6, 25.6, 24.7, 13.9. **FTIR** (neat film) 2933, 2852, 2793, 1539, 1440, 1277, 1259, 1026 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0953.



2-(Methylthio)-3a,4,5,6,7,8-hexahydro-3*H*-pyrazolo[1,5-*a*]azepine (**3e**). Following the general procedure **B** and starting from **3e** (105.4 mg, 0.50 mmol), elution with CH_2Cl_2/TBME (90:10 to 60:40) gave the monomer **3e** (23.7 mg, 26%, 99% estimated purity by NMR), and its quasidimer (21.6 mg, 22%, characterized below) as yellowish oils. When this reaction was conducted three times more diluted (0.10 M), **3e** was obtained in 35% and its quasidimer only in a 4% yield. **3e**: **TLC** R_f 0.62 (70:30 CH_2Cl_2/TBME). **^{1}H-NMR** (600 MHz, C_6D_6) δ 4.00 (dt, *J* = 12.1, 5.8 Hz, 1H), 2.86 (dtd, *J* = 13.4, 9.6, 3.8 Hz, 1H), 2.63 (ddd, *J* = 12.1, 8.9, 4.8 Hz, 1H), 2.51 (dd, *J* = 15.7, 9.6 Hz, 1H), 2.26 (s, 3H), 2.24 – 2.14 (m, 1H), 1.75 – 1.67 (m, 1H), 1.59 – 1.49 (m, 2H), 1.48 – 1.16 (m, 5H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 148.7, 69.1, 57.3, 45.9, 33.9, 28.5, 27.5, 26.3, 13.9. **FTIR** (neat film) 2924, 1660, 1502, 1463, 1442, 1136 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_2S$ (M+H) 185.1112, found 185.1106.

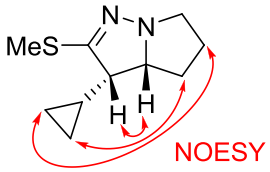


(3*R,3a*R**)-3-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3H-pyrrolo-[1,2-*b*]pyrazole** (**3g**). Following the general procedure **B** and starting from **2g** (63.1 mg, 0.32 mmol), elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **3g** as a yellowish oil (34.9 mg, 64%), d.r. (19:1 dr). Major diastereomer: **TLC** R_f 0.28 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.72 – 3.63 (m, 1H), 3.15 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 2.94 (ddd, *J* = 12.2, 9.1, 7.1 Hz, 1H), 2.54 (qd, *J* = 7.2, 1.4 Hz, 1H), 2.25 (s, 3H), 1.54 – 1.42 (m, 1H), 1.42 – 1.31 (m, 1H), 1.29 – 1.19 (m, 1H), 1.13 – 1.07 (m, 4H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 155.5, 73.2, 54.8, 51.6, 30.7, 24.3, 18.1, 13.5. **FTIR** (neat film) 2966, 2928, 2870, 1558, 1452, 1119, 1021 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0948.

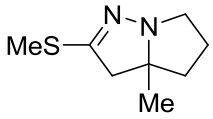


(3*S,3a*R**)-3-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo-[1,2-*b*]pyrazole** (**3h**). Following the general procedure **B** and starting from *Z*-**2h** (103.7 mg, 0.52 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3h** as a yellowish oil (55.3 mg, 62%), d.r. (18:2). Major diastereomer: **TLC** R_f 0.34 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.66 (m, 1H), 3.46 (dd, *J* = 14.7, 8.2 Hz, 1H), 3.12 (dt, *J* = 12.1, 7.5 Hz, 1H), 3.04 (dq, *J*

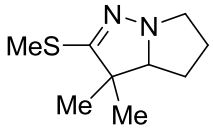
= 14.7, 7.3 Hz, 1H), 2.25 (s, 3H), 1.54 – 1.40 (m, 1H), 1.39 – 1.31 (m, 1H), 1.31 – 1.21 (m, 1H), 1.07 – 0.96 (m, 1H), 0.94 (d, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 154.8, 70.4, 55.8, 46.8, 25.1, 24.2, 13.8, 12.0. **FTIR** (neat film) 2927, 1670, 1561, 1451, 1378, 1184 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0958.



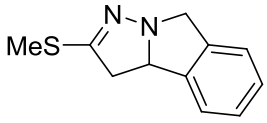
(3*S,3a*R**)-3-Cyclopropyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3i**). Following the general procedure **B** and starting from **2i** (38.1 mg, 0.17 mmol), elution with CH_2Cl_2/TBME (30:70 to 20:80) gave **3i** as a yellowish oil (20.3 mg, 61%), d.r. (17:3). Major diastereomer: **TLC** R_f 0.18 (75:25 CH_2Cl_2/TBME). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.71 (ddd, *J* = 12.2, 7.6, 4.9 Hz, 1H), 3.56 (dd, *J* = 16.5, 8.0 Hz, 1H), 3.12 (dt, *J* = 12.2, 7.6 Hz, 1H), 2.31 (s, 3H), 2.11 (dd, *J* = 10.4, 8.9 Hz, 1H), 1.66 – 1.50 (m, 2H), 1.39 – 1.22 (m, 2H), 0.65 – 0.48 (m, 2H), 0.32 – 0.13 (m, 2H), -0.13 – -0.24 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 154.8, 69.7, 58.9, 55.9, 25.4, 25.2, 13.8, 8.8, 6.1, 3.8. **FTIR** (neat film) 3095, 2961, 2870, 1553, 1430, 1250, 1154, 1021 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{17}N_2S$ (M+H) 197.1112, found 197.1115.



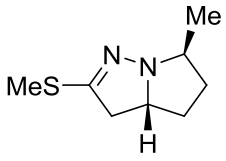
3a-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole (**3j**). Following the general procedure **B** and starting from **2j** (62.8 mg, 0.32 mmol), elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **3j** as a yellowish oil (37.9 mg, 70%, 99% estimated purity by NMR). **TLC** R_f 0.30 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.66 – 3.60 (m, 1H), 3.04 – 2.98 (m, 1H), 2.46 (d, *J* = 16.0 Hz, 1H), 2.42 (d, *J* = 16.0 Hz, 1H), 2.25 (s, 3H), 1.59 – 1.51 (m, 1H), 1.42 – 1.32 (m, 2H), 1.21 – 1.14 (m, 1H), 1.06 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 150.0, 73.1, 53.9, 50.8, 37.4, 26.2, 24.9, 13.5. **FTIR** (neat film) 2961, 2927, 2869, 1562, 1449, 1313, 1149, 1062 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0953.



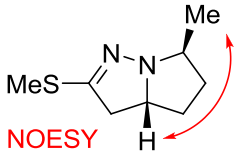
3,3-Dimethyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole (**3k**). Following the general procedure **B** and starting from **2k** (65.6 mg, 0.31 mmol), elution with hexane/EtOAc (60:40 to 40:60) gave **3k** as a yellowish oil (38.2 mg, 67%, 96% estimated purity by NMR). **TLC** R_f 0.21 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.64 (ddd, *J* = 7.8, 6.8, 4.2 Hz, 1H), 3.21 – 3.11 (m, 1H), 3.11 – 3.03 (m, 1H), 2.25 (s, 3H), 1.61 – 1.48 (m, 1H), 1.42 – 1.28 (m, 2H), 1.26 (s, *J* = 4.4 Hz, 3H), 1.12 – 1.03 (m, 1H), 1.01 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 157.9, 77.4, 54.9, 51.5, 26.5, 25.2, 25.1, 20.2, 13.3. **FTIR** (neat film) 2964, 2927, 1553, 1443, 1286, 1109 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_2S$ (M+H) 185.1112, found 185.1108.



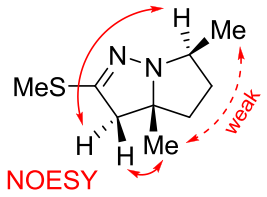
2-(Methylthio)-3a,8-dihydro-3*H*-pyrazolo[5,1-*a*]isoindole (**3l**). Following the general procedure **B** and starting from **2l** (59.3 mg, 0.26 mmol), elution with hexane/EtOAc (60:40 to 50:50) gave **3l** as a yellowish oil (36.5 mg, 70%). **TLC** R_f 0.31 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.04 – 6.97 (m, 2H), 6.88 (d, *J* = 5.8 Hz, 1H), 6.75 (d, *J* = 5.8 Hz, 1H), 4.83 (d, *J* = 15.7 Hz, 1H), 4.59 (d, *J* = 9.5 Hz, 1H), 4.36 (d, *J* = 15.7 Hz, 1H), 2.78 (dd, *J* = 15.9, 9.5 Hz, 1H), 2.67 (dd, *J* = 15.9, 1.4 Hz, 1H), 2.09 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.3, 143.6, 140.2, 128.7, 127.6, 123.6, 123.2, 70.6, 61.0, 43.2, 14.0. **FTIR** (neat film) 2923, 2848, 1562, 1431, 1287, 1156, 1117 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{13}N_2S$ (M+H) 205.0799, found 205.0791.



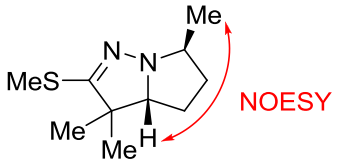
(3a*R,6*S*)-6-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]-pyrazole** (**3m**). Following the general procedure **B** and starting from **2m** (57.7 mg, 0.29 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3m** as a yellowish oil (37.8 mg, 76%), d.r. (17:3).



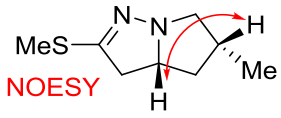
Major diastereomer: **(3a*R*,6*S*)-6-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole.** **TLC** R_f 0.47 (70:30 CH_2Cl_2/THF). $[\alpha]_D^{19}$ +36.5° (c 0.39, $CHCl_3$). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.74 (dq, *J* = 13.0, 6.7 Hz, 1H), 3.60 – 3.52 (m, 1H), 2.57 (dd, *J* = 16.1, 9.6 Hz, 1H), 2.26 (s, 3H), 2.23 (dd, *J* = 16.1, 2.3 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.48 – 1.38 (m, 1H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.12 – 1.00 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 150.0, 64.2, 62.5, 43.3, 32.5, 31.5, 21.7, 14.2. **FTIR** (neat film) 2958, 2924, 2853, 1660, 1632, 1601, 1456, 1377 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0958.



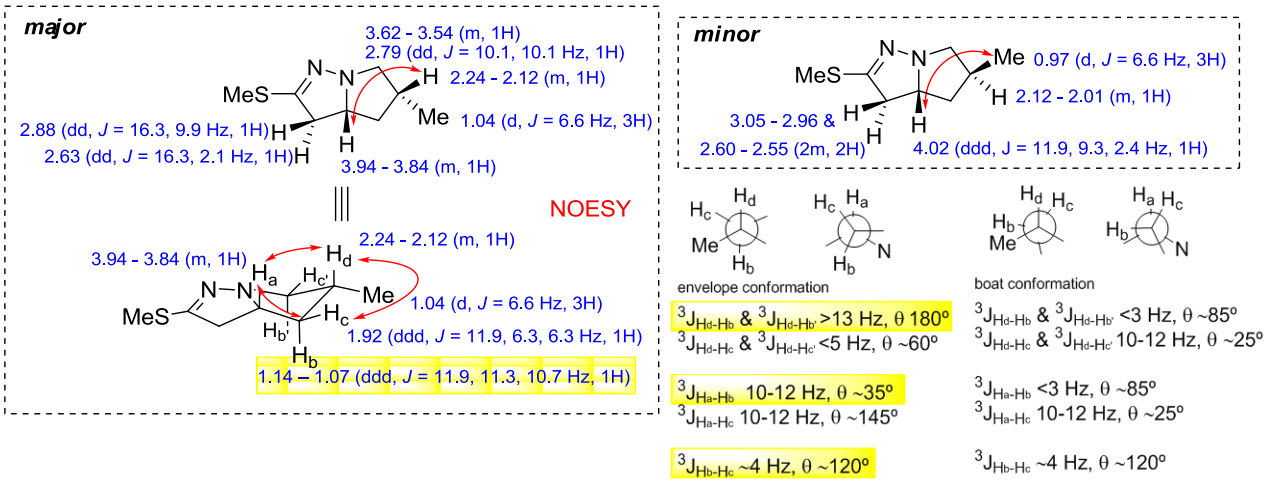
(3a*R,6*S**)-3a,6-Dimethyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3n**). Following the general procedure **B** and starting from **2n** (33.9 mg, 0.16 mmol), elution with hexane/EtOAc (80:20 to 70:30) gave **3n** as a yellowish oil (21.2 mg, 72%), d.r. (17:3). Major diastereomer: **TLC** R_f 0.50 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 3.40 (dq, *J* = 15.1, 6.7 Hz, 1H), 2.78 (d, *J* = 16.5 Hz, 1H), 2.61 (d, *J* = 16.5 Hz, 1H), 2.41 (s, 3H), 2.01 (dtd, *J* = 12.7, 7.1, 2.8 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.56 – 1.45 (m, 1H), 1.32 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 151.2, 71.8, 62.4, 50.4, 37.3, 32.2, 27.6, 22.5, 13.7. **FTIR** (neat film) 2941, 2883, 1539, 1440, 1396, 1332, 1303, 1216, 1118 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_2S$ (M+H) 185.1112, found 185.1118.



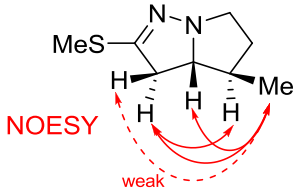
(3a*R,6*S**)-3,3,6-Trimethyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3o**). Following the general procedure **B** and starting from **2o** (57.9 mg, 0.26 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3o** as a yellowish oil (38.0 mg, 75%), d.r. (16:4). Major diastereomer: **TLC** R_f 0.61 (70:30 CH_2Cl_2/ THF). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 3.61 (dd, *J* = 13.7, 6.8 Hz, 1H), 3.48 (t, *J* = 8.2 Hz, 1H), 2.39 (s, 3H), 2.01 – 1.93 (m, 1H), 1.61 – 1.55 (m, 2H), 1.36 – 1.30 (m, 1H), 1.25 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.13 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 158.9, 76.0, 62.0, 51.0, 32.9, 26.8, 25.8, 21.7, 20.2, 13.3. **FTIR** (neat film) 2924, 2854, 1684, 1570, 1458, 1377 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{19}N_2S$ (M+H) 199.1269, found 199.1272.



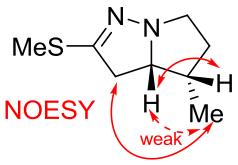
(3a*R,5*R**)-5-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo-[1,2-*b*]pyrazole** (**3p**). Following the general procedure **B** and starting from **2p** (61.8 mg, 0.31 mmol), elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **3p** as a yellowish oil (38.2 mg, 72%), d.r. (16:4). **TLC** R_f 0.32 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, $CDCl_3$) *Major diastereomer:* δ 3.94 – 3.84 (m, 1H), 3.62 – 3.54 (m, 1H), 2.88 (dd, *J* = 16.3, 9.9 Hz, 1H), 2.79 (dd, *J* = 10.1, 10.1 Hz, 1H), 2.63 (dd, *J* = 16.3, 2.1 Hz, 1H), 2.43 (s, 3H), 2.24 – 2.12 (m, 1H), 1.92 (dt, *J* = 12.3, 6.3 Hz, 1H), 1.14 – 1.07 (m, 1H), 1.04 (d, *J* = 6.6 Hz, 3H). *Minor diastereomer:* δ 4.02 (ddd, *J* = 11.9, 9.3, 2.4 Hz, 1H), 3.68 – 3.59 (m, 2H), 3.05 – 2.96 (m, 1H), 2.60 – 2.55 (m, 1H), 2.42 (s, 3H), 2.12 – 2.01 (m, 1H), 1.63 (ddd, *J* = 12.9, 8.5, 4.6 Hz, 1H), 1.48 (dt, *J* = 12.8, 9.0 Hz, 1H), 0.97 (d, *J* = 6.6 Hz, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) *Major diastereomer:* δ 151.2, 65.5, 62.3, 42.0, 39.6, 34.0, 18.3, 13.9. *Minor diastereomer:* δ 152.7, 64.2, 62.6, 44.9, 40.7, 31.8, 17.3. **FTIR** (neat film) 2921, 2850, 1670, 1559, 1457, 1267, 1126 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0949.



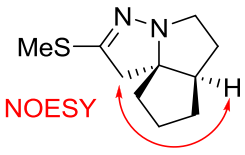
(3a*S,4*R**)-4-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3q**) and **(3a*S**,4*S**)-4-Methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3q'**). Following the general procedure **B** and starting from **2q** (63.5 mg, 0.32 mmol), elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **3q** (33.3 mg, 61%) and **3q'** (8.2 mg, 15%) as yellowish oils, d.r. (16:4).



3q: **TLC** R_f 0.27 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.48 (dt, *J* = 11.8, 7.7 Hz, 1H), 3.40 – 3.34 (m, 1H), 2.99 (td, *J* = 9.2, 1.8 Hz, 1H), 2.56 (dd, *J* = 16.1, 9.4 Hz, 1H), 2.29 – 2.23 (m, 4H), 1.64 (dtd, *J* = 12.6, 7.7, 5.0 Hz, 1H), 1.36 – 1.28 (m, 1H), 0.99 (ddd, *J* = 16.4, 12.4, 8.1 Hz, 1H), 0.59 (d, *J* = 6.7 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 149.0, 72.6, 54.4, 41.4, 38.0, 33.7, 17.1, 13.8. **FTIR** (neat film) 2955, 2928, 1561, 1459, 1434, 1274, 1145 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0951.

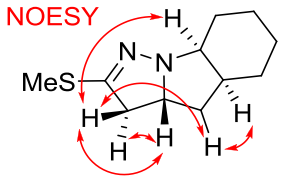


3q': **TLC** R_f 0.24 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.69 (ddd, *J* = 12.0, 6.7, 2.6 Hz, 1H), 3.59 (ddd, *J* = 9.4, 9.4, 3.0 Hz, 1H), 2.91 (ddd, *J* = 12.0, 10.7, 5.8 Hz, 1H), 2.52 – 2.37 (m, 2H), 2.24 (s, *J* = 3.1 Hz, 3H), 1.69 – 1.57 (m, 1H), 1.48 – 1.38 (m, 1H), 1.08 (dddd, *J* = 12.0, 10.6, 9.3, 6.7 Hz, 1H), 0.64 (d, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.2, 67.4, 54.4, 38.4, 35.5, 33.6, 16.2, 13.8. **FTIR** (neat film) 2960, 1561, 1509, 1459 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_8H_{15}N_2S$ (M+H) 171.0956, found 171.0955.

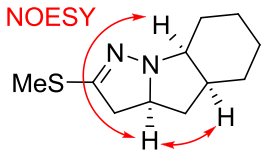


(3a*S,6a*R**)-2-(Methylthio)-4,5,6,6a,7,8-hexahydro-3*H*-cyclopenta[2,3]-pyrrolo[1,2-*b*]pyrazole** (**3r**). Following the general procedure **B** and starting from **2r** (65.1 mg, 0.29 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3r** as a yellowish oil (43.9 mg, 77%), d.r. (19:1). Major diastereomer: **TLC** R_f 0.47 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.74 (dd, *J* = 12.5, 7.2 Hz, 1H), 2.93 (ddd, *J* = 12.5, 12.5, 5.9 Hz, 1H), 2.63 (d, *J* = 16.2 Hz, 1H), 2.56 (d, *J* = 16.2 Hz, 1H), 2.25 (s, 3H), 1.88 – 1.80 (m, 2H), 1.76 (ddd, *J* = 16.5, 10.7, 7.0 Hz, 1H), 1.60 (dt, *J* = 13.4, 6.5 Hz, 1H), 1.57 – 1.48 (m, 1H), 1.39 (dt, *J* = 12.3, 6.1 Hz, 1H), 1.18 – 1.07 (m, 1H), 1.06 – 0.92 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.3, 84.6, 54.4, 51.0, 50.2, 39.4, 34.7, 32.8, 27.3, 13.9. **FTIR** (neat film) 2950, 2863, 1563, 1431, 1291, 1136 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{17}N_2S$ (M+H) 197.1112, found 197.1109.

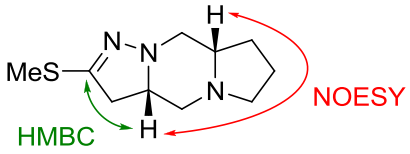
(3a*R,4a*S**,8a*S**)-2-(Methylthio)-3a,4,4a,5,6,7,8,8a-octahydro-3*H*-pyrazolo[1,5-*a*]indole** (**3s**); **(3a*S**,4a*S**,8a*S**)-2-(Methylthio)-3a,4,4a,5,6,7,8,8a-octahydro-3*H*-pyrazolo[1,5-*a*]indole** (**3s'**). Following the general procedure **B** and starting from **2s** (58.2 mg, 0.24 mmol), elution with CH_2Cl_2/TBME (70:30 to 60:40) gave **3s** (35.3 mg, 69%) and **3s'** (14.0 mg, 27%) as yellowish oils.



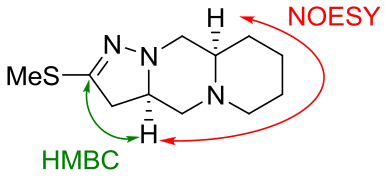
3s: **TLC** R_f 0.50 (50:50 CH_2Cl_2/TBME). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.85 – 3.78 (m, 1H), 3.59 – 3.48 (m, 1H), 2.65 (dd, *J* = 16.4, 10.4 Hz, 1H), 2.30 (s, 3H), 2.25 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.81 – 1.72 (m, 1H), 1.60 – 1.56 (m, 1H), 1.54 – 1.44 (m, 2H), 1.37 – 1.43 (m, 1H), 1.37 – 1.28 (m, 1H), 1.25 – 1.10 (m, 3H), 1.06 – 0.96 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.3, 65.9, 62.8, 44.5, 36.8, 36. 7, 28.6, 26.8, 24.0, 22.4, 14.2. **FTIR** (neat film) 2926, 2854, 1563, 1447, 1298, 1268, 1137 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{19}N_2S$ (M+H) 211.1269, found 211.1267.



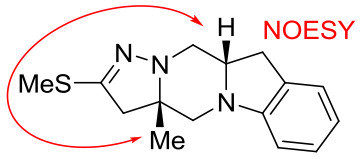
3s': **TLC** R_f 0.28 (50:50 CH_2Cl_2/TBME). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.69 – 3.61 (m, 1H), 3.30 (dd, *J* = 11.9, 5.9 Hz, 1H), 2.57 (dd, *J* = 16.3, 10.4 Hz, 1H), 2.28 (s, 3H), 2.22 (dd, *J* = 16.3, 4.2 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.89 – 1.82 (m, 2H), 1.82 – 1.73 (m, 1H), 1.68 – 1.57 (m, 1H), 1.47 – 1.29 (m, 3H), 1.20 – 1.11 (m, 2H), 1.04 – 0.96 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 149.6, 64.4, 62.5, 44.2, 39.4, 37.9, 29.9, 26.9, 24.3, 24.2, 14.1. **FTIR** (neat film) 2925, 2854, 1561, 1447, 1293, 1264, 1158, 1127 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{19}N_2S$ (M+H) 211.1269, found 211.1263.



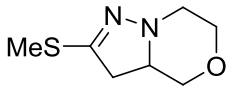
(3a*S*,8a*S*)-2-(Methylthio)-3,3a,4,6,7,8,8a,9-octahydro-pyrazolo[1,5-*d*]pyrrolo[1,2-*a*]pyrazine (**3t**). Following the general procedure **B** and starting from **2t** (71.2 mg, 0.30 mmol), elution with CH_2Cl_2/MeOH (95:5 to 85:15) gave **3t** as a yellowish oil (39.3 mg, 63%, 98% estimated purity by NMR). $[\alpha]_D^{18}$ -92.6º (c 0.53, $CHCl_3$). **TLC** R_f 0.38 (90:10 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, C_6D_6) δ 4.07 (dd, *J* = 12.8, 2.9 Hz, 1H), 3.58 – 3.50 (m, 1H), 2.97 (dd, *J* = 12.8, 10.5 Hz, 1H), 2.79 (td, *J* = 8.7, 1.9 Hz, 1H), 2.51 (dd, *J* = 15.2, 8.1 Hz, 1H), 2.30 – 2.25 (m, 4H), 2.06 – 1.97 (m, 1H), 1.96 – 1.88 (m, 2H), 1.77 (dt, *J* = 8.7, 8.7 Hz, 1H), 1.60 – 1.50 (m, 1H), 1.50 – 1.41 (m, 1H), 1.39 – 1.29 (m, 1H), 1.17 – 1.10 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 149.0, 61.5, 60.4, 56.4, 54.4, 53.4, 41.4, 28.0, 21.6, 14.0. **FTIR** (neat film) 2961, 2795, 1555, 1428, 1287, 1169 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{10}H_{18}N_3S$ (M+H) 212.1221, found 212.1219.



(3a*R*, 9a*R*)-2-(Methylthio)-3a,4,6,7,8,9,9a,10-octahydro-3*H*-pyrazolo[1,5-*d*]pyrido[1,2-*a*]pyrazine (**3u**). Following the general procedure **B** and starting from **2u** (64.6 mg, 0.26 mmol), elution with CH_2Cl_2/MeOH (100:0 to 90:10) gave **3u** as a yellowish oil (35.0 mg, 61%, 99% estimated purity by NMR). **TLC** R_f 0.21 (90:10 CH_2Cl_2/MeOH). $[\alpha]_D^{18}$ +70.4º (c 0.75, $CHCl_3$). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.90 – 3.80 (m, 1H), 3.38 – 3.32 (m, 1H), 3.30 (dd, *J* = 14.4, 4.1 Hz, 1H), 2.98 (dd, *J* = 13.9, 11.9 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.66 (d, *J* = 14.4 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.43 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.27 (s, 3H), 2.04 – 1.97 (m, 1H), 1.82 (dd, *J* = 15.2, 4.4 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.58 – 1.50 (m, 1H), 1.47 – 1.34 (m, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 147.5, 56.9, 56.7, 55.6, 53.3, 49.1, 41.6, 33.8, 32.9, 27.2, 14.1. **FTIR** (neat film) 2926, 2853, 1433, 1367, 1292, 1261, 1066 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{20}N_3S$ (M+H) 226.1378, found 226.1380.



(3a*R*,10a*S*)-3a-Methyl-2-(methylthio)-3,3a,4,10,10a,11-hexahydropyrazolo[1',5':4,5]pyrazino[1,2-*a*]indole (**3v**). Following the general procedure **B** and starting from **2v** (39.7 mg, 0.13 mmol), elution with hexane/EtOAc (90:10 to 80:20) gave **3v** as a yellowish oil (15.1 mg, 42%). **TLC** R_f 0.38 (75:25 hexane/EtOAc). $[\alpha]_D^{19}$ -30.8º (c 0.37, $CHCl_3$). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.11 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.31 (d, *J* = 7.7 Hz, 1H), 3.77 (dd, *J* = 13.7, 3.0 Hz, 1H), 3.31 – 3.25 (m, 1H), 3.10 (dd, *J* = 13.7, 11.2 Hz, 1H), 2.64 (d, *J* = 11.9 Hz, 1H), 2.59 (d, *J* = 11.9 Hz, 1H), 2.48 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.39 (d, *J* = 15.3 Hz, 1H), 2.25 (s, 3H), 2.21 – 2.07 (m, 1H), 1.92 (d, *J* = 15.3 Hz, 1H), 1.26 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 152.5, 148.3, 129.5, 127.9, 125.4, 118.9, 106.9, 65.1, 61.0, 52.0, 48.8, 48.7, 32.9, 21.9, 13.8. **FTIR** (neat film) 2924, 2810, 1607, 1482, 1294, 1233 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{15}H_{20}N_3S$ (M+H) 274.1378, found 274.1382.



2-(Methylthio)-3a,4,6,7-tetrahydro-3*H*-pyrazolo[5,1-*c*][1,4]oxazine (**3w**). Following the general procedure **B** and starting from **2w** (69.0 mg, 0.35 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3w** as a yellowish oil (41.5 mg, 70%, 98% estimated purity by NMR). **TLC** R_f 0.47 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.51 (dd, *J* = 13.5, 2.1 Hz, 1H), 3.45 (ddd, *J* = 11.5, 11.5, 2.4 Hz, 1H), 3.39 (dd, *J* = 11.5, 3.9 Hz, 1H), 3.35 – 3.27 (m, 1H), 3.23 – 3.14 (m, 1H), 3.12 (dd, *J* = 10.5, 5.4 Hz, 2H), 2.28 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.22 (s, 3H), 1.66 (dd, *J* = 15.5, 4.1 Hz, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 150.6, 66.5, 65.5, 61.1, 51.0, 39.9, 14.0. **FTIR** (neat film) 2924, 2854, 1668, 1457, 1261, 1107 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{13}N_2OS$ (M+H) 173.0749, found 173.0742.

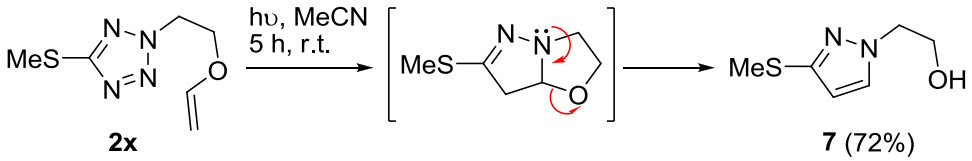
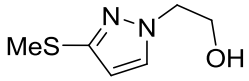
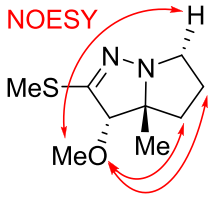


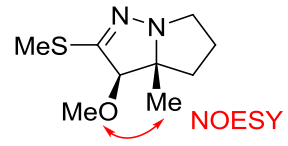
Figure SI 1. Aromatization via hemiaminal cleavage.



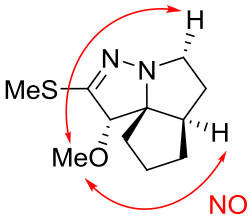
2-(3-(Methylthio)-1*H*-pyrazol-1-yl)ethanol (**7**). Following the general procedure **B** and starting from **2x** (66.9 mg, 0.36 mmol), elution with CH_2Cl_2/THF (90:10 to 80:20) gave **8** as a yellowish oil (40.9 mg, 72%, 97% estimated purity by NMR). **TLC** R_f 0.41 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 6.81 (d, *J* = 1.9 Hz, 1H), 5.99 (d, *J* = 1.9 Hz, 1H), 3.68 – 3.54 (m, 4H), 2.25 (s, 3H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 148.0, 132.1, 105.7, 62.0, 54.4, 16.0. **FTIR** (neat film) 3401, 2916, 1652, 1495, 1416, 1134 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_6H_{11}N_2OS$ (M+H) 159.0592, found 159.0594.



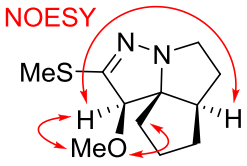
(3*S,3a*R**)-3-Methoxy-3a-methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3y**). Following the general procedure **B** and starting from *Z*-**2y** (46.2 mg, 0.20 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3y** as a yellowish oil (28.4 mg, 70%), d.r. (18:2). Major diastereomer: **TLC** R_f 0.58 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 4.03 (s, 1H), 3.63 – 3.53 (m, 1H), 3.08 (s, 3H), 3.01 (ddd, *J* = 12.2, 9.5, 7.0 Hz, 1H), 2.28 (ddd, *J* = 6.9, 6.5, 3.5 Hz, 1H), 2.25 (s, 3H), 1.64 – 1.54 (m, 1H), 1.48 – 1.36 (m, 1H), 1.17 (s, 3H), 1.09 – 0.99 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 153.4, 94.7, 76.5, 59.2, 55.2, 30.1, 27.2, 25.6, 13.6. **FTIR** (neat film) 2923, 2851, 1681, 1456, 1204, 1134 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_2OS$ (M+H) 201.1062, found 201.1063.



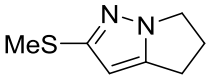
(3*R,3a*R**)-3-Methoxy-3a-methyl-2-(methylthio)-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole** (**3z**). Following the general procedure **B** and starting from *E*-**2z** (54.8 mg, 0.24 mmol), elution with CH_2Cl_2/THF (80:20 to 70:30) gave **3z** as a yellowish oil (31.5 mg, 66%), d.r. (15:5). Major diastereomer: **TLC** R_f 0.62 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 3.95 (s, 1H), 3.71 – 3.63 (m, 1H), 3.34 (s, 3H), 3.01 (ddd, *J* = 12.9, 9.3, 6.5 Hz, 1H), 2.21 (s, 3H), 1.55 – 1.42 (m, 1H), 1.37 – 1.25 (m, 2H), 1.18 (s, 3H), 1.17 – 1.13 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.1, 91.8, 75.6, 57.4, 53.2, 35.5, 24.5, 19.0, 13.9. **FTIR** (neat film) 2929, 1681, 1450, 1203, 1110 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{17}N_2OS$ (M+H) 201.1062, found 201.1066.



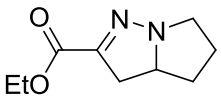
(3*S,3a*R**,6a*R**)-3-Methoxy-2-(methylthio)-4,5,6,6a,7,8-hexahydro-3*H*-cyclopenta[2,3]pyrrolo[1,2-*b*]pyrazole** (**3aa**). Following the general procedure **B** and starting from *Z*-**2aa** (66.0 mg, 0.26 mmol), elution with hexane/EtOAc (60:40 to 50:50) gave **3aa** as a yellowish oil (36.4 mg, 62%), d.r. > (20:1). **TLC** R_f 0.27 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 4.22 (s, 1H), 3.66 (dd, *J* = 12.5, 7.3 Hz, 1H), 3.17 (s, 3H), 3.03 – 2.89 (m, 2H), 2.25 (s, 3H), 2.01 (dt, *J* = 13.7, 7.0 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.73 – 1.63 (m, 2H), 1.47 – 1.32 (m, 2H), 1.17 – 1.08 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 154.1, 94.9, 88.1, 60.0, 55.8, 40.9, 39.9, 34. 7, 33.0, 27.0, 13.6. **FTIR** (neat film) 2952, 2929, 2864, 1681, 1453, 1111 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{19}N_2OS$ (M+H) 227.1218, found 227.1218.



(3*R,3a*R**,6a*R**)-3-Methoxy-2-(methylthio)-4,5,6,6a,7,8-hexahydro-3*H*-cyclopenta[2,3]pyrrolo[1,2-*b*]pyrazole** (**3bb**). Following the general procedure **B** and starting from *E*-**2bb** (64.6 mg, 0.25 mmol), elution with hexane/EtOAc (70:30 to 60:40) gave **3bb** as a yellowish oil (24.6 mg, 43%, 96% estimated purity by NMR), d.r. (>20:1). **TLC** R_f 0.45 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 4.20 (s, 1H), 3.71 (dd, *J* = 12.6, 7.4 Hz, 1H), 3.32 (s, 3H), 2.91 (ddd, *J* = 12.6, 12.6, 6.3 Hz, 1H), 2.33 – 2.25 (m, 1H), 2.24 (s, 3H), 1.88 – 1.78 (m, 1H), 1.69 – 1.49 (m, 3H), 1.48 – 1.39 (m, 1H), 1.27 – 1.17 (m, 1H), 1.03 – 0.95 (m, 1H), 0.91 (dd, *J* = 12.5, 6.3 Hz, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.8, 90.6, 87.0, 55.3, 53.9, 47.9, 34.2, 32.1, 30.3, 27.2, 13.7. **FTIR** (neat film) 2924, 2853, 1734, 1676, 1445, cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{11}H_{19}N_2OS$ (M+H) 227.1218, found 227.1211.

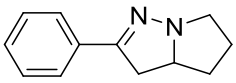


2-(Methylthio)-5,6-dihydro-4*H*-pyrrolo[1,2-*b*]pyrazole (**8**). Following the general procedure **B** and starting from **2cc** (56.2 mg, 0.31 mmol), elution with CH_2Cl_2/THF (90:10 to 80:20) gave **9** as a yellowish oil (9.2 mg, 19%). **TLC** R_f 0.49 (25:75 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 5.94 (s, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.56 (tt, *J* = 7.3, 7.2 Hz, 2H), 2.48 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 150.5, 147.0, 99.6, 47.9, 25.8, 23.2, 16.9. **FTIR** (neat film) 2955, 2924, 1655, 1531, 1456, 1359, 1315 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_7H_{11}N_2S$ (M+H) 155.0643, found 155.0642.



Ethyl 3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole-2-carboxylate (**14**). Following the general procedure **B** and starting from **13** (52.0 mg, 0.25 mmol), elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **14** as a yellowish oil (30.8 mg, 68%, 96% estimated purity by NMR). **TLC** R_f 0.68 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, C_6D_6) δ 4.09 (q, *J* = 7.1 Hz, 2H), 3.62 – 3.53 (m, 1H), 3.33 – 3.25 (m, 1H), 2.95 (ddd, *J* = 12.0, 7.7, 7.7, Hz, 1H), 2.71 – 2.68 (m, 2H), 1.27 – 1.18 (m, 1H), 1.14 (dddd, *J* = 12.8, 7.7, 7.7, 5.2 Hz, 1H), 1.10 – 1.03 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.90 – 0.81 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 162.9, 143.8,

65.1, 60.7, 53.0, 38.2, 30.1, 23.9, 14.3. **FTIR** (neat film) 2964, 1704, 1561, 1380, 1251, 1135 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_9H_{15}N_2O_2$ (M+H) 183.1134, found 183.1139.



2-Phenyl-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole (**16**). Following the general procedure **B** and starting from **15** (69.0 mg, 0.32 mmol), elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **16** as a yellowish oil (53.4 mg, 89%). **TLC** R_f 0.62 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.16 – 7.12 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.79 (ddd, *J* = 11.8, 7.3, 4.1 Hz, 1H), 3.57 – 3.50 (m, 1H), 3.13 – 3.06 (m, 1H), 2.71 (dd, *J* = 16.3, 9.6 Hz, 1H), 2.53 (dd, *J* = 16.3, 1.9 Hz, 1H), 1.47 – 1.34 (m, 2H), 1.29 – 1.22 (m, 1H), 1.06 – 0.99 (m, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 151.1, 134.1, 128.6, 128.6, 126.5, 64.3, 54.5, 39.5, 31.4, 24.4. **FTIR** (neat film) 2924, 1682, 1603, 1437, 1173, 1119 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{12}H_{15}N_2$ (M+H) 187.1235, found 187.1230.

D. Isomerization Studies of Model Olefin Substrates under the Reaction Conditions.

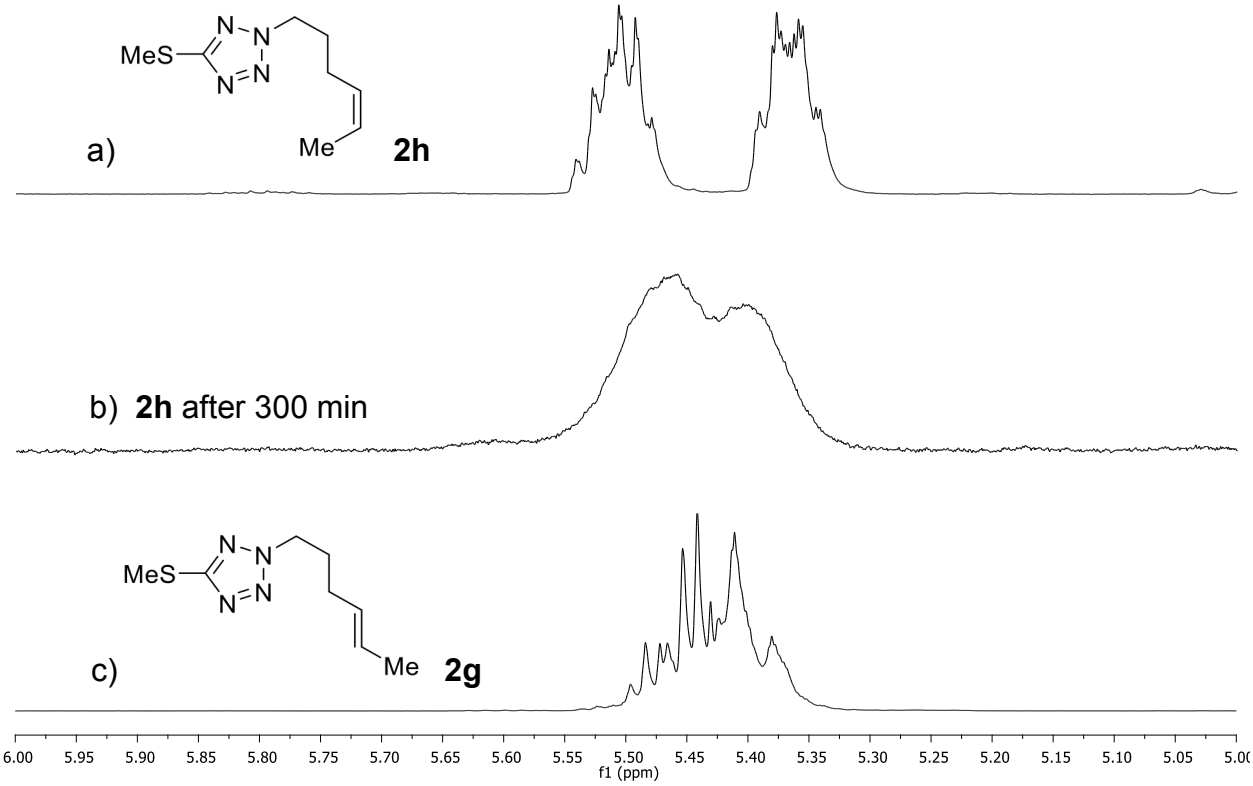


Figure SI 2. Isomerization of 2h under the reaction conditions. Stacked CD_3CN spectra of a) **2h**, b) **2h** after 300 min of reaction time and c) **2g**.

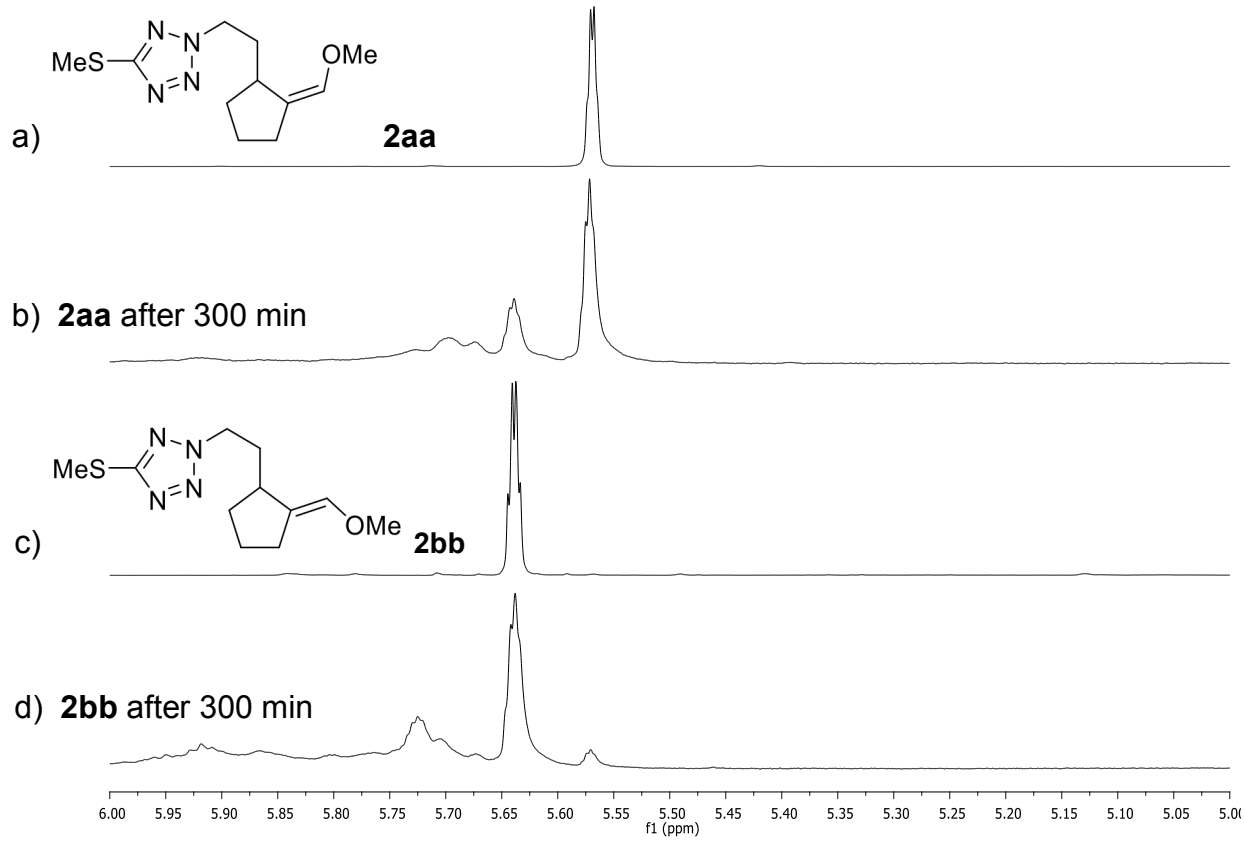


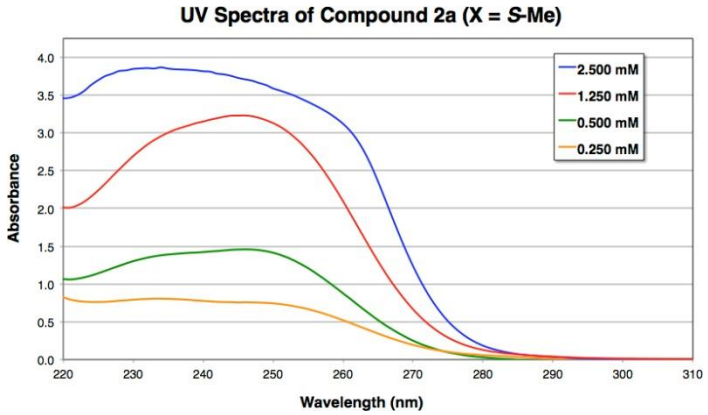
Figure SI 3. Isomerization of 2aa and 2bb under the reaction conditions. Stacked CD_3CN spectra of a) **2aa**, b) **2aa** after 300 min of reaction time, c) **2bb**, and d) **2bb** after 300 min of reaction time.

E. UV Absorbance Spectra of Tetrazole Substrates.

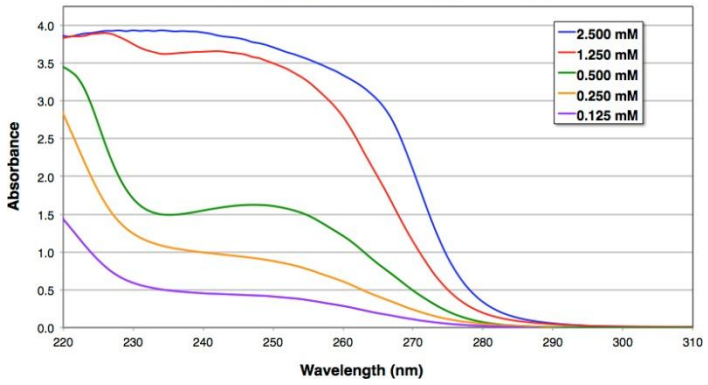
Substrates were dissolved in EtOH at various concentrations and UV spectra were recorded. All spectra in Figure 2 of the manuscript were recorded at 1.25 mM concentration for consistency. ε_{254} values (Avg*) were determined based on sample concentrations resulting in $0.1 < A_{254} < 3.0$.

Table 1. UV Absorbance Spectra of Tetrazole Substrates

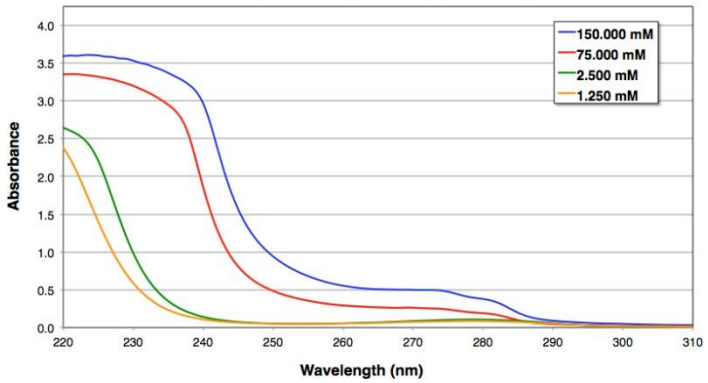
Compound	[mM]	150	75.0	25.0	12.5	2.50	1.25	0.500	0.250	0.125	0.050	Avg*
2a	A_{254}					3.45	2.86	1.26	0.688			
(X = SMe)	ε_{254}					1380	2290	2520	2750			**2520**
5	A_{254}					3.58	3.32	1.52	0.798	0.376		
(X = SBn)	ε_{254}					1430	2650	3040	3190	3010		**3080**
11	A_{254}	0.719	0.374			0.0495	0.0494					
(X = Me)	ε_{254}	4.79	4.99			19.8	39.5					**4.89**
13	A_{254}			1.60	0.785	0.195	0.107					
(X = CO_2Et)	ε_{254}			63.8	62.8	78.0	85.8					**72.6**
15	A_{254}					3.72	3.51	3.01	2.09	1.09	0.444	
(X = Ph)	ε_{254}					1490	2810	6030	8360	8750	8880	**8670**



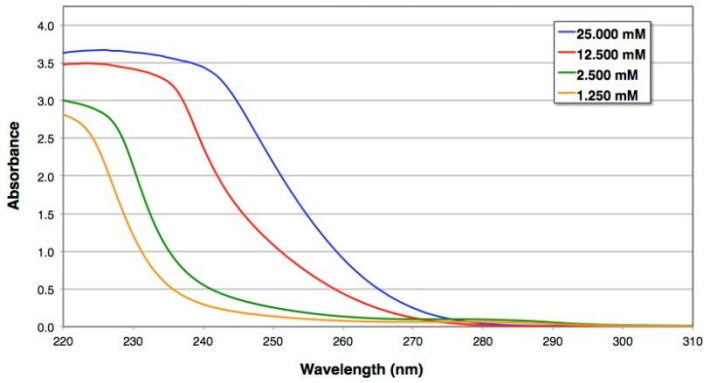
UV Spectra of Compound 5 (X = *S*-Bn)



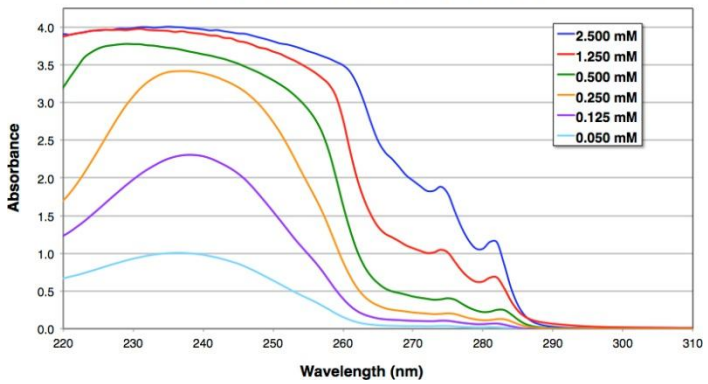
UV Spectra of Compound 11 (X = Me)



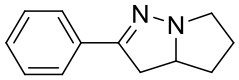
UV Spectra of Compound 13 (X = COOEt)



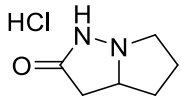
UV Spectra of Compound 15 (X = Ph)



F. Further Functionalization of Pyrazoline Scaffolds: Synthesis of 8, 16, 17, 18.



2-Phenyl-3a,4,5,6-tetrahydro-3*H*-pyrrolo[1,2-*b*]pyrazole (**16**). Copper (I) 3-methylsalicylate (CuMeSal) (110.3 mg, 0.51 mmol) and $Pd(Ph_3P)_4$ (27.0 mg, 0.02 mmol, 10 mol%) were added to a degassed solution of **3a** (36.5 mg, 0.23 mmol) and phenylboronic acid (62.7 mg, 0.51 mmol) in THF (5 mL) under Ar. The reaction mixture was heated to 80 ºC for 13 h. Then, the solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography and elution with CH_2Cl_2/THF (90:10 to 80:20) gave **16** as a yellowish oil (33.5 mg, 77%). The spectroscopic data is identical to the product described above.

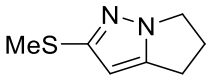


Tetrahydro-1*H*-pyrrolo[1,2-*b*]pyrazol-2(3*H*)-one hydrochloride (**17**). A solution of **3a** (23.6 mg, 0.15 mmol) in 4M HCl (2 mL) was heated to 100 ºC for 22 h. The solvent was removed under reduced pressure to give **17** as its hydrochloride salt (18.0 mg, 96%, 97% estimated purity by NMR).

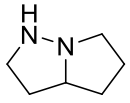
^{1}H-NMR (600 MHz, CD_3OD) δ 4.84 – 4.74 (m, 1H), 3.79 (dt, *J* = 12.1, 7.5 Hz, 1H), 3.47 (dt, *J* = 12.1, 6.1 Hz, 1H), 3.12 (dd, *J* = 17.7, 9.9 Hz, 1H), 2.74 (dd, *J* = 17.7, 5.2 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.29 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.19 – 2.11 (m, 1H), 2.11 – 2.00 (m, 1H). **^{13}C-NMR** (151 MHz, CD_3OD) δ 174.3, 67.6, 59.9, 36.1, 32.2, 24.5. MS (ESI) *m/z*: 127 (M+H, 100), 162 (M+HCl, 34). **HRMS** (ESI) *m/z*: Calcd for $C_6H_{11}N_2O$ (M+H) 127.0871, found 127.0870.

Confirmation of the structural assignment was achieved by liberation of the free base upon column chromatography on silica gel and elution with CH_2Cl_2/MeOH/NH_4OH (90:10:0.6). The resulting spectroscopic data matches that reported in literature:[24]

TLC R_f 0.28 (90:10:0.6 CH_2Cl_2/MeOH/NH_4OH). **^{1}H-NMR** ($CDCl_3$, 600 MHz) 4.07 – 4.04 (m, 1H), 3.10 (td, *J* = 11.0, 6.3 Hz, 1H), 2.86 (td, *J* = 11.0, 6.7 Hz, 1H), 2.62 (dd, *J* = 17.1, 9.3 Hz, 1H), 2.43 (dd, *J* = 17.1, 8.0 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.82 – 1.74 (m, 2H). **^{13}C-NMR** ($CDCl_3$, 150 MHz) 174.5, 62.0, 57.9, 37.5, 31.2, 23.7.



2-(Methylthio)-5,6-dihydro-4*H*-pyrrolo[1,2-*b*]pyrazole (**8**). A mixture of **3a** (24.9 mg, 0.16 mmol) and DDQ (43.4 mg, 0.19 mmol) in dry $CHCl_3$ (2 mL) was purged with Ar in a sealed vessel and microwaved at 120 ºC for 10 min. Purification by column chromatography on silica gel eluting with hexane/EtOAc (70:30 to 60:40) gave **8** as a yellowish oil (20.3 mg, 83%). Spectroscopic data matches the previously described.

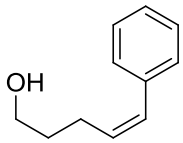


Hexahydro-1*H*-pyrrolo[1,2-*b*]pyrazole (**18**). A 15 mL flame dried schlenk tube was charged with **3a** (24.8 mg, 0.16 mmol) and AgOTf (61.2 mg, 0.24 mmol). The residue was azeotroped, and dissolved with dry THF (3 mL). The reaction mixture appeared to be a white precipitate and it was stirred at r.t. for 10 min. Then, $LiAlH_4$ (30.1 mg, 0.79 mmol) was added, and the reaction mixture immediately turned into a black precipitate. The suspension was stirred at r.t. for 1 h. Then, H_2O (0.25 mL) was added dropwise, followed by NaOH 15% aq. sol (0.25

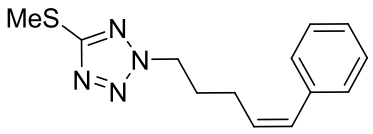
mL) and additional H_2O (0.25 mL) and stirred vigorously for 10 min. Then $MgSO_4$ was added, the solvents were filtered off and the solid residue was washed 3x CH_2Cl_2. 12 N HCl (1.5 mL) was added to the organic solution, and the resulting biphasic white suspension was evaporated under reduced pressure, and then lyophilized. The semisolid residue was triturated for 5 min under sonication with MeCN-benzene (50:50, 3 mL) and the resulting suspension was kept overnight at the freezer. Then, the clear supernatant solution was discarded and the solid residue was dried under reduced pressure to yield hexahydro-1H-pyrrolo[1,2-*b*]pyrazole **18** hydrochloride as a semisolid (21.2 mg, 90%, 98% estimated purity by NMR).

TLC (alumina) R_f 0.32 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 4.44 (tt, *J* = 8.5, 5.5 Hz, 1H), 3.77 – 3.65 (m, 1H), 3.35 (dt, *J* = 12.3, 6.3 Hz, 1H), 3.27 – 3.15 (m, 2H), 2.49 – 2.36 (m, 1H), 2.34 – 2.22 (m, 1H), 2.14 (tt, *J* = 13.4, 6.8 Hz, 1H), 2.07 – 1.87 (m, 2H), 1.79 (ddd, *J* = 13.0, 6.6, 6.4 Hz, 1H). **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 68.8, 57.7, 47.3, 33.0, 30.5, 23.8. **FTIR** (neat film) 3356, 2922, 2851, 1260, 1110 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_6H_{13}N_2$ (M+H) 113.1079, found 113.1077.

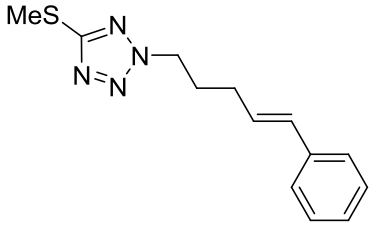
G. Total Syntheses of (±)-Newbouldine and Withasomnine 19-28.



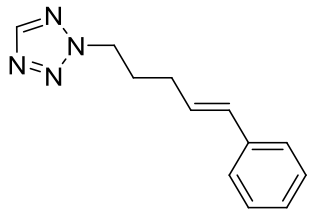
(*Z*)-5-Phenylpent-4-en-1-ol. ^{t}BuOK (1.004 g, 8.94 mmol) was added to a 0 ºC cooled suspension of [3-(ethoxycarbonyl)propyl]triphenylphosphonium bromide **28** (4.090 g, 8.94 mmol) in anhydrous THF (30 mL). The resulting orange colored solution was allowed to warm to r.t. and stirred for 30 min. Then benzaldehyde (695 µL, 6.88 mmol) was added dropwise and the reaction mixture was stirred for additional 1 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc (95:5 to 85:15) gave ethyl (*Z*)-5-phenylpent-4-enoate (846.4 mg, 60%).[25] $LiAlH_4$ (181.8 mg, 4.78 mmol) was added to a 0 ºC cooled solution of ethyl (*Z*)-5-phenylpent-4-enoate (751.0 g, 3.68 mmol) in THF (35 mL). The suspension was allowed to warm to r.t. and stirred for 1 h. Then, H_2O (0.5 mL) was added dropwise, followed by 15% aq. NaOH (0.5 mL), and H_2O (1.5 mL). The resulting mixture was stirred for 15 min. The resulting suspension was filtered through a pad of Celite, and the pad was washed with methanol. The combined organic fractions were concentrated under reduced pressure to give (*Z*)-5-phenylpent-4-en-1-ol (596 mg, quant.) as a colorless oil.[25a, 26]



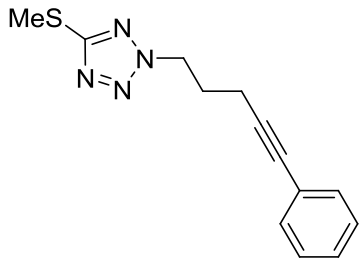
(*Z*)-5-(Methylthio)-2-(5-phenylpent-4-enyl)-2*H*-tetrazole (***Z*-22**). Following the general procedure **A** and starting from (*Z*)-5-phenylpent-4-en-1-ol (305.1 mg, 1.88 mmol, 1.1 equiv.), elution with hexane/EtOAc (90:10 to 80:20) gave ***Z*-22** (376.7 mg, 85%, 94:6 *Z*/*E*) as a colorless oil. **TLC** R_f 0.60 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.18 – 7.13 (m, 2H), 7.11 – 7.07 (m, 2H), 7.07 – 7.03 (m, 1H), 6.33 (d, *J* = 11.6 Hz, 1H), 5.23 (dt, *J* = 11.6, 7.3 Hz, 1H), 3.78 (t, *J* = 7.3 Hz, 2H), 2.26 (s, 3H), 1.99 – 1.91 (m, 2H), 1.60 – 1.49 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.6, 137.9, 131.0, 130.7, 129.4, 128.9, 127.5, 52.6, 29.6, 25.8, 14.3. **FTIR** (neat film) 2928, 1724, 1400, 1376, 1177, 1137, 1054 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{17}N_4S$ (M+H) 261.1174, found 261.1175.



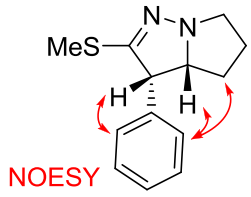
(*E*)-5-(Methylthio)-2-(5-phenylpent-4-enyl)-2*H*-tetrazole (***E*-22**). Following the general procedure **A** and starting from (*E*)-5-phenylpent-4-en-1-ol[27] (1.1775 g, 7.26 mmol, 1.1 equiv.), elution with hexane/EtOAc (85:15 to 75:25) gave ***E*-22** (1.4259 g, 83%, >99:1 *E*/*Z*) as a colorless oil. **TLC** R_f 0.55 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.24 – 7.17 (m, 2H), 7.14 (dd, *J* = 9.9, 8.5 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.16 (d, *J* = 15.8 Hz, 1H), 5.82 – 5.64 (m, 1H), 3.96 – 3.78 (m, 2H), 2.29 (s, 3H), 1.80 – 1.68 (m, 2H), 1.62 – 1.50 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.7, 138.1, 132.2, 129.2, 128.7, 127.8, 126.8, 52.5, 30.0, 29.0, 14.3. **FTIR** (neat film) 2933, 1723, 1496, 1401, 1364, 1288, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{17}N_4S$ (M+H) 261.1174, found 261.1166.



(*E*)-2-(5-Phenylpent-4-enyl)-2*H*-tetrazole. A 0.54 M MeCN solution of 1*H*-tetrazole (4.21 mL, 2.28 mmol) and diisopropyl azodicarboxylate (0.740 mL, 3.76 mmol) were added to a stirred solution of PPh_3 (985.3 mg, 3.76 mmol) and (*E*)-5-phenylpent-4-en-1-ol[27] (406.3 mg, 2.51 mmol) in THF (20 mL) at r.t. under Ar. The resulting mixture was heated to 80 ºC for 16 h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Elution with hexane/EtOAc (90:10 to 80:20) gave the entitled product (402.3 mg mg, 75%) as a colorless oil. **TLC** R_f 0.34 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.34 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.70 (t, *J* = 6.8 Hz, 2H), 2.27 (dd, *J* = 14.2, 6.8 Hz, 2H), 2.25 – 2.17 (m, 2H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 152.8, 137.1, 131.8, 128.5, 127.7, 127.3, 126.0, 52.3, 29.5, 28.8. **FTIR** (neat film) 3140, 3026, 2935, 1598, 1493, 1446, 1359, 1282, 1131, 1008 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{12}H_{15}N_4$ (M+H) 215.1297, found 215.1299.

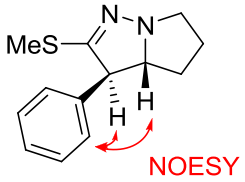


5-(Methylthio)-2-(5-phenylpent-4-ynyl)-2*H*-tetrazole (**27**). Following the general procedure **A** and starting from 5-phenylpent-4-yn-1-ol[4b, 28] (429.2 mg, 2.68 mmol, 1.1 equiv.), elution with hexane/EtOAc (80:20 to 70:30) gave **26** (491.6 mg, 78%) as a colorless oil. **TLC** R_f 0.53 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.45 – 7.41 (m, 2H), 7.02 – 6.96 (m, 3H), 4.02 (t, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 1.94 (t, *J* = 6.9 Hz, 2H), 1.65 (tt, *J* = 6.9, 6.8 Hz, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.8, 132.3, 128.9, 128.5, 124.5, 88.2, 82.8, 52.1, 28.4, 17.0, 14.3. **FTIR** (neat film) 3055, 2932, 2230, 1598, 1490, 1400, 1286, 1070, 757 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{17}N_4S$ (M+H) 259.1017, found 259.1014.

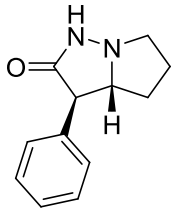


(3*S,3a*R**)-2-(Methylthio)-3-phenyl-3a,4,5,6-tetrahydro-3*H*-pyrrolo-[1,2-*b*]pyrazole** (***anti*-23**). Following the general procedure **B** with 8 h irradiation time and starting from ***Z*-22** (271.9 mg, 1.04 mmol), elution with hexane/EtOAc (50:50 to 20:80) gave ***anti*-23** (104.9 mg, 43%), and the C3 epimer ***syn*-23** (67.4 mg 28%) as yellowish oils. ***Anti*-22**: **TLC** R_f 0.26 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.13 – 7.09 (m, 2H), 7.08 (d, *J* = 6.7 Hz, 2H), 7.04 (t, *J* = 7.1 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 3.83 (ddd, *J* = 10.0, 8.3, 7.2 Hz, 1H), 3.70 (ddd, *J* = 12.0, 7.2, 4.5 Hz, 1H), 3.10 (ddd, *J* = 12.0, 8.0, 7.2 Hz, 1H), 2.28 (s, 3H), 1.44 (ddd, *J* = 15.4, 12.0, 7.2 Hz, 1H), 1.36 (td, *J* = 13.0, 6.5 Hz, 1H), 1.26 – 1.15 (m, 1H), 0.83 (ddd, *J* = 15.4, 13.0, 7.5 Hz, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 152.6, 136.3, 130.5, 128.8,

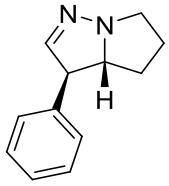
127.8, 71.0, 59.4, 56.1, 26.4, 24.9, 14.4. **FTIR** (neat film) 3029, 2926, 2869, 1603, 1550, 1494, 1453, 1238, 1155 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{17}N_2S$ (M+H) 233.1112, found 233.1110.



(3*R,3a*R**)-2-(Methylthio)-3-phenyl-3a,4,5,6-tetrahydro-3*H*-pyrrolo-[1,2-*b*]pyrazole** (***syn*-23**). Following the general procedure **B** with 16 h irradiation time and starting from ***E*-22** (100.2 mg, 0.39 mmol), elution with hexane/EtOAc (50:50 to 40:60) gave ***syn*-23** as a yellowish oil (65.3 mg, 73%). **TLC** R_f 0.43 (50:50 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 7.34 (bd, *J* = 8.0 Hz, 2H), 7.15 – 7.11 (m, 2H), 7.04 (dd, *J* = 7.0, 2.4 Hz, 1H), 3.79 – 3.68 (m, 2H), 3.57 (td, *J* = 6.8, 3.4 Hz, 1H), 2.95 (ddd, *J* = 12.2, 8.8, 6.8 Hz, 1H), 2.19 (s, 3H), 1.58 – 1.40 (m, 2H), 1.30 – 1.18 (m, 2H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 155.0, 141.6, 129.4, 128.3, 127.8, 74.7, 64.1, 55.1, 31.7, 24.6, 14.2. **FTIR** (neat film) 3061, 2928, 2869, 1602, 1557, 1494, 1453, 1175, 1121 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{17}N_2S$ (M+H) 233.1112, found 233.1107.

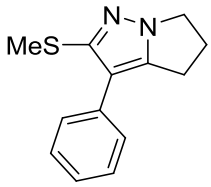


(3*R,3a*R**)-3-Phenyltetrahydro-1*H*-pyrrolo[1,2-*b*]pyrazol-2(3*H*)-one** (**24**). 12 M HCl (20 mL) was added to a solution of ***syn*-23** (135.1 mg, 0.58 mmol) in THF (1 mL). The resulting solution was heated to 100 ºC for 24 h. Then, the solvent was removed under reduced pressure. The residue was purified by basic alumina gel chromatography and elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave **24** (94.3 mg, 80%) as a pinkish solid. m.p. (MeOH) 120.0 – 121.4 ºC. **Basic alumina TLC** R_f 0.47 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 8.06 (bs, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.25 (m, 3H), 4.10 – 4.02 (m, 1H), 3.70 (d, *J* = 9.6 Hz, 1H), 3.31 – 3.21 (m, 1H), 3.01 – 2.88 (m, 1H), 2.17 – 2.06 (m, 2H), 1.96 – 1.86 (m, 2H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 175.2, 137.2, 128.9, 128.5, 127.5, 71.8, 57.7, 54.0, 29.1, 23.8. **FTIR** (neat film) 3186, 3063, 2968, 1690, 1497, 1454, 1293, 1071 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{12}H_{15}N_2O$ (M+H) 203.1184, found 203.1180.

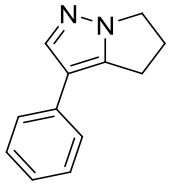


(±)-Newbouldine (**19**). Cp_2ZrHCl (48.1 mg, 0.19 mmol) was added in one solid portion to a –20 °C solution of **24** (13.2 mg, 0.07 mmol) in THF (5 mL). After stirring 2 h at this temperature, silica gel was added to the reaction mixture and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography and elution with $CHCl_3$/MeOH (100:0 to 95:5) gave (±)-newbouldine (**19**) (10.2 mg, 84%) as a yellowish oil. **TLC** R_f 0.32 (95:5 $CHCl_3$/MeOH). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 6.85 (bs, 1H), 3.99 (bs, 1H), 3.72 – 3.65 (m, 2H), 3.23 – 3.17 (m, 1H), 2.03 – 1.95

(m, 1H), 1.76 – 1.67 (m, 2H), 1.65 – 1.54 (m, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 147.1, 140.3, 128.9, 127.3, 127.2, 71.2, 60.9, 53.5, 31.2, 23.7. **HRMS** (ESI) *m/z*: Calcd for $C_{12}H_{15}N_2$ (M+H) 187.1235, found 187.1228. Spectroscopic data identical to the reported in literature.[29]



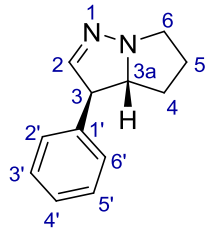
2-(Methylthio)-3-phenyl-5,6-dihydro-4*H*-pyrrolo[1,2-*b*]pyrazole (**25**). A mixture of ***syn*-23** (9.0 mg, 0.04 mmol) and DDQ (10.6 mg, 0.05 mmol) in dry $CHCl_3$ (0.5 mL) was purged with Ar in a sealed vessel and microwaved at 120 ºC for 10 min. Purification by column chromatography on silica gel eluting with CH_2Cl_2/MeOH (95:5 to 85:15) gave **25** (8.0 mg, 90%) as a yellowish oil. **TLC** R_f 0.75 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.25 – 7.21 (m, 1H), 4.17 (t, *J* = 7.3 Hz, 2H), 3.07 – 2.97 (m, 2H), 2.68 – 2.56 (m, 2H), 2.51 (s, 3H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 147.5, 144.8, 133.0, 128.5, 127.2, 126.0, 114.7, 48.1, 25.8, 24.0, 16.3. **FTIR** (neat film) 2958, 2924, 1602, 1574, 1384, 1003 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{13}H_{15}N_2S$ (M+H) 231.0956, found 231.0947.



Withasomnine (**20**). Raney Ni was washed 4 times with EtOH prior to use. A portion of the slurry was added to a solution of **25** (8.1 mg, 0.04 mmol) in EtOH (5 mL) and the reaction mixture was stirred at r.t. for 2 h. Then, the mixture was filtered through a pad of Celite, and the pad was washed with methanol. The combined organic fractions were concentrated under reduced pressure. The residue was purified by silica gel chromatography and elution with CH_2Cl_2/MeOH (100:0 to 95:5) gave withasomnine (**20**) (6.2 mg, 95%) as a yellowish oil. **TLC** R_f 0.55 (95:5 CH_2Cl_2/MeOH). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.45 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.18 (t, *J* = 7.3 Hz, 2H), 3.10 (t, *J* = 7.3 Hz, 2H), 2.73 – 2.66 (m, 2H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 142.6, 140.9, 133.4, 128.8, 125.6, 125.0, 115.3, 47.6, 26.4, 23.9. Spectroscopic data identical to the reported in literature.[29]

H. NMR Data of Natural and Synthetic 19.

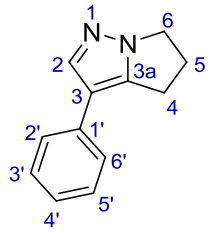
Table 2. NMR data of natural and synthetic **19**



	Natural 18[29]		**Trauner's Synthetic 18**[30]		**Synthetic 18**	
Position	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	6.82 bs	147.0	6.84 bs	147.0	6.85 bs	147.1
3	4.05 bs	61.1	4.00 bs	61.0	3.99 bs	60.9
3a	3.68 m	71.4	3.72 – 3.64 m	71.2	3.72 – 3.65 m	71.2
4	α 2.00 m β 1.56 m	31.4	α 2.03 – 1.95 m β 1.59 – 1.55 m	31.2	α 2.03 – 1.95 m β 1.65 – 1.54 m	31.2
5	1.70 m	23.9	1.74 – 1.67 m	23.7	1.76 – 1.67 m	23.7
6	3.69 m 3.17 m	53.6	3.72 – 3.64 m 3.23 – 3.16 m	53.5	3.72 – 3.65 m 3.23 – 3.17 m	53.5
1'		140.5		140.3		140.3
2', 6' 3', 5' 4'	} 7.34 – 7.26 m	127.3 129.0 127.4	} 7.36 – 7.21 m	127.1 128.9 127.3	} 7.33 – 7.29 m 7.26 – 7.21 m	127.2 128.9 127.3

I. NMR Data of Natural and Synthetic 20.

Table 3. NMR data of natural and synthetic **20**



	Natural 19[29]		**Odom's Synthetic 18**[31]		**Synthetic 19**	
Position	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.73 bs	141.0	7.79 s	140.9	7.82 s	140.9
3		115.4		115.3		115.3
3a		142.7		142.6		142.6
4	3.07 t	26.5	3.08 t	26.4	3.10 t	26.4
5	2.67 m	23.9	2.70 – 2.64 m	23.8	2.73 – 2.66 m	23.9
6	4.13 t	47.6	4.16 t	47.6	4.18 t	47.6
1'		133.5		133.4		133.4
2', 6' 3', 5' 4'	} 7.13 – 7.43	125.1 128.9 125.7	} 7.16 tt 7.33 d 7.44 – 7.42 m	125.0 128.8 125.6	} 7.19 t 7.38 – 7.34 m 7.45 dd	125.0 128.8 125.6

J. Synthesis of Azetidine, Azepane and Azocane Quasidimer Structures.

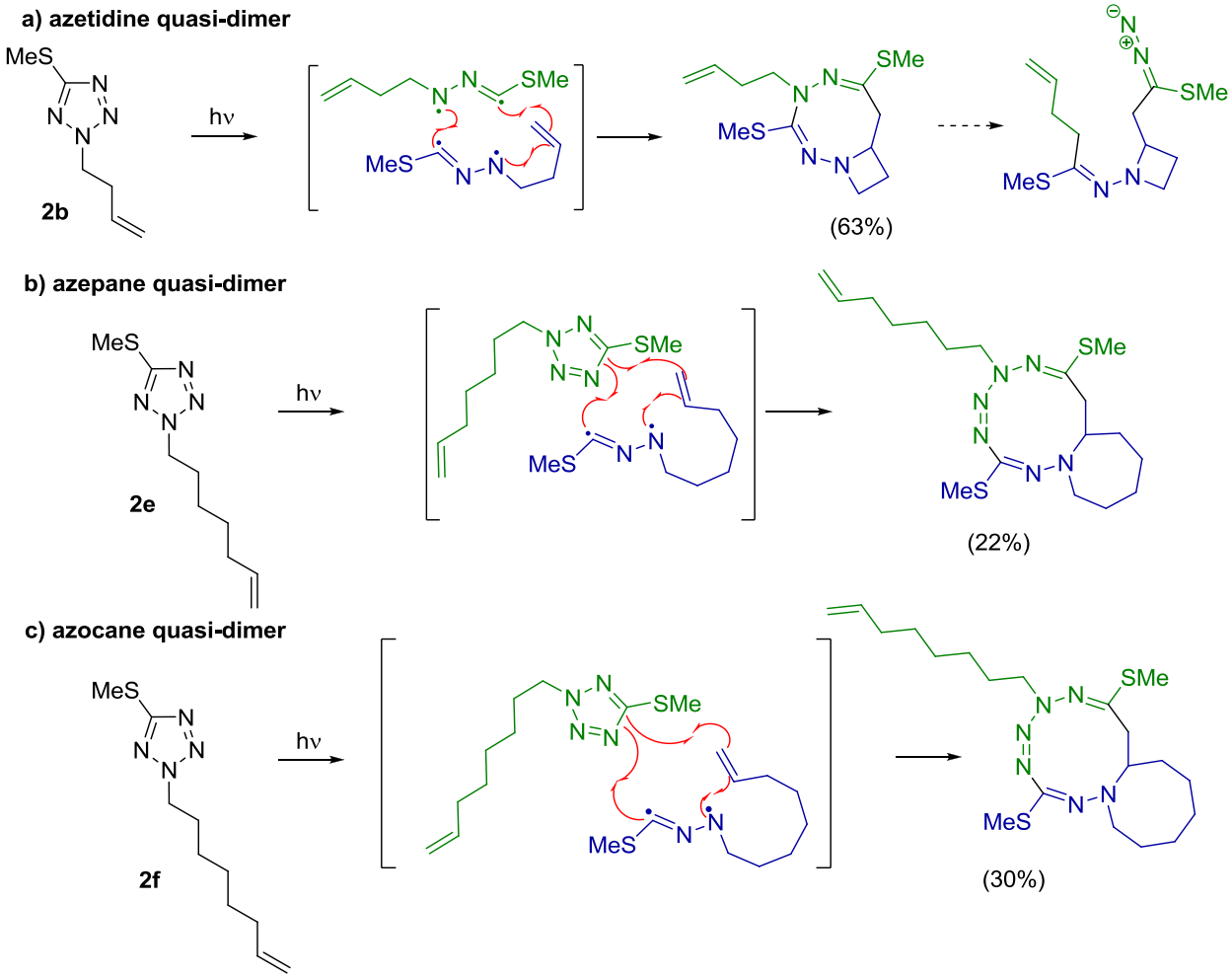
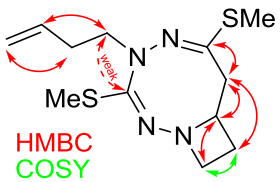
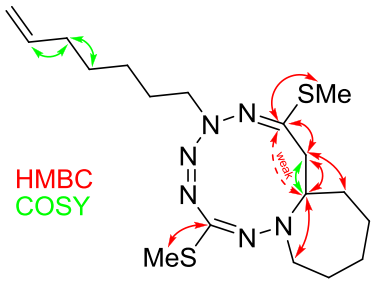


Figure SI 4. Proposed quasidimer structures from the 4-, 7- and 8-membered ring substrates (entries 2, 5 and 6 in Table 2):

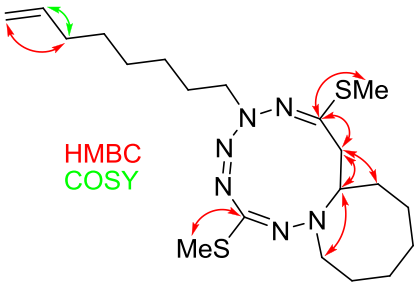


(2*E*)-4-(But-3-enyl)-3,6-bis(methylthio)-1,2,4,5-tetraazabicyclo[6.2.0]deca-2,5-diene (proposed structure). Following the general procedure **B** and starting from **2c** (56.0 mg, 0.33 mmol), elution with hexane/EtOAc (80:20 to 70:30) gave the entitled compound as a yellowish oil (29.3 mg, 63%). **TLC** R_f 0.37 (75:25 hexane/EtOAc). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.92 – 5.82 (m, 1H), 5.13 – 5.01 (m, 2H), 3.95 (ddd, *J* = 13.9, 8.3, 5.9 Hz, 1H), 3.79 (ddd, *J* = 13.9, 8.2, 7.1 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.58 – 2.47 (m, 3H), 2.28 (s, 3H), 2.21 – 2.09 (m, 5H), 1.92 – 1.81 (m, 2H), 1.64 (dtd, *J* = 14.3, 8.3, 6.0 Hz, 1H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.9, 150.3, 137.4, 116.1, 64.9, 55.3, 50.3, 42.1, 33.3, 32.1, 14.3, 13.7. **FTIR** (neat film) 3074, 2927, 2832,

1640, 1563, 1433, 1285, 1055 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{12}H_{21}N_4S_2$ (M+H) 285.1212, found 285.1208.



(3*Z*,6*E*)-5-(Hept-6-enyl)-2,7-bis(methylthio)-5,8,8a,9,10,11,12,13-octahydroazepino-[1,2-*g*][1,2,3,4,6,7]hexazecine (proposed structure). Following the general procedure **B** and starting from **2e** (105.4 mg, 0.50 mmol), elution with CH_2Cl_2/TBME (90:10 to 60:40) gave the monomer **3e** (23.7 mg, 26%, characterized above), and the entitled compound (21.6 mg, 22%) as yellowish oils. **TLC** R_f 0.94 (70:30 CH_2Cl_2/TBME). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 4.90 (m, 2H), 3.88 (t, *J* = 7.0 Hz, 2H), 2.75 (dt, *J* = 12.0, 7.8 Hz, 1H), 2.70 – 2.60 (m, 2H), 2.36 (dd, *J* = 15.4, 9.1 Hz, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 2.12 (dd, *J* = 15.4, 13.5 Hz, 1H), 2.07 – 2.01 (m, 2H), 1.98 – 1.93 (m, 1H), 1.92 – 1.83 (m, 1H), 1.53 – 1.46 (m, 1H), 1.46 – 1.37 (m, 5H), 1.34 (ddd, *J* = 10.1, 6.0, 2.4 Hz, 1H), 1.22 – 1.11 (m, 1H), 0.86 – 0.70 (m, 4H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.8, 149.7, 139.6, 114.9, 68.7, 55.8, 53.1, 43.0, 34.6, 32.9, 29.7, 29.5, 28.9, 27.7, 26.8, 26.2, 14.3, 13.8. **FTIR** (neat film) 3075, 2929, 2858, 1641, 1564, 1375, 1283, 1056 cm^{-1}. **HRMS** (ESI) m/z: Calcd for $C_{18}H_{33}N_6S_2$ (M+H) 397.2208, found 397.2214.



(3*Z*,6*E*)-2,7-bis(Methylthio)-5-(oct-7-enyl)-8,8a,9,10,11,12,13,14-octahydro-5*H*-azocino-[1,2-*g*][1,2,3,4,6,7]hexazecine (proposed structure). Following the general procedure **B** and starting from **2g** (68.4 mg, 0.30 mmol), elution with CH_2Cl_2/THF (95:5 to 85:15) gave the entitled compound as a yellowish oil (19.4 mg, 30%). **TLC** R_f 0.94 (70:30 CH_2Cl_2/THF). **^{1}H-NMR** (600 MHz, C_6D_6) δ 5.84 – 5.71 (m, 1H), 5.10 – 4.92 (m, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 2.82 (dt, *J* = 12.0, 7.8 Hz, 1H), 2.78 – 2.66 (m, 1H), 2.41 (dd, *J* = 15.4, 9.1 Hz, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 2.17 (dd, *J* = 15.4, 13.6 Hz, 1H), 2.05 – 1.90 (m, 3H), 1.95 – 1.87 (m, 2H), 1.52 – 1.19 (m, 10H), 0.95 – 0.76 (m, 6H). **^{13}C-NMR** (151 MHz, C_6D_6) δ 165.8, 149.7, 139.6, 114.9, 68.9, 56.0, 53.2, 43.1, 34.6, 33.3, 29.8, 29.7, 29.5, 29.4, 29.1, 28.1, 26.8, 26.7, 14.3, 13.8. **FTIR** (neat film) 3073, 2927, 2855, 1639, 1562, 1433, 1282, 1148, 1054 cm^{-1}. **HRMS** (ESI) *m/z*: Calcd for $C_{20}H_{37}N_6S_2$ (M+H) 425.2521, found 425.2532.

K. References and Notes.

1. C. F. Purchase and A. D. White, *Synth. Commun.*, 1996, **26**, 2687-2694.

2. In general, reactions proceed cleanly from starting material to product under the optimized reaction conditions. The moderate yields are due to incomplete conversions, but longer irradiation times were not beneficial and provided a higher extent of the corresponding thiopyrazolone by-products **4**.

3. (a) Synthesized as a colorless oil (827.7 mg, 99%) by $LiAlH_4$ reduction of (*Z*)-ethyl 5-cyclopropylpent-4-enoate. Spectroscopic data identical to the reported in literature; (b) C. Paolucci and P. Righi, *Tetrahedron*, 2007, **63**, 12763-12768.

4. (a) Z. Cai, N. Yongpruksa and M. Harmata, *Org. Lett.*, 2012, **14**, 1661-1663; (b) Synthesized as described in literature.

5. (a) Synthesized as a colorless oil (1.119 g, 92%) by $LiAlH_4$ reduction of methyl 5-methylhex-4-enoate in THF. Spectroscopic data identical to the reported in literature; (b) E. J. Corey, H. Cheng, C. H. Baker, S. P. T. Matsuda, D. Li and X. Song, *J. Am. Chem. Soc.*, 1997, **119**, 1277-1288.

6. P. M. Tadross, P. Bugga and B. M. Stoltz, *Org. Biomol. Chem.* , 2011, 5354-5357.

7. (a) M. R. Ashcroft, P. Bougeard, A. Bury, C. J. Cooksey, M. D. Johnson, J. M. Hungerford and G. M. Lampman, *J. Org. Chem.*, 1984, **49**, 1751-1761; (b) K. A. McManus and D. R. Arnold, *Can. J. Chem.*, 1995, **73**, 2158-2169.

8. (a) Synthesized as described in literature. Spectroscopic data identical to the reported in literature; (b) S. Raghavan and V. Sudheerbabu, *Chemistry - A European Journal*, 2011, **17**, 8487 - 8494.

9. F. C. Courchay, T. W. Baughman and K. B. Wagener, *J. Organomet. Chem.*, 2006, **691**, 585-594.

10. Synthesized as a colorless oil (160.0 mg, quant.) by $LiAlH_4$ reduction of methyl 2-(2-methylenecyclopentyl)acetate. Spectroscopic data identical to the reported in literature.

11. R. G. Salomon, S. Ghosh, M. G. Zagorski and M. Reitz, *J. Org. Chem.*, 1982, **47**, 829-836.

12. L. Wang, K. Thai and M. Gravel, *Org. Lett.*, 2009, **11**, 891-893.

13. S. H. Park, H. J. Kang, S. Ko, S. Park and S. Chang, *Tetrahedron: Asymmetry*, 2001, **12**, 2621-2624

14. (*R*)-methyl 1-allylpiperidine-2-carboxylate was synthesized using the following procedure: allyl bromide (3.4 mL, 38.7 mmol) was added to a mixture of (*R*)-methyl piperidine-2-carboxylate hydrochloride (3.477 g, 19.4 mmol) and Et_3N (10.8 mL, 77.4 mmol) in THF/DMF (95:5, 40 mL) at r.t. After stirring for 20 h at r.t., the reaction mixture was evaporated under reduced pressure. The residue was purified by silica gel chromatography and elution with hexane/EtOAc (85:15 to 75:25) gave the entitled product (3.325 g, 94%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.87 (dddd, *J* = 17.1, 10.1, 7.9, 5.6 Hz, 1H), 5.18 – 5.09 (m, 2H), 3.71 (s, 3H), 3.26 – 3.19 (m, 1H), 3.08 – 2.99 (m, 2H), 2.91 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.87 – 1.79 (m, 1H), 1.77 – 1.69 (m, 1H), 1.68 – 1.57 (m, 3H), 1.32 (tdd, *J* = 10.8, 8.6, 4.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 134.6, 118.1, 65.0, 59.7, 51.6, 50.9, 29.7, 25.2, 22.7. (*R*)-Methyl piperidine-2-carboxylate hydrochloride precursor was synthesized from (*R*)-Piperidine-2-carboxylic acid and using the same procedure as described in literature for the *S*-enantiomer.

15. P. Zajdel, G. Nomezine, N. Masurier, M. Amblard, M. Pawłowski, J. Martinez and G. Subra, *Chemistry – A European Journal*, 2010, **16**, 7547-7553.

16. The desired product was obtained with traces of the corresponding 1-substituted tetrazole regioisomer as an impurity.

17. C. Pasquier, S. Naili, L. Pelinski, J. Brocard, A. Mortreux and F. Agbossou, *Tetrahedron: Asymmetry*, 1998, **9**, 193-196.

18. K. C. Nicolaou, D. A. Claremon and W. E. Barnette, *J. Am. Chem. Soc.*, 1980, **102**, 6611-6612.

19. Synthesized as a colorless oil (525.3 mg, 99%) by $LiAlH_4$ reduction of methyl (*E*/*Z*)-2-(2-(methoxymethylene)cyclopentyl)acetate. Spectroscopic data identical to the reported in literature.

20. D. A. Frey, S. H. Krishna Reddy and K. D. Moeller, *J. Org. Chem.*, 1999, **64**, 2805-2813.

21. (a) Synthesized as a colorless oil (762.3 mg, 94%) by $LiAlH_4$ reduction of methyl 4,4-dimethoxybutyrate as described in literature. Spectroscopic data identical to the reported in literature; (b) J. R. Hazen, *J. Org. Chem.*, 1970, **35**, 973-978; (c) R. W. Hoffmann and I. Münster, *Liebigs Annalen*, 1997, **1997**, 1143-1150.

22. (a) F. F. Blicke and B. A. Brown, *J. Org. Chem.*, 1961, **26**, 3685-3691; (b) H. M. Deutsch, X. Ye, Q. Shi, Z. Liu and M. M. Schweri, *European Journal of Medicinal Chemistry*, 2001, **36**, 303-311.

23. A. Padwa, S. Nahm and E. Sato, *J. Org. Chem.*, 1978, **43**, 1664-1671.

24. J.-G. Roveda, C. Clavette, A. D. Hunt, S. I. Gorelsky, C. J. Whipp and A. M. Beauchemin, *J. Am. Chem. Soc.*, 2009, **131**, 8740-8741.

25. (a) Spectroscopic data identical to the reported in literature; (b) *US Pat.,* US 2006/0205955 A1, 2006.

26. T. Zheng, R. S. Narayan, J. M. Schomaker and B. Borhan, *J. Am. Chem. Soc.*, 2005, **127**, 6946-6947.

27. (a) Synthesized as a colorless oil (4.20 g, 99%) by $LiAlH_4$ reduction of (*E*)-5-phenylpent-4-enoic acid. Spectroscopic data identical to the reported in literature; (b) M. Abul Hashem and P. Weyerstahl, *Tetrahedron*, 1984, **40**, 2003-2009; (c) S. E. Denmark and M. T. Burk, *Org. Lett.*, 2012, **14**, 256-259.

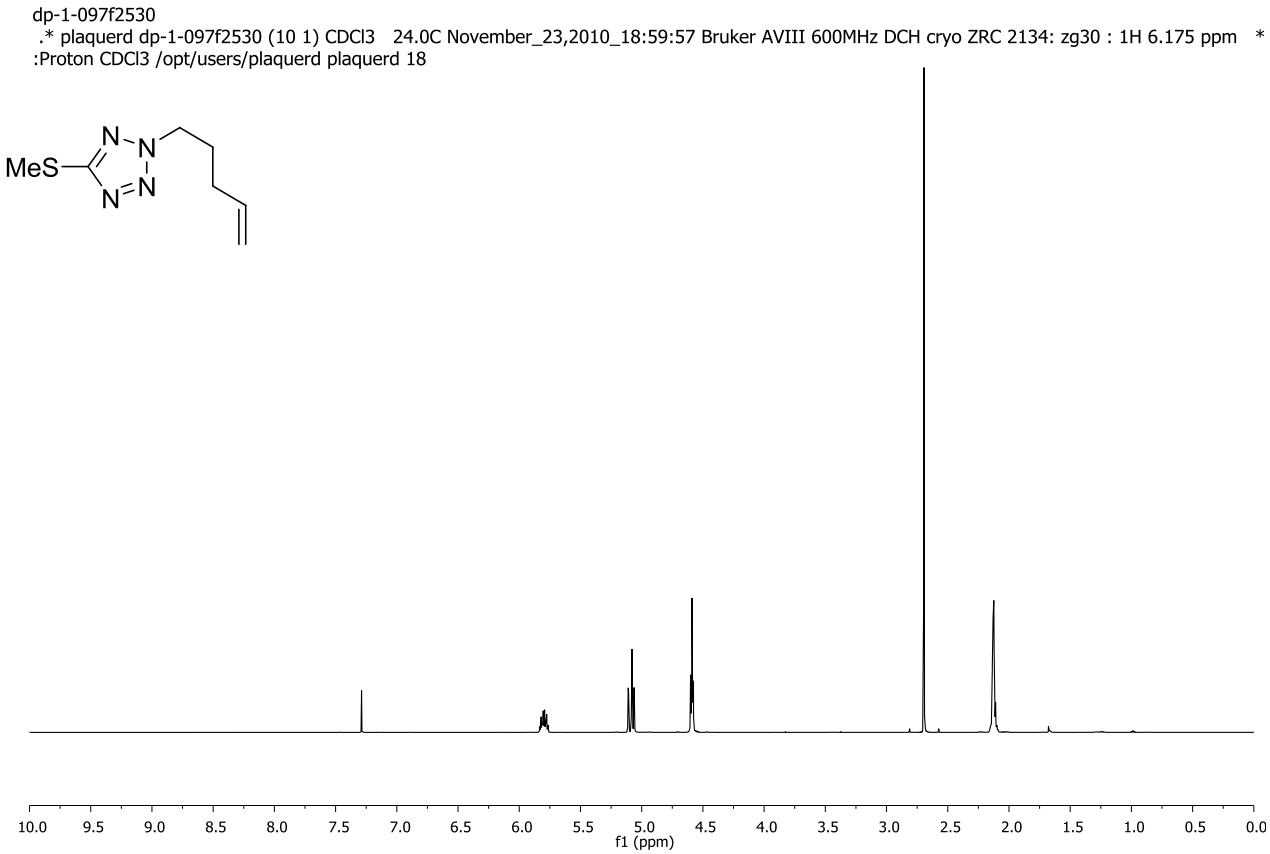
28. G. Liu and S. S. Stahl, *J. Am. Chem. Soc.*, 2007, **129**, 6328-6335.

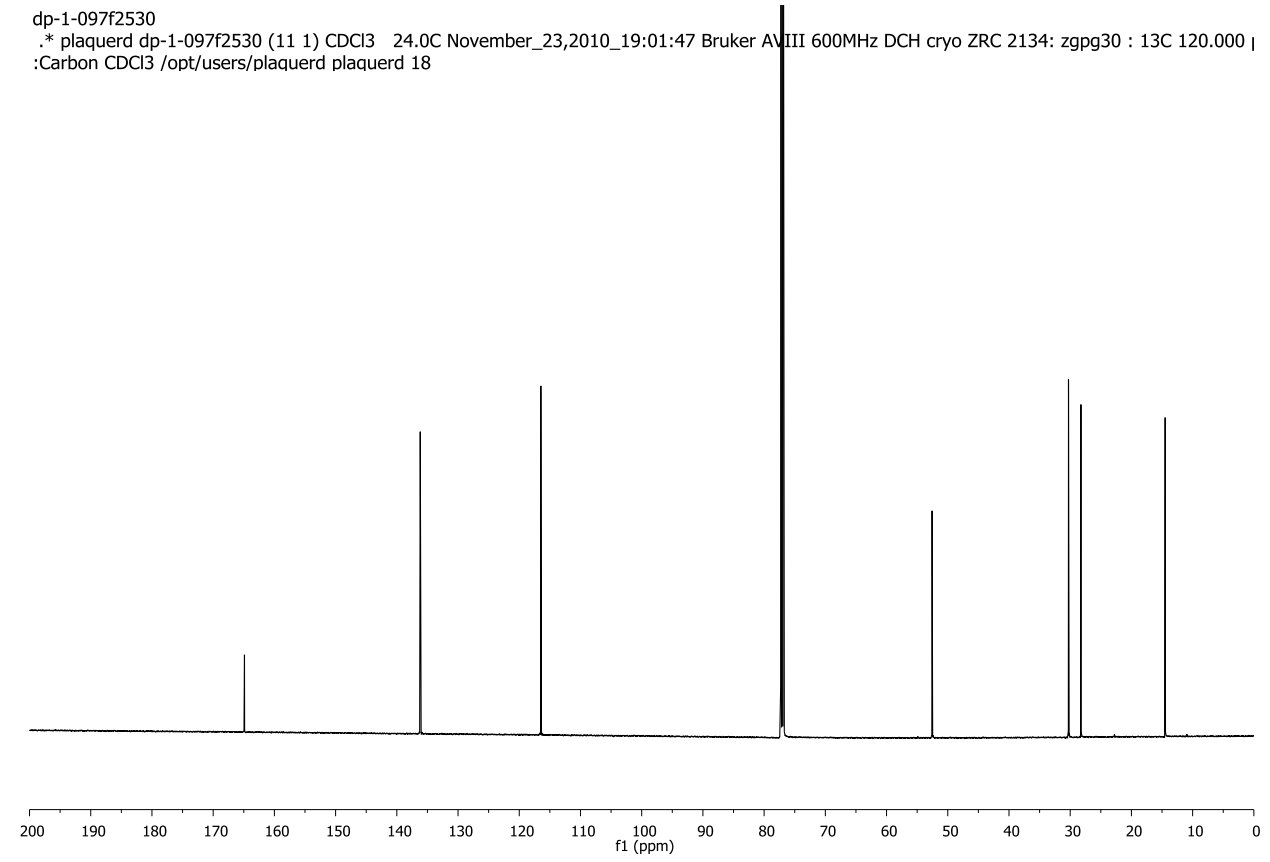
29. S. A. Adesanya, R. Nia, C. Fontaine and M. Païs, *Phytochemistry*, 1994, **35**, 1053 -1055.

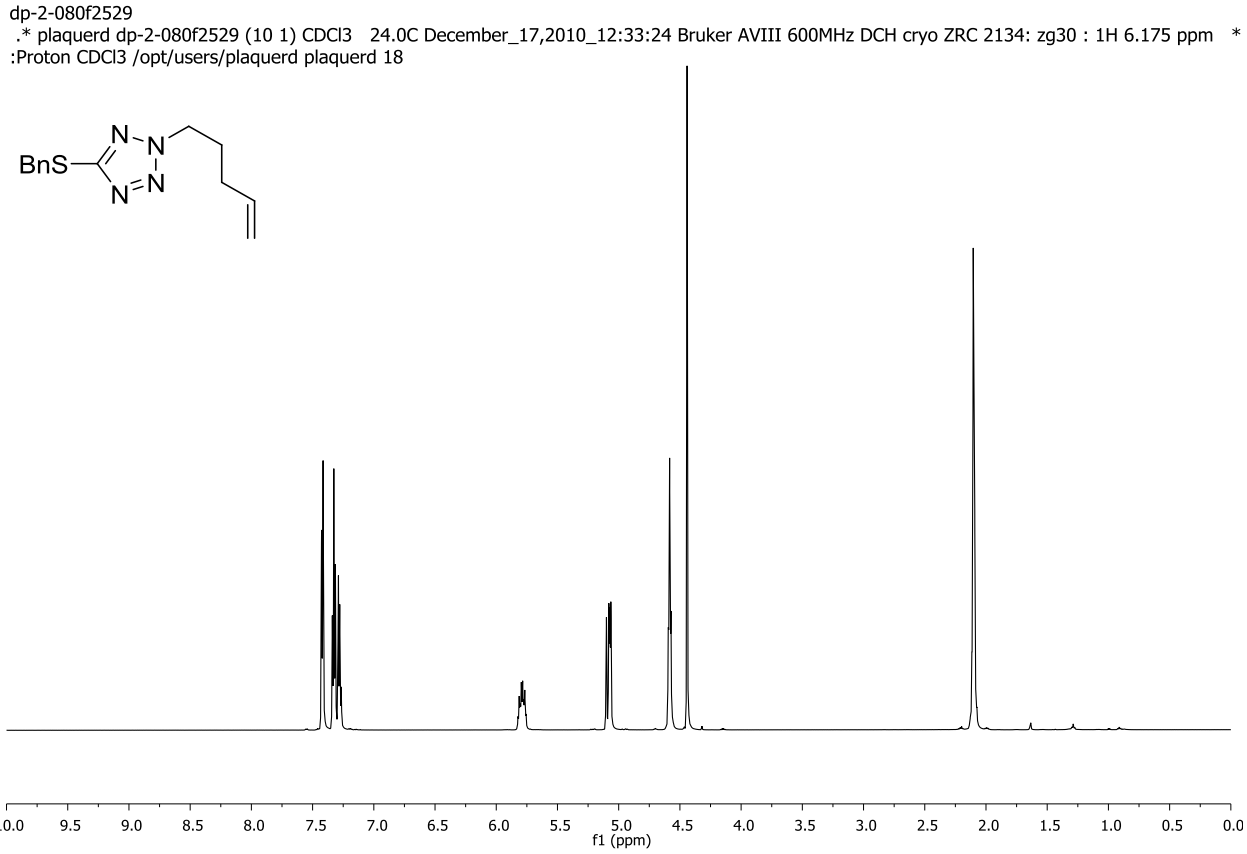
30. M. Pangerl, C. C. Hughes and D. Trauner, *Tetrahedron*, 2010, **66**, 6626-6631.

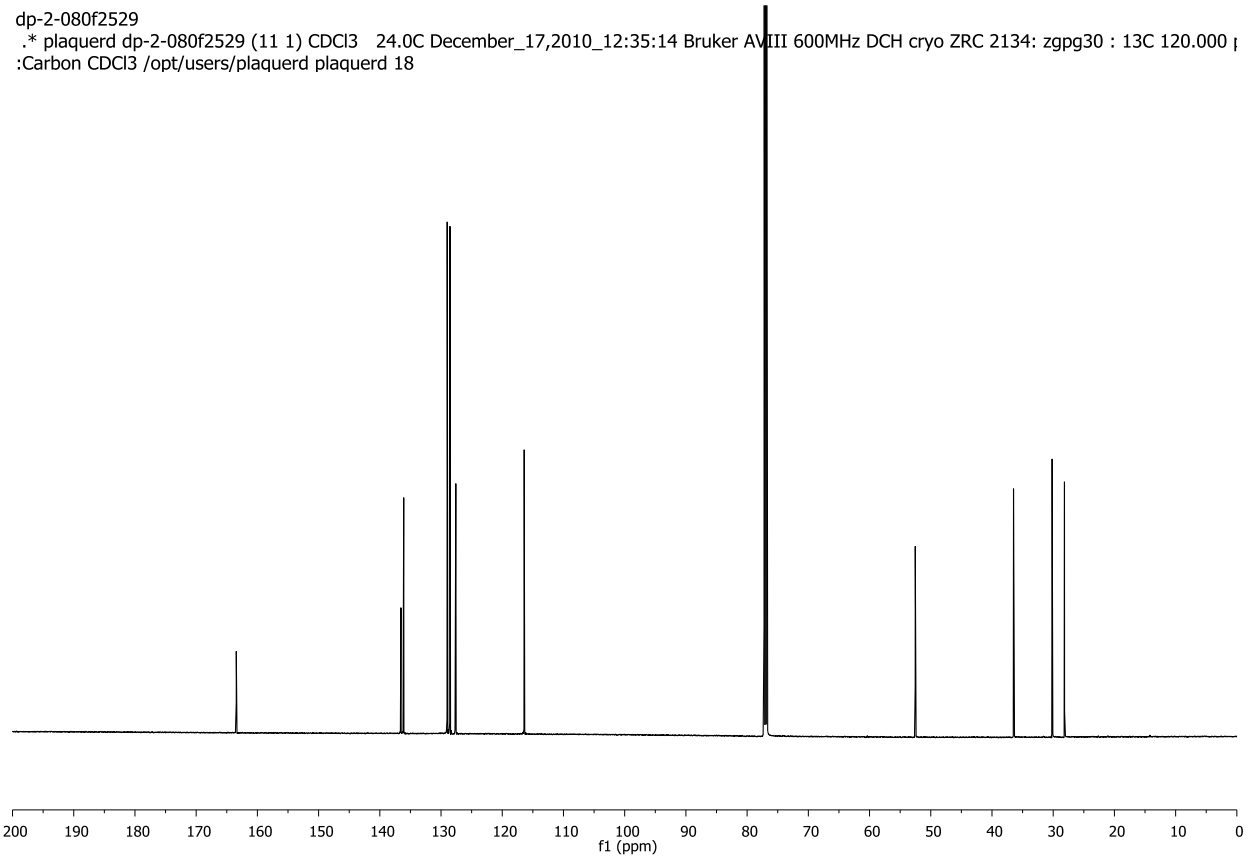
31. S. Majumder, K. R. Gipson, R. J. Staples and A. L. Odom, *Adv. Synth. Catal.*, 2009, **351**, 2013-2023.

L. ^{1}H and ^{13}C-NMR Spectra.

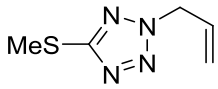




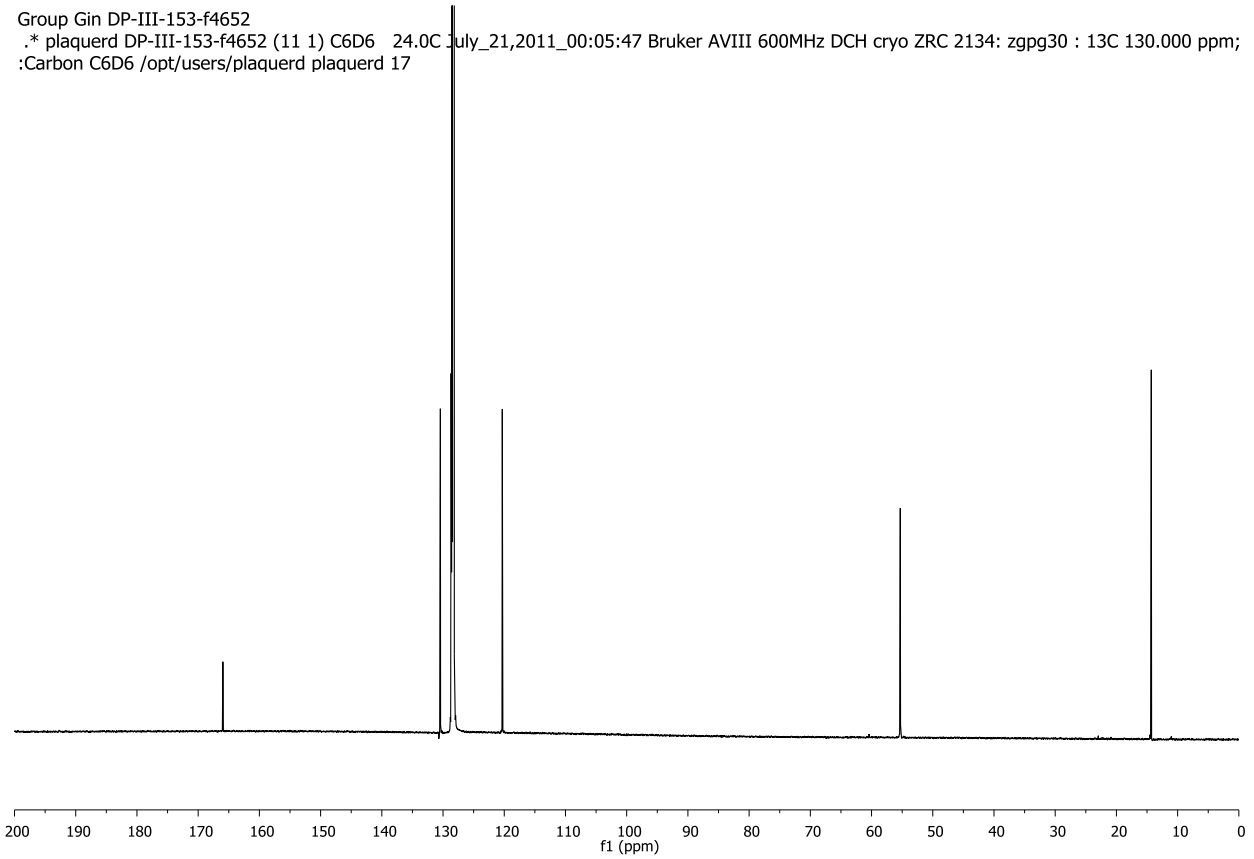

dp-2-080f2529
.* plaquerd dp-2-080f2529 (10 1) CDCl3 24.0C December_17,2010_12:33:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton CDCl3 /opt/users/plaquerd plaquerd 18
BnS
N
N
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


dp-2-080f2529
.* plaquerd dp-2-080f2529 (11 1) CDCl3 24.0C December_17,2010_12:35:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

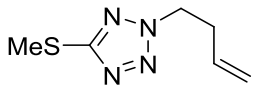
Group Gin DP-III-153-f4652
.* plaquerd DP-III-153-f4652 (10 1) C6D6 24.0C July_21,2011_00:03:57 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 17



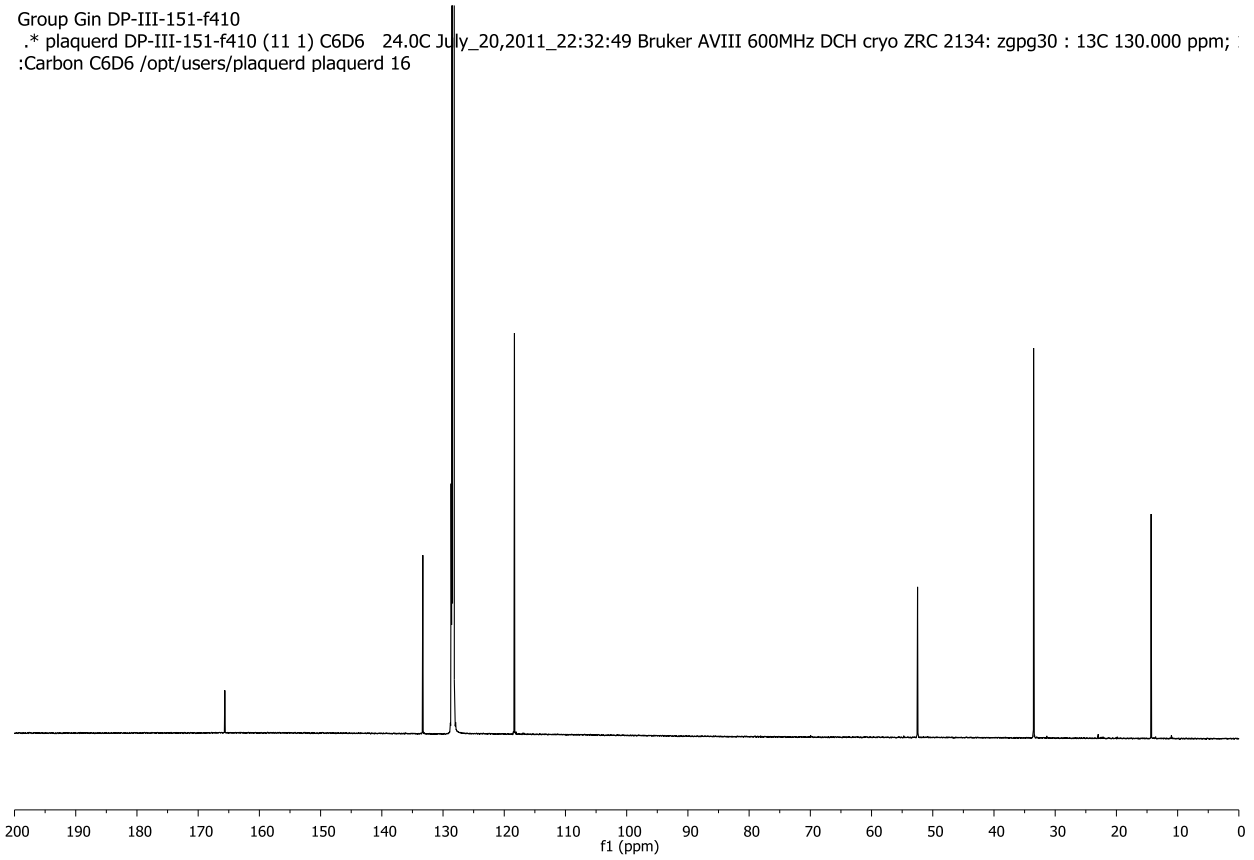
Group Gin DP-III-153-f4652
.* plaquerd DP-III-153-f4652 (11 1) C6D6 24.0C July_21,2011_00:05:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 17



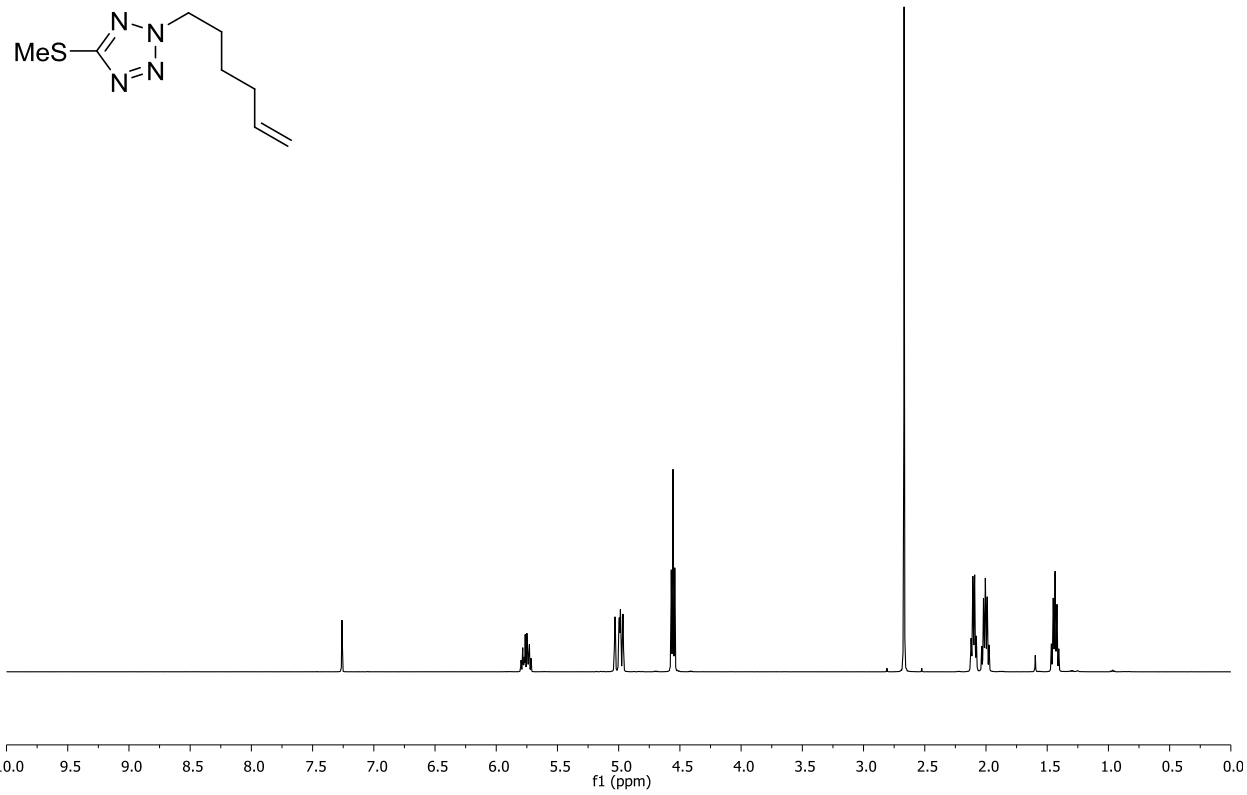
Group Gin DP-III-151-f410
.* plaquerd DP-III-151-f410 (10 1) C6D6 24.0C July_20,2011_22:30:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 16



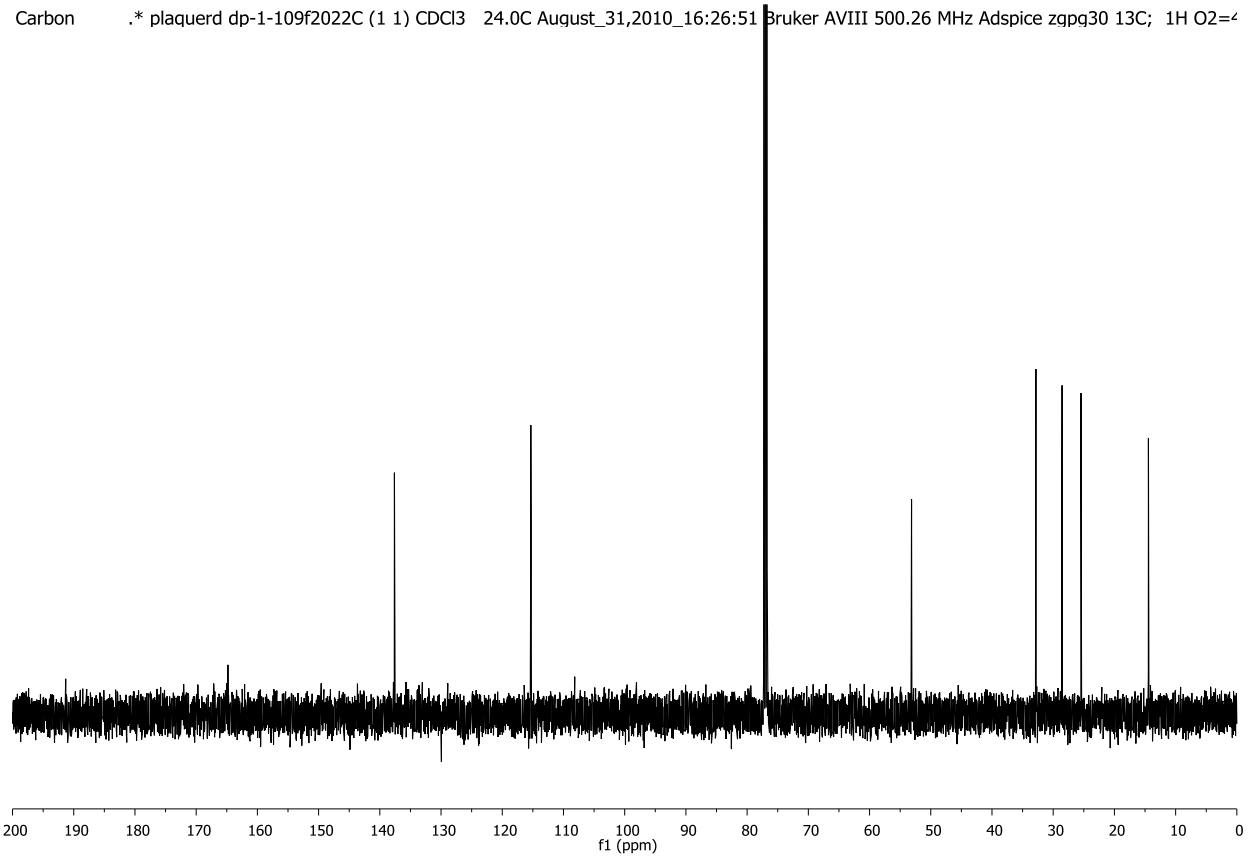
Group Gin DP-III-151-f410
.* plaquerd DP-III-151-f410 (11 1) C6D6 24.0C July_20,2011_22:32:49 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 16

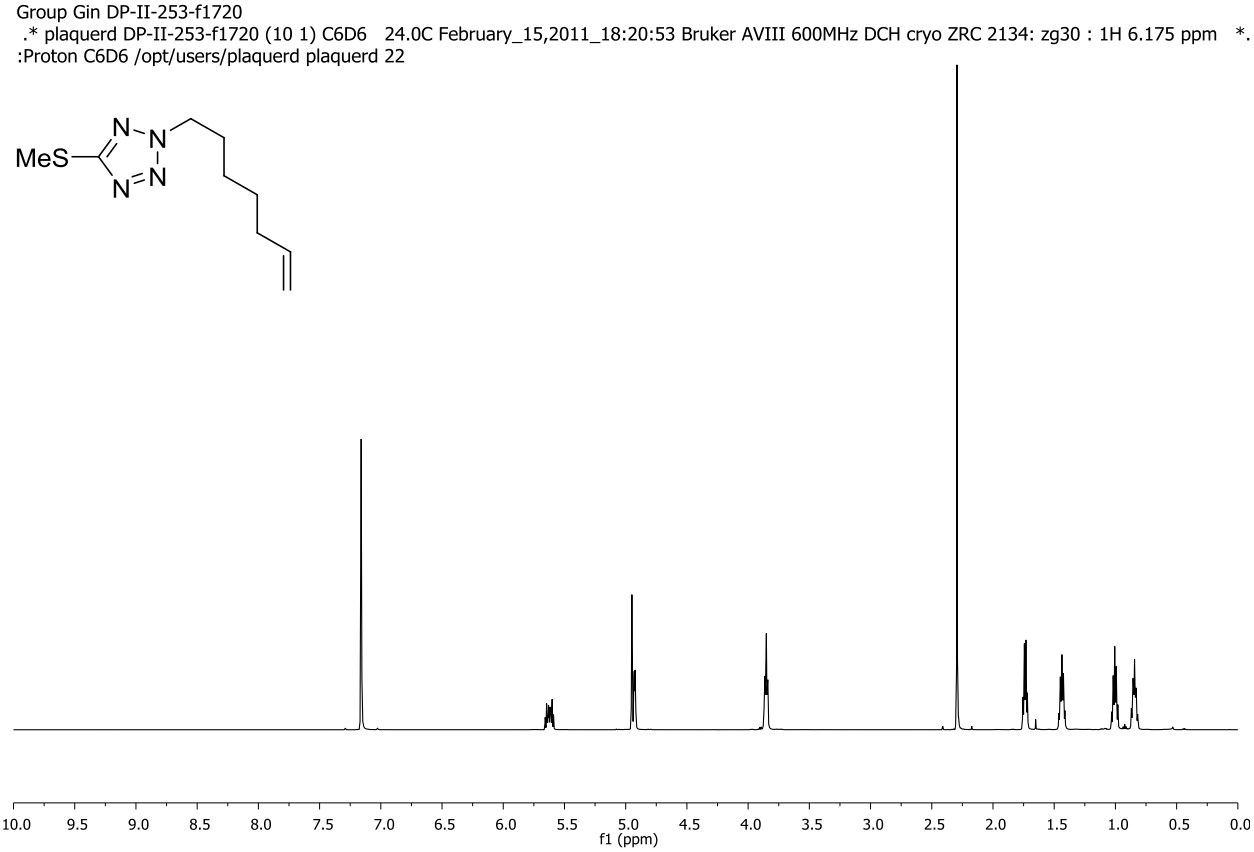


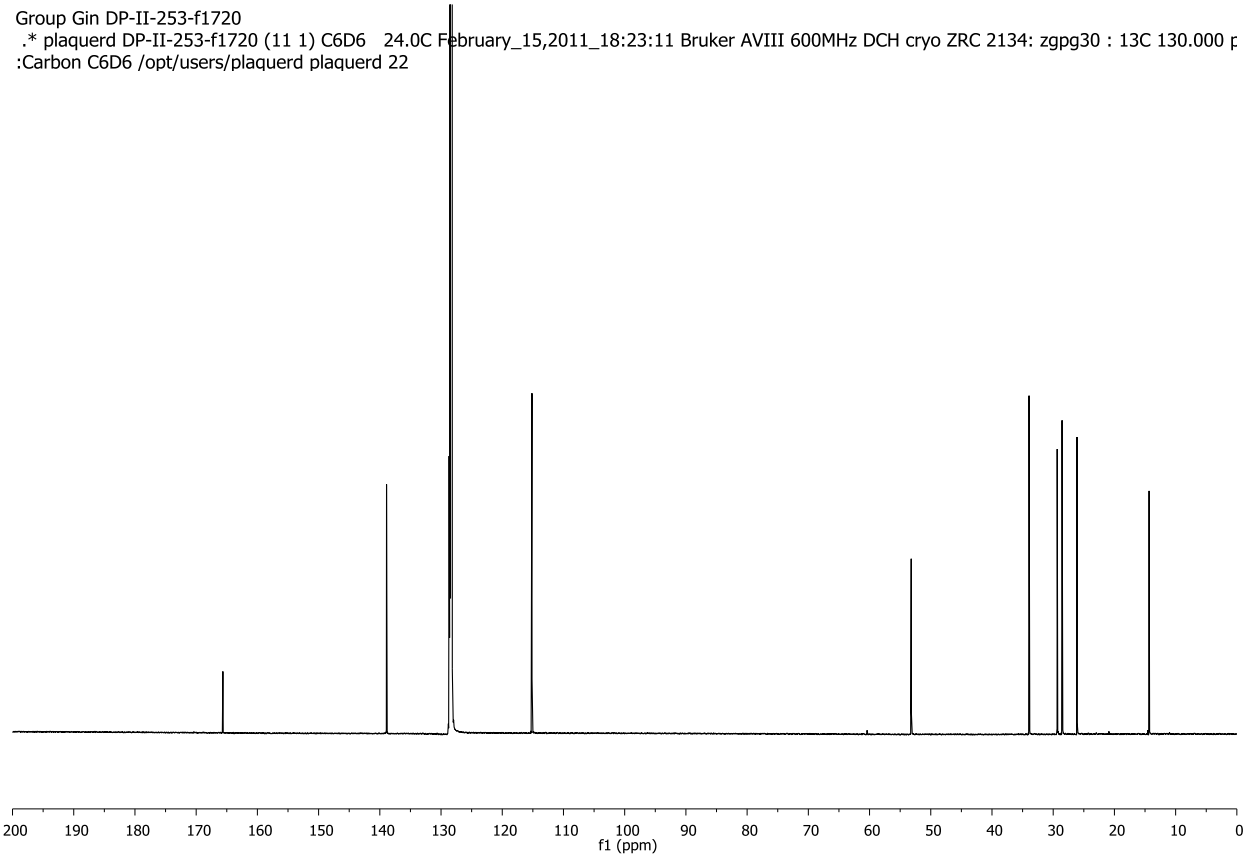
Proton .* plaquerd dp-1-109f2022 (1 1) CDCl3 24.0C August_31,2010_16:24:07 Bruker AVIII 500.26 MHz Adspice zg30 1H *.

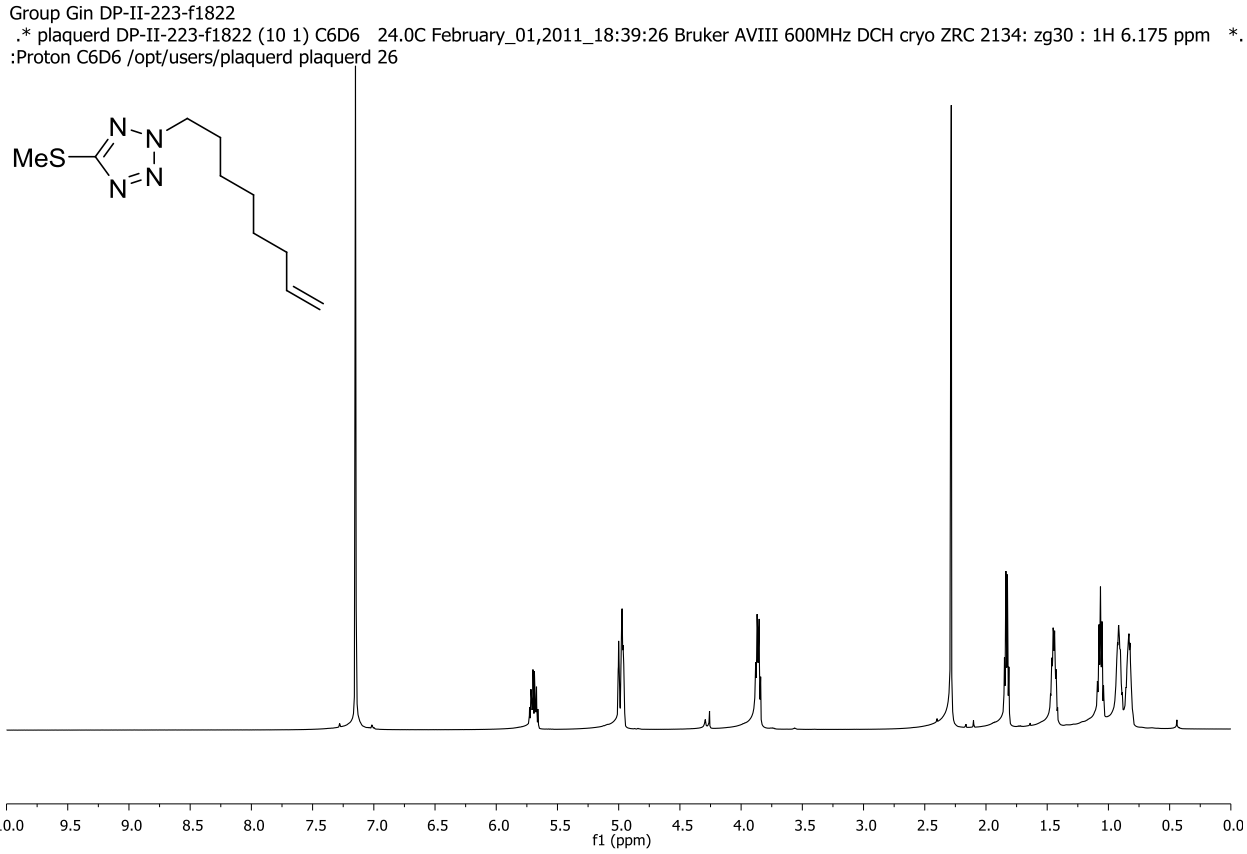


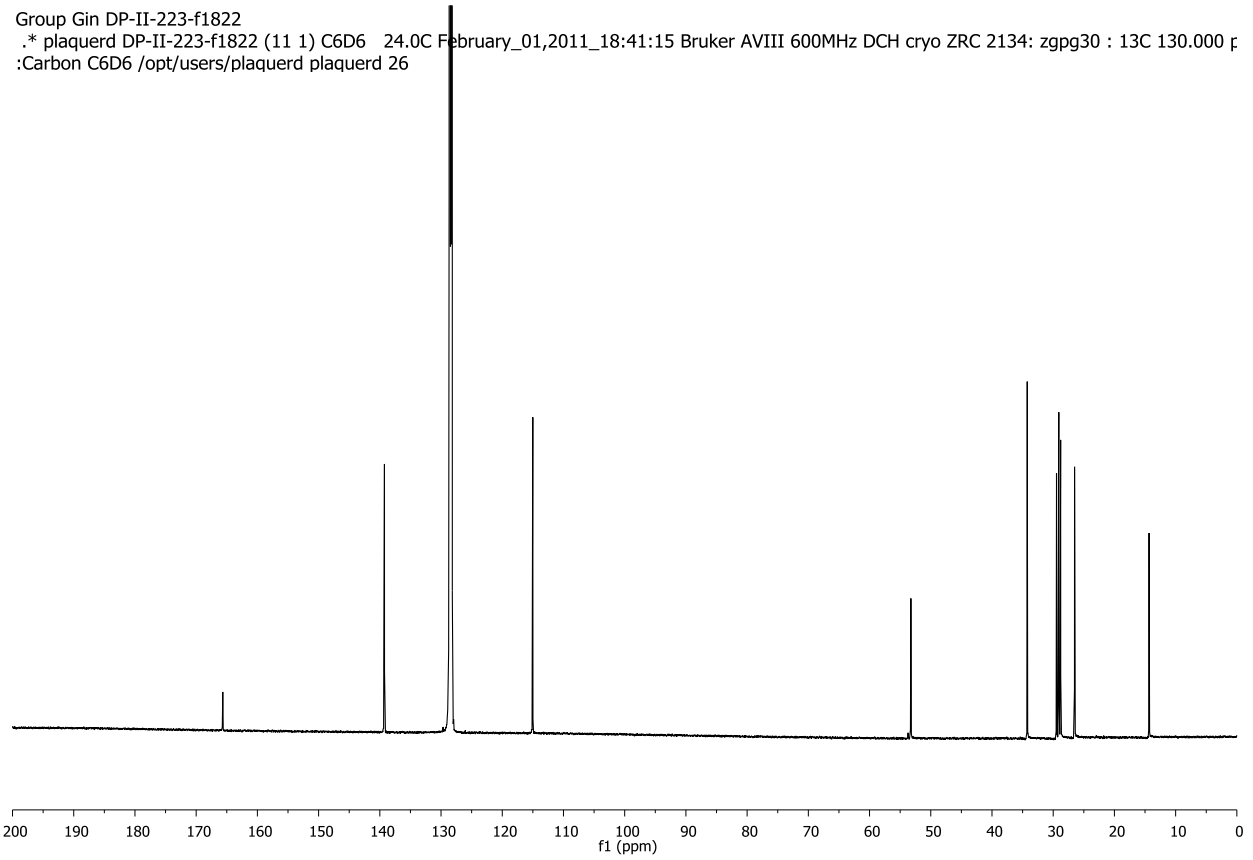
Carbon .* plaquerd dp-1-109f2022C (1 1) CDCl3 24.0C August_31,2010_16:26:51 Bruker AVIII 500.26 MHz Adspice zgpg30 13C; 1H O2=4



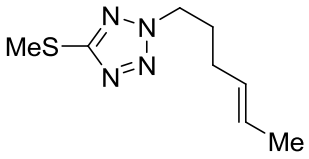

Group Gin DP-II-253-f1720
.* plaquerd DP-II-253-f1720 (10 1) C6D6 24.0C February_15,2011_18:20:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 22
MeS
N
N
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Group Gin DP-II-253-f1720
.* plaquerd DP-II-253-f1720 (11 1) C6D6 24.0C February_15,2011_18:23:11 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Group Gin DP-II-223-f1822
.* plaquerd DP-II-223-f1822 (10 1) C6D6 24.0C February_01,2011_18:39:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 26
MeS
N
N
N
N
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
f1 (ppm)

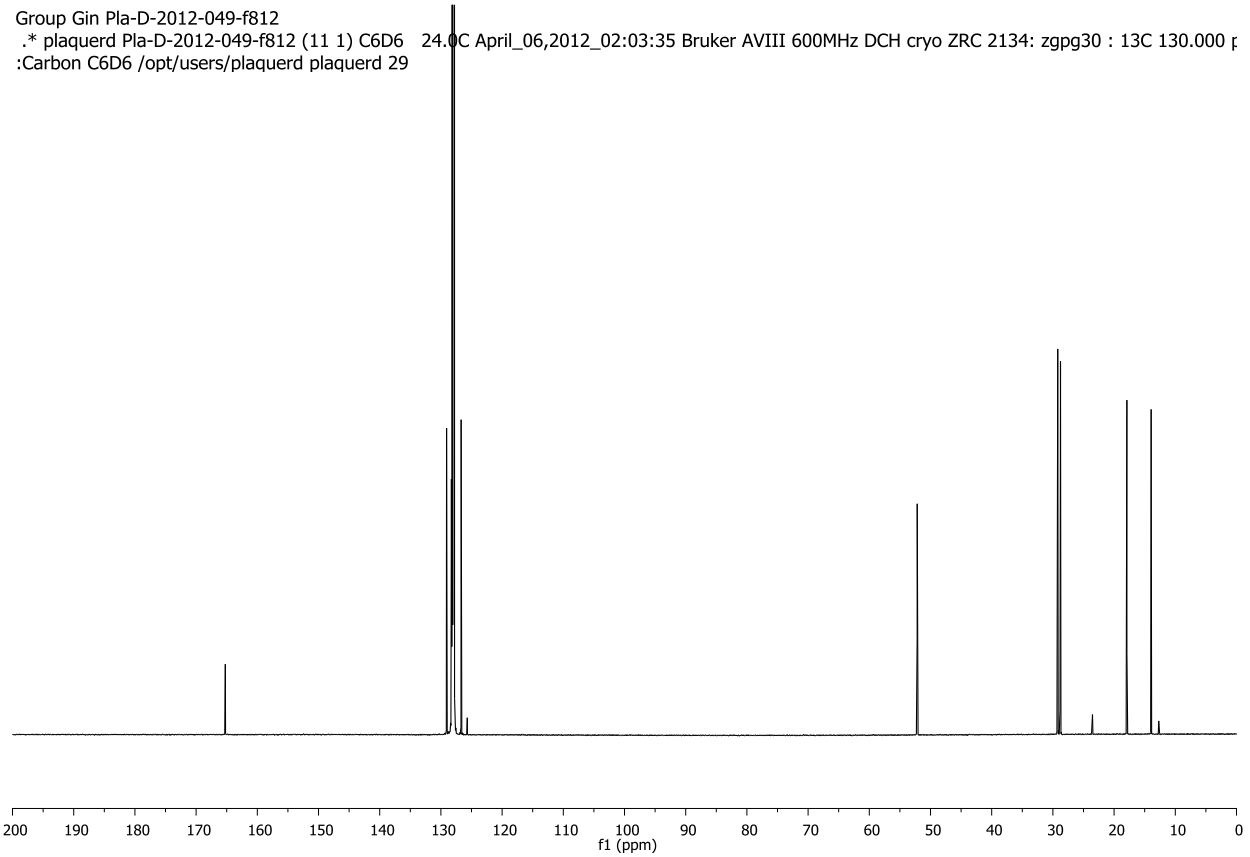

Group Gin DP-II-223-f1822
.* plaquerd DP-II-223-f1822 (11 1) C6D6 24.0C February_01,2011_18:41:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Group Gin Pla-D-2012-049-f812
.* plaquerd Pla-D-2012-049-f812 (10 1) C6D6 24.0C April_06,2012_02:01:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 29

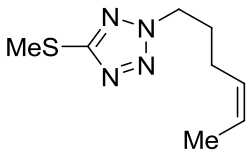


(96:4 *E*/*Z*)

Group Gin Pla-D-2012-049-f812
.* plaquerd Pla-D-2012-049-f812 (11 1) C6D6 24.0C April_06,2012_02:03:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 29

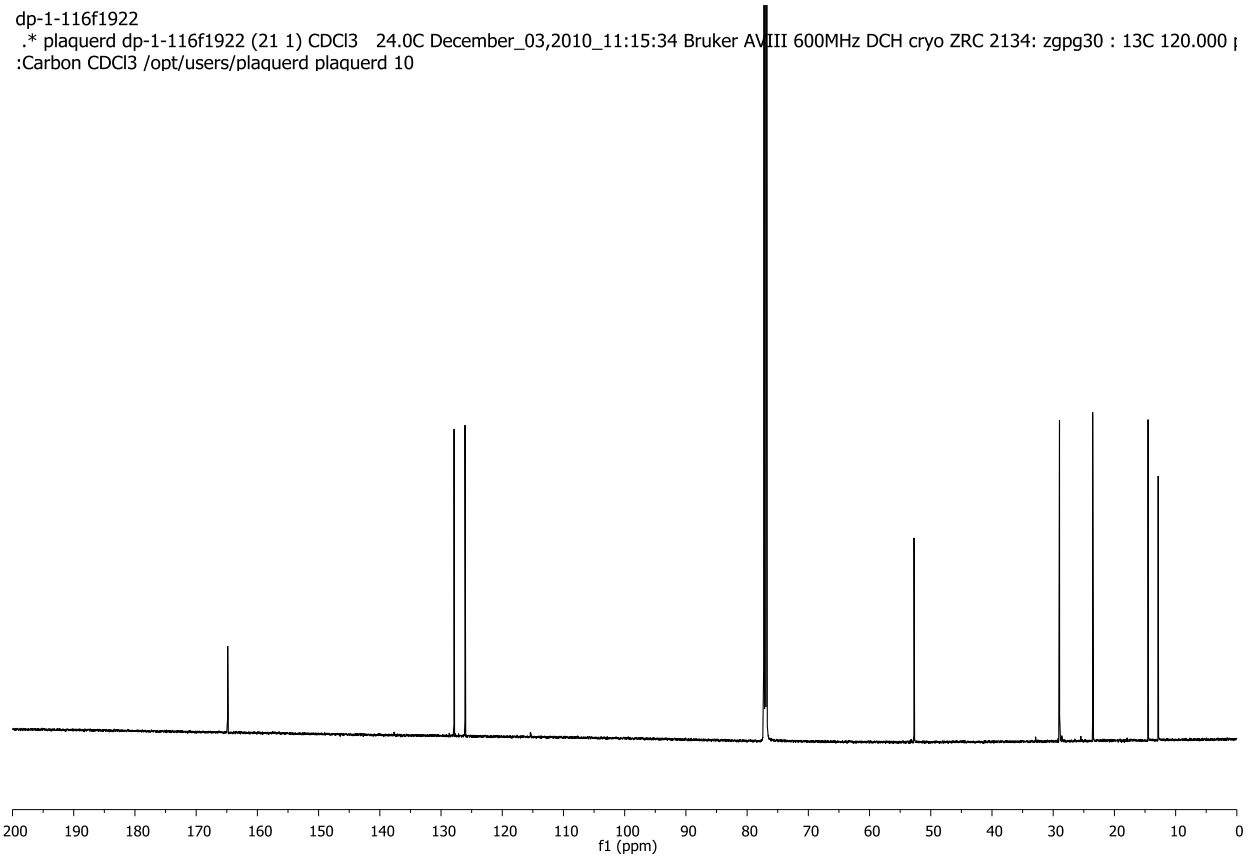


dp-1-116f1922
.* plaquerd dp-1-116f1922 (20 1) CDCl3 24.0C December_03,2010_11:13:38 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 10

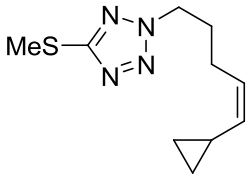


(>99:1 *Z*/*E*)

dp-1-116f1922
.* plaquerd dp-1-116f1922 (21 1) CDCl3 24.0C December_03,2010_11:15:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 I
:Carbon CDCl3 /opt/users/plaquerd plaquerd 10

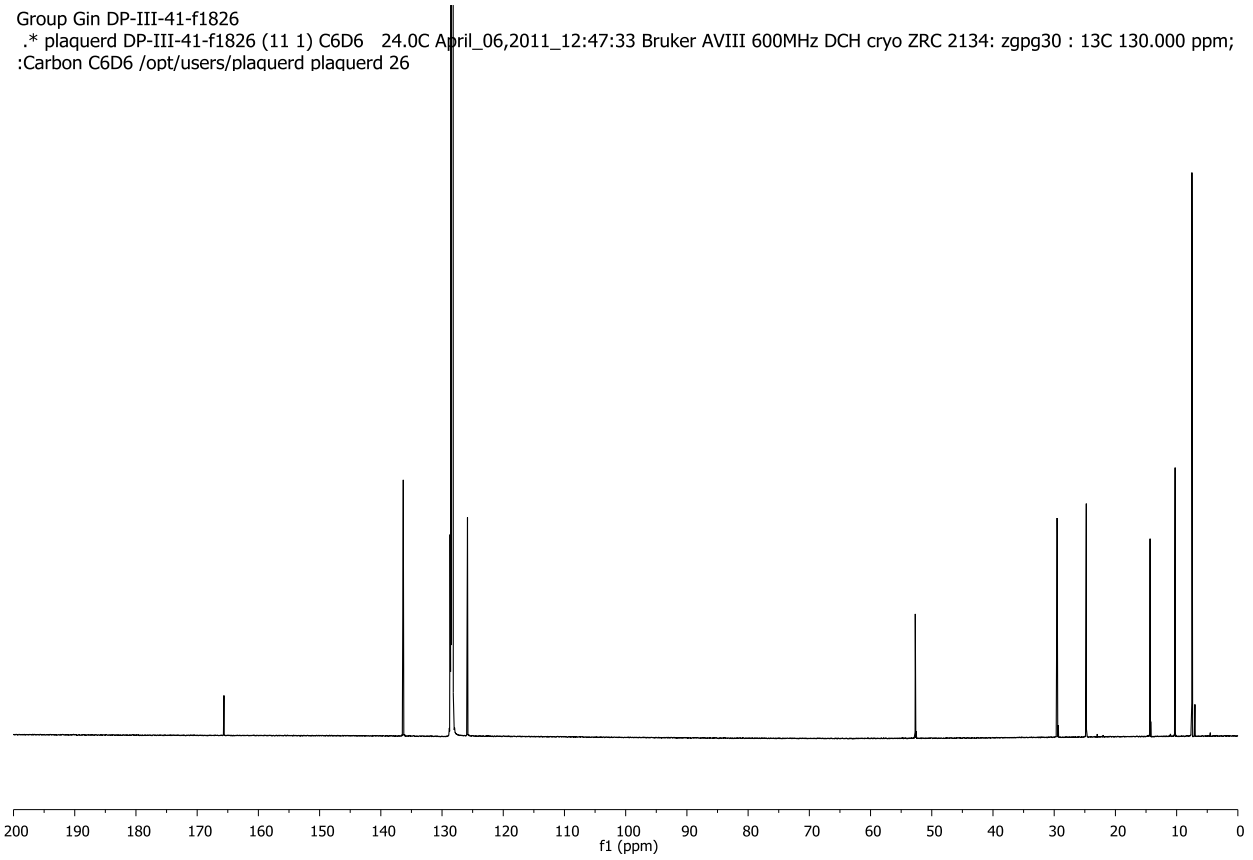


Group Gin DP-III-41-f1826
.* plaquerd DP-III-41-f1826 (10 1) C6D6 24.0C April_06,2011_12:45:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 26

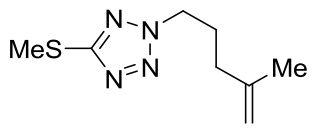


(94:6 *Z*/*E*)

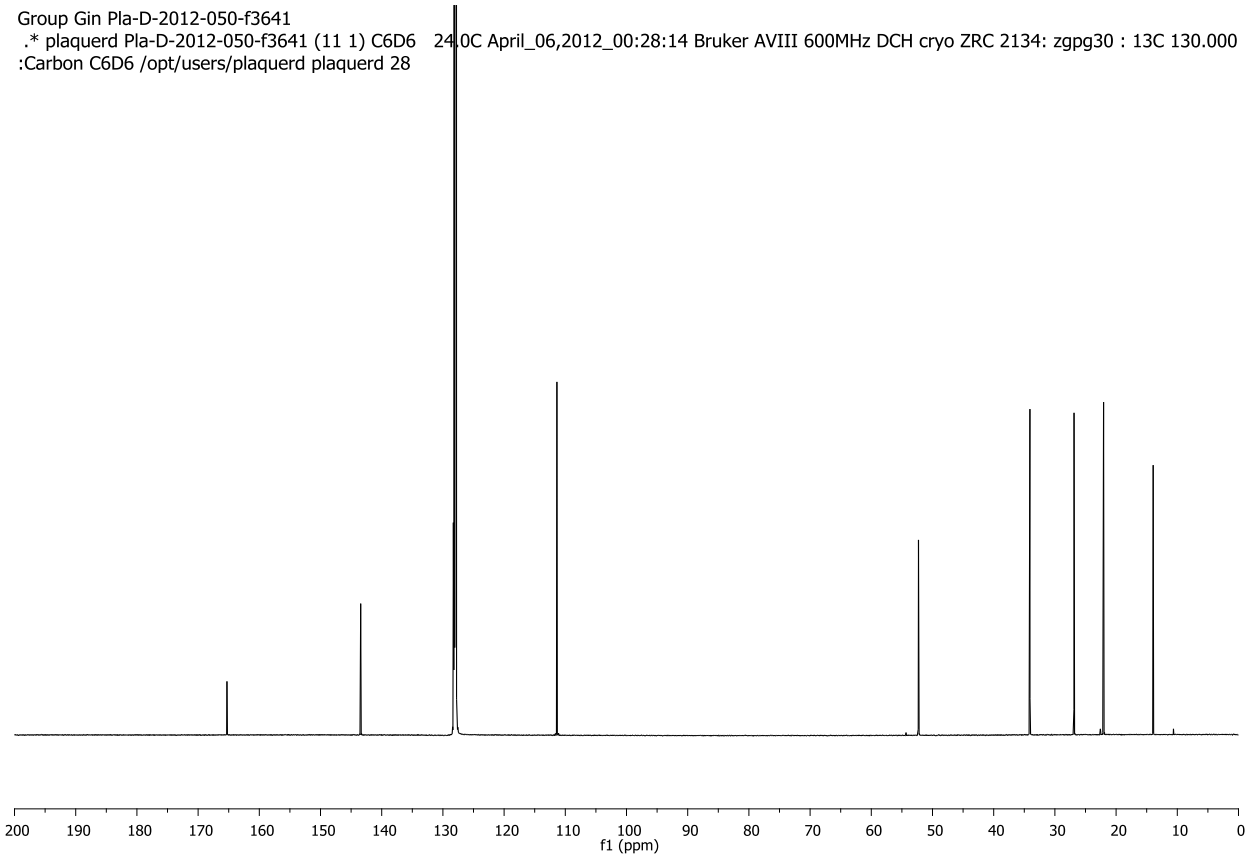
Group Gin DP-III-41-f1826
.* plaquerd DP-III-41-f1826 (11 1) C6D6 24.0C April_06,2011_12:47:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 26

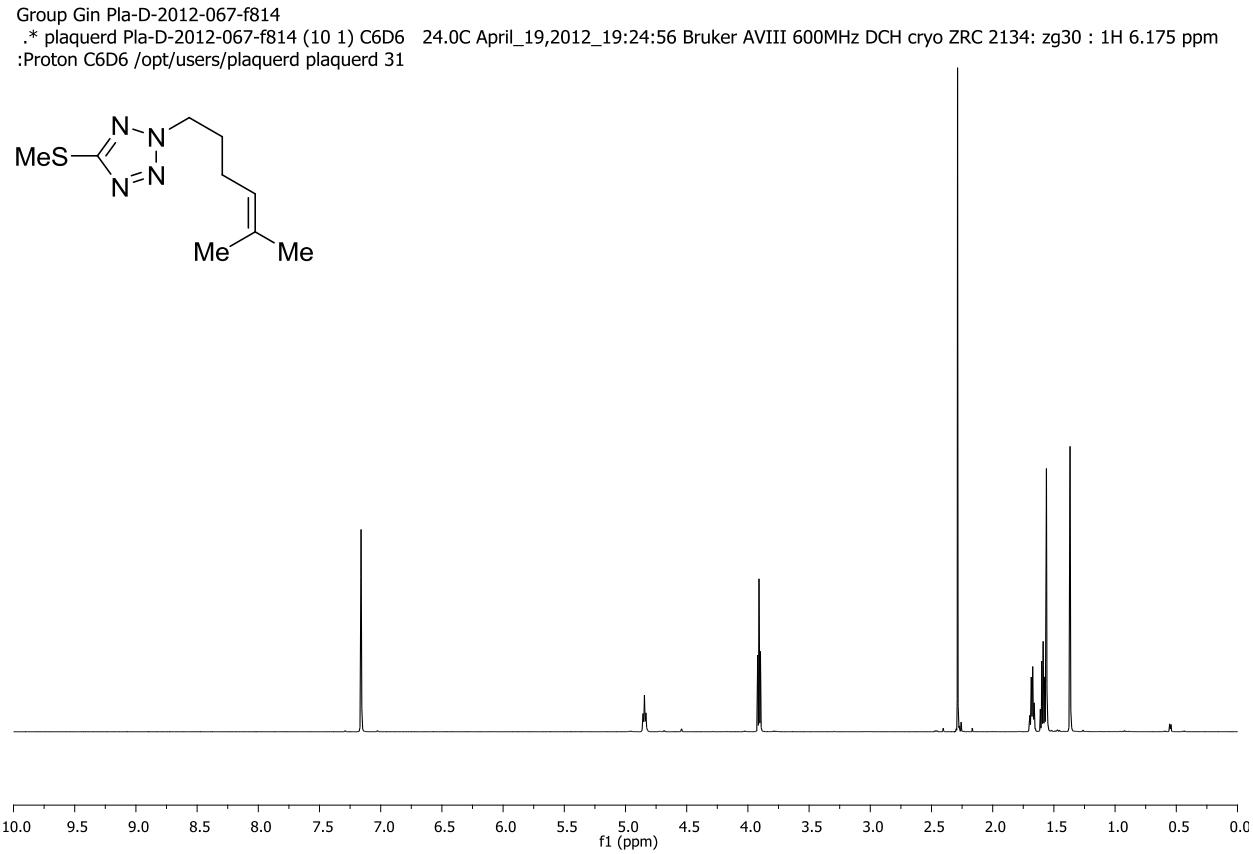


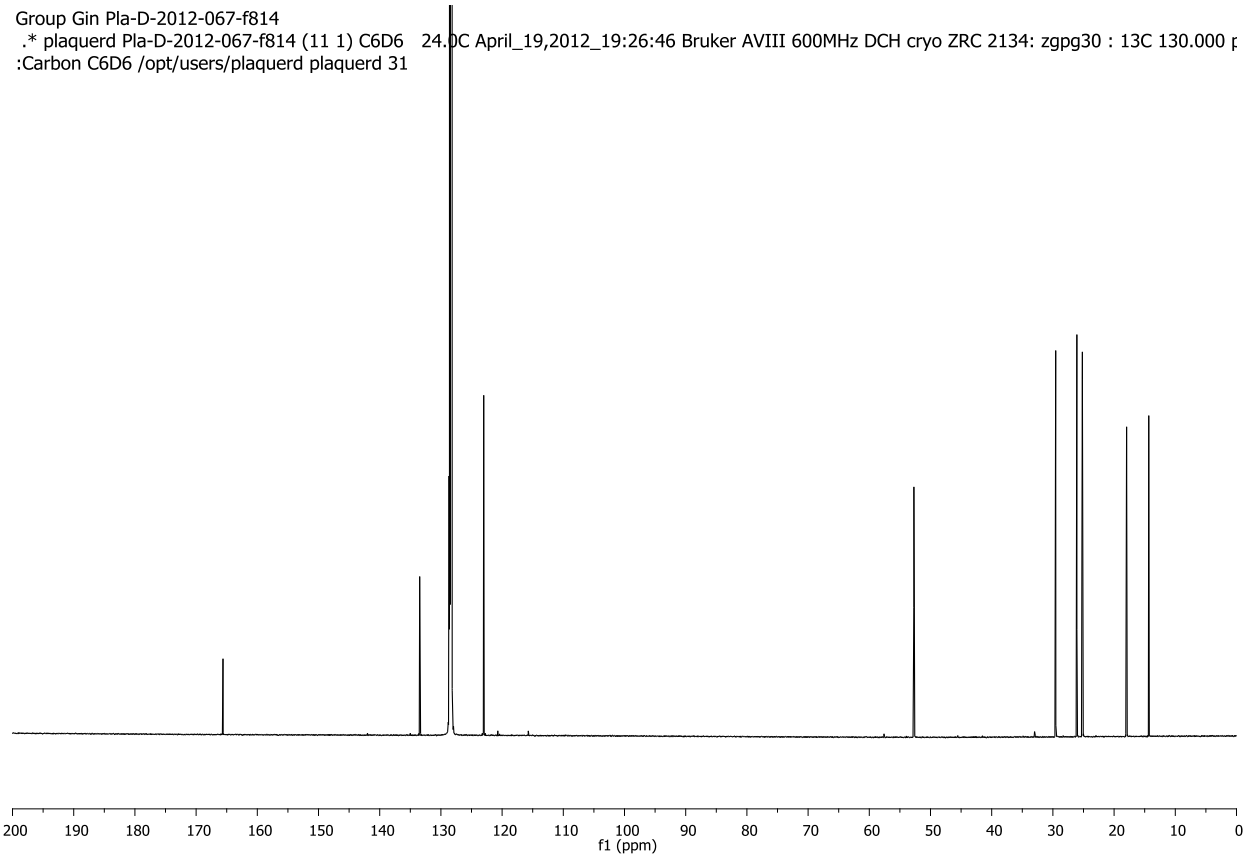
Group Gin Pla-D-2012-050-f3641
.* plaquerd Pla-D-2012-050-f3641 (10 1) C6D6 24.0C April_06,2012_00:26:25 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 28

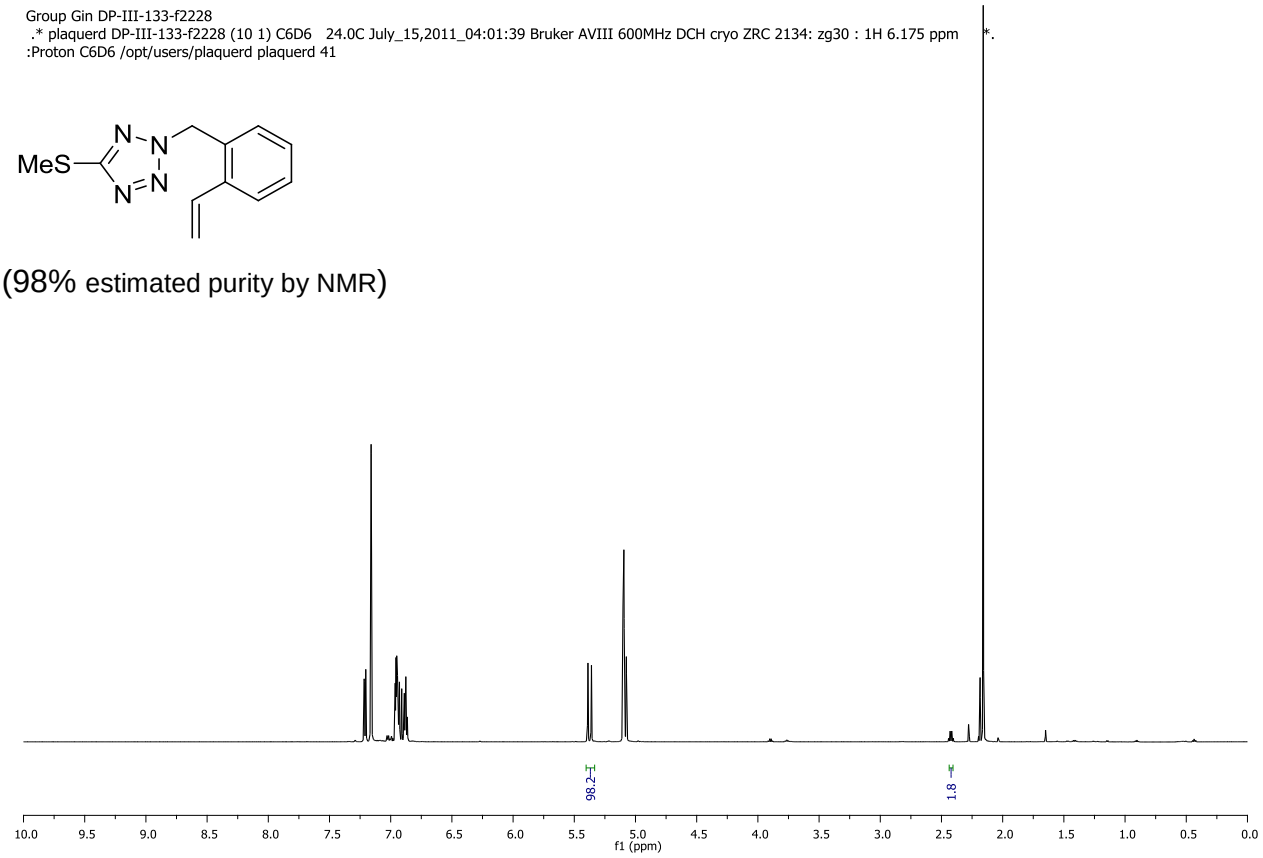


Group Gin Pla-D-2012-050-f3641
.* plaquerd Pla-D-2012-050-f3641 (11 1) C6D6 24.0C April_06,2012_00:28:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 28

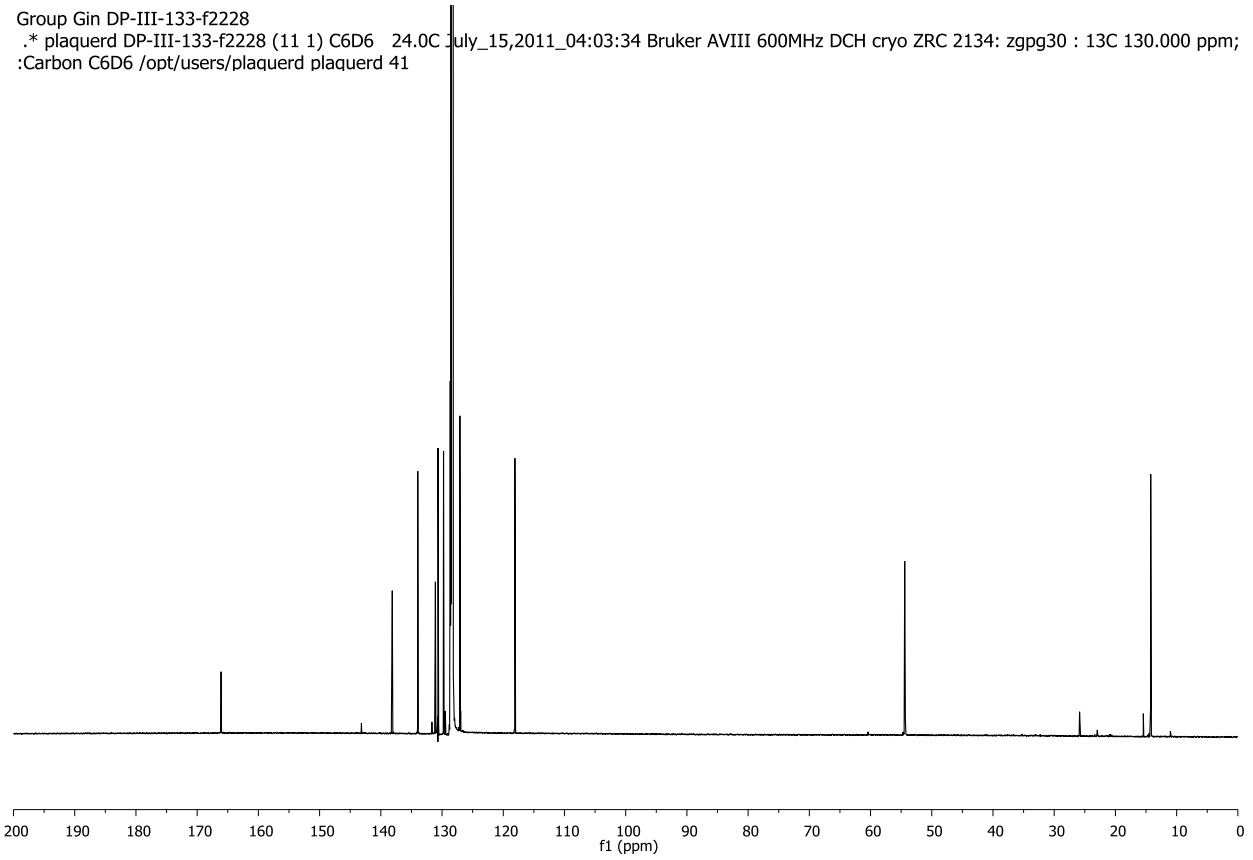


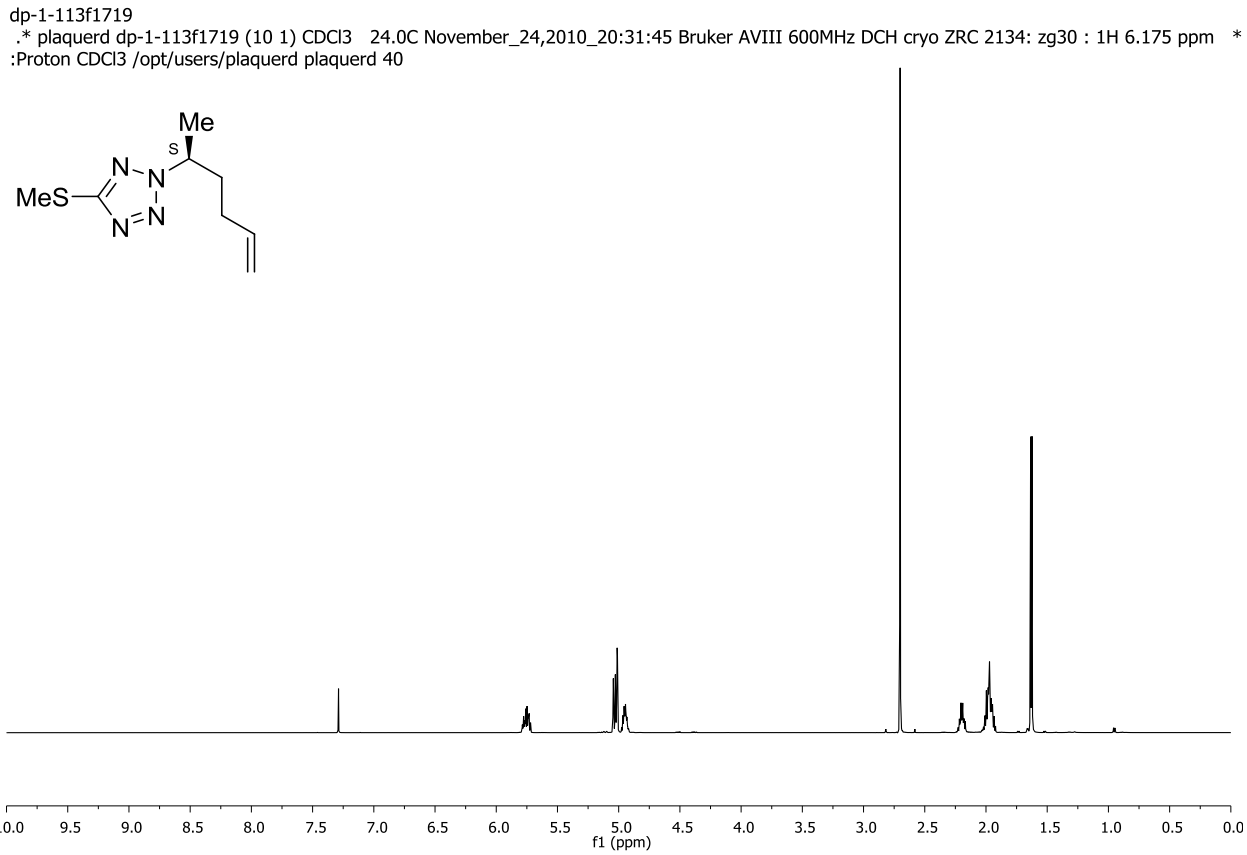

Group Gin Pla-D-2012-067-f814
.* plaquerd Pla-D-2012-067-f814 (10 1) C6D6 24.0C April_19,2012_19:24:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 31
MeS
N
N
N
N
Me
Me
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

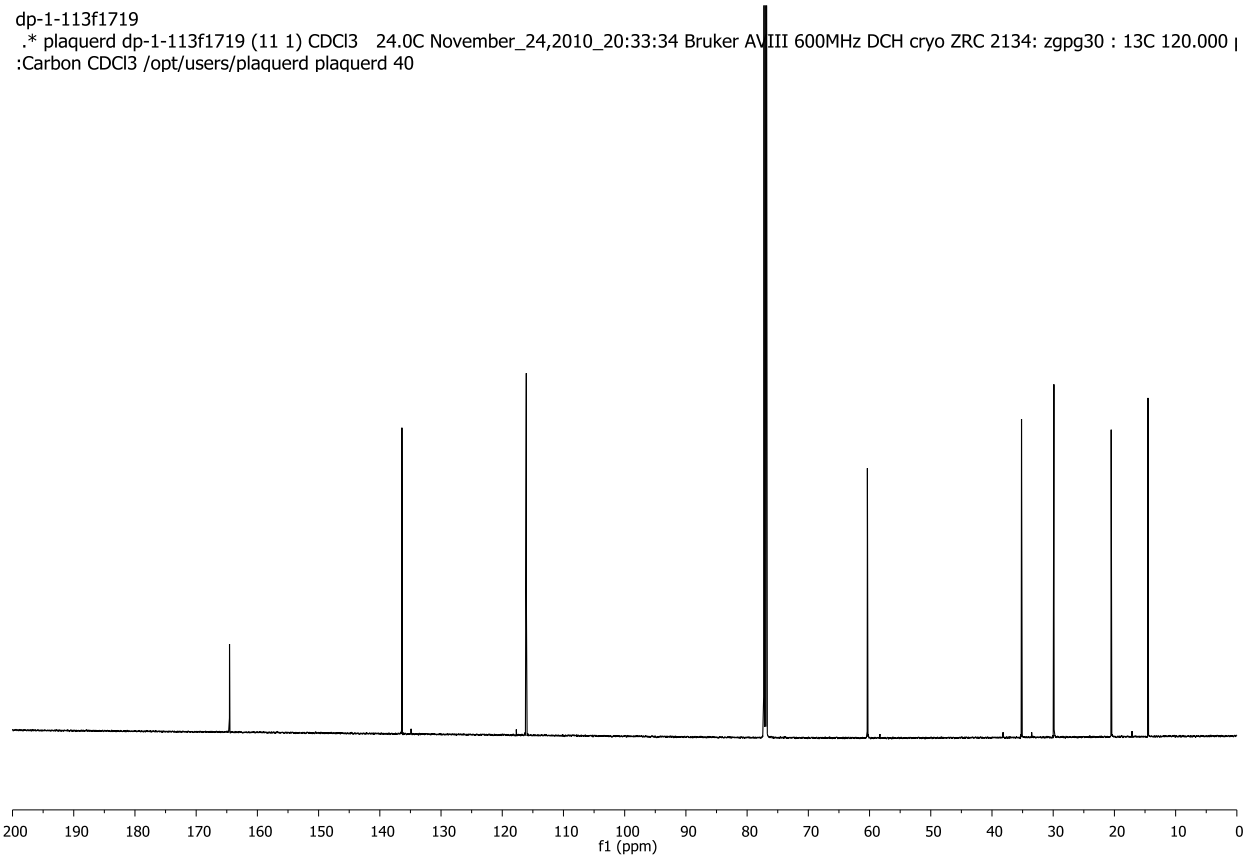

Group Gin Pla-D-2012-067-f814
.* plaquerd Pla-D-2012-067-f814 (11 1) C6D6 24.0C April_19,2012_19:26:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



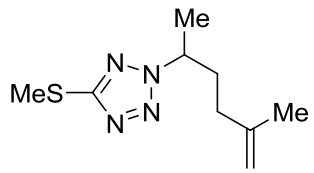
(98% estimated purity by NMR)



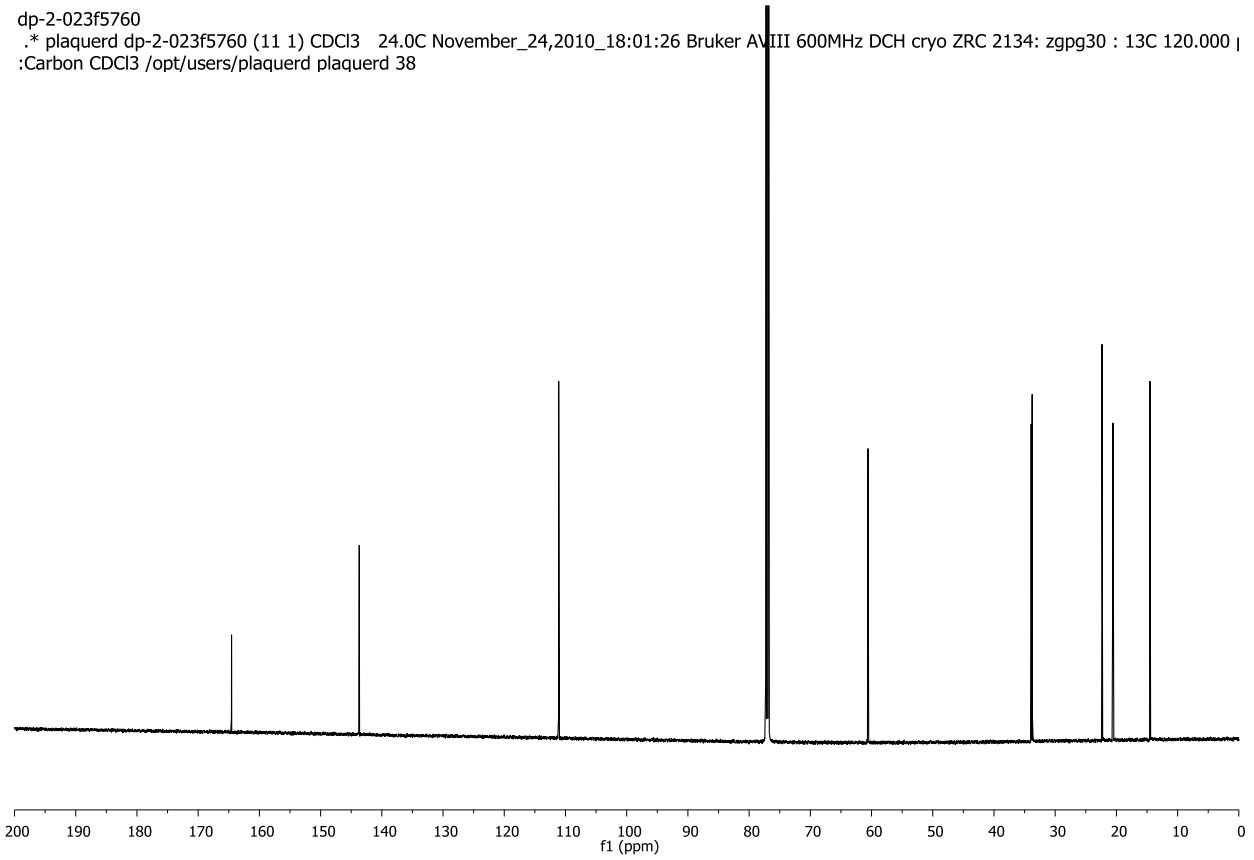

dp-1-113f1719
.* plaquerd dp-1-113f1719 (10 1) CDCl3 24.0C November_24,2010_20:31:45 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton CDCl3 /opt/users/plaquerd plaquerd 40
Me
S
N
N
N
N
MeS
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

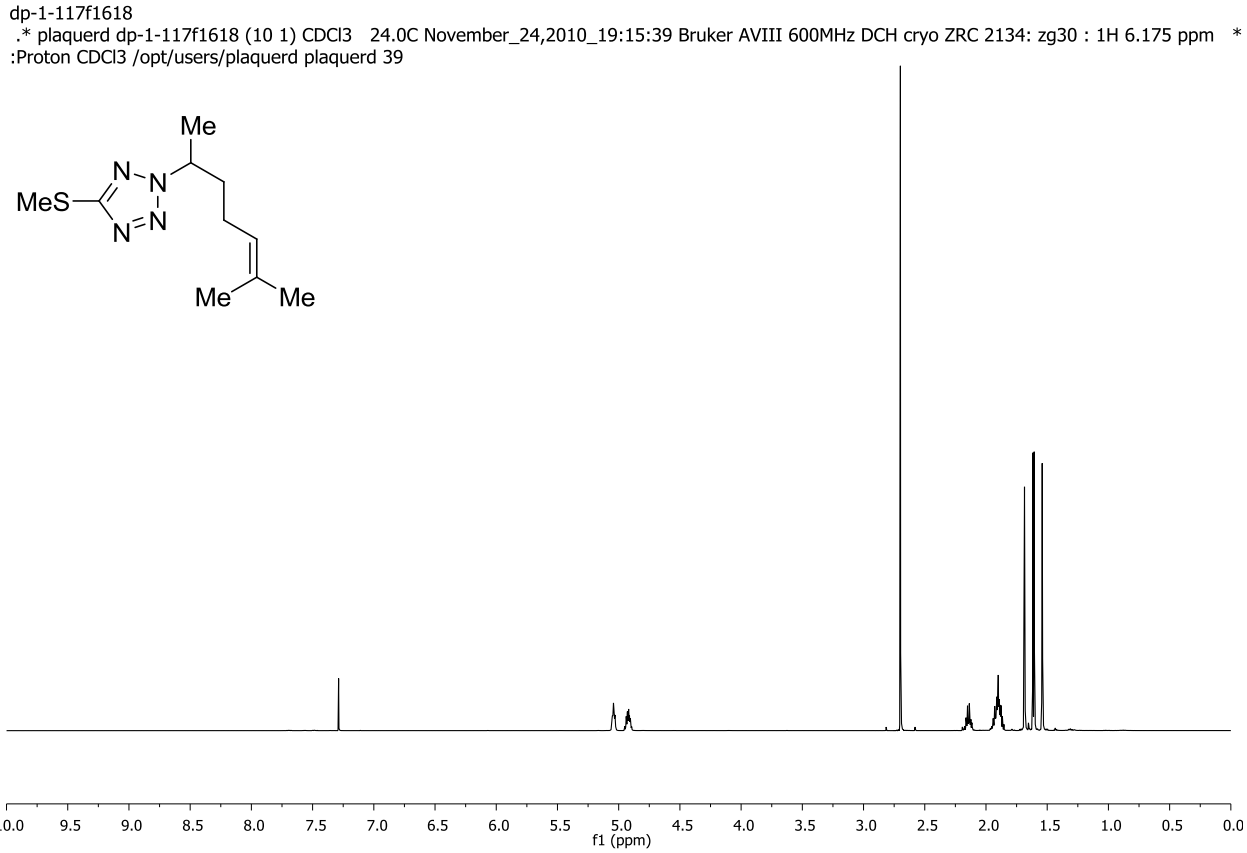

dp-1-113f1719
.* plaquerd dp-1-113f1719 (11 1) CDCl3 24.0C November_24,2010_20:33:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

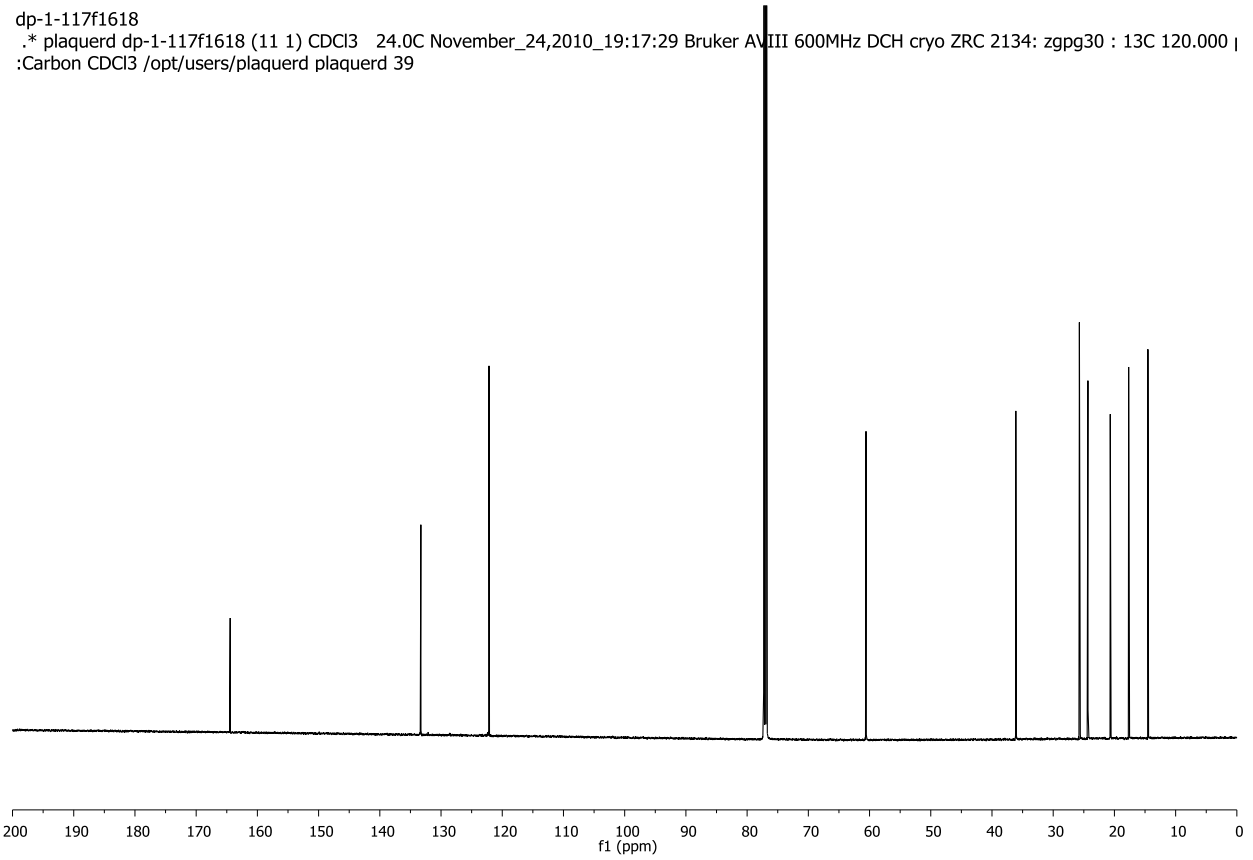
dp-2-023f5760
.* plaquerd dp-2-023f5760 (10 1) CDCl3 24.0C November_24,2010_17:59:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton CDCl3 /opt/users/plaquerd plaquerd 38



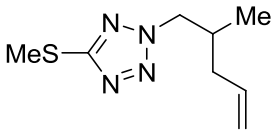
dp-2-023f5760
.* plaquerd dp-2-023f5760 (11 1) CDCl3 24.0C November_24,2010_18:01:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 38



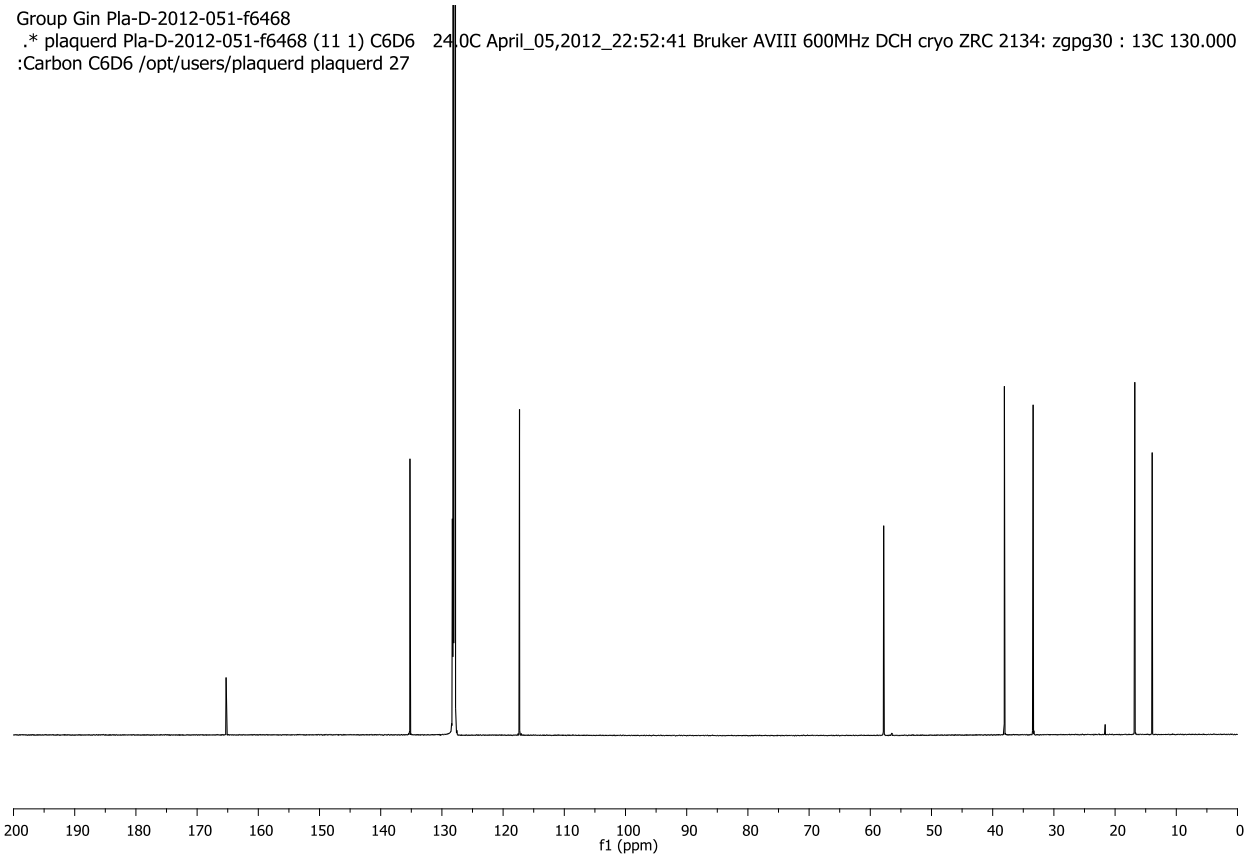

dp-1-117f1618
.* plaquerd dp-1-117f1618 (10 1) CDCl3 24.0C November_24,2010_19:15:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton CDCl3 /opt/users/plaquerd plaquerd 39
Me
N
N
MeS
N
N
Me
Me
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


dp-1-117f1618
.* plaquerd dp-1-117f1618 (11 1) CDCl3 24.0C November_24,2010_19:17:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 39
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

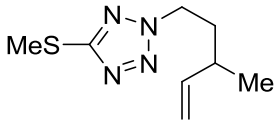
Group Gin Pla-D-2012-051-f6468
.* plaquerd Pla-D-2012-051-f6468 (10 1) C6D6 24.0C April_05,2012_22:50:52 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 27



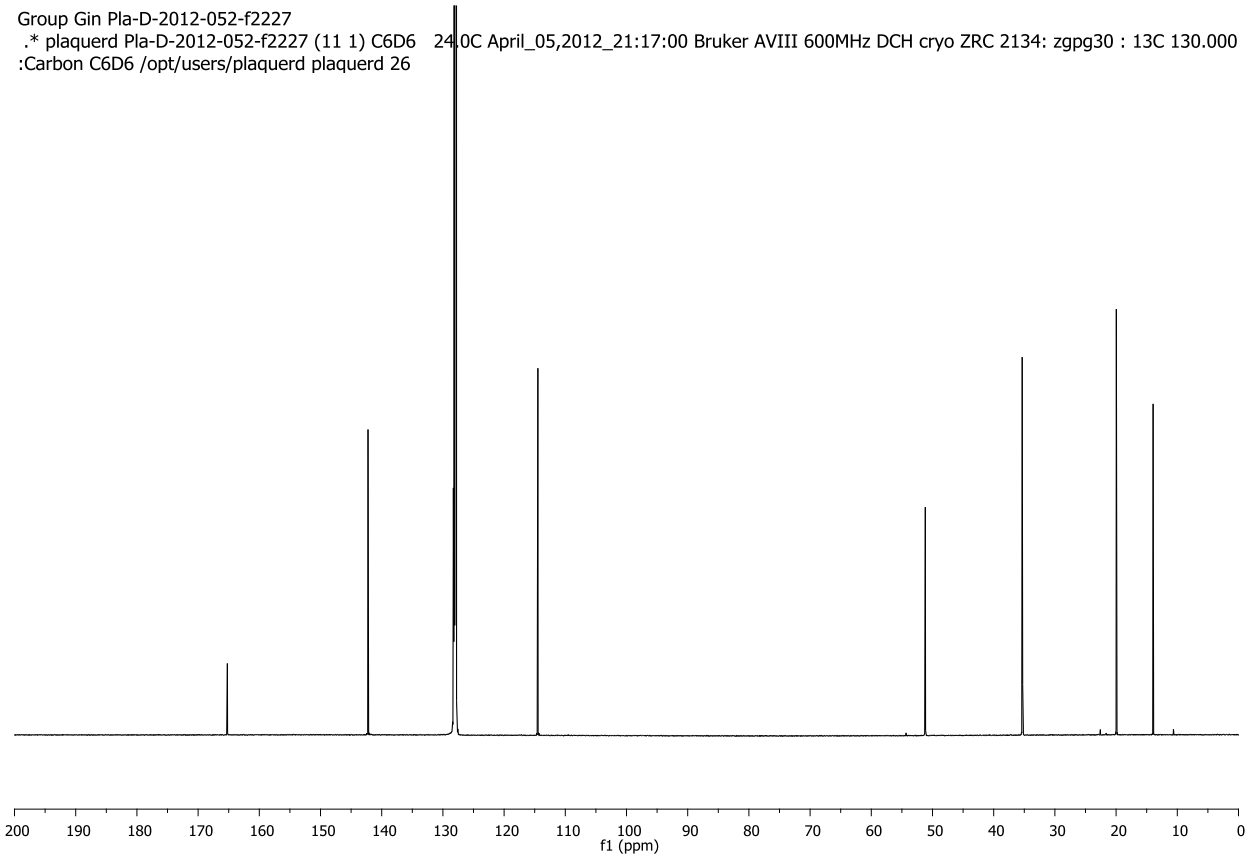
Group Gin Pla-D-2012-051-f6468
.* plaquerd Pla-D-2012-051-f6468 (11 1) C6D6 24.0C April_05,2012_22:52:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 27



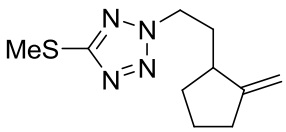
Group Gin Pla-D-2012-052-f2227
.* plaquerd Pla-D-2012-052-f2227 (10 1) C6D6 24.0C April_05,2012_21:15:01 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 26



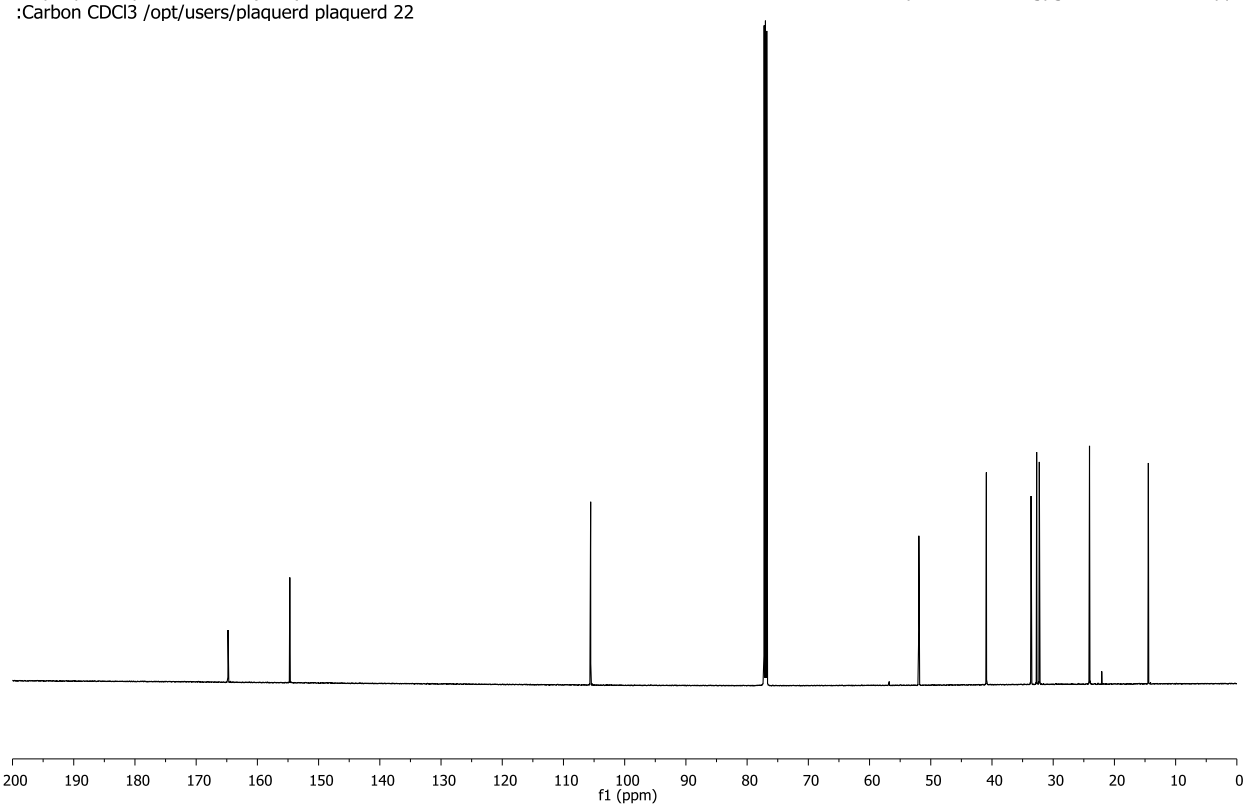
Group Gin Pla-D-2012-052-f2227
.* plaquerd Pla-D-2012-052-f2227 (11 1) C6D6 24.0C April_05,2012_21:17:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 26



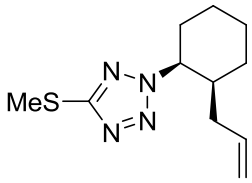
dp-2-033f2127
.* plaquerd dp-2-033f2127 (10 1) CDCl3 24.0C October_28,2010_13:49:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 22



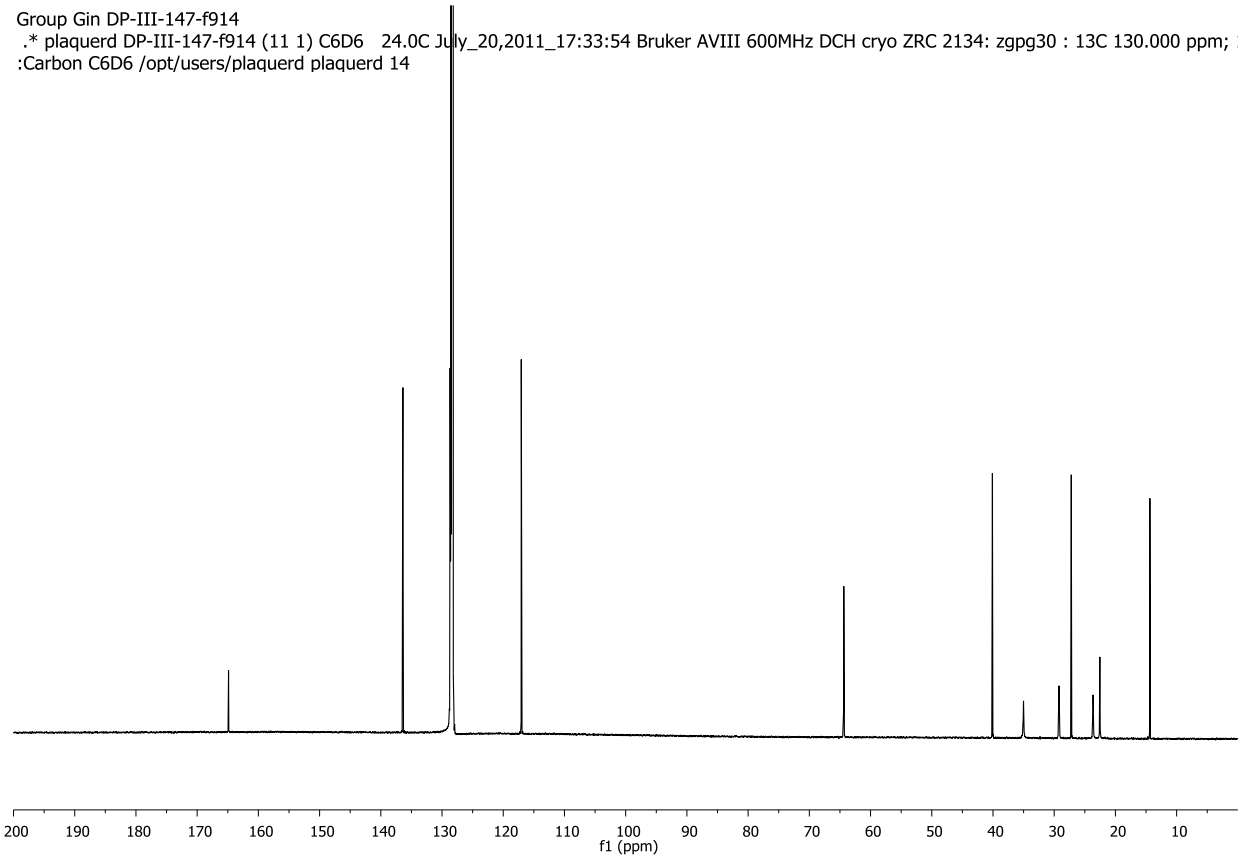
dp-2-033f2127
.* plaquerd dp-2-033f2127 (11 1) CDCl3 24.0C October_28,2010_13:50:31 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 pp
:Carbon CDCl3 /opt/users/plaquerd plaquerd 22



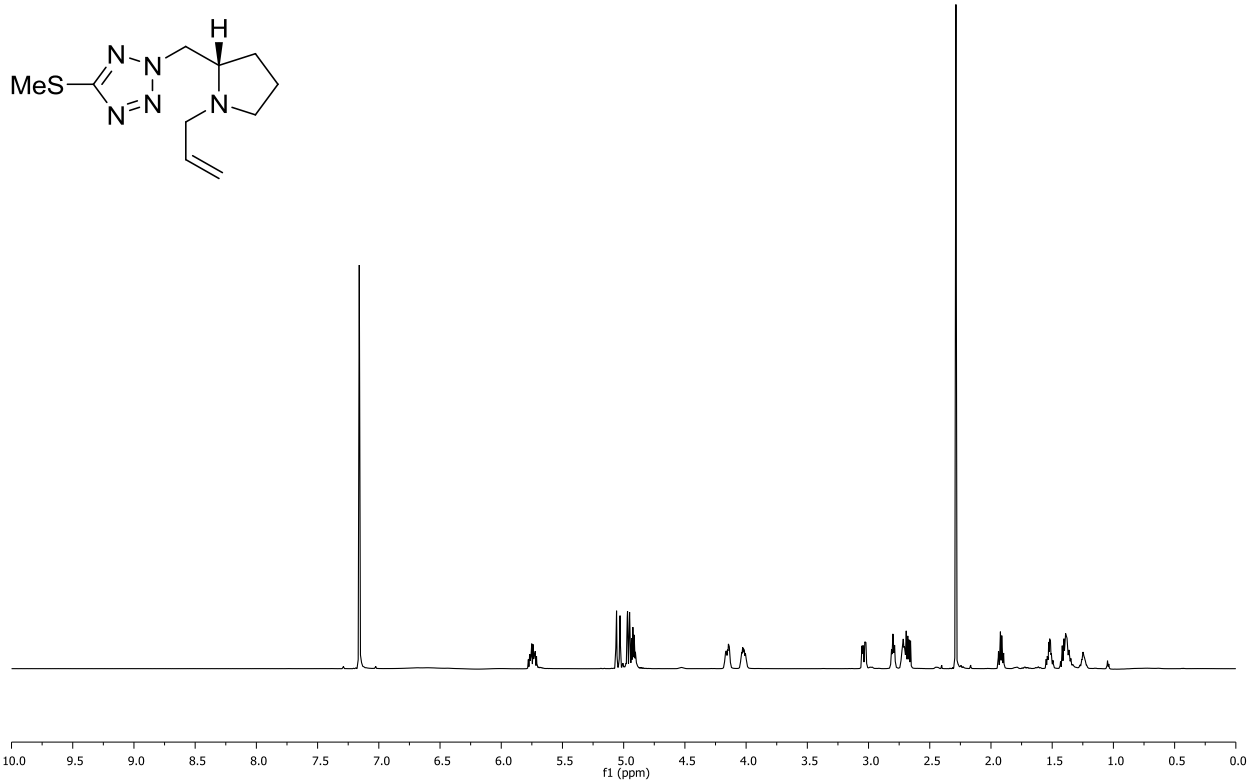
Group Gin DP-III-147-f914
.* plaquerd DP-III-147-f914 (10 1) C6D6 24.0C July_20,2011_17:32:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 14



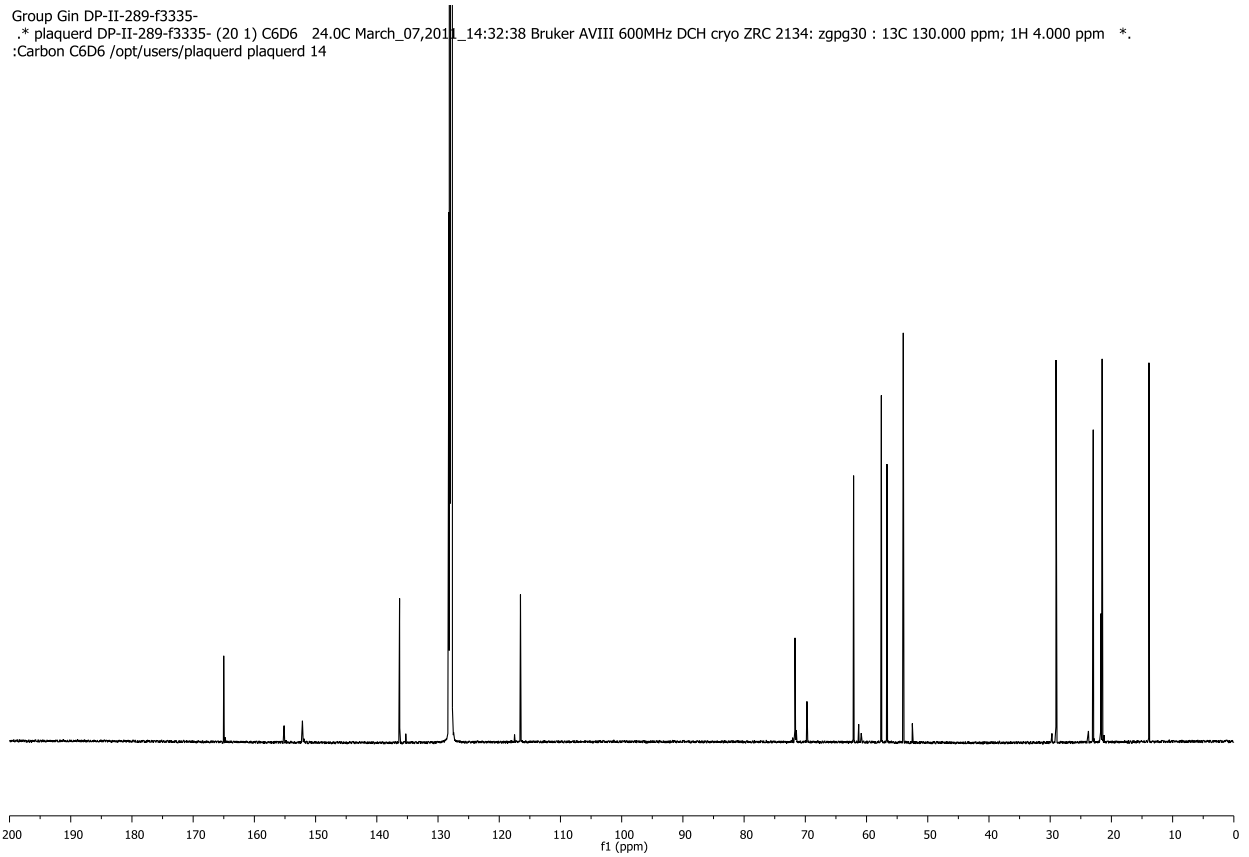
Group Gin DP-III-147-f914
.* plaquerd DP-III-147-f914 (11 1) C6D6 24.0C July_20,2011_17:33:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 14



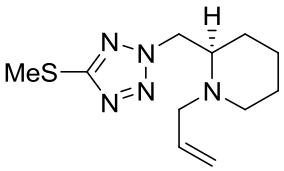
Group Gin DP-II-289-f3335-
.* plaquerd DP-II-289-f3335- (30 1) C6D6 24.0C March_07,2011_14:30:16 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 14



Group Gin DP-II-289-f3335-
.* plaquerd DP-II-289-f3335- (20 1) C6D6 24.0C March_07,2011_14:32:38 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
:Carbon C6D6 /opt/users/plaquerd plaquerd 14

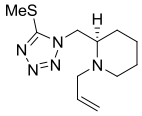


Group Gin DP-III-39-f5259
.* plaquerd DP-III-39-f5259 (10 1) C6D6 24.0C April_06,2011_11:11:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 25

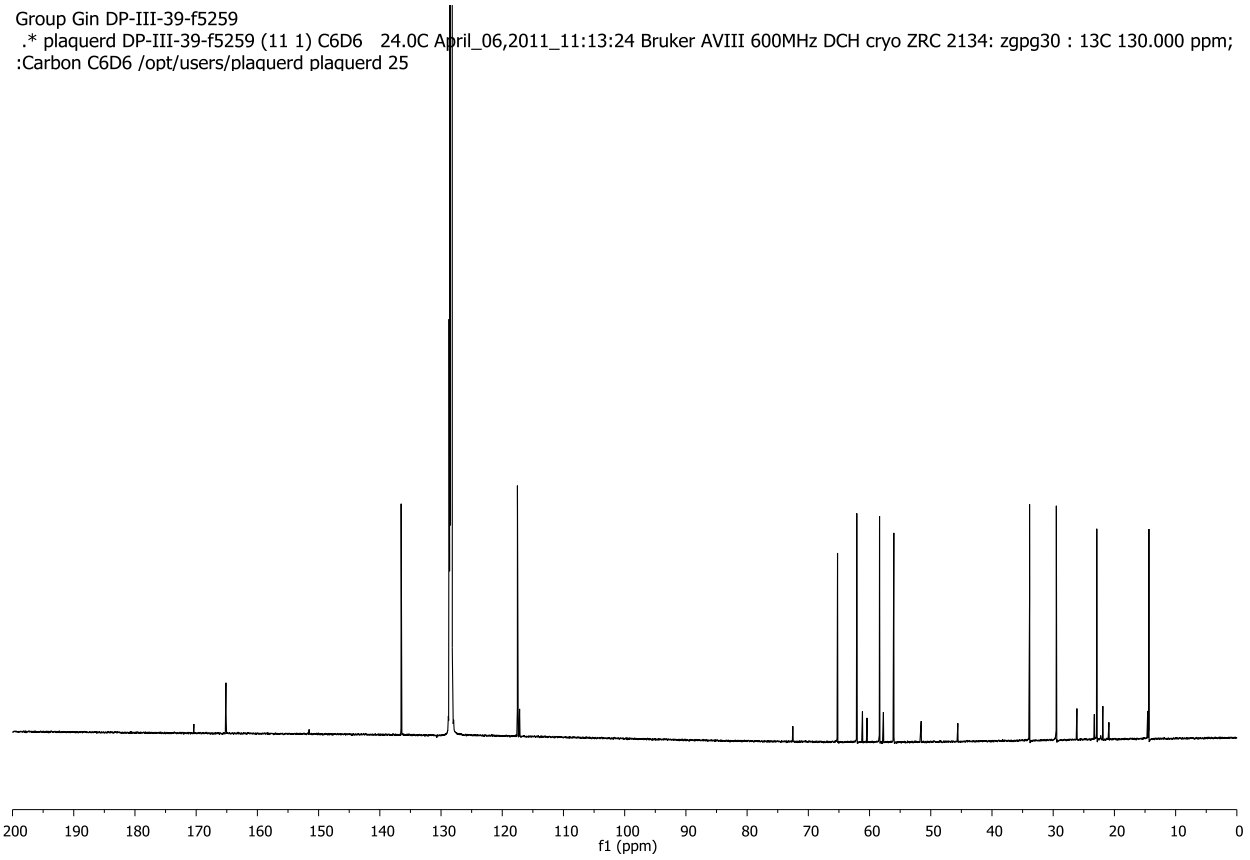


(96% estimated purity by NMR)

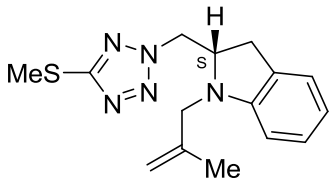
Impurity:



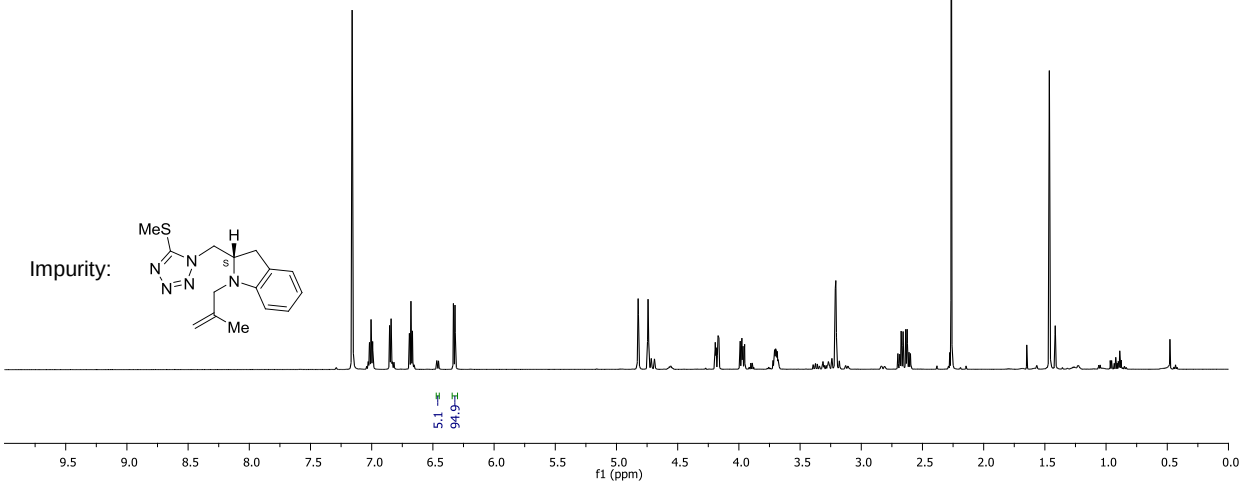
Group Gin DP-III-39-f5259
.* plaquerd DP-III-39-f5259 (11 1) C6D6 24.0C April_06,2011_11:13:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 25



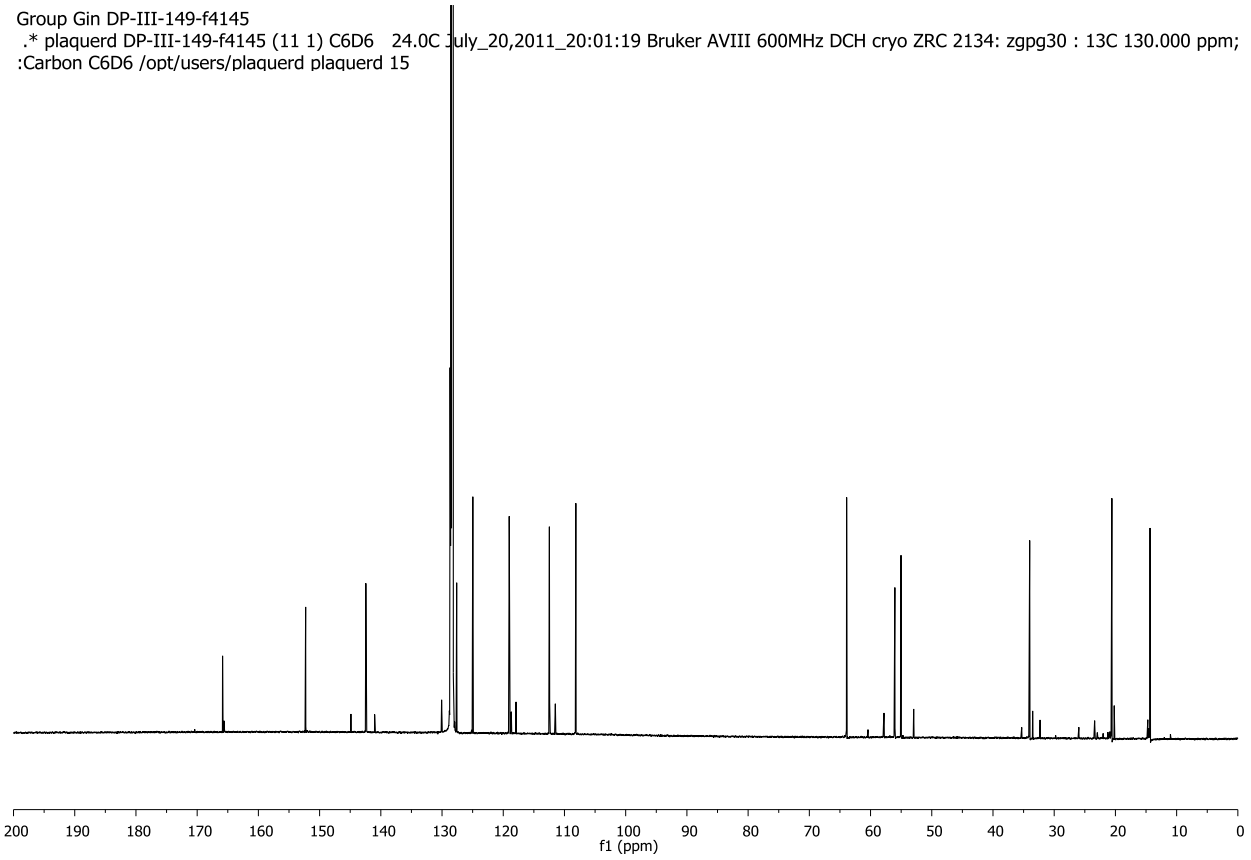
Group Gin DP-III-149-f4145
.* plaquerd DP-III-149-f4145 (10 1) C6D6 24.0C July_20,2011_17:26:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 15

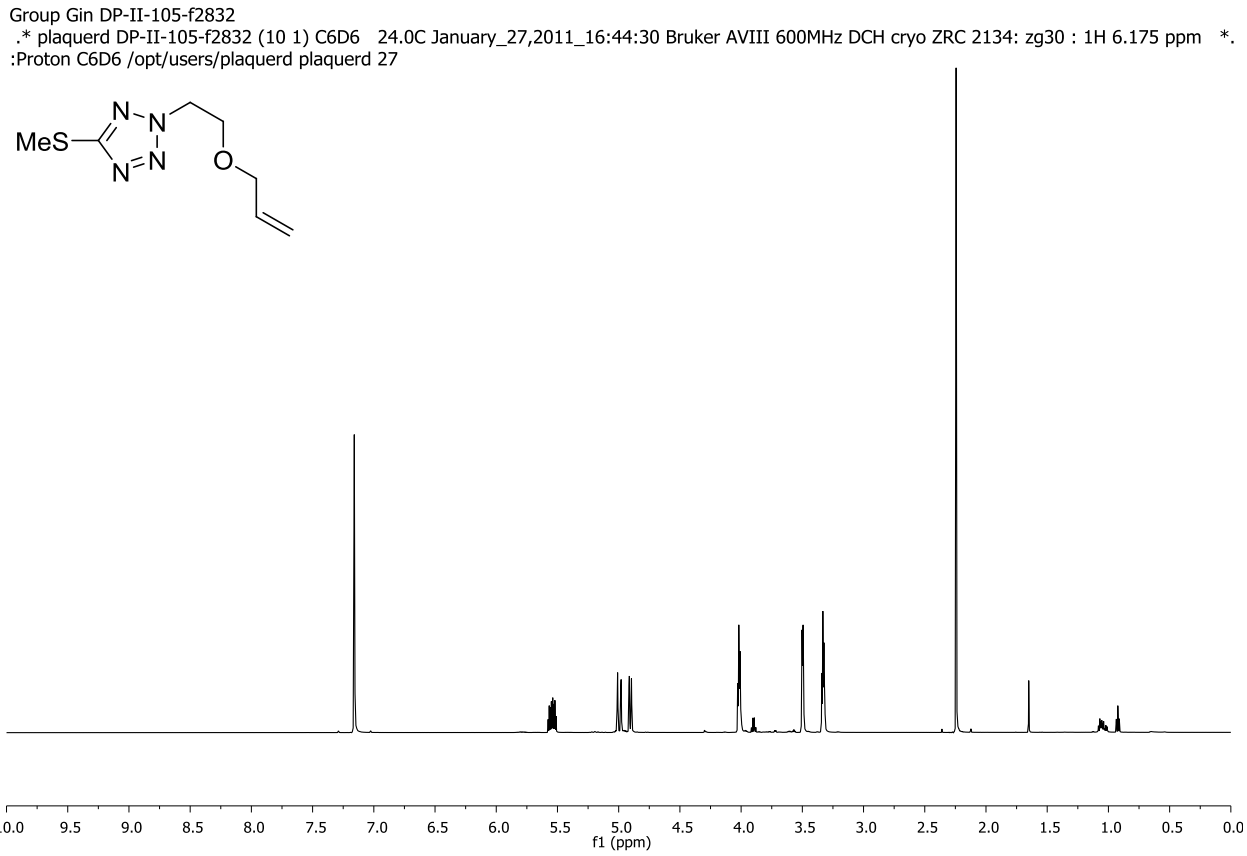


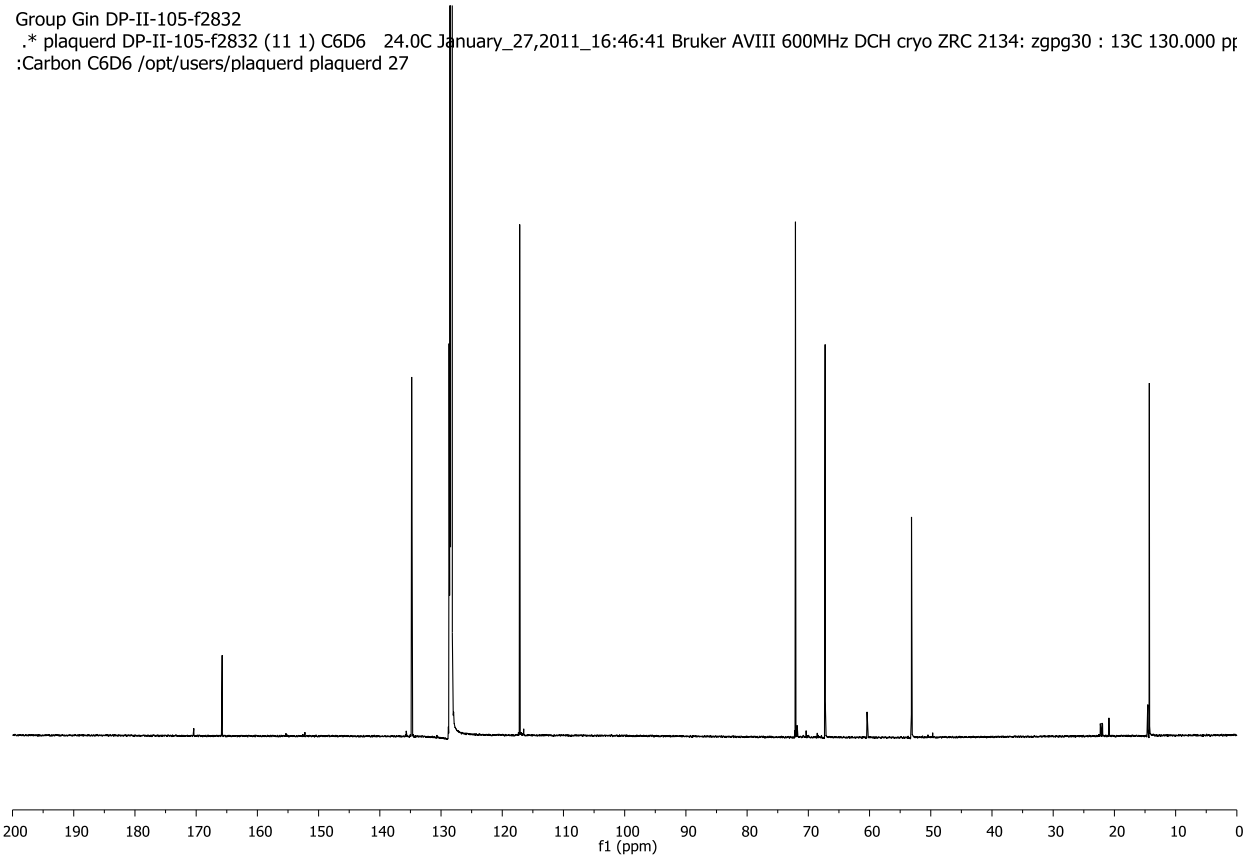
(95% estimated purity by NMR)



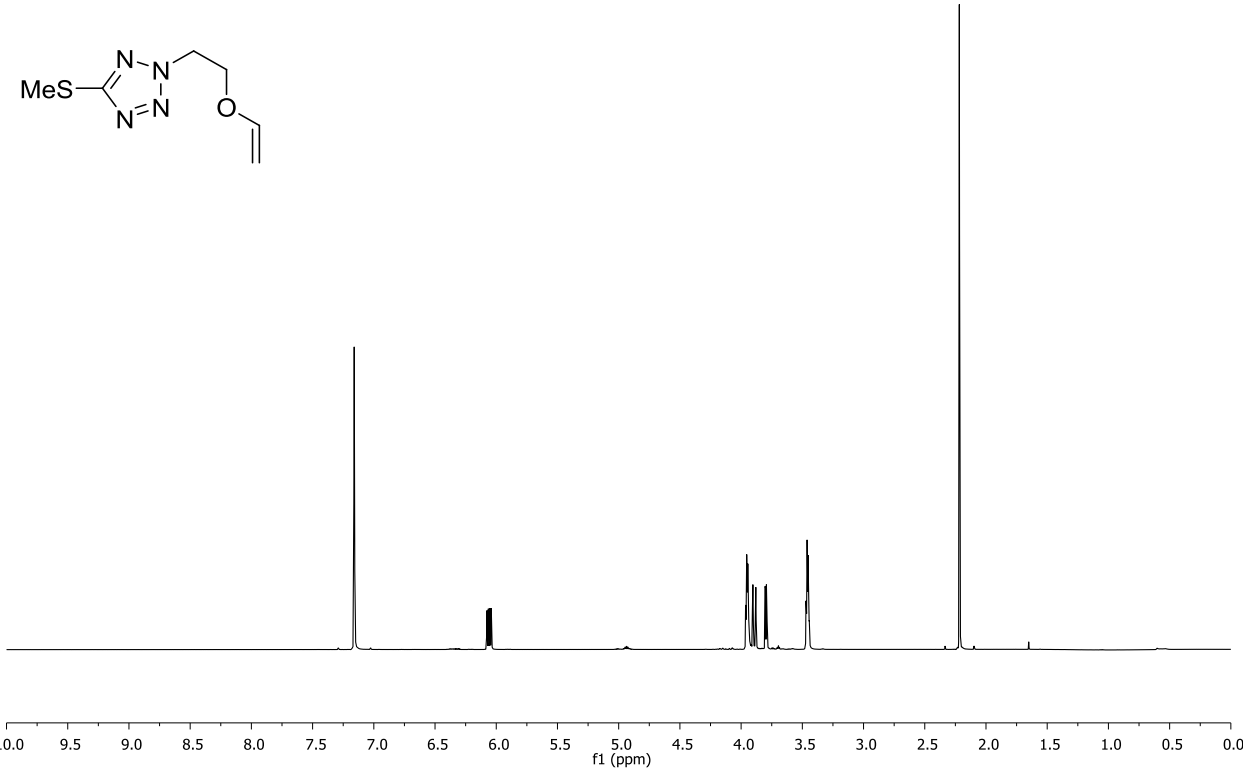
Group Gin DP-III-149-f4145
.* plaquerd DP-III-149-f4145 (11 1) C6D6 24.0C July_20,2011_20:01:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 15



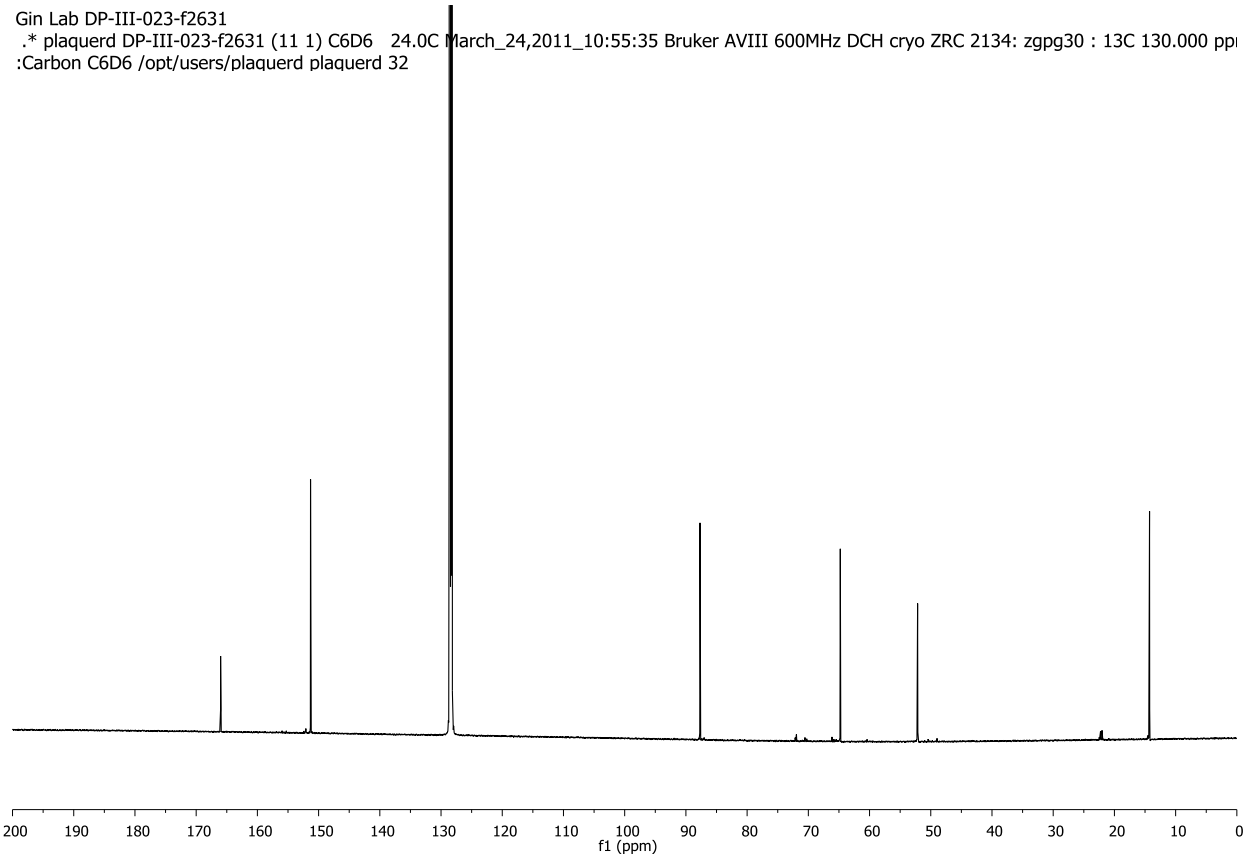

Group Gin DP-II-105-f2832
.* plaquerd DP-II-105-f2832 (10 1) C6D6 24.0C January_27,2011_16:44:30 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 27
MeS
N
N
N
N
O
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Group Gin DP-II-105-f2832
.* plaquerd DP-II-105-f2832 (11 1) C6D6 24.0C January_27,2011_16:46:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 pr
:Carbon C6D6 /opt/users/plaquerd plaquerd 27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

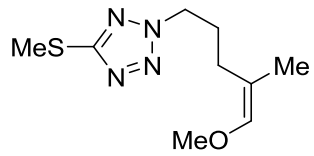
Gin Lab DP-III-023-f2631
.* plaquerd DP-III-023-f2631 (10 1) C6D6 24.0C March_24,2011_08:54:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 32



Gin Lab DP-III-023-f2631
.* plaquerd DP-III-023-f2631 (11 1) C6D6 24.0C March_24,2011_10:55:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppı
:Carbon C6D6 /opt/users/plaquerd plaquerd 32

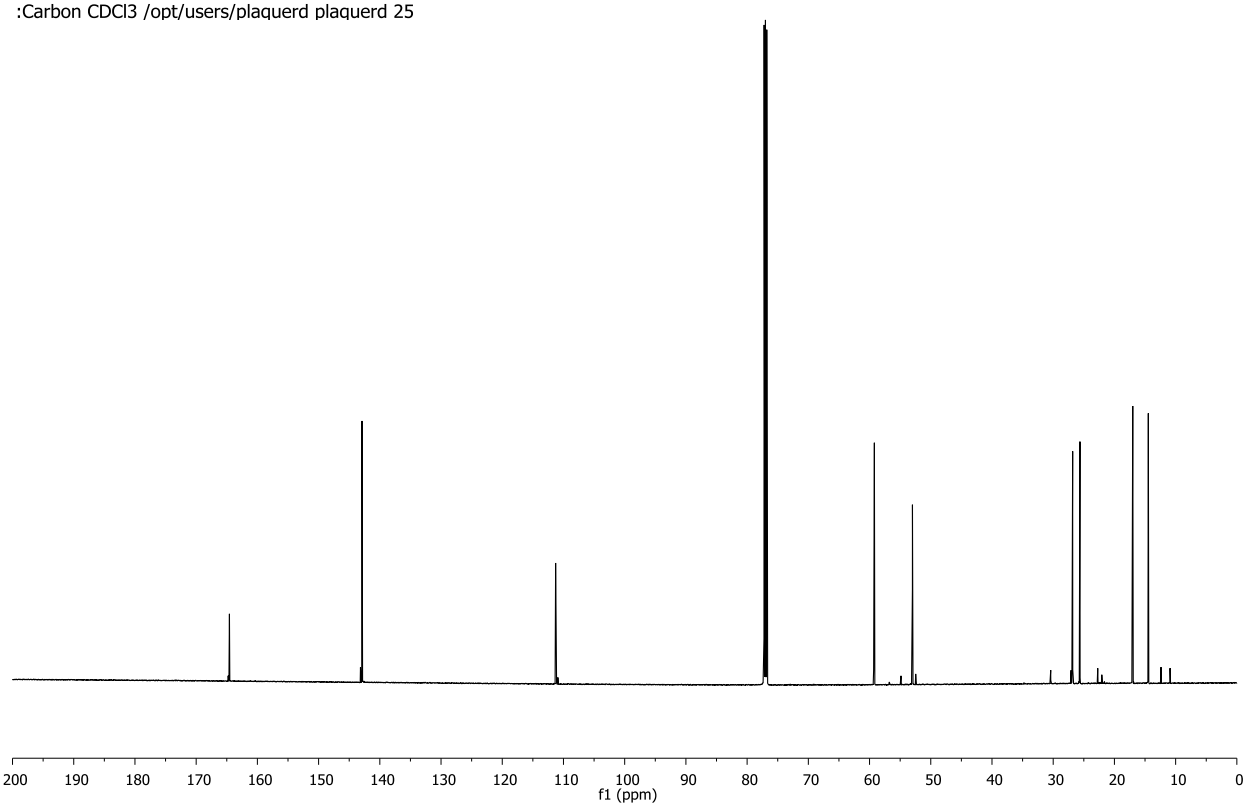


dp-2-032f2127
.* plaquerd dp-2-032f2127 (10 1) CDCl3 24.0C October_28,2010_17:38:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 25

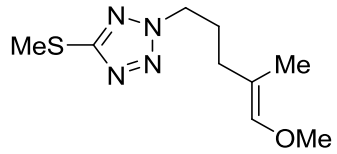


(95:5 *Z*/*E*)

dp-2-032f2127
.* plaquerd dp-2-032f2127 (11 1) CDCl3 24.0C October_28,2010_17:39:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 pp
:Carbon CDCl3 /opt/users/plaquerd plaquerd 25

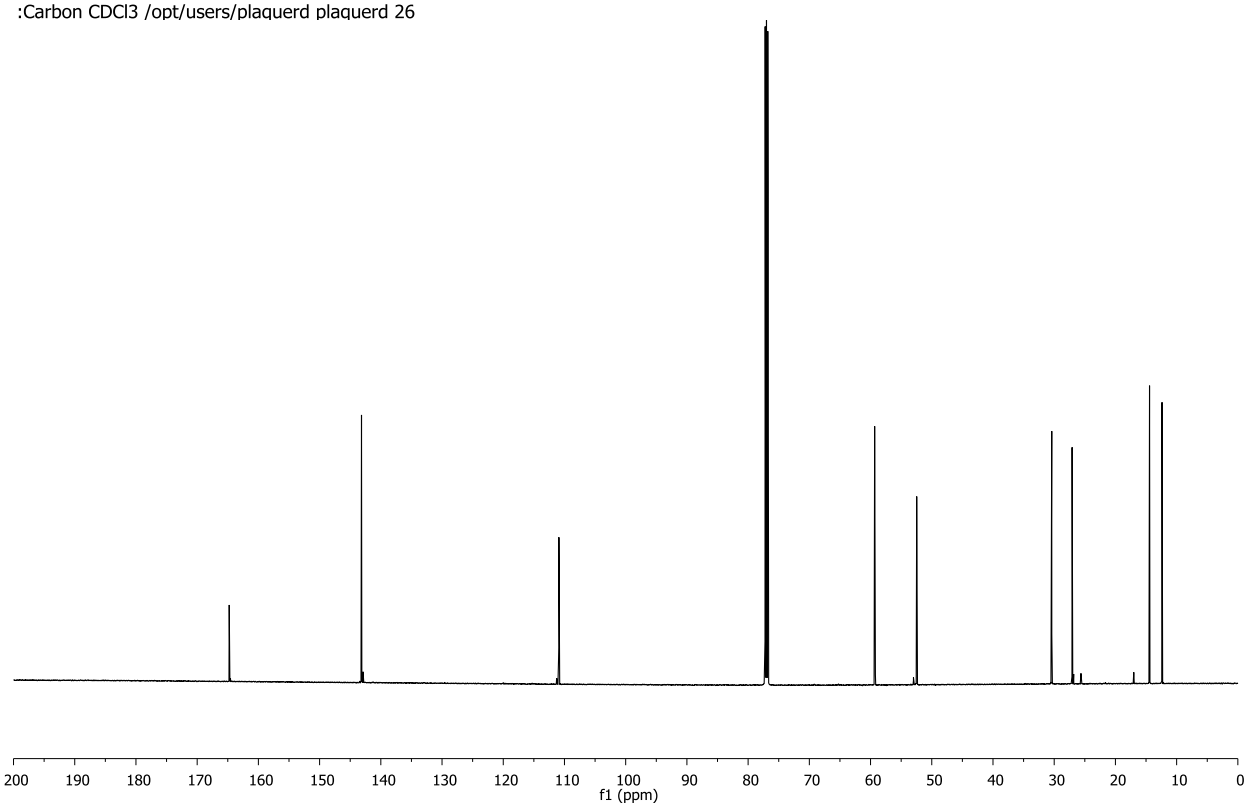


dp-2-032f2938
.* plaquerd dp-2-032f2938 (10 1) CDCl3 24.0C October_28,2010_19:03:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 26

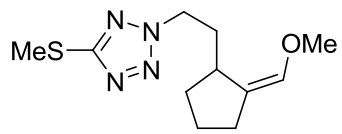


(97:3 *E*/*Z*)

dp-2-032f2938
.* plaquerd dp-2-032f2938 (11 1) CDCl3 24.0C October_28,2010_19:04:13 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 pp
:Carbon CDCl3 /opt/users/plaquerd plaquerd 26

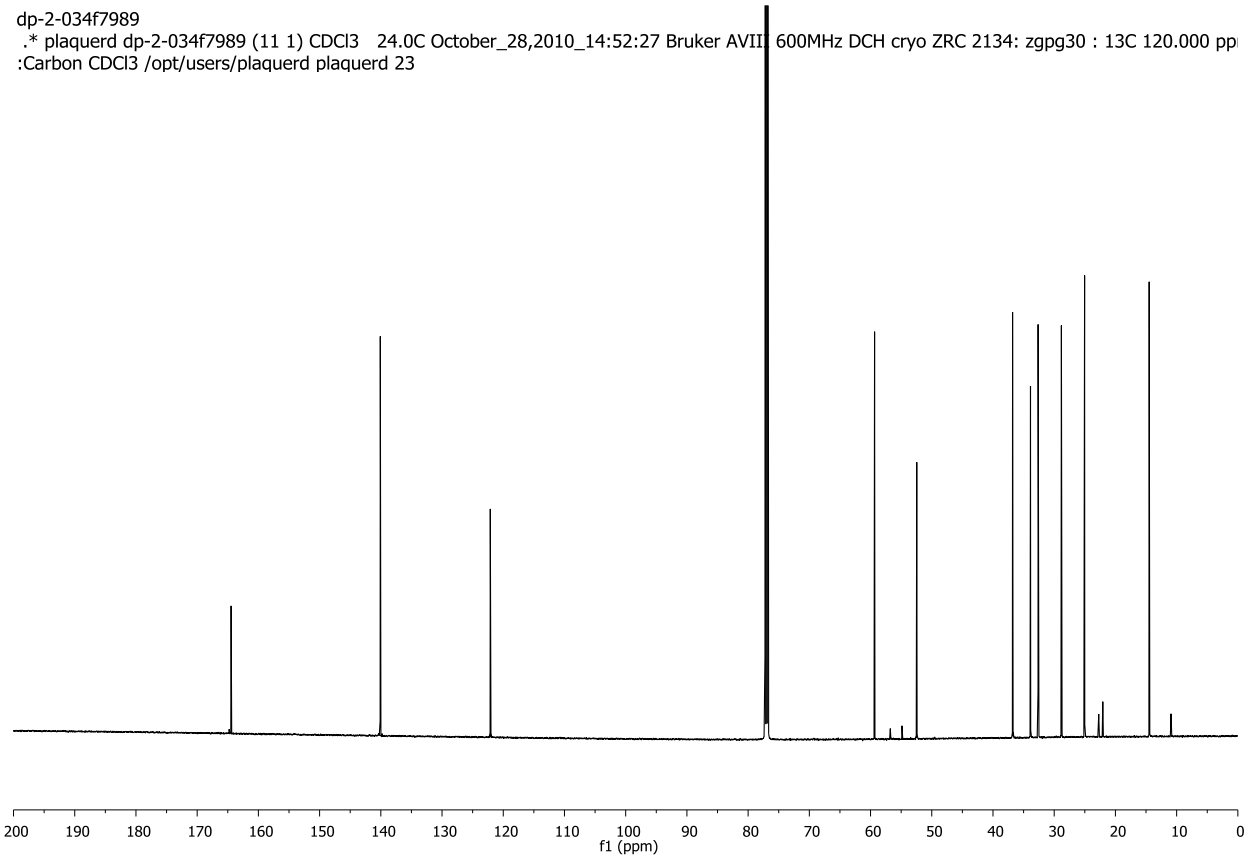


dp-2-034f7989
.* plaquerd dp-2-034f7989 (10 1) CDCl3 24.0C October_28,2010_14:51:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 23

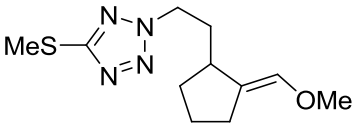


(>99:1 *Z*/*E*)

dp-2-034f7989
.* plaquerd dp-2-034f7989 (11 1) CDCl3 24.0C October_28,2010_14:52:27 Bruker AVII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 pp
:Carbon CDCl3 /opt/users/plaquerd plaquerd 23

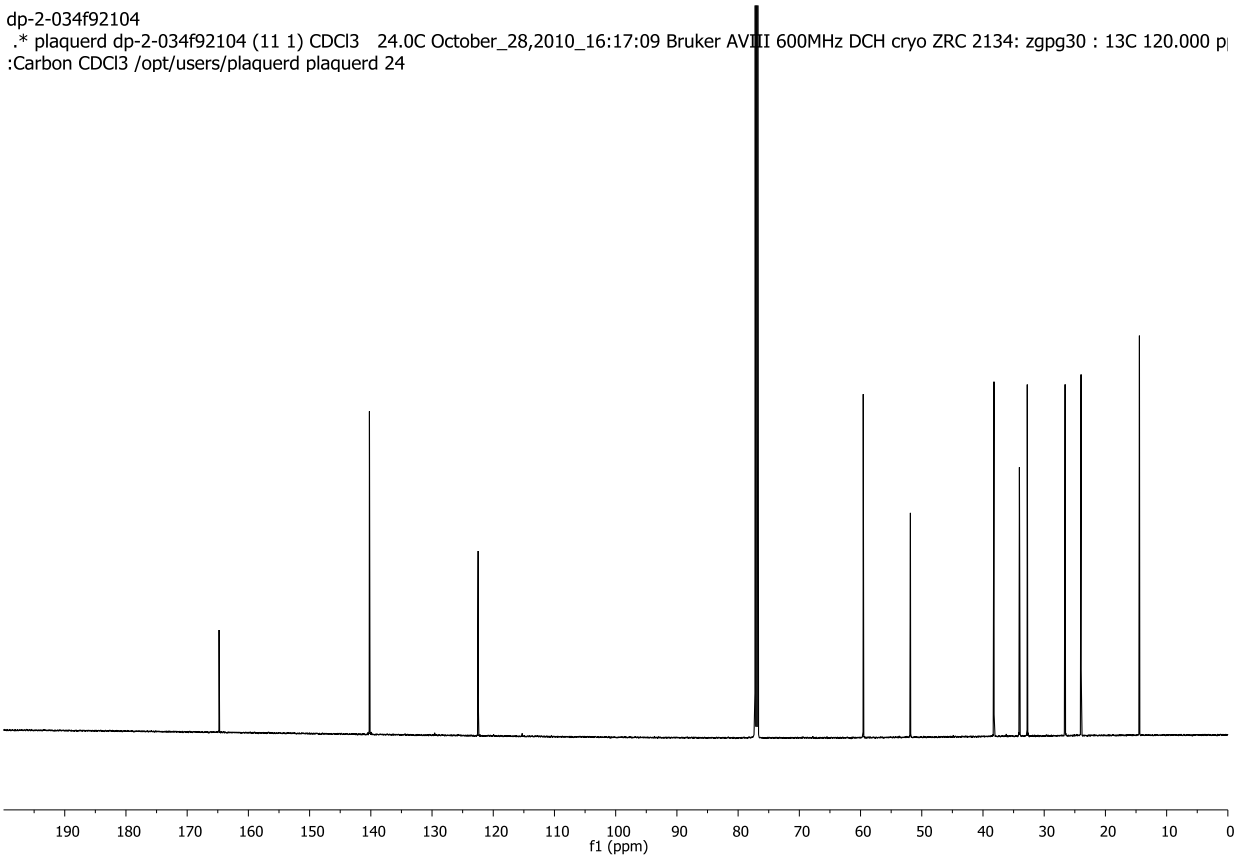


dp-2-034f92104
.* plaquerd dp-2-034f92104 (10 1) CDCl3 24.0C October_28,2010_16:16:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 24

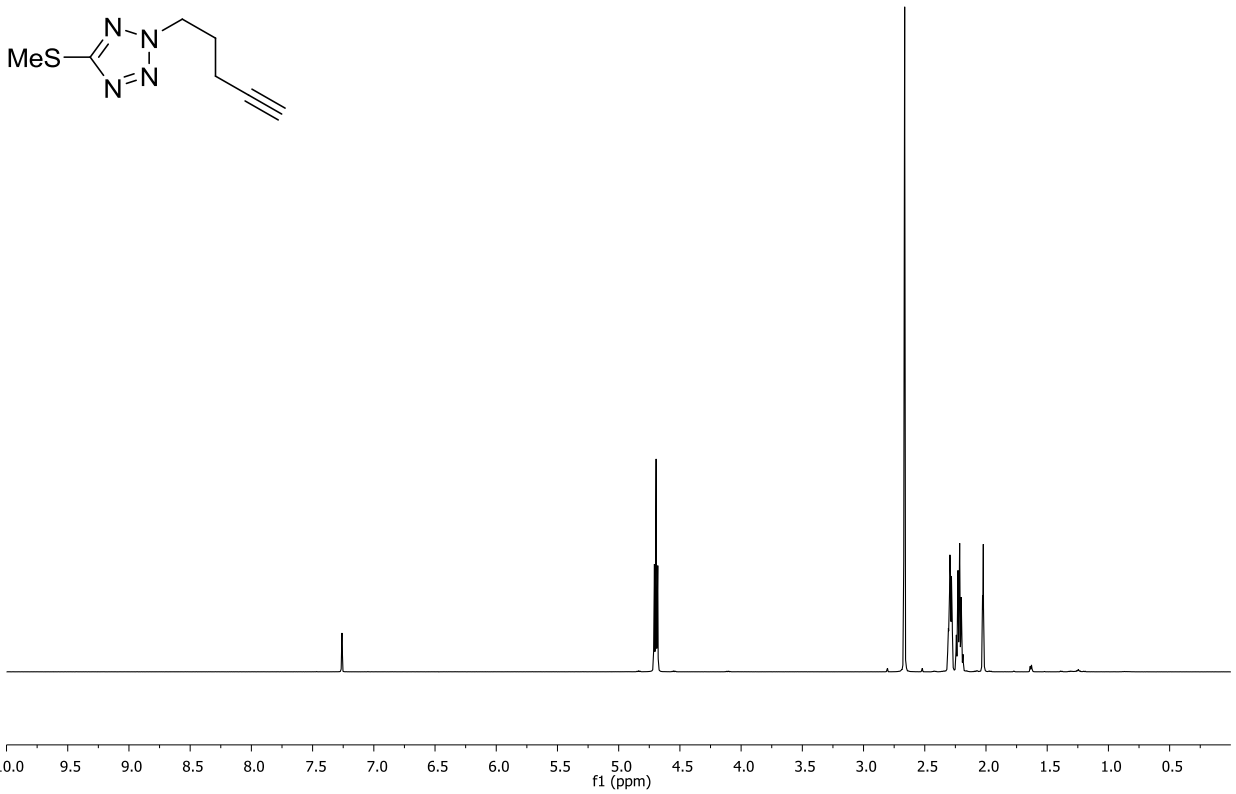


(>99:1 *E*/*Z*)

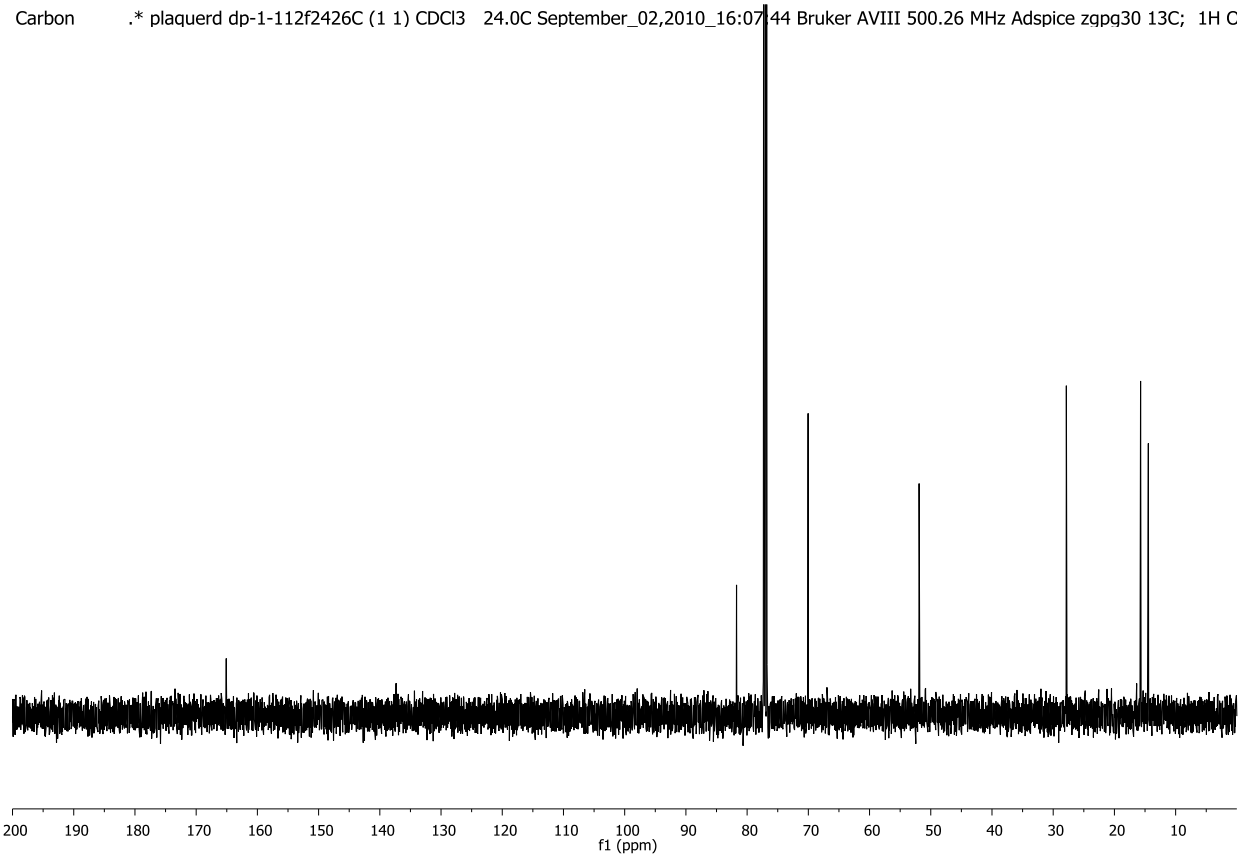
dp-2-034f92104
.* plaquerd dp-2-034f92104 (11 1) CDCl3 24.0C October_28,2010_16:17:09 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 p
:Carbon CDCl3 /opt/users/plaquerd plaquerd 24



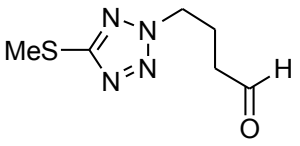
Proton .* plaquerd dp-1-112f2426 (1 1) CDCl3 24.0C September_02,2010_16:04:31 Bruker AVIII 500.26 MHz Adspice zg30 1H *.



Carbon .* plaquerd dp-1-112f2426C (1 1) CDCl3 24.0C September_02,2010_16:07:44 Bruker AVIII 500.26 MHz Adspice zgpg30 13C; 1H C

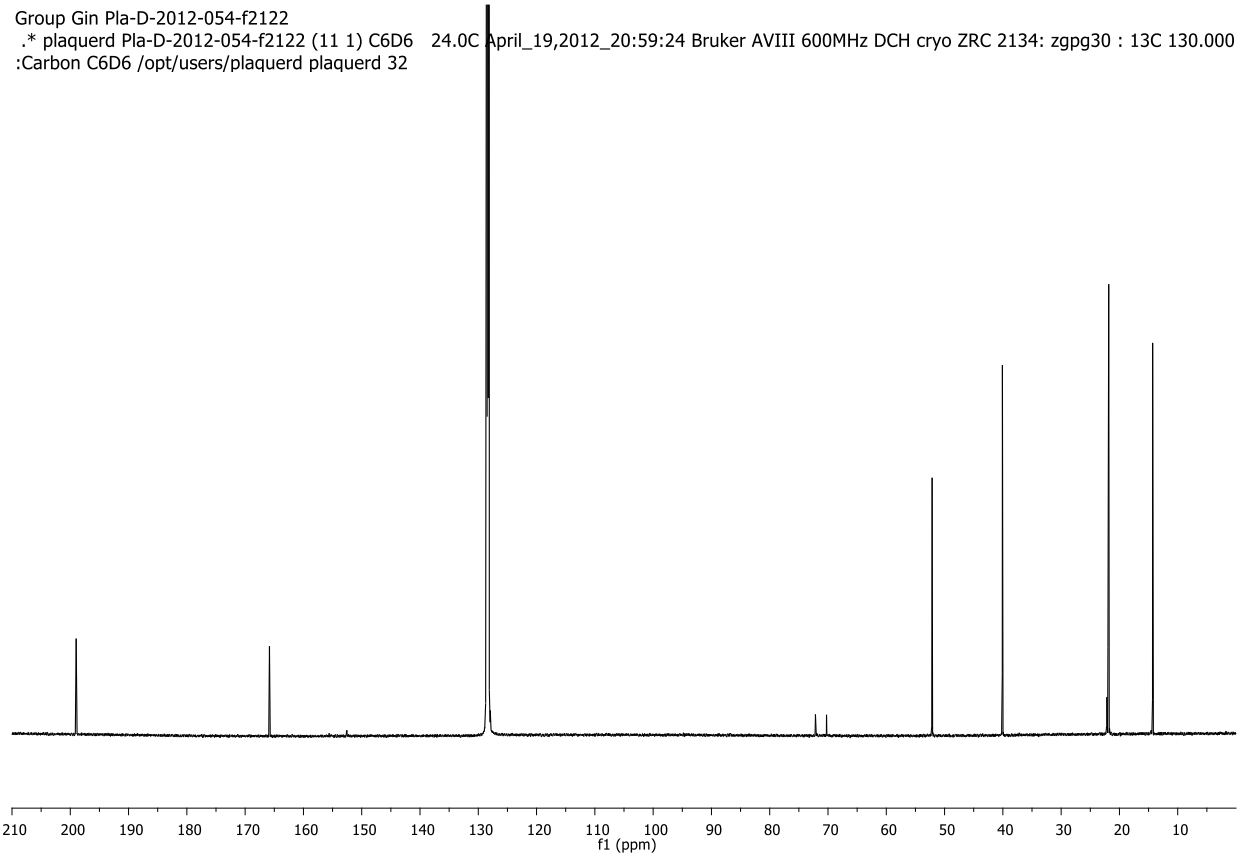


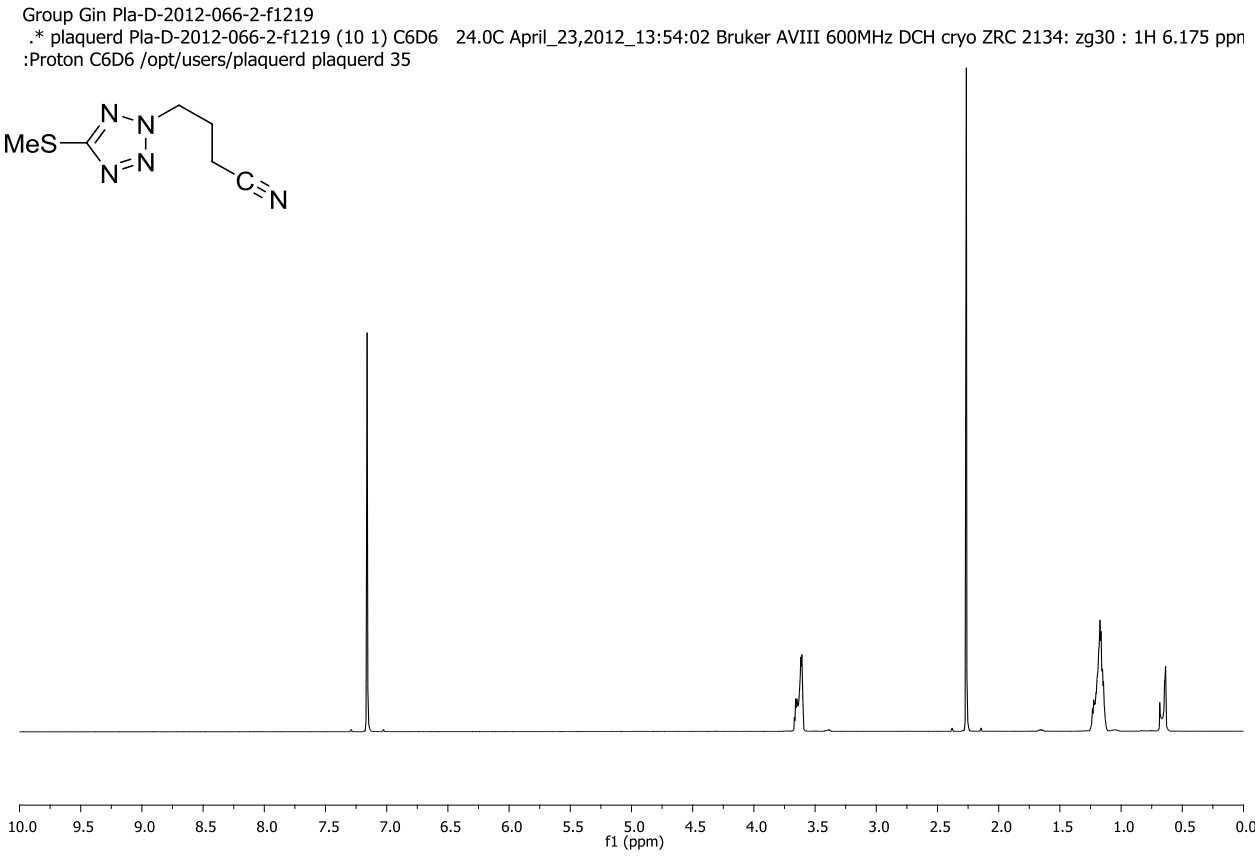
Group Gin Pla-D-2012-054-f2122
.* plaquerd Pla-D-2012-054-f2122 (10 1) C6D6 24.0C April_19,2012_20:57:28 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 32

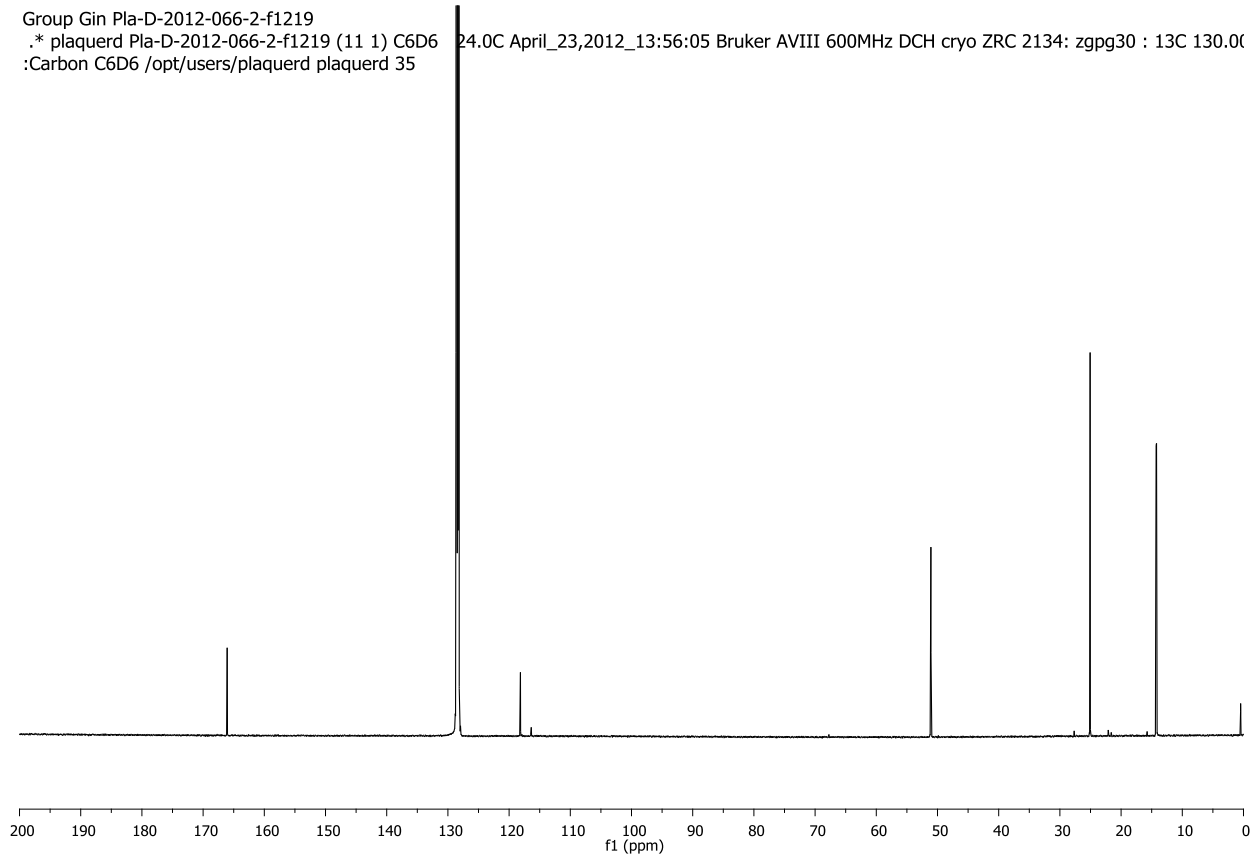


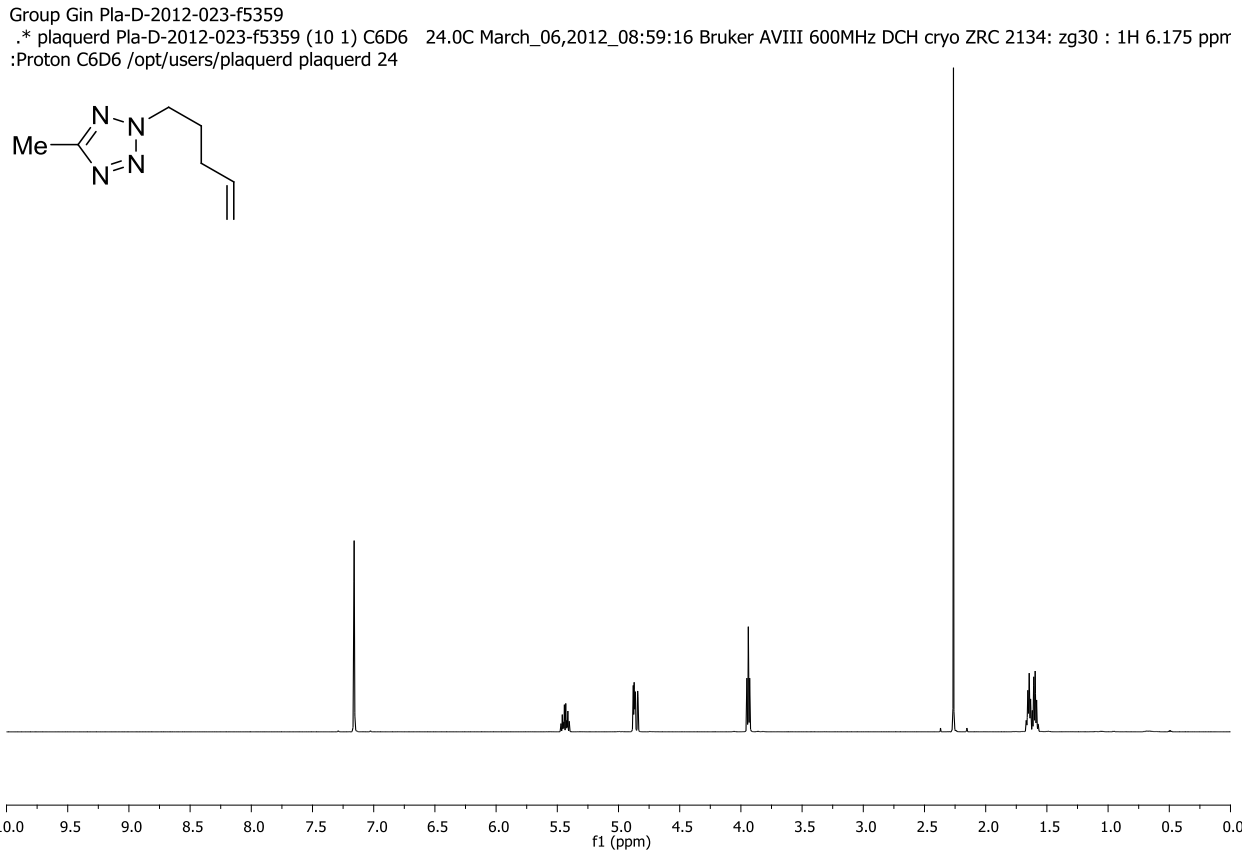
(98% estimated purity by NMR)

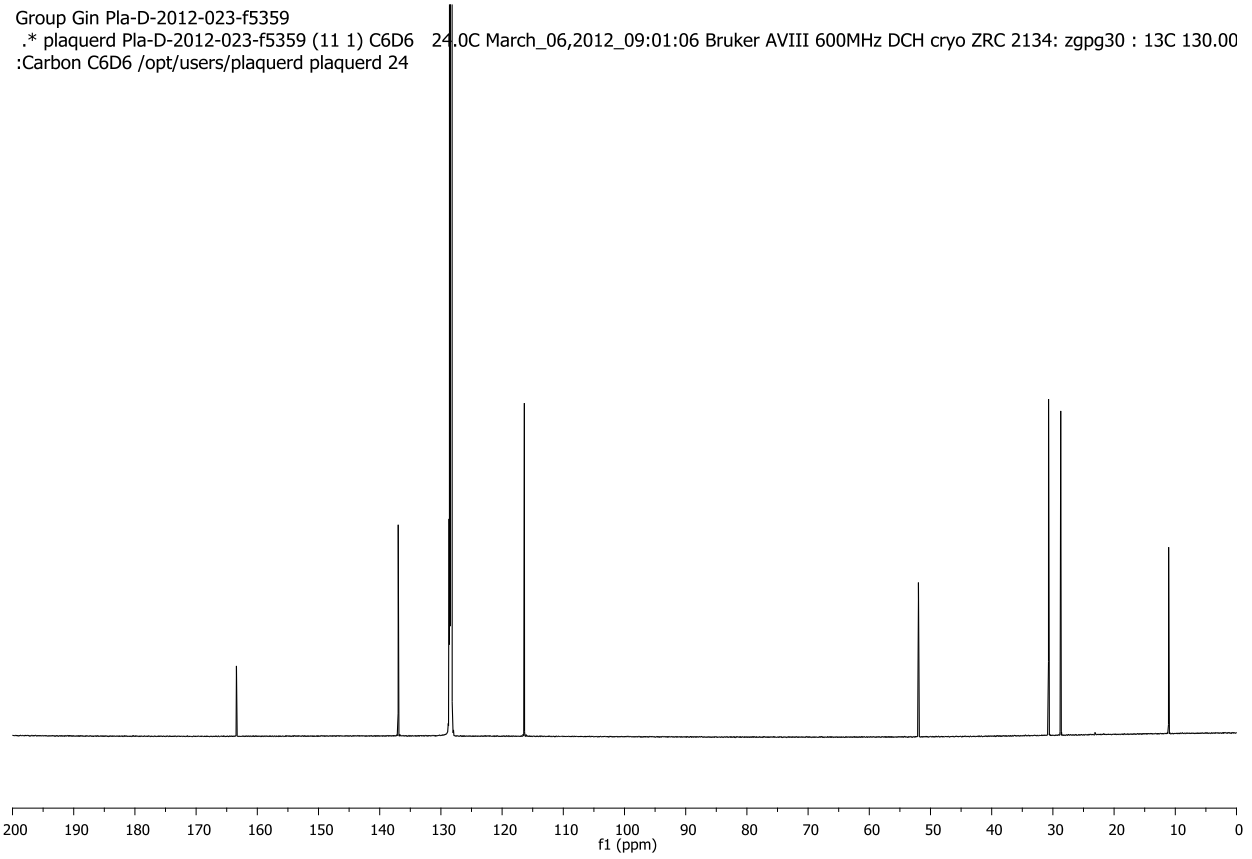
Group Gin Pla-D-2012-054-f2122
.* plaquerd Pla-D-2012-054-f2122 (11 1) C6D6 24.0C April_19,2012_20:59:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 32

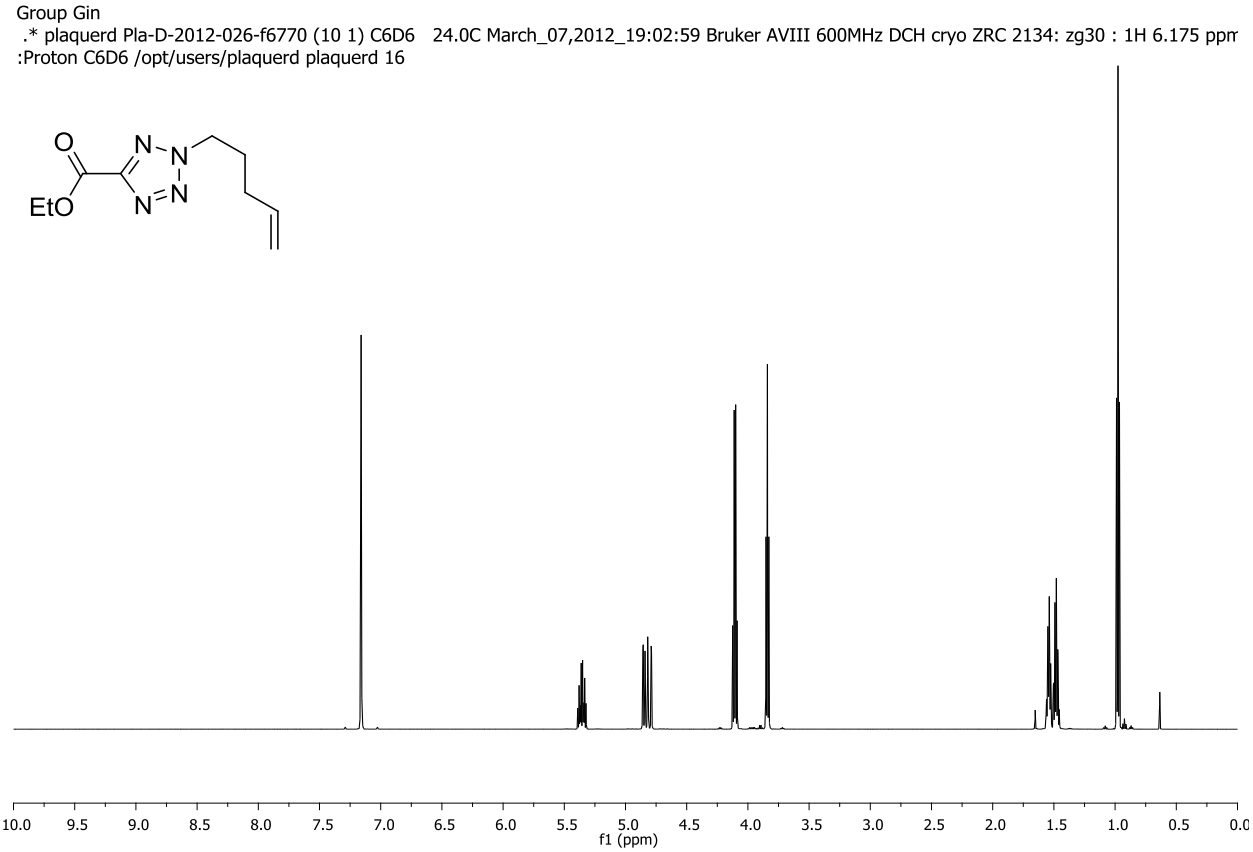


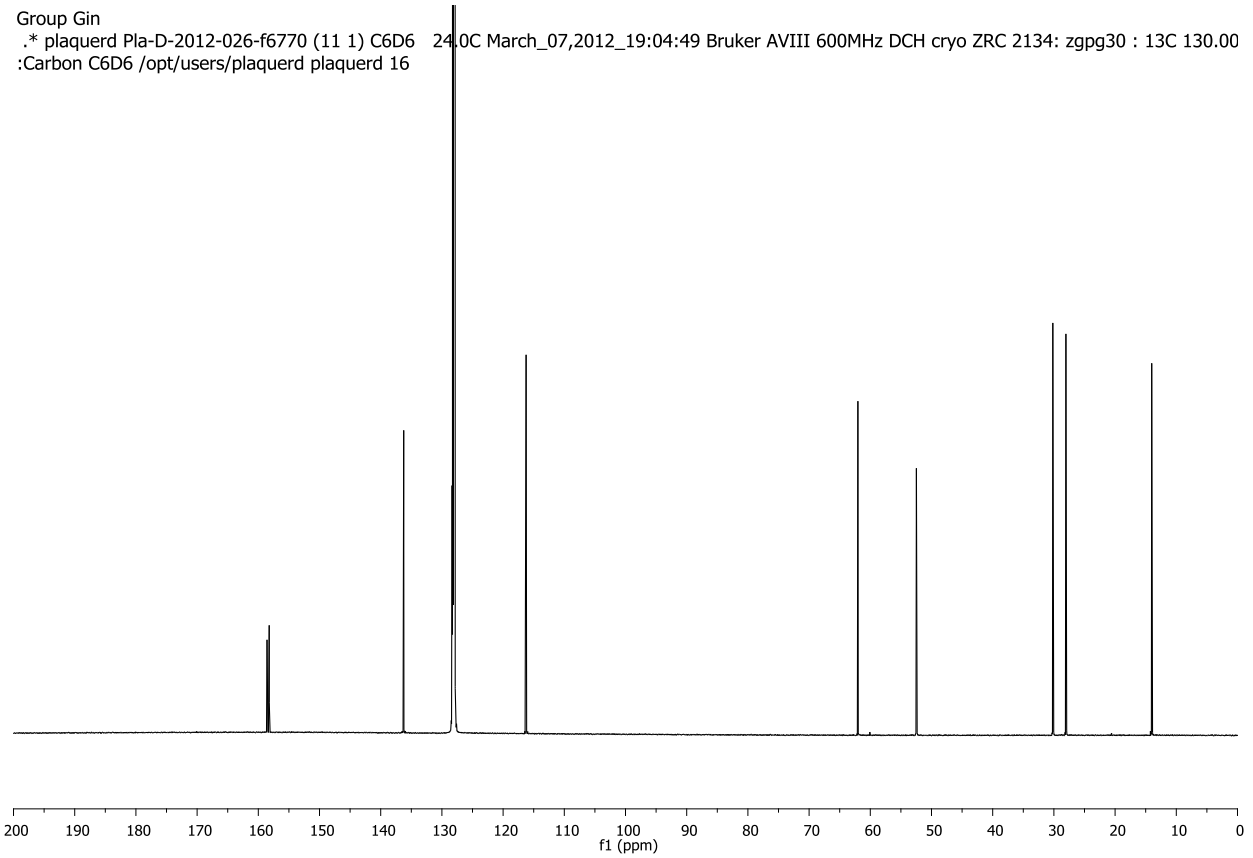

Group Gin Pla-D-2012-066-2-f1219
.* plaquerd Pla-D-2012-066-2-f1219 (10 1) C6D6 24.0C April_23,2012_13:54:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 35
MeS
N
N
N
N
C
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

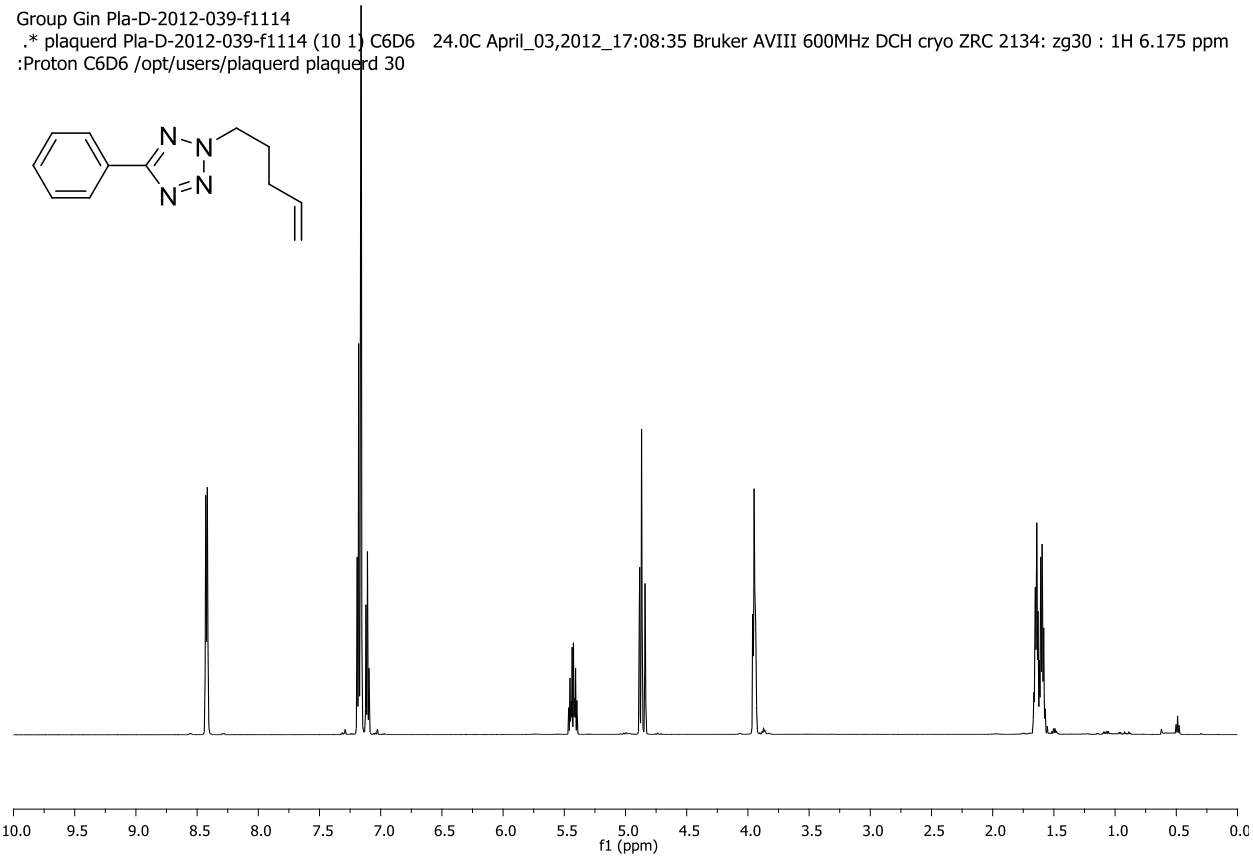

Group Gin Pla-D-2012-066-2-f1219
.* plaquerd Pla-D-2012-066-2-f1219 (11 1) C6D6 24.0C April_23,2012_13:56:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.0
:Carbon C6D6 /opt/users/plaquerd plaquerd 35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

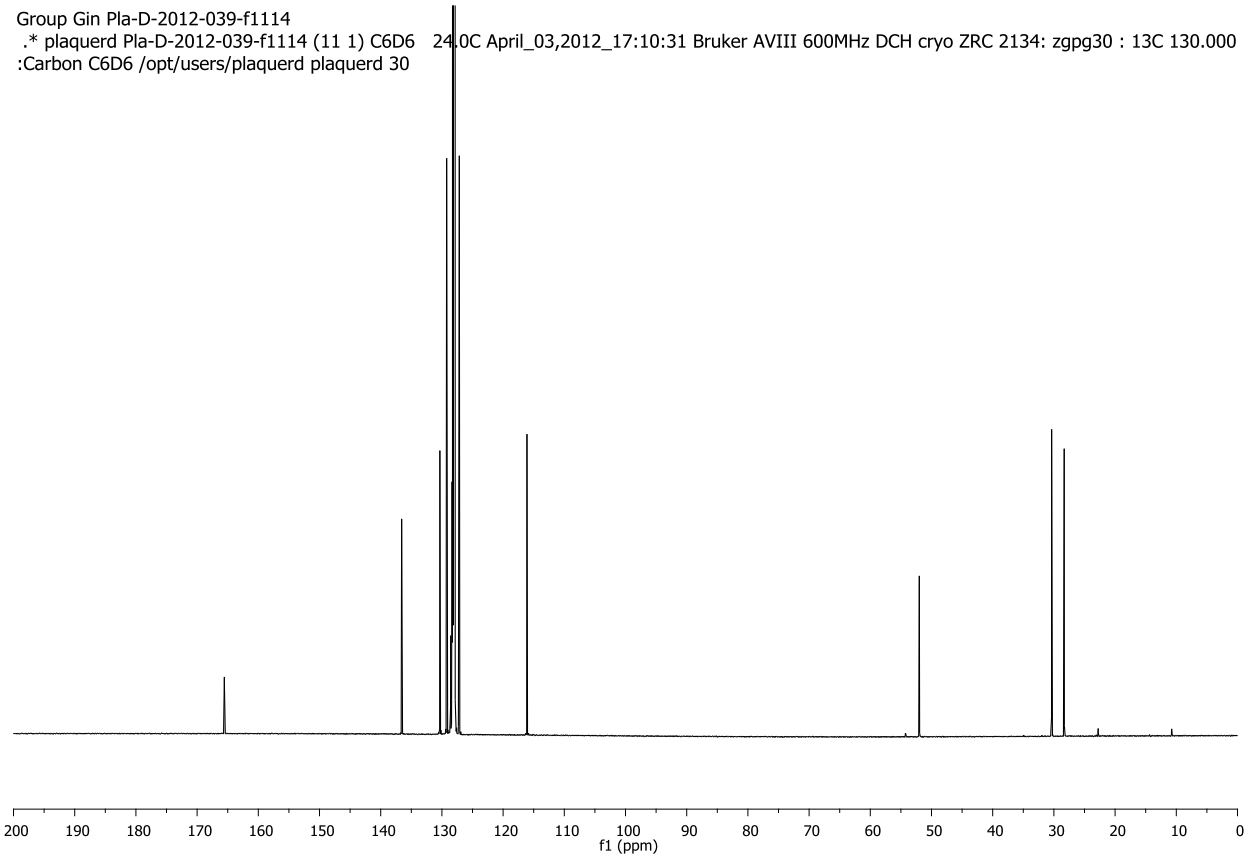

Group Gin Pla-D-2012-023-f5359
.* plaquerd Pla-D-2012-023-f5359 (10 1) C6D6 24.0C March_06,2012_08:59:16 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 24
Me
N
N
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Group Gin Pla-D-2012-023-f5359
.* plaquerd Pla-D-2012-023-f5359 (11 1) C6D6 24.0C March_06,2012_09:01:06 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.00
:Carbon C6D6 /opt/users/plaquerd plaquerd 24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

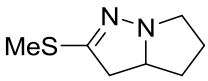

Group Gin
.* plaquerd Pla-D-2012-026-f6770 (10 1) C6D6 24.0C March_07,2012_19:02:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 16
O
EtO
N
N
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Group Gin
.* plaquerd Pla-D-2012-026-f6770 (11 1) C6D6 24.0C March_07,2012_19:04:49 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.00
:Carbon C6D6 /opt/users/plaquerd plaquerd 16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

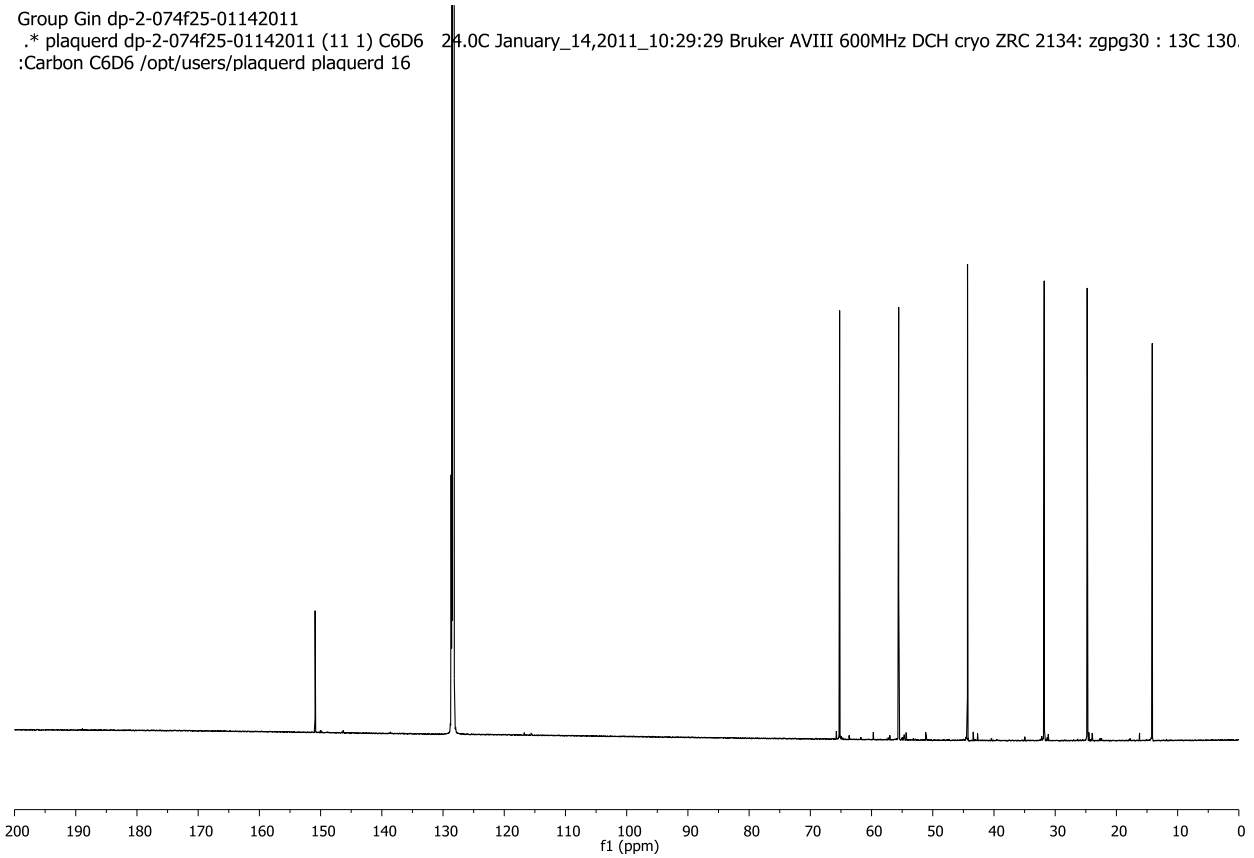

Group Gin Pla-D-2012-039-f1114
.* plaquerd Pla-D-2012-039-f1114 (10 1) C6D6 24.0C April_03,2012_17:08:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm
:Proton C6D6 /opt/users/plaquerd plaquerd 30
N
N
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Group Gin Pla-D-2012-039-f1114
.* plaquerd Pla-D-2012-039-f1114 (11 1) C6D6 24.0C April_03,2012_17:10:31 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

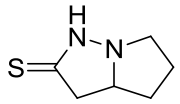
Group Gin dp-2-074f25-01142011
.* plaquerd dp-2-074f25-01142011 (10 1) C6D6 24.0C January_14,2011_10:27:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 p
:Proton C6D6 /opt/users/plaquerd plaquerd 16



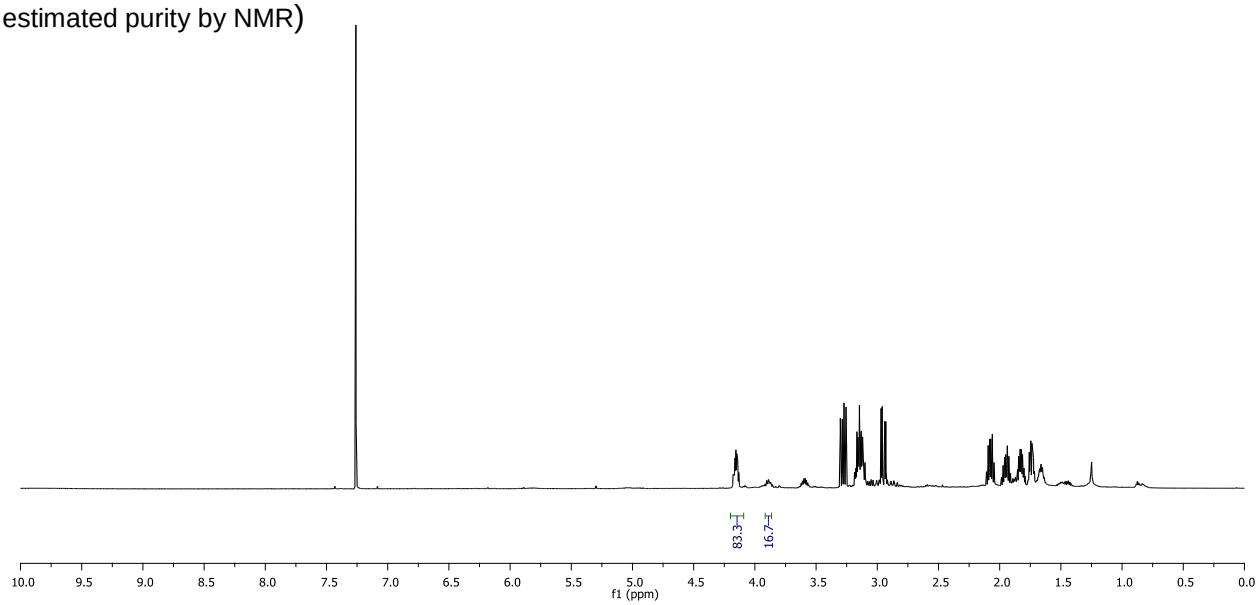
Group Gin dp-2-074f25-01142011
.* plaquerd dp-2-074f25-01142011 (11 1) C6D6 24.0C January_14,2011_10:29:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.
:Carbon C6D6 /opt/users/plaquerd plaquerd 16



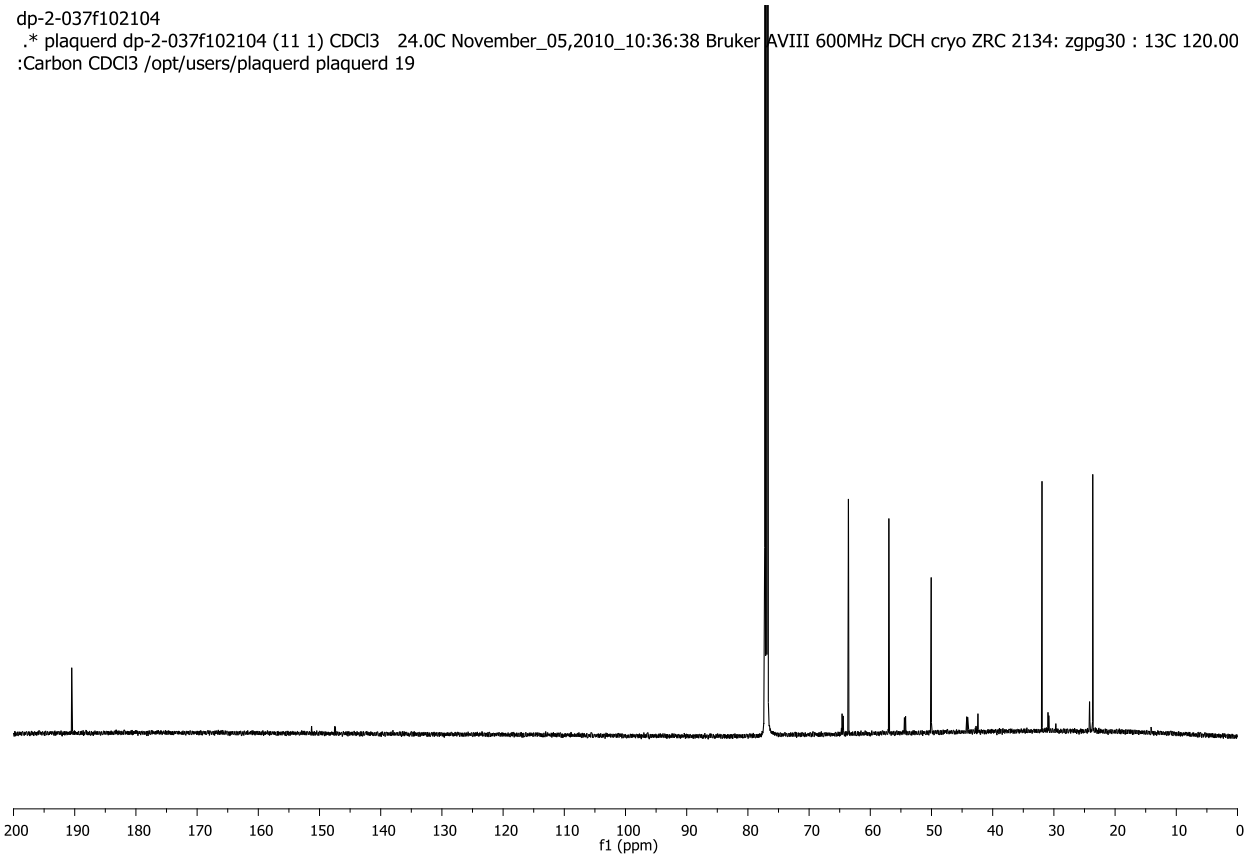
dp-2-037f102104
.* plaquerd dp-2-037f102104 (10 1) CDCl3 24.0C November_05,2010_10:35:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 19



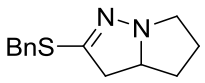
(83% estimated purity by NMR)



dp-2-037f102104
.* plaquerd dp-2-037f102104 (11 1) CDCl3 24.0C November_05,2010_10:36:38 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.00
:Carbon CDCl3 /opt/users/plaquerd plaquerd 19

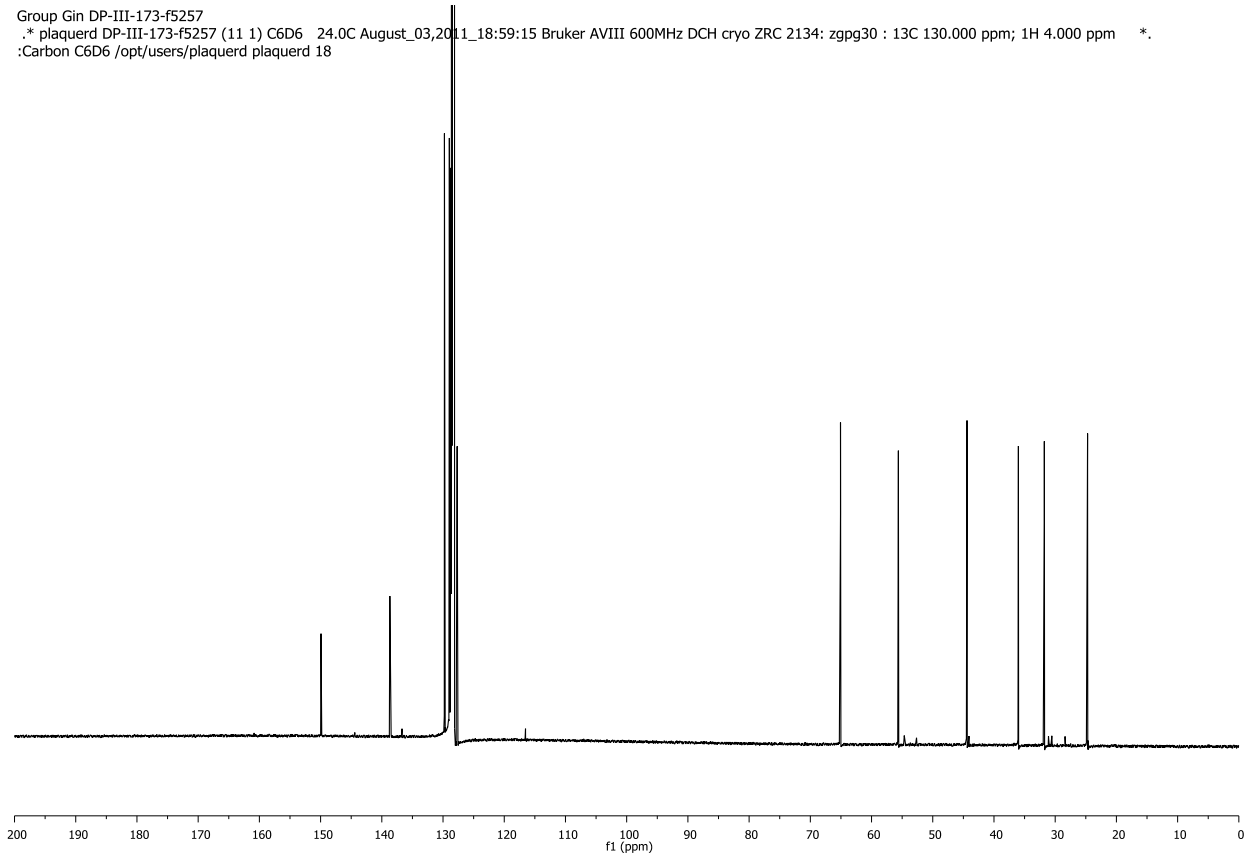


Group Gin DP-III-173-f5257
.* plaquerd DP-III-173-f5257 (10 1) C6D6 24.0C August_03,2011_18:57:25 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 18

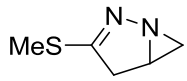


(98% estimated purity by NMR)

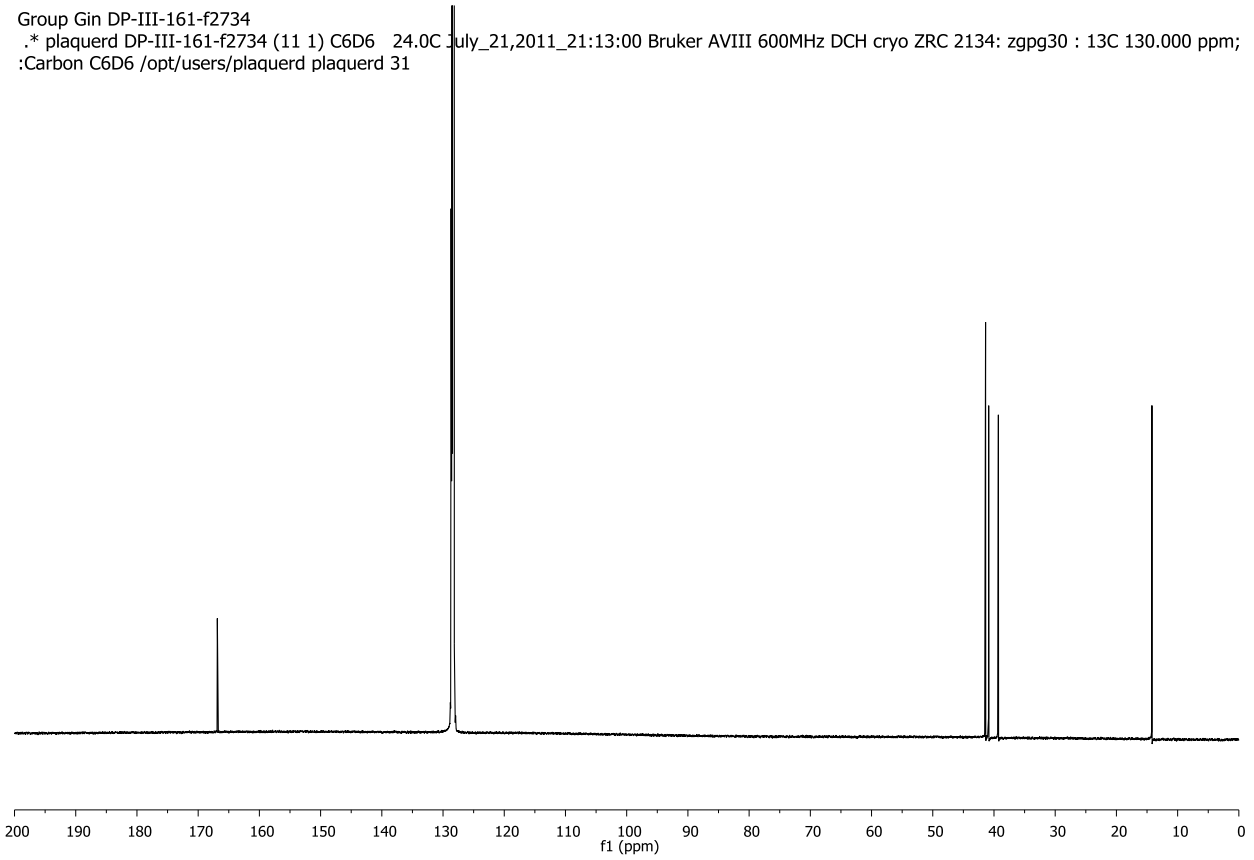
Group Gin DP-III-173-f5257
.* plaquerd DP-III-173-f5257 (11 1) C6D6 24.0C August_03,2011_18:59:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
:Carbon C6D6 /opt/users/plaquerd plaquerd 18



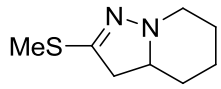
Group Gin DP-III-161-f2734
.* plaquerd DP-III-161-f2734 (10 1) C6D6 24.0C July_21,2011_21:11:03 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 31



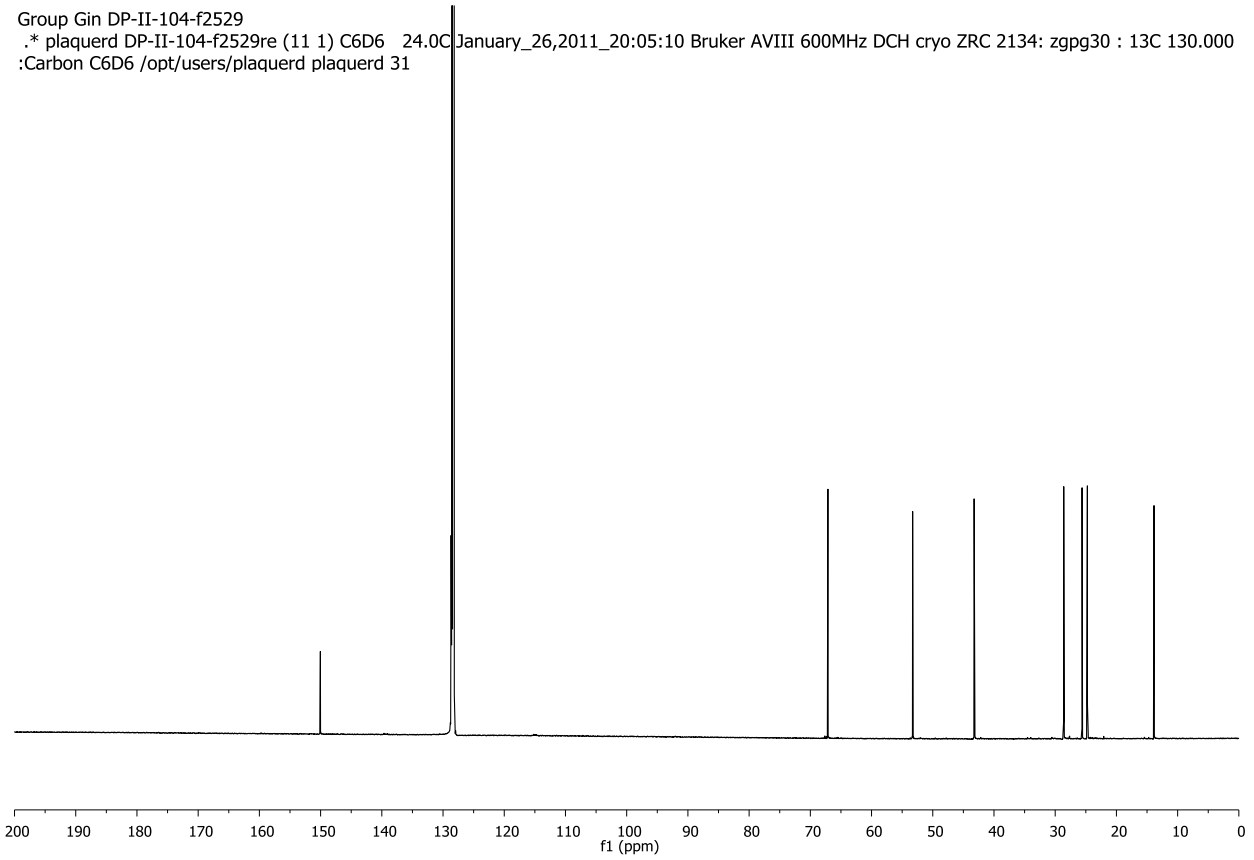
Group Gin DP-III-161-f2734
.* plaquerd DP-III-161-f2734 (11 1) C6D6 24.0C July_21,2011_21:13:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 31

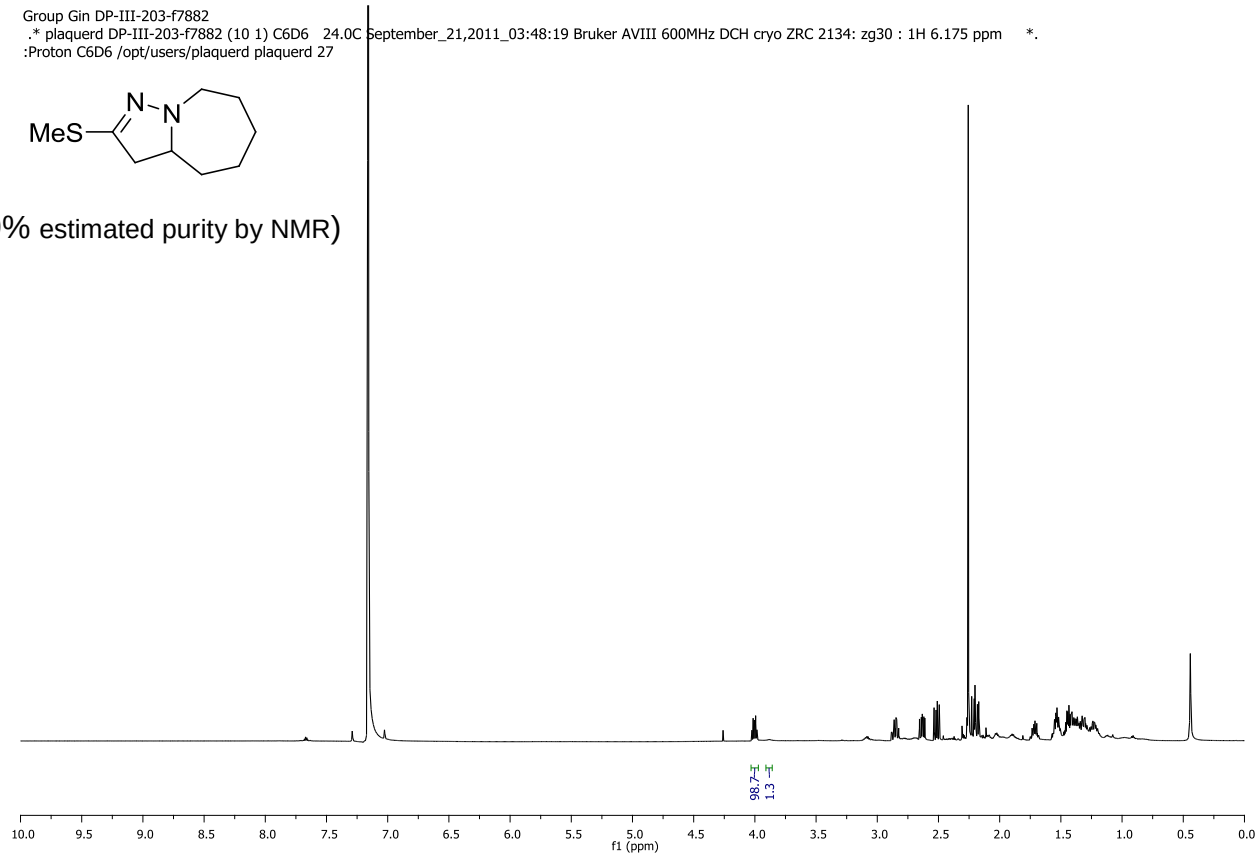


Group Gin DP-II-104-f2529
.* plaquerd DP-II-104-f2529re (10 1) C6D6 24.0C January_26,2011_20:03:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton C6D6 /opt/users/plaquerd plaquerd 31

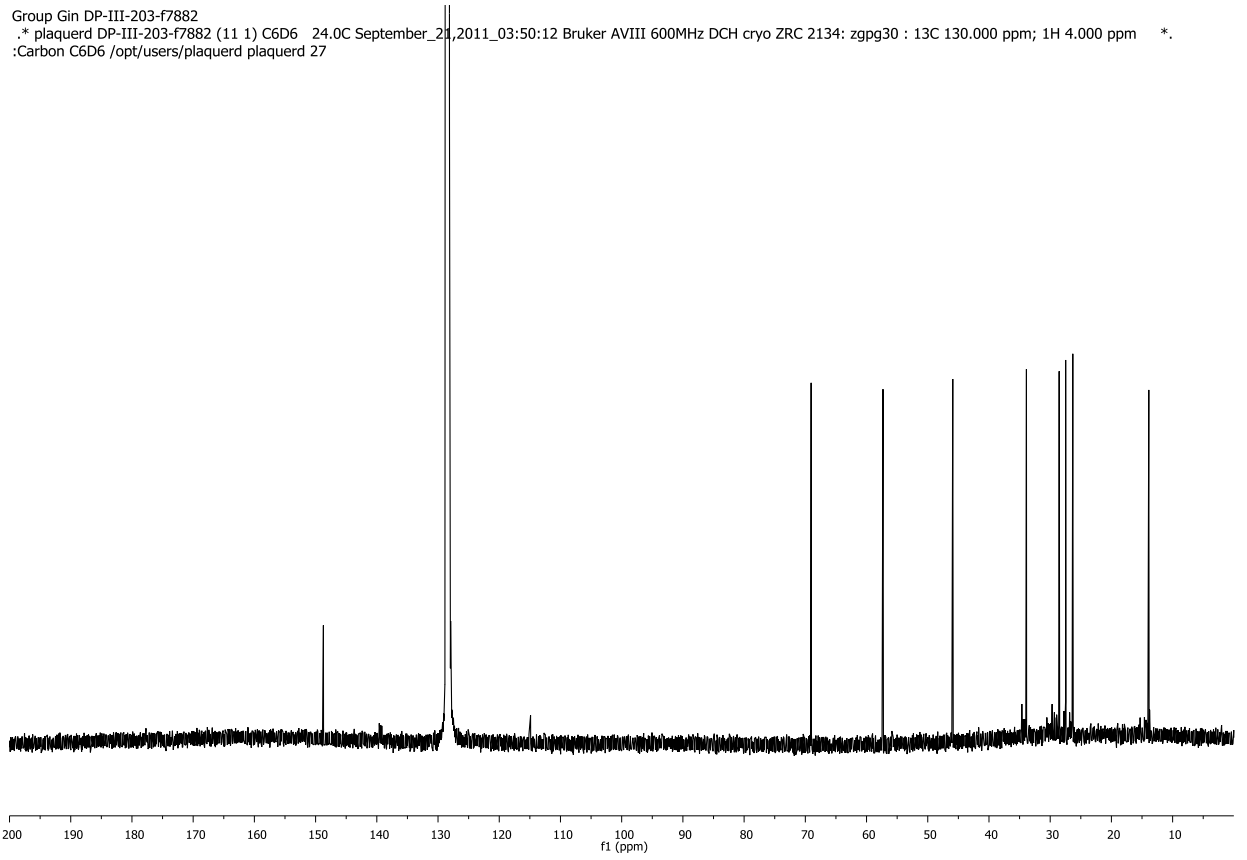


Group Gin DP-II-104-f2529
.* plaquerd DP-II-104-f2529re (11 1) C6D6 24.0C January_26,2011_20:05:10 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 31

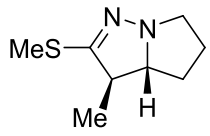




(99% estimated purity by NMR)

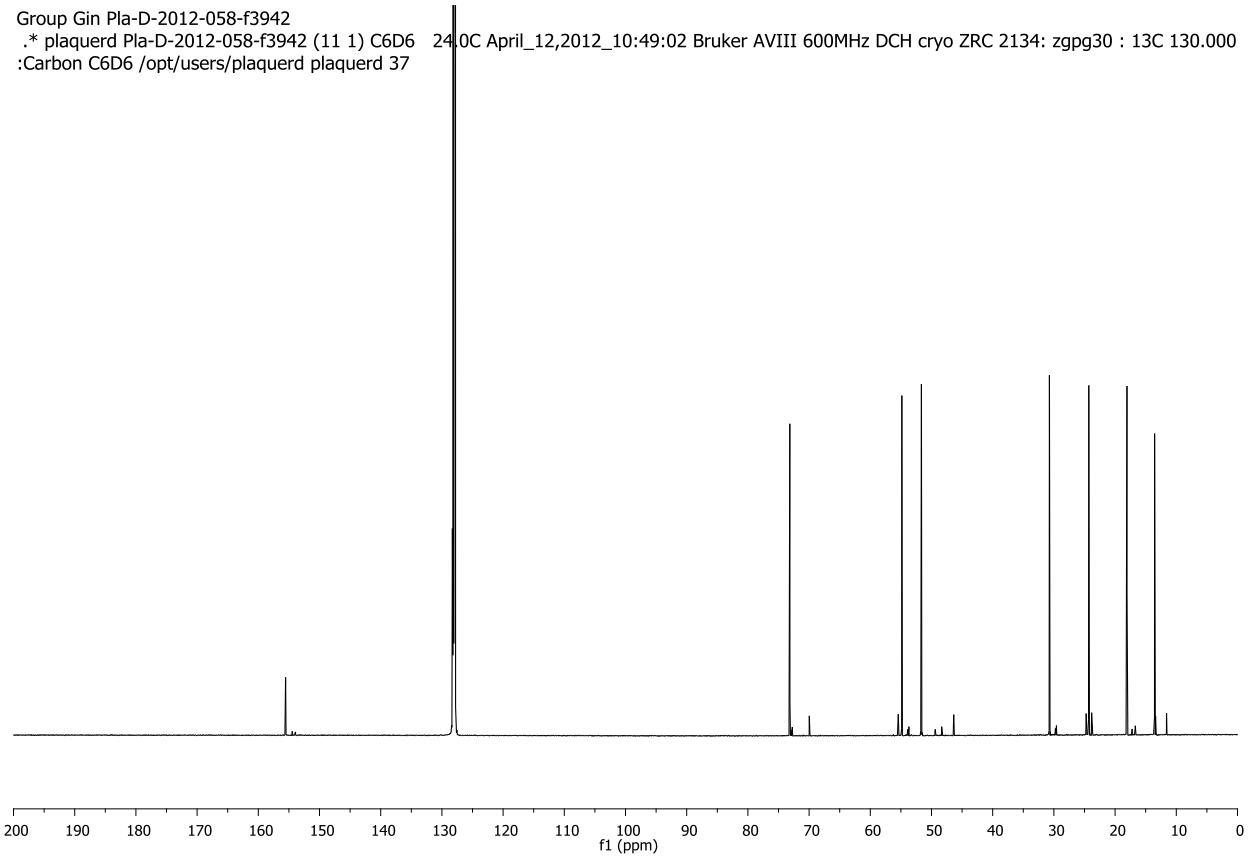


Group Gin Pla-D-2012-058-f3942
.* plaquerd Pla-D-2012-058-f3942 (10 1) C6D6 24.0C April_12,2012_10:47:10 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 37

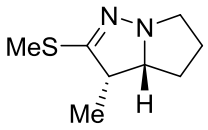


(19:1 dr)

Group Gin Pla-D-2012-058-f3942
.* plaquerd Pla-D-2012-058-f3942 (11 1) C6D6 24.0C April_12,2012_10:49:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 37

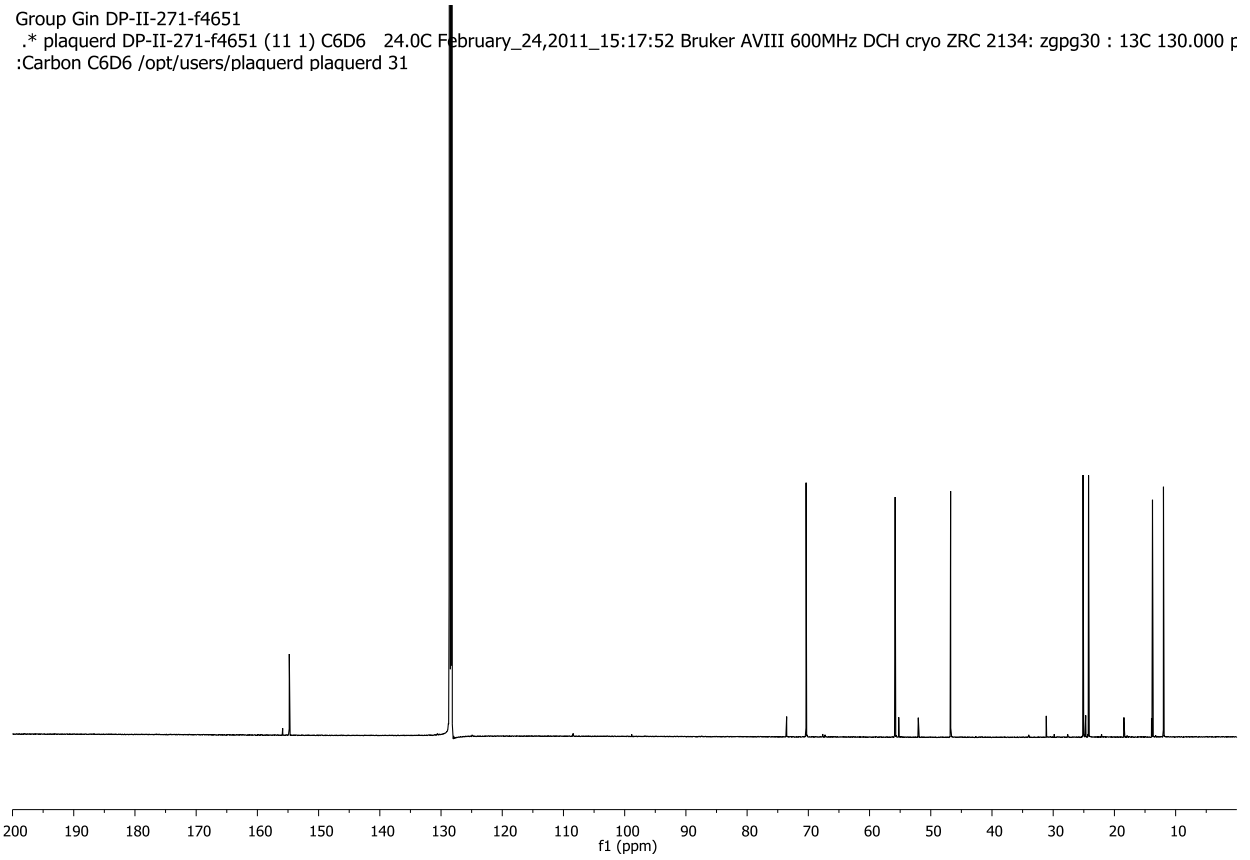


Group Gin DP-II-271-f4651
.* plaquerd DP-II-271-f4651 (10 1) C6D6 24.0C February_24,2011_15:15:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 31

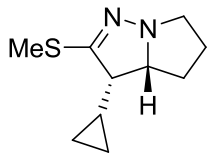


(19:1 dr)

Group Gin DP-II-271-f4651
.* plaquerd DP-II-271-f4651 (11 1) C6D6 24.0C February_24,2011_15:17:52 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 31

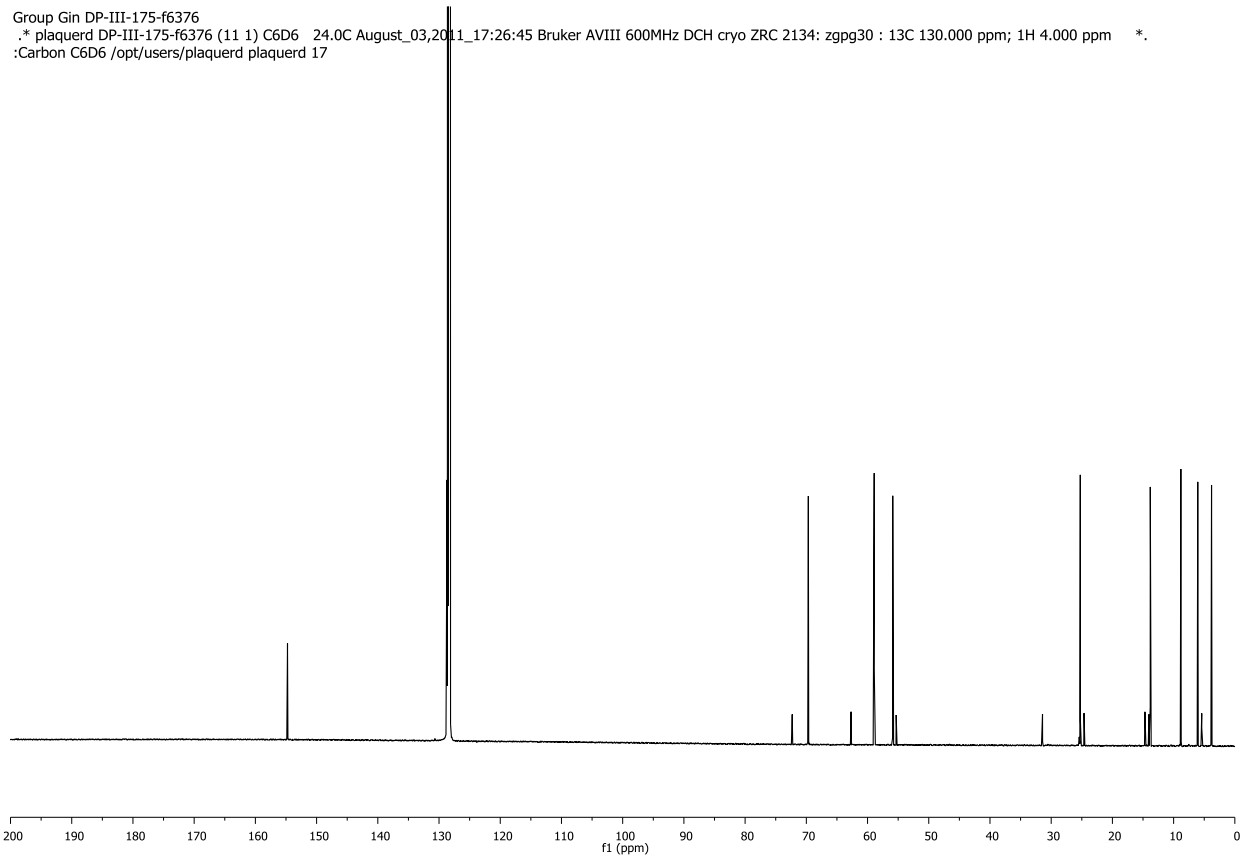


Group Gin DP-III-175-f6376
.* plaquerd DP-III-175-f6376 (10 1) C6D6 24.0C August_03,2011_17:24:51 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 17

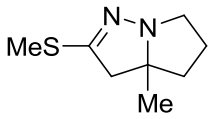


(18:2 dr)

Group Gin DP-III-175-f6376
.* plaquerd DP-III-175-f6376 (11 1) C6D6 24.0C August_03,2011_17:26:45 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
:Carbon C6D6 /opt/users/plaquerd plaquerd 17

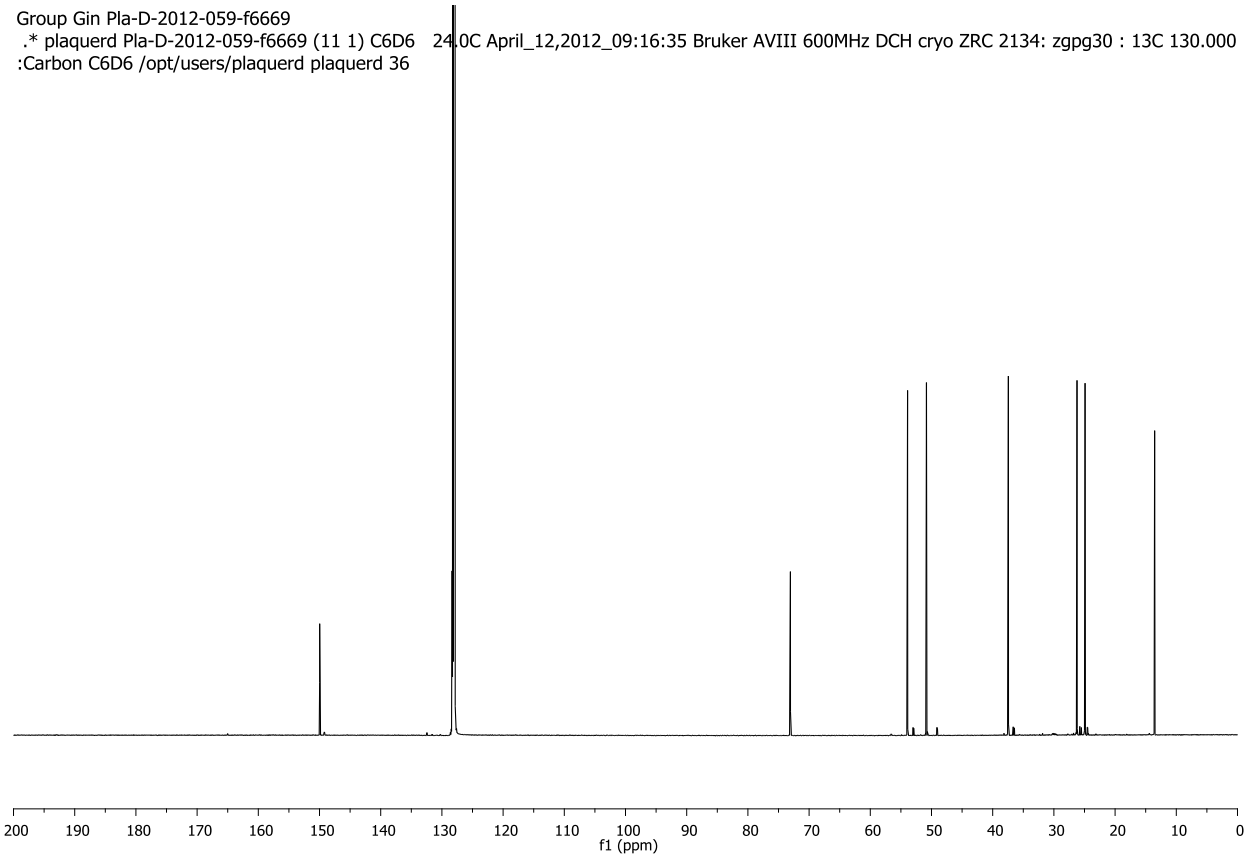


Group Gin Pla-D-2012-059-f6669
.* plaquerd Pla-D-2012-059-f6669 (10 1) C6D6 24.0C April_12,2012_09:14:45 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 36

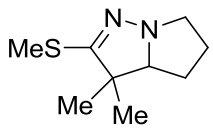


(99% estimated purity by NMR)

Group Gin Pla-D-2012-059-f6669
.* plaquerd Pla-D-2012-059-f6669 (11 1) C6D6 24.0C April_12,2012_09:16:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 36

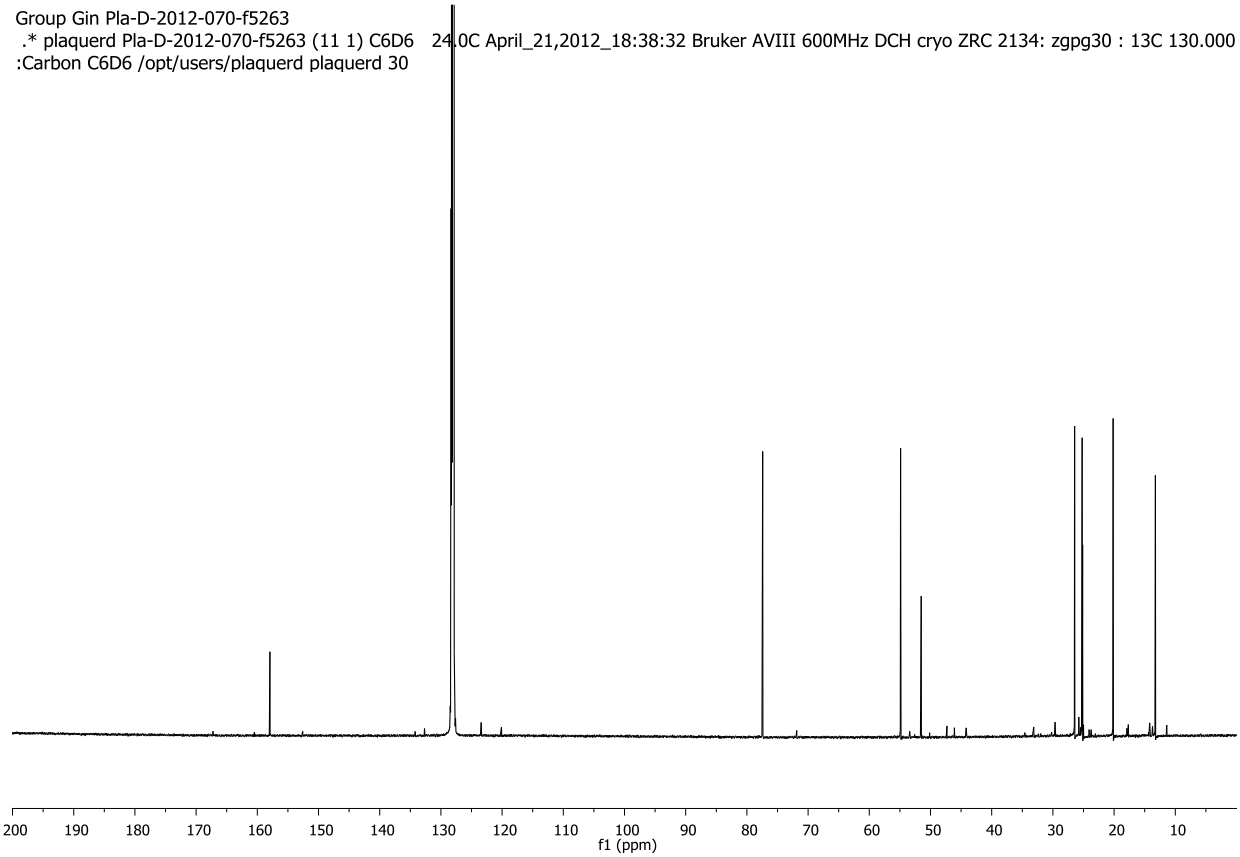


Group Gin Pla-D-2012-070-f5263
.* plaquerd Pla-D-2012-070-f5263 (10 1) C6D6 24.0C April_21,2012_18:36:40 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 30

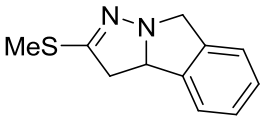


(96% estimated purity by NMR)

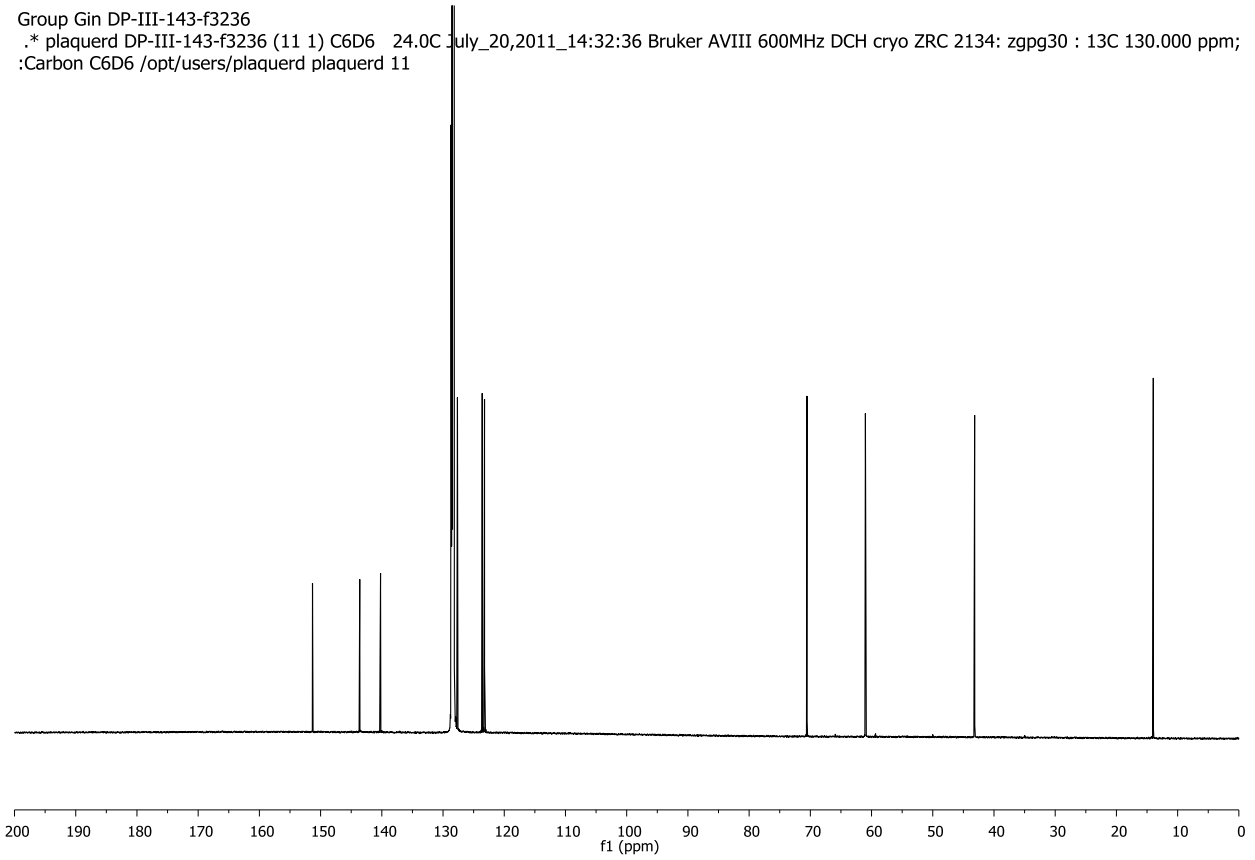
Group Gin Pla-D-2012-070-f5263
.* plaquerd Pla-D-2012-070-f5263 (11 1) C6D6 24.0C April_21,2012_18:38:32 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 30



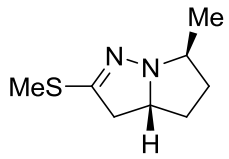
Group Gin DP-III-143-f3236
.* plaquerd DP-III-143-f3236 (10 1) C6D6 24.0C July_20,2011_14:30:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 11



Group Gin DP-III-143-f3236
.* plaquerd DP-III-143-f3236 (11 1) C6D6 24.0C July_20,2011_14:32:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 11

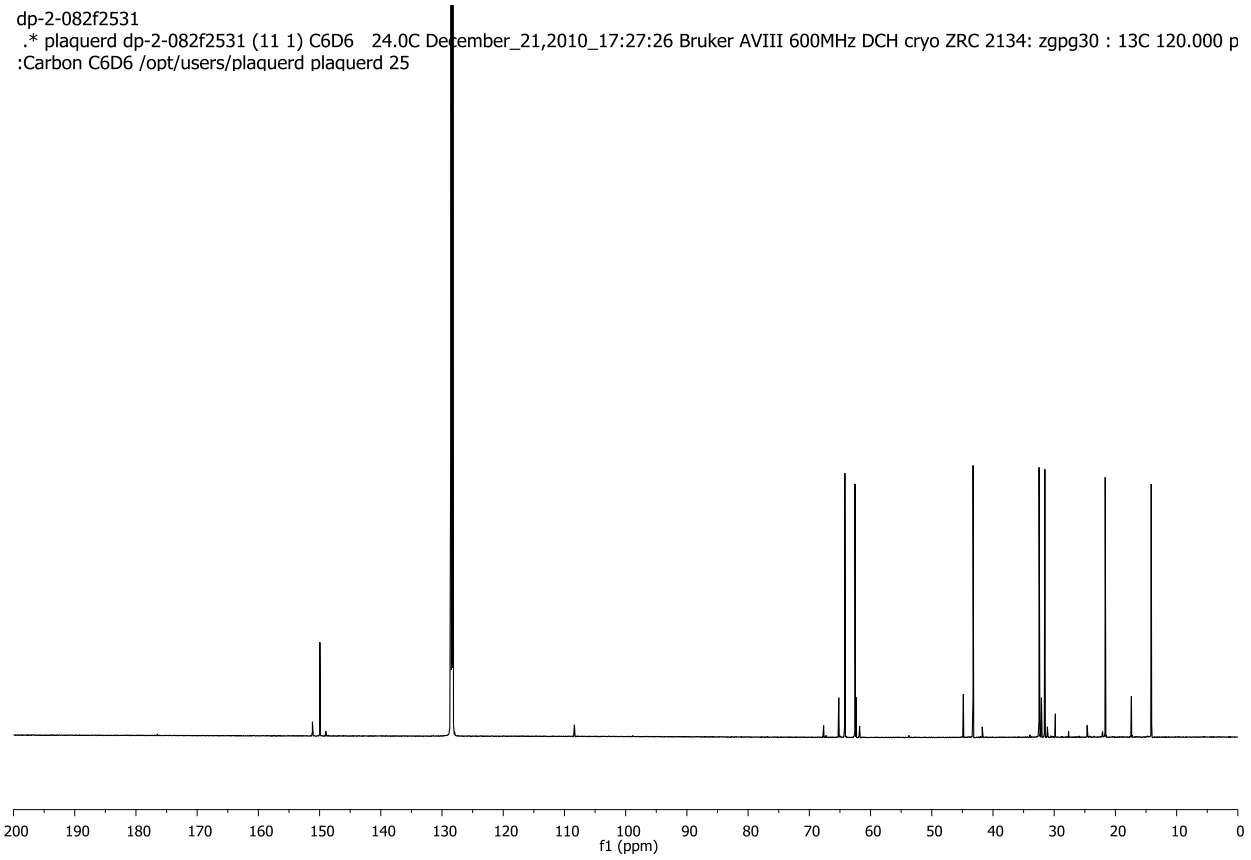


dp-2-082f2531
.* plaquerd dp-2-082f2531 (10 1) C6D6 24.0C December_21,2010_17:25:13 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 25

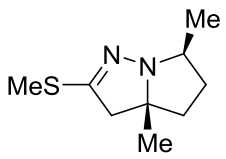


(17:3 dr)

dp-2-082f2531
.* plaquerd dp-2-082f2531 (11 1) C6D6 24.0C December_21,2010_17:27:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 25

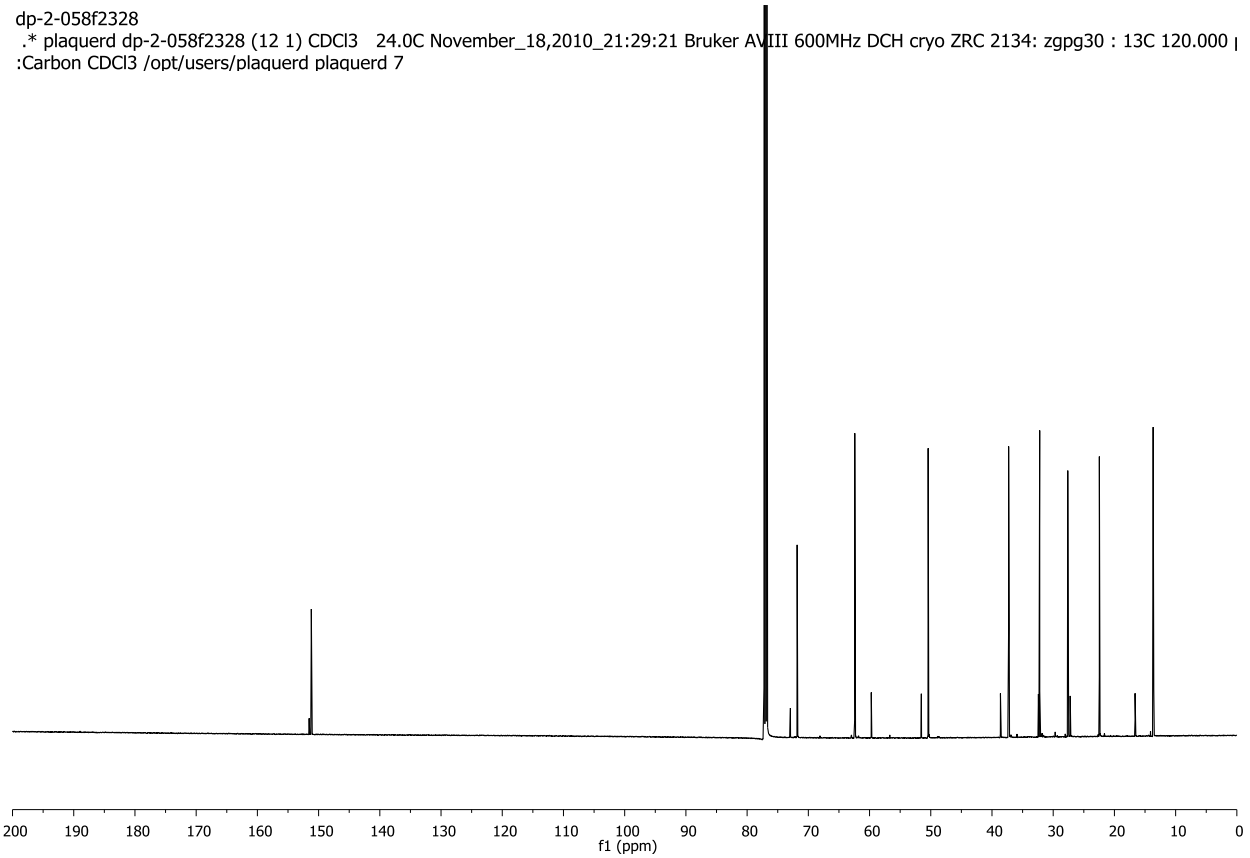


dp-2-058f2328
.* plaquerd dp-2-058f2328 (10 1) CDCl3 24.0C November_18,2010_21:27:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 7

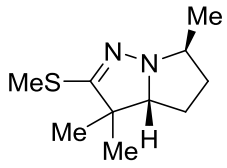


(18:2 dr)

dp-2-058f2328
.* plaquerd dp-2-058f2328 (12 1) CDCl3 24.0C November_18,2010_21:29:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 7

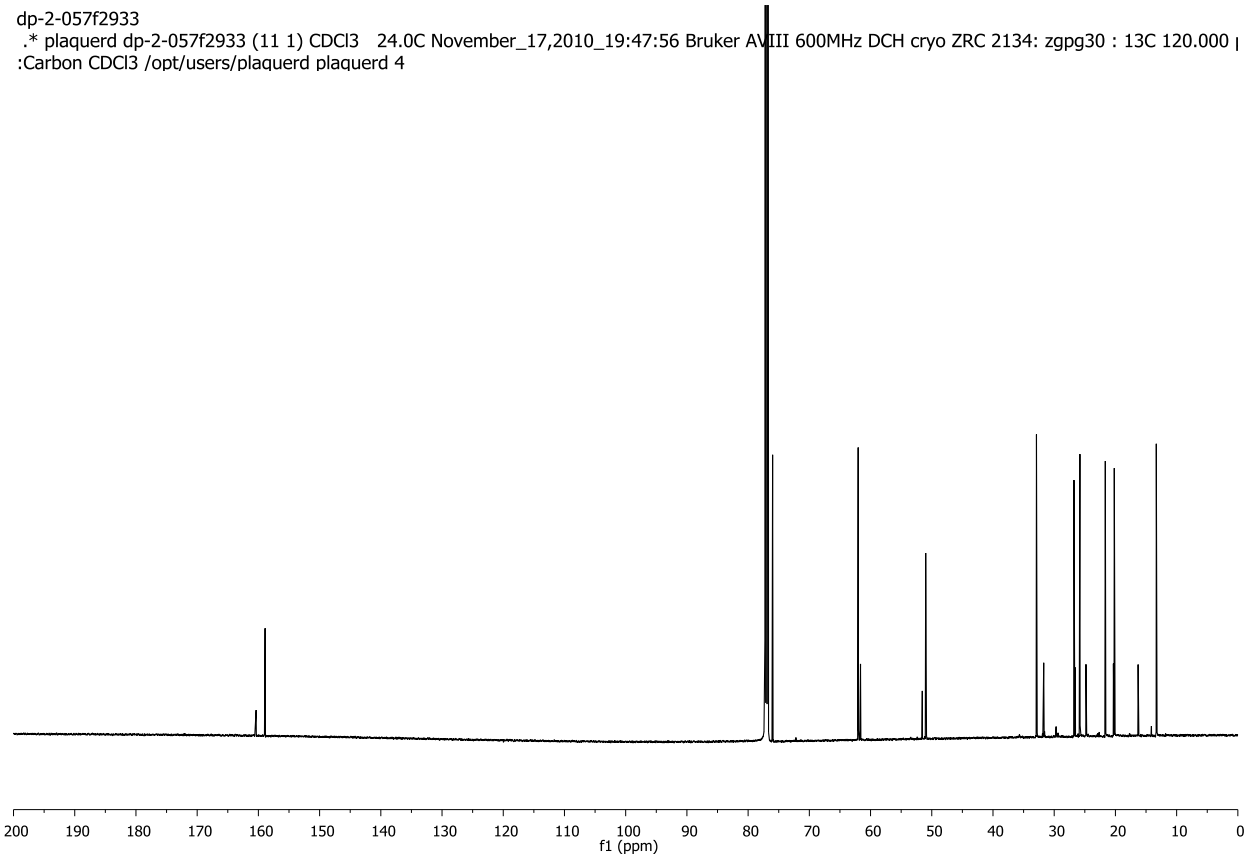


dp-2-057f2933
.* plaquerd dp-2-057f2933 (10 1) CDCl3 24.0C November_17,2010_19:46:06 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 4

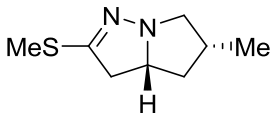


(16:4 dr)

dp-2-057f2933
.* plaquerd dp-2-057f2933 (11 1) CDCl3 24.0C November_17,2010_19:47:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 4

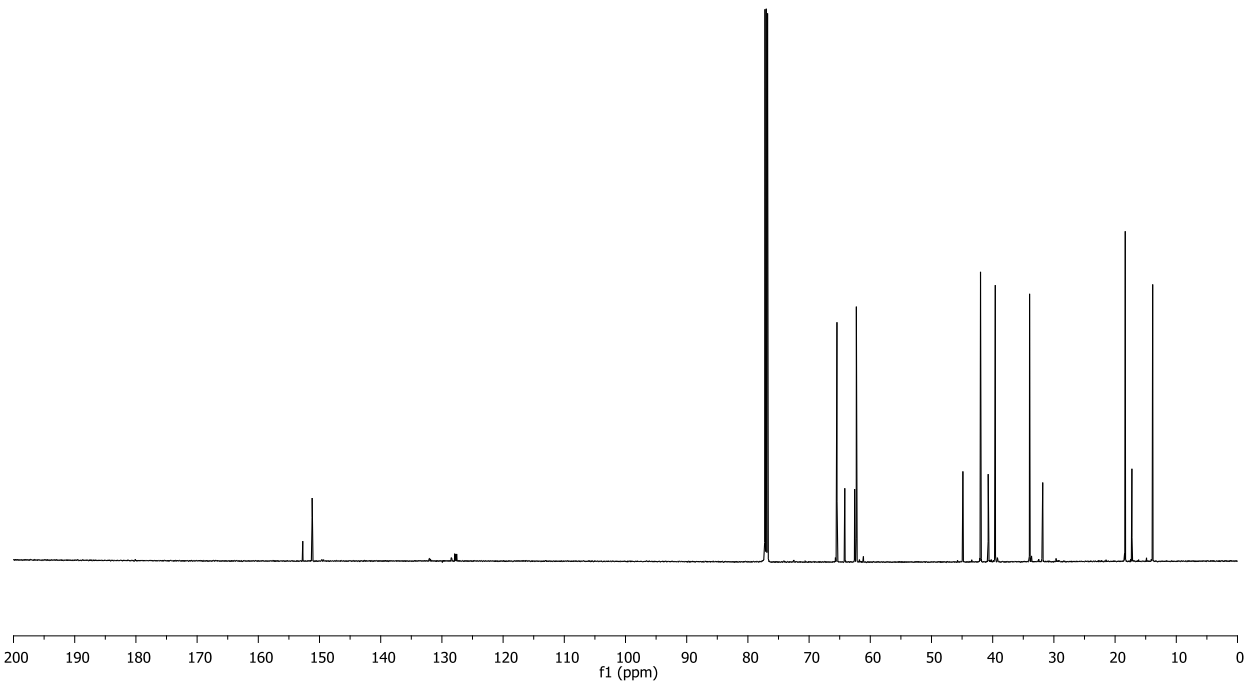


Group Gin Pla-D-2012-060-f1520-CDCl3
.* plaquerd Pla-D-2012-060-f1520-CDCl3 (10 1) CDCl3 24.0C April_21,2012_15:35:57 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 29

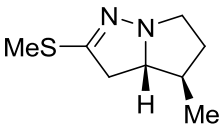


(16:4 dr)

Group Gin Pla-D-2012-060-f1520-CDCl3
.* plaquerd Pla-D-2012-060-f1520-CDCl3 (11 1) CDCl3 24.0C April_21,2012_15:37:57 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 1
:Carbon CDCl3 /opt/users/plaquerd plaquerd 29

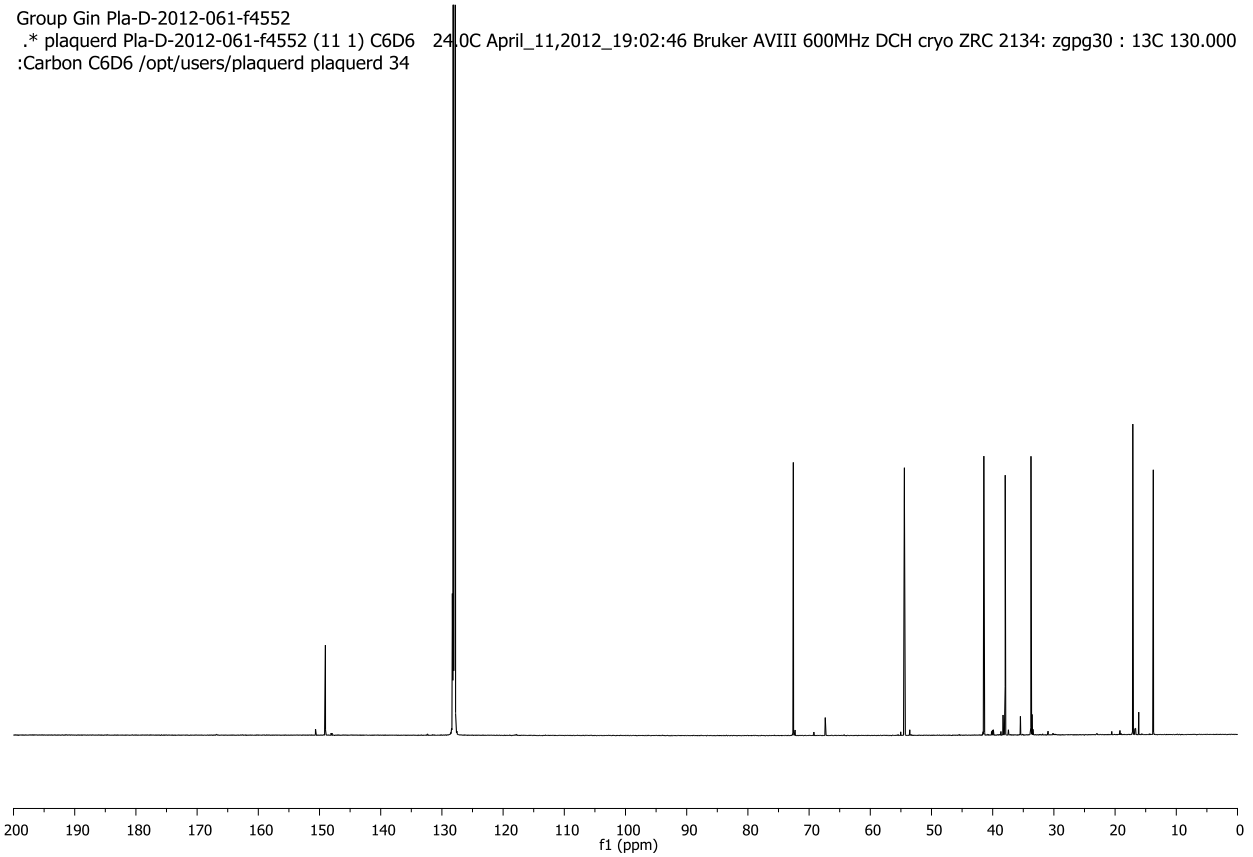


Group Gin Pla-D-2012-061-f4552
.* plaquerd Pla-D-2012-061-f4552 (10 1) C6D6 24.0C April_11,2012_19:00:55 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 34

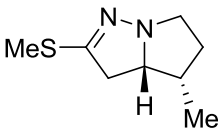


(>20:1 dr)

Group Gin Pla-D-2012-061-f4552
.* plaquerd Pla-D-2012-061-f4552 (11 1) C6D6 24.0C April_11,2012_19:02:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 34

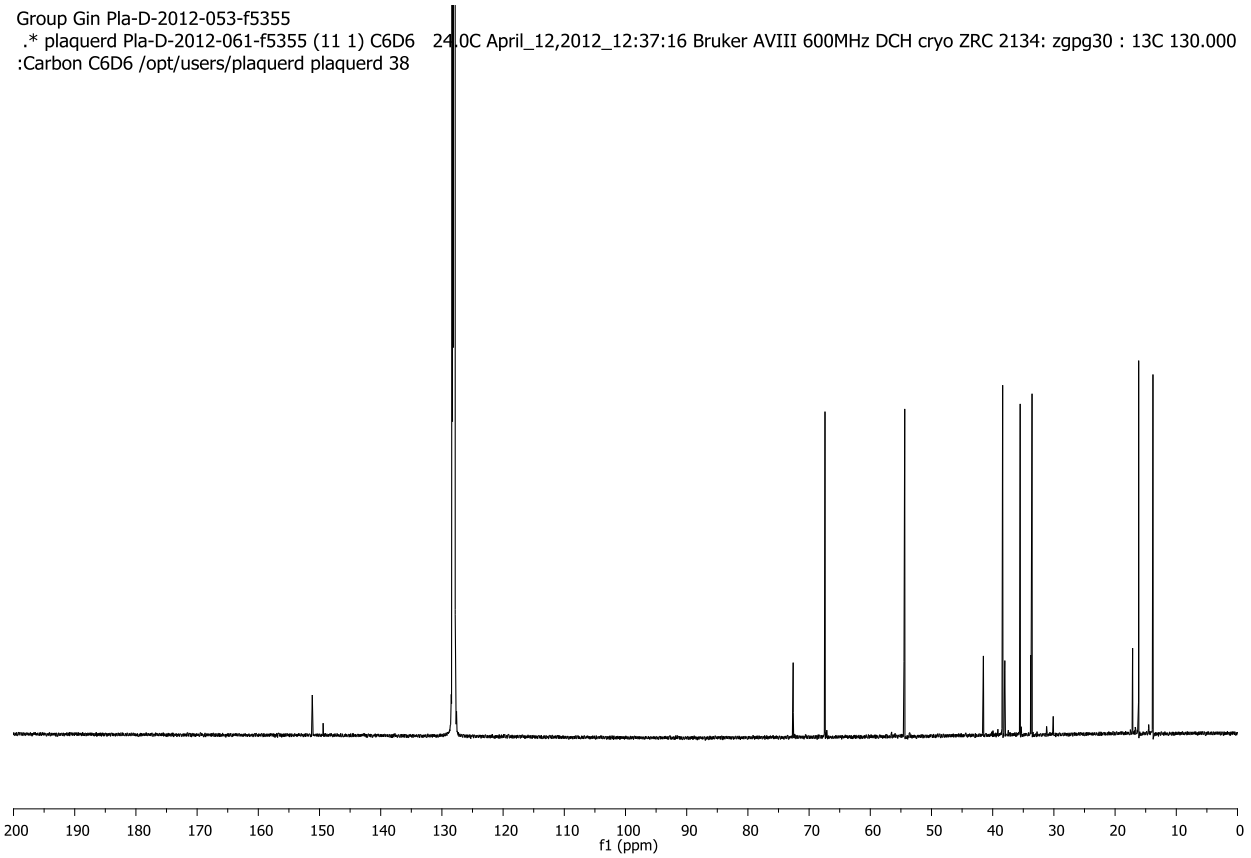


Group Gin Pla-D-2012-053-f5355
.* plaquerd Pla-D-2012-061-f5355 (10 1) C6D6 24.0C April_12,2012_12:35:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 38

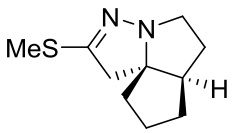


(17:3 dr)

Group Gin Pla-D-2012-053-f5355
.* plaquerd Pla-D-2012-061-f5355 (11 1) C6D6 24.0C April_12,2012_12:37:16 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon C6D6 /opt/users/plaquerd plaquerd 38

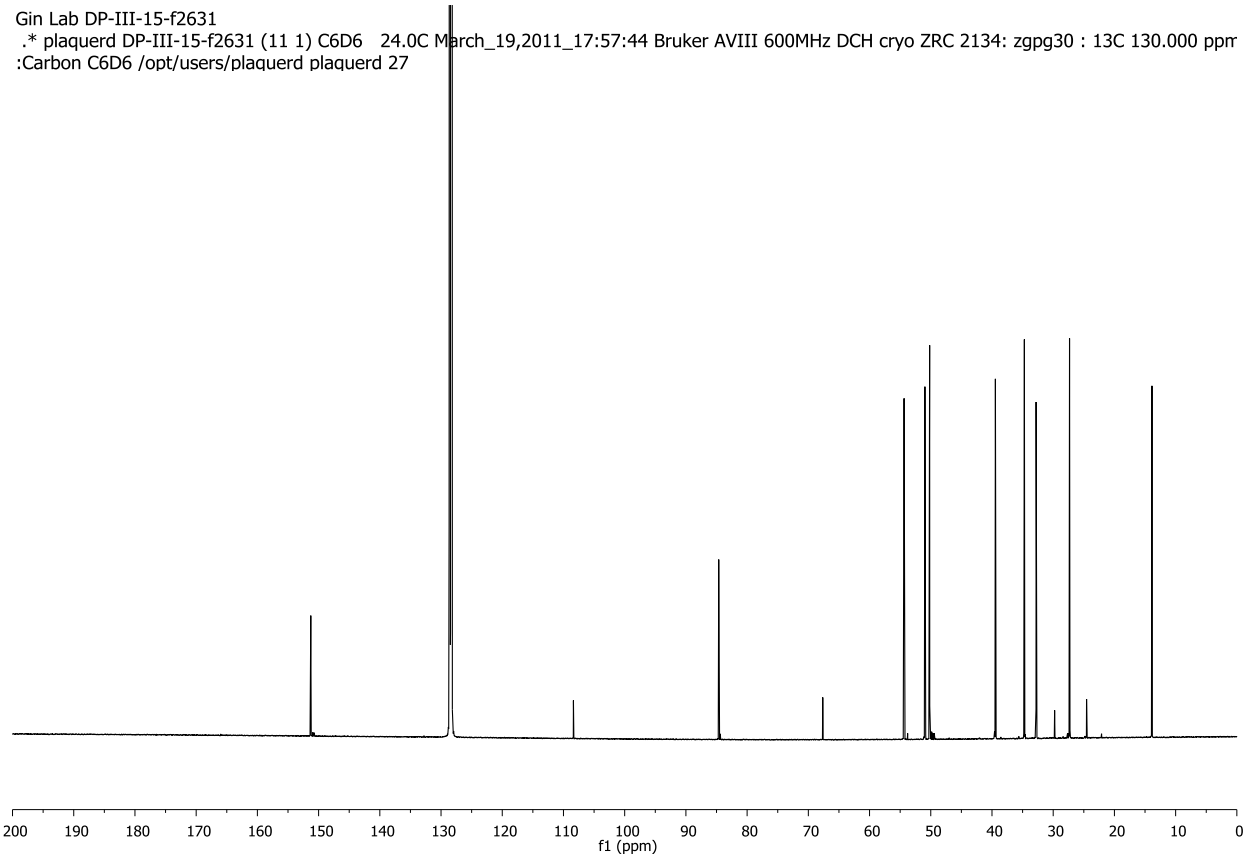


Gin Lab DP-III-15-f2631
.* plaquerd DP-III-15-f2631 (10 1) C6D6 24.0C March_19,2011_17:55:23 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 27

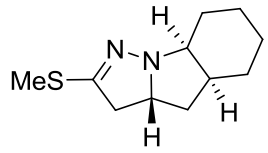


(19:1 dr)

Gin Lab DP-III-15-f2631
.* plaquerd DP-III-15-f2631 (11 1) C6D6 24.0C March_19,2011_17:57:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm
:Carbon C6D6 /opt/users/plaquerd plaquerd 27

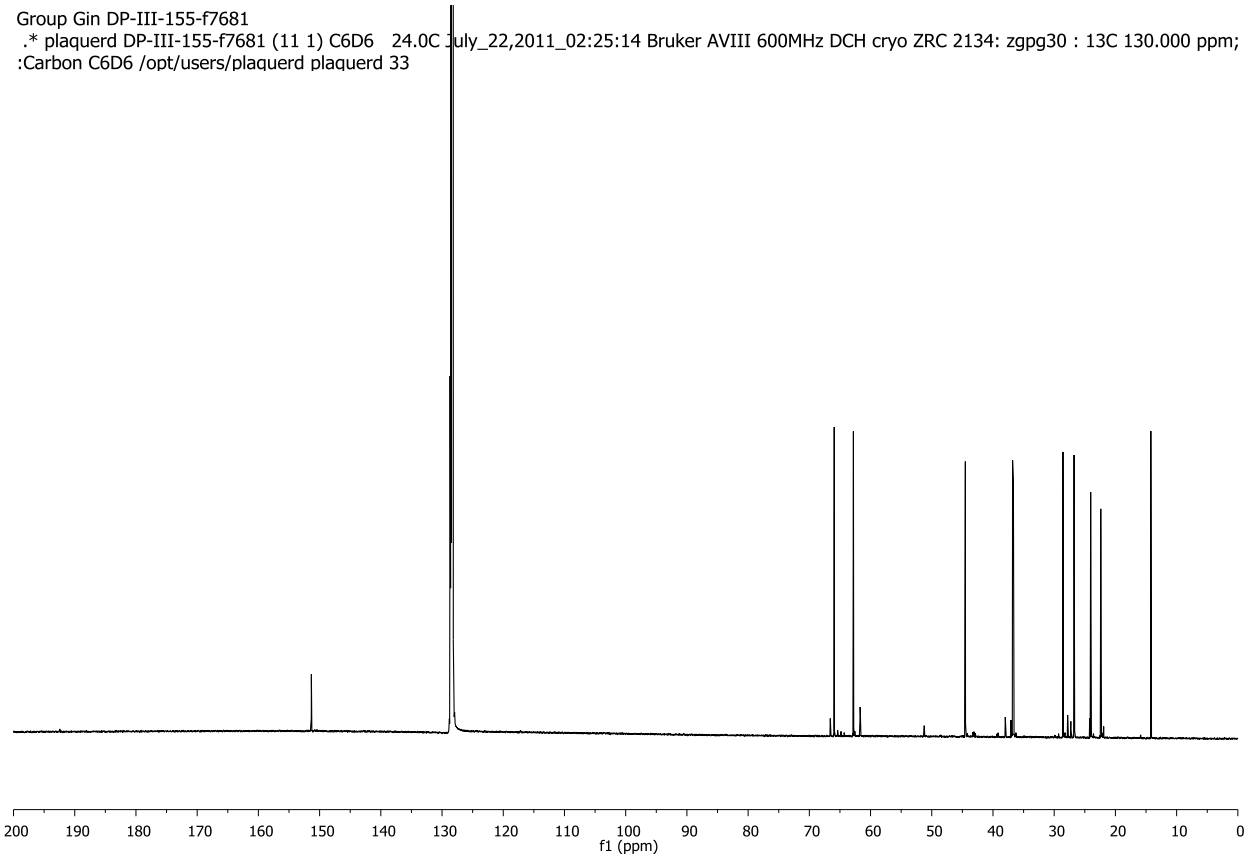


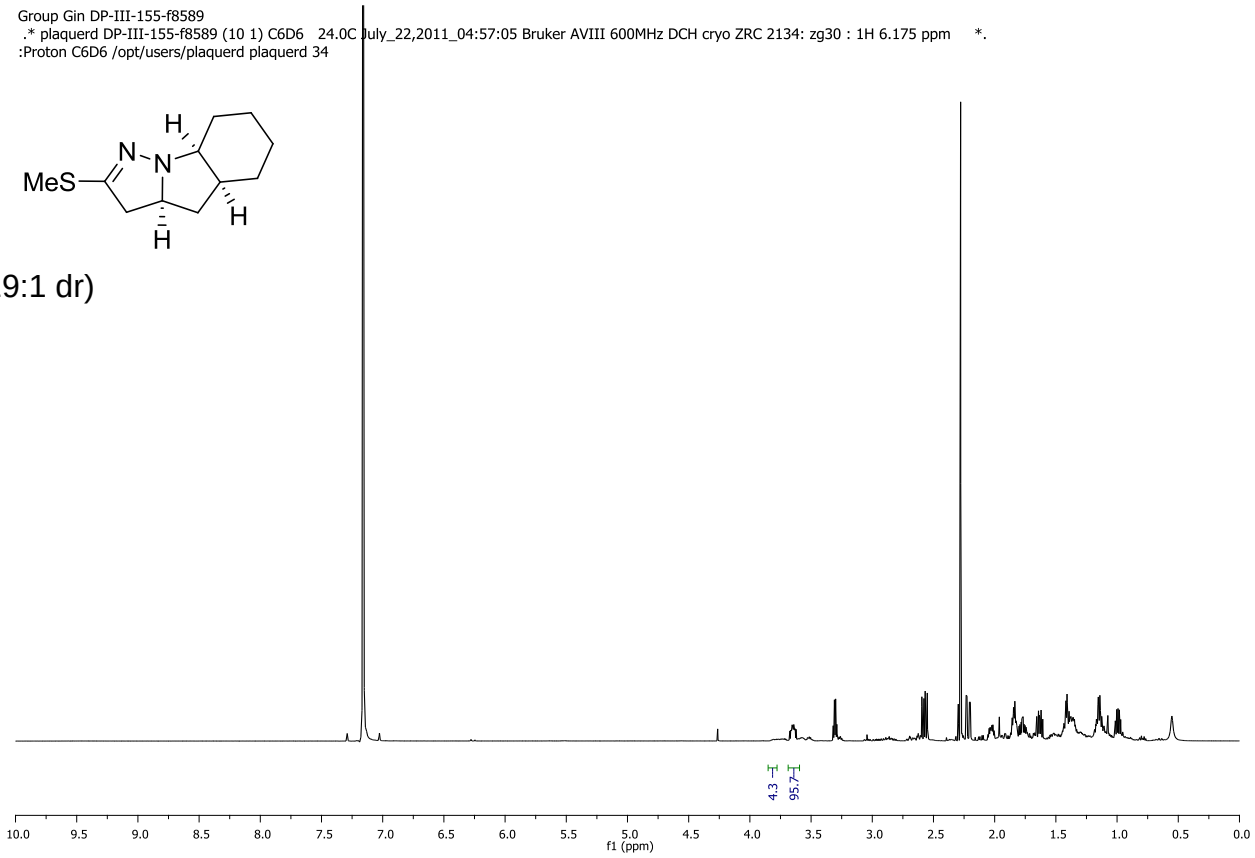
Group Gin DP-III-155-f7681
.* plaquerd DP-III-155-f7681 (10 1) C6D6 24.0C July_22,2011_02:23:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 33



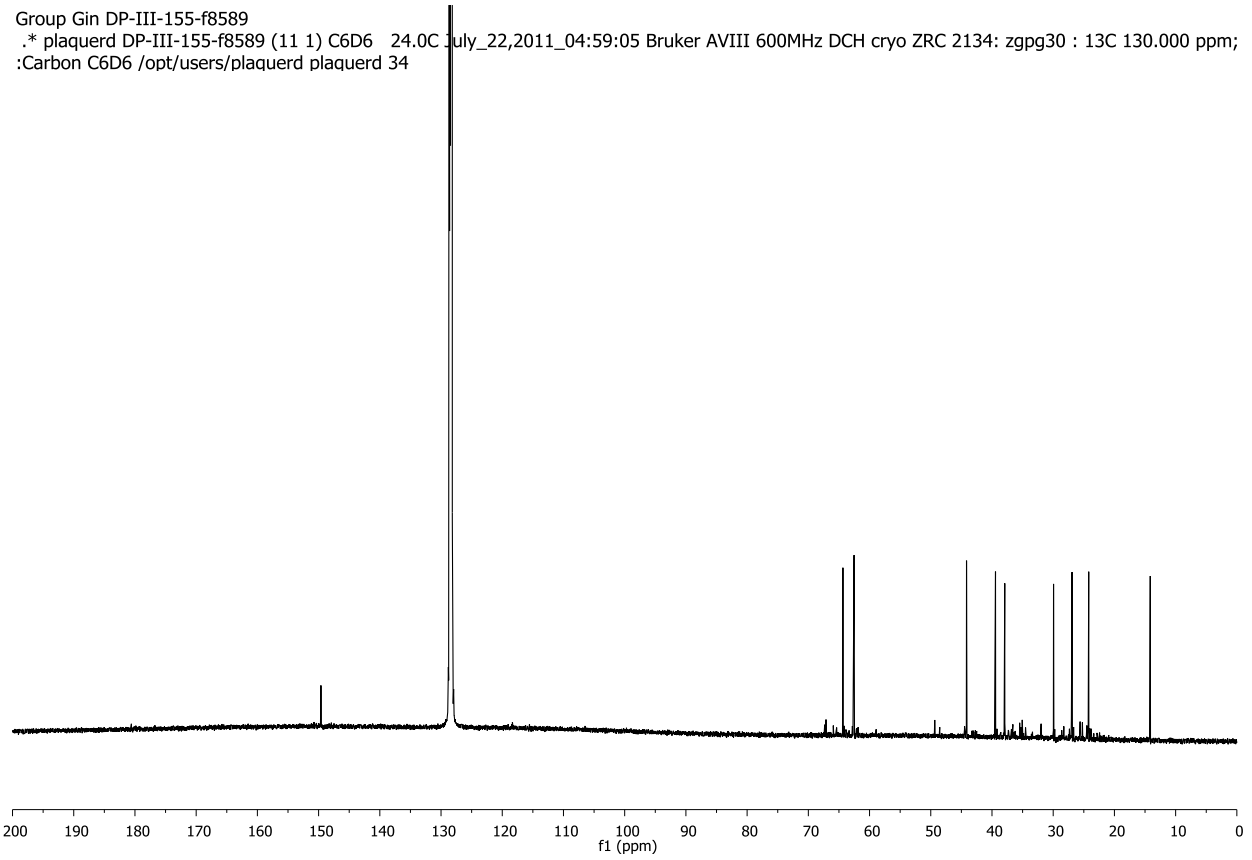
(19:1 dr)

Group Gin DP-III-155-f7681
.* plaquerd DP-III-155-f7681 (11 1) C6D6 24.0C July_22,2011_02:25:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 33

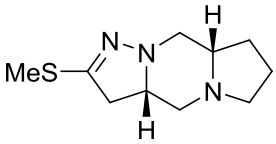



Group Gin DP-III-155-f8589
.* plaquerd DP-III-155-f8589 (10 1) C6D6 24.0C July_22,2011_04:57:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 34
MeS
N
N
H
H
H
4.3
95.7
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(19:1 dr)

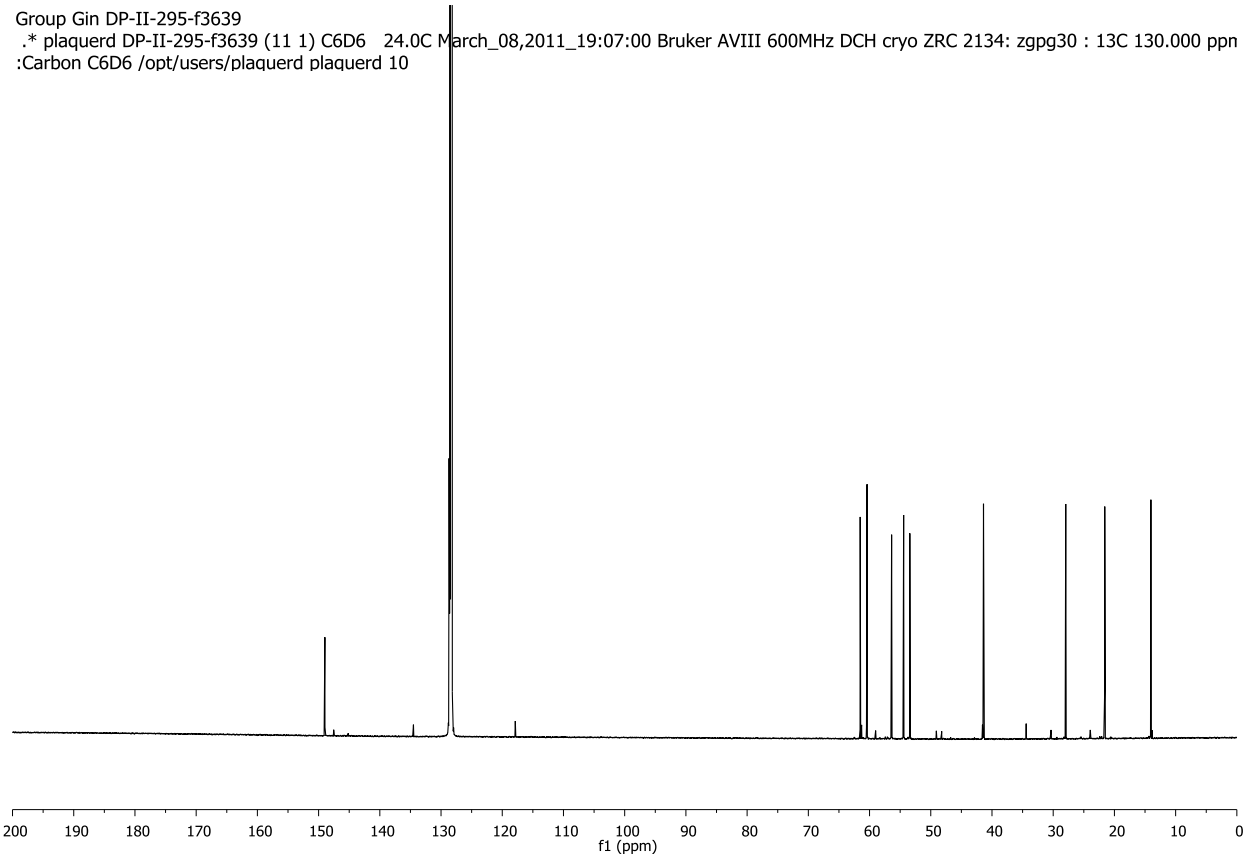

Group Gin DP-III-155-f8589
.* plaquerd DP-III-155-f8589 (11 1) C6D6 24.0C July_22,2011_04:59:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Group Gin DP-II-295-f3639
.* plaquerd DP-II-295-f3639 (10 1) C6D6 24.0C March_08,2011_19:04:40 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 10

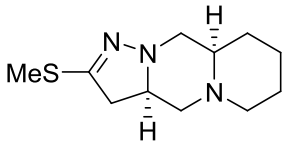


(98% estimated purity by NMR)

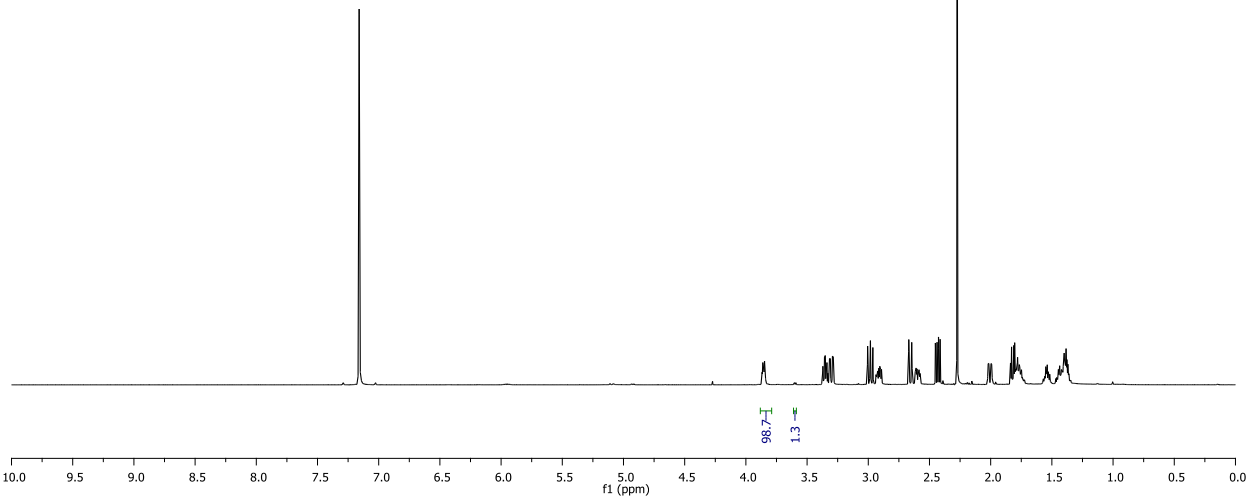
Group Gin DP-II-295-f3639
.* plaquerd DP-II-295-f3639 (11 1) C6D6 24.0C March_08,2011_19:07:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppn
:Carbon C6D6 /opt/users/plaquerd plaquerd 10



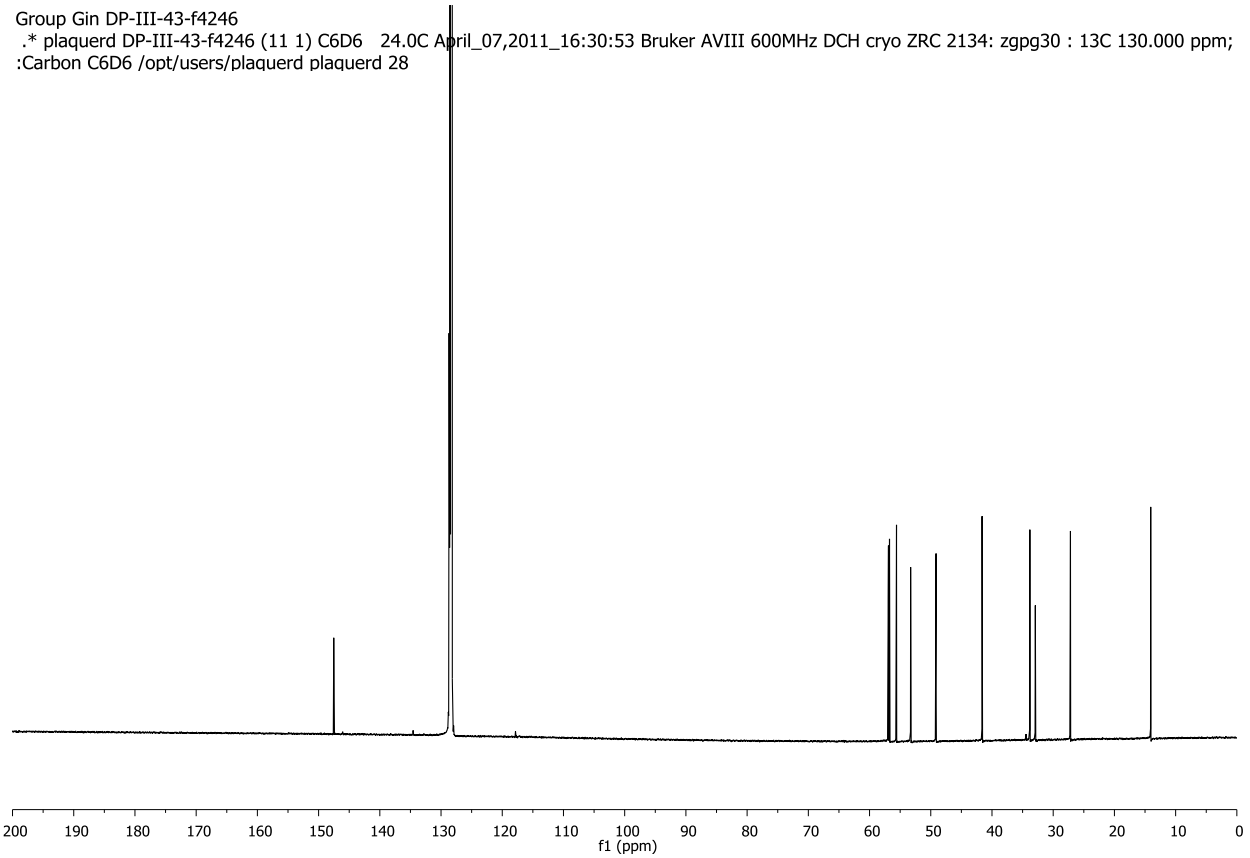
Group Gin DP-III-43-f4246
.* plaquerd DP-III-43-f4246 (10 1) C6D6 24.0C April_07,2011_16:29:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 28



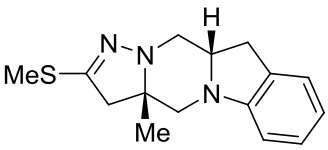
(99% estimated purity by NMR)



Group Gin DP-III-43-f4246
.* plaquerd DP-III-43-f4246 (11 1) C6D6 24.0C April_07,2011_16:30:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 28

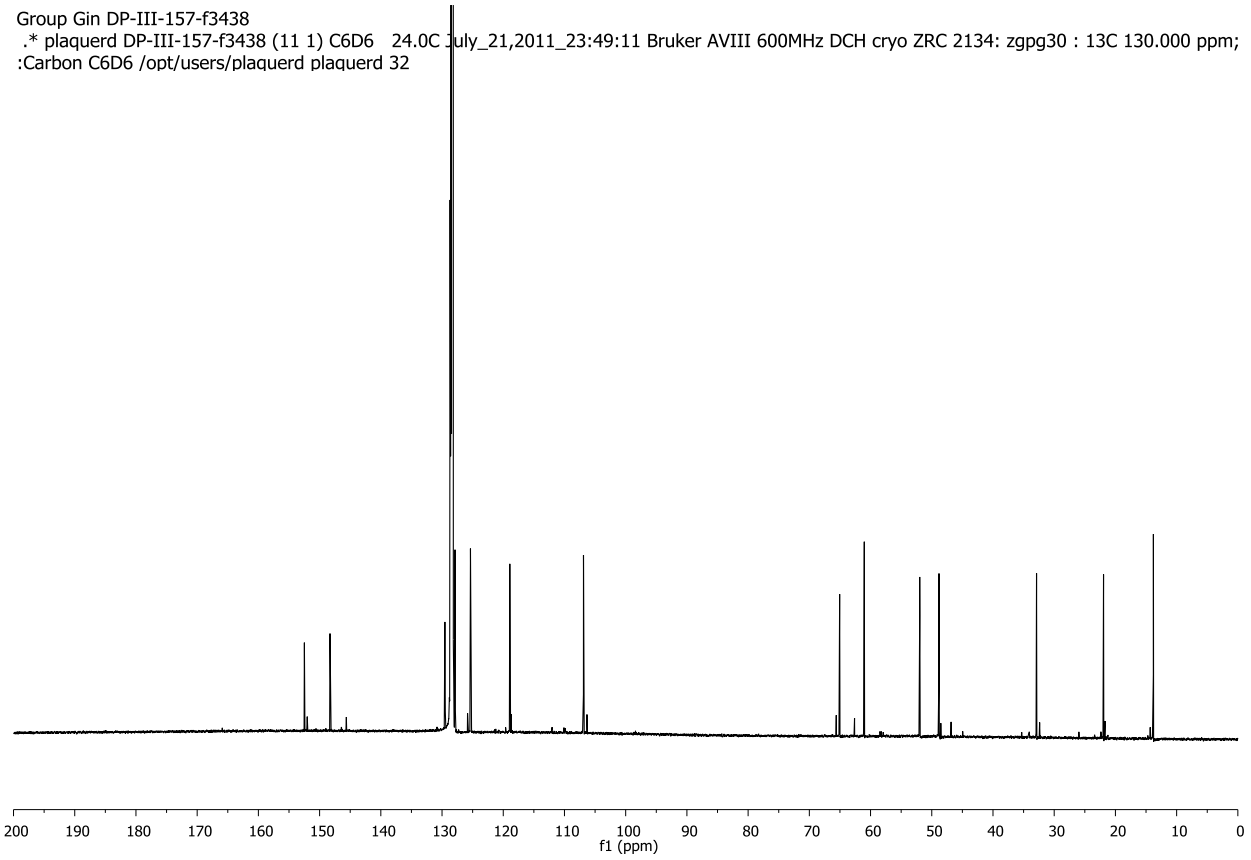


Group Gin DP-III-157-f3438
.* plaquerd DP-III-157-f3438 (10 1) C6D6 24.0C July_21,2011_23:47:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 32

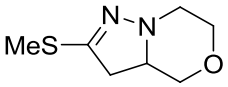


(18:2 dr)

Group Gin DP-III-157-f3438
.* plaquerd DP-III-157-f3438 (11 1) C6D6 24.0C July_21,2011_23:49:11 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 32

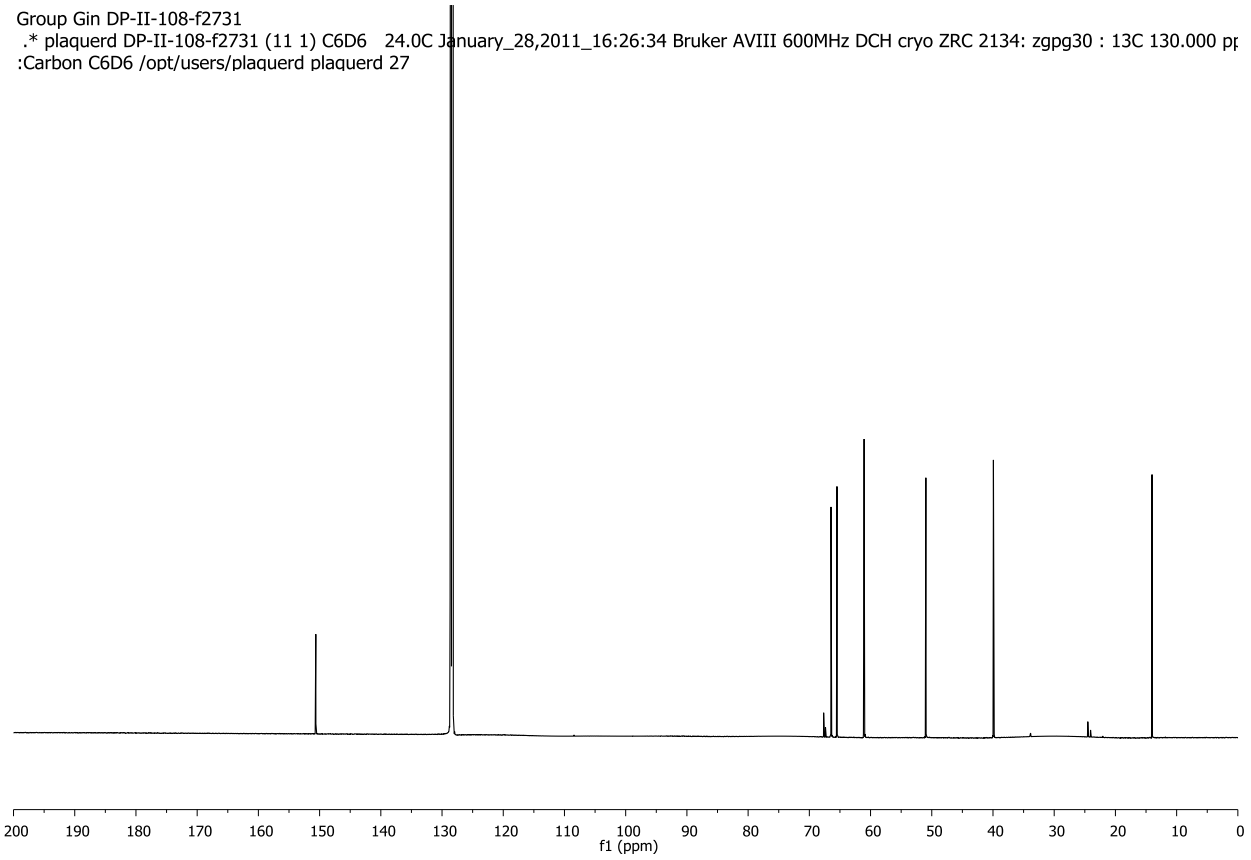


Group Gin DP-II-108-f2731
.* plaquerd DP-II-108-f2731 (10 1) C6D6 24.0C January_28,2011_16:24:42 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 27

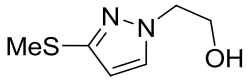


(98% estimated purity by NMR)

Group Gin DP-II-108-f2731
.* plaquerd DP-II-108-f2731 (11 1) C6D6 24.0C January_28,2011_16:26:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 pp
:Carbon C6D6 /opt/users/plaquerd plaquerd 27

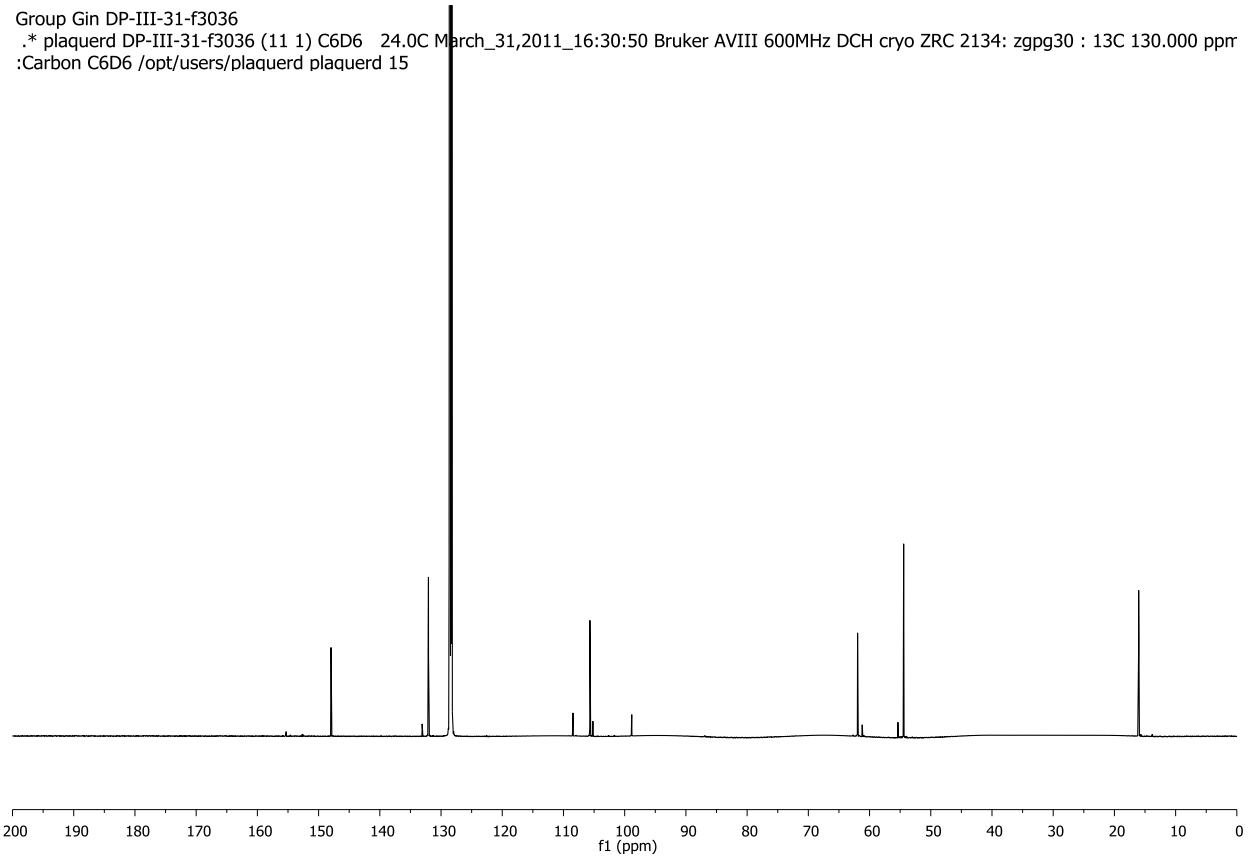


Group Gin DP-III-31-f3036
.* plaquerd DP-III-31-f3036 (10 1) C6D6 24.0C March_31,2011_16:28:22 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 15

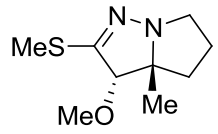


(97% estimated purity by NMR)

Group Gin DP-III-31-f3036
.* plaquerd DP-III-31-f3036 (11 1) C6D6 24.0C March_31,2011_16:30:50 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm
:Carbon C6D6 /opt/users/plaquerd plaquerd 15

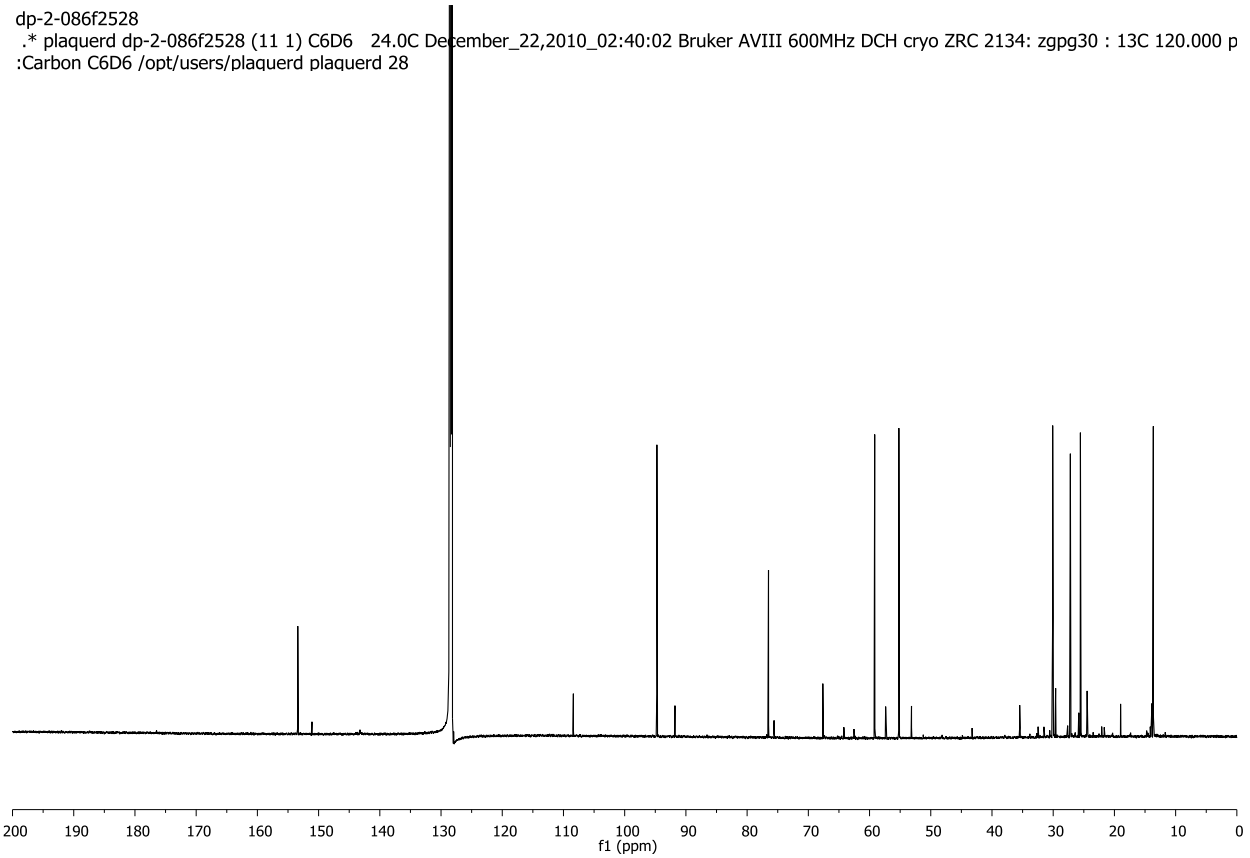


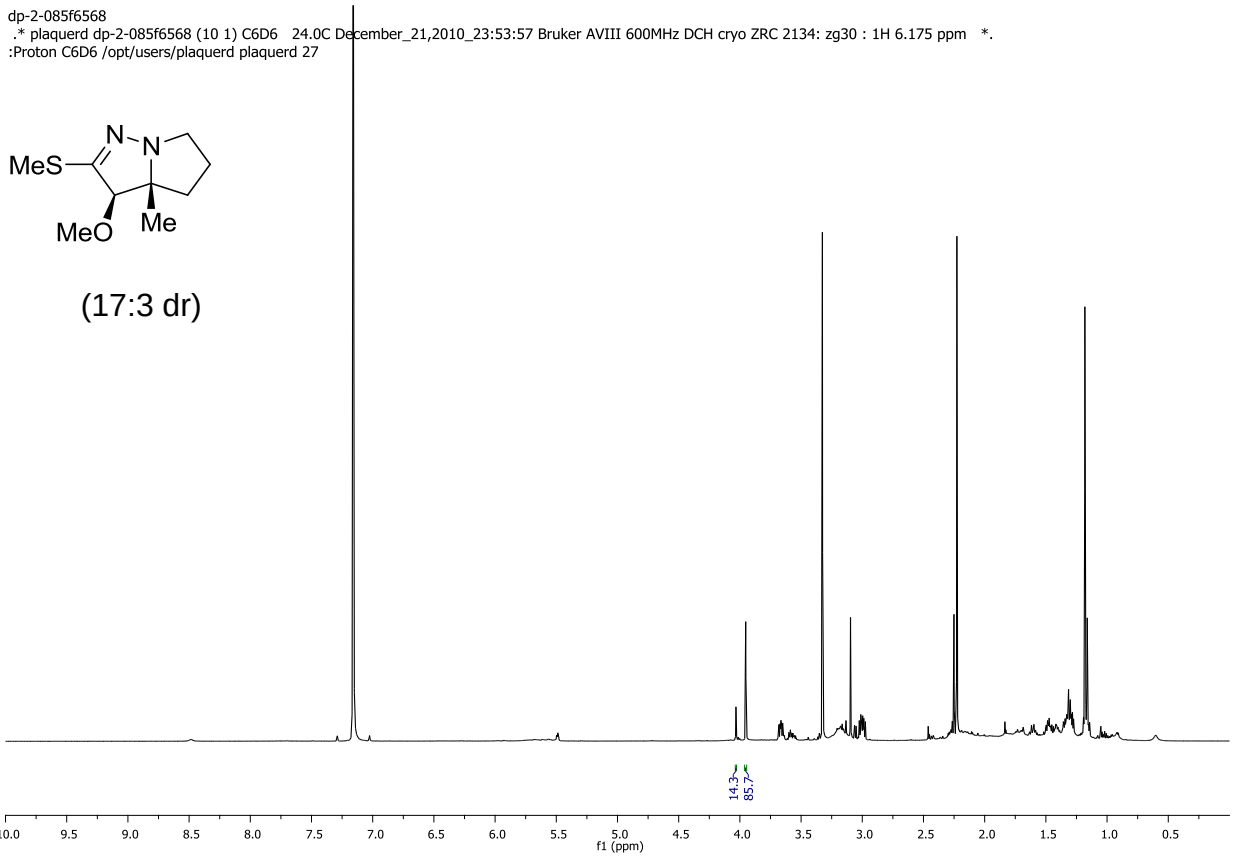
dp-2-086f2528
.* plaquerd dp-2-086f2528 (10 1) C6D6 24.0C December_22,2010_02:38:13 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 28

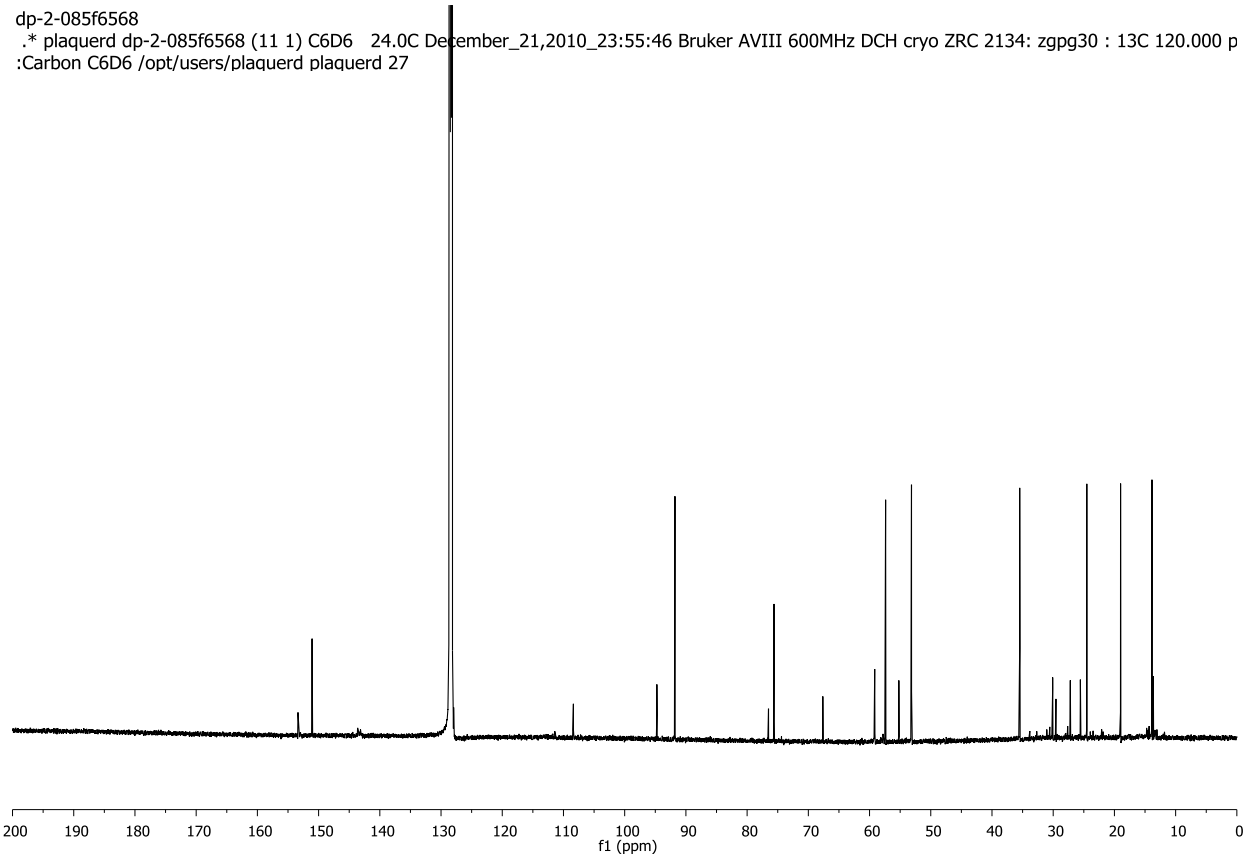


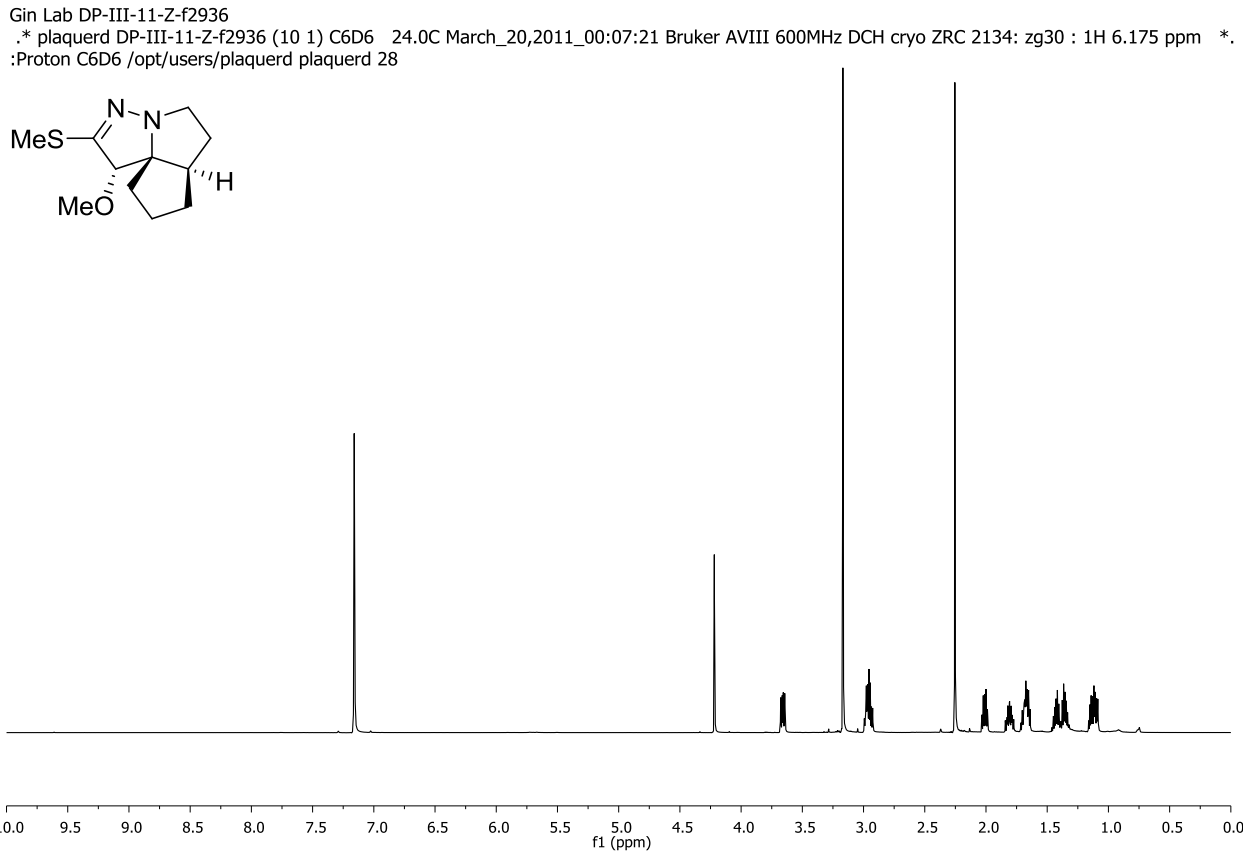
(18:2 dr)

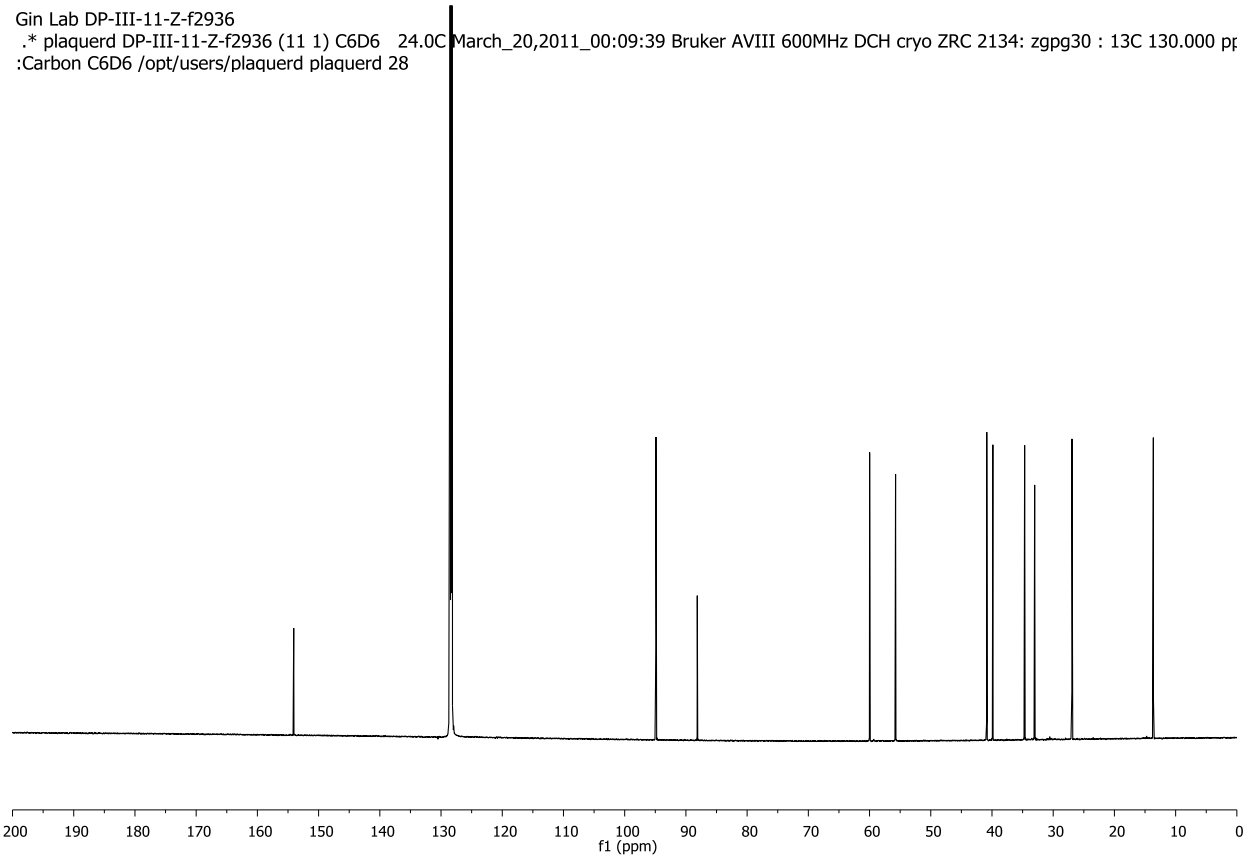
dp-2-086f2528
.* plaquerd dp-2-086f2528 (11 1) C6D6 24.0C December_22,2010_02:40:02 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 28

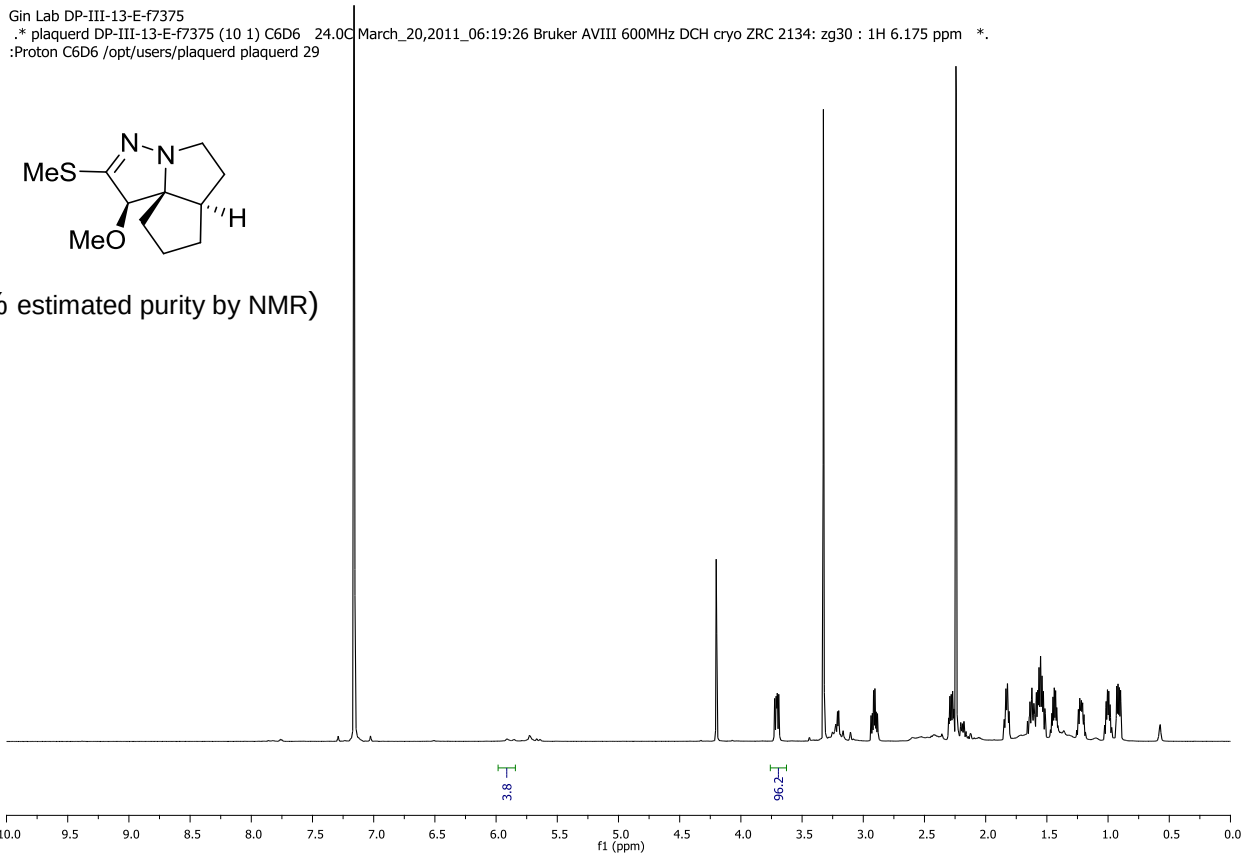



dp-2-085f6568
.* plaquerd dp-2-085f6568 (10 1) C6D6 24.0C December_21,2010_23:53:57 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 27
MeS
N
N
MeO
Me
(17:3 dr)
14.3
85.7
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

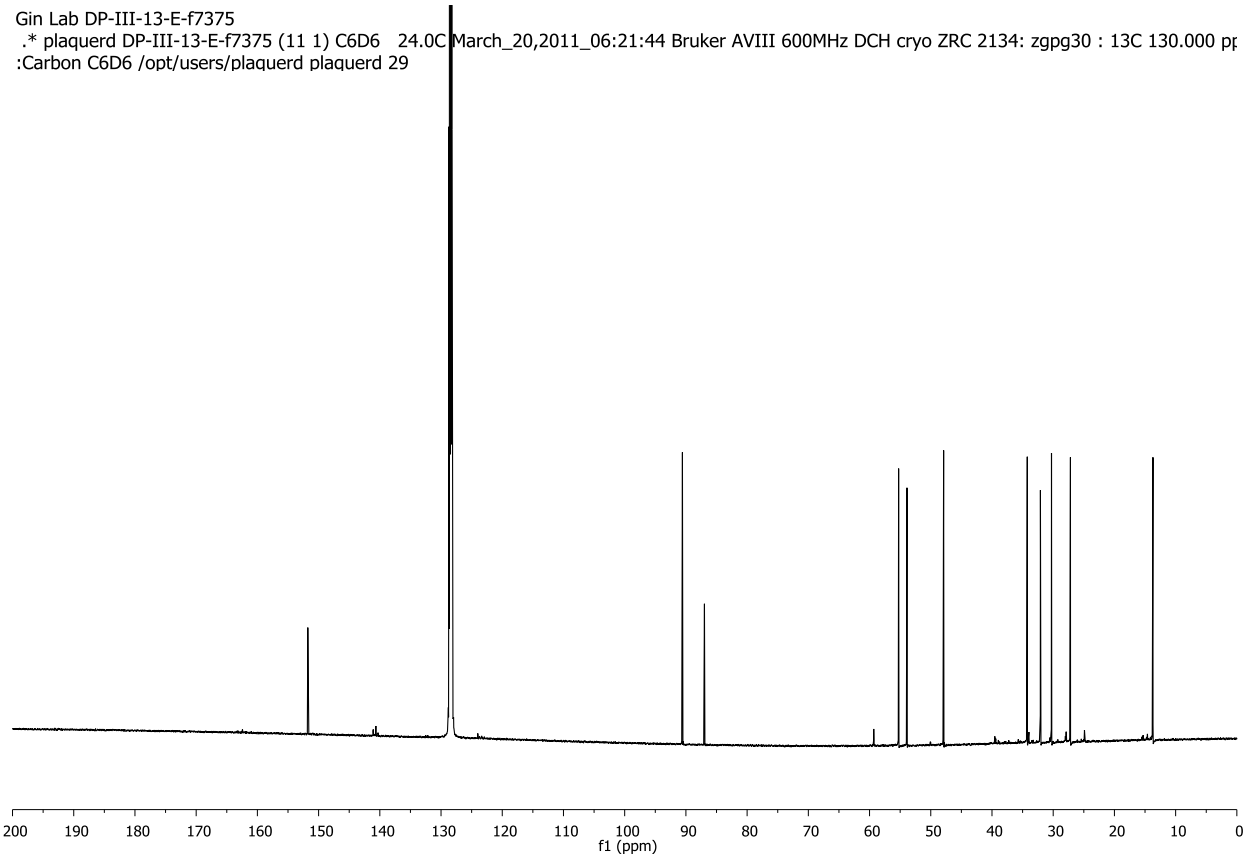

dp-2-085f6568
.* plaquerd dp-2-085f6568 (11 1) C6D6 24.0C December_21,2010_23:55:46 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Gin Lab DP-III-11-Z-f2936
.* plaquerd DP-III-11-Z-f2936 (10 1) C6D6 24.0C March_20,2011_00:07:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 28
MeS
N
N
H
MeO
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
f1 (ppm)

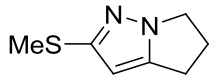

Gin Lab DP-III-11-Z-f2936
.* plaquerd DP-III-11-Z-f2936 (11 1) C6D6 24.0C March_20,2011_00:09:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 pp
:Carbon C6D6 /opt/users/plaquerd plaquerd 28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



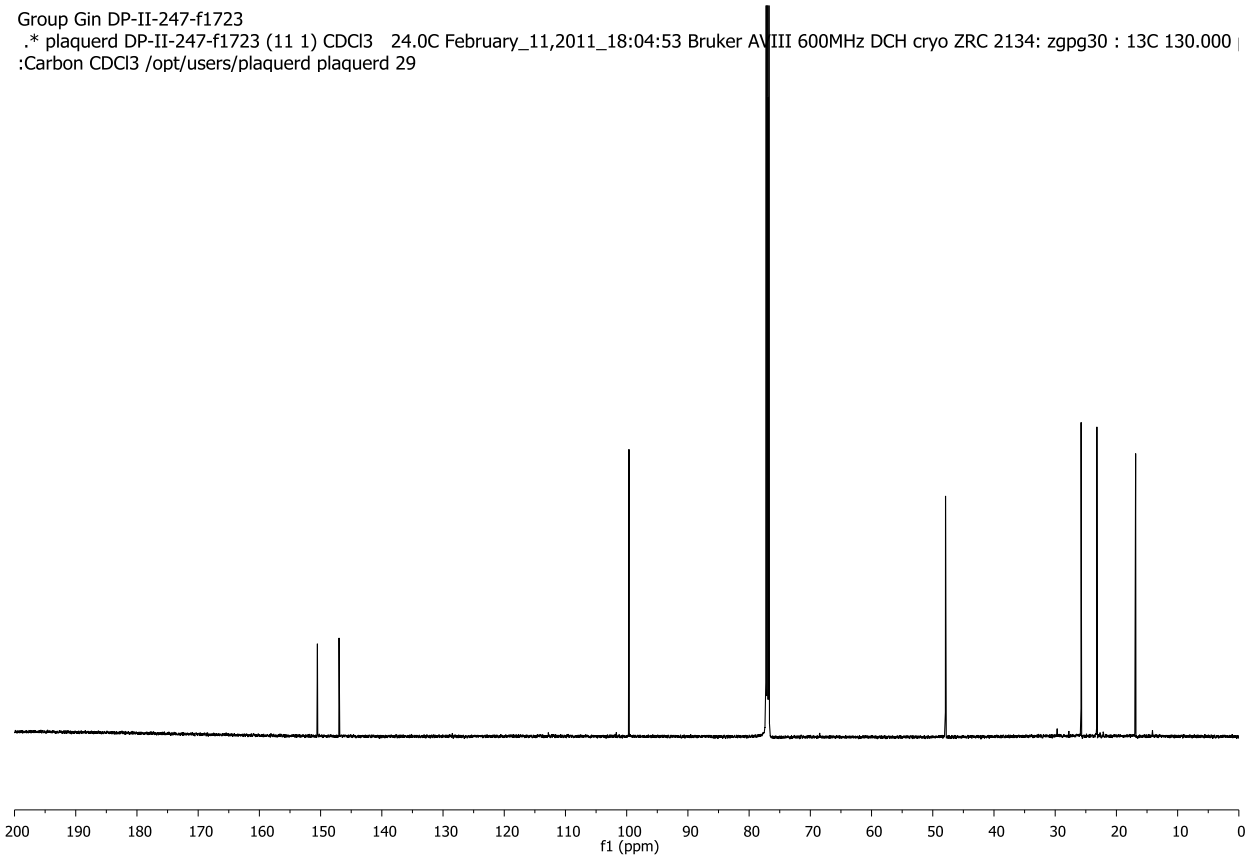
(96% estimated purity by NMR)



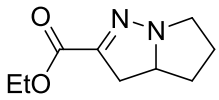
Group Gin DP-II-247-f1723
.* plaquerd DP-II-247-f1723 (10 1) CDCl3 24.0C February_11,2011_18:02:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton CDCl3 /opt/users/plaquerd plaquerd 29



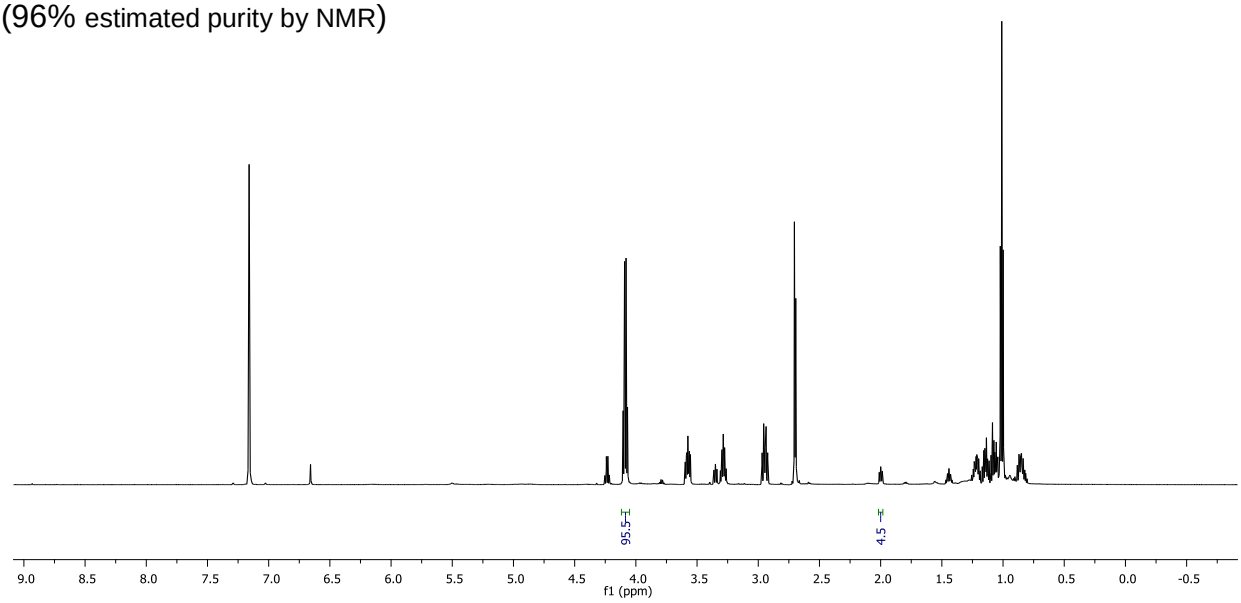
Group Gin DP-II-247-f1723
.* plaquerd DP-II-247-f1723 (11 1) CDCl3 24.0C February_11,2011_18:04:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000
:Carbon CDCl3 /opt/users/plaquerd plaquerd 29



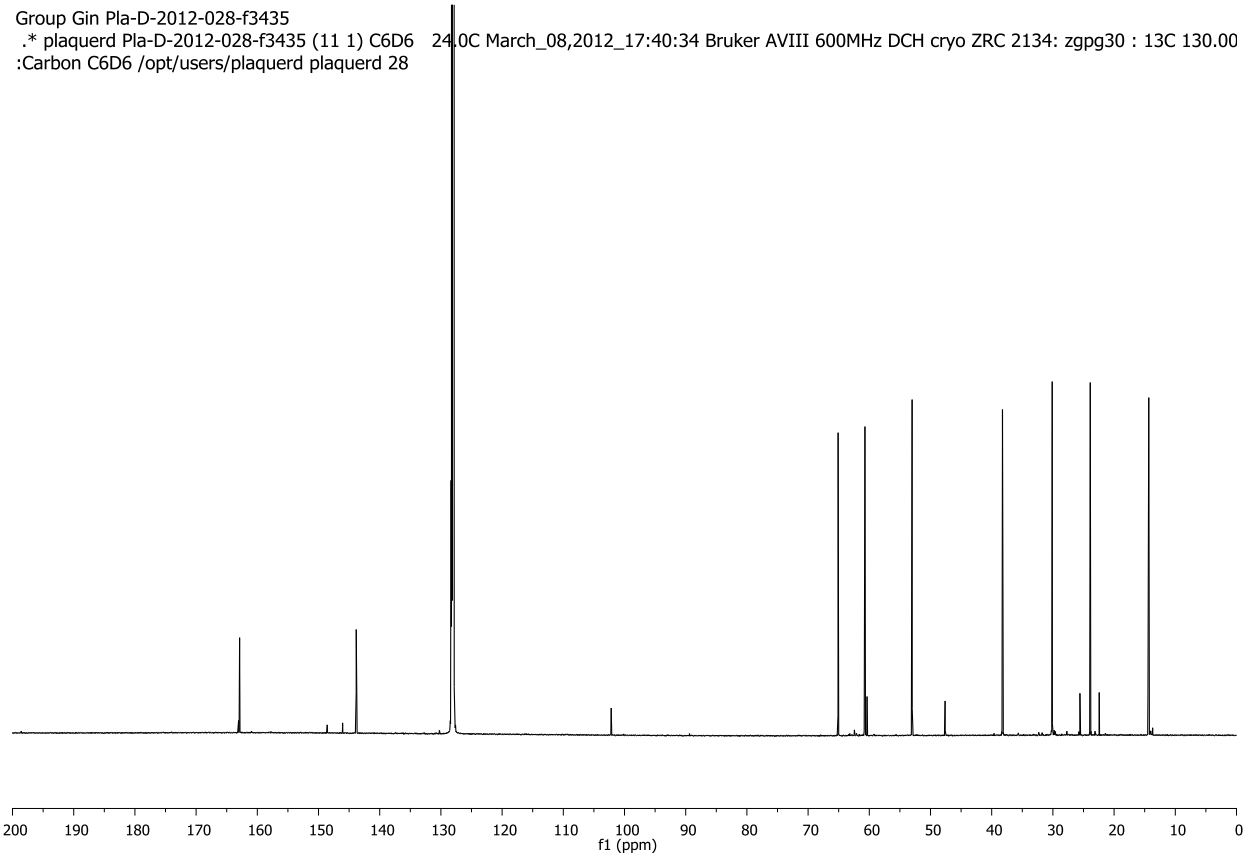
Group Gin Pla-D-2012-028-f3435
.* plaquerd Pla-D-2012-028-f3435 (10 1) C6D6 24.0C March_08,2012_17:38:19 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 28

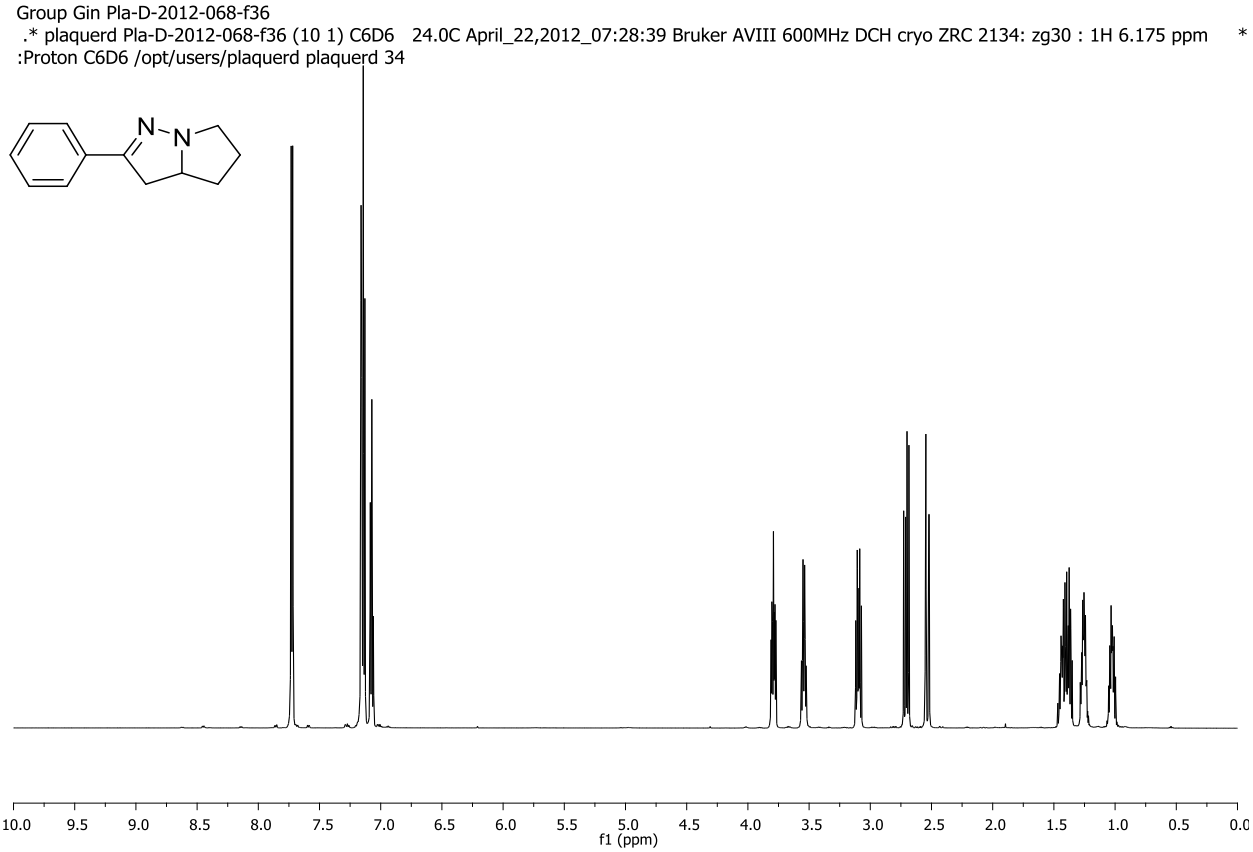


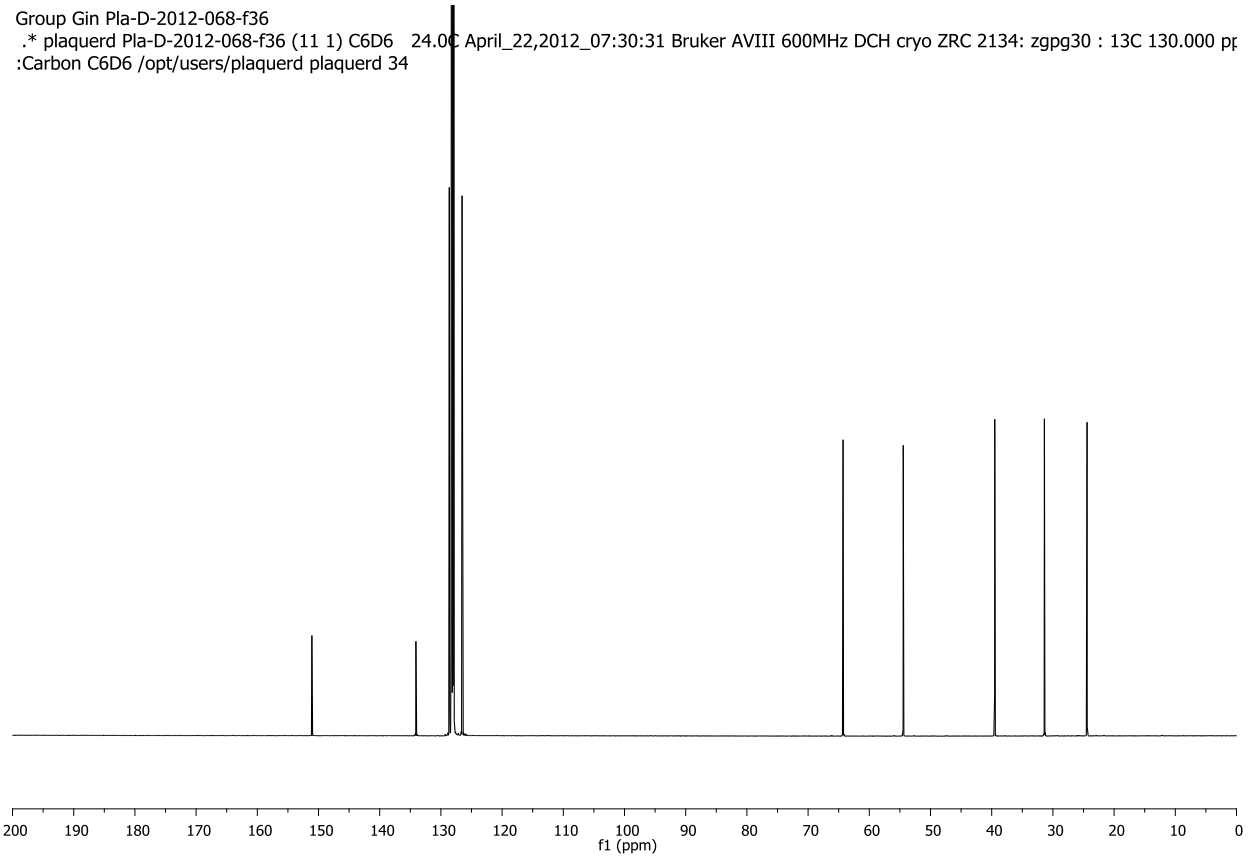
(96% estimated purity by NMR)



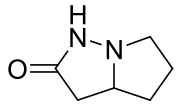
Group Gin Pla-D-2012-028-f3435
.* plaquerd Pla-D-2012-028-f3435 (11 1) C6D6 24.0C March_08,2012_17:40:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.00
:Carbon C6D6 /opt/users/plaquerd plaquerd 28




Group Gin Pla-D-2012-068-f36
.* plaquerd Pla-D-2012-068-f36 (10 1) C6D6 24.0C April_22,2012_07:28:39 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *
:Proton C6D6 /opt/users/plaquerd plaquerd 34
N
N
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
f1 (ppm)

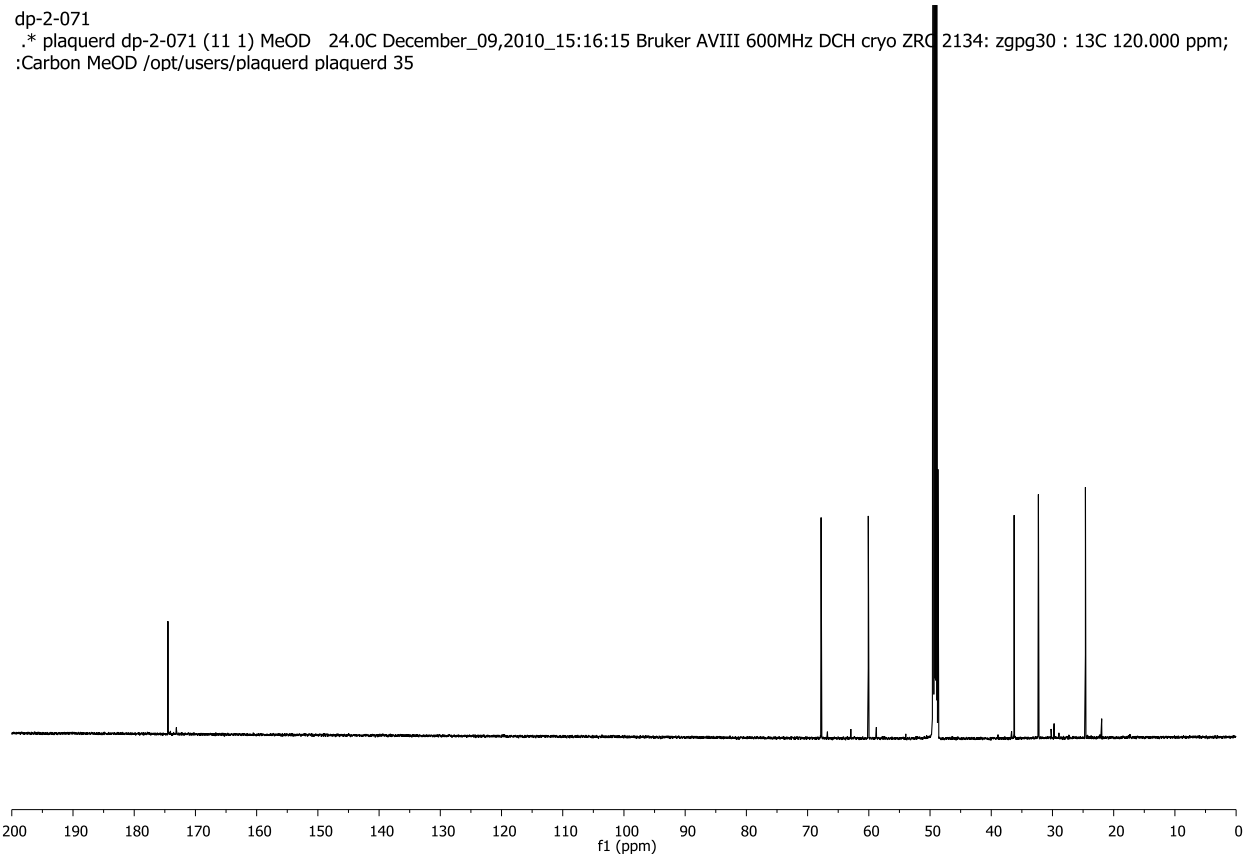

Group Gin Pla-D-2012-068-f36
.* plaquerd Pla-D-2012-068-f36 (11 1) C6D6 24.0C April_22,2012_07:30:31 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 pp
:Carbon C6D6 /opt/users/plaquerd plaquerd 34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

dp-2-071
.* plaquerd dp-2-071 (10 1) MeOD 24.0C December_09,2010_15:14:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton MeOD /opt/users/plaquerd plaquerd 35

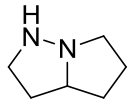


(97% estimated purity by NMR)

dp-2-071
.* plaquerd dp-2-071 (11 1) MeOD 24.0C December_09,2010_15:16:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 120.000 ppm;
:Carbon MeOD /opt/users/plaquerd plaquerd 35

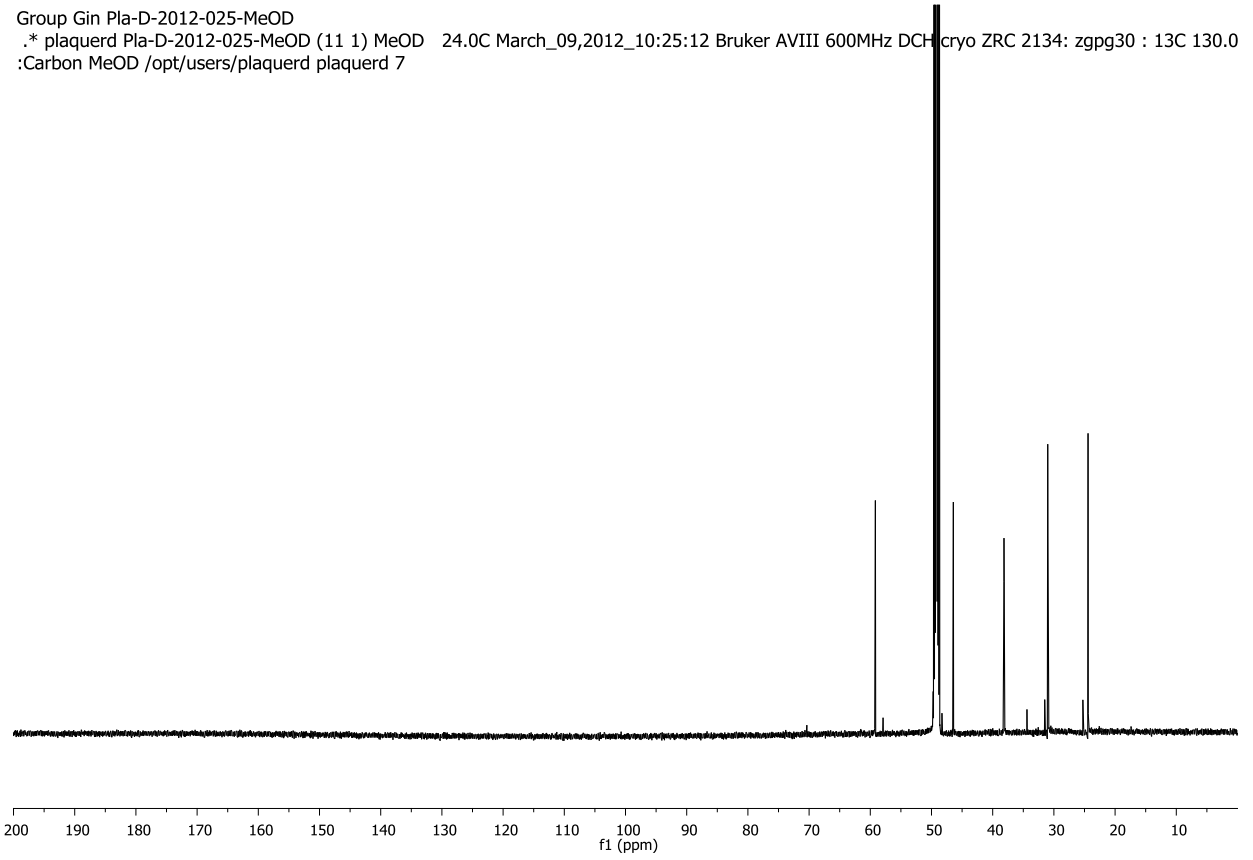


Group Gin Pla-D-2012-025-MeOD
.* plaquerd Pla-D-2012-025-MeOD (10 1) MeOD 24.0C March_09,2012_10:23:17 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton MeOD /opt/users/plaquerd plaquerd 7

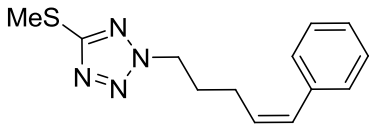


(98% estimated purity by NMR)

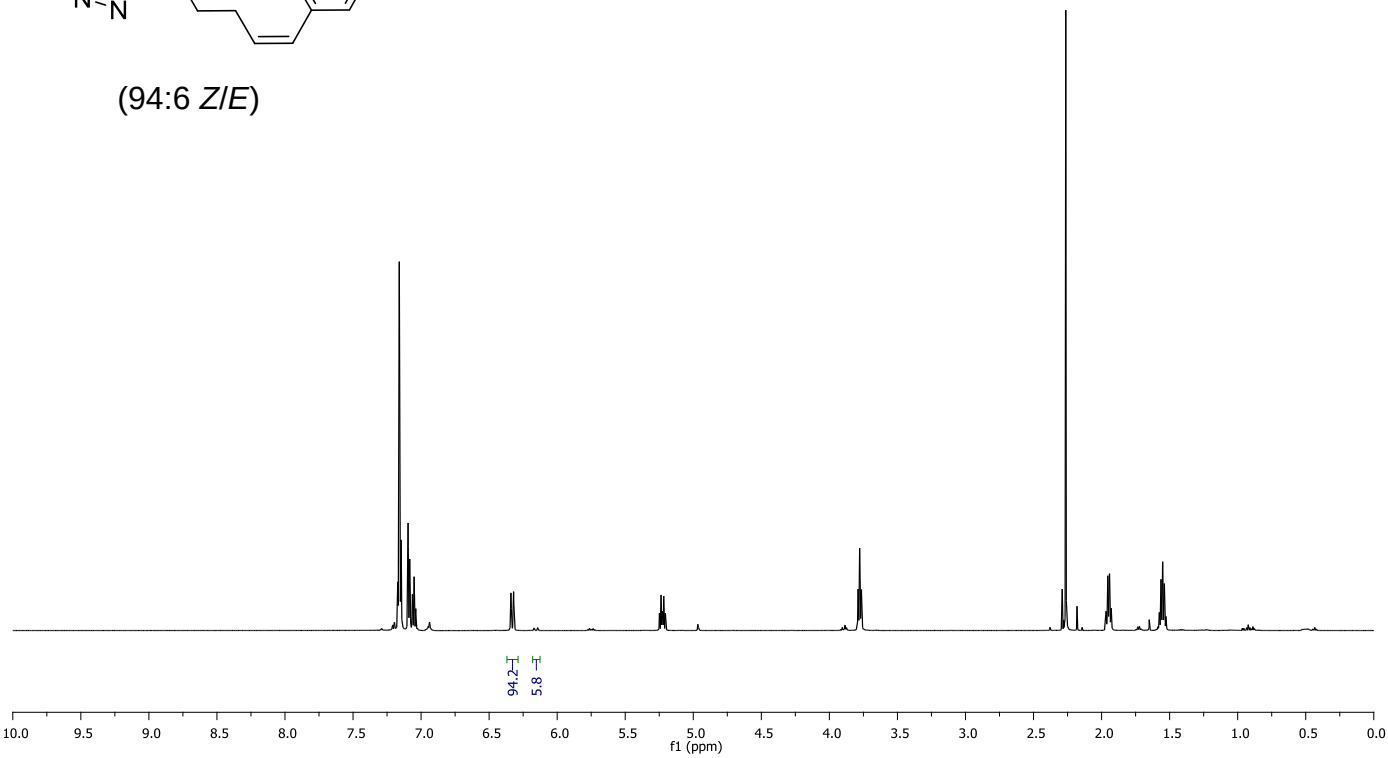
Group Gin Pla-D-2012-025-MeOD
.* plaquerd Pla-D-2012-025-MeOD (11 1) MeOD 24.0C March_09,2012_10:25:12 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.0
:Carbon MeOD /opt/users/plaquerd plaquerd 7



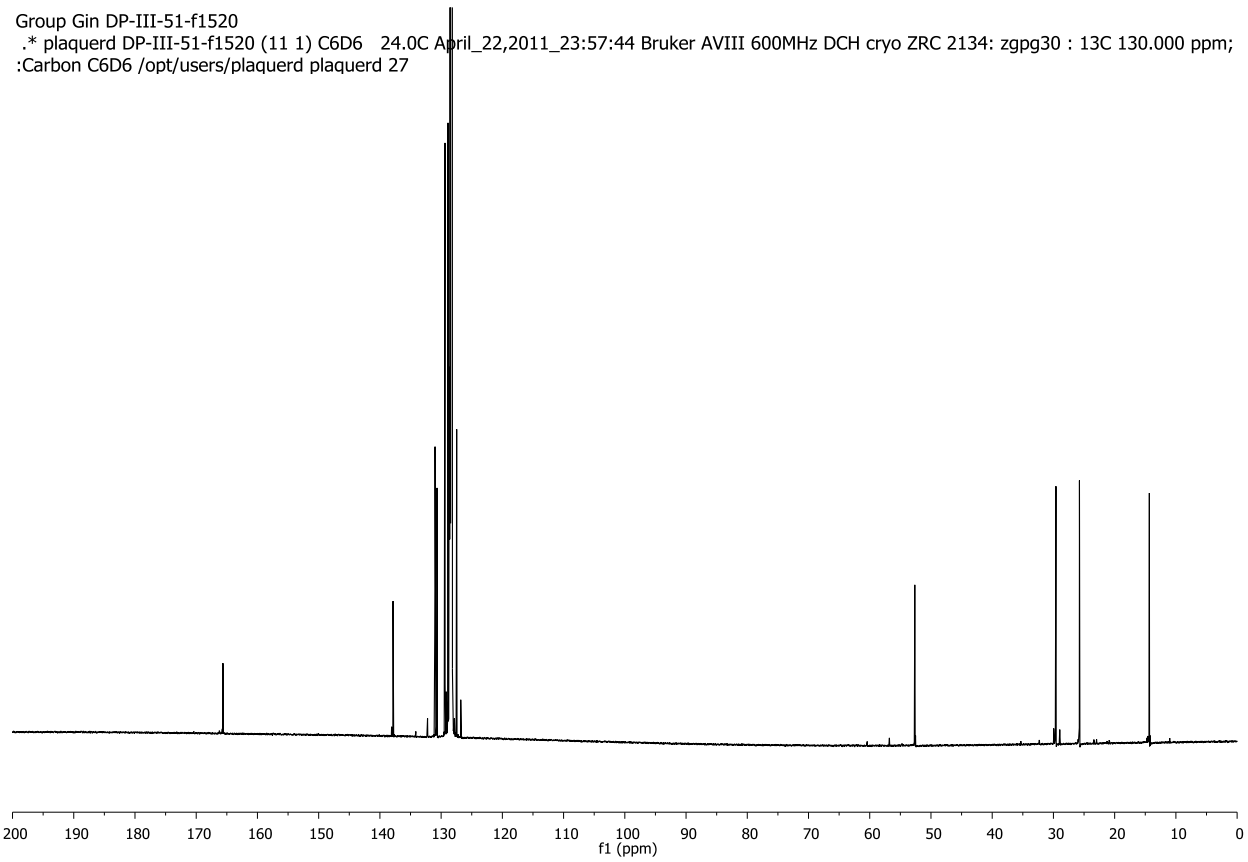
Group Gin DP-III-51-f1520
.* plaquerd DP-III-51-f1520 (10 1) C6D6 24.0C April_22,2011_23:55:51 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 27



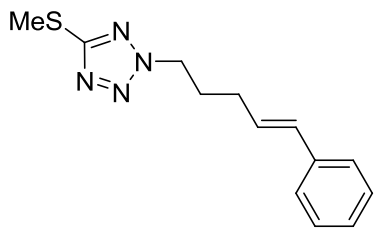
(94:6 *Z*/*E*)



Group Gin DP-III-51-f1520
.* plaquerd DP-III-51-f1520 (11 1) C6D6 24.0C April_22,2011_23:57:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 27

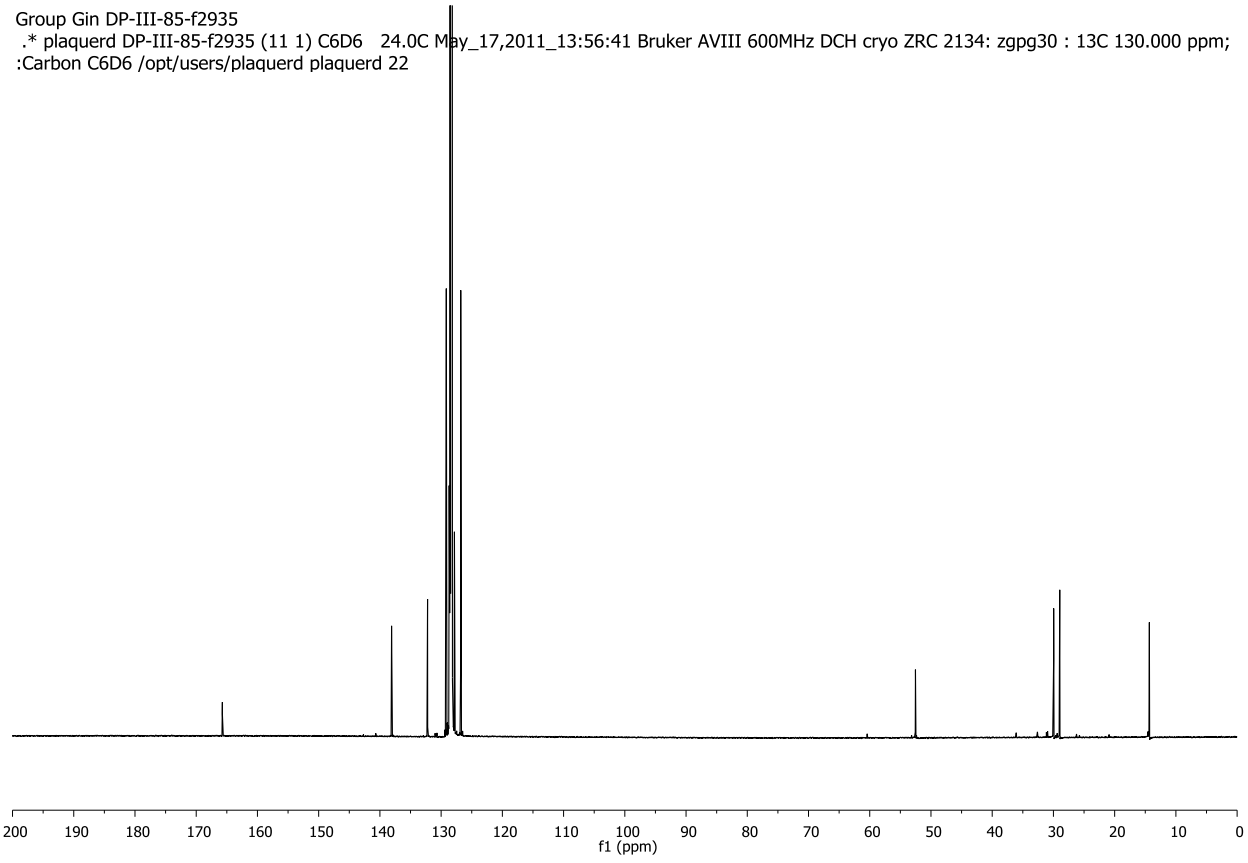


Group Gin DP-III-85-f2935
.* plaquerd DP-III-85-f2935 (10 1) C6D6 24.0C May_17,2011_13:54:48 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 22

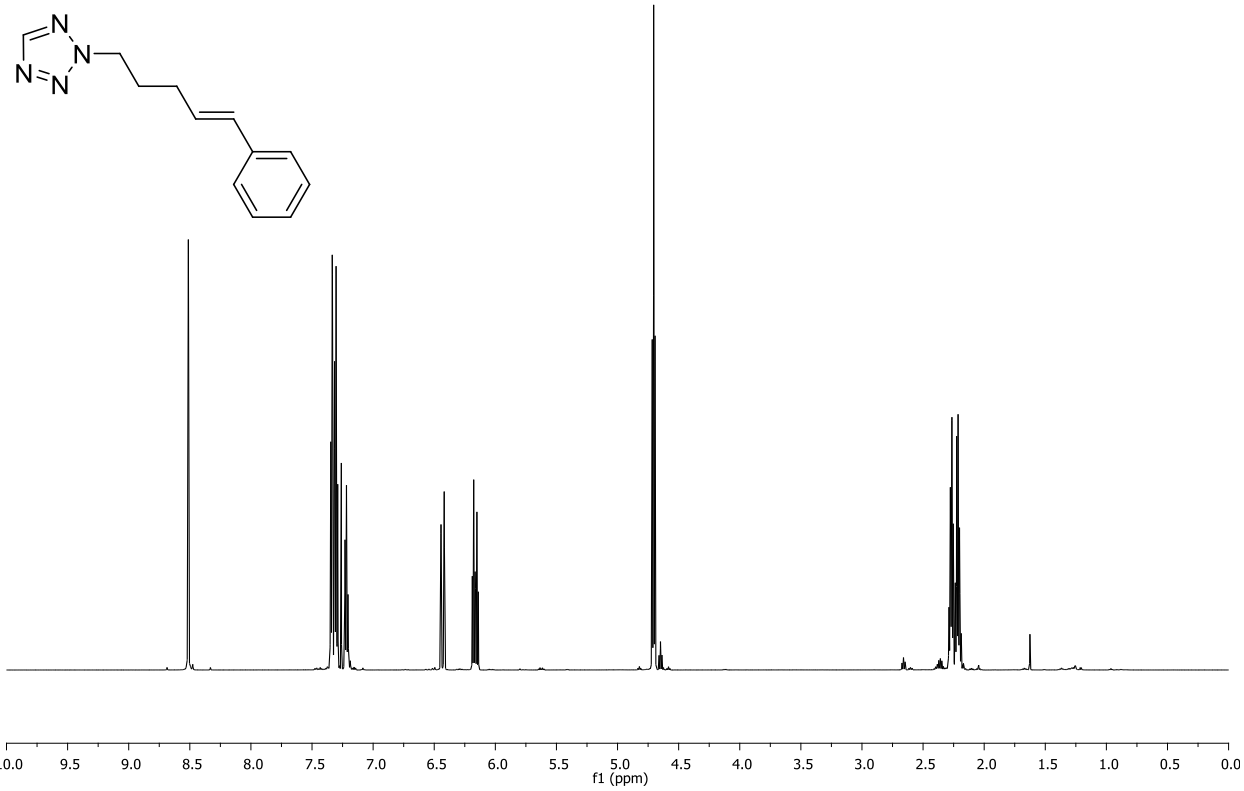


(>99:1 *E*/*Z*)

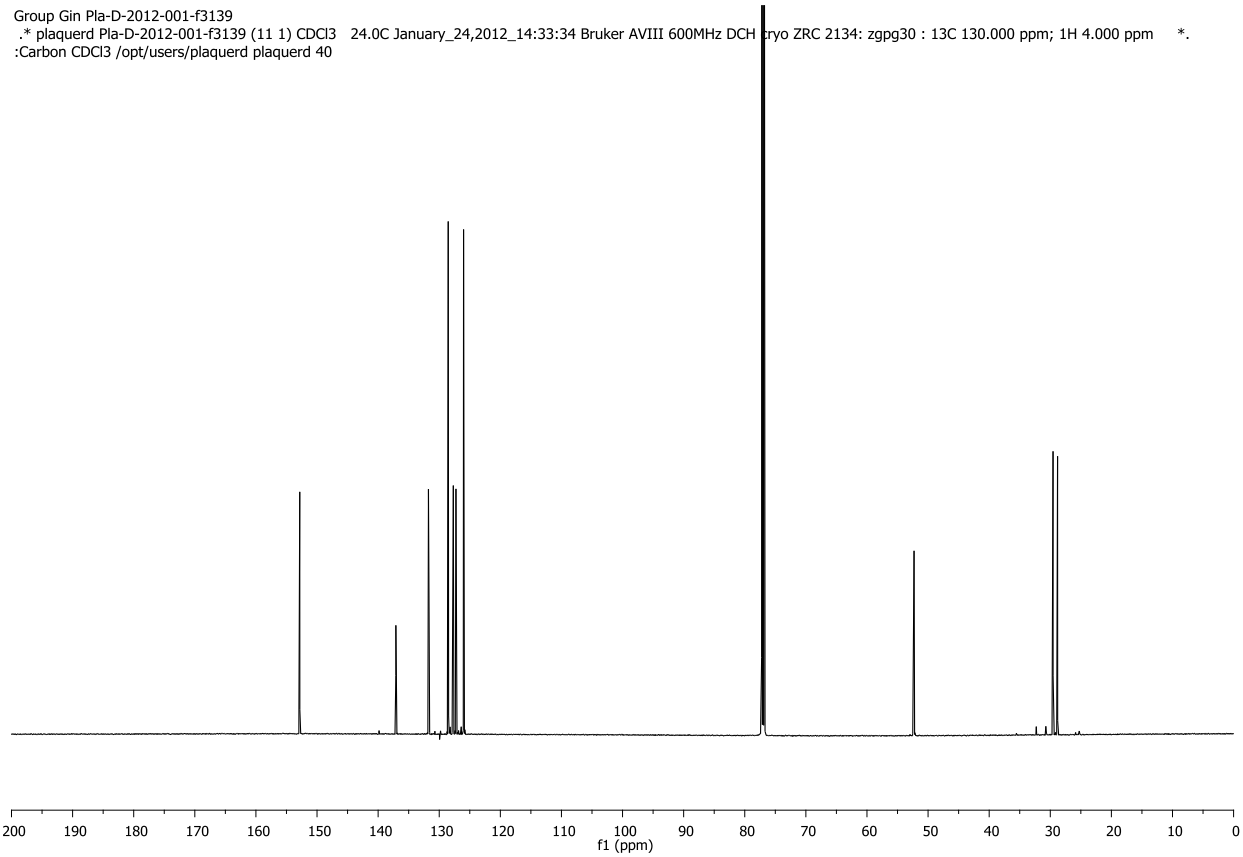
Group Gin DP-III-85-f2935
.* plaquerd DP-III-85-f2935 (11 1) C6D6 24.0C May_17,2011_13:56:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 22



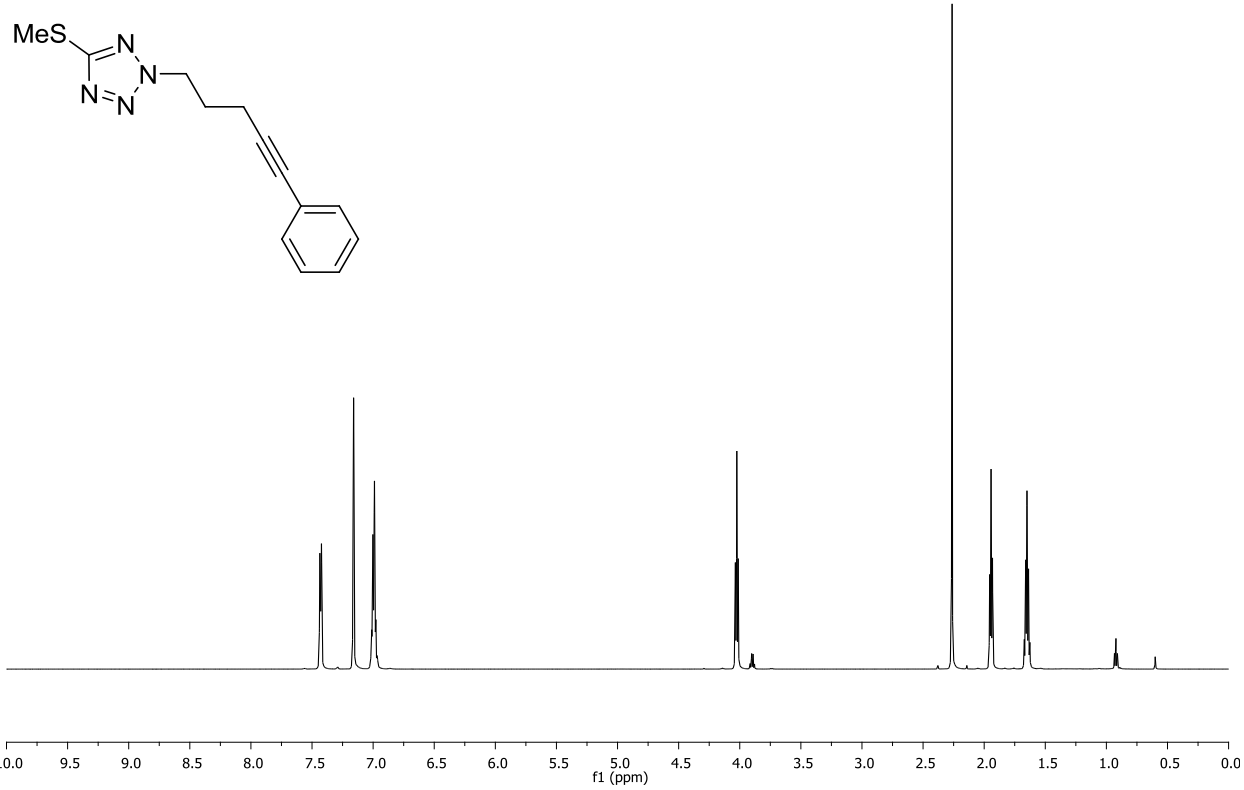
Group Gin Pla-D-2012-001-f3139
.* plaquerd Pla-D-2012-001-f3139 (10 1) CDCl3 24.0C January_24,2012_14:31:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 40



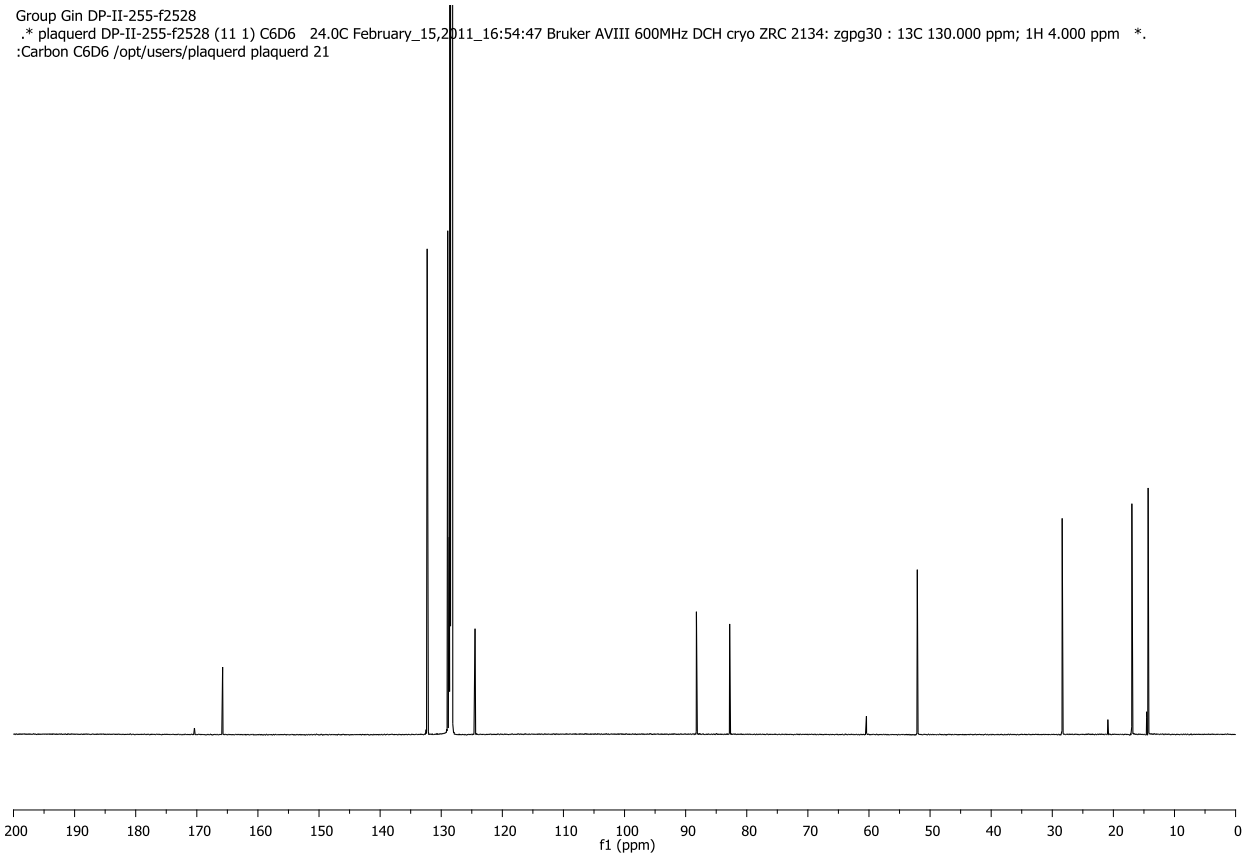
Group Gin Pla-D-2012-001-f3139
.* plaquerd Pla-D-2012-001-f3139 (11 1) CDCl3 24.0C January_24,2012_14:33:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
:Carbon CDCl3 /opt/users/plaquerd plaquerd 40



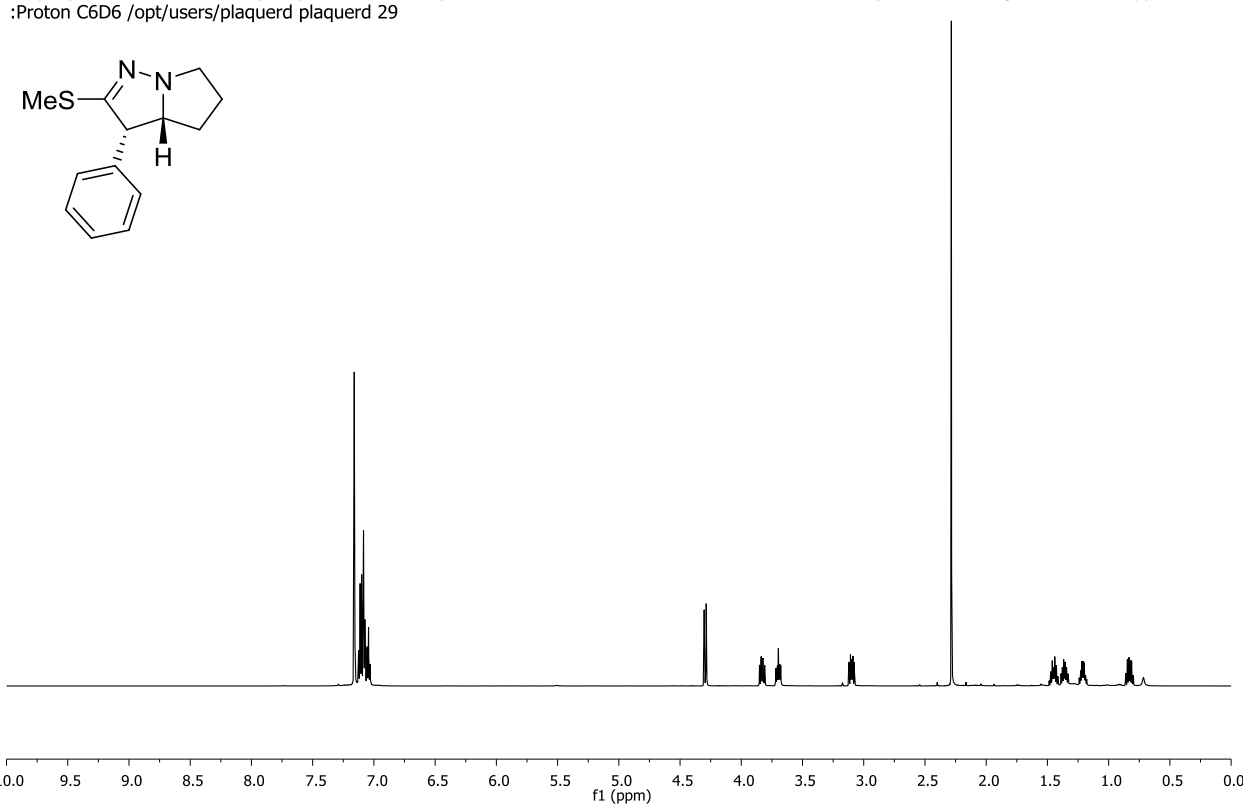
Group Gin DP-II-255-f2528
.* plaquerd DP-II-255-f2528 (10 1) C6D6 24.0C February_15,2011_16:52:28 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 21



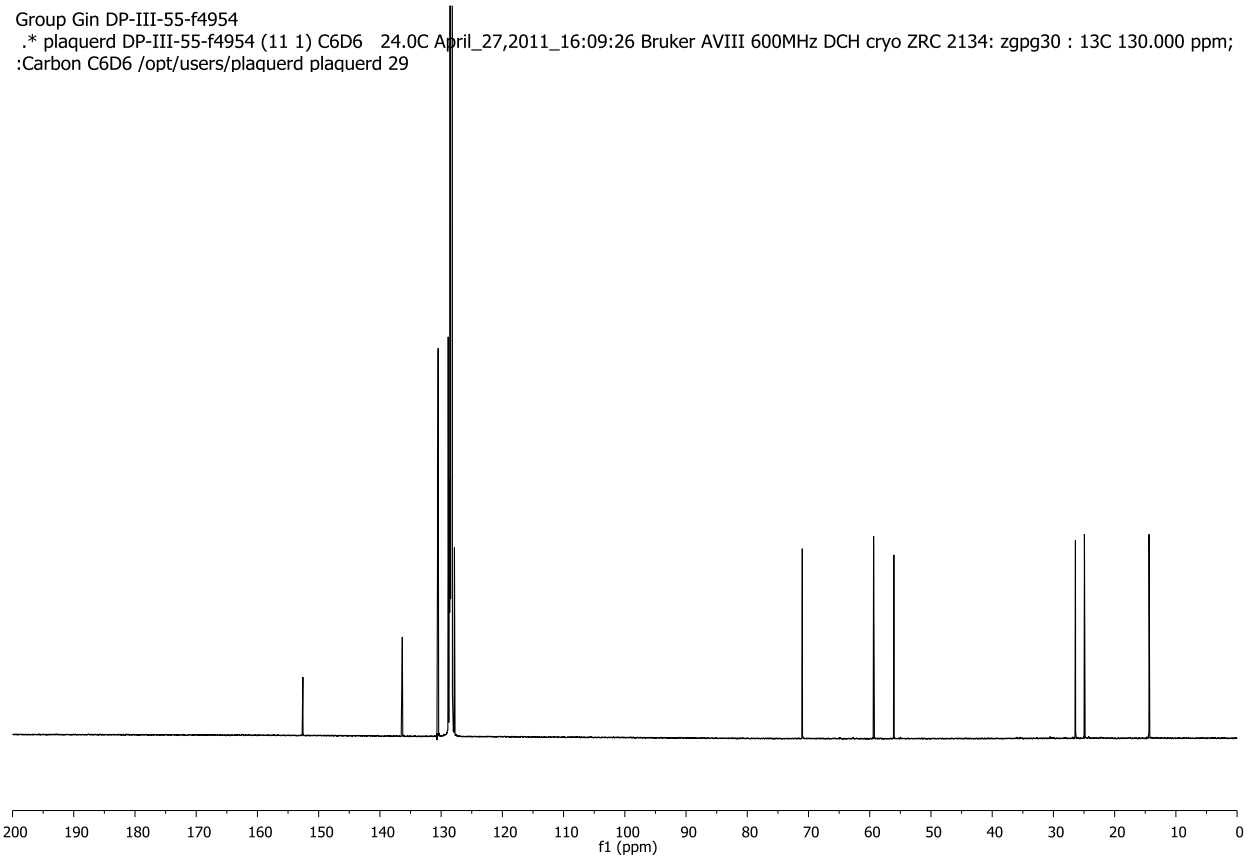
Group Gin DP-II-255-f2528
.* plaquerd DP-II-255-f2528 (11 1) C6D6 24.0C February_15,2011_16:54:47 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm; 1H 4.000 ppm *.
:Carbon C6D6 /opt/users/plaquerd plaquerd 21



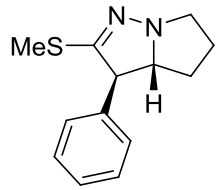
Group Gin DP-III-55-f4954
.* plaquerd DP-III-55-f4954 (10 1) C6D6 24.0C April_27,2011_16:07:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 29

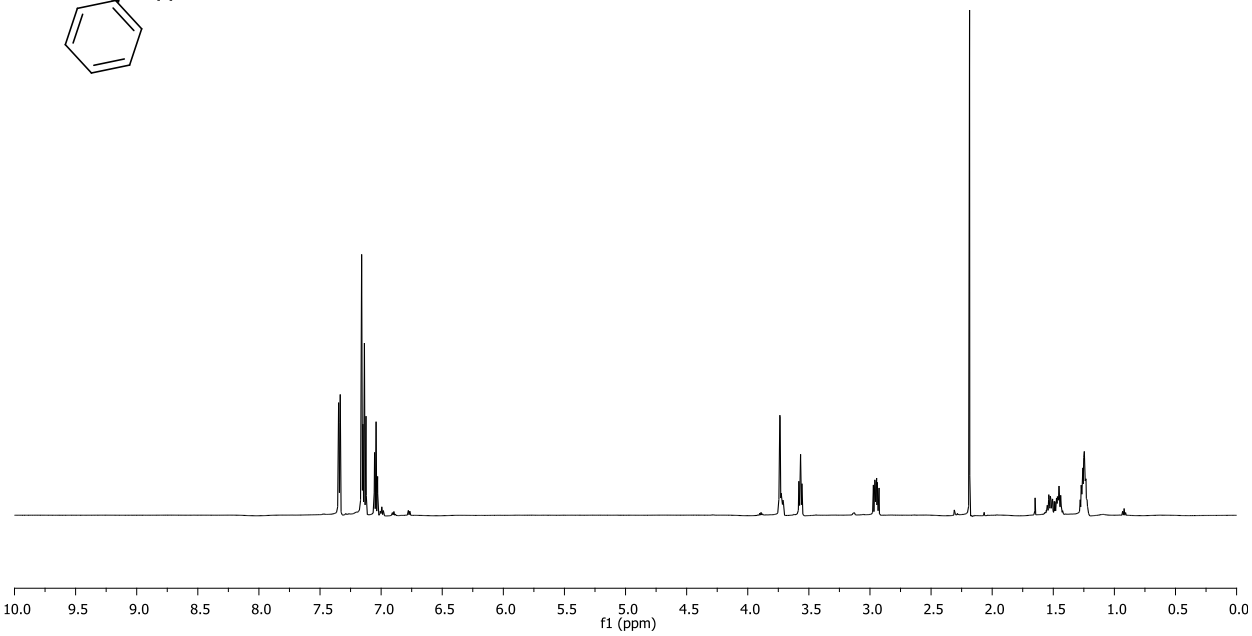


Group Gin DP-III-55-f4954
.* plaquerd DP-III-55-f4954 (11 1) C6D6 24.0C April_27,2011_16:09:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 29

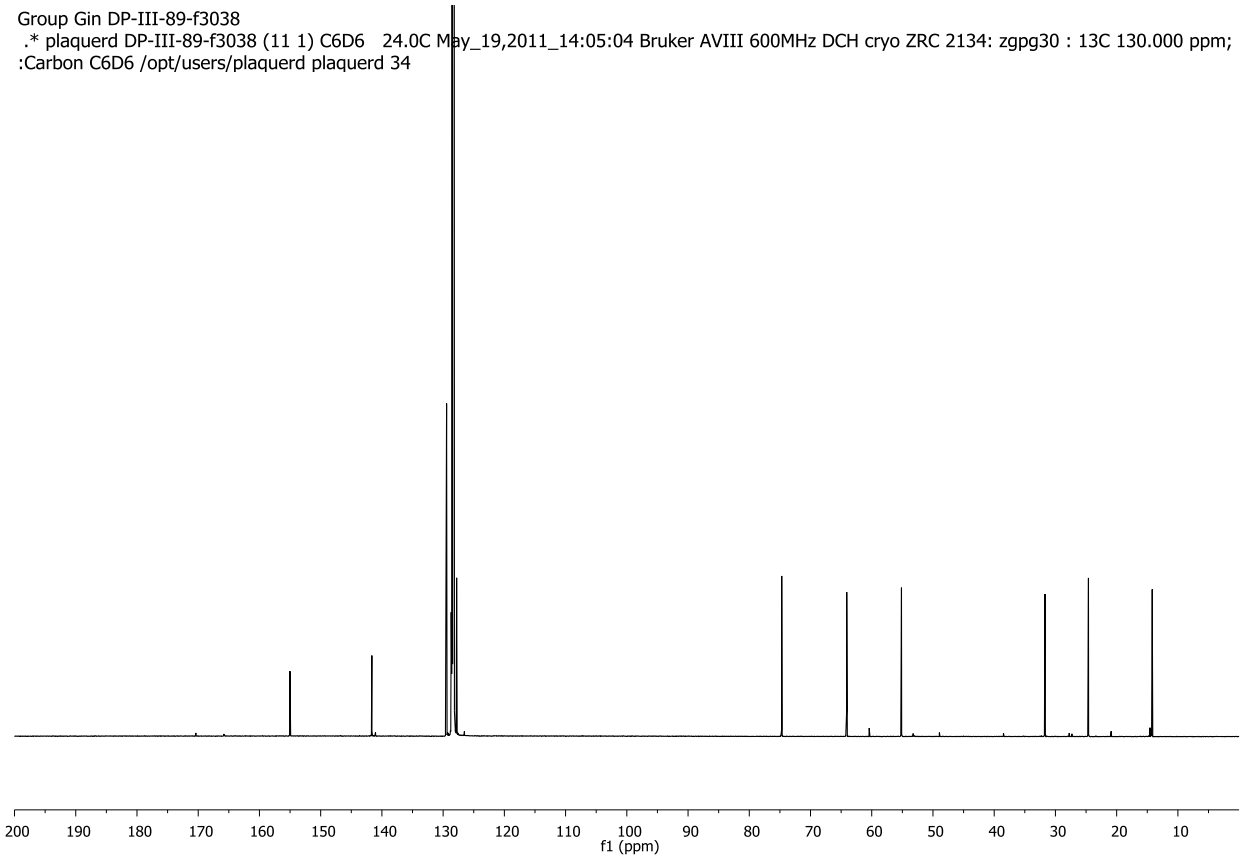


Group Gin DP-III-89-f3038
.* plaquerd DP-III-89-f3038 (10 1) C6D6 24.0C May_19,2011_14:03:06 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 34

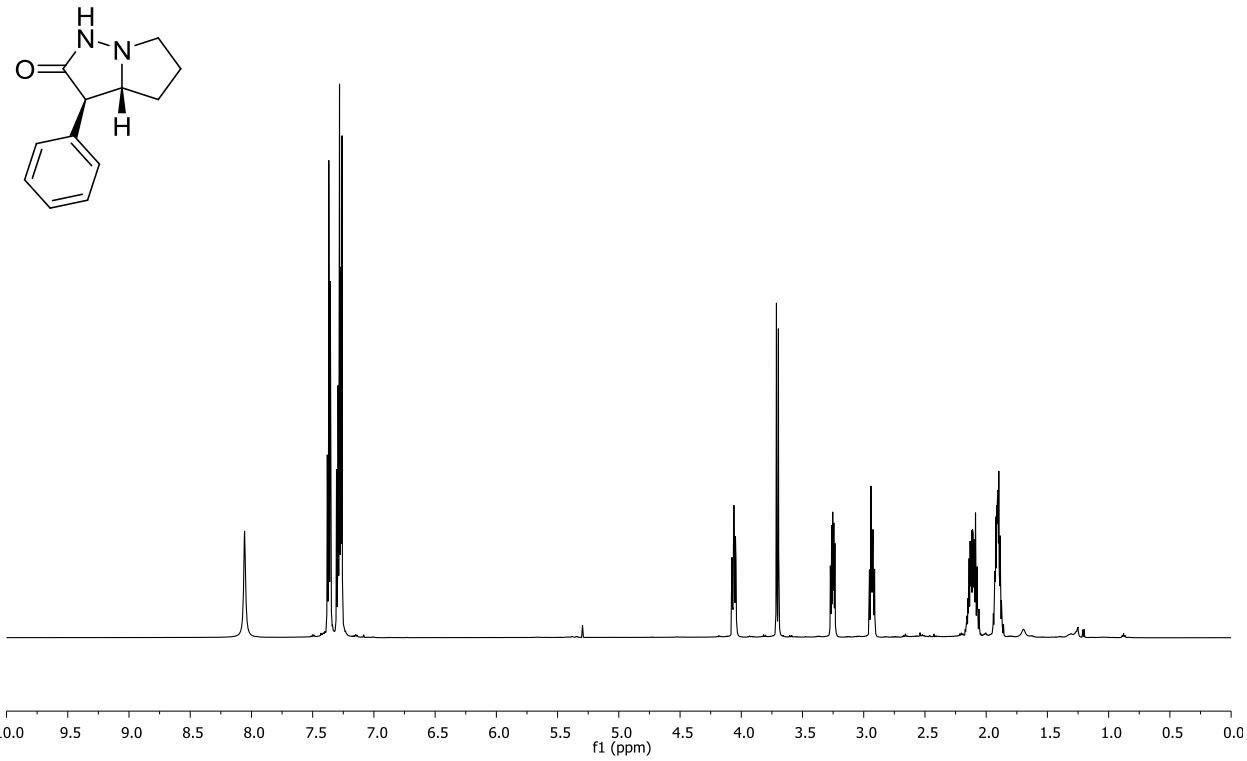




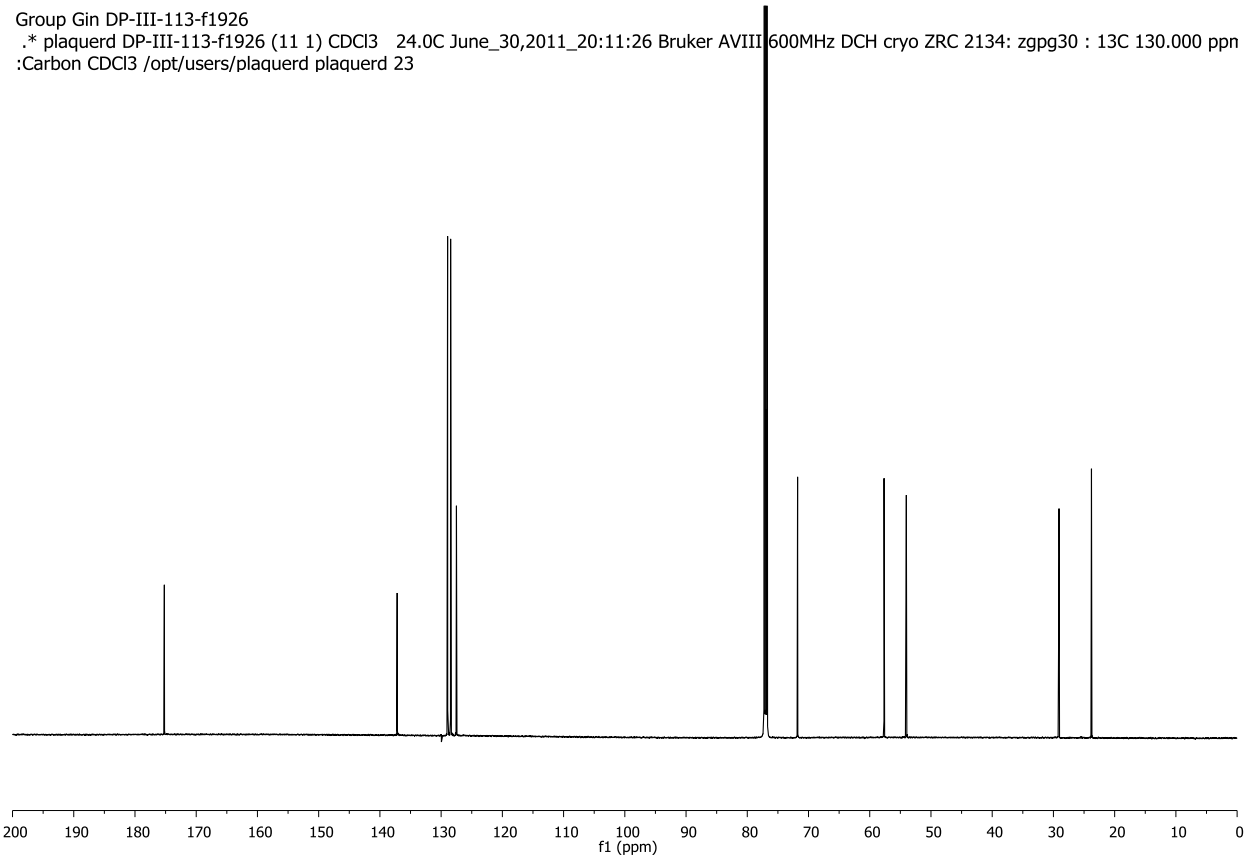
Group Gin DP-III-89-f3038
.* plaquerd DP-III-89-f3038 (11 1) C6D6 24.0C May_19,2011_14:05:04 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 34



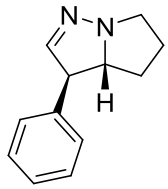
Group Gin DP-III-113-f1926
.* plaquerd DP-III-113-f1926 (10 1) CDCl3 24.0C June_30,2011_20:09:37 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 23



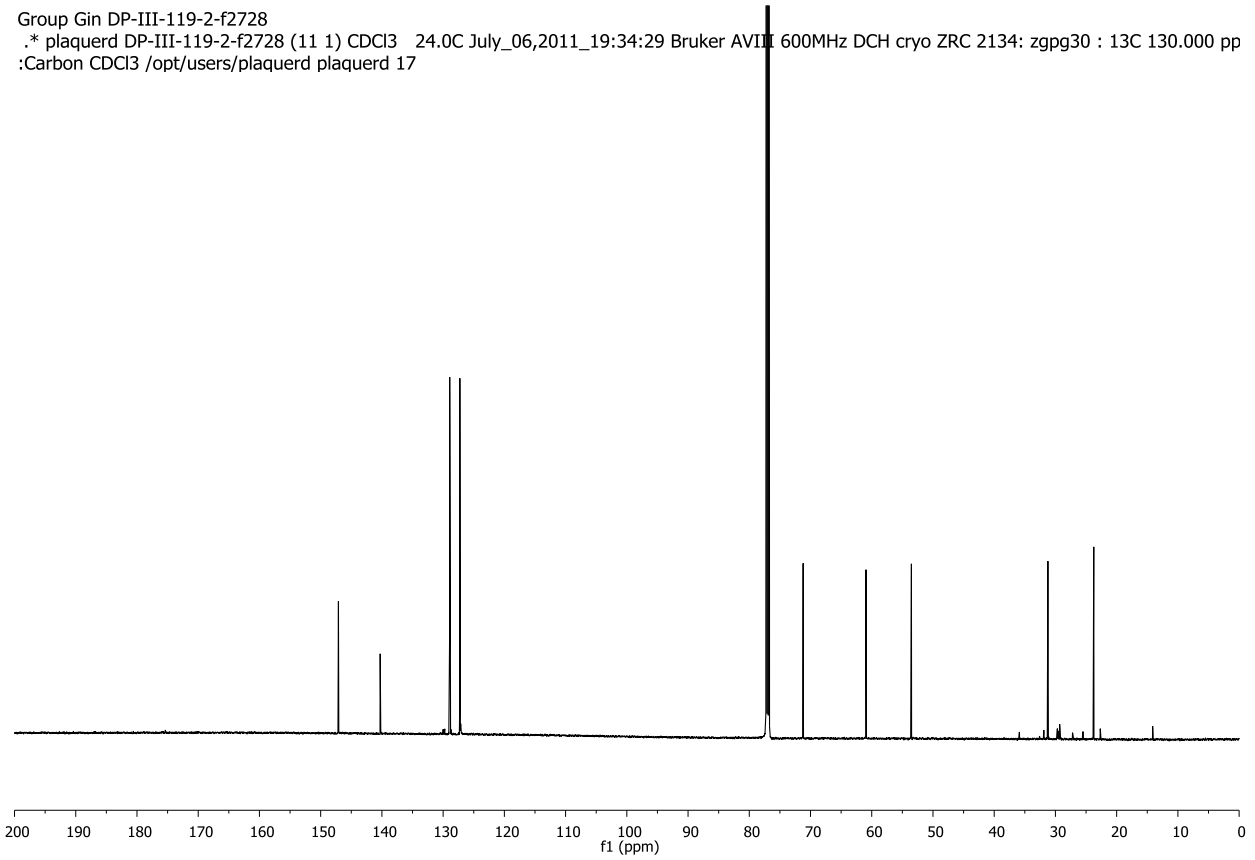
Group Gin DP-III-113-f1926
.* plaquerd DP-III-113-f1926 (11 1) CDCl3 24.0C June_30,2011_20:11:26 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppn
:Carbon CDCl3 /opt/users/plaquerd plaquerd 23



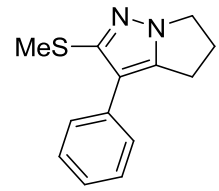
Group Gin DP-III-119-2-f2728
.* plaquerd DP-III-119-2-f2728 (10 1) CDCl3 24.0C July_06,2011_19:32:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 17



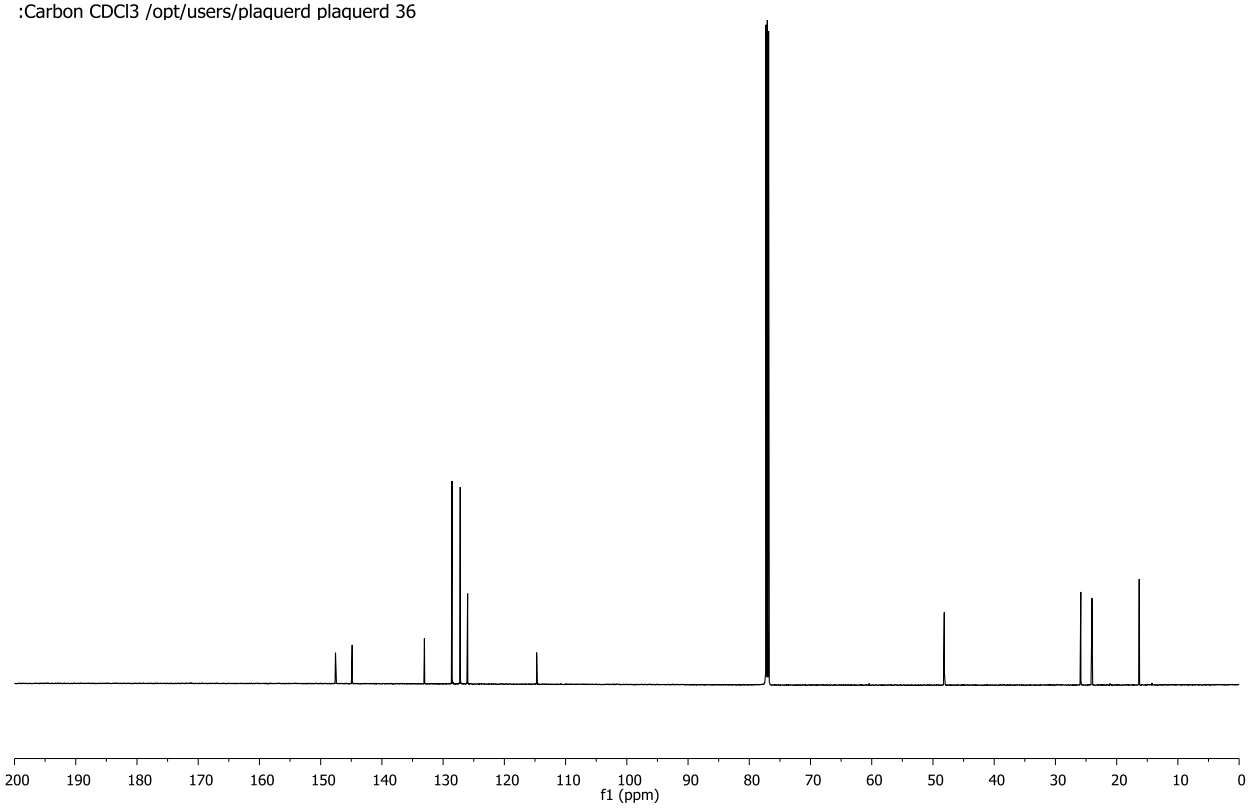
Group Gin DP-III-119-2-f2728
.* plaquerd DP-III-119-2-f2728 (11 1) CDCl3 24.0C July_06,2011_19:34:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 pp
:Carbon CDCl3 /opt/users/plaquerd plaquerd 17

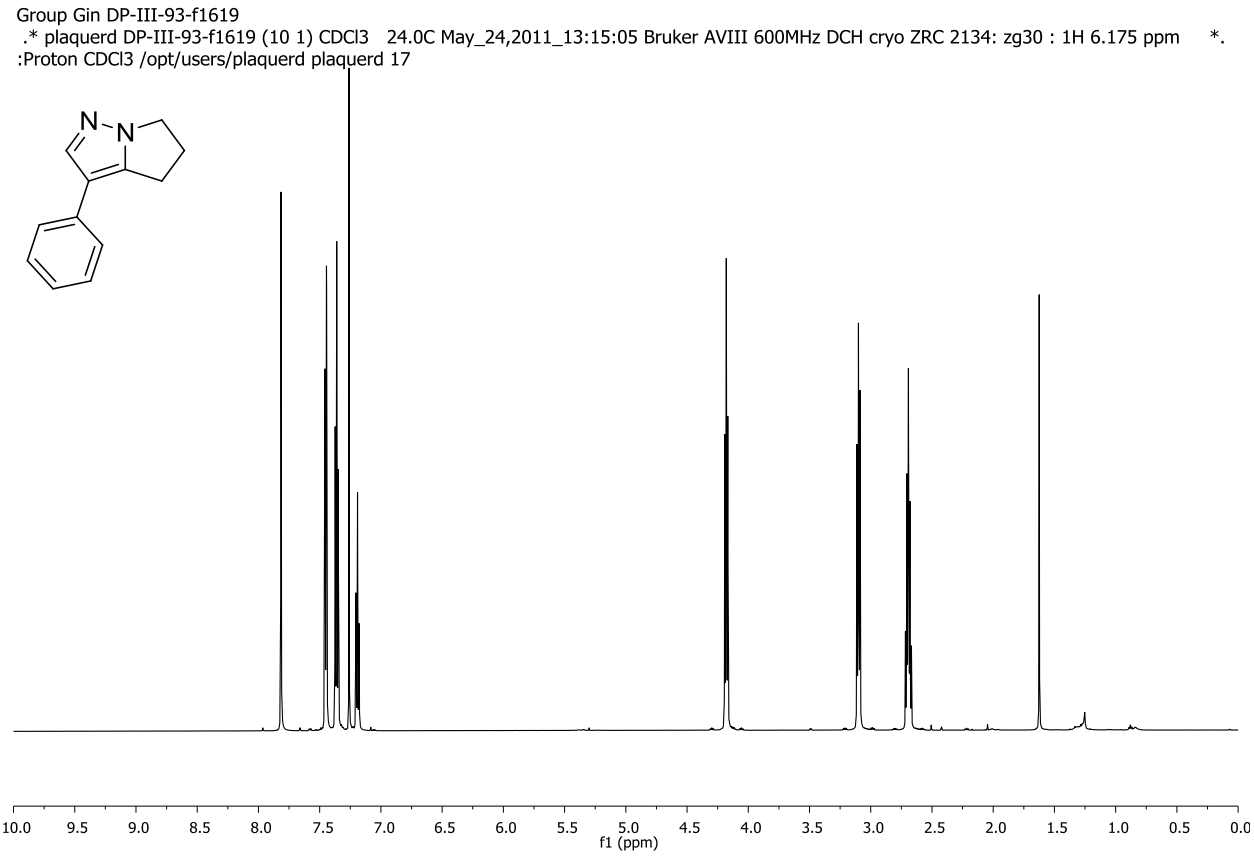


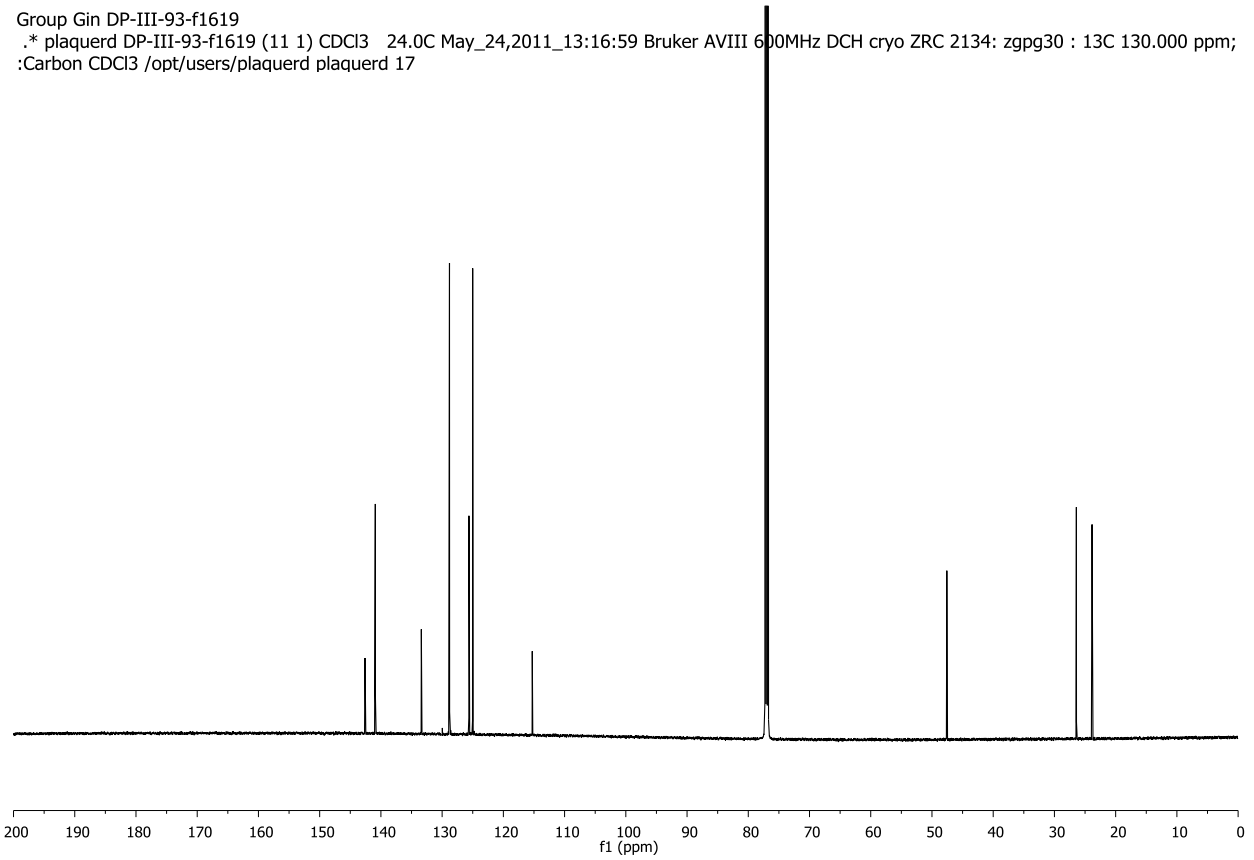
Group Gin DP-III-81-f5269
.* plaquerd DP-III-81-f5269 (10 1) CDCl3 24.0C May_19,2011_20:12:36 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 36



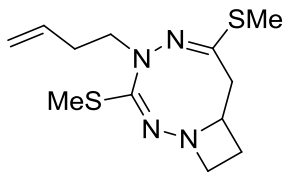
Group Gin DP-III-81-f5269
.* plaquerd DP-III-81-f5269 (11 1) CDCl3 24.0C May_19,2011_20:14:35 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon CDCl3 /opt/users/plaquerd plaquerd 36




Group Gin DP-III-93-f1619
.* plaquerd DP-III-93-f1619 (10 1) CDCl3 24.0C May_24,2011_13:15:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton CDCl3 /opt/users/plaquerd plaquerd 17
N
N
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
f1 (ppm)

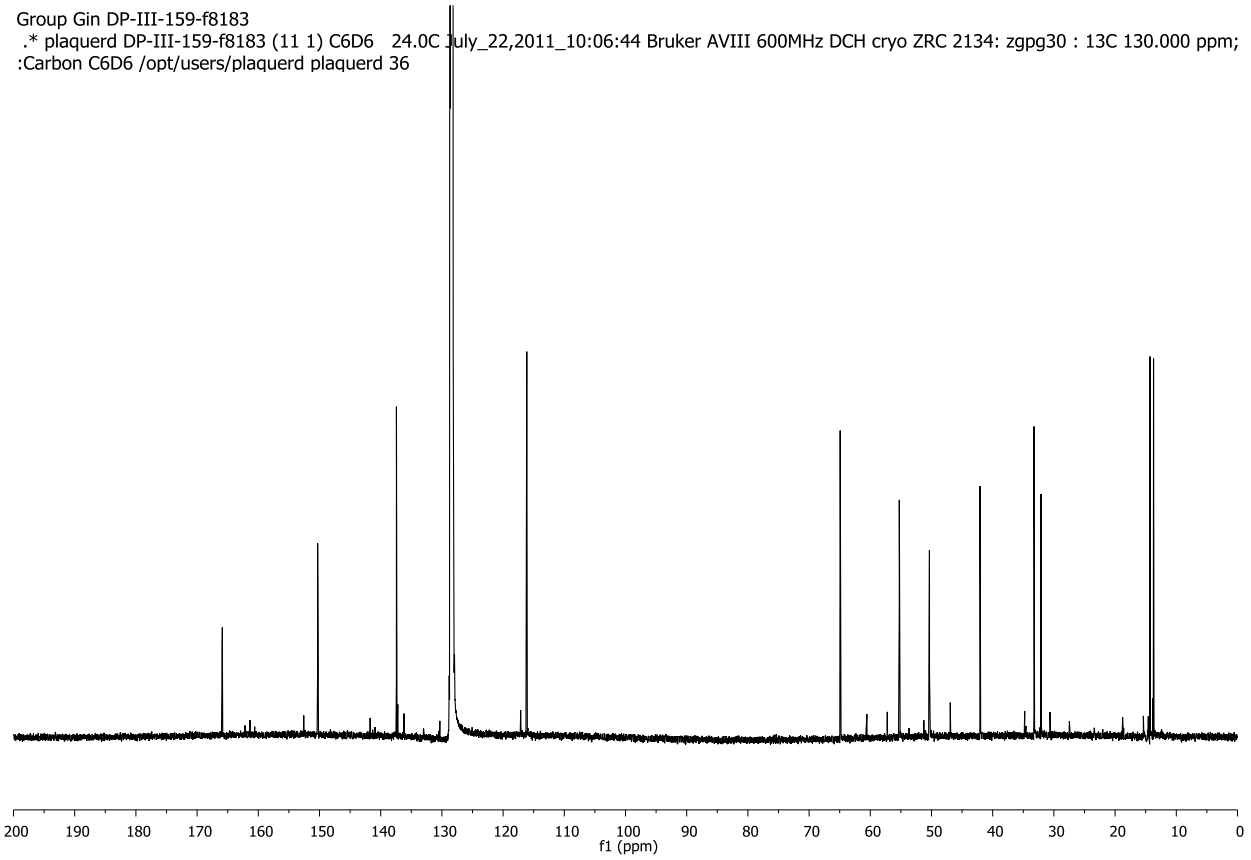

Group Gin DP-III-93-f1619
.* plaquerd DP-III-93-f1619 (11 1) CDCl3 24.0C May_24,2011_13:16:59 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon CDCl3 /opt/users/plaquerd plaquerd 17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Group Gin DP-III-159-f8183
.* plaquerd DP-III-159-f8183 (10 1) C6D6 24.0C July_22,2011_10:04:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 36

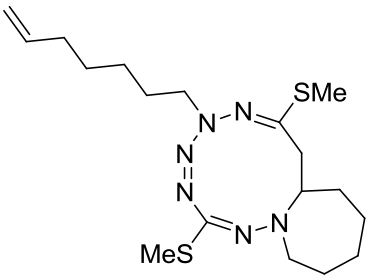


proposed structure

Group Gin DP-III-159-f8183
.* plaquerd DP-III-159-f8183 (11 1) C6D6 24.0C July_22,2011_10:06:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 ppm;
:Carbon C6D6 /opt/users/plaquerd plaquerd 36

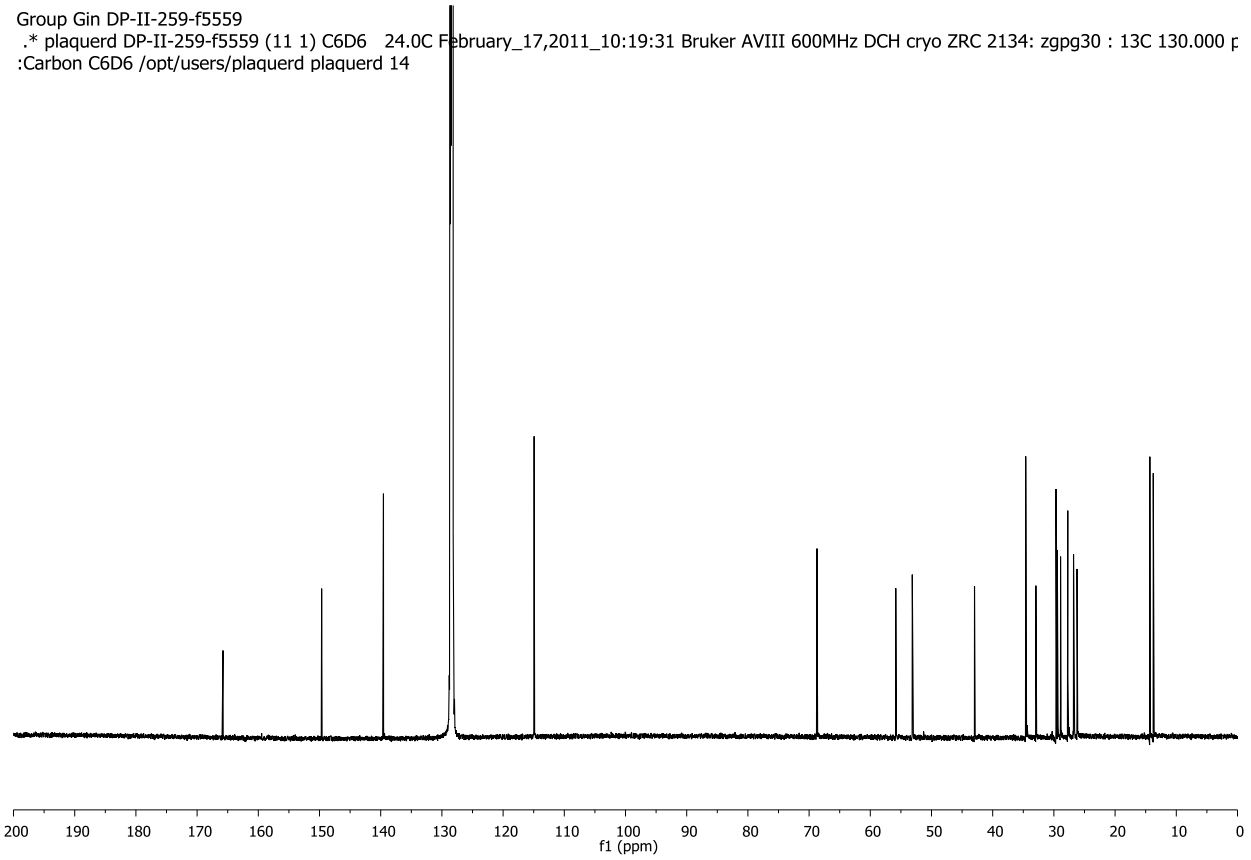


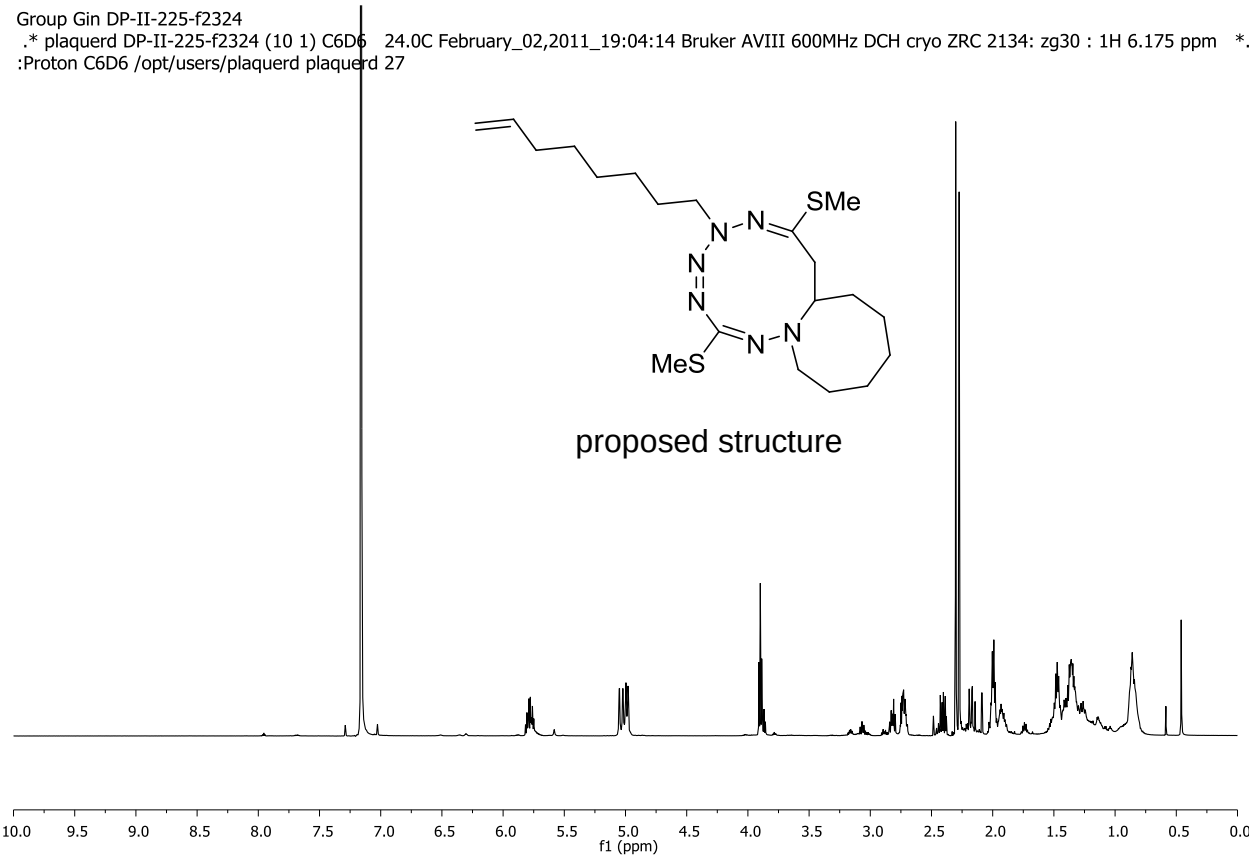
Group Gin DP-II-259-f5559
.* plaquerd DP-II-259-f5559 (10 1) C6D6 24.0C February_17,2011_10:17:10 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 14

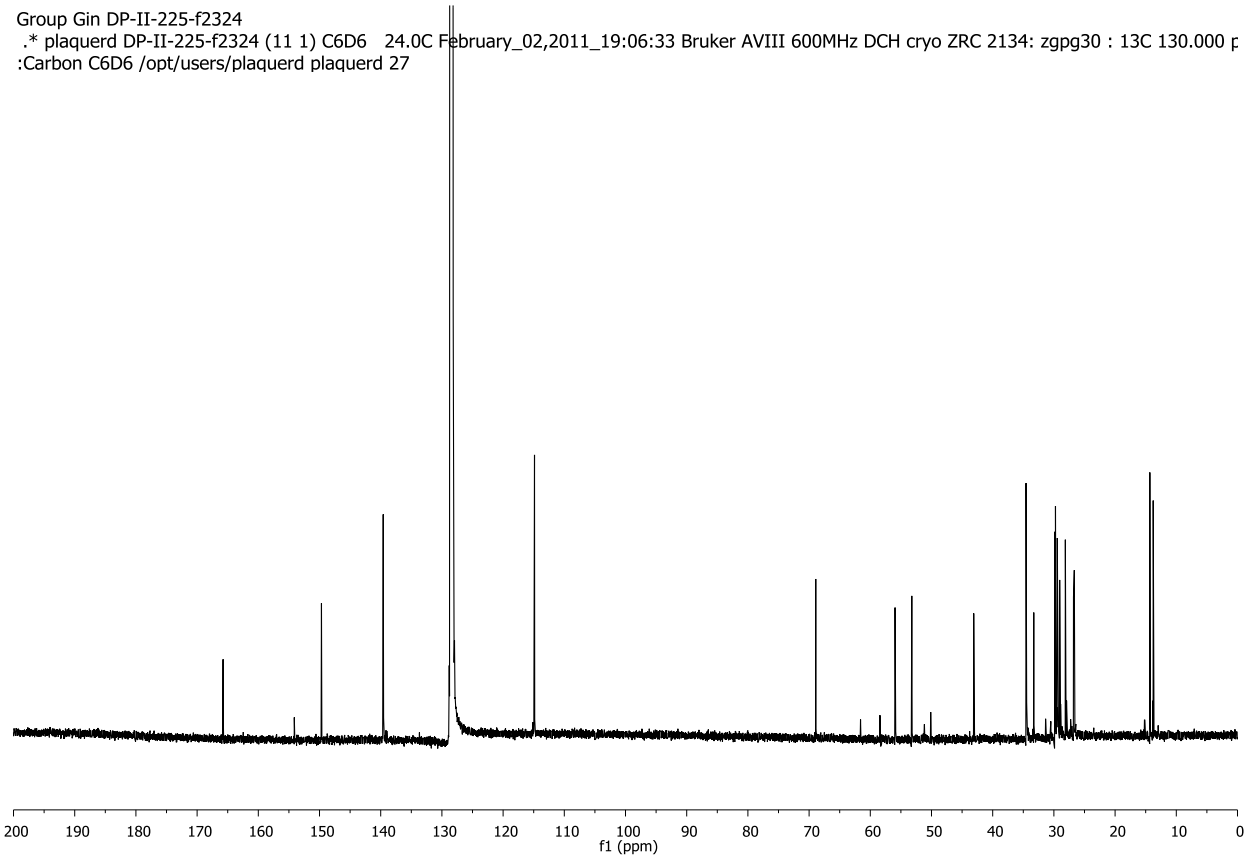


proposed structure

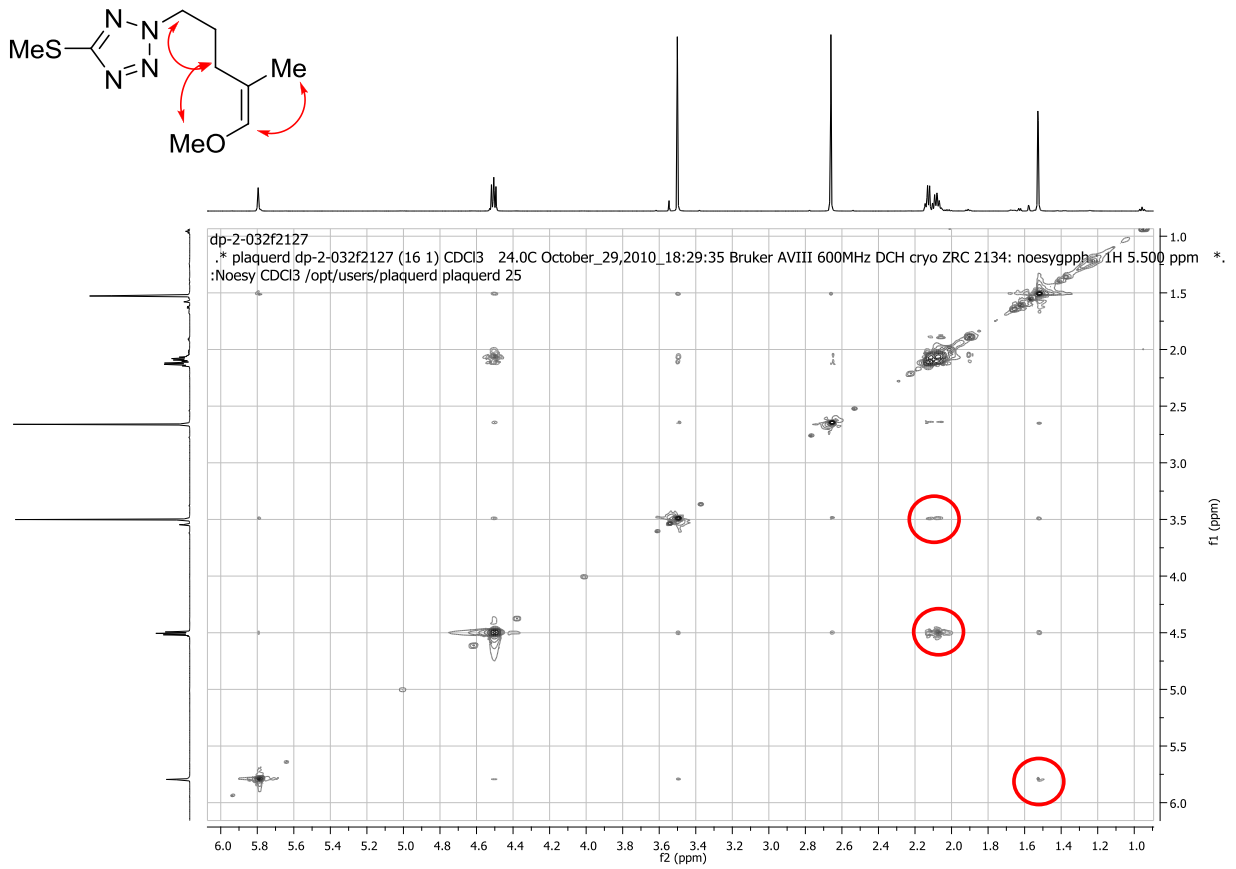
Group Gin DP-II-259-f5559
.* plaquerd DP-II-259-f5559 (11 1) C6D6 24.0C February_17,2011_10:19:31 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 14

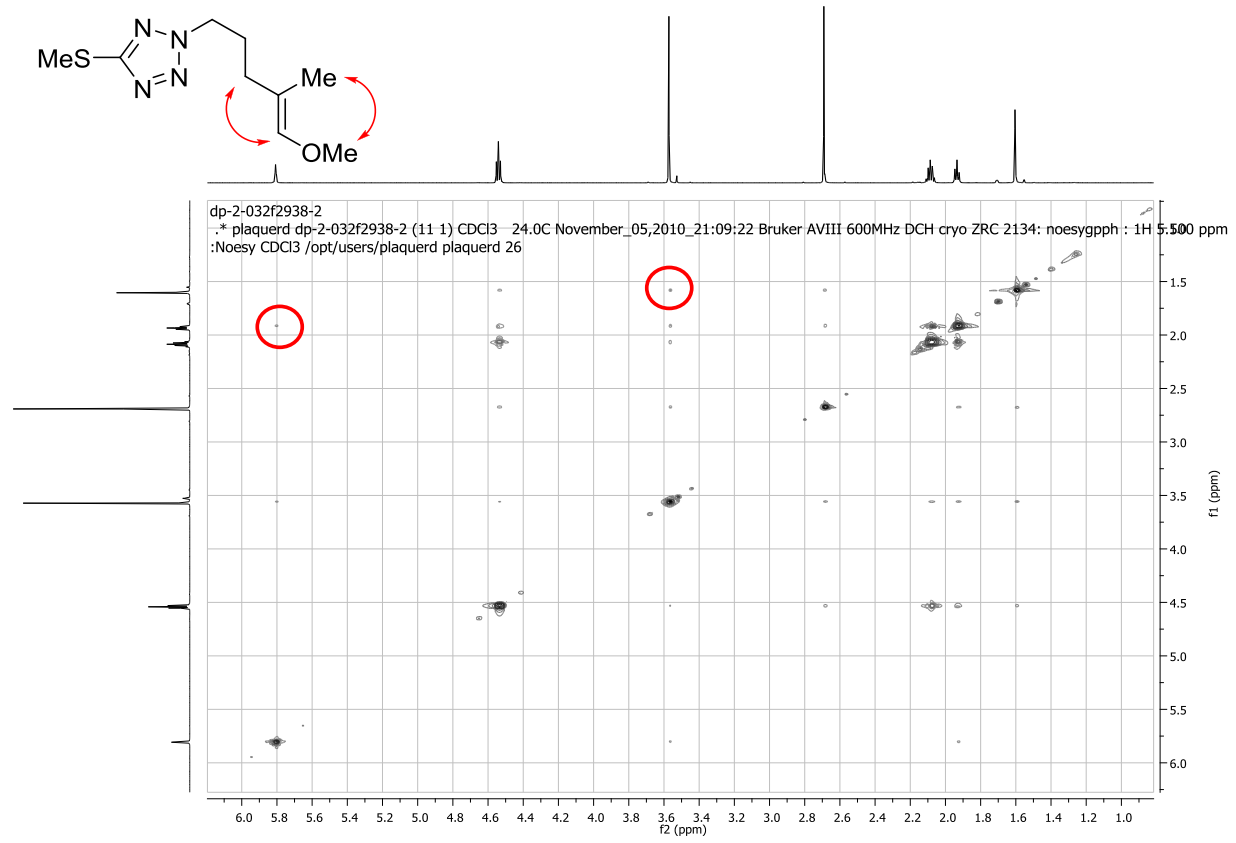


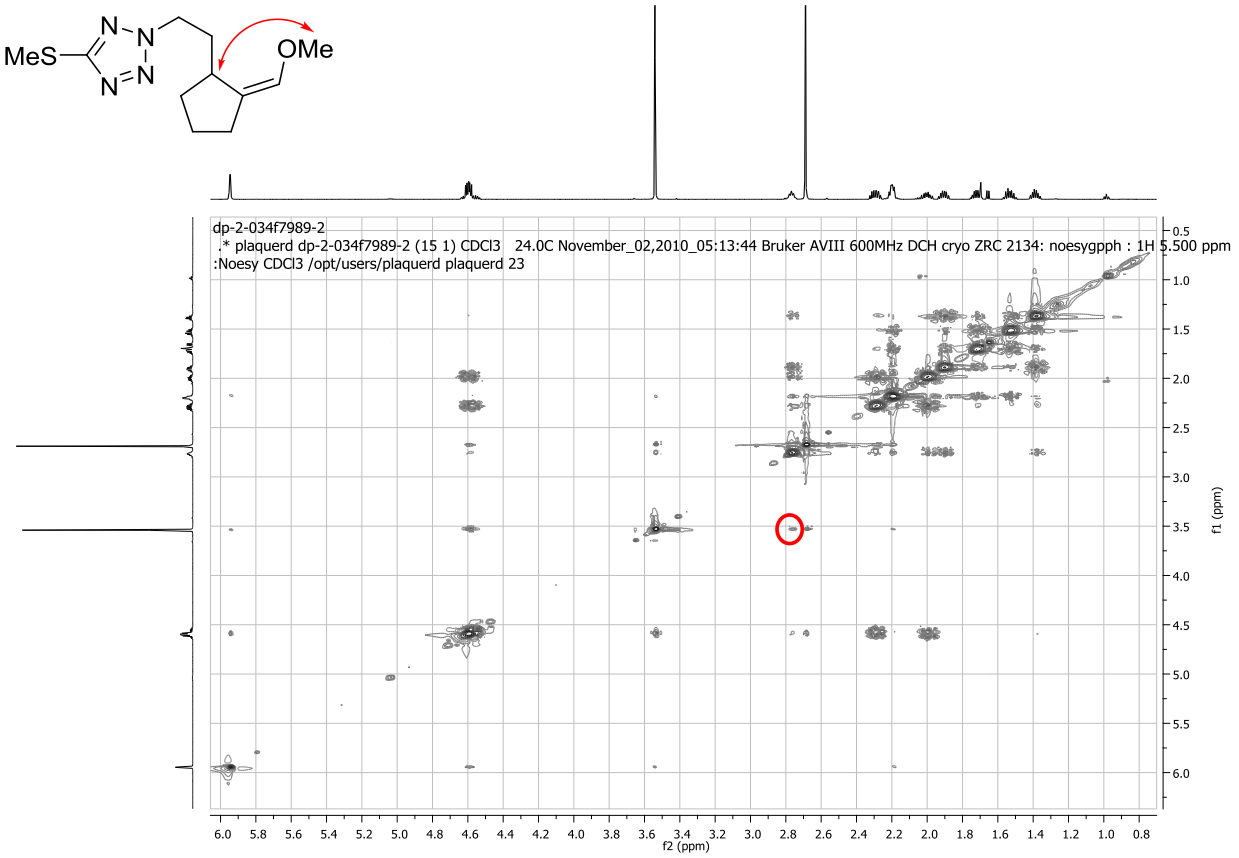

Group Gin DP-II-225-f2324
.* plaquerd DP-II-225-f2324 (10 1) C6D6 24.0C February_02,2011_19:04:14 Bruker AVIII 600MHz DCH cryo ZRC 2134: zg30 : 1H 6.175 ppm *.
:Proton C6D6 /opt/users/plaquerd plaquerd 27
SMe
MeS
proposed structure
f1 (ppm)

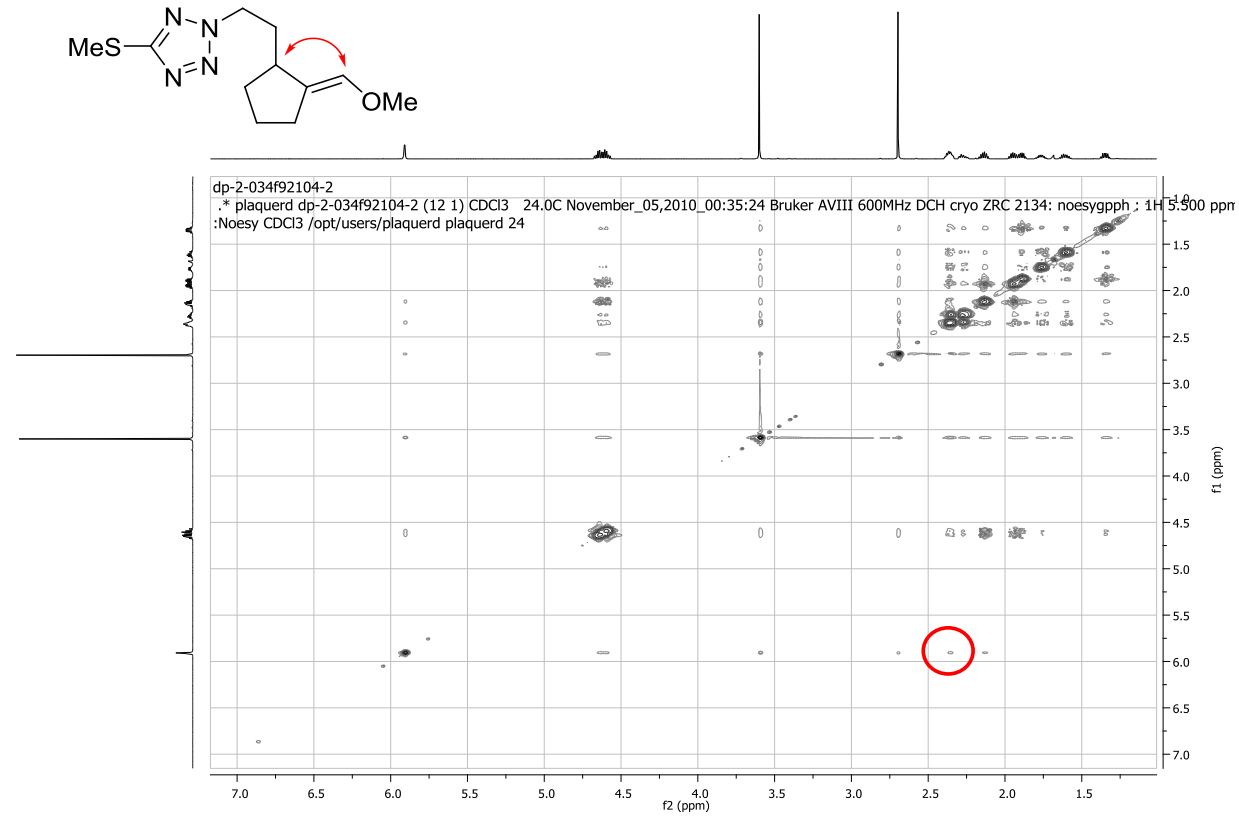

Group Gin DP-II-225-f2324
.* plaquerd DP-II-225-f2324 (11 1) C6D6 24.0C February_02,2011_19:06:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: zgpg30 : 13C 130.000 p
:Carbon C6D6 /opt/users/plaquerd plaquerd 27
f1 (ppm)

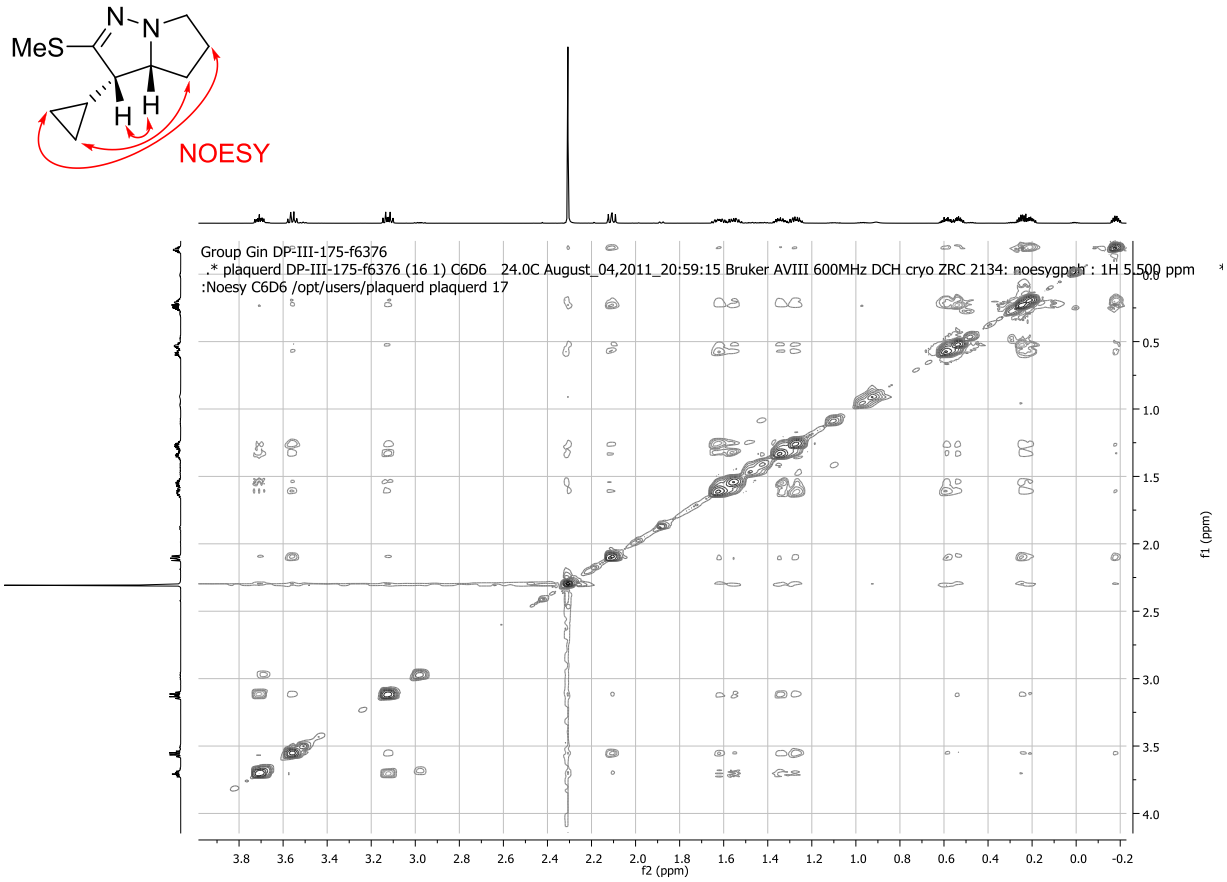
M. NOESY, COSY, HSQC and HMBC Spectra of Selected Compounds.

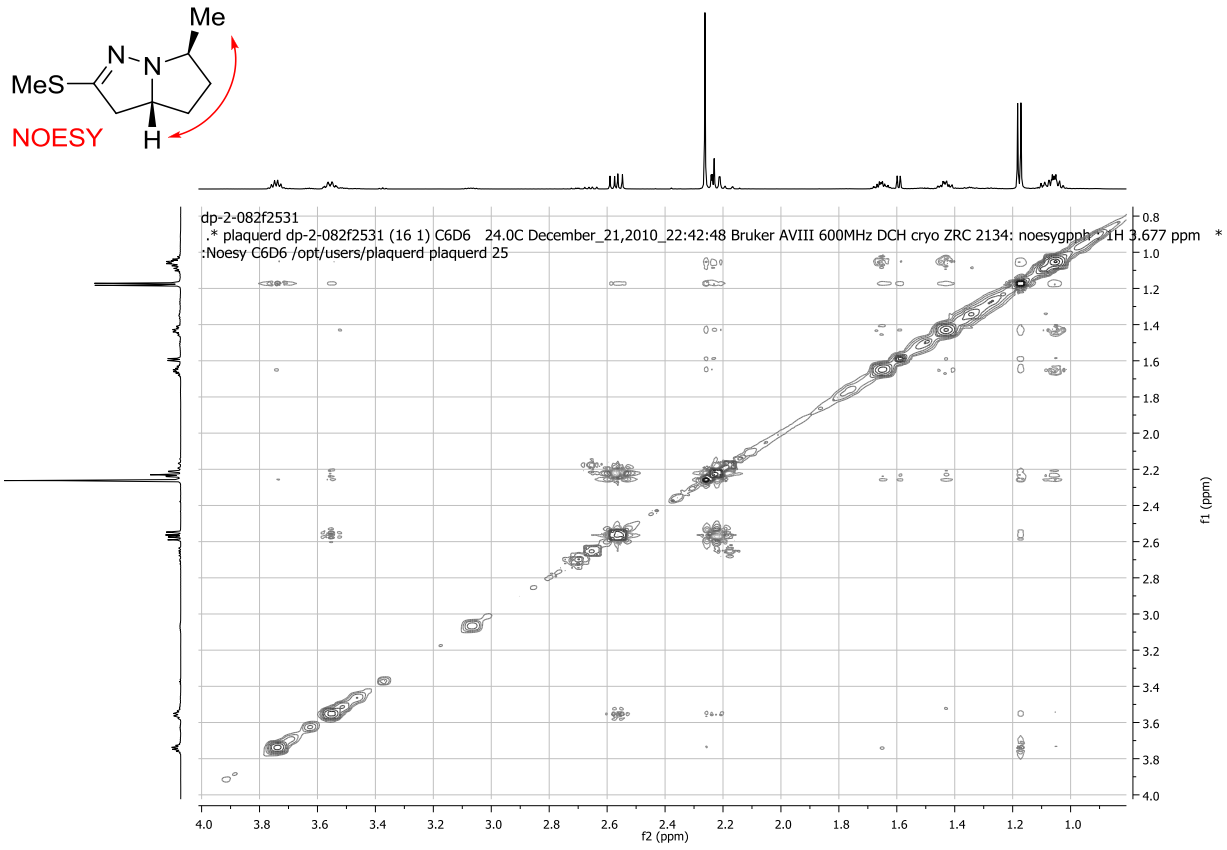


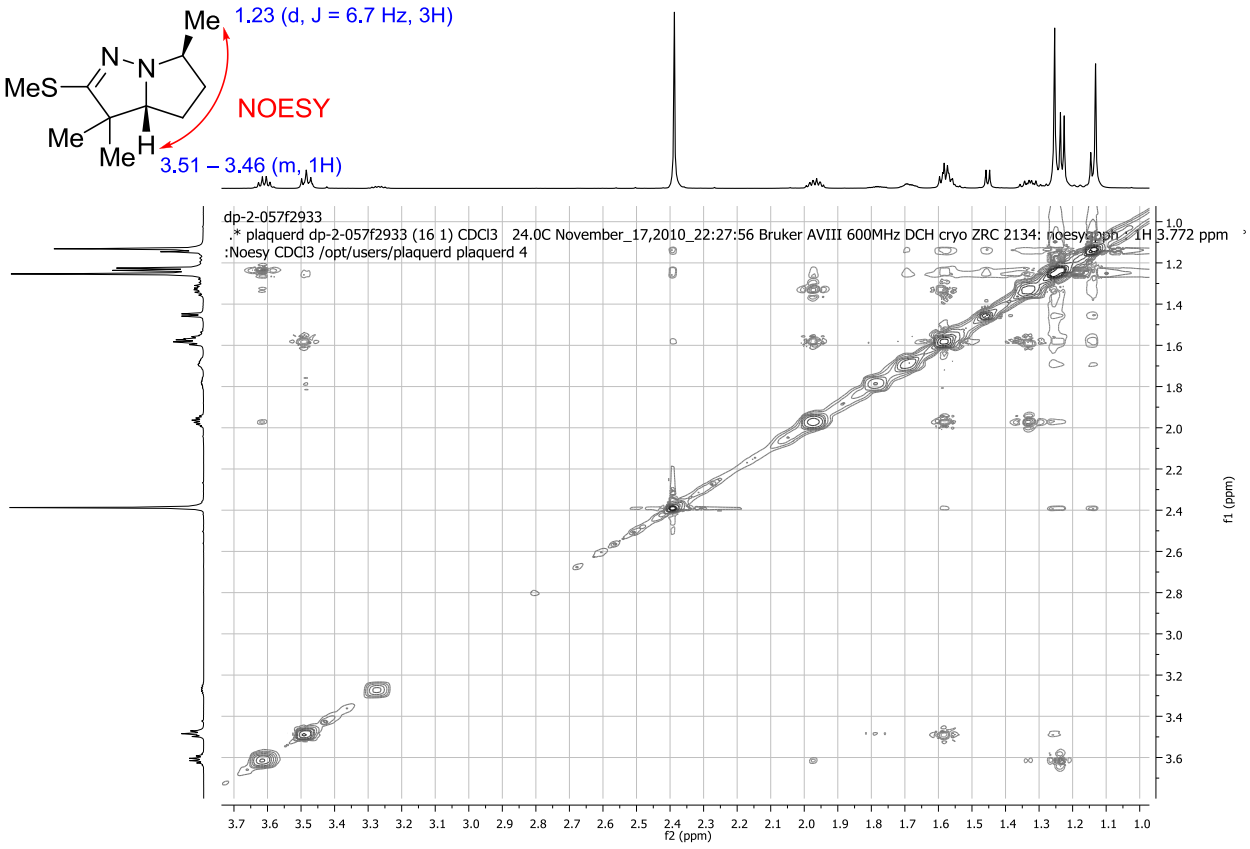


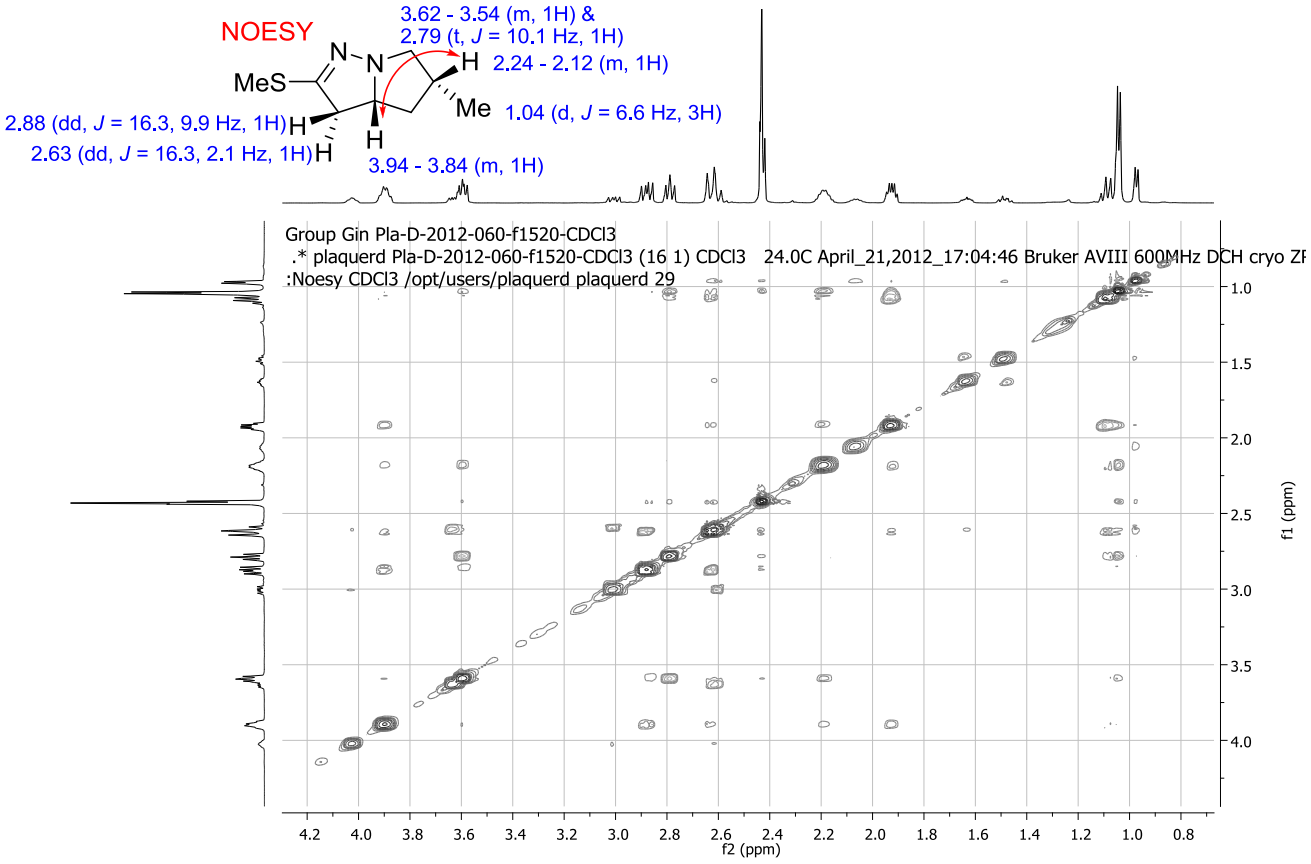

MeS
N
N
N
N
OMe
dp-2-034f7989-2
.* plaquerd dp-2-034f7989-2 (15 1) CDCl3 24.0C November_02,2010_05:13:44 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 5.500 ppm
:Noesy CDCl3 /opt/users/plaquerd plaquerd 23
f1 (ppm)
f2 (ppm)

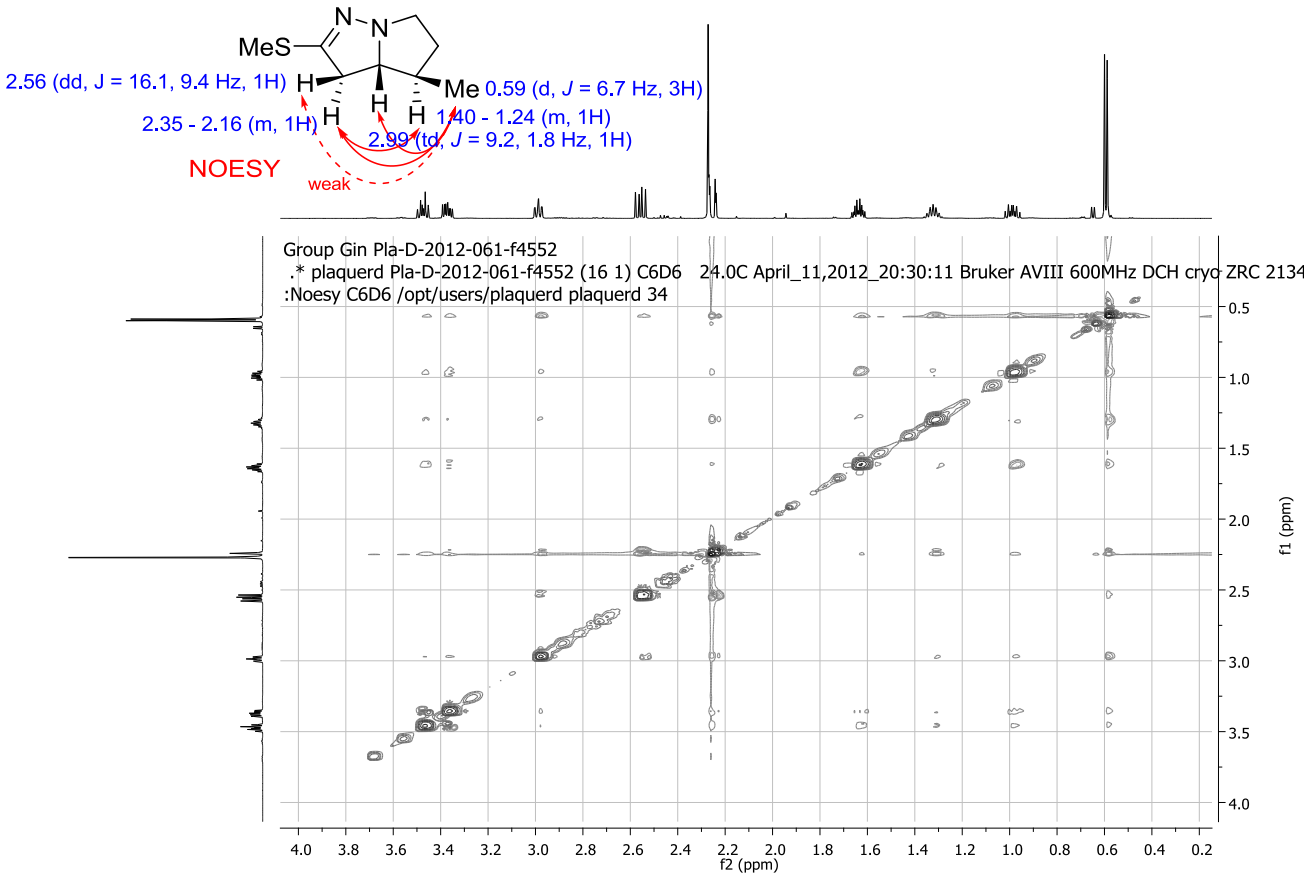

MeS
N
N
N
N
OMe
dp-2-034f92104-2
.* plaquerd dp-2-034f92104-2 (12 1) CDCl3 24.0C November_05,2010_00:35:24 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 5.500 ppm
:Noesy CDCl3 /opt/users/plaquerd plaquerd 24
f1 (ppm)
f2 (ppm)

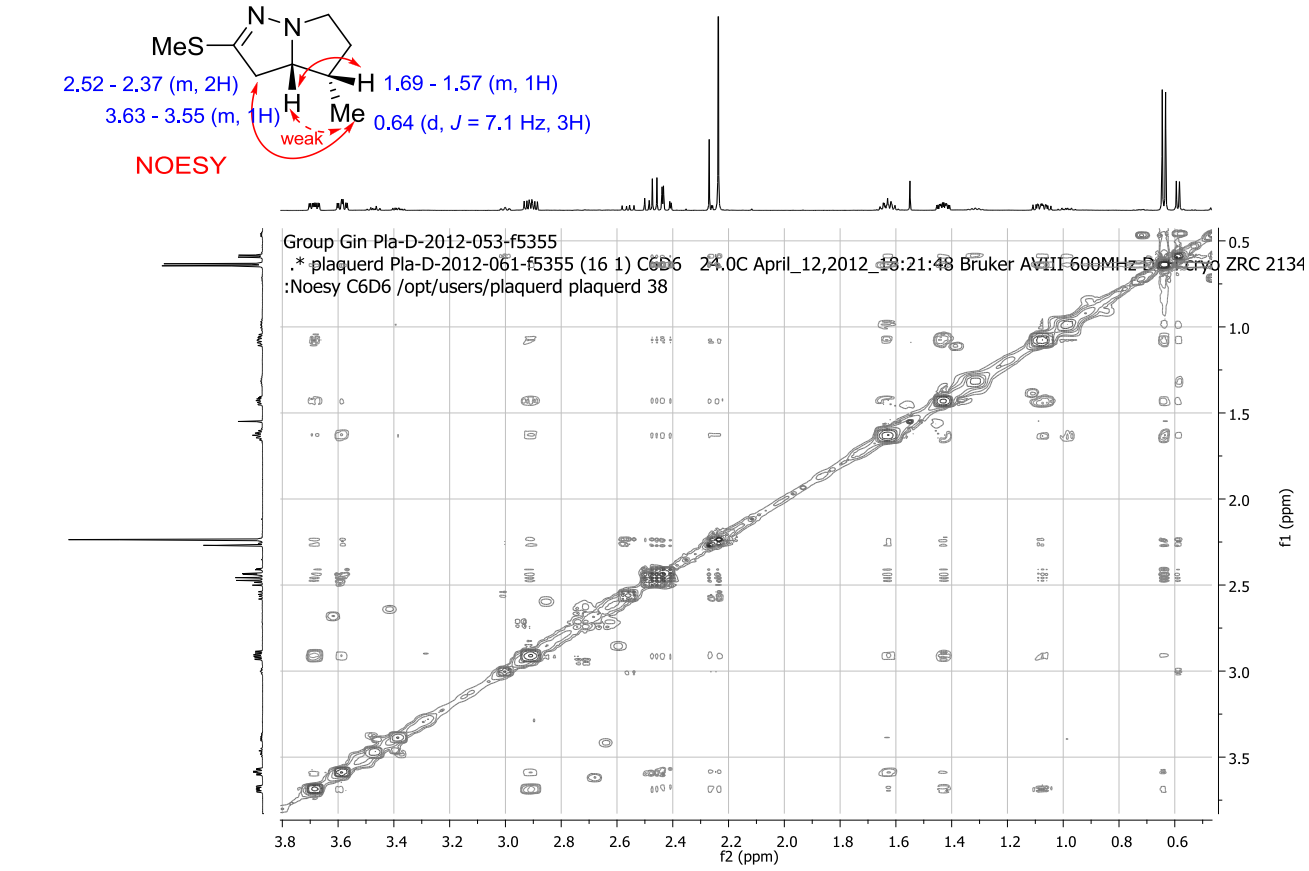

MeS
N
N
H
H
NOESY
Group Gin DP-III-175-f6376
.* plaquerd DP-III-175-f6376 (16 1) C6D6 24.0C August_04,2011_20:59:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 5.500 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 17
f1 (ppm)
f2 (ppm)

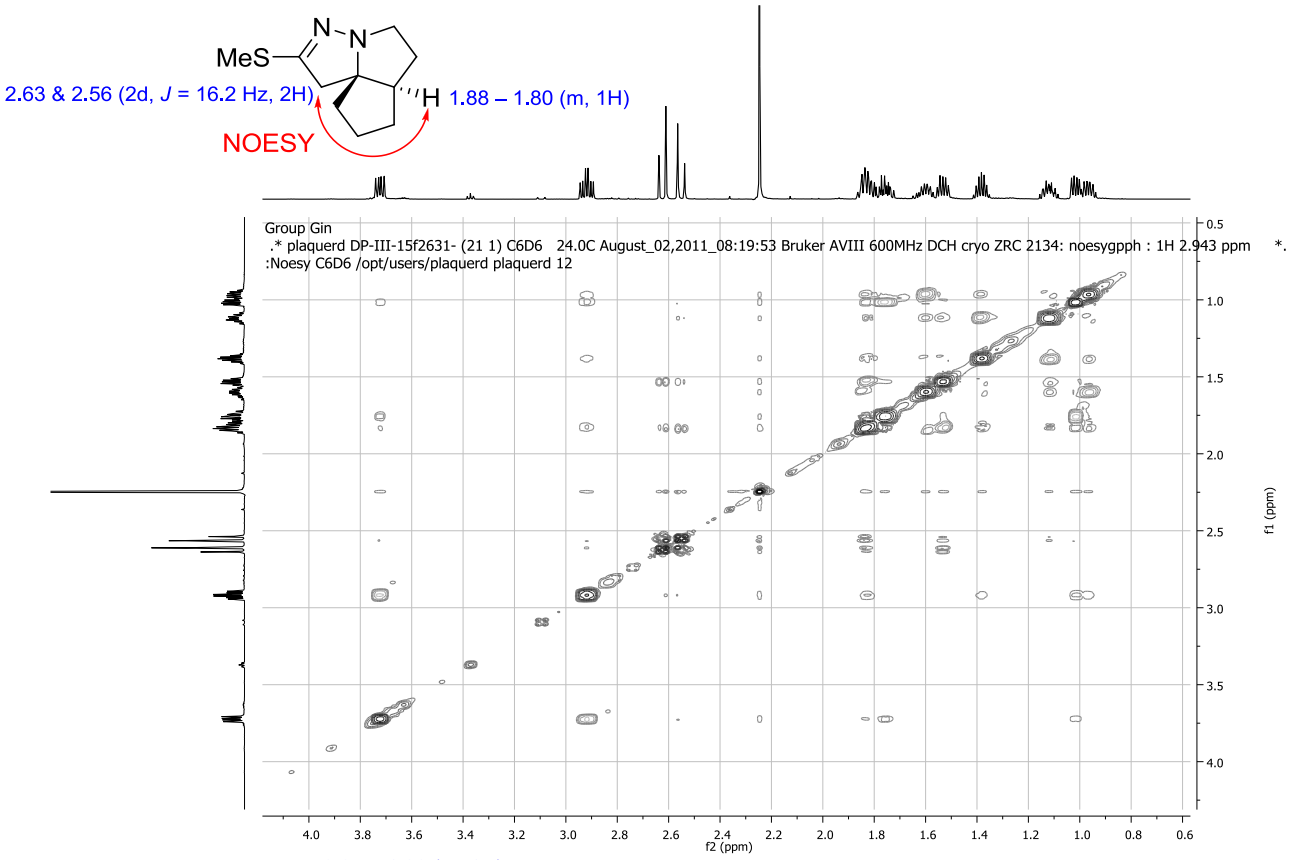

Me
MeS
N
N
NOESY
H
dp-2-082f2531
.* plaquerd dp-2-082f2531 (16 1) C6D6 24.0C December_21,2010_22:42:48 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.677 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 25
f1 (ppm)
f2 (ppm)

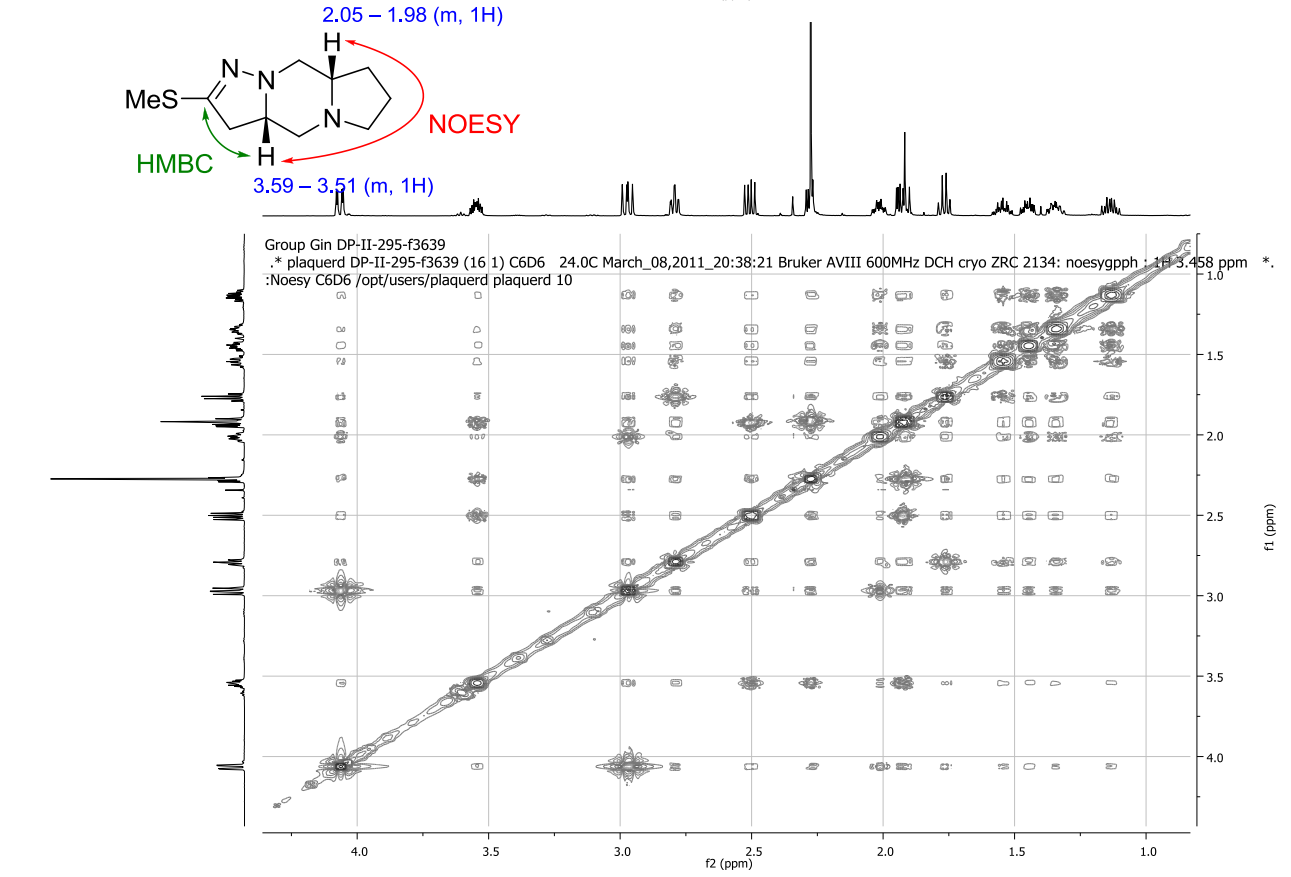

Me
1.23 (d, J = 6.7 Hz, 3H)
N
N
MeS
NOESY
Me
Me
H
3.51 – 3.46 (m, 1H)
dp-2-057f2933
.* plaquerd dp-2-057f2933 (16 1) CDCl3 24.0C November_17,2010_22:27:56 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesy.ppn 1H 3.772 ppm
:Noesy CDCl3 /opt/users/plaquerd plaquerd 4
f1 (ppm)
f2 (ppm)

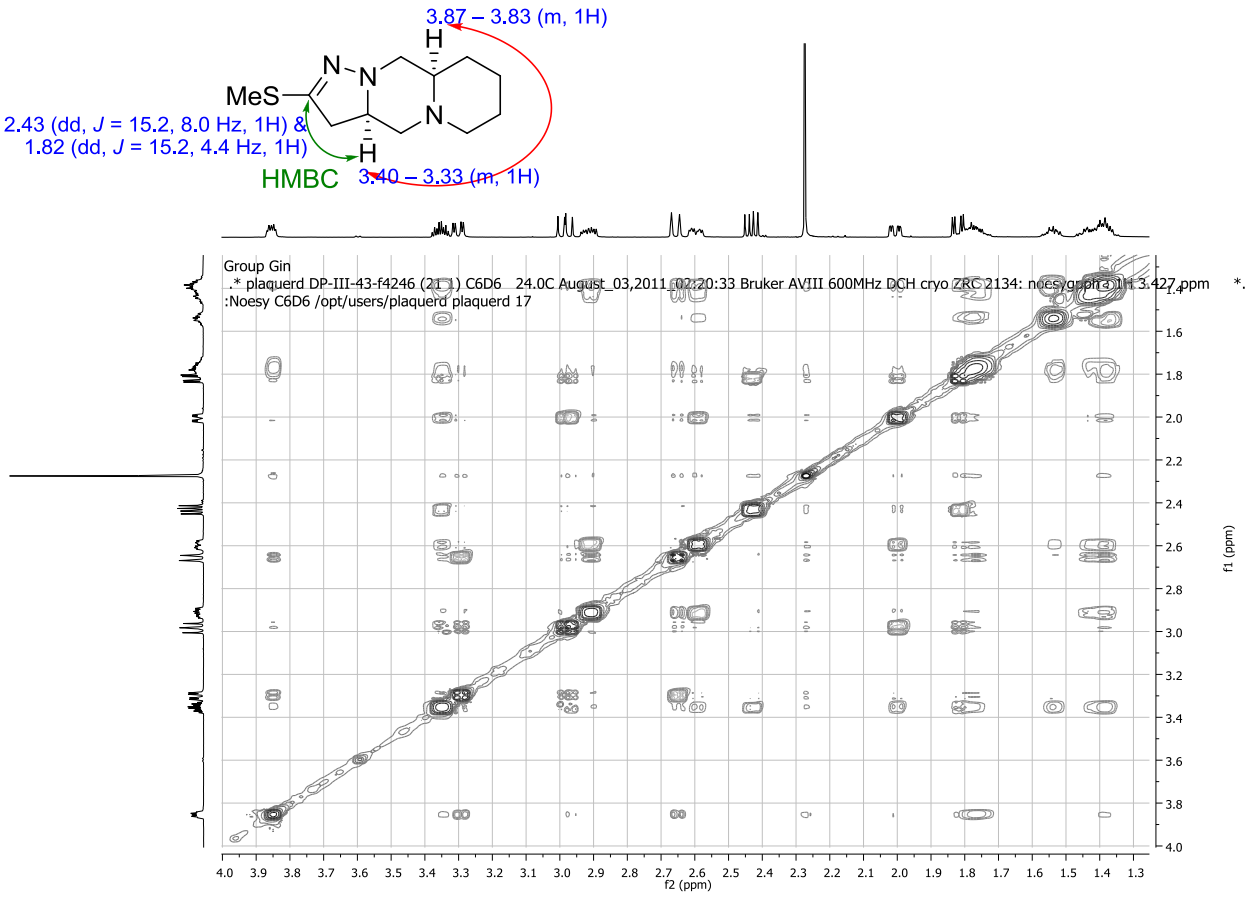

NOESY
3.62 - 3.54 (m, 1H) &
2.79 (t, J = 10.1 Hz, 1H)
N
N
H
2.24 - 2.12 (m, 1H)
MeS
Me
1.04 (d, J = 6.6 Hz, 3H)
2.88 (dd, J = 16.3, 9.9 Hz, 1H)
H
2.63 (dd, J = 16.3, 2.1 Hz, 1H)
H
H
3.94 - 3.84 (m, 1H)
Group Gin Pla-D-2012-060-f1520-CDCl3
.* plaquerd Pla-D-2012-060-f1520-CDCl3 (16 1) CDCl3 24.0C April_21,2012_17:04:46 Bruker AVIII 600MHz DCH cryo ZF
:Noesy CDCl3 /opt/users/plaquerd plaquerd 29
f1 (ppm)
f2 (ppm)

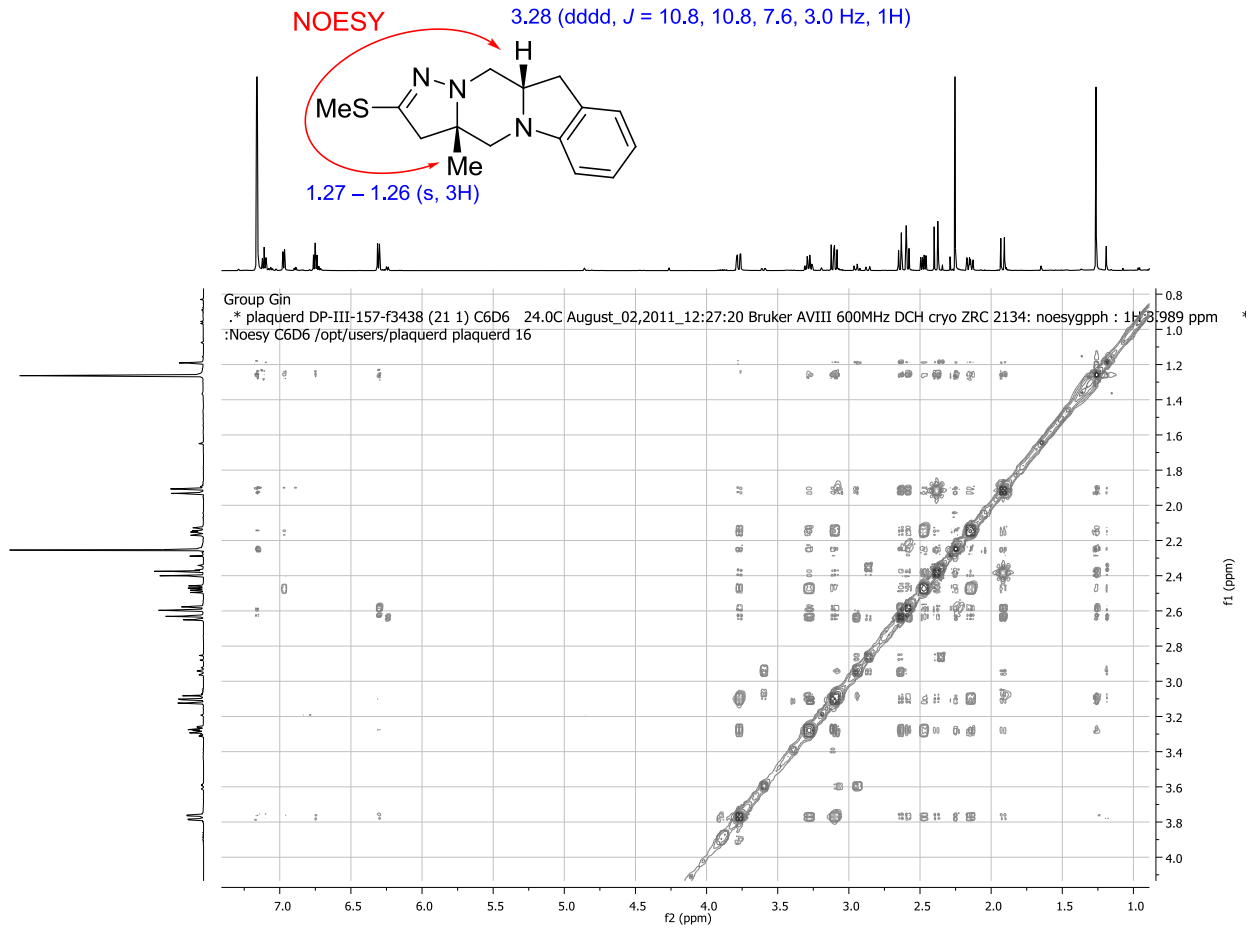

MeS
N
N
H
H
H
H
Me
2.56 (dd, J = 16.1, 9.4 Hz, 1H)
0.59 (d, J = 6.7 Hz, 3H)
2.35 - 2.16 (m, 1H)
1.40 - 1.24 (m, 1H)
2.99 (td, J = 9.2, 1.8 Hz, 1H)
NOESY
weak
Group Gin Pla-D-2012-061-f4552
.* plaquerd Pla-D-2012-061-f4552 (16 1) C6D6 24.0C April_11,2012_20:30:11 Bruker AVIII 600MHz DCH cryo ZRC 2134
:Noesy C6D6 /opt/users/plaquerd plaquerd 34
f1 (ppm)
f2 (ppm)

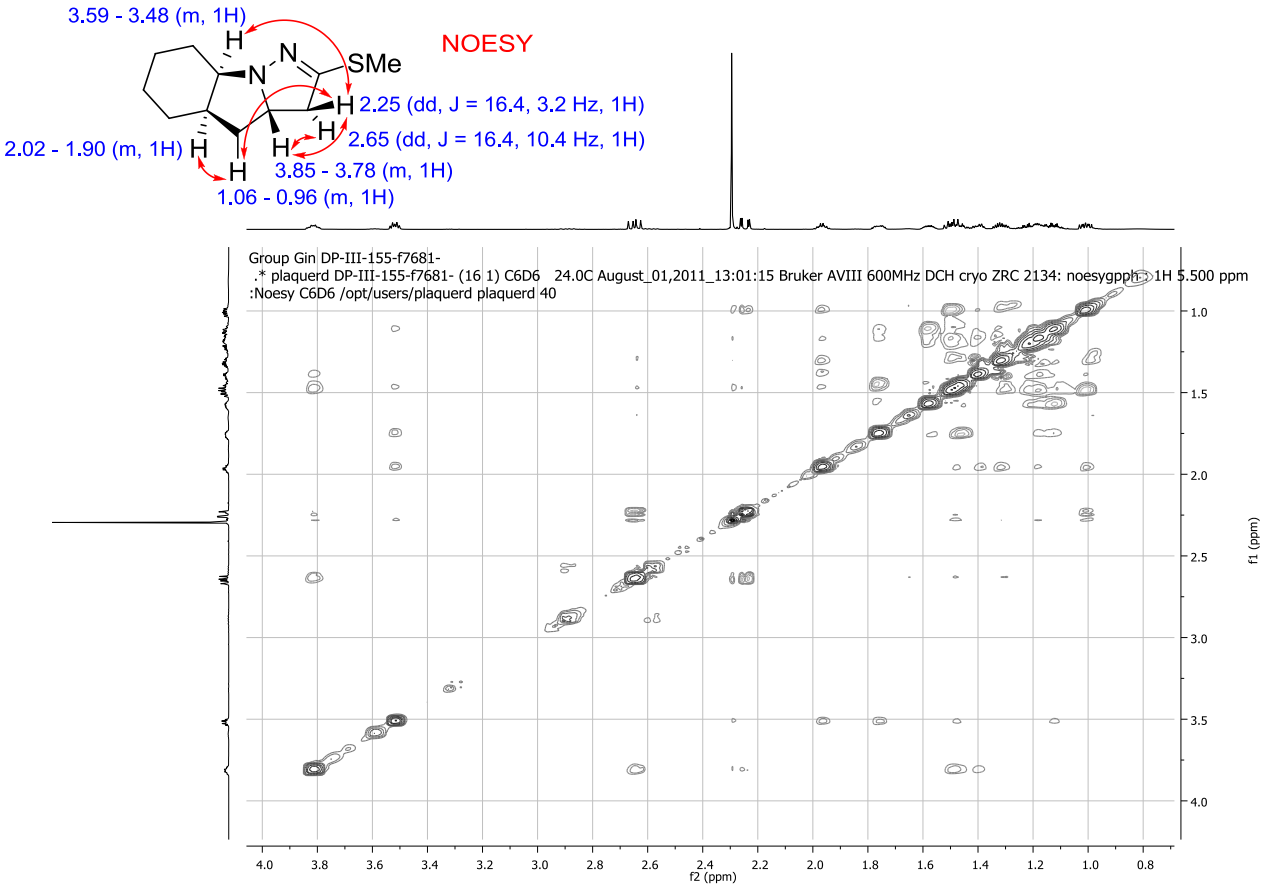

MeS
N
N
H
Me
2.52 - 2.37 (m, 2H)
1.69 - 1.57 (m, 1H)
3.63 - 3.55 (m, 1H)
0.64 (d, J = 7.1 Hz, 3H)
weak
NOESY
Group Gin Pla-D-2012-053-f5355
.* plaquerd Pla-D-2012-061-f5355 (16 1) C6D6 24.0C April_12,2012_18:21:48 Bruker AVIII 600MHz DCH cryo ZRC 2134
:Noesy C6D6 /opt/users/plaquerd plaquerd 38
f1 (ppm)
f2 (ppm)

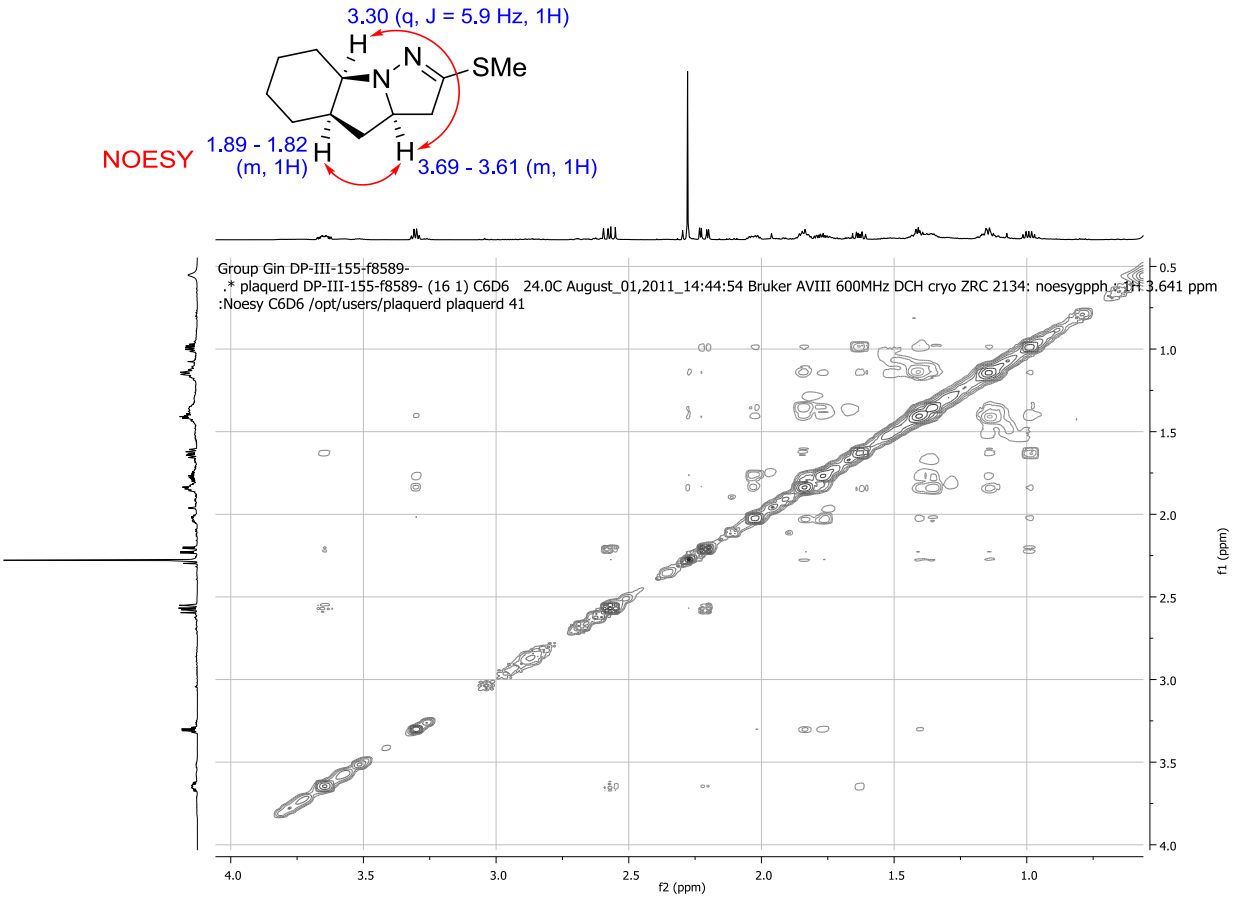

MeS
N
N
H
2.63 & 2.56 (2d, J = 16.2 Hz, 2H)
1.88 – 1.80 (m, 1H)
NOESY
Group Gin
.* plaquerd DP-III-15f2631- (21 1) C6D6 24.0C August_02,2011_08:19:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 2.943 ppm *.
:Noesy C6D6 /opt/users/plaquerd plaquerd 12
f1 (ppm)
f2 (ppm)

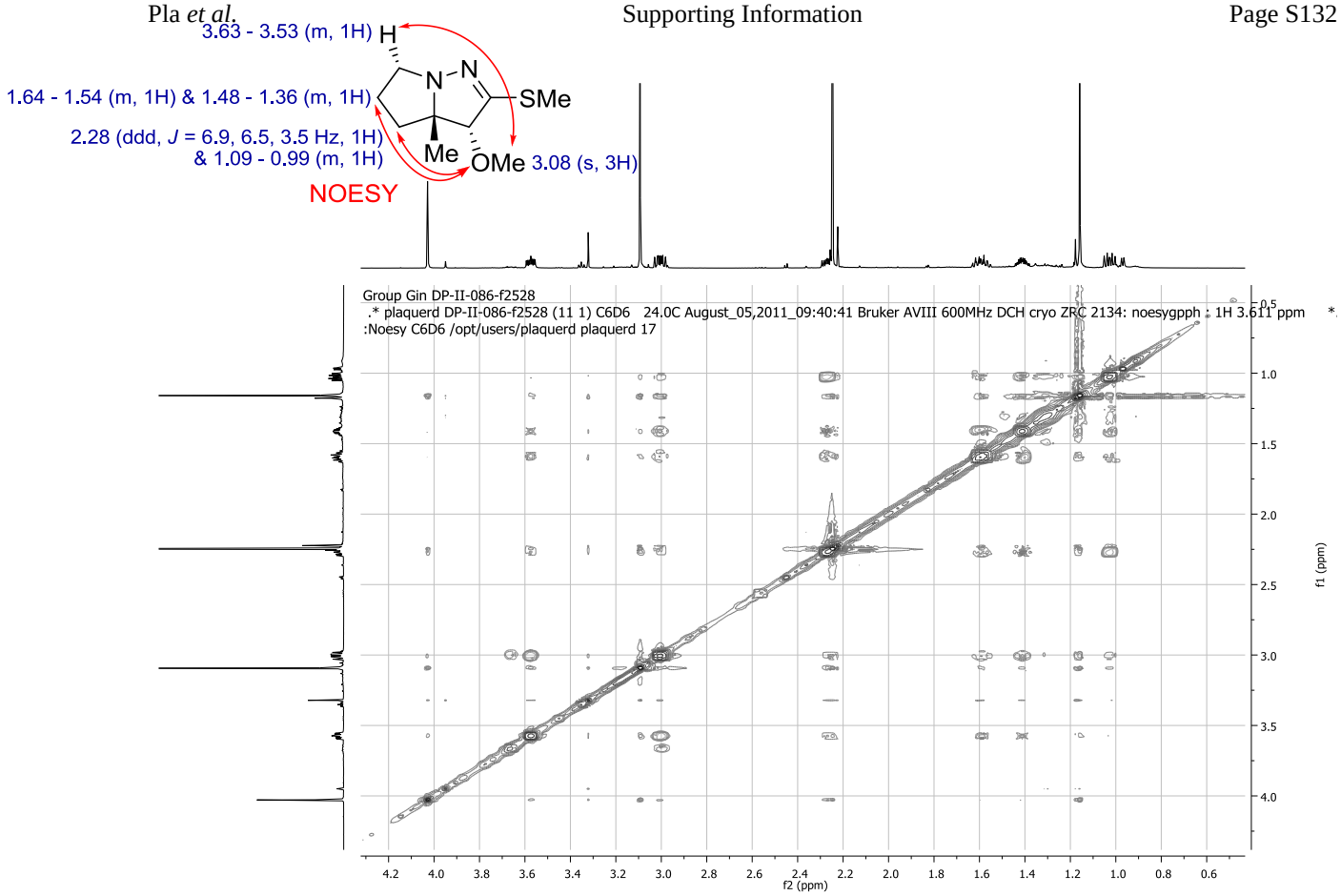

2.05 – 1.98 (m, 1H)
MeS
N
N
H
N
H
NOESY
HMBC
3.59 – 3.51 (m, 1H)
Group Gin DP-II-295-f3639
.* plaquerd DP-II-295-f3639 (16 1) C6D6 24.0C March_08,2011_20:38:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.458 ppm *.
:Noesy C6D6 /opt/users/plaquerd plaquerd 10
f1 (ppm)
f2 (ppm)

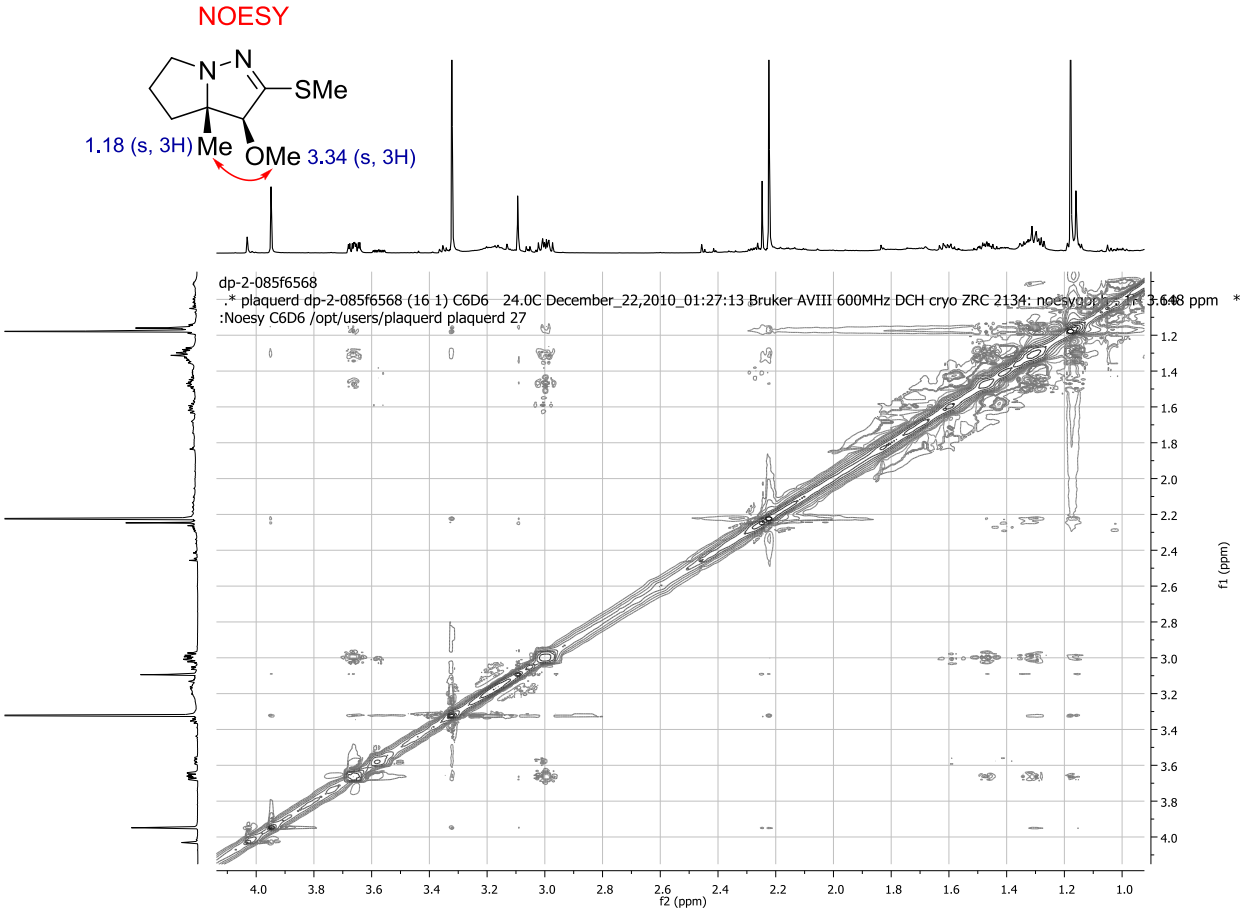

3.87 – 3.83 (m, 1H)
MeS
2.43 (dd, J = 15.2, 8.0 Hz, 1H) &
1.82 (dd, J = 15.2, 4.4 Hz, 1H)
HMBC
3.40 – 3.33 (m, 1H)
Group Gin
.* plaquerd DP-III-43-f4246 (21 1) C6D6 24.0C August_03,2011_02:20:33 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.427 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 17
f1 (ppm)
f2 (ppm)

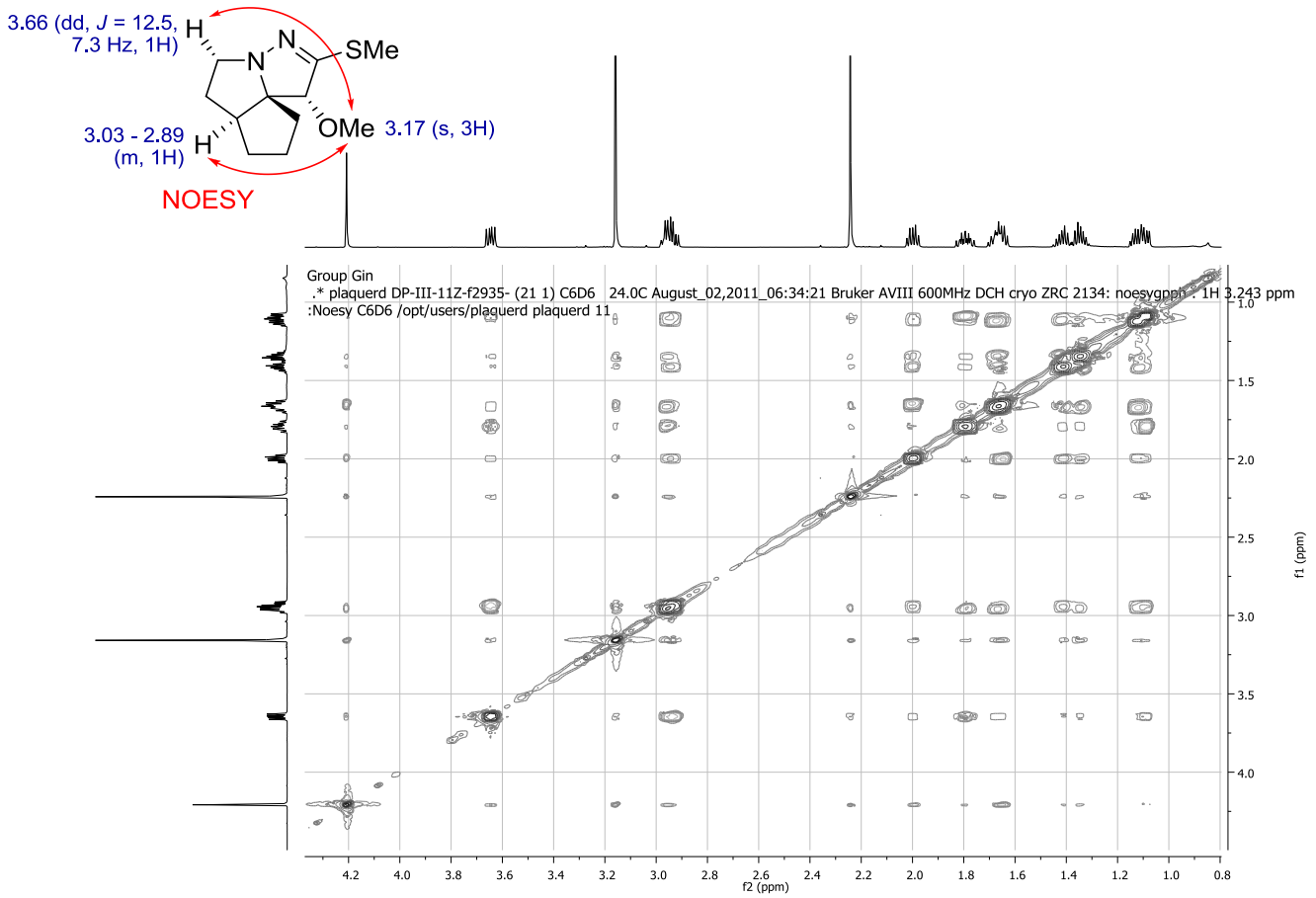

NOESY
3.28 (dddd, J = 10.8, 10.8, 7.6, 3.0 Hz, 1H)
MeS
Me
1.27 – 1.26 (s, 3H)
Group Gin
.* plaquerd DP-III-157-f3438 (21 1) C6D6 24.0C August_02,2011_12:27:20 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.989 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 16
f1 (ppm)
f2 (ppm)

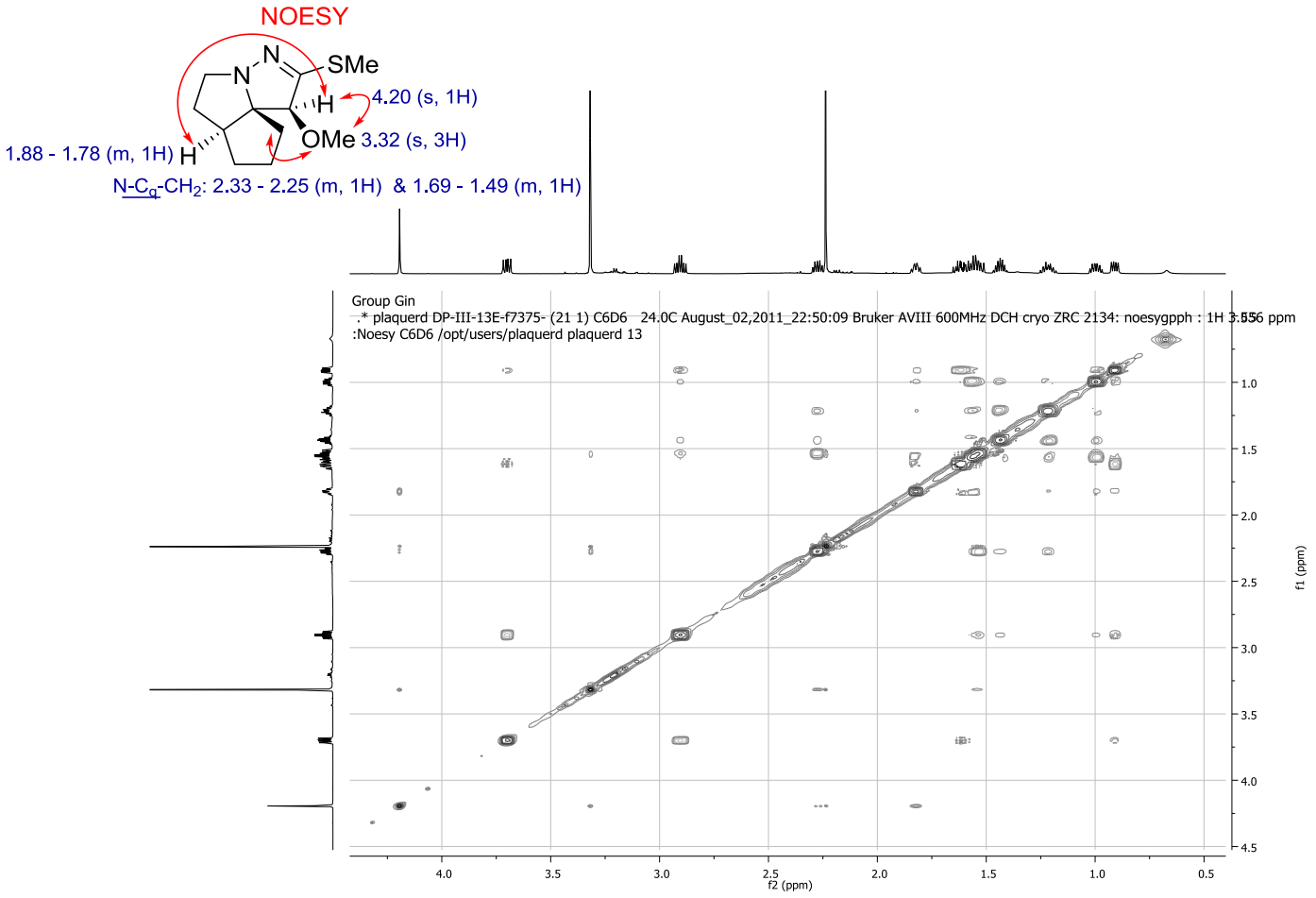

3.59 - 3.48 (m, 1H)
NOESY
SMe
2.25 (dd, J = 16.4, 3.2 Hz, 1H)
2.65 (dd, J = 16.4, 10.4 Hz, 1H)
2.02 - 1.90 (m, 1H)
3.85 - 3.78 (m, 1H)
1.06 - 0.96 (m, 1H)
Group Gin DP-III-155-f7681-
.* plaquerd DP-III-155-f7681- (16 1) C6D6 24.0C August_01,2011_13:01:15 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph 1H 5.500 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 40
f2 (ppm)
f1 (ppm)

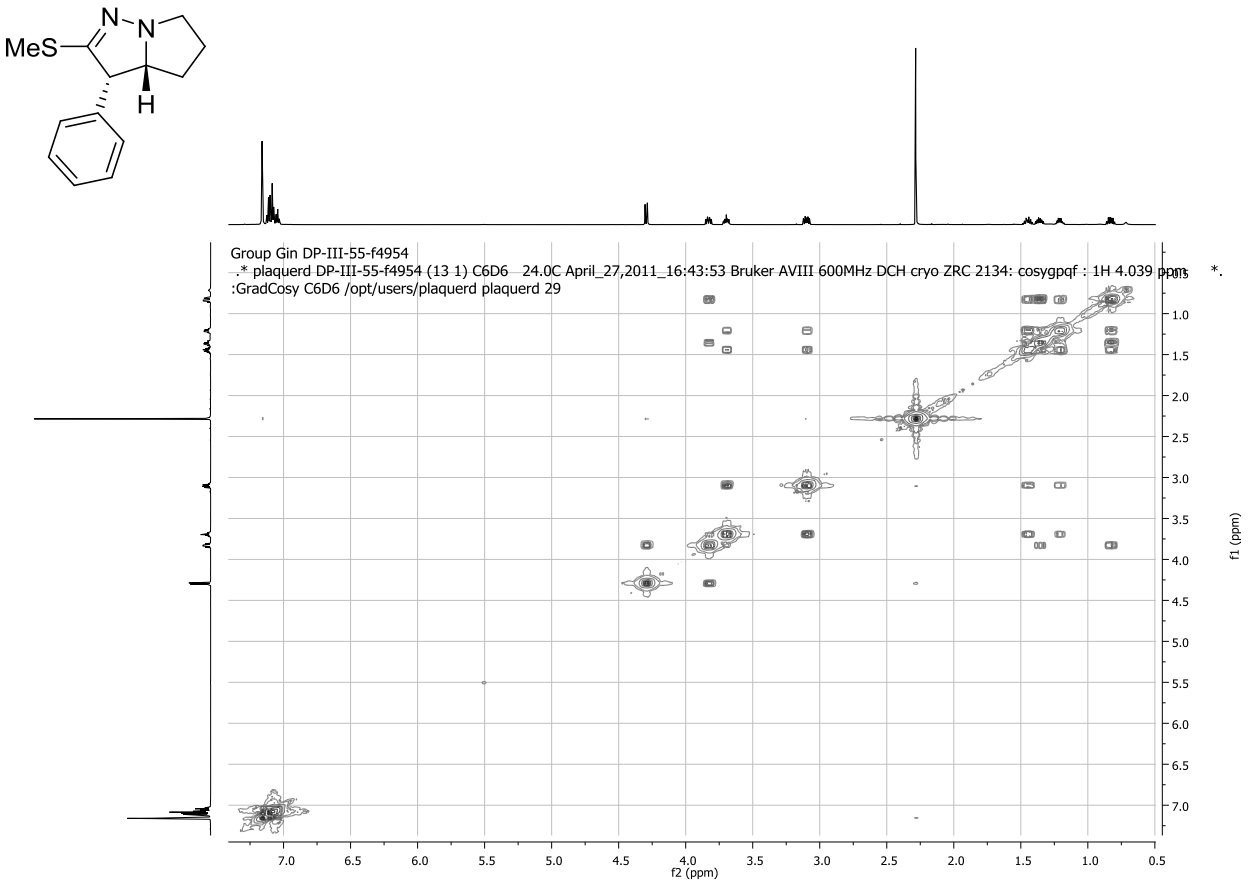

3.30 (q, J = 5.9 Hz, 1H)
SMe
NOESY
1.89 - 1.82 (m, 1H)
3.69 - 3.61 (m, 1H)
Group Gin DP-III-155-f8589-
.* plaquerd DP-III-155-f8589- (16 1) C6D6 24.0C August_01,2011_14:44:54 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph 1H 3.641 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 41
f2 (ppm)
f1 (ppm)

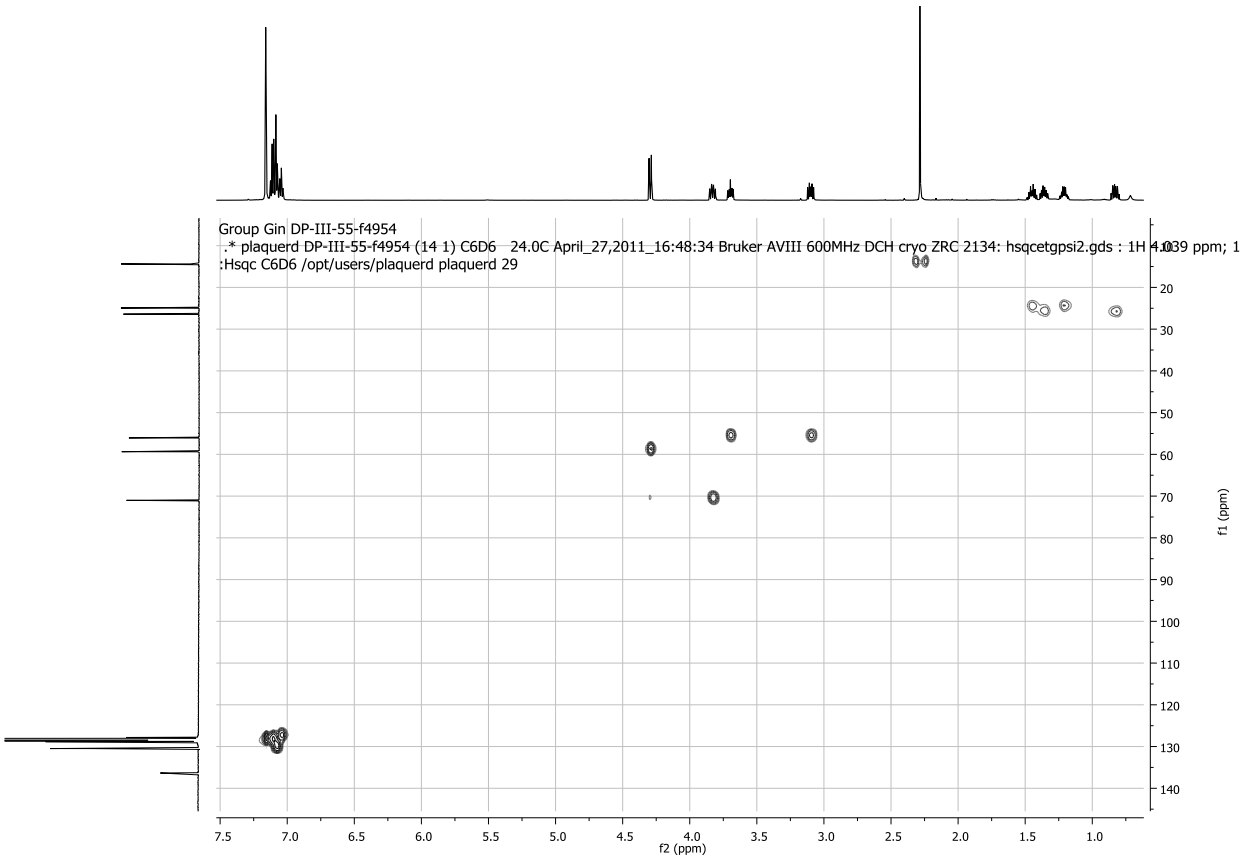

3.63 - 3.53 (m, 1H)
1.64 - 1.54 (m, 1H) & 1.48 - 1.36 (m, 1H)
2.28 (ddd, J = 6.9, 6.5, 3.5 Hz, 1H)
& 1.09 - 0.99 (m, 1H)
NOESY
SMe
Me
OMe 3.08 (s, 3H)
Group Gin DP-II-086-f2528
.* plaquerd DP-II-086-f2528 (11 1) C6D6 24.0C August_05,2011_09:40:41 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.611 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 17
f1 (ppm)
f2 (ppm)

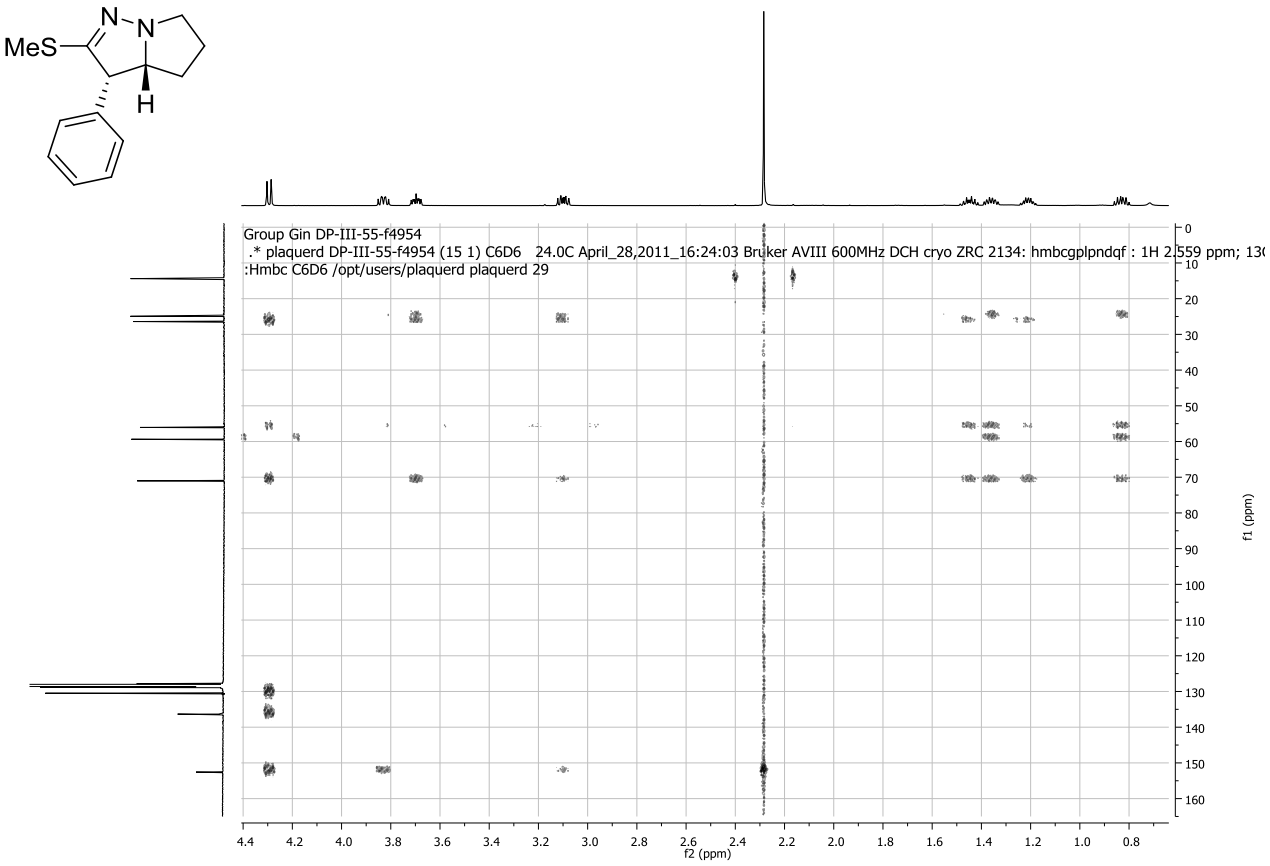

NOESY
SMe
1.18 (s, 3H)
Me
OMe 3.34 (s, 3H)
dp-2-085f6568
.* plaquerd dp-2-085f6568 (16 1) C6D6 24.0C December_22,2010_01:27:13 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.648 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 27
f1 (ppm)
f2 (ppm)

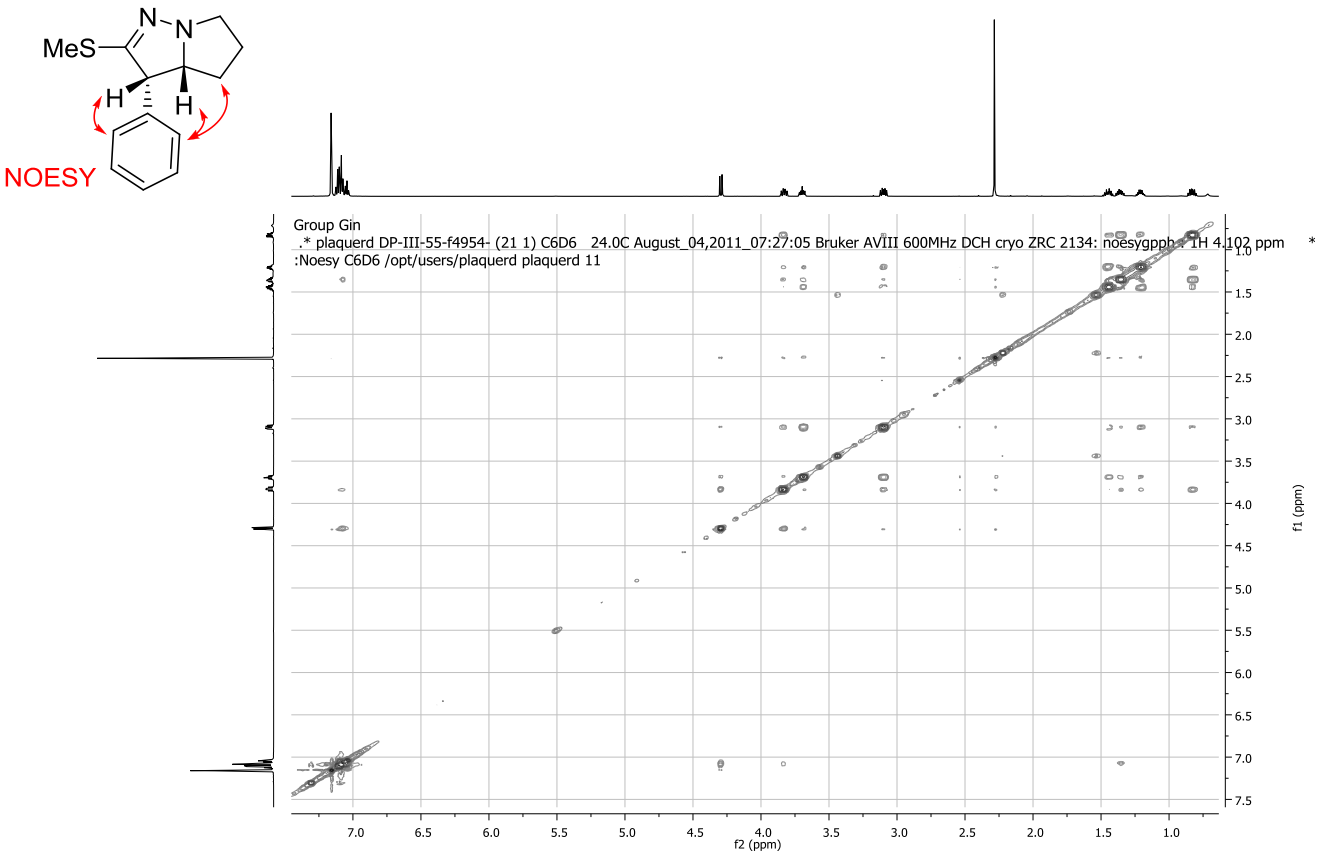

3.66 (dd, J = 12.5, 7.3 Hz, 1H)
SMe
3.03 - 2.89 (m, 1H)
OMe 3.17 (s, 3H)
NOESY
Group Gin
.* plaquerd DP-III-11Z-f2935- (21 1) C6D6 24.0C August_02,2011_06:34:21 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.243 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 11
f2 (ppm)
f1 (ppm)

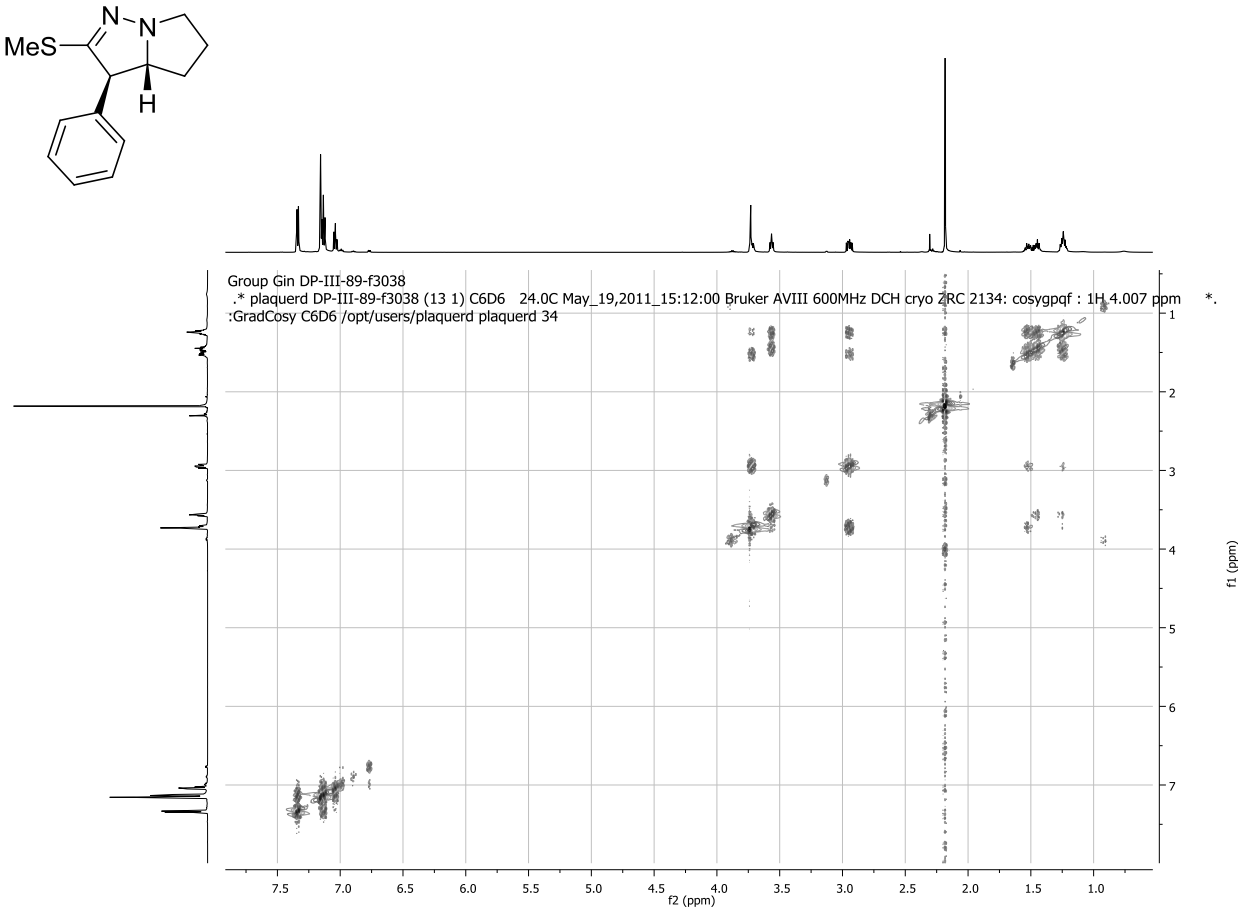

NOESY
SMe
4.20 (s, 1H)
OMe 3.32 (s, 3H)
1.88 - 1.78 (m, 1H)
N-Cq-CH2: 2.33 - 2.25 (m, 1H) & 1.69 - 1.49 (m, 1H)
Group Gin
.* plaquerd DP-III-13E-f7375- (21 1) C6D6 24.0C August_02,2011_22:50:09 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 3.556 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 13
f2 (ppm)
f1 (ppm)

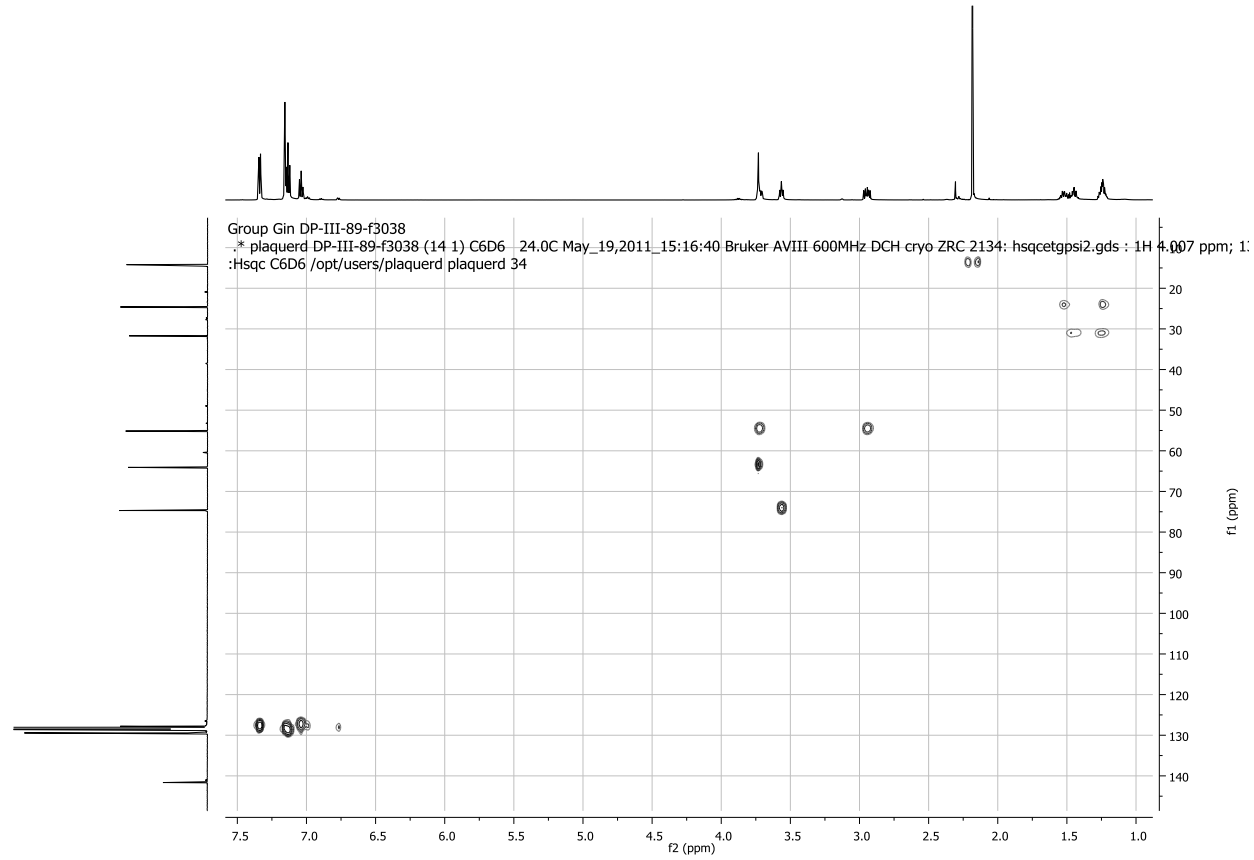

MeS
N
N
H
Group Gin DP-III-55-f4954
.* plaquerd DP-III-55-f4954 (13 1) C6D6 24.0C April_27,2011_16:43:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: cosygpqf : 1H 4.039 ppm *.
:GradCosy C6D6 /opt/users/plaquerd plaquerd 29
f1 (ppm)
f2 (ppm)

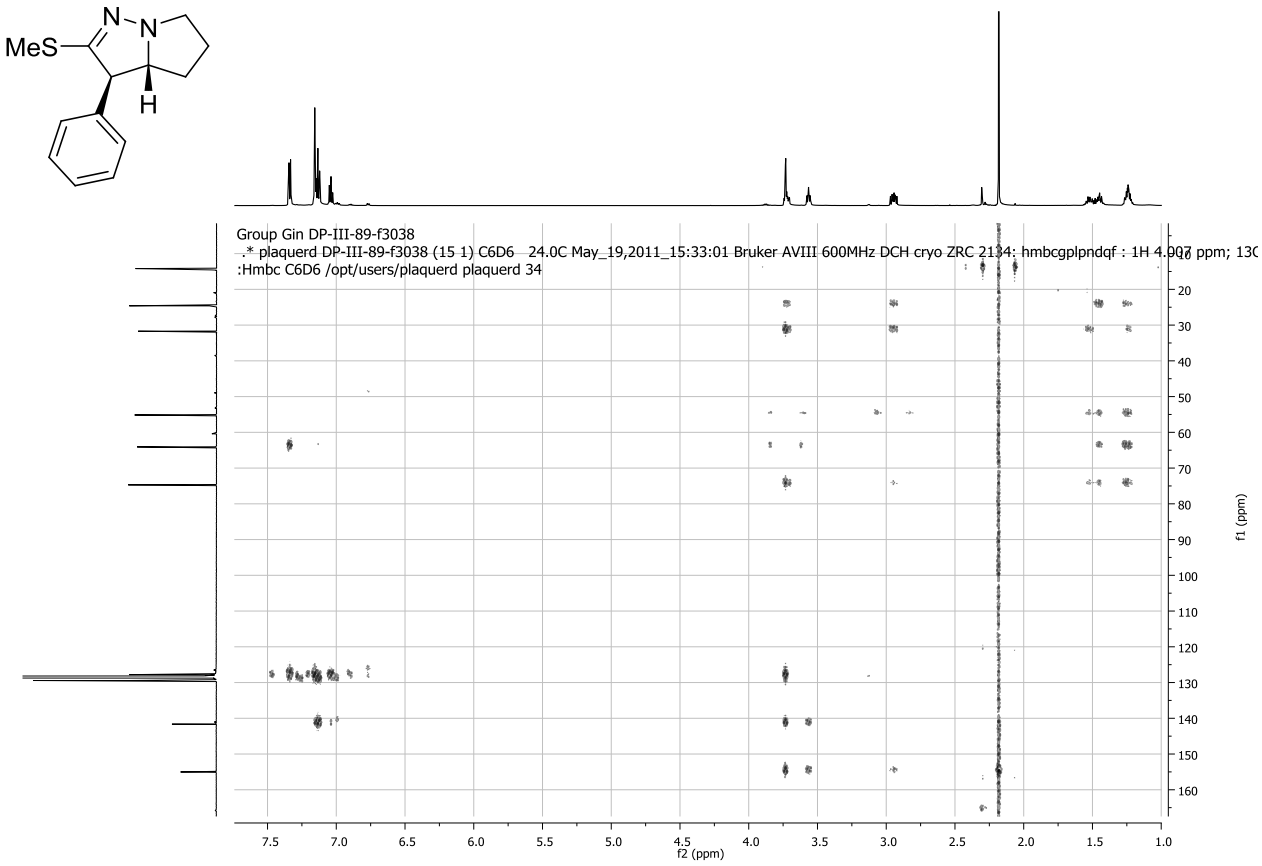

Group Gin DP-III-55-f4954
.* plaquerd DP-III-55-f4954 (14 1) C6D6 24.0C April_27,2011_16:48:34 Bruker AVIII 600MHz DCH cryo ZRC 2134: hsqcetgpsi2.gds : 1H 4.039 ppm; 1
:Hsqc C6D6 /opt/users/plaquerd plaquerd 29
f1 (ppm)
f2 (ppm)

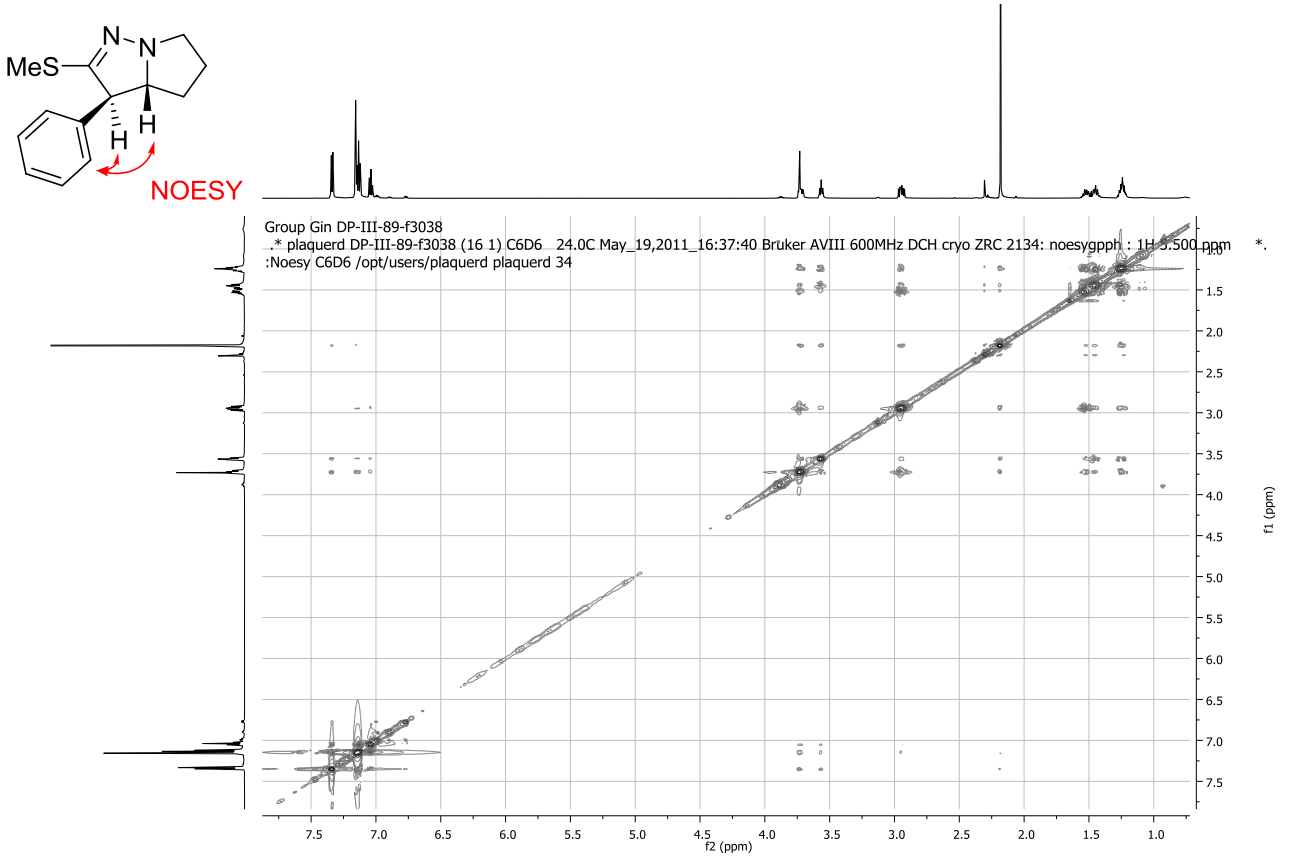

MeS
N
N
H
Group Gin DP-III-55-f4954
.* plaquerd DP-III-55-f4954 (15 1) C6D6 24.0C April_28,2011_16:24:03 Bruker AVIII 600MHz DCH cryo ZRC 2134: hmbcgplpndqf : 1H 2.559 ppm; 13(
:Hmbc C6D6 /opt/users/plaquerd plaquerd 29
f1 (ppm)
f2 (ppm)

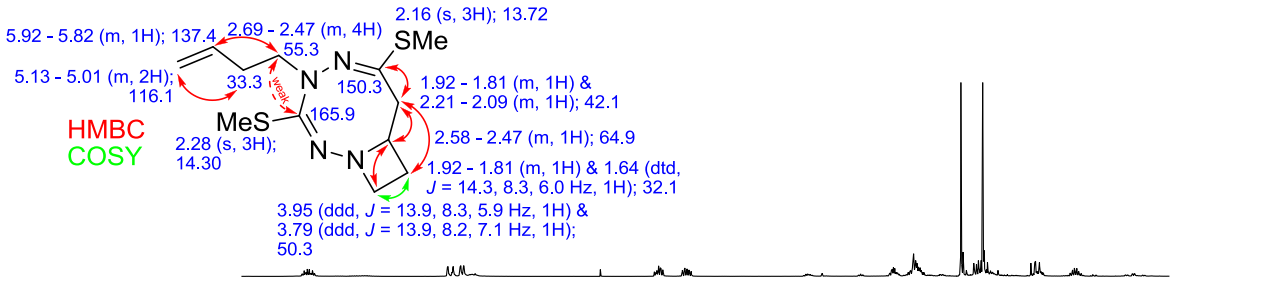

MeS
N
N
H
H
NOESY
Group Gin
.* plaquerd DP-III-55-f4954- (21 1) C6D6 24.0C August_04,2011_07:27:05 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 4.102 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 11
f1 (ppm)
f2 (ppm)


MeS
N
N
H
Group Gin DP-III-89-f3038
.* plaquerd DP-III-89-f3038 (13 1) C6D6 24.0C May_19,2011_15:12:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: cosygpqf : 1H 4.007 ppm *.
:GradCosy C6D6 /opt/users/plaquerd plaquerd 34
f2 (ppm)
f1 (ppm)

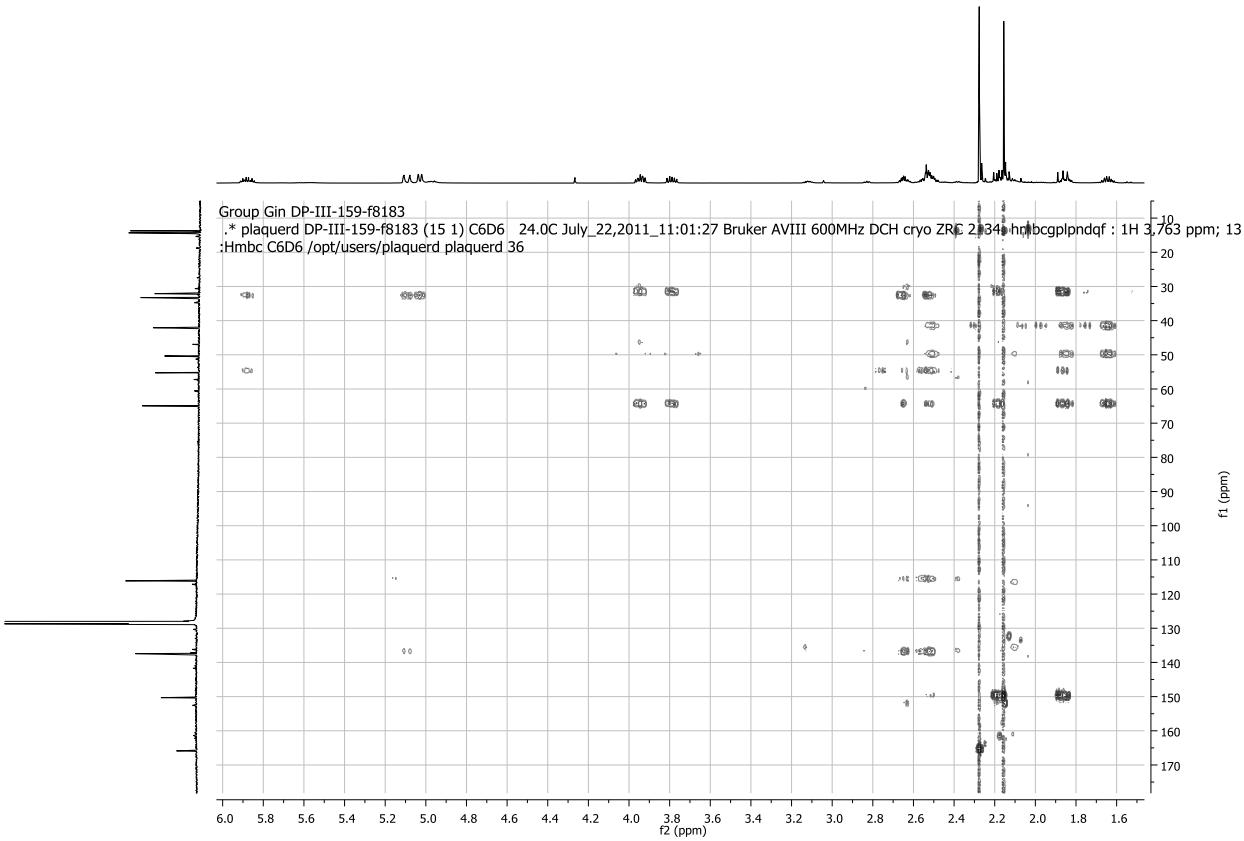

Group Gin DP-III-89-f3038
.* plaquerd DP-III-89-f3038 (14 1) C6D6 24.0C May_19,2011_15:16:40 Bruker AVIII 600MHz DCH cryo ZRC 2134: hsqcetgpsi2.gds : 1H 4.007 ppm; 1
:Hsqc C6D6 /opt/users/plaquerd plaquerd 34
f2 (ppm)
f1 (ppm)

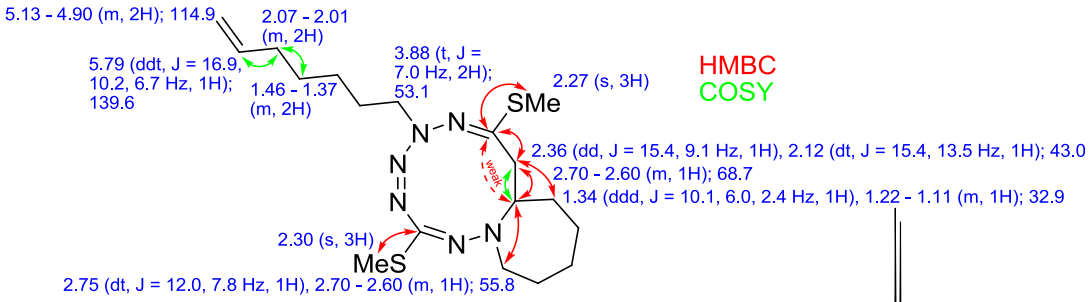

MeS
N
N
H
Group Gin DP-III-89-f3038
.* plaquerd DP-III-89-f3038 (15 1) C6D6 24.0C May_19,2011_15:33:01 Bruker AVIII 600MHz DCH cryo ZRC 2134: hmbcgplpndqf : 1H 4.907 ppm; 13C
:Hmbc C6D6 /opt/users/plaquerd plaquerd 34
f1 (ppm)
f2 (ppm)

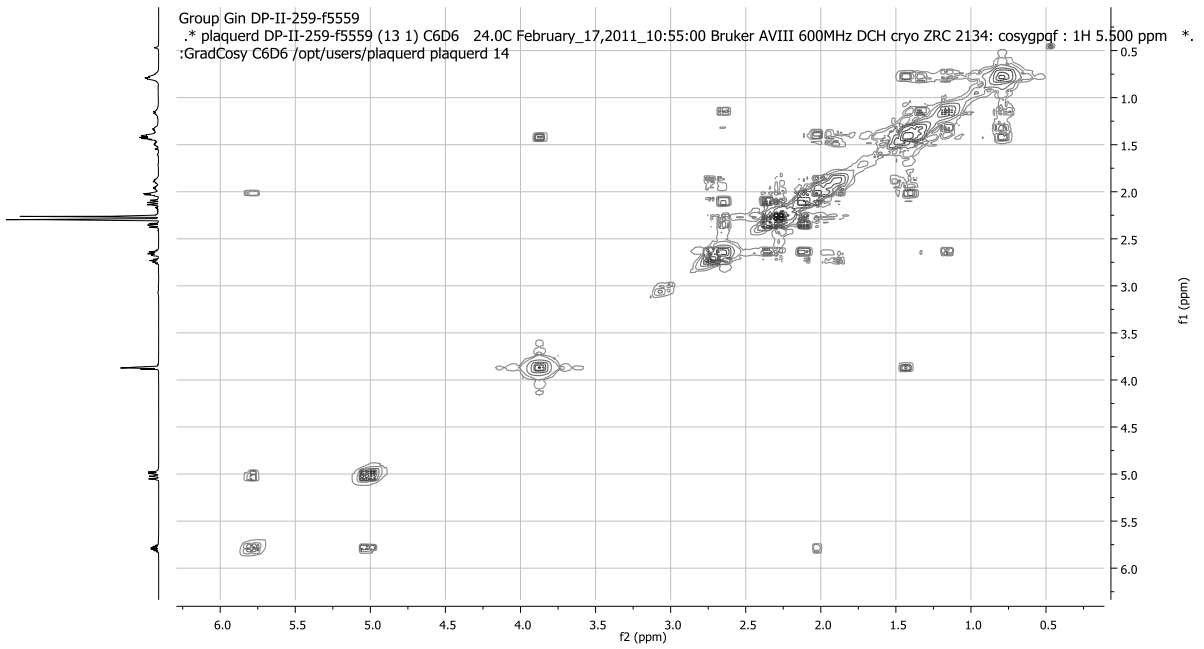

MeS
N
N
H
H
NOESY
Group Gin DP-III-89-f3038
.* plaquerd DP-III-89-f3038 (16 1) C6D6 24.0C May_19,2011_16:37:40 Bruker AVIII 600MHz DCH cryo ZRC 2134: noesygpph : 1H 9.500 ppm
:Noesy C6D6 /opt/users/plaquerd plaquerd 34
f1 (ppm)
f2 (ppm)

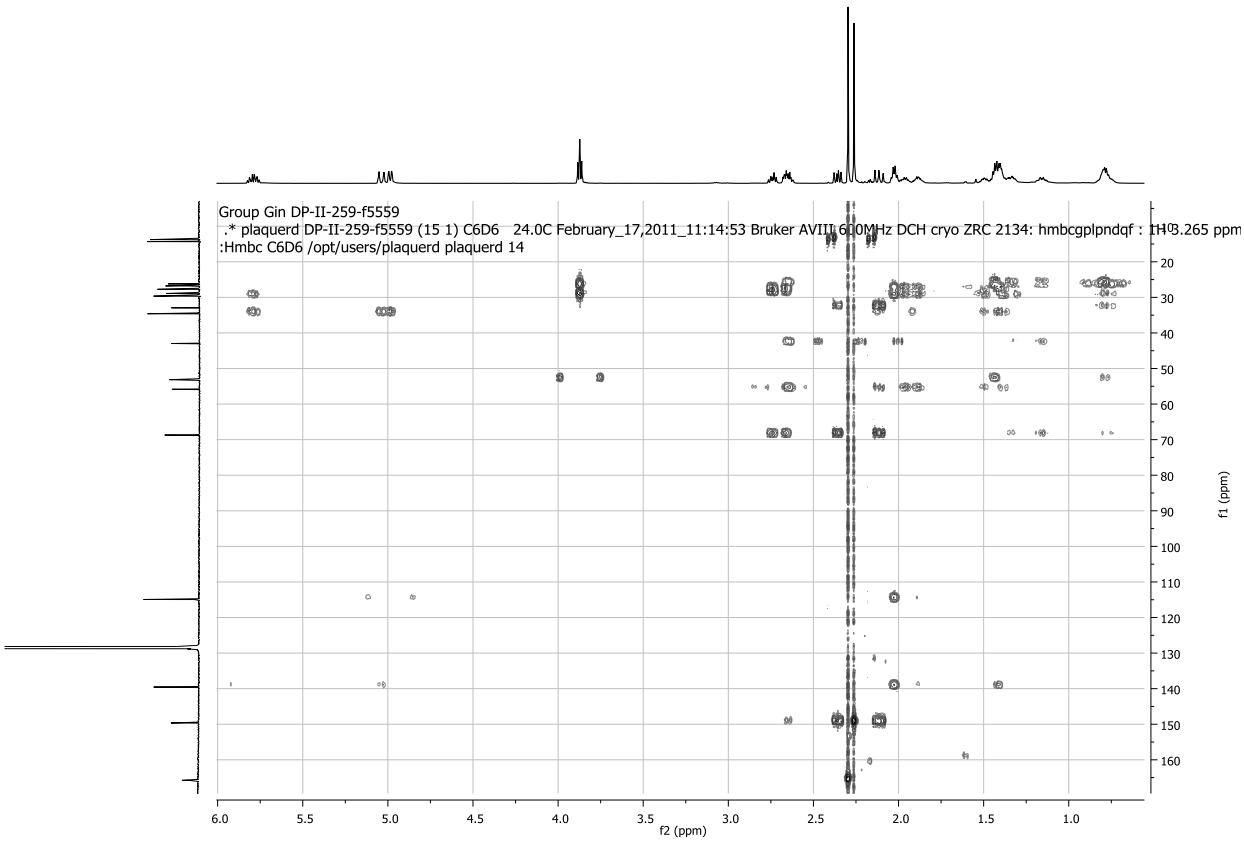

5.92 - 5.82 (m, 1H); 137.4
2.69 - 2.47 (m, 4H)
55.3
2.16 (s, 3H); 13.72
SMe
5.13 - 5.01 (m, 2H);
116.1
33.3
weak
150.3
1.92 - 1.81 (m, 1H) &
2.21 - 2.09 (m, 1H); 42.1
HMBC
COSY
MeS
2.28 (s, 3H);
14.30
165.9
2.58 - 2.47 (m, 1H); 64.9
1.92 - 1.81 (m, 1H) & 1.64 (dtd,
J = 14.3, 8.3, 6.0 Hz, 1H); 32.1
3.95 (ddd, J = 13.9, 8.3, 5.9 Hz, 1H) &
3.79 (ddd, J = 13.9, 8.2, 7.1 Hz, 1H);
50.3

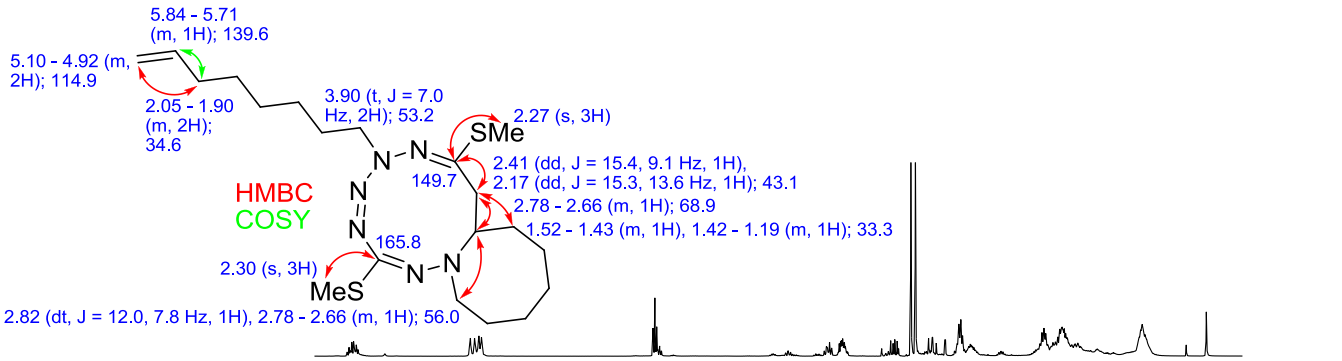
Group Gin DP-III-159-f8183
.* plaquerd DP-III-159-f8183 (13 1) C6D6 24.0C July_22,2011_10:41:13 Bruker AVIII 600MHz DCH cryo ZRC 2134: cosygpqf : 1H 3.462 ppm
:GradCosy C6D6 /opt/users/plaquerd plaquerd 36
f2 (ppm)
f1 (ppm)

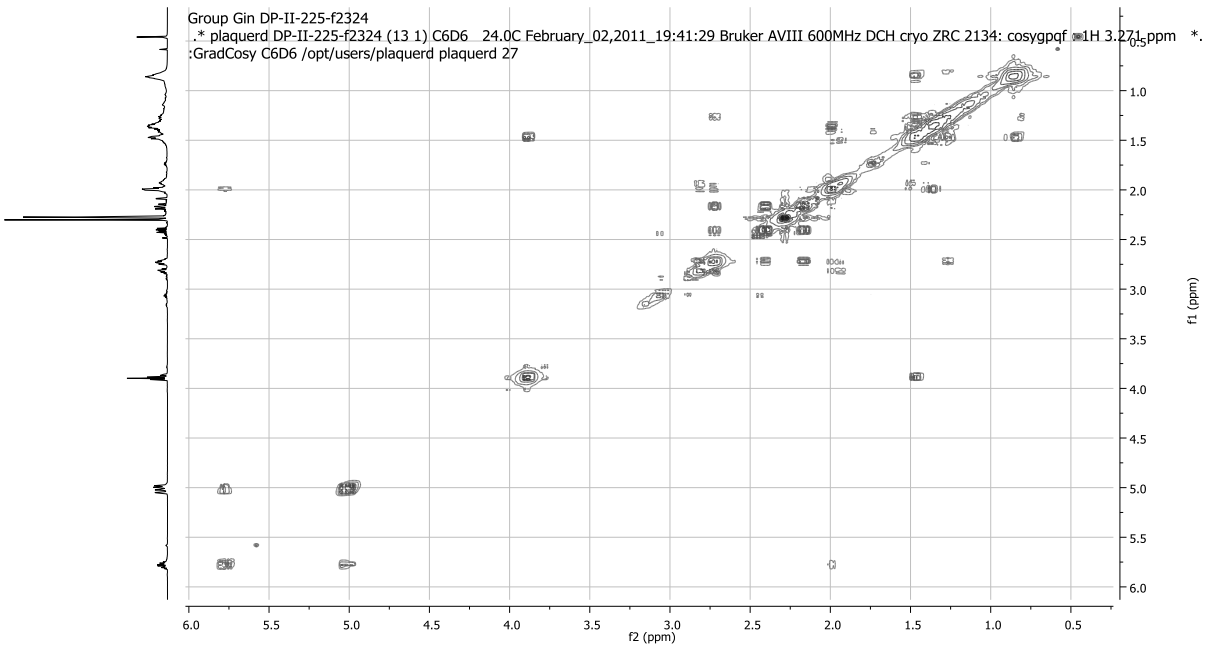

Group Gin DP-III-159-f8183
.* plaquerd DP-III-159-f8183 (15 1) C6D6 24.0C July_22,2011_11:01:27 Bruker AVIII 600MHz DCH cryo ZRC 2134: hmbcgplpndqf : 1H 3.763 ppm; 13
:Hmbc C6D6 /opt/users/plaquerd plaquerd 36
f2 (ppm)
f1 (ppm)

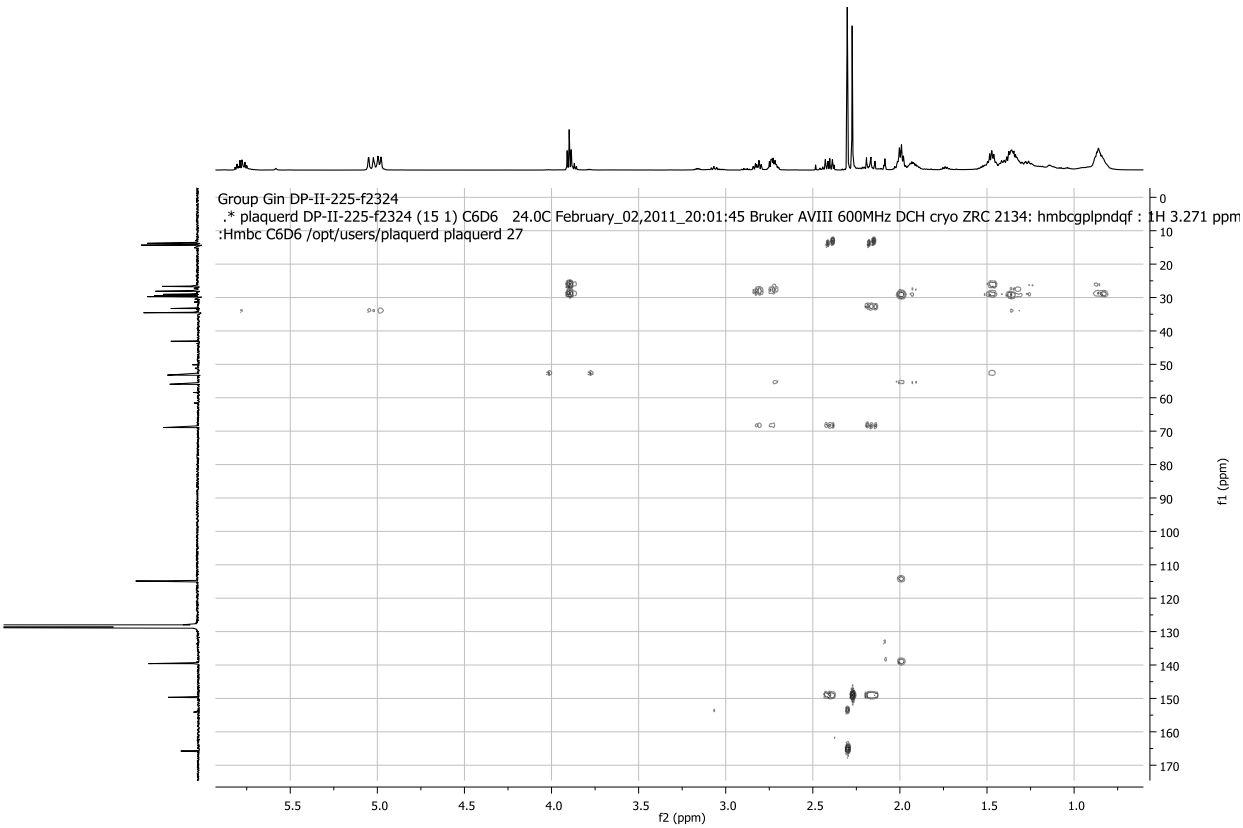

5.13 - 4.90 (m, 2H); 114.9
2.07 - 2.01 (m, 2H)
5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H); 139.6
1.46 - 1.37 (m, 2H)
3.88 (t, J = 7.0 Hz, 2H); 53.1
2.27 (s, 3H)
SMe
HMBC
COSY
2.36 (dd, J = 15.4, 9.1 Hz, 1H), 2.12 (dt, J = 15.4, 13.5 Hz, 1H); 43.0
2.70 - 2.60 (m, 1H); 68.7
1.34 (ddd, J = 10.1, 6.0, 2.4 Hz, 1H), 1.22 - 1.11 (m, 1H); 32.9
2.30 (s, 3H)
MeS
2.75 (dt, J = 12.0, 7.8 Hz, 1H), 2.70 - 2.60 (m, 1H); 55.8


Group Gin DP-II-259-f5559
.* plaquerd DP-II-259-f5559 (13 1) C6D6 24.0C February_17,2011_10:55:00 Bruker AVIII 600MHz DCH cryo ZRC 2134: cosygpqf : 1H 5.500 ppm *.
:GradCosy C6D6 /opt/users/plaquerd plaquerd 14
f1 (ppm)
f2 (ppm)


Group Gin DP-II-259-f5559
.* plaquerd DP-II-259-f5559 (15 1) C6D6 24.0C February_17,2011_11:14:53 Bruker AVIII 600MHz DCH cryo ZRC 2134: hmbcgplpndqf : 1H 3.265 ppm
:Hmbc C6D6 /opt/users/plaquerd plaquerd 14
f1 (ppm)
f2 (ppm)


5.84 - 5.71 (m, 1H); 139.6
5.10 - 4.92 (m, 2H); 114.9
2.05 - 1.90 (m, 2H); 34.6
3.90 (t, J = 7.0 Hz, 2H); 53.2
2.27 (s, 3H)
SMe
149.7
2.41 (dd, J = 15.4, 9.1 Hz, 1H), 2.17 (dd, J = 15.3, 13.6 Hz, 1H); 43.1
2.78 - 2.66 (m, 1H); 68.9
1.52 - 1.43 (m, 1H), 1.42 - 1.19 (m, 1H); 33.3
HMBC
COSY
165.8
2.30 (s, 3H)
MeS
2.82 (dt, J = 12.0, 7.8 Hz, 1H), 2.78 - 2.66 (m, 1H); 56.0


Group Gin DP-II-225-f2324
.* plaquerd DP-II-225-f2324 (13 1) C6D6 24.0C February_02,2011_19:41:29 Bruker AVIII 600MHz DCH cryo ZRC 2134: cosygpqf 1H 3.271 ppm *.
:GradCosy C6D6 /opt/users/plaquerd plaquerd 27
f2 (ppm)
f1 (ppm)


Group Gin DP-II-225-f2324
.* plaquerd DP-II-225-f2324 (15 1) C6D6 24.0C February_02,2011_20:01:45 Bruker AVIII 600MHz DCH cryo ZRC 2134: hmbcgplpndqf : 1H 3.271 ppm
:Hmbc C6D6 /opt/users/plaquerd plaquerd 27
f2 (ppm)
f1 (ppm)