Acta Crystallographica Section D

Biological Crystallography

High-Affinity Inhibitors of *Zymomonas mobilis* tRNA–Guanine Transglycosylase through Convergent Optimization

Supplementary Material

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List of Abbreviations

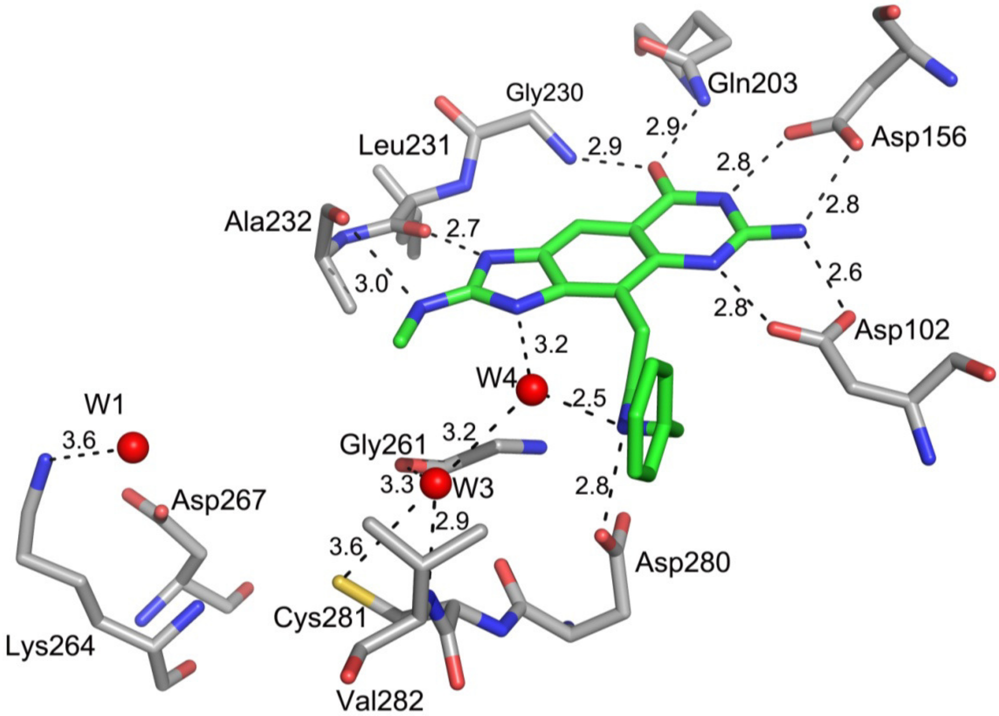
3-HPA	3-hydroxypicolinic acid
9-BBN	9-borabicyclo[3.3.1]nonane
Å	Ångström (1 Å = 10^{-10} m)
aq.	aqueous
Ar	argon
ax	axial
br.	broad
c	centi-
C	Celsius
calcd	calculated
conc.	concentrated
d	doublet
decomp	decomposition
DEPT	distortionless enhancement by polarization transfer
DIAD	*N,N*-diisopropyl azodicarboxylate
DIPA	*N,N*-diisopropylamine
DME	1,2-dimethoxyethane
DMF	*N,N*-dimethylformamide
Me_2SO	dimethylsulfoxide
eq	equivalent; equatorial
ESI	electron spray ionization
Et	ethyl
EtOAc	ethyl acetate
eV	electron volt
FC	flash column chromatography
FT	fourier transform
g	gram(s)
GP	general procedure
h	hour(s)
HPLC	high performance liquid chromatography
HR	high resolution
HSQC	heteronuclear single quantum coherence

Hz	Hertz
IR	infrared spectroscopy
J	coupling constant (NMR) in Hz
L	liter
LC/MS	liquid chromatography/mass spectrometry
Lit.	literature (value)
M	Mega
M	molar
m	mili-; medium; meter; multiplet
m.p.	melting point
m/z	mass over charge ratio
MALDI	matrix-assisted laser desorption/ionization
Me	methyl
MeCN	acetonitrile
mg	milligram(s)
min	minute(s)
MPLC	medium pressure liquid chromatography
MS	mass spectrometry
n	nano
n	*normal*
NMR	nuclear magnetic resonance
org.	organic
PDB	protein data bank
ppm	parts per million
q	quartet
R_f	retention factor
RP	reverse phase
s	singlet; strong
sat.	saturated
sh.	shoulder
t	triplet
t	*tert*
TGT	tRNA–guanine transglycosylase

THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	tetramethylsilane
tRNA	transfer ribonucleic acid
UV	ultraviolet
w	weak
Z. mobilis	*Zymomonas mobilis*
δ	chemical shift in ppm relative to TMS
$\tilde{\nu}$	wavenumber(s)
°	degree
µm	micrometer(s)

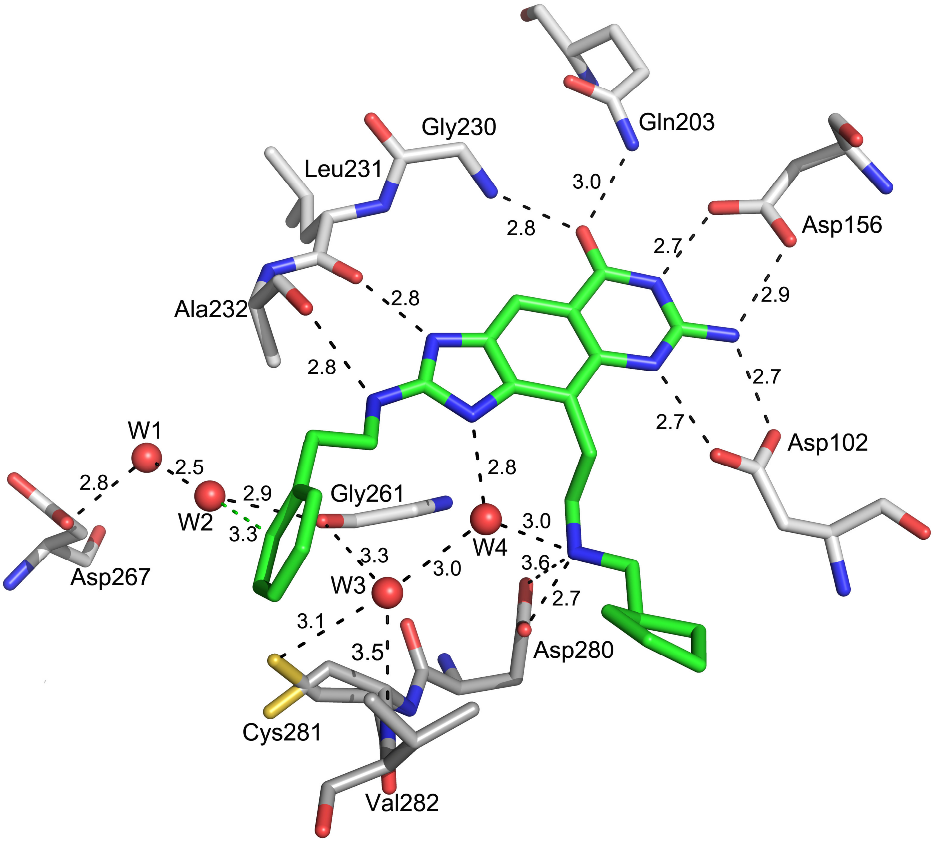
The three-letter code for amino acids is used.

Supplementary Figure S1. Crystal Structure with 6a



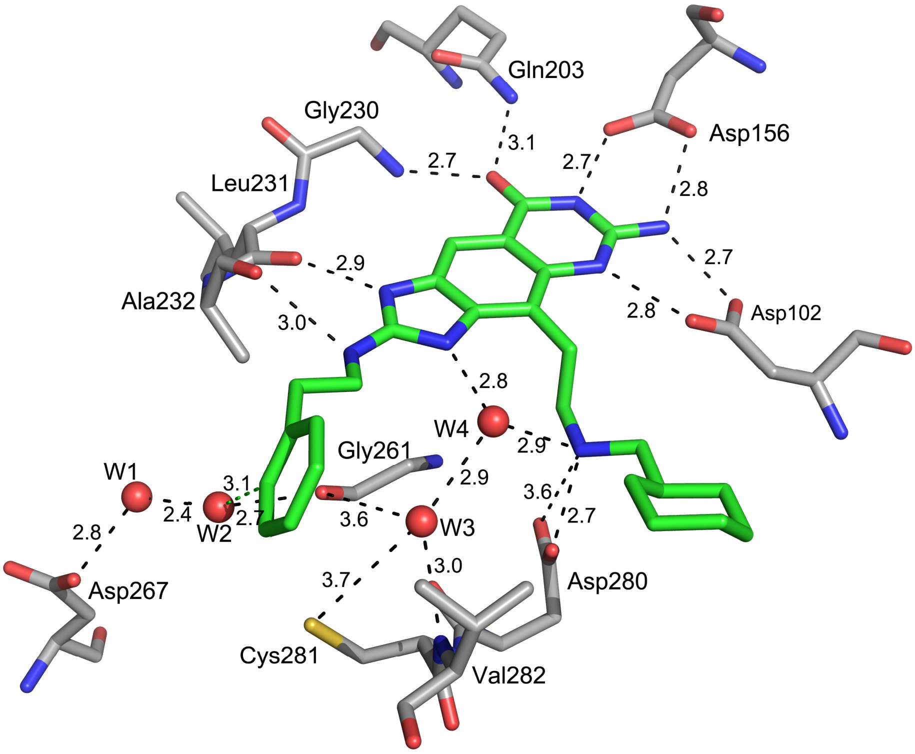
Crystal structure of *Z. mobilis* TGT·**6a** (PDB code: 4gi4), obtained by soaking. Color code: C_{enzyme} gray, C_{ligand} green, O red, N blue. Selected water molecules are shown as spheres. H-bonds are shown as dashed lines and distances are given in Å. The substituent in the ribose-33 pocket is not resolved.

Supplementary Figure S2. Crystal Structure with 6b



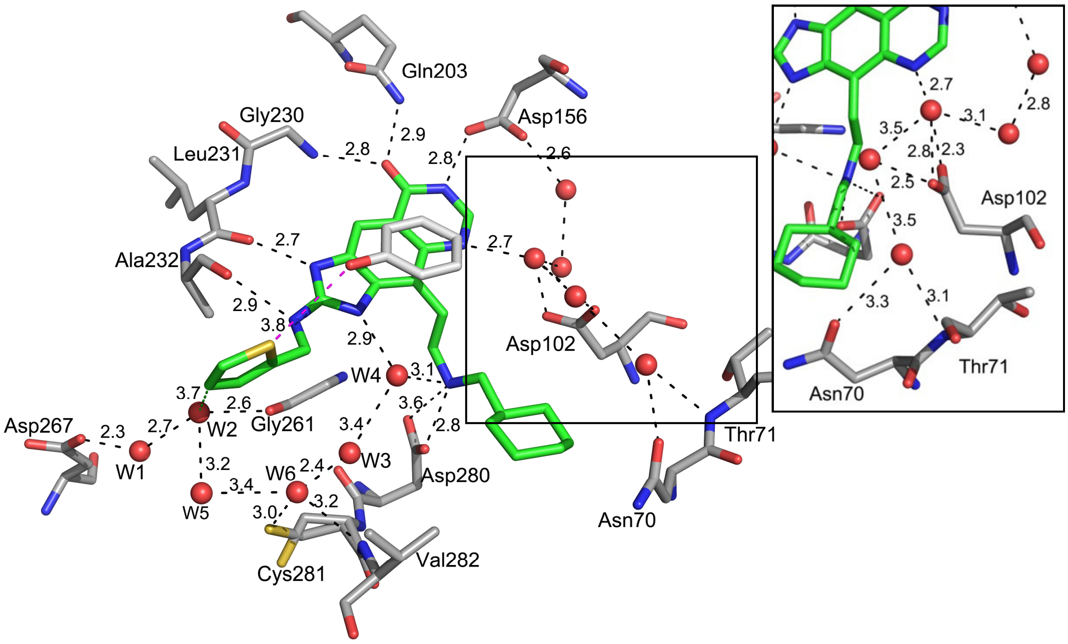
Crystal structure of *Z. mobilis* TGT·**6b** (PDB code: 4gkt), obtained by cocrystallization. Color code: C_{enzyme} gray, C_{ligand} green, O red, N blue. Selected water molecules are shown as spheres. H-bonds are shown as black dashed lines and the C_{Ph}–H···O_{W2} interaction as green dashed line. Distances are given in Å.

Supplementary Figure S3. Crystal Structure with 6c



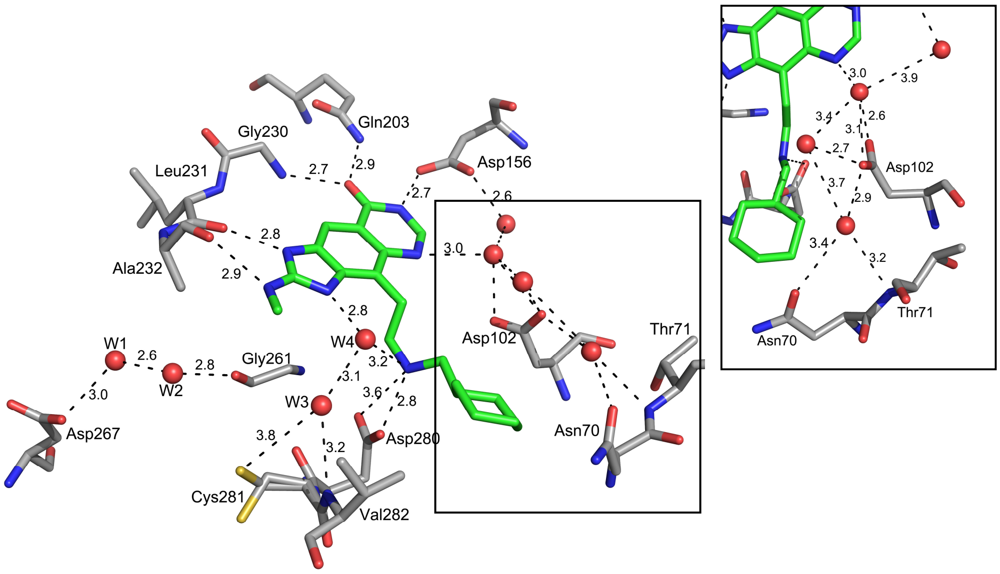
Crystal structure of *Z. mobilis* TGT·**6c** (PDB code: 4giy), obtained by cocrystallization. Color code: C_{enzyme} gray, C_{ligand} green, O red, N blue. Selected water molecules are shown as spheres. H-bonds are shown as black dashed lines and the C_{Ph}–H···O_{W2} interaction as green dashed line. Distances are given in Å.

Supplementary Figure S4: Crystal Structure with 7a



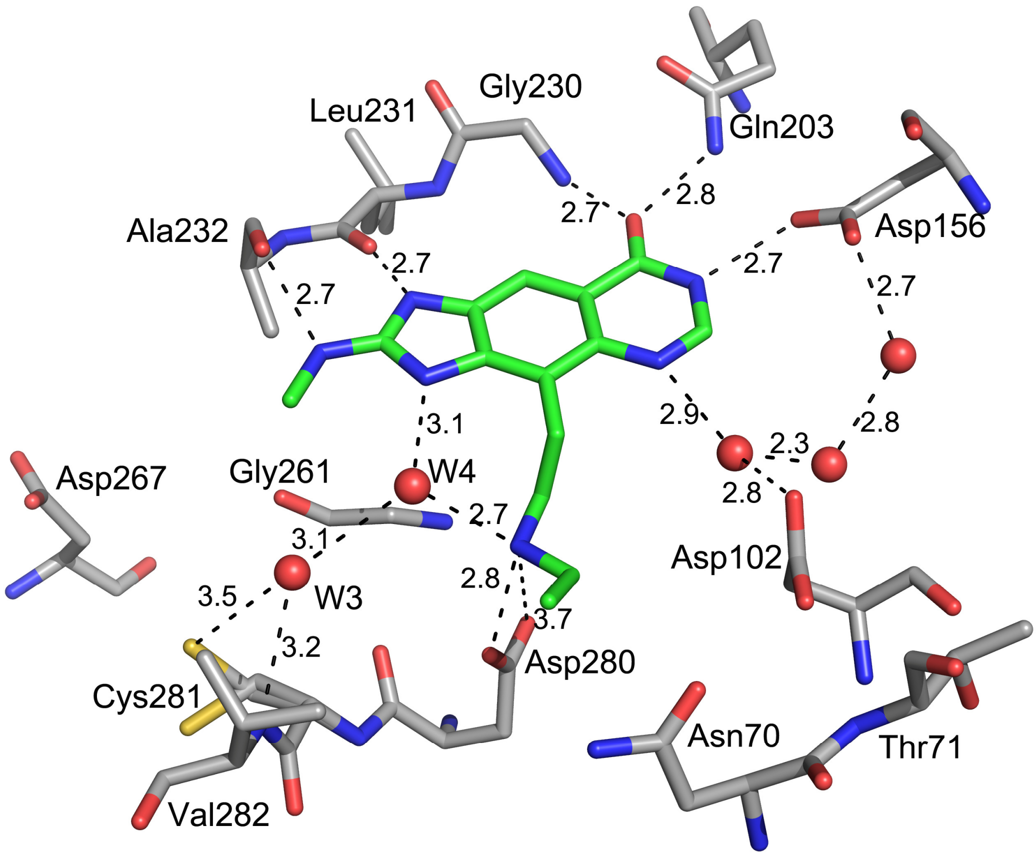
Crystal structure of *Z. mobilis* TGT·**7a** (PDB code: 4gg9), obtained by cocrystallization. Color code: C_{enzyme} gray, C_{ligand} green, O red, N blue. Selected water molecules are shown as spheres. H-bonds are shown as black dashed lines, the C_{Ph}–H···O_{W2} interaction as green dashed line, and the $S_{thiophene}$···O_{Tyr106} interaction as magenta dashed line. Distances are given in Å.

Supplementaary Figure S5. Crystal Structure with 7b



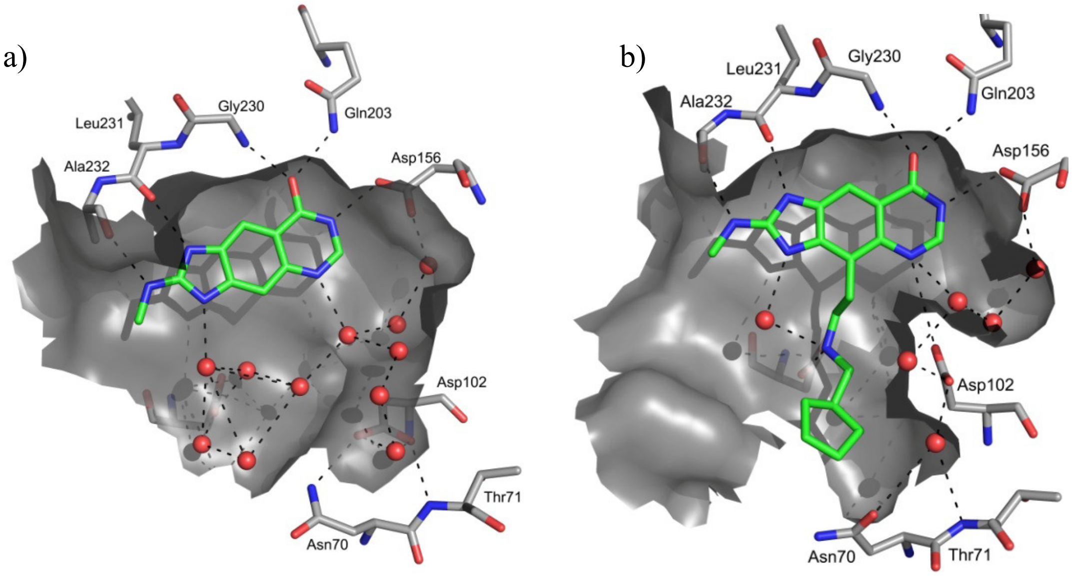
Crystal structure of *Z. mobilis* TGT·**7b** (PDB code: 4gh1), obtained by cocrystallization. The substituent in the ribose-33 pocket (morpholino) is not resolved. Color code: C_{enzyme} gray, C_{ligand} green, O red, N blue. Selected water molecules are shown as spheres. H-bonds are shown as dashed lines and distances are given in Å.

Supplementary Figure 6. Crystal Structure with 7c



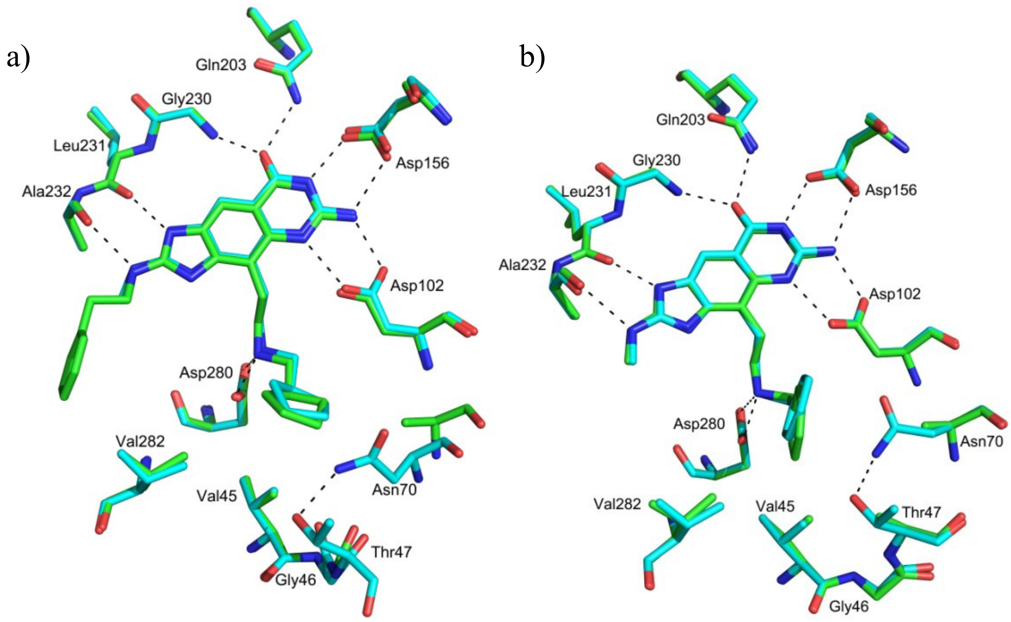
Crystal structure of *Z. mobilis* TGT·**7c** (PDB code: 4gh3), obtained by cocrystallization. The substituents in the ribose-33 (phenyl) and ribose-34 (cyclohexyl) pocket are not resolved. Color code: C_{enzyme} gray, C_{ligand} green, O red, N blue. Selected water molecules are shown as spheres. H-bonds are shown as dashed lines and distances are given in Å.

Supplementary Figure S7. Binding Mode of Mono-Functionalized *lin*-Benzohypoxanthines



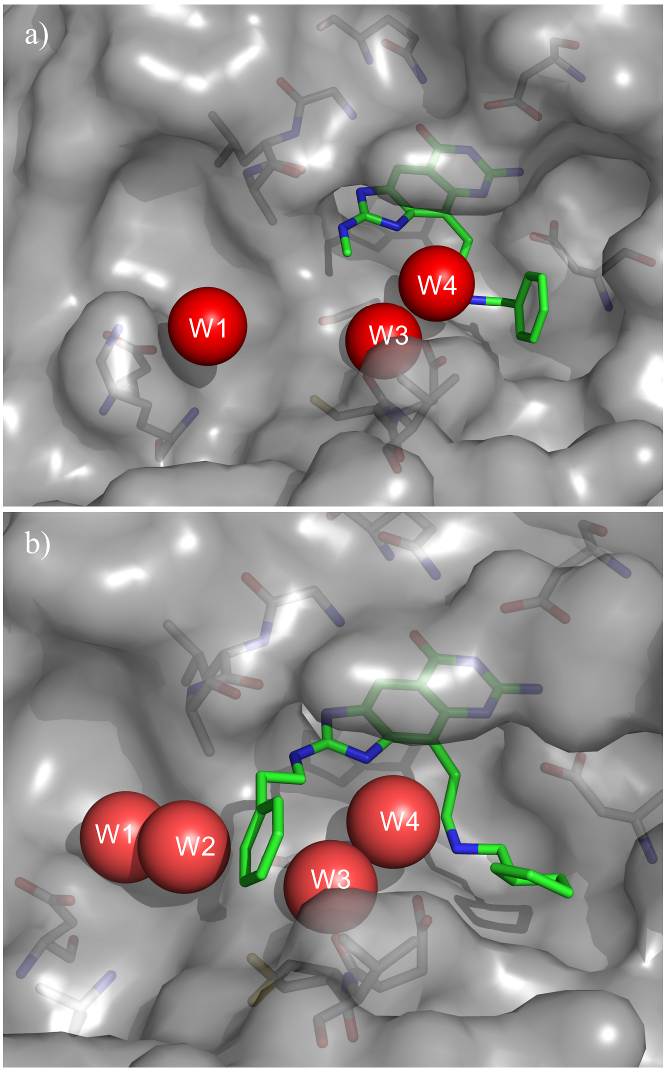
Binding mode of mono-functionalized *lin*-benzohypoxanthines. Crystal structure of *Z. mobilis* TGT with a) **2a** (PDB code: 3s1g[2]) and b) **5a** (PDB code: 3sm0[2]), both obtained by cocrystallization. Color code: C_{ligand} green, C_{enzyme} gray, O red, N blue. The pocket is indicated as gray surface. Selected water molecules are shown as red spheres, H-bonds as dashed lines.

Supplementary Figure 8. Comparison Crystal Structures of 4a,b with 6a,b



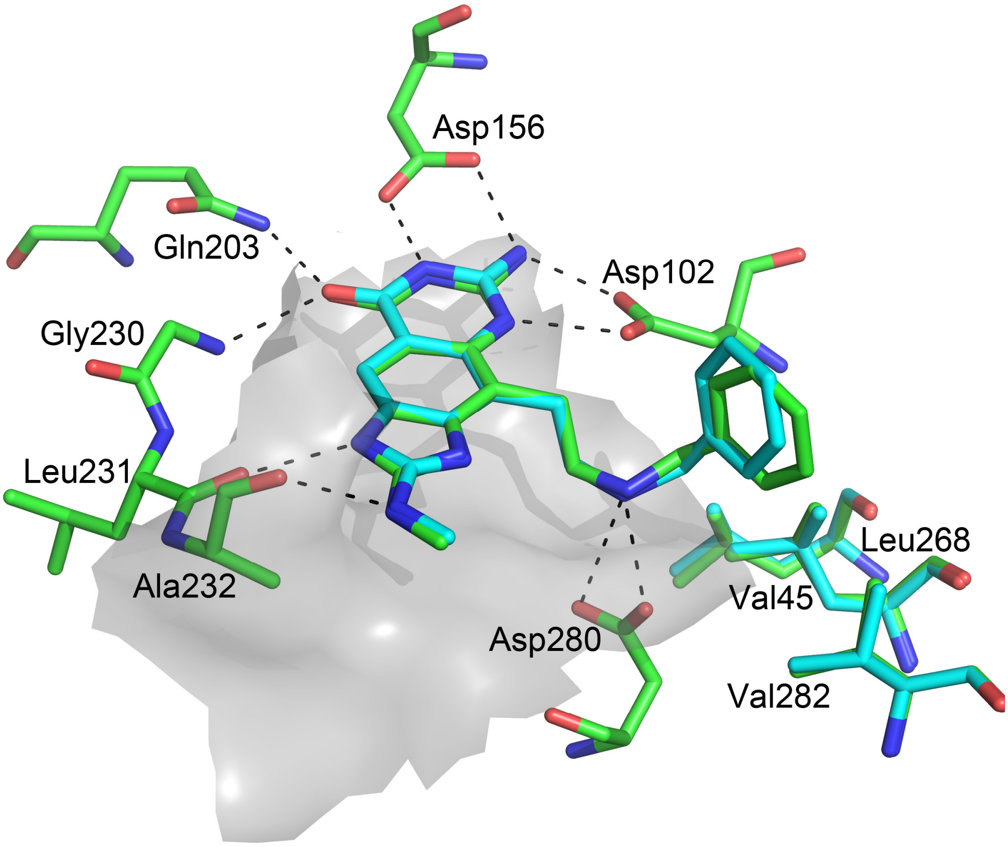
Comparison of the crystal structures of the bifunctionalized *lin*-benzoguanines **6a**,**b** (C green) with their mono-functionalized analogues **4a**,**b** (C cyan). a) **4a** (PDB code: 3ge7[1]; soaking) and **6b** (PDB code: 4gkt; cocrystallization). b) **4b** (PDB code: 3gc4[1]; soaking) and **6a** (PDB code: 4gi4; soaking). H-bonds shown as dashed lines, O red, N blue.

Supplementary Figure S9. Cocrystallization versus Soaking of Ligands



Comparison of available space in the ribose-33 pocket for the ligand in a) the soaked crystal structure (**6a**, PDB code: 4gi4) and b) the cocrystallized structure (**6b**, PDB code: 4gkt). Color code: C_{ligand} green, C_{enzyme} gray, O red, N blue. The pocket is indicated as gray surface. Selected water molecules (W1–W4) are shown as space-filling, red spheres.

Supplementary Figure S10. Comparison of the Binding Mode of 4c and 6a

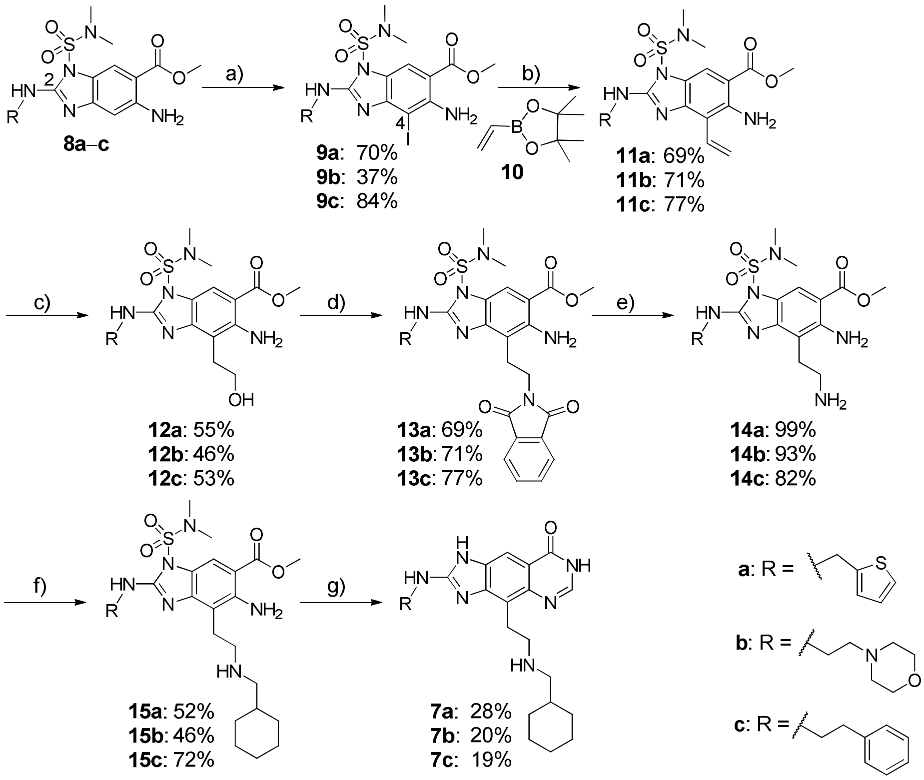


Comparison of the X-ray crystal structures of *Z. mobilis* TGT with **4c** (C cyan; PDB code: 3gc4[1]) and **6a** (C green; PDB code: 4gi4), both obtained by soaking. The phenyl substituent of **6a** is shifted by about 1 Å deeper into the ribose-34 pocket. Color code: O red, N blue. The active site is indicated as gray surface. Hydrogen bonds are shown as black dashed lines.

11 Synthetic Details and Experimental Data

11.1 Synthesis of the *lin*-Benzopurines

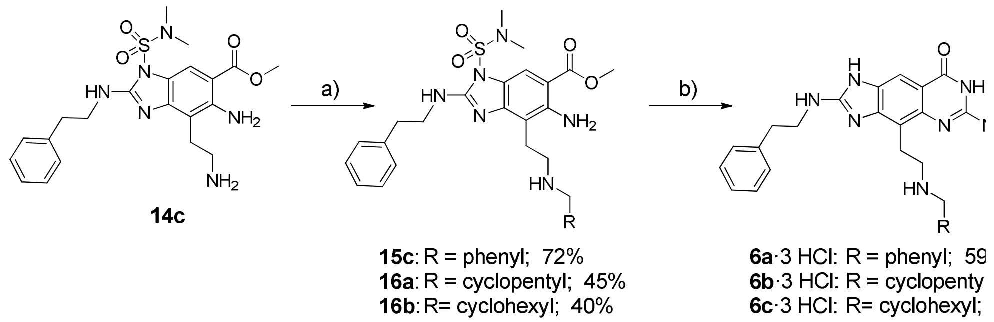
The 5-aminobenzimidazoles **8a–c** were prepared according to previously described procedures (Scheme S1).[3,4] Iodination at C(4) furnished **9a–c**, which were used for Suzuki cross-coupling reaction with borolane **10**. The obtained 4-vinylbenzimidazoles **11a–c** were transformed to the corresponding alcohols **12a–c** by hydroboration with 9-BBN, followed by oxidative workup. Subsequent Mitsunobu reaction furnished phthalimides **13a–c**, which were cleaved with hydrazine to give the amines **14a–c**.



Supplementary Scheme S1.

Synthesis of *lin*-benzohypoxanthines **7a–c**. a) I_2, $NaHCO_3$, CH_2Cl_2/H_2O, 25 °C, 1–3 d; **9a**: 70%, **9b**: 37%, **9c**: 84%. b) **10**, Et_3N, $[PdCl_2(PPh_3)_2]$, DME/H_2O, 85 °C, 3 h; **11a**: 69%, **11b**: 71%, **11c**: 77%. c) i) 9-BBN, THF, 25 °C, 3 h; ii) H_2O_2, NaOH, H_2O, 0 to 25 °C, 4 h; **12a**: 55%, **12b**: 46%, **12c**: 53%. d) PPh_3, DIAD, phthalimide, THF, 0 to 25 °C, 40 min; **13a**: 69%, **13b**: 71%, **13c**: 77%. e) $H_2NNH_2{\cdot}H_2O$, MeOH/THF, 50 °C, 2 h; **14a**: 99%, **14b**: 93%, **14c**: 82%. f) Cyclohexanecarb-aldehyde, $NaBH(OAc)_3$, 0 to 25 °C, 13–19 h; **15a**: 52%, **15b**: 46%, **15c**: 72%. g) i) Formamide, 140 °C, 18–22 h; ii) aq. HCl, MeOH, 65 °C, 18–24 h; **7a**: 28%, **7b**: 20%, **7c**: 19%. 9-BBN = 9-borabicyclo[3.3.1]nonane, DIAD = *N,N*-diisopropyl azodicarboxylate, DME =1,2-dimethoxyethane, THF = tetrahydrofuran.

Reductive amination of the amines using either cylcohexyl-, cyclopentyl-, or benzaldehyde furnished the benzimidazoles **15a**–**c** and **16a**,**b** (Schemes S1 and S2). The *lin*-benzohypoxanthines **7a**–**c** were accessible by cyclization using formamide followed by acidic deprotection. The *lin*-benzoguanines **6a**–**c** were directly obtained as trihydrochloride salts by cyclization with chloroformamidinium chloride.



Supplementary Scheme S2.

Synthesis of *lin*-benzoguanines **6a**–**c**. a) Benzaldehyde, cyclopentanecarbaldehyde, or cyclohexanecarbaldehyde, $NaBH(OAc)_3$, 0 to 25 °C, 13–19 h; **15c**: 72%, **16a**: 45%, **16b**: 40%. b) Chloroformamidinium chloride, Me_2SO_2, 130 °C, 1–2 h; **6a**·3 HCl: 59%, **6b**·3 HCl: 53%, **6c**·3 HCl: 48%.

11.2 Materials and Methods

Commercial reagents (ABCR, Aldrich, AlfaAesar, Acros, Fluka, and TCI Deutschland) were purchased as reagent-grade and used without further purification.

Solvents for extraction or column chromatography were of technical quality and were distilled before use.

Anhydrous solvents (CH_2Cl_2, DMF, and THF) for reactions were purified by a solvent drying system from LC Technology Solutions Inc. SP-105 under nitrogen atmosphere (H_2O content < 10 ppm as determined by Karl-Fischer titration). Formamide was dried by storing over 4 Å molecular sieves.

Evaporation was performed at ≤ 40 °C and ~10 mbar. Further drying of the compounds was carried out at ~10^{-2} mbar.

All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise stated. Reactions mixtures were stirred with a magnetic stirring bar and monitored by liquid chromatography/mass spectrometry (LC/MS) or by thin-layer chromatography (TLC).

TLC was carried out on SiO_2-layered glass plates (60 F_{254}, Merck). Visualization was achieved using UV light with a wavelength of 254 nm.

LC/MS was performed on an Ultimate 3000 series LC instrument combined with an MSQ Plus mass spectrometer from Dionex, using a Zorbax Eclipse Plus C18 column (30 x 3 mm; 3.5 µm pore size) from Agilent.

Flash column chromatography (FC) was performed using SiO_2-60 (230–400 mesh ASTM, 0.040–0.063 mm from Fluka) or MCI gel (CHP20P, styrene-divinylbenzene, 75–150 µm, from Supelco) at 25 °C with a head pressure of 0.0–0.4 bar. The solvent compositions are reported individually.

Medium pressure liquid chromatography (MPLC) was conducted on a Büchi MPLC System with pump module C-601 & C-605 and fraction collector C-660 with a gradient using the solvent mixtures indicated individually.

High performance liquid chromatography (HPLC) was carried out using a Merck Hitachi L-7100 pump (for analytic HPLC) or a Merck Hitachi L-7150 pump (for preparative HPLC), equipped with a Merck Hitachi D-7000 interface and a Merck Hitachi L-7614 degasser. For detection, a Merck Hitachi L-7400 UV detector (254 nm) was used. The analytical samples were injected using a Merck Hitachi L-7200 auto sampler. The column used was Phenomenex, 50 x 21.1 mm, Gemini 5 µm, C18, 110 A, AXIA, with a flow rate of 12 mL/min.

Melting points (m.p.) were determined on a B-540 apparatus from Büchi in open capillaries and are not corrected.

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian Gemini 300, a Varian Mercury 300, a Bruker AV 400, a Bruker DRX 400, a Bruker DRX 500, or a Bruker DRX 600 spectrometer. All spectra were measured at 25 °C. The residual solvent peak was used as the internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; $(CD_3)_2SO$: δ_H = 2.50 ppm, δ_C = 39.52 ppm; CD_3OD: δ_H = 3.31 ppm). The ^{1}H NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS (δ = 0 ppm) (multiplicity, coupling constant J in Hz, number of protons; suggested assignment). The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), sept. (septet) combinations thereof, or m (multiplet). Broad signals are described with br. (broad). The ^{13}C NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS ($\delta = 0$ ppm) (number of nuclei if greater than 1; suggested assignment if possible).

Infrared (IR) spectra were recorded on an ATR-unit-upgraded (Golden Gate) Perkin-Elmer FT-IR Spectrum 1600 spectrometer. The spectra were measured between 4000−600 cm^{-1}. Selected absorption bands are reported in wave numbers (cm^{-1}) with relative intensities described as s (strong), m (medium), or w (weak).

High resolution mass spectrometry (HR-MS) was performed by the MS service of the Laboratorium für Organische Chemie der ETH Zürich. High resolution electrospray ionization (ESI) spectra were measured on a Bruker maXis spectrometer. High-resolution matrix-assisted laser desorption/ionization (MALDI) spectra were measured on an Ionspec (Varian) Ultima FT-ICR or a Solarix (Bruker) FT-ICR mass spectrometer using 3-hydroxypicolinic acid (3-HPA) as a matrix.

Elemental analyses were measured by the Mikroanalytisches Laboratorium für Organische Chemie der ETH Zürich.

Nomenclature follows the suggestions proposed by the computer program ACD Name from ACD/Labs. Numbering of the atoms in the figures was defined arbitrarily to allow an unambiguous assignment of the NMR peaks.

11.3 General Procedures (GPs)

GP 1 for the Cyclization to the *lin*-Benzoguanines:

A suspension of the benzimidazole (1 eq), chloroformamidinium chloride (2 eq), and Me_2SO_2 was stirred at 130 °C for 1–2 h. The mixture was diluted with sat. aq. $NaHCO_3$ solution and the precipitate collected by centrifugation. FC (MCI gel; H_2O + 0.1 vol-% conc. HCl/MeOH) and evaporation gave the *lin*-benzoguanines.

GP 2 for the Cyclization to the *lin*-Benzohypoxanthines:

A solution of the benzimidazole (1 eq) in anhydrous formamide was heated at 140 °C for 18–22 h under Ar and evaporated by bulb-to-bulb distillation (0.5 mbar, 140 °C). A solution of the residue in aq. conc. HCl/MeOH 1:2 (6.0 mL) was stirred at 65 °C for 18–24 h, neutralized (pH 6–7) with aq. sat. $NaHCO_3$ solution, and evaporated. HPLC ([Phenomenex, 50x21.1 mm, Gemini 5 µm, C18, 110 A, AXIA]; flow rate 12 mL/min, H_2O + 0.1 vol-% HCOOH/MeCN 100:0 for 10 min, 100:0 to 80:20 within 40 min), evaporation, and lyophilization gave the *lin*-benzohypoxanthines.

GP 3 for the Iodination of 5-Aminobenzimidazoles:

A solution of the aminobenzimidazole (1 eq) and iodine (1.2 eq) in CH_2Cl_2/sat. aq. $NaHCO_3$ solution 2:1 was vigorously stirred at 25 °C for 1–3 d, diluted with sat. aq. $Na_2S_2O_3$ solution, and extracted with CH_2Cl_2 (2x). The combined org. layers were dried over Na_2SO_4, filtered, and evaporated. The residue was purified chromatographically.

GP 4 for the *Suzuki* Cross-Coupling Reaction:

A suspension of the aryl iodide (1 eq), vinylboronic acid pinacol ester (**10**; 1.6 eq), and Et_3N (3 eq) in DME/H_2O 5:1 was degassed in an ultra sonicator with Ar and treated with $[PdCl_2(PPh_3)_2]$ (0.05 eq). The mixture was stirred at 85 °C for 3 h, diluted with aq. sat. $NaHCO_3$ solution, and extracted with EtOAc (3x). The combined org. layers were dried over Na_2SO_4, filtered, and evaporated. The residue was purified chromatographically.

GP 5 for the Hydroboration:

The neat olefin (1 eq) was treated with a 0.5 M solution of 9-BBN in THF (3 eq) under Ar. After stirring at 25 °C for 3 h, 30% H_2O_2 in H_2O (10 eq) and 1 M aq. NaOH solution (10 eq) were added dropwise at 0 °C. The mixture was stirred vigorously at 25 °C for 4 h, diluted with sat. aq. NH_4Cl solution, and extracted with EtOAc (3x 50 mL). The combined org. layers were dried over Na_2SO_4, filtered, and evaporated. The residue was purified chromatographically.

GP 6 for the *Mitsunobu* Reaction with Phthalimide:

A solution of PPh_3 (2 eq) in anhydrous THF was treated with DIAD (1 eq) at 0 °C and stirred for 10 min until a pale yellow precipitate was formed. A solution of the alcohol (1 eq) and phthalimide (2 eq) in anhydrous THF was added. The mixture was stirred at 25 °C for 30 min and evaporated. The residue was purified chromatographically.

GP 7 for the Cleavage of Phthalimide:

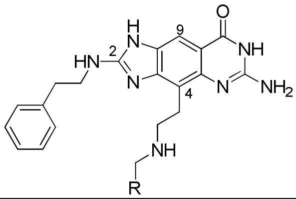
A solution of the phthalimide (1 eq) and hydrazine monohydrate (10 eq) in MeOH/THF 95:5 was stirred at 50 °C for 2 h. After evaporation, the mixture was taken up in 1 M aq. NaOH solution and extracted with CH_2Cl_2 (3x 50 mL). The combined org. layers were dried over Na_2SO_4, filtered, and evaporated to yield the amine.

GP 8 for the Reductive Amination:

A solution of the amine (1 eq) and the aldehyde (1 eq) in anhydrous CH_2Cl_2 over 4 Å molecular sieves was stirred at 25 °C for 1 h under Ar, cooled to 0 °C, and treated with $NaBH(OAc)_3$ (4 eq). The mixture was stirred at 25 °C for 13–19 h, diluted with 2 M aq. NH_3 solution, and extracted with EtOAc (3x). The combined org. layers were dried over Na_2SO_4, filtered, and evaporated. After purification by MPLC, the residue was dissolved in *t*BuOH and lyophilized to give the amine.

11.4 Compilation of ^{1}H and ^{13}C NMR Data

Table S1. Selected ^{1}H NMR data (400 MHz) of **6a**–**c**. The atom numbering for some compounds differs from the numbering in the experimental part.



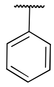
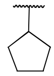
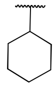
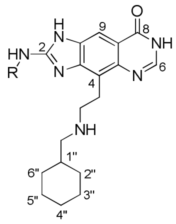
		6a·3 HCl	**6b**·3 HCl	**6c**·3 HCl
	R =			
	Solvent	CD_3OD	$(CD_3)_2SO$ + 1 drop TFA	$(CD_3)_2SO$ + 1 drop TFA
δ_H / ppm	C*H*$_2$CH$_2$NH–C(2)	3.04 (t, *J* = 6.6 Hz)	2.96 (t, *J* = 7.3 Hz)	2.95 (t, *J* = 7.3 Hz)
	CH$_2$–C(4)	3.38–3.43 (m)	3.23 (t, *J* = 6.9 Hz)	3.16–3.22 (m)
	C*H*$_2$CH$_2$–C(4)	3.58–3.65 (m)	3.53 (t, *J* = 6.9 Hz)	3.44–3.50 (m)
	C*H*$_2$NH–C(2)	3.83–3.88 (m)	3.77–3.84 (m)	3.70–3.79 (m)
	CH$_2$–R	4.24–4.40 (m)	3.01 (d, *J* = 7.5)	2.86 (br. d, *J* ≈ 6.2 Hz)
	H–C(9)	7.90 (s)	7.77 (s)	7.67 (s)

Table S2. Selected [1]H (600 MHz) and [13]C (150 MHz) NMR data of **7a–c** in $(CD_3)_2SO$. The atom numbering for some compounds differs from the numbering in the experimental part.



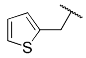
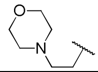
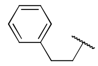
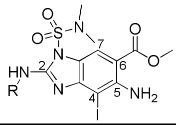
		7a	**7b**	**7c**
	R =			
δ_H / ppm	H_{ax}–C(2",6")	0.97 (qd, J = 12.6, 2.9 Hz)	0.95 (qd, J = 11.9, 3.0 Hz)	0.91 (qd, J = 11.9, 2.1 Hz)
	H_{ax}–C(4")	1.13 (tt, J = 12.3, 2.8 Hz)	1.13 (tt, J = 12.3, 3.1 Hz)	1.10 (tt, J = 12.0, 3.0 Hz)
	H_{ax}–C(3",5")	1.20 (qt, J = 12.6, 3.3 Hz)	1.19 (tt, J = 12.3, 3.1 Hz)	1.16 (br. tt, $J \approx$ 12.0, 3.0 Hz)
	H–C(1")	1.65–1.73 (m)	1.59–1.83 (m)	1.18–1.23 (m)
	H_{eq}–C(2",3",4", 5",6")	1.57–1.86 (m)	1.59–1.82 (m)	1.16 (br. d, $J \approx$ 12.6 Hz) 1.58–1.66 (m)
	CH_2–C(1")	2.87 (t, J = 6.2 Hz)	2.87 (d, J = 7.0 Hz)	2.79 (d, J = 7.2 Hz)
	CH_2–C(4)	3.21 (br. t, $J \approx$ 6.6 Hz)	2.73–2.78 (m)	2.93 (t, J = 7.2 Hz)
	CH_2CH_2NH–C(2)	--	3.23 (t, J = 7.3 Hz)	3.16 (t, J = 7.5 Hz)
	CH_2CH_2–C(4)	3.73 (br. t, $J \approx$ 6.6 Hz)	3.58 (t, J = 7.5 Hz)	3.52 (t, J = 7.2 Hz)
	CH_2NH–C(2)	5.08–5.19 (m)	3.58 (t, J = 7.5 Hz)	3.61 (t, J = 7.2 Hz)
	H–C(9)	7.95 (s)	7.76 (s)	7.71 (s)
	H–C(6)	8.13 (s)	8.15 (s)	7.95 (s)
δ_C / ppm	CH_2–C(4)	22.71	22.13	22.75
	C(3",5")	25.00	24.92	24.96
	C(4")	25.57	25.49	25.56
	C(2",6")	30.02	29.92	29.99
	C(1")	34.43	34.27	34.72
	CH_2NH–C(2)	41.46	46.95	43.63
	CH_2CH_2–C(4)	46.94	52.78	52.71
	CH_2–C(1")	52.71	52.24	47.27
	CH_2CH_2NH–C(2)	--	56.96	35.27
	C(8a)	105.77	103.67	103.86
	C(9)	116.91	115.30	115.26
	C(4)	118.65	116.53	116.07
	C(3a)	129.53	141.29	136.71
	C(9a)	134.60	141.39	141.07
	C(4a)	143.21	146.19	145.65
	C(6)	143.70	158.04	158.49
	C(2)	151.85	161.21	161.30
	C(8)	160.74	162.90	165.18

Table S3. Selected [1]H (400 MHz) and [13]C (100 MHz) NMR data of **9a–c** in $CDCl_3$.



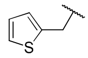
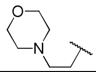
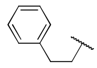
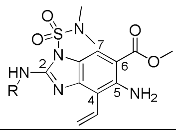
		9a	**9b**	**9c**
	R =			
δ_H / ppm	CH_2CH_2NH	--	2.67 (t, *J* = 5.9 Hz)	3.04 (t, *J* = 6.8 Hz)
	NMe_2	2.89 (s)	2.93 (s)	2.73 (s)
	OMe	3.90 (s)	3.89 (s)	3.86 (s)
	CH_2NH	4.99 (d, *J* = 5.1 Hz)	3.70–3.75 (m)	3.89 (td, *J* = 6.8, 5.4 Hz)
	NH_2	6.46 (br. s)	6.44 (br. s)	6.42 (br. s)
	NH	6.69 (t, *J* = 5.6 Hz)	7.07 (t, *J* = 4.4 Hz)	6.37 (t, *J* = 5.4 Hz)
	H–C(7)	8.08 (s)	8.06 (s)	8.01 (s)
δ_C / ppm	NMe_2	38.79	38.80	38.76
	CH_2NH	42.01	34.41	44.52
	OMe	51.85	51.80	51.92
	CH_2CH_2NH	--	56.51	35.29
	C(4)	73.44	73.03	73.37
	C(6)	104.35	104.01	104.21
	C(7)	114.35	114.12	114.27
	C(7a)	121.77	121.82	121.82
	C(3a)	148.65	148.58	148.76
	C(5)	149.75	150.04	150.17
	C(2)	154.19	154.86	154.78
	C=O	168.05	168.10	168.22

Table S4. Selected [1]H (400 MHz) and [13]C NMR (100 MHz) data of **11a–c** in $CDCl_3$



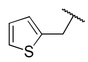
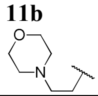
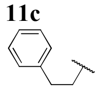
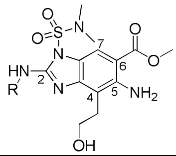
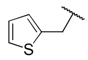
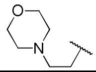
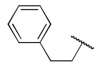
		11a	**11b**	**11c**
	R =			
δ_H / ppm	NMe_2	2.89 (s)	2.93 (s)	2.74 (s)
	OMe	3.89 (s)	3.88 (s)	3.85 (s)
	CH_2NH	4.95 (d, *J* = 5.4 Hz)	3.68 (q, *J* = 5.5 Hz)	3.84 (td, *J* = 7.0, 5.4 Hz)
	CH=CH_E	5.72 (dd, *J* = 11.8, 2.0 Hz)	5.68 (dd, *J* = 11.8, 2.1 Hz)	5.69 (dd, *J* = 11.8, 2.1 Hz)
	NH_2	6.16 (br. s)	6.16 (br. s)	6.13 (br. s)
	CH=CH_Z	6.30 (dd, *J* = 17.8, 2.0 Hz)	6.20 (dd, *J* = 17.9, 2.1 Hz)	6.25 (dd, *J* = 17.8, 2.1 Hz)
	NH	6.67 (t, *J* = 5.8 Hz)	6.99 (t, *J* = 4.8 Hz)	6.34 (t, *J* = 5.4 Hz)
	CH=CH_2	6.93 (dd, *J* = 17.8, 11.8 Hz)	6.92 (dd, *J* = 17.9, 11.8 Hz)	6.92 (dd, *J* = 17.8, 11.8 Hz)
	H–C(7)	8.05 (s)	8.04 (s)	7.99 (s)
δ_C / ppm	NMe_2	38.79	38.81	38.78
	CH_2NH	41.93	39.41	44.49
	OMe	51.61	51.58	51.68
	C(6)	104.70	104.31	104.55
	C(4)	111.37	110.99	111.24
	C(7)	113.46	113.27	113.43
	CH=CH_2	119.72	119.41	119.57
	C(7a)	123.40	123.42	123.45
	CH=CH_2	128.42	128.68	126.82
	C(3a)	145.77	146.18	146.31
	C(5)	146.79	146.76	146.94
	C(2)	154.39	155.01	154.98
	C=O	168.96	169.03	169.14

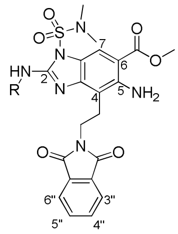
Table S5. Selected ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data of **12a–c** in $CDCl_3$.



		12a	**12b**	**12c**
	R =			
δ_H / ppm	OH	1.60–1.86 (br. s)	1.48–1.78 (br. s)	1.52–1.73 (br. s)
	CH_2CH_2NH	--	2.67 (t, J = 5.9 Hz)	2.97–3.03 (m)
	NMe_2	2.89 (s)	2.96 (s)	2.75 (s)
	CH_2CH_2OH	3.04 (t, J = 5.6 Hz)	2.99 (t, J = 5.6 Hz)	2.97–3.03 (m)
	OMe	3.88 (s)	3.89 (s)	3.85 (s)
	CH_2OH	4.04 (t, J = 5.6 Hz)	4.02 (t, J = 5.6 Hz)	4.03 (t, J = 5.5 Hz)
	CH_2NH	4.89 (d, J = 5.5 Hz)	3.61 (q, J = 5.5 Hz)	3.78 (td, J = 6.9, 5.5 Hz)
	NH_2	5.97 (br. s)	--[a]	5.94 (br. s)
	NH	6.73 (t, J = 5.7 Hz)	7.03 (t, J = 4.8 Hz)	6.37 (t, J = 5.5 Hz)
	H–C(7)	8.03 (s)	8.03 (s)	7.97 (s)
δ_C / ppm	CH_2CH_2OH	29.47	29.53	29.82
	NMe_2	38.77	38.79	35.32
	CH_2NH	41.98	39.44	44.56
	OMe	51.62	51.61	51.79
	CH_2CH_2NH	--	56.26	38.84
	CH_2OH	61.80	61.71	61.84
	C(6)	105.16	104.90	104.94
	C(4)	112.22	111.95	112.09
	C(7)	112.55	112.39	112.41
	C(7a)	123.04	123.09	122.93
	C(3a)	145.84	145.90	145.83
	C(5)	147.55	147.36	147.39
	C(2)	153.93	154.40	154.21
	C=O	169.00	169.05	168.97

[a] Signal not observed.

Table S6. Selected [1]H (400 MHz) and [13]C (100 MHz) NMR data of **13a**–**c** in $CDCl_3$. The atom numbering for some compounds differs from the numbering in the experimental part.



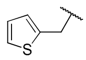
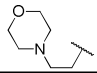
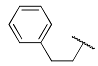
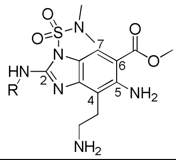
		13a	13b	13c
	R =			
δ_H / ppm	CH_2CH$_2$NH	--	2.60 (t, J = 5.7 Hz)	3.22 (t, J = 6.8 Hz)
	NMe$_2$	2.84 (s)	2.87 (s)	2.71 (s)
	CH$_2$–C(4)	3.26 (t, $J \approx$ 7.6 Hz)	3.17 (t, J = 7.7 Hz)	2.97 (t, J = 6.9 Hz)
	OMe	3.88 (s)	3.85 (s)	3.85 (s)
	CH_2CH$_2$–C(4)	3.98 (t, $J \approx$ 7.6 Hz)	3.92 (t, J = 7.7 Hz)	3.96 (t, J = 6.8 Hz)
	CH_2NH	4.81 (d, J = 5.6 Hz)	3.54 (q, J = 5.4 Hz)	3.70 (td, J = 6.9, 5.6 Hz)
	NH$_2$	6.29 (br. s)	6.25 (br. s)	6.24 (br. s)
	NH	6.52 (t, J = 5.7 Hz)	6.79 (t, J = 4.9 Hz)	6.21 (br. t, $J \approx$ 5.6 Hz)
	H–C(7)	8.02 (s)	7.98 (s)	7.80 (s)
δ_C / ppm	CH$_2$–C(4)	24.27	24.38	24.40
	CH$_2$CH$_2$–C(4)	35.84	35.91	35.95
	NMe$_2$	38.79	38.95	38.77
	CH$_2$NH	41.79	39.41	44.33
	OMe	51.51	51.62	51.57
	CH$_2$CH$_2$NH	--	56.79	35.43
	C(6)	104.50	104.29	104.35
	C(4)	109.76	109.47	109.68
	C(7)	112.98	112.94	112.92
	C(7a)	122.82	123.01	122.86
	C(3",6")	123.16	123.29	123.25
	C(1",2")	132.30	132.46	132.45
	C(4",5")	133.87	133.97	133.91
	C(3a)	147.02	147.55	147.53
	C(5)	147.42	147.55	147.55
	C(2)	154.16	154.95	154.76
	2 C=O	168.43	168.56	168.50
	C=O	169.04	169.24	169.19

Table S7. Selected ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data of **14a**–**c** in $CDCl_3$.



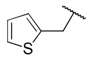
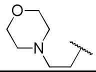
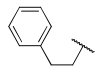
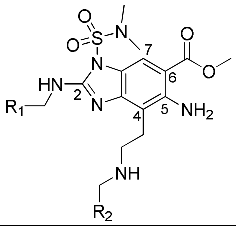
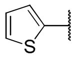
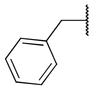
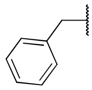
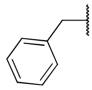
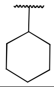
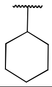
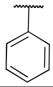
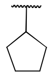
		14a	**14b**	**14c**
	R =			
δ_H / ppm	CH_2CH_2NH (*CH*)	--	2.63 (t, *J* = 6.0 Hz)	2.96–3.01 (m)
	NMe_2	2.88 (s)	2.92 (s)	2.72 (s)
	CH_2CH_2–C(4)	3.04–3.10 (m)	2.97–3.07 (m)	2.96–3.01 (m)
	OMe	3.88 (s)	3.85 (s)	3.82 (s)
	CH_2NH	4.92 (d, *J* = 5.5 Hz)	3.62 (q, *J* = 5.6 Hz)	3.80 (td, *J* = 6.8, 5.5 Hz)
	NH	6.64 (t, *J* = 5.8 Hz)	6.88 (t, *J* = 4.6 Hz)	6.28 (t, *J* = 5.5 Hz)
	H–C(7)	8.01 (s)	7.97 (s)	7.93 (s)
δ_C / ppm	CH_2–C(4)	29.51	29.39	29.45
	NMe_2	38.76	38.79	38.62
	CH_2CH_2–C(4)	41.06	40.98	41.05
	CH_2NH	41.88	39.43	44.24
	OMe	51.54	51.51	51.50
	CH_2CH_2NH	--	56.60	35.23
	C(6)	104.85	104.49	104.42
	C(4)	112.33	112.14	112.08
	C(7)	112.59	112.14	112.08
	C(7a)	123.11	123.16	122.97
	C(3a)	146.97	147.32	147.27
	C(5)	147.57	147.55	147.58
	C(2)	154.06	154.64	154.40
	C=O	169.11	167.17	169.12

Table S8. Selected ^{1}H NMR data of **15a**,**c** and **16a**,**b** in $CDCl_3$.



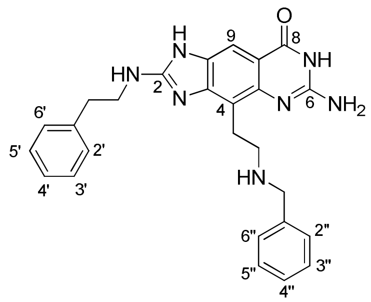
	15a	**15c**	**16a**	**16b**
R^1 =				
R^2 =				
Frequency	400 MHz	400 MHz	300 MHz	300 MHz
δ_H / ppm				
CH_2–R^2	2.57 (d, *J* = 6.7 Hz)	2.49 (d, *J* = 6.7 Hz)	3.76–3.82 (m)	2.59 (d, *J* = 7.3 Hz)
CH_2–R^1	--	2.98–3.07 (m)	2.97–3.02 (m)	2.98–3.07 (m)
NMe_2	2.88 (s)	2.74 (s)	2.75 (s)	2.74 (s)
CH_2–C(4)	3.00 (t, *J* = 6.6 Hz)	2.90 (t, *J* = 6.4 Hz)	2.97–3.02 (m)	2.92 (t, *J* = 6.2 Hz)
*CH_2*CH_2–C(4)	3.15 (t, *J* = 6.7 Hz)	2.98–3.07 (m)	3.10 (br. t, *J* ≈ 6.0 Hz)	2.98–3.07 (m)
OMe	3.87 (s)	3.84 (s)	3.85 (s)	3.84 (s)
*CH_2*NH–C(2)	4.93 (d, *J* = 5.5 Hz)	3.82 (td, *J* = 6.8, 5.5 Hz)	3.79 (td, *J* = 6.9, 5.6 Hz)	3.81 (td, *J* = 6.9, 5.5 Hz)
NH–C(2)	6.63 (t, *J* = 5.8 Hz)	6.27 (t, *J* = 5.5 Hz)	--[a]	6.27 (t, *J* = 5.5 Hz)
H–C(7)	7.99 (s)	7.93 (s)	7.95 (s)	7.93 (s)
Frequency	100 MHz	75 MHz	75 MHz	75 MHz
δ_C / ppm				
CH_2–C(4)	25.59	26.23	26.09	26.38
CH_2–R^1	--	38.33	35.18	40.23
NMe_2	38.77	38.83	38.57	38.66
*CH_2*NH–C(2)	41.91	44.46	44.19	44.29
*CH_2*CH_2–C(4)	48.69	49.33	48.21	49.14
OMe	51.50	51.63	51.42	54.45
CH_2–R^2	56.22	57.04	53.90	55.80
C(6)	104.75	104.42	104.37	104.25
C(4)	112.42	112.03	112.90	113.27
C(7)	112.42	113.42	112.02	111.86
C(7a)	122.91	122.86	122.85	122.69
C(3a)	146.60	146.92	146.97	146.76
C(5)	148.01	148.06	147.81	147.91
C(2)	154.02	154.30	154.29	154.12
C=O	169.06	169.11	169.09	168.94

[a] Signal not observed.

11.5 Experimental Data

Compounds **8a–c** were prepared as described in literature.[3]

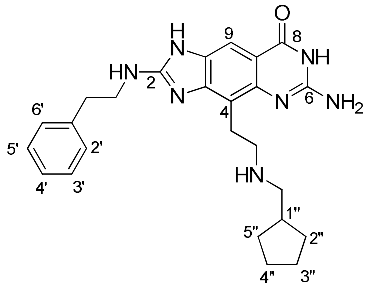
6-Amino-4-{2-[(benzylamino)amino]ethyl}-2-[(2-phenylethyl)amino]-1,7-dihydro-8*H*-imidazo[4,5-*g*]quinazolin-8-one Trihydrochloride (6a·3 HCl):



According to **GP 1**, starting from **15c** (43 mg, 0.08 mmol), chloroformamidinium chloride (15 mg, 0.16 mmol), and Me_2SO_2 (400 mg). The mixture was diluted with sat. aq. $NaHCO_3$ solution (5 mL) and the precipitate collected by centrifugation. FC (MCI gel; H_2O + 0.1 vol-% conc. HCl/MeOH 70:30 to 60:40) and evaporation yielded **6a**·3 HCl (21 mg, 48%) as a white solid.

M.p. > 225 °C (decomp.); ^{1}H NMR (400 MHz, CD_3OD): δ = 3.04 (t, J = 6.6 Hz, 2 H; CH_2–C(1')), 3.38–3.43 (m, 2 H; CH_2–C(4)), 3.58–3.65 (m, 2 H; C$H_2$$CH_2$–C(4)), 3.83–3.88 (m, 2 H; CH_2NH–C(2)), 4.55 (br. s, 2 H; CH_2–C(1")), 7.17 (t, J = 7.3 Hz, 1 H; H–C(4) of C_6H_5), 7.25–7.36 (m, 4 H of C_6H_5), 7.43–7.46 (m, 3 H of C_6H_5), 7.59–7.62 (m, 2 H of C_6H_5), 7.90 ppm (s, 1 H; H–C(9)); ^{13}C NMR (100 MHz, $(CD_3)_2SO$ + 1 drop TFA): δ = 22.38 (CH$_2$–C(4)), 34.80 (CH$_2$–C(1')), 44.29 (CH$_2$NH–C(2)), 45.51(CH$_2$CH$_2$–C(4)), 49.97 (CH$_2$–C(1")), 106.64 (C(9)), 128.64128.28, and 128.98 (8 C; C(2',3',5',6',2",3",5",6")), 128.91 (2 C; C(4',4")), 138.28 (2 C; C(1',1")), 151.39 ppm (C(2)), 7 signals hidden by noise; IR (ATR): $\tilde{\nu}$ = 3408 (w), 3338 (w), 2953 (br. w), 1678 (s), 1579 (m), 1453 (m), 1267 (w), 1209 (w), 1154 (w), 1073 (w), 739 (m), 696 cm^{-1} (s); HR-MALDI-MS: m/z (%): 455.2379 (31), 454.2344 (100, $[M + H]^+$, calcd for $C_{26}H_{28}N_7O^+$: 454.2350).

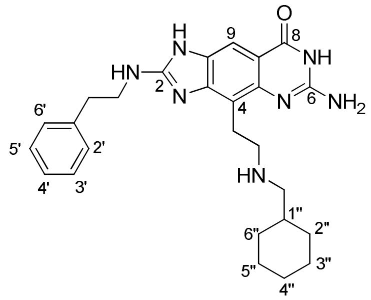
6-Amino-4-{2-[(cyclopentylmethyl)amino]ethyl}-2-[(2-phenylethyl)amino]-1,7-dihydro-8*H*-imidazo[4,5-*g*]quinazolin-8-one Trihydrochloride (6b·3 HCl):



According to **GP 1**, starting from **16a** (29 mg, 0.05 mmol), chloroformamidinium chloride (11 mg, 0.10 mmol), and Me_2SO_2 (400 mg). The mixture was diluted with sat. aq. $NaHCO_3$ solution (5 mL) and the precipitate collected by centrifugation. FC (MCI gel; H_2O + 0.1 vol-% conc. HCl/MeOH 60:40 to 50:50) and evaporation yielded **6b**·3 HCl (16 mg, 53%) as a white solid.

M.p. > 250 °C (decomp.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$ + 1 drop TFA; assignments based on a DQF-COSY spectrum): δ = 1.19–1.29 (m, 2 H; H_a–C(2",5")), 1.46–1.63 (m, 4 H; H_2C(3",4")), 1.75–1.83 (m, 2 H; H_b–C(2",5")), 2.16 (sept., J = 7.5 Hz, 1 H; H–C(1")), 2.96 (t, J = 7.3 Hz, 2 H; CH_2–C(1')), 3.01 (d, J = 7.5 Hz, CH_2–C(1")), 3.23 (t, J = 6.9 Hz, 2 H; CH_2–C(4)), 3.53 (t, J = 6.9 Hz, 2 H; C*H*$_2$CH$_2$–C(4)), 3.77–3.84 (m, 2 H; C*H*$_2$NH–C(2)), 7.16–7.22 (m, 1 H; H–C(4')), 7.27–7.36 (m, 4 H; H–C(2',3',5',6')), 7.77 (s, 1 H; H–C(9)), 8.04 (br. s, 1 H; NH), 8.83 (br. s, 2 H; NH_2), 9.21 ppm (br. s, 1 H; NH); ^{13}C NMR (125 MHz, $(CD_3)_2SO$ + 1 drop TFA): δ = 22.22 (*C*H$_2$–C(4)), 24.58 (2 C; C(3",4")), 30.09 (2 C; C(2",5")), 34.72 (*C*H$_2$–C(1')), 36.45 (C(1")), 44.25 (*C*H$_2$NH–C(2)), 45.87 (*C*H$_2$CH$_2$–C(4)), 51.46 (*C*H$_2$–C(1")), 106.80 (C(9)), 109.51 (C(4)), 126.42 (C(4')), 128.32 and 128.94 (4 C; C(2',3',5',6')), 138.21 (C(1")), 151.40 ppm (C(2)), 6 signals hidden by noise; IR (ATR): $\tilde{\nu}$ = 3424 (w), 2948 (w), 1678 (s), 1575 (w), 1447 (m), 1386 (w), 1200 (w), 1140 (w), 1014 (w), 984 (w), 745 (m), 696 cm^{-1} (s); HR-MALDI-MS: *m*/*z* (%): 446.2664 (100, $[M+H]^+$, calcd for $C_{25}H_{32}N_7O^+$: 446.2663).

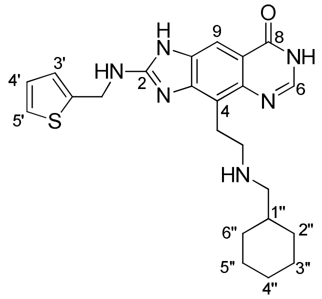
6-Amino-4-{2-[(cyclohexylmethyl)amino]ethyl}-2-[(2-phenylethyl)amino]-1,7-dihydro-8*H*-imidazo[4,5-*g*]quinazolin-8-one Trihydrochloride (6c·3 HCl):



According to **GP 1**, starting from **15c** (35 mg, 0.06 mmol), chloroformamidinium chloride (13 mg, 0.12 mmol), and Me_2SO_2 (400 mg). The mixture was diluted with sat. aq. $NaHCO_3$ solution (5 mL) and the precipitate collected by centrifugation. FC (MCI gel; H_2O + 0.1 vol-% conc. HCl/MeOH 60:40 to 50:50) and evaporation yielded **6c**·3 HCl (21 mg, 59%) as a white solid.

M.p. > 225 °C (decomp.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$ + 1 drop TFA; assignments based on a DQF-COSY spectrum): δ = 0.94 (qd, J = 11.7, 2.4 Hz, 2 H; H_{ax}–C(2",6")), 0.89–0.99 (m, 4 H; H_{ax}–C(3",5"), H_2C(4")), 1.56–1.78 (m, 5 H; H_{eq}–C(2",3",5",6"), H–C(1")), 2.86 (br. d, $J \approx$ 6.2 Hz, 2 H; CH_2–C(1")), 2.95 (t, J = 7.3 Hz, 2 H; CH_2–C(1')), 3.16–3.22 (m, 2 H; CH_2–C(4)), 3.44–3.50 (m, 2 H; CH_2CH_2–C(4)), 3.70–3.79 (m, 2 H; CH_2NH–C(2)), 6.35 (br. s, 1 H; NH), 7.21–7.23 (m, 1 H; H–C(4')), 7.26–7.35 (m, 4 H; H–C(2',3',5',6')), 7.67 (s, 1 H; H–C(9)), 8.79 ppm (br. s, 2 H; NH_2); ^{13}C NMR (125 MHz, $(CD_3)_2SO$ + 1 drop TFA): δ = 22.31 (CH$_2$–C(4)), 24.93 (2 C; C(3",5")), 25.50 (C(4")), 29.94 (2 C; C(2",6")), 34.34 (CH$_2$–C(1')), 34.88 (C(1")), 44.05 (CH$_2$NH–C(2)), 52.67 (CH$_2$–C(1")), 63.18 (CH$_2$CH$_2$–C(4)), 126.29 (C(4')), 128.26 and 128.88 (4 C; C(2',3',5',6')), 138.43 (C(1')), 150.91 ppm (C(2)), 8 signals hidden by noise; IR (ATR): $\tilde{\nu}$ = 3215 (w), 2924 (w), 2851 (br w), 1674 (s), 1651 (s), 1524 (w), 1445 (s), 1080 (m), 1009 (m), 778 (w), 694 cm^{-1} (w); HR-MALDI-MS: m/z (%): 461.2850 (33), 460.2816 (100, $[M + H]^+$, calcd for $C_{26}H_{34}N_7O^+$: 460.2819), 235.0713 (27).

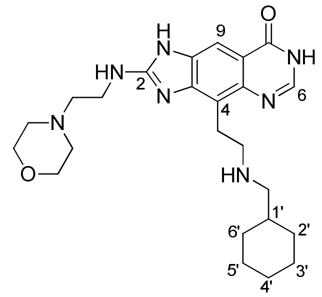
4-{2-[(Cyclohexylmethyl)amino]ethyl}-2-[(thien-2-ylmethyl)amino]-1,7-dihydro-8*H*-imidazo[4,5-*g*]quinazolin-8-one (7a):



According to **GP 2**, starting from **15a** (68 mg, 0.12 mmol) in anhydrous formamide (2.0 mL). HPLC, evaporation, and lyophilization yielded **7a** (15 mg, 28%) as a white solid.

M.p. > 188 °C (decomp); ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ = 0.97 (qd, J = 12.6, 2.9 Hz, 2 H; H_{ax}–C(2",6")), 1.13 (tt, J = 12.3, 2.8 Hz, 1 H; H_{ax}–C(4")), 1.20 (qt, J = 12.6, 3.3 Hz, 2 H; H_{ax}–C(3",5")), 1.57–1.86 (m, 6 H; H–C(1"), H_{eq}–C(2"–6")), 2.87 (t, J = 6.2 Hz, 2 H; CH_2–C(1")), 3.21 (br. t, $J \approx$ 6.6 Hz, 2 H; CH_2–C(4)), 3.73 (br. t, $J \approx$ 6.6 Hz, 2 H; CH_2CH_2–C(4)), 5.08–5.19 (m, 2 H; CH_2NH–C(2)), 7.03 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(3')), 7.36 (br. s, 1 H; H–C(2')), 7.51 (dd, J = 5.1, 1.1 Hz, 1 H; H–C(4')), 7.95 (s, 1 H; H–C(9)), 8.13 (s, 1 H; H–C(6)), 8.87 (br. s, 2 H; 2 NH), 9.98 (br. s, 1 H; NH), 12.36 ppm (br. s, 1 H; NH); ^{13}C NMR (150 MHz, $(CD_3)_2SO$): δ = 22.71 (CH_2–C(4)), 25.00 (2 C; C(3",5")), 25.57 (C(4")), 30.02 (2 C; C(2",6")), 34.43 (C(1")), 41.46 (CH_2NH–C(2)), 46.94 (CH_2CH_2–C(4)), 52.71 (CH_2–C(1")), 105.77 (C(8a)), 116.91 (C(9)), 118.65 (C(4)), 126.30 (C(5')), 126.93 and 127.29 (2 C; C(3',4')), 129.53 (C(3a)), 134.60 (C(9a)), 139.27 (C(2')), 143.21 (C(4a)), 143.70 (C(6)), 151.85 (C(2)), 160.74 ppm (C(8)); IR (ATR): $\tilde{\nu}$ = 2926 (m), 2839 (m), 1669 (s), 1631 (m), 1598 (m), 1447 (m), 1370 (w), 1297 (w), 1277 (w), 1209 (m), 1075 (w), 1013 (w), 891 (w), 848 (w), 792 (w), 699 cm^{-1} (m); HR-MALDI-MS: m/z (%): 438.2164 (24), 437.2124 (100, $[M + H]^+$, calcd for $C_{23}H_{29}N_6OS^+$: 437.2118).

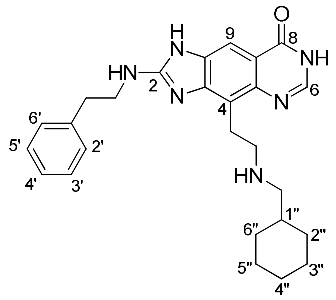
4-{2-[(Cyclohexylmethyl)amino]ethyl}-2-{[2-(morpholin-4-yl)ethyl]amino}-1,7-dihydro-8*H*-imidazo[4,5-*g*]quinazolin-8-one (7b):



According to **GP 2**, starting from **15b** (140 mg, 0.25 mmol) in anhydrous formamide (4.0 mL). HPLC, evaporation, and lyophilization yielded **7b** (22 mg, 20%) as a pale yellow solid.

M.p. > 235 °C (decomp); ^{1}H NMR (600 MHz, $(CD_3)_2SO$, assignments based on a DQF-COSY spectrum): δ = 0.95 (qd, J = 11.9, 3.0 Hz, 2 H; H_{ax}–C(2',6')), 1.13 (tt, J = 12.3, 3.1 Hz, 1 H; H_{ax}–C(4')), 1.19 (tt, J = 12.3, 3.1 Hz, 2 H; H_{ax}–C(3',5')), 1.59–1.82 (m, 6 H; H–C(1'), H_{eq}–C(2'–6')), 2.67 (br. s, 4 H; $N(CH_2)_2$), 2.73–2.78 (br. s, 2 H; CH_2–C(4)), 2.87 (d, J = 7.0 Hz, 2 H; CH_2–C(1')), 3.23 (t, J = 7.3 Hz, 2 H; CH_2CH$_2$NH–C(2)), 3.58 (t, J = 7.5 Hz, 4 H; CH_2NH–C(2), CH_2CH$_2$–C(4)), 3.67 (br. t, $J \approx$ 4.8 Hz, 4 H; $O(CH_2)_2$), 6.98 (br. s, 0.2 H; NH), 7.29 (br. s, 0.8 H; NH), 7.76 (s, 1 H; H–C(9)), 7.97 (br. s, 1 H; NH), 8.15 (s, 1 H; H–C(6)), 8.98 (br. s, 1 H; NH), 11.94 ppm (br. s, 1 H; NH); ^{13}C NMR (150 MHz, $(CD_3)_2SO$): δ = 22.13 (CH$_2$–C(4)), 24.92 (2 C; C(3',5')), 25.49 (C(4')), 29.92 (2 C; C(2',6')), 34.27 (C(1')), 46.95 (CH$_2$NH–C(2)), 52.24 (CH$_2$–C(1')), 52.78 (CH$_2$CH$_2$–C(4)), 56.96 (3 C; $N(CH_2)_3$), 65.41 (2 C; $O(CH_2)_2$), 103.67 (C(8a)), 115.30 (C(9)), 116.53 (C(4)), 141.29 (C(3a)), 141.39 (C(9a)), 146.19 (C(4a)), 158.04 (C(6)), 161.21 (C(2)), 162.90 ppm (C(8)); IR (ATR): $\tilde{\nu}$ = 2923 (m), 2852 (m), 1639 (s), 1621 (s), 1595 (s), 1572 (s), 1435 (s), 1373 (m), 1342 (m), 1304 (m), 1275 (m), 1220 (m), 1182 (m), 1100 (m), 1018 (m), 873 (m), 796 (m), 760 cm^{-1} (m); HR-MALDI-MS: m/z (%): 455.2964 (25), 454.2931 (100, $[M+H]^+$, calcd for $C_{24}H_{36}N_7O_2$+: 454.2925).

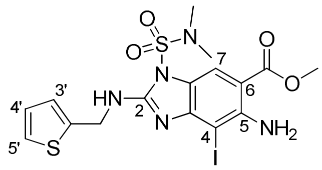
4-{2-[(Cyclohexylmethyl)amino]ethyl}-2-[(2-phenylethyl)amino]-1,7-dihydro-8*H*-imidazo[4,5-*g*]quinazolin-8-one (7c):



According to **GP 2**, starting from **15c** (140 mg, 0.25 mmol) in anhydrous formamide (4.0 mL). HPLC, evaporation, and lyophilization yielded **7c** (22 mg, purity 95%, yield 19%) as a pale yellow solid.

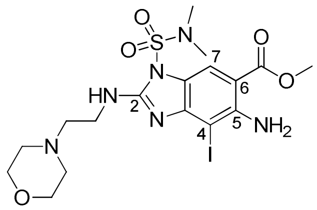
M.p. > 150 °C (decomp); ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ = 0.91 (qd, J = 11.9, 2.1 Hz, 2 H; H_{ax}–C(2",6")), 1.10 (tt, J = 12.0, 3.0 Hz, 1 H; H_{ax}–C(4")), 1.16 (br. tt, $J \approx$ 12.0, 3.0 Hz, 2 H; H_{ax}–C(3",5")), 1.18–1.23 (m, 1 H; H–C(1")), 1.26 (br. d, $J \approx$ 12.6 Hz, 2 H; H_{eq}–C(3",5")), 1.58–1.66 (m, 3 H; H_{eq}–C(2",4",6")), 2.79 (d, J = 7.2 Hz, 2 H; CH_2–C(1")), 2.93 (t, J = 7.2 Hz, 2 H; CH_2–C(4)), 3.16 (t, J = 7.5 Hz, 2 H; CH_2–C(1')), 3.52 (t, J = 7.2 Hz, 2 H; C$H_2$$CH_2$–C(4)), 3.61 (t, J = 7.2 Hz, 2 H; CH_2NH–C(2)), 7.20–7.22 (m, 1 H; NH), 7.30–7.32 (m, 5 H; C_6H_5), 7.70 (br. s, 1 H; NH), 7.71 (s, 1 H; H–C(9)), 7.95 (s, 1 H; H–C(6)), 8.37 ppm (br. s, 1 H; NH); ^{13}C NMR (150 MHz, $(CD_3)_2SO$): δ = 22.75 (CH_2–C(4)), 24.96 (2 C; C(3",5")), 25.56 (C(4")), 29.99 (2 C; C(2",6")), 34.72 (C(1")), 35.27 (CH_2–C(1')), 43.63 (CH_2NH–C(2)), 47.29 (CH_2–C(1")), 52.71 (CH_2CH_2–C(4)), 103.86 (C(9)), 115.26 (C(4)), 116.07 (C(8a)), 126.04 (C(4')), 128.22 (2 C; C(2',6')), 128.65 (2 C; C(3',5')), 136.71 (C(3a)), 139.28 (C(1')), 141.07 (C(9a)), 145.65 (C(4a)), 158.49 (C(6)), 161.30 (C(2)), 165.18 ppm (C(8)); IR (ATR): $\tilde{\nu}$ = 3046 (w), 2923 (w), 2847 (w), 1622 (s), 1601 (s), 1570 (s), 1435 (m), 1362 (m), 1343 (m), 1186 (m), 1084 (m), 901 (m), 876 (m), 798 (m), 749 (m), 698 cm^{-1} (m); HR-MALDI-MS: m/z (%): 446.2755 (28), 445.2720 (100, $[M + H]^+$, calcd for $C_{26}H_{33}N_6O^+$: 445.2710).

Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-iodo-2-[(thien-2-ylmethyl)amino]-1*H*-benzimidazole-6-carboxylate (9a):



According to **GP 3**, starting from **8a** (1.28 g, 3.13 mmol) and iodine (925 mg, 3.76 mmol) in CH_2Cl_2/sat. aq. $NaHCO_3$ solution 2:1 (90 mL); workup with sat. aq. $Na_2S_2O_3$ (35 mL) solution and CH_2Cl_2 (2x 80 mL). FC (SiO_2; cyclohexane/EtOAc 80:20) yielded **9a** (1.16 g, 70%) as a yellow solid.
R_f = 0.46 (SiO_2; cyclohexane/EtOAc 80:20, UV 254 nm); m.p. 175–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 6 H; NMe_2), 3.90 (s, 3 H; OMe), 4.99 (d, J = 5.1 Hz, 2 H; CH_2NH), 6.46 (br. s, 2 H; NH_2), 6.69 (t, J = 5.6 Hz, 1 H; NH), 7.00 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(4')), 7.15 (dd, J = 3.4, 1.0 Hz, 1 H; H–C(3')), 7.27 (dd, J = 5.1, 1.2 Hz, 1 H; H–C(5')), 8.08 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.79 (2 C; NMe_2), 42.01 (CH_2NH), 51.85 (OMe), 73.44 (C(4)), 104.35 (C(6)), 114.35 (C(7)), 121.77 (C(7a)), 125.62 (C(5')), 126.88 and 126.92 (2 C; C(3',4')), 139.85 (C(2')), 148.65 (C(3a)), 149.75 (C(5)), 154.19 (C(2)), 168.05 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3461 (w), 3401 (w), 3341 (w), 3117 (w), 2951 (w), 1769 (w), 1685 (m), 1631 (m), 1568 (s), 1538 (m), 1507 (m), 1446 (m), 1424 (m), 1386 (m), 1372 (m), 1334 (m), 1287 (m), 1258 (s), 1222 (m), 1186 (s), 1151 (s), 1107 (m), 1074 (m), 1032 (m), 1003 (m), 958 (s), 887 (m), 821 (m), 784 (m), 762 (m), 745 (m), 737 (m), 704 (s), 674 (m), 625 cm^{-1} (m); HR-ESI-MS: m/z (%): 535.9920 (100, $[M + H]^+$, calcd for $C_{16}H_{19}IN_5O_4S_2^+$: 535.9918), 279.1589 (24); elemental analysis calcd (%) for $C_{16}H_{18}IN_5O_4S_2$ (535.39): C 35.89, H 3.39, N 13.08; found: C 36.06, H 3.45; N 13.04.

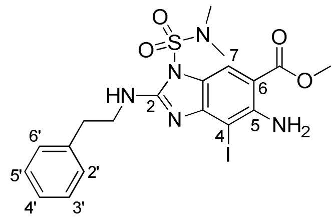
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-iodo-2-{[2-(morpholin-4-yl)ethyl]amino}-1*H*-benzimidazole-6-carboxylate (9b):



According to **GP 3**, starting from **8b** (1.21 g, 2.84 mmol) and iodine (865 mg, 3.42 mmol) in CH_2Cl_2/sat. aq. $NaHCO_3$ solution 2:1 (90 mL); workup with sat. aq. $Na_2S_2O_3$ (35 mL) solution and CH_2Cl_2 (2x 80 mL). FC (SiO_2; hexane/EtOAc 30:70 to 40:60) yielded **9b** (577 mg, 37%) as a pale brown solid.

R_f = 0.44 (SiO_2; EtOAc, UV 254 nm); m.p. 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.55 (br. t, J = 4.2 Hz, 4 H; $N(CH_2)_2$), 2.67 (t, J = 5.9 Hz, 2 H; CH_2CH$_2$NH), 2.93 (s, 6 H; NMe_2), 3.70–3.75 (m, 6 H; C*H*$_2$NH and $O(CH_2)_2$), 3.89 (s, 3 H; OMe), 6.44 (br. s, 2 H; NH_2), 7.07 (t, J = 4.4 Hz, 1 H; NH), 8.06 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.80 (2 C; NMe_2), 39.41 (*C*H$_2$NH), 51.80 (OMe), 53.26 (2 C; $N(CH_2)_2$), 56.51 (*C*H$_2$CH$_2$NH), 67.05 (2 C; $O(CH_2)_2$), 73.03 (C(4)), 104.01 (C(6)), 114.12 (C(7)), 121.82 (C(7a)), 148.58 (C(3a)), 150.04 (C(5)), 154.86 (C(2)), 168.10 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3459 (w), 3421 (w), 3334 (w), 2949 (w), 2866 (w), 2810 (w), 1686 (m), 1631 (w), 1568 (s), 1511 (m), 1451 (m), 1435 (m), 1422 (m), 1389 (m), 1373 (m), 1354 (m), 1286 (m), 1262 (s), 1229 (m), 1190 (s), 1155 (s), 1109 (s), 1068 (m), 1031 (s), 1020 (s), 992 (m), 968 (s), 929 (m), 912 (m), 891 (m), 827 (m), 784 (m), 736 (s), 714 (s), 707 cm^{-1} (s); HR-ESI-MS: m/z (%): 553.0712 (100, $[M + H]^+$, calcd for $C_{17}H_{26}IN_6O_5S^+$: 553.0725), 358.2733 (81); elemental analysis calcd (%) for $C_{17}H_{25}IN_6O_5S$ (552.39): C 36.96, H 4.56, N 15.21; found: C 37.34, H 4.57; N 14.88.

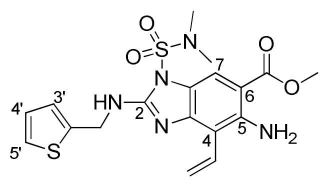
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-iodo-2-[(2-phenylethyl)amino]-1*H*-benzimidazole-6-carboxylate (9c):



According to **GP 3**, starting from **8c** (1.85 g, 4.44 mmol) and iodine (1.40 g, 5.51 mmol) in CH_2Cl_2/sat. aq. $NaHCO_3$ solution 2:1 (150 mL); workup with sat. aq. $Na_2S_2O_3$ (50 mL) solution and CH_2Cl_2 (2x 100 mL). FC (SiO_2; cyclohexane/EtOAc 80:20) yielded **9c** (2.06 g, 86%) as a red-brown foam.

$R_f = 0.38$ (SiO_2; cyclohexane/EtOAc 70:30, UV 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.73$ (s, 6 H; NMe_2), 3.04 (t, $J = 6.8$ Hz, 2 H, CH_2–C(1')), 3.86 (s, 3 H; OMe), 3.89 (td, $J = 6.8$, 5.4 Hz, 2 H; CH_2NH), 6.37 (t, $J = 5.4$ Hz, 1 H; NH), 6.42 (br. s, 2 H; NH_2), 7.21–7.36 (m, 5 H; C_6H_5), 8.01 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 35.29$ (CH_2–C(1')), 38.76 (2 C; NMe_2), 44.52 (CH_2NH), 51.92 (OMe), 73.37 (C(4)), 104.21 (C(6)), 114.27 (C(7)), 121.82 (C(7a)), 126.87 (C(4')), 128.89 (2 C; C(2',6')), 128.97 (2 C; C(3',5')), 138.57 (C(1')), 148.76 (C(3a)), 150.17 (C(5)), 154.78 (C(2)), 168.22 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3469 (w), 3399 (w), 3354 (w), 3027 (w), 2948 (w), 1680 (w), 1568 (s), 1423 (m), 1391 (m), 1262 (m), 1188 (s), 1152 (s), 960 (m), 786 (w), 712 cm^{-1} (s); HR-MALDI-MS: *m*/*z* (%): 545.0549 (23), 544.0516 (100, $[M + H]^+$, calcd for $C_{19}H_{23}IN_5O_4S^+$: 544.0510), 511.1757 (33), 436.0393 (72), 418.1540 (46), 310.1422 (47).

Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-2-[(thien-2-ylmethyl)amino]-4-vinyl-1*H*-benzimidazole-6-carboxylate (11a):

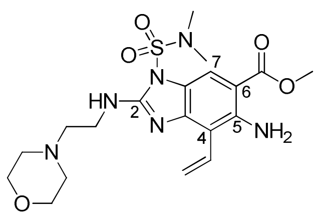


According to **GP 4**, starting from **9a** (1.16 g, 2.17 mmol), vinylboronic acid pinacol ester (**10**; 0.59 mL, 3.49 mmol), and Et_3N (0.9 mL, 6.33 mmol) in DME/H_2O 5:1 (6.0 mL); $[PdCl_2(PPh_3)_2]$ (36 mg, 0.05 mmol). Workup with aq. sat.

$NaHCO_3$ solution (30 mL) and EtOAc (3x 30 mL) and FC (SiO_2; cyclohexane/EtOAc 80:20) yielded crude **11a** (769 mg, ca. 81%) as a pale brown solid.

R_f = 0.24 (SiO_2; cyclohexane/EtOAc 80:20, UV 254 nm); m.p. 135–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 6 H; NMe_2), 3.89 (s, 3 H; OMe), 4.95 (d, J = 5.4 Hz, 2 H; CH_2NH), 5.72 (dd, J = 11.8, 2.0 Hz, 1 H; CH=CH_E), 6.16 (br. s, 2 H; NH_2), 6.30 (dd, J = 17.8, 2.0 Hz, 1 H; CH=CH_Z), 6.67 (t, J = 5.8 Hz, 1 H; NH), 6.93 (dd, J = 17.8, 11.8 Hz, 1 H; C*H*=CH_2), 6.99 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(4')), 7.10 (dd, J = 3.5, 1.1 Hz, 1 H; H–C(3')), 7.25 (dd, J = 5.1, 1.1 Hz, 1 H; H–C(5')), 8.05 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.79 (2 C; NMe_2), 41.93 (CH_2NH), 51.61 (OMe), 104.70 (C(6)), 111.37 (C(4)), 113.46 (C(7)), 119.72 (CH=CH_2), 123.40 (C(7a)), 125.46 (C(5')), 126.49 and 126.82 (2 C; C(3',4')), 128.42 (*C*H=CH_2), 140.39 (C(2')), 145.77 (C(3a)), 146.79 (C(5)), 154.39 (C(2)), 168.96 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3472 (w), 3401 (w), 2949 (w), 1683 (w), 1570 (s), 1505 (w), 1451 (w), 1429 (w), 1411 (w), 1371 (m), 1334 (w), 1306 (w), 1289 (m), 1261 (m), 1207 (s), 1156 (s), 1105 (w), 1050 (m), 1032 (m), 961 (s), 884 (w), 850 (w), 822 (w), 796 (m), 772 (w), 757 (w), 743 (w), 718 (s), 700 cm^{-1} (s); HR-ESI-MS: m/z (%): 437.1125 (23), 436.1096 (100, $[M + H]^+$, calcd for $C_{18}H_{22}N_5O_4S_2^+$: 436.1108).

Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-2-{[2-(morpholin-4-yl)ethyl]amino}-4-vinyl-1*H*-benzimidazole-6-carboxylate (11b):

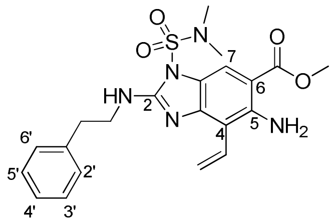


According to **GP 4**, starting from **9b** (577 mg, 1.04 mmol), vinylboronic acid pinacol ester (**10**; 0.28 mL, 1.67 mmol), and Et_3N (0.43 mL, 3.03 mmol) in DME/H_2O 5:1 (3.0 mL); $[PdCl_2(PPh_3)_2]$ (17 mg, 0.024 mmol). Workup with aq. sat. $NaHCO_3$ solution (15 mL) and EtOAc (3x 15 mL) and FC (SiO_2; cyclohexane/EtOAc 30:70) yielded crude **11b** (368 mg, 78 %) as a pale brown solid.

R_f = 0.25 (SiO_2; cyclohexane/EtOAc 30:70, UV 254 nm); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (t, J = 4.4 Hz, 4 H; $N(CH_2)_2$), 2.67 (t, J = 6.0 Hz, 2 H;

CH_2CH_2NH), 2.93 (s, 6 H; NMe_2), 3.68 (q, J = 5.5 Hz, 2 H; CH_2NH), 3.75 (t, J = 4.6 Hz, 4 H; $O(CH_2)_2$), 3.88 (s, 3 H; OMe), 5.68 (dd, J = 11.8, 2.1 Hz, 1 H; CH=CH_E), 6.16 (br. s, 2 H; NH_2), 6.20 (dd, J = 17.9, 2.1 Hz, 1 H; CH=CH_Z), 6.92 (dd, J = 17.9, 11.8 Hz, 1 H; CH=CH_2), 6.99 (t, J = 4.8 Hz, 1 H; NH), 8.04 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.81 (2 C; NMe_2), 39.41 (CH_2NH), 51.58 (OMe), 53.28 (2 C; $N(CH_2)_2$), 56.55 (CH_2CH_2NH), 67.04 (2 C; $O(CH_2)_2$), 104.31 (C(6)), 110.99 (C(4)), 113.27 (C(7)), 119.41 (CH=CH_2), 123.42 (C(7a)), 128.68 (CH=CH_2), 146.18 (C(3a)), 146.76 (C(5)), 155.01 (C(2)), 169.03 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3359 (w), 2948 (w), 1683 (w), 1640 (w), 1579 (s), 1455 (w), 1429 (m), 1385 (m), 1347 (m), 1271 (m), 1205 (m), 1155 (s), 1115 (m), 1051 (m), 964 (m), 914 (w), 854 (w), 796 (w), 748 (m), 713 cm^{-1} (s); HR-ESI-MS: m/z (%): 453.1905 (100, $[M + H]^+$, calcd for $C_{19}H_{29}N_6O_5S^+$: 453.1915), 454.1936 (27).

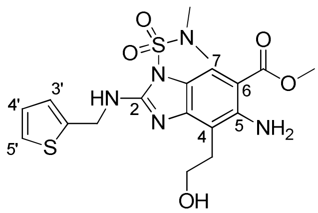
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-2-[(2-phenylethyl)amino]-4-vinyl-1*H*-benzimidazole-6-carboxylate (11c):



According to **GP 4**, starting from **9c** (1.35 g, 2.49 mmol), vinylboronic acid pinacol ester (**10**; 0.67 mL, 3.98 mmol), and Et_3N (1.02 mL, 7.22 mmol) in DME/H_2O 5:1 (6.0 mL); $[PdCl_2(PPh_3)_2]$ (41 mg, 0.06 mmol). Workup with aq. sat. $NaHCO_3$ solution (30 mL) and EtOAc (3x 30 mL) and FC (SiO_2; cyclohexane/EtOAc 80:20 to 70:30) yielded **11c** (920 mg, 83%) as a green oil.

R_f = 0.23 (SiO_2; cyclohexane/EtOAc 80:20, UV 254 nm); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.74 (s, 6 H; NMe_2), 3.02 (t, J = 7.0 Hz, 2 H; CH_2–C(1')), 3.84 (td, J = 7.0, 5.4 Hz, 2 H; CH_2NH), 3.85 (s, 3 H; OMe), 5.69 (dd, J = 11.8, 2.1 Hz, 1 H; CH=CH_E), 6.13 (br. s, 2 H; NH_2), 6.25 (dd, J = 17.8, 2.1 Hz, 1 H; CH=CH_Z), 6.34 (t, J = 5.4 Hz, 1 H; NH), 6.92 (dd, J = 17.8, 11.8 Hz, 1 H; CH=CH_2), 7.20–7.35 (m, 5 H; C_6H_5), 7.99 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.39 (CH_2–C(1')), 38.78 (2 C; NMe_2), 44.49 (CH_2NH), 51.68 (OMe), 104.55 (C(6)), 111.24 (C(4)), 113.43 (C(7)), 119.57 (CH=CH_2), 123.45 (C(7a)), 126.82 (CH=CH_2), 128.75 (C(4')), 128.86 (2 C; C(2',6')), 128.94 (2 C; C(3',5')), 138.73 (C(1')), 146.31 (C(3a)), 146.94 (C(5)), 154.98 (C(2)), 169.14 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3477 (w), 3424 (w), 3343 (w), 3021 (w), 2867 (w), 1682 (w), 1576 (s), 1498 (w), 1431 (m), 1386 (m), 1263 (m), 1210 (s), 1140 (s), 1024 (w), 953 (m), 901 (w), 797 (w), 705 cm^{-1} (s); HR-MALDI-MS: *m/z* (%): 444.1701 (50, $[M+H]^+$, calcd for $C_{14}H_{20}N_5O_4S^+$: 444.1700), 336.1578 (100), 235.0713 (21), 232.0954 (24).

Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-(2-hydroxyethyl)-2-[(thien-2-ylmethyl)amino]-1*H*-benzimidazole-6-carboxylate (12a):

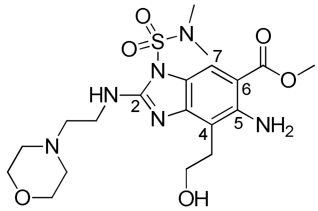


According to **GP 5**, starting from **11a** (769 mg, 1.76 mmol) and a 0.5 M solution 9-BBN in THF (10.5 mL, 5.25 mmol); 30 % H_2O_2 in H_2O (1.80 mL, 17.6 mmol) and 1 M aq NaOH solution (18.2 ml, 17.6 mmol). Workup with sat. aq. NH_4Cl solution (50 mL) and EtOAc (3x 50 mL) and FC (SiO_2; cyclohexane/EtOAc 50:50 to 40:60) yielded crude **12a** (439 mg, 55%) as a yellow solid.

R_f = 0.26 (SiO_2; cyclohexane/EtOAc 50:50, UV 254 nm); m.p. 130–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60–1.86 (br. s, 1 H; OH), 2.89 (s, 6 H; NMe_2), 3.04 (t, J = 5.6 Hz, 2 H; CH_2CH_2OH), 3.88 (s, 3 H; OMe), 4.04 (t, J = 5.6 Hz, 2 H; CH_2CH_2OH), 4.89 (d, J = 5.5 Hz, 2 H; CH_2NH), 5.97 (br. s, 2 H; NH_2), 6.73 (t, J = 5.7 Hz, 1 H; NH), 6.97 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(4')), 7.09 (dd, J = 3.5, 1.1 Hz, 1 H; H–C(3')), 7.24 (dd, J = 5.1, 1.1 Hz, 1 H; H–C(5')), 8.03 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.47 (CH_2CH_2OH), 38.77 (2 C; NMe_2), 41.98 (CH_2NH), 51.62 (OMe), 61.80 (CH_2OH), 105.16 (C(6)), 112.22 (C(4)), 112.55 (C(7)), 123.04 (C(7a)), 125.47 (C(5')), 126.51 and 126.89 (2 C; C(3',4')), 140.15 (C(2')), 145.84 (C(3a)), 147.55 (C(5)), 153.93 (C(2)), 169.00 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3372 (w), 2948 (w), 1683 (w), 1574 (s), 1504 (w), 1456 (w), 1426 (m), 1370 (m), 1273 (m), 1202 (s), 1152 (s), 1077 (m), 1036 (m), 963 (s), 891 (w), 852 (m), 791 (m), 743 (m), 706 (s), 615 cm^{-1} (m); HR-ESI-MS:

m/*z* (%): 455.1243 (24), 454.1207 (100, $[M + H]^+$, calcd for $C_{18}H_{24}N_5O_5S_2^+$: 454.1213); elemental analysis: calcd (%) for $C_{18}H_{23}N_5O_5S_2$ (453.54): C 47.67, H 5.11; found: C 47.84, H 5.31.

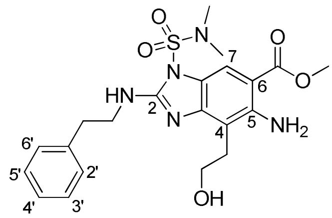
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-(2-hydroxyethyl)-2-{[(2-morpholin-4-yl)ethyl]amino}-1*H*-benzimidazole-6-carboxylate (12b):



According to **GP 5**, starting from **11b** (368 mg, 0.81 mmol) and a 0.5 M solution of 9-BBN in THF (4.9 mL, 2.45 mmol); 30 % H_2O_2 in H_2O (0.82 mL, 8.10 mmol) and 1 M aq NaOH solution (4.4 mL, 8.10 mmol). Workup with sat. aq. NH_4Cl solution (25 mL) and EtOAc (3x 25 mL) and FC (SiO_2; EtOAc/MeOH 95:5) yielded crude **12b** (176 mg, 46%) as a brown solid.

R_f = 0.19 (SiO_2; EtOAc/MeOH 95:5, UV 254 nm); m.p. 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48–1.78 (br. s, 1 H; OH), 2.54 (br. s, 4 H; $N(CH_2)_2$), 2.67 (t, J = 5.9 Hz, 2 H; C*H*$_2$CH$_2$NH), 2.96 (s, 6 H; NMe_2), 2.99 (t, J = 5.6 Hz, 2 H; C*H*$_2$CH$_2$OH), 3.61 (q, J = 5.5 Hz, 2 H; C*H*$_2$NH), 3.75 (br. t, J = 4.4 Hz, 4 H; $O(CH_2)_2$), 3.89 (s, 3 H; OMe), 4.02 (t, J = 5.6 Hz, 2 H; C*H*$_2$OH), 7.03 (t, J = 4.8 Hz, 1 H; NH), 8.03 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.53 (*C*H$_2$CH$_2$OH), 38.79 (2 C; NMe_2), 39.44 (CH_2NH), 51.61 (OMe), 53.23 (2 C; $N(CH_2)_2$), 56.26 (*C*H$_2$CH$_2$NH), 61.71 (CH$_2$*C*H$_2$OH), 66.95 (2 C; $O(CH_2)_2$), 104.90 (C(6)), 111.95 (C(4)), 112.39 (C(7)), 123.09 (C(7a)), 145.90 (C(3a)), 147.36 (C(5)), 154.40 (C(2)), 169.05 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3361 (w), 2949 (w), 2855 (w), 1683 (w), 1581 (s), 1455 (m), 1427 (m), 1376 (m), 1348 (m), 1272 (m), 1202 (s), 1154 (s), 1114 (s), 1068 (m), 1035 (m), 961 (m), 914 (m), 858 (m), 792 (m), 745 (m), 714 cm^{-1} (s); HR-ESI-MS: *m*/*z* (%): 472.2038 (27), 471.2008 (100, $[M + H]^+$, calcd for $C_{19}H_{31}N_6O_6S^+$: 471.2020).

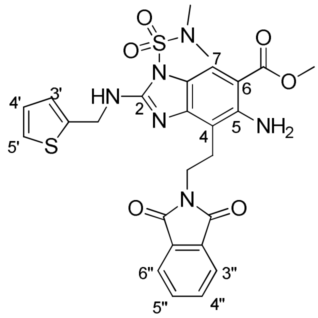
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-(2-hydroxyethyl)-2-[(2-phenylethyl)amino]-1*H*-benzimidazole-6-carboxylate (12c):



According to **GP 5**, starting from **11c** (403 mg, 0.91 mmol) and a 0.5 M solution of 9-BBN in THF (1.8 mL, 0.91 mmol); 30 % H_2O_2 in H_2O (0.46 mL, 4.5 mmol) and 1 M aq NaOH solution (4.5 mL, 4.5 mmol). Workup with sat. aq. NH_4Cl solution (30 mL) and EtOAc (3x 30 mL) and FC (SiO_2; cyclohexane/EtOAc 50:50 to 0:100) yielded **12c** (250 mg, 60%) as a yellow solid.

R_f = 0.20 (SiO_2; cyclohexane/EtOAc 50:50, UV 254 nm); m.p. 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52–1.73 (br. s, 1 H; OH), 2.75 (s, 6 H; NMe_2), 2.97–3.03 (m, 4 H; 2 CH_2), 3.78 (td, J = 6.9, 5.5 Hz, 2 H; CH_2NH), 3.85 (s, 3 H; OMe), 4.03 (t, J = 5.5 Hz, 2 H; CH_2OH), 5.94 (br. s, 2 H; NH_2), 6.37 (t, J = 5.5 Hz, 1 H; NH), 7.20–7.35 (m, 5 H; C_6H_5), 7.97 ppm (s, 1 H; H–C(7)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.82 (*C*H_2CH_2OH), 35.32 (2 C; NMe_2), 38.84 (*C*H_2CH_2NH), 44.56 (CH_2NH), 51.79 (OMe), 61.84 (CH_2OH), 104.94 (C(6)), 112.09 (C(4)), 112.41 (C(7)), 122.93 (C(7a)), 126.76 (C(4')), 128.78 (2 C; C(2',6')), 128.81 (2 C; C(3',5')), 138.32 (C(1')), 145.83 (C(3a)), 147.39 (C(5)), 154.21 (C(2)), 168.97 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3468 (w), 3402 (w), 3342 (w), 1686 (m), 1569 (s), 1453 (w), 1425 (m), 1368 (m), 1266 (m), 1192 (s), 1150 (s), 967 (m), 787 (w), 719 cm^{-1} (s); HR-MALDI-MS: *m/z* (%): 463.1832 (26), 462.1800 (100, $[M + H]^+$, calcd for $C_{21}H_{28}N_5O_5S^+$: 462.1806), 355.1758 (98), 354.1683 (85).

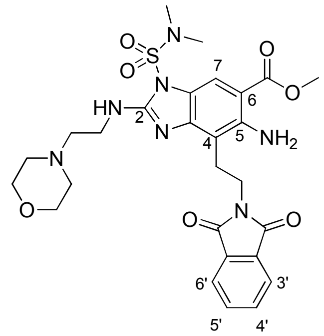
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-(2-phthalimidoethyl)-2-[(thien-2-yl-methyl)amino]-1*H*-benzimidazole-6-carboxylate (13a):



According to **GP 6**, starting from PPh_3 (508 mg, 1.93 mmol) in anhydrous THF (4.4 mL), DIAD (0.39 mL; 1.94 mmol), **12a** (439 mg, 0.96 mmol), and phthalimide (288 mg, 1.95 mmol) in anhydrous THF (7 mL). FC (SiO_2; cyclohexane/EtOAc 70:30 to 60:40), yielded **13a** (386 mg, 69 %) as a yellow solid.

R_f = 0.44 (SiO_2; cyclohexane/EtOAc 50:50, UV 254 nm); m.p. 215–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (s, 6 H; NMe_2), 3.26 (t, $J \approx$ 7.6 Hz, 2 H; CH_2–C(4)), 3.88 (s, 3 H; OMe), 3.98 (t, $J \approx$ 7.6 Hz, 2 H; CH_2CH$_2$–C(4)), 4.81 (d, J = 5.6 Hz, 2 H; CH_2NH), 6.29 (br. s, 2 H; NH_2), 6.52 (t, J = 5.7 Hz, 1 H; NH), 6.99 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(4')), 7.12 (dd, J = 3.5, 1.0 Hz, 1 H; H–C(3')), 7.25 (dd, J = 5.1, 1.0 Hz, 1 H; H–C(5')), 7.68–7.76 (m, 2 H; H–C(4",5")), 7.81–7.89 (m, 2 H; H–C(3",6")), 8.02 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.27 (CH$_2$–C(4)), 35.84 (CH$_2$CH$_2$–C(4)), 38.79 (2 C; NMe_2), 41.79 (CH_2NH), 51.51 (OMe), 104.50 (C(6)), 109.76 (C(4)), 112.98 (C(7)), 122.82 (C(7a)), 123.16 (2 C; C(3",6")), 125.44 (C(5')), 126.71 and 126.80 (2 C; C(3',4')), 132.30 (2 C; C(1",2")), 133.87 (2 C; C(4",5")), 140.32 (C(2')), 147.02 (C(3a)), 147.42 (C(5)), 154.16 (C(2)), 168.43 (2 C; N(C=O)$_2$), 169.04 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3463 (w), 3415 (w), 3347 (w), 2944 (w), 1767 (w), 1702 (s), 1640 (w), 1582 (s), 1502 (w), 1466 (w), 1425 (m), 1395 (m), 1368 (m), 1356 (m), 1341 (m), 1314 (w), 1295 (w), 1272 (s), 1196 (m), 1142 (s), 1114 (s), 1050 (s), 964 (s), 940 (m), 892 (m), 868 (w), 856 (w), 837 (w), 810 (w), 792 (m), 769 (w), 743 (m), 710 (s), 666 (m), 621 cm^{-1} (m); HR-ESI-MS: m/z (%): 584.1442 (35), 583.1409 (100, $[M+H]^+$, calcd for $C_{26}H_{27}N_6O_6S_2^+$: 583.1428).

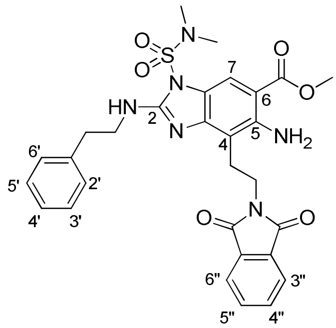
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-(2-phthalimidoethyl)-2-{[(2-morpholin-4-yl)ethyl]amino}-1*H*-benzimidazole-6-carboxylate (13b):



According to **GP 6**, starting from PPh_3 (144 mg, 0.71 mmol) in anhydrous THF (2.0 mL), DIAD (0.14 mL; 0.71 mmol), **12b** (167 mg, 0.36 mmol), and phthalimide (105 mg, 0.71 mmol) in anhydrous THF (2.0 mL). MPLC (SiO_2; CH_2Cl_2/EtOAc 100:0 to 0:100 within 30 min, 0:100 for 12 min) yielded **13b** (150 mg, 71%) as a yellow foam.

R_f = 0.18 (SiO_2; EtOAc, UV 254 nm); m.p. 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46–2.56 (m, 4 H; $N(CH_2)_2$), 2.60 (t, J = 5.7 Hz, 2 H; C$H_2$$CH_2$NH), 2.87 (s, 6 H; NMe_2), 3.17 (t, J = 7.7 Hz, 2 H; CH_2–C(4)), 3.54 (q, J = 5.4 Hz, 2 H; CH_2NH), 3.72 (br. t, J = 4.4 Hz, 4 H; $O(CH_2)_2$), 3.85 (s, 3 H; OMe), 3.92 (t, J = 7.7 Hz, 2 H; C$H_2$$CH_2$–C(4)), 6.25 (br. s, 2 H; NH_2), 6.79 (t, J = 4.9 Hz, 1 H; NH), 7.68–7.74 (m, 2 H; H–C(4',5')), 7.80–7.85 (m, 2 H; H–C(3',6')), 7.98 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.38 (CH_2–C(4)), 35.91 (CH_2CH_2–C(4)), 38.95 (2 C; NMe_2), 39.41 (CH_2NH), 51.62 (OMe), 53.45 (2 C; $N(CH_2)_2$), 56.79 (CH_2CH_2NH), 61.17 (2 C; $O(CH_2)_2$), 104.29 (C(6)), 109.47 (C(4)), 112.94 (C(7)), 123.01 (C(7a)), 123.29 (2 C; C(3',6')), 132.46 (2 C; C(1',2')), 133.97 (2 C; C(4',5')), 147.55 (2 C; C(3a,5)), 154.95 (C(2)), 168.56 (2 C; $N(C{=}O)_2$), 169.24 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3476 (w), 3363 (w), 2948 (w), 2860 (w), 2811 (w), 1771 (w), 1707 (s), 1585 (s), 1456 (w), 1428 (m), 1393 (m), 1349 (m), 1274 (m), 1204 (m), 1155 (m), 1114 (m), 1067 (m), 960 (m), 792 (m), 715 cm^{-1} (s); HR-ESI-MS: m/z (%): 601.2249 (38), 600.2216 (100, $[M+H]^+$, calcd for $C_{27}H_{34}N_7O_7S^+$: 600.2235), 358.2739 (36), 334.2161 (47), 295.1324 (42), 279.1376 (26), 239.1061 (21), 217.0828 (21), 177.0901 (26).

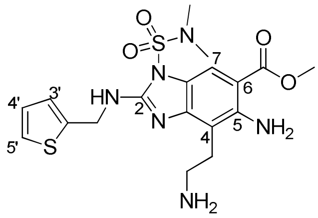
Methyl 5-Amino-1-(*N*,*N*-dimethylsulfamoyl)-4-(2-phthalimidoethyl)-2-[(2-phenylethyl)amino]-1*H*-benzimidazole-6-carboxylate (13c):



According to **GP 6**, starting from PPh_3 (696 mg, 2.65 mmol) in anhydrous THF (6.0 mL), DIAD (0.53 mL, 2.67 mmol), **12c** (613 mg, 1.33 mmol), and phthalimide (394 mg, 2.68 mmol) in anhydrous THF (10 mL). FC (SiO_2; cyclohexane/AcOEt 67:33 to 50:50) yielded **13c** (733 mg, 93%) as a yellow solid.

R_f = 0.54 (SiO_2; cyclohexane/EtOAc 50:50, UV 254 nm); m.p. 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 6 H; NMe_2), 2.97 (t, J = 6.9 Hz, 2 H; CH_2–C(4)), 3.22 (t, J = 6.8 Hz, 2 H; CH_2–C(1')), 3.70 (td, J = 6.9, 5.6 Hz, 2 H; CH_2NH), 3.85 (s, 3 H; OMe), 3.96 (t, J = 6.8 Hz, 2 H; CH_2CH_2–C(4)), 6.21 (br. t, $J \approx$ 5.6 Hz, 1 H; NH), 6.24 (br. s, 2 H; NH_2), 7.21–7.35 (m, 5 H; C_6H_5), 7.66–7.71 (m, 2 H; H–C(4",5")), 7.77–7.83 (m, 2 H; H–C(3",6"), 7.80 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.40 (CH_2–C(4)), 35.43 (CH_2–C(1')), 35.95 (CH_2CH_2–C(4)), 38.77 (2 C; NMe_2), 44.33 (CH_2NH), 51.57 (OMe), 104.35 (C(6)), 109.68 (C(4)), 112.92 (C(7)), 122.86 (C(7a)), 123.25 (2 C; C(3",6")), 126.72 (C(4')), 128.80 (2 C; C(2',6')), 129.00 (2 C; C(3',5')), 132.45 (2 C; C(1",2")), 133.91 (2 C; C(4",5")), 138.81 (C(1')), 147.53 (C(3a)), 147.55 (C(5)), 154.76 (C(2)), 168.50 (2 C; $N(C=O)_2$), 169.19 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3388 (w), 3030 (w), 2946 (w), 1771 (w), 1710 (m), 1684 (w), 1591 (s), 1516 (w), 1427 (m), 1392 (m), 1273 (m), 1208 (s), 1154 (s), 1106 (m), 1068 (w), 955 (m), 794 cm^{-1} (w); HR-MALDI-MS: m/z (%): 592.2051 (24), 591.2020 (68, $[M+H]$+, calcd for $C_{29}H_{31}N_6O_6S^+$: 591.2020), 483.1906 (100); elemental analysis calcd (%) for $C_{29}H_{30}N_6O_6S$ (590.66): C 58.97, H 5.12, N 14.23; found C 58.77, H 5.16, N 14.04.

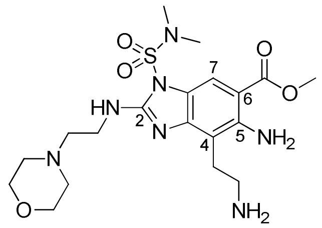
Methyl 5-Amino-4-(2-aminoethyl)-1-(*N*,*N*-dimethylsulfamoyl)-2-[(thien-2-ylmethyl)amino]-1*H*-benzimidazole-6-carboxylate (14a):



According to **GP 7**, starting from **13a** (386 mg, 0.66 mmol) and hydrazine monohydrate (0.32 mL, 6.66 mmol) in MeOH/THF 95:5 (14 mL). Workup with 1 M aq. NaOH solution (54 mL) and CH_2Cl_2 (3x 50 mL) yielded crude **14a** (300 mg, 99%) as a yellow solid.

R_f = 0.14 (SiO_2; CH_2Cl_2/MeOH/25% aq. NH_3 94:5:1, UV 254 nm); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (s, 6 H; NMe_2), 3.04–3.10 (m; 4 H; C$H_2$$CH_2$–C(4)), 3.88 (s, 3 H; OMe), 4.92 (d, J = 5.5 Hz, 2 H; CH_2NH–C(2)), 6.64 (t, J = 5.8 Hz, 1 H; NH), 6.98 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(4')), 7.09 (br. d, J = 3.5 Hz, 1 H; H–C(3')), 7.24 (dd, J = 5.1, 1.2 Hz, 1 H; H–C(5')), 8.01 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.51 (*C*H_2–C(4)), 38.76 (2 C; NMe_2), 41.06 (*C*$H_2$$CH_2$–C(4)), 41.88 ($CH_2$NH), 51.54 (OMe), 104.85 (C(6)), 112.33 (C(4)), 112.59 (C(7)), 123.11 (C(7a)), 125.41 (C(5')), 126.37 and 126.76 (2 C; C(3',4')), 140.61 (C(2')), 146.97 (C(3a)), 147.57 (C(5)), 154.06 (C(2)), 169.11 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3398 (w), 3348 (w), 2925 (w), 1682 (m), 1582 (s), 1502 (w), 1455 (m), 1425 (m), 1388 (m), 1366 (m), 1334 (w), 1273 (m), 1245 (m), 1201 (s), 1153 (s), 1100 (m), 1036 (m), 965 (m), 901 (m), 859 (w), 839 (m), 791 (m), 761 (w), 743 (m), 721 (s), 646 (w), 615 cm^{-1} (m); HR-ESI-MS: *m*/*z* (%): 454.1408 (23), 453.1382 (100, [M + H]$^+$, calcd for $C_{18}H_{25}N_6O_4S_2^+$: 453.1373).

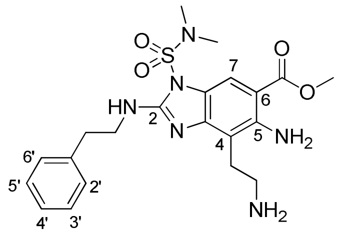
Methyl 5-Amino-4-(2-aminoethyl)-1-(*N*,*N*-dimethylsulfamoyl)-2-{[(2-morpholin-4-yl)ethyl]amino}-1*H*-benzimidazole-6-carboxylate (14b):



According to **GP 7**, starting from **13b** (150 mg, 0.25 mmol) and hydrazine monohydrate (122 µL, 2.50 mmol) in MeOH/THF 95:5 (14 mL). Workup with 1 M aq. NaOH solution (54 mL) and CH_2Cl_2 (3x 50 mL) yielded **14b** (109 mg, 93%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$; assignments based on a DQF-COSY spectrum): δ = 2.51 (br. t, J = 4.4 Hz, 4 H; $N(CH_2)_2$), 2.63 (t, J = 6.0 Hz, 2 H; CH_2CH_2NH), 2.92 (s, 6 H; NMe_2), 2.97–3.07 (m, 4 H; CH_2CH_2–C(4)), 3.62 (q, J = 5.6 Hz, 2 H; CH_2NH), 3.72 (br. t, J = 4.4 Hz, 4 H; $O(CH_2)_2$), 3.85 (s, 3 H; OMe), 6.88 (t, J = 4.6 Hz, 1 H; NH), 7.97 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$; assignments based on a DEPT and a HSQC spectrum): δ = 29.39 (CH_2–C(4)), 38.79 (2 C; NMe_2), 39.43 (CH_2NH), 40.98 (CH_2CH_2–C(4)), 51.51 (OMe), 53.30 (2 C; $N(CH_2)_2$), 56.60 (CH_2CH_2NH), 67.04 (2 C; $O(CH_2)_2$), 104.49 (C(6)), 112.14 (2 C; C(4,7)), 123.16 (C(7a)), 147.32 (C(3a)), 147.55 (C(5)), 154.64 (C(2)), 169.17 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3419 (w), 3366 (w), 2950 (w), 2855 (w), 1683 (w), 1585 (s), 1456 (w), 1431 (m), 1392 (w), 1349 (w), 1274 (m), 1207 (m), 1156 (m), 1115 (m), 1051 (w), 966 (w), 906 (s), 794 (w), 725 (s), 647 cm^{-1} (m); HR-ESI-MS: m/z (%): 471.2210 (29), 470.2183 (100, $[M+H]^+$, calcd for $C_{19}H_{32}N_7O_5S^+$: 470.2180).

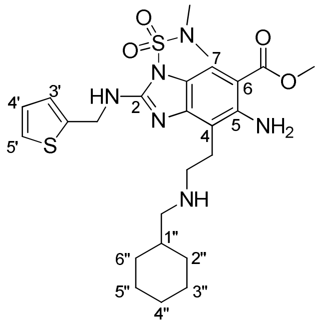
Methyl 5-Amino-4-(2-aminoethyl)-1-(*N*,*N*-dimethylsulfamoyl)-2-[(2-phenyl-ethyl)amino]-1*H*-benzimidazole-6-carboxylate (14c):



According to **GP 7**, starting from **13c** (714 mg, 1.21 mmol) and hydrazine monohydrate (0.59 mL, 12.2 mmol) in MeOH/THF 95:5 (30 mL). Workup with 1 M aq. NaOH solution (100 mL) and CH_2Cl_2 (3x 100 mL) yielded **14c** (452 mg, 81%) as a pale yellow solid.

R_f = 0.16 (SiO_2; CH_2Cl_2/MeOH/25% aq. NH_3 94:5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72 (s, 6 H; NMe_2), 2.96–3.01 (m, 6 H; CH_2CH_2–C(4), CH_2–C(1')), 3.80 (td, *J* = 6.8, 5.5 Hz, 2 H; C*H*$_2$NH), 3.82 (s, 3 H; OMe), 6.28 (t, *J* = 5.5 Hz, 1 H; NH), 7.17–7.32 (m, 5 H; C_6H_5), 7.93 ppm (s, 1 H; H–C(7)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.45 (*C*H$_2$–C(4)), 35.23 (*C*H$_2$–C(1')), 38.62 (2 C; NMe_2), 41.05 (*C*H$_2$CH$_2$–C(4)), 44.24 (CH_2NH), 51.50 (OMe), 104.42 (C(6)), 112.08 (2 C; C(4,7)), 122.97 (C(7a)), 126.62 (C(4')), 128.66 (2 C; C(2',6')), 128.77 (2 C; C(3',5')), 138.65 (C(1')), 147.27 (C(3a)), 147.58 (C(5)), 154.40 (C(2)), 169.12 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3408 (w), 2947 (w), 1682 (w), 1574 (s), 1426 (m), 1362 (w), 1270 (m), 1201 (s), 1150 (s), 1046 (w), 961 (m), 792 (w), 742 (w), 700 cm^{-1} (m); HR-MALDI-MS: *m/z* (%): 501.2270 (100), 461.1961 (83, $[M+H]^+$, calcd for $C_{21}H_{29}N_6O_4S^+$: 461.1966), 393.2145 (53), 353.1842 (75).

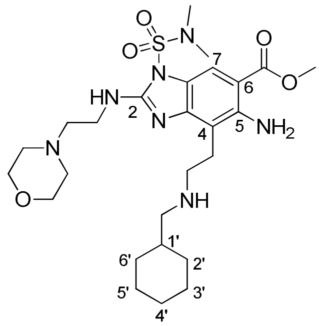
Methyl 5-Amino-4-{2-[(cyclohexylmethyl)amino]ethyl}-1-(*N*,*N*-dimethylsulfamoyl)-2-[(thien-2-ylmethyl)amino]-1*H*-benzimidazole-6-carboxylate (15a):



According to **GP 8**, starting from **14a** (300 mg, 0.66 mmol) and cyclohexanecarb-aldehyde (83 µL, 0.66 mmol) in anhydrous CH_2Cl_2 (9.0 mL) over 4 Å molecular sieves (ca. 400 mg), then with $NaBH(OAc)_3$ (562 mg, 2.64 mmol). Workup with aq. 2 M NH_3 solution (30 mL) and EtOAc (3x 30 mL), FC (SiO_2; CH_2Cl_2/MeOH 98:2 to 93:7), and lyophilization from *t*BuOH yielded **15a** (190 mg, 52%) as a yellow oil.

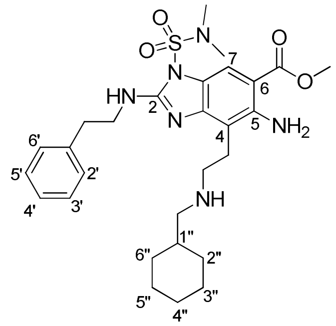
R_f = 0.38 (SiO_2; CH_2Cl_2/MeOH/25% aq. NH_3 95:4:1, UV 254 nm); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (qd, J = 12.1, 2.6 Hz, 2 H; H_{ax}–C(2",6")), 1.14–1.28 (m, 3 H; H_{ax}–C(3",4",5")), 1.52–1.54 (m, 1 H; H–C(1")), 1.62–1.80 (m, 5 H; H_{eq}–C(2"–6")), 2.57 (d, J = 6.7 Hz; CH_2–C(1")), 2.88 (s, 6 H; NMe_2), 3.00 (t, J = 6.6 Hz, 2 H; CH_2–C(4)), 3.15 (t, J = 6.7 Hz, 2 H; CH_2CH_2–C(4)), 3.87 (s, 3 H; OMe), 4.93 (d, J = 5.5 Hz, 2 H; CH_2NH–C(2)), 6.63 (t, J = 5.8 Hz, 1 H; NH–C(2)), 6.98 (dd, J = 5.1, 3.5 Hz, 1 H; H–C(4')), 7.09 (br. d, J = 3.5 Hz, 1 H; H–C(3')), 7.24 (dd, J = 5.1, 1.2 Hz, 1 H; H–C(5')), 7.99 ppm (s, 1 H; H–C(7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.59 (CH_2–C(4)), 25.95 (2 C; C(3",5")), 26.54 (C(4"), 31.35 (2 C; C(2",6")), 37.47 (C(1")), 38.77 (2 C; NMe_2), 41.91 (CH_2NH–C(2)), 48.69 (CH_2CH_2–C(4)), 51.50 (OMe), 56.22 (CH_2–C(1")), 104.75 (C(6)), 112.42 (2 C; C(4,7)), 122.91 (C(7a)), 125.42 (C(5')), 126.42 and 126.79 (2 C; C(3',4')), 140.52 (C(2')), 146.60 (C(3a)), 148.01 (C(5)), 154.02 (C(2)), 169.06 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3406 (w), 2922 (w), 2850 (w), 1685 (w), 1574 (s), 1504 (w), 1426 (m), 1392 (m), 1371 (m), 1272 (m), 1202 (s), 1153 (s), 1100 (m), 1034 (w), 964 (m), 892 (w), 852 (w), 793 (m), 734 (s), 702 (s), 618 cm^{-1} (m); HR-ESI-MS: *m*/*z* (%): 550.2350 (30), 549.2322 (100, $[M + H]^+$, calcd for $C_{25}H_{37}N_6O_4S_2^+$: 549.2312).

Methyl 5-Amino-4-{2-[(cyclohexylmethyl)amino]ethyl}-1-(*N*,*N*-dimethyl-sulfamoyl)-2-{[2-(morpholin-4-yl)ethyl]amino}-1*H*-benzimidazole-6-carboxy-late (15b):



According to **GP 8**, starting from **14b** (105 mg, 0.22 mmol) and cyclohexanecarb-aldehyde (28 µL, 0.22 mmol) in anhydrous CH_2Cl_2 (3.0 mL) over 4 Å molecular sieves (ca. 200 mg), then with $NaBH(OAc)_3$ (190 mg, 0.89 mmol). Workup with aq. 2 M NH_3 solution (10 mL) and EtOAc (3x 10 mL), MPLC (SiO_2; CH_2Cl_2/MeOH/Et_3N 100:0:0 to 80:19.4:0.6 within 60 min), and lyophilization from *t*BuOH yielded crude **15b** (58 mg, ca. 46%; purity: ca. 85%) as a yellow oil.
R_f = 0.40 (SiO_2; CH_2Cl_2/MeOH/Et_3N 90:9.9:0.1, UV 254 nm); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (qd, J = 12.0, 2.8 Hz, 2 H; H_{ax}–C(2',6')), 1.08–1.30 (m, 3 H; H_{ax}–C(3',4',5')), 1.36–1.54 (m, 1 H; H–C(1')), 1.60–1.72 (m, 5 H; H_{eq}–C(2'–6')), 2.46–2.50 (m, 2 H; CH_2–C(1')), 2.50 (br. t, J = 4.2 Hz, 4 H; $N(CH_2)_2$), 2.63 (t, J = 6.0 Hz, 2 H; C$H_2$$CH_2$NH–C(2)), 2.86–2.93 (m, 2 H; CH_2–C(4)), 2.90 (s, 6 H; NMe_2), 3.02 (t, J = 6.4 Hz, 2 H; C$H_2$$CH_2$–C(4)), 3.62 (q, J = 5.6 Hz, 2 H; CH_2NH–C(2)), 3.71 (br. t, J = 4.6 Hz, 4 H; $O(CH_2)_2$), 3.84 (s, 3 H; OMe), 6.89 (t, J = 4.8 Hz, 1 H; NH–C(2)), 7.95 ppm (s, 1 H; H–C(7)); IR (ATR): $\tilde{\nu}$ = 3410 (w), 3362 (w), 2921 (w), 2850 (w), 1684 (w), 1585 (s), 1476 (w), 1455 (w), 1429 (m), 1379 (w), 1348 (w), 1274 (m), 1203 (m), 1157 (m), 1117 (m), 1055 (w), 964 (w), 912 (w), 793 (w), 717 cm^{-1} (m); HR-ESI-MS: *m*/*z* (%): 567.3143 (28), 566.3115 (100, [*M* + H]+, calcd for $C_{26}H_{44}N_7O_5S^+$: 566.3119).

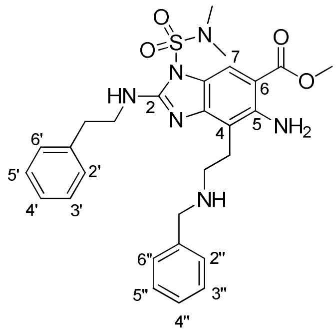
Methyl 5-Amino-4-{2-[(cyclohexylmethyl)amino]ethyl}-1-(*N*,*N*-dimethyl-sulfamoyl)-2-[(2-phenylethyl)amino]-1*H*-benzimidazole-6-carboxylate (15c):



According to **GP 8**, starting from **14c** (314 mg, 0.68 mmol) and cyclohexanecarb-aldehyde (84 µL,0.68 mmol) in anhydrous CH_2Cl_2 (9.0 mL) over 4 Å molecular sieves (ca. 300 mg), then with $NaBH(OAc)_3$ (576 mg, 2.70 mmol). Workup with aq. 2 M NH_3 solution (30 mL) and EtOAc (3x 30 mL), FC (SiO_2; CH_2Cl_2/MeOH 98:2 to 95:5), and lyophilization from *t*BuOH yielded **15c** (273 mg, 72%) as a yellow oil.

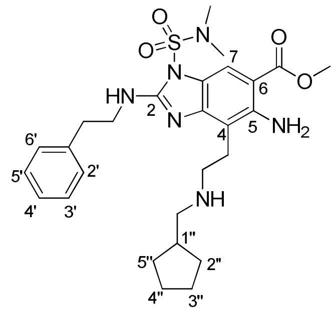
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (qd, J = 15.9, 3.8 Hz, 2 H; H_{ax}–C(2'',6'')), 1.10–1.30 (m, 3 H; H_{ax}–C(3'',4'',5'')), 1.36–1.51 (m, 1 H; H–C(1'')), 1.62–1.77 (m, 5 H; H_{eq}–C(2''–6'')), 2.49 (d, J = 6.7 Hz, 2 H; CH_2–C(1'')), 2.74 (s, 6 H; NMe_2), 2.90 (t, J = 6.4 Hz, 2 H; CH_2–C(4)), 2.98–3.07 (m, 4 H; CH_2CH$_2$–C(4), CH_2–C(1')), 3.82 (td, J = 6.8, 5.5 Hz, 2 H; CH_2NH–C(2)), 3.84 (s, 3 H; OMe), 6.20–6.50 (br. s, 2 H; NH_2), 6.27 (t, J = 5.5 Hz, 1 H; NH), 7.20–7.34 (m, 5 H; C_6H_5), 7.93 ppm (s, 1 H; H–C(7)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.32 (CH$_2$–C(4)), 26.52 (2 C; C(3'',5'')), 26.90 (C(4')), 31.70 (2 C; C(2'',6'')), 35.47 (C(1'')), 38.33 (CH$_2$–C(1')), 38.83 (2 C; NMe_2), 44.46 (CH$_2$NH–C(2)), 49.33 (CH$_2$CH$_2$–C(4)), 51.63 (OMe), 57.04 (CH$_2$–C(1'')), 104.42 (C(6)), 112.03 (C(4)), 113.42 (C(4)), 122.86 (C(7)), 126.66 (C(4')), 128.69 (2 C; C(2',6')), 128.80 (2 C; C(3',5')), 138.65 (C(1')), 146.92 (C(3a)), 148.06 (C(5)), 154.30 (C(2)), 169.11 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3406 (w), 2922 (w), 1685 (w), 1576 (s), 1427 (m), 1365 (w), 1273 (m), 1204 (s), 1153 (s), 1104 (w), 964 (m), 793 (w), 715 cm^{-1} (s); HR-MALDI-MS: m/z (%): 558.2931 (31), 557.2902 (100, $[M+H]^+$, calcd for $C_{28}H_{41}N_6O_4S^+$: 557.2904), 449.2782 (52), 324.1574 (45).

Methyl 5-Amino-4-[2-(benzylamino)ethyl]-1-(*N*,*N*-dimethylsulfamoyl)-2-[(2-phenylethyl)amino]-1*H*-benzimidazole-6-carboxylate (16a):



According to **GP 8**, starting from **14c** (68 mg, 0.15 mmol), benzaldehyde (16 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (1.0 mL) over 4 Å molecular sieves (ca. 100 mg), then with and $NaBH(OAc)_3$ (90 mg, 0.43 mmol). Workup with 2 M aq. NH_3 solution (10 mL) and EtOAc (3x 10 mL), FC (SiO_2; CH_2Cl_2/MeOH/Et_3N 97:2:1), and lyophilization from *t*BuOH yielded **16a** (48 mg, 59%) as a white solid R_f = 0.20 (SiO_2; CH_2Cl_2/MeOH/Et_3N 97:2:1, UV 254 nm); m.p. 107–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.75 (s, 6 H; NMe_2), 2.97–3.02 (m, 4 H; CH_2–C(4) and CH_2–C(1')), 3.10 (br. t, $J \approx$ 6.0 Hz, 2 H; $CH_2$$CH_2$–C(4)), 3.79 (td, J = 6.9, 5.6 Hz, 2 H; CH_2NH–C(2)), 3.76–3.82 (m, 2 H; CH_2–C(1")), 3.85 (s, 3 H; OMe), 6.28 (t, J = 5.6 Hz, 1 H; NH–C(2)), 7.21–7.35 (m, 10 H; 2x C_6H_5), 7.95 ppm (s, 1 H; H–C(7)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.09 (CH$_2$–C(4)), 35.18 (CH$_2$–C(1')), 38.57 (2 C; NMe_2), 44.19 (CH$_2$NH–C(2)), 48.21 (CH$_2$CH$_2$–C(4)), 51.42 (OMe), 53.90 (CH$_2$–C(1")), 104.37 (C(6)), 112.02 (C(7)), 112.90 (C(4)), 122.85 (C(7a)), 126.57 and 126.84 (2 C; C(4',4")), 127.99, 128.32, 128.62, and 128.72 (8 C; C(2',3',5',6',2",3",5",6")), 138.59 and 140.28 (2 C; C(1',1")), 146.97 (C(3a)), 147.81 (C(5)), 154.29 (C(2)), 169.09 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3443 (w), 3406 (w), 3338 (w), 3028 (w), 2951 (w), 1681 (w), 1583 (s), 1423 (m), 1373 (m), 1264 (m), 1205 (s), 1155 (s), 1072 (m), 959 (m), 793 (w), 738 (s), 696 cm^{-1} (s); HR-MALDI-MS: m/z (%): 552.2461 (34), 551.2432 (100, $[M + H]^+$, calcd for $C_{28}H_{35}N_6O_5S^+$: 551.2435), 444.2377 (100), 324.1574 (56).

Methyl 5-Amino-4-{2-[(cyclopentylmethyl)amino]ethyl}-1-(*N*,*N*-dimethyl-sulfamoyl)-2-[(2-phenylethyl)amino]-1*H*-benzimidazole-6-carboxylate (16b):



According to **GP 8**, starting from **14c** (62 mg, 0.14 mmol), cyclopentanecarb-aldehyde (13 mg, 0.13 mmol) in anhydrous CH_2Cl_2 (1.0 mL) over 4 Å molecular sieves (ca. 100 mg), then with and $NaBH(OAc)_3$ (110 mg, 0.52 mmol). Workup with 2 M aq. NH_3 solution (10 mL) and EtOAc (3x 10 mL), FC (SiO_2; CH_2Cl_2/MeOH/Et_3N 97:2:1), and lyophilization from *t*BuOH yielded **16b** (29 mg, 40%) as a colorless oil.

R_f = 0.17 (SiO_2; CH_2Cl_2/MeOH/Et_3N 97:2:1, UV 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08–1.19 (m, 2 H; H_a–C(2",5")), 1.46–1.62 (m, 4 H; H_2C(3",4")), 1.69–1.80 (m, 2 H; H_b–C(2",5")), 1.99 (sept., J = 7.3 Hz, 1 H; H–C(1")), 2.59 (d, J = 7.3 Hz, 2 H; CH_2–C(1")), 2.74 (s, 6 H; NMe_2), 2.92 (t, J = 6.2 Hz, 2 H; CH_2–C(4)), 2.98–3.07 (m, 4 H; C$H_2$$CH_2$–C(4) and CH_2–C(1')), 3.81 (td, J = 6.9, 5.5 Hz, 2 H; CH_2NH–C(2)), 3.84 (s, 3 H; OMe), 6.27 (t, J = 5.5 Hz, 1 H; NH–C(2)), 6.30–6.55 (br. s, 2 H; NH_2), 7.19–7.34 (m, 5 H; C_6H_5), 7.93 ppm (s, 1 H; H–C(7)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.38 (2 C; C(3",4")), 26.38 (CH$_2$–C(4)), 30.95 (2 C; C(2",5")), 35.29 (C(1")), 38.66 (2 C; NMe_2), 40.23 (CH$_2$–C(1')), 44.29 (CH$_2$NH–C(2)), 49.14 (CH$_2$CH$_2$–C(4)), 51.45 (OMe), 55.80 (CH$_2$–C(1")), 104.25 (C(6)), 111.86 (C(7)), 113.27 (C(4)), 122.69 (C(7a)), 126.48 (C(4')), 128.51 and 128.63 (4 C; C(2',3',5',6')), 138.49 (C(1')), 146.76 (C(3a)), 147.91 (C(5)), 154.12 (C(2)), 168.94 ppm (C=O); IR (ATR): $\tilde{\nu}$ = 3405 (w), 2947 (w), 2864 (w), 1684 (w), 1574 (s), 1426 (m), 1365 (w), 1272 (m), 1203 (s), 1151 (s), 1107 (w), 962 (m), 792 (w), 714 cm^{-1} (m); HR-MALDI-MS: m/z (%): 544.2781 (34), 543.2746 (100, $[M+H]^+$, calcd for $C_{27}H_{39}N_6O_4S^+$: 543.2754), 435.2627 (78), 324.1583 (75).

12 References

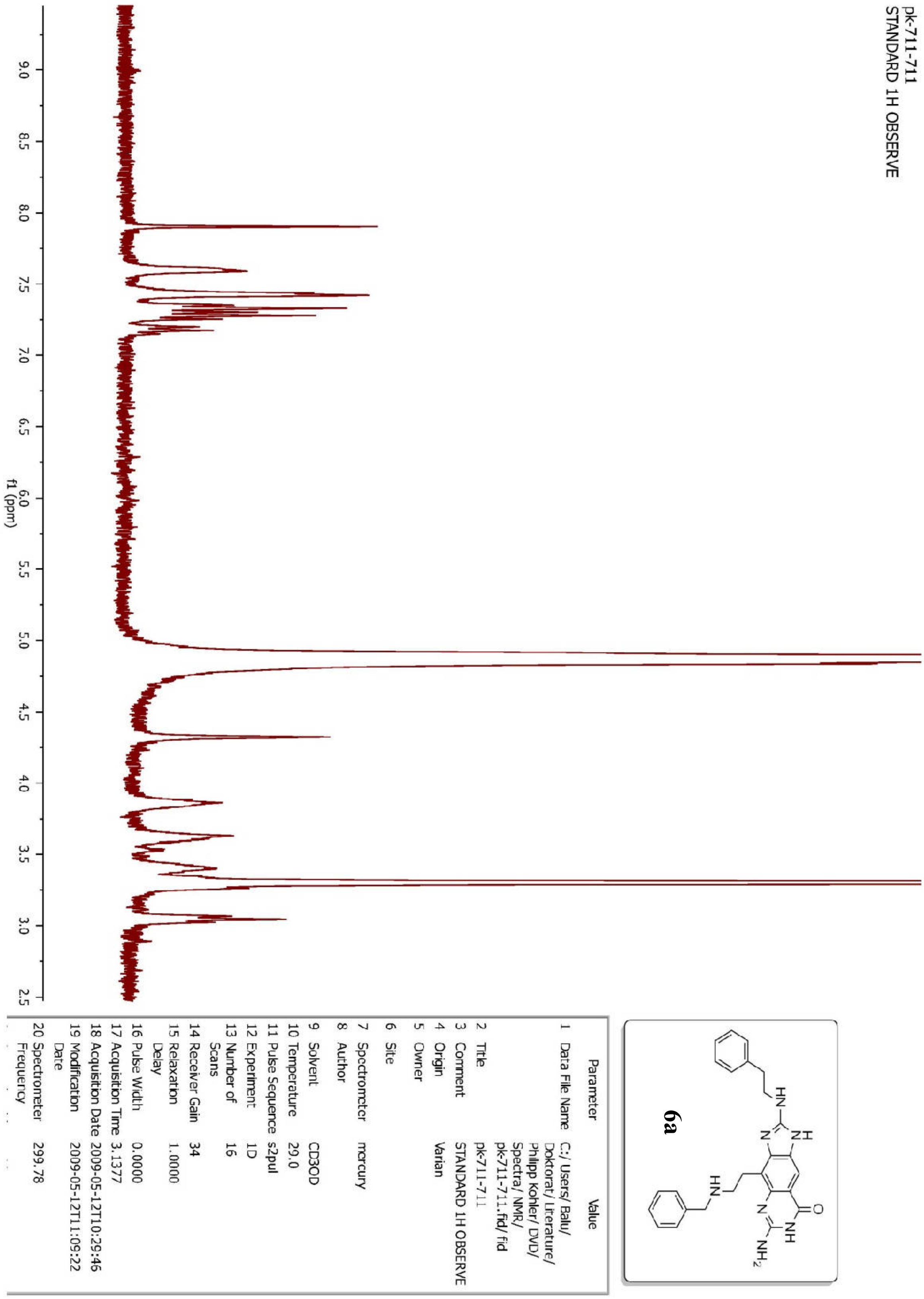
[1] T. Ritschel, P. C. Kohler, A. Heine, F. Diederich, G. Klebe, *ChemMedChem* **2009**, *4*, 2012–2023. How to Replace the Residual Solvation Shell of Polar Active Site Residues to Achieve Nanomolar Inhibition of tRNA-Guanine Transglycosylase.

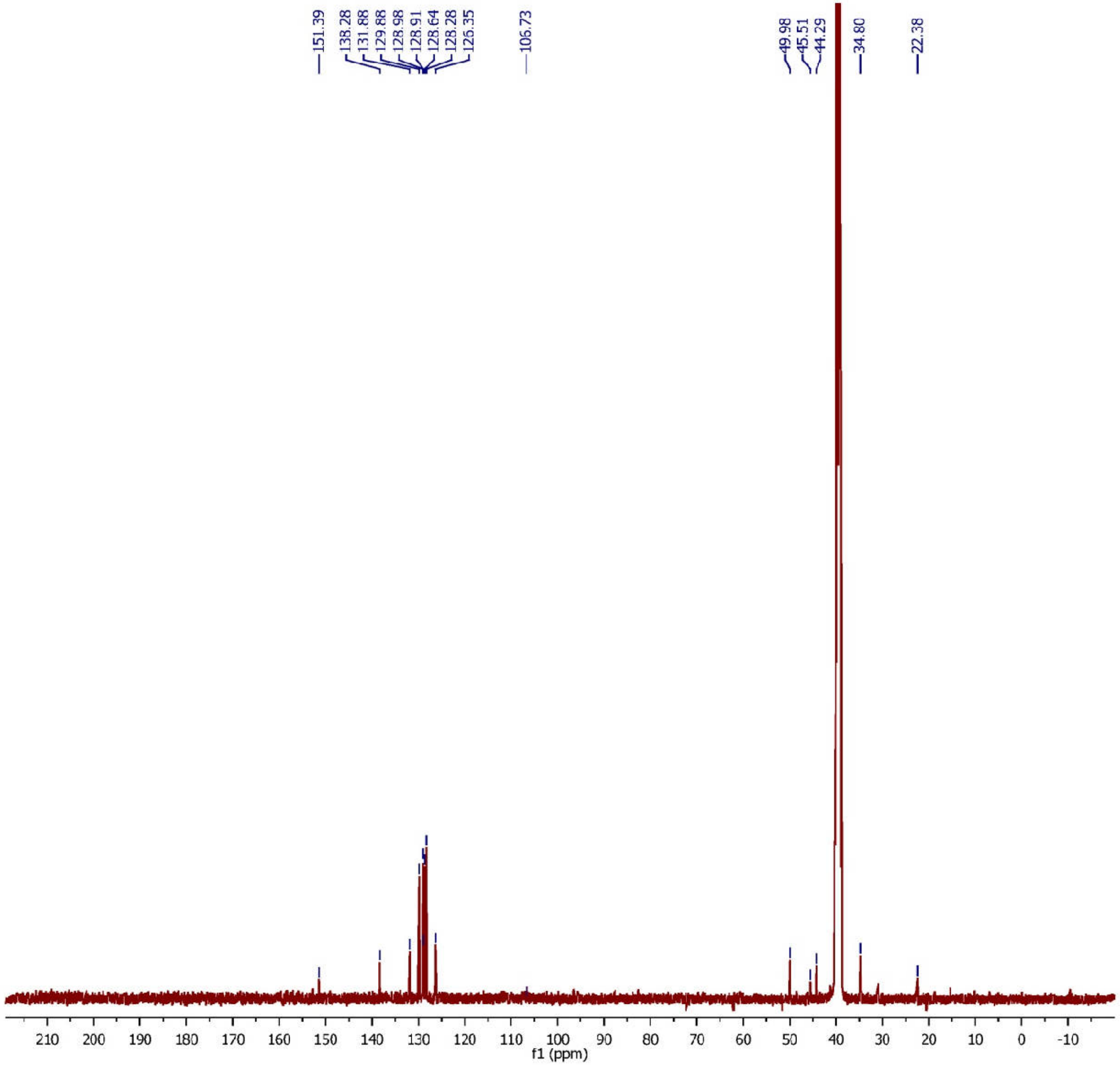
[2] L. J. Barandun, F. Immekus, P. C. Kohler, S. Tonazzi, B. Wagner, S. Wendelspiess, T. Ritschel, A. Heine, M. Kansy, G. Klebe, F. Diederich, *Chem. Eur. J.* **2012**, *18*, 9246–9257. From *lin*-Benzoguanines to *lin*-Benzoyhpoxanthines as Ligands for *Z. mobilis* TGT: Replacement of Protein-Ligand Hydrogen Bonding by Import of Water Clusters.

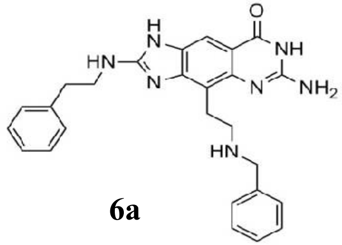
[3] S. R. Hörtner, T. Ritschel, B. Stengl, C. Kramer, W. B. Schweizer, B. Wagner, M. Kansy, G. Klebe, F. Diederich, *Angew. Chem. Int. Ed.* **2007**, *46*, 8266–8269; *Angew. Chem.* **2007**, *119*, 8414–8417. Potent Inhibitors of tRNA-Guanine Transglycosylase, an Enzyme Linked to the Pathogenicity of the *Shigella* Bacterium: Charge-Assisted Hydrogen Bonding.

[4] P. C. Kohler, T. Ritschel, W. B. Schweizer, G. Klebe, F. Diederich, *Chem. Eur. J.* **2009**, *15*, 10809–10817. High-Affinity Inhibitors of tRNA-Guanine Transgycosylase Replacing the Function of Structural Water Cluster.

13 NMR Spectra







6a

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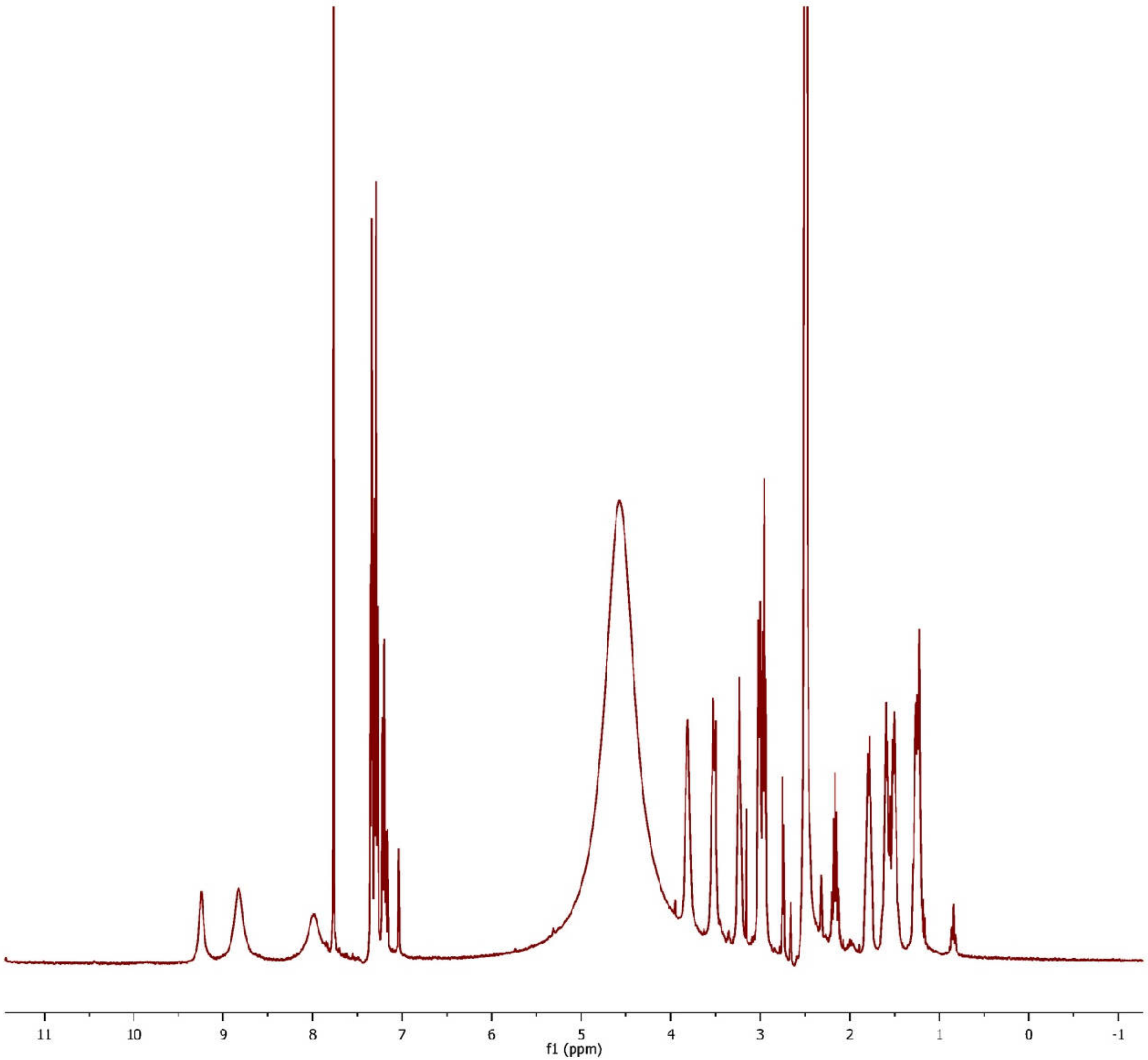
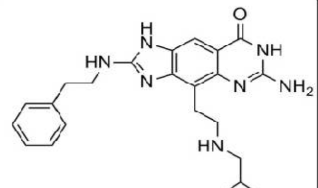
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	DMSO
7	Temperature	303.8
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	8192
11	Receiver Gain	7298
12	Relaxation Delay	2.0000
13	Pulse Width	7.8000
14	Acquisition Time	1.3632
15	Acquisition Date	2009-05-18T19:08:00
16	Spectrometer Frequency	100.61
17	Spectral Width	24038.5
18	Lowest Frequency	-2008.7
19	Nucleus	13C
20	Acquired Size	32768





6b

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3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	DMSO
7	Temperature	301.9
8	Pulse Sequence	zg30
9	Experiment	1D
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11	Receiver Gain	144
12	Relaxation Delay	1.0000
13	Pulse Width	10.9000
14	Acquisition Time	3.9716
15	Acquisition Date	2009-04-26T12:16:00
16	Spectrometer Frequency	400.13
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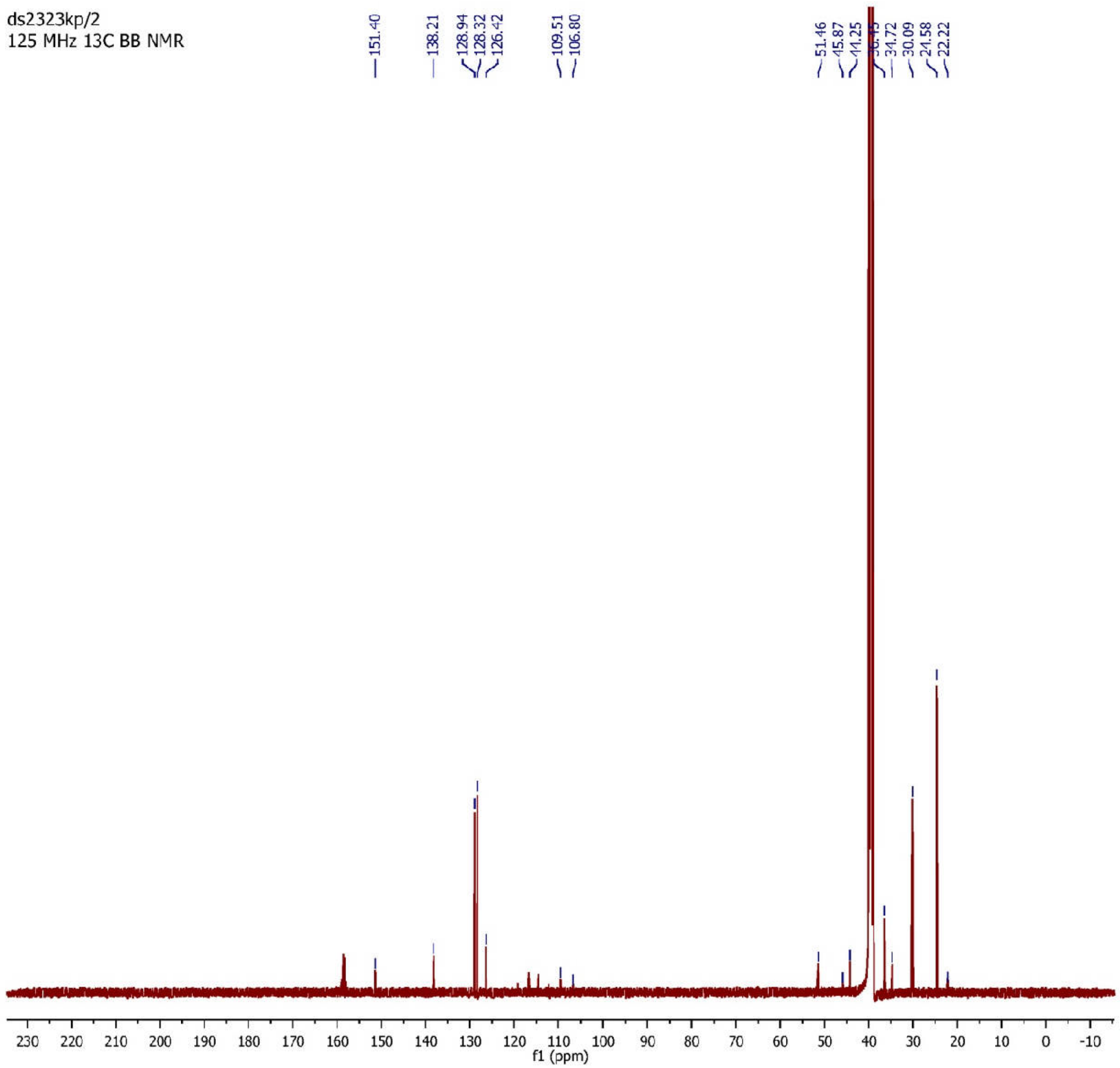
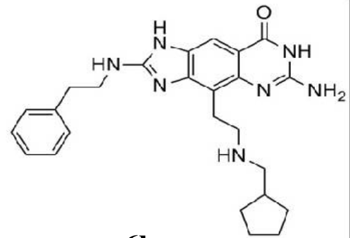
19	Nucleus	1H
20	Acquired Size	32768
21	Spectral Size	65536





6b

	Parameter	Value
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4	Owner	root
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	300.0
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9	Experiment	1D
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11	Receiver Gain	11585
12	Relaxation Delay	2.0000
13	Pulse Width	9.7000
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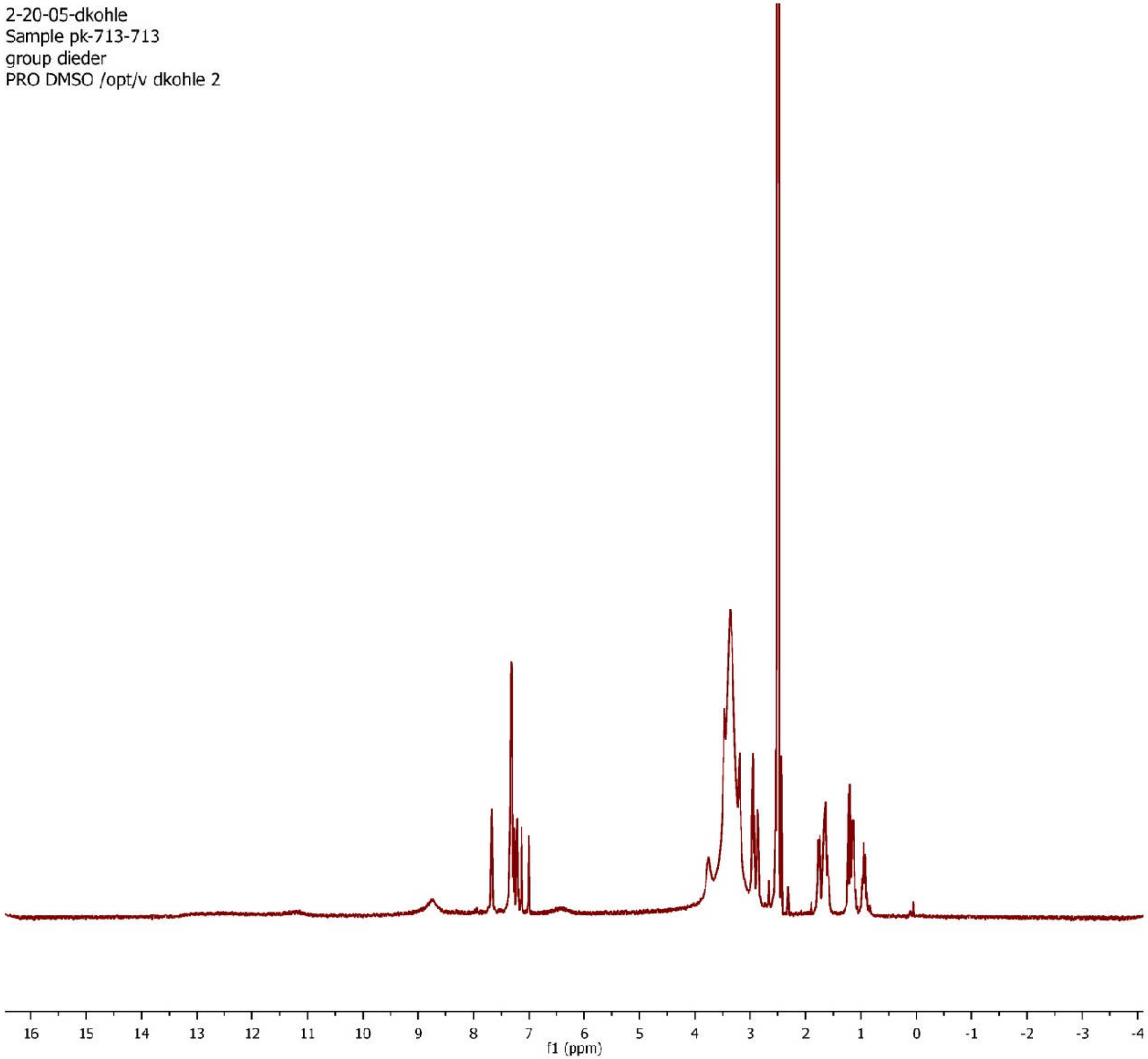

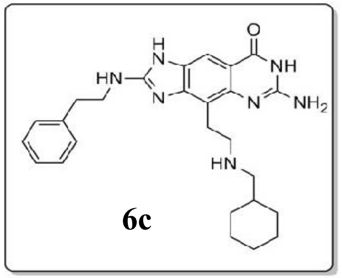

6c

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4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	DMSO
7	Temperature	300.0
8	Pulse Sequence	zg30
9	Experiment	1D
10	Number of Scans	64
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12	Relaxation Delay	1.0000
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16	Spectrometer Frequency	400.13
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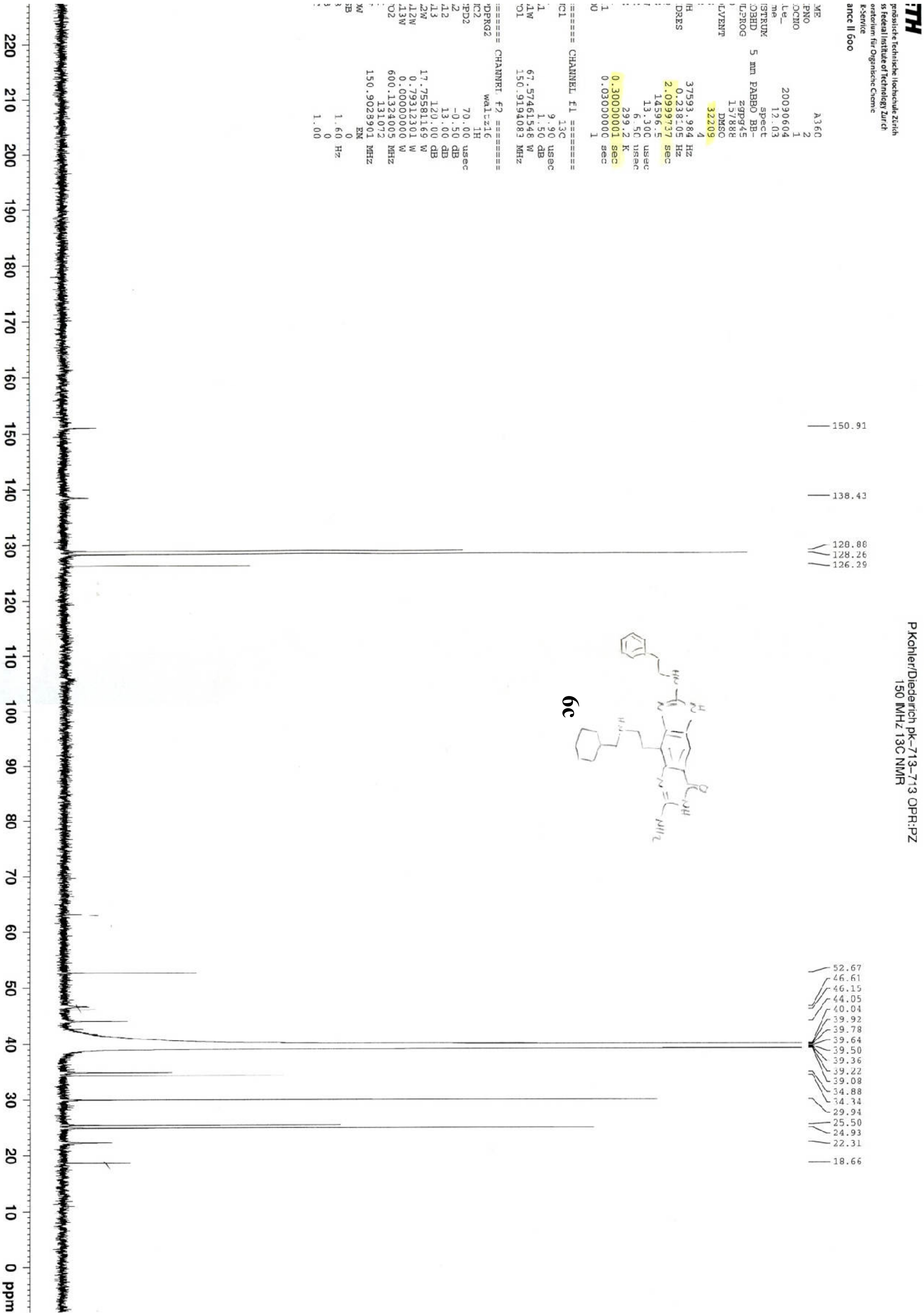
P.Kohler/Diederich pk-713-713 OPR:PZ
150 MHz 13C NMR
6c
150.91
138.43
128.88
128.26
126.29
52.67
46.61
46.15
44.05
40.04
39.92
39.78
39.64
39.50
39.36
39.22
39.08
34.88
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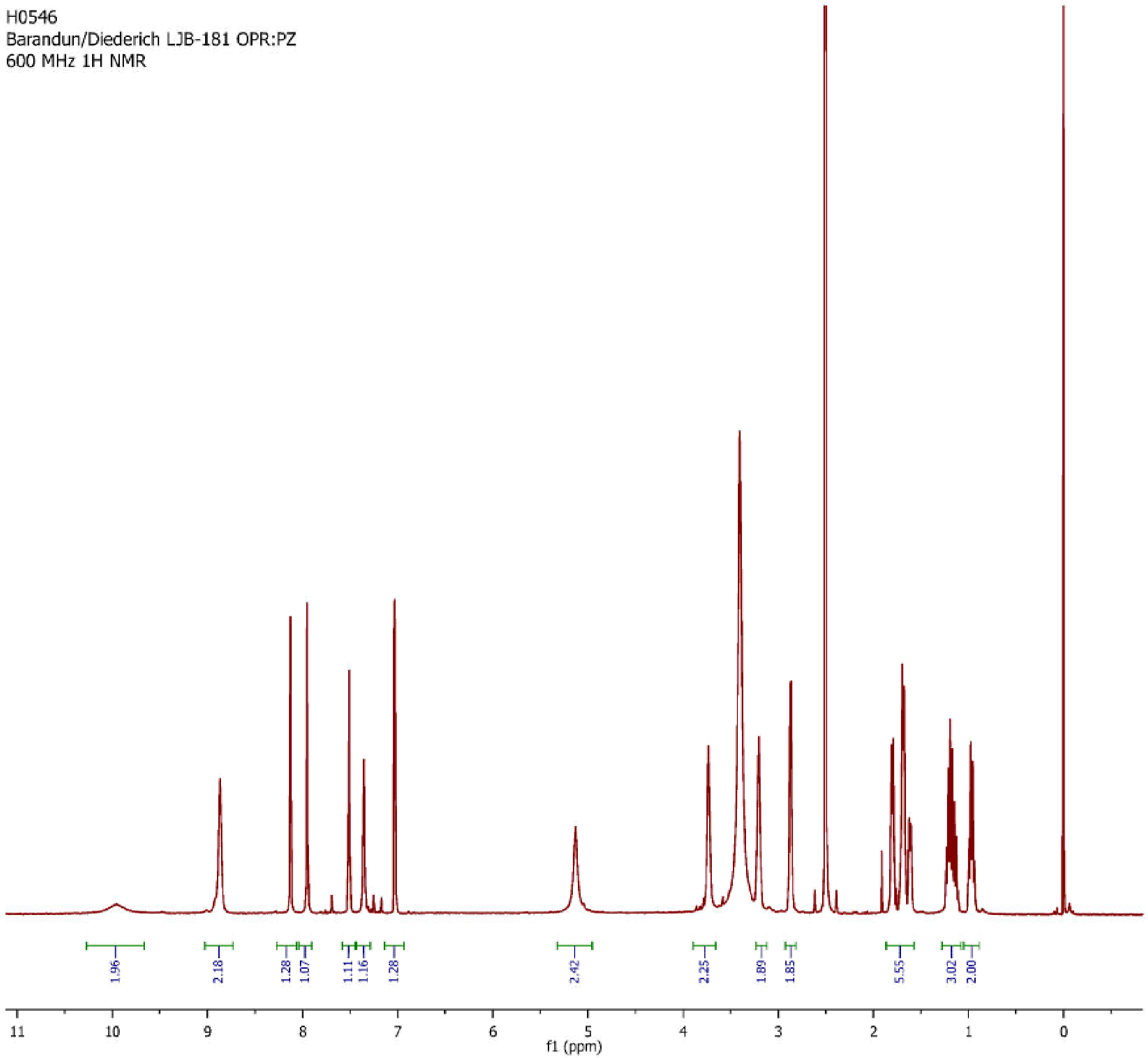
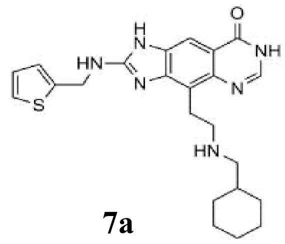
25.50
24.93
22.31
18.66
ppm





7a

Parameter		Value
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12	Relaxation Delay	0.0100
13	Pulse Width	9.6000
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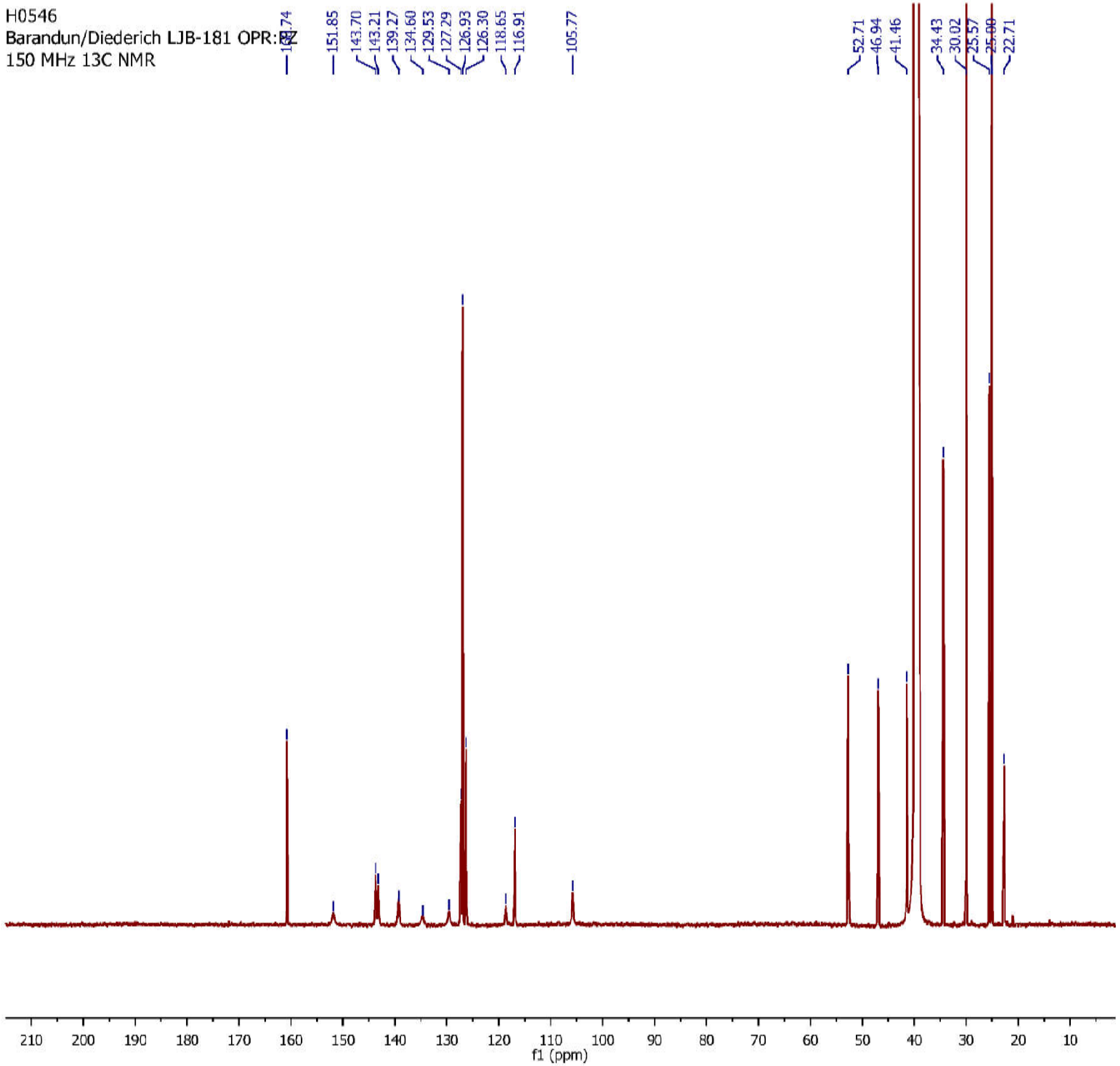

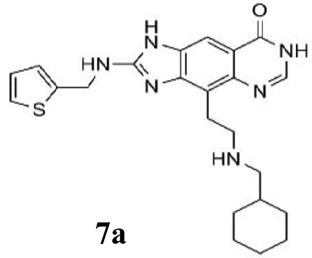

7a

	Parameter	Value
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4	Owner	sv
5	Spectrometer	spect
6	Solvent	DMSO
7	Temperature	298.3
8	Pulse Sequence	zgpg45
9	Experiment	1D
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11	Receiver Gain	128
12	Relaxation Delay	3.0000
13	Pulse Width	9.7000
14	Acquisition Time	2.1052
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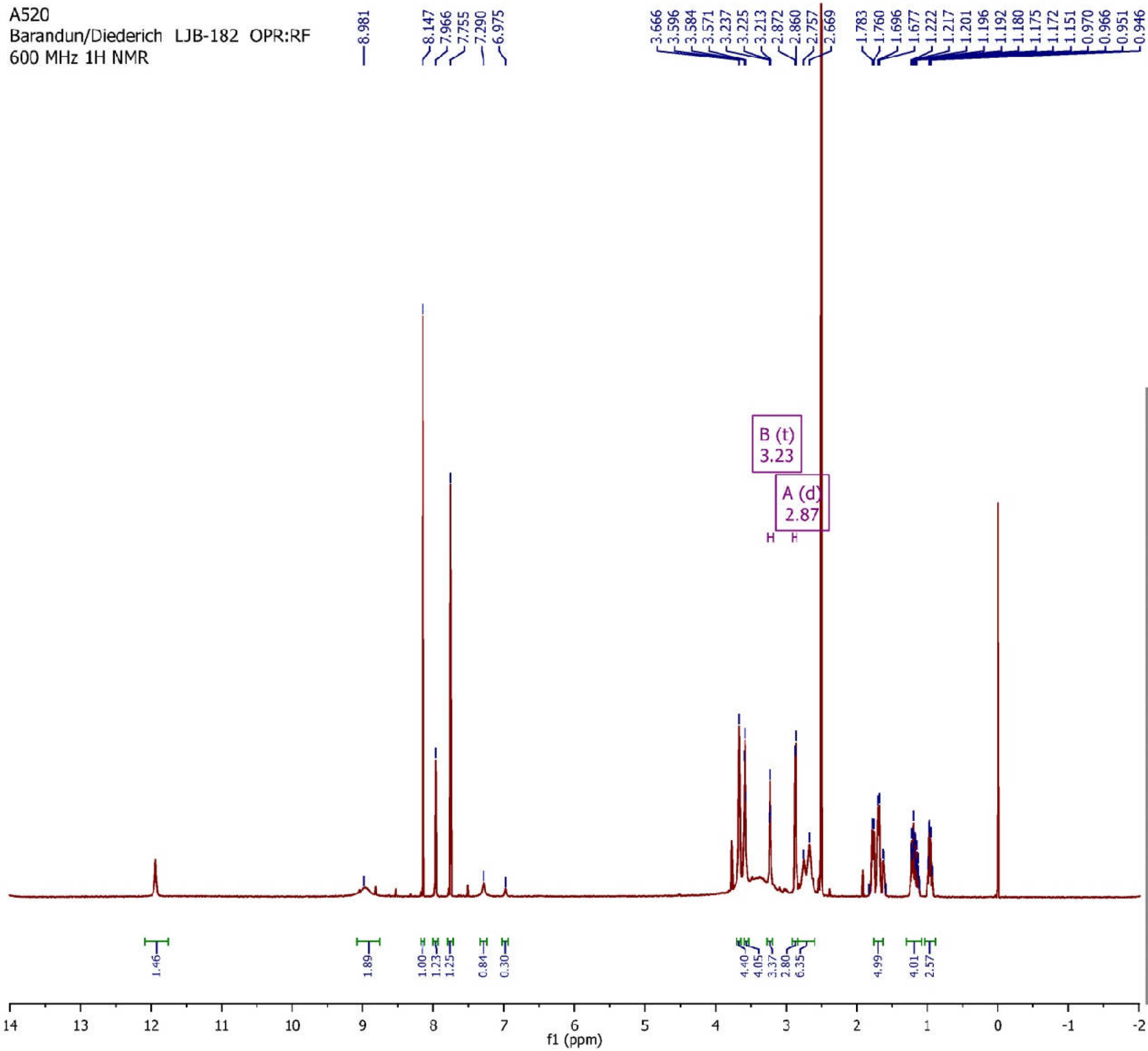
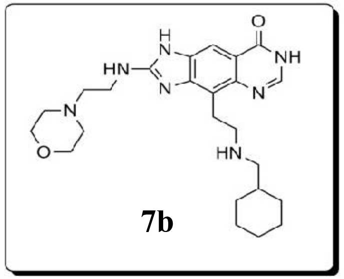
16	Modification Date	2010-10-15T11:25:50
17	Spectrometer Frequency	150.92
18	Nucleus	13C

^{13}C NMR (151 MHz, DMSO) δ 160.74, 151.85, 143.70, 143.21, 139.27, 134.60, 129.53, 127.29, 126.93, 126.30, 118.65, 116.91, 105.77, 52.71, 46.94, 41.46, 34.43, 30.02, 25.57, 25.00, 22.71.





7b

	Parameter	Value
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4	Owner	sv
5	Spectrometer	spect
6	Solvent	DMSO
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8	Pulse Sequence	zg30
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10	Number of Scans	64
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20	Nucleus	1H
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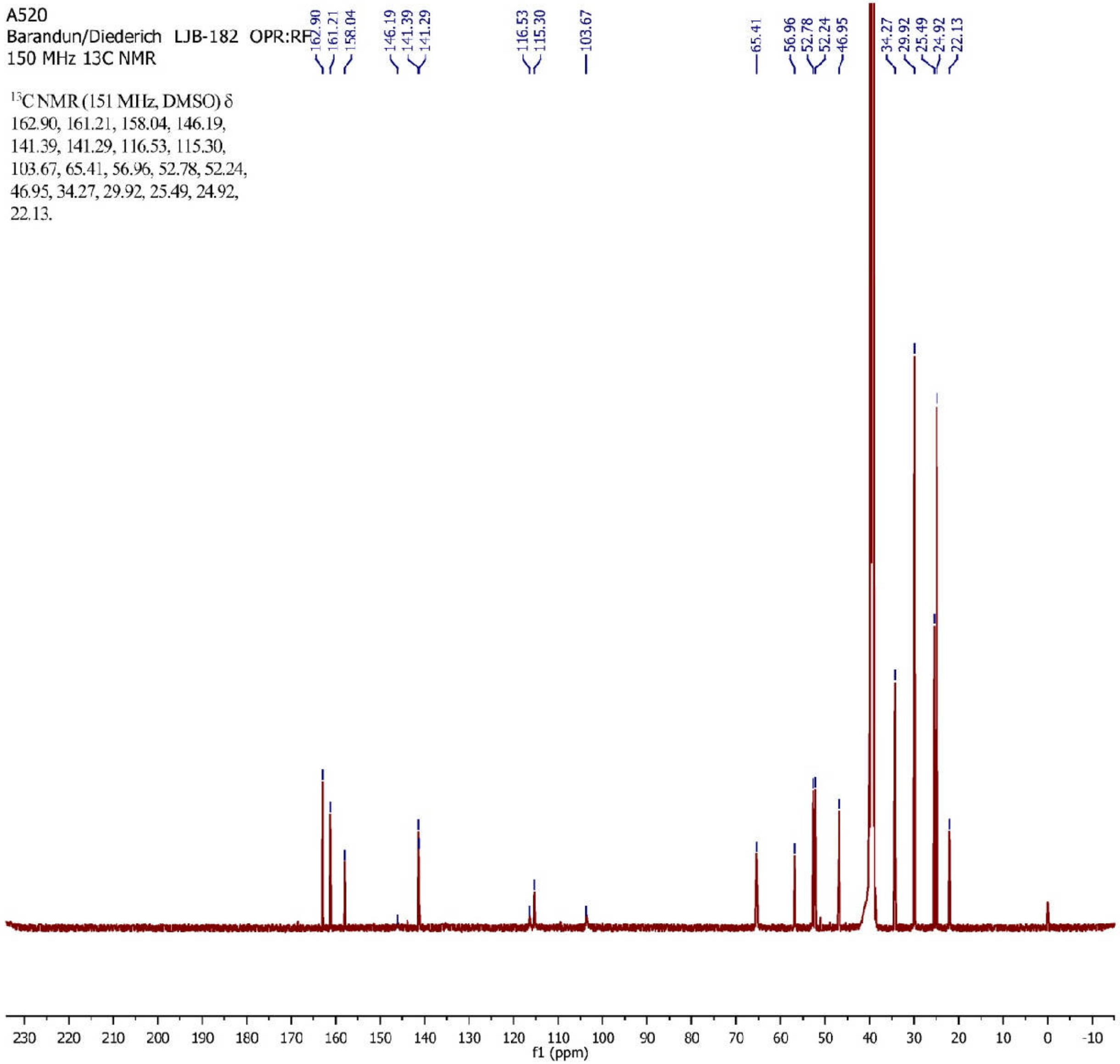
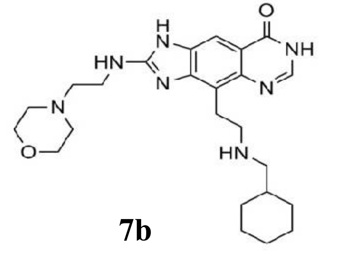
22	Spectral Size	131072

A520
Barandun/Diederich LJB-182 OPR:RF
150 MHz 13C NMR

^{13}C NMR (151 MHz, DMSO) δ 162.90, 161.21, 158.04, 146.19, 141.39, 141.29, 116.53, 115.30, 103.67, 65.41, 56.96, 52.78, 52.24, 46.95, 34.27, 29.92, 25.49, 24.92, 22.13.





7b

Parameter		Value
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4	Owner	sv
5	Spectrometer	spect
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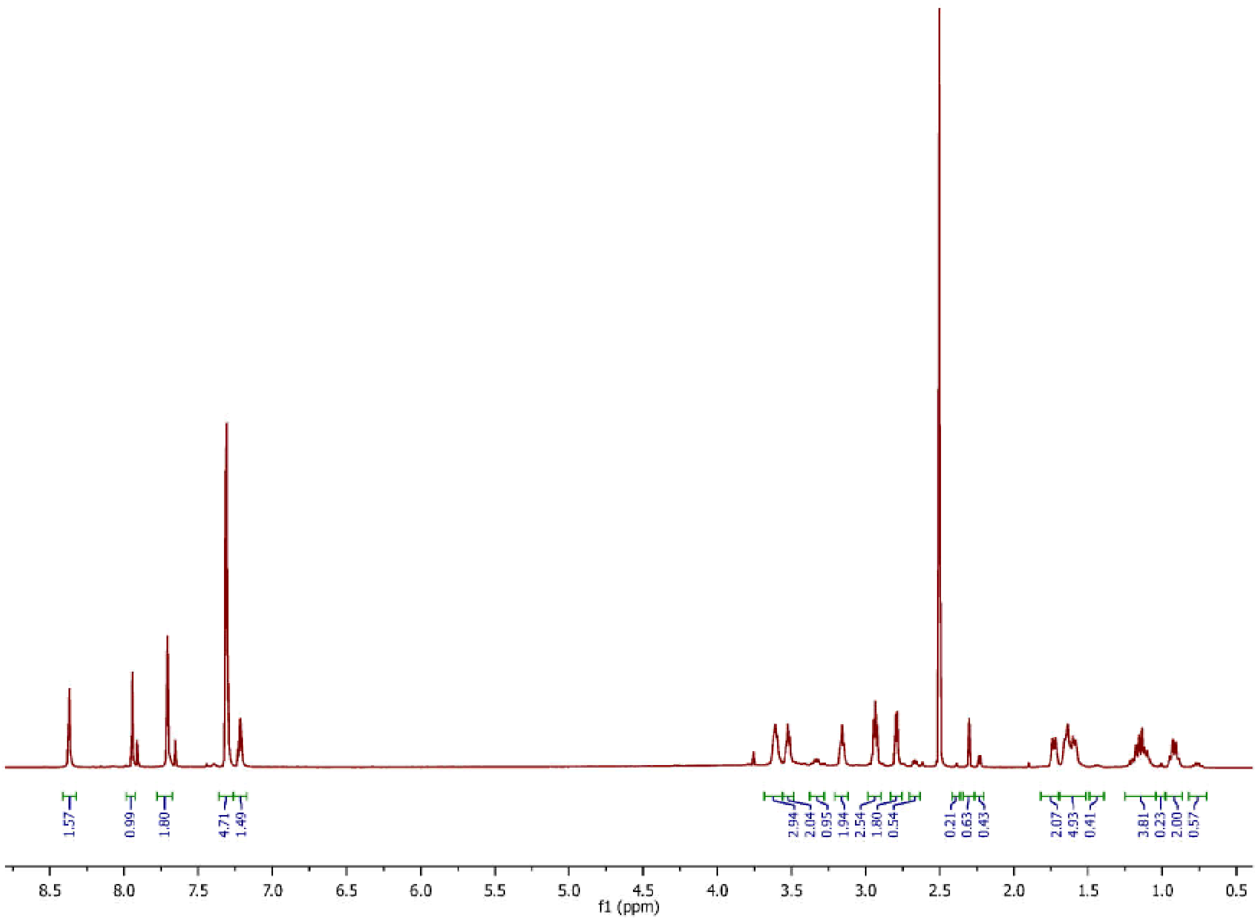
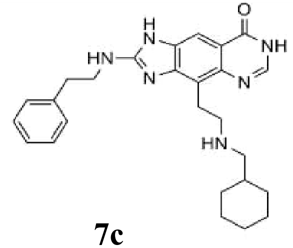
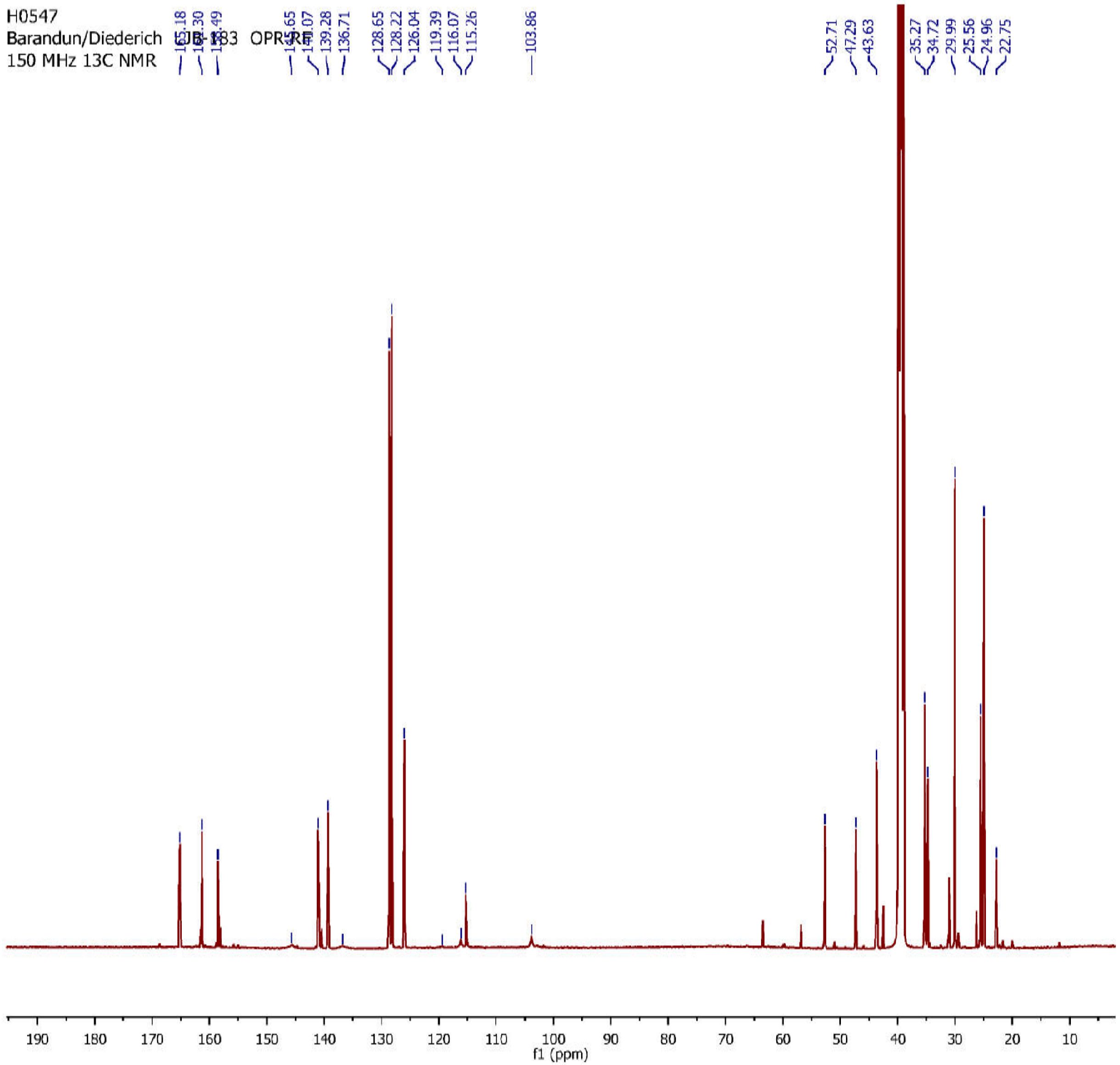
H0547
Barandun/Diederich LJB-183 OPR:RF
600 MHz 1H NMR

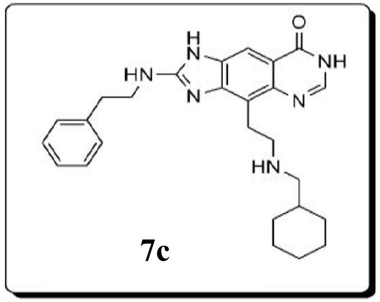




7c

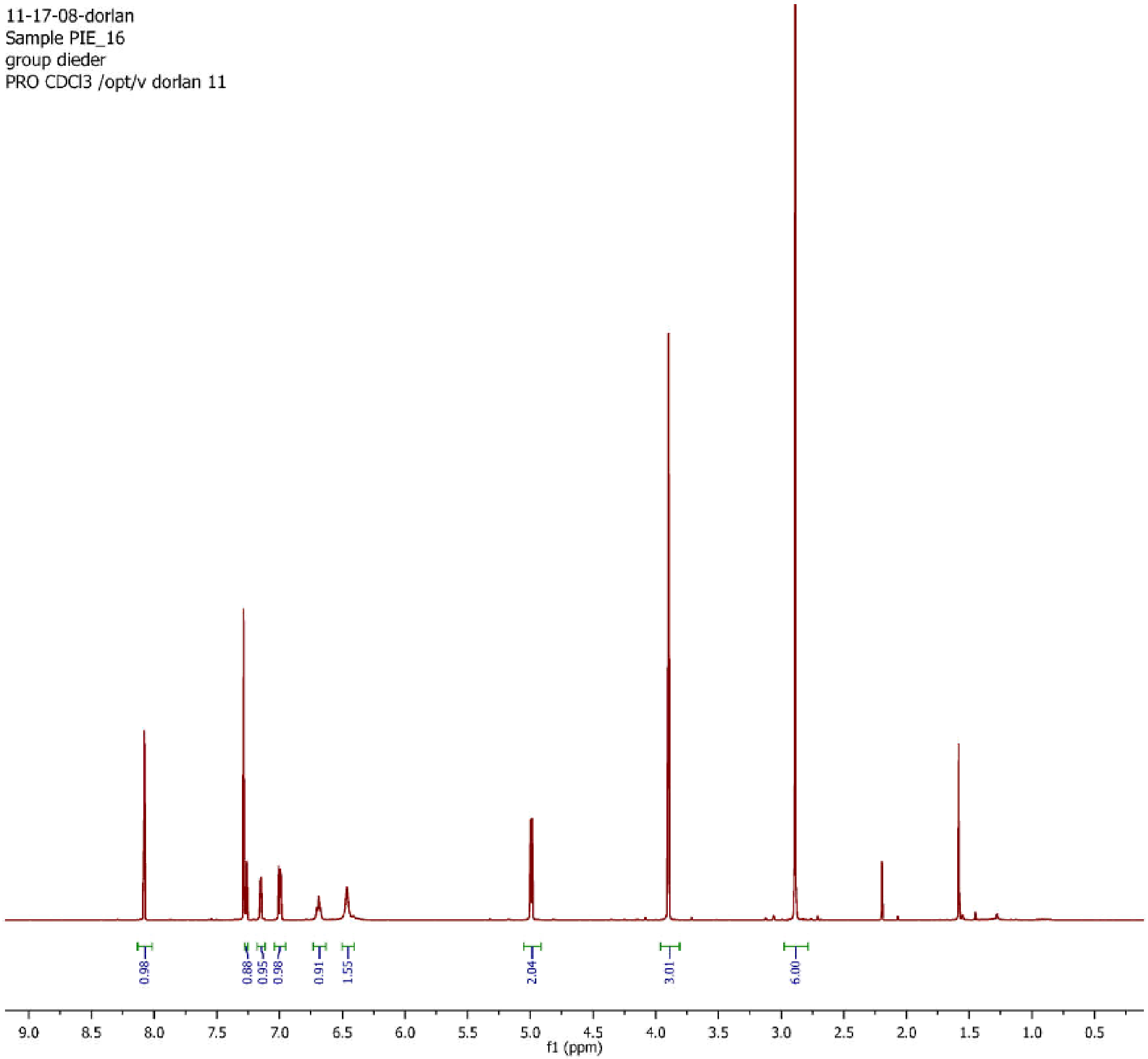
	Parameter	Value
1	Title	H0547
2	Comment	Barandun/ Diederich LJB-183 OPR:RF 600 MHz 1H NMR
3	Origin	Bruker BioSpin GmbH
4	Owner	sv
5	Spectrometer	spect
6	Solvent	DMSO
7	Temperature	298.3
8	Pulse Sequence	zg30
9	Experiment	1D
10	Number of Scans	64
11	Receiver Gain	23
12	Relaxation Delay	0.0100
13	Pulse Width	9.6000
14	Acquisition Time	5.0000
15	Acquisition Date	2010-10-11T10:31:00
16	Modification Date	2010-10-12T16:28:28
17	Spectrometer Frequency	600.18
18	Nucleus	1H

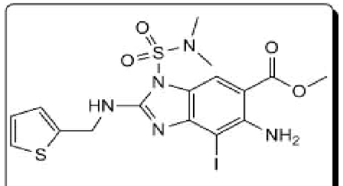




7c

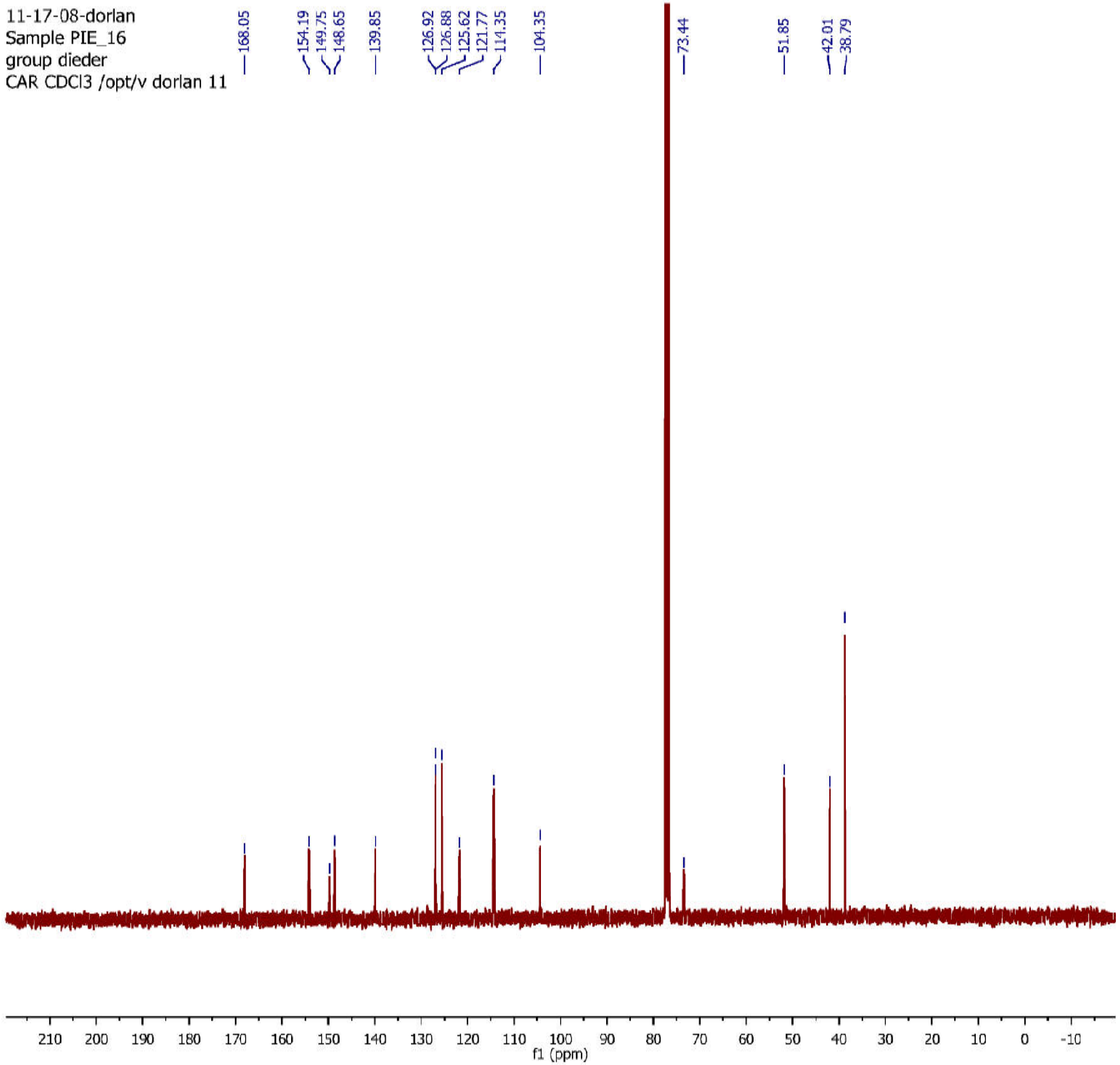
	Parameter	Value
1	Title	H0547
2	Comment	Barandun/ Diederich LJB-183 OPR:RF 150 MHz 13C NMR
3	Origin	Bruker BioSpin GmbH
4	Owner	sv
5	Spectrometer	spect
6	Solvent	DMSO
7	Temperature	298.3
8	Pulse Sequence	zgpg45
9	Experiment	1D
10	Number of Scans	15000
11	Receiver Gain	128
12	Relaxation Delay	0.3000
13	Pulse Width	9.7000
14	Acquisition Time	2.1052
15	Acquisition Date	2010-10-11T12:26:00
16	Modification Date	2010-10-12T16:28:31
17	Spectrometer Frequency	150.92
18	Nucleus	13C

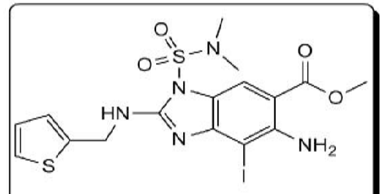




9a

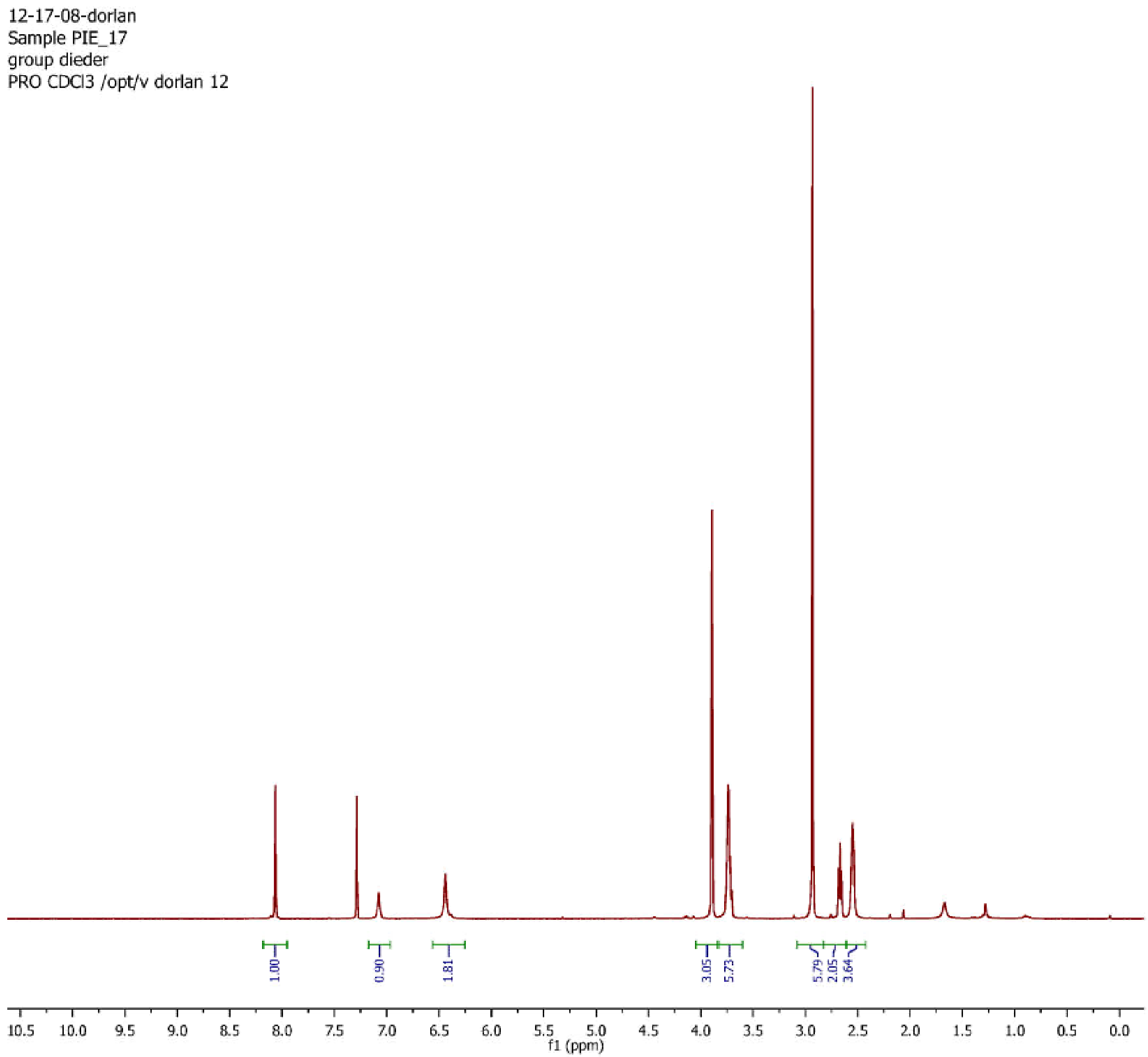
	Parameter	Value
1	Title	11-17-08-dorlan
2	Comment	Sample PIE_16 group dieder PRO CDCl3 / opt/ v dorlan 11
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	298.0
8	Pulse Sequence	zg30
9	Experiment	1D
10	Number of Scans	16
11	Receiver Gain	203
12	Relaxation Delay	1.0000
13	Pulse Width	12.1000
14	Acquisition Time	3.9846
15	Acquisition Date	2010-08-18T07:18:00
16	Modification Date	2010-08-18T09:40:54
17	Spectrometer Frequency	400.13
18	Nucleus	1H

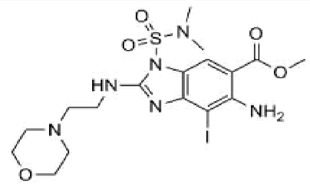




9a

	Parameter	Value
1	Title	11-17-08-dorlan
2	Comment	Sample PIE_16 group dieder CAR CDCl3 / opt/ v dorlan 11
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	298.0
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	1500
11	Receiver Gain	203
12	Relaxation Delay	2.0000
13	Pulse Width	9.1000
14	Acquisition Time	1.3632
15	Acquisition Date	2010-08-18T08:45:00
16	Modification Date	2010-08-18T09:40:56
17	Spectrometer Frequency	100.61
18	Nucleus	13C





9b

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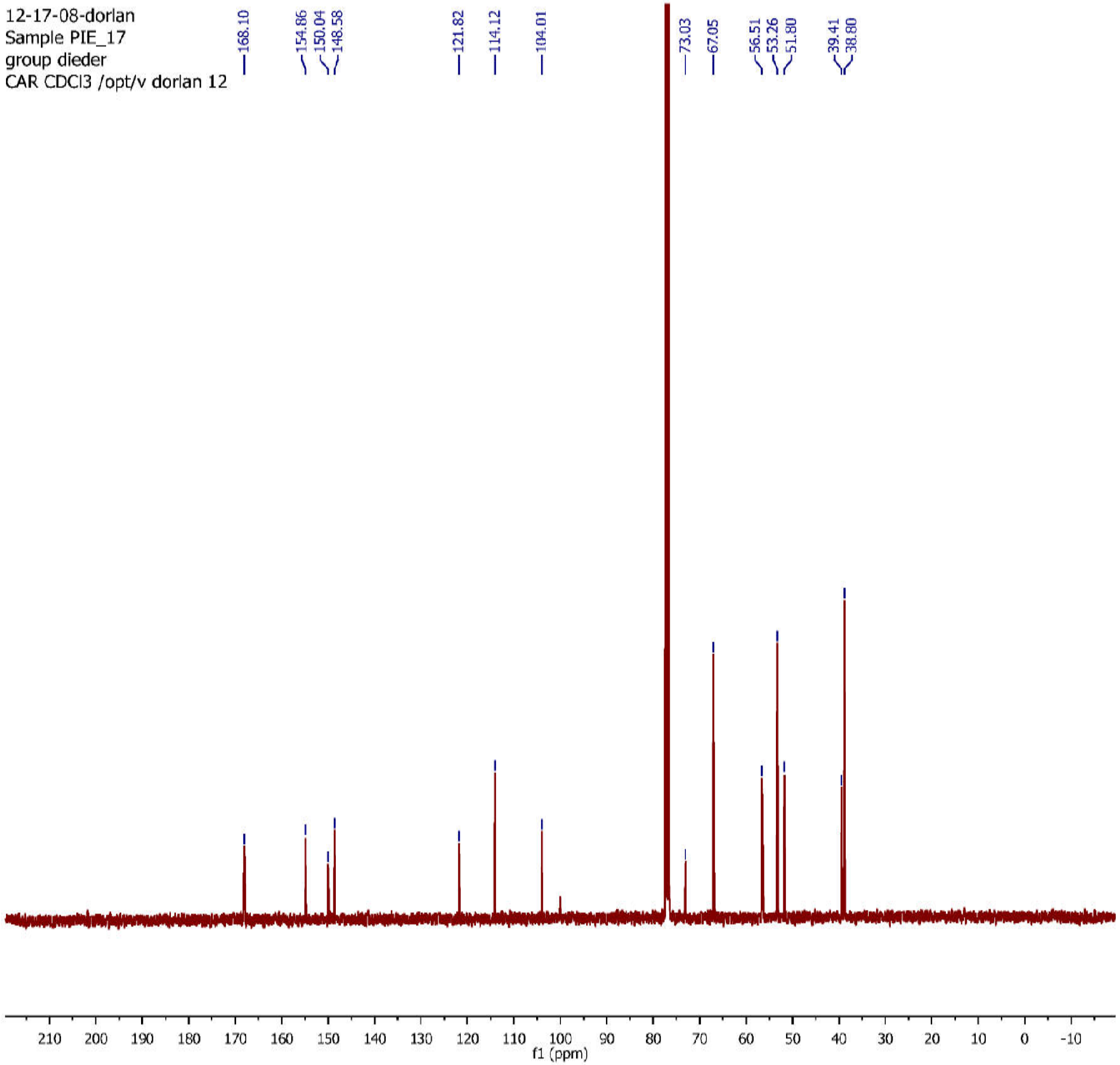
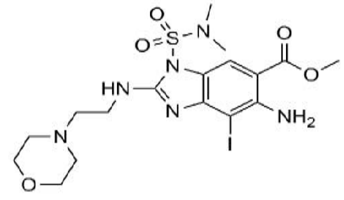
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 12-17-08-dorlan/ 10/ fid
2	Title	12-17-08-dorlan
3	Comment	Sample PIE_17 group dieder PRO CDCl3 / opt/ v dorlan 12
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-08-18T08:52:00
19	Modification	2010-08-18T09:41:04

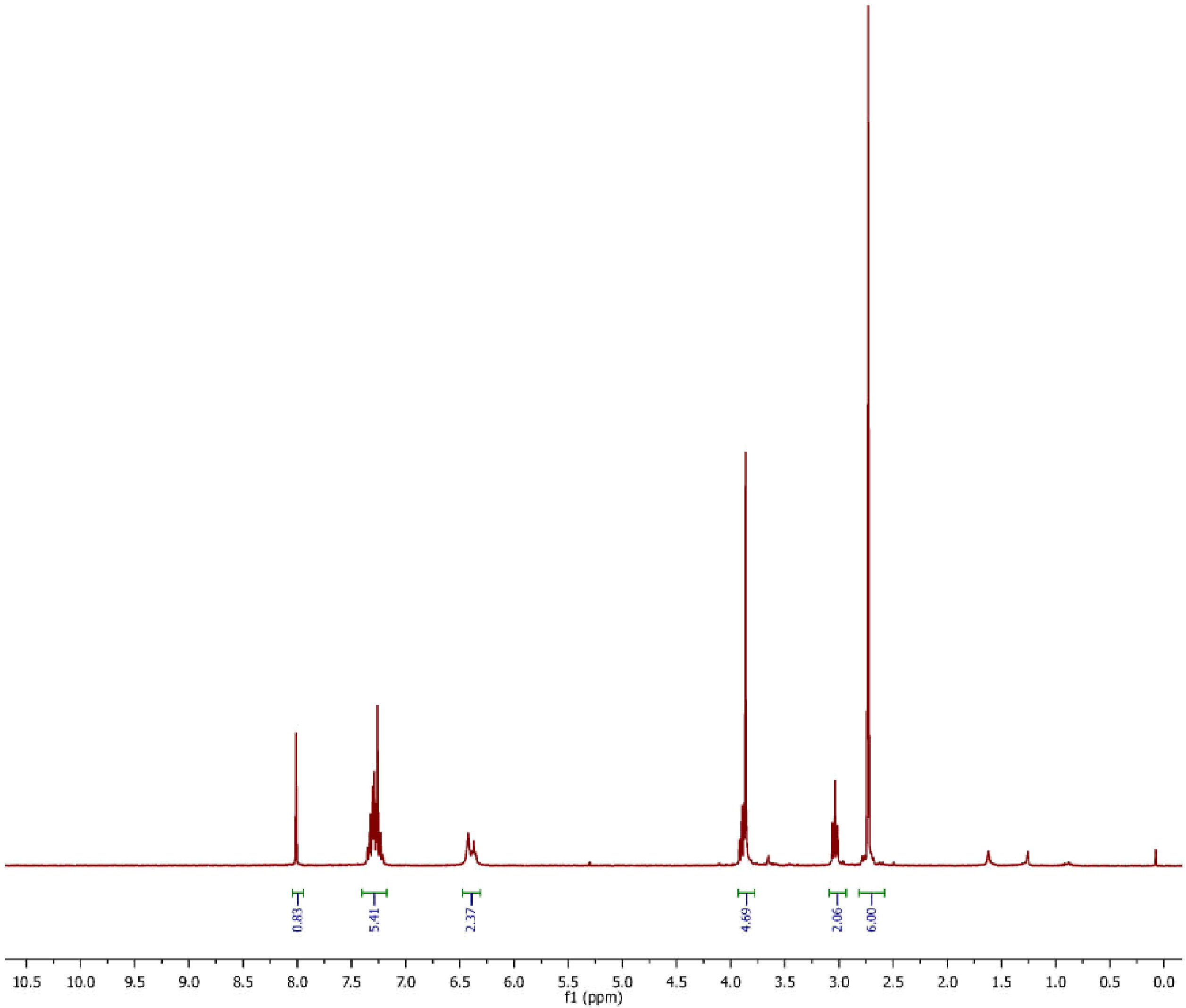


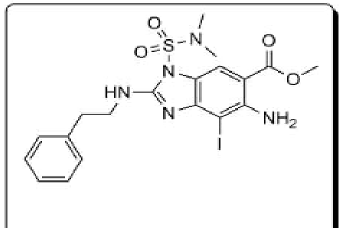


9b

	Parameter	Value
1	Title	12-17-08-dorlan
2	Comment	Sample PIE_17 group dieder CAR CDCl3 / opt/ v dorlan 12
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	298.0
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	1500
11	Receiver Gain	203
12	Relaxation Delay	2.0000
13	Pulse Width	9.1000
14	Acquisition Time	1.3632
15	Acquisition Date	2010-08-18T10:18:00
16	Modification Date	2010-08-18T09:41:08
17	Spectrometer Frequency	100.61
18	Nucleus	13C

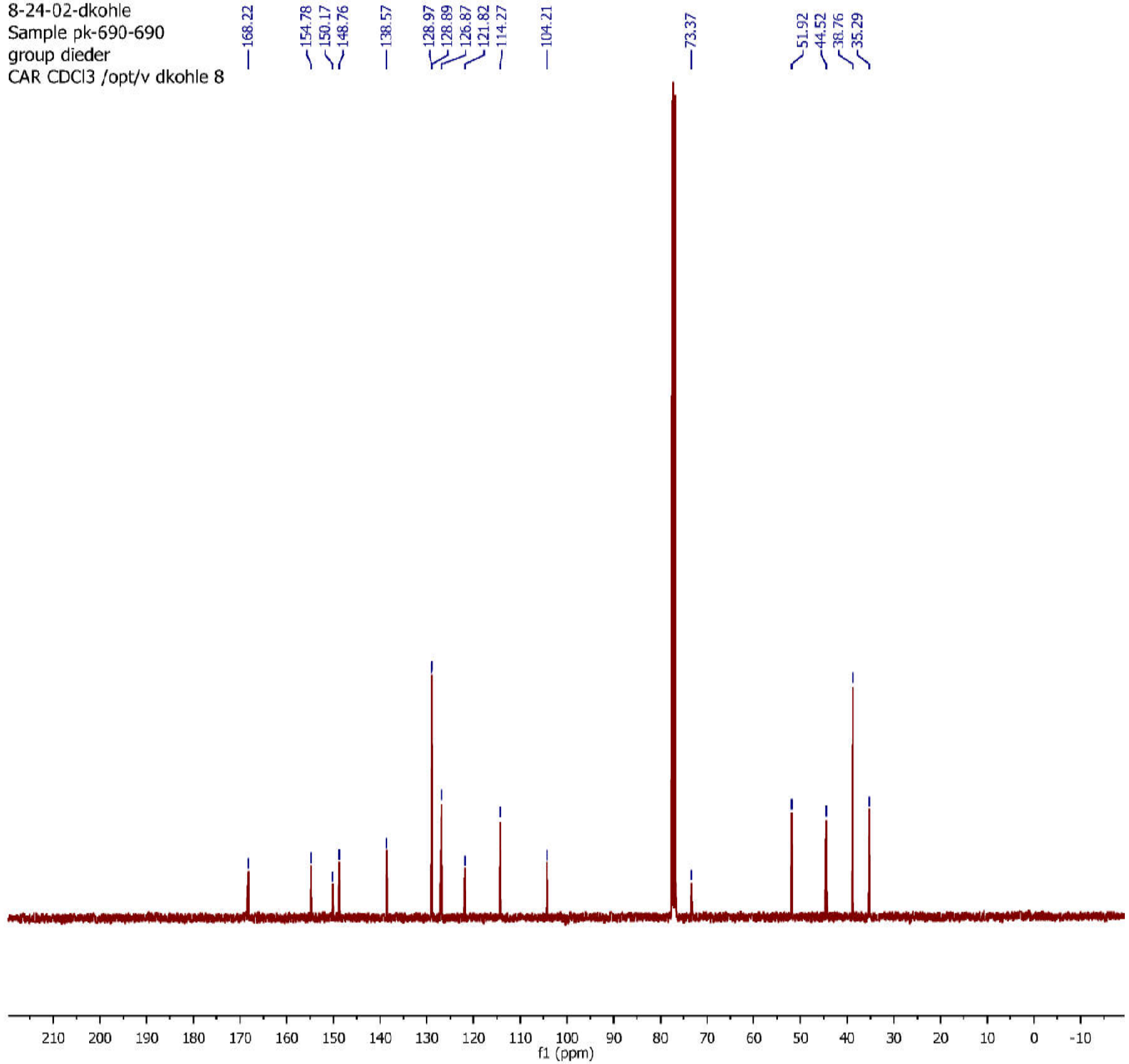
pk-690-690
STANDARD 1H OBSERVE

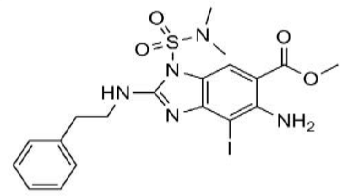




9c

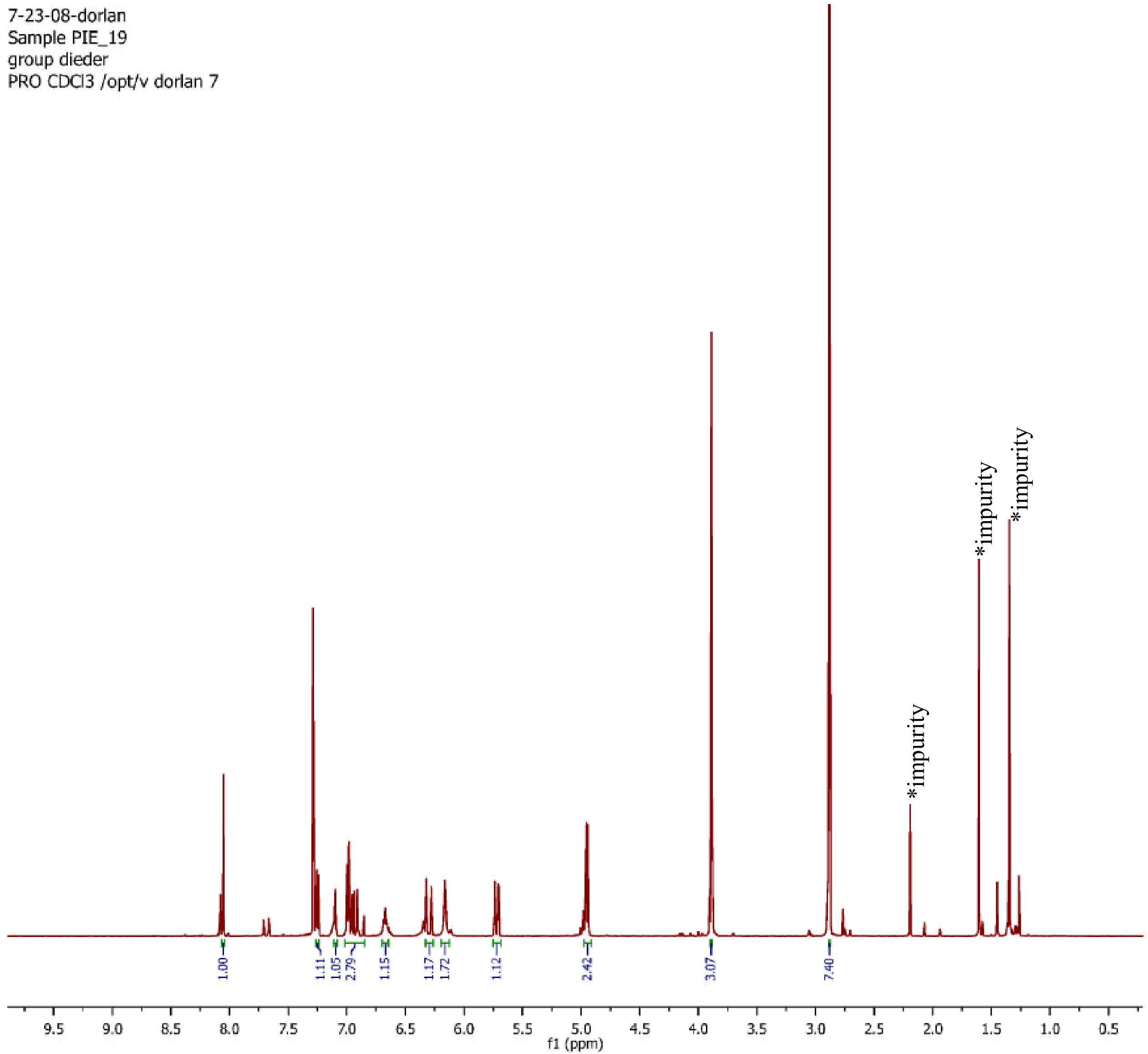
	Parameter	Value
1	Title	pk-690-690
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	16
10	Receiver Gain	32
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	3.1376
14	Acquisition Date	2009-02-24T09:34:44
15	Modification Date	2009-02-24T10:16:40
16	Spectrometer Frequency	300.22
17	Spectral Width	5099.4
18	Lowest Frequency	-640.4
19	Nucleus	1H
20	Acquired Size	16000
21	Spectral Size	32768

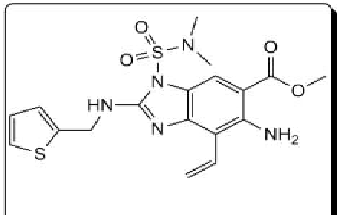




9c

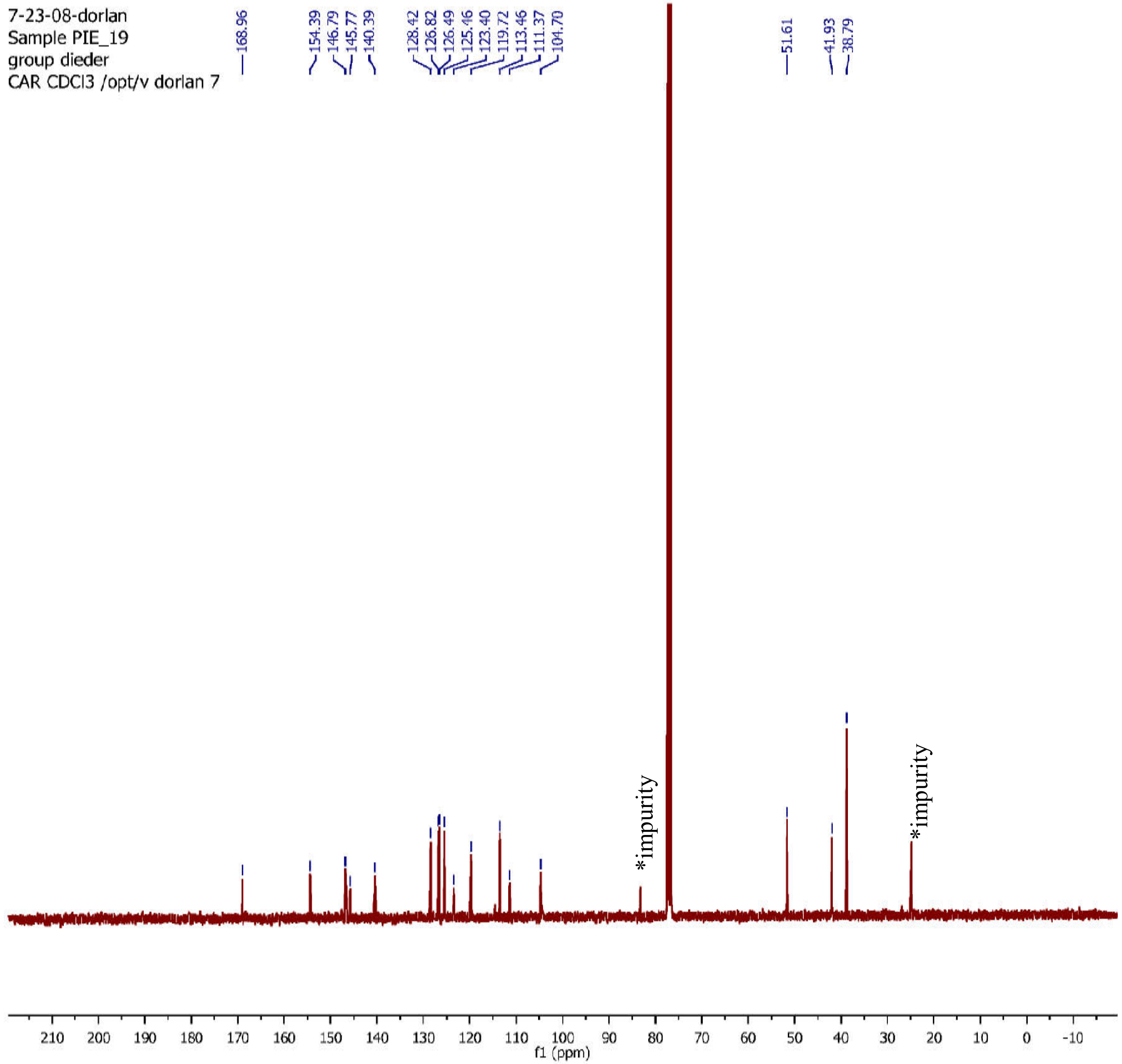
	Parameter	Value
1	Title	8-24-02-dkohle
2	Comment	Sample pk-690-690 group dieder CAR CDCl3 / opt/ v dkohle 8
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	300.0
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	1024
11	Receiver Gain	203
12	Relaxation Delay	2.0000
13	Pulse Width	9.1000
14	Acquisition Time	1.3632
15	Acquisition Date	2009-02-24T14:03:00
16	Modification Date	2009-02-24T14:39:30
17	Spectrometer Frequency	100.61
18	Nucleus	13C

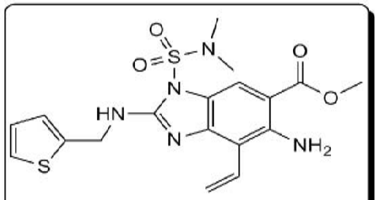




11a

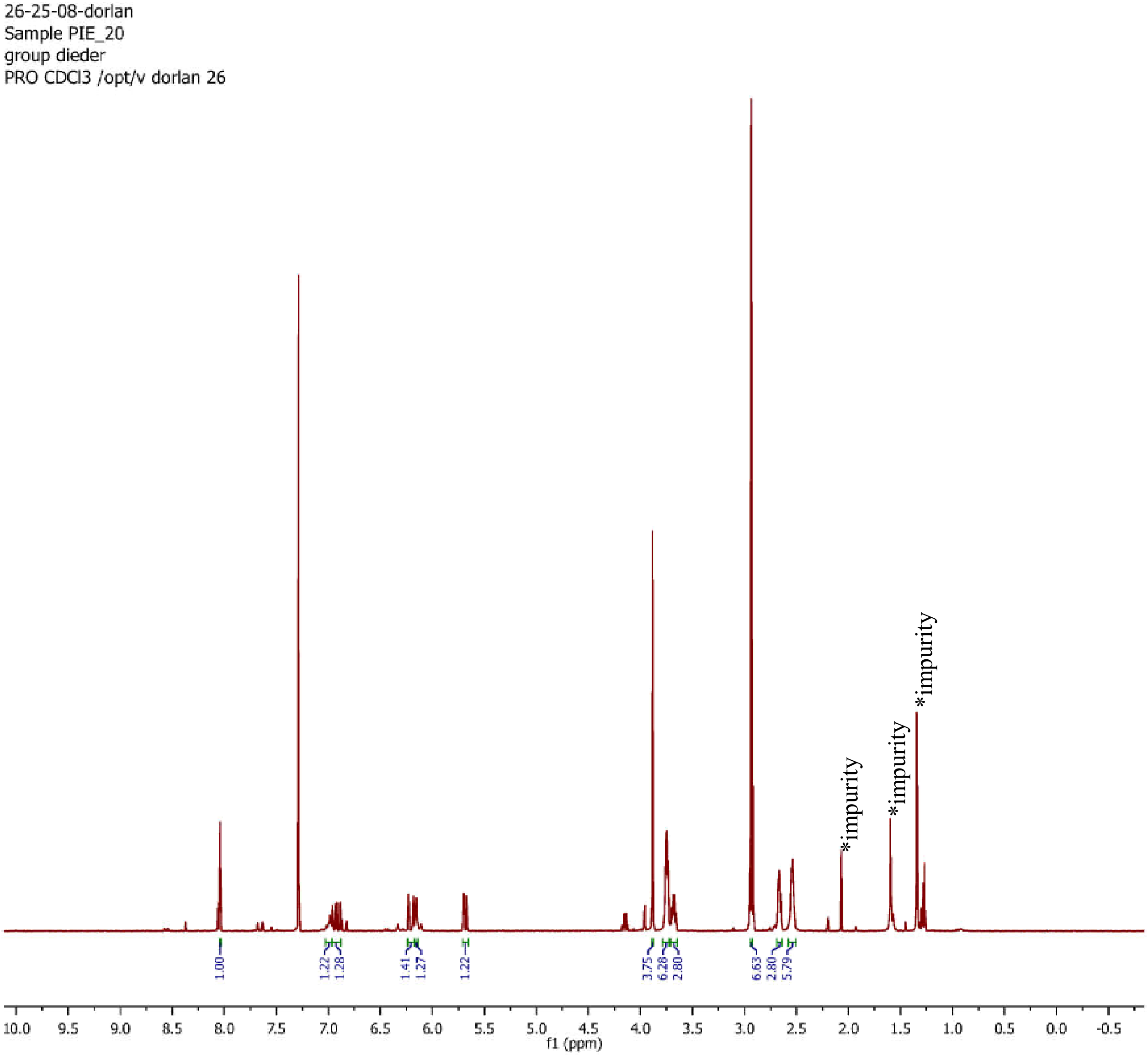
	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 7-23-08-dorlan/ 10/ fid
2	Title	7-23-08-dorlan
3	Comment	Sample PIE_19 group dieder PRO CDCl3 / opt/ v dorlan 7
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-08-23T19:36:00
19	Modification	2010-08-24T09:31:59

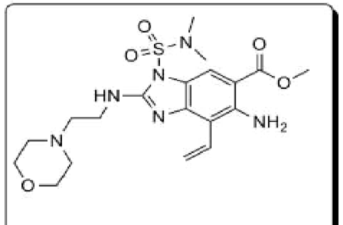




11a

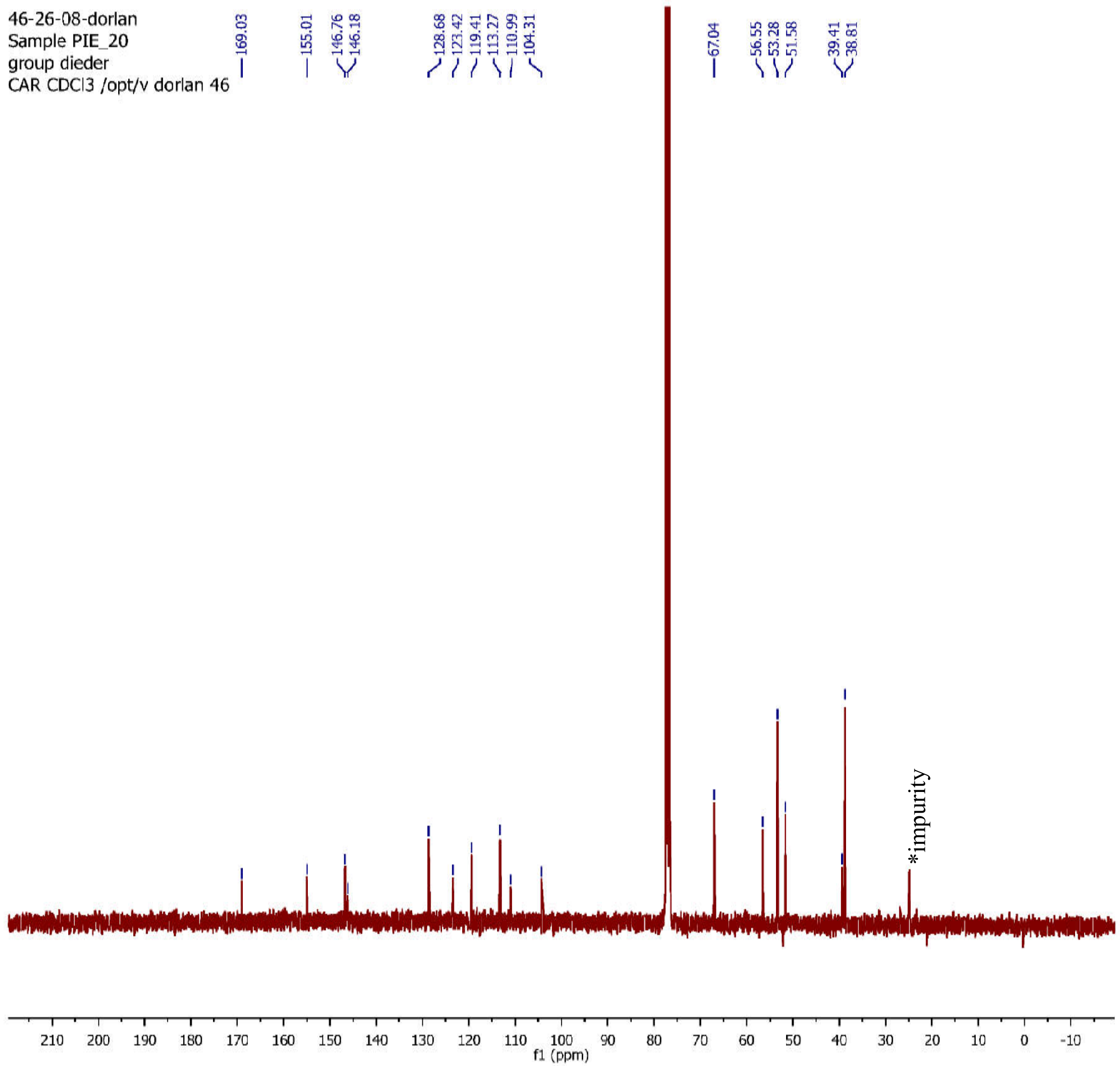
	Parameter	Value
1	Title	7-23-08-dorlan
2	Comment	Sample PIE_19 group dieder CAR CDCl3 / opt/ v dorlan 7
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	298.0
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	1500
11	Receiver Gain	203
12	Relaxation Delay	2.0000
13	Pulse Width	9.1000
14	Acquisition Time	1.3632
15	Acquisition Date	2010-08-23T21:03:00
16	Modification Date	2010-08-24T09:32:02
17	Spectrometer Frequency	100.61
18	Nucleus	13C

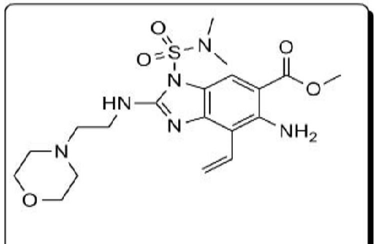




11b

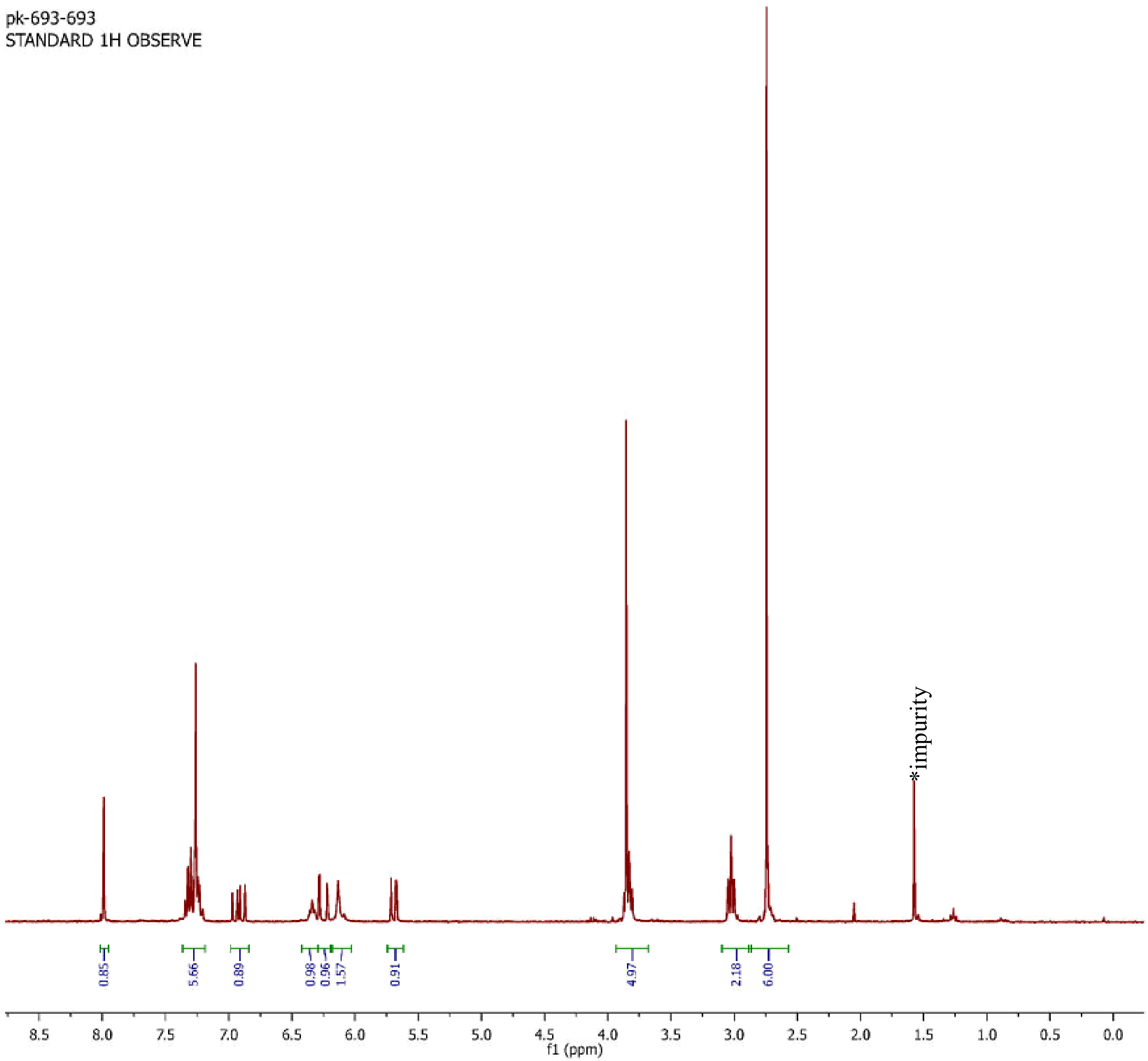
	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 26-25-08-dorlan/ 10/ fid
2	Title	26-25-08-dorlan
3	Comment	Sample PIE_20 group dieder PRO CDCl3 / opt/ v dorlan 26
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-08-25T18:45:00
19	Modification	2010-08-26T09:40:39

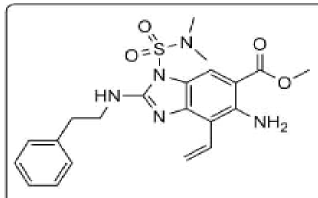




11b

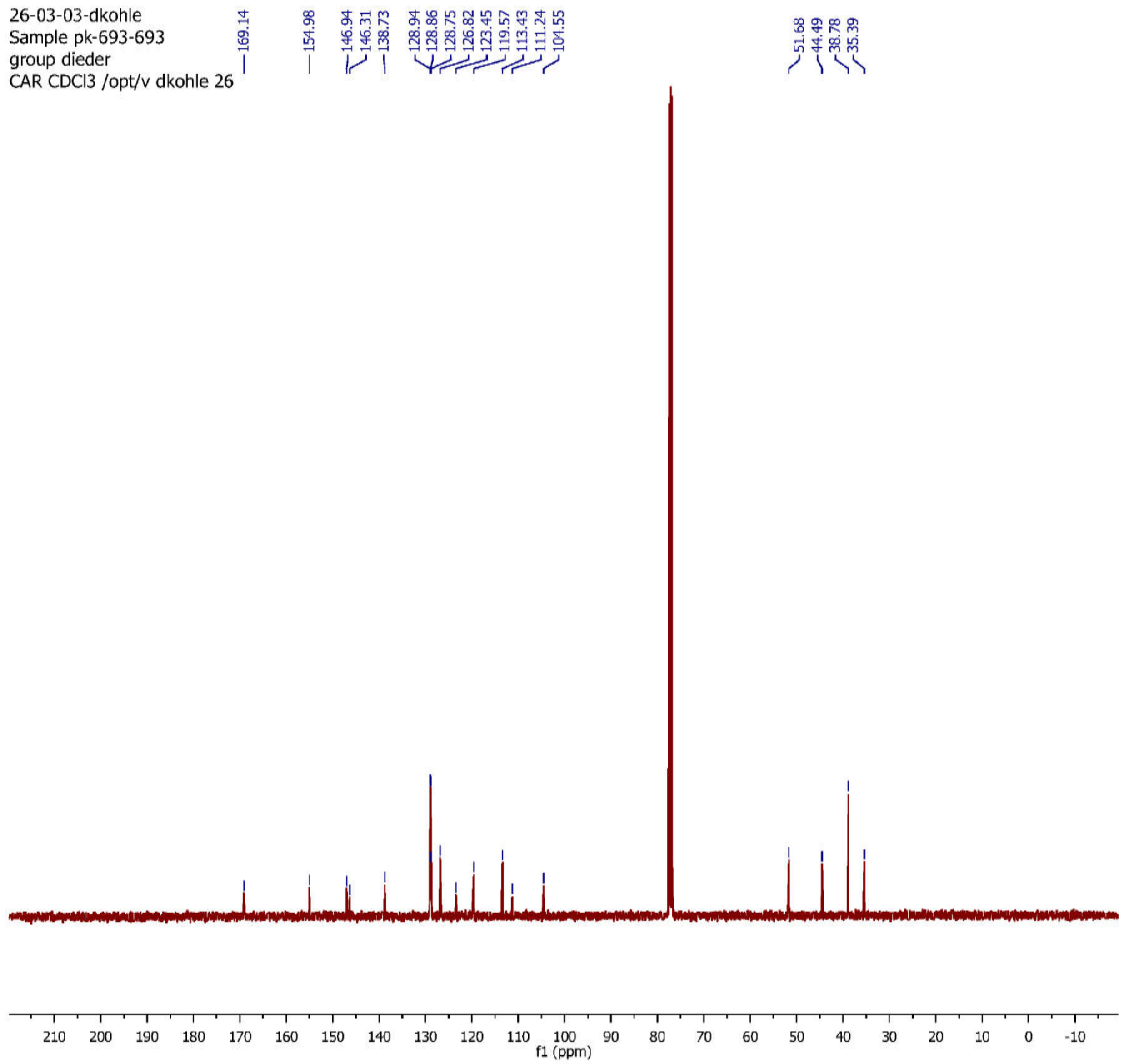
Parameter	Value
1 Title	46-26-08-dorlan
2 Comment	Sample PIE_20 group dieder CAR CDCl3 / opt/ v dorlan 46
3 Origin	Bruker BioSpin GmbH
4 Owner	locnmr
5 Spectrometer	spect
6 Solvent	CDCl3
7 Temperature	298.1
8 Pulse Sequence	zgpg30
9 Experiment	1D
10 Number of Scans	5500
11 Receiver Gain	2299
12 Relaxation Delay	2.0000
13 Pulse Width	7.8000
14 Acquisition Time	1.3632
15 Acquisition Date	2010-08-26T18:57:00
16 Modification Date	2010-08-27T10:26:18
17 Spectrometer Frequency	100.61
18 Nucleus	13C

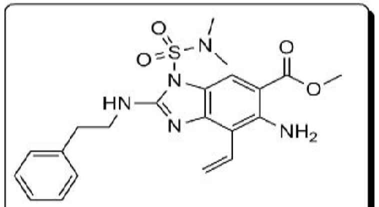




11c

	Parameter	Value
1	Title	pk-693-693
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	16
10	Receiver Gain	36
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	3.1376
14	Acquisition Date	2009-03-03T10:00:24
15	Modification Date	2009-03-03T10:24:48
16	Spectrometer Frequency	300.22
17	Spectral Width	5099.4
18	Lowest Frequency	-640.7
19	Nucleus	1H
20	Acquired Size	16000
21	Spectral Size	32768

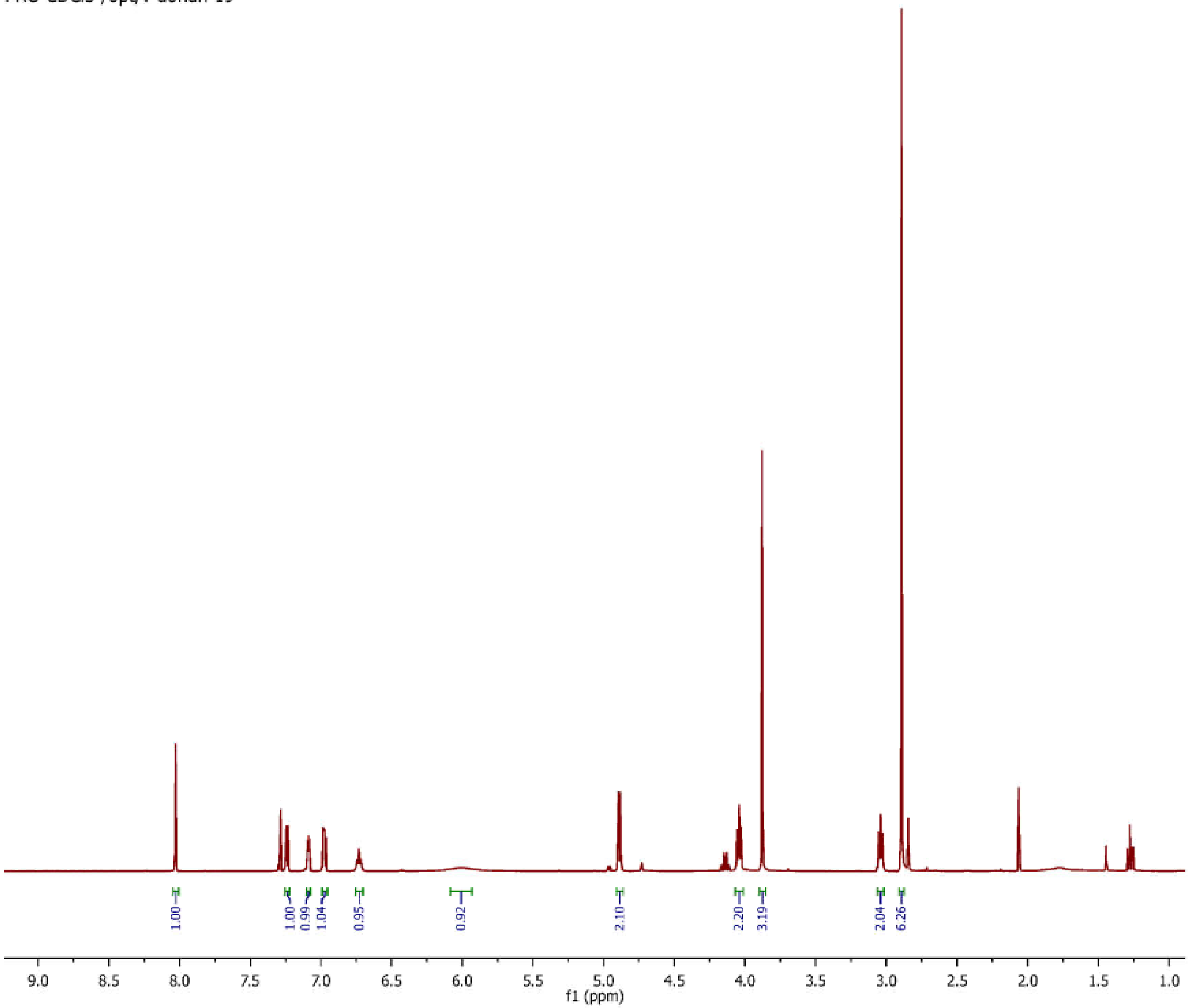


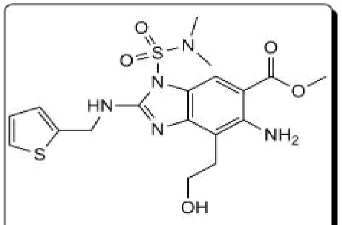


11c

	Parameter	Value
1	Title	26-03-03-dkohle
2	Comment	Sample pk-693-693 group dieder CAR CDCl3 / opt/ v dkohle 26
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	300.0
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	1024
11	Receiver Gain	203
12	Relaxation Delay	2.0000
13	Pulse Width	9.1000
14	Acquisition Time	1.3632
15	Acquisition Date	2009-03-03T12:00:00
16	Modification Date	2009-03-03T14:26:40
17	Spectrometer Frequency	100.61
18	Nucleus	13C

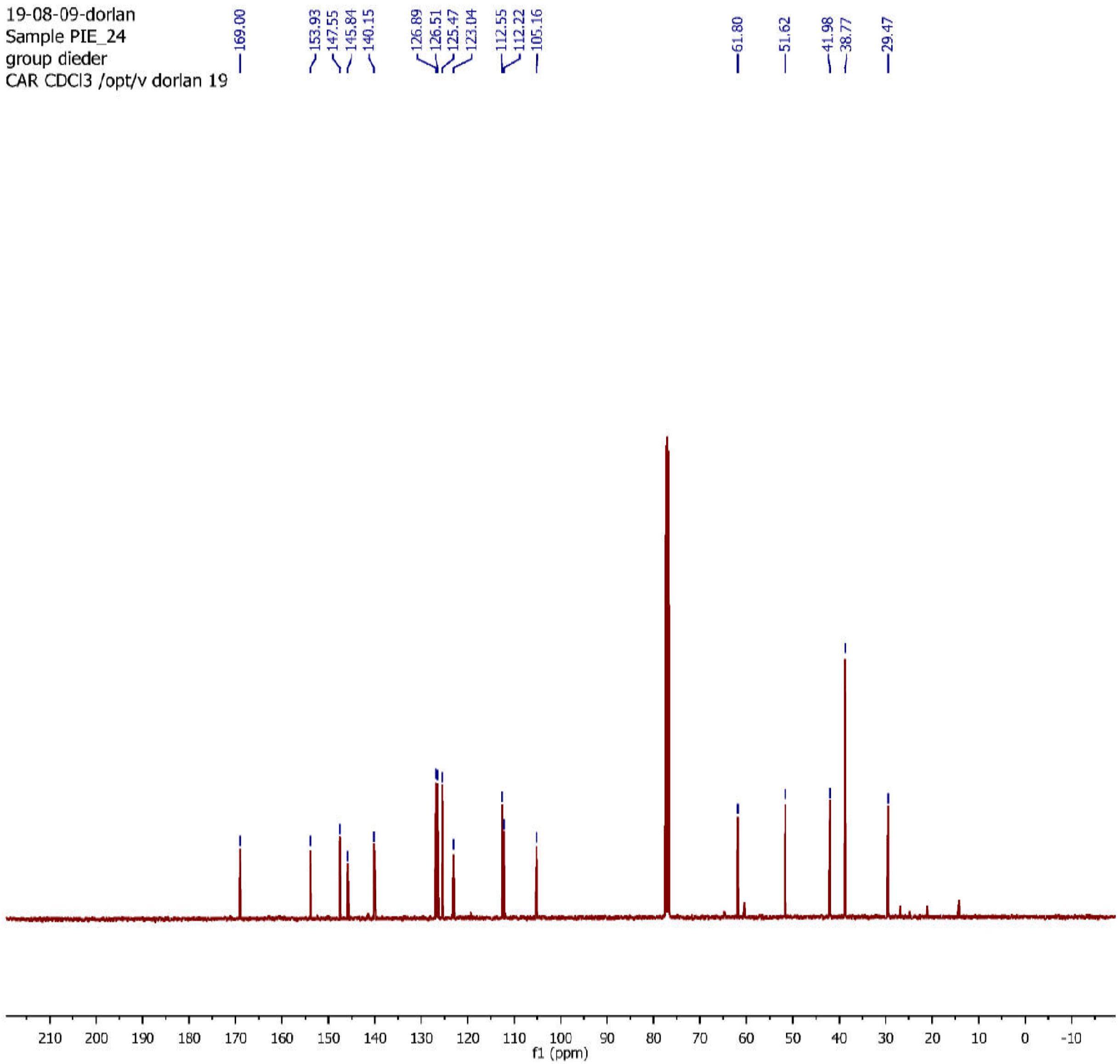
19-08-09-dorlan
Sample PIE_24
group dieder
PRO CDCl3 /opt/v dorlan 19

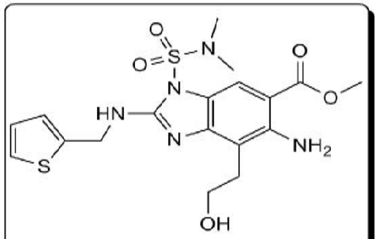




12a

	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 19-08-09-dorlan/ 10/ fid
2	Title	19-08-09-dorlan
3	Comment	Sample PIE_24 group dieder PRO CDCl3 / opt/ v dorlan 19
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	144
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-09-08T20:06:00
19	Modification	2010-09-09T09:41:53

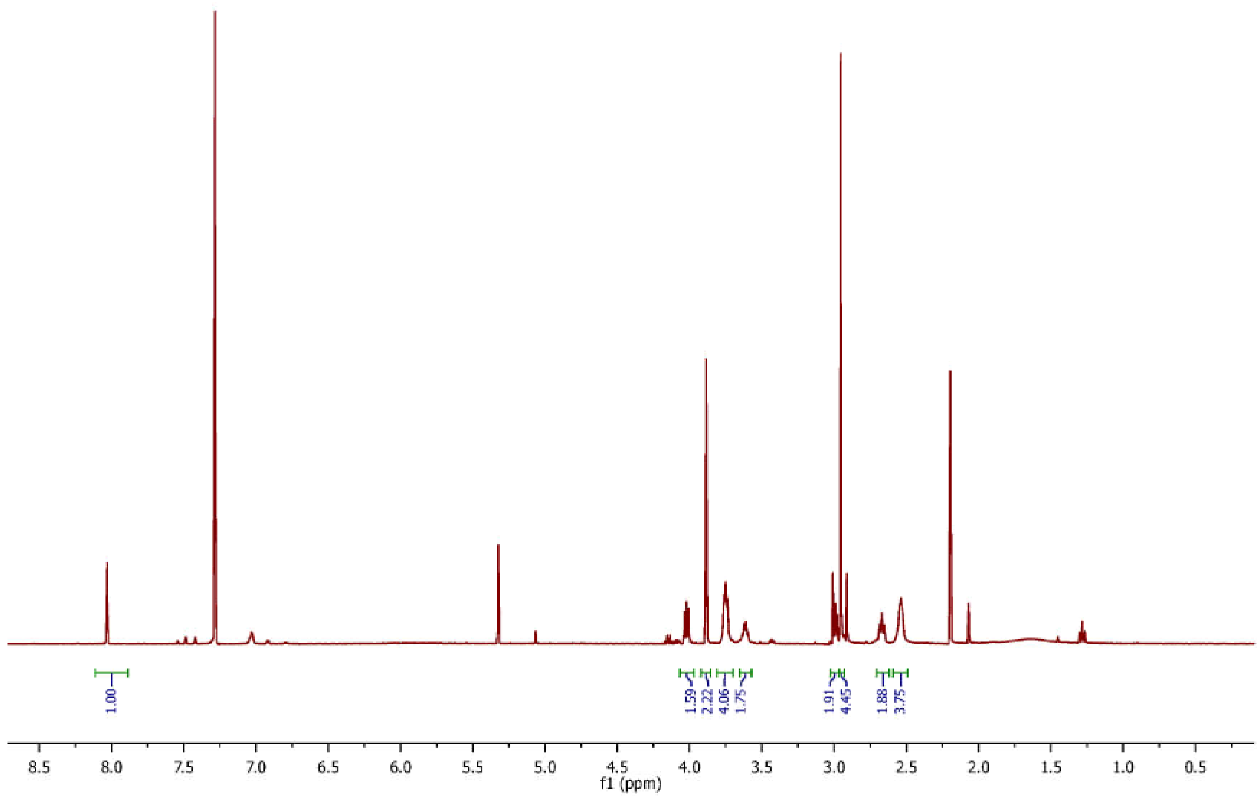


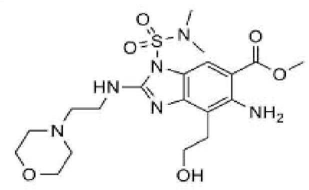


12a

	Parameter	Value
1	Title	19-08-09-dorlan
2	Comment	Sample PIE_24 group dieder CAR CDCl3 / opt/ v dorlan 19
3	Origin	Bruker BioSpin GmbH
4	Owner	locnmr
5	Spectrometer	spect
6	Solvent	CDCl3
7	Temperature	298.0
8	Pulse Sequence	zgpg30
9	Experiment	1D
10	Number of Scans	1500
11	Receiver Gain	203
12	Relaxation Delay	2.0000
13	Pulse Width	9.1000
14	Acquisition Time	1.3632
15	Acquisition Date	2010-09-08T21:32:00
16	Modification Date	2010-09-09T09:41:56
17	Spectrometer Frequency	100.61
18	Nucleus	13C

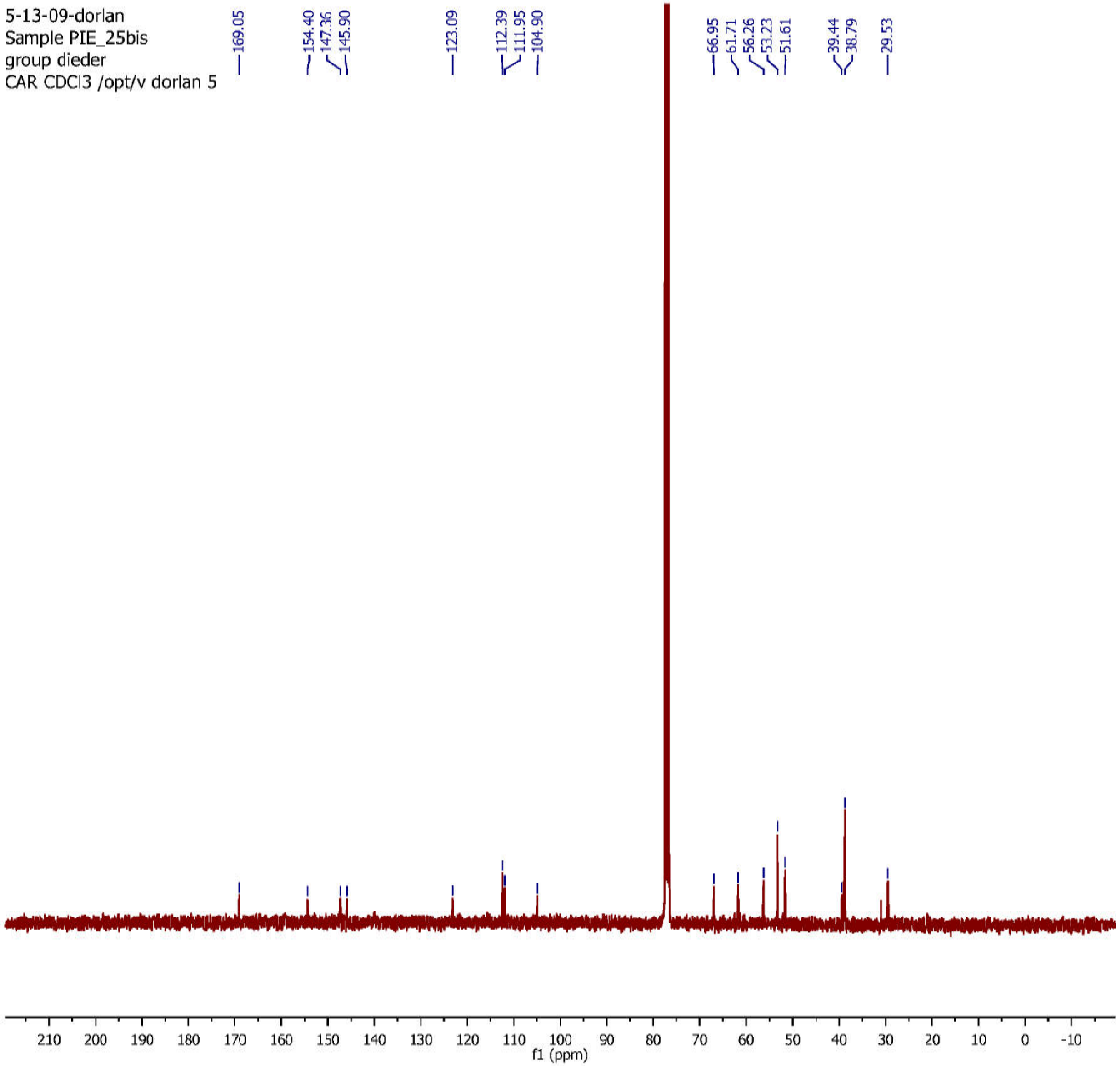
48-13-09-dorlan
Sample PIE_25
group dieder
PRO CDCl3 /opt/v dorlan 48

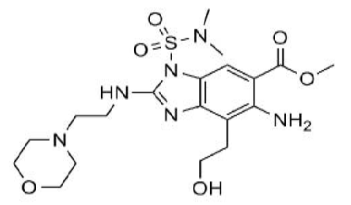




12b

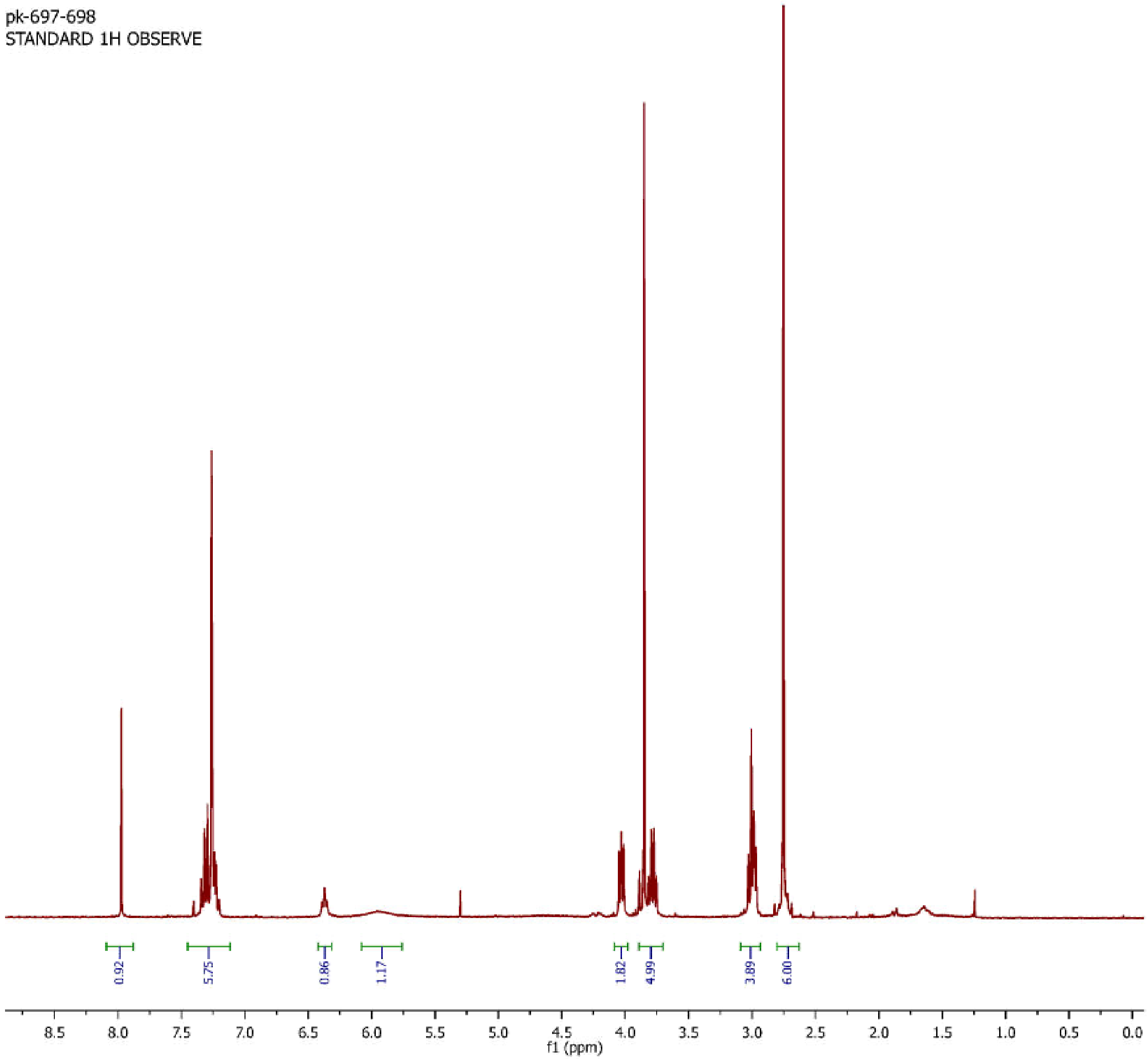
Parameter	Value
1 Title	48-13-09-dorlan
2 Origin	Bruker BioSpin GmbH
3 Owner	locnmr
4 Spectrometer	spect
5 Solvent	CDCl3
6 Temperature	298.0
7 Pulse Sequence	zg30
8 Experiment	1D
9 Number of Scans	16
10 Receiver Gain	203
11 Relaxation Delay	1.0000
12 Pulse Width	12.1000
13 Acquisition Time	3.9846
14 Acquisition Date	2010-09-13T13:05:00
15 Modification Date	2010-09-13T15:31:50
16 Spectrometer Frequency	400.13
17 Nucleus	1H

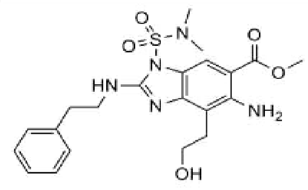




12b

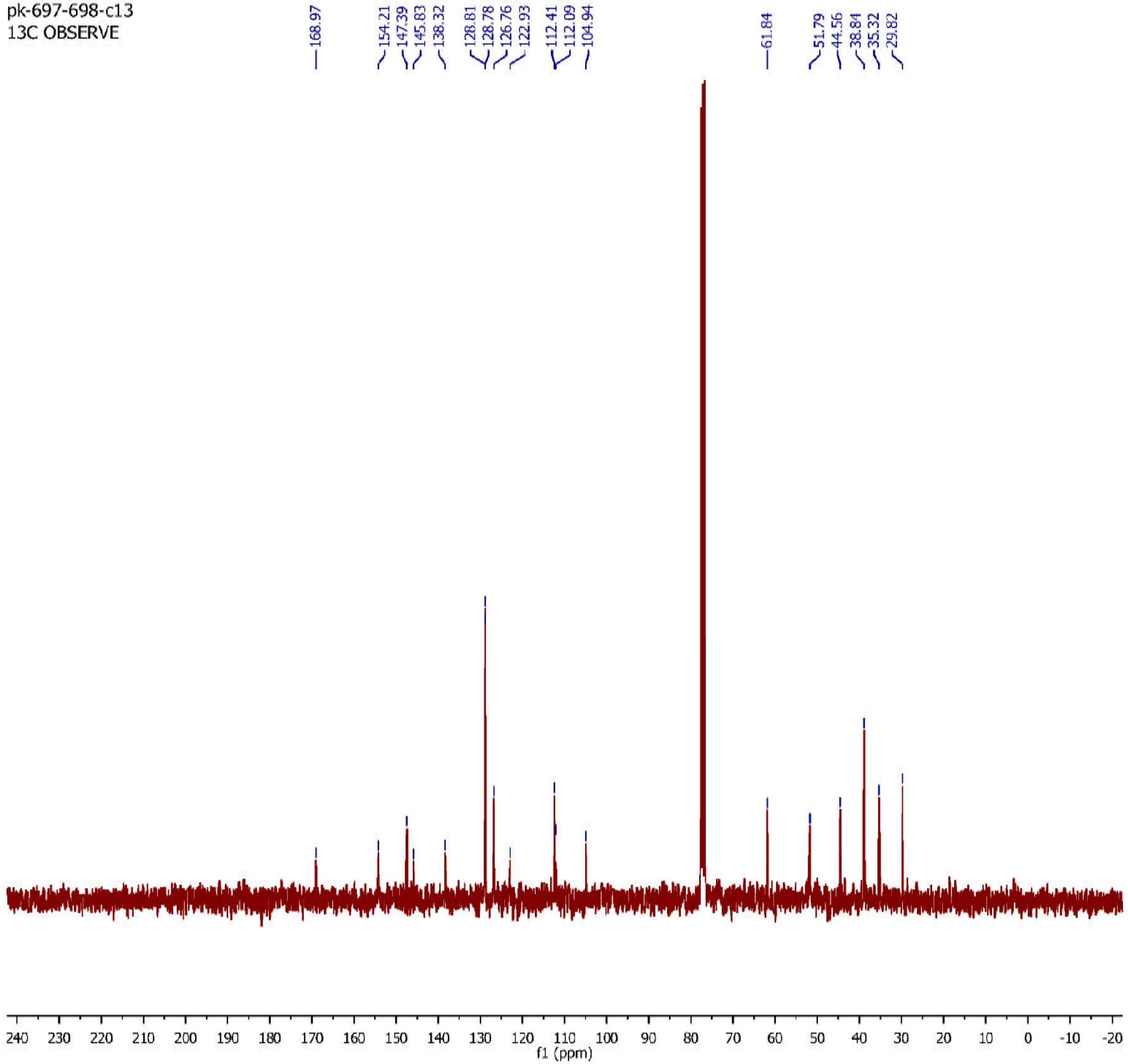
	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 5-13-09-dorlan/ 10/ fid
2	Title	5-13-09-dorlan
3	Comment	Sample PIE_25bis group dieder CAR CDCl3 / opt/ v dorlan 5
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.1
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	5000
14	Receiver Gain	6502
15	Relaxation Delay	2.0000
16	Pulse Width	7.8000
17	Acquisition Time	1.3632
18	Acquisition Date	2010-09-14T21:33:00

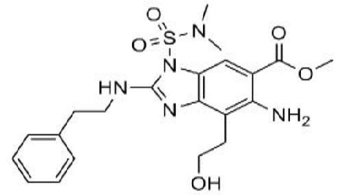




12c

	Parameter	Value
1	Title	pk-697-698
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	16
10	Receiver Gain	32
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	3.1376
14	Acquisition Date	2009-03-18T13:46:46
15	Modification Date	2009-03-18T14:12:34
16	Spectrometer Frequency	300.22
17	Spectral Width	5099.4
18	Lowest Frequency	-640.4
19	Nucleus	1H
20	Acquired Size	16000
21	Spectral Size	32768

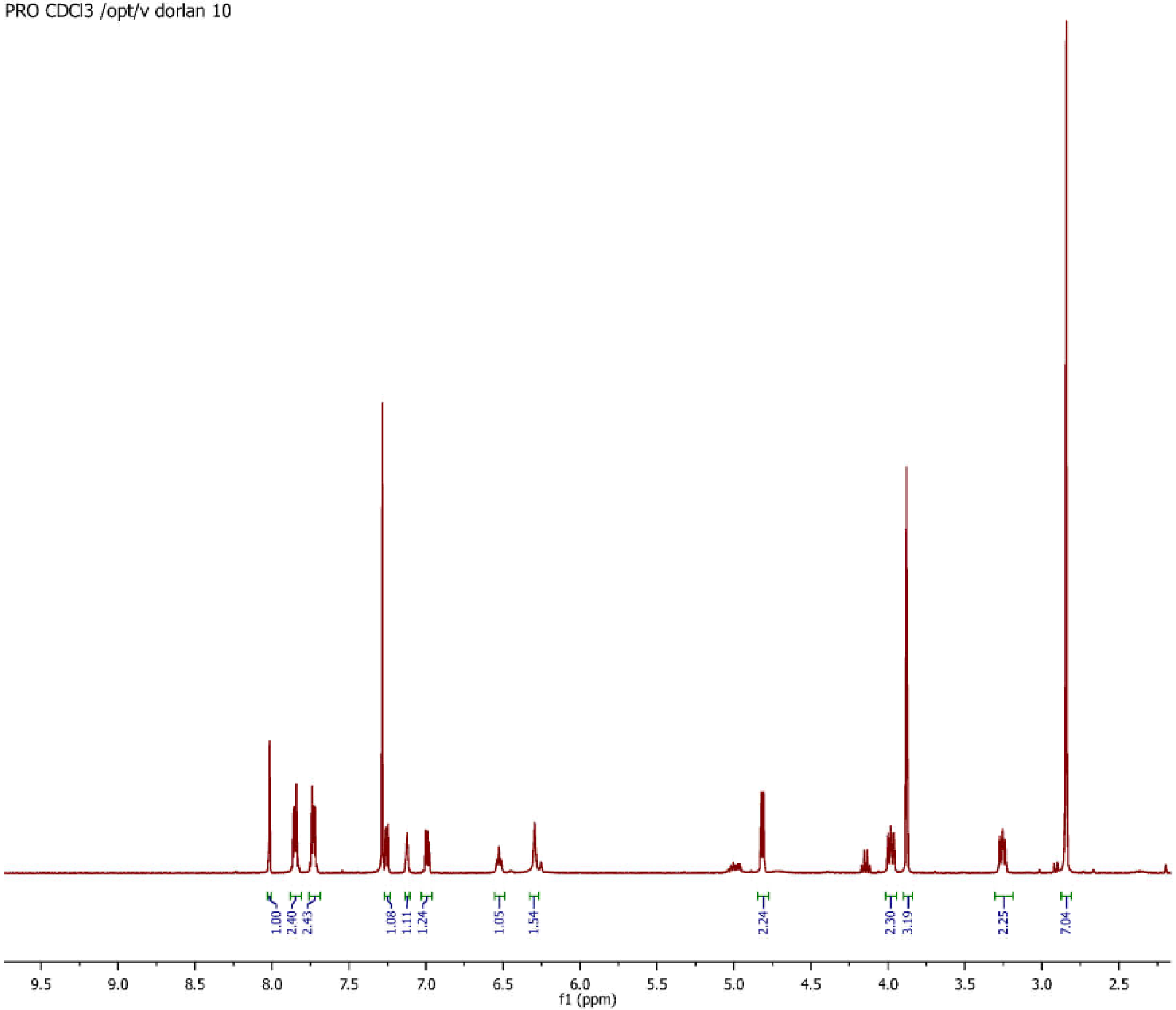


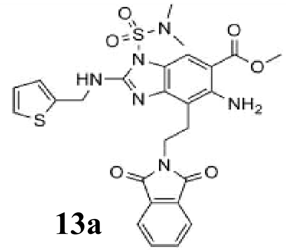


12c

	Parameter	Value
1	Title	pk-697-698-c13
2	Comment	13C OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	760
10	Receiver Gain	36
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.3000
14	Acquisition Date	2009-03-18T13:47:04
15	Modification Date	2009-03-18T14:33:56
16	Spectrometer Frequency	75.50
17	Spectral Width	20000.0
18	Lowest Frequency	-1711.2
19	Nucleus	13C
20	Acquired Size	26000
21	Spectral Size	65536

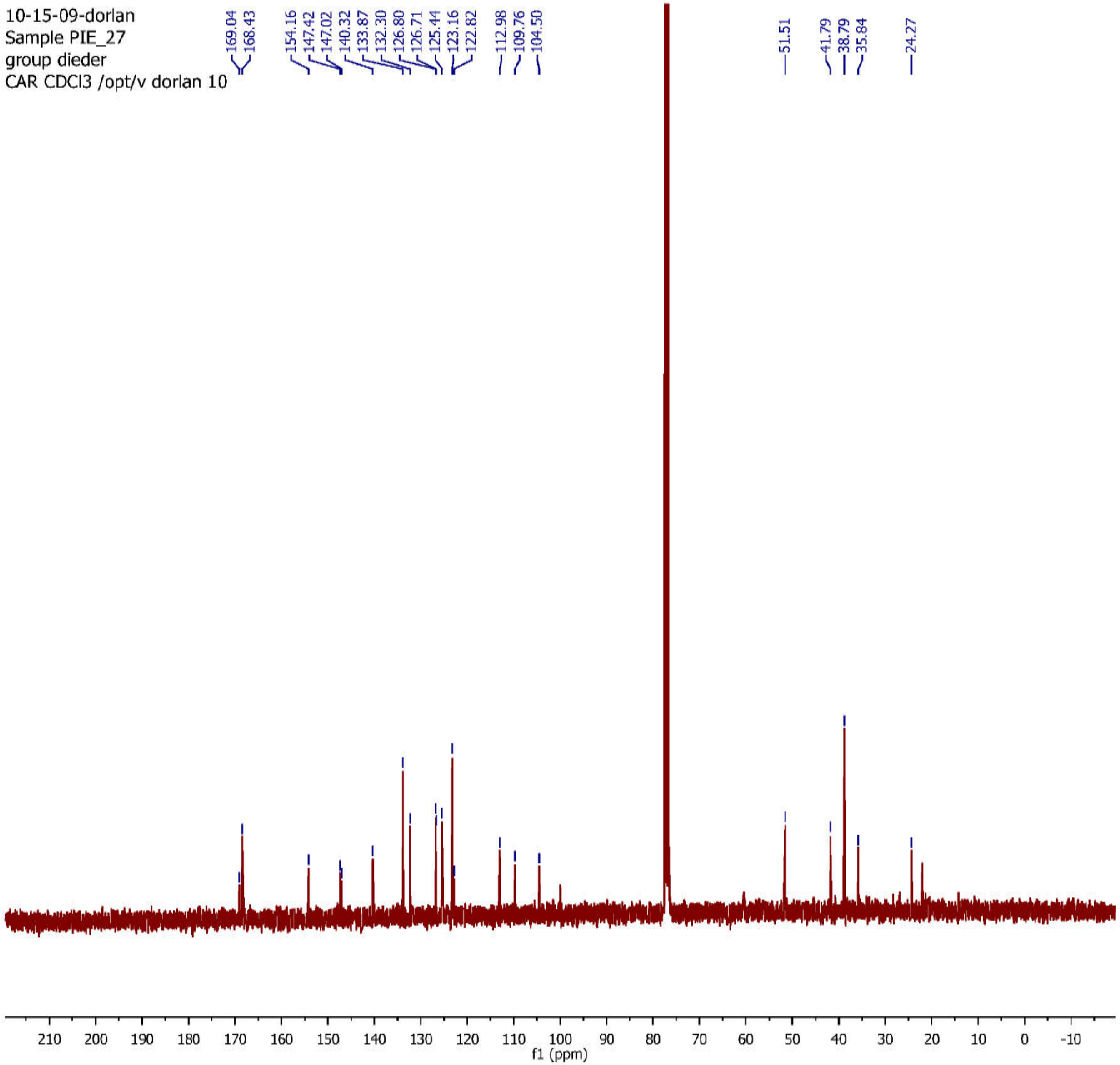
10-15-09-dorlan
Sample PIE_27
group dieder
PRO CDCl3 /opt/v dorlan 10

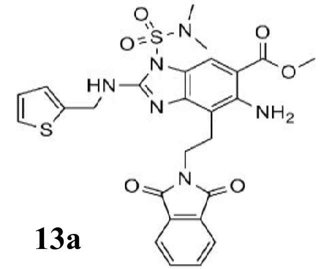




13a

	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 10-15-09-dorlan/ 10/ fid
2	Title	10-15-09-dorlan
3	Comment	Sample PIE_27 group dieder PRO CDCl3 / opt/ v dorlan 10
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-09-15T17:24:00
19	Modification	2010-09-16T12:05:37

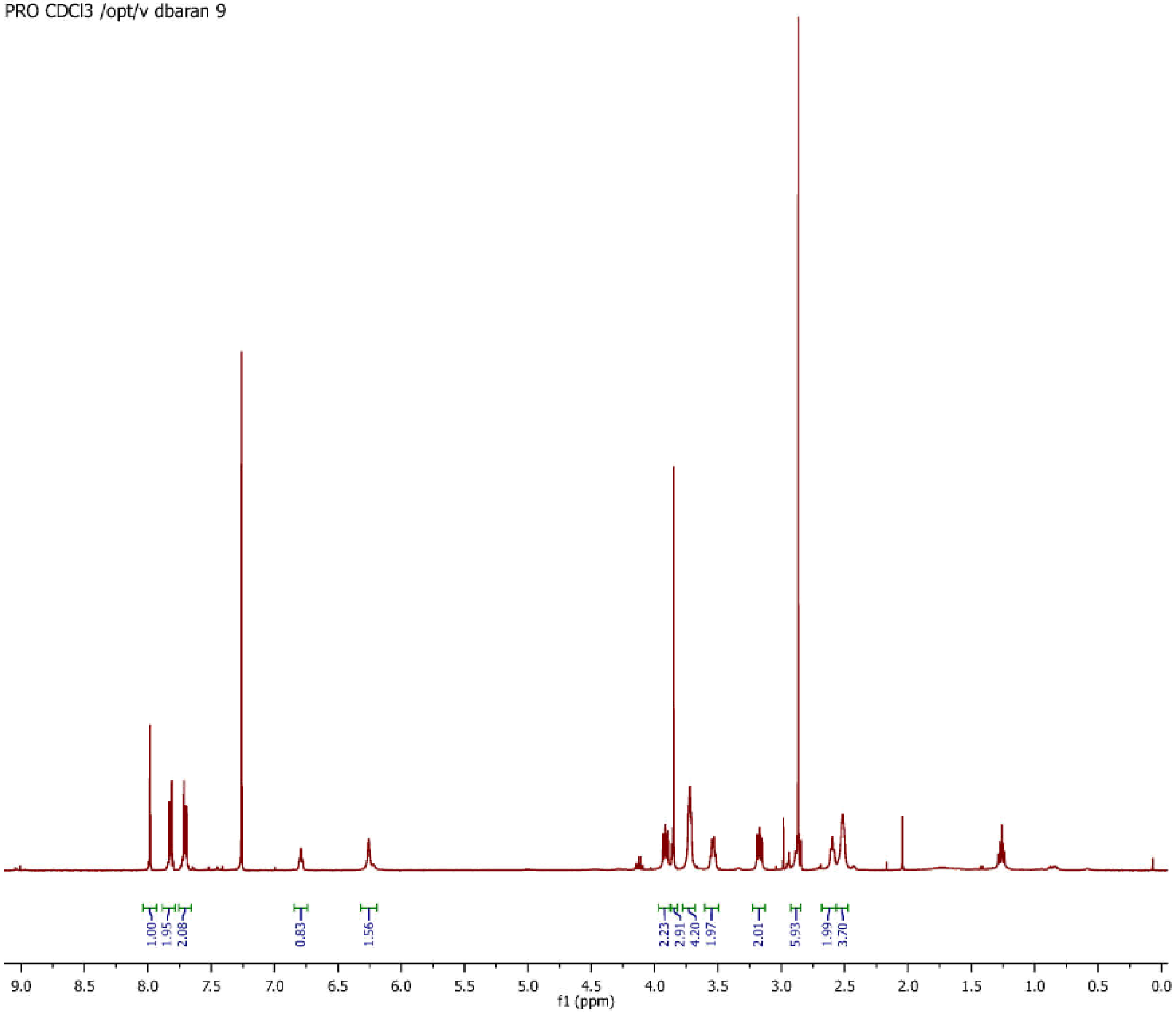


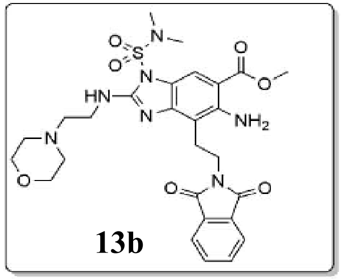


13a

	Parameter	Value
1	Title	10-15-09-dorlan
2	Origin	Bruker BioSpin GmbH
3	Owner	locnmr
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	298.0
7	Pulse Sequence	zgpg30
8	Experiment	1D
9	Number of Scans	1500
10	Receiver Gain	203
11	Relaxation Delay	2.0000
12	Pulse Width	9.1000
13	Acquisition Time	1.3632
14	Acquisition Date	2010-09-15T18:50:00
15	Modification Date	2010-09-16T12:05:40
16	Spectrometer Frequency	100.61
17	Nucleus	13C

9-15-09-dbaran
Sample LJB-170
group dieder
PRO CDCl3 /opt/v dbaran 9

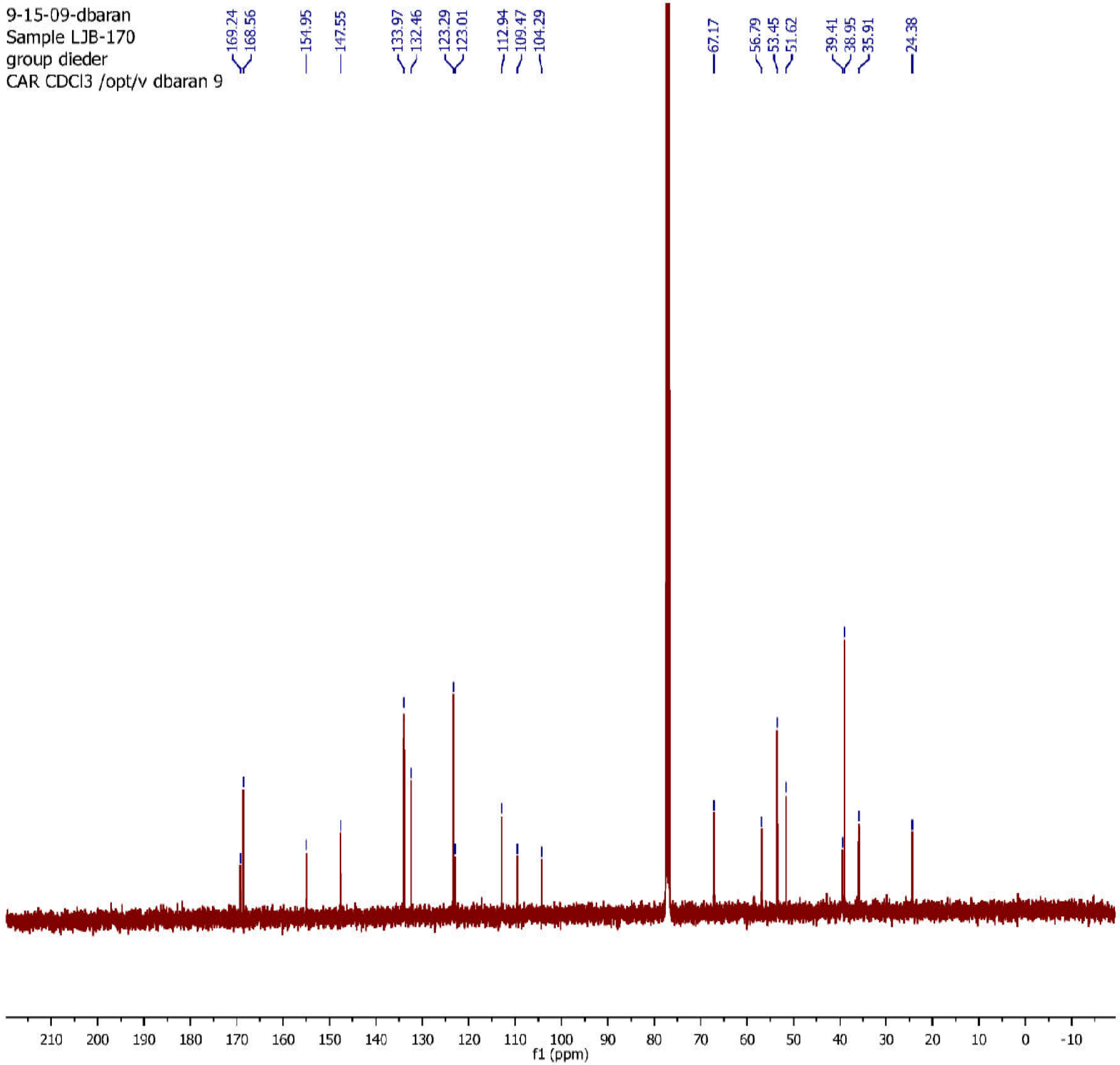


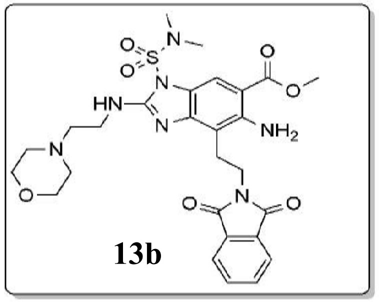


13b

Parameters

Parameter	Value
Title	9-15-09-dbaran
Origin	Bruker BioSpin GmbH
Owner	locnmr
Solvent	CDCl3
Pulse Sequence	zg30
Acquisition Date	2010-09-15T15:20:00
Modification Date	2010-09-17T08:28:18
Temperature	298.0
Number of Scans	16
Spectrometer Frequency	400.13
Spectral Width	8223.7
Lowest Frequency	-1640.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



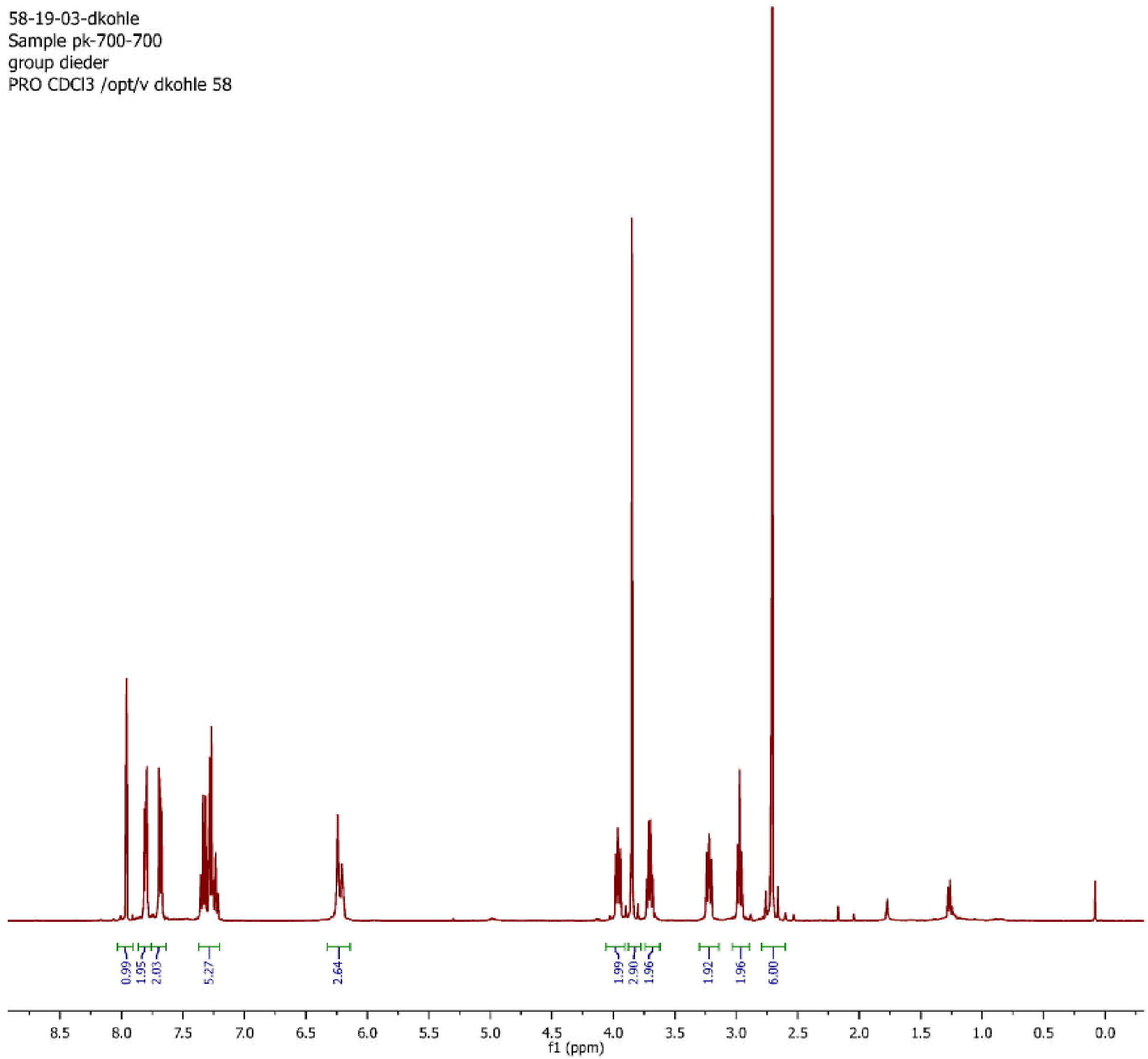


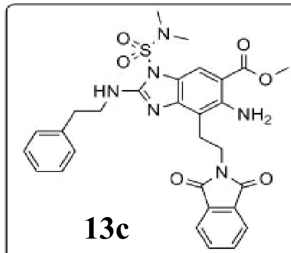
13b

Parameters

Parameter	Value
Title	9-15-09-dbaran
Origin	Bruker BioSpin GmbH
Owner	locnmr
Solvent	CDCl3
Pulse Sequence	zgpg30
Acquisition Date	2010-09-15T17:15:00
Modification Date	2010-09-17T08:28:26
Temperature	298.0
Number of Scans	2000
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1958.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

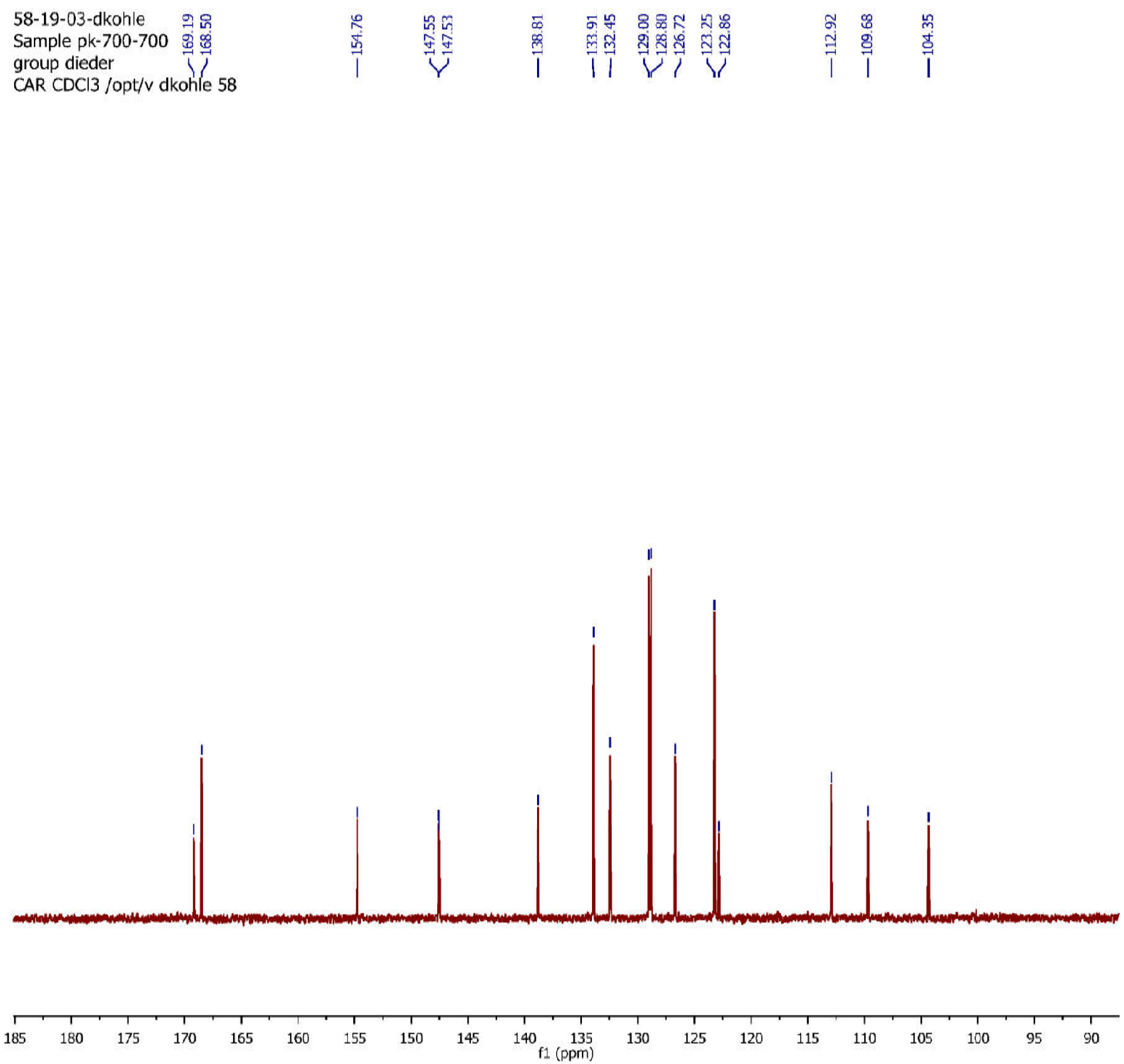
58-19-03-dkohle
Sample pk-700-700
group dieder
PRO CDCl3 /opt/v dkohle 58

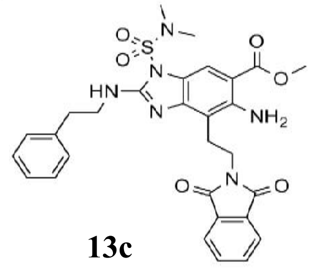




13c

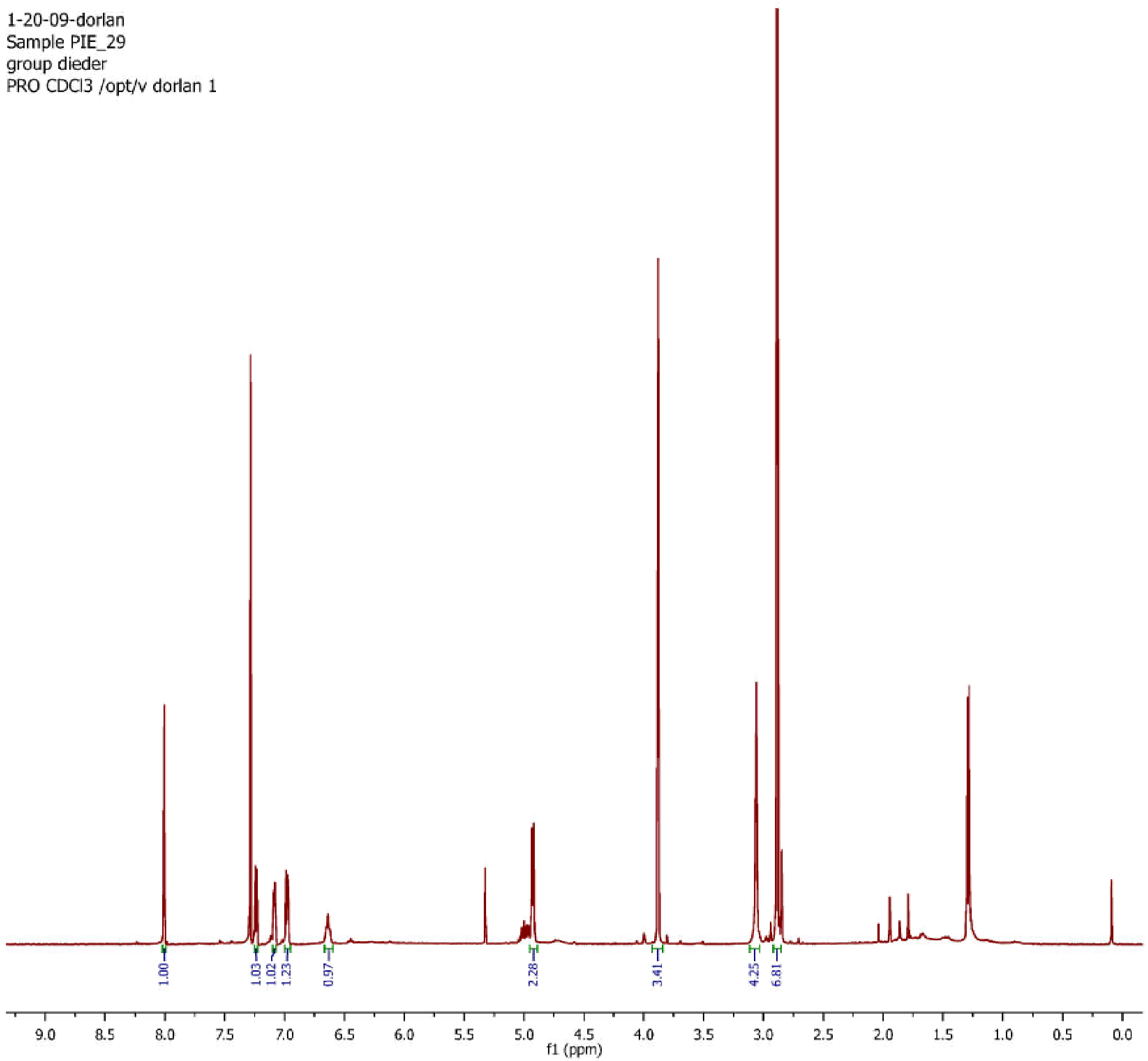
	Parameter	Value
1	Title	58-19-03-dkohle
2	Origin	Bruker BioSpin GmbH
3	Owner	locnmr
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	300.0
7	Pulse Sequence	zg30
8	Experiment	1D
9	Number of Scans	16
10	Receiver Gain	114
11	Relaxation Delay	1.0000
12	Pulse Width	12.1000
13	Acquisition Time	3.9846
14	Acquisition Date	2009-03-19T13:58:00
15	Modification Date	2009-03-19T15:47:00
16	Spectrometer Frequency	400.13
17	Nucleus	1H

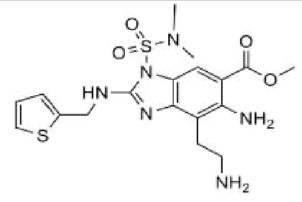




13c

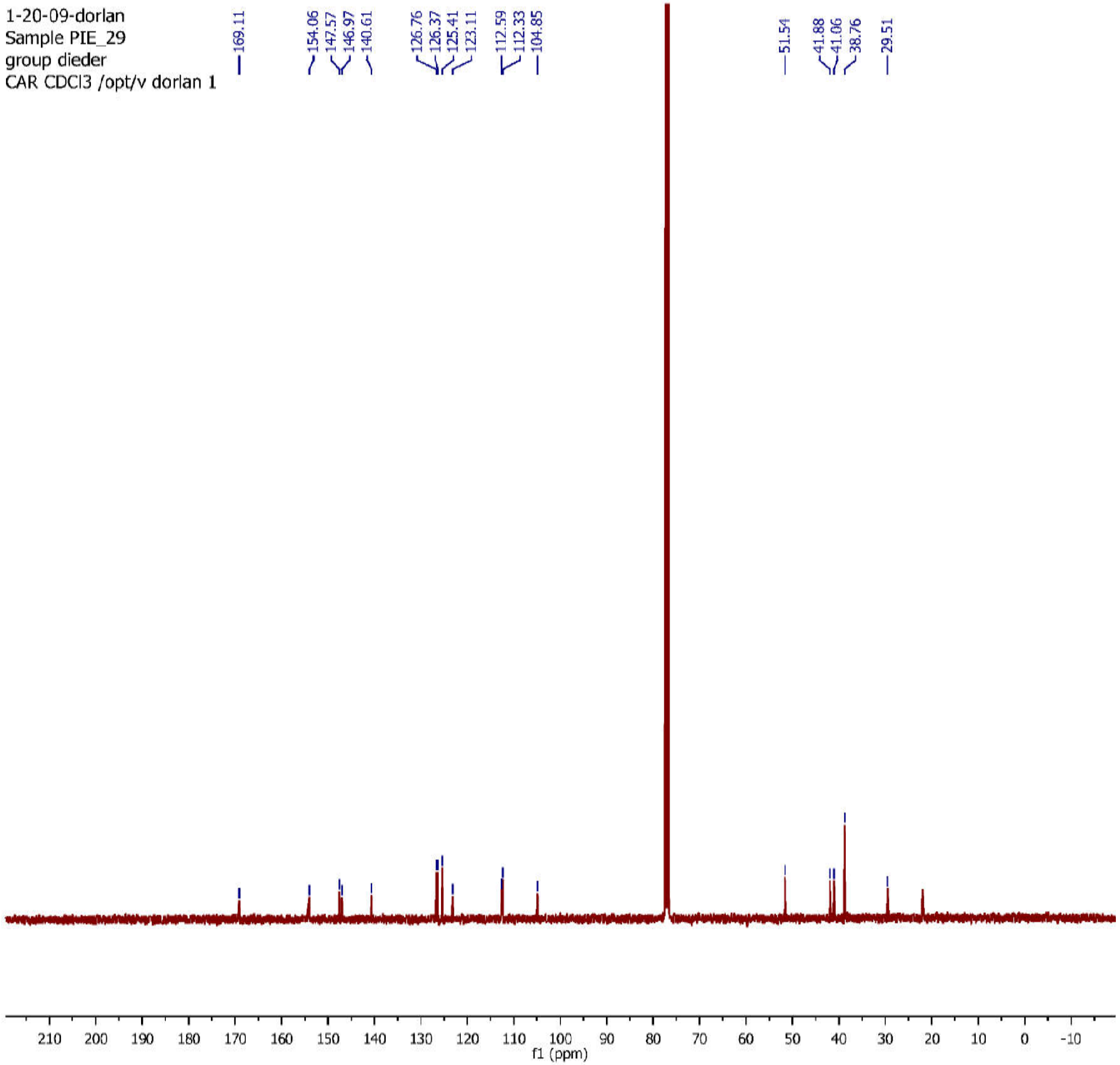
	Parameter	Value
1	Title	58-19-03-dkohle
2	Origin	Bruker BioSpin GmbH
3	Owner	locnmr
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	300.0
7	Pulse Sequence	zgpg30
8	Experiment	1D
9	Number of Scans	1024
10	Receiver Gain	203
11	Relaxation Delay	2.0000
12	Pulse Width	9.1000
13	Acquisition Time	1.3632
14	Acquisition Date	2009-03-19T14:58:00
15	Modification Date	2009-03-19T15:46:50
16	Spectrometer Frequency	100.61
17	Nucleus	13C

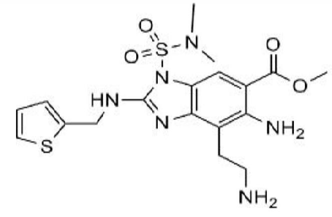




14a

	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 1-20-09-dorlan/ 10/ fid
2	Title	1-20-09-dorlan
3	Comment	Sample PIE_29 group dieder PRO CDCl3 / opt/ v dorlan 1
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-09-20T17:17:00
19	Modification	2010-09-21T15:28:18

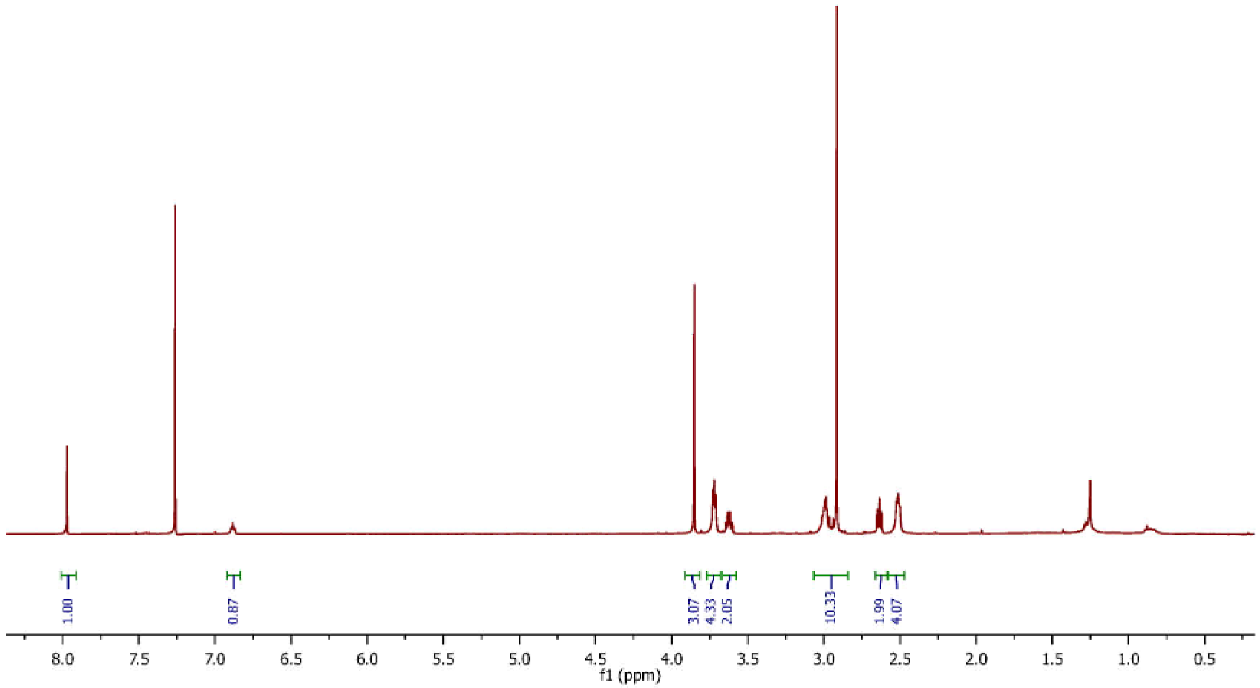


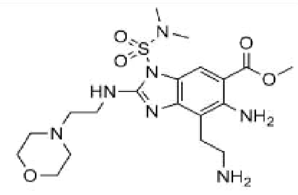


14a

Parameter		Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 1-20-09-dorlan/ 11/ fid
2	Title	1-20-09-dorlan
3	Comment	Sample PIE_29 group dieder CAR CDCl3 / opt/ v dorlan 1
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	1500
14	Receiver Gain	203
15	Relaxation Delay	2.0000
16	Pulse Width	9.1000
17	Acquisition Time	1.3632
18	Acquisition Date	2010-09-20T18:44:00

39-18-09-dbaran
Sample LJB2-173-I
group dieder
PRO CDCl3 /opt/v dbaran 39

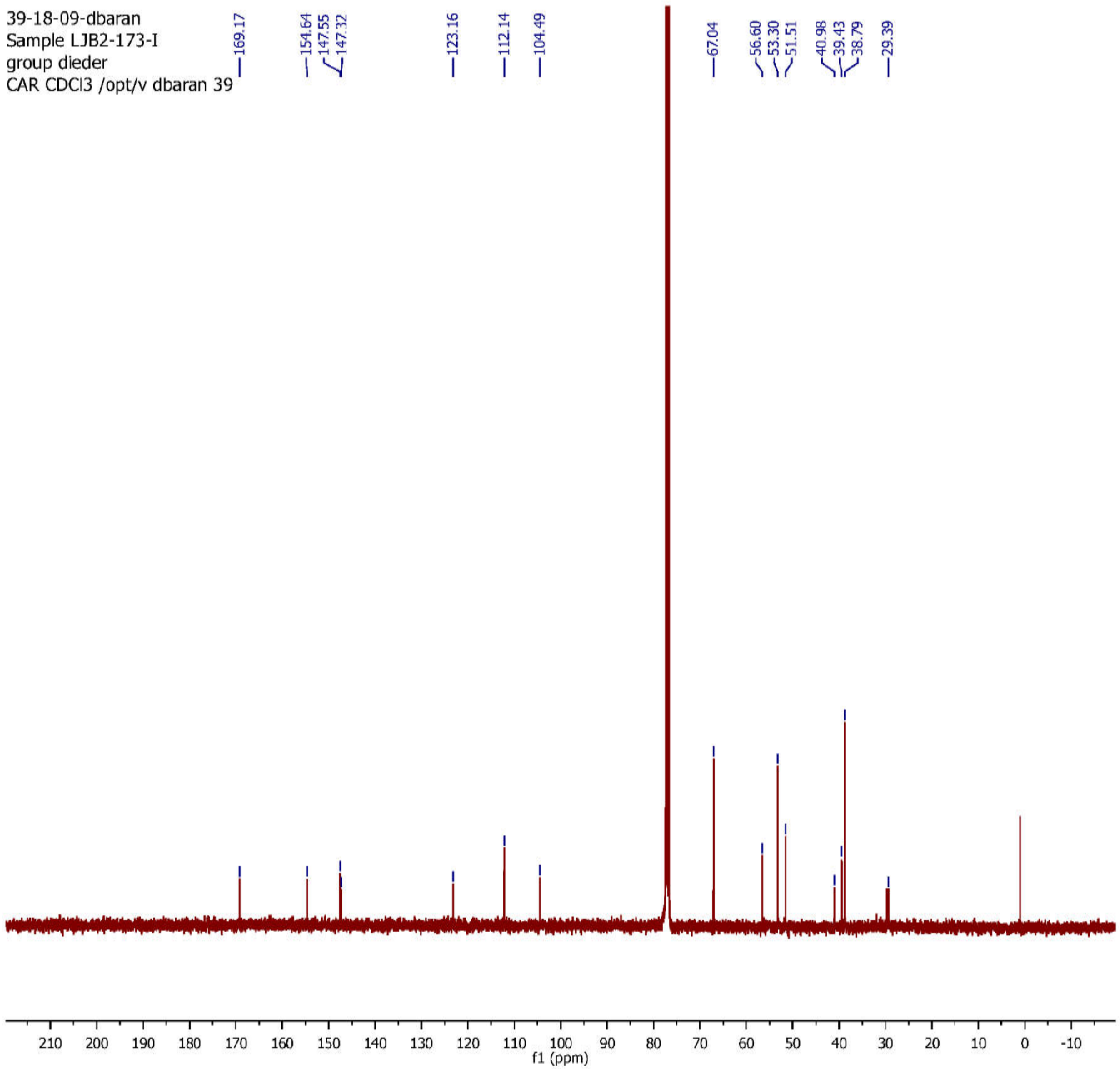


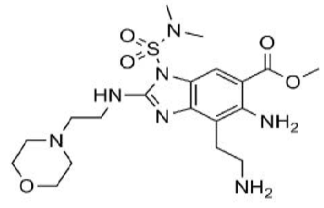


14b

Parameters

Parameter	Value
Title	39-18-09-dbaran
Origin	Bruker BioSpin GmbH
Owner	locnmr
Solvent	CDCl3
Pulse Sequence	zg30
Acquisition Date	2010-09-18T19:43:00
Modification Date	2010-09-19T14:52:27
Temperature	298.1
Number of Scans	16
Spectrometer Frequency	400.13
Spectral Width	8250.8
Lowest Frequency	-1654.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



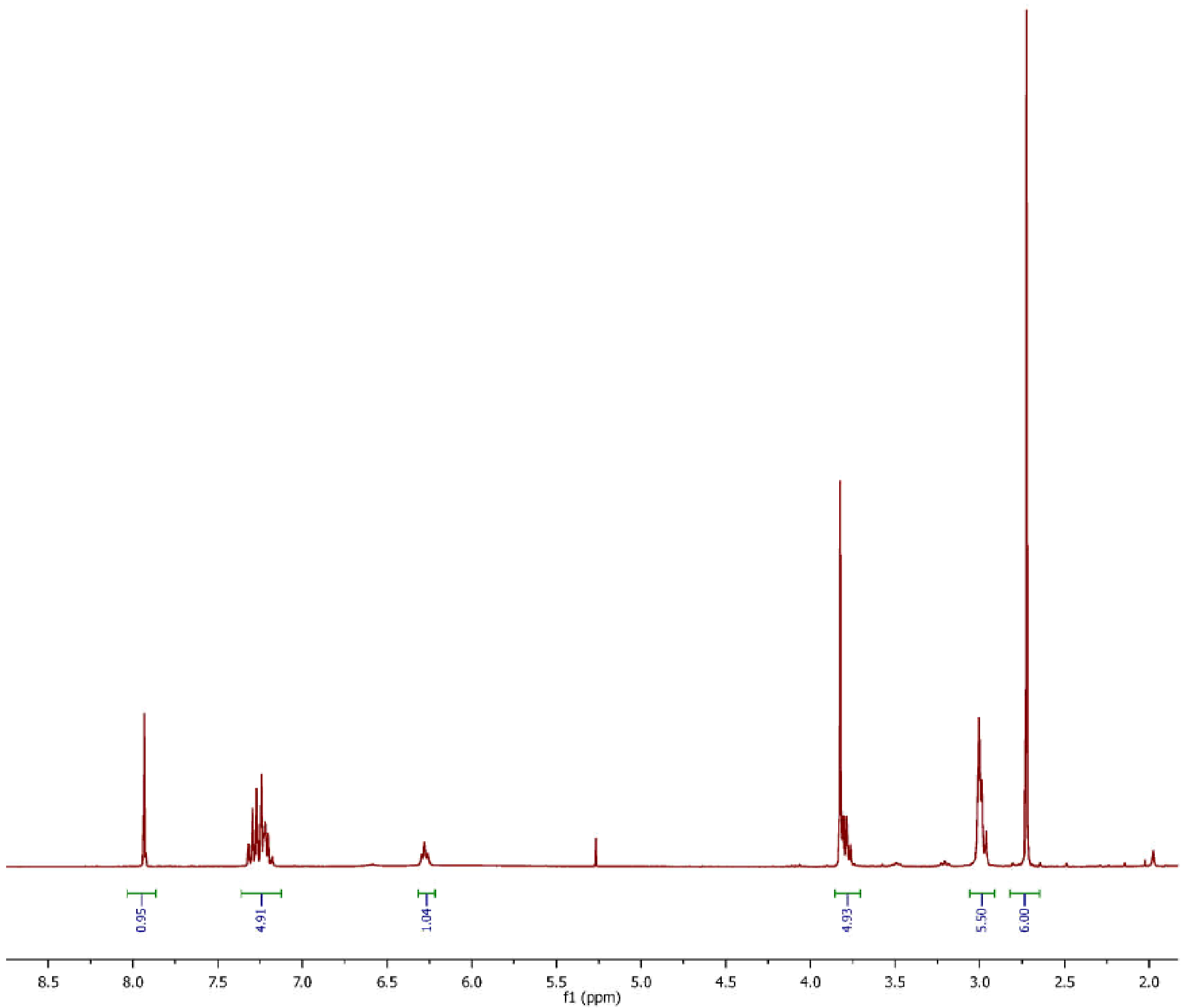


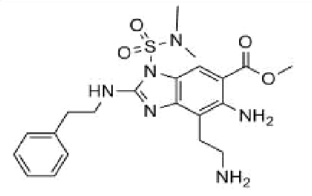
14b

Parameters

Parameter	Value
Title	39-18-09-dbaran
Origin	Bruker BioSpin GmbH
Owner	locnmr
Solvent	CDCl3
Pulse Sequence	zgpg30
Acquisition Date	2010-09-19T00:09:00
Modification Date	2010-09-19T14:52:30
Temperature	298.1
Number of Scans	4500
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

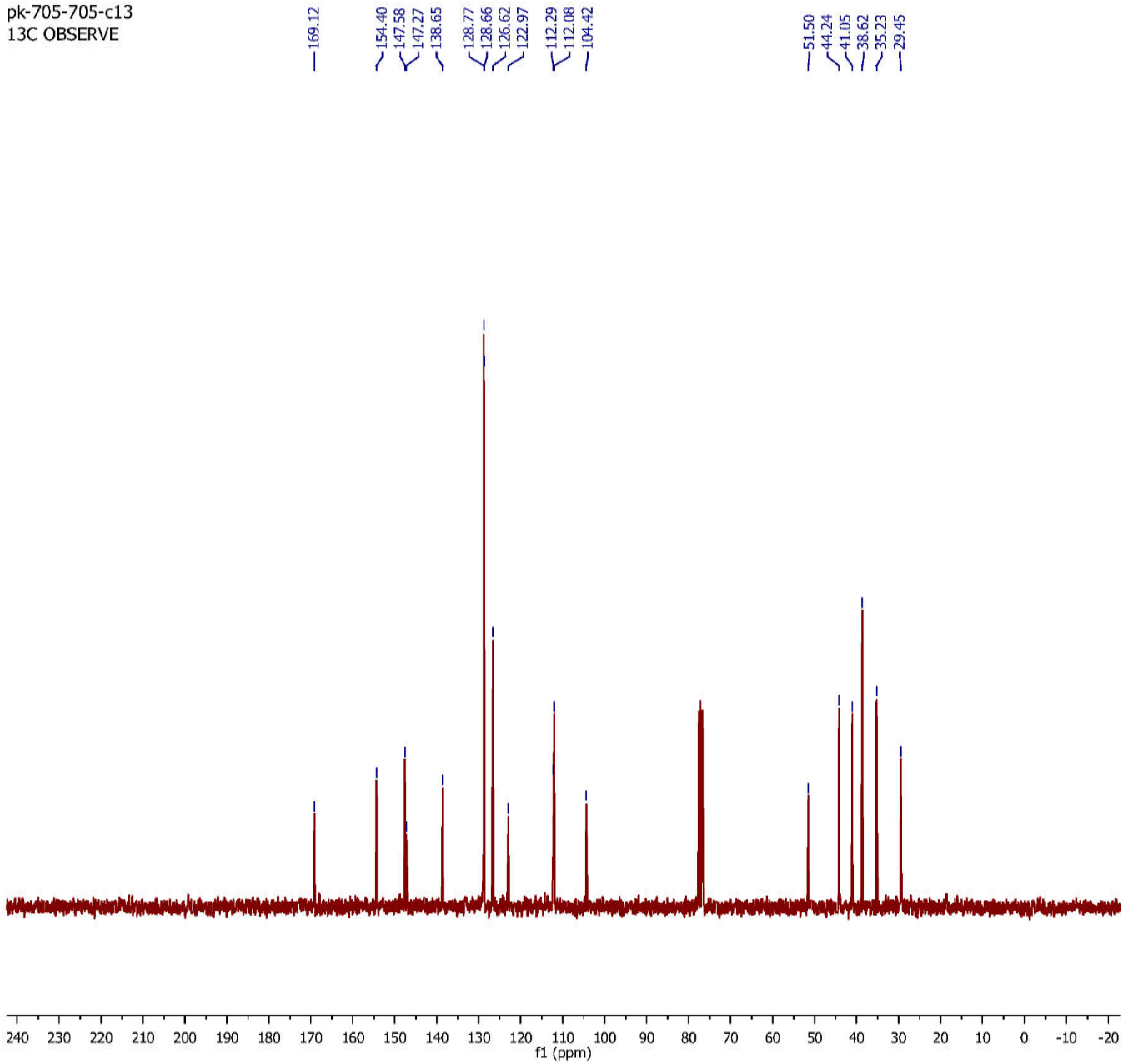
pk-705-705
STANDARD 1H OBSERVE

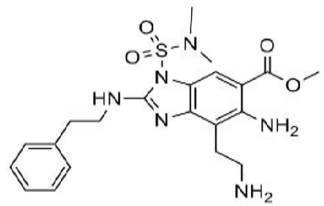




14c

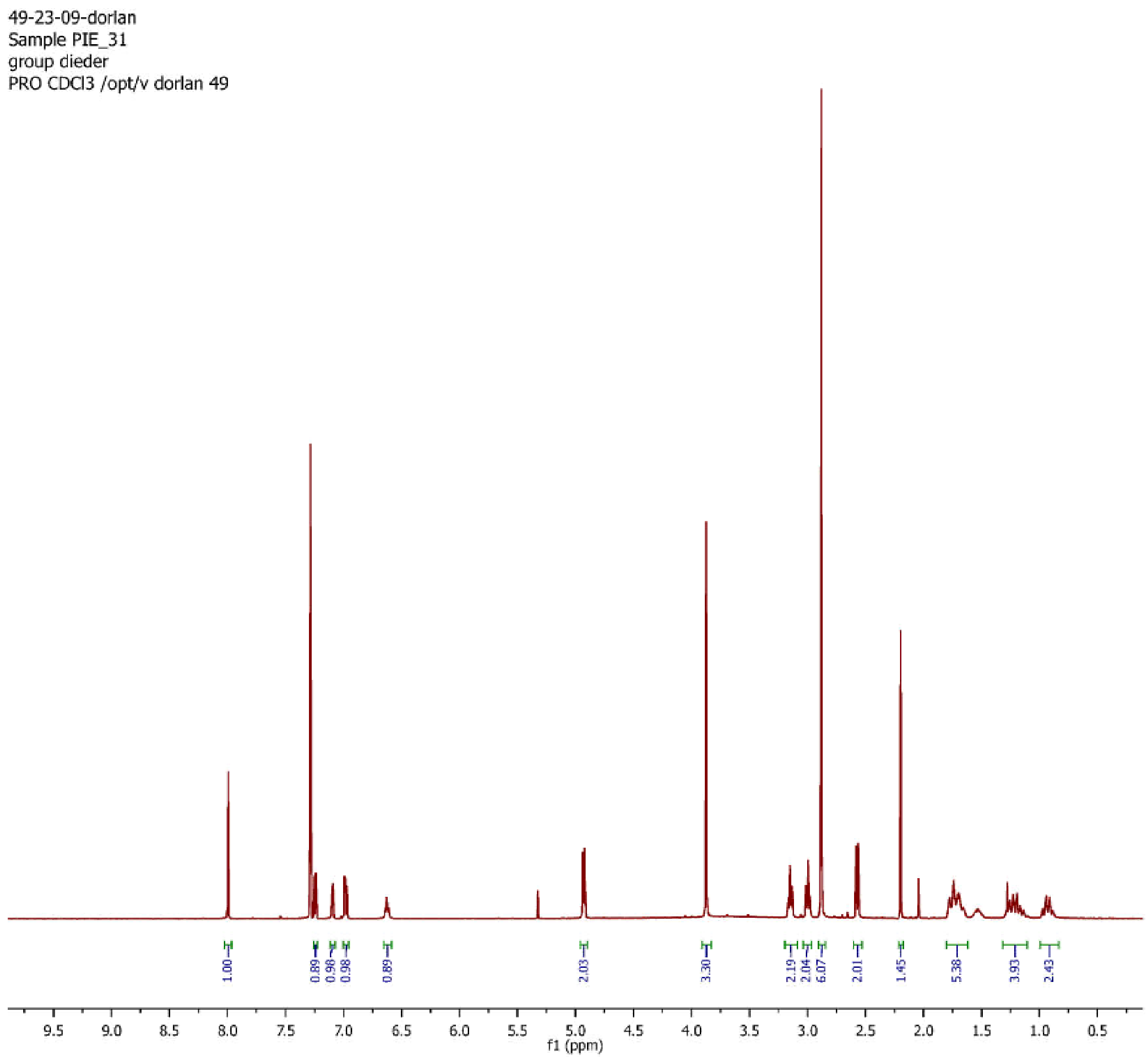
	Parameter	Value
1	Title	pk-705-705
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	16
10	Receiver Gain	12
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	3.1377
14	Acquisition Date	2009-04-02T09:15:16
15	Modification Date	2009-05-07T15:30:04
16	Spectrometer Frequency	299.77
17	Spectral Width	4500.5
18	Lowest Frequency	-363.9
19	Nucleus	1H
20	Acquired Size	14121
21	Spectral Size	32768

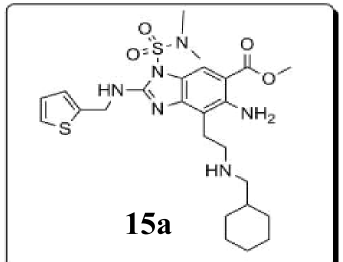




14c

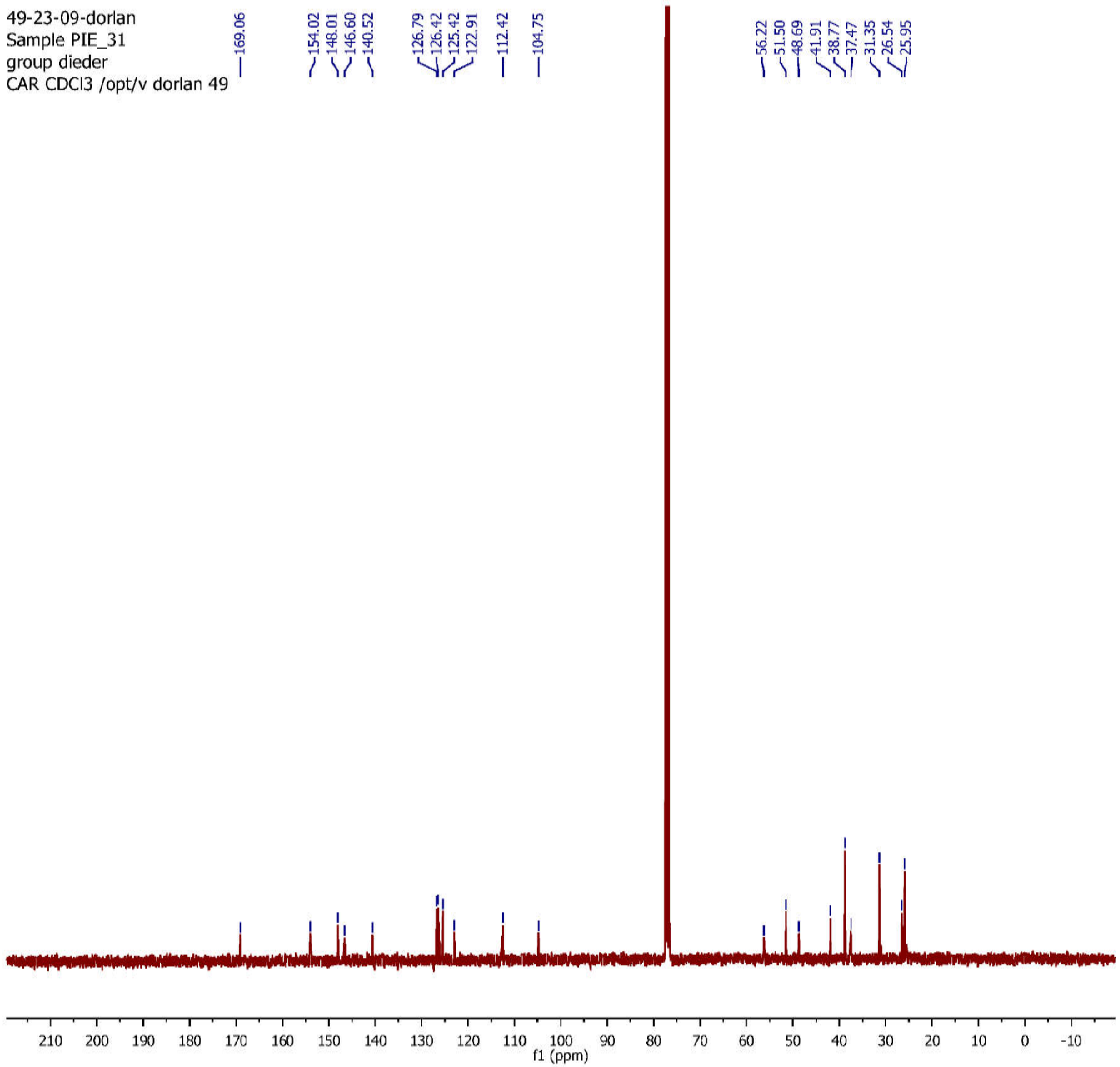
	Parameter	Value
1	Title	pk-705-705-c13
2	Comment	13C OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	64
10	Receiver Gain	30
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.3000
14	Acquisition Date	2009-04-02T09:15:35
15	Modification Date	2009-05-07T15:30:02
16	Spectrometer Frequency	75.39
17	Spectral Width	20000.0
18	Lowest Frequency	-1732.1
19	Nucleus	13C
20	Acquired Size	26000
21	Spectral Size	65536

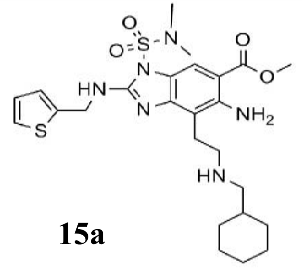




15a

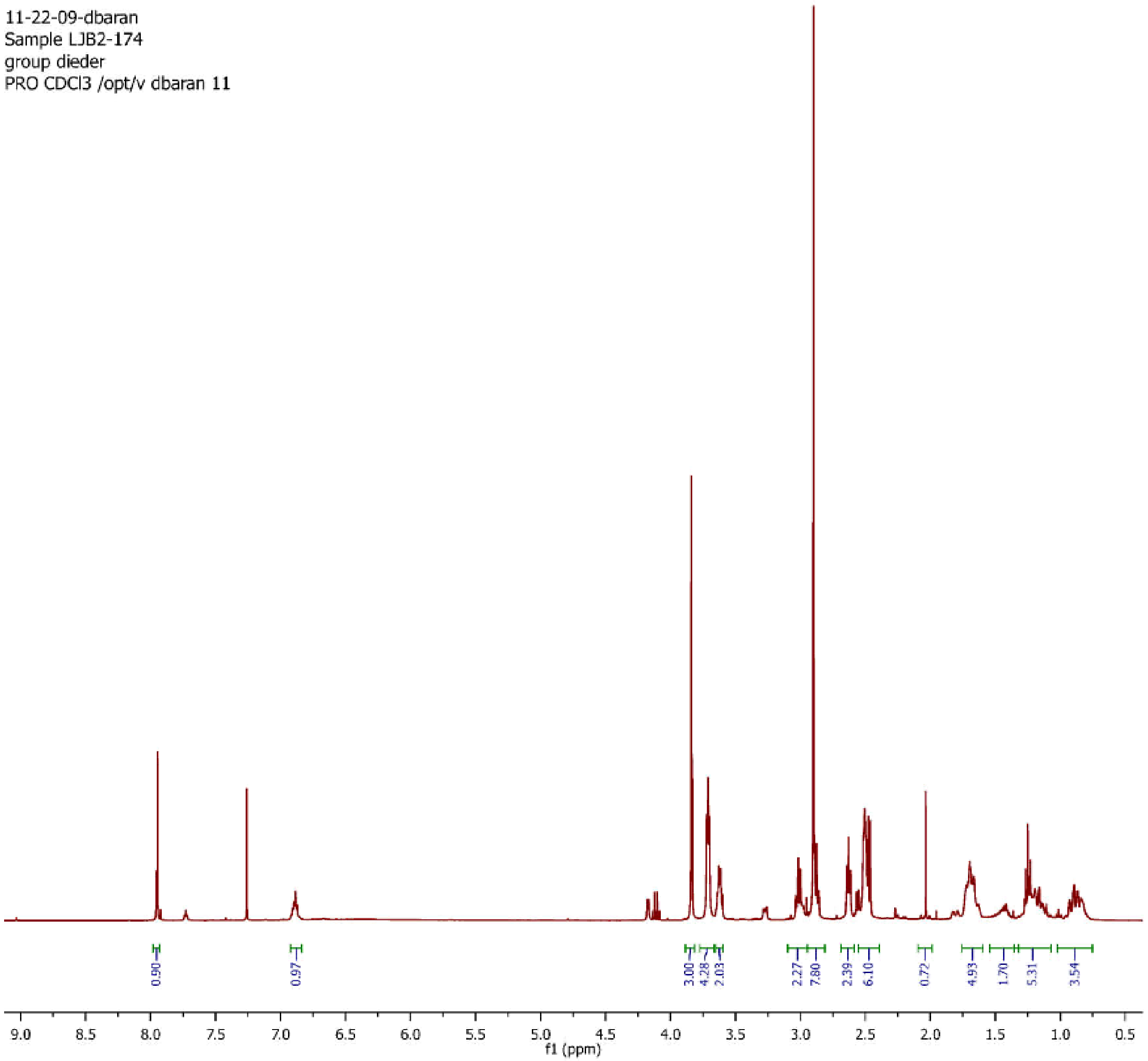
	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 49-23-09-dorlan/ 10/ fid
2	Title	49-23-09-dorlan
3	Comment	Sample PIE_31 group dieder PRO CDCl3 / opt/ v dorlan 49
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.1000
17	Acquisition Time	3.9846
18	Acquisition Date	2010-09-24T01:52:00
19	Modification	2010-09-24T11:00:40

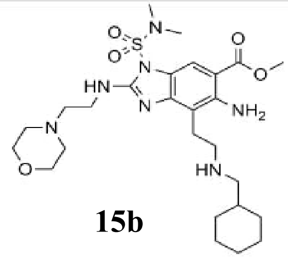




15a

	Parameter	Value
1	Data File Name	C:/ Users/ pierfrancesco/ Desktop/ dorlan/ 49-23-09-dorlan/ 11/ fid
2	Title	49-23-09-dorlan
3	Comment	Sample PIE_31 group dieder CAR CDCl3 / opt/ v dorlan 49
4	Origin	Bruker BioSpin GmbH
5	Owner	locnmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.0
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	1500
14	Receiver Gain	203
15	Relaxation Delay	2.0000
16	Pulse Width	9.1000
17	Acquisition Time	1.3632
18	Acquisition Date	2010-09-24T03:19:00

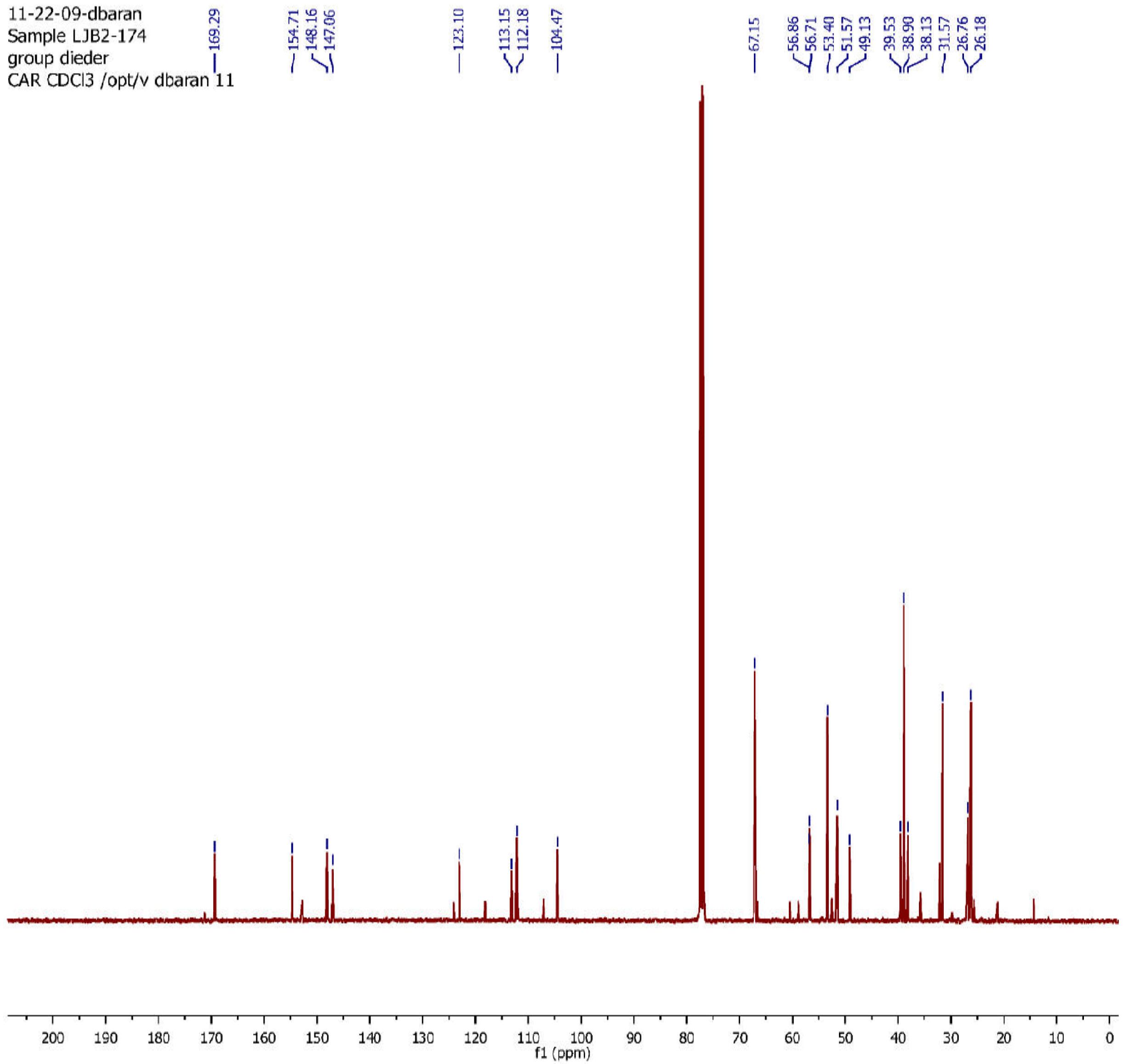


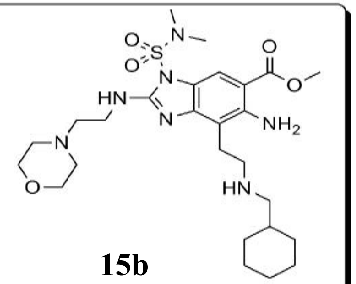


15b

Parameters

Parameter	Value
Title	11-22-09-dbaran
Origin	Bruker BioSpin GmbH
Owner	locnmr
Solvent	CDCl3
Pulse Sequence	zg30
Acquisition Date	2010-09-23T02:32:00
Modification Date	2010-09-23T08:19:19
Temperature	298.0
Number of Scans	16
Spectrometer Frequency	400.13
Spectral Width	8250.8
Lowest Frequency	-1654.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



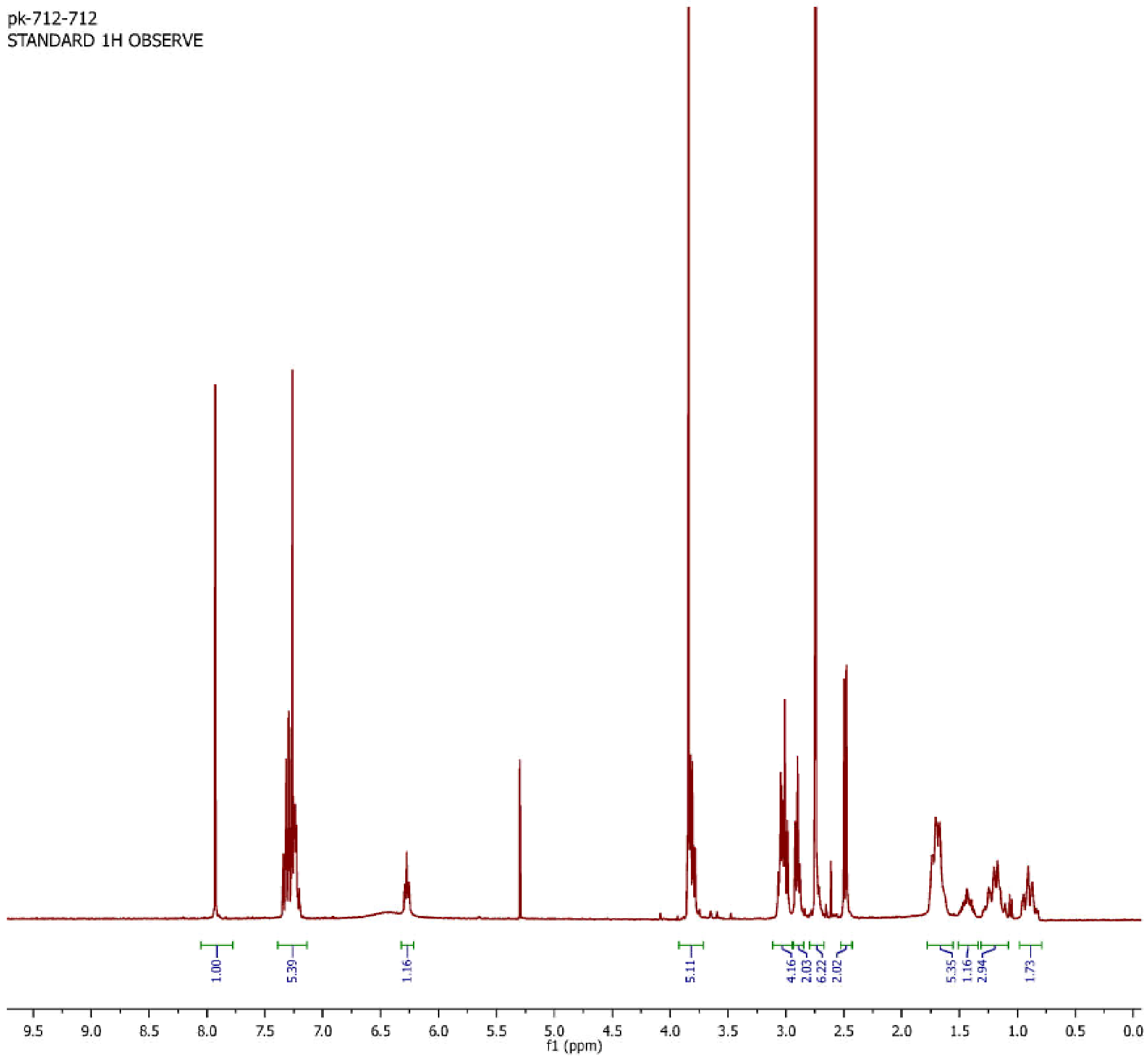


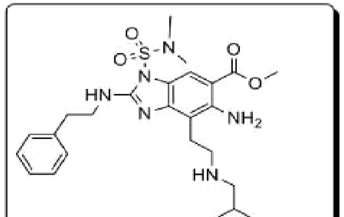
15b

Parameters

Parameter	Value
Title	11-22-09-dbaran
Origin	Bruker BioSpin GmbH
Owner	locnmr
Solvent	CDCl3
Pulse Sequence	zgpg30
Acquisition Date	2010-09-23T07:27:00
Modification Date	2010-09-23T08:19:22
Temperature	298.1
Number of Scans	5000
Spectrometer Frequency	100.61
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

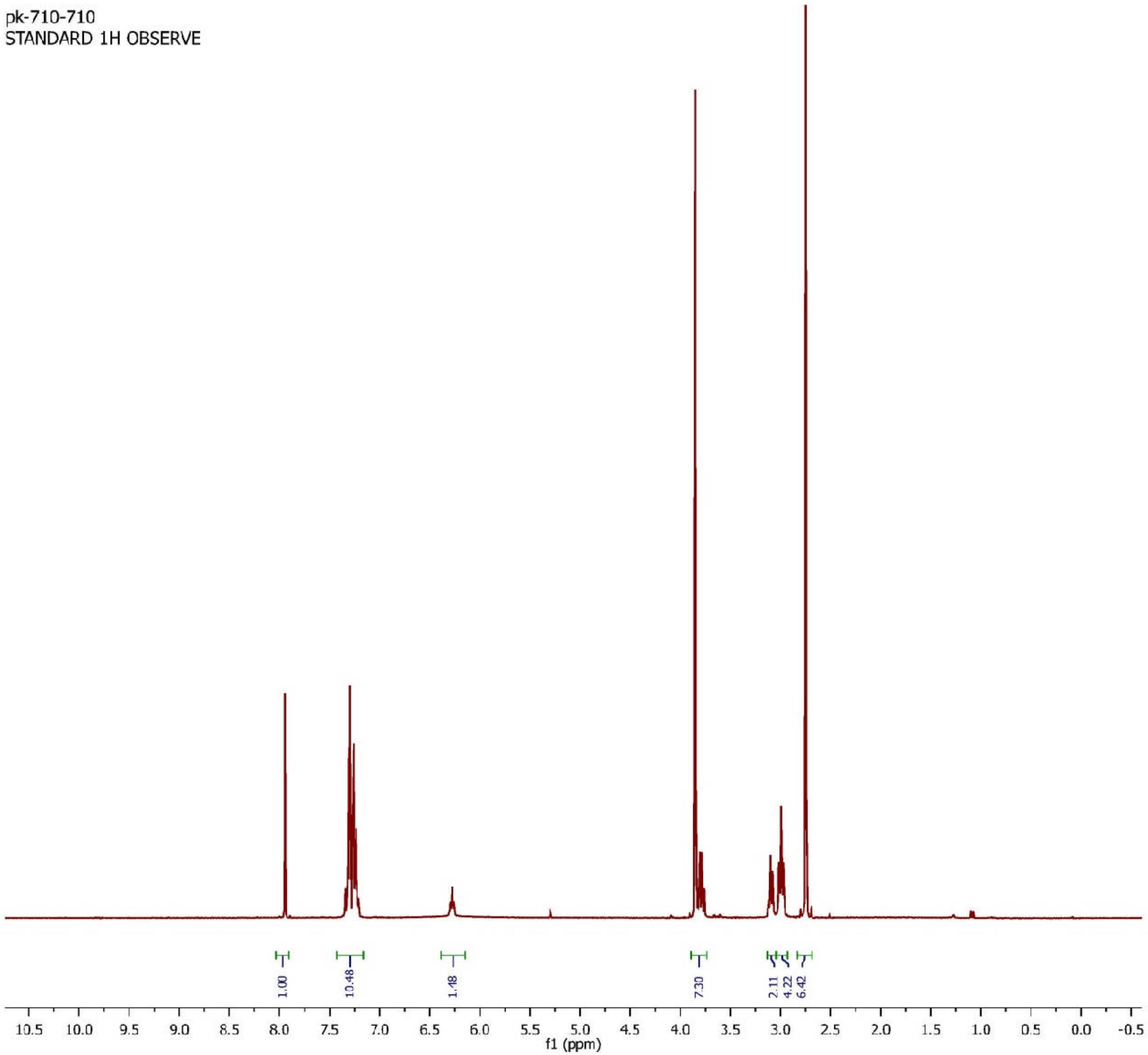
pk-712-712
STANDARD 1H OBSERVE

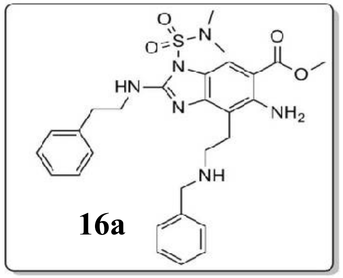




15c

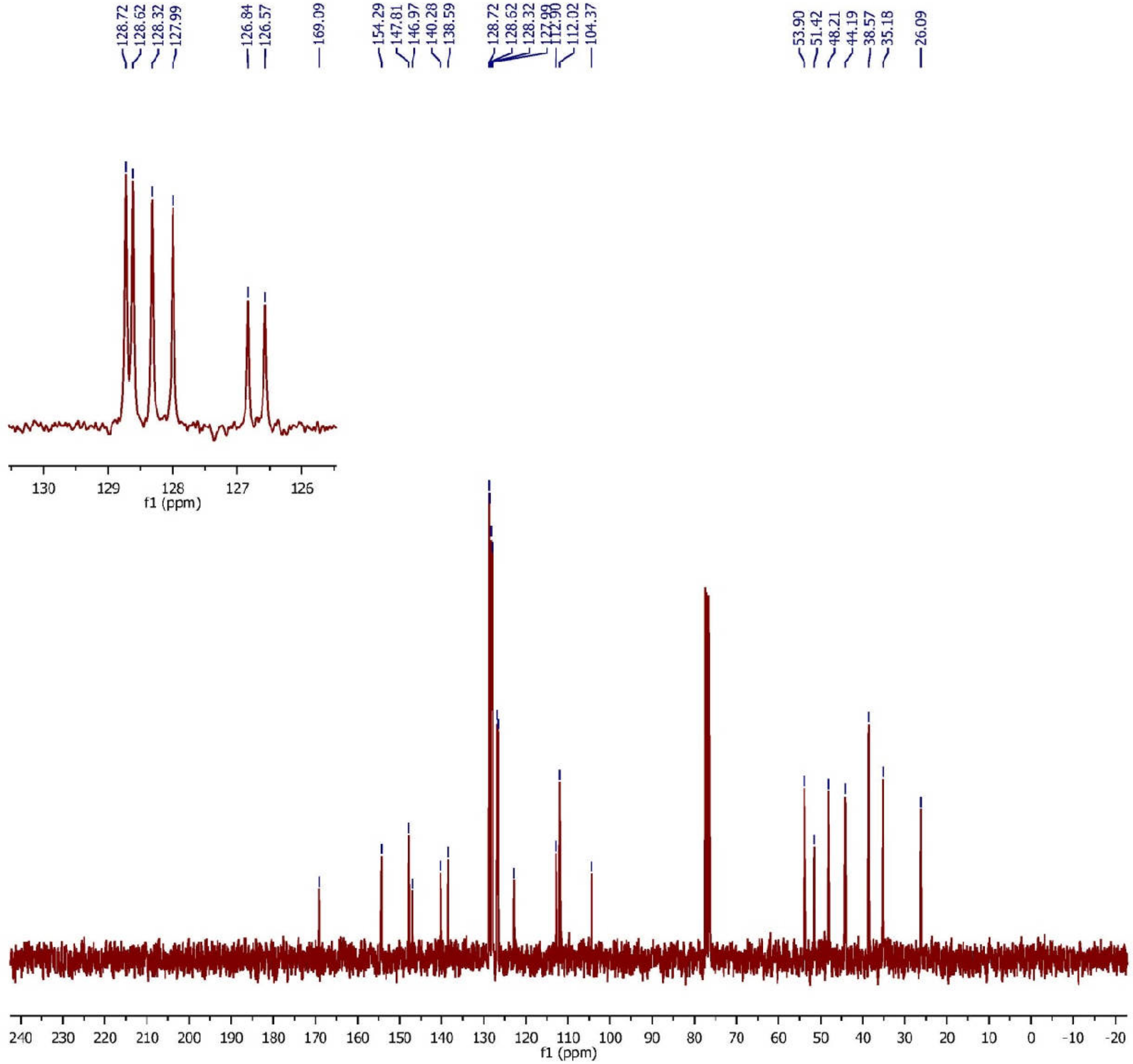
	Parameter	Value
1	Title	pk-712-712
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Solvent	CDCl3
6	Temperature	29.0
7	Pulse Sequence	s2pul
8	Experiment	1D
9	Number of Scans	16
10	Receiver Gain	26
11	Relaxation Delay	0.0000
12	Pulse Width	0.0000
13	Acquisition Time	3.1376
14	Acquisition Date	2009-05-12T19:19:30
15	Modification Date	2009-05-13T10:32:52
16	Spectrometer Frequency	300.22
17	Spectral Width	5099.4
18	Lowest Frequency	-640.4
19	Nucleus	1H
20	Acquired Size	16000
21	Spectral Size	32768

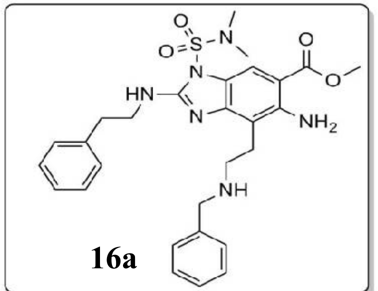




16a

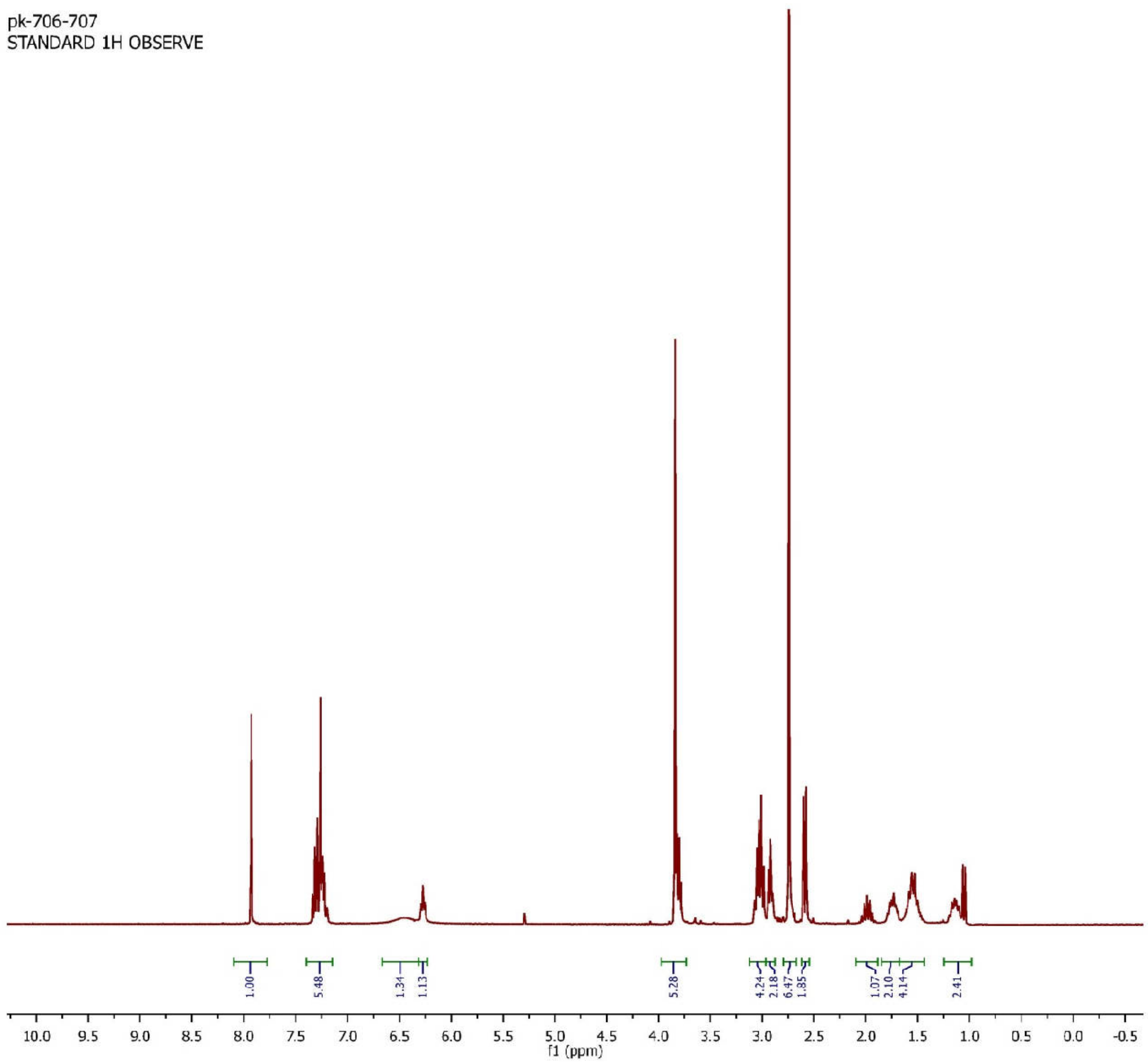
	Parameter	Value
1	Title	pk-710-710
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Author	
6	Solvent	CDCl3
7	Temperature	29.0
8	Pulse Sequence	s2pul
9	Experiment	1D
10	Number of Scans	16
11	Receiver Gain	24
12	Relaxation Delay	1.0000
13	Pulse Width	0.0000
14	Acquisition Time	3.1377
15	Acquisition Date	2009-05-07T08:19:00
16	Modification Date	2009-05-07T08:43:28
17	Spectrometer Frequency	299.77
18	Spectral Width	4500.5
19	Lowest Frequency	-362.4
20	Nucleus	1H
21	Acquired Size	14121
22	Spectral Size	32768

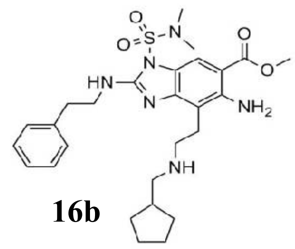




16a

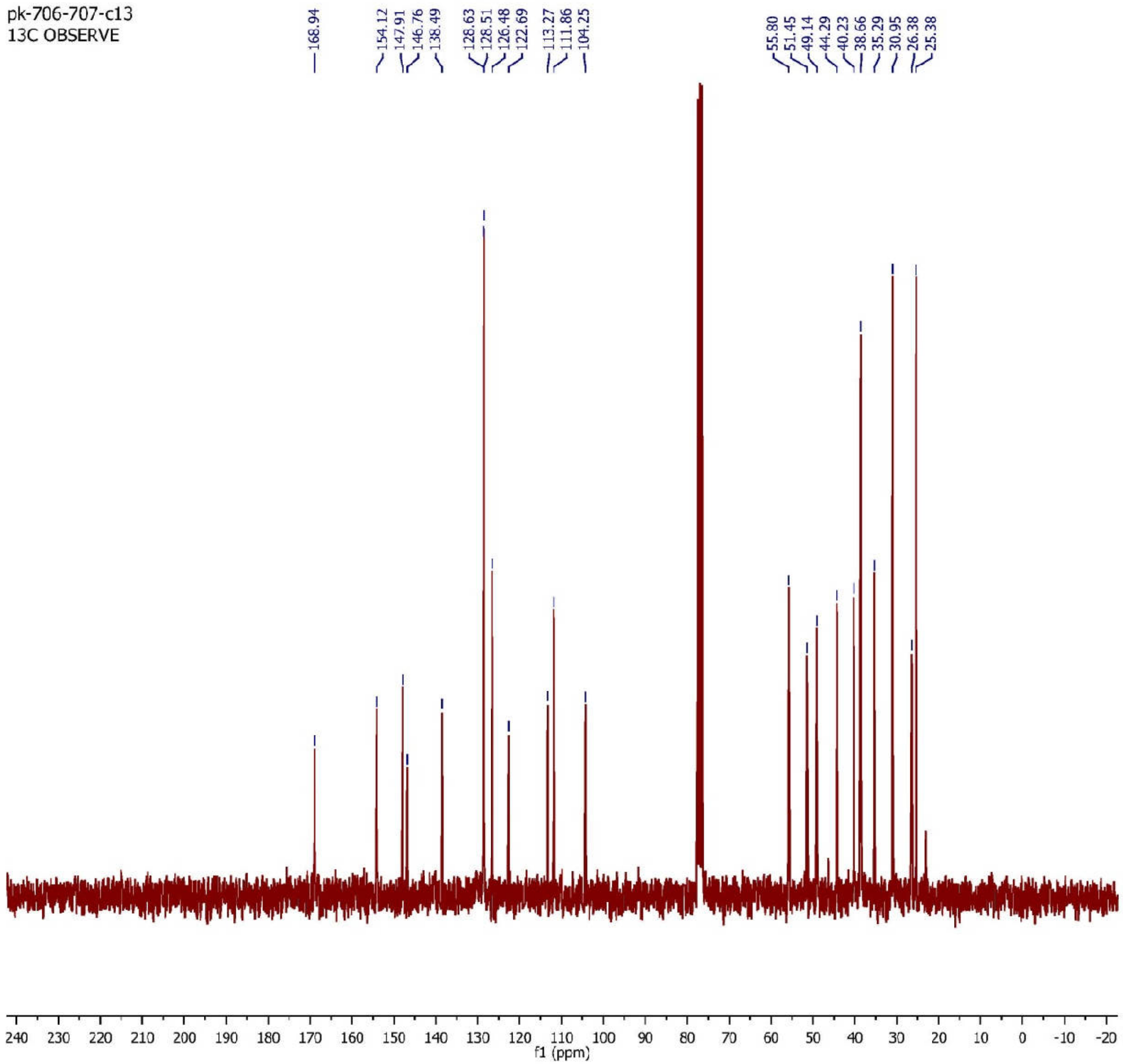
Parameter	Value
1 Title	pk-710-710-c13
2 Comment	13C OBSERVE
3 Origin	Varian
4 Spectrometer	mercury
5 Author	
6 Solvent	CDCl3
7 Temperature	29.0
8 Pulse Sequence	s2pul
9 Experiment	1D
10 Number of Scans	128
11 Receiver Gain	36
12 Relaxation Delay	1.0000
13 Pulse Width	0.0000
14 Acquisition Time	1.3000
15 Acquisition Date	2009-05-07T08:19:18
16 Modification Date	2009-05-07T08:43:24
17 Spectrometer Frequency	75.39
18 Spectral Width	20000.0
19 Lowest Frequency	-1724.8
20 Nucleus	13C
21 Acquired Size	26000
22 Spectral Size	65536

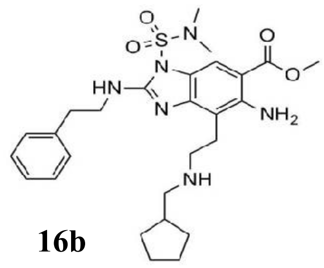




16b

Parameter		Value
1	Title	pk-706-707
2	Comment	STANDARD 1H OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Author	
6	Solvent	CDCl3
7	Temperature	29.0
8	Pulse Sequence	s2pul
9	Experiment	1D
10	Number of Scans	16
11	Receiver Gain	20
12	Relaxation Delay	0.0000
13	Pulse Width	0.0000
14	Acquisition Time	3.1376
15	Acquisition Date	2009-04-09T11:49:09
16	Modification Date	2009-04-09T12:10:32
17	Spectrometer Frequency	300.22
18	Spectral Width	5099.4
19	Lowest Frequency	-640.7
20	Nucleus	1H
21	Acquired Size	16000
22	Spectral Size	32768





16b

	Parameter	Value
1	Title	pk-706-707-c13
2	Comment	13C OBSERVE
3	Origin	Varian
4	Spectrometer	mercury
5	Author	
6	Solvent	CDCl3
7	Temperature	29.0
8	Pulse Sequence	s2pul
9	Experiment	1D
10	Number of Scans	484
11	Receiver Gain	36
12	Relaxation Delay	1.0000
13	Pulse Width	0.0000
14	Acquisition Time	1.3000
15	Acquisition Date	2009-04-09T11:52:22
16	Modification Date	2009-04-09T12:49:24
17	Spectrometer Frequency	75.50
18	Spectral Width	20000.0
19	Lowest Frequency	-1712.4
20	Nucleus	13C
21	Acquired Size	26000
22	Spectral Size	65536