Supporting Information

The Bull-James Assembly as a Chiral Auxiliary and Shift Reagent in Kinetic Resolution of Alkyne Amines by the CuAAC Reaction

William D. G. Brittain,[a,b] Brette M. Chapin,[a,b] Wenlei Zhai,[a,b] Vincent M. Lynch,[b] Benjamin R. Buckley,[c] Eric V. Anslyn[b] and John S. Fossey[a]

[a]School of Chemistry, University of Birmingham, Edgbaston, Birmingham, West Midlands, B15 2TT, UK
[b]Department of Chemistry, The University of Texas at Austin, Austin, Texas, 78712, USA
[c] Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

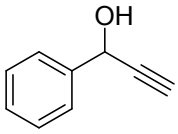
Contents

General

Reagents were used as purchased from suppliers without further purification; in cases where anhydrous solvents were required they were dried using a solvent purification system (SPS) which is monitored by Karl-Fisher titrations for water levels. 2-Formylphenylboronic acid was recrystallised from dichloromethane and hexane before use. ^{1}H NMR spectra were recorded at 300 MHz and 400 MHz using Bruker AVIII 300 and Bruker AVIII 400 NMR, Varian DirectDrive 400 spectrometers. ^{13}C NMR experiments were carried out on a Bruker AVIII 400 NMR and Varian DirectDrive 400 NMR spectrometer recorded at 101 MHz; in cases where it was required 2D NMR techniques were used to confirm compound identity. ^{1}H NMR chemical shifts are reported in ppm relative to TMS (δ 0.00) and ^{13}C NMR relative to chloroform (δ 77.36). Reactions carried out at low temperatures were cooled using a Lab Plant Cryoprobe or dry ice / acetone bath on a case by case basis. Melting points were carried out in triplicate and an average of the values taken and reported as a range using Stuart SMP10 melting point apparatus. IR spectra were recorded on a PerkinElmer 100FT-IR spectrometer at room temperature using ATR. HPLC analysis was carried out using an Agilent 1260 Infinity and Chiralpak IA column, and traces were recorded at eight UV wavelengths 210, 214, 230, 250, 254, 260, 273 and 280 nm. Calculations were carried out using the supplied traces recorded at 254 nm. GC analysis was carried out on a Varian 430-GC using a Chiralsil-Dex CB chiral column using a UV detector. Column chromatography was carried out using a Combiflash R*f* 200i, column traces were recorded at two UV wavelengths (254 nm and 280 nm).

Synthesis

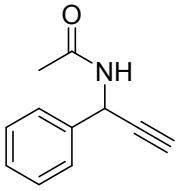
Synthesis of 1-phenylprop-2-yn-1-ol (8)



Under an atmosphere of nitrogen, a solution of benzaldehyde (1.0 mL, 10.0 mmol) in THF (10 mL) was stirred at -78 °C using a dry ice and acetone bath. To this solution ethynylmagnesium bromide (24 mL, 0.5 M in THF) was added dropwise over a period of 10 minutes with stirring. This was then allowed to slowly warm to room temperature and stirred for a further 3 h. The reaction mixture was then quenched with sat. NH_4Cl solution, and extracted with DCM (3 x 50 mL). The combined organic fractions were washed with water (100 mL), dried with $MgSO_4$ and concentrated *in vacuo*. The resulting brown oil was purified by automated flash column chromatography combiflash Rf (0-100% EtOAc : hexane gradient, 20 mins) to yield the product as a yellow oil 1.2 g, 91% yield.

Characterisation was consistent with literature.[1] δ_H (400 MHz, $CDCl_3$) 7.58 – 7.51 (2 H, m), 7.41 – 7.31 (3 H, m), 5.45 (1 H, d, *J* 1.5), 2.66 (1 H, d, *J* 2.3), 2.44 (1 H, br s); δ_C (101 MHz, $CDCl_3$) 140.05, 128.70, 128.58, 126.63, 83.52, 74.86, 64.43; IR ν_{max} (ATR)/cm^{-1} 3431, 3289, 3066, 3032, 1453, 1019, 947; MS AP$^-$ *m/z* 131.0 $[M-H]^-$; HRMS (AP$^-$-TOF) Calculated for $C_9H_7O^-$ = 131.0502 Found = 131.0494

Synthesis of *N*-(1-phenylprop-2-yn-1-yl)acetamide (9)

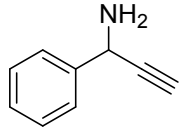


To a mixture of 1-phenyl-2-propynyl-1-ol (**13**) (1.11 g, 8.4 mmol) and anhydrous sodium sulphate (1.2 g, 8.4 mmol) in acetonitrile (20 mL) at 0 °C was added a solution of 95% sulphuric acid (4.28 g, 42 mmol, 2.9 mL) in acetonitrile (10 mL). The mixture was allowed to warm to room temperature and stirred for 48h. The solution

was then concentrated in *vacuo* and the residue poured onto ice. This mixture was then extracted with EtOAc (3 x 50mL) and then DCM (50 mL). The combined organic fractions were dried with $MgSO_4$ and concentrated *in vacuo*. The crude mixture was subjected to automated flash column chromatography combiflash Rf (0-100% EtOAc : Hexane gradient, 20 mins) to yield the product as a cream coloured solid 0.87 g, 59% yield.

Characterisation was consistent with literature.[2] δ_H (400 MHz, $CDCl_3$) 7.51 – 7.49 (2 H, m), 7.40 – 7.30 (3 H, m), 6.03 (1 H, s), 2.51 – 2.48 (1 H, m), 2.02 (3 H, s); δ_C (101 MHz, $CDCl_3$) 168.79, 138.27, 128.78, 128.29, 127.05, 81.70, 72.99, 44.53, 23.18; IR ν_{max} (ATR)/cm^{-1} 3280, 3038, 1648, 1532, 1452, 1371, 1309, 1092; MS AP+ *m/z* 174.1 $[M+H]^+$; HRMS (AP^+-TOF) Calculated for $C_{11}H_{12}NO^+$ = 174.0913 Found = 174.0913; MP 89 – 90 °C

Synthesis of 1-phenylprop-2-yn-1-amine (1)

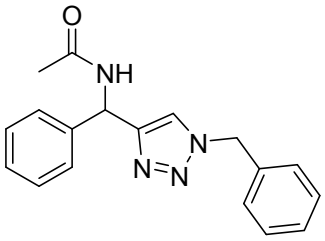


To a solution of *N*-(1-phenylprop-2-yn-1-yl)acetamide (**14**) (0.10 g, 0.76 mmol) in methanol (1 mL) was added 3.0 N aqueous HCl (20 mL) and the reaction mixture heated to 70°C for 18 h. The resulting solution was extracted with EtOAc (50 mL). The aqueous phase was basified with aqueous 2.0 N NaOH solution to pH ~ 10. This was then extracted with EtOAc (3 x 50mL), the organic layers were combined, dried with $MgSO_4$ and concentrated *in vacuo* to afford sufficiently pure 1-phenylprop-2-yn-1-amine as a yellow oil 0.036 g 35% yield. It was found that this compound will degrade if stored in its pure form, material was stored as a solution in chloroform in the freezer.

Characterisation was consistent with literature.[3] δ_H (300 MHz, $CDCl_3$) 7.58 – 7.50 (2 H, m), 7.40 – 7.29 (3 H, m), 4.78 (1 H, d, *J* 1.9), 2.49 (1 H, d, *J* 2.3), 1.91 (2 H, br s); δ_C (101 MHz,

$CDCl_3$) 141.59, 128.67, 127.82, 126.67, 86.01, 72.30, 47.31; IR ν_{max} (ATR)/cm^{-1} 3666, 3288, 1492, 1451, 1275; MS AP^+ *m/z* 132.1 $[M+H]^+$; HRMS (AP^+-TOF) Calculated for $C_{11}H_{12}NO^+$ = 132.0913 Found = 132.0814

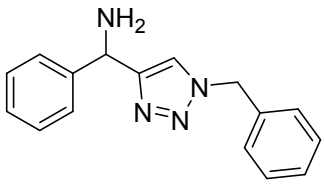
Synthesis of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)acetamide (10)



To a solution of *N*-(1-phenylprop-2-yn-1-yl)acetamide (**14**) (0.050 g, 0.30 mmol) and benzyl azide (0.044 g, 0.33 mmol) in methanol (20 mL) was added sodium L ascorbate (0.059 g, 0.30 mmol) and copper sulphate pentahydrate (0.008 g, 0.03 mmol). The mixture was allowed to stir at 50 °C for 3 h. The reaction mixture was quenched with 5% aqueous ammonia solution (10 mL). The solution extracted with EtOAc (3 x 25 mL) the combined organic extracts were washed with water (100 mL) dried with $MgSO_4$ and concentrated *in vacuo*. To give the pure triazole as a cream coloured solid 0.081 g 87% yield.

Characterisation was consistent with literature.[4] δ_H (400 MHz, $CDCl_3$) 7.39 – 7.21 (11 H, m), 6.95 (1 H, d, *J* 7.7), 6.27 (1 H, d, *J* 7.9), 5.47 (2 H, q, *J* 14.8), 2.01 (3 H, s); δ_C (101 MHz, $CDCl_3$) 169.26, 147.98, 140.88, 134.30, 129.17, 128.86, 128.71, 128.11, 127.73, 127.26, 121.53, 54.25, 49.56, 23.27; IR ν_{max} (ATR)/cm^{-1} 1721, 1653, 1489, 1345, 1278, 1154; MS ESI *m/z* 329.1 [M+Na]; MP 155 – 156 °C

Synthesis of (1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanamine (6)

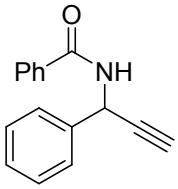


To a solution of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)acetamide (**15**) (0.25 g, 3.24 mmol) in methanol (2 mL) was added 3.0 N aqueous HCl (20 mL). The mixture heated to 70 °C for 18 h, after which the reaction mixture was extracted with EtOAc (50 mL), the aqueous

phase basified to pH ~ 10 with 2.0 N aqueous NaOH, extracted with EtOAc (3 x 50 mL) dried with $MgSO_4$ and concentrated *in vacuo*. To give the product as a cream coloured solid 0.48g 56% yield.

δ_H (400 MHz, $CDCl_3$) 7.44 – 7.13 (11 H, m), 5.45 (2 H, s), 5.36 (1 H, s) δ_C (101 MHz, $CDCl_3$) 152.76, 143.79, 134.64, 129.07, 128.66, 128.05, 127.50, 126.86, 120.73, 54.15, 52.54. IR ν_{max} (ATR)/cm^{-1} 3366, 3122, 3064, 2925, 2853, 1494, 1454, 1216; MS ESI *m/z* 287.1 $[M+Na]^-$; HRMS (ESI-TOF) Calculated for $C_{16}H_{16}N_4Na^-$ = 287.1278 Found = 287.1274.; MP 86 - 88°C

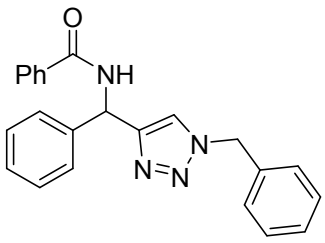
Synthesis of *N*-(1-phenylprop-2-yn-1-yl)benzamide (11)



To a solution of 1-phenylprop-2-yn-1-amine (**8**) (10 mg, 0.08 mmol) in DCM (10 mL) cooled in an ice bath was added benzoyl chloride (11 mg, 8.8 μL, 0.08 mmol) and TEA (8.0 mg, 10 μL, 0.08 mmol). The reaction was allowed to warm to room temperature and stirred for 2 h. The reaction was then quenched with water (10 mL) and extracted with EtOAc (3 x 25 mL) the organic fractions combined, dried over MgSO4 and concentrated *in vacuo*. The crude mixture was purified by automated flash column chromatography combiflash Rf (0-100% EtOAc : Hexane gradient, 20 mins) to yield the product as a white solid 15 mg, 84% yield.

δ_H (400 MHz, $CDCl_3$) 7.83 – 7.77 (2 H, m), 7.62 – 7.57 (2 H, m), 7.55 – 7.49 (1 H, m), 7.47 – 7.31 (5 H, m), 6.57 (1 H, d, *J* 7.9), 6.25 (1 H, dd, *J* 8.4, 2.4), 2.55 (1 H, d, *J* 2.4); δ_C (101 MHz, $CDCl_3$) 166.20, 138.21, 133.67, 131.92, 128.85, 128.66, 128.36, 127.11, 81.64, 73.33, 44.99; IR ν_{max} (ATR)/cm^{-1} 3291, 3034, 1639, 1522, 1488, 1331; MS AP^+ *m/z* 236.1 $[M+H]^+$; HRMS (AP^+-TOF) Calculated for $C_{16}H_{14}NO^+$ = 236.1070 Found = 236.1073; MP 131 – 132 °C; HPLC (IA) Hexane/IPA 80:20, 1.0 mL/min, λ = 254 nm, t_{major} = 7.9 min, t_{minor} = 8.8 min.

Synthesis of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)benzamide (12)

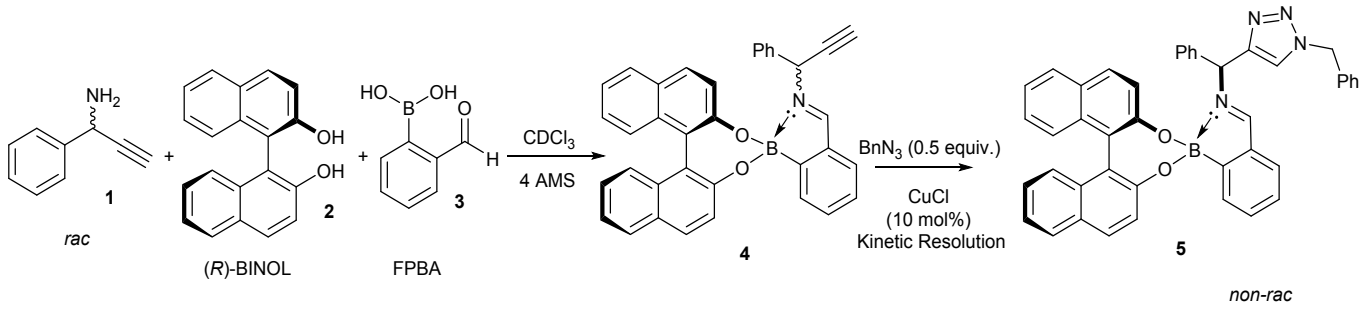


To a solution of (1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanamine (**11**) (0.079 g, 0.3 mmol) in DCM (10 mL) cooled in an ice bath was added benzoyl chloride (0.042 g, 35 μL, 0.3 mmol) and TEA (0.030 g, 42 μL, 0.3 mmol). The reaction allowed to warm to room temperature and stirred for 2 h. The reaction was then quenched with water (10 mL) and extracted with EtOAc (3 x 25 mL) the organic fractions combined, dried over $MgSO_4$ and concentrated in vacuo. The crude mixture was purified by automated flash column chromatography combiflash Rf (0-100% EtOAc : Hexane gradient, 20 mins) to yield the product as a white solid 0.102 g, 93% yield.

δ_H (400 MHz, $CDCl_3$) 7.83 (2 H, dd, *J* 5.2, 3.3), 7.58 (1 H, d, *J* 7.4), 7.52 – 7.21 (13 H, m), 6.46 (1 H, d, *J* 7.5), 5.49 (2 H, ABq, *J* 14.8); δ_C (101 MHz, $CDCl_3$) 166.51, 147.97, 140.93, 134.29, 134.03, 131.68, 129.18, 128.87, 128.77, 128.55, 128.13, 127.79, 127.30, 127.18, 121.58, 54.30, 50.12; IR ν_{max} (ATR)/cm^{-1} 3378, 3116, 1639, 1515, 1487, 1354; MS ESI *m/z* 391.2 $[M+Na]^-$; HRMS (ESI-TOF) Calculated for $C_{23}H_{20}N_4ONa^-$ = 391.1540 Found = 391.1541; MP 207 – 209 °C; HPLC (IA) Hexane/IPA 80:20, 1.0 mL/min, λ = 214 nm, t_{major} = 16.7 min, t_{minor} = 18.3 min.

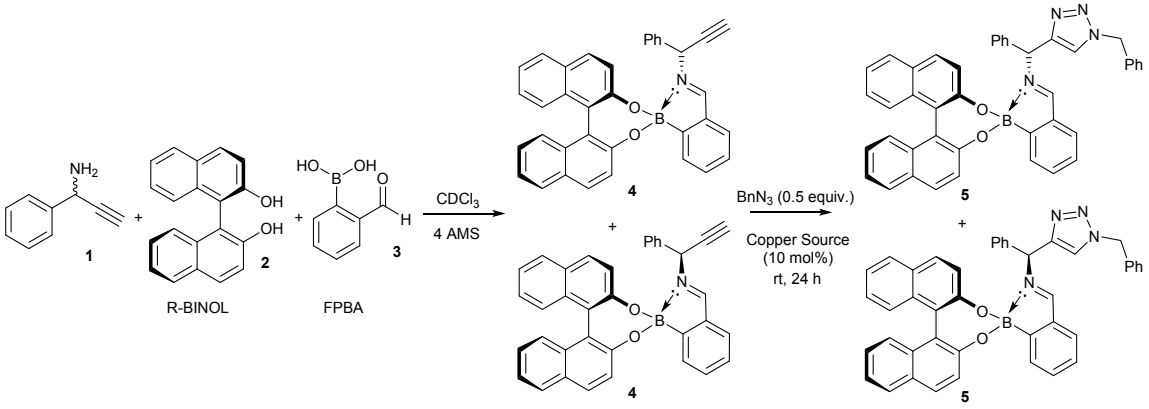
Catalysis

Representative assembly based reaction



A mixture of FPBA (5.7 mg, 0.038 mmol, 1 equiv.) and R-BINOL (10.9 mg, 0.038 mmol, 1 equiv.) were placed in a vial and dried under high vacuum for 2 hours, the mixture was removed from high vaccum and a solution of amine 8 (5.0 mg, 0.038 mmol, 1 equiv.) in $CDCl_3$ (0.5 mL) and dried over 4A MS was added. A small number of 4A MS were added to the vial and the contents stirred at rt for 20 mins. To this 0.1 mL of benzyl azide stock solution (24 µL per 1 mL, 0.5 equiv.) was added along with CuCl (0.19 mg, 0.0019 mmol, 5 mol%), the reaction was allowed to stir at rt for 24 h. After this time a ^1H NMR was taken of the reaction mixture to give the conversion and enantiomeric excess of **1** and **6**. To recover the alkyne **1** and triazole **6** after the reaction was completed 2.0 N HCl solution (5 mL) was added to the NMR sample and the combined solution was left to stir vigorously for 30 minutes. The mixture was then extracted with EtOAc (25 mL) and water (25 mL). The aqueous phase was then basified to pH ~ 10 using 2.0 N NaOH. The basified solution was then extracted with EtOAc (3 x 25 mL) the combined organic fractions were dried with $MgSO_4$ and concentrated *in vacuo* to give amine **1** and triazole **6** with minimal amounts of the other assembly components. Selected examples *e.e.* were verified *via* either chiral GC or chiral HPLC methodology. For HPLC determination benzoylation of the recovered mixture of components was carried out as detailed above.

Copper Source Screening table

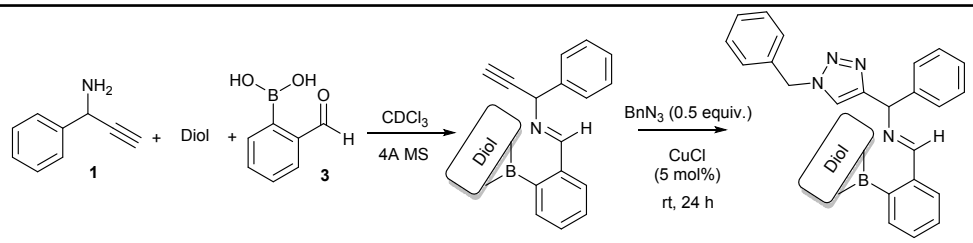


Entry	Copper Source	Conversion (%)[a]	eeSM (%)[b]	eeP (%)[b]	s
1	CuCl	30	23	39	4.1
2	CuBr	34	25	48	3.7
3	CuI[c]	39	21	13	2.4
2	Cu(OAc)	0	5	NA	NA
3	$Cu(OAc)_2$	11	6	19	3.1
4	$Cu(MeCN)_4 \bullet BF_4$	54	25	15	1.9
5	$CuSO_4$	0	0	NA	NA
6	$Cu(OTf)_2$	22	10	28	2.3
7	Cu(OTf) •0.5Toluene[c]	31	18	31	2.8
10	CuCl + TBTA 1:1[d]	68	30	13	1.7
11	Cu powder	0	0	NA	NA
12	Cu turnings	36	25	23	3.3
13	Copper acetylacetonate	0	0	NA	NA
14	Copper carbonate basic	0	0	NA	NA

15	$[Cu(CH_3CN)_4]PF_6$	50	36	16	3.0
16	$Cu(NO_3)_2*xH_2O$	0	0	NA	NA

[a]Conversion was determined by integration of ^{1}H NMR of the assembly comparing the imine proton of the starting material and triaolic product. [b]ee was determined via comparison of the integration values of the imine region diastereomers in the ^{1}H NMR of the assembly. [c]reaction was slow thus reaction time was increased to 48 h. [d]TBTA = Tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine

Diol Screening Table



Entry	Diol	Conversion (%)[a]	eeSM (%)[b]	eeP (%)[b]	s
1	Dimethyl-L-tartrate	25	15	5	3.0
3	(*S*)-1,2-propane diol	40	3	2	1.1
2	2*S*, 3*S*-butanediol	3	NA	NA	NA
3	*R*-1,1,2-triphenyl-1,2-ethanediol	40	29	19	3.3
4	*R*,*R*- 1,2 dicyclohexyl-1,2-ethanediol	82	2	9	1.0
7	(*S*)-(+)-1-phenyl-1,2-ethanediol	0	NA	NA	NA

[a]Conversion was determined via HPLC using the formula C = eeSM/(eeSM+eeP) where C = conversion, eeSM = ee of recovered starting material, eeP = ee of product. [b]ee was determined via chiral HPLC

Chromatography

Gas Chromatography

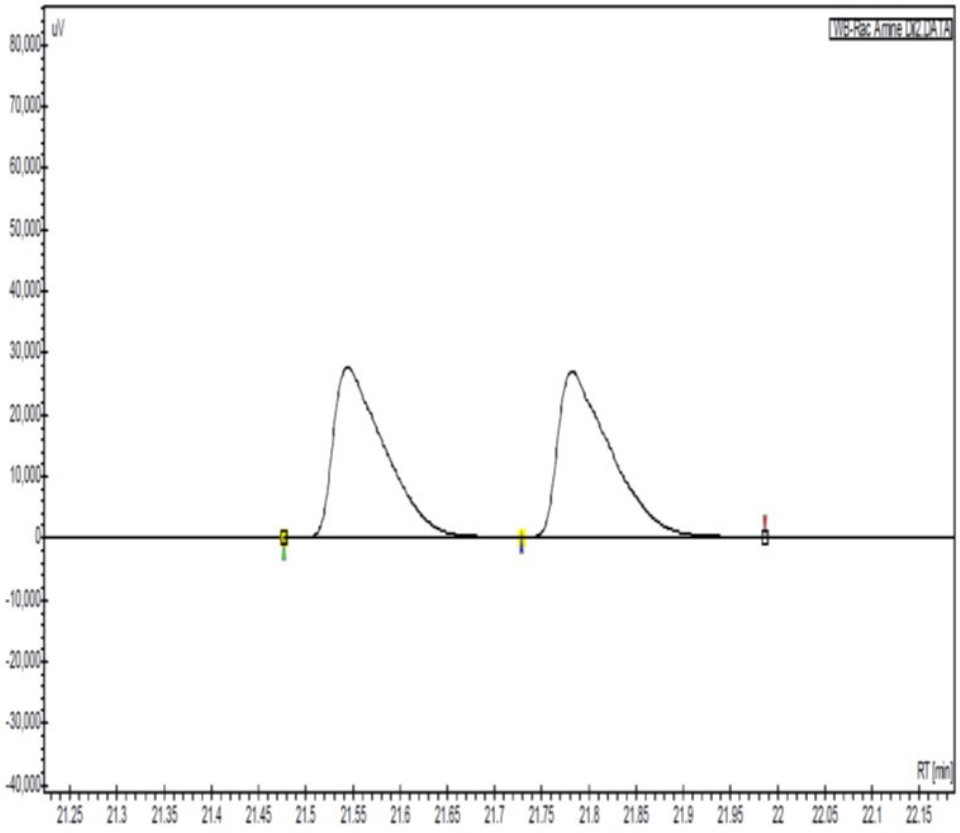
GC analysis was run on a Varian 430-GC using a Varian WCOT fused silica 25M x 0.25 mm, Chirasil-DEX CB DF = 0.25 column. The injector was given a setpoint of 200 °C, split state was on with a split ratio of 500. The column stabilisation time was set at 0.50 min. The column oven program was set to an initial temperature of 50 °C, which was then ramped at 3.7 °C per min until 200 °C was reached, and the oven held at 200 °C for 10 minutes to give an overall run length of 50.54 mins.

Chiral GC Trace of Racemic 1-phenylprop-2-yn-1-amine (1)

Rac Amine

Vial- 3
Method- GB METHOD.METH
Acq time- 04/11/2015 10:58:36
Injection volume- 5.000 µL
Sampelname- N.A.

UNIVERSITY OF BIRMINGHAM



Peak results :

WB-Rac Amine Dil2.DATA [FID]

Index	Time [Min]	Area [uV.Min]	Area % [%]
1	21.55	1742.3	49.858
2	21.78	1752.2	50.142

Rac Amine

Vial- 3
Method- GB METHOD.METH
Acq time- 04/11/2015 10:58:36
Injection volume- 5.000 µL
Sampelname- N.A.

UNIVERSITY OF BIRMINGHAM

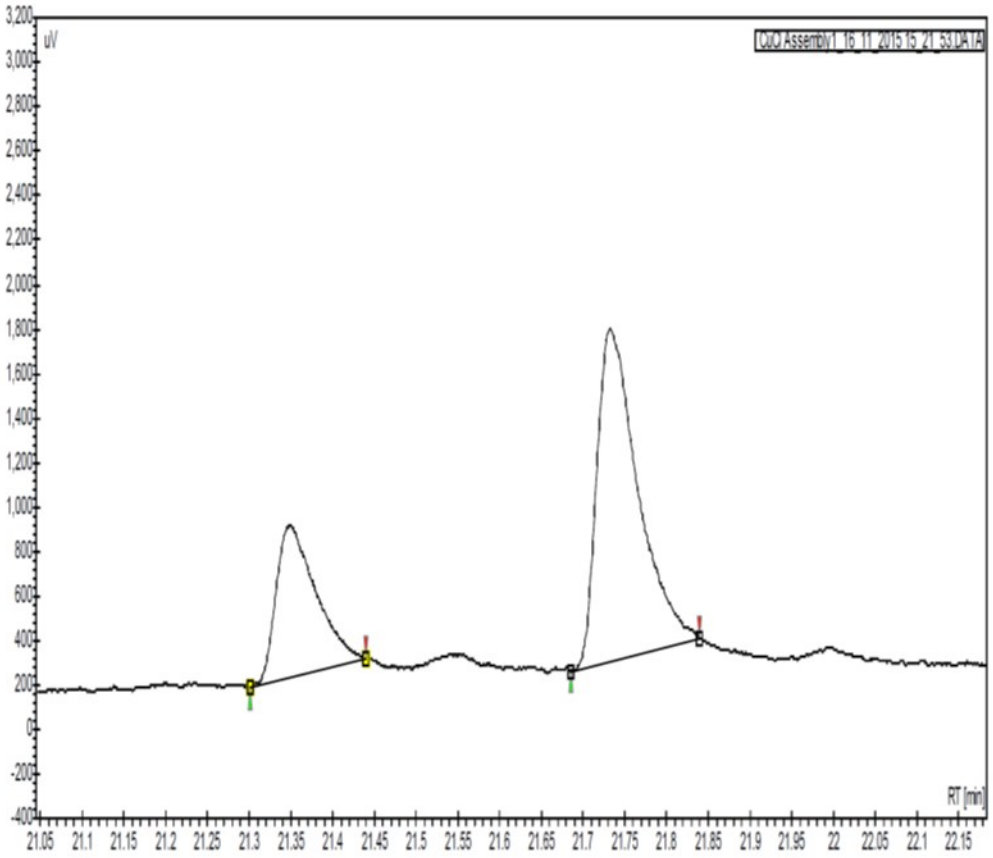
Index	Time [Min]	Area [uV.Min]	Area % [%]
Total		3494.5	100.000

Chiral GC Trace of 1-phenylprop-2-yn-1-amine (1) After Kinetic Resolution

CuCl Assembly

Vial- 15
Method- GB METHOD.METH
Acq time- 16/11/2015 15:30:42
Injection volume- 8.000 µL
Sampelname- N.A.

UNIVERSITY OF BIRMINGHAM



Peak results :

CuCl Assembly1_16_11_2015 15_21_53.DATA [FID]

Index	Time [Min]	Area [uV.Min]	Area % [%]
1	21.35	37.6	30.707
2	21.73	85.0	69.293

CuCl Assembly

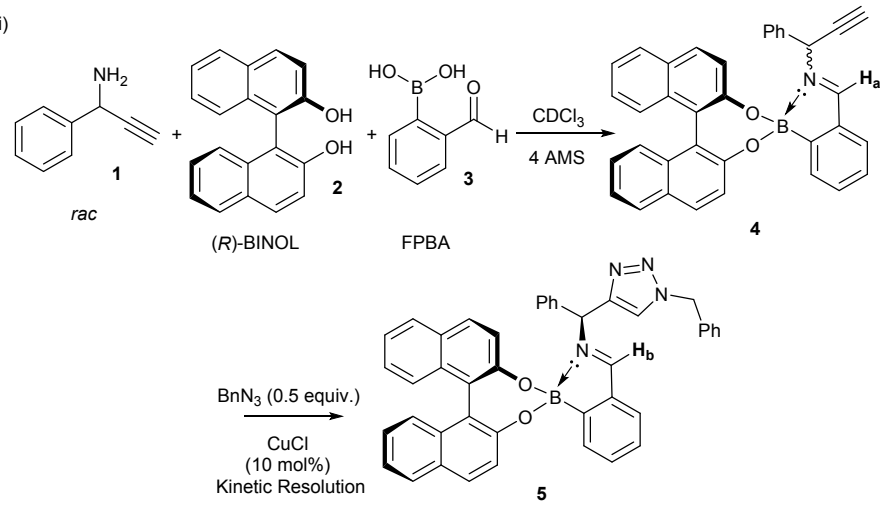
Vial- 15
Method- GB METHOD.METH
Acq time- 16/11/2015 15:30:42
Injection volume- 8.000 µL
Sampelname- N.A.

UNIVERSITY OF BIRMINGHAM

Index	Time [Min]	Area [uV.Min]	Area % [%]
Total		122.6	100.000

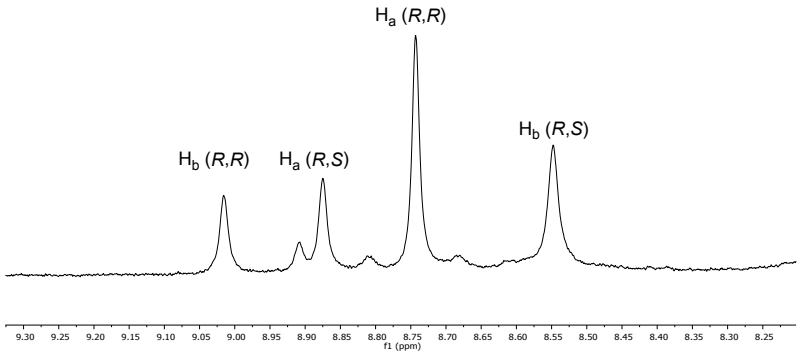
Comparison of NMR and Chiral GC

i)



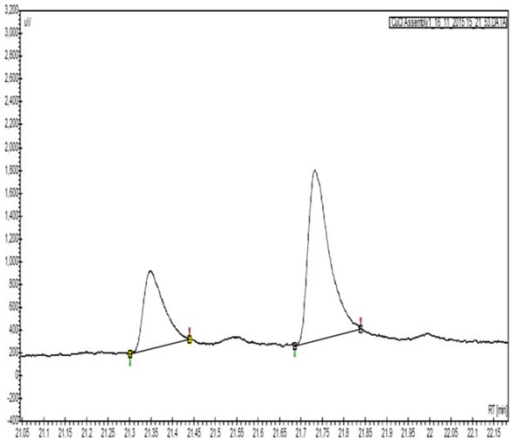
+ **9** Non 1:1 mixture of diastereoisomers

ii)



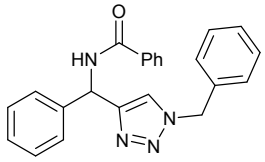
Highlighted peaks at 8.87ppm and 8.74 corresponding to the imine proton of the mixture of diastereoisomers of complex **4** after kinetic resolution. Integration gives 1.34 and 2.31 and thus an inferred *ee* of 37%

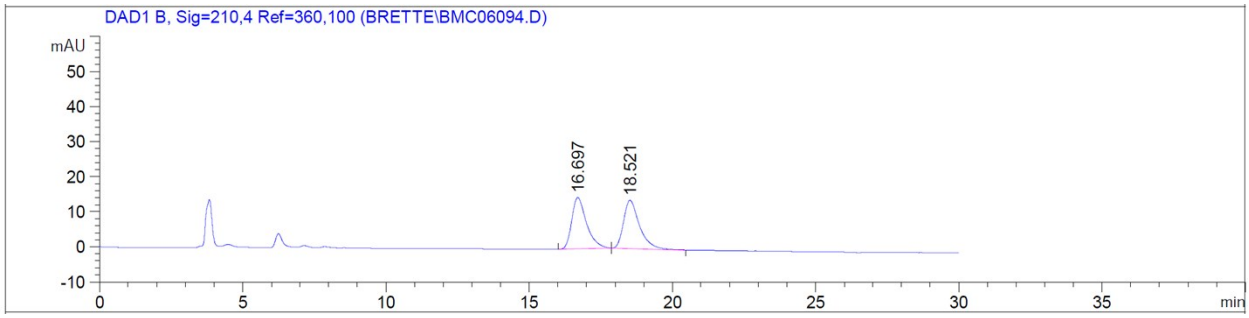
iii)



Chiral GC trace of amine **1** after hydrolysis of the assembly. Integration of area gives 30.7% and 69.3% an *ee* of 39%

HPLC Trace of Racemic *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl) benzamide (12)

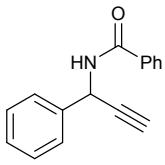


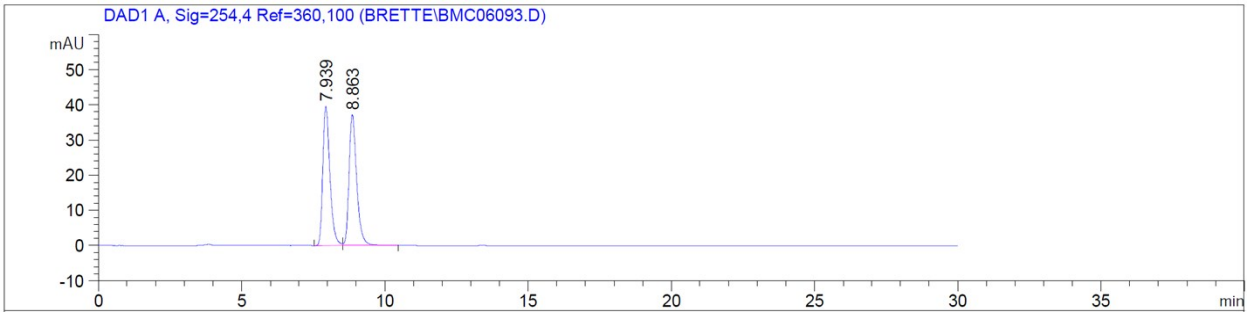


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.697	BB	0.5409	525.99249	14.65044	49.7732
2	18.521	BB	0.5775	530.78601	13.77542	50.2268
Totals :				1056.77850	28.42586	

HPLC Trace of Racemic *N*-(1-phenylprop-2-yn-1-yl)benzamide (11)

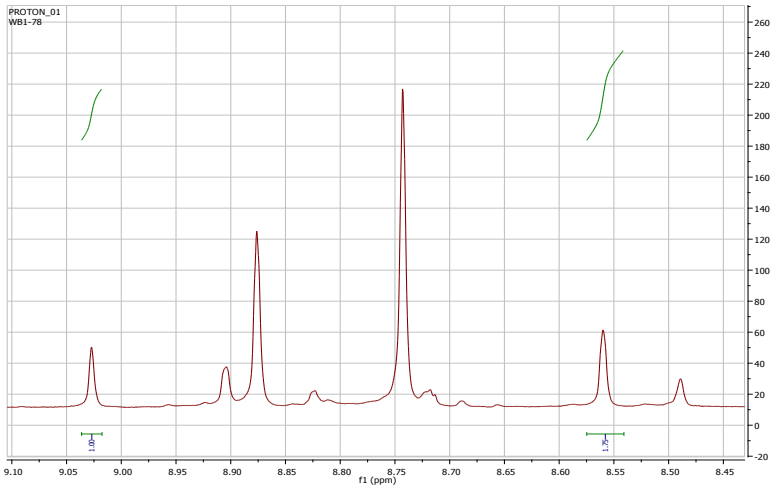


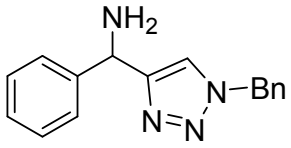


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.939	BV	0.2637	683.91754	39.56554	49.6011
2	8.863	VB	0.2838	694.91681	37.22253	50.3989
Totals :				1378.83435	76.78807	

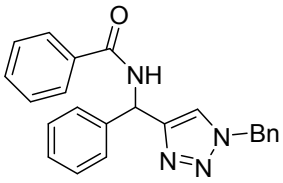
Representative HPLC Trace and NMR after Reaction



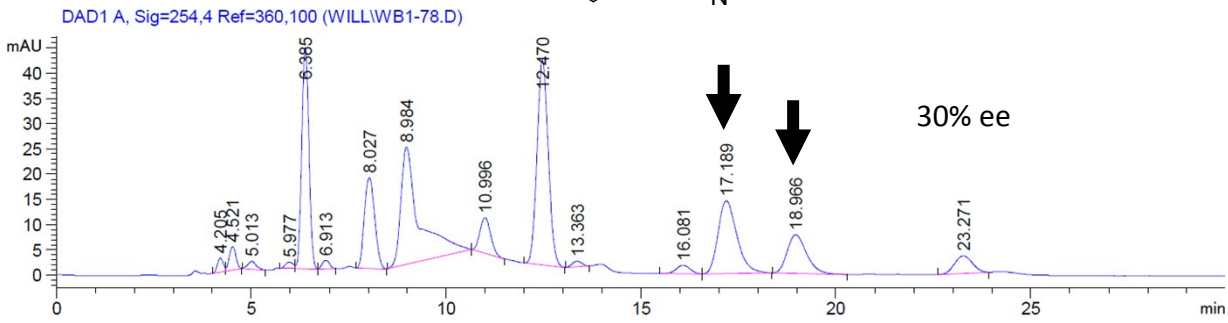


11

27% ee



17



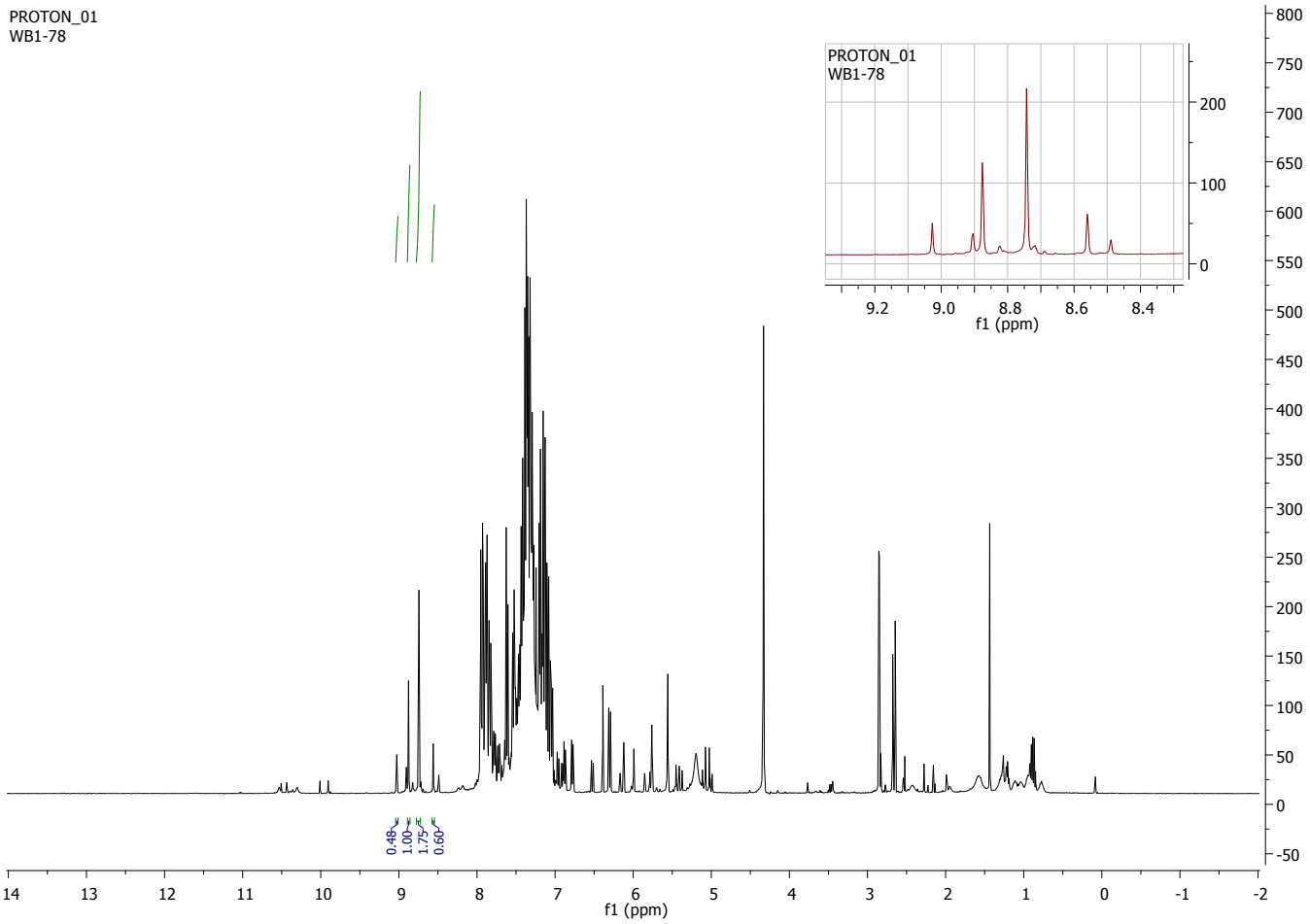
30% ee

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.205	BV	0.1619	28.00682	2.77047	0.7608
2	4.521	VB	0.1889	55.45269	4.65666	1.5064
3	5.013	BB	0.2212	23.97193	1.57793	0.6512
4	5.977	BV	0.2339	18.17609	1.26267	0.4937
5	6.385	VB	0.2033	560.42828	43.78338	15.2239
6	6.913	BB	0.2135	21.79398	1.67842	0.5920
7	8.027	BB	0.2982	332.82602	17.96015	9.0411
8	8.984	BB	0.4726	773.41614	23.21893	21.0097
9	10.996	BB	0.3039	135.17021	7.04374	3.6719
10	12.470	BB	0.3146	815.18677	40.53689	22.1444
11	13.363	BB	0.2802	18.35928	1.06970	0.4987
12	16.081	BB	0.3835	40.36820	1.64978	1.0966
13	17.189	BB	0.5187	483.66547	14.36969	13.1387
14	18.966	BB	0.5327	263.20996	7.66274	7.1500
15	23.271	BB	0.4996	111.20368	3.51008	3.0208
Totals :				3681.23552	172.75122	

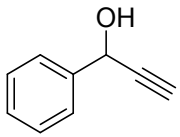
NMR

Representative assembly NMR after reaction



^{1}H NMR of 1-phenylprop-2-yn-1-ol (8)

WB-alkynealcohol



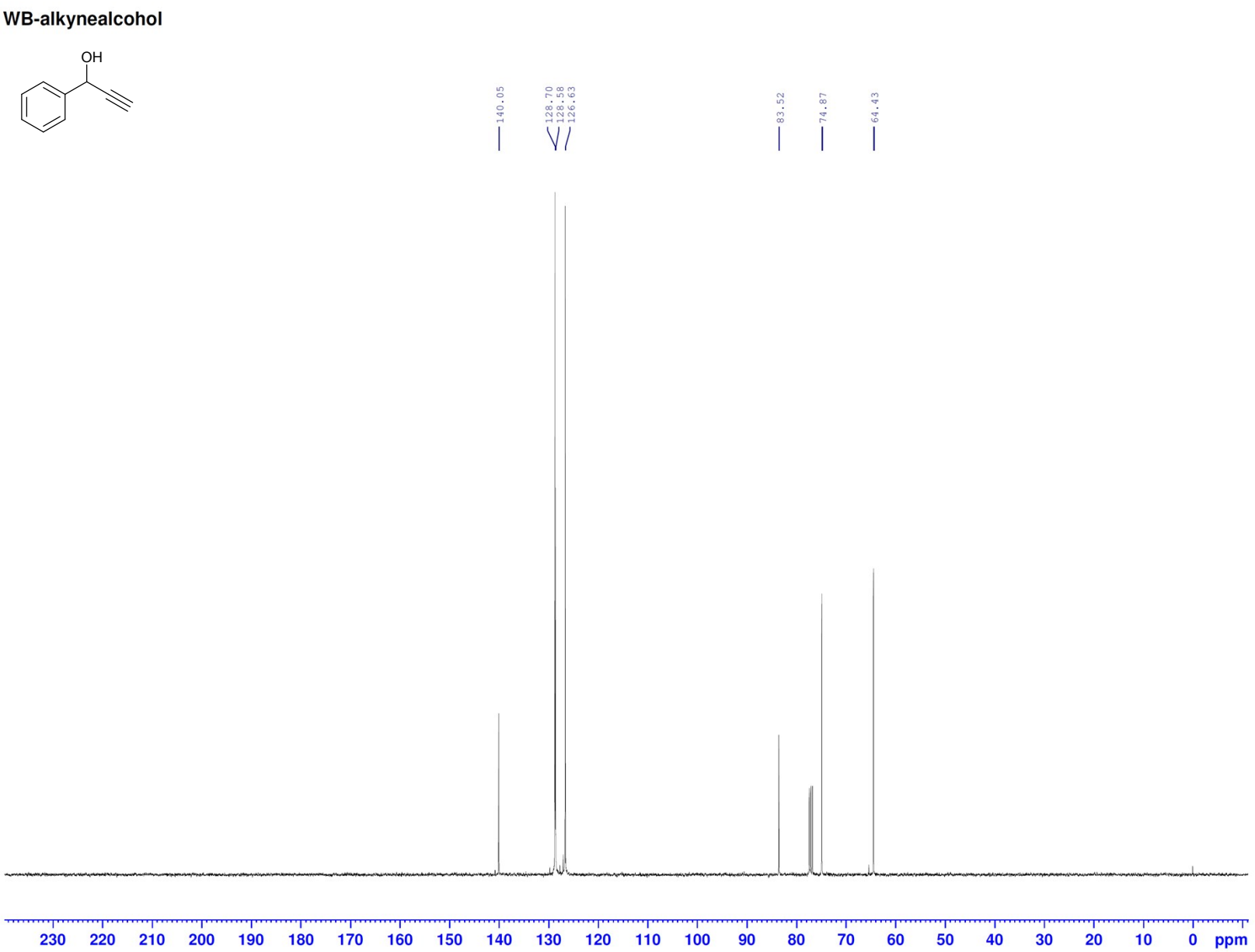
Current Data Parameters
NAME 11-17-Fossey-37
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151117
Time 16.22
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 181
DW 60.800 usec
DE 16.98 usec
TE 294.0 K
D1 1.50000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324008 MHz
NUC1 1H
P1 9.50 usec
PLW1 24.29199982 W

F2 - Processing parameters
SI 32768
SF 400.1300149 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

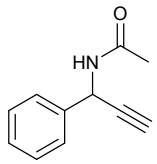
^{13}C NMR of 1-phenylprop-2-yn-1-ol (8)

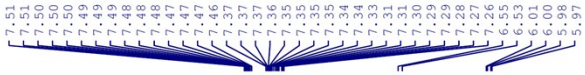


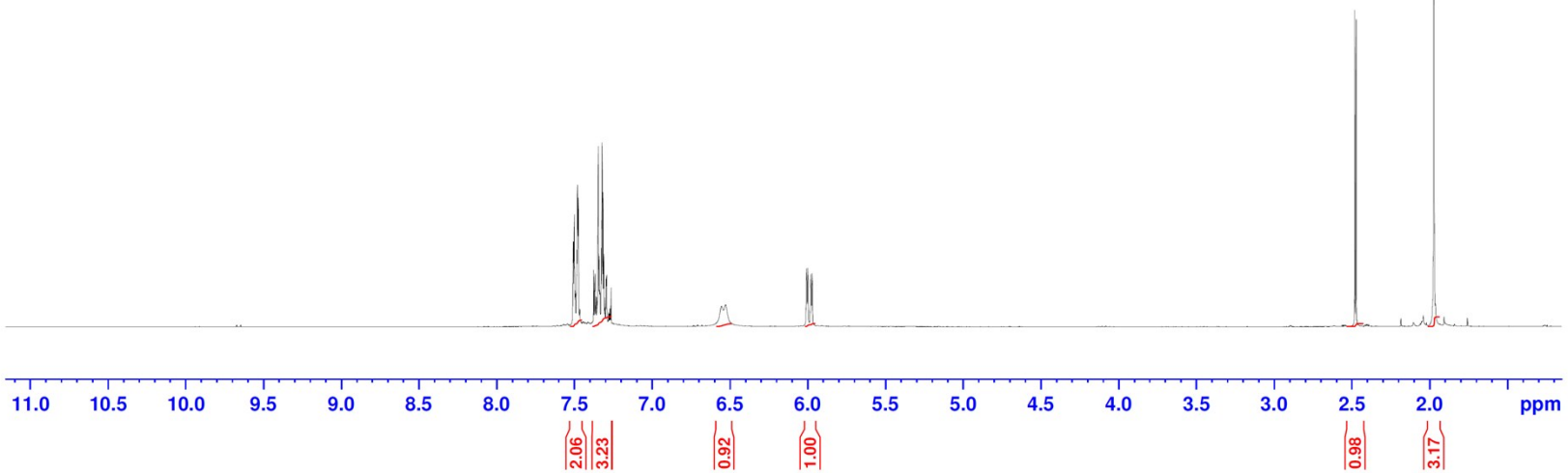

```
Current Data Parameters
NAME      11-17-Fossey-37
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151117
Time              16.32
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG           udeft
TD                18178
SOLVENT           CDCl3
NS                  380
DS                    0
SWH           25252.525 Hz
FIDRES         1.389181 Hz
AQ            0.3599244 sec
RG                 2050
DW               19.800 use
DE                8.20 use
TE               294.1 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                380

======== CHANNEL f1 ========
SFO1        100.6242690 MHz
NUC1               13C
P1                8.80 use
P13            2000.00 use
P26             500.00 use
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5           0.500
SPOFFS5  0 Hz
SPW5          6.93809986 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8           0.500
SPOFFS8  0 Hz
SPW8          6.93809986 W

======== CHANNEL f2 ========
SFO2        400.1320000 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             90.00 use
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                65536
SF           100.6127690 MHz
WDW                EM
SSB       0
LB               2.00 Hz
GB        0
PC               1.00
```

^{1}H NMR of *N*-(1-phenylprop-2-yn-1-yl)acetamide (9)

WB Amide 2



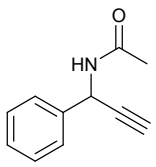





```
Current Data Parameters
NAME      03-10-Fossey-22
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150310
Time               18.56
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7262976 sec
RG                  80.6
DW                83.200 use
DE                12.89 use
TE                294.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 12.80 use
PLW1          9.57730007 W

F2 - Processing parameters
SI                 32768
SF           300.1300066 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

^{13}C NMR of *N*-(1-phenylprop-2-yn-1-yl)acetamide (9)

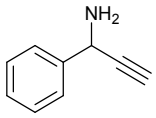
WB-MeAmide




```
Current Data Parameters
NAME      11-18-Fossey-57
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151119
Time               15.57
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES          1.389181 Hz
AQ             0.3599244 sec
RG                  2050
DW                19.800 use
DE                 8.20 use
TE                294.4 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                  380

======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                13C
P1                 8.80 use
P13             2000.00 use
P26              500.00 use
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          6.93809986 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          6.93809986 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 use
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                  65536
SF           100.6127690 MHz
WDW                    EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

^{1}H NMR of 1-phenylprop-2-yn-1-amine (1)

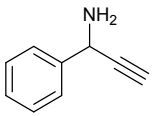
WB-Amine




```
Current Data Parameters
NAME      11-19-Fossey-48
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151119
Time               18.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7262976 sec
RG                   181
DW                83.200 use
DE                12.89 use
TE                294.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                   1H
P1                 12.80 use
PLW1          9.57730007 W

F2 - Processing parameters
SI                 32768
SF           300.1300085 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of 1-phenylprop-2-yn-1-amine (1)

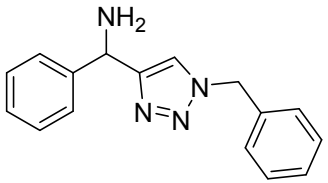
WB-Amine

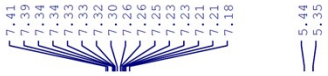


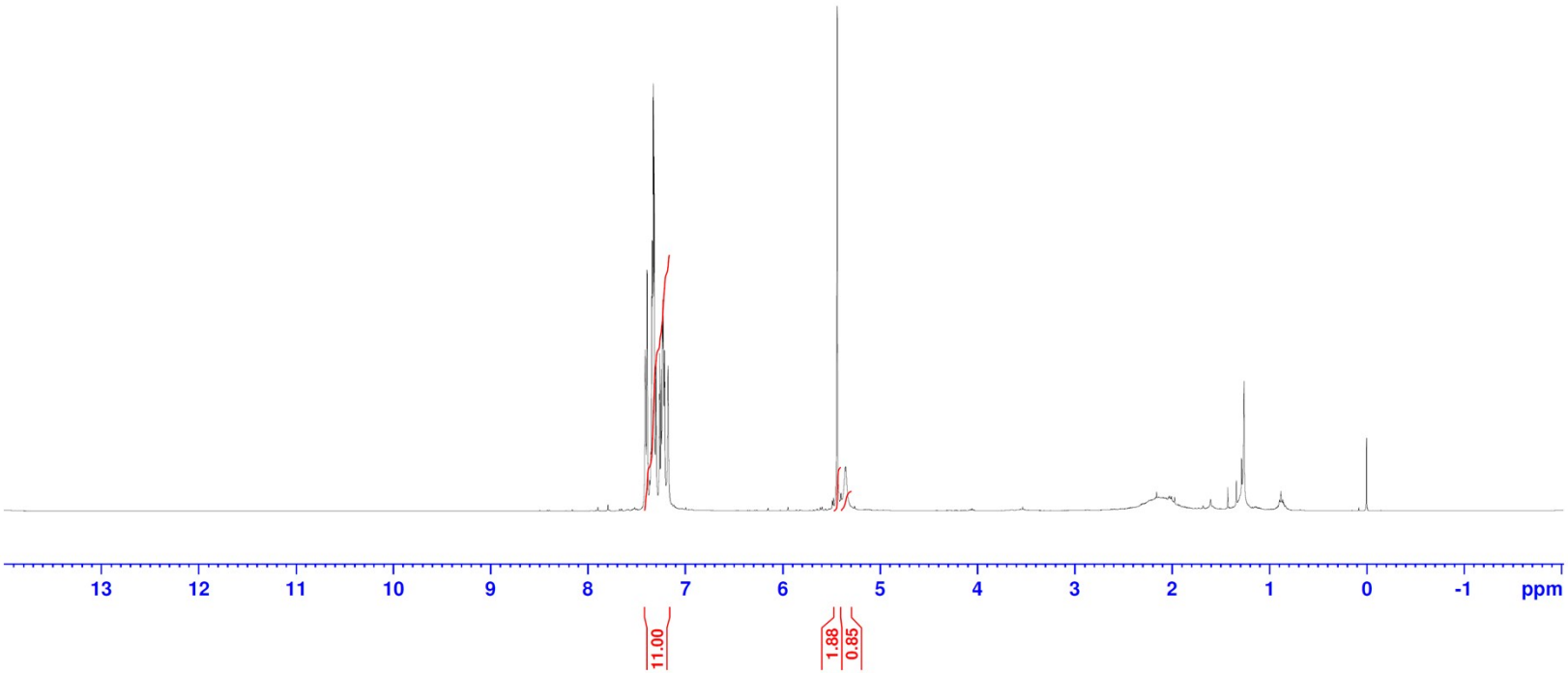

```
Current Data Parameters
NAME      11-20-Fossey-30
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151124
Time               17.46
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES          1.389181 Hz
AQ             0.3599244 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                294.4 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                  380

======== CHANNEL f1 ========
SFO1        100.6242690 MHz
NUC1                13C
P1                 8.80 usec
P13             2000.00 usec
P26              500.00 usec
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          6.93809986 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          6.93809986 W

======== CHANNEL f2 ========
SFO2        400.1320000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                 65536
SF          100.6127690 MHz
WDW                  EM
SSB      0
LB                 2.00 Hz
GB       0
PC                 1.00
```

^{1}H NMR of (1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanamine (6)

WB-NH2 Triazole
1D 1H spectrum before longer 1D 13C spectrum
Not spinning
CSLD on AV400 - 2015/12/17

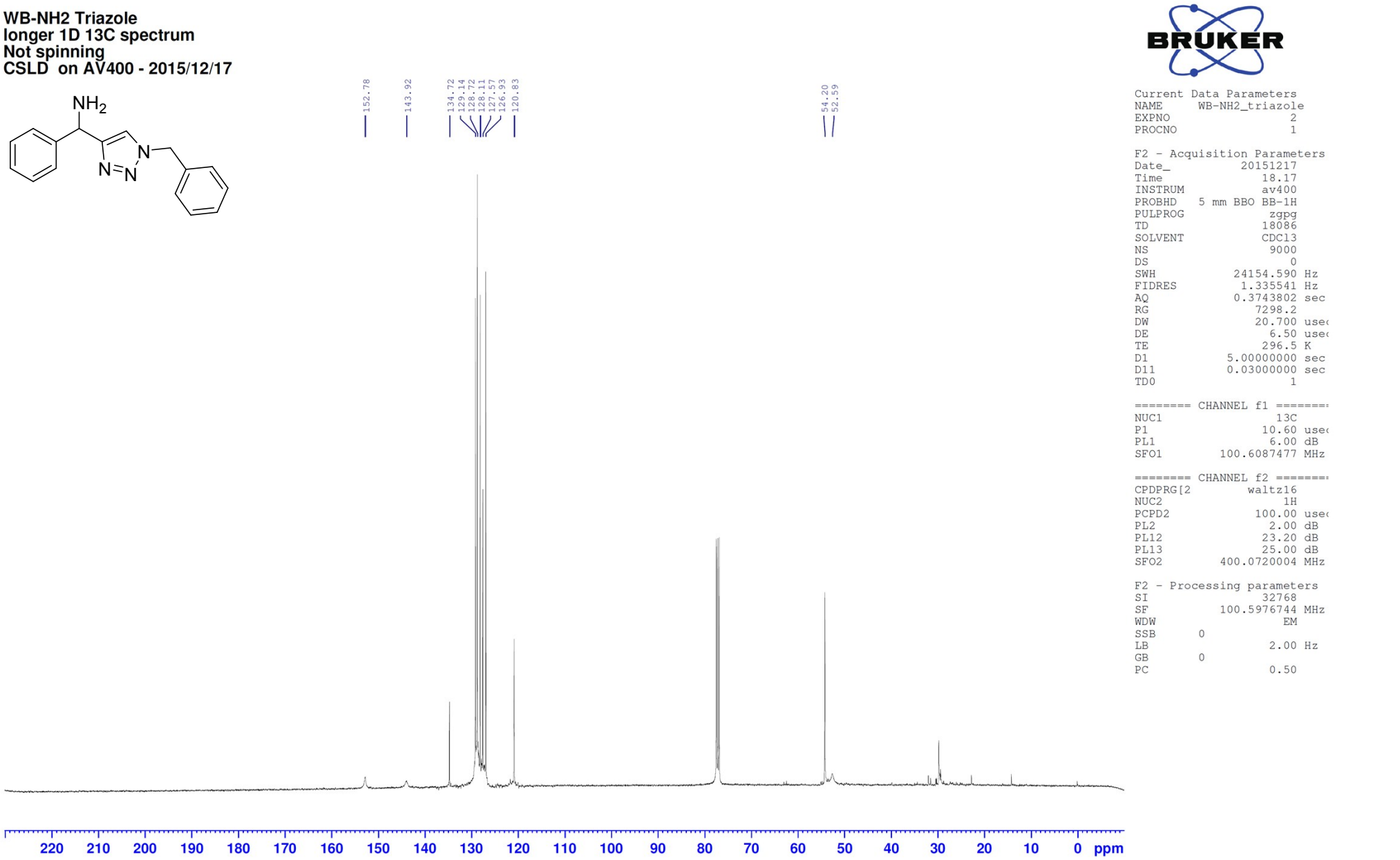







```
Current Data Parameters
NAME      WB-NH2_triazole
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151217
Time               16.47
INSTRUM            av400
PROBHD   5 mm BBO BB-1H
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ              2.5559039 sec
RG                 90.5
DW                78.000 use
DE                 6.50 use
TE                296.1 K
D1           15.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.30 use
PL1                 2.00 dB
SFO1         400.0724004 MHz

F2 - Processing parameters
SI                 32768
SF           400.0700047 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 4.50
```

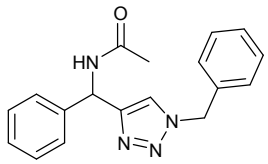
^{1}H NMR of (1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanamine (6)

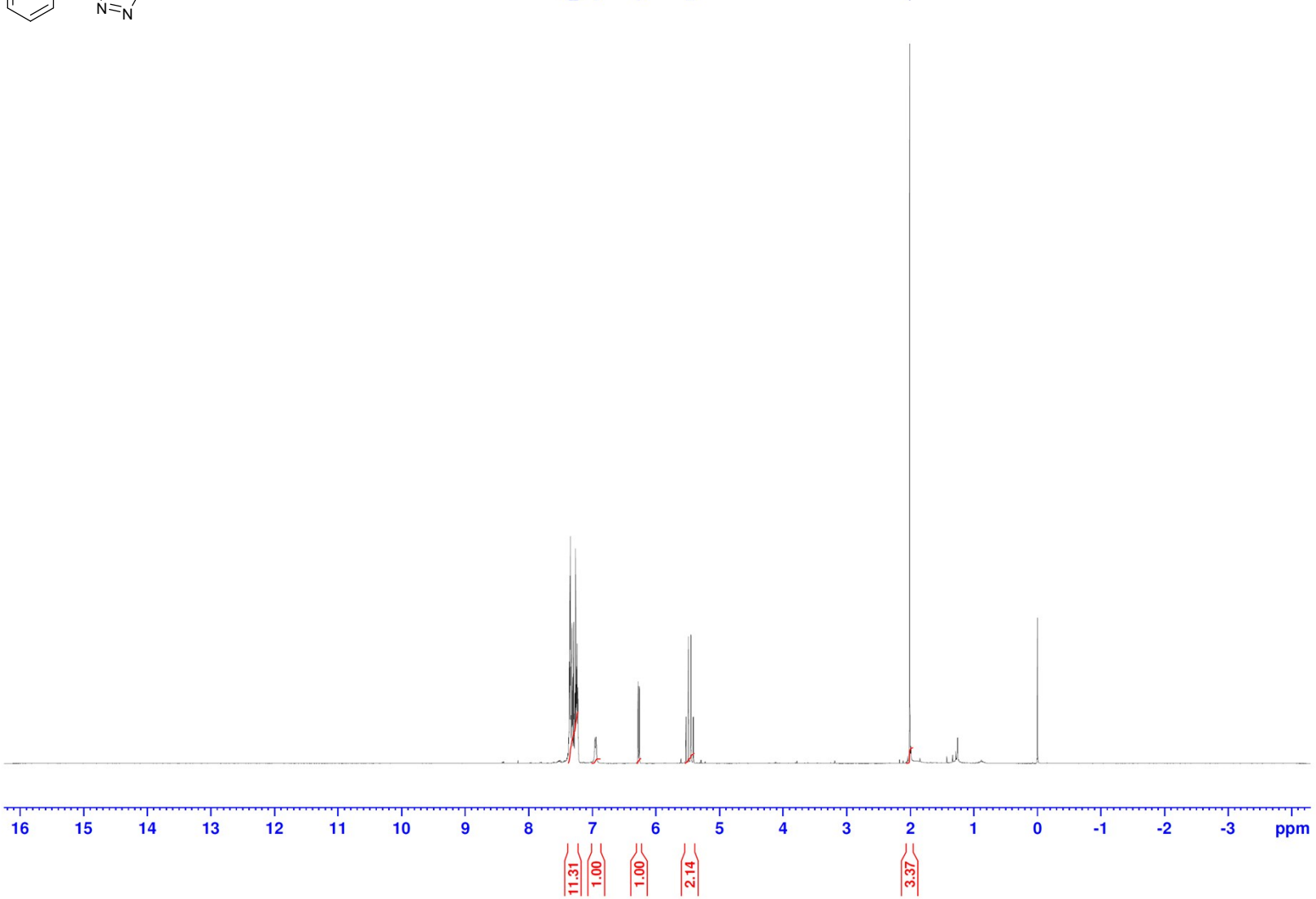



```
Current Data Parameters
NAME      WB-NH2_triazole
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151217
Time               18.17
INSTRUM          av400
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg
TD               18086
SOLVENT          CDCl3
NS                9000
DS                   0
SWH          24154.590 Hz
FIDRES        1.335541 Hz
AQ           0.3743802 sec
RG              7298.2
DW              20.700 usec
DE               6.50 usec
TE              296.5 K
D1           5.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               10.60 usec
PL1               6.00 dB
SFO1        100.6087477 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2               1H
PCPD2           100.00 usec
PL2               2.00 dB
PL12              23.20 dB
PL13              25.00 dB
SFO2        400.0720004 MHz

F2 - Processing parameters
SI                32768
SF          100.5976744 MHz
WDW                EM
SSB       0
LB                2.00 Hz
GB        0
PC                0.50
```

^{1}H NMR of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)acetamide (10)

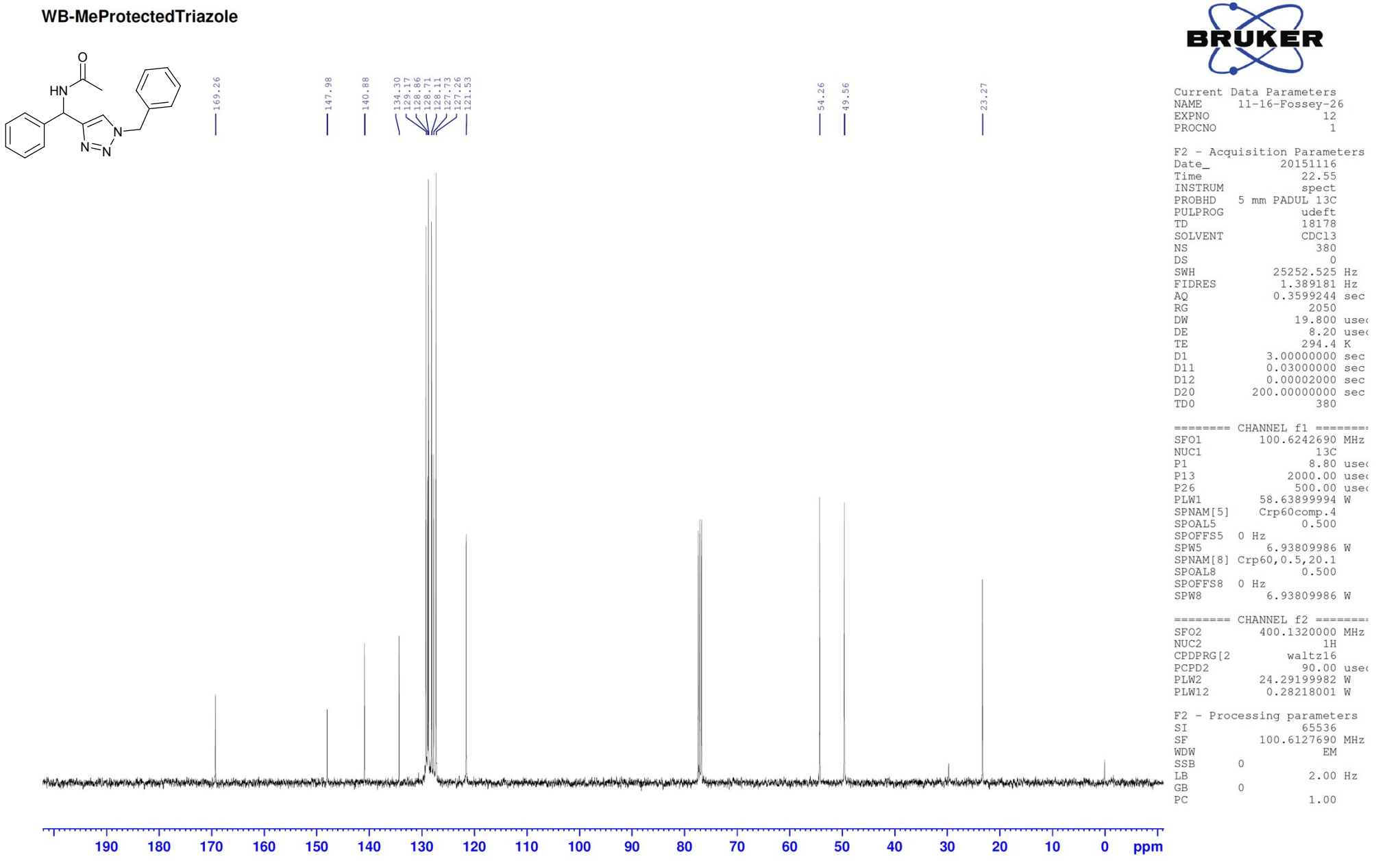
WB-MeProtectedTriazole






```
Current Data Parameters
NAME      11-16-Fossey-26
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151116
Time               22.19
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ             1.9922944 sec
RG                   256
DW                60.800 use
DE                16.98 use
TE                294.2 K
D1            1.50000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                   9.50 use
PLW1        24.29199982 W

F2 - Processing parameters
SI                 32768
SF           400.1300089 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)acetamide (10)

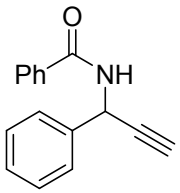


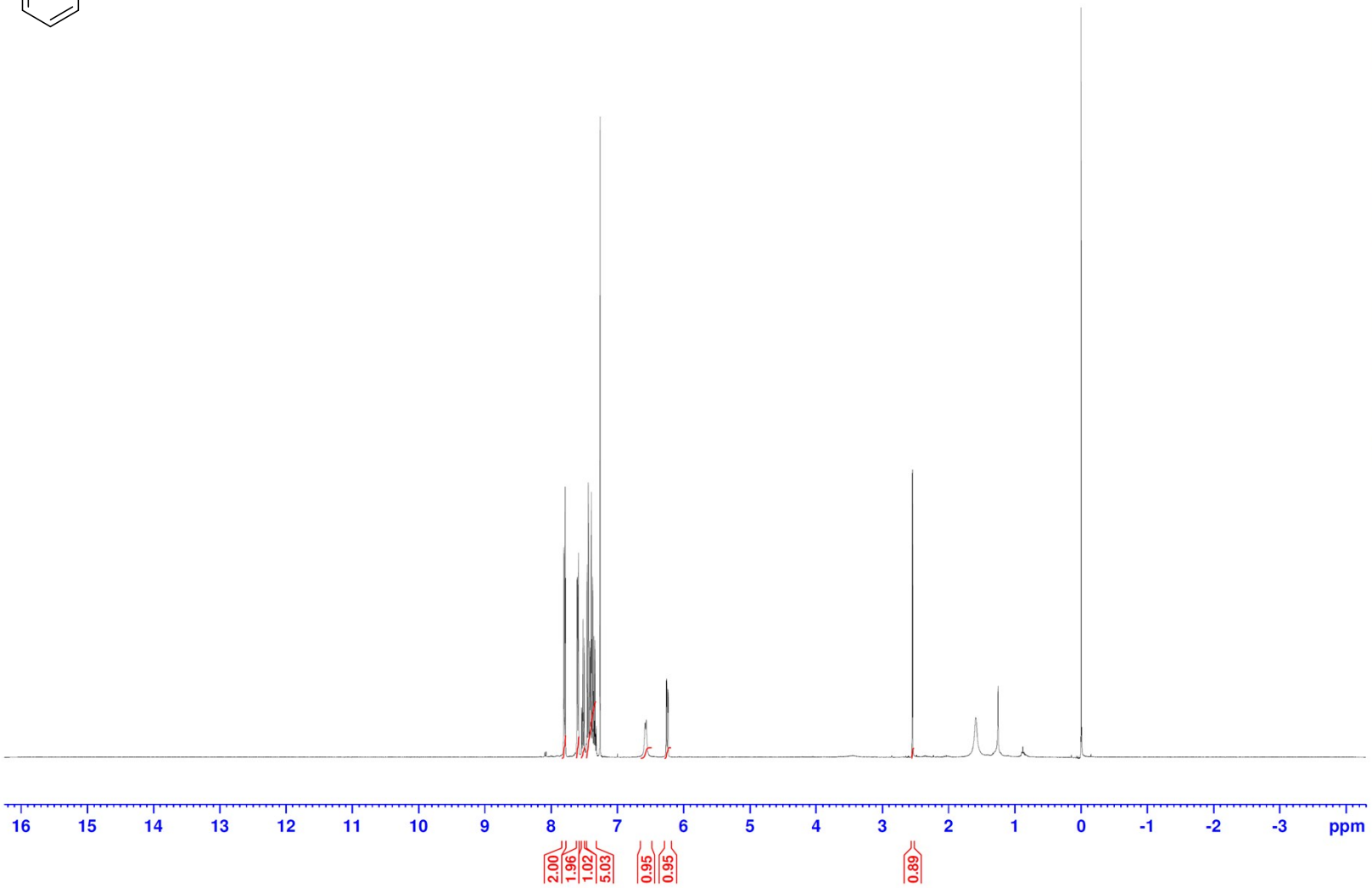
BRUKER

```
Current Data Parameters
NAME      11-16-Fossey-26
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151116
Time               22.55
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES          1.389181 Hz
AQ             0.3599244 sec
RG                  2050
DW                19.800 use
DE                 8.20 use
TE                294.4 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                 380

======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                13C
P1                 8.80 use
P13             2000.00 use
P26              500.00 use
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          6.93809986 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          6.93809986 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 use
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                 65536
SF           100.6127690 MHz
WDW                EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

^{1}H NMR of *N*-(1-phenylprop-2-yn-1-yl)benzamide (11)

WB-PhAlkyne

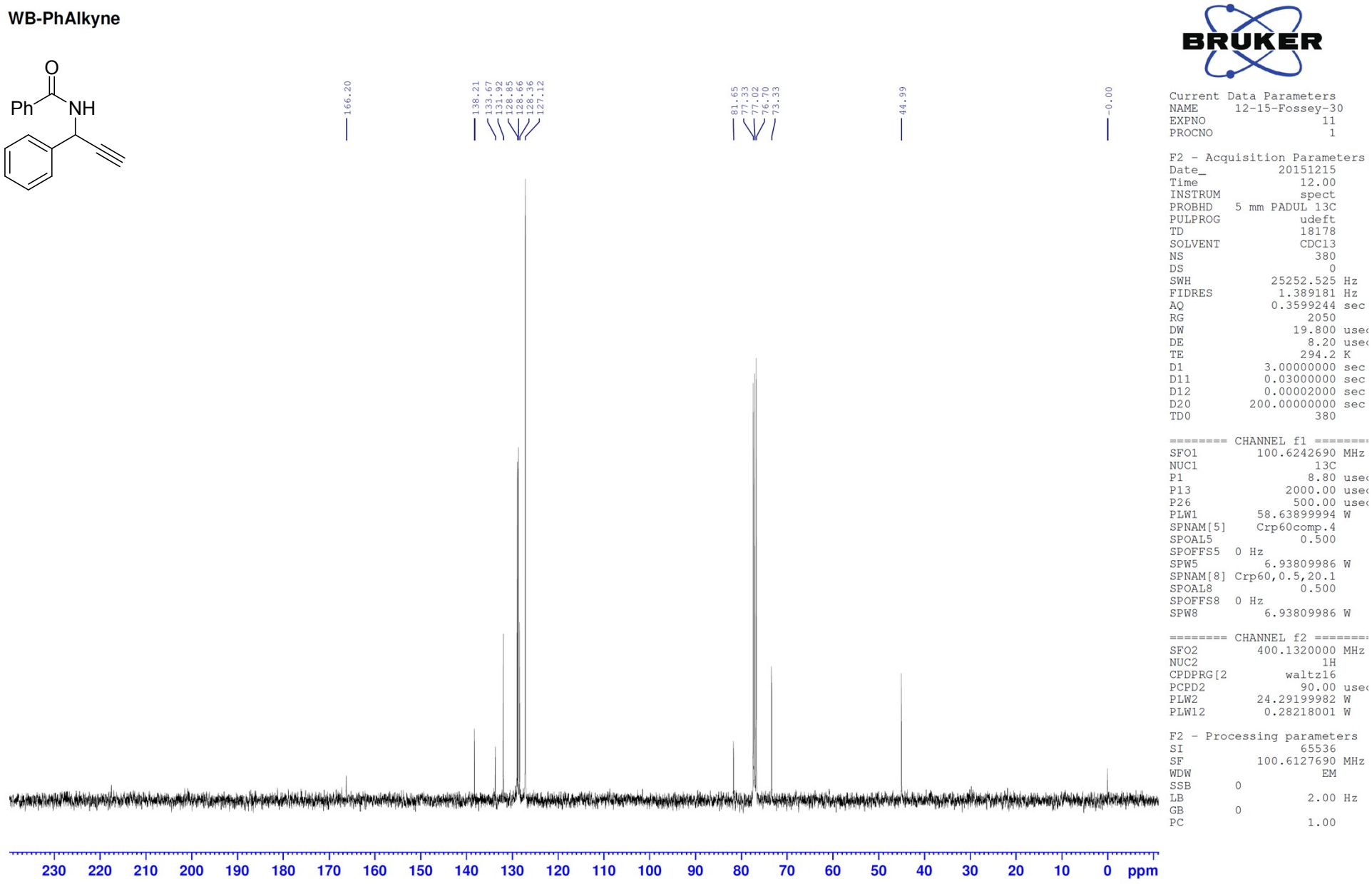




BRUKER

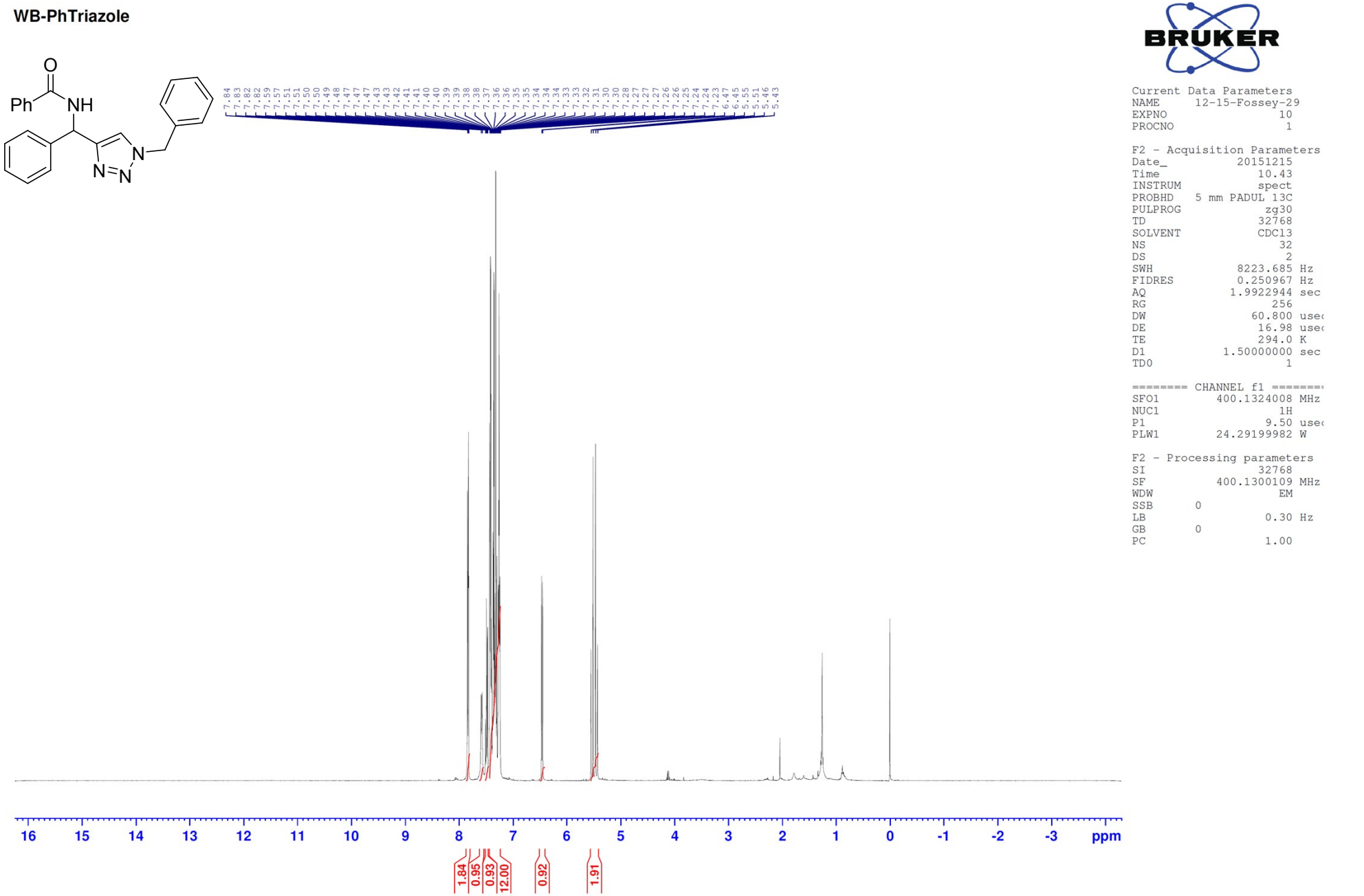
```
Current Data Parameters
NAME      12-15-Fossey-30
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151215
Time               11.50
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ             1.9922944 sec
RG                   456
DW                60.800 use
DE                16.98 use
TE                294.3 K
D1           1.50000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                 1H
P1                 9.50 use
PLW1        24.29199982 W

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of *N*-(1-phenylprop-2-yn-1-yl)benzamide (11)




```
Current Data Parameters
NAME      12-15-Fossey-30
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151215
Time               12.00
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES          1.389181 Hz
AQ             0.3599244 sec
RG                  2050
DW                19.800 usec
DE                 8.20 usec
TE                294.2 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                  380

======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                 13C
P1                  8.80 usec
P13              2000.00 usec
P26               500.00 usec
PLW1          58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5           6.93809986 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8           6.93809986 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2          24.29199982 W
PLW12          0.28218001 W

F2 - Processing parameters
SI                  65536
SF           100.6127690 MHz
WDW                  EM
SSB      0
LB                2.00 Hz
GB       0
PC                1.00
```

^{1}H NMR of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)benzamide (12)

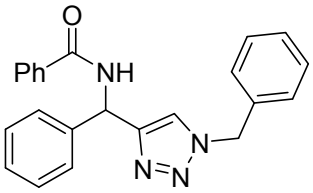


BRUKER

```
Current Data Parameters
NAME      12-15-Fossey-29
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151215
Time               10.43
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ             1.9922944 sec
RG                   256
DW                60.800 usec
DE                16.98 usec
TE                294.0 K
D1            1.50000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324008 MHz
NUC1                   1H
P1                  9.50 usec
PLW1         24.29199982 W

F2 - Processing parameters
SI                 32768
SF           400.1300109 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{13}C NMR of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methyl)benzamide (12)

WB-PhTriazole




```
Current Data Parameters
NAME      12-15-Fossey-29
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20151215
Time               10.53
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            udeft
TD                 18178
SOLVENT            CDCl3
NS                   380
DS                     0
SWH            25252.525 Hz
FIDRES          1.389181 Hz
AQ             0.3599244 sec
RG                  2050
DW                19.800 use
DE                 8.20 use
TE                294.1 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        200.00000000 sec
TD0                  380

======== CHANNEL f1 ========
SFO1         100.6242690 MHz
NUC1                 13C
P1                  8.80 use
P13              2000.00 use
P26               500.00 use
PLW1         58.63899994 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5          6.93809986 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8             0.500
SPOFFS8  0 Hz
SPW8          6.93809986 W

======== CHANNEL f2 ========
SFO2         400.1320000 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2               90.00 use
PLW2         24.29199982 W
PLW12         0.28218001 W

F2 - Processing parameters
SI                 65536
SF           100.6127690 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```

Crystallographic Information

General - CCDC deposit number 1477891

X-Ray Experimental for $C_{43}H_{31}N_3O_2B$: Crystals grew as colorless triangular prisms by slow evaporation from acetonitrile. The data crystal had approximate dimensions; 0.15 x 0.10 x 0.07 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 1688 frames of data were collected using □-scans with a scan range of 1° and a counting time of 9 seconds per frame for frames collected with a detector offset of +/- 40.8° and 28 seconds per frame with frames collected with a detector offset of +/- 108.3°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.[5] The structure was solved by direct methods using SuperFlip[6] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[7] Structure analysis was aided by use of the programs PLATON98[8] and WinGX.[9] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The absolute configuration was determined by internal comparison to the known configuration of the binapthalene group.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\square(F_o))^2 + (0.0505*P)^2 + (0.4821*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0831, with R(F) equal to 0.0313 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[10] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[11] All figures were generated using SHELXTL/PC.[12] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below.

Figure 1. View of **13** showing the atom labelling scheme. Displacement ellipsoids are scaled to the 50% probability level.

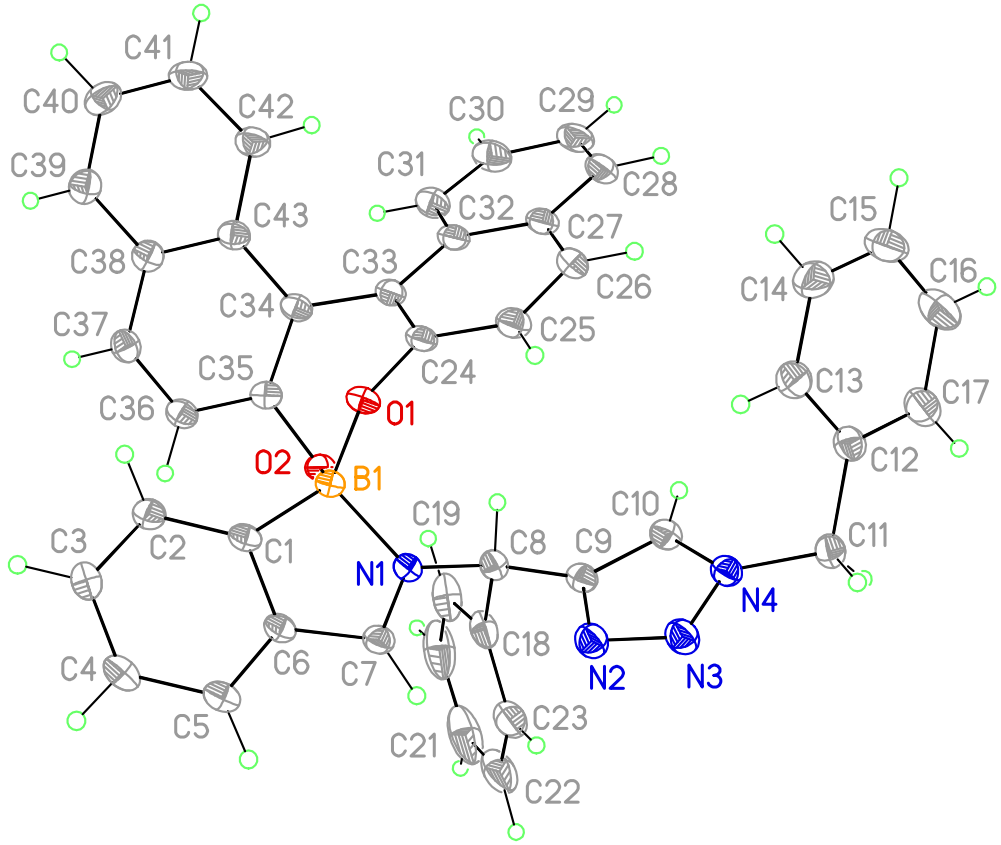


Table 1. Crystal data and structure refinement for 13.

Empirical formula	C43 H31 B N4 O2	
Formula weight	646.53	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.4858(12) Å	α= 90°.

	b = 16.647(2) Å	β= 90°.
	c = 20.977(2) Å	γ = 90°.
Volume	3312.5(7) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.631 mm^{-1}	
F(000)	1352	
Crystal size	0.150 x 0.100 x 0.070 mm^3	
Theta range for data collection	3.389 to 74.310°.	
Index ranges	-11<=h<=11, -20<=k<=20, -26<=l<=26	
Reflections collected	32887	
Independent reflections	6697 [R(int) = 0.0342]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.940	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6697 / 0 / 452	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0819	
R indices (all data)	R1 = 0.0326, wR2 = 0.0831	
Absolute structure parameter	-0.2(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.173 and -0.199 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	3973(2)	791(1)	9489(1)	18(1)
C2	2555(2)	911(1)	9613(1)	21(1)
C3	2145(2)	1441(1)	10098(1)	23(1)
C4	3142(2)	1864(1)	10453(1)	24(1)
C5	4571(2)	1768(1)	10329(1)	21(1)
C6	4962(2)	1227(1)	9856(1)	18(1)
C7	6387(2)	988(1)	9676(1)	19(1)
C8	7680(2)	21(1)	9011(1)	20(1)
C9	8780(2)	575(1)	8744(1)	19(1)
C10	9647(2)	444(1)	8234(1)	21(1)
C11	11585(2)	1292(1)	7745(1)	23(1)
C12	11129(2)	1146(1)	7063(1)	23(1)
C13	9823(2)	1408(1)	6846(1)	27(1)
C14	9419(2)	1283(2)	6218(1)	34(1)
C15	10303(3)	877(2)	5803(1)	39(1)
C16	11602(3)	609(2)	6016(1)	40(1)
C17	12023(2)	750(1)	6643(1)	31(1)
C18	8200(2)	-536(1)	9538(1)	25(1)
C19	7670(2)	-1316(1)	9566(1)	34(1)
C20	8128(3)	-1842(2)	10033(1)	49(1)
C21	9107(3)	-1590(2)	10484(1)	54(1)
C22	9607(3)	-809(2)	10470(1)	47(1)
C23	9165(2)	-280(2)	9995(1)	32(1)
C24	5057(2)	79(1)	7831(1)	18(1)
C25	6095(2)	411(1)	7427(1)	23(1)
C26	6568(2)	-13(1)	6911(1)	24(1)
C27	6052(2)	-796(1)	6786(1)	22(1)
C28	6605(2)	-1268(1)	6280(1)	28(1)
C29	6186(2)	-2042(1)	6187(1)	30(1)
C30	5184(2)	-2389(1)	6600(1)	29(1)
C31	4601(2)	-1945(1)	7087(1)	25(1)

C32	5007(2)	-1132(1)	7193(1)	21(1)
C33	4449(2)	-661(1)	7710(1)	19(1)
C34	3304(2)	-956(1)	8133(1)	19(1)
C35	3514(2)	-942(1)	8786(1)	18(1)
C36	2506(2)	-1242(1)	9217(1)	21(1)
C37	1249(2)	-1527(1)	8998(1)	22(1)
C38	914(2)	-1491(1)	8340(1)	22(1)
C39	-452(2)	-1693(1)	8119(1)	25(1)
C40	-816(2)	-1592(1)	7491(1)	28(1)
C41	200(2)	-1307(1)	7055(1)	28(1)
C42	1546(2)	-1130(1)	7248(1)	24(1)
C43	1948(2)	-1205(1)	7900(1)	21(1)
N1	6407(2)	450(1)	9233(1)	17(1)
N2	9081(2)	1308(1)	8995(1)	24(1)
N3	10098(2)	1639(1)	8655(1)	24(1)
N4	10441(2)	1111(1)	8196(1)	20(1)
O1	4622(1)	539(1)	8337(1)	19(1)
O2	4737(1)	-629(1)	9034(1)	19(1)
B1	4824(2)	240(1)	8985(1)	18(1)

Table 3. Bond lengths [Å] and angles [°] for 13.

C1-C2	1.384(3)	C16-C17	1.395(3)
C1-C6	1.414(2)	C16-H16	0.95
C1-B1	1.616(3)	C17-H17	0.95
C2-C3	1.401(3)	C18-C23	1.391(3)
C2-H2	0.95	C18-C19	1.394(3)
C3-C4	1.394(3)	C19-C20	1.383(3)
C3-H3	0.95	C19-H19	0.95
C4-C5	1.390(3)	C20-C21	1.391(5)
C4-H4	0.95	C20-H20	0.95
C5-C6	1.390(2)	C21-C22	1.384(5)
C5-H5	0.95	C21-H21	0.95
C6-C7	1.460(3)	C22-C23	1.394(3)
C7-N1	1.288(2)	C22-H22	0.95
C7-H7	0.95	C23-H23	0.95
C8-N1	1.479(2)	C24-O1	1.372(2)
C8-C9	1.501(3)	C24-C33	1.384(3)
C8-C18	1.525(3)	C24-C25	1.412(3)
C8-H8	1.00	C25-C26	1.369(3)
C9-N2	1.359(2)	C25-H25	0.95
C9-C10	1.367(3)	C26-C27	1.417(3)
C10-N4	1.342(2)	C26-H26	0.95
C10-H10	0.95	C27-C28	1.422(3)
C11-N4	1.471(2)	C27-C32	1.422(3)
C11-C12	1.514(2)	C28-C29	1.364(3)
C11-H11A	0.99	C28-H28	0.95
C11-H11B	0.99	C29-C30	1.410(3)
C12-C17	1.389(3)	C29-H29	0.95
C12-C13	1.390(3)	C30-C31	1.376(3)
C13-C14	1.388(3)	C30-H30	0.95
C13-H13	0.95	C31-C32	1.425(3)
C14-C15	1.384(4)	C31-H31	0.95
C14-H14	0.95	C32-C33	1.438(2)
C15-C16	1.385(4)	C33-C34	1.486(3)
C15-H15	0.95	C34-C35	1.385(2)

C34-C43	1.437(3)	C40-C41	1.412(3)
C35-O2	1.374(2)	C40-H40	0.95
C35-C36	1.408(3)	C41-C42	1.371(3)
C36-C37	1.363(3)	C41-H41	0.95
C36-H36	0.95	C42-C43	1.426(3)
C37-C38	1.419(3)	C42-H42	0.95
C37-H37	0.95	N1-B1	1.628(2)
C38-C39	1.417(3)	N2-N3	1.320(2)
C38-C43	1.428(3)	N3-N4	1.344(2)
C39-C40	1.372(3)	O1-B1	1.459(2)
C39-H39	0.95	O2-B1	1.453(2)

C2-C1-C6	117.89(17)	N1-C8-H8	106.4
C2-C1-B1	133.63(16)	C9-C8-H8	106.4
C6-C1-B1	108.48(16)	C18-C8-H8	106.4
C1-C2-C3	119.79(18)	N2-C9-C10	108.63(16)
C1-C2-H2	120.1	N2-C9-C8	123.52(16)
C3-C2-H2	120.1	C10-C9-C8	127.85(16)
C4-C3-C2	121.16(18)	N4-C10-C9	104.61(16)
C4-C3-H3	119.4	N4-C10-H10	127.7
C2-C3-H3	119.4	C9-C10-H10	127.7
C5-C4-C3	120.22(17)	N4-C11-C12	111.34(16)
C5-C4-H4	119.9	N4-C11-H11A	109.4
C3-C4-H4	119.9	C12-C11-H11A	109.4
C6-C5-C4	117.90(18)	N4-C11-H11B	109.4
C6-C5-H5	121.0	C12-C11-H11B	109.4
C4-C5-H5	121.0	H11A-C11-H11B	108.0
C5-C6-C1	123.00(18)	C17-C12-C13	119.00(18)
C5-C6-C7	127.52(17)	C17-C12-C11	120.12(18)
C1-C6-C7	109.43(16)	C13-C12-C11	120.88(18)
N1-C7-C6	112.93(16)	C14-C13-C12	120.6(2)
N1-C7-H7	123.5	C14-C13-H13	119.7
C6-C7-H7	123.5	C12-C13-H13	119.7
N1-C8-C9	112.87(15)	C15-C14-C13	120.2(2)
N1-C8-C18	109.27(14)	C15-C14-H14	119.9
C9-C8-C18	114.87(16)	C13-C14-H14	119.9

C14-C15-C16	119.6(2)	C26-C27-C28	121.25(18)
C14-C15-H15	120.2	C26-C27-C32	119.46(17)
C16-C15-H15	120.2	C28-C27-C32	119.23(18)
C15-C16-C17	120.2(2)	C29-C28-C27	121.44(19)
C15-C16-H16	119.9	C29-C28-H28	119.3
C17-C16-H16	119.9	C27-C28-H28	119.3
C12-C17-C16	120.3(2)	C28-C29-C30	119.72(18)
C12-C17-H17	119.8	C28-C29-H29	120.1
C16-C17-H17	119.8	C30-C29-H29	120.1
C23-C18-C19	119.6(2)	C31-C30-C29	120.47(19)
C23-C18-C8	121.65(19)	C31-C30-H30	119.8
C19-C18-C8	118.73(19)	C29-C30-H30	119.8
C20-C19-C18	120.4(3)	C30-C31-C32	121.16(19)
C20-C19-H19	119.8	C30-C31-H31	119.4
C18-C19-H19	119.8	C32-C31-H31	119.4
C19-C20-C21	120.0(3)	C27-C32-C31	117.94(17)
C19-C20-H20	120.0	C27-C32-C33	119.62(17)
C21-C20-H20	120.0	C31-C32-C33	122.38(17)
C22-C21-C20	119.8(2)	C24-C33-C32	118.09(17)
C22-C21-H21	120.1	C24-C33-C34	119.18(15)
C20-C21-H21	120.1	C32-C33-C34	122.66(16)
C21-C22-C23	120.4(3)	C35-C34-C43	118.00(17)
C21-C22-H22	119.8	C35-C34-C33	118.74(17)
C23-C22-H22	119.8	C43-C34-C33	123.12(15)
C18-C23-C22	119.7(2)	O2-C35-C34	120.14(16)
C18-C23-H23	120.1	O2-C35-C36	117.71(15)
C22-C23-H23	120.1	C34-C35-C36	122.15(17)
O1-C24-C33	120.97(16)	C37-C36-C35	120.13(16)
O1-C24-C25	117.08(16)	C37-C36-H36	119.9
C33-C24-C25	121.87(16)	C35-C36-H36	119.9
C26-C25-C24	120.13(18)	C36-C37-C38	120.55(17)
C26-C25-H25	119.9	C36-C37-H37	119.7
C24-C25-H25	119.9	C38-C37-H37	119.7
C25-C26-C27	120.49(18)	C39-C38-C37	120.85(18)
C25-C26-H26	119.8	C39-C38-C43	119.73(17)
C27-C26-H26	119.8	C37-C38-C43	119.33(17)

C40-C39-C38	121.01(19)	C7-N1-B1	111.51(14)
C40-C39-H39	119.5	C8-N1-B1	123.29(13)
C38-C39-H39	119.5	N3-N2-C9	108.61(15)
C39-C40-C41	119.48(19)	N2-N3-N4	106.88(15)
C39-C40-H40	120.3	C10-N4-N3	111.27(15)
C41-C40-H40	120.3	C10-N4-C11	128.39(15)
C42-C41-C40	121.07(18)	N3-N4-C11	120.32(15)
C42-C41-H41	119.5	C24-O1-B1	119.36(13)
C40-C41-H41	119.5	C35-O2-B1	113.49(14)
C41-C42-C43	120.92(19)	O2-B1-O1	113.45(14)
C41-C42-H42	119.5	O2-B1-C1	119.40(15)
C43-C42-H42	119.5	O1-B1-C1	110.50(14)
C42-C43-C38	117.74(17)	O2-B1-N1	104.11(14)
C42-C43-C34	122.71(17)	O1-B1-N1	110.23(14)
C38-C43-C34	119.42(16)	C1-B1-N1	97.40(13)
C7-N1-C8	125.00(16)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 13. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	22(1)	18(1)	14(1)	1(1)	-1(1)	0(1)
C2	22(1)	23(1)	18(1)	1(1)	-1(1)	0(1)
C3	22(1)	24(1)	23(1)	0(1)	5(1)	1(1)
C4	32(1)	22(1)	17(1)	-3(1)	5(1)	1(1)
C5	28(1)	20(1)	15(1)	-1(1)	0(1)	-1(1)
C6	22(1)	20(1)	13(1)	1(1)	0(1)	0(1)
C7	21(1)	21(1)	15(1)	1(1)	-1(1)	-2(1)
C8	19(1)	22(1)	18(1)	-1(1)	2(1)	1(1)
C9	21(1)	20(1)	16(1)	0(1)	-1(1)	2(1)
C10	23(1)	21(1)	18(1)	-1(1)	0(1)	0(1)
C11	20(1)	27(1)	21(1)	3(1)	2(1)	-1(1)
C12	25(1)	23(1)	20(1)	4(1)	2(1)	-3(1)
C13	27(1)	31(1)	25(1)	5(1)	0(1)	-3(1)
C14	31(1)	42(1)	30(1)	10(1)	-7(1)	-8(1)
C15	47(1)	49(1)	20(1)	2(1)	-4(1)	-13(1)
C16	47(1)	50(1)	24(1)	-3(1)	7(1)	-1(1)
C17	31(1)	38(1)	25(1)	2(1)	4(1)	2(1)
C18	24(1)	29(1)	23(1)	5(1)	7(1)	7(1)
C19	31(1)	30(1)	42(1)	10(1)	16(1)	7(1)
C20	44(1)	44(1)	59(2)	28(1)	26(1)	14(1)
C21	50(2)	67(2)	44(1)	35(1)	23(1)	30(1)
C22	36(1)	81(2)	23(1)	13(1)	5(1)	23(1)
C23	28(1)	45(1)	22(1)	4(1)	3(1)	10(1)
C24	21(1)	22(1)	12(1)	0(1)	-2(1)	3(1)
C25	27(1)	23(1)	18(1)	1(1)	-2(1)	-4(1)
C26	24(1)	34(1)	16(1)	2(1)	2(1)	-3(1)
C27	24(1)	29(1)	14(1)	-1(1)	-2(1)	4(1)
C28	27(1)	40(1)	16(1)	-3(1)	1(1)	5(1)
C29	33(1)	39(1)	19(1)	-10(1)	-2(1)	10(1)
C30	38(1)	25(1)	25(1)	-8(1)	-2(1)	5(1)
C31	30(1)	24(1)	22(1)	-3(1)	0(1)	2(1)

C32	23(1)	24(1)	14(1)	-2(1)	-2(1)	3(1)
C33	21(1)	21(1)	15(1)	-1(1)	-1(1)	2(1)
C34	24(1)	17(1)	16(1)	-3(1)	0(1)	1(1)
C35	22(1)	16(1)	18(1)	0(1)	-2(1)	1(1)
C36	25(1)	19(1)	18(1)	1(1)	0(1)	1(1)
C37	24(1)	21(1)	23(1)	1(1)	4(1)	-1(1)
C38	23(1)	18(1)	23(1)	-2(1)	0(1)	-1(1)
C39	24(1)	22(1)	30(1)	-3(1)	0(1)	-2(1)
C40	24(1)	26(1)	34(1)	-7(1)	-7(1)	-2(1)
C41	31(1)	31(1)	22(1)	-6(1)	-7(1)	2(1)
C42	28(1)	25(1)	20(1)	-5(1)	-2(1)	1(1)
C43	24(1)	18(1)	20(1)	-3(1)	-1(1)	0(1)
N1	18(1)	19(1)	15(1)	0(1)	1(1)	0(1)
N2	25(1)	23(1)	23(1)	-3(1)	4(1)	-2(1)
N3	27(1)	23(1)	22(1)	-3(1)	4(1)	-1(1)
N4	21(1)	22(1)	17(1)	1(1)	0(1)	1(1)
O1	24(1)	18(1)	14(1)	-2(1)	-1(1)	1(1)
O2	20(1)	20(1)	16(1)	-1(1)	-2(1)	-1(1)
B1	18(1)	21(1)	14(1)	-1(1)	-1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 13.

	x	y	z	U(eq)
H2	1863	634	9371	25
H3	1171	1513	10186	28
H4	2842	2218	10781	29
H5	5259	2064	10559	25
H7	7214	1205	9864	23
H8	7372	-332	8652	24
H10	9681	-15	7966	25
H11A	12411	950	7844	27
H11B	11872	1860	7795	27
H13	9202	1676	7131	33
H14	8534	1476	6072	41
H15	10020	784	5375	46
H16	12209	327	5733	48
H17	12924	576	6783	37
H19	6991	-1488	9263	41
H20	7774	-2375	10045	58
H21	9431	-1953	10802	65
H22	10255	-632	10785	56
H23	9521	253	9982	38
H25	6465	930	7514	27
H26	7247	220	6634	29
H28	7283	-1038	6000	33
H29	6566	-2347	5845	36
H30	4909	-2933	6542	35
H31	3917	-2185	7357	30
H36	2702	-1246	9661	25
H37	591	-1752	9290	27
H39	-1126	-1902	8410	30
H40	-1745	-1712	7352	33
H41	-52	-1238	6620	33

H42	2219	-954	6943	29

Table 6. Torsion angles [°] for 13.

C6-C1-C2-C3	-1.0(3)	C8-C18-C19-C20	179.29(19)
B1-C1-C2-C3	179.67(17)	C18-C19-C20-C21	1.0(3)
C1-C2-C3-C4	1.1(3)	C19-C20-C21-C22	0.8(4)
C2-C3-C4-C5	0.3(3)	C20-C21-C22-C23	-1.8(4)
C3-C4-C5-C6	-1.7(3)	C19-C18-C23-C22	0.9(3)
C4-C5-C6-C1	1.9(3)	C8-C18-C23-C22	179.71(18)
C4-C5-C6-C7	-175.30(18)	C21-C22-C23-C18	1.0(3)
C2-C1-C6-C5	-0.5(3)	O1-C24-C25-C26	-179.48(16)
B1-C1-C6-C5	179.02(16)	C33-C24-C25-C26	-2.5(3)
C2-C1-C6-C7	177.10(16)	C24-C25-C26-C27	-1.7(3)
B1-C1-C6-C7	-3.37(19)	C25-C26-C27-C28	-175.35(18)
C5-C6-C7-N1	177.65(17)	C25-C26-C27-C32	1.7(3)
C1-C6-C7-N1	0.2(2)	C26-C27-C28-C29	175.16(19)
N1-C8-C9-N2	38.8(2)	C32-C27-C28-C29	-1.9(3)
C18-C8-C9-N2	-87.4(2)	C27-C28-C29-C30	-0.2(3)
N1-C8-C9-C10	-142.40(18)	C28-C29-C30-C31	1.6(3)
C18-C8-C9-C10	91.4(2)	C29-C30-C31-C32	-1.0(3)
N2-C9-C10-N4	-0.2(2)	C26-C27-C32-C31	-174.66(17)
C8-C9-C10-N4	-179.14(17)	C28-C27-C32-C31	2.4(3)
N4-C11-C12-C17	-135.90(19)	C26-C27-C32-C33	2.4(3)
N4-C11-C12-C13	44.6(2)	C28-C27-C32-C33	179.50(16)
C17-C12-C13-C14	-0.5(3)	C30-C31-C32-C27	-1.0(3)
C11-C12-C13-C14	179.07(19)	C30-C31-C32-C33	-178.03(18)
C12-C13-C14-C15	1.5(3)	O1-C24-C33-C32	-176.65(15)
C13-C14-C15-C16	-1.0(3)	C25-C24-C33-C32	6.5(3)
C14-C15-C16-C17	-0.5(4)	O1-C24-C33-C34	0.4(2)
C13-C12-C17-C16	-1.0(3)	C25-C24-C33-C34	-176.49(17)
C11-C12-C17-C16	179.5(2)	C27-C32-C33-C24	-6.4(3)
C15-C16-C17-C12	1.5(4)	C31-C32-C33-C24	170.55(17)
N1-C8-C18-C23	-90.0(2)	C27-C32-C33-C34	176.72(16)
C9-C8-C18-C23	38.0(2)	C31-C32-C33-C34	-6.3(3)
N1-C8-C18-C19	88.9(2)	C24-C33-C34-C35	-50.0(2)
C9-C8-C18-C19	-143.11(18)	C32-C33-C34-C35	126.82(19)
C23-C18-C19-C20	-1.8(3)	C24-C33-C34-C43	125.61(19)

C32-C33-C34-C43	-57.5(2)	C10-C9-N2-N3	0.5(2)
C43-C34-C35-O2	-173.14(15)	C8-C9-N2-N3	179.45(17)
C33-C34-C35-O2	2.7(3)	C9-N2-N3-N4	-0.5(2)
C43-C34-C35-C36	6.9(3)	C9-C10-N4-N3	-0.1(2)
C33-C34-C35-C36	-177.20(16)	C9-C10-N4-C11	178.16(17)
O2-C35-C36-C37	177.17(16)	N2-N3-N4-C10	0.4(2)
C34-C35-C36-C37	-2.9(3)	N2-N3-N4-C11	-178.03(15)
C35-C36-C37-C38	-3.0(3)	C12-C11-N4-C10	50.7(2)
C36-C37-C38-C39	-172.11(18)	C12-C11-N4-N3	-131.20(17)
C36-C37-C38-C43	4.4(3)	C33-C24-O1-B1	63.9(2)
C37-C38-C39-C40	174.26(18)	C25-C24-O1-B1	-119.16(18)
C43-C38-C39-C40	-2.3(3)	C34-C35-O2-B1	72.0(2)
C38-C39-C40-C41	2.1(3)	C36-C35-O2-B1	-108.09(18)
C39-C40-C41-C42	-0.1(3)	C35-O2-B1-O1	-54.2(2)
C40-C41-C42-C43	-1.8(3)	C35-O2-B1-C1	78.87(19)
C41-C42-C43-C38	1.6(3)	C35-O2-B1-N1	-174.03(13)
C41-C42-C43-C34	-174.16(18)	C24-O1-B1-O2	-31.8(2)
C39-C38-C43-C42	0.4(3)	C24-O1-B1-C1	-169.02(15)
C37-C38-C43-C42	-176.22(17)	C24-O1-B1-N1	84.46(18)
C39-C38-C43-C34	176.33(17)	C2-C1-B1-O2	-65.2(3)
C37-C38-C43-C34	-0.3(3)	C6-C1-B1-O2	115.37(17)
C35-C34-C43-C42	170.50(17)	C2-C1-B1-O1	69.1(3)
C33-C34-C43-C42	-5.2(3)	C6-C1-B1-O1	-110.33(16)
C35-C34-C43-C38	-5.2(3)	C2-C1-B1-N1	-176.02(19)
C33-C34-C43-C38	179.08(16)	C6-C1-B1-N1	4.56(17)
C6-C7-N1-C8	-171.93(15)	C7-N1-B1-O2	-127.55(15)
C6-C7-N1-B1	3.1(2)	C8-N1-B1-O2	47.62(19)
C9-C8-N1-C7	-60.7(2)	C7-N1-B1-O1	110.45(16)
C18-C8-N1-C7	68.4(2)	C8-N1-B1-O1	-74.38(19)
C9-C8-N1-B1	124.81(16)	C7-N1-B1-C1	-4.65(17)
C18-C8-N1-B1	-106.08(18)	C8-N1-B1-C1	170.52(14)

References

1) L. Ye, W. He and L. Zhang, *J. Am. Chem. Soc.*, 2010, 132, 8550-8551.
2) Z. Ni, L. Giordano and A. Tenaglia, *Chem. Eur. J.*, 2014, 20, 11703-11706.
3) B. M. Nilsson and U. Hacksell, *J. Heterocycl. Chem.*, 1989, 26, 269-275.
4) 4. D. Castagnolo, F. Dessì, M. Radi and M. Botta, *Tetrahedron: Asymmetry*, 2007, 18, 1345-1350.

5) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.

6) SuperFlip. (2007). A program for crystal structure solution. Palatinus, L. and Chapuis, G. J. Appl. Cryst. 40, 786-790.

7) Sheldrick, G. M. (2015). SHELXL-2014/7. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.

8) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.

9) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.

10) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

11) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

12) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.