Supporting Information

Open aryl triazole receptors: Planar sheets, spheres and anion binding

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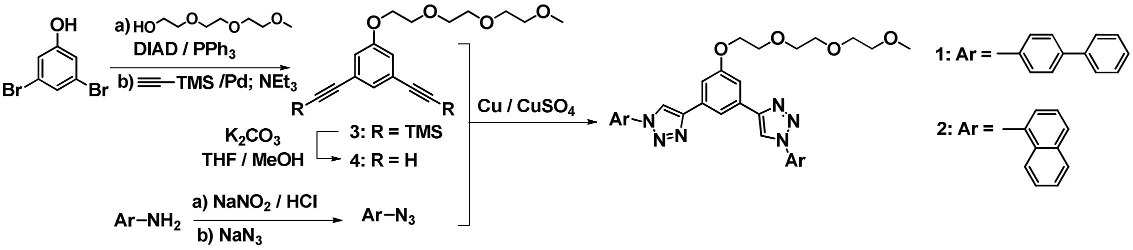
1. Supplementary Figures



Scheme S1. Synthesis of aryl triazole receptors **1** and **2**

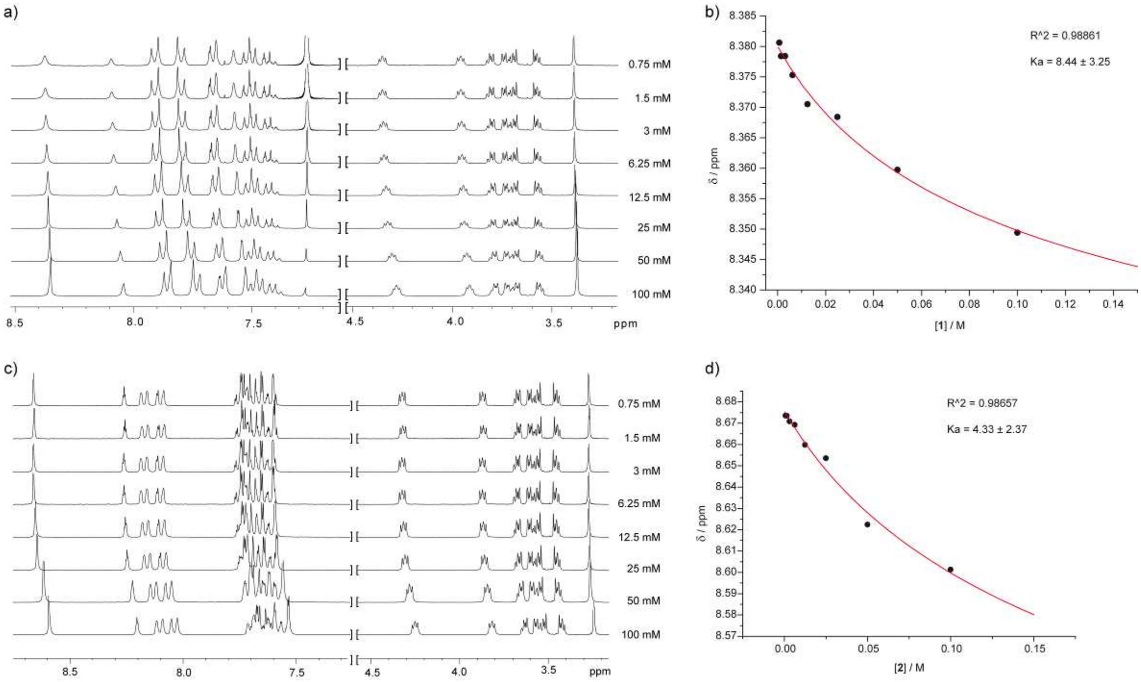


Figure S1. Partial ^{1}H NMR spectra at different concentrations of aryl triazoles **1** ($CDCl_3$, 300 MHz, 298 K) (a), and **2** (CD_3CN, 300 MHz, 298 K) (c). (b and d) Concentration dependence of the chemical shift corresponding to the proton in the 1,2,3-triazole ring (H_b in Figure 1) with increasing concentration and fit to the isodesmic model.

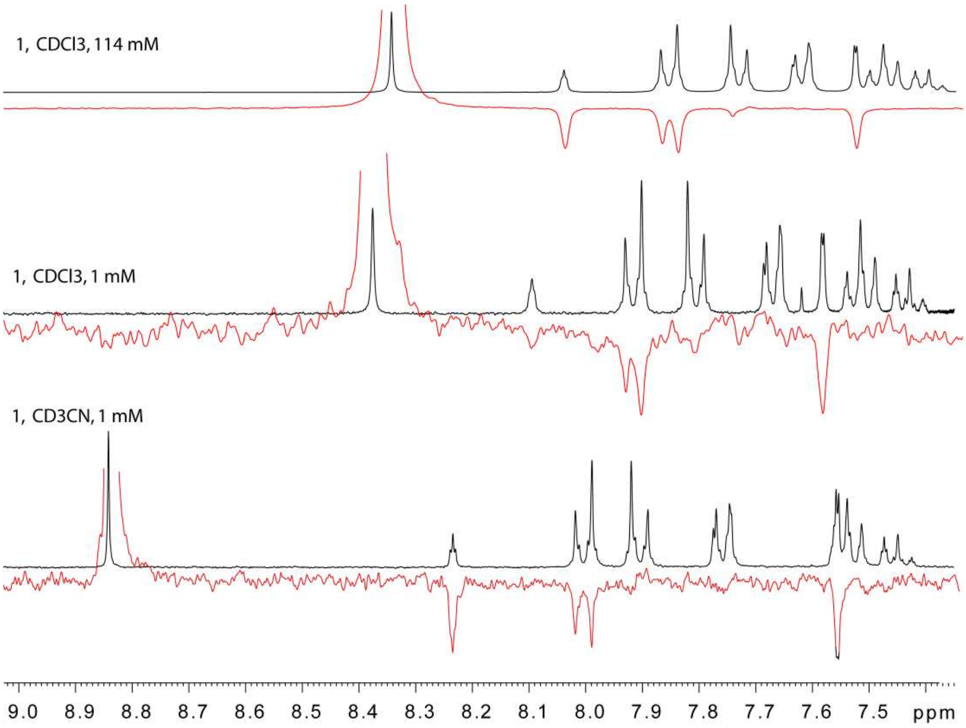


Figure S2. Partial ^{1}H NMR spectra (300 MHz, 298 K) (black) and NOE experiments (red) of aryl triazole **1** in $CDCl_3$ at 114 mM (top), 1 mM (middle) and CD_3CN 1 mM (bottom).

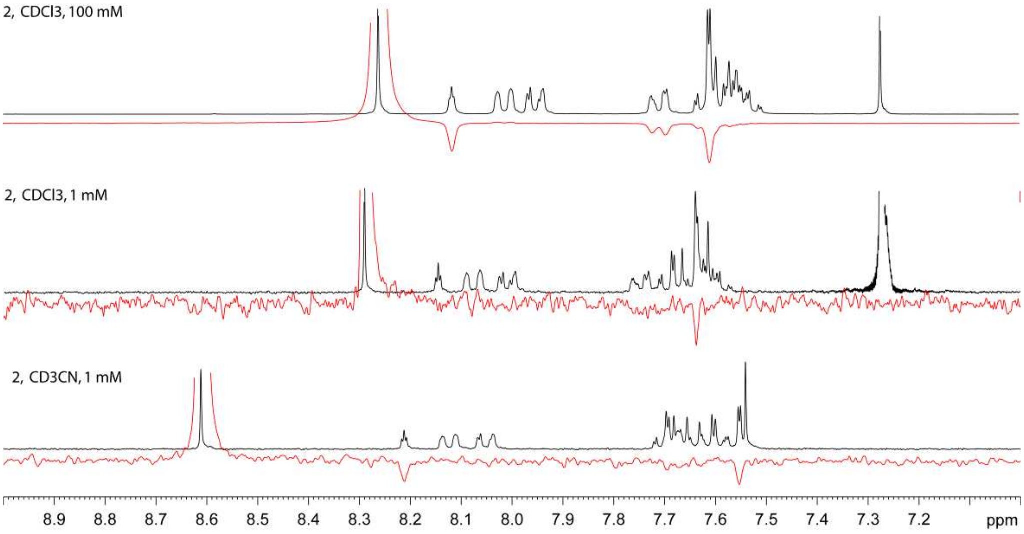


Figure S3. Partial ^{1}H NMR spectra (300 MHz, 298 K) (black) and NOE experiments (red) of aryl triazole **2** in $CDCl_3$ at 100 mM (top), 1 mM (middle) and CD_3CN 1 mM (bottom).

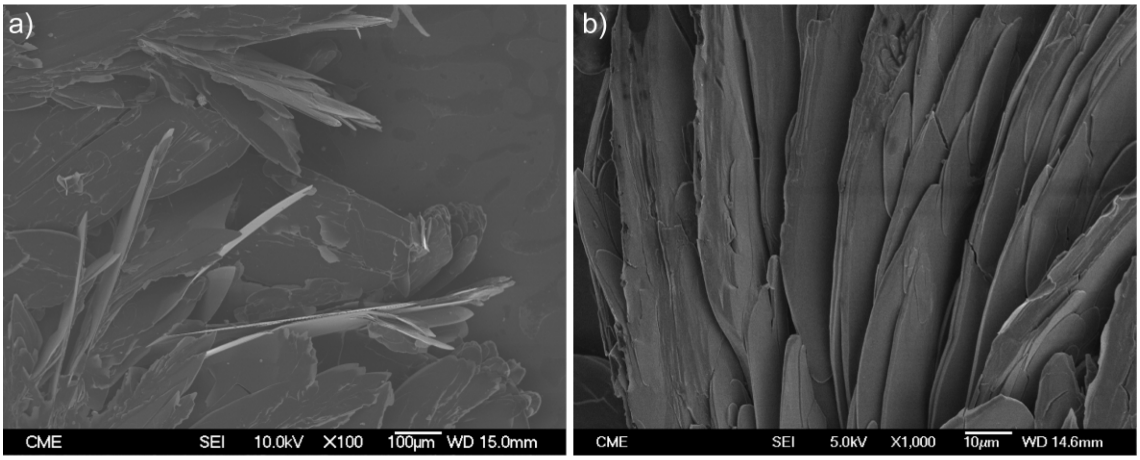


Figure S4. SEM images (298 K, 1 x 10^{-4} M in acetonitrile, glass substrate) of stratified flat lamellae formed from **1** (a).

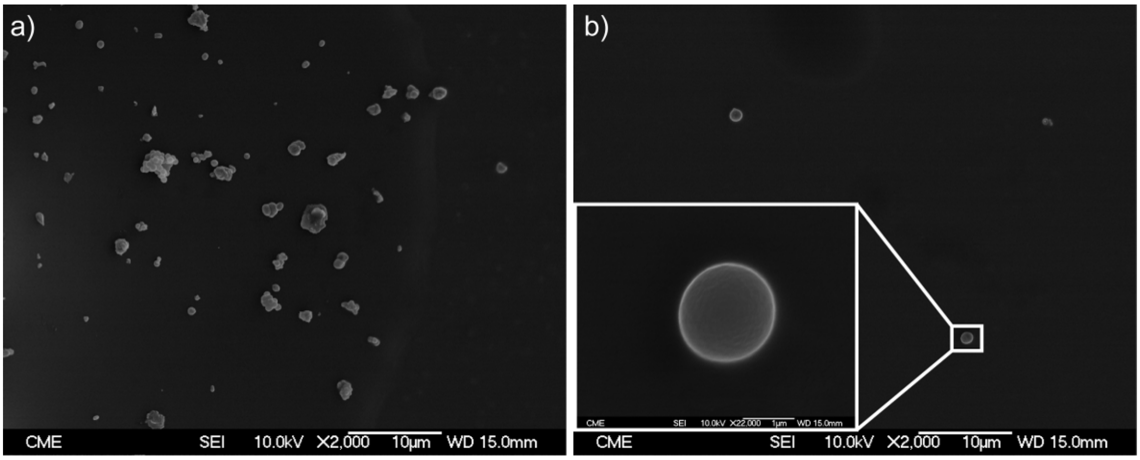


Figure S5. SEM images (298 K, 1 x 10^{-4} M in acetonitrile, glass substrate) of the spherical objects formed from **2**.

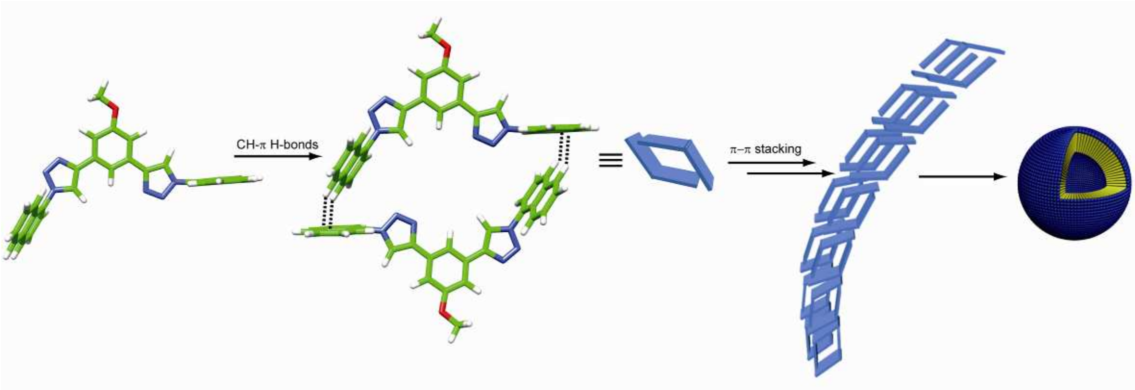


Figure S6. Schematic illustration of the self-assembly process of compound **2**.

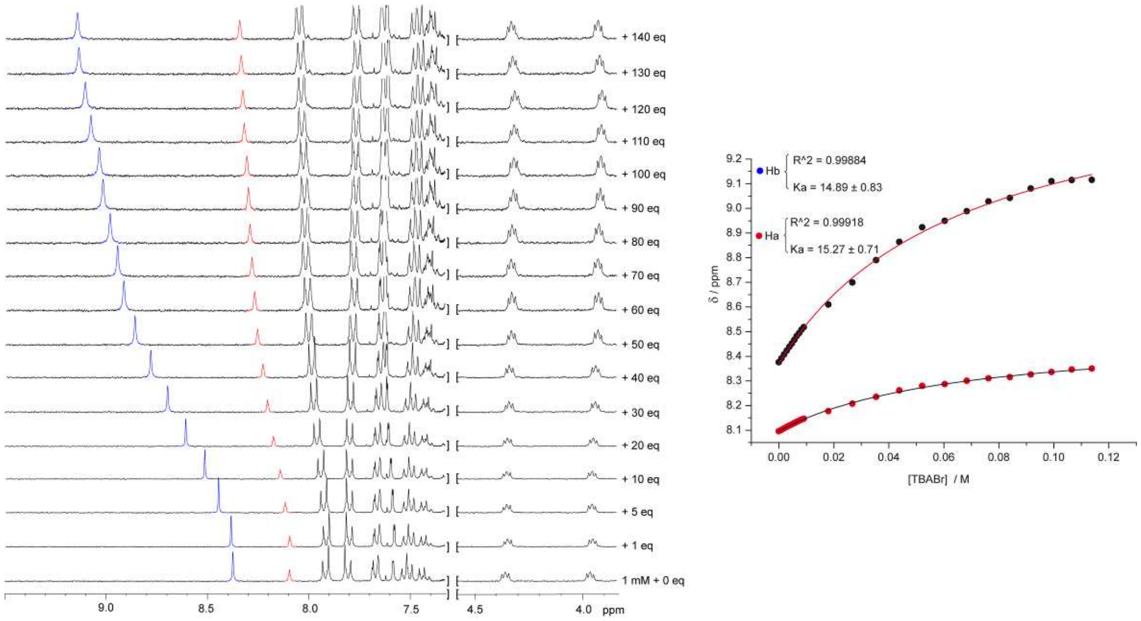


Figure S7. (a) Partial ^{1}H NMR spectra (300 MHz, 298 K, 1 mM, $CDCl_3$) of aryl triazole **1** upon titrational addition of TBABr. (b) Binding isotherms corresponding to the variation of the chemical shift of H_a (red) and H_b (blue) upon addition of TBABr and fitting to the model of 1:1 complexation.

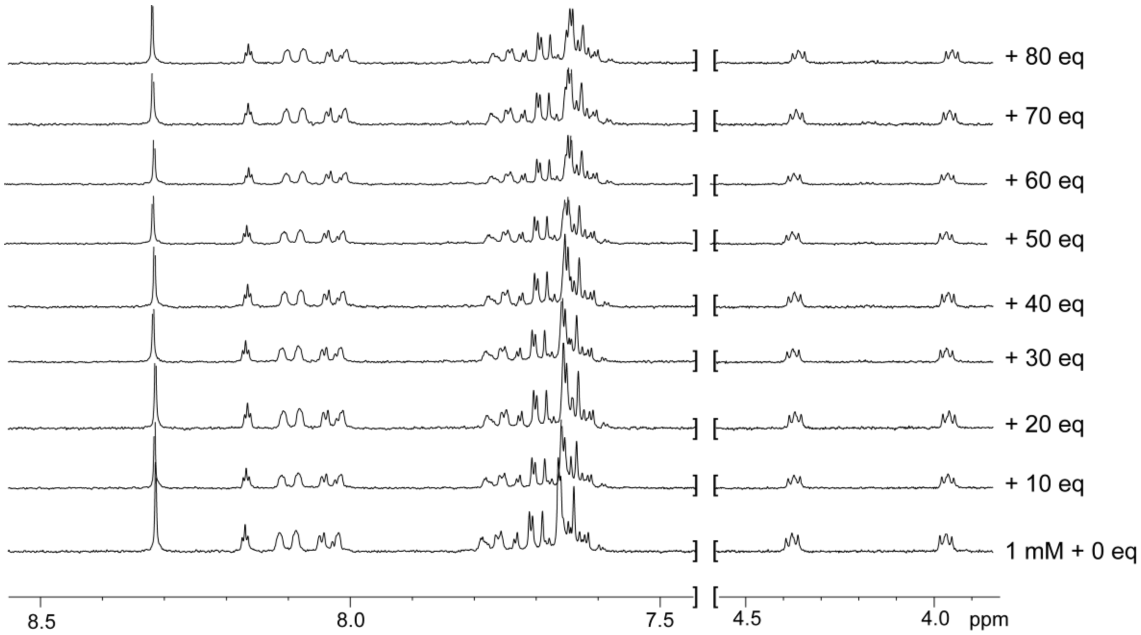


Figure S8. Partial ^{1}H NMR spectra (300 MHz, 298 K, 1 mM, $CDCl_3$) of aryl triazole **2** upon titrational addition of TBABr.

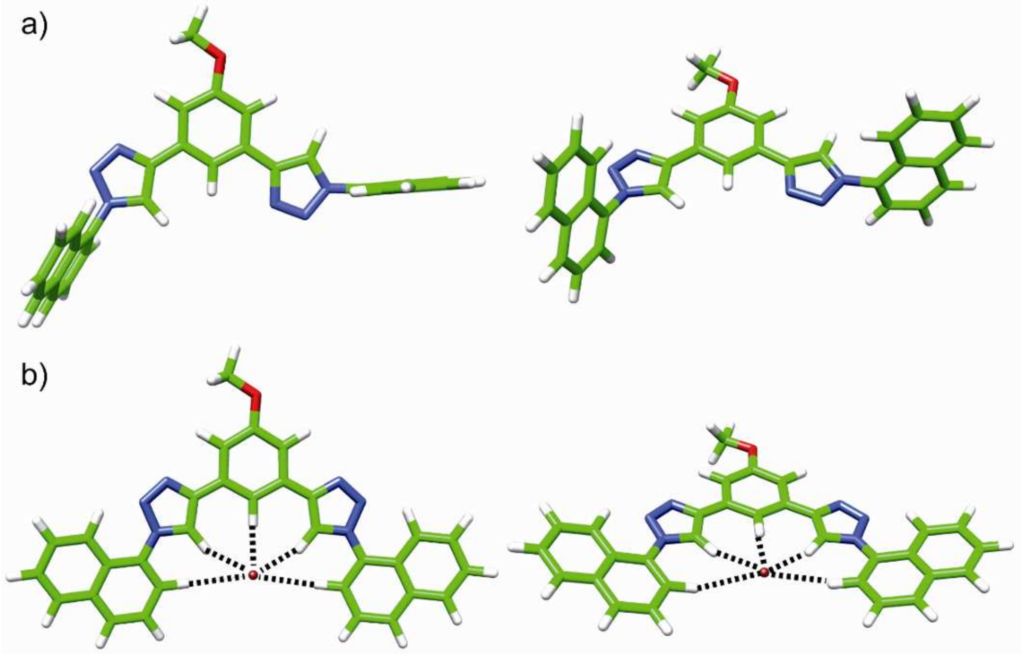


Figure S9. Calculated molecular geometry of aryl-triazole receptor **2** without (a) and with (b) TBABr (the TEG chains have been replaced by a methyl group for simplicity purposes).

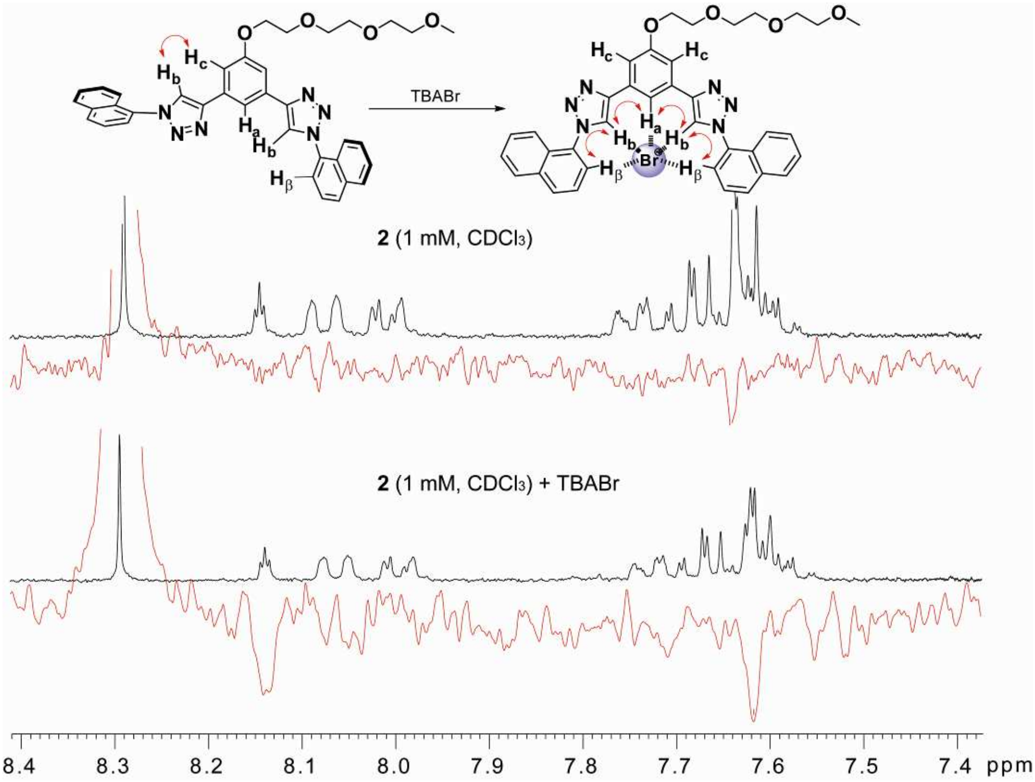


Figure S10. Partial ^{1}H NMR spectra (300 MHz, 298 K) (black) and NOE experiments (red) of aryl triazole **2** in $CDCl_3$ at 1 mM without (top) and with TBABr (bottom). In the upper part of the spectra, the NOE contacts are represented by curved arrows.

2. Experimental Section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. High resolution Electrospray ionization experiments FTMS were recorded on a Bruker APEX Q IV spectrometer. SEM images were obtained from on a JEOL JSM 6335F microscope working at 5kV. The samples for SEM imaging were prepared by slow diffusion of acetonitrile vapour into a solution of the corresponding triazole in chloroform. The obtained suspension was deposited onto a glass substrate and the remaining solvent dried at the air.

3. X-Ray data collection and structure refinement

Data collection was carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) operating at 50 kV and 35 mA. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 20s covered 0.3 in ϖ. The cell parameters were determined and refined by a least-squares fit of all reflections. The first 100 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. A summary of the fundamental crystal and refinement data is given in Table S1. The structure was solved by direct methods and refined by full-matrix least-square procedures on F^2 (SHELXL-97)*. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in their calculated positions and refined riding on the respective carbon atoms. Some atoms from the molecule were disordered over two sites with occupancies of approximately 50%. The disordered ring C17-C22 was refined using rigid body constrains and some atoms of the chain C40-O4-C41 were refined using geometrical restrains and variable common C-C distances (see Figure).

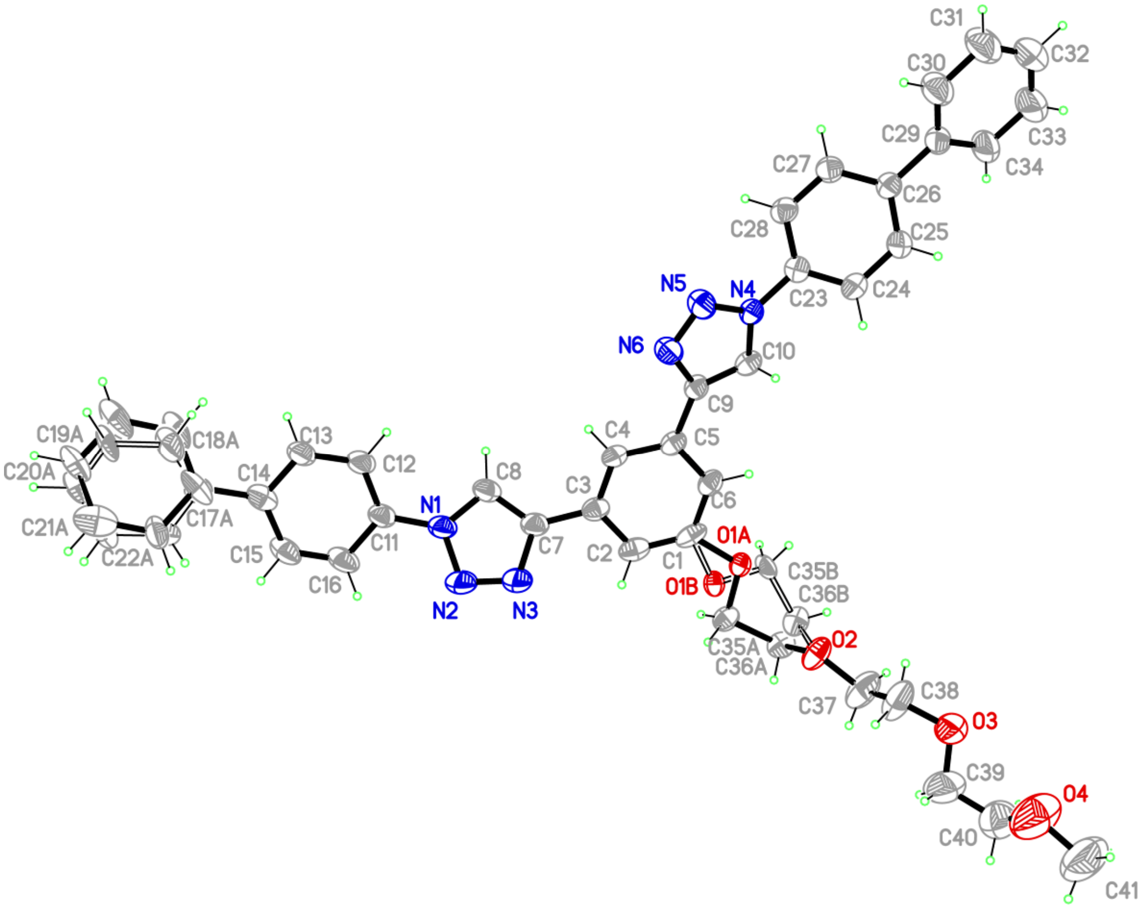


Figure S11. ORTEP diagram (50% probability level) of compound **1**.

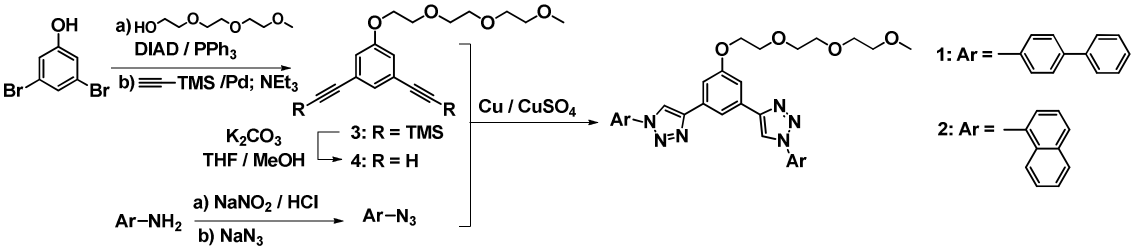
Further crystallographic details for the structure reported in this paper may be obtained from the Cambridge Crystallographic Data Center, on quoting the depository number CCDC: **804817**

*G.M. Sheldrick, 'SHELX97, Program for Refinement of Crystal Structure', University of Göttingen, Göttingen, Germany, 1997

Table S1. Crystal data and structure refinement for $C_{41}H_{38}N_6O_4$ (compound **1**).

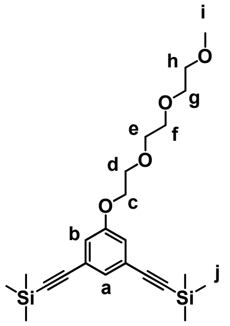
Identification code	p21c	
Empirical formula	C41 H38 N6 O4	
Formula weight	678.77	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 33.436(4) Å	a= 90°.
	b = 5.8453(6) Å	b= 96.269(2)°.
	c = 17.8776(19) Å	g = 90°.
Volume	3473.2(6) Å3	
Z	4	
Density (calculated)	1.298 mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	1432	
Crystal size	0.48 x 0.27 x 0.05 mm3	
Theta range for data collection	1.23 to 25.00°.	
Index ranges	-39<=h<=39, -6<=k<=6, -21<=l<=15	
Reflections collected	25183	
Independent reflections	6101 [R(int) = 0.1344]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	6101 / 11 / 520	
Goodness-of-fit on F2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0906, wR2 = 0.2322	
R indices (all data)	R1 = 0.2415, wR2 = 0.3279	
Extinction coefficient	0.0036(13)	
Largest diff. peak and hole	0.554 and -0.297 e.Å-3	

4. Synthetic details and characterization



1-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)-3,5-dibromobenzene and 1-azidonaphthalene were prepared according to previously reported synthetic procedures (see: Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* ***2004***, *126*, 12796; and Hu, M.; Li, J.; Yao, S. Q. *Org. Lett.* **2008**, *10*, 5529–5531) and showed identical spectroscopic properties to those reported therein. 4-Azido-1,1'-biphenyl was prepared by a slightly modified procedure than reported in Hu, M.; Li, J.; Yao, S. Q. *Org. Lett.* **2008**, *10*, 5529–5531.

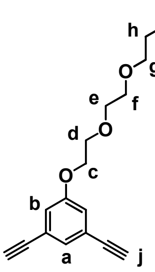
1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-3,5-bis(2-(trimethylsilyl)ethynyl)benzene (3)



$C_{23}H_{36}O_4Si_2$
Exact Mass: 432,2152

1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-3,5-dibromobenzene (4.8 g, 12.06 mmol), bis-(triphenylphosphine)-palladium(II)-chloride (849 mg, 1.21 mmol) and copper (I) iodide (114 mg, 0.60 mmol), triethylamine (6.7 mL, 48.24 mL) were dissolved in dry THF (20 mL). The mixture was subjected to several vacuum/argon cycles and trimethylsilylacetylene (5.1 mL, 36.18 mmol) was added. The mixture was heated at 70 ºC and stirred for 3 hours. After evaporation of the solvent under reduced pressure, the crude was washed with HCl 1N, NH_4Cl saturated solution, water and extracted with methylenechloride. The residue was purified by column chromatography (silica gel, $CHCl_3$) affording compound **3** as a brown oil (4.42 g, 85%). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.19 (1H, H_a, t, J = 1.3Hz), 6.96 (2H, H_b, d, J = 1.3Hz), 4.11 (2H, H_c, t, J = 4.8 Hz), 3.84 (2H, H_d, t, J = 4.8 Hz), 3.74 -3.65 (6H, H_{e+f+g}, m), 3.56 (2H, H_h, m), 3.39 (3H, H_i, s), 0.24 (18H, H_j, s);^{13}C NMR ($CDCl_3$, 75Mz) δ 158.6, 128.7, 124.6, 118.8, 104.3, 95.0, 72.3, 71.2, 71.0, 70.9, 69.9, 68.1, 59.4, 0.2; FTIR (neat) 650, 690, 760, 845, 985, 1066, 1115, 1250, 1297, 1328, 1417, 1582, 2160, 2880, 2958 cm^{-1}.

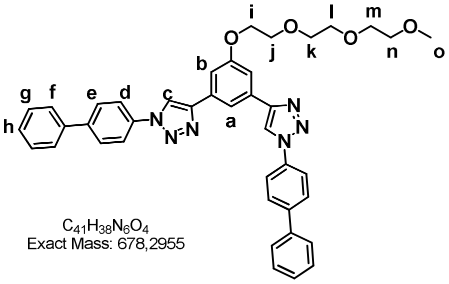
1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-3,5-diethynylbenzene (4)



$C_{17}H_{20}O_4$
Exact Mass: 288,1362

Compound **3** (4.42 g, 10.22 mmol) was dissolved in 60 mL of a THF:methanol mixture (1:1) and potassium carbonate was added (3.11 g, 22.50 mmol). The reaction mixture was stirred for one hour. After evaporation of the solvent, the residue was washed with water, extracted with methylene chloride, dried over $MgSO_4$ and evaporated the solvent. The residue was purified by column chromatography (silica gel, hexane:diethyl ether 1:2) affording compound **4** as a brown oil (2.03 g, 69%).^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (1H, H_a, br), 7.02 (2H, H_b, br), 4.11 (2H, H_c, t, J = 4.4 Hz), 3.84 (2H, H_d, t, J = 4.4 Hz), 3.74 -3.64 (6H, H_{e+f+g}, m), 3.54 (2H, H_h, m), 3.38 (3H, H_i, s), 3.07 (2H, H_j, s);^{13}C NMR ($CDCl_3$, 75Mz) δ 158.7, 128.8, 123.7, 119.3, 82.9, 72.3, 71.3, 71.0, 70.9, 69.9, 68.1, 59.4; FTIR (neat) 673, 803, 862, 942, 1066, 1107, 1199, 1250, 1294, 1322, 1353, 1420, 1453, 1582, 1726, 2110, 2880, 3244, 3288 cm^{-1}.

Compound 1

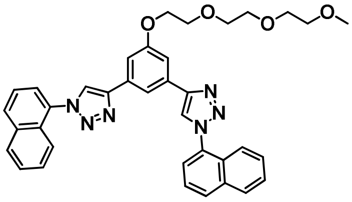


$C_{41}H_{38}N_6O_4$
Exact Mass: 678,2955

Compound **4** (516 mg, 1.79 mmol), 4-biphenyl azide (1.00 g, 5.38 mmol), copper sulphate pentahydrate (9 mg, 0.04 mmol) and sodium ascorbate (18 mg, 0.09 mmol) were dissolved in 40 mL of a dichloromethane:water mixture (1:1) under Argon atmosphere. The reaction mixture was stirred for 72 hours and then the organic layer was separate, dried over $MgSO_4$ and filtered. After evaporation of the solvent under reduced pressure, the residue was purified under by column chromatography (silica gel, chloroform:methanol 100:1) affording compound **1** as a white solid (300 mg, 25%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35 (2H, H_c, s), 8.05 (1H, H_a, s), 7.87 (4H, H_d, d, J=8.6Hz), 7.75 (4H, H_e, d, J=8.6Hz), 7.63 (4H, H_f, d, J=7.1Hz), 7.54-7.40 (8H, H_{b+g+h}, m), 4.30 (2H,

H_i, t, J = 4.7 Hz), 3.92 (2H, H_j, t, J = 4.7 Hz), 3.79 (2H, H_k, t, J=4.7 Hz), 3.74 -3.55 (6H, H_{l+m+n}, m), 3.38 (3H, H_o, s); ^{13}C NMR ($CDCl_3$, 75Mz) δ 160.1, 148.2, 142.1, 139.9, 136.4, 132.4, 129.3, 128.7, 128.3, 127.4, 121.0, 118.4, 116.2, 112.3, 72.3, 71.2, 71.0, 70.9, 70.1, 68.2, 59.3; FTIR (neat) 647, 696, 768, 807, 844, 942, 995, 1041, 1071, 1106, 1200, 1235, 1354, 1403, 1454, 1490, 1525, 1561, 1603, 2880, 2922, 3066, 3135 cm^{-1}; ESI-FTMS: calcd. for $C_{41}H_{38}NaO_4$ $[M+Na]^+$,701.28467; found, 701.28610.

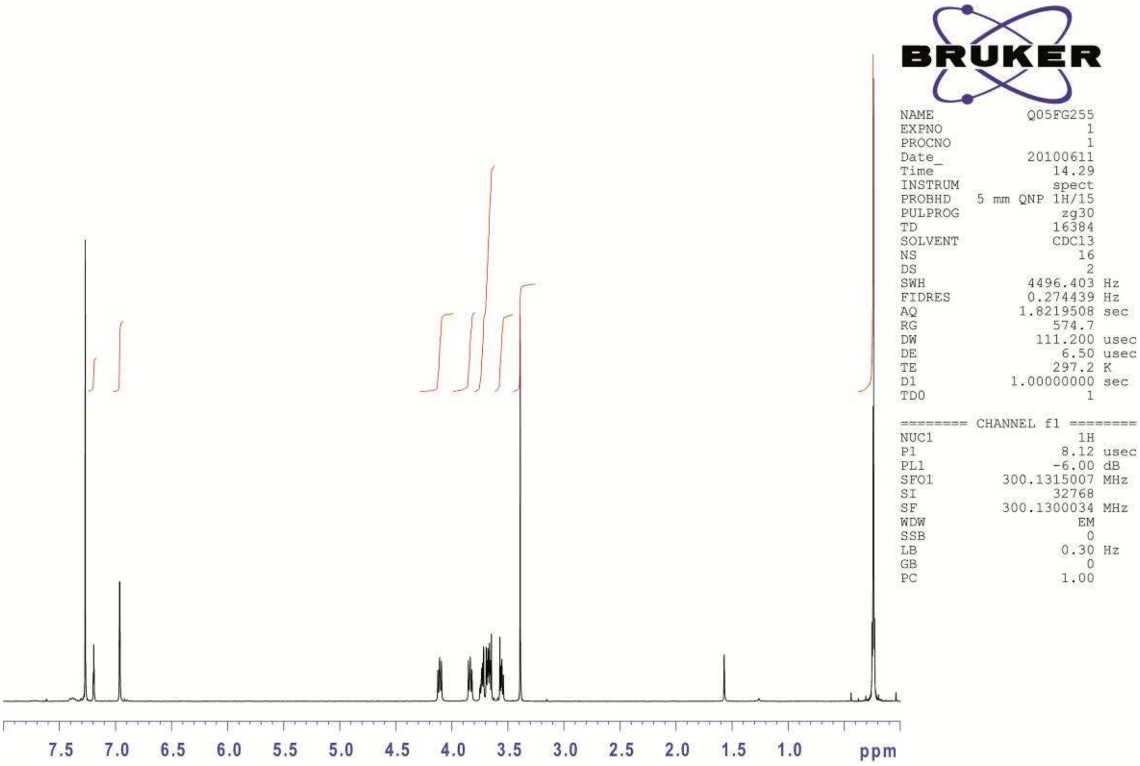
4-(3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-(1-(naphthalen-1-yl)-1H-1,2,3-triazol-4-yl)phenyl)-1-(naphthalen-1-yl)-1H-1,2,3-triazole (2)



$C_{37}H_{34}N_6O_4$
Exact Mass: 626,2642

A mixture of compound **4** (312 mg, 1.08 mmol), 1-naphtyl azide (529 mg, 3.25 mmol), copper sulphate pentahydrate (5 mg, 0.04 mmol), sodium ascorbate (10 mg, 0.09 mmol) and metallic copper in 4 mL of a dichloromethane:water mixture (1:1), under Argon atmosphere, was stirred for 25 hours. After that, the organic layer was separate, dried over $MgSO_4$ and filtered. After evaporation of the solvent under reduced pressure, the residue was purified under by column chromatography (silica gel, chloroform:methanol 100:1) affording compound **2** as a brown oil (600 mg, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26 (2H, s), 8.11 (1H, t, J=1.4 Hz), 8.01 (2H, d, J=7.8Hz), 7.95 (2H, m), 7.71 (2H, m), 7.64-7.51 (10H, m); 4.33 (2H, m), 3.93 (2H, t, J = 4.7 Hz), 3.77 (2H, t, J=4.7 Hz), 3.72-3.64 (4H, m), 3.53 (2H, m), 3.35 (3H, s); ^{13}C NMR ($CDCl_3$, 75Mz) δ 160.2, 147.5, 134.4, 133.9, 132.5, 130.7, 128.7, 128.6, 128.2, 125.3, 123.8, 123.1, 122.6, 116.2, 112.3, 72.2, 71.1, 71.0, 70.8, 70.0, 68.1, 59.2; FTIR (neat) 664, 689, 772, 802, 861, 949, 1038, 1068, 1111, 1207, 1351, 1442, 1472, 1512, 1555, 1600, 2878, 3064, 3126 cm^{-1}; ESI-FTMS: calcd. for $C_{37}H_{35}N_6O_4$ $[M+H]^+$,627.27143; found, 627.26851.

5. Collection of spectra



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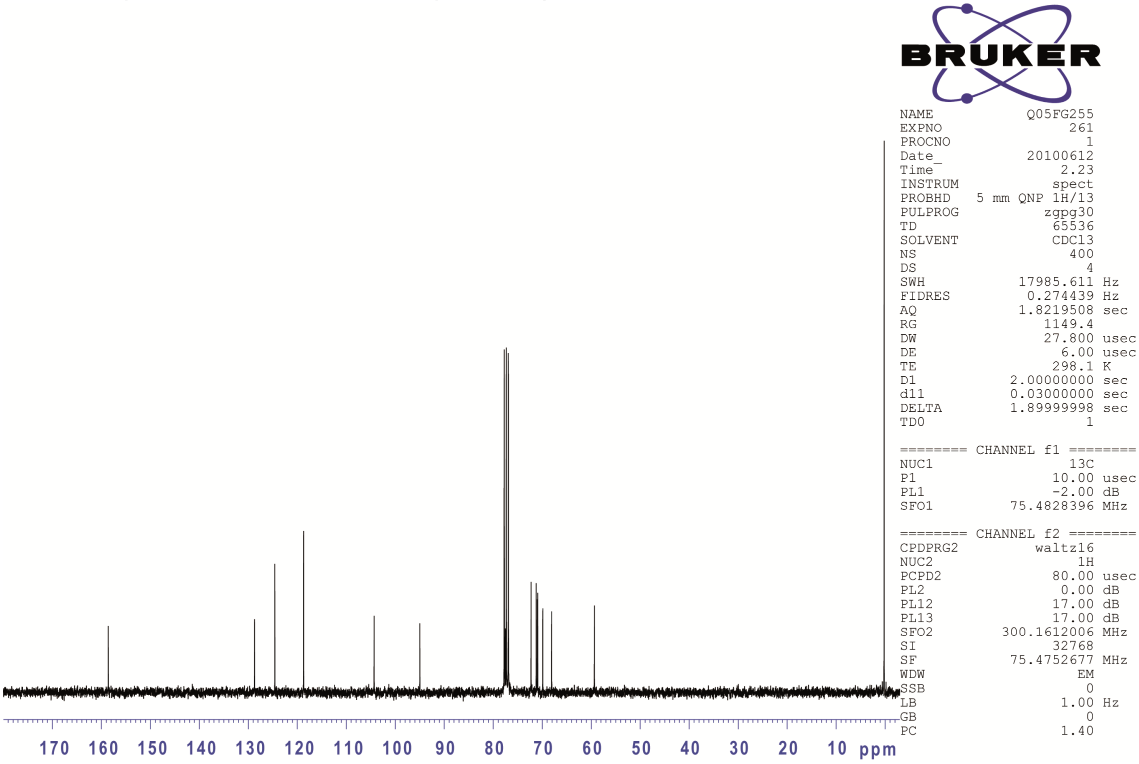
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **3**



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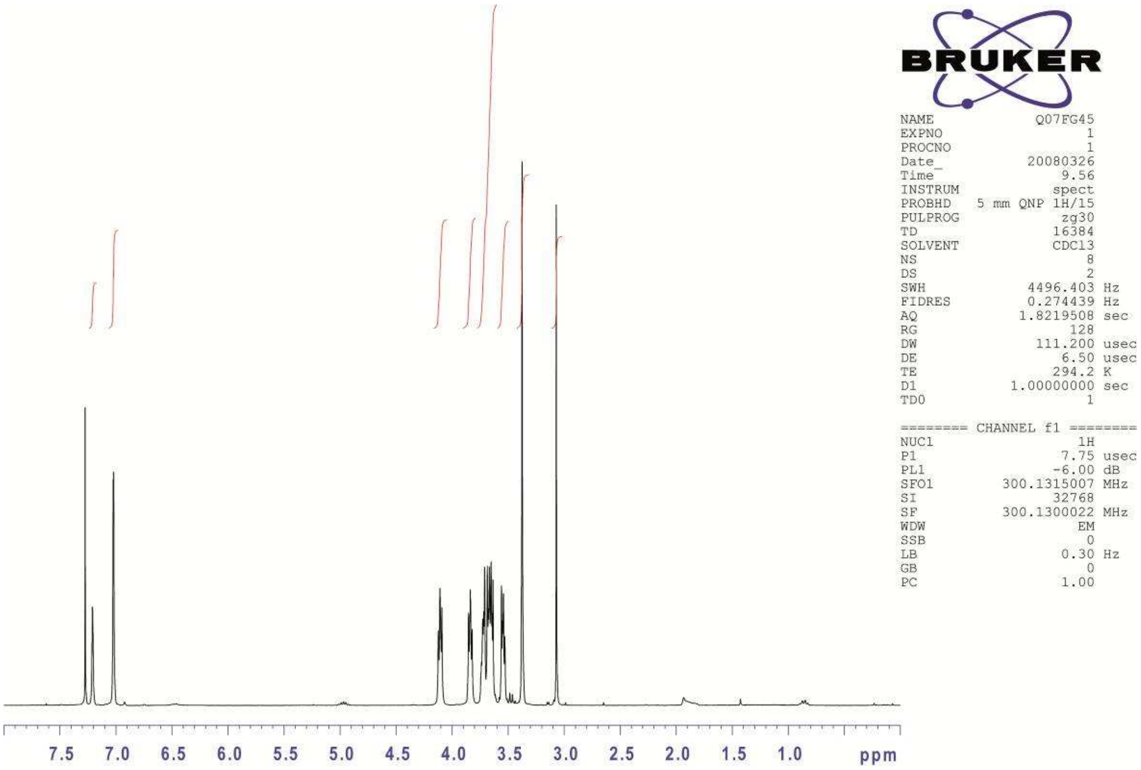
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **3**



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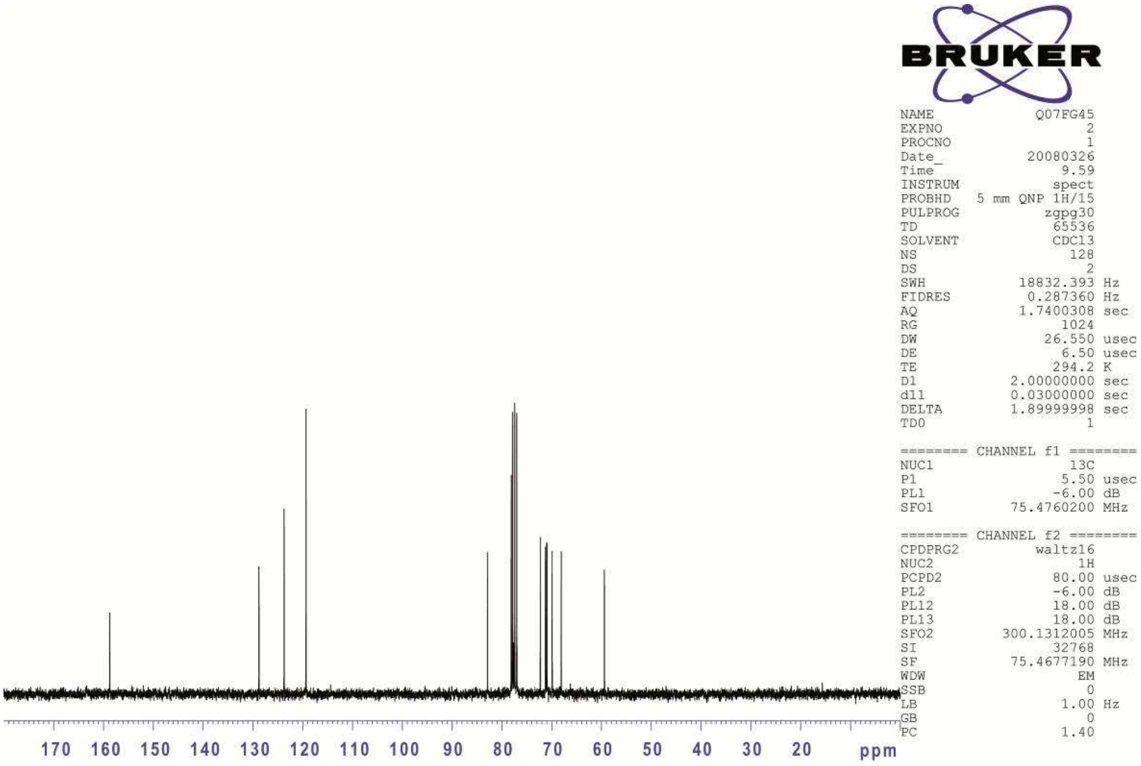
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **4**



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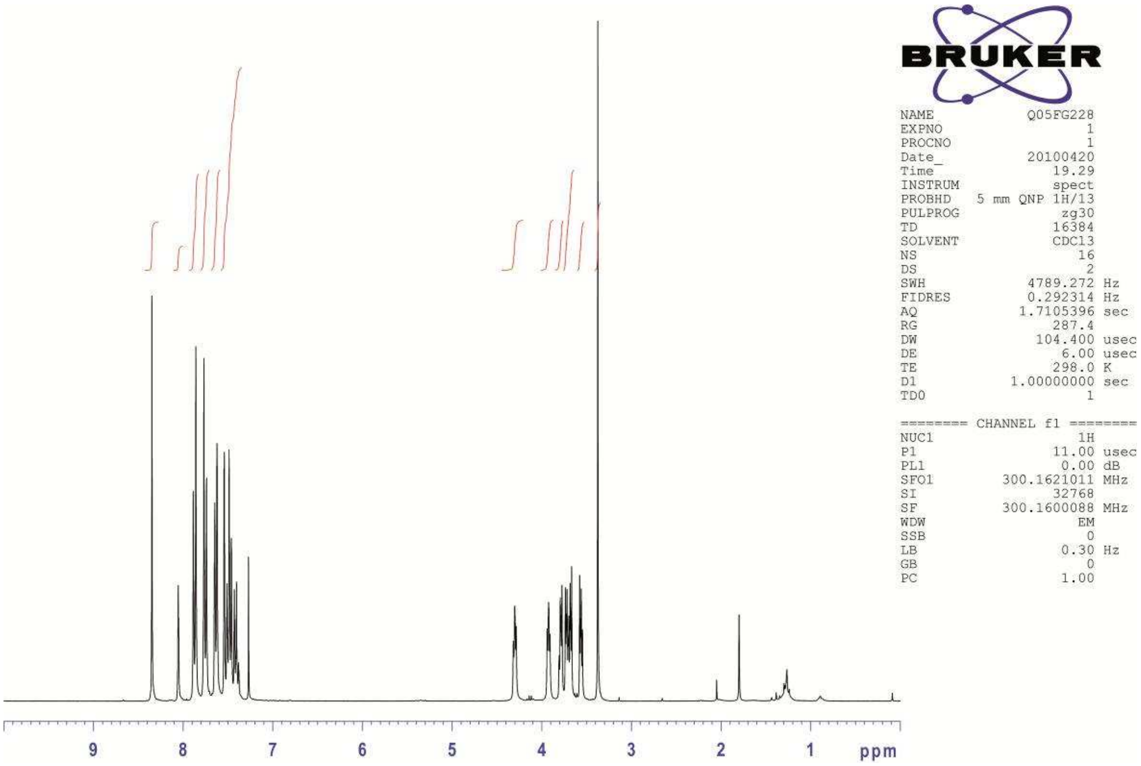
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **4**



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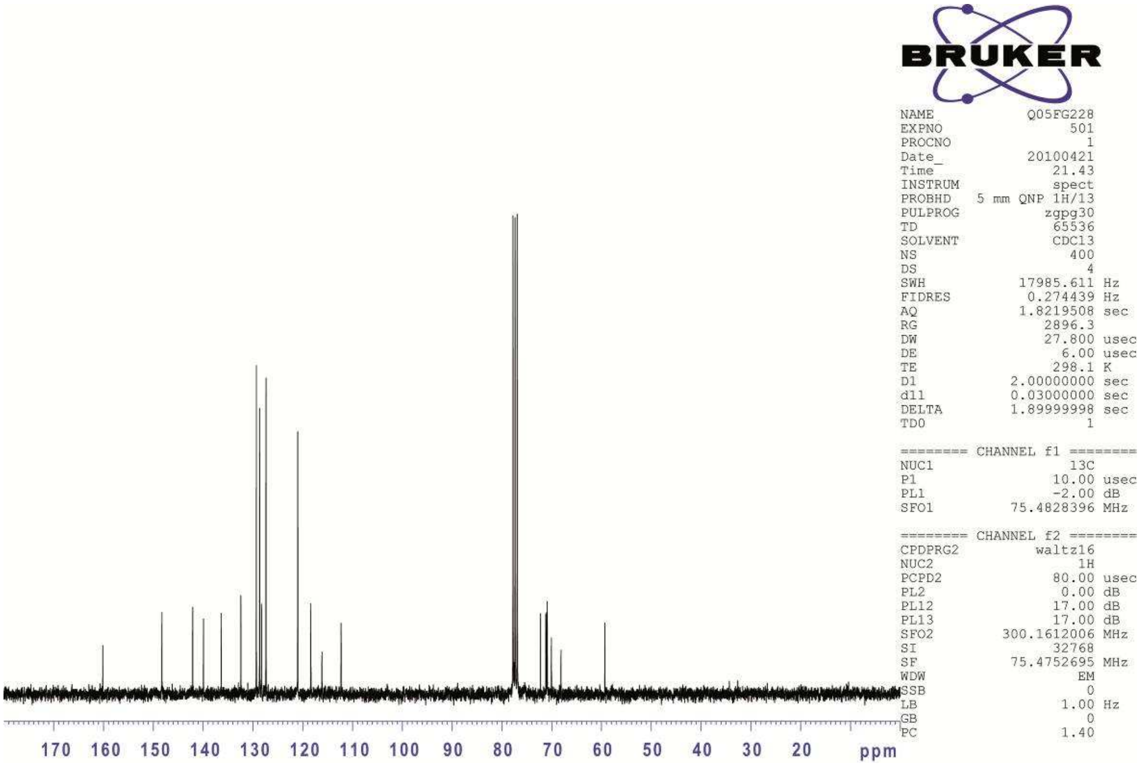
Time               19.29
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4789.272 Hz
FIDRES          0.292314 Hz
AQ             1.7105396 sec
RG                 287.4
DW               104.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 0.00 dB
SFO1         300.1621011 MHz
SI                 32768
SF           300.1600088 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) of compound **1**

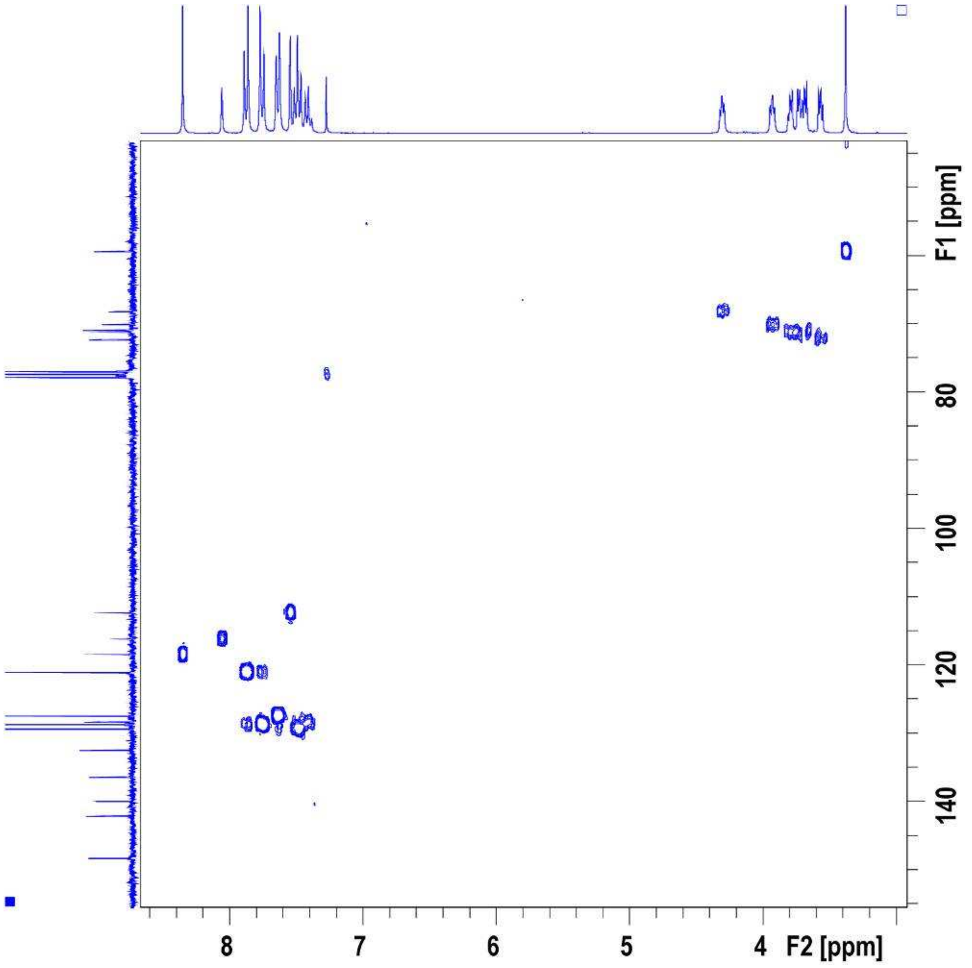


```
NAME            Q05FG228
EXPNO                501
PROCNO                 1
Date_           20100421
Time               21.43
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   400
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                2896.3
DW                27.800 usec
DE                  6.00 usec
TE                 298.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

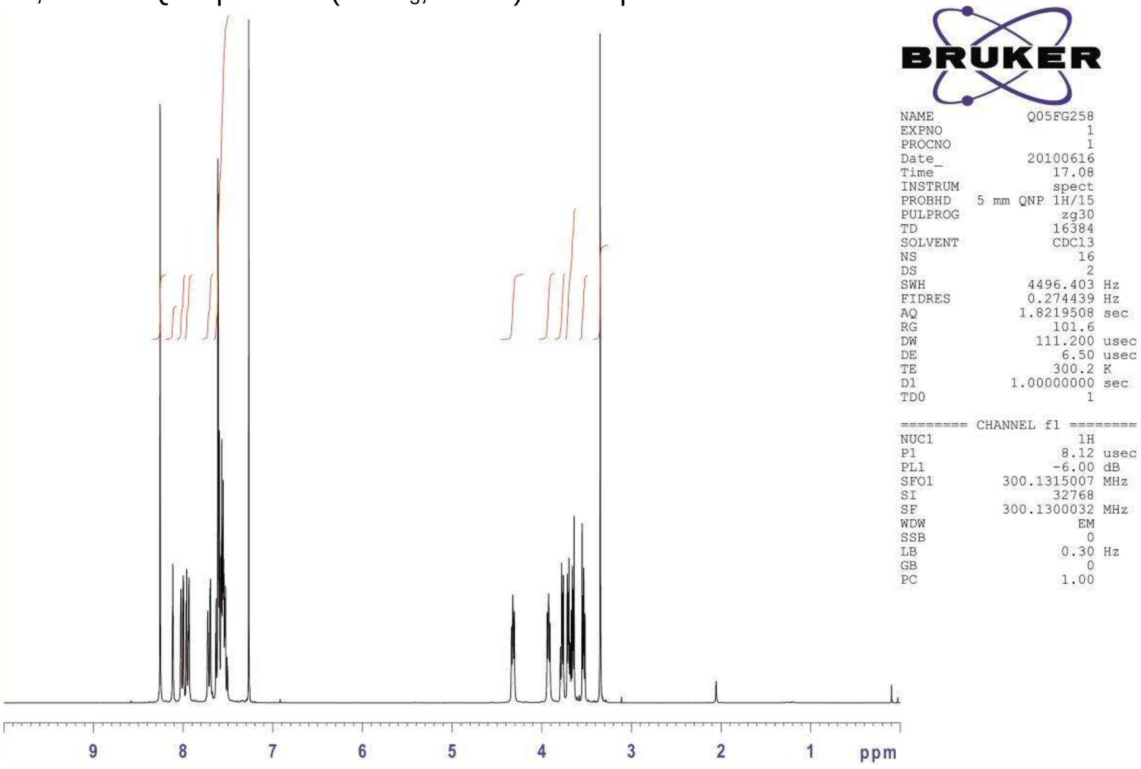
======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                -2.00 dB
SFO1          75.4828396 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.00 dB
PL13               17.00 dB
SFO2         300.1612006 MHz
SI                 32768
SF            75.4752695 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) of compound **1**



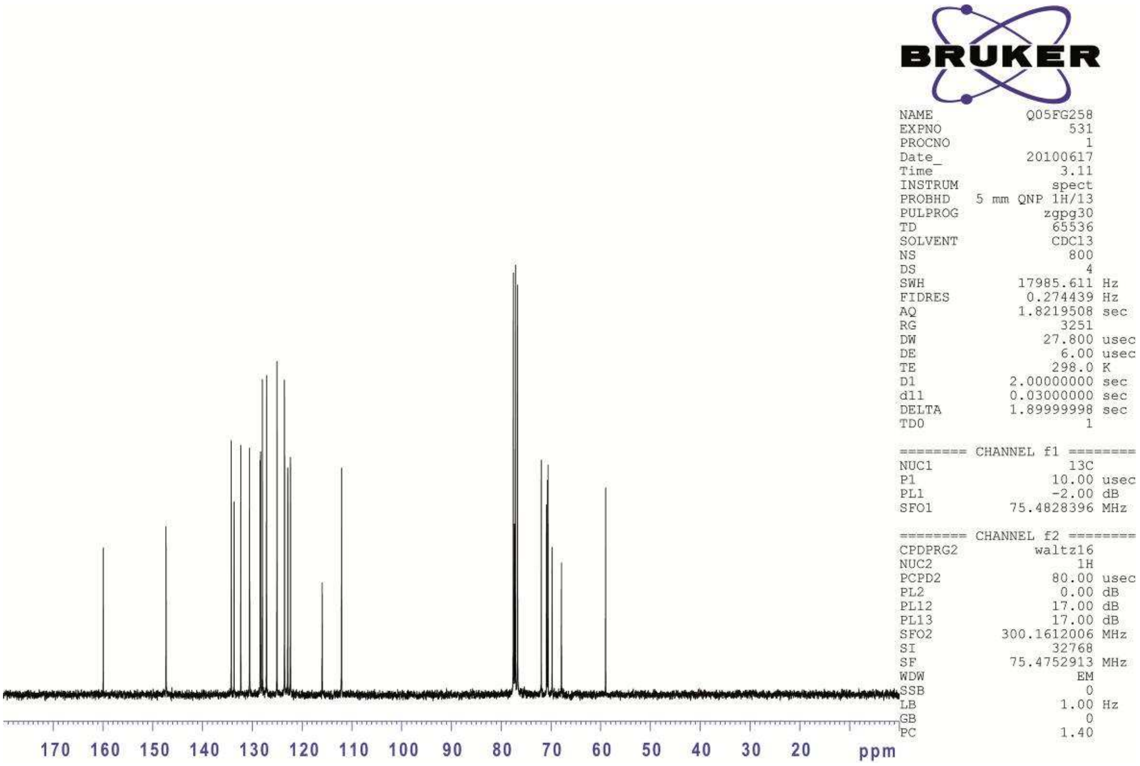
^{1}H, ^{13}C-HMQC spectrum (CDCl$_3$, 298 K) of compound **1**



```
NAME             Q05FG258
EXPNO                   1
PROCNO                  1
Date_            20100616
Time                17.08
INSTRUM             spect
PROBHD   5 mm QNP 1H/15
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4496.403 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  101.6
DW                111.200 usec
DE                   6.50 usec
TE                  300.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.12 usec
PL1                 -6.00 dB
SFO1          300.1315007 MHz
SI                  32768
SF            300.1300032 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR (CDCl$_3$, 300 MHz, 298 K) of compound **2**

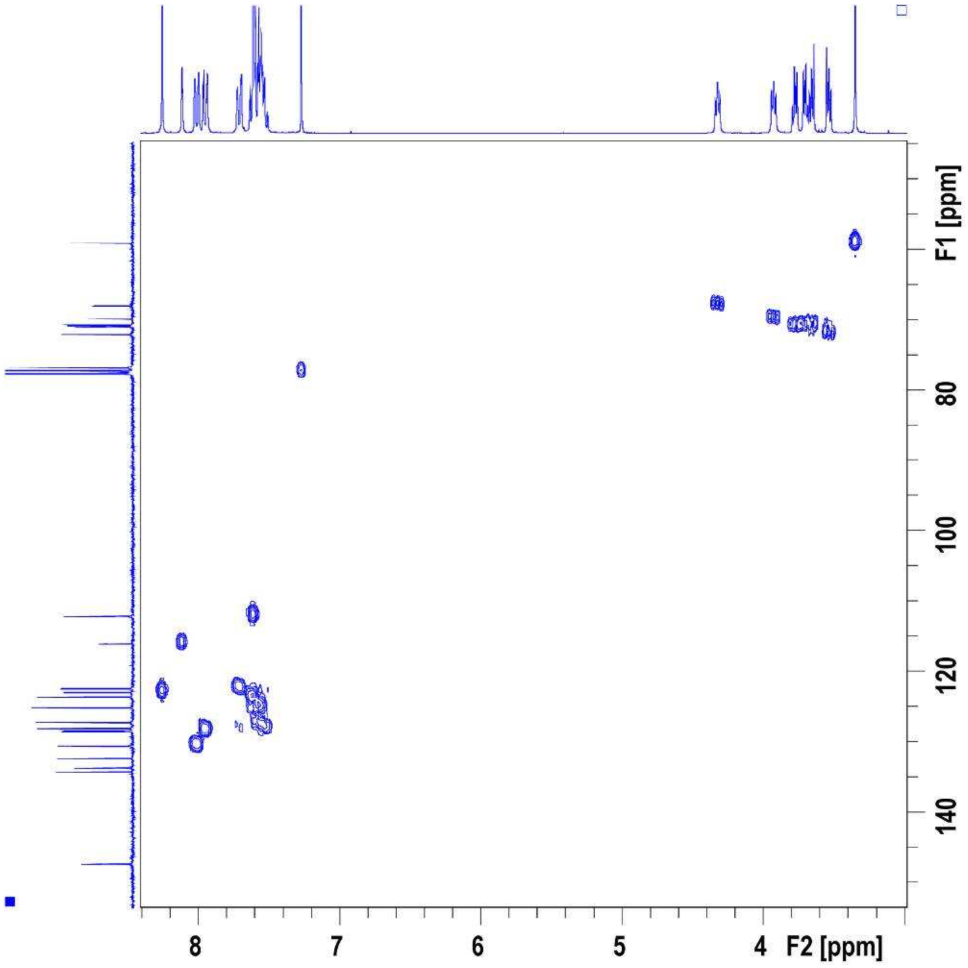


```
NAME              Q05FG258
EXPNO                  531
PROCNO                   1
Date_             20100617
Time                  3.11
INSTRUM              spect
PROBHD     5 mm QNP 1H/13
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     800
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                    3251
DW                  27.800 usec
DE                    6.00 usec
TE                   298.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

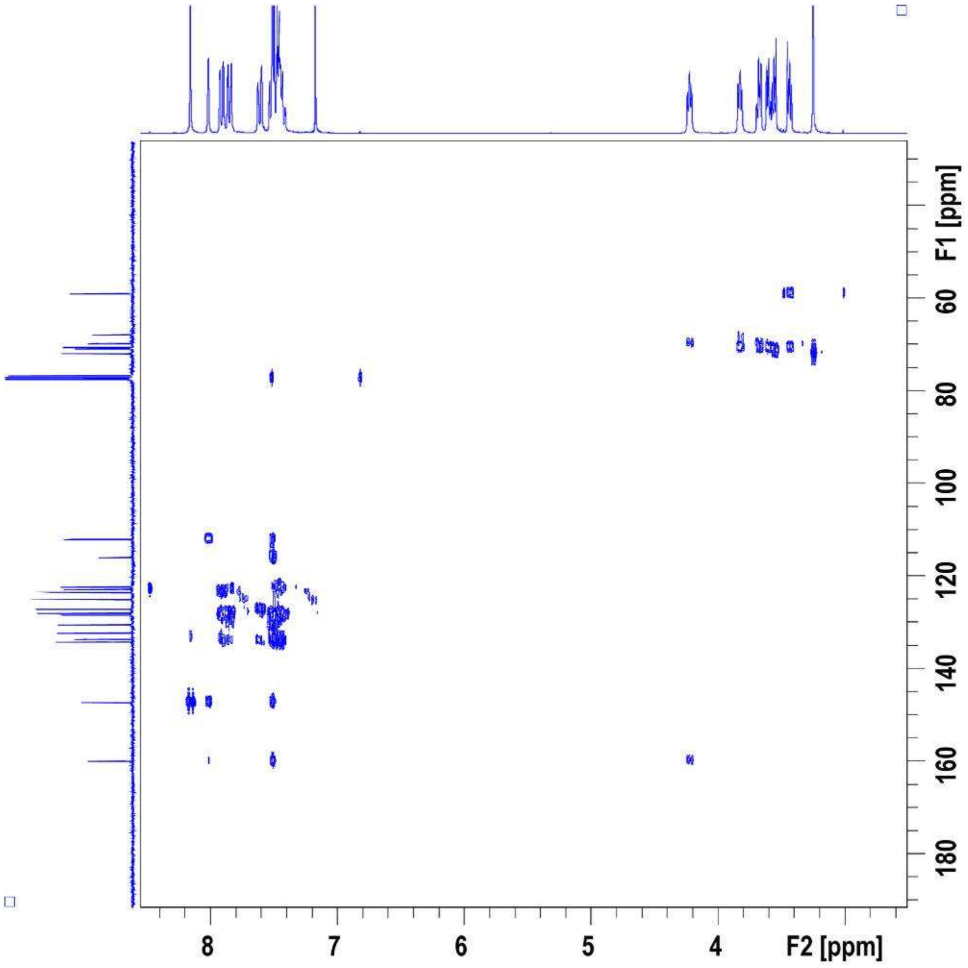
======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                  -2.00 dB
SFO1            75.4828396 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.00 dB
PL13                 17.00 dB
SFO2           300.1612006 MHz
SI                   32768
SF              75.4752913 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{13}C NMR (CDCl$_3$, 75 MHz, 298 K) of compound **2**



^{1}H, ^{13}C-HMQC spectrum (CDCl$_3$, 298 K) of compound **2**



^{1}H, ^{13}C-HMBC spectrum ($CDCl_3$, 298 K) of compound **2**