

Supporting Information

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Octamethylbicyclo[3.2.1]octadienes from the Rhizobacterium *Serratia odorifera***

*Stephan H. von Reuß, Marco Kai, Birgit Piechulla, and Wittko Francke**

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Experimental Part

General Information: ^1H NMR spectra were recorded with a Bruker WM 500 instrument (500.1 MHz). Broadband decoupled ^{13}C $\{^1\text{H}\}$ NMR and ^{13}C PENDANT spectra were run on a Bruker AV 400 instrument (100.6 MHz) or Bruker WM 500 instrument (125.8 MHz). Two dimensional NMR experiments (COSY-90, HMQC, HMBC and *gp*-NOESY) were carried out using the Bruker WM 500 instrument (^1H : 500.13 MHz, ^{13}C : 125.8 MHz). $[\text{D}_6]$ Benzene was used as the solvent, and tetramethylsilane (TMS) served as the internal standard ($\delta = 0$ ppm). 70 eV EI-MS measurements were obtained with a VG Analytical 70-250S mass spectrometer coupled to a HP 5890 gas chromatograph (Hewlett Packard) equipped with a 25 m CPSil-5 CB (Chrompack) fused-silica capillary. Temperature program from 80 °C to 270 °C at 10 °C/min. 70 eV HR-MS measurements at a resolution of 6000 were carried out on a VG Analytical 70-SE mass spectrometer coupled to a HP 5890 gas chromatograph (Hewlett Packard) equipped with a 50 m FFAP fused-silica capillary. Preparative GC was performed with a modified Varian 1400 gas chromatograph equipped with a stainless steel column (1.85 m x 4.3 mm; Silcosteel, Amchro) packed with 10 % Polydimethylsiloxane SE-30 on Chromosorb W-HP. Helium was used as the carrier gas at a flow rate of approximately 120 ml/min at 120 °C. Eluting compounds were trapped in Teflon[®] tubes cooled with liquid N_2 .

Bacteria and Growth Conditions: *Serratia odorifera* 4Rx13 was obtained from the Strain Collection of Antagonistic Microorganisms (SCAM; University of Rostock, Microbiology). Previously, it had been isolated from the rhizosphere of *Brassica napus*. *S. odorifera* was incubated on nutrient broth agar II (NA II; peptone from casein 3.5 g l⁻¹, peptone from meat 2.5 g l⁻¹, peptone from gelatine 2.5 g l⁻¹, yeast extract 1.5 g l⁻¹, NaCl 5 g l⁻¹, agar-agar 15 g l⁻¹, pH 7.2), for 12–24 h at 30°C. NBII liquid culture medium is identical to NAII without addition of agar.

Collection of volatiles: A single colony of *S. odorifera* was picked and suspended in 6 ml of NBII media. After incubation for 24 hours at 30°C and shaking at 180 rpm, 1 ml (OD₆₀₀ 0,8 – 1,4) was used to inoculate 250 ml NBII. Of this preculture 100 ml were used to inoculate a 10 l culture in a 20 l wide-necked glass flask closed with a glass lid, which had an inlet and an outlet. During growth, the bacterial culture was kept at 30°C and stirred with a magnetic stir bar at 600 rpm. A diaphragm pump (Rietschle, Puchheim, Germany) pulled charcoal-purified air at a flow rate of 3 l h⁻¹, and volatiles released during 30 hours of growth of *S. odorifera* were trapped on 100 mg SuperQ (Alltech Associates, Deerfield, IL, USA). The collected volatiles were eluted from SuperQ with 3 batches of 500 µl dichloromethane.

Cycloaddition: Under N₂ atmosphere a solution of 272 mg 1,2,3,4,5-pentamethylcyclopentadiene (**2**, 2 mmol) in 1.4 ml dry acetonitrile was treated with 480 mg sodium iodide (3.2 mmol; dried at 150 °C for 24 h and powdered) and 160 mg copper powder (2.4 mmol). A solution of 200 mg 2,4-dibromopentan-3-one (**3**, 0.8 mmol) in 0.6 ml acetonitrile was added dropwise, and the resulting mixture was stirred for 4 h. Subsequently, 10 ml diethyl ether were added and the resulting mixture poured on 10 ml ice cold 15 % aqueous ammonia solution. The organic layer was separated and the aqueous layer extracted with 3 x 5 ml diethyl ether. The combined organic solutions were washed with 3 x 10 ml ice cold 5 % aqueous ammonia solution until free of blue colored copper salts and with 5 x 10 ml ice-water until neutral pH. The organic solution was dried over Na₂SO₄, and the solvent was removed in vacuo under N₂ at 30 °C. The residue was cooled to 0 °C, the flask filled with N₂ and the residue dissolved in 1 ml pentane. Upon storage at – 20 °C the majority of **5** precipitated. The supernatant solution was fractionated by column chromatography on silica gel using pentane to afford 39 mg **4** as a colorless oil (0.18 mmol, 22 % yield). Precipitated **5** and the amount of **5** obtained upon chromatography made up 90 mg (0.4 mmol, 50 % yield).

8-*anti*-2,4-*bisaxial*-1,2,4,5,6,7,8-heptamethylbicyclo[3.2.1]oct-6-en-3-one (**4**): ^1H NMR (500 MHz, $[\text{D}_6]$ benzene, TMS): $\delta = 0.63$ (d, $^3J = 6.6$ Hz, 3H; 8-CH₃), 0.66 (s, 6H; 1-CH₃, 5-CH₃), 1.00 (d, $^3J = 7.6$ Hz, 6H; 2-CH₃, 4-CH₃), 1.26 (s, 6H; 6-CH₃, 7-CH₃), 2.03 (q, $^3J = 6.7$ Hz, 1H; 8-H), 2.16 (q, $^3J = 7.2$ Hz, 2H; 2-CH, 4-CH); ^{13}C PENDANT (125 MHz, $[\text{D}_6]$ benzene, TMS): $\delta = 9.5$ (q; 6-CH₃, 7-CH₃), 10.7 (q; 8-CH₃), 15.1 (q; 1-CH₃, 5-CH₃), 16.8 (q; 2-CH₃, 4-CH₃), 40.5 (d; 8-CH), 49.8 (s; 1-C, 5-C), 51.9 (d; 2-CH, 4-CH), 136.1 (s; 6-C, 7-C), 216.0 (s; 3-CO); MS (70 eV): m/z (%): 220 (19) [M^+], 205 (1), 163 (16), 149 (9), 136 (54), 135 (61), 134 (100), 121 (23), 119 (14), 105 (16), 91 (15), 85 (7), 77 (4), 67 (5), 55 (8); HR-MS (70 eV): m/z 220.1834 [M^+], calcd for C₁₆H₂₆: 220.1827.

8-*anti*-2,4-*bisequatorial*-1,2,4,5,6,7,8-heptamethylbicyclo[3.2.1]oct-6-en-3-one (**5**): ^1H NMR (500 MHz, $[\text{D}_6]$ benzene, TMS): $\delta = 0.64$ (d, $^3J = 6.9$ Hz, 3H; 8-CH₃), 0.81 (s, 6H; 1-CH₃, 5-CH₃), 1.14 (d, $^3J = 6.9$ Hz, 6H; 2-CH₃, 4-CH₃), 1.37 (s, 6H; 6-CH₃, 7-CH₃), 1.56 (q, $^3J = 6.9$ Hz, 1H, 8-H), 2.03 (q, $^3J = 6.9$ Hz, 2H, 2-CH, 4-CH); ^{13}C PENDANT (125 MHz, $[\text{D}_6]$ benzene, TMS): $\delta = 11.3$ (q, 6-CH₃, 7-CH₃), 11.9 (q, 8-CH₃), 12.8 (q, 1-CH₃, 5-CH₃), 16.9 (q, 2-CH₃, 4-CH₃), 52.2 (s, 1-C, 5-C), 56.4 (d, 2-CH, 4-CH), 58.9 (d, 8-CH), 134.7 (s, 6-C, 7-C), 210.7 (s, 3-CO); MS (70 eV): m/z (%): 220 (19) [M^+], 205 (1), 163 (16), 149 (9), 136 (54), 135 (61), 134 (100), 121 (23), 119 (14), 105 (16), 91 (15), 85 (7), 77 (4), 67 (5), 55 (8); HR-MS (70 eV): m/z 220.1837 [M^+], calcd for C₁₆H₂₆: 220.1827.

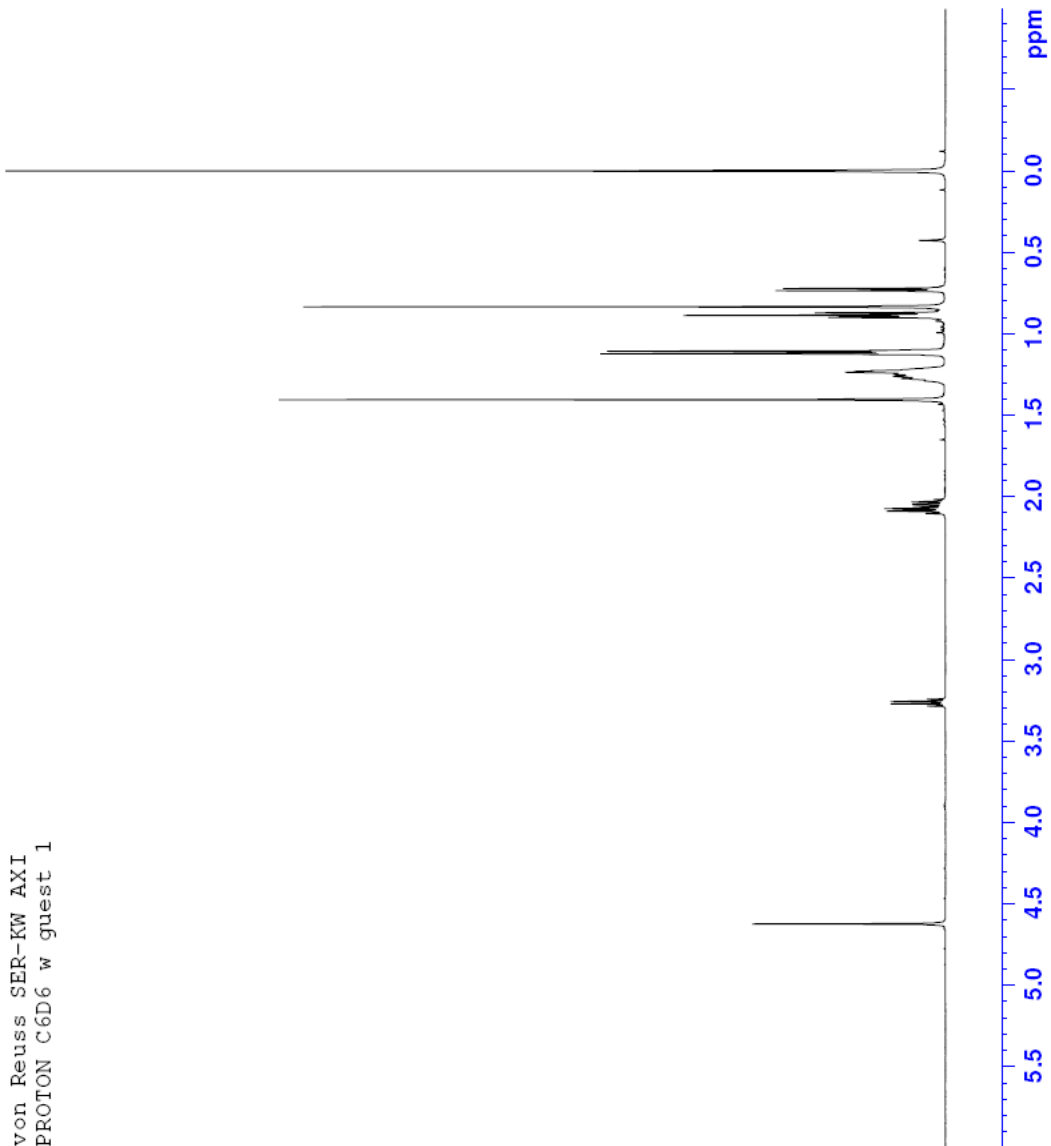
Olefination: Under N₂ atmosphere a solution of 220 mg **4** or **5** (1 mmol) in 5 ml THF at 0 °C was treated with 3 ml 0.5 M Tebbe's reagent (1.5 mmol) in toluene. After stirring for 1 h, the mixture was treated with 10 ml diethyl ether and 5 ml 1 M aqueous sodium hydroxide solution. Subsequently, the organic layer was washed with water, dried over Na₂SO₄, and concentrated in vacuo. Column chromatography on silica gel using pentane as the eluent followed by preparative gas chromatography afforded 170 mg 8-*anti*-2,4-*bisaxial*-1,2,4,5,6,7,8-heptamethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**1**, 780 μmol , 78 % yield) as a

white solid and 185 mg 8-*anti*-2,4-*bisequatorial*-1,2,4,5,6,7,8-heptamethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**6**, 850 μ mol, 85 % yield) as a colorless oil.

8-*anti*-2,4-*bisaxial*-1,2,4,5,6,7,8-heptamethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**1**): ^1H NMR (500 MHz, $[\text{D}_6]$ benzene, TMS): δ = 0.73 (3H, d, 3J = 6.9 Hz, 8-CH₃), 0.83 (6H, s, 1-CH₃, 5-CH₃), 1.12 (6H, d, 3J = 7.3 Hz, 2-CH₃, 4-CH₃), 1.41 (6H, s, 6-CH₃, 7-CH₃), 2.04 (1H, q, 3J = 6.9 Hz, 8-H), 2.08 (2H, q, 3J = 7.2 Hz, 2-CH, 4-CH), 4.63 (2H, s, 3-CH₂); ^{13}C PENDANT (125 MHz, $[\text{D}_6]$ benzene, TMS): δ = 9.6 (q, 6-CH₃, 7-CH₃), 11.0 (q, 8-CH₃), 17.7 (q, 1-CH₃, 5-CH₃), 19.5 (q, 2-CH₃, 4-CH₃), 39.9 (d, 8-CH), 44.1 (d, 2-CH, 4-CH), 51.5 (s, 1-C, 5-C), 111.1 (t, 3-CH₂), 134.2 (s, 6-C, 7-C), 156.0 (s, 3-C); MS (70 eV): m/z (%): 218 (30) [M^+], 203 (8), 189 (3), 162 (11), 148 (4), 136 (100), 135 (89), 134 (70), 121 (28), 105 (18), 91 (14), 83 (28), 67 (9), 55 (18), 41 (21); HR-MS (70 eV): m/z 218.2044 [M^+], calcd for C₁₆H₂₆: 218.2035.

8-*anti*-2,4-*bisequatorial*-1,2,4,5,6,7,8-heptamethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**6**): ^1H NMR (500 MHz, $[\text{D}_6]$ benzene, TMS): δ = 0.73 (3H, d, 3J = 6.6 Hz, 8-CH₃), 0.92 (6H, s, 1-CH₃, 5-CH₃), 1.07 (6H, d, 3J = 6.9 Hz, 2-CH₃, 4-CH₃), 1.47 (6H, s, 6-CH₃, 7-CH₃), 1.52 (1H, q, 3J = 6.6 Hz, 8-H), 2.10 (2H, q, 3J = 6.9 Hz, 2-CH, 4-CH), 4.88 (2H, s, 3-CH₂); ^{13}C PENDANT (125 MHz, $[\text{D}_6]$ benzene, TMS): δ = 12.4 (q, 6-CH₃, 7-CH₃), 14.3 (q, 8-CH₃), 15.3 (q, 1-CH₃, 5-CH₃), 17.2 (q, 2-CH₃, 4-CH₃), 59.7 (d, 8-CH), 47.7 (d, 2-CH, 4-CH), 52.4 (s, 1-C, 5-C), 106.2 (t, 3-CH₂), 133.1 (s, 6-C, 7-C), 157.0 (s, 3-C); MS (70 eV): m/z (%): 218 (30) [M], 203 (8), 189 (3), 162 (11), 148 (4), 136 (100), 135 (89), 134 (70), 121 (28), 105 (18), 91 (14), 83 (28), 67 (9), 55 (18), 41 (21); HRMS (70 eV): m/z 218.2047 [M^+], calcd for C₁₆H₂₆: 218.2035.

von Reuss SER-KW AXI
PROTON C6D6 w guest 1



NAME 070613
EXPNO 10
PROCNO 1
Date_ 20070613
Time 11.41
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 128
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 60.6
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec
MCREST 0.0000000 sec
MCWRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 11.50 usec
PL1 -1.00 dB
SF01 500.1330885 MHz
SI 32768
SF 500.1300588 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 1: 500 MHz ¹H NMR spectrum of **1** in [D₆]benzene.

von Reuss SER-KW AXI
C13APT C6D6 w guest 1



```
NAME 070613
EXPNO 12
PROCNO 1
Date_ 20070614
Time 8.01
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 5120
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 13004
DW 16.650 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.0001137 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.50 usec
P2 21.00 usec
PL1 -2.00 dB
SFO1 125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 20.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577587 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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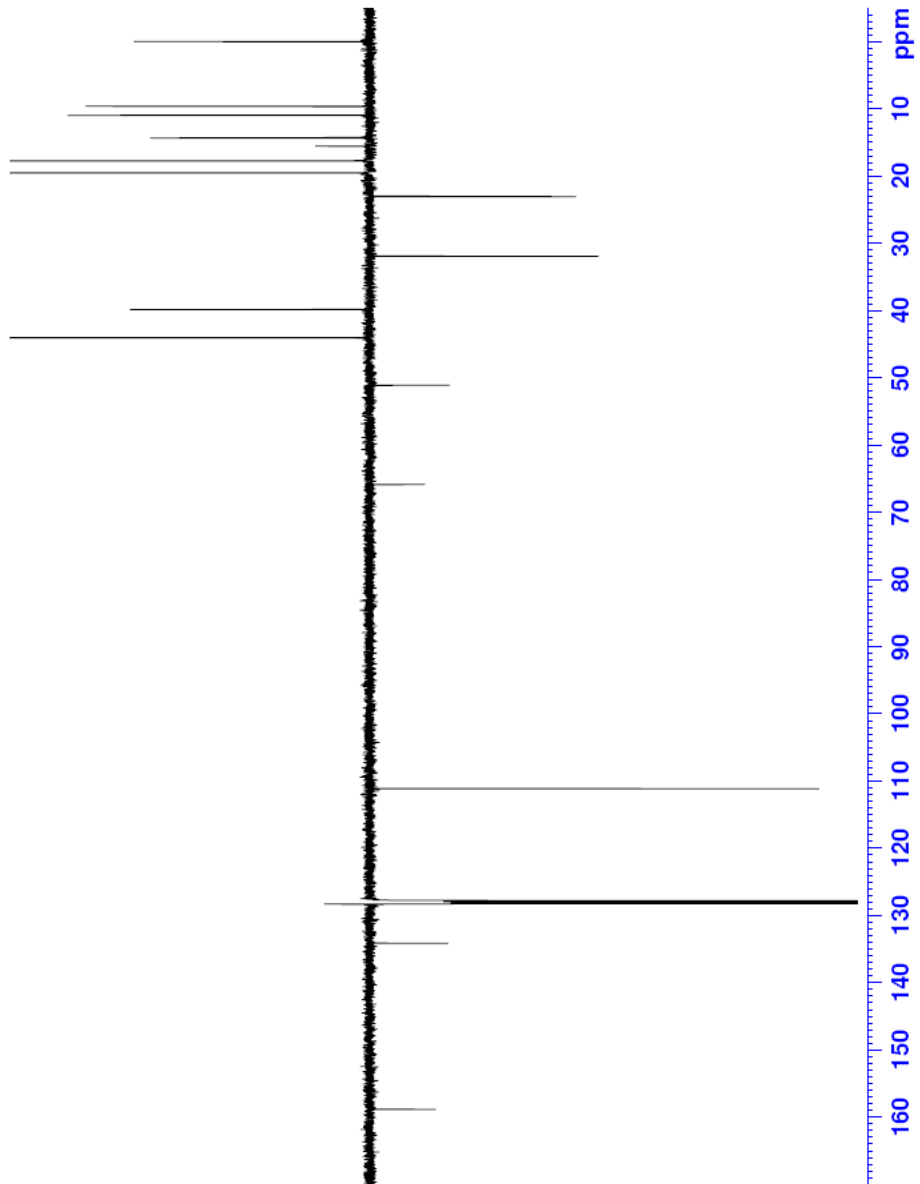


Figure 2: 125 MHz ^{13}C PENDANT spectrum of **1** in $[\text{D}_6]\text{benzene}$.

von reuss ser kw axi
 COSY90SW C6D6 w guest 8



```

NAME 070619
EXPNO 81
PROCNO 1
Date_ 20070620
Time 2.41
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG cosydf90
TD 4096
SOLVENT C6D6
NS 32
DS 16
SWH 4222.973 Hz
FIDRES 1.030999 Hz
AQ 0.4850164 sec
RG 114
DE 118.400 usec
TE 300.0 K
d0 0.00000300 sec
D1 0.91316420 sec
IN0 0.00023680 sec
MCREST 0.00000000 sec
MCWRK 0.91316420 sec

===== CHANNEL f1 =====
NUC1 1H
P1 11.50 usec
PL1 -1.00 dB
SFO1 500.1318099 MHz
ND0 1
TD 256
SFO1 500.1318 MHz
FIDRES 16.495989 Hz
SW 8.444 PPM
FMODE QF
SI 4096
SF 500.1300587 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 4096
MC2 QF
SF 500.1300587 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0
  
```

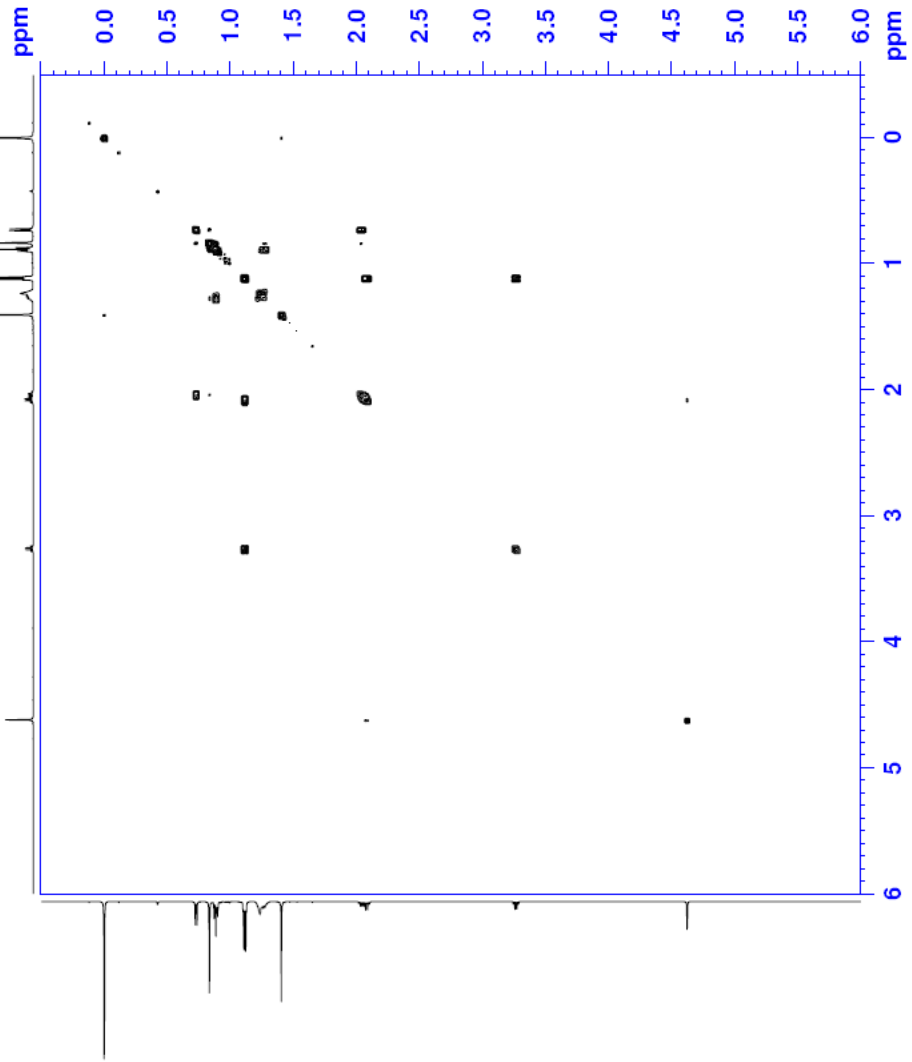


Figure 3: COSY-90 spectrum of **1** in [D₆]benzene.

von Reuss SER-KW AXI
 NOESYPSHW C6D6 w guest 1



```

NAME 070613
EXPNO 11
PROCNO 1
Date_ 20070613
Time 11.45
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG noesyph
TD 4866
SOLVENT C6D6
NS 64
DS 16
SWH 4310.345 Hz
FIDRES 1.052330 Hz
AQ 0.4751860 sec
RG 101.6
DW 116.000 usec
DE 6.00 usec
TE 300.10 K
d0 0.00010136 sec
D1 1.12463295 sec
D8 0.60000002 sec
IN0 0.00023200 sec
MCREST 0.00000000 sec
MCWBK 0.56231648 sec
STICNT 0

===== CHANNEL f1 =====
NUC1 1H
P1 11.50 usec
PL1 -1.00 dB
SFO1 500.1318391 MHz
ND0 1
TD 400
SFO1 500.1318 MHz
FIDRES 10.775862 Hz
SW 8.618 ppm
FMODE States-TFPI
SI 2048
SF 500.1300588 MHz
WDW QSI
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 2048
MC2 States-TFPI
SF 500.1300588 MHz
WDW QSI
SSB 2
LB 0.00 Hz
GB 0
  
```

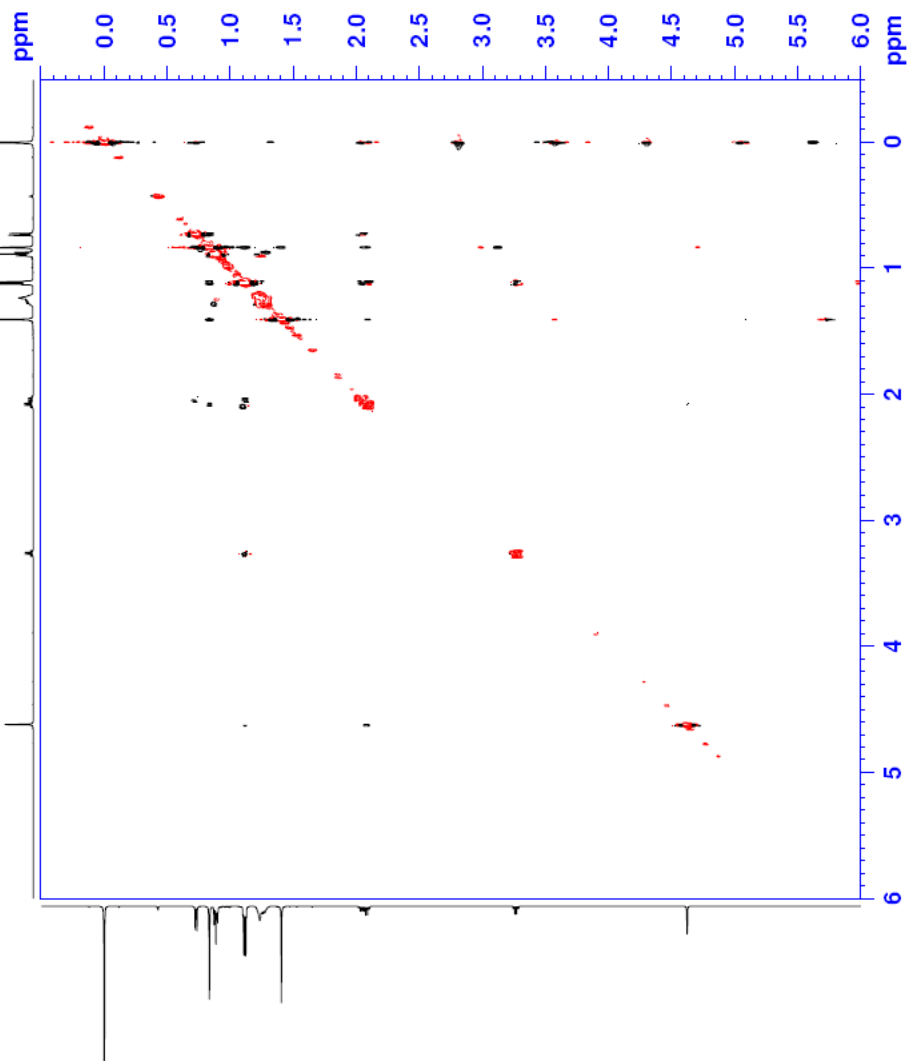


Figure 4: NOESY spectrum of **1** in $[D_6]$ benzene.

von Reuss SER-KW EQu
PROTON C6D6 w guest 11



```
NAME 070622
EXPNO 110
PROCNO 1
Date_ 20070624
Time 3.15
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 128
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 203.2
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 11.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300586 MHz
WDW EM
SSE 0
LB 0.30 Hz
GB 0
PC 1.00
```

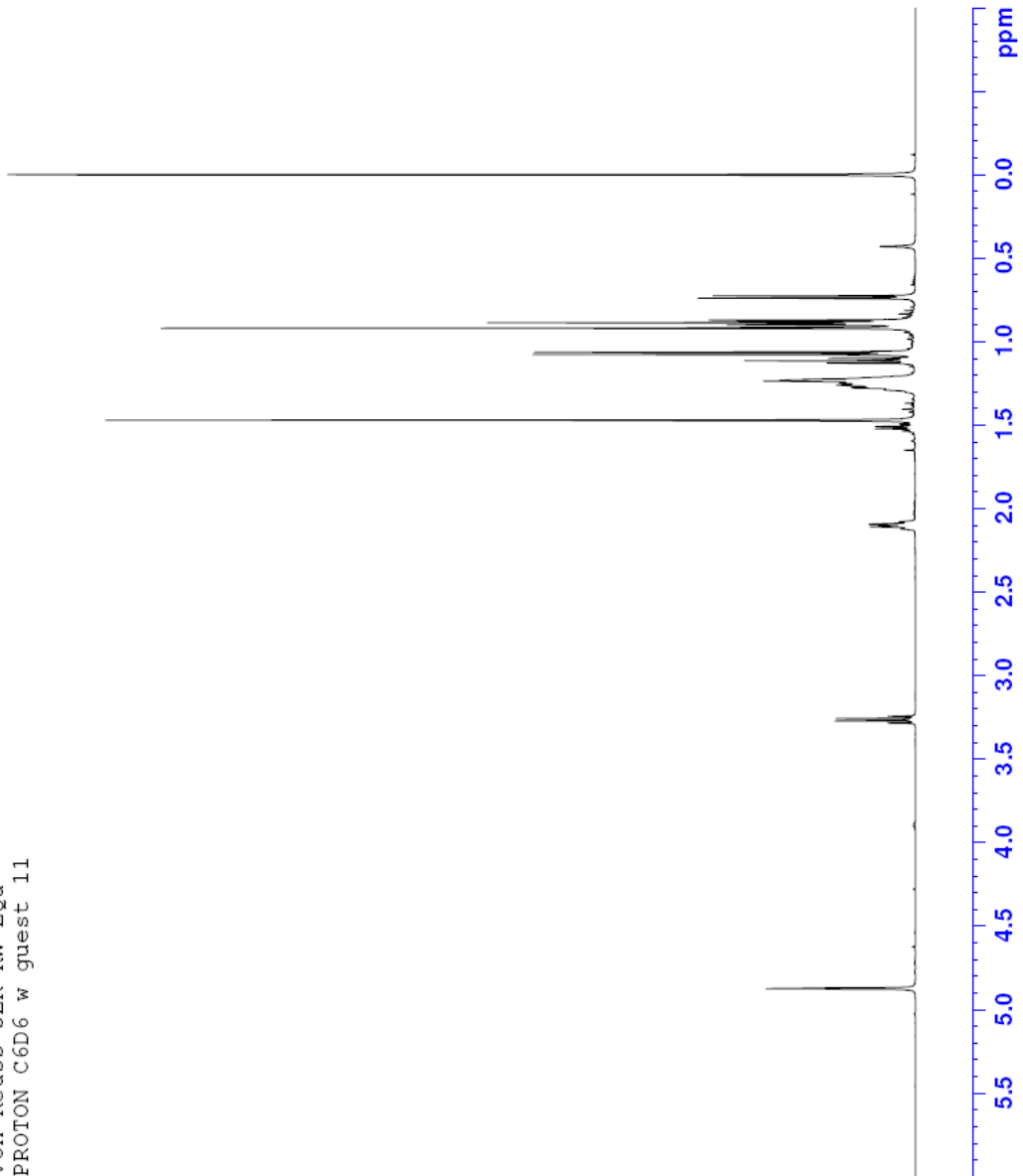


Figure 6: 500 MHz ^1H NMR spectrum of **6** in $[\text{D}_6]$ benzene.

von Reuss SER-KW EQU
C13APT C6D6 w guest 2



```
NAME 070611
EXPNO 22
PROCNO 1
Date_ 20070612
Time 6.51
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG 65536
TD 686
SOLVENT C6D6
NS 5120
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 9195.2
DW 16.650 usec
DE 6.00 usec
TE 300.0 K
CNS12 145.0000000
CNS11 1.0000000
D1 2.0000000 sec
d20 0.00689655 sec
DELTA 0.00001337 sec
MCREST 0.0000000 sec
MCWRK 0.015000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.50 usec
P2 21.00 usec
PL1 -2.00 dB
SFO1 125.7703643 MHz

===== CHANNEL f2 =====
CFPPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 20.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577584 MHz
WDW EM
SSE 0
LB 1.00 Hz
GB 0
PC 1.40
```

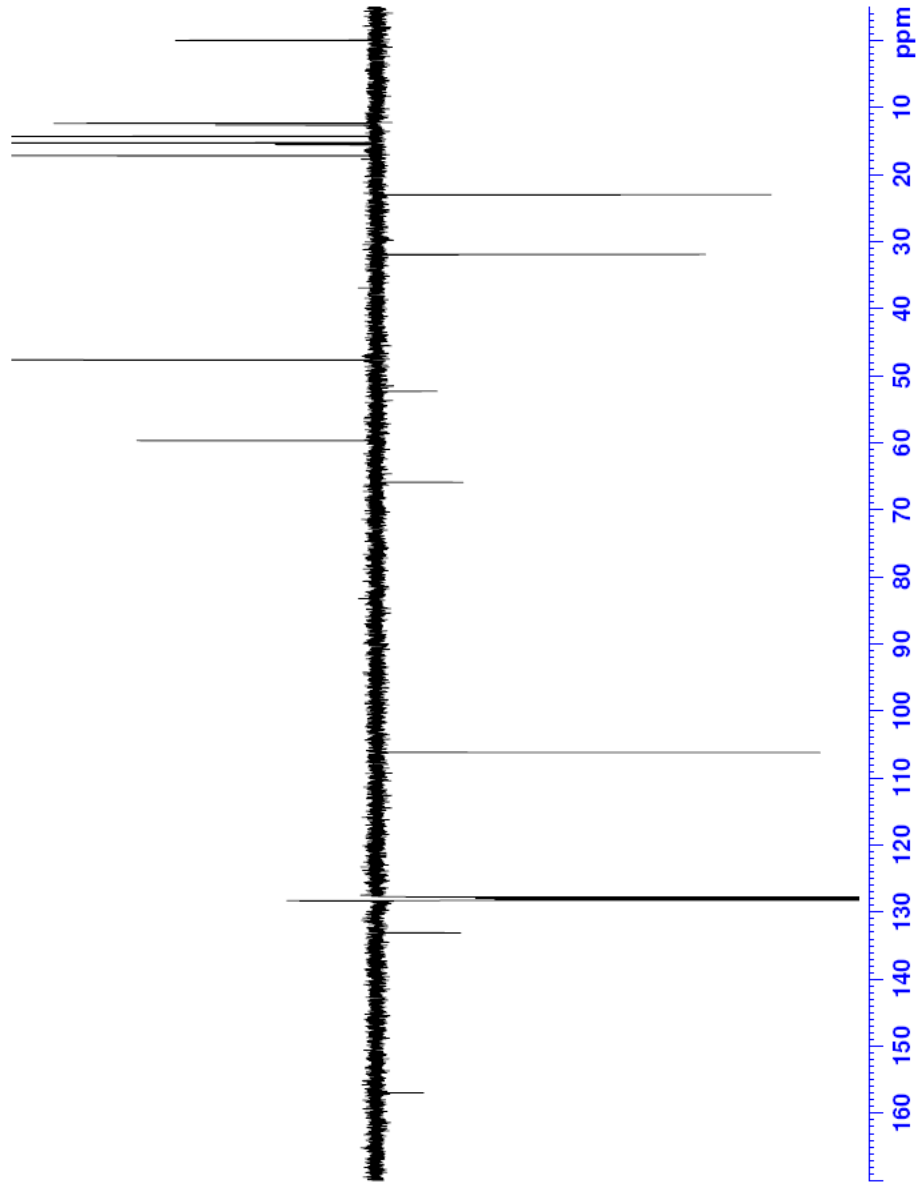


Figure 7: 125 MHz ^{13}C PENDANT spectrum of **6** in $[\text{D}_6]\text{benzene}$.

von Reuss SER-KW EQu
 COSY90SW C6D6 w guest 11



```

NAME 070622
EXPNO 112
PROCNO 1
Date_ 20070624
Time 10.39
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG cosyzf90
TD 4096
SOLVENT C6D6
NS 16
DS 16
SWH 4222.973 Hz
FIDRES 1.030999 Hz
AQ 0.4850164 sec
RG 181
DW 118.400 usec
DE 6.00 usec
TE 300.0 K
d0 0.0000300 sec
d1 1.11316395 sec
INO 0.00023680 sec
MCREST 0.0000000 sec
MCWRK 1.11316395 sec
===== CHANNEL f1 =====
NUC1 1H
P1 11.50 usec
PL1 -1.00 dB
SFO1 500.1318629 MHz
ND0 1
TD 256
SFO1 500.1319 MHz
FIDRES 16.495989 Hz
SW 8.444 Ppm
F1MODE QF
SI 2048
SF 500.1300586 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 2048
MC2 QF
SF 500.1300586 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0
  
```

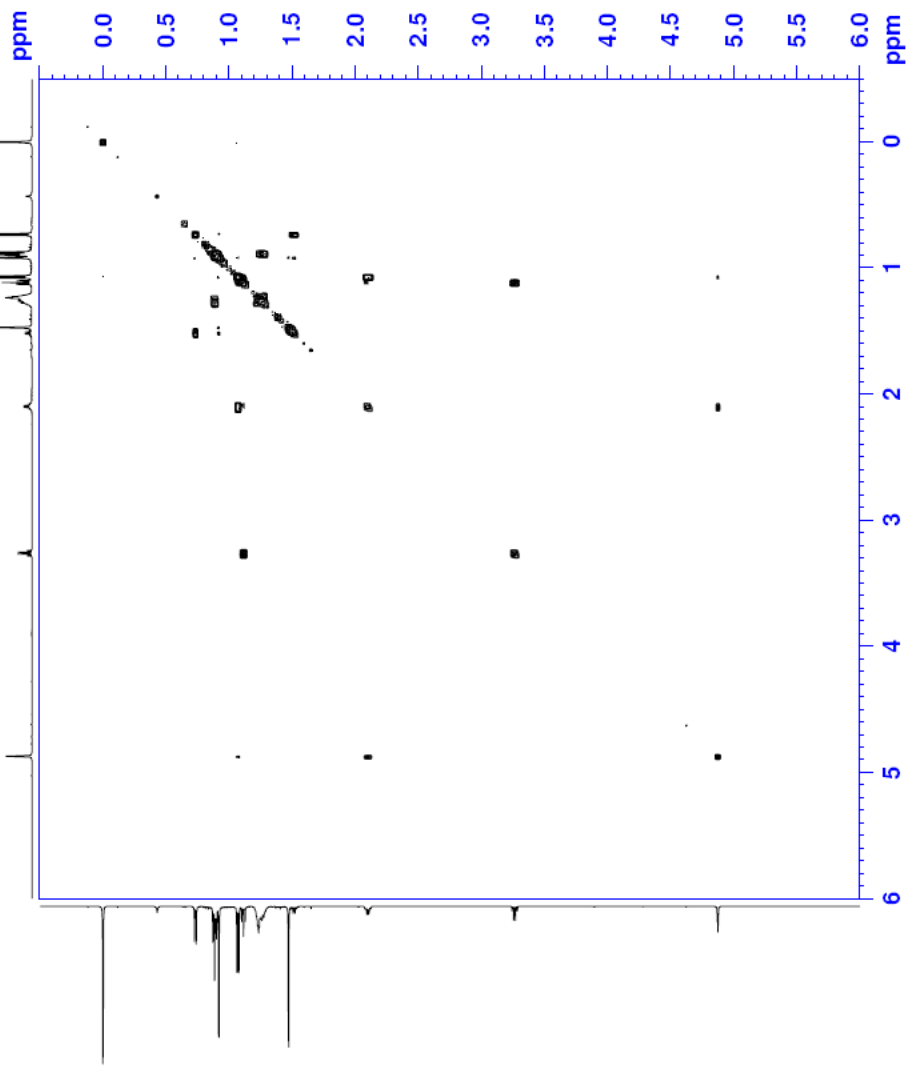


Figure 8: COSY-90 spectrum of **6** in [D₆]benzene.

von Reuss SER-KW EQU
 NOESYHSW C6D6 w guest 2



```

NAME 070611
EXPNO 21
PROCNO 1
Date_ 20070611
Time 10.35
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG noesyph
TD 4096
SOLVENT C6D6
NS 64
DS 16
SWH 4194.631 Hz
FIDRES 1.024080 Hz
AQ 0.4882932 sec
RG 64
DW 119.200 usec
DE 6.00 usec
TE 300.0 K
G0 0.00010456 sec
D1 1.11234498 sec
D8 0.60000002 sec
IN0 0.00023840 sec
MCREST 0.00000000 sec
MCWRK 0.55617249 sec
STICNT 0
  
```

```

===== CHANNEL f1 =====
NUC1 1H
P1 11.50 usec
PL1 -1.00 dB
SFO1 500.1318232 MHz
ND0 1
TD 400
SFO1 500.1318 MHz
FIDRES 10.46577 Hz
SW 8.387 PPM
FMODE States-TPPI
SI 4096
SF 500.1300586 MHz
WDW COSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 4096
MC2 States-TPPI
SF 500.1300586 MHz
WDW COSINE
SSB 2
LB 0.00 Hz
GB 0
  
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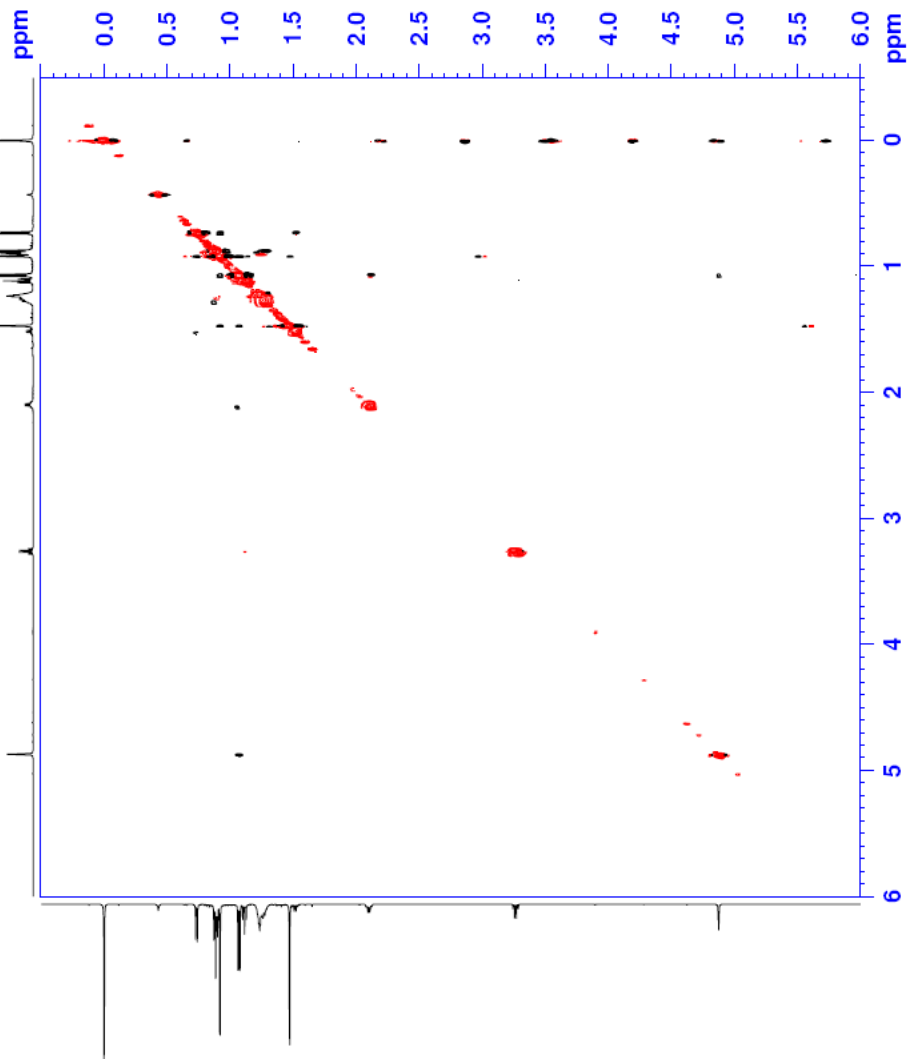


Figure 9: NOESY spectrum of **6** in $[D_6]$ benzene.

