Supporting Information

for

Single-Chain Folding of Diblock Copolymers Driven by Orthogonal H-Donor and Acceptor Units

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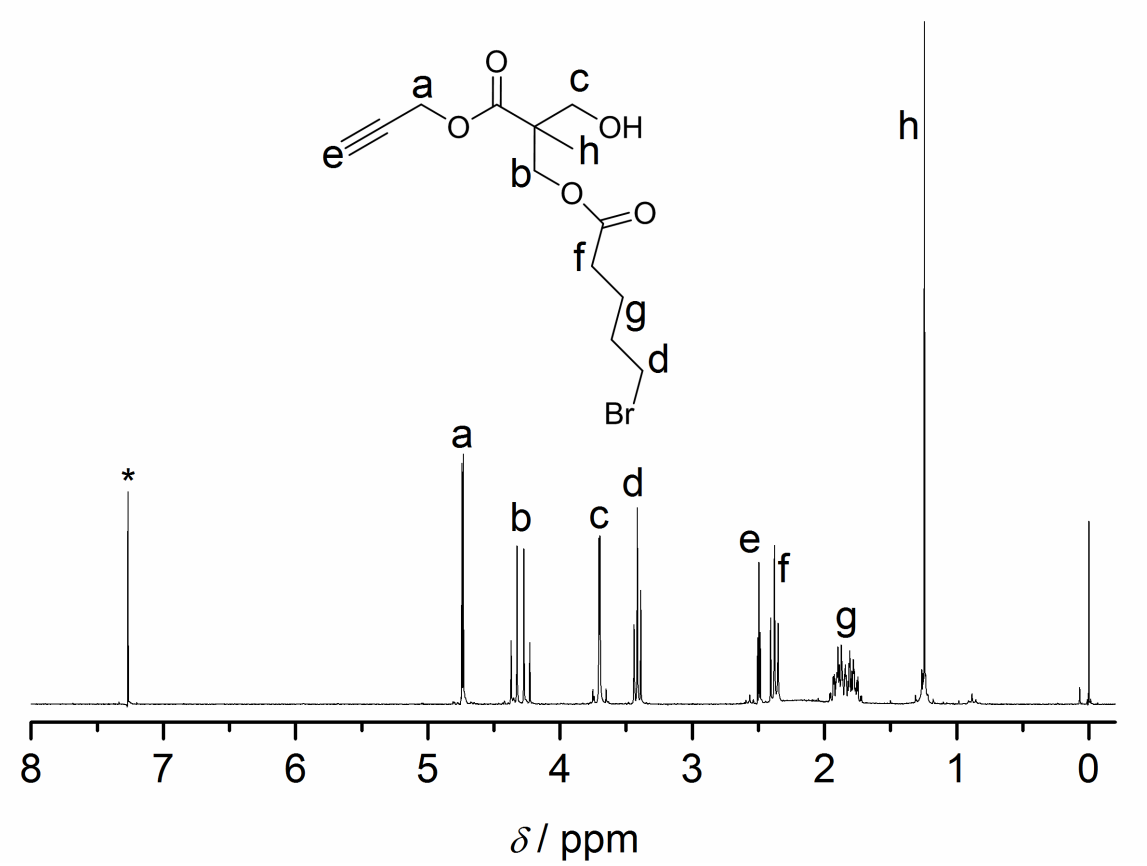


Figure S1. ^{1}H NMR spectrum of 2-(hydroxymethyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy)propyl 5-bromopentanoate (**2**) in $CDCl_3$ at ambient temperature. The peak marked with an asterisk is due to solvent.

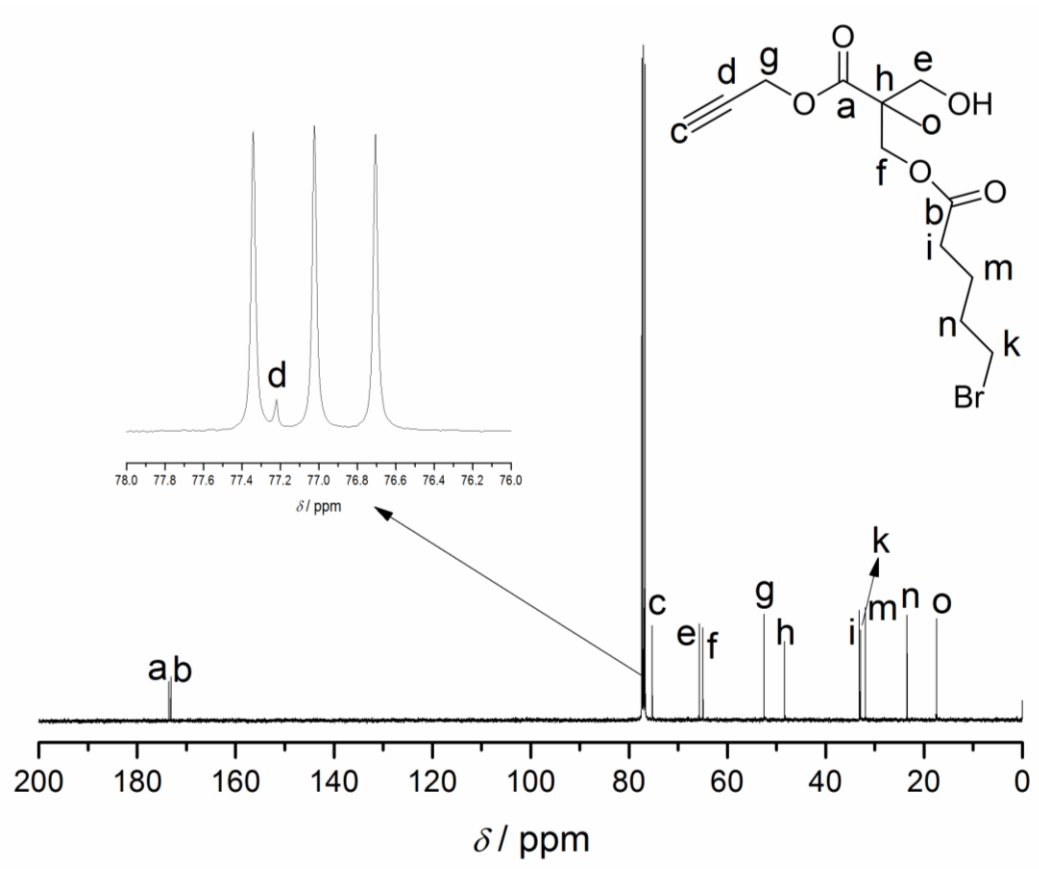


Figure S2. ^{13}C NMR spectrum of 2-(hydroxymethyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy)propyl 5-bromopentanoate (**2**) in $CDCl_3$ at ambient temperature.

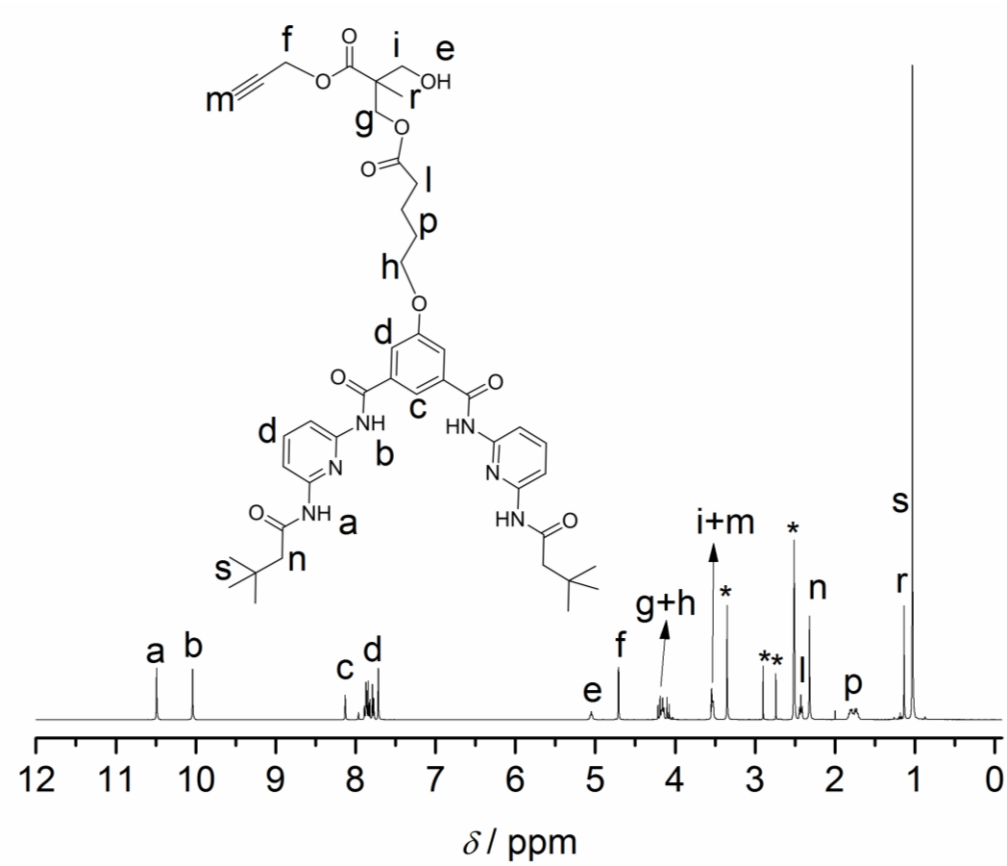


Figure S3. ^{1}H NMR spectrum of 2-(hydroxymethyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy) propyl5-(3,5-bis((6-(3,3-dimethylbutanamido)pyridin-2-yl)carbamoyl)phenoxy)pentanoate (**4**) in DMSO-d_6 at ambient temperature. The peak marked with an asterisk is due to solvent.

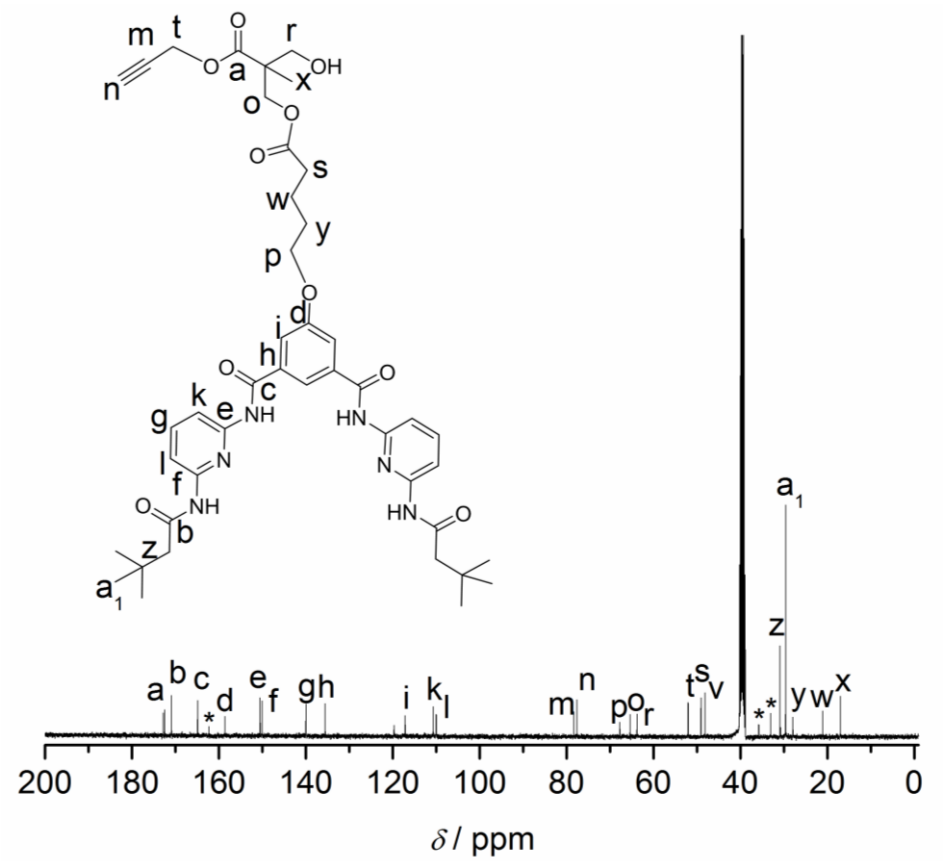


Figure S4. ^{13}C NMR spectrum of 2-(hydroxymethyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy) propyl5-(3,5-bis((6-(3,3-dimethylbutanamido)pyridin-2-yl)carbamoyl)phenoxy)pentanoate (**4**) in DMSO-d_6 at ambient temperature. The peak marked with an asterisk is due to solvent.

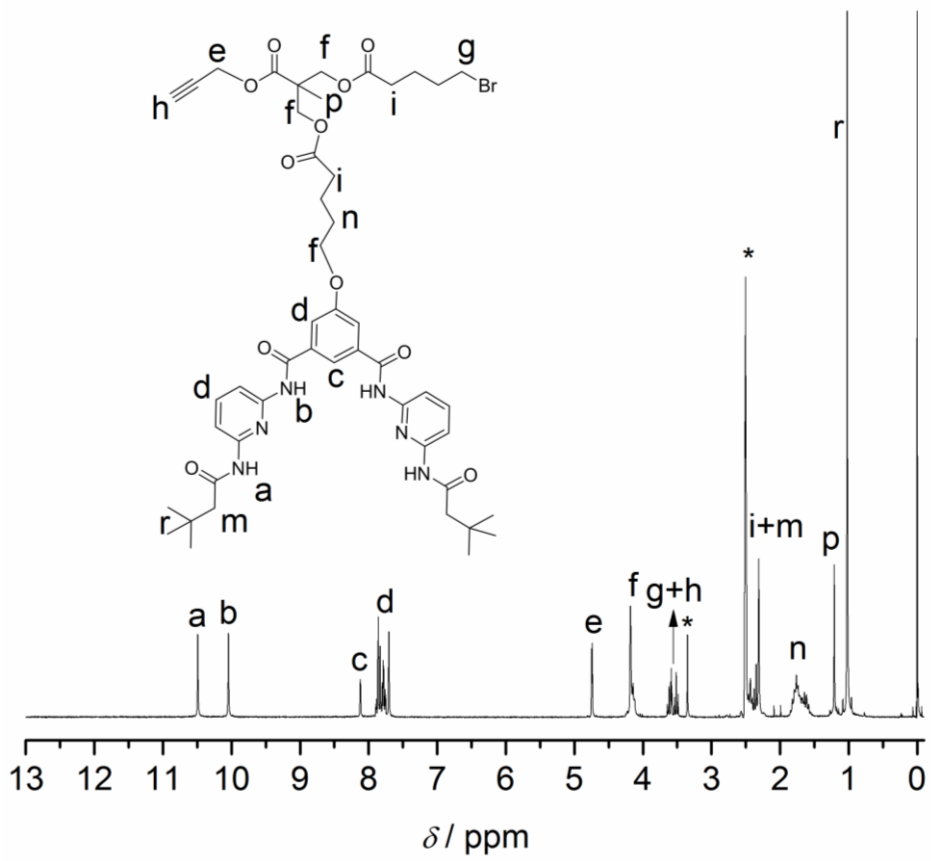


Figure S5. ^{1}H NMR spectrum of 2-(((5-(3,5-bis((6-(3,3-dimethylbutanamido)pyridin-2-yl)carbamoyl)phenoxy)pentanoyl)oxy)methyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy)propyl 5-bromopentanoate (**5**) in DMSO-d_6 at ambient temperature. The peak marked with an asterisk is due to solvent.

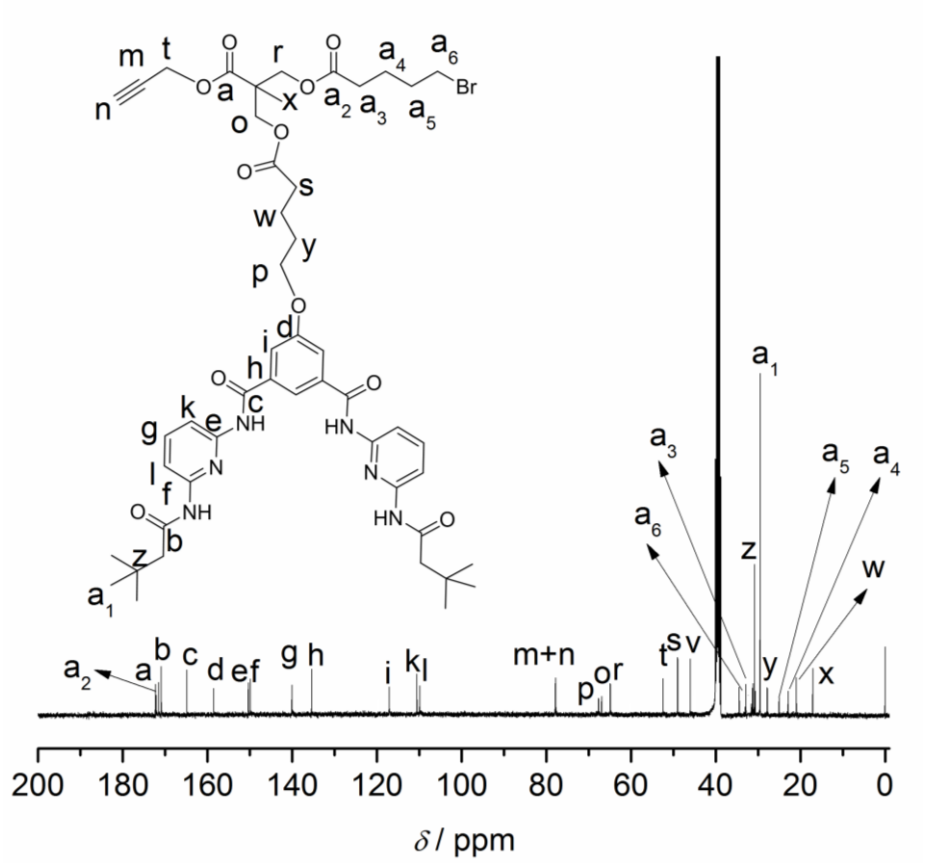


Figure S6. ^{13}C NMR spectrum of 2-(((5-(3,5-bis((6-(3,3-dimethylbutanamido)pyridin-2-yl)carbamoyl)phenoxy)pentanoyl)oxy)methyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy)propyl 5-bromopentanoate (**5**) in DMSO-d_6 at ambient temperature.

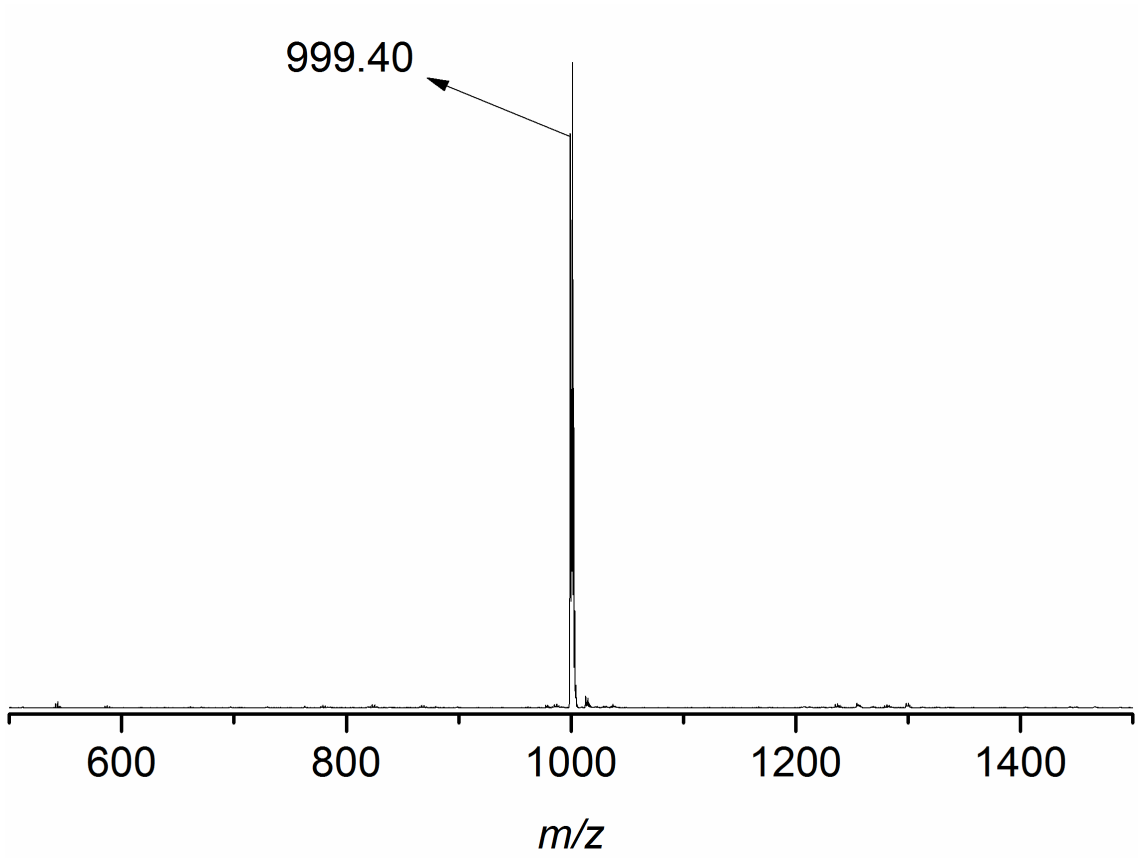


Figure S7. ESI-MS-spectrum of **5** (ionized with NaI)

Table S1. Theoretical and experimental *m/z* of **5** (ionized with NaI).

Species	m/z_{theo}	m/z_{exp}	$\Delta m/z$
[**5**+Na]$^+$	999.35	999.50	0.15

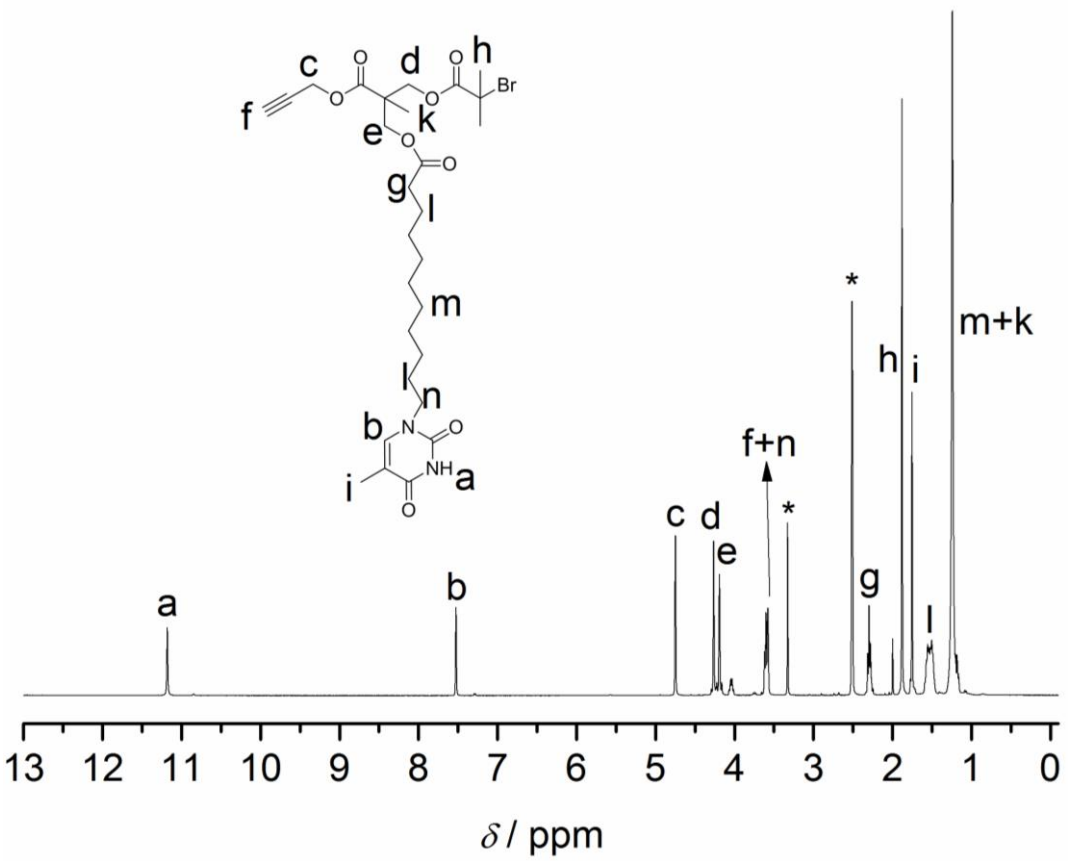


Figure S8. ^{1}H NMR spectrum of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy)propyl 11-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)undecanoate (**8**) in DMSO-d_6 at ambient temperature. The peak marked with an asterisk is due to solvent.

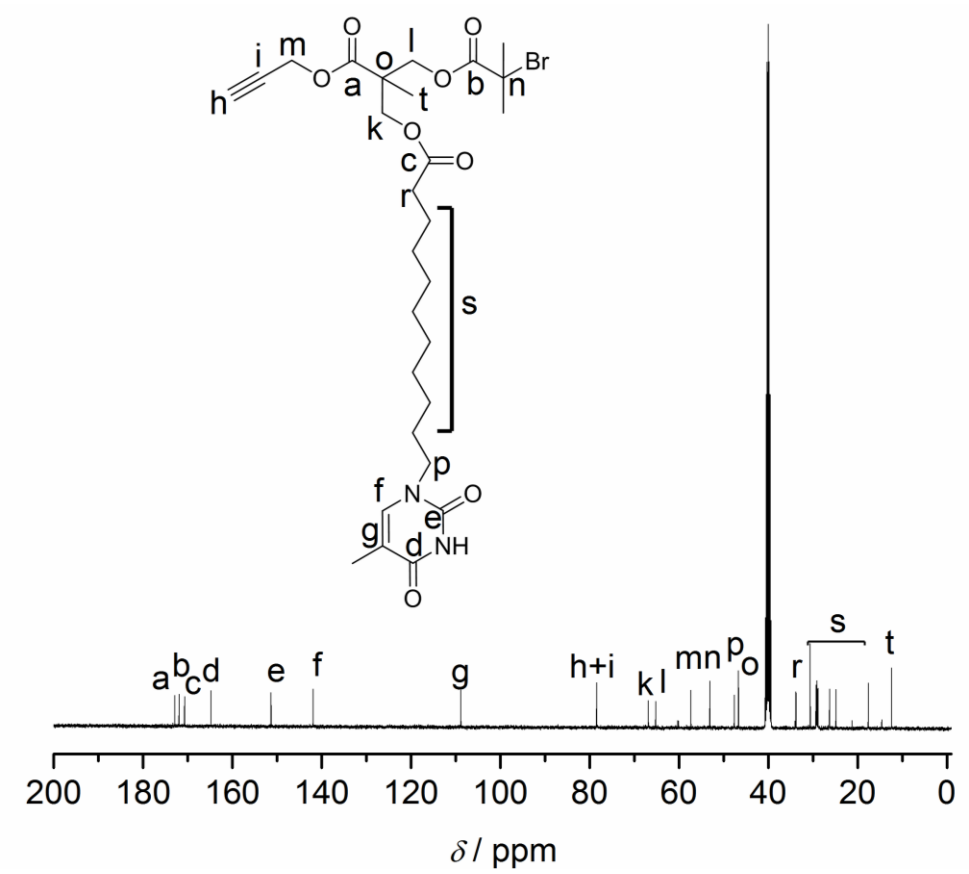


Figure S9. ^{13}C NMR spectrum of 2-(((2-bromo-2-methylpropanoyl)oxy)methyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy)propyl 11-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)undecanoate (**8**) in DMSO-d_6 at ambient temperature.

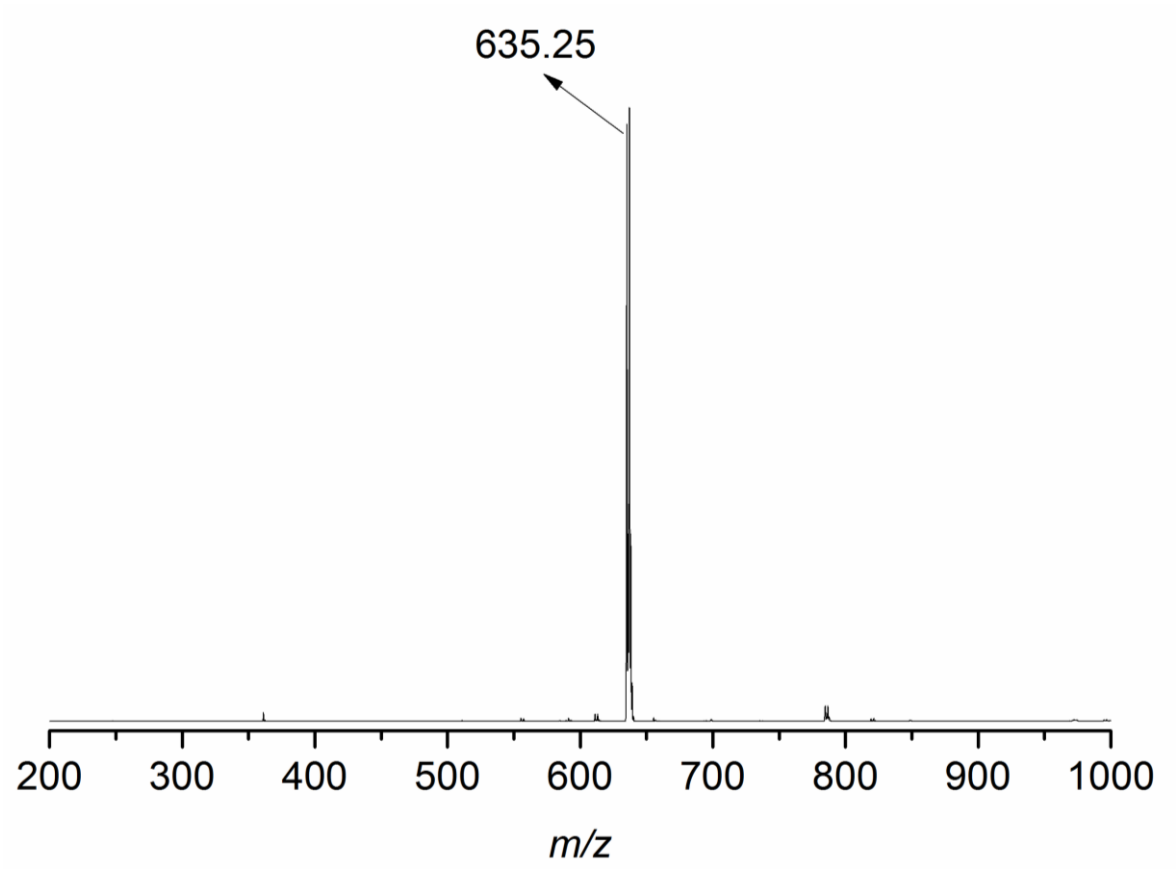


Figure S10. ESI-MS-spectrum of **8** (ionized with NaI)

Table S2. Theoretical and experimental *m/z* of **8** (ionized with NaI).

Species	m/z_{theo}	m/z_{exp}	$\Delta m/z$
[**8**+Na]$^+$	635.19	635.33	0.14

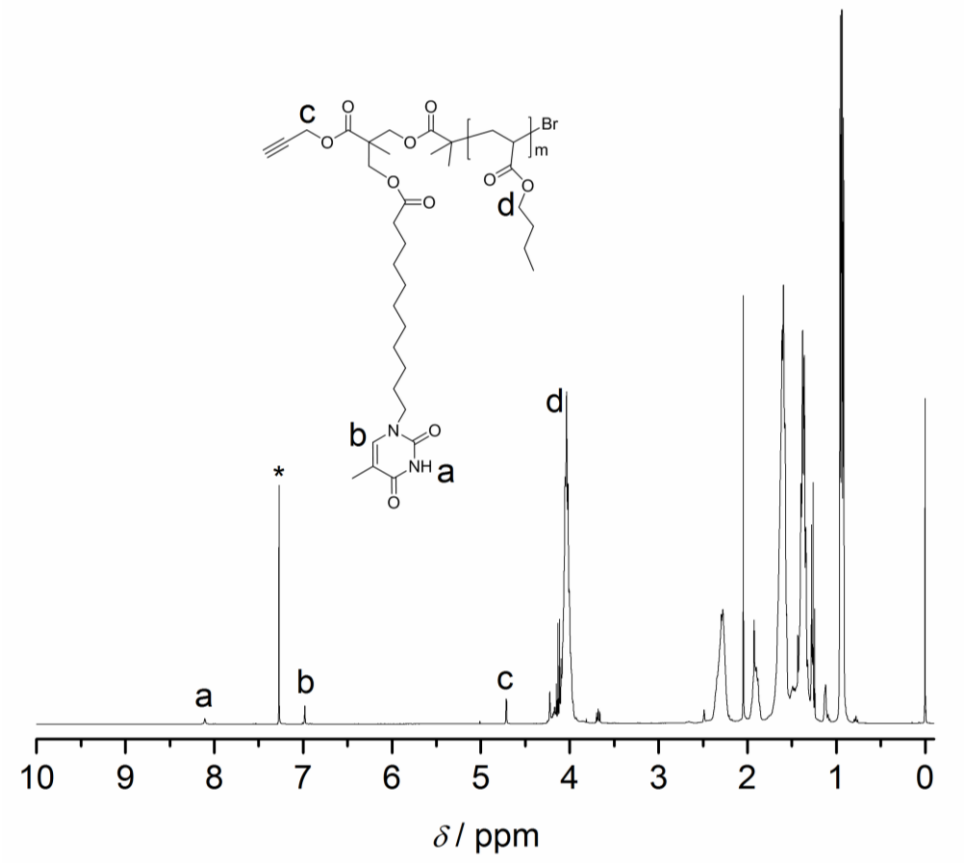


Figure S11. ^{1}H NMR spectrum of α-(alkyne/thymine) functional poly(*n*-butylacrylate) (**9**) in $CDCl_3$ at ambient temperature. The peak marked with an asterisk is due to solvent.

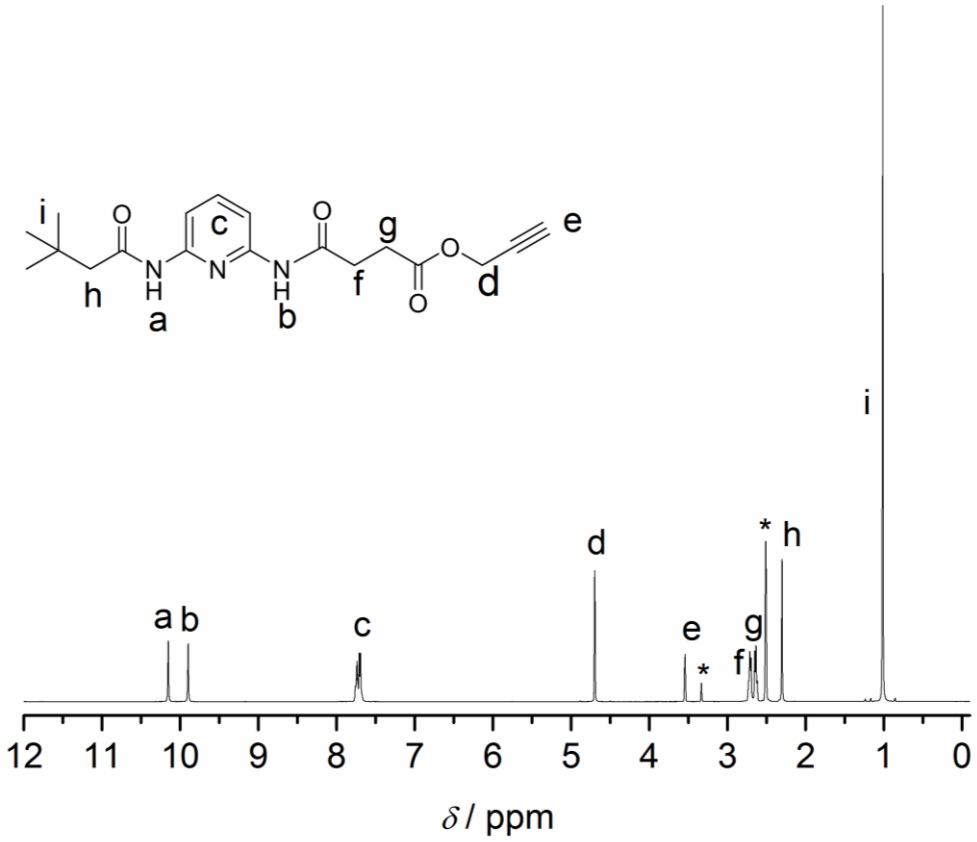


Figure S12. ^{1}H NMR spectrum of prop-2-yn-1-yl 4-((6-(3,3-dimethylbutanamido)pyridin-2-yl)amino)-4-oxobutanoate (**12**) in DMSO-d_6 at ambient temperature. The peak marked with an asterisk is due to solvent.

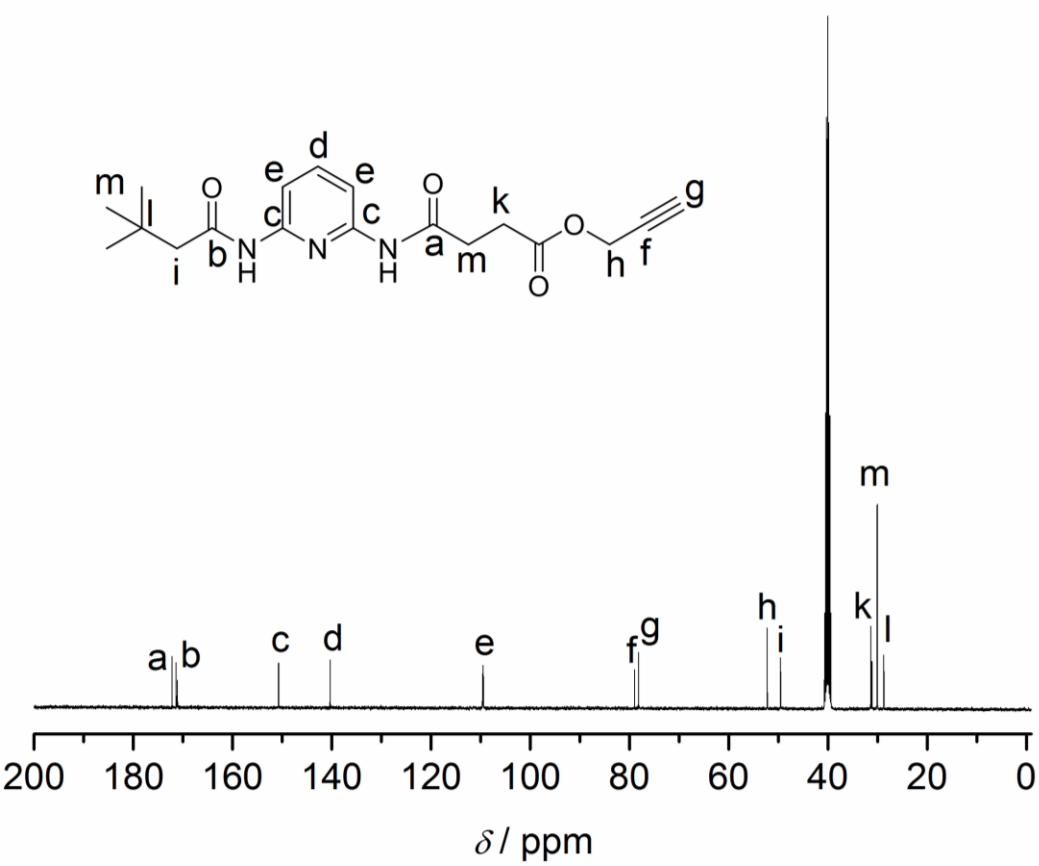


Figure S13. ^{13}C NMR spectrum of prop-2-yn-1-yl 4-((6-(3,3-dimethylbutanamido)pyridin-2-yl)amino)-4-oxobutanoate (**12**) in DMSO-d_6 at ambient temperature.

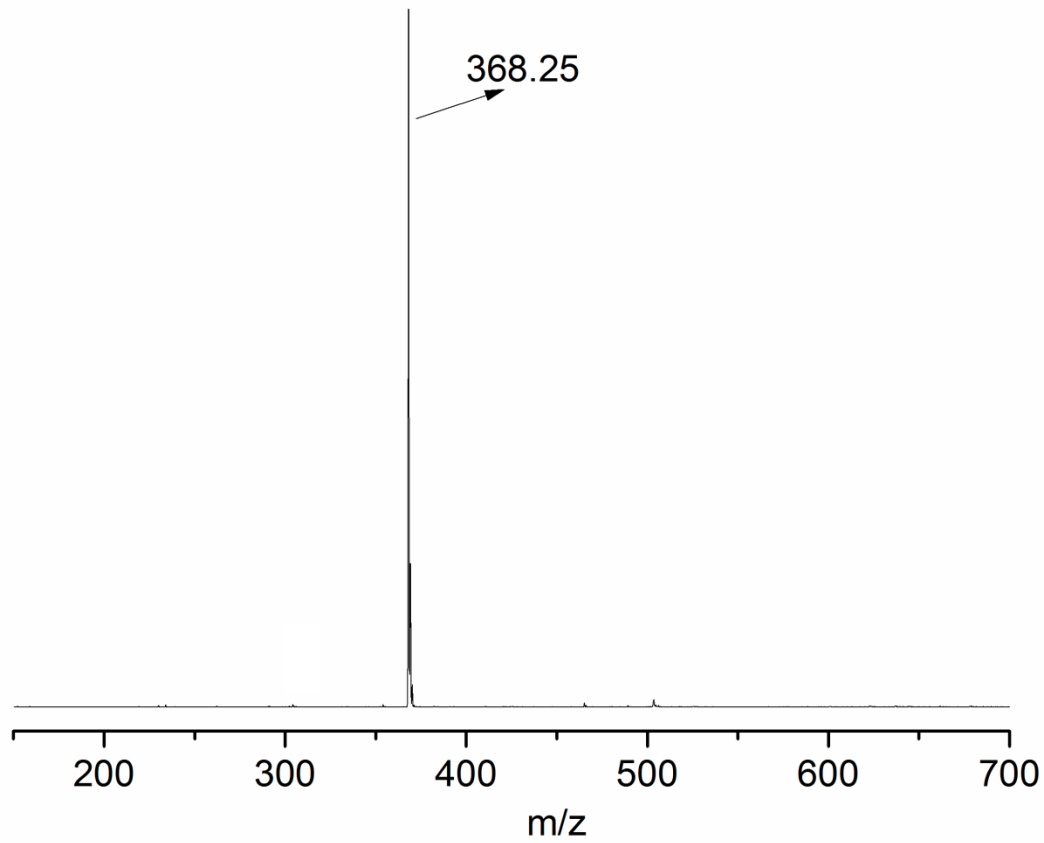


Figure S14. ESI-MS-spectrum of **12** (ionized with NaI)

Table S3. Theoretical and experimental *m/z* of **12** (ionized with NaI).

Species	m/z_{theo}	m/z_{exp}	$\Delta m/z$
[**12**+Na]$^+$	368.16	368.25	0.09

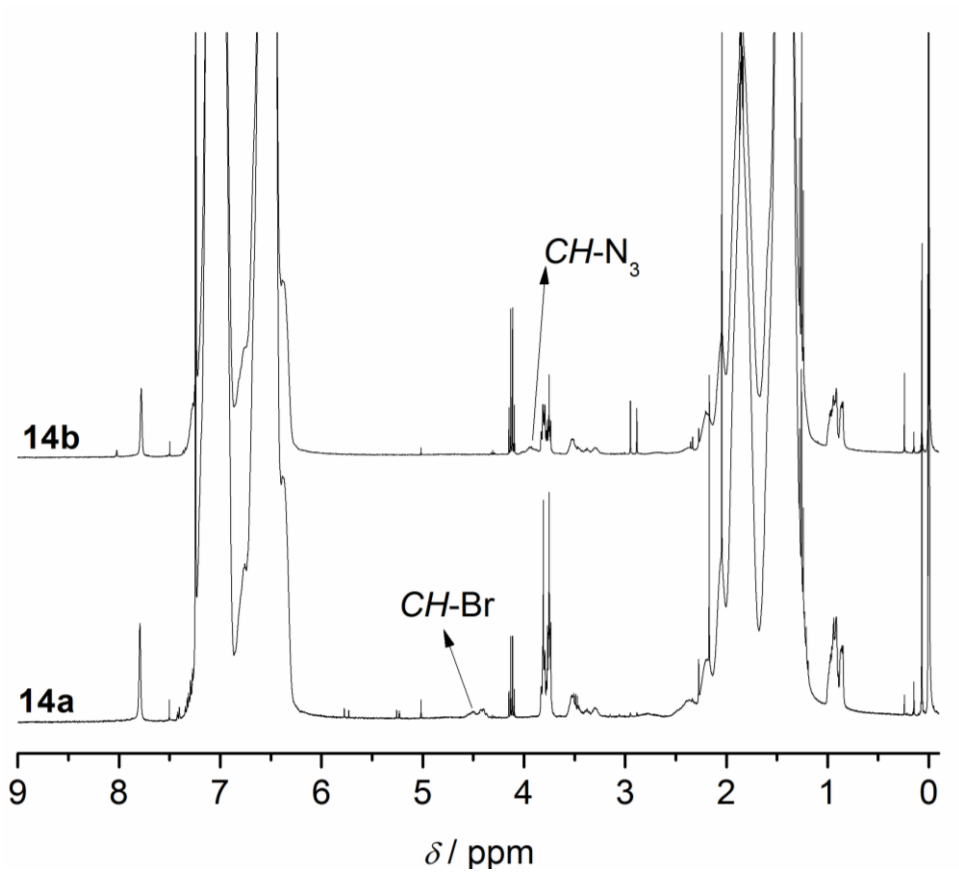


Figure S15. ^{1}H NMR spectrum of α-cyanuric acid and ω-azide functional polystyrene (**14**) in $CDCl_3$ at ambient temperature.

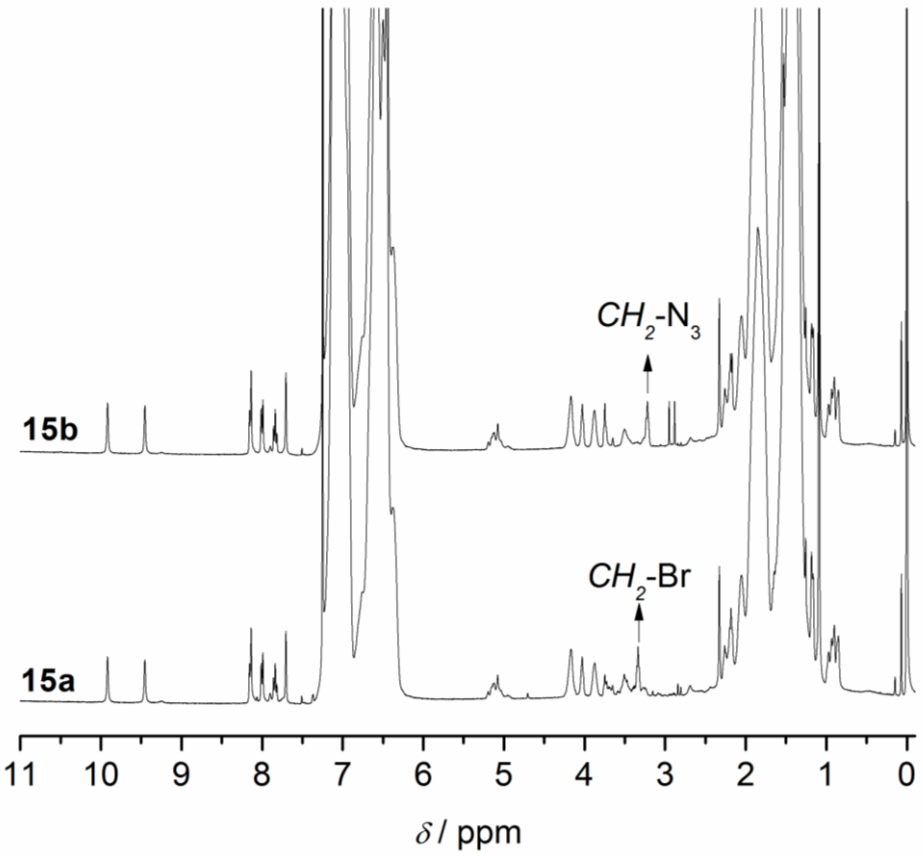


Figure S16. ^{1}H NMR spectrum of α-cyanuric acid and ω-(Hamilton wedge/azide) functional polystyrene (**15**) in $CDCl_3$ at ambient temperature.

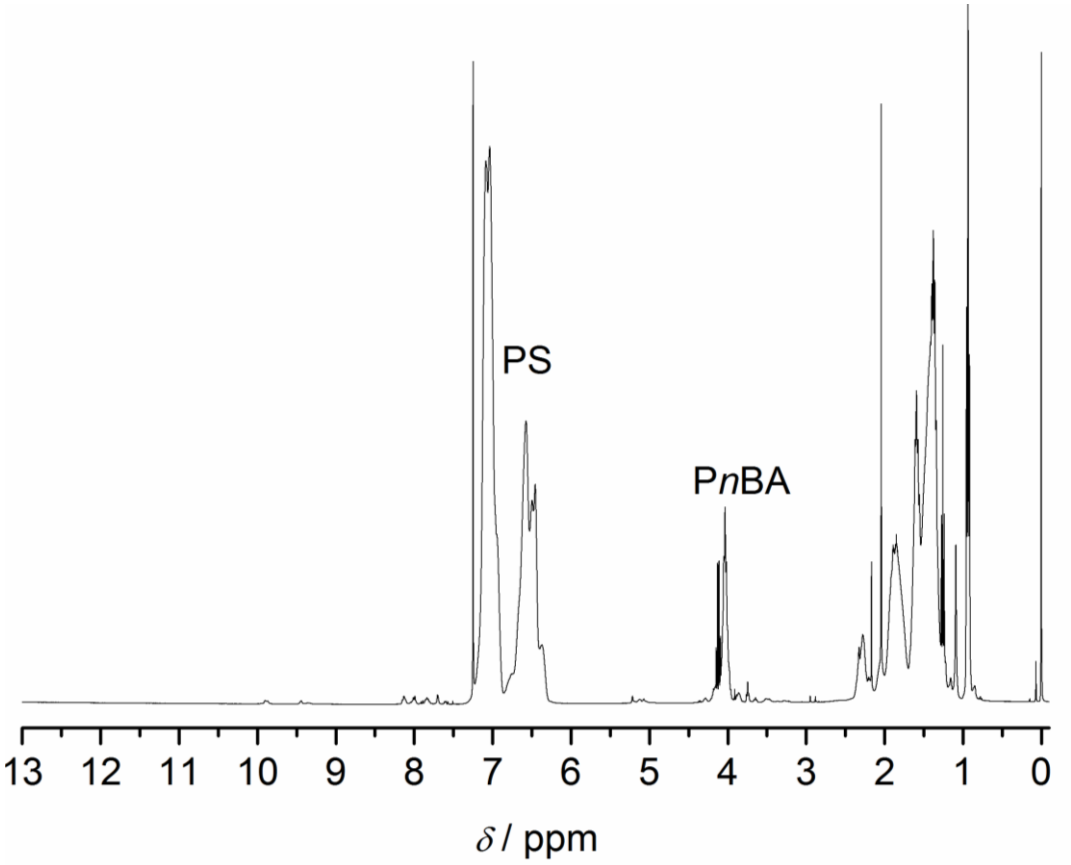


Figure S17. ^{1}H NMR spectrum of α-cyanuric acid, mid-chain (Hamilton wedge/thymine) and ω-azide functional diblock block copolymer (PS-*b*-P*n*BA) (**16a**) in $CDCl_3$ at ambient temperature.

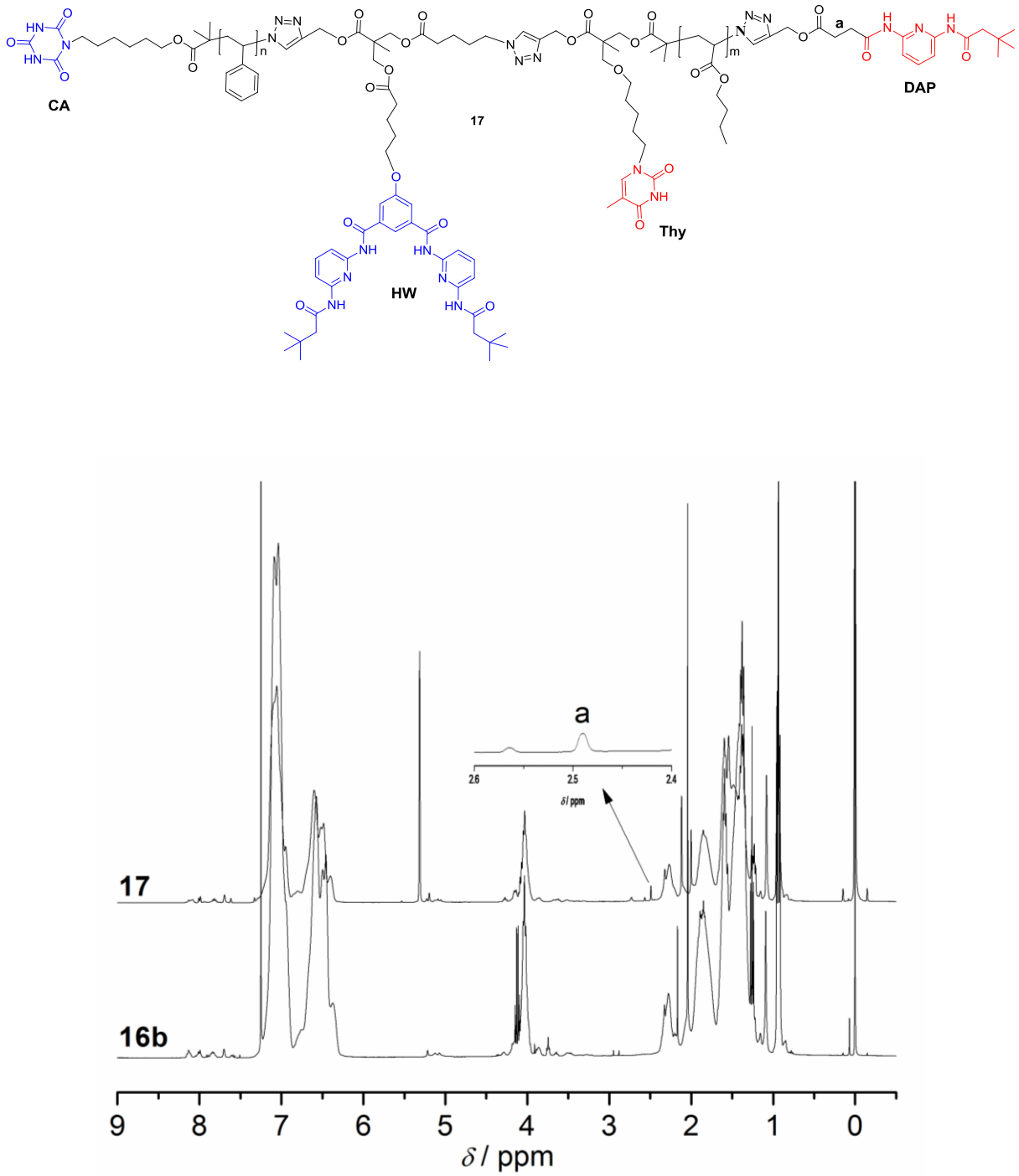


Figure S18. ^{1}H NMR spectrum of α-cyanuric acid (CA), mid-chain (Hamilton wedge (HW)/thymine (Thy)) and ω-diaminopyridine (DAP) functional diblock block copolymer (PS-*b*-P*n*BA) (**17**) in CD_2Cl_2 and its precursor polymer before attaching DAP motif (**16b**) in $CDCl_3$ at ambient temperature. New proton resonances for C=OCH_2CH_2C=O were observed

at 2.49 ppm indicating the DAP motif was successfully attached at the chain end of the polymer **17**.

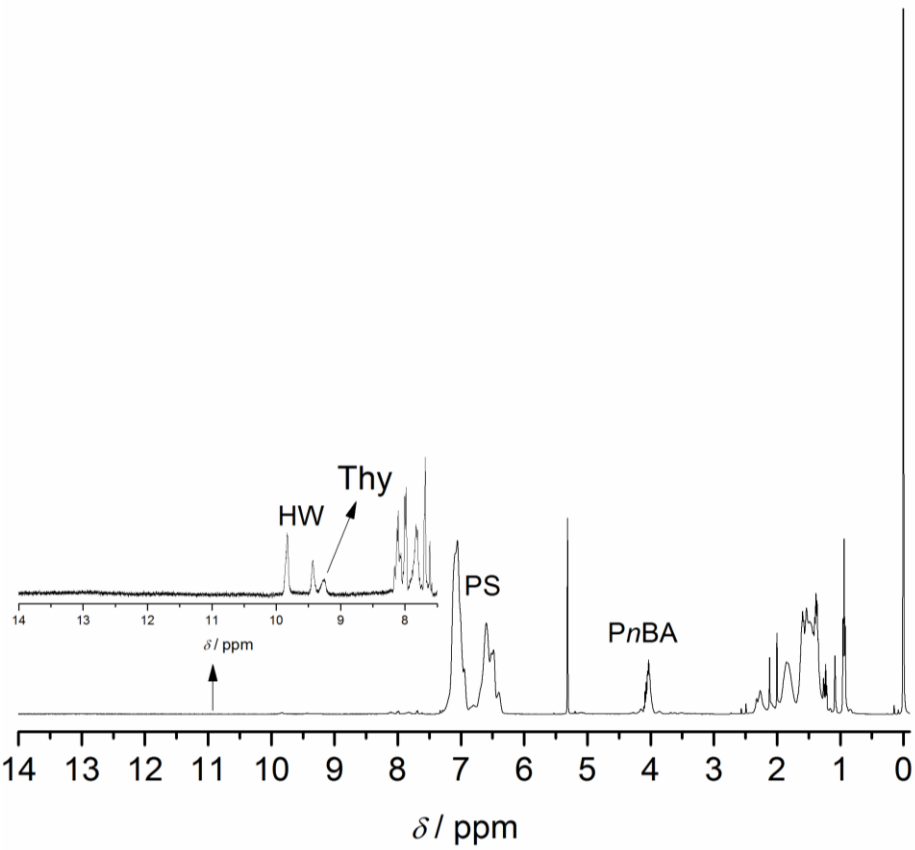


Figure S19. ^{1}H NMR spectrum of α-cyanuric acid (CA), mid-chain (Hamilton wedge (HW)/thymine (Thy)) and ω-diaminopyridine (DAP) functional diblock block copolymer (PS-*b*-P*n*BA) (**17**) in CD_2Cl_2 at ambient temperature.

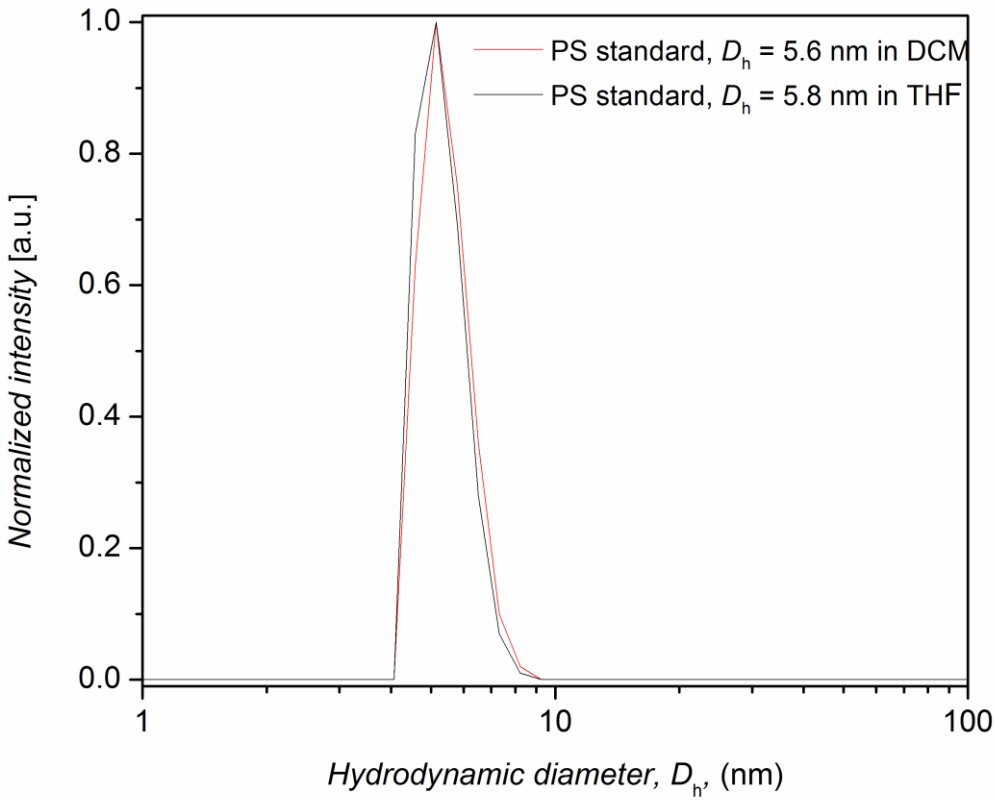


Figure S20. Mean hydrodynamic diameters of the polystyrene standard ($M_{n,SEC}$ = 17400 Da, $Đ$ = 1.11) recorded at a 90° angle in tetrahydrofuran (THF) or dichloromethane (DCM) at 25 °C.

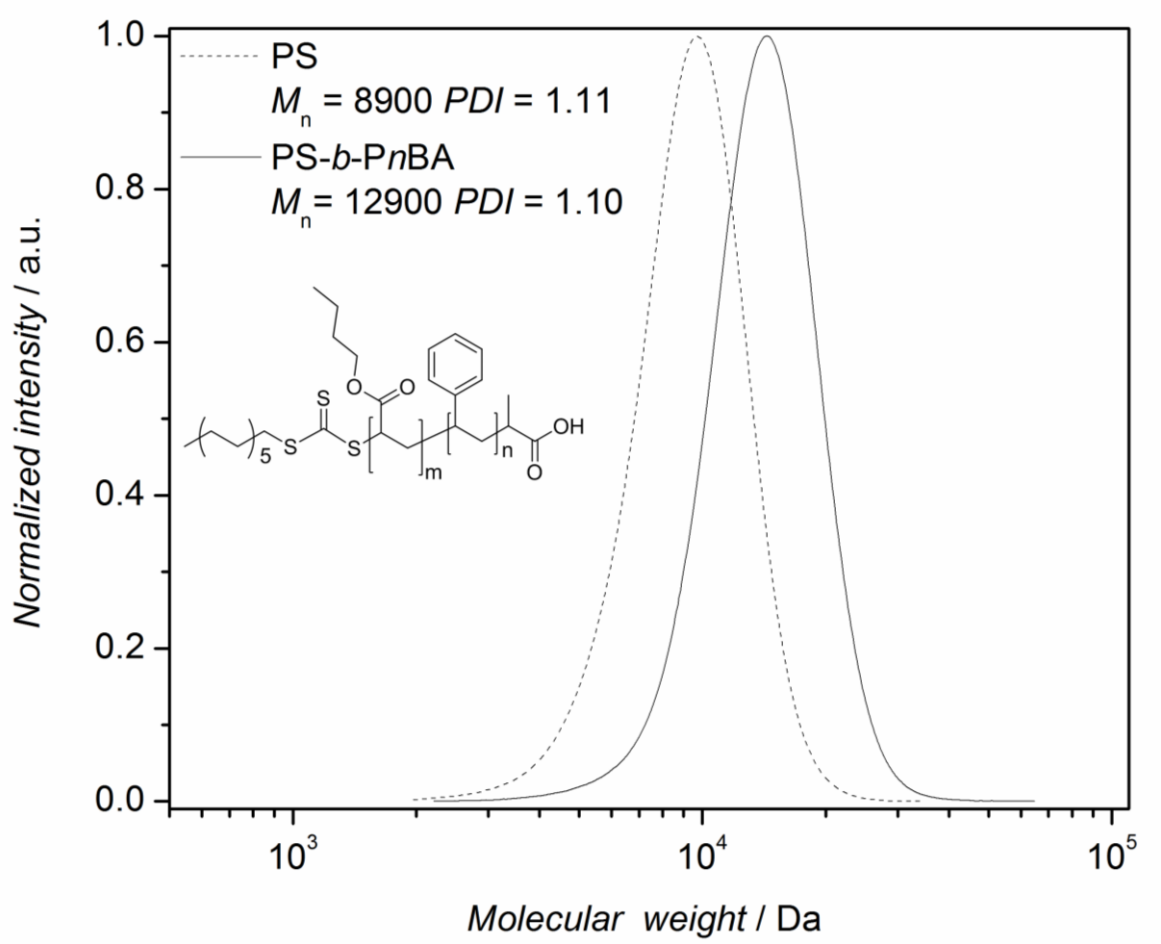


Figure S21. SEC traces of the polystyrene (PS) homopolymer and the polystyrene-*b*-poly(*n*-butylacrylate) (PS-*b*-P*n*BA) block copolymer.

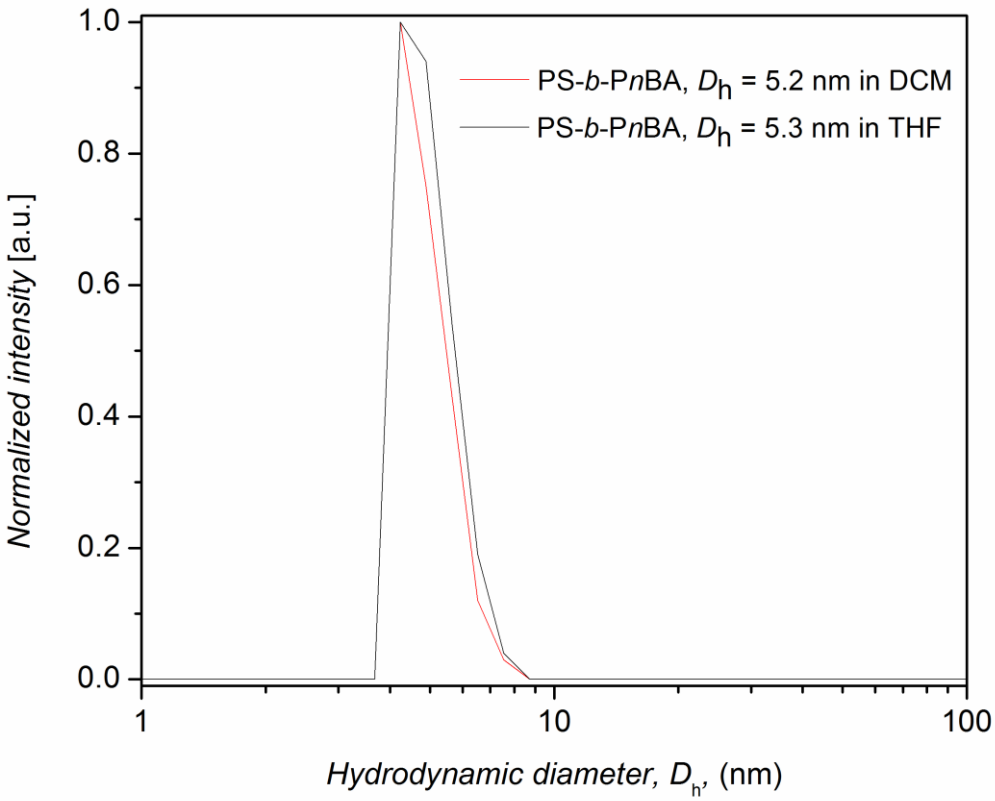


Figure S22. Mean hydrodynamic diameters of the non-functional block copolymer PS-*b*-P*n*BA ($M_{n,SEC}$ = 12900 Da, $Đ$ = 1.10) recorded at a 90° angle in tetrahydrofuran (THF) or dichloromethane (DCM) at 25 °C.

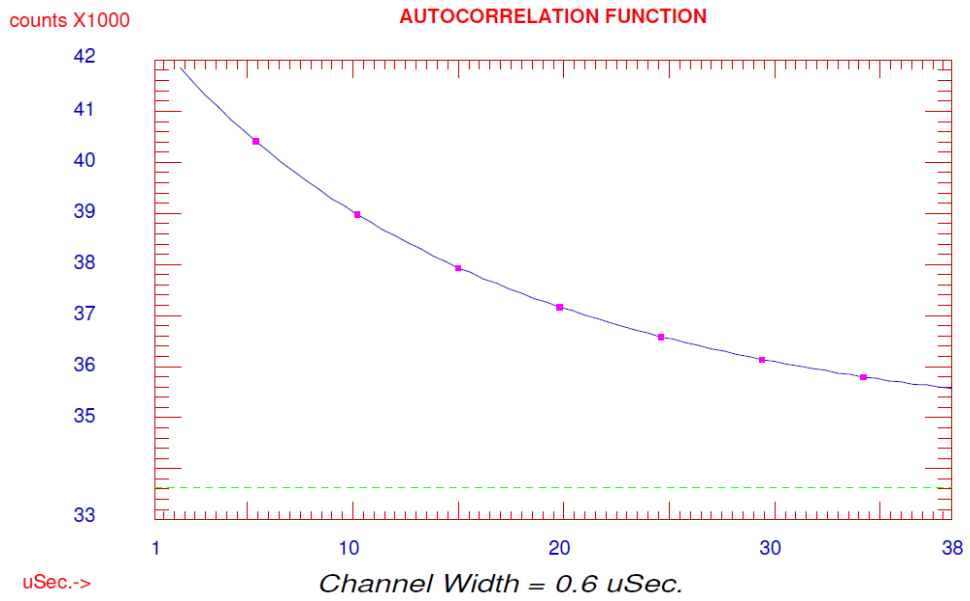


Figure S23. Autocorrelation function for the DLS measurement of polymer **17** in THF at 25 °C.

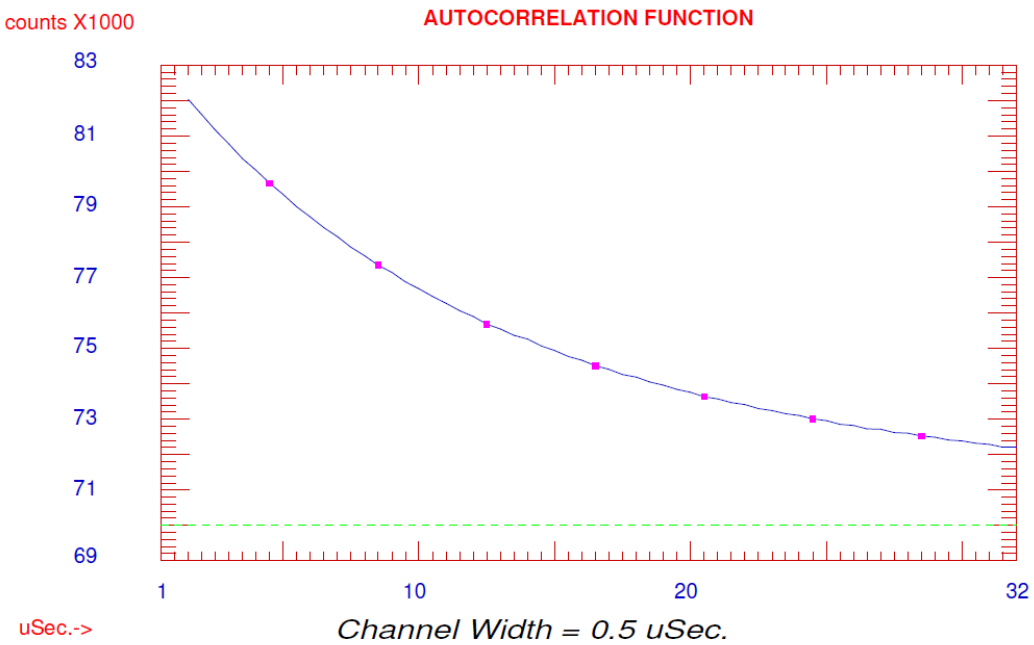


Figure S24. Autocorrelation function for the DLS measurement of polymer **17** in DCM at 25 °C.

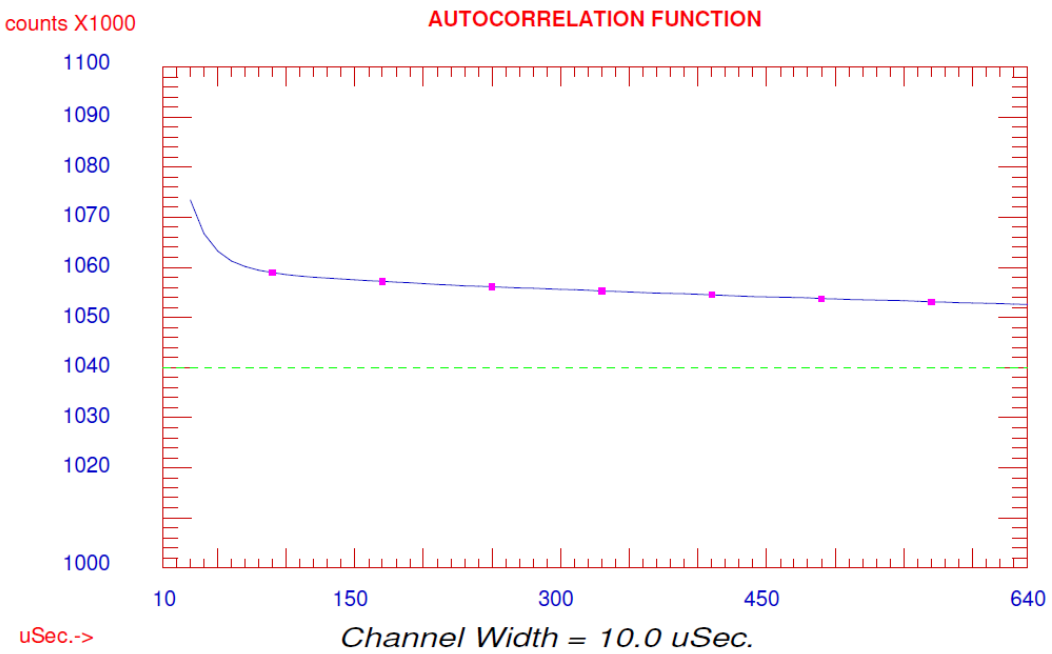


Figure S25. Autocorrelation function for the DLS measurement of the polystyrene standard in THF at 25 °C.

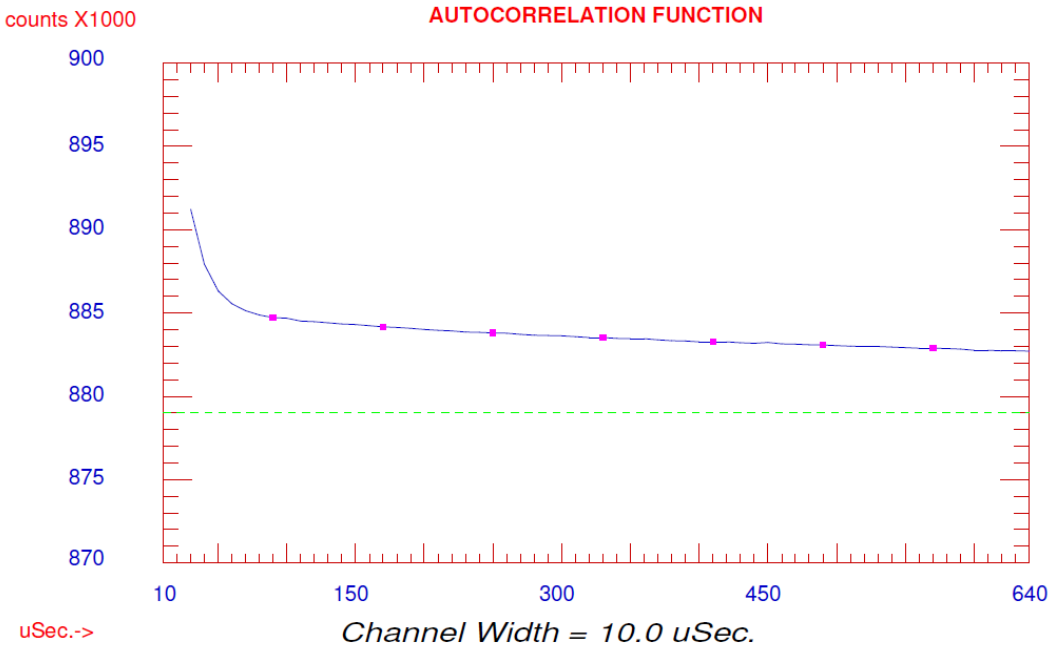


Figure S26. Autocorrelation function for the DLS measurement of the polystyrene standard in DCM at 25 °C.

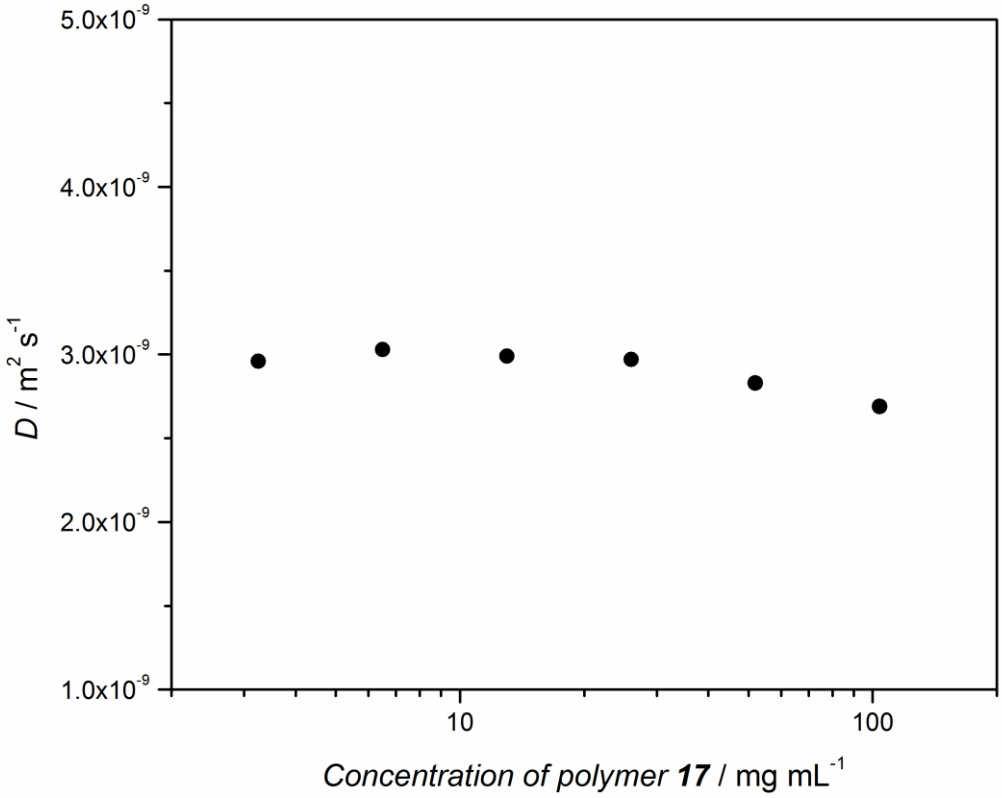


Figure S27. Diffusion coefficient of deuterated dichloromethane as a function of the concentration of polymer **17**, indicating that the diffusion coefficient is almost not affected by the increasing viscosity of the solution.

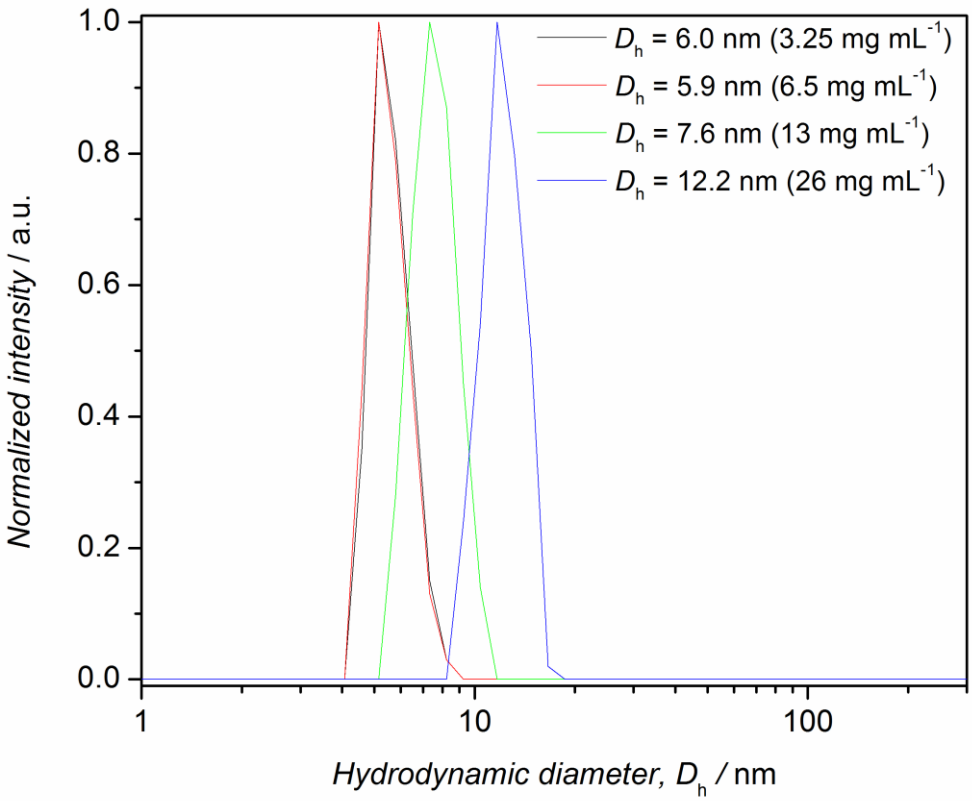


Figure S28. Hydrodynamic diameter, D_h, distributions as a function of the concentration of polymer **17** recorded at a 90° angle in DCM at 25 °C.

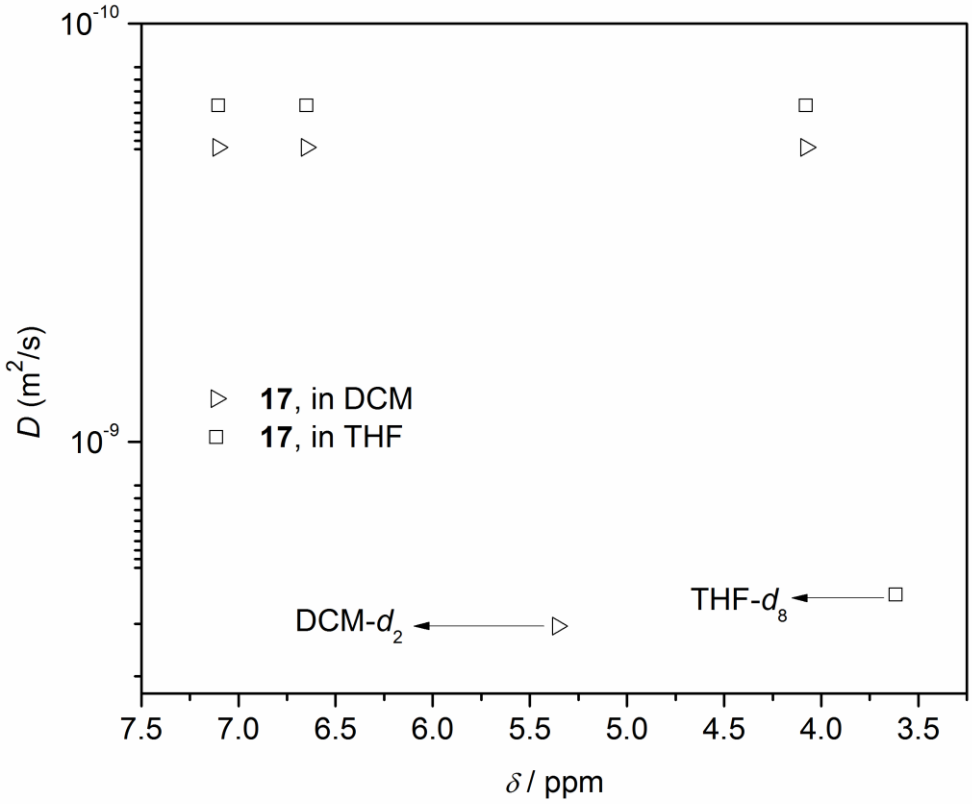
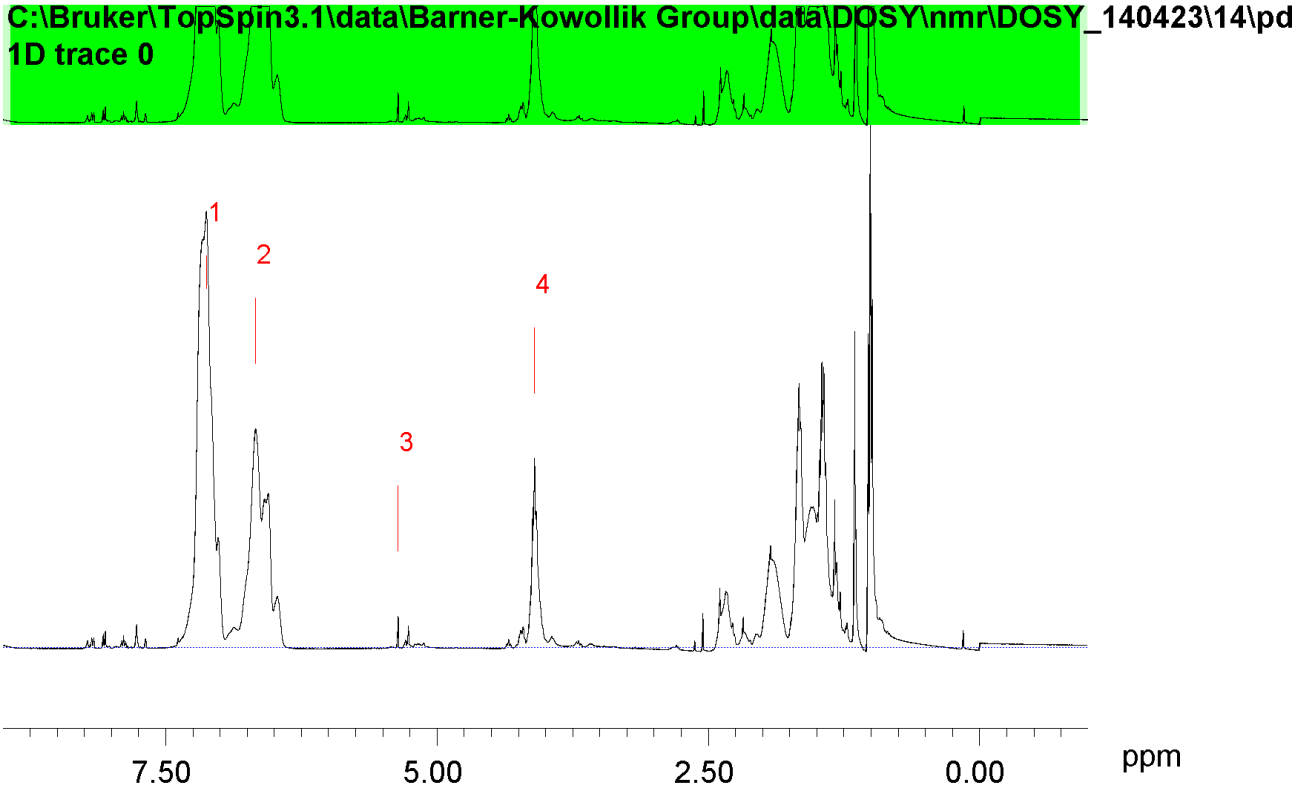


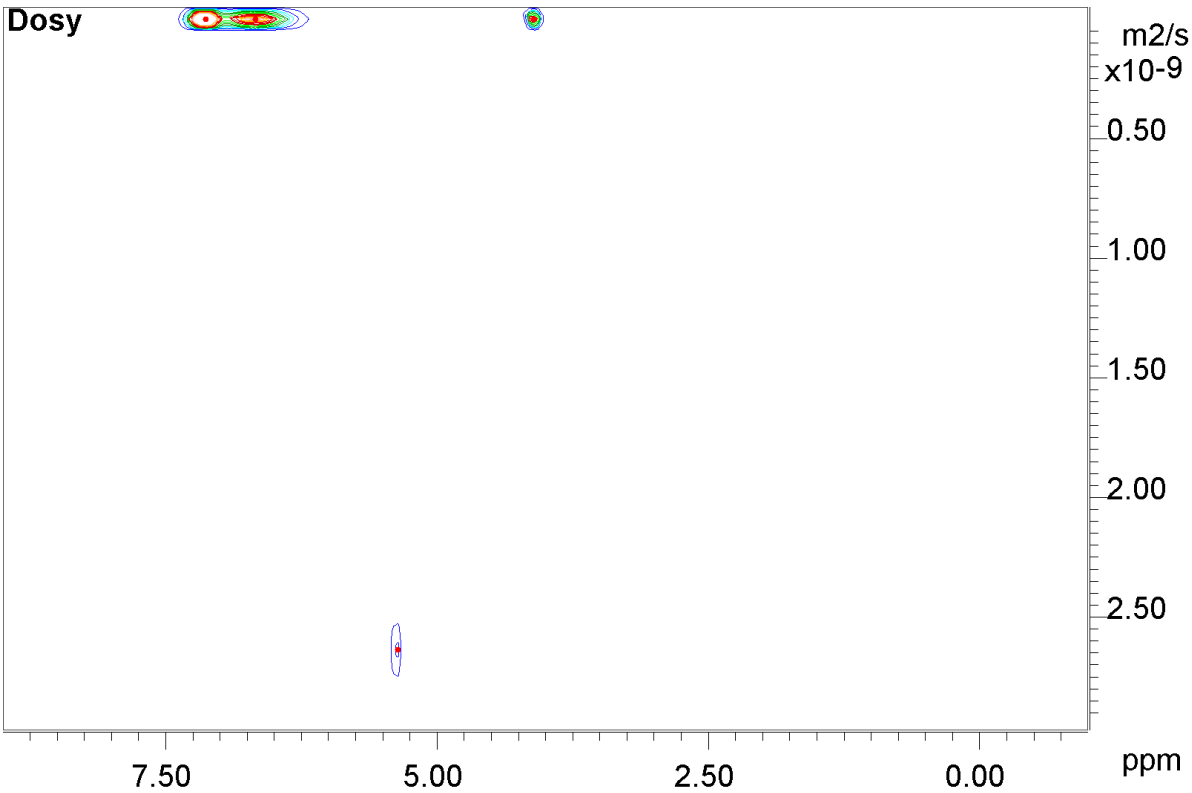
Figure S29. Diffusion coefficients, *D*, as a function of the chemical shifts of the resonances associated with the polymer **17** in tetrahydrofuran (THF-d_8) or dichloromethane (DCM-d_2) at 25 °C.

Appendix: Primary DOSY data of the concentration study depicted in Figure 5

Diffusion Analysis

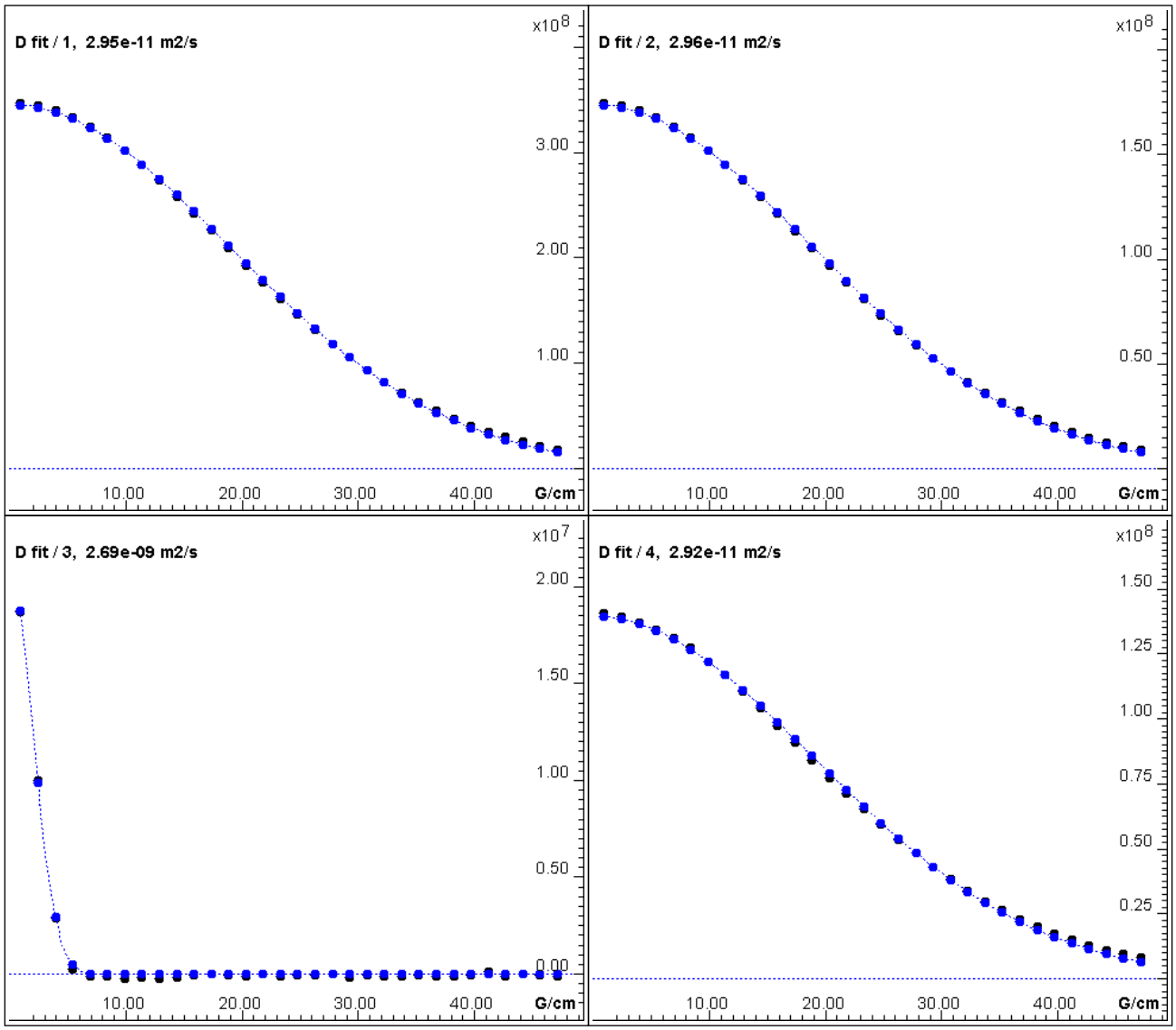
sample name:	104 mg/mL
Description/Title:	
Origin:	in-house
Date of preparation:	04 / 2014
Temperature (K):	298.0
Weight (Daltons):	15400


C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\14\pd
1D trace 0
1
2
3
4
7.50
5.00
2.50
0.00
ppm


Dosy
m2/s
x10-9
0.50
1.00
1.50
2.00
2.50
7.50
5.00
2.50
0.00
ppm

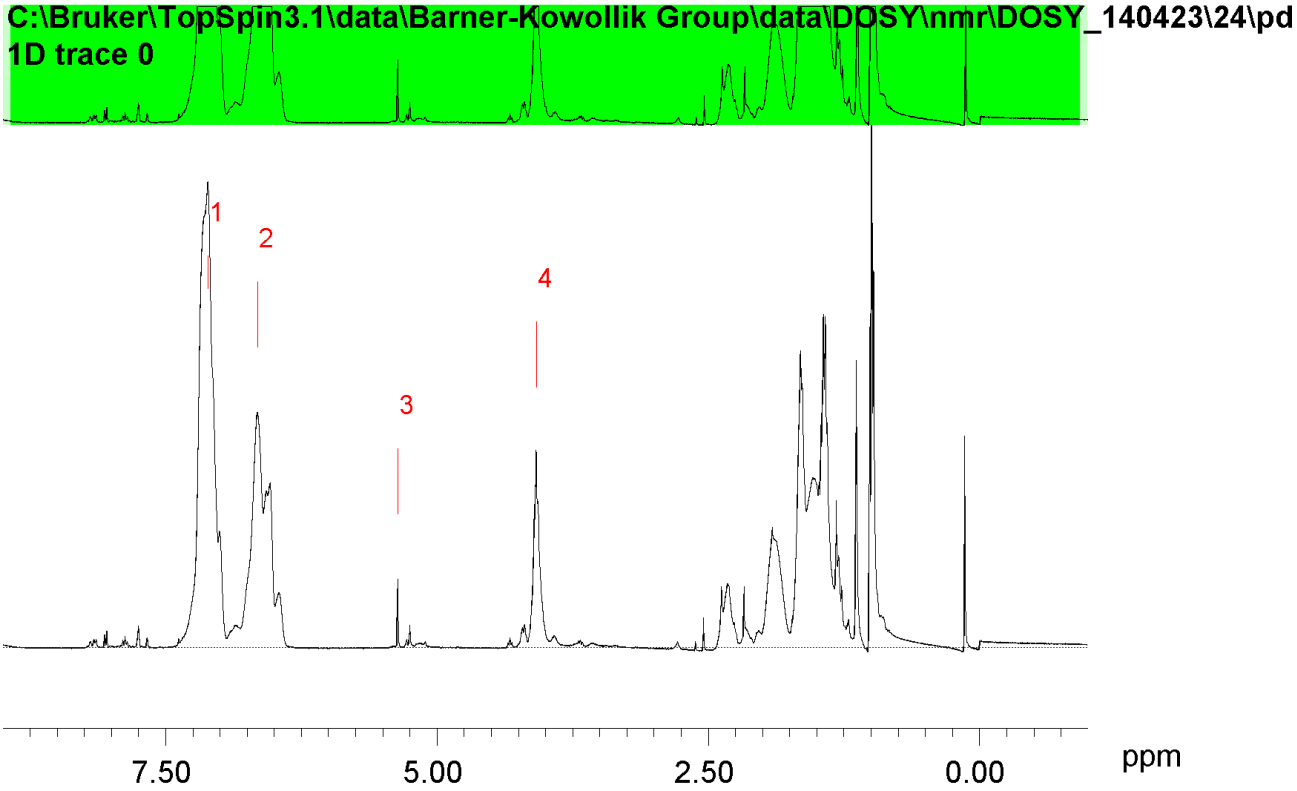
Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0082000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\11\pdata\1\peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error
1	7.124	2.95e-11	2.691e-13
2	6.669	2.96e-11	2.604e-13
3	5.358	2.69e-09	7.974e-11
4	4.101	2.92e-11	4.111e-13


D fit / 1, 2.95e-11 m2/s
x10^8
3.00
2.00
1.00
10.00
20.00
30.00
40.00
G/cm
D fit / 2, 2.96e-11 m2/s
x10^8
1.50
1.00
0.50
10.00
20.00
30.00
40.00
G/cm
D fit / 3, 2.69e-09 m2/s
x10^7
2.00
1.50
1.00
0.50
0.00
10.00
20.00
30.00
40.00
G/cm
D fit / 4, 2.92e-11 m2/s
x10^8
1.50
1.25
1.00
0.75
0.50
0.25
10.00
20.00
30.00
40.00
G/cm

Diffusion Analysis

sample name:	52 mg/mL
Description/Title:	
Origin:	in-house
Date of preparation:	04 / 2014
Temperature (K):	298.0
Weight (Daltons):	15400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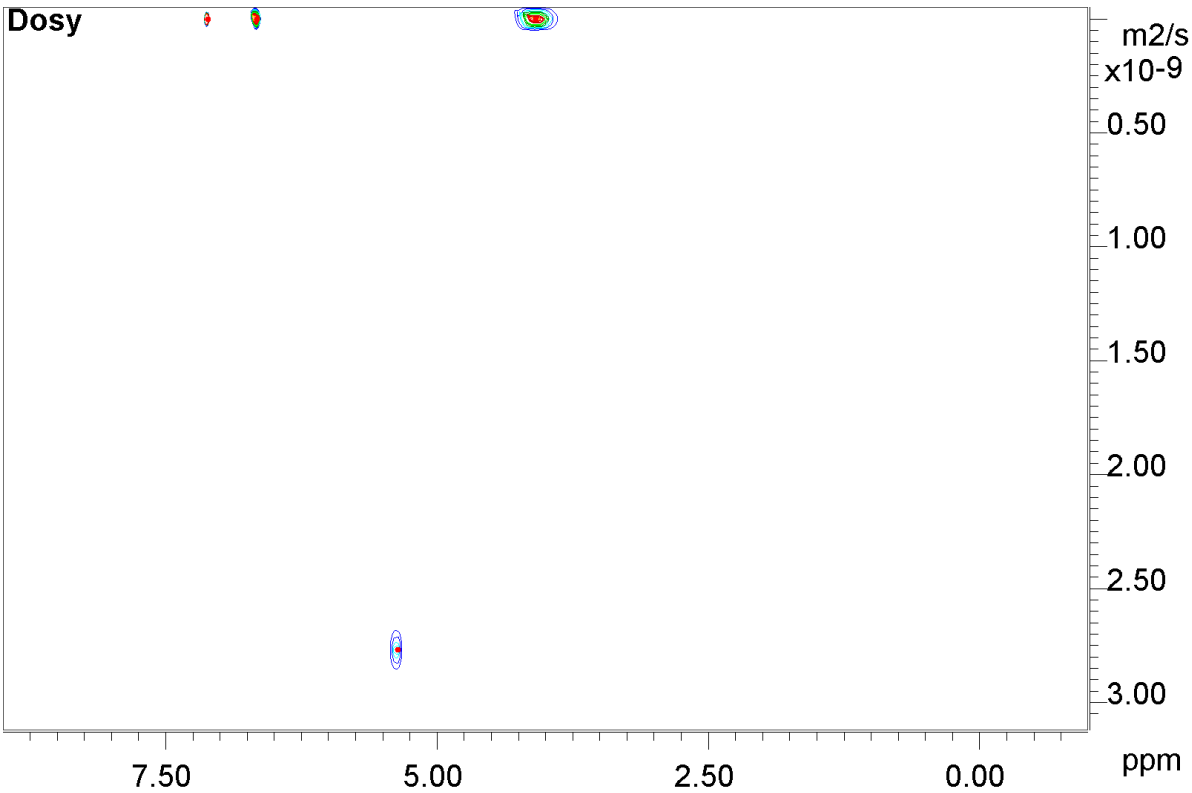
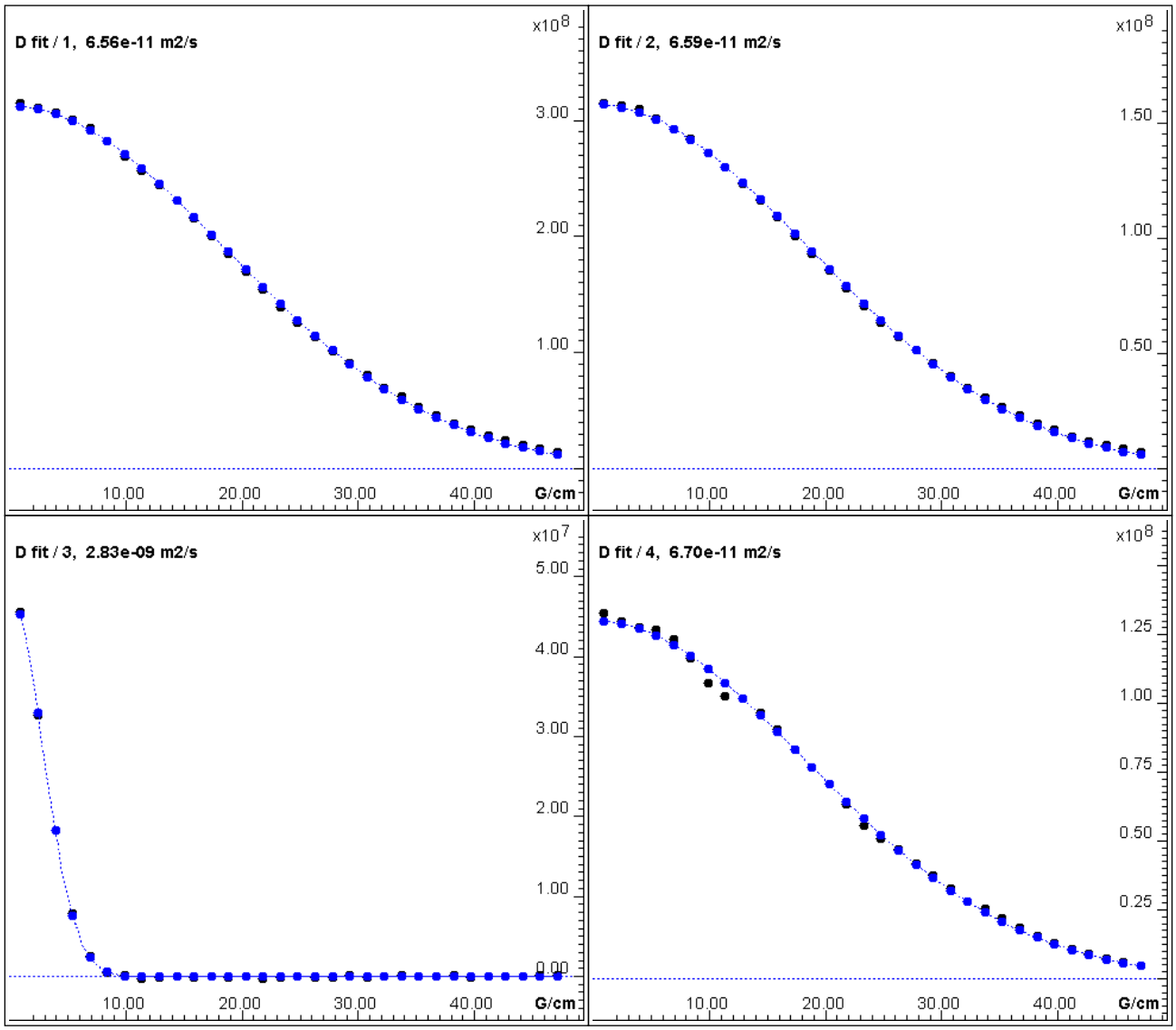
1D trace 0
1
2
3
4
7.50
5.00
2.50
0.00
ppm


Dosy
m2/s
x10-9
0.50
1.00
1.50
2.00
2.50
3.00
7.50
5.00
2.50
0.00
ppm

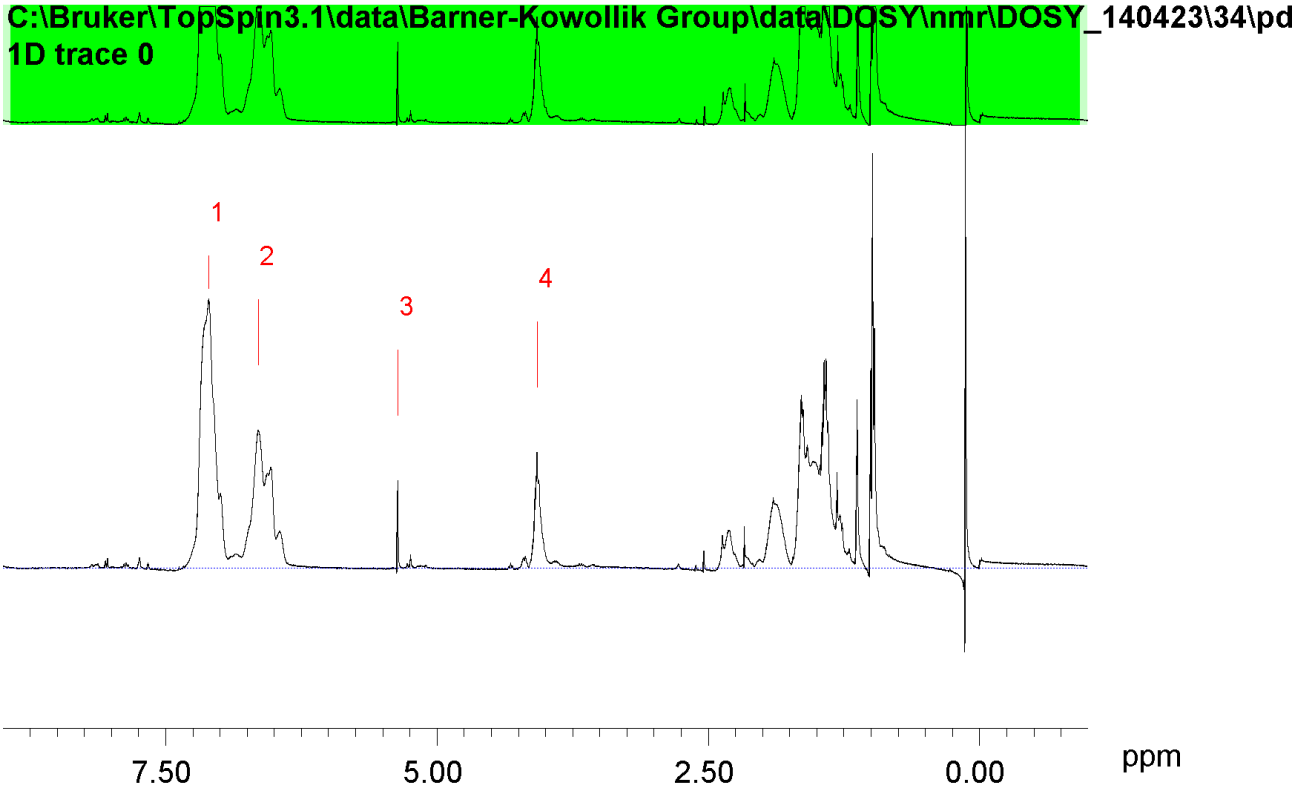
Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0056000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\21\pdata\1\peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

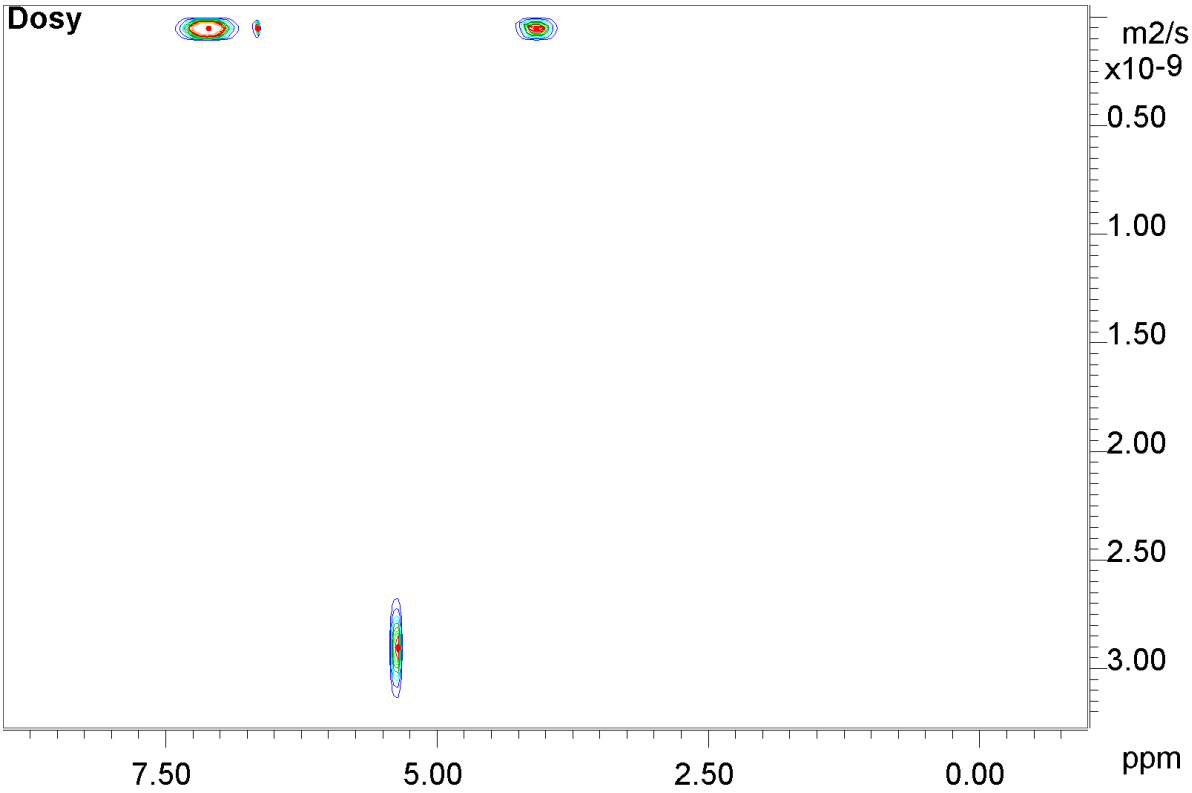
Peak name	F2 [ppm]	D [m2/s]	error
1	7.109	6.56e-11	7.410e-13
2	6.652	6.59e-11	6.440e-13
3	5.358	2.83e-09	4.186e-11
4	4.084	6.70e-11	1.569e-12


D fit / 1, 6.56e-11 m2/s
x10^8
3.00
2.00
1.00
10.00
20.00
30.00
40.00
G/cm
D fit / 2, 6.59e-11 m2/s
x10^8
1.50
1.00
0.50
10.00
20.00
30.00
40.00
G/cm
D fit / 3, 2.83e-09 m2/s
x10^7
5.00
4.00
3.00
2.00
1.00
0.00
10.00
20.00
30.00
40.00
G/cm
D fit / 4, 6.70e-11 m2/s
x10^8
1.25
1.00
0.75
0.50
0.25
10.00
20.00
30.00
40.00
G/cm

Diffusion Analysis

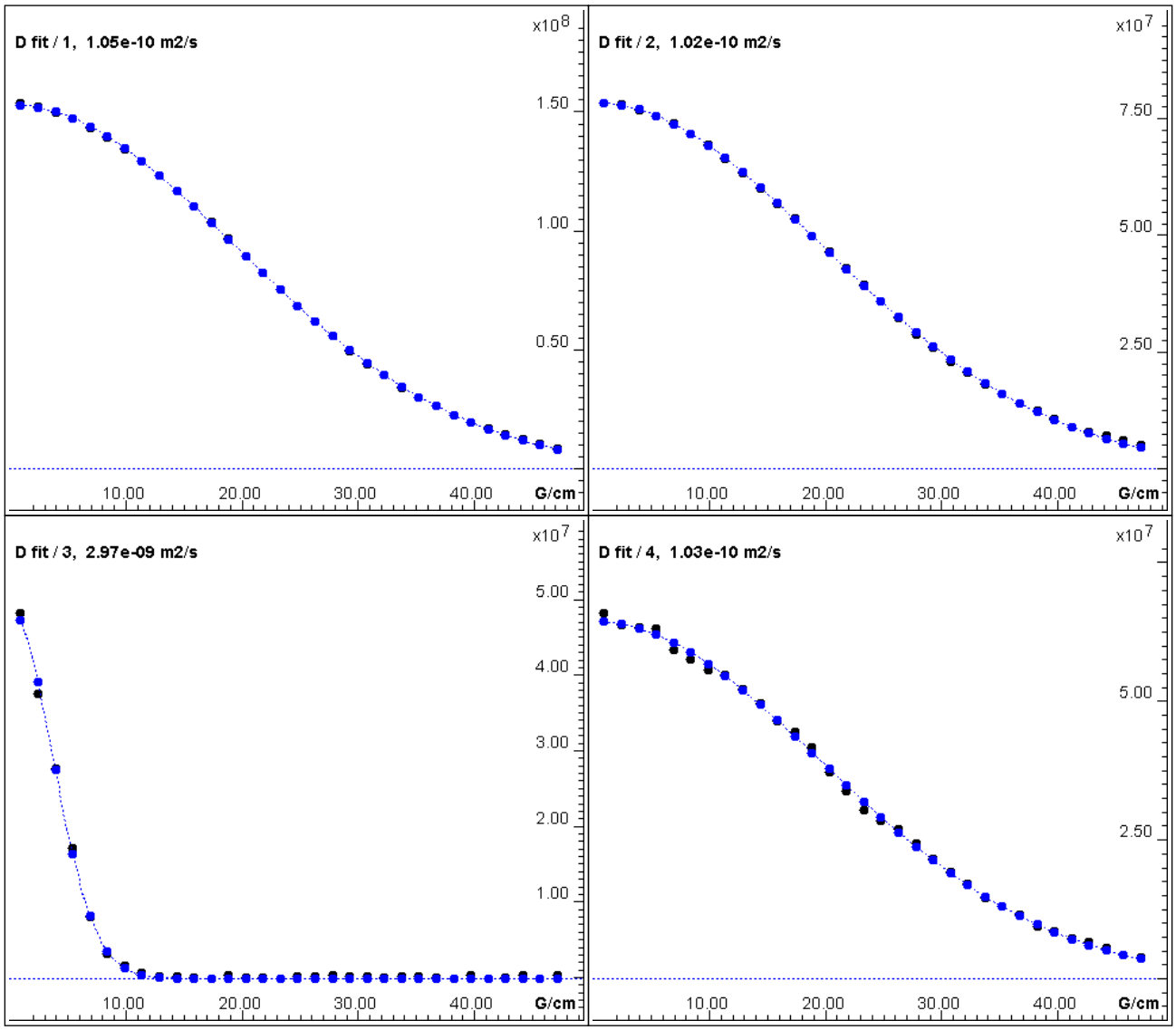
sample name:	26 mg/mL
Description/Title:	
Origin:	in-house
Date of preparation:	04 / 2014
Temperature (K):	298.0
Weight (Daltons):	15400


C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\34\pd
1D trace 0
1
2
3
4
7.50
5.00
2.50
0.00
ppm


Dosy
m2/s
x10-9
0.50
1.00
1.50
2.00
2.50
3.00
7.50
5.00
2.50
0.00
ppm

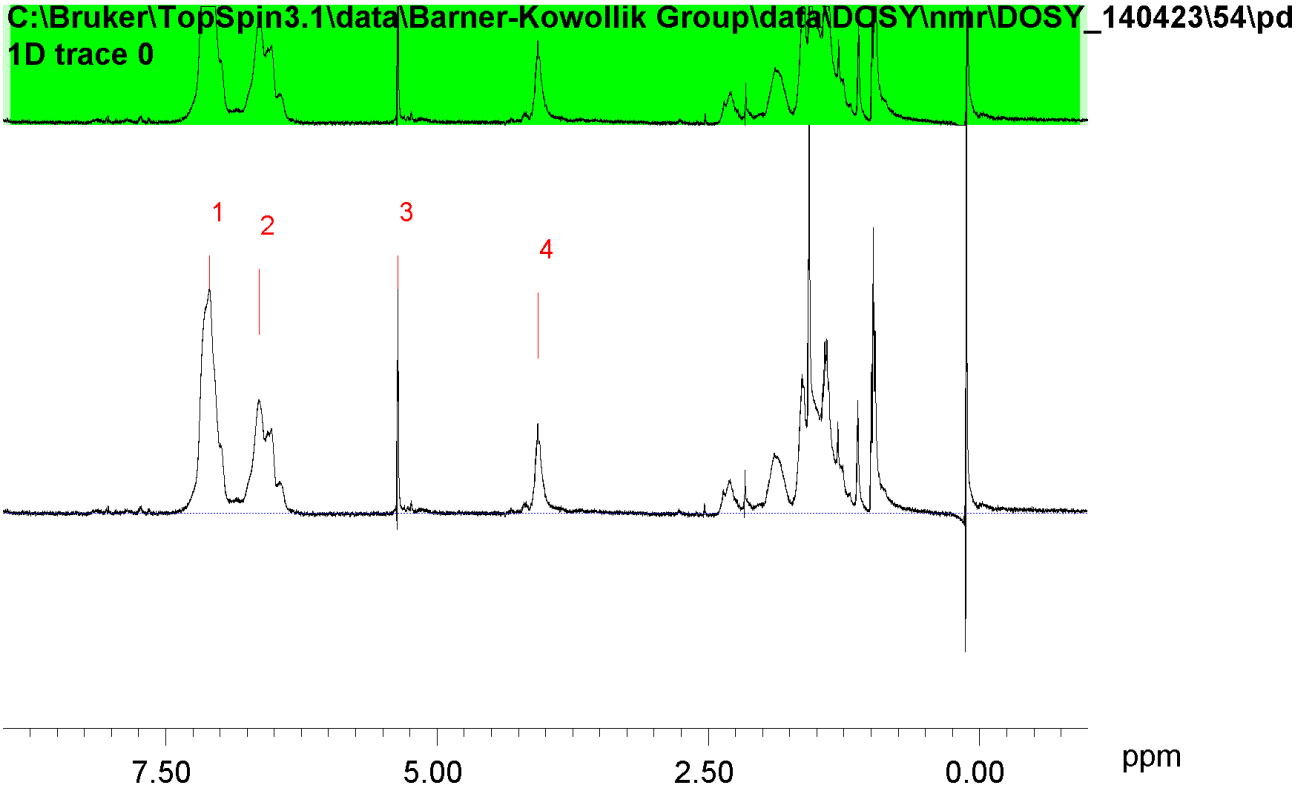
Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0042000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\31\pdata\1\peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

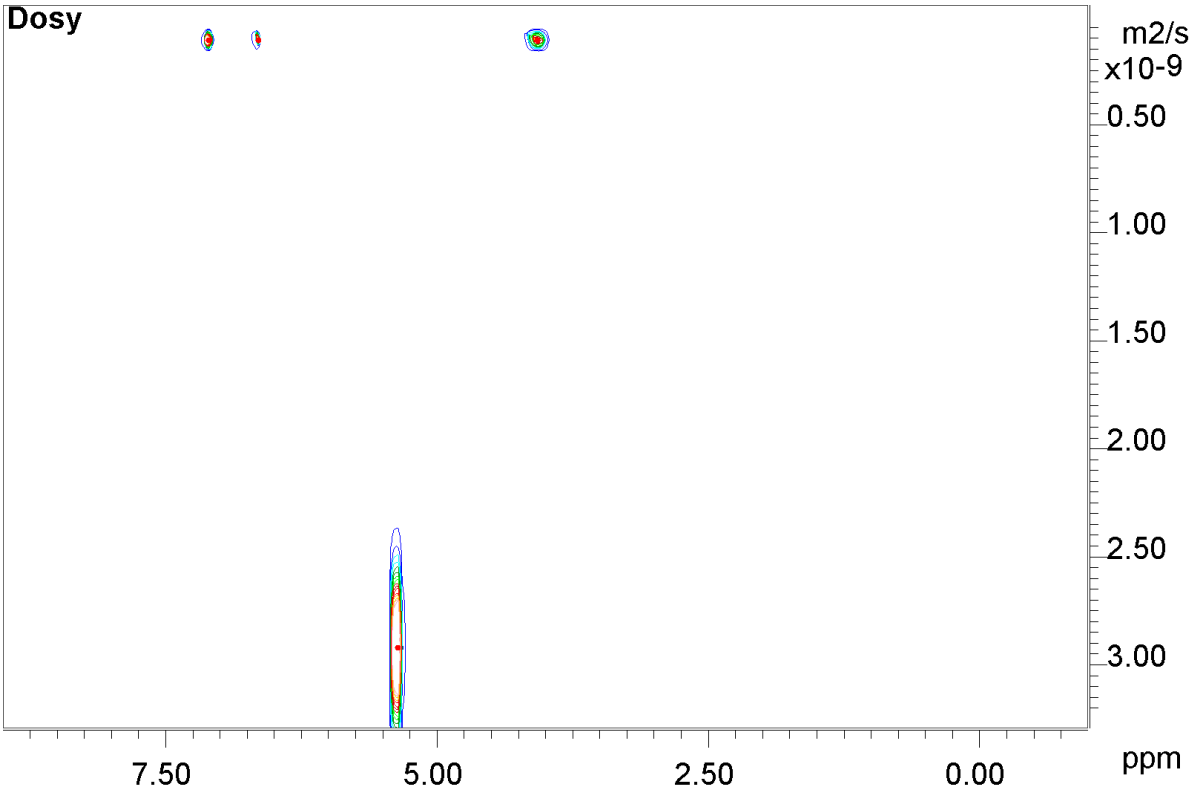
Peak name	F2 [ppm]	D [m2/s]	error
1	7.101	1.05e-10	4.402e-13
2	6.644	1.02e-10	6.643e-13
3	5.358	2.97e-09	1.080e-10
4	4.076	1.03e-10	2.027e-12


D fit / 1, 1.05e-10 m2/s
x10^8
1.50
1.00
0.50
10.00
20.00
30.00
40.00
G/cm
D fit / 2, 1.02e-10 m2/s
x10^7
7.50
5.00
2.50
10.00
20.00
30.00
40.00
G/cm
D fit / 3, 2.97e-09 m2/s
x10^7
5.00
4.00
3.00
2.00
1.00
10.00
20.00
30.00
40.00
G/cm
D fit / 4, 1.03e-10 m2/s
x10^7
5.00
2.50
10.00
20.00
30.00
40.00
G/cm

Diffusion Analysis

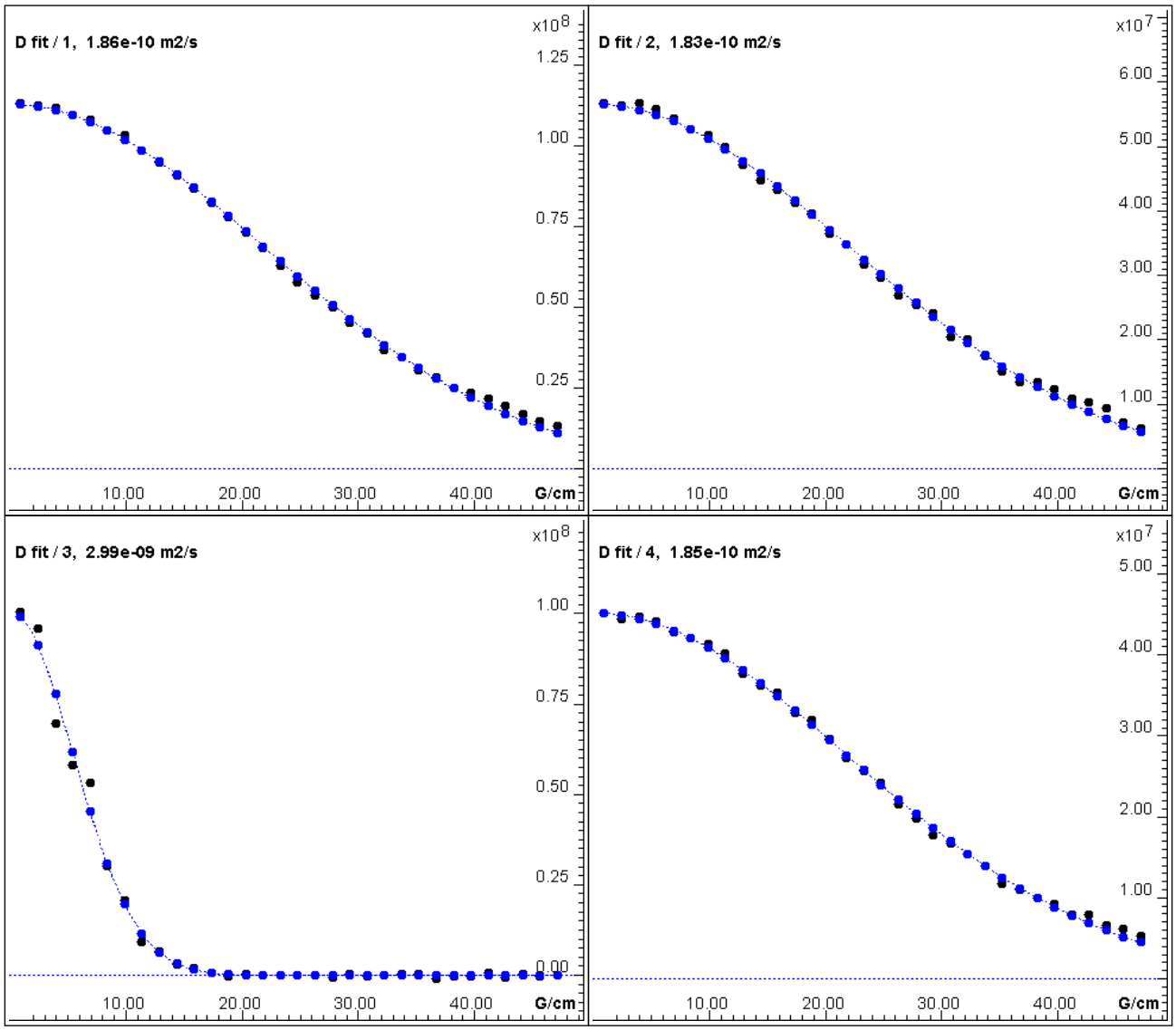
sample name:	13 mg/mL
Description/Title:	
Origin:	in-house
Date of preparation:	04 / 2014
Temperature (K):	298.0
Weight (Daltons):	15400


C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\54\pd
1D trace 0
1
2
3
4
7.50
5.00
2.50
0.00
ppm


Dosy
m2/s
x10-9
0.50
1.00
1.50
2.00
2.50
3.00
7.50
5.00
2.50
0.00
ppm

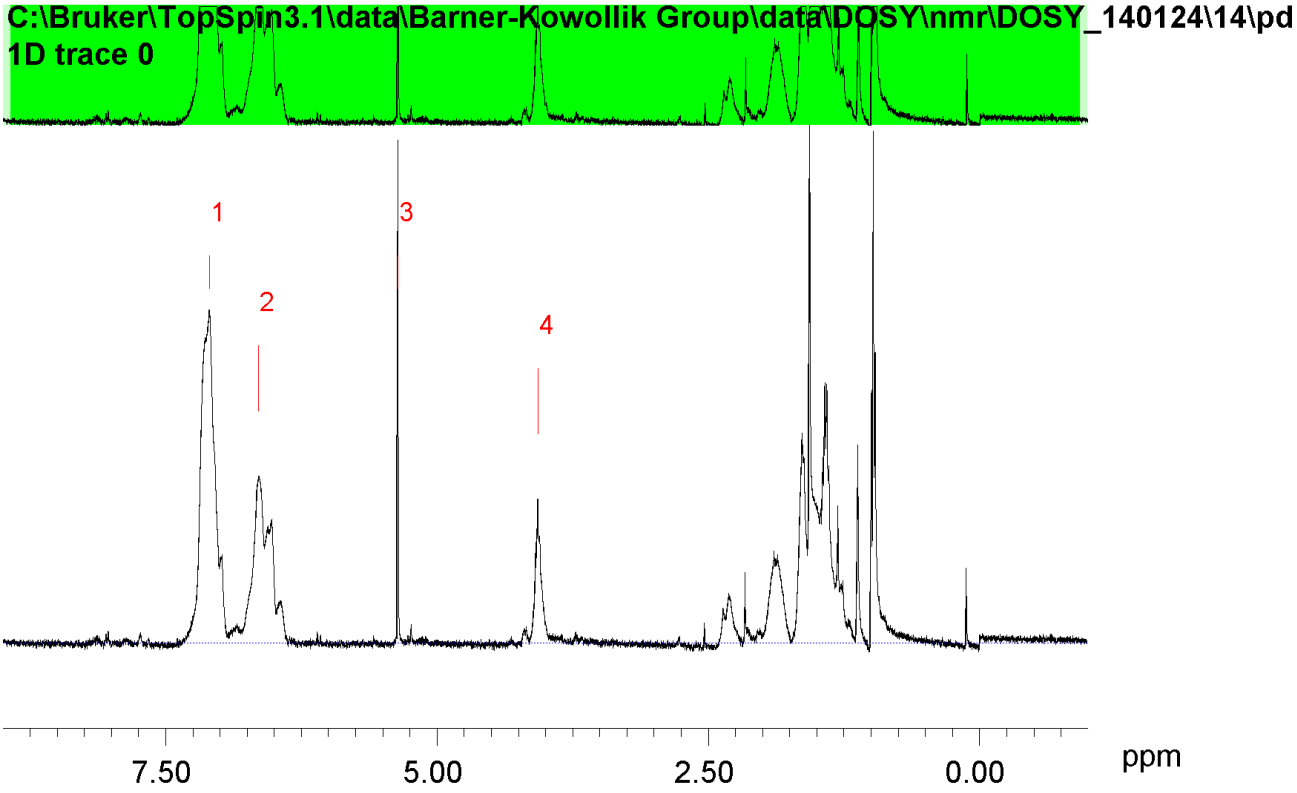
Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0028000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\51\pdata\1\peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

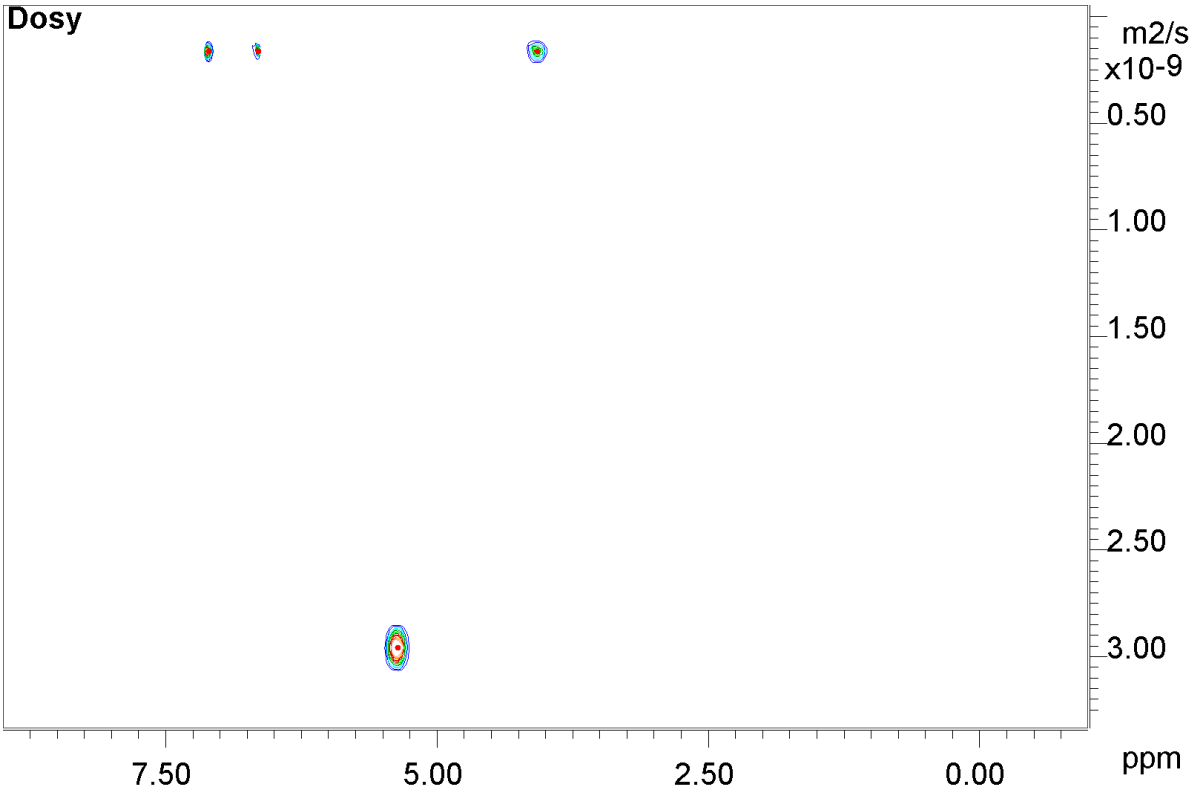
Peak name	F2 [ppm]	D [m2/s]	error
1	7.097	1.86e-10	3.359e-12
2	6.638	1.83e-10	4.325e-12
3	5.359	2.99e-09	2.296e-10
4	4.068	1.85e-10	3.549e-12


D fit / 1, 1.86e-10 m2/s
x10^8
1.25
1.00
0.75
0.50
0.25
10.00
20.00
30.00
40.00
G/cm
D fit / 2, 1.83e-10 m2/s
x10^7
6.00
5.00
4.00
3.00
2.00
1.00
10.00
20.00
30.00
40.00
G/cm
D fit / 3, 2.99e-09 m2/s
x10^8
1.00
0.75
0.50
0.25
0.00
10.00
20.00
30.00
40.00
G/cm
D fit / 4, 1.85e-10 m2/s
x10^7
5.00
4.00
3.00
2.00
1.00
10.00
20.00
30.00
40.00
G/cm

Diffusion Analysis

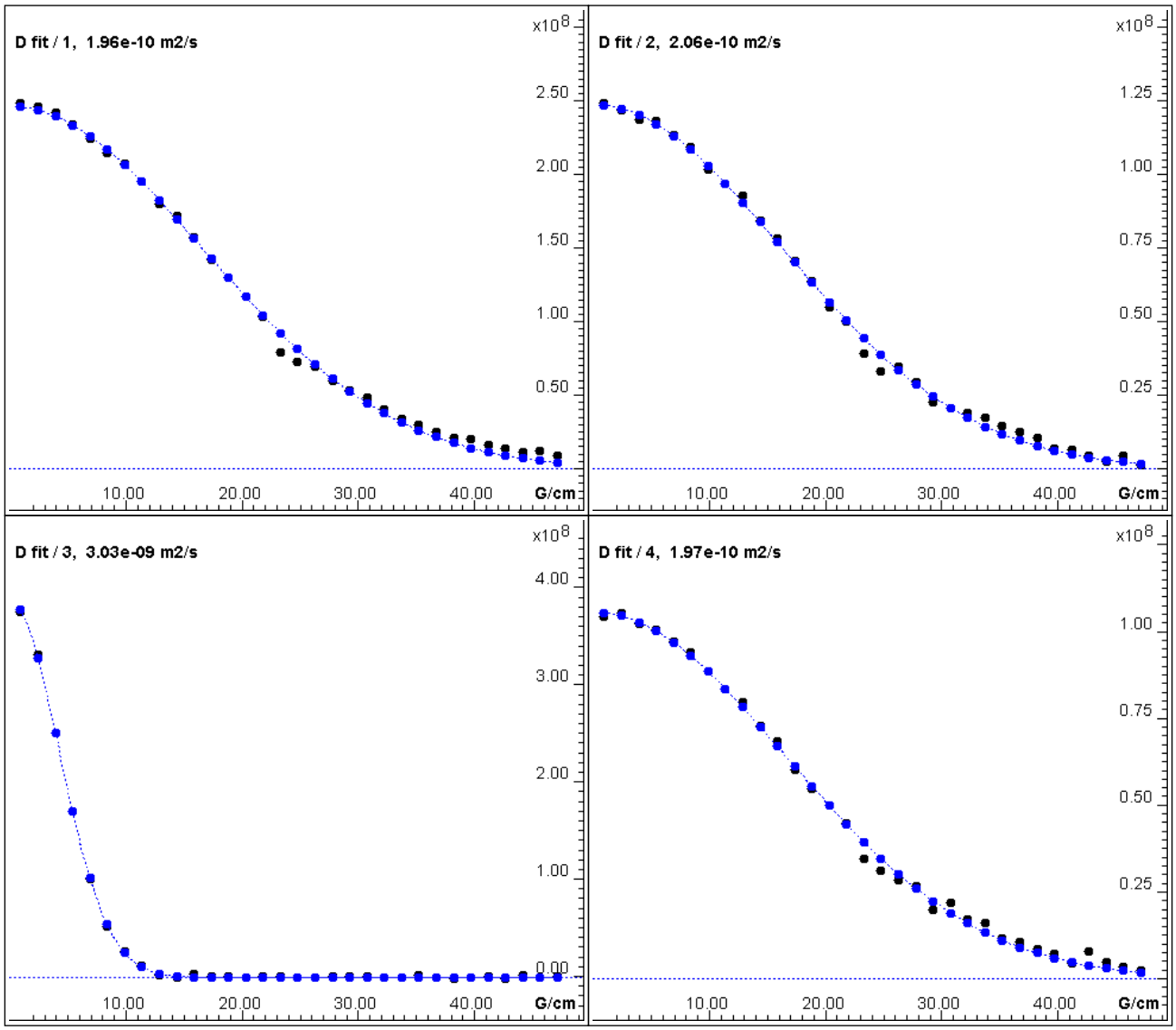
sample name:	6.5 mg/mL
Description/Title:	
Origin:	in-house
Date of preparation:	04 / 2014
Temperature (K):	298.0
Weight (Daltons):	15400


C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140124\14\pd
1D trace 0
1
2
3
4
7.50
5.00
2.50
0.00
ppm


Dosy
m2/s
x10-9
0.50
1.00
1.50
2.00
2.50
3.00
7.50
5.00
2.50
0.00
ppm

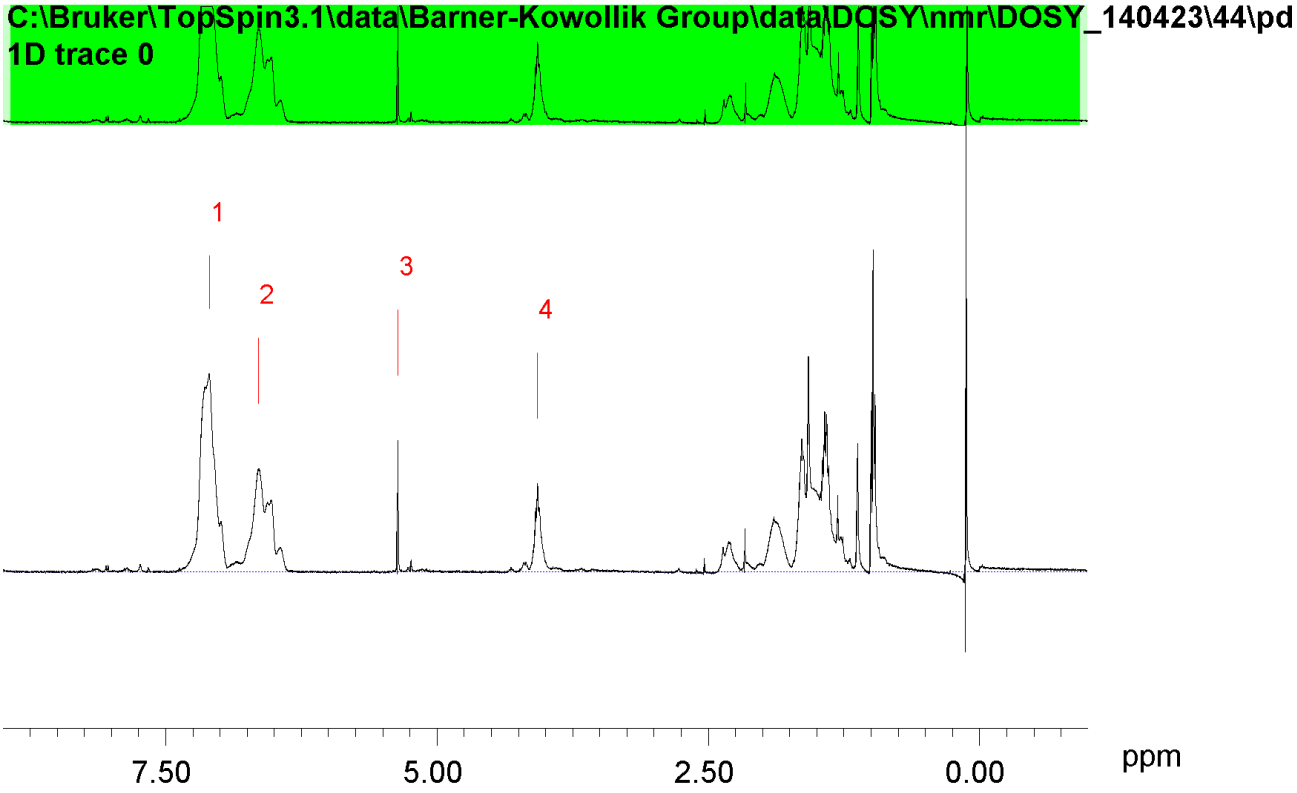
Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0036000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140124\11\pdata\1\peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

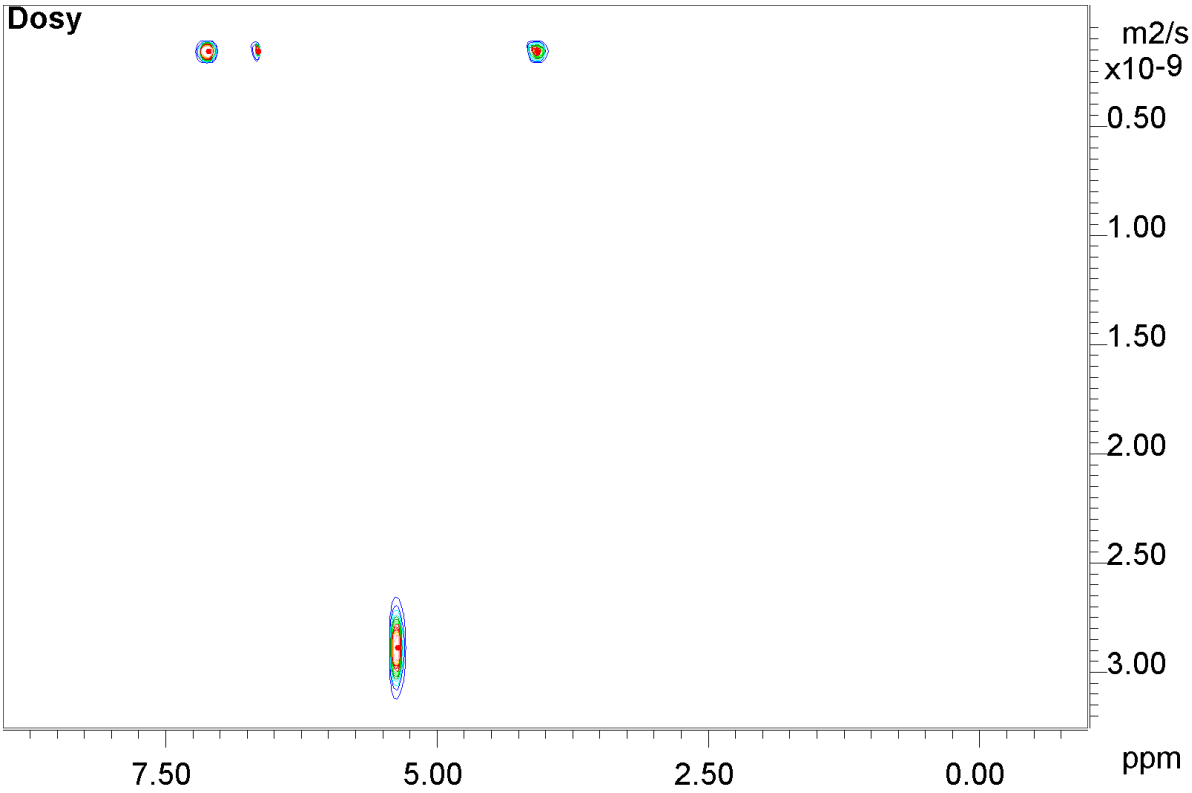
Peak name	F2 [ppm]	D [m2/s]	error
1	7.096	1.96e-10	6.288e-12
2	6.642	2.06e-10	6.372e-12
3	5.358	3.03e-09	4.336e-11
4	4.070	1.97e-10	6.429e-12


D fit / 1, 1.96e-10 m2/s
x10^8
2.50
2.00
1.50
1.00
0.50
10.00
20.00
30.00
40.00
G/cm
D fit / 2, 2.06e-10 m2/s
x10^8
1.25
1.00
0.75
0.50
0.25
10.00
20.00
30.00
40.00
G/cm
D fit / 3, 3.03e-09 m2/s
x10^8
4.00
3.00
2.00
1.00
0.00
10.00
20.00
30.00
40.00
G/cm
D fit / 4, 1.97e-10 m2/s
x10^8
1.00
0.75
0.50
0.25
10.00
20.00
30.00
40.00
G/cm

Diffusion Analysis

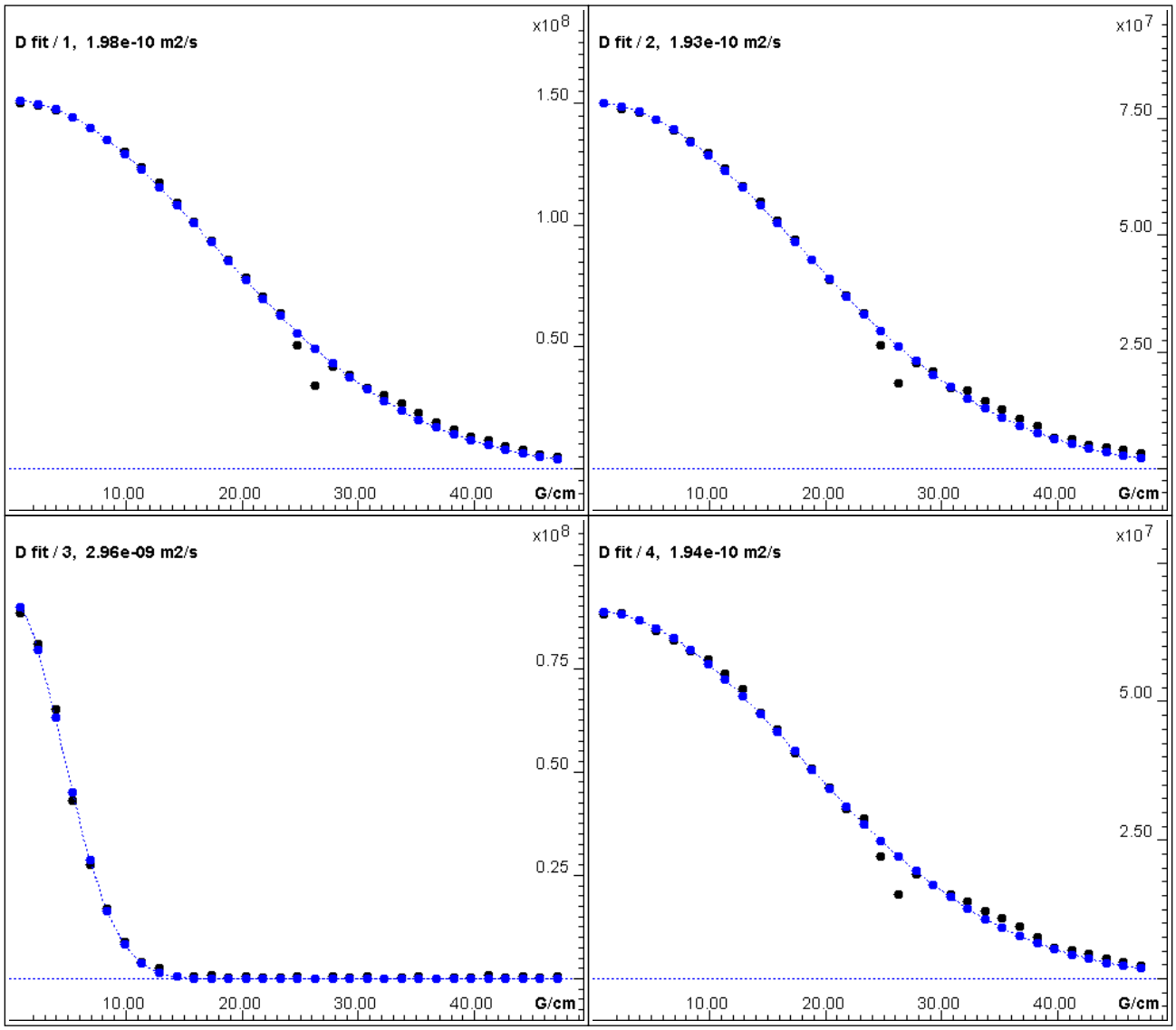
sample name:	3.25 mg/mL
Description/Title:	
Origin:	in-house
Date of preparation:	04 / 2014
Temperature (K):	298.0
Weight (Daltons):	15400


C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\44\pd
1D trace 0
1
2
3
4
7.50
5.00
2.50
0.00
ppm


Dosy
m2/s
x10-9
0.50
1.00
1.50
2.00
2.50
3.00
7.50
5.00
2.50
0.00
ppm

Fitted function:	f (x) = A * exp (-D * x^2 * gamma^2 * littleDelta^2 (bigDelta-littleDelta/3)* 10^4
used gamma:	26752 rad/(s*Gauss)
used little delta:	0.0034000 s
used big delta:	0.099900 s
used gradient strength:	variable
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitray y uncertainties
Confidence level:	95%
Used peaks:	peaks from C:\Bruker\TopSpin3.1\data\Barner-Kowollik Group\data\DOSY\nmr\DOSY_140423\41\pdata\1\peaklist.xml
Used integrals:	peak intensities
Used Gradient strength:	all values (including replicates) used

Peak name	F2 [ppm]	D [m2/s]	error
1	7.099	1.98e-10	7.553e-12
2	6.642	1.93e-10	7.886e-12
3	5.358	2.96e-09	9.862e-11
4	4.072	1.94e-10	8.298e-12


D fit / 1, 1.98e-10 m2/s
x10^8
1.50
1.00
0.50
10.00
20.00
30.00
40.00
G/cm
D fit / 2, 1.93e-10 m2/s
x10^7
7.50
5.00
2.50
10.00
20.00
30.00
40.00
G/cm
D fit / 3, 2.96e-09 m2/s
x10^8
0.75
0.50
0.25
10.00
20.00
30.00
40.00
G/cm
D fit / 4, 1.94e-10 m2/s
x10^7
5.00
2.50
10.00
20.00
30.00
40.00
G/cm