

Chemo-enzymatic synthesis and characterization of renewable thermoplastic and thermoset isocyanate-free poly(hydroxy)urethanes from ferulic acid derivatives

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Supporting Information contains 1 table, 28 figures and comprises a total of 30 pages

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Figure S1: ^1H -NMR spectrum of IDF2Cy C₅-precursor

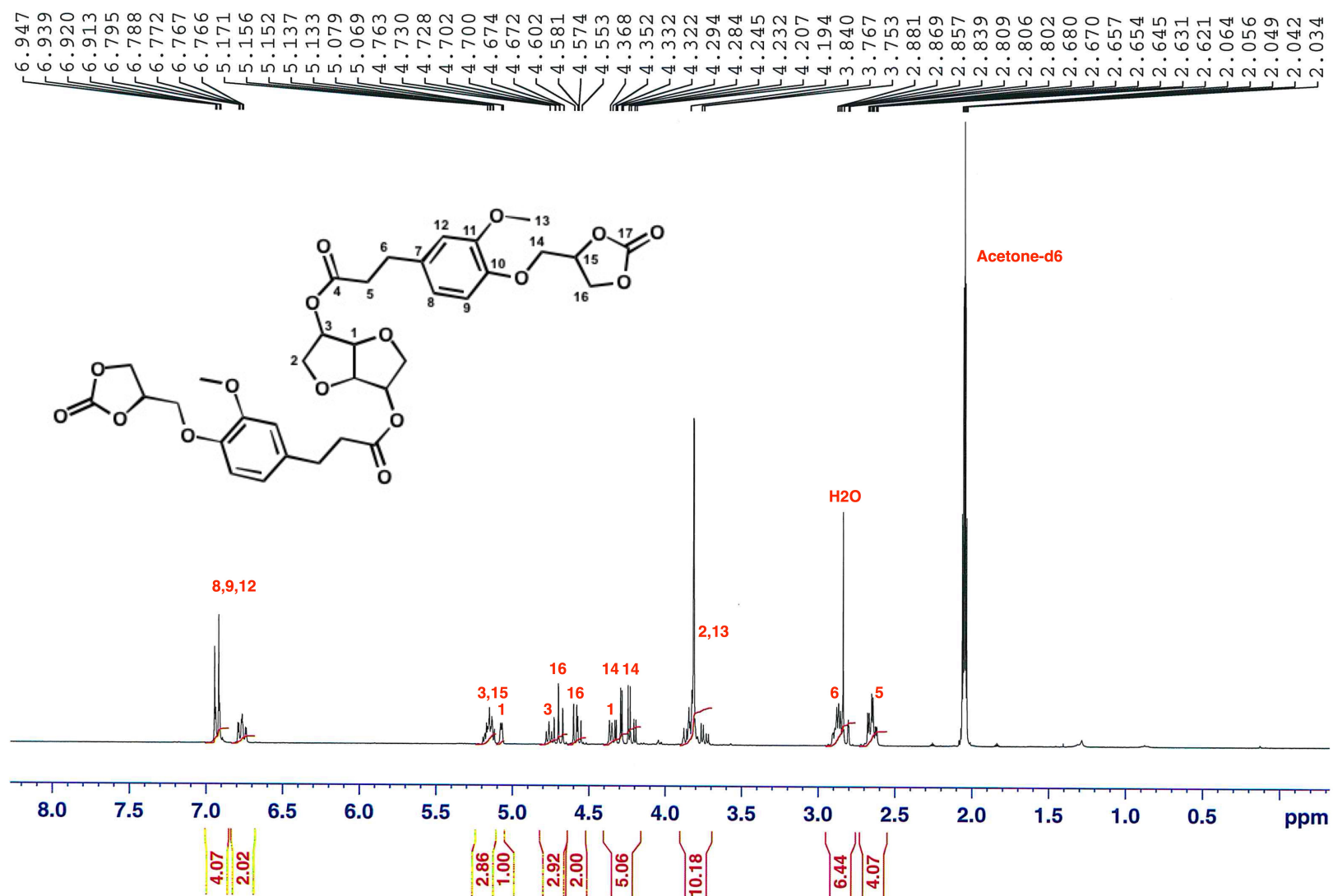


Figure S2: ^1H -NMR spectrum of GTF3Cy C₅-precursor

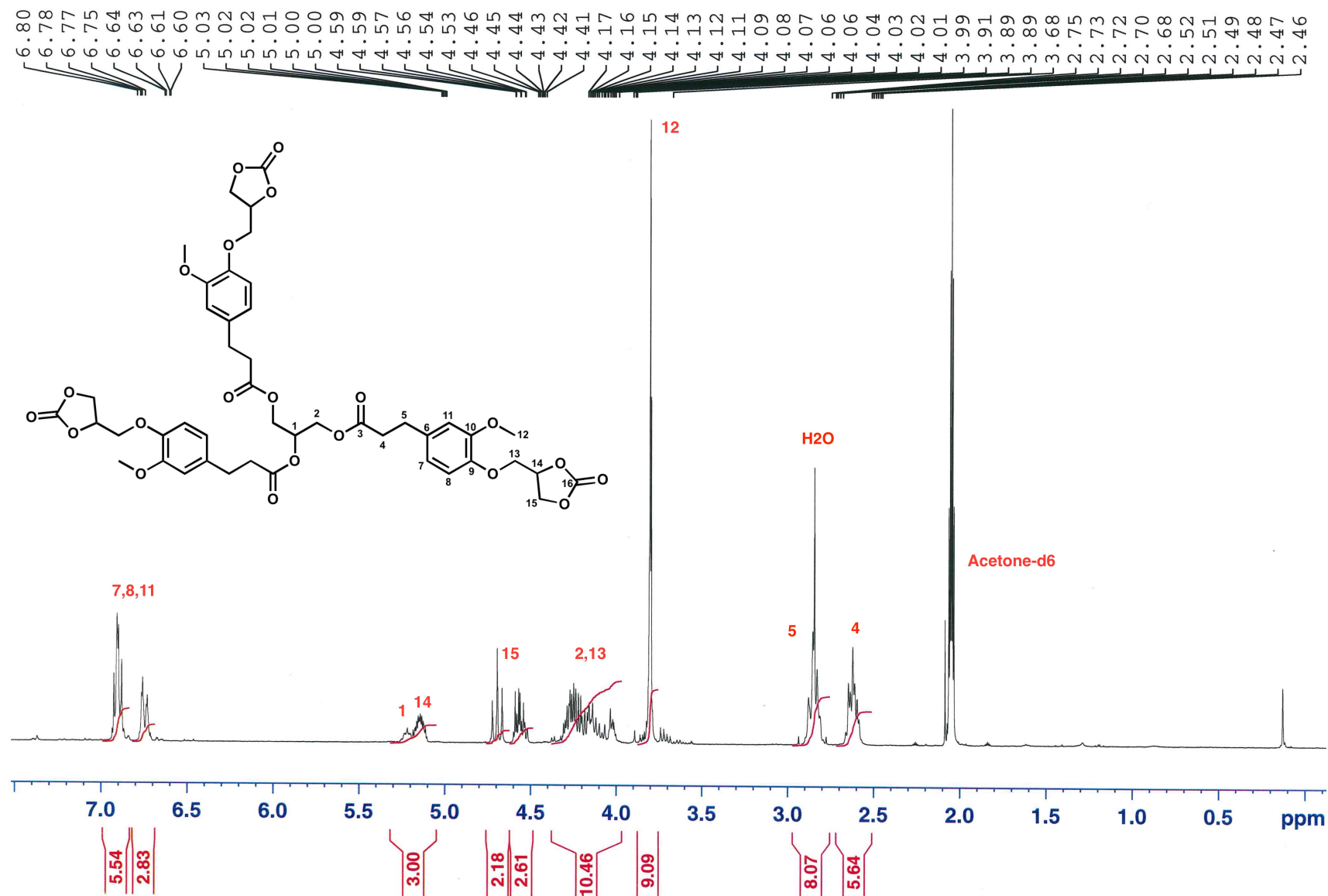


Figure S3: ^{13}C -NMR spectrum of BDF2Cy C₅-precursor

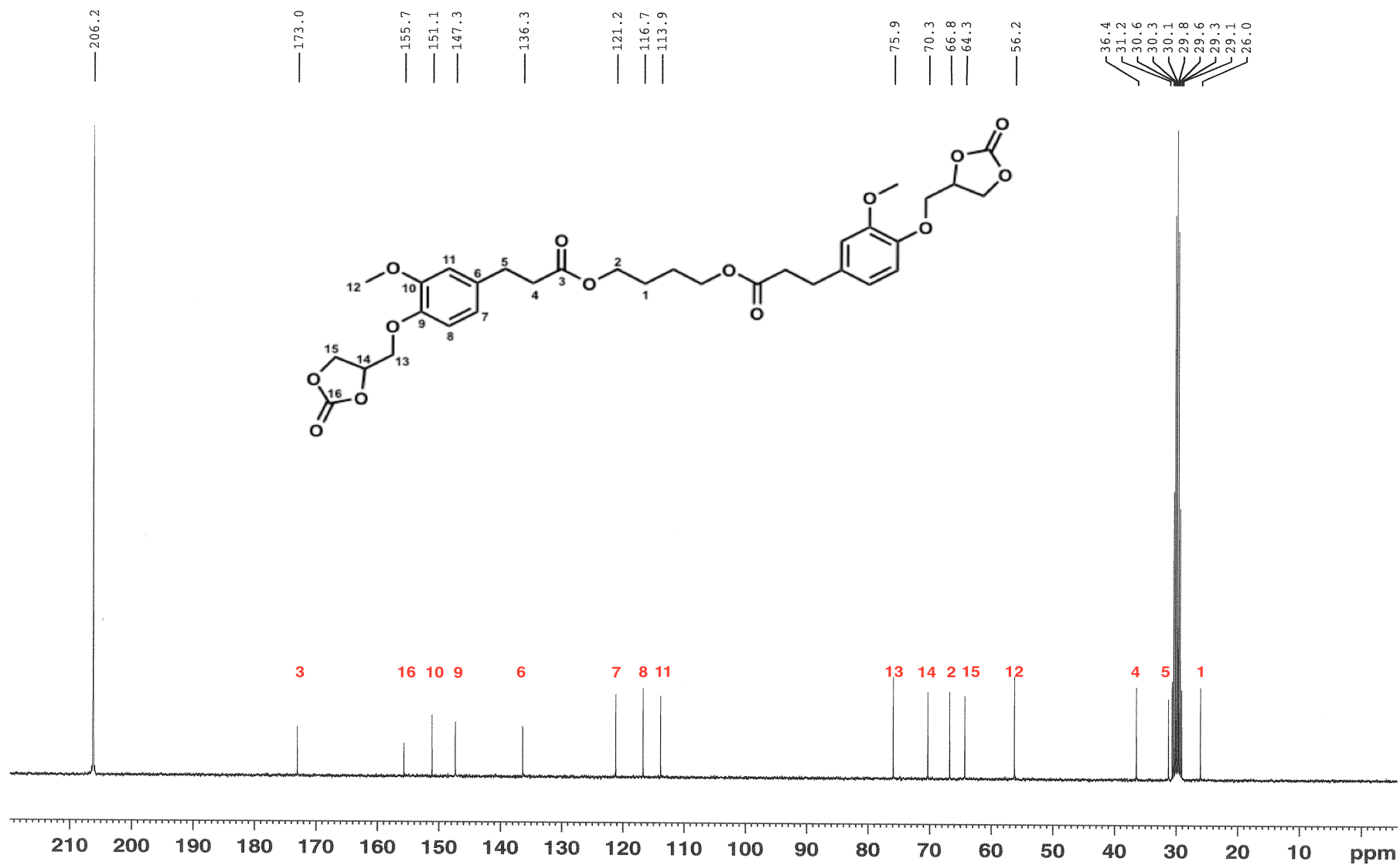


Figure S4: ^1H -NMR spectrum of DIFFA

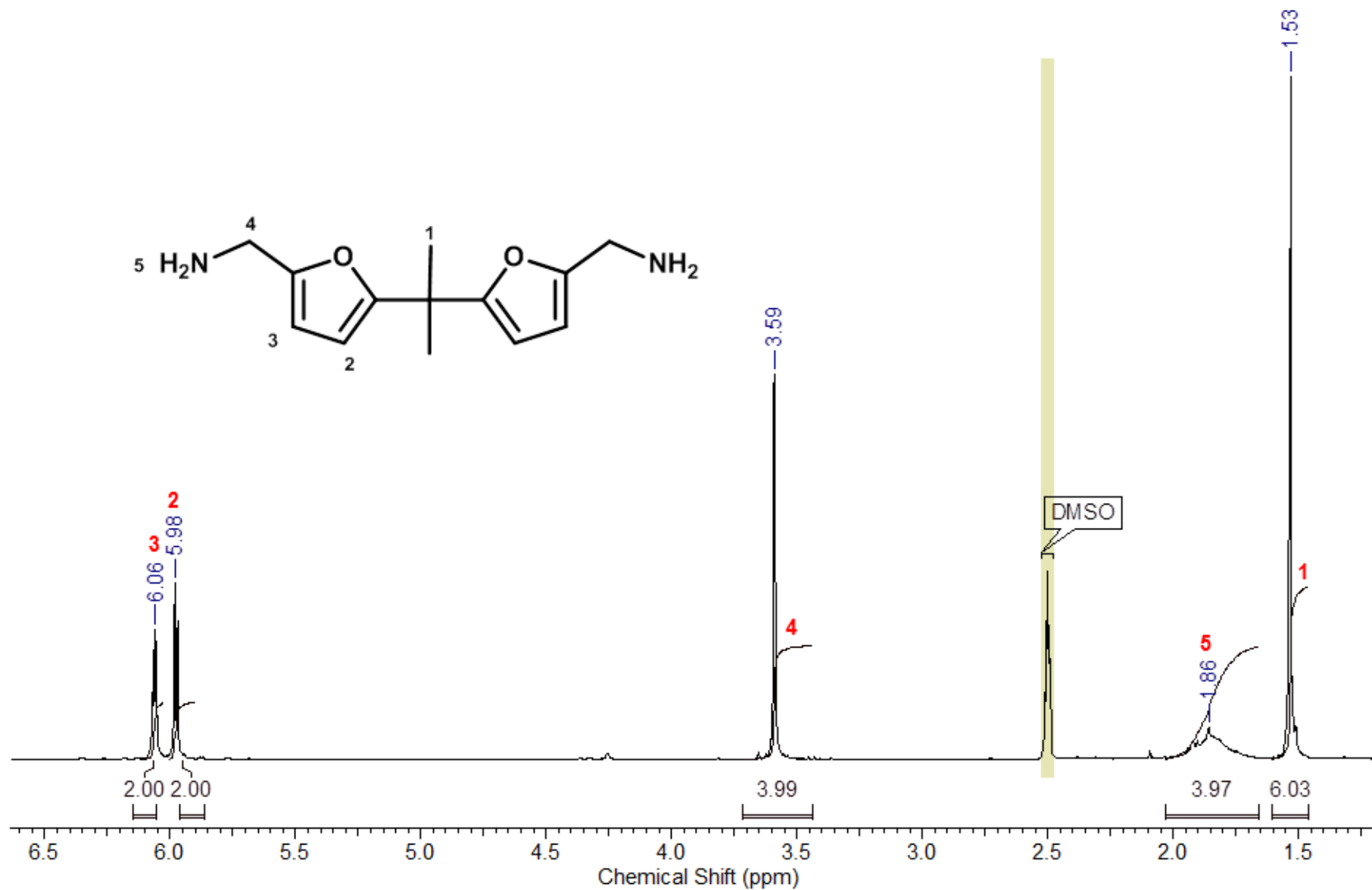


Table S5: Compositions of the formulated NIPUs

NIPU	C₅-precursor (w%)	Diamine (w%)
BDF2Cy-IPDA	BDF2Cy (79.2)	IPDA (20.8)
BDF2Cy-DA10	BDF2Cy (79.0)	DA10 (21.0)
BDF2Cy-DIFFA	BDF2Cy (73.4)	DIFFA (26.6)
BDF2Cy-EDR148	BDF2Cy (81.3)	EDR148 (18.7)
IDF2Cy-IPDA	IDF2Cy (81.7)	IPDA (18.3)
IDF2Cy-DA10	IDF2Cy (81.5)	DA10 (18.5)
IDF2Cy-DIFFA	IDF2Cy (76.5)	DIFFA (23.5)
IDF2Cy-EDR148	IDF2Cy (83.7)	EDR148 (16.3)
GTF3Cy-IPDA	GTF3Cy (82.0)	IPDA (18.0)
GTF3Cy-DA10	GTF3Cy (81.8)	DA10 (18.2)
GTF3Cy-DIFFA	GTF3Cy (76.7)	DIFFA (23.3)
GTF3Cy-EDR148	GTF3Cy (83.9)	EDR148 (16.1)

Figure S6: ^{13}C -NMR spectrum of BDF2CY-DIFFA

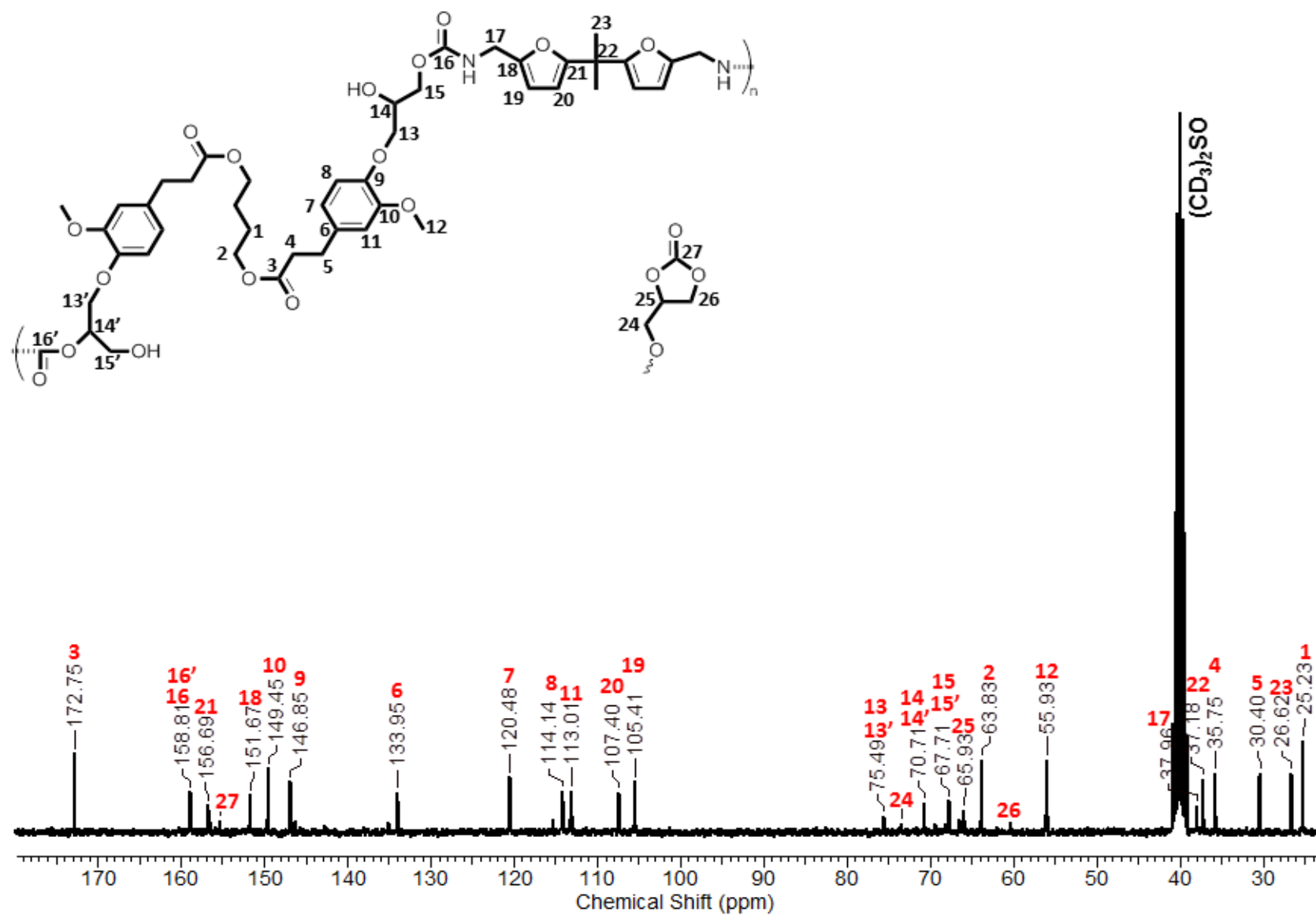


Figure S7: FTIR spectrum of BDF2CY-DIFFA

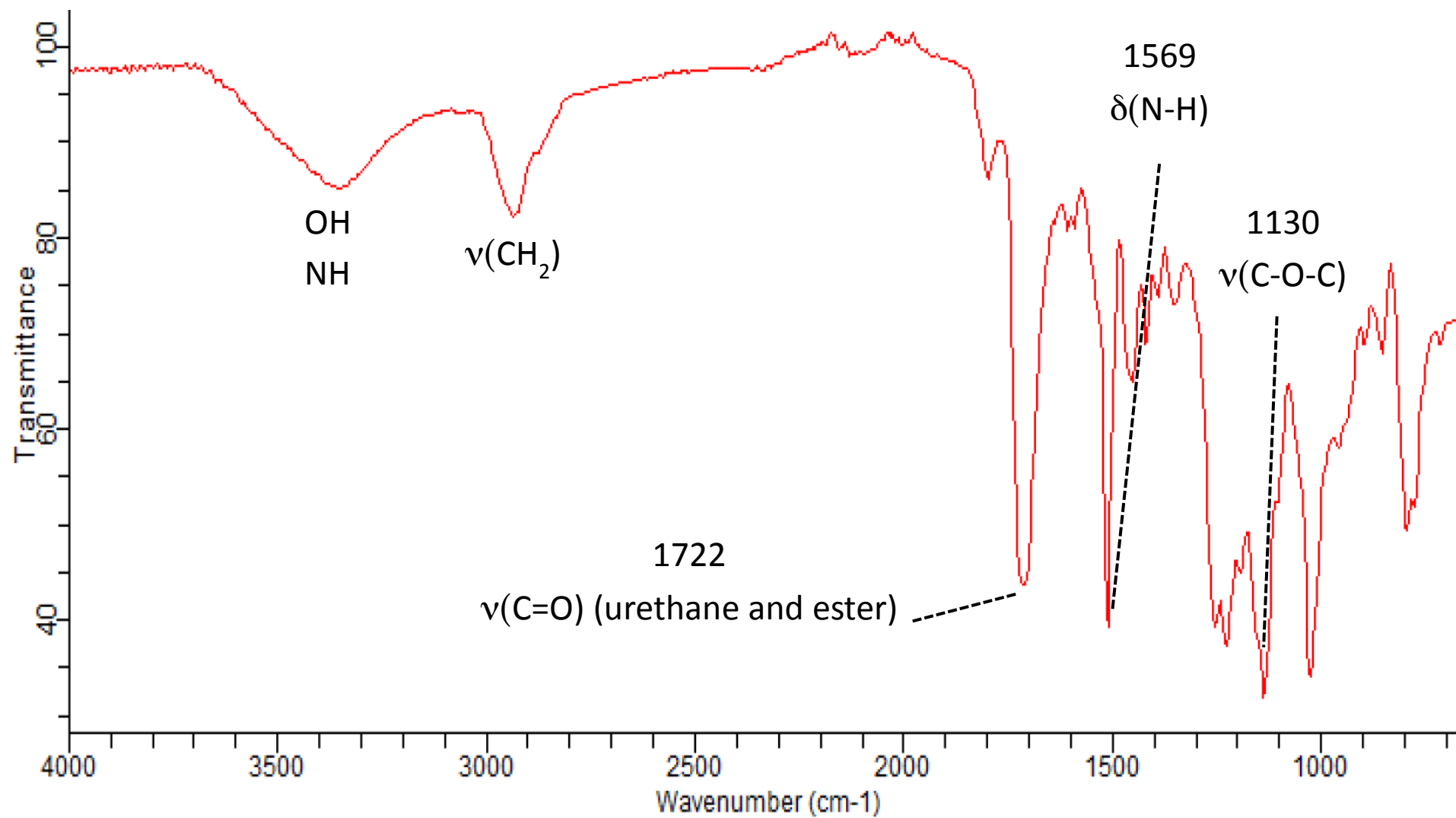


Figure S8: Thermograms of the IPDA-containing series (10 °C/min, under nitrogen)

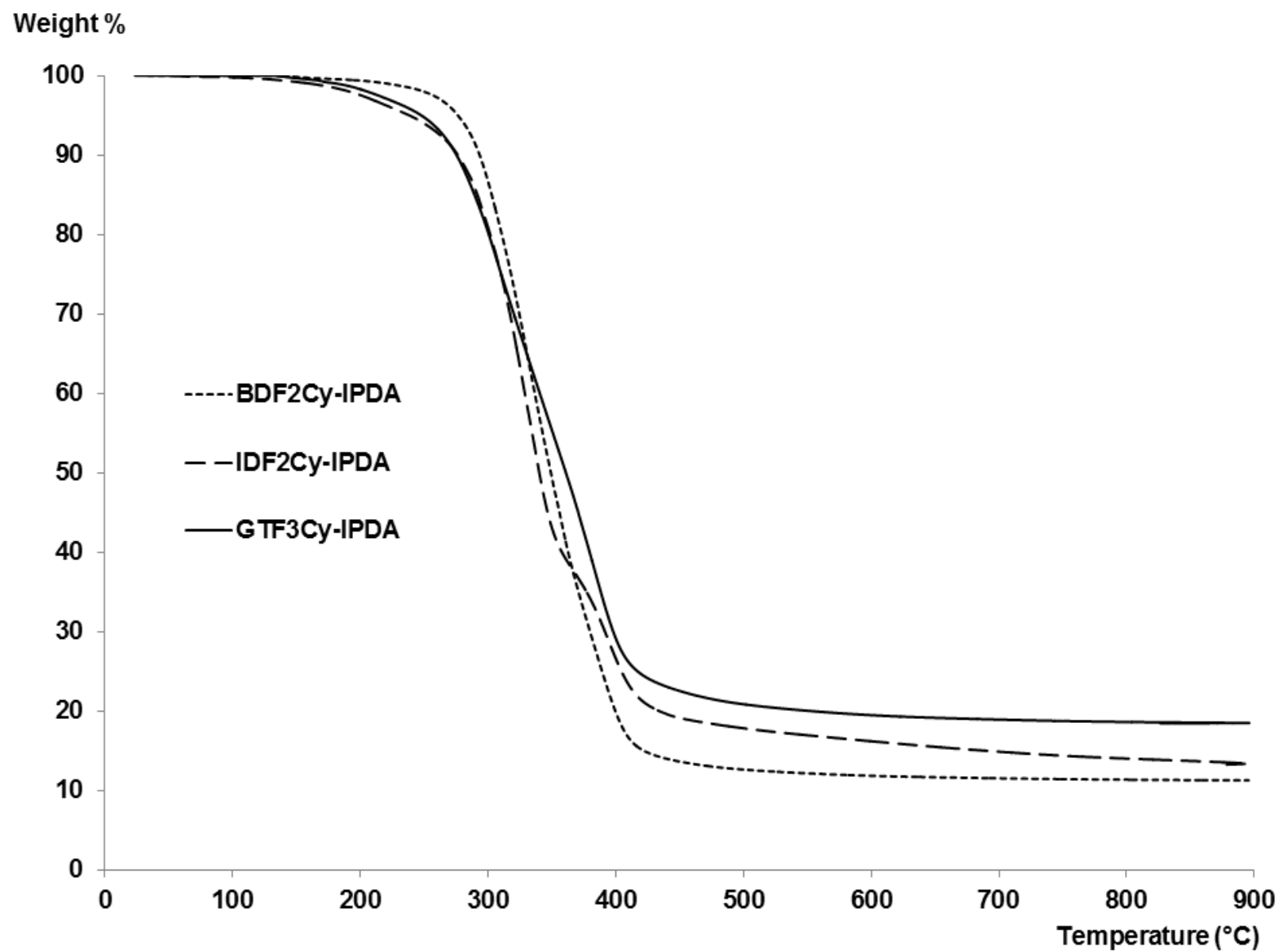


Figure S9: Thermograms of the DIFFA-containing series (10 °C/min, under nitrogen)

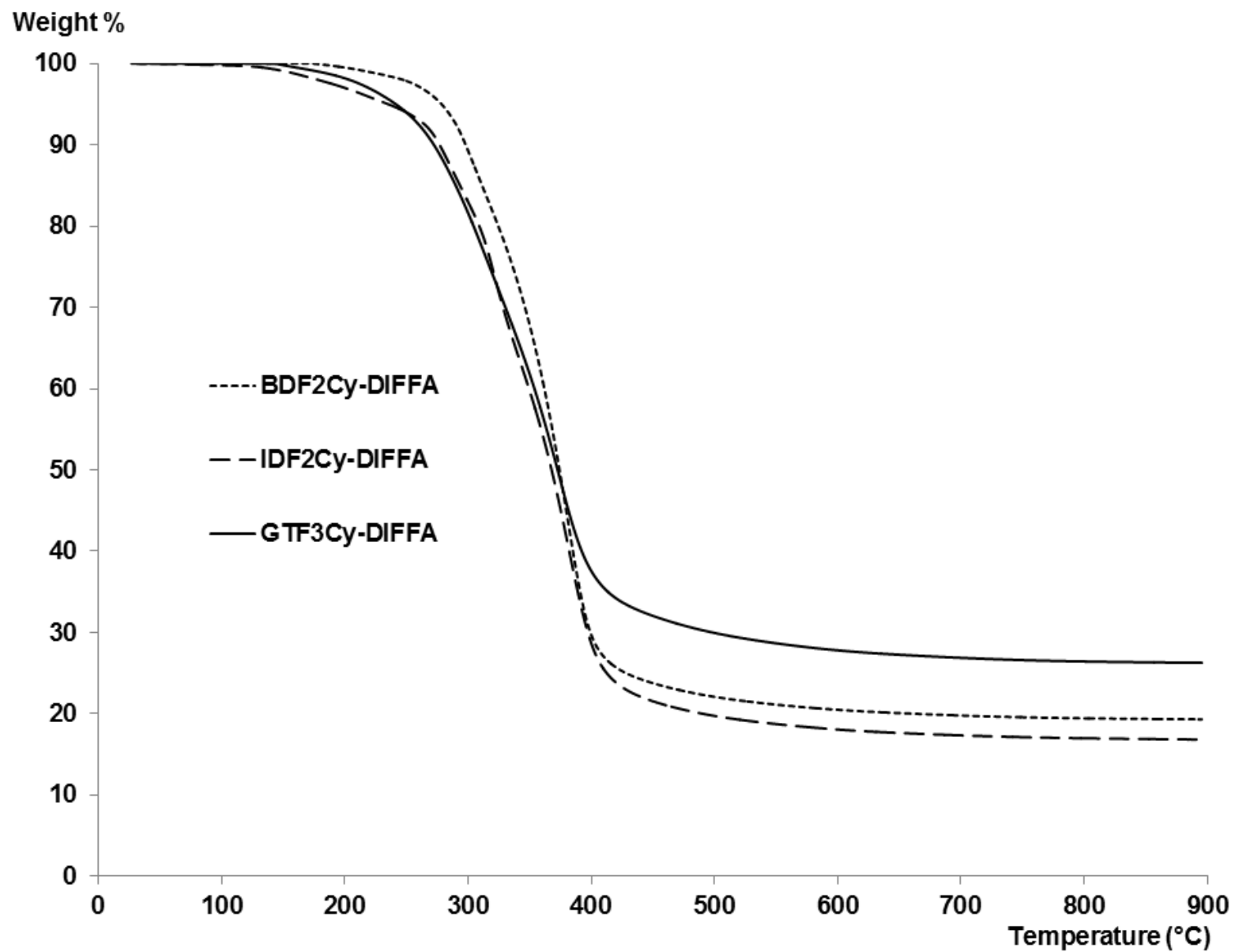


Figure S10: Thermograms of the EDR148-containing series (10 °C/min, under nitrogen)

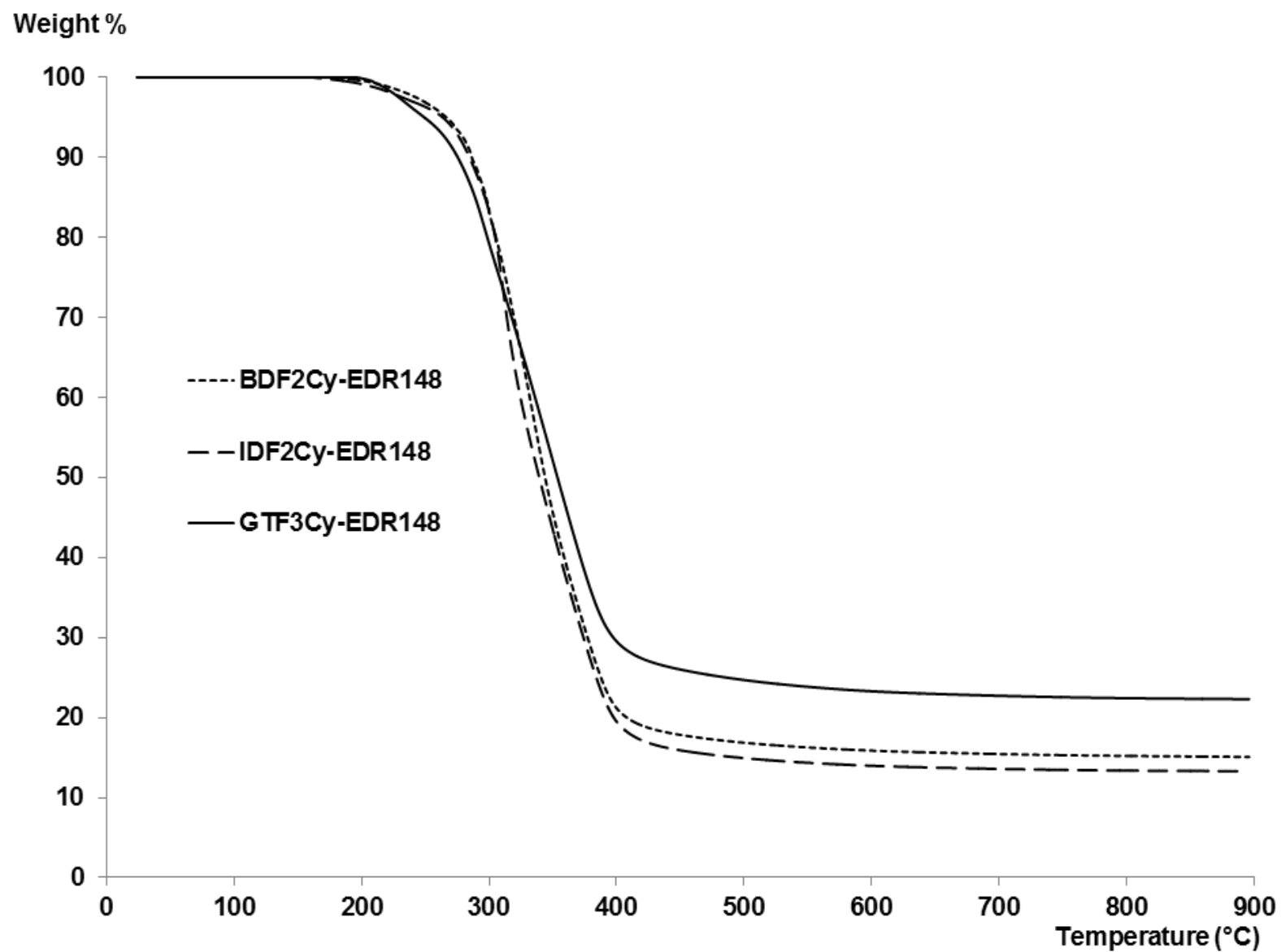


Figure S11: Thermograms of the BDF2Cy-containing series (10 °C/min, under nitrogen)

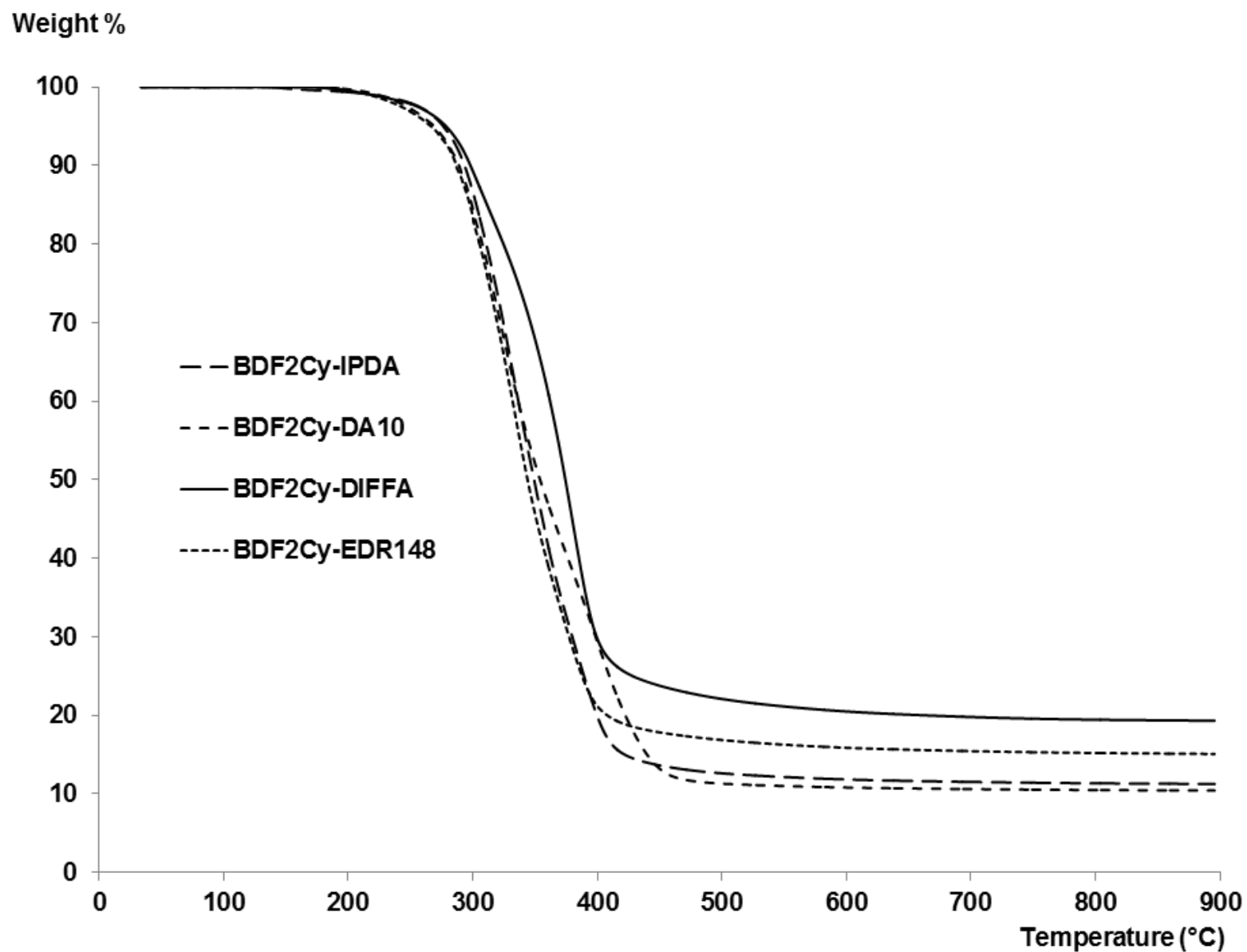


Figure S12: DSC curves of the three C₅ series (10 °C/min, under nitrogen)

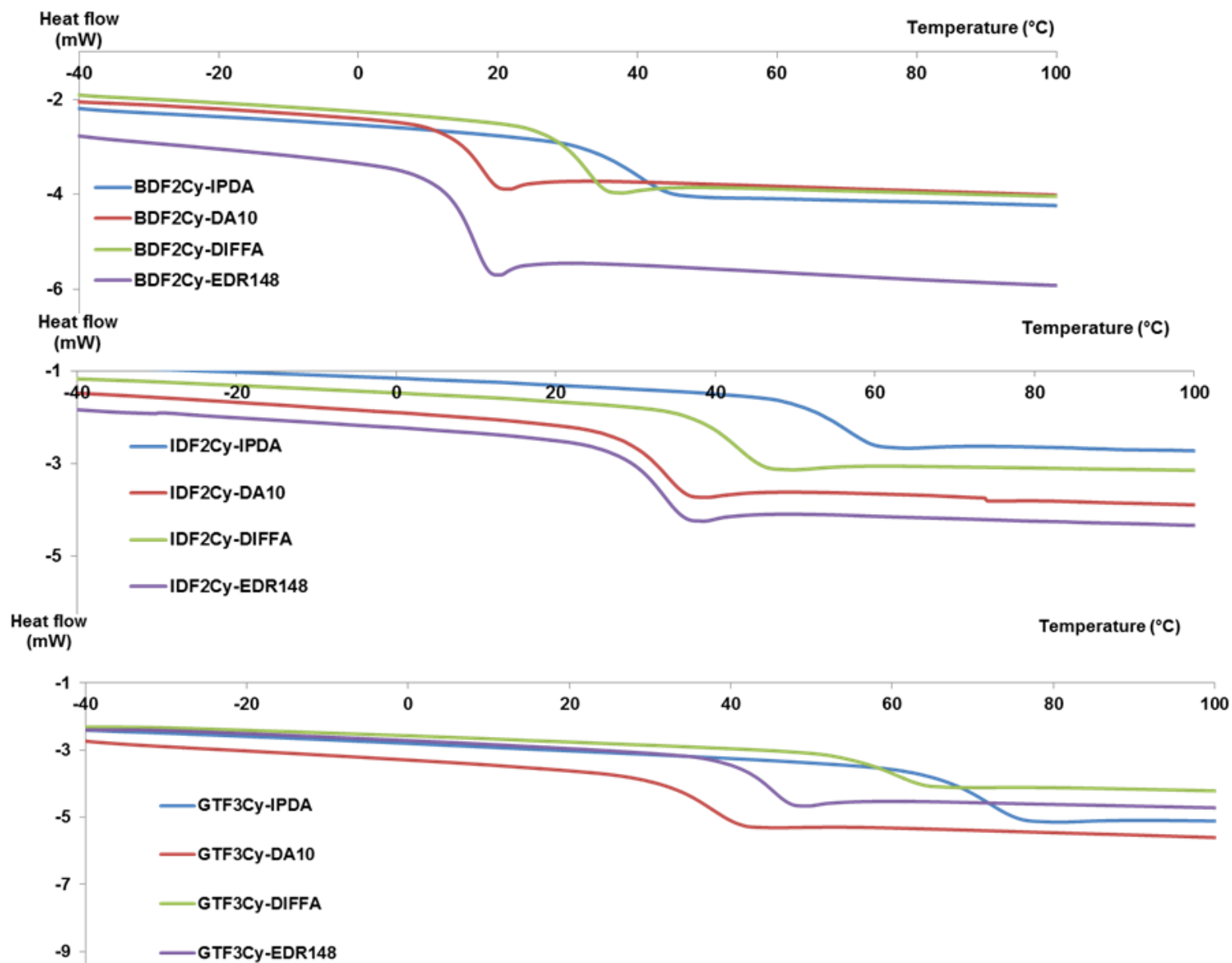


Figure S13: ^1H -NMR spectrum of BDF2Cy-IPDA

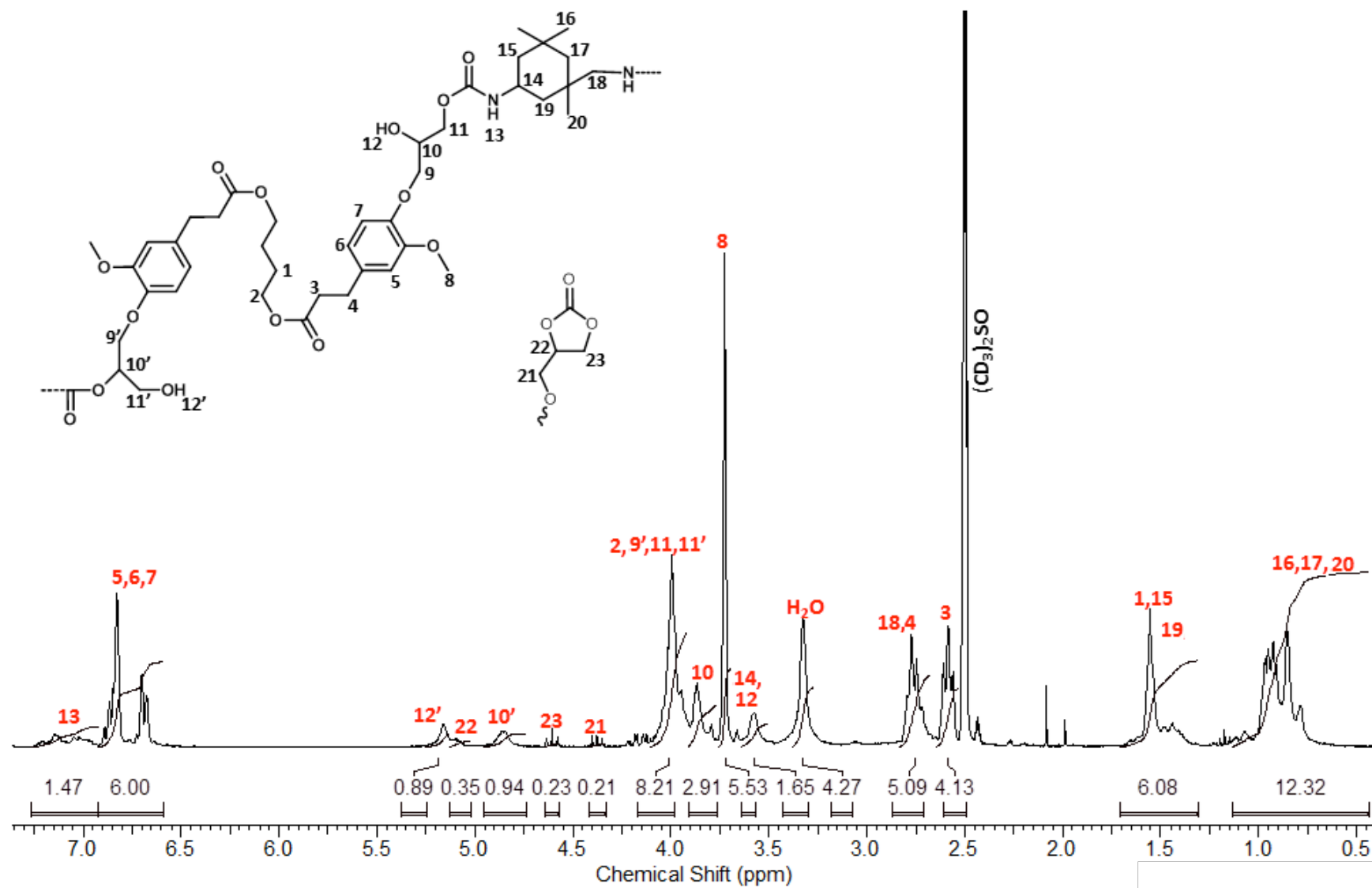


Figure S14: ^1H -NMR spectrum of BDF2Cy-EDR148

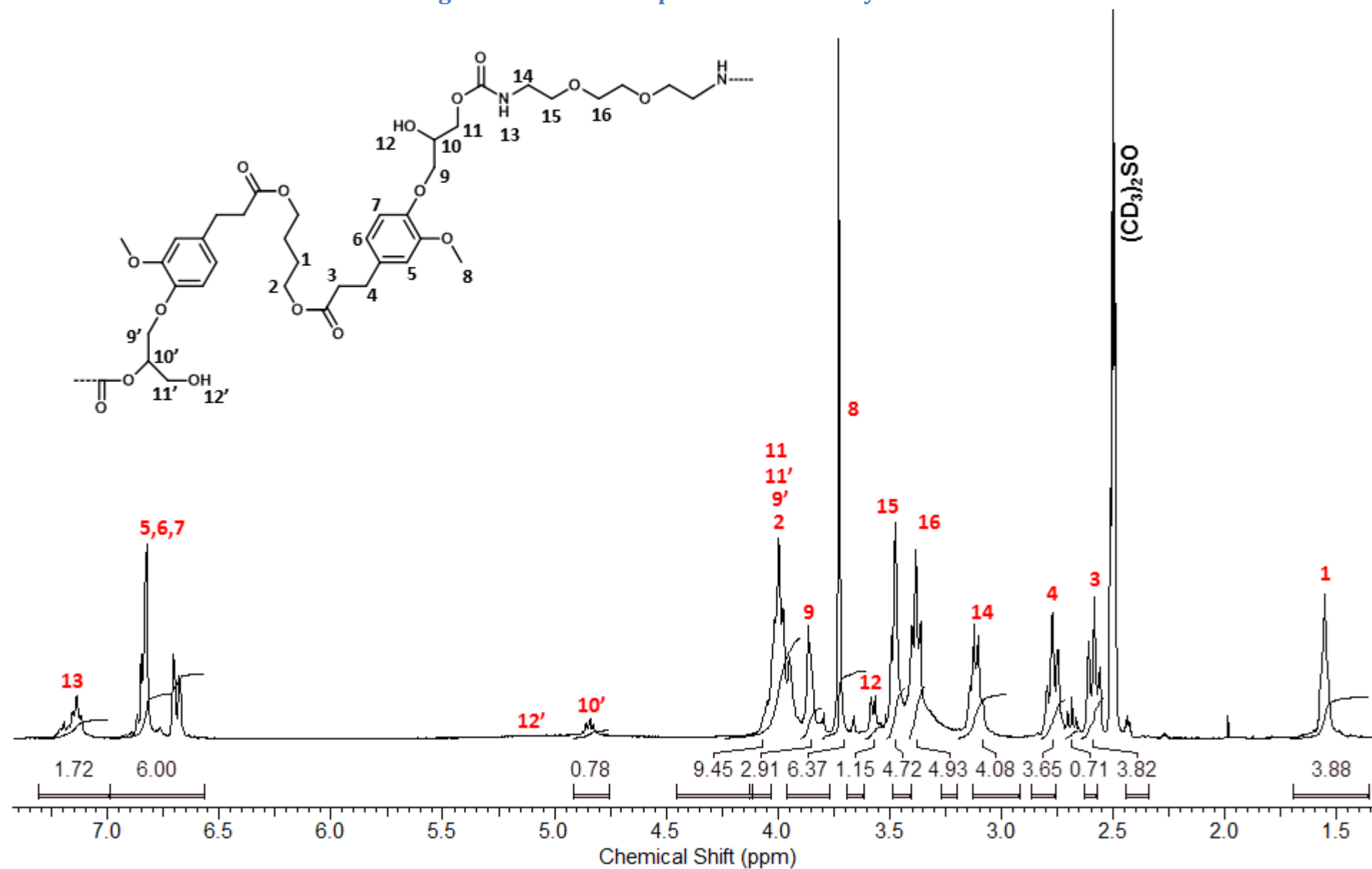


Figure S15: ^1H -NMR spectrum of BDF2Cy-DA10

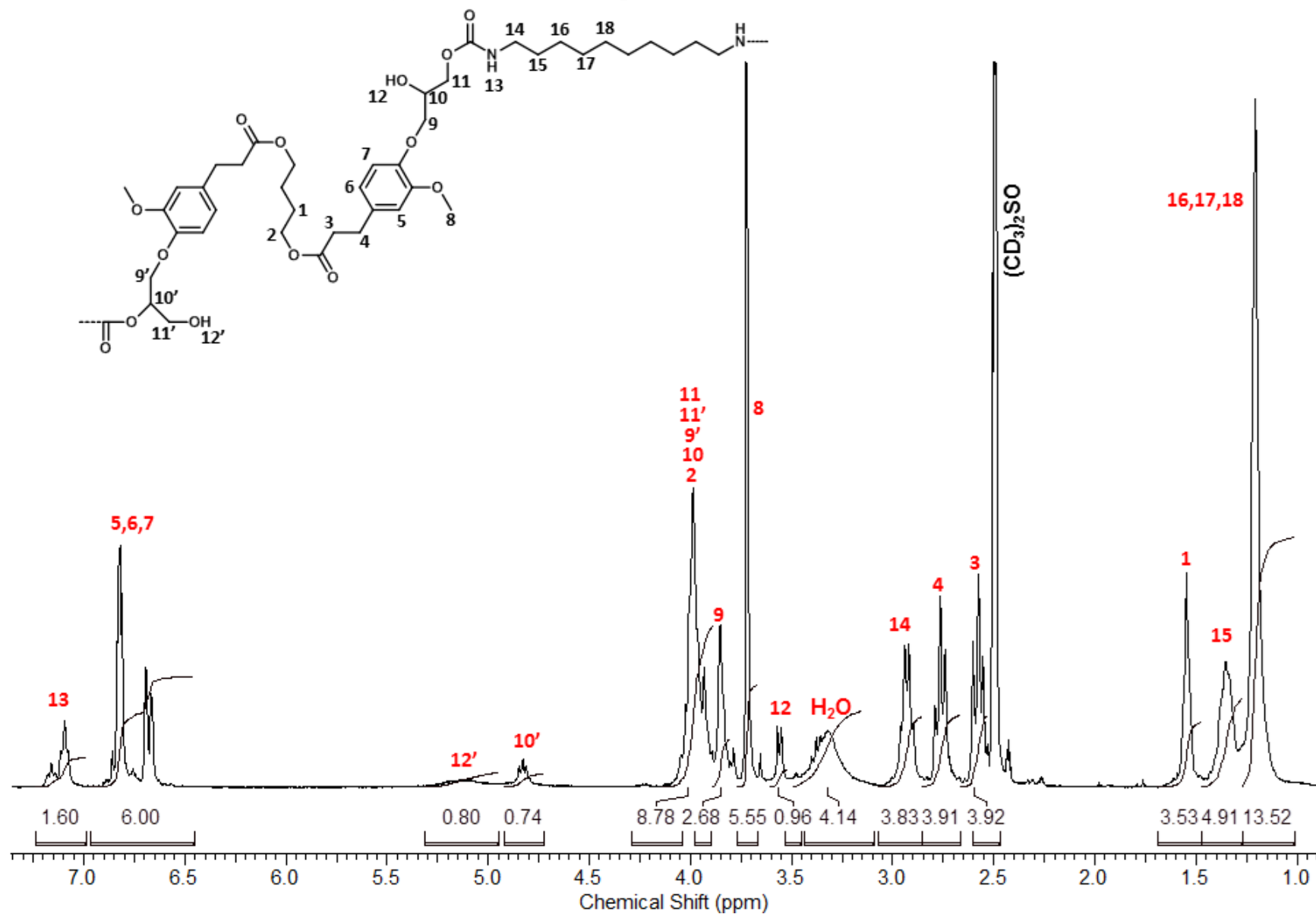


Figure S16: ^1H -NMR spectrum of BDF2Cy-DIFFA

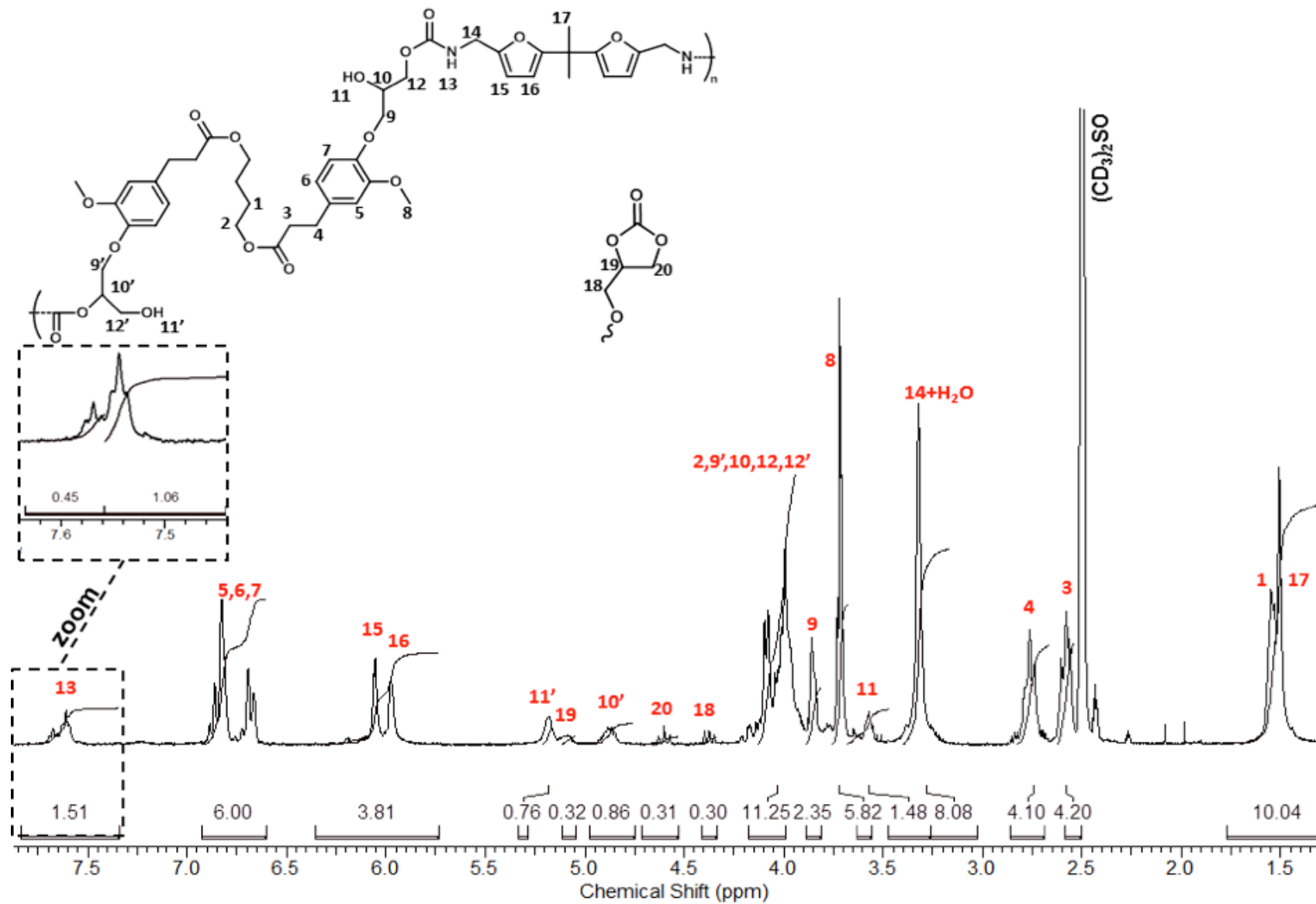


Figure S17: ^1H -NMR spectrum of IDF2Cy-IPDA

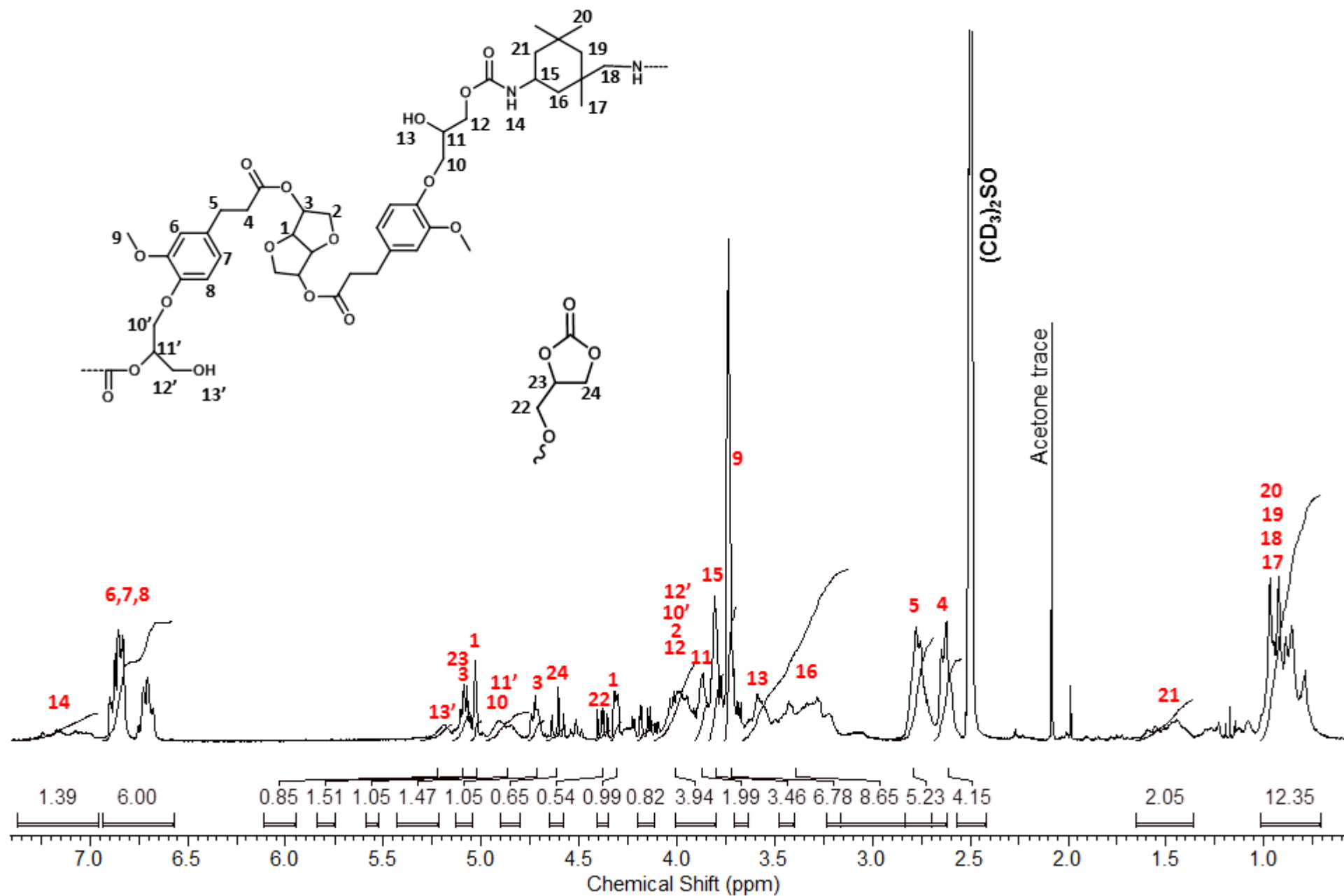


Figure S18: ^1H -NMR spectrum of IDF2Cy-DA10

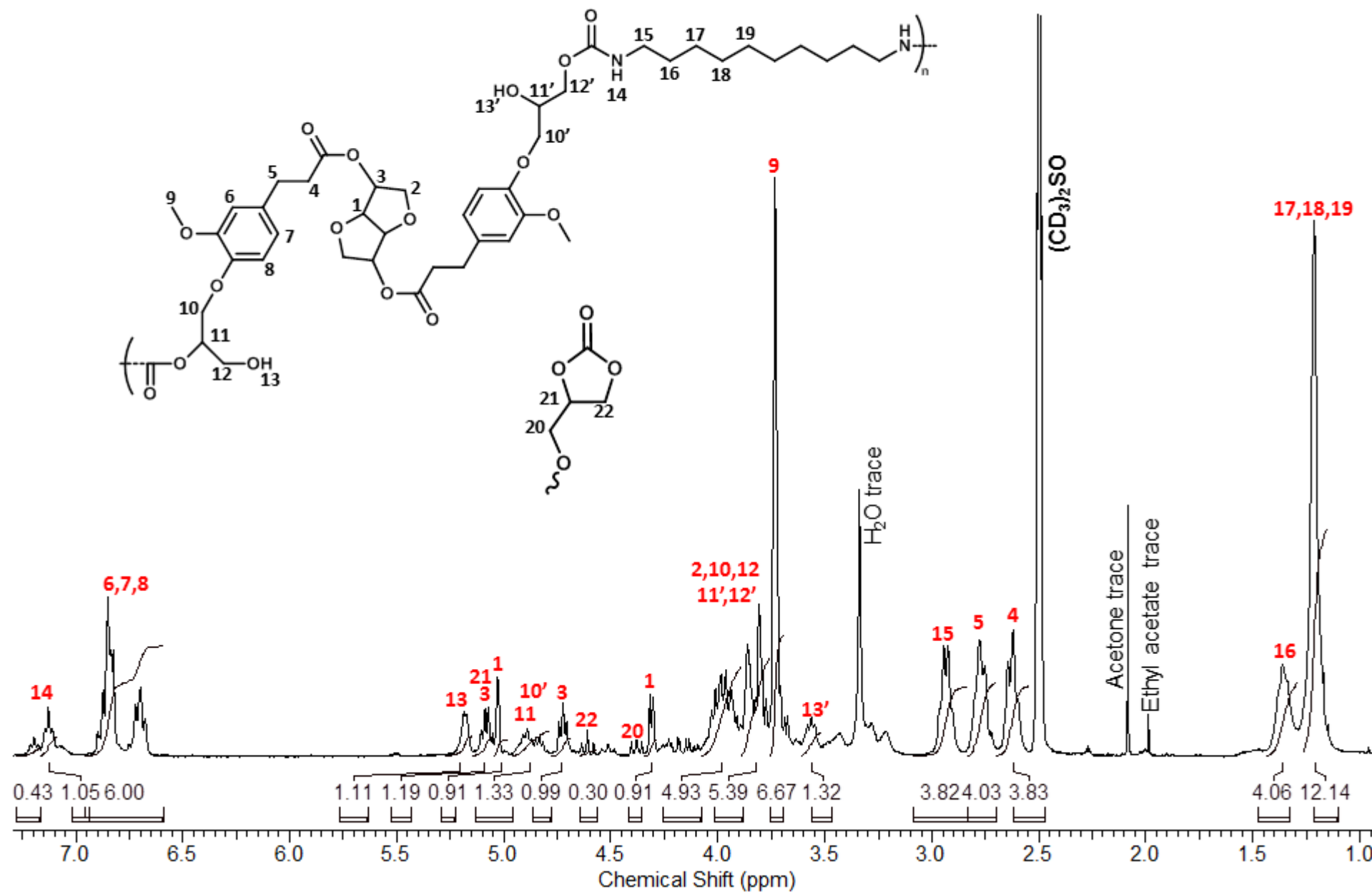


Figure S19: ^1H -NMR spectrum of IDF2Cy-EDR148

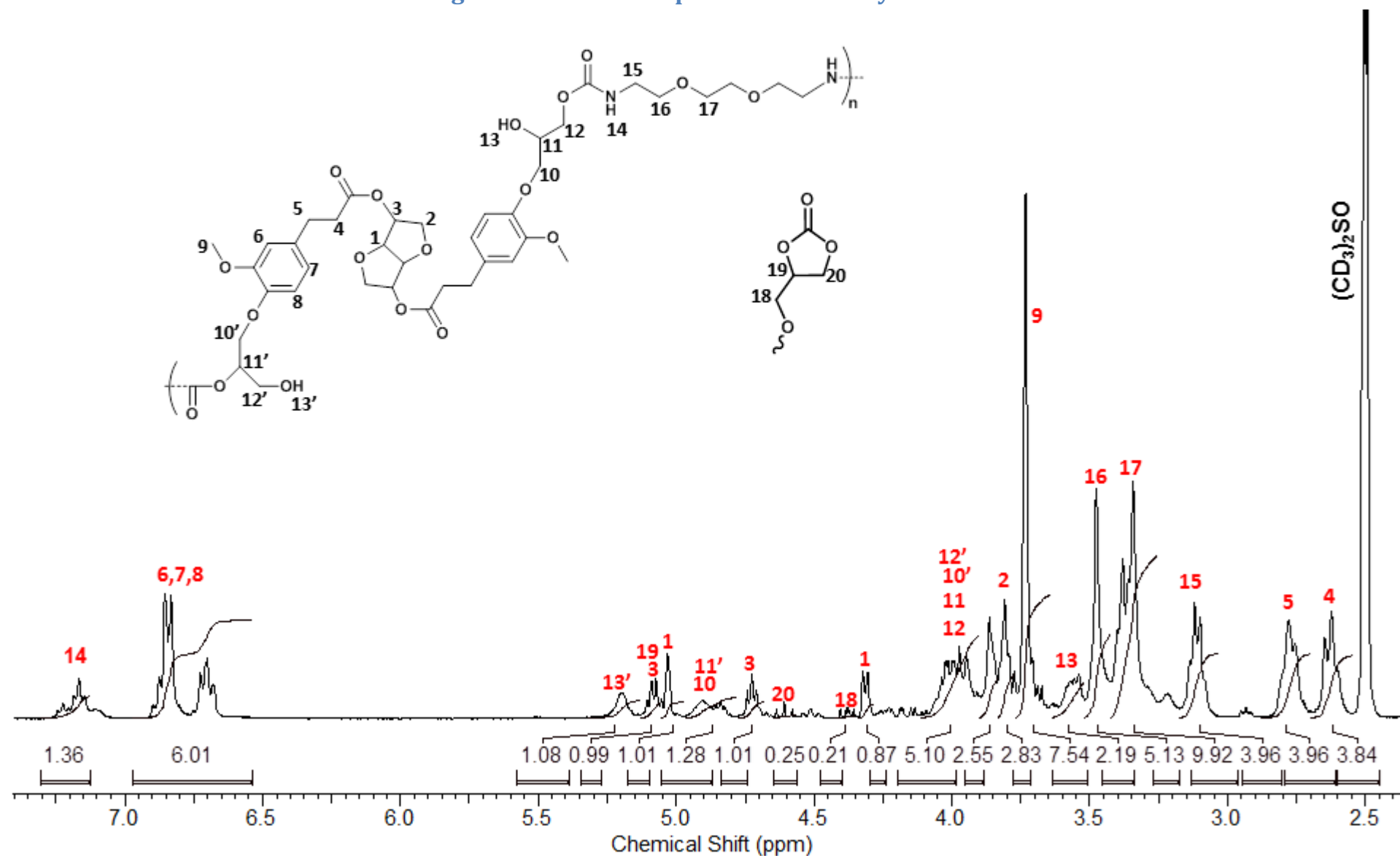


Figure S20: ^1H -NMR spectrum of IDF2Cy-DIFFA

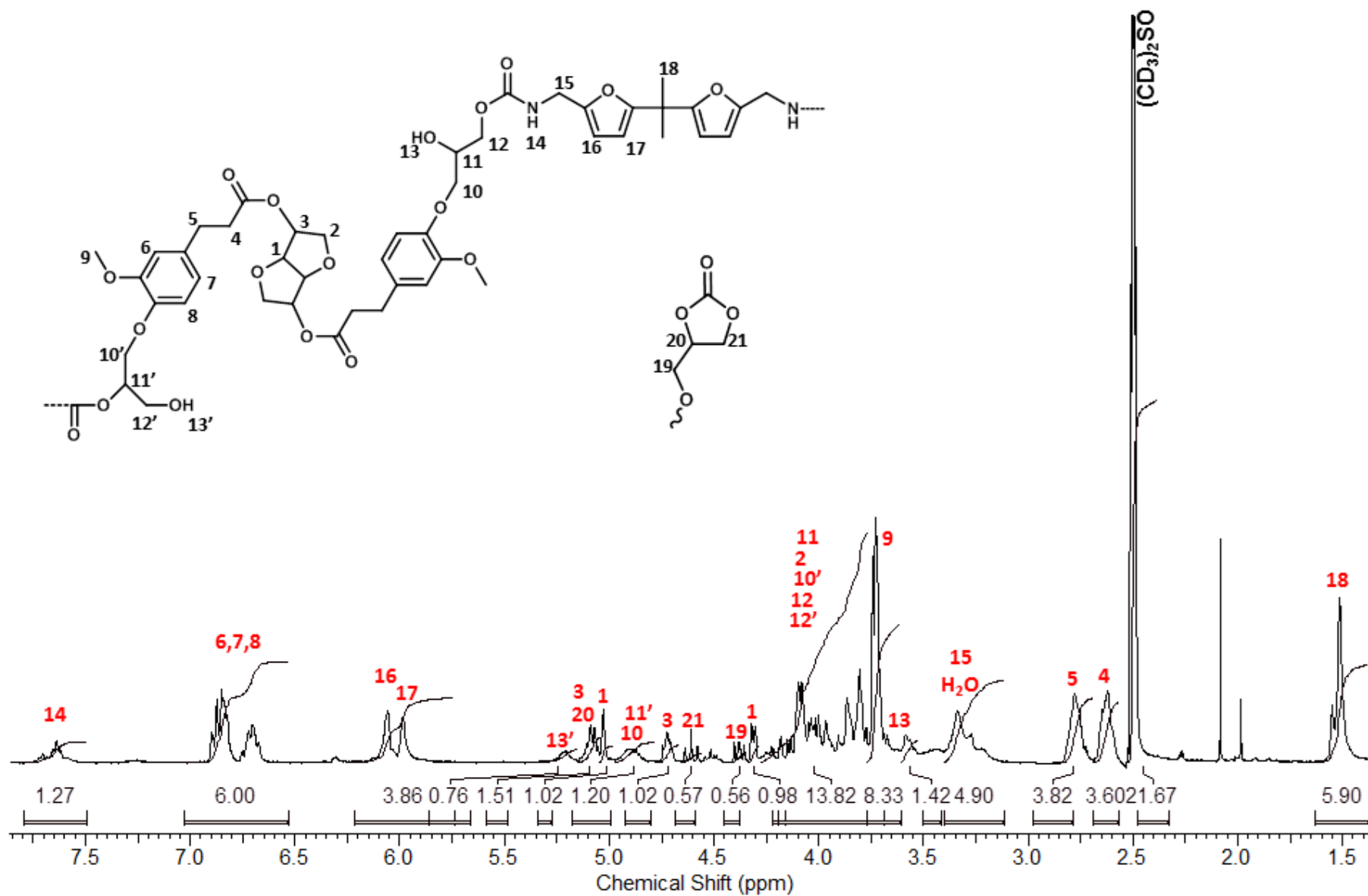


Figure S21: GPC chromatogram of BDF2Cy-IPDA

Sample Details

Sample Name: BDF2 CY-IPDA

Acquired: 16/06/2016 15:08:52

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0001.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0001.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

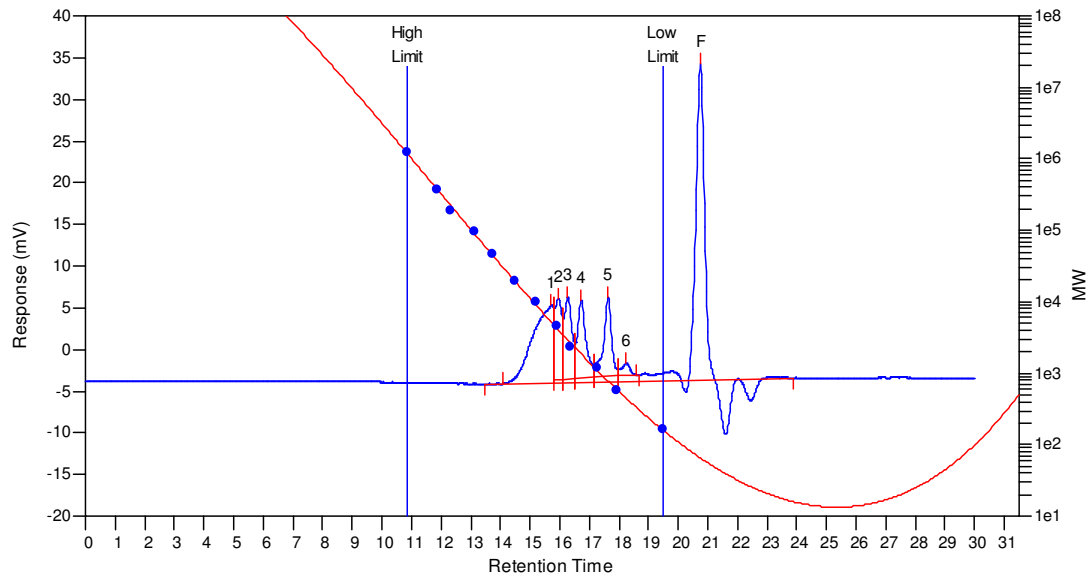
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5192	7651	8138	9696	11342	7872	1.06365
2	4073	4680	3451	4055	4079	3226	0.737393
3	2943	3133	2597	2893	2919	2486	0.828918
4	1842	1838	1711	1821	1851	1674	0.930903
5	776	818	807	843	865	798	0.986553
6	450	470	439	462	467	431	0.934043
7	0	0	0	0	0	0	0

Figure S22: GPC chromatogram of BDF2Cy-DA10

Sample Details

Sample Name: BDF2 CY-DA10

Acquired: 16/06/2016 16:16:06

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0003.cgrm

Injection Volume: 20.0 ul

By Analyst: SEC THF - UV

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0003.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

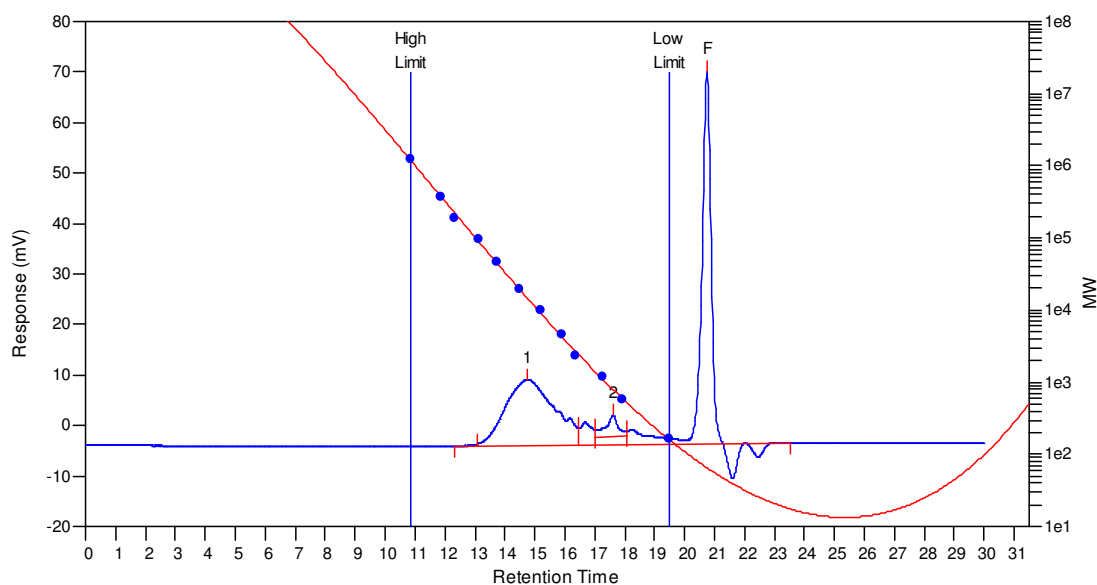
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14851	9477	16773	27427	38895	15423	1.76986
2	788	857	849	918	964	833	0.990665
3	0	0	0	0	0	0	0

Figure S23: GPC chromatogram of BDF2Cy-DIFFA

Sample Details

Sample Name: BDF2 CY-DIFFA

Acquired: 16/06/2016 16:49:44

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0004.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0004.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

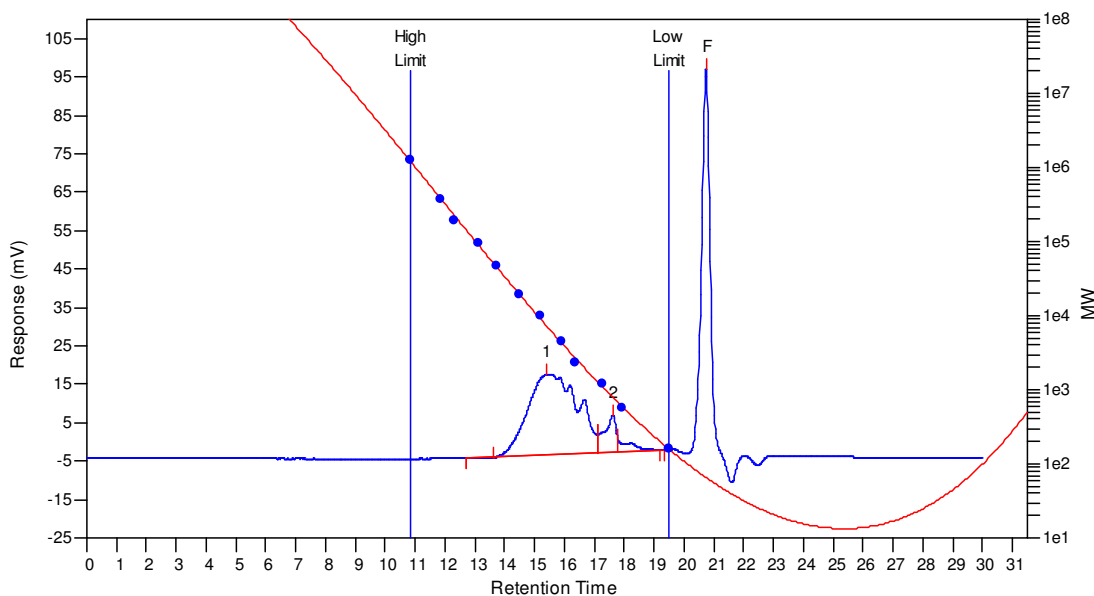
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7250	4388	7360	11868	16923	6798	1.6773
2	788	925	864	932	959	843	0.934054
3	0	0	0	0	0	0	0

Figure S24: GPC chromatogram of BDF2Cy-EDR148

Sample Details

Sample Name: BDF2 CY- EDR148

Acquired: 16/06/2016 15:42:30

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0002.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0002.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

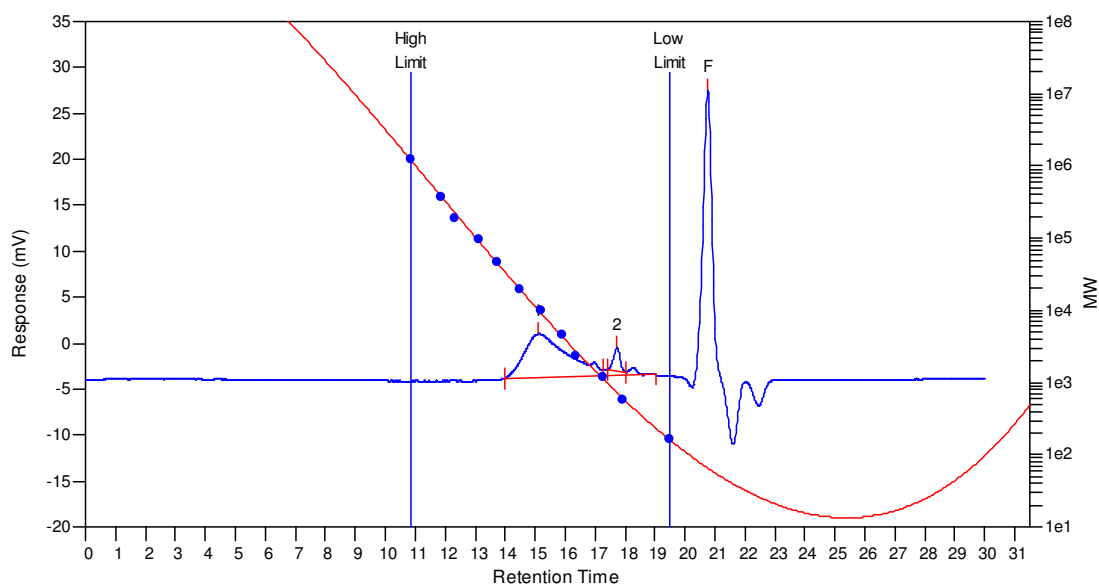
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9940	4924	8377	12131	15333	7829	1.70126
2	717	725	730	736	742	729	1.0069
3	0	0	0	0	0	0	0

Figure S25: GPC chromatogram of IDF2Cy-IPDA

Sample Details

Sample Name: IDF2 CY-IPDA

Acquired: 16/06/2016 17:23:20

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0005.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0005.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

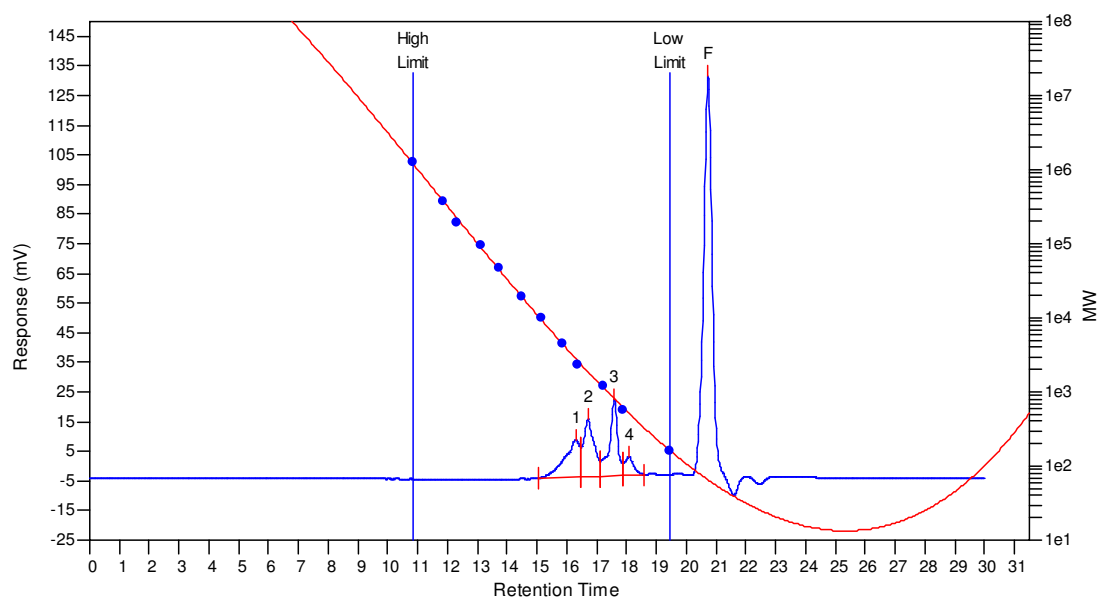
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2855	3526	3602	4141	4678	3500	1.02155
2	1879	1832	1699	1821	1856	1659	0.927402
3	802	858	830	875	899	817	0.967366
4	508	521	476	507	513	464	0.913628
5	0	0	0	0	0	0	0

Figure S26: GPC chromatogram of IDF2Cy-DA10

Sample Details

Sample Name: IDF2 CY-DA10

Acquired: 16/06/2016 18:30:32

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0007.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0007.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

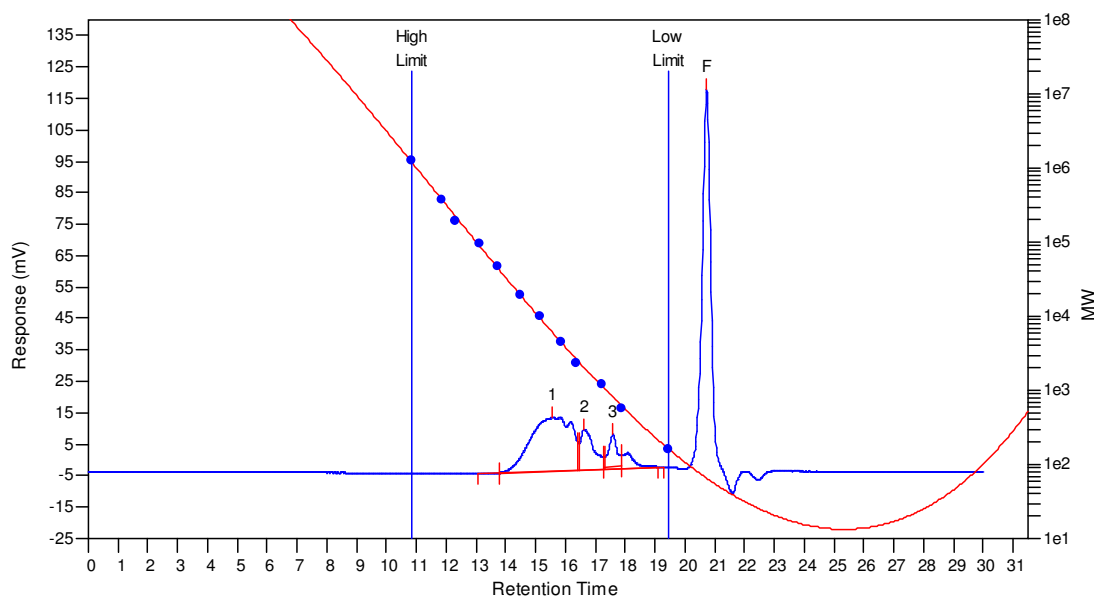
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5999	5784	7894	11225	15059	7464	1.3648
2	2008	1759	1675	1822	1883	1632	0.952246
3	802	844	776	828	840	758	0.919431
4	0	0	0	0	0	0	0

Figure S27: GPC chromatogram of IDF2Cy-DIFFA

Sample Details

Sample Name: IDF2 CY-DIFFA

Acquired: 16/06/2016 19:04:10

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0008.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0008.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

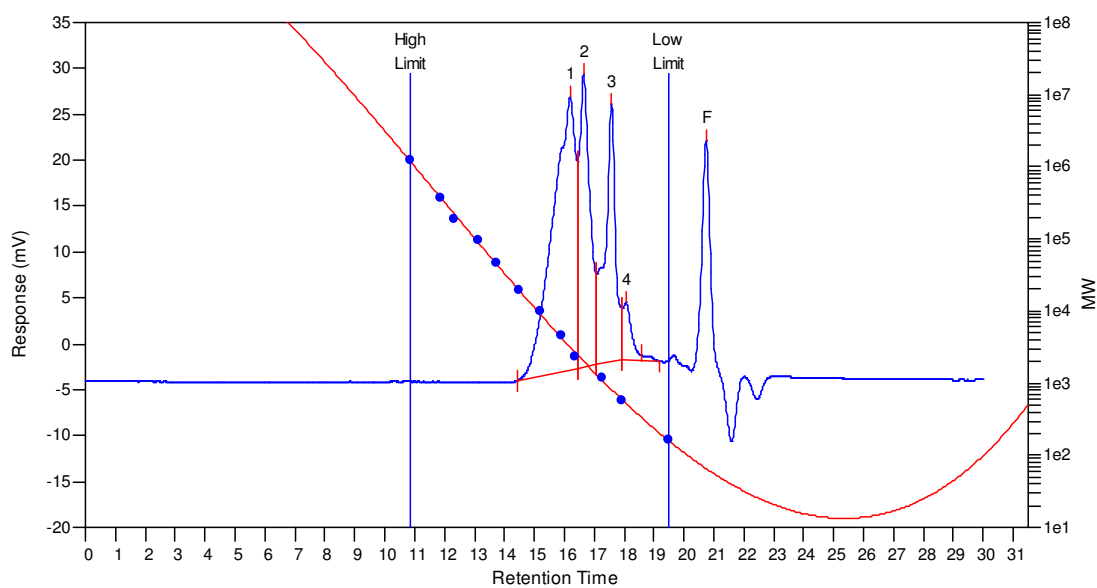
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3204	4238	4729	5849	7203	4563	1.11586
2	2001	1974	1800	1952	1994	1749	0.911854
3	813	890	861	921	953	844	0.967416
4	530	522	456	498	505	441	0.873563
5	0	0	0	0	0	0	0

Figure S28: GPC chromatogram of IDF2Cy-EDR148

Sample Details

Sample Name: IDF2 CY-EDR148

Acquired: 16/06/2016 17:56:56

By Analyst: SEC THF - UV

Batch Name: RAPH

Filename: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0006.cgrm

Injection Volume: 20.0 ul

K of Sample: 14.1000

Alpha of Sample: 0.7000

Analysis Using Method: METHODE PS

Comments:

Results File: C:\Cirrus Workbooks\PASSEUR S1 2016 THF RI\raph-0006.rst

Calibration Used: 12/01/2016 17:25:22

Calibration Type: Narrow Standard

Curve Fit Used: 3

Calibration Curve: $y = 10.063018 - 0.134224x^1 - 0.031098x^2 + 0.000887x^3$

High Limit MW RT: 10.86 mins

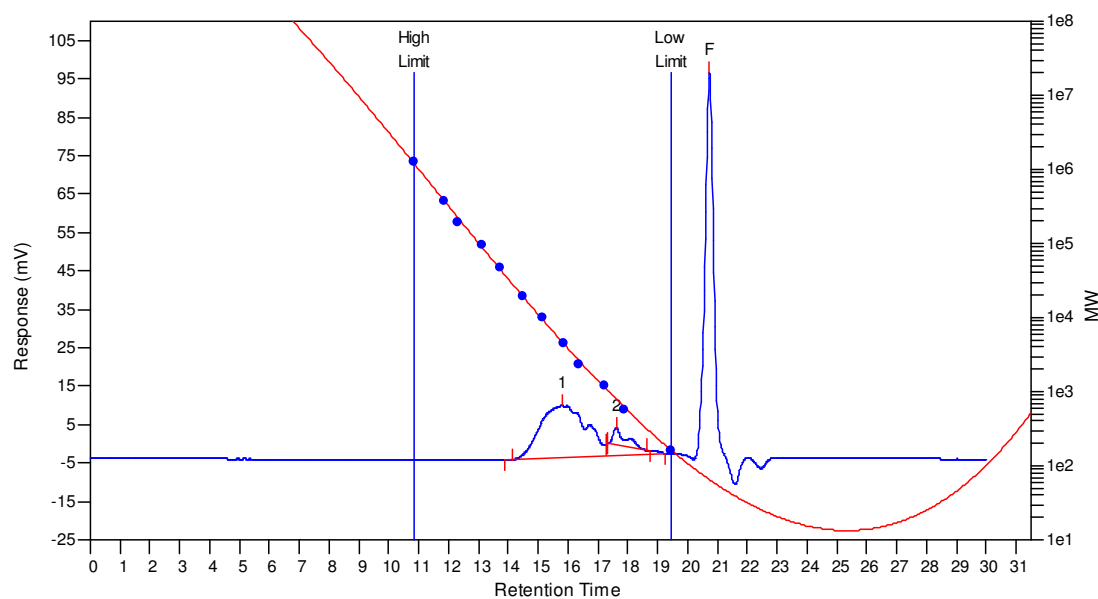
Low Limit MW RT: 19.48 mins

High Limit MW: 1186822

Low Limit MW: 159

K: 14.1000

Alpha: 0.7000



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4863	3604	5527	8140	10837	5180	1.53357
2	790	627	663	697	727	658	1.05742
3	0	0	0	0	0	0	0