SUPPORTING INFORMATION TO THE MANUSRIPT

Star-shaped D–π–A oligothiophenes with *tris*(2-methoxyphenyl)amine core and alkyldicyanovinyl groups: synthesis, physical and photovoltaic properties

Yuriy N. Luponosov,[1,*,†] Jie Min,[2,*,†] Alexander N. Solodukhin,[1] Artem V. Bakirov,[1,3] Petr V. Dmitryakov,[3] Maxim A. Shcherbina,[1,4] Svetlana M. Peregudova,[1,5] Georgiy V. Cherkaev,[1] Sergei N. Chvalun,[1,3] Christoph J. Brabec,[2,6] Sergei A. Ponomarenko[1,7]

[1]Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya st. 70, Moscow 117393, Russia

[2]Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany

[3]National Research Centre "Kurchatov Institute", 1, Akademika Kurchatova pl., Moscow, 123182, Russia

[4]Moscow Institute of Physics and Technology, 4 Institutsky line, Dolgoprudny, Moscow region, 141700 Russian Federation

[5]Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, Moscow, 119991, Russia

[6]Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstraße 2a, 91058 Erlangen, Germany

[7]Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia

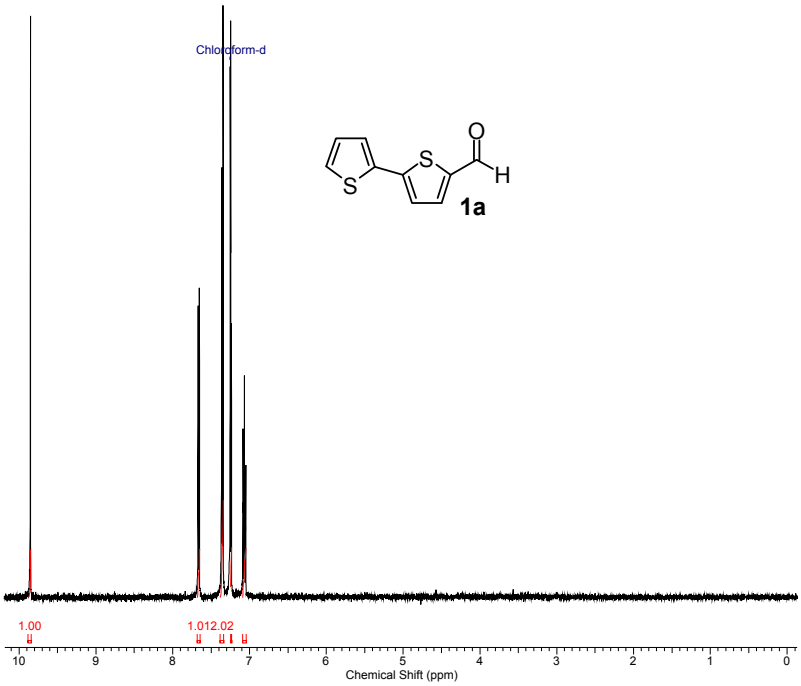
[*]Corresponding authors: E-mail: luponosov@ispm.ru (Y. N. Luponosov)

Min.Jie@fau.de (J. Min)

† These authors contributed equally to this work.

CONTENTS

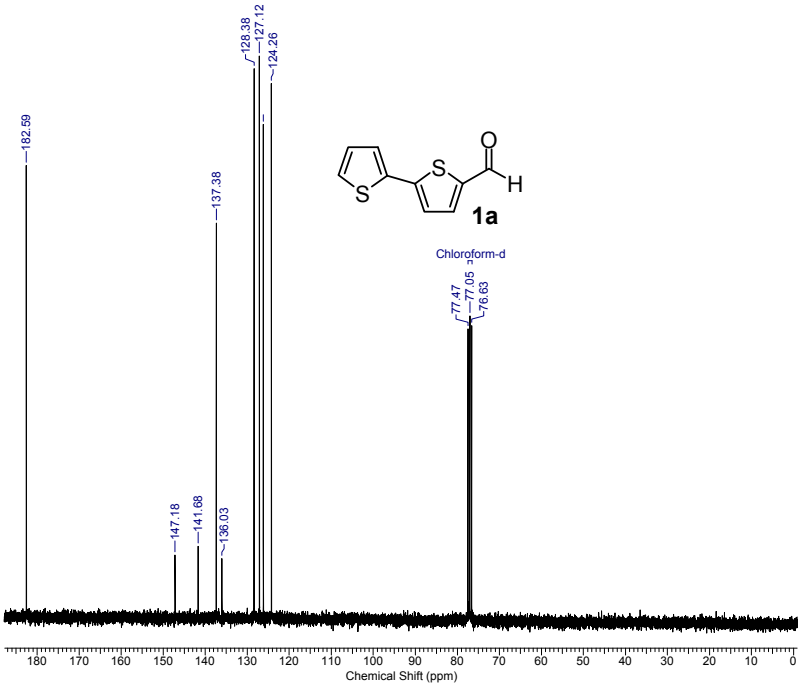
1. ^{1}H and ^{13}C NMR Spectra



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[7.04 .. 7.09]	1.020	1.76243e+7
2	[7.23 .. 7.25]	1.040	1.79740e+7
3	[7.34 .. 7.38]	2.018	3.48873e+7
4	[7.65 .. 7.68]	1.005	1.73800e+7
5	[9.84 .. 9.89]	1.000	1.72867e+7

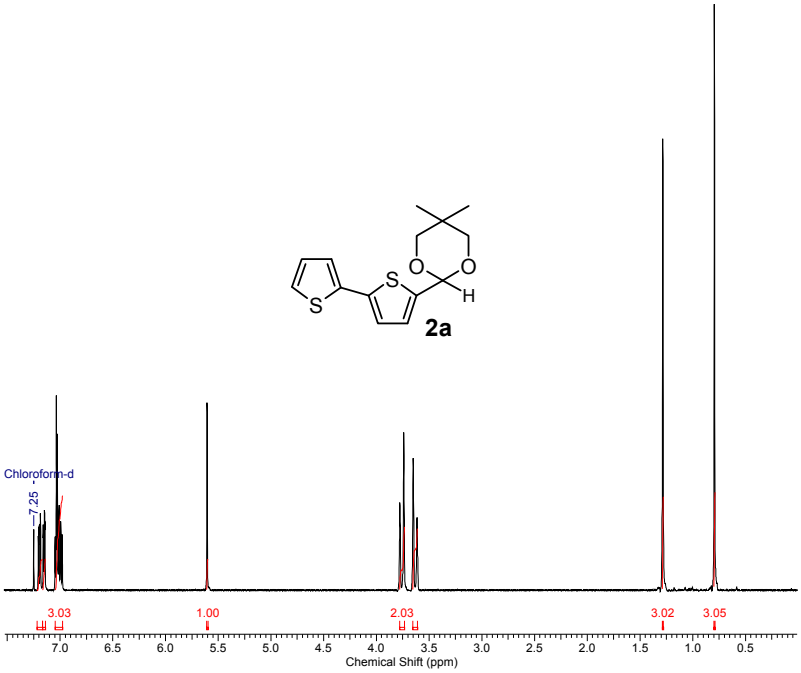
Figure S1. ^{1}H NMR spectrum of compound **1a** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	76.63	5783.6	0.5291
2	77.05	5815.5	0.5461
3	77.47	5847.5	0.5234
4	124.26	9378.9	0.9516
5	126.17	9523.3	0.8801
6	127.12	9594.8	1.0000
7	128.38	9689.9	0.9775
8	136.03	10267.2	0.1219
9	137.38	10369.2	0.7083
10	141.68	10693.4	0.1436
11	147.18	11108.7	0.1281
12	182.59	13781.5	0.8087

No.	Annotation	(ppm)
1	Chloroform-d	[76.53 .. 77.48]

Figure S2. ^{13}C NMR spectrum of compound **1a** in $CDCl_3$

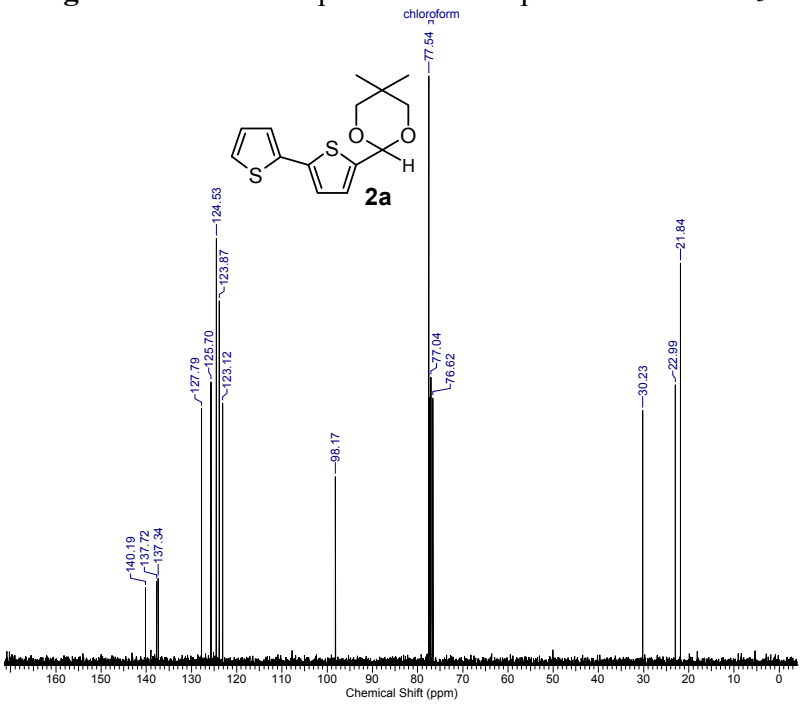


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.1036

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.79 .. 0.80]	3.048	7.34085e+9
2	[1.28 .. 1.29]	3.022	7.27915e+9
3	[3.61 .. 3.66]	2.025	4.87848e+9
4	[3.73 .. 3.78]	2.032	4.89439e+9
5	[5.60 .. 5.61]	1.000	2.40759e+9
6	[6.98 .. 7.05]	3.033	7.30557e+9
7	[7.14 .. 7.16]	1.006	2.42320e+9
8	[7.17 .. 7.22]	0.996	2.39841e+9

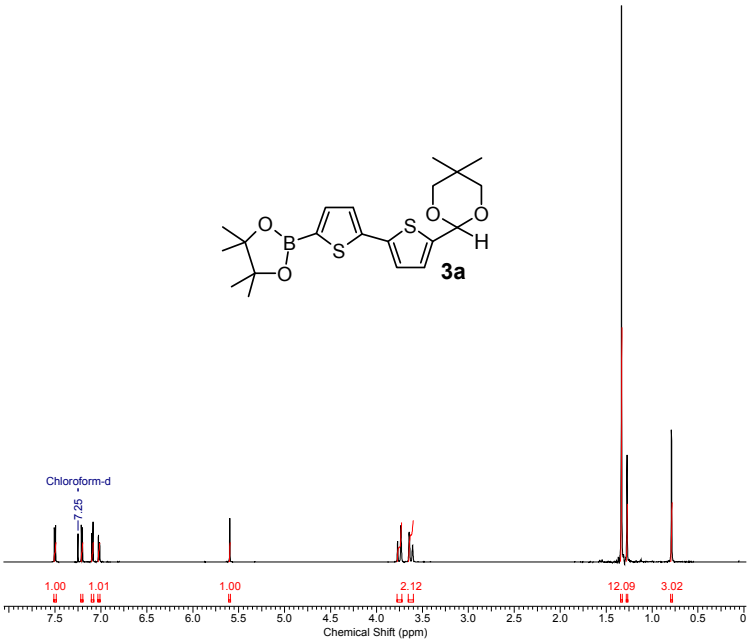
Figure S3. ^{1}H NMR spectrum of compound **2a** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	21.84	1648.9	0.4351
2	22.99	1735.2	0.3052
3	30.23	2281.5	0.2780
4	76.62	5783.6	0.2914
5	77.04	5815.5	0.3134
6	77.46	5847.3	0.2919
7	77.54	5852.9	1.0000
8	98.17	7410.3	0.2074
9	123.12	9293.6	0.2859
10	123.87	9350.3	0.3949
11	124.53	9400.2	0.4614
12	125.70	9488.3	0.3083
13	127.79	9646.1	0.2800
14	137.34	10366.9	0.0989
15	137.72	10396.0	0.0958
16	140.19	10582.0	0.0889

No.	Annotation	(ppm)
1	chloroform	[76.52 .. 77.50]

Figure S4. ^{13}C NMR spectrum of compound **2a** in $CDCl_3$

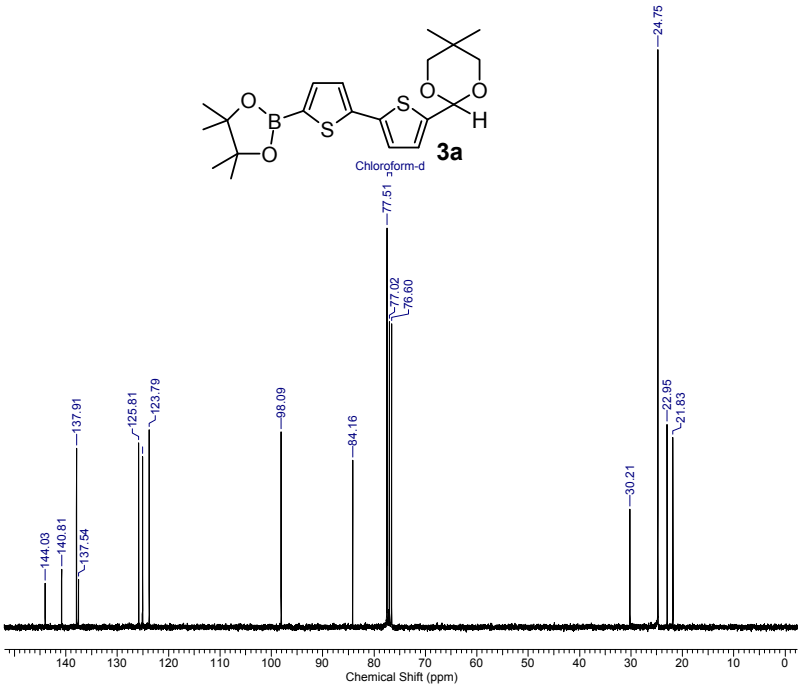


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.0450

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.78 .. 0.80]	3.022	1.21637e+9
2	[1.27 .. 1.28]	3.026	1.21769e+9
3	[1.33 .. 1.34]	12.093	4.86692e+9
4	[3.60 .. 3.65]	2.124	8.54874e+8
5	[3.73 .. 3.78]	2.071	8.33436e+8
6	[5.59 .. 5.61]	1.003	4.03803e+8
7	[7.01 .. 7.03]	1.010	4.06606e+8
8	[7.08 .. 7.10]	0.999	4.02136e+8
9	[7.20 .. 7.22]	1.002	4.03288e+8
10	[7.48 .. 7.51]	1.000	4.02459e+8

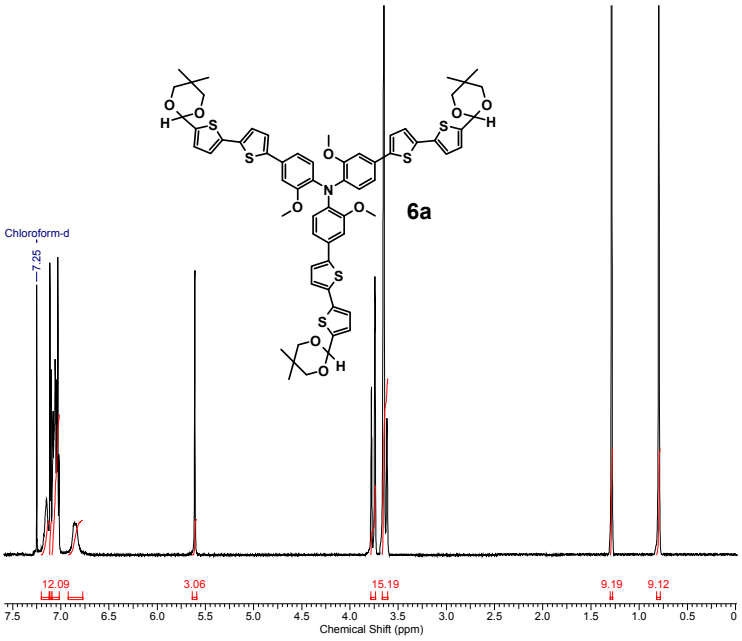
Figure S5. ^{1}H NMR spectrum of compound **3a** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	21.83	1647.3	0.2789
2	22.95	1732.4	0.2983
3	24.75	1867.9	1.0000
4	30.21	2280.2	0.1731
5	76.60	5781.3	0.4458
6	77.02	5813.4	0.4493
7	77.44	5845.2	0.4473
8	77.51	5850.1	0.5868
9	84.16	6352.4	0.2453
10	98.09	7403.4	0.2868
11	123.79	9343.6	0.2900
12	125.07	9440.0	0.2506
13	125.81	9496.1	0.2708
14	137.54	10380.9	0.0700
15	137.91	10409.1	0.2628
16	140.81	10628.1	0.0852
17	144.03	10871.2	0.0645

No.	Annotation	(ppm)
1	Chloroform-d	[76.60 .. 77.43]

Figure S6. ^{13}C NMR spectrum of compound 3**a** in $CDCl_3$

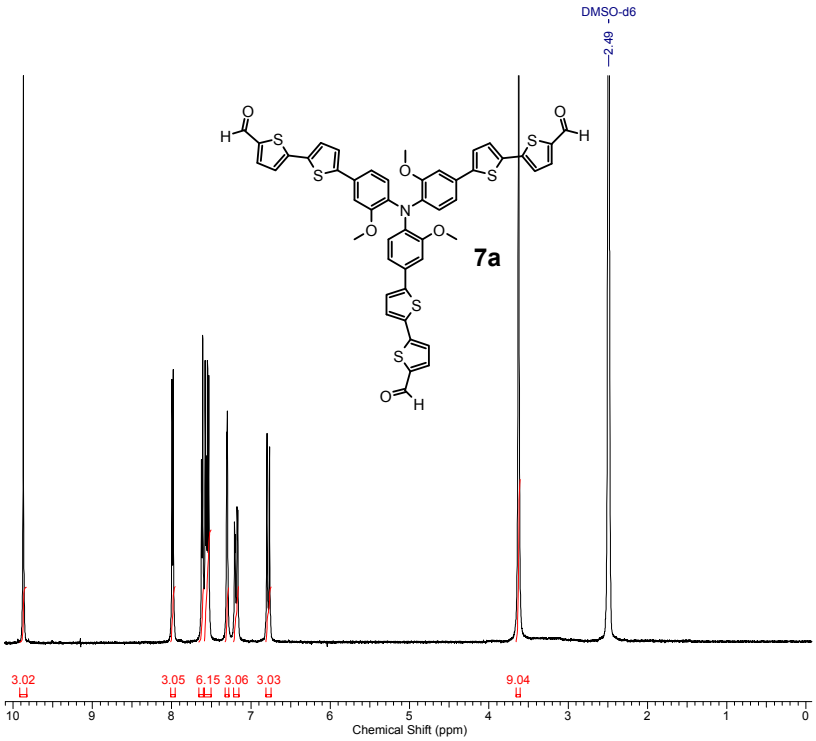


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.3101

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.78 .. 0.82]	9.120	7.26799e+9
2	[1.28 .. 1.30]	9.188	7.32241e+9
3	[3.61 .. 3.67]	15.191	1.21065e+10
4	[3.73 .. 3.79]	6.047	4.81900e+9
5	[5.59 .. 5.64]	3.061	2.43947e+9
6	[6.77 .. 6.92]	3.000	2.39080e+9
7	[7.02 .. 7.09]	12.090	9.63531e+9
8	[7.10 .. 7.12]	3.118	2.48496e+9
9	[7.12 .. 7.20]	3.020	2.40703e+9

Figure S7. ^{1}H NMR spectrum of purified product **6a** in $CDCl_3$

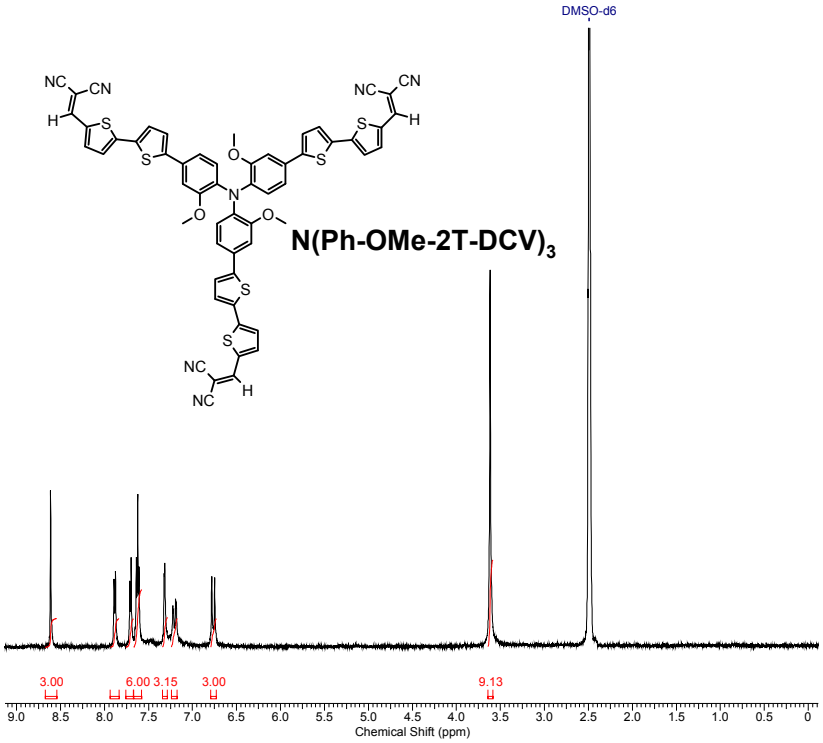


No.	(ppm)	(Hz)	Height
1	2.49	622.8	0.9298

No.	Annotation	(ppm)
1	DMSO-d6	2.49

No.	(ppm)	Value	Absolute Value
1	[3.60 .. 3.66]	9.039	6.41419e+6
2	[6.75 .. 6.81]	3.030	2.15010e+6
3	[7.15 .. 7.22]	3.058	2.16998e+6
4	[7.28 .. 7.33]	3.032	2.15154e+6
5	[7.50 .. 7.59]	6.146	4.36157e+6
6	[7.60 .. 7.66]	3.042	2.15876e+6
7	[7.95 .. 8.01]	3.052	2.16592e+6
8	[9.83 .. 9.92]	3.015	2.13990e+6

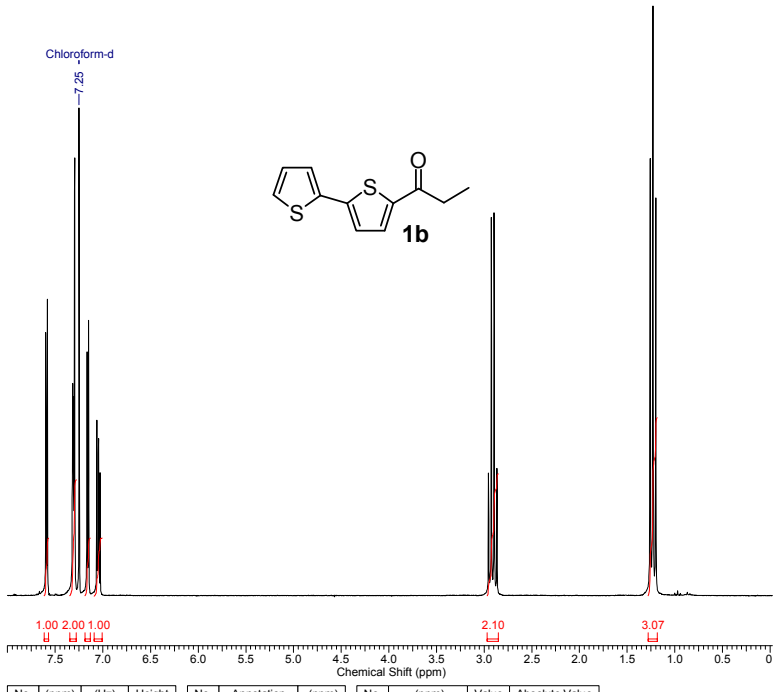
Figure S8. ^{1}H NMR spectrum of purified product **7a** in DMSO-d6



No.	Annotation	(ppm)
1	DMSO-d6	2.49

No.	(ppm)	Value	Absolute Value
1	[3.59 .. 3.64]	9.130	7.40200e+6
2	[6.73 .. 6.79]	2.998	2.43076e+6
3	[7.18 .. 7.24]	3.023	2.45079e+6
4	[7.29 .. 7.34]	3.150	2.55386e+6
5	[7.58 .. 7.67]	6.003	4.86666e+6
6	[7.67 .. 7.76]	2.993	2.42632e+6
7	[7.83 .. 7.93]	2.989	2.42309e+6
8	[8.54 .. 8.67]	3.000	2.43214e+6

Figure S9. ^{1}H NMR spectrum of **N(Ph-OMe-2T-DCV)$_3$** in DMSO-d6

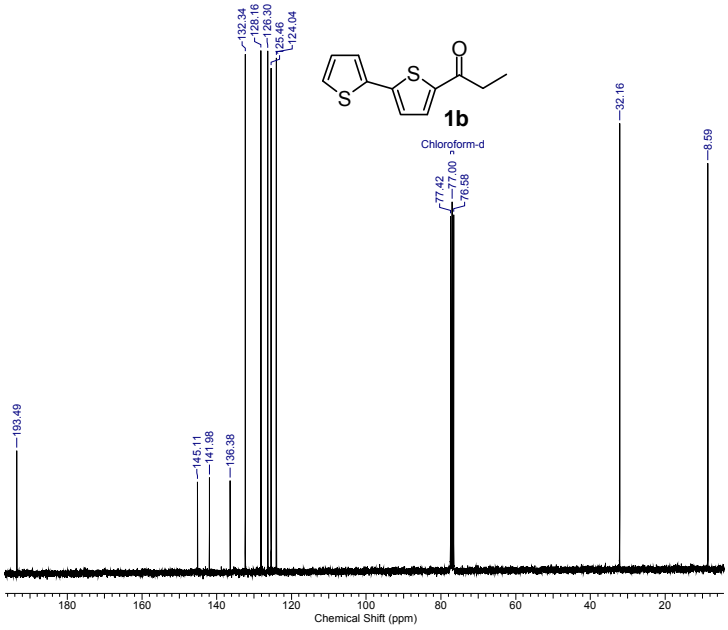


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	0.5702

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.19 .. 1.28]	3.068	1.58990e+7
2	[2.85 .. 2.97]	2.100	1.08817e+7
3	[7.01 .. 7.09]	1.000	5.18183e+6
4	[7.13 .. 7.19]	0.997	5.16502e+6
5	[7.28 .. 7.35]	2.004	1.03831e+7
6	[7.57 .. 7.62]	0.995	5.15731e+6

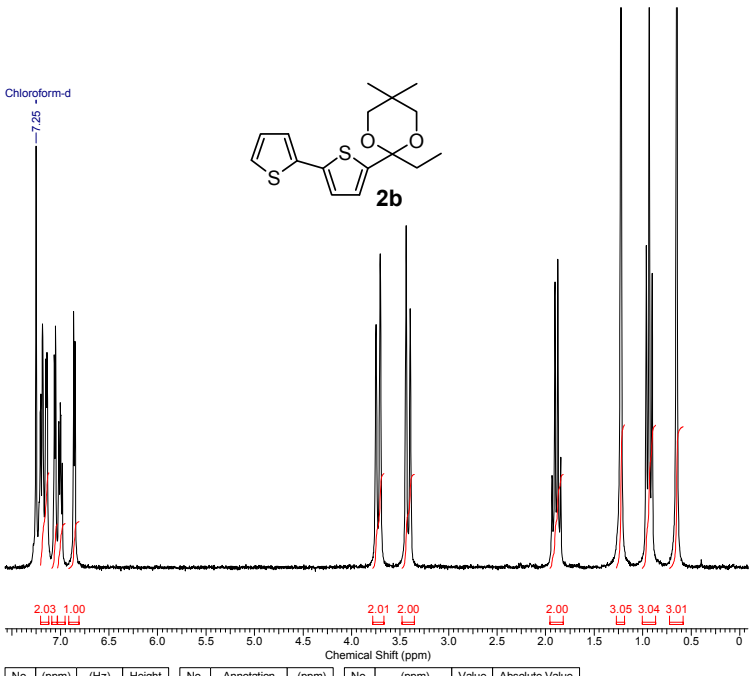
Figure S10. ^{1}H NMR spectrum of purified product **1b** in $CDCl_3$.



No.	(ppm)	(Hz)	Height
1	8.59	648.4	0.7838
2	32.16	2427.3	0.8600
3	76.58	5779.7	0.6844
4	77.00	5811.6	0.7095
5	77.42	5843.7	0.6812
6	124.04	9362.5	0.9857
7	125.46	9469.8	0.9663
8	126.30	9532.9	0.9995
9	128.16	9673.0	1.0000
10	132.34	9988.4	0.9931
11	136.38	10293.5	0.1741
12	141.98	10716.3	0.1797
13	145.11	10952.5	0.1716
14	193.49	14603.9	0.2315

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

Figure S11. ^{13}C NMR spectrum of purified product **1b** in $CDCl_3$

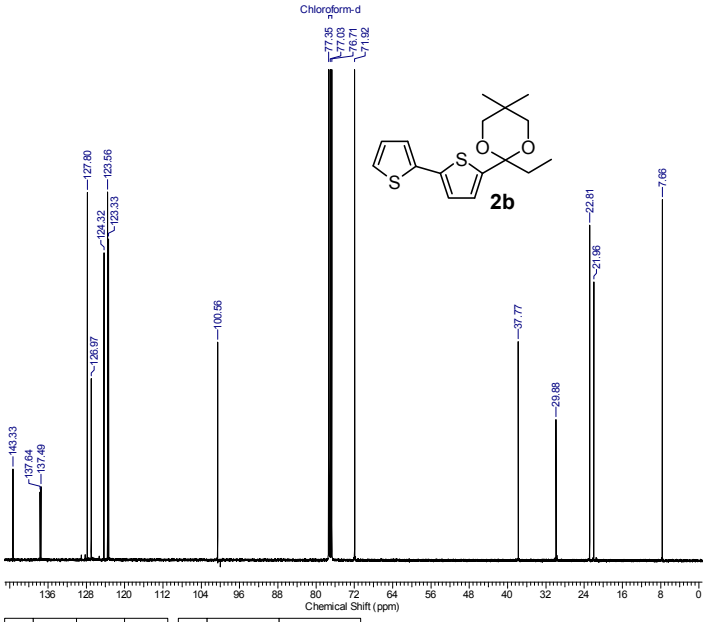


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	0.3640

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.58 .. 0.72]	3.008	1.99891e+7
2	[0.87 .. 1.00]	3.037	2.01856e+7
3	[1.19 .. 1.27]	3.049	2.02603e+7
4	[1.82 .. 1.95]	2.000	1.32919e+7
5	[3.36 .. 3.48]	1.998	1.32785e+7
6	[3.67 .. 3.78]	2.014	1.33871e+7
7	[6.81 .. 6.91]	0.995	6.61338e+6
8	[6.95 .. 7.03]	0.952	6.32795e+6
9	[7.03 .. 7.09]	0.949	6.30624e+6
10	[7.12 .. 7.21]	2.031	1.34975e+7

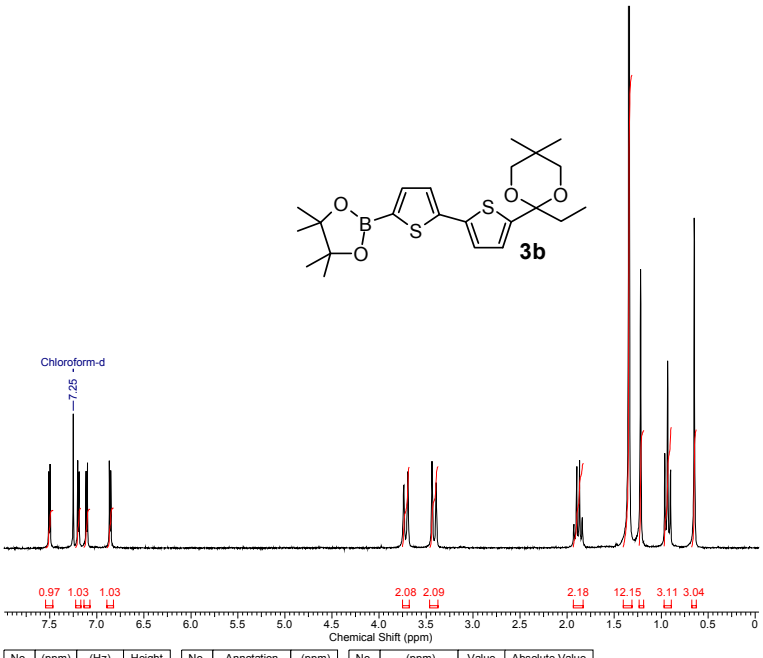
Figure S12. ^{1}H NMR spectrum of purified product **2b** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	7.66	770.7	0.6127
2	21.96	2210.0	0.4731
3	22.81	2295.9	0.5689
4	29.88	3006.8	0.2391
5	37.77	3800.5	0.3718
6	71.92	7237.5	1.0000
7	76.71	7719.5	0.8893
8	77.03	7751.8	0.9992
9	77.35	7784.1	0.8943
10	100.56	10119.2	0.3703
11	123.33	12411.0	0.5458
12	123.56	12433.7	0.6258
13	124.32	12510.8	0.5224
14	126.97	12777.1	0.3086
15	127.80	12860.7	0.6250
16	137.49	13835.7	0.1250
17	137.64	13850.4	0.1158
18	143.33	14423.3	0.1550

No.	Annotation	(ppm)
1	Chloroform-d	[76.71 .. 77.35]

Figure S13. ^{13}C NMR spectrum of purified product **2b** in $CDCl_3$

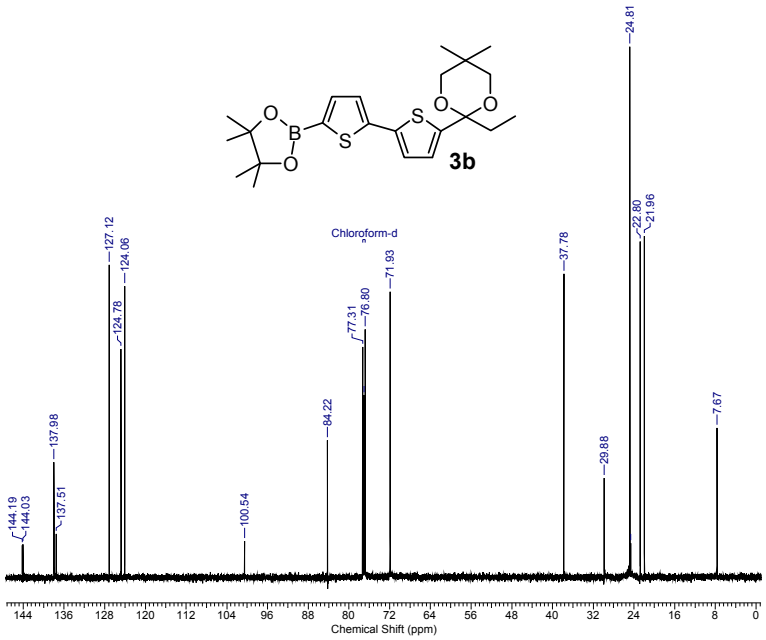


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	0.0912

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.63 .. 0.68]	3.042	4.18531e+6
2	[0.89 .. 0.97]	3.106	4.27341e+6
3	[1.19 .. 1.23]	3.023	4.16022e+6
4	[1.31 .. 1.41]	12.153	1.67232e+7
5	[1.83 .. 1.93]	2.182	3.00209e+6
6	[3.37 .. 3.46]	2.093	2.88022e+6
7	[3.68 .. 3.75]	2.081	2.86323e+6
8	[6.83 .. 6.89]	1.032	1.41976e+6
9	[7.07 .. 7.14]	1.000	1.37603e+6
10	[7.17 .. 7.23]	1.029	1.41606e+6
11	[7.47 .. 7.55]	0.973	1.33910e+6

Figure S14. ^{1}H NMR spectrum of purified product **3b** in $CDCl_3$

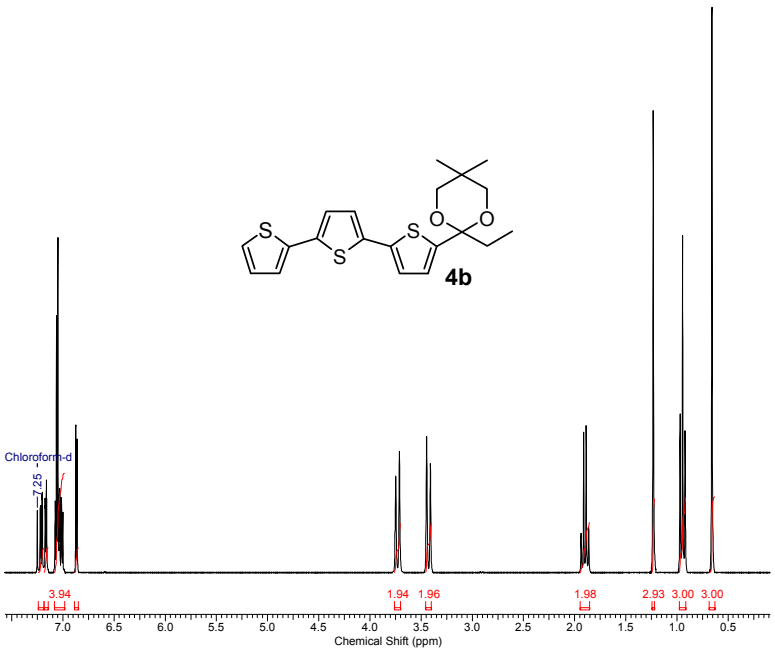


No.	(ppm)	(Hz)	Height
1	7.67	965.1	0.2807
2	21.96	2761.4	0.6427
3	22.80	2867.7	0.6323
4	24.62	3096.9	0.0635
5	24.81	3120.7	1.0000
6	29.88	3758.6	0.1866
7	37.78	4752.1	0.5712
8	71.93	9046.8	0.5377
9	76.80	9659.0	0.4666
10	77.05	9690.2	0.3425

No.	(ppm)	(Hz)	Height
11	77.31	9723.2	0.4336
12	84.22	10592.0	0.2575
13	100.54	12645.0	0.0674
14	124.06	15603.4	0.5484
15	124.78	15693.2	0.4297
16	127.12	15988.4	0.5884
17	137.51	17295.3	0.0814
18	137.98	17353.9	0.2160
19	144.03	18114.6	0.0617
20	144.19	18134.8	0.0597

No.	Annotation	(ppm)
1	Chloroform-d	[76.80 .. 77.31]

Figure S15. ^{13}C NMR spectrum of purified product **3b** in $CDCl_3$

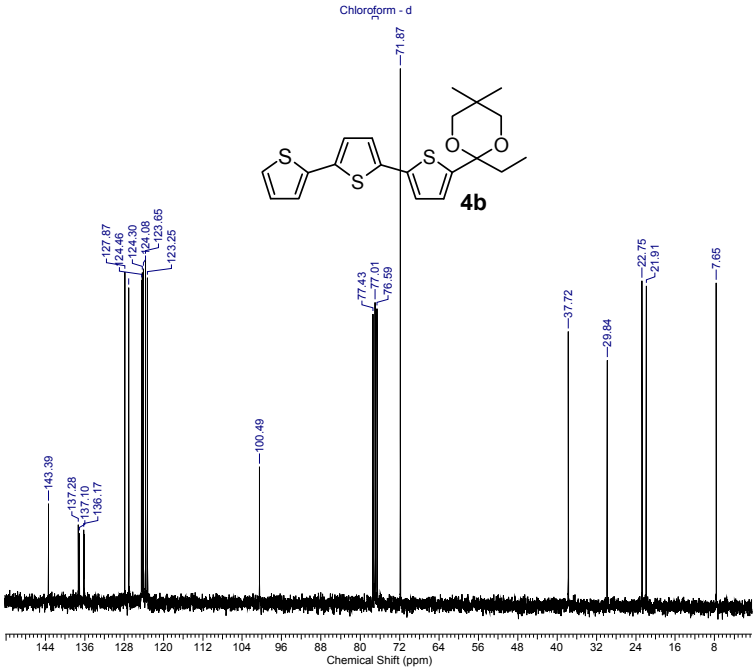


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.1099

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.63 .. 0.68]	3.000	8.99774e+9
2	[0.91 .. 0.98]	3.002	9.00377e+9
3	[1.22 .. 1.24]	2.926	8.77700e+9
4	[1.85 .. 1.94]	1.982	5.94490e+9
5	[3.40 .. 3.46]	1.962	5.88442e+9
6	[3.70 .. 3.76]	1.944	5.82905e+9
7	[6.85 .. 6.89]	0.981	2.94110e+9
8	[6.98 .. 7.08]	3.943	1.18251e+10
9	[7.14 .. 7.19]	0.984	2.95073e+9
10	[7.19 .. 7.24]	0.953	2.85728e+9

Figure S16. ^{1}H NMR spectrum of purified product **4b** in $CDCl_3$

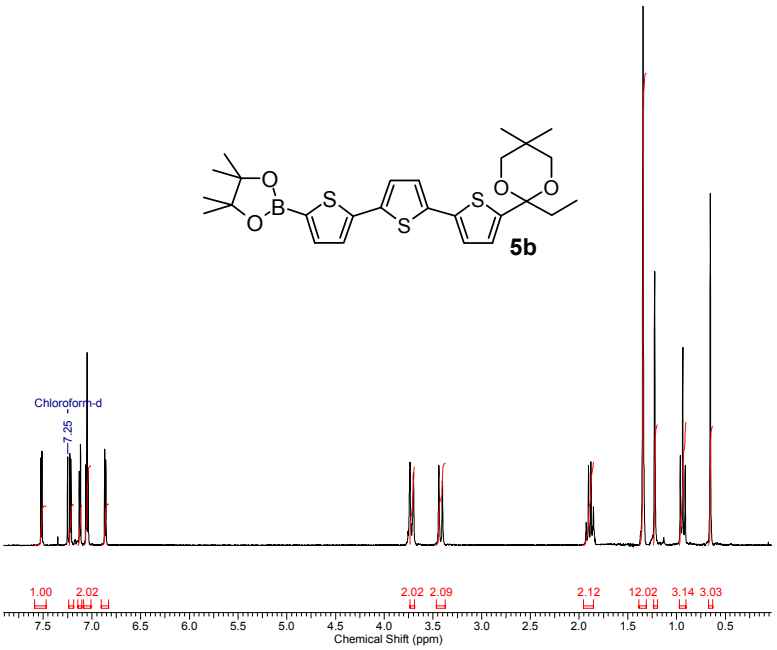


No.	(ppm)	(Hz)	Height
1	7.65	577.6	0.6040
2	21.91	1653.5	0.5982
3	22.75	1717.4	0.6078
4	29.84	2252.5	0.4608
5	37.72	2847.1	0.5141
6	71.87	5424.9	1.0000
7	76.59	5780.6	0.5560
8	77.01	5812.7	0.5674
9	77.43	5844.5	0.5463
10	100.49	7584.9	0.2636
11	123.25	9302.9	0.6131

No.	(ppm)	(Hz)	Height
12	123.65	9332.8	0.6520
13	124.08	9365.1	0.6297
14	124.30	9381.7	0.6227
15	124.46	9393.9	0.6079
16	127.06	9589.9	0.5950
17	127.87	9651.5	0.6243
18	136.13	10274.8	0.1398
19	136.17	10277.6	0.1471
20	137.10	10348.1	0.1404
21	137.28	10361.4	0.1566
22	143.39	10822.7	0.1953

No.	Annotation	(ppm)
1	Chloroform - d	[76.40 .. 77.57]

Figure S17. ^{13}C NMR spectrum of purified product **4b** in $CDCl_3$

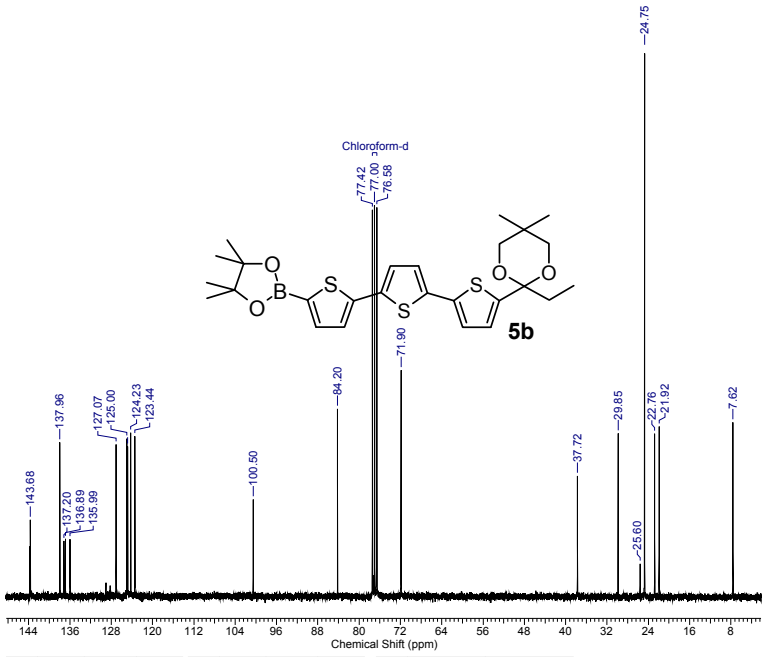


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.0578

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.63 .. 0.67]	3.029	1.91806e+9
2	[0.90 .. 0.97]	3.143	1.99027e+9
3	[1.20 .. 1.24]	3.074	1.94626e+9
4	[1.31 .. 1.39]	12.019	7.61038e+9
5	[1.85 .. 1.95]	2.119	1.34162e+9
6	[3.37 .. 3.47]	2.089	1.32299e+9
7	[3.69 .. 3.74]	2.018	1.27798e+9
8	[6.83 .. 6.90]	1.048	6.63748e+8
9	[7.01 .. 7.09]	2.019	1.27835e+9
10	[7.10 .. 7.14]	1.007	6.37840e+8
11	[7.19 .. 7.24]	1.043	6.60399e+8
12	[7.47 .. 7.59]	1.000	6.33220e+8

Figure S18. ^{1}H NMR spectrum of purified product **5b** in $CDCl_3$

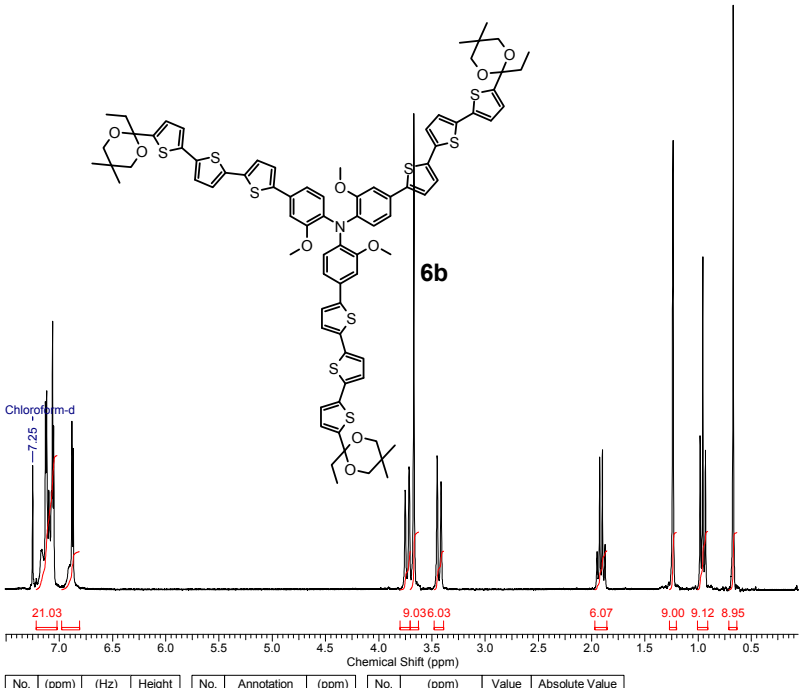


No.	(ppm)	(Hz)	Height
1	7.62	575.3	0.3026
2	21.92	1654.2	0.2955
3	22.76	1717.9	0.2833
4	24.75	1868.1	1.0000
5	25.60	1932.2	0.0655
6	29.85	2252.7	0.2838
7	37.72	2847.1	0.2129
8	71.90	5426.6	0.3896
9	76.58	5779.9	0.6623
10	77.00	5811.7	0.6655
11	77.42	5843.8	0.6582
12	84.20	6355.6	0.3251

No.	(ppm)	(Hz)	Height
13	100.50	7585.8	0.1731
14	123.44	9317.0	0.2790
15	124.23	9376.3	0.2851
16	124.82	9421.0	0.2621
17	125.00	9434.9	0.2751
18	127.07	9590.6	0.2655
19	135.99	10263.9	0.1070
20	136.89	10332.0	0.1074
21	137.20	10355.3	0.1038
22	137.96	10413.2	0.2687
23	143.68	10844.7	0.1393
24	143.75	10850.2	0.0950

No.	Annotation	(ppm)
1	Chloroform-d	[76.58 .. 77.42]

Figure S19. ^{13}C NMR spectrum of purified product **5b** in $CDCl_3$

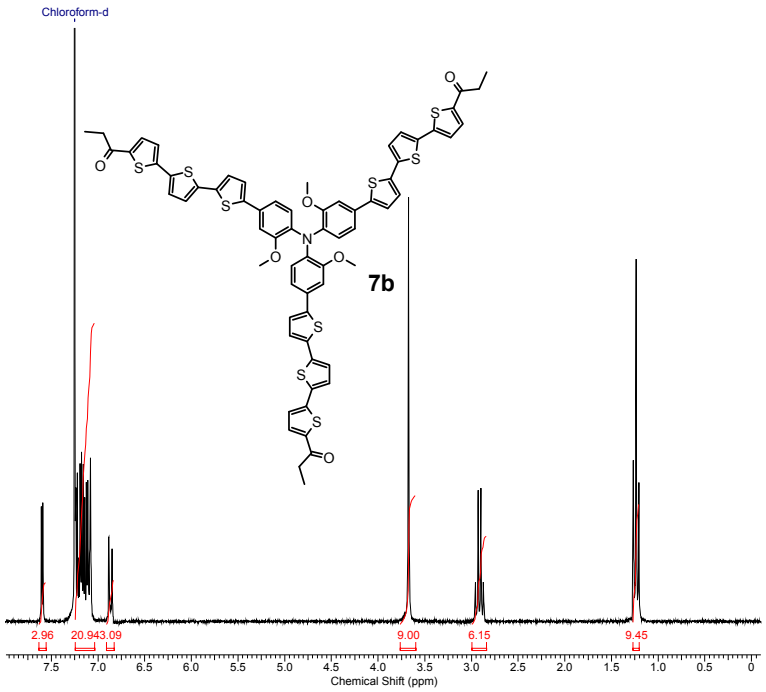


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.2125

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.64 .. 0.71]	8.953	6.88099e+9
2	[0.91 .. 1.00]	9.121	7.00999e+9
3	[1.20 .. 1.27]	9.000	6.91663e+9
4	[1.86 .. 1.97]	6.065	4.66120e+9
5	[3.39 .. 3.48]	6.030	4.63461e+9
6	[3.63 .. 3.70]	9.028	6.93860e+9
7	[3.70 .. 3.80]	6.017	4.62410e+9
8	[6.81 .. 6.98]	5.970	4.58788e+9
9	[7.02 .. 7.21]	21.026	1.61591e+10

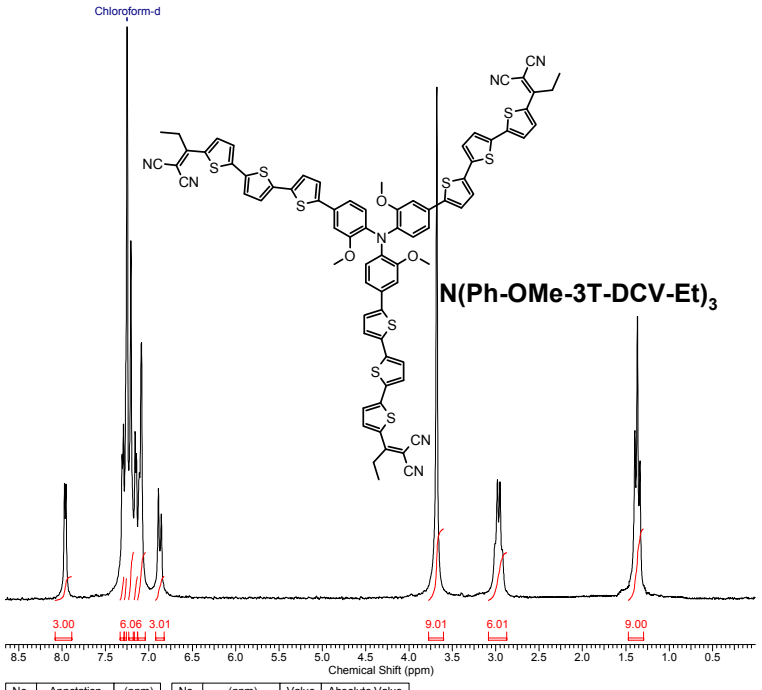
Figure S20. ^{1}H NMR spectrum of purified product **6b** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.20 .. 1.27]	9.455	8.39118e+6
2	[2.84 .. 3.00]	6.149	5.45764e+6
3	[3.59 .. 3.76]	9.000	7.98770e+6
4	[6.83 .. 6.91]	3.094	2.74576e+6
5	[7.04 .. 7.24]	20.941	1.85853e+7
6	[7.56 .. 7.63]	2.965	2.63113e+6

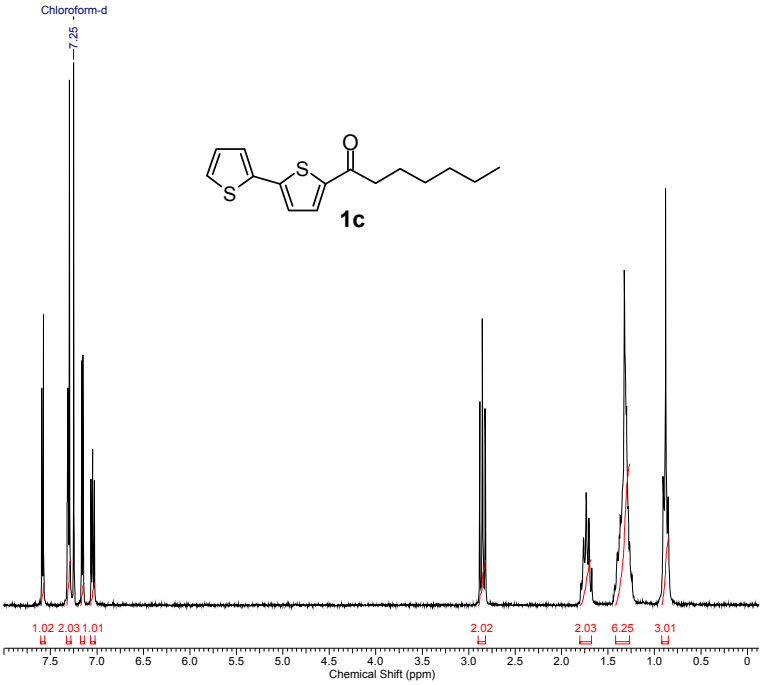
Figure S21. ^{1}H NMR spectrum of purified product **7b** in $CDCl_3$



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[1.30 .. 1.47]	8.998	3.86748e+7
2	[2.88 .. 3.08]	6.010	2.58323e+7
3	[3.60 .. 3.77]	9.008	3.87148e+7
4	[6.82 .. 6.92]	3.009	1.29315e+7
5	[7.04 .. 7.13]	6.012	2.58391e+7
6	[7.13 .. 7.17]	2.986	1.28337e+7
7	[7.18 .. 7.23]	6.060	2.60458e+7
8	[7.26 .. 7.28]	2.991	1.28574e+7
9	[7.29 .. 7.33]	3.015	1.29565e+7
10	[7.89 .. 8.08]	3.000	1.28940e+7

Figure S22. ^{1}H NMR spectrum of **N(Ph-OMe-3T-DCV-Et)$_3$** in $CDCl_3$

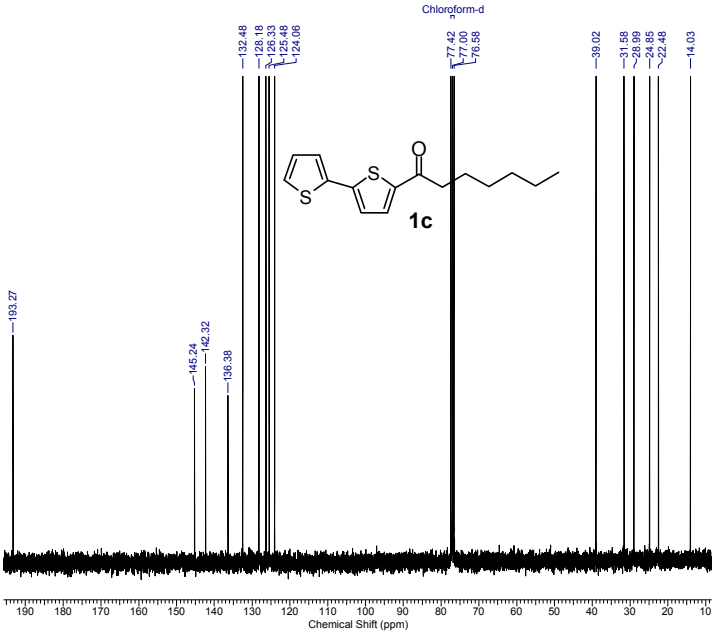


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	1.0000

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.85 .. 0.92]	3.014	1.35978e+7
2	[1.27 .. 1.42]	6.248	2.81922e+7
3	[1.68 .. 1.80]	2.028	9.14952e+6
4	[2.82 .. 2.90]	2.019	9.10944e+6
5	[7.02 .. 7.07]	1.007	4.54583e+6
6	[7.14 .. 7.18]	1.000	4.51207e+6
7	[7.28 .. 7.33]	2.028	9.15194e+6
8	[7.56 .. 7.60]	1.023	4.61635e+6

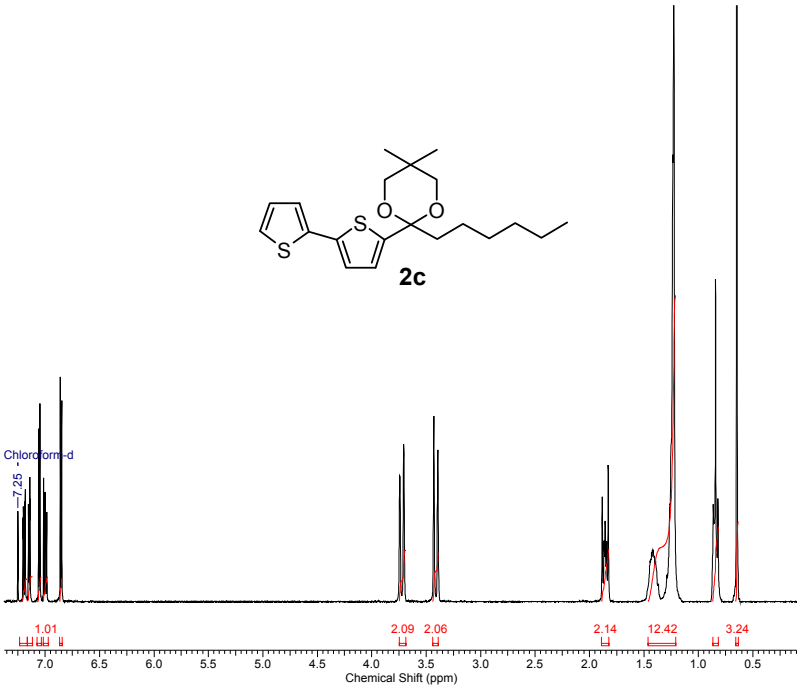
Figure S23. ^{1}H NMR spectrum of **1c** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	14.03	1059.0	0.8162
2	22.48	1696.9	0.8974
3	24.85	1875.4	0.9101
4	28.99	2188.3	0.9814
5	31.58	2383.8	0.9315
6	39.02	2944.9	0.9517
7	76.58	5779.7	0.8886
8	77.00	5811.8	0.9006
9	77.42	5843.9	0.8767
10	124.06	9363.5	0.9655
11	125.48	9470.8	1.0000
12	126.33	9534.9	0.9453
13	128.18	9674.5	0.9957
14	132.48	9999.6	0.9426
15	136.38	10293.6	0.2042
16	142.32	10742.4	0.2422
17	145.24	10962.2	0.2139
18	193.27	14587.3	0.2828

No.	Annotation	(ppm)
1	Chloroform-d	[76.56 .. 77.43]

Figure S24. ^{13}C NMR spectrum of **1c** in $CDCl_3$

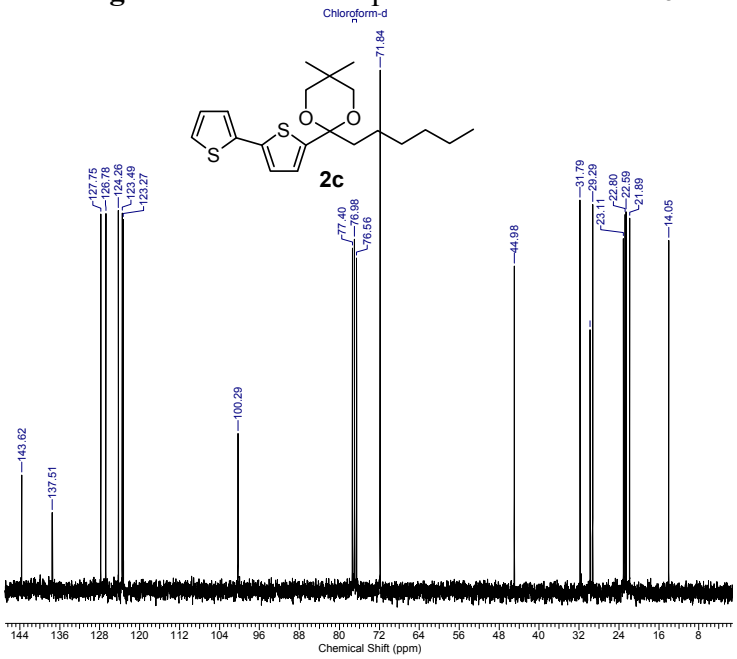


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.1133

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.63 .. 0.66]	3.240	5.68342e+9
2	[0.82 .. 0.87]	3.044	5.33939e+9
3	[1.21 .. 1.46]	12.419	2.17848e+10
4	[1.82 .. 1.89]	2.141	3.75600e+9
5	[3.39 .. 3.44]	2.063	3.61891e+9
6	[3.69 .. 3.75]	2.085	3.65799e+9
7	[6.85 .. 6.87]	1.001	1.75572e+9
8	[6.97 .. 7.02]	1.010	1.77137e+9
9	[7.03 .. 7.07]	0.999	1.75192e+9
10	[7.12 .. 7.17]	0.986	1.72979e+9
11	[7.17 .. 7.23]	0.929	1.63027e+9

Figure S25. ^{1}H NMR spectrum of **2c** in $CDCl_3$

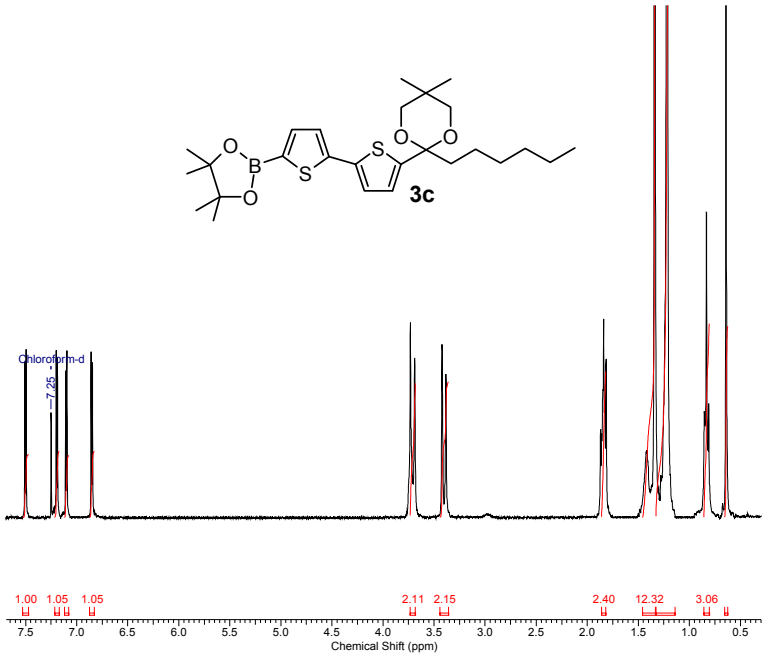


No.	(ppm)	(Hz)	Height
1	14.05	1060.2	0.5626
2	21.89	1652.3	0.5974
3	22.59	1705.1	0.6072
4	22.80	1720.6	0.6032
5	23.11	1744.4	0.5653
6	29.29	2210.4	0.6188
7	29.80	2249.4	0.4214
8	31.79	2399.2	0.6257
9	44.98	3394.6	0.5219
10	71.84	5422.5	1.0000
11	76.56	5778.3	0.5345

No.	(ppm)	(Hz)	Height
12	76.98	5810.1	0.5642
13	77.40	5842.2	0.5501
14	100.29	7569.6	0.2579
15	123.27	9304.5	0.5951
16	123.49	9321.1	0.6054
17	124.26	9379.1	0.6095
18	126.78	9569.0	0.6047
19	127.75	9642.6	0.6036
20	137.43	10372.9	0.1148
21	137.51	10379.2	0.1329
22	143.62	10839.8	0.1919

No.	Annotation	(ppm)
1	Chloroform-d	[76.56 .. 77.40]

Figure S26. ^{13}C NMR spectrum of **2c** in $CDCl_3$

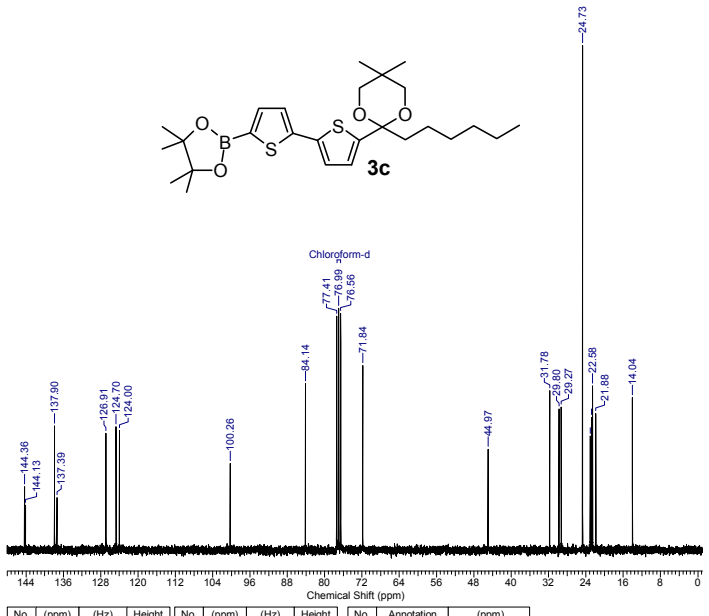


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.0356

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.63 .. 0.65]	3.019	2.02352e+9
2	[0.80 .. 0.86]	3.058	2.04925e+9
3	[1.14 .. 1.33]	12.064	8.08548e+9
4	[1.33 .. 1.46]	12.322	8.25812e+9
5	[1.82 .. 1.86]	2.399	1.60806e+9
6	[3.36 .. 3.44]	2.150	1.44067e+9
7	[3.68 .. 3.73]	2.114	1.41714e+9
8	[6.83 .. 6.88]	1.051	7.04390e+8
9	[7.08 .. 7.12]	0.984	6.59701e+8
10	[7.17 .. 7.21]	1.051	7.04214e+8
11	[7.47 .. 7.53]	1.000	6.70202e+8

Figure S27. ^{1}H NMR spectrum of purified product **3c** in $CDCl_3$

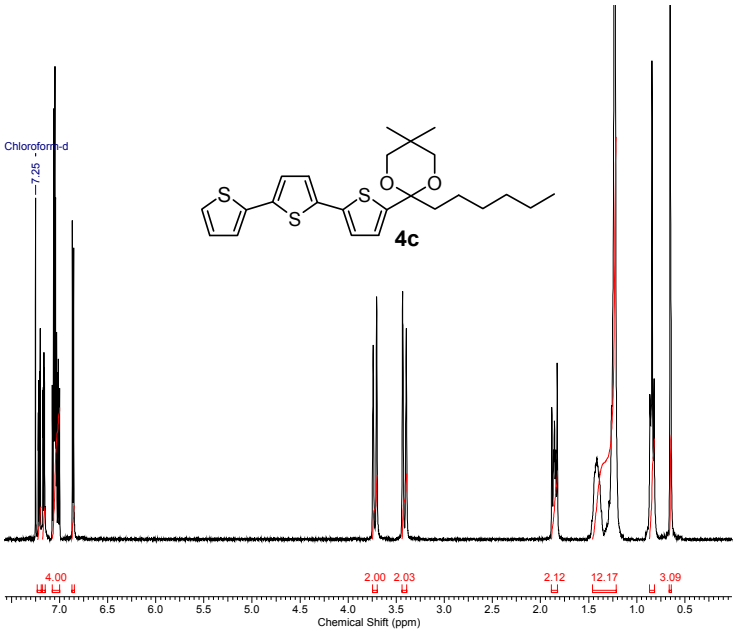


No.	(ppm)	(Hz)	Height
1	14.04	1060.0	0.3024
2	21.88	1651.3	0.2709
3	22.58	1704.4	0.3256
4	22.78	1719.2	0.2634
5	23.09	1742.7	0.2259
6	24.73	1866.6	1.0000
7	29.27	2209.2	0.2841
8	29.80	2249.2	0.2804
9	31.78	2398.4	0.3159
10	44.97	3394.5	0.2002
11	71.84	5422.4	0.3657
12	76.56	5778.7	0.4693

No.	(ppm)	(Hz)	Height
13	76.99	5810.7	0.4797
14	77.41	5842.6	0.4639
15	84.14	6350.4	0.3302
16	100.26	7567.5	0.1721
17	124.00	9358.9	0.2373
18	124.70	9411.8	0.2447
19	126.91	9578.6	0.2314
20	137.39	10369.8	0.1040
21	137.90	10408.5	0.2462
22	144.13	10878.5	0.0893
23	144.36	10896.3	0.1257

No.	Annotation	(ppm)
1	Chloroform-d	[76.56 .. 77.38]

Figure S28. ^{13}C NMR spectrum of purified product **3c** in $CDCl_3$

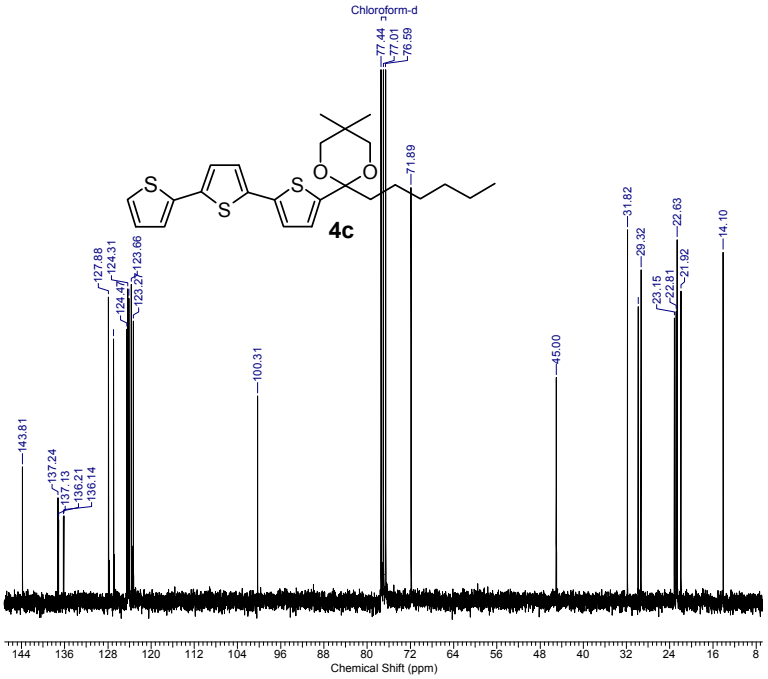


No.	(ppm)	(Hz)	Height
1	7.25	2176.2	0.2826

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.64 .. 0.66]	3.086	7.67765e+9
2	[0.82 .. 0.87]	3.049	7.58745e+9
3	[1.22 .. 1.46]	12.168	3.02762e+10
4	[1.82 .. 1.89]	2.124	5.28579e+9
5	[3.39 .. 3.44]	2.031	5.05384e+9
6	[3.70 .. 3.75]	2.000	4.97547e+9
7	[6.85 .. 6.87]	1.035	2.57425e+9
8	[7.00 .. 7.07]	3.997	9.94437e+9
9	[7.15 .. 7.18]	1.005	2.50084e+9
10	[7.19 .. 7.23]	0.998	2.48285e+9

Figure S29. ^{1}H NMR spectrum of purified product **4c** in $CDCl_3$

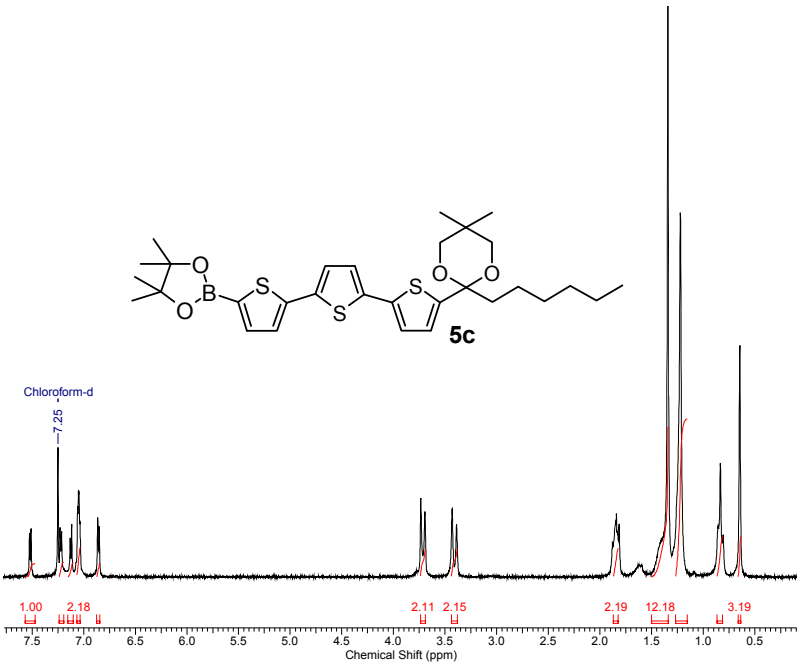


No.	(ppm)	(Hz)	Height
1	14.10	1064.2	0.4435
2	21.92	1654.6	0.3967
3	22.63	1708.4	0.4585
4	22.81	1722.0	0.3721
5	23.15	1747.4	0.3642
6	29.32	2213.0	0.4223
7	29.85	2252.9	0.3779
8	31.82	2402.0	0.4705
9	45.00	3396.4	0.2926
10	71.89	5425.9	0.5217
11	76.59	5781.0	0.9689
12	77.01	5812.9	1.0000
13	77.44	5844.9	0.9677

No.	(ppm)	(Hz)	Height
14	100.31	7570.8	0.2705
15	123.28	9304.5	0.3606
16	123.66	9333.8	0.4047
17	124.09	9365.9	0.3882
18	124.31	9382.7	0.3994
19	124.47	9394.7	0.3511
20	126.92	9579.8	0.3393
21	127.88	9652.5	0.3896
22	136.14	10275.9	0.1261
23	136.21	10280.8	0.1251
24	137.13	10350.2	0.1216
25	137.24	10358.5	0.1479
26	143.81	10854.8	0.1851

No.	Annotation	(ppm)
1	Chloroform-d	[76.55 .. 77.37]

Figure S30. ^{13}C NMR spectrum of purified product **4c** in $CDCl_3$

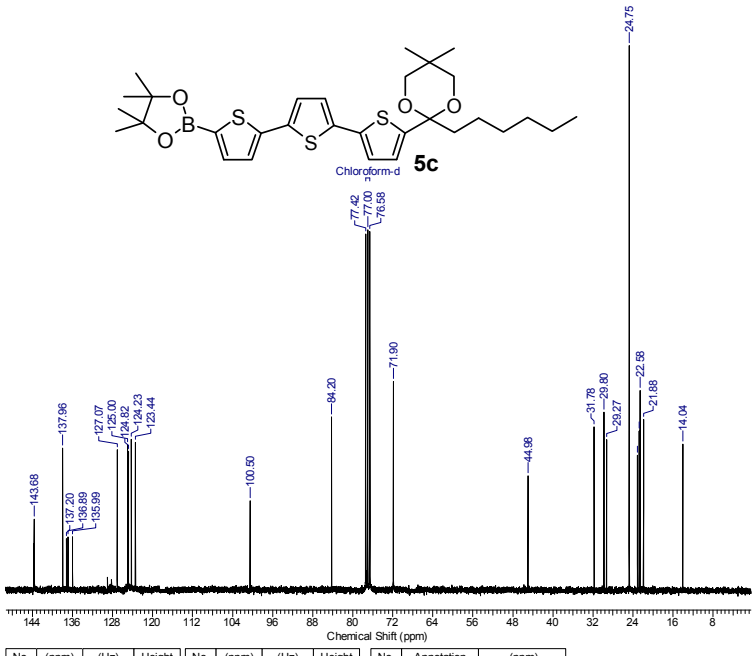


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	0.1622

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.64 .. 0.66]	3.191	1.09865e+7
2	[0.81 .. 0.87]	3.110	1.07086e+7
3	[1.16 .. 1.27]	12.045	4.14698e+7
4	[1.34 .. 1.50]	12.181	4.19386e+7
5	[1.83 .. 1.87]	2.193	7.55150e+6
6	[3.38 .. 3.44]	2.152	7.40840e+6
7	[3.69 .. 3.74]	2.111	7.26802e+6
8	[6.84 .. 6.87]	1.080	3.71939e+6
9	[7.03 .. 7.07]	2.184	7.51986e+6
10	[7.10 .. 7.15]	1.090	3.75420e+6
11	[7.19 .. 7.24]	1.157	3.98214e+6
12	[7.47 .. 7.56]	1.000	3.44299e+6

Figure S31. ^{1}H NMR spectrum of purified product **5c** in $CDCl_3$

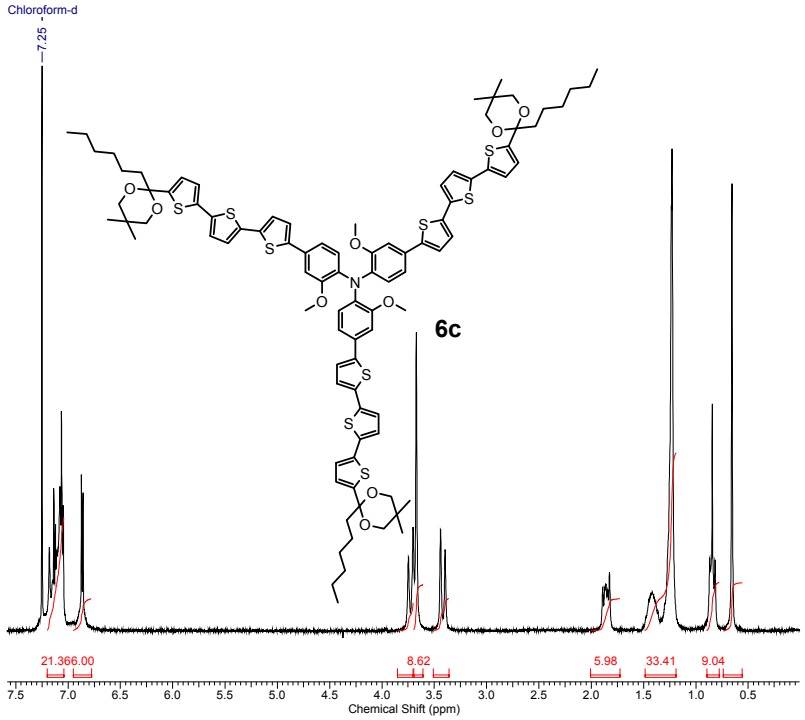


No.	(ppm)	(Hz)	Height
1	14.04	1059.8	0.2758
2	21.88	1651.6	0.3210
3	22.58	1704.2	0.3737
4	22.78	1719.2	0.2994
5	23.09	1743.0	0.2555
6	24.75	1868.1	1.0000
7	29.27	2209.1	0.2840
8	29.80	2249.2	0.3339
9	31.78	2398.5	0.3070
10	44.98	3395.0	0.2184
11	71.90	5426.6	0.3896
12	76.58	5779.9	0.6623
13	77.00	5811.7	0.6655
14	77.42	5843.8	0.6582

No.	(ppm)	(Hz)	Height
15	84.20	6355.6	0.3251
16	100.50	7585.8	0.1731
17	123.44	9317.0	0.2790
18	124.23	9376.3	0.2851
19	124.82	9421.0	0.2621
20	125.00	9434.9	0.2751
21	127.07	9590.6	0.2655
22	135.99	10263.9	0.1070
23	136.89	10332.0	0.1074
24	137.20	10355.3	0.1038
25	137.96	10413.2	0.2687
26	143.68	10844.7	0.1393
27	143.75	10850.2	0.0950

No.	Annotation	(ppm)
1	Chloroform-d	[76.57 .. 77.41]

Figure S32. ^{13}C NMR spectrum of purified product **5c** in $CDCl_3$

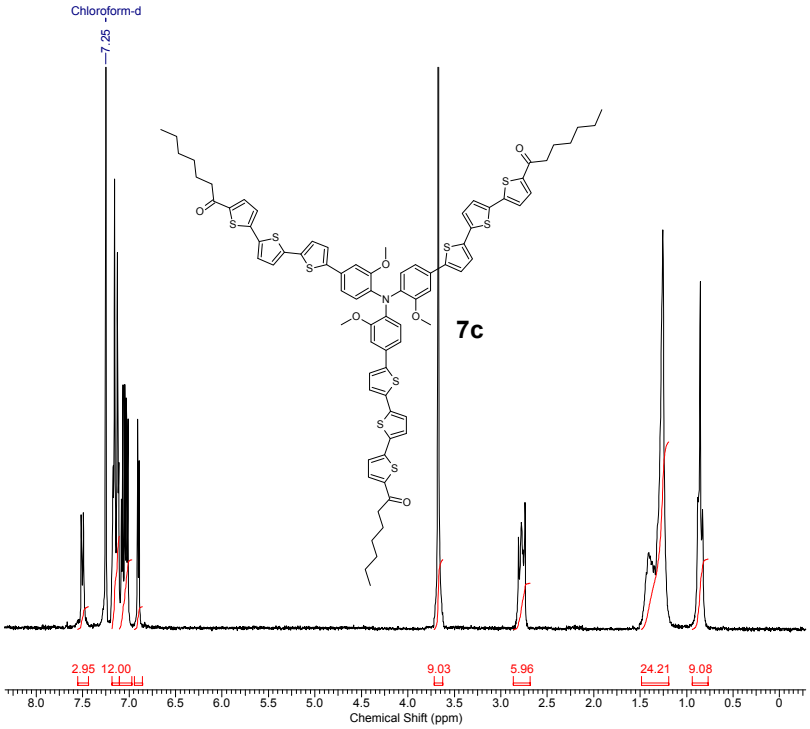


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	1.0000

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.56 .. 0.74]	9.013	2.88291e+7
2	[0.78 .. 0.90]	9.044	2.89290e+7
3	[1.19 .. 1.48]	33.406	1.06856e+8
4	[1.72 .. 2.01]	5.978	1.91212e+7
5	[3.36 .. 3.51]	6.000	1.91922e+7
6	[3.61 .. 3.69]	8.619	2.75692e+7
7	[3.70 .. 3.85]	5.263	1.68348e+7
8	[6.78 .. 6.95]	5.998	1.91868e+7
9	[7.04 .. 7.20]	21.359	6.83209e+7

Figure S33. ^{1}H NMR spectrum of purified product **6c** in $CDCl_3$

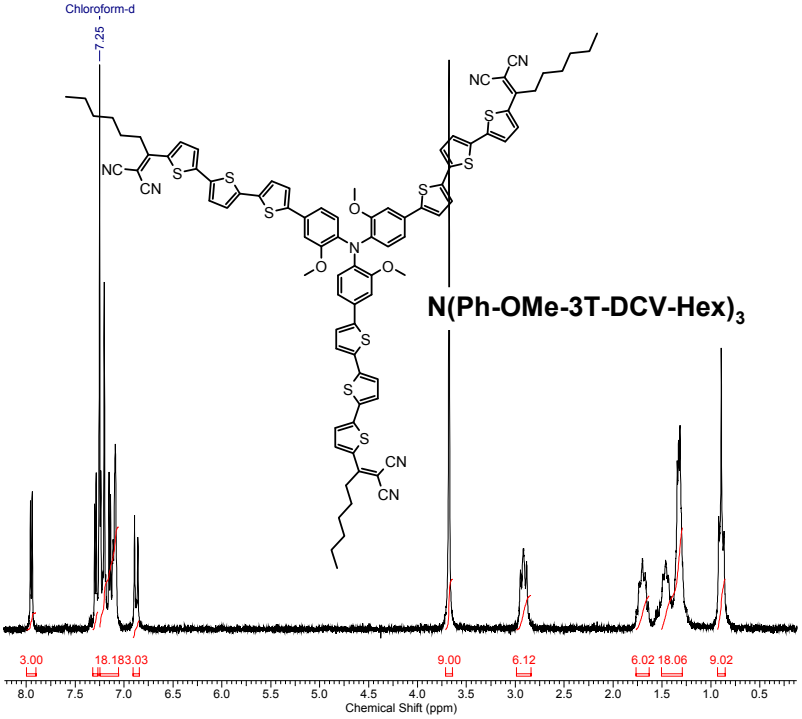


No.	(ppm)	(Hz)	Height
1	7.25	1813.5	1.0000

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.77 .. 0.94]	9.084	1.95713e+7
2	[1.19 .. 1.49]	24.215	5.21695e+7
3	[2.68 .. 2.86]	5.959	1.28385e+7
4	[3.62 .. 3.72]	9.034	1.94640e+7
5	[6.85 .. 6.94]	2.953	6.36140e+6
6	[6.97 .. 7.10]	9.016	1.94243e+7
7	[7.11 .. 7.18]	12.000	2.58534e+7
8	[7.44 .. 7.55]	2.955	6.36572e+6

Figure S34. ^{1}H NMR spectrum of purified product **7c** in $CDCl_3$



No.	(ppm)	(Hz)	Height
1	7.25	1813.5	0.9916

No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.85 .. 0.93]	9.025	4.58930e+7
2	[1.29 .. 1.51]	18.058	9.18271e+7
3	[1.63 .. 1.76]	6.020	3.06147e+7
4	[2.84 .. 2.99]	6.121	3.11273e+7
5	[3.64 .. 3.71]	8.997	4.57486e+7
6	[6.85 .. 6.91]	3.032	1.54171e+7
7	[7.06 .. 7.25]	18.178	9.24382e+7
8	[7.27 .. 7.32]	3.187	1.62041e+7
9	[7.90 .. 8.00]	3.000	1.52556e+7

Figure S35. ^{1}H NMR spectrum of purified product **N(Ph-OMe-3T-DCV-Hex)$_3$** in $CDCl_3$

2. Molecular Modelling and X-Ray diffraction data

First stage of the modelling of a crystal structure of the compounds under investigation included refinement of the structure of single molecules. Based on the CCDC crystallographic data for TPA [i] and m-TPA-OMe [ii] we studied the optimal way of attachment of bithiophene-dicyanovinyl fragments to the TPA or m-TPA "core" of the star molecule. One can find widely different values of the central (43°÷60°) and attachment (0°÷28°) torsion angles. As can be seen from Figure S36, the energy minimum is rather a shallow for the rotation around the attachment bond (providing the tilt of the planes of bithiophene fragments respectively to the plane of TPA or TPA-OMe core), allowing an easy adjustment of the molecular shape. However, application of the close packing principle made us to suggest the torsion angles to be 39° and 50.5° for the central bonds and 26° for the attachment bonds, so that the overall shape of the molecule is almost planar both for **N(Ph-2T-DCV-Me)$_3$** and **N(Ph-OMe-2T-DCV-Me)$_3$** compounds, respectively. It should also be noted that the height of the energy barrier on Figure S36b is in a good agreement with conjugation energy between the benzene ring and the bithiophene fragments**.**

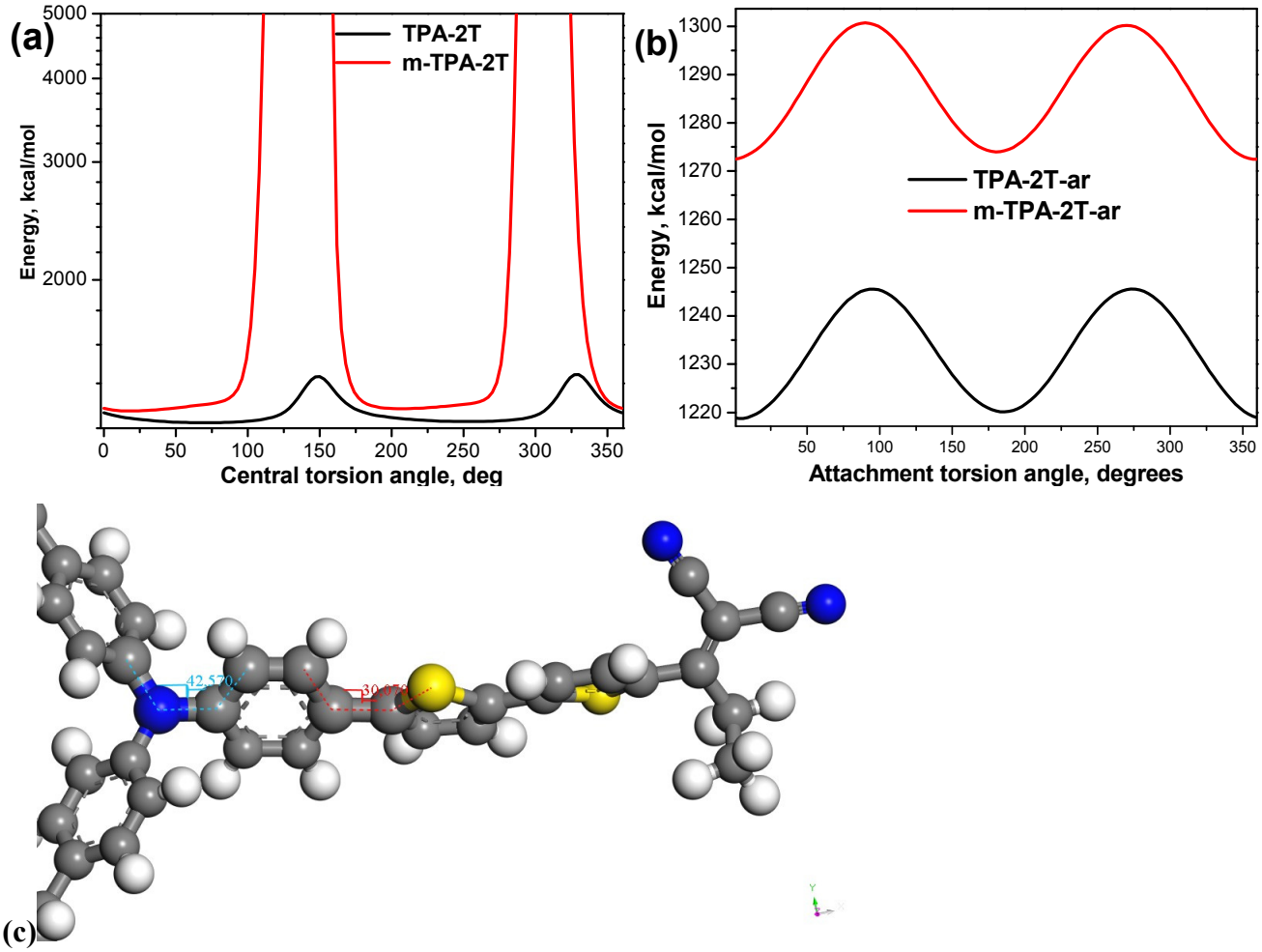


Figure S36. Energy dependence on central (a) and aromatic (b) torsion angle for TPA and m-TPA cores with 2T fragments. Corresponding torsion angles are illustrated on figure (c): central in green color and aromatic in red color.

Second stage of the modelling includes optimization of the mutual arrangement of two molecules in the supramolecular column. We applied COMPASS-II force field, assuming columnar organization of the molecules with molecular planes orthogonal to the column axis. Calculating energy of the system versus distance between the molecules and the rotation angle chi, one can build the energy maps of these interactions allowing definition of the optimal stacking position. The distance in these pairs varied from 0.2 to 12 Å and the chi angle from -60° to 60° as the molecules of all compounds possess the rotation axis of the 3rd order. Moreover, while TPA-based molecules are almost flat, m-TPA ones lack the mirror plane coinciding with the general plane of the molecule. Thus, tree ways of the interaction between two m-TPA molecules are possible: all methoxy groups oriented in the same way, both facing inwards of the pair, and both facing outwards.

As Figure S37 reveals, energy maps of **N(Ph-2T-DCV-Me)$_3$** are rather symmetrical for positive and negative chi angles, thus no chirality can be found. Some deviations observed may be due to the interaction of DCV-groups facing in the same direction. Four minimums were attributed to the optimal stacking of the central TPA core. The optimal distance between two **N(Ph-2T-DCV-Me)$_3$** molecules is 4.7 Å and the optimal orientation angle is 21°. Pattern of the interaction between **N(Ph-OMe-2T-DCV-Me)$_3$** molecules is drastically different. Introducing OMe groups changes the type of interaction. As energy maps unequivocally show (same color map is applied), the most likely stacking of two molecules is when their methoxy groups are looking outwards the pair. The energy maps are also asymmetrical respectively to the chi rotation. Two best possible stacking positions are available: χ = -40° and χ = -14°, corresponding to the distance of 4.8 Å between the molecules. In conclusion, the molecular modelling study performed revealed that the basic unit of the structure in the crystal of such compounds is the pair of molecules whose methoxy groups look outwards.

Finally, after building such pairs an attempt was made to pack them into columns (Figure S39). For pair modelling we took Z as a distance between identical central atoms and each pair to be "rigid". As expected, the optimal χ angle between the pairs for the first case was 14° and for the second case 40°, confirming the symmetry of the model. Overall, optimal distance was found to be 12 Å, which confirms the stacking of 6 molecules in a crystal cell within a fiber repeat c ~ 30 Å. Packing of three pairs in a column repeat unit agrees well with the stacking angle of pairs equal to 40 degrees.

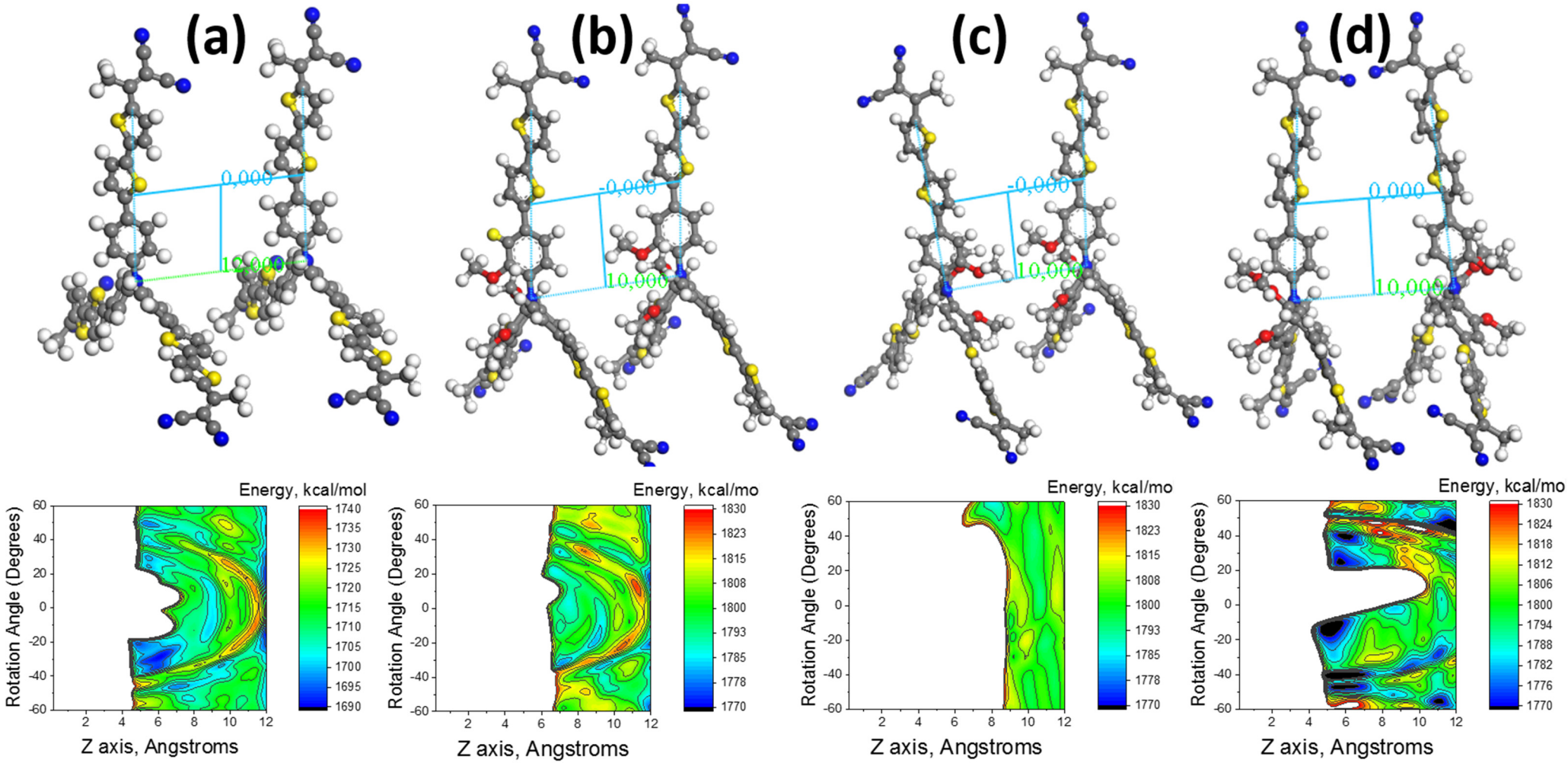


Figure S38. Energy maps for pair interactions depending on torsion angle chi and intermolecular distance Z for following molecules: 2x **N(Ph-2T-DCV-Me)$_3$** (a), 2x **N(Ph-OMe-2T-DCV-Me)$_3$** with OMe facing same the direction (b), inside (c) and outside (d)

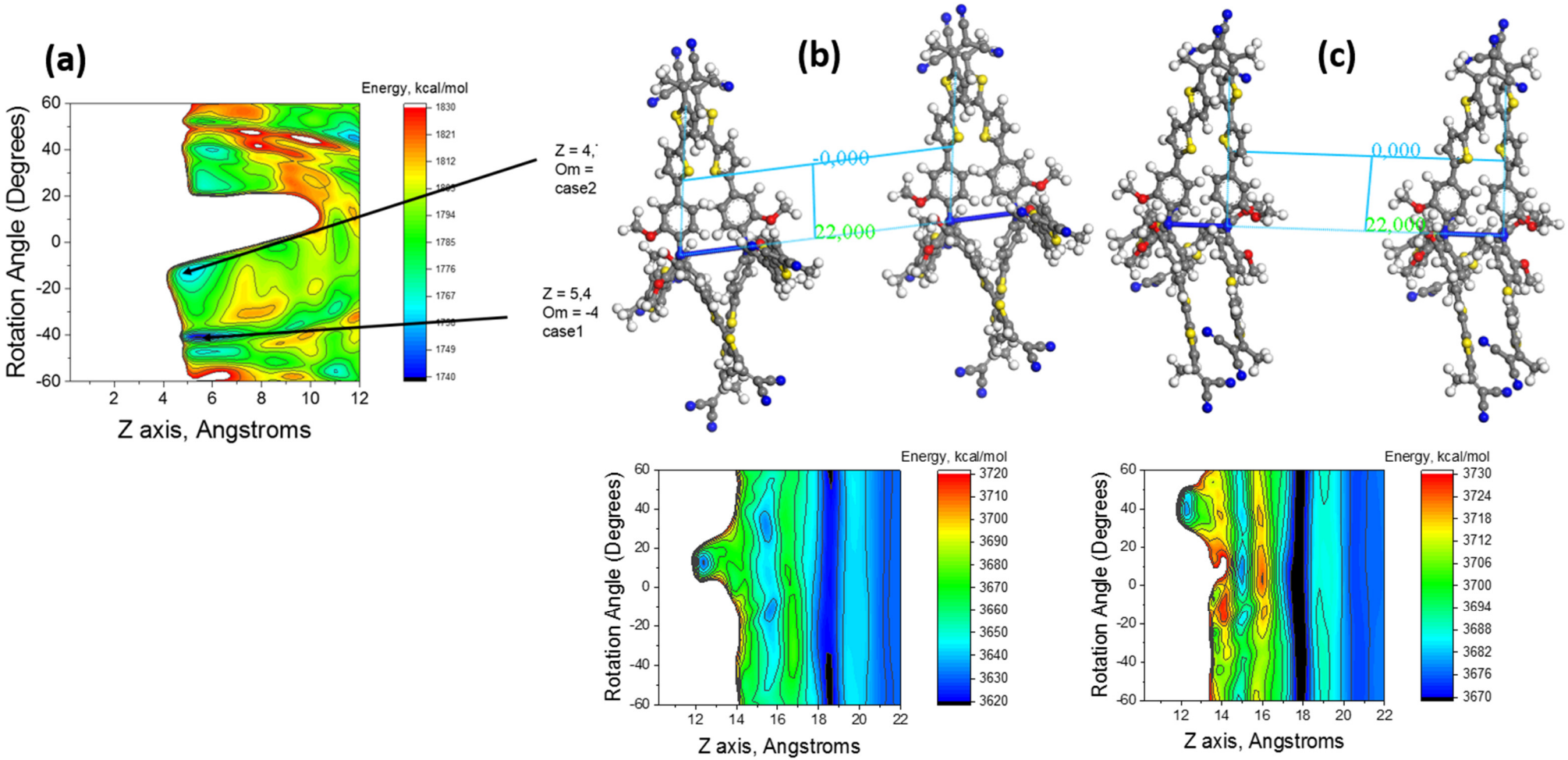


Figure S39. Two possible optimal solutions for MeO "outside" packing of **N(Ph-OMe-2T-DCV-Me)$_3$** pair (a). Energy maps for two pairs interactions depending on torsion angle chi and intermolecular distance Z for pairs with 40 degrees torsion angle (b) and 14 degrees torsion angle(c).

Table S1. Table of registered XRD reflections for N(Ph-OMe-2T-DCV)$_3$

d obs, A	d calc, A	Difference, A	hkl
20,722	20,798	-0,076	010
15,311	15,344	-0,033	002
13,137	13,163	-0,026	102
12,788	12,807	-0,019	200
11,554	11,819	-0,265	201
9,231	9,193	0,038	121
7,681	7,672	0,009	004
7,030	6,933	0,097	030
6,568	6,599	-0,031	320
5,477	5,561	-0,084	224
5,367	5,453	-0,086	420
4,867	4,876	-0,009	116
4,770	4,75	0,020	206
4,014	4,036	-0,022	440
3,798	3,825	-0,027	622
3,391	3,381	0,010	062
3,223	3,227	-0,004	056

Table S2. Table of registered XRD reflections for N(Ph-OMe-2T-DCV-Me)$_3$

d obs, A	d calc, A	Difference, A	hkl
33,266	33,236	0,030	001
18,802	18,802	0,000	010
17,559	17,559	0,000	101
16,929	16,633	0,296	002
10,837	10,670	0,167	112
9,788	9,772	0,016	103
9,038	9,058	-0,020	021
8,444	8,317	0,127	004
8,215	8,184	0,031	022
7,765	7,716	0,049	104
7,260	7,171	0,089	023
6,636	6,748	-0,112	301
6,484	6,480	0,004	204
6,032	6,030	0,002	312
5,948	5,964	-0,016	124
5,610	5,642	-0,032	132
5,466	5,456	0,010	033
5,349	5,355	-0,006	106
5,178	5,168	0,010	400
5,008	5,005	0,003	034
4,853	4,825	0,028	233
4,761	4,776	-0,015	026
4,586	4,584	0,002	140
4,537	4,529	0,008	420
4,307	4,279	0,028	240
4,242	4,244	-0,002	241
4,119	4,135	-0,016	500
4,010	4,013	-0,003	502
3,868	3,874	-0,006	503
3,816	3,805	0,011	244
3,693	3,691	0,002	522
3,636	3,633	0,003	514
3,518	3,519	-0,001	344
3,475	3,477	-0,002	440
3,325	3,321	0,004	612
3,237	3,237	0,000	436
3,136	3,134	0,002	060

Table S3. Table of registered XRD reflections for N(Ph-OMe-3T-DCV-Et)$_3$

d obs, A	d calc, A	Difference, A	hkl
27,917	28,43	-0,513	001
16,467	16,453	0,014	200
15,613	15,615	-0,002	110
14,060	14,215	-0,155	002
13,742	13,686	0,056	111
12,657	13,049	-0,392	102
9,361	9,329	0,032	310
7,099	7,108	-0,009	004
6,876	6,843	0,033	222
6,667	6,648	0,019	313
6,047	6,032	0,015	420
5,704	5,863	-0,159	413
5,337	5,343	-0,006	115
4,923	4,916	0,007	612
4,568	5,578	-1,010	016
4,087	4,069	0,018	341
3,750	3,758	-0,008	516
3,615	3,609	0,006	443
3,541	3,528	0,013	526

Table S4. Table of registered SAXS reflections for N(Ph-OMe-3T-DCV-Hex)$_3$

dobs, A	d calc, A	Difference, A	hkl
31,205	31,205	0,000	010
27,722	27,722	0,000	001
17,677	17,677	0,000	111
17,041	16,932	0,109	200
15,580	15,603	-0,023	020
14,180	14,171	0,009	120
13,764	13,861	-0,097	002
11,326	11,288	0,038	300
10,291	10,362	-0,071	022
6,940	6,931	0,009	004
6,361	6,334	0,027	024
6,130	6,121	0,009	413
5,674	5,644	0,030	600
5,529	5,531	-0,002	601
5,045	5,054	-0,009	424
4,839	4,869	-0,030	062
4,393	4,43	-0,037	026
3,732	3,733	-0,001	464
3,656	3,655	0,001	381
3,574	3,575	-0,001	606
3,469	3,486	-0,017	626

3. Photovoltaic data

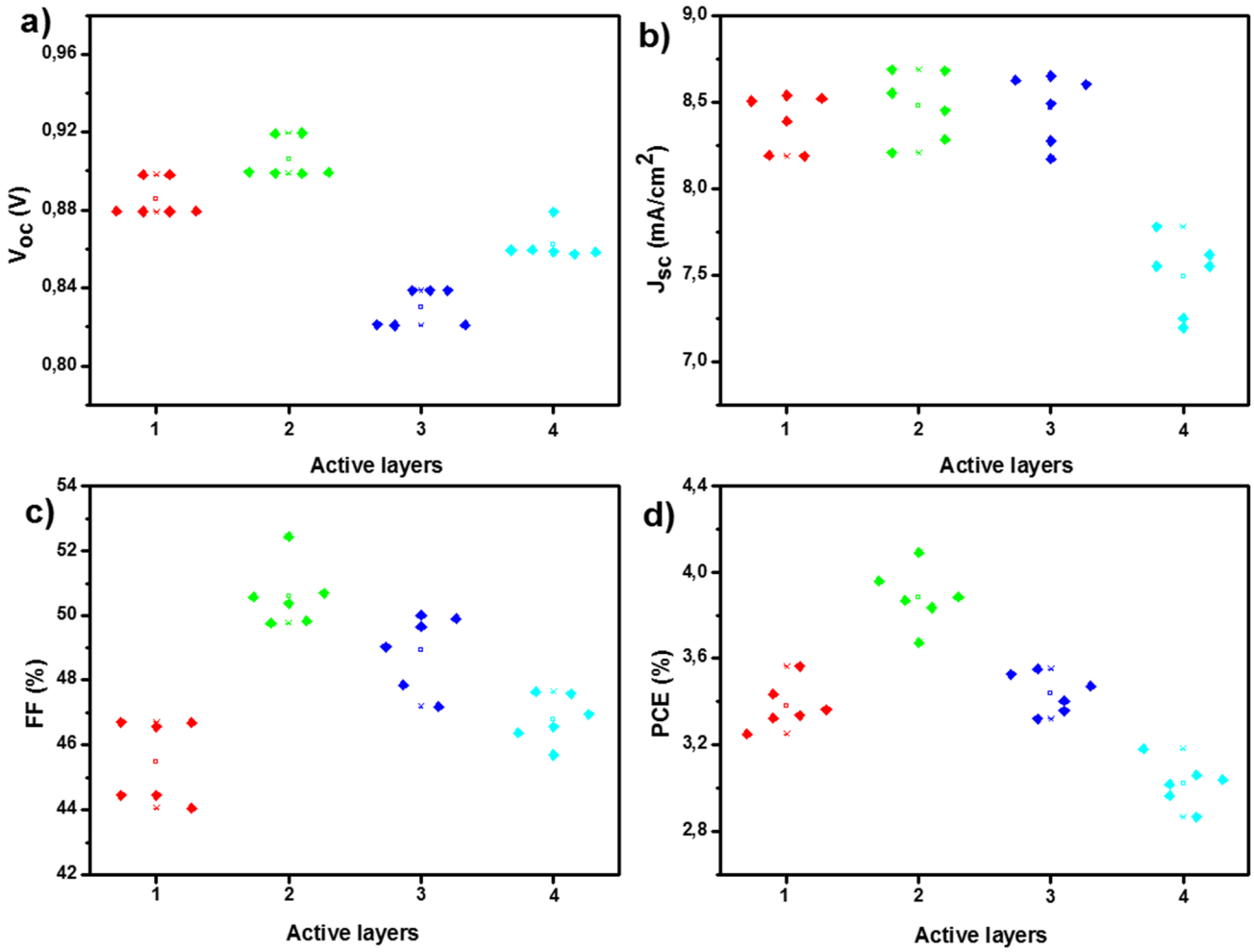


Figure S40. The ranges of (a) V_{oc}, (b) J_{sc}, (c) fill factor and (d) PCE from six devices for OSCs based on oligomers:$PC_{70}BM$ active layer, namely, **N(Ph-OMe-2T-DCV)$_3$**:$PC_{70}BM$ = 1:2.5 **(1)**, **N(Ph-OMe-2T-DCV-Me)$_3$**:$PC_{70}BM$ = 1:2 **(2)**; **N(Ph-OMe-3T-DCV-Et)$_3$**:$PC_{70}BM$ = 1:2 **(3)**; **N(Ph-OMe-2T-DCV-Me)$_3$**:$PC_{70}BM$ = 1:2.5 **(4)**.

---

[i] Sobolev et al. Acta Cryst. 1985, C41, 967-971

[ii] C.Soulie, P.Bassoul, J.Simon // New J.Chem., 1993, 17, 787

(iii) (a) HyperChem 7, Hypercube, Inc. Publication HC70-00-01-00, 2002. (b) TURBOMOLE: COSMOlogic GmbH and Co. KG, ImbacherWeg 46, 51379 Leverkusen, Germany. (c) Brabec et al. J. Phys. Chem. B, 2016, DOI: 10.1021/acs.jpcb.6b00787.