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Supporting Information

Structure-Photovoltaic Performance Relationships for DSSC Sensitizers Having Heterocyclic and Benzene Spacers.

Bo Hyung Kim and Harold S. Freeman

Fiber and Polymer Science Program, North Carolina State University, Raleigh, NC 27695, USA

bkim6@ncsu.edu, hfreeman@ncsu.edu

1 Synthetic procedures for intermediates

1-(Furan-2-yl)-2-methylpropan-1-one (2a)[1]

Furan (5g, 73.4 mmol) and isobutyric anhydride (13.5 g, 85.3 mmol) were placed in a flask under N_2 gas. To the rapidly stirred mixture at room temperature was added $BF_3{\cdot}O(C_2H_5)_2$ (1.0 g, 7.3 mmol) all at once. The reaction mixture was then heated to 100 °C and stirred for 30 min, and cooled to room temperature, Water (50 ml) was added to the reaction mixture followed by extraction twice with ether. The combined ether extracts were shaken with sat. $NaHCO_3$ to remove acid and the solvent was removed. The crude product was purified by column chromatography (DCM (dichloromethane)/ hexane, 2/1, v/v) on silica gel to produce a colorless oil. Yield: 54 %. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52 (dd, 1H, J = 1.7 Hz, 0.9 Hz), 7.13 (dd, 1H, J = 3.6 Hz, 0.9 Hz), 6.47 (dd, 1H, J = 3.6 Hz, 1.5 Hz), 3.27 (sept, 1H, J = 6.9 Hz), 1.15 (d, 6H, J = 6.9 Hz).

2-Methyl-1-(thiazol-5-yl)propan-1-one (3a)[2]

A solution of isobutyric chloride (0.68g, 6.38 mmol) in DCM (95 ml) was added to a stirred solution of 2-trimethyl silyl thiazole (0.5 g, 3.18 mmol) in DCM (62 ml) under N_2 gas. After stirring for 6 h at room temperature, the reaction mixture was treated with sat. $NaHCO_3$ followed by stirring for 30 min. The reaction mixture was extracted with DCM and dried using anhydrous $MgSO_4$. The crude product was distilled to afford a colorless oil. Yield: 75 %, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, 1H, J = 3Hz), 7.60 (d, 1H, J = 3 Hz), 3.78 (sept, 1H, J = 6.9 Hz), 1.28 (d, 6H, J = 6.9 Hz)

1-(4-Bromophenyl)-2-methylpropan-1-one (5a)

To a solution of iodobenzene (5 g, 24.5 mmol) and $AlCl_3$ (7.84 g, 58.8 mmol) was added dropwise isobutyric chloride (3.13 g, 29.4 mmol). The reaction mixture was stirred at 40 °C until HCl evolution ceased, poured into ice water, extracted with ether, and the organic layer was washed with water. Purification of crude **5a** was carried out by column chromatography (toluene/hexane, 4/1, v/v) on silica gel to yield a colorless oil. Yield: 32 %, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.76 (AA'BB', 2H), 7.60 (AA'BB', 2H), 3.42 (sept, 1H, J = 6.9 Hz), 1.14 (d, 6H, J = 6.9 Hz).

5-Bromo-2-(furan-2-yl)-3,3-dimethyl-3H-indole (2b)

To a solution of 4-bromophenyl hydrazine hydrochloride (4.85 g, 21.7 mmol) and **2a** (3 g, 21.7 mmol) in ethanol was added *p*-toluenesulfonic acid monohydrate (4.13 g, 21.7 mmol). The reaction mixture was stirred at 100 °C until **2a** was consumed as determined by TLC. The solution was diluted with ether followed by neutralization using *aq*. $NaHCO_3$, and extraction with ethyl acetate. The organic extracts were dried using anhydrous MgSO4 and concentrated under vacuum. The crude product was purified by column chromatography (ethyl acetate/hexane, 1/15, v/v) on silica gel, to produce a pale yellow-white solid. Yield: 19 %, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.60 (dd, 1H, J = 1.6 Hz, 0.9 Hz), 7.47 - 7.41 (m, 2H), 7.38 (dd, 1H, J = 1.5 Hz, 0.6 Hz), 7.10 (dd, 1H, J = 3.6 Hz, 0.6 Hz), 6.54 (dd, 1H, J = 3.6 Hz, 1.8 Hz), 1.48 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 174.30, 152.50, 148.63, 148.23, 146.41, 130.69, 124.84, 121.94, 118.45, 115.38, 112.64, 53.33, 23.59.

5-Bromo-3,3-dimethyl-2-(thiazol-2-yl)-3H-indole (3b)

Compound **3b** was prepared using the procedure given for **2b** except that **3a** was used in lieu of **2a**. Crude **3b** was purified by column chromatography (ethyl acetate/hexane, 1/20, v/v) over silica gel to produce an off-white solid. Yield: 44 %, ^{1}H NMR (300 MHz, DMSO-d6) δ = 8.17 (d, 1H, J = 3 Hz), 8.05 (d, 1H, J = 3.3 Hz), 7.86 (d, 1H, J = 2.1 Hz), 7.63 (d, 1H, J = 8.4 Hz), 7.57 (dd, 1H, J = 8.4 Hz, 1.8 Hz), 1.60 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 177.62, 161.54, 151.63, 149.66, 145.19, 130.95, 125.17, 124.19, 122.74, 119.92, 54.33, 23.14.

5-Bromo-2-(4-iodophenyl)-3,3-dimethyl-3H-indole (5b)

Compound **5b** was prepared using the procedure given for **2b** except that **5a** was used in lieu of **2a**. The crude product was purified by column chromatography (ethyl acetate/hexane, 1/20, v/v) over silica gel to produce an off-white solid. Yield: 57 %, ^{1}H NMR (500 MHz, DMSO-d6) δ = 7.95 (AA'BB', 2H), 7.90 (AA'BB', 2H), 7.81 (d, 1H, J = 1.5 Hz), 7.56 (d, 1H, J = 8.4 Hz), 7.53 (dd, 1H, J = 8.4 Hz, 2.0 Hz), 1.53 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 182.30, 151.45, 150.30, 137.73, 131.44, 130.65, 130.05, 124.91, 122.22, 119.07, 98.73, 53.59, 23.64.

2-(Furan-2-yl)-3,3-dimethyl-N,N-diphenyl-3H-indol-5-amine (2c)

An oven dried 1-neck flask containing a magnetic stirrer was evacuated and backfilled with argon gas. The flask was then charged with tris(dibenzylideneacetone) dipalladium(0) (0.05 g, 0.05 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.1 g, 0.21 mmol), sodium *tert*-butoxide (0.34 g, 3.62 mmol), **2b** (0.75 g, 2.58 mmol), diphenylamine (0.52 g, 3.10 mmol) followed, by addition of toluene (20 ml) using a syringe. The flask was sealed under a positive pressure of argon using a Teflon screw cap and the solution was stirred at 80 °C for 1 day. The solution was cooled to room temperature and diluted by adding ethyl acetate. The mixture was filtered through Celite and the solvent was removed The crude product was purified by column chromatography (ethyl acetate/hexane, 1/4, v/v) to yield a yellow solid **2c**. Yield: 87 %, ^{1}H NMR (300 MHz, CDCl3) δ = 7.61 (d, 1H, J = 1.8 Hz), 7.5 (dd, 1H, J = 8.4 Hz, 1.6 Hz), 7.26 ~ 6.97 (m, 13H), 6.57 (dd, 1H, J = 3.6 Hz, 1.8 Hz), 1.47 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 172.98, 149.20, 148.69, 147.72, 147.47, 145.76, 145.24, 129.47, 124, 123.38, 122.69, 121.01, 117.63, 114.17, 112.48, 52.88, 23.81.

3,3-Dimethyl-N,N-diphenyl-2-(thiazol-2-yl)-3H-indol-5-amine (3c)

Compound **3c** was prepared using the same procedure as in **2c** except the **3b** was used in lieu of **2b**. The crude product was purified by column chromatography (ethyl acetate/hexane, 1/11, v/v) to yield a brownish yellow solid **3c**. Yield: 28 %, ^{1}H NMR (300 MHz, DMSO-d*6*) δ = 8.11 (d, 1H, J = 3 Hz), 7.98 (d, 1H, J = 3.3 Hz), 7.57 (d, 1H, J = 8.1 Hz), 7.34 - 7.29 (m, 4H), 7.20 (d, 1H, J = 2.4 Hz), 7.08 - 7.03 (m, 6H), 6.94 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.52 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 175.80, 162.16, 149.04, 147.84, 147.25, 146.65, 144.92, 129.59, 123.91, 123.34, 123.19, 121.85, 116.77, 53.77, 23.62.

4-(5-Bromo-3,3-dimethyl-3H-indol-2-yl)benzaldehyde (5c)

Compound **5c** was produced using the same procedure as for **2d** except that **5b** was used in lieu of **2c**. The crude product obtained from evaporation of solvent was purified by column chromatography (ethyl acetate/hexane, 1/6, v/v) on silica gel, to yield a pale yellow solid. Yield: 41 %, ^{1}H NMR (300 MHz, DMSO-d6) δ = 10.10 (s, 1H), 8.39 (d, 2H, J = 8.4 Hz), 8.05 (d, 2H, J = 8.1 Hz), 7.87 (d, 1H, J = 1.8 Hz), 7.62 (d, 1H, J = 8.4 Hz, 7.56 (dd, 1H, J = 8.1 Hz, J = 2.1 Hz), 1.58 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 193.17, 182.11, 151.42, 150.34, 137.16, 137.05, 130.73, 129.69, 128.81, 124.98, 122.59, 119.59, 53.83, 23.64.

5-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)furan-2-carbaldehyde (2d)

A solution of **2c** (0.8 g, 2.11 mmol) in THF (80 ml) was cooled to -78 °C while the system was purged with N_2. n-BuLi (3.3 ml, 5.28 mmol) was added dropwise over 10 min and the reaction mixture was stirred at -78 °C for 1 h. The solution was kept at -78 °C for a dropwise addition of dry N,N-dimethylformamide (0.4 ml, 5.28 mmol). The reaction mixture was stirred for additional 1 h at -78 °C, allowed to warm to 0 °C, and the solution was neutralized using 10 % HCl. The crude product obtained from extractions using DCM was dried over anhydrous $MgSO_4$ and and solvent removal, and purified by column chromatography on silica gel (ethyl acetate/hexane, 1/3, v/v) to yield an orange solid. Yield: 15 %, ^{1}H NMR (300 MHz, DMSO-d*6*) δ = 9.73 (s, 1H), 7.70 (d, 1H, J = 3.9 Hz), 7.55 (d, 1H, J = 8.1 Hz), 7.50 (d, 1H, J = 3.6 Hz), 7.34 ~ 7.29 (m, 4H), 7.21 (d, 1H, J = 2.7 Hz), 7.08 - 7.02 (m, 6H), 6.94 (dd, 1H, J = 8.1Hz, 2.4 Hz), 1.45 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 178.81, 172.10, 152.65, 152.46, 148.40, 148.10, 147.24, 146.46, 129.57, 123.85, 123.54, 123.33, 123.10, 121.88, 116.81, 115.13, 53.25, 23.25.

2-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)thiazole-5-carbaldehyde (3d)

Compounds **3d** was prepared using the same procedure as for **2d** except that **3c** was used as a starting material instead of **2c**. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/6, v/v) to yield a reddish orange solid. Yield: 51 %, ^{1}H NMR (300 MHz, DMSO-d6) δ = 10.12 (s, 1H), 8.89 (s, 1H), 7.64 (d, 1H, J = 8.4 Hz), 7.36 - 7.31 (m, 4H), 7.19 (d, 1H, J = 1.8 Hz), 7.12 - 7.06 (m, 6H), 6.93 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.53 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 184.72, 167.84, 153.44, 149.56, 147.63, 147.14, 146.96, 139.56, 124.35, 123.61, 122.63, 122.42, 115.78, 54.08, 23.14.

4-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)benzaldehyde (5d)

Compound **5d** was prepared using the similar procedure as for **2c** using **5c** in lieu of **2b** with a use of CS_2CO_3 as a base. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/5, v/v) to yield a yellow-orange solid. Yield: 73 %, ^{1}H NMR (300 MHz, DMSO-d*6*) δ = 10.09 (s, 1H), 8.35 (d, 2H, J = 8.4 Hz), 8.09 (d, 2H, J = 8.4 Hz), 7.58 (d, 1H, J = 8.4 Hz), 7.34 - 7.29 (m, 4H), 7.23 (d, 1H, J = 2.1 Hz), 7.08 ~ 7.02 (m, 6H), 6.95 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.51 (s, 6H). ^{13}C NMR (500 MHz, DMSO-d_6) δ = 192.70, 180.26, 149.62, 147.95, 147.28, 146.20, 137.60, 136.84, 129.73, 129.52, 128.46, 123.70, 123.39, 122.97, 121.70, 116.94, 53.17, 23.78.

2 Modeling studies

DFT (density functional theory) calculations were conducted using Gaussian 03 software. Geometries were optimized using the B3LYP hybrid functional (Beck's three-parameter functional and Lee-Yang-Parr functional) as an exchange-correlation functional and 3-21G(d) or 6-31G(d) was used as the basis set. HOMO and LUMO orbitals were determined using optimized geometries. Transition energies were calculated using TDDFT (time-dependent density functional theory). using BHandH (designed by Becke with 50% of LSDA exchange) were implemented to study electronic transitions. Basis sets 3-21G(d), 6-31G(d), or 6-31+G(d,p) were used to determine the one most suitable for predicting excited state properties. The normal dipole moments and polarizabilities were obtained using single point calculation after geometry optimzation.

Table S1. Calculated electronic transition energies and oscillator strengths (f) for 5 dyes.[a]

Dyes	Transition state	Main Configurations	λ_{max} (nm)	f
DP-T	$S_0 \rightarrow S_1$	H → L (83 %) H-1 → L (6 %)	466	1.168
	$S_0 \rightarrow S_2$	H-1 → L (76 %) H → L (8 %)	330	0.340
	$S_0 \rightarrow S_3$	H → L+2 (74 %) H → L+3 (5 %)	289	0.166
DP-F	$S_0 \rightarrow S_1$	H → L (82 %) H-1 → L (6 %)	464	0.978
	$S_0 \rightarrow S_2$	H-1 → L (77 %) H → L (9 %)	331	0.346
	$S_0 \rightarrow S_3$	H → L+1 (80 %)	290	0.311
DP-TZ	$S_0 \rightarrow S_1$	H → L (85 %) H-1 → L (4 %)	478	1.129
	$S_0 \rightarrow S_2$	H-1 → L (77 %) H → L (6 %)	328	0.453
	$S_0 \rightarrow S_3$	H-7 → L (70 %) H-7 → L +1 (15 %)	305	0.003
DP-P	$S_0 \rightarrow S_1$	H → L (77 %) H-1 → L (10 %)	432	1.188
	$S_0 \rightarrow S_2$	H-1 → L (73 %) H → L (10 %)	325	0.250
	$S_0 \rightarrow S_3$	H → L+1 (74 %) H → L (6 %) H-1 → L +1 (5 %)	290	0.208
DP-B	$S_0 \rightarrow S_1$	H → L (83 %) H-1 → L (6 %) H → L+1 (5 %)	423	1.174
	$S_0 \rightarrow S_2$	H-1 → L (73 %) H → L (7 %) H-6 → L (6 %)	304	0.570
	$S_0 \rightarrow S_3$	H → L+1 (69 %) H → L+5 (7 %) H → L (6 %) H-8 → L (6 %)	283	0.127

[a] Values were predicted using TDDFT-PCM-BHandH/3-21G(d)//B3LYP/3-21G(d). H and L represent HOMO and LUMO, respectively.

Table S2. Calculated electronic transition energies using different basis set[a].

Basis set used	DP-T		DP-F		DP-TZ		DP-P		DP-B	
	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$
TD-PCM-BHandH/6-31+G(d,p)//B3LYP/6-31G(d)	504	348	498	346	514	341	462	340	459	320
TD-PCM-BHandH/6-31G(d,p)//B3LYP/6-31G(d)	494	343	485	340	-	-	-	-	-	-
TD-PCM-BHandH/6-31G(d)//B3LYP/6-31G(d)	494	343	485	340	504	337	449	333	448	315
TD-PCM-BHandH/3-21G(d)//B3LYP/3-21G(d)	466	330	464	331	478	328	432	325	423	304

[a] unit of nm

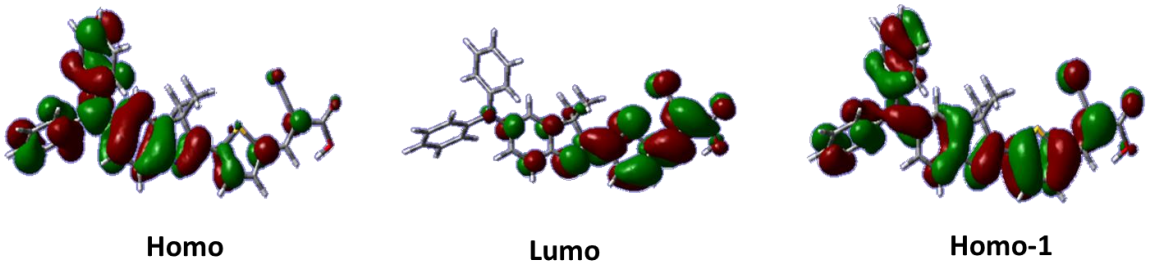


Figure S1. Representative examples of isodensity surface plots of HOMO, LUMO, and HOMO-1 for **DP-T** obtained using TDDFT-PCM-BHandH/3-21G(d)//B3LYP/3-21G(d).

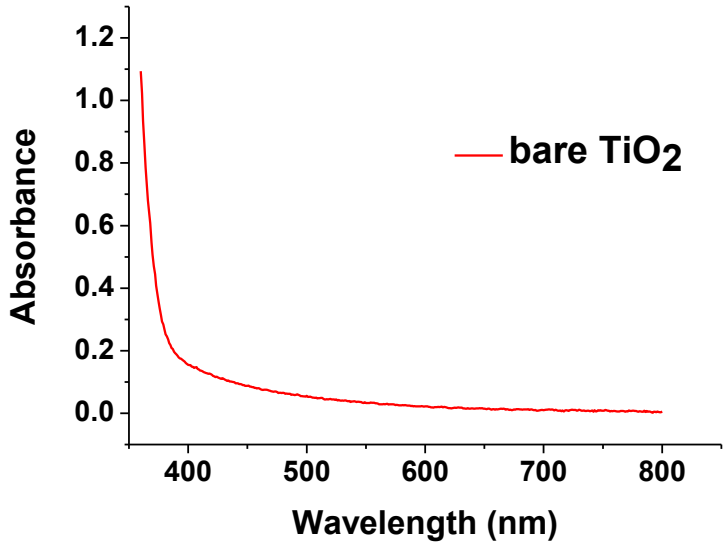


Figure S2. Absorption spectrum of blank TiO_2 film (6μm).

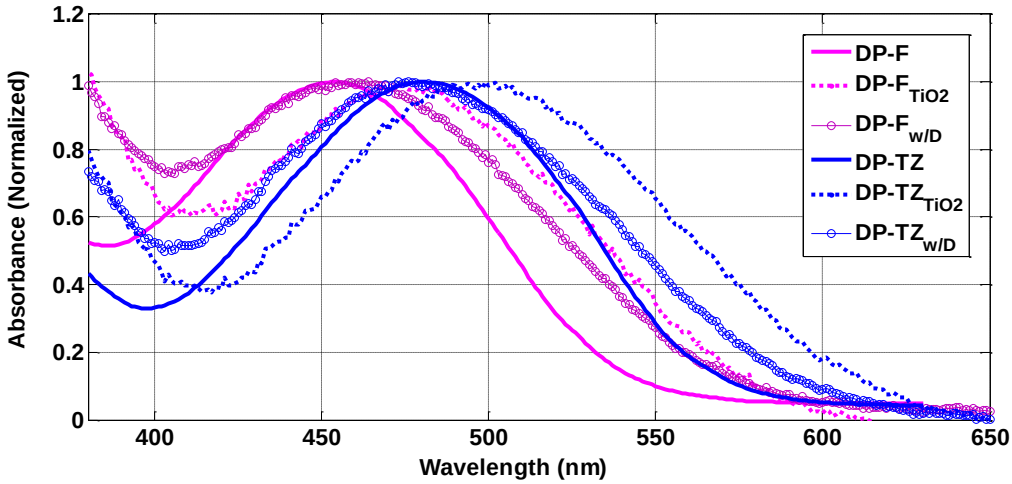


Figure S3. Absorption spectra based on dyes **DP-F** and **DP-TZ**. (line; absorption of dyes measured in THF solution, dashed line; absorption of dye loaded TiO_2 films, line with circle; absorption of dye/DCA loaded TiO_2 films.)

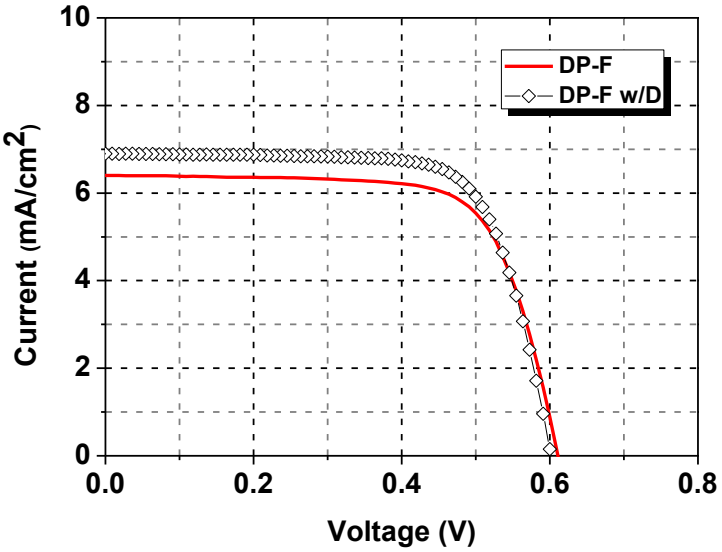
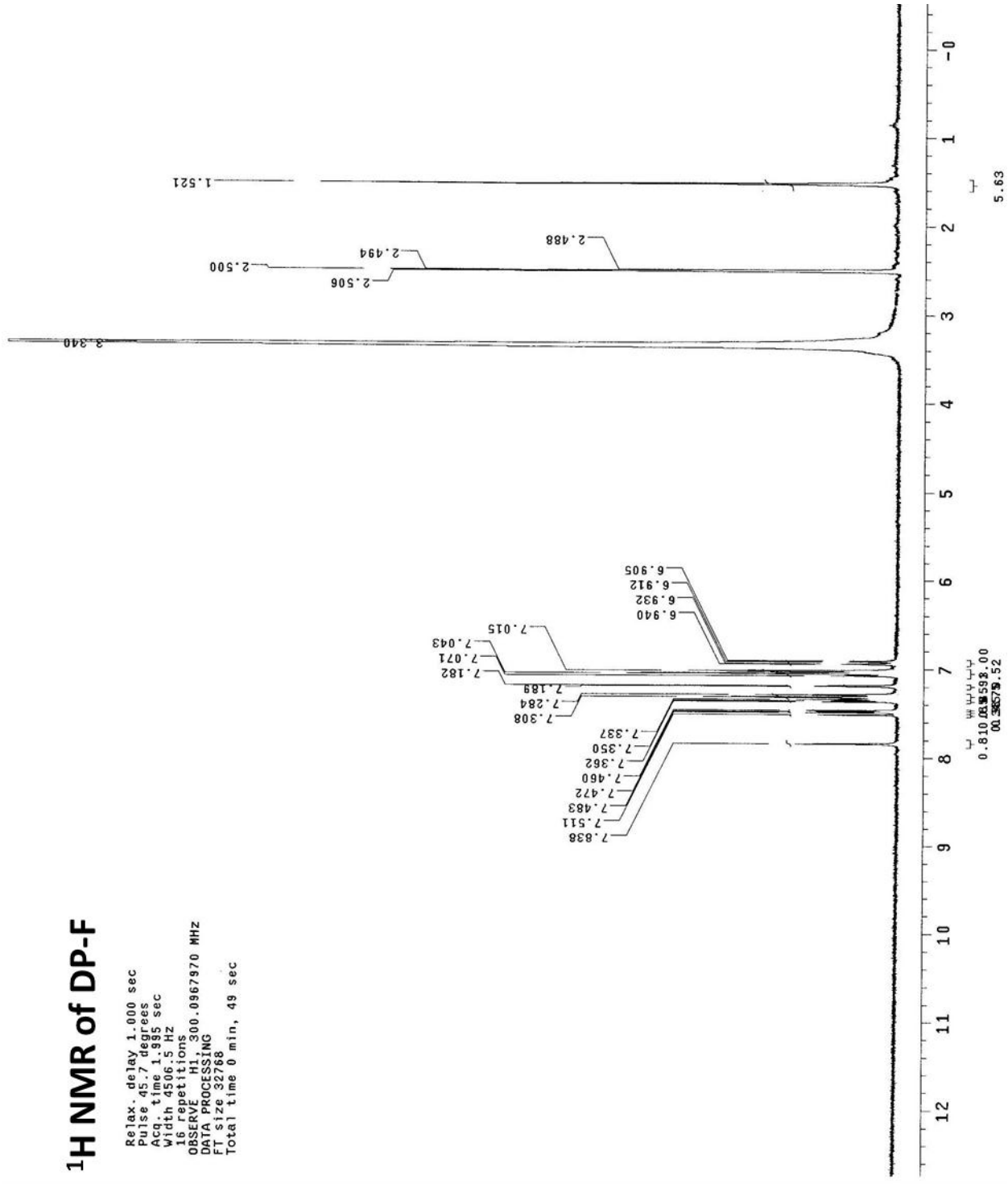
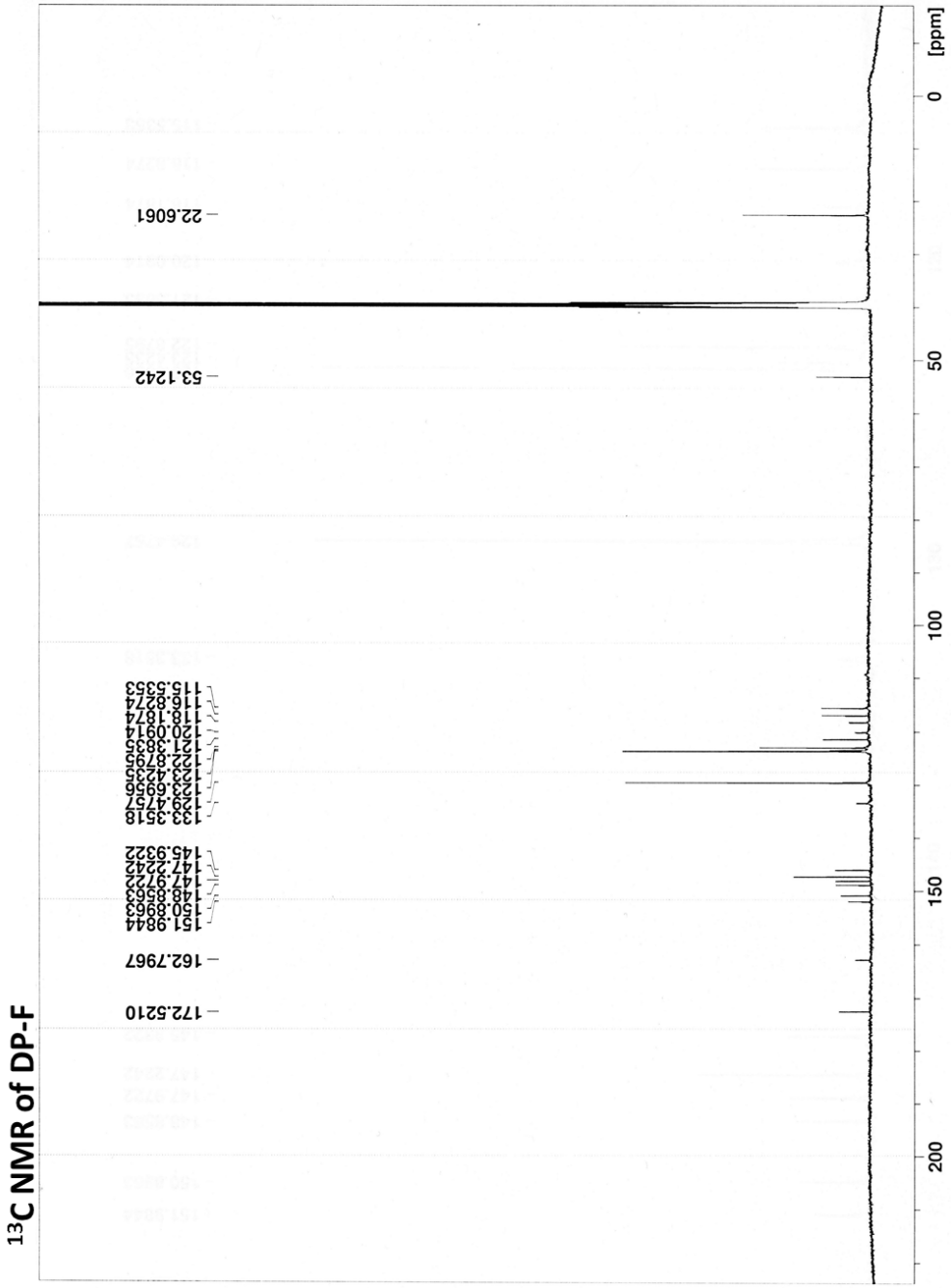


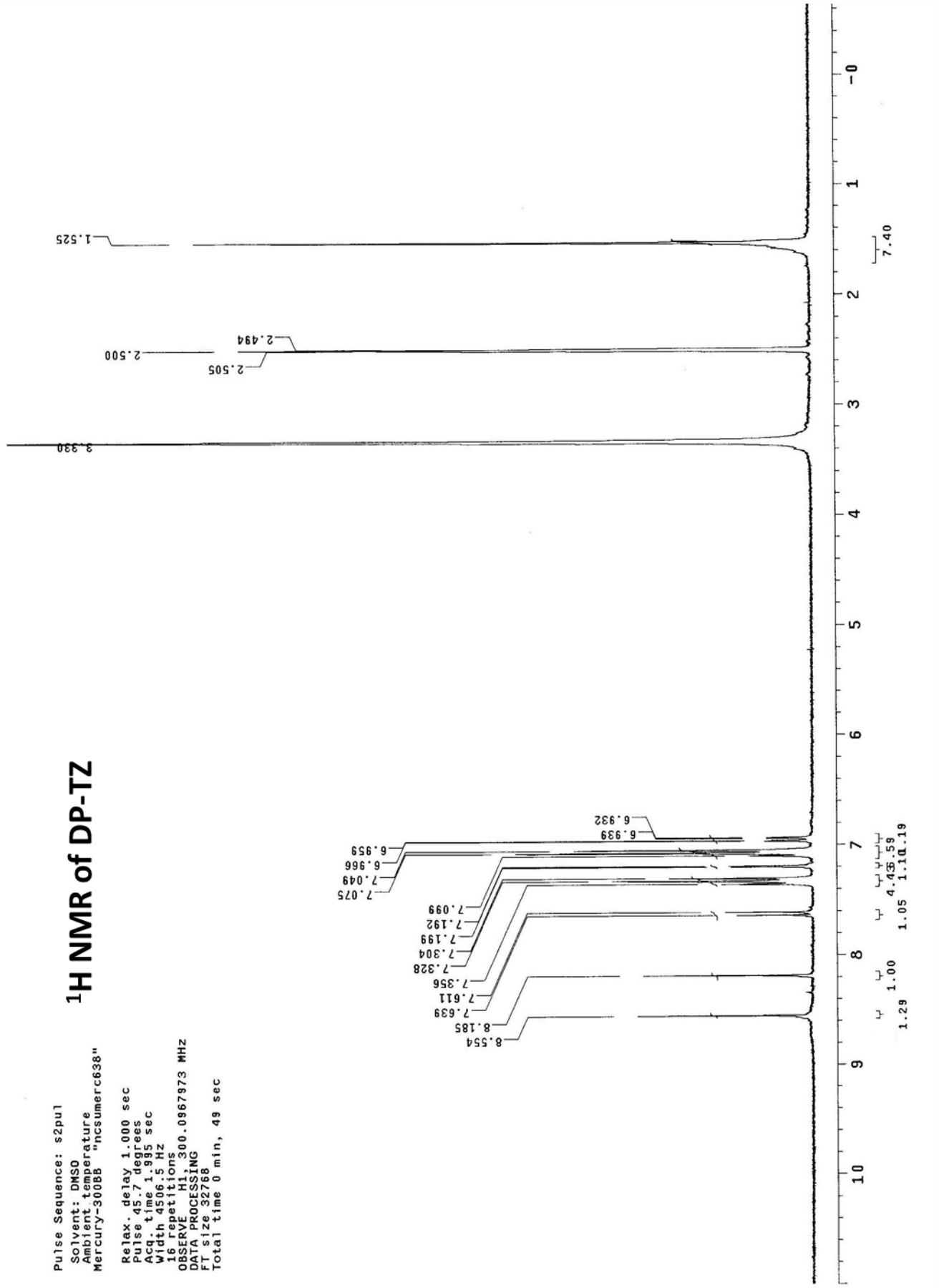
Figure S4. I-V curves of devices based on **DP-F**.

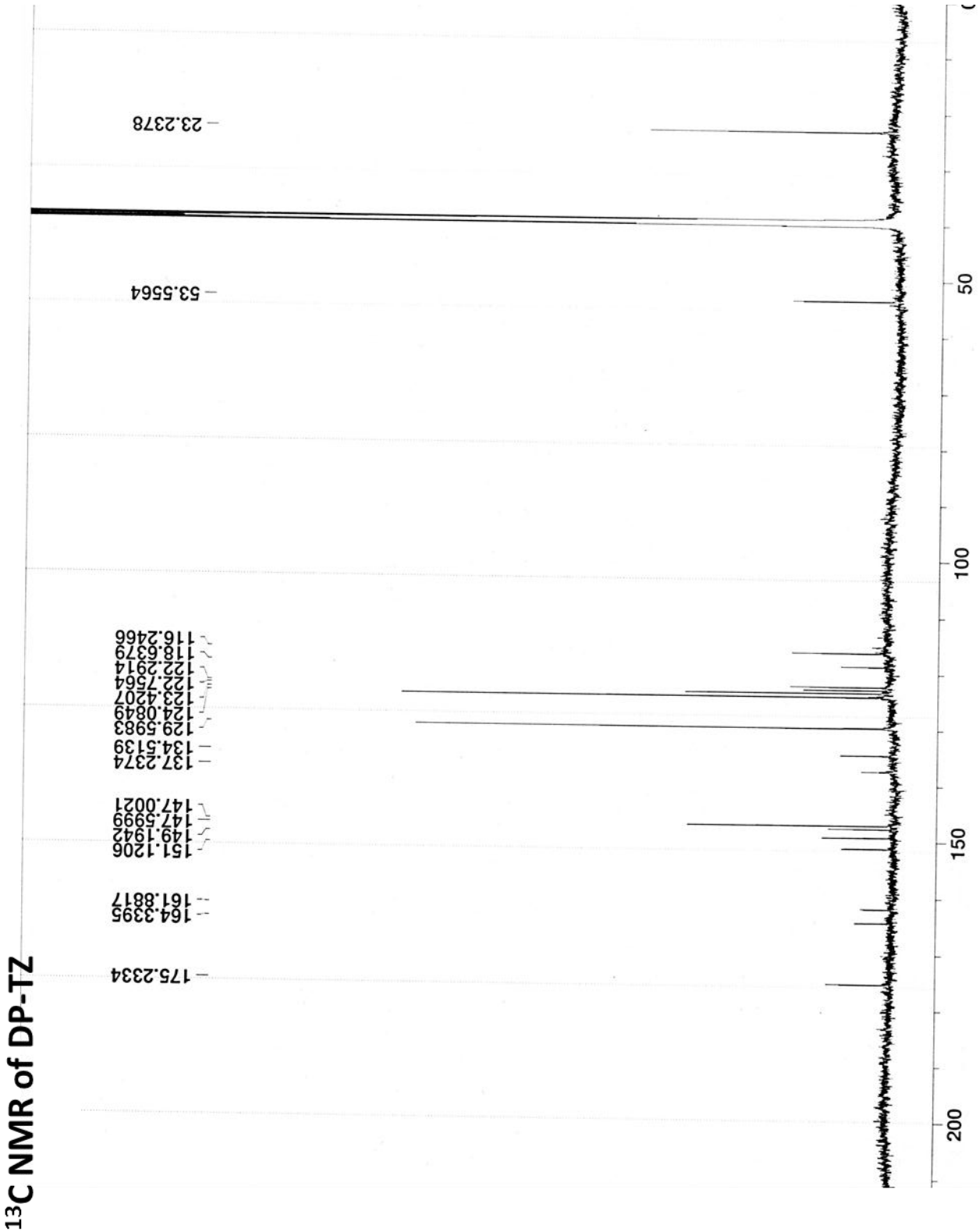
(w/D means the cell with dye (0.3 mM)/DCA (1 mM) loaded TiO_2 anode under same composition of electrolyte).

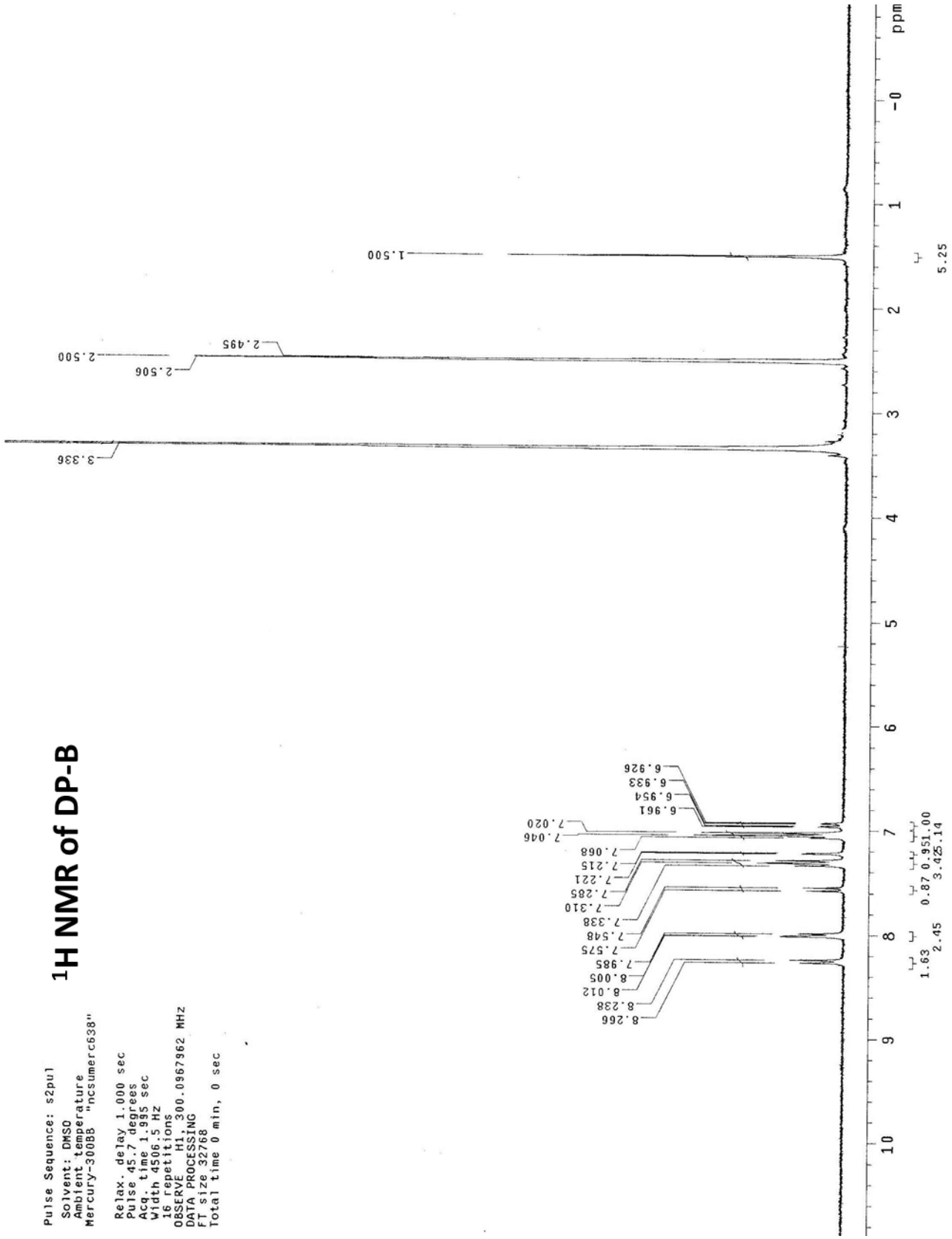
3 ^{1}H NMR and Mass spectra











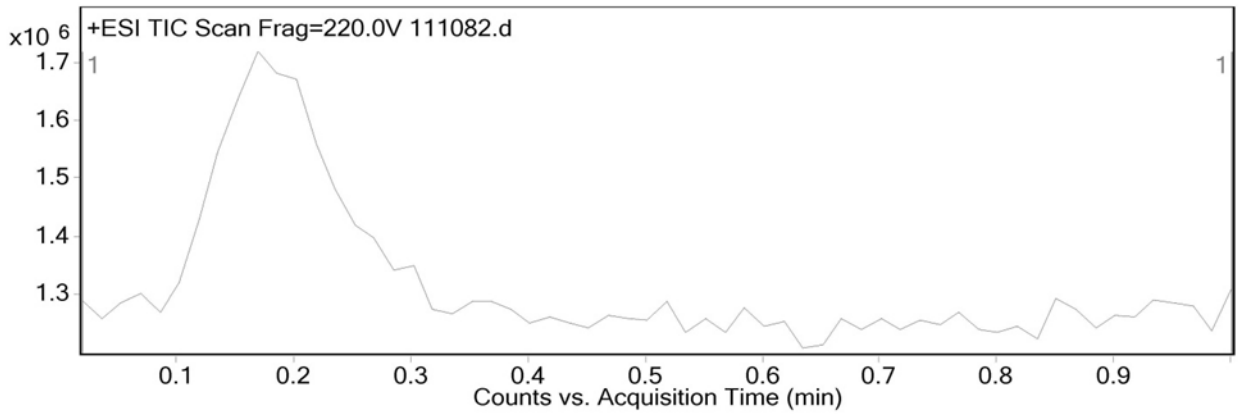
Mass spectrum of DP-F

Instrument Name Agilent Technologies 6210 LC-TOF

IRM Calibration Status Success

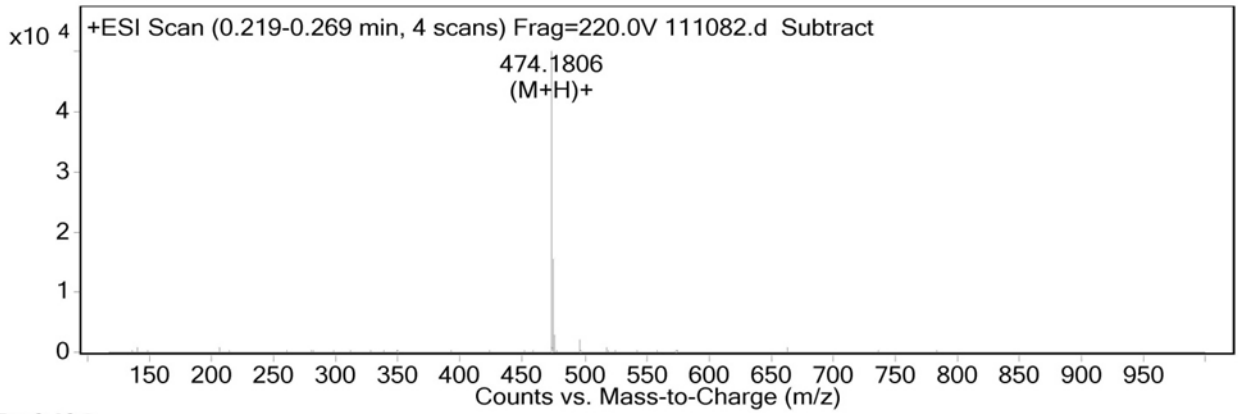
User Chromatograms

Fragmentor Voltage 220 **Collision Energy** 0 **Ionization Mode** Esi



User Spectra

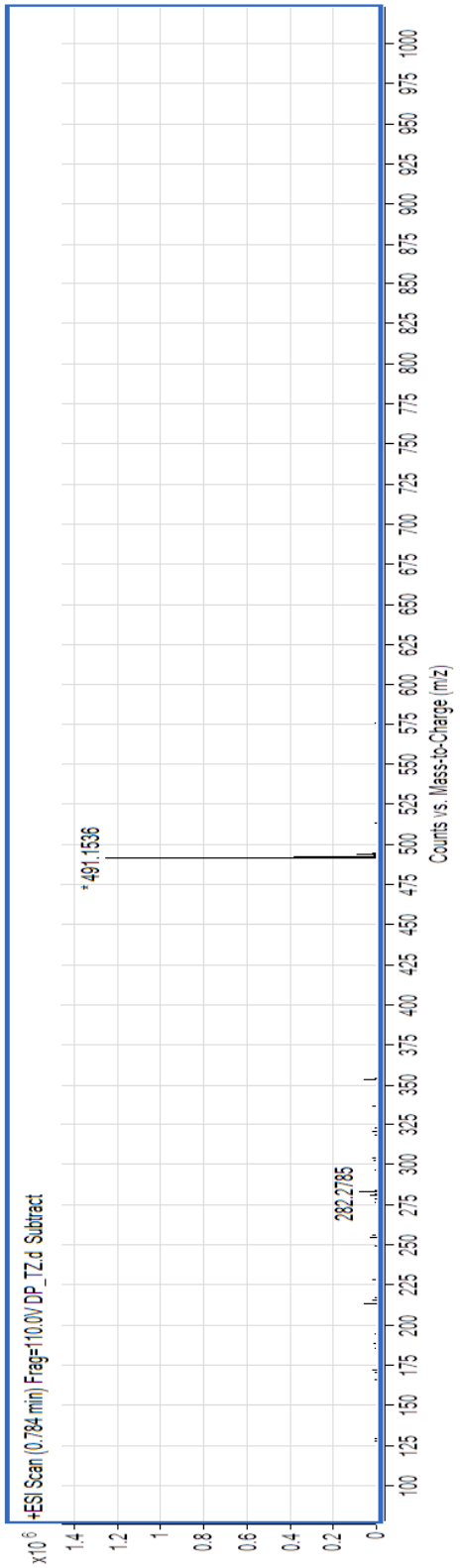
Fragmentor Voltage 220 **Collision Energy** 0 **Ionization Mode** Esi



Peak List

m/z	z	Abund	Formula	Ion
474.1806	1	56227	C30 H24 N3 O3	(M+H)+
475.1839	1	16724	C30 H24 N3 O3	(M+H)+

Mass spectrum of DP-TZ



Mass spectrum of DP-B

Instrument Name Agilent Technologies 6210 LC-TOF

IRM Calibration Status Success

User Chromatograms

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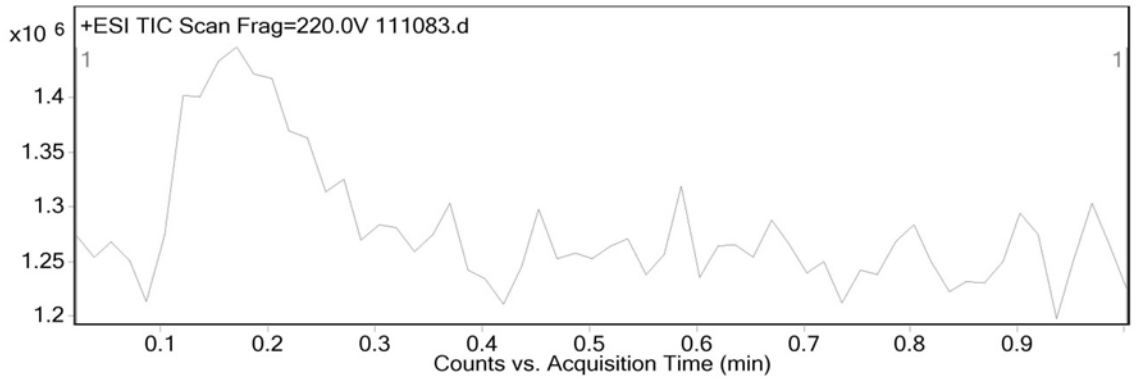
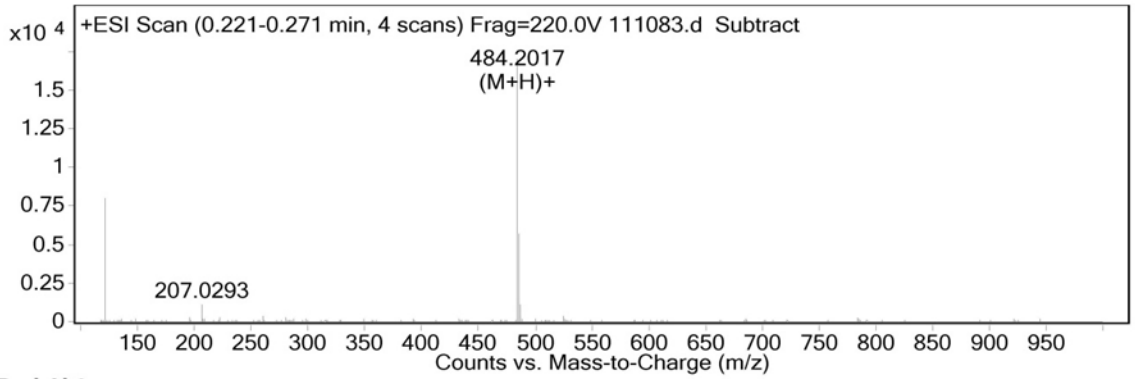


User Spectra

Fragmentor Voltage 220 **Collision Energy** 0 **Ionization Mode** Esi



Peak List

m/z	z	Abund	Formula	Ion
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207.0293		1086		
484.2017	1	17026	C32 H26 N3 O2	(M+H)+
485.2055	1	5726	C32 H26 N3 O2	(M+H)+
486.2149	1	3922	C32 H26 N3 O2	(M+H)+
487.2202	1	1146	C32 H26 N3 O2	(M+H)+

4 References

(1) Komoto, I.; Matsuo, J.-I.; Kobayashi, S. *Top. Catal.* **2002**, *19*, 43.
(2) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *J. Org. Chem.* **1988**, *53*, 1748.