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Supporting Information

Tuning Pentacene Based Dye-Sensitized Solar Cells

Andreas Kunzmann,[a] Marco Gruber,[b] Rubén Casillas,[a] Rik R. Tykwinski,[b,c*] Rubén D. Costa,[a*] and Dirk M. Guldi[a*]

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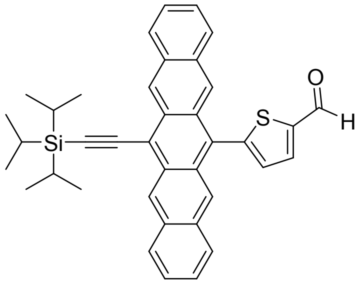
General procedures and methods

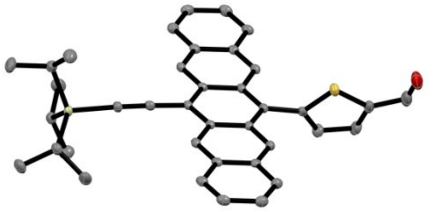
Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium/benzophenone. *i*-Pr_2NH was dried over $CaCl_2$. $MgSO_4 \bullet 2H_2O$ was used as the drying reagent after aqueous (aq) work-up. Saturated (satd) NH_4Cl and brine refer to saturated aqueous solutions of NH_4Cl and NaCl, respectively. Deoxygenated solutions were prepared by bubbling nitrogen through the solution for at least 20 min. All solutions containing pentacene were covered in foil to prevent decomposition. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance (300 and 400) spectrometers at 300 MHz (^1H NMR) and 100 or 75 MHz ($^{13}C\{^1H\}$ NMR), respectively. NMR spectra were referenced to the residual solvent signal (^1H: $CDCl_3$, 7.24 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; ^1H: THF-d_8, 1.72 ppm, 3.58 ppm; ^{13}C: THF-d_8, 25.3 ppm, 67.2 ppm) and recorded at ambient probe temperature. $CDCl_3$ (99.8%, Deutero GmbH) and THF-d_8 (99.5%, Deutero GmbH) were stored over 4 Å molecular sieves. UV/Vis measurements were carried out in CH_2Cl_2 and THF on a Varian Cary 5000 UV/Vis–NIR spectrophotometer at rt with quartz cuvettes having 1 cm path length. Mass spectra were obtained from either a Bruker micro TOF II or Bruker maxis 4G (APPI, ESI) instrument. IR spectra were recorded as solids on a Varian 660-IR spectrometer in ATR-mode. Melting points were measured with an Electrothermal 9100 instrument. TLC analyses were carried out on TLC plates from Macherey-Nagel (ALUGRAM® SIL G/UV254) and visualized via UV-light (264/364 nm). Column chromatography was performed using Silica Gel 60M (Merck).

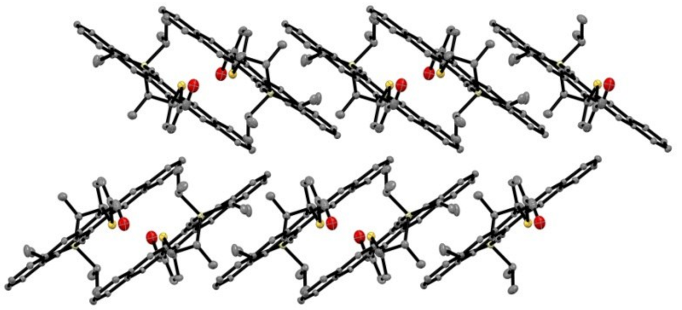
Synthesis

Compound **5** has been obtained by protection of 2-bromo-5-thiophenecarboxaldehyde as the cyclic acetal according to a literature procedure.[1] The synthesis of compounds **1**,[4] **2**,[4]**6**,[2] and **8**,[3] and have been described elsewhere.

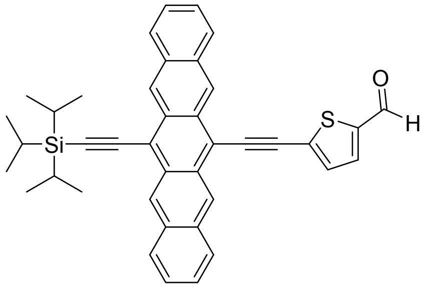


Compound **3**: To a solution of **5** (2.01 g, 8.56 mmol) in dry THF (100 mL) at –78 °C was added *n*-BuLi (2.5 M in hexanes, 3.3 mL, 8.3 mmol). After stirring for 30 min at –78 °C, **6** (1.40 g, 2.85 mmol) was added as a solid. The resulting mixture was warmed to rt and stirred for 16 h. After quenching the reaction *via* the addition of satd aq NH_4Cl, the mixture was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic phases were washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The crude intermediate **7** was obtained as dark brown oil and subjected to reductive aromatization without further purification. Therefore, the residue was dissolved in THF (50 mL) and $SnCl_2 \cdot 2H_2O$ (2.00 g, 8.85 mmol) and 10% aq sulfuric acid (5.0 mL) were added. To minimize light exposure, the flask was wrapped in aluminum foil. The reaction mixture was stirred for 3 h at rt. After quenching the reaction via the addition of satd aq NH_4Cl, the mixture was extracted with CH_2Cl_2 (2 x 100 mL). The organic phases were combined and washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The residue was passed through a pad of silica (CH_2Cl_2/hexanes, 3:1). After removal of the solvent, the blue residue was purified by recrystallization from CH_2Cl_2/MeOH at –18 °C to obtain **3** (1.24 g, 76%) as a deep blue crystalline solid. Mp 387 °C (decomp). R_f = 0.74 (CH_2Cl_2). UV/Vis (CH_2Cl_2) λ_{max} (ε) 270 (29 600), 309 (370 000), 347 (10 300), 410 (2 000), 436 (2 800), 538 (4 600), 577 (11 500), 624 (19 000) nm. IR (ATR): 3042 (w), 2940 (m), 2857 (m), 2124 (w), 1667 (s), 1453 (m), 1360 (m), 1209 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 10.14 (s, 1H), 9.35 (s, 2H), 8.36 (s, 2H), 8.10 (d, J = 3.6 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 3.6 Hz, 1H), 7.40–7.30 (m, 4H), 1.40–1.35 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.0, 149.9, 145.3, 136.7, 132.02, 131.96, 131.6, 130.4, 129.1, 128.52, 128.49, 127.4, 126.14, 126.07, 126.03, 125.0, 120.0, 107.1, 104.4, 19.0, 11.6. APPI HRMS (CH_3CN/CH_2Cl_2/THF) *m/z* calcd for $C_{38}H_{37}OSSi$ ($[M + H]^+$), 569.2329, found 569.2330.

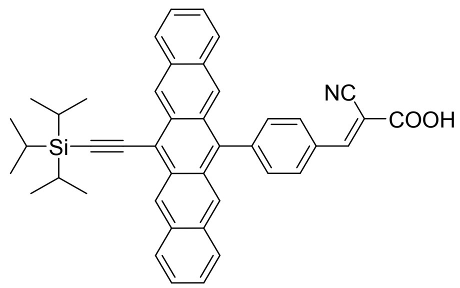




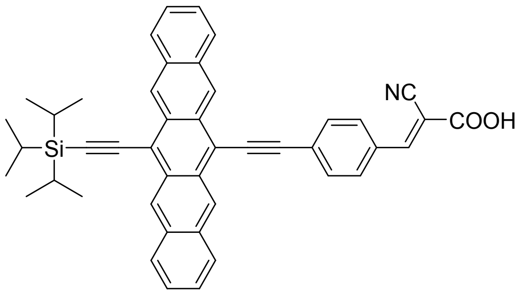
A crystal of **3** suitable for X-ray crystallographic analysis has been grown from a solution of **3** in CH_2Cl_2/MeOH (3:1) by slow evaporation at rt. X-ray data for **3** ($C_{38}H_{36}OSSi \bullet CH_2Cl_2$), F_w = 653.74; monoclinic crystal system; space group $P2_1/c$; a = 11.8379(3) Å, b = 16.8043(5) Å, c = 17.9233(4) Å; β = 106.646(3)°, V = 3416.03(16) Å^3; Z = 4; $\rho_{(calcd)}$ = 1.271 g cm^{-3}; $2\theta_{max}$ = 123.8°; μ = 2.840 mm^{-1}; T = 173.0(1) K; total data collected = 8398; R_1 = 0.0635 [5117 independent reflections with $I > 2\sigma(I)$]; ωR_2 = 0.1854 for 5117 data, 403 variables, and 0 restraints; largest difference, peak and hole = 0.97 and –0.88 e Å^{-3}. CCDC 1456574



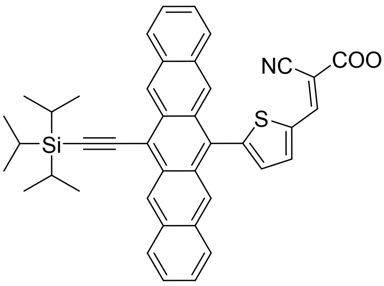
Compound **4:** Compound **8** (1.55 g, 2.85 mmol) and 5-bromothiophene-2-carbaldehyde (665 mg, 0.412 mL, 3.48 mmol) were dissolved in a mixture of dry, deoxygenated THF (35 mL) and *i*-Pr_2NH (12 mL). $PdCl_2(PPh_3)_2$ (100 mg, 0.142 mmol) and CuI (40 mg, 0.21 mmol) were added and the reaction mixture stirred for 16 h at reflux. The reaction was quenched by addition of satd aq NH_4Cl and the resulting solution extracted with CH_2Cl_2 (2 x 100 mL). The organic phase was washed with satd aq NH_4Cl (100 mL), H_2O (100 mL), and brine (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude intermediate **9** was obtained as yellow-brown foamy residue and subjected to reductive aromatization without further purification. Therefore, the residue was dissolved in THF (50 mL) and $SnCl_2 \bullet 2H_2O$ (2.00 g, 8.85 mmol) and 10% aq sulfuric acid (5.0 mL) were added. The mixture was stirred for 3 h at rt. To minimize light exposure, the flask was wrapped in aluminum foil. The reaction was quenched *via* the addition of satd aq NH_4Cl and the mixture extracted with CH_2Cl_2 (2 x 100 mL). The organic phases were washed with H_2O (100 mL) and brine (100 mL), and dried ($MgSO_4$). After filtration and concentration, a dark green residue was obtained. The residue was dissolved in CH_2Cl_2 (50 mL), poured onto a pad of silica, and eluted with CH_2Cl_2. Prepurification was achieved by precipitation from a concentrated CH_2Cl_2 solution by the addition of MeOH and concentration of this mixture at 50 °C. The precipitate was filtered and further purified by column chromatography (silica gel, CH_2Cl_2) to obtain pure **4** (1.38 g, 82%) as a green powder. Mp 362 °C (decomp). $R_f = 0.74$ (CH_2Cl_2). UV/Vis (CH_2Cl_2) λ_{max} (ε) 272 (28 100), 314 (269 000), 390 (15 400), 441 (6 200), 409 (23 200), 617 (14 300), 668 (23 400) nm. IR (ATR): 3044 (w), 2941 (m), 2857 (m), 2169 (w), 2123 (w), 1659 (s), 1452 (s), 1219 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.95 (s, 1H), 9.21 (s, 2H), 8.97 (s, 2H), 7.99–7.96 (m, 2H), 7.90–7.87 (m, 2H), 7.78 (d, J = 3.9 Hz, 1H), 7.55 (d, J = 3.9 Hz, 1H), 7.43–7.38 (m, 4H), 1.39–1.35 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.3, 144.2, 136.2, 132.9, 132.5, 132.4, 132.2, 130.3, 130.0, 128.6, 128.5, 126.6, 126.4, 126.1, 125.3, 120.0, 115.8, 108.3, 104.5, 96.9, 96.6, 19.0, 11.6. ESI HRMS (CH_2Cl_2/THF) *m/z* calcd for $C_{40}H_{37}OSSi$ ($[M + H]^+$), 593.2329, found 593.2330.



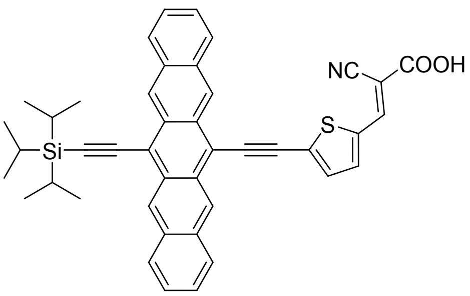
Compound **DPV1:** To a solution of **1** (281 mg, 0.500 mmol) and cyanoacetic acid (425 mg, 5.00 mmol) in deoxygenated $CHCl_3$ (75 mL) was added piperidine (298 mg, 0.345 mL, 3.50 mmol). The flask was wrapped in aluminum foil to minimize light exposure and the mixture stirred for 16 h at reflux. After allowing to cool to rt, the reaction mixture was poured into 1M aq HCl (50 mL) and extracted with toluene (2 x 100 mL). The combined organic phases were washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. Ultrasonication in pentane for 10 min, filtration, and drying *in vacuo* gave the desired product **DPV1** (251 mg, 80%) as a greyish-blue solid. Mp 291 °C (decomp). R_f = 0.18 (CH_2Cl_2/MeOH, 10:1). UV/Vis (THF) λ_{max} (ε) 309 (305 400), 348 (13 400), 434 (4 100), 544 (5 800), 577 (11 200), 623 (15 300) nm. IR (ATR): 3039 (w), 2938 (m), 2860 (m), 2131 (w), 1696 (m), 1591 (s), 1375 (m), 1280 (m) cm^{-1}. ^1H NMR (300 MHz, THF-d_8): δ 9.39 (s, 2H), 8.53 (s, 1H), 8.45 (d, J = 8.1 Hz, 2H), 8.32 (s, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.1 Hz, 4H), 7.41–7.28 (m, 4H), 1.45–1.40 (m, 21H); the acidic carboxyl proton is not observed. ^{13}C NMR (75 MHz, THF-d_8): δ 163.8, 154.2, 145.0, 138.0, 133.5, 133.1, 132.8, 132.2, 131.7, 129.5, 129.05, 128.98, 127.1, 126.63, 126.59, 126.4, 118.5, 116.4, 106.3, 105.9, 105.1, 19.4, 12.6 (one signal coincident or not observed). APPI HRMS (CH_3CN/CH_2Cl_2/THF) *m/z* calcd for $C_{43}H_{40}NO_2Si$ ([M + H]$^+$), 630.2823, found 630.2828.



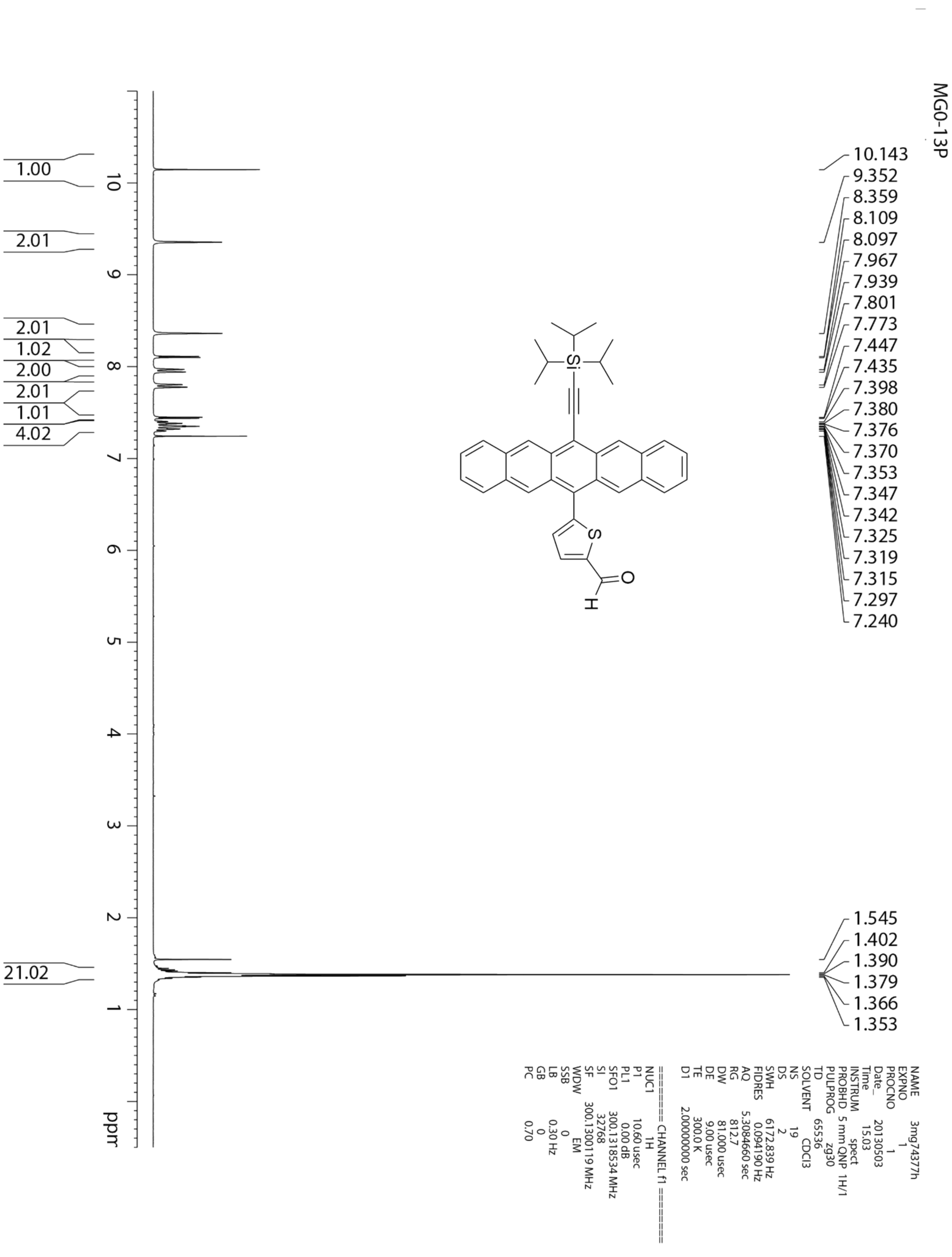
Compound **DPV2**: To a solution of **2** (235 mg, 0.400 mmol) and cyanoacetic acid (340 mg, 4.00 mmol) in deoxygenated $CHCl_3$ (60 mL) was added piperidine (238 mg, 0.277 mL, 2.80 mmol). The flask was wrapped in aluminum foil to minimize light exposure and the mixture stirred for 16 h at reflux. After allowing to cool to rt, the reaction mixture was poured into 1M aq HCl (50 mL) and extracted with toluene (2 x 100 mL). The combined organic phases were washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. Ultrasonication in pentane for 10 min, filtration, and drying *in vacuo* gave the desired product **DPV2** (194 mg, 74%) as a dark green solid. Mp 282 °C (decomp). $R_f = 0.13$ (CH_2Cl_2/MeOH, 10:1). UV/Vis (THF) λ_{max} (ε) 272 (30 400), 312 (231 000), 347 (18 300), 402 (20 400), 571 (5 700), 611 (14 600), 665 (25 000) nm. IR (ATR): 3039 (w), 2940 (m), 2861 (m), 2173 (w), 2122 (w), 1693 (s), 1575 (vs), 1417 (m), 1281 (s) cm^{-1}. ^1H NMR (300 MHz, THF-d_8): δ 9.32 (s, 4H), 8.36 (s, 1H), 8.25 (d, $J = 8.4$ Hz, 2H), 8.15–8.09 (m, 4H), 7.98–7.94 (m, 2H), 7.48–7.43 (m, 4H), 1.45–1.38 (m, 21H); the acidic carboxyl proton is not observed. ^{13}C NMR (100 MHz, THF-d_8): δ 163.6, 153.4, 133.6, 133.5, 133.2, 133.1, 131.9, 131.4, 131.1, 129.5, 129.2, 128.6, 127.32, 127.28, 127.0, 126.7, 119.8, 118.2, 116.3, 108.4, 105.8, 105.4, 105.3, 92.1, 19.4, 12.6. APPI HRMS (CH_3CN, CH_2Cl_2/THF) *m/z* calcd for $C_{45}H_{40}NO_2Si$ ($[M + H]^+$), 654.2823, found 654.2826.



Compound **DPV3**: To a solution of **3** (284 mg, 0.500 mmol) and cyanoacetic acid (425 mg, 5.00 mmol) in deoxygenated $CHCl_3$ (75 mL) was added piperidine (298 mg, 0.347 mL, 3.50 mmol). The flask was wrapped in aluminum foil to minimize light exposure and the mixture stirred for 16 h at reflux. After allowing to cool to rt, the reaction mixture was poured into 1M aq HCl (50 mL) and extracted with toluene (2 x 100 mL). The combined organic phases were washed with H_2O (100 mL) and brine (100 mL), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. Ultrasonication in pentane for 10 min, filtration, and drying *in vacuo* gave the desired product **DPV3** (273 mg, 86%) as a blue-greyish solid. Mp 320 °C (decomp). R_f = 0.20 (CH_2Cl_2/MeOH, 10:1). UV/Vis (THF) λ_{max} (ε) 270 (25 000), 308 (302 000), 345 (27 200), 538 (4 500), 578 (11 200), 625 (18 200) nm. IR (ATR): 3041 (w), 2938 (m), 2861 (m), 2126 (m), 1690 (s), 1572 (vs), 1419 (m), 1327 (m), 1272 (s) cm^{-1}. ^1H NMR (300 MHz, THF-d_8): δ 9.38 (s, 2H), 8.63 (s, 1H), 8.51 (s, 2H), 8.31 (d, J = 3.9 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 3.9 Hz, 1H), 7.42–7.30 (m, 4H), 1.45–1.40 (m, 21H); the acidic carboxyl proton is not observed. ^{13}C NMR (75 MHz, THF-d_8): δ 163.9, 149.6, 146.6, 139.3, 138.7, 133.20, 133.15, 133.1, 131.4, 130.2, 129.4, 129.05, 128.98, 127.3, 126.9, 126.5, 126.2, 120.3, 116.5, 107.5, 105.7, 101.4, 19.4, 12.6. APPI HRMS (CH_3CN, CH_2Cl_2/THF) *m/z* calcd for $C_{41}H_{38}NO_2SSi$ ($[M + H]^+$), 636.2387, found 636.2391.



Compound **DPV4**: To a solution of **4** (300 mg, 0.500 mmol) and cyanoacetic acid (430 mg, 5.06 mmol) in deoxygenated $CHCl_3$ (75 mL) was added piperidine (300 mg, 349 mL, 3.52 mmol). The flask was wrapped in aluminum foil to minimize light exposure and the mixture stirred for 3 h at reflux. After cooling to rt, the reaction mixture was poured into 1M aq HCl (200 mL) and extracted with CH_2Cl_2/THF, 9:1 (400 mL). The combined organic phases were washed with H_2O (200 mL) and brine (200 mL), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. Recrystallization from THF/pentane at –18 °C yielded the desired product **DPV4** (273 mg, 83%) as a dark green solid. Mp 307 °C (decomp). R_f = 0.12 (CH_2Cl_2/MeOH, 10:1). UV/Vis (THF) λ_{max} (ε) 271 (32 700), 313 (145 000), 347 (19 000), 442 (19 400), 628 (11 800), 677 (18 100) nm. IR (ATR): 3043 (w), 2939 (m), 2861 (m), 2150 (w), 2142 (w), 1688 (m), 1564 (vs), 1410 (s), 1252 (s), 1213 (vs) cm^{-1}. ^{1}H NMR (300 MHz, THF-d_8): δ 9.30 (s, 2H), 9.21 (s, 2H), 8.46 (s, 1H), 8.12–8.09 (m, 2H), 7.98–7.94 (m, 3H), 7.81 (d, J = 3.9 Hz, 1H), 7.49–7.42 (m, 4H), 1.44–1.39 (m, 21H); the acidic carboxyl proton is not observed. ^{13}C NMR (75 MHz, THF-d_8): δ 163.8, 146.0, 139.0, 138.9, 134.2, 133.5, 133.3, 132.4, 131.0, 130.6, 129.4, 129.2, 127.3, 127.2, 127.0, 126.3, 120.1, 117.1, 116.6, 108.6, 105.7, 101.6, 98.3, 97.9, 19.4, 12.6. ESI HRMS (CH_3CN, toluene/MeOH) *m/z* calcd for $C_{43}H_{36}NO_2SSi$ ([M – H]), 658.2242, found 658.2235.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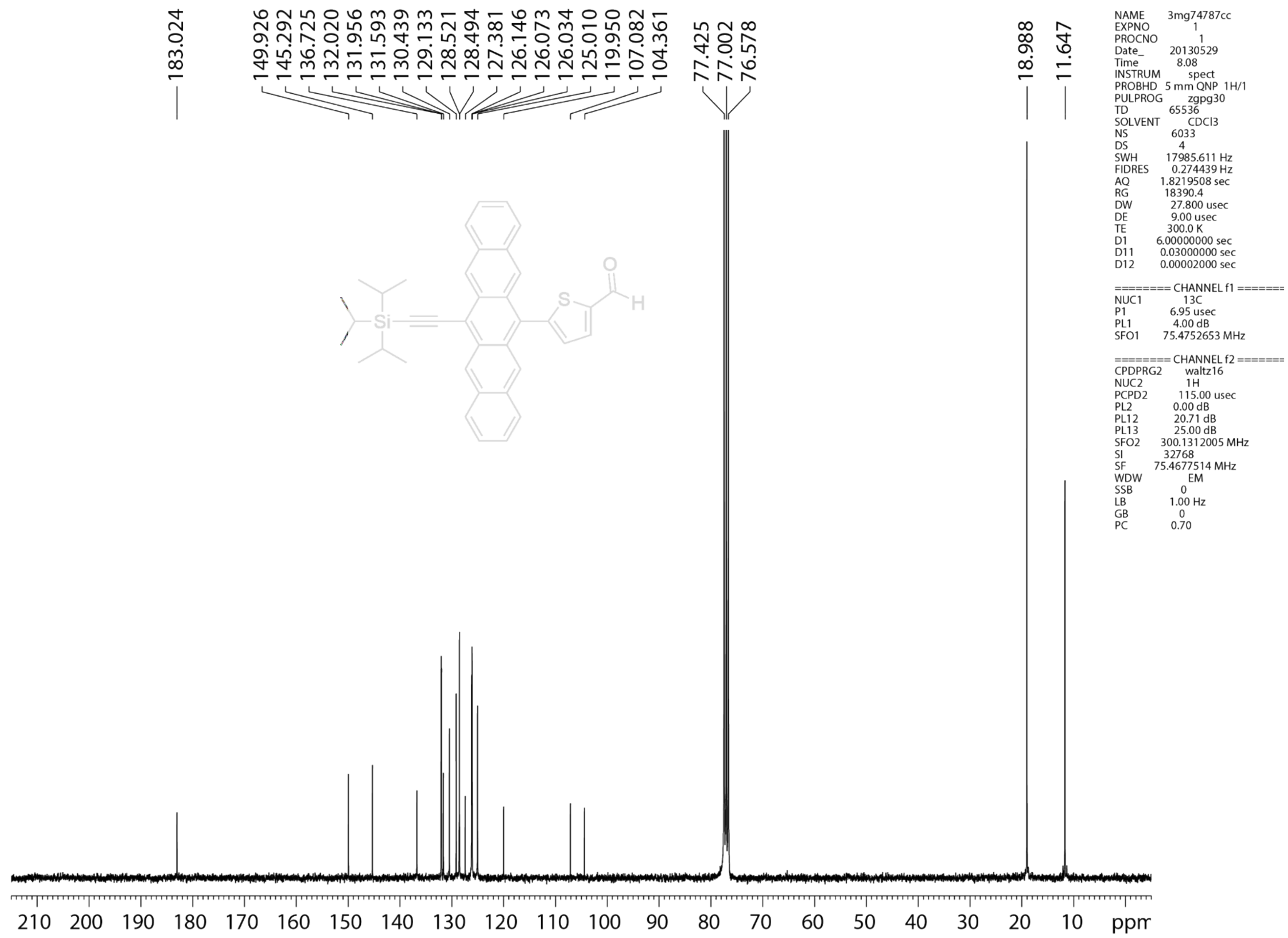

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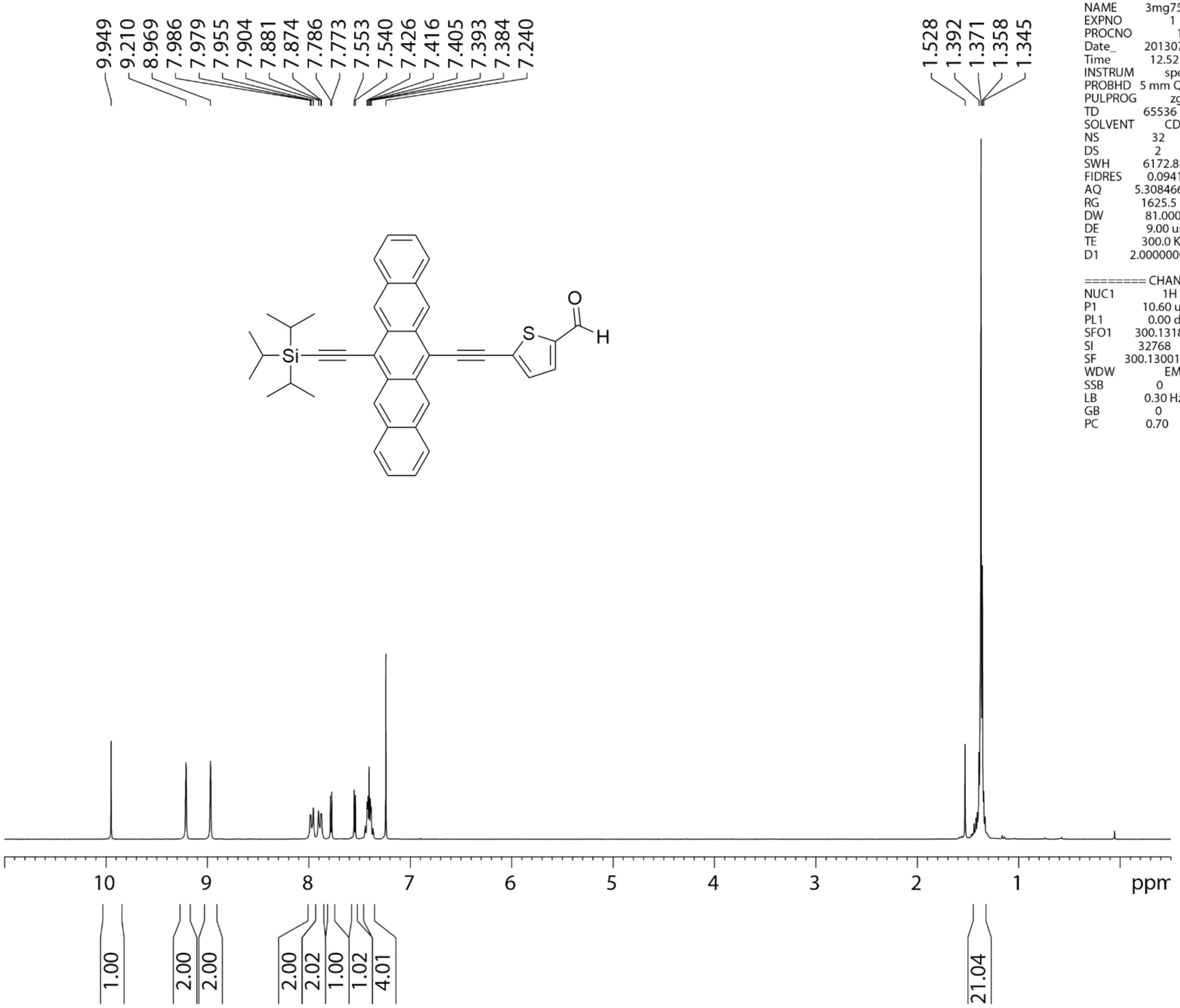

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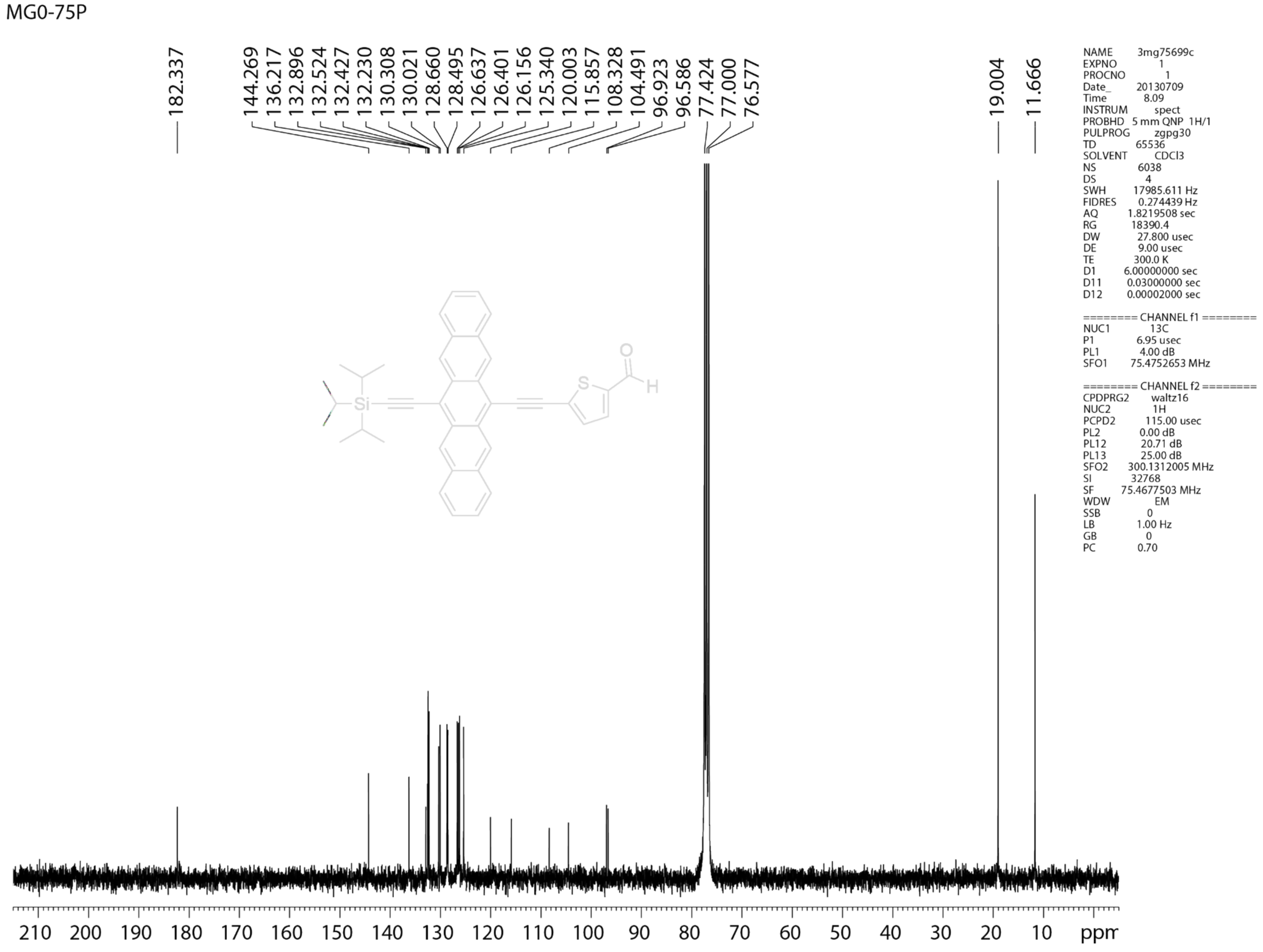
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H
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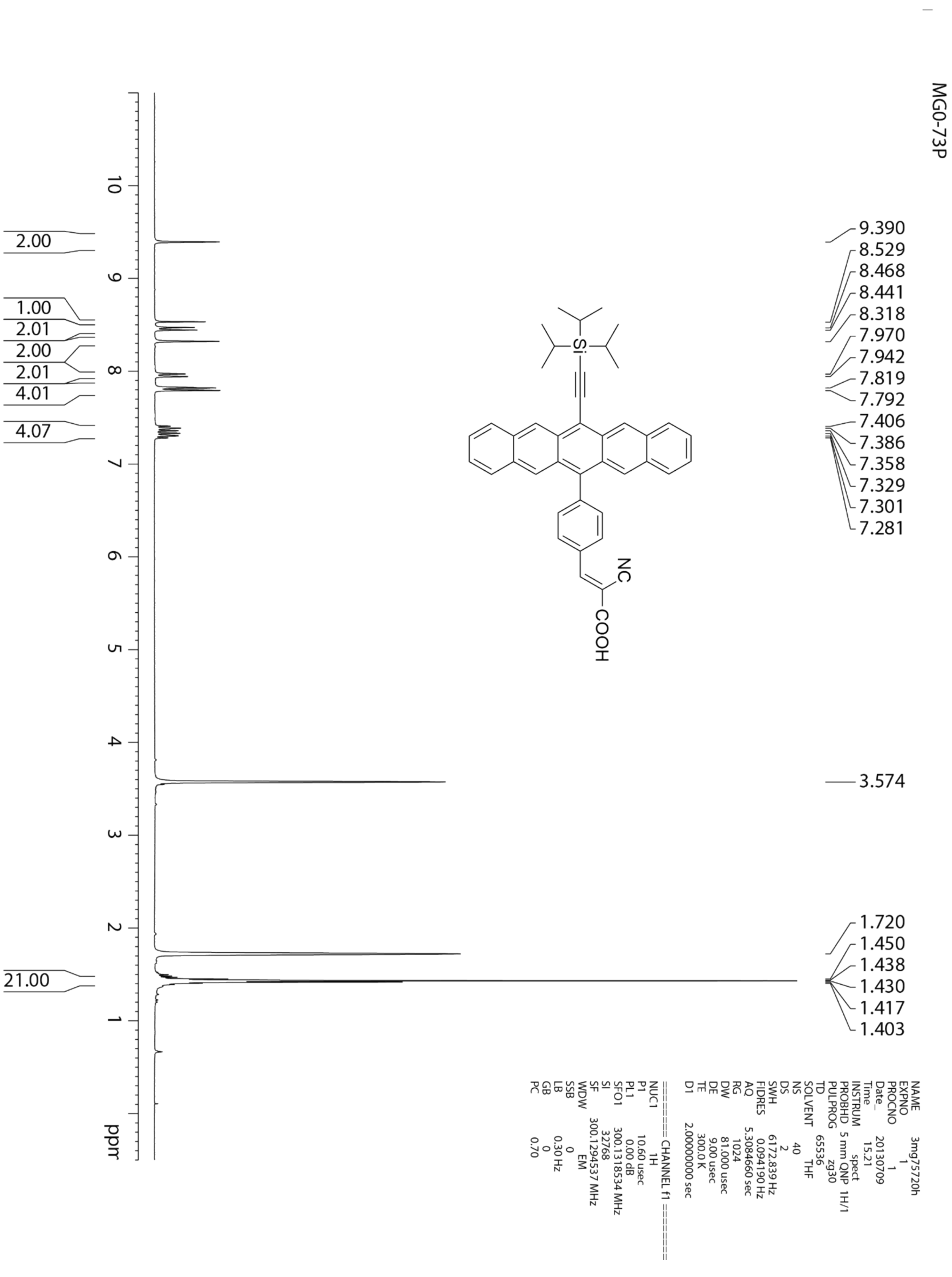
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1.00
2.01
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PROCNO 1
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DE 9.00 usec
TE 300.0 K
D1 2.00000000 sec
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LB 0.30 Hz
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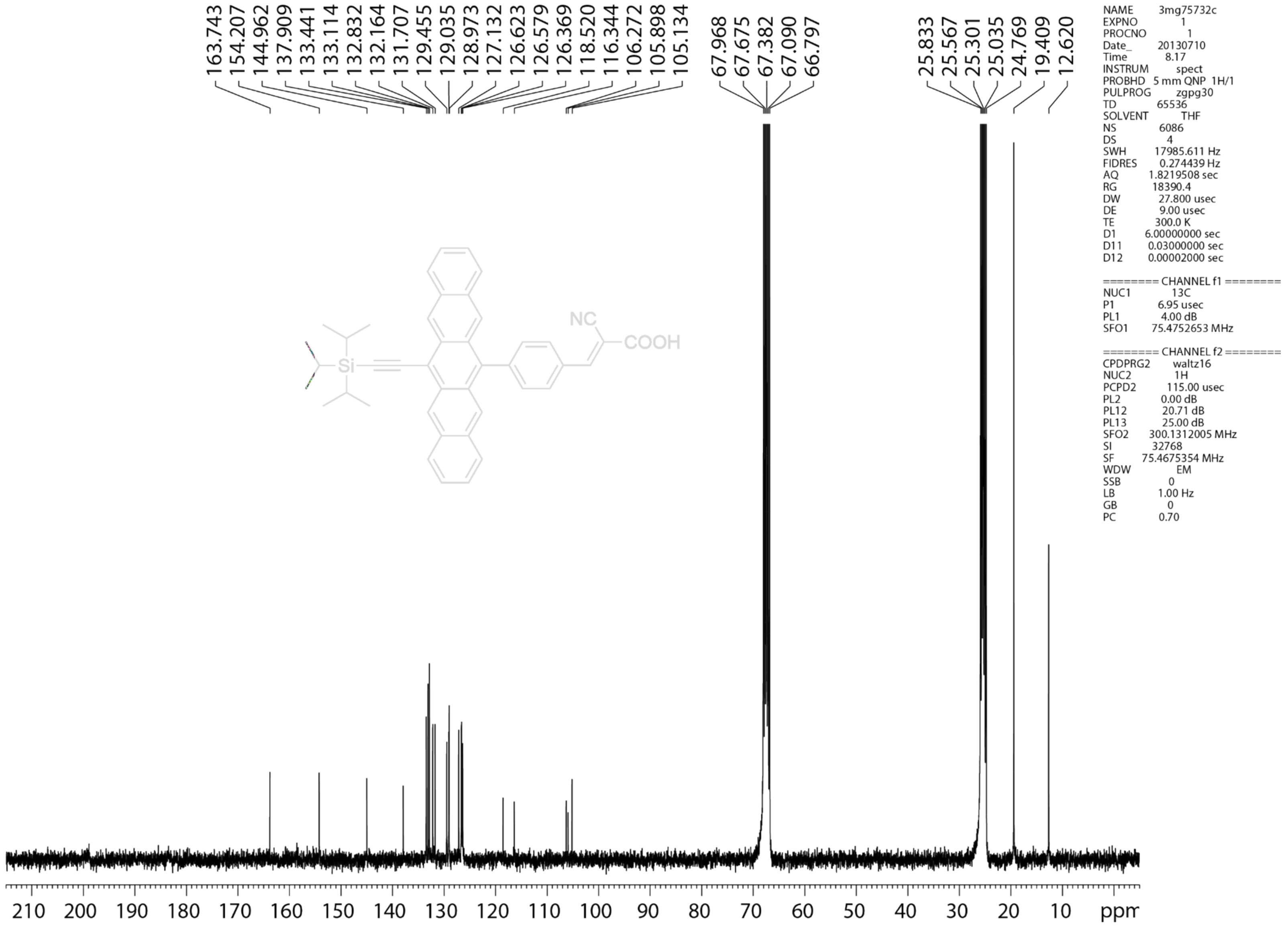
MG0-73P



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FIDRES   0.274439 Hz
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RG          18390.4
DW       27.800 usec
DE         9.00 usec
TE          300.0 K
D1    6.00000000 sec
D11   0.03000000 sec
D12   0.00002000 sec

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SFO1  75.4752653 MHz

======== CHANNEL f2 ========
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NUC2             1H
PCPD2   115.00 usec
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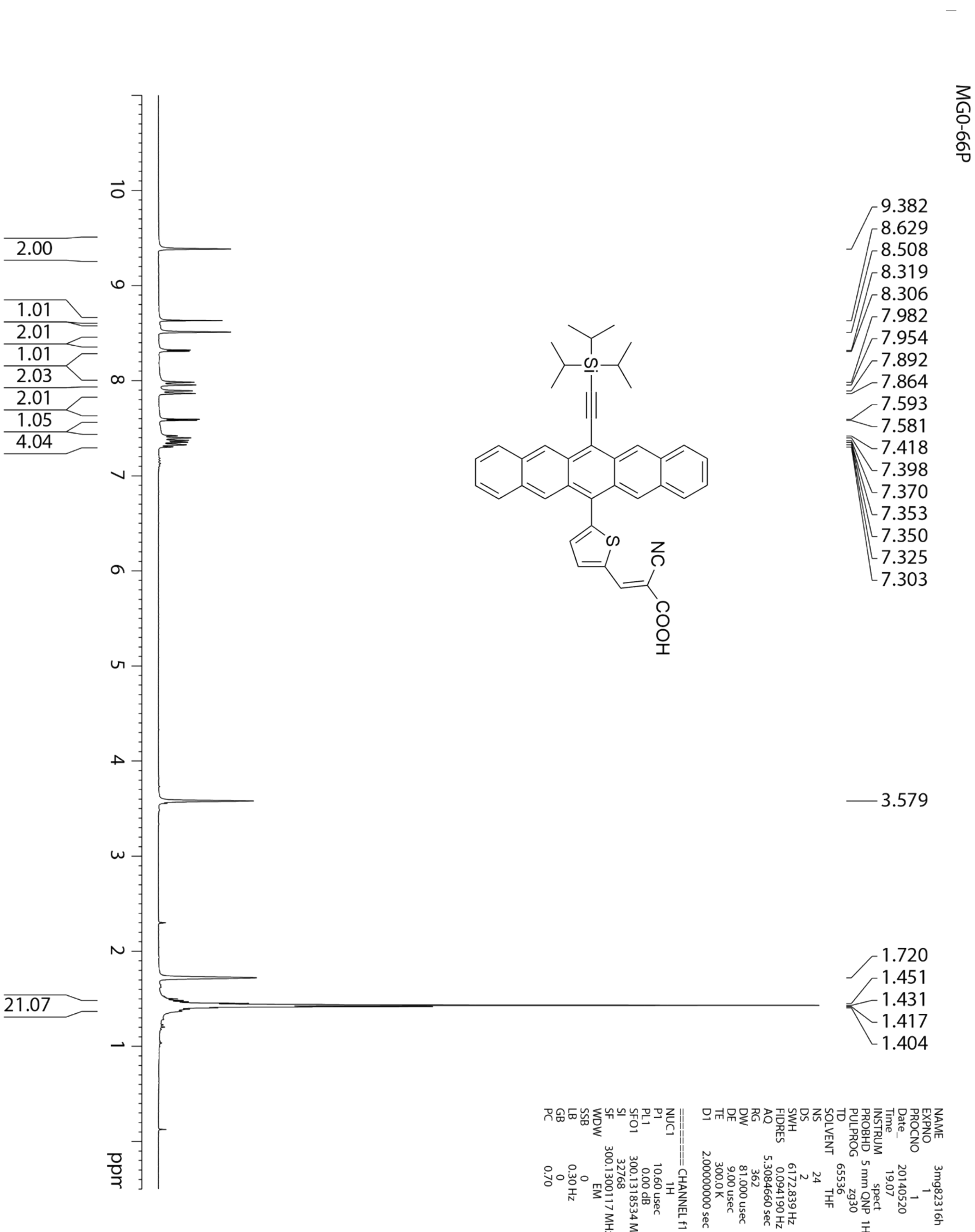
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PROCNO 1
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TE 300.0 K
D1 2.00000000 sec
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PL1 0.00 dB
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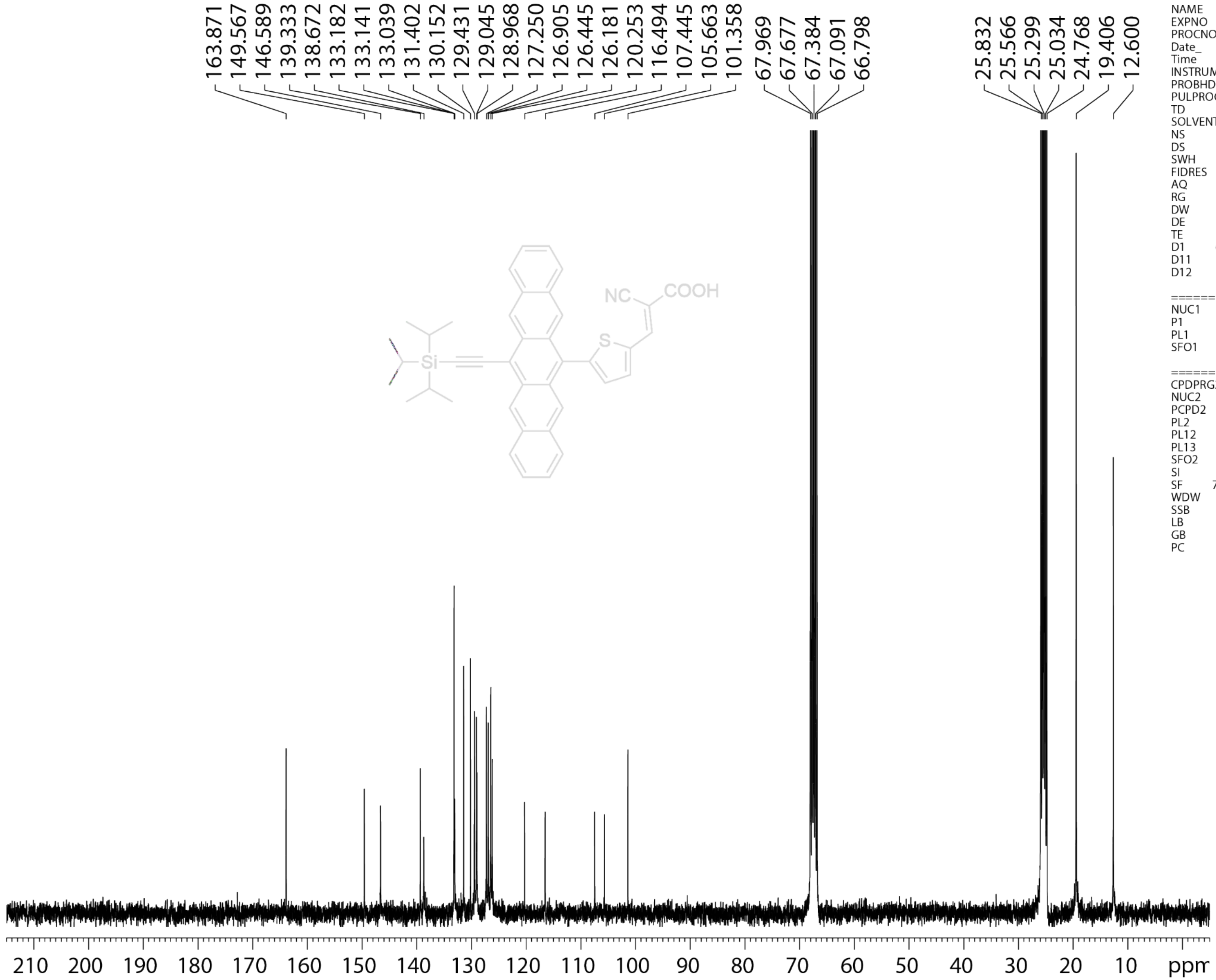

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SOLVENT           THF
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FIDRES      0.274439 Hz
AQ         1.8219508 sec
RG             46341
DW            27.800 usec
DE              9.00 usec
TE             300.0 K
D1        6.00000000 sec
D11       0.03000000 sec
D12       0.00002000 sec

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P1              18.00 usec
PL1              4.00 dB
SFO1      75.4752653 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2          115.00 usec
PL2              0.00 dB
PL12            20.00 dB
PL13            23.00 dB
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LB                1.00 Hz
GB                   0
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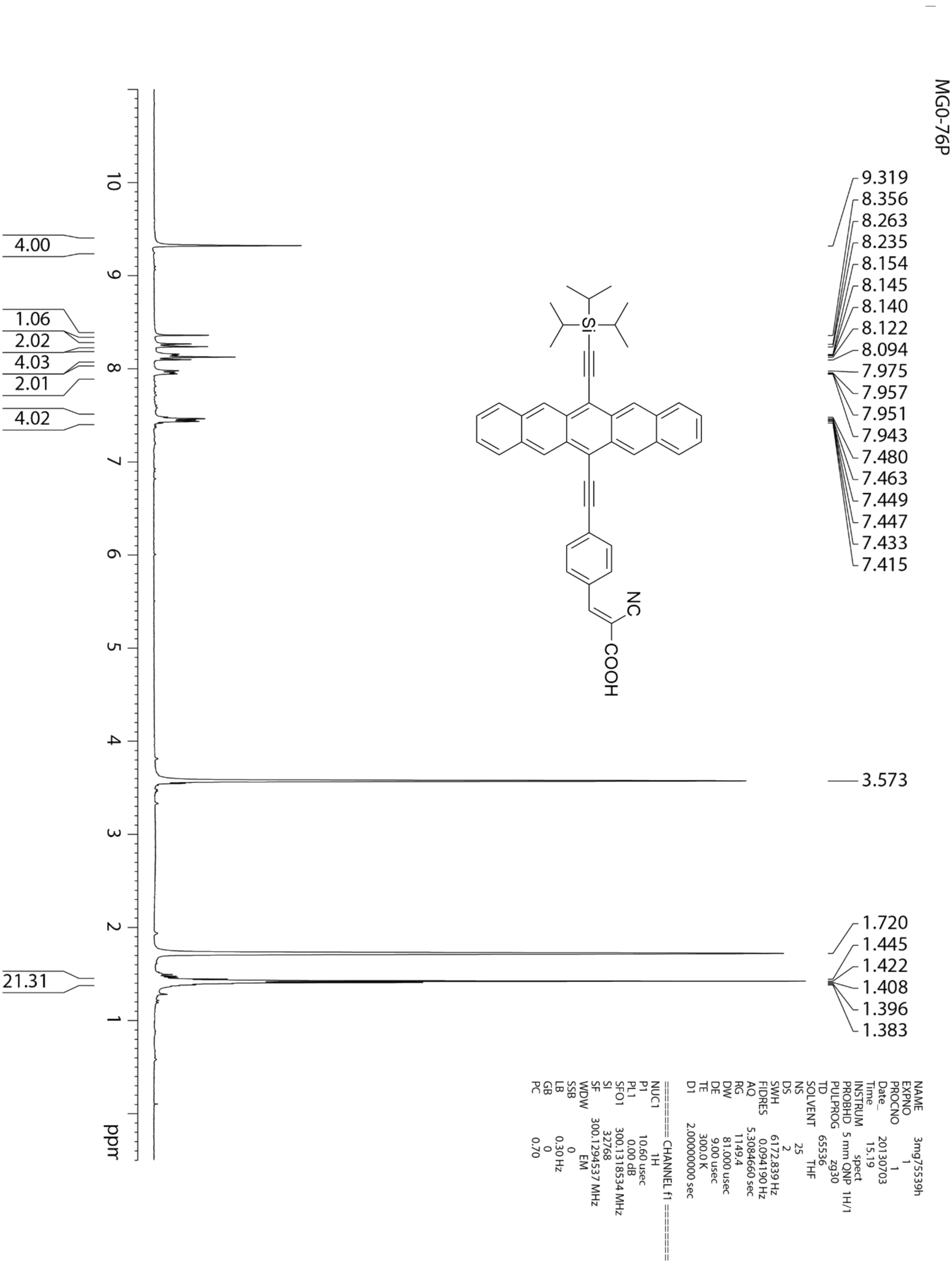
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7.463
7.449
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7.433
7.415
3.573
1.720
1.445
1.422
1.408
1.396
1.383
4.00
1.06
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PROCNO 1
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Time 15.19
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TD 65536
SOLVENT THF
NS 25
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SWH 6172.839 Hz
FIDRES 0.094190 Hz
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RG 1149.4
DW 81.000 usec
DE 9.00 usec
TE 300.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
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PL1 0.00 dB
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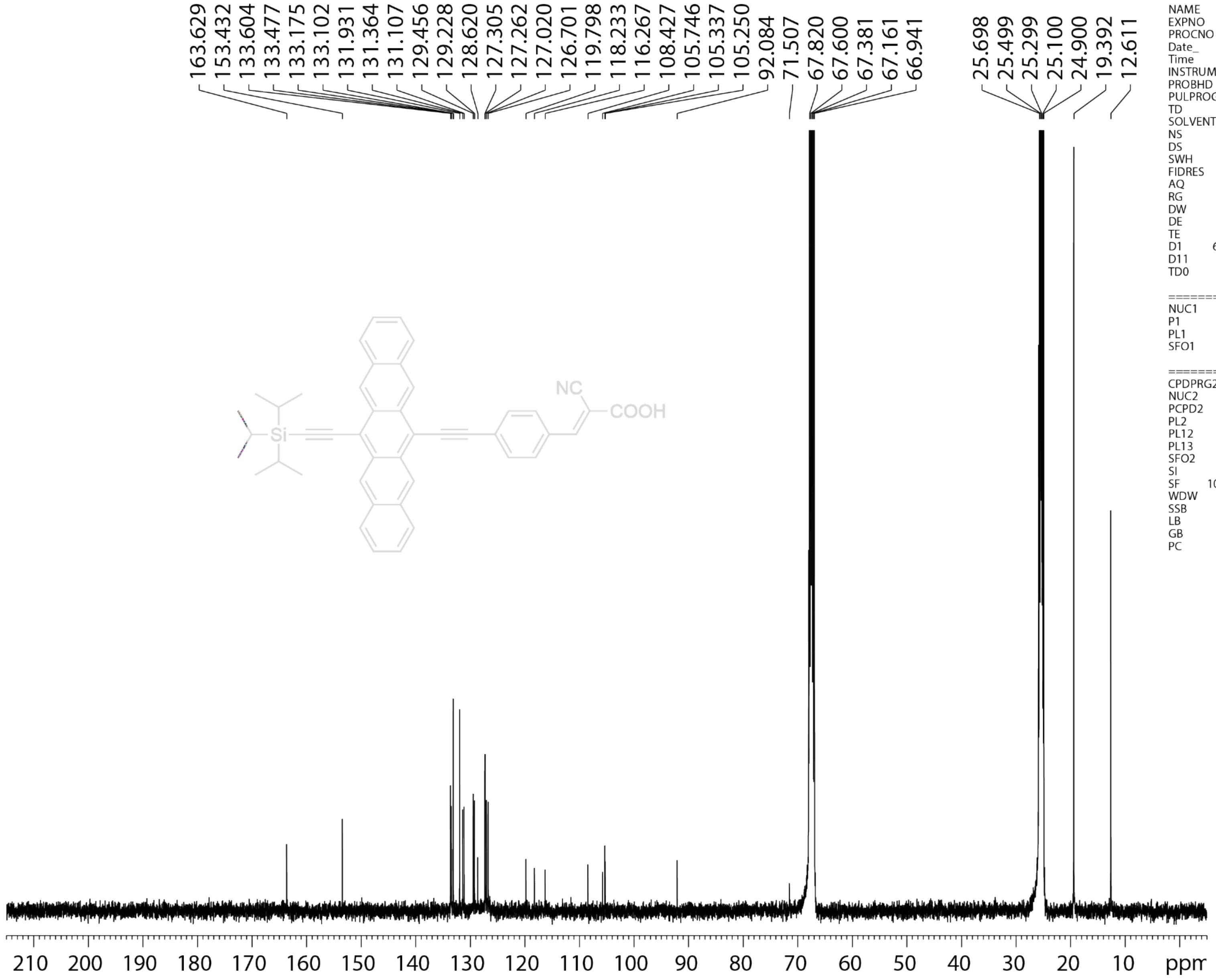
MG0-76P



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PULPROG       zgpg30
TD             65536
SOLVENT          THF
NS              6347
DS                 4
SWH       23980.814 Hz
FIDRES     0.365918 Hz
AQ        1.3664756 sec
RG           18390.4
DW           20.850 usec
DE             9.00 usec
TE            298.2 K
D1       6.00000000 sec
D11      0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1             13C
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PL1             0.00 dB
SFO1     100.6227898 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2              1H
PCPD2         116.00 usec
PL2             0.00 dB
PL12           21.25 dB
PL13           25.00 dB
SFO2     400.1316005 MHz
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SF       100.6126719 MHz
WDW               EM
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GB                 0
PC              1.40
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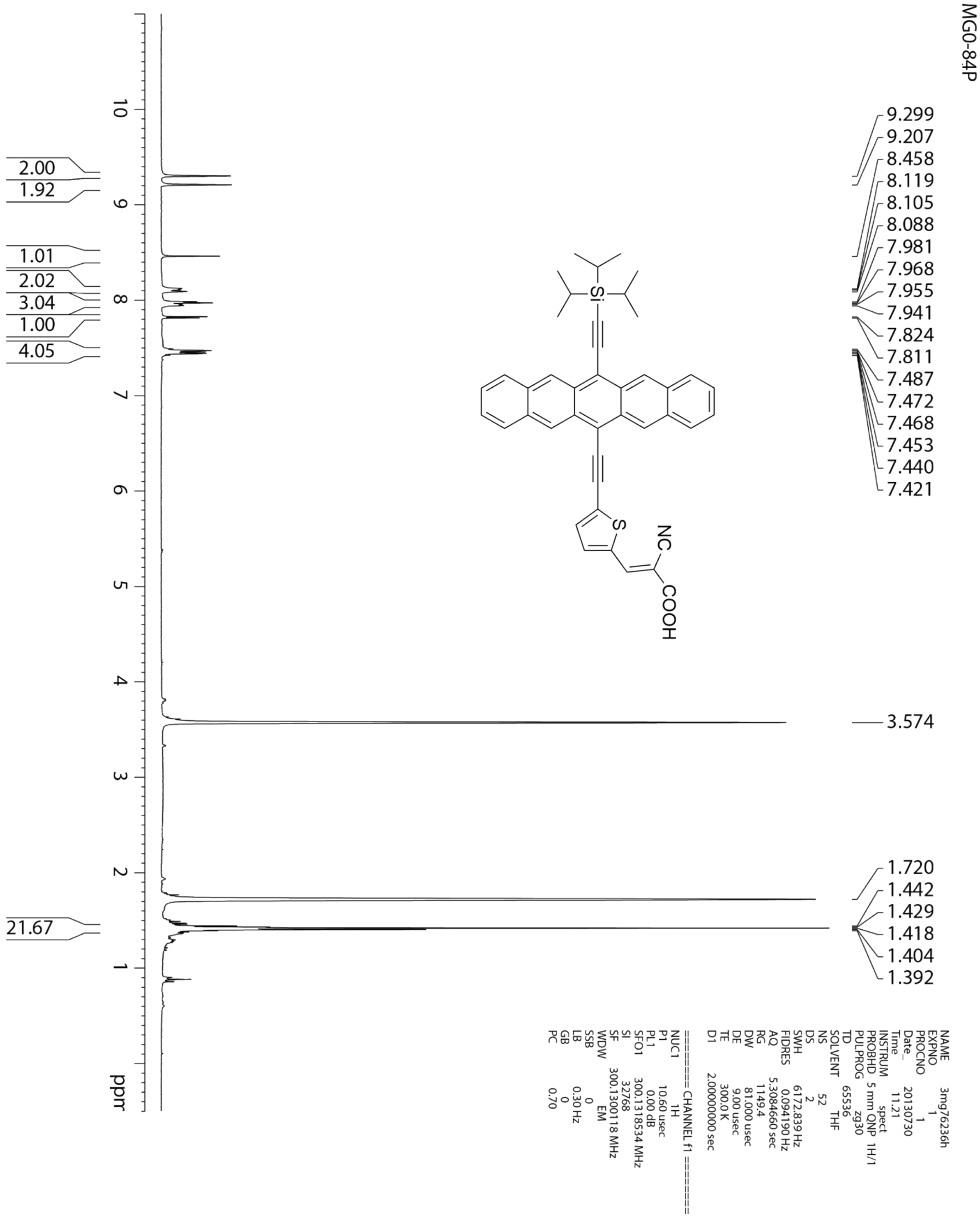
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7.472
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COOH
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PROCNO 1
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Time 11.21
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PULPROG zg30
TD 65536
SOLVENT THF
NS 52
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 1149.4
DW 81.000 usec
DE 9.00 usec
TE 300.0 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.60 usec
PL1 0.00 dB
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SI 32768
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WDW EM
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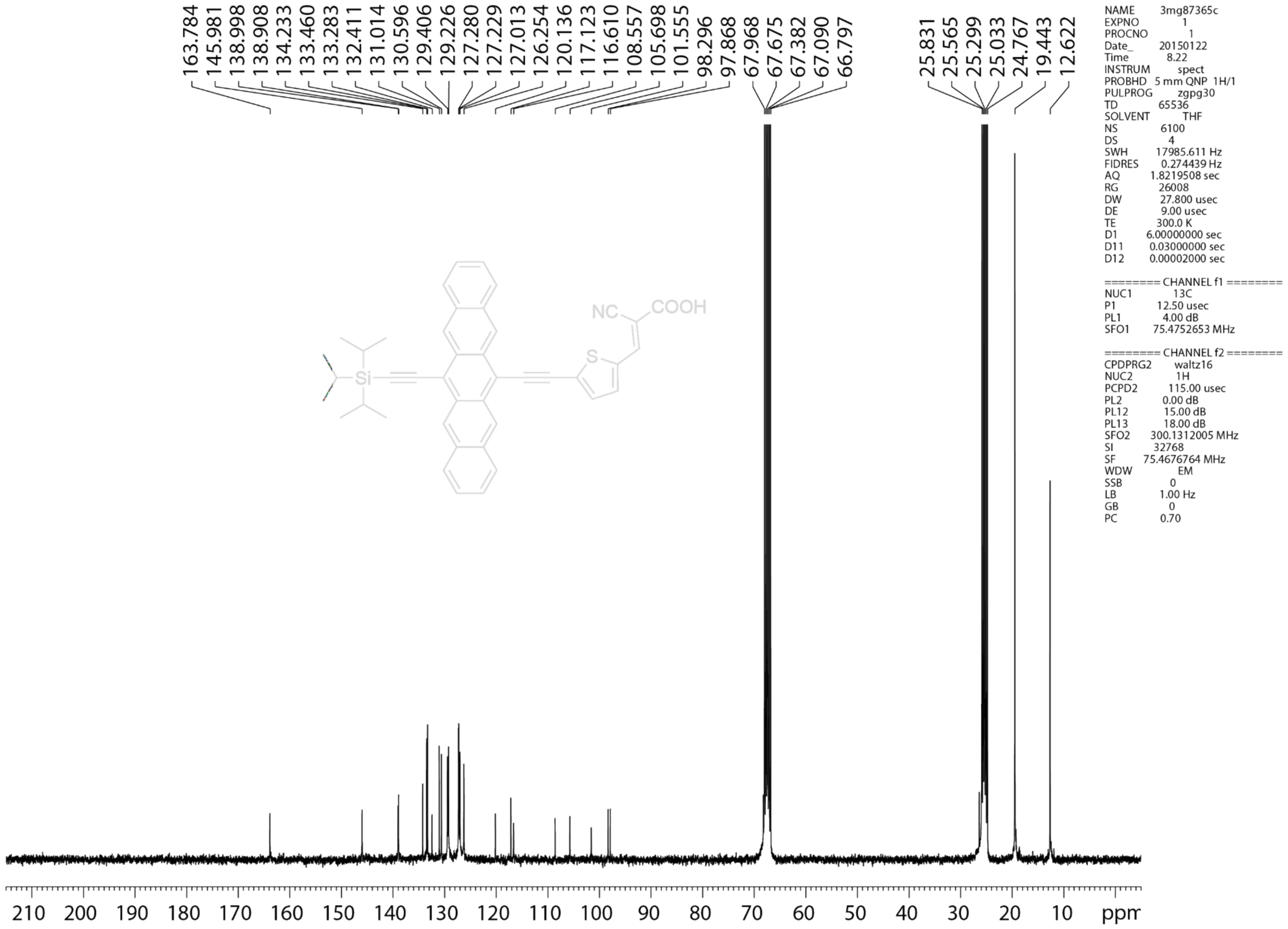
LB 0.30 Hz
GB 0
PC 0.70

MG0-84P



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PULPROG       zgpg30
TD             65536
SOLVENT          THF
NS              6100
DS                 4
SWH       17985.611 Hz
FIDRES     0.274439 Hz
AQ        1.8219508 sec
RG             26008
DW            27.800 usec
DE              9.00 usec
TE             300.0 K
D1        6.00000000 sec
D11       0.03000000 sec
D12       0.00002000 sec

======== CHANNEL f1 ========
NUC1             13C
P1             12.50 usec
PL1             4.00 dB
SFO1      75.4752653 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2              1H
PCPD2         115.00 usec
PL2             0.00 dB
PL12           15.00 dB
PL13           18.00 dB
SFO2     300.1312005 MHz
SI             32768
SF        75.4676764 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              0.70
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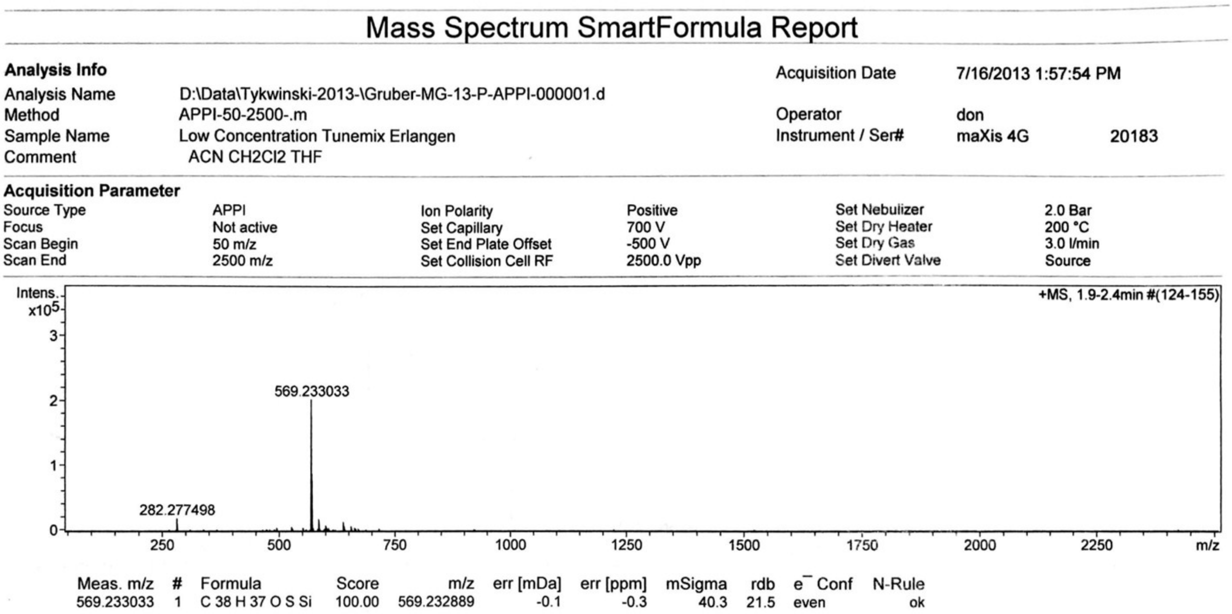

Mass Spectrum SmartFormula Report

Analysis Info

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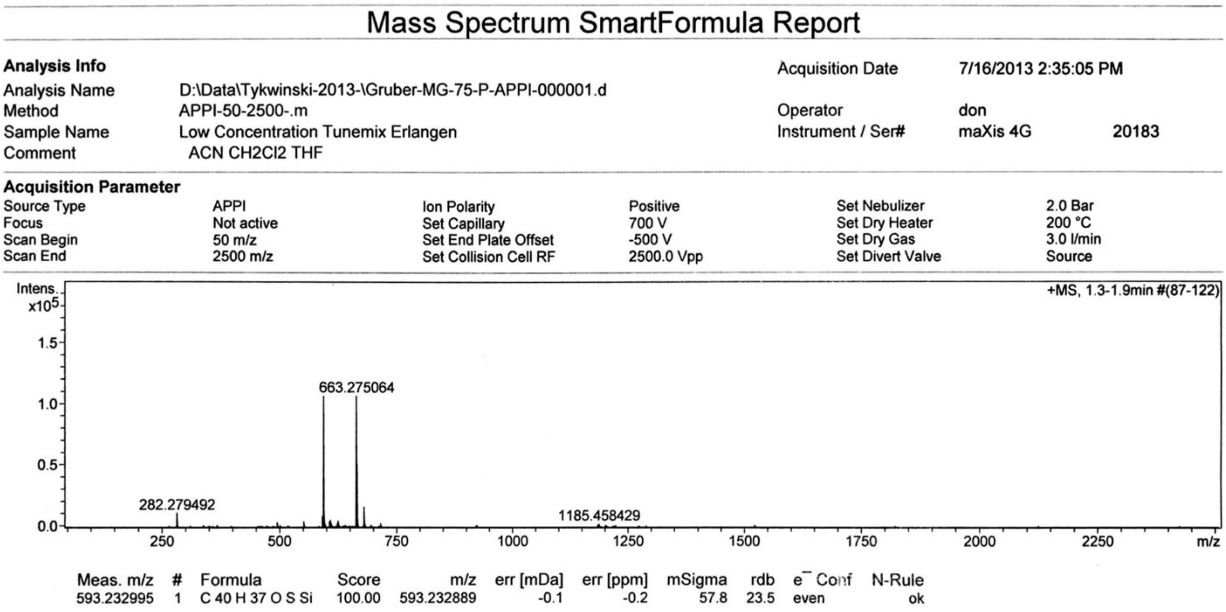
Method	APPI-50-2500-.m	Operator	don
Sample Name	Low Concentration Tunemix Erlangen	Instrument / Ser#	maXis 4G 20183
Comment	ACN CH2Cl2 THF		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
569.233033	1	C 38 H 37 O S Si	100.00	569.232889	-0.1	-0.3	40.3	21.5	even	ok

APPI HRMS of compound 3 (NCCH$_3$, CH$_2$Cl$_2$, THF).



Mass Spectrum SmartFormula Report

Analysis Info

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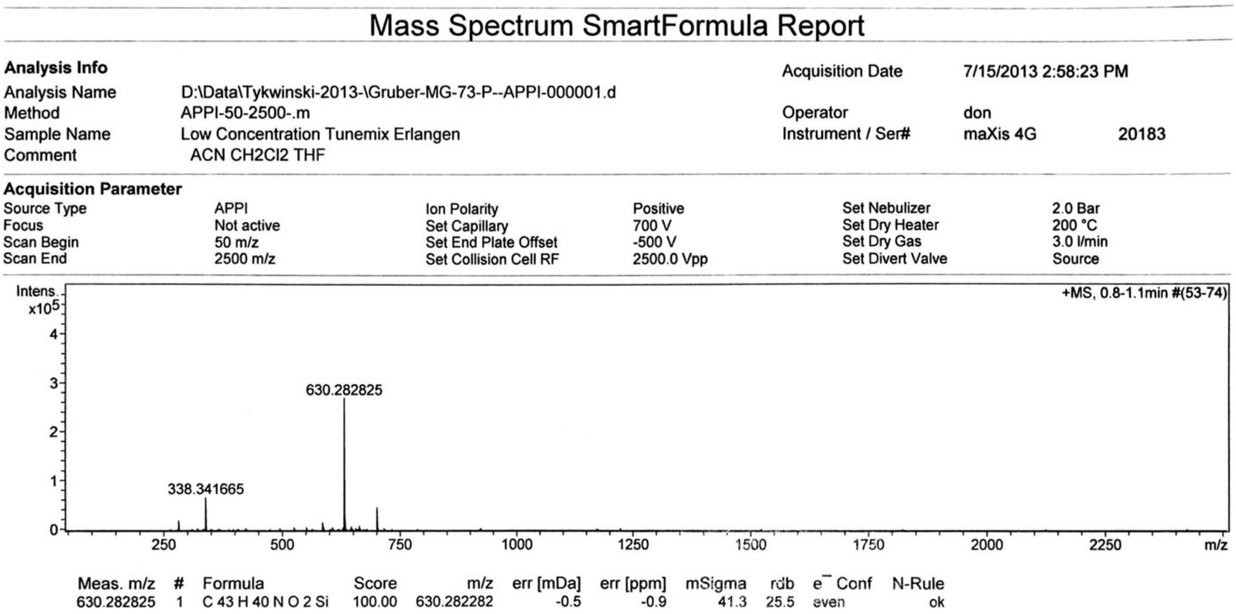
Sample Name	Low Concentration Tunemix Erlangen	Instrument / Ser#	maXis 4G 20183
Comment	ACN CH2Cl2 THF		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
593.232995	1	C 40 H 37 O S Si	100.00	593.232889	-0.1	-0.2	57.8	23.5	even	ok

ESI HRMS of compound 4 (NCCH$_3$, CH$_2$Cl$_2$, THF).



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\Tykwinski-2013-\Gruber-MG-73-P--APPI-000001.d
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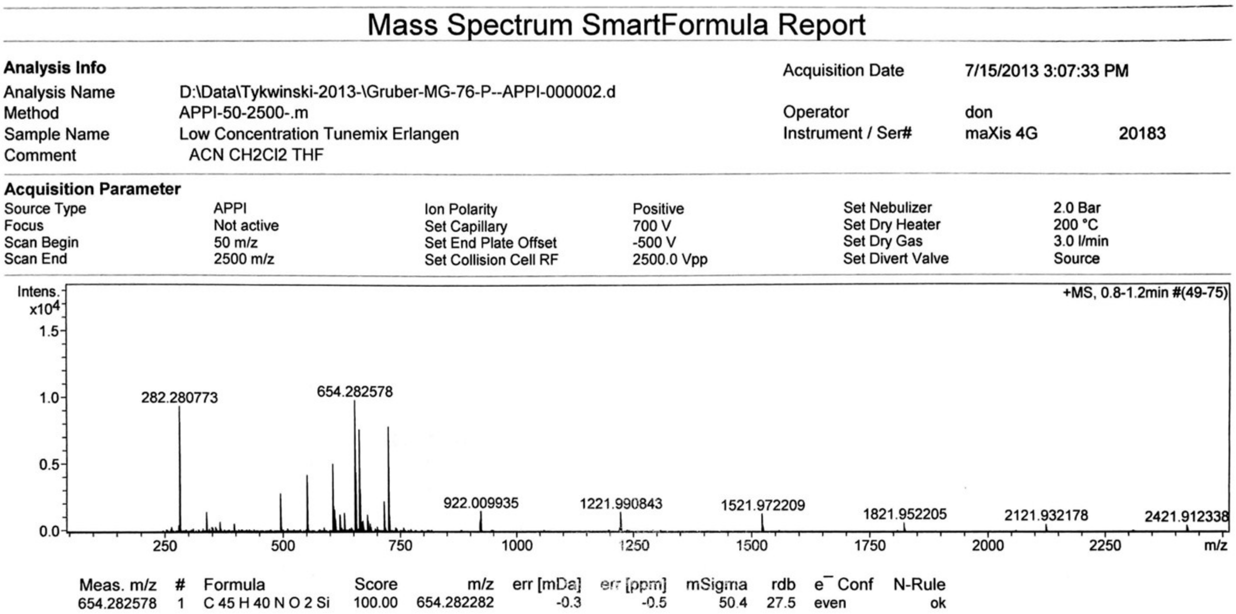
Sample Name Low Concentration Tunemix Erlangen
Comment ACN CH2Cl2 THF
Acquisition Date 7/15/2013 2:58:23 PM
Operator don
Instrument / Ser# maXis 4G 20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
630.282825	1	C 43 H 40 N O 2 Si	100.00	630.282282	-0.5	-0.9	41.3	25.5	even	ok

APPI HRMS of compound DPV1 ($NCCH_3$, CH_2Cl_2, THF).



Mass Spectrum SmartFormula Report

Analysis Info

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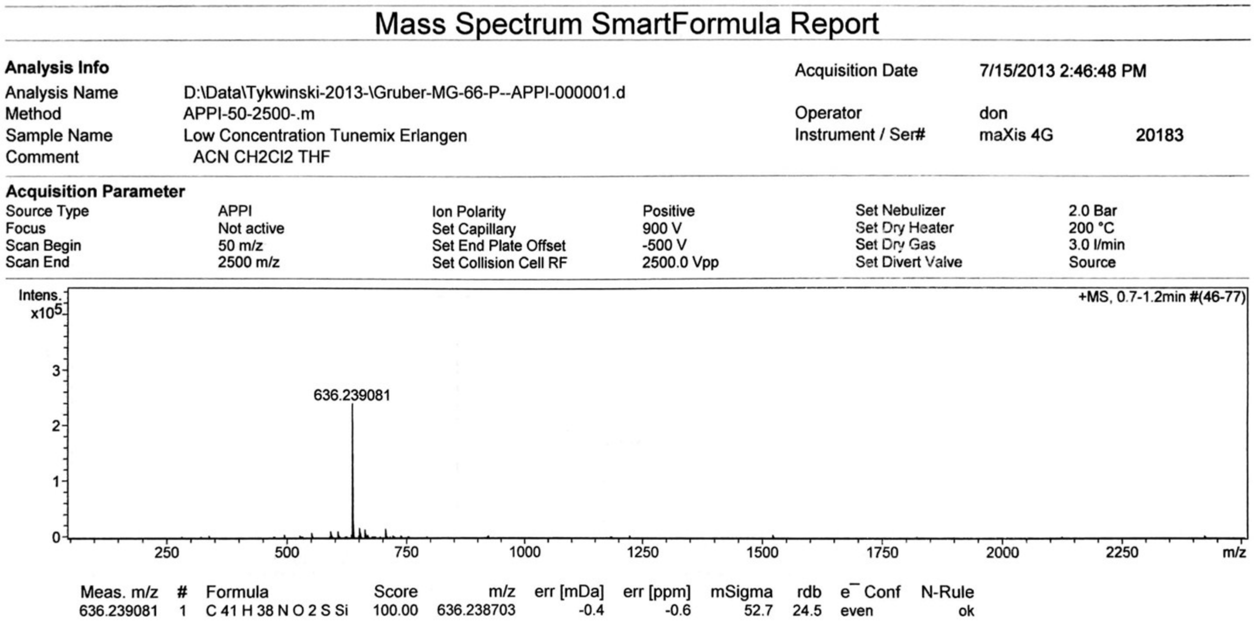
Method APPI-50-2500-.m
Sample Name Low Concentration Tunemix Erlangen
Comment ACN CH2Cl2 THF
Acquisition Date 7/15/2013 3:07:33 PM
Operator don
Instrument / Ser# maXis 4G 20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
654.282578	1	C 45 H 40 N O 2 Si	100.00	654.282282	-0.3	-0.5	50.4	27.5	even	ok

APPI HRMS of compound DPV2 ($NCCH_3$, CH_2Cl_2, THF).



Mass Spectrum SmartFormula Report

Analysis Info

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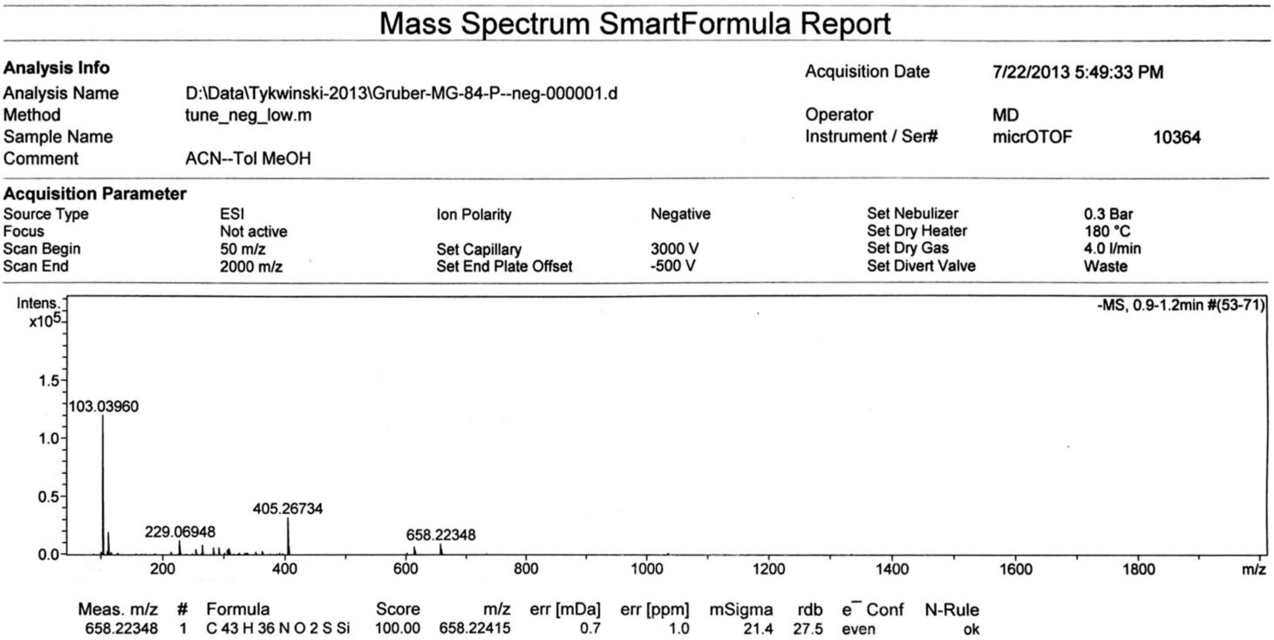
Method	APPI-50-2500-.m	Operator	don
Sample Name	Low Concentration Tunemix Erlangen	Instrument / Ser#	maXis 4G 20183
Comment	ACN CH2Cl2 THF		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	900 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	2500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
636.239081	1	C 41 H 38 N O 2 S Si	100.00	636.238703	-0.4	-0.6	52.7	24.5	even	ok

APPI HRMS of compound DPV3 ($NCCH_3$, CH_2Cl_2, THF).



Mass Spectrum SmartFormula Report

Analysis Info

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Method	tune_neg_low.m	Operator	MD
Sample Name		Instrument / Ser#	micrOTOF 10364
Comment	ACN--Tol MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.3 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	3000 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
658.22348	1	C 43 H 36 N O 2 S Si	100.00	658.22415	0.7	1.0	21.4	27.5	even	ok

ESI HRMS of compound DPV4 ($NCCH_3$, PhMe, MeOH).

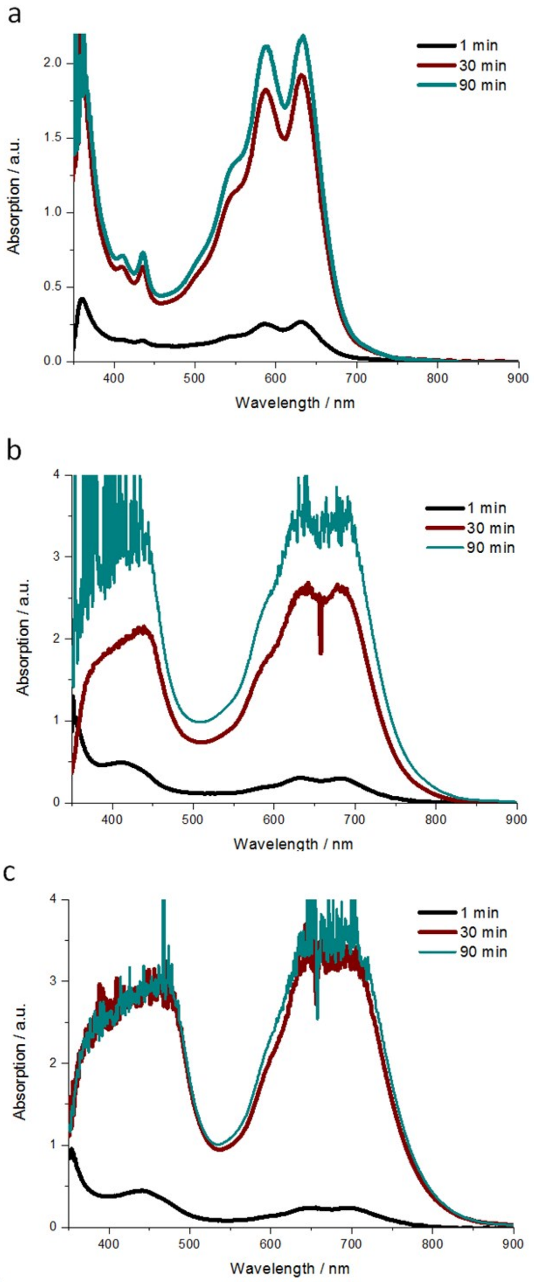

Figure S1. Absorption spectra of TiO_2 electrodes with **DPV1** a), **DPV2** b), **DPV4** c) after 1 (black), 30 (red), and 90 min (blue) uptake.

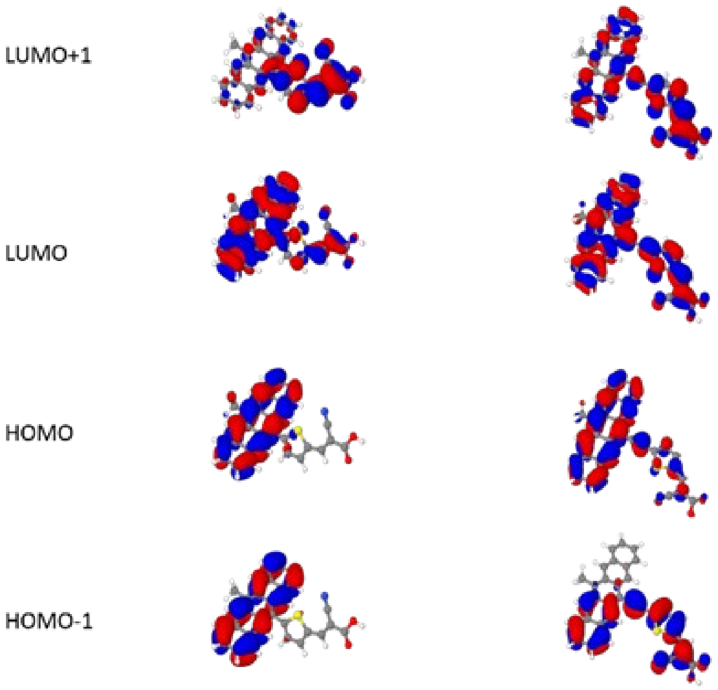

Figure S2. Molecular orbital representation of the HOMO-1, HOMO, LUMO and LUMO+1 of **DPV3** (right) and **DPV4** (left). Isovalue 0.01 in gas phase. Optimized geometries via B3lyp-6311 G* and def-TZVP basis set.

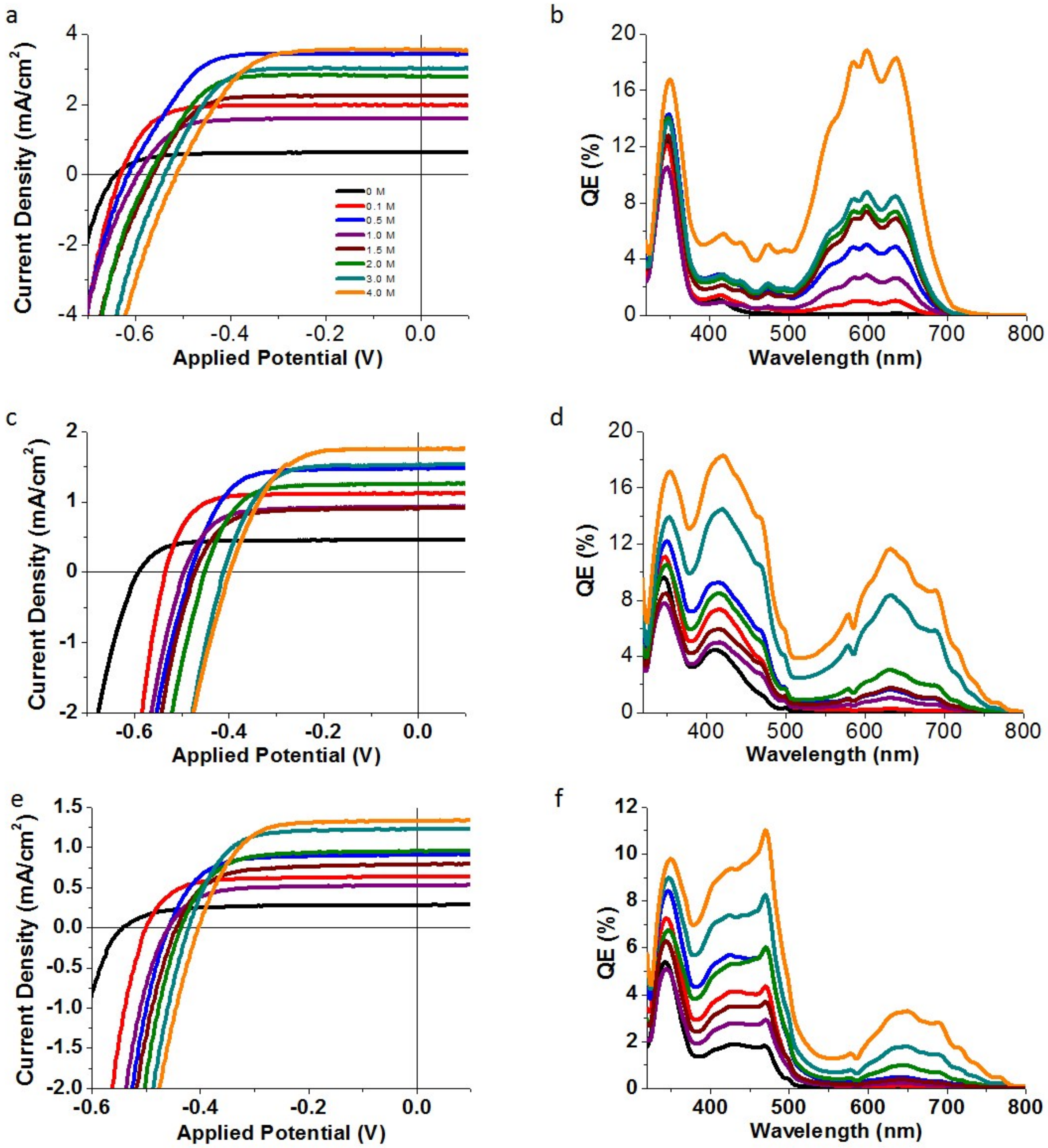

Figure S3. J-V curves a), c), and e) and IPCE spectra b), d), and f) of devices with **DPV1** a) and b), **DPV2** c) and d) and **DPV4** e) and f) with different Li$^+$ concentrations in the electrolyte redox couple (see figure legend for details) under 1 sun AM 1.5 solar intensity.

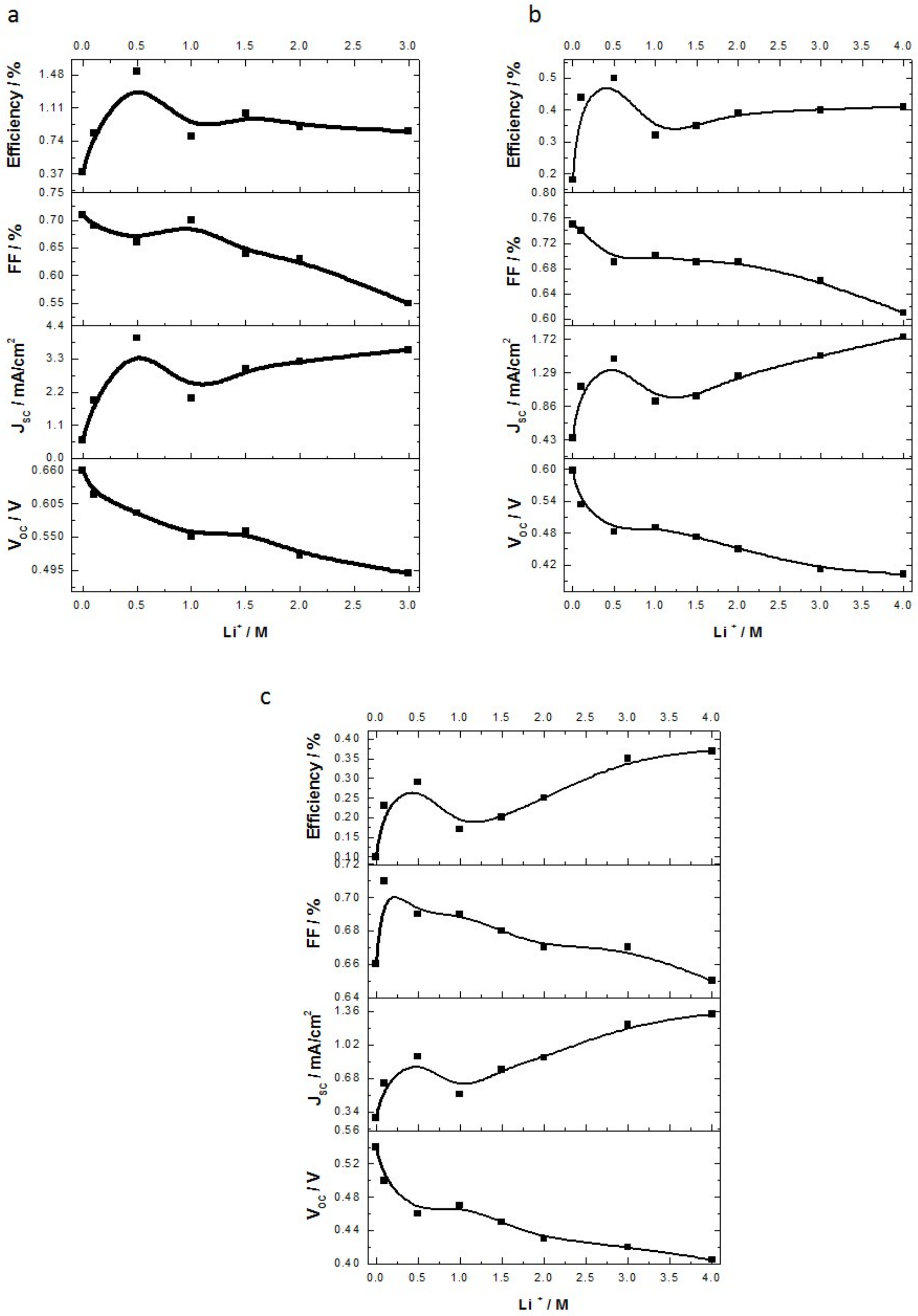

Figure S4. Figures-of-merit for devices with **DPV1** a), **DPV2** b), and **DPV4** c) as a function of Li^+ concentration in the electrolyte redox couple under 1 sun AM 1.5 solar intensity.

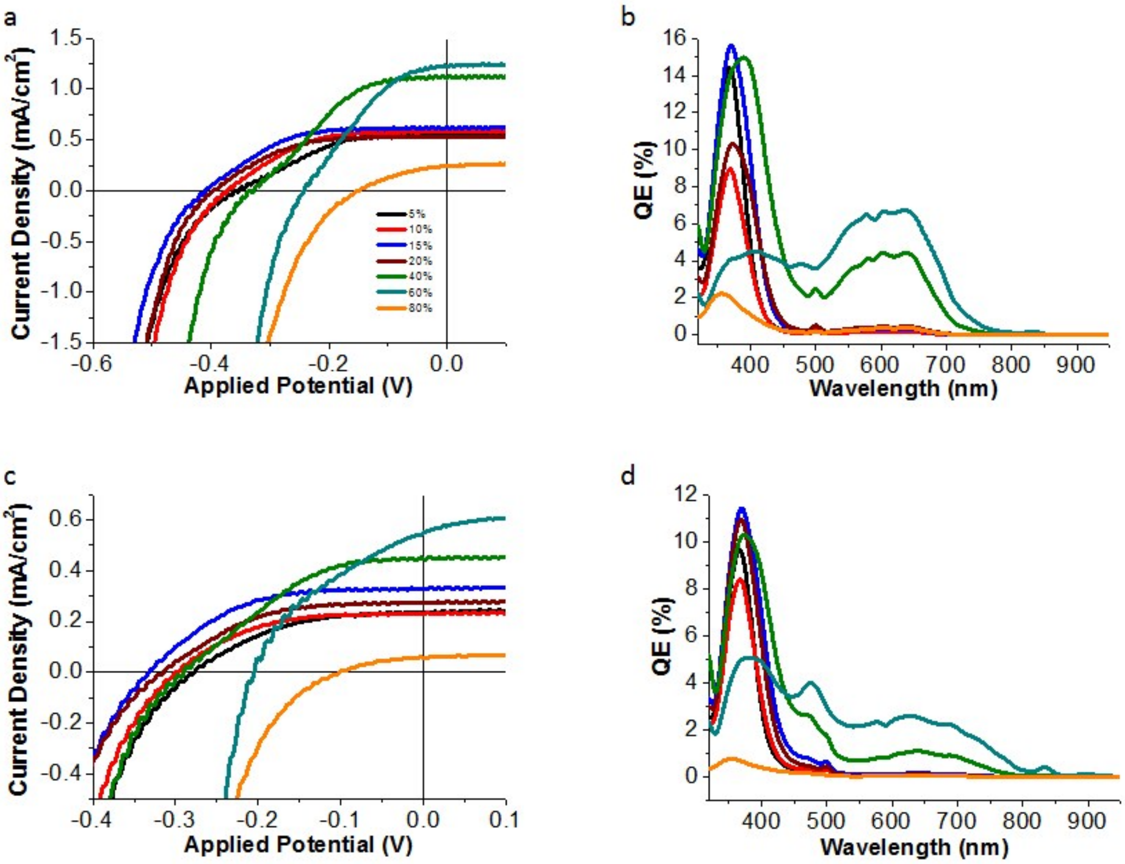

Figure S5. J-V curves a) and c) and IPCE spectra b) and d) of In_xZn_yO based devices with increasing In concentration (see figure legend for details) as well as with **DPV3** a) and b) and **DPV4** c) and d) under 1 sun AM 1.5 solar intensity.

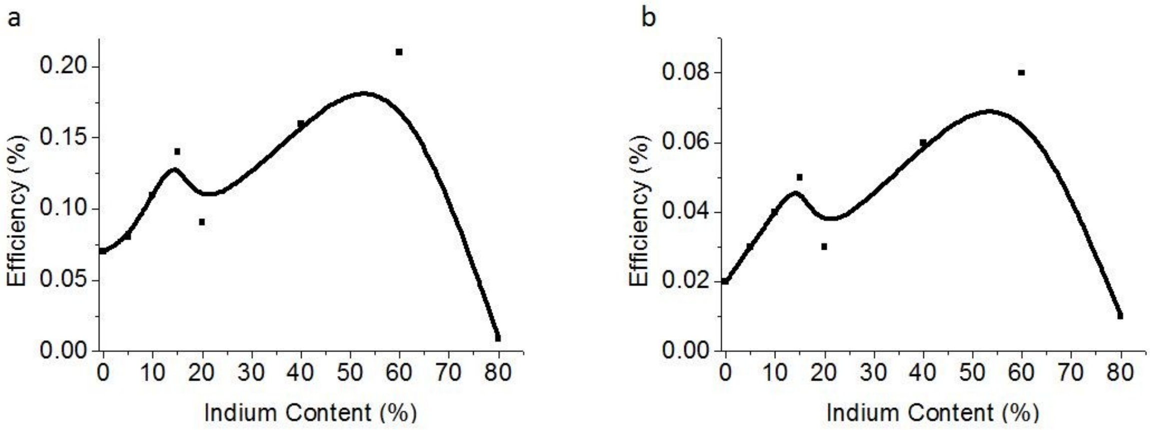

Figure S6. Changes in the efficiency of In_xZn_yO based devices with increasing In concentration in the electrode for **DPV3** a) and **DPV4** b) under 1 sun AM 1.5 solar intensity.

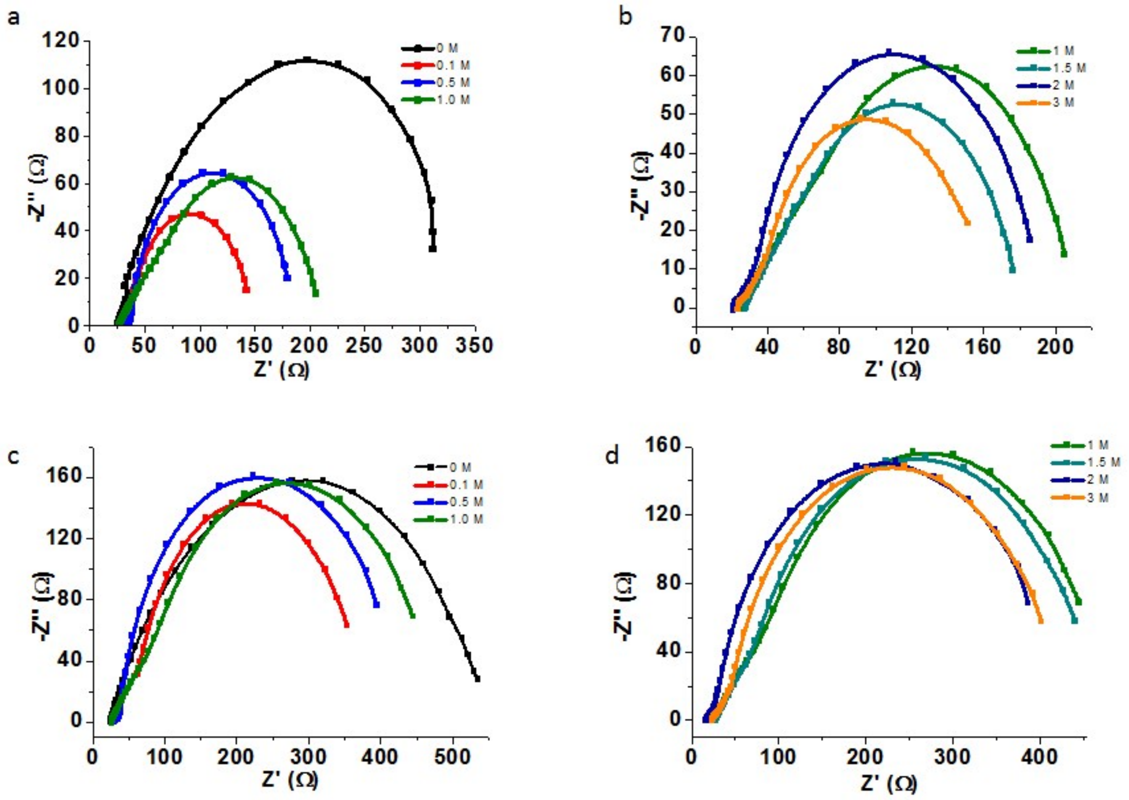

Figure S7. Nyquist plots for devices with **DPV1** as a function of Li$^+$ concentration in the electrolyte redox couple (see figure legends for details) under 1 sun AM 1.5 solar intensity a) and b) and dark conditions c) and d).

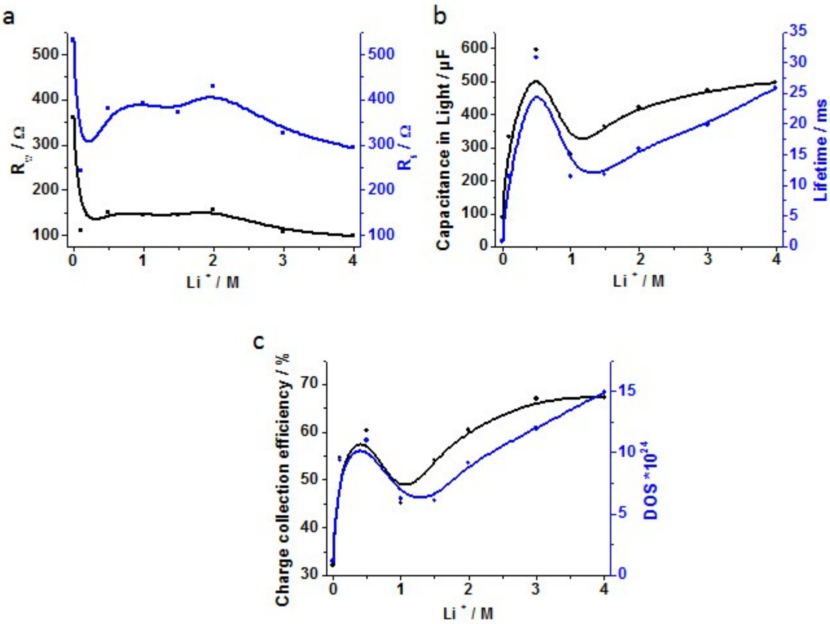

Figure S8. EIS figures-of-merit of sensitized solar cells with **DPV1** as a function of Li^+ concentration in the electrolyte redox couple. a) Resistance changes under 1 sun AM 1.5 solar intensity (R_w, Black) and dark (R_k, Blue) conditions; b) Capacitance (C, Black) and lifetime (τ, Blue) under 1 sun AM 1.5 solar intensity; c) Charge collection efficiency (, Black) and the density of states (DOS, Blue) under 1 sun AM 1.5 solar intensity.

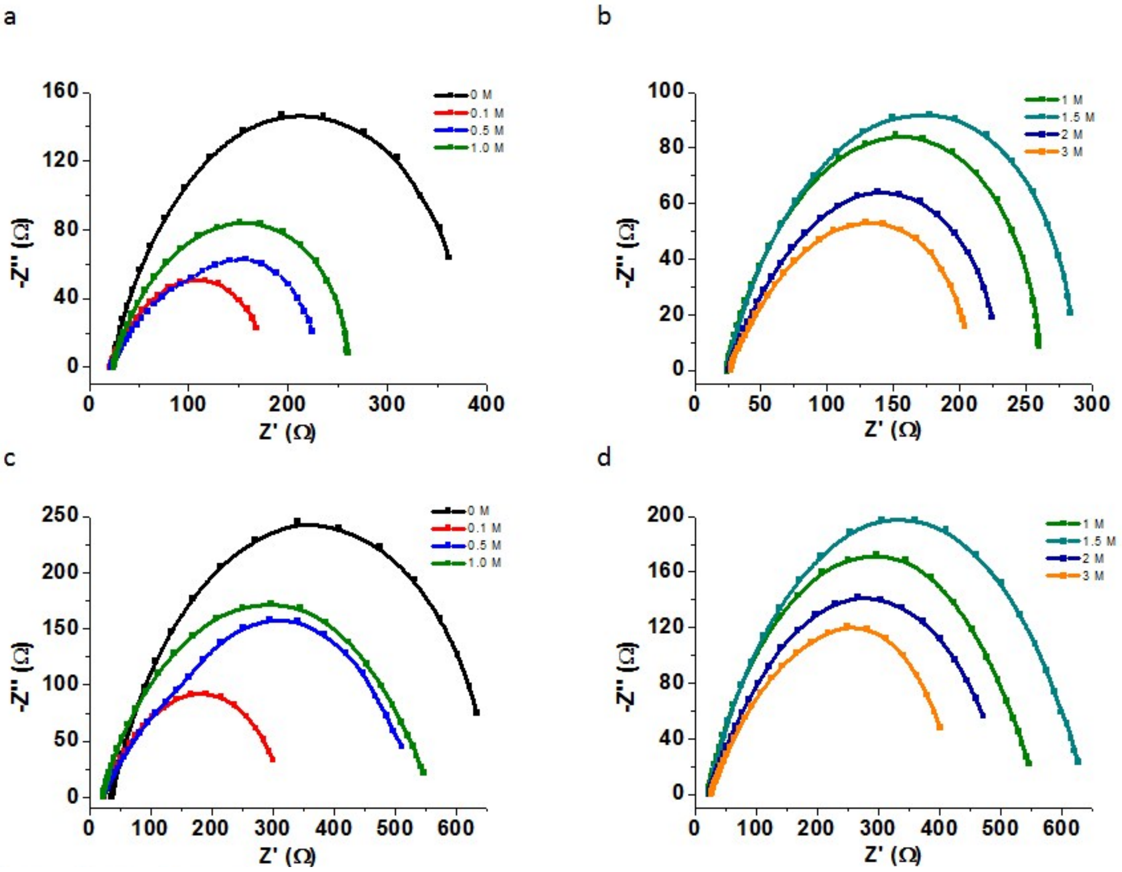

Figure S9. Nyquist plots for devices with **DPV2** as a function of Li^+ concentration in the electrolyte redox couple (see figure legends for details) under 1 sun AM 1.5 solar intensity a) and b) and dark conditions c) and d).

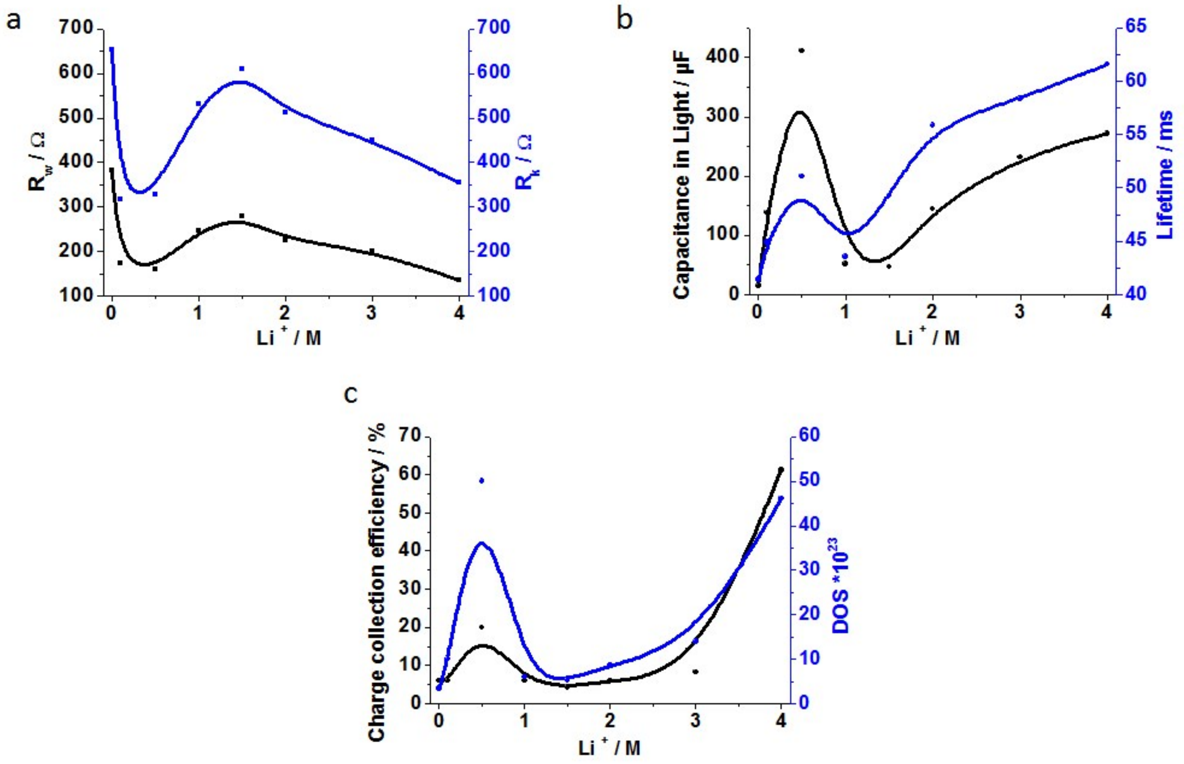

Figure S10. EIS figures-of-merit of DSSCs with **DPV2** as a function of Li^+ concentration in the electrolyte redox couple. a) Resistance changes under 1 sun AM 1.5 solar intensity (R_w, black) and dark ($R_{k,}$ blue) conditions; b) Capacitance (C, black) and lifetime (τ, blue) under 1 sun AM 1.5 solar intensity; c) Charge collection efficiency (η_{coll}, black) and the density of states (DOS, blue) under 1 sun AM 1.5 solar intensity.

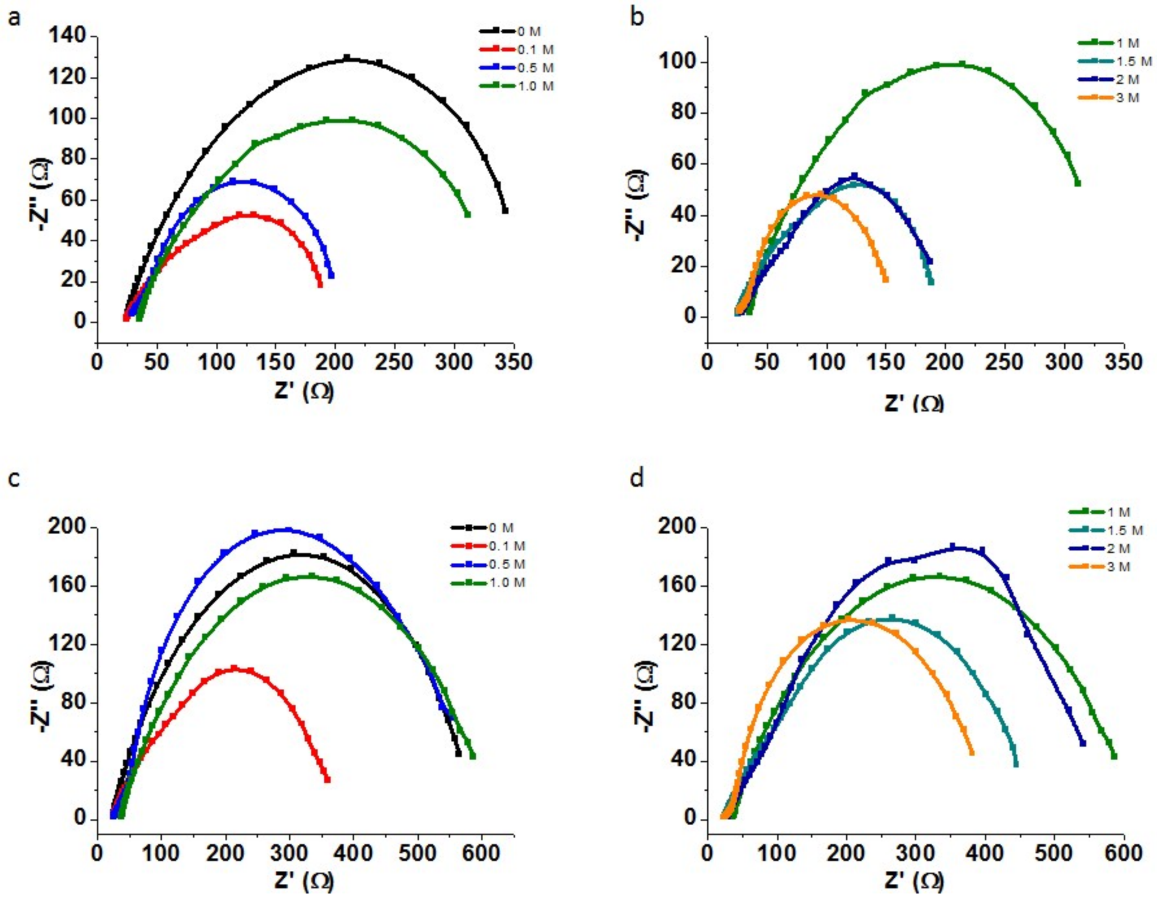

Figure S11. Nyquist plots for devices with **DPV3** as a function of Li^+ concentration in the electrolyte redox couple (see figure legends for details) under 1 sun AM 1.5 solar intensity a) and b) and dark conditions c) and d).

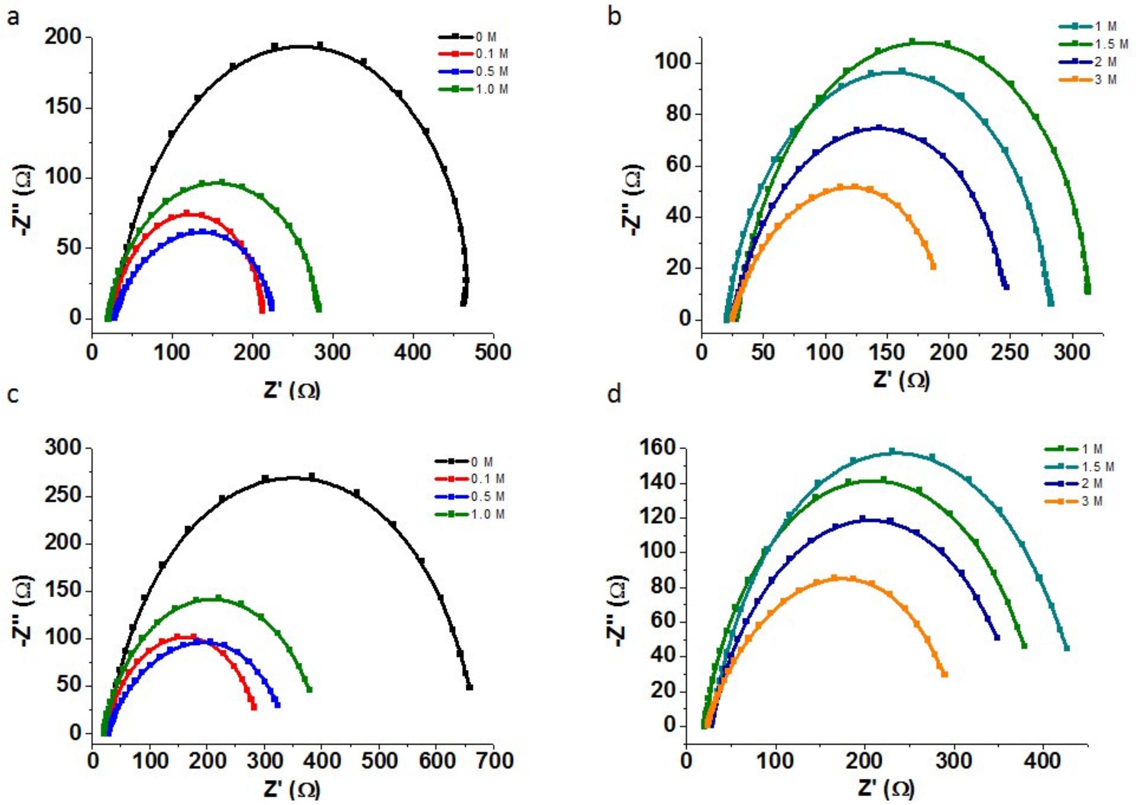

Figure S12. Nyquist plots for devices with **DPV3** as a function of Li^+ concentration in the electrolyte redox couple (see figure legends for details) under 1 sun AM 1.5 solar intensity a) and b) and dark conditions c) and d).

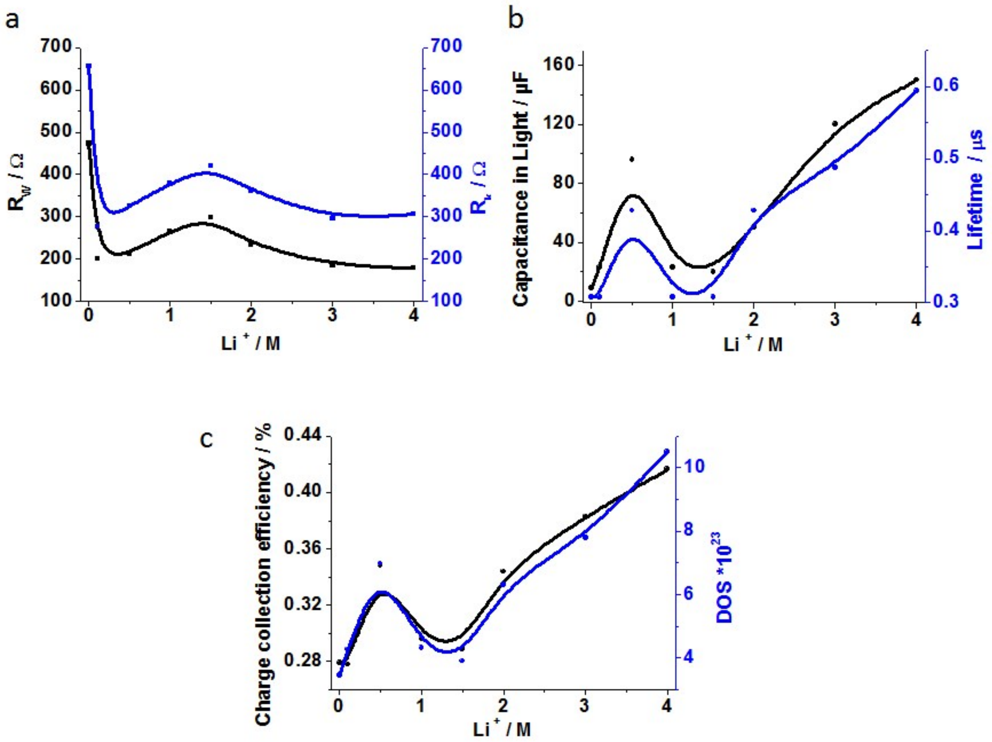

Figure S13. EIS figures-of-merit of DSSCs with **DPV4** as a function of Li$^+$ concentration in the electrolyte redox couple. a) Resistance changes under 1 sun AM 1.5 solar intensity (R_w, black) and dark ($R_{k,}$ blue) conditions; b) Capacitance (C, black) and lifetime (τ, blue) under 1 sun AM 1.5 solar intensity; c) Charge collection efficiency (η_{coll}, black) and the density of states (DOS, blue) under 1 sun AM 1.5 solar intensity.

Table S1: Injection kinetics for devices with **DPV3@DSSC** (left) and **DPV4@DSSC** (right) upon increasing the Li+ concentration in the electrolyte.

	[Li$^+$] [M]	*Injection (s^{-1})*		*[Li$^+$] [M]*	*Injection (s^{-1})*
DPV3	0	4.4 x 10^{10}	*DPV4*	0	9.3 x 10^{10}
	0.5	5.5 x 10^{10}		0.5	1.3 x 10^{11}
	1	5.5 x 10^{10}		1	1.4 x 10^{11}
	3	1.4 x 10^{11}		3	1.5 x 10^{11}

References:

[1] T.-J. Lu, J.-F. Yang, L.-J. Sheu, *J. Org. Chem.,* **1995**, *60*, 2931.

[2] D. Lehnherr, R. McDonald, R. R. Tykwinski, *Org. Lett.,* **2008**, *10*, 4163.

[3] D. Lehnherr, A. H. Murray, R. McDonald, R. R. Tykwinski, *Angew. Chem., Int. Ed.,* **2010**, *49*, 6190.

[4] E. T. Chernick, R. Casillas, J. Zirzlmeier, D. M. Gardner, M. Gruber, H. Kropp, K. Meyer, M. R. Wasielewski, D. M. Guldi, R. R. Tykwinski, *J. Am. Chem. Soc.,* **2015**, *137*, 857.