Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

Highly Efficency Triarylene Conjugation Contains subsitution groups for Dye-Sensitized Soalr Cells

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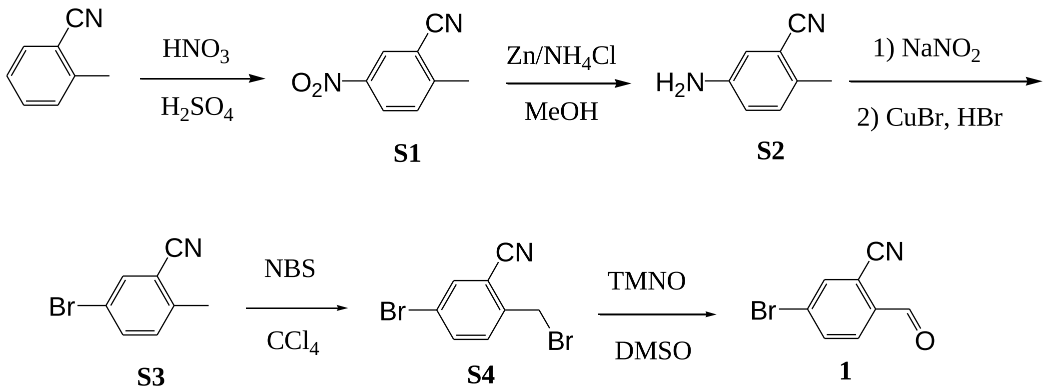
1. The synthesis of compound 1

General Information

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on Brucker (AV 400/AV 500 MHz) spectrometer in $CDCl_3$, THF-d_8, and DMSO-d_6 as a solvent. Chemical shifts are reported in scale downfield from the peak for tetramethylsilane. Absorption spectra were recorded on a Jasco-550 spectrophotometer. Emission spectra and photoluminescence quantum yield were obtained from a Hitachi F-4500 spectrofluorimeter. The emission spectra in solutions were measured in spectral grade solvent by a 90° angle detection, and those of thin film were recorded by front-face detection. The redox potentials were measured by using cyclic voltammetry on CHI 620 analyzer. All measurements were carried out in THF solutions containing 0.1 M tetrabutylammonium hexaflouro-phosphate ($TBAPF_6$) as supporting electrolyte at ambient condition after purging 10 minutes with N_2. The conventional three electrode configuration was employed, which consists of a glassy carbon working electrode, a platinum counter electrode, and a Ag/Ag$^+$ reference electrode calibrated with ferrocene/-ferrocenium (Fc/Fc$^+$) as an internal reference. Mass spectra were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

All chemicals were purchased from ACROS, Merck, Lancaster, TCI, Sigma-Aldrich, separately, and purified before use. Chromatographic separations were carried out by using silica gel from Merk, Kieselgel si 60 (40 - 63 μm).



Scheme S1. The synthetic route of **1**.

2-Methyl-5-nitrobenzonitrile (S1)

A mixture of fuming nitric acid (10 mL) and sulphuric acid (20 mL) in a two-necked flask was stirred at room temperature for 1 h. To it was added *o*-tolunitrile (9 mL, 76.8 mmol) slowly in an ice-bath, then the mixture was stirred for 1 hour at room temperature. The resulted solution was poured into ice-water, and the white solids were collected by filtration. Compound **S1** was purified by recrystallization from ethanol in 90% yield (11.2 g, 69.12 mmol). Spectroscopic data of **S1**: δ_H (400 MHz, $CDCl_3$) 8.46 (d, 1H, *J* = 2.4 Hz), 8.33 (dd, 1H, *J* = 2.4, 8.4 Hz), 7.53 (d, 1H, *J* = 8.8 Hz), 2.68 (s, 3H); δ_C (100 MHz,$CDCl_3$) 149.2, 146.1, 131.5, 127.5, 127.2, 115.9, 114.2, 20.8; *m/z* (EI) 162.0425 (M^+, $C_8H_6N_2O_2$ requires 162.0429).

5-Amino-2-methylbenzonitrile (S2)

A mixture of compound **S1** (5 g, 30.8 mmol) and Zn powder (7.5 g, 114.7 mmol) in methanol (200 mL) was placed in a three-necked flask and was stirred at room temperature for 4 h under a nitrogen atmosphere. The reaction was quenched by adding 0.1 N $NaOH_{(aq)}$, then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The products were purified by silica gel column chromatograph eluted with dichloromethane. Yellow solids of **S2** were obtained in 85% yield (3.46 g, 26.18 mmol). Spectroscopic data of **S2**: δ_H (400 MHz, $CDCl_3$) 7.03 (d, 1H, *J* = 8.5 Hz), 6.84 (d, 1H, *J* = 2.5 Hz), 6.76 (dd, 1H, *J* = 2.5, 8.0 Hz), 3.68 (br, s, 2H), 2.39 (s, 3H); δ_C NMR (100 MHz, $CDCl_3$) 144.4, 131.3, 130.9, 119.6, 118.3, 117.7, 112.9, 19.2; *m/z* (EI) 132.0687 (M^+, $C_8H_8N_2$ requires 132.0687).

5-Bromo-2-methylbenzonitrile (S3)

A mixture of compound **S2** (3 g, 22.65 mmol), water (36 mL) and 48% HBr (10.8 mL) was stirred for 2 h. To it was then added an aqueous solution (20.3 mL) of $NaNO_2$ (17.1 g, 2.7 mmol), followed by CuBr (9.75 g, 67.65 mmol) after 30 mins. To the mixture was again added a combined solution of 48% HBr (22.5 mL) and water (54 mL) at 70 °C in a period of 30 mins. Then the mixture was heated to reflux for 2 h. After being cooled, the reaction was quenched by adding $KOH_{(aq)}$, then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The products were purified by silica gel column chromatograph eluted with dichloromethane/hexane (1/1). Colorless crystalline solids of **S3** were obtained in 56% yield (2.47 g, 12.68 mmol). Spectroscopic data of **S3**: δ_H ($CDCl_3$) 7.7 (d, 1H, *J* = 2.0 Hz), 7.59 (dd, 1H, *J* = 2, 8.4 Hz), 7.19 (d, 1H, *J* = 8.0 Hz), 2.49 (s, 3H); δ_C ($CDCl_3$) 140.8, 135.7, 134.7, 131.7, 119.2, 116.6, 114.5, 19.9; *m/z* (EI)

194.9682 (M^+, C_8H_6BrN requires 194.9684).

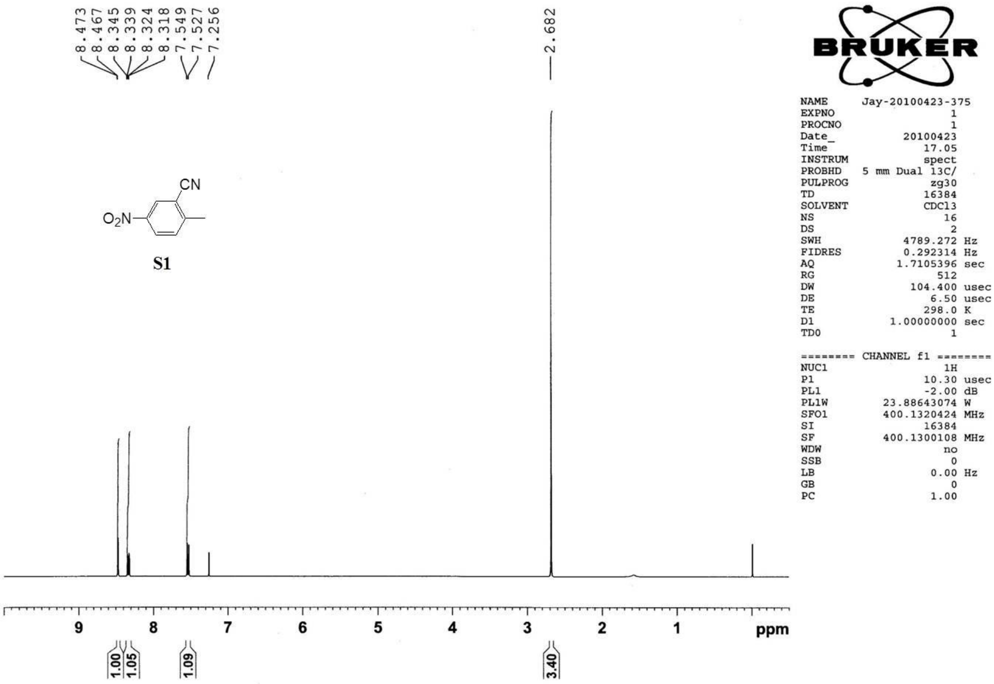
5-Bromo-2-(bromomethyl)benzonitrile (S4)

A mixture of compound **S3** (1 g, 5.13 mmol), NBS (1.0 g, 5.64 mmol), and BPO (40 mg, 0.165 mmol) was dissolved in CCl_4 (20 mL), then the solution was heated to 90 °C with stirring for 9 h. After cooling, the reaction was quenched by adding water, then was extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The products were purified by silica gel column chromatograph eluted with ethyl acetate/hexane (1/9). White solids of **S4** were obtained in 90% yield (1.26 g, 4.62 mmol). Spectroscopic data of **S4**: δ_H (400 MHz, $CDCl_3$) 7.78 (d, 1H, J = 2.0 Hz), 7.71 (dd, 1H, J = 2, 8.4 Hz), 7.42 (d, 1H, J = 8.4 Hz), 4.57 (s, 2H); δ_C (100 MHz, $CDCl_3$) 140.0, 136.4, 135.5, 131.8, 122.4, 115.2, 114.0, 28.3; *m/z* (EI) 272.8793 (M^+, $C_8H_5Br_2N$ requires 272.8789).

5-Bromo-2-formylbenzonitrile (1)

The solution of trimethylamine N-oxide (1.1 g, 14.64 mmol) in DMSO (8 mL) was kept in an ice bath, and to it was added dropwise compound **S4** (1.0 g, 3.66 mmol) in dry CH_2Cl_2, and the resulted solution was warm to room temperature and stirred with a magnetic bar for 8 h. The reaction was quenched by adding saturated $NaCl_{(aq)}$, then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under vacuum. The products were purified by silica gel column chromatograph eluted with dichloromethane. White solids of **1** were obtained in 56% yield (428 mg, 2.05 mmol). Spectroscopic data of **1**: δ_H (400 MHz, $CDCl_3$) 10.30 (s, 1H), 7.97 (s, 1H), 7.91 (s, 2H); δ_C (100 MHz, $CDCl_3$) 187.4, 136.7, 136.6, 135.4, 130.56, 129.3, 115.3, 114.5; *m/z* (EI) 208.9477 (M^+, C_8H_4BrNO requires 208.9476).

2. ^{1}H and ^{13}C NMR spectra



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RG                       512
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DE                      6.50 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

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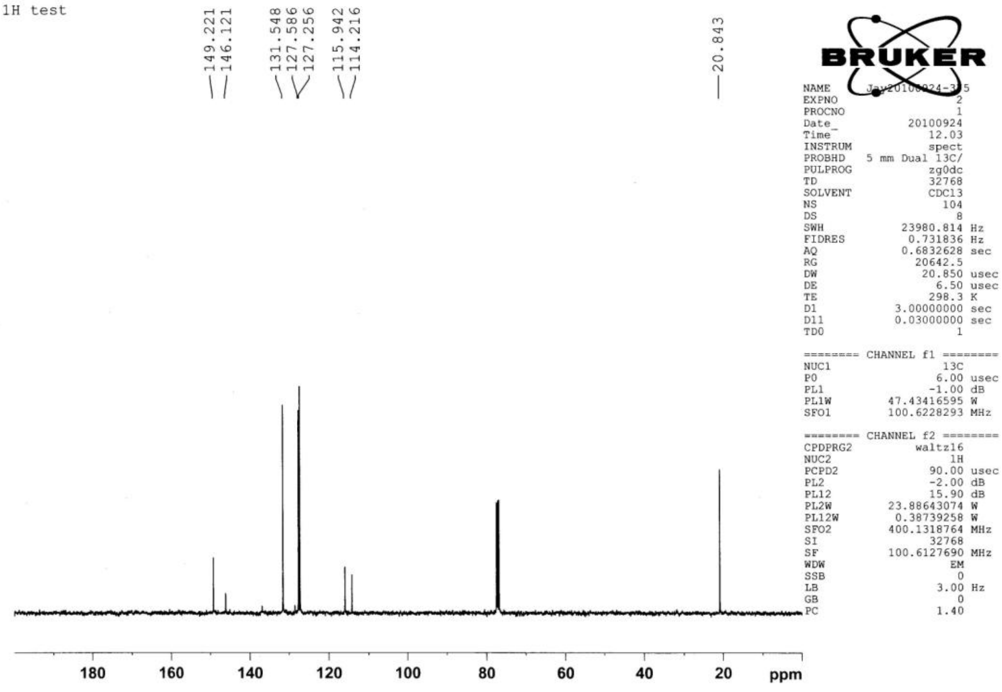

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AQ                 0.6832628 sec
RG                   20642.5
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DE                      6.50 usec
TE                     298.3 K
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D11               0.03000000 sec
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PL1                    -1.00 dB
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PL12                   15.90 dB
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PL12W             0.38739258 W
SFO2             400.1318764 MHz
SI                     32768
SF               100.6127690 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40
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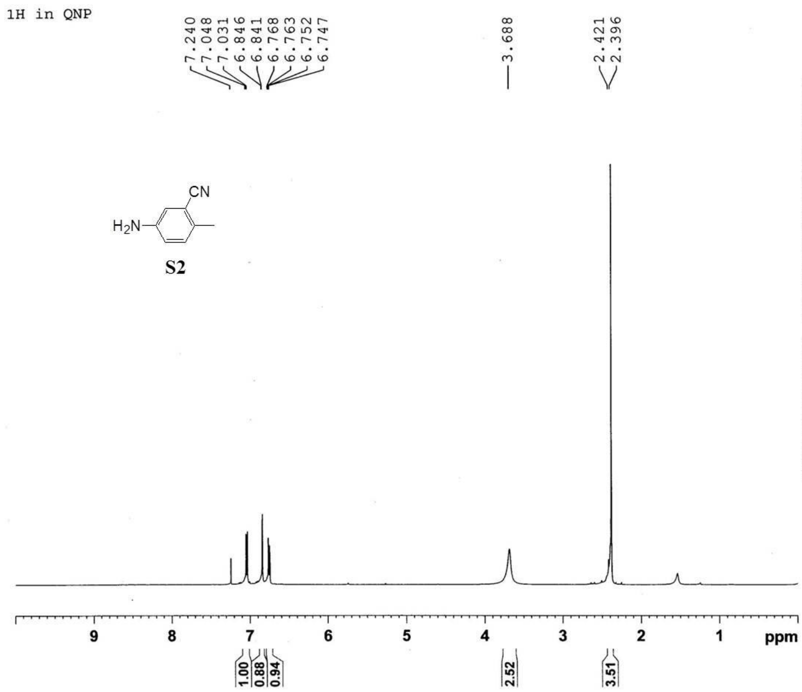
Figure S1: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **S1** in $CDCl_3$.



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PULPROG                   zg
TD                     32768
SOLVENT                CDCl3
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DS                         2
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FIDRES              0.198682 Hz
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RG                       256
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TE                     312.2 K
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TD0                        1

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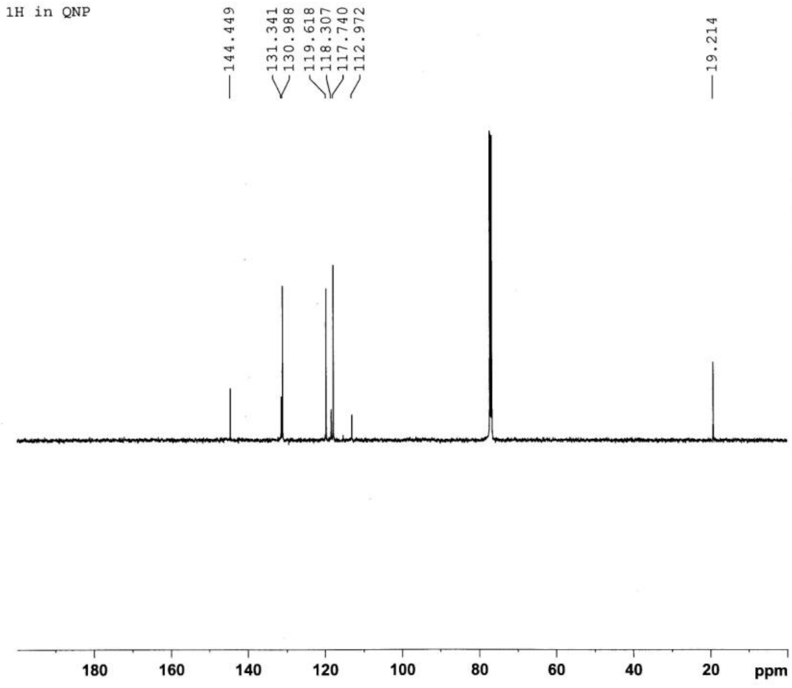

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TD                     32768
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FIDRES              1.038013 Hz
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RG                      4096
DW                    14.700 usec
DE                      6.00 usec
TE                     301.1 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
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PL1                     3.00 dB
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SFO1             125.7898571 MHz

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PL12W             0.61838412 W
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SI                     32768
SF               125.7753975 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.00
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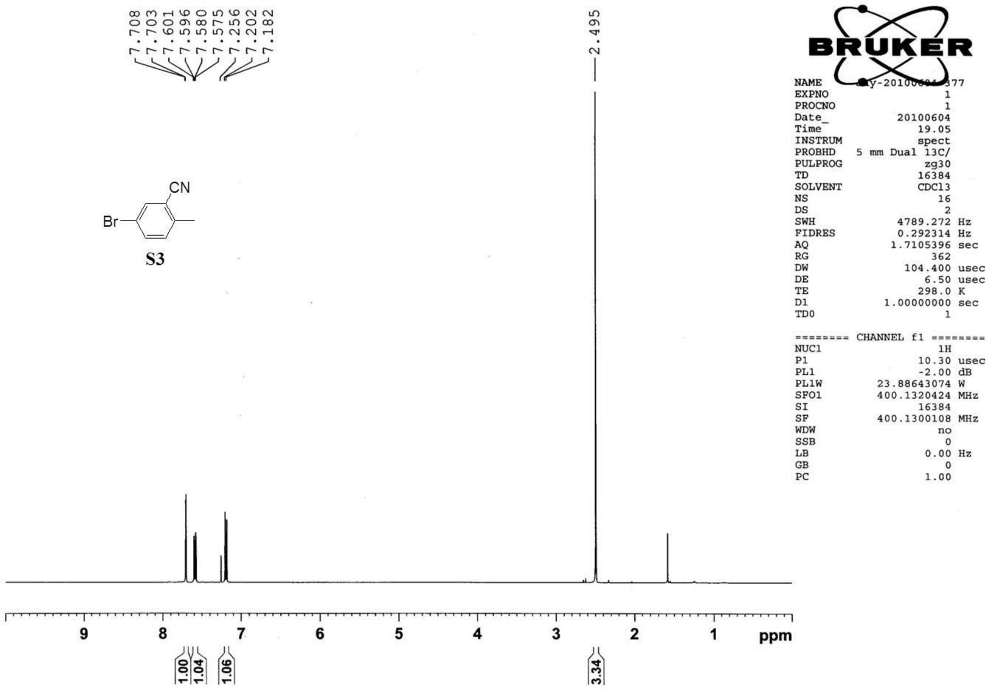
Figure S2: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **S2** in $CDCl_3$.



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TD                   16384
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DS                       2
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FIDRES            0.292314 Hz
AQ               1.7105396 sec
RG                     362
DW                 104.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.30 usec
PL1                  -2.00 dB
PL1W           23.88643074 W
SFO1           400.1320424 MHz
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SF             400.1300108 MHz
WDW                     no
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LB                    0.00 Hz
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PC                    1.00
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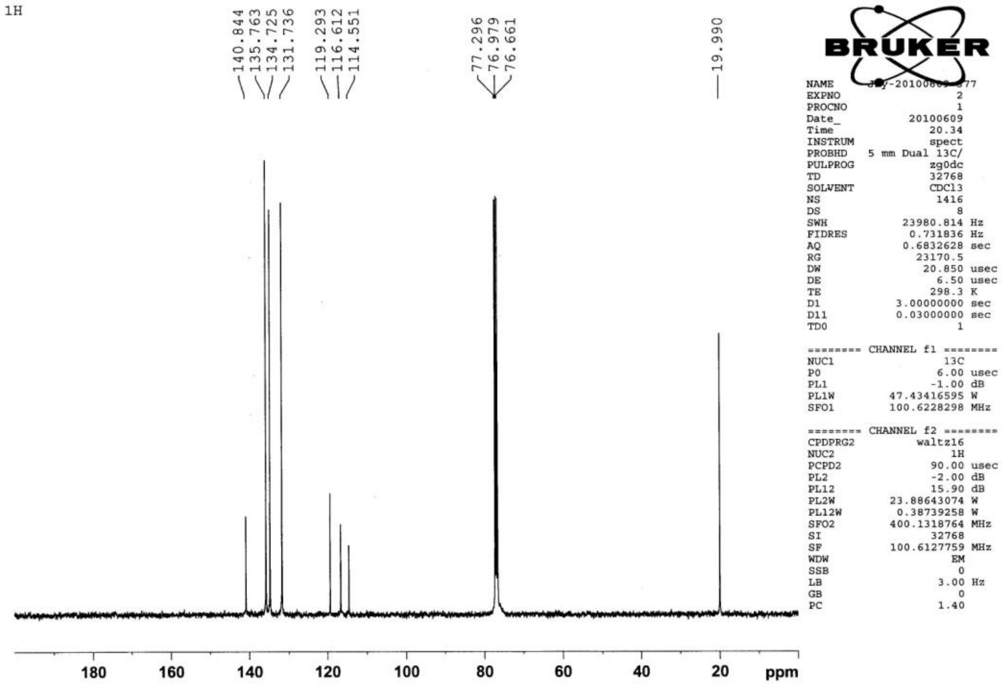

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TD                   32768
SOLVENT              CDCl3
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DS                       8
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ               0.6832628 sec
RG                 23170.5
DW                  20.850 usec
DE                    6.50 usec
TE                   298.3 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P0                    6.00 usec
PL1                  -1.00 dB
PL1W           47.43416595 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
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NUC2                    1H
PCPD2                90.00 usec
PL2                  -2.00 dB
PL12                 15.90 dB
PL2W           23.88643074 W
PL12W           0.38739258 W
SFO2           400.1318764 MHz
SI                   32768
SF             100.6127759 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
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Figure S3: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **S3** in $CDCl_3$.

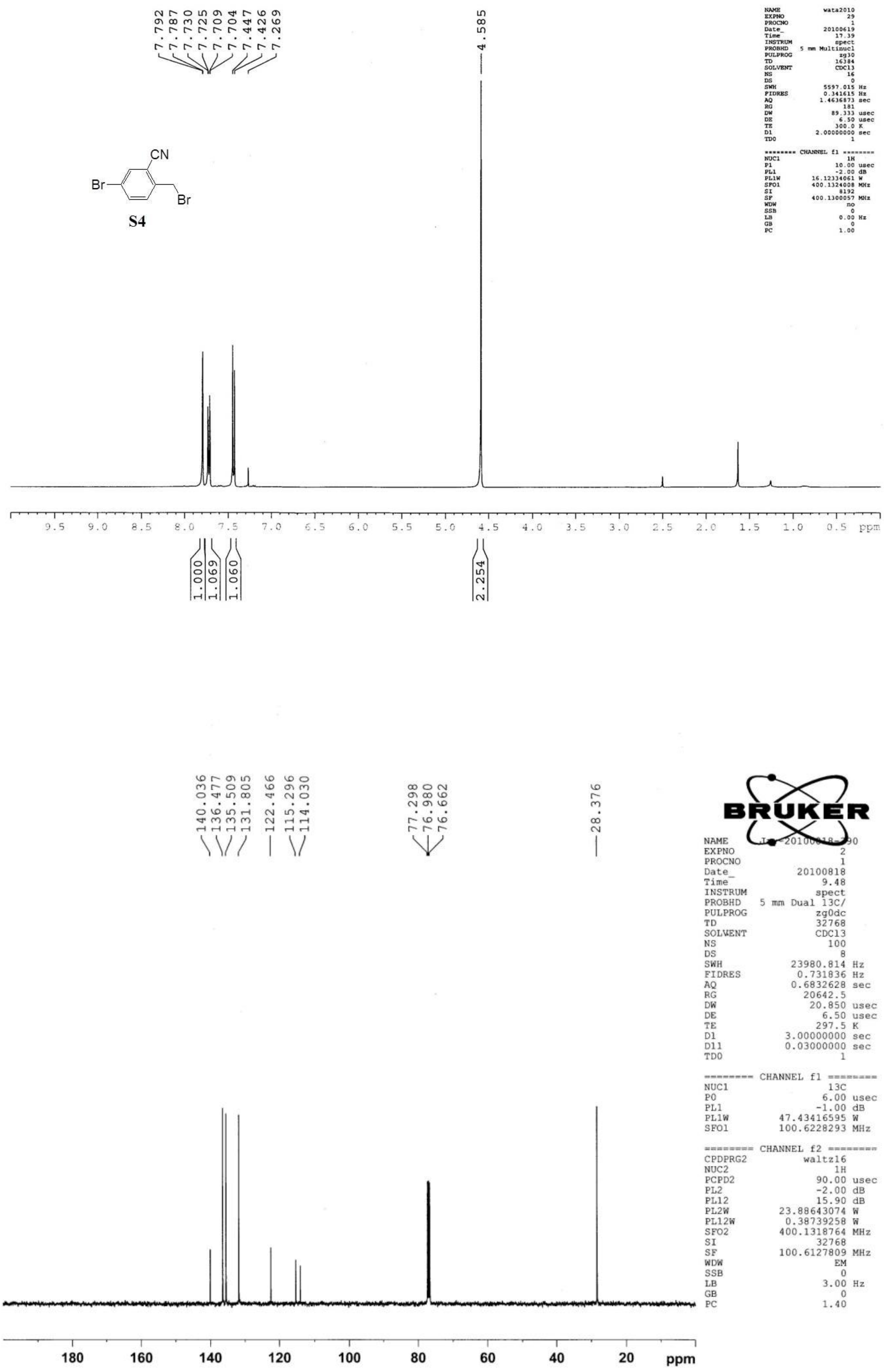
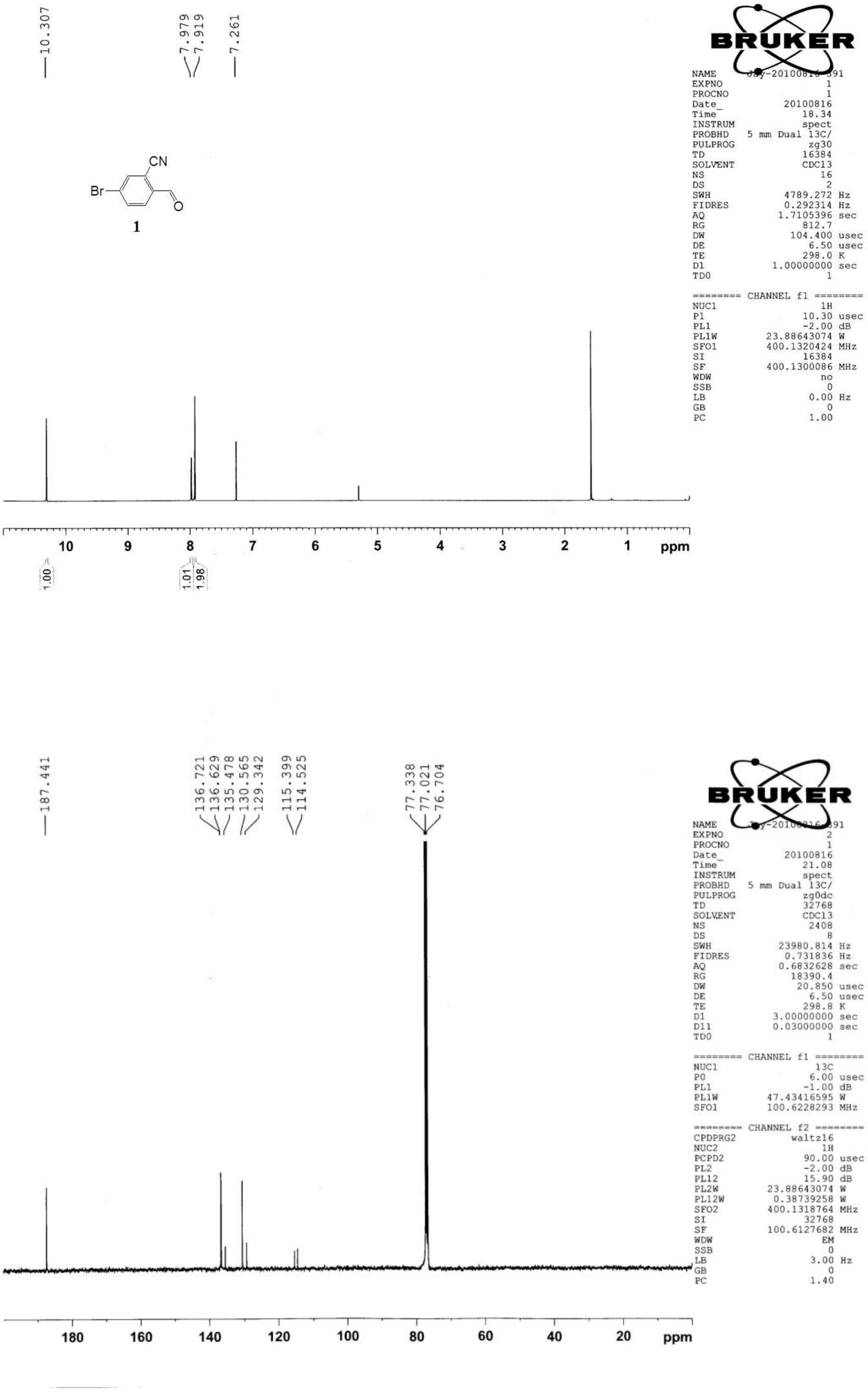


Figure S4: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **S4** in $CDCl_3$.



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TE                    298.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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GB                        0
PC                     1.00
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TD                    32768
SOLVENT               CDCl3
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FIDRES             0.731836 Hz
AQ                0.6832628 sec
RG                  18390.4
DW                   20.850 usec
DE                     6.50 usec
TE                    298.8 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P0                     6.00 usec
PL1                   -1.00 dB
PL1W            47.43416595 W
SFO1            100.6228293 MHz

======== CHANNEL f2 ========
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NUC2                     1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  15.90 dB
PL2W            23.88643074 W
PL12W            0.38739258 W
SFO2            400.1318764 MHz
SI                    32768
SF              100.6127682 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     1.40
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Figure S5: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **1** in $CDCl_3$.

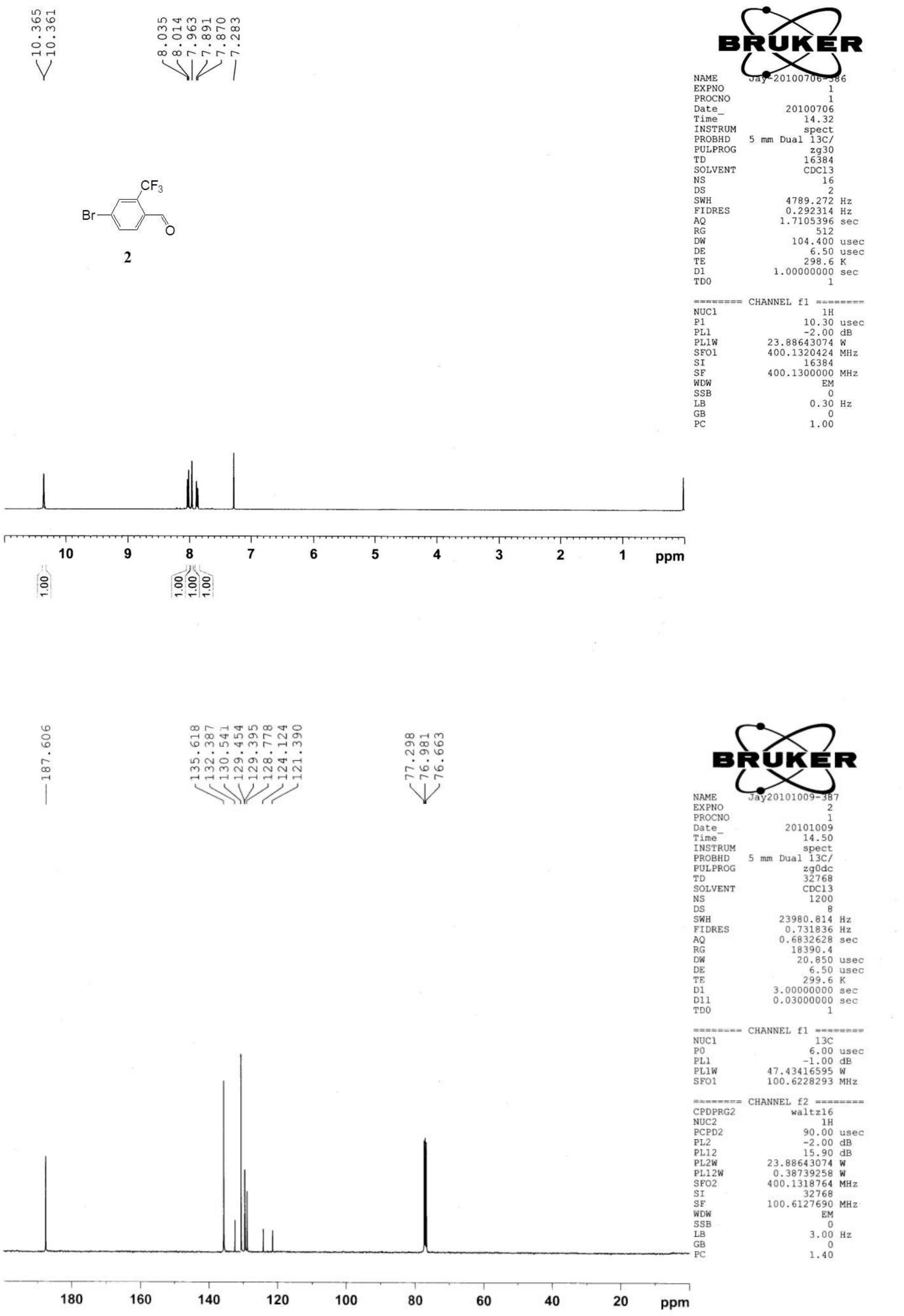
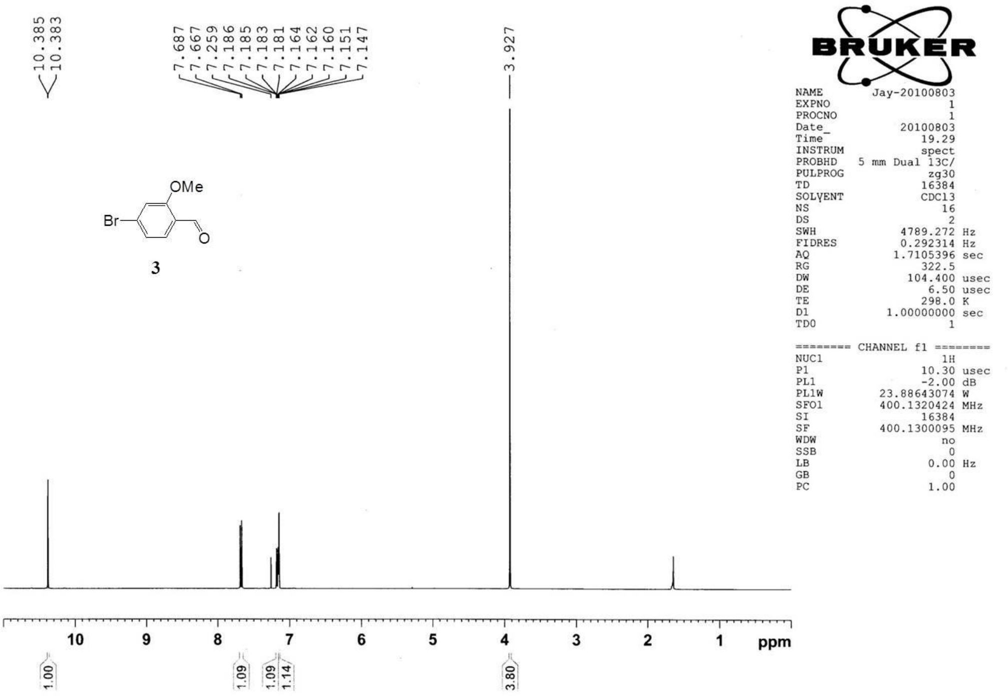


Figure S6: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **2** in $CDCl_3$.



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TD                   16384
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DS                       2
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FIDRES            0.292314 Hz
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RG                   322.5
DW                 104.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.30 usec
PL1                  -2.00 dB
PL1W           23.88643074 W
SFO1           400.1320424 MHz
SI                   16384
SF             400.1300095 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
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PC                    1.00
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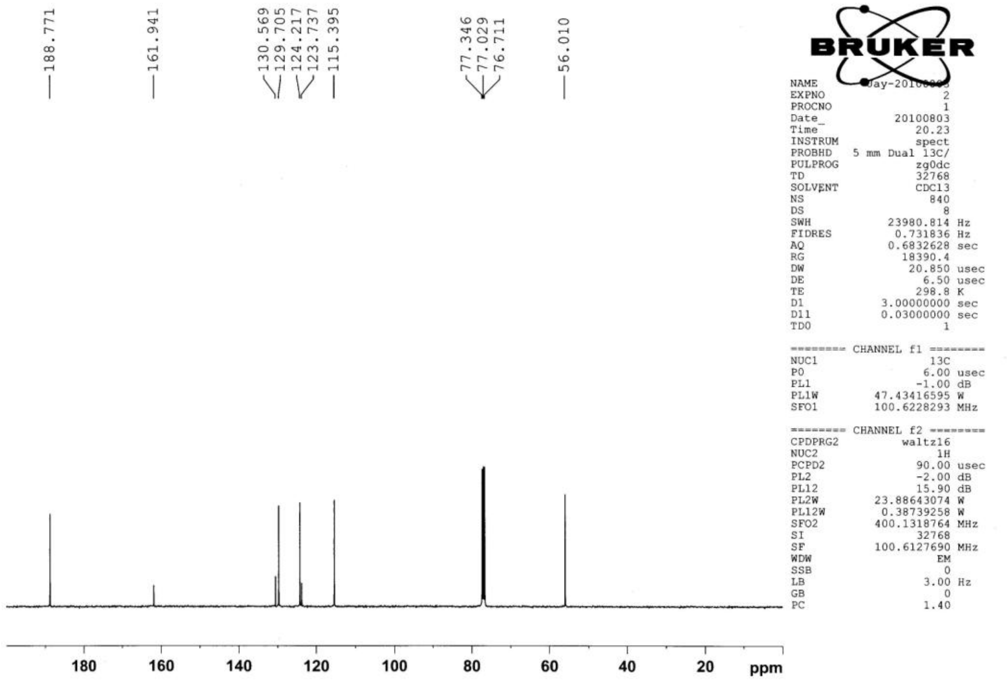

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PULPROG             zg0dc
TD                   32768
SOLVENT              CDC13
NS                     840
DS                       8
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ               0.6832628 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.50 usec
TE                   298.8 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P0                    6.00 usec
PL1                  -1.00 dB
PL1W           47.43416595 W
SFO1           100.6228293 MHz

======== CHANNEL f2 ========
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NUC2                    1H
PCPD2                90.00 usec
PL2                  -2.00 dB
PL12                 15.90 dB
PL2W           23.88643074 W
PL12W           0.38739258 W
SFO2           400.1318764 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
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Figure S7: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **3** in $CDCl_3$.

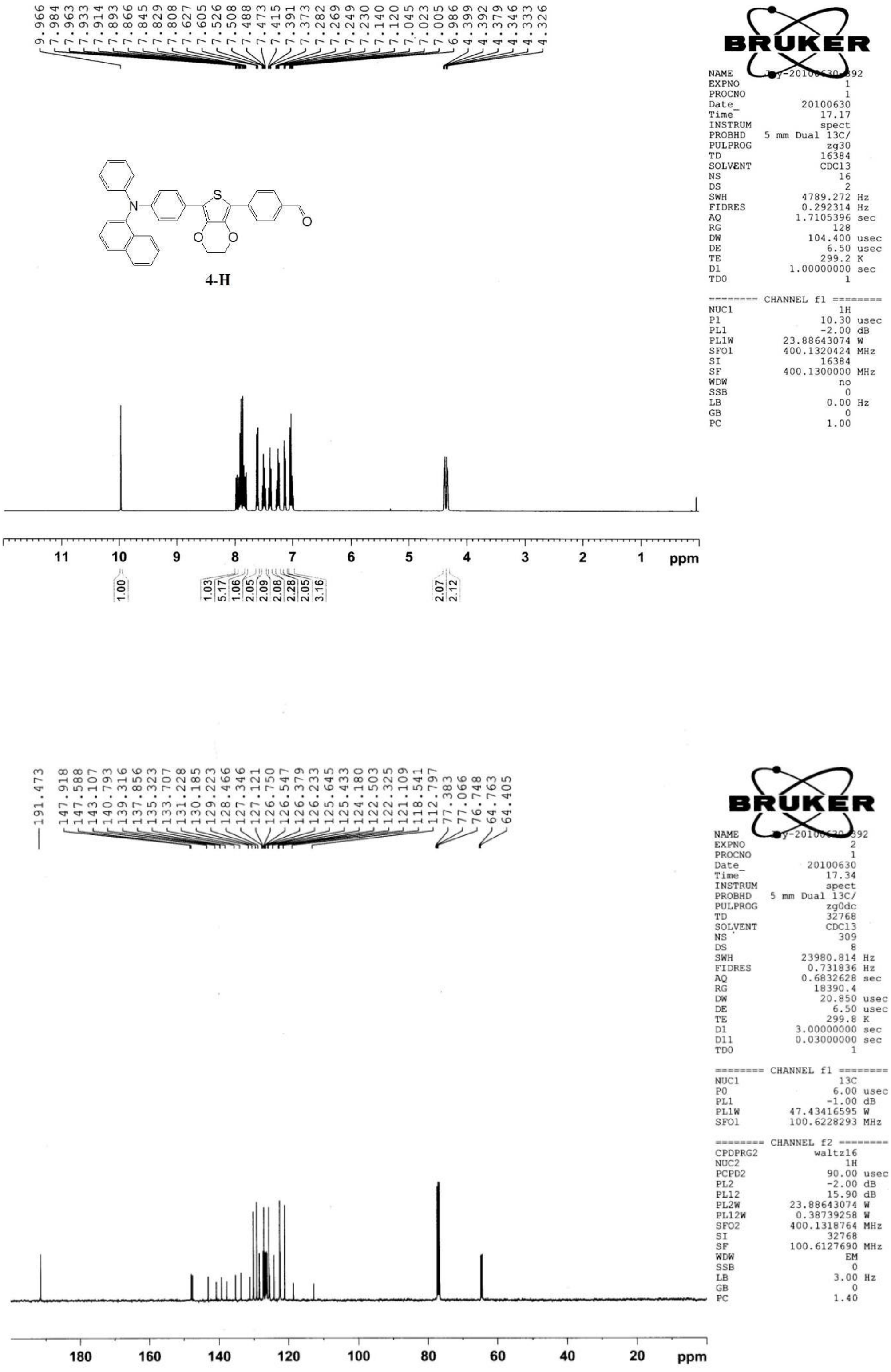
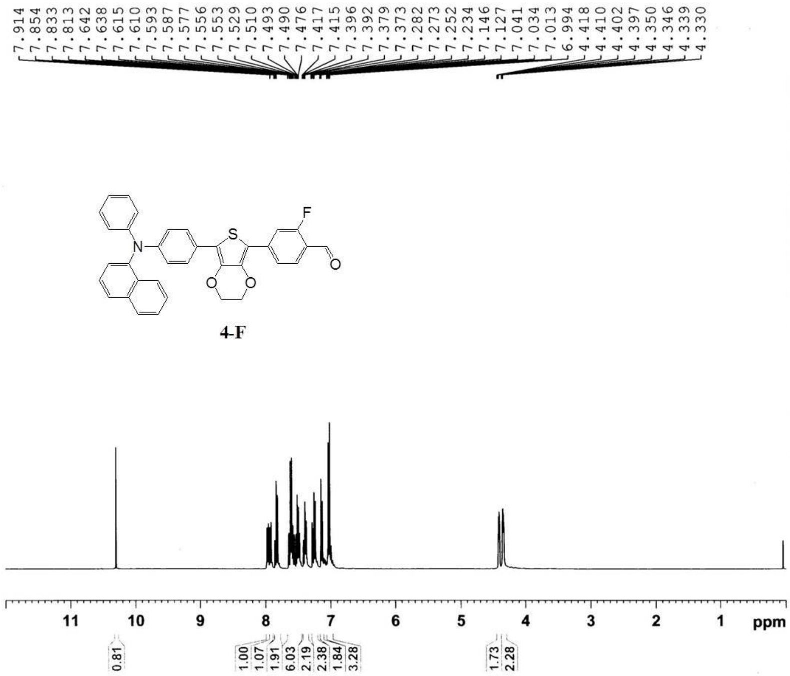


Figure S8: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **4-H** in $CDCl_3$.



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RG                      161.3
DW                    104.400 usec
DE                       6.50 usec
TE                      299.4 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.30 usec
PL1                     -2.00 dB
PL1W              23.88643074 W
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SI                      16384
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SSB                         0
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PC                       1.00
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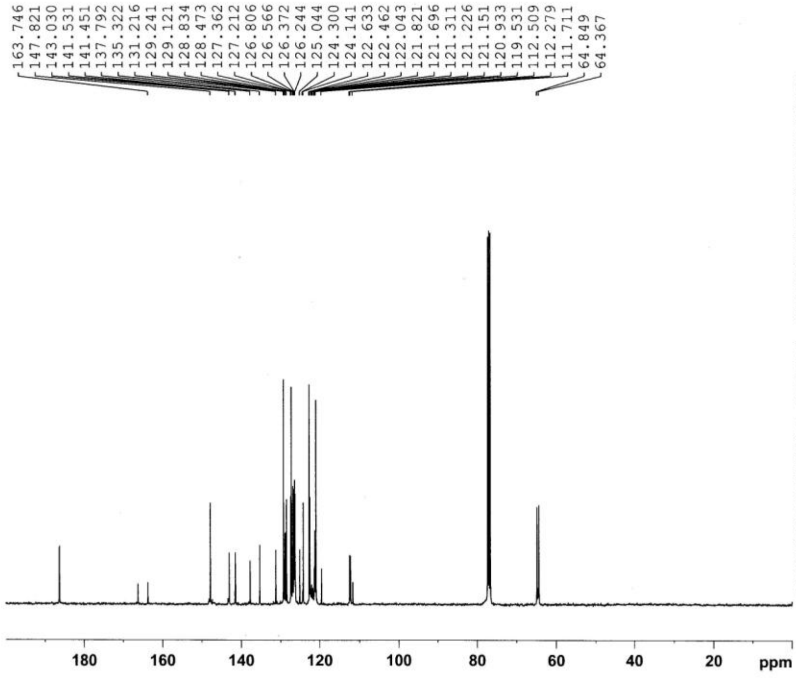

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PULPROG                zg0dc
TD                      32768
SOLVENT                 CDC13
NS                       3114
DS                          8
SWH                 23980.814 Hz
FIDRES               0.731836 Hz
AQ                  0.6832628 sec
RG                      16384
DW                     20.850 usec
DE                       6.50 usec
TE                      299.8 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P0                       6.00 usec
PL1                     -1.00 dB
PL1W              47.43416595 W
SFO1              100.6228293 MHz

======== CHANNEL f2 ========
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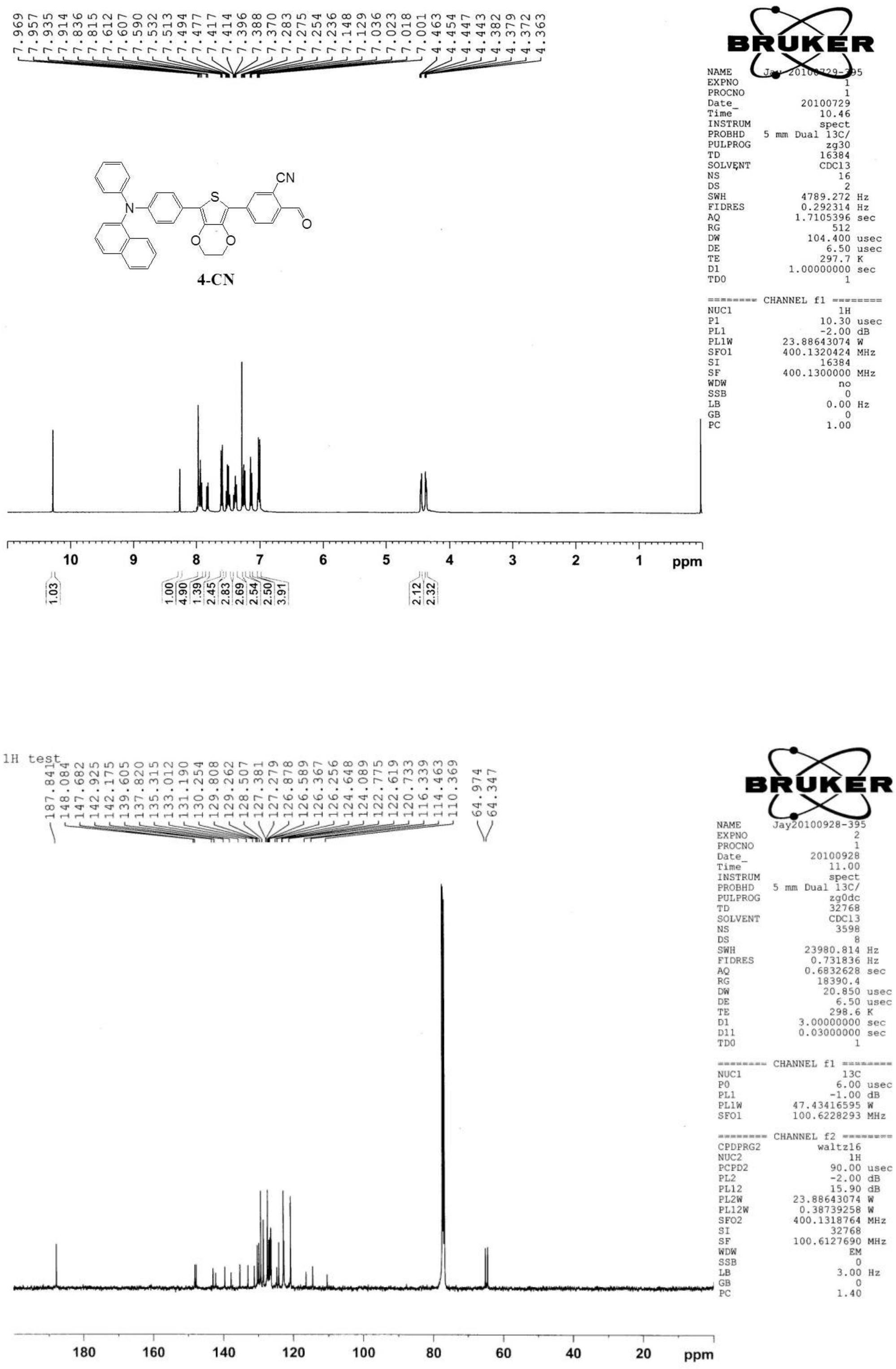
NUC2                       1H
PCPD2                   90.00 usec
PL2                     -2.00 dB
PL12                    15.90 dB
PL2W              23.88643074 W
PL12W              0.38739258 W
SFO2              400.1318764 MHz
SI                      32768
SF                100.6127690 MHz
WDW                        EM
SSB                         0
LB                       3.00 Hz
GB                          0
PC                       1.40
```

Figure S9: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **4-F** in $CDCl_3$.



```
NAME          Jay20100729-395
EXPNO                       1
PROCNO                      1
Date_                20100729
Time                    10.46
INSTRUM                 spect
PROBHD     5 mm Dual 13C/
PULPROG                  zg30
TD                      16384
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  4789.272 Hz
FIDRES               0.292314 Hz
AQ                  1.7105396 sec
RG                        512
DW                    104.400 usec
DE                       6.50 usec
TE                      297.7 K
D1                 1.00000000 sec
TD0                         1

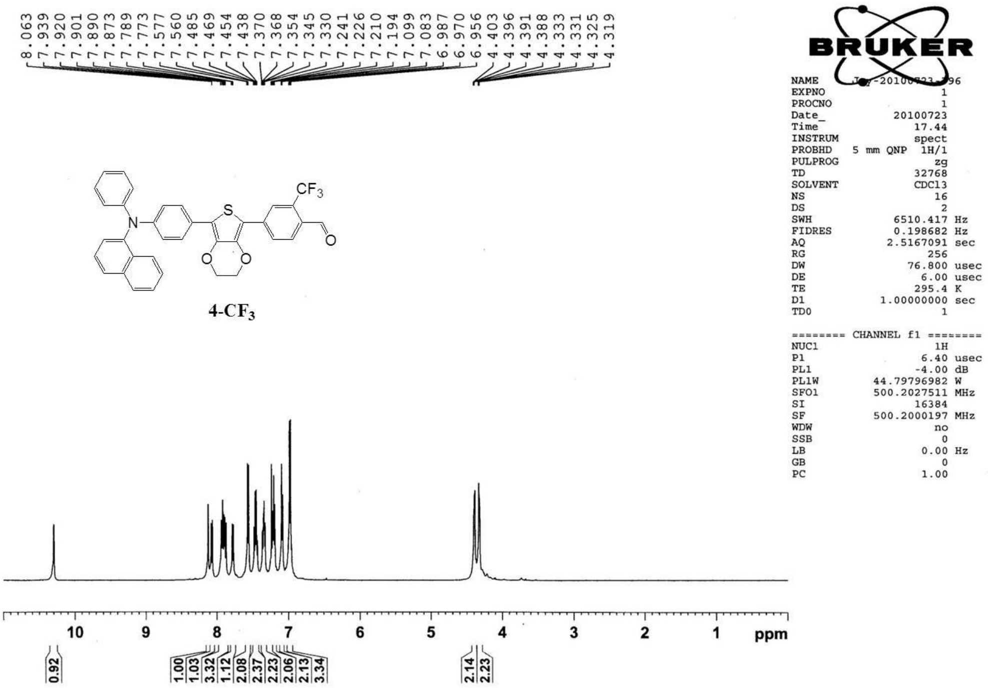
======== CHANNEL f1 ========
NUC1                       1H
P1                      10.30 usec
PL1                     -2.00 dB
PL1W              23.88643074 W
SFO1              400.1320424 MHz
SI                      16384
SF                400.1300000 MHz
WDW                        no
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00
```

```
NAME          Jay20100928-395
EXPNO                       2
PROCNO                      1
Date_                20100928
Time                    11.00
INSTRUM                 spect
PROBHD     5 mm Dual 13C/
PULPROG                 zg0dc
TD                      32768
SOLVENT                 CDCl3
NS                       3598
DS                          8
SWH                 23980.814 Hz
FIDRES               0.731836 Hz
AQ                  0.6832628 sec
RG                    18390.4
DW                     20.850 usec
DE                       6.50 usec
TE                      298.6 K
D1                 3.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P0                       6.00 usec
PL1                     -1.00 dB
PL1W              47.43416595 W
SFO1              100.6228293 MHz

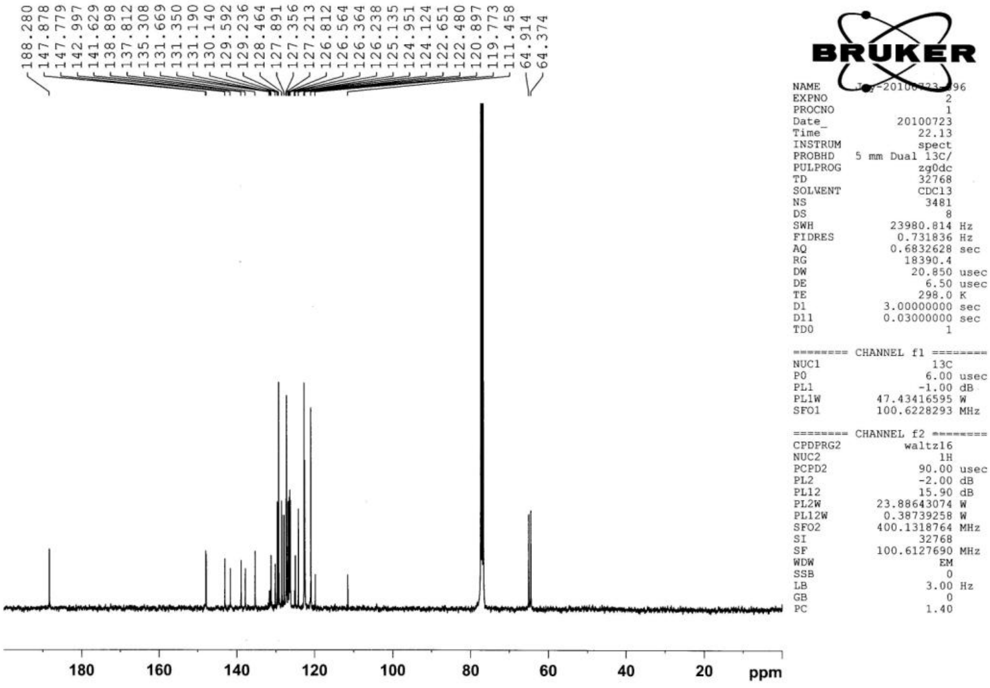
======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                   90.00 usec
PL2                     -2.00 dB
PL12                    15.90 dB
PL2W              23.88643074 W
PL12W              0.38739258 W
SFO2              400.1318764 MHz
SI                      32768
SF                100.6127690 MHz
WDW                        EM
SSB                         0
LB                       3.00 Hz
GB                          0
PC                       1.40
```

Figure S10: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **4-CN** in $CDCl_3$.



```
NAME       J[illegible]-20100723-[illegible]96
EXPNO                    1
PROCNO                   1
Date_             20100723
Time                 17.44
INSTRUM              spect
PROBHD   5 mm QNP  1H/1
PULPROG                 zg
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6510.417 Hz
FIDRES            0.198682 Hz
AQ               2.5167091 sec
RG                     256
DW                  76.800 usec
DE                    6.00 usec
TE                   295.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    6.40 usec
PL1                  -4.00 dB
PL1W           44.79796982 W
SFO1           500.2027511 MHz
SI                   16384
SF             500.2000197 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

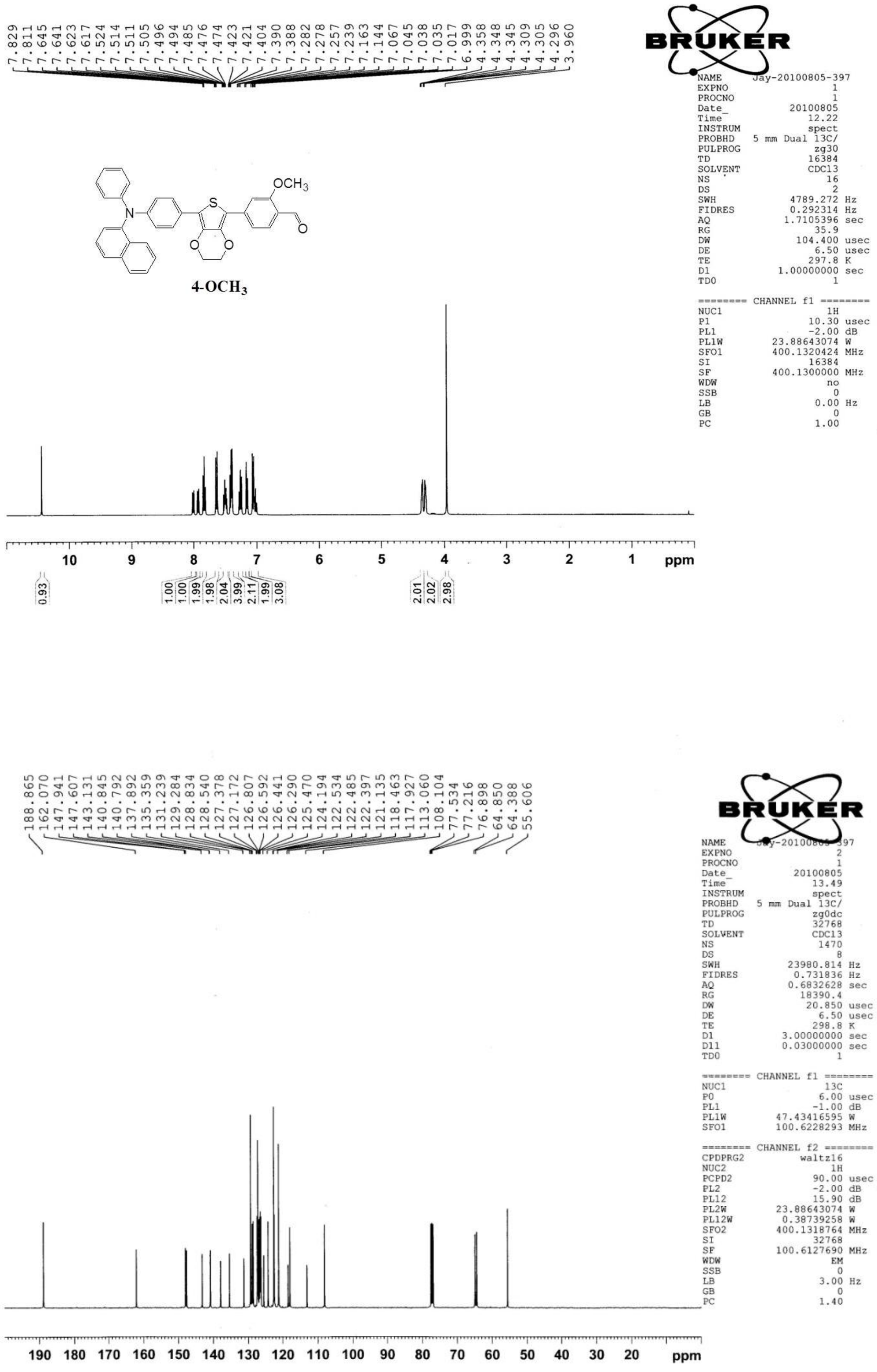


```
NAME       J[illegible]-20100723-[illegible]96
EXPNO                    2
PROCNO                   1
Date_             20100723
Time                 22.13
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG              zg0dc
TD                   32768
SOLVENT              CDCl3
NS                    3481
DS                       8
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ               0.6832628 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.50 usec
TE                   298.0 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P0                    6.00 usec
PL1                  -1.00 dB
PL1W           47.43416595 W
SFO1           100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -2.00 dB
PL12                 15.90 dB
PL2W           23.88643074 W
PL12W           0.38739258 W
SFO2           400.1318764 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
```

Figure S11: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **4-CF$_3$** in CDCl$_3$.



```
NAME      Jay-20100805-397
EXPNO                    1
PROCNO                   1
Date_             20100805
Time                 12.22
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4789.272 Hz
FIDRES            0.292314 Hz
AQ               1.7105396 sec
RG                    35.9
DW                 104.400 usec
DE                    6.50 usec
TE                   297.8 K
D1              1.00000000 sec
TD0                      1

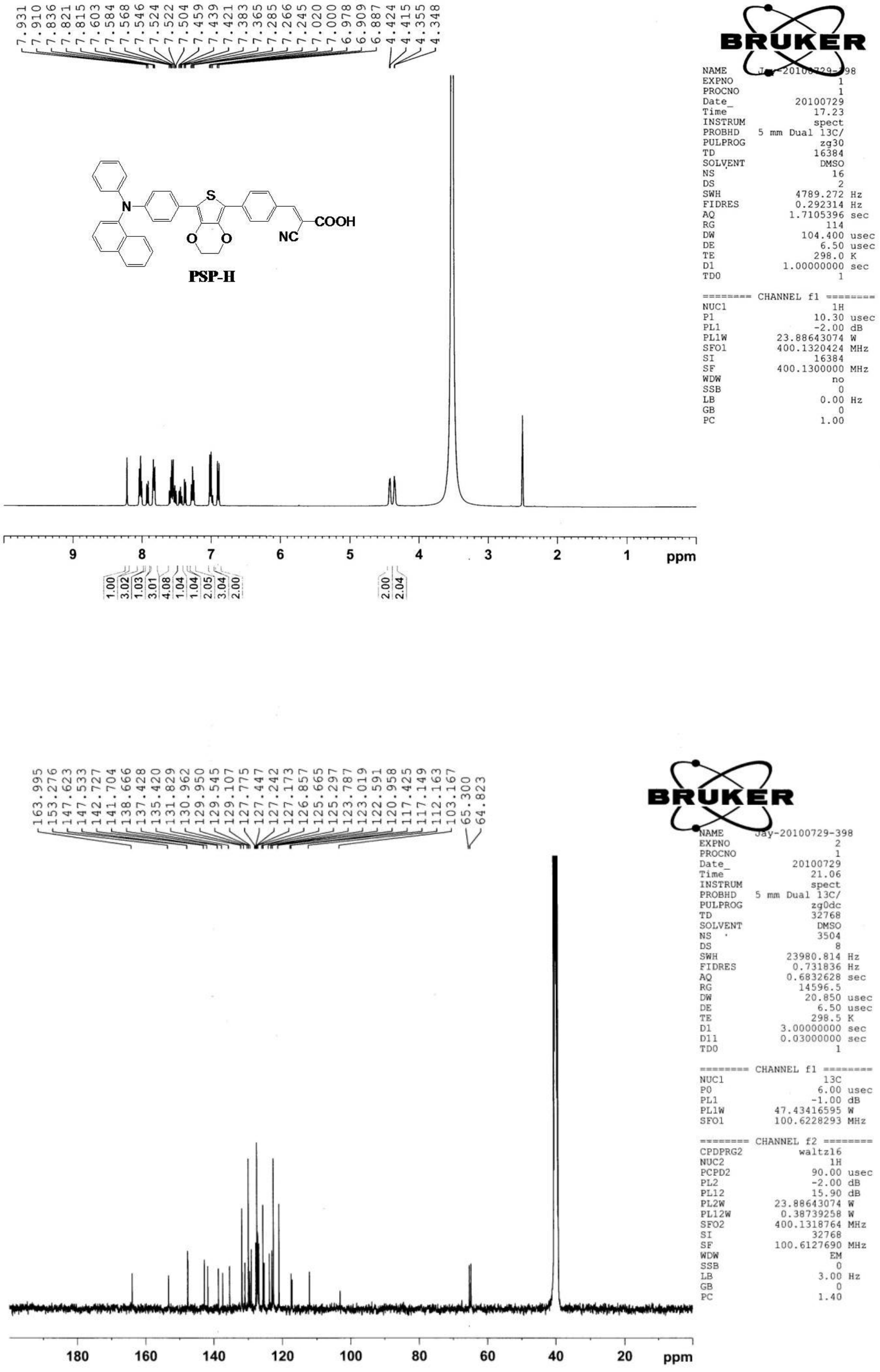
======== CHANNEL f1 ========
NUC1                    1H
P1                   10.30 usec
PL1                  -2.00 dB
PL1W           23.88643074 W
SFO1           400.1320424 MHz
SI                   16384
SF             400.1300000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

```
NAME      Jay-20100805-397
EXPNO                    2
PROCNO                   1
Date_             20100805
Time                 13.49
INSTRUM              spect
PROBHD   5 mm Dual 13C/
PULPROG              zg0dc
TD                   32768
SOLVENT              CDCl3
NS                    1470
DS                       8
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ               0.6832628 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.50 usec
TE                   298.8 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P0                    6.00 usec
PL1                  -1.00 dB
PL1W           47.43416595 W
SFO1           100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -2.00 dB
PL12                 15.90 dB
PL2W           23.88643074 W
PL12W           0.38739258 W
SFO2           400.1318764 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
```

Figure S12: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **4-OCH$_3$** in CDCl$_3$.



```
NAME        Jay-20100729-398
EXPNO                      1
PROCNO                     1
Date_               20100729
Time                   17.23
INSTRUM                spect
PROBHD   5 mm Dual 13C/
PULPROG                 zg30
TD                     16384
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.292314 Hz
AQ                 1.7105396 sec
RG                       114
DW                   104.400 usec
DE                      6.50 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

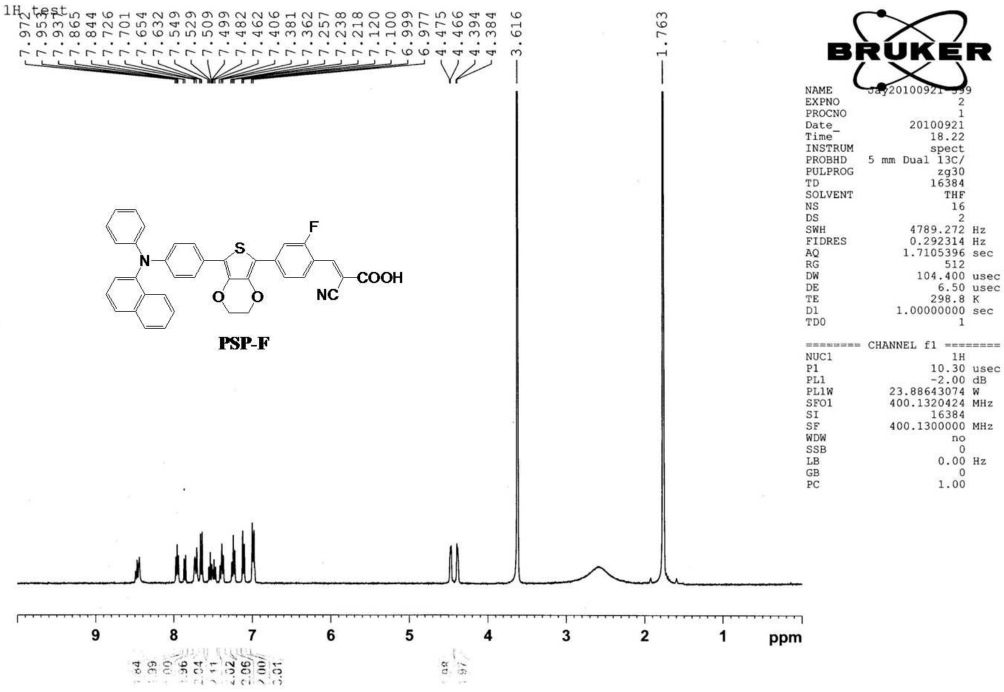
======== CHANNEL f1 ========
NUC1                      1H
P1                     10.30 usec
PL1                    -2.00 dB
PL1W             23.88643074 W
SFO1             400.1320424 MHz
SI                     16384
SF               400.1300000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

```
NAME        Jay-20100729-398
EXPNO                      2
PROCNO                     1
Date_               20100729
Time                   21.06
INSTRUM                spect
PROBHD   5 mm Dual 13C/
PULPROG                 zg0dc
TD                     32768
SOLVENT                 DMSO
NS                      3504
DS                         8
SWH                23980.814 Hz
FIDRES              0.731836 Hz
AQ                 0.6832628 sec
RG                   14596.5
DW                    20.850 usec
DE                      6.50 usec
TE                     298.5 K
D1                3.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P0                      6.00 usec
PL1                    -1.00 dB
PL1W             47.43416595 W
SFO1             100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  90.00 usec
PL2                    -2.00 dB
PL12                   15.90 dB
PL2W             23.88643074 W
PL12W             0.38739258 W
SFO2             400.1318764 MHz
SI                     32768
SF               100.6127690 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40
```

Figure S13: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PSP-H** in DMSO-d_6.



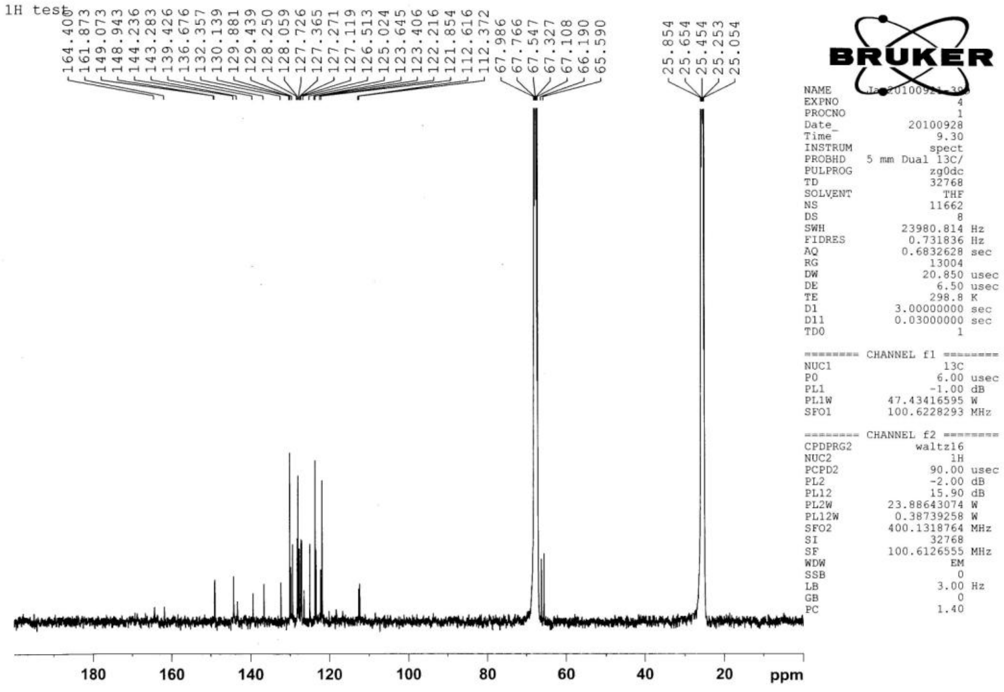
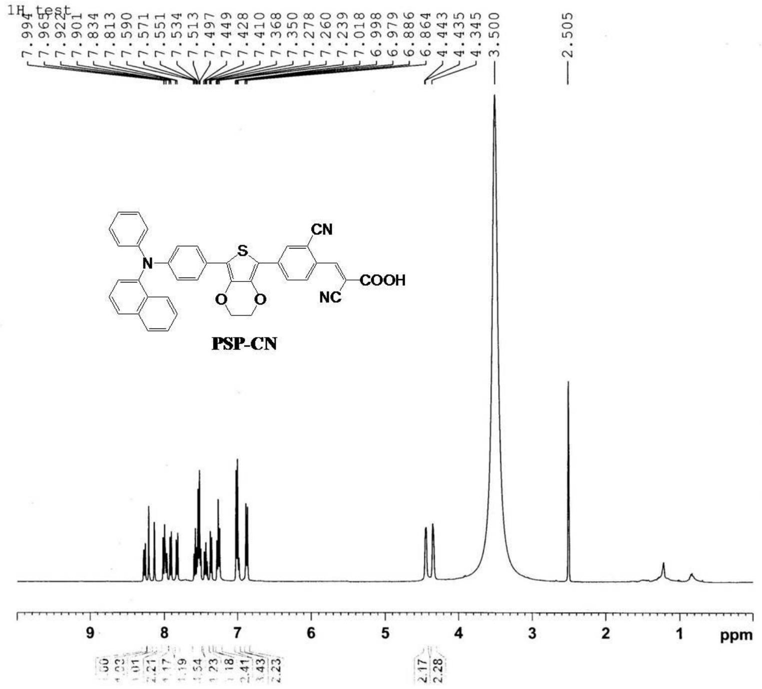
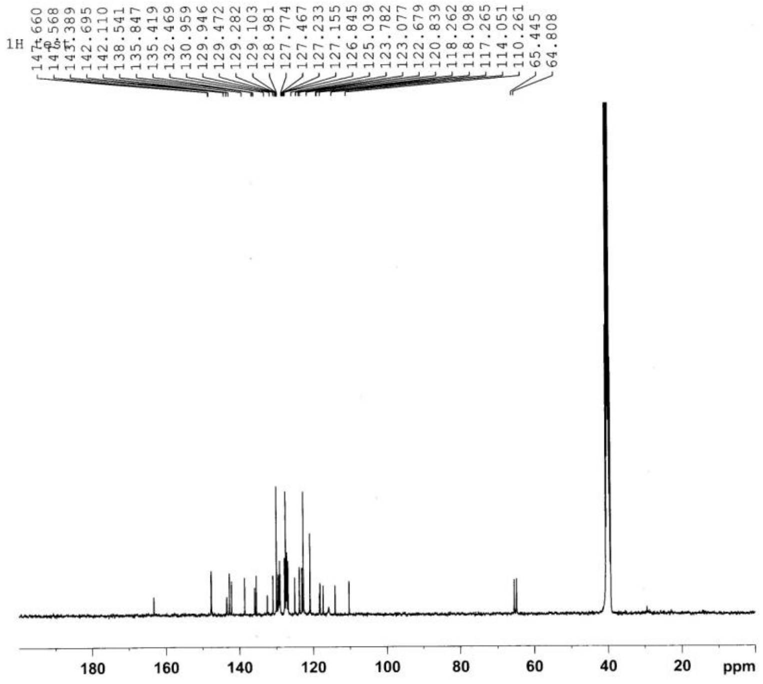


Figure S14: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PSP-F** in THF-d_8.



```
NAME          Jay20100921
EXPNO                   1
PROCNO                  1
Date_            20100921
Time                16.32
INSTRUM             spect
PROBHD   5 mm Dual 13C/
PULPROG              zg30
TD                  16384
SOLVENT              DMSO
NS                     16
DS                      2
SWH              4789.272 Hz
FIDRES           0.292314 Hz
AQ              1.7105396 sec
RG                    128
DW                104.400 usec
DE                   6.50 usec
TE                  297.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.30 usec
PL1                 -2.00 dB
PL1W          23.88643074 W
SFO1          400.1320424 MHz
SI                  16384
SF            400.1300000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

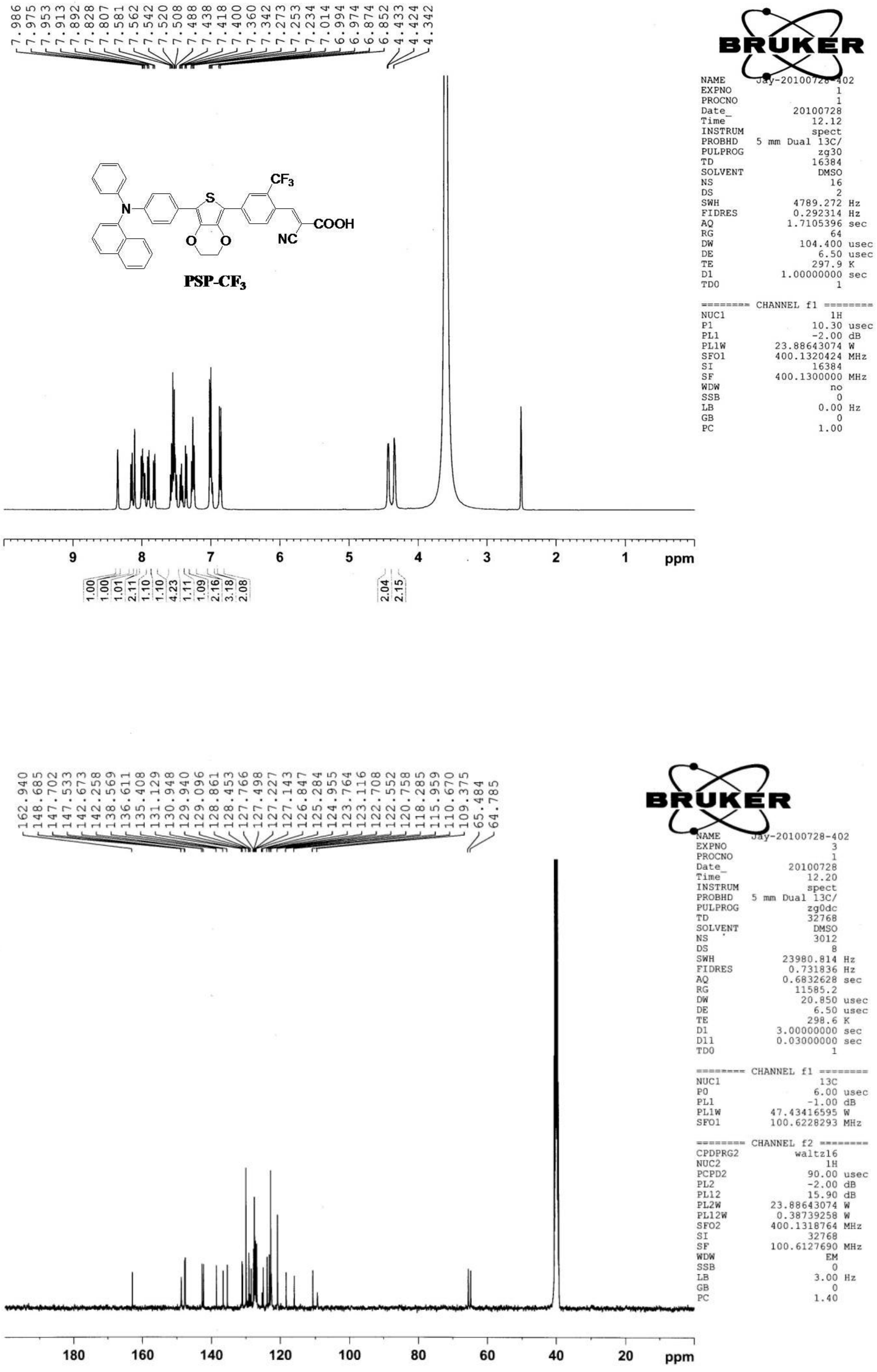


```
NAME     Jay20100923-4[illegible]1
EXPNO                   2
PROCNO                  1
Date_            20100924
Time                 8.00
INSTRUM             spect
PROBHD   5 mm Dual 13C/
PULPROG             zg0dc
TD                  32768
SOLVENT              DMSO
NS '                10000
DS                      8
SWH             23980.814 Hz
FIDRES           0.731836 Hz
AQ              0.6832628 sec
RG                11585.2
DW                 20.850 usec
DE                   6.50 usec
TE                  299.1 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P0                   6.00 usec
PL1                 -1.00 dB
PL1W          47.43416595 W
SFO1          100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -2.00 dB
PL12                15.90 dB
PL2W          23.88643074 W
PL12W          0.38739258 W
SFO2          400.1318764 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40
```

Figure S15: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PSP-CN** in DMSO-d_6.



```
NAME       Jay-20100728-402
EXPNO                     1
PROCNO                    1
Date_              20100728
Time                  12.12
INSTRUM               spect
PROBHD     5 mm Dual 13C/
PULPROG                zg30
TD                    16384
SOLVENT                DMSO
NS                       16
DS                        2
SWH                4789.272 Hz
FIDRES             0.292314 Hz
AQ                1.7105396 sec
RG                       64
DW                  104.400 usec
DE                     6.50 usec
TE                    297.9 K
D1               1.00000000 sec
TD0                       1

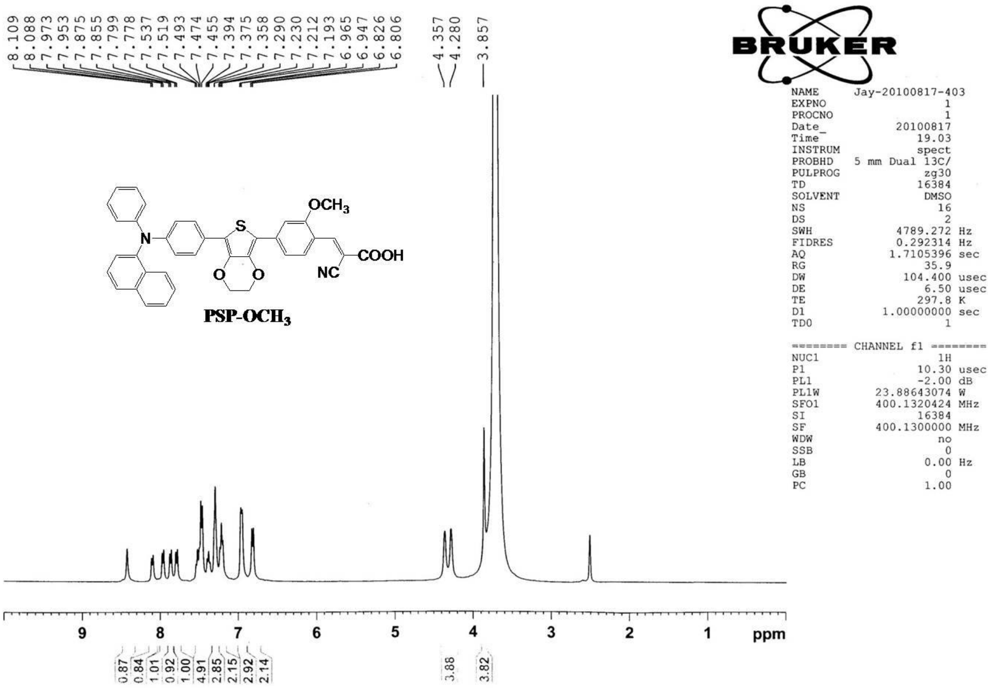
======== CHANNEL f1 ========
NUC1                     1H
P1                    10.30 usec
PL1                   -2.00 dB
PL1W            23.88643074 W
SFO1            400.1320424 MHz
SI                    16384
SF              400.1300000 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

```
NAME       Jay-20100728-402
EXPNO                     3
PROCNO                    1
Date_              20100728
Time                  12.20
INSTRUM               spect
PROBHD     5 mm Dual 13C/
PULPROG              zg0dc
TD                    32768
SOLVENT                DMSO
NS                     3012
DS                        8
SWH               23980.814 Hz
FIDRES             0.731836 Hz
AQ                0.6832628 sec
RG                  11585.2
DW                   20.850 usec
DE                     6.50 usec
TE                    298.6 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P0                     6.00 usec
PL1                   -1.00 dB
PL1W            47.43416595 W
SFO1            100.6228293 MHz

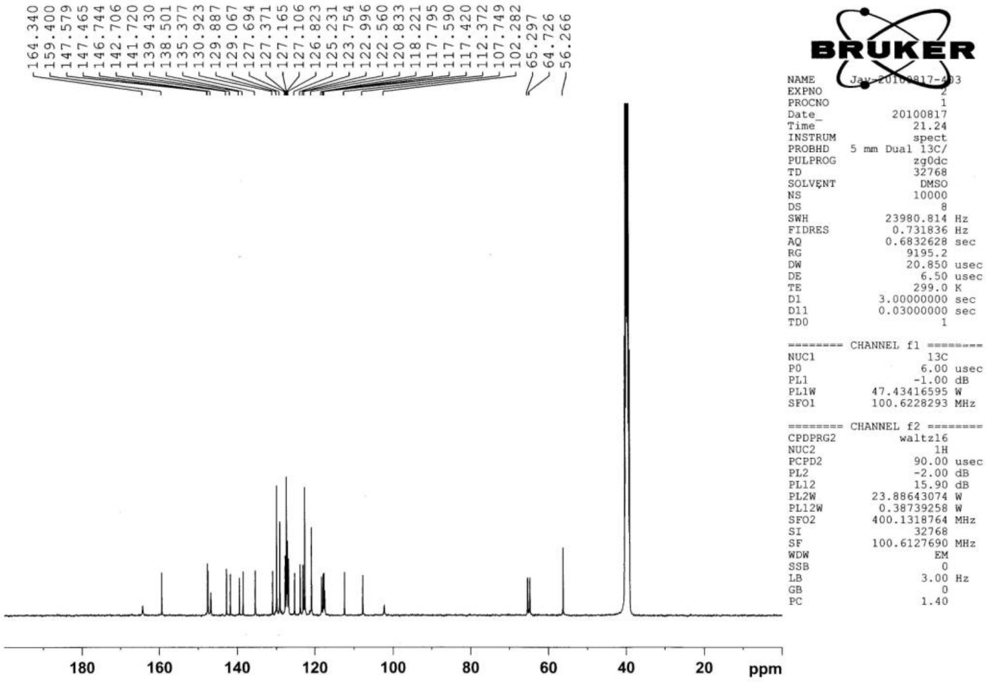
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  15.90 dB
PL2W            23.88643074 W
PL12W            0.38739258 W
SFO2            400.1318764 MHz
SI                    32768
SF              100.6127690 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     1.40
```

Figure S16: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PSP-CF$_3$** in DMSO-d_6.



```
NAME          Jay-20100817-403
EXPNO                        1
PROCNO                       1
Date_                 20100817
Time                     19.03
INSTRUM                  spect
PROBHD    5 mm Dual 13C/
PULPROG                   zg30
TD                       16384
SOLVENT                   DMSO
NS                          16
DS                           2
SWH                   4789.272 Hz
FIDRES                0.292314 Hz
AQ                   1.7105396 sec
RG                        35.9
DW                     104.400 usec
DE                        6.50 usec
TE                       297.8 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       10.30 usec
PL1                      -2.00 dB
PL1W               23.88643074 W
SFO1               400.1320424 MHz
SI                       16384
SF                 400.1300000 MHz
WDW                         no
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.00
```



```
NAME          Jay-20100817-403
EXPNO                        2
PROCNO                       1
Date_                 20100817
Time                     21.24
INSTRUM                  spect
PROBHD    5 mm Dual 13C/
PULPROG                  zg0dc
TD                       32768
SOLVENT                   DMSO
NS                       10000
DS                           8
SWH                  23980.814 Hz
FIDRES                0.731836 Hz
AQ                   0.6832628 sec
RG                      9195.2
DW                      20.850 usec
DE                        6.50 usec
TE                       299.0 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P0                        6.00 usec
PL1                      -1.00 dB
PL1W               47.43416595 W
SFO1               100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -2.00 dB
PL12                     15.90 dB
PL2W               23.88643074 W
PL12W               0.38739258 W
SFO2               400.1318764 MHz
SI                       32768
SF                 100.6127690 MHz
WDW                         EM
SSB                          0
LB                        3.00 Hz
GB                           0
PC                        1.40
```

Figure S17: ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **PSP-OCH$_3$** in DMSO-d_6.

3. Infrared spectra

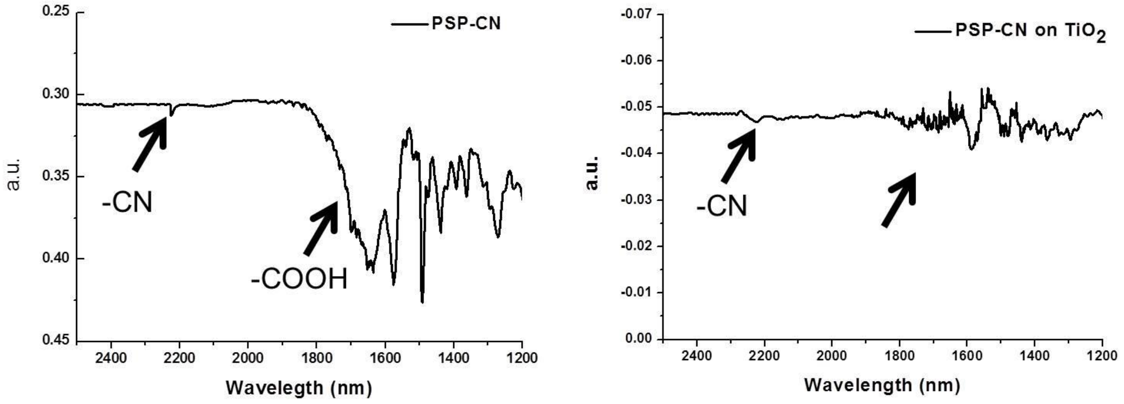


Figure S18. The IR spectra of **PSP-CN** (Left: neat; Right: dye on TiO$_2$ film).

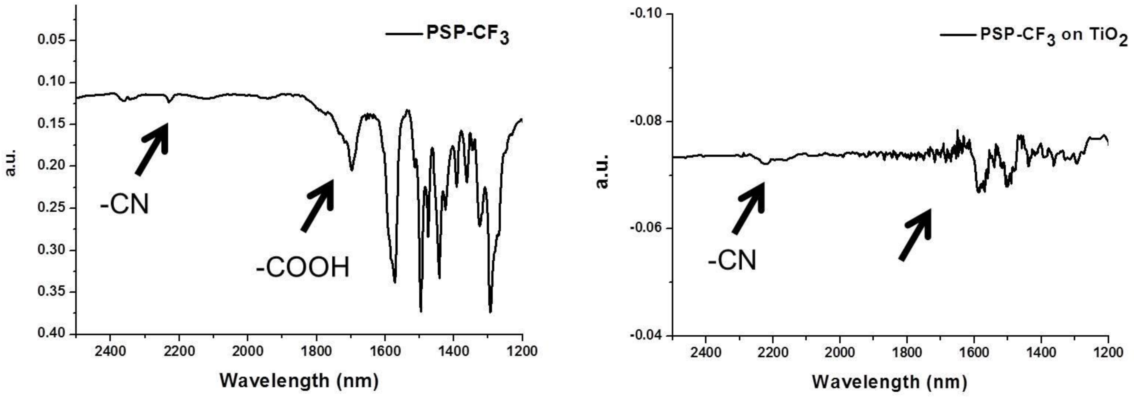
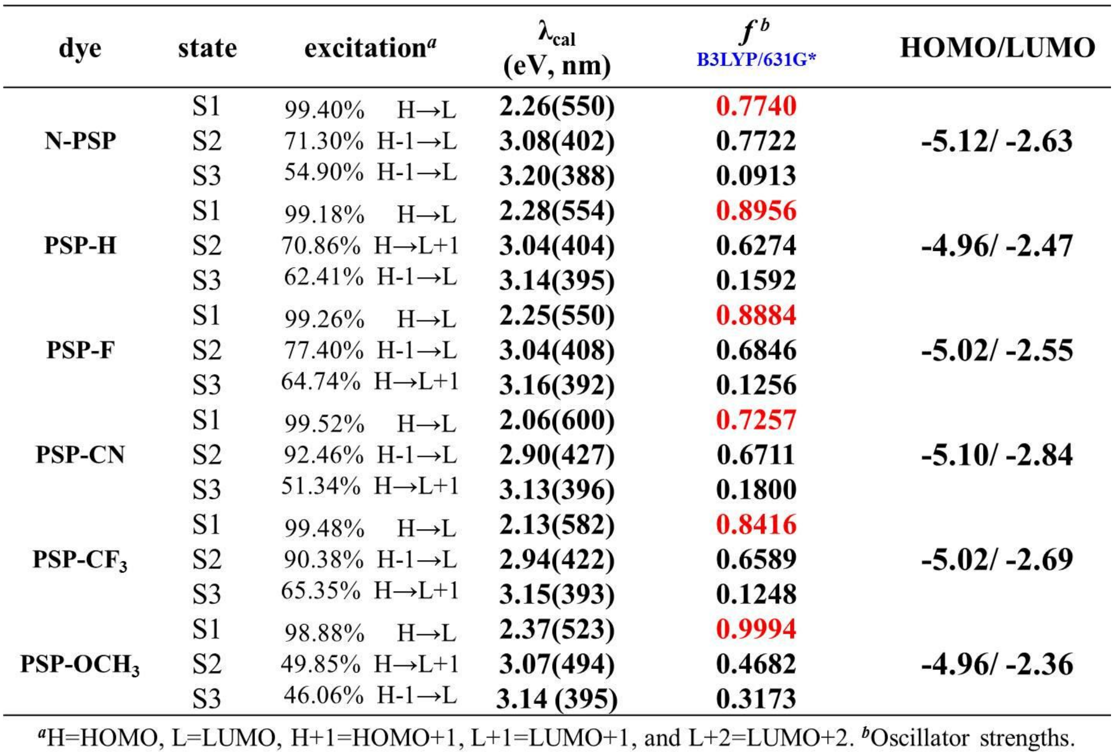


Figure S19. The IR spectra of **PSP-CF$_3$** (Left: neat; Right: dye on TiO$_2$ film).

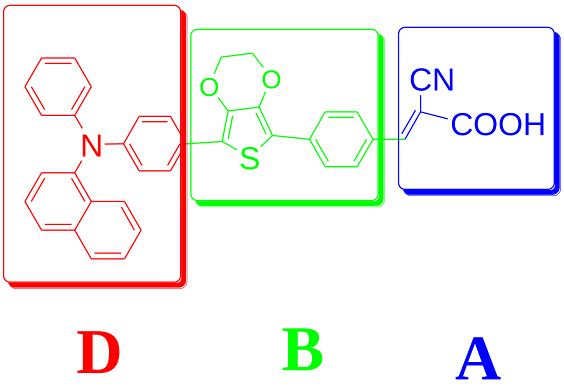
4. Theoretical calculation

Table S1. Calculated Low-Lying Transition for dyes.



dye	state	excitation[a]	λ_{cal} (eV, nm)	f [b] B3LYP/631G*	HOMO/LUMO
N-PSP	S1	99.40% H→L	**2.26(550)**	**0.7740**	**-5.12/ -2.63**
	S2	71.30% H-1→L	**3.08(402)**	**0.7722**	
	S3	54.90% H-1→L	**3.20(388)**	**0.0913**	
PSP-H	S1	99.18% H→L	**2.28(554)**	**0.8956**	**-4.96/ -2.47**
	S2	70.86% H→L+1	**3.04(404)**	**0.6274**	
	S3	62.41% H-1→L	**3.14(395)**	**0.1592**	
PSP-F	S1	99.26% H→L	**2.25(550)**	**0.8884**	**-5.02/ -2.55**
	S2	77.40% H-1→L	**3.04(408)**	**0.6846**	
	S3	64.74% H→L+1	**3.16(392)**	**0.1256**	
PSP-CN	S1	99.52% H→L	**2.06(600)**	**0.7257**	**-5.10/ -2.84**
	S2	92.46% H-1→L	**2.90(427)**	**0.6711**	
	S3	51.34% H→L+1	**3.13(396)**	**0.1800**	
PSP-CF_3	S1	99.48% H→L	**2.13(582)**	**0.8416**	**-5.02/ -2.69**
	S2	90.38% H-1→L	**2.94(422)**	**0.6589**	
	S3	65.35% H→L+1	**3.15(393)**	**0.1248**	
PSP-OCH_3	S1	98.88% H→L	**2.37(523)**	**0.9994**	**-4.96/ -2.36**
	S2	49.85% H→L+1	**3.07(494)**	**0.4682**	
	S3	46.06% H-1→L	**3.14 (395)**	**0.3173**	

[a] H=HOMO, L=LUMO, H+1=HOMO+1, L+1=LUMO+1, and L+2=LUMO+2. [b] Oscillator strengths.



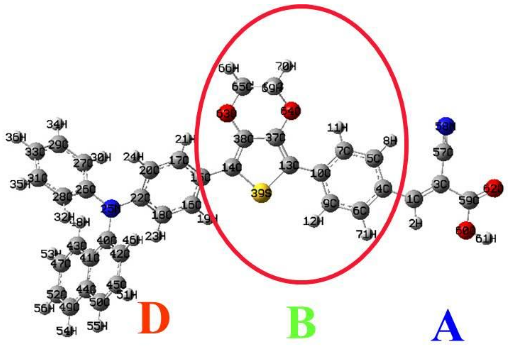
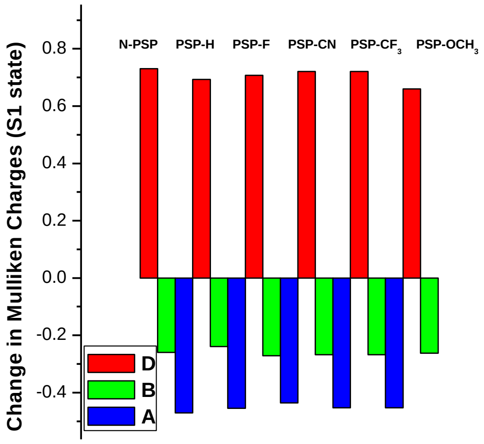


Table S2. Difference of Mulliken charges between ground state (S_0) and excited state (S_1), estimated by time dependent DFT/B3LYP model.

dye	D	B	A
N-PSP	0.73091	-0.26014	-0.47078
PSP-H	0.69312	-0.23877	-0.45435
PSP-F	0.70760	-0.27141	-0.43619
PSP-CN	0.75501	-0.30760	-0.44741
PSP-CF3	0.72077	-0.26813	-0.45263
PSP-OMe	0.66031	-0.26239	-0.39792

Difference of Mulliken charge between ground state and excited state.



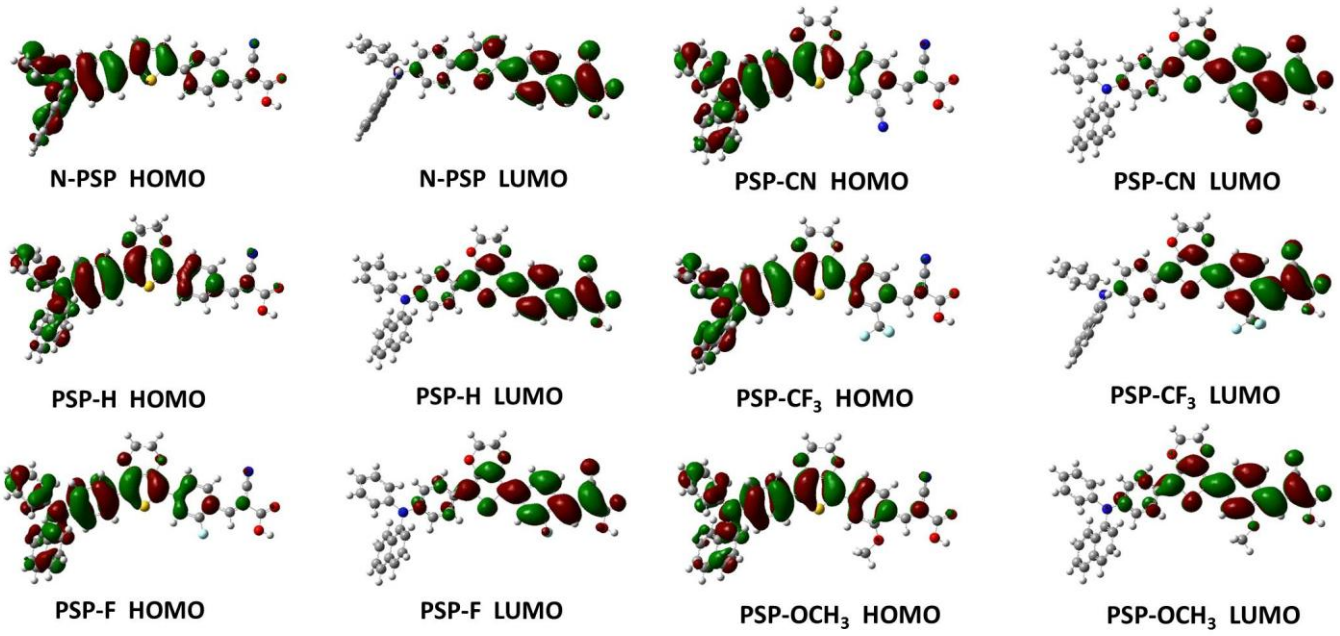


Figure S20. Bar-chart plots foe the difference of Mulliken charge listed in Table S2.

Figure S21. Computed HOMO and LUMO orbitals of **PSP-** series compounds.

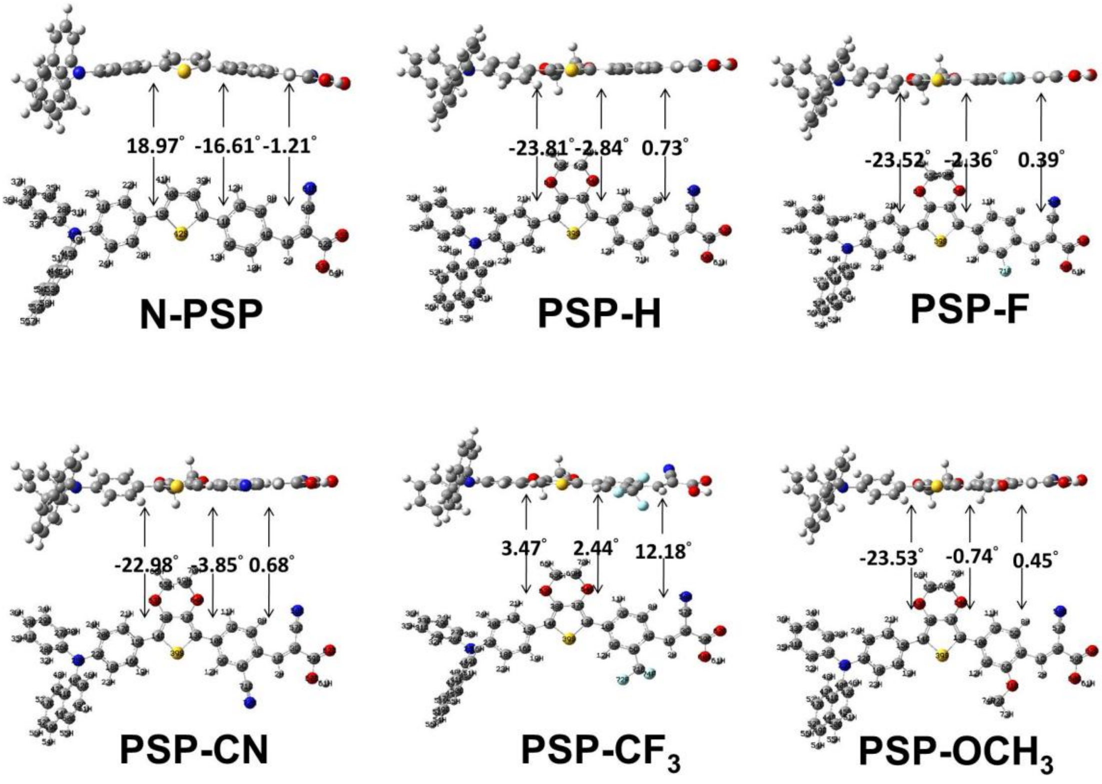


Figure S22. Computed dihedral angles of **PSP**-series.

5. Loading amount

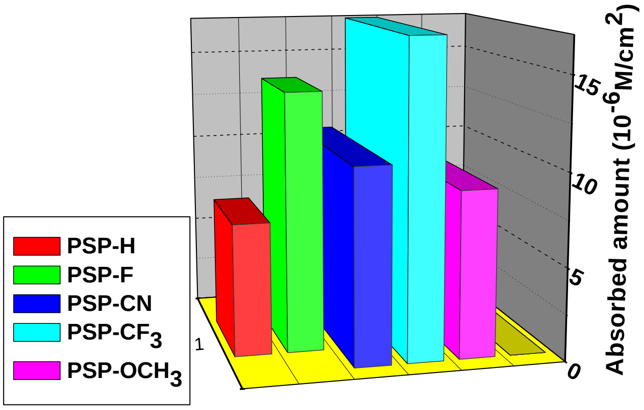


Figure S23. Loading amount of organic dyes on TiO_2 film.

6. HOMO-LUMO level

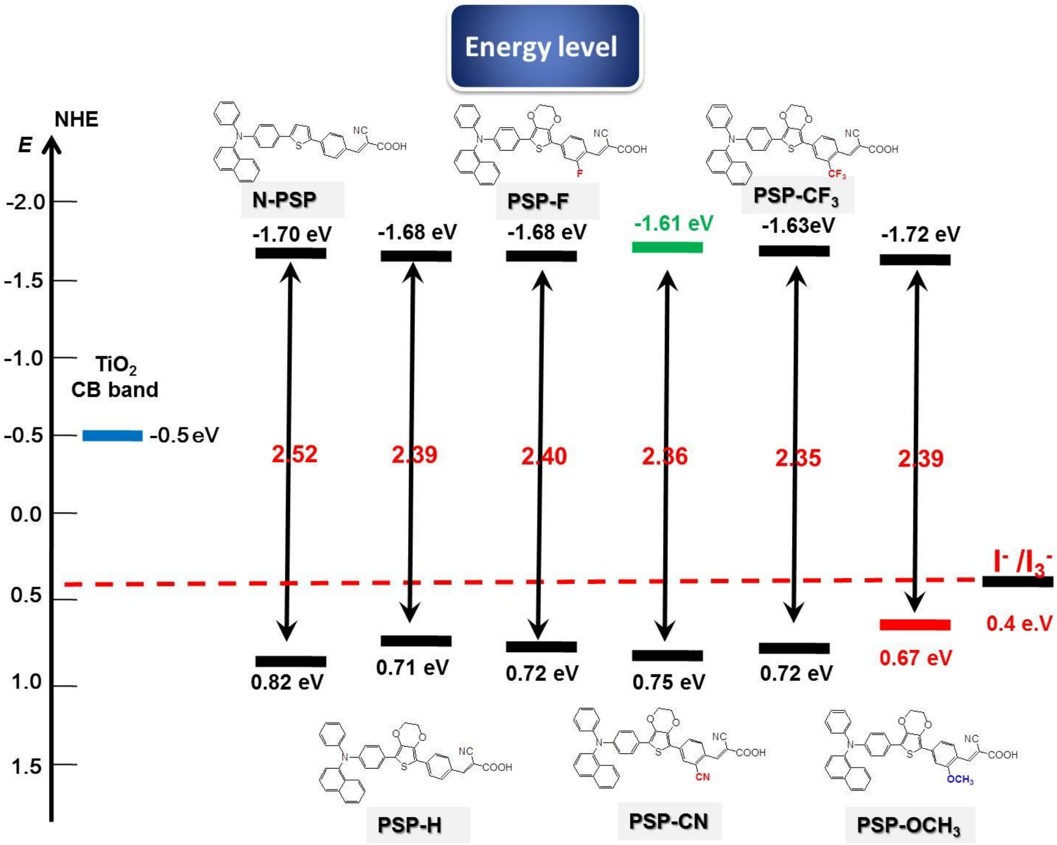
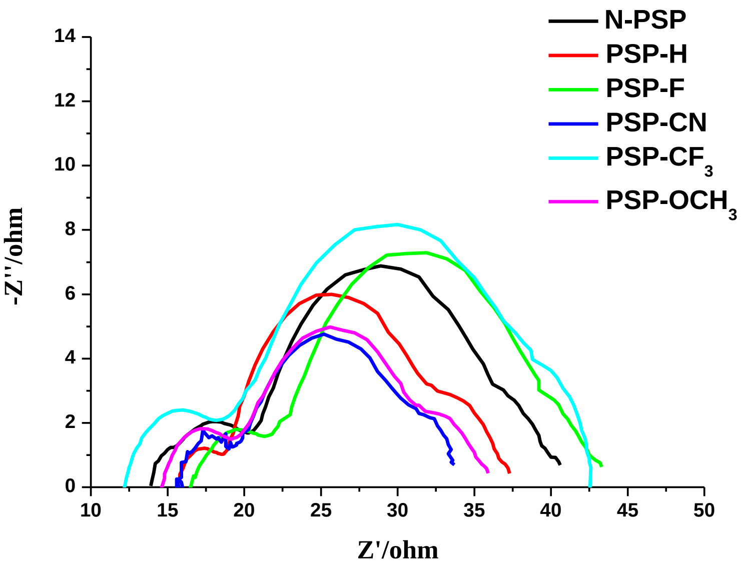


Figure S24. HOMO - LUMO energy levels of **PSP**-series.

7. EIS spectra



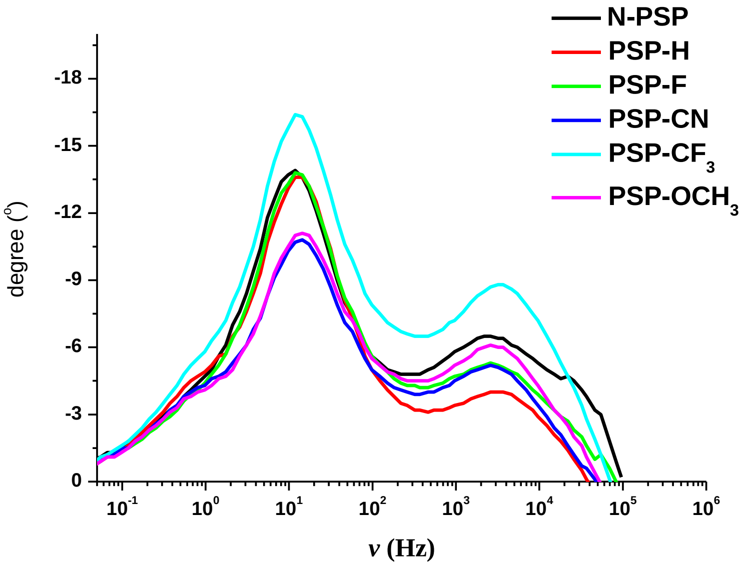


Figure S25. Impendance spectra of **PSP**-series organic dyes at -0.73 V bais in the dark. (upper) Nyquist plots; (lower) Bode phase plots.