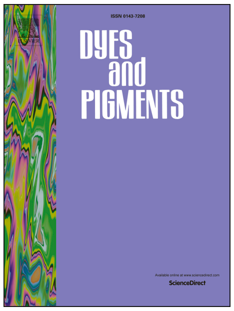

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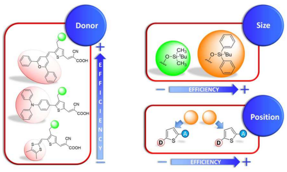
Donor
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Size
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Organic sensitizers bearing a trialkylsilylether group for liquid dye sensitized solar cells

Raquel Pérez-Tejada[a], Natalia Martínez de Baroja[a], Santiago Franco[a*], Laia Pellejà[b*], Jesús Orduna[a], Raquel Andreu[a], Javier Garín[a]

[a]*Departamento de Química Orgánica - Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza - CSIC, E-50009 Zaragoza, Spain*
[b]*Institute of Chemical Research of Catalonia (ICIQ), Avda Països Catalans 16, Tarragona E-43007 Spain*

* Corresponding author. Tel.: +34 976762283; E-mail address: sfranco@unizar.es (S. Franco)

Abstract

In this work we present the synthesis, optical characterization and performance of five metal-free sensitizers for dye-sensitized solar cells (DSSC). All dyes include, for the first time, a trialkylsilyl ether group in the π-conjugated bridge (a thiophene ring). The influence of different donor unities, like triarylamine (TPA), 4*H*-pyranylidene and dithiafulvene have been evaluated in DSSC with a liquid I_3/I^- electrolyte, obtaining the best results with the 4*H*-pyranylidene moiety. The size and the position of the bulky group have a great importance in the efficiency of the final devices.

In order to explain the recombination processes and electron life-time, charge extraction (CE) and transient photovoltaic (TPV) experiments have been carried out.

1. Introduction

Solar energy offers a clean, well-spread and inexhaustible energy source. Although the market is dominated by silicon-based photovoltaic devices, in recent years the interest on alternatives more environment-friendly has increased, specially focused on reducing mass during cell manufacture processes and the thickness of the final device.

Organic Photovoltaic Cells (OPVs) [1, 2] and particularly Dye Sensitized Solar Cells (DSSCs)[3, 4] constitute an interesting alternative due to their low manufacturing cost, flexibility of molecular design, light-weight and great aesthetic features, like color and transparency. The key element in a DSSC device is probably the sensitizer dye and over the last years, thousands of new dyes have been investigated. The most efficient organic sensitizers are based on Donor-π spacer-acceptor (D-π-A) structures,[5] a type of push-pull systems which lead to effective photoinduced intramolecular charge-transfer (ICT). In these systems small variations in the different parts of the molecule (mostly in the donor and the π-bridge) may result in significant changes in the photovoltaic properties. Triphenylamine (TPA)-based metal free organic dyes are one of the most common donor groups in DSSCs,[6, 7] as it presents several advantages, like a non-planar structure, which suppresses the formation of aggregates. Furthermore, the physical properties can be easily modulated by introduction of bulky or donor groups.[8-13] Recently, proaromatic systems like 4*H*-pyranylidene[14-17] and dithiafulvene[18-20] have been introduced as alternative and efficient donor unities in DSSCs, but no studies comparing their properties have been reported.

When designing a new sensitizer, one important factor to take into account is related to the minimization of aggregates by π-π stacking. This may be performed by using additives, such as deoxycholic acid (DCA) [21, 22] or by the introduction of bulky groups both, in the donor or in the π-bridge.[12, 23-26] However, it is relatively difficult to synthesize dyes with bulky chains in the conjugated spacer, requiring tedious and multiple reaction steps.

Silicon-based dyes have been very promising for DSSCs due to its photo and thermal stability.[27, 28] Examples of organic sensitizers bearing a dithienosilole (DTS) as a π-linker have been reported with high efficiencies.[29-34] However, to the best of our knowledge, organic dyes featuring a trialkylsilyl ether ($R_1R_2R_3SiO-$) were never used to preclude the π-aggregation on the TiO_2 in DSSCs. This popular protecting group can be easily introduced from alcohols[35] and the overall size and the stability depends on the nature of the R_1, R_2 or R_3. Moreover, the silylether group greatly enhances the solubility of the sensitizer that facilitates its adsorption on the TiO_2 surface.

In the present work, a series of five new metal-free organic sensitizers for DSSCs with a trialkylsilyloxy group have been designed, synthesized and characterized. In order to evaluate the donor influence on the photovoltaic properties a TPA and two proaromatic donor unities (4*H*-pyranylidene and dithiafulvene) have been used (Figure 1).

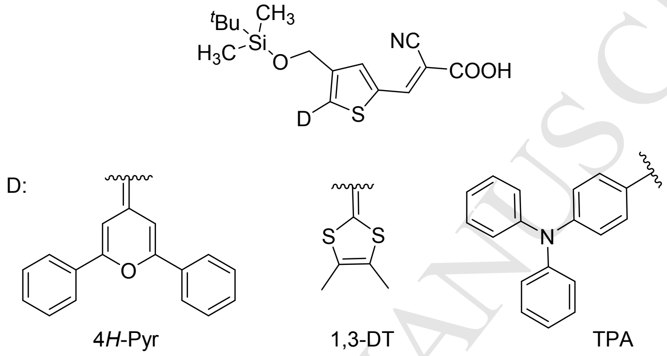
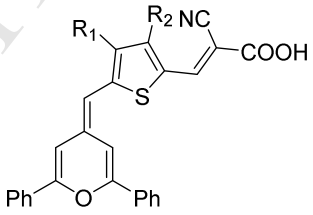


Fig 1. Molecular structures of TBDMS organic sensitizers

The influence of the size and the relative position on the heterocyclic linker of two bulky groups, *tert*-butyldimethyl (TBDMS) or *tert*-butyldiphenyl silylether (TBDPS) are also studied (Figure 2). Finally, the photophysical properties, molecular orbital calculations and the performance of DSSCs based on these organic dyes are reported.



$R_1 = CH_2OTBDPS$ or $CH_2OTBDMS$, $R_2 = H$
$R_1 = H$, $R_2 = CH_2OTBDPS$

Fig. 2. Molecular structures of 4*H*-pyranylidene organic sensitizers

2. Experimental section

2.1. General information

Infrared measurements were carried out in KBr or neat using a Perkin-Elmer Fourier Transform Infrared 1600 spectrometer. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or

400 MHz and 75 or 100 MHz respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), and m (multiplet). ^{1}H-^{1}H COSY and ^{1}H-^{13}C-HSQC experiments were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz in order to establish peaks assignment and spatial relationships. Electrospray mass spectra were recorded on a Bruker Microtof-Q spectrometer; accurate mass measurements were achieved using sodium formate as external reference. UV-Visible spectra were recorded with an UV-Vis UNICAM UV4 spectrophotometer. Pulse differential voltammetry measurements were performed with a μ-Autolab type III potentiostat using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon in CH_2Cl_2, with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 0.01V s^{-1}, modulation amplitude 0.025V and modulation time 0.05 s^{-1}.

2.2. Synthesis

4-((tert-butyldimethylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)thiophene-2-carbaldehyde ***(7)***

A solution of 2,6-diphenyl-(4*H*-pyran-4ylidene)-diphenylphosphine oxide **5** (680 mg, 1.56 mmol) in anhydrous THF (12 ml) was prepared, purged with argon and cooled to −78ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (1.2 mL, 2.08 mmol) was added dropwise and the resulting mixture was stirred for 15 min. Then 3-((*tert*-butyldimethylsilyloxy)methyl)thiophene-2-carbaldehyde **4** (472 mg; 1.84 mmol) in anhydrous THF (5 mL) was added dropwise and the mixture was warmed to 0 ºC for 3 hours (TLC monitoring using 10% EtOAc in hexanes). Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with EtOAc (2 × 25 mL) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was dissolved in EtOAc/hexanes (3/97) and filtered over silica gel to give the crude *tert*-butyl((2-((2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)thiophen-3-yl)methoxy)dimethylsilane **6** as an intermediate. Then, a solution of 2,2,6,6-tetramethylpiperidine (0.27 mg, 1.58 mmol) in THF (8.4 mL) was prepared, purged with argon and cooled to −78 ºC. To this solution, ^{t}BuLi (1.7 M in pentane) (1.01 mL, 1.71 mmol) was added dropwise and the resulting mixture was stirred for 1h and then a solution of **6** (676.0 mg, 1.41 mmol) in THF (33.6 mL) was added. The resulting mixture was stirred for an additional hour, DMF (0.28 mL, 3.70 mmol) was added dropwise and the mixture was warmed to −30 ºC. The reaction was quenched by the addition of saturated NH_4Cl solution and the solvent was evaporated under reduced pressure. The organic layer was extracted with EtOAc (2 × 20 mL) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the aldehyde **7** was purified by silica gel column chromatography (6% EtOAc in hexanes). Yield: red oil (583.0 mg, 1.16 mmol; 82%).

IR (neat): cm^{-1} 1648 (C=O), 1573 (C=C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.81 (s, 1H), 7.90−7.76 (m, 4H), 7.69 (s, 1H), 7.55−7.43 (m, 6H), 7.29 (d, *J* = 2.0 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.07 (s, 1H), 4.75 (s, 2H), 0.96 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 182.1, 155.3, 152.6, 146.6, 139.0, 137.9, 137.0, 132.8, 132.5, 132.5, 130.2, 129.7, 128.9, 128.8, 125.3, 124.7, 109.0, 104.7, 102.9, 59.7, 26.0, 18.4, −5.2. HRMS (ESI$^+$): *m/z* calcd for $[C_{30}H_{33}O_3SSi]^+$: 501.1914, found: 501.1914 $[M+H]^+$; calcd for $[C_{30}H_{32}NaO_3SSi]^+$: 523.1734, found: 523.1721 $[M+Na]^+$.

4-((tert-butyldimethylsilyloxy)methyl)-5-((4,5-dimethyl-1,3-dithiol-2ylidene)methyl)thiophene-2-carbaldehyde ***(10)***

A solution of tributyl(4,5-dimethyl-1,3-dithiol-2-yl)phosphonium hexafluorophosphate **8** (317.7 mg, 0.66 mmol) and 3-((*tert*-butyldimethylsilyloxy)methyl)thiophene-2-carbaldehyde **4** (131.0 mg, 0.51 mmol) in anhydrous THF (16 mL) was prepared, purged with argon and cooled to −78ºC. To this solution, Et_3N (352.4 μL, 2.51 mmol) was added dropwise and the resulting mixture was stirred for 15 min. After the removal of the solvent, the residue was dissolved in EtOAc/hexanes (1:9) and filtered over neutral aluminum oxide to give compound **9** as an intermediate. Then, a solution of **9** in THF (10 mL) was prepared, purged with argon and cooled to −45 ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (0.53 mL, 0.85 mmol) was added dropwise and the resulting mixture was stirred for 1h. DMF (0.09 mL, 1.2 mmol) was added dropwise and then, the mixture was warmed to room temperature over 24h. Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. After the removal of the solvent, the aldehyde **10** was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: red oil (136.2 mg, 0.34 mmol; 67%).

IR (neat): cm^{-1} 1649 (C=O), 1492 (C=C). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.80 (s, 1H), 7.65 (s, 1H), 6.82 (s, 1H), 4.69 (s, 2H), 2.09 (s, 3H), 2.03 (s, 3H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 181.9, 146.6, 142.5, 137.9, 137.3, 135.8, 124.4, 123.4, 102.9, 59.6, 25.9, 18.3, 13.8, 13.1, −5.2. HRMS (ESI^+): *m/z* calcd for $[C_{18}H_{27}O_2S_3Si]^+$: 399.0937, found: 399.0961 $[M+H]^+$; calcd for $[C_{18}H_{26}NaO_2S_3Si]^+$: 421.0756, found: 421.0784 $[M+Na]^+$.

4-(3-((tert-butyldimethylsilyloxy)methyl)thiophen-2-yl)-N,N-diphenylaniline ***(13)***

A solution of the stannyl derivative **12** (990.0 mg, 1.87 mmol) and compound **11** (668.2 mg, 1.87 mmol) in anhydrous toluene (24 mL) was prepared, purged with argon for 15 min before addition of $Pd(PPh_3)_4$ (112.3 mg, 0.10 mmol). The reaction mixture was refluxed for 15 h under an argon atmosphere. After addition of water (30 mL), the mixture was extracted with toluene (2 × 30 mL). The organic phase was washed with a saturated aqueous solution of NH_4Cl (30 mL) and water (3 × 10 mL) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the compound was purified by silica gel column chromatography (2% diethyl ether in hexanes). Yield: light yellow oil (392.4 mg, 0.83 mmol; 44%).

IR (neat): cm^{-1} 1592 (C=C). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.39−7.33 (m, 2H), 7.32−7.24 (m, 4H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.15−7.02 (m, 9H), 4.68 (s, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 148.1, 148.0, 140.6, 137.6, 130.4, 130.3, 129.9, 128.4, 125.2, 123.7, 59.9, 26.3, 18.8, −5.02. HRMS (ESI^+): *m/z* calcd for $[C_{29}H_{34}NOSSi]^+$: 472.2125, found: 472.2109 $[M+H]^+$; calcd for $[C_{29}H_{33}NNaOSSi]^+$: 494.1944, found: 494.1930 $[M+Na]^+$.

4-((tert-butyldimethylsilyloxy)methyl)-5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde ***(14)***

A solution of **13** (352.4 mg, 0.75 mmol) in anhydrous THF (17 mL) was prepared, purged with argon and cooled to −30 ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (0.78 mL, 1.25 mmol) was added dropwise and the resulting mixture was stirred for 1 hour. Then, DMF (173 µL, 2 mmol) was added dropwise and the mixture was warmed to room temperature (TLC monitoring using 2% diethyl ether in hexanes). Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with diethyl ether (15 × 3 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde **14** was purified by column chromatography on silica gel (2% ethylic ether in hexanes). Yield: yellow oil (298.6 mg, 0.50 mmol; 80%).

IR (neat): cm^{-1} 1670 (C=O), 1445 (C=C). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.84 (s, 1H), 7.80 (s, 1H), 7.41−7.38 (m, 2H), 7.33−7.29 (m, 4H), 7.16−7.05 (m, 8H), 4.72 (s, 2H), 0.91 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 183.2, 150.3, 149.4, 147.7, 141.0, 139.5, 139.2, 130.4, 130.0, 126.5, 125.7, 124.4, 122.7, 60.0, 26.3, 18.8, −4.5. HRMS (ESI^+): *m/z* calcd for $[C_{30}H_{34}NO_2SSi]^+$: 500.2074, found: 500.2045 $[M+H]^+$.

3-(4-((tert-butyldimethylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl) thiophen-2-yl)-2-cyanoacrylic acid ***(1)***

To a solution of aldehyde **7** (122 mg, 0.24 mmol) and 2-cyanoacetic acid (33 mg, 0.38 mmol) in chloroform (5 mL) was added piperidine (160 µL; 1.62 mmol). The mixture was refluxed for 24 hours under an argon atmosphere and then cooled down to room temperature. HCl (1N) was added until pH=3, the organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Then, hexane was added and a solid appeared. This compound was filtered under reduced pressure and washed with a mixture hexane/CH_2Cl_2 (9/1) to afford **1** Yield: dark purple solid (134 mg, 0.24 mmol; 96%).

Mp 215−218 ºC. IR (KBr): cm^{-1} 3100−2600 (COO−H), 2210 (C≡N), 1672 (C=O), 1652 (C=C). ^1H NMR (400 MHz, dmso-d_6): δ (ppm) 8.33 (s, 1H), 8.02−7.89 (m, 4H), 7.86 (s, 1H), 7.63−7.45 (m, 6H), 7.37 (d, *J* = 1.5 Hz, 1H), 7.11 (d, *J* = 1.5 Hz, 1H), 6.37 (s, 1H), 4.76 (s, 2H), 0.90 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (75 MHz, dmso-d_6): δ (ppm) 164.1, 154.8, 151.9, 145.7, 144.9, 139.3, 132.2, 131.6, 131.5, 130.5, 130.0, 129.9, 129.1, 128.9, 124.8, 124.5, 117.7, 109.1, 105.3, 102.4, 58.7, 25.7, 17.9, −5.4. HRMS (ESI^+): *m/z* calcd for $[C_{33}H_{34}NO_4SSi]^+$: 568.1972, found: 568.1945 $[M+H]^+$.

*3-(4-((tert-butyldimethylsilyloxy)methyl)-5-((4,5-dimethyl-1,3-dithiol-2-ylidene)methyl)thiophen-2-yl)-2-cyanoacrylic acid **(2)***

To a solution of aldehyde **10** (136.4 mg, 0.34 mmol) and 2-cyanoacetic acid (45.4 mg, 0.53 mmol) in chloroform (32 mL) was added piperidine (226.4 µL, 2.25 mmol). The mixture was refluxed for 85h under an argon atmosphere and then cooled down to room temperature. The reaction crude was chromatographied on reverse C18 silica gel (50 % $AcONH_4$ (20 mM) in acetonitrile). After the addition of acetic acid a solid appeared. This compound was filtered under reduced pressure to afford **2**. Yield: dark purple solid (68.7 mg, 0.15 mmol; 43%).

Mp 170−174 ºC. IR (KBr): cm^{-1} 2211 (C≡N), 1673 (C=O), 1531 (C=C). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.21 (s, 1H), 7.68 (s, 1H), 6.84 (s, 1H), 4.69 (s, 2H), 2.14 (s, 3H), 2.07 (s, 3H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.1, 149.1, 146.5, 145.5, 139.8, 136.6, 130.9, 125.6, 124.5, 116.9, 103.1, 91.5, 59.5, 25.9, 18.3, 14.0, 13.1, −5.3. HRMS (ESI^+): *m/z* calcd for $[C_{21}H_{28}NO_3S_3Si]^+$: 466.0995, found: 466.1040 $[M+H]^+$. HRMS (ESI^+): *m/z* calcd for $[C_{21}H_{27}NNaO_3S_3Si]^+$: 488.0815, found: 488.0793 $[M+Na]^+$.

*3-(4-((tert-butyldimethylsilyloxy)methyl)-5-(4-(diphenylamino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid **(3)***

To a solution of aldehyde **14** (139.2 mg; 0.29 mmol) and 2-cyanoacetic acid (45.4 mg; 0.53 mmol) in chloroform (26 mL) was added piperidine (200.6 µL; 1.90 mmol). The mixture was refluxed for 5 days under an argon atmosphere and then cooled down to room temperature. The reaction crude was chromatographied on reverse C18 silica gel (50 % $AcONH_4$ (20 mM) in acetonitrile). After the addition of acetic acid a solid appeared. This compound was filtered under reduced pressure to afford **3**. Yield: pinkish solid (113.1 mg, 0.20 mmol; 70%).

Mp 196−200 ºC. IR (KBr): cm^{-1} 2223 (C≡N), 1679 (C=O), 1566 (C=C). ^1H NMR (400 MHz, acetone-d_6): δ *(*ppm*)* 8.42 (s, 1H), 8.05 (s, 1H), 7.58−7.53 (m, 2H), 7.39−7.33 (m, 4H), 7.18−7.11 (m, 6H) 7.11−7.06 (m, 2H), 4.83 (s, 2H), 0.91 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, acetone-d_6): δ (ppm) 167.8, 151.5, 150.9, 148.9, 148.3, 143.4, 140.7, 134.9, 131.8, 131.5, 127.4, 127.2, 126.0, 123.6, 117.8, 100.1, 60.9, 27.3, 19.8, −4.1. HRMS (ESI^-): *m/z* calcd for $[C_{33}H_{33}N_2O_3SSi]^-$: 565.1987, found: 565.2014 $[M-H]^-$.

*3-((tert-butyldiphenylsilyloxy)methyl)thiophene-2-carbaldehyde **(18)***

A solution of *tert*-butyldiphenyl(thiophen-3-ylmethoxy)silane **17** (2.2 g, 6.2 mmol) in anhydrous diethyl ether (10 mL) was prepared, purged with argon and cooled to −10 ºC. To this solution, *t*-BuLi (1.7 M in pentane) (4 mL, 6.2 mmol) was added dropwise for a period of 20 min and the resulting mixture was stirred at −10 ºC for 1h. Then, DMF (0.75 mL, 9.6 mmol) was added dropwise and the mixture was warmed to 0 ºC and stirred at this temperature overnight (TLC monitoring using 20% hexanes in dichloromethane). Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with diethyl ether (10 × 3 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde **18** was purified by silica gel column chromatography (20% hexanes in dichloromethane). Yield: yellow oil (454.9 mg, 1.20 mmol; 20%).

IR (neat): cm^{-1} 1664 (C=O), 1588 (C=C). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.95 (d, *J* = 0.9 Hz, 1H), 7.68−7.66 (m, 5H), 7.48−7.37 (m, 6H), 7.25 (d, *J* = 5.0 Hz, 1H), 5.06 (s, 2H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 182.9, 150.9, 138.1, 136.1, 134.5, 133.5, 130.5, 130.0, 128.5, 61.4, 27.2, 19.7. HRMS (ESI$^+$): *m/z* calcd for $[C_{22}H_{25}O_2SSi]^+$: 381.1339, found: 381.1313 [M+H]$^+$; calcd for $[C_{22}H_{24}NaO_2SSi]^+$: 403.1158, found: 403.1139 [M+Na]$^+$.

4-((tert-butyldiphenylsilyloxy)methyl)thiophene-2-carbaldehyde ***(19)***

A solution of *tert*-butyldiphenyl(thiophen-3-ylmethoxy)silane **17** (1.6 g, 4.5 mmol) in anhydrous THF (39 mL) was prepared, purged with argon and cooled to −10 ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (2.8 mL, 4.5 mmol) was added dropwise and the resulting mixture was stirred at −10 ºC for 1h and 30 min. Then, DMF (0.54 mL, 6.9 mmol) was added dropwise and the mixture was warmed to 0 ºC and stirred at this temperature overnight (TLC monitoring using 20% ethyl acetate in hexanes). Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with diethyl ether (15 × 2 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde **19** was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: white solid (465.3 mg, 1.22 mmol; 21%).

Mp 76−78 ºC. IR (KBr): cm^{-1} 1666 (C=O), 1466 (C=C). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.86 (d, *J* = 1.3 Hz, 1H), 7.69−7.65 (m, 5H), 7.59−7.58 (m, 1H), 7.47−7.37 (m, 6H), 4.77 (d, *J* = 0.6 Hz, 2H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 183.5, 144.7, 144.5, 136.1, 135.8, 133.7, 130.8, 130.4, 128.4, 62.2, 27.1, 19.7. HRMS (ESI$^+$): *m/z* calcd for $[C_{22}H_{25}O_2SSi]^+$: 381.1339, found: 381.1320 [M+H]$^+$; calcd for $[C_{22}H_{24}NaO_2SSi]^+$: 403.1158, found: 403.1144 [M+Na]$^+$.

4-((tert-butyldiphenylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)thiophene-2-carbaldehyde ***(21)***

A solution of **5** (22.6 mg, 0.51 mmol) in anhydrous THF (5 mL) was prepared, purged with argon and cooled to −78ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (0.32 mL, 0.51 mmol) was added dropwise and the resulting mixture was stirred for 20 min. Then 3-((*tert*-butyldiphenylsilyloxy)methyl)thiophene-2-carbaldehyde **18** (151.1 mg; 0.40 mmol) in anhydrous THF (5 mL) was added dropwise and the mixture was warmed to room temperature for 21 hours (TLC monitoring using 10% dichloromethane in hexanes). Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with hexanes (25 × 2 mL) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was dissolved in hexanes/CH_2Cl_2 (9/1) and filtered over silica gel to give the compound **20** as an intermediate. A solution of **20** in THF (10 mL) was prepared, purged with argon and cooled to −78 ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (0.36 mL, 0.58 mmol) was added dropwise and the resulting mixture was stirred for 1h and 30 min. DMF (0.08 mL, 1.03 mmol) was added dropwise and the mixture stirred for 2h. Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with hexanes (15 × 2 mL) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the aldehyde **21** was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: red oil (136.4 mg, 0.22 mmol; 55%).

IR (neat): cm^{-1} 1643 (C=O), 1518 (C=C). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.77 (s, 1H), 7.92−7.89 (m, 2H), 7.80−7.78 (m, 2H), 7.75−7.67 (m, 4H), 7.64 (s, 1H), 7.55−7.38 (m, 12H), 7.27 (d, *J* = 2.0 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 6.00 (s, 1H), 4.81 (s, 2H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 182.4, 155.8, 153.0, 147.1, 139.1, 138.5, 137.8, 136.2, 133.8, 133.2, 133.1, 133.0, 130.7, 130.4, 130.2, 129.4, 129.3, 128.4, 125.9, 125.2, 109.5, 105.4, 103.3, 60.9, 27.2, 19.7. HRMS (ESI$^+$): *m/z* calcd for $[C_{40}H_{37}O_3SSi]^+$: 625.2227, found: 625.2235 [M+H]$^+$.

3-((tert-butyldiphenylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)thiophene-2-carbaldehyde ***(23)***

A solution of 2,6-diphenyl(4*H*-pyran-4ylidene)diphenylphosphine oxide **5** (222.6 mg, 0.51 mmol) in anhydrous THF (5 ml) was prepared, purged with argon and cooled to −78ºC. To the solution, *n*-BuLi (1.6 M in hexanes) (0.32 mL, 0.51 mmol) was added dropwise and the resulting mixture was stirred for 20 min. Then 4-((*tert*-butyldiphenylsilyloxy)methyl)thiophene-2-carbaldehyde **19** (150.0 mg; 0.39 mmol) in anhydrous THF (5 mL) was added dropwise and the mixture was warmed to room temperature for 21 h (TLC monitoring using 20% ethyl acetate in hexanes). Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with EtOAc and dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was dissolved in EtOAc/hexanes (2:8) and filtered over silica gel to give the crude *tert*-butyl((5-((2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)thiophen-3-yl)methoxy)diphenylsilane **22** as an intermediate. A solution of **22** in THF (10 mL) was prepared, purged with argon and cooled to −78 ºC. To this solution, *n*-BuLi (1.6 M in hexanes) (0.42 mL, 0.68 mmol) was added dropwise and the resulting mixture was stirred for 2h. DMF (0.09 mL, 1.2 mmol) was added dropwise and the mixture stirred for 2h. Saturated NH_4Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with EtOAc (15 × 3 mL) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the aldehyde **23** was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: dark red oil (138.9 mg, 0.22 mmol; 56%).

IR (neat): cm^{-1} 1643 (C=O), 1579 (C=C). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.86 (s, 1H), 7.90−7.88 (m, 2H), 7.82−7.80 (m, 2H), 7.73−7.70 (m, 4H), 7.50−7.41 (m, 12H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.05 (s, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 6.14 (s, 1H), 5.02 (s, 2H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ (ppm) 181.4, 155.6, 153.1, 151.5, 151.3, 136.1, 133.7, 133.5, 133.3, 133.2, 133.1, 130.7, 130.5, 130.2, 129.4, 129.3, 128.4, 127.8, 125.9, 125.3, 109.1, 107.6, 103.2, 61.2, 27.2, 19.7. HRMS (ESI$^+$): *m/z* calcd for $[C_{40}H_{37}O_3SSi]^+$: 625.2227, found: 625.2244 $[M+H]^+$.

*3-(4-((tert-butyldiphenylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)thiophen-2-yl)-2-cyanoacrylic acid **(15)***

To a solution of aldehyde **21** (97.9 mg, 0.157 mmol) and 2-cyanoacetic acid (20.8 mg, 0.24 mmol) in chloroform (16 mL) was added piperidine (109.9 µL, 1.04 mmol). The mixture was refluxed for 72h under an argon atmosphere and then cooled down to room temperature. The reaction crude was chromatographied on reverse C18 silica gel (started 50 % $AcONH_4$ (20 Mm) in acetonitrile and finished 30%). After the addition of acetic acid a solid appeared. This compound was filtered under reduced pressure to afford **15**. Yield: dark purple solid (83.4 mg, 0.12 mmol; 77%).

Mp 208−211 ºC. IR (KBr): cm^{-1} 2207 (C≡N), 1652 (C=O), 1539 (C=C). ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) 8.29 (s, 1H), 8.01−7.98 (m, 2H), 7.88−7.85 (m, 2H), 7.79 (s, 1H), 7.76−7.70 (m, 4H), 7.59−7.32 (m, 13H), 6.76 (d, *J* = 1.6 Hz, 1H), 6.12 (s, 1H), 4.87 (s, 2H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, THF-d_8): δ (ppm) 164.9, 156.6, 153.8, 147.8, 146.1, 139.8, 139.8, 136.6, 134.3, 134.0, 133.7, 133.5, 131.9, 130.9, 130.6, 130.0, 129.7, 128.8, 126.2, 125.7, 117.9, 110.2, 106.2, 104.0, 96.6, 61.3, 27.4, 20.1. HRMS (ESI$^+$): *m/z* calcd for $[C_{43}H_{38}NO_4SSi]^+$: 692.2285, found: 692.2248 $[M+H]^+$; calcd for $[C_{43}H_{37}NNaO_4SSi]^+$: 714.2105, found: 714.2066 $[M+Na]^+$.

*3-(3-((tert-butyldiphenylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)thiophen-2-yl)-2-cyanoacrylic acid **(16)***

To a solution of aldehyde **23** (120.4 mg, 0.192 mmol) and 2-cyanoacetic acid (25.6 mg, 0.30 mmol) in chloroform (18 mL) was added piperidine (134.6 µL, 1.28 mmol). The mixture was refluxed for 20h under an argon atmosphere, then cooled down to room temperature. The reaction crude was chromatographed on reverse C18 silica gel (started 50 % $AcONH_4$ (20 mM) in acetonitrile and finished 33%). After the addition of acetic acid a solid appeared. This compound was filtered under reduced pressure to afford **16.** Yield: dark purple solid (86.0 mg, 0.12 mmol; 65%).

Mp 219−226 ºC. IR (KBr): cm^{-1} 2209 (C≡N), 1651 (C=O), 1541 (C=C).^{1}H NMR (400 MHz, THF-d$_8$): δ (ppm) 8.51 (s, 1H), 7.99−7.88 (m, 4H), 7.74−7.72 (m, 4H), 7.49−7.34 (m, 14H), 6.99 (s, 1H), 6.81 (br s, 1H), 4.92 (s, 2H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, THF-d$_8$): δ (ppm) 164.9, 156.4, 154.0, 152.5, 151.7, 143.7, 136.6, 134.3, 134.0, 133.7, 133.5, 131.9, 131.2, 130.9, 130.7, 130.0, 129.8, 128.8, 128.1, 126.2, 125.8, 118.1, 109.8, 108.4, 103.9, 95.8, 61.3, 27.4, 20.0. HRMS (ESI$^+$): *m/z* calcd for $[C_{43}H_{38}NO_4SSi]^+$: 692.2285, found: 692.2313

2.3. Device preparation and characterization

The working and counter electrodes consisted of TiO_2 and thermalized platinum films, respectively, and were deposited onto F-doped tin oxide (FTO, Pilkington Glass Inc., with 15 Ω sq^{-1} sheet resistance) conducting glass substrates. Efficient DSC devices were made using 9 µm thick films consisting of 20 nm TiO_2 nanoparticles (Dyesol© paste) and a scattering layer of 4 µm of 400 nm TiO_2 particles (Dyesol© paste). Prior to the deposition of the TiO_2 paste, the conducting glass substrates were immersed in a solution of $TiCl_4$ (40 mM) for 30 minutes and then dried. The TiO_2 nanoparticle paste was deposited onto a conducting glass substrate using the screen printing technique. The TiO_2 electrodes were gradually heated under an air flow at 325 ºC for 5 min, 375 ºC for 5 min, 450 ºC for 15 min and 500 ºC for 15 min. The heated TiO_2 electrodes were immersed again in a solution of $TiCl_4$ (40 mM) at 70 ºC for 30 min and then washed with ethanol. The electrodes were heated again at 500 ºC for 30 min and cooled before dye adsorption. The active area for devices was 0.16 cm^2. The counter electrode was made by spreading a 5 mM solution of H_2PtCl_6 in isopropyl alcohol onto a conducting glass substrate containing a small hole to allow the introduction of the liquid electrolyte using vacuum, followed by heating at 390 ºC for 15 minutes. All films were sensitized in 0.3 mM dye solutions in dichloromethane for 2 hours at room temperature (optimized dye loading conditions). The sensitized electrodes were washed with dichloromethane and dried under air. Finally, the working and counter electrodes were sandwiched together using a thin thermoplastic (Surlyn) frame that melts at 100 ºC. Electrolyte LP1 was used: consisted of 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M *tert*-butylpyridine in acetonitrile.

The J/V curves of the cells were measured using a Sun 2000 solar simulator equipped with a 150W xenon lamp. The illumination intensity was measured to be 100 mW cm^{-2} with a calibrated silicon photodiode. The appropriate filters were utilized to faithfully simulate the AM 1.5G spectrum. The applied potential and cell current were measured using a Keithley 2400 digital source meter. The IPCE (incident photon to current conversion efficiency) was measured using a home-made set up consisting of a 150 W Oriel xenon lamp, a motorized monochromator and a Keithley 2400 digital source meter.

Transient photovoltage (TPV) and charge extraction (CE) measurements were carried out alike reported before.[36] In CE measurements, white light from a series of LEDs was used as the light source. When the LEDs are turned off, the cell is immediately short-circuited and the charge is extracted allowing the electron density in the cells to be calculated. By changing the intensity of the LEDs, the electron density can be estimated as a function of cell voltage. In TPV measurements, in addition to the white light applied by the LEDS, a diode pulse (660 nm, 10 mW) is applied to the sample inducing a change of 2–3 mV within the cell. The resulting photovoltage decay transients are collected and the τ values are determined by fitting the data to the equation $\exp(-t/\tau)$.

2.4. Computational details

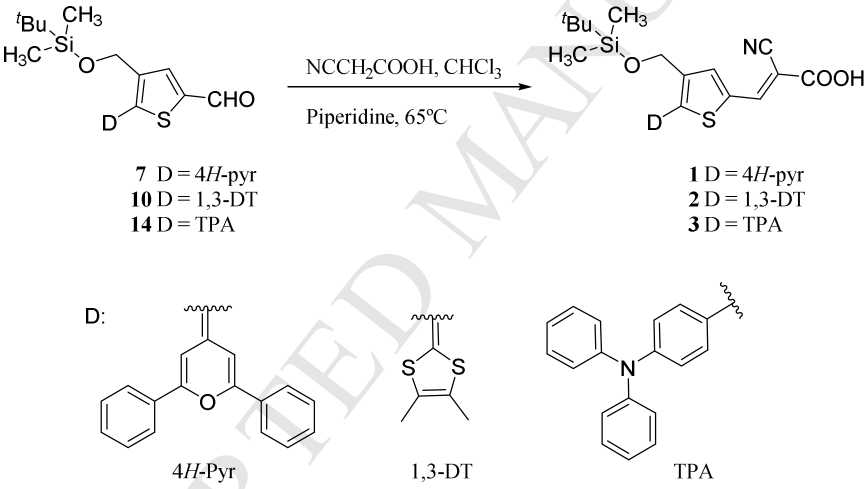
Density Functional Theory (DFT) calculations were performed using Gaussian 09[37] with the ultrafine integration grid. Solvent effects were estimated using a Conductor-like Polarizable Continuum Model (CPCM).[38, 39] Equilibrium geometries were optimized using the M06-2x hybrid meta-GGA exchange

correlation functional [40] and the medium size 6-31G* base.[41] Ground state geometries were characterized as minima by frequency calculations. Excitation energies were calculated by time-dependent single point calculations using the M06-2x/6-311+G (2d,p) model chemistry. Absorption spectra were estimated through the calculation of vertical excitations at the ground state geometry and emission spectra, through the calculation of vertical excitations at the excited state geometry. Due to the large computational cost required to calculate excited state vibrational energies, $E_{0\text{-}0}$ were approached to adiabatic excitation energies (E_{Adia}). Ground state oxidation potentials (E_{OX}) were calculated using the M06-2x/6-311+G (2d,p) energies and calculating the thermal corrections to Gibbs free energy at the M06-2x/6-31G* level. Excited state oxidation potentials (E^*_{OX}) were estimated substracting $E_{0\text{-}0}$ from Eox.
Molecular Orbital contour plots were obtained using the Avogadro software [42] at 0.04 isosurface value.

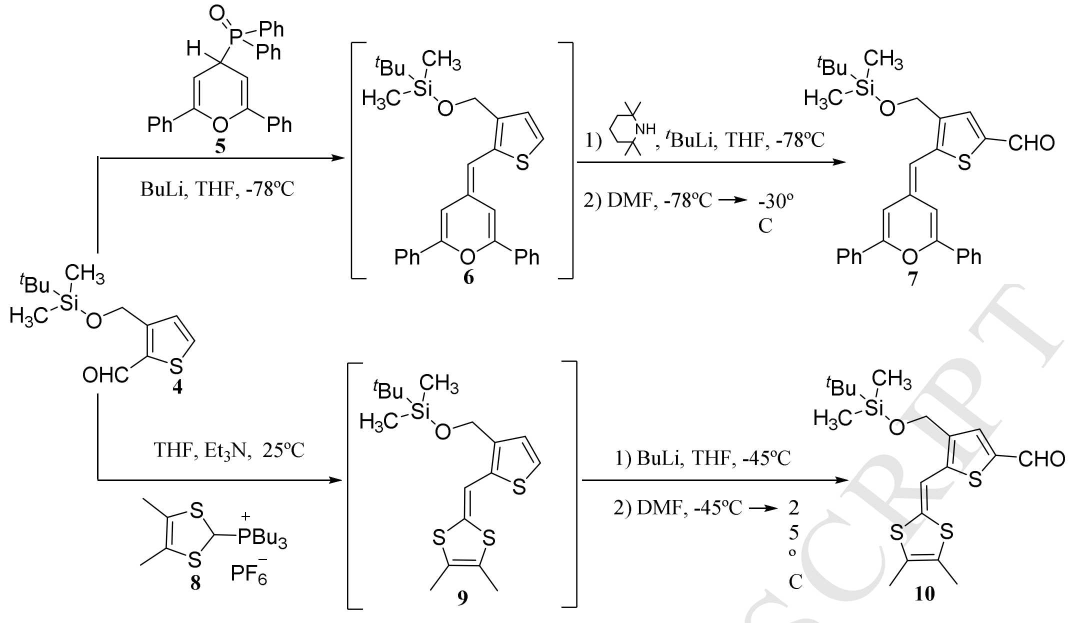
3. Results and discussion

3.1. Synthesis

The target compounds **1**, **2**, and **3** were prepared via condensation of the corresponding aldehyde derivative (**7**, **10**, **14**) and cyanoacetic acid in the presence of piperidine (Scheme 1).

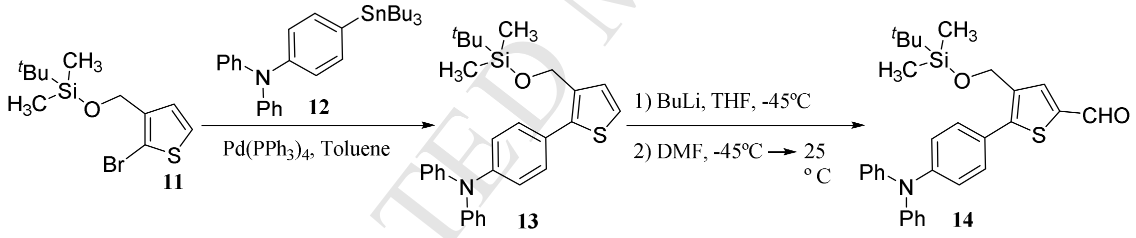


Scheme 1. Synthesis of dyes **1−3**



Scheme 2. Synthesis of aldehydes **7, 10**

Aldehydes **7** and **10** were synthesized by a Wittig-Horner or Wittig reaction of the diphenylphosphine oxide **5**[43] or the phosphonium salt **8**[44] with aldehyde **4**,[45] followed by lithiation of the resulting intermediates **6** and **9** and reaction with anhydrous DMF (Scheme 2). A different approach was adopted for the aldehyde **14** (Scheme 3) which was prepared through a Stille reaction between the stannane **12**[46] and the compound **11**,[47] followed by lithiation and formylation with DMF.



Scheme 3. Synthesis of aldehyde **14**

3.2. Optical properties

The absorption spectra of the synthesized dyes were studied in 10^{-5}M CH_2Cl_2 solution (Fig. 3) and the relevant optical data are listed in Table 1. Two absorption bands can be observed for all dyes, one between 300−400 nm assigned to a π–π* transition and the main band between 400−700 nm due to the ICT among the donor and the acceptor units. The inclusion of a proaromatic donor like 4*H*-pyranylidene or dithiafulvene results in a red-shift of the absorption when compared to the triarylamine dye. The molar extinction coefficients of the dyes increase in the order triarylamine < 4*H*-pyranylidene < dithiafulvene, being for the last one 37108 M^{-1} cm^{-1}. When the dyes are attached to TiO_2 surface, they present broader bands than in solution and the maximum absorption peaks are around 30 nm blue-shifted. In general, the blue shifts of the absorption spectra on TiO_2 are ascribed to the deprotonation of the carboxylic acid when anchored on the titanium surface and/or to the formation of H-aggregates.[48]

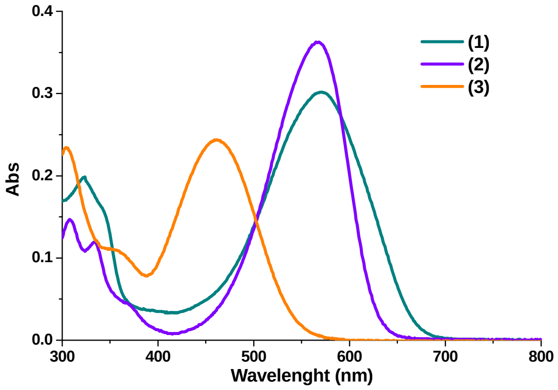


Fig. 3. Normalized UV-vis absorption of compounds **1**−**3**

Table 1. Optical and electrochemical properties of dyes **1**−**3.**

dye	λ_{abs}, nm (ε, $M^{-1}cm^{-1}$)^a	λ_{abs} (nm)^b	λ_{em} (nm)^c	E_{ox} ^{d} V (*vs*. NHE)	$E_{0\text{-}0}$ ^{e} (eV)	E^*_{ox} ^{f} V (*vs*. NHE)
1	570 (30370)	522	659	0.87	1.97	−1.10
2	568 (37108)	518	630	0.93	2.06	−1.12
3	460 (23958)	432	611	1.22	2.29	−1.08

[a]Absorption maxima in CH_2Cl_2 solution. [b] Absorption maxima on TiO_2 films. [c] Emission spectra were recorded in CH_2Cl_2. [d] First oxidation potentials were measured from three electrode electrochemical cell in CH_2Cl_2 containing 0.1 M $TBAPF_6$. A glassy carbon, Ag/AgCl (KCl 3M), and Pt were used as working, reference, and counter electrode respectively. [e] Zeroth-zeroth transition energies estimated from the intersection of normalized absorption and emission spectra in CH_2Cl_2 solution. [f] Excited-state oxidation potentials of the dyes obtained from $E_{ox} - E_{0\text{-}0.}$

3.3. Electrochemical Properties

The oxidation potential (E_{ox}) of each dye was determined in solution by differential pulse voltammetry (DPV) methods. E^*_{ox} was estimated from E_{ox}−$E_{0\text{-}0}$ (Table 1, see also energy diagram shown in SI Figure S-33).

The donor unit affects significantly the oxidation potential values, with an increase on the ease of oxidation in the order **3** < **2** < **1**, pointing to the superior donor ability of the 4*H*-pyranylidene moiety. The regeneration of the oxidized dye after electron injection into the conduction band of TiO_2 is guaranteed in all cases, as the E_{ox} values are more positive than the potential of the iodide/triiodide redox couple (+0.42 *vs* NHE), indicating that the oxidized dyes formed after the electron injection into the TiO_2 electrode could thermodynamically accept electrons from I^- ions.

The resulting E_{ox}* values for all the dyes were almost similar and sufficiently more negative than the energy conduction band edge energy level of TiO_2 (−0.5 V vs NHE), indicating an efficient injection of electrons into the TiO_2 from the excited dyes.

3.4. Photovoltaic properties of DSSCs

The device performance (with an effective area of 0.16 cm^2) were measured under sun-simulated AM 1.5 G irradiation (100 mW/cm^2). The optimized conditions for these dyes are determined to be 0.3 mM of dye in dichloromethane solution, 2 h of immersion and LP1 (0.5 M BMII/ 0.05M I_2/ 0.5M TBP/ 0.1M LiI in acetonitrile) as electrolyte. The relevant photovoltaic parameters V_{oc}, J_{sc}, *ff*, and solar-to-electrical energy conversion efficiencies (η) are collected in Table 2. Moreover, current density-voltage (*J*-*V*) curves and incident photon- to- current conversion efficiencies (IPCE) of devices based on these dyes are represented in Fig. 4.

Table 2. Photovoltaic properties of DSSCs constructed using the dyes **1**−**3.**

dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	*ff*	η (%)
1	11.74	0.644	74	5.56
2	6.99	0.609	69	2.91
3	7.26	0.759	74	4.09

The IPCE tendencies of these dyes are in accordance with their UV-vis absorption spectra on the TiO_2 film. The onset of the IPCE spectra for dyes **1** and **2** are significantly broadened compared with the obtained for dye **3**. These results confirm the higher J_{sc} value obtained for devices based on dye **1**, with a broad and roughly constant photoresponse (~ 60%) in the range 450−600 nm. Dye **3** presents a maximum IPCE value of 93% at 475 nm and the highest V_{oc} value (0.759V) of all the molecules studied, suggesting a decrease in the charge recombination processes for this molecule. However, its J_{sc} is 60% lower than obtained for compound **1**, probably due to the narrower IPCE observed band.

Data in Table 2 indicate that the more efficient donor system is the 4*H*-pyranylidene ($\eta = 5.56\%$), followed by the triarylamine system ($\eta = 4.09\%$) and finally the 1,3-dithiole ($\eta = 2.91\%$).

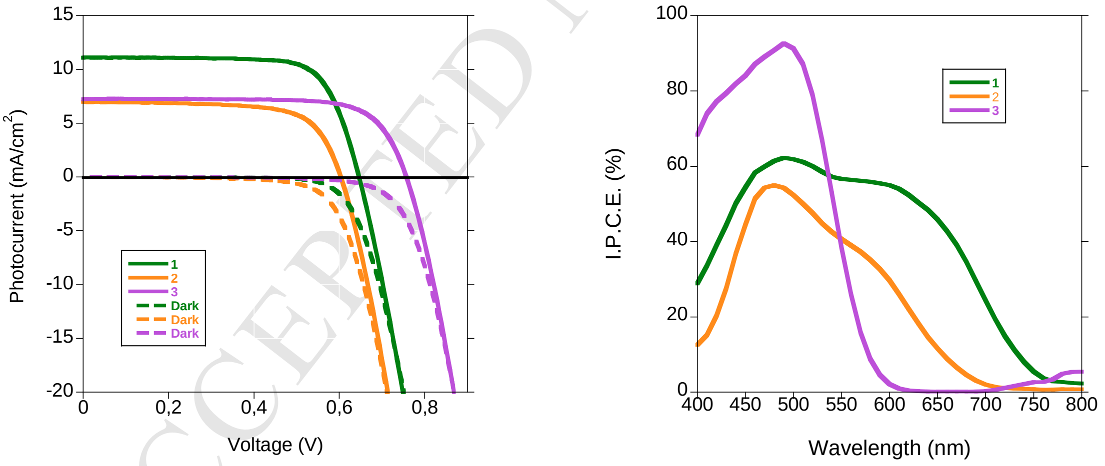
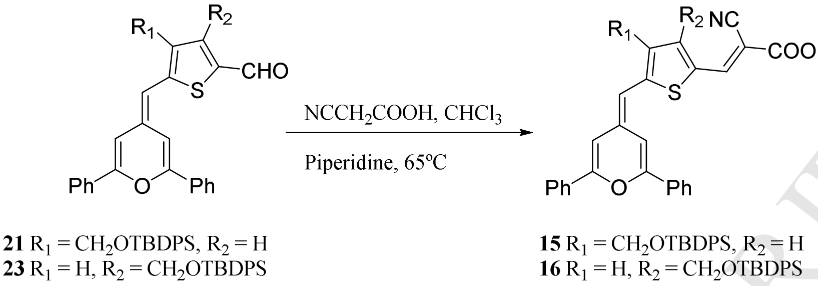


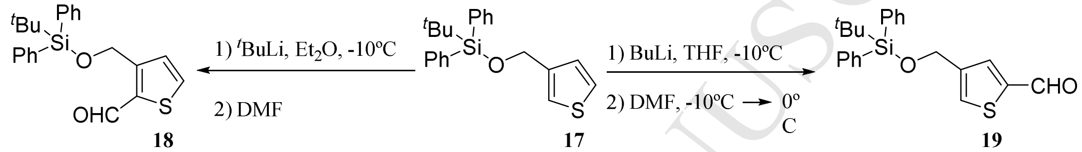
Fig. 4. *J*-*V* curves of compounds **1**−**3** (left) and IPCE curves of **1**−**3** (right)

3.5. Structural modification of the thiophene ring and physical properties

With the aim of understanding the influence of a different bulky silyl ether group and its position in the thiophene ring, dyes **15** and **16** were synthesized by a Knoevenagel condensation of the unreported aldehydes **21** and **23** with 2-cyanoacetic acid (Scheme 4). We have chosen the pyranylidene system as donor group due to the best results obtained in the previous section. These precursors were obtained in a three-step synthetic route starting in both cases from compound **17**.[49] Lithiation conditions (base and solvent) were finely tuned in order to activate position 2 (*tert*-BuLi, Et_2O) or position 5 (BuLi, THF) (Scheme 5). Finally, compounds **18** and **19** were obtained by reaction of the organolithium intermediates with DMF. Next, a Horner reaction of diphenylphosphine oxide **5** with **18** or **19** afforded the corresponding pyranylidene-thiophene derivatives **20** and **22**, which by lithiation and reaction with DMF yielded final aldehydes **21** and **23** respectively (Scheme 6).

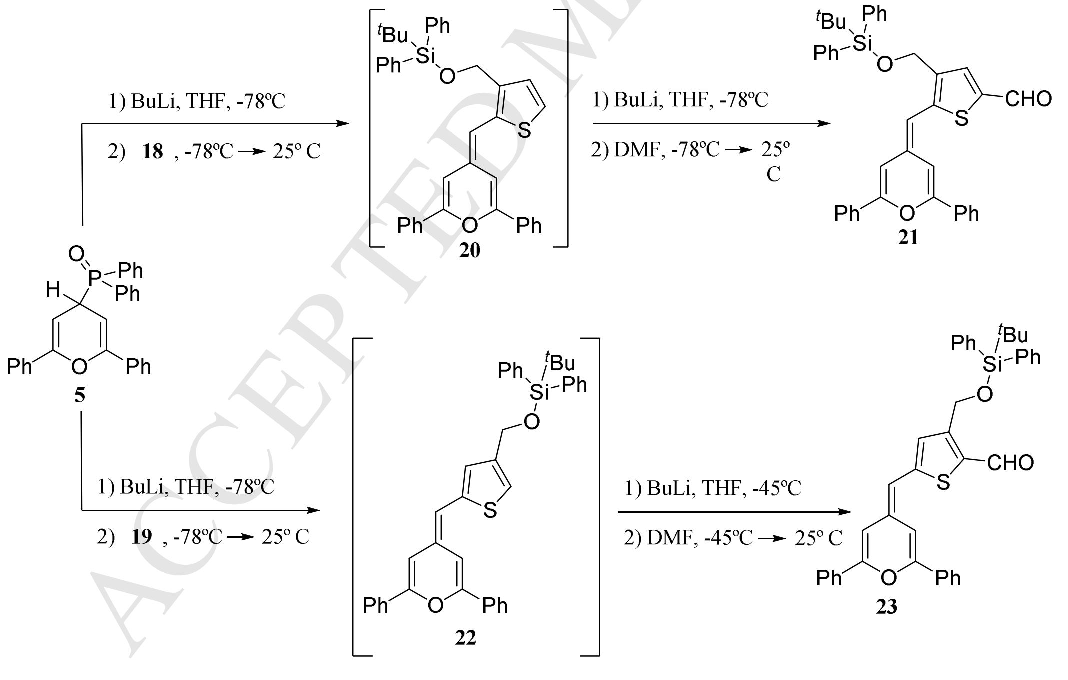


Scheme 4. Synthesis of dyes **15**, **16**



18 **17** **19**

Scheme 5. Synthesis of thiophene-aldehydes **18**, **19**



Scheme 6. Synthesis of aldehydes **21**, **23**

The substitution of a TBDMS group (**1**) by a *tert*-butyldiphenylsilyl (TBDPS (**15**)) does not change significantly the maximum absorption peak (570 nm for **1** and 573 nm for **15**). By contrast, the molar extinction coefficient (ε) is enhanced on passing from TBDMS to TBDPS (30370 $M^{-1}cm^{-1}$ (**1**) to 33618 $M^{-1}cm^{-1}$ (**15**)), probably due to the incorporation of two additional phenyl groups. Moreover, a bigger enhancement of the ε is found when the silyloxy substituent is located at the position 3 of the thiophene ring instead of the position 4 (from 33618 (**15**) to 39963 M^{-1} cm^{-1} (**16**)).

Regarding the electrochemical properties, it has to be pointed that the E_{ox} values for systems **1**, **15** and **16** are very similar (+0.87, +0.90, and +0.88V respectively, measured in conditions indicated in Table 1) and hence, the influence of the bulky substituent and its position is fairly null (See SI Figure S-34).

We have tested the photovoltaic response of dyes **15** and **16** (Figure 5) in DSSCs and their results were compared with those of compound **1** (Table 3). The substitution of a TBDMS group (**1**) by the bulkier group (TBDPS) (**15**) improve slightly the efficiency (from 5.56% to 5.86%), mostly due to a better value of the V_{oc} for the last one. This result suggests that a TBDPS group retards the recombination of TiO_2 conduction band electrons with the electrolyte as it has been shown from charge extraction and transient photovoltage experiments (see below).[50]

The influence of the position of the silyl ether group was also studied and we have found that the solar cell based on dye **16** (with a higher molecular extinction coefficient) shows an efficiency of 3.42%, 42% lower that obtained for dye **15**. The decrease in the efficiency is mainly due to a lower J_{sc} and V_{oc}, to a lesser extent. The remarkable decrease of J_{sc} was attributed to the lower injection efficiency, probably affected by the amount of dye absorbed to the TiO_2 surface.

Desorption experiments (0.1M NaOH, EtOH:H_2O (1:1)) determined that dye **16** is less adsorbed (106 nmol/cm^2) than dye **15** (140 nmol/cm^2) and this observation was attributed to the steric hindrance of the TBDPS group which is closer to the anchor group. Moreover, a lower amount of dye absorbed could result in higher I_3^- concentration in the interface TiO_2/electrolyte, increasing the recombination processes.

Table 3. Photovoltaic properties of DSSCs constructed using the dyes **1, 15** and **16**

dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	*ff*	η (%)
1	11.74	0.644	74	5.56
15	11.44	0.689	74	5.86
16	7.71	0.624	71	3.42

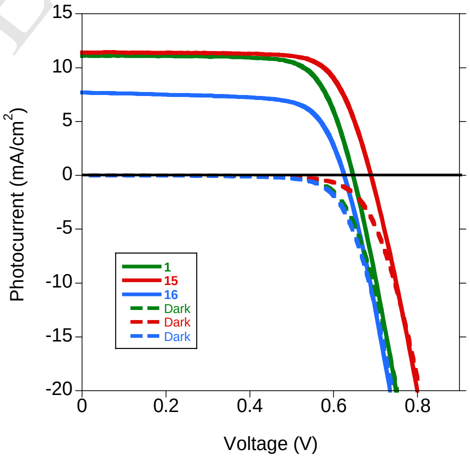


Fig. 5- *J*-*V* curves of compounds **1, 15** and **16**

Figure 6 illustrates the charge density (charge accumulated at the device under different light bias) and the charge lifetime at a given charge. As it can be seen, the solar cells made using dye **15** have the slowest charge recombination under working conditions. Moreover, it is worthy to mention that a shift on the measured charge vs voltage is observed for the solar cells made using dye **16**. This shift can be attributed to the lower coverage of dyes at the surface of the TiO_2, which has as a consequence the lower concentration of protons at the surface of the TiO_2. In fact, this is also in good agreement with the lower photocurrent measured.

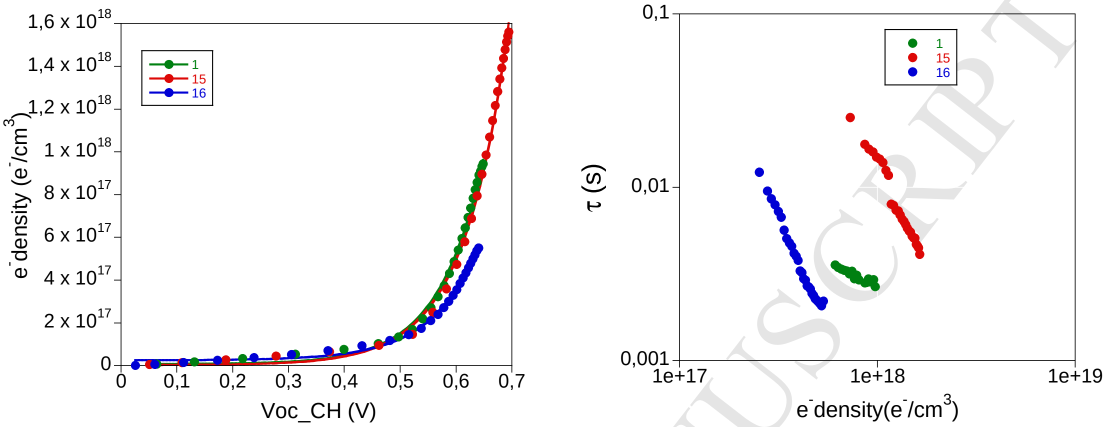


Fig. 6- Charge Extraction (left) and Transient Photovoltage (right) curves of compounds **1, 15** and **16**

3.6. Theoretical calculations

The electronic structures of the new synthesized compounds have been studied using density functional theory methods and the most relevant parameters derived from these calculations are gathered in table 4. There is a good agreement with the experimental values described above, with estimated error of less than 0.25 eV in the excitation energies, less than 0.1 V in E_{OX} and less than 0.2 V in E^{*}_{OX}.

Table 4. Results of DFT Calculations.

	E_{HOMO} (eV)	E_{LUMO} (eV)	λ_{Abs} (nm)	f^{a}	λ_{em} (nm)	$E_{0\text{-}0}$ (eV)	E_{OX} V (*vs.* NHE)	E^{*}_{OX} V (*vs.* NHE)
1	−6.38	−2.29	558	1.24	666	2.03	0.95	−1.08
2	−6.38	−2.13	528	1.00	605	2.18	1.00	−1.18
3	−6.58	−2.11	431	1.23	565	2.50	1.24	−1.26
15	−6.39	−2.30	559	1.23	666	2.03	0.93	−1.10
16	−6.40	−2.33	564	1.25	663	2.03	0.95	−1.08

[a] Oscillator strength

Calculations describe the first excited state as the consequence of a one-electron transition from the HOMO to the LUMO (see Figure 7). Excitation involves some charge transfer from the donor to the cyanoacetic acid acceptor, with a large HOMO-LUMO overlap that gives rise to large oscillator strengths and therefore to great molar extinction coefficients.

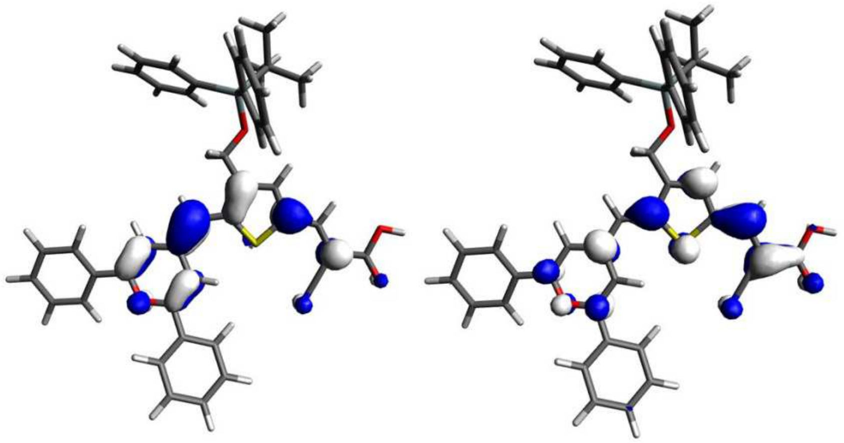


Figure 7. HOMO (left) and LUMO (right) for compound **15**.

Unfortunately, a direct correlation between the oscillator strengths (proportional to the peak area) and the molar extinction coefficients (related to peak height) is not possible for compounds giving rise to absorption bands of different width. Thus, compound **2** having the largest ε gives rise to the narrowest absorption band and also the lowest *f*.

4*H*-pyranylidene compounds **1, 15** and **16** display similar HOMO and LUMO energies and therefore their excitation energies and oxidation potentials are also similar. Compound **2**, with a weak donor group has a lower HOMO energy compared to the other studied dyes and, therefore, displays higher excitation energies and E_{OX}.

Conclusions

A series of five new metal free sensitizers (D-π-A) for DSSC with a trialkylsilyl ether group in the spacer have been synthesized and characterized. Several donor unities have been studied, obtaining the best performances with 4*H*-pyranylidene, followed by triphenylamine (TPA) and dithiafulvene moieties respectively. Two trialkylsilyl ether groups (TBDMS and TBDPS) were compared in order to study the influence of their molecular size in the photovoltaic properties. The best efficiencies values were obtained for a TBDPS group at the position 4 of the thiophene ring. This observation indicates that trialkylsilyl ethers can be promising substituents for future more efficient sensitizers.

Acknowledgements

We gratefully acknowledge the financial support from the Spanish Ministry of Science and Innovation, MICINN-FEDER (project CTQ2011-22727), MINECO (project CTQ2014-52331-R) and the Gobierno de Aragón-Fondo Social Europeo (E39). A predoctoral fellowship to R. Pérez-Tejada (CSIC, JAE 2011) is also acknowledged. The authors thank Prof. Emilio Palomares for the use of the equipment at ICIQ and the helpful comments on the results. Dr. Laia Pellejà thanks MICINN for the Severo Ochoa Excellence Accreditation 2014.2018 (SEV-2013-0319).

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version at

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Synthesis and characterization of organic sensitizers with a trialkylsilyloxy group on the π-spacer

DSSC efficiency was highly dependent on the size and position of the silyloxy group

Best efficiencies were obtained with the 4H-pyranylidene, followed by TPA and dithiafulvene systems

Organic sensitizers bearing a trialkylsilylether group for liquid dye sensitized solar cells

Raquel Pérez-Tejada[a], Natalia Martínez de Baroja[a], Santiago Franco*[a], Laia Pellejà*[b], Jesús Orduna[a], Raquel Andreu[a], Javier Garín[a],

[a] *Departamento de Química Orgánica-Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain.*

[b] *Institute of Chemical Research of Catalonia (ICIQ). Avda. Països Catalans, 16. Tarragona. E-43007. Spain.*

* Corresponding author. Tel.: +34 976762283; *E-mail address*: sfranco@unizar.es

TABLE OF CONTENTS

General Experimental Methods:

Infrared measurements were carried out in KBr or neat using a Perkin-Elmer Fourier Transform Infrared 1600 spectrometer. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz and 75 or 100 MHz respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), and m (multiplet). ^{1}H-^{1}H COSY and ^{1}H-^{13}C-HSQC experiments were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz in order to establish peaks assignment and spatial relationships. Electrospray mass spectra were recorded on a Bruker Q-ToF spectrometer; accurate mass measurements were achieved using sodium formate as external reference. UV-Visible spectra were recorded with an UV-Vis UNICAM UV4 spectrophotometer. Pulse differential voltammetry measurements were performed with a µ-Autolab type III potentiostat using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon in CH_2Cl_2, with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 0.01V s^{-1}, modulation amplitude 0.025V and modulation time 0.05 s^{-1}.

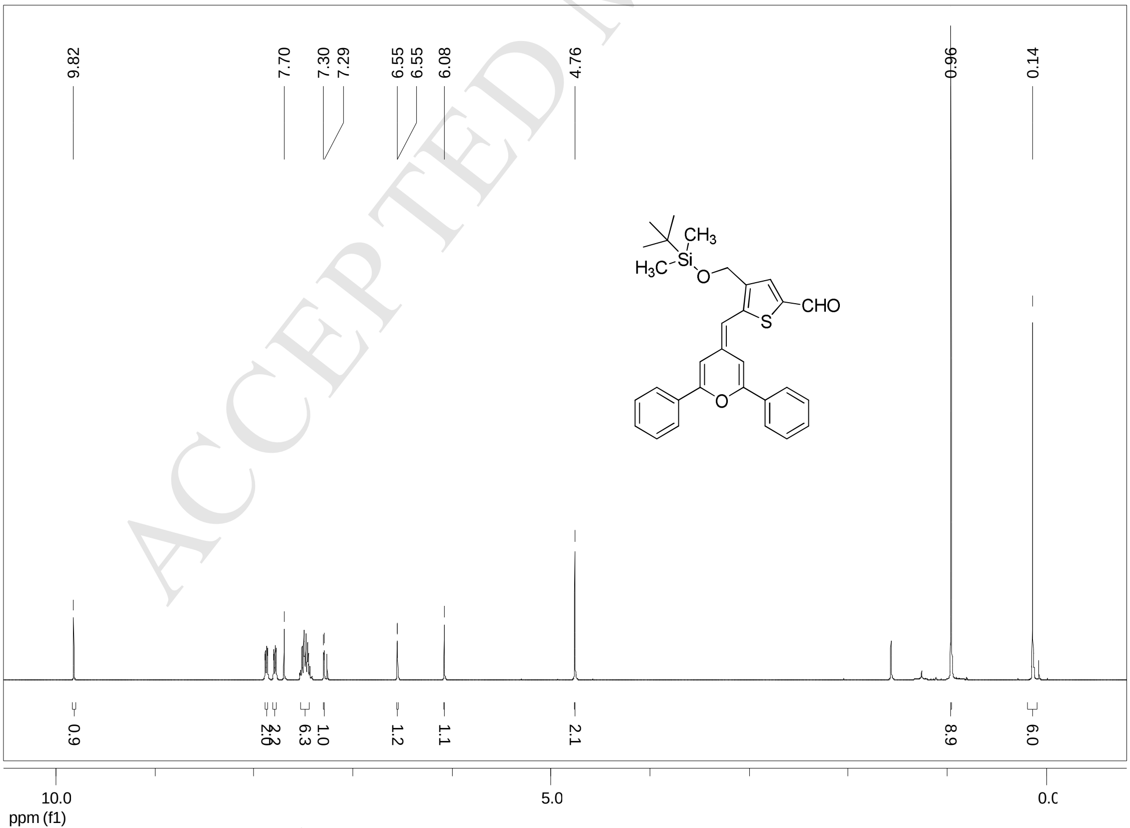

Figure S-1: ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

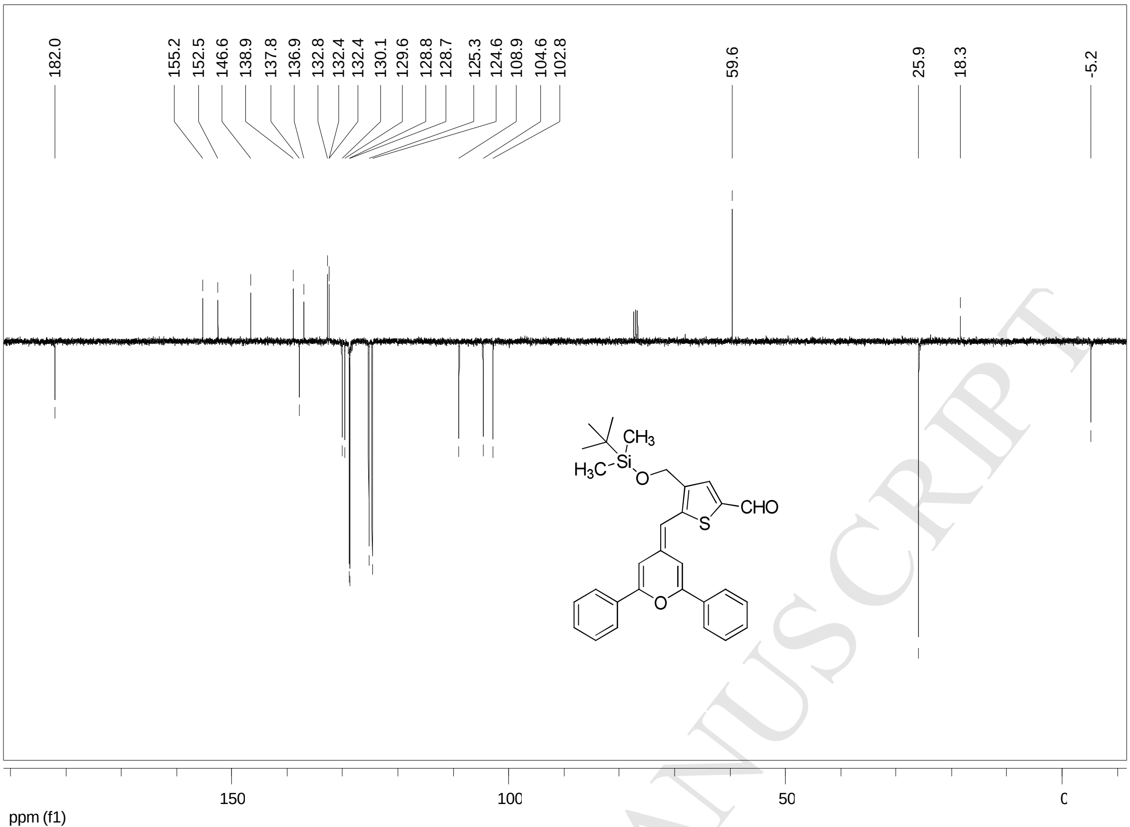

Figure S-2: ^{13}C NMR (APT) spectrum of compound **7** (100 MHz, CDCl$_3$).

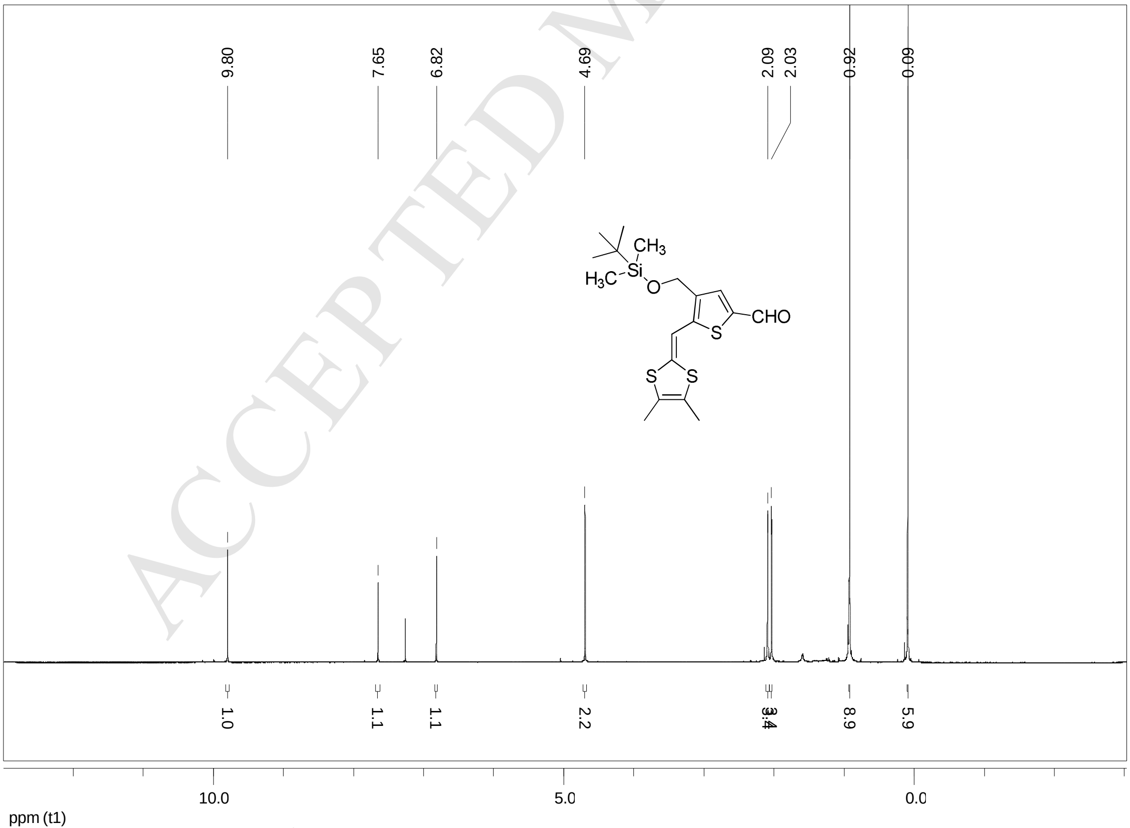

Figure S-3: ^{1}H NMR spectrum of compound **10** (400 MHz, CDCl$_3$).

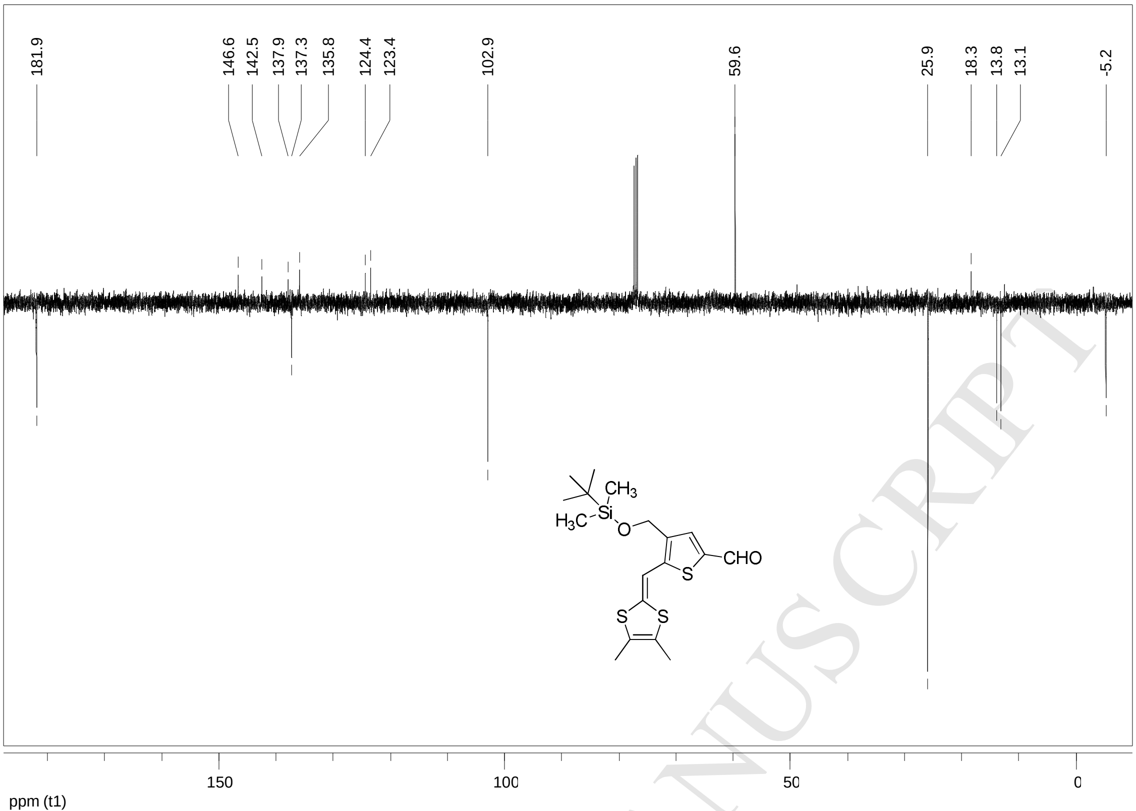

Figure S-4: ^{13}C NMR (APT) spectrum of compound **10** (100 MHz, $CDCl_3$).

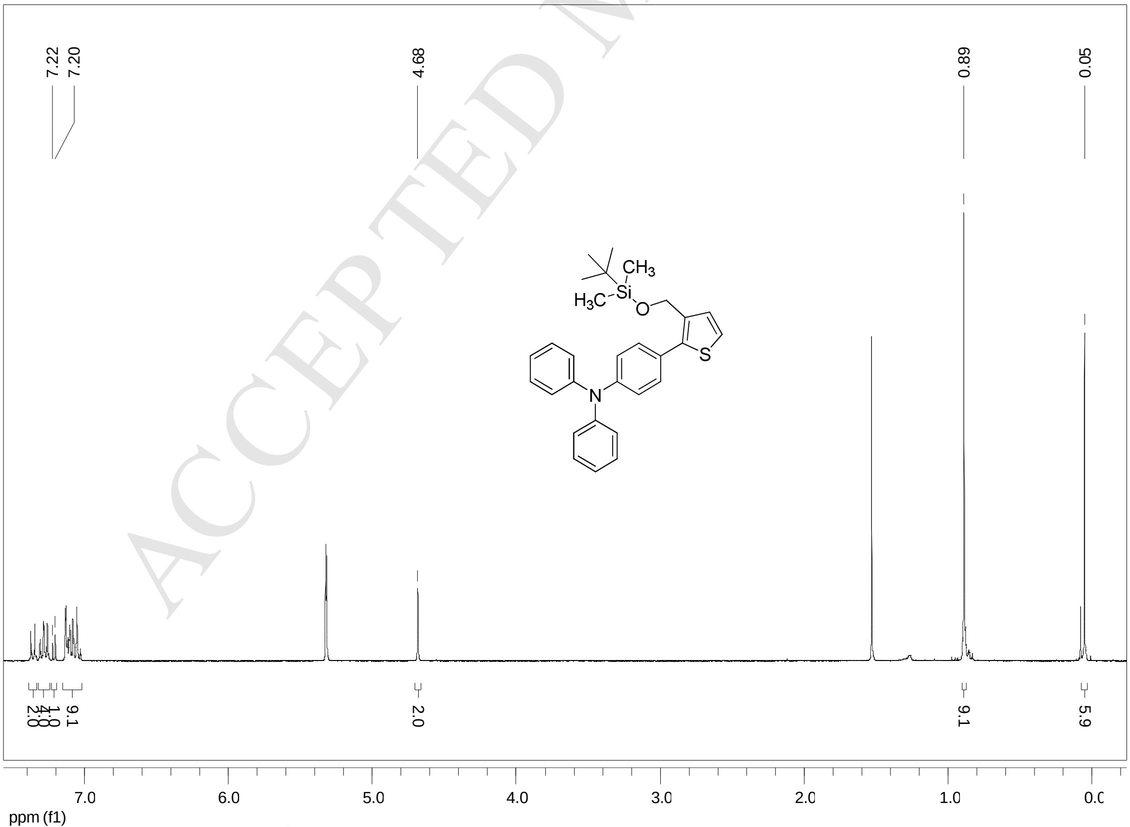

Figure S-5: ^{1}H NMR spectrum of compound **13** (300 MHz, CD_2Cl_2).

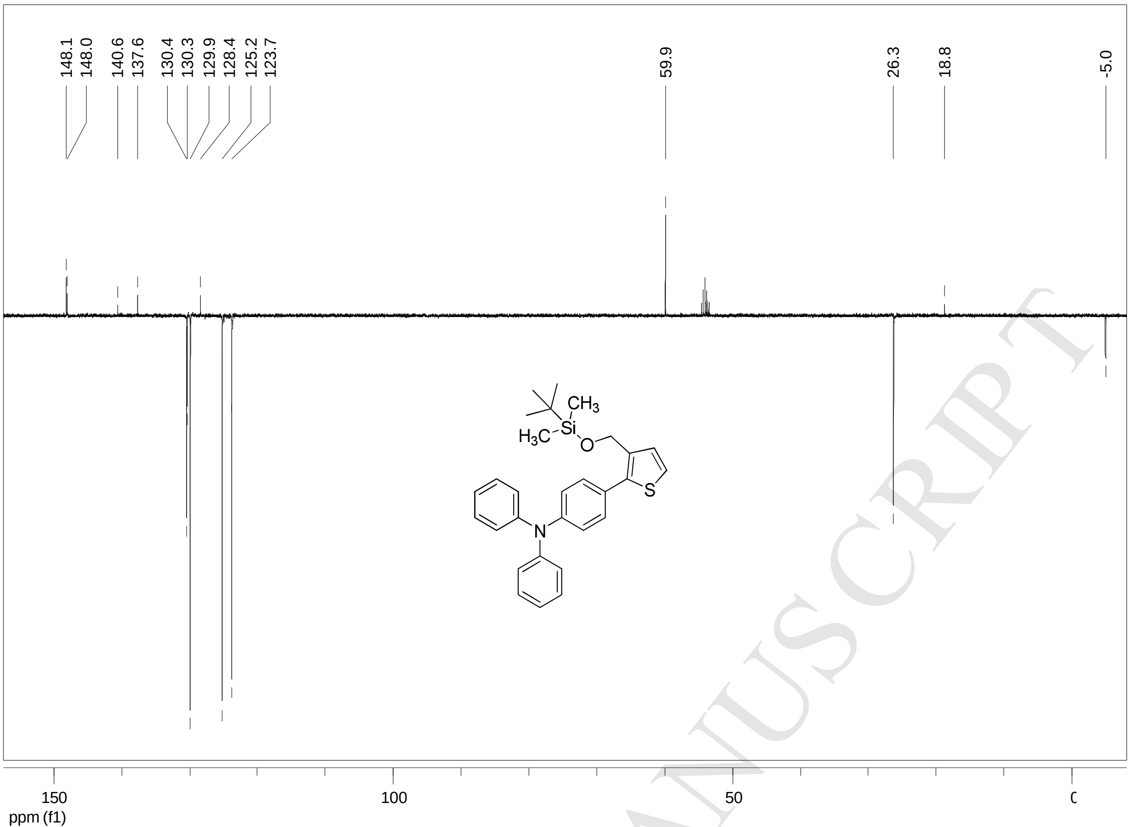

Figure S-6: ^{13}C NMR (APT) spectrum of compound **13** (100 MHz, CD_2Cl_2).

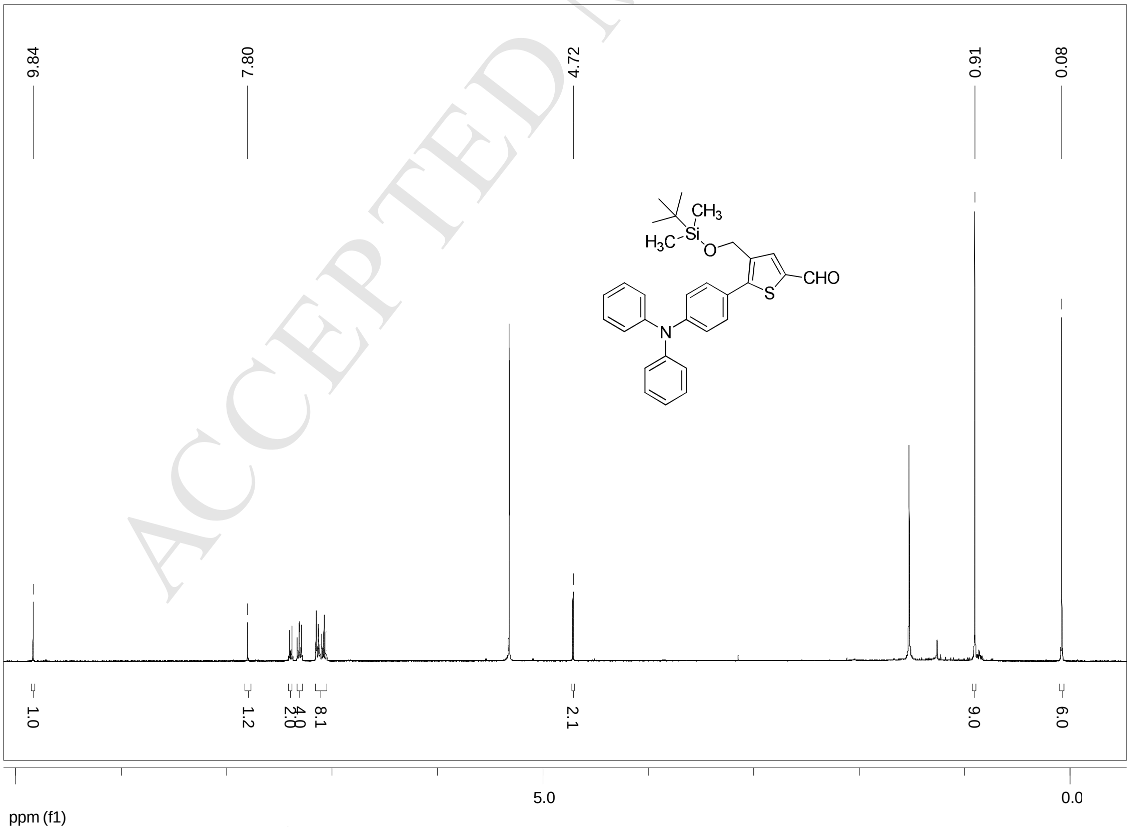

Figure S-7: ^{1}H NMR spectrum of compound **14** (400 MHz, CD_2Cl_2).

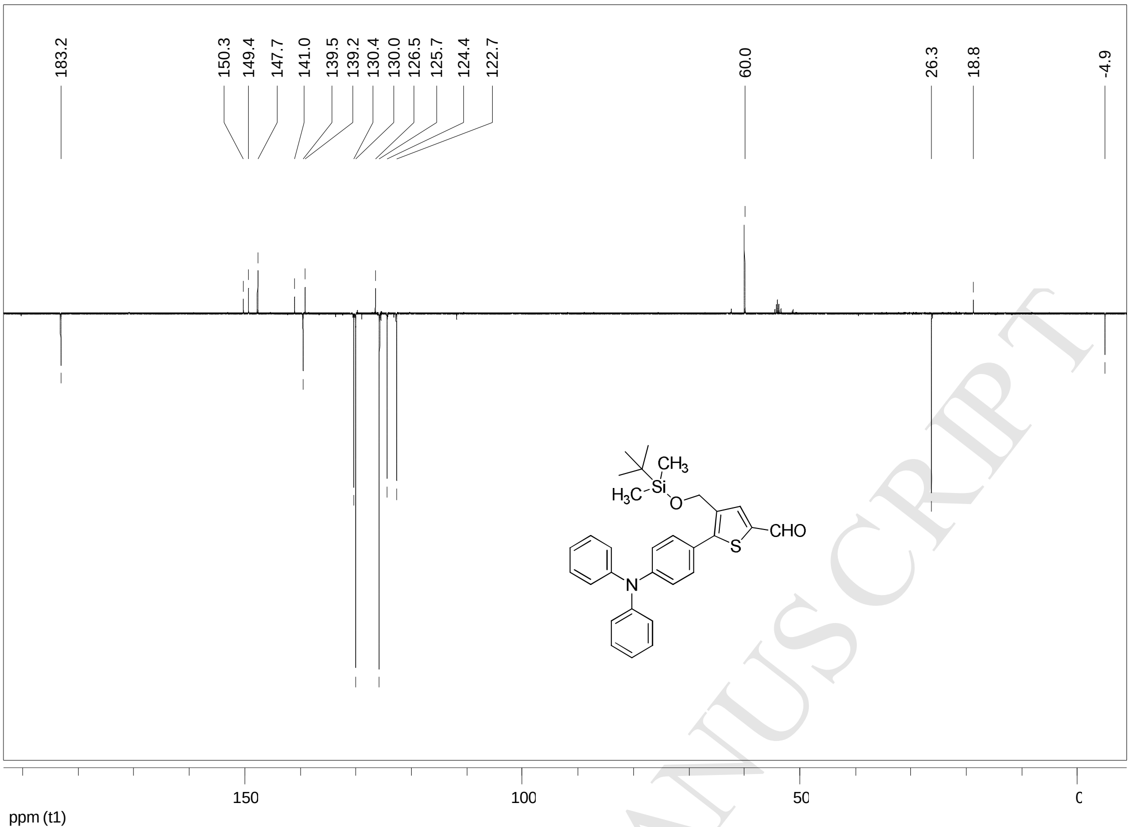

Figure S-8: ^{13}C NMR (APT) spectrum of compound **14** (100 MHz, CD_2Cl_2).

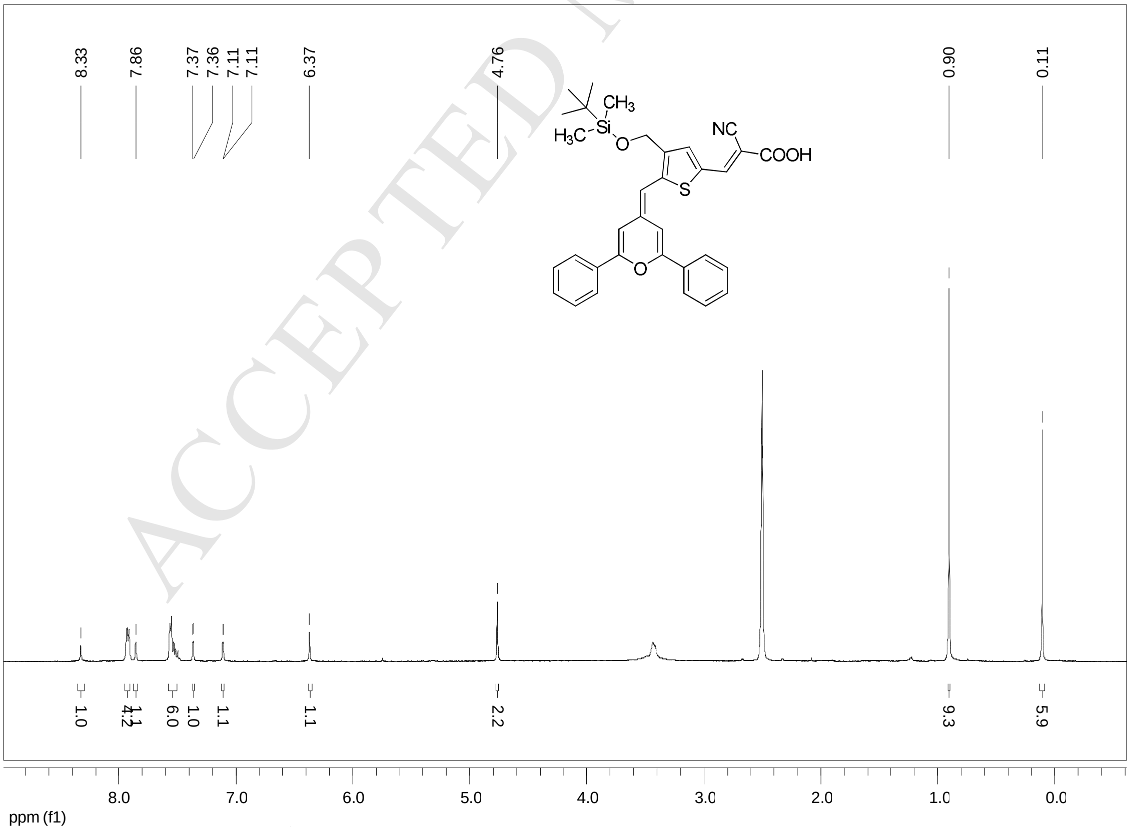

Figure S-9: ^{1}H NMR spectrum of compound **1** (400 MHz, dmso-d_6).

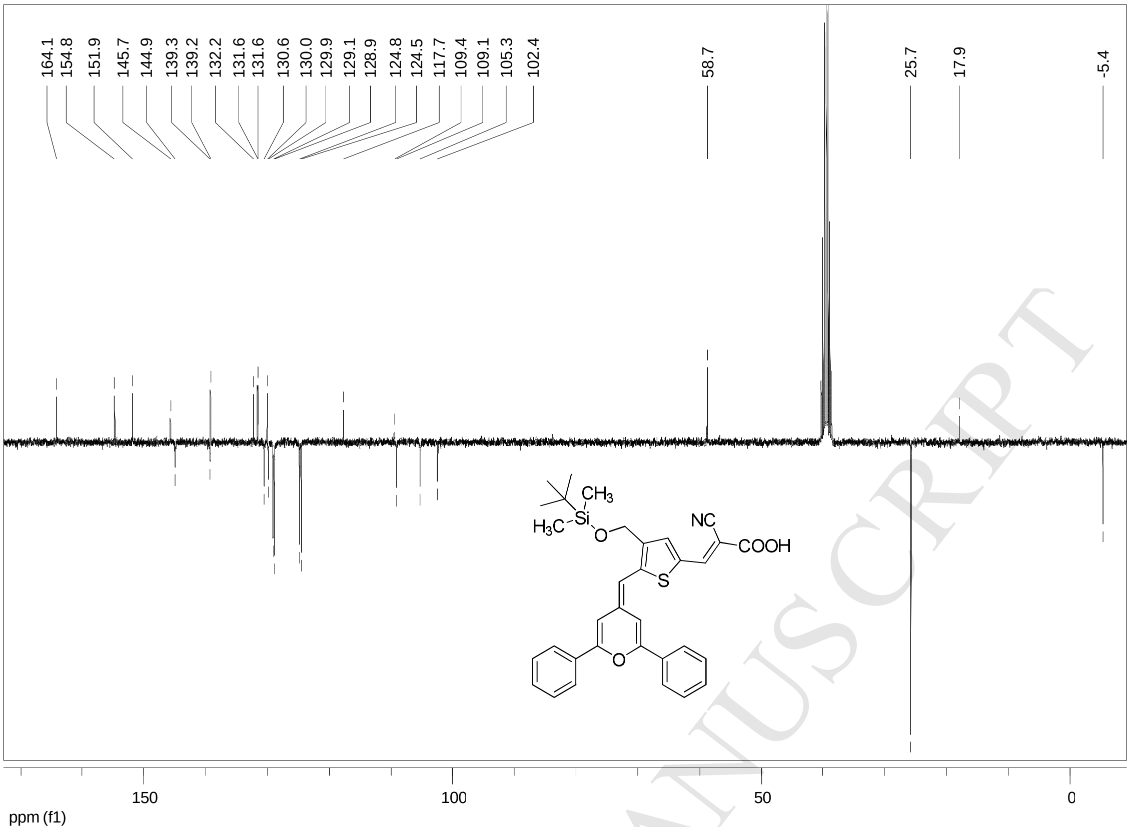

Figure S-10: ^{13}C NMR (APT) spectrum of compound **1** (75 MHz, dmso-d_6).

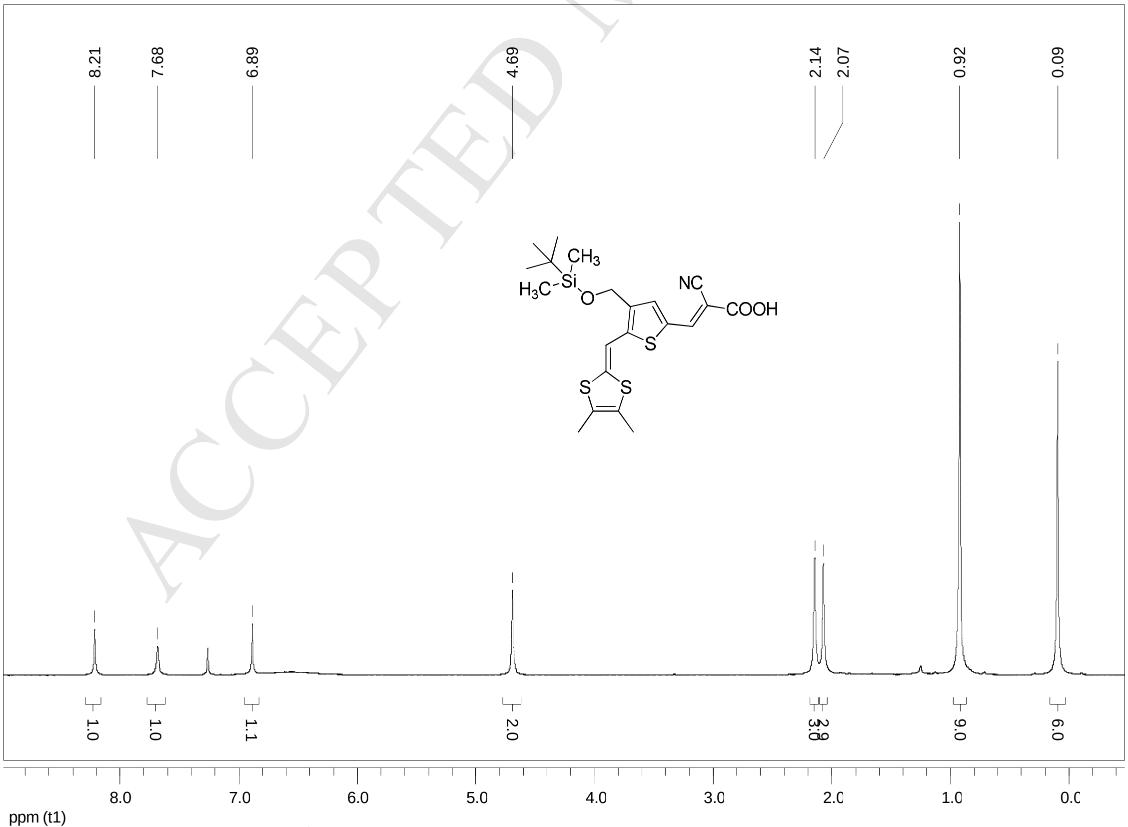

Figure S-11: ^{1}H NMR spectrum of compound **2** (300 MHz, $CDCl_3$).

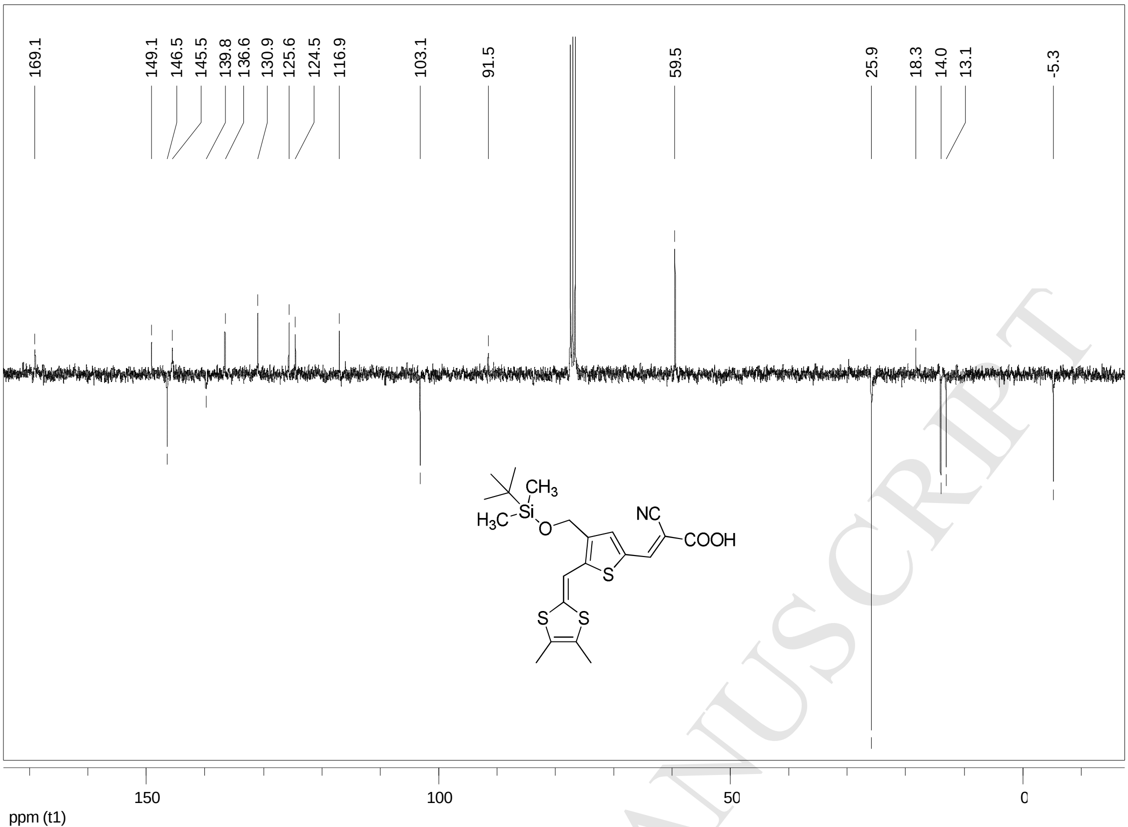

Figure S-12: ^{13}C NMR (APT) spectrum of compound **2** (75 MHz, CDCl$_3$).

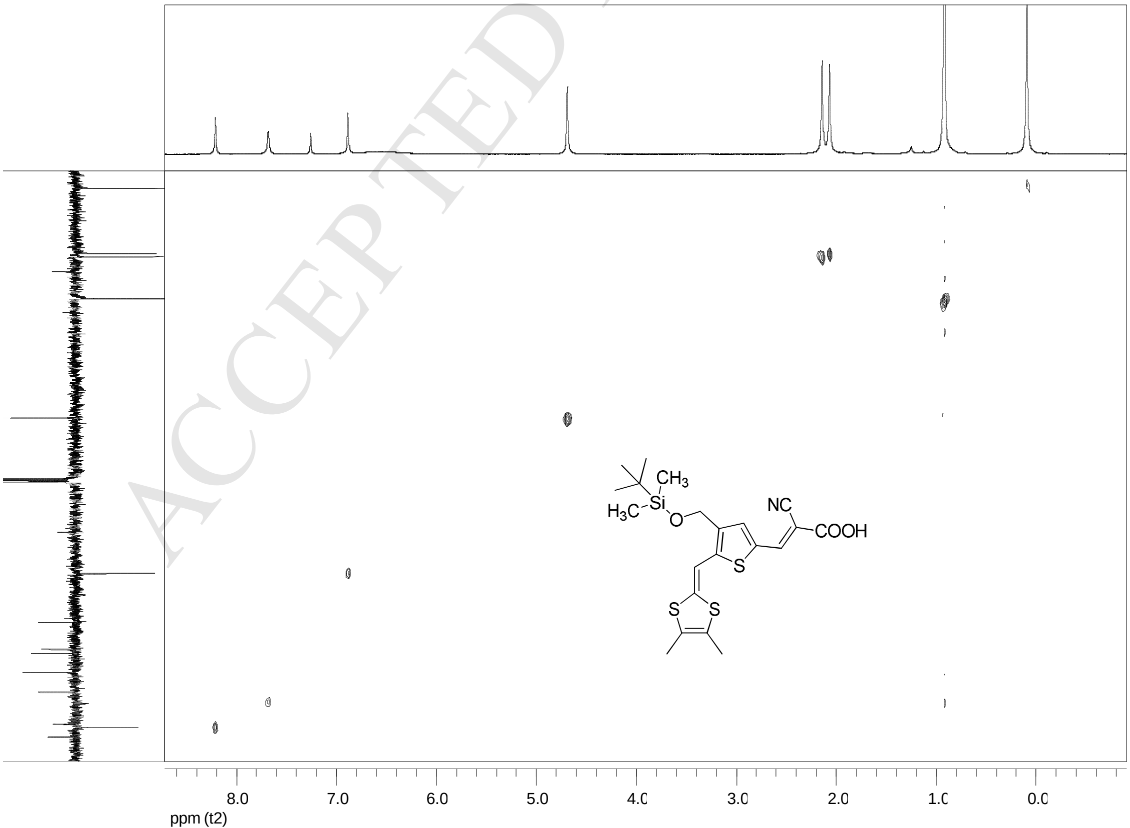

Figure S-13 ^{1}H-^{13}C HSQC spectrum of compound **2**.

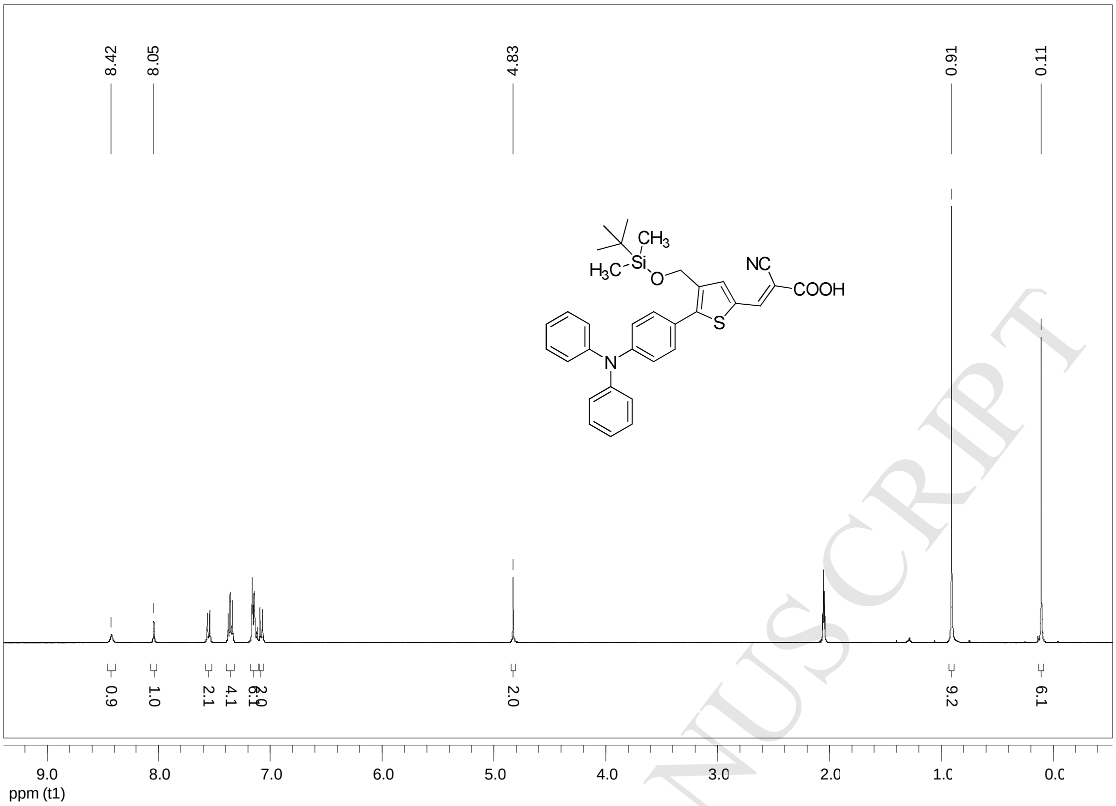

Figure S-14: ^{1}H NMR spectrum of compound **3** (400 MHz, acetone-d$_6$).

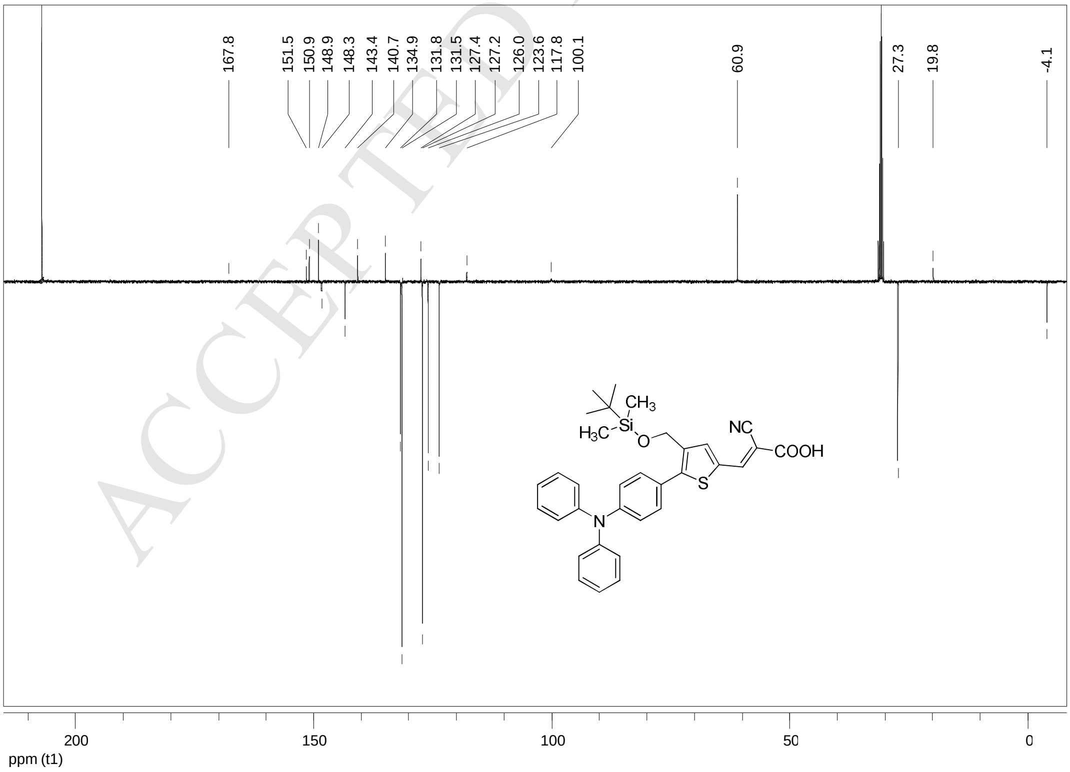

Figure S-15: ^{13}C NMR (APT) spectrum of compound **3** (100 MHz, acetone-d$_6$).

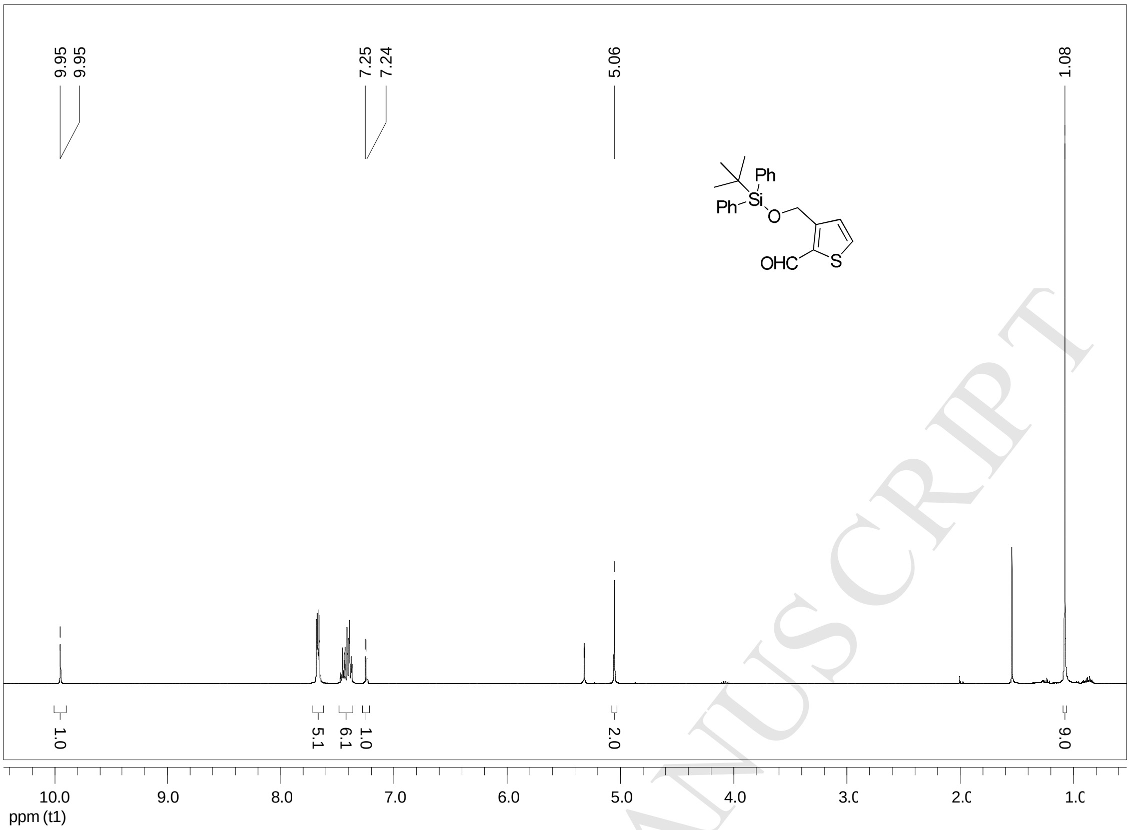

Figure S-16: ^{1}H NMR spectrum of compound **18** (400 MHz, CD_2Cl_2).

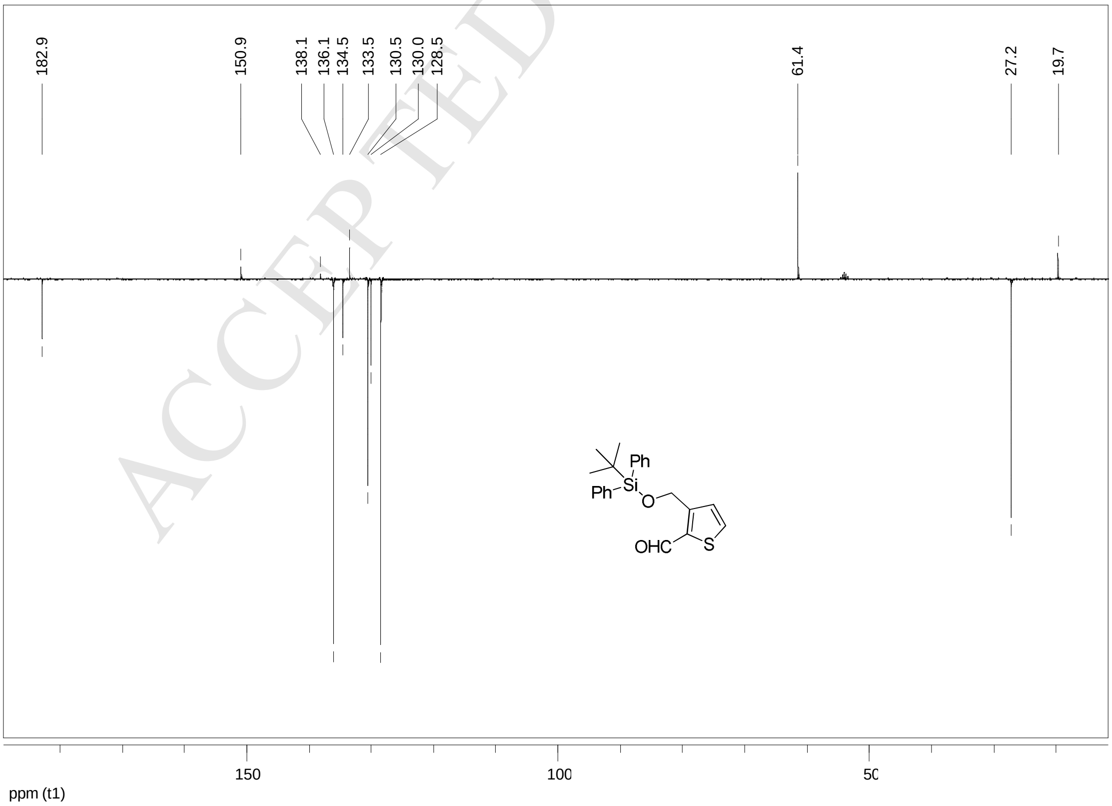

Figure S-17: ^{13}C NMR (APT) spectrum of compound **18** (100 MHz, CD_2Cl_2).

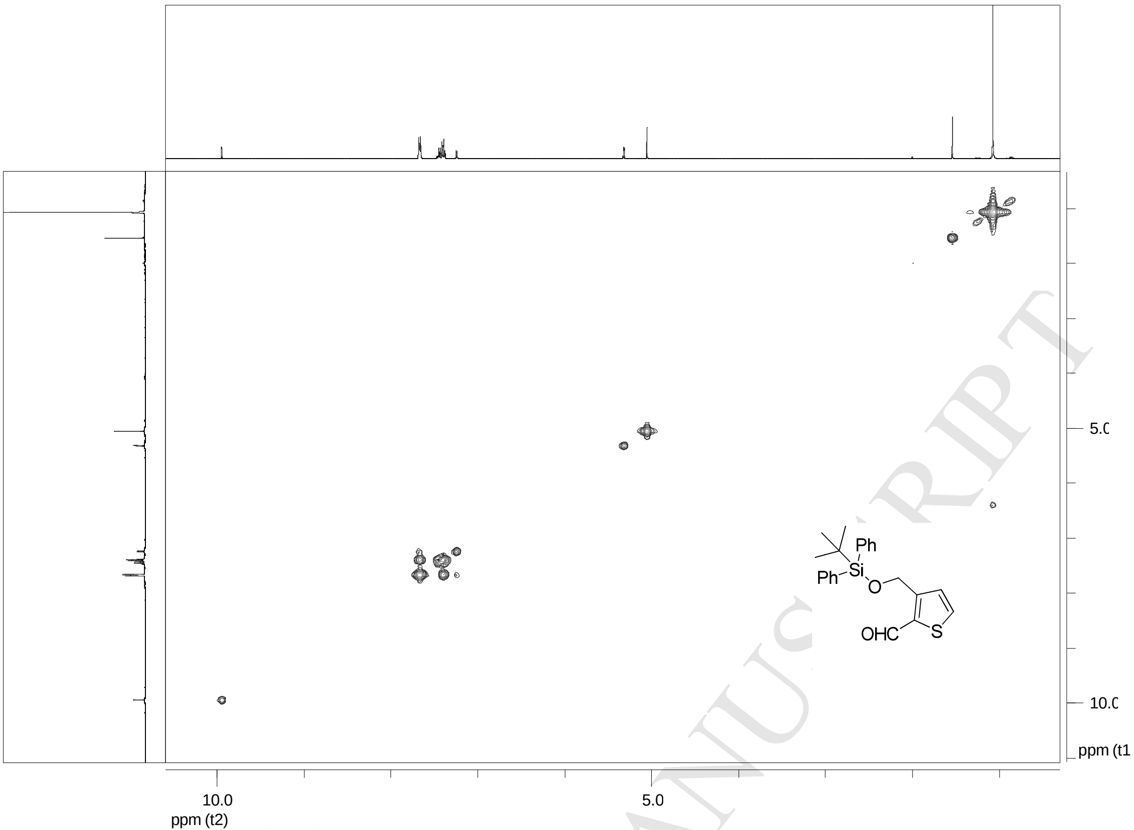

Figure S-18: ^{1}H-^{1}H COSY spectrum of compound **18** (400 MHz, CD_2Cl_2).

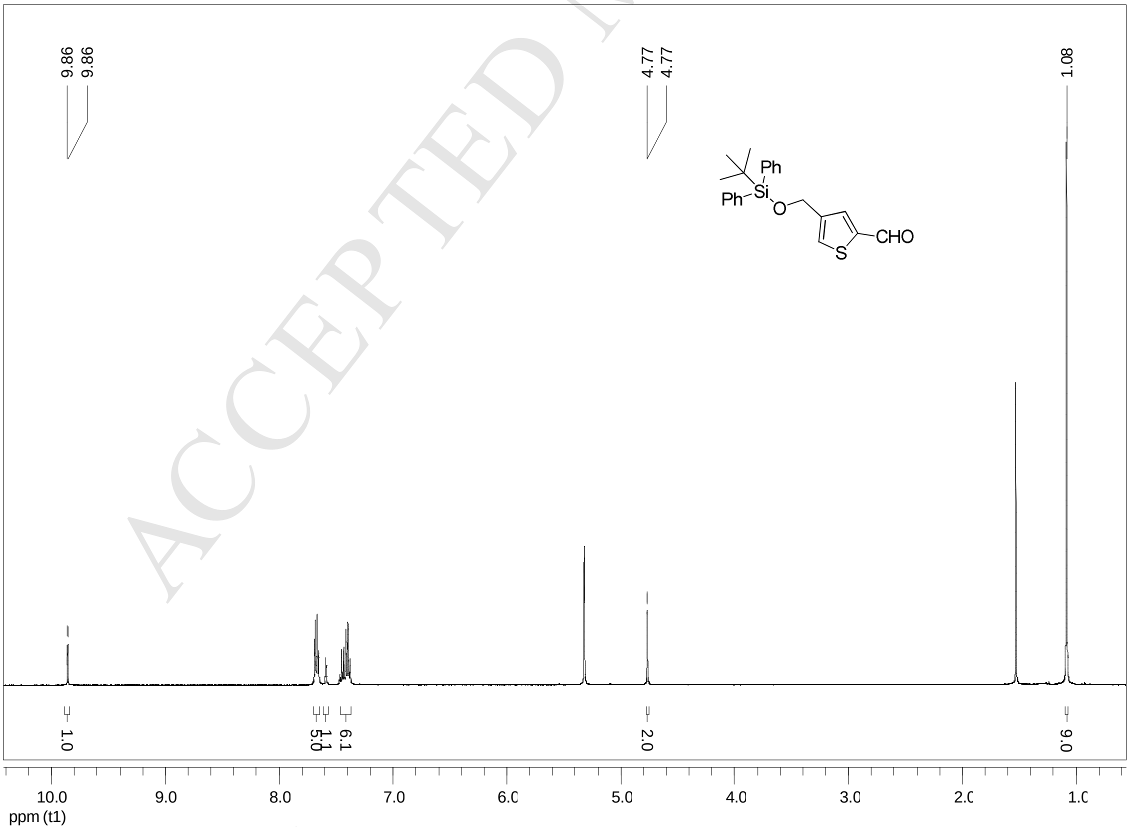

Figure S-19: ^{1}H NMR spectrum of compound **19** (400 MHz, CD_2Cl_2).

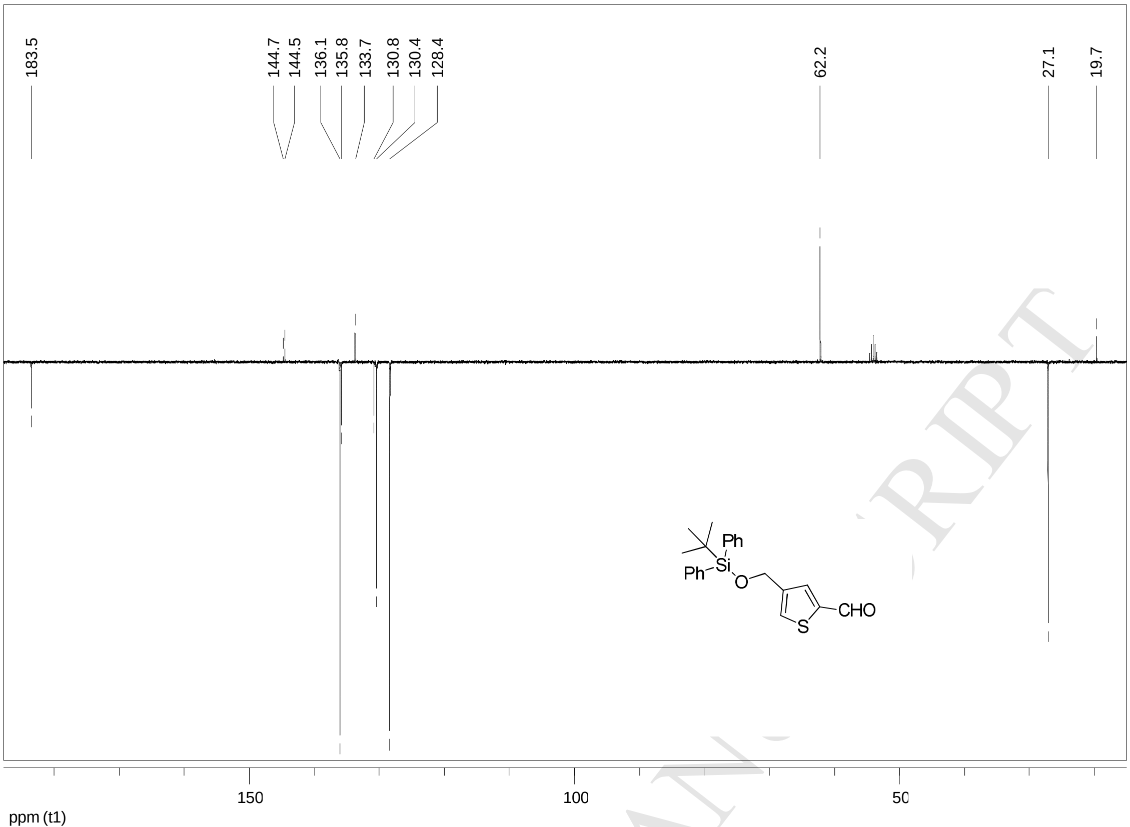

Figure S-20: ^{13}C NMR (APT) spectrum of compound **19** (100 MHz, CD_2Cl_2).

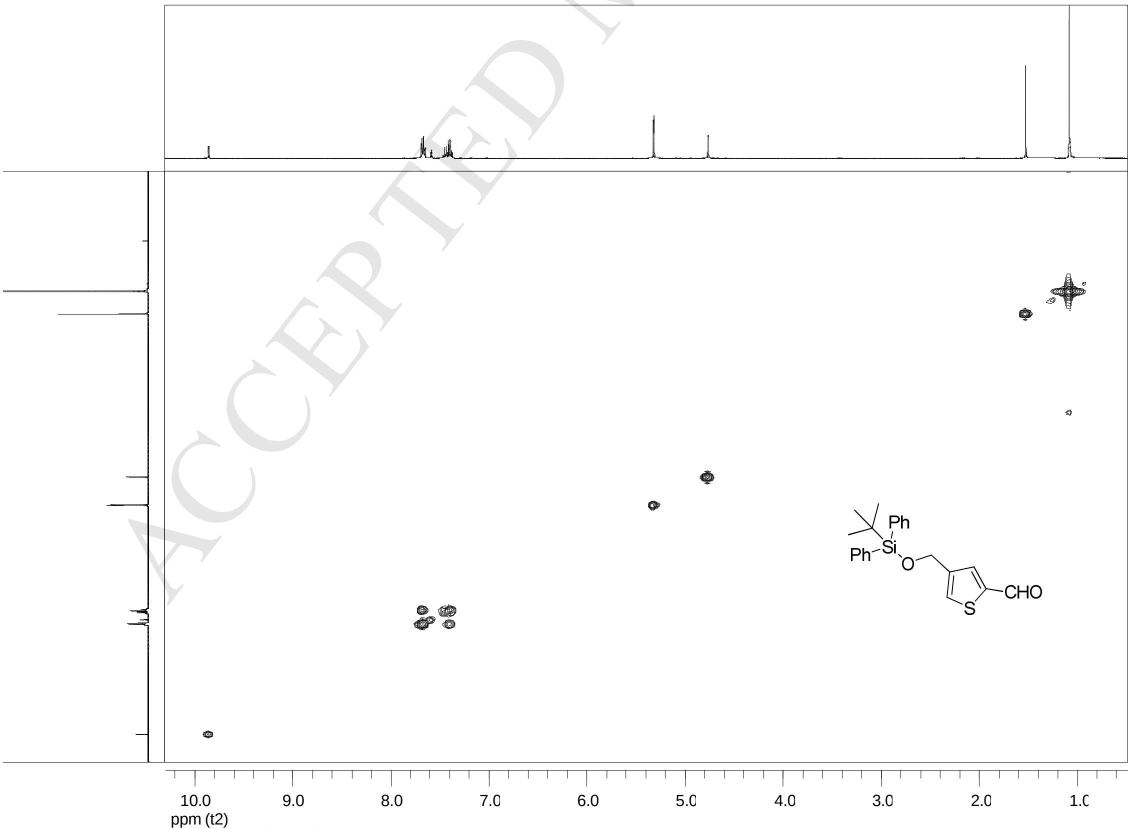

Figure S-21: ^{1}H-^{1}H COSY spectrum of compound **19** (400 MHz, CD_2Cl_2).

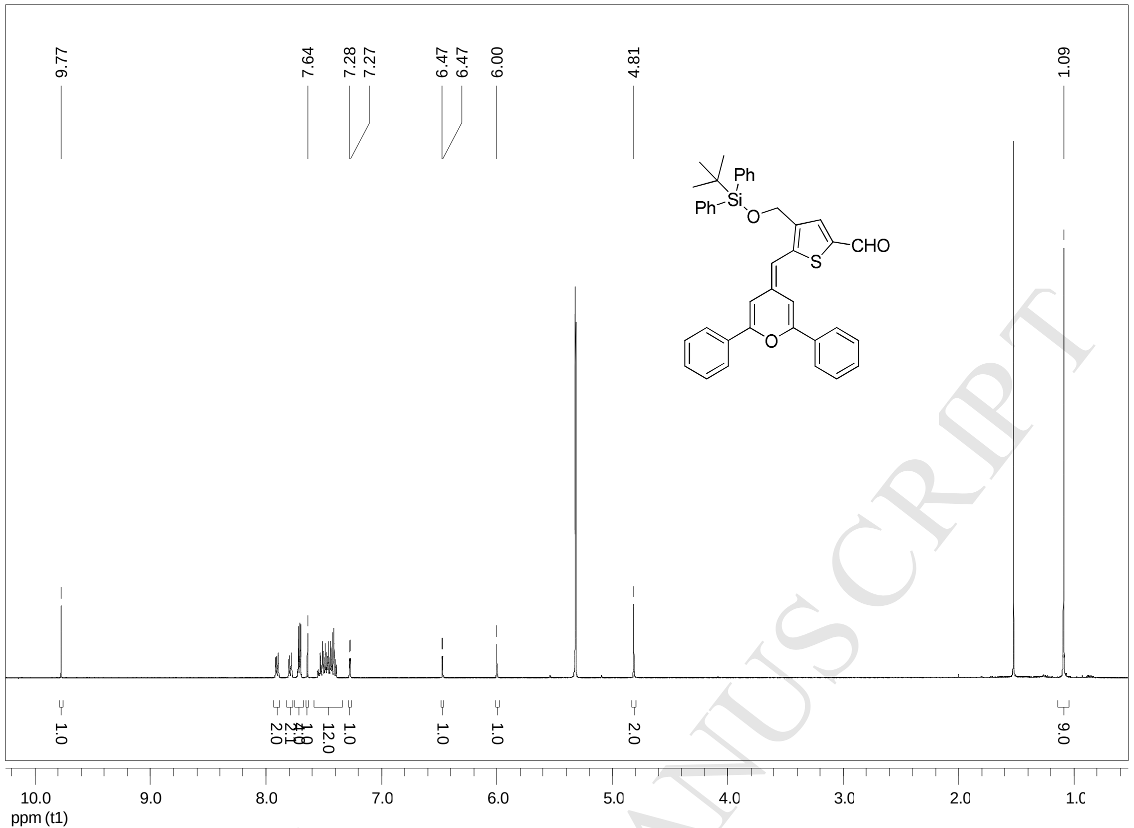

Figure S-22: ^{1}H NMR spectrum of compound **21** (400 MHz, CD_2Cl_2).

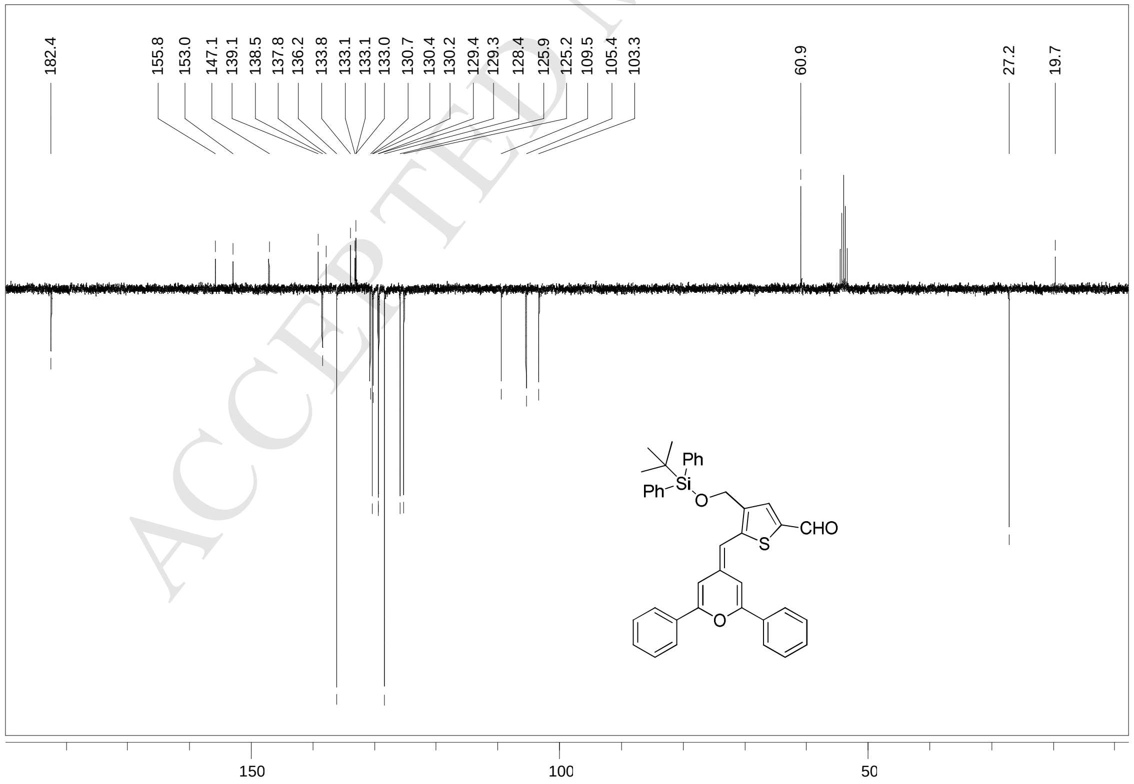

Figure S-23 ^{13}C NMR (APT) spectrum of compound **21** (100 MHz, CD_2Cl_2).

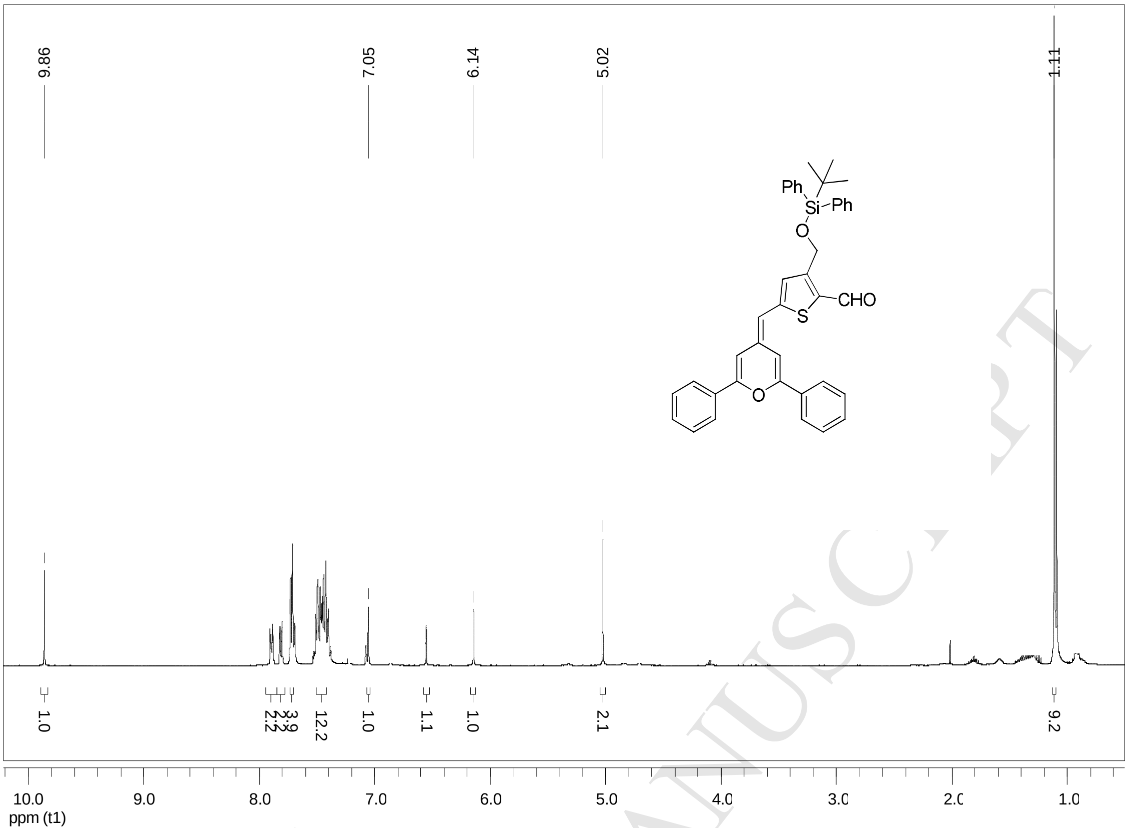

Figure S-24: ^{1}H NMR spectrum of compound **23** (400 MHz, CD_2Cl_2).

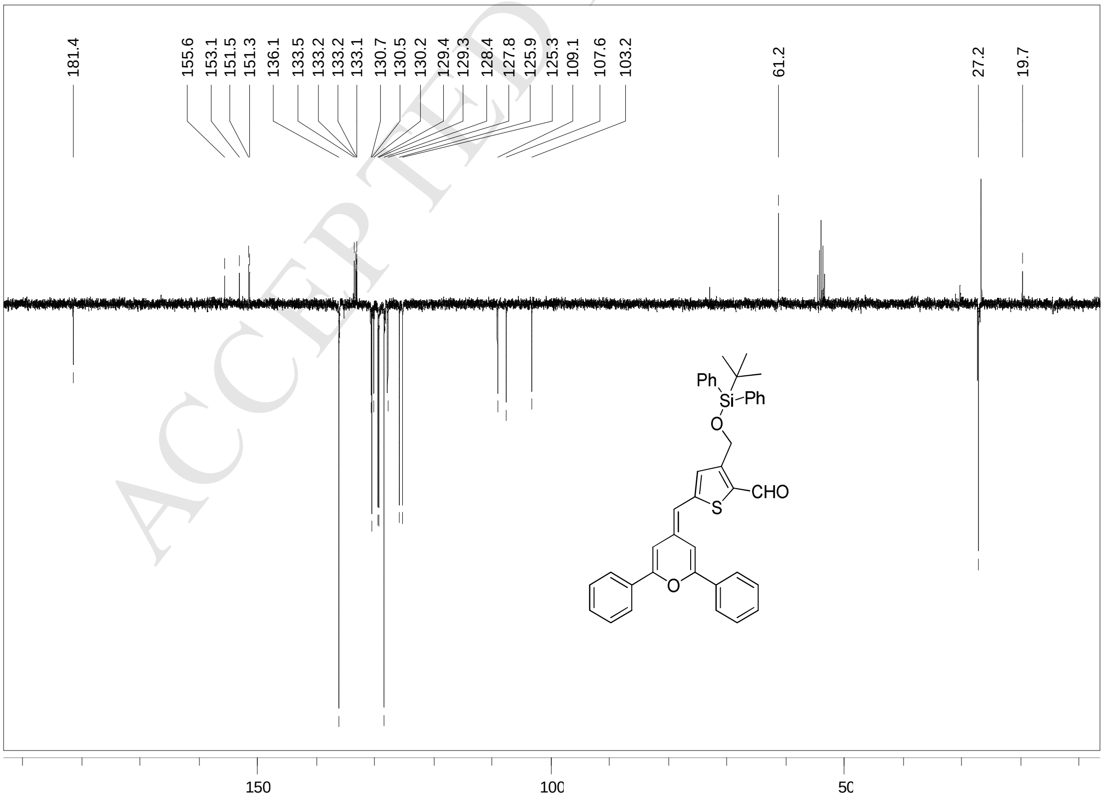

Figure S-25: ^{13}C NMR (APT) spectrum of compound **23** (100 MHz, CD_2Cl_2).

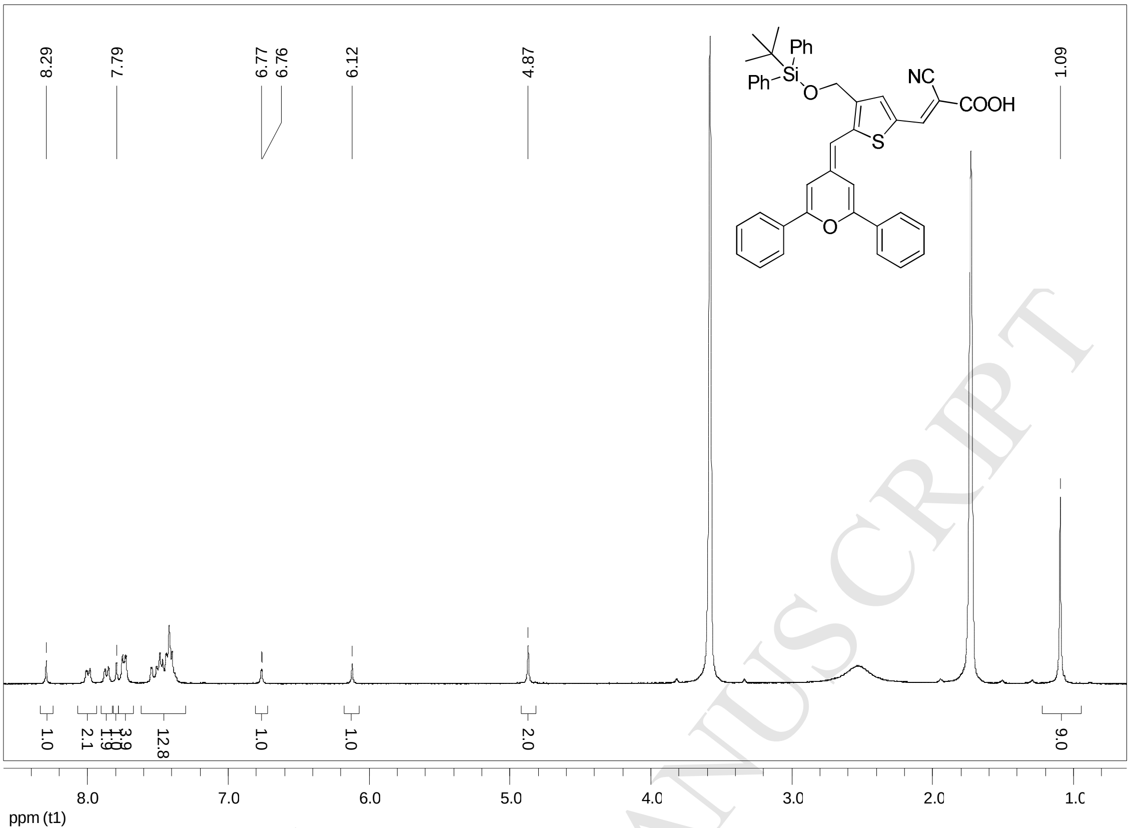

Figure S-26: ^{1}H NMR spectrum of compound **15** (300 MHz, THF-d_8).

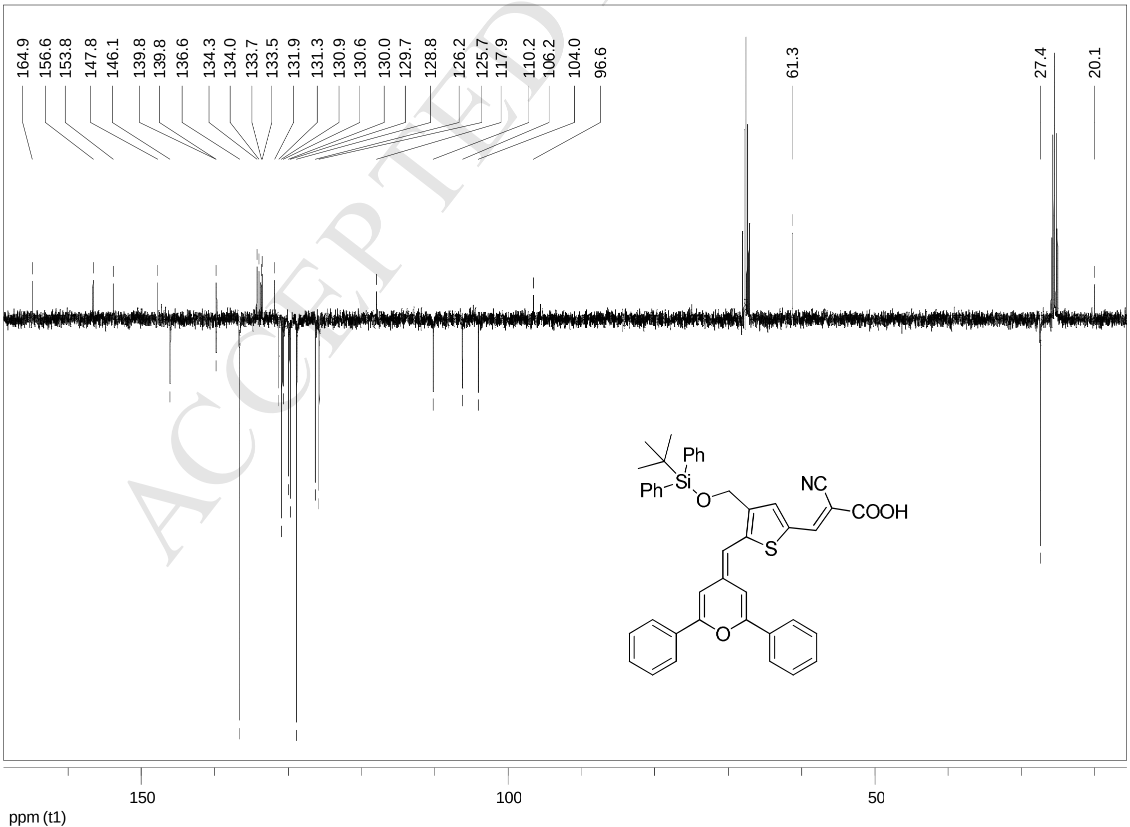

Figure S-27: ^{13}C NMR (APT) spectrum of compound **15** (100 MHz, THF-d_8).

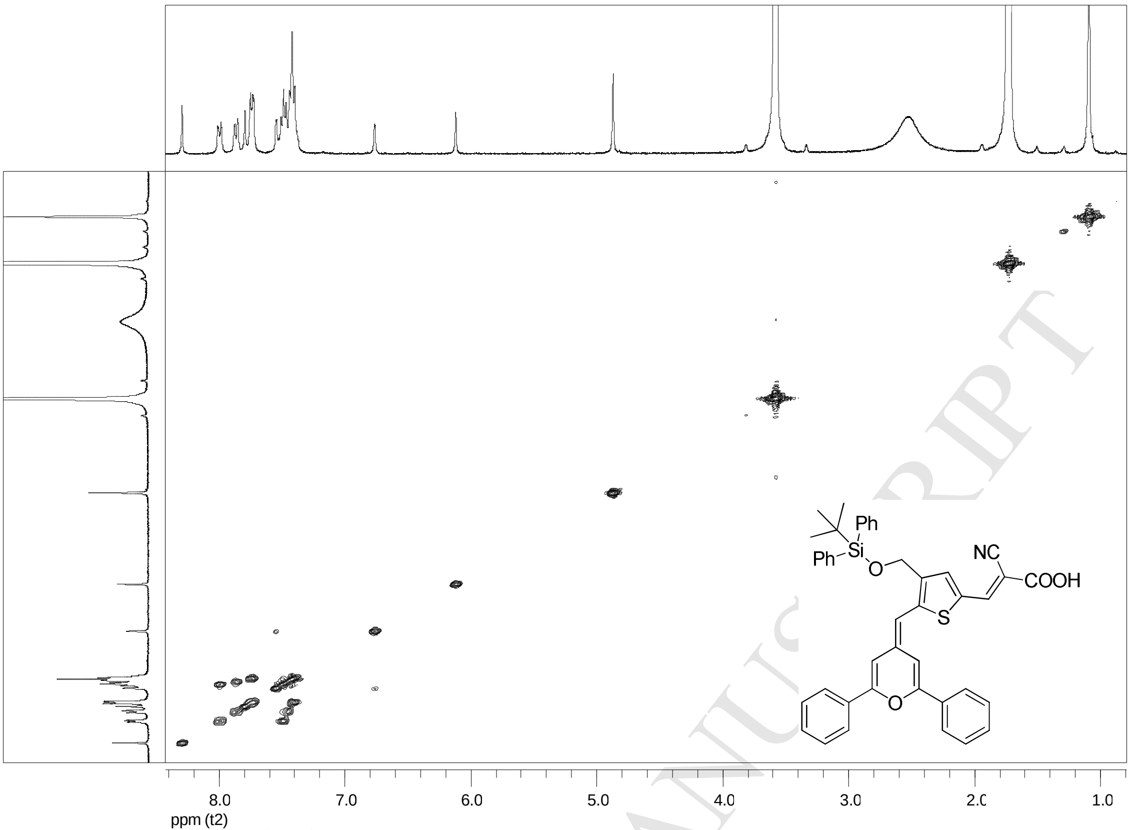

Figure S-28: ^{1}H-^{1}H COSY spectrum of compound **15** (300 MHz, THF-d_8).

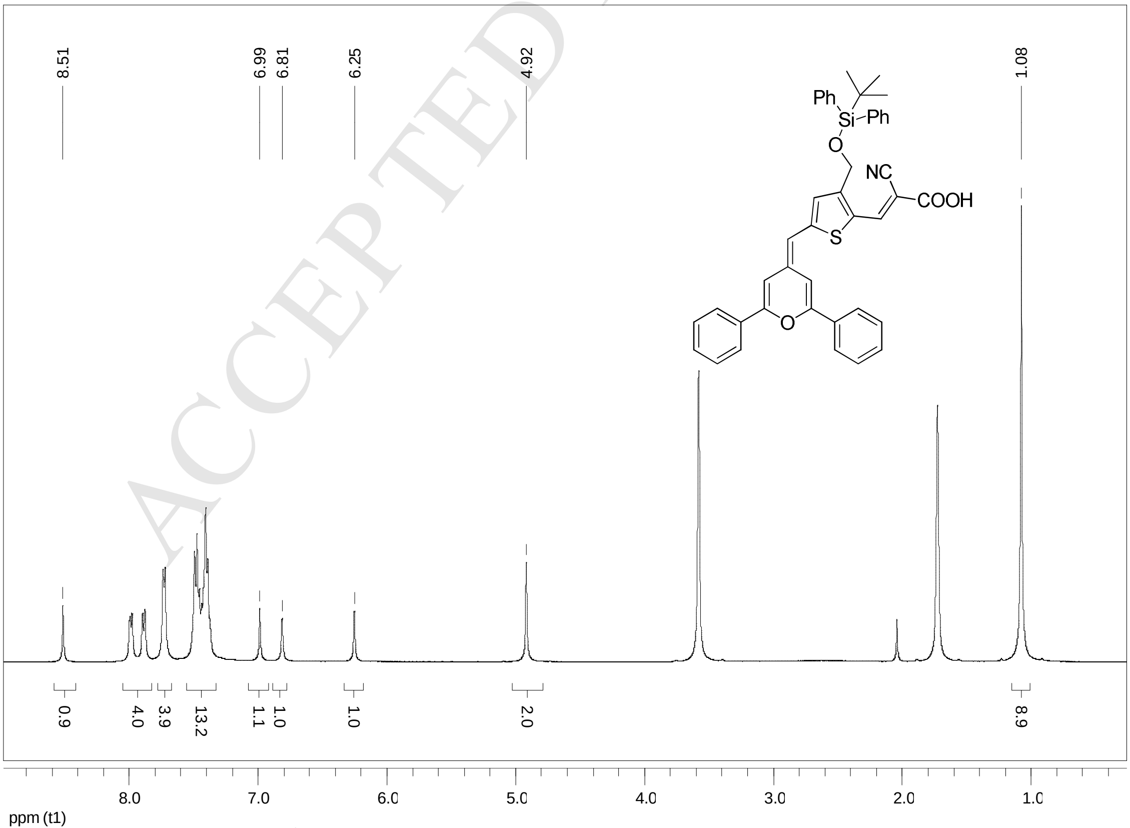

Figure S-29: ^{1}H NMR spectrum of compound **16** (400 MHz, THF-d_8).

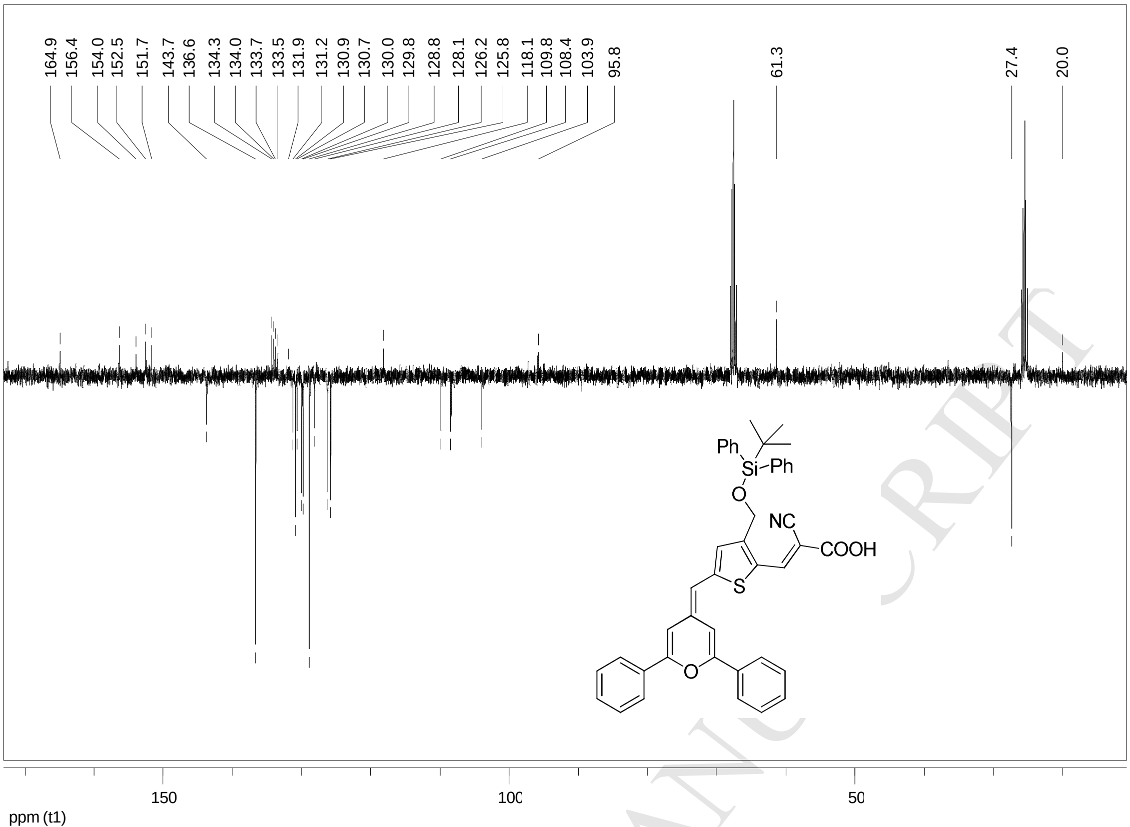

Figure S-30: ^{13}C NMR (APT) spectrum of compound **16** (100 MHz, THF-d$_8$).

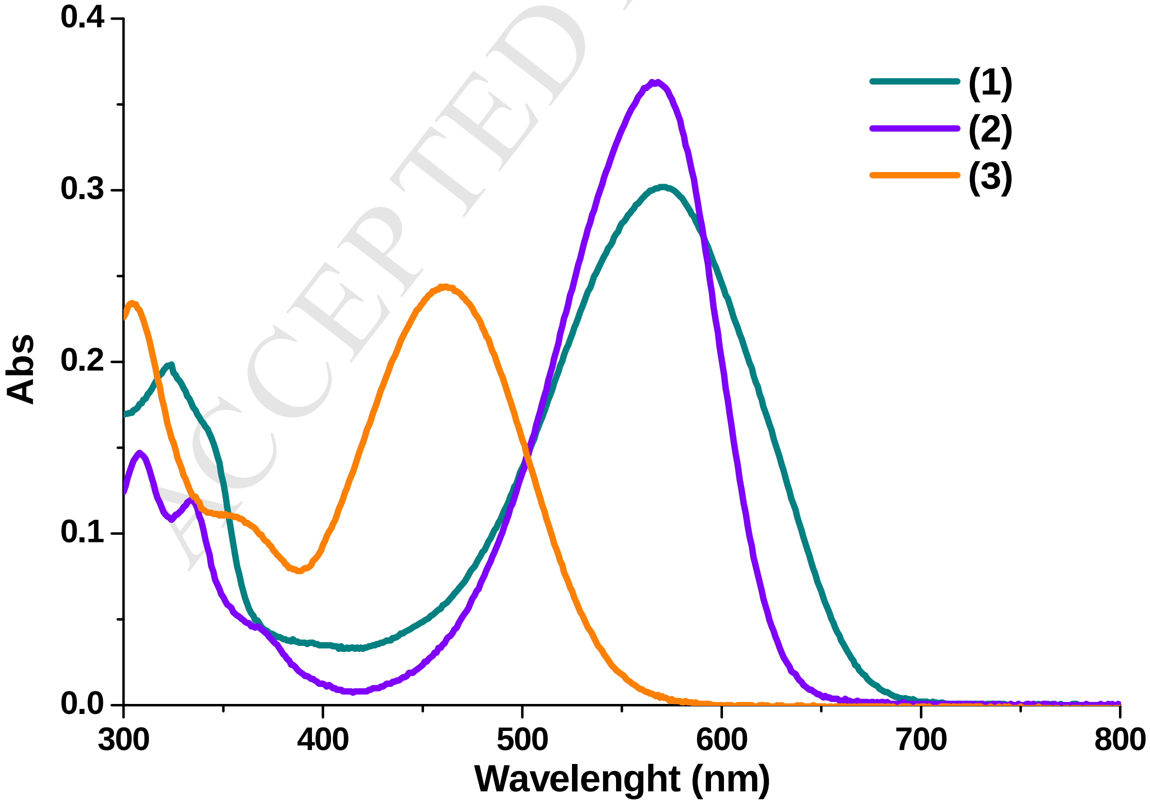

Figure S-31: Normalized UV-vis absorption of compounds (**1-3**)

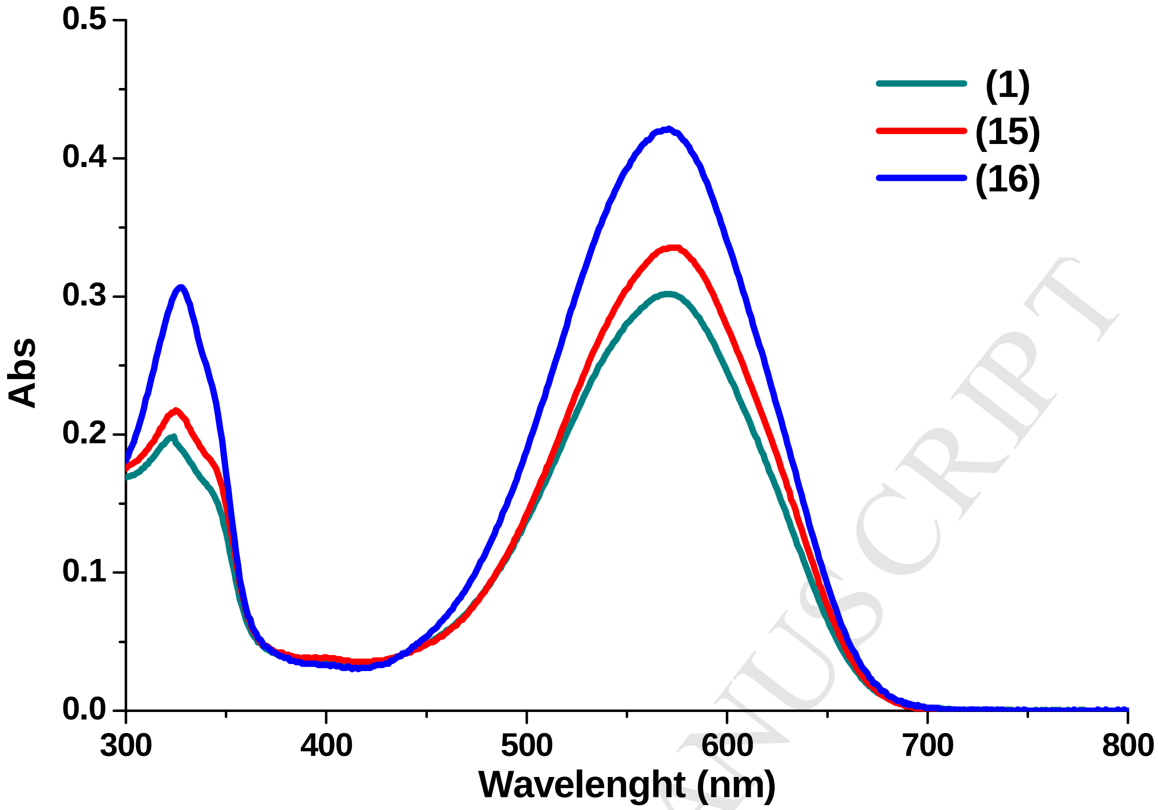

Figure S-32: Normalized UV-vis absorption of compounds (**1, 15 and 16**)

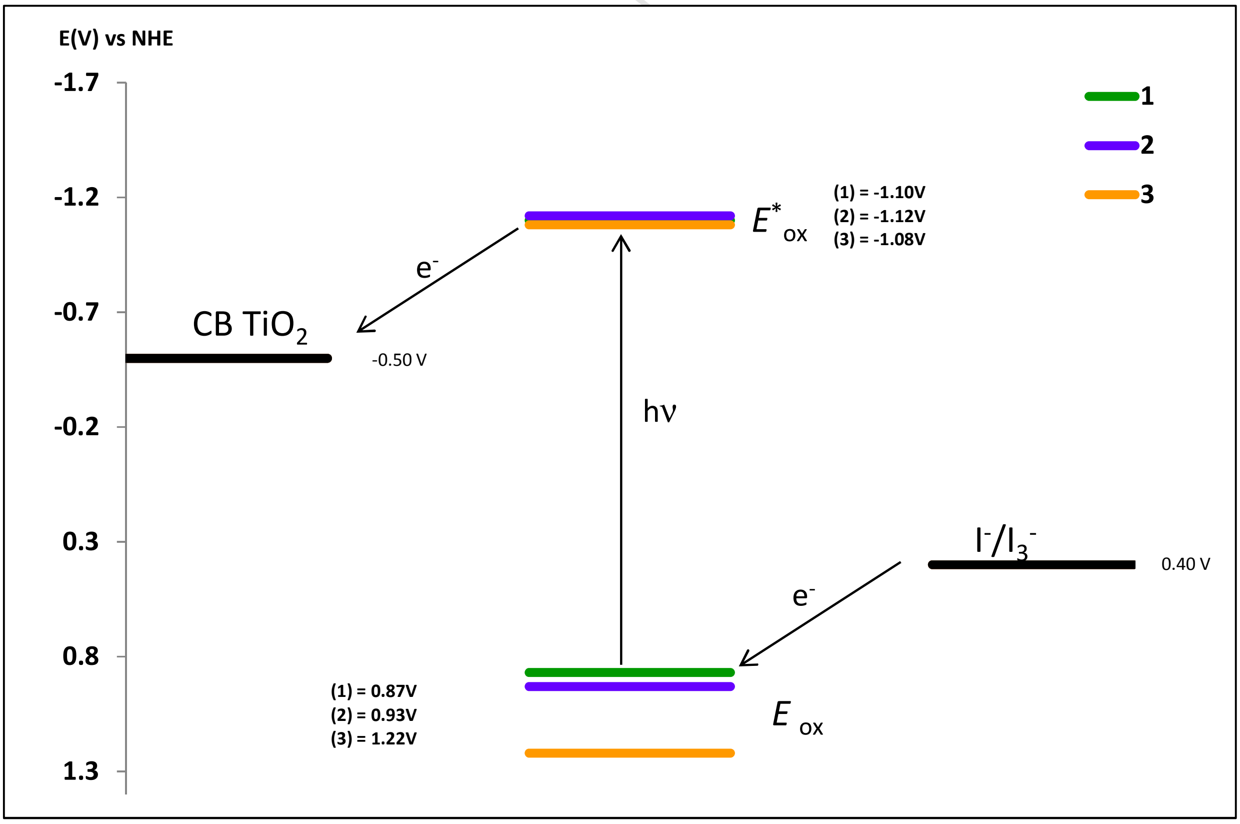

Figure S-33: Energy diagram of compounds (**1-3**)

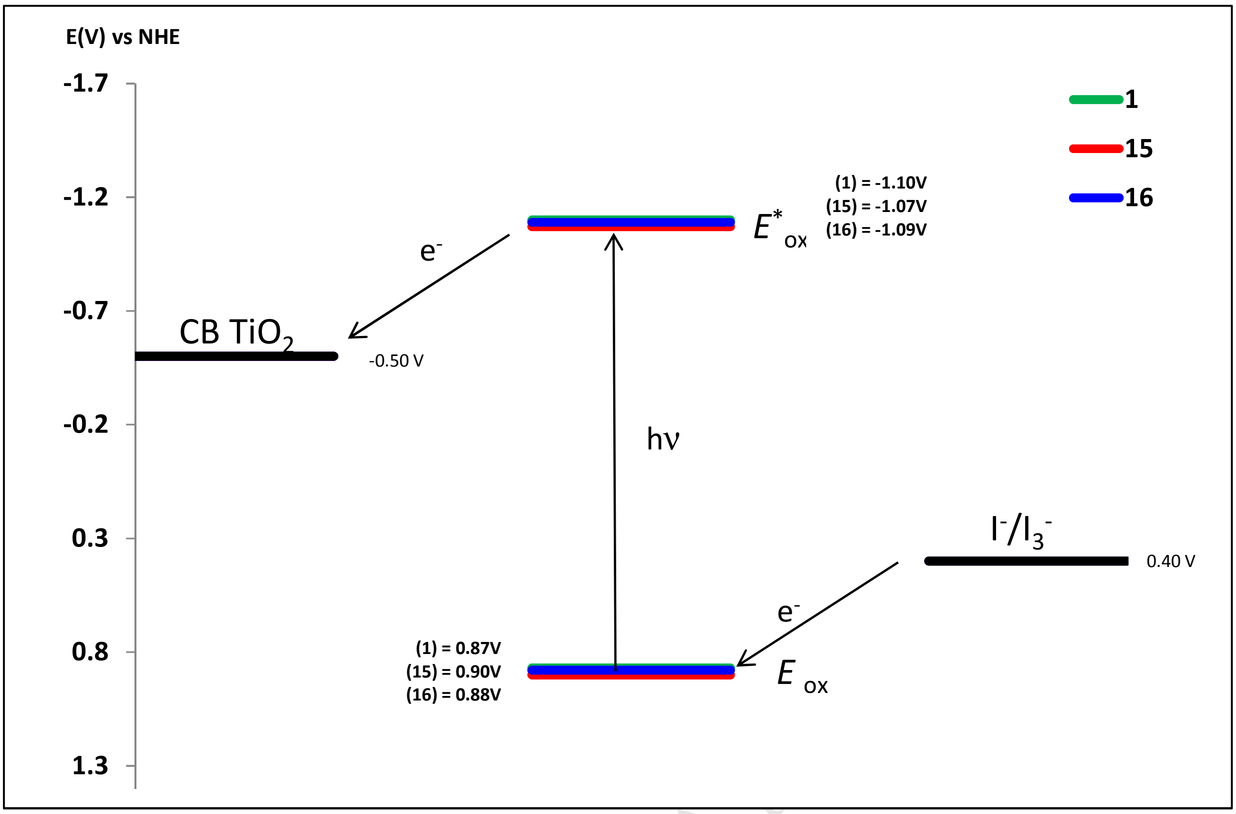

Figure S-34: Energy diagram of compounds (**1, 15 and 16**)

Calculated molecular geometries and energies (M06-2x/6-31G* PCM-Dichloromethane)

Compound 1: Ground State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        3.829068    0.342082    0.207179
      2          6           0        2.478089    0.326360    0.247164
      3          6           0        1.731942   -0.892423    0.028851
      4          6           0        2.564467   -2.070627   -0.092789
      5          6           0        3.912057   -1.990169   -0.096131
      6          1           0        1.981432    1.251855    0.495987
      7          1           0        2.094994   -3.038354   -0.226174
      8          8           0        4.551757   -0.789206    0.006538
      9          6           0        0.365498   -1.000661   -0.060482
     10          6           0       -0.629703    0.027659   -0.076143
     11          6           0       -2.010315   -0.207906   -0.063898
     12         16           0       -0.302215    1.731147   -0.194028
     13          6           0       -2.763090    0.966586   -0.132055
     14          6           0       -2.002098    2.128615   -0.204331
     15          1           0       -3.847412    0.976890   -0.123754
     16          1           0       -0.029902   -2.008728   -0.161306
     17          6           0       -2.544154    3.435840   -0.260948
     18          6           0       -1.913927    4.650039   -0.317747
     19          1           0       -3.631334    3.469993   -0.256994
     20          6           0       -2.612789   -1.585528    0.019983
     21          1           0       -2.278136   -2.188277   -0.839224
     22          1           0       -2.253256   -2.092671    0.928396
     23          6           0       -0.492120    4.790478   -0.332263
     24          7           0        0.663384    4.891731   -0.343831
     25          6           0       -2.657749    5.922795   -0.367085
     26          8           0       -2.134075    7.014452   -0.420847
     27          8           0       -3.990355    5.753046   -0.346417
     28          1           0       -4.392111    6.639242   -0.380817
     29          8           0       -4.018277   -1.479167    0.034402
     30         14           0       -4.999634   -2.846555    0.090944
     31          6           0       -4.816614   -3.818593   -1.504009
     32          1           0       -3.778480   -4.130953   -1.660826
     33          1           0       -5.429549   -4.725896   -1.474552
     34          1           0       -5.125731   -3.228056   -2.372478
     35          6           0       -4.487610   -3.907903    1.553904
     36          1           0       -4.423236   -3.313236    2.471208
     37          1           0       -5.213668   -4.710786    1.722829
     38          1           0       -3.512502   -4.377580    1.386236
     39          6           0       -6.744843   -2.154285    0.295155
     40          6           0       -6.866241   -1.467502    1.662589
     41          6           0       -7.025867   -1.129039   -0.812023
     42          6           0       -7.770280   -3.293237    0.203372
     43          1           0       -6.712658   -2.176170    2.484736
     44          1           0       -6.134951   -0.658233    1.770875
     45          1           0       -7.868193   -1.032724    1.781113
     46          1           0       -6.952751   -1.578621   -1.809370
     47          1           0       -8.042076   -0.725656   -0.703841
     48          1           0       -6.323787   -0.289436   -0.767002
     49          1           0       -8.785384   -2.897665    0.344165
     50          1           0       -7.741206   -3.787721   -0.774706
     51          1           0       -7.605519   -4.056479    0.973437
     52          6           0        4.855745   -3.111812   -0.242315
     53          6           0        6.163844   -2.874641   -0.682069
     54          6           0        4.459138   -4.421588    0.055315
     55          6           0        7.052623   -3.933559   -0.835810
     56          1           0        6.477081   -1.861900   -0.912125
     57          6           0        5.350763   -5.475813   -0.101663
     58          1           0        3.460276   -4.615887    0.433294
     59          6           0        6.649344   -5.235704   -0.549181
     60          1           0        8.062636   -3.739914   -1.182854
     61          1           0        5.034268   -6.486085    0.137019
     62          1           0        7.345593   -6.059797   -0.668074
     63          6           0        4.675973    1.532870    0.392938
     64          6           0        6.022594    1.390435    0.748475
     65          6           0        4.143206    2.817146    0.216961
     66          6           0        6.816772    2.515999    0.940871
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     67          1           0        6.440660    0.398578    0.883721
     68          6           0        4.940125    3.937364    0.415601
     69          1           0        3.111633    2.948415   -0.096955
     70          6           0        6.278417    3.790793    0.779189
     71          1           0        7.858306    2.395931    1.221487
     72          1           0        4.515437    4.926174    0.275007
     73          1           0        6.900173    4.667618    0.930565
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E(RM062X) =  -2320.01579137
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Compound 1: First Excited State.

```
                         Standard orientation:
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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      3          6           0        1.736599   -0.910680    0.091749
      4          6           0        2.513623   -2.089577   -0.101965
      5          6           0        3.877057   -2.045331   -0.106981
      6          1           0        1.979051    1.201536    0.609828
      7          1           0        2.015515   -3.036345   -0.274620
      8          8           0        4.525935   -0.857127    0.044060
      9          6           0        0.315085   -0.997692    0.046313
     10          6           0       -0.626250    0.015848   -0.019158
     11          6           0       -2.048843   -0.177854   -0.018474
     12         16           0       -0.254543    1.735927   -0.182879
     13          6           0       -2.760202    0.990737   -0.123002
     14          6           0       -1.958884    2.161669   -0.216274
     15          1           0       -3.843023    1.031773   -0.132816
     16          1           0       -0.082820   -2.010871    0.032661
     17          6           0       -2.454264    3.464019   -0.313147
     18          6           0       -1.759528    4.673012   -0.395421
     19          1           0       -3.538013    3.544080   -0.322958
     20          6           0       -2.674385   -1.538972    0.093305
     21          1           0       -2.320850   -2.169321   -0.738804
     22          1           0       -2.337091   -2.019978    1.024816
     23          6           0       -0.341497    4.768637   -0.392845
     24          7           0        0.819216    4.851907   -0.390109
     25          6           0       -2.447120    5.960517   -0.485148
     26          8           0       -1.894690    7.043534   -0.559455
     27          8           0       -3.792795    5.844001   -0.478304
     28          1           0       -4.149143    6.747423   -0.538939
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     30         14           0       -5.074803   -2.775302    0.118099
     31          6           0       -4.886190   -3.747060   -1.476130
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     35          6           0       -4.586712   -3.841472    1.585513
     36          1           0       -4.527406   -3.248093    2.504002
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     38          1           0       -3.613478   -4.318463    1.427430
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     40          6           0       -6.941275   -1.379382    1.674346
     41          6           0       -7.066952   -1.027400   -0.800615
     42          6           0       -7.851078   -3.187103    0.196000
     43          1           0       -6.806775   -2.093817    2.494840
     44          1           0       -6.201191   -0.580035    1.795197
     45          1           0       -7.938965   -0.932467    1.783028
     46          1           0       -6.989611   -1.473813   -1.799042
     47          1           0       -8.078356   -0.610079   -0.701277
     48          1           0       -6.353160   -0.198483   -0.744111
     49          1           0       -8.862656   -2.779769    0.327954
     50          1           0       -7.817288   -3.676743   -0.784355
     51          1           0       -7.703952   -3.956239    0.963822
     52          6           0        4.788257   -3.173490   -0.296833
     53          6           0        6.137887   -2.944796   -0.607073
     54          6           0        4.331022   -4.495002   -0.168961
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     57          6           0        5.201485   -5.558708   -0.360083
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     60          1           0        8.043541   -3.825831   -1.040705
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     62          1           0        7.219481   -6.158311   -0.822326
     63          6           0        4.688931    1.460290    0.469502
     64          6           0        6.053946    1.303679    0.755247
     65          6           0        4.152552    2.755126    0.365923
     66          6           0        6.858532    2.419784    0.949465
     67          1           0        6.474300    0.307304    0.840287
     68          6           0        4.963130    3.863634    0.564319
     69          1           0        3.108758    2.905490    0.104830
     70          6           0        6.317602    3.701451    0.858171
     71          1           0        7.911561    2.287942    1.176611
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E(TD-HF/TD-KS) =  -2319.93927608
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Compound 1: Radical-Cation.

```
                         Standard orientation:
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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          6           0       -3.844499    0.307557   -0.323411
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      3          6           0       -1.761967   -0.908539   -0.213348
      4          6           0       -2.526790   -2.078722    0.019185
      5          6           0       -3.893090   -2.011443    0.088762
      6          1           0       -1.992378    1.202245   -0.748441
      7          1           0       -2.032388   -3.027062    0.188082
      8          8           0       -4.510870   -0.824664   -0.053489
      9          6           0       -0.338670   -1.011889   -0.209182
     10          6           0        0.608967    0.001030   -0.134891
     11          6           0        2.017138   -0.223569   -0.145388
     12         16           0        0.262852    1.704529    0.075109
     13          6           0        2.744651    0.945671    0.000564
     14          6           0        1.953456    2.092265    0.131188
     15          1           0        3.827731    0.973318    0.015204
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     19          1           0        3.576066    3.455413    0.313371
     20          6           0        2.646003   -1.580333   -0.298536
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     22          1           0        2.312237   -2.029260   -1.246666
     23          6           0        0.403578    4.703881    0.393401
     24          7           0       -0.752468    4.778623    0.373699
     25          6           0        2.547257    5.886858    0.570840
     26          8           0        1.978262    6.946049    0.681406
     27          8           0        3.874578    5.739312    0.576486
     28          1           0        4.273412    6.622230    0.681552
     29          8           0        4.040339   -1.441273   -0.265091
     30         14           0        5.075781   -2.777760   -0.268082
     31          6           0        4.593929   -3.914577    1.145637
     32          1           0        3.641183   -4.418794    0.952024
     33          1           0        5.351574   -4.693056    1.287251
     34          1           0        4.500872   -3.361580    2.086201
     35          6           0        4.922033   -3.676624   -1.906721
     36          1           0        5.215853   -3.038781   -2.746372
     37          1           0        5.559782   -4.567014   -1.917113
     38          1           0        3.893239   -4.010813   -2.079965
     39          6           0        6.786901   -2.019348   -0.026422
     40          6           0        7.028263   -0.939942   -1.091032
     41          6           0        6.874752   -1.383336    1.368003
     42          6           0        7.858289   -3.111761   -0.158076
     43          1           0        6.978043   -1.351778   -2.105863
     44          1           0        6.291557   -0.132702   -1.016134
     45          1           0        8.026197   -0.499737   -0.961074
     46          1           0        6.749079   -2.129571    2.160917
```

```
     47          1           0        7.857517   -0.912856    1.507334
     48          1           0        6.110558   -0.609585    1.505232
     49          1           0        8.855910   -2.680935    0.001463
     50          1           0        7.722539   -3.909260    0.582259
     51          1           0        7.851679   -3.568965   -1.154478
     52          6           0       -4.814736   -3.119341    0.344774
     53          6           0       -6.114154   -2.858032    0.801288
     54          6           0       -4.401945   -4.442265    0.135009
     55          6           0       -6.983202   -3.911609    1.053637
     56          1           0       -6.433859   -1.835630    0.971723
     57          6           0       -5.278438   -5.489161    0.387273
     58          1           0       -3.410153   -4.656314   -0.249840
     59          6           0       -6.567837   -5.226384    0.848553
     60          1           0       -7.985422   -3.706407    1.414497
     61          1           0       -4.957329   -6.511009    0.216000
     62          1           0       -7.250255   -6.046885    1.045434
     63          6           0       -4.704569    1.479539   -0.486655
     64          6           0       -6.066674    1.319504   -0.775666
     65          6           0       -4.163793    2.766589   -0.352800
     66          6           0       -6.872729    2.438272   -0.941623
     67          1           0       -6.484570    0.324459   -0.886028
     68          6           0       -4.977618    3.878638   -0.519733
     69          1           0       -3.119355    2.908062   -0.090656
     70          6           0       -6.330667    3.716920   -0.816102
     71          1           0       -7.925029    2.312279   -1.172835
     72          1           0       -4.555388    4.871559   -0.407921
     73          1           0       -6.964344    4.588511   -0.945140
 ---------------------------------------------------------------------
E(UM062X) =  -2319.82537035     A.U.
```

Compound 2: Ground State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.426071   -1.571114   -0.022272
      2          6           0        0.711921   -0.328655   -0.025472
      3          6           0       -0.681025   -0.222364   -0.039683
      4         16           0        1.460585    1.238451   -0.010271
      5          6           0       -1.117116    1.104975   -0.038003
      6          6           0       -0.089779    2.040866   -0.023001
      7          1           0       -2.164696    1.384772   -0.046952
      8          1           0        0.799835   -2.459782   -0.030767
      9          6           0       -0.302107    3.444352   -0.018660
     10          6           0        0.596543    4.473113   -0.002133
     11          1           0       -1.350089    3.734676   -0.030105
     12          6           0       -1.607567   -1.410134   -0.052109
     13          6           0        2.010941    4.270792    0.015196
     14          7           0        3.157349    4.097411    0.029225
     15          6           0        0.176179    5.888404   -0.000155
     16          8           0        0.945564    6.823941    0.015778
     17          8           0       -1.158206    6.038083   -0.017922
     18          1           0       -1.339809    6.994649   -0.015071
     19          8           0       -2.941178   -0.957986   -0.087731
     20         14           0       -4.233903   -2.036519   -0.011307
     21          6           0       -5.758459   -0.924935    0.036404
     22          6           0       -5.779506   -0.138449    1.354840
     23          6           0       -5.717196    0.061447   -1.139171
     24          6           0       -7.028140   -1.782392   -0.065349
     25          1           0       -5.854584   -0.804909    2.221817
     26          1           0       -4.876762    0.471860    1.472905
     27          1           0       -6.646140    0.536309    1.378863
     28          1           0       -5.710755   -0.458075   -2.104596
     29          1           0       -6.603676    0.710096   -1.118720
     30          1           0       -4.829465    0.701245   -1.093266
     31          1           0       -7.919832   -1.143425   -0.009092
     32          1           0       -7.072952   -2.329038   -1.014330
     33          1           0       -7.095518   -2.512687    0.750007
     34          1           0       -1.390079   -2.041124   -0.927562
     35          1           0       -1.429915   -2.026374    0.842899
     36          6           0        2.770362   -1.783043   -0.009761
     37          6           0        5.399790   -1.652791    0.015415
     38          6           0        5.124736   -2.964653    0.009282
     39         16           0        3.419890   -3.415068   -0.007517
     40         16           0        4.015137   -0.551172    0.005602
```

```
     41          6           0        6.093490   -4.110816    0.014888
     42          1           0        5.958392   -4.734837   -0.873769
     43          1           0        7.123289   -3.753503    0.027620
     44          1           0        5.939199   -4.742485    0.894972
     45          6           0        6.742121   -0.983506    0.029590
     46          1           0        6.849881   -0.351124    0.916132
     47          1           0        7.546028   -1.719844    0.036322
     48          1           0        6.867229   -0.348235   -0.852590
     49          6           0       -4.074756   -3.074099    1.545733
     50          1           0       -3.893162   -2.444601    2.423049
     51          1           0       -4.992319   -3.645309    1.724776
     52          1           0       -3.252212   -3.792837    1.468171
     53          6           0       -4.219131   -3.143530   -1.526925
     54          1           0       -4.324564   -2.564679   -2.450109
     55          1           0       -3.286261   -3.713942   -1.591336
     56          1           0       -5.041352   -3.865907   -1.483483
 ---------------------------------------------------------------------
E(RM062X) =  -2580.41952258     A.U.
```

Compound 2: First Excited State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.389727   -1.532117   -0.023849
      2          6           0        0.713844   -0.312847   -0.026747
      3          6           0       -0.709313   -0.175246   -0.044129
      4         16           0        1.485606    1.271611   -0.007967
      5          6           0       -1.130702    1.132643   -0.042974
      6          6           0       -0.079211    2.088298   -0.024602
      7          1           0       -2.173851    1.425073   -0.054182
      8          1           0        0.756721   -2.417562   -0.034009
      9          6           0       -0.261717    3.471900   -0.019795
     10          6           0        0.693637    4.495984   -0.001339
     11          1           0       -1.298292    3.796699   -0.031841
     12          6           0       -1.636833   -1.357858   -0.059072
     13          6           0        2.094186    4.265414    0.016025
     14          7           0        3.244376    4.086297    0.030200
     15          6           0        0.318486    5.906457    0.001104
     16          8           0        1.101064    6.841227    0.016851
     17          8           0       -1.019994    6.099903   -0.016201
     18          1           0       -1.158107    7.063035   -0.013037
     19          8           0       -2.970451   -0.914380   -0.094808
     20         14           0       -4.259388   -1.997600   -0.009832
     21          6           0       -5.786752   -0.890529    0.036483
     22          6           0       -5.808223   -0.100396    1.352774
     23          6           0       -5.749423    0.092621   -1.141987
     24          6           0       -7.053972   -1.752106   -0.061321
     25          1           0       -5.880555   -0.764592    2.221733
     26          1           0       -4.907065    0.512771    1.467943
     27          1           0       -6.676649    0.572035    1.375794
     28          1           0       -5.742406   -0.429639   -2.105943
     29          1           0       -6.637903    0.738506   -1.122436
     30          1           0       -4.863649    0.735255   -1.098652
     31          1           0       -7.947409   -1.115607   -0.005307
     32          1           0       -7.098558   -2.301166   -1.008921
     33          1           0       -7.118055   -2.480605    0.755928
     34          1           0       -1.412076   -1.986749   -0.934910
     35          1           0       -1.452373   -1.974345    0.835142
     36          6           0        2.763034   -1.796113   -0.010148
     37          6           0        5.363997   -1.762249    0.015204
     38          6           0        5.031403   -3.074676    0.008910
     39         16           0        3.325952   -3.437114   -0.007570
     40         16           0        4.037902   -0.622532    0.003689
     41          6           0        5.959399   -4.253978    0.017524
     42          1           0        5.772796   -4.895648   -0.848411
     43          1           0        7.000325   -3.933566   -0.013737
     44          1           0        5.810559   -4.853245    0.920547
     45          6           0        6.739154   -1.163399    0.030250
     46          1           0        6.869953   -0.524525    0.908493
     47          1           0        7.503633   -1.939395    0.055673
     48          1           0        6.900794   -0.549372   -0.860589
     49          6           0       -4.090865   -3.026322    1.552038
     50          1           0       -3.905561   -2.391446    2.424697
```

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     51          1           0       -5.007143   -3.597033    1.739104
     52          1           0       -3.268345   -3.745130    1.474659
     53          6           0       -4.243039   -3.111305   -1.520412
     54          1           0       -4.352764   -2.536791   -2.445793
     55          1           0       -3.308117   -3.678446   -1.584418
     56          1           0       -5.062336   -3.836684   -1.472066
 ---------------------------------------------------------------------
E(TD-HF/TD-KS) =  -2580.33519498
```

Compound 2: Radical-Cation.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.434745   -1.526387   -0.045285
      2          6           0        0.729910   -0.317292   -0.043559
      3          6           0       -0.684074   -0.233605   -0.061785
      4         16           0        1.455360    1.268302   -0.018197
      5          6           0       -1.133821    1.081451   -0.057469
      6          6           0       -0.108057    2.025469   -0.035199
      7          1           0       -2.183118    1.350989   -0.069270
      8          1           0        0.826009   -2.427095   -0.066110
      9          6           0       -0.347769    3.438235   -0.028236
     10          6           0        0.546845    4.458820   -0.002524
     11          1           0       -1.397858    3.717051   -0.046100
     12          6           0       -1.600897   -1.425962   -0.077576
     13          6           0        1.964450    4.261601    0.024512
     14          7           0        3.108953    4.085108    0.046112
     15          6           0        0.122246    5.887938    0.000304
     16          8           0        0.904310    6.806908    0.024423
     17          8           0       -1.205582    6.025345   -0.026776
     18          1           0       -1.408498    6.978566   -0.023251
     19          8           0       -2.929251   -0.980886   -0.115080
     20         14           0       -4.224838   -2.064435   -0.002578
     21          6           0       -5.744502   -0.949554    0.044307
     22          6           0       -5.748140   -0.140277    1.349185
     23          6           0       -5.717974    0.015311   -1.149562
     24          6           0       -7.015169   -1.809307   -0.025969
     25          1           0       -5.813200   -0.791237    2.228564
     26          1           0       -4.843862    0.471732    1.445558
     27          1           0       -6.613950    0.535231    1.371615
     28          1           0       -5.723690   -0.521250   -2.105524
     29          1           0       -6.604529    0.663482   -1.129095
     30          1           0       -4.830647    0.657059   -1.126485
     31          1           0       -7.905607   -1.168972    0.030278
     32          1           0       -7.072258   -2.372667   -0.964376
     33          1           0       -7.072234   -2.524587    0.803268
     34          1           0       -1.368548   -2.050683   -0.953697
     35          1           0       -1.410458   -2.036262    0.818993
     36          6           0        2.817292   -1.742757   -0.023340
     37          6           0        5.392648   -1.615272    0.034400
     38          6           0        5.100742   -2.944162    0.011147
     39         16           0        3.424706   -3.350647   -0.029410
     40         16           0        4.039080   -0.536769    0.016769
     41          6           0        6.125805   -4.040936    0.026903
     42          1           0        5.669500   -5.021471   -0.115634
     43          1           0        6.855769   -3.880385   -0.770907
     44          1           0        6.655528   -4.044118    0.984268
     45          6           0        6.778862   -1.042547    0.052883
     46          1           0        6.775691    0.009741    0.341026
     47          1           0        7.398763   -1.593300    0.764851
     48          1           0        7.233761   -1.127335   -0.938925
     49          6           0       -4.031850   -3.066573    1.572237
     50          1           0       -3.832844   -2.418301    2.431920
     51          1           0       -4.946948   -3.631185    1.781912
     52          1           0       -3.213616   -3.790216    1.494695
     53          6           0       -4.215204   -3.193251   -1.500129
     54          1           0       -4.329022   -2.629054   -2.431245
     55          1           0       -3.282193   -3.763748   -1.562331
     56          1           0       -5.035554   -3.916415   -1.439292
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```

```
E(UM062X) =  -2580.22366026     A.U.
```

Compound 3: Ground State.

```
                         Standard orientation:                         
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.925769   -0.944905    0.261375
      2          6           0        1.923397    0.004844    0.398190
      3         16           0        1.575201   -2.548047    0.150145
      4          6           0        3.209647   -0.575905    0.397114
      5          6           0        3.207690   -1.951553    0.265228
      6          1           0        4.122339    0.006035    0.464269
      7          6           0        4.402672   -2.734928    0.229696
      8          6           0        4.562616   -4.078900    0.100391
      9          1           0        5.317668   -2.154693    0.322422
     10          6           0        1.714312    1.495480    0.480880
     11          6           0        3.464826   -4.987564   -0.028644
     12          7           0        2.572131   -5.719066   -0.131938
     13          6           0        5.898194   -4.719873    0.082678
     14          8           0        6.069834   -5.912338   -0.027903
     15          8           0        6.900302   -3.837555    0.201818
     16          1           0        7.733946   -4.340659    0.179960
     17          8           0        2.873811    2.144414    0.006013
     18         14           0        2.966249    3.825584   -0.065986
     19          6           0        4.766248    4.172780   -0.515505
     20          6           0        5.672341    3.805607    0.668150
     21          6           0        5.165513    3.332655   -1.736784
     22          6           0        4.938127    5.662531   -0.845460
     23          1           0        5.455321    4.420481    1.549195
     24          1           0        5.556256    2.753125    0.952043
     25          1           0        6.726101    3.966419    0.402382
     26          1           0        4.543327    3.564287   -2.609394
     27          1           0        6.209387    3.537986   -2.010996
     28          1           0        5.073560    2.260989   -1.531113
     29          1           0        5.990533    5.879400   -1.073444
     30          1           0        4.343618    5.954889   -1.718614
     31          1           0        4.644916    6.304434   -0.005835
     32          1           0        0.829402    1.775670   -0.109146
     33          1           0        1.519695    1.793299    1.522219
     34          6           0       -0.524459   -0.747416    0.198444
     35          6           0       -1.331030   -1.547293   -0.626088
     36          6           0       -1.153454    0.241112    0.969903
     37          6           0       -2.701070   -1.358456   -0.693243
     38          1           0       -0.873336   -2.307060   -1.253688
     39          6           0       -2.525385    0.430776    0.915925
     40          1           0       -0.568973    0.841662    1.659998
     41          6           0       -3.323552   -0.362656    0.077423
     42          1           0       -3.298253   -1.974997   -1.356369
     43          1           0       -2.989120    1.188983    1.537712
     44          7           0       -4.711628   -0.167362    0.012081
     45          6           0       -5.583155   -1.259161   -0.248861
     46          6           0       -6.639823   -1.109742   -1.152527
     47          6           0       -5.402127   -2.482572    0.404461
     48          6           0       -7.505371   -2.171734   -1.393928
     49          1           0       -6.777079   -0.158945   -1.658479
     50          6           0       -6.261190   -3.545121    0.142966
     51          1           0       -4.587226   -2.593881    1.113395
     52          6           0       -7.318471   -3.395157   -0.752870
     53          1           0       -8.322674   -2.043741   -2.096791
     54          1           0       -6.109985   -4.490526    0.654540
     55          1           0       -7.991157   -4.223720   -0.948538
     56          6           0       -5.270770    1.124691    0.202414
     57          6           0       -4.691321    2.245276   -0.402367
     58          6           0       -6.418959    1.281374    0.985417
     59          6           0       -5.247659    3.505774   -0.210886
     60          1           0       -3.806256    2.121520   -1.019036
     61          6           0       -6.979507    2.543079    1.155948
     62          1           0       -6.866821    0.410293    1.453875
     63          6           0       -6.395403    3.661866    0.564535
     64          1           0       -4.788057    4.367932   -0.684102
```

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     65          1           0       -7.871511    2.651557    1.765030
     66          1           0       -6.831167    4.645531    0.705215
     67          6           0        2.512934    4.538197    1.611434
     68          1           0        1.442082    4.434249    1.816014
     69          1           0        3.061919    4.037416    2.415806
     70          1           0        2.753185    5.606308    1.654541
     71          6           0        1.783804    4.463395   -1.376720
     72          1           0        2.059032    4.107788   -2.374841
     73          1           0        0.757045    4.139781   -1.174785
     74          1           0        1.784185    5.558586   -1.394529
 ---------------------------------------------------------------------
E(RM062X) =  -2300.17371142     A.U.
```

Compound 3: First Excited State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.797953    0.864027   -0.000994
      2          6           0       -1.918820   -0.020630    0.098354
      3         16           0       -1.360879    2.537309   -0.144039
      4          6           0       -3.128739    0.635088    0.064069
      5          6           0       -3.042983    2.047078   -0.062855
      6          1           0       -4.080942    0.121732    0.116251
      7          6           0       -4.145173    2.900988   -0.117365
      8          6           0       -4.188293    4.296482   -0.236267
      9          1           0       -5.110220    2.405643   -0.058968
     10          6           0       -1.848652   -1.524089    0.193785
     11          6           0       -3.030560    5.113552   -0.314177
     12          7           0       -2.088265    5.794062   -0.377223
     13          6           0       -5.446841    5.031769   -0.284527
     14          8           0       -5.551543    6.242676   -0.384284
     15          8           0       -6.534245    4.230222   -0.206489
     16          1           0       -7.309515    4.816652   -0.246296
     17          8           0       -3.143833   -2.062787    0.096727
     18         14           0       -3.413082   -3.723320    0.206764
     19          6           0       -5.293079   -3.882601    0.214813
     20          6           0       -5.852874   -3.279557    1.511071
     21          6           0       -5.880859   -3.129659   -0.987110
     22          6           0       -5.688276   -5.363771    0.128933
     23          1           0       -5.496721   -3.820390    2.395463
     24          1           0       -5.568368   -2.226580    1.619425
     25          1           0       -6.950167   -3.332191    1.509527
     26          1           0       -5.512292   -3.532514   -1.937842
     27          1           0       -6.975565   -3.222072   -0.991040
     28          1           0       -5.631967   -2.063665   -0.952060
     29          1           0       -6.781507   -5.464726    0.163174
     30          1           0       -5.343467   -5.821624   -0.805366
     31          1           0       -5.278370   -5.945815    0.963156
     32          1           0       -1.205189   -1.914422   -0.609238
     33          1           0       -1.390660   -1.812895    1.152717
     34          6           0        0.592186    0.610750   -0.007353
     35          6           0        1.525493    1.664653   -0.289491
     36          6           0        1.166000   -0.671864    0.274549
     37          6           0        2.877933    1.463402   -0.296449
     38          1           0        1.155990    2.652754   -0.543509
     39          6           0        2.518464   -0.881158    0.261615
     40          1           0        0.534982   -1.503844    0.553282
     41          6           0        3.421309    0.179731   -0.023890
     42          1           0        3.543567    2.282104   -0.545905
     43          1           0        2.912109   -1.859046    0.515353
     44          7           0        4.782220   -0.029224   -0.025009
     45          6           0        5.682335    1.031069    0.275173
     46          6           0        6.829582    1.208907   -0.505471
     47          6           0        5.426351    1.879083    1.358488
     48          6           0        7.711121    2.239221   -0.202339
     49          1           0        7.015055    0.546949   -1.345372
     50          6           0        6.312648    2.909853    1.647086
     51          1           0        4.545162    1.716324    1.971196
     52          6           0        7.455830    3.093965    0.870167
     53          1           0        8.596860    2.380223   -0.812914
     54          1           0        6.114524    3.562835    2.490639
     55          1           0        8.146587    3.898016    1.101013
     56          6           0        5.326717   -1.308948   -0.321439
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     57          6           0        4.821563   -2.054911   -1.392437
     58          6           0        6.380541   -1.808630    0.451927
     59          6           0        5.364572   -3.302647   -1.675698
     60          1           0        4.020874   -1.646268   -2.001058
     61          6           0        6.918823   -3.054106    0.153922
     62          1           0        6.760933   -1.222695    1.282500
     63          6           0        6.412828   -3.806357   -0.906410
     64          1           0        4.975068   -3.876414   -2.510144
     65          1           0        7.731533   -3.442304    0.758929
     66          1           0        6.836046   -4.779010   -1.133890
     67          6           0       -2.646263   -4.363497    1.796825
     68          1           0       -1.552347   -4.366351    1.743312
     69          1           0       -2.942160   -3.749769    2.654034
     70          1           0       -2.967167   -5.392552    1.992612
     71          6           0       -2.640022   -4.582281   -1.272187
     72          1           0       -3.087489   -4.245748   -2.212861
     73          1           0       -1.562819   -4.390151   -1.323350
     74          1           0       -2.775341   -5.666888   -1.200771
 ---------------------------------------------------------------------
E(TD-HF/TD-KS) =  -2300.07905494
```

Compound 3: Radical-Cation.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.868945   -0.932596    0.206689
      2          6           0        1.883486    0.004093    0.339982
      3         16           0        1.491000   -2.546760    0.070216
      4          6           0        3.157925   -0.600968    0.321433
      5          6           0        3.124909   -1.975192    0.186217
      6          1           0        4.080716   -0.036223    0.387404
      7          6           0        4.310364   -2.786667    0.158314
      8          6           0        4.433632   -4.130680    0.036854
      9          1           0        5.237018   -2.225646    0.249667
     10          6           0        1.720088    1.501336    0.433476
     11          6           0        3.311534   -5.011274   -0.091420
     12          7           0        2.396370   -5.713616   -0.194554
     13          6           0        5.756507   -4.810063    0.026252
     14          8           0        5.888250   -6.006182   -0.080019
     15          8           0        6.776259   -3.953044    0.146386
     16          1           0        7.600981   -4.471576    0.129962
     17          8           0        2.915642    2.111005    0.012969
     18         14           0        3.094685    3.790511    0.006290
     19          6           0        4.921345    4.056197   -0.381717
     20          6           0        5.772705    3.603047    0.812886
     21          6           0        5.312250    3.238182   -1.620706
     22          6           0        5.177685    5.545578   -0.654444
     23          1           0        5.561942    4.198618    1.708510
     24          1           0        5.595704    2.548971    1.056857
     25          1           0        6.840266    3.718108    0.581314
     26          1           0        4.727550    3.530302   -2.501008
     27          1           0        6.372237    3.399817   -1.859436
     28          1           0        5.162306    2.165988   -1.455423
     29          1           0        6.245920    5.714941   -0.845289
     30          1           0        4.625020    5.897244   -1.533171
     31          1           0        4.892875    6.173347    0.198612
     32          1           0        0.869257    1.821851   -0.185594
     33          1           0        1.496085    1.785265    1.473306
     34          6           0       -0.570894   -0.715926    0.153241
     35          6           0       -1.401337   -1.574572   -0.598912
     36          6           0       -1.169039    0.346671    0.861538
     37          6           0       -2.763342   -1.381731   -0.652563
     38          1           0       -0.961194   -2.377565   -1.181112
     39          6           0       -2.530026    0.559323    0.809395
     40          1           0       -0.567102    0.976595    1.505732
     41          6           0       -3.347629   -0.304404    0.049626
     42          1           0       -3.381973   -2.021463   -1.271768
     43          1           0       -2.980971    1.352267    1.395278
     44          7           0       -4.721654   -0.099541   -0.001629
     45          6           0       -5.605476   -1.194909   -0.140361
```

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     46          6           0       -6.726812   -1.074052   -0.975192
     47          6           0       -5.358161   -2.381300    0.567066
     48          6           0       -7.589998   -2.151004   -1.106213
     49          1           0       -6.890739   -0.156348   -1.530014
     50          6           0       -6.235563   -3.446337    0.428235
     51          1           0       -4.507628   -2.444467    1.237713
     52          6           0       -7.348182   -3.335537   -0.407300
     53          1           0       -8.449320   -2.070537   -1.762508
     54          1           0       -6.058235   -4.360535    0.983563
     55          1           0       -8.030011   -4.172599   -0.512073
     56          6           0       -5.255365    1.207153    0.085611
     57          6           0       -4.621903    2.262899   -0.587686
     58          6           0       -6.420900    1.426765    0.835329
     59          6           0       -5.158686    3.538752   -0.500574
     60          1           0       -3.743272    2.068189   -1.193712
     61          6           0       -6.939989    2.709841    0.916001
     62          1           0       -6.885154    0.602098    1.365575
     63          6           0       -6.313290    3.765409    0.250348
     64          1           0       -4.682847    4.356101   -1.030777
     65          1           0       -7.830916    2.889827    1.507188
     66          1           0       -6.727382    4.765872    0.314657
     67          6           0        2.627353    4.457244    1.697814
     68          1           0        1.547365    4.399340    1.870011
     69          1           0        3.129271    3.900184    2.495873
     70          1           0        2.917568    5.509769    1.789301
     71          6           0        1.980352    4.527698   -1.310992
     72          1           0        2.263411    4.189975   -2.313080
     73          1           0        0.933368    4.251902   -1.144779
     74          1           0        2.037151    5.621402   -1.293060
 ---------------------------------------------------------------------
E(UM062X) =  -2299.97188393     A.U.
```

Compound 15: Ground State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -4.674455   -0.199336   -0.213047
      2          6           0       -3.371845    0.145756   -0.103460
      3          6           0       -2.358469   -0.833897    0.216520
      4          6           0       -2.860025   -2.189491    0.290046
      5          6           0       -4.172128   -2.470769    0.144806
      6          1           0       -3.115398    1.173603   -0.311376
      7          1           0       -2.169309   -2.996929    0.503332
      8          8           0       -5.089269   -1.483297   -0.067510
      9          6           0       -1.025346   -0.584664    0.436844
     10          6           0       -0.327588    0.661524    0.508944
     11          6           0        1.062806    0.779645    0.639258
     12         16           0       -1.076809    2.230274    0.519961
     13          6           0        1.489688    2.106787    0.730148
     14          6           0        0.460695    3.041331    0.678921
     15          1           0        2.532553    2.388729    0.827819
     16          1           0       -0.399430   -1.457907    0.604113
     17          6           0        0.653298    4.443379    0.738410
     18          6           0       -0.261379    5.460233    0.685483
     19          1           0        1.691989    4.748655    0.841677
     20          6           0        1.990786   -0.405955    0.662887
     21          1           0        1.726059   -1.082151    1.488292
     22          1           0        1.873825   -0.982036   -0.268853
     23          6           0       -1.666299    5.237443    0.550598
     24          7           0       -2.805033    5.045577    0.441233
     25          6           0        0.132001    6.879588    0.762047
     26          8           0       -0.649314    7.804939    0.716882
     27          8           0        1.458718    7.049753    0.888374
     28          1           0        1.621270    8.008733    0.930596
     29          8           0        3.322510    0.038854    0.826444
     30         14           0        4.603130   -0.785269    0.124669
     31          6           0        6.147076   -0.007454    0.881498
     32          6           0        6.110975    1.505497    0.617994
     33          6           0        6.175894   -0.259069    2.395497
     34          6           0        7.406070   -0.608839    0.241765
```

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     35          1           0        6.077334    1.727825   -0.455012
     36          1           0        5.239447    1.972140    1.090128
     37          1           0        7.011901    1.979426    1.030421
     38          1           0        6.255398   -1.327335    2.625638
     39          1           0        7.046039    0.243128    2.839418
     40          1           0        5.276997    0.131294    2.886086
     41          1           0        8.302781   -0.192962    0.720279
     42          1           0        7.442686   -1.699095    0.359740
     43          1           0        7.465491   -0.377760   -0.827593
     44          6           0       -4.796211   -3.802431    0.222542
     45          6           0       -6.163276   -3.921379    0.502257
     46          6           0       -4.034809   -4.960255    0.018535
     47          6           0       -6.752130   -5.178550    0.591471
     48          1           0       -6.758821   -3.028571    0.659111
     49          6           0       -4.628029   -6.213471    0.110494
     50          1           0       -2.982389   -4.883190   -0.235251
     51          6           0       -5.987623   -6.327061    0.398774
     52          1           0       -7.811132   -5.259757    0.814217
     53          1           0       -4.029212   -7.103311   -0.054160
     54          1           0       -6.449338   -7.306844    0.466883
     55          6           0       -5.781096    0.723115   -0.518910
     56          6           0       -6.988919    0.227869   -1.025500
     57          6           0       -5.636669    2.101120   -0.308495
     58          6           0       -8.028056    1.100584   -1.331463
     59          1           0       -7.105546   -0.838174   -1.188407
     60          6           0       -6.676998    2.967894   -0.619394
     61          1           0       -4.721110    2.500849    0.117334
     62          6           0       -7.874809    2.471023   -1.132543
     63          1           0       -8.958536    0.708322   -1.728951
     64          1           0       -6.554051    4.032699   -0.450010
     65          1           0       -8.687261    3.149920   -1.370980
     66          6           0        4.523765   -0.496270   -1.729396
     67          6           0        5.398512   -1.113805   -2.639369
     68          6           0        3.582547    0.411280   -2.240370
     69          6           0        5.327710   -0.846002   -4.004569
     70          1           0        6.154020   -1.811751   -2.284214
     71          6           0        3.505870    0.682160   -3.605387
     72          1           0        2.901350    0.920070   -1.560483
     73          6           0        4.377670    0.051138   -4.489821
     74          1           0        6.013993   -1.335514   -4.688846
     75          1           0        2.767820    1.386282   -3.977519
     76          1           0        4.320221    0.260183   -5.553700
     77          6           0        4.397509   -2.601592    0.559971
     78          6           0        4.028100   -2.934287    1.875356
     79          6           0        4.568574   -3.649074   -0.356049
     80          6           0        3.852055   -4.259660    2.263953
     81          1           0        3.868084   -2.143541    2.606399
     82          6           0        4.398413   -4.978629    0.027632
     83          1           0        4.823782   -3.430547   -1.389568
     84          6           0        4.042588   -5.285314    1.338818
     85          1           0        3.564764   -4.493006    3.284704
     86          1           0        4.537296   -5.773661   -0.698711
     87          1           0        3.906982   -6.320140    1.638361
 ---------------------------------------------------------------------
 E(RM062X) =  -2703.34040424     A.U.
```

Compound 15: First Excited State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -4.657042   -0.232123   -0.342067
      2          6           0       -3.336126    0.095355   -0.239489
      3          6           0       -2.369149   -0.875053    0.141789
      4          6           0       -2.856000   -2.203534    0.313153
      5          6           0       -4.180371   -2.494992    0.167142
      6          1           0       -3.047749    1.101264   -0.508830
      7          1           0       -2.169237   -2.993493    0.593252
      8          8           0       -5.071864   -1.507508   -0.125210
      9          6           0       -0.983697   -0.610758    0.344922
     10          6           0       -0.330364    0.603043    0.476173
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   11          6           0        1.088030    0.762265    0.632787
   12         16           0       -1.124174    2.180280    0.546638
   13          6           0        1.478185    2.069640    0.782790
   14          6           0        0.410140    3.008574    0.758307
   15          1           0        2.510386    2.374497    0.911219
   16          1           0       -0.356751   -1.495247    0.440763
   17          6           0        0.561640    4.391669    0.881409
   18          6           0       -0.408219    5.395553    0.846092
   19          1           0        1.584238    4.731384    1.021575
   20          6           0        2.030711   -0.406727    0.614450
   21          1           0        1.754762   -1.124475    1.400927
   22          1           0        1.927586   -0.936529   -0.346550
   23          6           0       -1.793723    5.145407    0.649971
   24          7           0       -2.928795    4.947328    0.487690
   25          6           0       -0.068487    6.809508    0.999885
   26          8           0       -0.868638    7.727191    0.970570
   27          8           0        1.253142    7.019530    1.183610
   28          1           0        1.370686    7.981422    1.272807
   29          8           0        3.353762    0.038014    0.818894
   30         14           0        4.649253   -0.752233    0.101830
   31          6           0        6.180161    0.008609    0.899886
   32          6           0        6.139076    1.529086    0.684359
   33          6           0        6.197049   -0.291719    2.405128
   34          6           0        7.447422   -0.566319    0.251827
   35          1           0        6.116806    1.785309   -0.381323
   36          1           0        5.259946    1.976762    1.160695
   37          1           0        7.032907    1.993614    1.122087
   38          1           0        6.280119   -1.366472    2.601377
   39          1           0        7.060881    0.200005    2.872408
   40          1           0        5.292189    0.078361    2.900407
   41          1           0        8.338037   -0.160276    0.749698
   42          1           0        7.489342   -1.659417    0.336913
   43          1           0        7.513617   -0.302555   -0.809578
   44          6           0       -4.811481   -3.804426    0.326235
   45          6           0       -6.203652   -3.900126    0.478362
   46          6           0       -4.040847   -4.978418    0.328790
   47          6           0       -6.805799   -5.142024    0.641695
   48          1           0       -6.807016   -2.999276    0.482420
   49          6           0       -4.649936   -6.214620    0.493030
   50          1           0       -2.967186   -4.930714    0.179907
   51          6           0       -6.033675   -6.302092    0.651503
   52          1           0       -7.882261   -5.202966    0.764495
   53          1           0       -4.043798   -7.114556    0.488369
   54          1           0       -6.506580   -7.270625    0.777665
   55          6           0       -5.738198    0.682697   -0.698825
   56          6           0       -6.976677    0.181201   -1.128693
   57          6           0       -5.552174    2.072872   -0.610860
   58          6           0       -7.999477    1.054468   -1.478336
   59          1           0       -7.125878   -0.890625   -1.201596
   60          6           0       -6.578784    2.937235   -0.964065
   61          1           0       -4.617385    2.485171   -0.242164
   62          6           0       -7.804739    2.432763   -1.400200
   63          1           0       -8.951175    0.657397   -1.816297
   64          1           0       -6.423808    4.008526   -0.887139
   65          1           0       -8.606144    3.111944   -1.672422
   66          6           0        4.585305   -0.396098   -1.740535
   67          6           0        5.462378   -0.985725   -2.666476
   68          6           0        3.656117    0.539226   -2.222904
   69          6           0        5.404680   -0.665080   -4.020875
   70          1           0        6.209904   -1.702344   -2.332165
   71          6           0        3.592875    0.862984   -3.577057
   72          1           0        2.975298    1.028819   -1.528455
   73          6           0        4.466065    0.258327   -4.478414
   74          1           0        6.092389   -1.133734   -4.718191
   75          1           0        2.864495    1.588054   -3.927380
   76          1           0        4.419023    0.508668   -5.533867
   77          6           0        4.445971   -2.582722    0.474078
   78          6           0        4.065244   -2.957813    1.774801
   79          6           0        4.626695   -3.600131   -0.473441
   80          6           0        3.888083   -4.295123    2.119402
   81          1           0        3.897004   -2.191056    2.529220
   82          6           0        4.455305   -4.941462   -0.133819
   83          1           0        4.890514   -3.348682   -1.497227
   84          6           0        4.088529   -5.290406    1.163739
   85          1           0        3.592239   -4.561275    3.129629
   86          1           0        4.601776   -5.712692   -0.883943
   87          1           0        3.952161   -6.334482    1.428821
```

```
 ---------------------------------------------------------------------
E(TD-HF/TD-KS) =  -2703.26408981
```

Compound 15: Radical-Cation.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -4.680240   -0.209540   -0.353717
      2          6           0       -3.356279    0.131598   -0.266250
      3          6           0       -2.393995   -0.841930    0.094933
      4          6           0       -2.858511   -2.169215    0.270433
      5          6           0       -4.191086   -2.459835    0.145926
      6          1           0       -3.079784    1.139695   -0.536399
      7          1           0       -2.166602   -2.955180    0.545356
      8          8           0       -5.064432   -1.476263   -0.136246
      9          6           0       -1.003378   -0.581370    0.282807
     10          6           0       -0.347503    0.635671    0.414654
     11          6           0        1.065155    0.761705    0.568813
     12         16           0       -1.114833    2.206936    0.494279
     13          6           0        1.468328    2.076800    0.728599
     14          6           0        0.414589    2.998283    0.709902
     15          1           0        2.503416    2.370763    0.857006
     16          1           0       -0.376732   -1.464816    0.371671
     17          6           0        0.601681    4.407760    0.849526
     18          6           0       -0.329372    5.399743    0.824722
     19          1           0        1.633511    4.718008    0.990449
     20          6           0        2.009429   -0.406821    0.543133
     21          1           0        1.728047   -1.131070    1.321408
     22          1           0        1.912010   -0.922993   -0.425317
     23          6           0       -1.728913    5.162203    0.640627
     24          7           0       -2.858301    4.952658    0.489339
     25          6           0        0.035408    6.835253    0.983119
     26          8           0       -0.776594    7.728478    0.959325
     27          8           0        1.348318    7.013131    1.151929
     28          1           0        1.510655    7.969327    1.247656
     29          8           0        3.321413    0.051453    0.758341
     30         14           0        4.640879   -0.770032    0.108349
     31          6           0        6.144875    0.016207    0.929457
     32          6           0        6.109656    1.529775    0.668474
     33          6           0        6.120732   -0.240640    2.442691
     34          6           0        7.429424   -0.576364    0.332510
     35          1           0        6.113515    1.755456   -0.404270
     36          1           0        5.220252    1.991567    1.111290
     37          1           0        6.992969    2.006241    1.114181
     38          1           0        6.200908   -1.308888    2.672186
     39          1           0        6.970652    0.266671    2.918335
     40          1           0        5.202435    0.141604    2.903065
     41          1           0        8.305656   -0.153573    0.841447
     42          1           0        7.470379   -1.666147    0.452334
     43          1           0        7.523621   -0.344874   -0.734251
     44          6           0       -4.824020   -3.767671    0.319492
     45          6           0       -6.200179   -3.851709    0.574342
     46          6           0       -4.057719   -4.938224    0.232225
     47          6           0       -6.796167   -5.093951    0.749662
     48          1           0       -6.793812   -2.947215    0.649908
     49          6           0       -4.662582   -6.175899    0.405830
     50          1           0       -2.998311   -4.888375    0.003498
     51          6           0       -6.030196   -6.255910    0.666723
     52          1           0       -7.859523   -5.155082    0.954411
     53          1           0       -4.067471   -7.079387    0.329848
     54          1           0       -6.499370   -7.224829    0.802568
     55          6           0       -5.780597    0.692785   -0.692381
     56          6           0       -6.994191    0.174706   -1.165714
     57          6           0       -5.621063    2.078172   -0.544382
     58          6           0       -8.030167    1.037986   -1.498235
     59          1           0       -7.115525   -0.896343   -1.286957
     60          6           0       -6.662920    2.933010   -0.877893
     61          1           0       -4.700595    2.492582   -0.144613
     62          6           0       -7.866293    2.415493   -1.356566
     63          1           0       -8.965503    0.635727   -1.872062
```

```
     64          1           0       -6.537340    4.003340   -0.755179
     65          1           0       -8.678521    3.086590   -1.615982
     66          6           0        4.627967   -0.469252   -1.743989
     67          6           0        5.523704   -1.097553   -2.625706
     68          6           0        3.725196    0.461367   -2.281859
     69          6           0        5.508342   -0.818287   -3.990270
     70          1           0        6.252620   -1.811912   -2.248332
     71          6           0        3.703823    0.743819   -3.646368
     72          1           0        3.032678    0.982276   -1.622940
     73          6           0        4.594604    0.101059   -4.502935
     74          1           0        6.209894   -1.315901   -4.652694
     75          1           0        2.995385    1.466486   -4.039728
     76          1           0        4.580899    0.319027   -5.566408
     77          6           0        4.407075   -2.583802    0.533088
     78          6           0        4.004093   -2.918006    1.838396
     79          6           0        4.585209   -3.628445   -0.384959
     80          6           0        3.802553   -4.242942    2.215614
     81          1           0        3.838775   -2.129721    2.571015
     82          6           0        4.389954   -4.957497   -0.011943
     83          1           0        4.866551   -3.408248   -1.411190
     84          6           0        4.001046   -5.266070    1.289319
     85          1           0        3.490521   -4.477920    3.228629
     86          1           0        4.535793   -5.750580   -0.738923
     87          1           0        3.846632   -6.300609    1.580389
 ---------------------------------------------------------------------
 E(UM062X) =  -2703.14956783     A.U.
```

Compound 16: Ground State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        5.284291    0.427806    0.107187
      2          6           0        3.936706    0.325973    0.071430
      3          6           0        3.284547   -0.934926   -0.202134
      4          6           0        4.198478   -2.051184   -0.320348
      5          6           0        5.535988   -1.885508   -0.248561
      6          1           0        3.369544    1.215398    0.301262
      7          1           0        3.800042   -3.041684   -0.506181
      8          8           0        6.088585   -0.650496   -0.073035
      9          6           0        1.933977   -1.139129   -0.343967
     10          6           0        0.861497   -0.194476   -0.352412
     11          6           0       -0.487941   -0.544564   -0.436346
     12         16           0        1.034191    1.532919   -0.325271
     13          6           0       -1.357867    0.547280   -0.467461
     14          6           0       -0.696152    1.779125   -0.413192
     15          1           0        1.608612   -2.166310   -0.490497
     16          6           0       -1.332998    3.041165   -0.422101
     17          6           0       -0.799624    4.302648   -0.365171
     18          1           0       -2.418427    3.008366   -0.484981
     19          6           0       -2.857477    0.405040   -0.527060
     20          6           0        0.603178    4.557978   -0.280325
     21          7           0        1.743379    4.760865   -0.212909
     22          6           0       -1.641297    5.512591   -0.390584
     23          8           0       -1.208725    6.644004   -0.344361
     24          8           0       -2.954700    5.237840   -0.471472
     25          1           0       -3.423962    6.090722   -0.484249
     26          8           0       -3.197523   -0.953141   -0.693495
     27         14           0       -4.671345   -1.554852   -0.157432
     28          6           0       -4.625847   -3.383058   -0.628326
     29          6           0       -4.226830   -3.573025   -2.099748
     30          6           0       -3.561371   -4.066797    0.247722
     31          6           0       -5.988726   -4.033948   -0.351913
     32          1           0       -4.947252   -3.132248   -2.795828
     33          1           0       -3.248360   -3.126298   -2.303426
     34          1           0       -4.164082   -4.645333   -2.328960
     35          1           0       -3.816457   -4.015464    1.311401
     36          1           0       -3.480604   -5.126174   -0.030088
     37          1           0       -2.573935   -3.609423    0.113138
     38          1           0       -5.937355   -5.111606   -0.556449
     39          1           0       -6.285205   -3.910435    0.697088
```

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     40          1           0       -6.783419   -3.612933   -0.976993
     41          6           0        6.557754   -2.938647   -0.375447
     42          6           0        7.870535   -2.602705   -0.729277
     43          6           0        6.232049   -4.281260   -0.144950
     44          6           0        8.834521   -3.596502   -0.865005
     45          1           0        8.129575   -1.564580   -0.907019
     46          6           0        7.198724   -5.269928   -0.283635
     47          1           0        5.228452   -4.553714    0.165767
     48          6           0        8.502181   -4.931411   -0.645599
     49          1           0        9.847510   -3.325940   -1.145006
     50          1           0        6.936025   -6.306282   -0.097921
     51          1           0        9.256117   -5.705033   -0.750154
     52          6           0        6.043252    1.663877    0.363086
     53          6           0        7.371411    1.594414    0.801123
     54          6           0        5.445911    2.917417    0.174282
     55          6           0        8.082954    2.761038    1.061432
     56          1           0        7.838419    0.626354    0.947152
     57          6           0        6.160661    4.078915    0.439588
     58          1           0        4.429073    2.992479   -0.199322
     59          6           0        7.480165    4.004640    0.884825
     60          1           0        9.110001    2.697231    1.406048
     61          1           0        5.687653    5.043752    0.288005
     62          1           0        8.037448    4.913493    1.087954
     63          1           0       -0.823173   -1.573710   -0.478926
     64          1           0       -3.264322    0.995913   -1.358582
     65          1           0       -3.288474    0.809298    0.402375
     66          6           0       -4.694040   -1.333841    1.707077
     67          6           0       -5.889196   -1.320212    2.441401
     68          6           0       -3.484296   -1.237125    2.412706
     69          6           0       -5.879023   -1.221350    3.831484
     70          1           0       -6.843738   -1.377682    1.921085
     71          6           0       -3.467325   -1.130648    3.801678
     72          1           0       -2.542052   -1.242509    1.865529
     73          6           0       -4.666621   -1.125342    4.512276
     74          1           0       -6.814558   -1.213688    4.382542
     75          1           0       -2.521709   -1.051188    4.329448
     76          1           0       -4.656397   -1.043363    5.594956
     77          6           0       -6.084910   -0.547661   -0.883574
     78          6           0       -6.794996   -0.921073   -2.035503
     79          6           0       -6.423407    0.676303   -0.280529
     80          6           0       -7.799288   -0.111915   -2.562654
     81          1           0       -6.571717   -1.859432   -2.534653
     82          6           0       -7.421226    1.494166   -0.805730
     83          1           0       -5.907651    0.993770    0.623830
     84          6           0       -8.112510    1.098950   -1.948997
     85          1           0       -8.336845   -0.427034   -3.451730
     86          1           0       -7.662235    2.435120   -0.320642
     87          1           0       -8.894388    1.731109   -2.358790
 ---------------------------------------------------------------------
E(RM062X) =  -2703.33896712     A.U.
```

Compound 16: First Excited State.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        5.282313    0.409001    0.220923
      2          6           0        3.925573    0.267248    0.196362
      3          6           0        3.325920   -0.984220   -0.117837
      4          6           0        4.225869   -2.072918   -0.310418
      5          6           0        5.576127   -1.894163   -0.244172
      6          1           0        3.328137    1.123601    0.474081
      7          1           0        3.833405   -3.055525   -0.543023
      8          8           0        6.093138   -0.655839   -0.011779
      9          6           0        1.926762   -1.210394   -0.240231
     10          6           0        0.887654   -0.295902   -0.318258
     11          6           0       -0.492240   -0.643953   -0.408367
     12         16           0        1.066908    1.458407   -0.393468
     13          6           0       -1.343768    0.425810   -0.517443
     14          6           0       -0.670682    1.689505   -0.519506
     15          1           0        1.623122   -2.253036   -0.312955
```

```
     16          6           0       -1.298749    2.933307   -0.605734
     17          6           0       -0.736228    4.213289   -0.596141
     18          1           0       -2.381839    2.910956   -0.691448
     19          6           0       -2.838417    0.312890   -0.620010
     20          6           0        0.657046    4.464412   -0.473696
     21          7           0        1.795878    4.680910   -0.371590
     22          6           0       -1.555361    5.419471   -0.703046
     23          8           0       -1.125275    6.559009   -0.699051
     24          8           0       -2.876042    5.155137   -0.810489
     25          1           0       -3.325986    6.015532   -0.875322
     26          8           0       -3.209949   -1.047614   -0.626451
     27         14           0       -4.701216   -1.553095   -0.044465
     28          6           0       -4.666554   -3.430141   -0.255113
     29          6           0       -4.232974   -3.826373   -1.674810
     30          6           0       -3.632328   -3.994466    0.734892
     31          6           0       -6.043048   -4.026129    0.072991
     32          1           0       -4.929409   -3.479308   -2.444450
     33          1           0       -3.243720   -3.421732   -1.911934
     34          1           0       -4.178764   -4.920694   -1.751749
     35          1           0       -3.913056   -3.793773    1.774143
     36          1           0       -3.557377   -5.082825    0.608775
     37          1           0       -2.636465   -3.568360    0.564316
     38          1           0       -5.997719   -5.122266    0.024646
     39          1           0       -6.365501   -3.753219    1.085465
     40          1           0       -6.816709   -3.692905   -0.626972
     41          6           0        6.605242   -2.915841   -0.433978
     42          6           0        7.938408   -2.538251   -0.658432
     43          6           0        6.278522   -4.281063   -0.394398
     44          6           0        8.917022   -3.506495   -0.849657
     45          1           0        8.200238   -1.486760   -0.696004
     46          6           0        7.261507   -5.241571   -0.587299
     47          1           0        5.260652   -4.596783   -0.190902
     48          6           0        8.583832   -4.859211   -0.816825
     49          1           0        9.943332   -3.202310   -1.027730
     50          1           0        6.996827   -6.293173   -0.549765
     51          1           0        9.350140   -5.613167   -0.964954
     52          6           0        6.007490    1.644913    0.506086
     53          6           0        7.364705    1.602561    0.860868
     54          6           0        5.356682    2.887665    0.424610
     55          6           0        8.049067    2.778488    1.143621
     56          1           0        7.872479    0.646621    0.928949
     57          6           0        6.047643    4.056668    0.711018
     58          1           0        4.317918    2.950978    0.113875
     59          6           0        7.394565    4.007369    1.072671
     60          1           0        9.096516    2.734745    1.423806
     61          1           0        5.534219    5.010099    0.640477
     62          1           0        7.932238    4.923887    1.293040
     63          1           0       -0.827063   -1.675041   -0.392823
     64          1           0       -3.193398    0.803173   -1.538032
     65          1           0       -3.296921    0.847587    0.227933
     66          6           0       -4.761408   -1.075695    1.770438
     67          6           0       -5.970803   -0.951933    2.470239
     68          6           0       -3.564982   -0.892832    2.481667
     69          6           0       -5.987182   -0.664263    3.833878
     70          1           0       -6.915260   -1.071791    1.942167
     71          6           0       -3.574487   -0.597657    3.843082
     72          1           0       -2.612511   -0.979127    1.959440
     73          6           0       -4.787665   -0.486154    4.520801
     74          1           0       -6.933378   -0.573667    4.358782
     75          1           0       -2.638821   -0.454222    4.375067
     76          1           0       -4.798145   -0.257386    5.582217
     77          6           0       -6.088119   -0.648165   -0.937261
     78          6           0       -6.773627   -1.175892   -2.042640
     79          6           0       -6.427628    0.651417   -0.522467
     80          6           0       -7.755326   -0.442382   -2.705431
     81          1           0       -6.547837   -2.177085   -2.397698
     82          6           0       -7.403033    1.393829   -1.184345
     83          1           0       -5.930134    1.090269    0.340451
     84          6           0       -8.069949    0.845665   -2.277919
     85          1           0       -8.273824   -0.876429   -3.554858
     86          1           0       -7.645395    2.396034   -0.844226
     87          1           0       -8.833979    1.419320   -2.793779
 ---------------------------------------------------------------------
E(TD-HF/TD-KS) =  -2703.26276188
```

Compound 16: Radical-Cation.

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        5.329078    0.405998    0.207354
      2          6           0        3.963247    0.300673    0.207992
      3          6           0        3.346578   -0.945772   -0.060415
      4          6           0        4.204065   -2.058860   -0.246372
      5          6           0        5.563929   -1.901975   -0.208743
      6          1           0        3.393785    1.179561    0.470161
      7          1           0        3.787109   -3.035584   -0.455845
      8          8           0        6.087880   -0.679523   -0.007771
      9          6           0        1.939181   -1.158160   -0.148537
     10          6           0        0.906447   -0.229033   -0.211102
     11          6           0       -0.461378   -0.591893   -0.279425
     12         16           0        1.076423    1.507687   -0.281820
     13          6           0       -1.322534    0.486086   -0.370692
     14          6           0       -0.644348    1.723004   -0.382485
     15          1           0        1.621376   -2.195882   -0.206227
     16          6           0       -1.297518    2.988316   -0.464733
     17          6           0       -0.753355    4.237258   -0.469952
     18          1           0       -2.381708    2.951015   -0.530146
     19          6           0       -2.821293    0.346697   -0.439948
     20          6           0        0.652889    4.488979   -0.388842
     21          7           0        1.793785    4.679953   -0.322496
     22          6           0       -1.591715    5.465017   -0.559913
     23          8           0       -1.129781    6.580542   -0.566033
     24          8           0       -2.896817    5.188889   -0.632206
     25          1           0       -3.378268    6.034116   -0.691435
     26          8           0       -3.148745   -1.019876   -0.462697
     27         14           0       -4.693872   -1.556931   -0.055825
     28          6           0       -4.600488   -3.427964   -0.285130
     29          6           0       -4.021578   -3.797269   -1.659538
     30          6           0       -3.660130   -3.988296    0.796544
     31          6           0       -5.992991   -4.049237   -0.102667
     32          1           0       -4.643969   -3.450601   -2.490252
     33          1           0       -3.020255   -3.374710   -1.792406
     34          1           0       -3.941667   -4.889312   -1.743694
     35          1           0       -4.046012   -3.806119    1.804984
     36          1           0       -3.554886   -5.073442    0.665905
     37          1           0       -2.659356   -3.544816    0.730625
     38          1           0       -5.924559   -5.143552   -0.160040
     39          1           0       -6.418977   -3.795519    0.875873
     40          1           0       -6.698501   -3.718296   -0.872131
     41          6           0        6.573385   -2.944376   -0.397336
     42          6           0        7.886316   -2.593906   -0.742833
     43          6           0        6.231577   -4.293996   -0.233394
     44          6           0        8.839935   -3.586061   -0.930908
     45          1           0        8.151351   -1.550926   -0.877734
     46          6           0        7.192158   -5.278879   -0.420672
     47          1           0        5.227669   -4.577005    0.065386
     48          6           0        8.495457   -4.927552   -0.771291
     49          1           0        9.852817   -3.311916   -1.205439
     50          1           0        6.925338   -6.321342   -0.285293
     51          1           0        9.243450   -5.699964   -0.917159
     52          6           0        6.099652    1.626499    0.446387
     53          6           0        7.441119    1.542787    0.844883
     54          6           0        5.496571    2.881419    0.279096
     55          6           0        8.163822    2.704339    1.084894
     56          1           0        7.906458    0.572539    0.981366
     57          6           0        6.227532    4.036957    0.520143
     58          1           0        4.469766    2.963948   -0.063742
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     61          1           0        5.758414    5.005281    0.383368
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     66          6           0       -4.955368   -1.097749    1.744864
     67          6           0       -6.236634   -0.964157    2.300035
     68          6           0       -3.848079   -0.936503    2.592629
     69          6           0       -6.408350   -0.686781    3.654944
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     70          1           0       -7.114407   -1.068995    1.664897
     71          6           0       -4.012590   -0.651638    3.946225
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     73          6           0       -5.295182   -0.529040    4.478524
     74          1           0       -7.408108   -0.588729    4.066794
     75          1           0       -3.143875   -0.525498    4.585248
     76          1           0       -5.426679   -0.308380    5.533464
     77          6           0       -5.973172   -0.648110   -1.090134
     78          6           0       -6.543902   -1.172080   -2.260603
     79          6           0       -6.347516    0.652729   -0.709855
     80          6           0       -7.449056   -0.432848   -3.019034
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     82          6           0       -7.246416    1.400357   -1.466883
     83          1           0       -5.940739    1.087879    0.201282
     84          6           0       -7.799904    0.856194   -2.623952
     85          1           0       -7.880422   -0.863654   -3.917315
     86          1           0       -7.518930    2.402789   -1.151325
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