Supporting Information

Linker effect in organic donor-acceptor dyes on p-type NiO dye sensitized solar cells

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General information

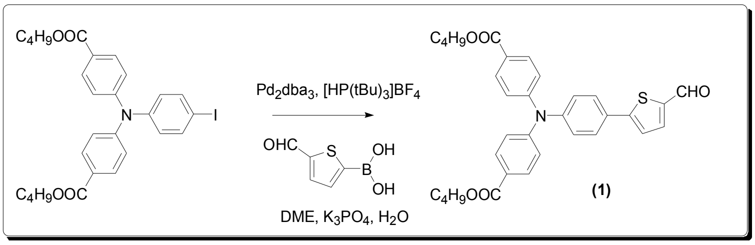
All reagents and solvents (analytical grade) were purchased from Fisher Scientific Company and used without further purification. The silica gel (60-200 μm) was purchased from Fisher Scientific. All products were characterized by ^1H NMR, ^{13}C NMR, and high resolution mass spectrometry (HRMS). All NMR spectra were obtained using a Bruker 250 or 400 MHz spectrometer. HRMS was conducted on a Bruker Daltonics BioTOF system with electrospray ionization (ESI) source. N,N-Di(4-benzoic acid tert-butyl ester)-4-iodo-phenylamine,[1] N,N-Di(4-benzoic acid tert-butyl ester)-4-(4,4,5,5,-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenylamine,[1] 4-[Bis-(4-bromo-phenyl)-amino]-benzoic acid,[2] 2-bromo-3,4-ethylenedioxy-5-aldhydethiophene[3] were prepared following the literature procedure and obtained with satisfactory purity. The absorption spectra were measured by Lamda 950 spectrophotometer (Perkin-Elmer). The emission spectra were obtained with Fluoromax 4 spectrofluorometer (Jobin yvon). Cyclic voltammetry and squarewave voltammetry was measured using a CV50W electrochemical workstation. The electrochemical cell consisted of a Pt working electrode, a Ag wire as reference electrode, and a Pt wire auxiliary electrode in a single compartment. $(TBA)ClO_4$ (recrystallized in EtOH twice before use, 0.1 M) in degassed dry DMF was used. The Scan rate is 100 mV/s. The ferrocenium-ferrocene ($Fc^{+/0}$) was used as internal reference, and all potentials were reported relative to NHE using Fc^+/Fc couple (0.64 versus NHE) as reference.

Solar cell fabrication and measurement

The NiO paste was prepared using polymer template methods adopted from literature.[4] Double layer NiO film was deposited on FTO with modification from Sun's method.[5] The thickness of the final NiO film is about 600 nm. The film area is proximately 0.7×0.7 cm^2. The film was soaked in dye solution (0.3 mM in CH_3CN) for 16 hrs. After washed with CH_3CN, and dried under air, the NiO electrode and platinized counter electrode was sealed by placing surlyn 60 film (Solaronix) in between. A CH_3CN electrolyte solution of 1.0 M LiI and 0.1 M I_2 was filled through the holes predrilled on the counter electrode by applying vaccum. The holes were sealed afterward with glass cover slide. The *J-V* curve was measured under 1 Sun AM 1.5G simulated sunlight (Small-Area Class-B Solar Simulator, PV Measurements) with a mask (0.225 cm^2) and recorded with a CV-50W voltammetric analyzer. The IPCE spectra were recorded by the QEX7 quantum efficiency measurement system from PVmeasurement using silicon diode as reference cell. The electrochemical impedance spectra were measured by an EIS600 potentionstat (Gamry Instruments, Warminster, PA) in the frequency range of 3×10^5 to 0.1 Hz at open circuit condition under 1 Sun illumination. The AC amplitude is 10 mV. Density functional theory (DFT) calculations were performed at the Ohio Supercomputer Center with Gaussian 03[6] at the B3LYP/6-31+G(d) level. The frontier molecular orbitals of the dyes O2, O6 and O7 are shown in Figure S4.

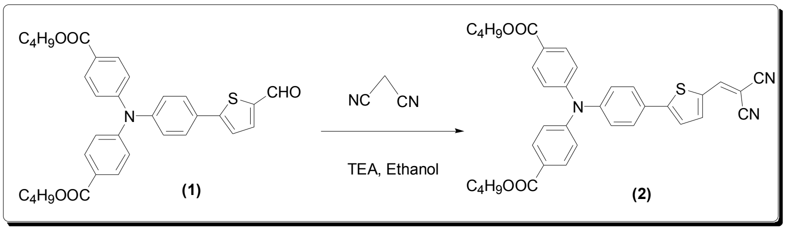
Synthesis

Compound 1



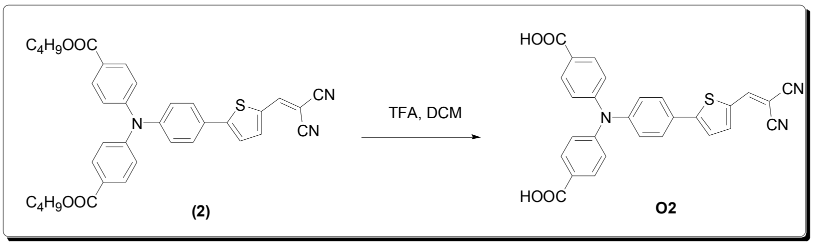
N,N-Di(4-benzoic acid tert-butyl ester)-4-iodo-phenylamine (114.3 mg, 0.2 mmol), 5-formyl-2-thiophene boronic acid (38 mg, 0.24 mmol), Pd_2dba (6 mg, 0.01 mmol), $HP(tBu)_3BF_4$ (6 mg, 0.02 mmol), and K_3PO_4 (0.5 mL, 1 M) were added in 2 mL DME. The mixture was stirred at room temperature under Ar for 24 hrs. After poured in 20 mL H_2O, the mixture was extracted by CH_2Cl_2, and dried under Na_2SO_4. The crude product was purified on Silica gel column using $CHCl_3$ and MeOH (1%) as eluent to give yellow oil (108 mg, 97%). ^{1}H NMR (CD_3COCD_3, 250 M Hz): δ 1.58 (18H, s), 7.65 (6H, m), 7.65 (1H, d, *J* = 4.8 Hz), 7.82 (2H, d, *J* = 9.8 Hz), 7.95 (5 H, m), 9.94 (1H, s) ppm. ESI_Mass (m/z): $[M+Na]^+$ = 578.2.

Compound 2



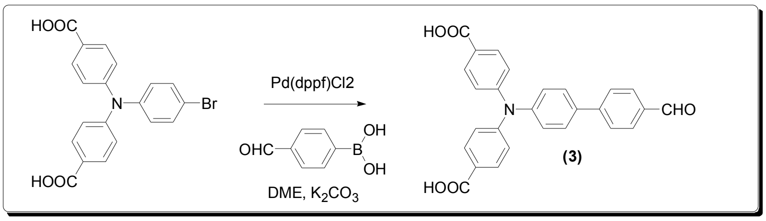
Compound 1 (118.5 mg, 0.21 mmol) and malonitrile (42 mg, 0.63 mg) were added in 50 mL ethanol. 10 drops of TEA was added. The mixture was heated at reflux under Ar. for 5 hrs. After the mixture was poured into water, it was extracted with $CHCl_3$ and dried under Na_2SO_4. The crude product was purified on Silica gel column using $CHCl_3$ and EtOAc (2%) as eluent to give red solid 85.5 mg (67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.59 (18H, s), 7.13 (6H, m), 7.39 (1H, d, *J* = 4.4 Hz), 7.61 (2H, d, *J* = 10.4 Hz), 7.71 (1H, d, *J* = 7.2 Hz), 7.78 (H, s), 97.91 (4H, m) ppm. ESI_Mass (m/z): $[M+Na]^+$ = 626.2.

O2



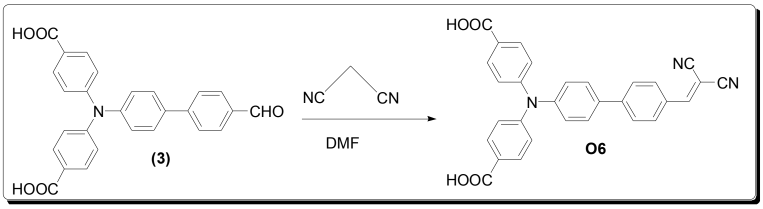
Compound 2 (72 mg, 0.12 mmol) was dissolved in CH_2Cl_2 5 mL and TFA (0.5 mL) was added. The mixture was stirred at r.t. for 5 hrs. After reaction, solvent was removed to give red solid, which was dried under vaccum for overnight. (50 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (6H, m), 7.76 (1H, d), 7.88 (2H, d, *J* = 12 Hz), 8.03 (5H, m), 8.42 (1 H, s), 97.91 (4H, m) ppm. ^{13}C NMR (CD_3COCD_3, 100 MHz): δ 75.5, 113.6, 114.3, 122.7, 123.5, 124.9, 125.6, 127.8, 128.4, 131.1, 134.2, 141.6, 147.9, 150.4, 151.5, 155.0, 166.1 ppm. ESI_Mass (m/z): $[M-H]^-$ = 490.1.

Compound 3



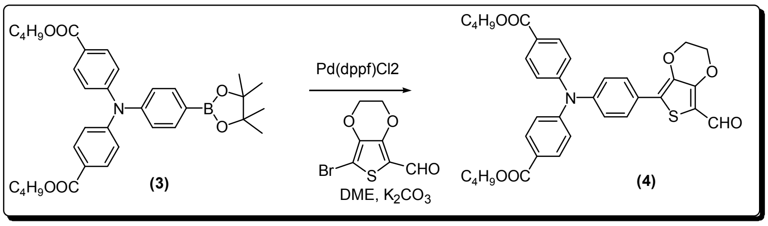
4-[Bis-(4-bromo-phenyl)-amino]-benzoic acid (206.1 mg, 0.5 mmol), 4-aldehyde-phenylbronic acid (90.0 mg, 0.6 mmol) were added to 15 mL DME. Pd(dppf)Cl_2 (40 mg, 0.05 mmol) and 3 mL 1 M K_2CO_3 aq. were added. The mixture was heated to reflux under Ar. for 17 hrs. Solvent was removed, and water (20 mL) was added. The pH was adjusted to about pH 7. The mixture was extracted by EtOAc. The organic phase was combined. The pure product was obtained by silica gel column eluted by CH_2Cl_2/HOAc (20/1, v/v) to give yellow solid 212 mg (97%). ^{1}H NMR (CD_3COCD_3, 250 MHz): δ 7.23 (4H, d, *J* = 10 Hz), 7.33 (2H, d, *J* = 6.3 Hz), 7.85 (2H, d, *J* = 13 Hz), 7.80 (8 H, m), 10.10 (1H, s) ppm. ESI_Mass (m/z): $[M+Na]^+$ = 460.1.

O6



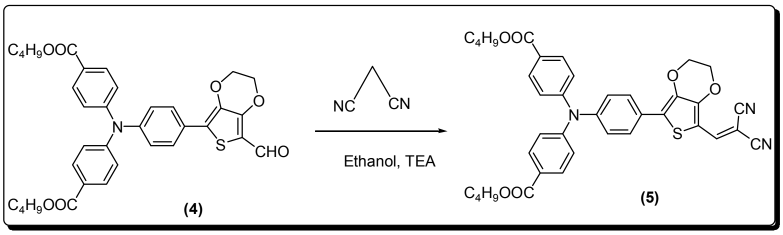
Compound 3 (43 mg, 0.1 mmol) and malonitrile (33 mg, 0.5 mmol) were added to 5 mL DMF. The mixture was heated at 85 C for 5 hrs. Solvent was removed. The crude product was purified on silica gel column eluted by solvent gradient from EtOAc to EtOAc/MeOH (200/1, v/v) to give 40 mg orange solid (82%). ^{1}H NMR (CD_3COCD_3, 250 MHz): δ 7.22 (4H, d, *J* = 8.5 Hz), 7.32 (2H, d, *J* = 8.5 Hz), 7.87 (2H, d, *J* = 9 Hz), 8.00 (6 H, m), 8.15 (2H, d, *J* = 8.5 Hz), 8.34 (1H, s) ppm. ^{13}C NMR (CD_3COCD_3, 100 M Hz): δ 81.3, 113.2, 114.1, 123.1, 125.1, 126.1, 126.2, 127.4, 128.6, 130.5, 131.6, 135.1, 145.6, 147.6, 150.8, 159.9, 1, 166.1 ppm. ESI_Mass (m/z): $(M-1)^-$= 484.1.

Compound 4



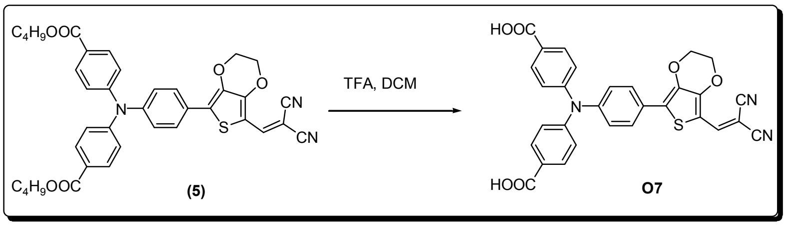
N,N-di(4-benzoic acid tert-butyl ester)-4-(4,4,5,5,-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenylamine (174 mg, 0.3 mmol) and 2-bromo,3,4-diethyleneoxy-thiophneylaldhdyde (82.2 mg, 0.33 mmol), Pd(dppf)$_2$ (30 mg) were added into 10 mL DME. 2 mL 1 M K_2CO_3 were added. The mixture was heated to reflux under Ar overnight. The mixture was extracted with EtOAc. The combined organic phase was dried on Na_2SO_4. The filtrate was evaporated. The residue was purified on Silica gel column eluted with Hexane/EtOAc (v/v, 2/1). The solvent was removed to give yellow solid (150 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 M Hz): δ 1.58 (18 H), 4.40 (4H, m) 7.16 (6H, m), 7.76 (2H, d, J = 12.5 Hz), 7.94 (4H, d, J = 7.5 Hz), 9.98 (1H, s) ppm. ESI_Mass (m/z): $[M+Na]^+$ = 636.2.

Compound 5



Compound 4 (123 mg, 0.20 mmol) and malonitrile (42 mg, 0.63 mmol) were added into ethanol (50 mL). 10 drop TEA was added. The mixture was heated at reflux for 6 hrs. The solvent was removed. The residue was purified on silica gel column eluted by 20/1 DCM/EtOAc to collect the red color band to give pure product 125 mg (94%). ^{1}H NMR ($CDCl_3$, 250 M Hz): δ 1.58 (18 H), 4.42 (4H, m) 7.11 (6H, m), 7.75 (2H, d, *J* = 10.0 Hz), 7.89 (5H, m) ppm. ESI_Mass (m/z): $[M+Na]^+$ = 684.2.

O7



Compound 5 (20 mg) was added in 20 mL DCM and 0.4 mL TFA was added. The mixture was stirred at r.t. overnight. Solvent was removed. The residue was loaded on silica gel column eluted by EtOAc/CH_2Cl_2 (1/20, v/v), then EtOAc/HOAc (20/1). The red band was collected. The solvent was removed to give pure red solid. (70%) ^{1}H NMR (d_6-DMSO, 250 MHz): δ 4.50 (4H, m) 7.19 (6H, m), 7.85 (2H, d, *J* = 7.5 Hz), 7.94 (4H, m), 8.02 (1H, s) ppm. ^{13}C NMR (d_6-DMSO, 100 MHz): δ 65.1, 66.3, 69.7, 109.2, 115.1, 115.7, 123.9, 124.5, 126.0, 128.7, 131.5, 138.4, 145.2, 148.0, 149.9, 151.0, 168.8 ppm. ESI_Mass (m/z): $[M+Na]^+$ = 548.1.

Table S1. Electrochemical data of O2, O6, and O7 dyes.

Dyes	**E_{-red}(V)**	**E_{ox} (V)/**	**E_{00}(ev)**	**$E^{*/-1}$(V)**
O2	-0.78	1.40, 1.88	2.19	1.41
O6	-0.62	1.44	2.18	1.56
O7	-0.84	1.35, 1.80	2.15	1.31

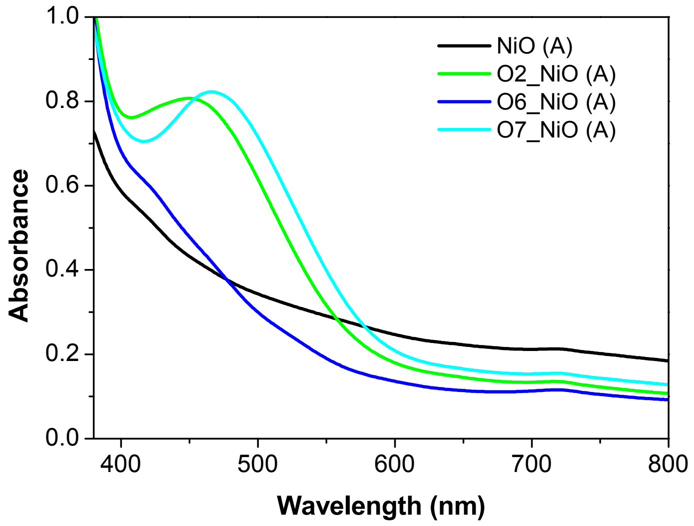


Figure S1. The absorption spectra of dye sensitized NiO film.

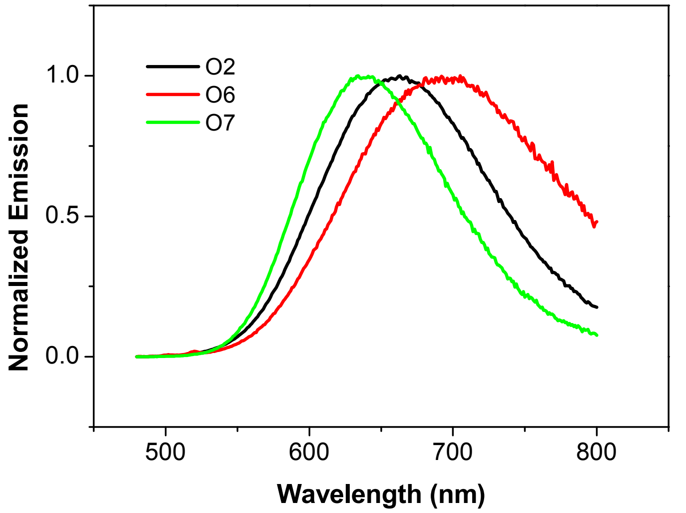
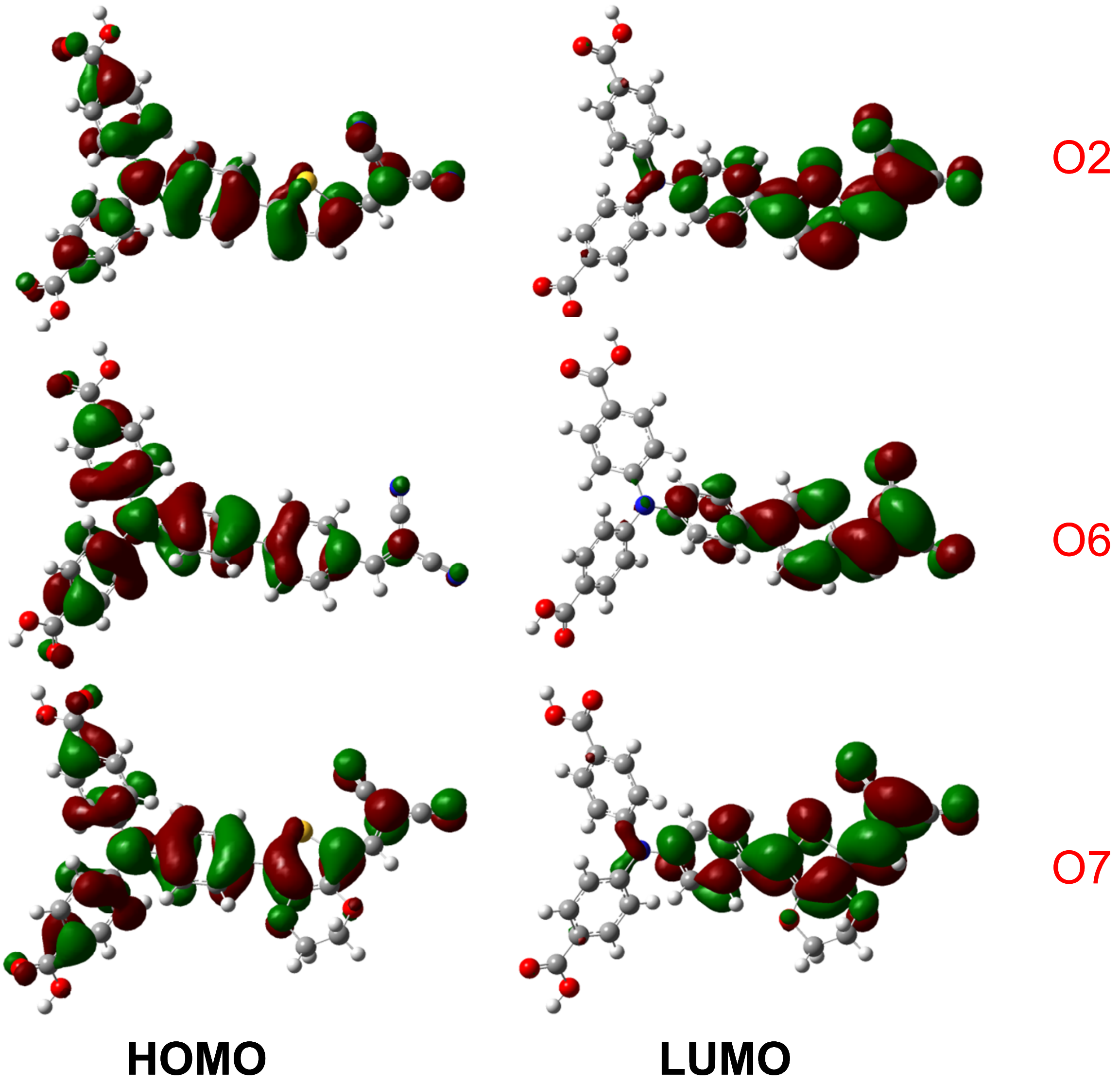


Figure S2. The room temperature emission spectra of dyes in CH_3CN.



	O2	O6	O7
HOMO	-6.06	-6.10	-5.92
LUMO	-3.41	-3.34	-3.25

FigureS3. Frontier orbital configuration and calculated HOMO and LUMO energy level (relative to vaccum) of O2, O6, and O7.

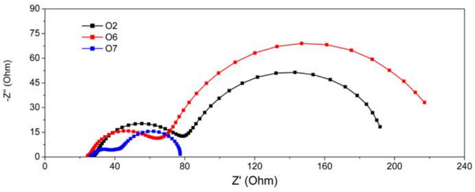


Figure S4. Electrochemical impedance spectra of DSCs made of O2, O6, and O7.

References

[1] J. Cremer, *PhD thesis, Univ. Ulm*, 2005.

[2] J. Seok, S. Park, M. E. El-Khouly, Y. Araki, O. Ito, and K. Kay, *J. Organomet. Chem.*, 2009, **694**, 1818.

[3] M. Jessing, M. Brandt, K. J. Jensen, J. B. Christensen, and U. Boas, *J. Org. Chem.*, **71**, 6734.

[4] S. Sumikura, S. Mori, S. Shimizu, H. Usami, and E. Suzuki, *J. Photochem. Photobiol., A*, 2008, **199**, 1.

[5] L. Li, E. A. Gibson, P. Qin, G. Boschloo, M. Gorlov, A. Hagfeldt, and L. Sun, *Adv. Mater.* , **22**, 1759.

[6] M. J. G. Frisch, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

Figure S5. ^{1}H NMR spectrum of O2.

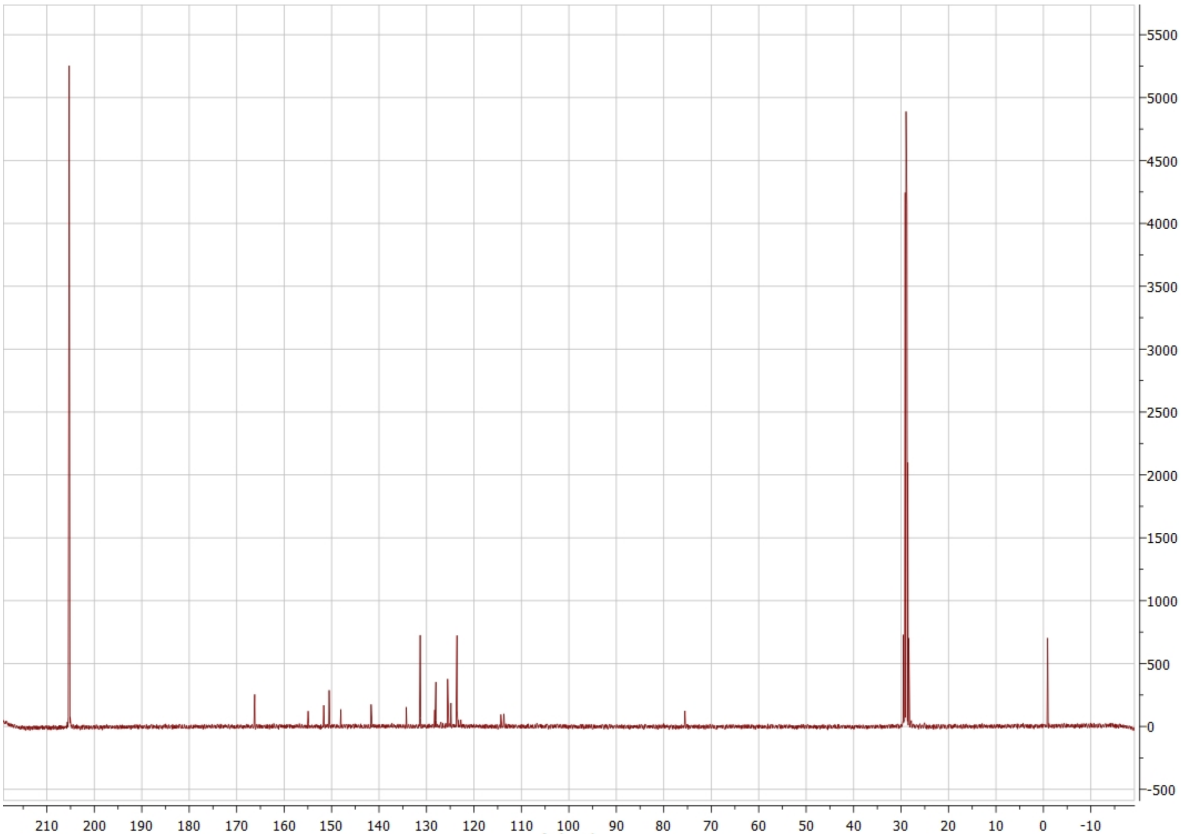


Figure S6. ^{13}C NMR spectrum of O2.

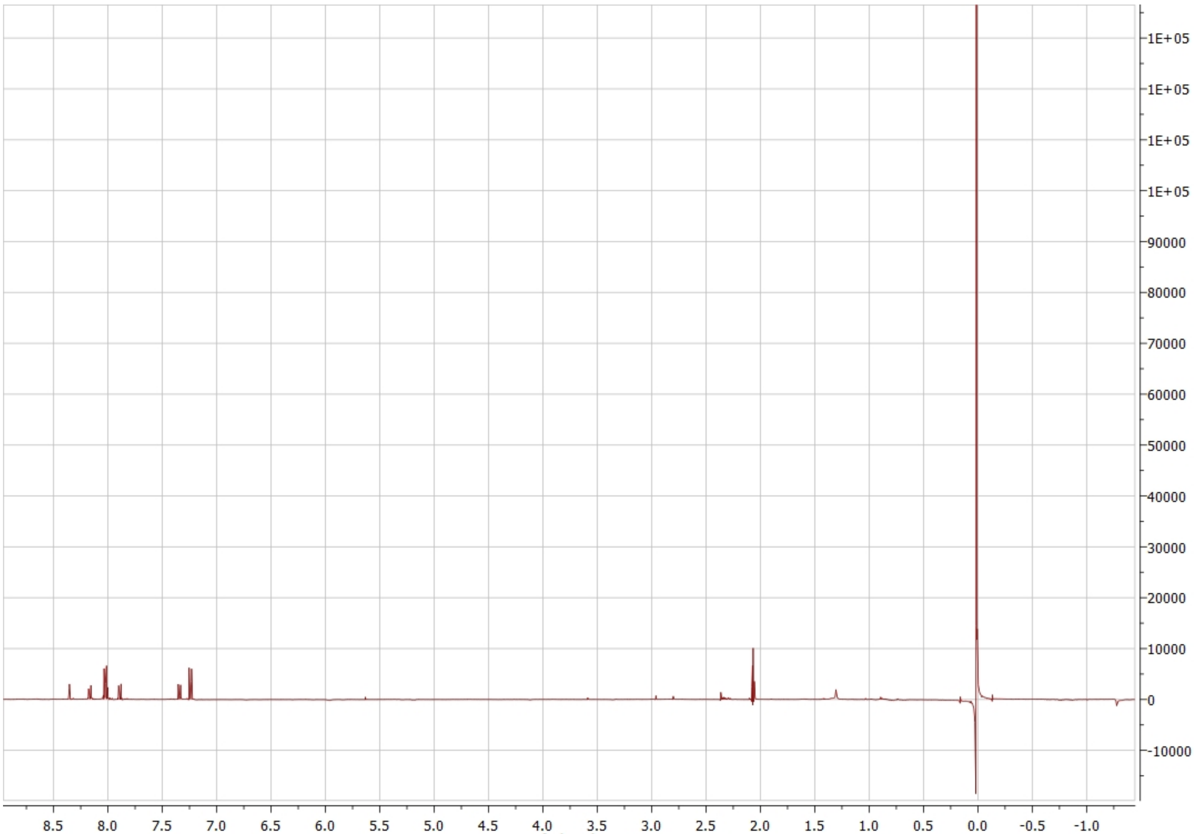


Figure S7. ^{1}H NMR Spectrum of O6.

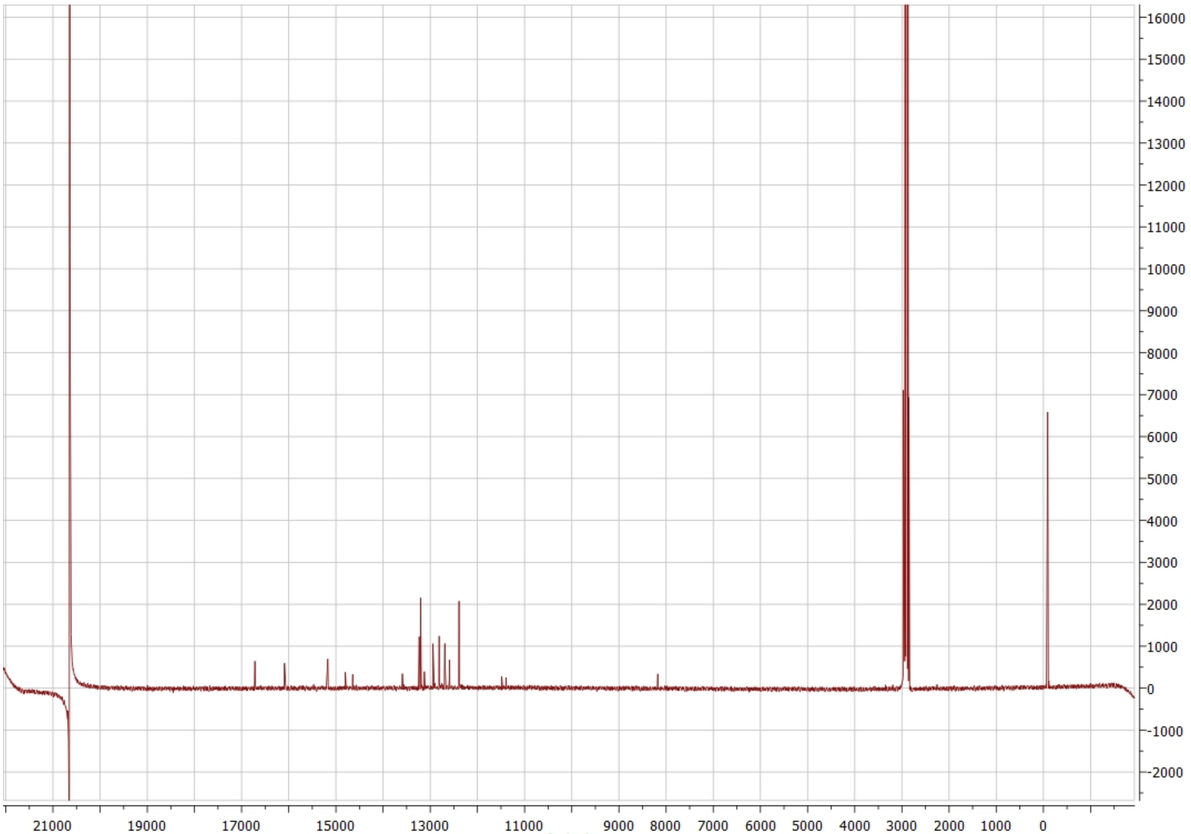


Figure S8. ^{13}C NMR spectrum of O6.

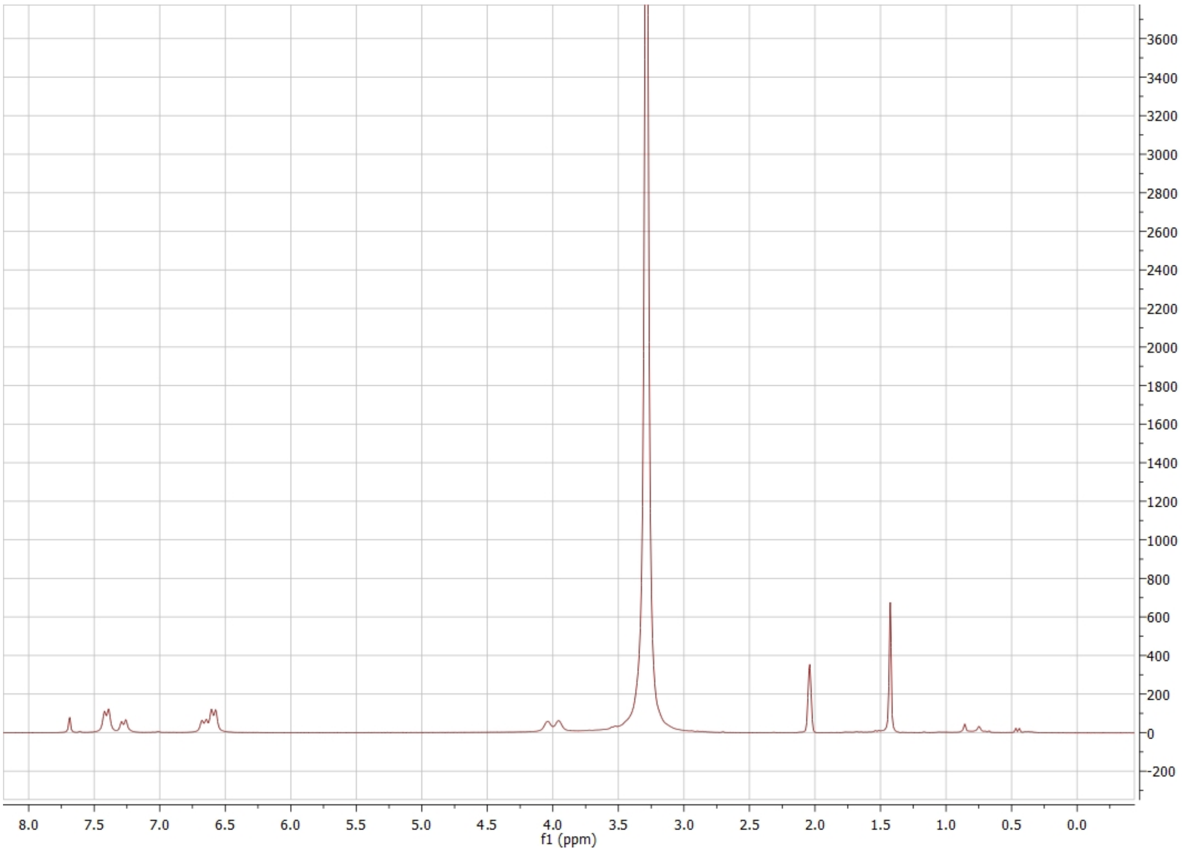


Figure S9. ^{1}H NMR spectrum of O7.

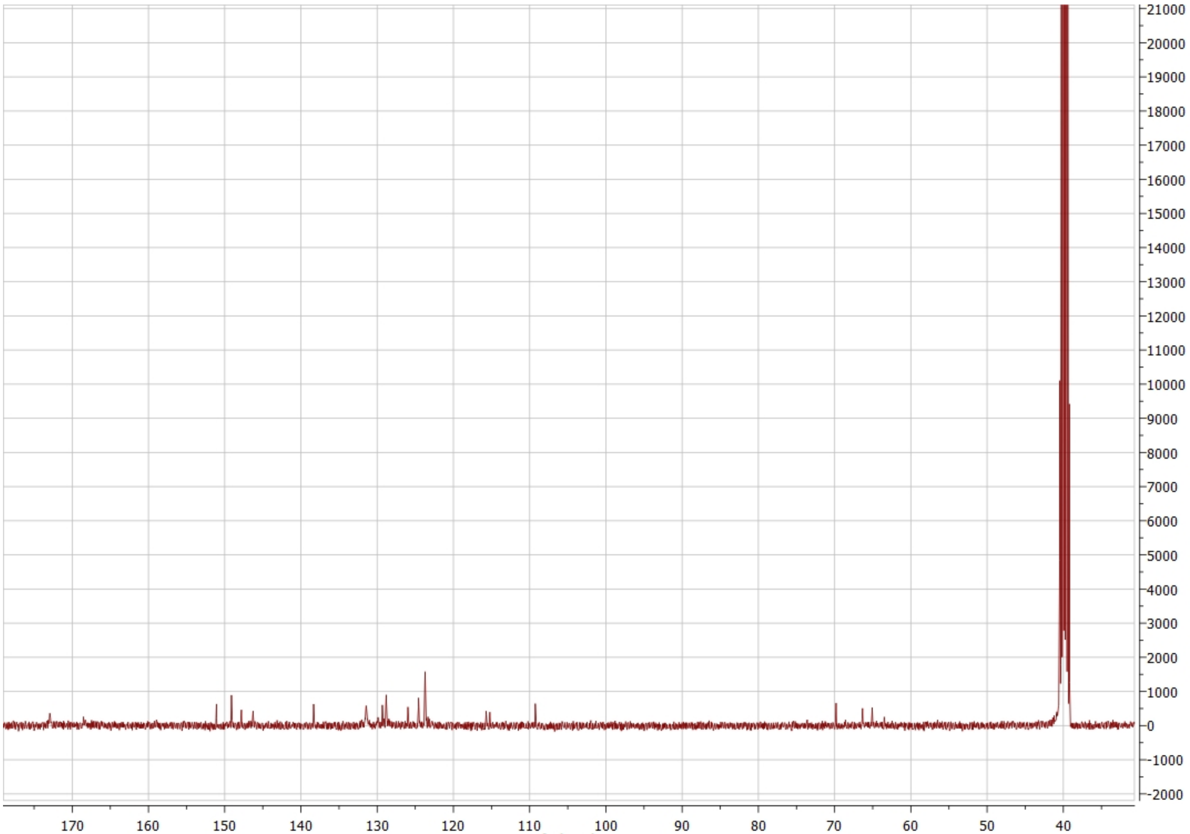


Figure S10. ^{13}C NMR spectrum of O7.