Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Low-polarity small organic molecule with stable keto form for photocatalytic H_2 evolution

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Experimental Details

Materials:

All chemicals were commercially available and used without further purification. Triformylphloroglucinol, and 4-Aminobenzonitrile were purchased from Alpha chemicals. 4-amino-3-methoxybenzonitrile, 4-amino-3-methylbenzonitrile, 4-amino-3-hydroxybenzonitrile, and 4-amino-3-fluorobenzonitrile were purchased from Fluorochem. p-nitroaniline, 4-aminophenol, 4-fluoroaniline, 4-aminobenzoic acid, and p-methyl aniline, $Ru_3(CO)_{12}$ were purchased from Aladdin chemicals. Salicylaldehyde, Aniline, acetone, mesitylene, 1,4-dioxane, ethanol, sodium sulphate, tetrahydrofuran (THF) and propan-2-ol were purchased from Kelong chemicals. 2,4-dihydroxyisophthalaldehyde was obtained from Bidepharm.

Synthesis of SOMs:

The synthesis method of SOMs was as shown below. Typically, Salicylaldehyde (12.2 mg, 0.10 mmol), 2,4-dihydroxyisophthalaldehyde (18.3 mg, 0.11 mmol), 2-hydroxybenzene-1,3,5-tricarbaldehyde (8.9 mg, 0.05 mmol), 2,4-dihydroxybenzene-1,3,5-tricarbaldehyde (10 mg, 0.05 mmol) or triformylphloroglucinol (Tp, 11.9 mg, 0.05 mmol) and 4-Aminobenzonitrile (ABN, 40.0 mg, 0.34 mmol) were ultrasonically dispersed into 4 mL ethanol homogeneously and then solvothermally treated at 80 ^{o}C for 24 hours, respectively (sample was noted as **1**, **2**, **3**, **4** and **5**). During the whole process, the light-yellow, orange, or red precipitate appeared. As comparison, other monomer with different substituent (-F, -Me, -OMe, -NO_2, -COOH, -OH) replacing β-H or -CN group of ABN was reacted with TP, respectively, in the same reaction

condition. The obtained product was immersed in acetone overnight and washed with ethanol, THF, acetone for several times until all residual unreacted reagents were cleaned, followed by dried at 70 ^{o}C under vacuum. Sample **1** and **3** was recrystallized for 2-3 times in ethanol. Sample **1**: the experimental elemental composition and containment ($C_{14}H_{10}N_2O$: C(73.25%), N(11.78%), O(8.67%), H(6.30%), ^{13}C solid state NMR(500 Hz): δ 112.3, 119.04, 129.0, 136.1, 147.8, 163.4 and the relative molecular mass (222.92 (m/z)), Anal. Calcld. for $C_{14}H_{10}N_2O$: C(75.66%), N(12.60%), O(7.20%), H(4.54%) and 222.25 (m/z). Sample **2**: the experimental elemental composition and containment ($C_{22}H_{14}N_4O_2$: C (71.26%), N (14.59%), O (11.06%), H (3.09%), ^{13}C solid state NMR(500 Hz): δ 108.3, 112.2, 118.2, 134.7, 142.8, 147.5, 184.3 and the relative molecular mass (366.91 (m/z)), Anal. Calcld. for $C_{22}H_{14}N_4O_2$: C (72.12%), N (15.29%), O (8.73%), H (3.85%) and 366.38 (m/z). Sample **3**: the relative molecular mass (479.27 (m/z)), ^{13}C solid state NMR (500 Hz): δ 108.8, 118.5, 132.1, 135.4, 156.4, 164.1. Anal. Calcld. For $C_{30}H_{18}N_6O$: 478.52. Sample **4**: the relative molecular mass (495.30 (m/z), ^{13}C solid state NMR (500 Hz): δ 108.4, 117.6, 121.4, 132.4, 150.1, 156.4, 184.1, Anal. Calcld. For $C_{30}H_{18}N_6O_2$: 494.15 (m/z). Sample **5**: the experimental elemental composition and containment ($C_{30}H_{18}N_6O_3$: C (70.06%), N (16.45%), O (10.38%), H (3.11%)) and the relative molecular mass (510.91(m/z), ^{13}C solid state NMR (500 Hz): δ 107.9, 118.7, 133.8, 141.3, 182.7, Anal. Calcld. for $C_{30}H_{18}N_6O_3$: C (70.58%), N (16.46%), O (9.40%), H (3.55%) and 510.51 (m/z).

Characterization: Firstly, the organic element analysis (elemental vario EL cube,

Germany) and MALDI-TOF-MS (AXIMA Performance) were applied to measure the element component, content and relative molecular mass. The solid state ^{13}C NMR (AVANCE III 500MHz), the liquid ^{1}H NMR (AVANCE III HD) and FT-IR (INVENIOR，bruker) were used to clarify the characteristic functional groups. The optical properties and charge separation ability were analyzed by UV-vis DRS (UV3600, Shimadzu) and fluorescence spectrometer (Hitachi F-7000). The Brunauer -Emmett-Teller (BET) surface area were obtained by using nitrogen adsorption-desorption curve (Micromeritics). The thermal properties were tested by METTLER TOLEDO DSC1, under N_2 flow and 10 ^{o}C/min heating rate between 30 ^{o}C and 600 ^{o}C. The X-ray photoelectron spectroscopy (XPS, Thermo Fisher 250 XI) was used for surface analysis of sample **5** after- or before- irradiation.

The analysis of photocurrent, electrochemical impedance spectroscopy (EIS) and Mott-Schottky curve were realized on electrochemical workstation (CHI660E). The fabrication of work electrode for the electrochemical test was as follows: 5 mg sample powder was placed into centrifuge tubes with the mixture solution of 150 μL ethanol, 150 μL isopropyl alcohol and 10 μL naphthol and formed the homogeneous dispersion by ultrasonic. Draw 40 μL dispersion to be coated on the surface of FTO conductive glass to generate uniformly 1.0 × 1.0 cm film. At last, the FTO plate was placed into vacuum oven to dry for 5 h at 70℃. The photoelectrochemical measurement was completed via a three-electrode model. Ag/AgCl electrode as the reference electrode, Pt piece as the counter electrode, and 0.1 M Na_2SO_4 as electrolyte solution in this model.

Photocatalytic measurement.

The photocatalytic water reduction reaction was performed in an airtight and homothermic glass photoreactor with external light lamp and gas circulation system. 10 mg SOM photocatalyst and quantitative H_2PtCl_6 solution were dropped in 200 mL aqueous triethanolamine (TEOA, 10 vol%). Before photocatalytic reaction, the whole system was evacuated to hold vacuum state. Prior to the catalytic reaction, Pt co-catalyst was loaded on sample **5** through the in-situ photoreduction of H_2PtCl_6 under the 30-min irradiation of full-spectrum 300W Xe lamp (Ceralux 300BF). After that, photocatalytic reaction was proceeded under the visible-light irradiation (300W Xe lamp installed with light filter, λ>400nm). The amount of photocatalytic H_2 production was monitored in real time by gas chromatograph (GC-112AT). The loading of RuO_2(consulting the previous literature [1]): 20 mg SOM-5 was impregnated in 15 mL THF solution with quantitative amount of $Ru_3(CO)_{12}$. The former was maintained at 60 ^oC. After the evaporation of the solvent, the photocatalyst powder was transferred to muffle furnace and heated at 300 ^oC for 1h.

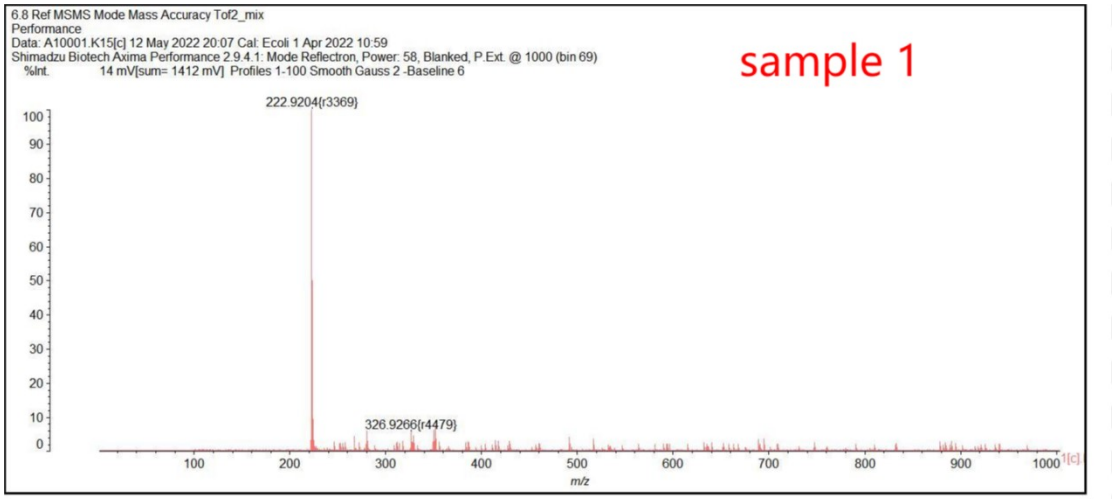
The calculation of apparent quantum yield (AQY): 0.1 g photocatalyst and 200 mL TEOA solution (Pt as cocatalyst) was dispersed in the same photocatalytic reaction apparatus, 300 W Xe lamp installed with optical filter (λ=425 nm) as incident light. The amount of H_2 production was detected by gas chromatograph. The amount of photon was tested by ThorLabs S120C photo-diode.

The calculation of AQY by the following formula:

$$\eta = \frac{2 \times \text{moles of H2 evolved}}{\text{moles of the incident photons}} \times 100\%$$

Theoretical calculation

Gaussian 09[2] program was employed to conduct all calculation, by using M062X[3,4]-D3[5,6] density functional with the 6-31+G(d,p) basis set. The chemical structure was optimized and characterized by frequency analysis at 298 K. The corresponding theoretical energy level was calculated by Time-dependent density functional theory (TD-DFT). Spin population was obtained using Multiwfn 3.8 software[7] , and the corresponding isosurface plots were generated by VMD 1.9.3 package [8]. The optimized geometries and the corresponding structural parameters are as shown in Figure S21 and Table S5.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Performance
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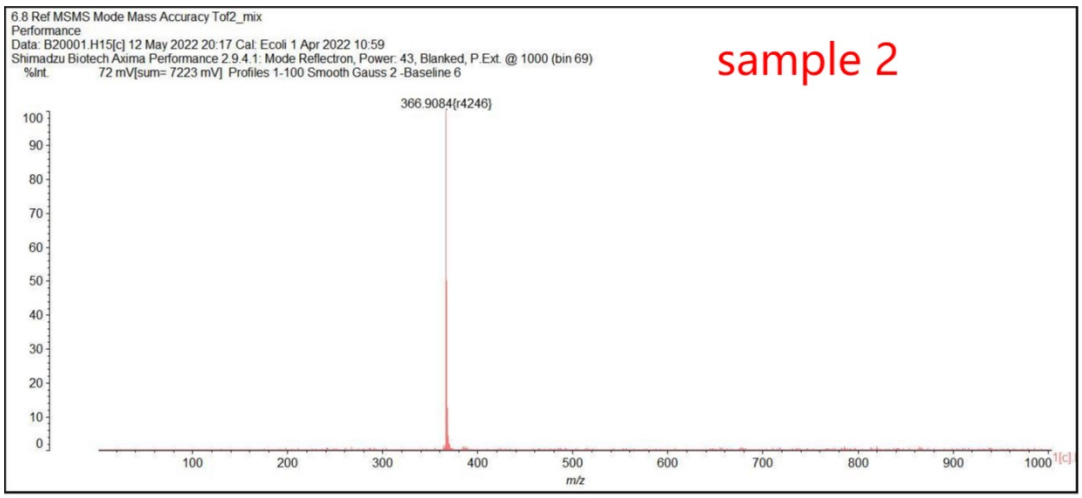
222.9204{r3369}
326.9266{r4479}
m/z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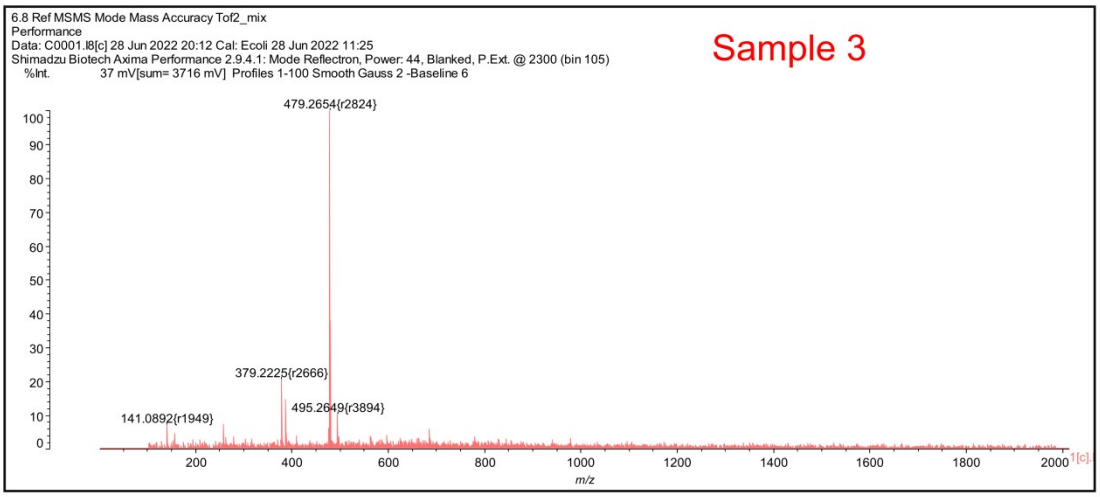
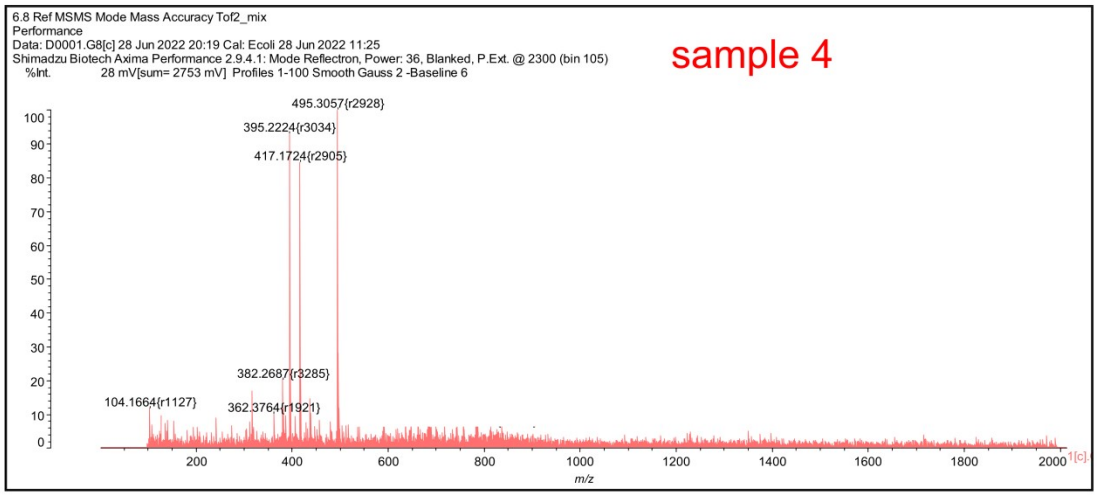
%Int. 72 mV[sum= 7223 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 2
366.9084{r4246}
m/z


6.8 Ref MSMS Mode Mass Accuracy Tof2_mix
Performance
Data: C0001.I8[c] 28 Jun 2022 20:12 Cal: Ecoli 28 Jun 2022 11:25
Shimadzu Biotech Axima Performance 2.9.4.1: Mode Reflectron, Power: 44, Blanked, P.Ext. @ 2300 (bin 105)
%Int. 37 mV[sum= 3716 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
Sample 3
479.2654{r2824}
379.2225{r2666}
495.2649{r3894}
141.0892{r1949}
m/z



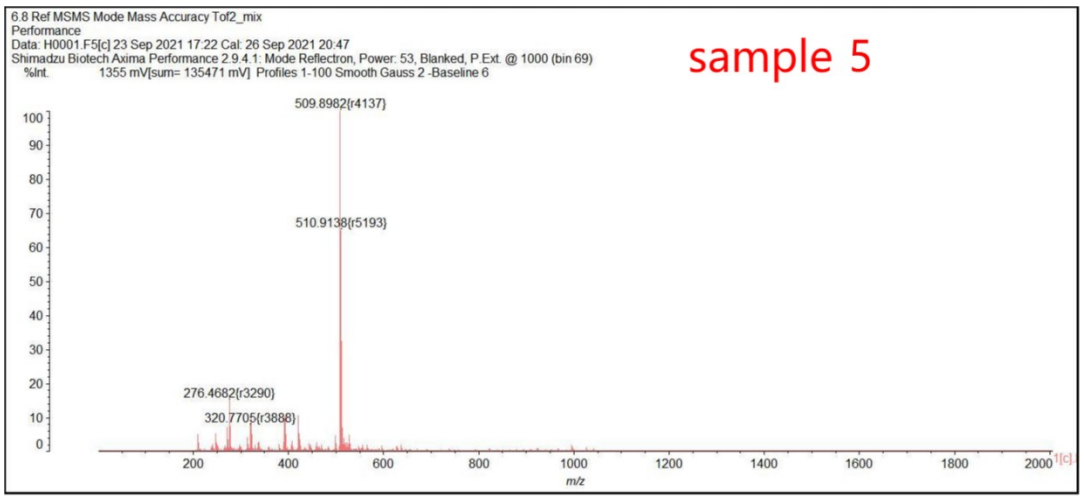


Figure S1: The MALDI-TOF-MS results of sample **1-5**.

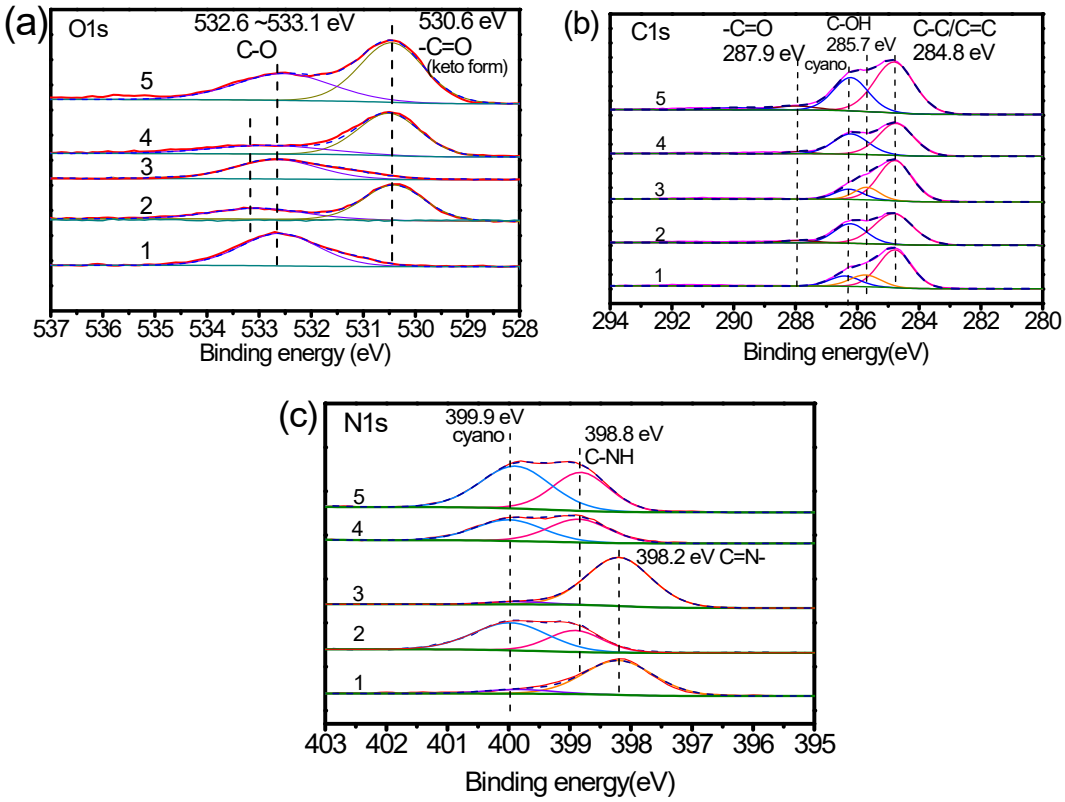


Figure S2. the O1s(a), C1s(b) and N1s(c) spectra of high-resolution XPS spectra of sample **1**-**5**.

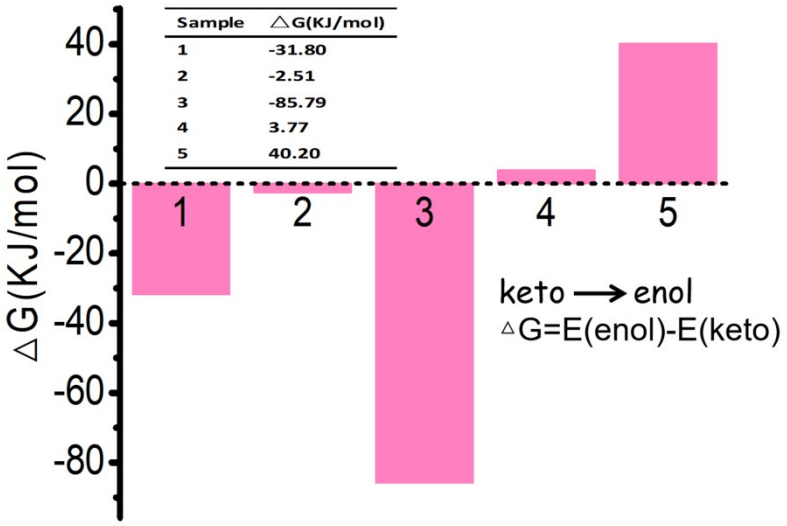


Figure S3. The energy difference between corresponding enol structure and keto form structure of sample **1**, **2**, **3**, **4** and **5**, respectively.

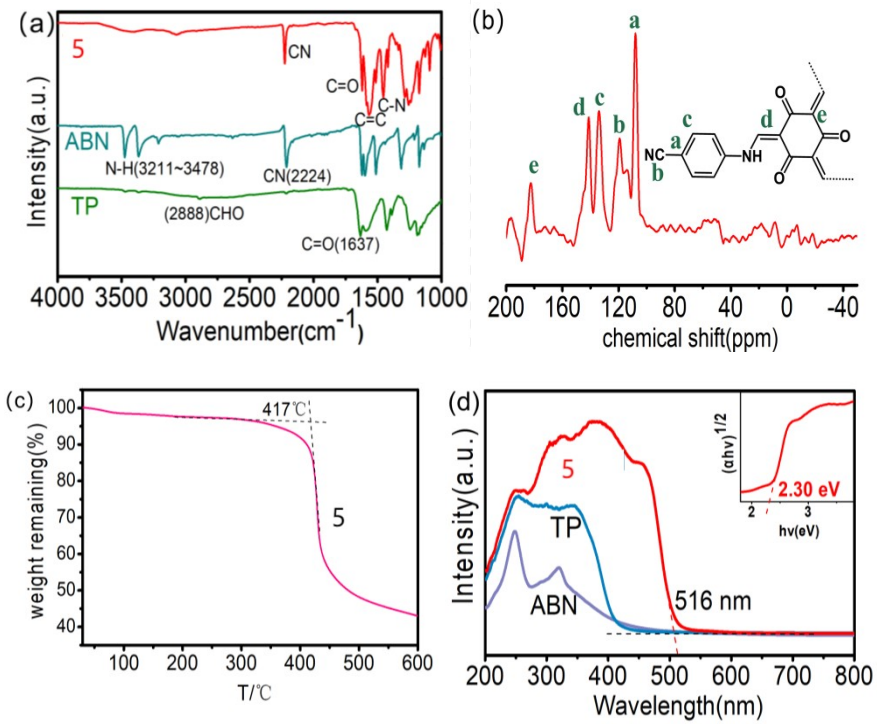


Figure S4. FT-IR spectra (a), ^{13}C solid-state NMR (b), thermogravimetry (TG) (c) and the UV-vis DRS (d) curve of **5**. The inset in (d) shows the bandgap of **5**.

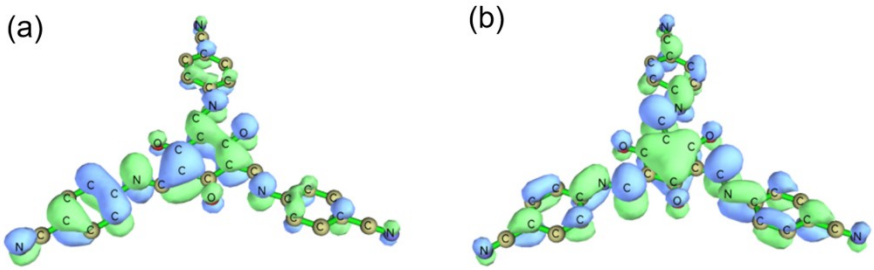


Figure S5. The HOMO(a) and LUMO(b) level of **5**.

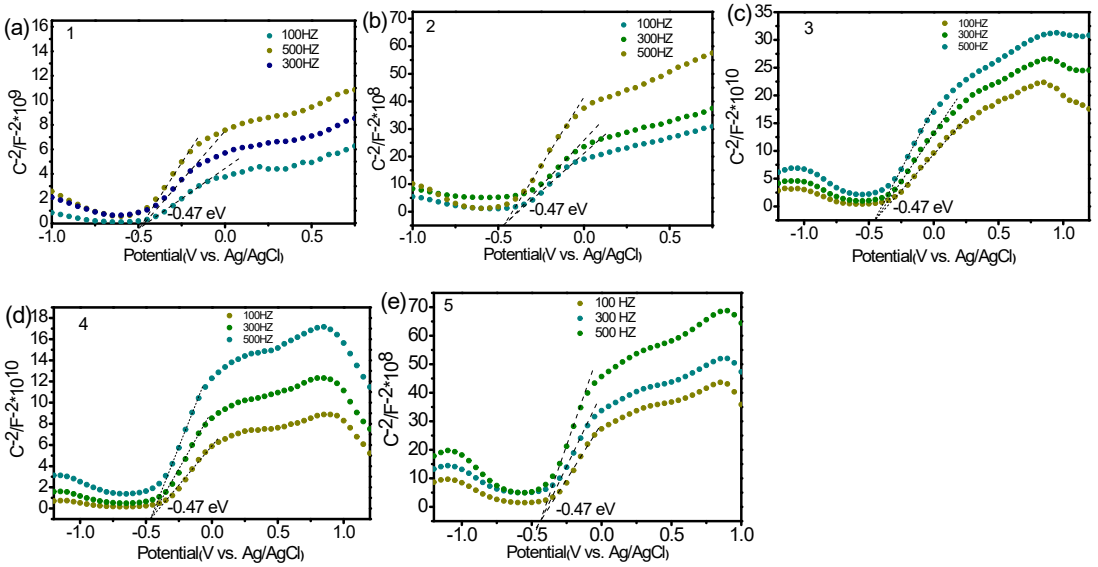


Figure S6. The Mott-Schottky curves of sample **1-5** (a)-(e) (100 HZ, 300HZ, 500HZ). The intercept on the x axis is the value of the flat band (vs. Ag/AgCl).

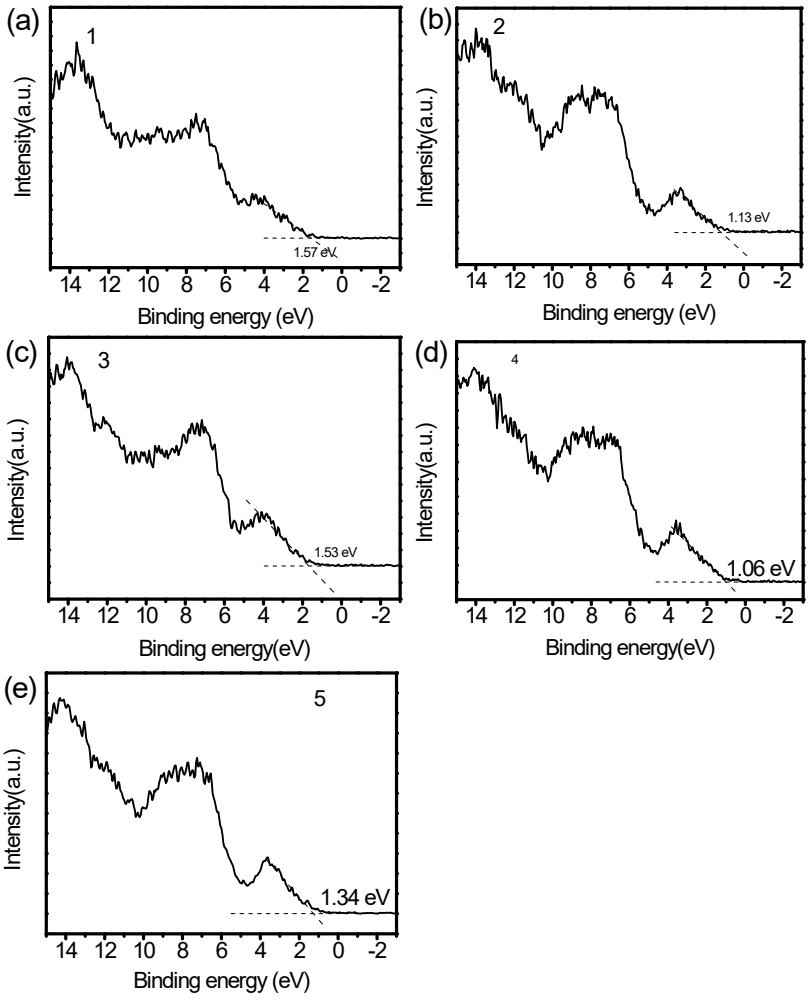


Figure S7. The VB-XPS of sample **1-5** (a-e).

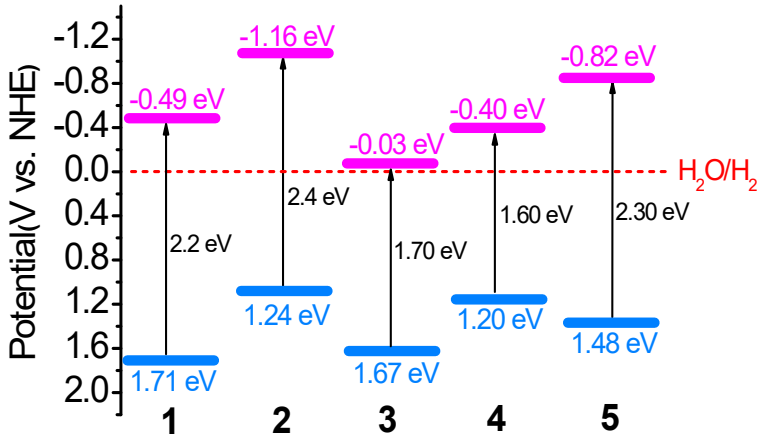


Figure S8. The energy band alignments of sample **1-5** respectively.

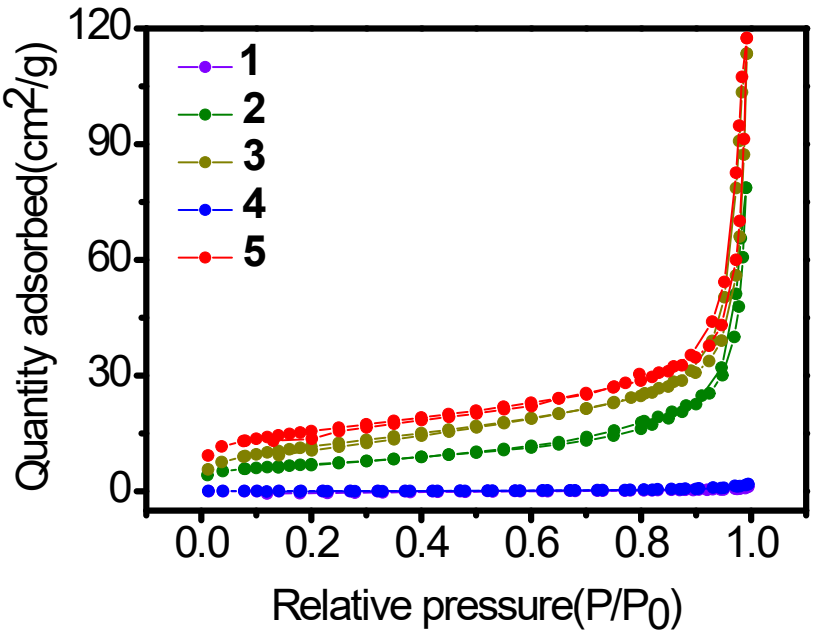


Figure S9. Nitrogen adsorption-desorption isotherm of sample **1-5**.

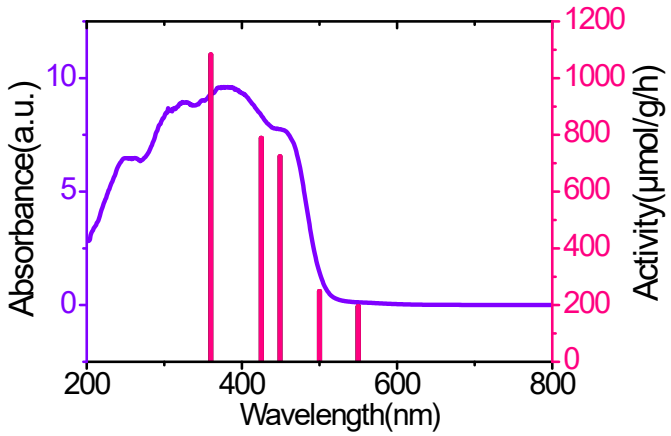


Figure S10. The activity of **5** with changing incident-light wavelength.

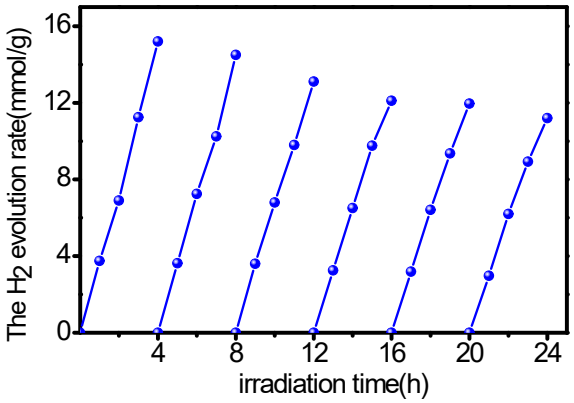


Figure S11. The photostability test of **5** (6 cycles, 24h-irradiation).

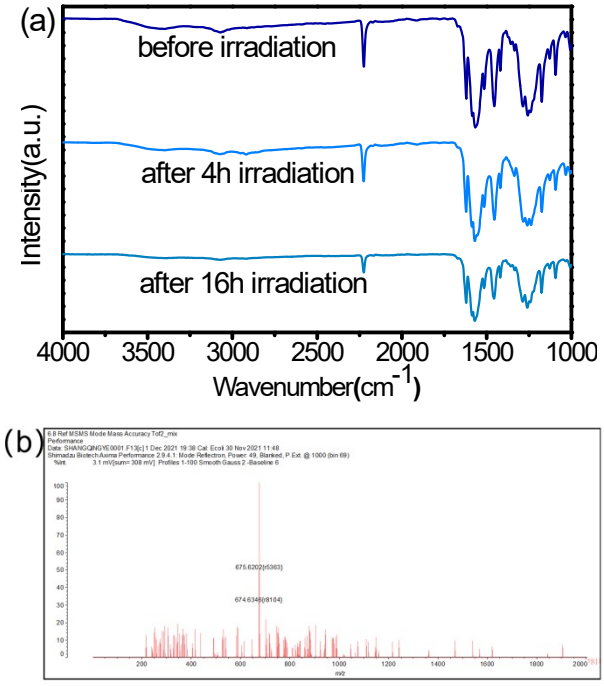


Figure S12. The FT-IR spectra of **5** after-irradiation and the MALDI-TOF-MS of supernatants from the reaction solution.

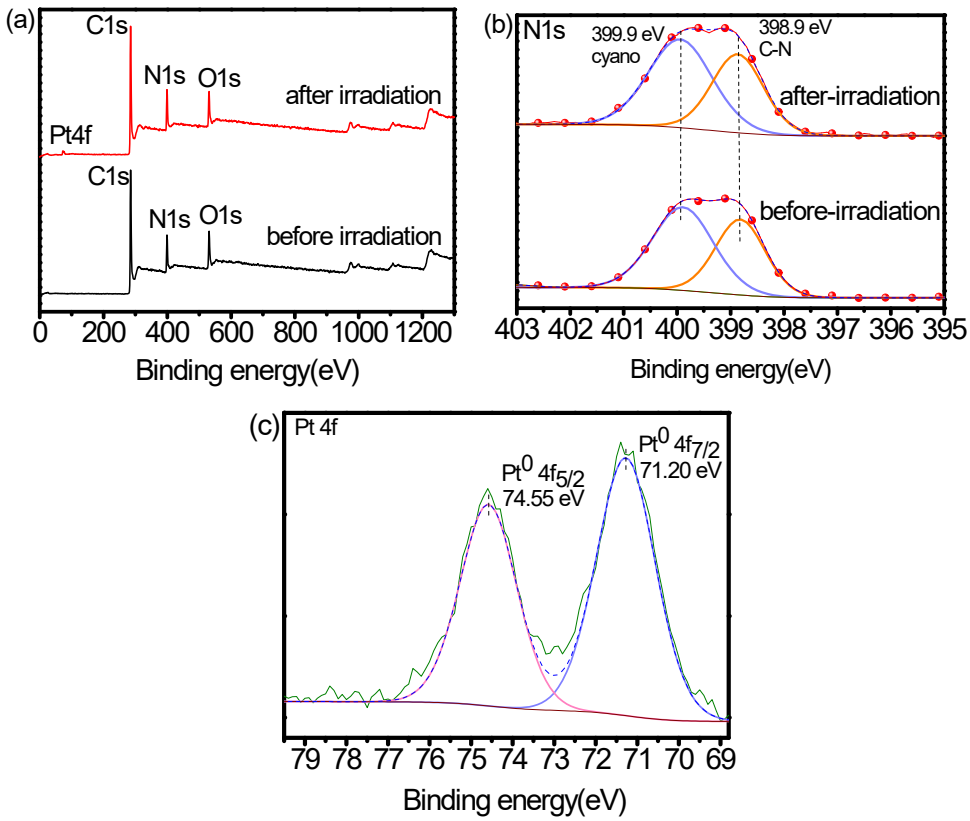


Figure S13. The high resolution XPS spectra of N 1s(a), Pt 4f (b).

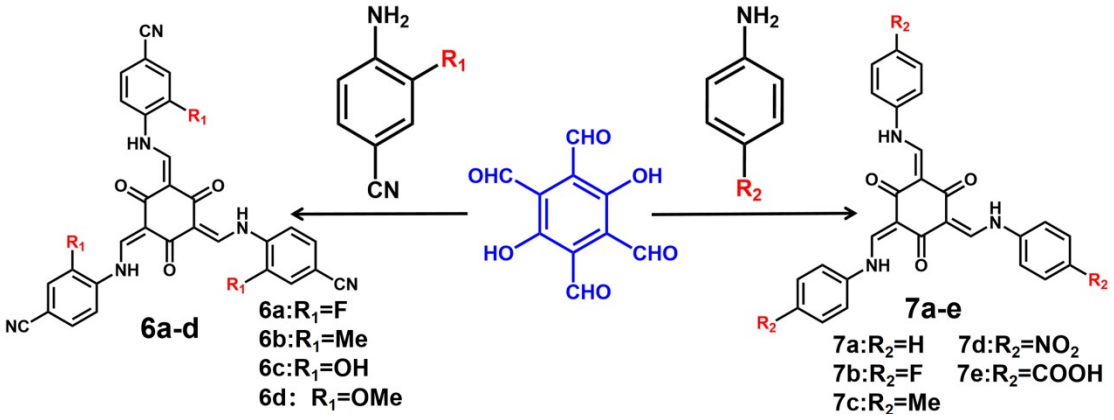
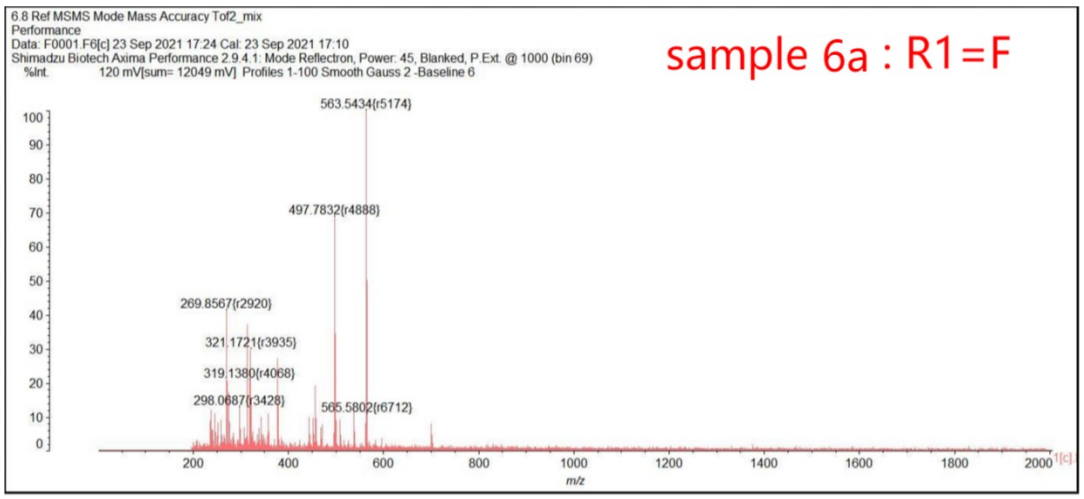


Figure S14. The synthetic route of **6a-d** and **7a-e**. (R_1 and R_2 substituent replace β-H or cyan group of ABN, respectively)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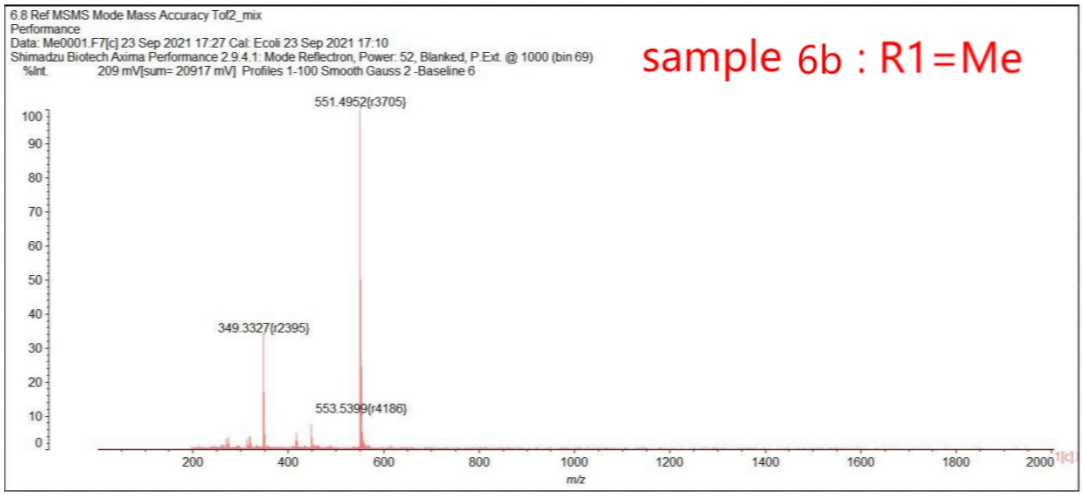
%Int. 120 mV[sum= 12049 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 6a : R1=F
563.5434{r5174}
497.7832{r4888}
269.8567{r2920}
321.1721{r3935}
319.1380{r4068}
298.0687{r3428}
565.5802{r6712}
m/z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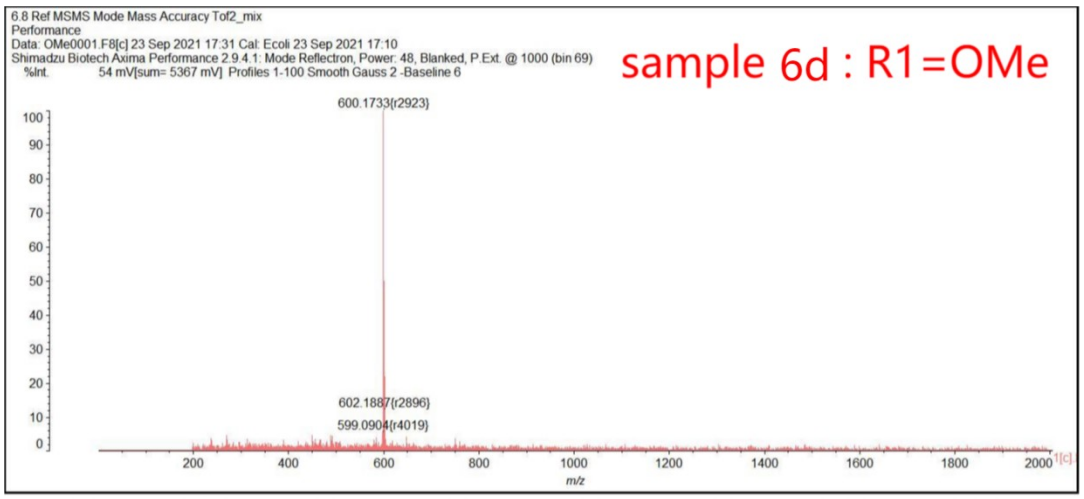
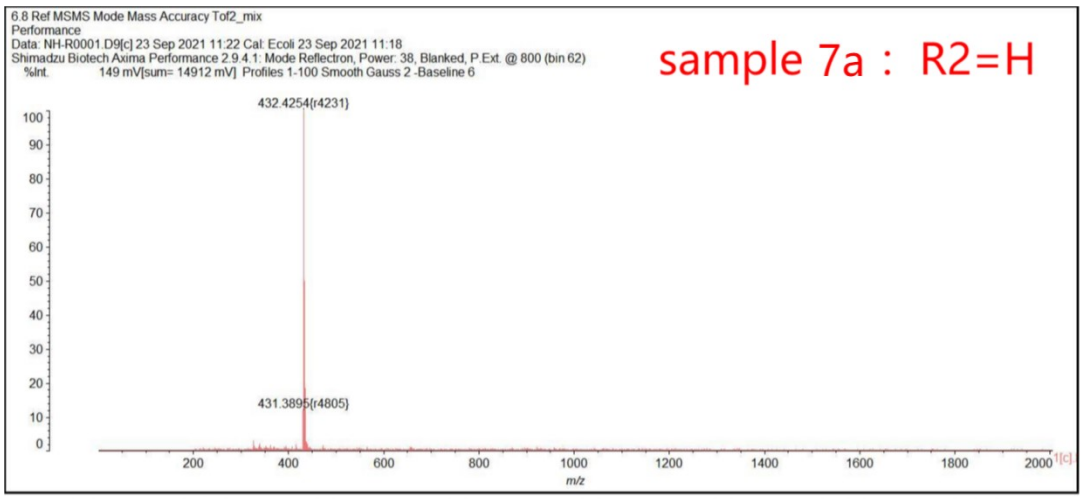
%Int. 209 mV[sum= 20917 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 6b : R1=Me
551.4952{r3705}
349.3327{r2395}
553.5399{r4186}
m/z


6.8 Ref MSMS Mode Mass Accuracy Tof2_mix
Performance
Data: OMe0001.F8[c] 23 Sep 2021 17:31 Cal: Ecoli 23 Sep 2021 17:10
Shimadzu Biotech Axima Performance 2.9.4.1: Mode Reflectron, Power: 48, Blanked, P.Ext. @ 1000 (bin 69)
%Int. 54 mV[sum= 5367 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 6d : R1=OMe
600.1733{r2923}
602.1887{r2896}
599.0904{r4019}
m/z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Performance
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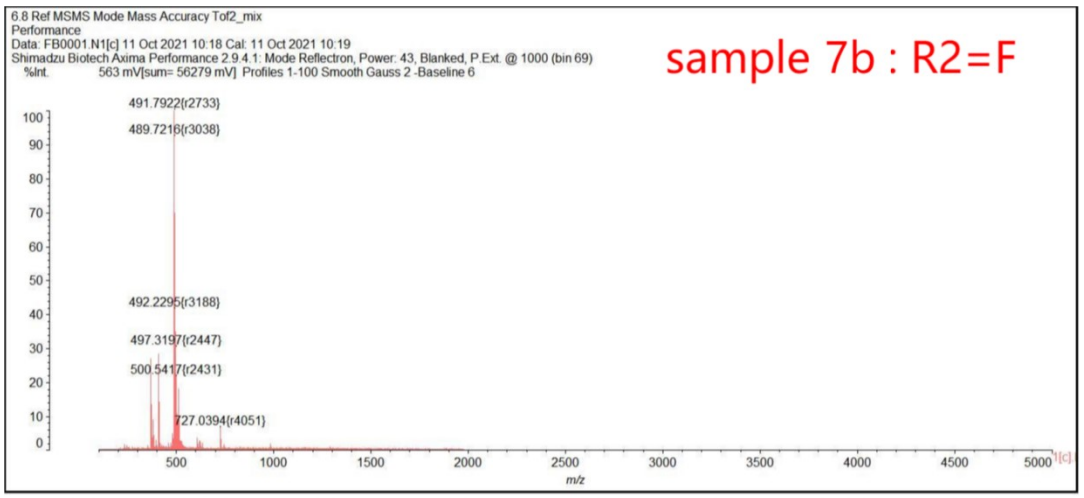
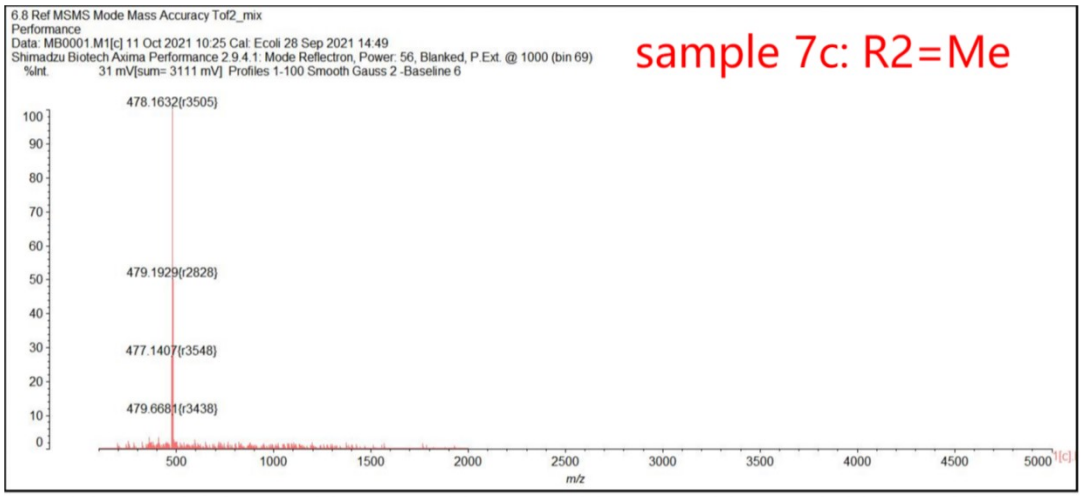
Shimadzu Biotech Axima Performance 2.9.4.1: Mode Reflectron, Power: 38, Blanked, P.Ext. @ 800 (bin 62)
%Int. 149 mV[sum= 14912 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 7a : R2=H
432.4254{r4231}
431.3895{r4805}
m/z


6.8 Ref MSMS Mode Mass Accuracy Tof2_mix
Performance
Data: FB0001.N1[c] 11 Oct 2021 10:18 Cal: 11 Oct 2021 10:19
Shimadzu Biotech Axima Performance 2.9.4.1: Mode Reflectron, Power: 43, Blanked, P.Ext. @ 1000 (bin 69)
%Int. 563 mV[sum= 56279 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 7b : R2=F
491.7922{r2733}
489.7216{r3038}
492.2295{r3188}
497.3197{r2447}
500.5417{r2431}
727.0394{r4051}
m/z


6.8 Ref MSMS Mode Mass Accuracy Tof2_mix
Performance
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%Int. 31 mV[sum= 3111 mV] Profiles 1-100 Smooth Gauss 2 -Baseline 6
sample 7c: R2=Me
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477.1407{r3548}
479.6681{r3438}
m/z

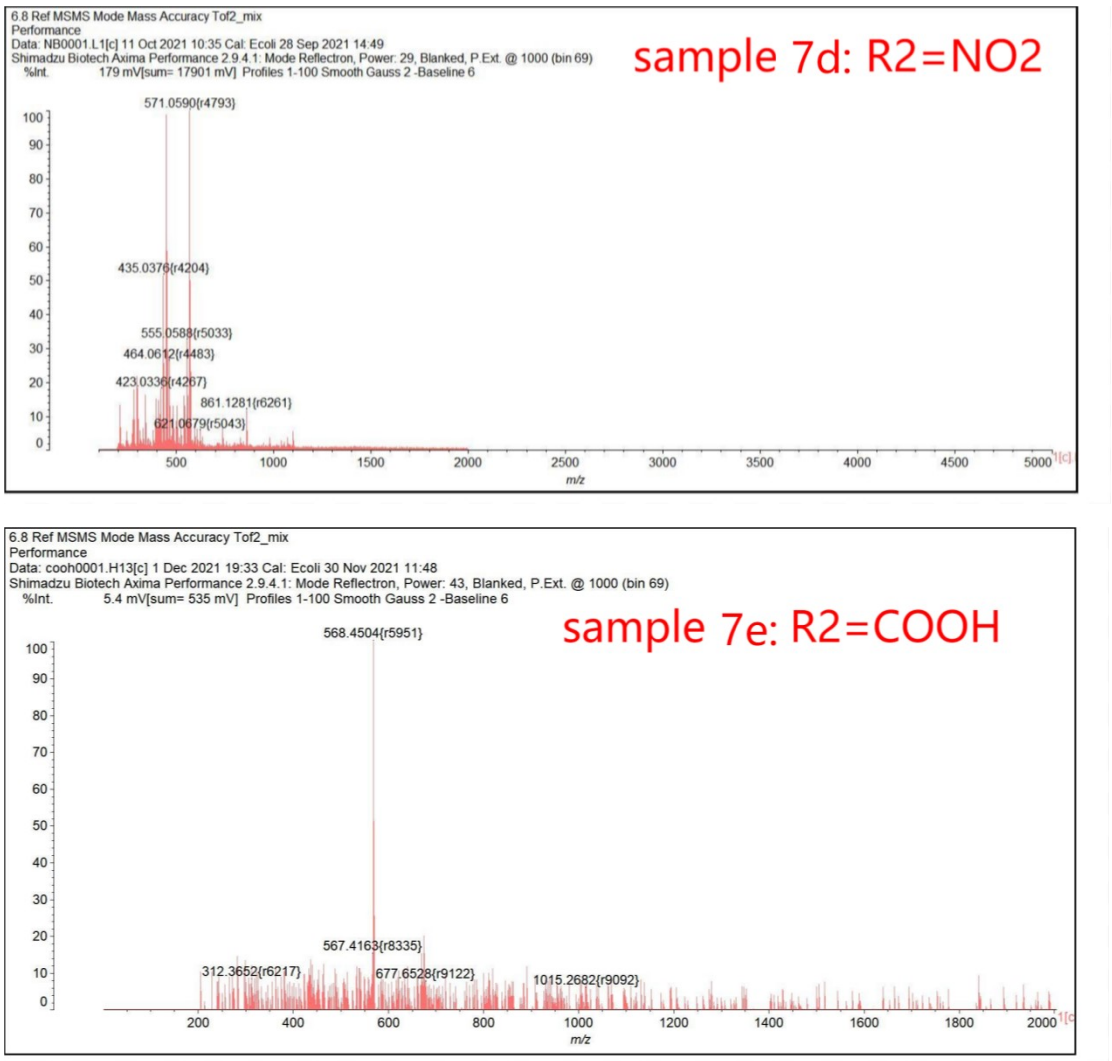


Figure S15. The MALDI-TOF-MS results of sample **1-3** and **4a-d**, **5a-e**.

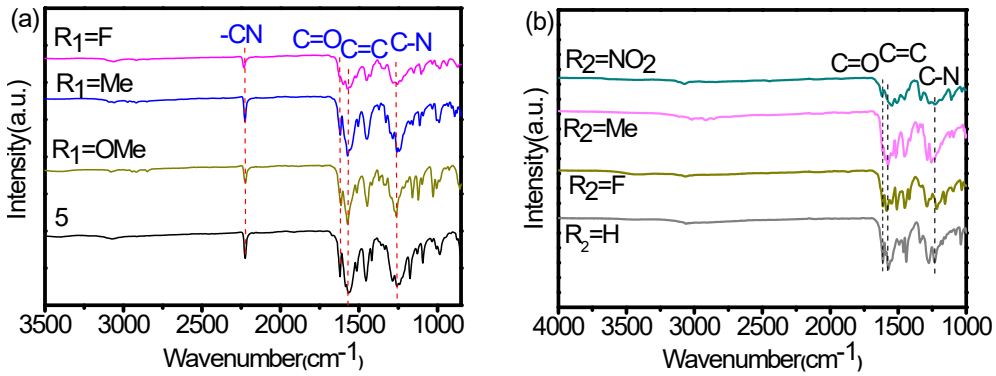


Figure S16. The Fourier Transform Infrared Spectra (FT-IR) of **5**, R_1=F, Me, OMe(a) and R_2=H, F, Me, NO_2(b).

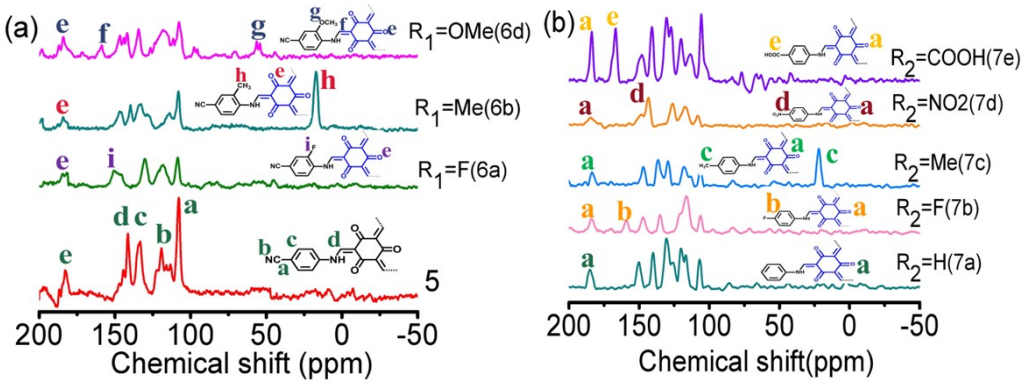


Figure S17. The ^{13}C solid-state nuclear magnetic resonance (NMR) of **5** (δ 107.9, 118.7, 133.8, 141.3, 182.7(C=O)), R1=F(δ 108.5, 118.2, 132.1, 150.5, 182.4(C=O)), R1=Me(δ 17.1, 108.2, 114.3, 133.7, 140.1, 146.5, 183.9(C=O)), R1=OMe(δ 56.2(OMe), 107.4, 118.2, 134.2, 142.0, 147.2, 158.9, 184.1(C=O)) (a) and R_2=H(δ 107.5, 117.2, 130.9, 140.1, 150.3, 184.6(C=O)), F(δ 108.2, 117.5, 135.1, 147.2, 159.2(F-C), 183.5(C=O)), Me(δ 21.8(Me), 107.2, 117.6, 130.1, 136.5, 146.9, 183.3(C=O)), NO_2(δ 108.2, 117.4, 126.2, 143.4(NO_2-C), 184.2(C=O)), COOH(δ 107.2, 116.9, 130.3, 140.9, 148.1, 166.9(COOH), 183.6(C=O))(b).

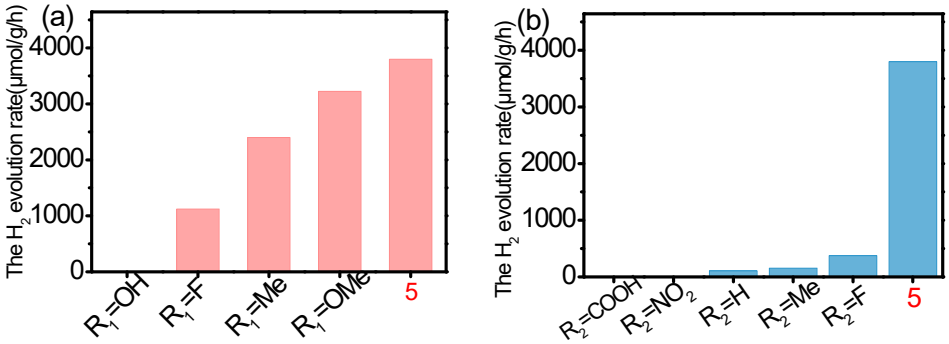


Figure S18. The photocatalytic activity of **6a-d** (**6a**:R_1=F,**6b**:R_1=Me, **6c**:R_1=OH, **6d**:R_1=OMe) (a) and **7a-e**(**7a**:R_2=H, **7b**:R_2=F,**7c**:R_2=Me, **7d**:R_2=NO_2, **7e**:R_2=COOH) (b).

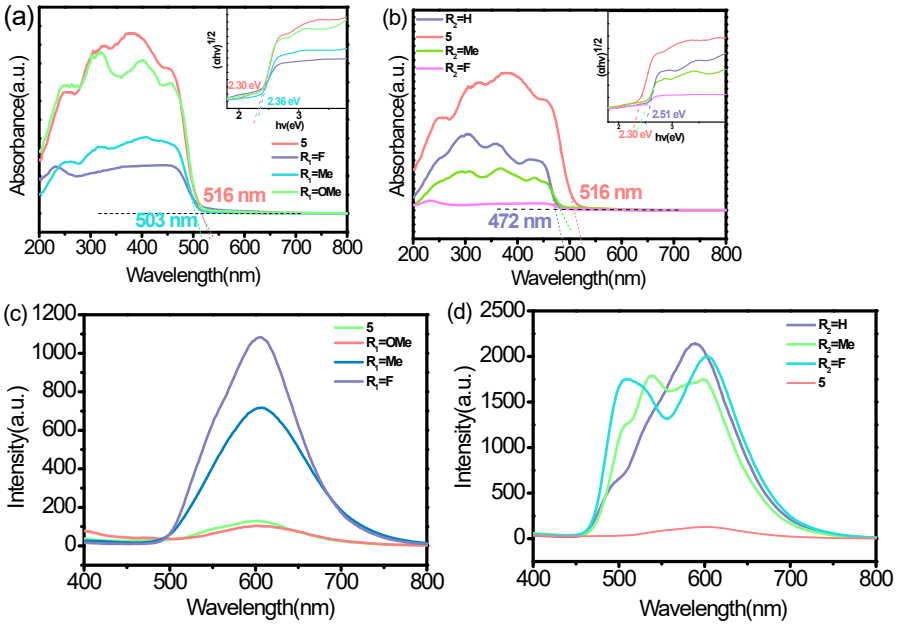


Figure S19. The UV-vis DRS (a)(b) and PL spectra(c)(d) of **6a-d** and **7a-e**, respectively.

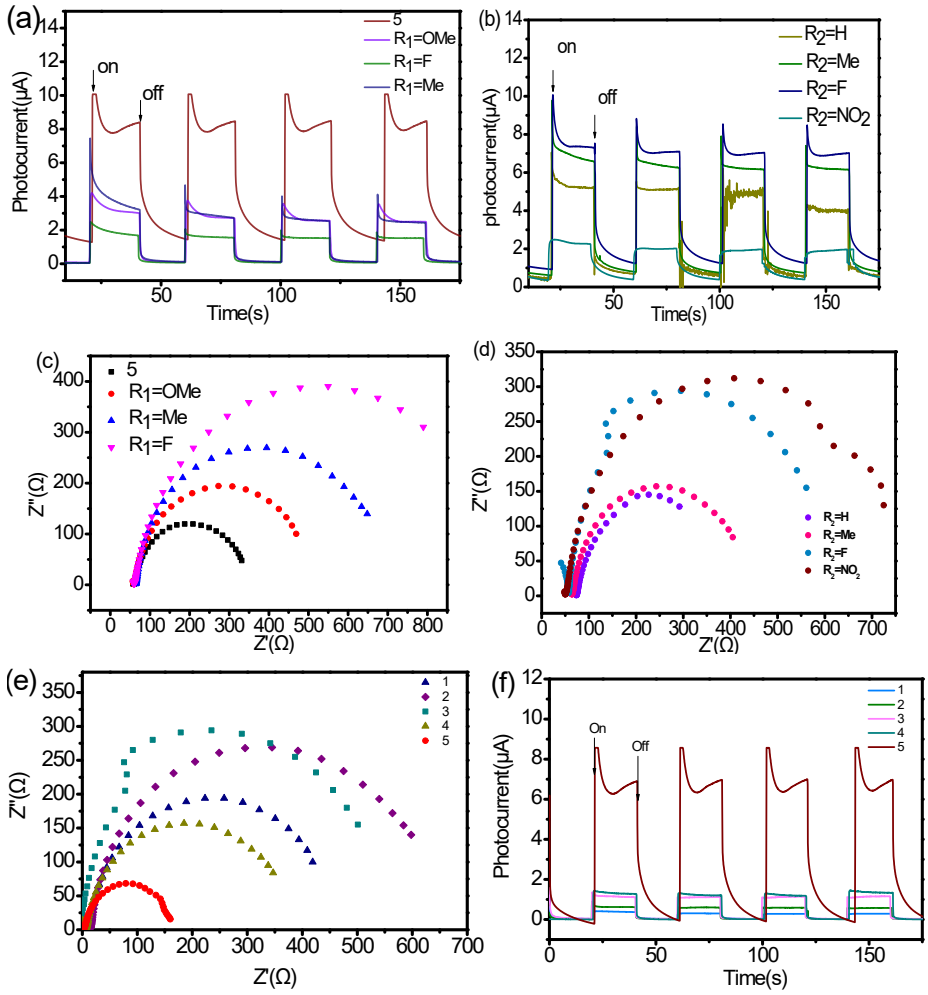


Figure S20. The photocurrent response(a)(b) and EIS spectra(c)(d) of sample with different R_1 or R_2 substitution. EIS spectra (f) and photocurrent response of **1-5** (e).

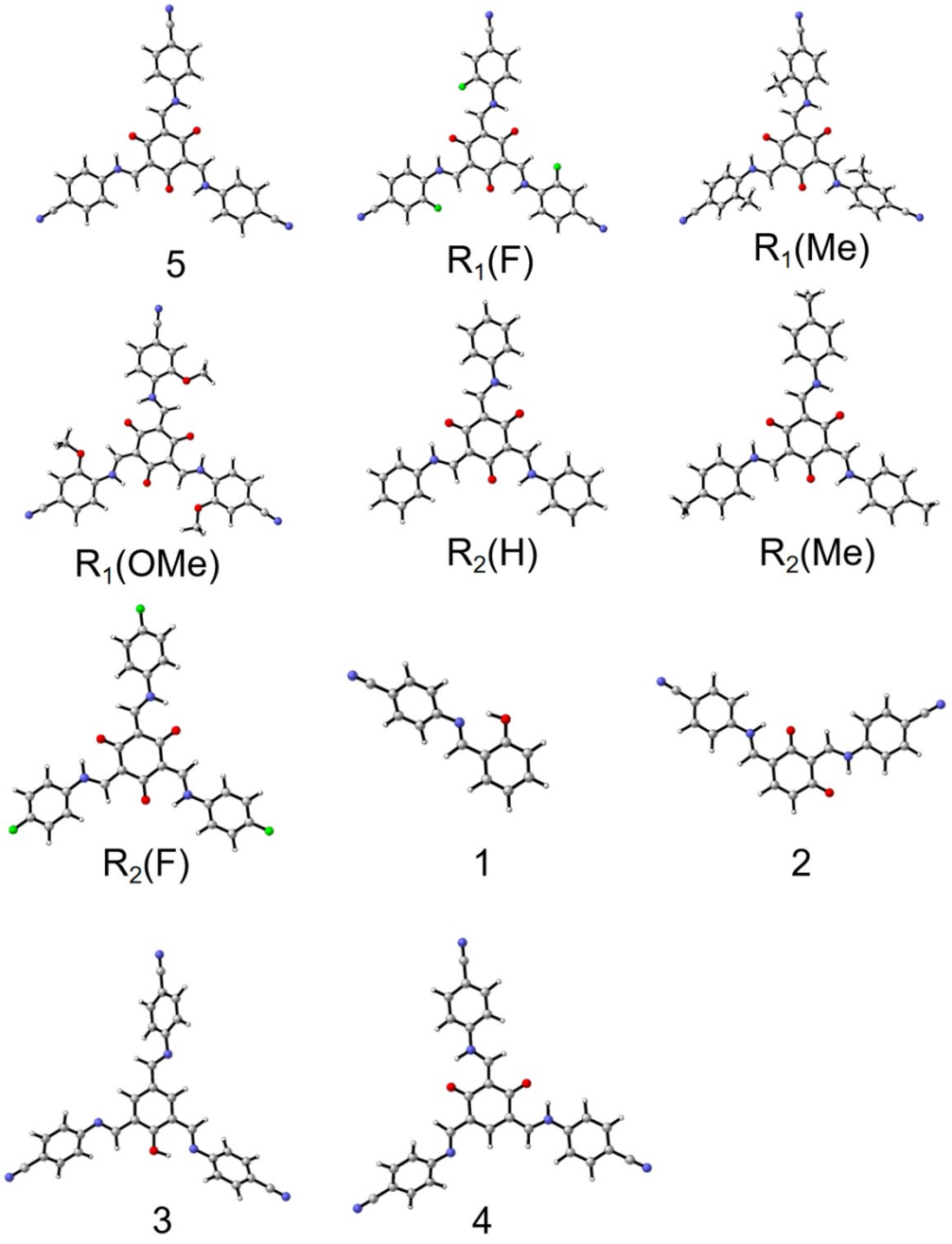
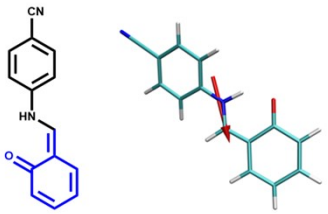


Figure S21. Optimized geometries and the corresponding structural parameters.

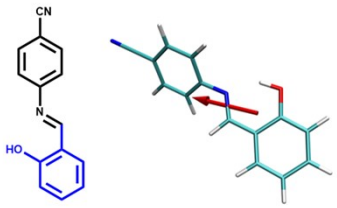
(a)



sample 1(keto structure)

4.3339

dipole moment (Debye)

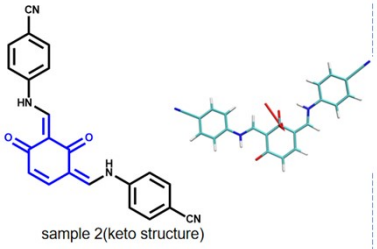


sample 1(enol structure)

5.1337

dipole moment (Debye)

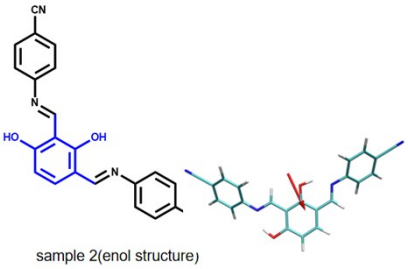
(b)



sample 2(keto structure)

3.8897

dipole moment (Debye)

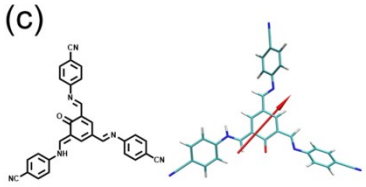


sample 2(enol structure)

4.7987

dipole moment (Debye)

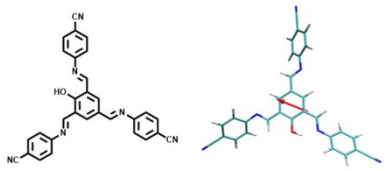
(c)



sample 3(keto structure)

7.91399

dipole moment (Debye)

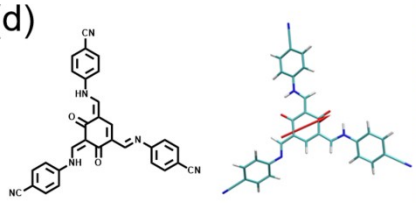


sample 3(enol structure)

2.94015

dipole moment (Debye)

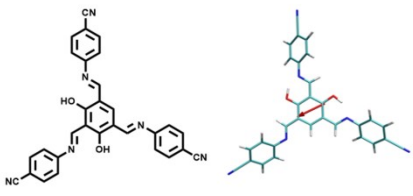
(d)



sample 4(keto strucutre)

4.41815

dipole moment (Debye)



sample 4(enol strucutre)

2.62187

dipole moment (Debye)

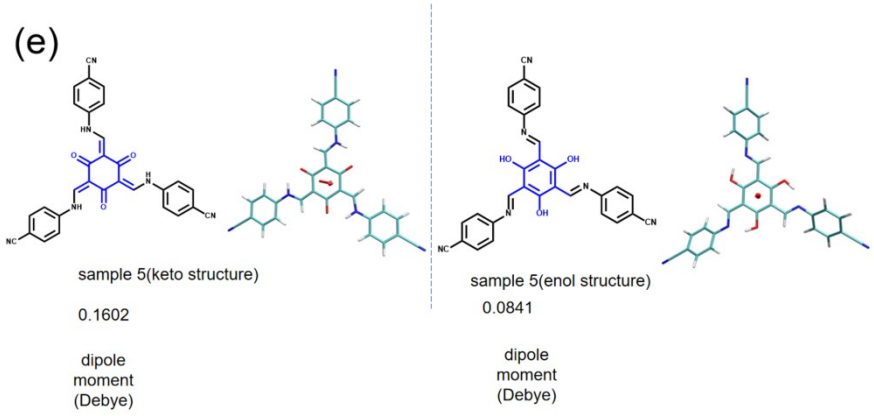


Figure S22. The dipole moment of sample **1**, **2**, **3**, **4** and **5** with keto or enol form respectively.

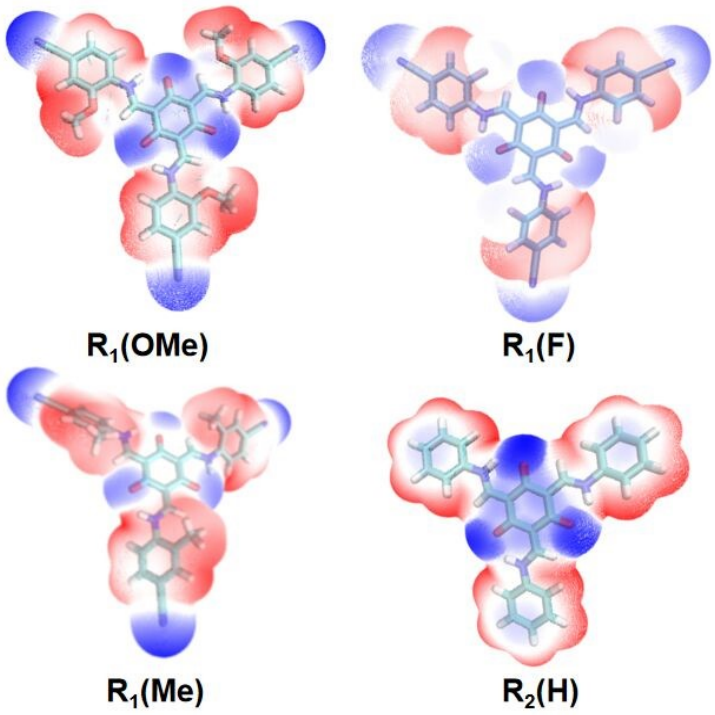


Figure S23. Electrostatic potential-mapped vdW molecular surface of **6a**, **6b**, **6d** and **7a** (isovalue=0.001 au, computed at the M062X-D3/6-31+G(d,p) level of theory) Isosurface map of electrostatic potential (ESP) (isovalue=0.001 au, computed at the M062X-D3/6-31+G(d,p) level of theory).

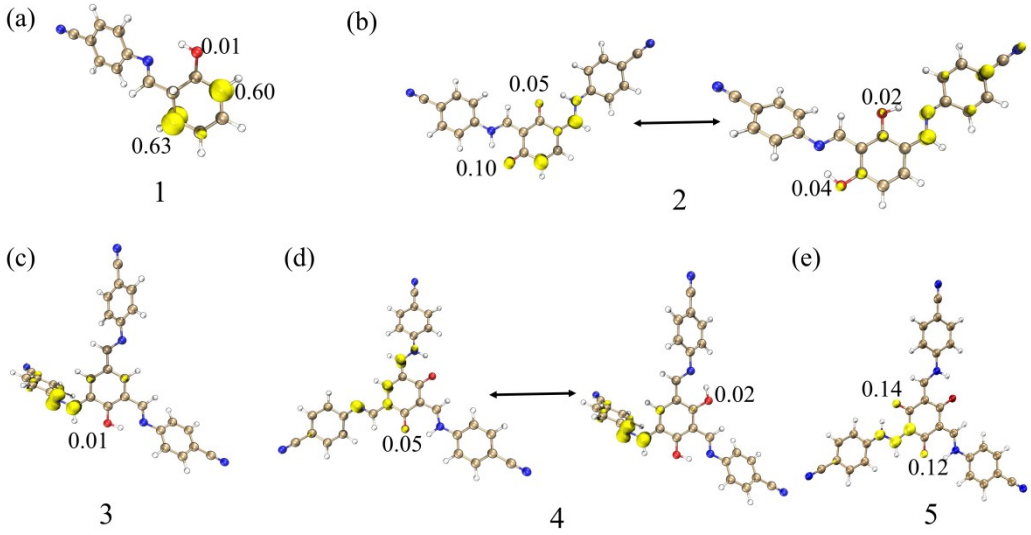


Figure S24. Spin electron density for **1**-**5** in the first excited triple state (T1, isovalue=0.02). The yellow domain represents the distribution of single electron.

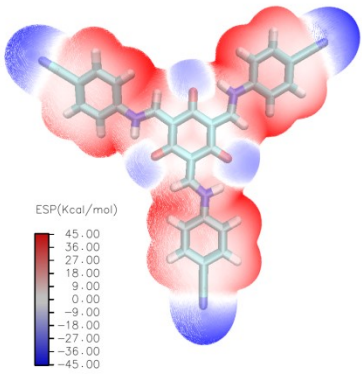


Figure S25. Electrostatic potential-mapped vdW molecular surface of **5** (isovalue=0.001 au, computed at the M062X-D3/6-31+G(d,p) level of theory) Isosurface map of electrostatic potential (ESP) (isovalue=0.001 au, computed at the M062X-D3/6-31+G(d,p) level of theory).

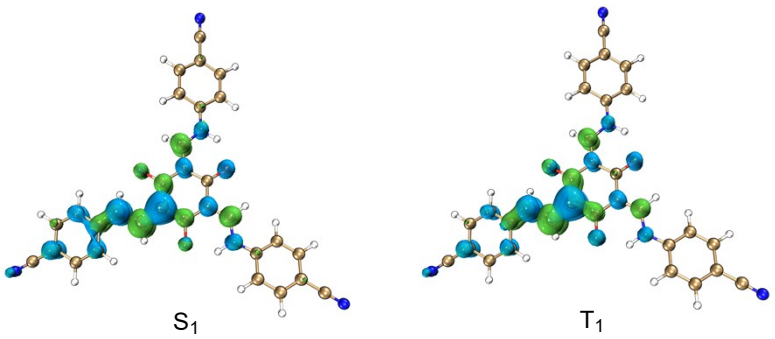


Figure S26. Space representation of hole and electron distributions of S_1 and T_1 states for 5, obtained by Mutilwfn software. Green and blue isosurfaces corresponding to electron and hole distributions, respectively (isovalue = 0.02 au).

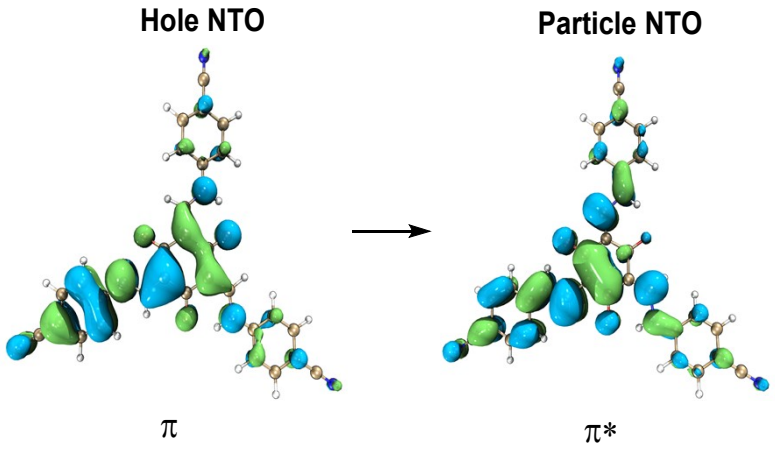


Figure S27. Dominant natural transition orbital (NTO) pair for the $S_0 \rightarrow S_1$ transition for **5**, obtained by Mutilwfn software (isovalue = 0.002 au). The associated eigenvalue λ is 0.883.

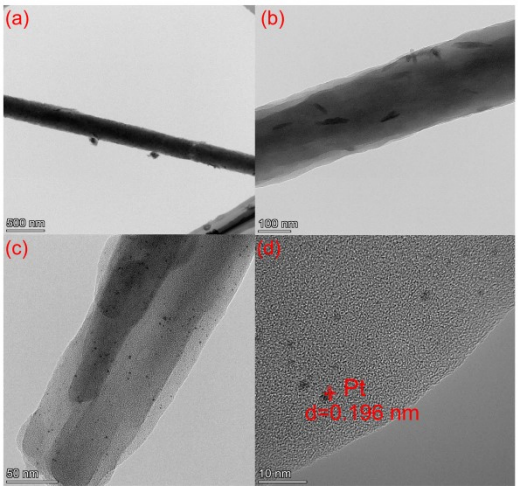


Figure S28. The TEM image of **5** before-irradiation (a and b) and after-irradiation SOM (c and d).

Table S1. The element containment of samples

Element analysis	C(wt%)	H(wt%)	O(wt%)	N(wt%)
1($C_{14}H_{10}N_2O$)	73.25	6.30	8.67	11.78
2($C_{22}H_{14}N_4O_2$)	71.26	3.09	11.06	14.59
5($C_{30}H_{18}N_6O_3$)	70.06	3.11	10.38	16.45
R_2=Me ($C_{33}H_{24}N_6O_3$)	69.88	4.91	11.17	14.04
R_1=OMe ($C_{33}H_{24}N_6O_6$)	65.74	4.89	16.25	13.12
R_2=H ($C_{27}H_{21}N_3O_3$)	72.94	5.17	12.78	9.11
R_2=Me ($C_{30}H_{27}N_3O_3$)	74.72	5.90	10.71	8.67
R_2=NO_2 ($C_{27}H_{18}N_6O_9$)	56.05	3.49	27.16	13.30

Table S2 The BET surface area of sample 1-5, 6a, 6b

sample	BET surface area	Pore volume(cm^3/g)	Pore size(nm)
1	0.10 m^2/g	0.0017	15.39
2	24.55 m^2/g	0.12	22.67
3	43.70 m^2/g	0.18	18.71
4	0.26 m^2/g	0.0027	16.78
5	48.54 m^2/g	0.20	18.32
6a(R_1=F)	0.15 m^2/g	0.0013	15.48
6b(R_1=Me)	0.60 m^2/g	0.0021	16.23

Table S3. The dihedral angle and dipole moment of samples.

Sample	dihedral angle(°)	Dipole(Debye)
1(enol form)	41.6	5.13
1(keto form)	17.2	3.90
2(enol form)	39.6	4.80
2(keto form)	0.3	3.89
3	0.7	0.16
R_1=OMe	1.1	0.14
R_1=F	29.5	2.04
R_1=Me	43.6	2.06

R_1=OH	1.2	0.20
R_2=H	1.5	0.48
R_2=Me	0.8	0.08
R_2=F	1.5	0.48
R_2=NO_2	1.5	0.42

Table S4. The spin population of main atoms of **5**.

5	Value	% of sum	% of sum abs
C1	0.05826158	2.913091	2.696225
C2	0.41842150	22.921170	21.214791
C3	0.03800227	1.900122	1.758666
C8	0.02176706	1.0088358	0.270390
O9	0.13931985	6.966021	6.447432
C10	0.41661284	20.830728	19.279974
O11	0.14108878	7.054468	6.529295
N31	0.26291206	13.145657	12.167022

Table S5. Electronic energies (EZ), enthalpy(H), and Gibbs free energies (G) for all stationary points (in Hartree), obtained at the M062X-D3/6-31+G** theoretical level.

Structures	[a]***ZPE***	E_z	[b]H_c	***H***	[c]G_c	***G***
1-enol	0.20132	-724.20560	0.21573	-723.98987	0.15976	-724.04584
1-keto	0.20071	-724.19242	0.21522	-723.97719	0.15872	-724.03370
2-enol	0.30503	-1216.1899	0.32863	-1215.8626	0.25020	-1215.94107
2-keto	0.30585	-1216.1899	0.32981	-1215.8602	0.24988	-1215.94009
3-enol	0.40325	-1632.9282	0.43557	-1557.2483	0.33552	-1632.59267
3-keto	0.40449	-1632.9293	0.43714	-1632.4926	0.33523	-1632.59407
4-enol	0.39894	-1557.6788	0.43049	-1557.2483	0.33113	-1557.34769
4-keto	0.39886	-1557.6462	0.43087	-1557.2153	0.33116	-1557.31500
5	0.42445	-1707.20146	0.45783	-1707.16808	0.35446	-1707.27145
R_1(F)	0.39951	-2004.83938	0.43541	-2004.80348	0.32670	-2004.91220
R_1(Me)	0.50864	-1825.00909	0.54643	-1824.97130	0.43551	-1825.08221
R_1(OMe)	0.52379	-2050.54306	0.56481	-2050.50204	0.44449	-2050.62236
R_2(H)	0.42866	-1430.54918	0.45651	-1430.52134	0.36663	-1430.61122
R_2(Me)	0.51142	-1548.36348	0.54477	-1548.33013	0.44204	-1548.43286
R_2(F)	0.40406	-1728.20387	0.43345	-1728.17448	0.34109	-1728.26684

a Zero-point correction energy;

b Thermal correction to Gibbs free energy;

c Gibbs free energy obtained using BP86-D3 and B3LYP-D3 with def2-TZVP basis set.

Table S6. Cartesian coordinates of all structures

1-enol form	X	Y	Z
C	-4.404434	-2.254705	0.272098
C	-3.881099	-3.523071	0.553176
C	-4.671188	-4.480414	1.169737
C	-5.999379	-4.205293	1.524722
C	-6.520416	-2.953947	1.249024
C	-5.744004	-1.962932	0.6229
C	-6.331125	-0.662994	0.352984
O	-3.609051	-1.357834	-0.321919
N	-5.672061	0.293603	-0.198275
C	-6.312996	1.512862	-0.480152
C	-5.597263	2.697795	-0.267441
C	-6.18352	3.926131	-0.531153
C	-7.489348	3.981145	-1.03636
C	-8.198132	2.799932	-1.279681
C	-7.611021	1.571738	-1.004864
C	-8.096357	5.254686	-1.320587
N	-8.584311	6.280059	-1.546481
H	-2.852157	-3.724968	0.275944
H	-4.24993	-5.458749	1.38042
H	-6.607787	-4.960691	2.00886
H	-7.54794	-2.717061	1.515466
H	-7.376468	-0.521719	0.661068
H	-4.117274	-0.519751	-0.441607
H	-4.585108	2.635689	0.11821
H	-5.637401	4.846709	-0.355001
H	-9.199888	2.850131	-1.692947
H	-8.145358	0.653648	-1.228145

1-keto form	X	Y	Z
C	-2.91807	0.917114	0.039819
C	-4.352934	1.096459	0.062384
C	-5.195239	0.041628	-0.129398
C	-4.716485	-1.289393	-0.36259
C	-3.374688	-1.517471	-0.3921
C	-2.443568	-0.448343	-0.191004
C	-1.076847	-0.700104	-0.222113
O	-2.121165	1.876051	0.205274
N	-0.171883	0.260675	-0.051292

C	1.218937	0.11078	-0.034332
C	2.000998	1.259735	-0.209056
C	3.383711	1.169347	-0.205788
C	4.002797	-0.074215	-0.028746
C	3.222097	-1.22011	0.159737
C	1.837859	-1.129338	0.165524
C	5.43757	-0.174724	-0.031555
N	6.592374	-0.25817	-0.035528
H	-4.720538	2.102067	0.236382
H	-6.268709	0.210314	-0.106583
H	-5.422949	-2.097662	-0.512155
H	-2.984683	-2.518283	-0.56611
H	-0.717344	-1.710745	-0.409494
H	-0.634189	1.195656	0.076092
H	1.513528	2.218392	-0.356597
H	3.989793	2.057672	-0.347013
H	3.705407	-2.178601	0.31542
H	1.250617	-2.021003	0.352865

2-enol form	X	Y	Z
C	-1.547137	0.389968	-0.546357
C	-0.991727	-0.89053	-0.361422
C	-1.817176	-1.935396	-0.015058
C	-3.205582	-1.769776	0.164173
C	-3.762697	-0.484772	-0.024804
C	-2.938054	0.603592	-0.381223
C	-3.529535	1.91358	-0.565633
C	-4.03514	-2.892089	0.532953
O	-5.068017	-0.263726	0.122305
O	-0.732669	1.383294	-0.875976
N	-5.310199	-2.781822	0.689402
C	-6.071064	-3.888284	1.104711
C	-7.347227	-4.053158	0.551816
C	-8.140542	-5.126133	0.928082
C	-7.67156	-6.037728	1.883006
C	-6.408928	-5.862709	2.459804
C	-5.614359	-4.791062	2.074584
N	-2.812121	2.937026	-0.878218
C	-3.429663	4.182782	-1.09409
C	-2.763373	5.331701	-0.650492
C	-3.32952	6.583939	-0.834702
C	-4.562572	6.701208	-1.48918
C	-5.218573	5.558881	-1.961115
C	-4.6528	4.305902	-1.766615

C	-5.148053	8.000531	-1.690046
N	-5.618616	9.04637	-1.849005
C	-8.494762	-7.147988	2.283969
N	-9.155221	-8.04268	2.606084
H	0.075461	-1.016053	-0.497557
H	-1.393629	-2.926605	0.129521
H	-4.609379	1.996377	-0.408674
H	-3.533438	-3.860703	0.659614
H	-5.500675	-1.132699	0.365371
H	-1.274976	2.21717	-0.965093
H	-7.695725	-3.334465	-0.182467
H	-9.123721	-5.264123	0.491338
H	-6.062854	-6.560317	3.215102
H	-4.651864	-4.633337	2.550785
H	-1.807554	5.222495	-0.148924
H	-2.822664	7.474869	-0.480041
H	-6.162031	5.659844	-2.486811
H	-5.144686	3.422517	-2.161298

2-keto from	X	Y	Z
C	-5.059277	-7.175998	-0.134002
C	-5.753228	-5.9769	-0.120189
C	-5.067619	-4.764061	0.025805
C	-3.674881	-4.765278	0.167936
C	-2.98108	-5.966642	0.14814
C	-3.665623	-7.177846	-0.002878
N	-5.830918	-3.589991	0.033307
C	-5.378585	-2.334599	0.015229
C	-6.189039	-1.217935	0.04299
C	-5.51651	0.081281	0.017293
C	-6.379875	1.26825	0.052898
C	-7.815335	1.101478	0.108081
C	-8.426562	-0.101886	0.129752
C	-7.649027	-1.339756	0.096911
O	-4.274704	0.176987	-0.029866
O	-8.208419	-2.449292	0.112346
C	-5.84422	2.53512	0.031992
N	-4.528756	2.803552	-0.021255
C	-3.916795	4.057238	-0.047965
C	-2.515112	4.086927	-0.089708
C	-1.837577	5.293782	-0.117427
C	-2.552698	6.49799	-0.103617
C	-3.950709	6.470876	-0.062684
C	-4.631787	5.262359	-0.035371

C	-2.940466	-8.419725	-0.018587
N	-2.358577	-9.420599	-0.03163
C	-1.855894	7.755168	-0.132435
N	-1.294963	8.767951	-0.155854
H	-5.591629	-8.113922	-0.248667
H	-6.833817	-5.970959	-0.227219
H	-3.124031	-3.842338	0.305191
H	-1.901955	-5.970588	0.258098
H	-6.856757	-3.655037	0.052167
H	-4.305037	-2.171922	-0.030567
H	-8.419387	2.007036	0.13252
H	-9.504867	-0.203945	0.17039
H	-6.518387	3.387597	0.060523
H	-3.943984	1.960728	-0.042942
H	-1.962812	3.152139	-0.099694
H	-0.75362	5.311374	-0.149608
H	-4.503797	7.403876	-0.05304
H	-5.714631	5.274268	-0.005671

3-keto form	X	Y	Z
C	-0.652938	-1.31353	-0.002425
C	0.803058	-1.209373	0.010242
C	1.490032	0.087666	0.036728
C	0.671079	1.295579	0.032108
C	-0.795508	1.243165	0.018529
C	-1.431788	-0.070074	0.010066
O	-1.47434	2.286895	0.010206
C	1.240621	2.549905	0.03828
O	2.733062	0.153937	0.0614
C	1.604622	-2.330122	-0.003777
O	-1.218964	-2.422686	-0.020341
C	-2.803291	-0.203075	0.007236
N	2.554448	2.795432	0.053691
C	3.166038	4.05547	0.03056
C	4.536327	4.120625	0.313559
C	5.195041	5.339642	0.305109
C	4.489636	6.513553	0.0149
C	3.122514	6.447457	-0.276046
C	2.463175	5.227147	-0.275838
C	5.168192	7.781516	0.008701
N	5.714852	8.802147	0.004167
N	-3.670207	0.814	0.010087
C	-5.067539	0.716869	0.032887
C	-5.805529	1.867669	-0.272059

C	-7.190722	1.831703	-0.267421
C	-7.85725	0.640019	0.041229
C	-7.119996	-0.507091	0.355875
C	-5.733215	-0.470561	0.359732
C	-9.294773	0.594933	0.042527
N	-10.451952	0.557111	0.042893
N	1.154673	-3.588425	-0.03013
C	1.920356	-4.759992	-0.052367
C	1.229387	-5.978724	-0.064828
C	1.92209	-7.178127	-0.087937
C	3.321827	-7.175468	-0.098761
C	4.012451	-5.958617	-0.08655
C	3.32063	-4.756386	-0.064005
C	4.048184	-8.416307	-0.124309
N	4.63372	-9.414929	-0.145846
H	0.563335	3.399564	0.041728
H	2.67879	-2.16826	0.007319
H	-3.202405	-1.213809	-0.011977
H	3.135714	1.952183	0.09048
H	5.078569	3.209678	0.548219
H	6.255411	5.389191	0.527549
H	2.580345	7.356161	-0.51415
H	-3.227463	1.738603	-0.016896
H	-5.284105	2.786676	-0.521874
H	-7.761638	2.721773	-0.508248
H	-7.639398	-1.424971	0.609144
H	0.131998	-3.660845	-0.035442
H	0.143558	-5.977625	-0.056347
H	1.384205	-8.11986	-0.09798
H	5.097046	-5.958336	-0.096087
H	1.410836	5.197461	-0.532455
H	-5.182293	-1.361729	0.636235
H	3.881553	-3.829655	-0.057354

R_2(H)	X	Y	Z
C	-0.549504	-1.307884	-0.01694
C	0.90522	-1.20798	-0.001345
C	1.595335	0.085645	0.034213
C	0.780483	1.294353	0.046222
C	-0.684943	1.246211	0.038907
C	-1.324118	-0.063636	0.01088
O	-1.362386	2.293412	0.048732
C	1.355767	2.548773	0.061982
O	2.840806	0.148811	0.05401

C	1.704255	-2.333685	-0.016246
O	-1.119153	-2.41732	-0.048102
C	-2.698642	-0.191477	0.001745
N	2.666551	2.793105	0.069149
C	3.277632	4.060423	0.049317
C	4.631445	4.140243	0.391293
C	5.280712	5.369597	0.384056
C	4.589693	6.531161	0.042244
C	3.242848	6.445617	-0.305514
C	2.584727	5.219468	-0.313289
N	-3.562736	0.823527	0.021541
C	-4.966194	0.723673	0.038599
C	-5.706513	1.860643	-0.301148
C	-7.096029	1.813824	-0.298012
C	-7.761272	0.635614	0.037883
C	-7.019426	-0.492407	0.383992
C	-5.628147	-0.454735	0.395826
N	1.254974	-3.588528	-0.049171
C	2.022434	-4.766341	-0.064484
C	1.331877	-5.982982	-0.066353
C	2.03052	-7.184525	-0.080735
C	3.424363	-7.189225	-0.093168
C	4.108557	-5.975205	-0.092492
C	3.420738	-4.765276	-0.079267
H	0.681231	3.400781	0.08034
H	2.778729	-2.173875	0.001934
H	-3.1013	-1.200471	-0.037571
H	3.2483	1.950333	0.094039
H	5.165877	3.236242	0.669374
H	6.331136	5.41801	0.653012
H	2.696062	7.339638	-0.588084
H	-3.119932	1.748043	0.014279
H	-5.185077	2.773452	-0.574978
H	-7.659634	2.701995	-0.565172
H	-7.525684	-1.411439	0.661943
H	0.232717	-3.660239	-0.060979
H	0.245481	-5.97855	-0.055544
H	1.480103	-8.119925	-0.081804
H	5.193856	-5.963402	-0.103876
H	1.545877	5.172521	-0.620534
H	-5.070872	-1.333347	0.701264
H	3.981035	-3.837464	-0.08268
H	5.096501	7.490216	0.040055
H	3.970876	-8.126069	-0.104157

H	-8.845342	0.598721	0.037069

R_2(Me)	X	Y	Z
C	-0.58262	-1.317694	0.05654
C	0.872063	-1.228225	0.049311
C	1.572799	0.05921	0.061098
C	0.767953	1.274184	0.059599
C	-0.69737	1.237569	0.053826
C	-1.347246	-0.066997	0.052983
O	-1.366573	2.290871	0.043429
C	1.354672	2.524158	0.062416
O	2.819502	0.112676	0.070809
C	1.660951	-2.361429	0.032104
O	-1.160065	-2.423893	0.068012
C	-2.723343	-0.183078	0.037541
N	2.667045	2.756089	0.065315
C	3.289851	4.018272	0.040819
C	4.637163	4.097527	0.39799
C	5.2922	5.324918	0.387822
C	4.628704	6.499971	0.029728
C	3.281229	6.400554	-0.332848
C	2.61373	5.181771	-0.34004
N	-3.57806	0.83918	0.028231
C	-4.982986	0.752498	0.024076
C	-5.71179	1.884711	-0.345439
C	-7.102278	1.846212	-0.36294
C	-7.800848	0.686085	-0.022305
C	-7.054728	-0.435127	0.35613
C	-5.665426	-0.41166	0.390563
N	1.207215	-3.61451	0.025712
C	1.99893	-4.77744	-0.04096
C	1.452474	-5.982367	0.403785
C	2.203302	-7.152591	0.345456
C	3.51028	-7.153636	-0.145954
C	4.037541	-5.938992	-0.596952
C	3.29763	-4.762903	-0.55839
H	0.688276	3.382753	0.074188
H	2.73869	-2.216394	0.036327
H	-3.134723	-1.189239	0.017687
H	3.240416	1.907417	0.095373
H	5.166742	3.196036	0.693408
H	6.340264	5.366645	0.672385
H	2.74144	7.296568	-0.629596
H	-3.126246	1.759223	0.007955

H	-5.183877	2.792103	-0.625205
H	-7.652768	2.737243	-0.65288
H	-7.572543	-1.346619	0.644695
H	0.186953	-3.692458	0.07363
H	0.441647	-5.997319	0.801554
H	1.762763	-8.081971	0.696633
H	5.045208	-5.913337	-1.00457
H	1.577893	5.143269	-0.659272
H	-5.124265	-1.291459	0.721501
H	3.723363	-3.847296	-0.954967
C	5.335329	7.831346	0.013069
H	5.432082	8.212726	-1.008621
H	4.783771	8.577962	0.592249
H	6.33916	7.74922	0.43649
C	-9.306681	0.63121	-0.065098
H	-9.652448	0.013141	-0.900309
H	-9.712471	0.199646	0.854547
H	-9.734529	1.62892	-0.188405
C	4.335258	-8.414772	-0.188313
H	4.799734	-8.549798	-1.169456
H	5.138484	-8.382405	0.55525
H	3.722002	-9.294627	0.020298

R2(F)	X	Y	Z
C	-0.569015	-1.31312	-0.044457
C	0.885737	-1.222227	-0.030858
C	1.584716	0.065655	0.008892
C	0.777901	1.27911	0.034885
C	-0.687174	1.240487	0.045579
C	-1.335061	-0.064694	0.010021
O	-1.357777	2.292169	0.074414
C	1.363805	2.528816	0.047171
O	2.83094	0.120627	0.023387
C	1.675026	-2.354473	-0.057593
O	-1.145263	-2.418475	-0.096983
C	-2.710601	-0.181966	0.016926
N	2.676608	2.760924	0.04267
C	3.287949	4.029052	0.001451
C	4.60019	4.148641	0.469771
C	5.247012	5.378803	0.44564
C	4.561959	6.480297	-0.043416
C	3.264201	6.388425	-0.521048
C	2.628522	5.150889	-0.509163
N	-3.564854	0.840178	0.064574

C	-4.968896	0.747583	0.108563
C	-5.714548	1.870194	-0.265609
C	-7.103821	1.83521	-0.238017
C	-7.730796	0.664605	0.159822
C	-7.016851	-0.459419	0.543459
C	-5.626165	-0.412746	0.528288
N	1.217924	-3.605984	-0.100884
C	2.003712	-4.774318	-0.0872
C	1.443016	-5.953401	-0.588226
C	2.174384	-7.135655	-0.590854
C	3.468989	-7.116791	-0.095402
C	4.046817	-5.964361	0.412718
C	3.30355	-4.787847	0.426915
H	0.699414	3.389353	0.074711
H	2.752935	-2.209602	-0.056601
H	-3.123621	-1.186747	-0.032781
H	3.252092	1.913185	0.066655
H	5.109229	3.274193	0.864001
H	6.262564	5.492884	0.807298
H	2.772733	7.271854	-0.912703
H	-3.113031	1.760877	0.063479
H	-5.199825	2.770381	-0.588162
H	-7.698844	2.694542	-0.525477
H	-7.548011	-1.348381	0.864546
H	0.19652	-3.676807	-0.147873
H	0.43259	-5.938138	-0.985678
H	1.758796	-8.059669	-0.976465
H	5.056182	-5.999434	0.806862
H	1.629164	5.063077	-0.920993
H	-5.064023	-1.277176	0.863692
H	3.735269	-3.892498	0.860379
F	5.180222	7.677246	-0.062509
F	4.186014	-8.258037	-0.100079
F	-9.077678	0.621149	0.182512

R1(OMe)	X	Y	Z
H	-2.836071	2.224038	0.012768
C	1.466515	-0.162807	-0.006203
C	0.861814	1.164584	-0.005023
C	-0.591593	1.352442	0.003065
C	-1.438652	0.165559	0.009065
C	-0.87464	-1.187461	0.008057
C	0.576981	-1.327431	0.000413
O	-1.617929	-2.191016	0.013406

C	-2.817698	0.252738	0.014927
C	1.62633	2.315741	-0.012392
O	2.707357	-0.304757	-0.012841
C	1.191575	-2.565042	-0.001405
N	-3.47908	1.419407	0.016369
C	-4.846963	1.701713	0.020557
C	-5.206399	3.053204	0.01947
C	-6.533268	3.456901	0.022967
C	-7.535158	2.487212	0.02769
C	-7.203317	1.126274	0.029033
C	-5.871715	0.726162	0.025533
C	-8.920792	2.872529	0.031033
N	-10.037485	3.179077	0.033522
N	0.512425	-3.721274	0.004013
C	0.950473	-5.047341	0.002514
C	-0.041677	-6.032765	0.00285
C	0.269096	-7.384503	0.002103
C	1.609228	-7.769626	0.000944
C	2.623146	-6.803535	0.000696
C	2.306948	-5.449331	0.00156
C	1.96558	-9.162993	0.000131
N	2.256352	-10.283889	-0.000479
N	2.967243	2.305801	-0.020628
C	3.896087	3.348824	-0.030666
C	5.245798	2.982586	-0.038373
C	6.260702	3.92763	-0.049337
C	5.924378	5.280959	-0.052972
C	4.58061	5.675652	-0.045072
C	3.566102	4.724767	-0.033772
C	6.952802	6.286237	-0.065711
N	7.778492	7.098137	-0.076433
H	-3.389446	-0.665213	0.018284
H	1.115496	3.269254	-0.01161
H	2.272532	-2.59989	-0.007659
H	-4.414861	3.796931	0.015527
H	-6.790768	4.509559	0.021923
H	-7.999575	0.392807	0.032909
H	-0.505739	-3.56675	0.009332
H	-1.080947	-5.717252	0.003614
H	-0.515438	-8.132226	0.002348
H	3.655717	-7.128604	-0.000009
H	3.343342	1.346965	-0.020329
H	5.492541	1.924927	-0.035772
H	7.300441	3.622161	-0.055285

H	4.346107	6.732337	-0.048159
O	-1.08908	2.498228	0.00442
O	-5.484238	-0.571813	0.026553
O	3.239595	-4.46688	0.001855
O	2.249123	5.041673	-0.025496
C	-6.483626	-1.577719	0.029648
H	-7.105579	-1.507343	0.928448
H	-7.110033	-1.50838	-0.866134
H	-5.945976	-2.524557	0.028908
C	1.882829	6.411719	-0.027455
H	2.266146	6.918788	0.864564
H	2.250038	6.911908	-0.930054
H	0.794215	6.42432	-0.017658
C	4.609451	-4.833392	0.002615
H	4.858375	-5.410277	0.899704
H	4.85967	-5.409325	-0.89472
H	5.16377	-3.896284	0.003495

R1=F	X	Y	Z
C	-0.626243	-1.318708	-0.053476
C	0.825302	-1.162472	-0.0517
C	1.462586	0.159123	-0.050005
C	0.602116	1.338481	-0.055046
C	-0.861015	1.229932	-0.056195
C	-1.450828	-0.105876	-0.064857
O	-1.577282	2.248789	-0.047149
C	1.123018	2.615391	-0.051234
O	2.703852	0.268293	-0.04079
C	1.671176	-2.251357	-0.039746
O	-1.151806	-2.448453	-0.042314
C	-2.816746	-0.29213	-0.067703
N	2.440311	2.8728	-0.04868
C	3.107972	4.09542	-0.026014
C	4.499423	4.076711	0.153855
C	5.242494	5.24499	0.180824
C	4.60208	6.479933	0.0273
C	3.217811	6.527062	-0.158839
C	2.500876	5.347452	-0.185168
C	5.362897	7.699871	0.056898
N	5.980869	8.678311	0.082
N	-3.703664	0.714405	-0.068693
C	-5.096375	0.639156	-0.031778
C	-5.814925	1.760438	0.405533
C	-7.199953	1.757375	0.449461

C	-7.905446	0.615168	0.054147
C	-7.212971	-0.511386	-0.398701
C	-5.833492	-0.478567	-0.441327
C	-9.342671	0.595716	0.107255
N	-10.499157	0.582117	0.1534
N	1.239	-3.521838	-0.034642
C	1.976571	-4.703787	0.006944
C	1.29407	-5.894159	0.298026
C	1.951109	-7.112447	0.345584
C	3.327894	-7.169565	0.101048
C	4.03059	-5.999367	-0.199646
C	3.350665	-4.798766	-0.245986
C	4.023465	-8.427049	0.155545
N	4.580032	-9.44091	0.202322
H	0.429921	3.448709	-0.047887
H	2.739467	-2.067026	-0.029603
H	-3.191304	-1.310256	-0.061593
H	3.009372	2.014979	-0.035874
H	4.991721	3.116909	0.277788
H	6.316378	5.207059	0.322988
H	2.692261	7.4663	-0.288789
H	-3.260537	1.642441	-0.037009
H	-5.261444	2.639677	0.720642
H	-7.738934	2.632399	0.79425
H	-7.731463	-1.404812	-0.727922
H	0.212341	-3.592499	-0.020694
H	0.227395	-5.844322	0.494461
H	1.405078	-8.019864	0.576286
H	5.094954	-6.010449	-0.405317
F	1.171313	5.42337	-0.381983
F	-5.188612	-1.559017	-0.916751
F	4.047419	-3.690716	-0.560044

R1=Me	X	Y	Z
C	-0.677161	-1.326279	-0.335321
C	0.776132	-1.213151	-0.319839
C	1.458224	0.084689	-0.287776
C	0.634686	1.286996	-0.252719
C	-0.83056	1.228261	-0.252938
C	-1.459999	-0.086787	-0.288709
O	-1.515347	2.269371	-0.225351
C	1.204143	2.543326	-0.243306
O	2.702893	0.156112	-0.29075
C	1.582116	-2.331295	-0.336313

O	-1.23489	-2.439662	-0.381991
C	-2.83239	-0.222297	-0.294509
N	2.516468	2.790849	-0.242081
C	3.107515	4.072129	-0.28739
C	4.195546	4.239487	-1.151807
C	4.838292	5.461915	-1.252651
C	4.381364	6.533694	-0.478722
C	3.310172	6.357317	0.400123
C	2.659789	5.129178	0.526284
C	5.025093	7.817867	-0.572583
N	5.541879	8.850893	-0.650397
N	-3.705894	0.78693	-0.251533
C	-5.110835	0.648937	-0.278658
C	-5.82283	1.526387	-1.104765
C	-7.203976	1.461927	-1.182456
C	-7.881843	0.501608	-0.42422
C	-7.170468	-0.357237	0.416496
C	-5.780171	-0.297194	0.51931
C	-9.316592	0.407456	-0.494127
N	-10.470274	0.330874	-0.552205
N	1.155467	-3.596525	-0.363566
C	2.002842	-4.727337	-0.361242
C	1.707993	-5.759728	-1.258367
C	2.495258	-6.898788	-1.308589
C	3.594638	-7.002591	-0.4501
C	3.872784	-5.980276	0.459827
C	3.082733	-4.832845	0.535131
C	4.4314	-8.17348	-0.487493
N	5.103739	-9.115366	-0.5174
H	0.53435	3.399158	-0.258228
H	2.657608	-2.172491	-0.341606
H	-3.236461	-1.229505	-0.356839
H	3.101795	1.951293	-0.308295
H	4.51794	3.39836	-1.757793
H	5.676006	5.594781	-1.928082
H	2.991615	7.192191	1.017353
H	-3.276614	1.717977	-0.275205
H	-5.273211	2.249895	-1.698951
H	-7.756706	2.13643	-1.826838
H	-7.716544	-1.074159	1.022626
H	0.139896	-3.704809	-0.44049
H	0.862453	-5.647621	-1.930001
H	2.273362	-7.696775	-2.008349
H	4.710311	-6.093102	1.141871

C	1.565428	4.973367	1.553627
H	0.571029	5.144814	1.129512
H	1.571109	3.972024	1.992813
H	1.708434	5.699326	2.356509
C	-5.074242	-1.192525	1.508087
H	-4.741664	-2.130887	1.053028
H	-4.196412	-0.701666	1.936533
H	-5.753673	-1.447523	2.323951
C	3.379249	-3.800824	1.595794
H	4.033113	-3.004059	1.227433
H	2.462323	-3.333843	1.964782
H	3.884002	-4.275117	2.439861

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