Electronic Supplementary Material (ESI) for Materials Advances.

Unusual Redshift due to Selective Hydrogen Bonding Between Fluoride ion and Sensor Motif: A Naked Eye Colorimetric Sensor for Fluoride ions in the Aqueous Environment.

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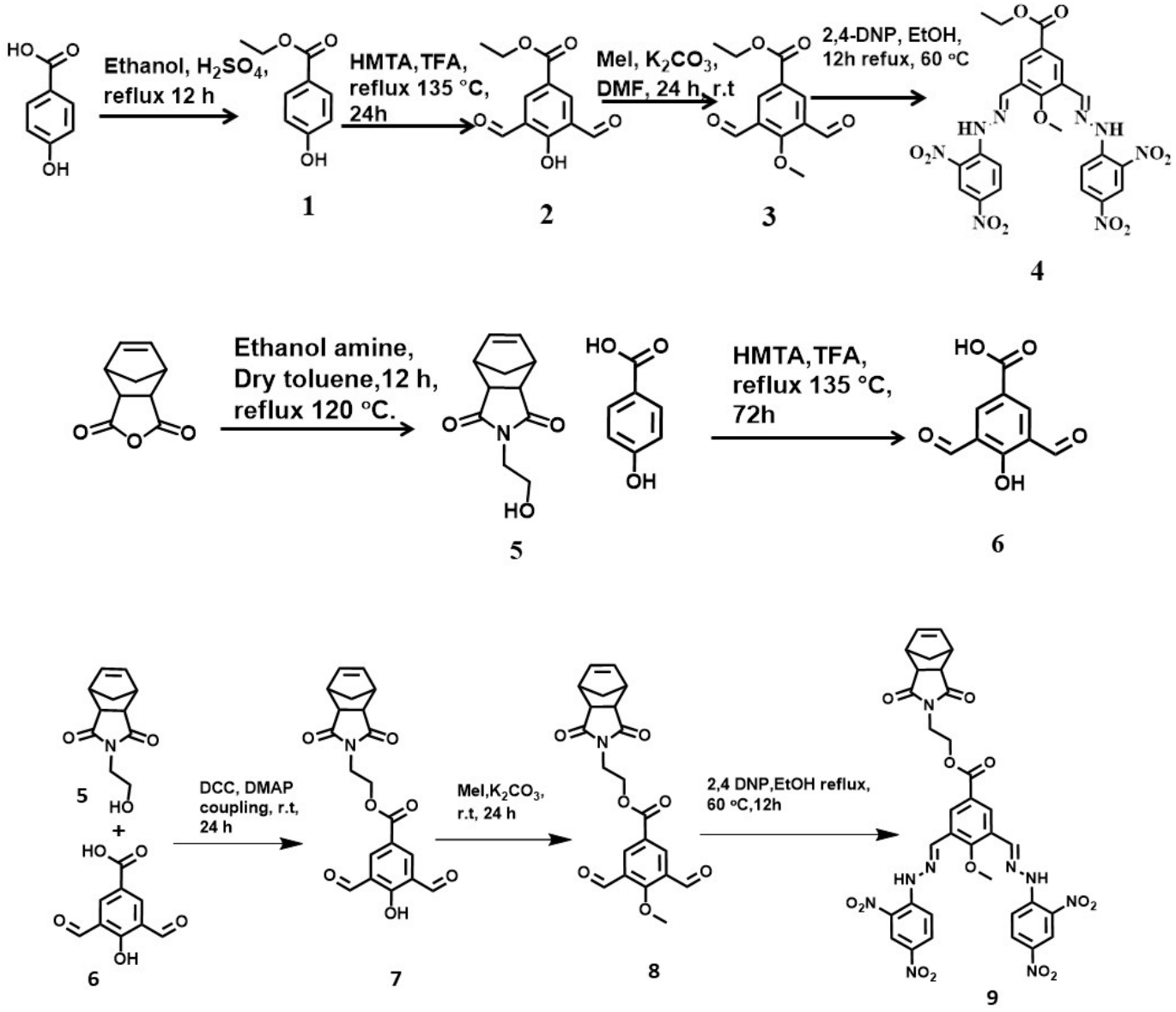
Table of content

29. Figure S29: Real sample analysis with compound 11 + Colgate toothpaste.

1.Synthetic scheme:



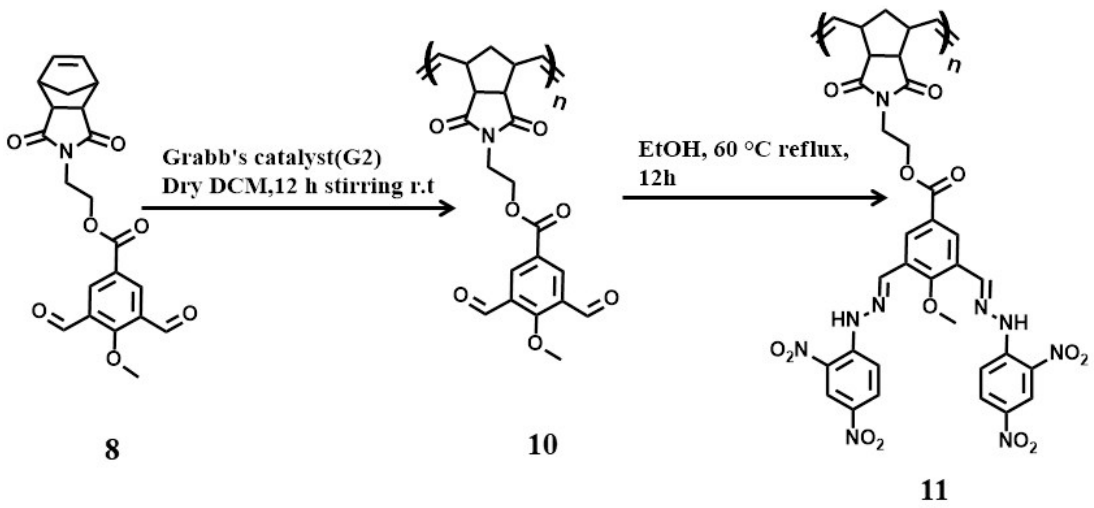


Figure S 1: synthetic scheme of the compound - 1 to11

2.Experimental procedure:

2.1. Materials used:

2,4-DNP, Ethanolamine, cis-5-norbornene-Exo-2,3-dicarboxylic acid, 4-hydroxybenzoic acid, Ethanol, concentrated sulfuric acid, glacial acetic acid, Methanol, Hexamethylenetetramine (HMTA), TFA, HCl, Sodium chloride, Chloroform-D, DMSO-d_6 from Sigma Aldrich, N, N-dimethylformamide, K_2CO_3, dry DCM, sodium bicarbonate, dry toluene, Ethyl acetate, Sodium hydroxide, Methyl iodide, dicyclohexylcarbodiimide (DCC), Tris-HCl buffer (pH 7.4), Grubbs' catalyst second generation (G2) catalyst from Sigma Aldrich.

2.2. The Technique of characterization:

^{1}H NMR and ^{13}C NMR spectroscopy: The nuclear magnetic resonance spectroscopy was carried out in Bruker 500 MHz spectrometer and Zeol 400 MHz respectively using $CDCl_3$ and DMSO-d_6

as NMR solvent. ^{1}H NMR spectrum was calibrated against Tetramethylsilane as an internal standard.

Fourier Transform Infra-Red (FT-IR): FT-IR spectroscopy were obtained at FT-IR Parkin-Elmer spectrometer at the normal resolution of 12 cm^{-1}.

UV-vis spectroscopy: UV-Visible absorption spectroscopy was carried out on the U-400 spectrometer HITACHI UV-Vis spectrometer taking scanning range from 700 nm to 300 nm with scanning rate 500 nm min^{-1}.

2.3.1 Preparation of compound 1:

4-Hydroxybenzoic acid (4 gm, 29.629 mmol) was dissolved in ethanol and a catalytic amount of glacial acetic acid was added to the reaction mixture. Then washed magnetic stirrer was added to the reaction mixture and the whole reaction mixture was stirring at 60 ℃ for 12 hours then sodium bicarbonate solution (1M) was added to the Ethanolic reaction mixture to neutralize the acetic acid (by checking pH paper). The ester of 4-hydroxybenzoic acid was extracted by diethyl ether and was washed with a brine solution. Diethyl ether layer was collected and dried by anhydrous sodium sulfate and concentrated by Rotavapor to get compound 2. Yield 90%. ^{1}H-NMR (DMSO-d_6, 400 MHz) (δ ppm): 12 (s, 1H), 6.8(s, 2H), 7.8 (s, 2H), 4.2 (q, 2H), 1.2 (t, 3H). $^{13}CNMR$ (DMSO-d_6, 500 MHz): 16, 65, 117, 121, 132, 165, 167.

2.3.2 Preparation of compound 2:

Compound 1 (3 gm, 18.07 mmol) was dissolved in TFA (50 ml) then HMTA (10.409 gm, 72.2 mmol) was added to the reaction mixture. The whole mixture was refluxed at 135 ℃ for 24 hours. Then the whole mixture was poured into 1M HCl solution and the reaction mixture was heated at 100 ℃ for 2 hours at the stirring condition to get precipitate. The precipitate was filtered and washed with water to get pure compound as a pale yellow powder. Yield 93% ^{1}H NMR (DMSO-d_6, 400 MHz) (δ ppm): 12 (s, 1H), 10.2 (s, 2H), 8.5 (s, 2H), 4.2 (q, 2H), 1.2 (t, 3H). $^{13}CNMR$ (DMSO-d_6, 500 MHz) (δ ppm): 190, 160, 165, 138, 123, 122, 61, 13. HRMS(+M): 222.05(expected) 222.9787(experimental).

2.3.3 Preparation of compound 3:

Compound 2 (1 gm, 4.5 mmol) was dissolved in dry DMF (7ml), K_2CO_3 (621 mg, 4.5mmol) was added to the reaction mixture. Then the whole reaction mixture was stirred room temperature for 30 min. After that Methyl Iodide (0.416 ml, 6.696 mmol) was added to the reaction mixture. Then the whole reaction mixture was stirred at room temperature for 24 hours. After completion of the reaction (monitored by TLC), the whole reaction mixture was poured into distilled water for precipitation. The resultant precipitate was filtered out and washed with water several times to remove DMF and other impurities completely to get compound 4. After drying, the pure product was formed with an 80% yield. ^{1}HNMR ($CDCl_3$, 400 MHz) (δ ppm): 12 (s, 1H), 10 (s, 2H), 8.5 (s, 2H), 3.8 (q, 2H), 3.5 (s, 3H), 1.2 (t, 3H). ^{13}CNMR (DMSO-d_6, 500 MHz) (δ ppm): 186, 166, 165, 137, 122, 124, 63, 45, 14.

2.3.4. Preparation of compound 4:

2,4-DNPH (166 mg, 0.84 mmol) was dissolved in excess dry Methanol followed by the addition of a catalytic amount of Glacial Acetic Acid. Then the reaction mixture was heated at 60 ℃ temperature for 30 min. Then compound 3 (100 mg, 0.42 mmol) was dissolved in methanol and the solution was added to the above reaction mixture. Then the whole reaction mixture was refluxed at 60 ℃ for 18 hours. After completion of the reaction, the solvent was evaporated under reduced pressure and was purified by column chromatography (ethyl acetate: hexane). Yield 70%. ^{1}HNMR (DMSO-d_6, 400MHz) (δ ppm): 12 (b, 2H), 8-9 (aromatic proton), 3.5 (s, 3H), 2.1 (t, 3H).

HRMS(M-H): 595.12(expected), 595.1252(experimental)

2.3.5. Preparation of compound 5:

cis-5-norbornene-Exo-2,3-dicarboxylic anhydride (1 gm, 10.3 mmol) was dissolved in dry toluene (30ml) in a washed and well-dried round-bottomed flux. Then ethanolamine (0.62 ml, 10.3mmol) was added to the reaction mixture under inert and dried condition (N_2 atmosphere). Then the whole reaction mixture was stirring at r.t for three hours. After three hours the reaction mixture was put for the refluxing at 120 ℃ for 12 hours. After completion of the reaction, toluene was evaporated and the crude was dissolved in DCM. Then the organic layer was washed with 2N HCl solution (3

times), then with distilled water (2 times), the crude was washed with brine solution (2times). The organic part was dried over anhydrous sodium sulfate and condensed under reduced pressure. The Pure compound we got as white crystalline form. 90% Yield. ^{1}HNMR ($CDCl_3$ -400 MHz) (δ ppm): 6.3 (s, 2H), 3.8 (t, 2H), 3.7 (t, 2H), 3.2 (s 2H), 2.7 (s, 2H), 2.4 (1H), 1.3 (m, 2H), ^{13}C NMR (DMSO-d_6, 500 MHz) (δ ppm): 177, 137.5, 57, 47, 45, 42, 40.5. HRMS(M+Na):230.08(expected), 230.0847(experimental).

2.3.6. Preparation of compound 6:

4-hydroxycarboxylic acid (3 gm, 18.07 mmol) was dissolved in TFA (50 ml) then HMTA (10.409 gm, 72.2 mmol) was added to the reaction mixture. The whole mixture was refluxed at 135 ℃ for 72 hours. Then the whole mixture was poured into 1M HCl solution and the reaction mixture was heated at 100 ℃ for 2 hours at the stirring condition to get precipitate. The precipitate was filtered and washed with water to get pure compound as a pale yellow powder. Yield 83% ^{1}H NMR (DMSO-d_6, 500 MHz) (δ ppm): 8.3 (s, 2H), 10.2 (s, 2H), 11.5 (s, 1H), 13.52 (s, 1H), ^{13}C NMR (DMSO-d_6, 500 MHz) (δ ppm): 187, 166, 135, 122, 121.

2.3.7. Preparation of compound 7:

Compound 6 (500 mg, 2.577mmol) (was taken in a well-dried round-bottomed flux under the N_2-atmosphere and was dissolved with dried DMF (8ml), then to the reaction mixture DCC (530mg, 2.577mmol) and catalytic amount (10 mol %) DMAP was added. Then the whole reaction mixture was stirred at room temperature for 30 minutes. After 30 minute compound-5 (414mg, 2.0mmol) was added to the reaction mixture and maintaining inert and dried condition. Then the whole reaction mixture was stirring for 36 hours at room temperature. After completion of the reaction (monitoring by TLC), the reaction mixture was dissolved into ethyl acetate and the organic layer was washed with distilled water (3 times), then brine solution (3 times). Then the organic layer was dried over anhydrous sodium sulfate and was condensed under reduced pressure. Then the product was purified using column chromatography by ethyl acetate: hexane as the eluting solvent.Yield-80%. ^{1}H NMR (DMSO-d_6, 400 MHz) (δ ppm). 11.8 (s, 1H), 10.2 (s, 2H), 8.2(s, 2H), 6.2 (s, 2H), 3.8 (t, 2H), 3,7 (t, 2H), 3.2 (s, 2H), 2.6 (s, 2H), 1.3 (m, 2H).

2.3.8. Preparation of compound 8:

Compound 7 (1 gm, 4.5 mmol) was dissolved in dry DMF (7ml), K_2CO_3 (621.9 mg, 4.5 mmol) was added to the reaction mixture. Then the whole reaction mixture was stirred room temperature for 30 min. After that Methyl Iodide (0.416 ml, 6.696 mmol) was added to the reaction mixture. Then the whole reaction mixture was stirred at room temperature for 24 hours. After completion of the reaction (monitored by TLC), the whole reaction mixture was poured into distilled water for precipitation. The resultant precipitate was filtered out and washed with water several times to remove DMF and other impurities completely to get compound 8. Then the compound was purified by column chromatography eluting with ethyl acetate: hexane as the eluting solvent. Yield 80%. ^{1}HNMR ($CDCl_3$, 400 MHz) (δ ppm): 10.3 (s, 2H), 8.2 (s, 2H), 6.2 (s, 2H), 4 (s, 3H), 3.6 (t, 2H), 3.5 (t, 2H), 3.2 (s, 2H), 2.6 (s, 2H), 1.3 (m, 2H).

2.3.9. Preparation of compound 9:

2,4-dinitrophenyl hydrazine (100 mg, 0.504 mmol) was taken in a well-dried round-bottomed flux and was dissolved with ethanol (30 ml). Then a magnetic bar was put into the reaction mixture and the whole reaction mixture was heated at 60 ℃ for 30 min (the clear solution of 2,4-DNPH). After getting a clear ethanolic solution of 2,4-DNPH compound 8 1(00 mg, 0.252mmol) was added to the reaction mixture. Then the whole reaction mixture was incorporated for refluxing for 12 hours. After completion of the reaction, ethanol was evaporated under reduced pressure and the resulting crude was purified by column chromatography using ethyl acetate: hexane as eluent. Yield 60%. ^{1}HNMR ($CDCl_3$, 400 MHz) (δ ppm): 12.2 (s, 2H), 7-9 (aromatic proton, 5H), 6.3 (s, 2H), 4.8 (s, 3H), 3.6 (m, 4H), 3.2 (s, 2H), 2.6 (s, 2H), 1.3 (m, 2H). HRMS(M+H):758.18(expected), 758.0320(experimental).

2.3.10. Preparation of compound 10:

Dried compound 8 (200mg, 0.503mmol) was taken in a dried vial under inert condition. Then dried DMF (2ml) was added to the vial for dissolving compound 8 and Grabber's catalyst (G-2)

(20mg) was added to the reaction mixture. Then putting a magnetic bar into the reaction vial, and making the vial reaction condition inert (glove box) the whole reaction mixture was stirring for 12 hours room temperature. After 12 hours the reaction was quenched by ethyl vinyl ether and the final polymer was precipitated with diethyl ether. And then dialysis was done to get the pure monomer free precipitate with DMF. The formation of a new peak at 5.5 confirms the formation of the polymer.

2.3.11. Preparation of compound 11:

2,4-dinitrophenyl hydrazine (100 mg, 0.504 mmol) was taken in a well-dried round-bottomed flux and was dissolved with DMF (10ml). Then a magnetic bar was put into the reaction mixture and the whole reaction mixture was heated at 60 ℃ for 30 min (for complete desolvation of 2,4-DNPH). After getting a clear solution of 2,4-DNPH compound 10 (50mg polymer) was added to the reaction mixture. Then the whole reaction mixture was incorporated for refluxing for 20 hours. After completion of the reaction, the polymer was precipitated from diethyl ether and was dialysis in DMF to get pure polymer.

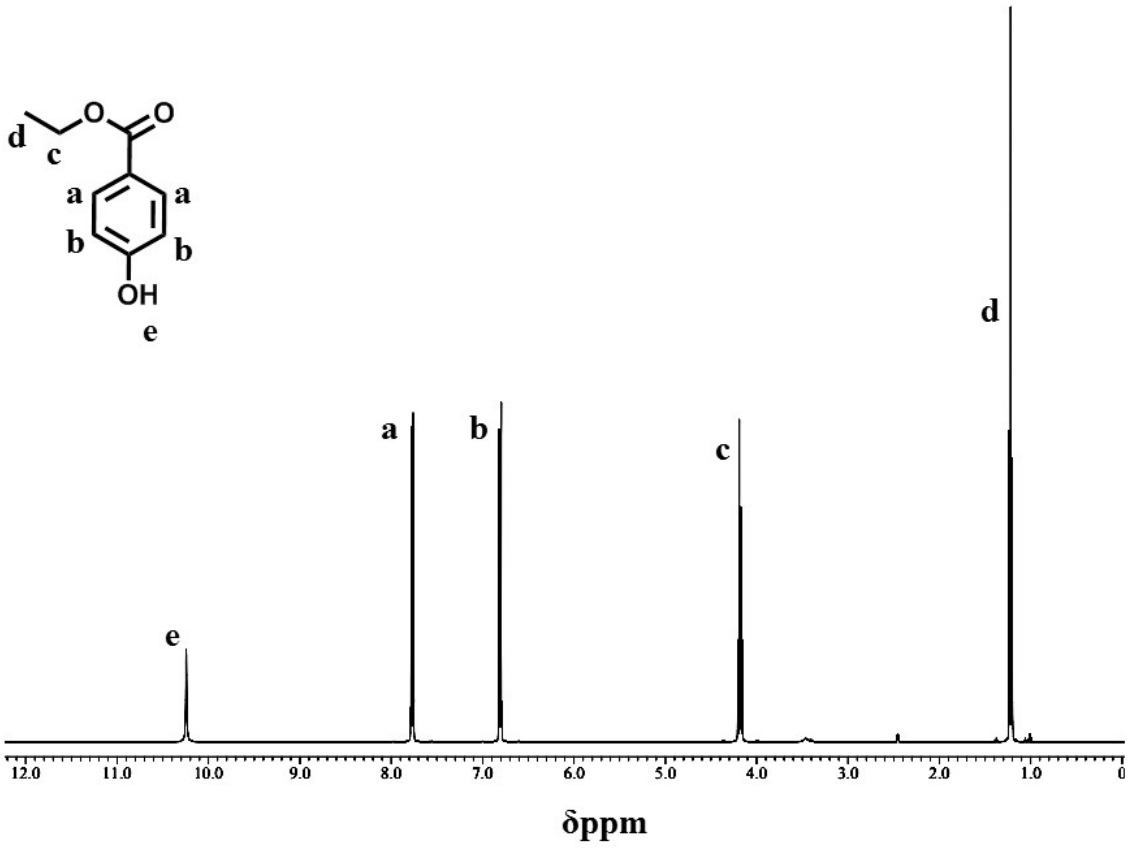


Figure S2: ^{1}H NMR spectroscopy of compound 1 in DMSO-d_6

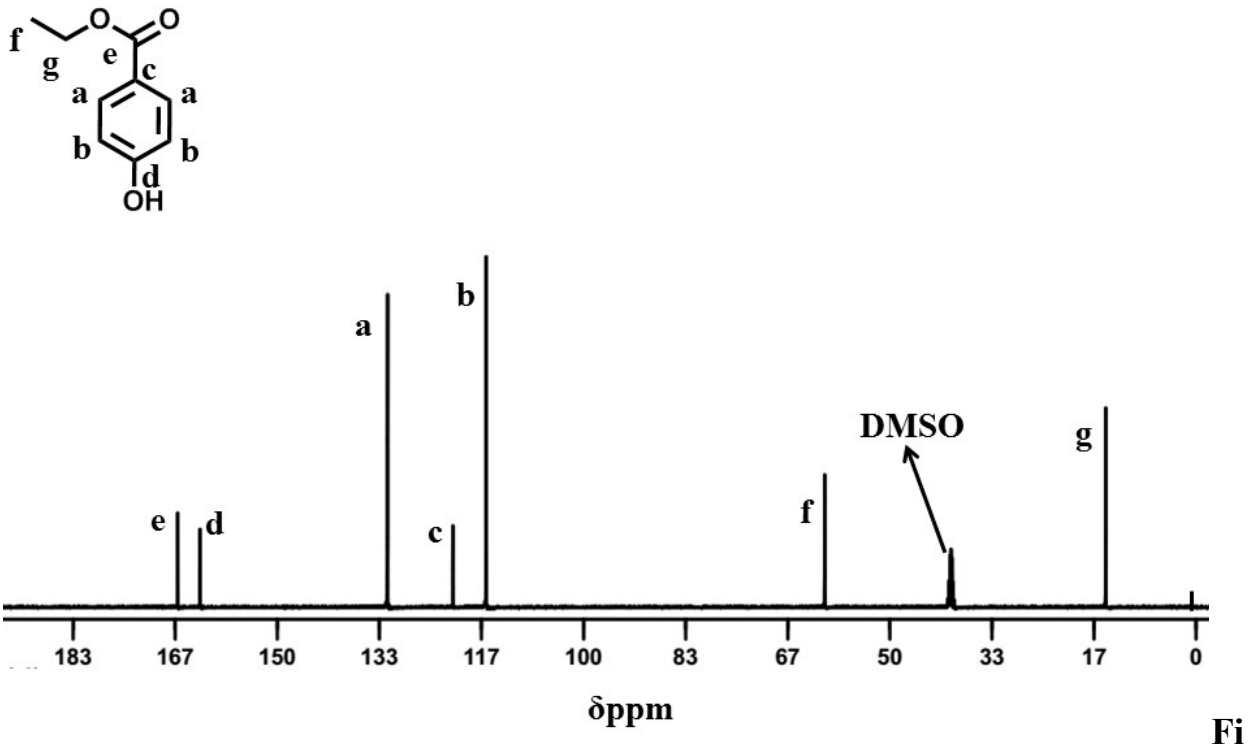


Figure S3: ^{13}C NMR spectroscopy of compound-1 in DMSO-d_6

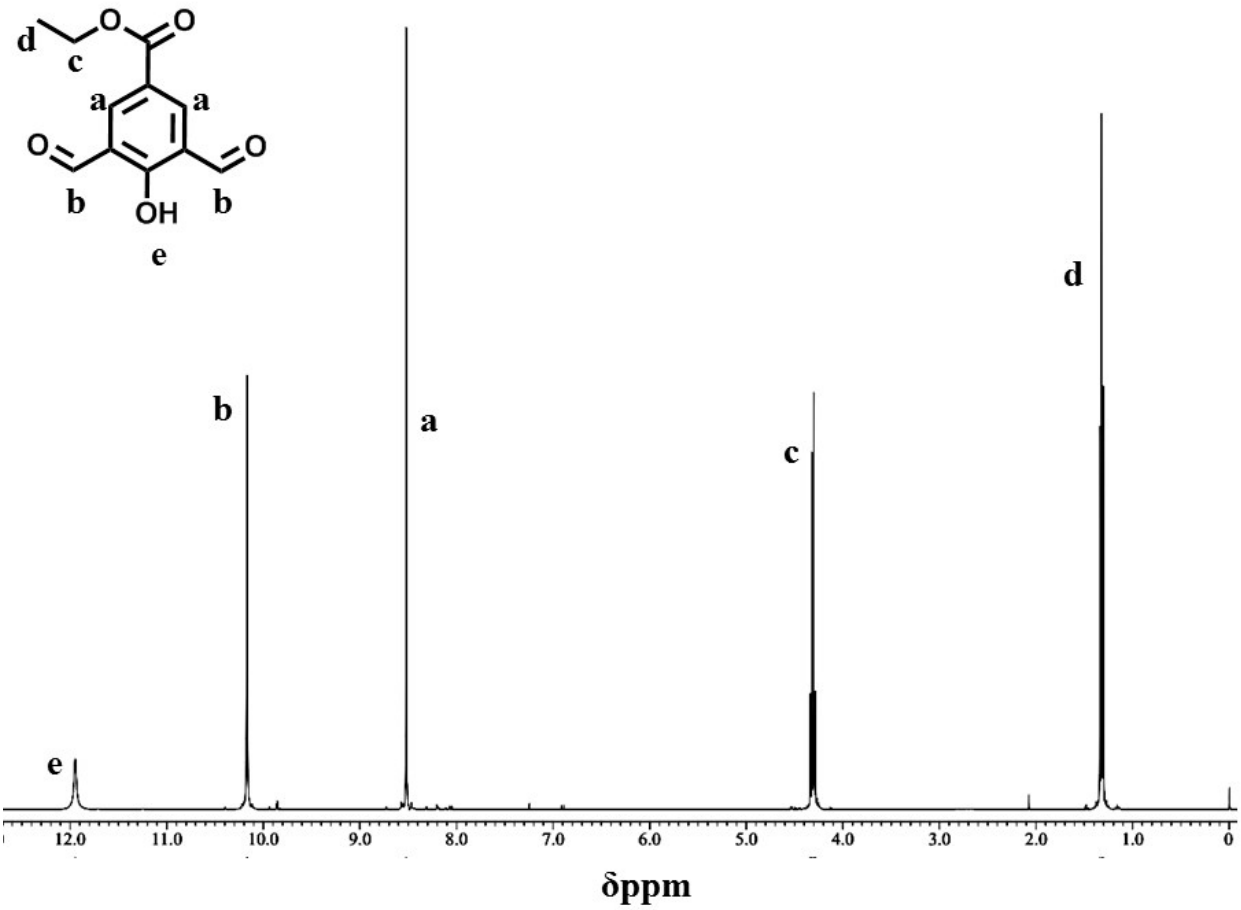


Figure S4: ^{1}H NMR spectroscopy of compound-2 in DMSO-d_6

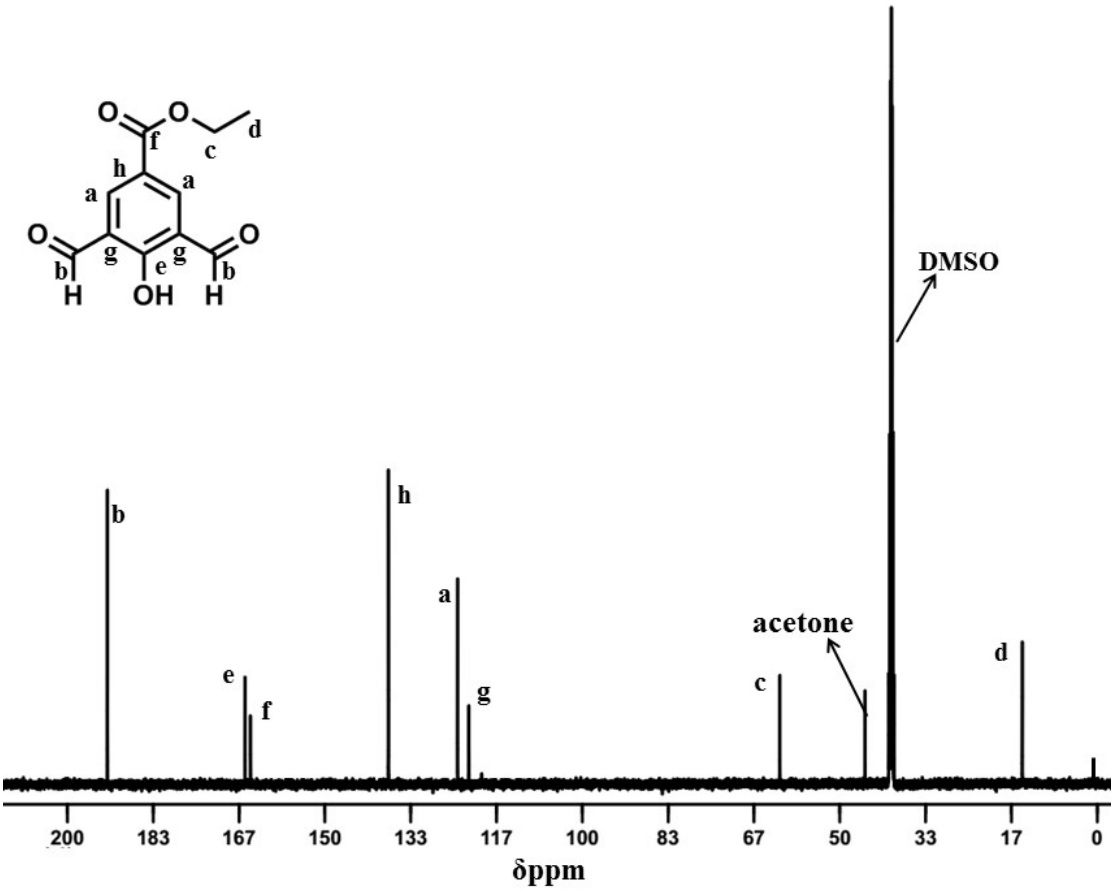


Figure S5: ^{13}C NMR spectroscopy of compound-2 in DMSO-d_6

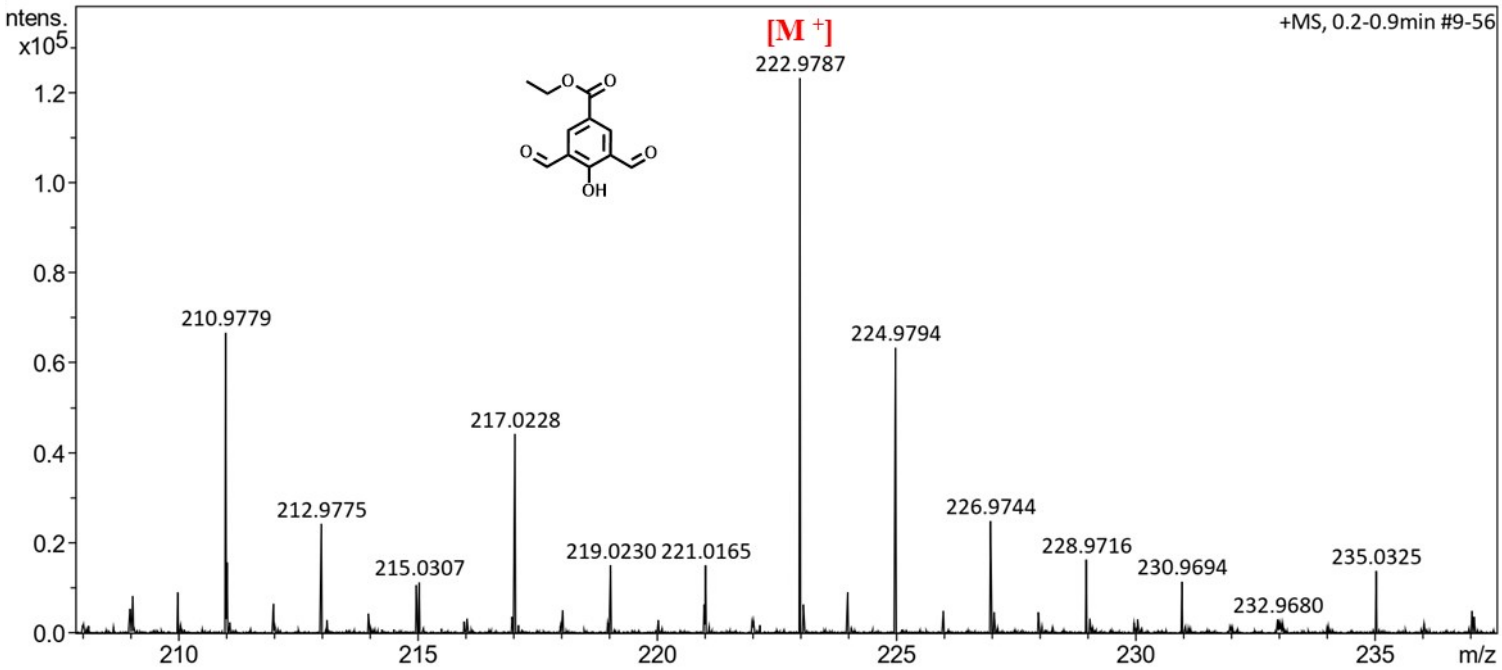


Figure S6: HRMS spectrum of compound-2 in methanol.

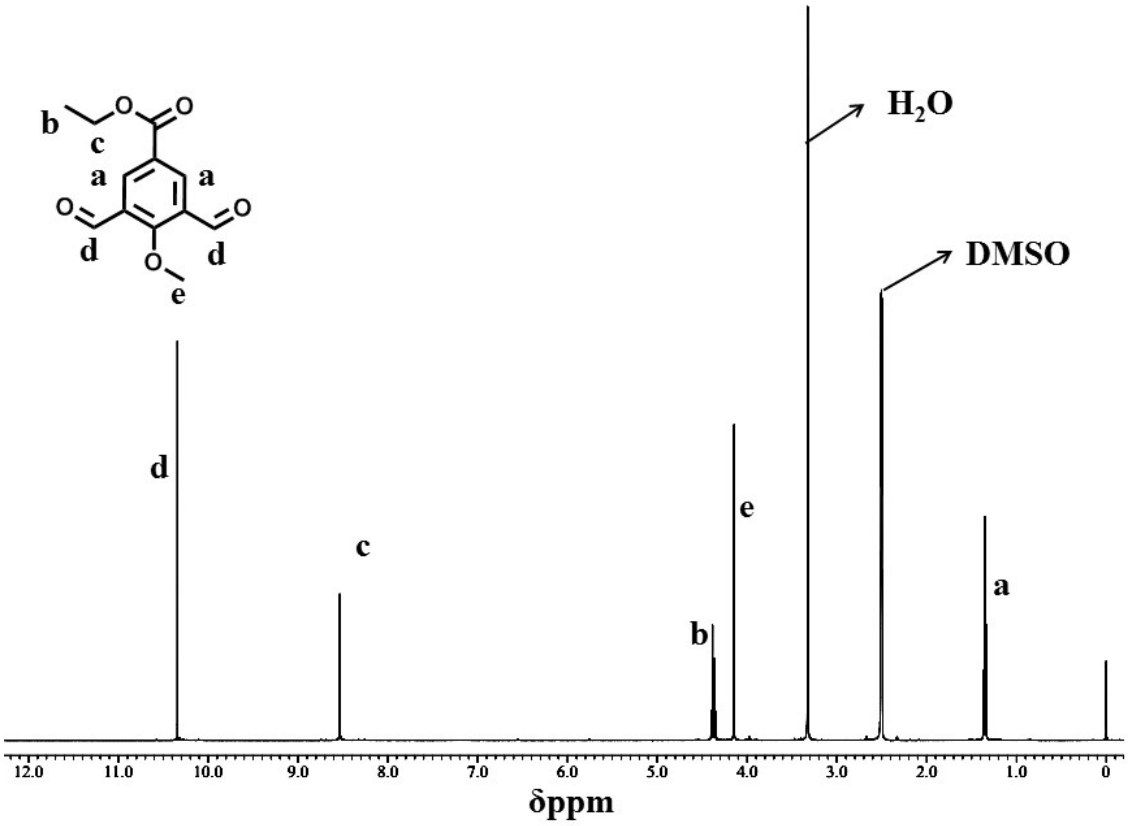
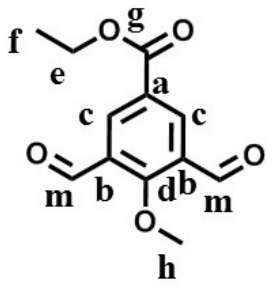


Figure S7: ^{1}H NMR spectroscopy of compound-3 in DMSO-d_6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O
g
O
e
a
c
c
O
O
m
b
d
b
m
O
h

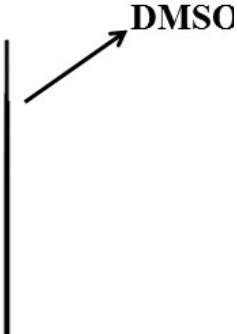

DMSO

Figure S8: ^{13}C NMR spectroscopy of compound-3 in DMSO-d_6

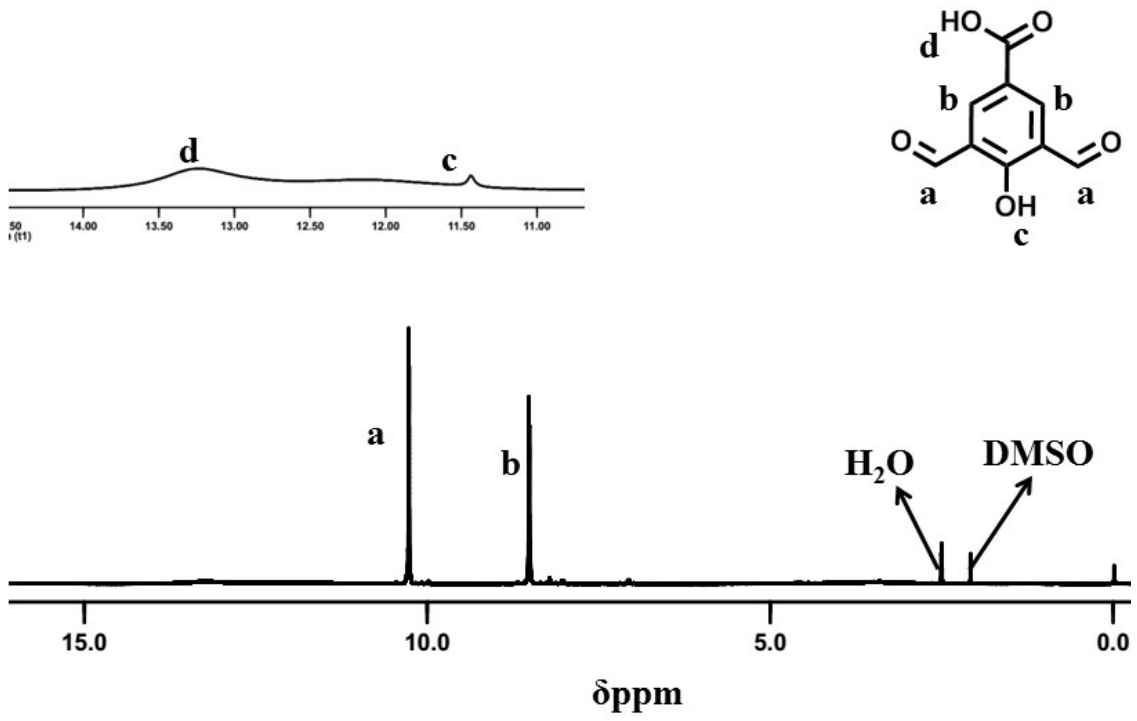


Figure S9: ^{1}H NMR spectroscopy of compound-6 in DMSO-d_6

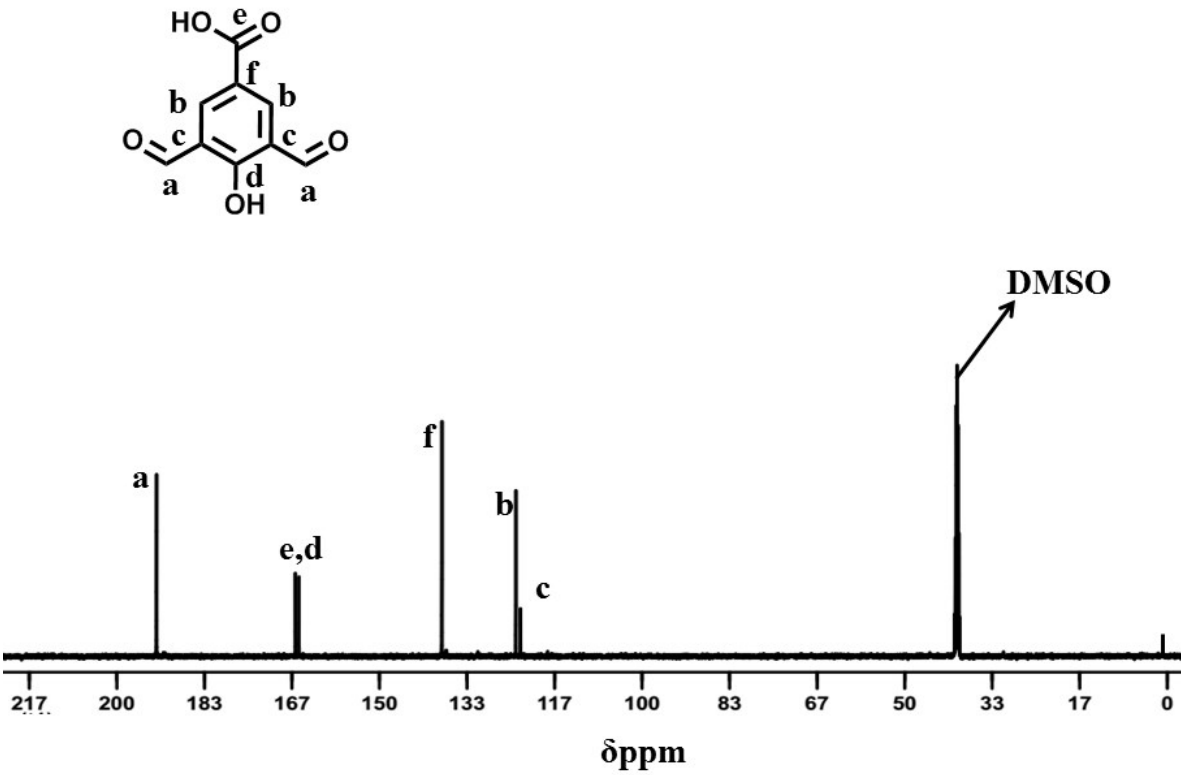


Figure S10: ^{13}C NMR spectroscopy of compound-6 in DMSO-d_6

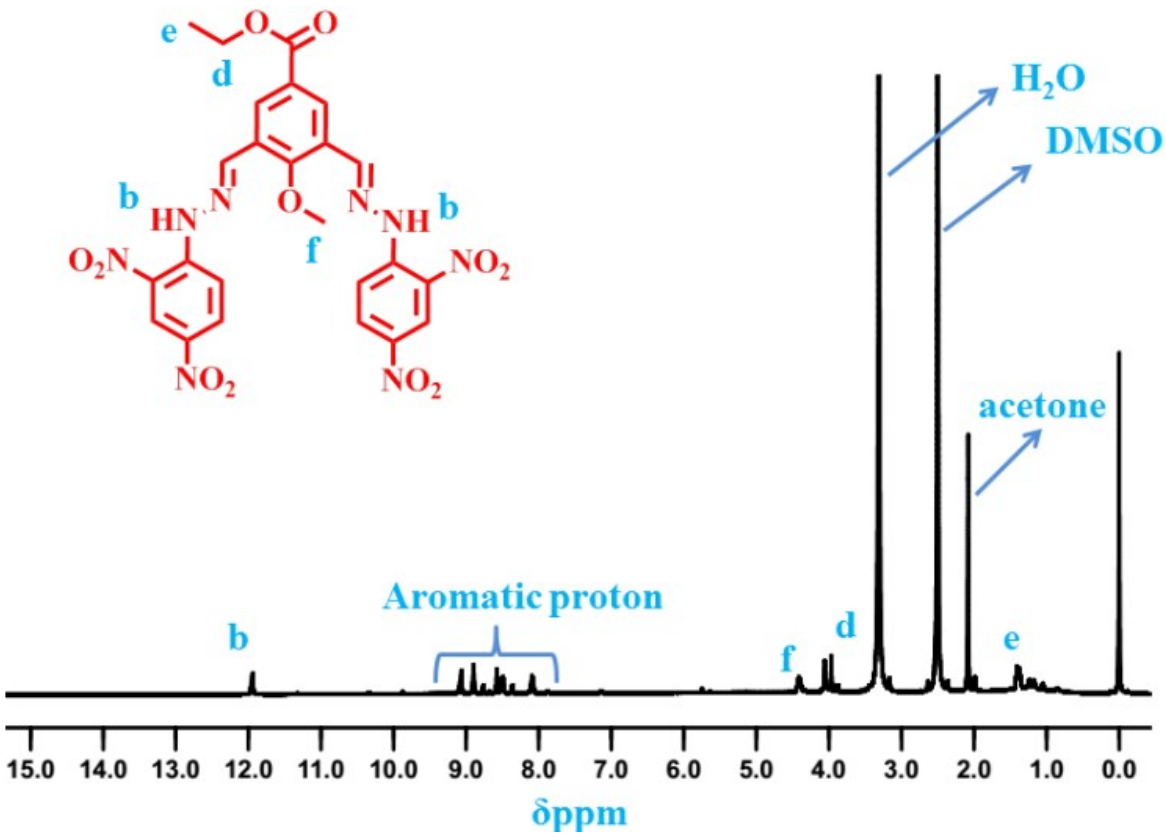


Figure S11: ^{1}H NMR spectroscopy of compound-4 in DMSO-d_6

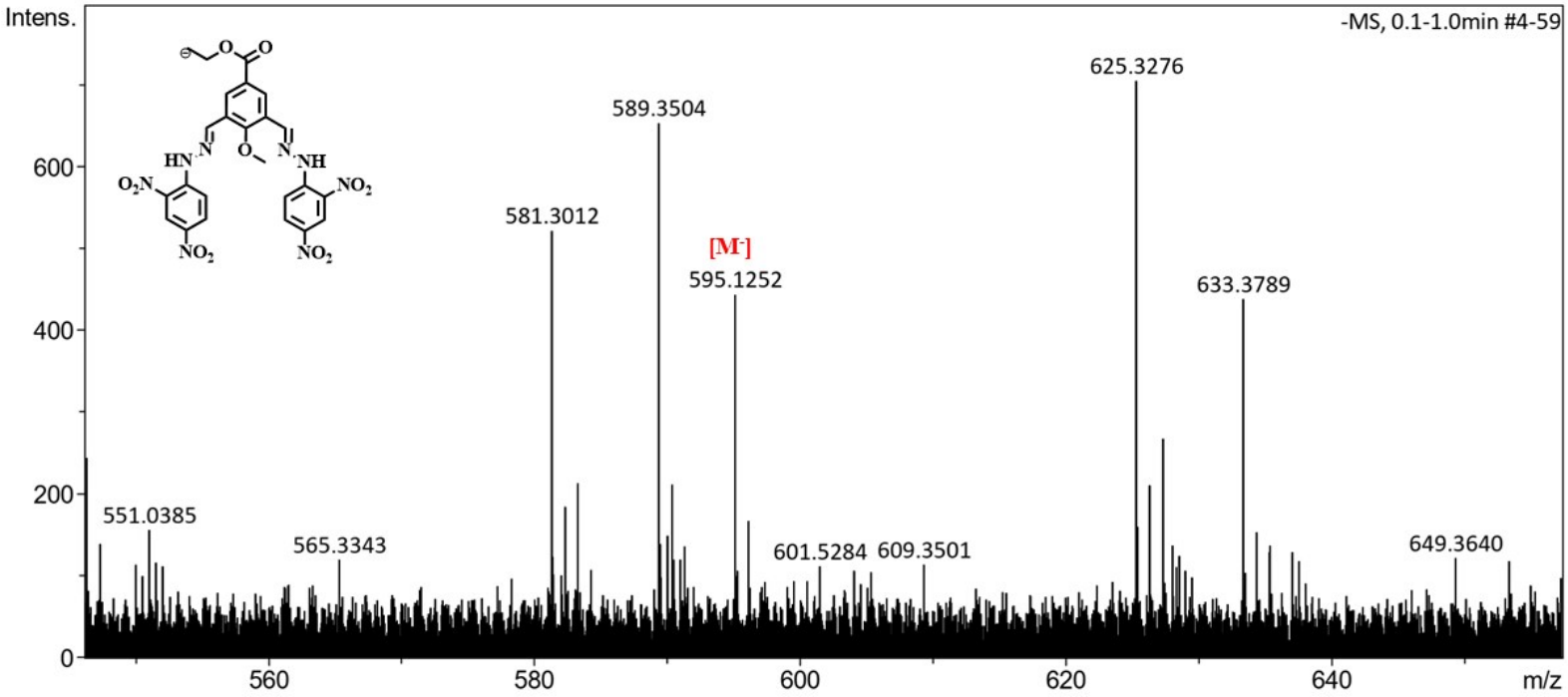


Figure S12: HRMS spectrum of compound-4 in methanol.

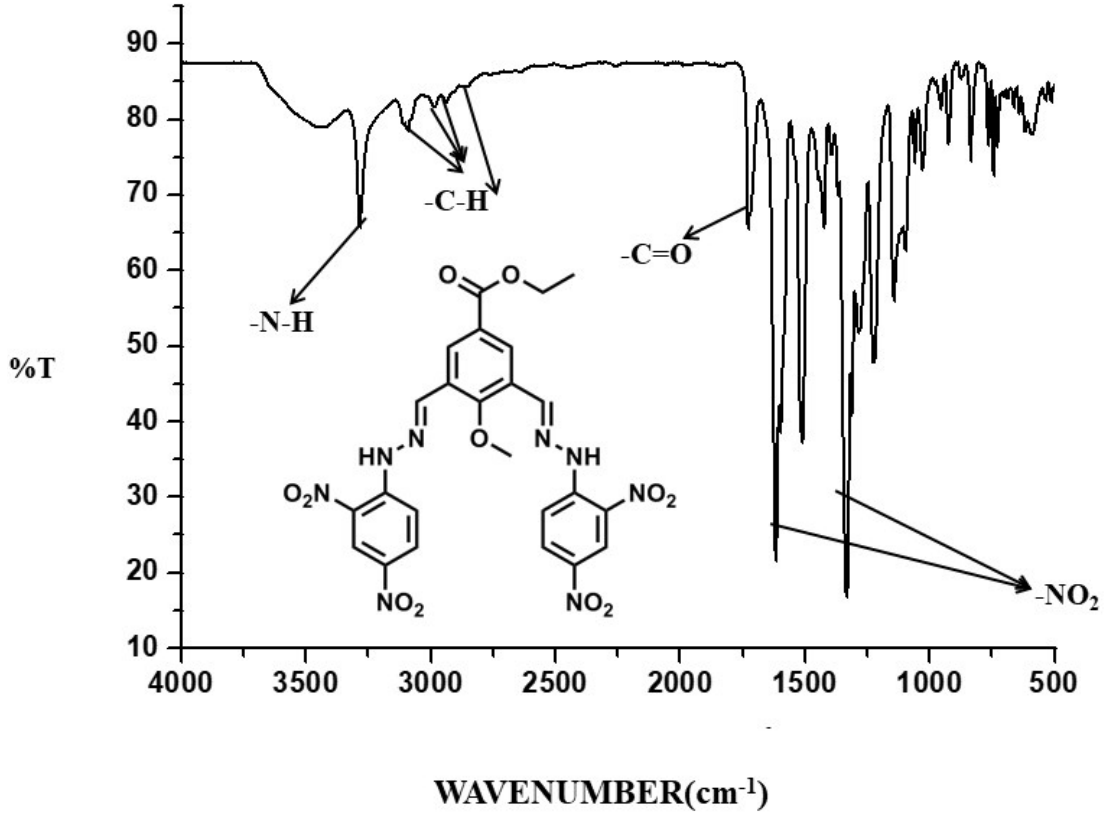


Figure S13: FTIR spectrum of compound-4.

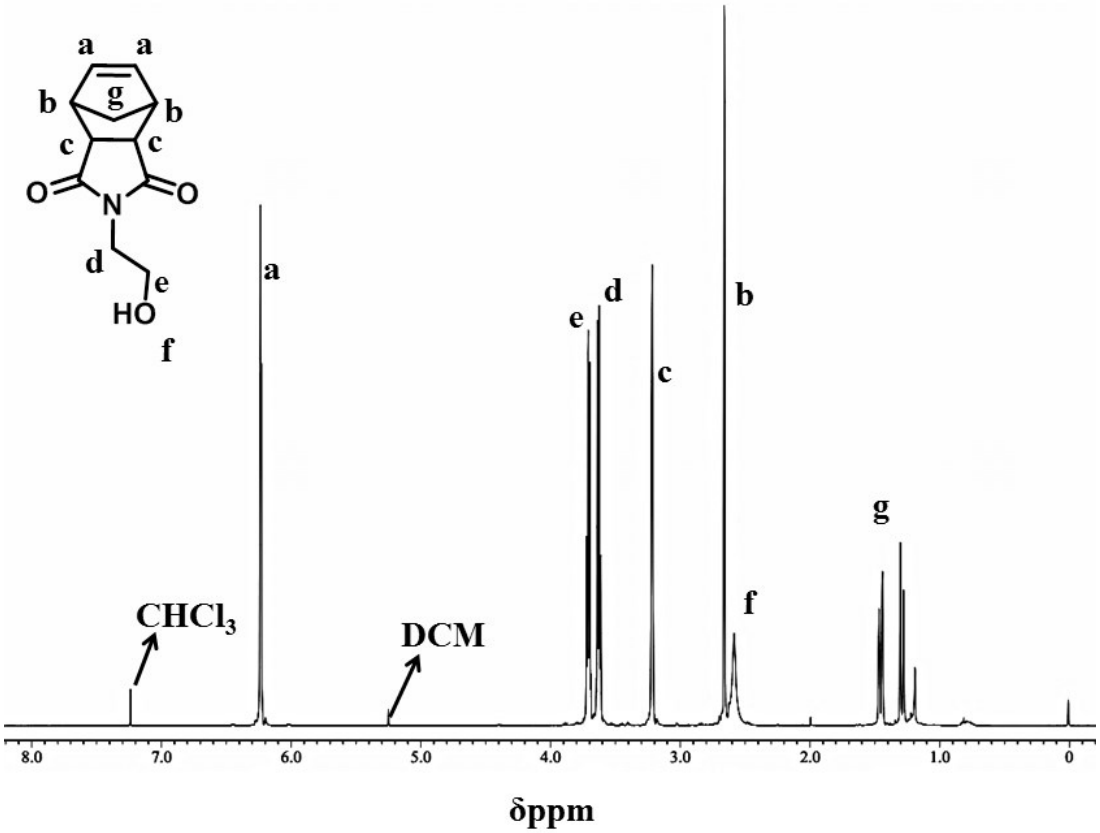


Figure S14: ^{1}H NMR spectroscopy of compound-5 in $CDCl_3$

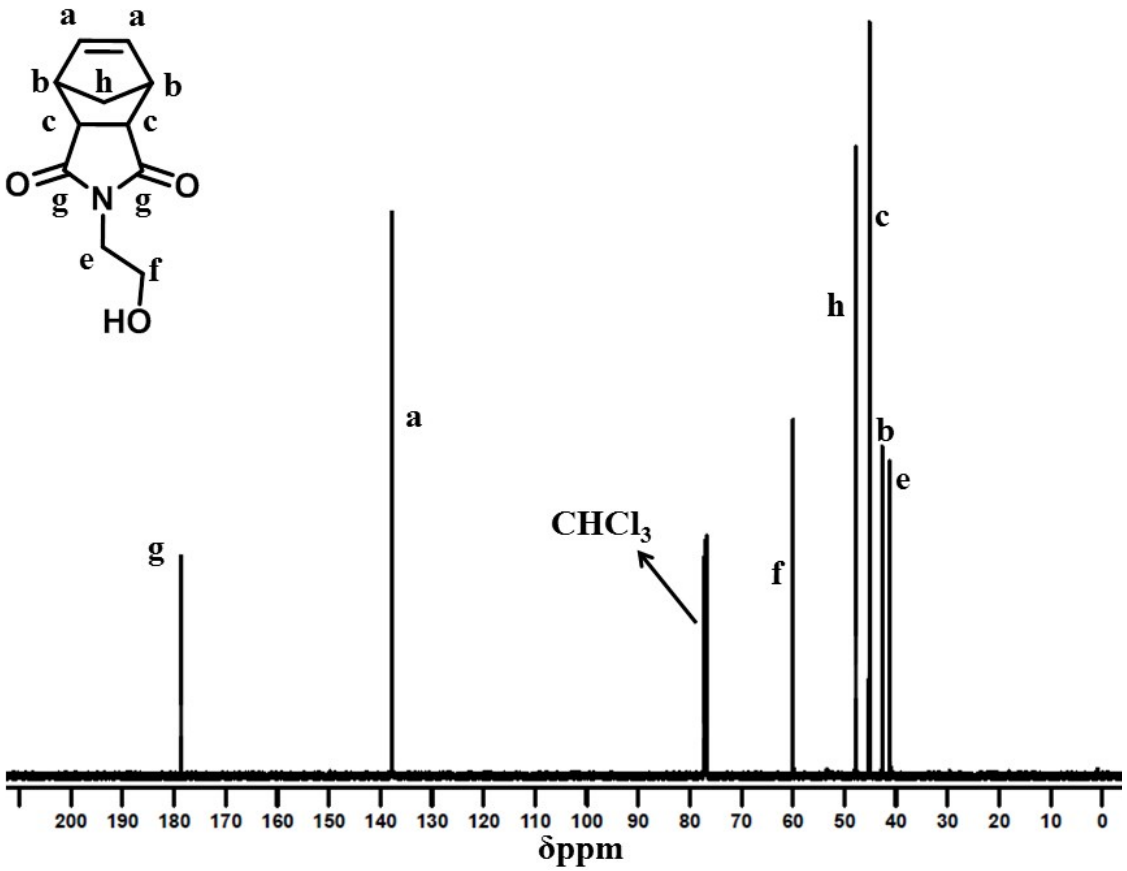


Figure S15: ^{13}C NMR spectroscopy of compound-5 in $CDCl_3$

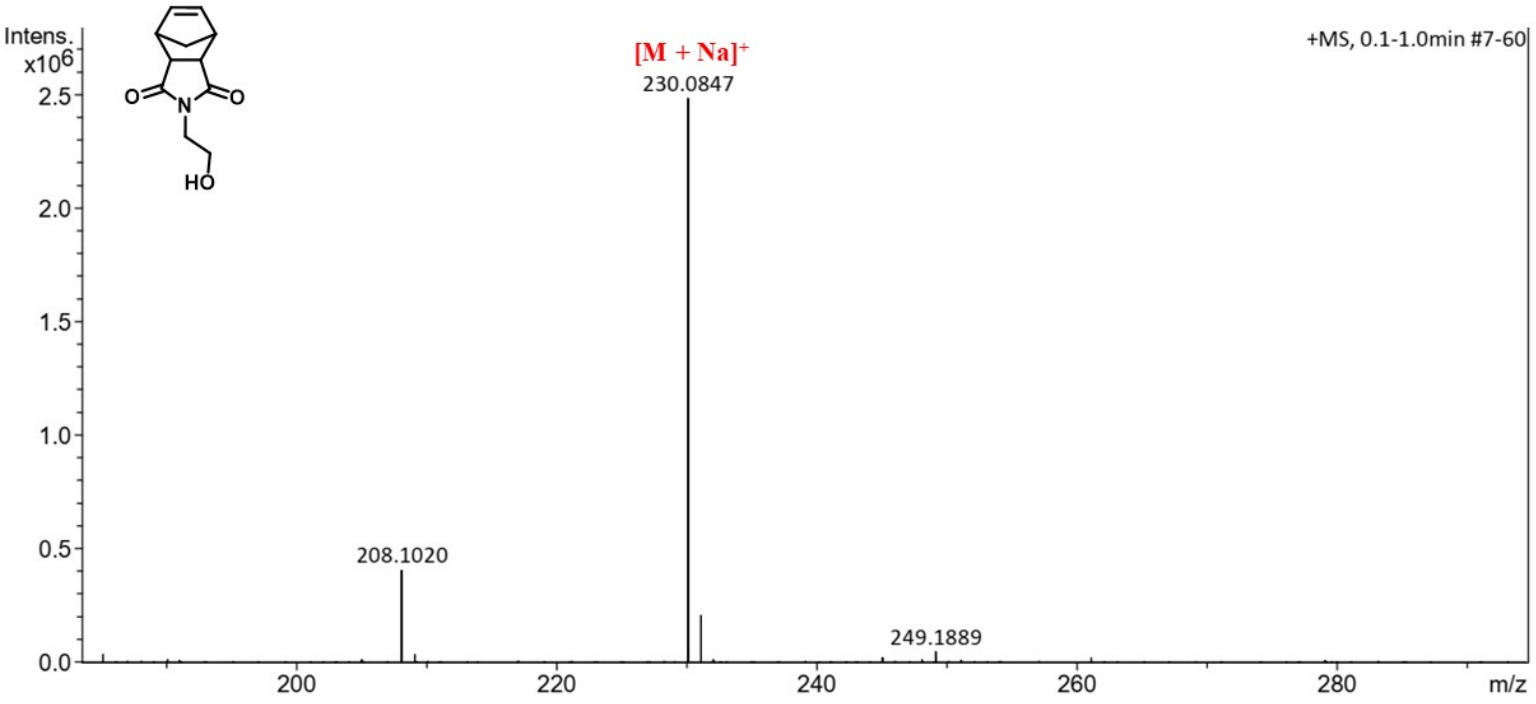


Figure S16: HRMS spectrum of compound-5 in methanol.

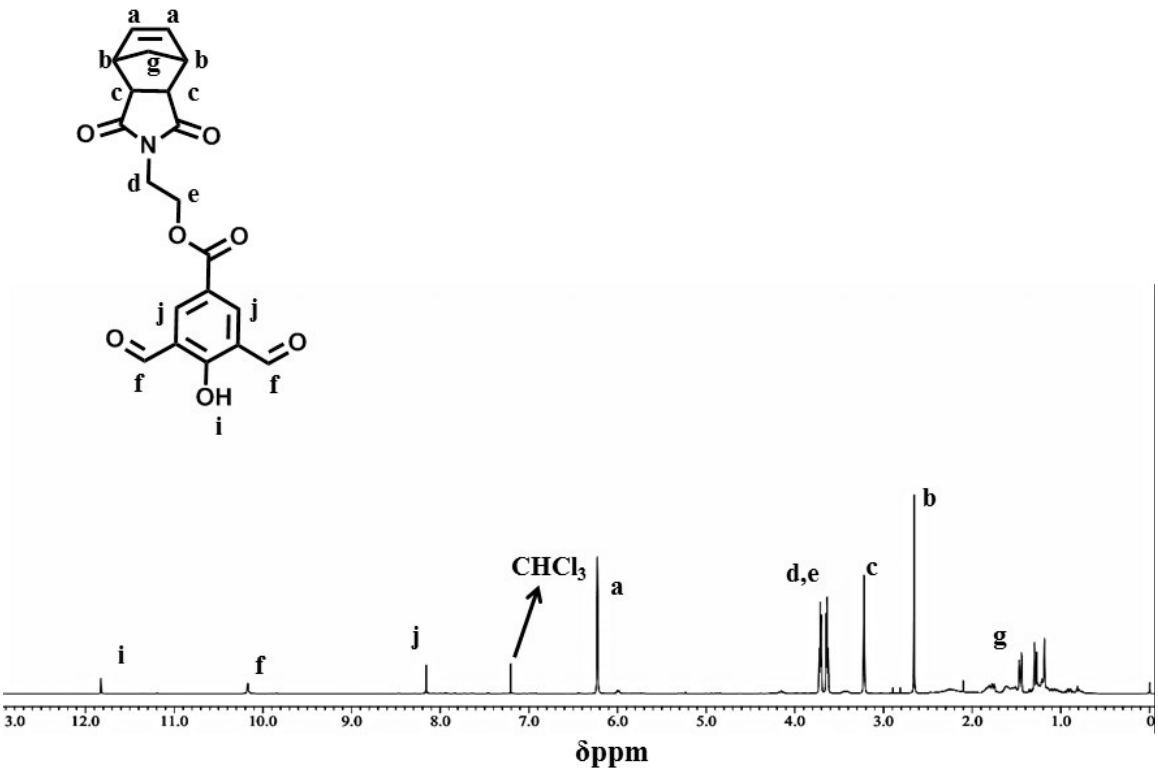


Figure S17: ^{1}H NMR spectroscopy of compound-7 in $CDCl_3$

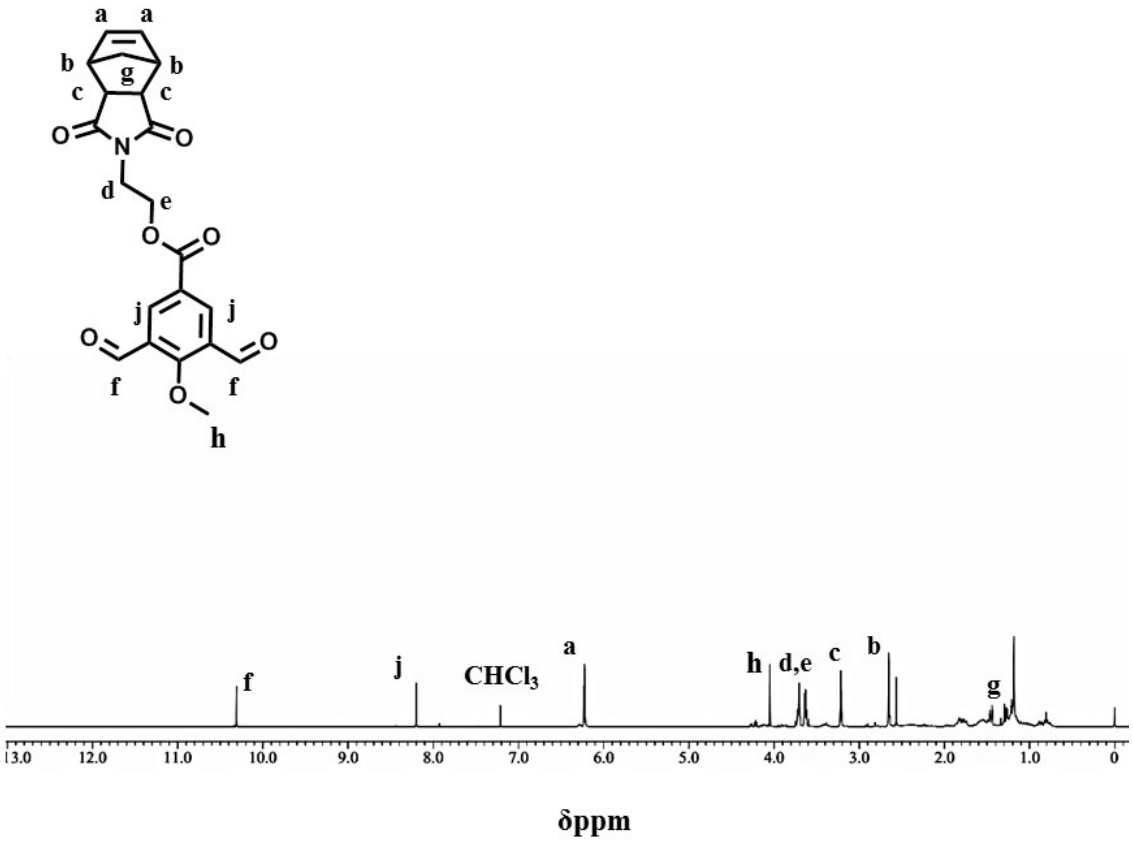


Figure S18: ^{1}H NMR spectroscopy of compound-8 in $CDCl_3$

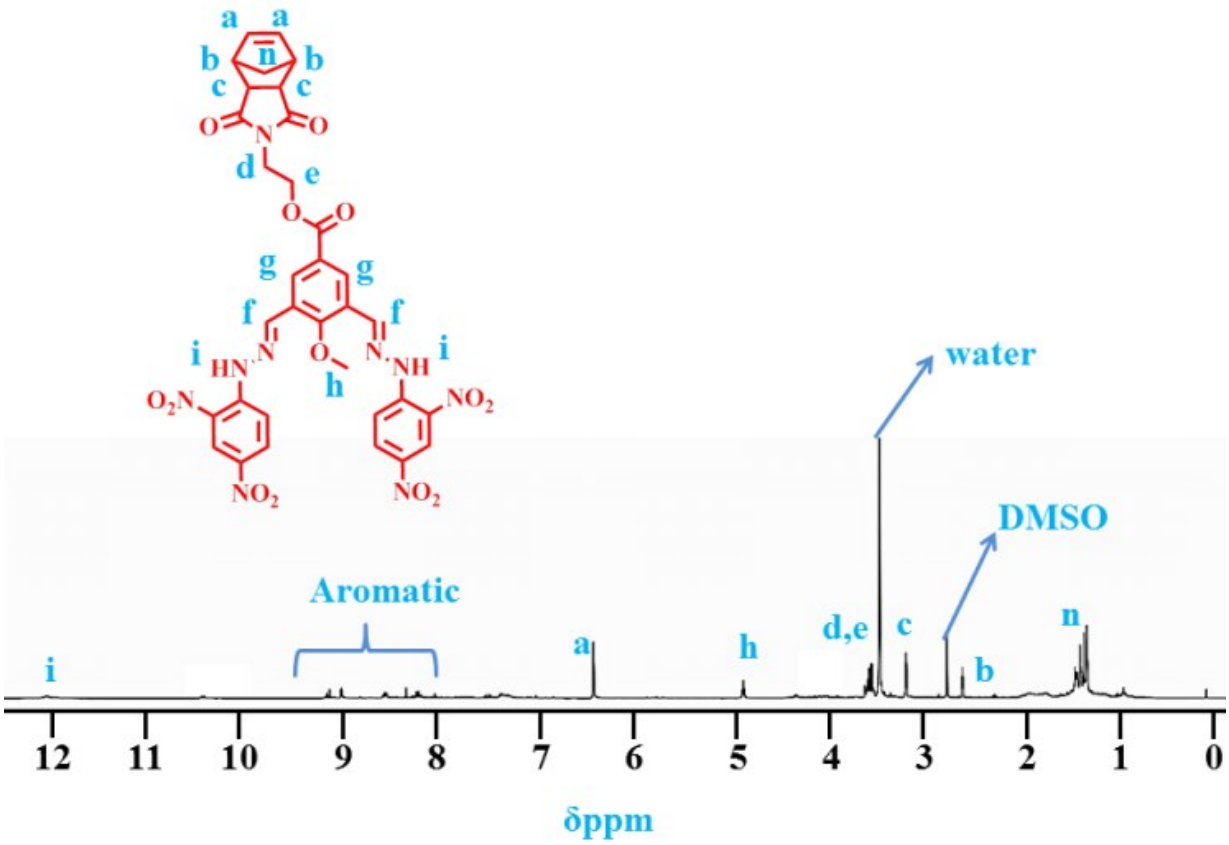


Figure S19: ^{1}H NMR spectroscopy of compound-9 in DMSO-d_6

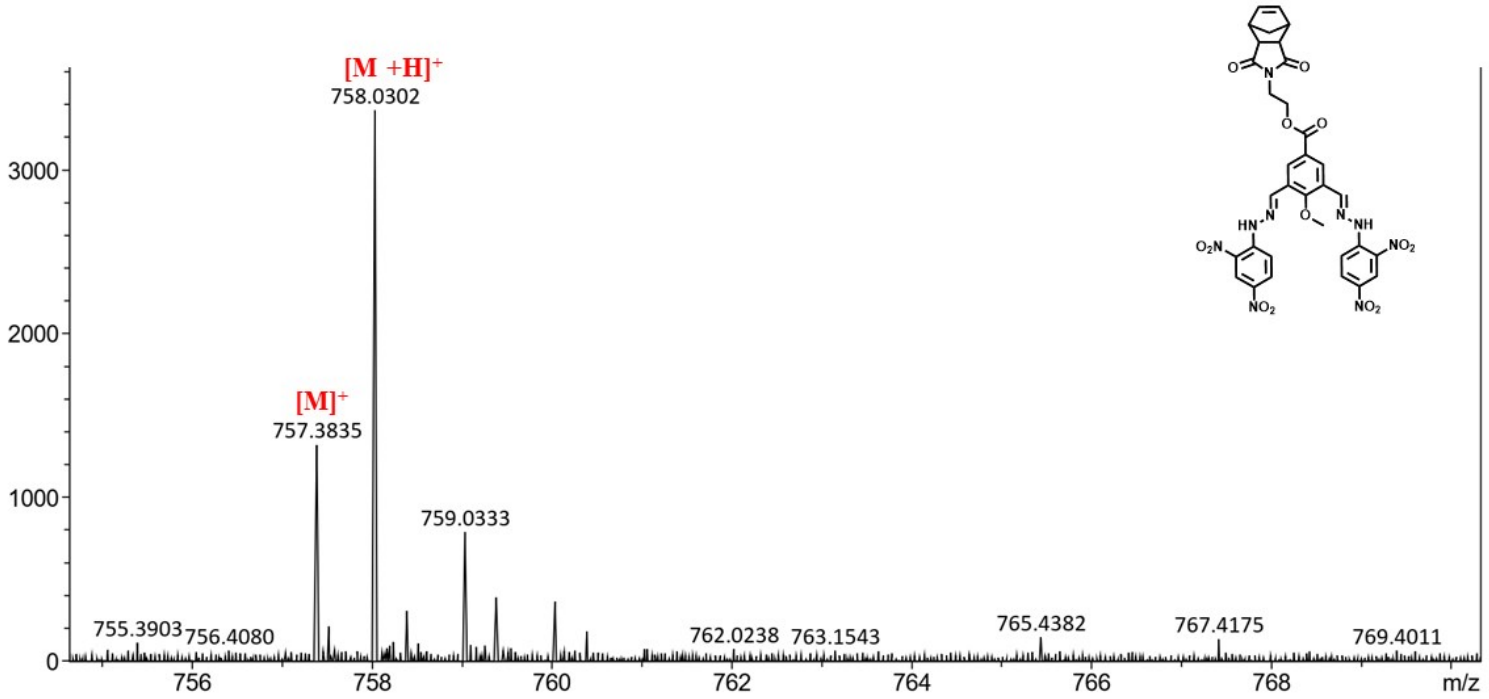


Figure S20: HRMS spectrum of compound-9 in methanol.

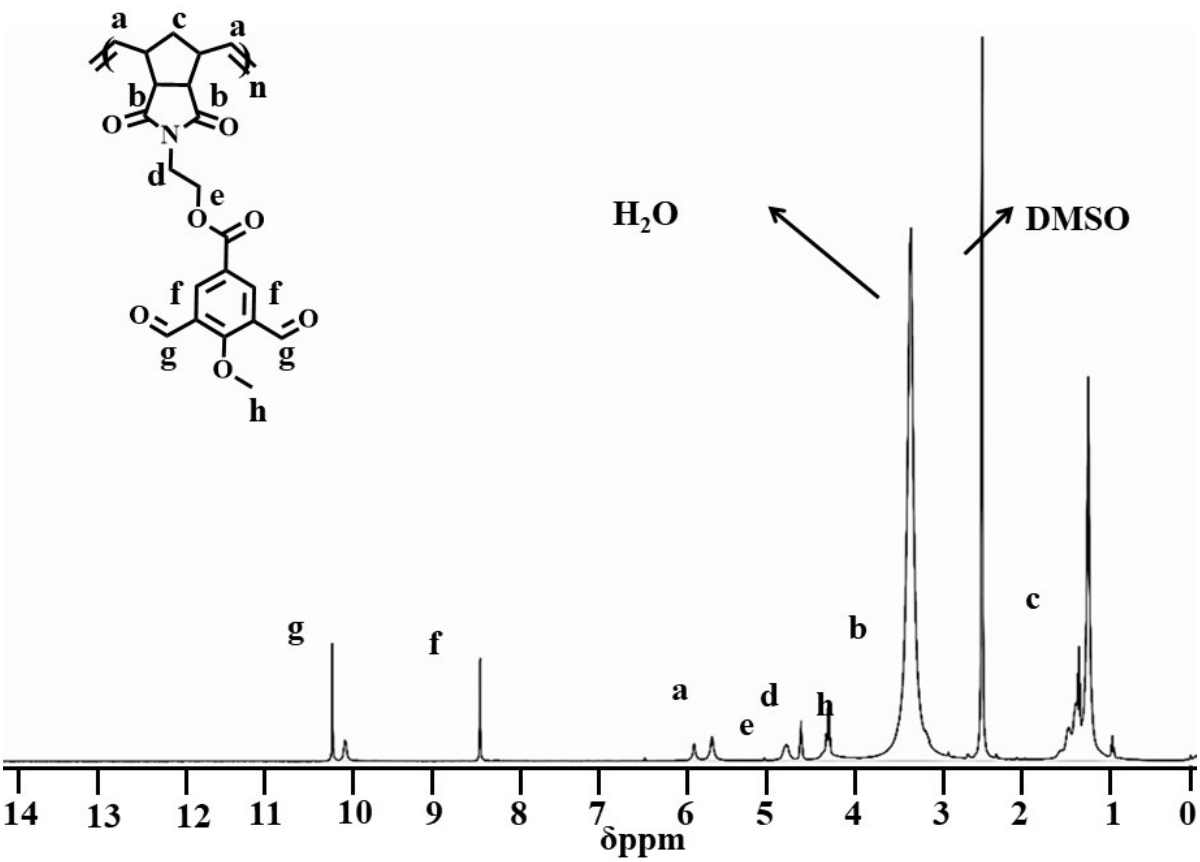


Figure S21:[1]H NMR spectroscopy of compound-10 in DMSO-d_6

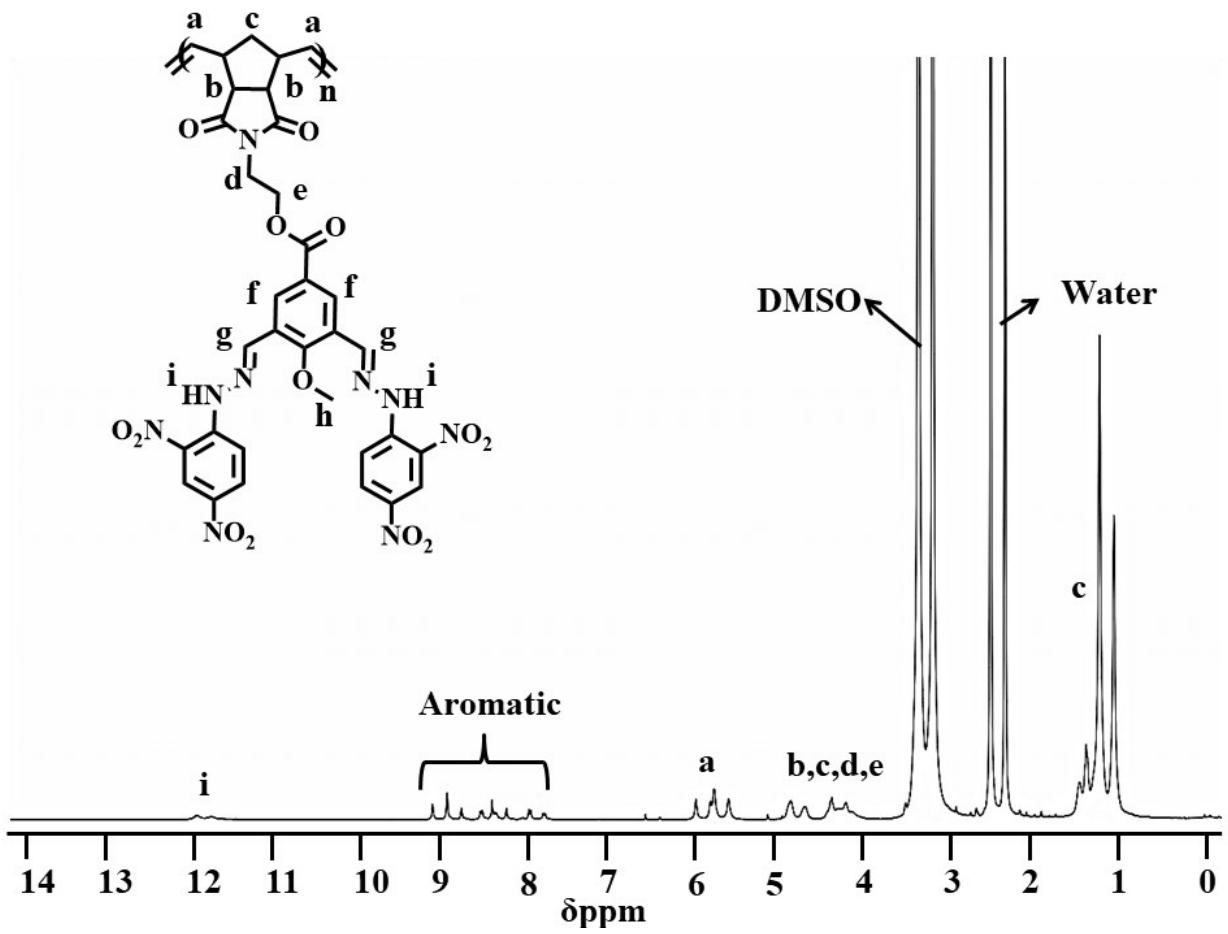


Figure S22: ^{1}H NMR spectroscopy of compound-11 in DMSO-d_6

Calculation of limit of detection (LOD):

the detection limit was calculated from UV-vis spectroscopy titration data based on the reported method. Compound 4 and compound 11 were titrated against the increasing concentration of fluoride anion. The linear relationship between absorbance and concentration of fluoride anion was fitted based on absorbance maxima.

Detection limit= $3\sigma/k$

Where sigma is the standard deviation of the blank sample and k is the slope of a linear regression equation.

Calculation of association constant:

Binding constant was calculated using Benesi- Hildebrand equation plotting $[A_{max}-A_0]/[A-A_0]$ vs concentration of anion from the Uv-vis titration diagram of Di-DNP and NorDi-DNP.

Binding constant =1/k

Where k is the slope of linear fitted spectra.

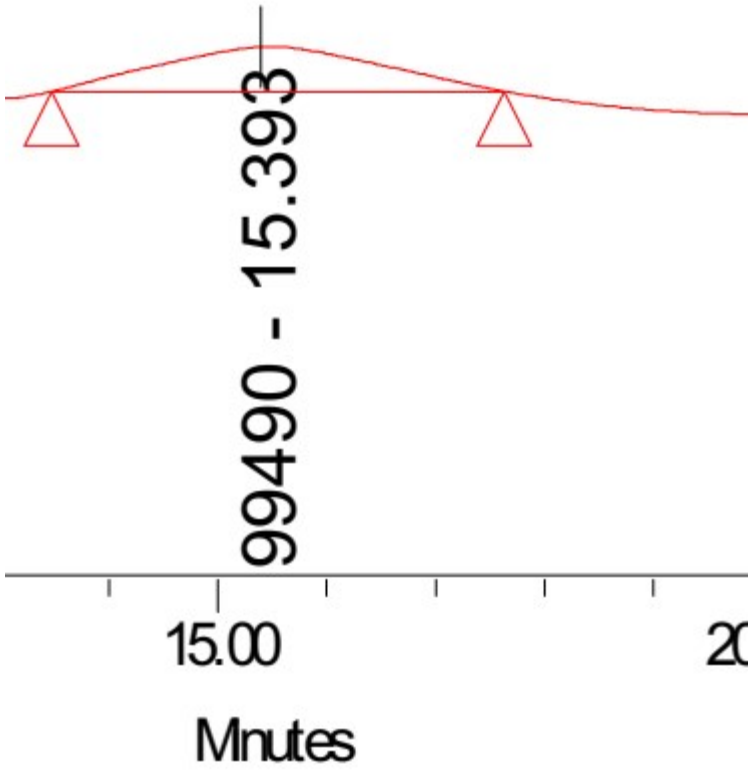
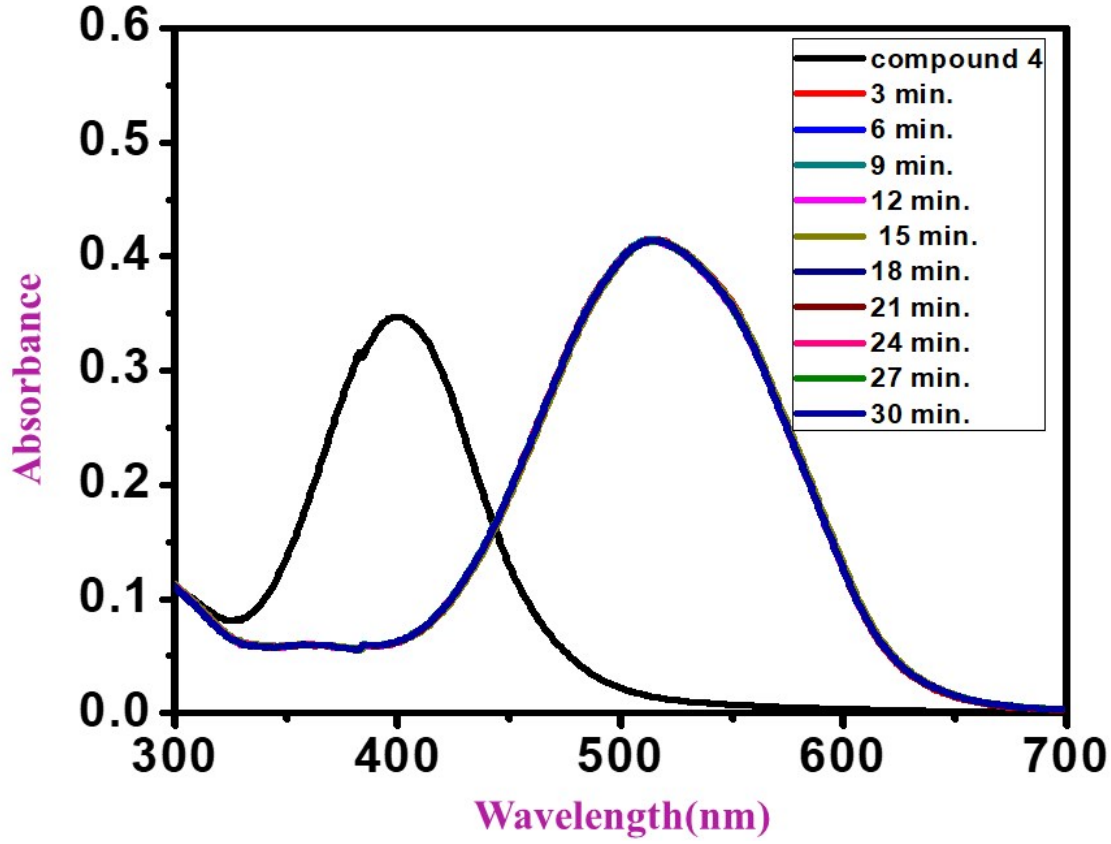


Figure S23: GPC data for compound 11.


0.6
0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
300
400
500
600
700
Wavelength(nm)
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15 min.
18 min.
21 min.
24 min.
27 min.
30 min.

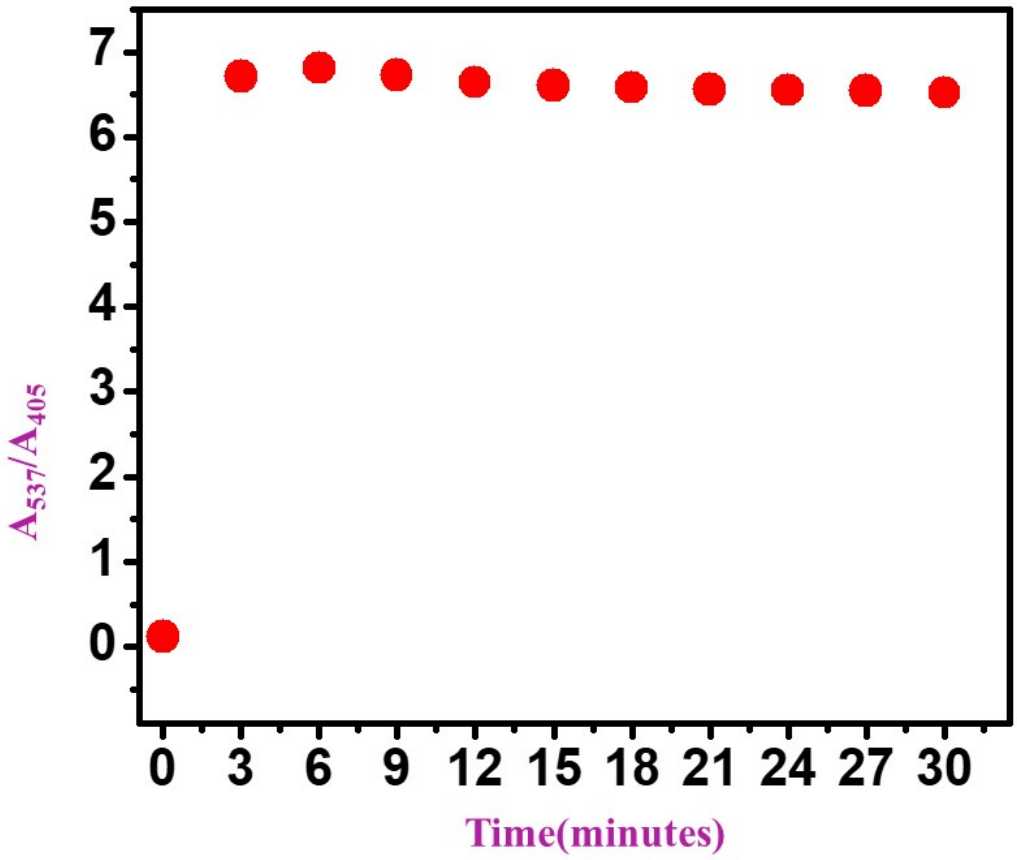
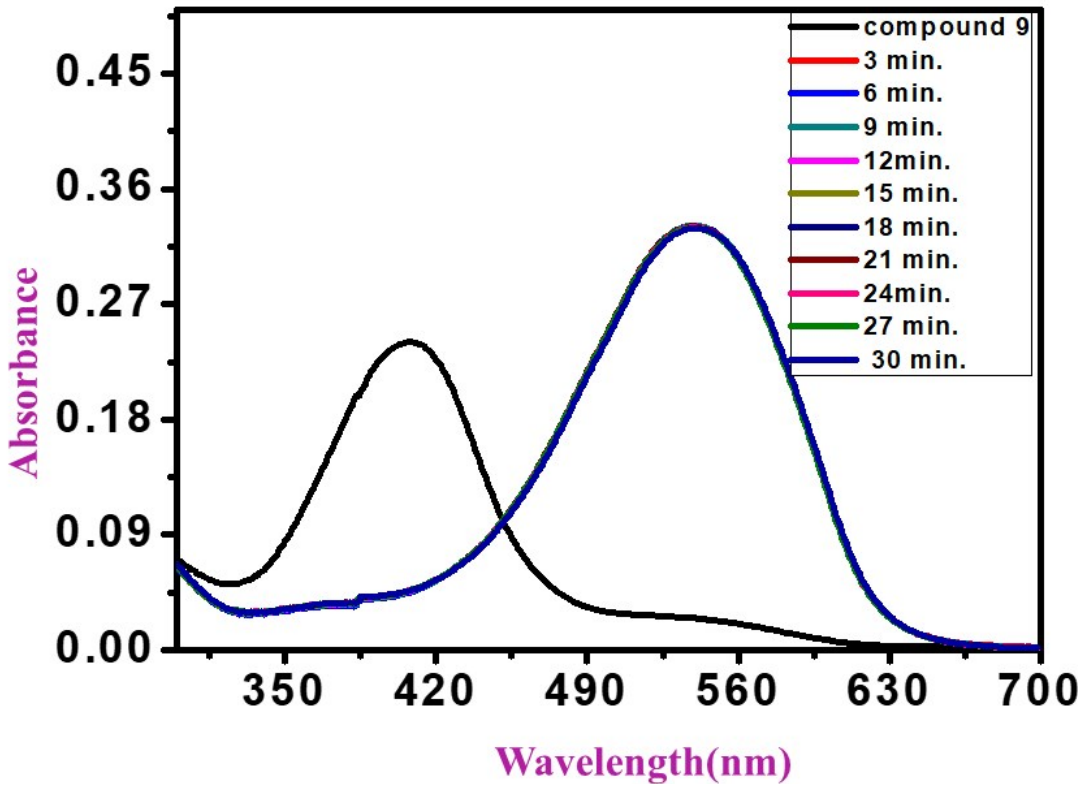


Figure S24: Time-dependent Uv-vis spectra for compound 4 (2.5×10^{-6}M) with a 1.0×10^{-6}M solution of TBAF solution in Tris-HCl buffer solution (pH-7.4) 9:1 DMSO: H_2O solvent mixture.


compound 9
3 min.
6 min.
9 min.
12min.
15 min.
18 min.
21 min.
24min.
27 min.
30 min.
Absorbance
0.45
0.36
0.27
0.18
0.09
0.00
350
420
490
560
630
700
Wavelength(nm)

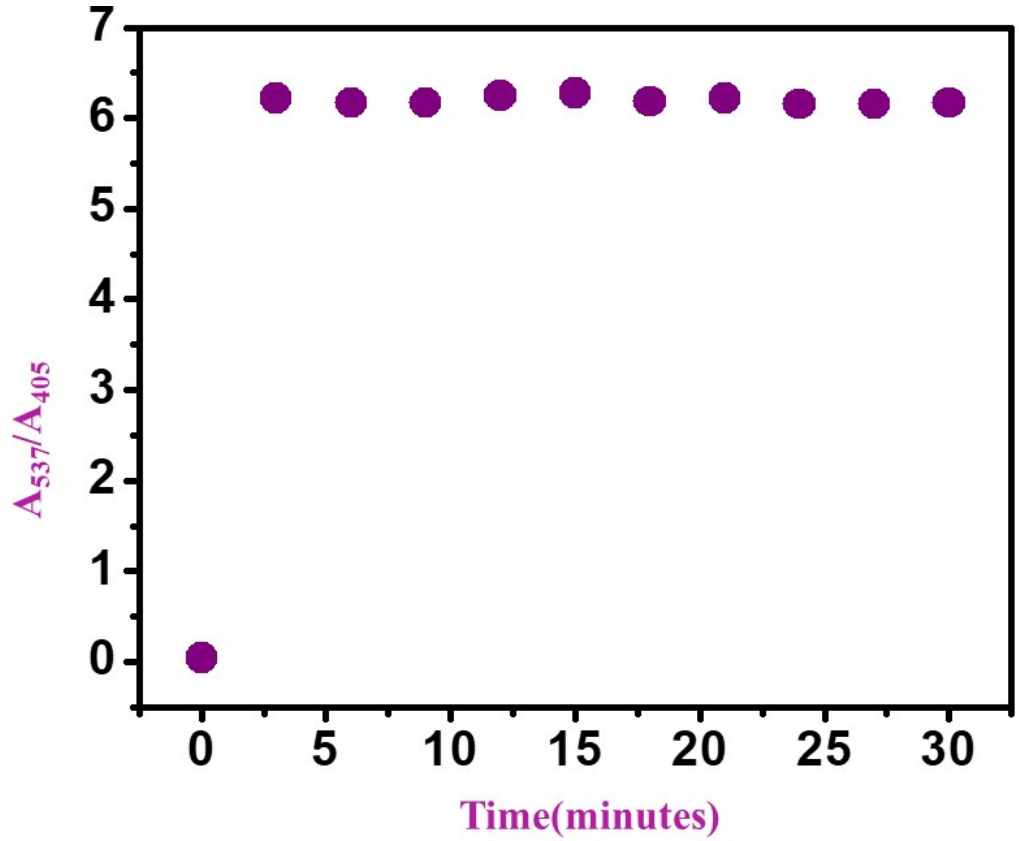

A_{537}/A_{405}
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
Time(minutes)

Figure S25: Time-dependent Uv-vis spectra for compound 9 (1.5×10^{-5}M) with a 0.5×10^{-4}M solution of TBAF solution in Tris-HCl buffer solution (pH-7.4) 9:1 DMSO: H_2O solvent mixture.

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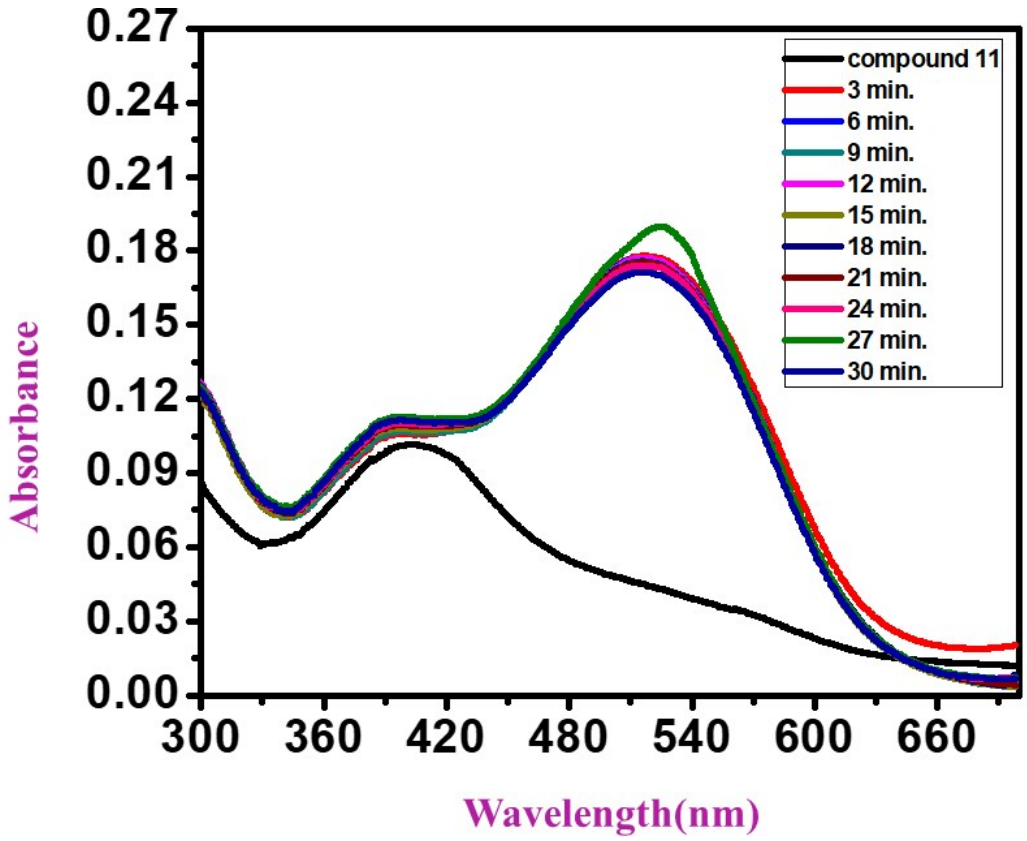


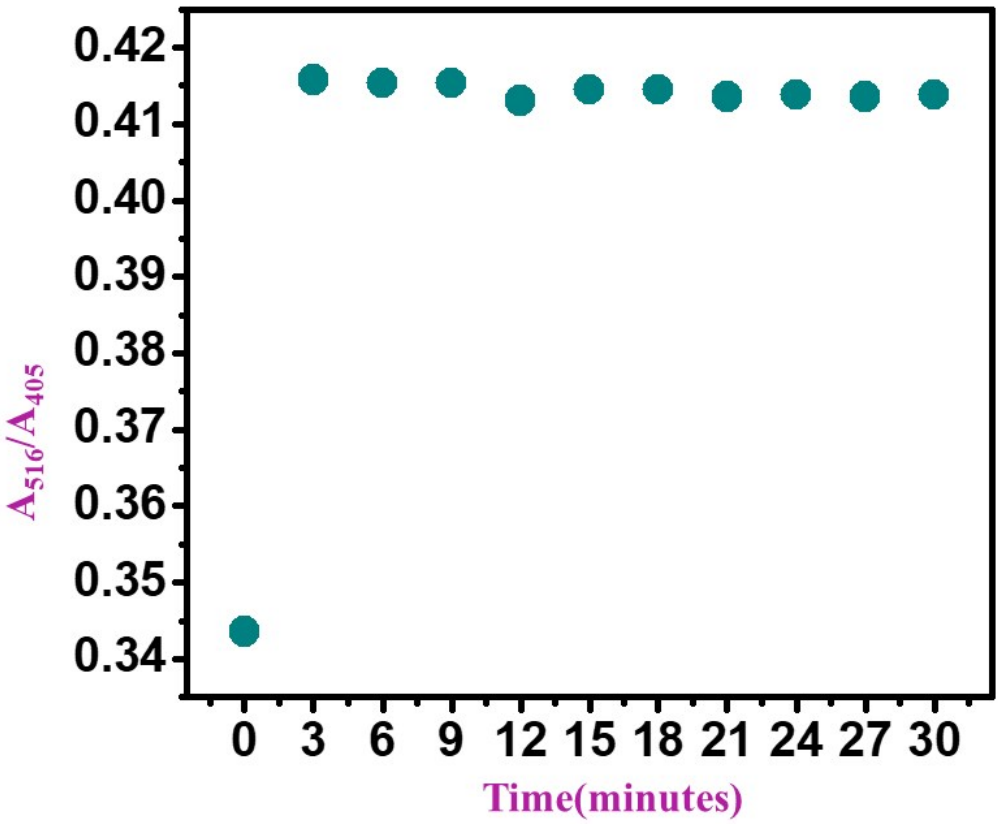


Figure S26: (A)Time-dependent Uv-vis spectra for compound 11(1mg/2ml DMSO solvent) with 0.5×10^{-4}M solution of TBAF solution in Tris-HCl buffer solution (pH-7.4) 9:1 DMSO:H_2O solvent mixture.(B)

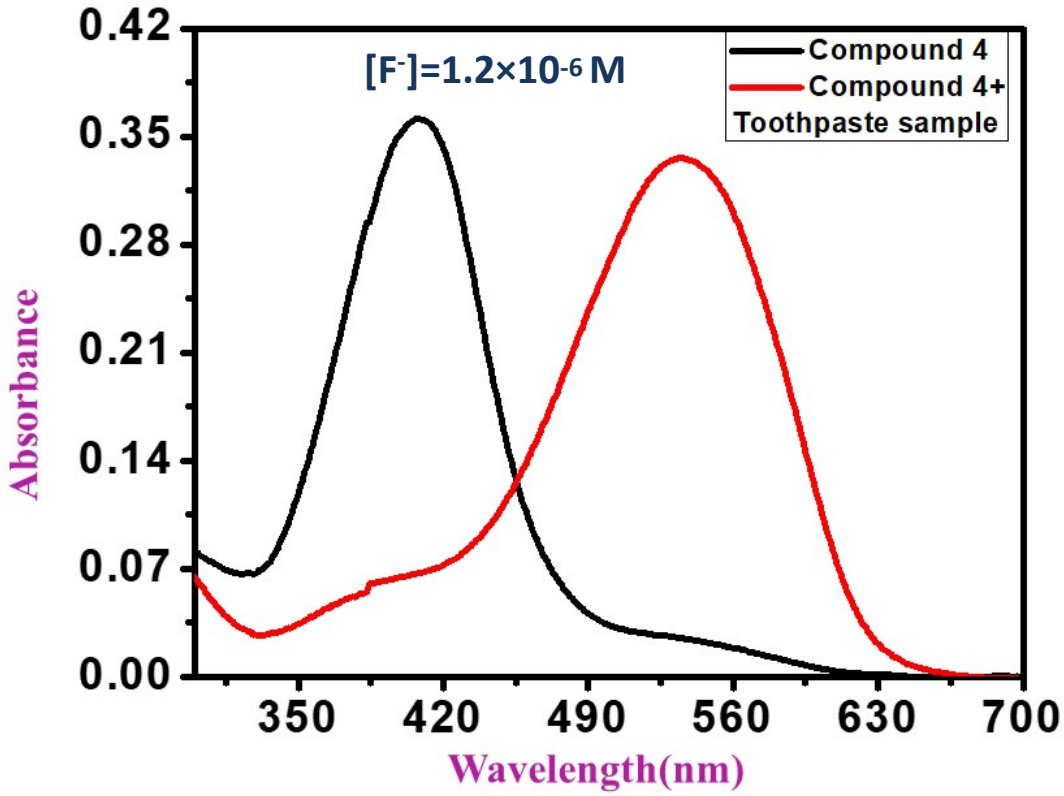


Figure S27:: Real sample analysis by compound 4 (2.5×10^{-6}M DMSO solution) with Colgate toothpaste sample (100µl) solution in Tris-HCl buffer solution (pH-7.4) 9:1 DMSO: H_2O solvent mixture.

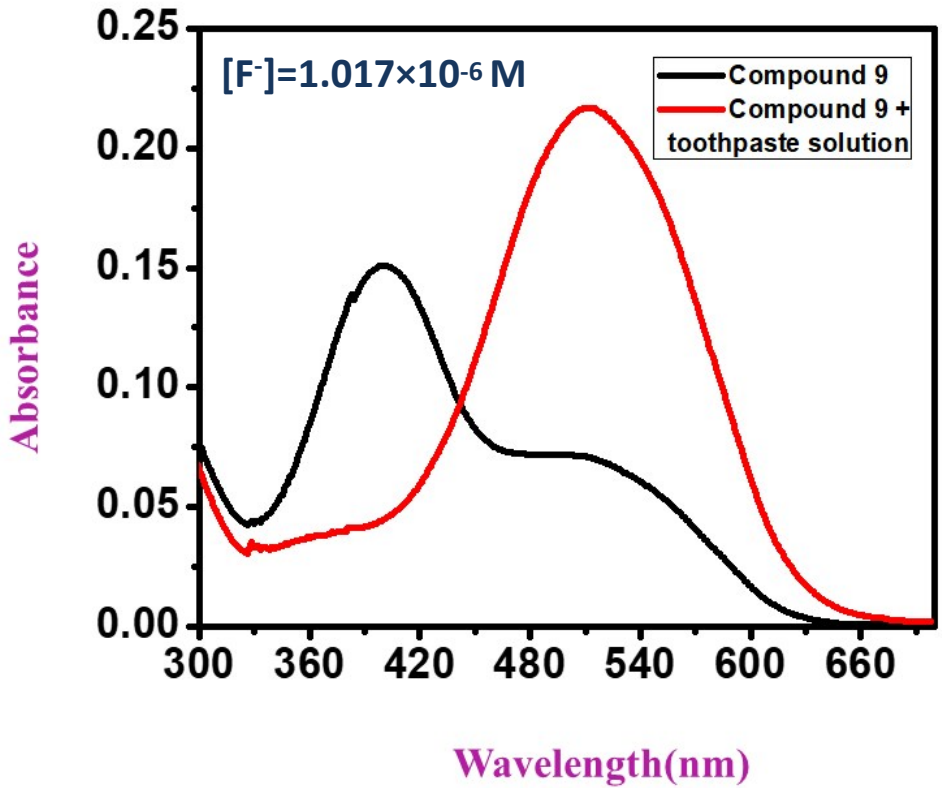


Figure S28: Real sample analysis by compound 9 (1.5×10^{-5}M) DMSO solution) with Colgate toothpaste sample (100µl) solution in Tris-HCl buffer solution (pH-7.4) 9:1 DMSO: H_2O solvent mixture.

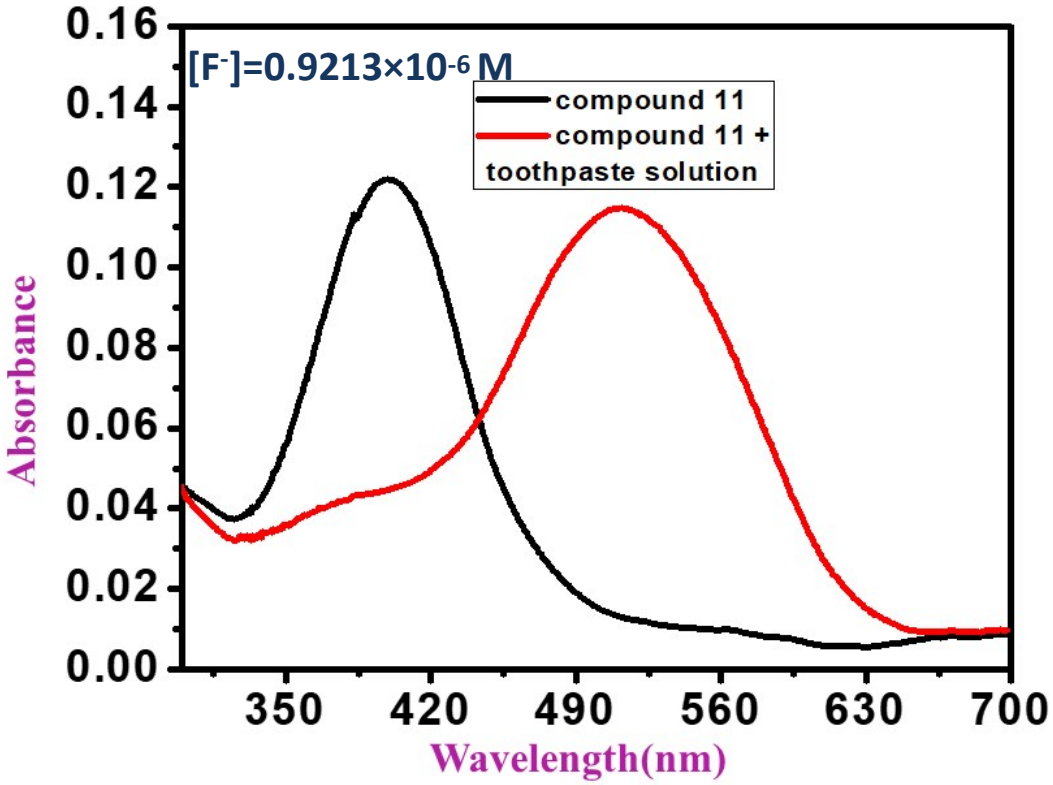
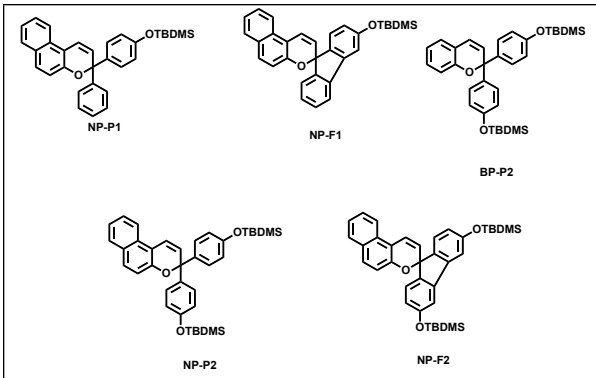
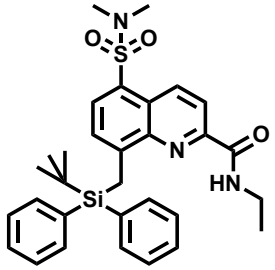
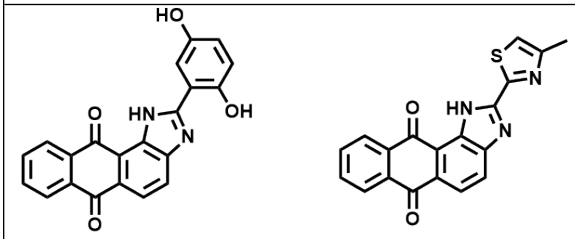
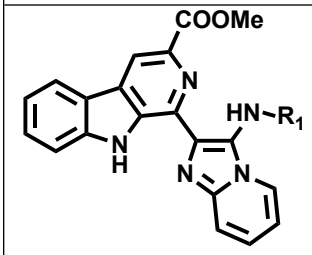
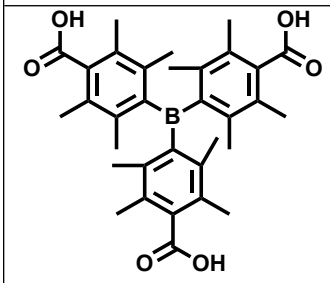
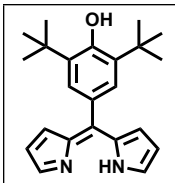
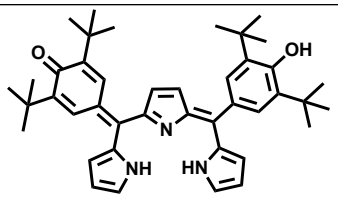
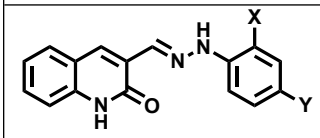
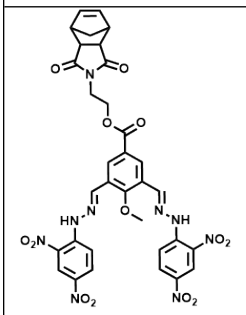
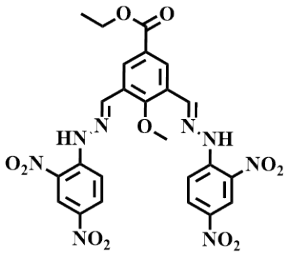
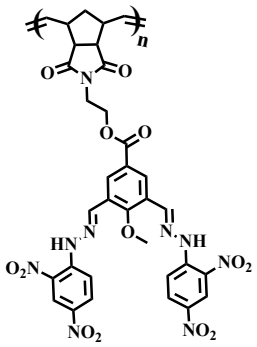


Figure S29: Real sample analysis by compound 11(1mg/2ml DMSO solution) with Colgate toothpaste sample (100µl) solution in Tris-HCl buffer solution (pH-7.4) 9:1 DMSO: H_2O solvent mixture.

Table 1. Limit of Detection (LOD) of representative probes for fluoride in aqueous sample

Sensors	limit of detection(µM)	Refferences

	NP-P1 = 0.57 NP-F1 = 0.51 BP-P2 = 7.03 NP-P2 = 0.47 NP-F2 = 0.42	J. Org. Chem. 2016, 81, 7741- 7750
	20	Anal. Chem. 2015, 87, 4081- 4086
 1	1 = 0.068 4= 0.081	New J. Chem., 2015, 39, 5984
 **S1 : R1= tert- butyl** **S2 : R1=CH2COOEt**	S1 = 0.177 S2 = 1.027	New J. Chem., 2018, 42, 10317
	0.1	J. Am. Chem. Soc. 2019, 141, 3052- 3058

 A  B	A = 2×10^{-4} M B= 2×10^{-5} M	Chem. Commun., 2010, 46, 3669- 3671
 3A:X=Y=H; 3B: X=H, Y= NO2; 3C:X=Y=NO2	3B = 1.42 3A = 3.11	Sensors and Actuator B. 245, 2017, 314-320
  A B  C		A= Limit of detection=72.432×10-9M B=Limit of detection=68.182×10-9M C= Limit of detection=18.981×10-9M

REFERENCES:

1. Gomez, D. E.; Fabbrizzi, L.; Licchelli, M., Why, on Interaction of Urea-Based Receptors with Fluoride, Beautiful Colors Develop. *J. Org.Chem.* ***2005****, 70,* 5717.
2. Kumaravel, M.; Tmague, J.; Baakrishna, M. Hydrazone derivatives appended to diphenylphosphine oxide as anion sensors. *J. Chem. Sci. 2017, 129,* 471.
3. Cao, X.; Lin, W.; Yu, Q.; Wang, J. Ratiometric sensing of fluoride anions based on a BODIPY-coumarin platform. *Org. Lett.* ***2011,*** *22,* 6098.
4. 3.Jose, D.; Kumar, D. K.; Ganguly, B.; Das, A. Efficient and simple colorimetric fluoride ion sensor based on receptors having urea and thiourea binding sites. *Org. Lett.* ***2004,*** *20,* 3445.
5. Sarkar, A.; Bhattacharya, S.; Mukherjee, A. Colorimetric detection of fluoride ions by anthraimidazoledione based sensors in the presence of Cu (II). *Dalton Trans.* ***2016,*** *45,* 1166.
6. Eun Jin Cho, Byung Ju Ryu, Young Ju Lee, Kye Chun Nam, *Organic Letter,* ***2005,*** *7,* 2607.
7. Kim, S. Y.; Hong, J. I. Chromogenic and Fluorescent Chemodosimeter for Detection of Fluoride in Aqueous Solution. *Organic Letter* ***2007,*** *9,* 3109.
8. Kumari, N.; Jha, S.; Bhattacharya, S. Colorimetric Probes Based on Anthraimidazolediones for Selective Sensing of Fluoride and Cyanide Ion via Intramolecular Charge Transfer. *J. Org. Chem. 2011,* ***76,*** 8215.
9. Roychowdhary, A.; Banerjee, P. A simple hydrazine-based molecule for selective detection of Fluoride ion in DMSO. *J. Chem. Sci.* ***2017,*** *129,* 463.