Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A phototunable anion receptor for C-H…X interactions with benzoate anion

Sk. Atiur Rahaman, Munshi Sahid Hossain, Sruthy Baburaj, Ankita Biswas, Arijit Bag, Subhajit Bandyopadhyay*

E-mail: sb1@iiserkol.ac.in

Table of Contents

Page

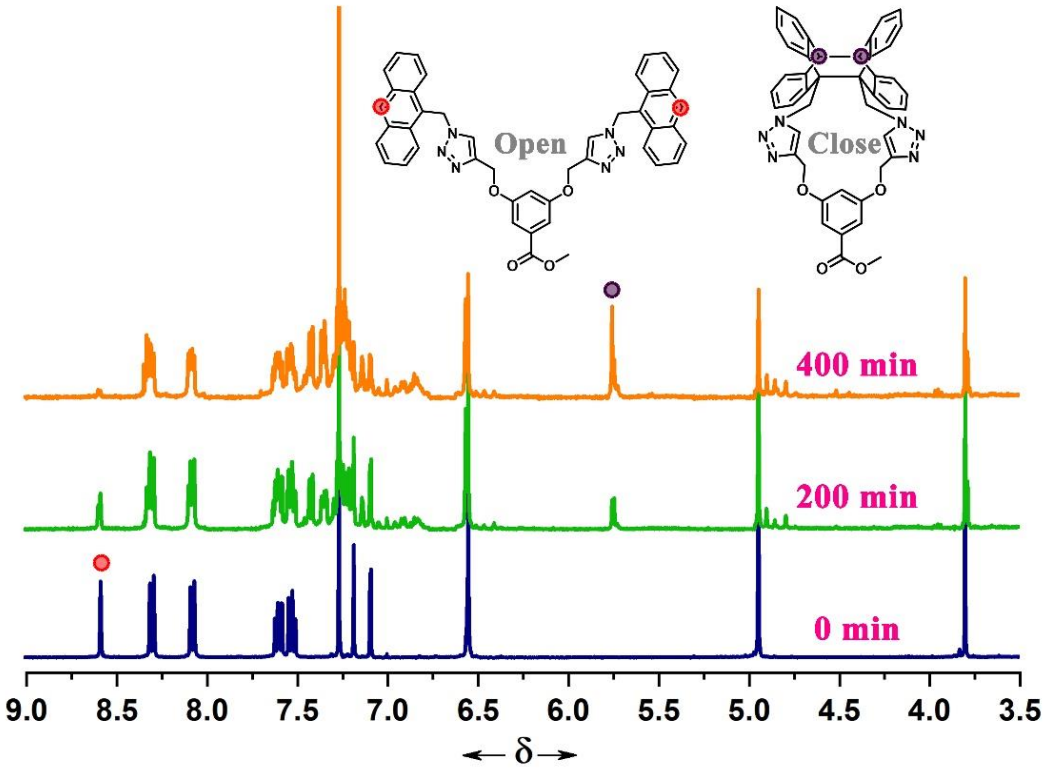

Figure S1. ^{1}H NMR of **1** (10^{-4} M) upon exposure at 366 nm UV light in $CDCl_3$ at 25 ^{o}C.

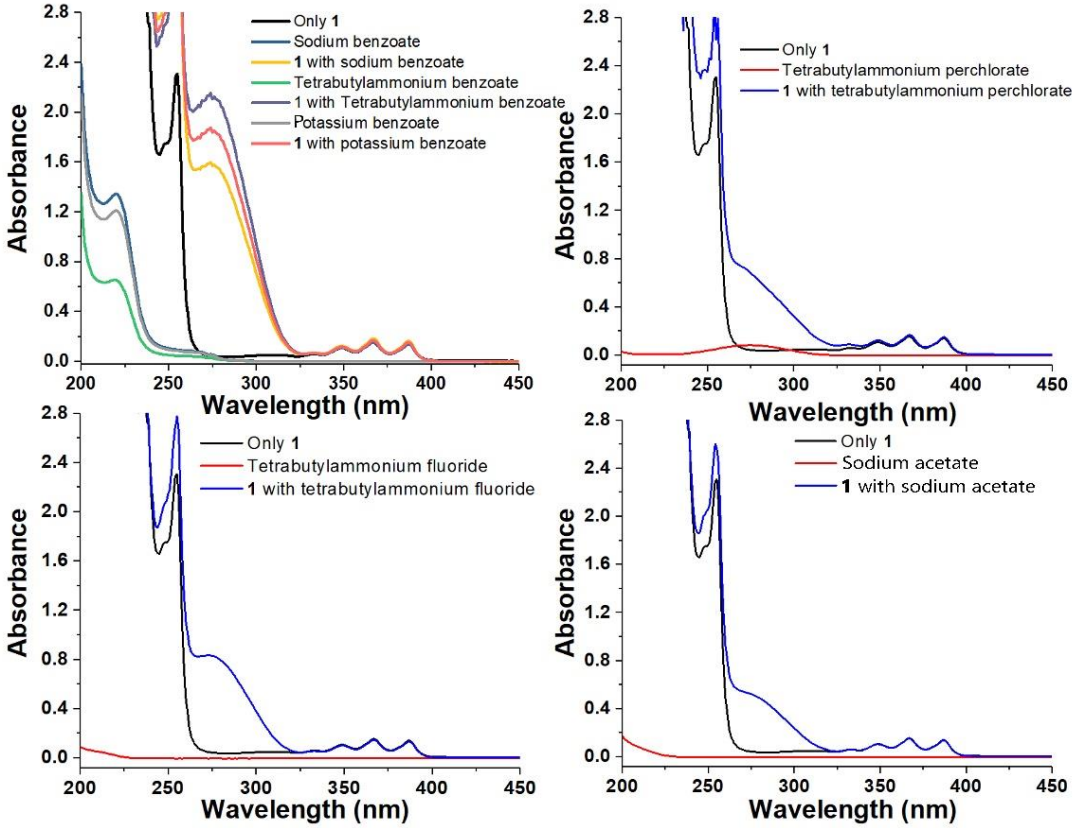

Figure S2. The changes in the UV-vis absorption spectra of ligand **1** (10 μM) upon titration with anions (100 μM) and anions (benzoate, perchlorate, fluoride, acetate: 100 μM each) without the receptor in CH_3CN media with 1% DMSO as a co-solvent at 25 ^{o}C.

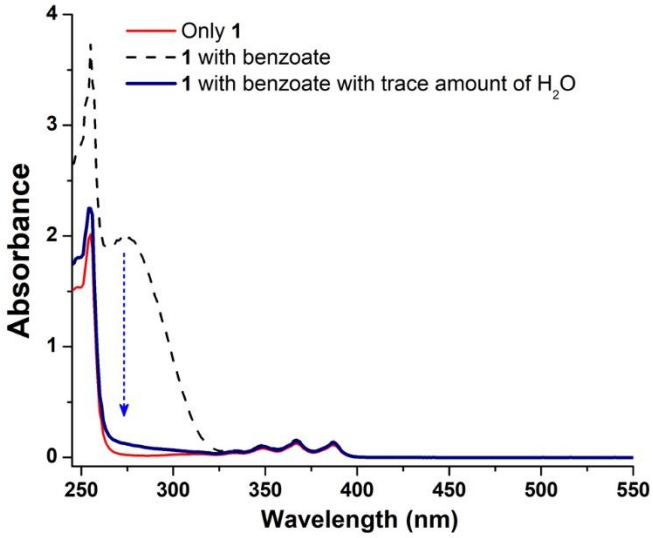

Figure S3. The changes in the UV-vis absorption spectrum of ligand **1**⊂$PhCOO^-$ with upon addition of a trace amount of water in CH_3CN media at 25 ^oC.

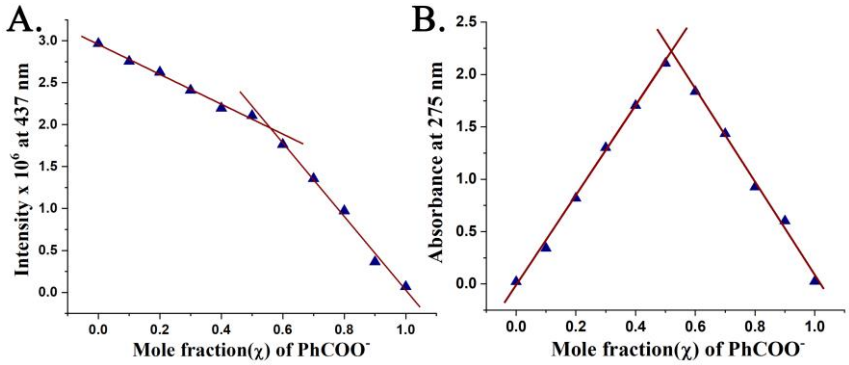

Figure S4. Fluorescence UV-vis Job's plots for benzoate bound receptor **1**.

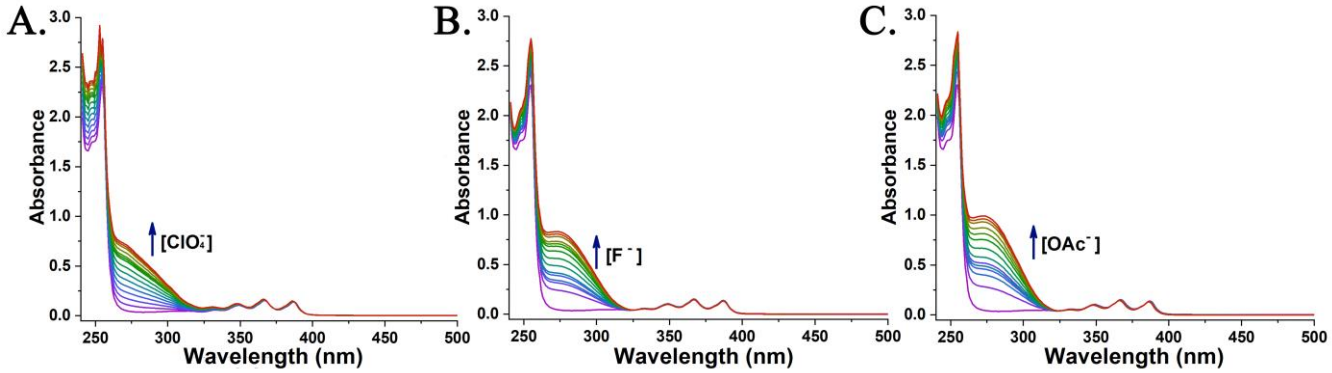

Figure S5. UV-vis absorption spectra of compound **1** (10 μM) upon addition of 0 to 100 μM of (A) ClO_4^-, (B) F^-, (C) OAc^-.

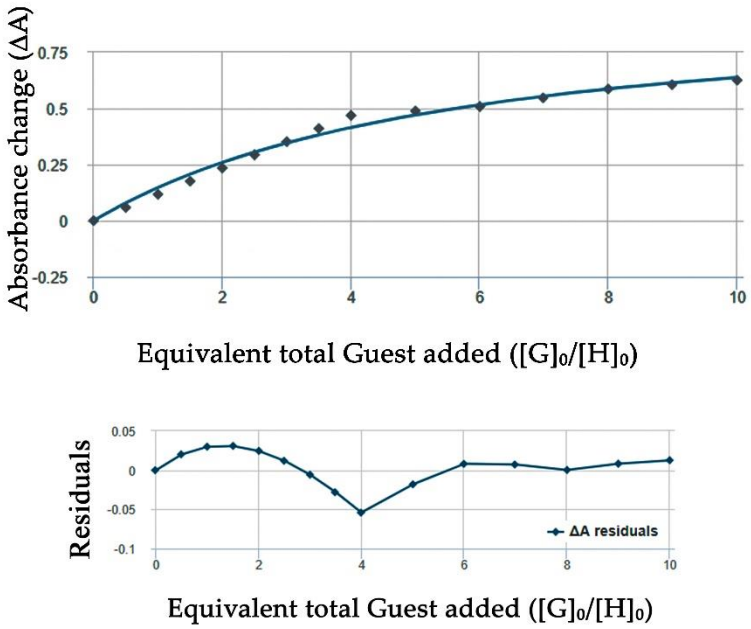

Figure S6. Determination of the binding constant for the benzoate-bound receptor **1**⊂ClO_4^-. (Non-linear data fitting of the absorbance data obtained from the titration). The value of the binding constant was 2.17 × 10^4 M^{-1}.

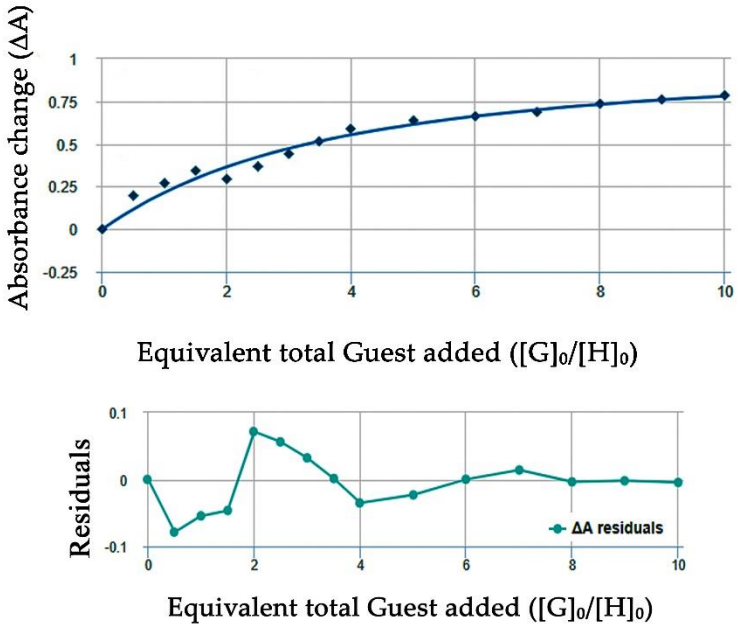

Figure S7. Determination of the binding constant for the benzoate-bound receptor **1**⊂F^-. (Non-linear data fitting of the absorbance data obtained from the titration). The value of the binding constant was 2.61 × 10^4 M^{-1}.

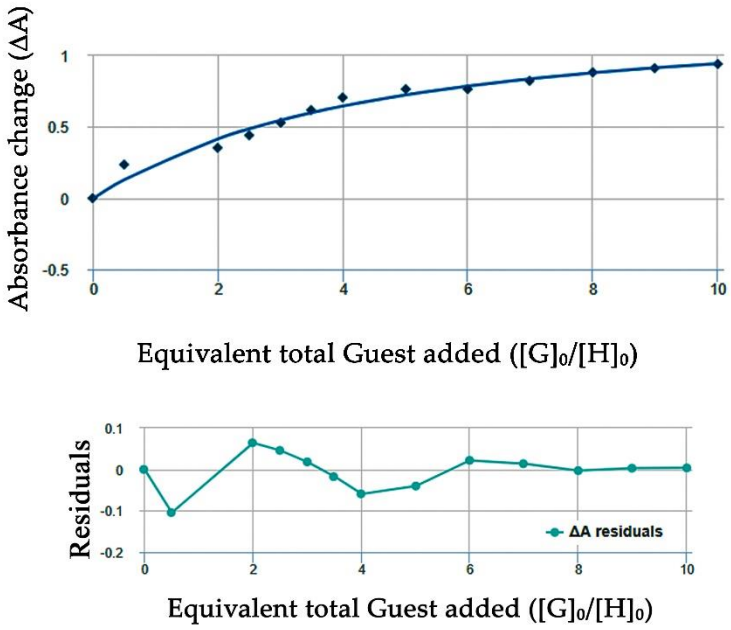

Figure S8. Determination of the binding constant for the benzoate-bound receptor **1**⊂OAc^-. (Non-linear data fitting of the absorbance data obtained from the titration). The value of the binding constant was 2.8×10^4 M^{-1}.

———

The Bindfit software for data analysis were used from ***supramolecular.org*** .

The constants K^{11} from the 1:1 binding data[ζ]

	Parameter (bounds)	Optimised (M^{-1})	Error (%)
1⊂$PhCOO^-$	K (0→ ∞)	28632.52	± 10.91
1⊂ClO_4^-	K (0→ ∞)	21719.72	± 7.42
1⊂OAc^-	K (0→ ∞)	28006.12	± 11.21
1⊂F^-	K (0→ ∞)	26117.54	± 11.43

ζ A 1:2 binding model was ignored because of the large errors associated with the fitting of the binding model.

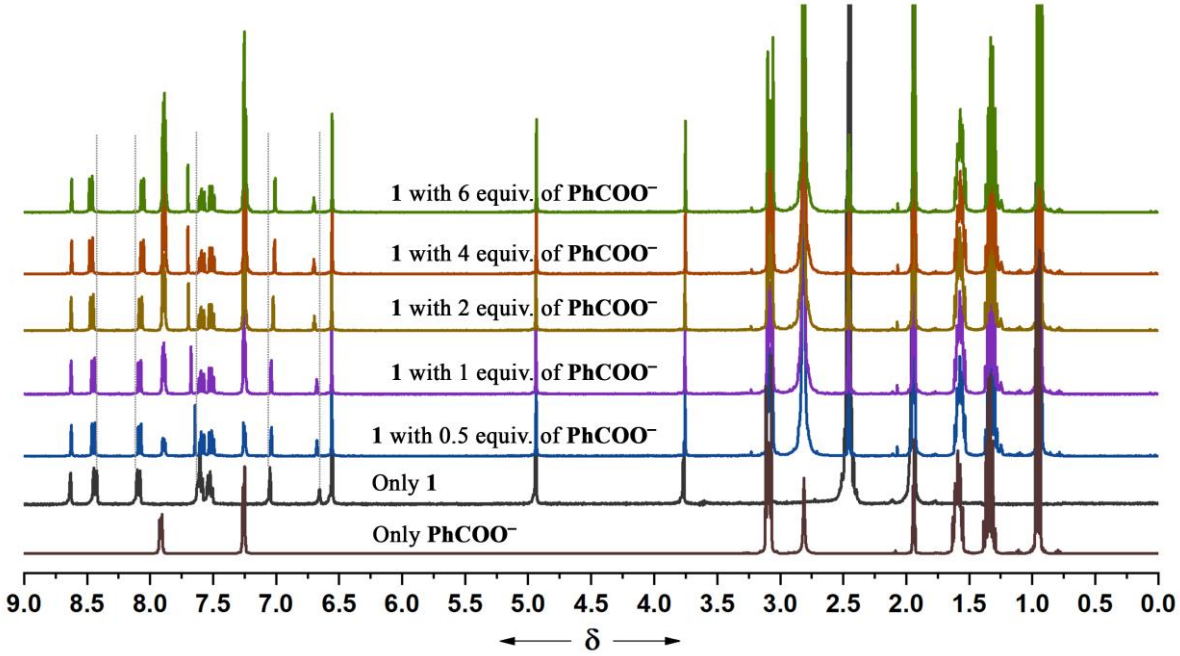

Figure S9. ^{1}H NMR titration of **1** (10^{-4} M) upon addition of TBA benzoate in CD_3CN at 25 ^{o}C. (See Figure 5, Main text for the peak assignments)

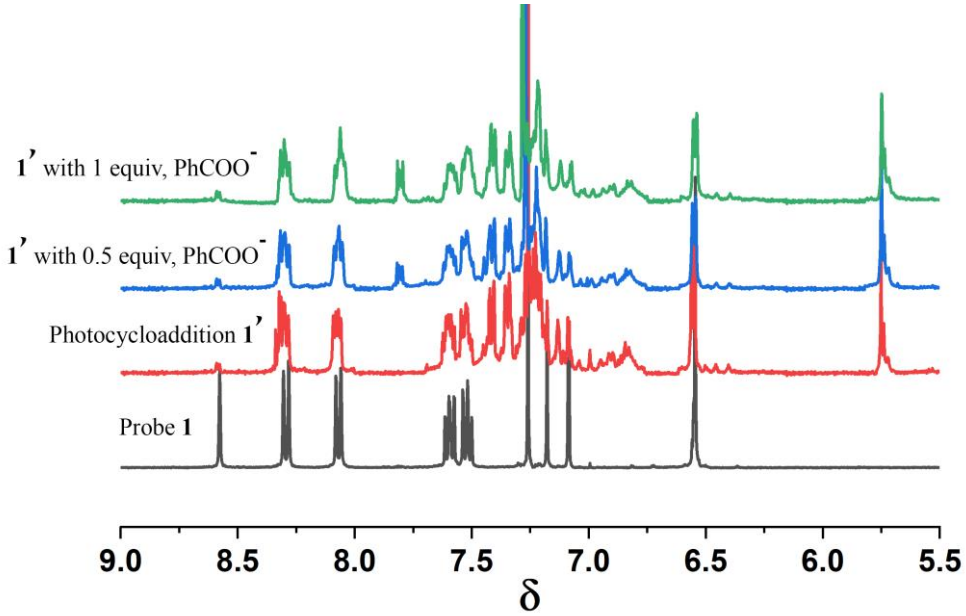

Figure S10. ^{1}H NMR titration of photocycloaddition **1'** (10^{-4} M) upon addition of TBA benzoate in $CDCl_3$ at 25 ^{o}C.

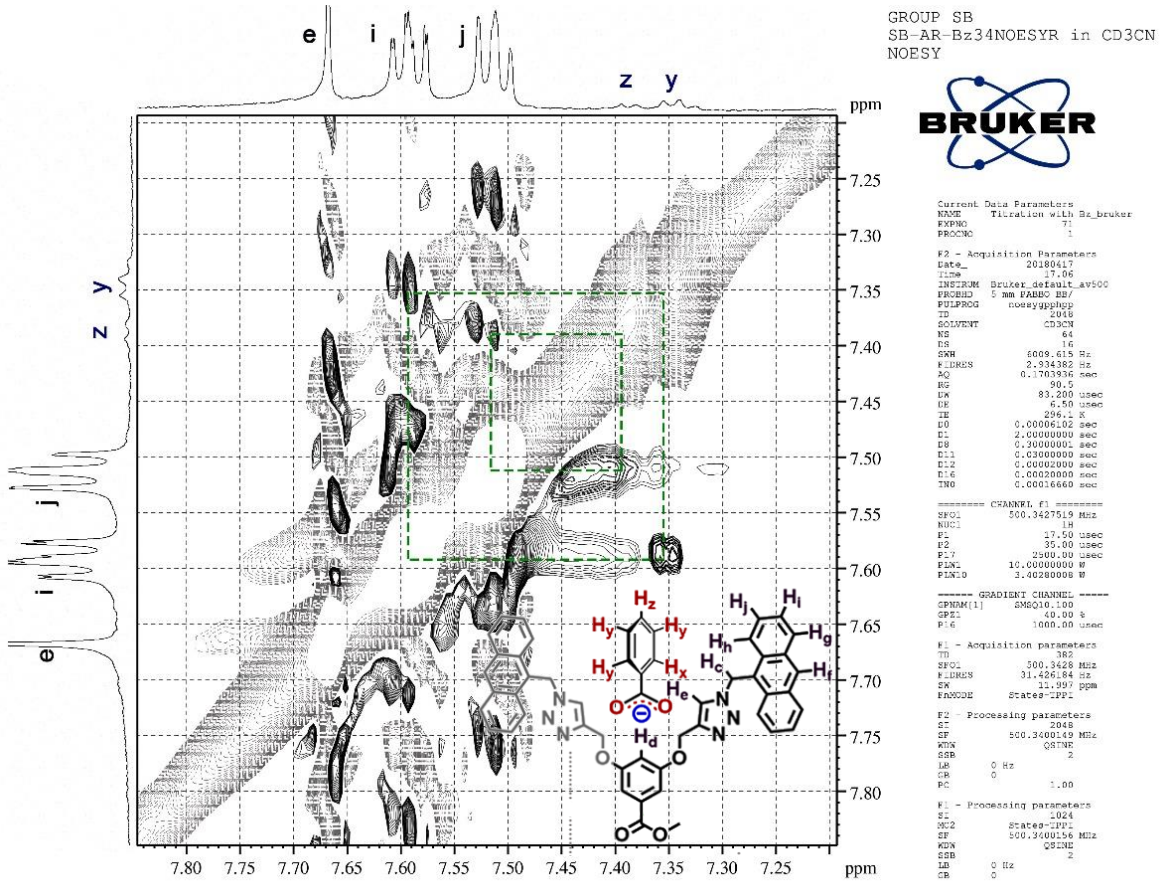

Figure S11. ^{1}H–^{1}H 2D NOESY NMR spectrum in CD_3CN (instrument frequency 500 MHz) at 25 °C of **1**⊂$PhCOO^-$.

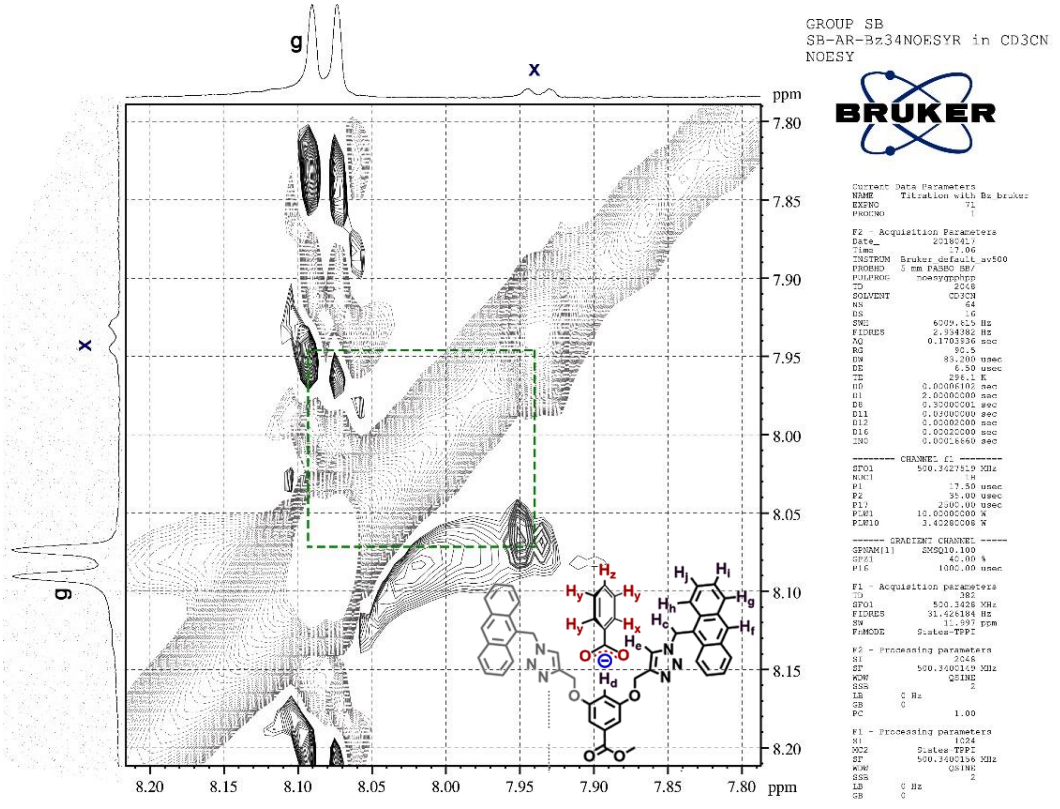

Figure S12. ^{1}H–^{1}H 2D NOESY NMR (500 MHz) spectrum in CD_3CN at 25 °C of **1**⊂$PhCOO^-$.

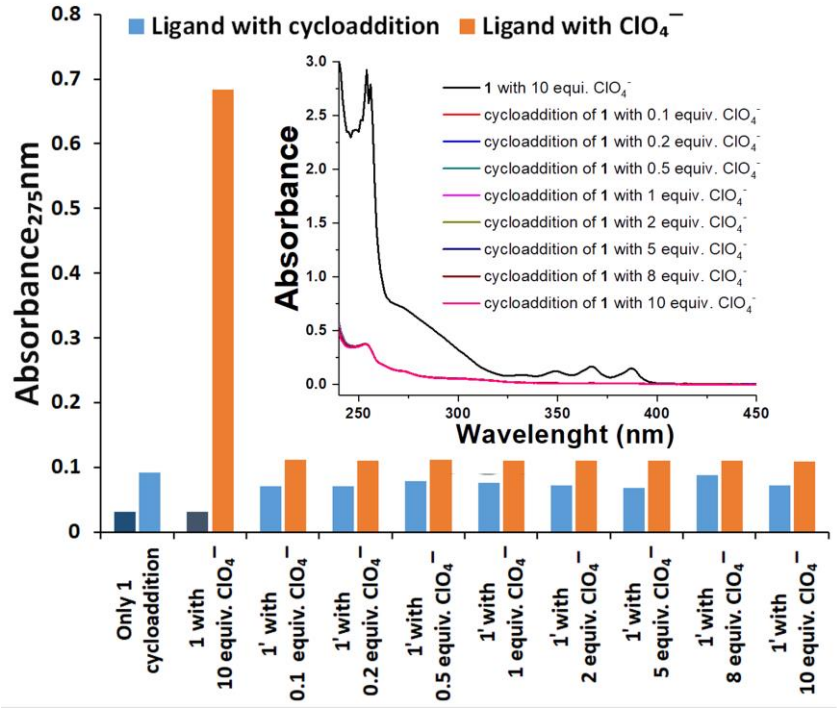

Figure S13. Change in the absorbance at absorbance at 275 nm upon the addition of 0−10 equiv. of ClO_4^- to the photocycloaddition adduct **1'** (10 μM) (inset: The absorption spectra of **1'** with the addition of 0−10 equiv. of ClO_4^-).

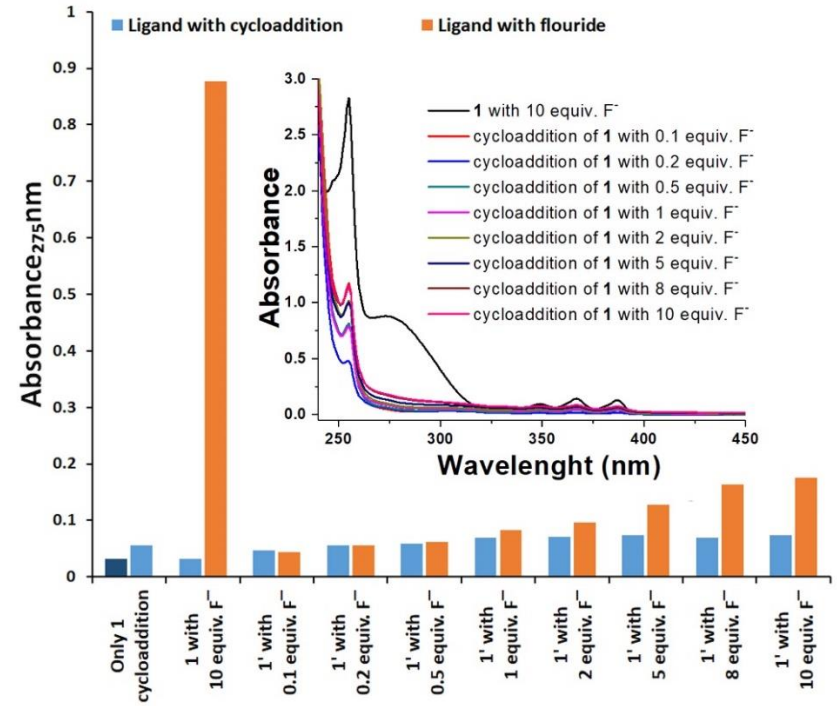

Figure S14. Change in the absorbance at absorbance at 275 nm upon the addition of 0−10 equiv. of F^- to the photocycloaddition adduct **1'** (10 μM) (inset: The absorption spectra of **1'** with the addition of 0−10 equiv. of F^-).

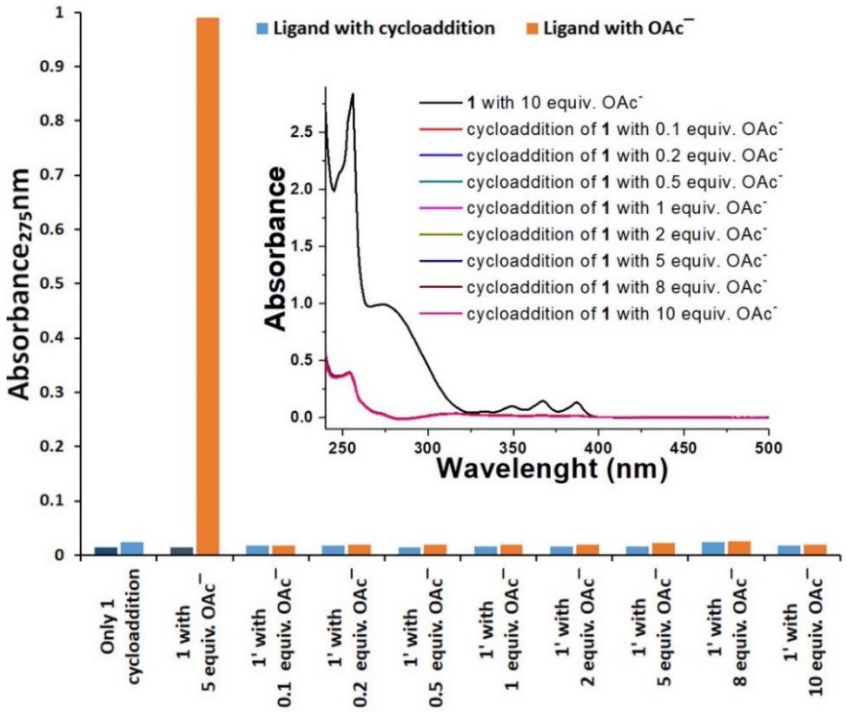

Figure S15. Change in the absorbance at absorbance at 275 nm upon the addition of 0−10 equiv. of OAc^- to the photocycloaddition adduct **1'** (10 μM) (inset: The absorption spectra of **1'** with the addition of 0−10 equiv. of OAc^-).

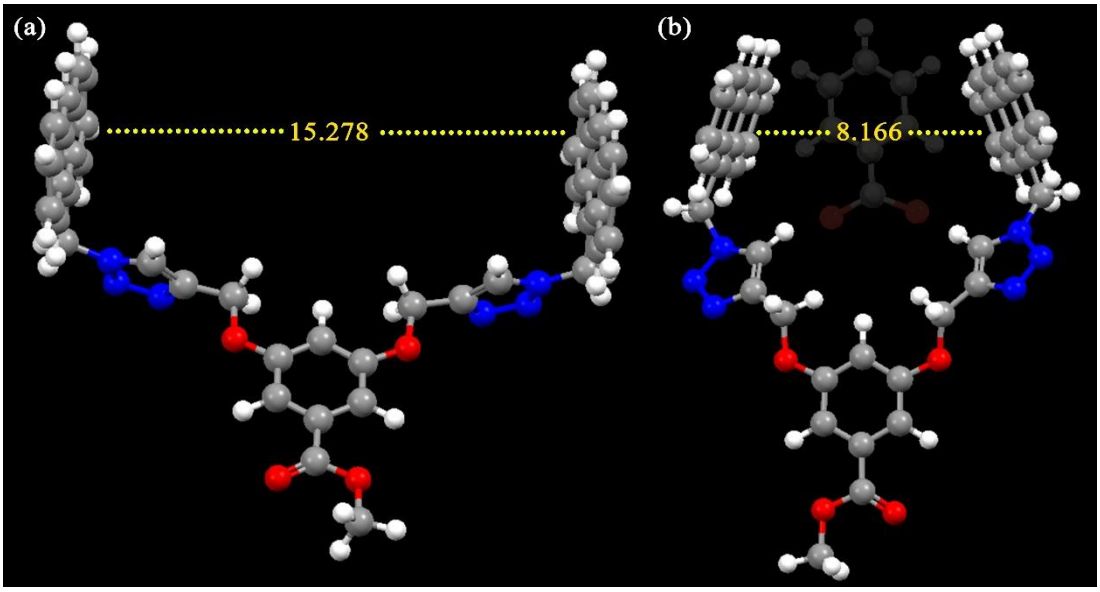

Figure S16. (a) The calculated energy minimized structures and the distance (Å) of (a) the probe **1** and (b) the $PhCOO^-$ bound **1** obtained from the DFT studies with 6-311G basis.

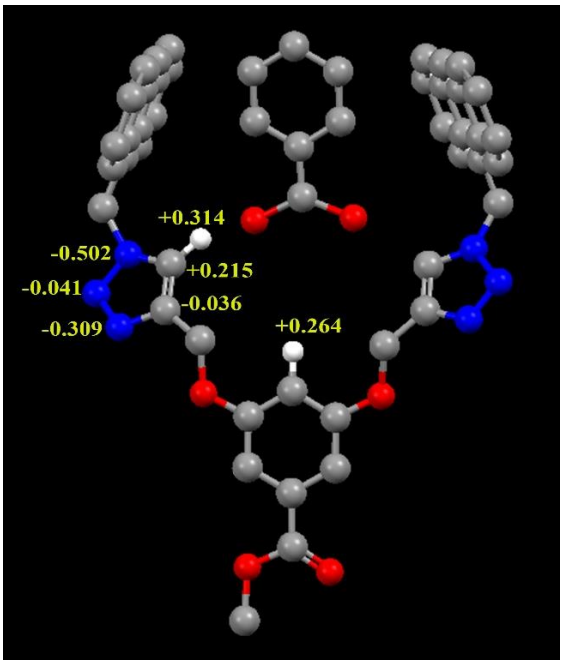

Figure S17. The calculated energy minimized structures and the charge distribution of the $PhCOO^-$ bound **1** obtained using from the DFT calculation with 6-311G basis. The numbers and the signs next to the atoms imply the respective partial charges on the atoms.

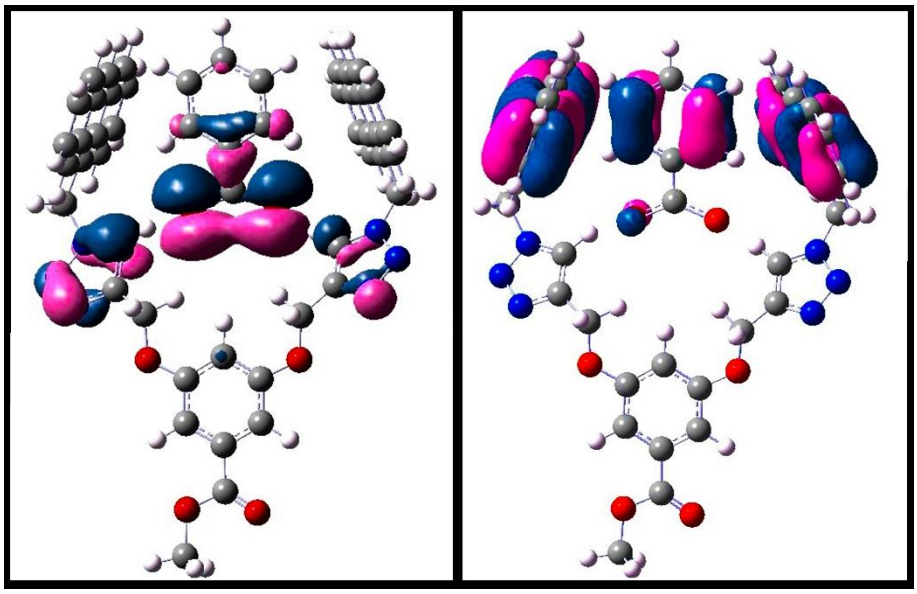

Figure S18. The molecular orbitals and energies for the HOMO-1, HOMO of the **1**•$PhCOO^-$ useing with 6-311G basis.

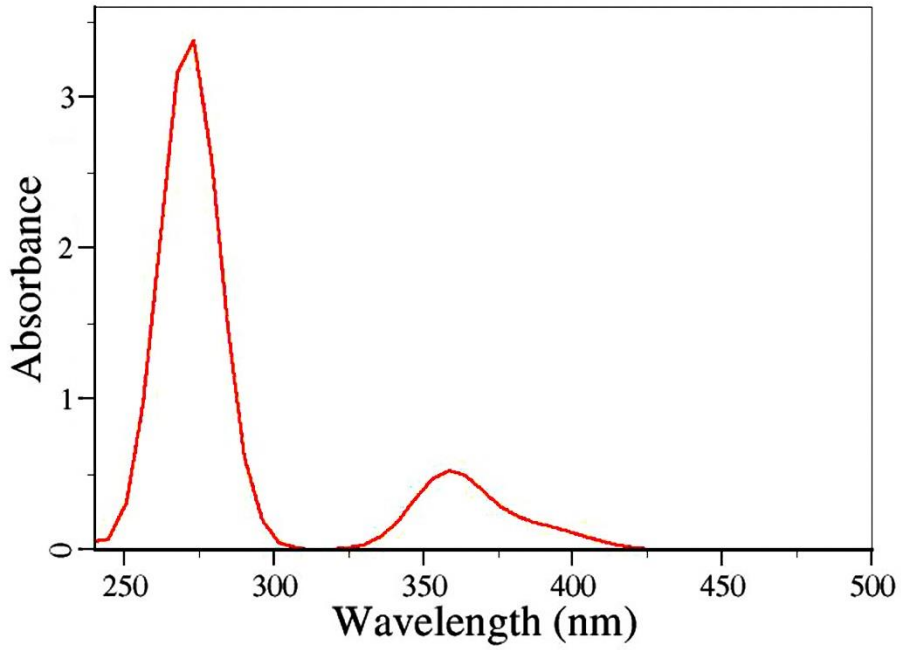

Figure S19. The calculated UV-vis spectrum of **1**⊂$PhCOO^-$ in CH_3CN using B3LYP/6-311G(d) method.

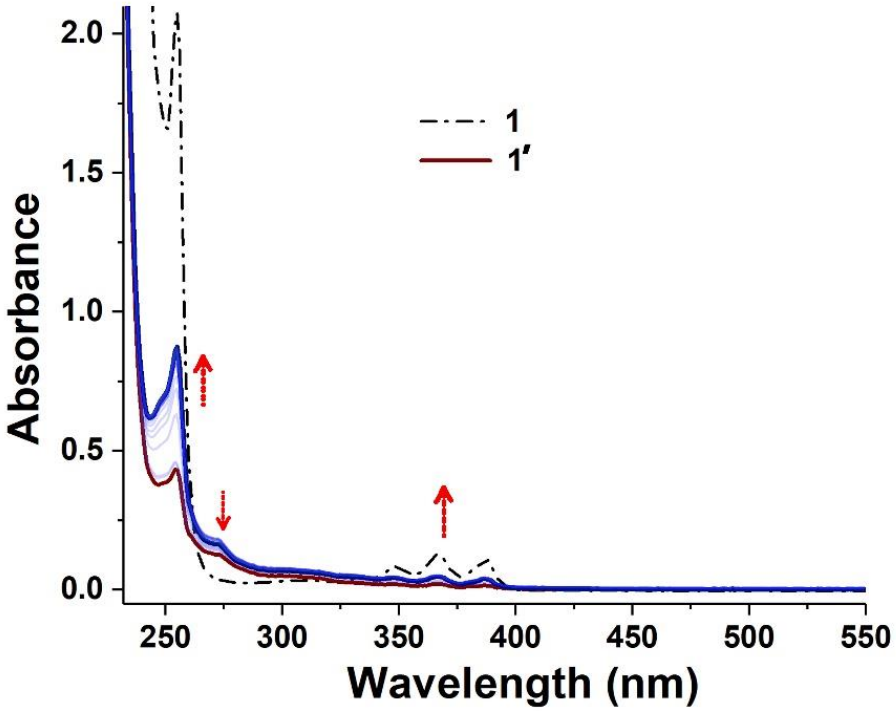

Figure S20. Reversal of **1'** (10 μM) to **1** upon radiation at 254 nm in CH_3CN at 25 °C.

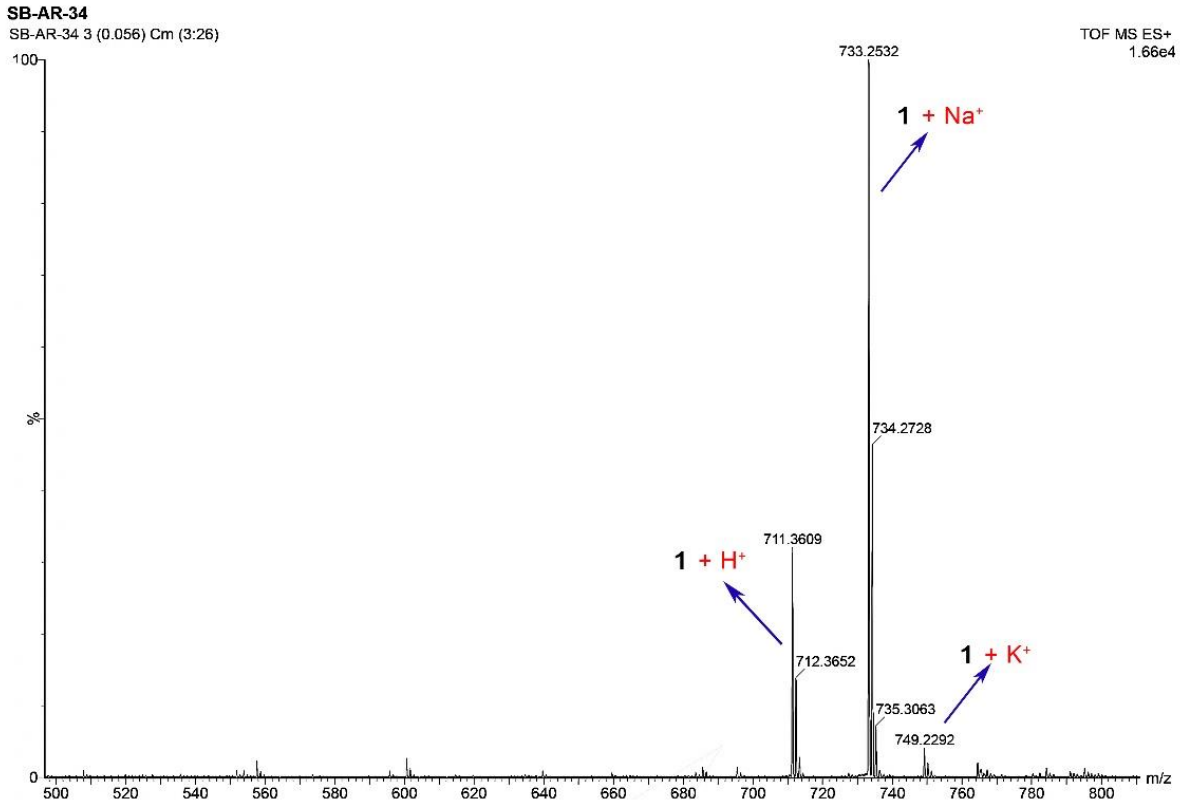

Figure S21. ESI mass spectrum of the compound **1**.

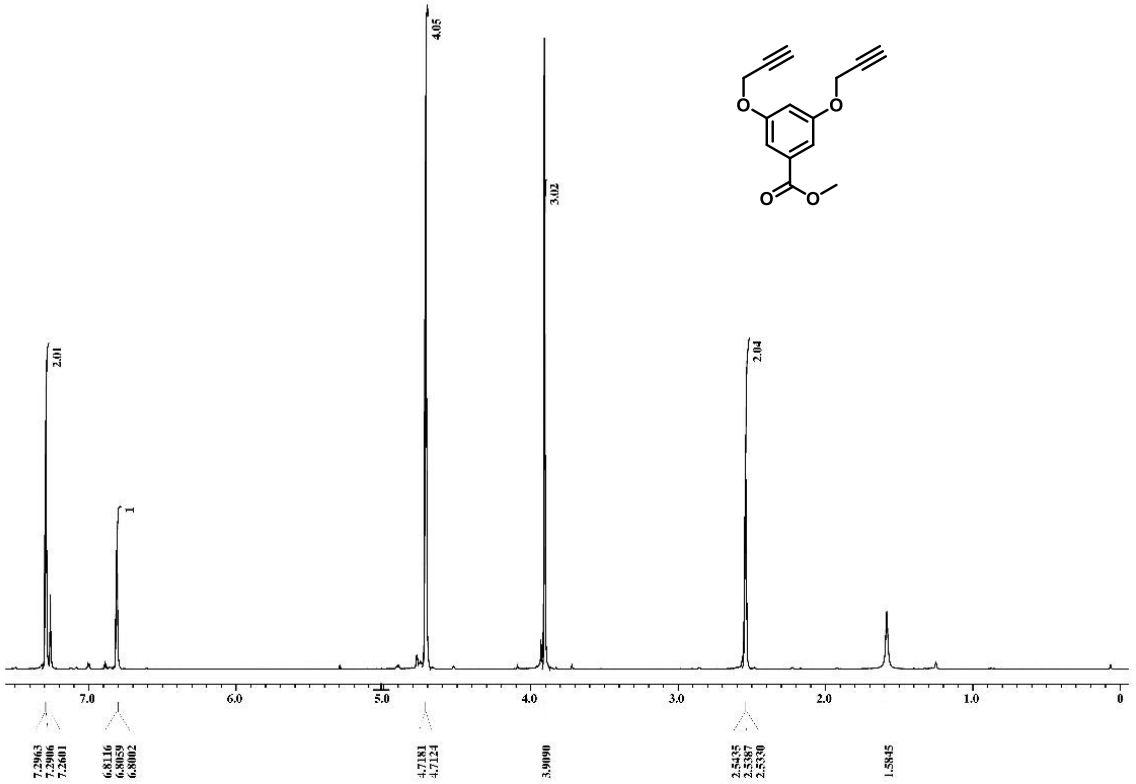

Figure S22. ^{1}H-NMR spectrum of compound **2** in $CDCl_3$ at 25 ^{o}C.

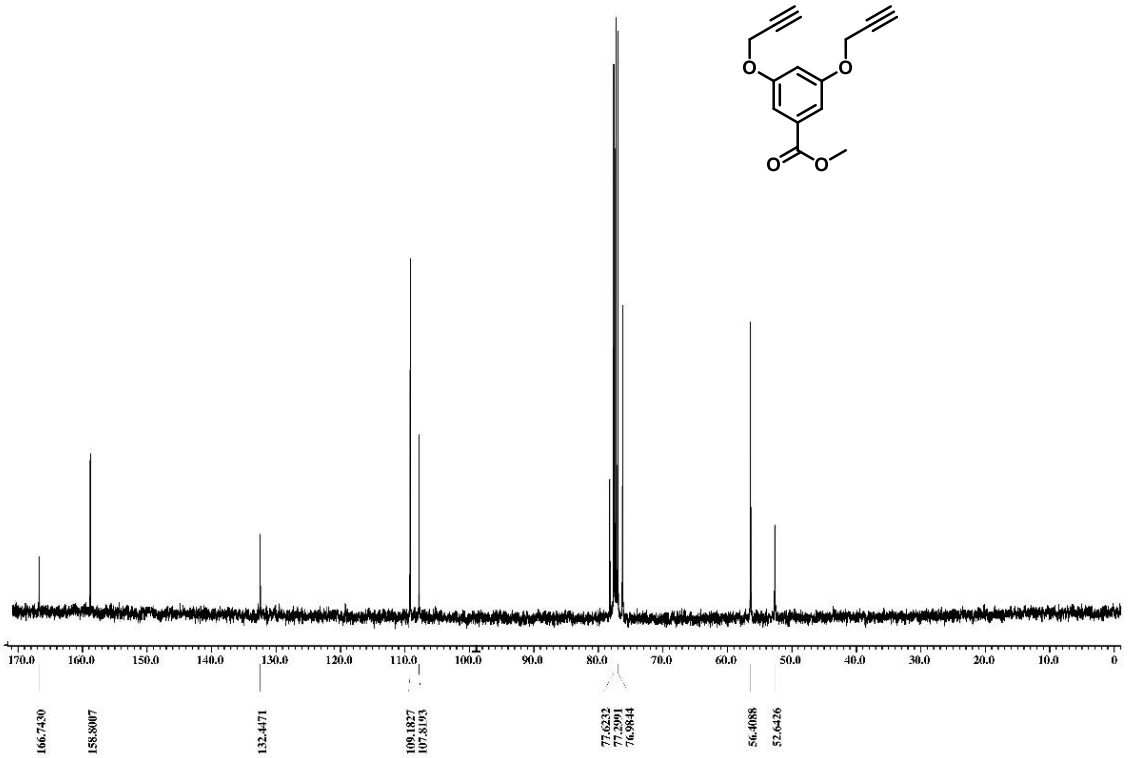

Figure S23. ^{13}C-NMR spectrum of compound **2** in $CDCl_3$ at 25 ^{o}C.

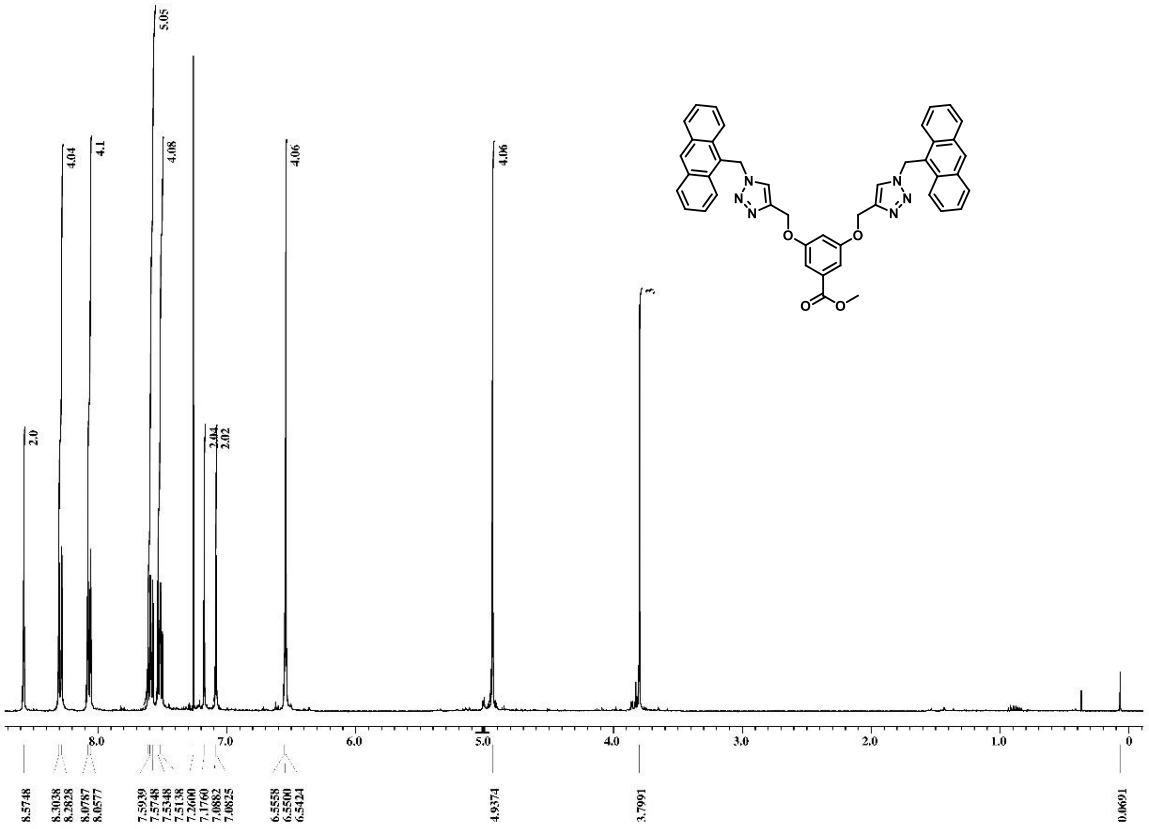

Figure S24. ^{1}H-NMR spectrum of compound **1** in $CDCl_3$ at 25 ^{o}C with 400 MHz.

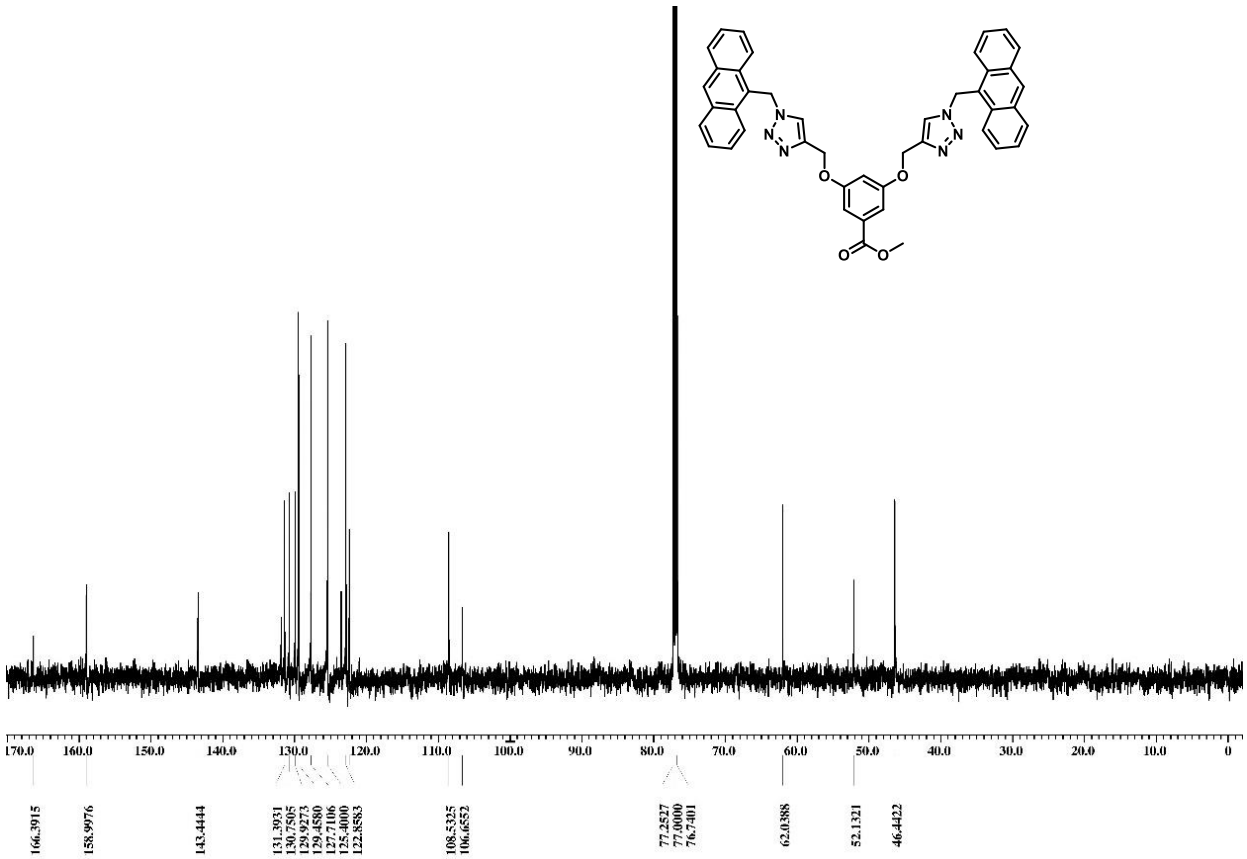

Figure S25. ^{13}C-NMR spectrum of compound **1** in $CDCl_3$ at 25 ^{o}C.

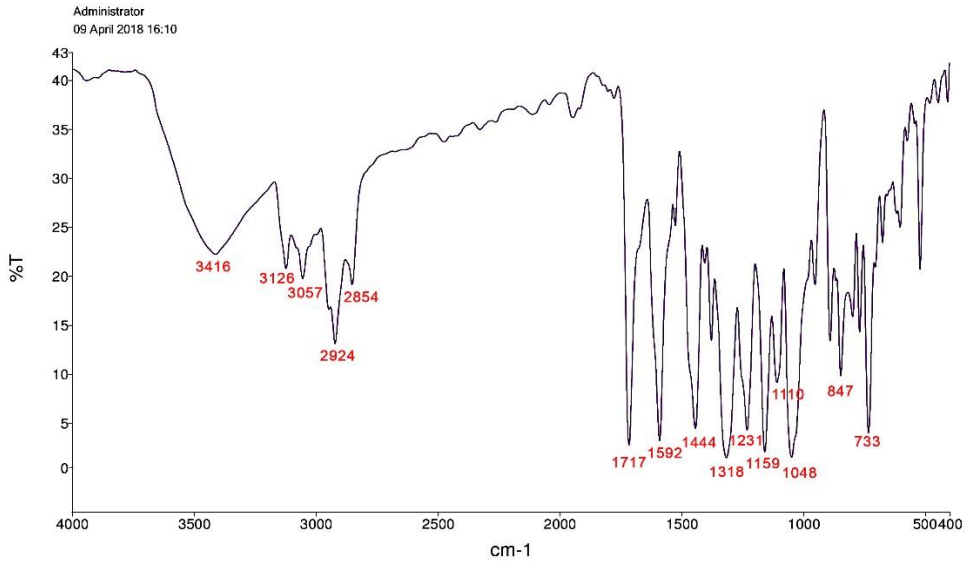

Figure S26. FT-IR spectra of compound **1**.

_____

DFT computational results:

Cartesian coordinates (X, Y, Z) table and the free energies in atomic unit (a.u.) for the optimized structure of the receptor **1** calculated by DFT methods at the B3LYP/6-31G(d) level.

Receptor **1** E = -2326.41217863 a.u.

Atom	X	Y	Z
C	1.326300000	-8.333100001	1.076700000

O	-1.039700000	-7.059800001	0.638900000
C	2.523300000	-1.042100000	-1.440300000
C	-2.571700000	-1.098400000	-1.428700000
C	7.410600001	0.180400000	-0.890200000
C	-7.483000001	0.025500000	-0.879600000
O	1.243000000	-6.943400001	0.590500000
O	2.453600000	-2.447700000	-0.988400000
O	-2.469600000	-2.501200000	-0.974000000
C	7.052400001	5.327100001	-1.514000000
C	7.991400001	0.919400000	4.262200001
C	-7.194600001	5.176300001	-1.504100000
C	-8.101600001	0.758700000	4.269600001
C	6.967100001	4.199900001	-2.382300000
C	7.908700001	-0.230000000	3.422600000
C	-7.090700001	4.050100000	-2.371600000
C	-7.998400001	-0.389800000	3.431200000
C	7.248400001	5.140700001	-0.170600000
C	7.883700001	2.170300000	3.715200000
C	-7.393800001	4.987800001	-0.161400000
C	-8.008100001	2.010700000	3.722500000
C	7.083800001	2.922300000	-1.892900000
C	7.728100001	-0.102800000	2.068300000
C	-7.192200001	2.771200000	-1.882100000
C	-7.812200001	-0.260800000	2.077800000
C	-0.008900000	-2.372000000	-1.011400000
C	1.233300000	-4.348900001	-0.314900000
C	-1.200700000	-4.373600001	-0.307700000
C	-4.971500001	-0.468700000	-0.651000000
C	7.571700001	3.629300000	1.754000000
C	-7.705600001	3.472900000	1.762200000
N	-4.607700001	-0.795800000	-2.838600000
C	-0.005200000	-6.412300001	0.408300000
C	3.953300000	-0.696300000	-1.606900000
C	-4.009100000	-0.784600000	-1.594800000
C	1.205300000	-3.031700000	-0.778300000
C	-1.207800000	-3.057500000	-0.771100000
C	0.023600000	-5.014600001	-0.082200000
C	7.432100001	1.371800000	0.047600000
C	-7.526300001	1.216700000	0.057800000
N	5.838000001	-0.368700000	-2.716900000
N	-6.122500001	-0.299000000	-1.353600000
C	7.373200001	3.824800000	0.382300000
C	7.690000001	2.349700000	2.306100000
C	-7.503300001	3.670500000	0.391500000
C	-7.809400001	2.192100000	2.314400000
C	7.298200001	2.675800000	-0.494300000
C	7.615900001	1.186700000	1.441500000
C	-7.408600001	2.522300000	-0.484300000
C	-7.714600001	1.029800000	1.450800000
N	4.551600001	-0.692300000	-2.850900000
N	6.056400001	-0.168500000	-1.365100000
C	4.909300001	-0.363000000	-0.662600000
N	-5.900300001	-0.498100000	-2.705000000
H	2.387500000	-8.536800001	1.146400000

H	0.846000000	-9.003200001	0.368300000
H	0.848300000	-8.415100001	2.049400000
H	2.010600000	-0.943300000	-2.396800000
H	2.038000000	-0.408900000	-0.696800000
H	-2.099800000	-0.452900000	-0.687200000
H	-2.062500000	-0.990200000	-2.386100000
H	7.984900001	0.378600000	-1.791100000
H	7.846300001	-0.701200000	-0.431900000
H	-8.060300001	0.213400000	-1.781000000
H	-7.903100001	-0.863700000	-0.421500000
H	6.958800001	6.324100001	-1.922000000
H	8.136200001	0.795100000	5.326400001
H	-7.112700001	6.174400001	-1.912000000
H	-8.250600001	0.633000000	5.333100001
H	6.804300001	4.356300001	-3.440100000
H	7.988100001	-1.214900000	3.862200000
H	-6.926000001	4.208300001	-3.428800000
H	-8.066500001	-1.375600000	3.870900000
H	7.311500001	5.987600001	0.500700000
H	7.940500001	3.052500000	4.339800001
H	-7.471300001	5.834000001	0.509200000
H	-8.080500001	2.892400000	4.346300001
H	6.992800001	2.092100000	-2.576900000
H	7.665200001	-1.001000000	1.472600000
H	-7.087800001	1.942200000	-2.565600000
H	-7.733600001	-1.158400000	1.483100000
H	-0.020700000	-1.358100000	-1.372500000
H	2.180000000	-4.833500001	-0.144500000
H	-2.132200000	-4.886500001	-0.128400000
H	-4.914800001	-0.354800000	0.414300000
H	7.631900001	4.491900001	2.406400000
H	-7.780900001	4.334900001	2.413900000
H	4.850700001	-0.253100000	0.403000000

Cartesian coordinates of the benzoate bound receptor

Benzoate bound receptor 1 : E = -2746.57466142 a.u.

Atom	X	Y	Z
C	10.909800001	-0.444600000	-0.426500000
O	9.358800001	1.777100000	-0.659600000
C	3.415100000	-2.127300000	0.955700000
C	3.078400000	2.962000000	0.311800000
C	-0.042200000	-5.620600001	-0.025800000
C	-1.167100000	5.389400001	-0.954400000
O	9.447800001	-0.468600000	-0.241400000
O	4.839900001	-1.994200000	0.568600000
O	4.429500001	2.826500000	-0.302300000
C	-2.897100000	-3.873100000	3.953500000
C	-4.234000001	-5.172700001	-3.131500000
C	-3.942700000	5.770800001	3.221900000
C	-4.530900001	2.248700000	-3.174900000
C	-1.532200000	-4.246900001	3.782300000
C	-2.875100000	-5.551500001	-3.338200000
C	-2.698100000	6.335500001	2.816300000

C	-3.287100000	2.793200000	-3.610700000
C	-3.754700000	-3.913400000	2.885300000
C	-4.651700001	-4.792100001	-1.884100000
C	-4.621700001	4.935000001	2.374200000
C	-5.016300001	2.569400000	-1.935100000
C	-1.060400000	-4.654800001	2.559100000
C	-1.976600000	-5.547100001	-2.301200000
C	-2.167400000	6.058300001	1.580600000
C	-2.568900000	3.642000000	-2.807000000
C	4.535500001	0.413600000	0.173000000
C	6.728900001	-0.653000000	0.119100000
C	6.525300001	1.736700000	-0.297100000
C	0.740600000	3.747000000	-0.435800000
C	-4.175300000	-4.369700001	0.496500000
C	-4.794200001	3.767200000	0.206500000
N	2.162800000	5.306000001	0.339400000
C	8.773300001	0.715700000	-0.385700000
C	2.651000000	-3.337800000	0.576900000
C	2.009300000	3.958200000	0.079900000
C	5.343500001	-0.723000000	0.292300000
C	5.143700001	1.642300000	-0.121700000
C	7.313300001	0.582600000	-0.185100000
C	-1.474200000	-5.145800001	0.133900000
C	-2.333900000	4.895200001	-0.635000000
N	2.333700000	-5.490500001	0.175000000
N	0.164400000	4.977300001	-0.473300000
C	-3.303300000	-4.329600001	1.590500000
C	-3.745700000	-4.768100001	-0.773400000
C	-4.103600000	4.618900001	1.076200000
C	-4.297100001	3.449500000	-1.061400000
C	-1.921400000	-4.721300001	1.411200000
C	-2.363600000	-5.163000001	-0.970600000
C	-2.845500000	5.196000001	0.653400000
C	-3.036000000	4.018000000	-1.500000000
N	3.225500000	-4.593800001	0.596000000
N	1.175200000	-4.790800001	-0.116400000
C	1.348500000	-3.463800000	0.124700000
N	1.040800000	5.943500001	0.003600000
C	-4.114200000	-1.613500000	0.409200000
C	-2.776600000	-1.516100000	0.015400000
C	-2.197900000	-0.264900000	-0.246200000
C	-2.983100000	0.889400000	-0.102500000
C	-4.322100001	0.795300000	0.285300000
C	-4.891400001	-0.457200000	0.543200000
C	-0.846000000	-0.118500000	-0.559000000
O	-0.407100000	1.356100000	-0.747200000
O	-0.103000000	-1.473300000	-0.740800000
H	11.224500001	-1.468100000	-0.264300000
H	11.366200001	0.223300000	0.299700000
H	11.151900001	-0.117800000	-1.434700000
H	3.348400000	-2.108300000	2.044000000
H	2.842100000	-1.293400000	0.553100000
H	2.482800000	2.071300000	0.113800000
H	3.221700000	3.090200000	1.385300000

H	0.119900000	-6.267600001	0.831900000
H	-0.077900000	-6.264600001	-0.898300000
H	-1.254100000	6.439500001	-0.687100000
H	-1.166300000	5.344000001	-2.038600000
H	-3.246700000	-3.556700000	4.926500001
H	-4.925200001	-5.185500001	-3.962900000
H	-4.341700001	6.003100001	4.199700001
H	-5.081300001	1.583500000	-3.825900000
H	-0.860400000	-4.203100001	4.628700001
H	-2.550100000	-5.843600001	-4.327500001
H	-2.164800000	6.986700001	3.495600000
H	-2.904900000	2.528500000	-4.587200001
H	-4.792900001	-3.628900000	2.999300000
H	-5.678800001	-4.496900001	-1.712000000
H	-5.565500001	4.495600001	2.670700000
H	-5.956600001	2.160800000	-1.587700000
H	-0.015300000	-4.907600001	2.462300000
H	-0.956600000	-5.835400001	-2.505300000
H	-1.211900000	6.485000001	1.315700000
H	-1.626900000	4.020600000	-3.173300000
H	3.460600000	0.337400000	0.240500000
H	7.325200001	-1.545000000	0.216600000
H	6.975800001	2.690300000	-0.522900000
H	0.269700000	2.816800000	-0.723200000
H	-5.210000001	-4.080600000	0.635600000
H	-5.737700001	3.340300000	0.524700000
H	0.575900000	-2.735000000	-0.028600000
H	-4.548100001	-2.583800000	0.611900000
H	-2.164600000	-2.399900000	-0.090600000
H	-2.525600000	1.848200000	-0.298000000
H	-4.918500001	1.692600000	0.389000000
H	-5.927800001	-0.531400000	0.845900000