Supporting Information:

Recognition of Carboxylate Anions and Carboxylic Acids by Selenium based New Chromogenic Fluorescent Sensor: A Remarkable Fluorescence Enhancement of Hindered Carboxylates

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Table of Contents:

1. Synthetic procedure of the receptor 1: 2,5,6-Triamino-3*H*-pyrimidin-4-one dihydrochloride (1 gm, 4.7 mmol) and selenium dioxide (0.51 g, 4.7 mmol) were thoroughly ground together. Then the mixture was irradiated at 400 Watt for 15 minutes in a microwave oven (SANYO 800W) taken in an open mouth conical flask. Water was added to it and the precipitate was filtered and dried well. The dry crude product was then heated at 100-120 °C with pivalic anhydride (2 ml) and a catalytic amount of DMAP for 6 hours. The product was purified through column chromatography (silica gel, 100-200 mesh) eluting 2% methanol in chloroform to get pure compound.

Mp 194-195 °C;

IR: 3295, 3136, 2967, 2873, 1673, 1624, 1512, 1455, 1372, 1239, 1147, 1021, 930, 800, 735, 614, 562, 473 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): 12.03 (bs, 1H), 8.54 (bs, 1H), 1.35 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): 181.1, 164.1, 155.2, 149.9, 147.2, 40.6, 26.9.

MS (ES): 302.1 [$(M+2H)^+$, 60], 300.1 [M^+, 30].

Anal. Calcd for $C_9H_{11}N_5O_2Se$: C, 36.01; H, 3.69; N, 23.33; Found: C, 35.93; H, 3.86; N, 23.20.

2. General procedure for UV-vis titration:

UV–vis spectra were recorded on a JASCO V-530. The stock solution of the receptor **1** was prepared in the order of 1.00 x 10^{-4} mL^{-1} in $CHCl_3$. The solutions of guest acids were also prepared in *ca* 1 x 10^{-3} mL^{-1} order in $CHCl_3$. Then the guest solution is added to the receptor solution (taking 2 mL in the UV-cell) and continuous decreases of absorbance in UV spectra were recorded each time. Association constants were calculated by plotting $1/\Delta I$ *vs* 1/[G].

3. General procedure for Fluorescence titration:

Fluorescence spectra were recorded on Perkin Elmer LS-55. The stock solution of receptor **1** was taken in the order of 1.87 x 10^{-4} mL^{-1} in $CHCl_3$. The solutions of guest acids were also prepared *ca* 1 x 10^{-3} mL^{-1} order. Then the guest solutions were added to the receptor solution (taking 2 mL in the cell) and continuous increase of intensity of

emission spectra was recorded each time. Association constants were calculated by plotting I_0/I_0-I *vs* 1/[G] (I_0 and I are the initial and final intensity of the receptor solution after each addition during titration).

4. ^{1}H NMR of receptor 1:

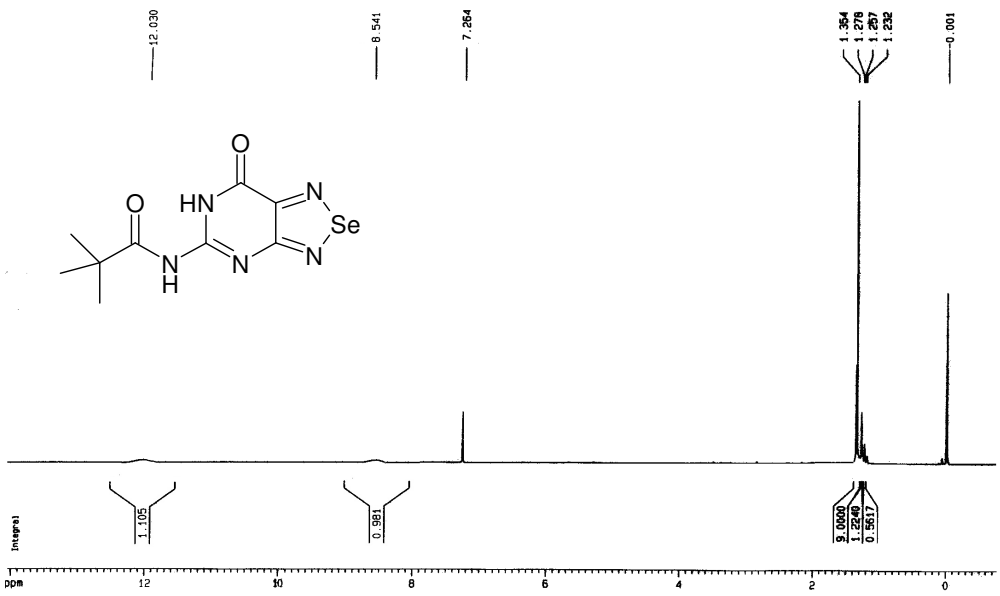


Figure S1

5. ^{13}C NMR of receptor 1:

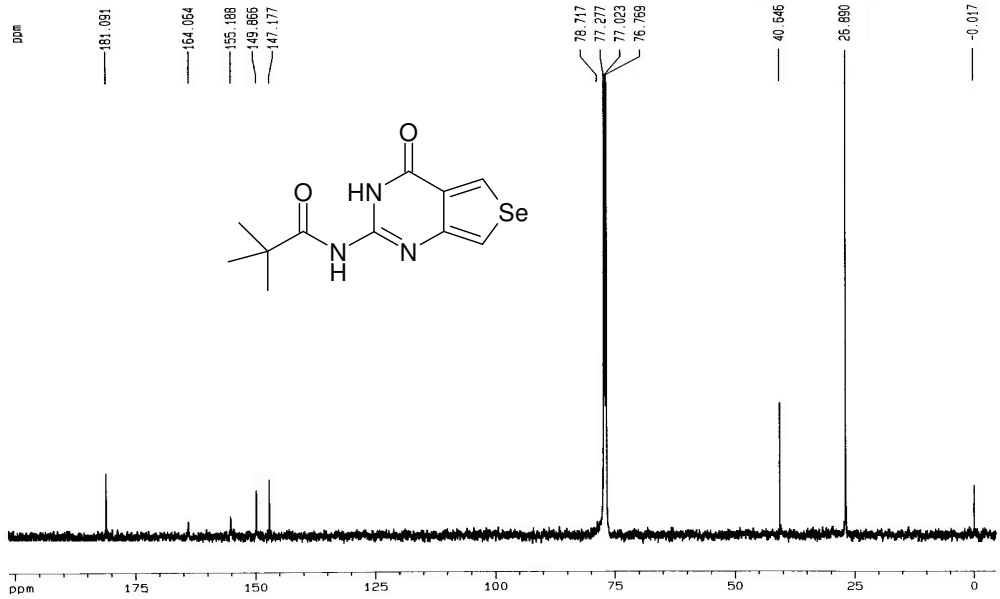


Figure S2

6. Mass spectra of receptor 1: 302.1 $(M+2H)^+$

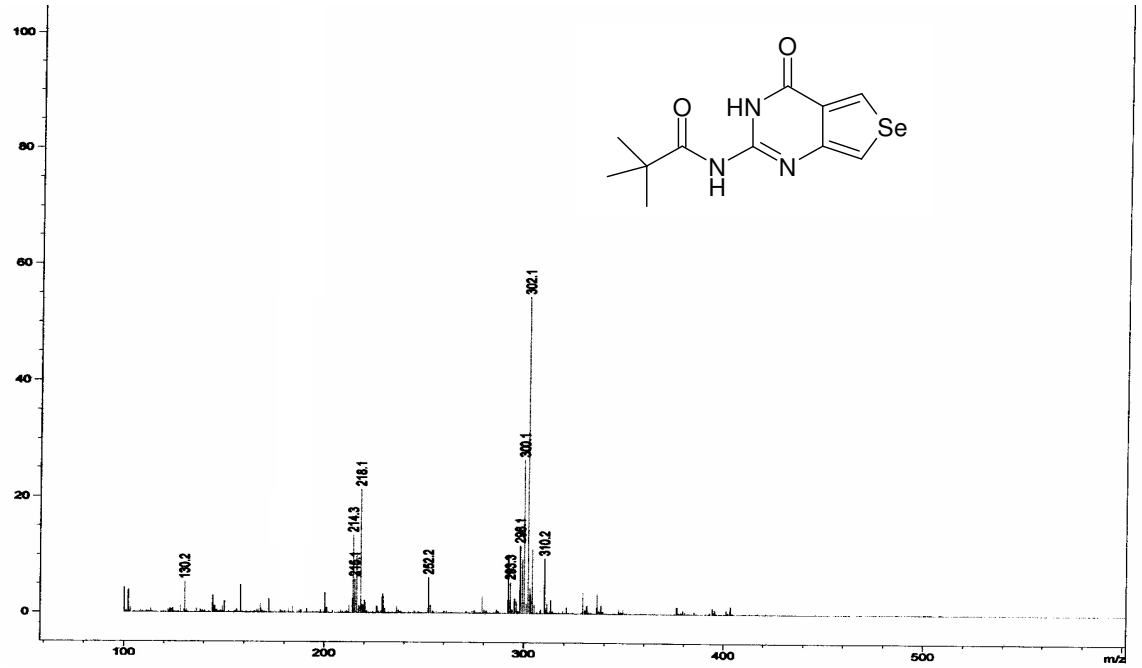


Figure S3

7. 1:1 ^{1}H NMR of receptor 1 with acetic acid:

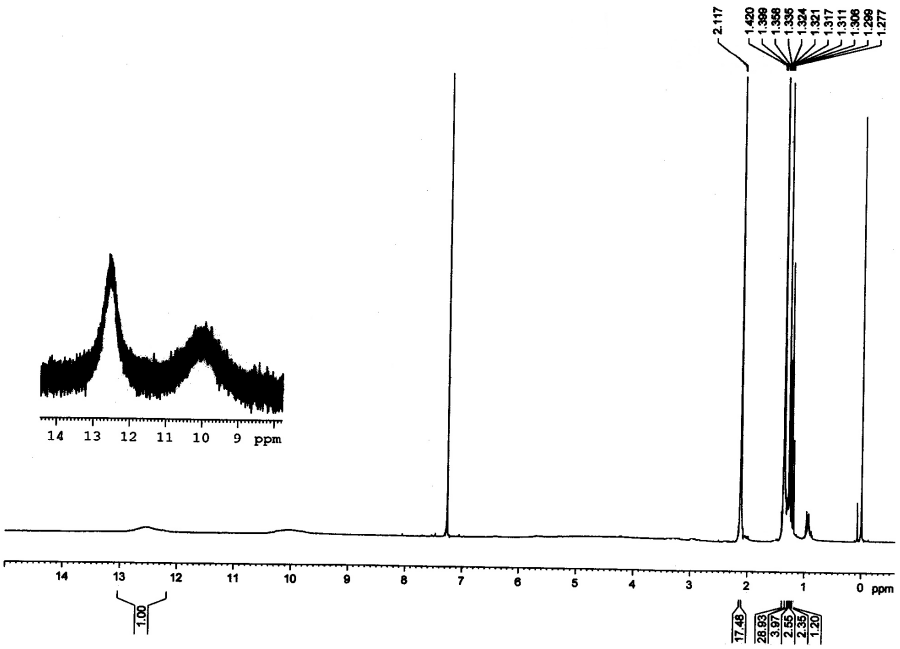


Figure S4

8. 1:1 ^{1}H NMR of receptor 1 with pivalic acid:

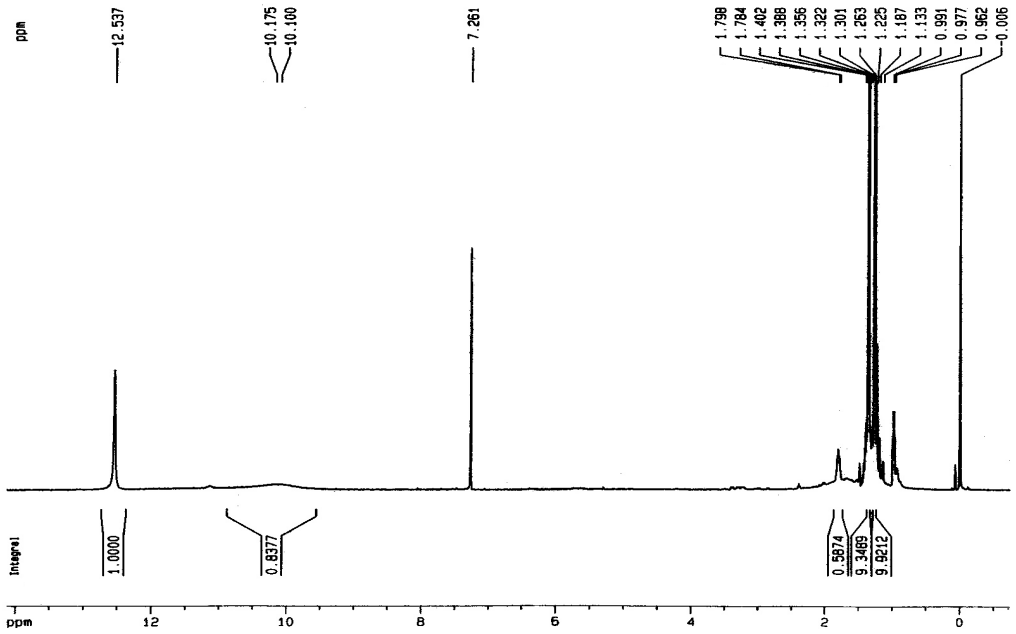


Figure S5

9. 1:1 ^{1}H NMR of receptor 1 with tetrabutylammonium adamantane-1-carboxylate:

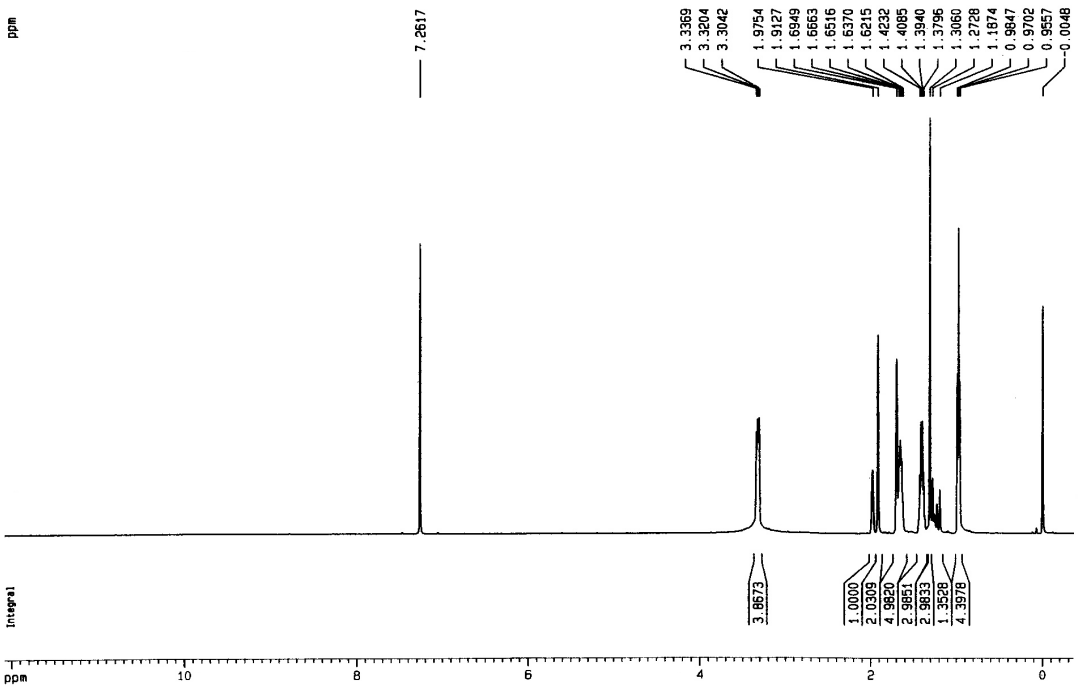
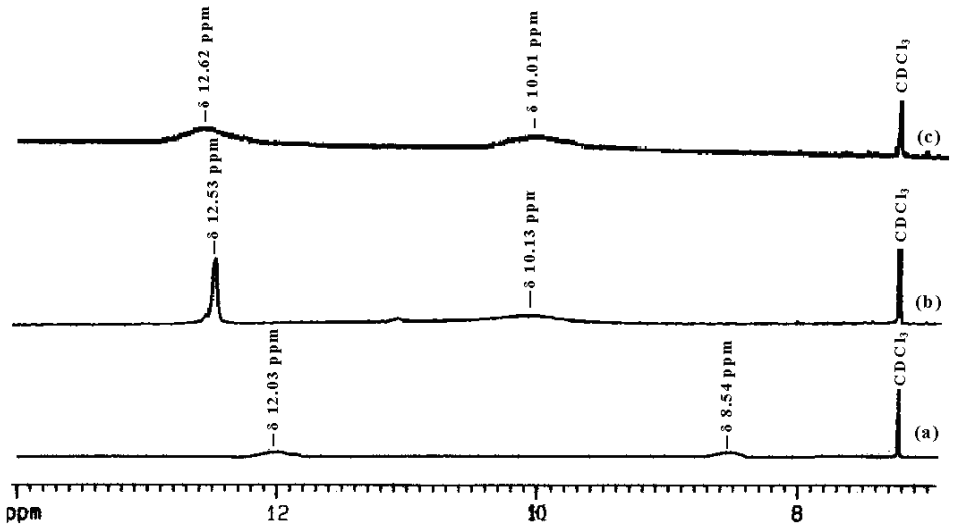
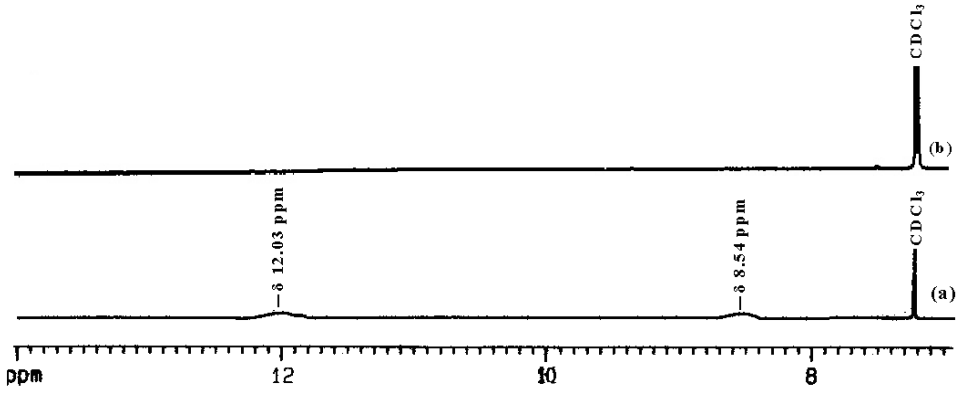


Figure S6



(i)



(ii)

Figure S7: Partial ^{1}H NMR (500 MHz) spectra of **(i)** receptor **1** (a), equivalent amount of pivalic acid (b) and equivalent amount of acetic acid (c) in $CDCl_3$; **(ii)** receptor **1** (a) and equivalent amount of tetrabutylammonium adamantine-1-carboxylate (b) in $CDCl_3$.

10. UV-vis titration spectra and association constant determination curve:

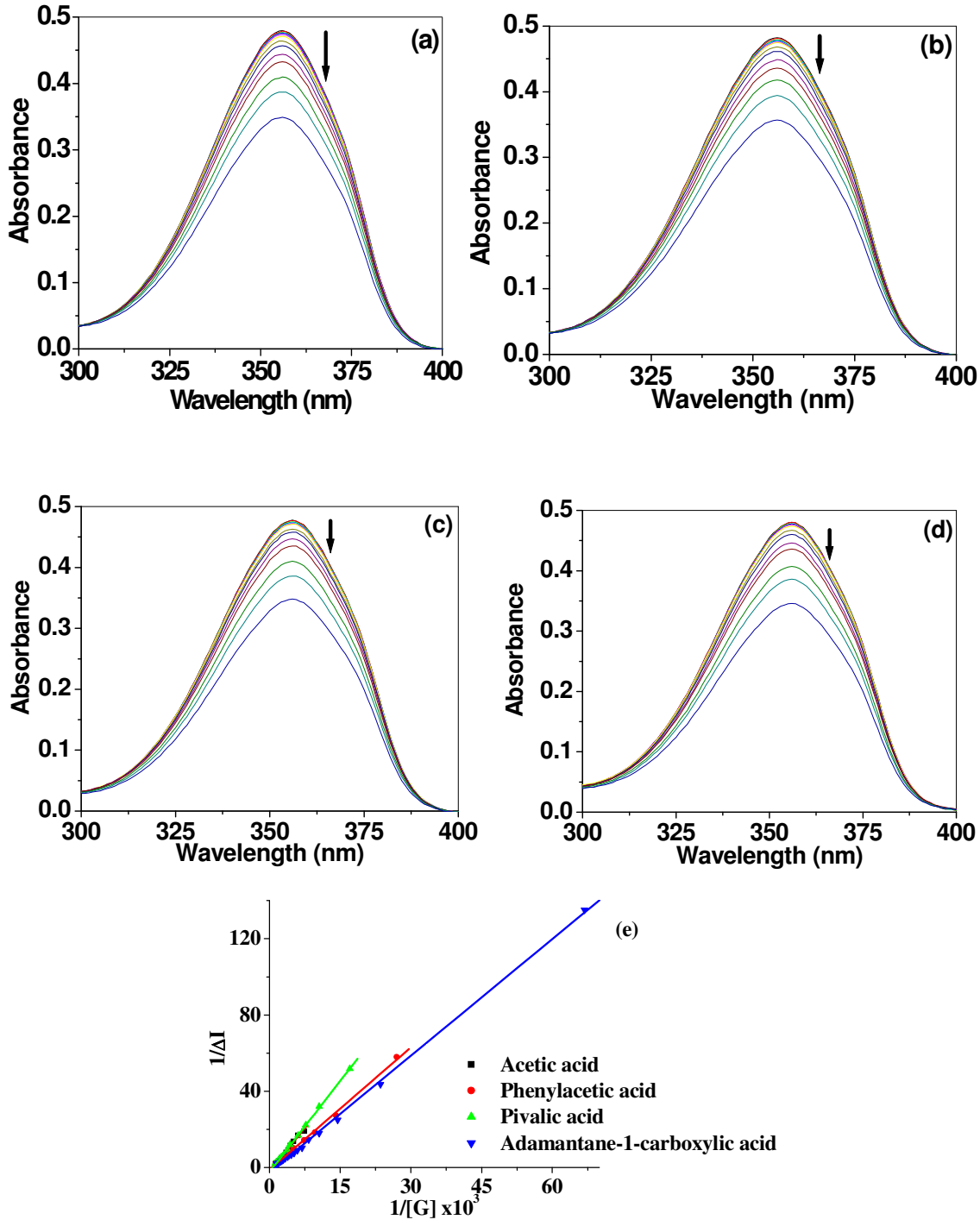
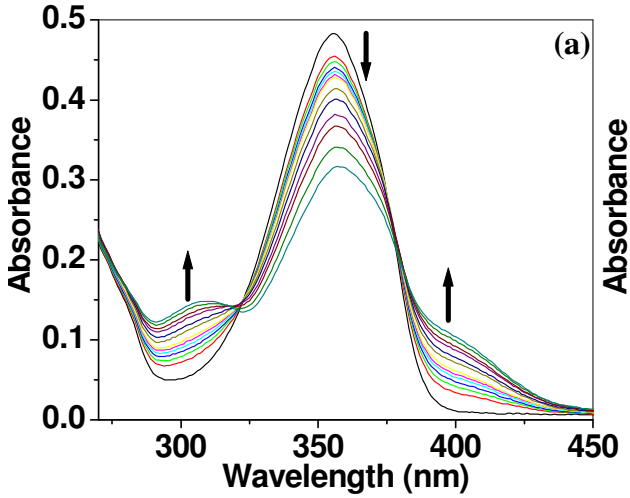
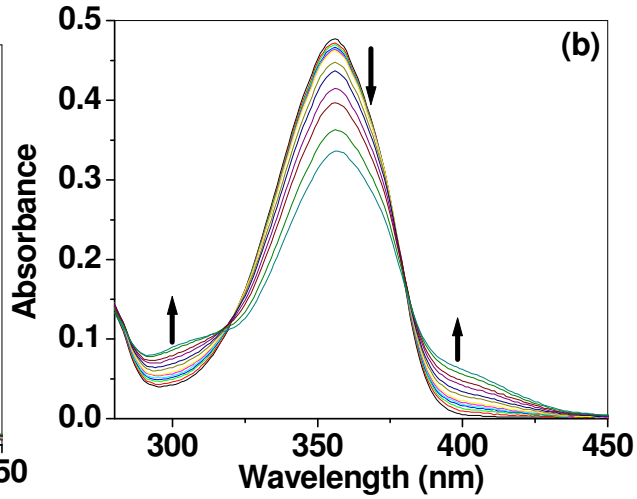
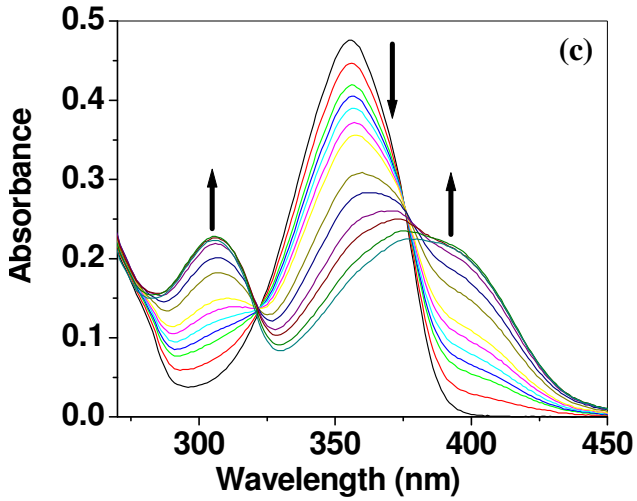
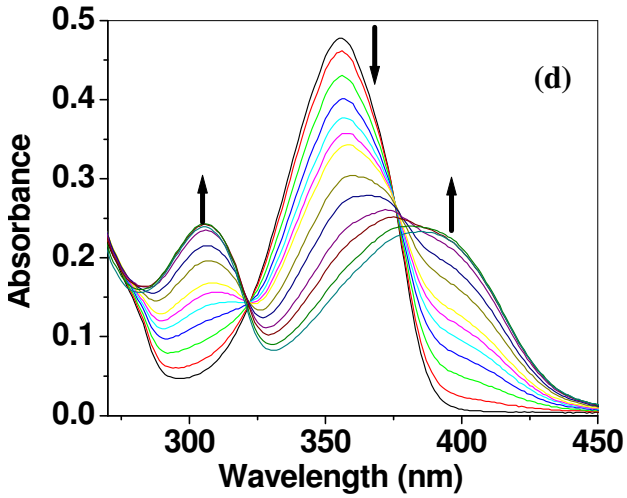


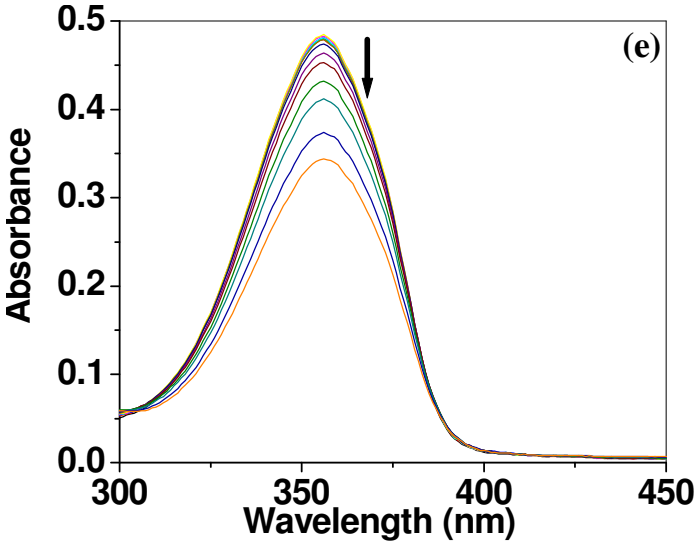
Figure S8: UV-vis titration spectra of receptor **1** (1.00 x 10^{-4} mL^{-1}) with different monocarboxylic acids in $CHCl_3$: (a) acetic acid; (b) phenylacetic acid; (c) pivalic acid; (d) adamantane-1-carboxylic acid; (e) association constant determination curve.

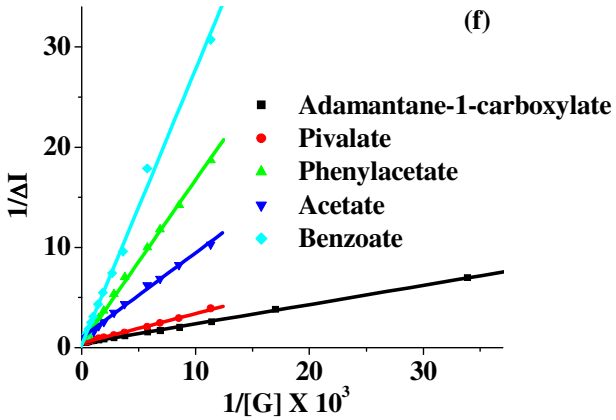

(a)
Absorbance
Wavelength (nm)


(b)
Absorbance
Wavelength (nm)


(c)
Absorbance
Wavelength (nm)


(d)
Absorbance
Wavelength (nm)


(e)
Absorbance
Wavelength (nm)


(f)
Adamantane-1-carboxylate
Pivalate
Phenylacetate
Acetate
Benzoate
1/ΔI
1/[G] X 10^3

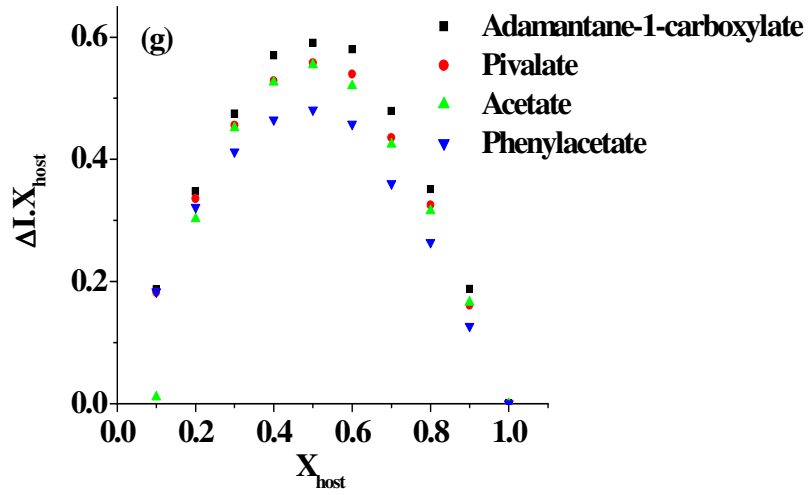


Figure S9: UV-vis titration spectra of receptor **1** (1.00 x 10^{-4} mL^{-1}) with different tertiary butylammonium monocarboxylate salts in $CHCl_3$: (a) acetate; (b) phenylacetate; (c) pivalate; (d) adamantane-1-carboxylate; (e) benzoate; (f) association constant determination curve; (g) Jobs plot.

11. Fluorescence titration spectra and Association constant determination curve:

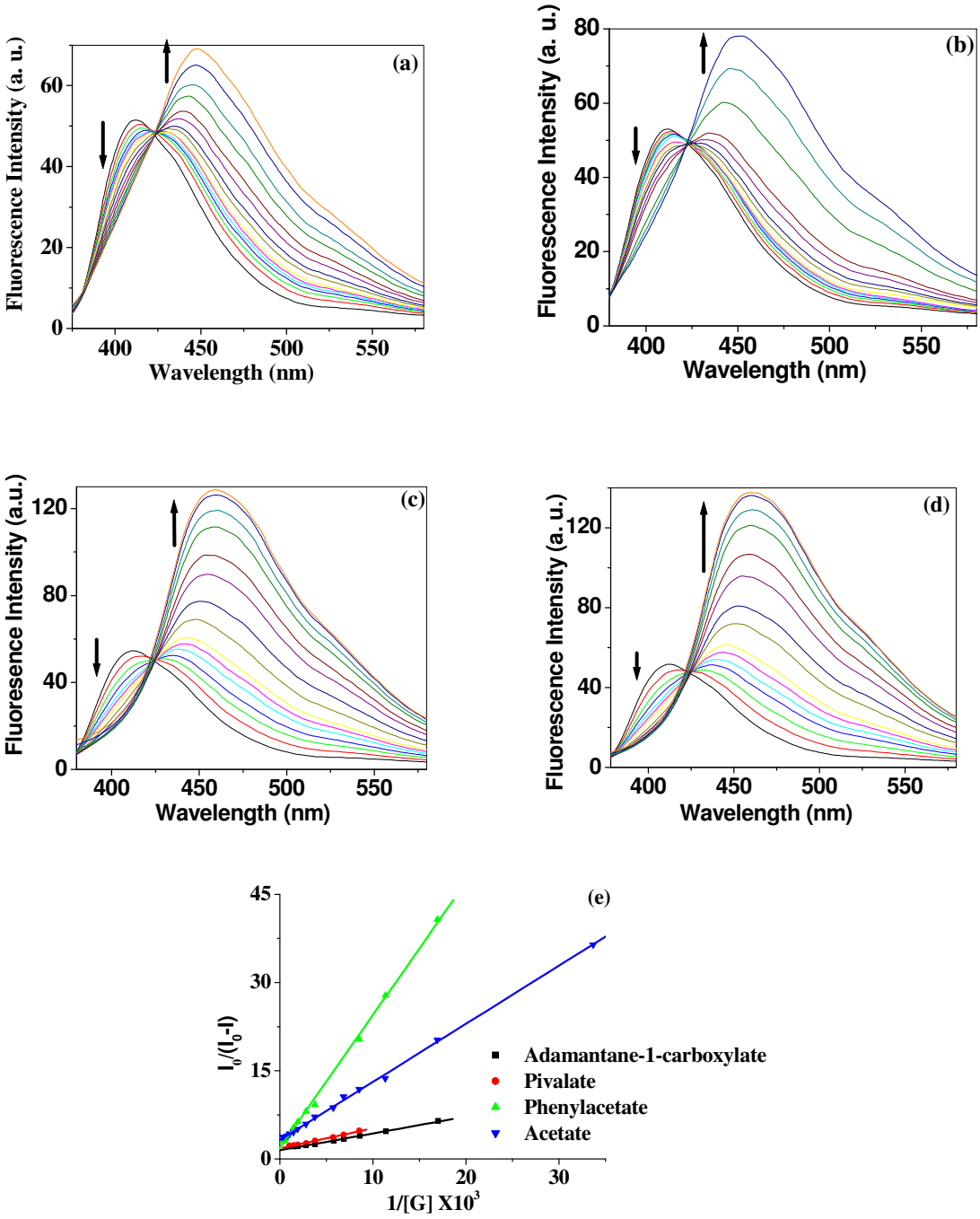


Figure S10: Fluorescence titration spectra of receptor **1** (2.133 x 10^{-4} mL^{-1}) with different monocarboxylic acids in $CHCl_3$: (a) acetate; (b) phenylacetate; (c) pivalate; (d) adamantane-1-carboxylilate; (e) association constant determination curve.

12. Table 1: Crystallographic data and structure refinement parameters of co crystal of receptor and pivalic acid:

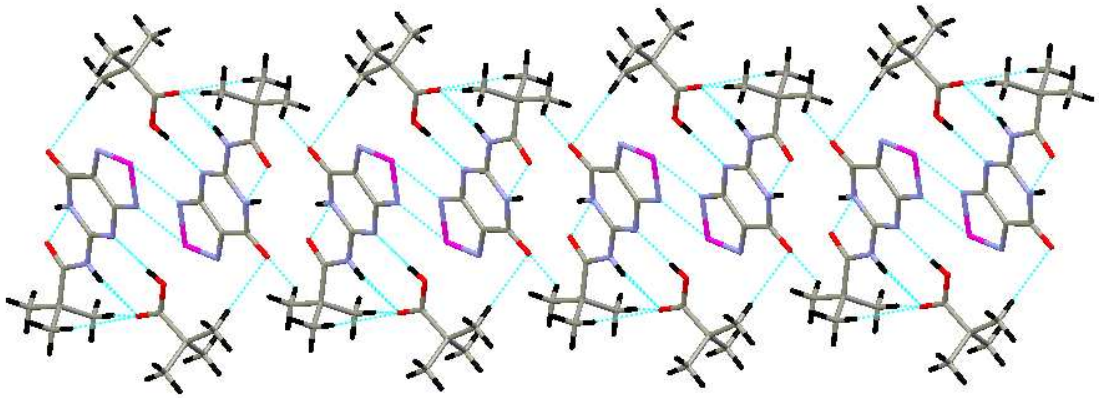
CCDC No.	**740531**
Empirical formula	$C_9H_{11}N_5O_2Se,C_5H_{10}O_2$
Formula weight [g mol^{-1}]	402.32
Crystal system	Triclinic
Space group	*P*-1
T [K]	100
a [Å]	6.20680(10)
b [Å]	10.0735(2)
c [Å]	14.6424(2)
α [deg]	105.5300(10)
β [deg]	94.3850(10)
γ [deg]	97.2430(10)
Z	2
V [$Å^3$]	869.20(3)
Ï [Å]	0.71073
D_{calc} [g/cm^3]	1.537
F [000]	412
Crystal size	0.14 x 0.23 x 0.60
Theta min-max [deg]	1.5 to 35.0
μ [mm^{-1}]	2.189
Index ranges	$-9 \leq h \leq 9$ $-16 \leq k \leq 16$ $-23 \leq l \leq 23$
Reflections collected	31047
Unique reflections	7552
Observed reflections [I > 2.0 sigma(I)]	6806
R_1 [$I > 2\sigma(I)$]	0.0217
wR_2	0.0596
GOF	1.08

13. Table 2: Hydrogen-bond parameters (Å, °) of the complex of receptor **1** with pivalic acid:

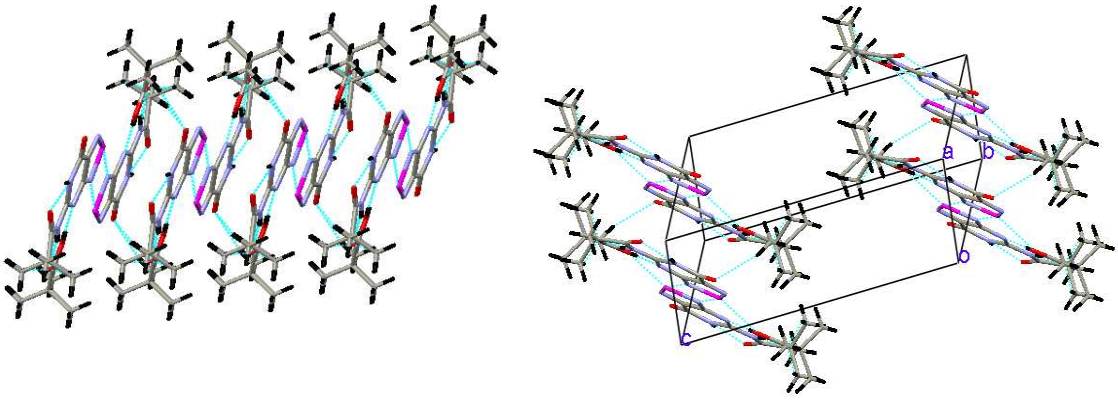
D--H....A	D – H	H...A	D...A	D - H...A
O4--H1...N1	0.775(18)	1.955(18)	2.7257(11)	173.6(19)
Intra N4--H1...O2	0.781(19)	2.027(18)	2.6313(11)	134.1(17)
N5--H1...O3	0.872(17)	2.035(17)	2.8966(11)	169.6(16)
C7--H7C...O3	0.96	2.57	3.4448(14	152
C9--H9A...O1^{i}	0.96	2.48	3.3030(13)	143
C12--H12A...O1^{ii}	0.96	2.59	3.5175(14)	162
C5--O2…*Cg*1^{iii}	1.2232(12)	3.7842(9)	4.3055(9)	107.09(6)
C5--O2…*Cg*2^{iii}	1.2232(12)	3.8278(9)	4.4438(10)	112.60(6)

Symmetry codes: (i) 2-x, -y, -z; (ii) 1-x, 1-y, -z; (iii) 1+x, y, z; *Cg*1 and *Cg*2 are the centroids of the rings C1/N2/Se1/N3/C2 and N1/C1/C2/C3/N4/C4.

14. Illustration of X-ray crystal structure:



(a)



(b) **(c)**

Figure S11: Illustrations for the X-ray crystal structure of receptor **1** with pivalic acid: (a) 2D polymeric chain viewed down along *a* axis; (b) 3D chair like motif; (c) crystal packing.