Supporting Information

A diminutive modification in arylamine electron donors: synthesis, photophysics and solvatochromic analysis – towards the understanding of dye sensitized solar cell performances

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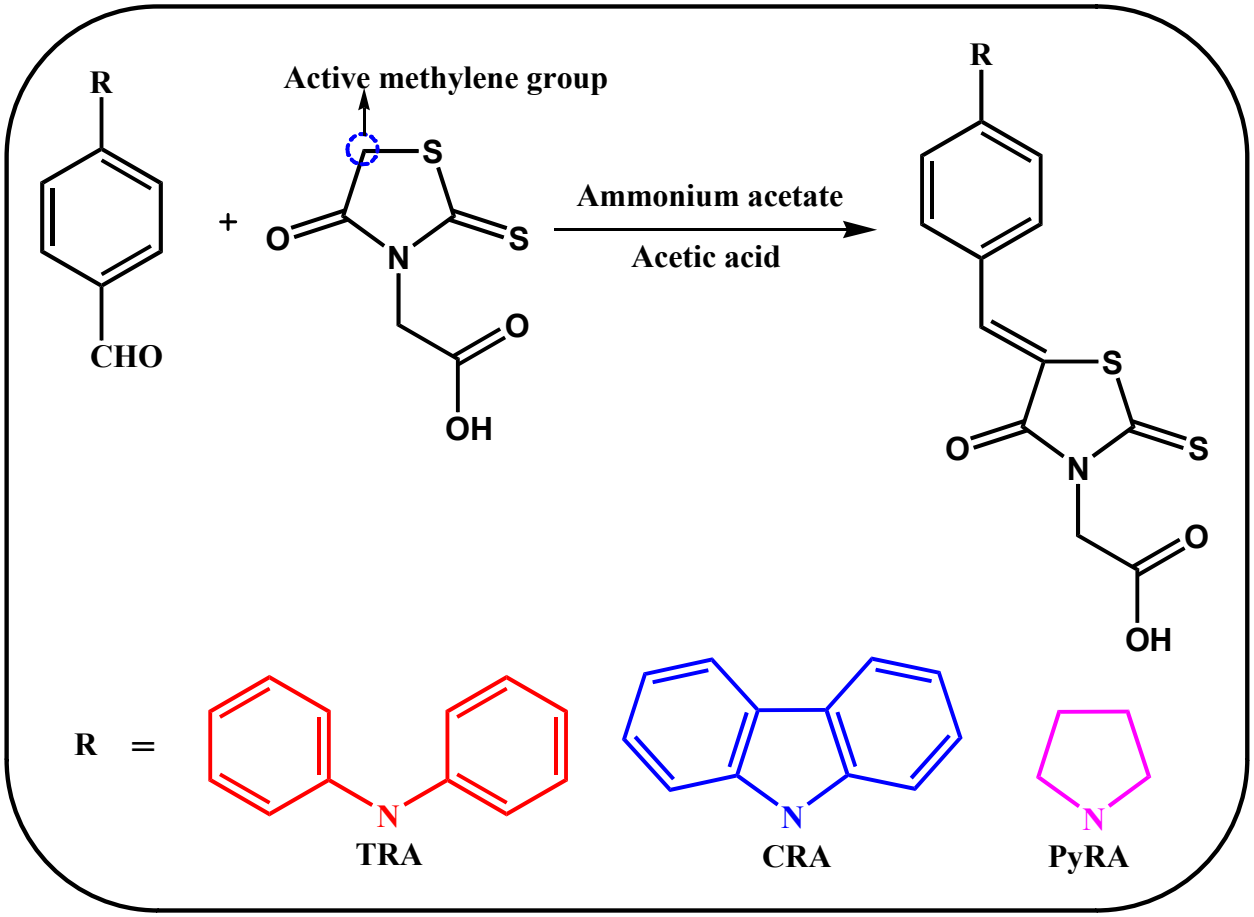

Scheme S1: Synthetic route of Arylamine dyes

Synthesis of [5-(4-Diphenylamino-benzaldene)-4-oxo-2-thioxo-thiozolidin-3-yl]-acetic acid (TRA):

A mixture of 4-(Diphenylamino) benzaldehyde (0.39 g, 1.46 mmol), 4-oxo-2-thioxo-3-thiozolidinyl acetic acid (0.41 g, 2.19 mmol), acetic acid (5 mL) and ammonium acetate (4 mg) was stirred at reflux 12 h. The resultant mixture was poured into ice-cold water to give a Orange colour precipitate. This was filtered, washed thoroughly with water and then dried. The crude product was purified by silica gel column chromatography using chloroform-methanol (v/v: 10: 0.5) to obtain a red solid. Yield: 53.1%. MP: > 200^{o}C. **IR (cm^{-1}) :** 1723 (-C=O-), 1702 (-C=O-), 1571 (-C=C-). **^{1}H NMR:** (DMSO-d_6, 400 MHz) δ ppm: 7.74 (s, 1H), 7.51-7.53 (d, J = 8 Hz, 2H**,** Aromatic), 7.38-7.42 (t, J = 16 Hz, 4H, aromatic), 7.18-7.23 (m, 6H, Aromatic), 6.89-6.91 (d, J=8Hz, 2H), 4.70 (s, 2H, CH_2COOH). **^{13}C NMR:** (DMSO-d_6, 100 MHz) δ ppm: 193.35, 167.84, 166.93, 150.66, 145.98, 134.47, 133.34, 130.49, 126.68, 125.85, 124.96, 119.76, 117.66, 45.48. MS-EI: (m/z) calcd for $C_{24}H_{18}N_2O_3S_2$: 446.08, Found: 446.09.

Synthesis of [5-(4-Carbazol-9-yl-benzylidene)-4-oxo-2-thioxo-thiazolidin-3-yl]-acetic acid (CRA):

A mixture of N-(4-Formyl phenyl) carbazole (0.40 g, 1.47 mmol), 4-oxo-2-thioxo-3-thiozolidinyl acetic acid (0.42 g, 2.20 mmol), acetic acid (5 mL) and ammonium acetate (4 mg) was stirred at reflux 12 h. The resultant mixture was poured into ice-cold water to give a yellow colour precipitate. This was filtered, washed thoroughly with water and then dried. The crude product was purified by silica gel column chromatography using chloroform-methanol (v/v: 10 : 0.5) to obtain a red solid. **Yield**: 74.99%. **Melting point :** > 200^{o}C. **IR (cm^{-1}):** 1746 (-C=O-), 1703 (-C=O-), 1583 (-C=C-). **^{1}H NMR :** (DMSO-d_6, 400 MHz) δ ppm: 13.50 (br s, 1H, COOH), 8.26-8.28 (d,2H,J=8Hz,Aromatic), 7.97-8.00 (d, J = 12 Hz, 2H, aromatic), 7.87-7.89 (d, J = 8 Hz, 2H, aromatic), 7.53-7.55 (d, J = 8Hz, 2H, aromatic), 7.45-7.49 (m, 2H),7.32-7.35 (m,2H,Aromatic), 4.79 (s,2H,CH_2COOH). **^{13}C NMR:**(DMSOd_6, 100MHz) δppm:193.54, 167.78, 166.89, 139.97, 139.6, 133.49, 133.13, 131.92, 127.54, 126.98, 123.65, 122.57, 121.18, 121.13, 110.37, 45.57. MS-EI :(m/z) calcd for $C_{24}H_{16}N_2O_3S_2$: 444.06, Found: 444.11.

Synthesis of [4-Oxo-5-(4-pyrrolidin-1-yl-benzylidene)-2-thioxo-thiazolidin-3-yl]-acetic acid (PyRA):

A mixture of 4-(1-Pyrrolidino) benzaldehyde (0.40 g, 2.29 mmol), 4-oxo-2-thioxo-3-thiozolidinyl acetic acid (0.65 g, 3.44 mmol), acetic acid (5 mL) and ammonium acetate (4 mg) was stirred at reflux 12 h. The resultant mixture was poured into ice-cold water to give a Dark Red colour precipitate. This was filtered, washed thoroughly with water and then dried. The crude product was purified by silica gel column chromatography using chloroform-methanol (v/v: 10: 0.5) to obtain a red solid. **Yield**: 72.1%. **Melting point:** > 200^{o}C. **IR (cm^{-1}) :** 1699 (-C=O-), 1612 (-C=O-), 1561 (-C=C-). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ ppm: 7.72 (s, 1H), 7.47-7.50 (d, J = 12 Hz, 2H, aromatic), 6.68-6.70 (d, J = 8 Hz, 2H, aromatic), 4.70 (s, 2H, CH_2COOH), 1.96-1.99 (m, 6H) **^{13}C NMR:** (DMSO-d_6, 100MHz) δ ppm: 192.94, 167.94, 166.87, 150.08, 136.03,134.06, 119.87, 113.04, 113.01, 47.89, 45.50,25.37. MS-EI:(m/z) calcd for $C_{16}H_{16}N_2O_3S_2$: 348.06, Found: 348.08.

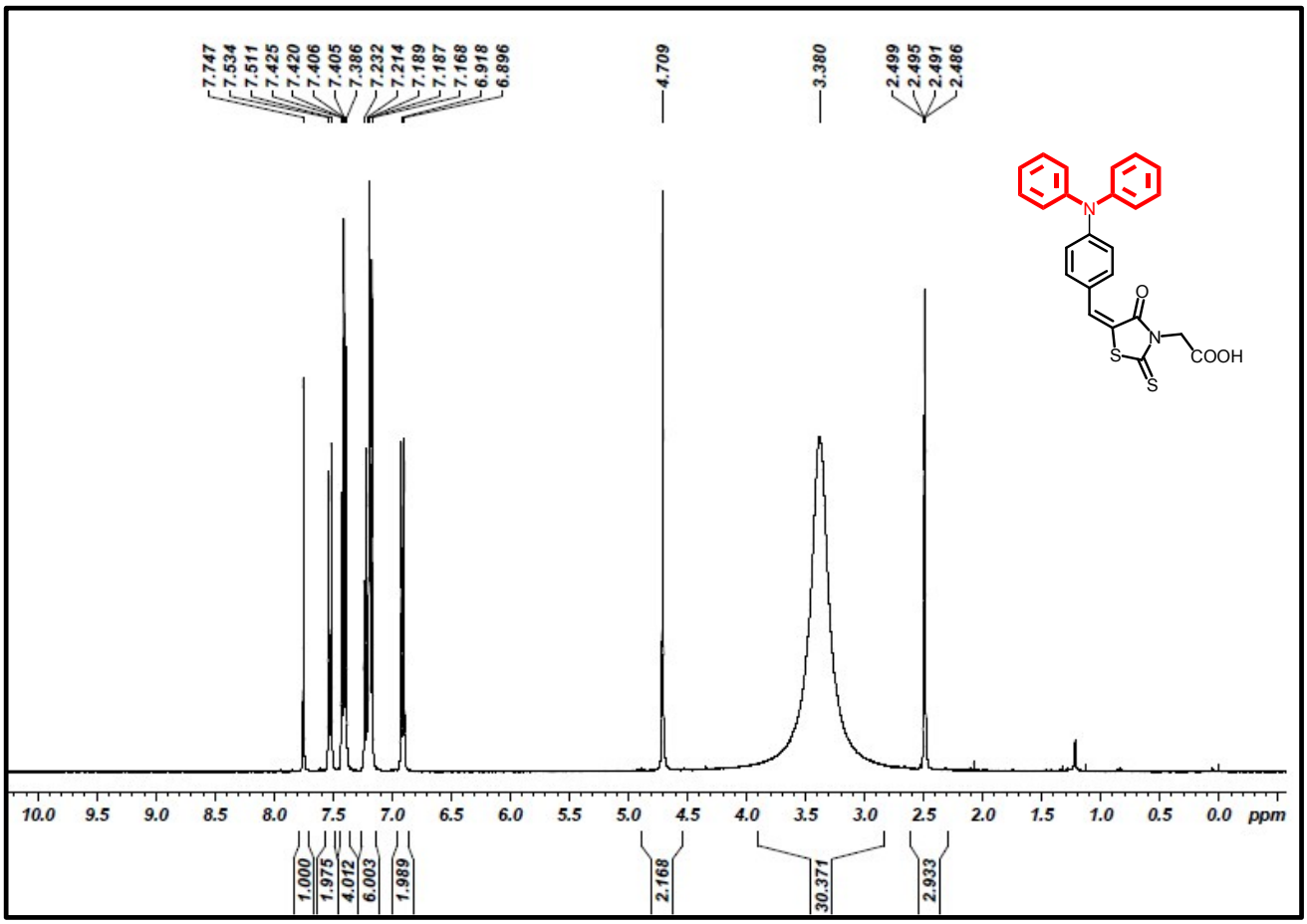

Figure S1: ^{1}H NMR spectrum of TRA in DMSO – d_6

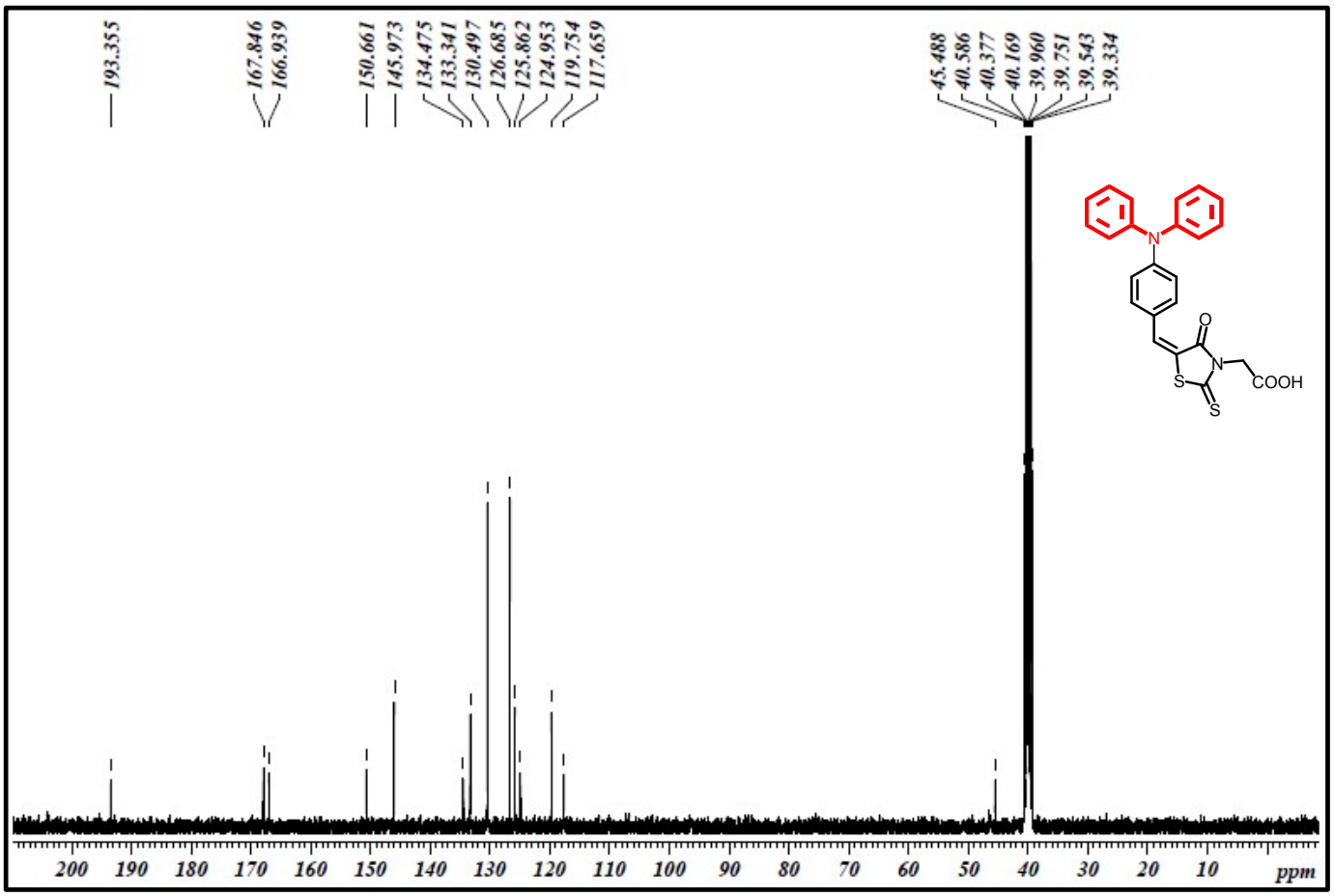

Figure S2: ^{13}C NMR spectrum of TRA in DMSO – d_6

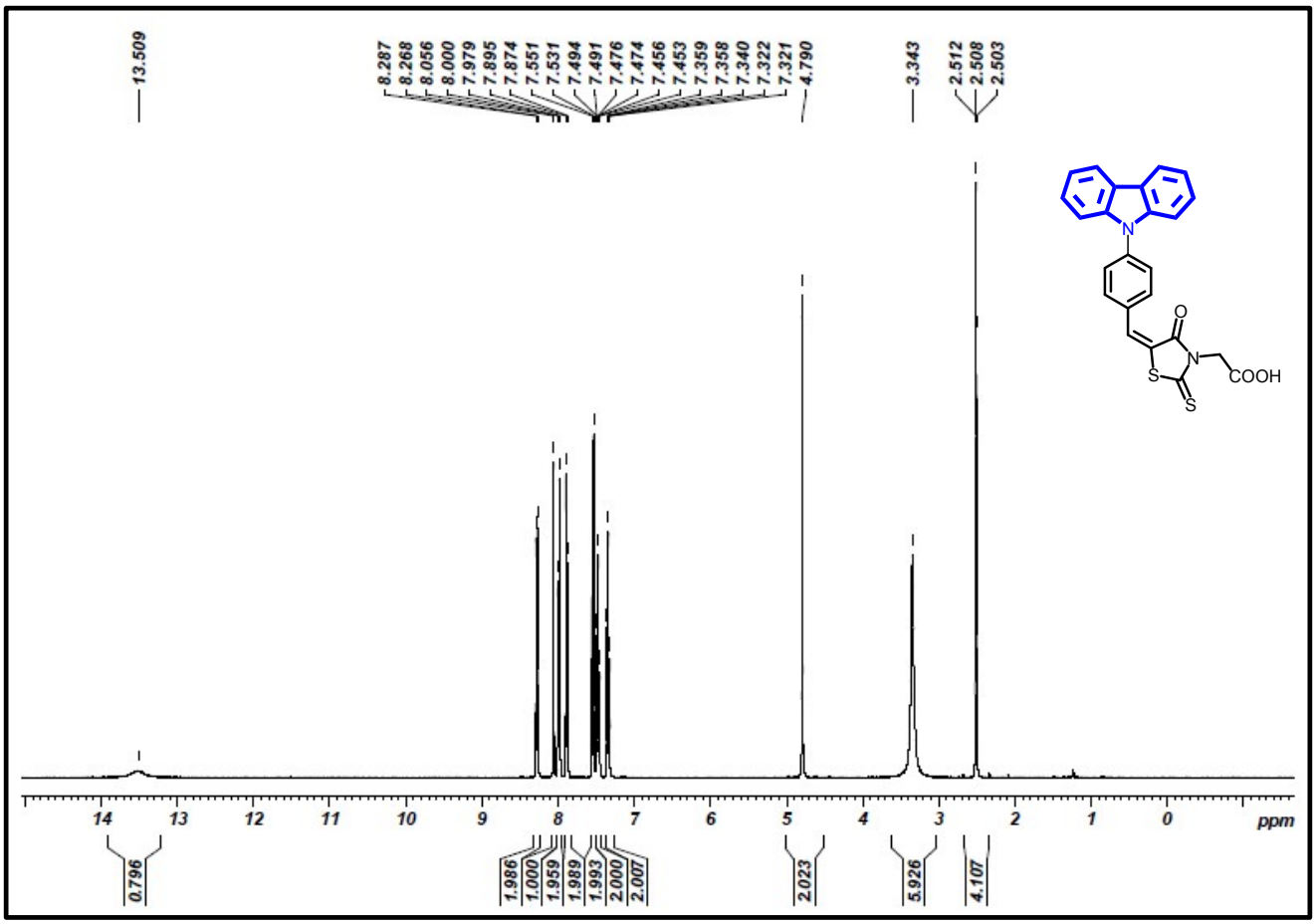

Figure S3: ^{1}H NMR spectrum of CRA in DMSO – d_6

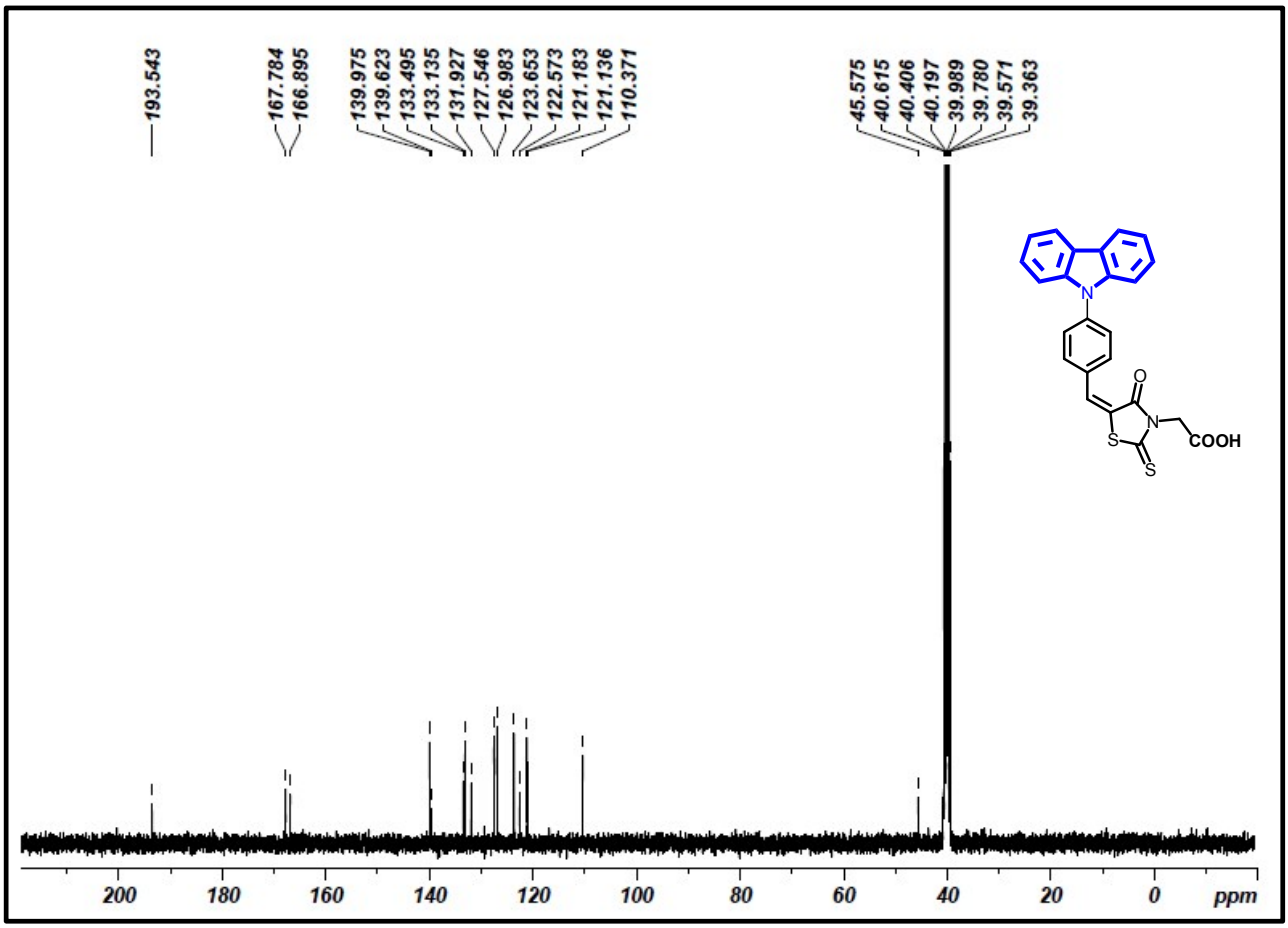

Figure S4: ^{13}C NMR spectrum of CRA in DMSO – d_6

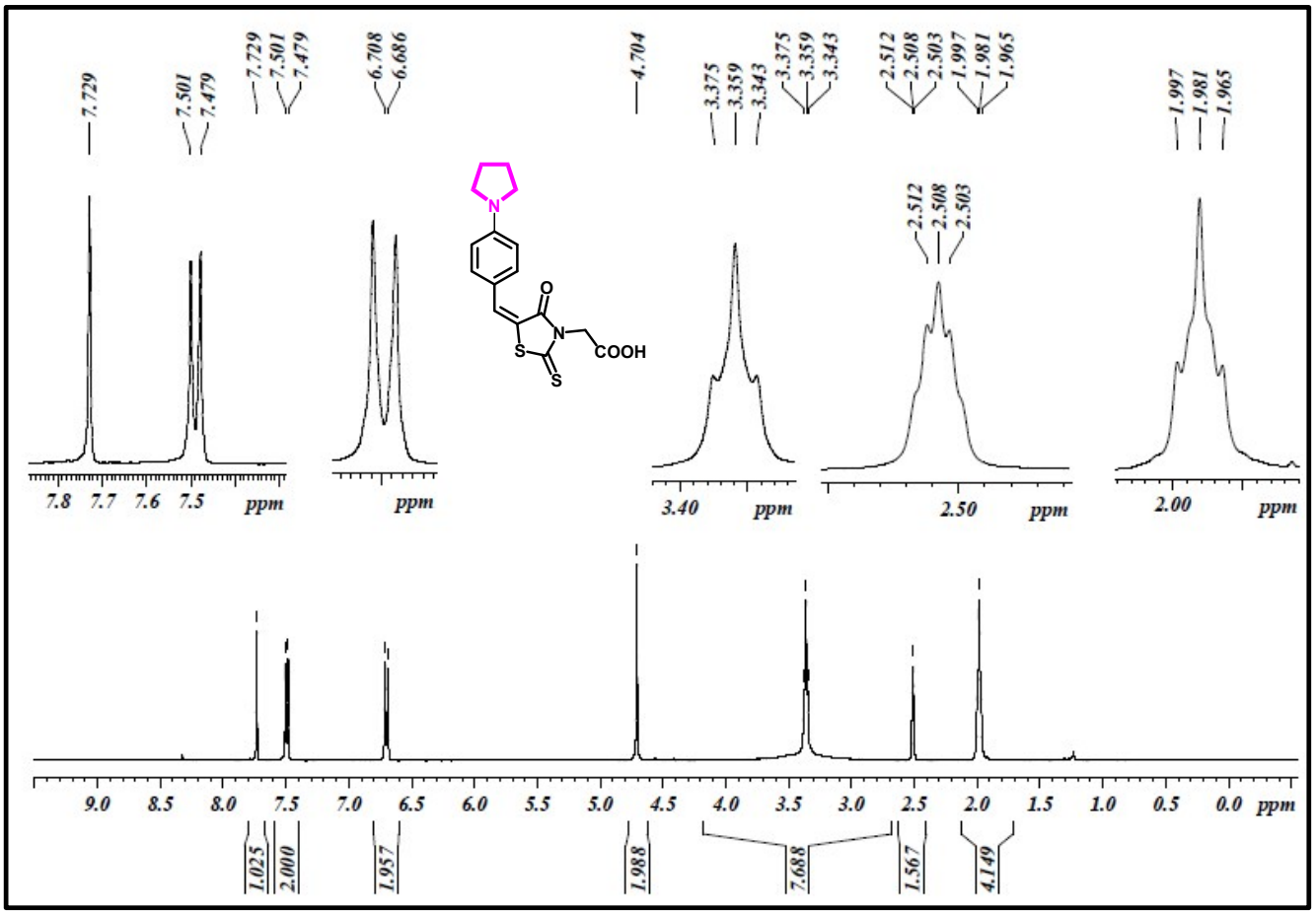

Figure S5: ^{1}H NMR spectrum of PyRA in DMSO – d_6

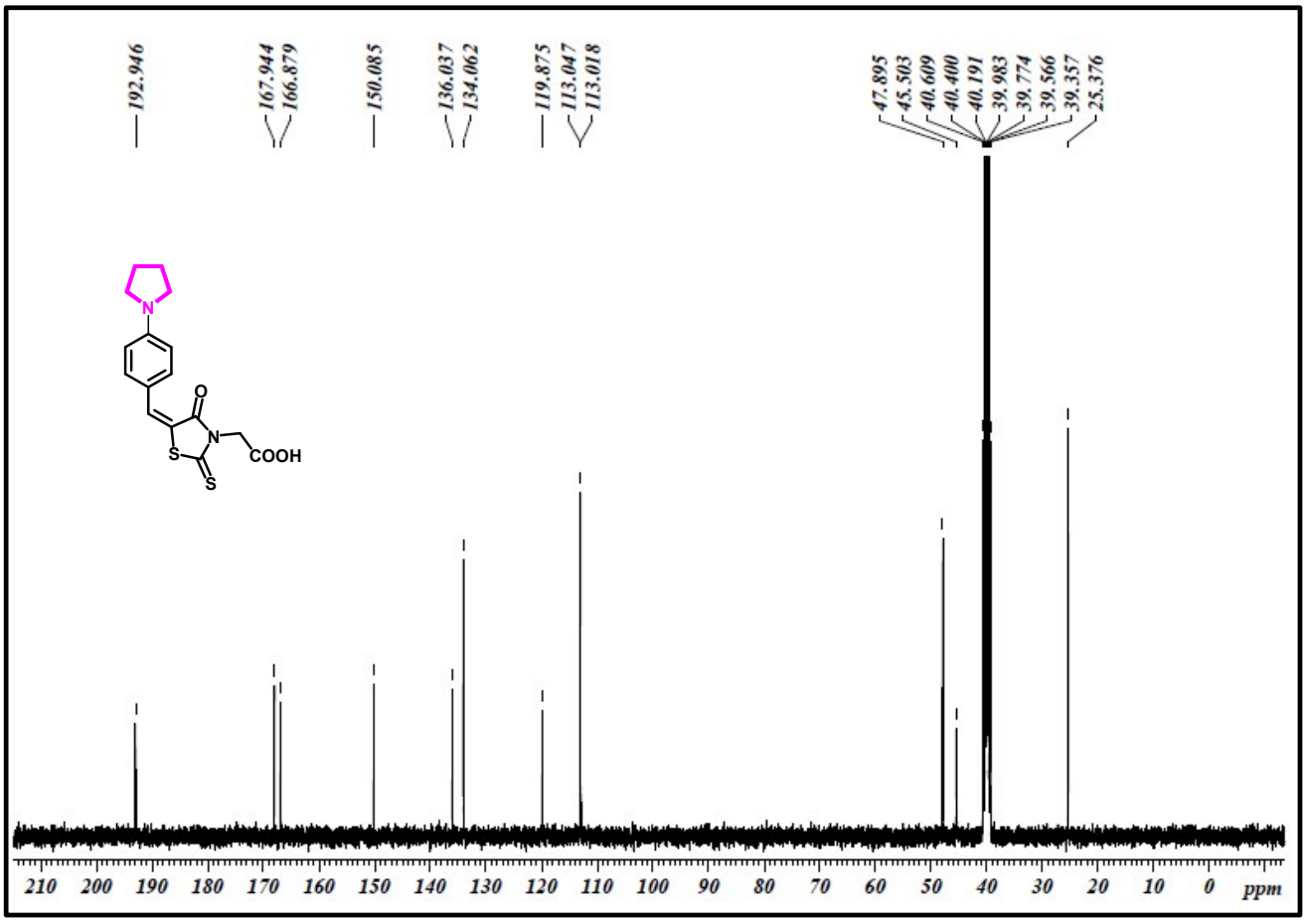

Figure S6: ^{13}C NMR spectrum of PyRA in DMSO – d_6

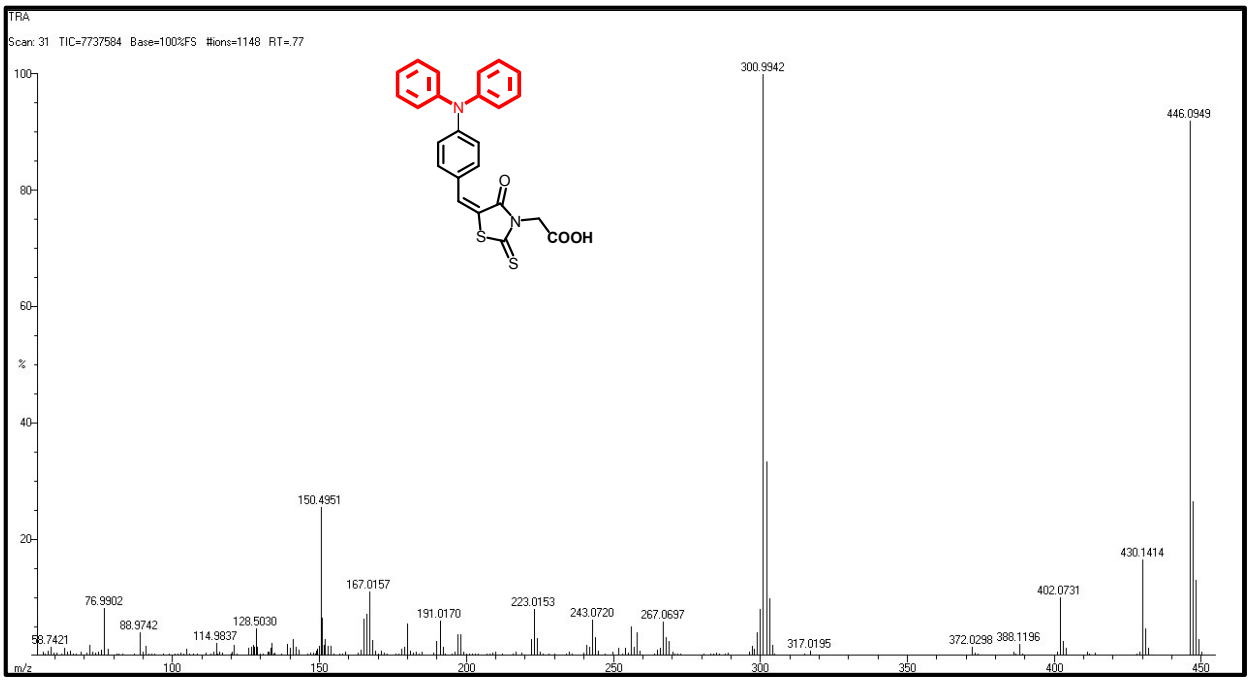

Figure S7: Mass spectrum of TRA

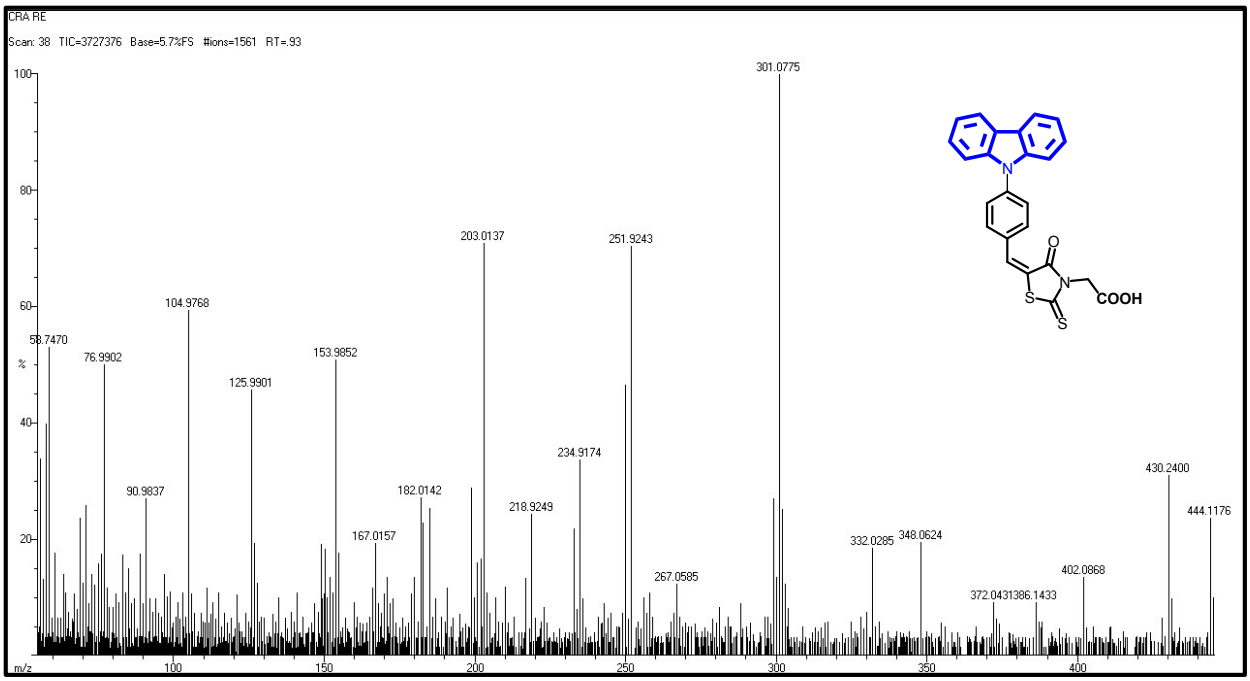

Figure S8: Mass spectrum of CRA

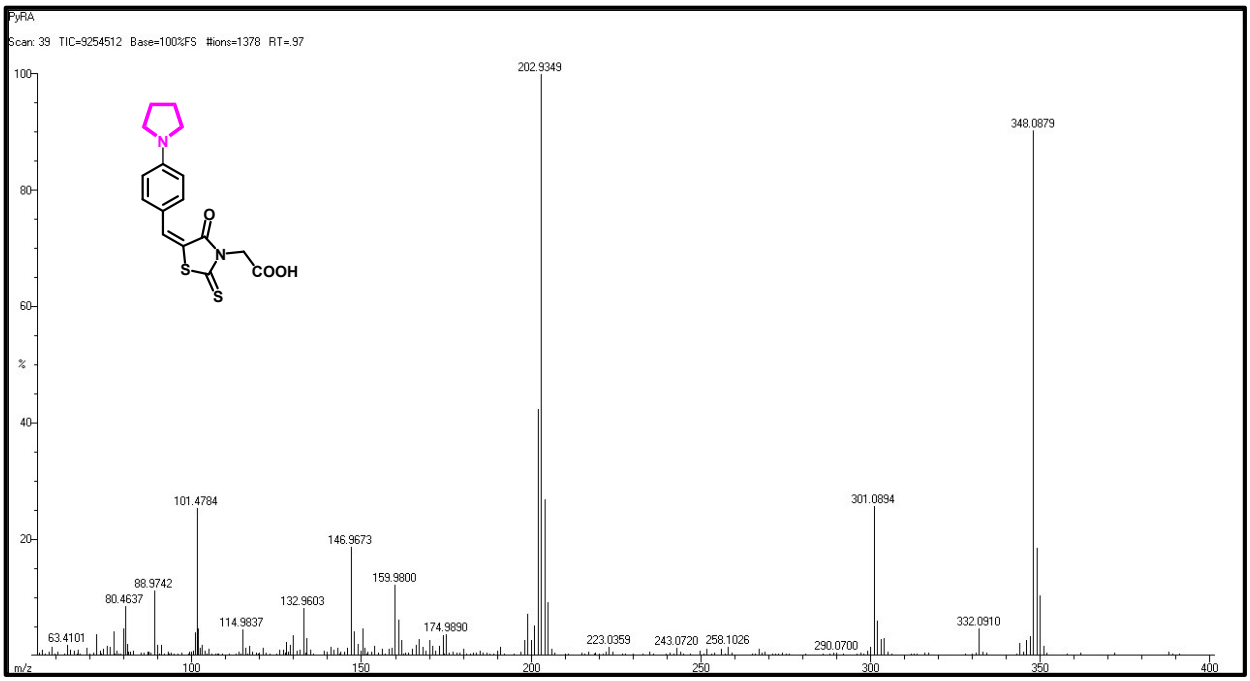

Figure S9: Mass spectrum of PyRA

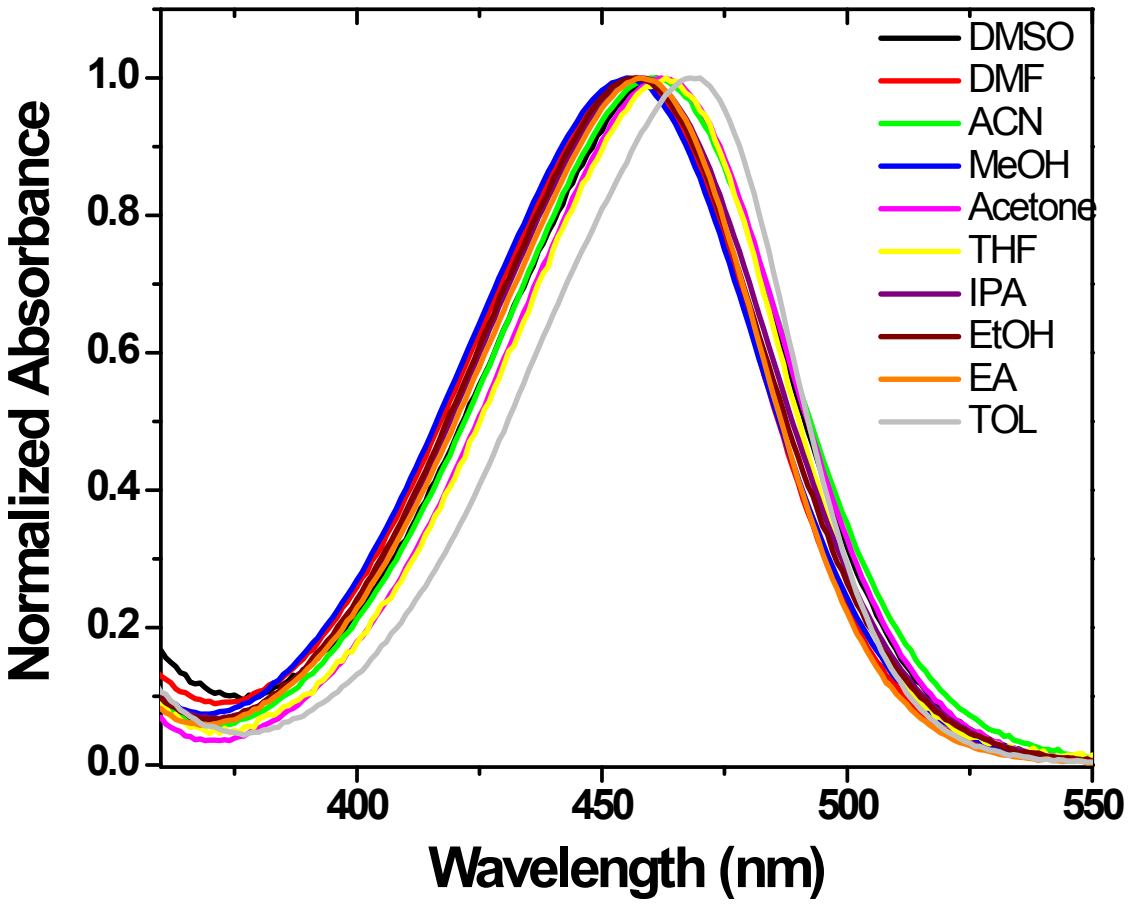

Figure S10: Normalized absorption spectra of TRA in various solvents

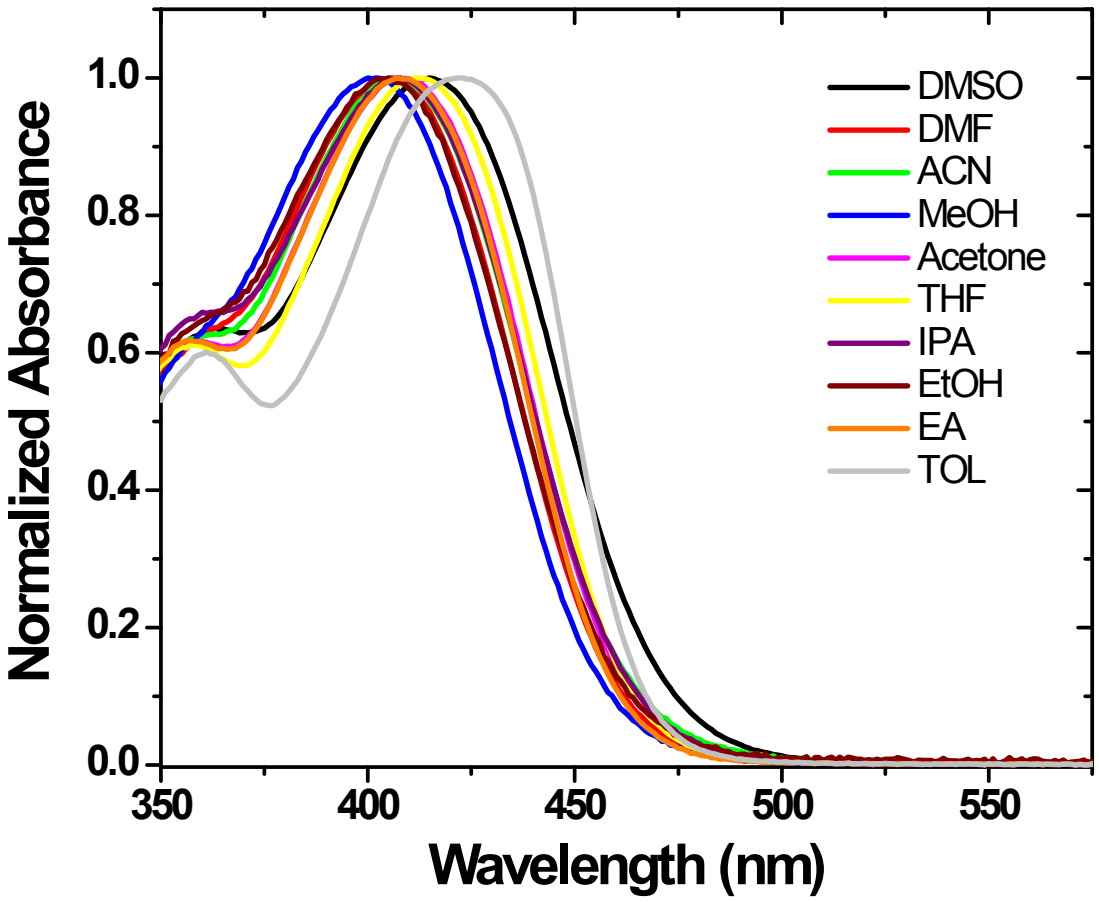

Figure S11: Normalized absorption spectra of CRA in various solvents

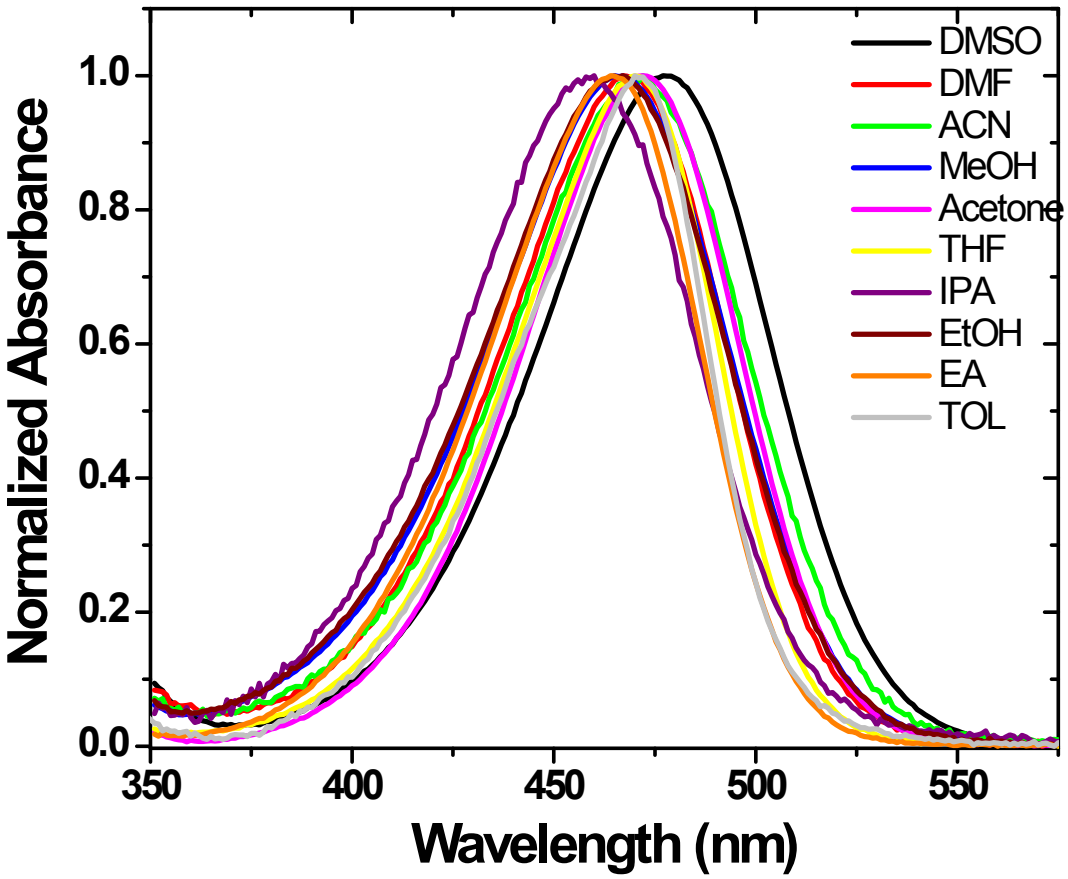

Figure S12: Normalized absorption spectra of PyRA in various solvents

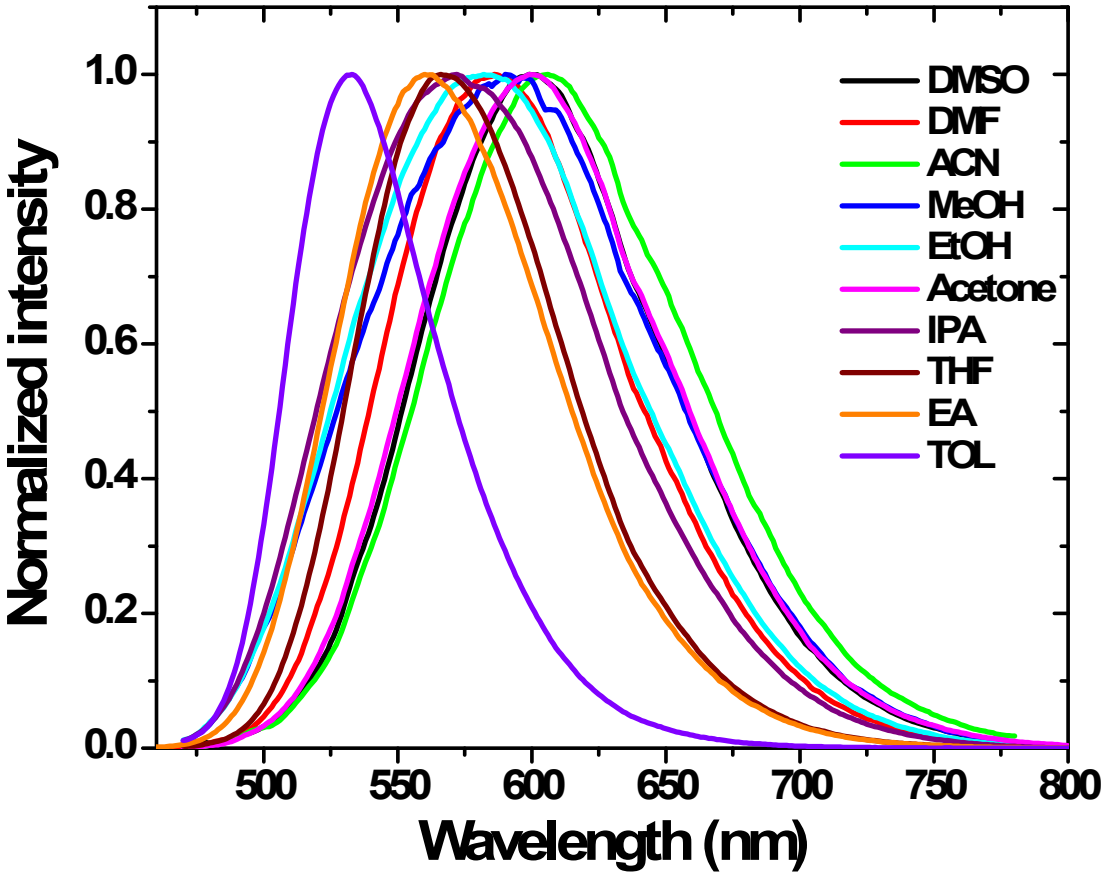

Figure S13: Normalized fluorescence spectra of TRA in various solvents

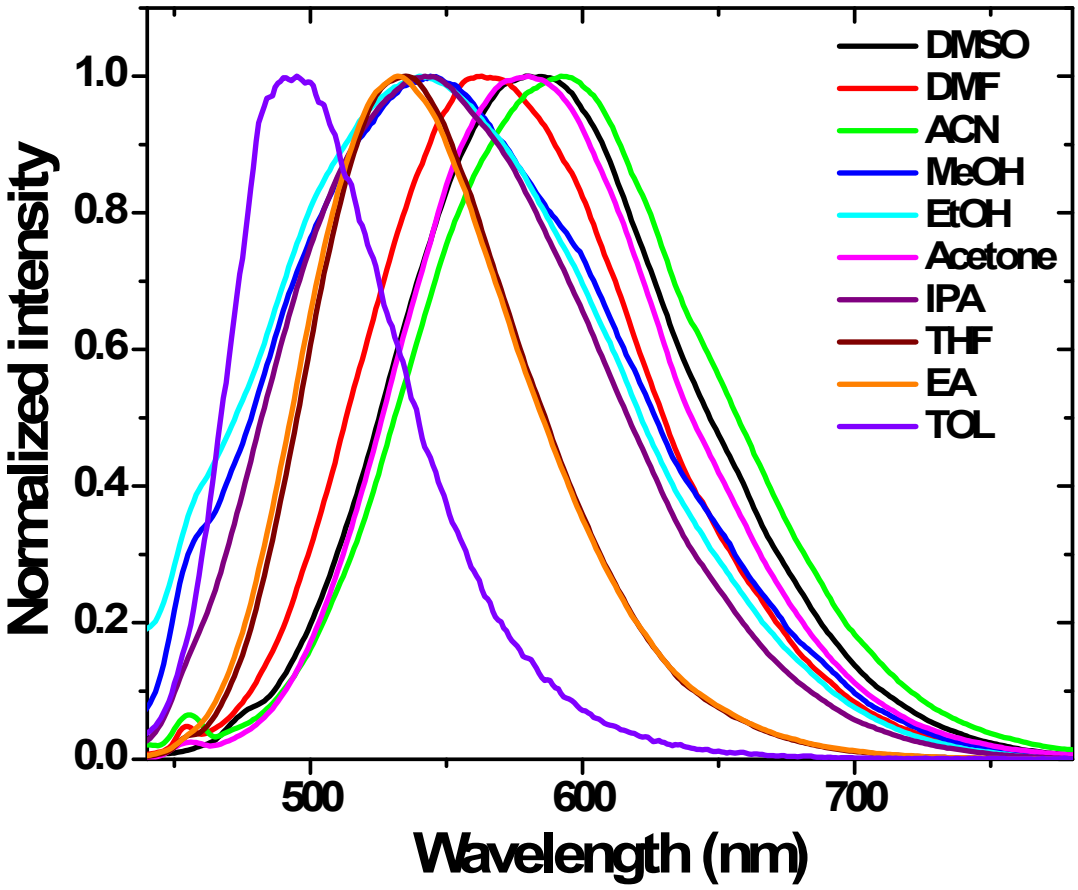

Figure S14: Normalized fluorescence spectra of CRA in various solvents

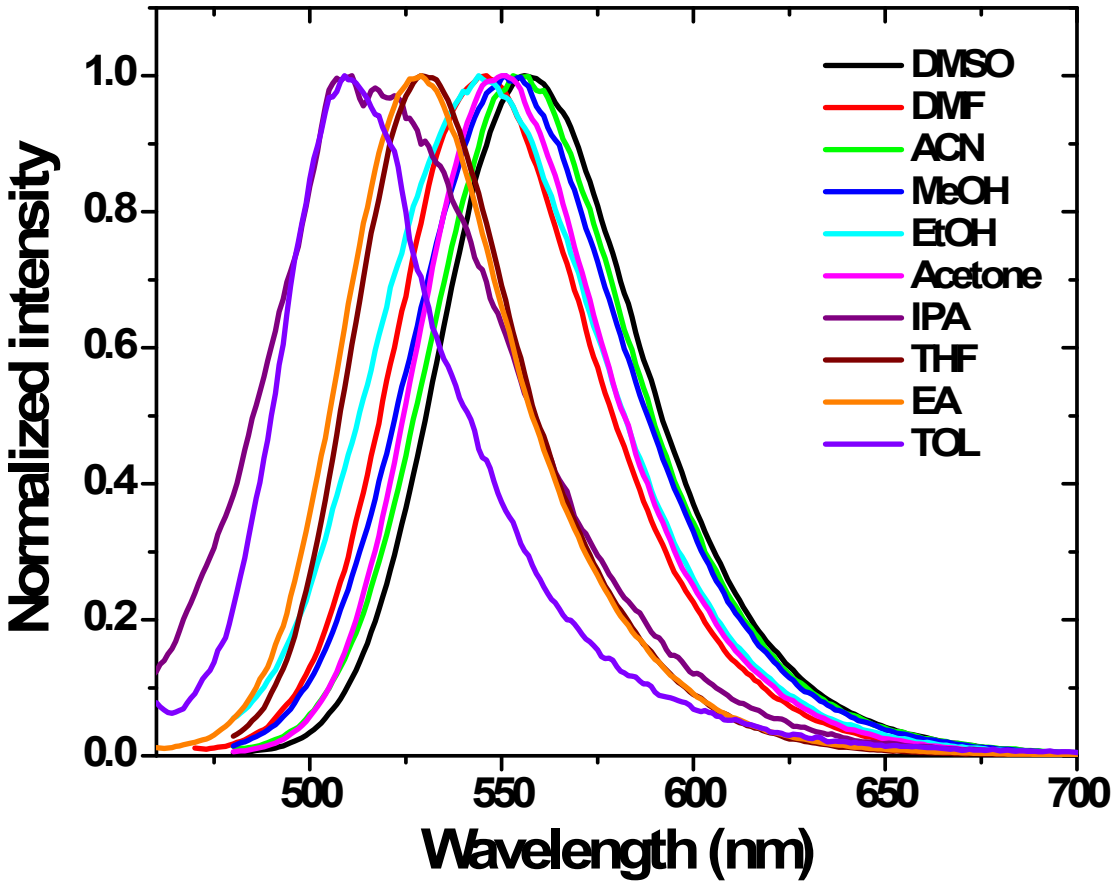

Figure S15: Normalized fluorescence spectra of PyRA in various solvents

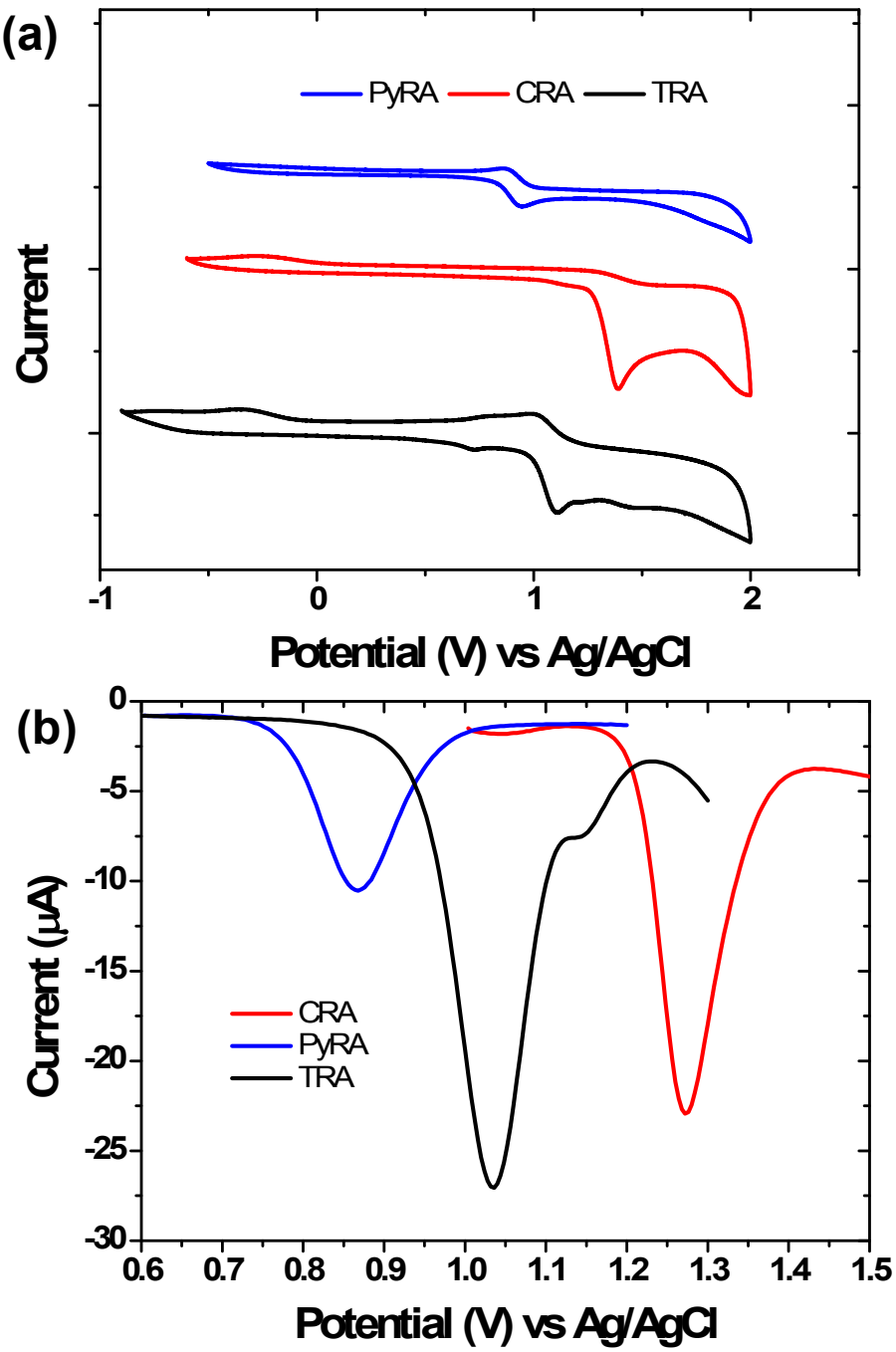

Figure S16: CV and DPV plots of arylamine dyes

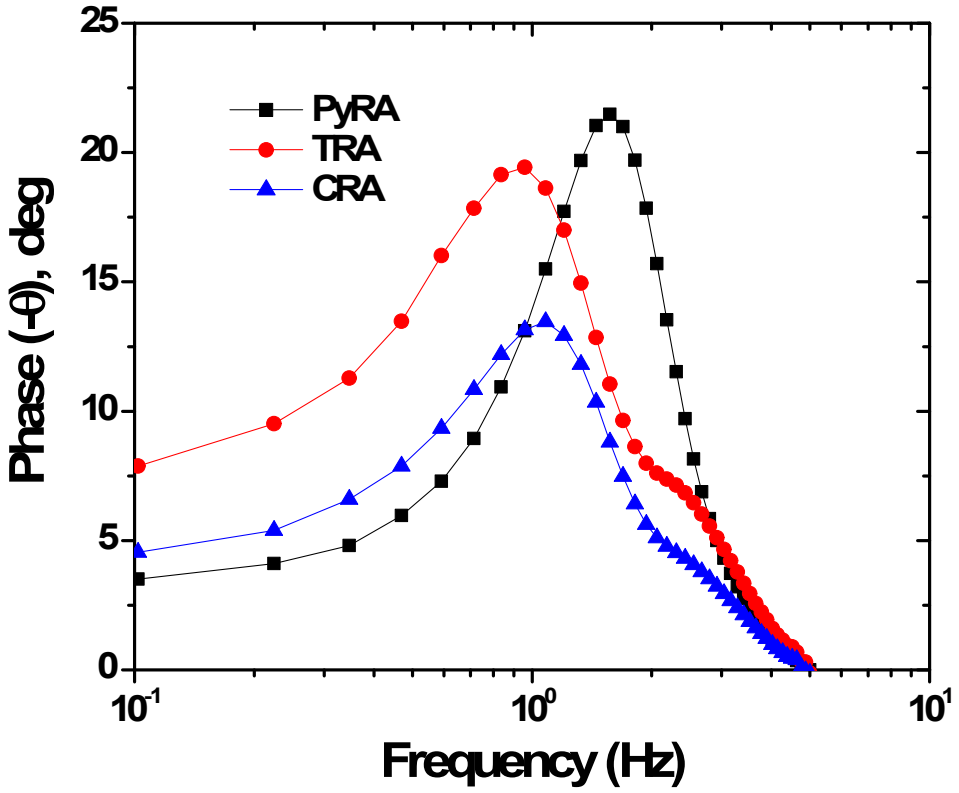

Figure S17: Bode phase plots of TRA, CRA and PyRA devices.

Table S1: Absorption maxima, emission maxima and Stokes' shift of dyes in various solvents

Solvents	Abs (nm)			Emi (nm)			Δν (cm^{-1})			Δ*f*
	TRA	CRA	PyRA	TRA	CRA	PyRA	TRA	CRA	PyRA	
DMSO	461	415	477	600	581	557	4950	6972	2967	0.2634
ACN	462	407	472	603	591	555	5210	7652	3213	0.3055
DMF	456	405	469	587	561	544	4865	7054	3006	0.2744
MeOH	456	402	466	587	543	550	4971	6487	3343	0.3086
EtOH	456	405	465	582	533	542	4670	5964	3009	0.2887
Acetone	463	409	472	600	578	550	4922	7266	3004	0.2843
IPA	458	407	460	571	543	516	4338	5913	2555	0.2721
THF	463	411	470	567	533	528	4054	5580	2408	0.2096
EA	458	408	465	560	531	529	4103	5748	2637	0.2010
Toluene	471	421	469	532	495	509	2434	3550	1675	0.0133
Dioxane	463	414	468	543	507	516	3296	4585	2545	0.0246
DCM	474	422	483	603	565	545	4513	5997	2355	0.2170