Electronic supporting information

Dipolar vinyl sulfur fluorescent dyes. Synthesis and photophysics of sulfides, sulfoxides and sulfones based D-π-A compounds

Matias Monçalves,[a] Gabriel M. Zanotto,[d] Josene M. Toldo,[d] Daniel S. Rampon,[c] Paulo H. Schneider,[b] Paulo F. B Gonçalves,[d] Fabiano S. Rodembusch*[b] and Claudio C. Silveira*[a]

[a]Departamento de Química, Universidade Federal de Santa Maria. Santa Maria, CEP 97105-900, RS, Brazil. Fax: +55 (55) 3220-8754; E-mail: silveira@quimica.ufsm.br

[b]Grupo de Pesquisa em Fotoquímica Orgânica Aplicada, Universidade Federal do Rio Grande do Sul - Instituto de Química, Avenida Bento Gonçalves 9500. CEP 91501-970 Porto Alegre-RS, Brazil. Fax: +55 51 33087204; Tel: +55 51 33087204; E-mail: fabiano.rodembusch@ufrgs.br

[c]Universidade Federal do Paraná, Departamento de Química, Laboratório de Polímeros e Catálise. CEP 81531-980 Curitiba, PR, Brazil

[d]Grupo de Química Teórica e Computacional, Universidade Federal do Rio Grande do Sul - Instituto de Química, Avenida Bento Gonçalves, 9500, CP 15003, CEP 91501-970 Porto Alegre-RS, Brazil.

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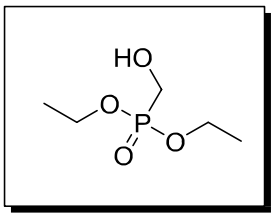
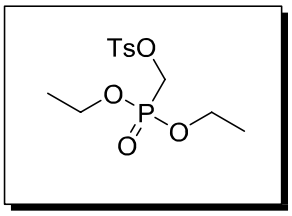
Synthesis of starting materials

Synthesis of diethyl (hydroxymethyl)phosphonate (M1)



Dimethyl hydrogenophosphonate (25.7 mL, 200 mmol) was added to a flask containing paraformaldehyde (7.2 g, 240 mmol), potassium carbonate (1.38 g, 10 mmol) and ethanol (150 mL), under an atmosphere of argon. The reaction mixture was heated to 70°C and stirring was maintained for 5 h. After this time, the reaction was filtered and the solvent were removed under reduced pressure to afford colorless oil. Yield: 100 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.1 Hz, 6H), 3.91 (d, $J_{P–H}$ = 5.9 Hz, 2H), 4.17 (m, J = 7.4 Hz, 4H), 4.5 (s, 1H) ppm.

Synthesis of (diethoxyphosphoryl)methyl 4-methylbenzenesulfonate (M2)



To a solution of diethyl (hydroxymethyl)phosphonate **M1** (16.8 g, 100 mmol) in CH_2Cl_2 (150 mL), under an atmosphere of argon, was added triethylamine (20 mL, 144 mmol) dropwise at 0°C. The reaction mixture was stirred 30 min at room temp., cooled to 0°C, and *p*-tosyl chloride (20.52 g, 108 mmol) was added. The reaction was kept at 0°C for 30 min and then 24 h at room temperature. After this time, the reaction mixture was filtered and extracted. The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel; using 5:95 to 30:70, v/v, EtOAc/hexanes) gave the product as colorless oil. Yield: 60 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (*t*, J = 7.6 Hz, 6H), 2.46 (*s*, 3H), 4.08-4.22 (*m*, 4H), 4.18 (*d*, $J_{P–H}$ = 9.9 Hz, 2H), 7.38 (*d*, J = 8.6 Hz, 2H), 7.8 (*d*, J = 8.3 Hz, 2H) ppm.

Additional Computational Data

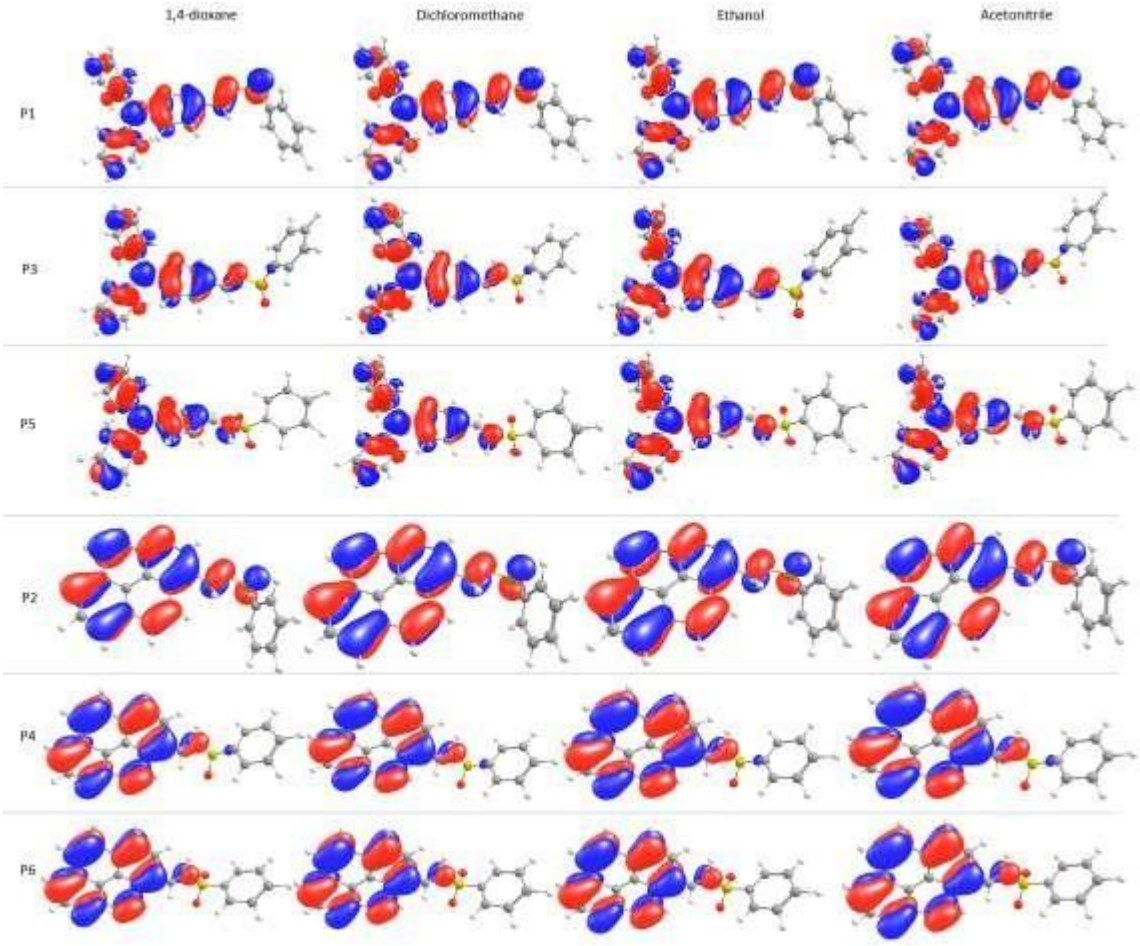


Figure ESI1. HOMO for **P1-P6** dyes. Calculated at CAM-B3LYP level in 1,4-dioxane, dichloromethane, ethanol and acetonitrile.

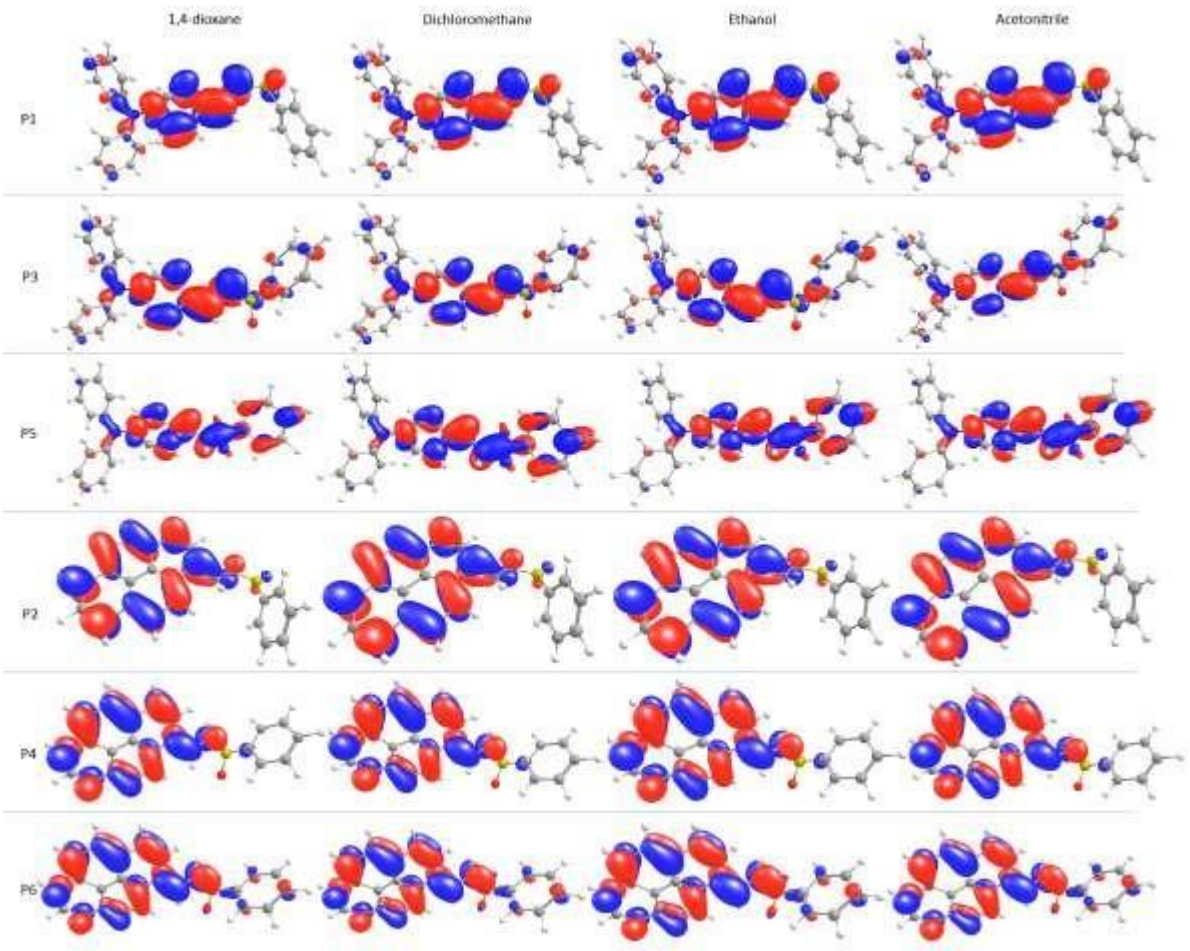


Figure ESI2. LUMO for **P1-P6** dyes. Calculated at CAM-B3LYP level in 1,4-dioxane, dichloromethane, ethanol and acetonitrile.

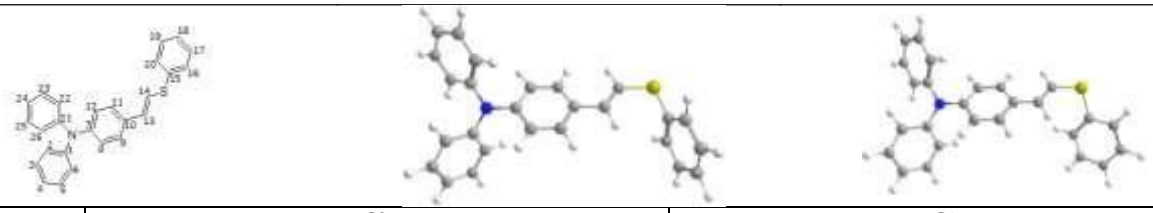
Table ESI1. Calculated photophysical data of the **P1–P6** dyes. The λ_{abs} is the absorption maxima (nm), λ_{em} is the emission maxima. E% is the relative error compared to experimental values, on the right.

		PBE1PBE				**CAM-B3LYP**				**Experimental**	
Dye	**Solvent**	**λ_{abs}**	**E%**	**λ_{em}**	**E%**	**λ_{abs}**	**E%**	**λ_{em}**	**E%**	**λ_{abs}**	**λ_{em}**
P1	DIO	368.38	-4.65	450.76	-8.36	329.48	6.40	412.13	0.93	352	416
	DCM	368.47	-4.09	464.20	-6.22	329.55	6.91	427.03	2.28	354	437
	Ethanol	367.65	-5.04	468.46	-7.94	328.86	6.04	431.32	0.62	350	434
	ACN	367.41	-5.58	469.38	-3.85	328.67	5.55	432.10	4.40	348	452
P3	DIO	373.62	-4.07	485.68	-7.93	331.40	7.69	385.44	14.35	359	450
	DCM	374.82	-2.97	483.18	-0.04	332.02	8.79	406.52	15.83	364	483
	EtOH	374.15	-2.51	481.95	4.75	331.41	9.20	412.41	18.50	365	506
	ACN	373.92	-4.16	480.81	4.03	331.22	7.74	413.55	17.45	359	501
P5	DIO	395.01	-5.06	531.38	-13.30	343.22	8.72	399.18	14.89	376	469
	DCM	400.10	-4.74	513.92	-1.17	346.09	9.40	419.16	17.49	382	508
	EtOH	400.12	-5.85	512.54	2.19	345.73	8.54	425.34	20.28	378	524
	ACN	400.21	-6.72	521.62	2.50	345.86	7.77	426.51	18.83	375	535
P2	DIO	395.99	-6.74	484.75	-13.26	353.89	4.61	447.20	-4.49	371	428
	DCM	396.96	-7.29	509.93	-17.23	354.26	4.25	471.19	-8.32	370	435
	EtOH	395.83	-7.86	517.05	-19.41	353.27	4.08	478.55	-10.52	367	433
	ACN	395.49	-7.47	518.34	-17.54	352.99	3.74	479.90	-8.82	368	441
P4	DIO	384.42	-6.19	443.92	-6.46	350.03	3.31	420.35	-0.80	362	417
	DCM	384.81	-4.28	468.42	-8.43	350.23	5.09	445.13	-3.04	369	432
	EtOH	383.83	-4.02	475.80	-7.16	349.31	5.34	452.56	-1.93	369	444
	ACN	383.54	-6.54	477.21	-10.21	349.04	3.04	453.96	-4.84	360	433
P6	DIO	402.93	-8.61	451.92	-5.10	362.32	2.34	428.24	0.41	371	430
	DCM	406.21	-9.20	468.06	-4.24	364.70	1.96	458.29	-2.07	372	449
	EtOH	405.65	-9.64	490.49	-7.80	363.99	1.62	467.70	-2.79	370	455
	ACN	405.41	-9.57	492.18	-8.17	363.74	1.69	469.48	-3.18	370	455

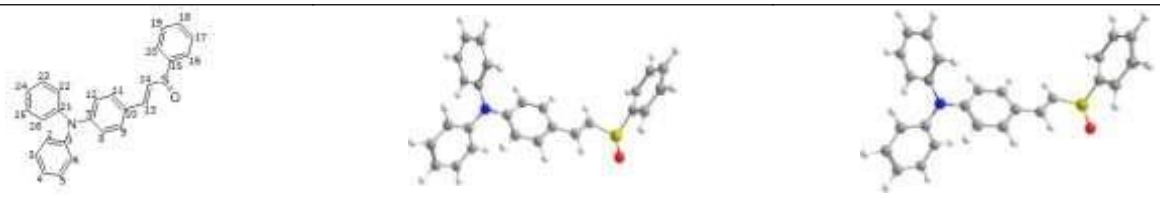
DIO = 1,4-dioxane, DCM=dichloromethane, ACN=acetonitrile.

Table ESI2. Theoretical structural data of **P1, P3, and P5** molecules in different organic solvents, where the bond lengths (**r**) are presented in Å and angles (**a**) and dihedral angles (**d**) are given in degrees. Geometries for S_0 and S_1 calculated with CAM-B3LYP/cc-pVDZ. The representative equilibrium structures are plotted at the same level using 1,4-dioxane as solvent. The ground state structures are given on the left and first excited state structures are given on the right. In 1,4-dioxane, the structural data is also given with PBE1PBE at the same level (marked with a *).

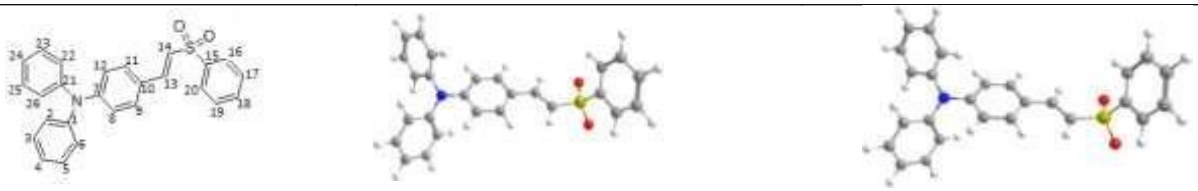
d1 = C_1-N-C_7-C_8 / **d2** = C_{11}-C_{10}-C_{13}-C_{14} / **d3** = C_{14}-S-C_{15}-C_{16} / **a1**= C_{14}-S-C_{15} / **r1** = C_{13}-C_{14}/ **r2** = C_{14}-S/ **r3** = S-C_{15}.



Dye	Solvent	S0							S1						
		d1	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**	**d1**	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**
P1	DIO*	33.02	0.67	100.86	96.66	1.340	1.797	1.819	49.47	2.16	19.68	106.56	1.391	1.739	1.780
	DIO	42.09	4.30	88.04	103.10	1.338	1.768	1.791	41.89	2.80	26.51	106.52	1.388	1.727	1.782
	DCM	42.32	3.80	88.09	103.26	1.338	1.768	1.791	42.90	2.64	27.54	106.70	1.403	1.727	1.785
	ACN	42.35	3.94	88.10	103.30	1.338	1.768	1.791	43.29	2.56	27.90	106.75	1.404	1.727	1.786
	EtOH	42.34	3.91	88.09	103.30	1.338	1.768	1.791	43.24	2.58	27.85	106.74	1.404	1.727	1.786



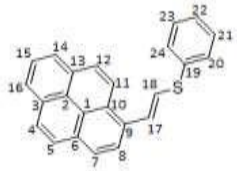
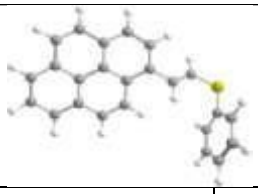
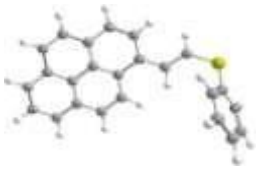
Dye	Solvent	S0							S1						
		d1	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**	**d1**	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**
P3	DIO*	31.72	1.12	95.86	103.99	1.343	1.766	1.792	28.18	2.71	84.06	101.22	1.381	1.757	1.835
	DIO	46.27	1.01	81.93	97.07	1.333	1.803	1.820	35.13	0.21	78.05	99.72	1.375	1.770	1.835
	DCM	47.06	1.24	82.19	97.31	1.333	1.801	1.837	38.48	0.68	72.98	101.05	1.383	1.761	1.837
	ACN	47.34	1.53	82.34	97.39	1.333	1.081	1.837	39.21	0.41	72.15	101.32	1.385	1.759	1.837
	EtOH	47.30	1.46	82.30	97.38	1.333	1.801	1.837	39.09	0.45	72.34	101.28	1.385	1.760	1.837



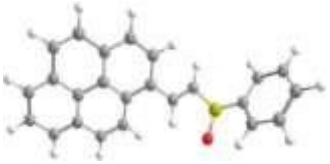
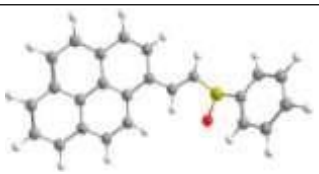
Dye	Solvent	S0							S1						
		d1	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**	**d1**	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**
P5	DIO*	58.95	1.04	89.33	102.95	1.344	1.756	1.786	65.35	0.34	88.81	107.18	1.410	1.728	1.740
	DIO	48.45	0.56	85.96	104.35	1.337	1.770	1.793	34.09	0,25	88.27	105.33	1.377	1.737	1.798
	DCM	49.49	0.99	86.45	104.79	1.338	1.767	1.791	37.08	0,20	88.43	106.20	1.384	1.730	1.797
	ACN	49.94	1.35	86.74	104.95	1.338	1.766	1.790	38.06	0,37	88.49	106.51	1.386	1.728	1.797
	EtOH	49.88	1.30	86.68	104.92	1.338	1.766	1.791	37.91	0,34	88.47	106.46	1.386	1.728	1.797

Table ESI3. Theoretical structural data of **P2, P4, and P6** molecules in different organic solvents, where the bond lengths (**r**) are presented in Å and angles (**a**) and dihedral angles (**d**) are given in degrees. Geometries for S0 and S1 calculated with CAM-B3LYP/ cc-pVDZ. The representative equilibrium structures are plotted at the same level using 1,4-dioxane as solvent. The ground state structures are given on the left and first excited state structures are given on the right. In 1,4-dioxane, the structural data is also given with PBE1PBE at the same level (marked with a *).

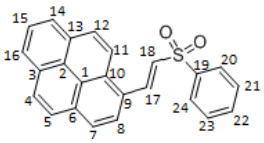
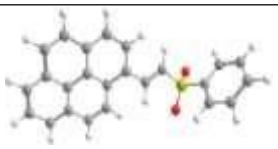
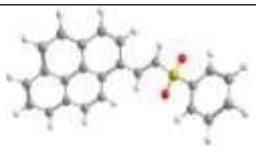
d1 = C_{10}-C_9-C_{17}-C_{18} / **d2** = C_{18}-S-C_{19}-C_{24}/ **a1**= C_{18}-S-C_{19} / **r1** = C_{17}-C_{18}/ **r2** = C_{18}-S/ **r3** = S-C_{19}.

Dye	Solvent	S0							S1						
		d1	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**	**d1**	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**
P2	DIO*	26.64	93.21	102.86	1.345	1.757	1.786	8.97	32.18	106.50	1.385	1.732	1.767	26.64	93.21
	DIO	30.40	89.76	102.93	1.339	1.766	1.791	7.01	44.04	106.20	1.382	1.734	1.781	30.40	89.76
	DCM	29.37	89.25	103.10	1.339	1.766	1.791	5.91	50.95	106.04	1.383	1.733	1.784	29.37	89.25
	ACN	28.99	88.87	103.15	1.339	1.766	1.792	5.55	53.22	105.95	1.383	1.733	1.784	28.99	88.87
	EtOH	29.05	88.95	103.15	1.339	1.766	1.792	5.60	52.83	105.97	1.383	1.733	1.784	29.05	88.95

Dye	Solvent	S0							S1						
		d1	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**	**d1**	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**
P4	DIO*	23.53	82.31	96.36	1.338	1.799	1.819	4.58	82.21	98.82	1.371	1.769	1.828	23.53	82.31
	DIO	25.20	82.46	96.88	1.333	1.804	1.820	3.45	81.12	98.28	1.364	1.782	1.828	25.20	82.46
	DCM	24.32	82.72	97.04	1.333	1.802	1.819	3.20	81.57	98.60	1.366	1.780	1.827	24.32	82.72
	ACN	23.72	82.50	97.09	1.333	1.802	1.819	3.12	81.77	98.67	1.367	1.780	1.827	23.72	82.50
	EtOH	23.83	82.55	97.08	1.333	1.802	1.819	3.13	81.76	98.66	1.367	1.780	1.827	23.83	82.55

Dye	Solvent	S0							S1						
		d1	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**	**d1**	**d2**	**d3**	**a1**	**r1**	**r2**	**r3**
P6	DIO*	15.86	95.89	103.75	1.342	1.770	1.791	2.05	87.01	103.84	1.373	1.746	1.789	15.86	95.89
	DIO	18.27	84.49	104.21	1.336	1.774	1.792	1.60	86.56	104.57	1.369	1.750	1.794	18.27	84.49
	DCM	16.25	84.75	104.59	1.337	1.771	1.790	0.43	87.26	105.34	1.373	1.744	1.793	16.25	84.75
	ACN	16.08	84.98	104.75	1.337	1.771	1.789	0.47	87.59	105.63	1.375	1.742	1.793	16.08	84.98
	EtOH	16.09	84.93	104.73	1.337	1.771	1.789	0.46	87.52	105.59	1.375	1.742	1.793	16.09	84.93

Characterization Data

Spectra data for compound P1

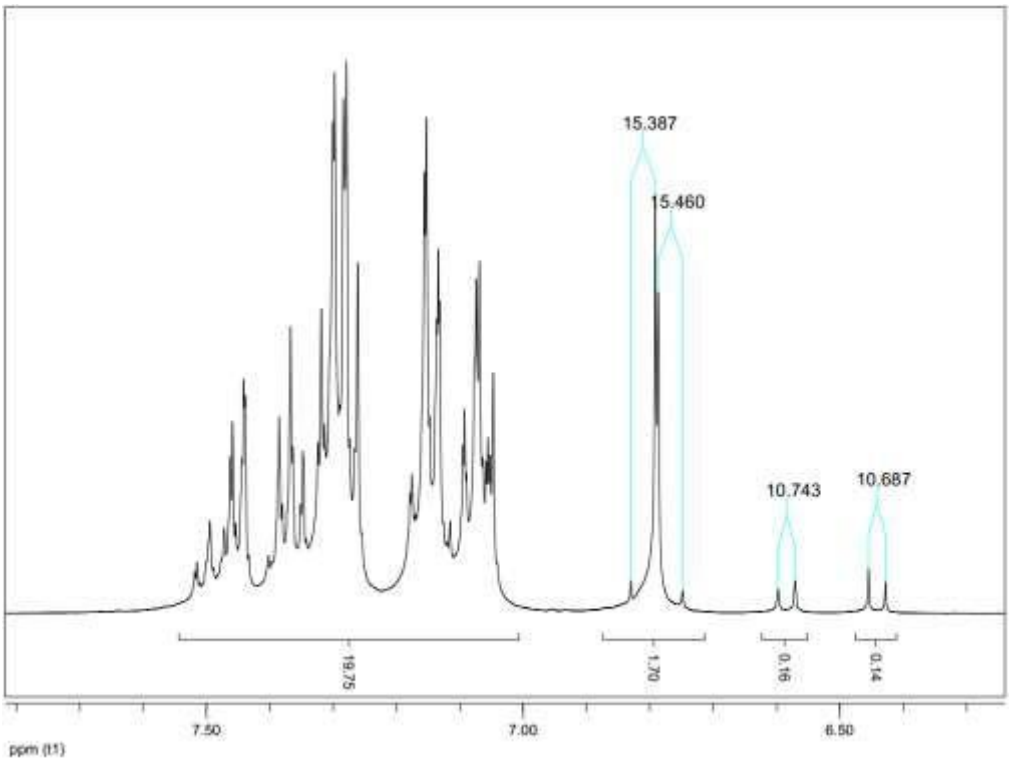


Figure ESI3. ^{1}H NMR spectra of **P1**.

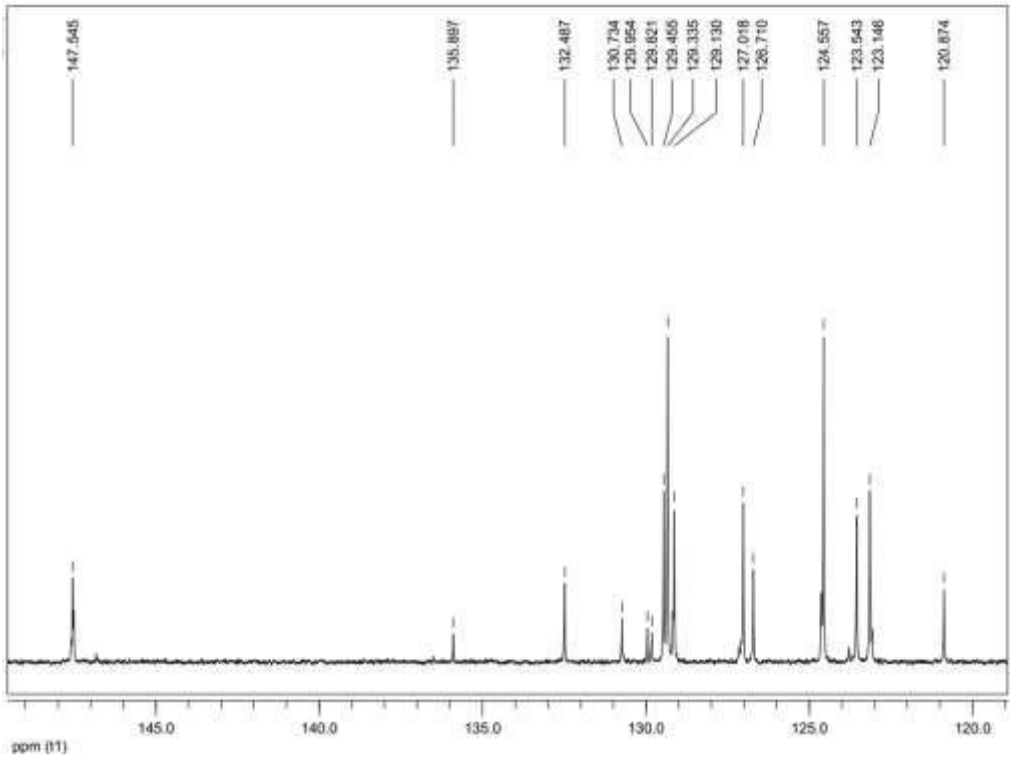


Figure ESI4. ^{13}C NMR spectra of **P1**.

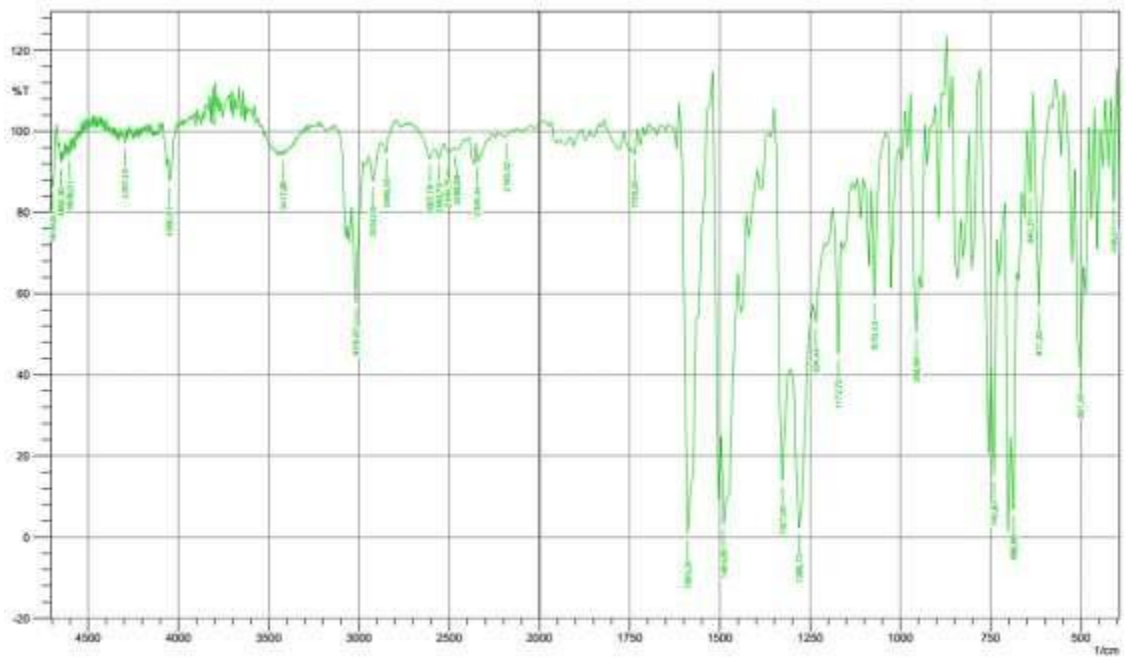


Figure ESI5. IR spectra of **P1**.

Spectra data for compound P3

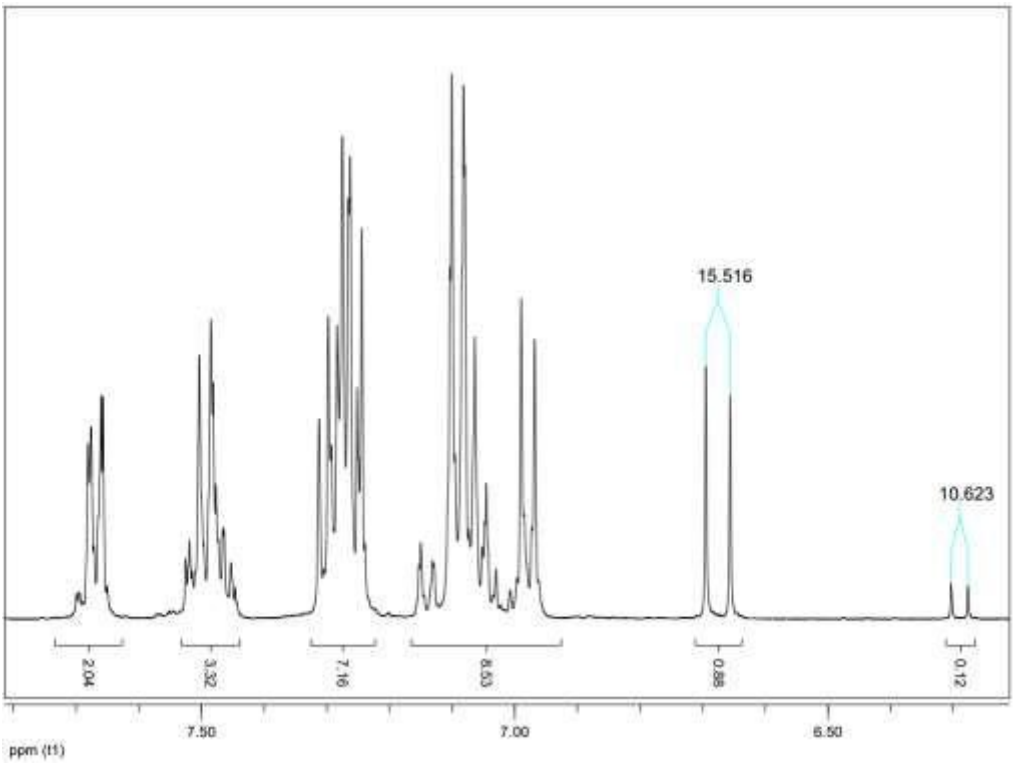


Figure ESI6. ^{1}H NMR spectra of **P3**.

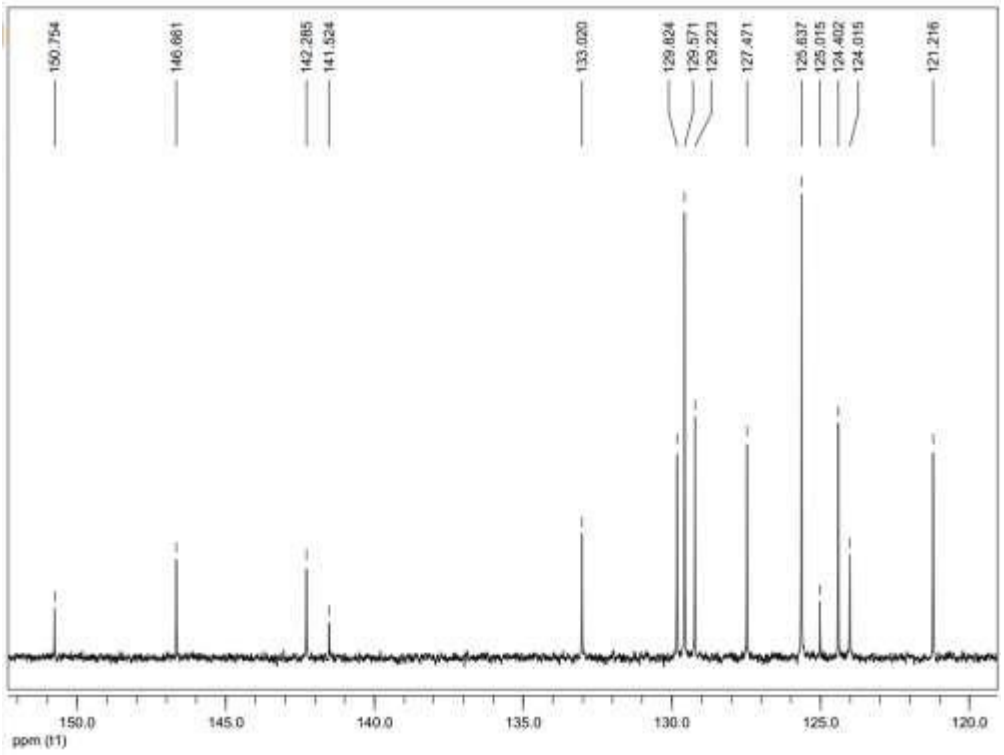


Figure ESI7. ^{13}C NMR spectra of **P3**.

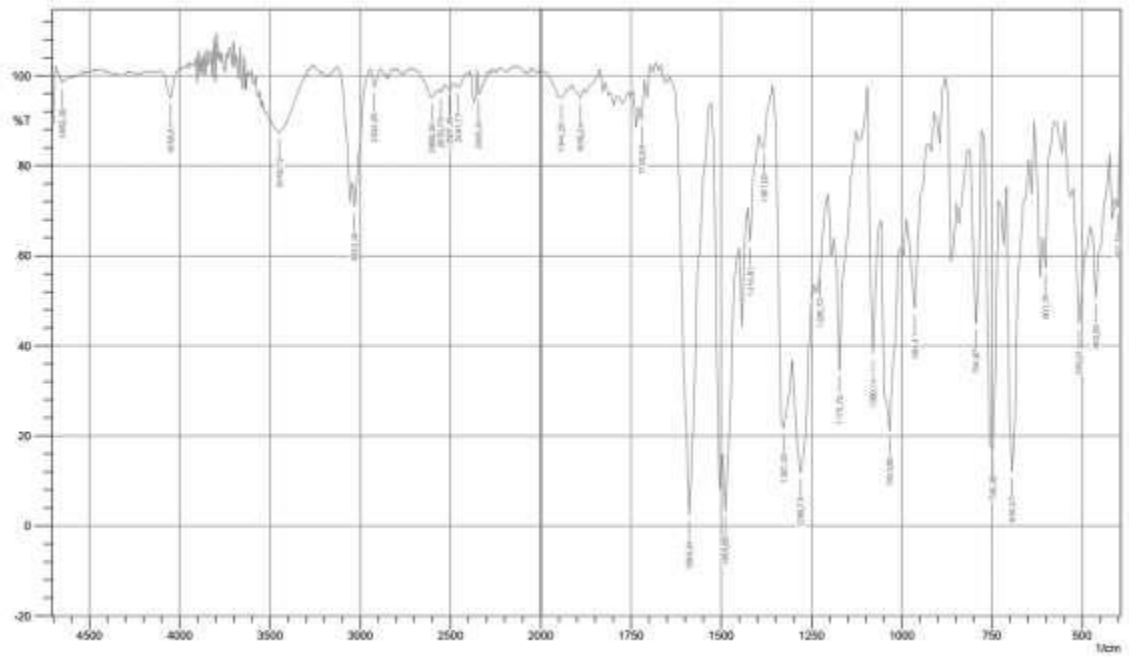


Figure ESI8. IR spectra of **P3**.

Spectra data for compound P5

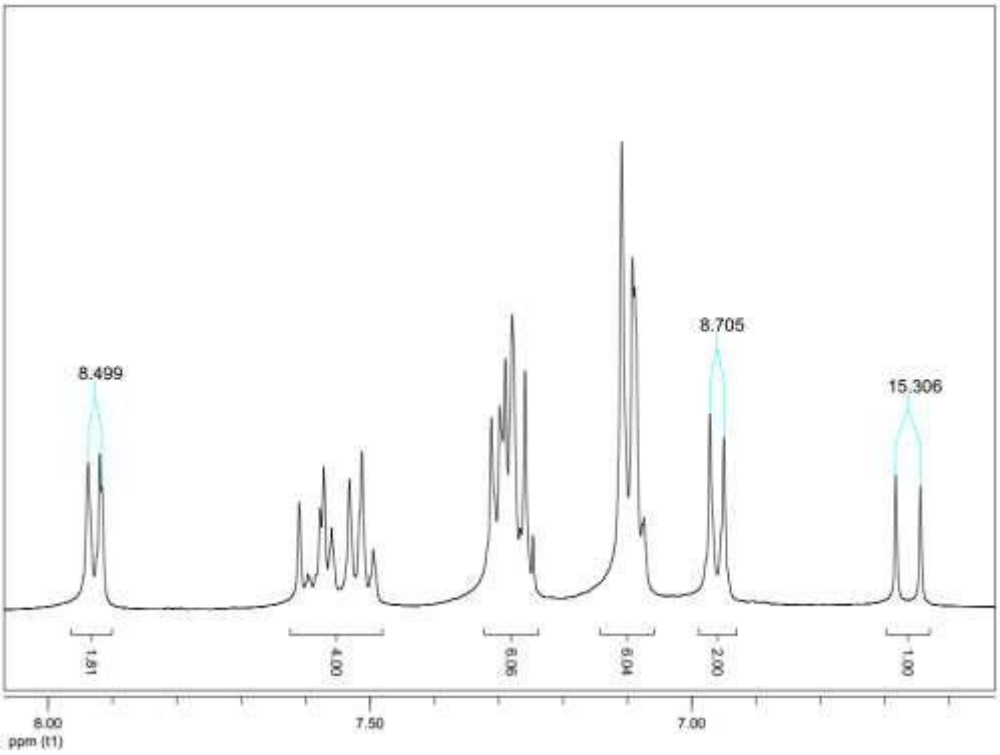


Figure ESI9. ^{1}H NMR spectra of **P5**.

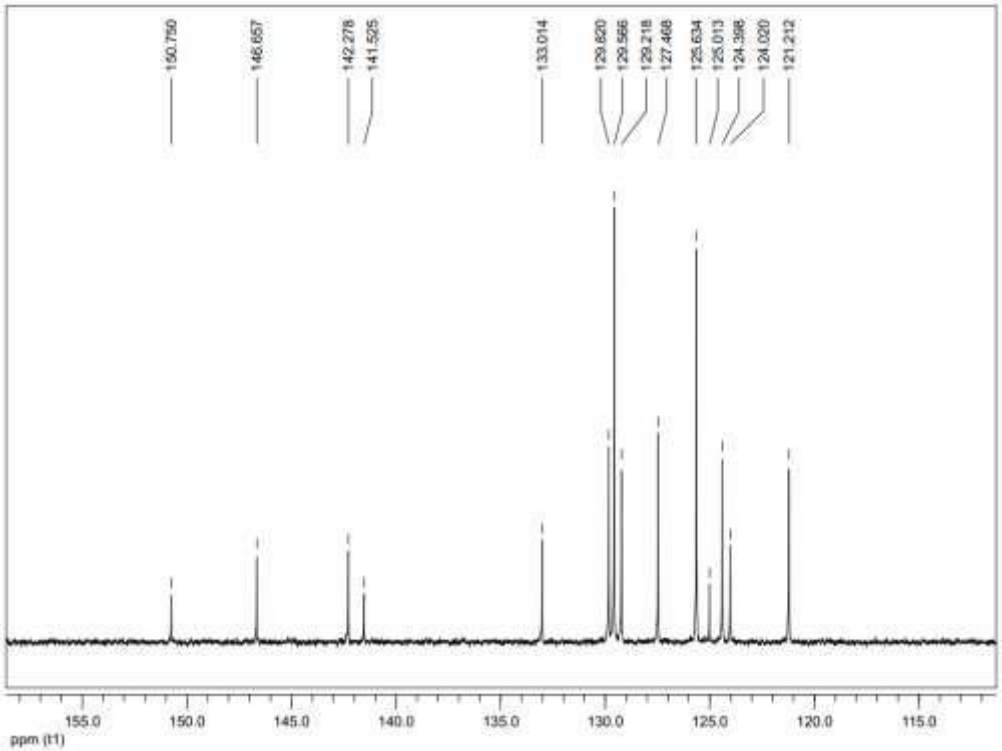


Figure ESI10. ^{13}C NMR spectra of **P5**.

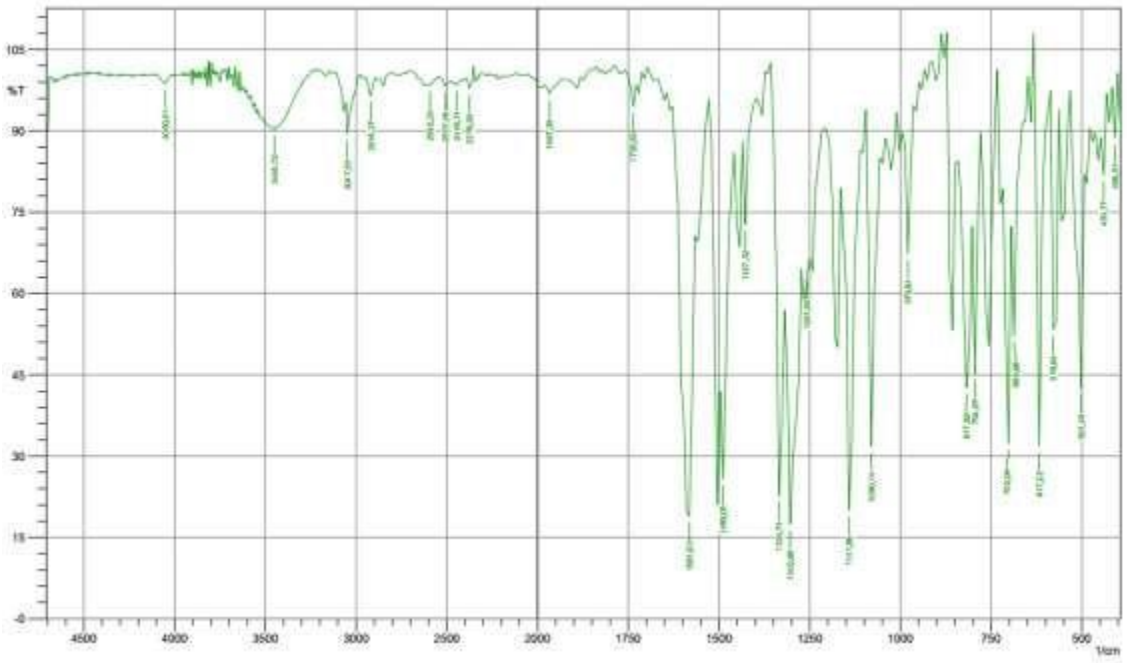


Figure ESI11. IR spectra of **P5**.

Spectra data for compound P2

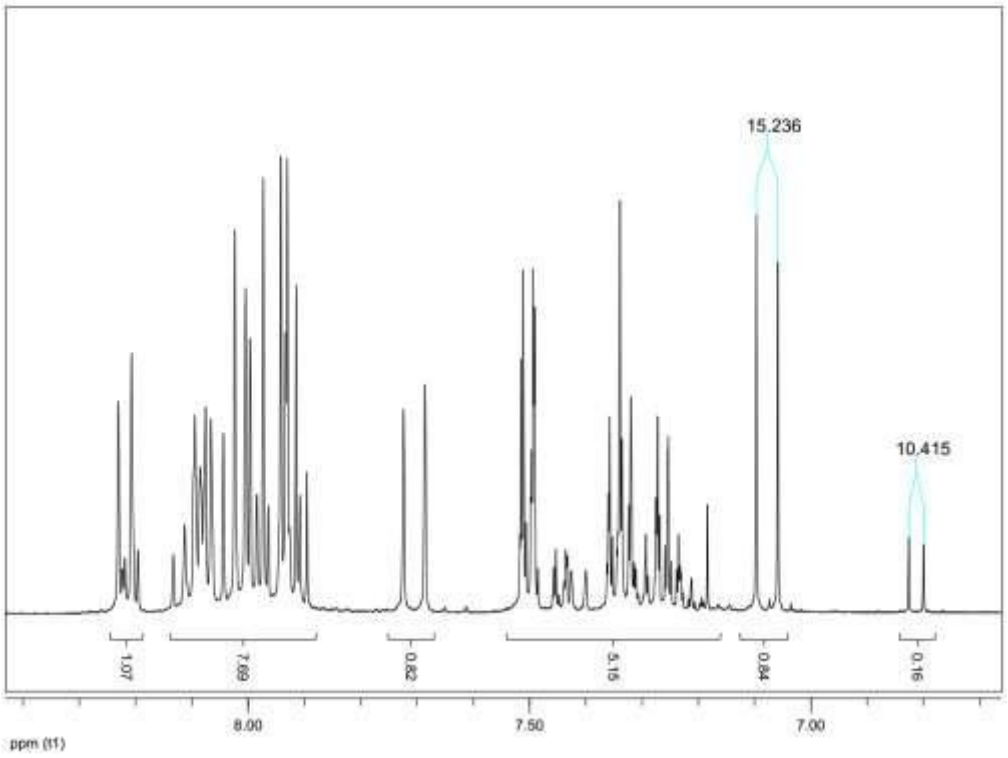


Figure ESI12. ^{1}H NMR spectra of **P2**.

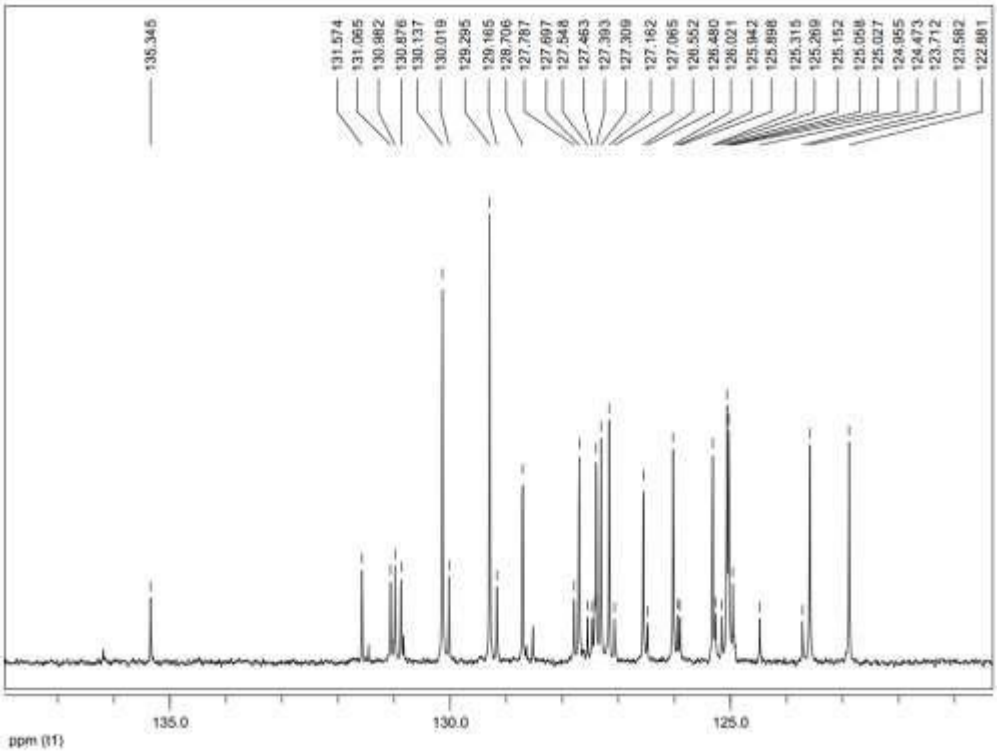


Figure ESI13. ^{13}C NMR spectra of **P2**.

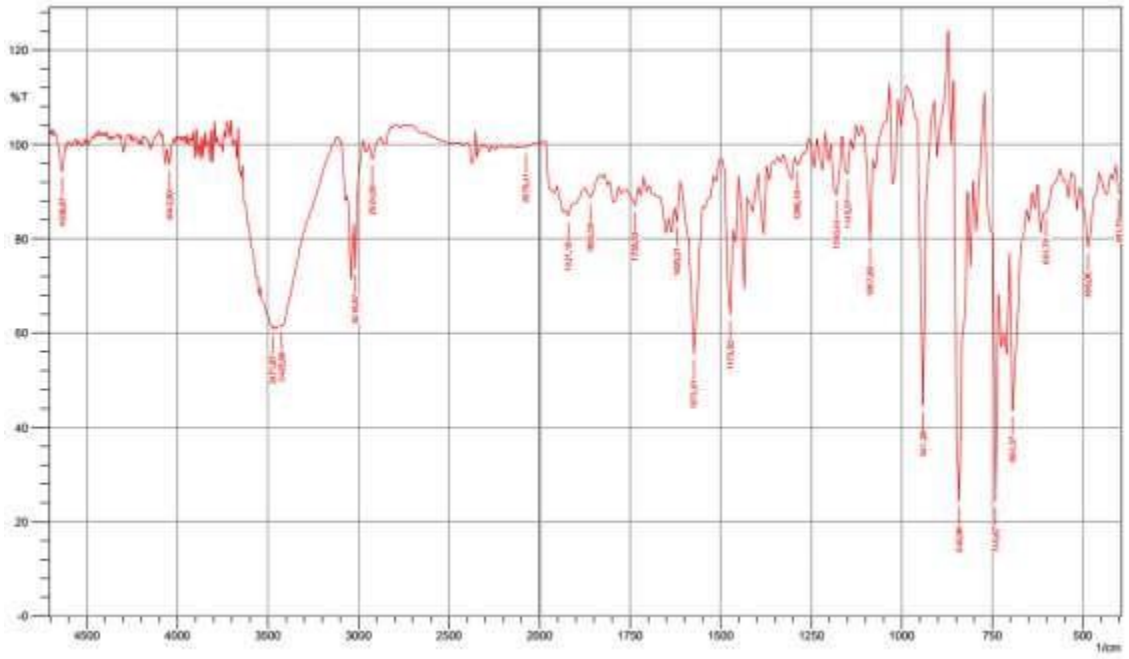


Figure ESI14. IR spectra of **P2**.

Spectra data for compound P4

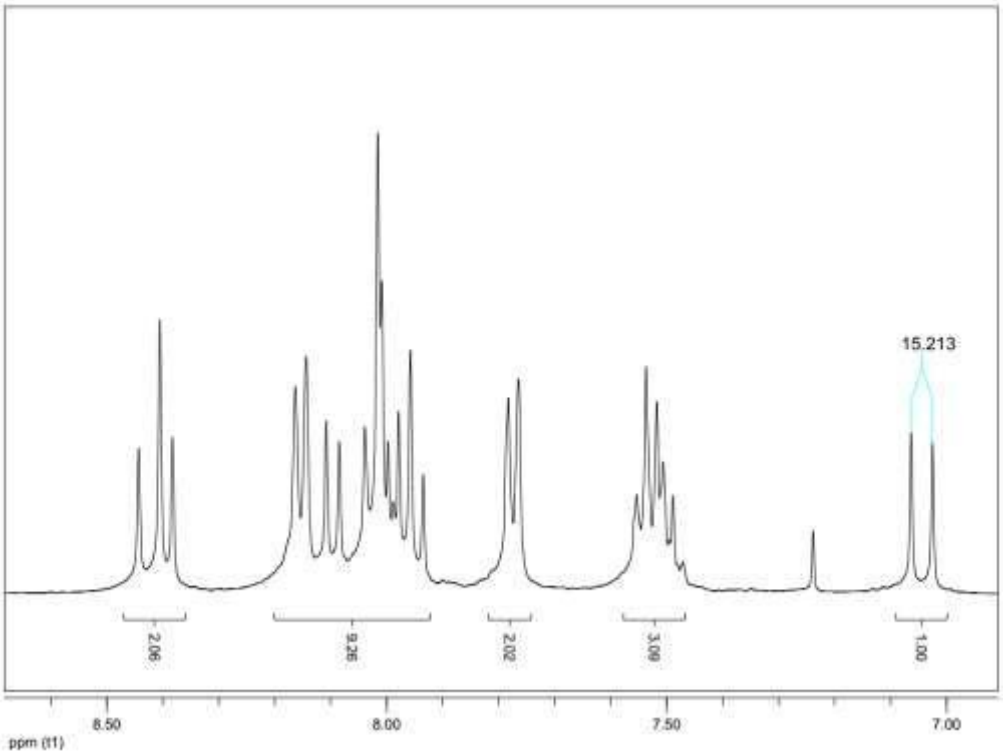


Figure ESI15. ^{1}H NMR spectra of **P4**.

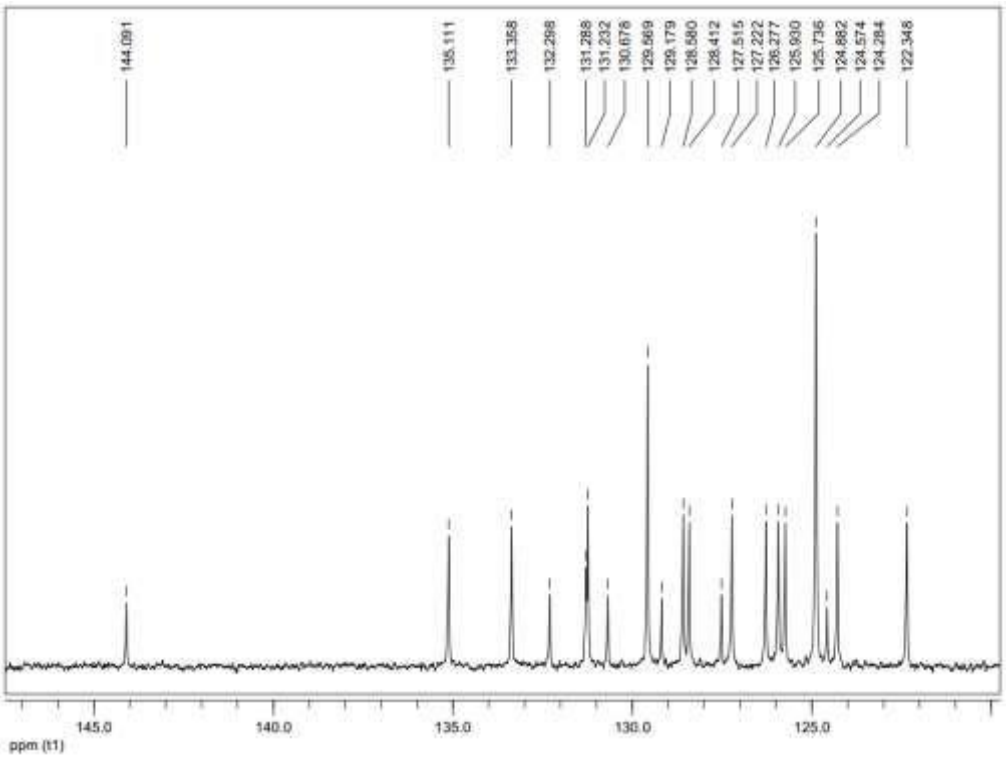


Figure ESI16. ^{13}C NMR spectra of **P4**.

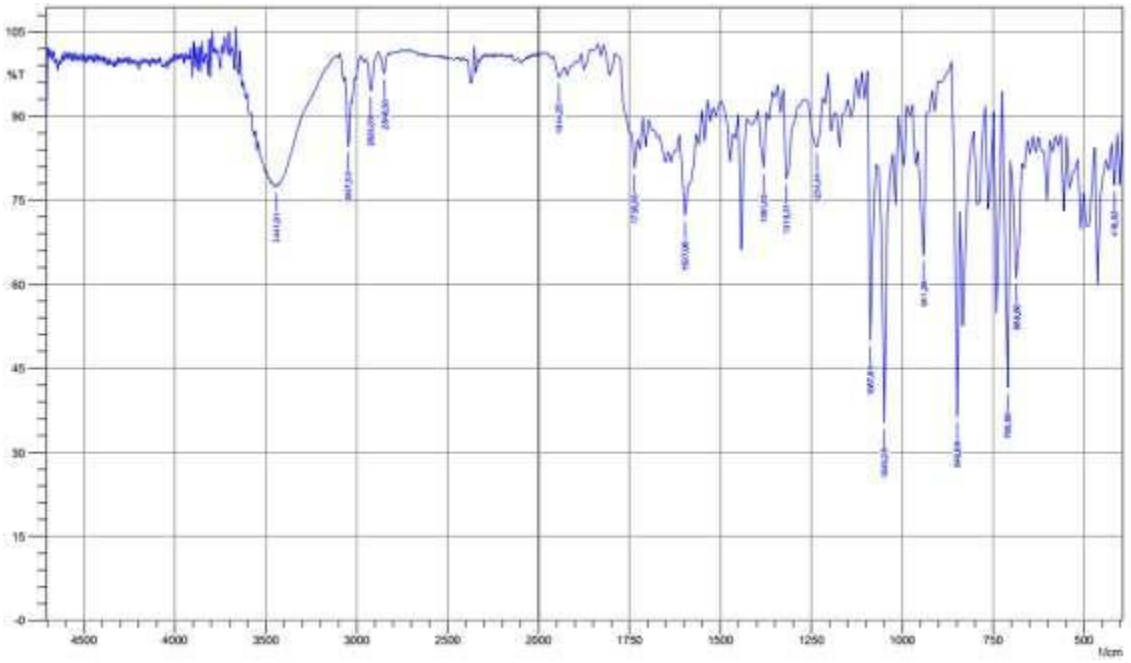


Figure ESI17. IR spectra of **P4**.

Spectra data for compound P6

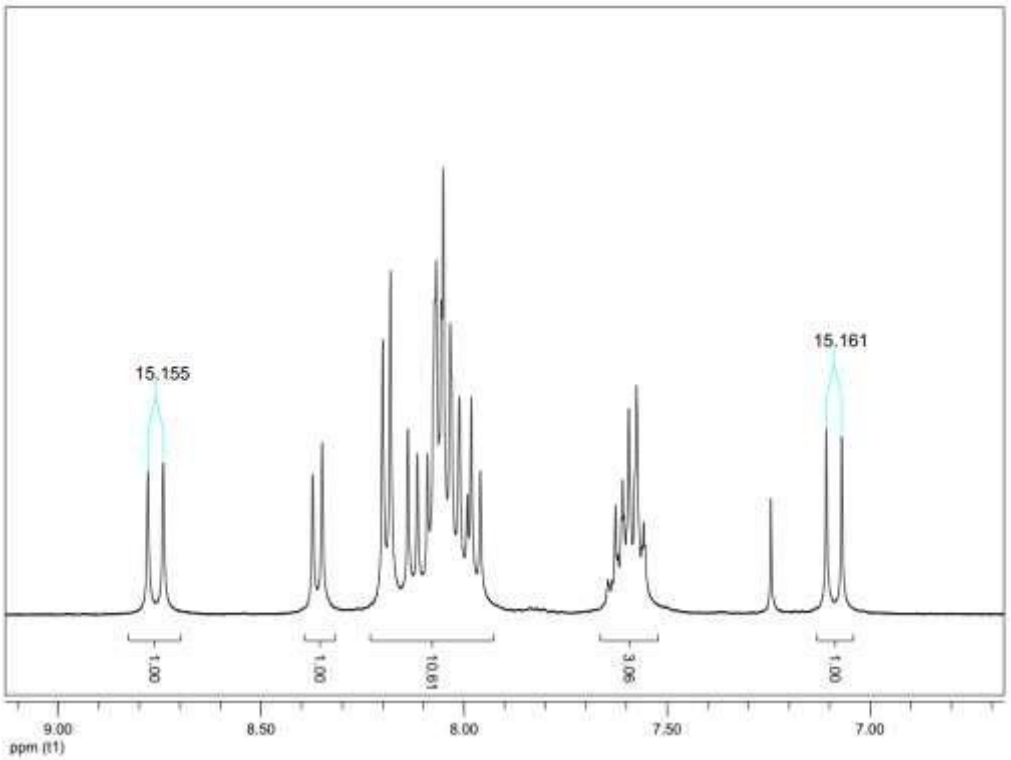


Figure ESI18. ^{1}H NMR spectra of **P6**.

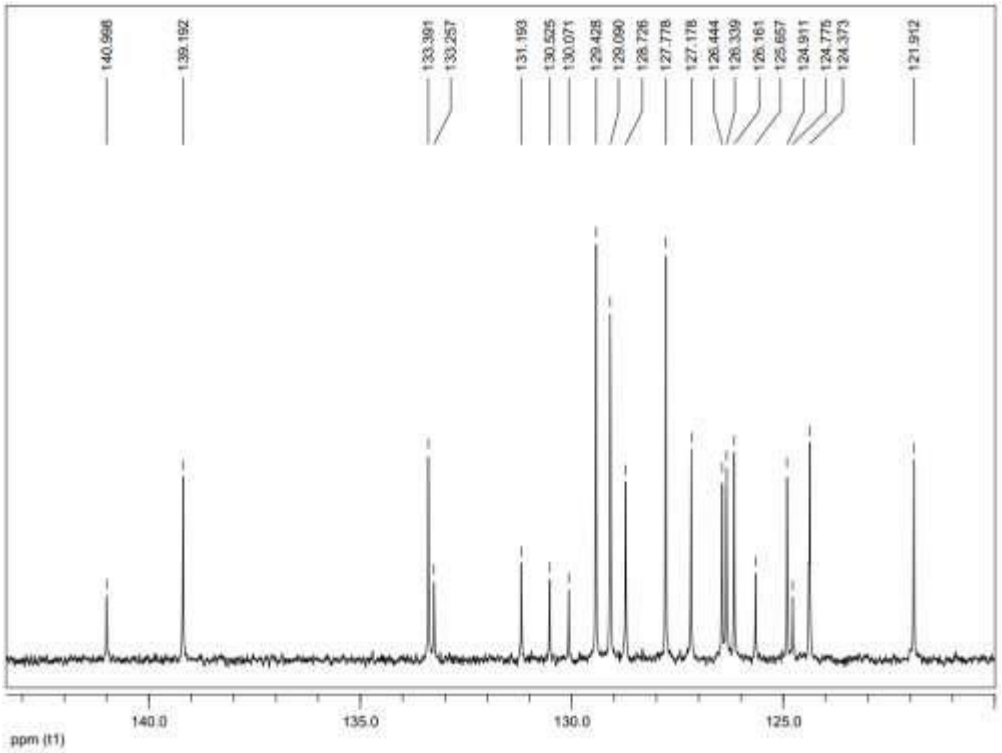


Figure ESI19. ^{13}C NMR spectra of **P6**.

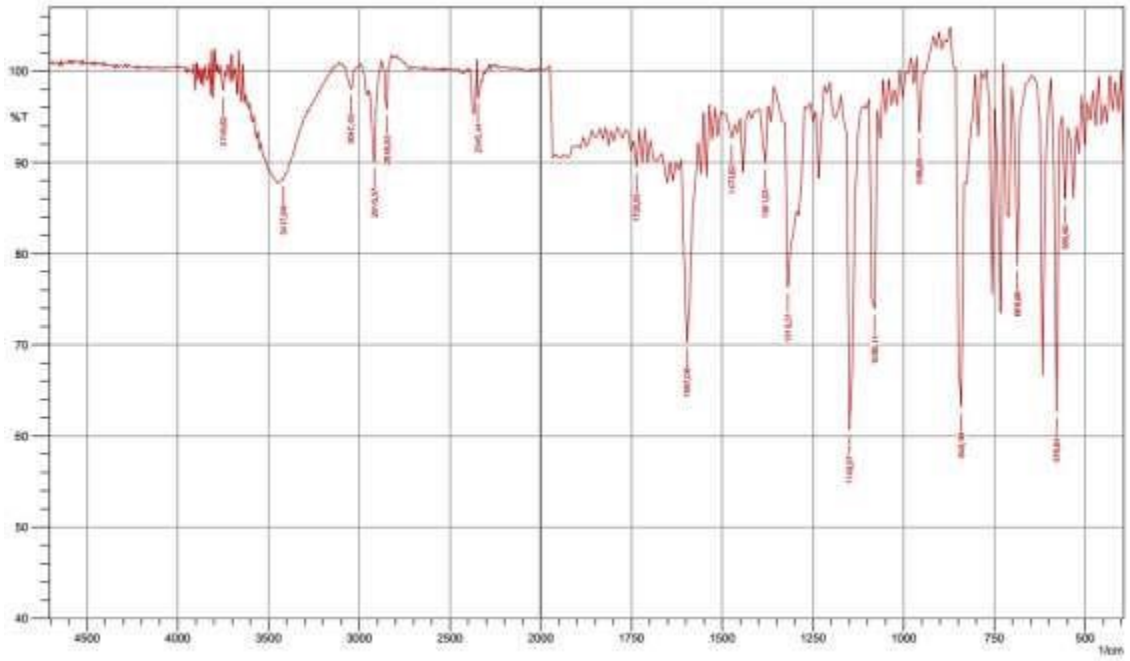


Figure ESI20. IR spectra of **P6**.