Quantum Chemical Prediction and Benchmark Study for Structural Isomers of Terpyridine: Electronic Structure Modulations and Charge Transfer Dynamics

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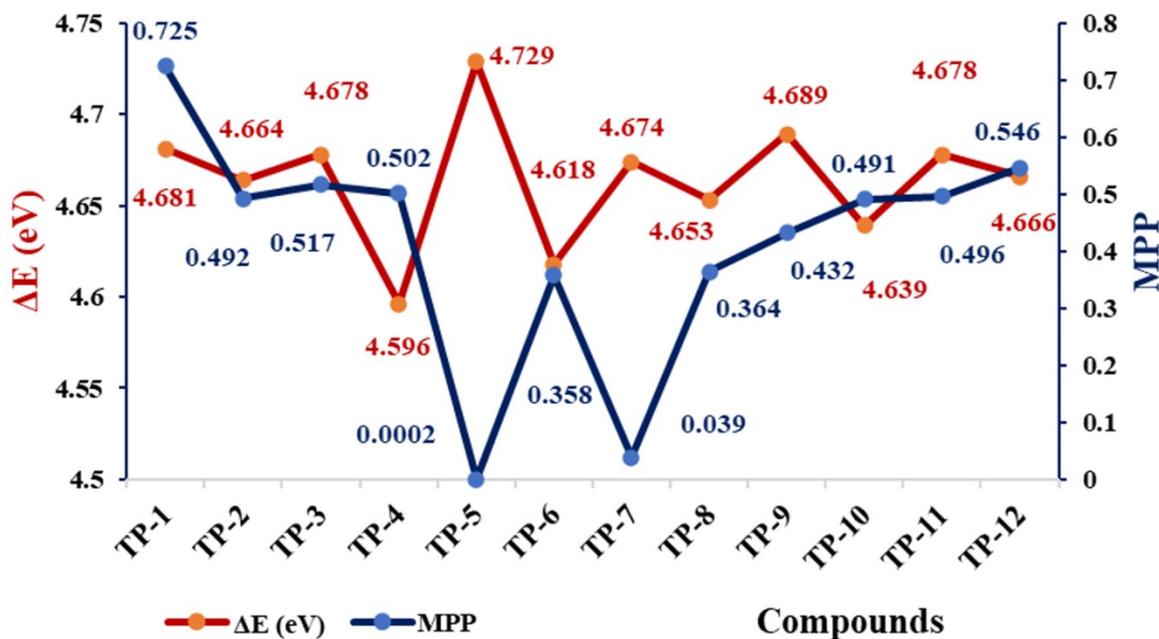[*] Corresponding Authors: SM: mshabbir@kku.edu.sa SB: shamsa.shafiq@uaf.edu.pk

Figure S1. Graphical representation of the correlation between the MPP of terpyridine isomers with their excitation energies
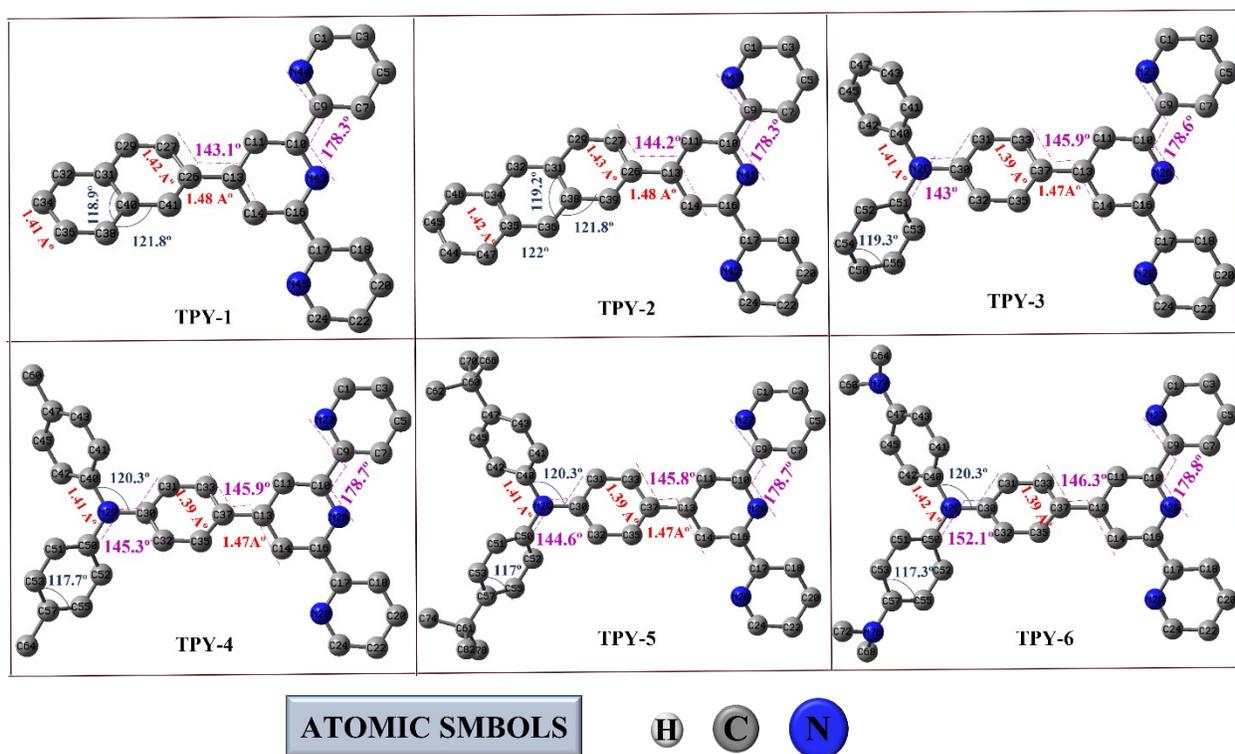
Figure S2. Optimized molecular geometries of the studied compounds were obtained at M06-2X/6-311G** calculations.

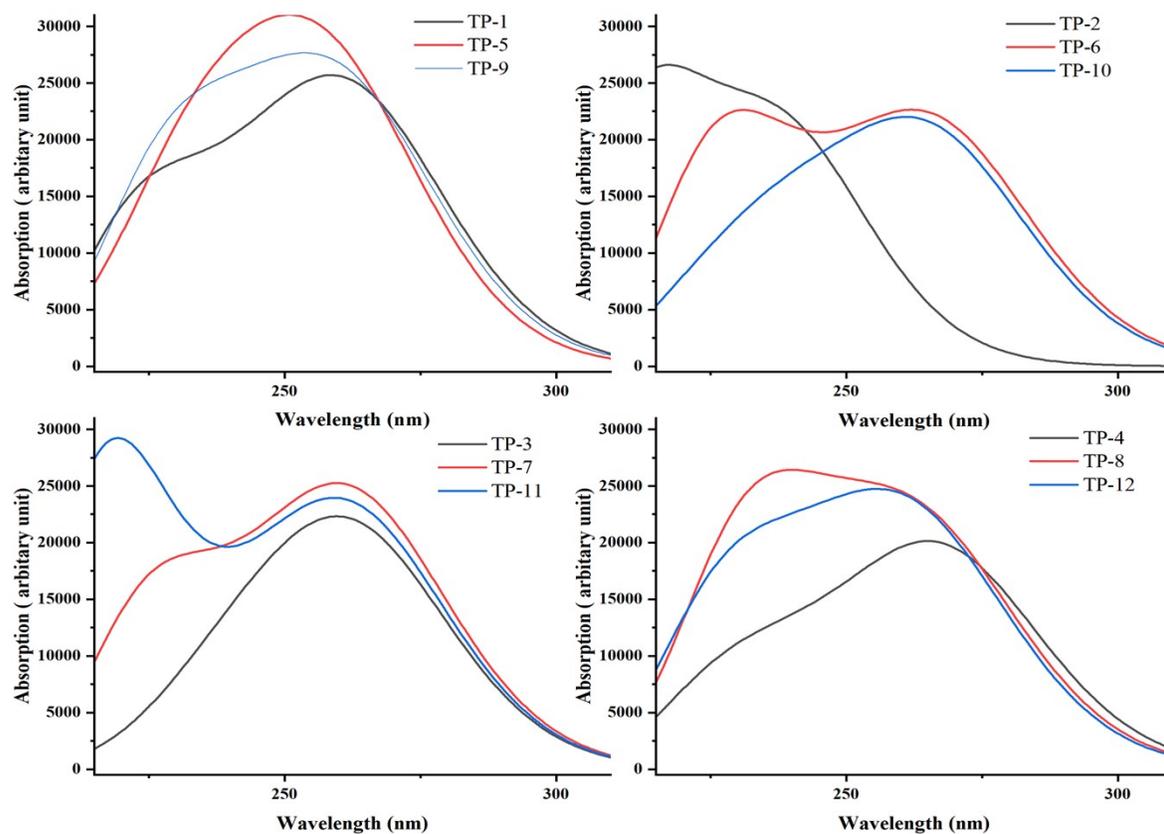**Figure S3.**   Graphical representation of UV spectra in THF solvent
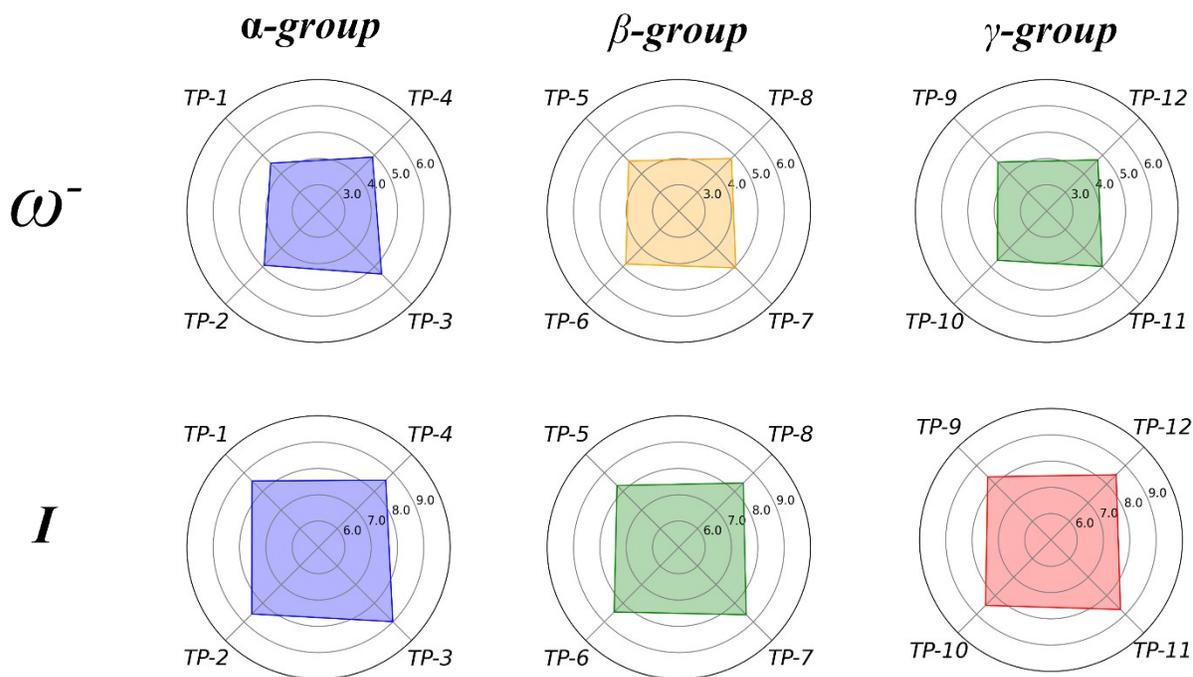
Figure S4 Ionization potential tendencies and Electro donating power tendencies under isomerization of terpyridine
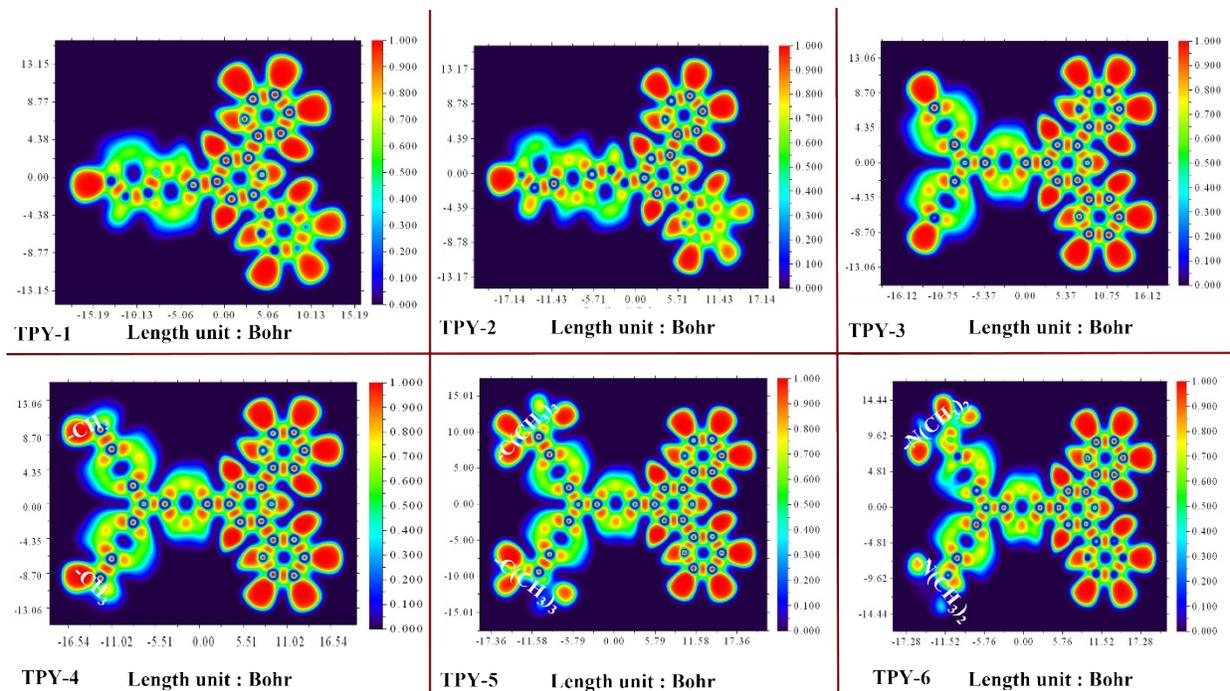
Figure S5. ELF (0-1) color-filled maps for **TPY-1** to **TPY-6** compounds, with color-coded scales: red regions correspond to high electron localization, while blue regions denote delocalized electron density.

Figure S6.   LOL (0-0.8) color-filled maps for **TPY-1** to **TPY-6** compounds, with color-coded scales: red regions correspond to high electron localization, while blue regions denote delocalized electron density.

Table S1.   Frontier molecular orbital (FMOs) analysis

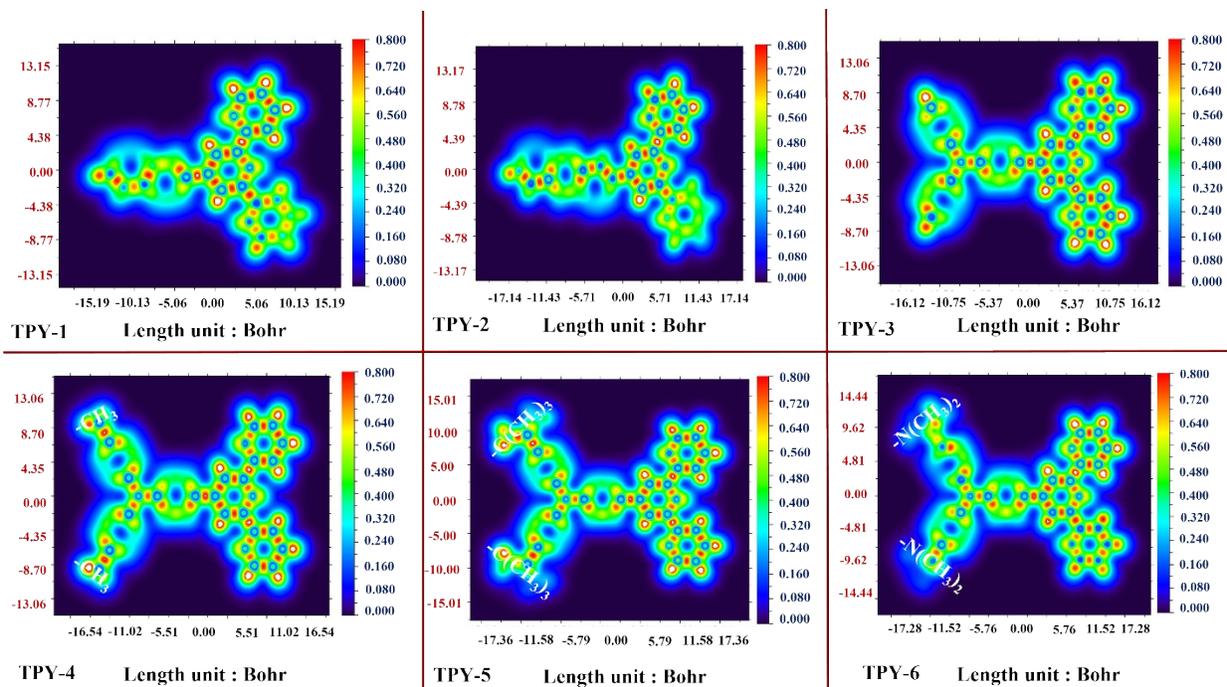| Compounds	E_{HOMO}	E_{LUMO}	ΔE	Electronegativity (χ)	Hardness (η)	Chemical potential (μ)
TP-1	-7.67	-0.58	7.09	8.84	4.15	-8.84
TP-2	-7.88	-0.83	7.04	4.34	4.24	-4.34
TP-3	-8.30	-1.07	7.22	4.66	4.32	-4.66
TP-4	-7.90	-0.91	6.99	4.33	4.27	-4.33
TP-5	-7.69	-0.62	7.07	4.16	4.15	-4.16
TP-6	-7.77	-0.82	6.95	4.28	4.19	-4.28
TP-7	-7.91	-0.96	6.96	4.42	4.19	-4.42
TP-8	-7.82	-0.91	6.96	4.27	4.18	-4.27
TP-9	-7.67	-0.63	7.05	4.25	4.15	-4.25
TP-10	-7.81	-0.66	7.14	4.33	4.18	-4.33
TP-11	-8.03	-0.80	7.23	4.40	4.33	-4.40
TP-12	-7.74	-0.73	7.01	4.27	4.23	-4.27

Table S2.   Accepting index of terpyridine isomers

Compounds	I	A	ω^{-}	ω^{+}
TP-1	8.570	0.270	4.575	8.307
TP-2	8.583	0.100	4.924	8.685
TP-3	8.999	0.340	5.395	9.353
TP-4	8.614	0.064	4.906	8.679
TP-5	8.326	0.007	4.690	8.333
TP-6	8.474	0.091	4.853	8.567
TP-7	8.620	0.226	5.067	8.853
TP-8	8.460	0.081	4.835	8.542
TP-9	8.403	0.097	4.637	8.306
TP-10	8.521	0.145	4.659	8.378
TP-11	8.741	0.067	4.981	8.810

TP-12	8.517	0.040	4.753	8.477

Table S3. Bond length, bond angle and dihedral angle comparison by using M06-2x/6-311G**

Bond length	Computed	Experimental	Difference
C_3-C_5	1.389	1.365	0.024
C_1-N_{44}	1.329	1.330	-0.001
N_{44}-C_9	1.335	1.342	-0.007
C_9-C_{10}	1.492	1.482	0.010
C_{10}-N_{43}	1.333	1.349	-0.016
N_{43}-C_{16}	1.333	1.338	-0.005
C_{16}-C_{17}	1.492	1.490	0.002
C_{17}-N_{45}	1.335	1.330	0.005
N_{45}-C_{24}	1.329	1.338	-0.009
C_{13}-C_{26}	1.482	1.476	0.006
C_{31}-C_{40}	1.420	1.410	0.010
C_{26}-C_{27}	1.422	1.416	0.006
C_{34}-C_{36}	1.415	1.395	0.020
C_{18}-C_{20}	1.386	1.369	0.017
C_{40}-C_{41}	1.416	1.413	0.003
		RMSD	0.019393

Bond angle	Computed	Experimental	Difference
N_{44}-C_9-C_{10}	116.6	116.2	0.4
C_{10}-N_{43}-C_{16}	118.3	117.5	0.8
N_{44}-C_9-C_7	122.5	121.8	0.7
N_{43}-C_{16}-C_{17}	116.9	116.3	0.6
C_{17}-N_{45}-C_{24}	118.1	117.3	0.8
C_{17}-C_{18}-C_{20}	118.6	118.8	-0.2
N_{45}-C_{17}-C_{18}	122.6	122.0	-0.6
C_{13}-C_{25}-C_{27}	120.0	120.0	0000
C_{38}-C_{40}-C_{41}	121.8	122.2	-0.4
C_{31}-C_{40}-C_{38}	118.9	118.7	-0.2

		RMSD	0.530094	
Dihedral angle	Computed	Experimental	Difference	
N_{44}-C_9-C_{10}-N_{43}	178.3	166.7	11.6	
C_7-C_9-C_{10}-C_{11}	177.9	170.6	7.3	
C_{11}-C_{13}-C_{26}-C_{41}	143.1	143.5	-0.4	
C_{29}-C_{31}-C_{40}-C_{38}	179.7	176.1	3.6	
		RMSD	3.93182283	

Table S4. Natural bond orbital (NBO) analysis for **TPY-1** to **TPY-6** computed at M06-2X/6-311G** level of theory

Compounds	Donor (i)	Type	Acceptor (j)	Type	$E^{(2)}$ kcal/mol	E(j)-E (i) (a.u.)	F (i;j) (a.u.)
TPY-1	π	C_{13}-C_{14}	π*	C_{16}-N_{43}	41.72	0.37	0.106
	π	C_{13}-C_{14}	π*	C_{26}-C_{41}	9.51	0.37	0.055
TPY-2	π	C_{26}-C_{39}	π*	C_{13}-C_{14}	11.37	0.38	0.06
	σ	C_{13}-C_{14}	σ*	C_{26}-C_{27}	2.21	1.35	0.049
TPY-3	LP (1)	N_{29}	π*	C_{40}-C_{42}	23.72	0.36	0.085
	σ	C_{52}-C_{54}	σ*	N_{29}-C_{51}	4.97	1.26	0.071
TPY-4	π	C_{13}-C_{14}	π*	C_{16}-N_{26}	42.33	0.33	0.107
	LP (1)	N_{29}	π*	C_{40}-C_{42}	22.31	0.36	0.082
TPY-5	LP (1)	N_{29}	π*	C_{40}-C_{41}	23.13	0.36	0.084
	σ	C_{40}-C_{41}	σ*	C_{40}-C_{42}	5.18	1.41	0.076
TPY-6	LP (1)	N_{77}	π*	C_{45}-C_{47}	46.34	0.37	0.122
	π	C_{13}-C_{14}	π*	C_{16}-N_{26}	42.84	0.33	0.107

Table S5. The centroid distance between two orbitals and HOMO–LUMO orbital overlap integral (S) for **TPY-1** to **TPY-6** computed at M06-2X/6-311G** level of theory

Compounds	Centroid distance (D_{CT})	Orbital overlap integral (S)
TPY-1	3.552	0.657
TPY-2	1.258	0.835
TPY-3	6.296	0.414

TPY-4	6.515	0.398
TPY-5	6.537	0.397
TPY-6	7.491	0.335

Table S6. Benchmark comparison of calculated $\langle\gamma\rangle$ ($\times$ 10^{-36} esu) using different density functionals (ωB97X-D[1], CAM-B3LYP[2], LC-BLYP[3], M05[4], M06[5], and M06-2X[5]) for **TPY-1** to **TPY-6** to assess the influence of range-separation and exchange contribution on the computed results.

Compound	ωB97X-D/ 6-311G**	CAM-B3LYP/ 6-311G**	M06/ 6-311G**	M05/ 6-311G**	M06-2X/ 6-311G**
TPY-1	59.51	63.21	89.66	86.78	63.83
TPY-2	96.89	105.8	161.0	154.5	108.5
TPY-3	137.0	153.9	266.2	258.2	163.4
TPY-4	161.0	182.4	324.9	314.3	194.7
TPY-5	178.5	201.8	360.8	349.6	219.1
TPY-6	205.9	235.6	410.2	398.5	291.4

Table S7: Literature summary table of $\langle\gamma\rangle$ values for similar terpyridine derivatives

Compounds	NLO values	Reference
Zn(II) complex [Zn(C27H35N3)Cl2] with 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine ligand	104.19 × 10^{-36} esu	Hussain S, Muhammad S, Chen X, Akkurt M, Alshehri AM, Din SU, Ullah H, Al-Sehemi AG. Synthesis, Crystal Structure, and Nonlinear Optical Properties of Zn (II) Complex with 4, 4', 4"-Tri-tert-Butyl-2, 2': 6', 2"-Terpyridine: A Dual Exploration. Russian Journal of Inorganic Chemistry. 2020 Mar;65(3):368-77.
[2,6-diphenyl-4-(3,4,5-trimethoxyphenyl) pyridine]	187.53 × 10^{-36} esu	Chaudhry, A.R., Muhammad, S., Haq, B.U., Kumar, S., Al-Sehemi, A.G., Irfan, A., Laref, A. and Hussain, A., 2019. Exploring the functional properties of Trimethoxy-Phenylpyridine as efficient optical and nonlinear optical material: A quantum chemical approach. *Journal of Molecular Structure, 1185*, pp.268-275.

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