Supplementary Materials

Structure of Tris[2-(4-pyridyl)ethyl]phosphine, Tris[2-(2-pyridyl)ethyl]phosphine, and Their Chalcogenides in Solution: Dipole Moments, IR Spectroscopy, DFT Study

Anastasiia A. Kuznetsova [1], Denis V. Chachkov [2], Natalia A. Belogorlova [3], Svetlana F. Malysheva [3] and Yana A. Vereshchagina [1,*]

[1] Department of Physical Chemistry, A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya 18, 420008 Kazan, Russia; kuznetsovaanastan@gmail.com
[2] Kazan Department of Joint Supercomputer Center of Russian Academy of Sciences–Branch of Federal Scientific Center "Scientific Research Institute for System Analysis of the RAS", Lobachevskogo 2/31, 420111 Kazan, Russia; de2005c@gmail.com
[3] A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Favorskogo 1, 664033 Irkutsk, Russia; mal@irioch.irk.ru
* Correspondence: jveresch@kpfu.ru

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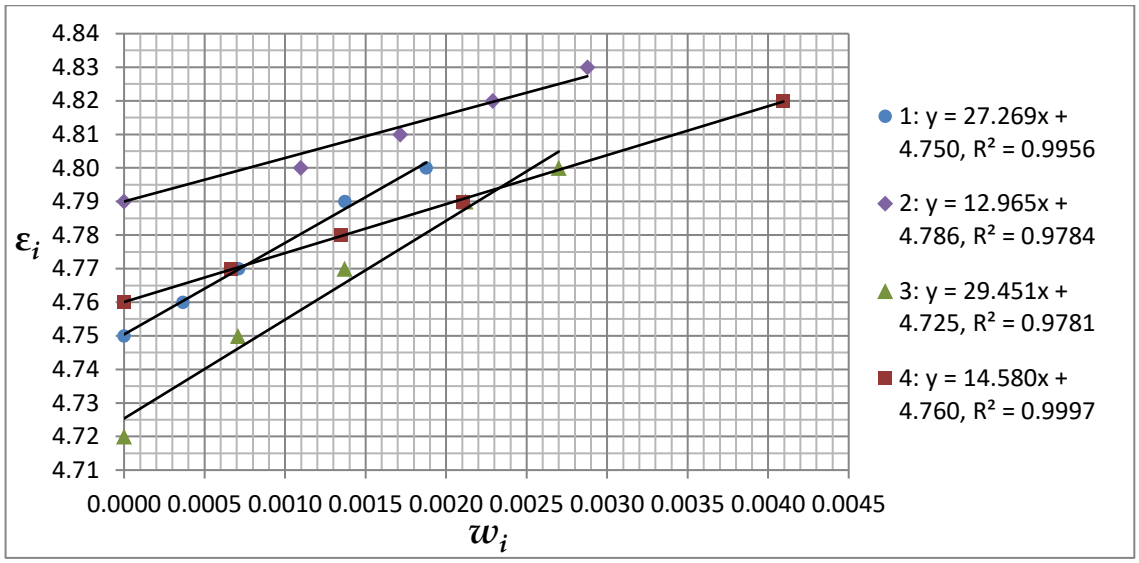
Equations for α and γ calculations (Guggenheim-Smith equation):

$$\alpha = \frac{\varepsilon_i - \varepsilon_0}{w_i},$$

$$\gamma = \frac{n_i^2 - n_0^2}{w_i},$$

where α and γ are slopes of the ε_i–w_i and n_i^2–w_i plots; ε_i, n_i, and w_i are the dielectric permittivity, refractive index, and weigh fraction of the solute of the i^{th} solution, respectively.



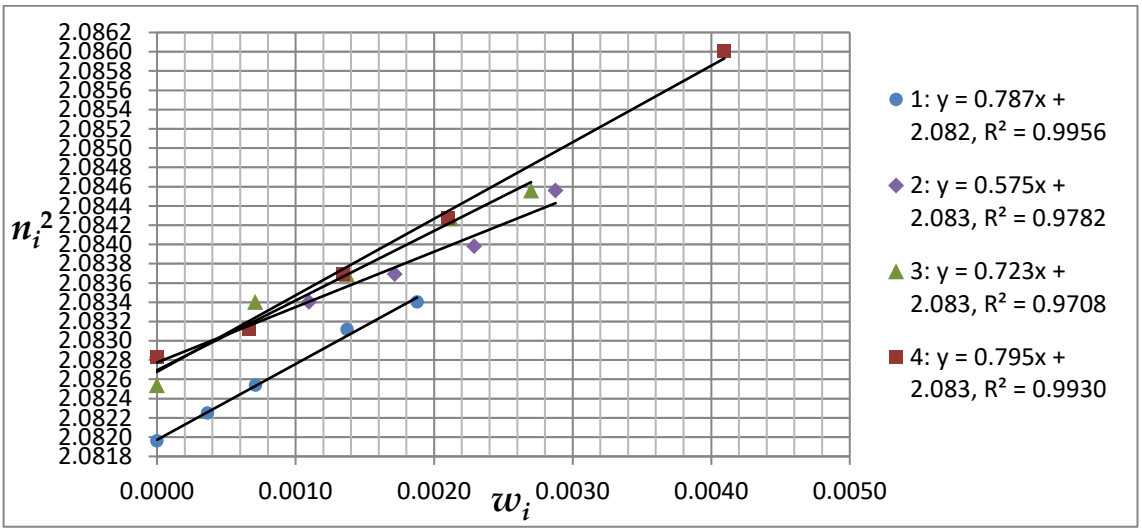
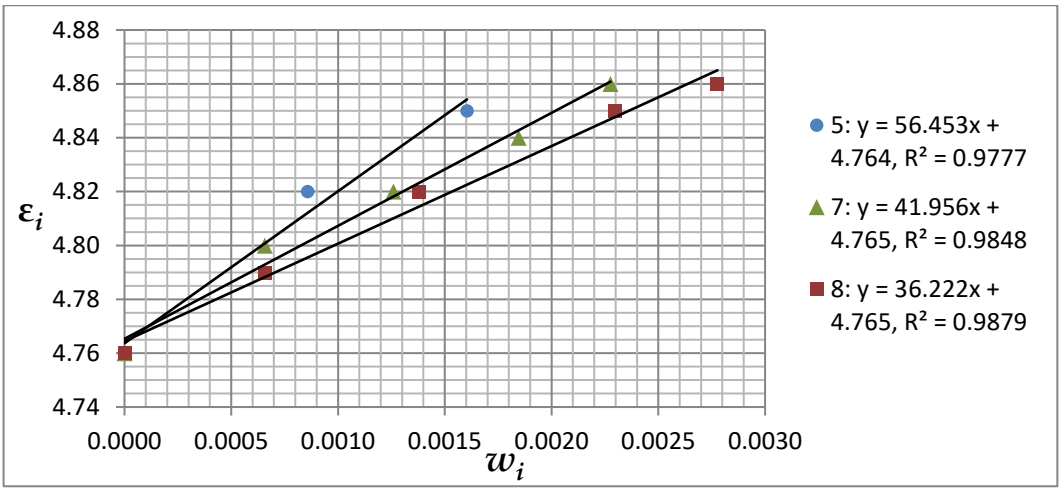


Figure S1. The εi–w_i and n_i^2–w_i plots for compounds **1-4**, trichloromethane solutions.



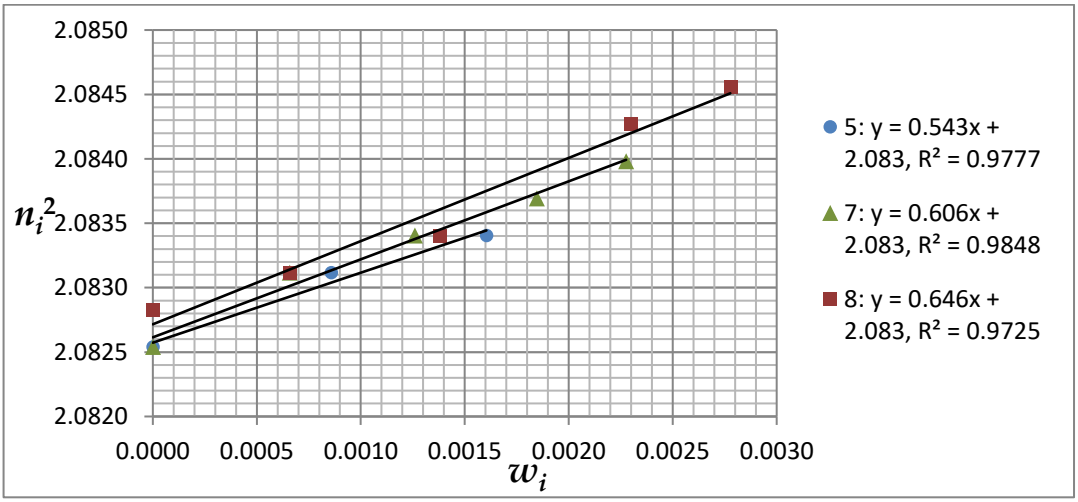
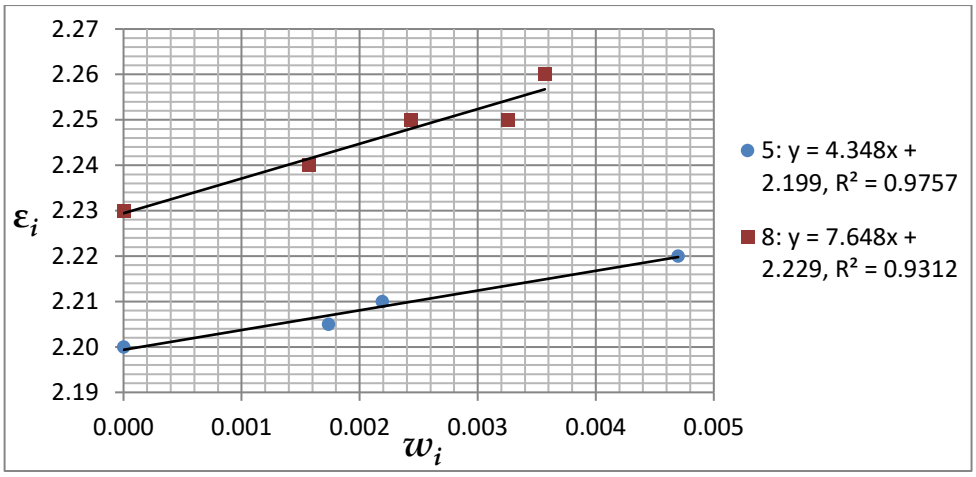
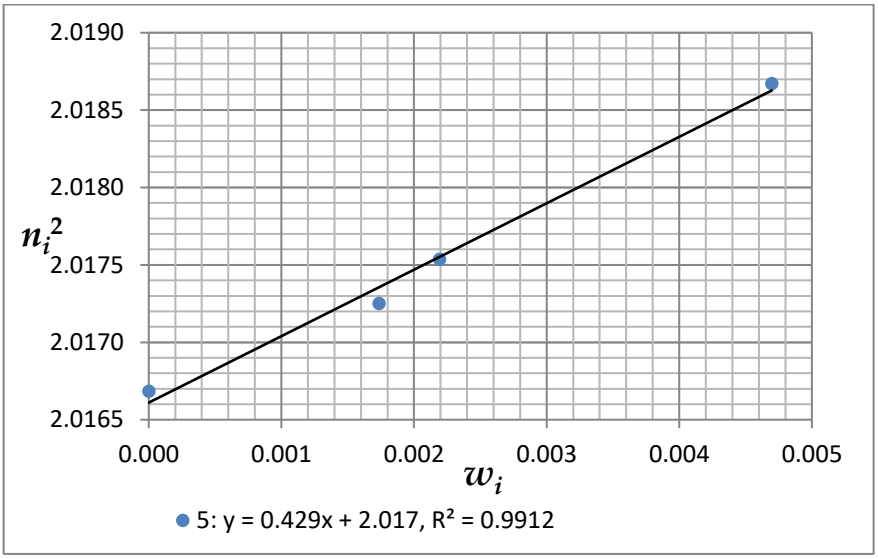


Figure S2. The ε_i–w_i and n_i^2–w_i plots for compounds **5**, **7**, and **8**, trichloromethane solutions.





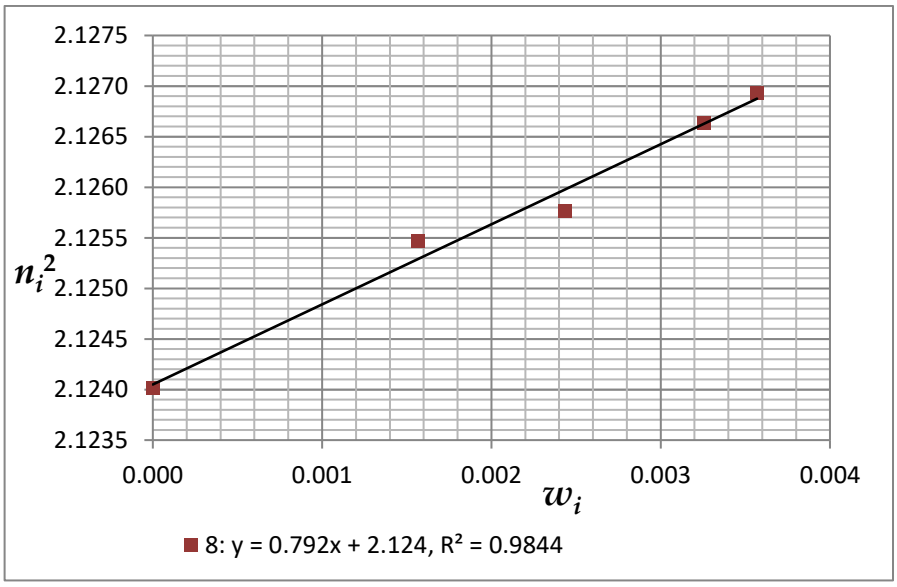


Figure S3. The ε_i–w_i and n_i^2–w_i plots for compounds **5** (1,4-dioxane solutions) and **8** (tetrachloromethane solutions).

Table S1. Values of the slope (α or γ) and the intercept of the linear ε_i–w_i and n_i^2–w_i dependences and standard errors of regression parameters for compounds **1–5**, **7**, **8**.

	Solvent	$\varepsilon_i = \alpha \cdot w_i + c_1$				$n_i^2 = \gamma \cdot w_i + c_2$			
		α	$\Delta\alpha$	c_1	Δc_1	γ	$\Delta\gamma$	c_2	Δc_2
1	Trichloromethane	27.27	1.05	4.76	0.00	0.787	0.030	2.0820	0.0000
2	Trichloromethane	12.97	1.10	4.79	0.00	0.575	0.050	2.0828	0.0001
3	Trichloromethane	29.45	2.54	4.73	0.00	0.723	0.072	2.0827	0.0001
4	Trichloromethane	14.58	0.16	4.76	0.00	0.795	0.038	2.0827	0.0001
5	Trichloromethane	56.45	8.52	4.76	0.01	0.543	0.082	2.0826	0.0001
	1,4-Dioxane	4.35	0.49	2.20	0.00	0.429	0.029	2.0166	0.0001
7	Trichloromethane	41.96	3.01	4.77	0.00	0.606	0.043	2.0826	0.0001
8	Trichloromethane	36.22	2.32	4.76	0.00	0.646	0.063	2.0827	0.0001
	Tetrachloromethane	7.65	1.20	2.23	0.00	0.792	0.057	2.1241	0.0001

Table S2. Selected vibration frequencies (cm^{-1}) of **2–4**; theoretical values are listed for conformers **a–f**.

Vibrations*	Experimental			Gas phase						Solution (CPCM model)					
	Solid	**Solution**	**Melt**	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
C–H(Pyridyl) (ω)	805	-	802	822	819, 825	817, 828	822	821	819	823	822	817, 825	823	823	820
C–H(Ethyl) (τ, ϱ)	953, 975	925, 939	948	948	925, 949	911, 929, 953	919, 948, 969	927, 945, 969	958	950	923, 952	902, 923, 956	926, 953, 970	930, 950, 971	959
C–H(Pyridyl) (τ)	994	995	991	1013	1014	1015	1016	1012	1017	1015	1014	1015	1015	1015	1015
P=O (ν)	1149, 1168	1167	1169	1211	1206	1204	1211	1196	1197	1181	1183	1283	1183	1172	1172
C–H(Pyridyl) (δ)	1415	1418	1414	1449	1449	1447	1449	1449	1447	1447	1446	1447	1446	1446	1446
C=C and C=N (ν)	1599	1603	1597	1647	1648	1648	1647	1646	1648	1648	1647	1648	1647	1647	1647
				3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**
C–H(Pyridyl) (ω)	799, 807	no	802	821	822	816, 822	822	820	821	823	824	816, 822	822	822	823
C–H(Ethyl) (τ, ϱ)	939, 956, 967	939, 953	952	945, 971	902, 923, 949, 964	905, 920, 932, 959	922, 949, 984	920, 964	939, 948, 972	950, 971	901, 924, 951, 963	902, 922, 934, 961	932, 949, 982	923, 964, 973	939, 950, 973
C–H(Pyridyl) (τ)	994	995	991	1015	1015	1015	1014	1014	1013	1015	1013	1014	1014	1014	1015
C–H(Pyridyl) (δ)	1418	1417	1414	1 448	1447	1447	1447	1448	1449	1446	1448	1447	1446	1449	1446
C=C and C=N (ν)	1602	1603	1597	1648	1648	1648	1648	1648	1647	1647	1647	1648	1647	1647	1647
				4a	**4b**	**4c**	**4d**	**4e**	**4f**	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**
C–H(Pyridyl) (ω)	807	no		822	822	815, 823	822	818	822	824	816, 822	815, 821	822	820	824
C–H(Ethyl) (τ, ϱ)	938, 956, 967	924, 939, 952,		946, 967	902, 922, 949, 961	903, 921, 933, 960	923, 946, 982	963, 968	937, 948, 972	951, 963	902, 922, 952, 964	901, 921, 933, 963	925, 952, 976	962, 974	939, 951, 974
C–H(Pyridyl) (τ)	995	995		1014	1014	1016	1014	1016	1013	1013	1014	1013	1014	1015	1016
C–H(Pyridyl) (δ)	1419	1418		1450	1449	1448	1448	1449	1449	1 447	1446	1445	1446	1446	1447
C=C and C=N (ν)	1602	1603		1647	1647	1649	1648	1647	1647	1648	1647	1647	1647	1647	1647

* ν – stretching, δ – scissoring, ϱ – rocking, ω – wagging, τ – twisting

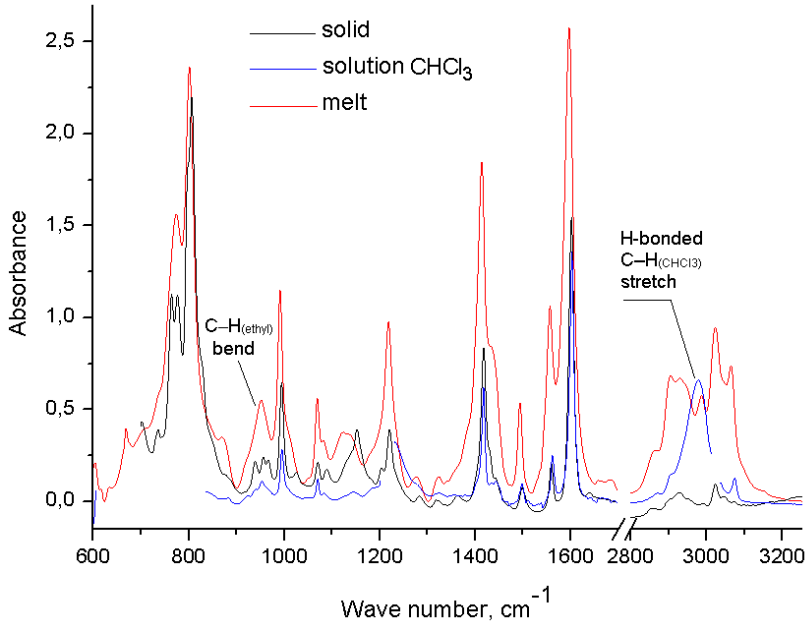


Figure S4. FT-IR spectra of compound **3** in different aggregate states.

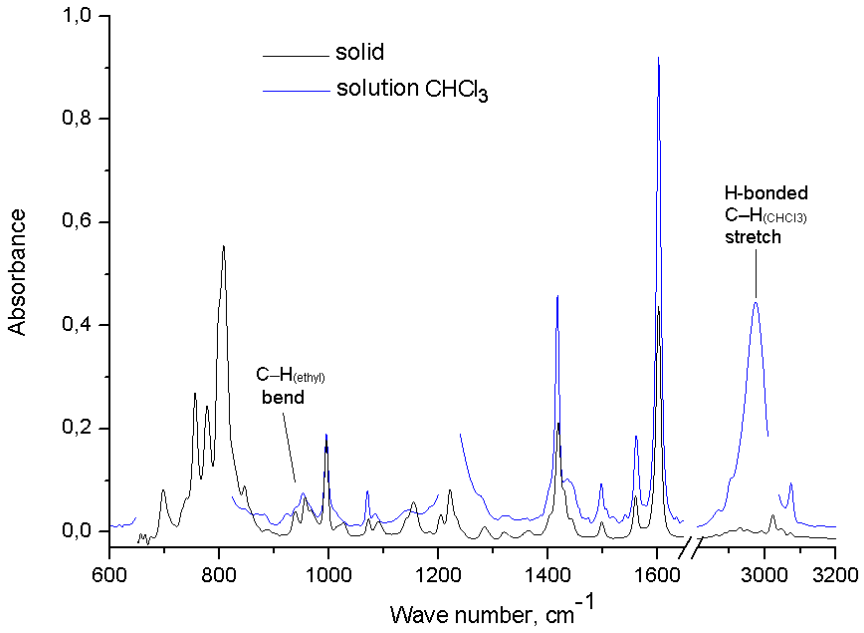


Figure S5. FT-IR spectra of compound **4** in different aggregate states.

Table S3. Selected vibration frequencies (cm^{-1}) of **7**, **8**; theoretical values are listed for conformers 7**a–c**, **7f**, **7h-j** and **8a–c**, **8e-g**, **8j**.

Vibrations*	Experimental		Gas phase							Solution (CPCM model)						
	Solid	**Solution**	**7a**	**7b**	**7c**	**7f**	**7h**	**7i**	**7j**	**7a**	**7b**	**7c**	**7f**	**7h**	**7i**	**7j**
C–H$_{(Pyridyl)}$ (ω)	798, 808	no	795	788, 797	778, 799	796, 801	794	790, 799	788, 797	798	785, 799	777, 797	799	789, 798	798	793, 799
C–H$_{(Ethyl)}$ (τ, ϱ)	940, 957, 968	939, 952, 965	950, 970	919, 930, 955, 966	968	953, 977, 989	951, 966	945, 974	953, 978, 990	950, 971	930, 954, 966	964, 973	953, 977	953, 970	943, 952, 973	953, 976
C–H$_{(Pyridyl)}$ (τ)	995	997	1012	1014	1012	1012	1013	1013	1013	1012	1013	1014	1013	1012	1012	1013
C–H$_{(Pyridyl)}$ (δ)	1419	1436	1466, 1478	1465, 1474	1466, 1476	1467, 1476	1470	1467, 1476	1467, 1476	1464, 1473	1471	1472	1465, 1474	1463, 1472	1463, 1472	1465, 1470
C–H$_{(Pyridyl)}$ (ϱ)	-	1475	1510	1510	1508	1509	1509	1509	1509	1508	1510	1508	1509	1508	1508	1509
C=C and C=N (ν)	1602	1593	1644	1643	1642	1642	1642	1642	1642	1642	1641	1641	1640	1642	1642	1640
			8a	**8b**	**8c**	**8e**	**8f**	**8g**	**8j**	**8a**	**8b**	**8c**	**8e**	**8f**	**8g**	**8j**
C–H$_{(Pyridyl)}$ (ω)	750, 766	-	765, 795	764, 785, 797	766, 775, 796	765, 795	761, 788, 796	764, 773, 788, 797	764, 773, 796	766, 799	764, 785, 797	765, 777, 798	767, 799	758, 767, 787, 799	768, 792	770, 797
C–H$_{(Ethyl)}$ (τ, ϱ)	938, 948, 966	922, 939, 951, 965	949, 967	931, 954, 966	965	953, 976, 988	951, 963	954, 978, 988	945, 954, 974	950, 965	955, 967	964, 973	954, 978	951, 968	955, 976	943, 952, 975
C–H$_{(Pyridyl)}$ (τ)	994	997	1015	1014	1013	1012	1013	1013	1013	1013	1014	1012	1013	1013	1014	1014
C–H$_{(Pyridyl)}$ (δ)	1435	1437	1465, 1477	1465, 1474	1467, 1476	1466, 1475	1470	1467, 1476	1467, 1476	1464, 1473	1463, 1472	1466, 1472	1465, 1474	1470	1463, 1472	1466, 1472
C–H$_{(Pyridyl)}$ (ϱ)	1475	1475	1510	1509	1508	1508	1509	1509	1509	1509	1507	1508	1507	1509	1508	1507
C=C and C=N (ν)	1589	1594	1643	1643	1642	1641	1642	1642	1642	1639	1641	1642	1640	1640	1641	1641

* ν – stretching, δ – scissoring, ϱ – rocking, ω – wagging, τ – twisting