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Solvent-Free Synthesis and Spectral Correlation of ^{1}*N*-Acetyl-3-(4-β-Methacrylate)-5-(Substituted Phenyl)-4,5-Dihydro-^{1}*H*-Pyrazolines

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Abstract. A series containing fourteen ^{1}*N*-acetyl-3-(4-β-methacrylate)-5-(substituted phenyl)-4, 5-dihydro-^{1}*H*-pyrazolines were synthesized by KF/Al_2O_3 catalyzed solvent-free condensation of ^{1}*N*-acetyl-3-(4-hydroxyphenyl)-5-(substituted phenyl)-4, 5-dihydro-^{1}*H*-pyrazolines and (*E*)-methyl-2-[2-(bromo methyl)-phenyl]-3-methoxyacrylate under microwave irradiation. The yields of the above ^{1}*N*-acetyl-3-(4-β-methacrylate)-5-(substituted phenyl)-4, 5-dihydro-^{1}*H*-pyrazolines were more than 90%. These pyrazolines were characterized by their physical constants, IR, NMR and Mass spectral data. The infrared spectral frequencies (ν, cm^{-1}) and NMR chemical shifts (δ, ppm) of proton and carbons of these pyrazolines were assigned and correlated with Hammett substituent constants, F and R parameters. From the results of statistical analyses, the effects of substituent on the above spectral data have been discussed.

Keywords: Solvent-free synthesis, KF/Al_2O_3, β-methacrylate-^{1}*N*-acetylpyrazolines, IR spectra, NMR spectra, Hammett correlation

1 Introduction

The ^{1}*H*-4,5-dihydropyrazoline and ^{1}*N*-acetyl-4,5-dihydroprazoline derivatives play structurally more important roles in pharmaceutical field of research because they possess numerous biological activities. The important biological activities of pyrazoline derivatives are anti-bacterial[1], anti-fungal[2], anti-depressants[3], anti-convulsant[4], anti-inflammatory[5], anti-tumour [6], anaesthetic[7], analgesic[8], anti-cancer[9], anti-Helicobacter pylori[10], MAO-B inhibitors[11], steroidal, nitric oxide synthase inhibitor, anti-viral and cannabinoid CBI receptor antagonists[5]. They belong to the bi-nitrogen five membered heterocyclic compounds containing three hydrogens in different planes[12-14]. This spatial arrangement of the protons was confirmed by ^{1}H NMR and XRD analysis. Many solvent assisted and solvent-free methods including cyclization[15,16], N-acetylation, N-thio-acetylation[17], N-phenylation[15], N-thio-amination[12,13] and condensation[14] were reported in the literature for synthesis of these pyrazoline derivatives. The catalysts such as, Lewis acids, weak acids [18], polyacids [19], sodium acetate [20], clays[21], fly-ash:H_2SO_4 [14], SiO_2-H_3PO_4 [22], preheated fly-ash[12], fly-ash:PTS [13], with or without microwave and ultrasound irradiation [23] were utilized for the above reactions. Now-a-days chemists and organic researchers have paid more attention to solvent-free methods. These methods are important and play vital role for synthesis of organics due to easy work-up procedure, technique, shorter time, less hazardousness, less pollution to the environment, higher yield. Sasikala et al.,[15] have synthesised some 5-chloro-2-thienyl based pyrazoline derivatives by solvent-free method and studied the antimicrobial activities. Sakthinathan et al.[20] have synthesised and studied the effects of substituent on 2-naphthyl based pyrazolines. Spectroscopic data were used for prediction of ground state equilibration of organic compounds such as, *E, Z* or *cis-trans* isomers of unsaturated compounds such as, alkenes, alkynes, polyenes, enol-enones, unsaturated acid chlorides, ω-halo-acyl compounds and pyrazoline derivatives. These spectroscopic data were applied for the study of spectral linear regression through Hammett equation. Thirunarayanan et al. have studied the effects of substituents and solvent-free synthesis of some 5-bromo-2-thienyl based pyrazolines [22]. The solvent-free synthesis and the

Hammett linearity on some pyrazoline-1-carbothioamides have been studied by Thirunarayanan and Sekar [12, 13]. Spectroscopic data are applied for prediction of ground sate equilibration of organic molecules such as unsaturated ketones, aldehydes, alkenes, alkynes, acyl halides and its esters [24]. The effect of substituents on the functional group of the molecules can be evaluated by the correlation of the respective spectral group frequencies with Hammett substituent constants, *F* and *R* parameters using linear regression analysis [25]. The correlation analysis has been applied for the study of electrochemical behaviour of organic molecules, *E*, Z, *s-cis*- and *s-trans* configuration and isomers of unsaturated systems, *cis*- and *gauche*- forms of rotamers of ω-halo acyl compounds [26]. There is no information available about solvent-free synthesis and the study of spectral linearity on ^{1}*N*-acetyl-3-(4-β-methacrylate)-5-(substituted phenyl)-4,5-dihydro-^{1}*H*-pyrazolines. Therefore the authors have taken efforts to synthesize of ^{1}*N*-acetyl-3-(4-β-methacrylate)-5-(substituted phenyl)-4,5-dihydro-^{1}*H*-pyrazolines by solvent-free by KF/Al_2O_3 catalyzed condensation of ^{1}*N*-acetyl-3-(4-hydroxyphenyl)-5-(substituted phenyl)-4,5-dihydro-^{1}*H*-pyrazolines and (*E*)-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate under microwave irradiation and record their infrared and NMR spectra in order to investigate the effect of substituents.

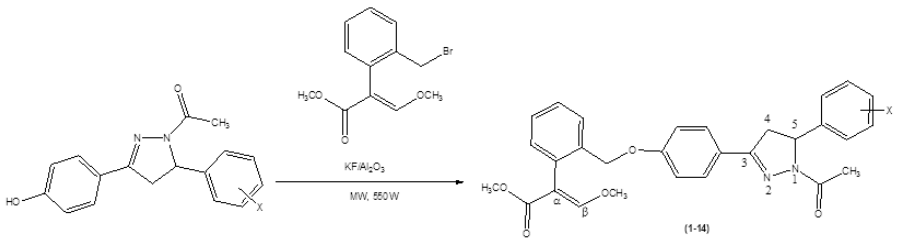
2 Experimental

2.1 General

All chemicals used were procured from Sigma-Aldrich and Merck chemical companies. The infrared spectra of all pyrazolines were recorded with KBr discs in SHIMADAZU Fourier Transform spectrophotometer. The NMR spectra of all synthesized compounds were recorded in BRUKER AV400 NMR spectrometer applying 400 MHz for ^{1}H and 100MHz frequencies for ^{13}C NMR spectra using $CDCl_3$ solvent and tetramethylsilane as standard. The mass spectra of all pyrazolines were recorded in SHIMADZU spectrometer using chemical ionization technique.

2.2 Synthesis of ^{1}*N*-acetyl-3-(4-β-methacrylate)-5-(substituted phenyl)-4,5-dihydro-^{1}*H*-pyrazolines

An appropriate equi-molar quantities of 3-(4-hydroxphenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones (2 mmol), *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate (2 mmol), and KF/Al_2O_3 (0.4 g) were taken in a 50 mL borosil beaker and closed with lid. The mixture has been subjected to microwave irradiation for 6-8 minutes in a microwave oven at 550 watts, 2540 MHz frequency (Scheme 1) (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50Hz, 2450Hz, 100-750W (IEC-705), and then cooled to room temperature. After separating the organic layer with dichloromethane, the solid product has been obtained on evaporation. The solid, on recrystallization from benzene-hexane mixture afforded glittering product. The insoluble catalyst has been recycled by washing with ethyl acetate (8 mL) followed by drying in an oven at 100°C for 1h and reused for further reactions.



Entry	1	2	3	4	5	6	7	8	9	10	11	12	13	14
X	H	4-Br	4-Cl	4-OEt	4-Et	2-F	3-F	4-F	3-OMe	4-OMe	4-Me	2-NO_2	3-NO_2	4-NO_2

Scheme 1. Structure of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones by solvent-free condensation of 3-(4-hydroxyphenyl)-5-(substitutedphenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)ethanones and *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate in the presence of KF/Al_2O_3 catalyst.

3 Results and Discussion

The authors have taken efforts for the synthesis of 3-(4-β-methoxyacrylate)-5-(substitutedphenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanone derivatives by condensation of 3-(4-hydroxyphenyl)-5-(substitutedphenyl)-4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones possessing electron withdrawing as well as electron donating groups as substituents in 5th positioned phenyl ring, and *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate in the presence of acidic catalyst KF/Al_2O_3 under microwave irradiation. Hence the authors have synthesized the 3-(4-β-methoxyacrylate)-5-(substitutedphenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanone derivatives by the cyclization of 2 mmol of corresponding ^{1}*N*-acetyl pyrazoline, 2 mmol of *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate under microwave irradiation with 0.4 g of KF/Al_2O_3 catalyst at 550 W, 6-8 minutes (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50Hz, 2450Hz, 100-750W (IEC-705), (Scheme 1). During the course of this reaction KF/Al_2O_3 catalyses condensation of 4-hydroxyphyenyl attached in the 3rd position of ^{1}*N*-acetyl pyrazolines and the *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate by elimination of HBr. The yield of the ^{1}*N*-acetyl pyrazolines in this reaction is more than 95%. The ^{1}N-acetyl pyrazolines containing electron donating substituent (OCH_3) gave higher yield than electron-withdrawing (halogens, NO_2) substituents. Further we have investigated this condensation with equimolar quantities of the 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanone (entry 1) and *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate under the above same condition. In this reaction the obtained yield was 92%. The effect of quantity on this reaction was studied by varying the catalyst quantity from 0.1 g to 1 g. As the catalyst quantity increased from 0.1 g to 0.4 g, the percentage of yield increased from 85 to 92%. Further increasing the catalyst amount beyond 0.4 g, there is no significant increasing in the percentage of the product. The effect of catalyst loading is shown in Figure 1. The optimum quantity of catalyst loading was found to be 0.4 g. The analytical results and mass spectral data are summarized in Table 1.

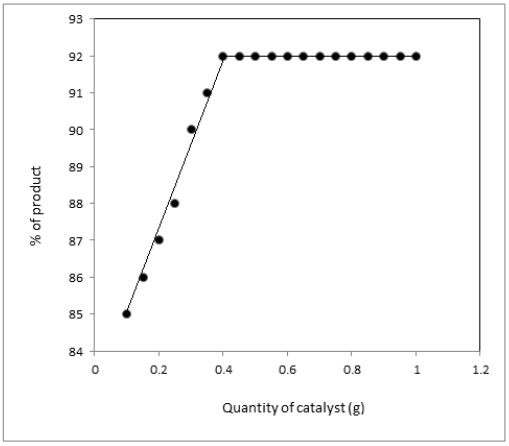


Figure 1. The effect of catalyst loading.

The reusability of this catalyst was studied for the condensation of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanone (entry 1), *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate was presented in Table 2. From Table 2, the first two runs gave 92% product. The third, fourth and fifth runs of reactions gave the yields 91.5% and 90%, of the targeted ^{1}*N*-acetyl pyrazolines. Here the authors observed the appreciable loss in its effect of catalytic activity up to the fifth run. The effect of solvents on the yield was also studied with methanol, ethanol, dichloromethane and tetrahydrofuran with the same quantity of catalyst (entry 1) in 6h reflux condition. The effect of solvents on the yield of the targeted ^{1}*N*-acetyl pyrazolines(entry 1) was presented in Table 3. From the table it can be seen that the highest yield of ^{1}*N*-acetyl pyrazolines (entry 1) was obtained from the condensation of 3-(4-hydroxyphenyl)-5-phenyl-4,5-dihydro^1*H*-pyrazole-1-yl) ethanone (entry 1) and *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate udner microwave irradiation.

Table 1. The physical constants, analytical and mass fragments (m/z) data of 3-(4-β-methoxyacrylate)-5-(substitutedphenyl)-(4,5-dihydro-1H-pyrazole-1-yl) ethanones[27].

No.	X	M. F.	M.W	Yield (%)	M.p. (°C)	Mass (m/z)
1	C_6H_5	$C_{23}H_{24}N_2O_5$	484	90	125-126	408[M^+]
2	4-Br	$C_{23}H_{23}BrN_2O_5$	563	90	79-80 (78-80)	487[M^+], 489[M^{2+}]
3	4-Cl	$C_{23}H_{23}ClN_2O_5$	518	90	87-88 (86-89)	443[M^+], 445[M^{2+}]
4	4-OCH_2CH_3	$C_{31}H_{32}N_2O_6$	529	91	68-69 (67-69)	453[M^+]
5	4-CH_2CH_3	$C_{31}H_{32}N_2O_5$	513	93	81-81 (79-80)	513[M^+]
6	2-F	$C_{23}H_{23}FN_2O_5$	503	90	153-154 (151-153)	426[M^+], 428[M^{2+}]
7	3-F	$C_{23}H_{23}FN_2O_5$	503	90	136-137 (135-137)	426[M^+], 428[M^{2+}]
8	4-F	$C_{23}H_{23}FN_2O_5$	503	90	87-88 (84-87)	426[M^+], 428[M^{2+}]
9	3-OCH_3	$C_{24}H_{26}N_2O_6$	515	95	77-78 (75-77)	438[M^+]
10	4-OCH_3	$C_{24}H_{26}N_2O_6$	515	95	80-81 (77-80)	438[M^+]
11	4-CH_3	$C_{24}H_{26}N_2O_5$	499	93	89-90 (85-88)	422[M^+]
12	2-NO_2	$C_{23}H_{23}N_3O_7$	530	90	107-108	453[M^+]
13	3-NO_2	$C_{23}H_{23}N_3O_7$	530	90	117-118	453[M^+]
14	4-NO_2	$C_{23}H_{23}N_3O_7$	530	90	129-130	453[M^+]

Table 2. Reusability of KF/Al_2O_3 catalyst for condensation of 3-(4-hydroxyphenyl)-5-phenyl-(4,5-dihydro-^1H-pyrazole-1-yl) ethanone and *E*-methyl-2-[2-(bromomethyl)-phenyl]-3-methoxyacrylate(entry 1).

Run	1	2	3	4	5
Yield(%)	92	92	91.5	91.5	90

Table 3. The effect of solvents in conventional heating and without solvent in microwave irradiation on the yield of 1-acetyl pyrazoline (entry 1).

Solvents				Microwave irradiation
MeOH	EtOH	DCM	THF	
77	79	75	81	92

*MeOH: Methanol; EtOH: Ethanol; DCM: Dichloromethane; THF: Tetrahydrofuron

3.1 Spectral Correlations

In the present spectral investigation, the spectral correlation of 3-(4-β-methoxyacrylate)-5-(substitutedphenyl)-(4,5-dihydro-^1H-pyrazole-1-yl) ethanones has been studied by assessment of the substituent effects[12-14, 22, 24, 26, 28, 29] on the absorption group frequencies of single substituted systems. The infrared spectral νC=N and C=O (cm^{-1}) frequencies, NMR chemical shifts (δ, ppm) of $CH_{3(keto)}$, H_4, H_4, H_5, CH_2, H_β, OCH_3, $CH_{3(ester)}$protons, C=O, $CH_{3(keto)}$, C=N, CH_2, C_α, C_β, OCH_3, $C{=}O_{(ester)}$, and $CH_{3(ester)}$ carbons of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl)

ethanones have been assigned and correlated with Hammett substituent constants and Swain-Lupton's [30] parameters using single and multi-regression analysis.

3.1.1 IR spectral study

The νCO and C=N stretching frequencies (cm^{-1}) of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl) ethanones of the present study are presented in Table 4. These data have been correlated with Hammett substituent constants [12-14, 22, 24, 26, 28, 29]. The results of statistical analyses were shown in Table 5. In this correlation, the structure parameter Hammett equation employed is as shown in the following equation (1)

$$\nu = \rho\sigma + \nu_0 \quad (1)$$

where ν is the carbonyl frequencies of substituted system and ν_0 is the corresponding σ quantity of unsubstituted system, σ is a Hammett substituent constant, which is characteristics of the substituent and ρ is a reaction constant which depends upon the nature of the reaction.

Table 4. The infrared and NMR spectral data of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl) ethanones.

No.	X	IR, (ν, cm^{-1})		^{1}H NMR (δ, ppm)									
		C=O	C=N	CH_3 (keto)	H_4	$H_{4'}$	H_5	CH_2	H_β (vinyl)	OCH_3	CH_3 (ester)	Ar-H	X
1	H	1654	1588	2.463	3.107	3.723	5.631	5.132	7.631	3.437	3.813	6.256-7.324	---
2	4-Br	1658	1592	2.381	3.217	3.691	5.593	5.214	7.537	3.394	3.794	6.345-7.567	---
3	4-Cl	1659	1590	2.411	3.178	3.654	5.453	5.174	7.673	3.531	3.781	6.223-7.082	---
4	4-OEt	1648	1564	2.367	3.215	3.741	5.717	5.072	7.610	3.432	3.870	6.120-7.032	3.722, 2.525
5	4-Et	1647	1586	2.417	3.213	3.661	5.677	5.213	7.543	3.471	3.861	6.653-7.675	2.546, 1.378
6	2-F	1651	1574	2.483	3.089	3.713	5.879	5.176	7.601	3.347	3.837	6.976-7.053	---
7	3-F	1657	1583	2.408	3.247	3.717	5.656	5.097	7.173	3.417	3.841	6.873-7.213	---
8	4-F	1660	1586	2.439	3.187	3.813	5.465	5.032	7.217	3.677	3.873	6.654-7.921	---
9	3-OMe	1650	1576	2.474	3.210	3.564	5.652	5.176	7.017	3.431	3.805	6.241-7.134	3.456
10	4-OMe	1648	1579	2.379	3.117	3.693	5.632	5.071	7.581	3.767	3.708	6.235-7.334	3.245
11	4-Me	1652	1584	2.497	3.126	3.647	5.523	5.021	7.589	3.817	3.716	6.043-7.762	2.563
12	2-NO_2	1664	1596	2.507	3.193	3.667	5.895	5.173	7.593	3.831	3.875	6.823-7.892	---
13	3-NO_2	1666	1595	2.556	3.207	3.679	5.621	5.783	7.617	3.617	3.871	6.842-7.889	---
14	4-NO_2	1669	1597	2.571	3.431	3.701	5.639	5.810	7.621	3.704	3.883	6.345-7.238	---

Table 4. continued

No.	X	^{13}C NMR (δ, ppm)										
		C=O (keto)	CH_3	C=N	CH_2	Cα	Cβ	OCH_3	CO (ester)	CH_3 (ester)	Ar-C	X
1	H	168.63	23.65	157.37	71.36	105.73	147.71	52.71	172.71	54.70	124.45-146.88	---
2	4-Br	168.71	23.64	157.56	77.41	105.87	147.84	52.93	171.89	53.45	119.44-145.98	---
3	4-Cl	168.81	24.01	157.63	71.87	106.07	148.71	53.45	171.19	54.21	123.54-146.98	---
4	4-OEt	168.08	24.17	157.82	71.86	105.89	148.66	54.83	1714.3	54.66	118.89-145.93	65.44, 15.66
5	4-Et	168.06	24.32	157.48	71.24	106.74	148.07	54.86	171.08	54.41	124.36-145.28	33.24, 15.03
6	2-F	169.17	24.93	158.04	71.94	107.06	148.98	54.96	171.70	54.94	117.02-137-98	---
7	3-F	169.27	24.88	158.07	72.00	107.31	148.84	54.67	171.84	54.63	121.36-147.25	---
8	4-F	169.34	24.67	158.27	72.06	107.15	148.67	54.47	171.36	54.24	122.52-146.35	---
9	3-OMe	167.07	23.54	157.21	71.24	107.02	148.01	53.07	171.10	54.09	123.68-146.25	65.98
10	4-OMe	167.12	23.84	157.24	71.32	106.84	147.94	53.17	171.15	54.17	125.69-147.30	66.35
11	4-Me	167.94	23.97	157.57	71.77	107.09	148.14	52.93	171.24	54.96	124.05-147.36	25.31
12	2-NO_2	168.94	24.89	158.74	72.84	107.15	148.99	54.46	171.64	54.89	125.36-147.25	---
13	3-NO_2	168.97	24.94	158.88	72.86	107.41	148.97	54.88	171.97	54.90	124.05-143.68	---
14	4-NO_2	169.01	24.97	158.92	72.90	107.49	148.96	54.98	171.98	54.92	123.06-147.25	---

Table 5. Results of statistical analysis of infrared stretches ν(cm^{-1}), NMR chemical shifts (δ, ppm) of protons and carbons of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones with Hammett σ, σ^+, σ_I σ_R constants and F and R parameters.

Functionality	Constants	r	I	ρ	s	n	Correlated derivatives
IR data Vs Hammett substituent constants, F and R parameters							
νC=O	σ	0.932	1653.21	16.601	3.40	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.906	1654.96	8.824	5.64	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.907	1647.96	21.483	4.80	11	4-Br, 4-Cl, 4-OEt, 2-F, 3-F, 4-F, 3-OCH_3,4-OCH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.905	1659.69	17.651	5.58	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.907	1648.77	19.127	5.07	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-

							NO_2
	R	0.906	1659.77	15.109	5.09	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
νC=N	σ	0.907	1582.06	17.70	6.67	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.937	1583.74	7.079	9.10	11	H, 4-Br, 4-Cl, 4-Et, 3-F, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 2-NO_2, 4-NO_2
	σ_I	0.937	1579.78	14.059	9.00	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.997	1596.48	30.370	5.06	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.903	1580.23	11.904	9.13	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.907	1591.30	24.774	6.45	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	^{1}H NMR data Vs Hammett substituent constants, F and R parameters						
δCH_3keto	σ	0.907	2.437	0.128	0.04	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.906	2.438	0.087	0.05	12	H, 4-Cl, 4-Et, 2-F,3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.803	2.422	0.078	0.06	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.906	2.489	0.165	0.04	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.832	2.429	0.060	0.06	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.906	2.492	0.151	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δH_4	σ	0.848	3.178	0.105	0.07	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.844	3.181	0.079	0.44	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.904	3.140	0.148	0.07	13	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.830	3.216	0.098	0.08	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.804	3.139	0.139	0.07	13	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.827	3.251	0.079	0.08	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F,

							3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
$\delta H_{4'}$	σ	0.811	0.369	0.017	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.792	0.366	0.059	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.825	3.678	0.054	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.834	3.661	0.071	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.818	3.680	0.033	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.801	3.571	0.049	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δH_5	σ	0.920	5.630	0.088	0.12	10	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3
	σ^+	0.904	5.624	0.114	0.14	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.818	5.690	0.095	0.13	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.803	5.648	0.016	0.13	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.807	5.630	0.035	0.13	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.815	5.662	0.069	0.13	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCH_2	σ	0.974	5.144	0.490	0.17	13	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.963	5.163	0.342	0.20	12	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2
	σ_I	0.848	5.043	0.487	0.22	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.963	5.355	0.612	0.19	12	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 4-NO_2
	F	0.831	5.086	0.345	0.24	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.964	5.770	0.532	0.19	12	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 4-NO_2
δH_β	σ	0.841	7.487	0.080	0.21	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.805	7.493	0.250	0.21	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F,

							3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.804	7.513	0.037	0.21	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.849	70582	0.387	0.38	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.826	7.580	0.201	0.20	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.906	7.617	0.461	0.16	11	H, 4-Br, 4-Cl, 4-OEt, 4-Et,2-F, 3-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δOCH_3	σ	0.925	3.543	0.13	0.19	12	H, 4-Br, 4-Cl, 4-OEt, 2-F, 3-F, 4-F, 3-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.913	3.570	0.048	0.17	12	H, 4-Br, 4-Cl, 4-OEt, 2-F, 3-F, 4-F, 3-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.811	3.533	0.078	0.17	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.843	3.621	0.278	0.15	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.835	3.526	0.880	0.17	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.831	3.611	0.191	0.16	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δ$CH_{3\ ester}$	σ	0.949	3.811	0.075	0.05	12	H, 4-Br, 4-Cl, 2-F,3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3,2-NO_2,3-NO_2, 4-NO_2
	σ^+	0.963	3.809	0.078	0.04	12	H, 4-Br, 4-Cl, 2-F,3-F, 4-F,3-OCH_3,4-OCH_3,4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.905	3.780	0.115	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.816	3.838	0.036	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.904	3.786	0.106	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.827	3.836	0.053	0.05	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	^{13}C NMR data Vs Hammett substituent constants, F and R parameters						
δC=Oketo	σ	0.954	168.33.	1.664	0.65	11	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3
	σ^+	0.946	168.37	1.743	0.68	11	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3
	σ_I	0.963	167.81	1.890	0.60	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

	σ_R	0.823	168.65	1.674	0.75	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.963	167.80	1.769	0.59	12	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.830	168.71	0.805	0.73	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCH_3 keto	σ	0.957	24.17	0.840	0.46	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.944	24.22	0.527	0.57	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.967	23.76	1.467	0.42	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.813	24.39	0.387	0.56	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.964	23.75	1.408	0.41	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.824	24.43	0.478	0.55	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δC=N	σ	0.980	157.70	1.263	0.36	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.966	157.76	0.843	0.46	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.907	157.22	0.184	0.38	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.848	158.14	1.006	0.54	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.907	157.25	1.645	0.40	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.849	158.18	1.025	0.53	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCH_2	σ	0.835	72.08	1.491	1.52	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.838	72.09	1.320	1.50	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.840	71.39	1.496	1.49	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

	σ_R	0.826	72.67	1.581	1.57	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.832	71.58	1.875	1.54	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.823	72.67	1.336	1.58	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCα	σ	0.944	106.65	0.31	0.57	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.921	106.72	0.293	0.62	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.841	106.39	1.031	1.54	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.814	106.84	0.328	0.63	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.905	106.30	1.164	0.54	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.804	106.79	0.199	0.63	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δC_β	σ	0.959	148.34	0.745	0.40	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.955	148.36	0.810	0.41	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.970	147.91	0.148	0.31	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.808	148.49	0.154	0.50	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.907	148.93	1.257	0.33	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.817	148.53	0.294	0.49	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δOCH_3	σ	0.834	58.89	0.849	0.88	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.838	53.89	0.875	0.87	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.905	53.22	1.880	0.80	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

	σ_R	0.802	54.01	0.574	0.94	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.905	53.33	1.424	0.81	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.809	54.10	0.302	0.94	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCO ester	σ	0.938	170.23	41.847	3.96	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.802	175.39	20.291	5.23	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.901	170.54	17.158	4.13	13	4-Br,4-Cl,4-OEt,4-Et, 2-F,3-F,4-F,3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.840	174.19	63.011	3.93	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.914	173.37	32.582	4.21	13	4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.825	178.17	36.854	4.59	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCH_3 ester	σ	0.829	54.45	0.337	0.43	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.824	54.47	0.234	0.44	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.806	54.47	0.110	0.45	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.831	54.62	0.511	0.43	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.803	54.48	0.060	0.45	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.804	54.67	0.632	0.41	14	H, 4-Br, 4-Cl, 4-OEt, 4-Et, 2-F, 3-F, 4-F, 3-OCH_3, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2

*r = correlation co-efficient; ρ = slope; I = intercept; s = standard deviation; n = number of substituents

The νC=O stretching frequencies (cm^{-1}) with Hammett σ, σ^+, σ_R constants, F and R parameters gave satisfactory correlations. The Hammett σ_I constant produced satisfactory correlations individually excluding H, 4-Et and 4-CH_3 substituents (σ: r=0.932, σ^+: r=0.906, σ_I: r=0.907, σ_R: r=0.905, F: r=0.907, R: r=906). The results of statistical analyses were presented in Table 5. All correlations gave positive ρ value. This means that the normal substituent effects operate in all systems.

The correlation of νC=N stretching frequencies (cm^{-1}) with Hammett σ and σ_R constants was satisfactory. The Hammett σ^+, σ_I, constants, F and R parameters have shown satisfactory correlation excluding H, 4-OEt, 2-F, 3-OMe and 4-Me substituents (σ: r=0.907, σ^+: r=0.931, σ_I: r=0.937, σ_R:

r=0.997, F: r=0.903, R: r=0.907). If these substituents were included in the correlations, they will reduce the correlations considerably. All correlations gave positive ρ value. This means that the normal substituent effects operate in all systems.

To study the application of multi-regression analysis of these data with σ_I and σ_R constants or Swain-Lupton's [30] F and R parameters gave satisfactory correlations. The correlation equations for CO and CN are given in equations (2)-(5).

$$\nu C=O(cm^{-1})=1652.01\left(\pm1.519\right)+19.222\left(\pm2.994\right)\sigma_I+15.022\left(\pm2.855\right)\sigma_R \quad \left(R=0.993,\ n=14,\ P>95\%\right) \tag{2}$$

$$\nu C=O(cm^{-1})=1652.08\left(\pm1.281\right)+19.480\left(\pm2.414\right)F+15.512\left(\pm2.302\right)R \quad \left(R=0.995,\ n=14,\ P>95\%\right) \tag{3}$$

$$\nu C=N(cm^{-1})=1587.61\left(\pm2.612\right)+9.689\left(\pm4.258\right)\sigma_I+29.044\left(\pm4.909\right)\sigma_R \quad \left(R=0.989,\ n=14,\ P>95\%\right) \tag{4}$$

$$\nu C=N(cm^{-1})=1586.37\left(\pm3.102\right)+12.474\left(\pm5.844\right)\ F+25.032\left(\pm5.572\right)R \quad \left(R=0.982,\ n=14,\ P>95\%\right) \tag{5}$$

3.2 ^{1}H NMR Spectral Study

The ^{1}H NMR spectra of synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones have been recorded in deuteriochloroform solution employing tetramethylsilane (TMS) as internal standard. The signals of the pyrazoline ring protons have been assigned. They have been calculated as AB or AA' systems respectively. The chemical shifts (ppm) of H_4 are at higher fields than those of $H_{4'}$ and H_5 in this series of ^{1}*N*-acetyl pyrazolines. This is due to the deshielding of $H_{4'}$ and H_5 which are in different chemical as well as magnetic environment. These H_4 protons gave an AB pattern and the $H_{4'}$ proton doublets of doublet in most cases were well separated from the signals H_5 and the aromatic protons. The assigned chemical shifts (ppm) of $CH_{3(keto)}$, H_4, $H_{4'}$, H_5, CH_2, H_β, OCH_3 and $CH_{3(ester)}$ protons are presented in Table 4.

In nuclear magnetic resonance spectra, the ^{1}H or the ^{13}C chemical shifts (δ) depend on the electronic environment of the nuclei concerned. The assigned vinyl proton chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation in the form of

$$\text{Log}\,\delta=\ \text{Log}\,\delta_0+\rho\sigma \tag{6}$$

where δ_0 is the chemical shift of unsubstituted ketones.

The assigned chemical shifts (ppm) of $CH_{3(keto)}$, H_4, $H_{4'}$, H_5, CH_2, H_β, OCH_3 and $CH_{3(ester)}$ protons of synthesised 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)-ethanones have been correlated with various Hammett sigma constants, F and R parameters. The results of statistical analysis [12-14, 22, 24, 26, 28, 29] are presented in Table 5. The $CH_{3(keto)}$ proton chemical shifts (δ, ppm) with Hammett σ, σ_R constants and R parameters gave satisfactory correlations. The Hammett σ^+ constant was correlated satisfactorily with the methyl proton chemical shifts excluding 4-Br and 4-OEt substituents. The Hammett σ_I constant and F parameters showed poor correlations (σ: r=0.907, σ^+: r=0.906, σ_I: r=0.803, σ_R: r=0.906, F: r=0.832, R: r=906). All correlations give positive ρ values and it implies that there is a normal substituent effect operates in all systems. The failure in correlation was the incapability of effect of substituents on the chemical shift and associated with the conjugative structure as shown in Figure 2.

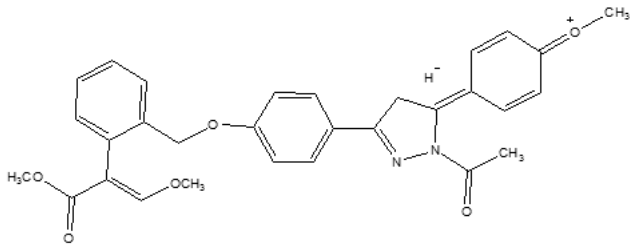


Figure 2. The resonance-conjugative structure.

The correlation of H_4 proton chemical shifts (δ, ppm) with Hammett substituent constants F and R parameters were shown in Table 5. The H_4 proton chemical shifts (δ, ppm) with Hammett σ_I constant and F parameters gave satisfactory correlation (σ: r=0.848, σ^+: r=0.844, σ_I: r=0.904, σ_R: r=0.830, F: r=0.904, R: r=827). The remaining Hammett substituent and R parameter gave poor correlation with the H_4 proton chemical shifts. The Hammett substituent constants, F and R parameters failed in correlation with $H_{4'}$ proton chemical shifts (δ, ppm) of synthesized 1-acetyl pyrazoline derivatives (σ: r=0.811, σ^+: r=0.792, σ_I: r=0.825, σ_R: r=0.834, F: r=0.818, R: r=0.801).

The H_5 proton chemical shifts (δ, ppm) with Hammett σ and σ^+ constants produced satisfactory correlation excluding 2-F and nitro substituents. The remaining Hammett substituent constants, F and R parameters were failed in correlation (σ: r=0.920, σ^+: r=0.904, σ_I: r=0.818, σ_R: r=0.803, F: r=0.807, R: r=0.815).

The assigned chemical shifts (δ, ppm) of methylene ($-CH_2-$) proton singlets of synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)-ethanones correlated satisfactorily with Hammett σ, σ^+, σ_R constant and R parameters excluding 2- and 3-NO_2 substituents(σ: r=0.974, σ^+: r=0.963, σ_I: r=0.848, σ_R: r=0.963, F: r=0.831, R: r=0.964). If these substituents will be included in the regression, they will reduce the correlations considerably. The remaining Hammett σ_I constant and F parameter failed in correlation.

The β-protons (H_β) singlet chemical shifts (δ, ppm) of synthesised 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)-ethanones are correlated satisfactorily with R parameter excluding 3-F, 4-F and 4-OMe substituents(σ: r=0.814, σ^+: r=0.805, σ_I: r=0.804, σ_R: r=0.849, F: r=0.826, R: r=0.906). The remaining Hammett substituent constants and F parameter failed in correlation.

The methoxy proton singlet chemical shifts (δ, ppm) of synthesised 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)-ethanones correlated satisfactorily with Hammett σ and σ^+ constants. The remaining Hammett σ_I and σ_R constants, F and R parameters failed in correlation (σ: r=0.925, σ^+: r=0.913, σ_I: r=0.811, σ_R: r=0.843, F: r=0.835, R: r=0.831). The methyl proton (CH_3, ester) singlet chemical shifts (δ, ppm) of synthesised 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)-ethanones correlated satisfactorily with Hammett σ, σ^+ constants gave satisfactory correlations excluding 4-OEt and 4-Et substituents. The Hammett σ_I constant and F parameters showed satisfactory correlations. The Hammett σ_R constant and R parameter were failed in correlation (σ: r=0.949, σ^+: r=0.963, σ_I: r=0.905, σ_R: r=0.816, F: r=0.904, R: r=0.827).

Some of the single regressions of the chemical shifts (ppm) of $CH_{3(keto)}$, H_4, $H_{4'}$, H_5, CH_2, H_β, OCH_3 and $CH_{3(ester)}$ protons of synthesised 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl)-ethanones gave poor correlations. All correlations gave positive ρ values. This means that the normal substituent effects operate in all regressions. The poor correlation was due to the absence or incapability of transmittance of effects of substituent to the proton chemical shifts (ppm) and it was associated with the resonance-conjugative structure as shown in Figure 2.

In view of the inability of some of the Hammett σ constants to produce satisfactory correlation individually for $CH_{3(keto)}$, H_4, $H_{4'}$, H_5, CH_2, OCH_3 and $CH_{3(ester)}$ proton chemical shifts, the authors think that it is worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's[30] F and R parameters. The correlation equations for $CH_{3(keto)}$, H_4, $H_{4'}$, H_5, CH_2, OCH_3 and $CH_{3(ester)}$ proton chemical shifts (δ, ppm) are given in equations (7-22).

$$\delta CH_{3(keto)}^{(ppm)} = 2.487(\pm 0.028) + 0.054(\pm 0.005)\sigma_I + 0.157(\pm 0.053)\sigma_R \quad (R = 0.974,\ n = 14, P > 95\%) \tag{7}$$

$$\delta CH_{3(keto)}^{(ppm)} = 2.466(\pm 0.026) + 0.056(\pm 0.002)\ F + 0.152(\pm 0.048)R \quad (R = 0.971,\ n = 14, P > 95\%) \tag{8}$$

$$\delta H_{4}^{(ppm)} = 3.161(\pm 0.044) + 0.136(\pm 0.087)\sigma_I + 0.079(\pm 0.008)\sigma_R \quad (R = 0.951,\ n = 14, P > 95\%) \tag{9}$$

$$\delta H_{4'}^{(ppm)} = 3.159(\pm 0.049) + 0.141(\pm 0.079)F + 0.082(\pm 0.005)R \quad (R = 0.952,\ n = 14, P > 95\%) \tag{10}$$

$$\delta H_{4'}^{(ppm)} = 3.651(\pm 0.031) + 0.068(\pm 0.062)\sigma_I + 0.063(\pm 0.005)\sigma_I \quad (R = 0.939,\ n = 14, P > 90\%) \tag{11}$$

$$\delta H_{4'}^{(ppm)} = 3.652(\pm 0.030) + 0.077(\pm 0.005)\ F + 0.532(\pm 0.003)R \quad (R = 0.938,\ n = 14, P > 90\%) \tag{12}$$

$$\delta H_{5}^{(ppm)} = 5.561(\pm 0.077) + 0.911(\pm 0.152)\sigma_I + 0.342(\pm 0.029)\sigma_R \quad (R = 0.918,\ n = 14, P > 90\%) \tag{13}$$

$$\delta H_{5}^{(ppm)} = 5.648(\pm 0.074) + 0.037(\pm 0.014)\ F + 0.774(\pm 0.012)\ R \quad (R = 0.917,\ n = 14, P > 95\%) \tag{14}$$

$$\delta CH_{2}^{(ppm)} = 5.193(\pm 0.110) + 0.403(\pm 0.119)\sigma_I + 0.559(\pm 0.190)\sigma_R \quad (R = 0.956,\ n = 14, P > 95\%) \tag{15}$$

$$\delta CH_{2}^{(ppm)} = 5.220(\pm 0.098) + 0.358(\pm 0.185)\ F + 0.580(\pm 0.172)R \quad (R = 0.975,\ n = 14, P > 95\%) \tag{16}$$

$$\delta H_{\beta}^{(ppm)} = 7.621(\pm 0.108) + 0.937(\pm 0.214)\sigma_I + 0.400(\pm 0.021)\sigma_R \quad (R = 0.951,\ n = 14, P > 95\%) \tag{17}$$

$$\delta H_{\beta}^{(ppm)} = 7.693(\pm 0.088) + 0.191(\pm 0.016)F + 0.453(\pm 0.159)R \quad (R = 0.968,\ n = 14, P > 95\%) \tag{18}$$

$$\delta OCH_{3}^{(ppm)} = 3.606(\pm 0.093) + 0.037(\pm 0.184)\sigma_I + 0.272(\pm 0.176)\sigma_R \quad (R = 0.943,\ n = 14, P > 90\%) \tag{19}$$

$$\delta OCH_{3}^{(ppm)} = 3.754(\pm 0.093) + 0.993(\pm 0.171)\ F + 0.193(\pm 0.016)R \quad (R = 0.935,\ n = 14, P > 90\%) \tag{20}$$

$$\delta CH_{3ester}^{(ppm)} = 3.786(\pm 0.038) + 0.112(\pm 0.060)\sigma_I + 0.021(\pm 0.005)\sigma_R \quad (R = 0.951,\ n = 14, P > 95\%) \tag{21}$$

$$\delta CH_{3ester}^{(ppm)} = 3.794(\pm 0.024) + 0.107(\pm 0.053)F + 0.055(\pm 0.010)R \quad (R = 0.956,\ n = 14, P > 95\%) \tag{22}$$

3.3 ^{13}C NMR Spectra

Organic chemists, spectral analysts, and physical organic chemists [12-14, 22, 24, 26, 28, 29] have made extensive study of ^{13}C NMR spectra for a large number of ketones, styrenes, keto-epoxides and pyrazolines. In their investigation, they assessed the linear correlation of the chemical shifts (ppm) of vinyl, C=N and carbonyl carbons with Hammett σ constants, F and R parameters. In the present study, the chemical shifts (δ,ppm) observed for the C=O, $CH_{3(keto)}$, C=N, CH_2, C_α, C_β, OCH_3, $C{=}O_{(ester)}$, and $CH_{3(ester)}$ carbons of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones are presented in Table 4. Attempts have been made to correlate the above assigned carbon chemical shifts (δ, ppm) with Hammett substituent constants, field and resonance parameters with the help of single and multi-regression analyses to study the reactivity through the effect of substituents.

The chemical shifts (δ, ppm) observed for the C=O, $CH_{3(keto)}$, C=N, C_4, C_5, CH_2, C_α, C_β, OCH_3, $C{=}O_{(ester)}$, and $CH_{3(ester)}$ carbons of 3-(4-β-methoxy acrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones have been correlated with Hammett substituent constants and the results of statistical analysis are presented in Table 5. The C=O chemical shifts (δ, ppm) were satisfactorily correlated with Hammett σ, σ^+, σ_I constants and F parameters excluding 3-OMe, 4-OMe and 3-NO_2 substituents. The remaining Hammett σ_R constant and R parameters failed in correlation (σ: r=0.954, σ^+: r=0.946, σ_I: r=0.963, σ_R: r=0.823, F: r=0.963, R: r=0.830). This is due to the reasons stated earlier and it is associated with the resonance-conjugated structure as shown in Figure 2.

The chemical shifts (δ,ppm) observed for the $CH_{3(keto)}$ carbons satisfactorily correlated with σ, σ^+, σ_I constants and F parameters(σ: r=0.957, σ^+: r=0.944, σ_I: r=0.967, σ_R: r=0.813, F: r=0.964, R: r=0.824). The remaining Hammett σ_R constant and R parameter failed in correlation.

The assigned C=N carbon chemical shifts (δ, ppm) have shown satisfactory correlation with σ, σ^+, σ_I constants and F parameters. The Hammett σ_R constants and R parameters were failed in correlation (σ: r=0.980, σ^+: r=0.966, σ_I: r=0.907, σ_R: r=0.818, F: r=0.907, R: r=0.849).

The chemical shifts (δ, ppm) observed for the CH_2 carbon of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones have been poorly correlated with Hammett substituent constants, F and R parameters(σ: r=0.835, σ^+: r=0.838, σ_I: r=0.840, σ_R: r=0.826, F: r=0.832, R: r=0.823).

The assigned α carbon chemical shifts (δ, ppm) of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones correlated with Hammett σ, σ^+ and F parameters satisfactorily (σ: r=0.944, σ^+: r=0.921, σ_I: r=0.841, σ_R: r=0.814, F: r=0.905, R: r=0.804). The Hammett σ_I, σ_R constants and R parameter were failed in correlation. The correlation of assigned β carbon chemical shifts (δ, ppm) of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4, 5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones with Hammett σ, σ^+, σ_I constants and F parameters found to be satisfactory. The Hammett σ_R constant and R parameters failed in correlation (σ: r=0.989, σ^+: r=0.955, σ_I: r=0.970, σ_R: r=0.808, F: r=0.907, R: r=0.817). The equal degree of transmittance of the effect of substituents was observed in Cα and Cβ carbons.

The OCH_3 carbon chemical shifts (δ, ppm) of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones gave satisfactory correlations with Hammett σ_I constant and F parameter (σ: r=0.834, σ^+: r=0.838, σ_I: r=0.905, σ_R: r=0.802, F: r=0.905, R: r=0.809). The remaining Hammett substituent constants and R parameters were failed in correlation.

The correlation of CO(ester) carbon chemical shifts (δ, ppm) of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones with Hammett σ, σ_I constants and F parameters are satisfactory excluding H substituent(σ: r=0.938, σ^+: r=0.802, σ_I: r=0.901, σ_R: r=0.840, F: r=0.914, R: r=0.825). The Hammett σ^+, σ_R constants and R parameters failed in correlation.

The assigned $CH_{3(ester)}$ carbon chemical shifts (δ, ppm) of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones have been satisfactorily correlated with Hammett σ, σ^+ and σ_R substituent constants and R parameter. The inductive and field effects of the substituents fail in predicting the regression coefficients (σ: r=0.903, σ^+: r=0.904, σ_I: r=0.822, σ_R: r=0.905, F: r=0.811, R: r=0.906).

Some of the single correlations of the chemical shifts (δ,ppm) C=O, $CH_{3(keto)}$, C=N, C_4, C_5, CH_2, C_α, C_β, OCH_3, $C{=}O_{(ester)}$, and $CH_{3(ester)}$ carbons of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^{1}*H*-pyrazole-1-yl) ethanones were failed with Hammett substituent constants, F and R

parameters. The failure in the correlation was due to the reason stated earlier and it is associated with the resonance - conjugative structure as shown in Figure 2. All correlations gave positive ρ values. This means that the normal substituent effect operates in all systems.

In view of the inability of some of the σ constants to produce individually satisfactory correlation for C=O, $CH_{3(keto)}$, C=N, CH_2, C_α, C_β, OCH_3, $C=O_{(ester)}$, and $CH_{3(ester)}$ carbons, the authors think that, it is worthwhile to seek multiple correlation involving either σ_I, σ_R or F and R parameters[30]. The formulated multi-correlation equations are given in (23-40).

$$\delta CO_{keto}^{(ppm)} = 167.92(\pm 0.349) + 1.815(\pm 0.689)\sigma_I + 0.425(\pm 0.065)\sigma_R \quad (R = 0.964,\ n = 14, P > 95\%) \tag{23}$$

$$\delta CO_{keto}^{(ppm)} = 168.00(\pm 0.317) + 1.788(\pm 0.558)F + 1.842(\pm 0.554)R \quad (R = 0.971,\ n = 14, P > 95\%) \tag{24}$$

$$\delta CH_{3keto}^{(ppm)} = 23.81(\pm 0.247) + 1.463(\pm 0.487)\sigma_I + 0.186(\pm 0.046)\sigma_R \quad (R = 0.968,\ n = 14, P > 95\%) \tag{25}$$

$$\delta CH_{3keto}^{(ppm)} = 23.87(\pm 0.224) + 1.419(\pm 0.417)\ F + 1.505(\pm 0.398)R \quad (R = 0.973,\ n = 14, P > 95\%) \tag{26}$$

$$\delta CN^{(ppm)} = 157.45(\pm 0.185) + 1.725(\pm 0.366)\sigma_I + 0.825(\pm 0.349)\sigma_R \quad (R = 0.986,\ n = 14, P > 95\%) \tag{27}$$

$$\delta CN^{(ppm)} = 157.52(\pm 0.146) + 1.670(\pm 0.278)\ F + 1.084(\pm 0.0.024)R \quad (R = 0.990,\ n = 14, P > 95\%) \tag{28}$$

$$\delta CH_2^{(ppm)} = 71.73(\pm 0.864) + 2.341(\pm 1.703)\sigma_I + 1.261(\pm 0.623)\sigma \quad (R = 0.945,\ n = 14, P > 90\%) \tag{29}$$

$$\delta CH_2^{(ppm)} = 71.92(\pm 0.855) + 1.906(\pm 1.611)\ F + 1.373(\pm 0.152)R \quad (R = 0.940,\ n = 14, P > 90\%) \tag{30}$$

$$\delta C_\alpha^{(ppm)} = 106.44(\pm 0.344) + 0.989(\pm 0.063)\sigma_I + 1.932(\pm 0.644)\sigma_R \quad (R = 0.942,\ n = 14, P > 90\%) \tag{31}$$

$$\delta C_\alpha^{(ppm)} = 106.33(\pm 0.032) + 1.167(\pm 0.562)F + 0.131(\pm 0.050)R \quad (R = 0.951,\ n = 14, P > 95\%) \tag{32}$$

$$\delta C_\beta^{(ppm)} = 147.89(\pm 0.189) + 1.496(\pm 0.372)\sigma_I + 0.514(\pm 0.301)\sigma_R \quad (R = 0.977,\ n = 14, P > 95\%) \tag{33}$$

$$\delta C_\beta^{(ppm)} = 148.01(\pm 1.333) + 0.321(\pm 0.033)F + 3.352(\pm 0.033)R \quad (R = 0.976,\ n = 14, P > 95\%) \tag{34}$$

$$\delta OCH_3^{(ppm)} = 53.23(\pm 0.447) + 1.939(\pm 0.939)\sigma_I + 1.329(\pm 0.813)\sigma_R \quad (R = 0.952,\ n = 14, P > 95\%) \tag{35}$$

$$\delta OCH_3^{(ppm)} = 53.42(\pm 0.462) + 1.728(\pm 0.782)F + 0.336(\pm 0.081)R \quad (R = 0.951,\ n = 14, P > 95\%) \tag{36}$$

$$\delta CO_{ester}^{(ppm)} = 178.44\left(\pm 23.211\right) + 78.135\left(\pm 8.257\right)\sigma_I + 61.935\left(\pm 4.373\right)\sigma_R \quad (37)$$
$$\left(R = 0.940,\ n = 14, P > 90\%\right)$$

$$\delta CO_{3ester}^{(ppm)} = 178.24\left(\pm 23.417\right) + 22.781\left(\pm 4.417\right)F + 37.073\left(\pm 4.271\right)R \quad (38)$$
$$\left(R = 0.929,\ n = 14, P > 90\%\right)$$

$$\delta OCH_3 ester^{(ppm)} = 54.60\left(\pm 0.527\right) + 0.325\left(\pm 0.052\right)\sigma_I + 0.952\left(\pm 0.0524\right)\sigma_R \quad (39)$$
$$\left(R = 0.930,\ n = 14, P > 90\%\right)$$

$$\delta OCH_3 ester^{(ppm)} = 54.64\left(\pm 0.238\right) + 0.075\left(\pm 0.004\right)\ F + 0.638\left(\pm 0.002\right)R \quad (40)$$
$$\left(R = 0.941,\ n = 14, P > 90\%\right)$$

4 Conclusions

Totally fourteen ^1N-acetyl pyrazolines, 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl) ethanones have been synthesised by microwave assisted KF/Al_2O_3 catalyzed solvent-free condensation of 3-(4-hydroxyphenyl)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl)-ethanones and *E*-methyl-2-[2-(bromo methyl)-phenyl]-3-methoxyacrylate. The yield of the synthesized 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl) ethanones is more than 90%. The correlation study of infrared spectral νC=N and C=O (cm^{-1}) frequencies, NMR chemical shifts (δ, ppm) of $CH_{3(keto)}$, H_4, $H_{4'}$, H_5, CH_2, H_β, OCH_3, $CH_{3(ester)}$protons, C=O, $CH_{3(keto)}$, C=N, CH_2, C_α, C_β, OCH_3, $C{=}O_{(ester)}$, and $CH_{3(ester)}$ carbons of 3-(4-β-methoxyacrylate)-5-(substituted phenyl)-(4,5-dihydro-^1H-pyrazole-1-yl) ethanones have been assigned and correlated with Hammett substituent constants and Swain-Lupton's parameters using single and multi-regression analysis. The results of statistical analyses show satisfactory correlation co-efficient in both single and multi-regressions.

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