Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Ni-NiO Heterojunction: A Versatile Nanocatalyst for the Regioselective Halogenation and Oxidative Esterification of Aromatics

Nivedita Bhardwaj[a], Ajit Kumar Singh[b], Nancy Tripathi[a], Bharat Goel[a], Arindam Indra*[b] and Shreyans K. Jain*[a]

[a]*Department of Pharmaceutical Engineering & Technology, Indian Institute of Technology (Banaras Hindu University) Varanasi-221005, India. Email:* sjain.phe@iitbhu.ac.in (SKJ)

[b]*Department of Chemistry, Indian Institute of Technology (Banaras Hindu University) Varanasi-221005, India. Email*: arindam.chy@iitbhu.ac.in (AI)

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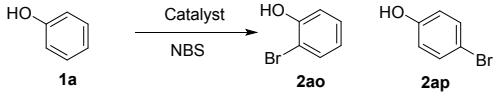
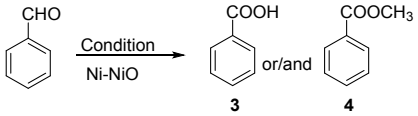
Table S1.1 Optimization of the nuclear bromination reaction.



Entry	Catalyst	Reaction conditions	% Conversion	Yield (%)[a]	
				ortho	*para*
1	NiO (commercial)	H_2O, 100 ^oC, 8 h	20	8	12
2	NiO (commercial)	MeOH:H_2O (8:2), 60 ^oC, 4 h	40	19	21
3	Ni-NiO (wt 25%)	H_2O, rt, 4 h	68	8	60
4	Ni-NiO (wt 25%)	MeOH:H_2O (8:2), rt, 1 h	100	10	90
5	Ni-NiO (wt 5%)	MeOH:H_2O (8:2), rt, 1 h	100	15	85
6	Ni-NiO (wt 10%)	MeOH:H_2O (8:2), rt, 1 h	100	8	92
7	Ni-NiO (wt 15%)	MeOH:H_2O (8:2), rt, 1 h	100	8	92

[a]Analyzed by GCMS.

Table S1.2 Oxidation of aromatic benzaldehydes with Ni-NiO nanoparticles.[a]



Entry	Solvent	Temperature (^oC)	Amount of NBS (eqv)	Catalyst	Time (h)	Major Product	Yield of major product
1.	H_2O	100	0	Ni-NiO	2	Benzoic acid	80[c]
2.	H_2O	100	0	No catalyst	16	Benzoic acid	40[c]
3.	MeOH: H_2O[b]	50	0	Ni-NiO	2	**4**	85
4	MeOH: H_2O[b]	50	0	No catalyst	16	Benzoic acid	55[c]
5	MeOH: H_2O[b]	35	0.25 eqv	Ni-NiO	1	**4**	95
6	MeOH: H_2O[b]	Rt	0.25 eqv	Ni-NiO	1	**4**	75
7	MeOH	80	0.25 eqv	No catalyst	12	**4**	50[c]
8	MeOH	80	1 eqv	No catalyst	12	Benzoic acid	50[c]

[a]Reaction conditions: aromatic carbonyl compound (**1**, 1 mmol), NBS (1 eqv.), catalyst Ni-NiO NPs (10 wt%) and solvent. [b]MeOH:H_2O in 8:2 ratio, [r]eaction didn't complete in given condition and starting material remain unreacted.

Energy dispersive X-ray spectroscopic study of synthesized Ni-NiO nanoparticle:

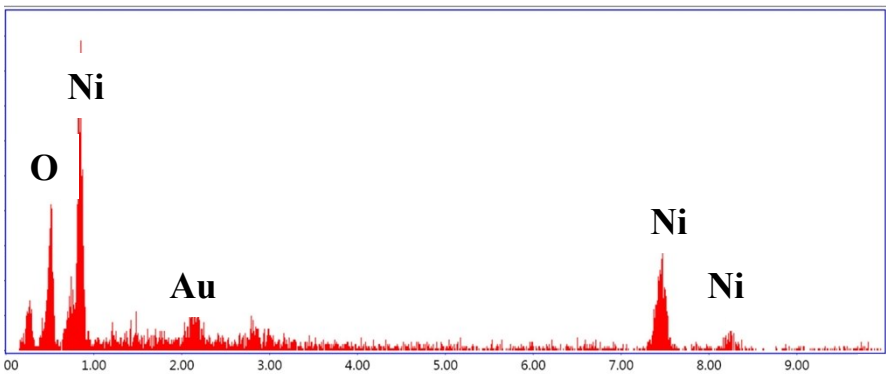
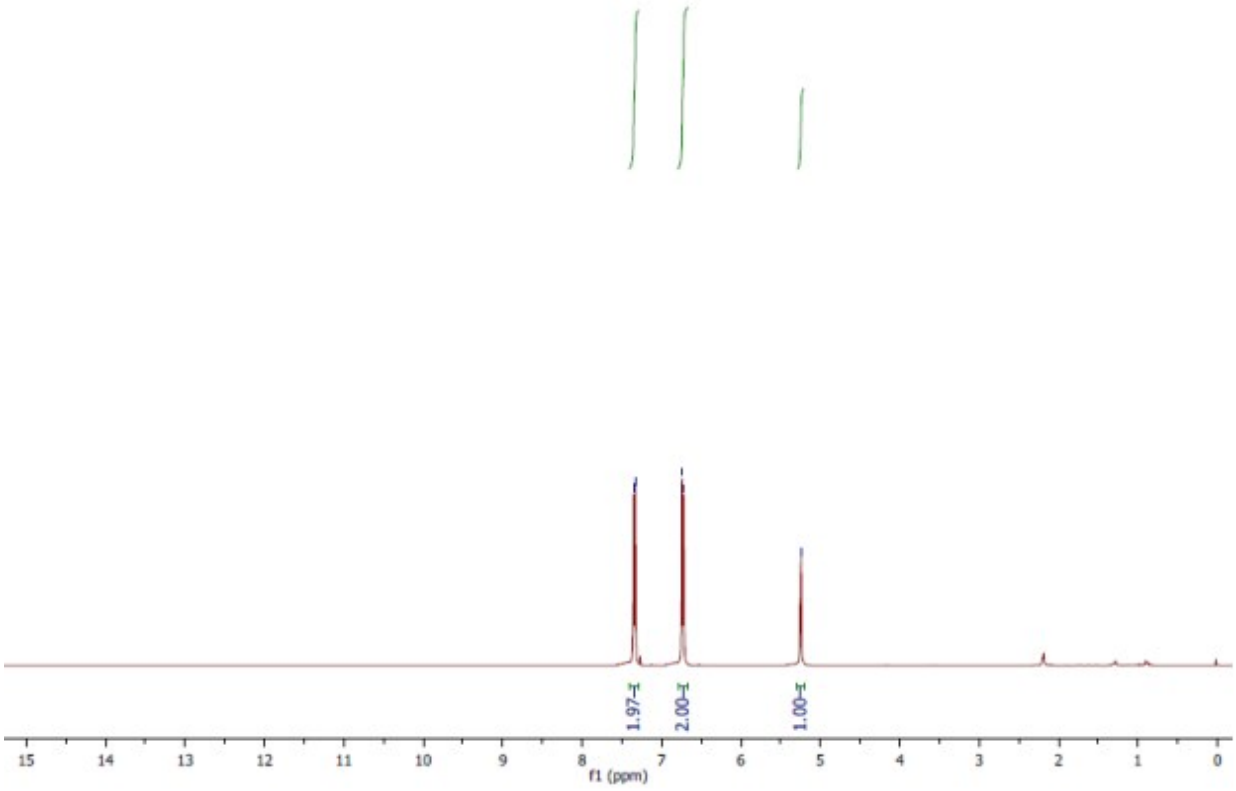


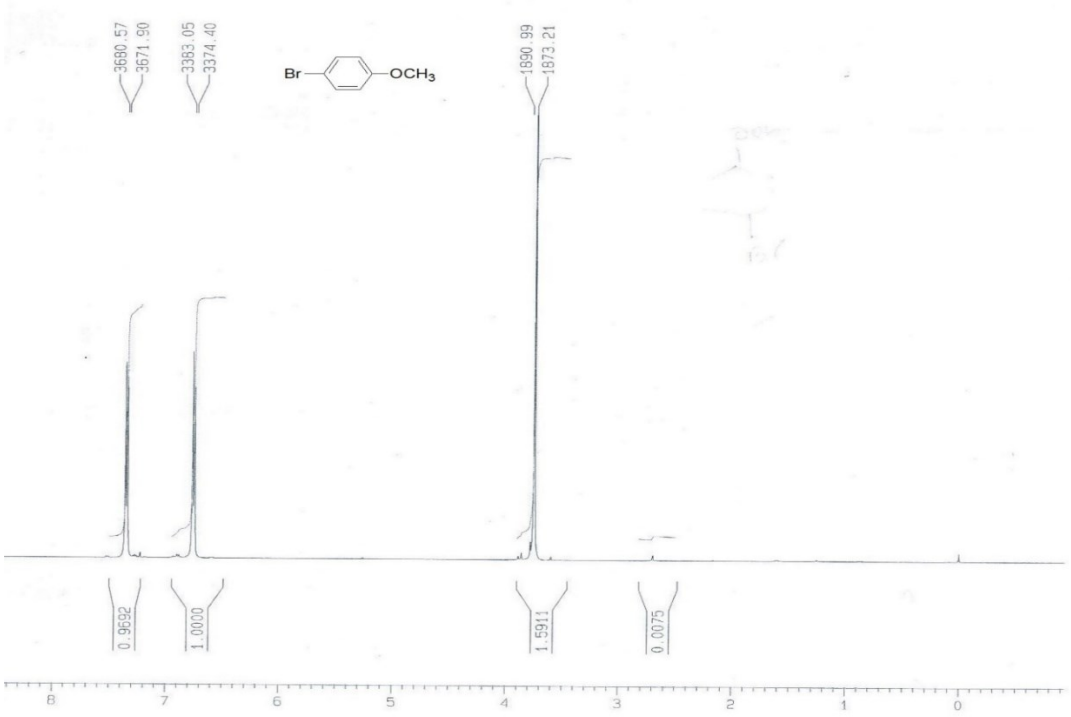
Figure S-2. EDX spectra of Ni-NiO nanoparticles.

S-3. SELECTED ^{1}H NMR SPECTRA

S-3.1: ^{1} H NMR spectrum of 4-bromo-phenol (**2a**) (CD_3OD, 500 MH_Z)

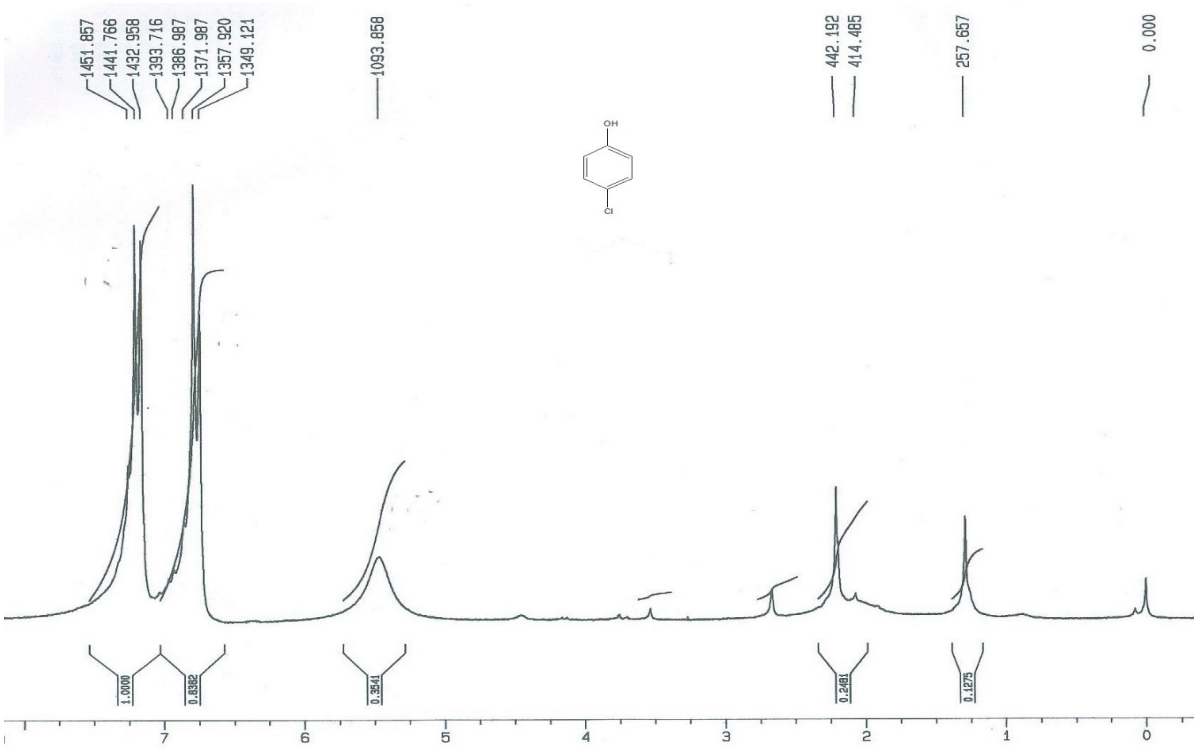


S-3.2: ^{1} H NMR spectrum of p-bromo anisol (CD_3OD, 500 MH_Z)

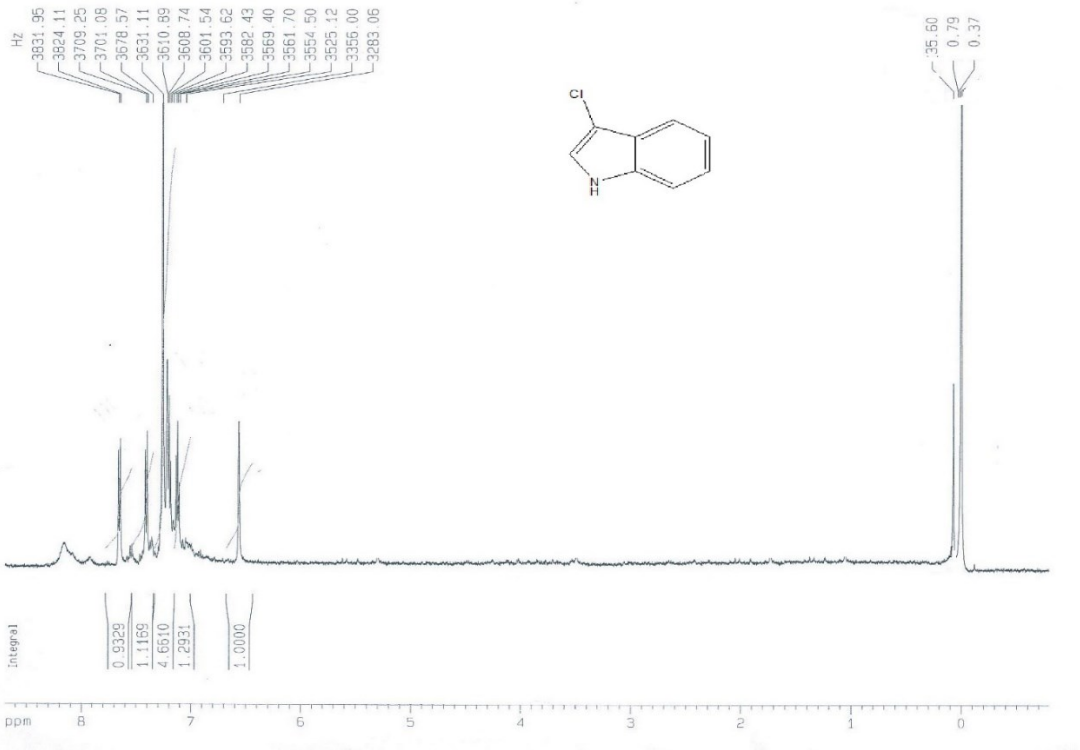


S-3.3: [1] H NMR spectrum of p-chloroanisol (CD_3OD, 500 MH_Z)

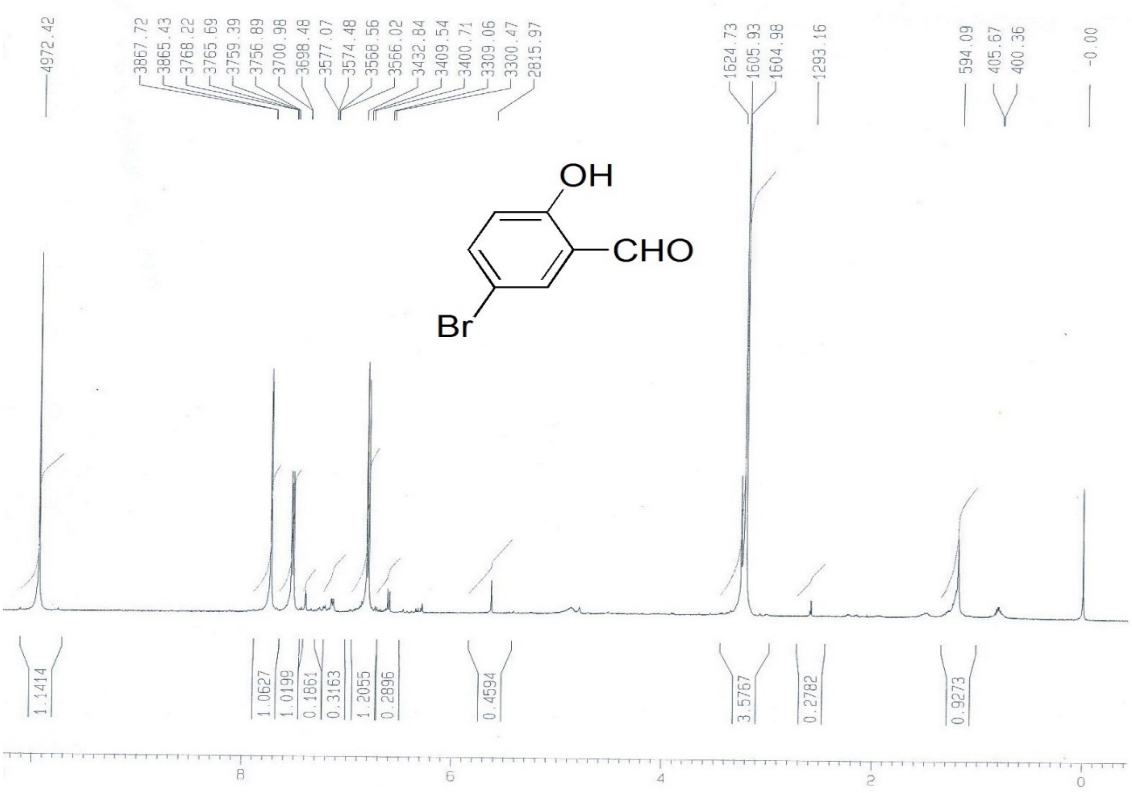
S-3.4: [1] H NMR spectrum of p-chlorophenol (CD_3OD, 500 MH_Z)



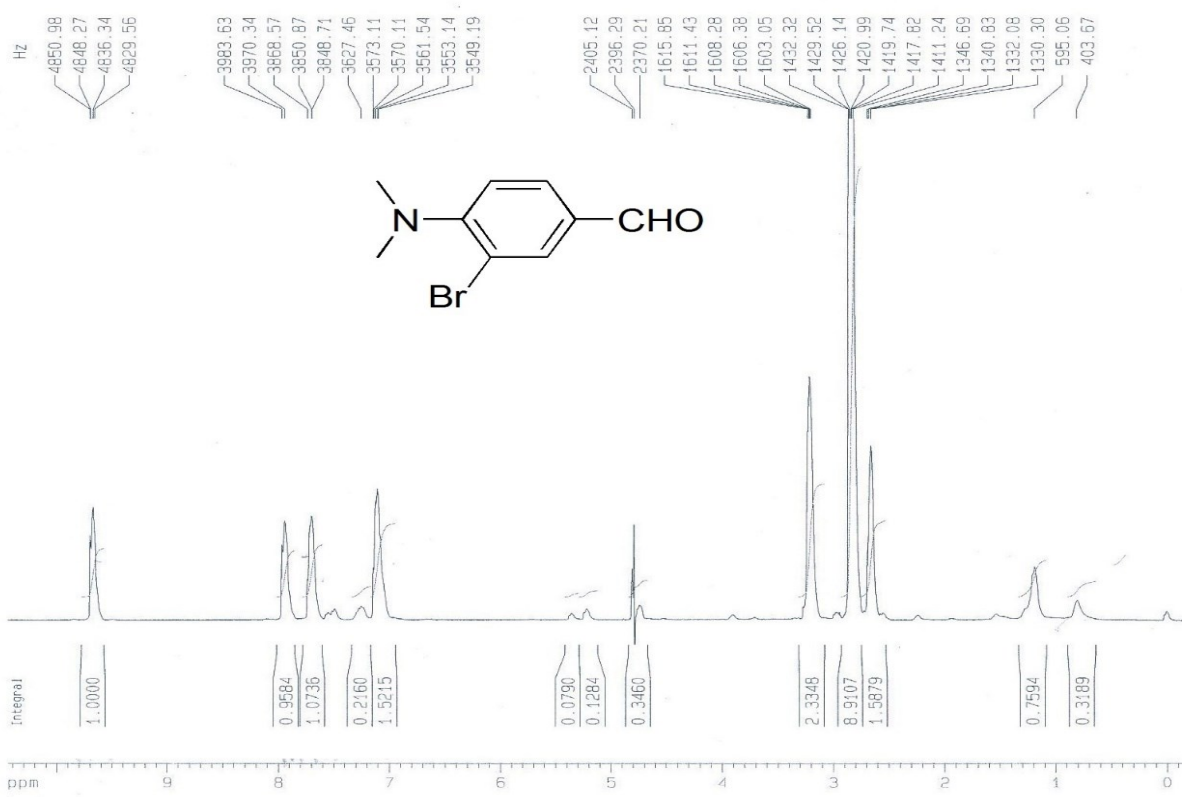
S-3.5: [1] H NMR spectrum of 3-chloro indol (CD_3OD, 500 MH_Z)



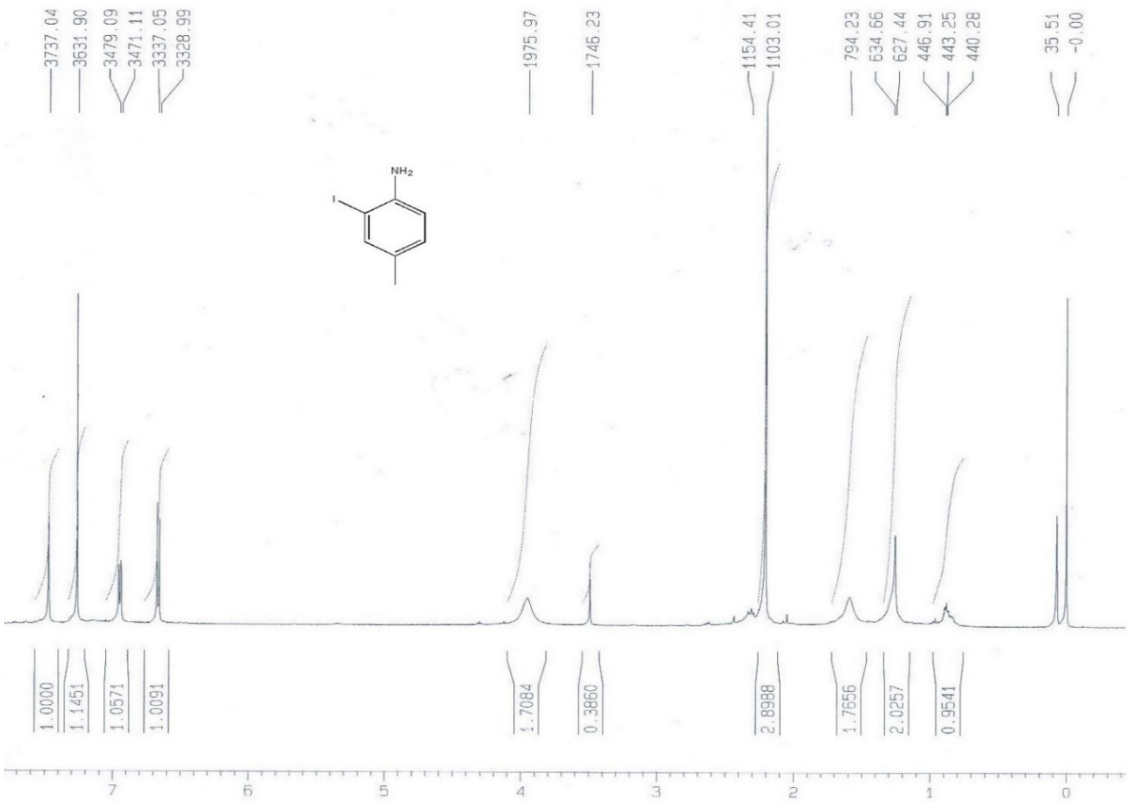
S-3.6: [1] H NMR spectrum of 5-bromo-2-hydroxybenzaldehyde (CD_3OD, 500 MH_Z)



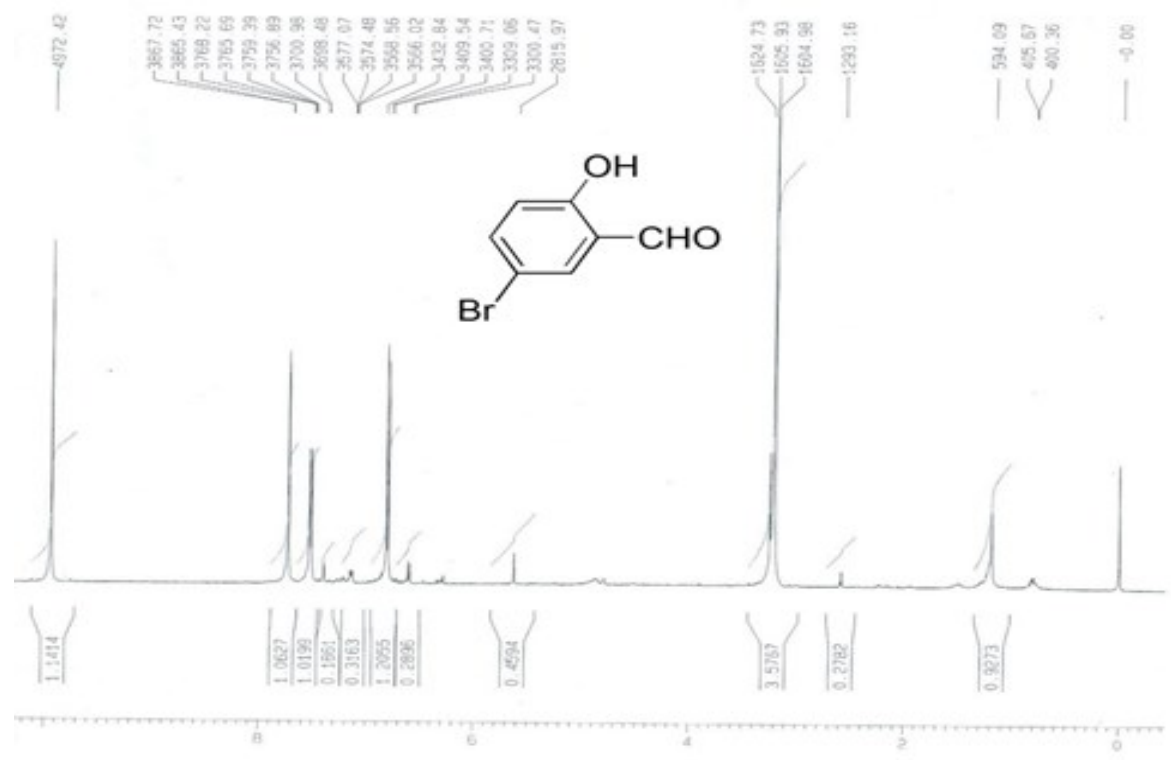
S-3.7: [1] H NMR spectrum of 3-bromo-4-(dimethylamino) benzaldehyde (CD_3OD, 500 MH_Z)



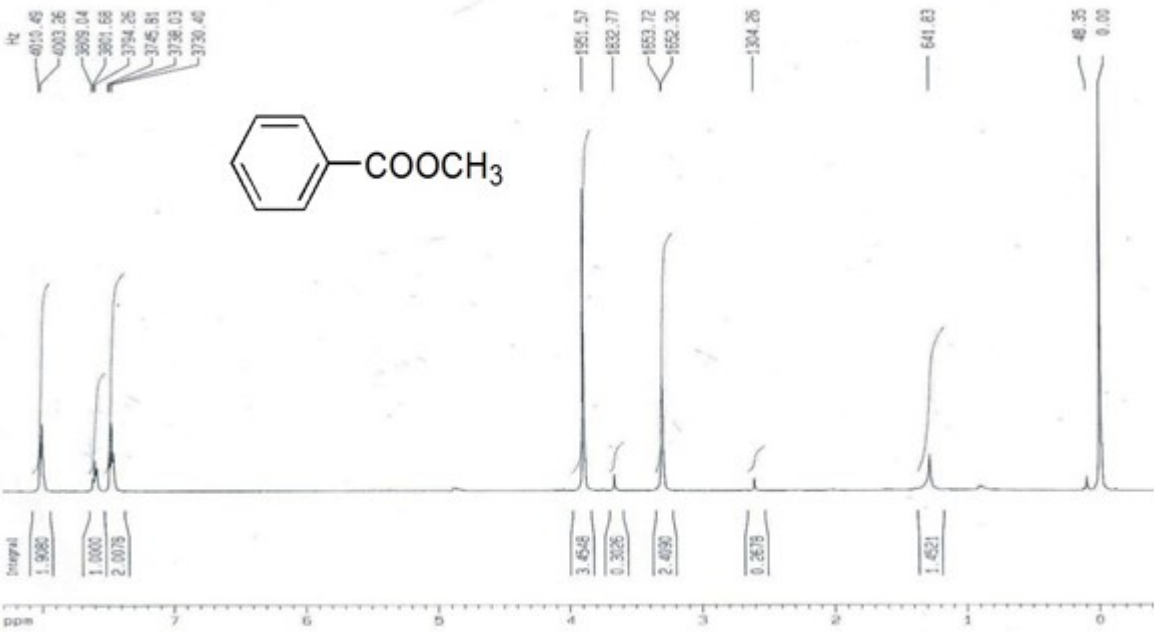
S-3.8: [1] H NMR spectrum of 2-iodo-4-methylbenzenamine (CD_3OD, 500 MH_Z)



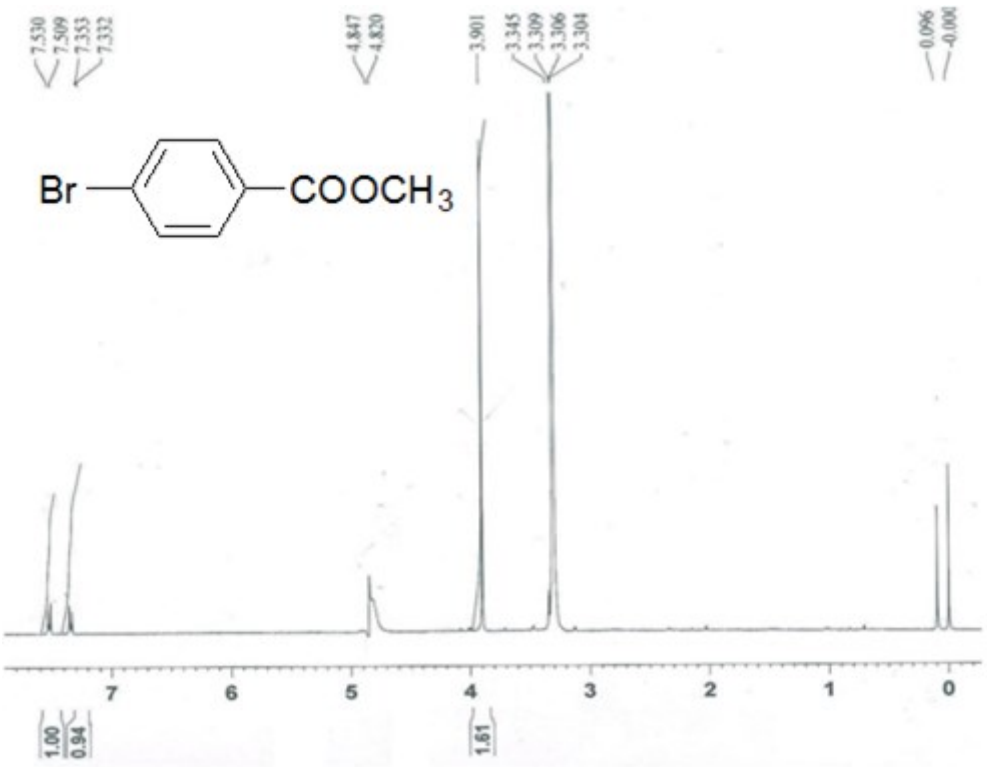
S-3.9: 5-Bromo-2-hydroxybenzaldehyde (**2b**) (CD_3OD, 500 MH_Z)



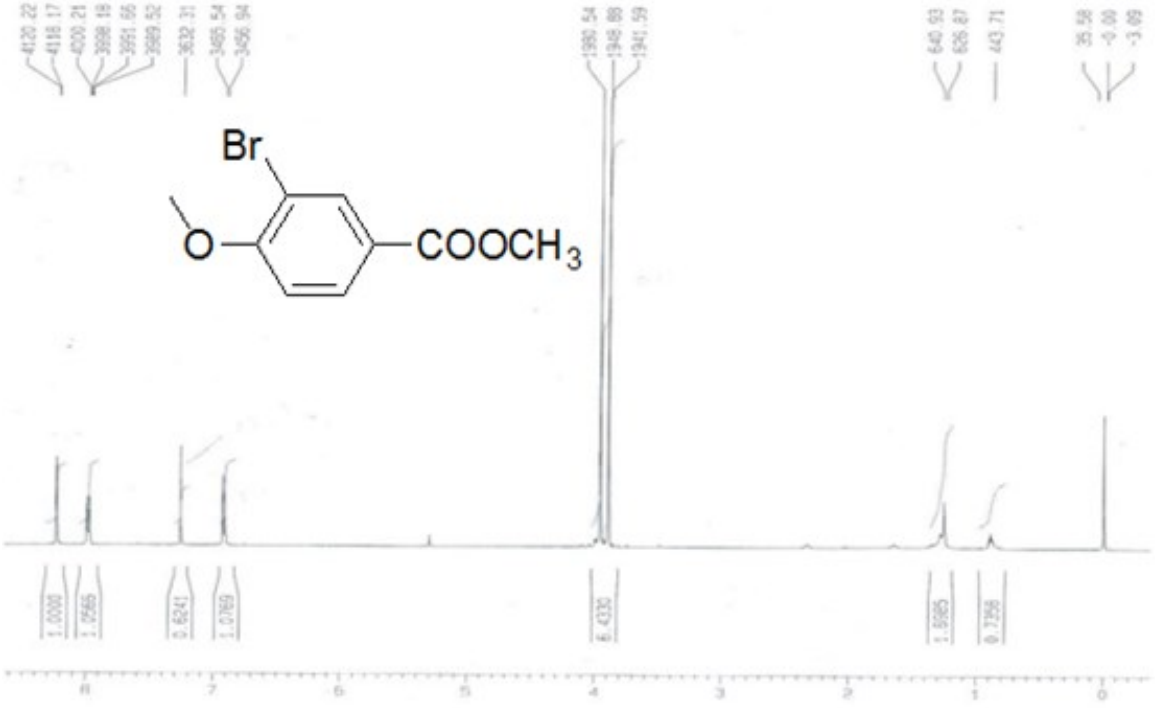
S-3.10: ^{1}H NMR spectrum of Methyl benzoate (**4**) (CD_3OD, 500 MH_Z)



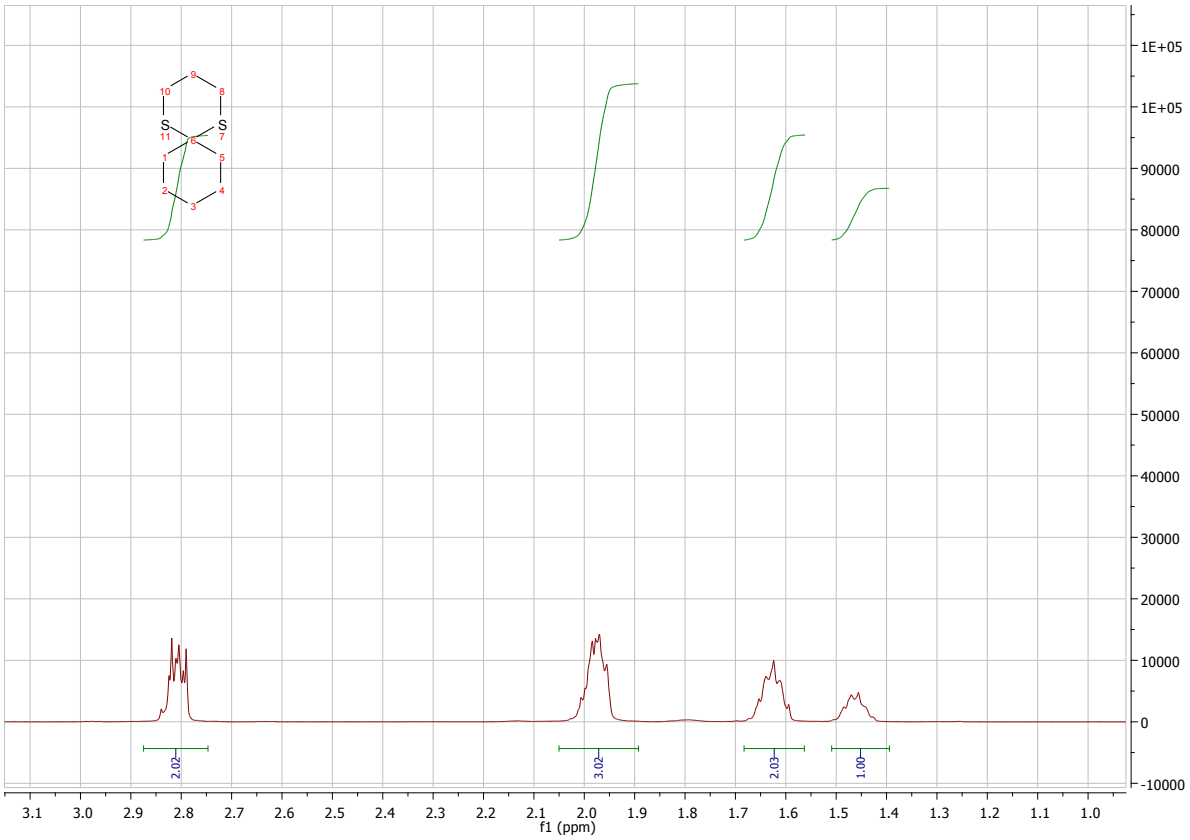
S-3.11: [1] H NMR spectrum of 4-Bromo methylbenzoate (**7e**) (CD_3OD, MeOD)



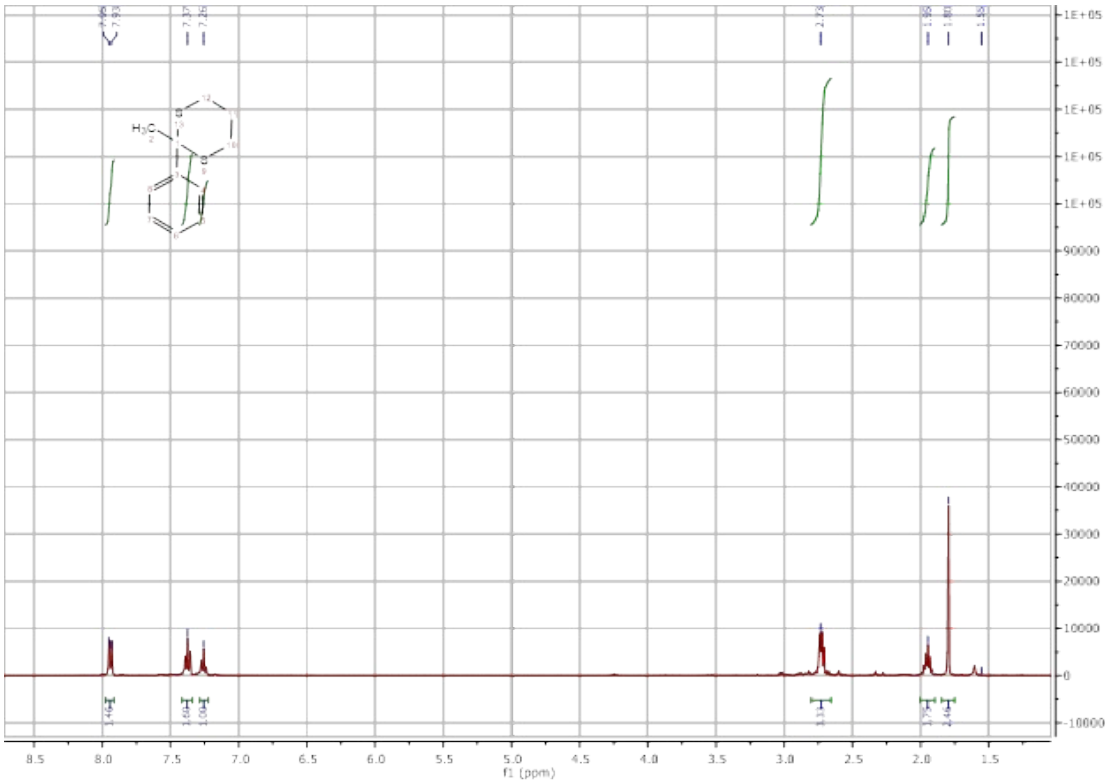
S-3.12: [1] H NMR spectrum of Methyl 3-bromo-4-methoxybenzoate (7f) ($CDCl_3$, 500 MH_z)



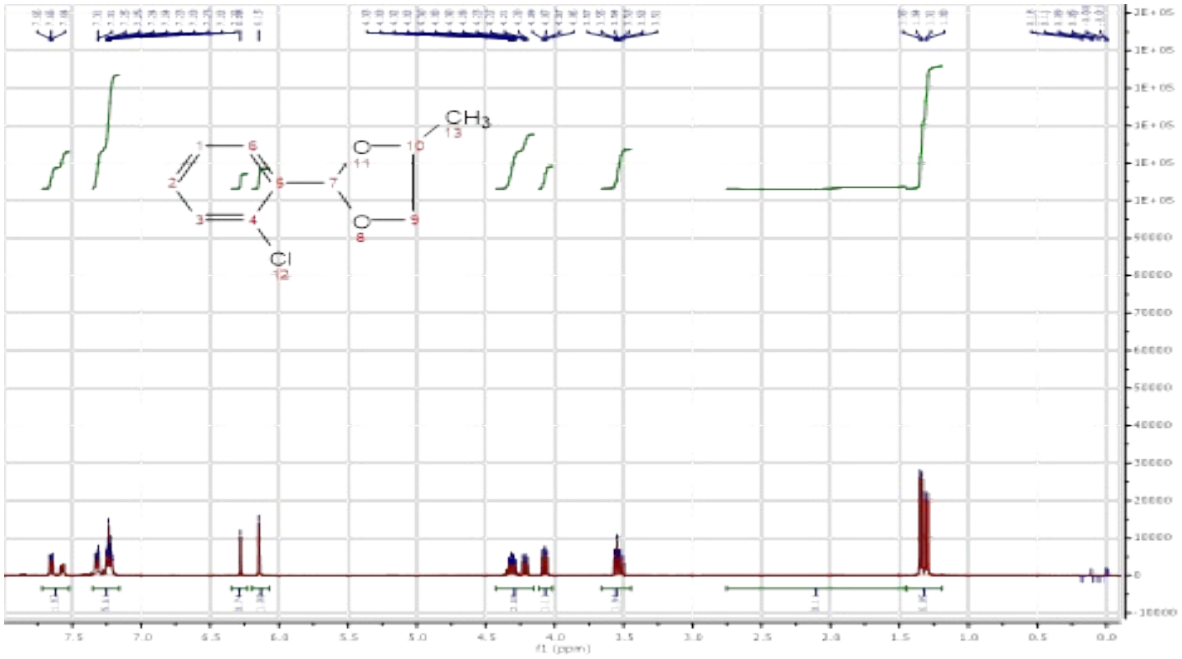
S-3.13: ^{1}H NMR spectrum of 1,5-dithiaspiro[5.5]undecane **(9a)** (CD_3OD, 500 MH_Z)



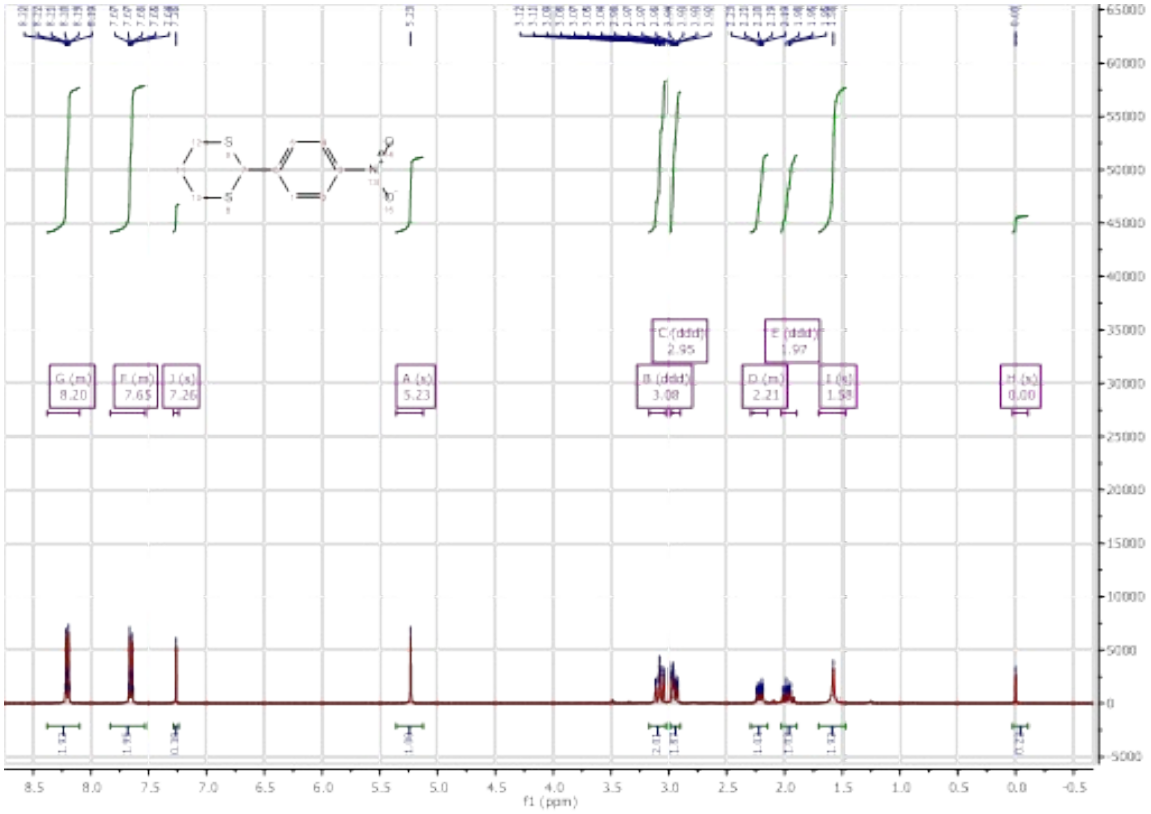
S-3.14: ^{1}H NMR spectrum of 2-methyl-2-phenyl-1,3-dithiane (**9e**)



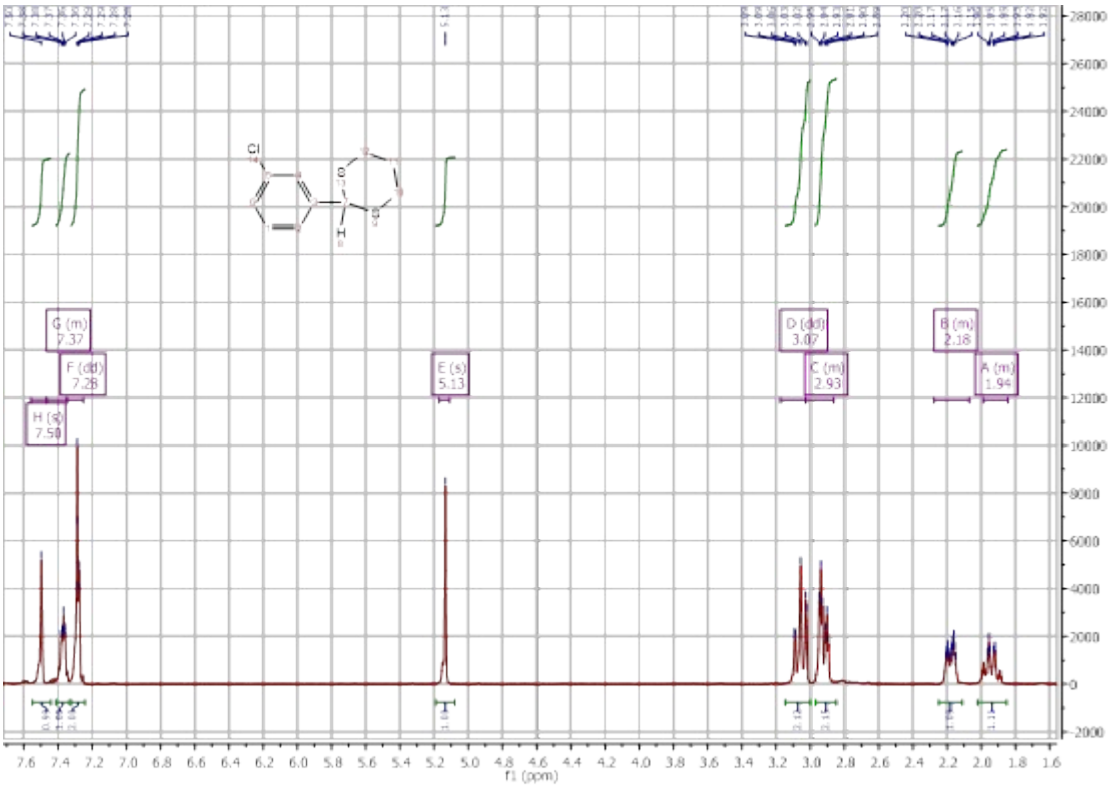
S-3.15: ^{1}H NMR spectrum of 2-(2-Chlorophenyl)-4-methyl-1,3-dioxolane (**10b**) ($CDCl_3$, 500 MH_Z, mix of two stereoisomer)



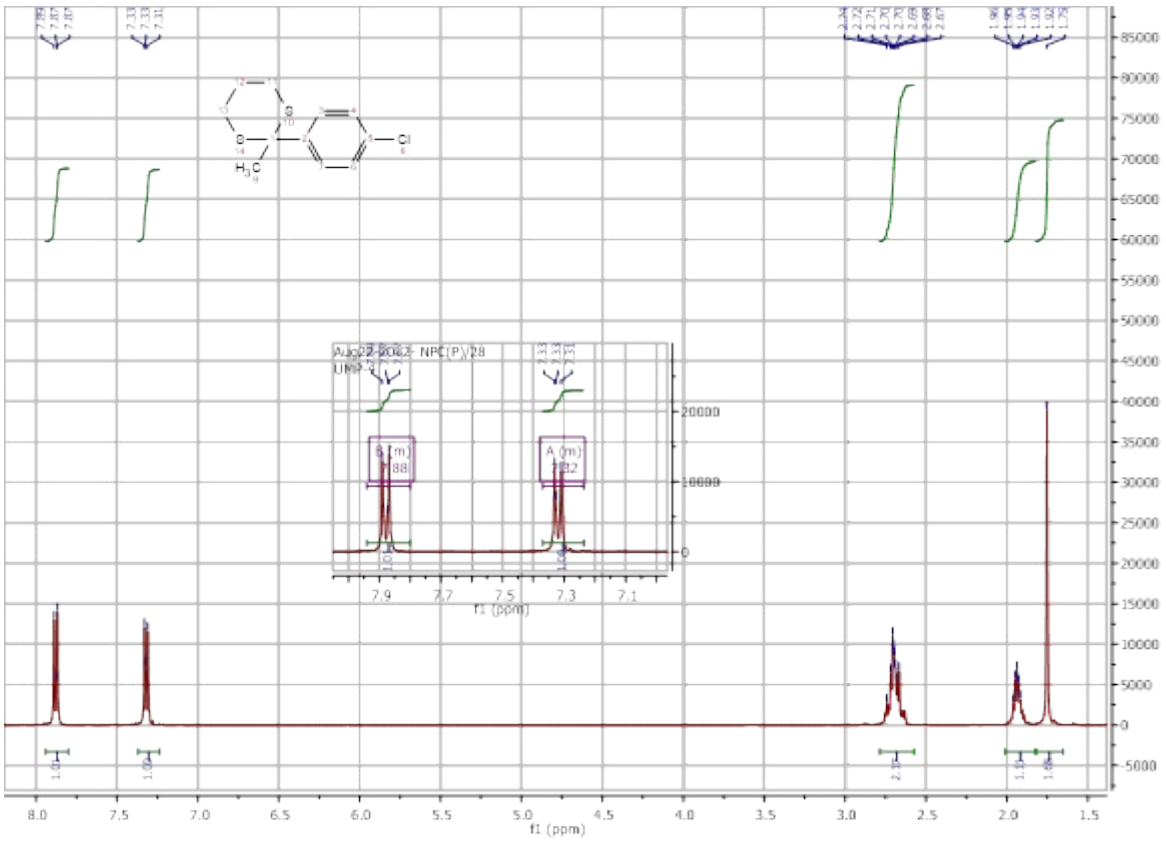
S-3.16: ^{1}H NMR spectrum of 2-(4-nitrophenyl)-1,3-dithiane (9d) ($CDCl_3$, 500 MH_Z)



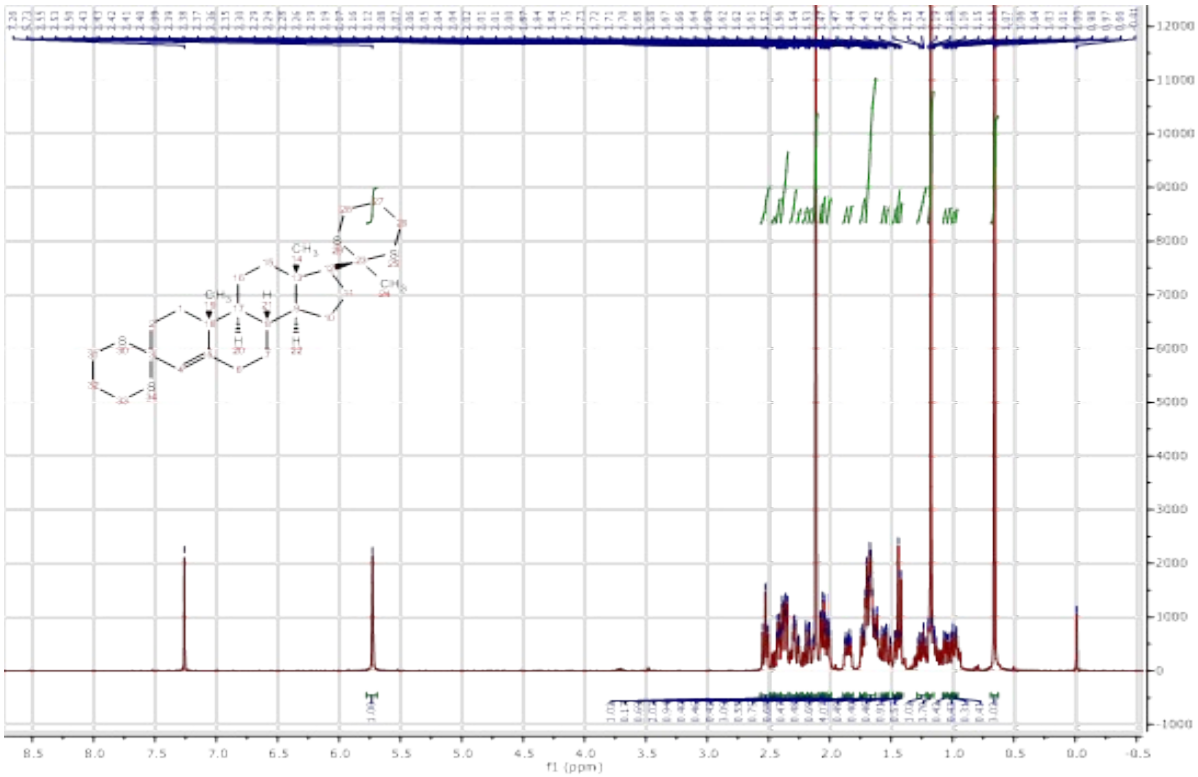
S-3.17: ^{1}H NMR spectrum of 2-(3-chlorophenyl)-1,3-dithiane (**9c**) ($CDCl_3$, 500 MH_Z)



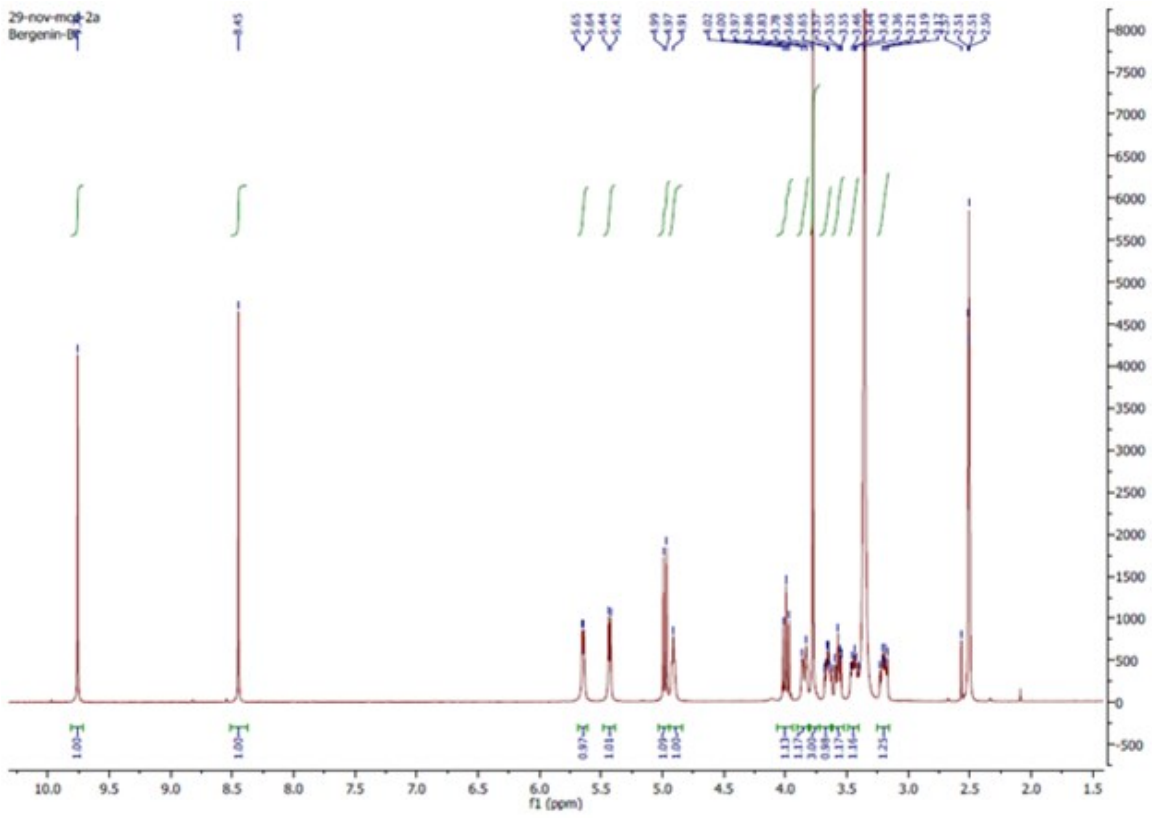
S-3.18: ^{1}H NMR 2-methyl-2-(4-nitrophenyl)-1,3-dithiane (9f) ($CDCl_3$, 500 MH_Z)



S-3.19: ^{1}H NMR spectrum of Thioketal derivative of progesterone (**14**) ($CDCl_3$, 500 MH_Z)



S-3.20: ^{1}H NMR spectrum of Bergenin (**11**) (CD_3OD, 500 MH_Z)



S-4: HRMS of progesterone thioketalization product **14**

Sample Group Info.

Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 60: C27 H42 S4	0.23	494.21862	C27 H42 S4	C27 H42 S4	-3.41	C27 H42 S4

Compound Label	m/z	RT	Algorithm	Mass
Cpd 60: C27 H42 S4	495.22591	0.23	Find by Molecular Feature	494.21862

MFE MS Spectrum