

Electronic Supplementary Information (ESI)

**Novel formazan derivatives containing phenylsulfanyl and carbonyl units: Synthesis,  
optical and electrochemical properties**

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**Table S1** UV-Vis. absorption  $\lambda_{\text{max}}$  values of formazans (**4a–4h**) in various solvents

Comp.	DMSO	DMF	EtOH	MeOH	Acetone	1,4-Dioxane	EtOAc
<b>4a</b>	517	515	517	505	504	512	509
	304	302	304	298		302	302
<b>4b</b>	521	512	499	490	498	501	499
	368, 311	361, 310	285	285	363	310	355
<b>4c</b>	537	531	522	521	521	525	522
	304	304	302	302		303	302
<b>4d</b>	537	531	526	527	526	527	526
	306	303	303	415, 304		303	305
<b>4e</b>	521	513	501	506	505	506	507
	303	302	300	301		302	301
<b>4f</b>	501	515	523	524	521	530	523
	378	374	364, 295	514, 362	364	364, 297	364, 295
<b>4g</b>	515	510	498	499	504	502	503
	308	309	304	305		306	304
<b>4h</b>	409	503	390	389	489	483	484
		369	294	289	365	363	365

Comp.	2-Propanol	CHCl <sub>3</sub>	THF	1-Butanol	Toluene	Cyclohexane	n-Hexane
<b>4a</b>	507	510	511	513	524	507	511
	299	303	302	303	304	405, 301	403
<b>4b</b>	499	502	507	497	515	495	490
	285	309	362	286	357	325, 310	361
<b>4c</b>	522	531	531	528	532	526	520
	303	307	303	302	306	304	414
<b>4d</b>	531	530	535	523	536	531	527
	303	306	305	303	305	419	415
<b>4e</b>	508	509	514	512	514	511	508
	302	301	304	301	305	300	406
<b>4f</b>	522	523	530	528	537	446	442
	361, 302	374	366, 300	364, 386	366	274	361, 286
<b>4g</b>	502	503	508	505	509	499	498
	304	309	308	307	309	405	354
<b>4h</b>	386	496	494	385	503	439	478
		368	365		367	370	431

**Table S2** UV-vis absorption  $\lambda_{\max}$  values of formazans (**5a–5h**) in different solvents

Comp.	DMSO	DMF	EtOH	MeOH	Acetone	Dioxane	EtOAc
<b>5a</b>	505	507	501 303	498	502	501	503
	307	305		303		305	304
<b>5b</b>	513	506	503	500	502	502	500
	372, 313	368, 313	364, 309	365, 310	365	365, 310	299, 272
<b>5c</b>	520	517	512	511	515	512	515
	313	309	307	307		307	309
<b>5d</b>	524	520	517	512	526	517	516
	311	310	307	308	364	308	310
<b>5e</b>	508	507	501	499	503	502	500
	307	306	306	305		305	306
<b>5f</b>	496	494	533	530	525	540	537
			377, 299	394, 289	372	368, 304	371, 304
<b>5g</b>	506	506	499	500	498	500	500
	311	310	309	306	359	311	308
<b>5h</b>	406	402	388	391	391	386	386

Comp.	Propanol	CHCl <sub>3</sub>	THF	1-Butanol	Toluene	Cyclohexane	n-Hexane
<b>5a</b>	500	503	506	503	509	505	504
	300	308	306	303	417, 306	304	302
<b>5b</b>	503	496	506	504	512	506	502
	365, 311	364, 314	368, 313	366, 310	367, 312	361, 312	361, 312
<b>5c</b>	511 308	509	520	513	518	516	516
		311	310	309	311	412, 309	461, 307
<b>5d</b>	531	515 312	517	519	523	518	517
	303		310	309	313	417, 310	311
<b>5e</b>	502	498	504	503	511 311	506	503
	303	309	308	305		303	426, 306
<b>5f</b>	534	548	539	538	552	549	568
	376, 310	372, 304	371	372, 303	367, 306	360, 307	363
<b>5g</b>	498	499	506	501	503	503	502
	309	312	311	307	311	308	310
<b>5h</b>	390	389	391	389	388	379	369
	303						

**Table S3.** Calculated sum of electronic and thermal free energies (SETFE) (in Hartree) of compounds **4a-4h** and **5a-5h** and some important bond distances of tautomer forms predicted at PBE1PBE/6-311g(2d,2p) level (in Å) in gas phase.

Comp.	SETFE		$\Delta_{KT}^a$	H-bond (Å)					
	Tautomer 1	Tautomer 2		Tautomeric form 1			Tautomeric form 2		
				H1...N2	H1...S1	H1...O1	H2...N1	H2...S1	H2...O1
<b>4a</b>	-1694.6068	-1694.6026	0.004	1.788	3.051	-	1.840	2.670	
<b>4b</b>	-1809.0035	-1809.0067	-0.003	1.772	3.045	-	1.842	2.671	
<b>4c</b>	-2154.0435	-2154.0459	-0.002	1.683	2.931	-	1.835	2.664	
<b>4d</b>	-4267.7524	-4267.7536	-0.001	1.784	3.042	-	1.837	2.665	
<b>4e</b>	-1793.7951	-1793.7945	0.001	1.782	3.045	-	1.840	2.666	
<b>4f</b>	-1898.9917	-1898.9912	0.001	1.804	3.038	-	1.825	2.662	
<b>4g</b>	-1773.0942	-1773.1009	-0.007	1.783	3.055	-	1.732	2.668	
<b>4h</b>	-2103.3694	-2103.3611	0.008	1.940	3.543	1.928	1.789	4.321	2.135
<b>5a</b>	-1869.251	-1869.246	0.005	1.850	-	2.313	1.799	-	3.480
<b>5b</b>	-1983.646	-1983.648	-0.002	1.832	-	2.297	1.807	-	3.491
<b>5c</b>	-2328.690	-2328.688	0.002	1.852	-	2.273	1.789	-	3.367
<b>5d</b>	-4442.355	-4442.396	-0.041	1.855	-	2.365	1.795	-	3.398
<b>5e</b>	-1968.437	-1968.437	0.000	1.749	-	2.139	1.791	-	3.352
<b>5f</b>	-2073.629	-2073.637	-0.008	1.783	-	2.132	1.917	-	1.982
<b>5g</b>	-1949.383	-1947.647	1.736	1.845	-	2.298	1.796	-	3.459
<b>5h</b>	-2278.007	-2278.010	-0.002	1.885	-	2.221	1.899	-	1.972

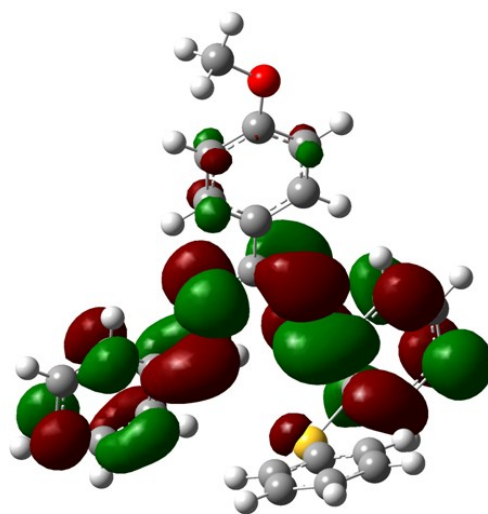
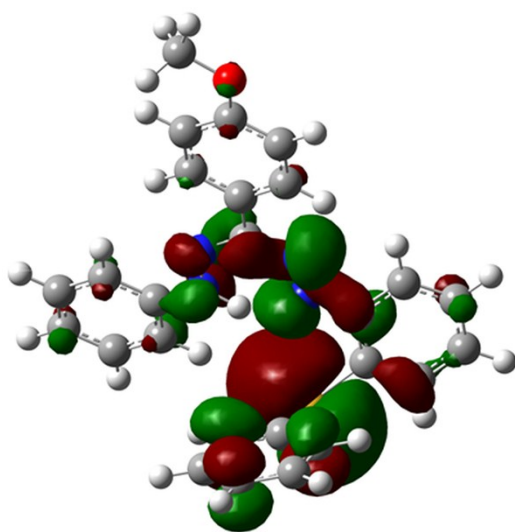
<sup>a</sup>  $\Delta_{KT} = E_{\text{tautomer form 2}} - E_{\text{tautomer form 1}}$ ,  $\Delta_{KT}$  constant stable between tautomer forms.

Comp.

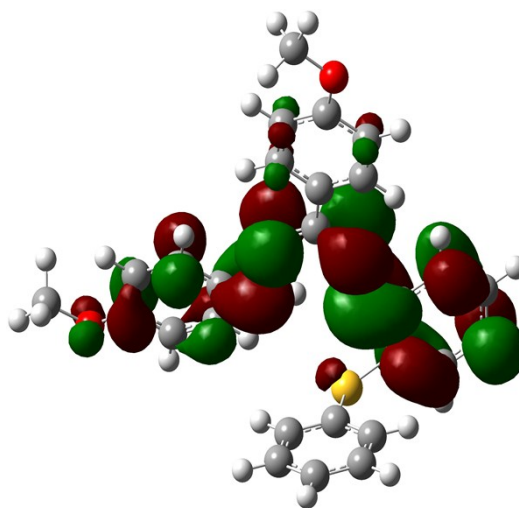
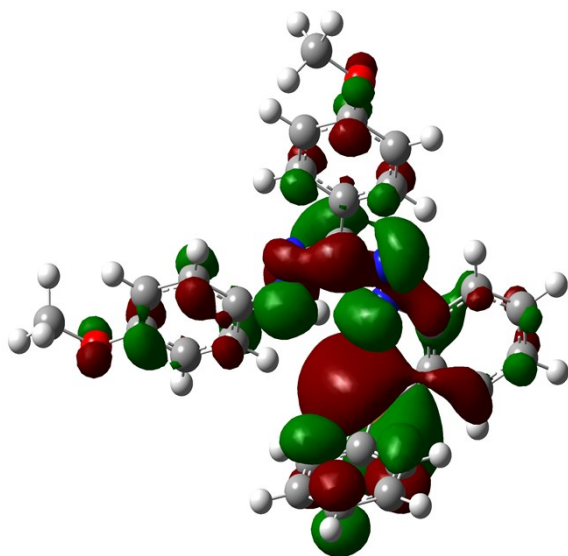
HOMO (eV)

LUMO (eV)

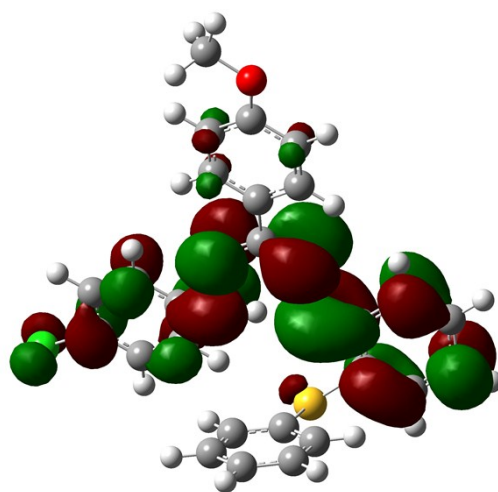
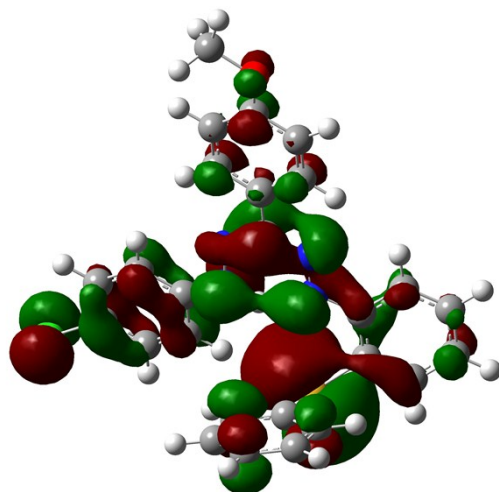
4a



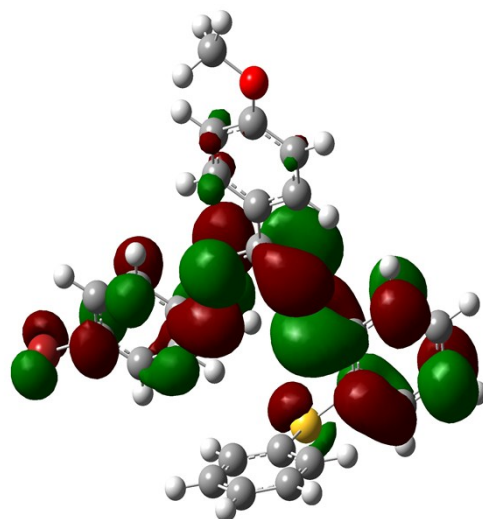
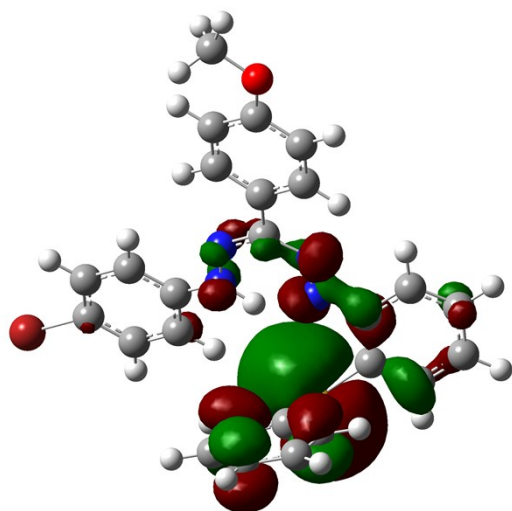
4b



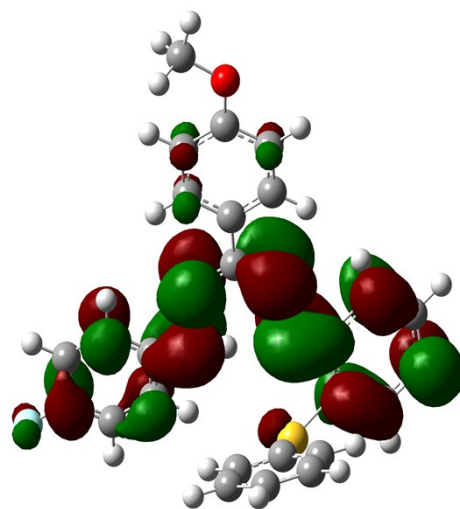
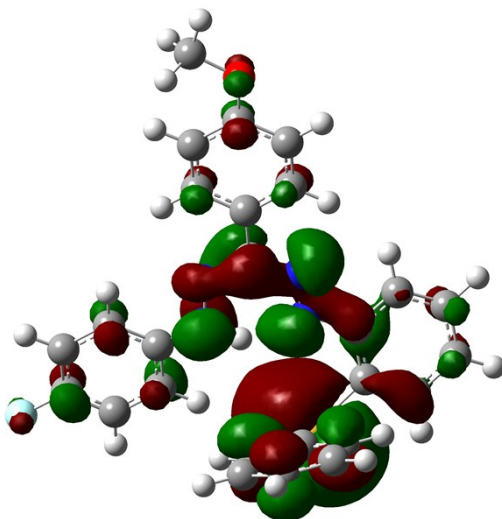
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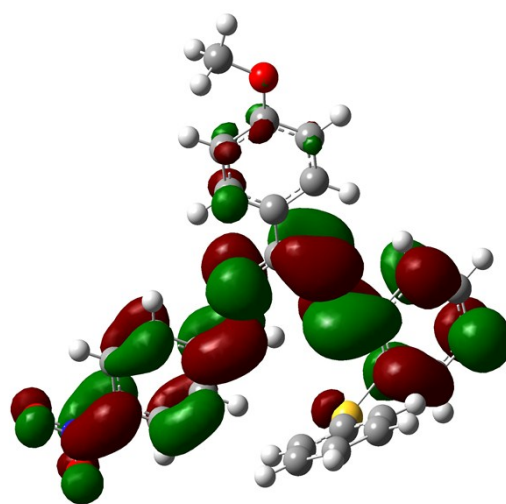
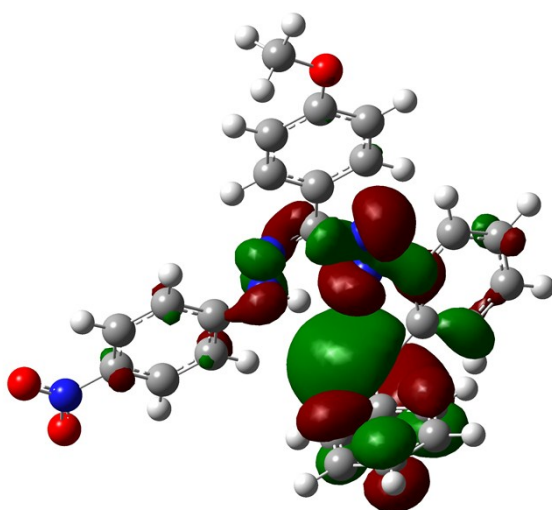
4d



4e



4f



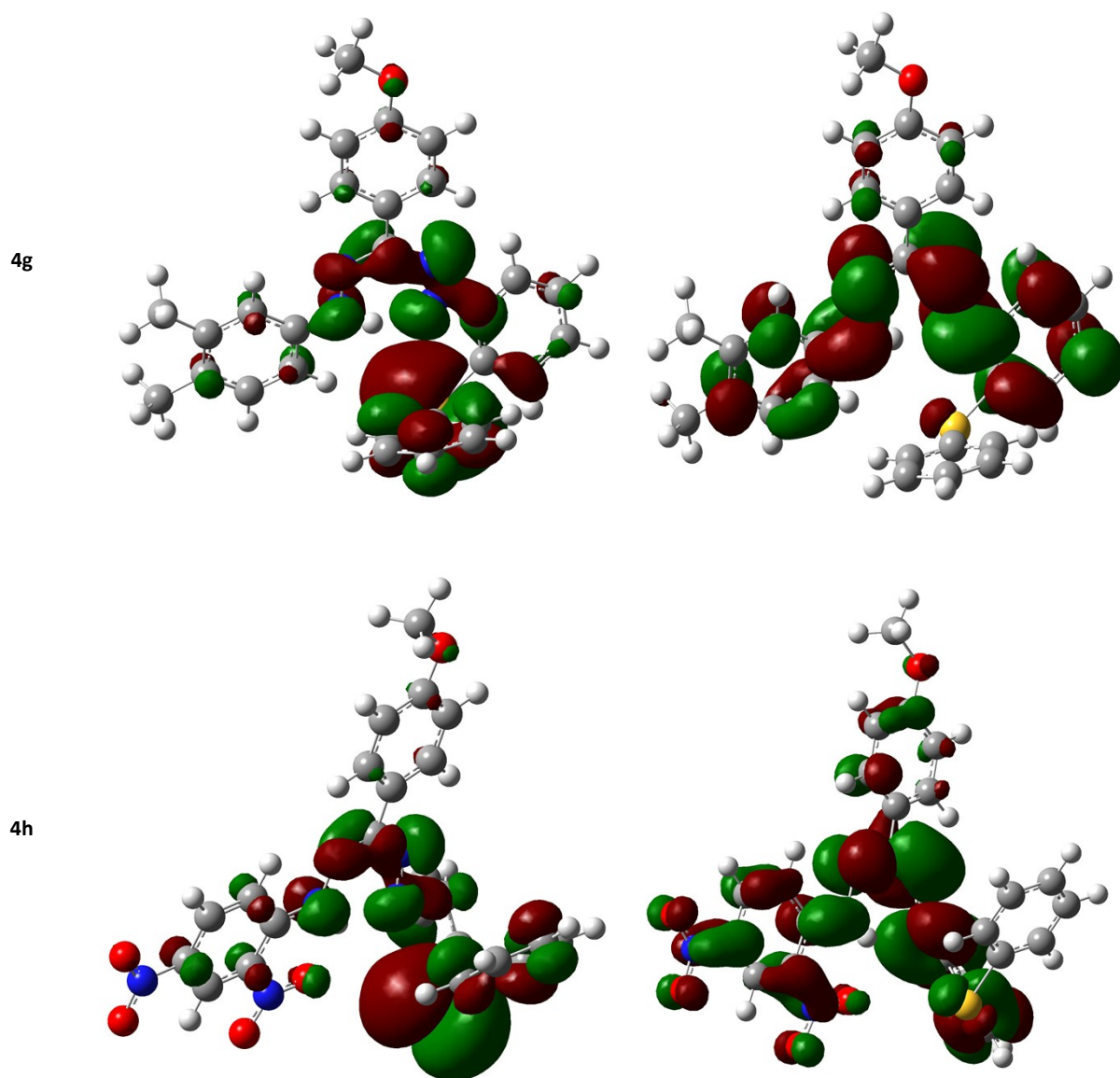


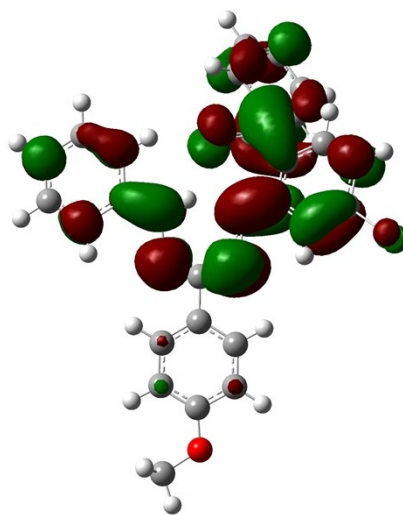
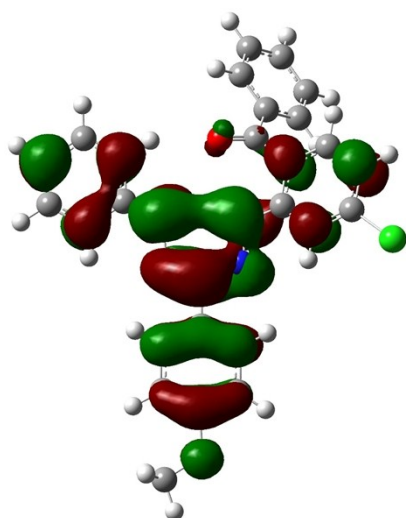
Figure S1 HOMO and LUMO electronic density distributions of **4a–4h** calculated at PBE1PBE/6-311g (2d,2p) level

Comp.

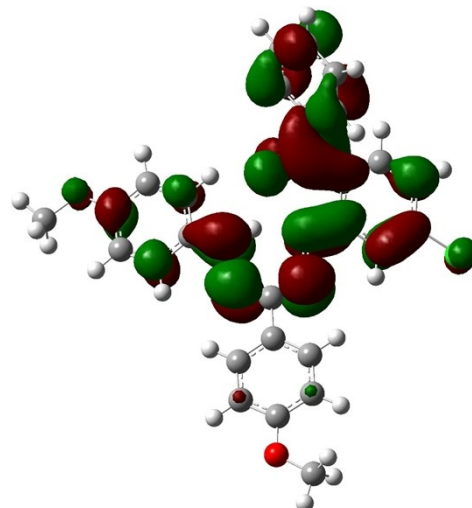
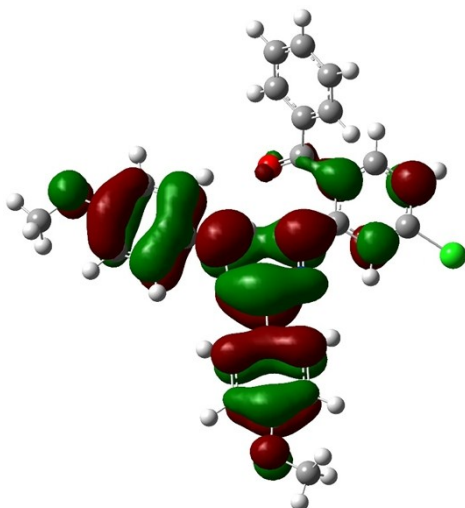
HOMO (eV)

LUMO (eV)

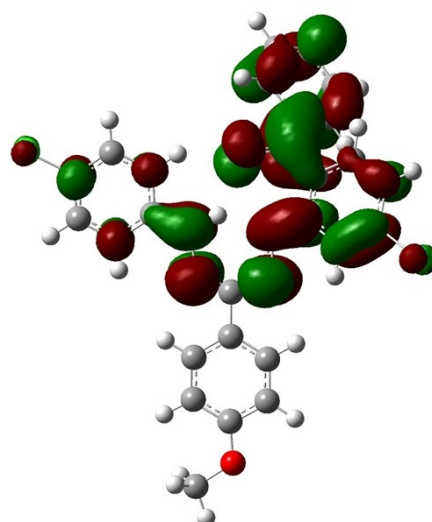
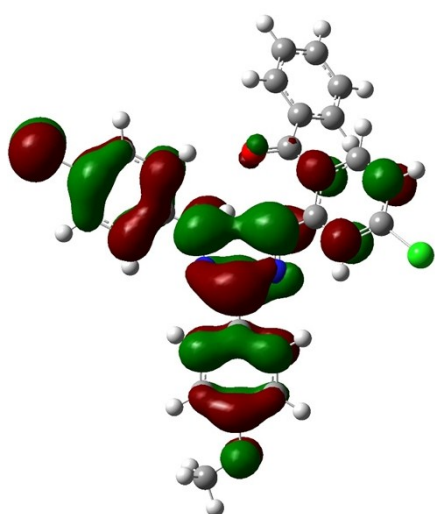
5a



5b

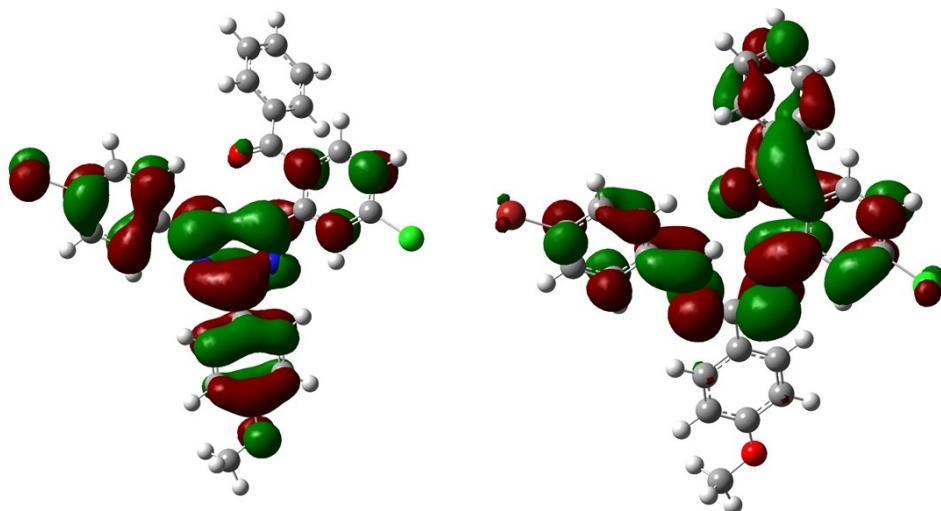


5c

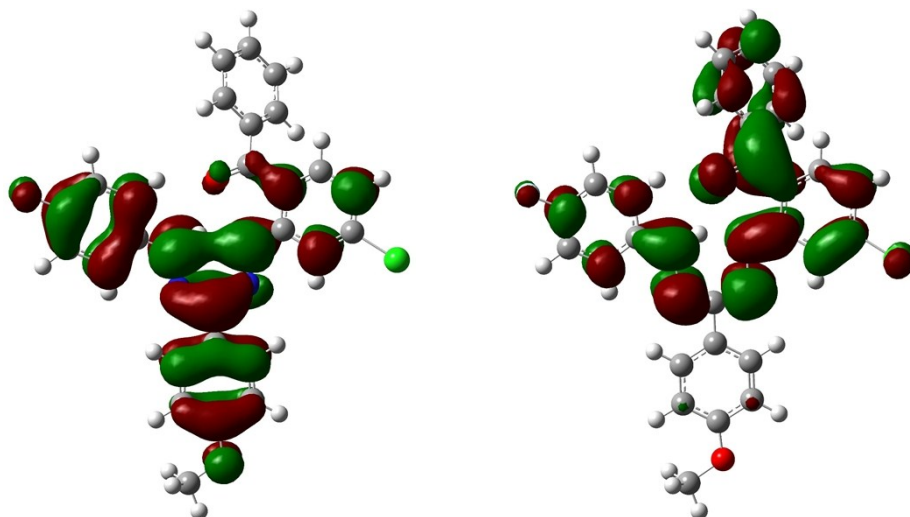




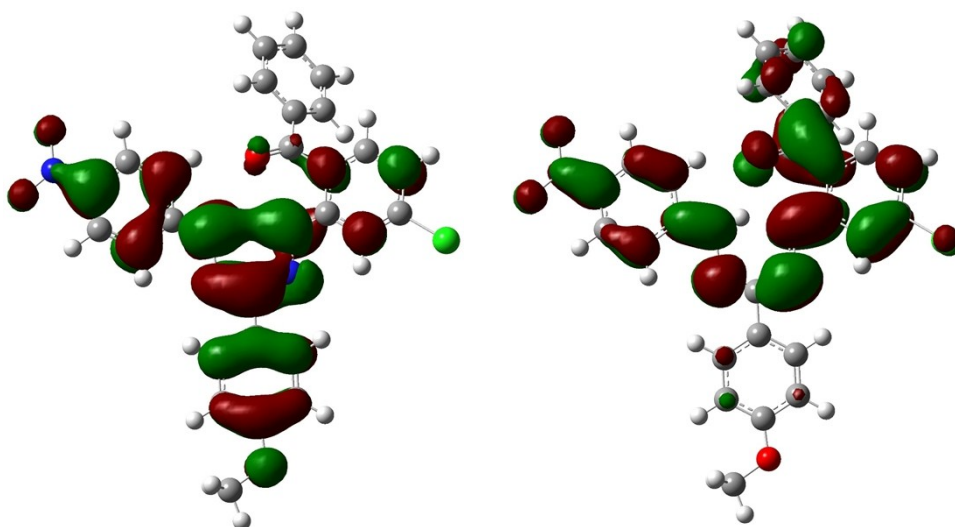
5d



5e



5f



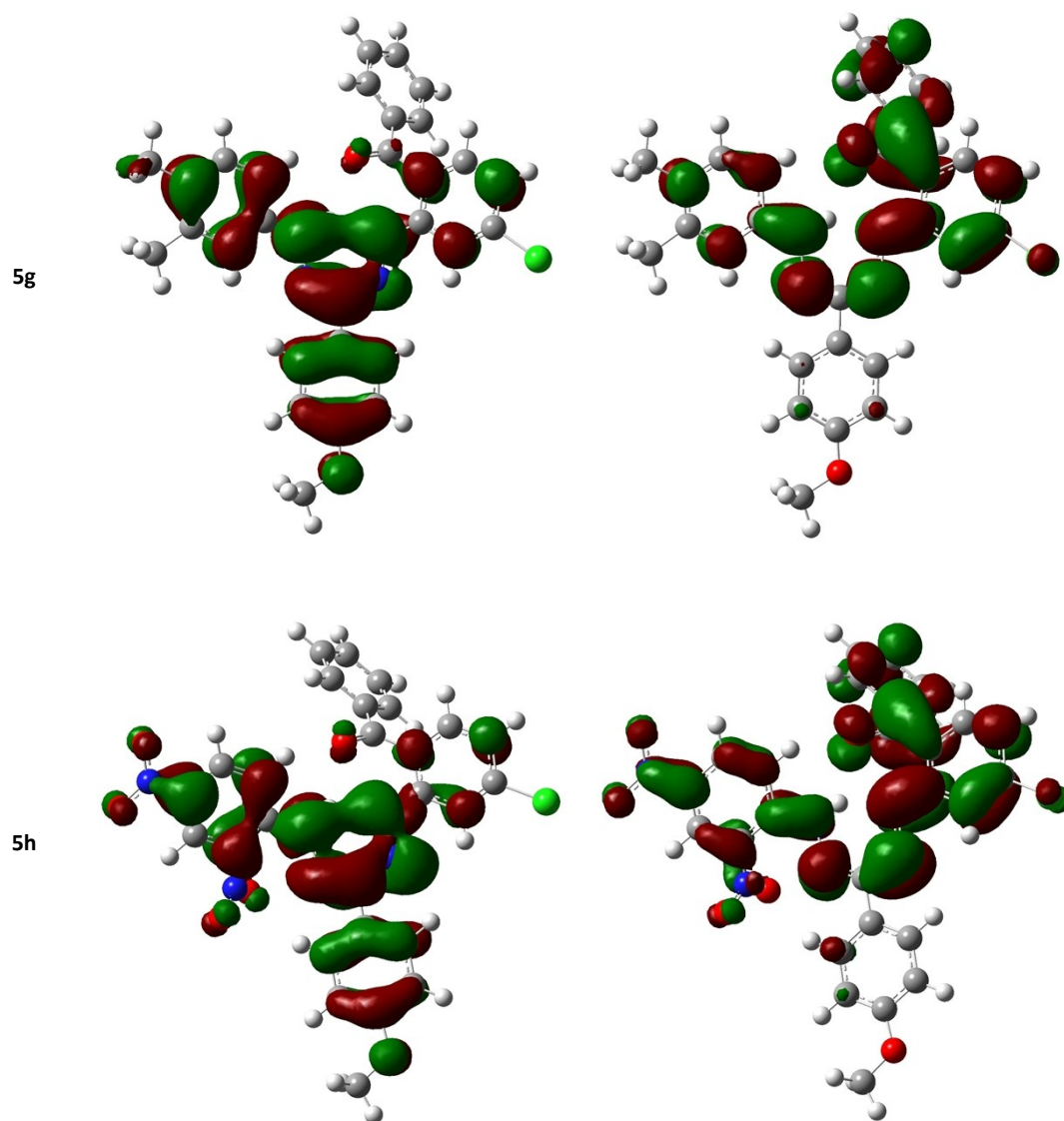
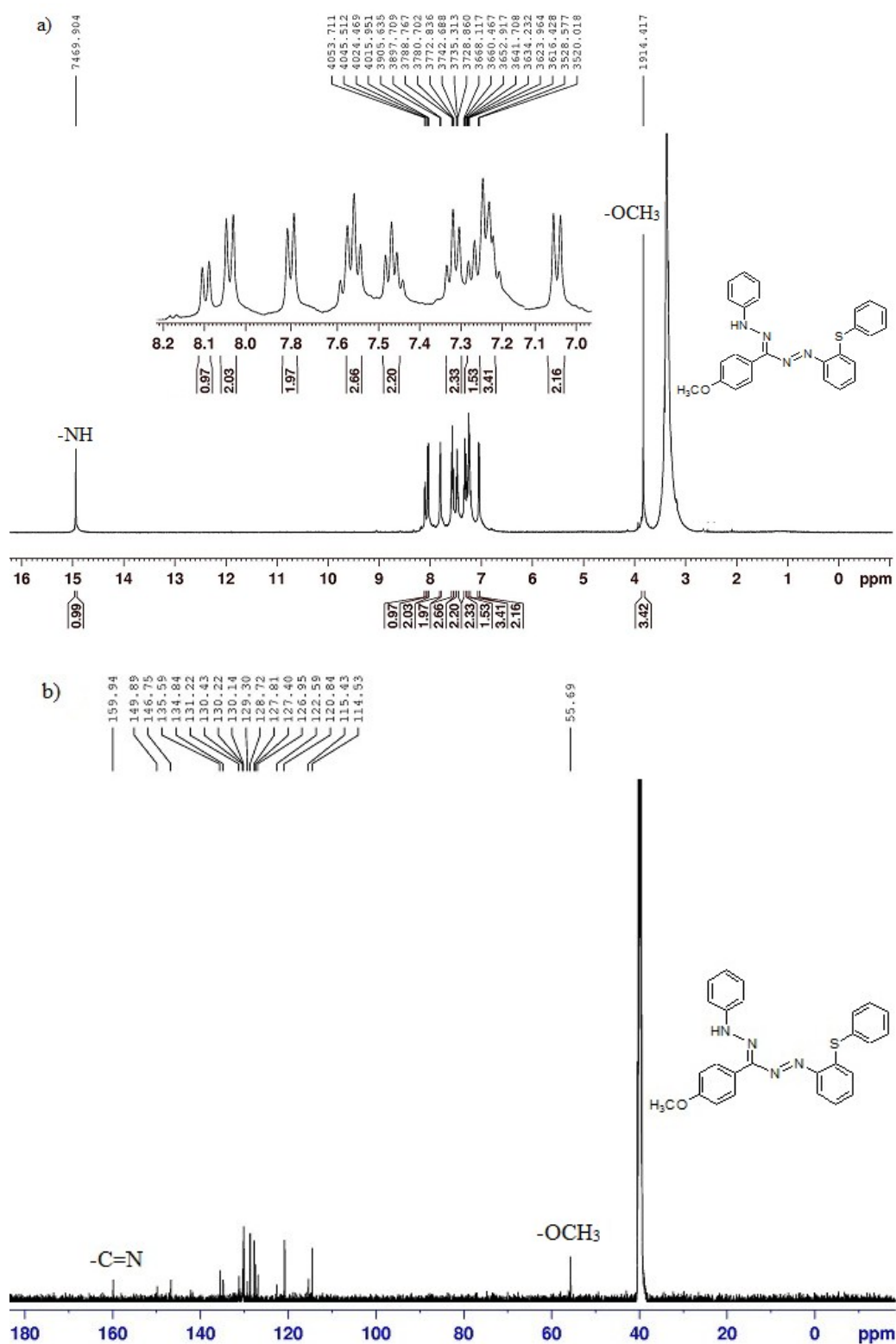
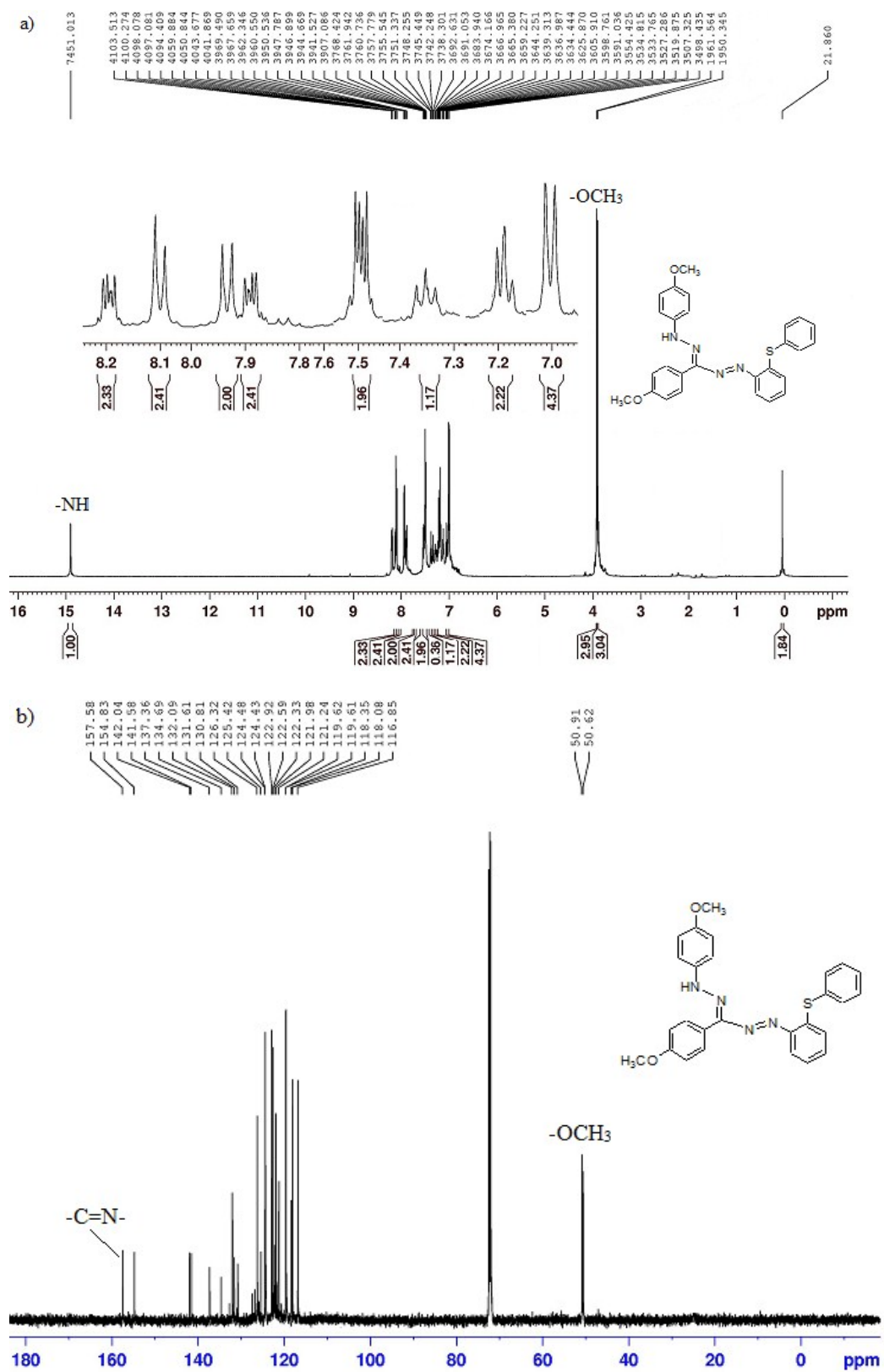


Figure S2 HOMO and LUMO electronic density distributions of **5a–5h** calculated at PBE1PBE/6-311g (2d,2p) level

## NMR spectra of target compounds

Figure S3 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) spectra of compound **4a**



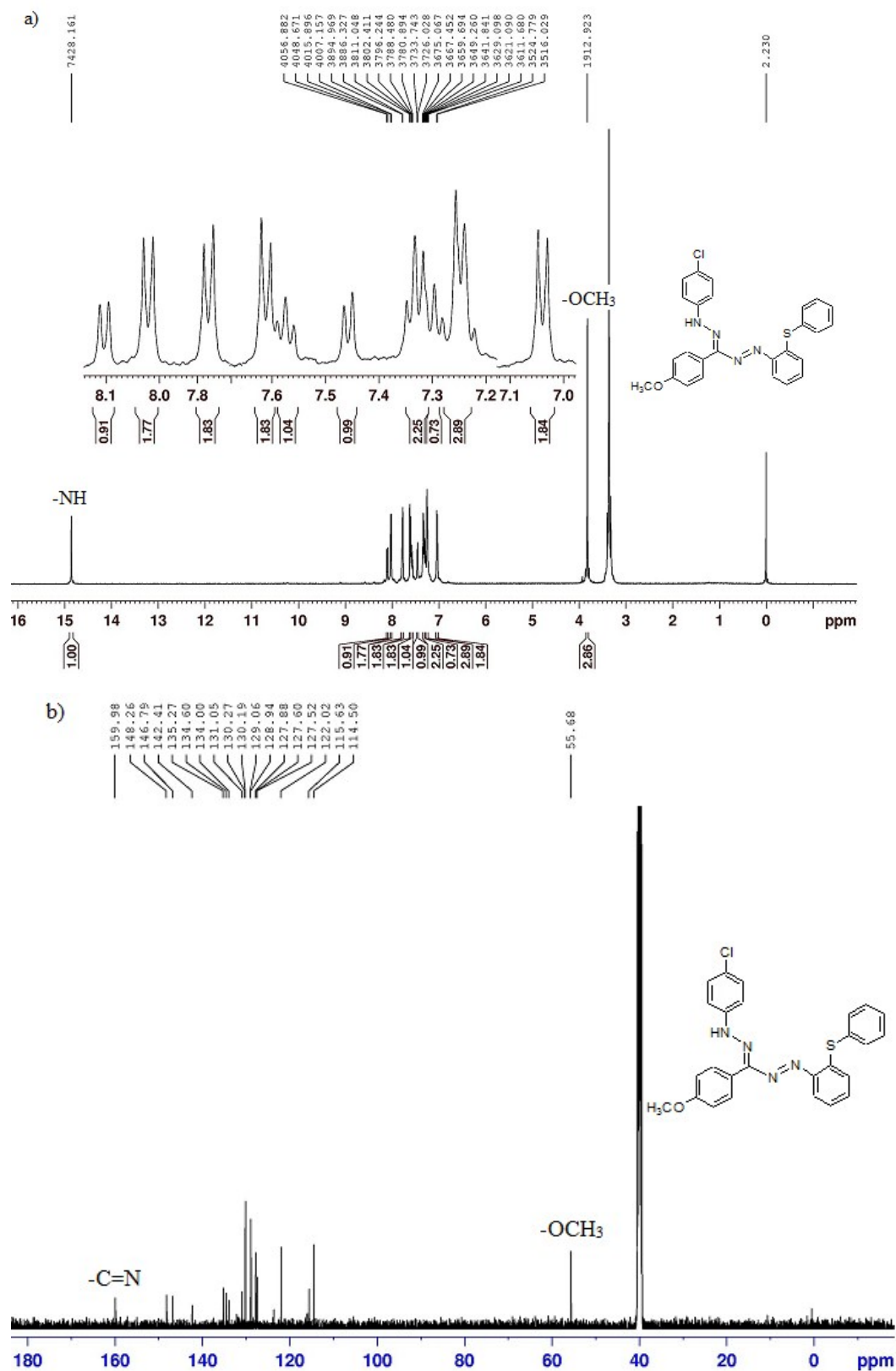


Figure S5 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) spectra of compound 4c

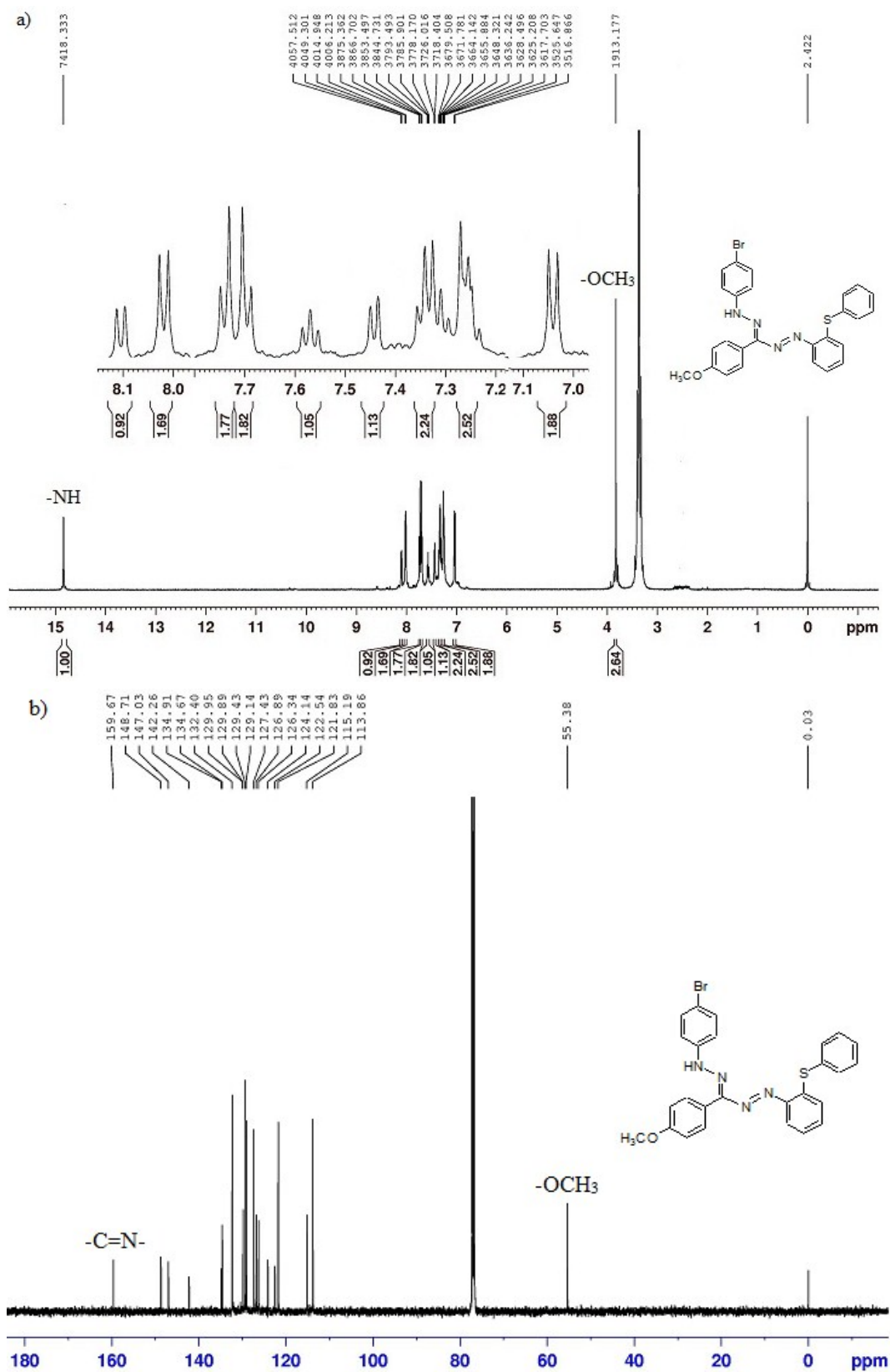


Figure S6 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectra of compound 4d

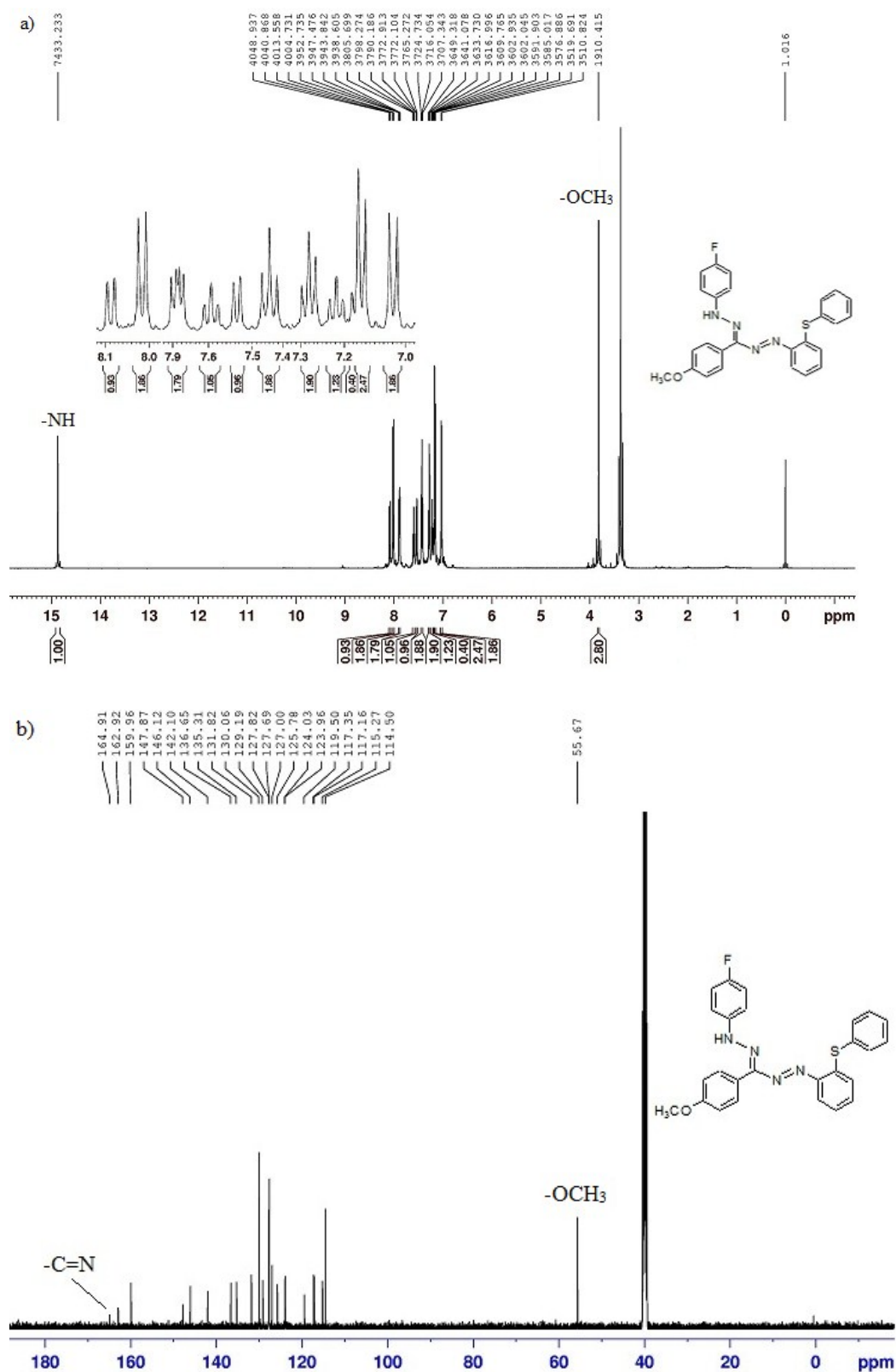


Figure S7 a)  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ), b)  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-d}_6$ ) spectra of compound **4e**

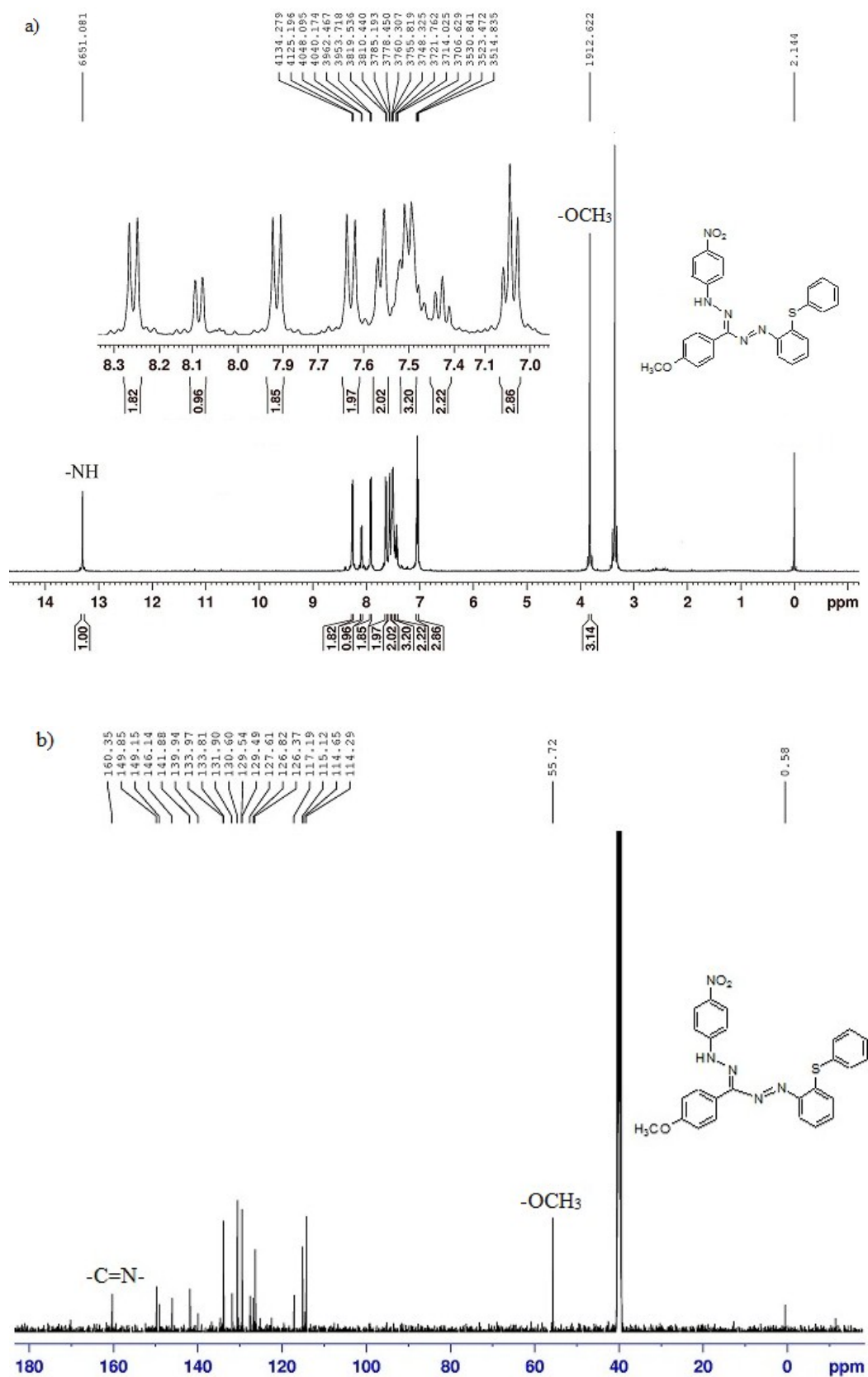


Figure S8 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) spectra of compound **4f**



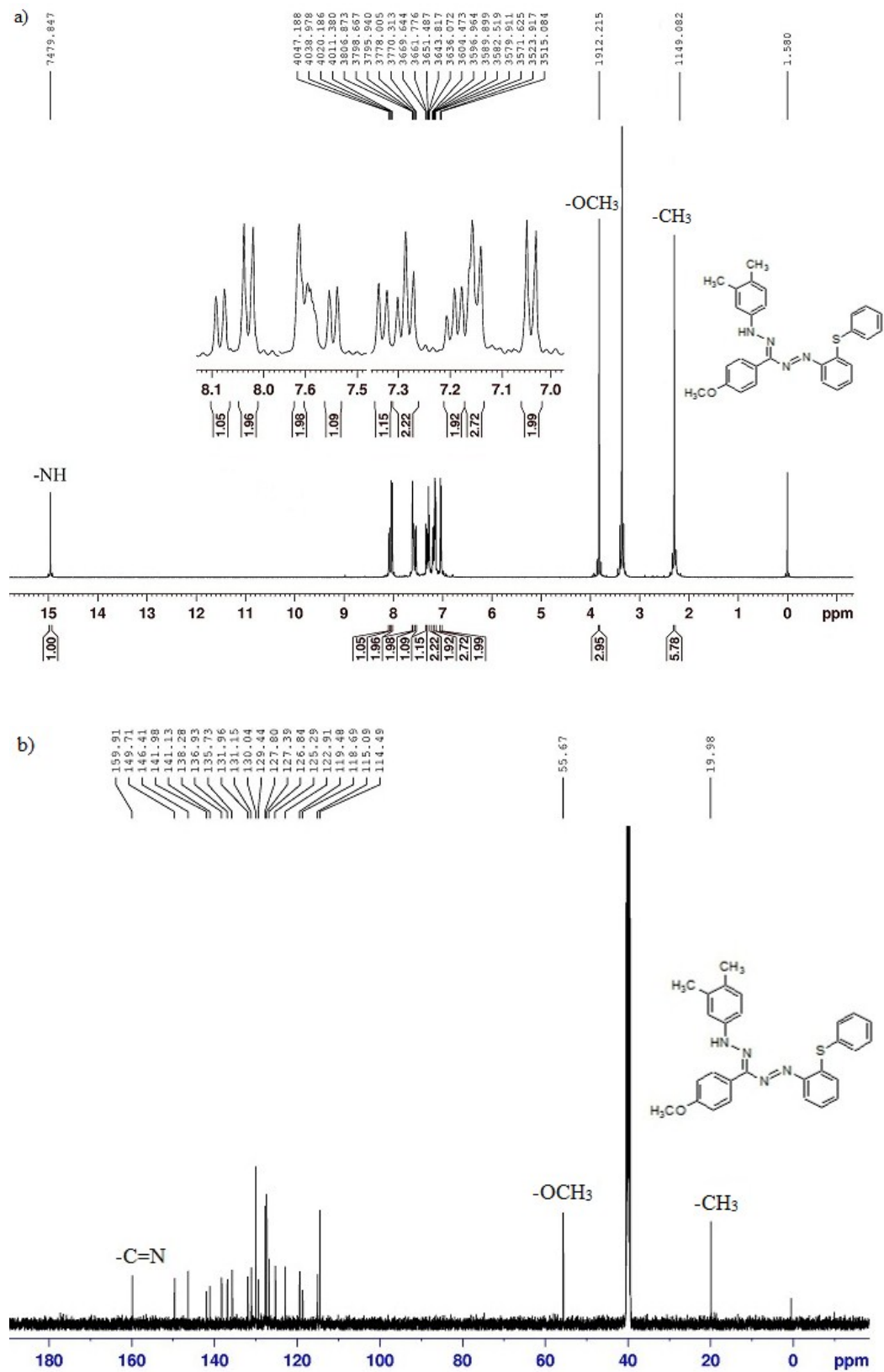


Figure S9 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) spectra of compound **4g**

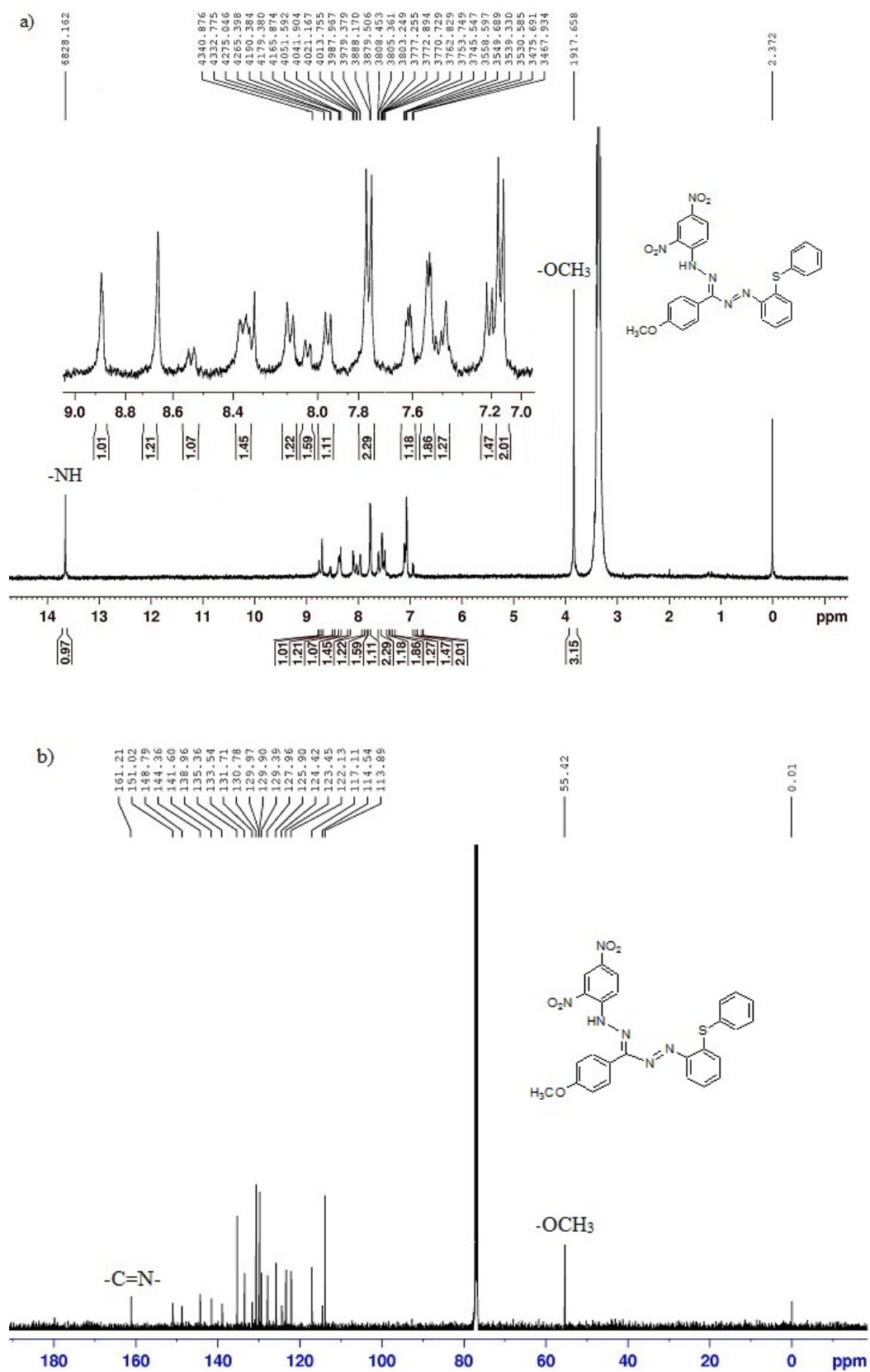


Figure S10 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectra of compound 4h

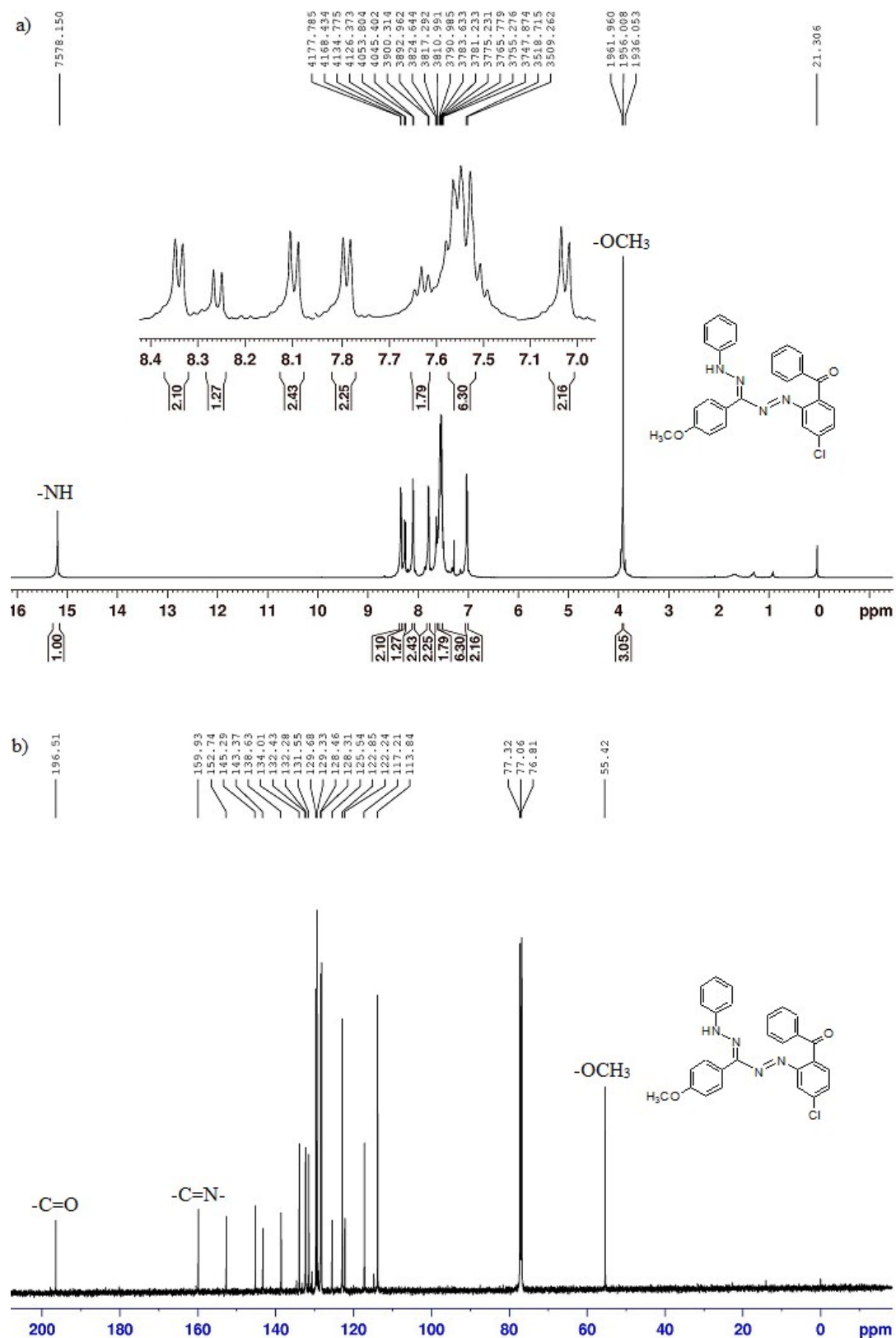
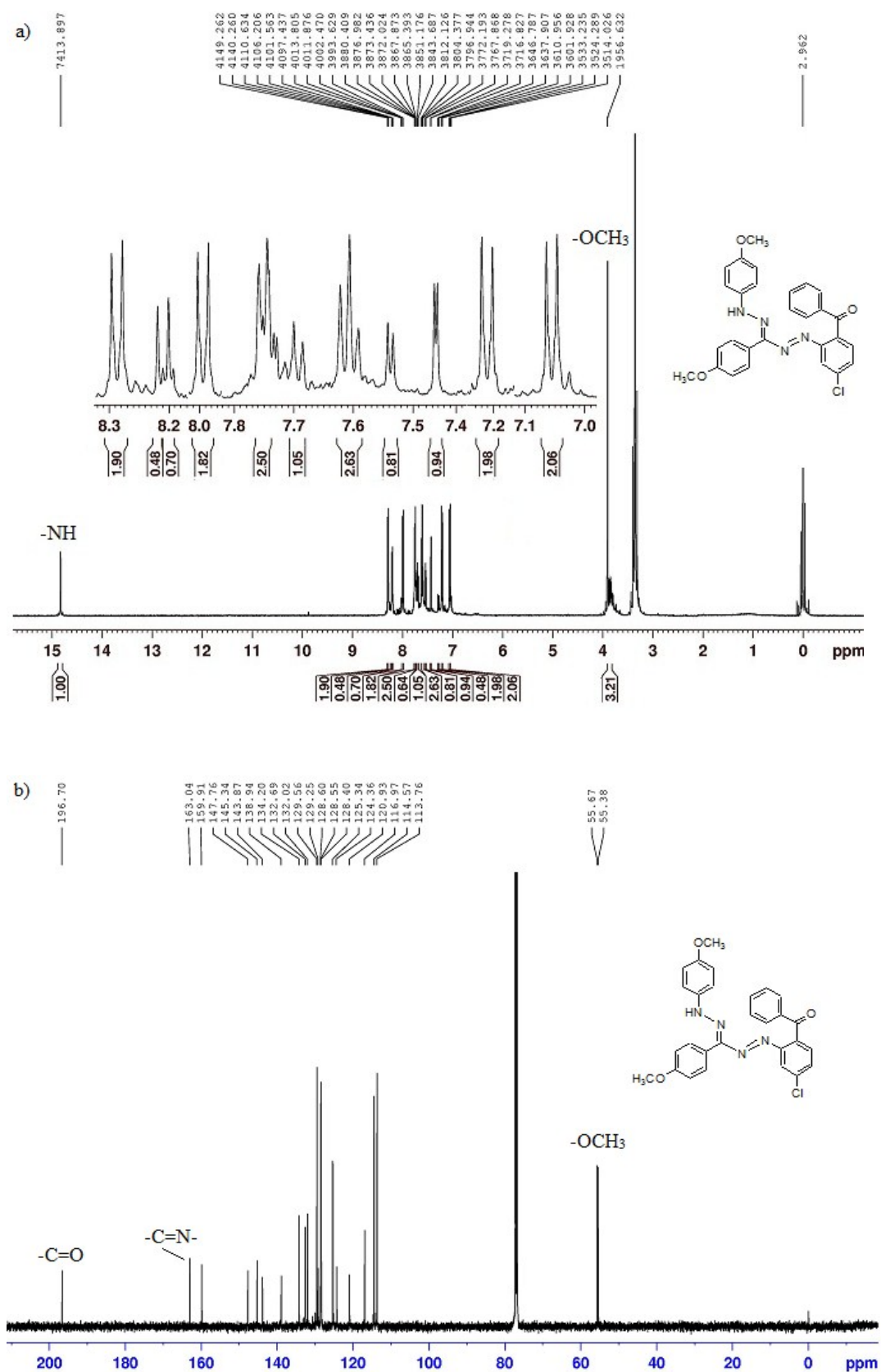


Figure S11 a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ), b)  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectra of compound 5a



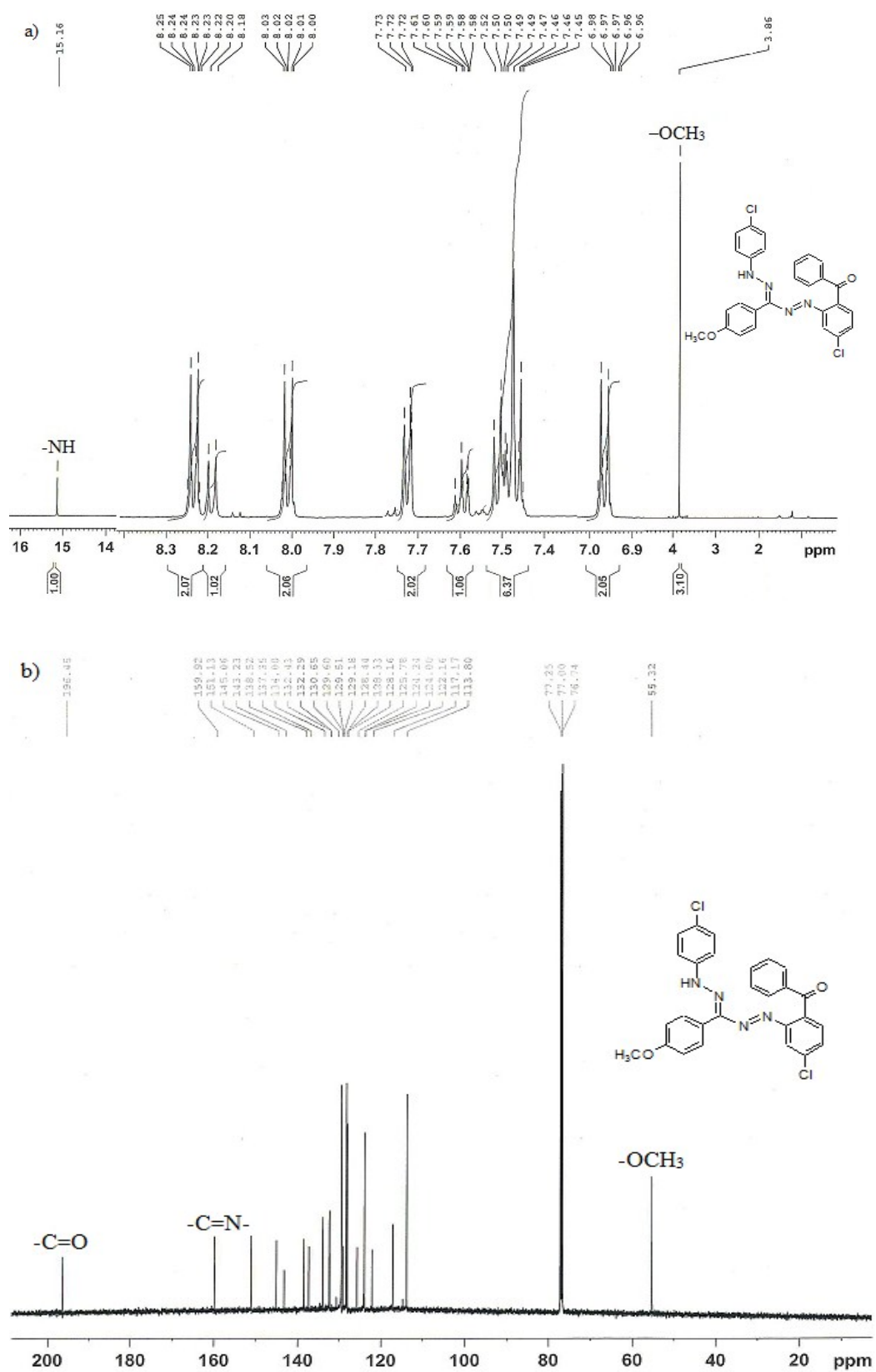


Figure S13 a) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), b) <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectra of compound 5c

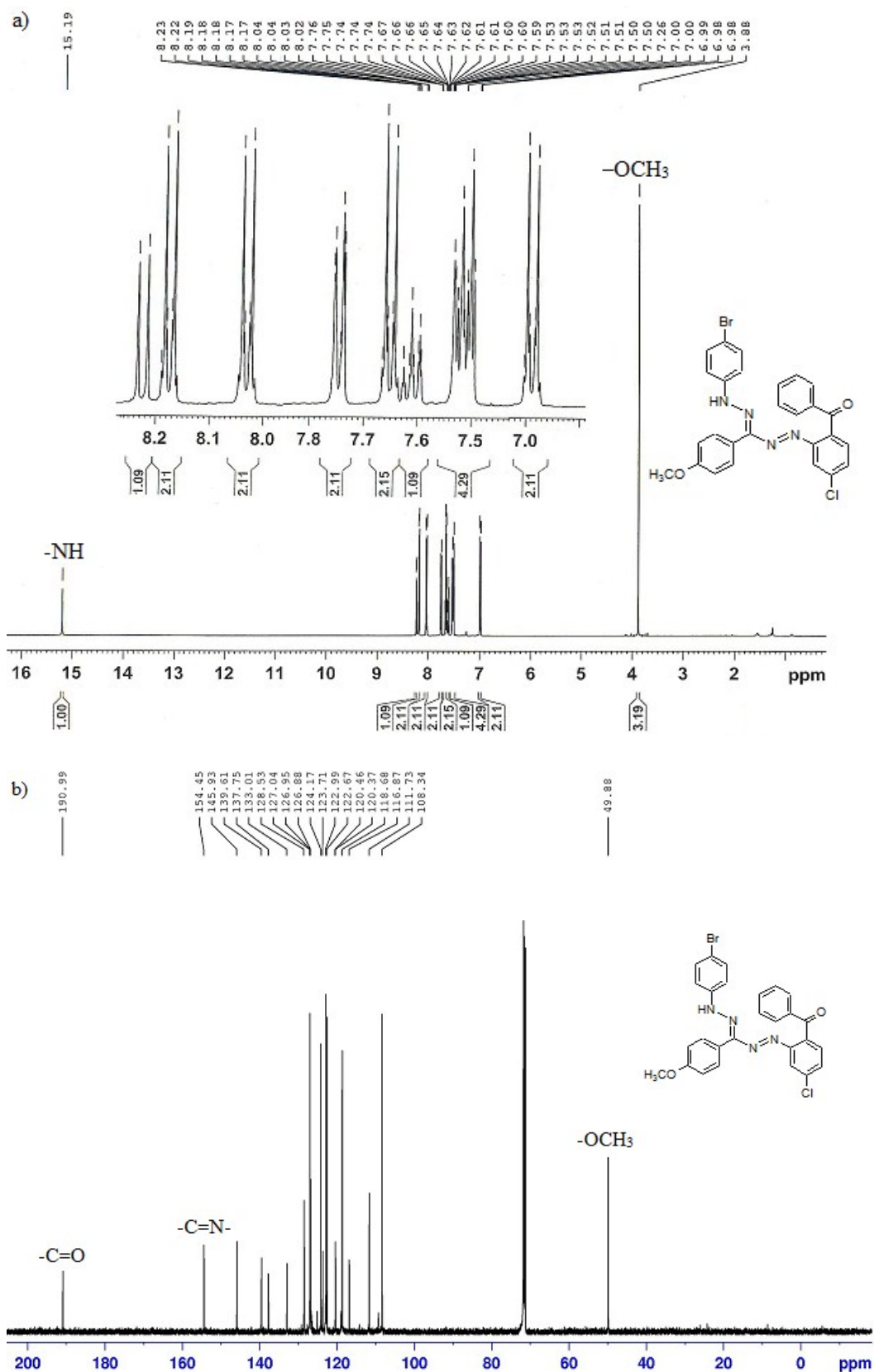
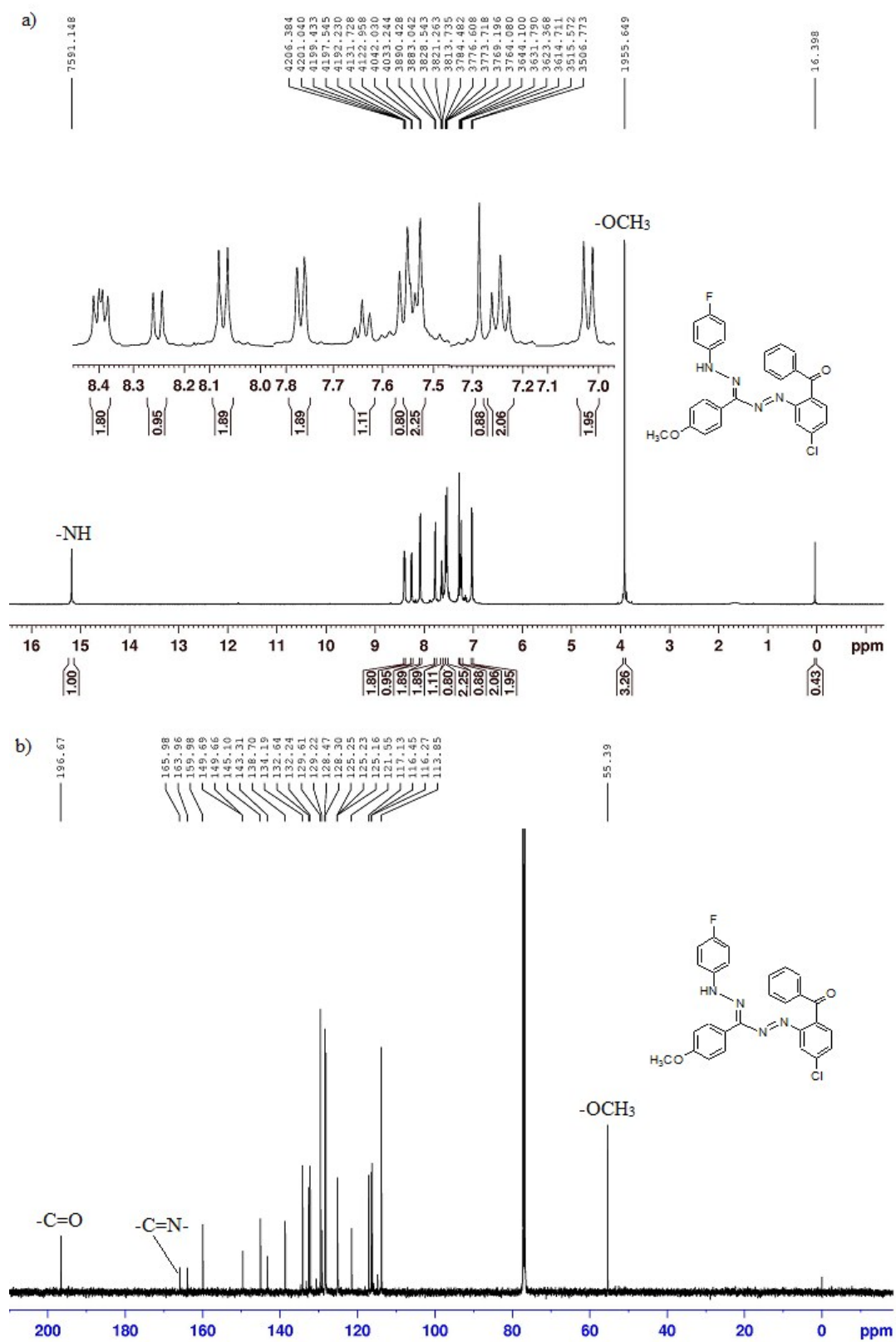
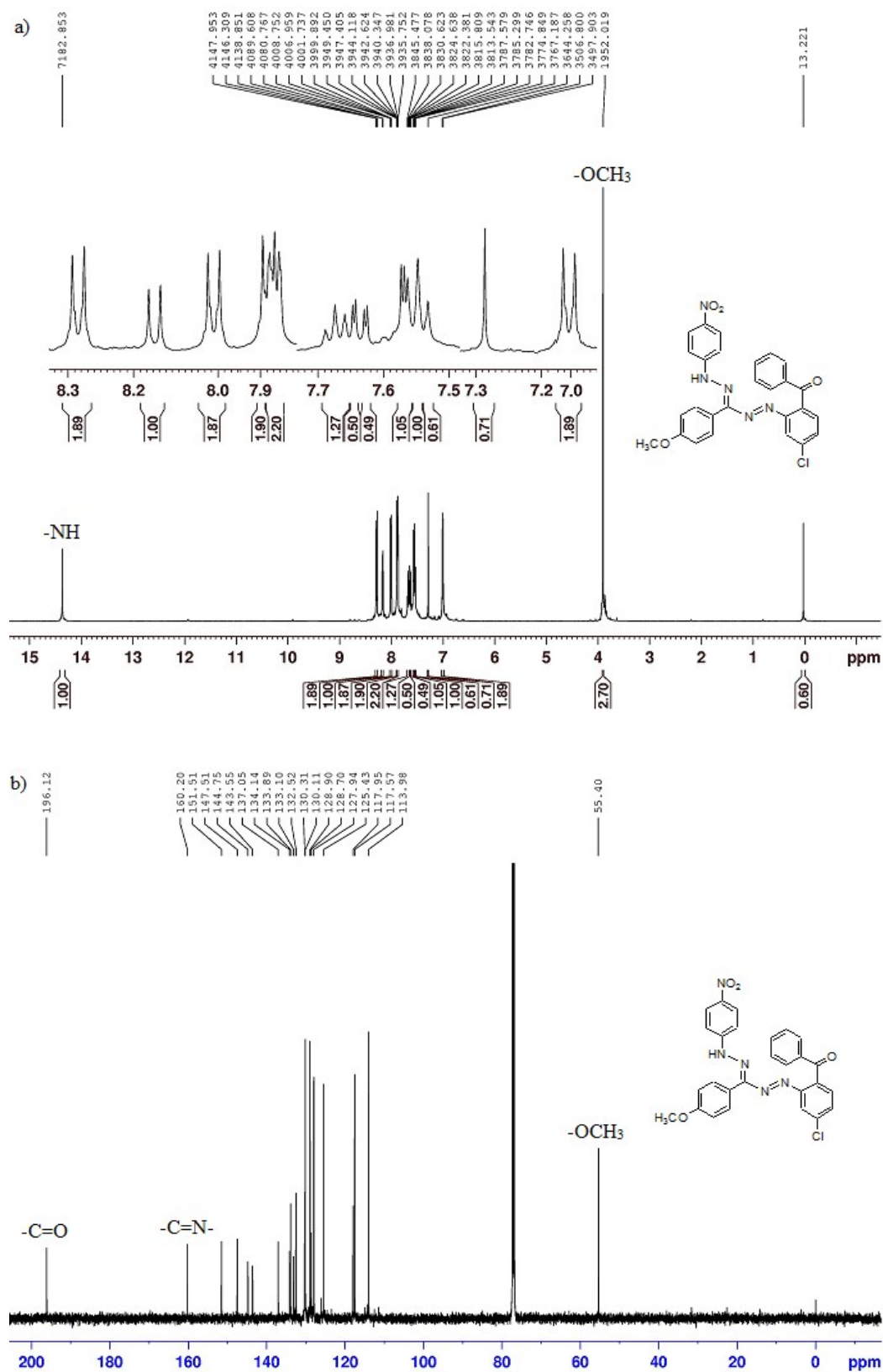


Figure S14 a) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), b) <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectra of compound 5d







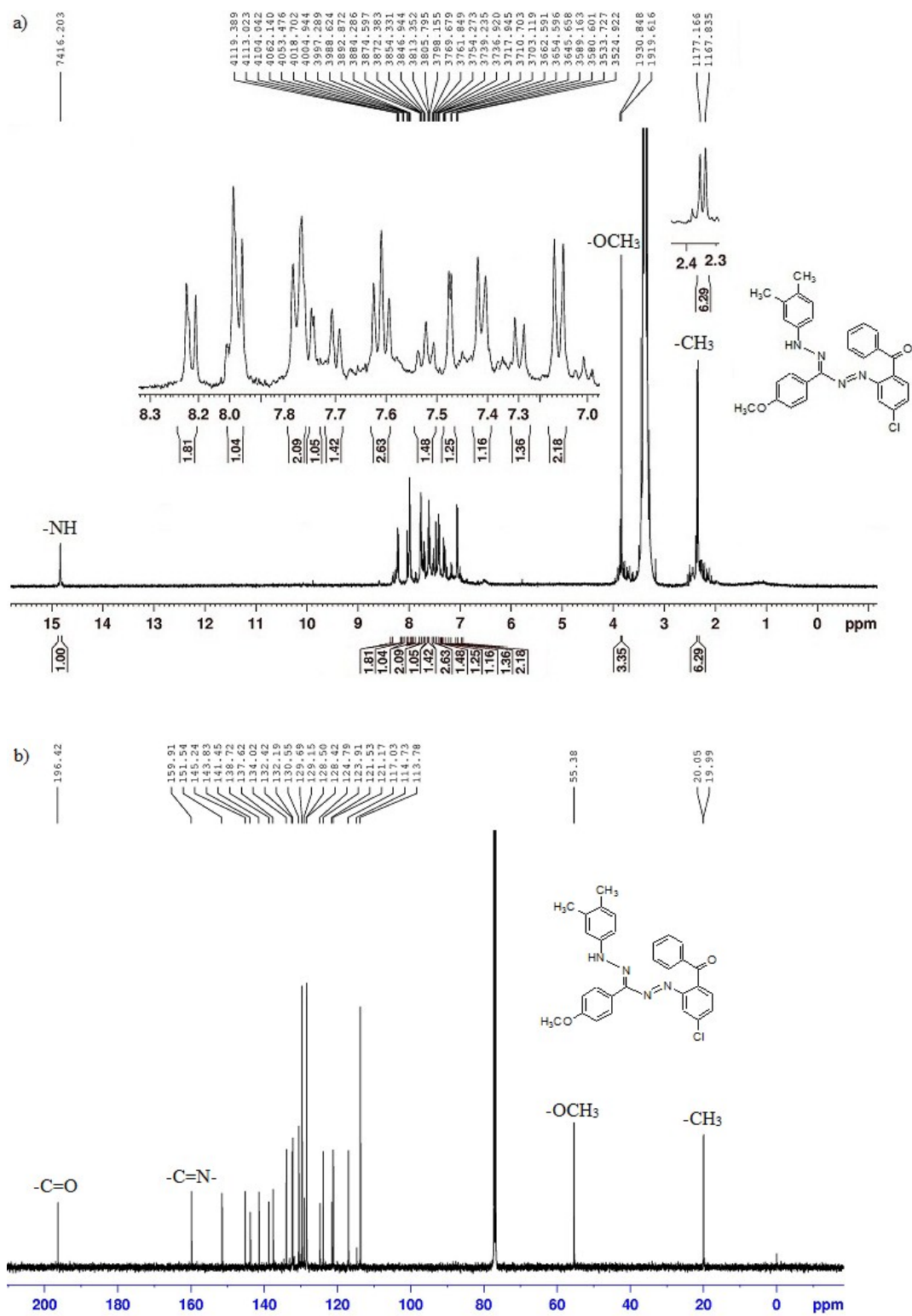


Figure S17 a) <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>), b) <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectra of compound **5g**

