Electronic Supplementary Information (ESI)

Synthesis, crystal structure, optical and electrochemical properties of novel diphenylether-based formazan derivatives

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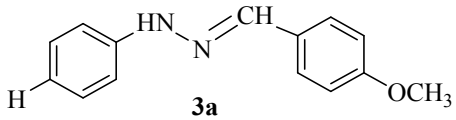
1. Experimental procedures and characterization data

General Procedure for the Synthesis of 1-(4-methoxybenzylidene)-2-phenylhydrazine (3a).

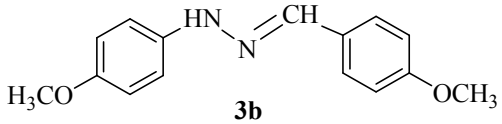


3a

To a solution of 1.36 g of 4-methoxybenzaldehyde (10.0 mmol) in 25 mL of methanol was added a solution of 1.09 g of phenylhydrazine (0.90 mL, 10.0 mmol) in 25 mL of methanol dropwise at 60 °C. The reaction mixture was stirred for 2 hours and cooled down to room temperature for 30 min. The yellow precipitate was filtered off and dried in an oven at 60 °C. The crude product was recrystallized from methanol. The compound **3a** was obtained as bright yellow needles in 98% yield (2.21 g); m.p. 130−131 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3315 (s), 1365 (s), 1527-1506 (s), 3022 (s), 1596 (s), 1296, 1244 (m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.60 (d, J = 8.70 Hz, 2H), 7.47 (s, 1H), 7.28 (t, J = 7.10 Hz, 2H), 7.11 (d, J = 8.50 Hz, 2H), 6.91 (d, J = 9.00 Hz, 2H), 6.85 (t, J = 7.25 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.98, 144.95, 137.36, 129.25, 127.56, 119.78, 114.10, 55.32. Anal. Calcd. for $C_{14}H_{14}N_2O$ (226.27, %): C, 74.31; H, 6.24; N, 12.38. Found: C, 74.06; H, 6.23; N, 12.37.

The other compounds (**3b−3h)** were prepared in a similar manner.

1-(4-Methoxybenzylidene)-2-(4-methoxyphenyl)hydrazine (3b).

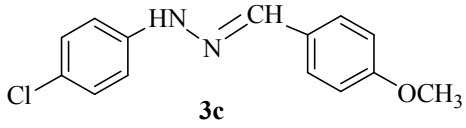


3b

Light cream solid (crystallized from methanol). Yield 2.11 g (83%); m.p. 138−139 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3309 (s), 1313 (s), 1524-1506 (s), 3031 (s), 1606 (s), 1245 (m). ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.06 (d, J = 9.05 Hz, 2H), 7.85 (d, J = 9.15 Hz, 2H), 7.64 (s, 1H), 7.01 (d, J = 8.10 Hz, 2H), 6.93 (d, J = 8.00 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.75, 136.84, 132.26, 131.98, 129.45, 127.37, 114.30, 113.91, 55.57, 55.45. Anal. Calcd. for $C_{15}H_{16}N_2O_2$ (256.30,

%): C, 70.29; H, 6.29; N, 10.93. Found: C, 70.45; H, 6.10; N, 11.20.

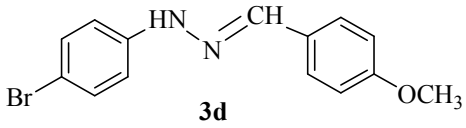
1-(4-Methoxybenzylidene)-2-(4-chlorophenyl)hydrazine (3c).



3c

Light white needles (crystallized from methanol). Yield 1.40 g (77%); m.p. 159−160 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3309 (s), 1357 (s), 1523-1506 (s), 3012 (s), 1606 (s), 1292-1253 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.65 (s, 1H), 7.58 (d, J = 8.52 Hz, 2H), 7.21 (dd, J = 8.15 and 2.32 Hz, 2H), 7.02 (d, J = 8.00 Hz, 2H), 6.91 (d, J = 8.48 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.60, 143.52, 138.07, 131.98, 129.36, 128.95, 127.65, 114.13, 113.73, 55.33. Anal. Calcd. for $C_{14}H_{13}ClN_2O$ (260.72, %): C, 64.49; H, 5.03; N, 10.74. Found: C, 64.33; H, 4.95; N, 10.73.

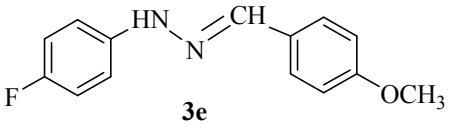
1-(4-Methoxybenzylidene)-2-(4-bromophenyl)hydrazine (3d).



3d

Light cream solid (crystallized from methanol). Yield 1.30 g (80%); m.p. 158−159 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3307 (s), 1357 (s), 1504 (s), 3006 (s), 1604 (s), 1292-1253 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.64 (s, 1H), 7.59 (d, J = 8.40 Hz, 2H), 7.34 (d, J = 9.12 Hz, 2H), 6.97 (d, J = 9.01 Hz, 2H), 6.90 (d, J = 8.28 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.20, 143.96, 138.18, 131.99, 127.68, 114.20, 114.14, 55.34. Anal. Calcd. for $C_{14}H_{13}BrN_2O$ (305.17, %): C, 55.10; H, 4.29; N, 9.18. Found: C, 54.98; H, 4.13; N, 9.06.

1-(4-Methoxybenzylidene)-2-(4-fluorophenyl)hydrazine (3e).

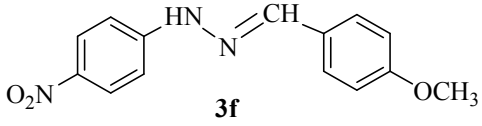


3e

Light brown solid (from methanol). Yield 2.03 g (83%); m.p. 140−141 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3311 (s), 1359 (s), 1595-1502 (s), 3020 (s),

1604 (s), 1245-1211 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.66 (s, 1H), 7.58 (d, J = 9.00 Hz, 2H), 7.04 (dd, J = 9.05, 4.53 Hz, 2H), 6.98 (d, J = 8.54 Hz, 2H), 6.90 (d, J = 8.28 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.04, 158.06, 156.17, 141.33, 137.61, 132.29, 129.71, 127.98, 115.81, 113.73, 55.32. Anal. Calcd. for $C_{14}H_{13}FN_2O$ (244.26, %): C, 68.84; H, 5.36; N, 11.47. Found: C, 68.60; H, 5.14; N, 11.20.

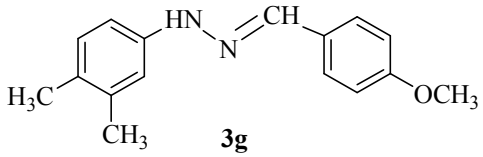
1-(4-Methoxybenzylidene)-2-(4-nitrophenyl)hydrazine (3f).



3f

Light red needles (from methanol). Yield 1.32 g (75%); m.p. 164−165 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3315 (s), 1365 (s), 1525-1500 (s), 3051 (s), 1618 (s), 1271-1209 (m), 1400 (s), 1298 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.86 Hz, 2H), 7.96 (s, 1H), 7.76 (s, 1H), 7.64 (d, J = 8.70 Hz, 2H), 7.10 (d, J = 8.24 Hz, 2H), 6.94 (d, J = 8.62 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.91, 149.64, 141.32, 140.07, 128.26, 126.82, 126.20, 114.29, 111.49, 55.38. Anal. Calcd. for $C_{14}H_{13}N_3O_3$ (271.27, %): C, 61.99; H, 4.83; N, 15.49. Found: C, 62.10; H, 4.84; N, 15.53.

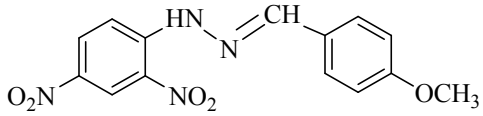
1-(4-Methoxybenzylidene)-2-(3,4-dimethylphenyl)hydrazine (3g).



3g

Light brown solid (from methanol). Yield 2.10 g (83%); m.p. 104−106 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3319 (s), 1353 (s), 1510 (s), 3020 (s), 1614 (s), 1298-1247 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.63 (s, 1H), 7.60 (d, J = 8.50 Hz, 2H), 7.43 (d, J = 7.80 Hz, 1H), 7.02 (d, J = 8.00 Hz, 1H), 6.91 (d, J = 8.50 Hz, 2H), 6.83 (d, J = 7.50 Hz, 1H), 3.84 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.83, 136.78, 136.71, 132.26, 130.22, 128.31, 127.54, 114.05, 110.16, 55.31, 20.03, 18.89. Anal. Calcd. for $C_{16}H_{18}N_2O$ (254.33, %): C, 75.56; H, 7.13; N, 11.01. Found: C, 75.38; H, 6.87; N, 10.92.

1-(4-Methoxybenzylidene)-2-(2,4-dinitrophenyl)hydrazine (3h).



3h

Light orange colored powder (from methanol). Yield 2.65 g (84%); m.p. 258−260 °C; FT-IR (KBr, cm^{-1}) ν_{max} : 3271 (s), 1330 (s), 1585-1510 (s), 3012 (s), 1622 (s), 1249 (m), 1330 (s). ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.07 (s, 1H), 8.94 (s, 1H), 8.14 (dd, J = 8.78, 2.65 Hz, 1H), 7.88 (d, J = 8.32 Hz, 2H), 7.52 (d, J = 8.10 Hz, 2H), 6.78 (d, J = 8.50 Hz, 2H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.52, 148.32, 145.33, 144.50, 130.47, 129.84, 126.29, 124.10, 1107.18, 115.04, 55.98. Anal. Calcd. for $C_{14}H_{12}N_4O_5$ (316.27, %): C, 53.17; H, 3.82; N, 17.71. Found: C, 52.89; H, 3.67; N, 17.64.

2. Crystallographic data for compound 5e.

Table S1 The some selected bond lengths (Å) and angles (°) of compound **5e**

C2-O2	1.374(3)	F1-C18	1.357(3)
N4-N3	1.277(3)	N4-C15	1.415(3)
N1-C8	1.307(3)	N1-N2	1.335(3)
N3-C8	1.407(3)	N2-C9	1.380(3)
C1-O2	1.422(3)	C9-C14	1.388(4)
C14-O1	1.396(3)	O1-C21	1.390(3)
N3-N4-C15	115.3(2)	N4-N3-C8	114.8(2)
C8-N1-N2	120.1(2)	N3-C8-C5	114.3(2)
C20-C15-N4	125.7(2)	C16-C15-N4	114.1(2)
N1-C8-C5	116.5(2)	C2-O2-C1	116.9(2)
F1-C18-C17	118.2(2)	N1-C8-N3	129.2(2)
N2-C9-C14	118.0(2)	F1-C18-C19	118.4(2)
N2-C9-C10	122.8(2)	N1-N2-C9	120.3(2)
C10-C11-Cl1	118.4(2)	C12-C11-Cl1	119.1(2)
C13-C14-O1	121.4(2)	C9-C14-O1	117.2(2)
C21-O1-C14	118.2(2)	C22-C21-O1	123.5(2)

3. Absorption spectra λ_{max} values of formazans 5a–5h in various solvents.

Table S2 Absorption spectral λ_{max} values of formazans **5a**–**5h** in various solvents.

4. NMR Spectra of Final Compounds (5a−5h)

	λ_{max}.(nm)						
Comp.	DMSO	DMF	EtOH	MeOH	Acetone	Dioxane	EtOAc
5a	513	515	501	506	504	507	507
	293	302	291	289		293	293
5b	521	513	511,	493	496	500	499
	301	301	499, 272	299		275	300, 272
5c	540	531	533	525	523	531	531
	299	299	522, 298	298		295	298
5d	533	532	531	521	523	531	531
	295	298	297	295		296	298
5e	512	507	508	504	506	507	508
	294	308	293	294		292	294
5f	475	499	533	546	526	545	534
	385	367	367, 301	393, 289	367	362, 300	362, 302
5g	513	508	501	501	504	504	502
	301	301	297	297		296	296
5h	400	390	388	390	384	375, 352	379
Comp.	Propanol	$CHCl_3$	THF	1-Butanol	Toluene	Cyclohexane	n-Hexane
5a	505	507	509	511	515	510	506
	293	296	288	293	295	291	291
5b	500	505	505	498	518	506	494
	301, 275	303	302	275	302	300, 275	366, 301
5c	531	531	534	532	538	535	532
	299	298	302	298	298	298	299
5d	532	530	530	531	535	533	528
	298	298	293	296	296	295	297
5e	509	509	511	510	522	519	516
	293	296	292	291		292	291
5f	535	546	537	534	554	551	541
	360, 304	371, 304	365, 303	365, 303	365	358, 299	360, 305
5g	503	504	508	504	516	500	500
	299	299	297	297	299	298	296
5h	385, 304	384	380, 292	391	378	366	421, 371

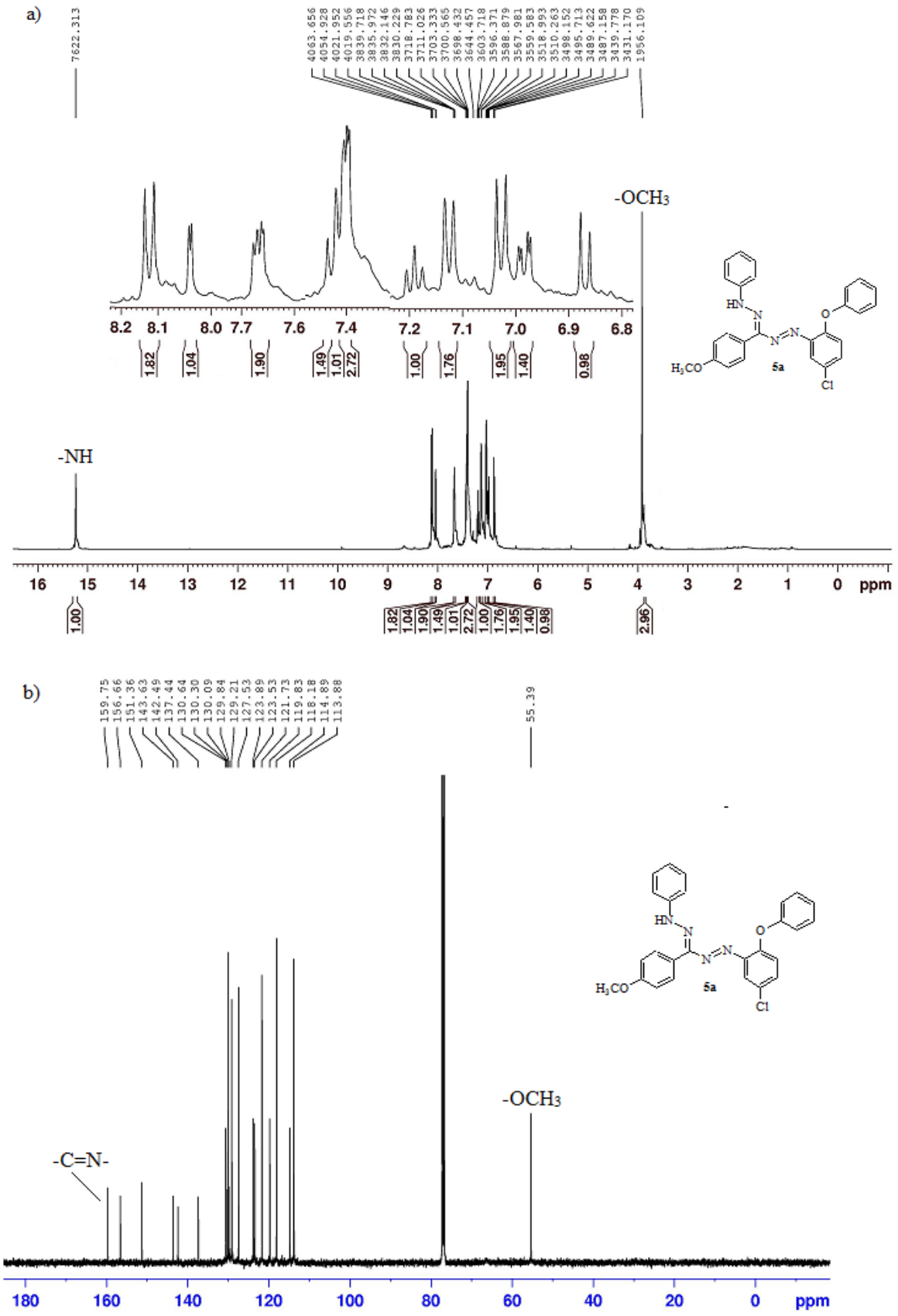


Figure S1 Compound **5a**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

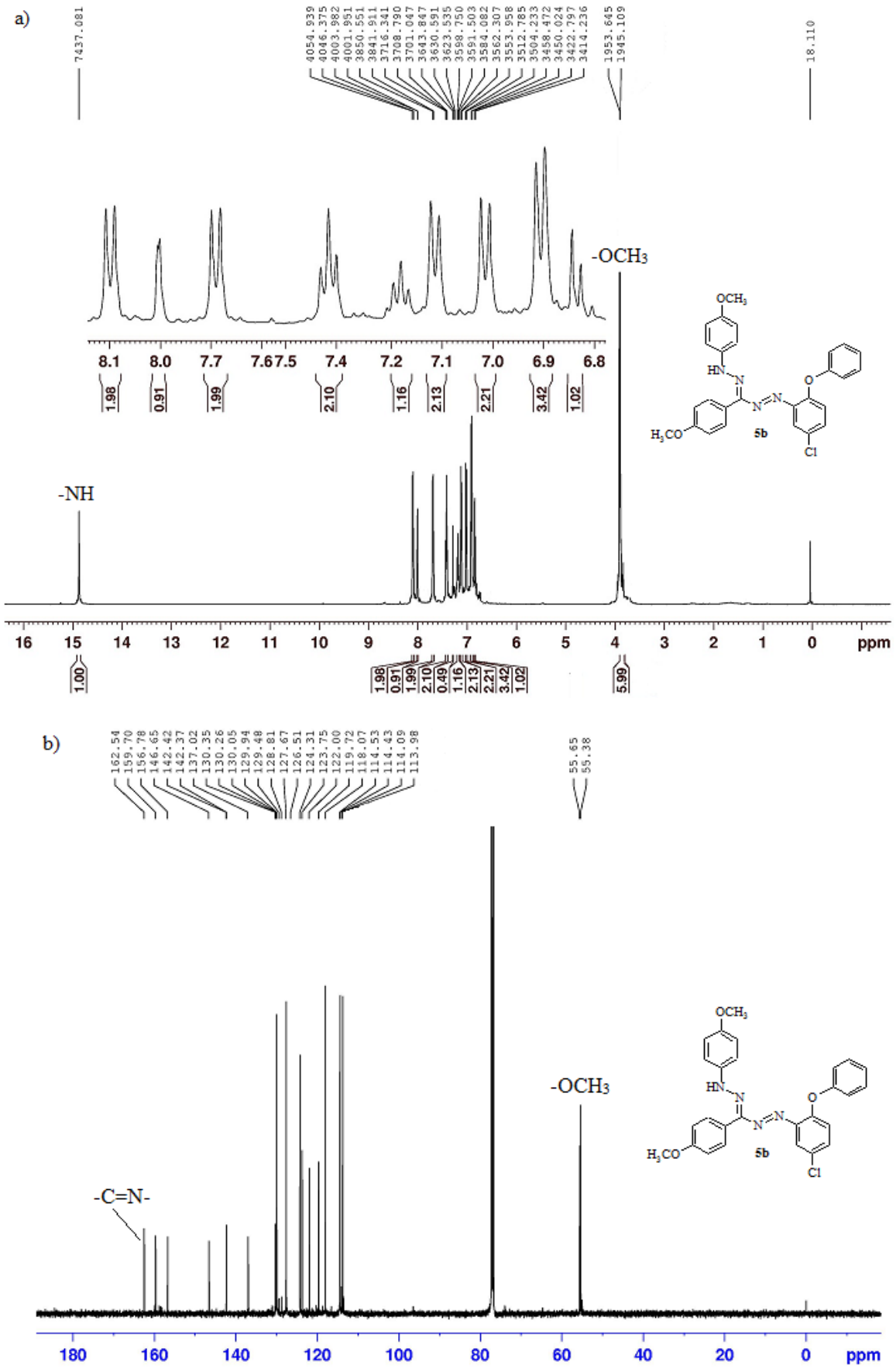


Figure S2 Compound **5b**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

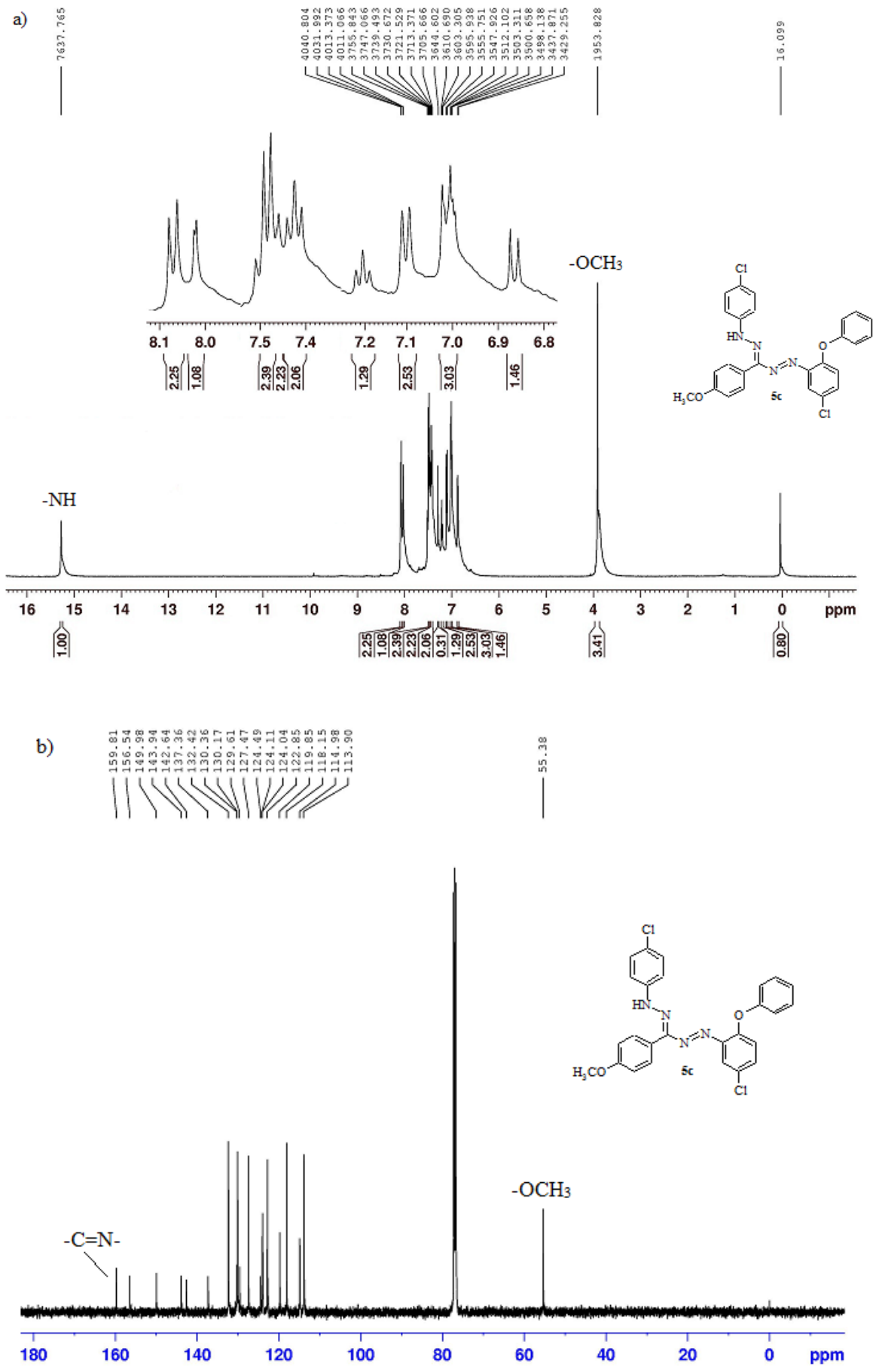


Figure S3 Compound **5c**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

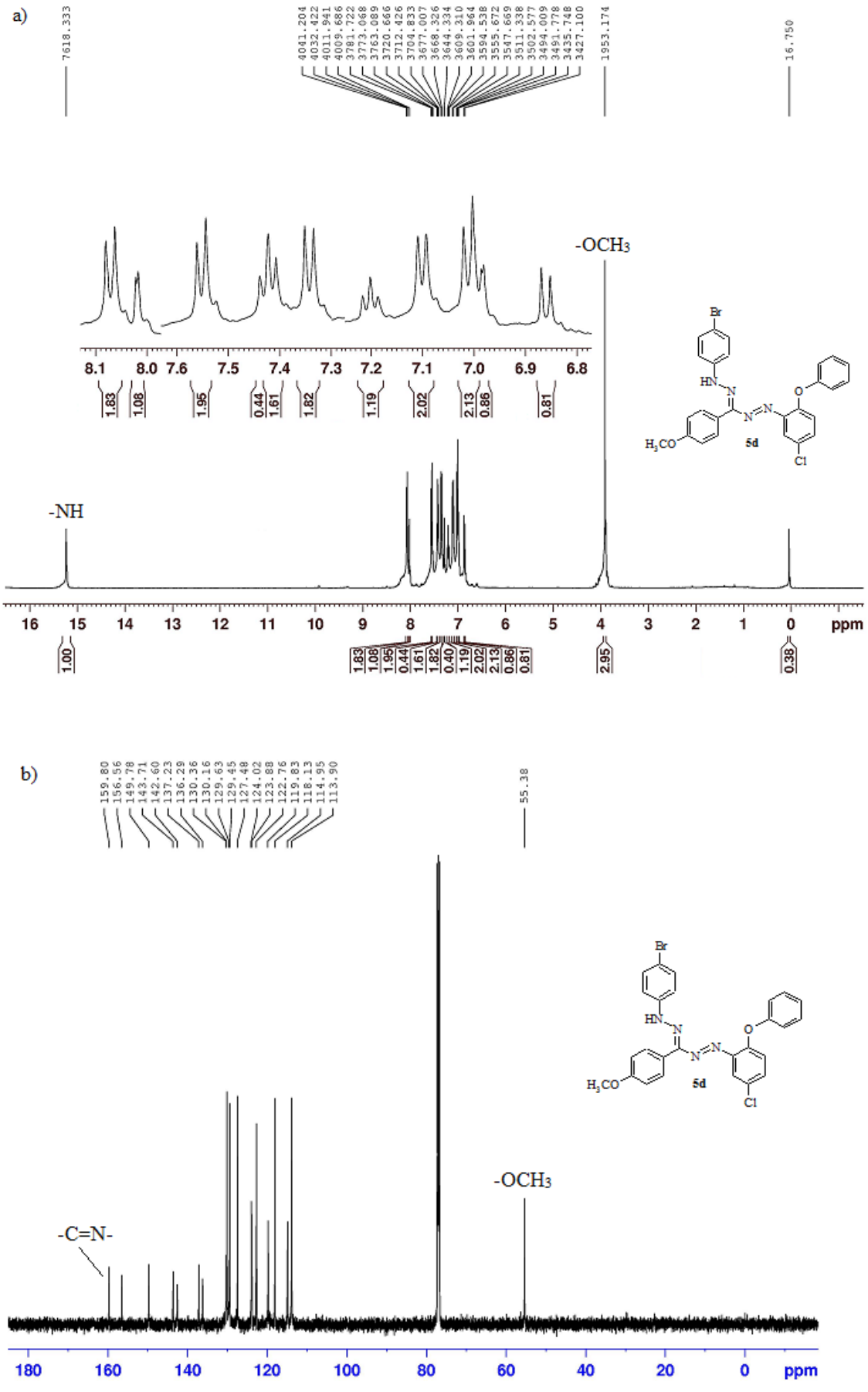


Figure S4 Compound **5d**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

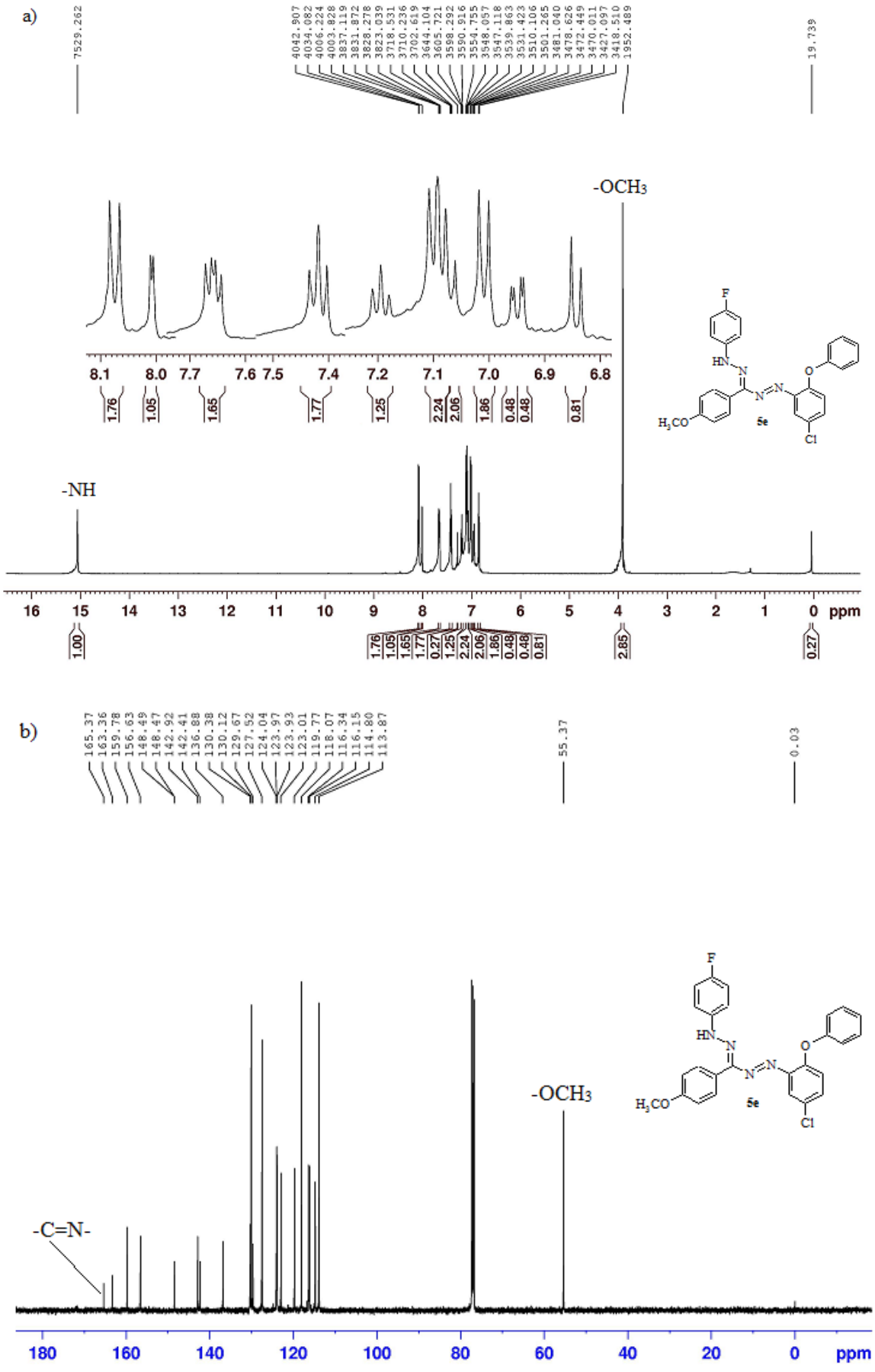


Figure S5 Compound **5e**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

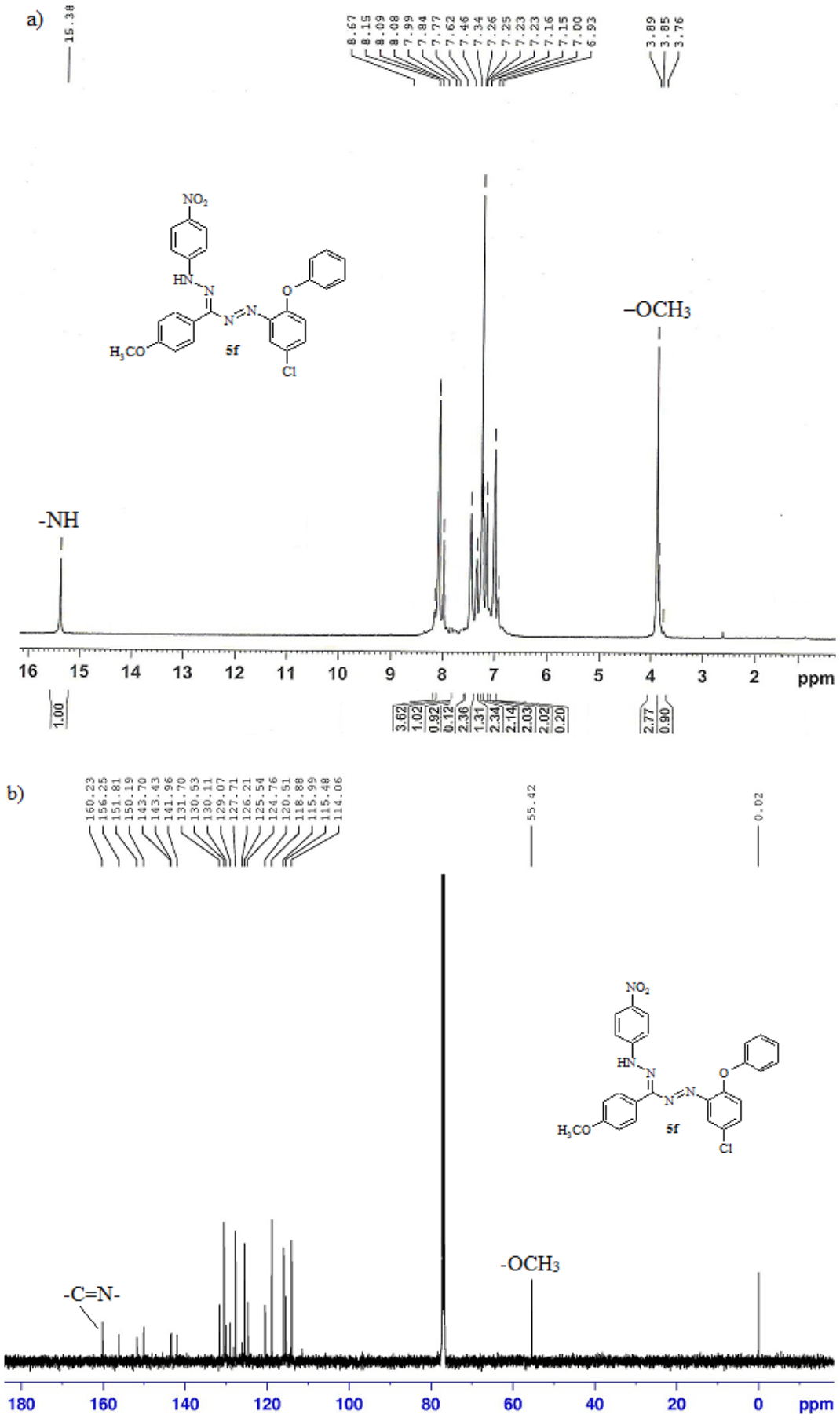


Figure S6 Compound **5f**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

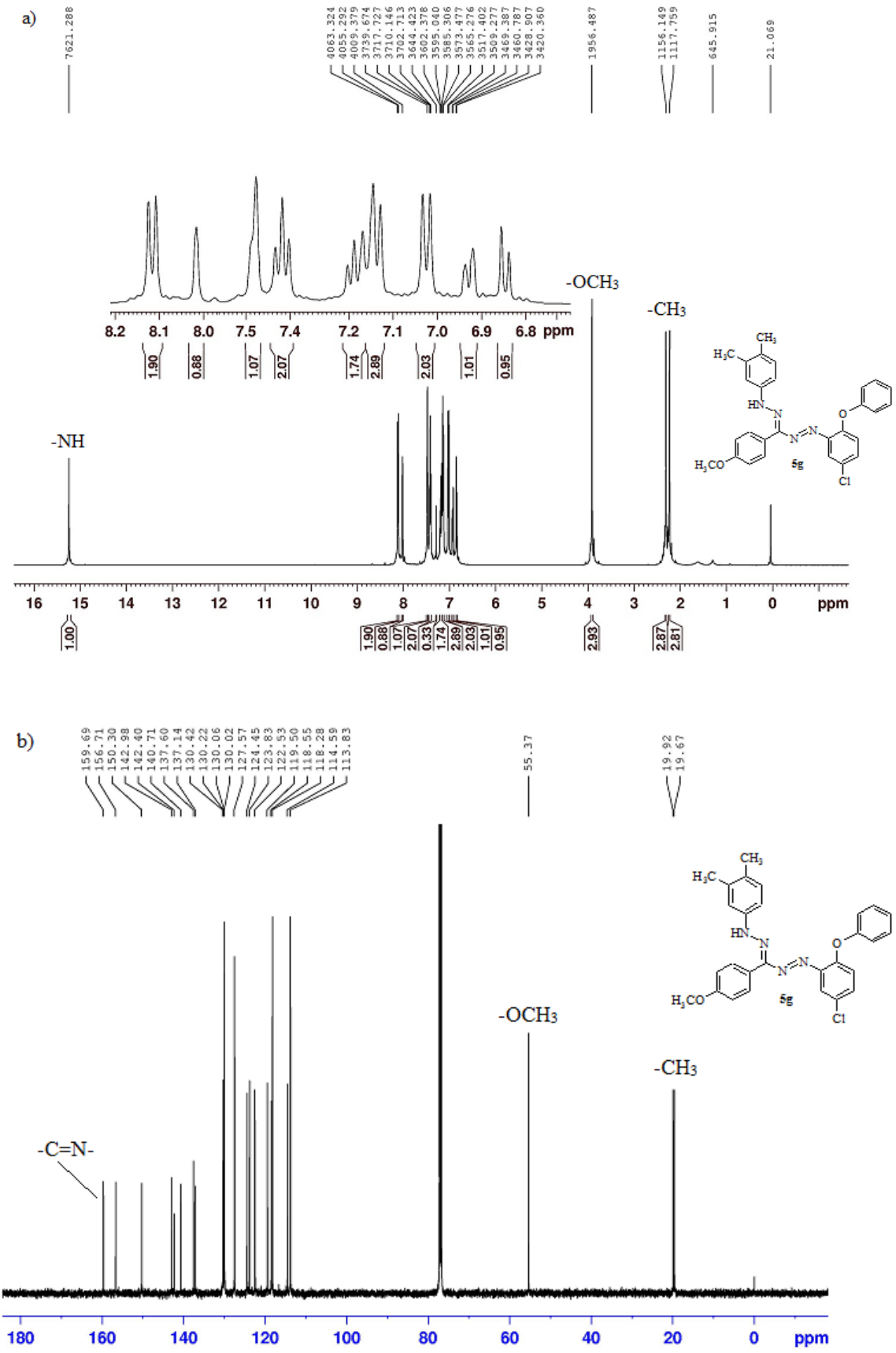


Figure S7 Compound **5g**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.

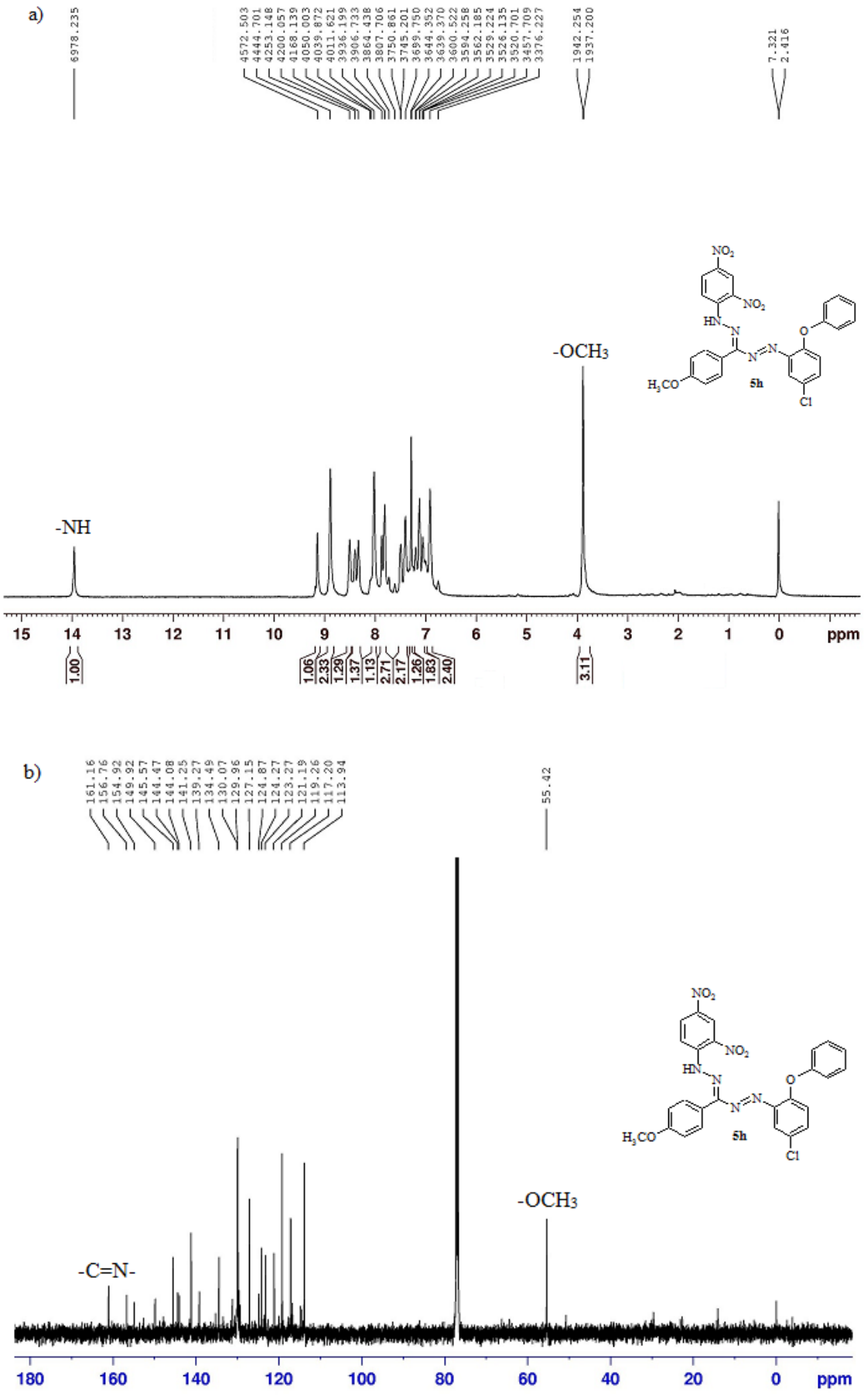


Figure S8 Compound **5h**: a) ^{1}H NMR, b) ^{13}C NMR spectrum.