Supplementary Information

High Selective *N*-Acylhydrazones Silver(I) Complexes against Tuberculosis

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Experimental procedures of compounds

(*E*)-*N*'-(Benzylidene)isonicotinohydrazide (IZBEN)

In a round bottom flask, 2.0 mmol (0.274 g) of INH, dissolved in 20.0 mL ethanol, were added. Then, 2.0 mmol (0.20 mL) of benzaldehyde were slowly added. Catalytic amount of glacial acetic acid was added, and the mixture was stirred at 70 ºC for 2 h. The colorless precipitate was collected by filtration, washed with ethanol and stored in a desiccator under silica.

(*E*)-*N*'-(2-Methoxybenzylidene)isonicohydrazide (IZoAN)

The IZoAN was synthesized following the same procedure described to IZBEN. However, 2-methoxybenzaldehyde was used instead of benzaldehyde.

(*E*)-*N'*-(3-Methoxybenzylidene)isonicohydrazide (IZmAN)

The IZmAN was synthesized following the same procedure described to IZBEN. However, 3-methoxybenzaldehyde was used instead of benzaldehyde.

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(*E*)-*N'*-(4-methoxybenzylidene)isonicohydrazide monohydrated (IZpAN)

The IZpAN was synthesized following the same procedure described to IZBEN. However, 4-methoxybenzaldehyde was used instead of benzaldehyde.

(*E*)-*N'*-(2-nitrobenzylidene)isonicohydrazide monohydrated (IZoNIT)

The IZoNIT was synthesized following the same procedure described to IZBEN. However, 2-nitrobenzaldehyde was used instead of benzaldehyde.

(*E*)-*N'*-(3-nitrobenzylidene)isonicohydrazidemonohydratate (IZmNIT)

The IZmNIT was synthesized following the same procedure described to IZBEN. However, 3-nitrobenzaldehyde was used instead of benzaldehyde.

(*E*)-*N'*-(4-nitrobenzylidene)isonicohydrazide (IZpNIT)

The IZpNIT was synthesized following the same procedure described to IZBEN. However, 4-nitrobenzaldehyde was used instead of benzaldehyde.

$[AgNO_3(C_{13}H_{11}N_3O)]$(AgIZBEN)

In a round bottom flask, 2.0 mmol (0.450 g) of IZBEN, dissolved in 20.0 mL acetonitrile, was added. Then, 1.0 mmol (0.169 g) of silver nitrate was slowly added and the mixture was stirred at 70 ºC for 2 h in the dark. The pale-yellow precipitate was collected by filtration, washed with ethanol and stored in a desiccator under silica.

$[Ag(C_{14}H_{13}N_3O_2)]NO_3$(AgIZoAN)

A solution of 10.0 mL of methanol containing silver nitrate (1.0 mmol, 0.169 g) was added to IZoAN (2.0 mmol, 0.510 g), previously dissolved in 30 mL of methanol. The final solution was stirred for 2.5 h, at 60 °C, in the dark. The silver(I) complex was obtained as a pale yellow polycrystalline solid, which was separated by simple filtration and stored in a desiccator under silica.

$[AgNO_3(C_{14}H_{13}N_3O_2)]$ (AgIZmAN)

The AgIZmAN was synthesized following the same procedure described to AgIZoAN. However, IZmAN was used as a ligand instead IZoAN. The silver(I) complex was obtained as a pale yellow polycrystalline solid, which was separated by simple filtration and stored in a desiccator under silica.

$[AgNO_3(C_{14}H_{13}N_3O_2)_2]H_2O$ (AgIZpAN)

The AgIZpAN was synthesized following the same procedure described toAgIZoAN. However, IZpAN was used as a ligand instead IZoAN. The yellow polycrystalline solid obtained was separated by simple filtration and stored in a desiccator under silica.

$[AgNO_3(C_{13}H_{10}N_4O_3)]$ (AgIZoNIT)

In a round bottom flask, 2.0 mmol (0.540 g) of IZoNIT was dissolved in 30.0 mL of ethanol in reflux. Then, 1.0 mmol (0.169 g) of silver nitrate were slowly added and the mixture was stirred for 2 h in the dark.

$[AgNO_3(C_{13}H_{10}N_4O_3)_2]$ (AgIZmNIT)

The AgIZmNIT was synthesized following the same procedure described to AgIZoNIT. However, IZmNIT were used instead IZoNIT.

$[AgNO_3(C_{13}H_{10}N_4O_3)_2]$ (AgIZpNIT)

The AgIZpNIT was synthesized following the same procedure described to IZoNIT. However, IZpNIT was used instead IZoNIT.

FTIR spectra

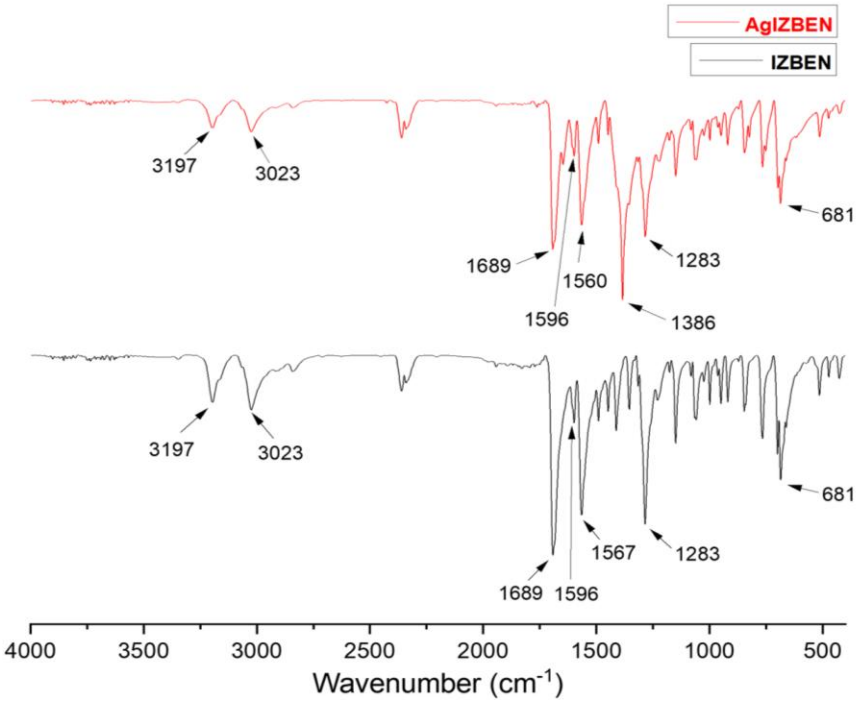


Figure S1. Experimental FTIR (KBr) spectra for IZBEN and AgIZBEN, range 4000-400 cm^{-1}.

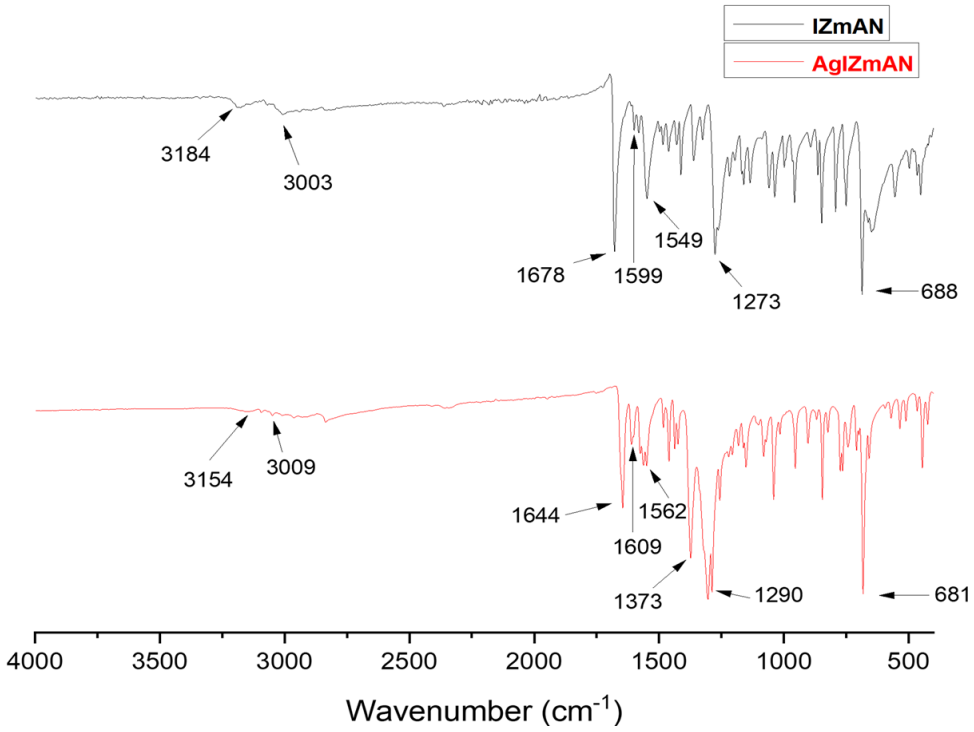


Figure S2. Experimental FTIR (KBr) spectra for IZmAN and AgIZmAN, range 4000-400 cm^{-1}.

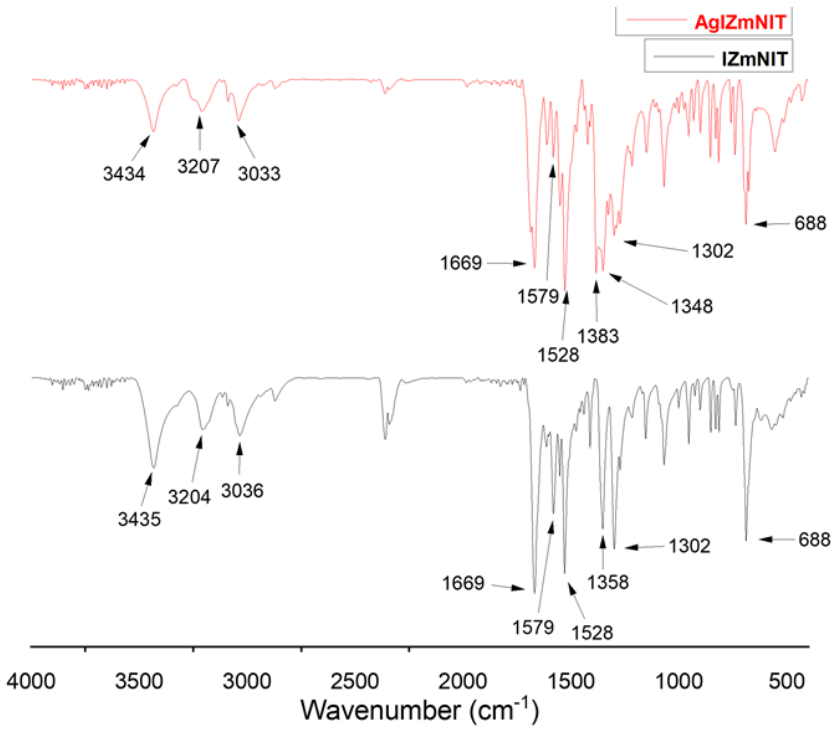


Figure S3. Experimental FTIR (KBr) spectra for IZmNIT and AgIZmNIT, range 4000-400 cm^{-1}.

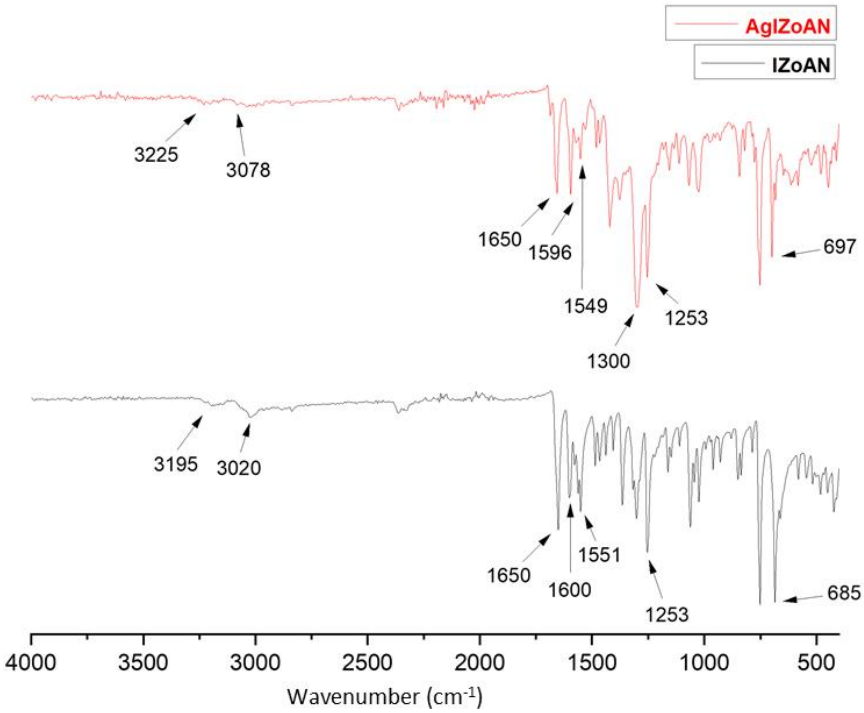


Figure S4. Experimental FTIR (KBr) spectra for IZoAN and AgIZoAN, range 4000-400 cm^{-1}.

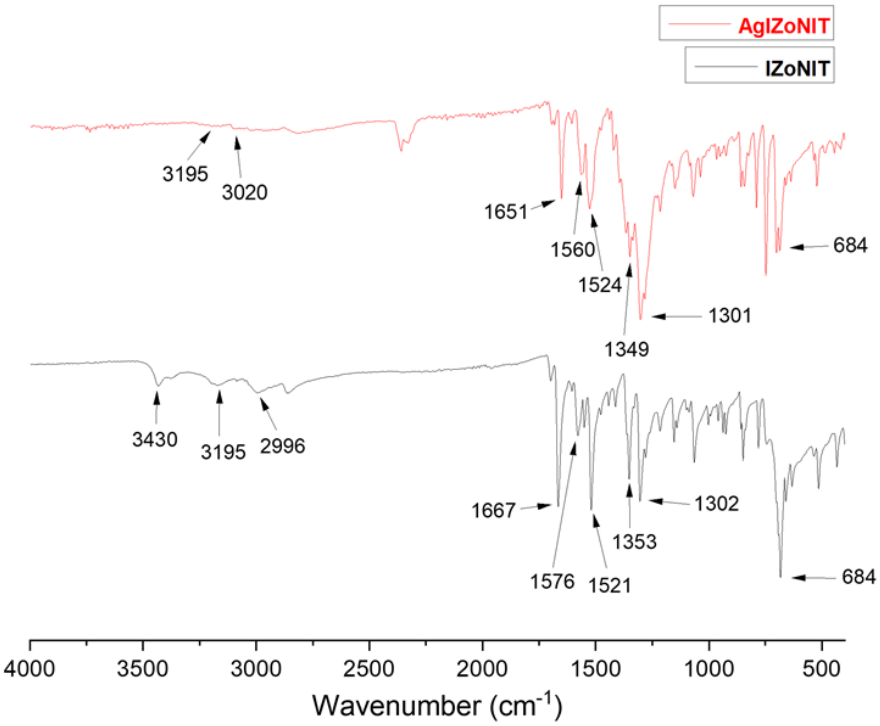


Figure S5. Experimental FTIR (KBr) spectra for IZoNIT and AgIZoNIT, range 4000-400 cm^{-1}.

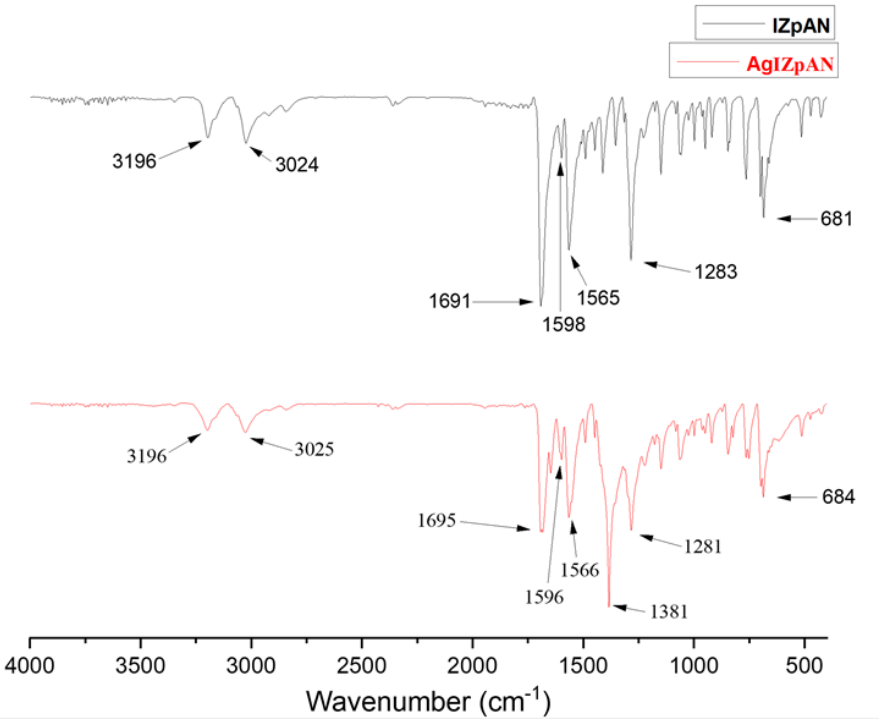


Figure S6. Experimental FTIR (KBr) spectra for IZpAN and AgIZpAN, range 4000-400 cm^{-1}.

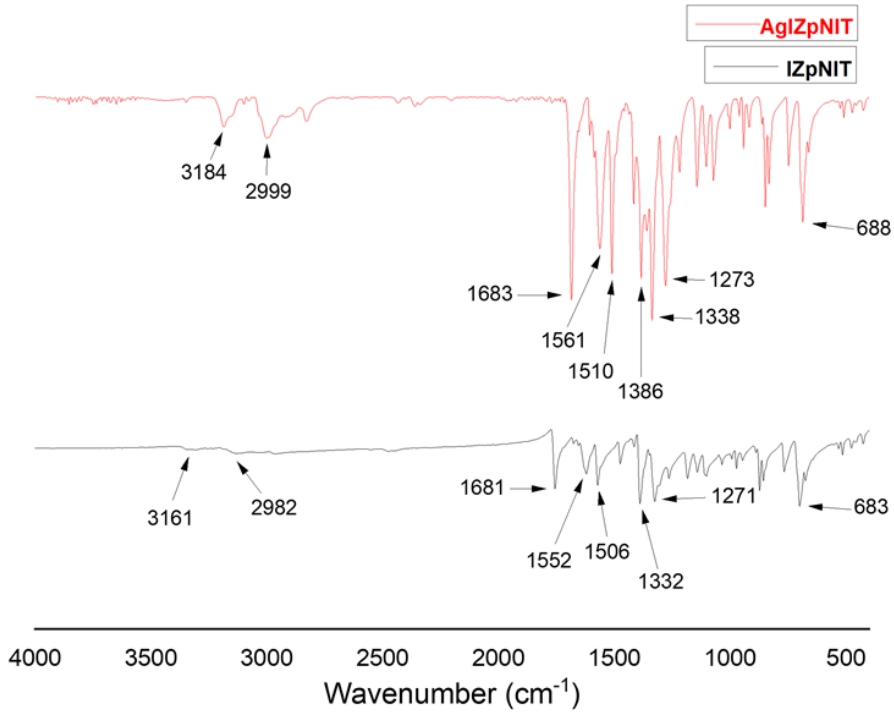


Figure S7. Experimental FTIR (KBr) spectra for IZpNIT and AgIZpNIT, range 4000-400 cm^{-1}.

^{1}H, $^{13}C\{^{1}H\}$, $\{^{1}H\text{-}^{15}N\}$ HMBC NMR (spectra and data)

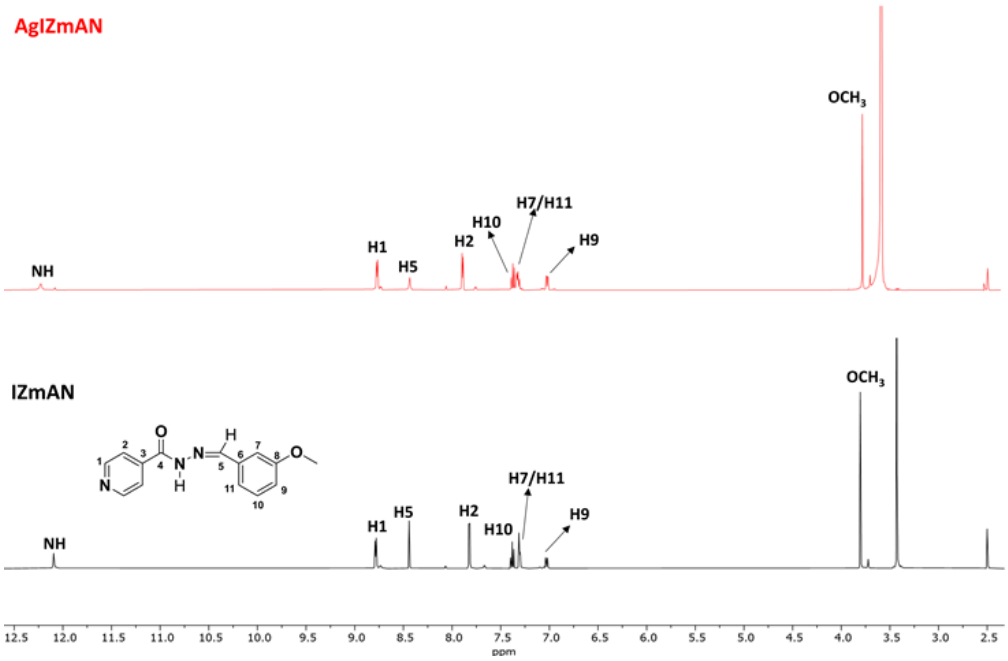


Figure S8. ^{1}H NMR (500 MHz, DMSO-d_6) of IZmAN and AgIZmAN.

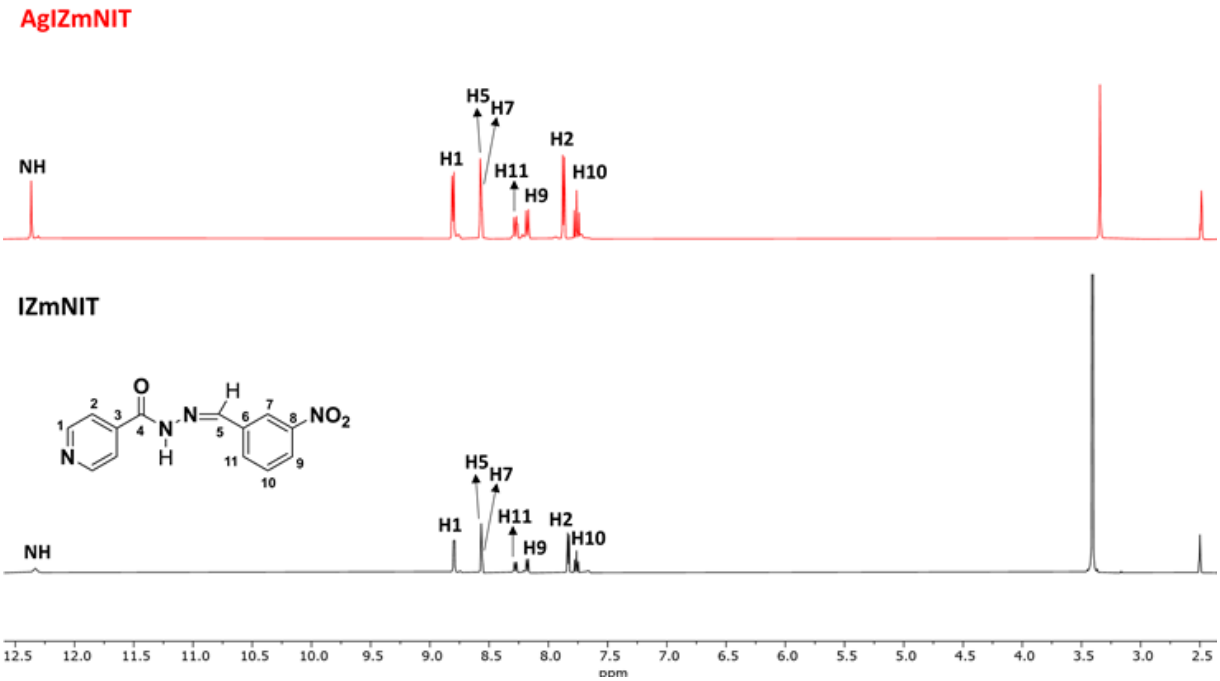


Figure S9. ^{1}H NMR (500 MHz, DMSO-d_6) of IZmNIT and AgIZmNIT.

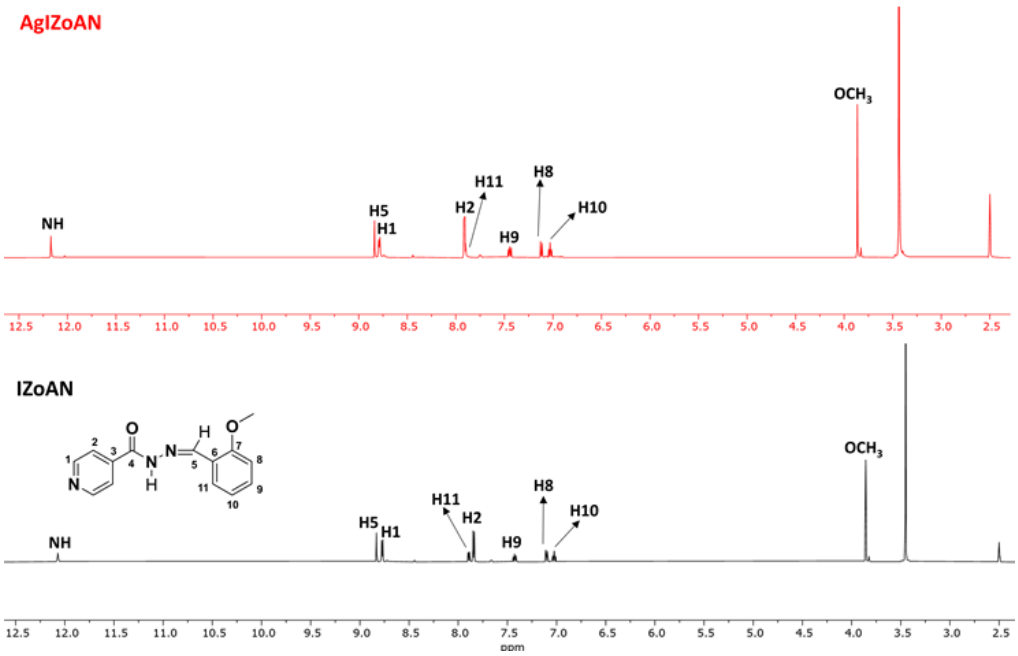


Figure S10. ^{1}H NMR (500 MHz, DMSO-d_6) of IZoAN and AgIZoAN.

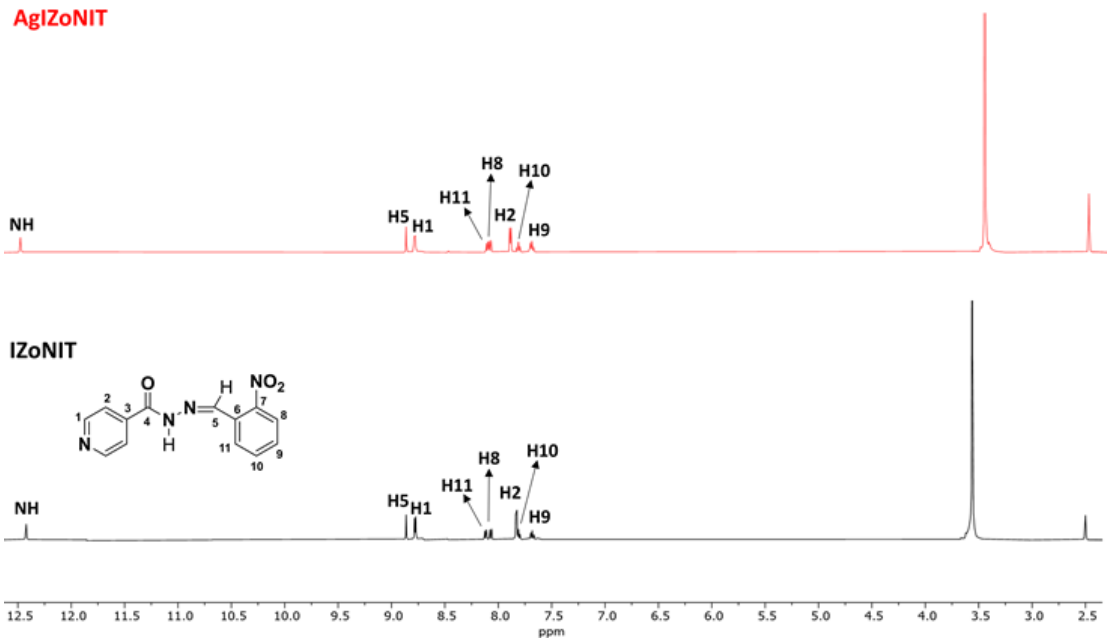


Figure S11. ^{1}H NMR (500 MHz, DMSO-d_6) of IZoNIT and AgIZoNIT.

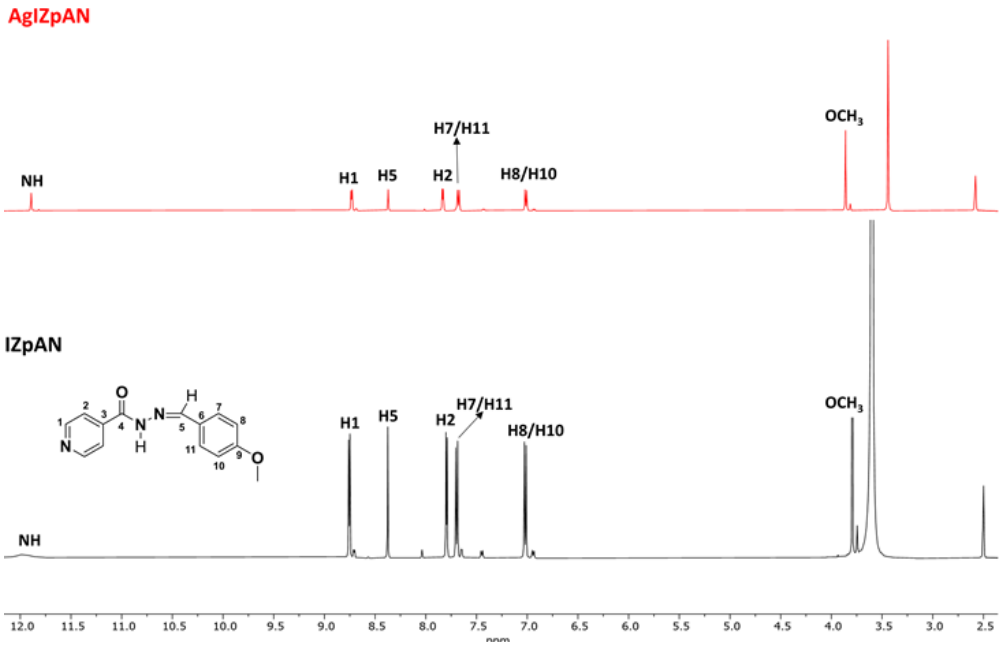


Figure S12. ^{1}H NMR (500 MHz, DMSO-d_6) of IZpAN and AgIZpAN.

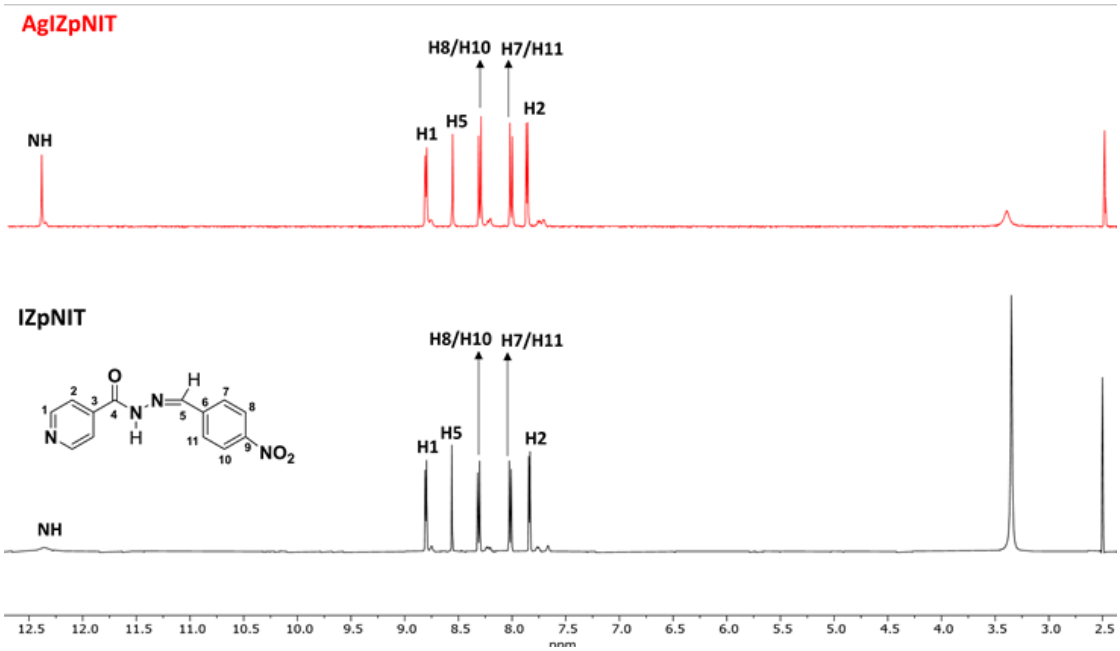


Figure S13. ^{1}H NMR (500 MHz, DMSO-d_6) of IZpNIT and AgIZpNIT.

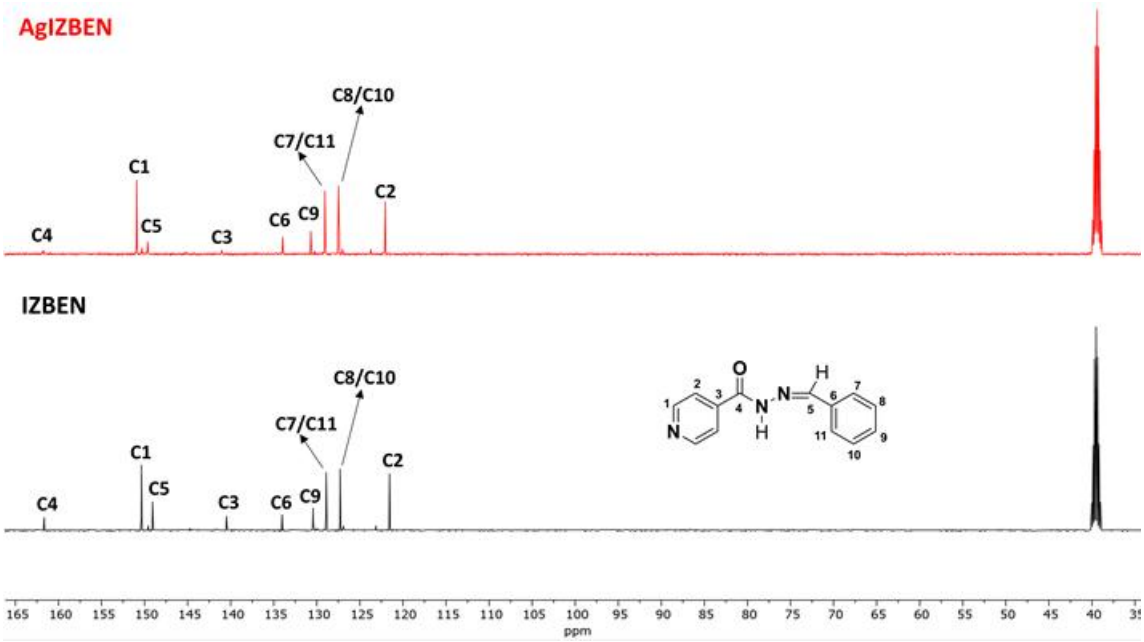


Figure S14. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZBEN and AgIZBEN.

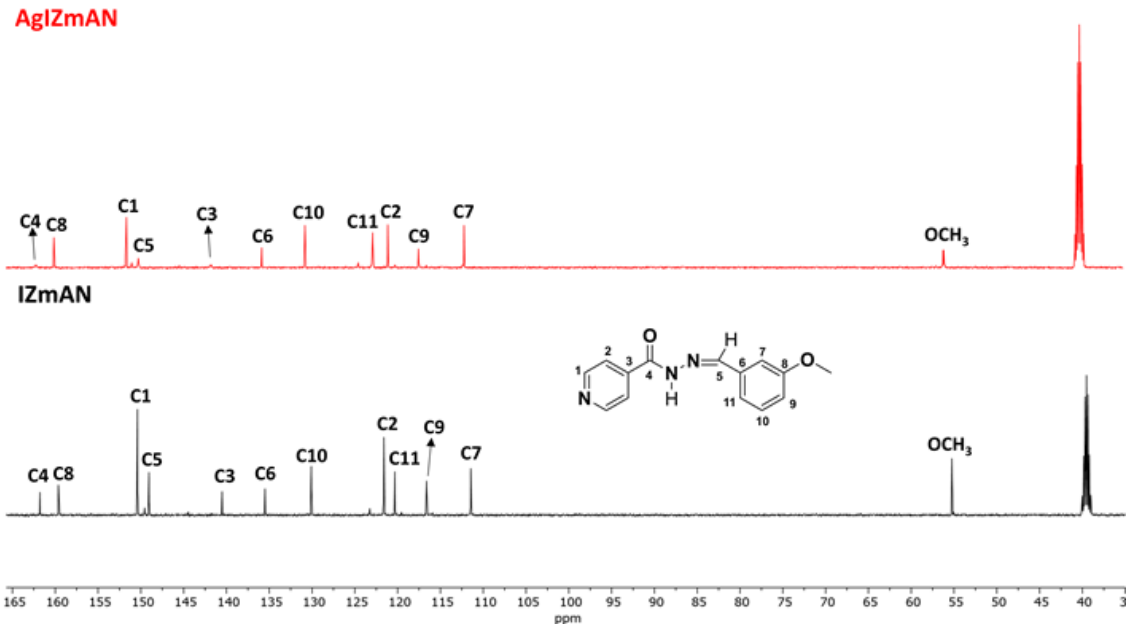


Figure S15. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZmAN and AgIZmAN.

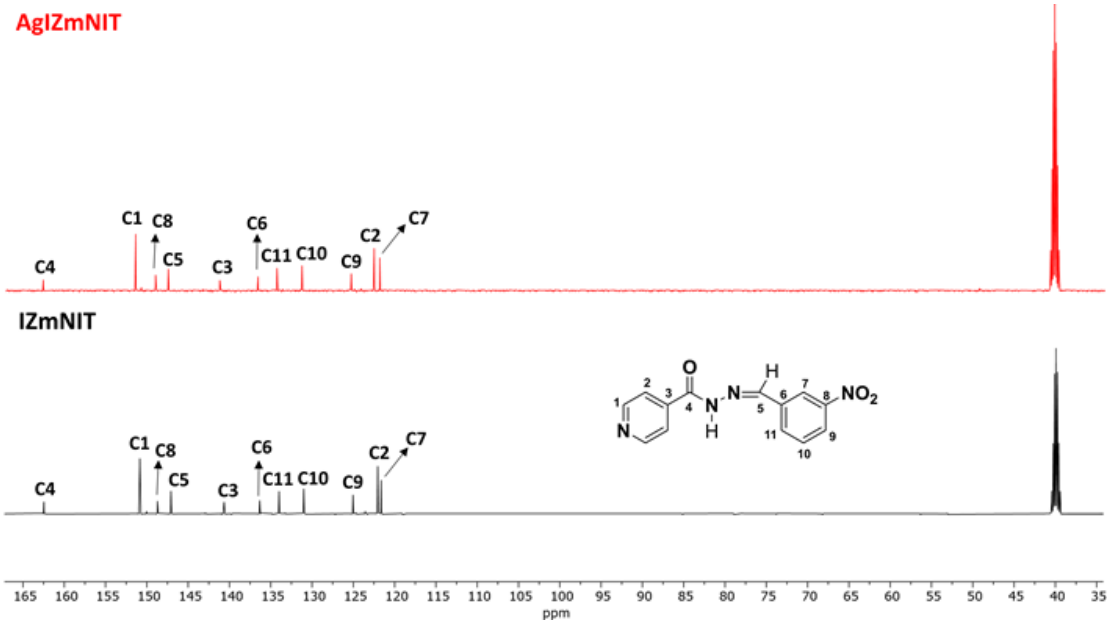


Figure S16. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZmNIT and AgIZmNIT.

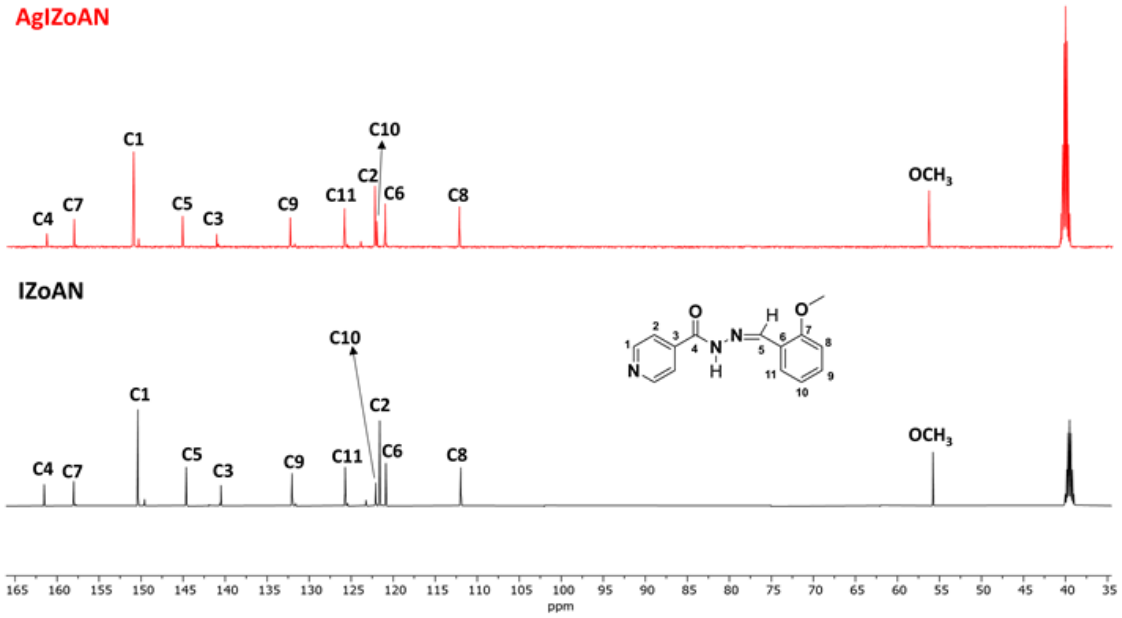


Figure S17. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZoAN and AgIZoAN.

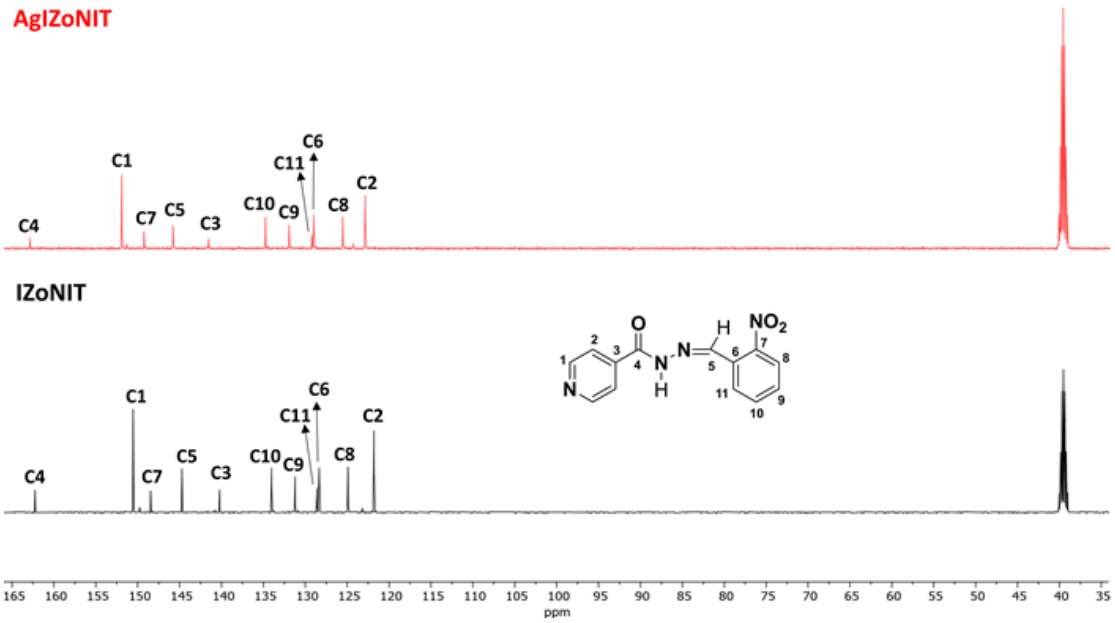


Figure S18. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZoNIT and AgIZoNIT.

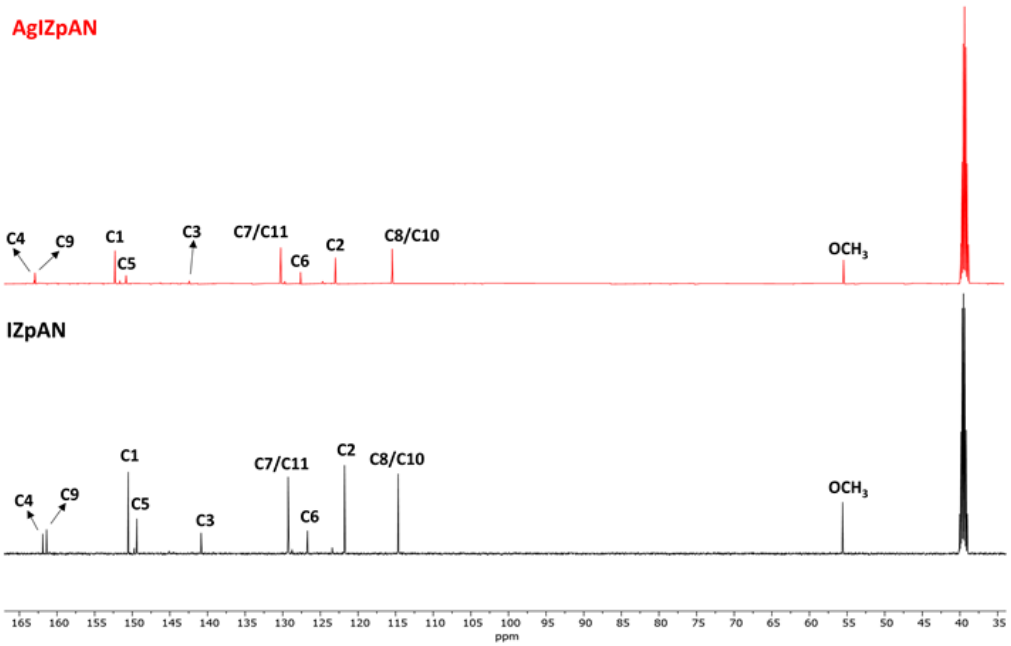


Figure S19. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZpAN and AgIZpAN.

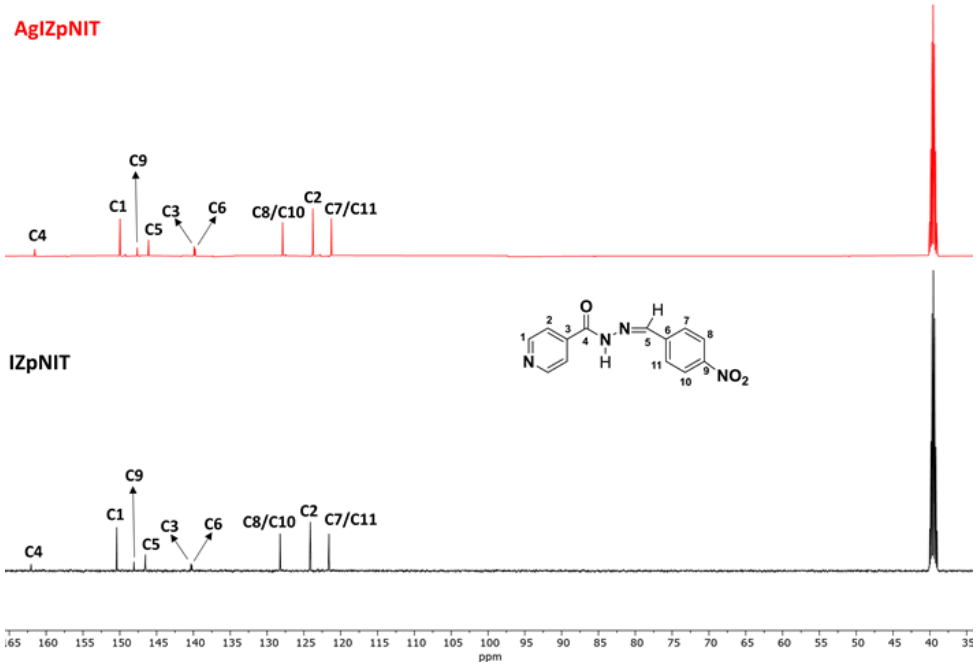


Figure S20. $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) of IZpNIT and AgIZpNIT.

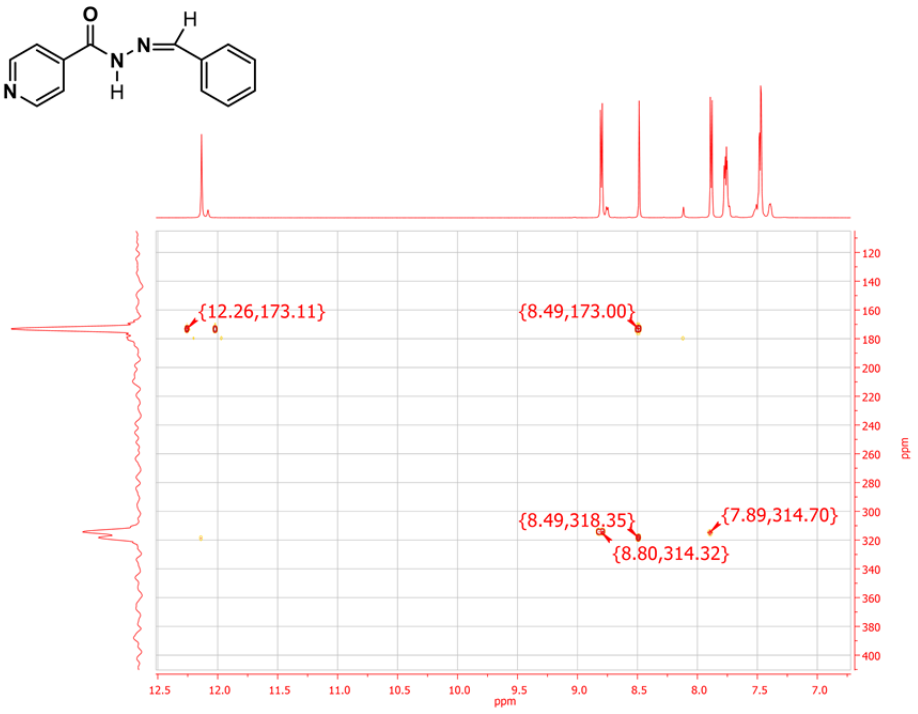


Figure S21. HMBC $\{^{1}H\text{-}^{15}N\}$ correlation maps (DMSO-d_6) of complex AgIZBEN.

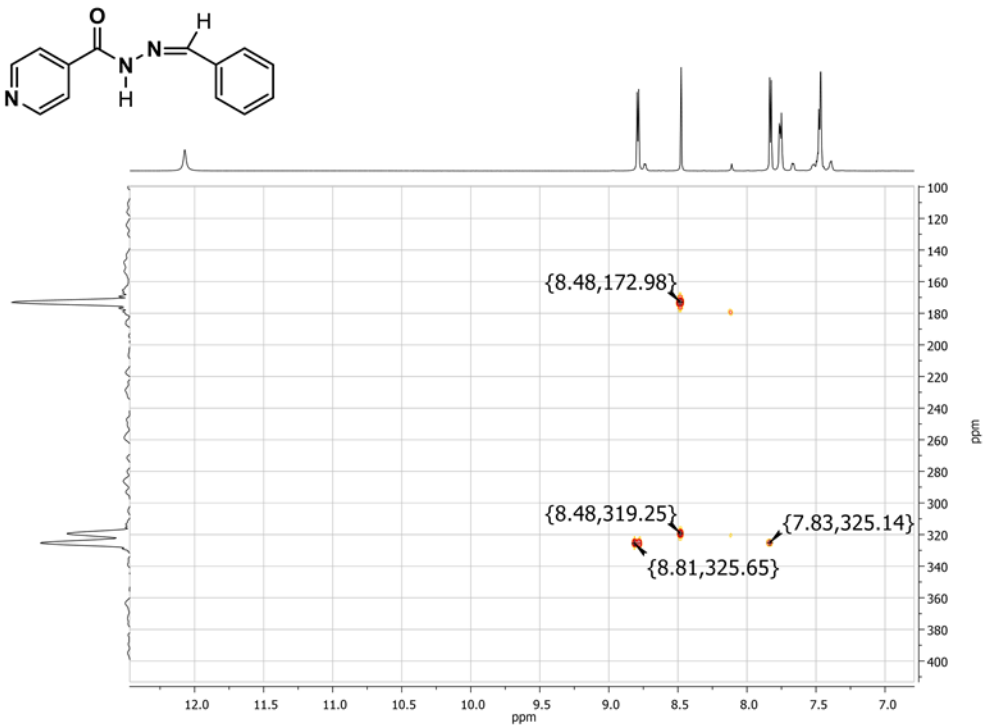


Figure S22. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of ligand IZBEN.

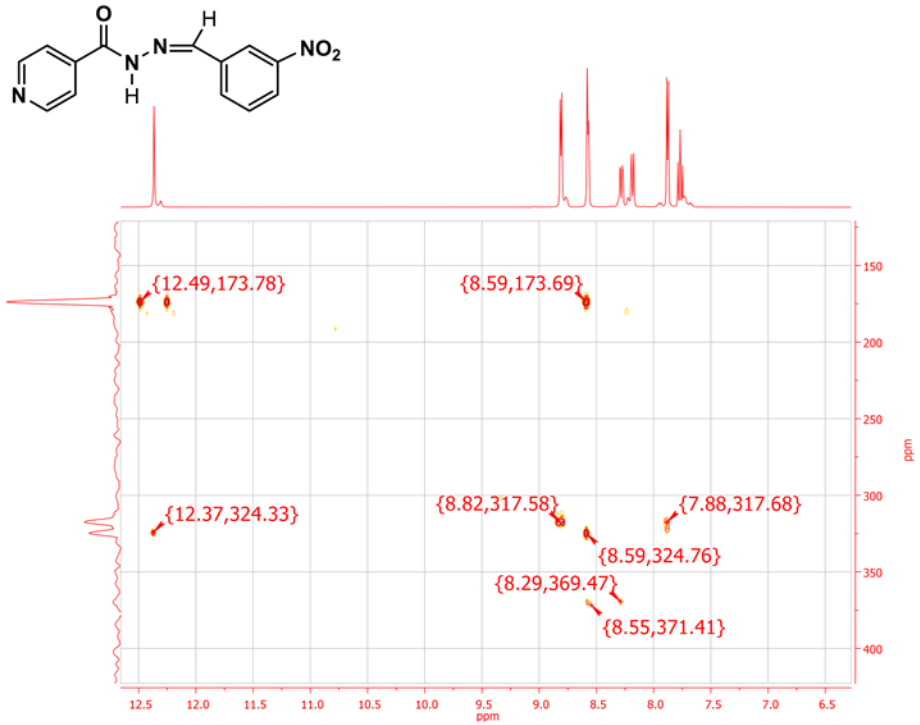


Figure S23. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of complex AgIZmNIT.

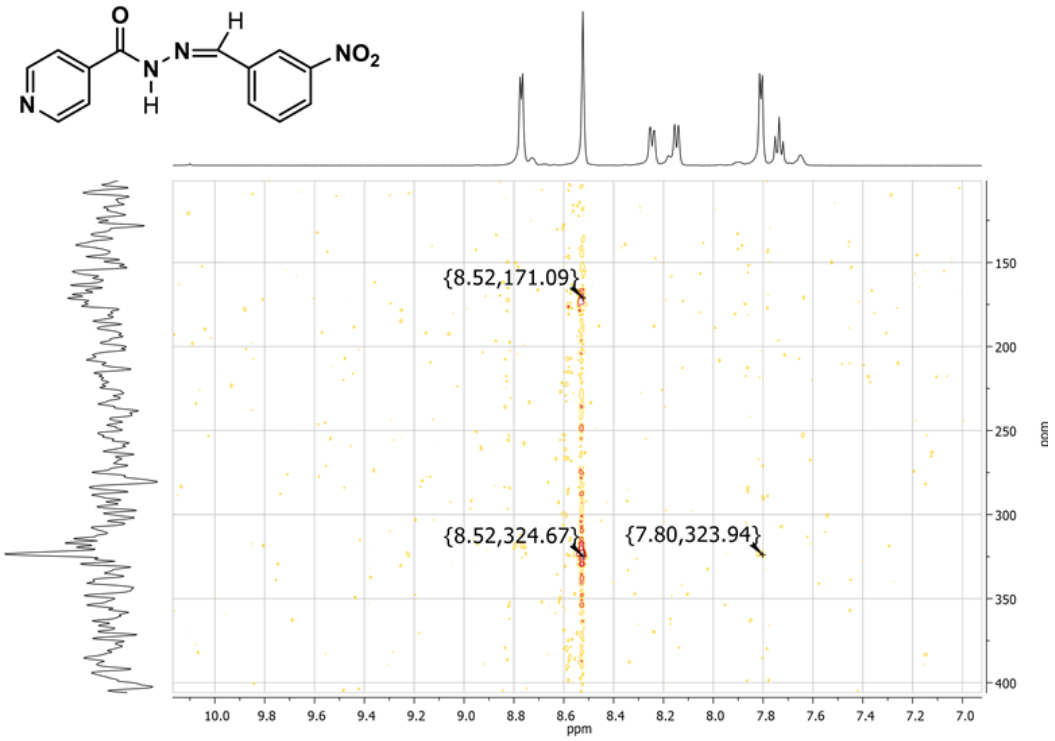


Figure S24. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of ligand IZmNIT.

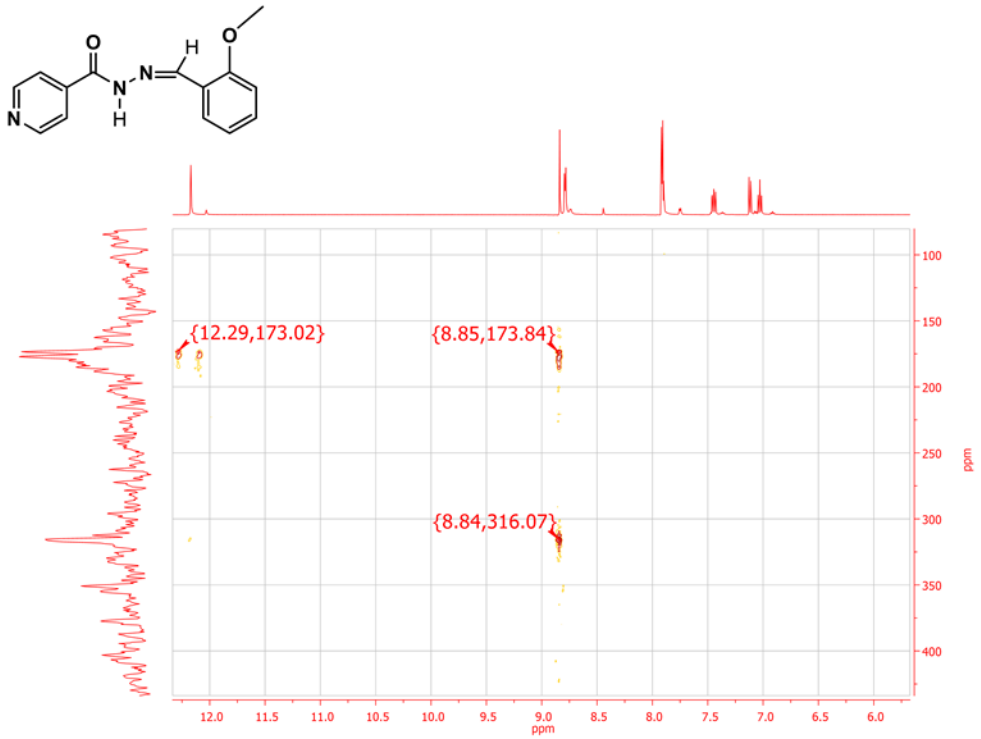


Figure S25. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of complex AgIZoAN.

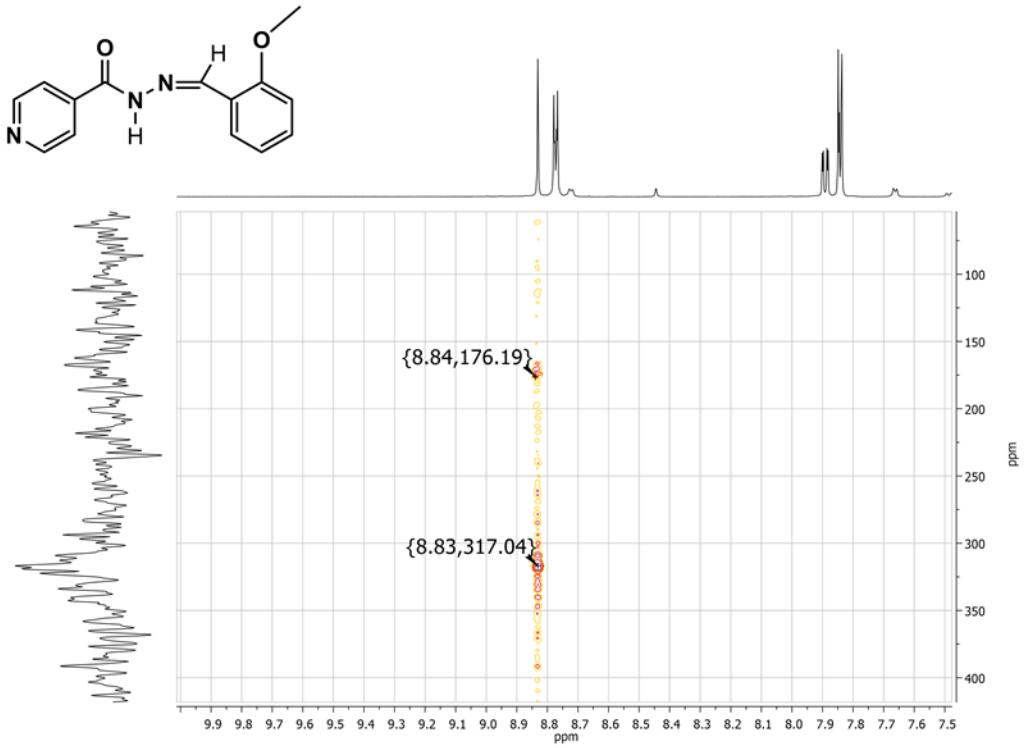


Figure S26. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of ligand IZoAN.

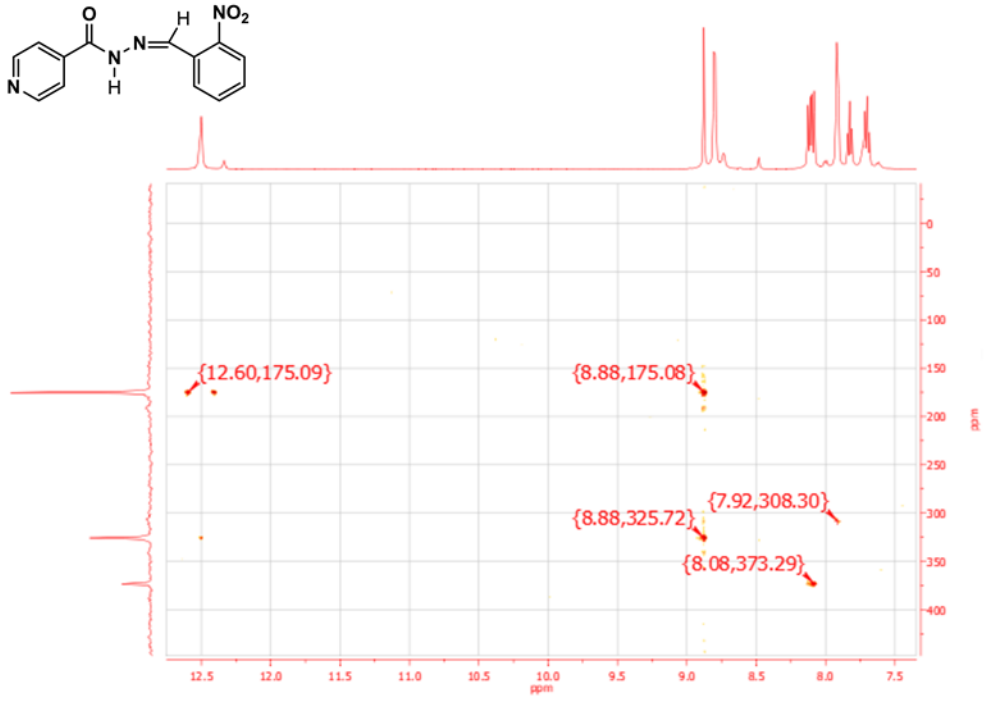


Figure S27. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of complex AgIZoNIT.

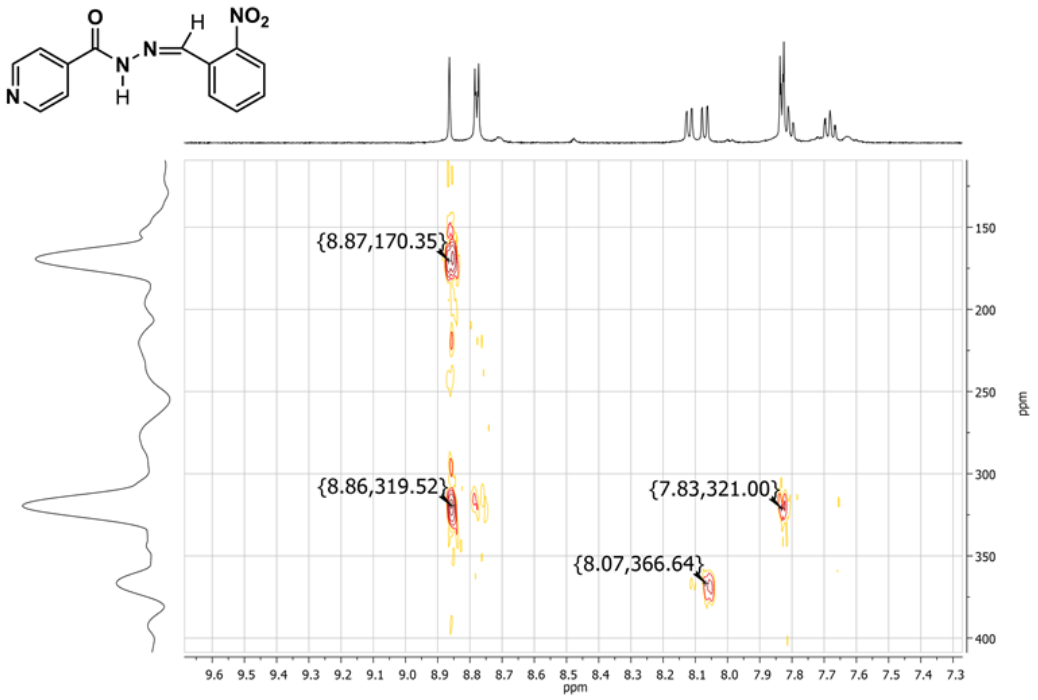


Figure S28. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of ligand IZoNIT.

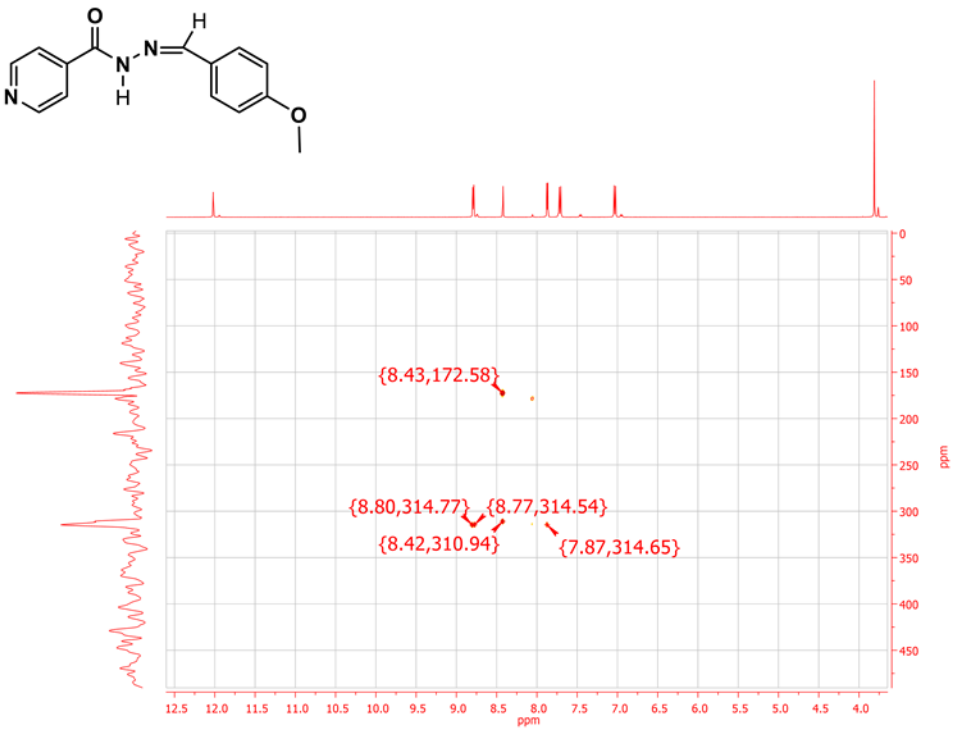


Figure S29. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of complex AgIZpAN.

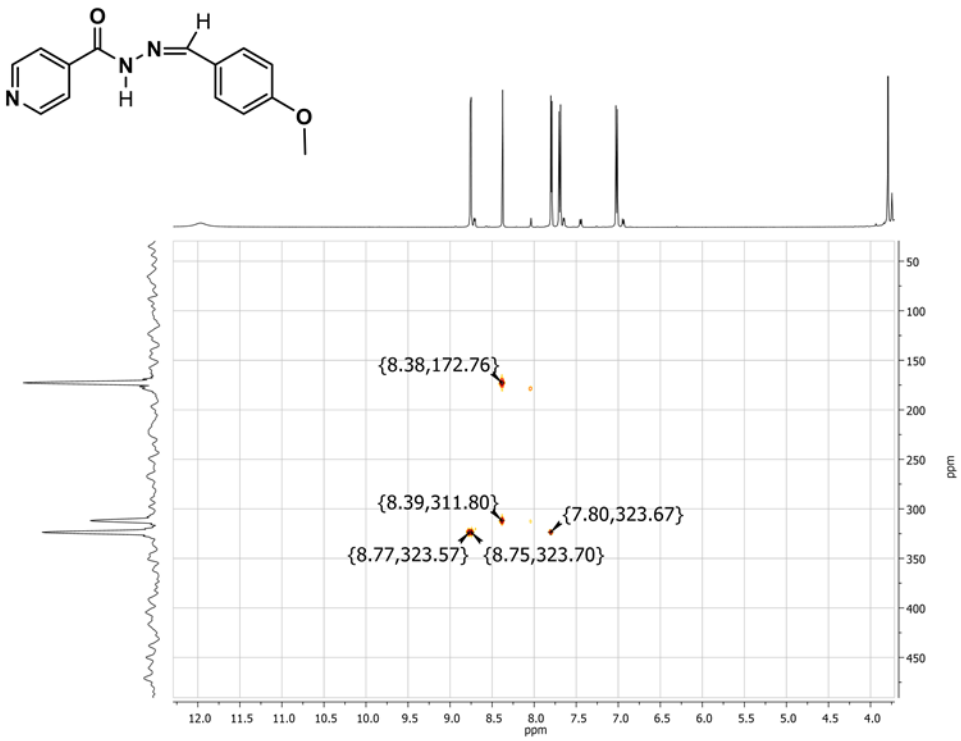


Figure S30. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of ligand IZpAN.

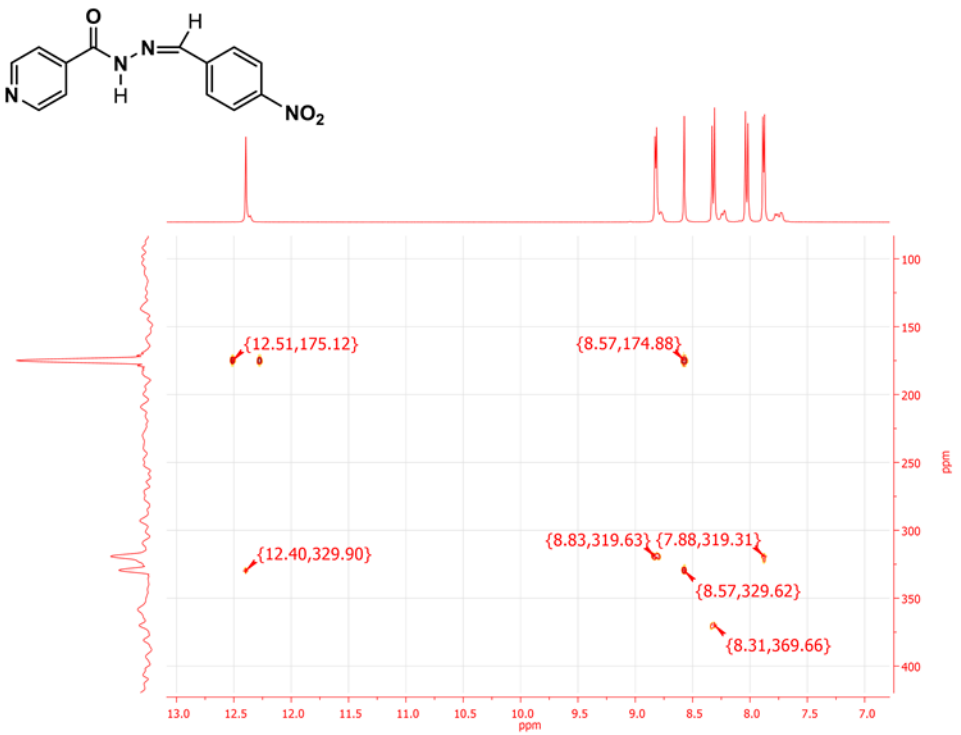
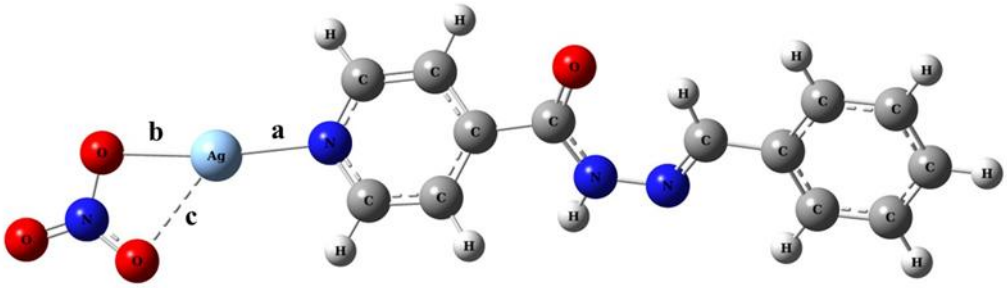
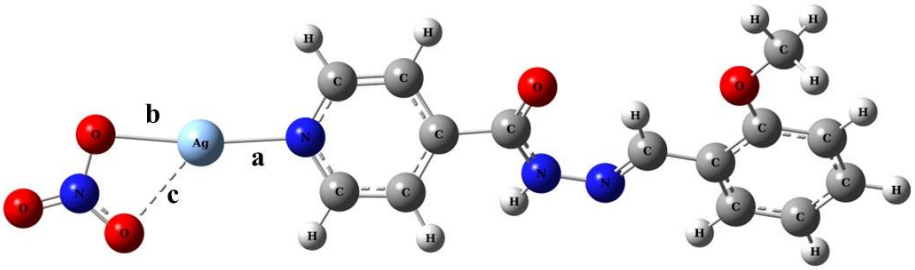


Figure S31. HMBC {^{1}H-^{15}N} correlation maps (DMSO-d_6) of complex AgIZpNIT.



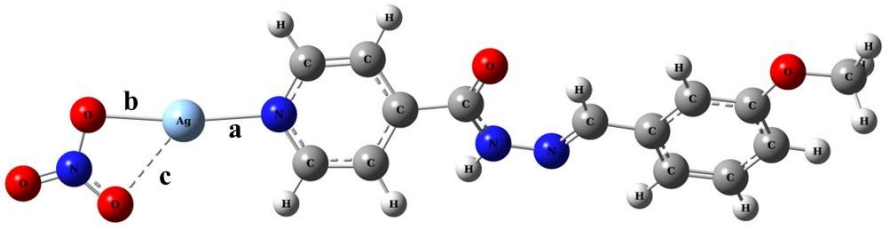
bond lengths		
a) 2.193 Å	b) 2.202 Å	c) 2.487 Å

Figure S32. Drawn from DFT studies of AgIZBEN.



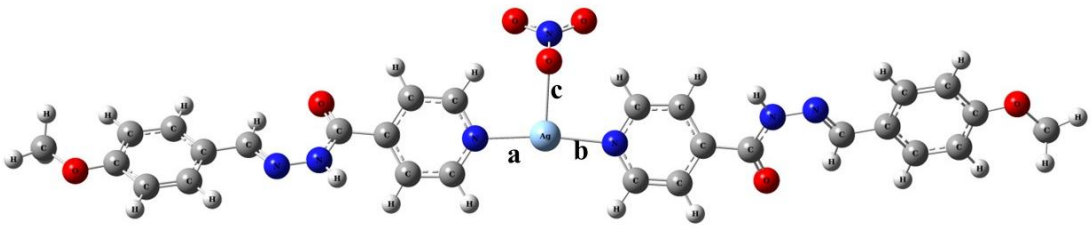
bond lengths		
a) 2.193 Å	b) 2.206 Å	c) 2.488Å

Figure S33. Drawn from DFT studies of AgIZoAN.



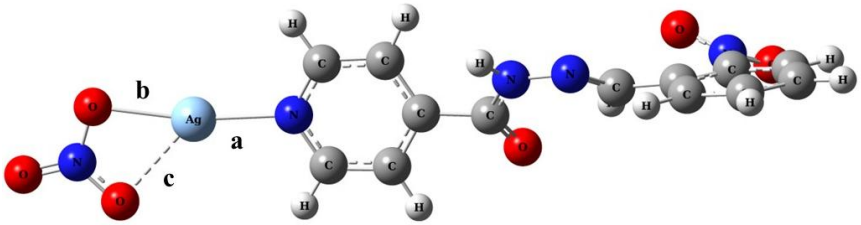
bond lengths		
a) 2.193 Å	b) 2.202 Å	c) 2.488 Å

Figure S34. Drawn from DFT studies of AgIZmAN.



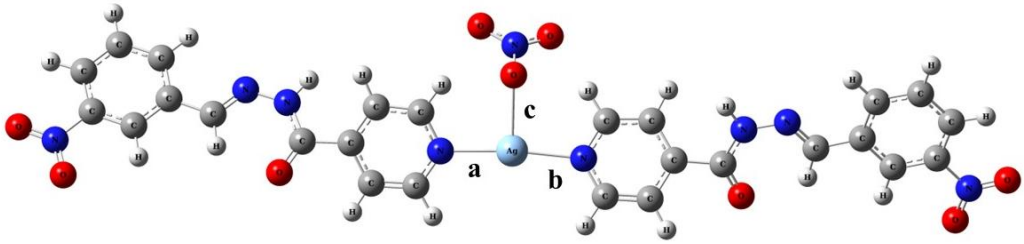
bond lengths		
a) 2.212 Å	b) 2.213 Å	c) 2.408 Å

Figure S35. Drawn from DFT studies of AgIZpAN.



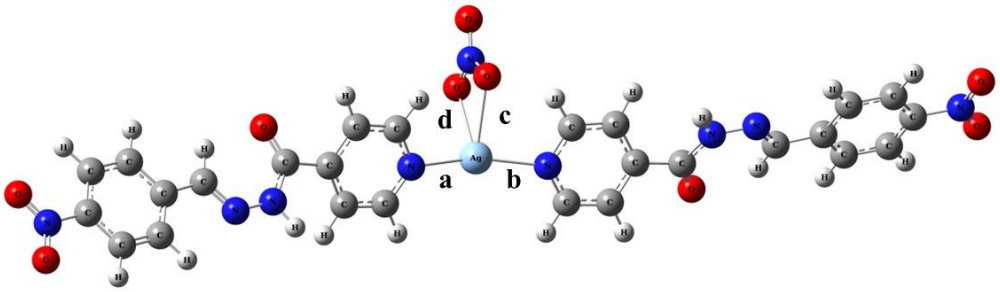
bond lengths		
a) 2.195 Å	b) 2.209 Å	c) 2.474 Å

Figure S36. Drawn from DFT studies of AgIZoNIT.



bond lengths		
a) 2.211 Å	b) 2.214 Å	c) 2.425 Å

Figure S37. Drawn from DFT studies of AgIZmNIT.



bond lengths			
a) 2.259 Å	b) 2.261 Å	c) 2.536 Å	d) 2.492 Å

Figure S38. Drawn from DFT studies of AgIZpNIT.

Table S1. δ values and comparison between shifts and assignments for $^{13}C\{^{1}H\}$ NMR signals observed in ligands and silver(I) complexes

Compound	Assignment / ppm											
	C4	C1	C5	C3	C6	C9	C7/C11	C8/C10	C2			
IZBEN	161.66	150.36	149.07	140.49	134.04	130.43	128.92	127.30	121.55			
AgIZBEN	161.79	150.99	149.71	141.12	134.04	130.78	129.14	127.56	122.15			
$\Delta\delta$	+ 0.13	+ 0.63	+ 0.64	+ 0.63	0	+ 0.35	+ 0.22	+ 0.26	+ 0.60			
AgIZBEN: molar ratio 1:1, electrolyte, partially, C1,C2,C3 (+, about 0.60),aromatic from aldehyde (+)												
	C4	C7	C1	C5	C3	C9	C11	C2	C10	C6	C8	OCH_3
IZoAN	161.53	158.00	150.38	144.63	140.50	132.03	125.72	122.06	121.61	120.88	111.96	55.77
AgIZoAN	161.37	158.09	150.99	145.14	141.06	132.24	125.75	122.12	121.89	120.91	112.02	55.83
$\Delta\delta$	– 0.16	+ 0.09	+ 0.61	+ 0.51	+ 0.56	+ 0.21	+ 0.03	+ 0.06	+ 0.28	+ 0.03	+0.06	+0.06
AgIZoAN: molar ratio 1:1, electrolyte, C1,C2,C3 (+, from 0.06 to 0.61),aromatic from aldehyde (+)												
	C4	C8	C1	C5	C3	C6	C10	C2	C11	C9	C7	OCH_3
IZmAN	161.78	159.63	150.40	149.05	140.51	135.49	130.08	121.60	120.32	116.62	111.45	55.25
AgIZmAN	161.99	159.81	151.30	149.90	141.35	135.43	130.36	122.41	120.64	117.03	111.70	55.51
$\Delta\delta$	+0.21	+ 0.18	+ 0.90	+ 0.85	+0.84	– 0.06	+ 0.28	+ 0.81	+0.32	+0.41	+0.25	+0.26
AgIZmAN: molar ratio 1:1, electrolyte, partially, C1,C2,C3 (+, nearly 0.85), aromatic from aldehyde (+)												
	C4	C9	C1	C5	C3	C7/11	C6	C2	C8/10	OCH_3		
IZpAN	161.89	161.39	150.54	149.39	140.85	129.29	126.72	121.80	114.60	55.58		
AgIZpAN	161.29	161.18	150.71	149.25	140.99	129.01	126.43	121.85	114.44	55.36		
$\Delta\delta$	– 0.60	– 0.21	+ 0.17	– 0.14	+ 0.14	– 0.28	– 0.29	+ 0.05	– 0.16	– 0.22		
AgIZpAN: molar ratio 2:1, electrolyte, partially, C1,C2,C3 (+, from 0.05 to 0.17), aromatic from aldehyde (–)												
	C4	C1	C7	C5	C3	C10	C9	C11	C6	C8	C2	
IZoNIT	162.50	150.54	148.46	144.71	140.23	134.03	131.21	128.60	128.34	124.91	121.80	
AgIZoNIT	161.92	151.03	148.41	144.98	140.74	134.02	131.23	128.54	128.31	124.87	122.20	
$\Delta\delta$	– 0.58	+ 0.49	– 0.05	+ 0.27	+ 0.51	– 0.01	+ 0.02	– 0.06	– 0.03	– 0.04	+ 0.40	
AgIZoNIT: molar ratio 1:1, electrolyte, partially, C1,C2,C3 (+, nearly 0.50), aromatic from aldehyde (–, from 0.06 to 0.01)												
	C4	C1	C8	C5	C3	C6	C11	C10	C9	C2	C7	
IZmNIT	162.45	150.85	148.71	147.09	140.65	136.34	133.99	131.00	125.04	122.05	121.63	
AgIZmNIT	161.83	150.66	148.26	146.71	140.49	135.87	133.58	130.55	124.60	121.83	121.14	
$\Delta\delta$	–0.62	–0.19	–0.45	–0.38	–0.16	–0.47	–0.41	–0.45	–0.44	–0.22	–0.49	
AgIZmNIT: molar ratio 2:1, electrolyte, partially, C1,C2,C3 (–), aromatic from aldehyde (–)												
	C4	C1	C9	C5	C3	C6	C8/10	C2	C7/11			
IZpNIT	162.04	150.42	148.07	146.52	140.32	140.19	128.24	124.12	121.59			
AgIZpNIT	162.04	150.42	148.08	146.53	140.32	140.18	128.24	124.12	121.59			
$\Delta\delta$	0	0	+0.01	+0.01	0	–0.01	0	0	0			
AgIZpNIT: molar ratio 2:1, non-electrolyte, nearly not changes												

δ: chemical shift; ppm: parts *per* million; $\Delta\delta$: difference between the chemical shift (complex) and the chemical shift (ligand).

Table S2. Conductivity variation in relation to time for the Ag^{I} complexes (1.0×10^{-3} mol L^{-1}, DMSO)

Complex	Conductivity variation / (μS cm^2 mol^{-1})						
	0 h	2 h	4 h	6 h	24 h	48 h	Average
AgIZBEN	42.74	44.38	44.18	43.70	44.20	44.5	44.2
AgIZoAN	58.15	56.76	56.36	56.22	55.77	55.03	56.4
AgIZmAN	40.28	40.44	40.29	40.53	41.22	41.70	40.4
AgIZpAN	21.58	23.29	21.15	22.43	22.91	22.88	22.4
AgIZoNIT	48.72	47.45	47.57	47.44	47.20	46.98	47.4
AgIZmNIT	32.25	31.39	30.08	29.97	29.83	29.70	30.1
AgIZpNIT	1.20	1.21	1.20	1.19	1.20	1.18	1.20

IZBEN: benzaldehyde; IZoAN: *o*-anisaldehyde; IZmAN: *m*-anisaldehyde; IZpAN: *p*-anisaldehyde; IZoNIT: *o*-nitrobenzaldehyde; IZmNIT: *m*-nitrobenzaldehyde; IZpNIT: *p*-nitrobenzaldehyde.