Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supporting Information

Surface immobilized Azomethine for Multiple Component Exchange

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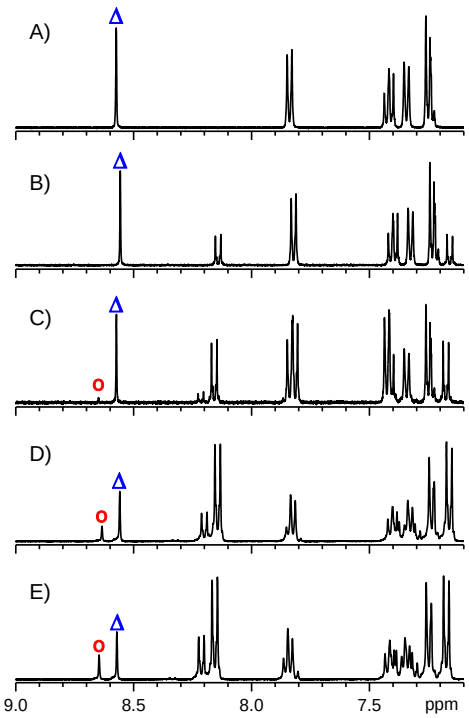


Figure S1. Component exchange of **2** monitored by ^{1}H NMR in DMSO-d_6 at 40^{o} C: **2** (A), **2** with equimolar 4-aminodinitrotriphenylamine after 6 hrs (B), with the addition of a catalytic amount of $Sc(Otf)_3$ after 6 hrs (C), after 8 additional hours (D), and after 24 hrs (E). Inset: sample (E) after the addition of 10 equivalents of 4-aminodinitrotriphenylamine. The imine proton of **2** (○) and **1** (△) are highlighted to illustrate dynamic component exchange.

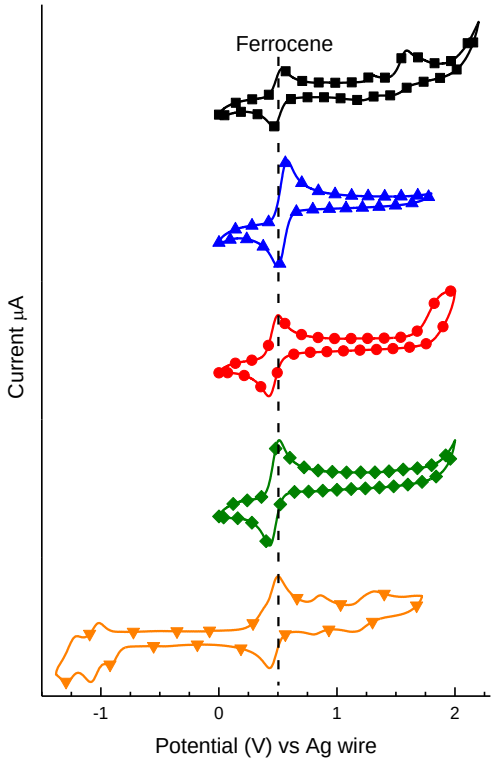


Figure S2. Cyclic voltammograms of **1** (■), **2** (●), **3** (◆), ***4*** (▲) and *N*,*N*-bis(4-nitrophenyl)-1,4-phenylenediamine (▼) in degassed acetonitrile with $TBAPF_6$ (0.1 M) as the electrolyte and ferrocene (0.1 mM) as internal reference measured at 100 mV/s, [C]=0.1 M.

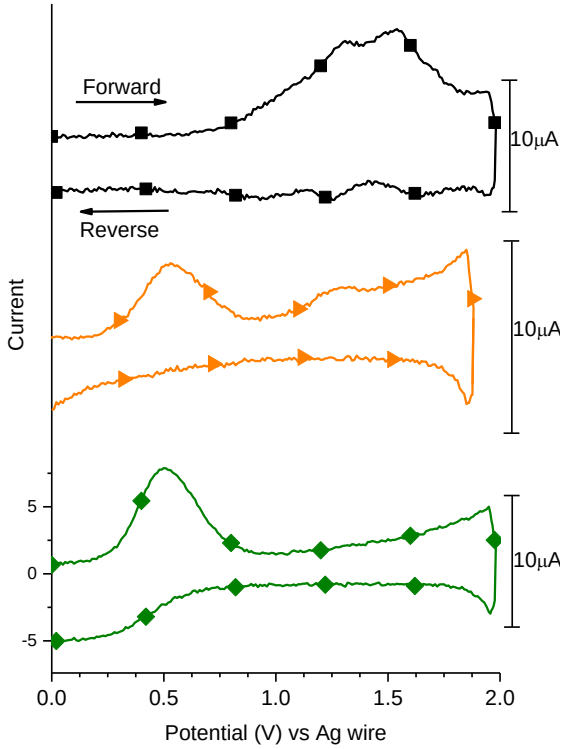


Figure S3. Square wave voltammograms of **1** (■), **3** (◆) and a mixture of **1** and **3** (▶) in degassed acetonitrile with 0.1 M $TBAPF_6$ as the electrolyte.

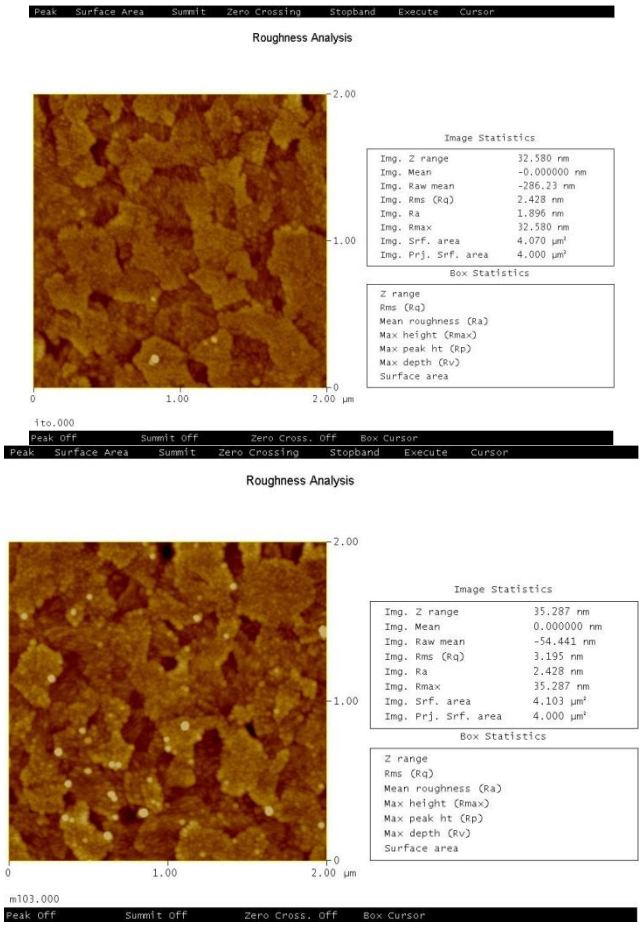


Figure S4. AFM micrograph illustrating the surface roughness of native ITO coated glass substrate (top) and **1s** (bottom).

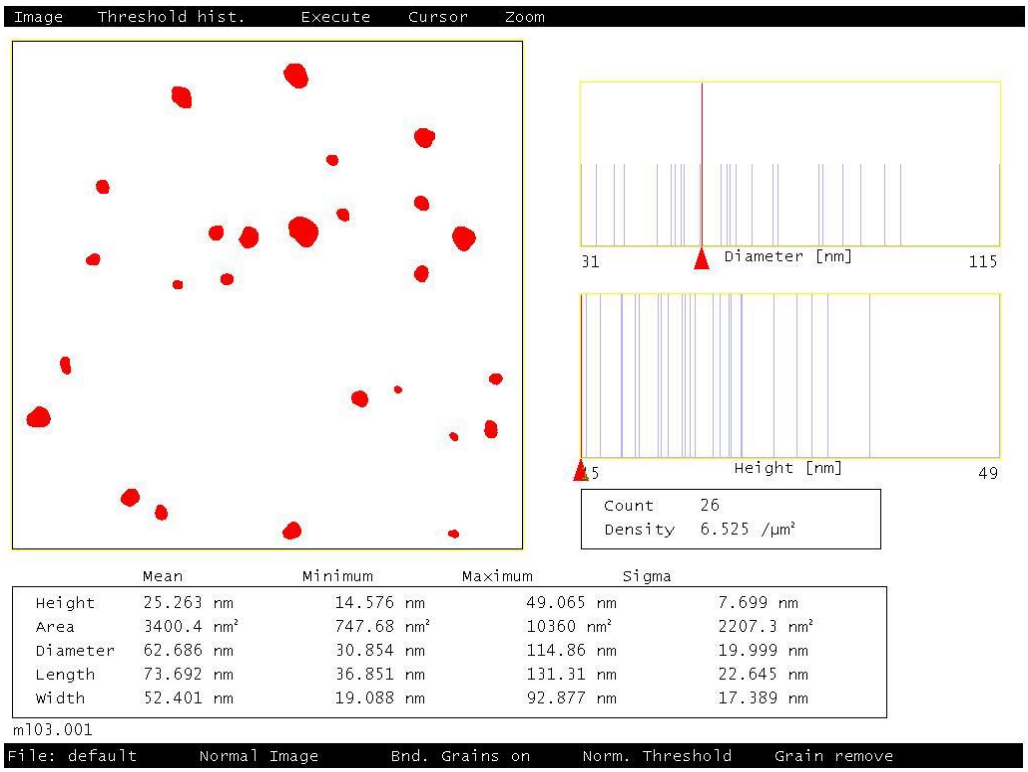


Figure S5. Particle size distribution of **1s** on an ITO coated glass substrate.

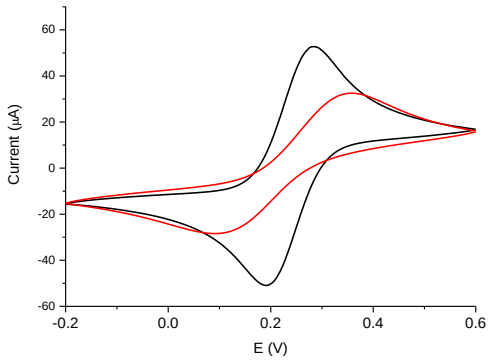


Figure S6. Cyclic voltammograms of a glassy carbon electrode before (black) and after immobilizing **4s** (red) in 5 mM solution of $K_3[Fe(CN)_6]$ and 5 mM $K_4[Fe(CN)_6]$ with 0.1 M KCl at pH=5 at 100 mV/s.

Table S1. ToF-SIMS data.

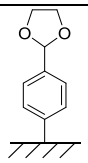
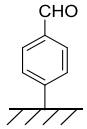
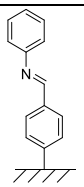
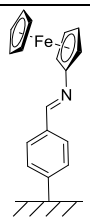
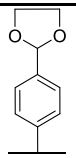
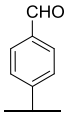
Molecular formula	Mass Center (u)	Compound			
			 **(4s)**	 **(2s)**	 **(3s)**
		Peak intensity			
$C_9H_9O^-$	133.0664	$1.5x10^{-4}$	$7.9x10^{-5}$		$4.6x10^{-5}$
$C_7H_5O^+$	105.0357	$1.1x10^{-3}$	$1.7x10^{-3}$		$3.8x10^{-4}$
$C_7H_4^+$	88.0284	$1.5x10^{-4}$	$4.7x10^{-4}$	$8.3x10^{-4}$	$2.1x10^{-4}$
$C_6H_4N^+$	90.0326			$3.2x10^{-4}$	
$C_6H_4N^-$	90.0328			$8.5x10^{-4}$	
$C_6H_5^+$	77.0384			$7.6x10^{-3}$	
$C_7H_6N^+$	104.0536			$8.9x10^{-4}$	$7.5x10^{-4}$
$C_7H_7N^+$	105.0592			$6.2x10^{-4}$	
$C_7H_7^+$	91.0538			$2.8x10^{-3}$	$1.7x10^{-3}$
$C_{10}H_9Fe^+$	184.9987				$6.7x10^{-4}$
$C_{10}H_{10}Fe^+$	186.0093				$2.6x10^{-3}$
$C_{10}H_{11}NFe^+$	201.0337				$4.8x10^{-3}$
$C_{13}H_{10}N^+$	180.0837			$2.6x10^{-4}$	
$C_{17}H_{14}NFe^+$	288.0539				$4.9x10^{-5}$

Table S2. XPS data expressed in atomic percentages.

Name	**BE (eV)**	**Assigned**	**ITO**[a]		 **(4s)**	**2s**	**1s**[b]		**3s**[c]		**1s→2s**[d]	**1s→3s**[e]	
				obs'd	obs'd	obs'd	obs'd	calc'd	obs'd	calc'd	obs'd	obs'd	calc'd
C1S	285.0	C-C, C=C	48.1	51.0	46.5	45.2	44.5		33.3		46.9	42.1	
	285.6	C-N				9.1	5.5	2.1	4.7	0.6	7.1	5.0	1.3
	286.5	C-O, C-O-C	7.0	17.7	12.6	11.3	11.4		10.2		11.0	9.8	
	287.9	C=O, O-C-O		4.8	4.1	4.9	3.9		6.3		5.0	4.9	
	289.2	O-C=O	4.0	2.5	5.0	2.0	3.9		3.9		2.5	4.1	
	291.2	π=>π* from C=C		0.6	0.9	7.5	0.7				0.8		
N1S	399.5	C-N, C=N, N=N		1.2	0.7	4.0	1.3	2.4	1.0	1.2	3.1	0.8	1.6
	402.6	N+		1.1	0.3	2.0			0.5		1.1	1.0	
	406.3	NO_2					0.7	ref[f]				0.4	ref[f,g]
O1S	530.5	In-O, Sn-O	21.0	1.9	2.1	2.6	1.4		1.9		1.4		
	531.9	C=O, In-OH, Sn-OH	14.4	6.9	9.0	5.2	7.8		10.5		5.7	11.7	
	532.9	C-O, C-O-C		8.8	12.5	10.9	11.7		9.7		11.5	9.4	
	533.3	C-O	5.5										
	533.8	O-C=O, NO_2		2.2	4.9	2.0	5.5	1.4	3.7		2.6	3.8	0.8
Fe2p3/2	708.0	ferrocene							0.6	ref[f]		0.1	ref[f]
	710.3	Iron oxide							2.0			0.7	

obs'd=observed; calc'd=calculated. ITO substrate cleaned by successive sonications in acetone, ethanol, and water, followed by air drying. [b] Average of two different samples. [c] Average of three different samples. [d] Exchanged by submerging the substrate in aniline with catalytic *p*TSOH overnight. [e] Exchanged by submerging the substrate in dichloromethane solution of aminoferrocene overnight. [f] Used as the reference to calculate the expected atomic percentages. [g] The reference takes into account 2xNO_2 per **1s**.

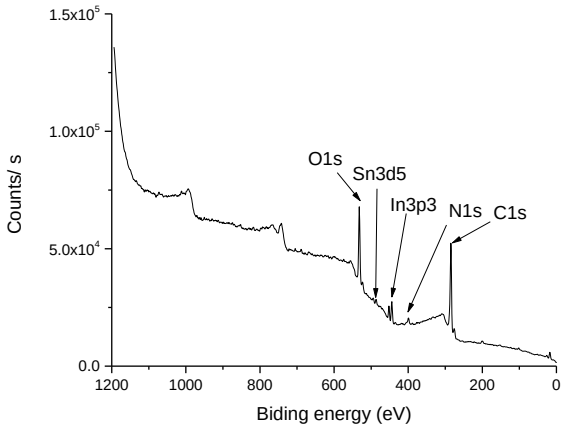


Figure S7. XPS survey spectrum of **4s**.

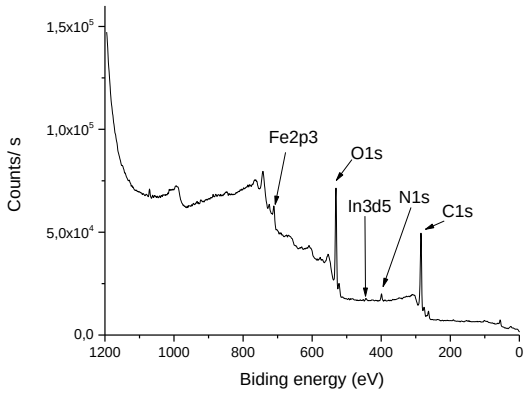


Figure S8. XPS survey spectrum of **3s**.

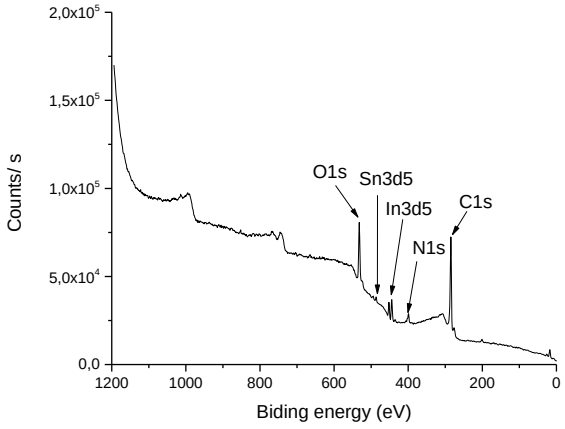


Figure S9. XPS survey spectrum of **2s** prepared by component exchange of **1s**.

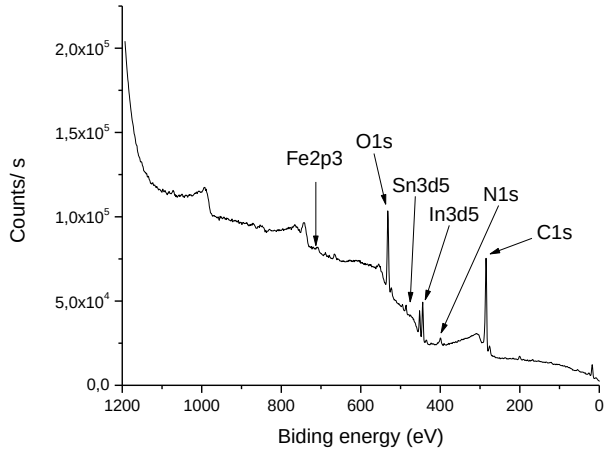


Figure S10. XPS survey spectrum of **3s** prepared by component exchange of **1s**.

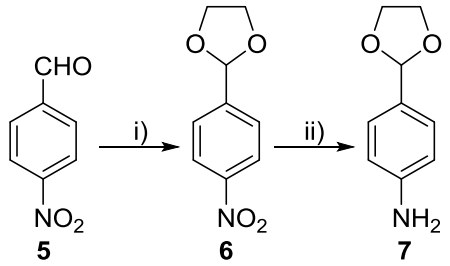


Figure S11. Synthetic scheme for the preparation of the reactive intermediate leading to **4s**: i) ethylene glycol, *p*-toluene sulfonic acid, anhydrous toluene, 120°C, overnight, and ii) PtO_2, $MgSO_4$, THF/EtOH, H_2 70 psi.

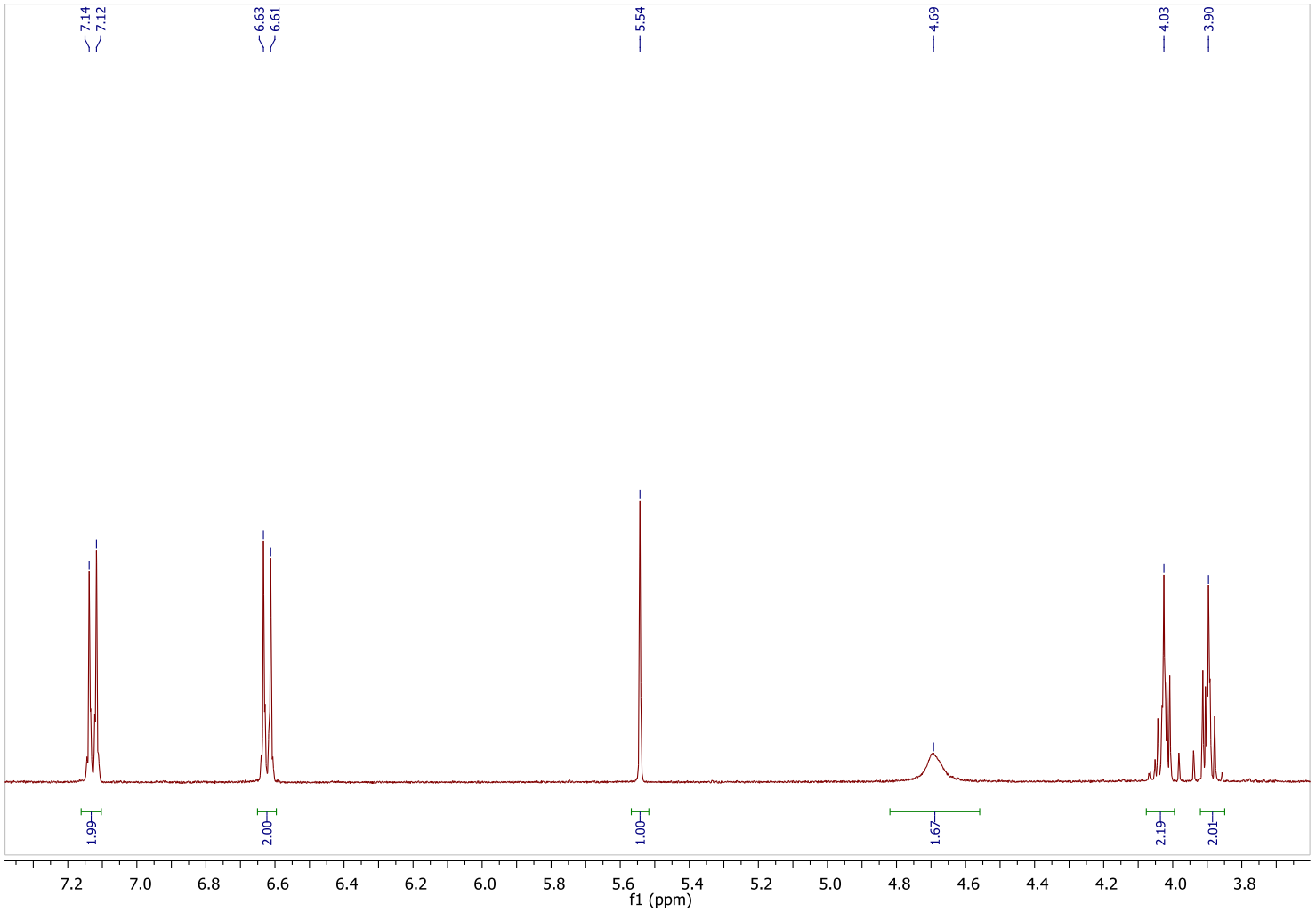


Figure S12. ^{1}H-NMR spectrum of 1,3-dioxolane-4-benzenamine (**7**) recorded in acetone-d_6.

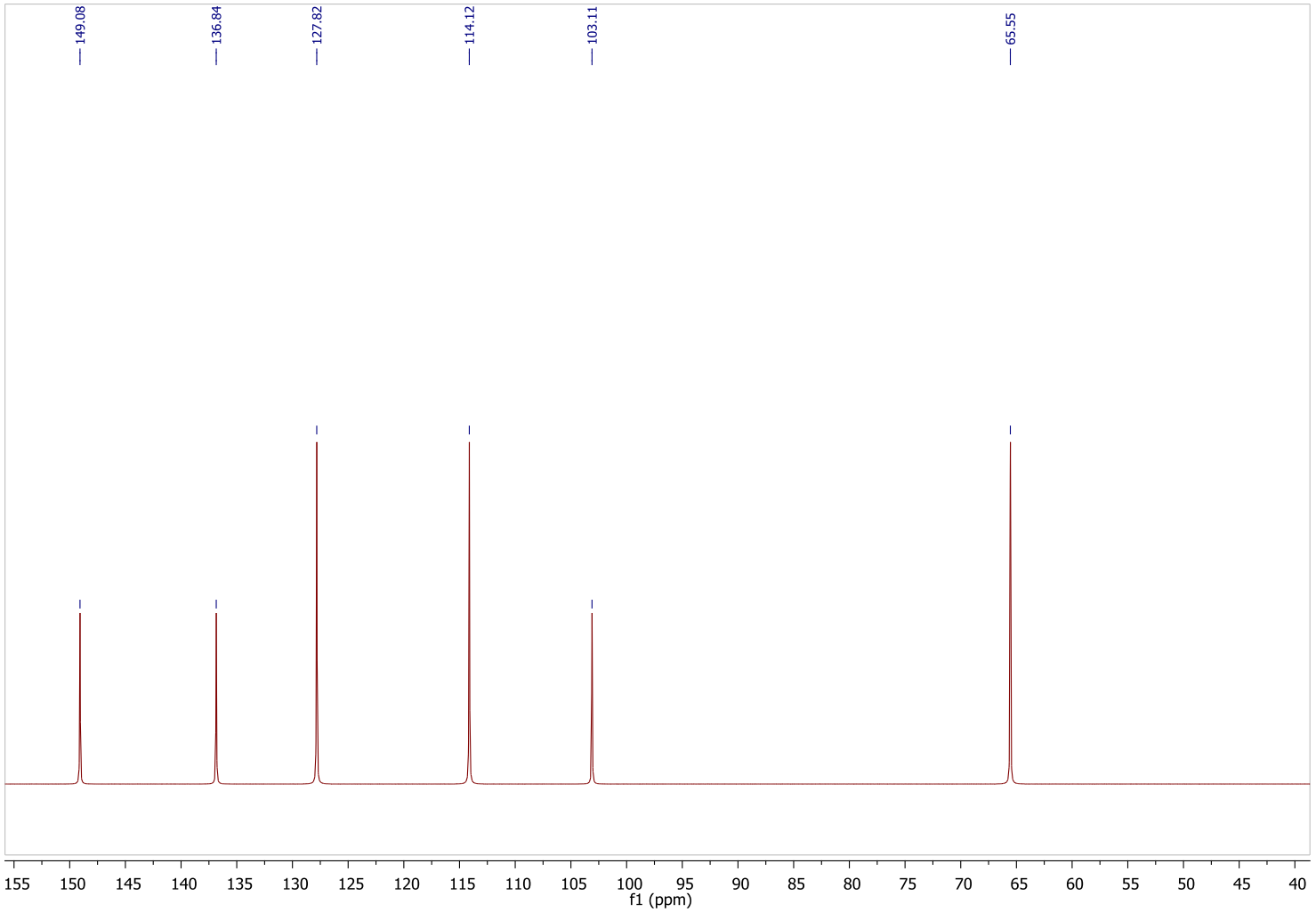


Figure S13. ^{13}C-NMR spectrum of 1,3-dioxolane-4-benzenamine (**7**) recorded in acetone-d_6.

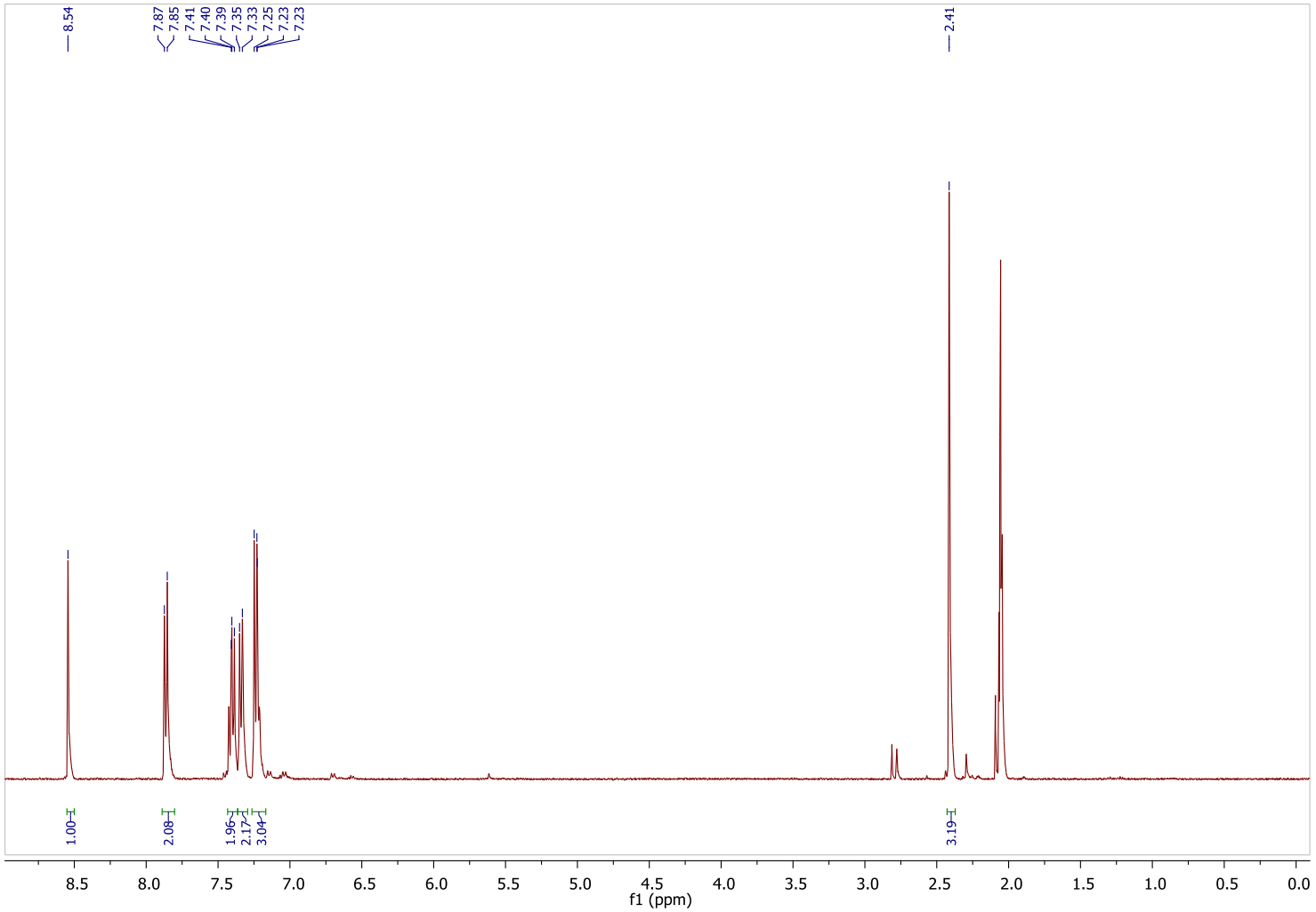


Figure S14. ^{1}H-NMR spectrum of *N*-phenyl-1-(*p*-tolyl)methanimine (**2**) recorded in acetone-d_6.

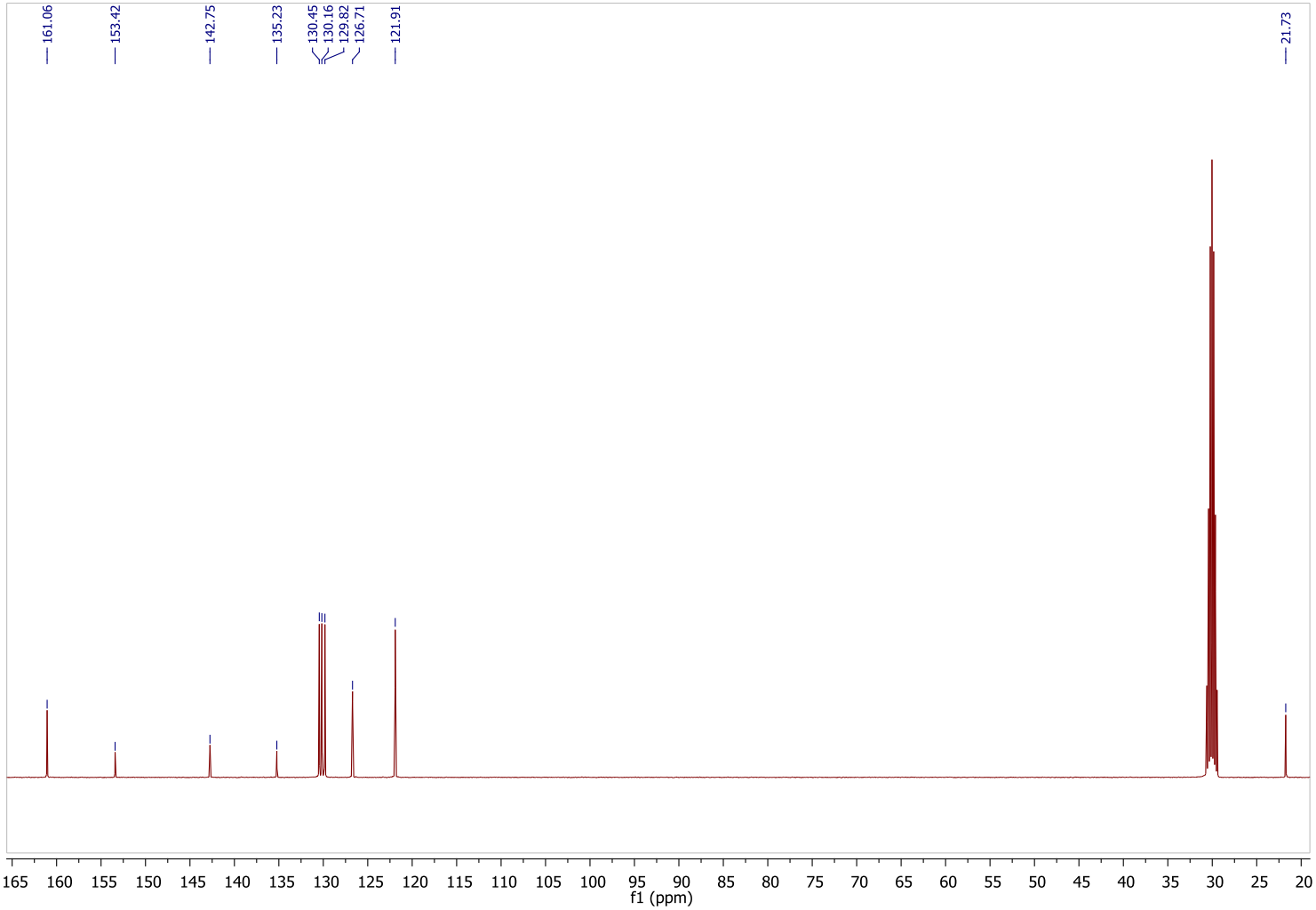


Figure S15. ^{13}C-NMR spectrum of *N*-phenyl-1-(*p*-tolyl)methanimine (**2**) recorded in acetone-d_6.

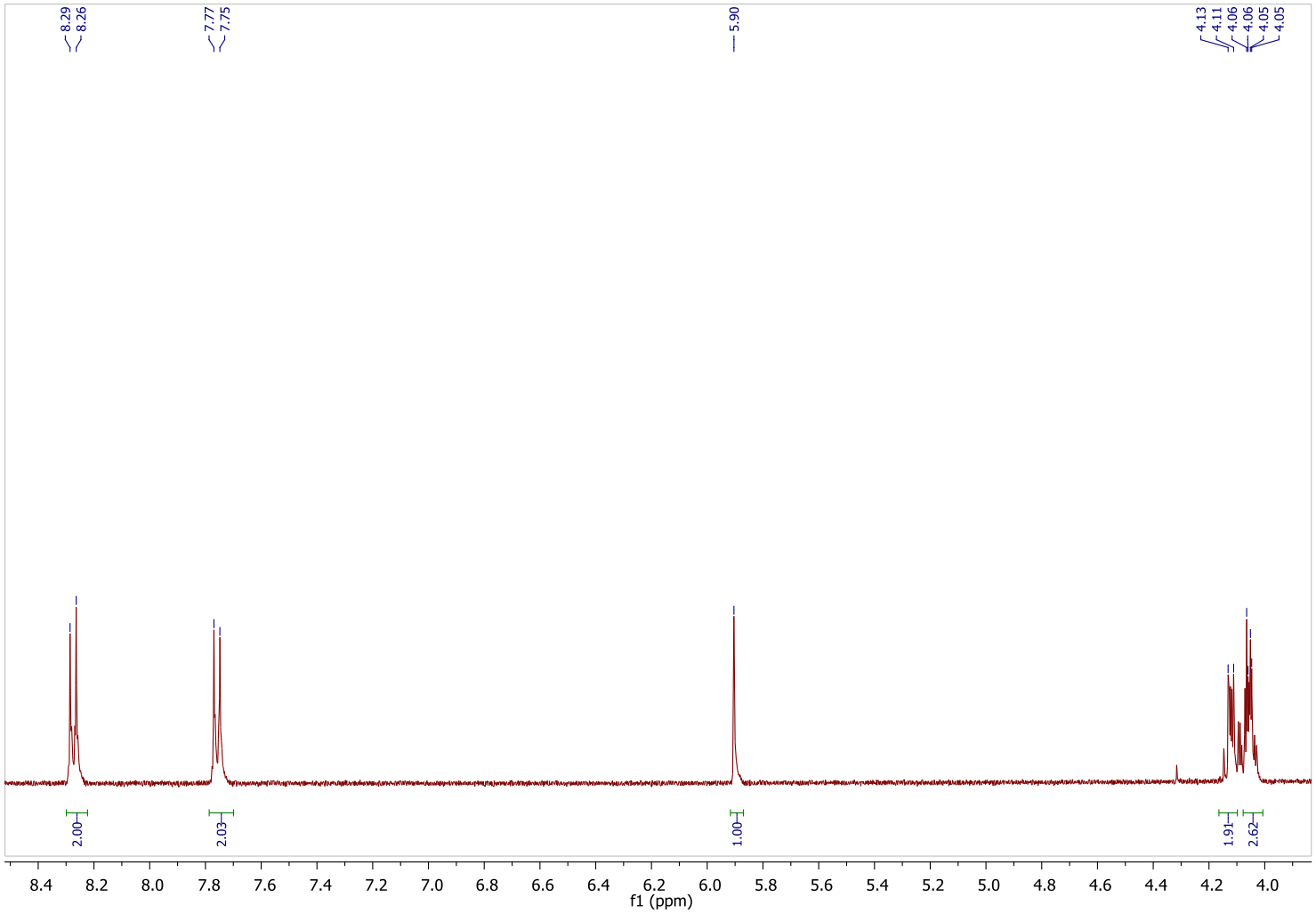


Figure S16. ^{1}H-NMR spectrum of 1,3-dioxolane-4-nitrobenzaldehyde (**6**) recorded in acetone-d_6.

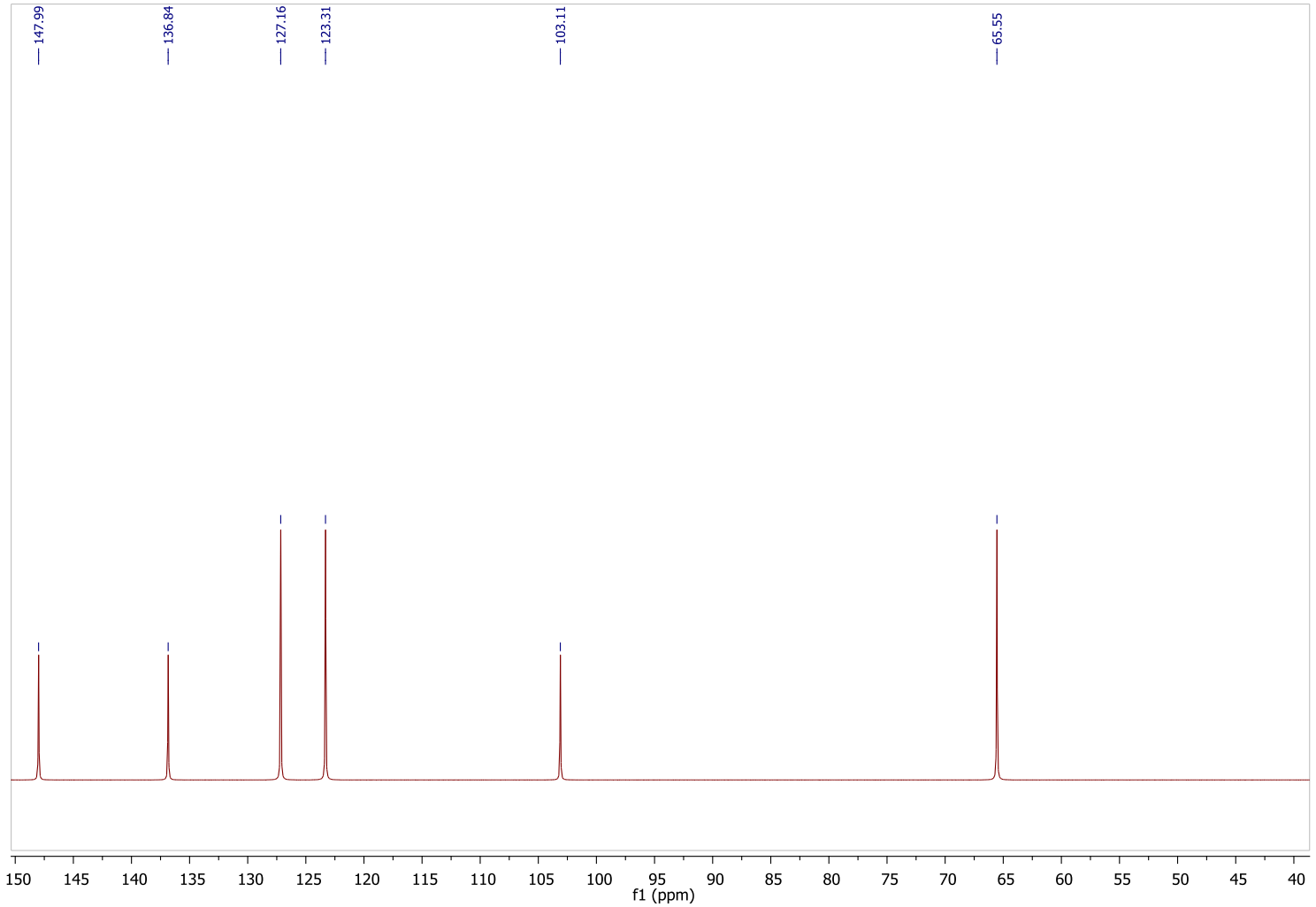


Figure S17. ^{13}C-NMR spectrum of 1,3-dioxolane-4-nitrobenzaldehyde (**6**) recorded in acetone-d_6.

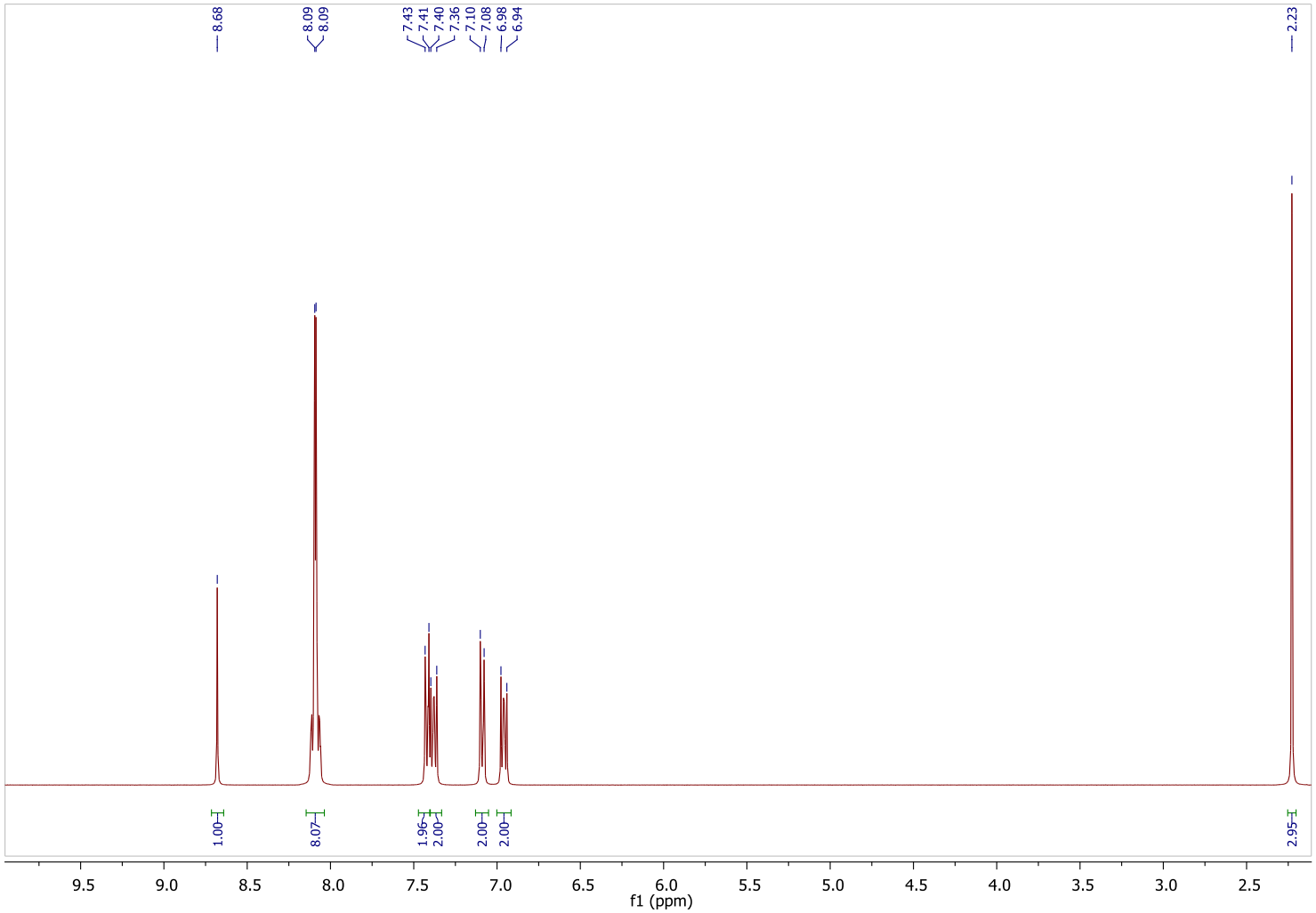


Figure S18. ^{1}H-NMR spectrum of *N*-dinitrotriphenylamine-1-(*p*-tolyl)methanimine (**1**) recorded recorded in acetone-d_6.

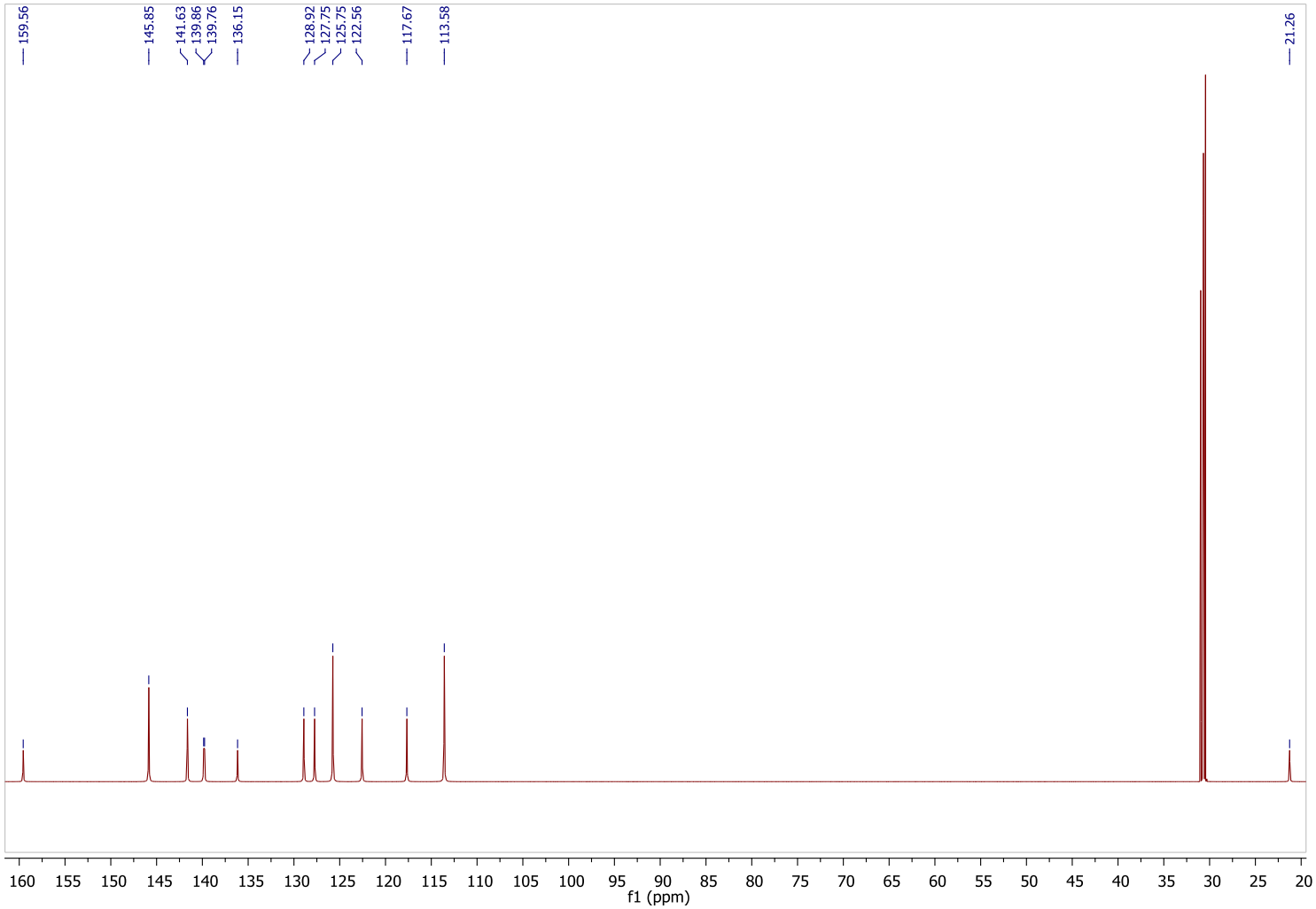


Figure S19. ^{13}C-NMR spectrum of *N*-dinitrotriphenylamine-1-(*p*-tolyl)methanimine (**1**) recorded in acetone-d_6.

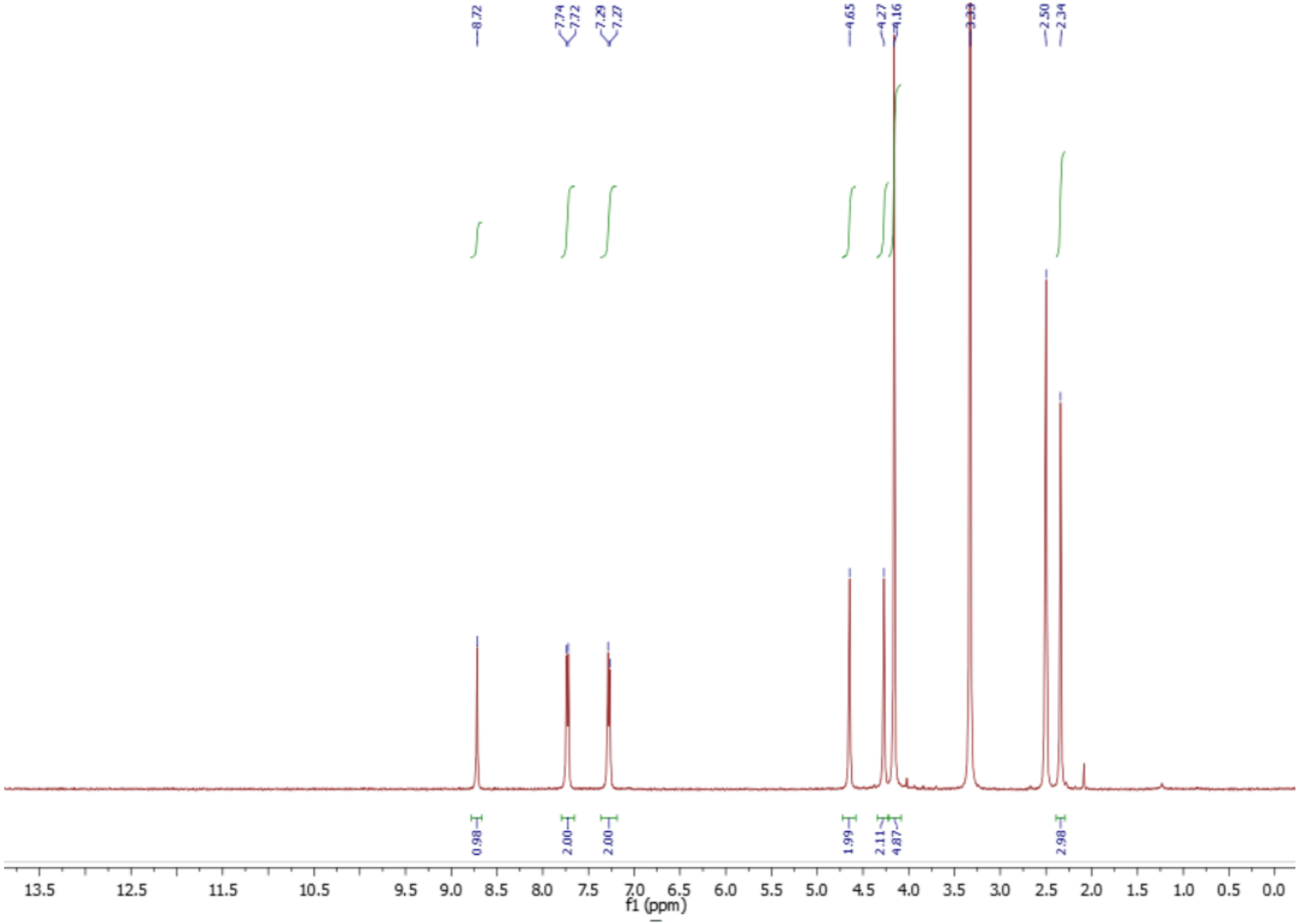


Figure S20. ^{1}H-NMR spectrum of *N*-ferrocene-1-(*p*-tolyl)methanimine (**3**) recorded in acetone-d_6.

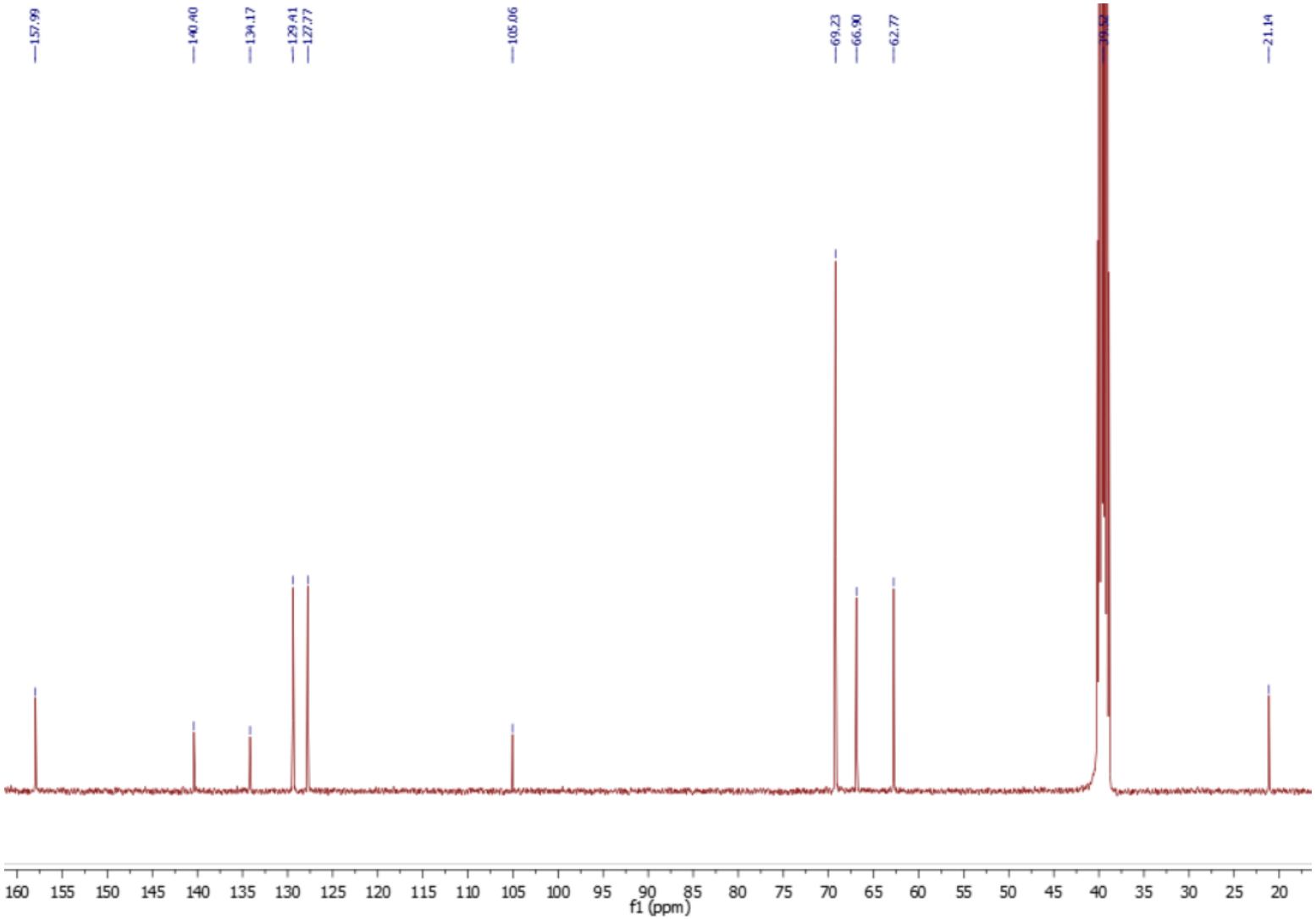


Figure S21. ^{13}C-NMR spectrum of *N*-ferrocene-1-(*p*-tolyl)methanimine (**3**) recorded in acetone-d_6.

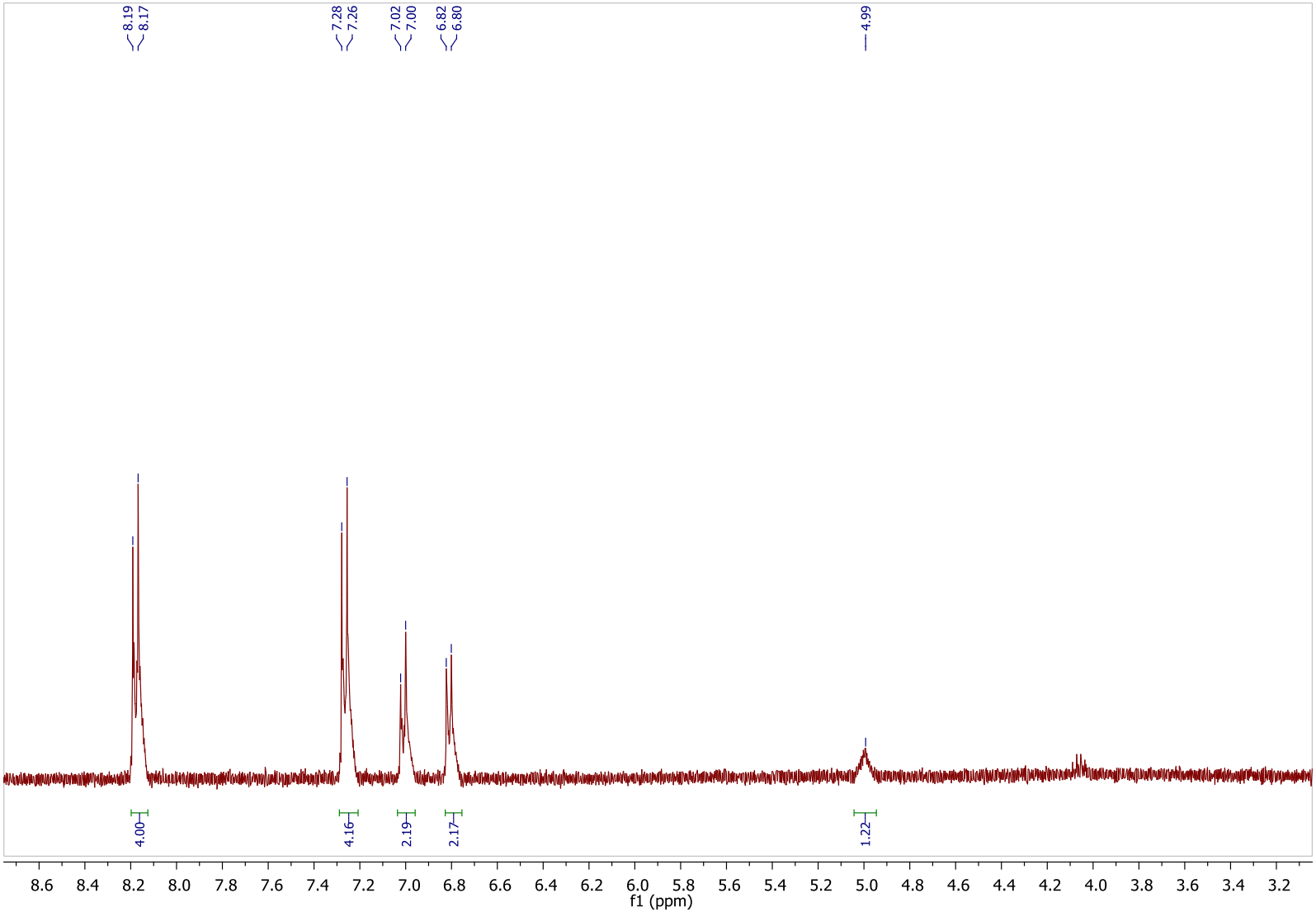


Figure S22. ^{1}H-NMR spectrum of *N*,*N*-bis(4-nitrophenyl)-1,4-phenylenediamine recorded in acetone-d_6.

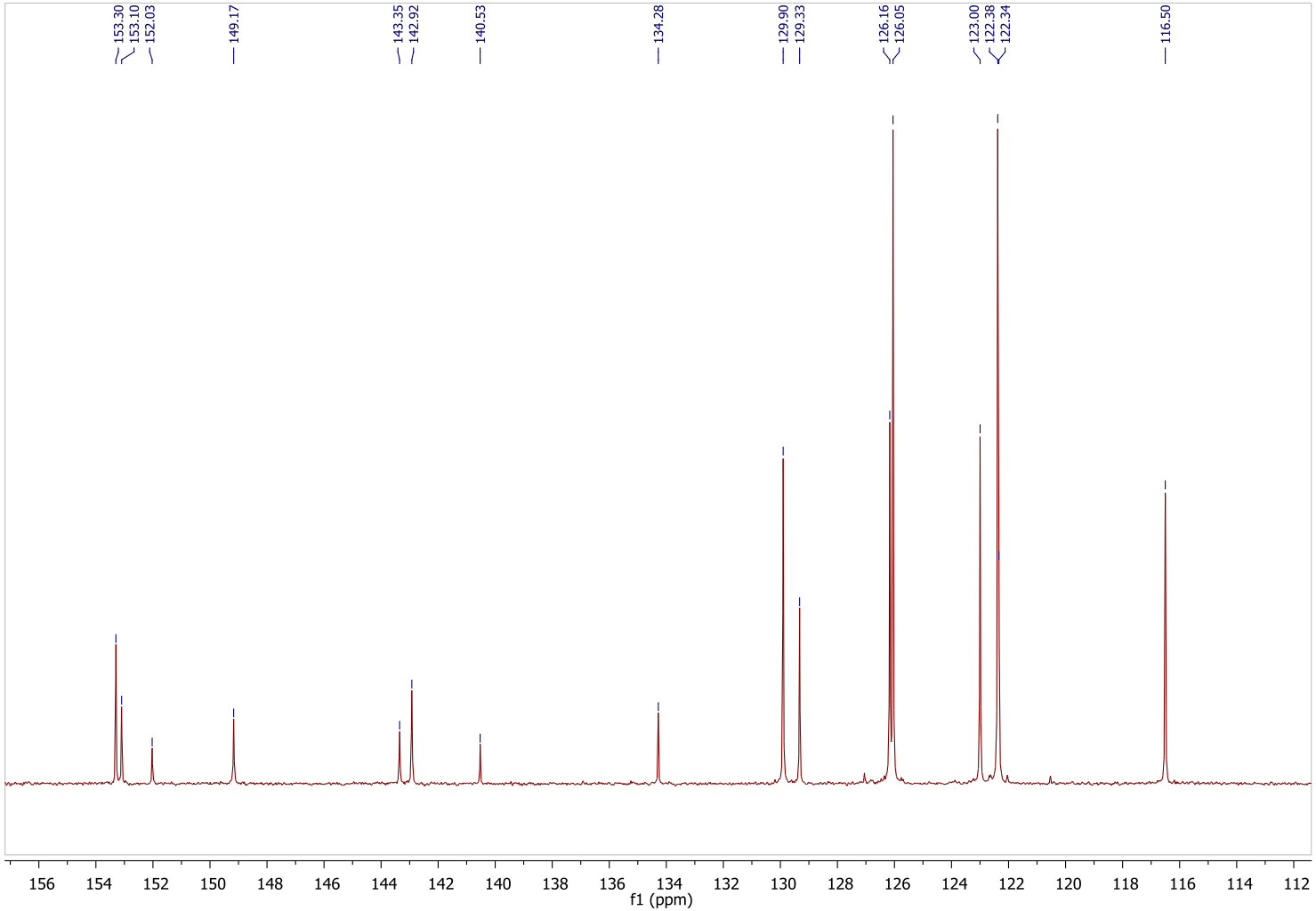


Figure S23. ^{13}C-NMR spectrum of *N*,*N*-bis(4-nitrophenyl)-1,4-phenylenediamine recorded in acetone-d_6.