Electronic Supplementary Information

A mineralogically-inspired silver-bismuth hybrid material: an efficient heterogeneous catalyst for the direct synthesis of nitriles from terminal alkynes

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1. Additional characterization data: as-prepared AgBi HM sample

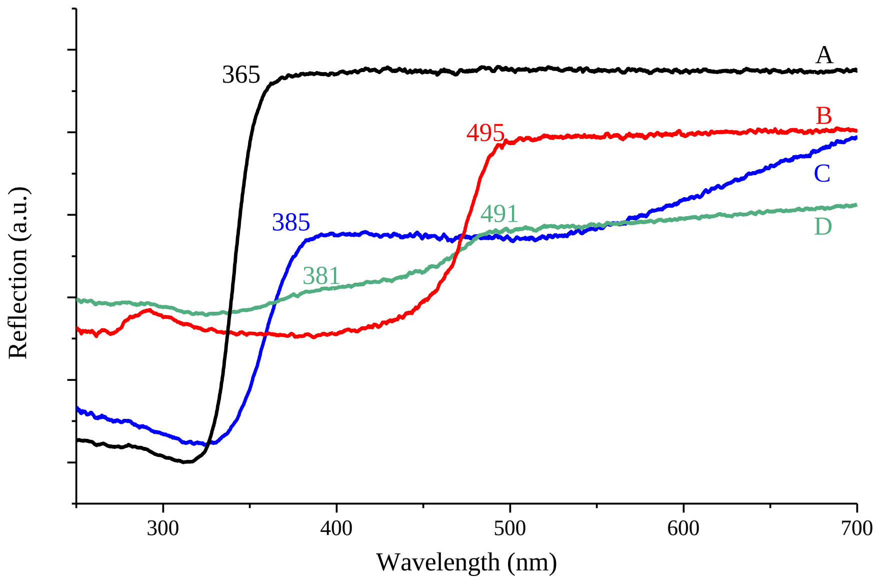


Fig. S1 UV–vis–near IR DRS spectra of materials A–D. (A: hydrolyzed $Bi(NO_3)_3{\cdot}5H_2O$, B: hydrolyzed mixture of Ag_2O–Ag_2CO_3–$AgNO_3$, C: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 130 °C and D: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 100 °C.)

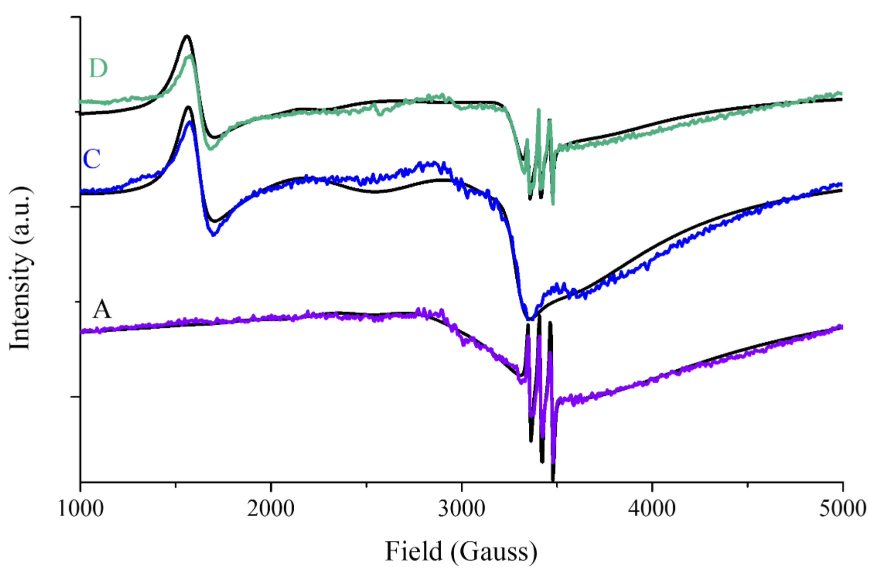


Fig. S2 EPR spectra of of materials A–D. (A: hydrolyzed $Bi(NO_3)_3{\cdot}5H_2O$, B: hydrolyzed mixture of Ag_2O–Ag_2CO_3–$AgNO_3$, C: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 130 °C and D: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 100 °C.)

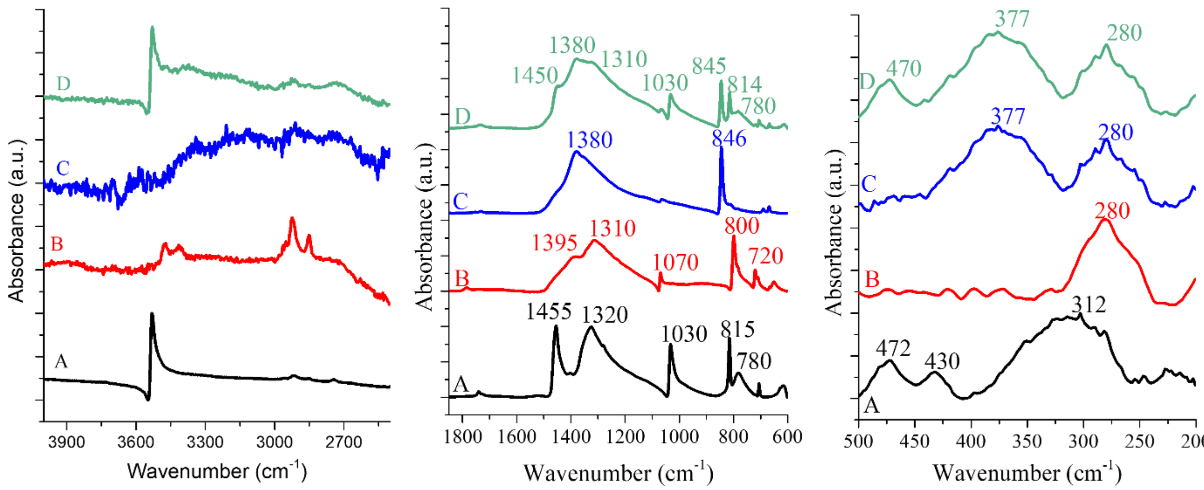


Fig. S3 IR spectra for materials A–D. (A: hydrolyzed $Bi(NO_3)_3{\cdot}5H_2O$, B: hydrolyzed mixture of Ag_2O–Ag_2CO_3–$AgNO_3$, C: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 130 °C and D: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 100 °C.)

Table S1 The observed vibrations by IR spectroscopy for samples A–D. (A: hydrolyzed $Bi(NO_3)_3{\cdot}5H_2O$, B: hydrolyzed mixture of Ag_2O–Ag_2CO_3–$AgNO_3$, C: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 130 °C and D: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 100 °C)

Sample	Vibration (cm^{-1})									
	a	b	c	d	e	f	g	h	i	j
A	–	312	430	472	780	815	–	1030	1320	1455
B	280	–	–	–	720	800	–	1070	1310	1395
C	280	–	377	–	–	–	846	–	1380	–
D	280	–	377	472	780	814	845	1030	1380/1310	1450

a Ag–O (carbonate) bending vibration[1]
b Bi–O–Bi vibration of the BiO_6 octahedral unit[2]
c ν_2 totally symmetric bending vibration of the Bi–O bonds in the BiO_3 units[3]
d Bi–O bending vibrations of the BiO_6 units[3]
e ν_4 in-plane deformation vibration mode of the carbonate or the nitrate ion[3, 4]
f ν_2 out-of-plane bending vibration mode of the nitrate or the carbonate ion[3, 4]
g ν_1 symmetric stretching vibrations of Bi–O bonds in BiO_3 units[3]
h ν_1 symmetric vibration of the nitrate or the carbonate ion[3, 4]
i ν_3 antisymmetric vibration of the nitrate or the carbonate ion[3, 4]
j ν_3 antisymmetric vibration of the nitrate or the carbonate ion[3, 4]

Table S2 The composition of materials A and C by ICP–AES measurements assuming the O_2CO_3 unit, the theoretical formula of the Bi subcarbonate is in parentheses. (A: hydrolyzed $Bi(NO_3)_3{\cdot}5H_2O$, C: $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 130 °C.)

Sample	Ag content (w%)	Bi content (w%)	Formula
A	–	77.9 (82.0)	$Bi_{1.6}O_2CO_3$ ($Bi_2O_2CO_3$)
C	6.1	62.7	$Ag_{0.17}Bi_{0.88}O_2CO_3$

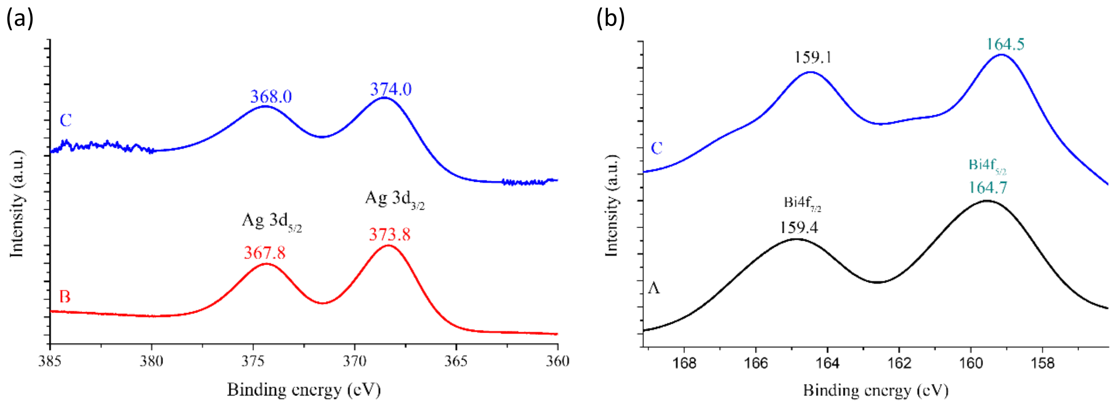


Fig. S4 The Ag3d (a) and Bi4f (b) XPS spectra of material C (the $Bi(NO_3)_3{\cdot}5H_2O$–$AgNO_3$ mixture co-hydrolyzed at 130°C) and materials A (hydrolyzed $Bi(NO_3)_3{\cdot}5H_2O$) and B (the hydrolyzed mixture of Ag_2O–Ag_2CO_3–$AgNO_3$).

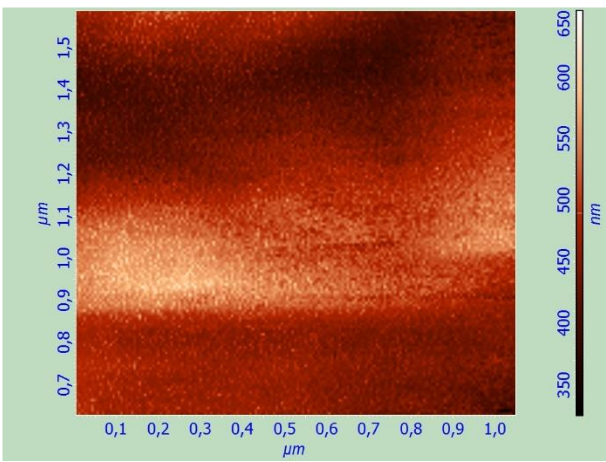


Fig. S5 The AFM (atomic force microscopy) image of the AgBi HM

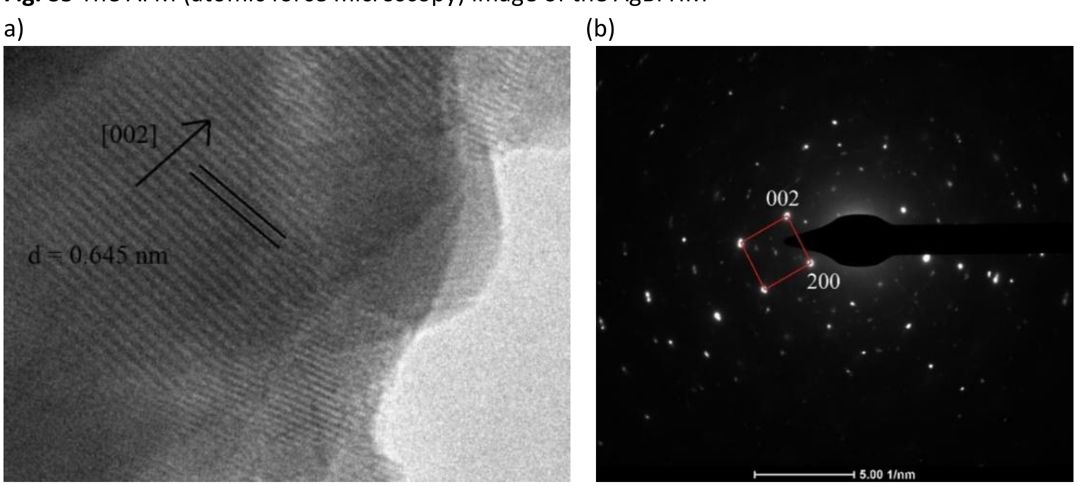


Fig. S6 The enlarged TEM (a) and the SAED (b) images of the AgBi HM.

2. Additional reaction optimization data

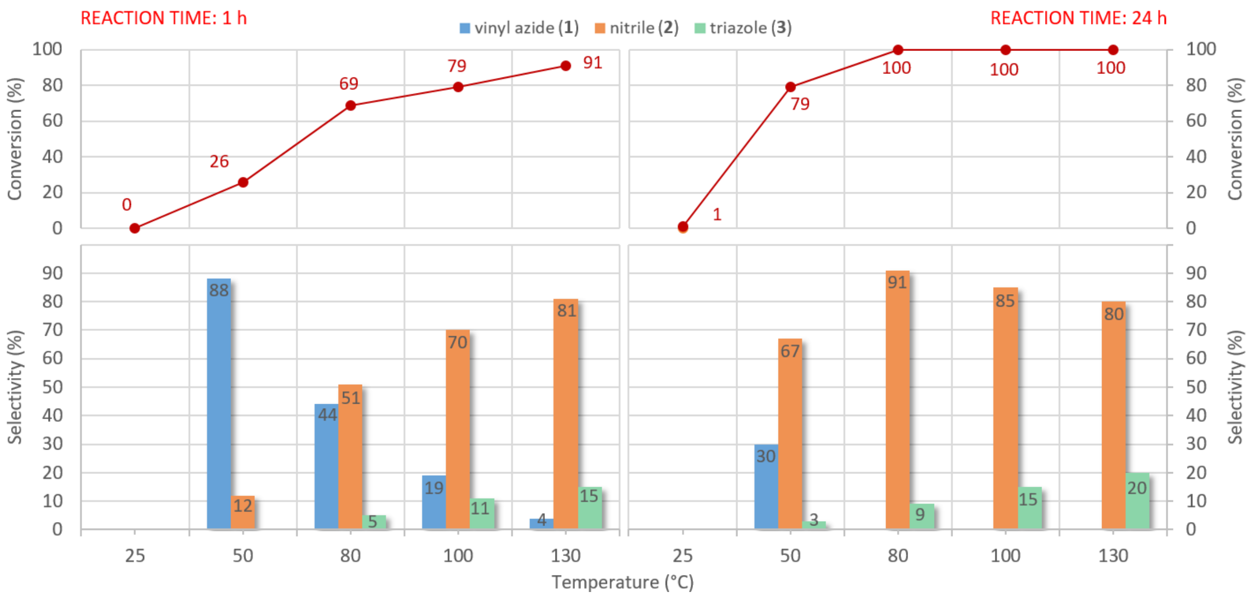


Fig. S7 Investigation of the effects of the reaction temperature on the AgBi HM-catalyzed nitrogenation of *p*-methoxy phenylacetylene with $TMSN_3$ (see Scheme 1 in the manuscript). Reaction conditions: 1 equiv. (0.25 M) alkyne, 2 equiv. $TMSN_3$, 10 mol% catalyst, solvent: DMSO, 1 h or 24 h reaction time.

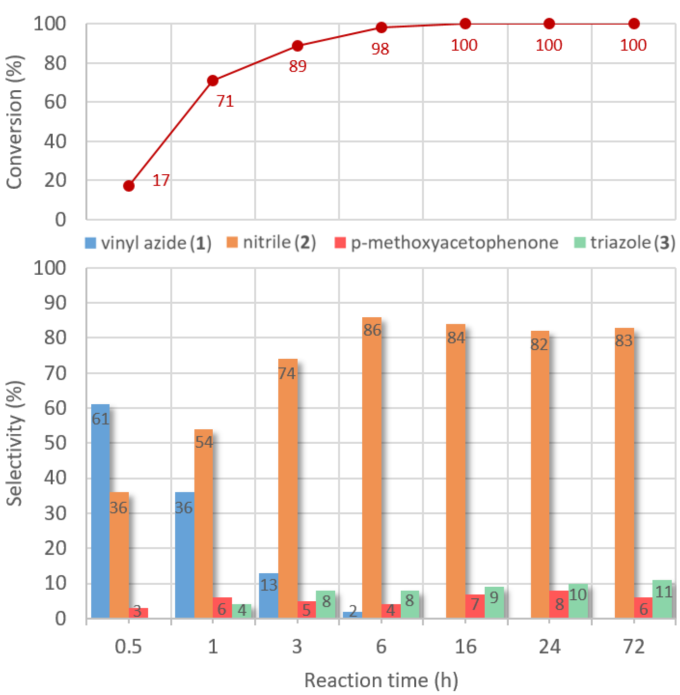


Fig. S8 Investigation of the effects of H_2O as an additive on the AgBi HM-catalyzed nitrogenation of *p*-methoxy phenylacetylene with $TMSN_3$ as nitrogen source (see Scheme 1 in the manuscript). Reaction conditions: 1 equiv. (0.25 M) alkyne, 2 equiv. $TMSN_3$, 2 equiv. H_2O, 10 mol% catalyst, solvent: DMSO, 80 °C, 0.5–72 h reaction time.

3. Additional characterization data: used AgBi HM sample

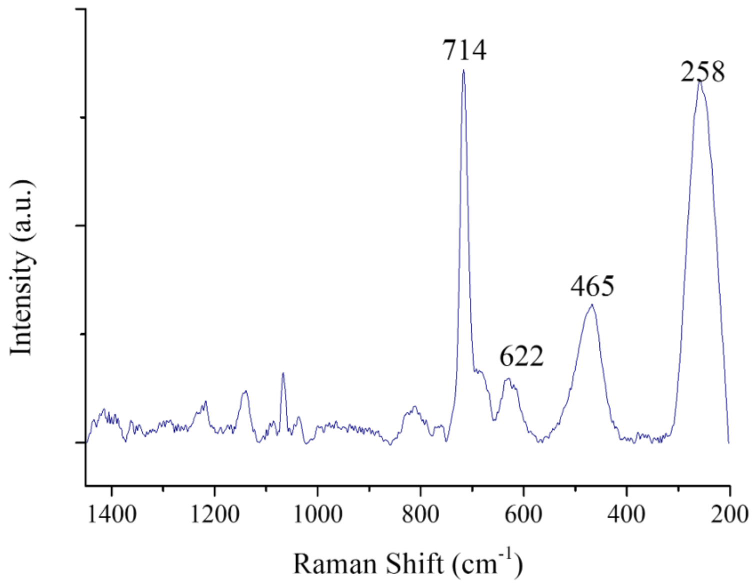


Fig. S9 The Raman spectrum of the used catalysts sample.

Table S3 The composition of the as-prepared vs. the used catalyst samples (materials C and C_{used}) by ICP-AES measurements

Sample	Ag content (w%)	Bi content (w%)	Formula
C	6.1	62.7	$Ag_{0.17}Bi_{0.88}O_2CO_3$
C_{used}	6.0	63.3	$Ag_{0.17}Bi_{0.91}O_2CO_3$

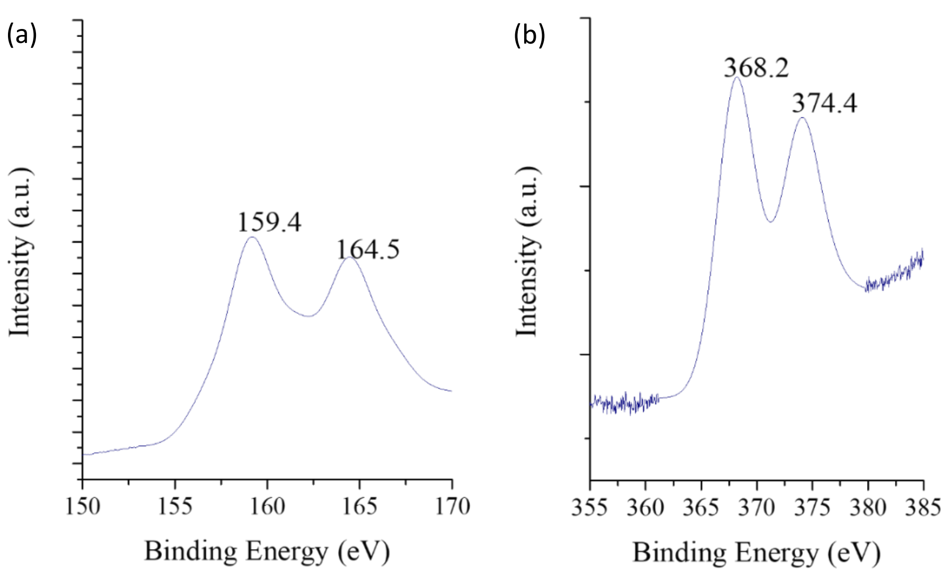
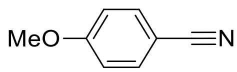


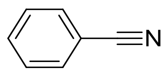
Fig. S10 Ag3d (a) and Bi4f (b) XPS spectra of the used catalyst sample.

4. Analytical data of the reaction products



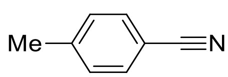
4-methoxybenzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.56–7.59 (d, J= 8.95 Hz, 2H); 6.93–6.96 (d, J= 8.95 Hz, 2H); 3.86 (s, 3H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 133 (M^+), 118, 103, 90, 76, 63.



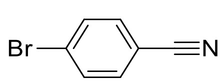
benzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.64–7.70 (d, J= 7.58 Hz, 2H); 7.59–7.63 (t, J= 7.87 Hz, 1H); 7.46–7.52 (t, J= 7.58 Hz, 2H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 103 (M^+), 86, 76, 63, 50, 39.



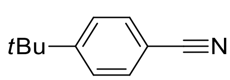
4-methylbenzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.53–7.55 (d, J= 8.10 Hz, 2H); 7.26–7.28 (d, J= 8.10 Hz, 2H); 2.42 (s, 3H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 117 (M^+), 90, 63, 51, 39.



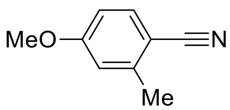
4-bromobenzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.63–7.65 (d, J= 8.42 Hz, 2H); 7.52–7.54 (d, J= 8.42 Hz, 2H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 181 (M^+), 102, 75, 51.



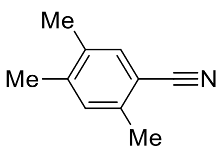
4-(*tert*-butyl)benzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.57–7.60 (d, J= 8.50 Hz, 2H); 7.47–7.49 (d, J= 8.50 Hz, 2H); 1.33 (s, 9H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 159 (M^+), 144, 116, 104, 89, 77, 63.



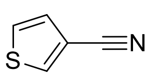
4-methoxy-2-methylbenzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.50–7.52 (d, J= 8.31, 1H); 6.75–6.79 (m, 2H); 3.84 (s, 3H); 2.51 (s, 3H). NMR data is in agreement with the literature reference.[6] MS (EI): m/z = 147 (M^+), 132, 117, 104, 90, 77, 63.



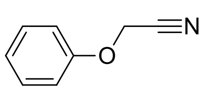
2,4,5-trimethylbenzonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.32 (s, 1H); 7.06 (s, 1H); 2.45 (s, 3H); 2.27 (s, 3H); 2.23 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 142.6; 139.6; 135.2; 133.5; 131.9; 119.0; 110.2; 20.4; 20.2; 19.4. MS (EI): m/z = 145 (M^+), 130, 115, 103, 89, 77, 63.



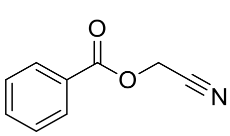
thiophene-3-carbonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.94–7.95 (d, J= 2.58 Hz, 1H); 7.42–7.44 (q, J= 8.31 Hz, 1H); 7.30–7.32 (d, J= 5.2 Hz, 1H). NMR data is in agreement with the literature reference.[7] MS (EI): m/z = 109 (M^+), 82, 64, 58, 45.



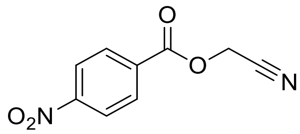
2-phenoxyacetonitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.33–7.37 (t, J= 8.28 Hz, 2H); 7.07–7.11 (t, J= 7.95 Hz, 1H); 7.00–6.96 (d, J= 7.95 Hz 2H); 4.76 (s, 2H). NMR data is in agreement with the literature reference.[8] MS (EI): m/z = 133 (M^+), 105, 93, 77, 65.



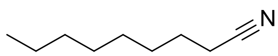
cyanomethyl benzoate

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.04–8.08 (d, J= 7.43 Hz, 2H); 7.61–7.65 (t, J= 7.63 Hz, 1H); 7.46–7.51 (t, J= 7.63 Hz, 2H); 4.97 (s, 2H). NMR data is in agreement with the literature reference.[9] MS (EI): m/z = 161 (M^+), 105, 77.



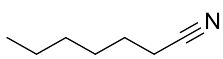
cyanomethyl 4-nitrobenzoate

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.33–8.35 (d, J= 7.46 Hz, 2H); 8.24–8.26 (d, J= 7.46 Hz, 2H); 5.02 (s, 2H). NMR data is in agreement with the literature reference.[9] MS (EI): m/z = 206 (M^+), 176, 150, 120, 104, 92, 76, 64.



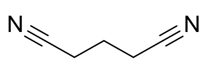
nonanenitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.30–2.37 (t, J= 7.25 Hz, 2H); 1.61–1.71 (m, 2H); 1.40–1.48 (m, 2H); 1.26–1.33 (m, 6H); 0.86–0.92 (m, 3H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 111, 97, 83, 71, 57, 44, 28.



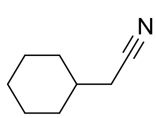
heptanenitrile

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.30–2.37 (t, J= 7.25 Hz, 2H); 1.60–1.69 (m, 2H); 1.41–1.49 (m, 2H); 1.29–1.35 (m, 4H); 0.85–0.93 (m, 3H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 96, 83, 55, 44, 28.



glutaronitrile

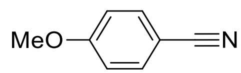
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.52–2.58 (t, J= 7.16 Hz, 4H); 2.01–2.09 (m, 2H). NMR data is in agreement with the literature reference.[10] MS (EI): m/z = 66, 54, 40, 28.



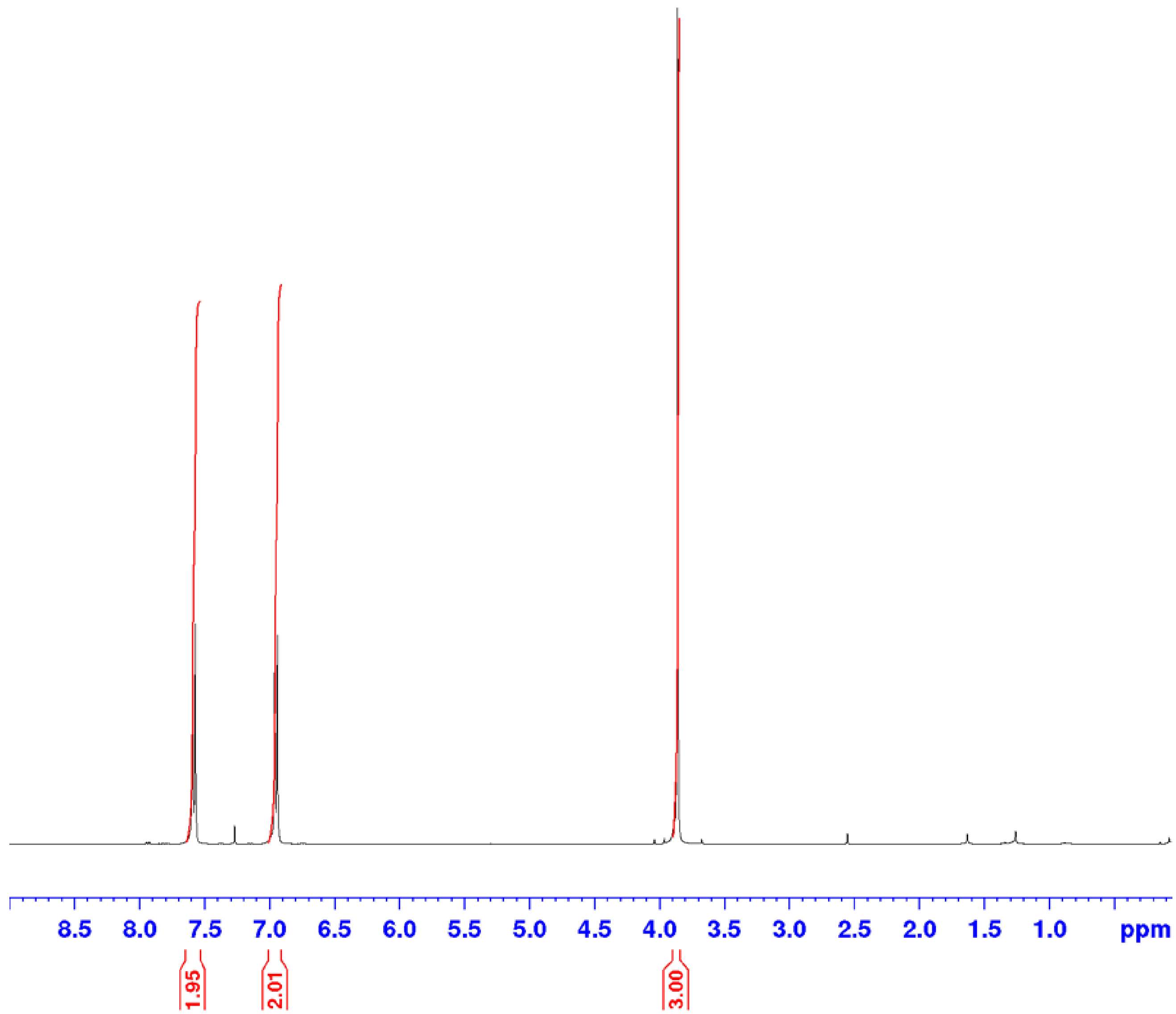
2-cyclohexylacetonitrile

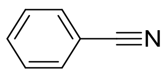
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.20–2.26 (d, J= 6.58 Hz, 2H); 1.63–1.86 (m, 6H); 1.00–1.34 (m, 5H). NMR data is in agreement with the literature reference.[5] MS (EI): m/z = 96, 83, 67, 55.

5. Collection of NMR and MS Spectra

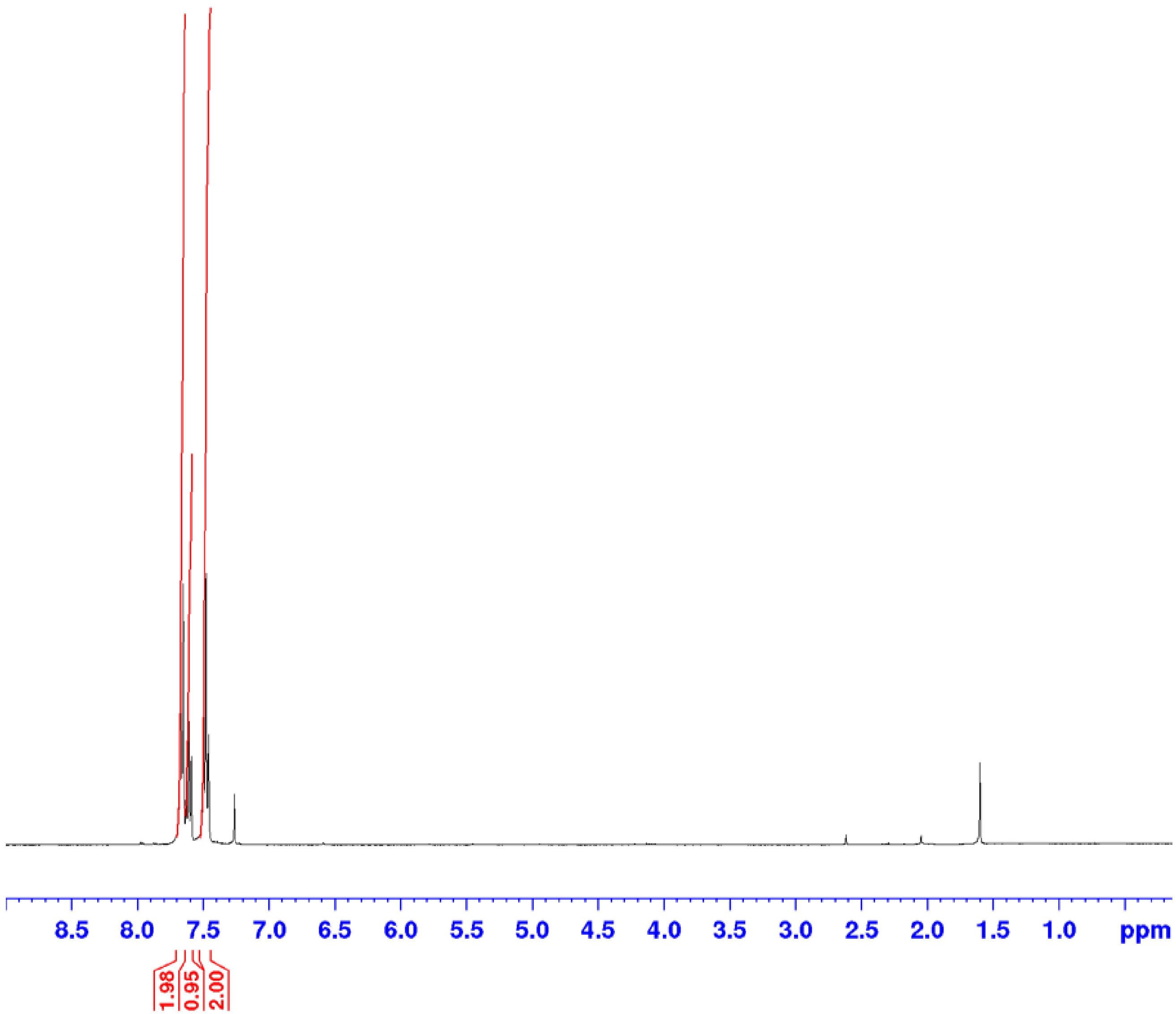


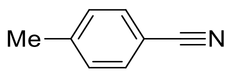
4-methoxybenzonitrile

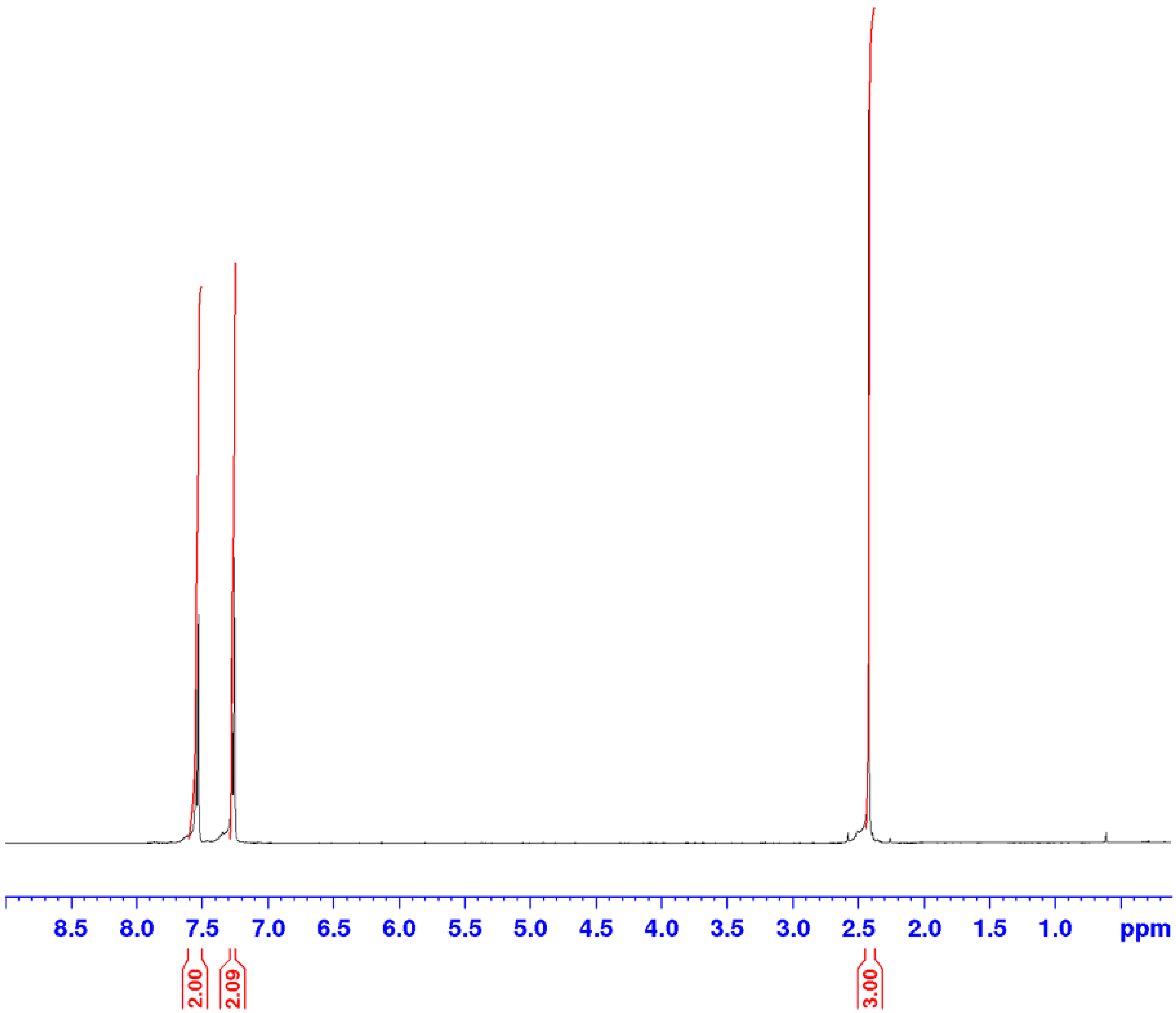


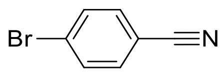


benzonitrile

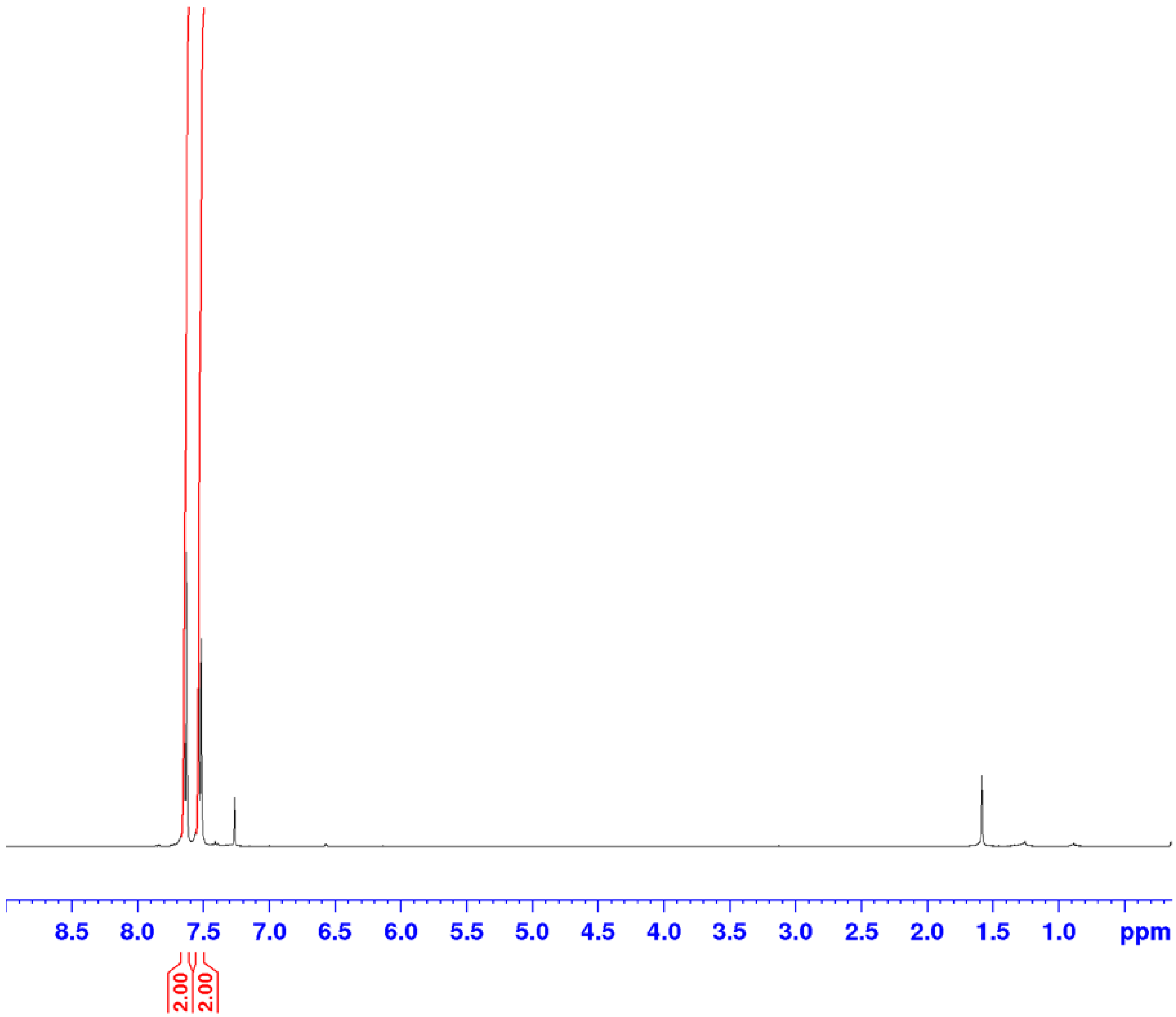


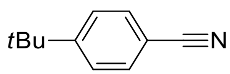

4-methylbenzonitrile



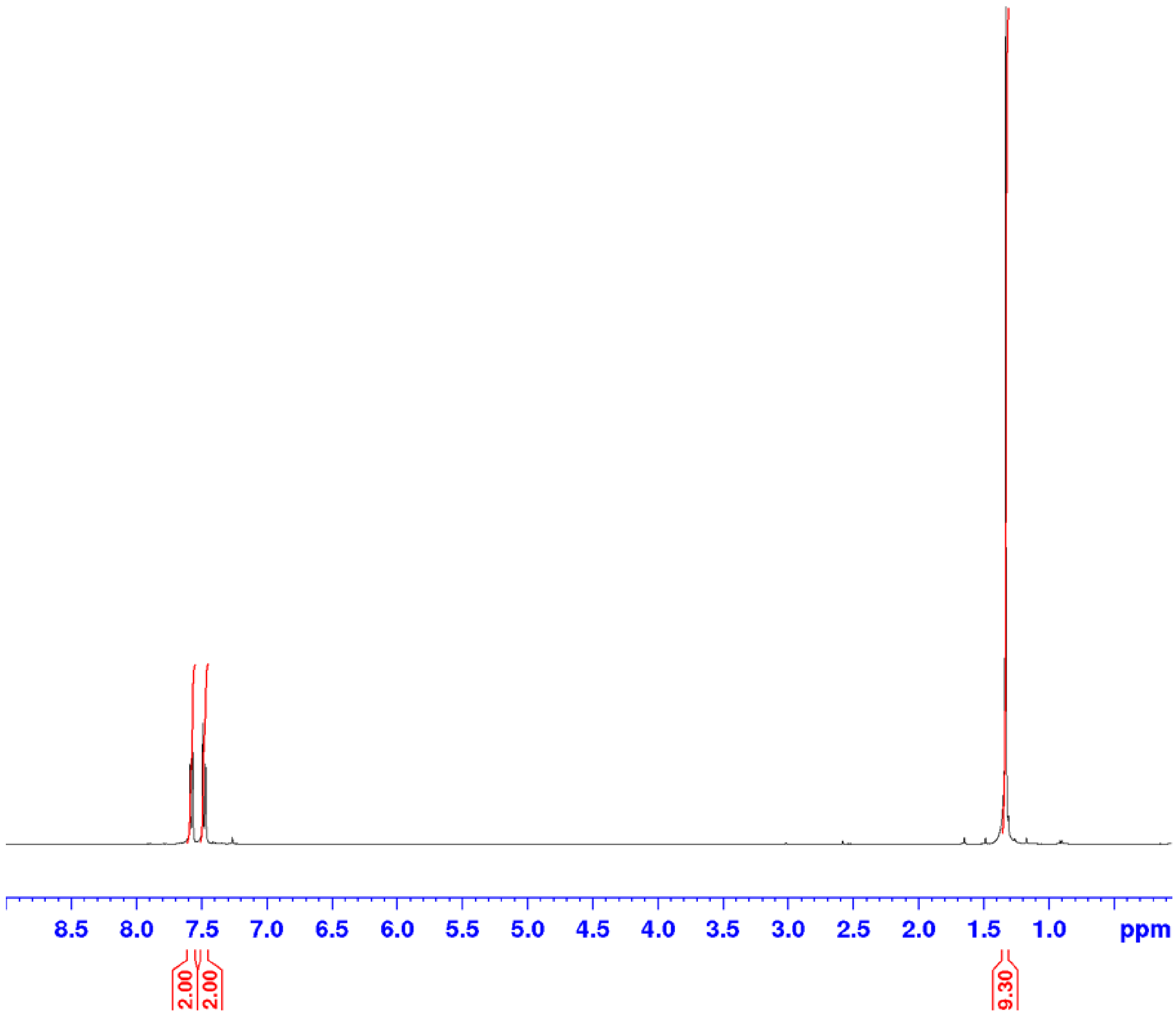


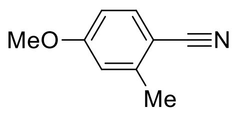
4-bromobenzonitrile



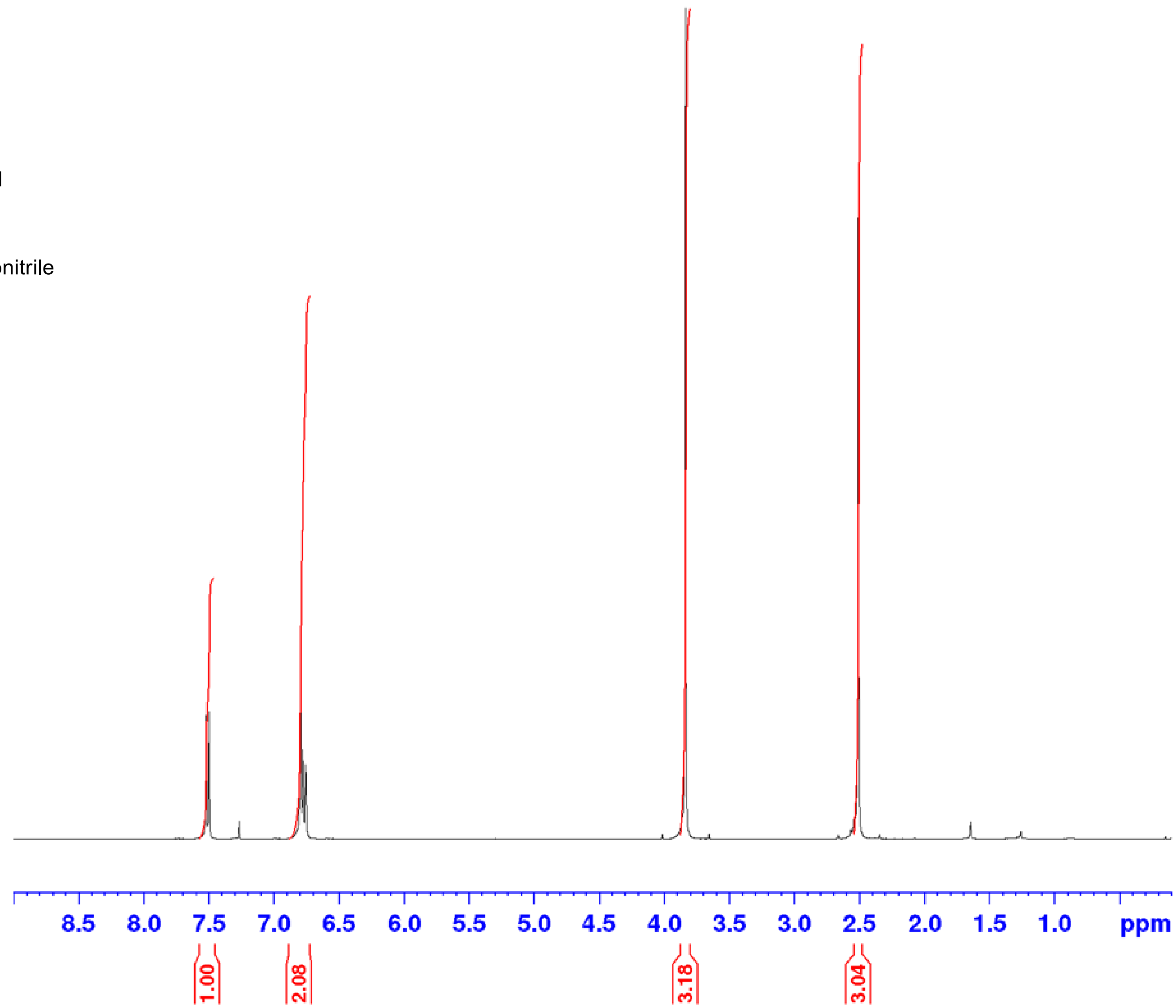


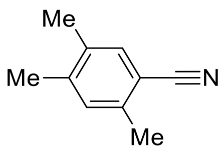
4-(*tert*-butyl)benzonitrile



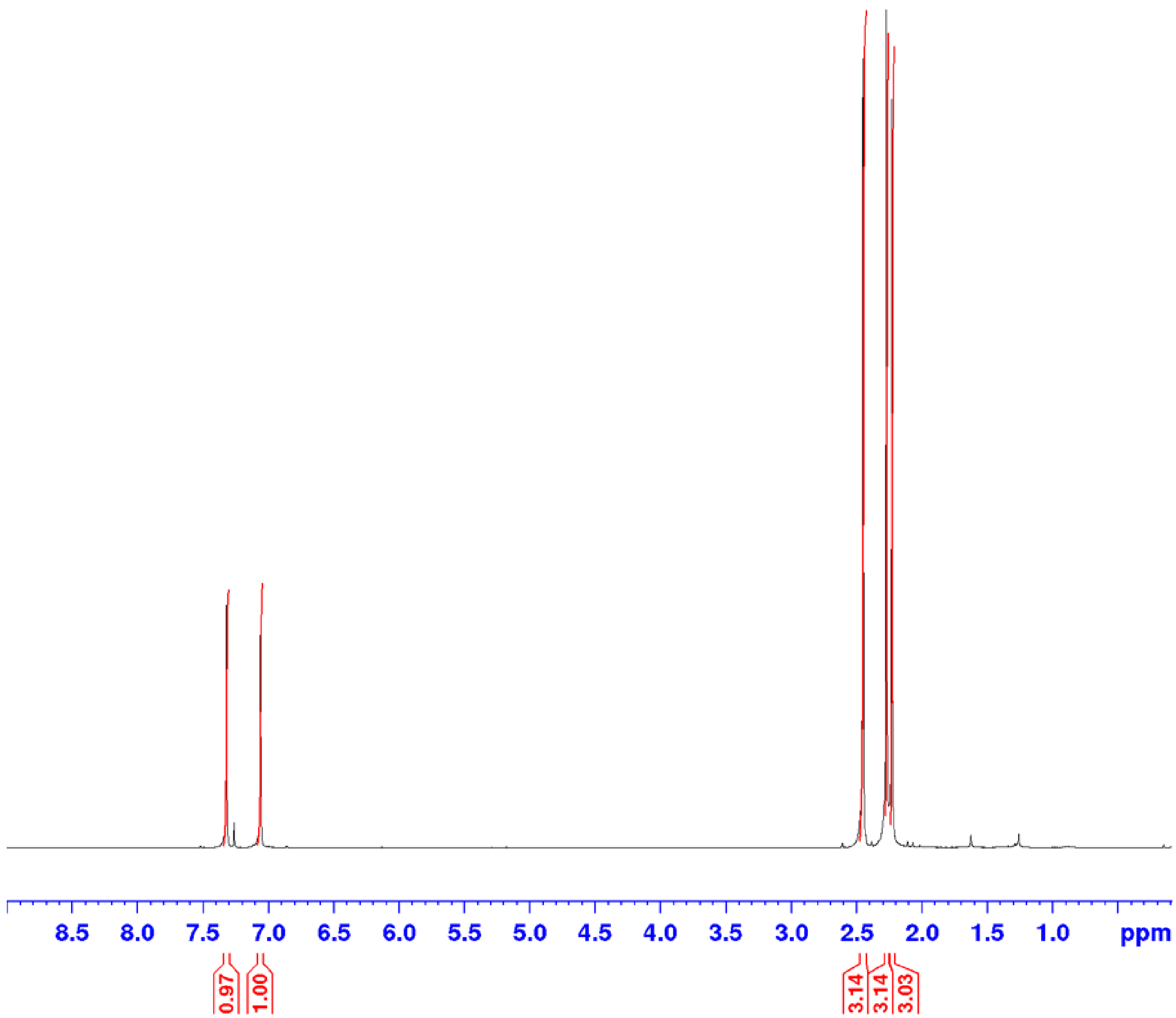


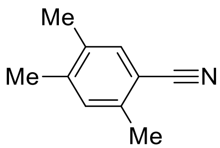
4-methoxy-2-methylbenzonitrile





2,4,5-trimethylbenzonitrile

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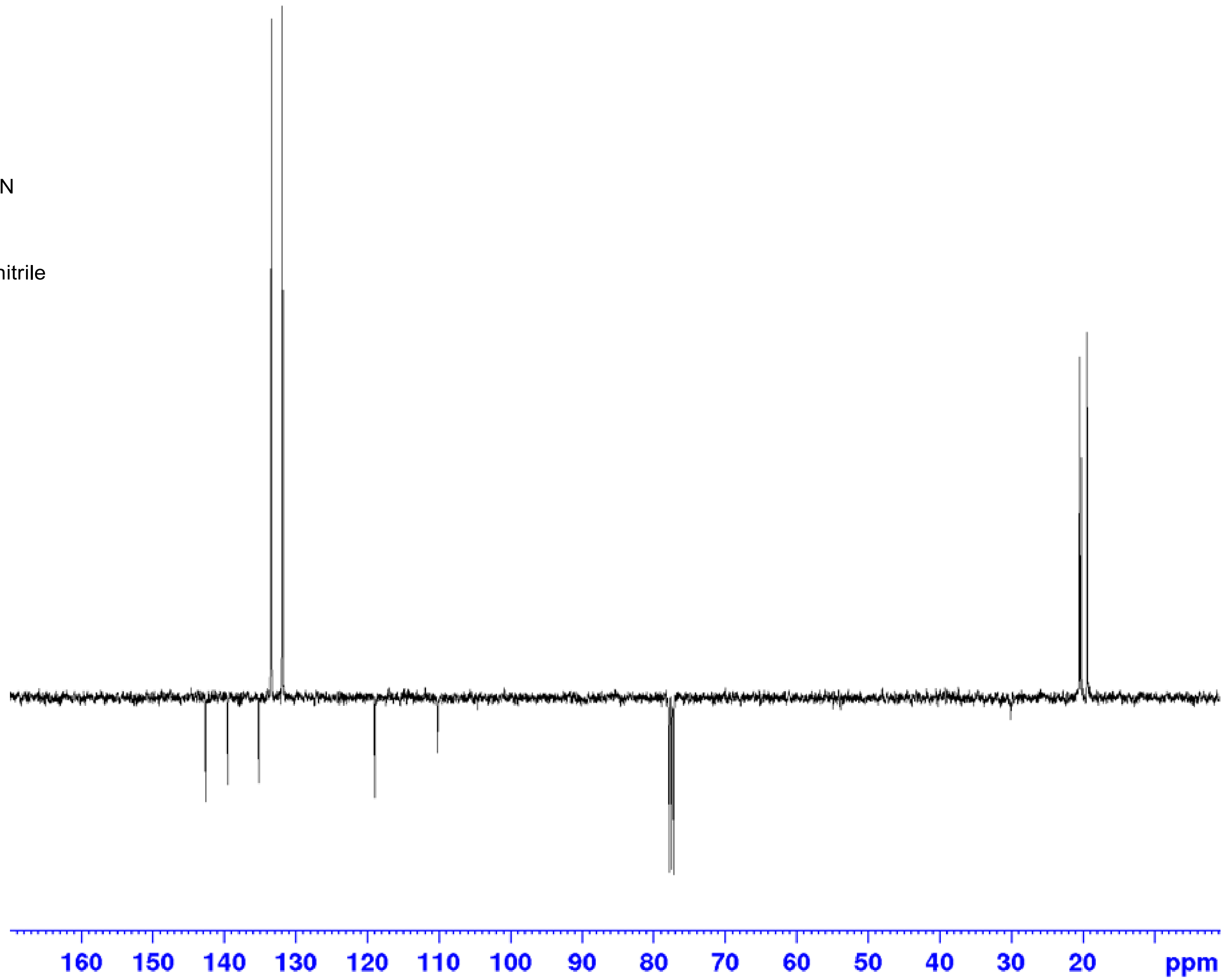

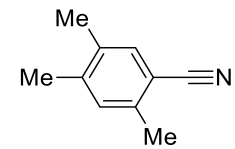

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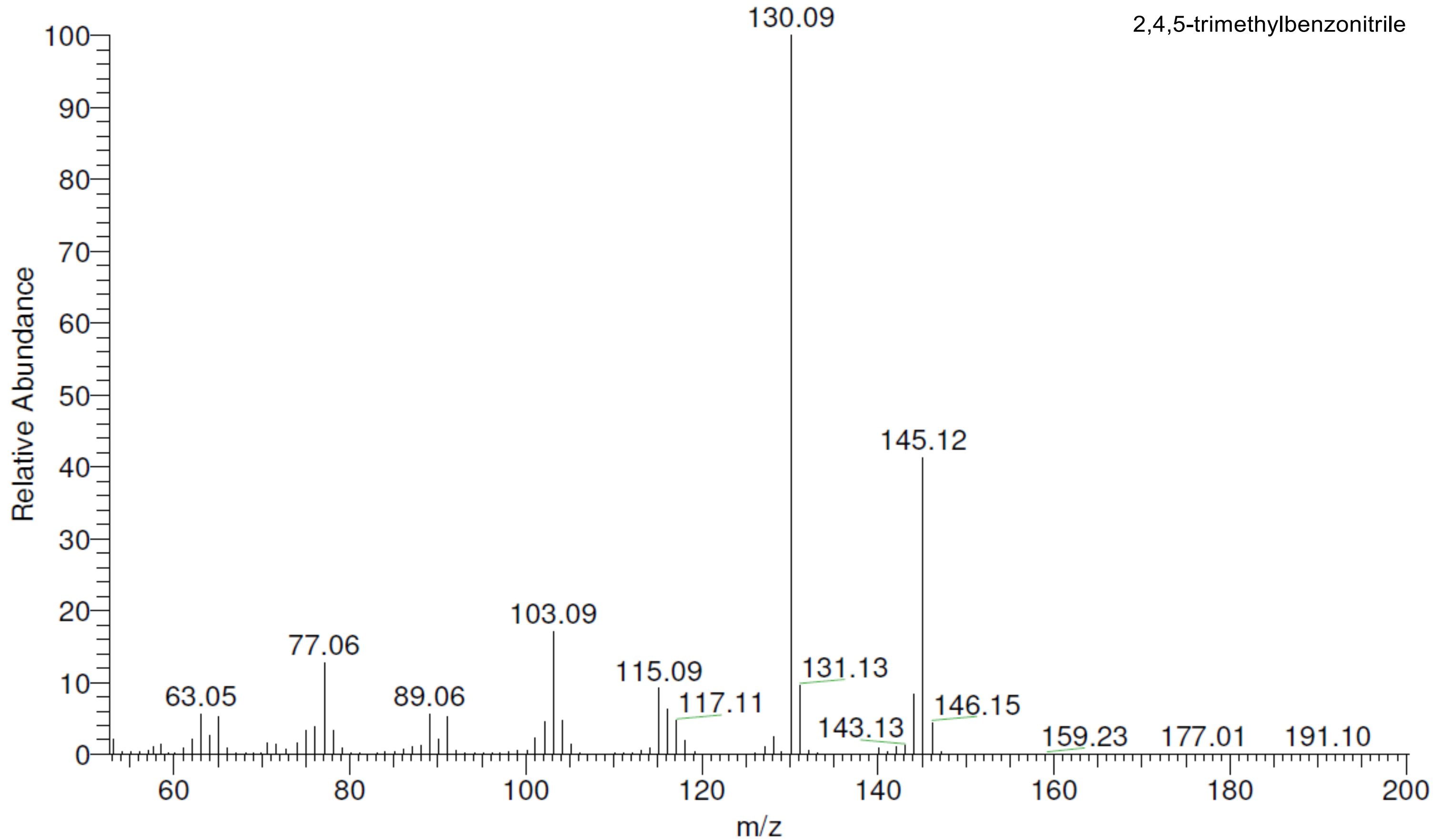

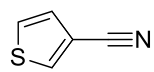

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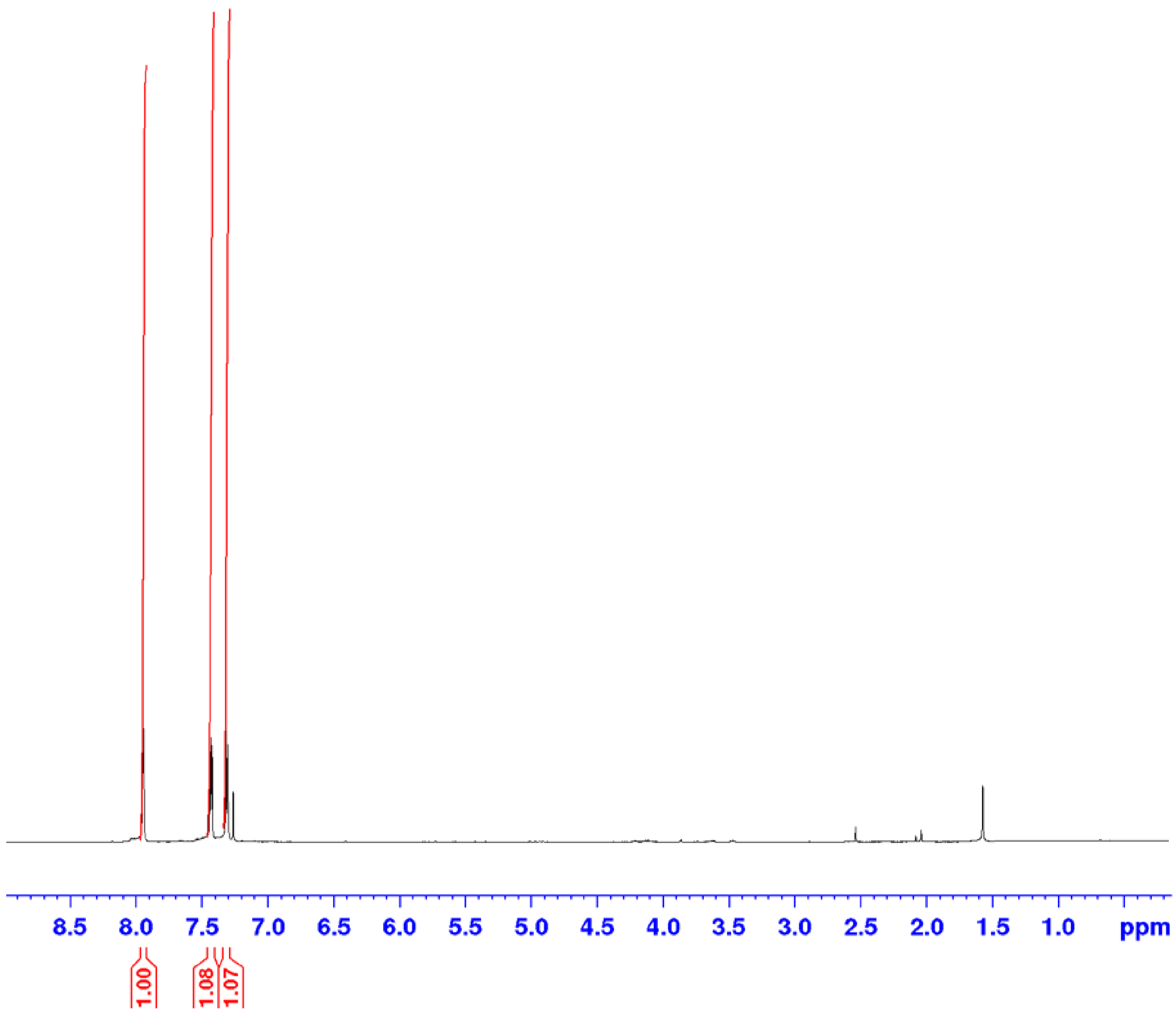

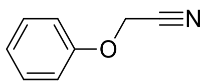

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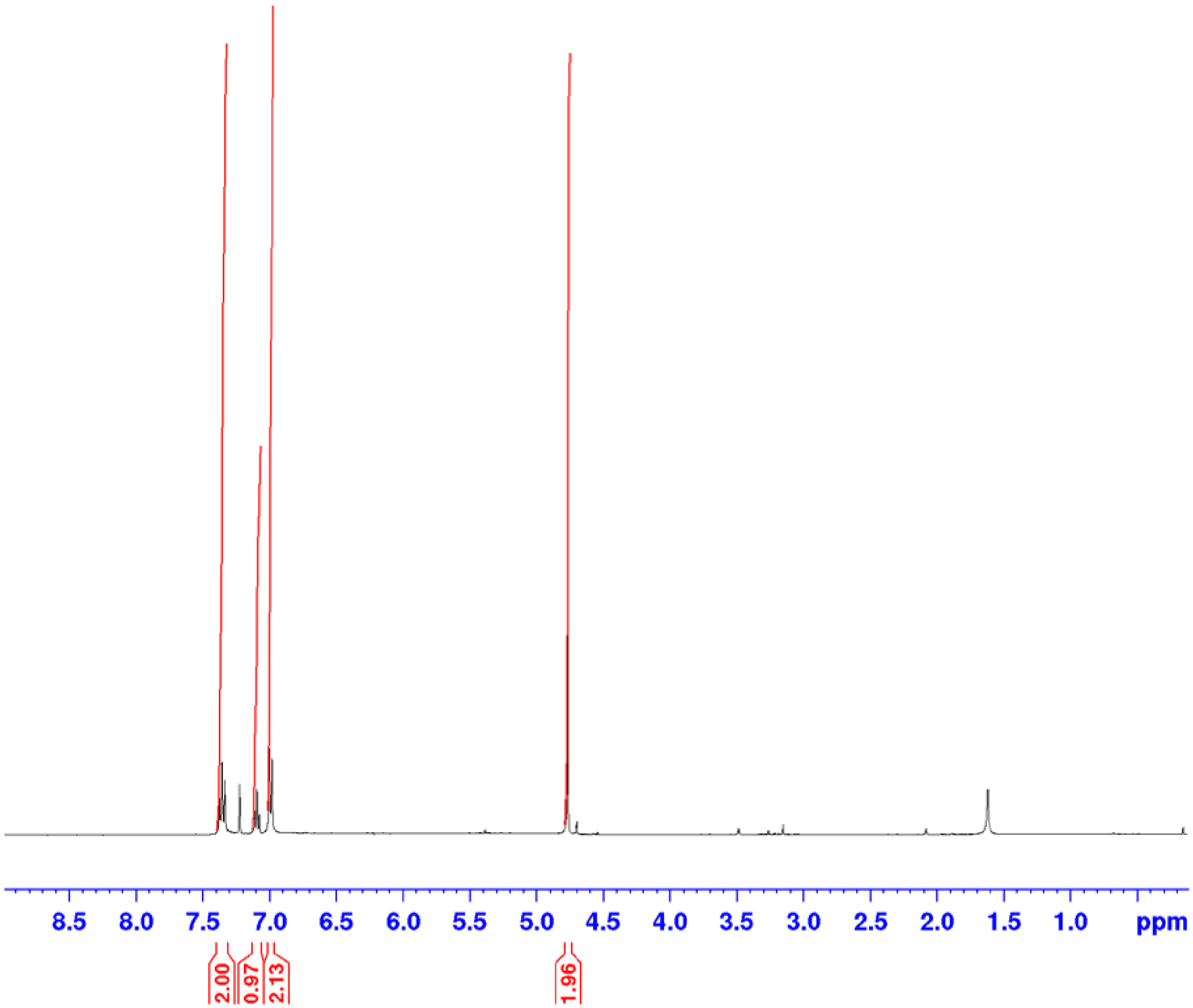
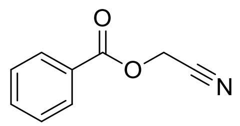
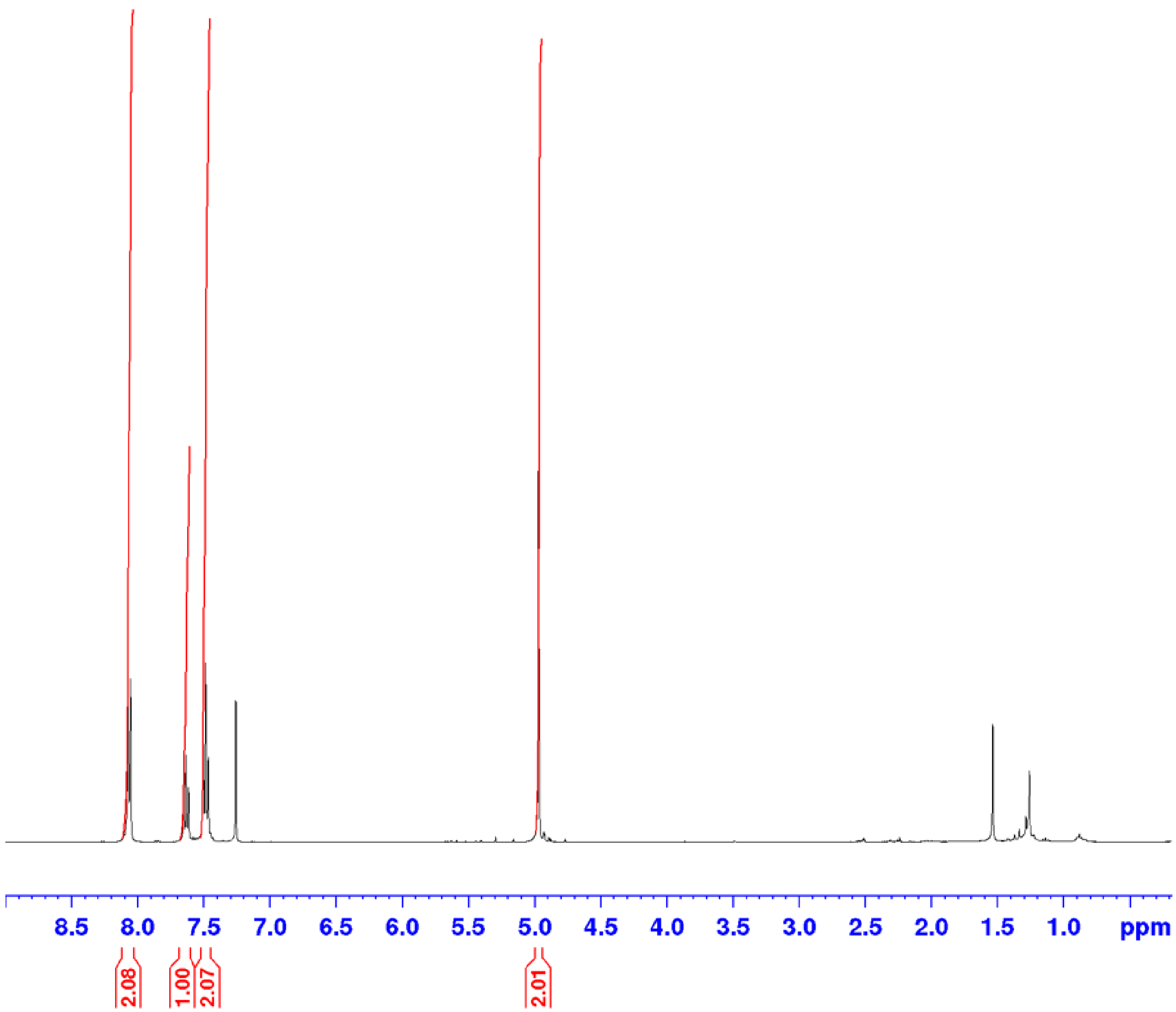
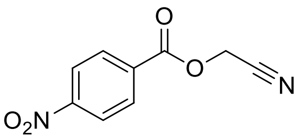




cyanomethyl benzoate





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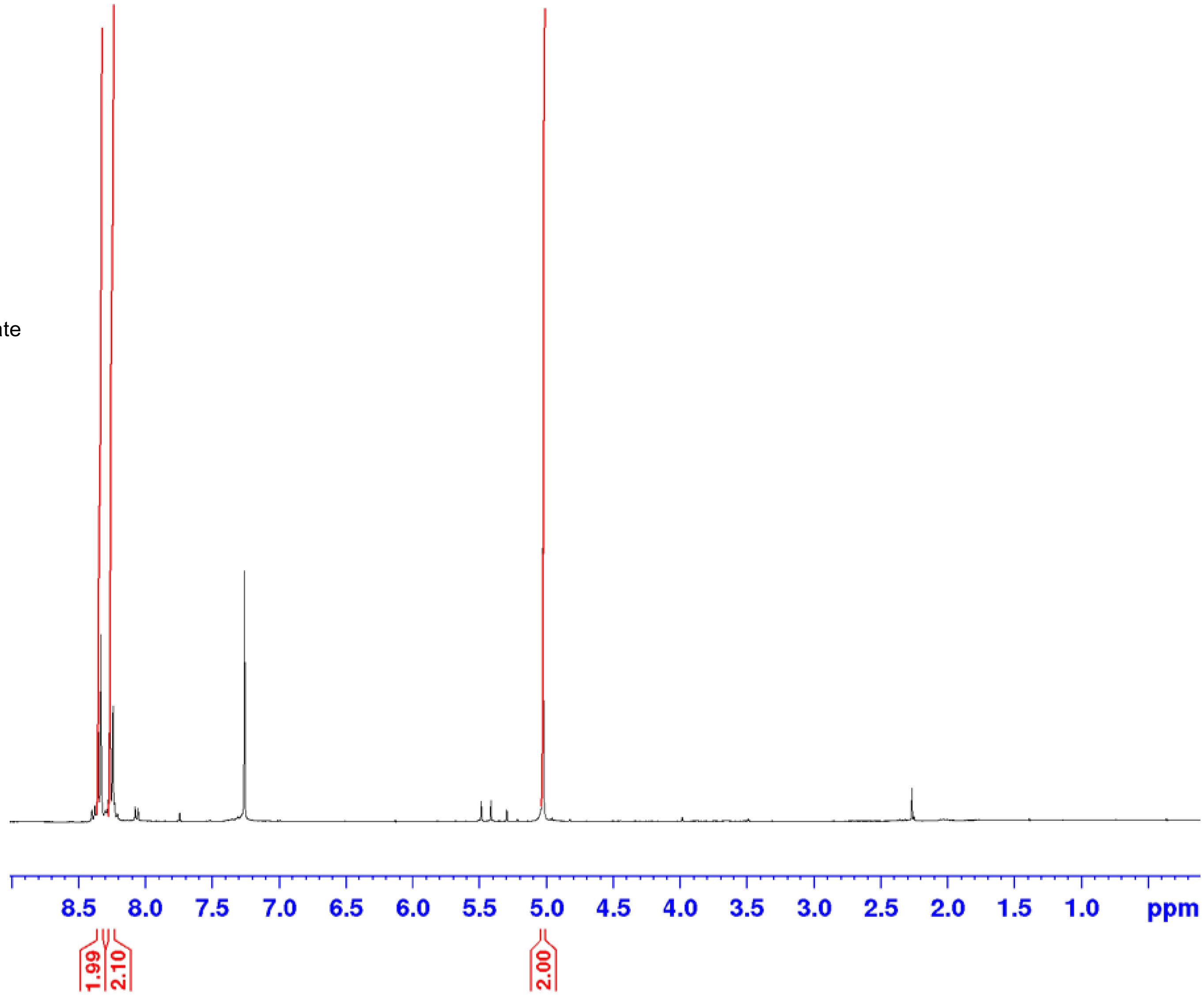
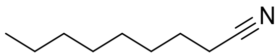
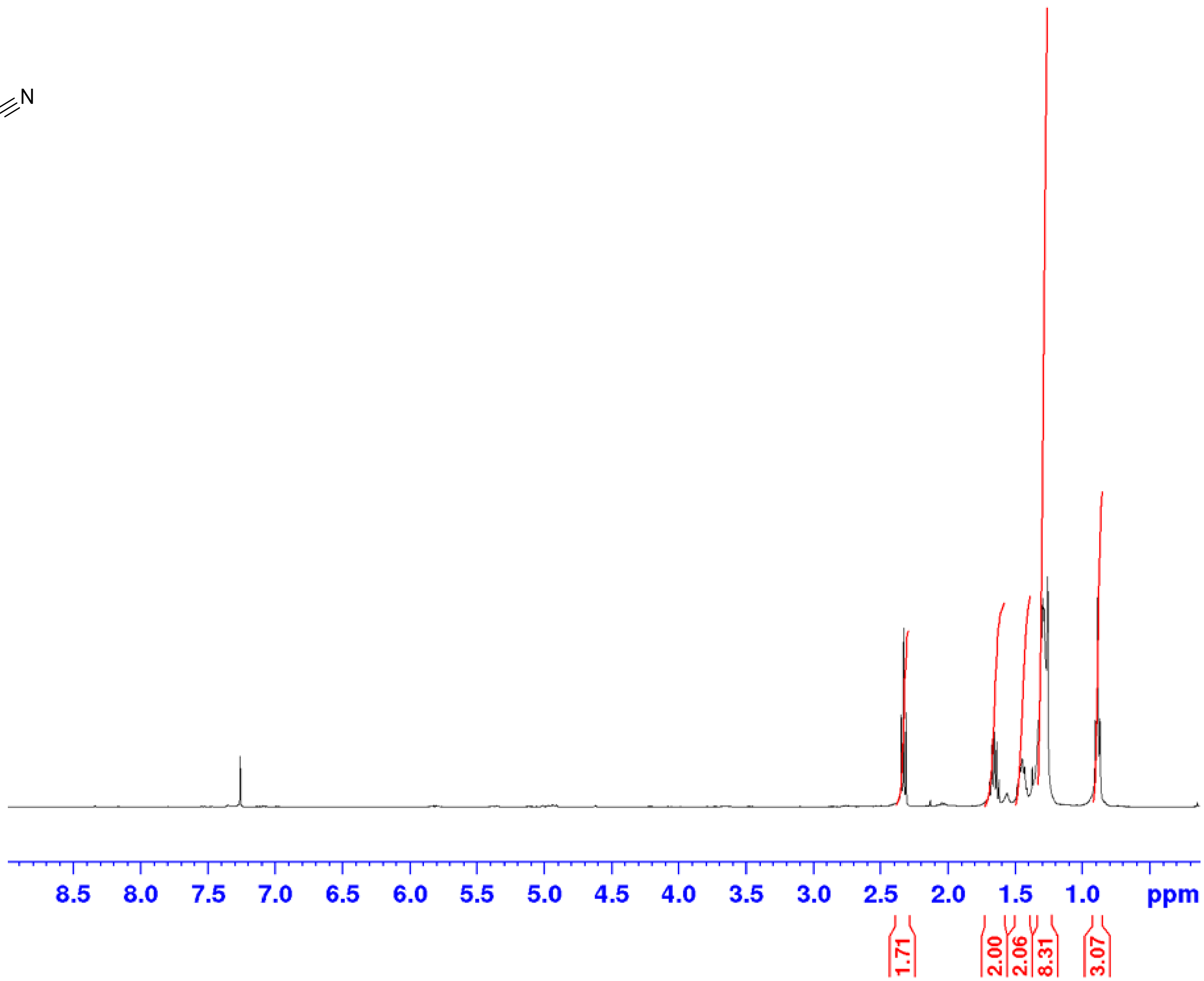
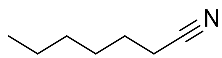




nonanenitrile





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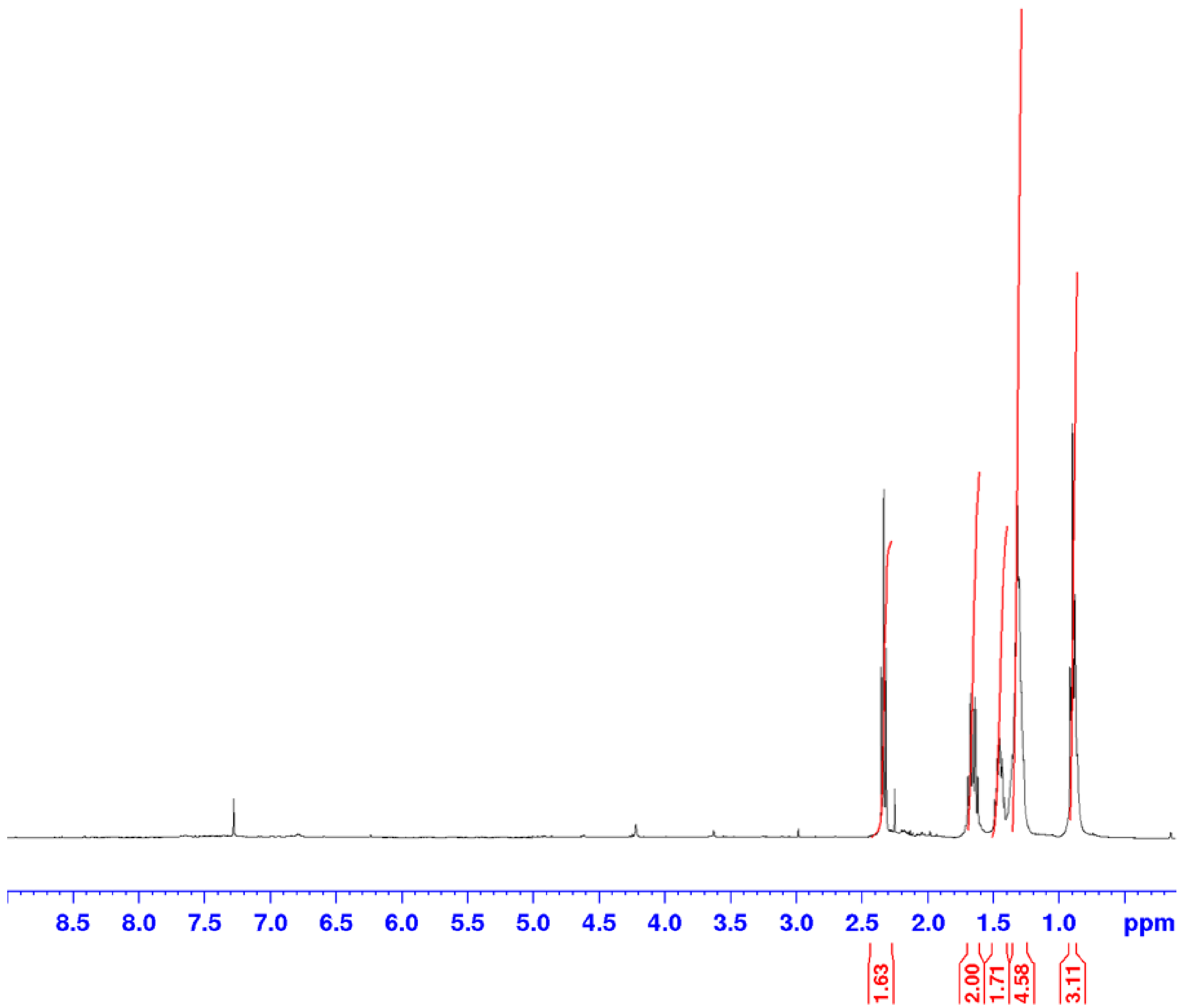

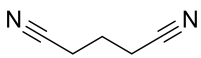
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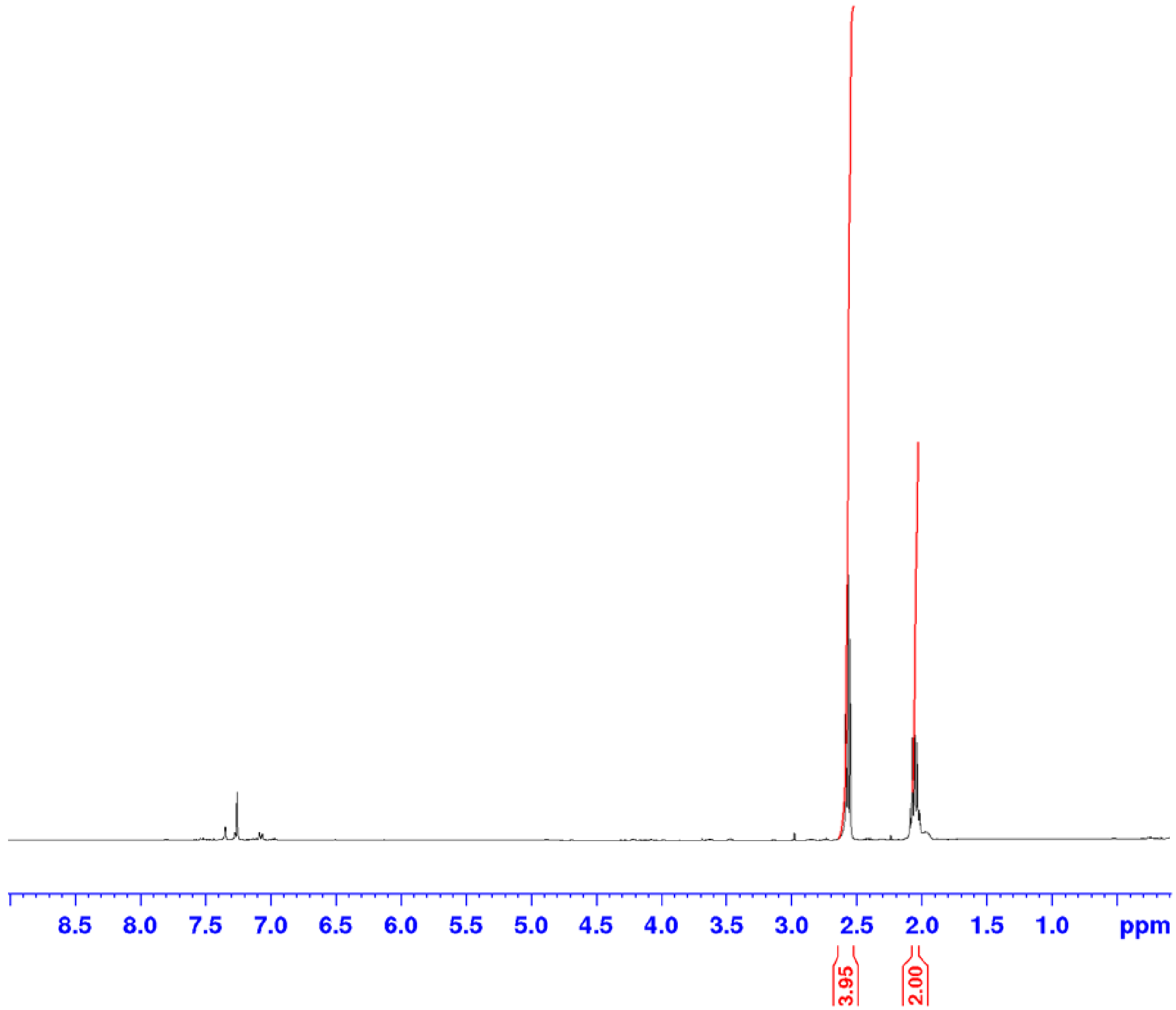
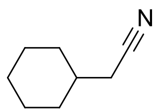
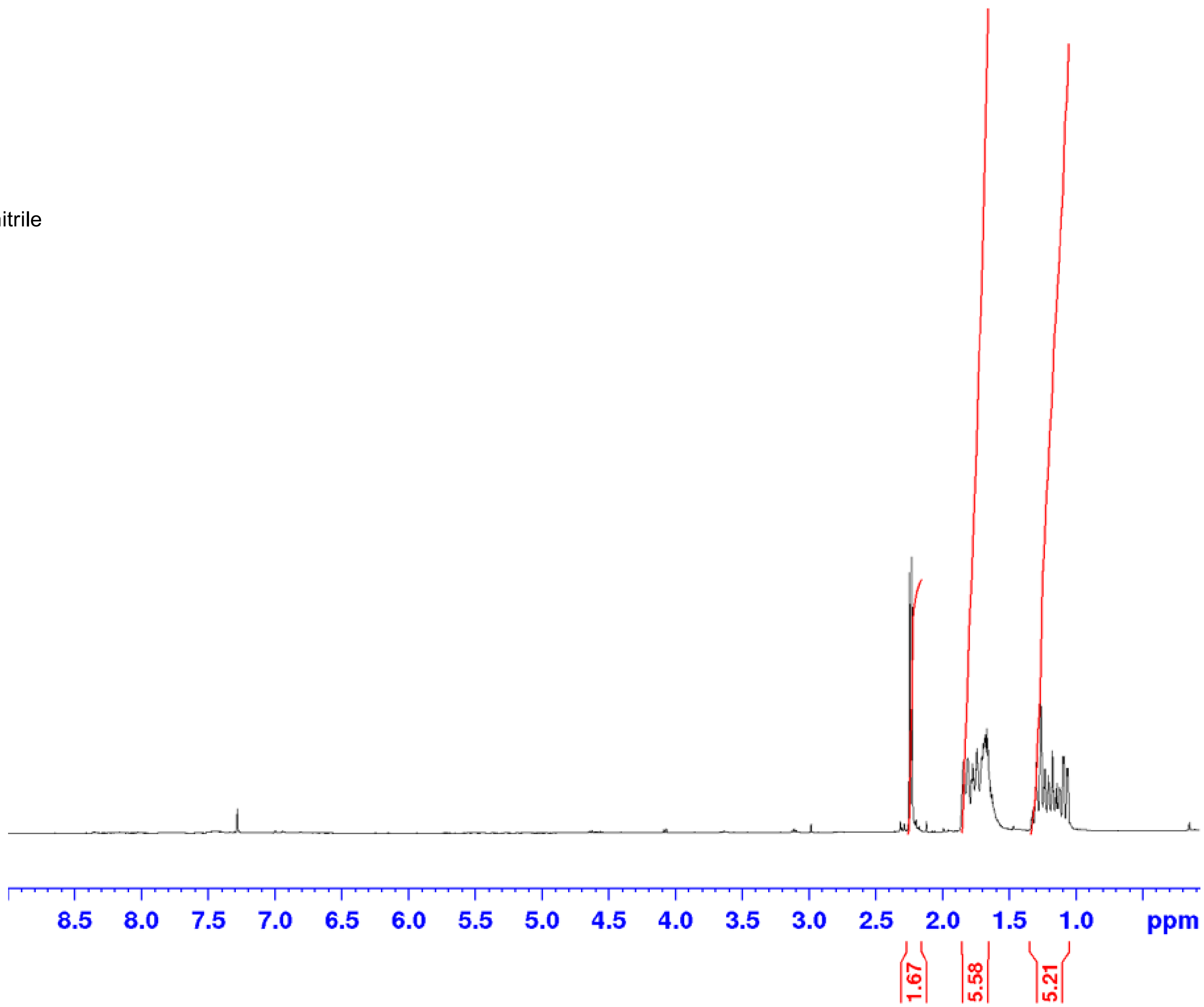




2-cyclohexylacetonitrile



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