Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Unlocking the catalytic potency of a magnetic responsive $CoFe_2O_4$/Ni-BTC MOF composite for the sustainable synthesis of tri and tetra-substituted imidazoles

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Experimental section

Materials and reagents

1,3,5-benzene tricarboxylic acid (BTC) was purchased from Tokyo Chemical Industry Pvt. Ltd. Nickel nitrate, ferric chloride and cobalt chloride were procured from Sisco Research Laboratory (SRL). Anhydrous sodium acetate, anhydrous sodium sulphate, ethyl acetate and ethanol were purchased from Merck. Rests of the reagents were obtained from Spectrochem Pvt. Ltd. Double distilled water was used throughout the whole protocol.

Instrumentation

FT-IR spectra of samples were carried out using KBr pellet from Perkin Elmer Spectrum 2000 FT-IR Spectrometer. SEM using a JEOL instrument was employed to gain an insight into the size, shape and morphological characteristics of the synthesized composites. For this, sample was kept on a carbon tape and coated with gold using a JEOL JEC-3000 FC gold sputtering machine. Similarly, TEM micrographs were obtained for confirming the shape and size and nanoparticles using a FEI TECHNAI G^2 T20 microscope operated at 200 kV. XRD spectra of all the samples were obtained from a Bruker D8 ADVANCE (Karlsruhe, bundesland, Germany) X-ray diffractometer in the 2Θ range of 5-80^o. A Fischerscope X-Ray XAN-FAD BC was employed to carry out the ED-XRF spectroscopic analysis. Magnetization studies of all the modified magnetic and non-magnetic samples were performed using a vibrating sample magnetometer (EV-9, Microsense, ADE). XPS analysis of samples was carried out using a Thermo Fischer ESCALAB XI+. The amount of nickel loading in the final composite was determined using a flame atomic absorption spectroscopy (model no. N3180021 PinAAcle 500) using an acetylene flame. Synthesized organic products were characterized by interpreting the fragmentation patterns of mass spectra obtained through an Agilent gas chromatogram (6850 GC) equipped 5975C mass selective detector (MSD) using helium as a carrier gas. ^{1}H and ^{13}C NMR of imidazole products were recorded using a JEOL JNM-EXCP-400 instrument.

Catalyst preparation

Synthesis of cobalt ferrite nanoparticles ($CoFe_2O_4$)

$CoFe_2O_4$ nanoparticles were prepared using a solvothermal strategy, wherein initial step involved the addition of 148.7 mg of $CoCl_2.6H_2O$ and 337.9 mg of $FeCl_3.6H_2O$ in 10 mL ethylene glycol under stirring till a homogeneous solution was obtained.[1] The subsequent step involved the addition of 900 mg of sodium acetate and 500 mg PEG-6000 in the above prepared mixture which was stirred for about 30 minutes. The homogeneous mixture so formed was transferred to a Teflon-lined autoclave and heated at 160 ^{o}C for 16 h. The black precipitate obtained was separated *via* external magnet, washed repeatedly with distilled water and eventually dried at 60 ^{o}C in an oven.

Synthesis of nickel benzene-1,3,5-tricarboxylate metal organic framework (Ni-BTC)

$Ni(NO_3)_2.6H_2O$ (1.5 mmol) and benzene-1,3,5-tricarboxylic acid (H_3BTC) (1.0 mmol) were dissolved ultrasonically in 15 mL dimethylformamide for 15 minutes.[2] The resulting solution was transferred to a Teflon lined autoclave and kept at 150 °C for 8 h. Once reaction completed, solution was cooled to r.t. and product was collected *via* centrifugation, washed with DMF, ethanol and dried in a vacuum oven at 60 °C for 12 h.

Synthesis of Ni-BTC decorated with $CoFe_2O_4$ nanoparticles ($CoFe_2O_4$/Ni-BTC)

The hybrid composite of $CoFe_2O_4$/Ni-BTC was prepared using a simple solvothermal approach. $Ni(NO_3)_2.6H_2O$ (1.5 mmol) and benzene-1,3,5-tricarboxylic acid (H_3BTC) (1.0 mmol) were dissolved ultrasonically in 15 mL dimethylformamide for 15 minutes. After this, the synthesized $CoFe_2O_4$ nanoparticles were added and stirred further for about 15 minutes. Ultimately, the solution obtained was transferred to a Teflon lined stainless steel autoclave and held at 150 °C for 8 h. Solution was then cooled to r.t. and product was collected *via* an external magnet, washed with DMF, ethanol and dried in a vacuum oven at 60 °C for 12 h.

General procedure for hybrid magnetic $CoFe_2O_4$/Ni-BTC mediated synthesis of 2,4,5-trisubstituted imidazoles

To a 25 mL round bottom flask, substituted 1,2-diketones (1 mmol), substituted benzaldehydes (1 mmol), ammonium acetate (2 mmol) and $CoFe_2O_4$/Ni-BTC (20 mg) were added and resulting mixture was stirred at 100 °C for 30 minutes. Once the reaction completed, mixture was cooled to r.t. and $CoFe_2O_4$/Ni-BTC was removed using external magnet. Reaction mixture was extracted using ethyl acetate, organic layer was separated and dried over sodium sulfate. Product obtained was recrystallized using ethanol to give pure 2,4,5-trisubstituted imidazoles which were then analyzed using GC-MS and NMR spectroscopy.

General procedure for hybrid magnetic $CoFe_2O_4$/Ni-BTC mediated synthesis of 1,2,4,5-tetrasubstituted imidazoles

To a 25 mL round bottom flask, 1,2-diketones (2.5 mmol), substituted benzaldehydes (2.5 mmol), benzylamine (2.5 mmol), ammonium acetate (2.5 mmol) and $CoFe_2O_4$/Ni-BTC (20 mg) were added and resulting mixture was stirred at 100 °C for 30 minutes. Once the reaction completed, mixture was cooled to r.t. with subsequent removal of $CoFe_2O_4$/Ni-BTC using external magnet. Reaction mixture was extracted using ethyl acetate, organic layer was separated and dried over sodium sulfate. Product obtained was recrystallized using ethanol to give pure 1,2,4,5-tetrasubstituted imidazoles which were then analyzed using NMR spectroscopy.

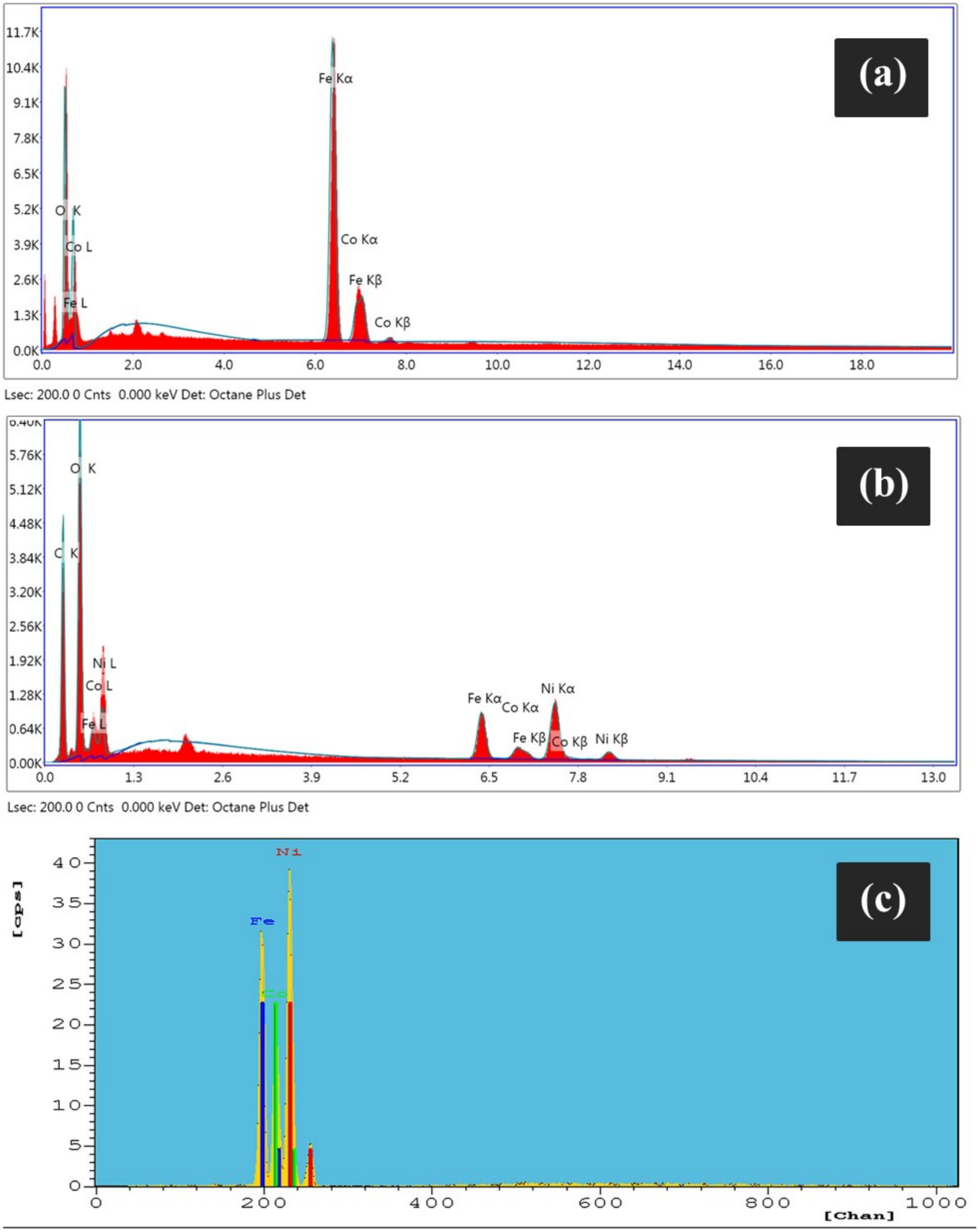


Fig. S1 EDS of (a) $CoFe_2O_4$, (b) $CoFe_2O_4$/Ni-BTC and ED-XRF of (c) $CoFe_2O_4$/Ni-BTC.

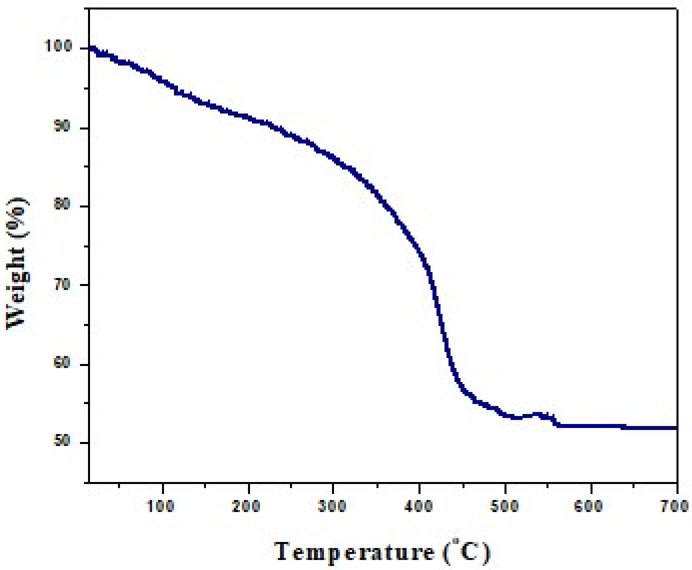


Fig. S2 Thermogravimetric analysis curve of $CoFe_2O_4$/Ni-BTC

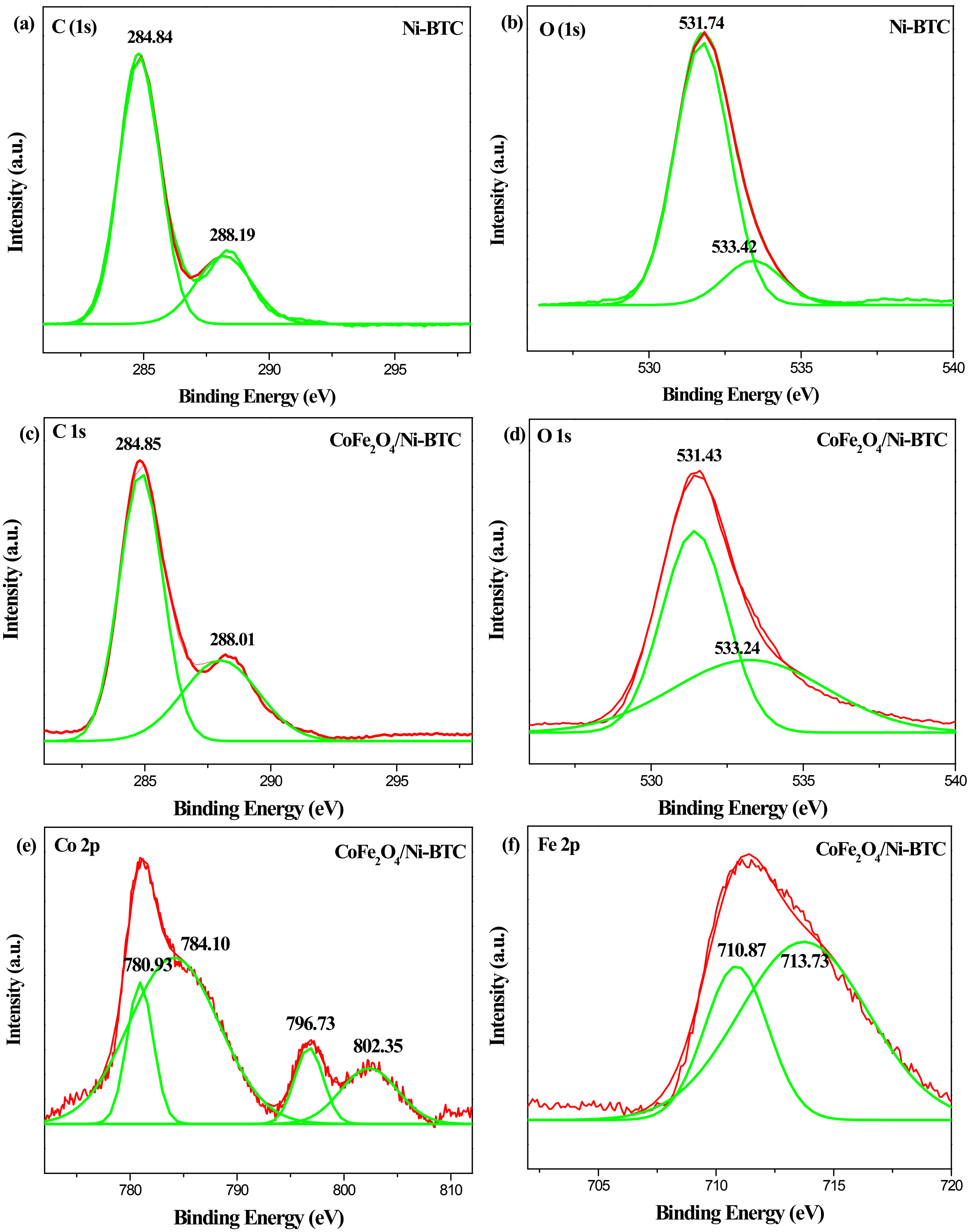

(a)
C (1s)
Ni-BTC
284.84
288.19
Intensity (a.u.)
285
290
295
Binding Energy (eV)
(b)
O (1s)
Ni-BTC
531.74
533.42
Intensity (a.u.)
530
535
540
Binding Energy (eV)
(c)
C 1s
$CoFe_2O_4$/Ni-BTC
284.85
288.01
Intensity (a.u.)
285
290
295
Binding Energy (eV)
(d)
O 1s
$CoFe_2O_4$/Ni-BTC
531.43
533.24
Intensity (a.u.)
530
535
540
Binding Energy (eV)
(e)
Co 2p
$CoFe_2O_4$/Ni-BTC
784.10
780.93
796.73
802.35
Intensity (a.u.)
780
790
800
810
Binding Energy (eV)
(f)
Fe 2p
$CoFe_2O_4$/Ni-BTC
710.87
713.73
Intensity (a.u.)
705
710
715
720
Binding Energy (eV)

Fig. S3 High resolution XPS spectrum of (a) C 1s (Ni-BTC) , (b) O 1s (Ni-BTC), (c) C 1s $CoFe_2O_4$/Ni-BTC, (d) O 1s ($CoFe_2O_4$/Ni-BTC), (e) Co 2p ($CoFe_2O_4$/Ni-BTC) and (f) Fe 2p ($CoFe_2O_4$/Ni-BTC).

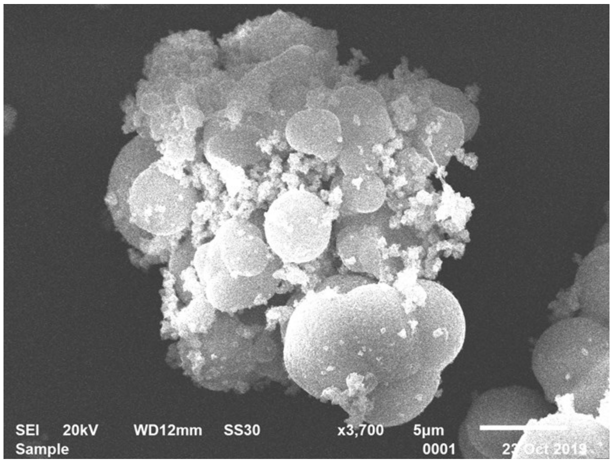


Fig. S4 SEM of recovered $CoFe_2O_4$/Ni-BTC

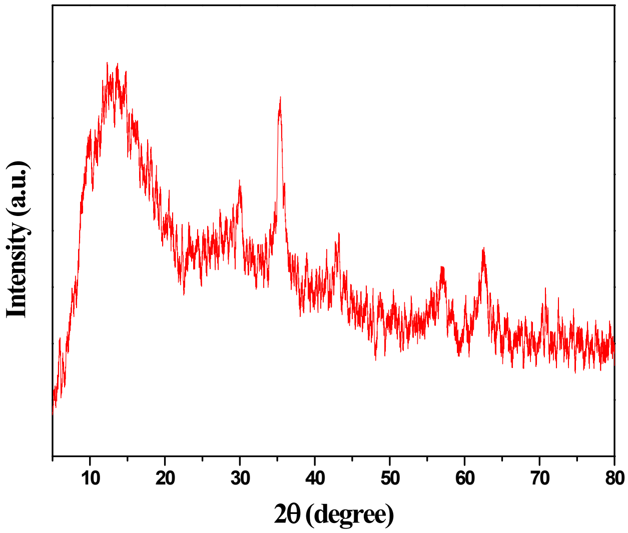


Fig. S5 XRD spectrum of recovered $CoFe_2O_4$/Ni-BTC

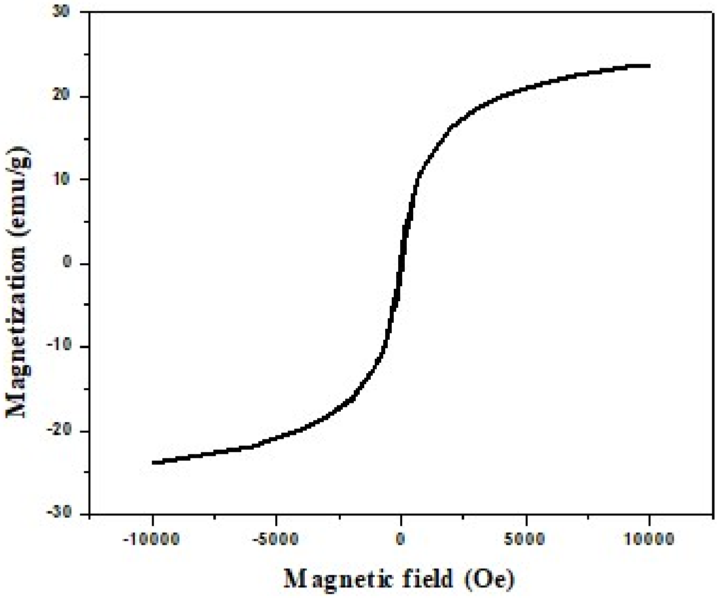


Fig. S6 VSM of recovered $CoFe_2O_4$/Ni-BTC

Table S1. Comparison of catalytic activity of $CoFe_2O_4$/Ni-BTC for synthesis of 2,4,5-trisubstituted imidazoles with literature precedents.

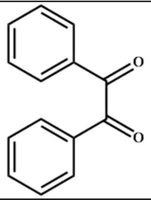
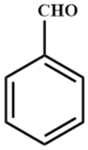
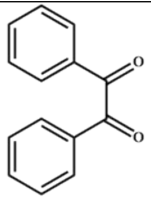
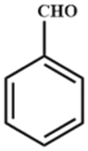
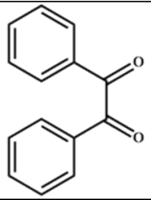
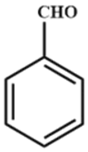
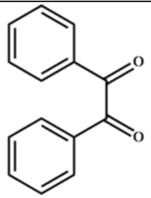
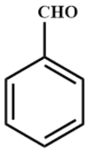
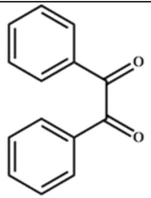
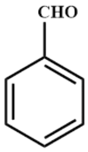
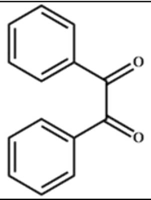
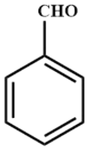
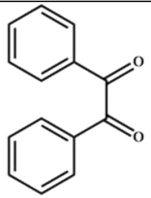
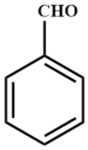
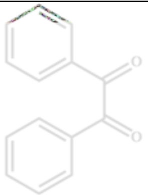
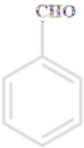
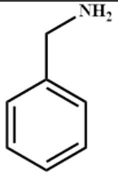
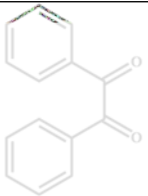
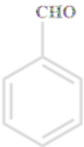
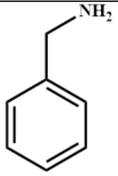
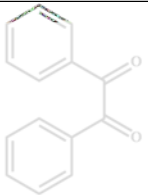
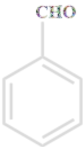
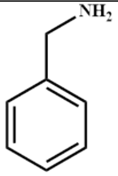
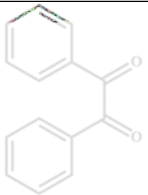
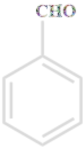
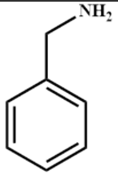
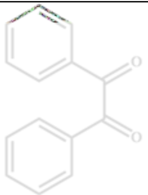
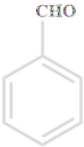
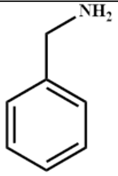
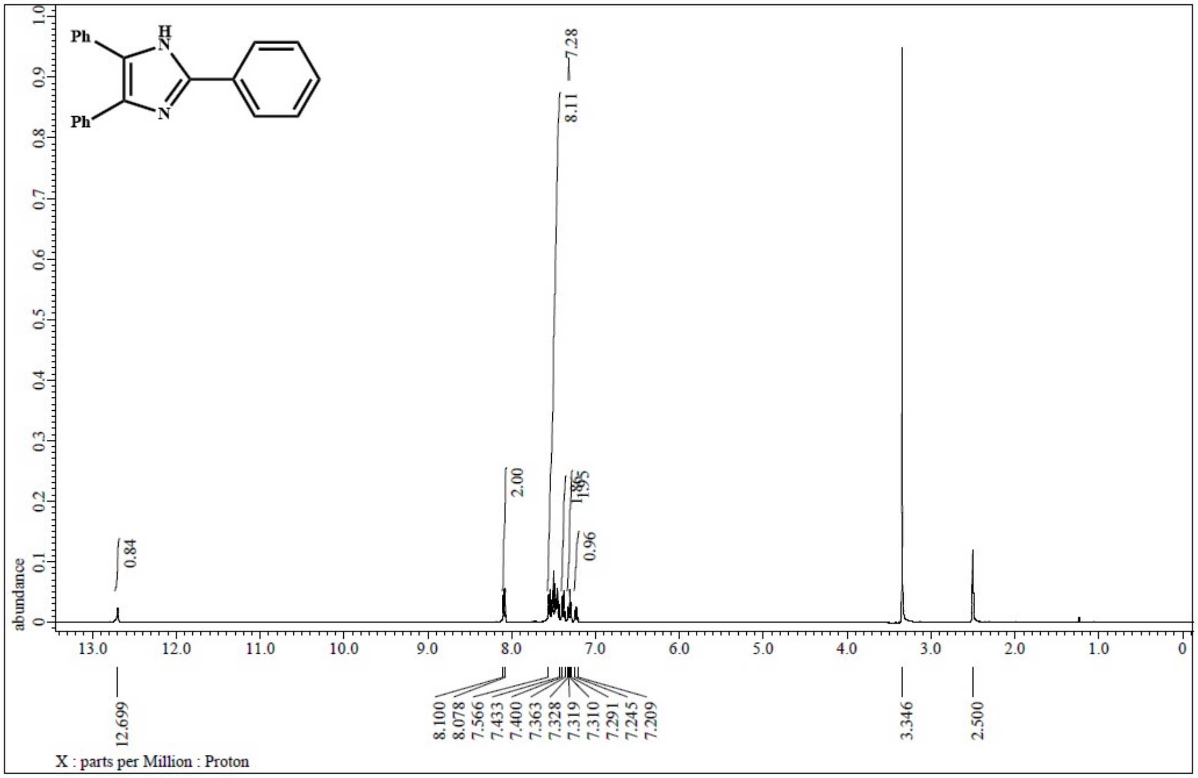
S. No.	Benzil	Substituted benzaldehyde	Catalytic conditions	Yield (%)	Ref.
1.			$InCl_3.3H_2O$, NH_4OAc, MeOH, r.t., 8-9 h	82	43
2.			AlOOH NPs, NH_4OAc, 120 °C, 80 min	98	45
3.			Dihydroquinoline, NH_4OAc, ethanol, reflux, 5-6 h	92	46
4.			$LiBF_4$, NH_4OAc, 120 °C, 20 min	90	47
5.			Molecularly imprinted polymer, NH_4OAc, EtOH, 78 °C, 30 min	90	48
6.			L-Proline, NH_4OAc, MeOH, 60 °C, 9 h	90	49
7.			$CoFe_2O_4$/Ni-BTC, NH_4OAc, 100 °C, 30 min	98	Present work

Table S2. Comparison of catalytic activity of $CoFe_2O_4$/Ni-BTC for synthesis of 1,2,4,5-tetrasubstituted imidazoles with literature precedents.

S. No.	Benzil	Substituted benzaldehyde	Benzylamine	Catalytic conditions	Yield (%)	Ref.
1.				AlOOH NPs, NH_4OAc, 120 °C, 50 min	96	45
2.				$Zn(BF_4)_2$, NH_4OAc, 120 °C, 12 min	92	47
3.				L-Proline, NH_4OAc, MeOH, 60 °C, 8.5 h	86	49
4.				Trityl chloride, NH_4OAc, 90 °C, 32 min	80	50
5.				$CoFe_2O_4$/Ni-BTC, NH_4OAc, 100 °C, 30 min	97	Present work

NMR Spectra of 2,4,5-trisubstituted imidazoles

Entry 3a ^{1}H NMR spectrum of 2,4,5-triphenyl-1H-imidazole (DMSO-d_6) Full



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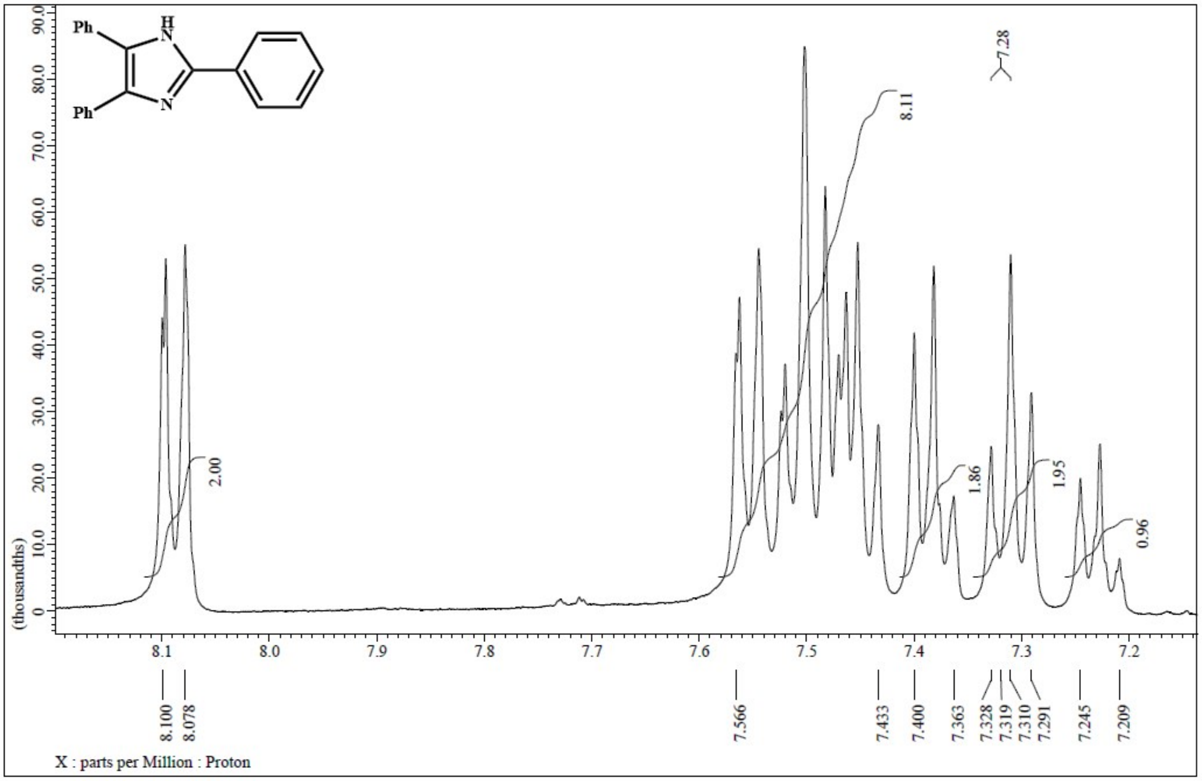

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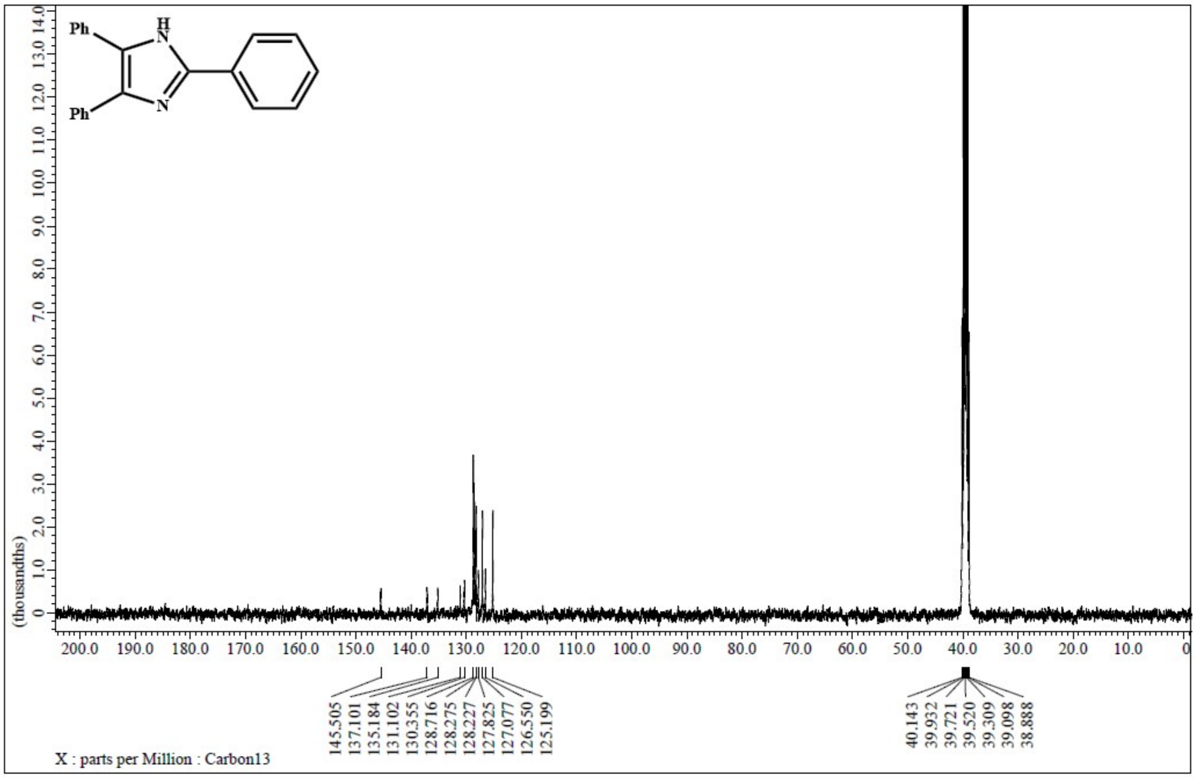
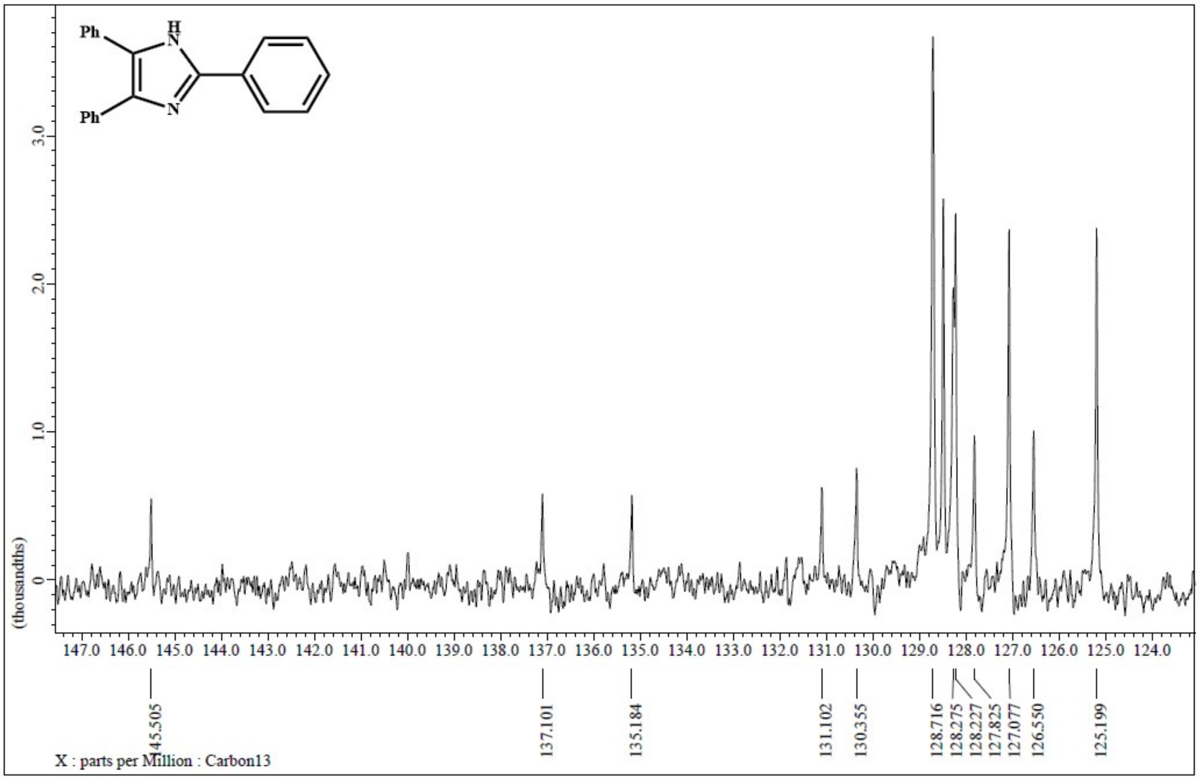


Entry 3a ^{13}C NMR spectrum of 2,4,5-triphenyl-1H-imidazole Expansion



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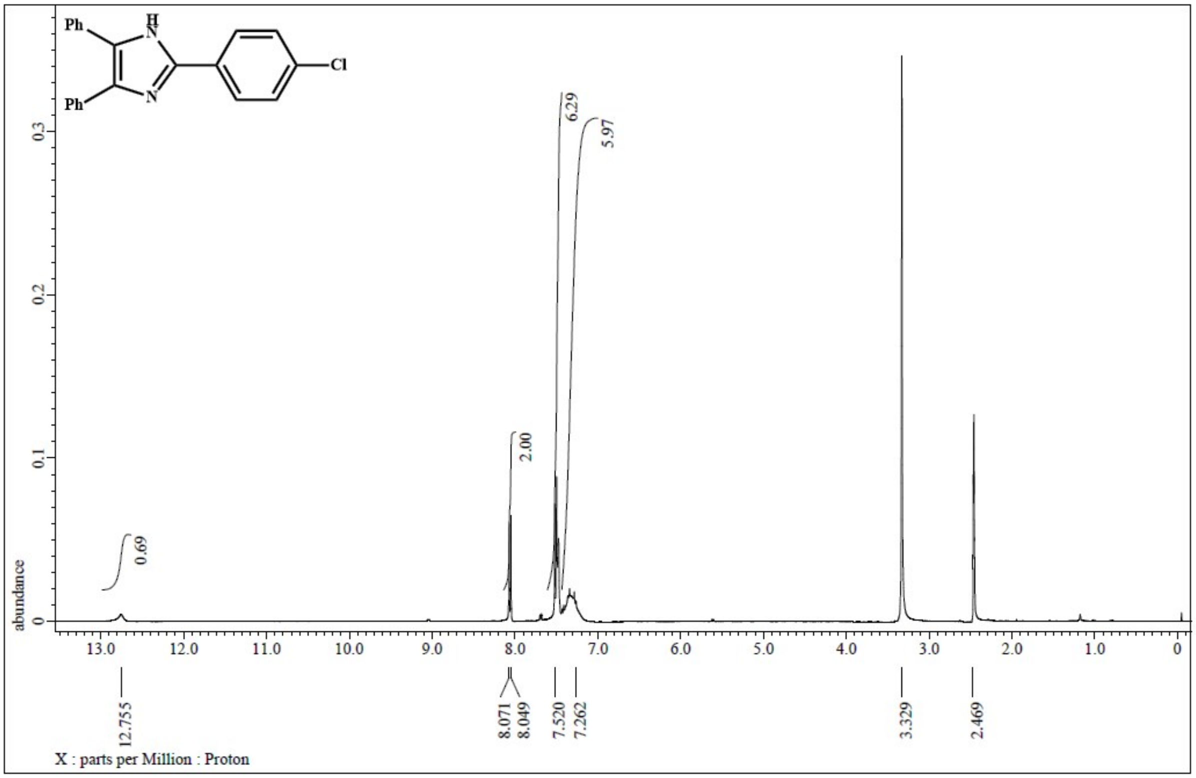
Full



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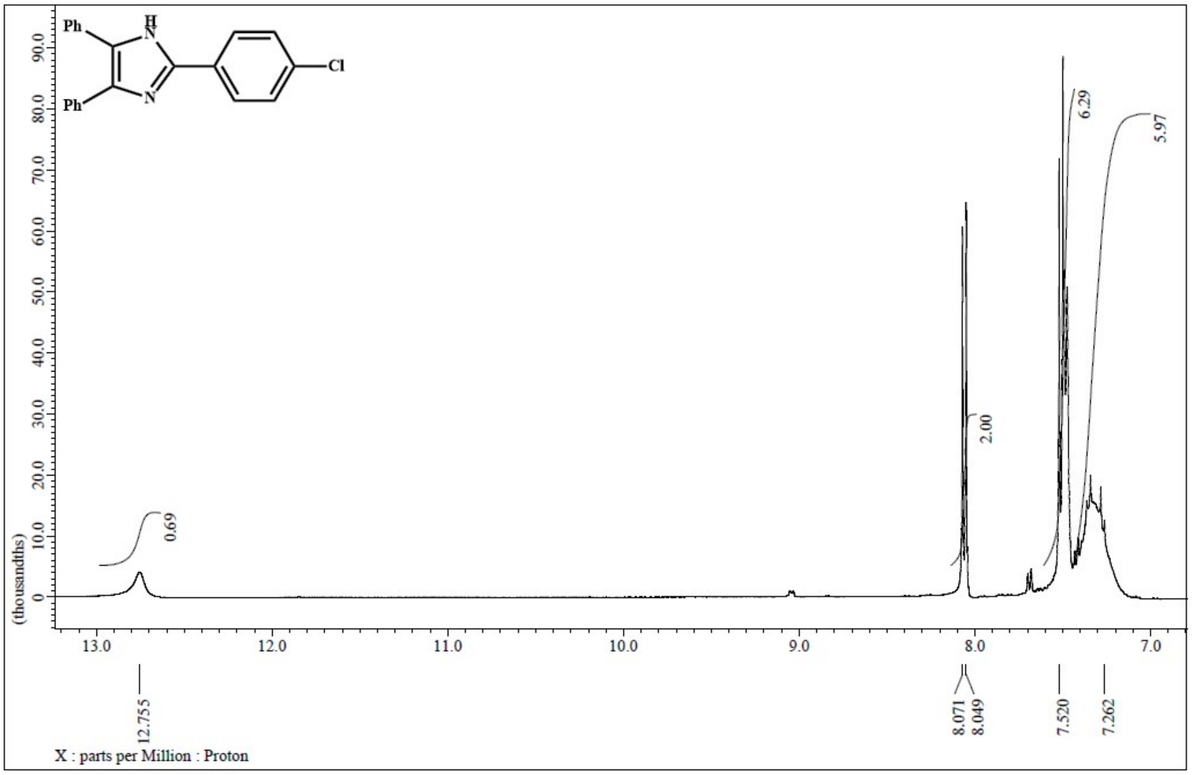

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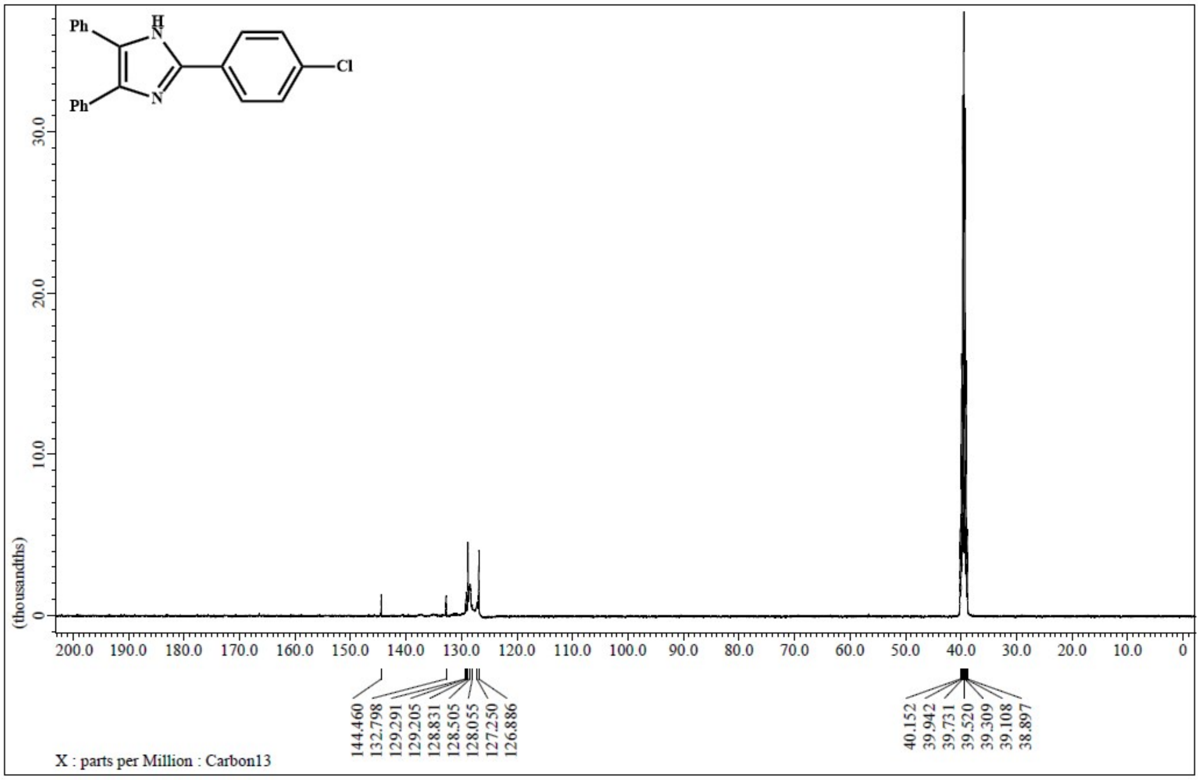
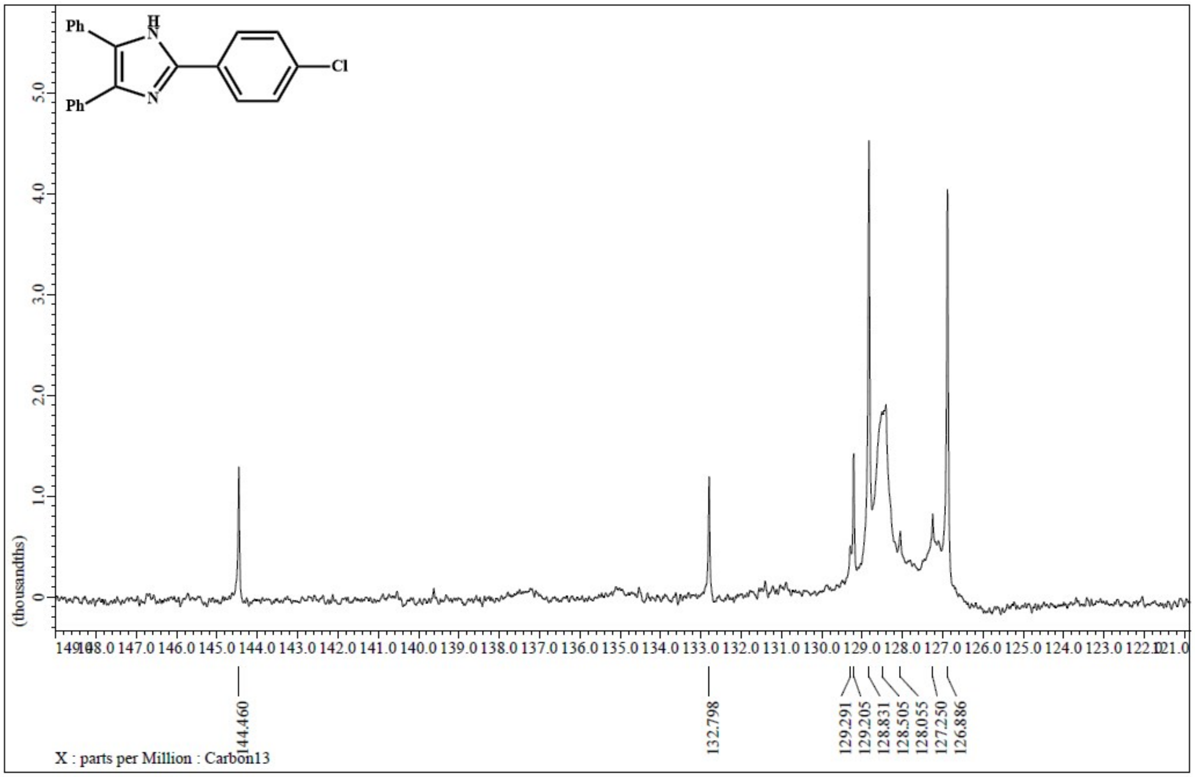
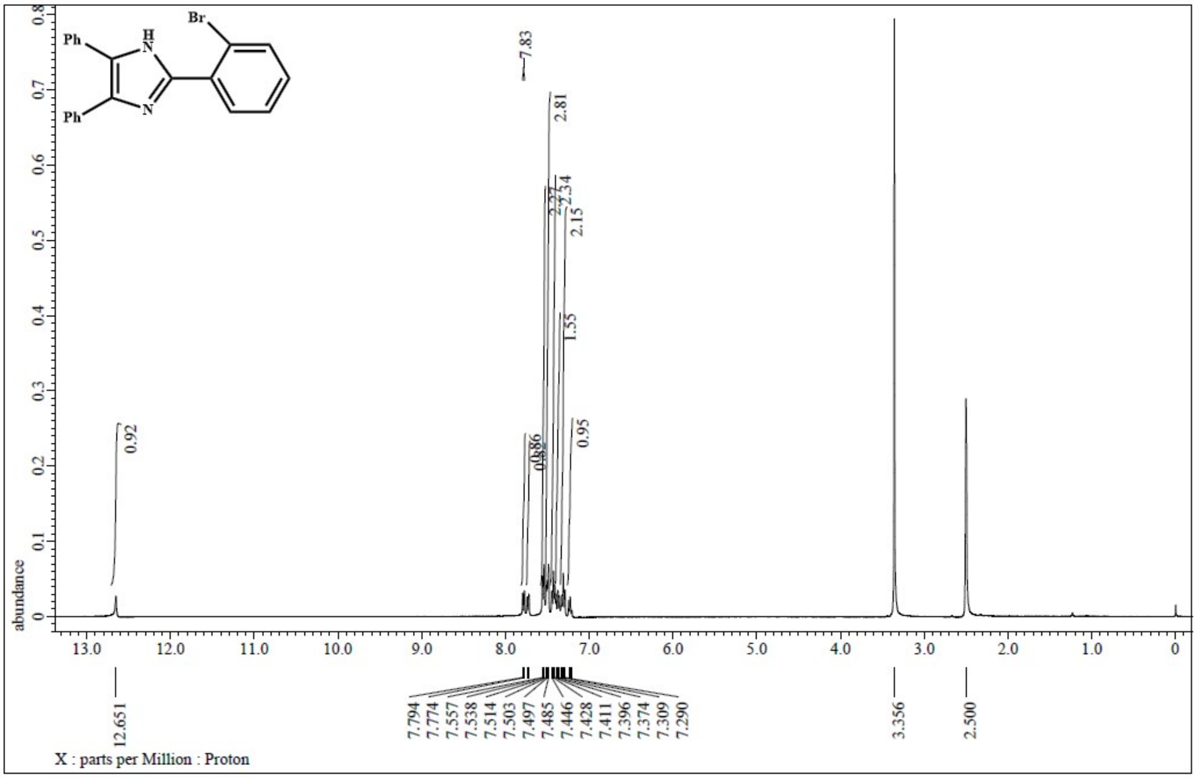


Entry 3b ^{13}C NMR spectrum of 2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole Expansion



Entry 3c ^{1}H NMR spectrum of 2-(2-bromophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

Full



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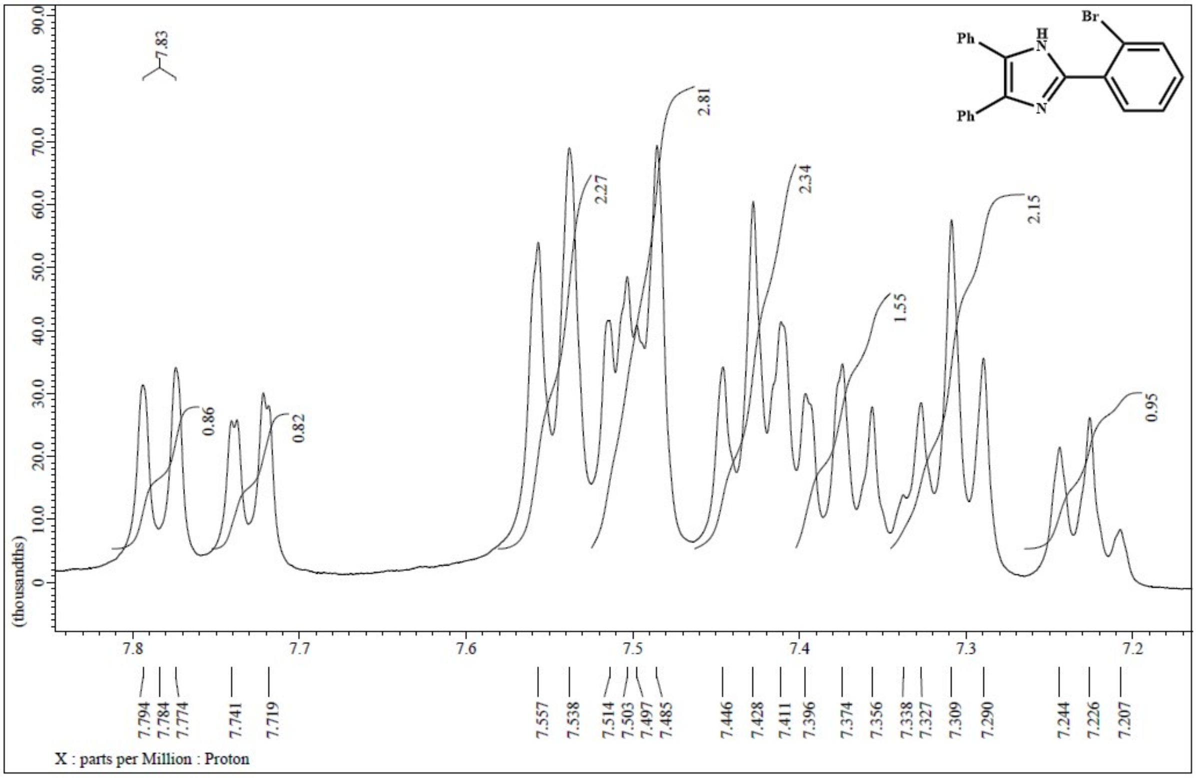
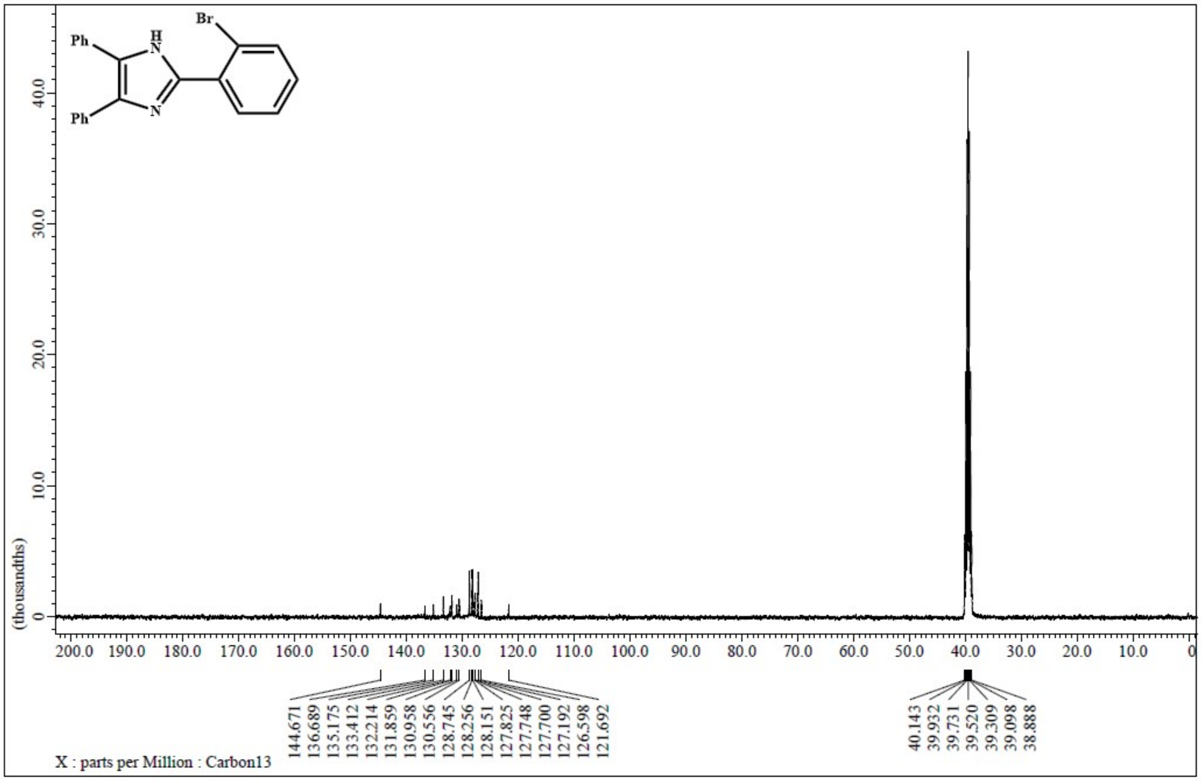
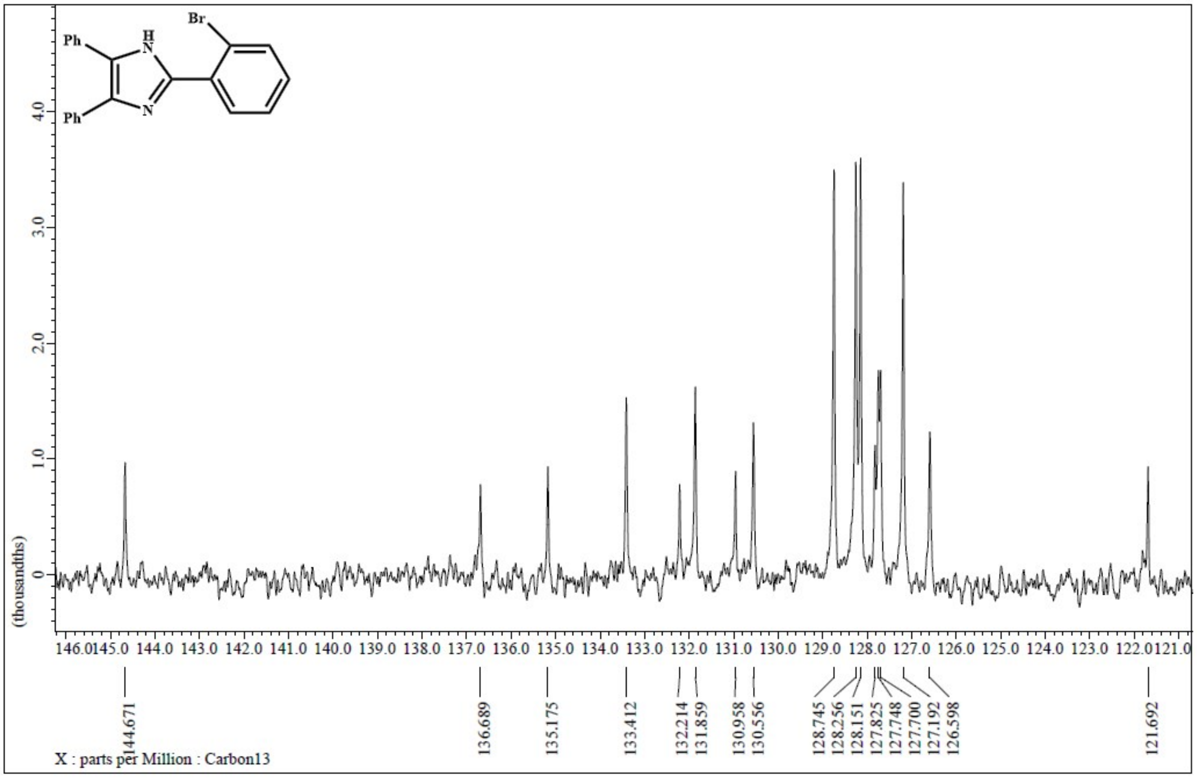


Entry 3c ^{13}C NMR spectrum of 2-(2-bromophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$)

Full

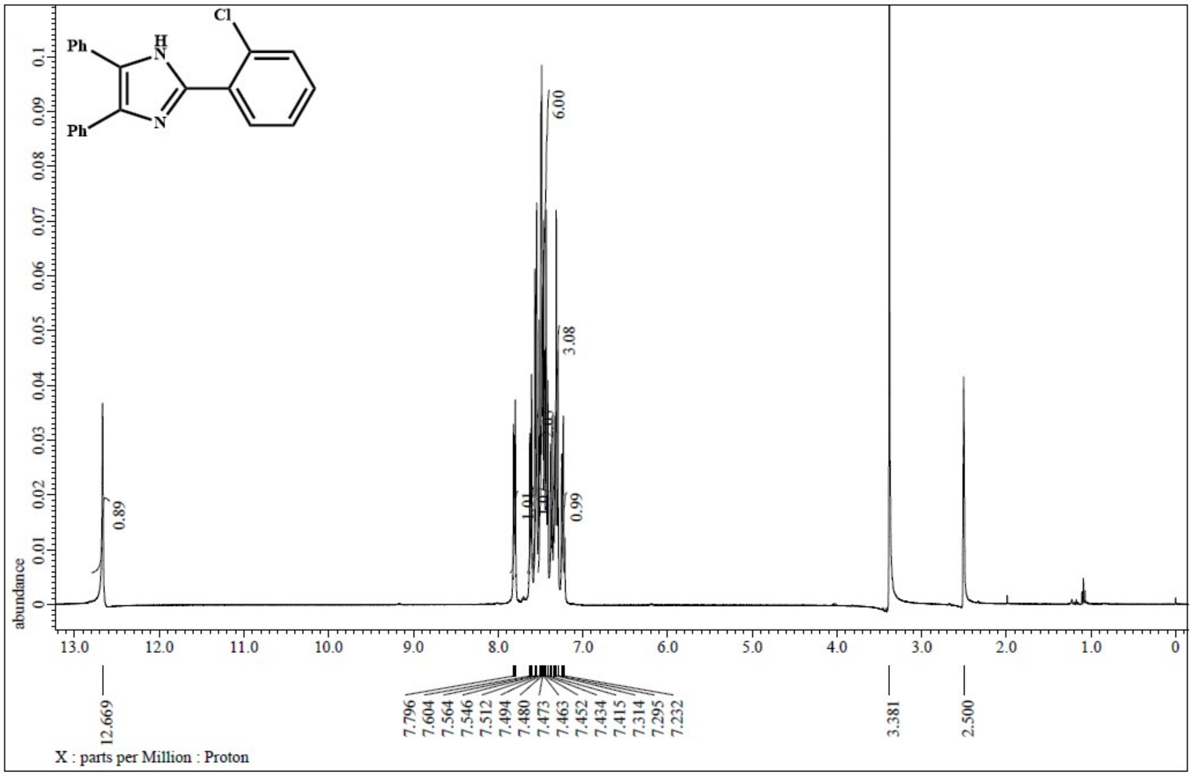


Entry 3c ^{13}C NMR spectrum of 2-(2-bromophenyl)-4,5-diphenyl-1H-imidazole Expansion

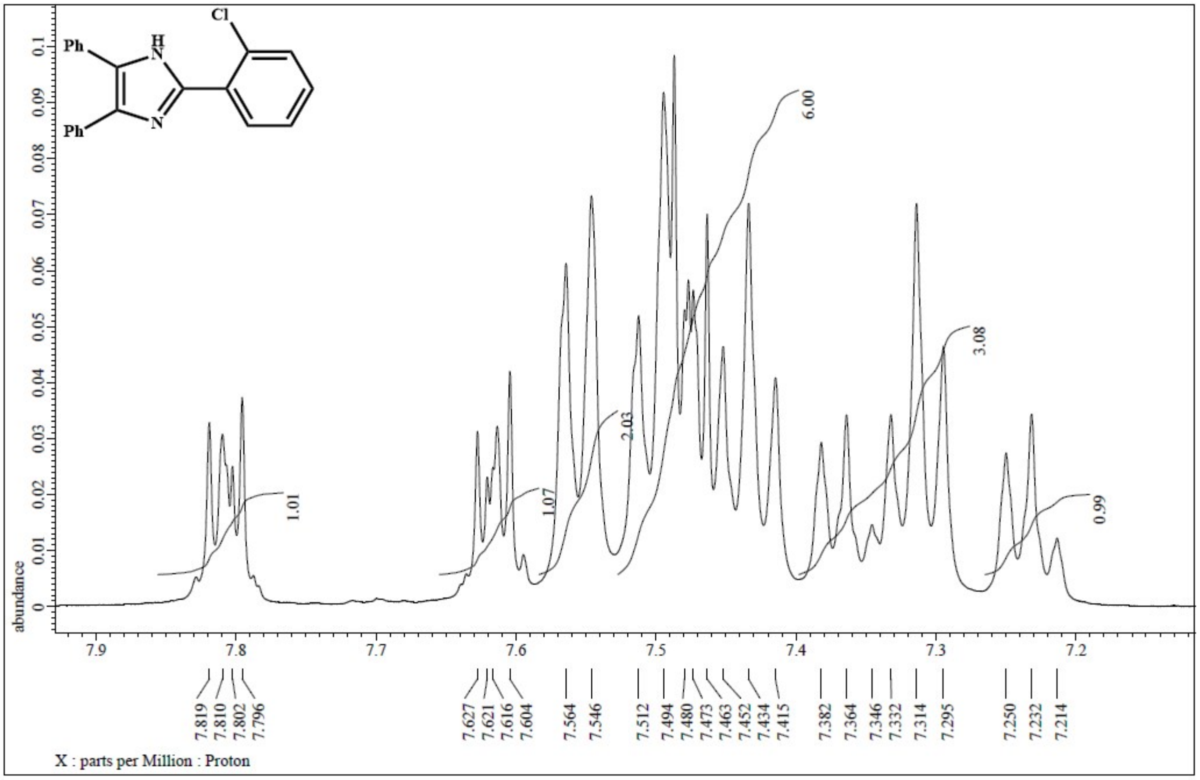


Entry 3d ^{1}H NMR spectrum of 2-(2-chlorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

Full

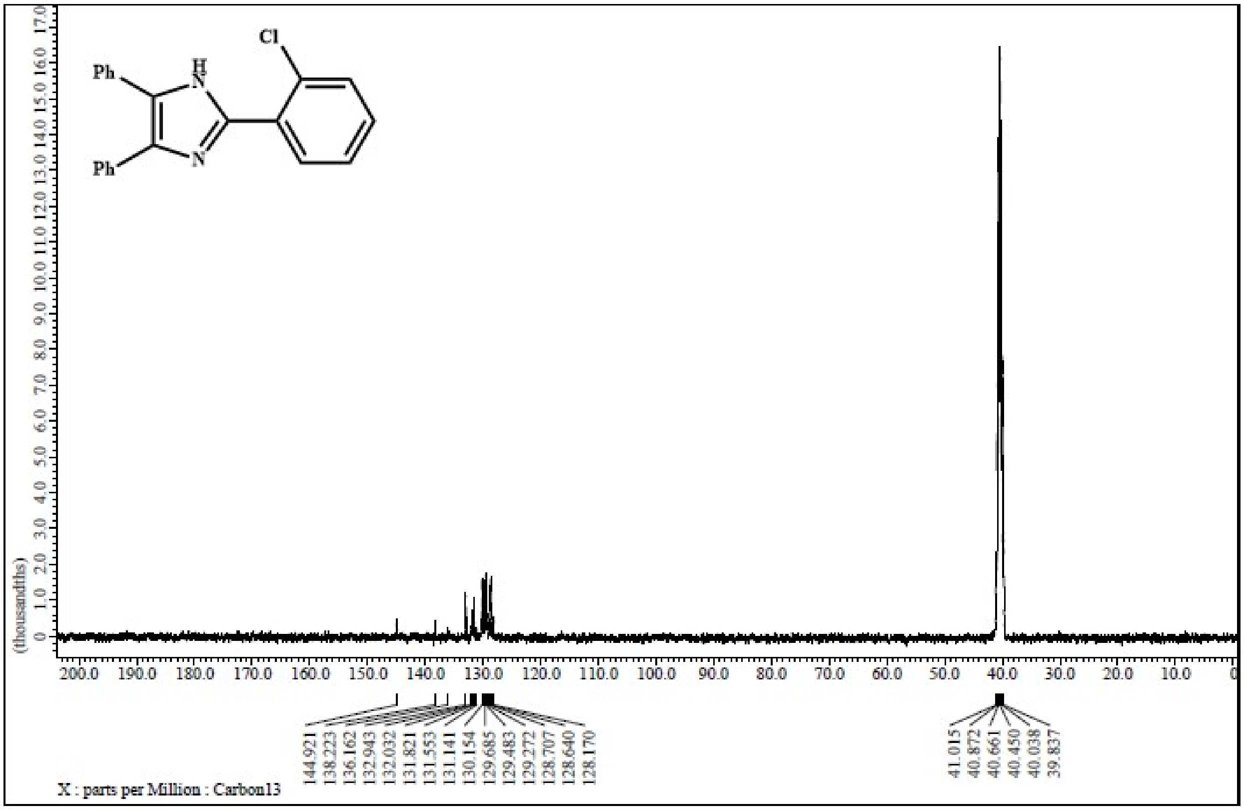


Entry 3d ^{1}H NMR spectrum of 2-(2-chlorophenyl)-4,5-diphenyl-1H-imidazole Expansion

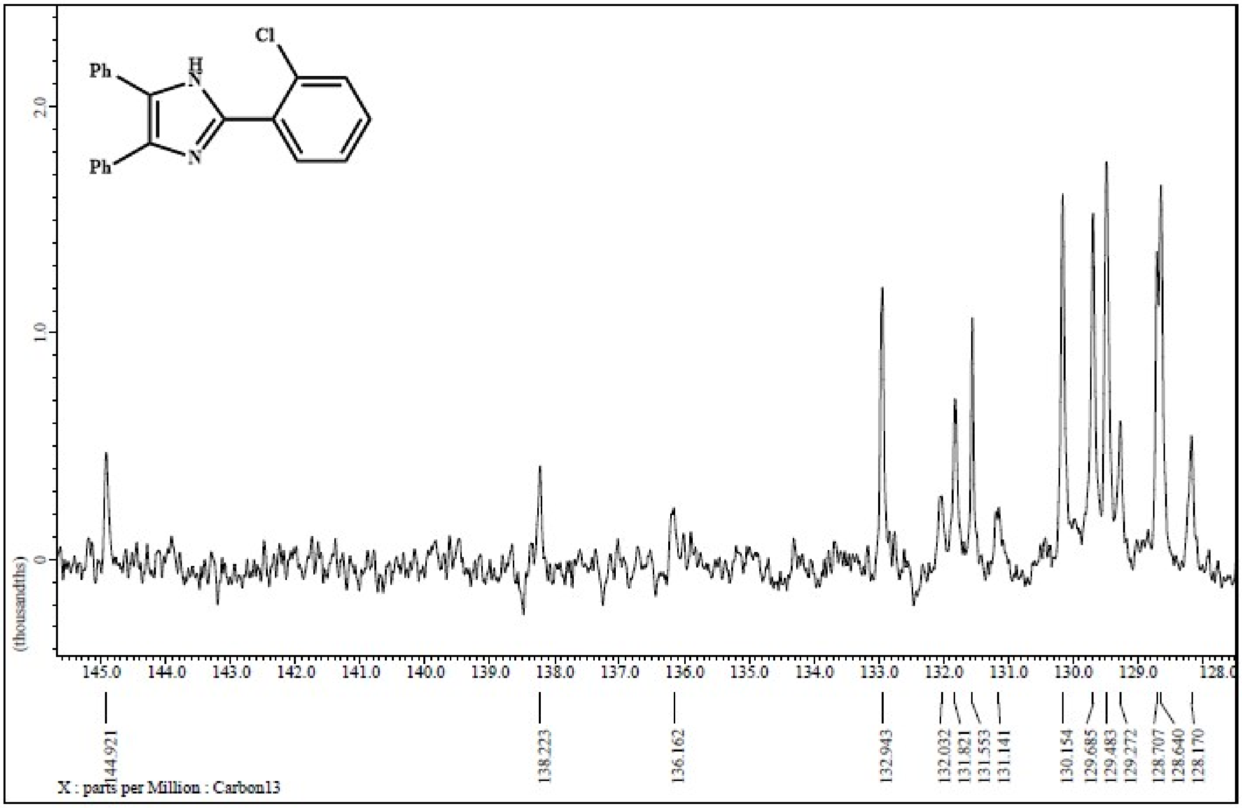


Entry 3d ^{13}C NMR spectrum of 2-(2-chlorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

Full

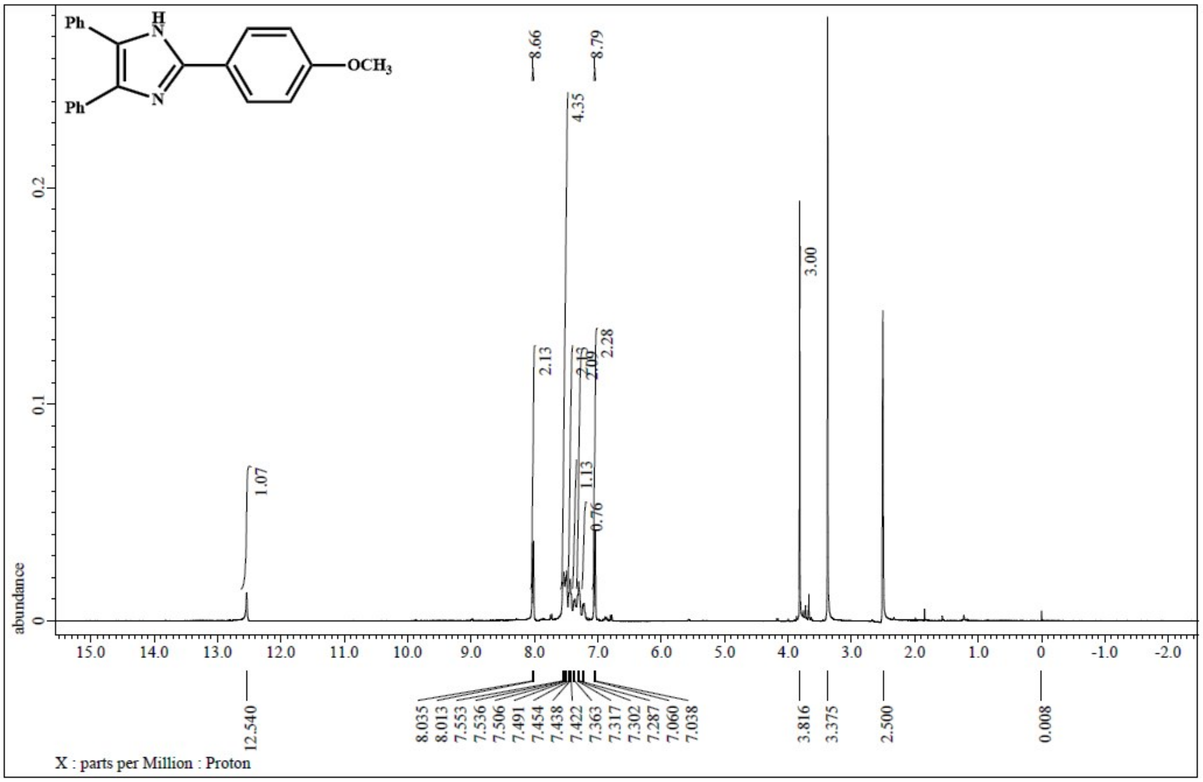


Entry 3d ^{13}C NMR spectrum of 2-(2-chlorophenyl)-4,5-diphenyl-1H-imidazole Expansion

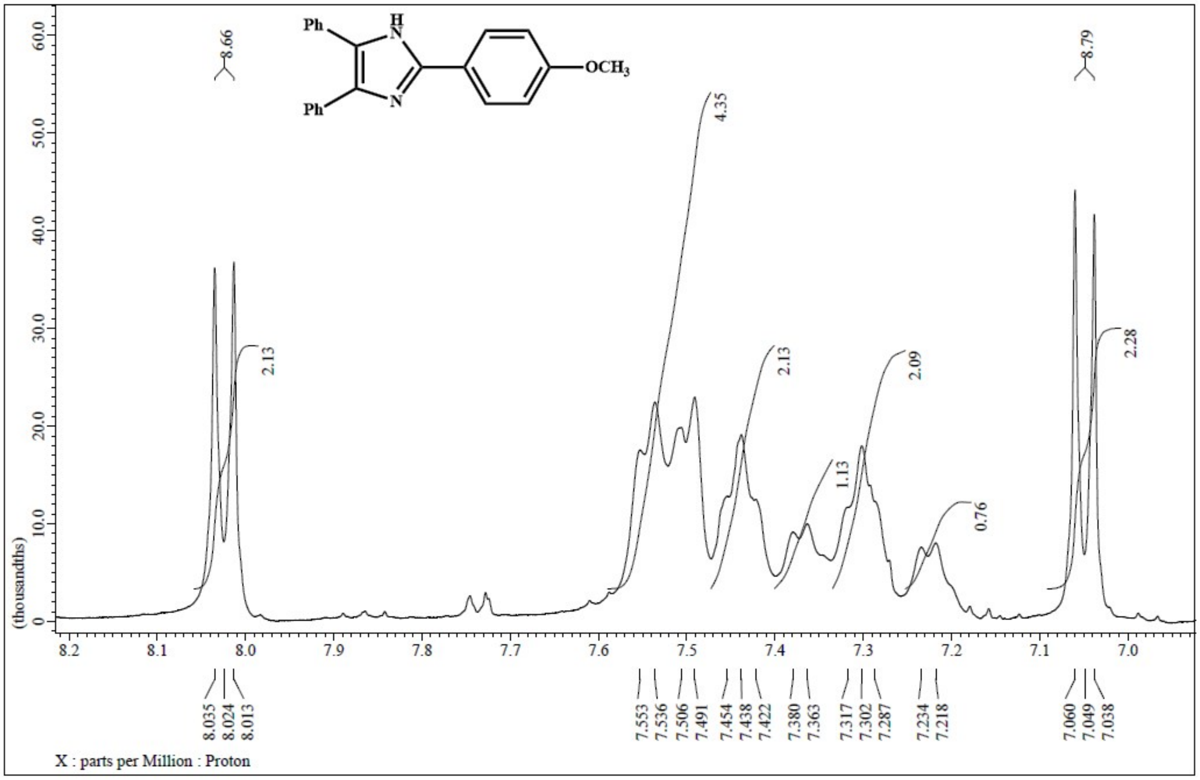


Entry 3e ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$)

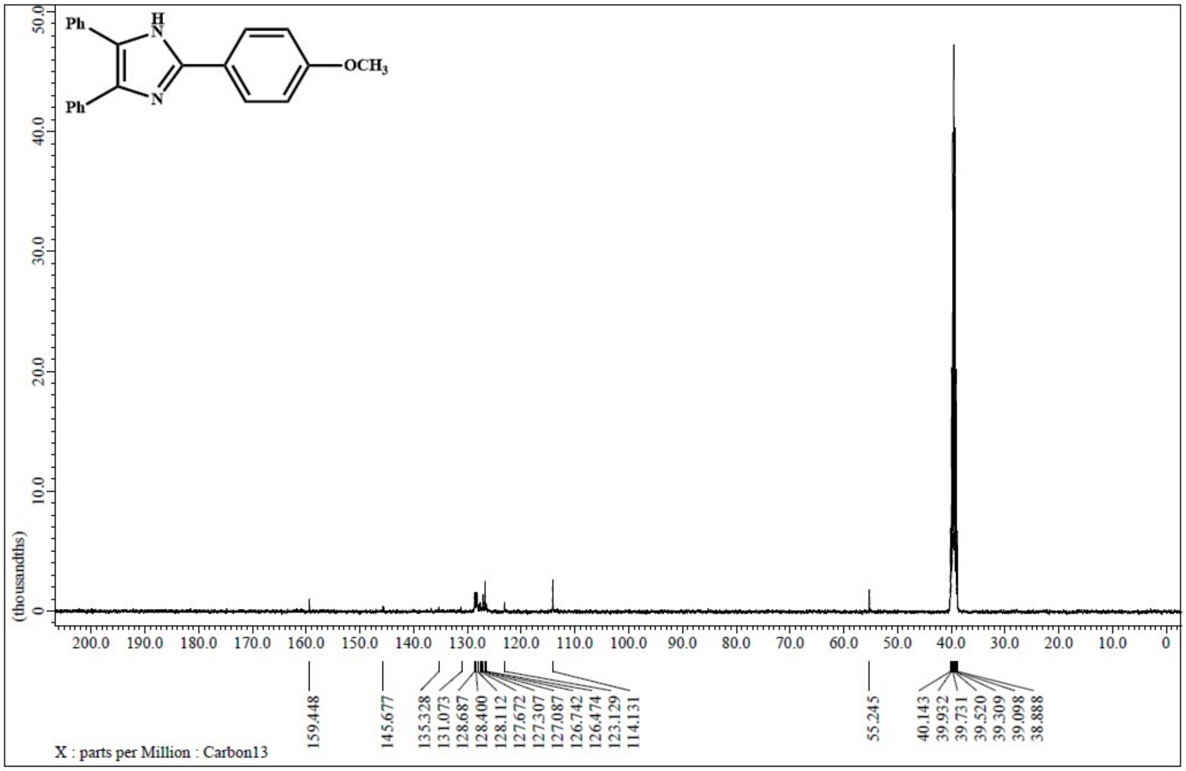
Full



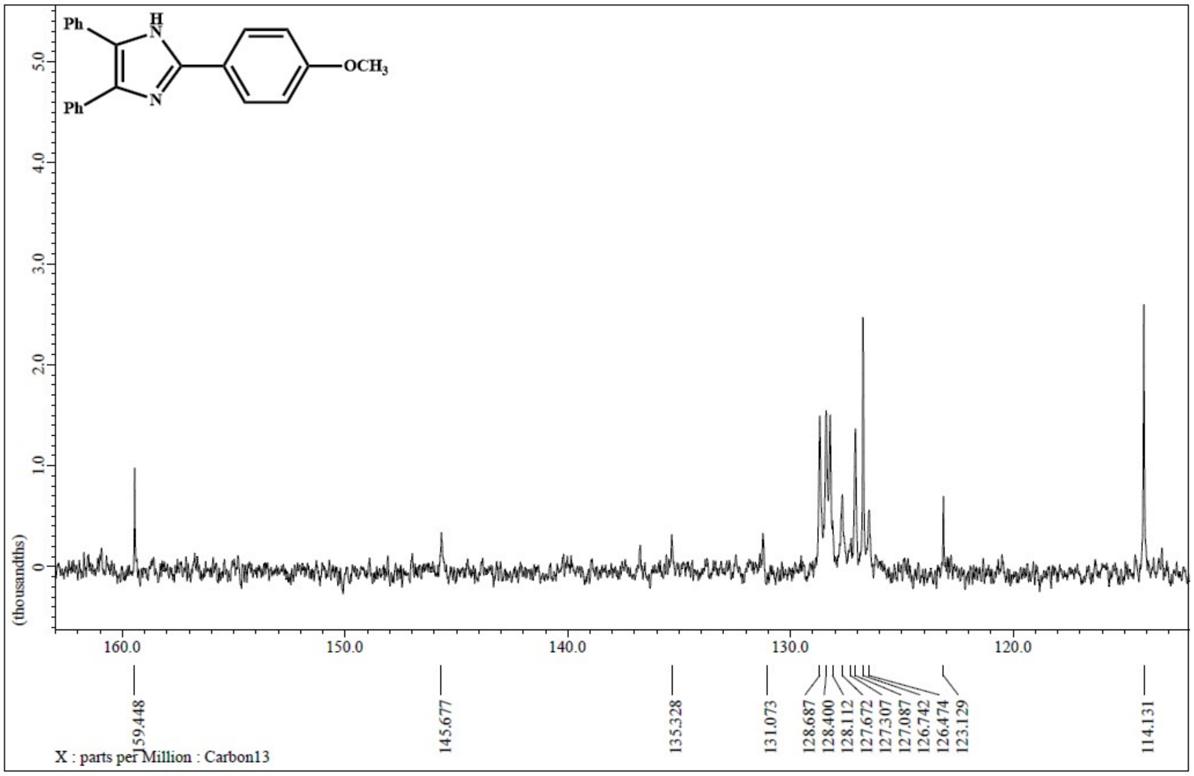
Entry 3e ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole Expansion



Entry 3e ^{13}C NMR spectrum of 2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$) Full

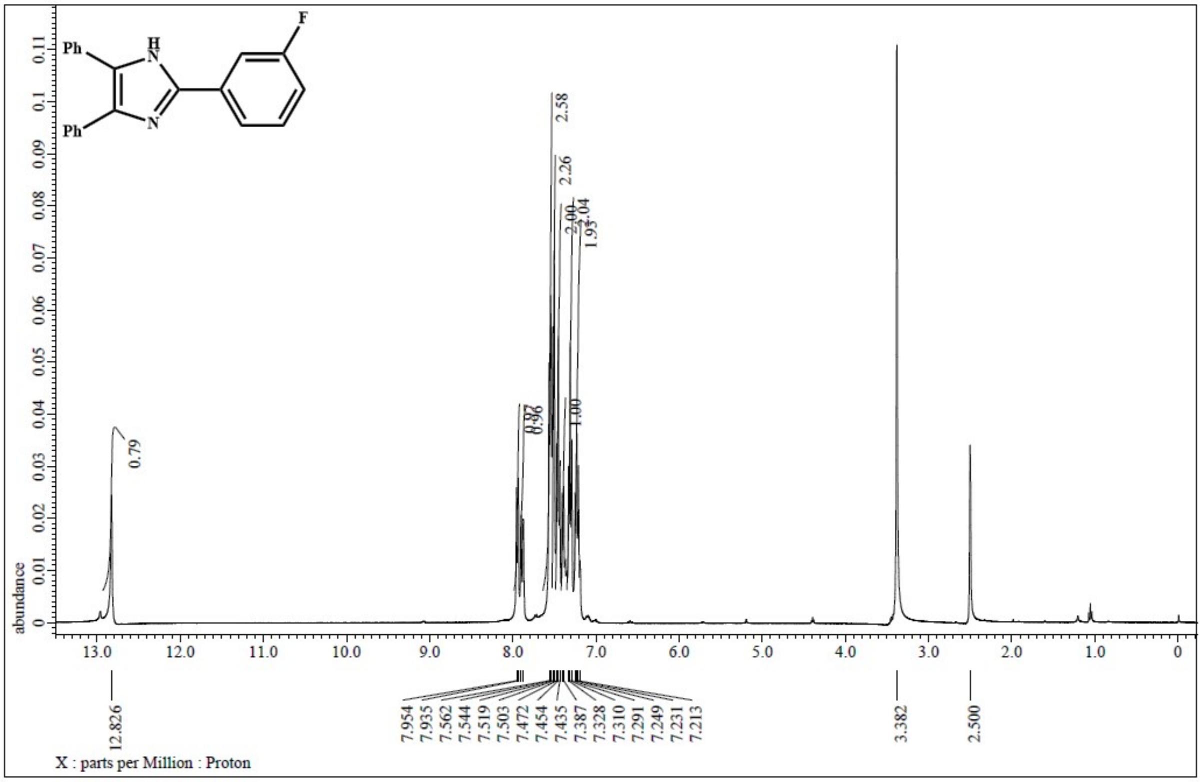


Entry 3e ^{13}C NMR spectrum of 2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole Expansion

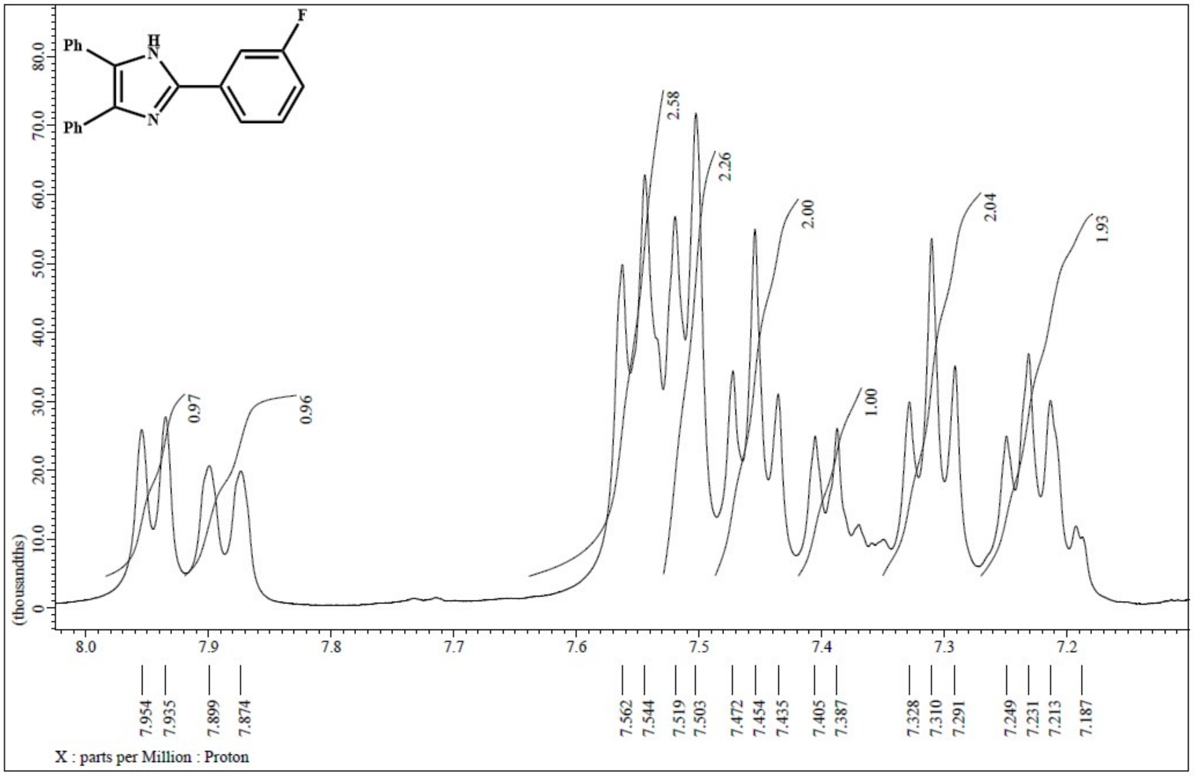


Entry 3f ^{1}H NMR spectrum of 2-(3-fluorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$)

Full

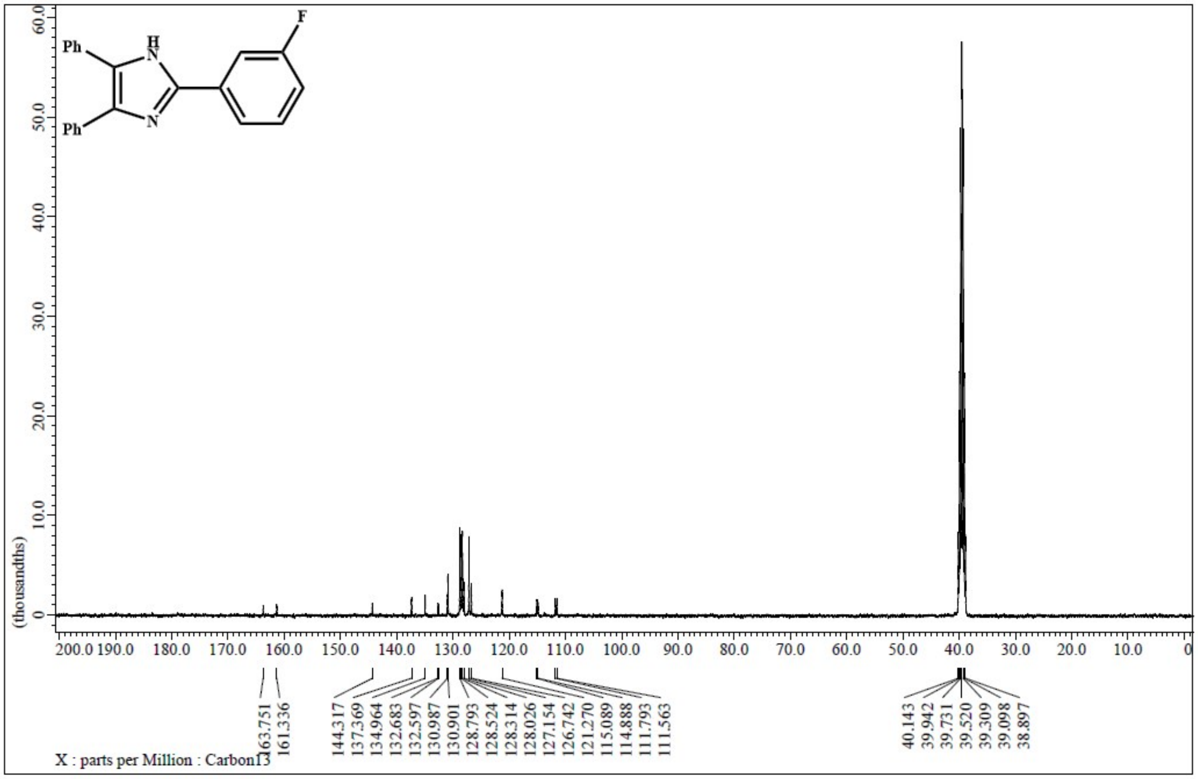


Entry 3f ^{1}H NMR spectrum of 2-(3-fluorophenyl)-4,5-diphenyl-1H-imidazole Expansion

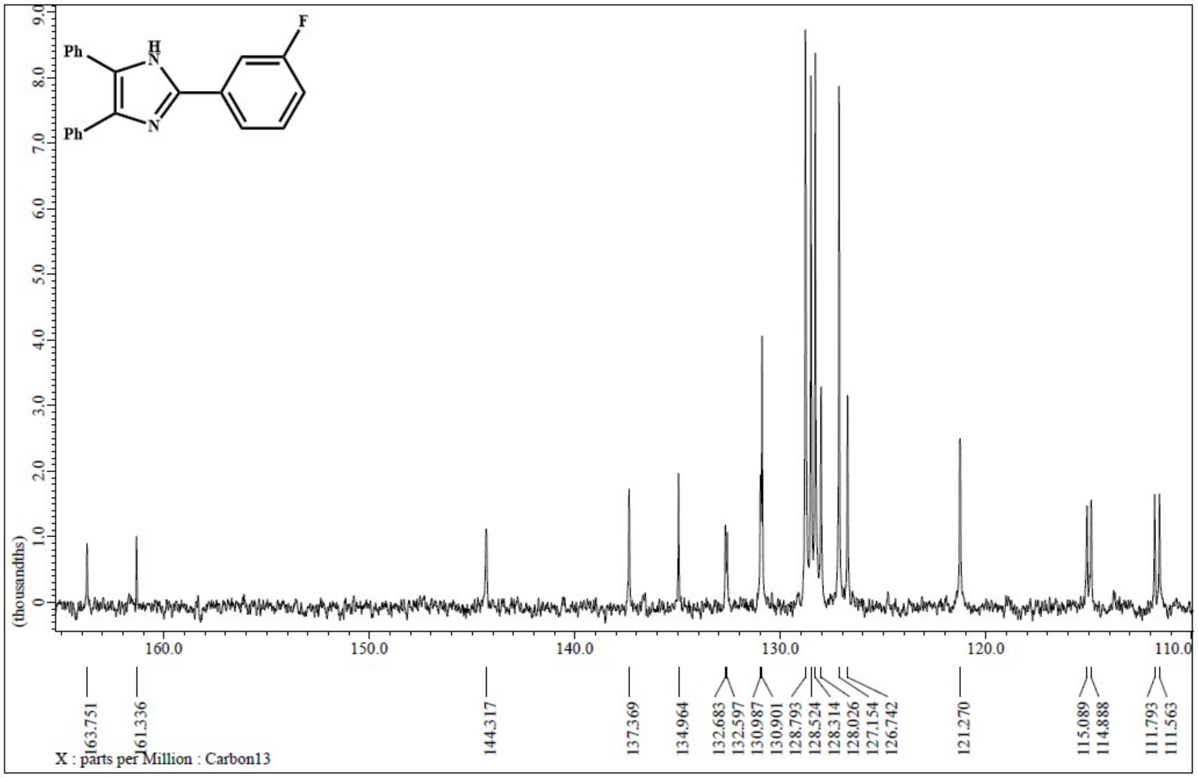


Entry 3f ^{13}C NMR spectrum of 2-(3-fluorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

Full

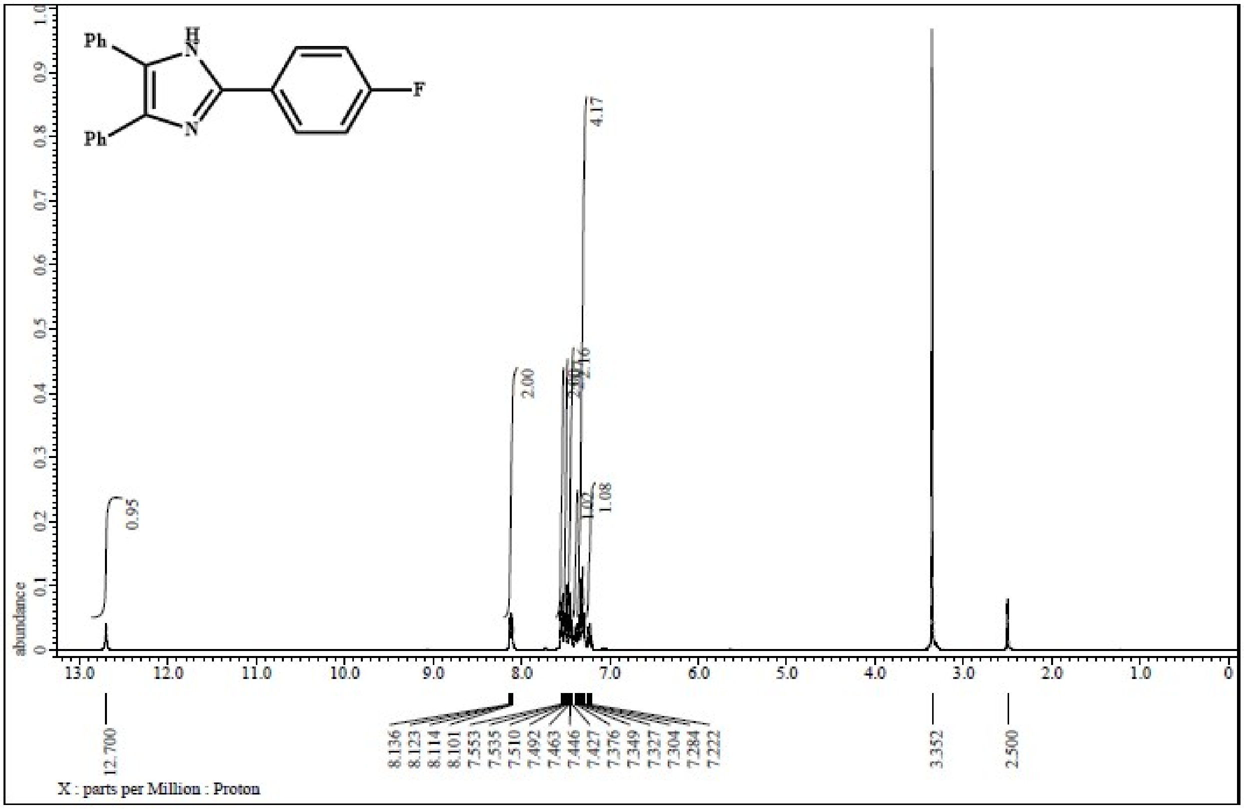


Entry 3f ^{13}C NMR spectrum of 2-(3-fluorophenyl)-4,5-diphenyl-1H-imidazole Expansion

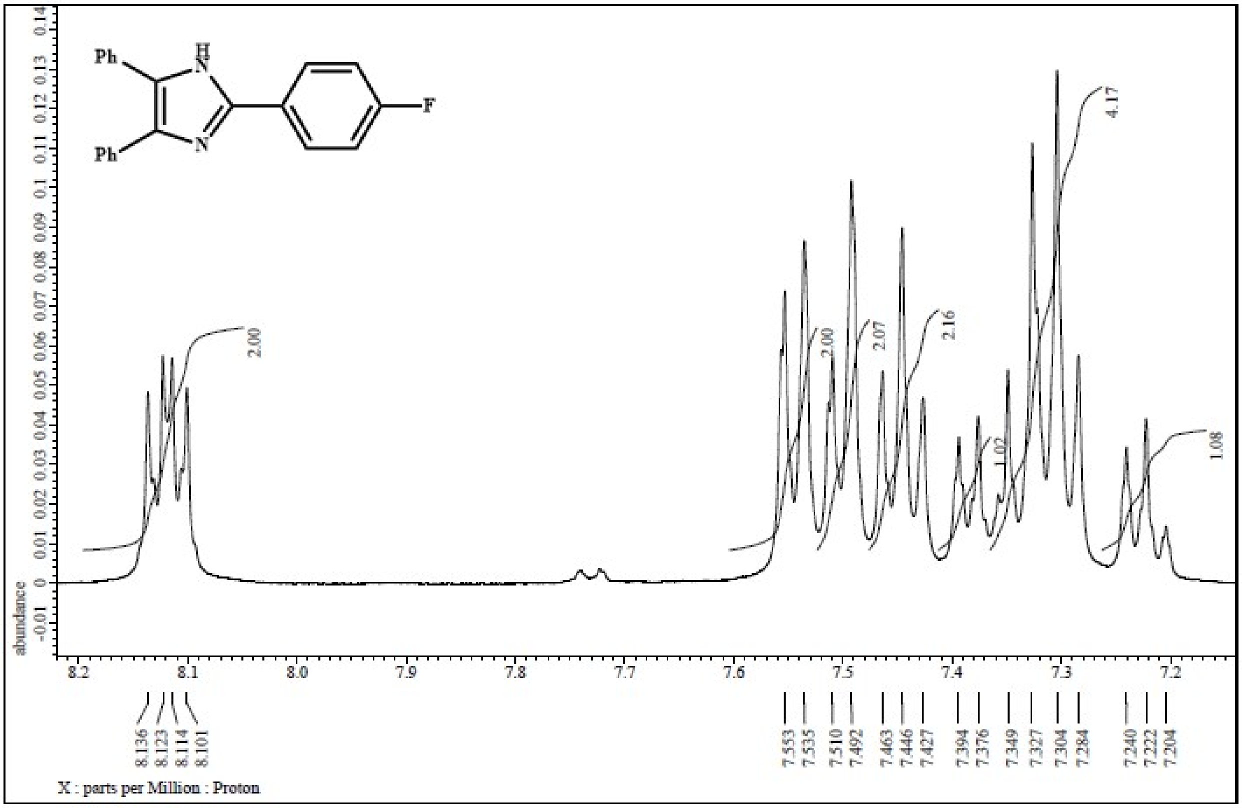


Entry 3g ^{1}H NMR spectrum of 2-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

Full

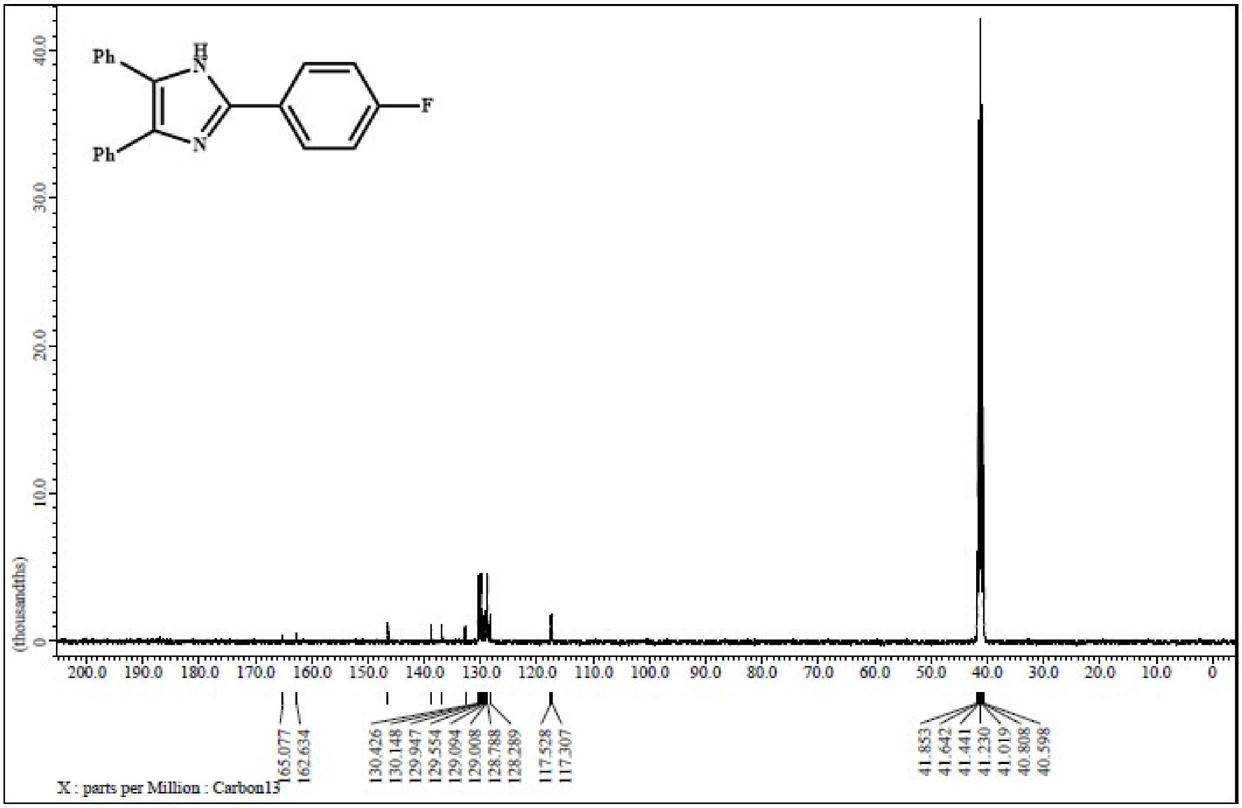


Entry 3g ^{1}H NMR spectrum of 2-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole Expansion

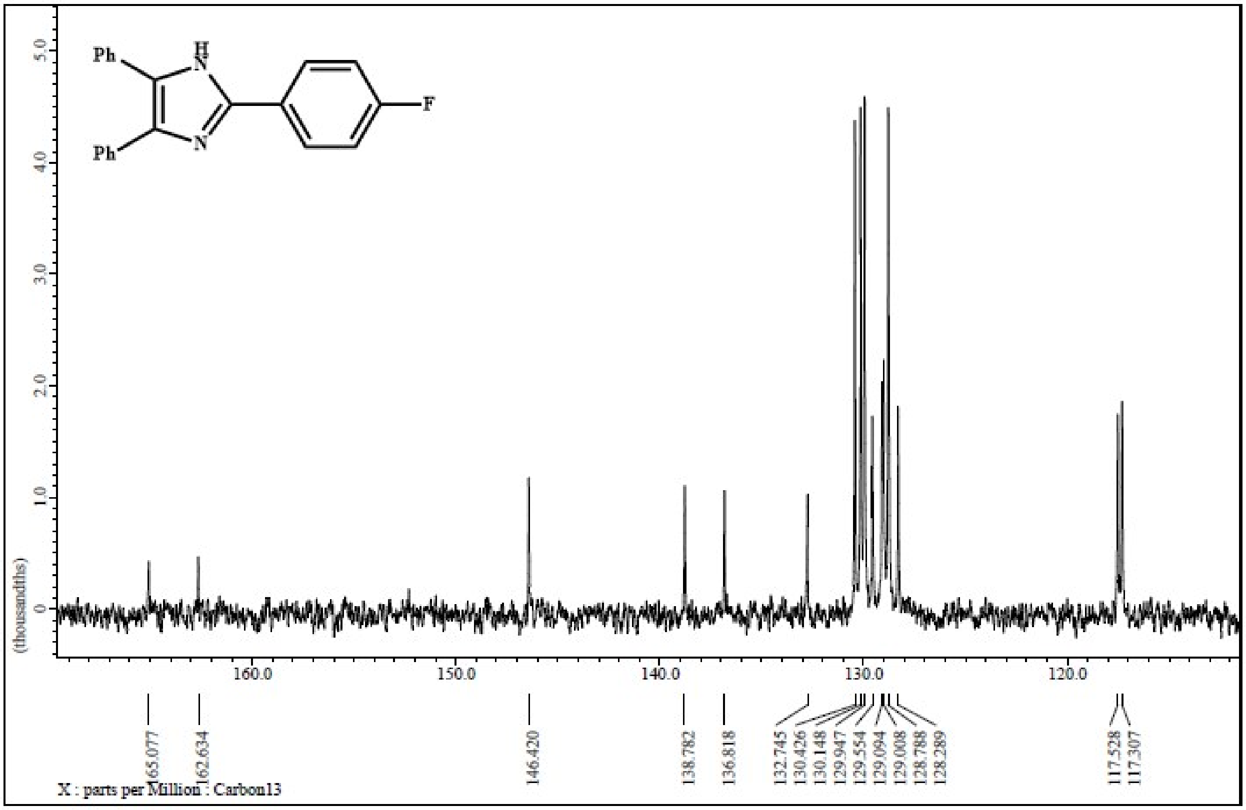


Entry 3g ^{13}C NMR spectrum of 2-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$)

Full

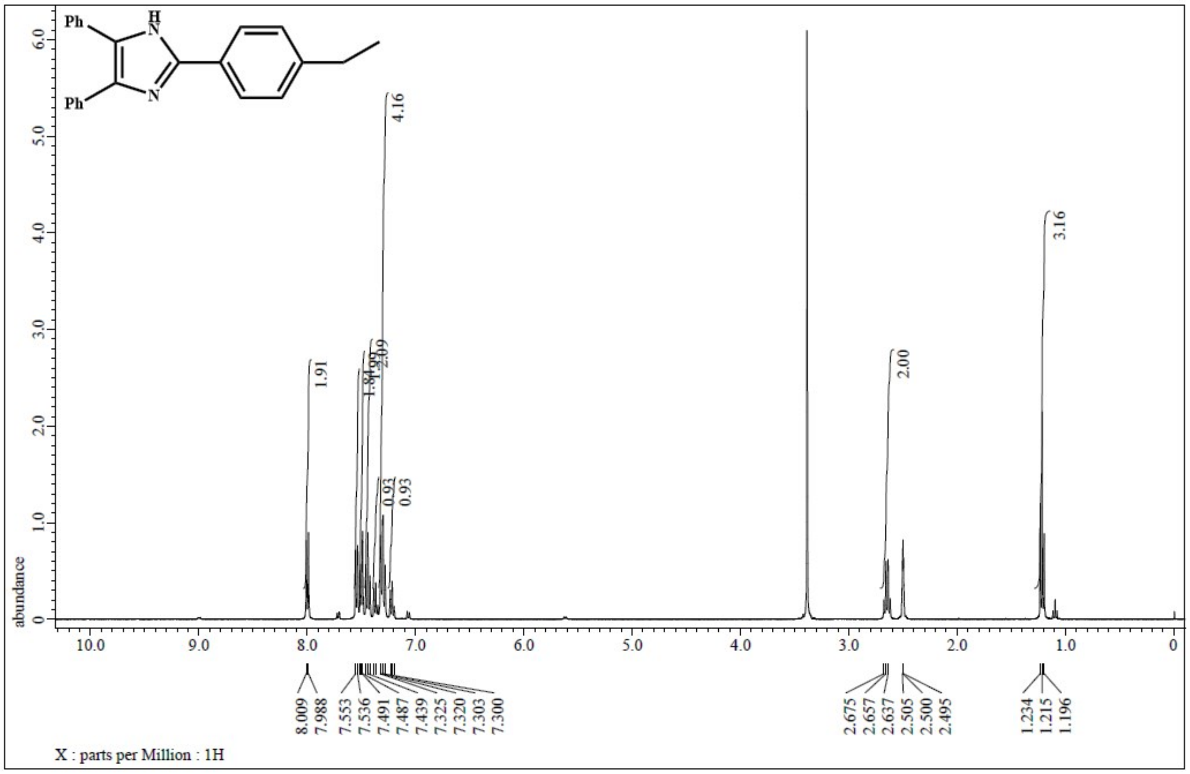


Entry 3g ^{13}C NMR spectrum of 2-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole Expansion

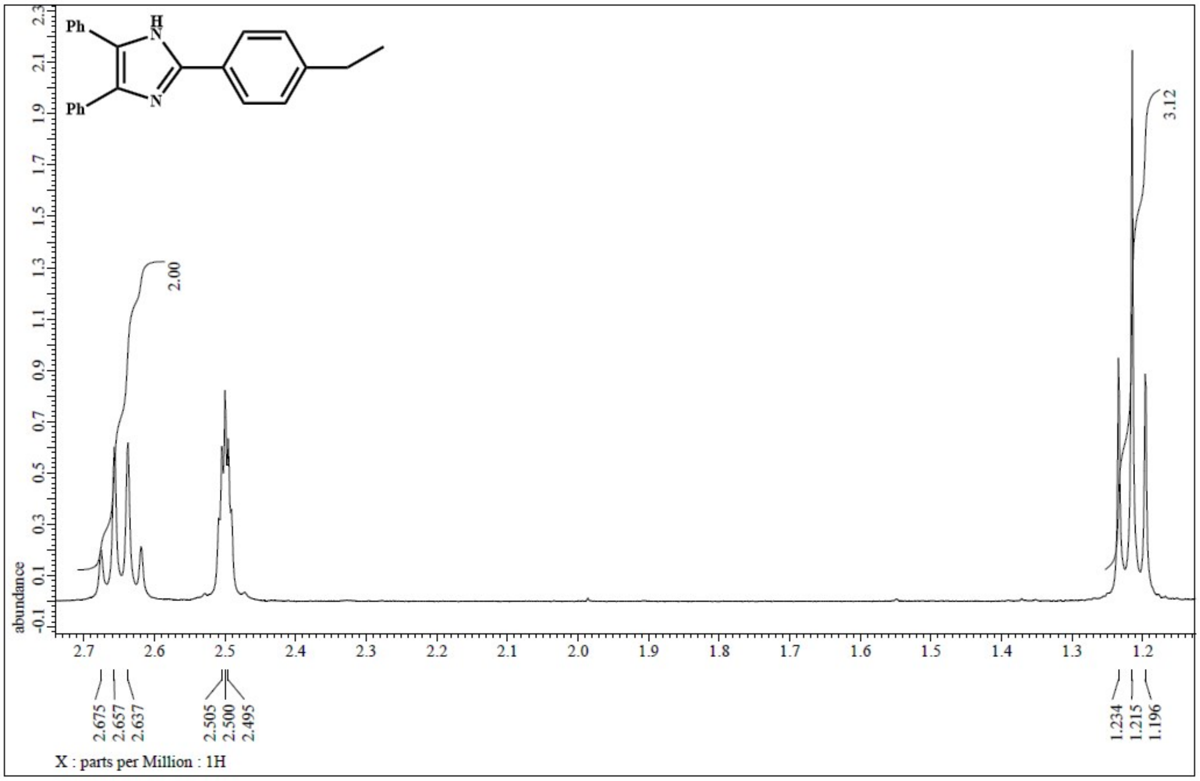


Entry 3h ^{1}H NMR spectrum of 2-(4-ethylphenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

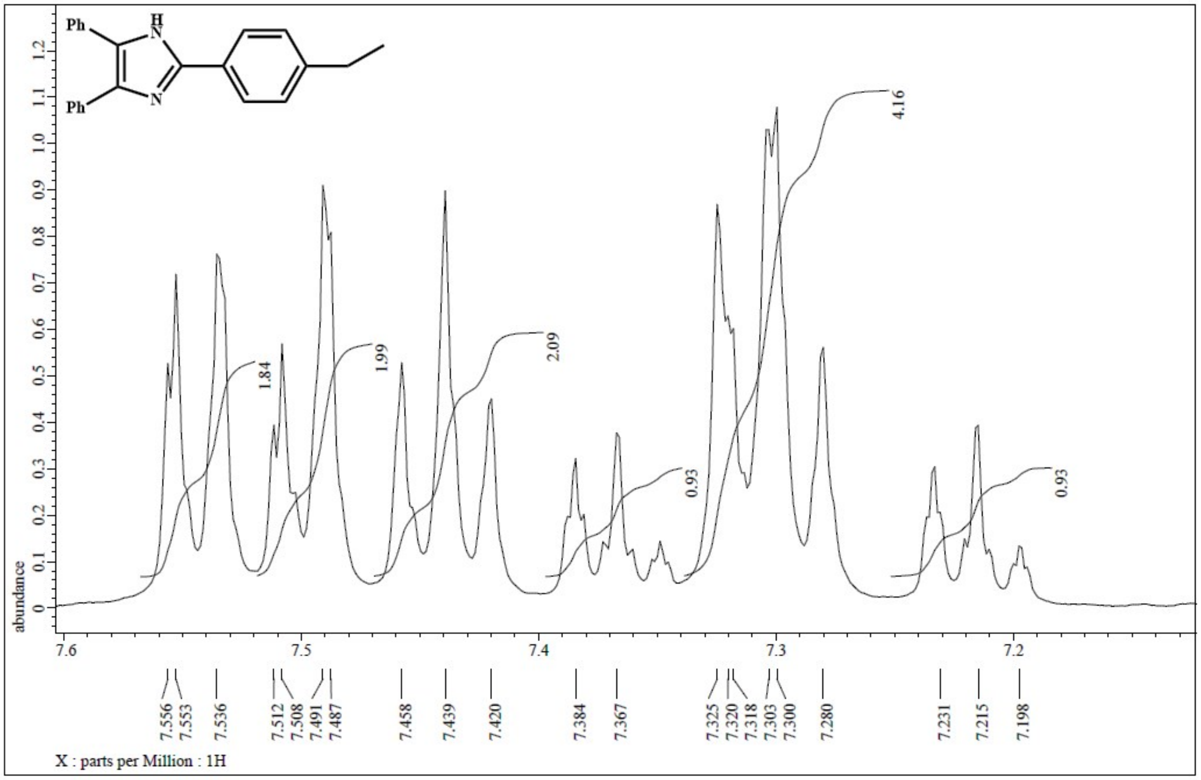
Full



Entry 3h ^{1}H NMR spectrum of 2-(4-ethylphenyl)-4,5-diphenyl-1H-imidazole Expansion

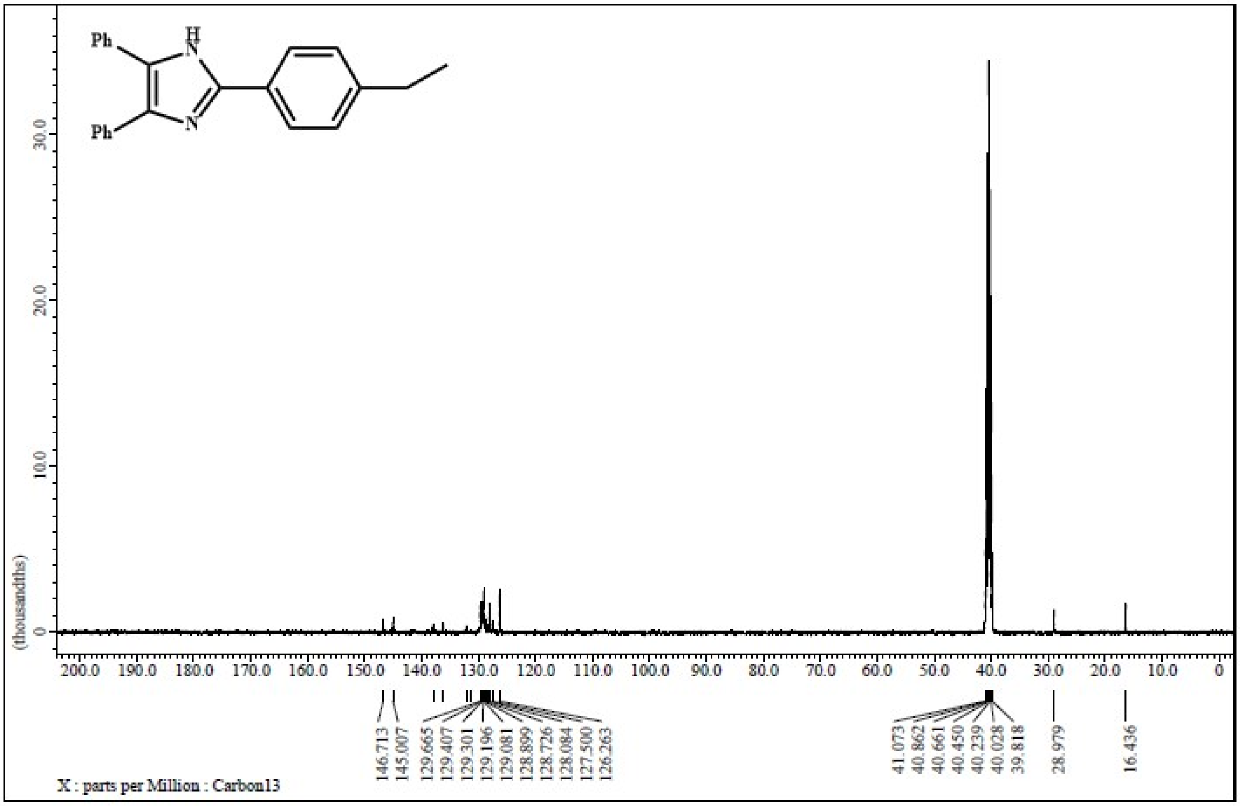


Entry 3h ^{1}H NMR spectrum of 2-(4-ethylphenyl)-4,5-diphenyl-1H-imidazole Expansion

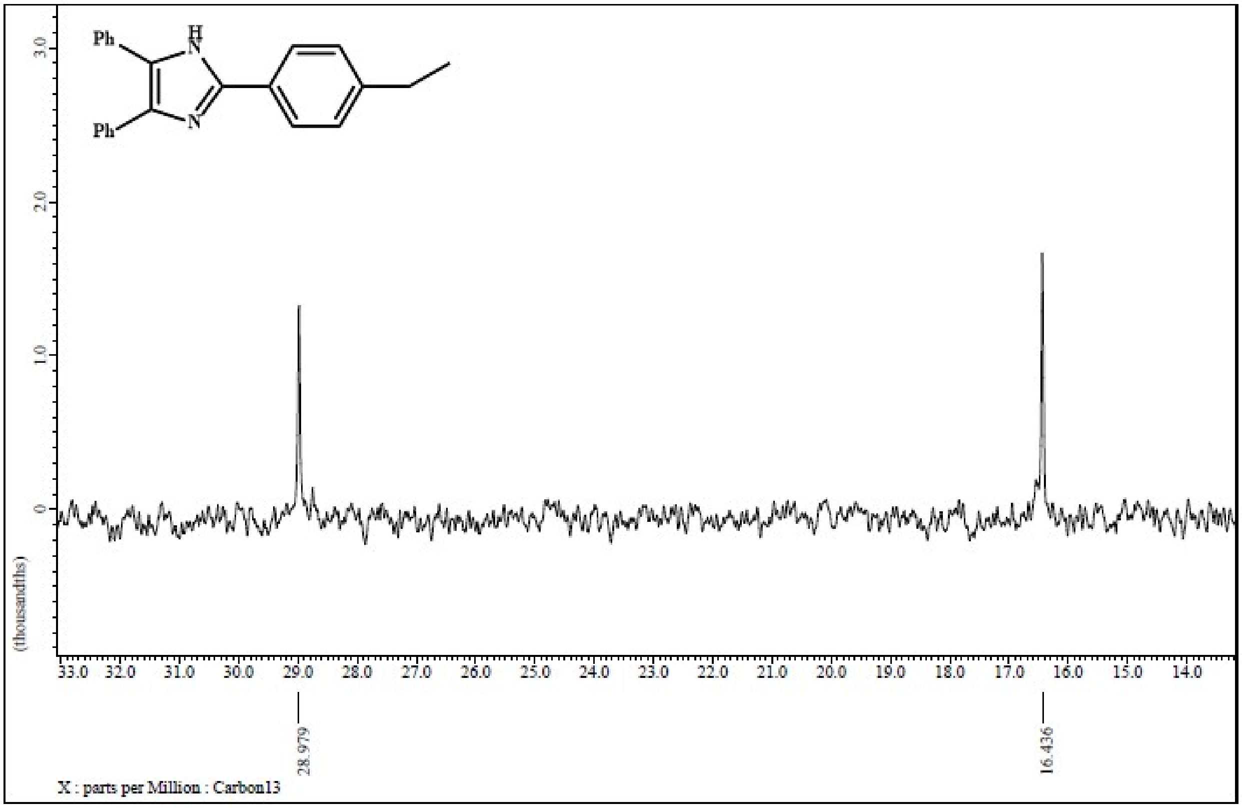


Entry 3h ^{13}C NMR spectrum of 2-(4-ethylphenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6)

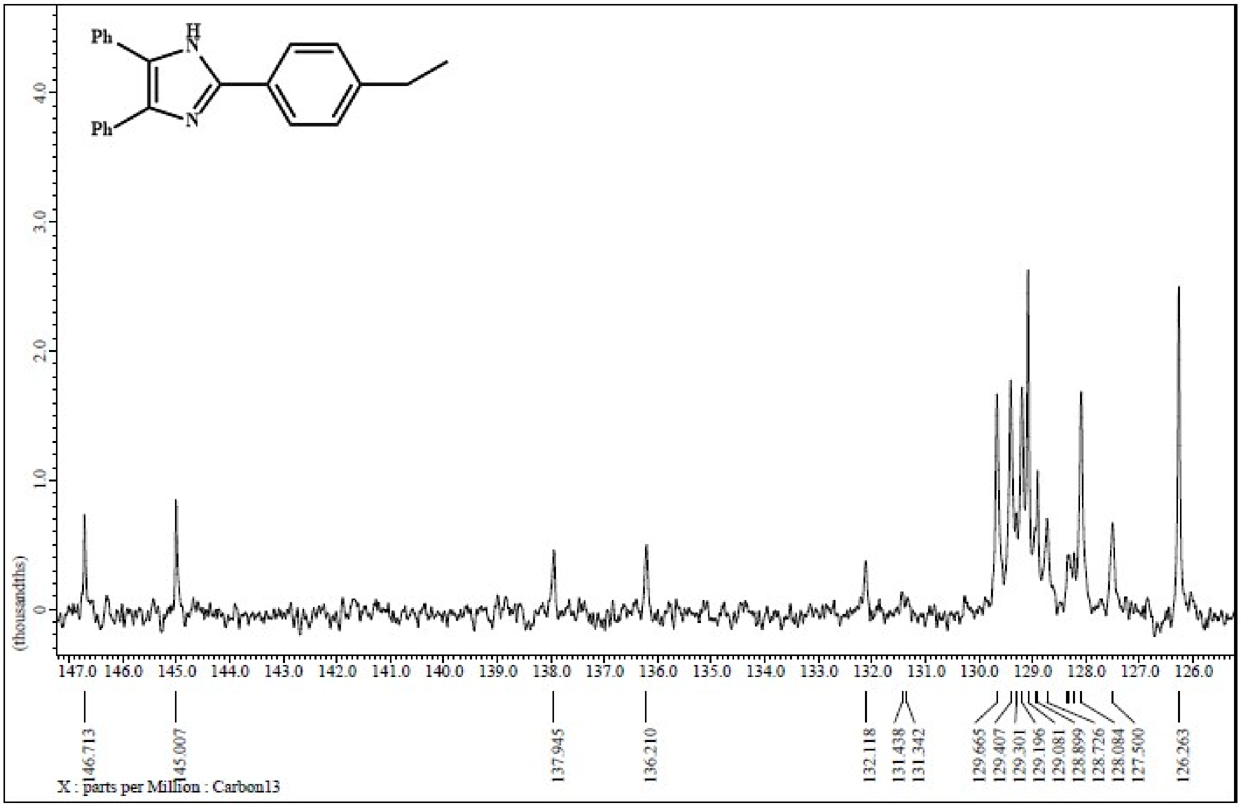
Full



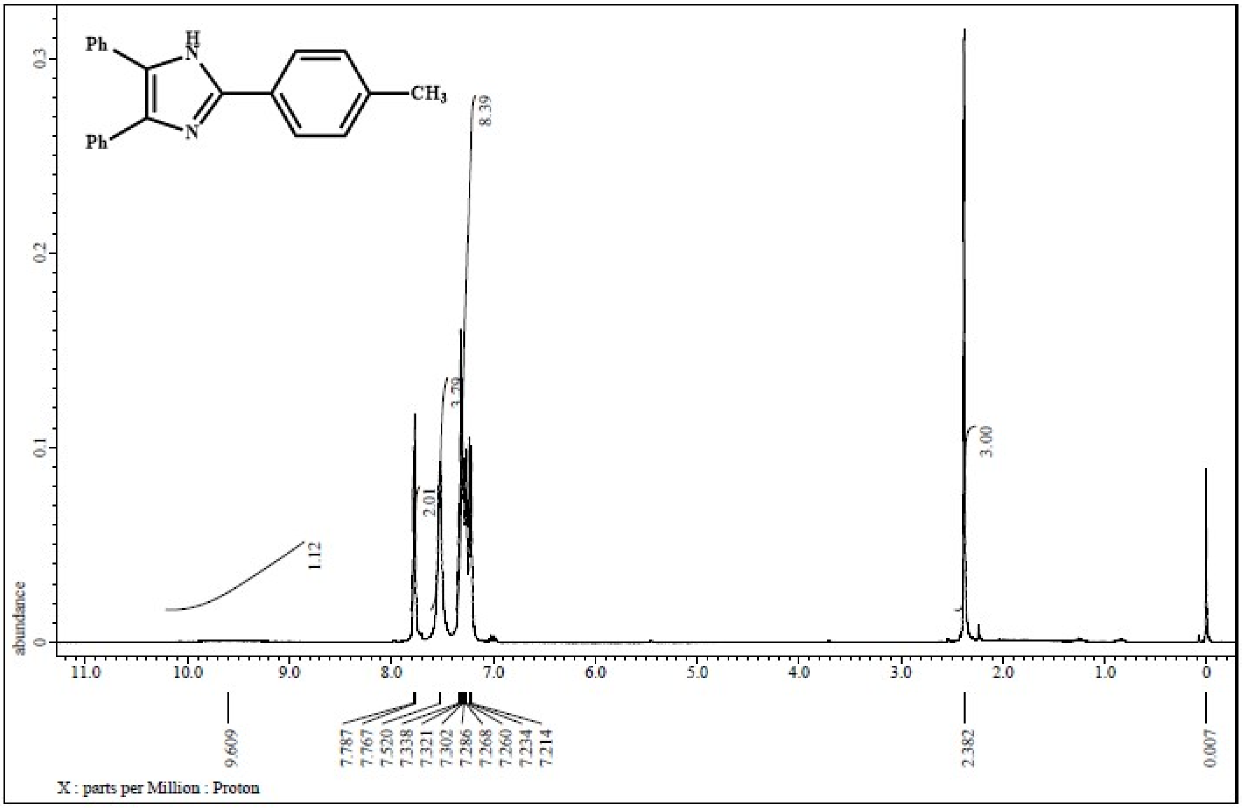
Entry 3h ^{13}C NMR spectrum of 2-(4-ethylphenyl)-4,5-diphenyl-1H-imidazole Expansion



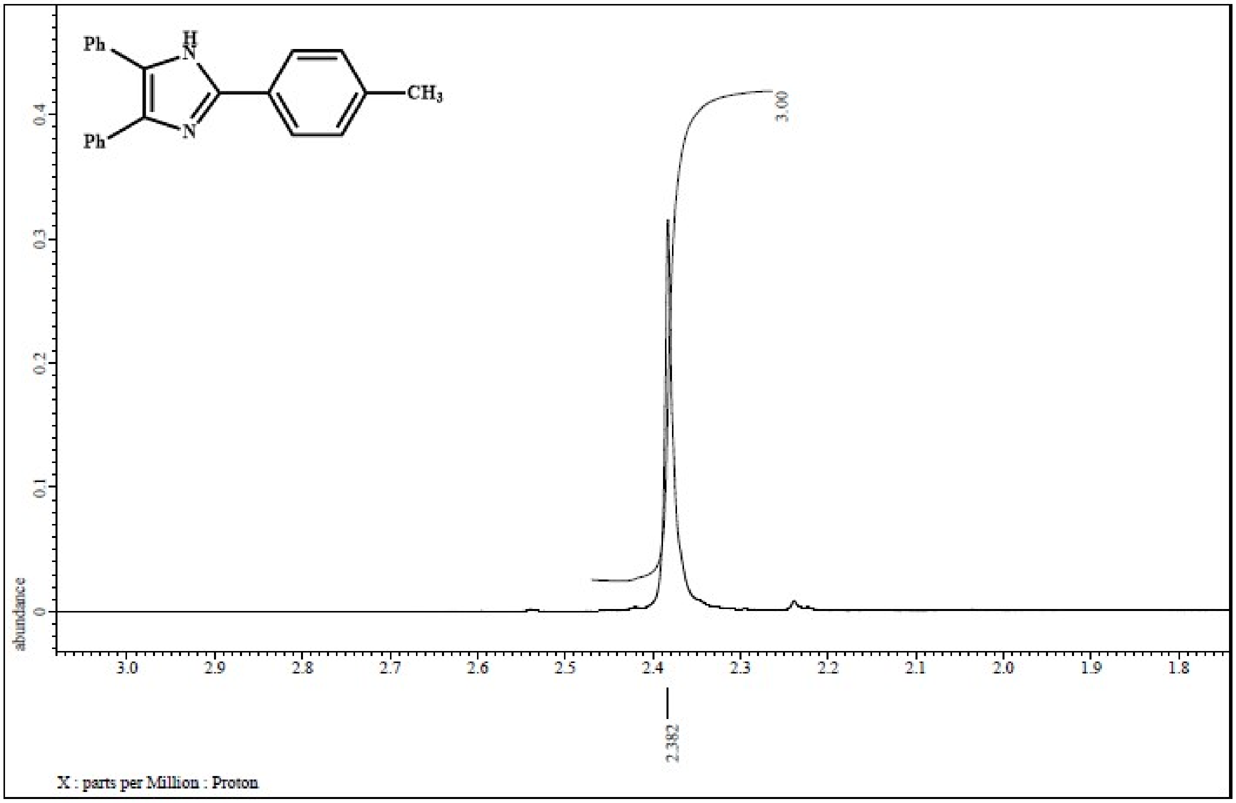
Entry 3h ^{13}C NMR spectrum of 2-(4-ethylphenyl)-4,5-diphenyl-1H-imidazole Expansion



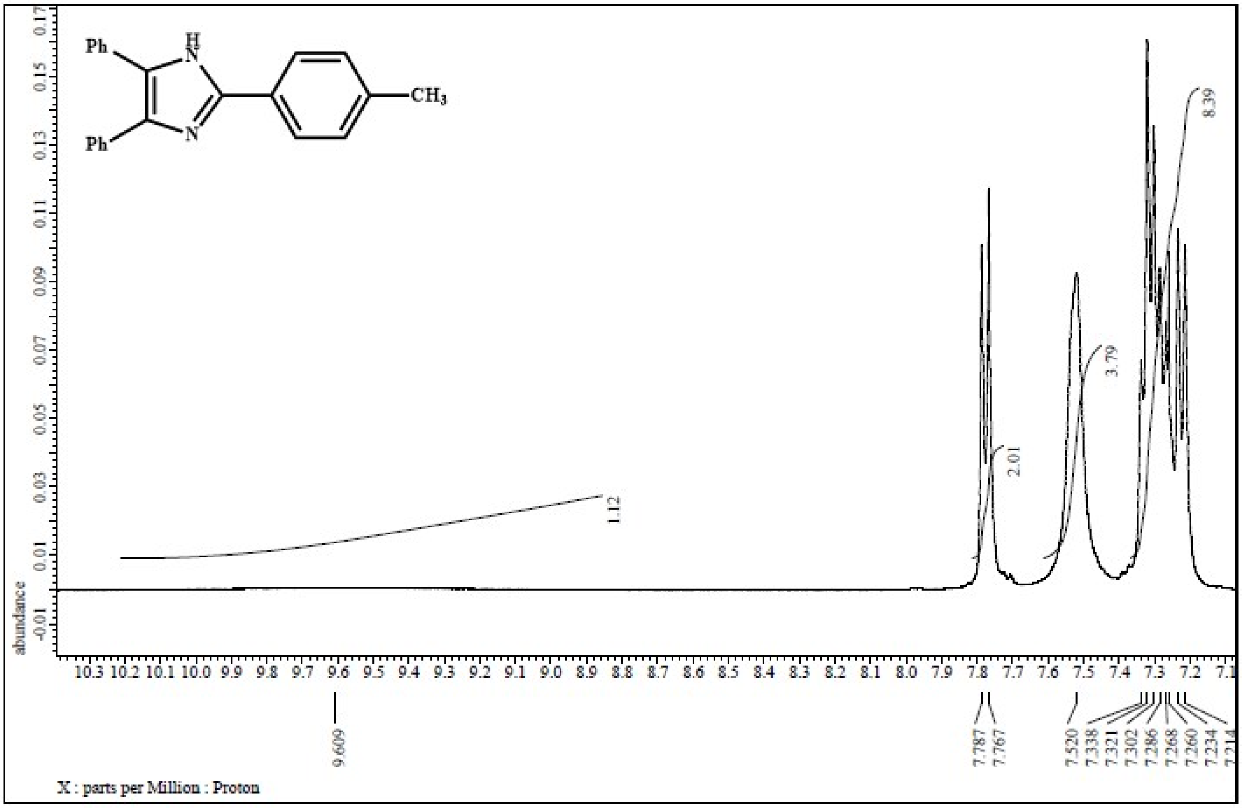
Entry 3i ^{1}H NMR spectrum of 4,5-diphenyl-2-(p-tolyl)-1H-imidazole (CDCl$_3$) Full



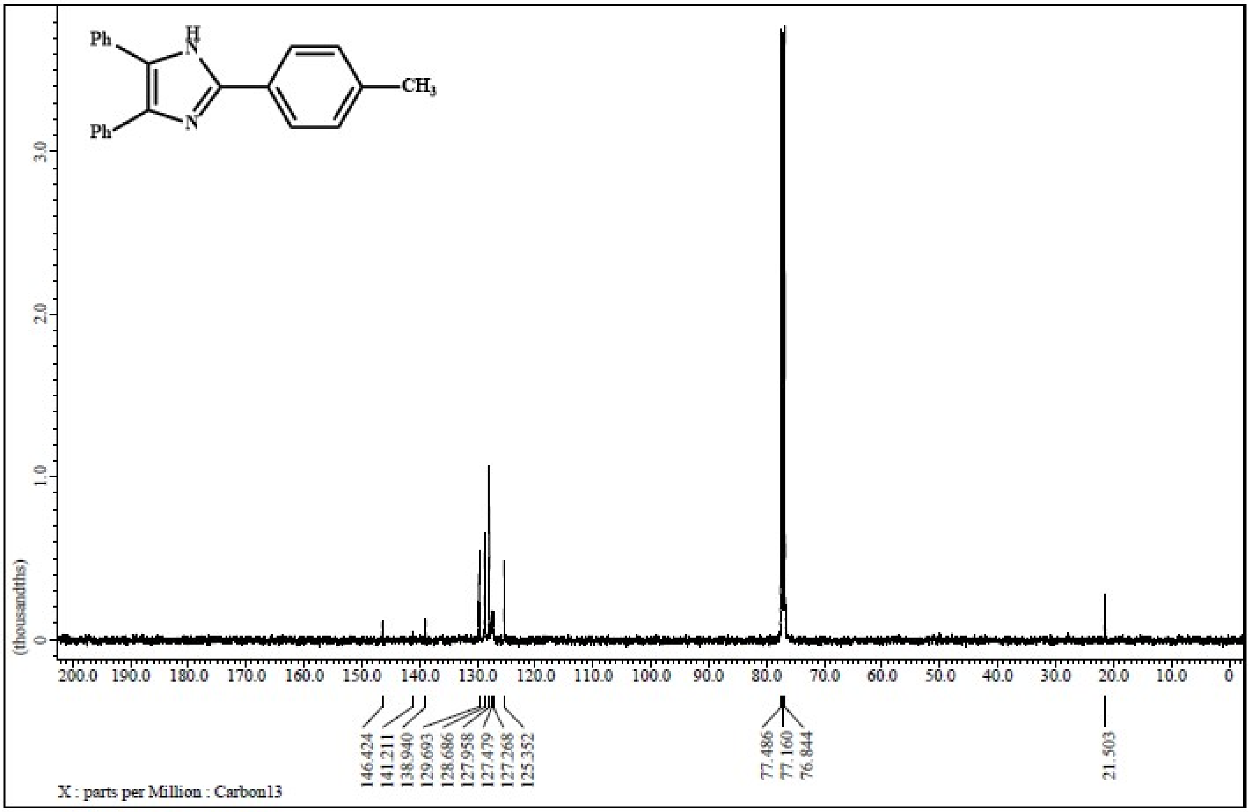
Entry 3i ^{1}H NMR spectrum of 4,5-diphenyl-2-(p-tolyl)-1H-imidazole Expansion



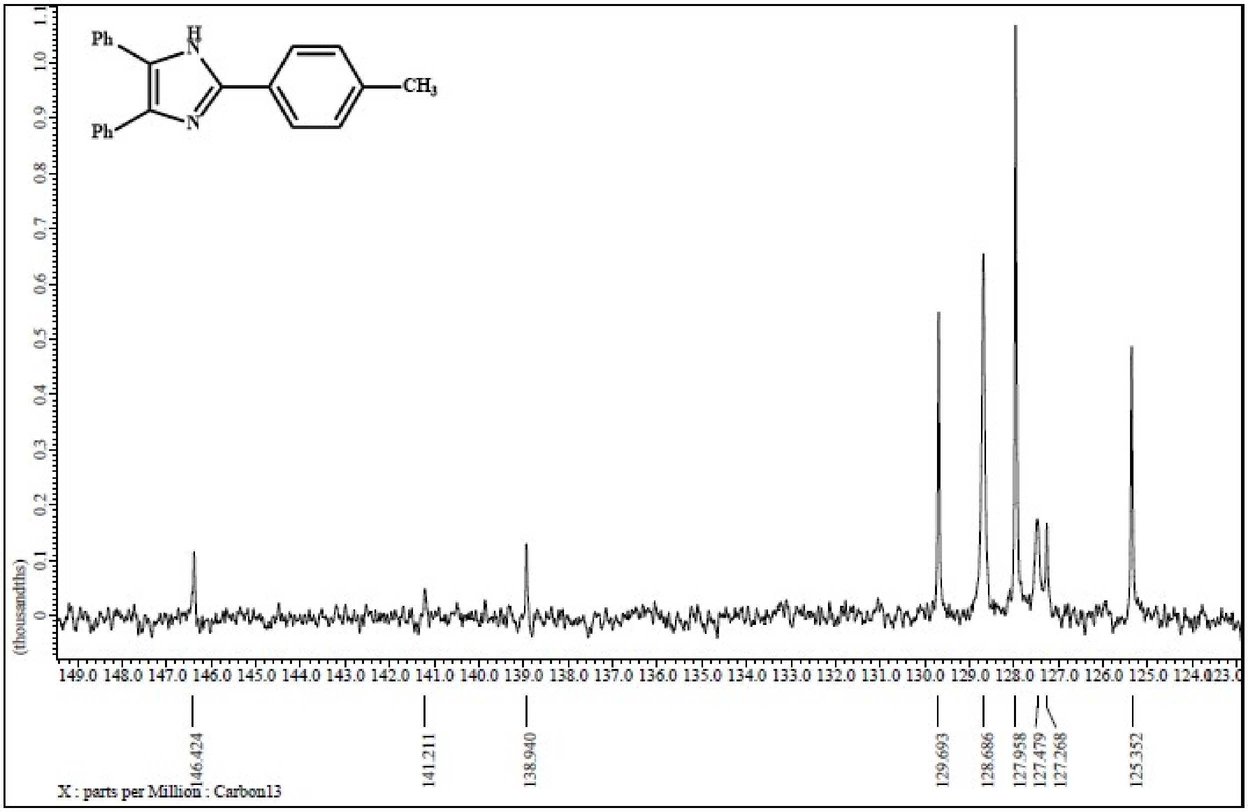
Entry 3i ^{1}H NMR spectrum of 4,5-diphenyl-2-(p-tolyl)-1H-imidazole Expansion



Entry 3i ^{13}C NMR spectrum of 4,5-diphenyl-2-(p-tolyl)-1H-imidazole ($CDCl_3$) Full

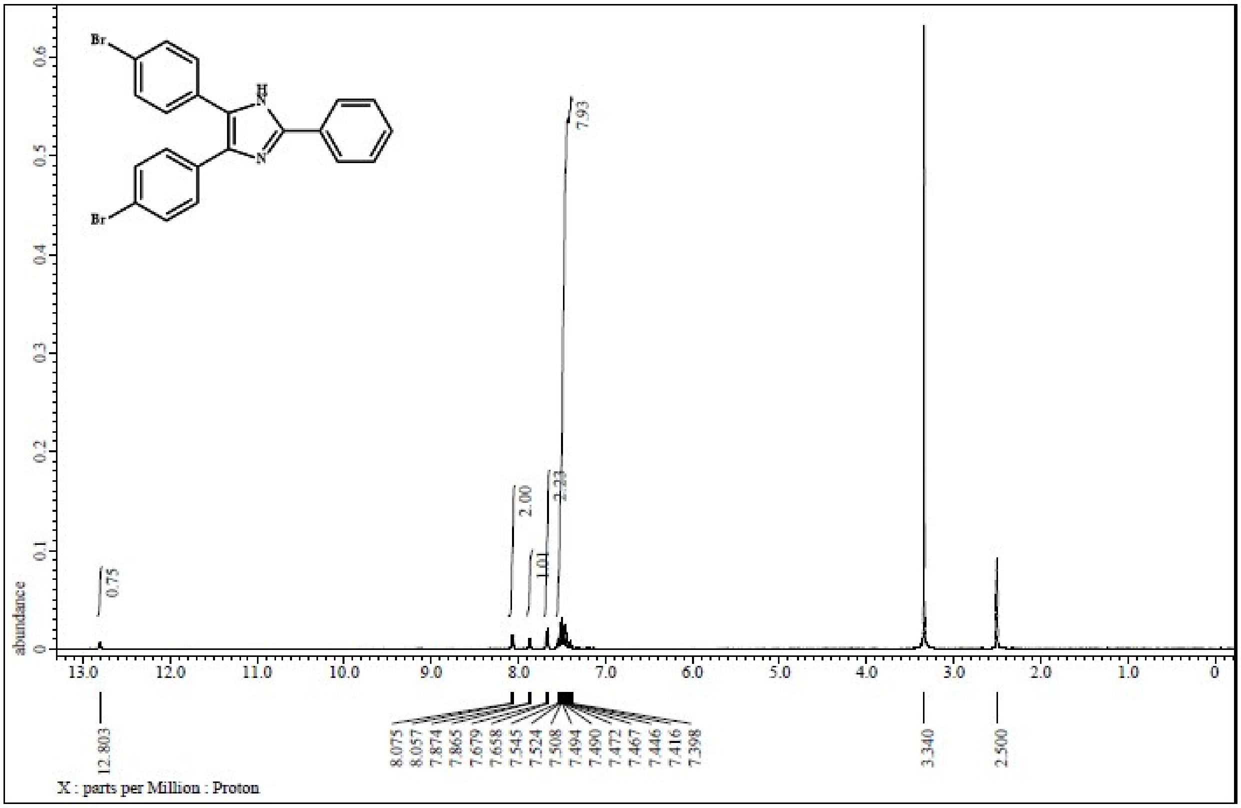


Entry 3i ^{13}C NMR spectrum of 4,5-diphenyl-2-(p-tolyl)-1H-imidazole ($CDCl_3$) Expansion

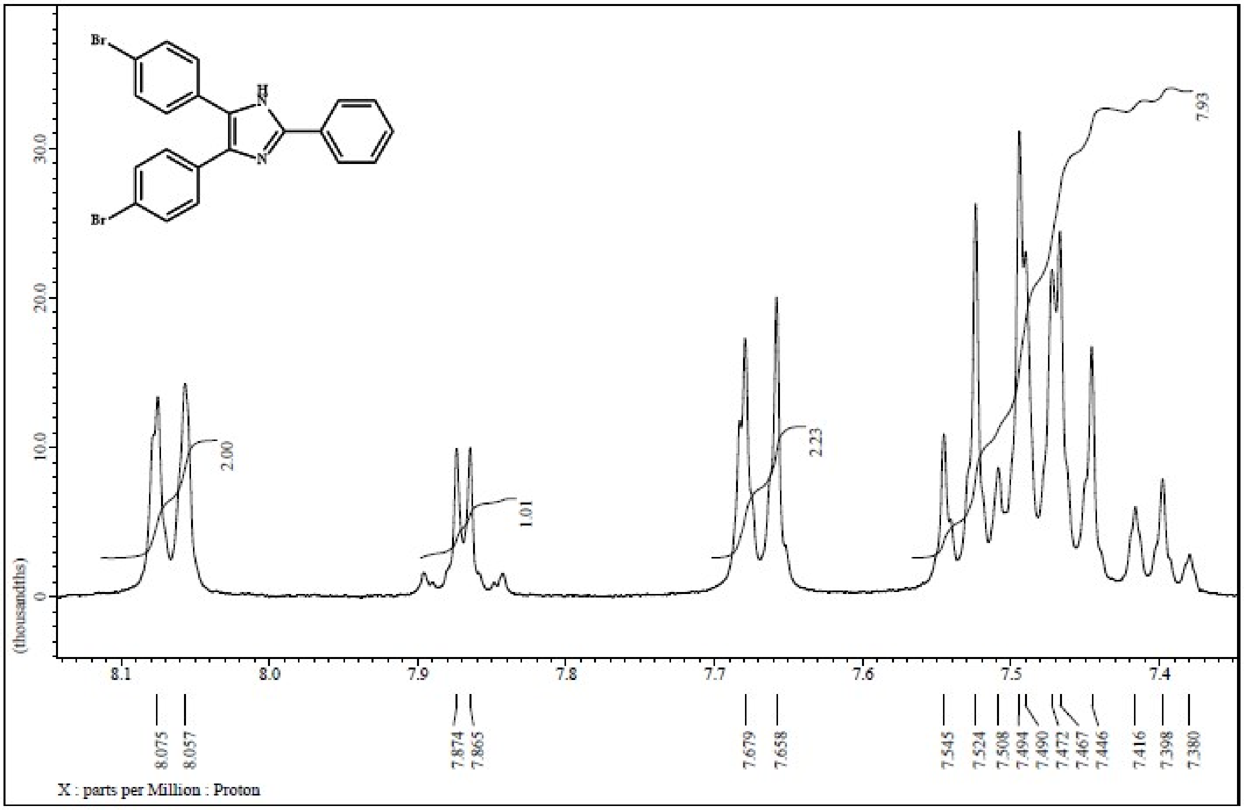


Entry 3j ^{1}H NMR spectrum of 4,5-bis(4-bromophenyl)-2-phenyl-1H-imidazole (DMSO-d_6)

Full

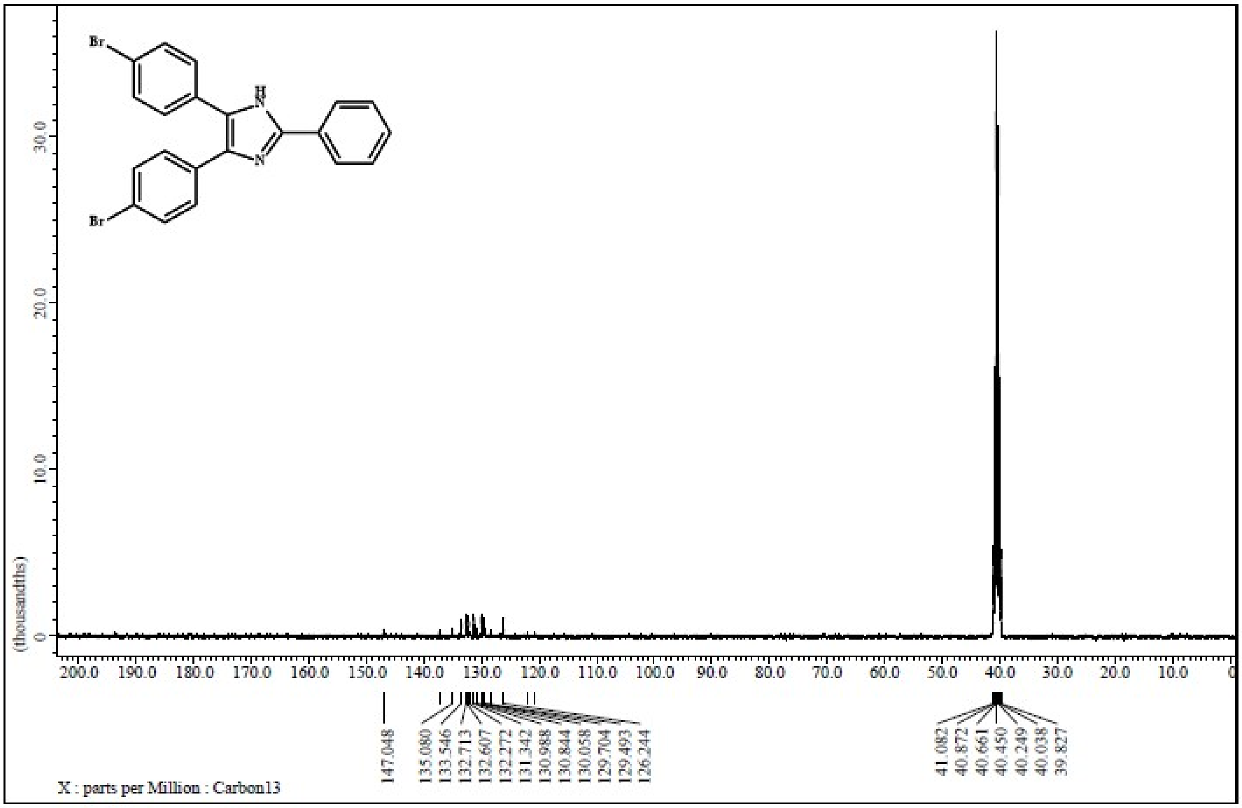


Entry 3j ^{1}H NMR spectrum of 4,5-bis(4-bromophenyl)-2-phenyl-1H-imidazole Expansion

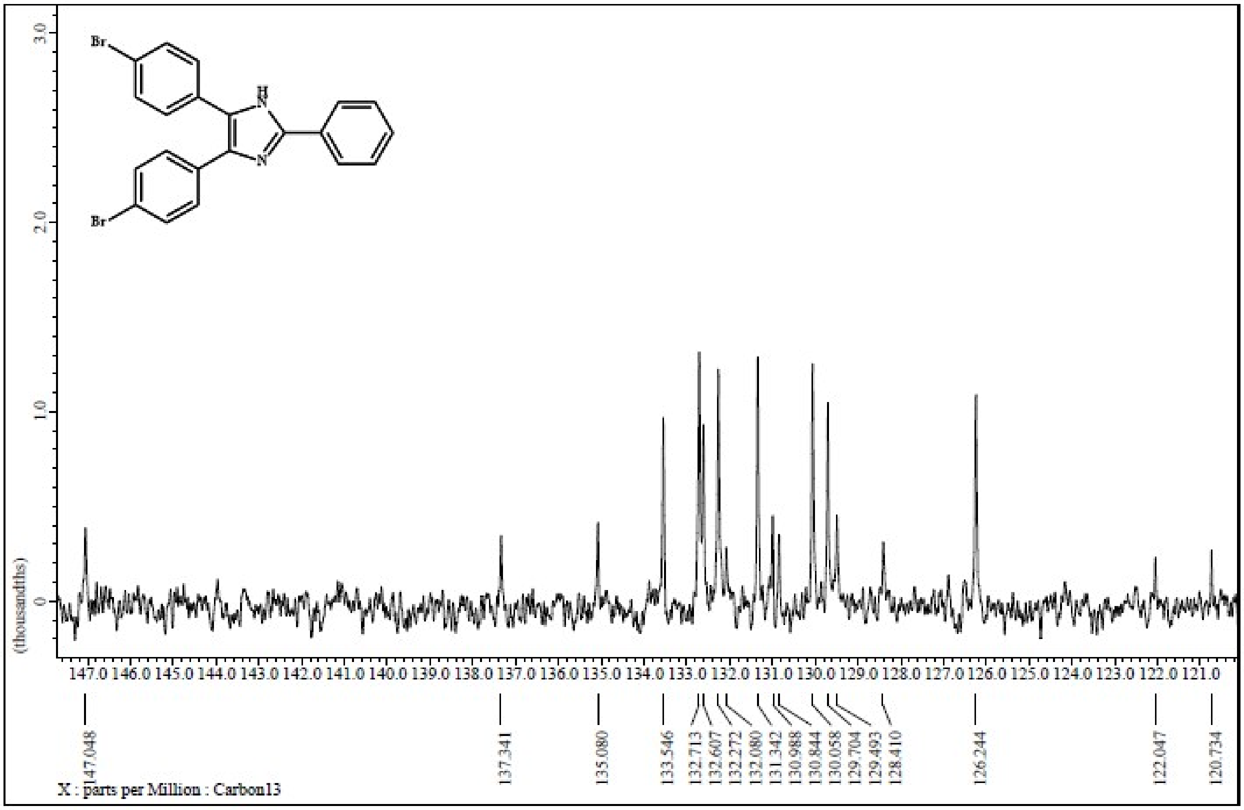


Entry 3j ^{13}C NMR spectrum of 4,5-bis(4-bromophenyl)-2-phenyl-1H-imidazole (DMSO-d_6)

Full

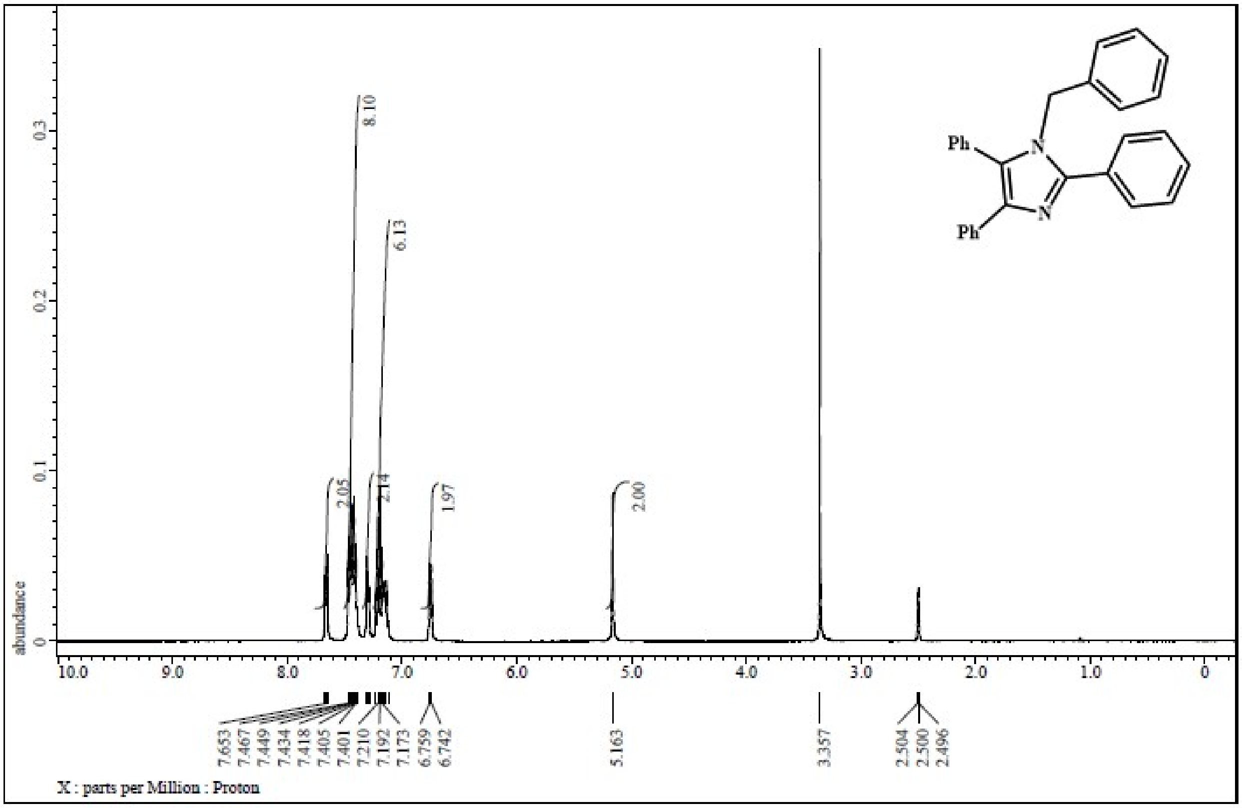


Entry 3j ^{13}C NMR spectrum of 4,5-bis(4-bromophenyl)-2-phenyl-1H-imidazole Expansion

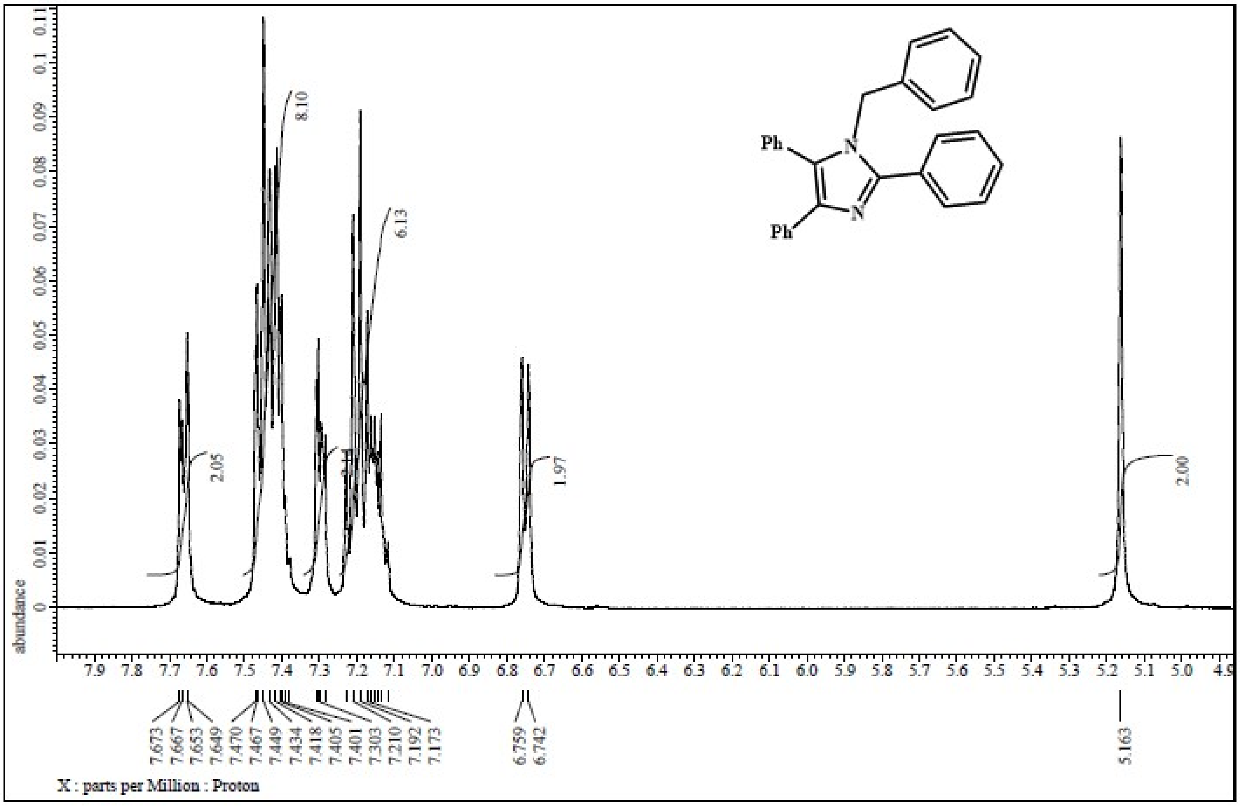


NMR Spectra of 1,2,4,5-tetrasubstituted imidazoles

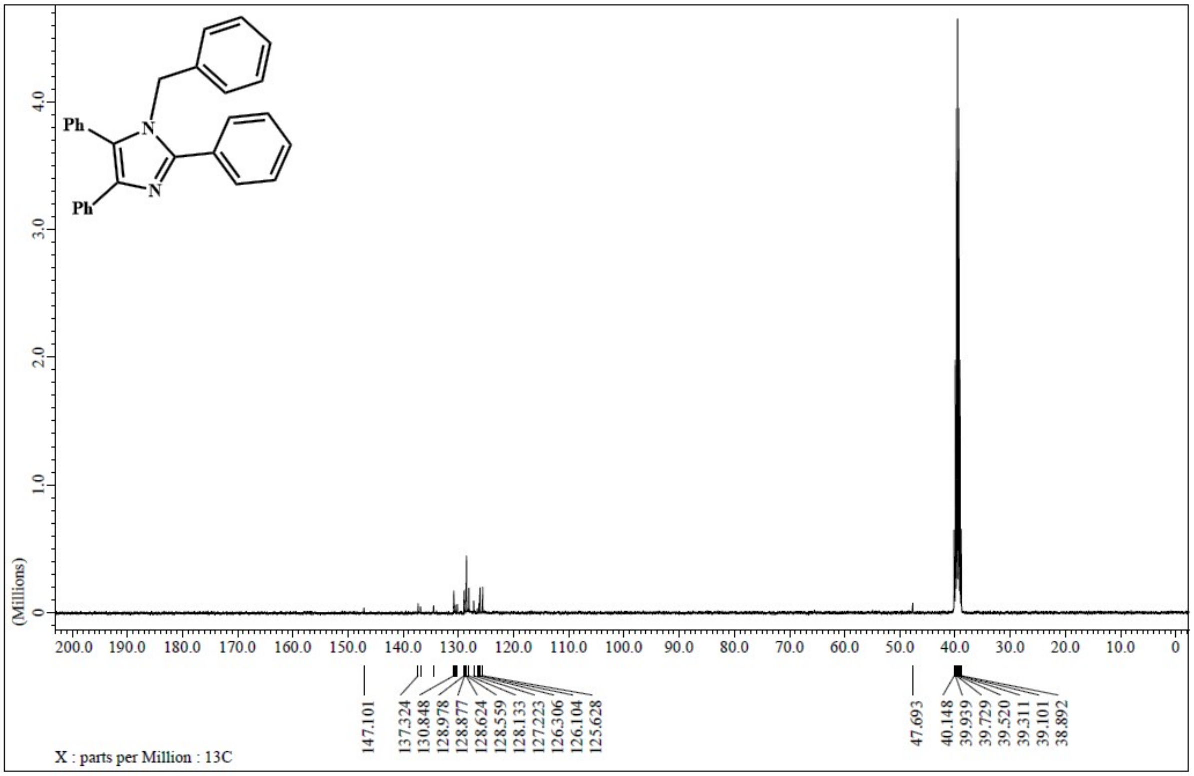
Entry 4a ^{1}H NMR spectrum of 1-benzyl-2,4,5-triphenyl-1H-imidazole (DMSO-d_6) Full



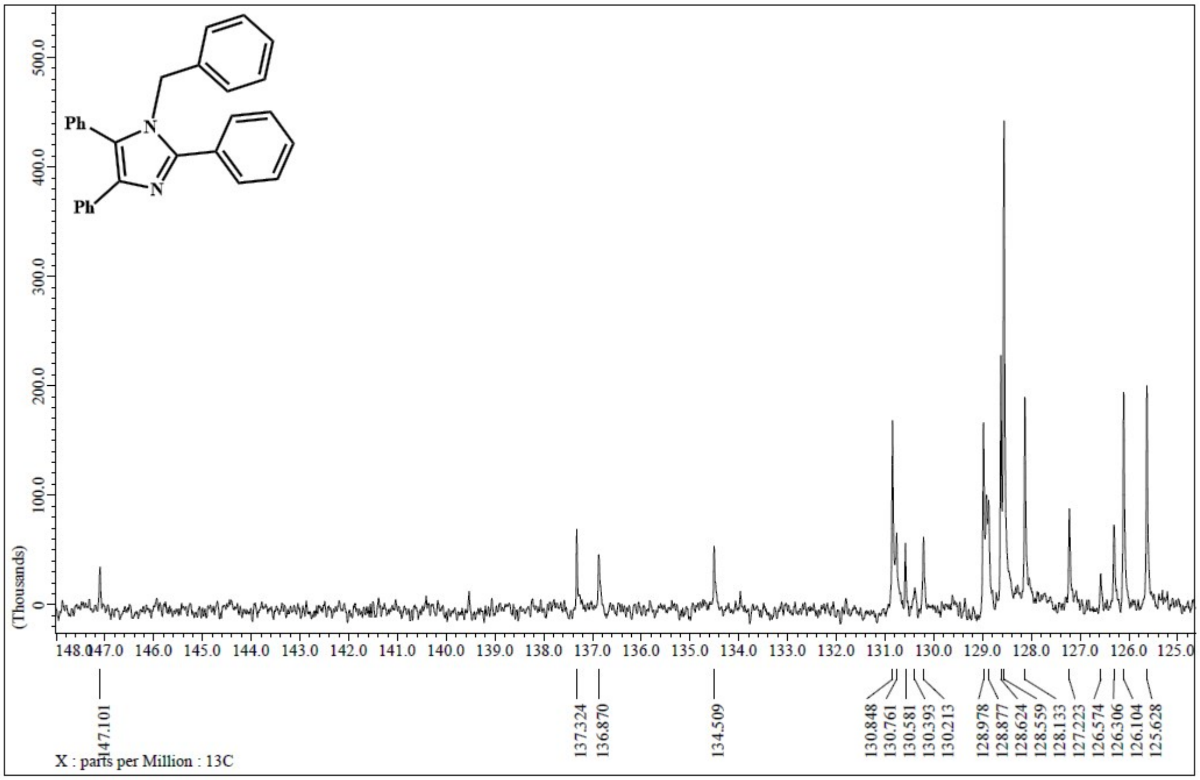
Entry 4a ^{1}H NMR spectrum of 1-benzyl-2,4,5-triphenyl-1H-imidazole Expansion



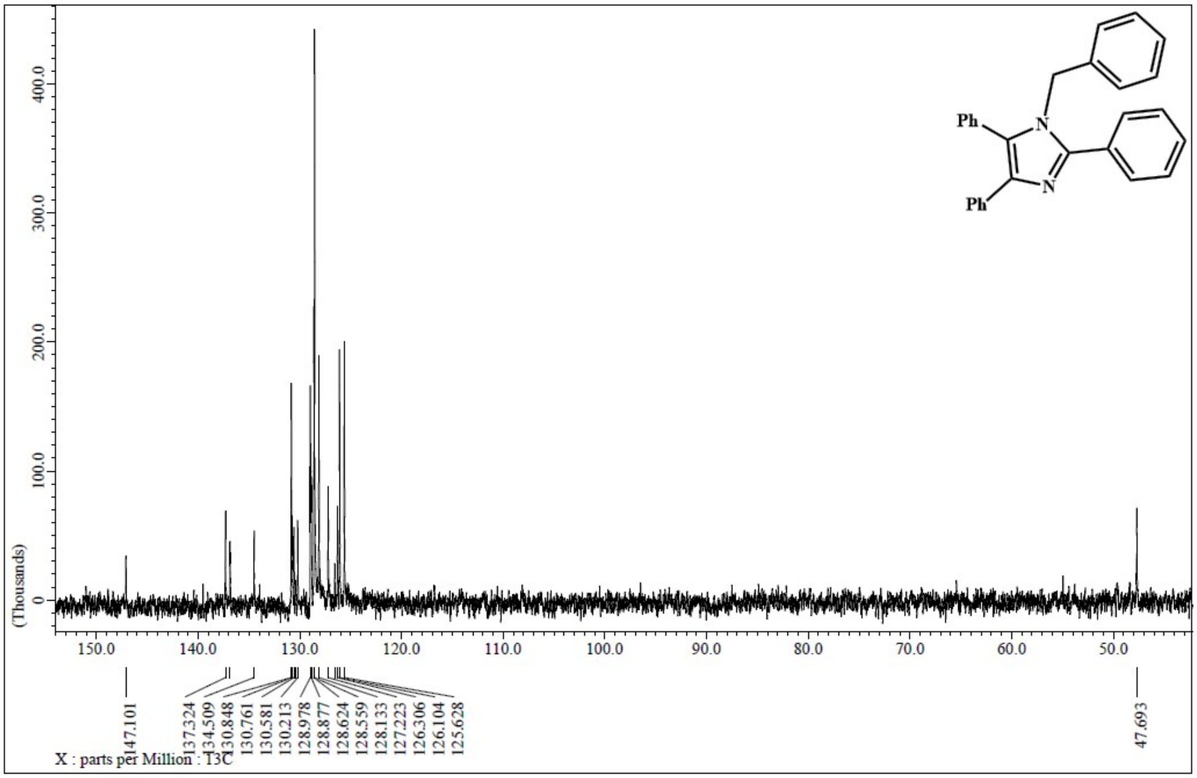
Entry 4a ^{13}C NMR spectrum of 1-benzyl-2,4,5-triphenyl-1H-imidazole (DMSO-d_6) Full



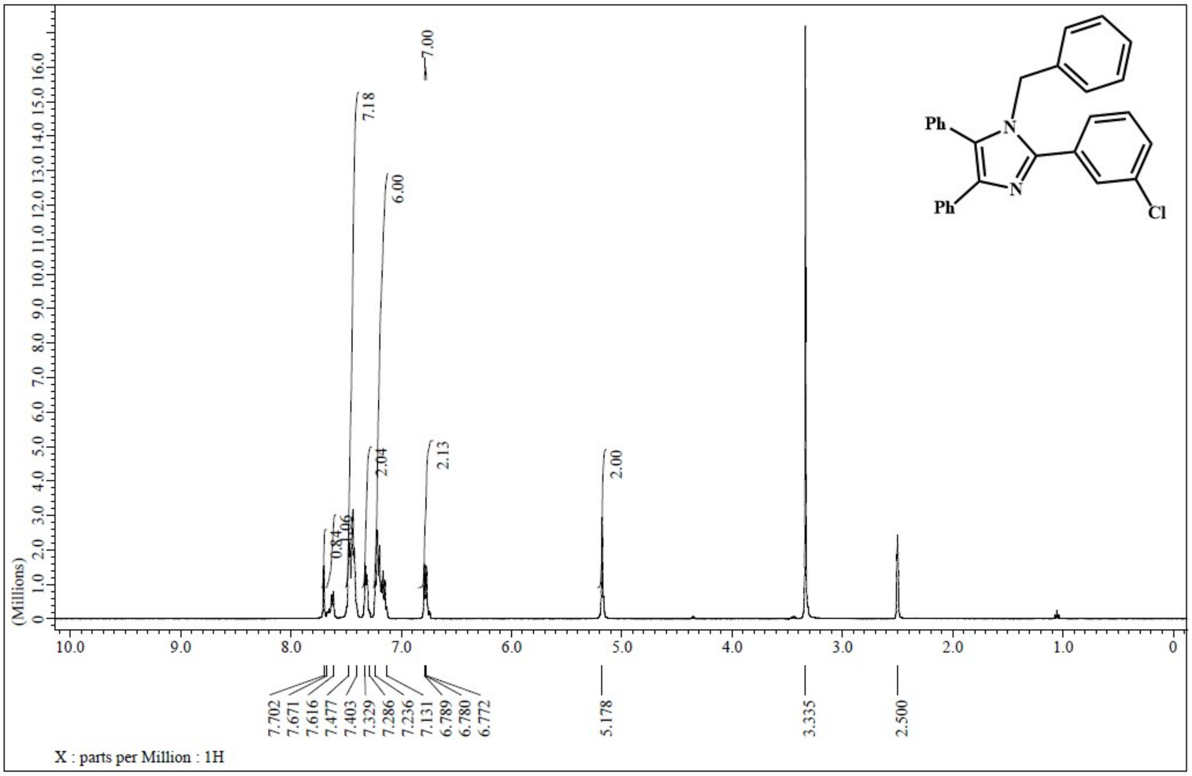
Entry 4a ^{13}C NMR spectrum of 1-benzyl-2,4,5-triphenyl-1H-imidazole Expansion



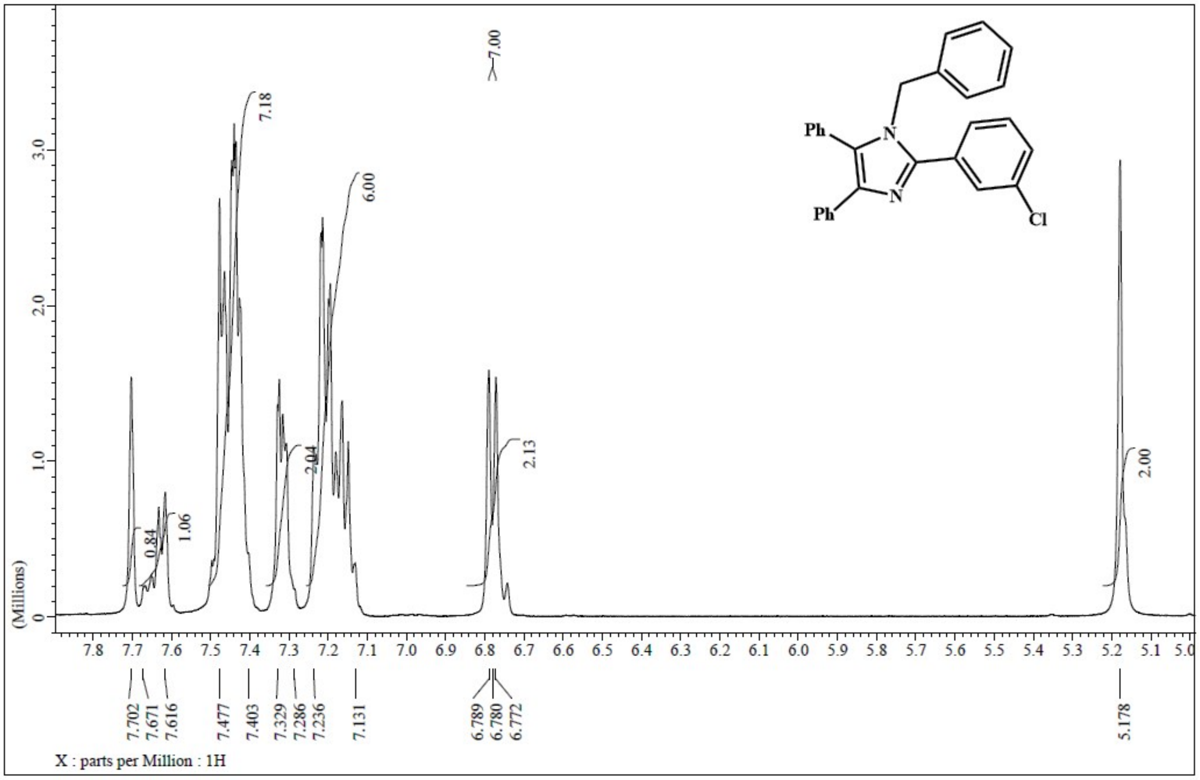
Entry 4a ^{13}C NMR spectrum of 1-benzyl-2,4,5-triphenyl-1H-imidazole Expansion



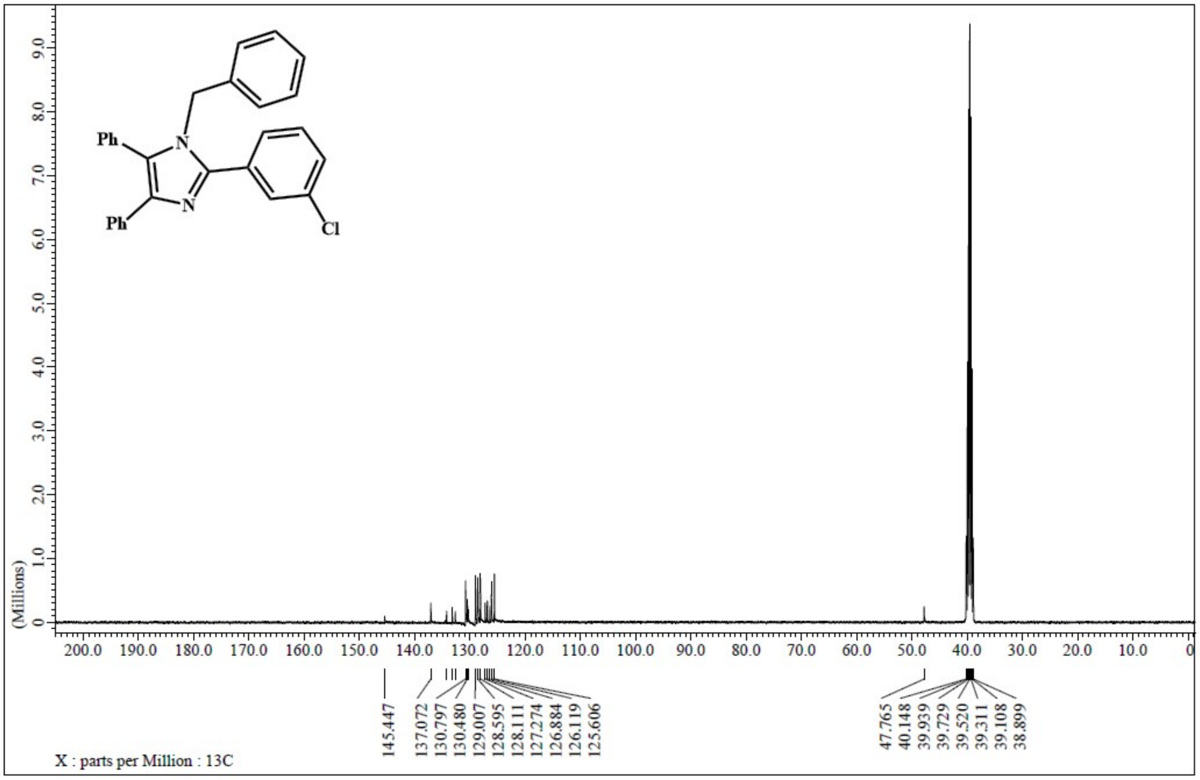
Entry 4b ^{1}H NMR spectrum of 1-benzyl-2-(3-chlorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$) Full



Entry 4b ^{1}H NMR spectrum of 1-benzyl-2-(3-chlorophenyl)-4,5-diphenyl-1H-imidazole Expansion

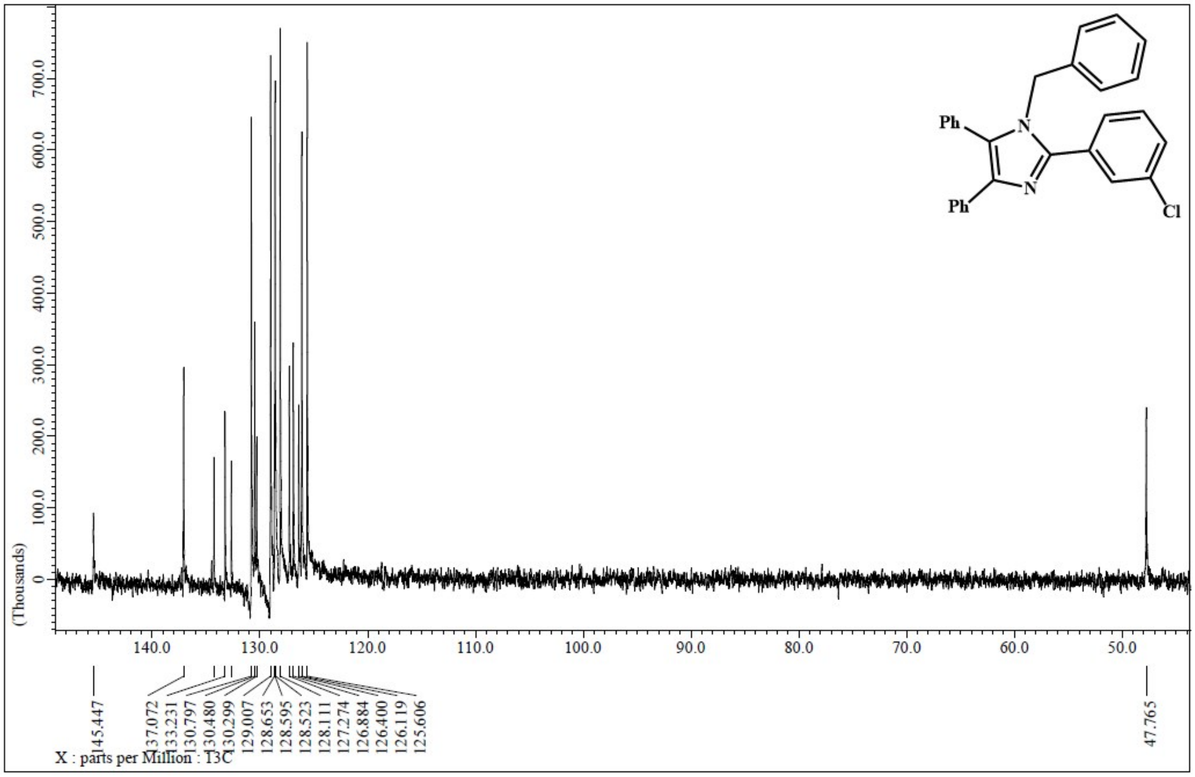


Entry 4b ^{13}C NMR spectrum of 1-benzyl-2-(3-chlorophenyl)-4,5-diphenyl-1H-imidazole (DMSO-d_6) Full



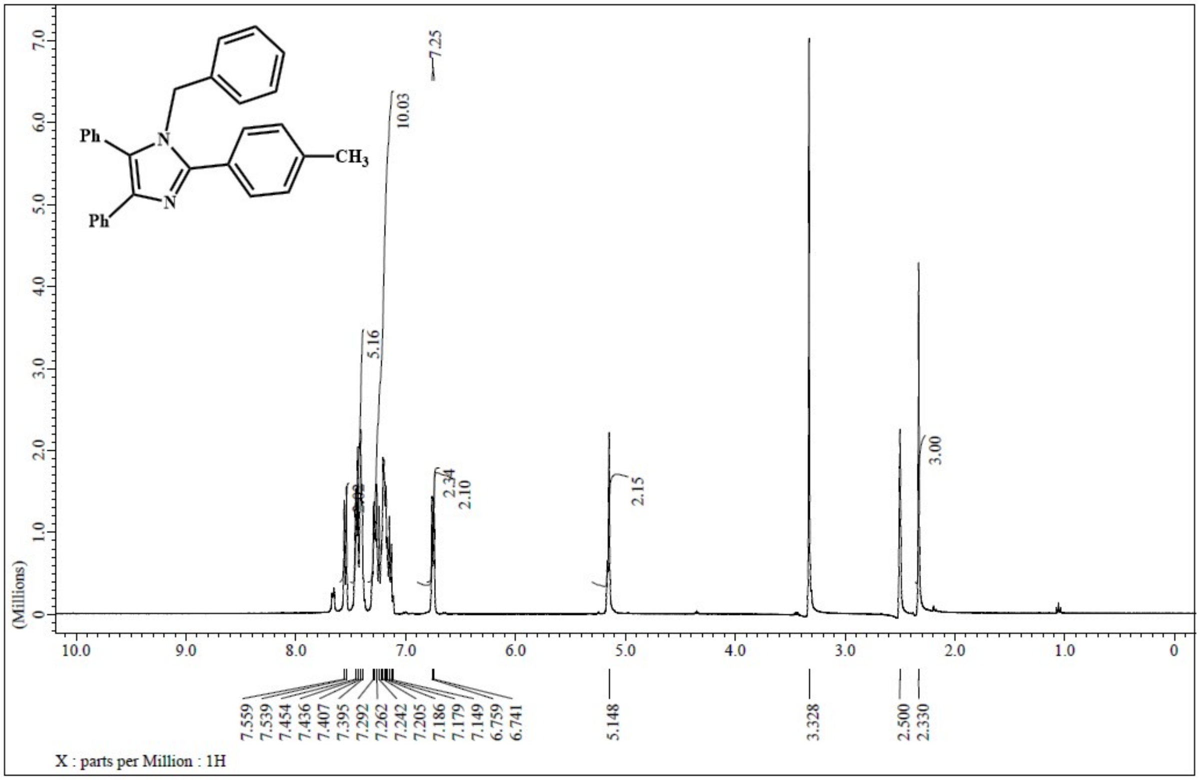
Entry 4b ^{13}C NMR spectrum of 1-benzyl-2-(3-chlorophenyl)-4,5-diphenyl-1H-imidazole

Expansion

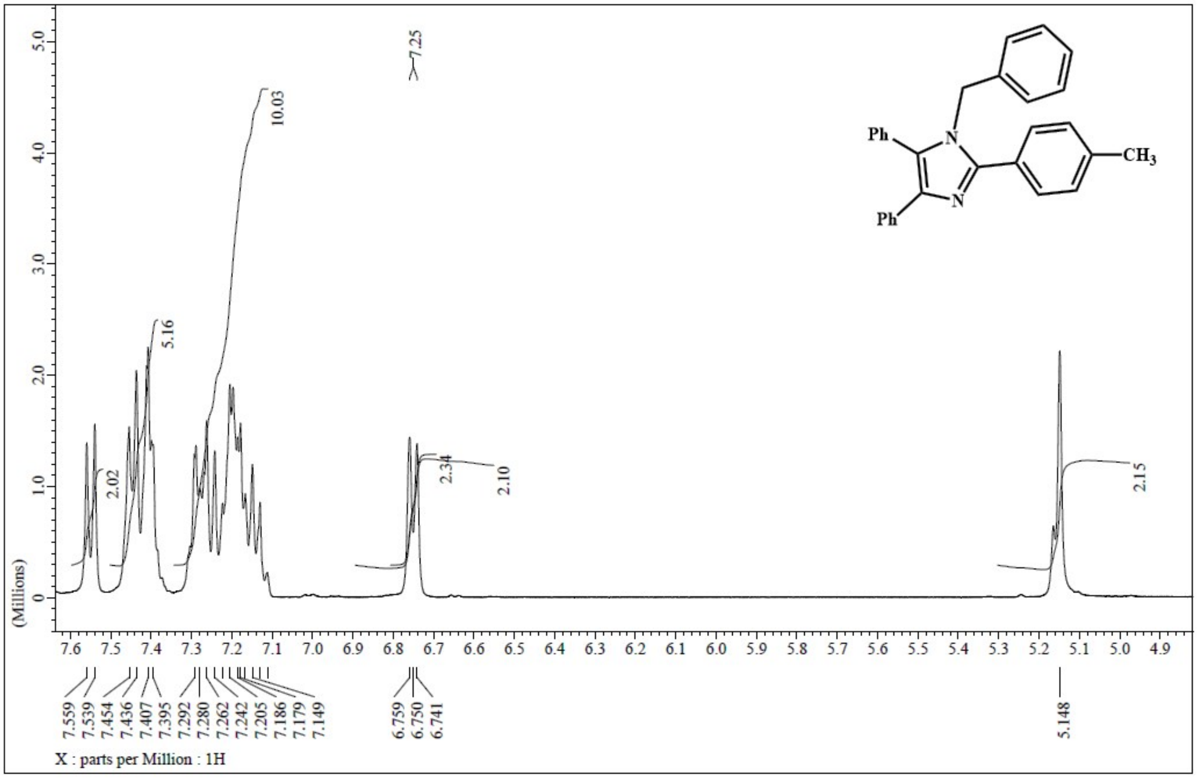


Entry 4c ^{1}H NMR spectrum of 1-benzyl-4,5-diphenyl-2-(p-tolyl)-1H-imidazole (DMSO-d_6)

Full

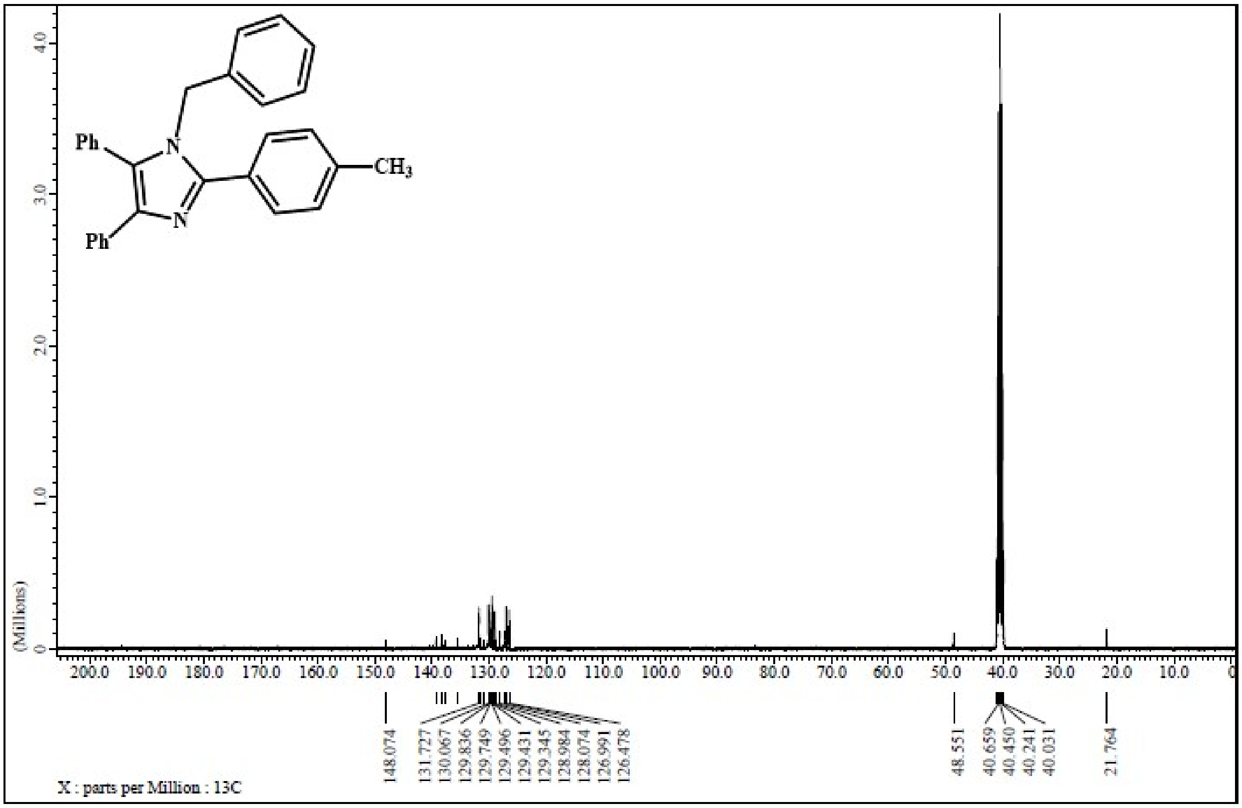


Entry 4c ^{1}H NMR spectrum of 1-benzyl-4,5-diphenyl-2-(p-tolyl)-1H-imidazole Expansion

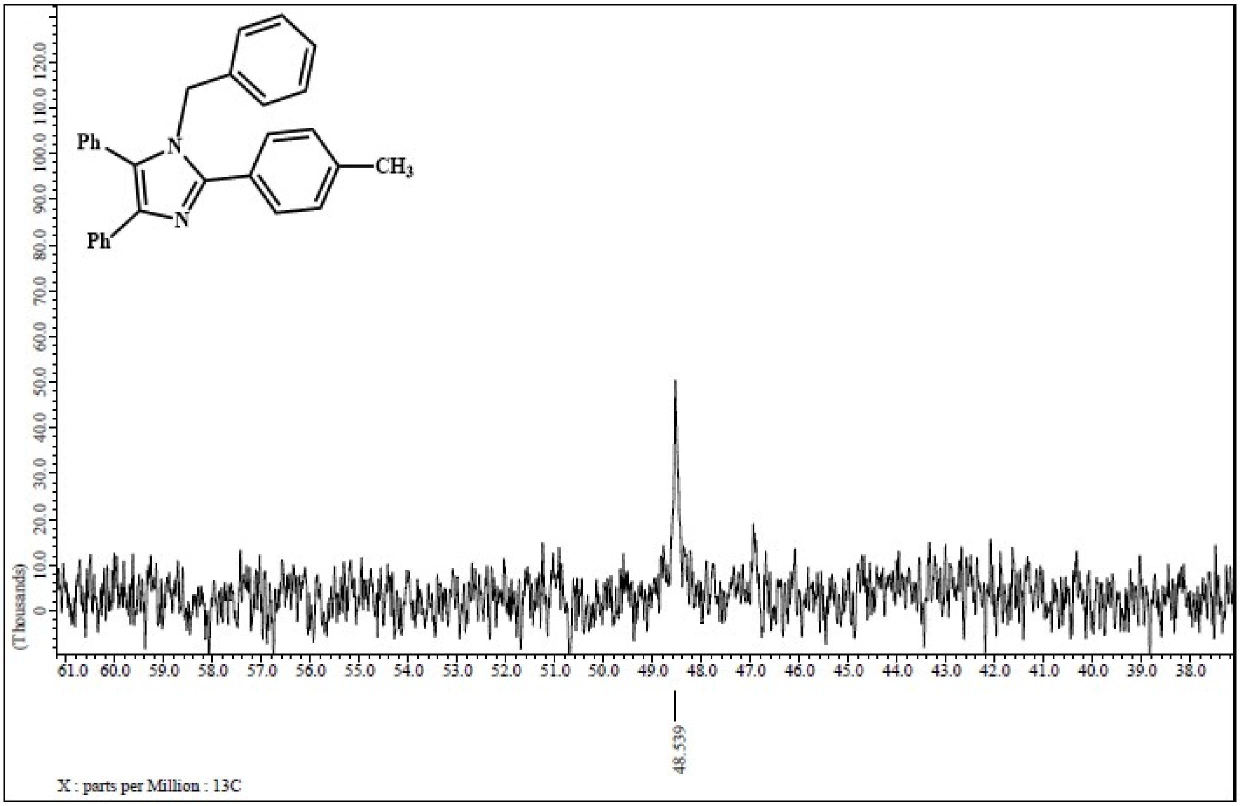


Entry 4c ^{13}C NMR spectrum of 1-benzyl-4,5-diphenyl-2-(p-tolyl)-1H-imidazole (DMSO-d_6)

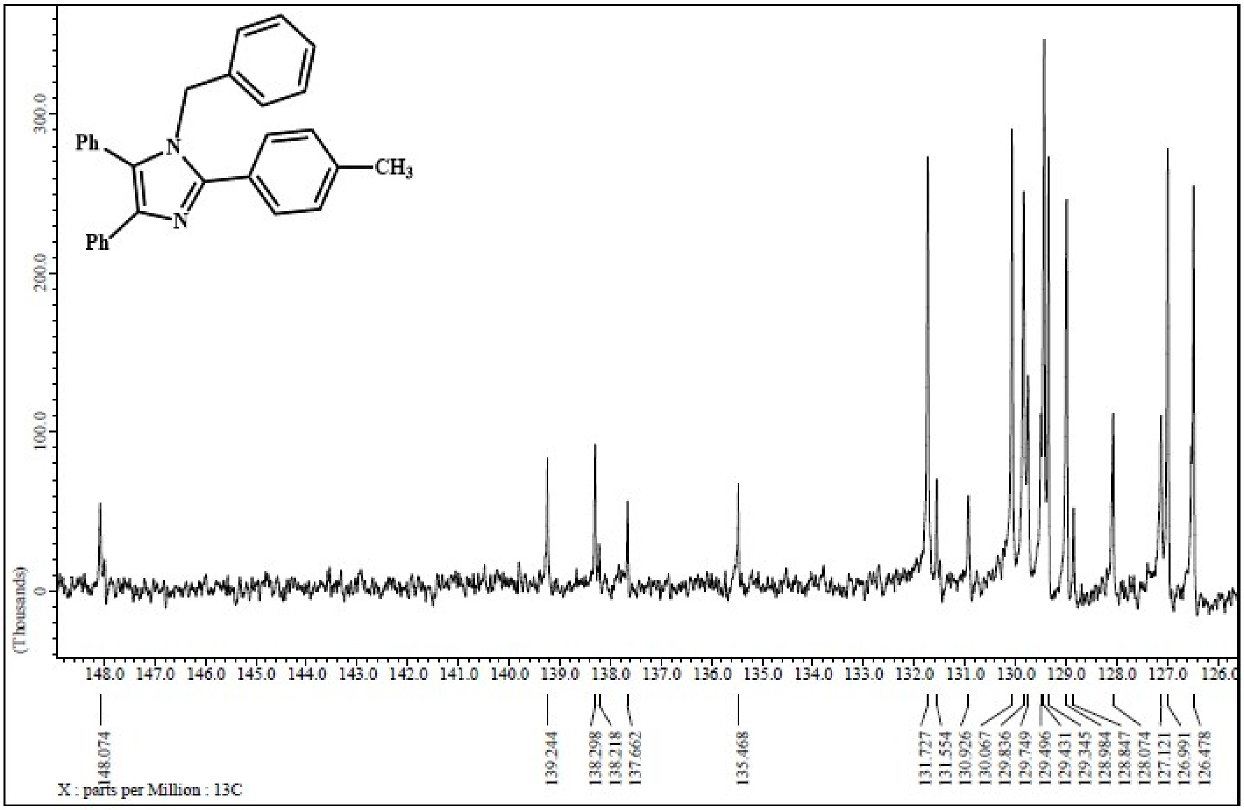
Full



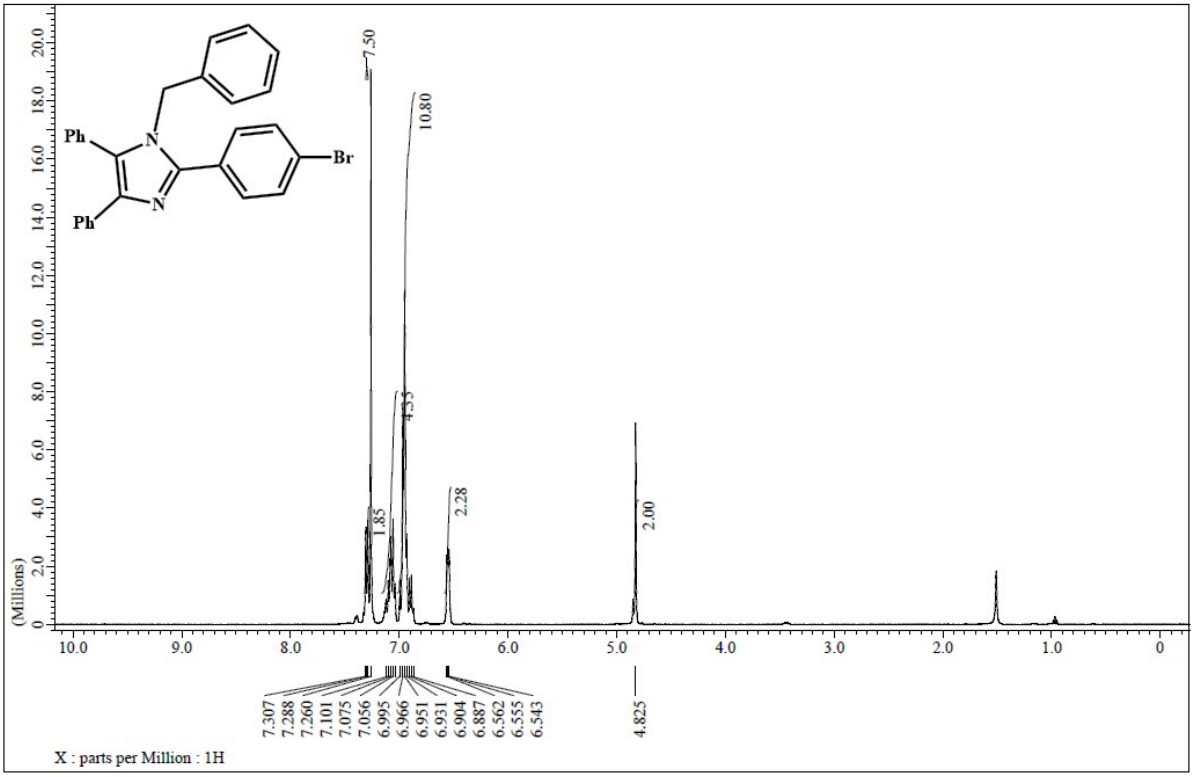
Entry 4c ^{13}C NMR spectrum of 1-benzyl-4,5-diphenyl-2-(p-tolyl)-1H-imidazole Expansion



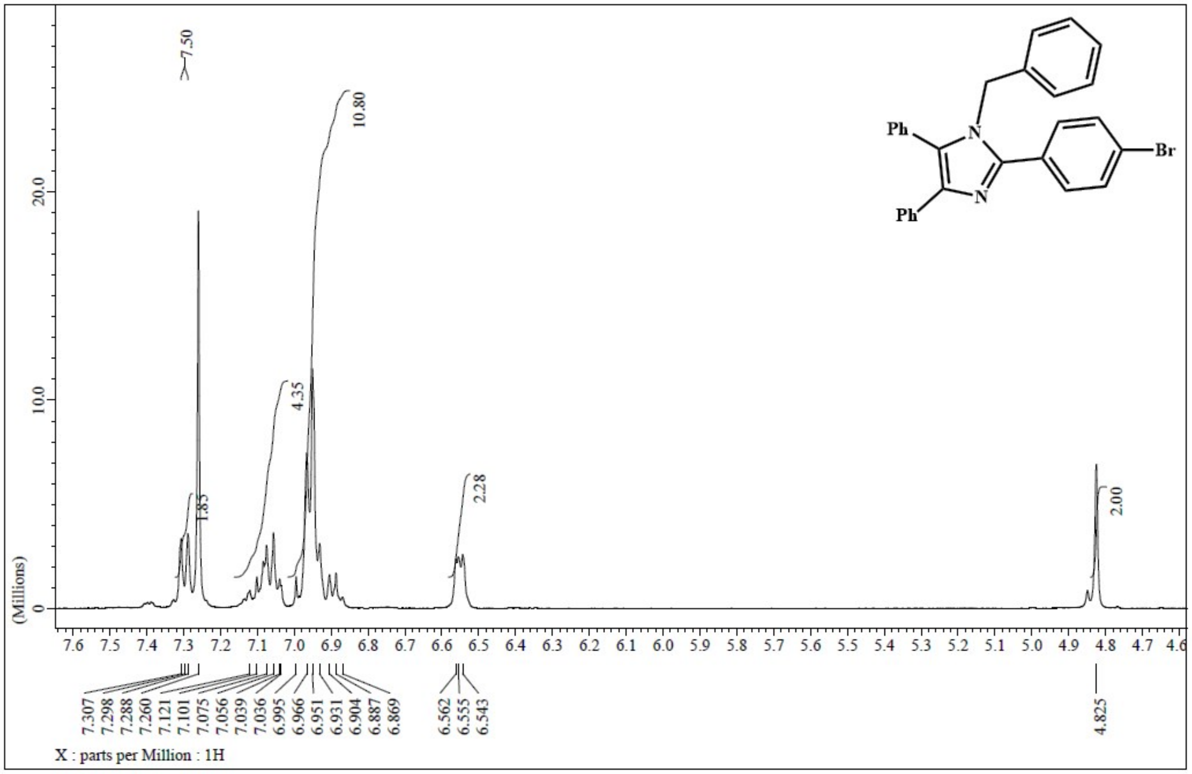
Entry 4c ^{13}C NMR spectrum of 1-benzyl-4,5-diphenyl-2-(p-tolyl)-1H-imidazole Expansion



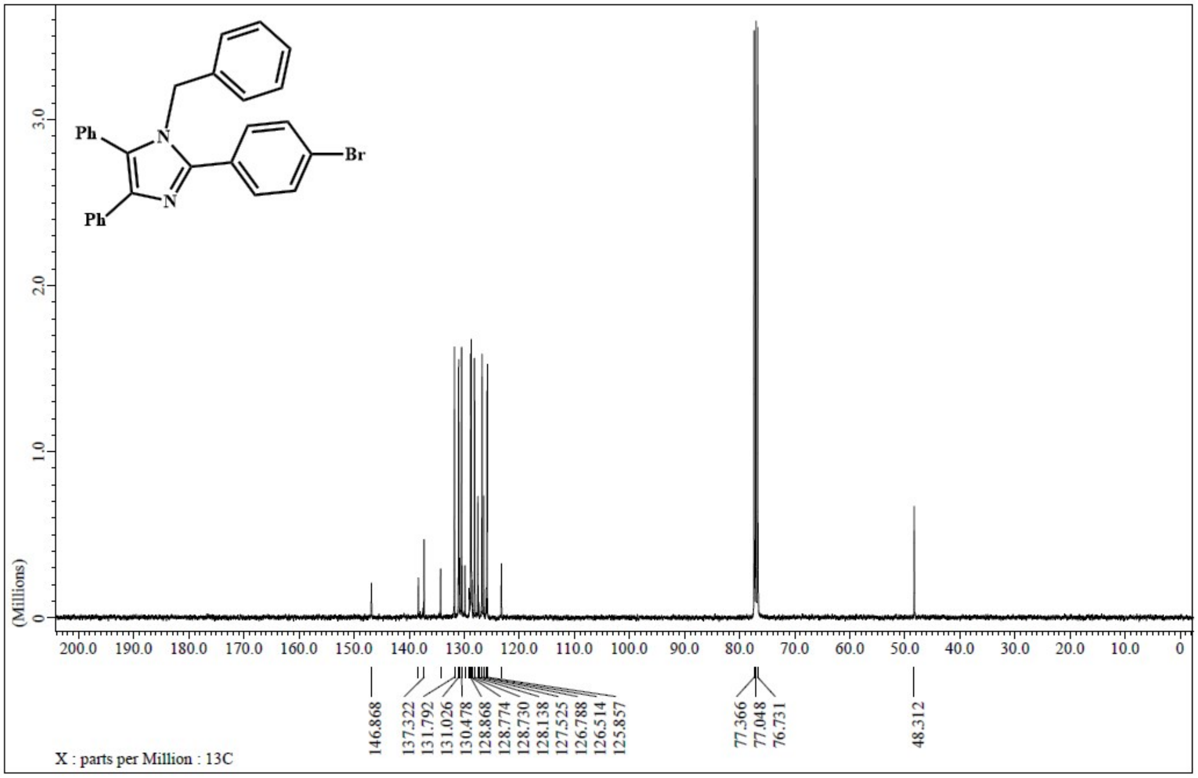
Entry 4d ^{1}H NMR spectrum of 1-benzyl-2-(4-bromophenyl)-4,5-diphenyl-1H-imidazole ($CDCl_3$) Full



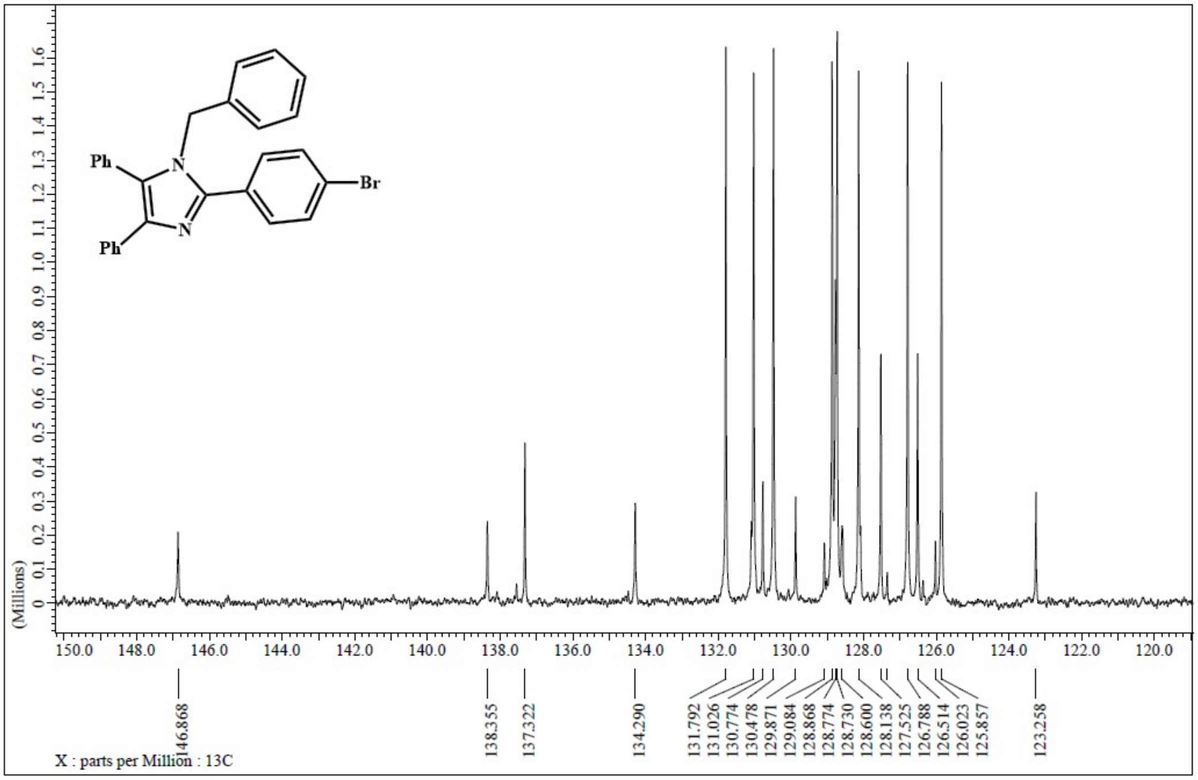
Entry 4d ^{1}H NMR spectrum of 1-benzyl-2-(4-bromophenyl)-4,5-diphenyl-1H-imidazole Expansion



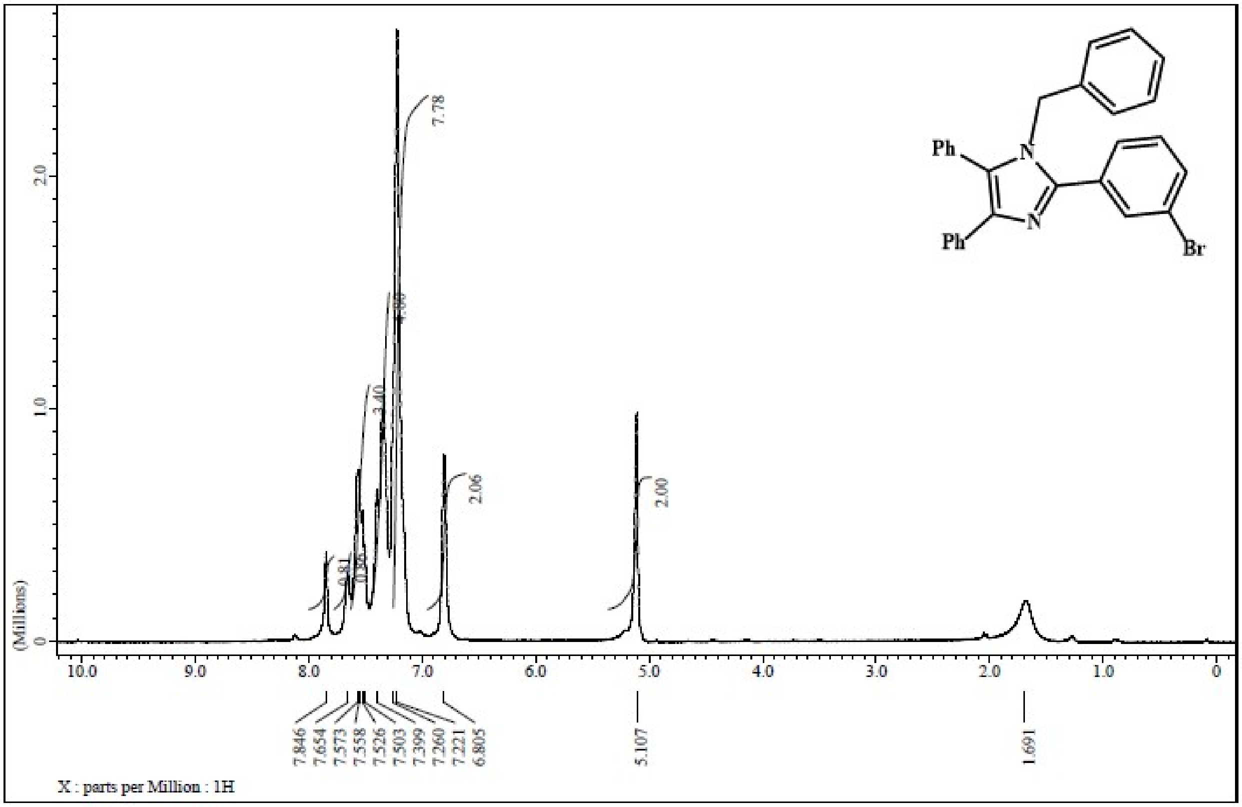
Entry 4d ^{13}C NMR spectrum of 1-benzyl-2-(4-bromophenyl)-4,5-diphenyl-1H-imidazole ($CDCl_3$) Full



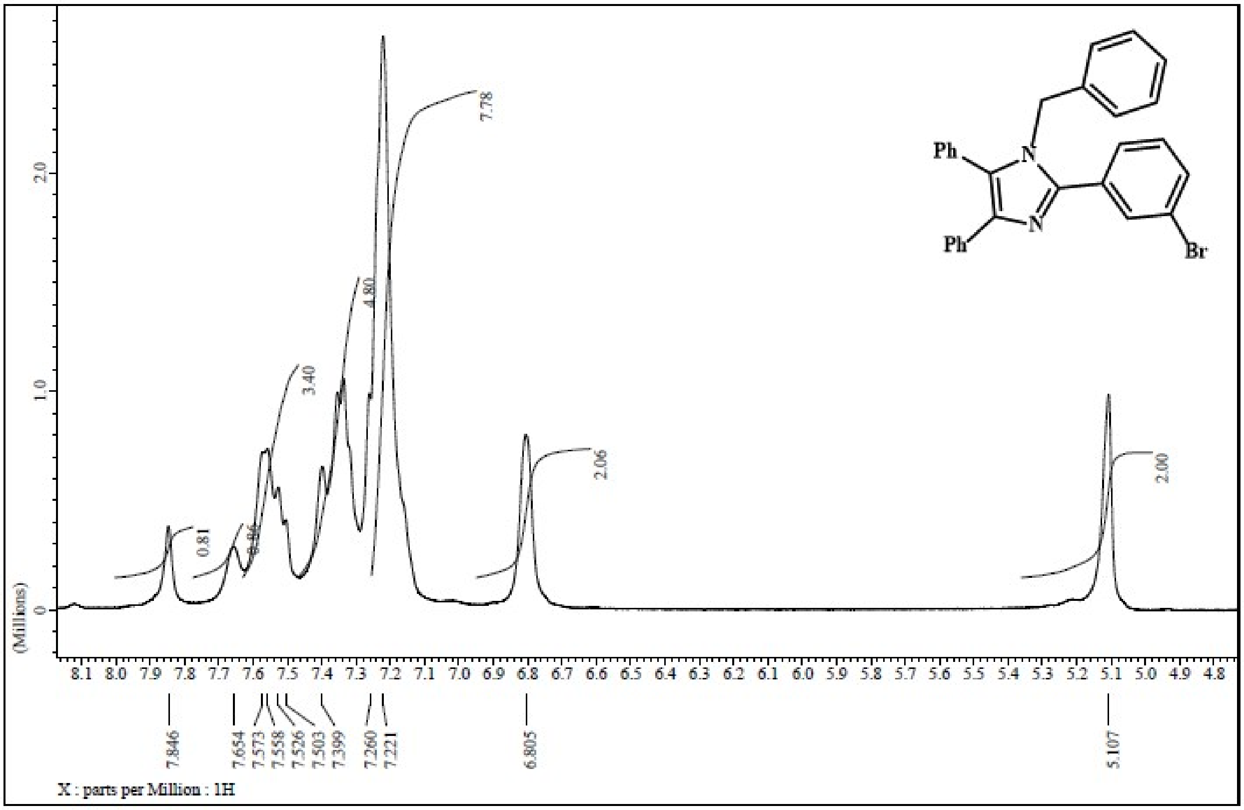
Entry 4d ^{13}C NMR spectrum of 1-benzyl-2-(4-bromophenyl)-4,5-diphenyl-1H-imidazole Expansion



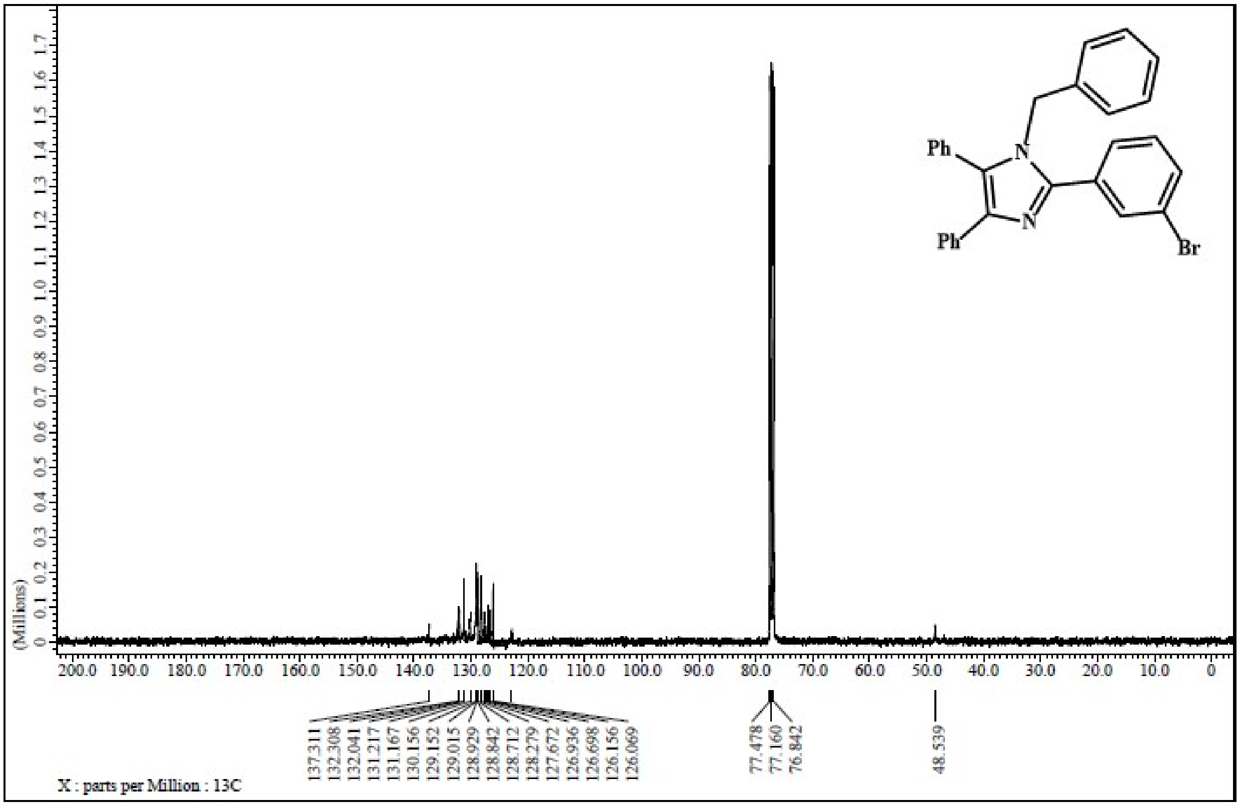
Entry 4e ^{1}H NMR spectrum of 1-benzyl-2-(3-bromophenyl)-4,5-diphenyl-1H-imidazole ($CDCl_3$) Full



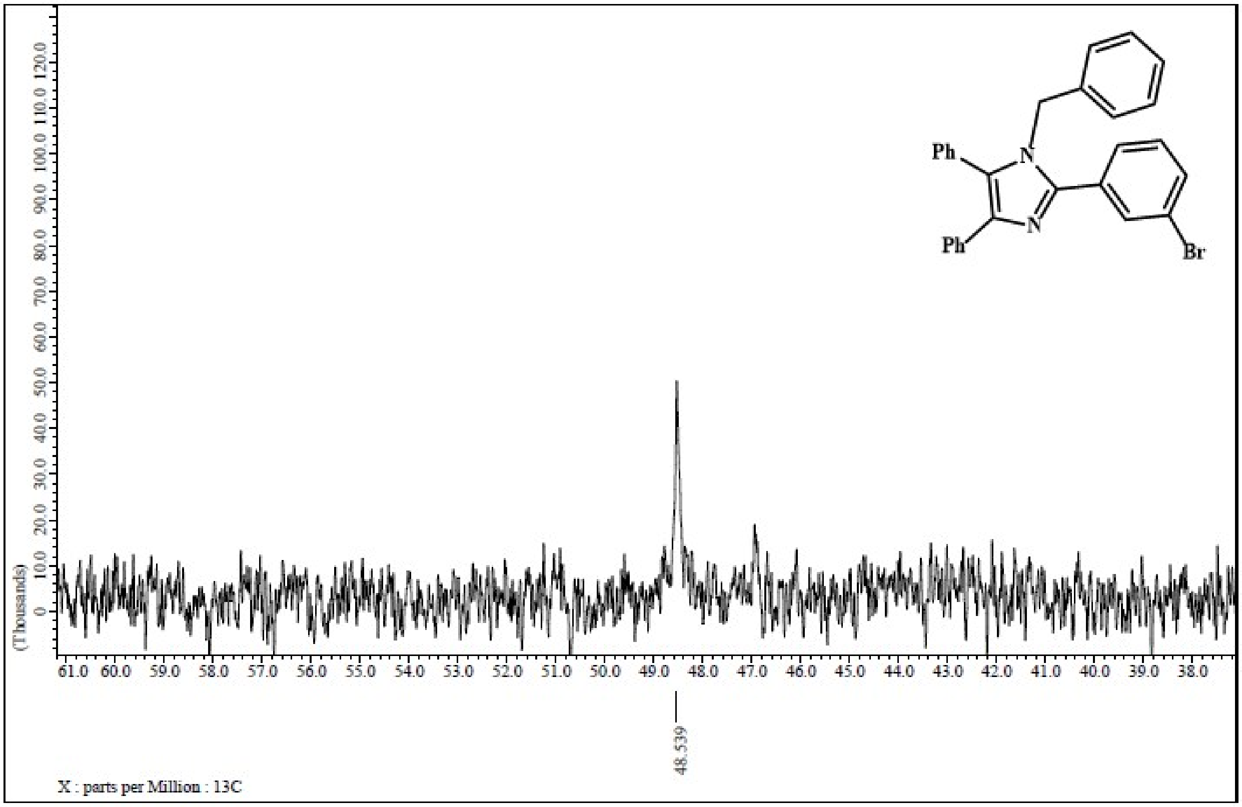
Entry 4e ^{1}H NMR spectrum of 1-benzyl-2-(3-bromophenyl)-4,5-diphenyl-1H-imidazole Expansion



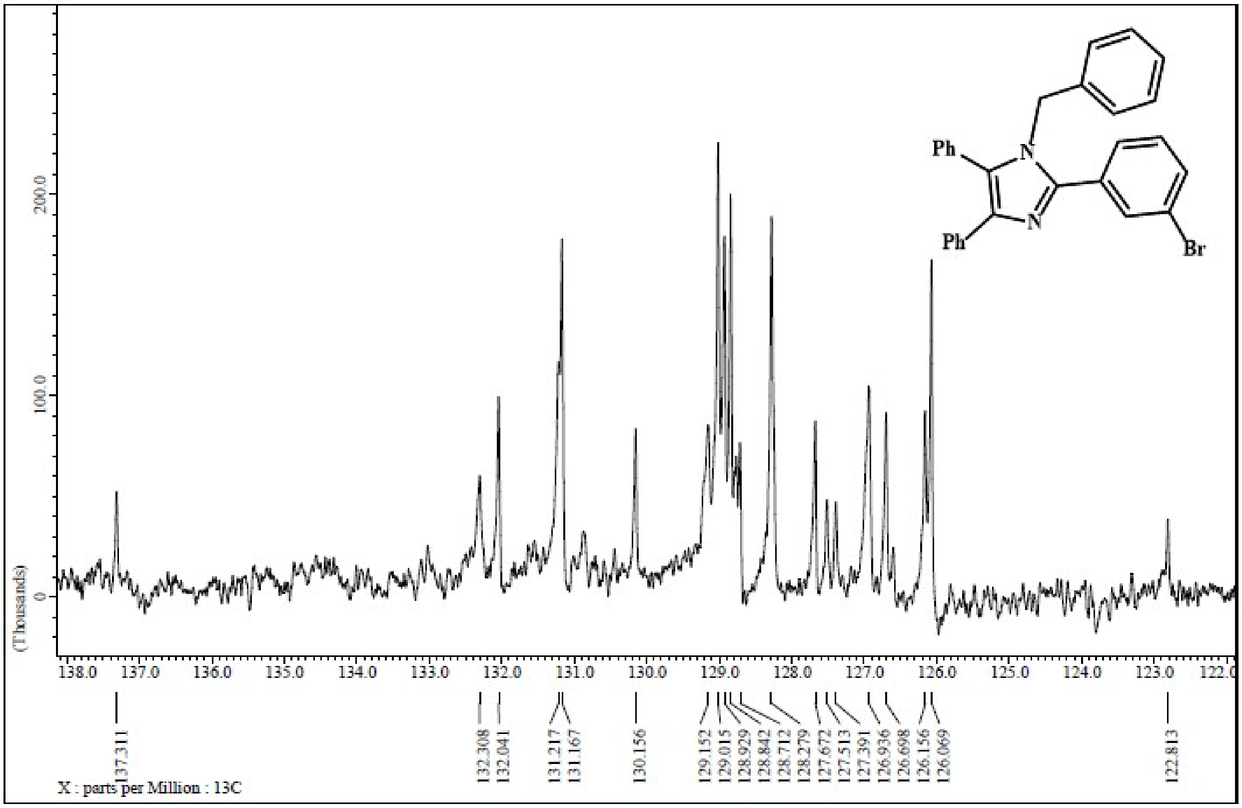
Entry 4e ^{13}C NMR spectrum of 1-benzyl-2-(3-bromophenyl)-4,5-diphenyl-1H-imidazole ($CDCl_3$) Full



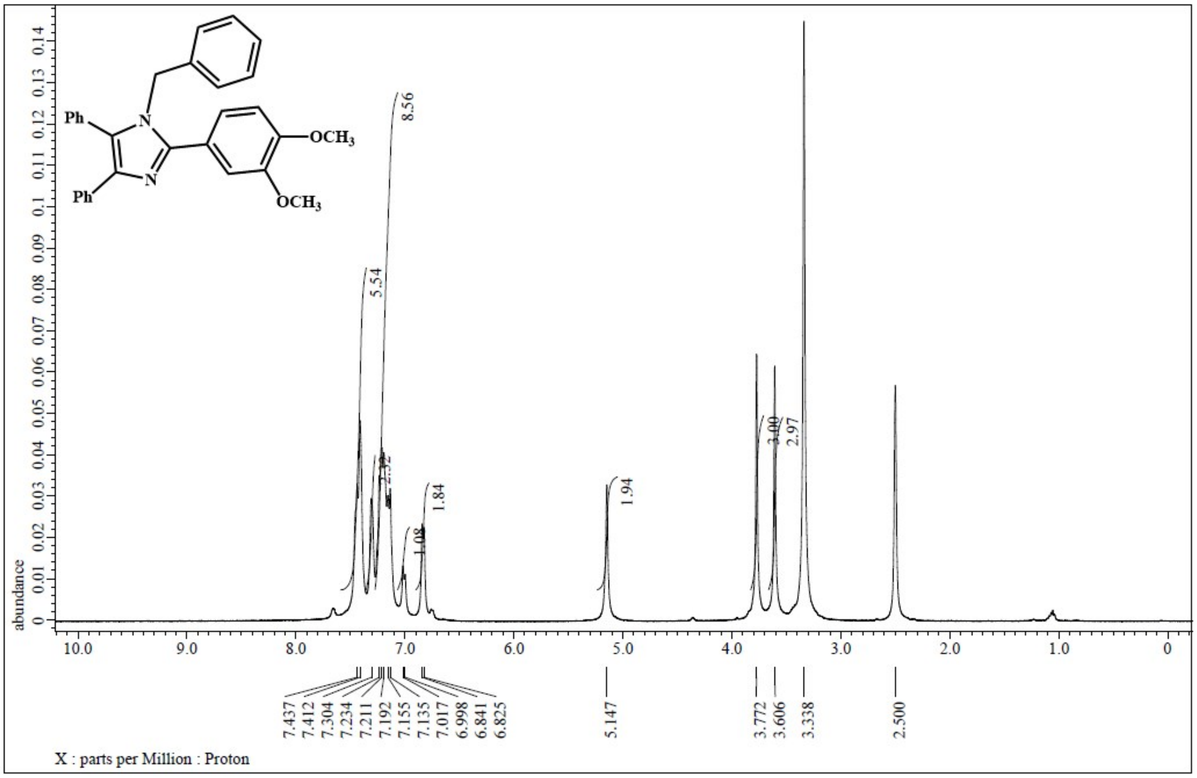
Entry 4e ^{13}C NMR spectrum of 1-benzyl-2-(3-bromophenyl)-4,5-diphenyl-1H-imidazole Expansion



Entry 4e ^{13}C NMR spectrum of 1-benzyl-2-(3-bromophenyl)-4,5-diphenyl-1H-imidazole Expansion



Entry 4f ^{1}H NMR spectrum of 1-benzyl-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$) Full



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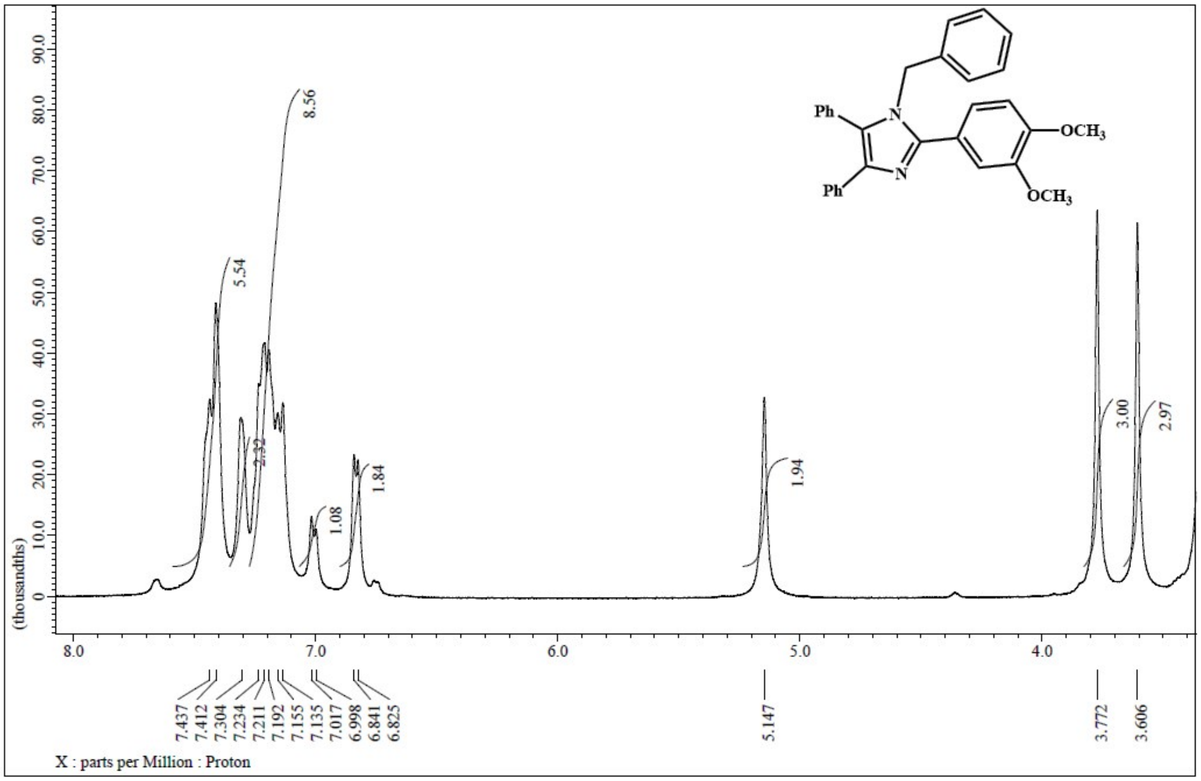
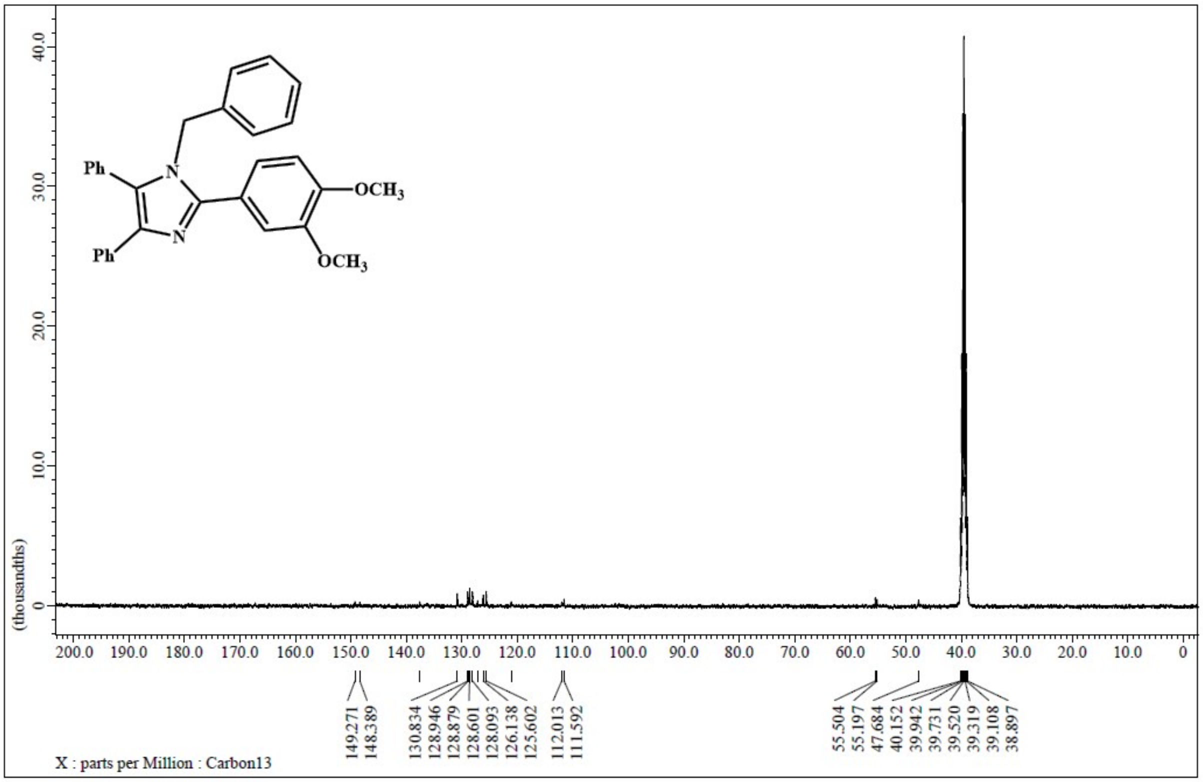
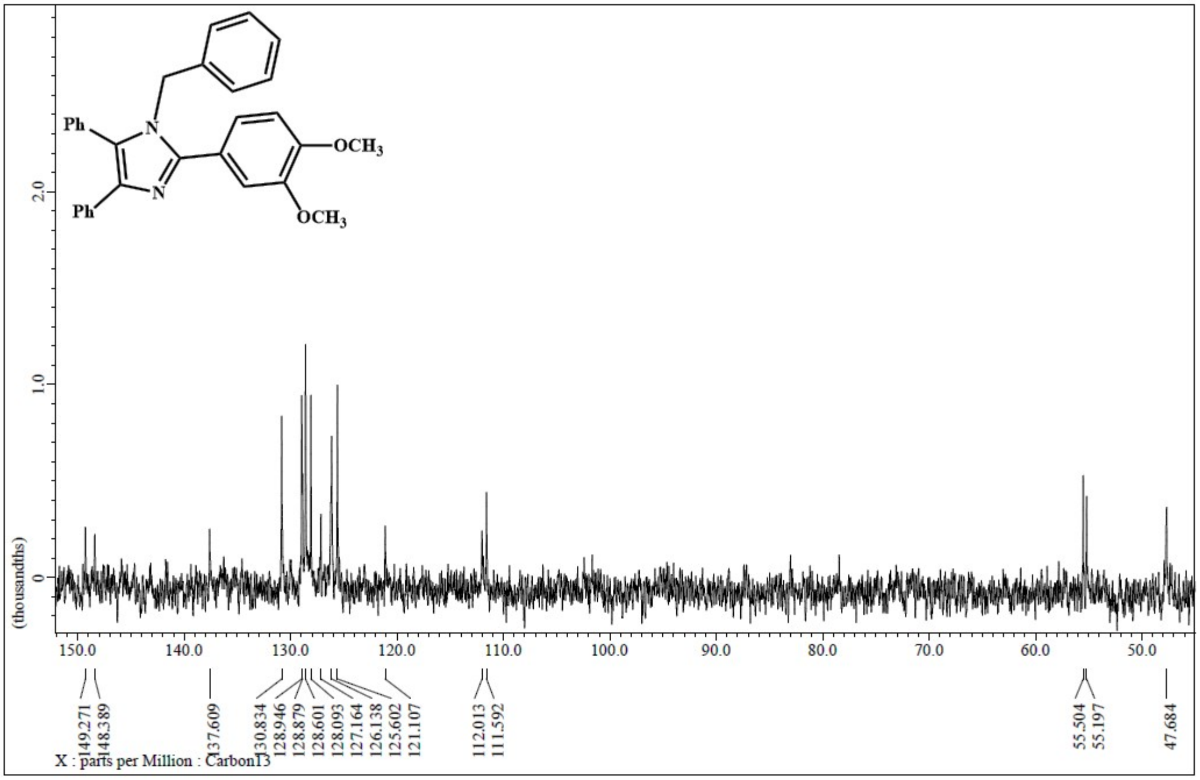


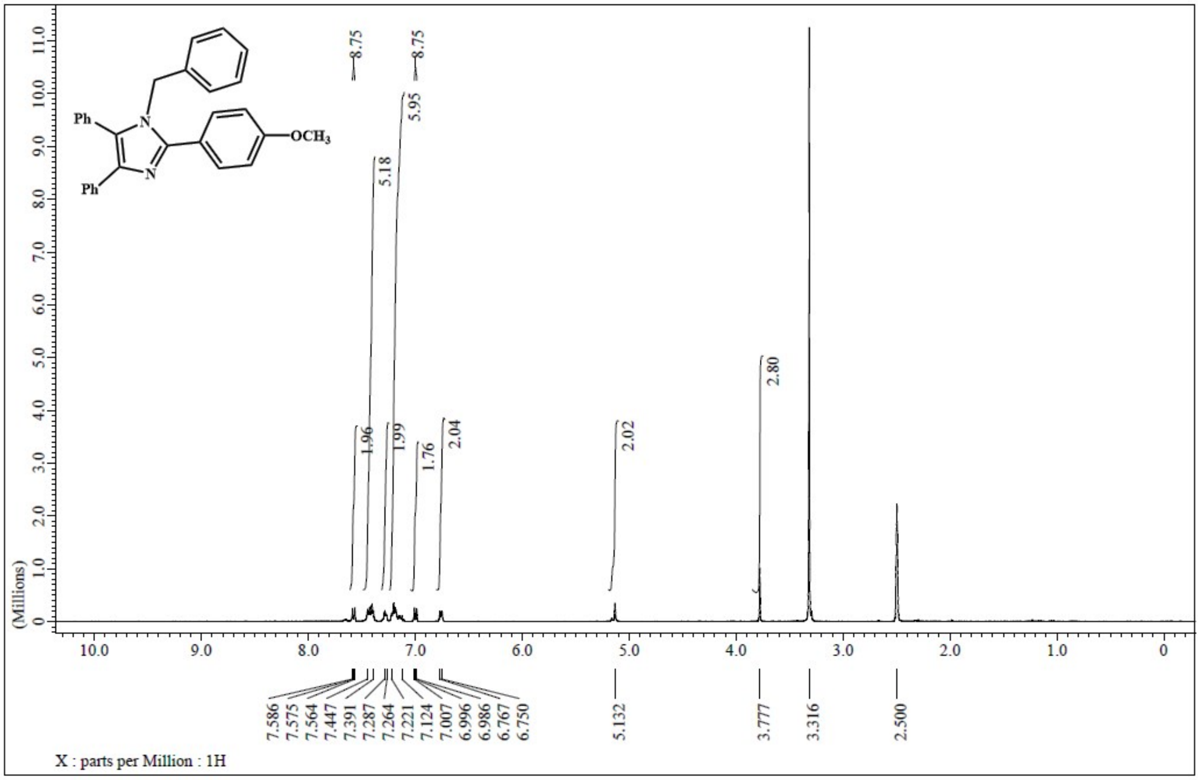
Entry 4f ^{13}C NMR spectrum of 1-benzyl-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (DMSO-d$_6$) Full



Entry 4f ^{13}C NMR spectrum of 1-benzyl-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole Expansion

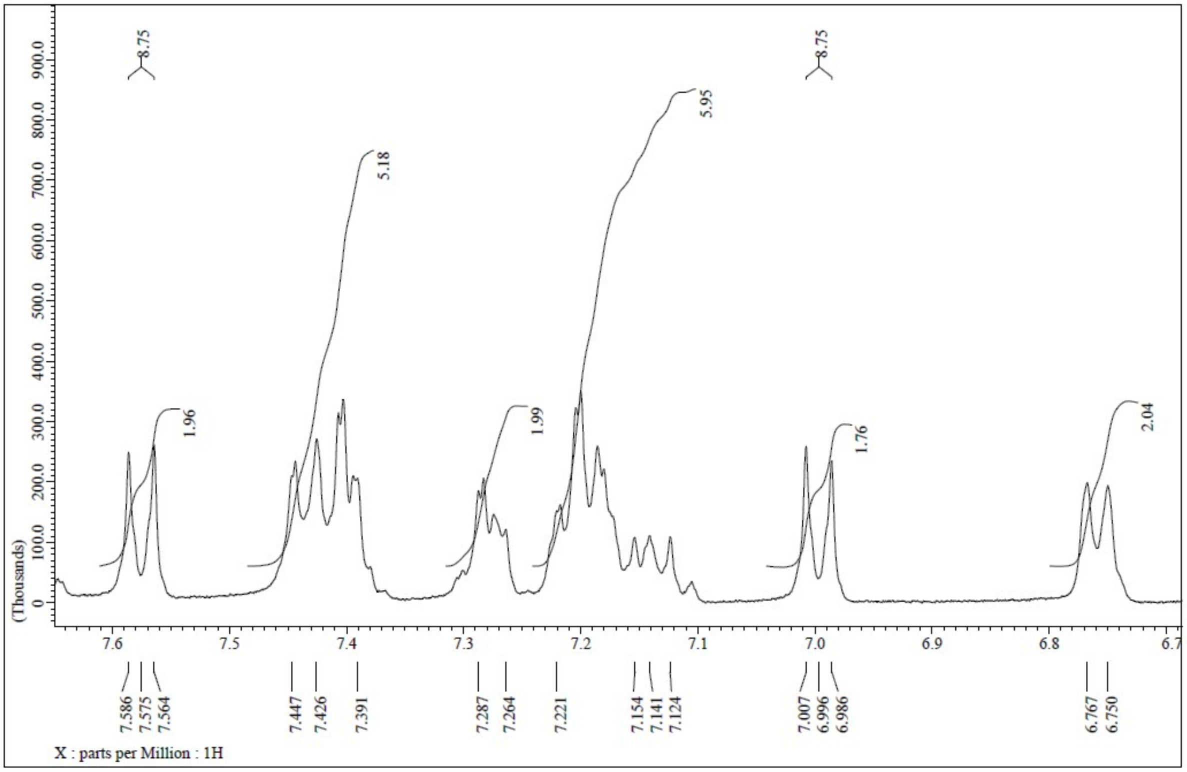


Entry 4g ^{1}H NMR spectrum of 1-benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole ($DMSO-d_6$) Full



Entry 4g ^{1}H NMR spectrum of 1-benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole

Expansion



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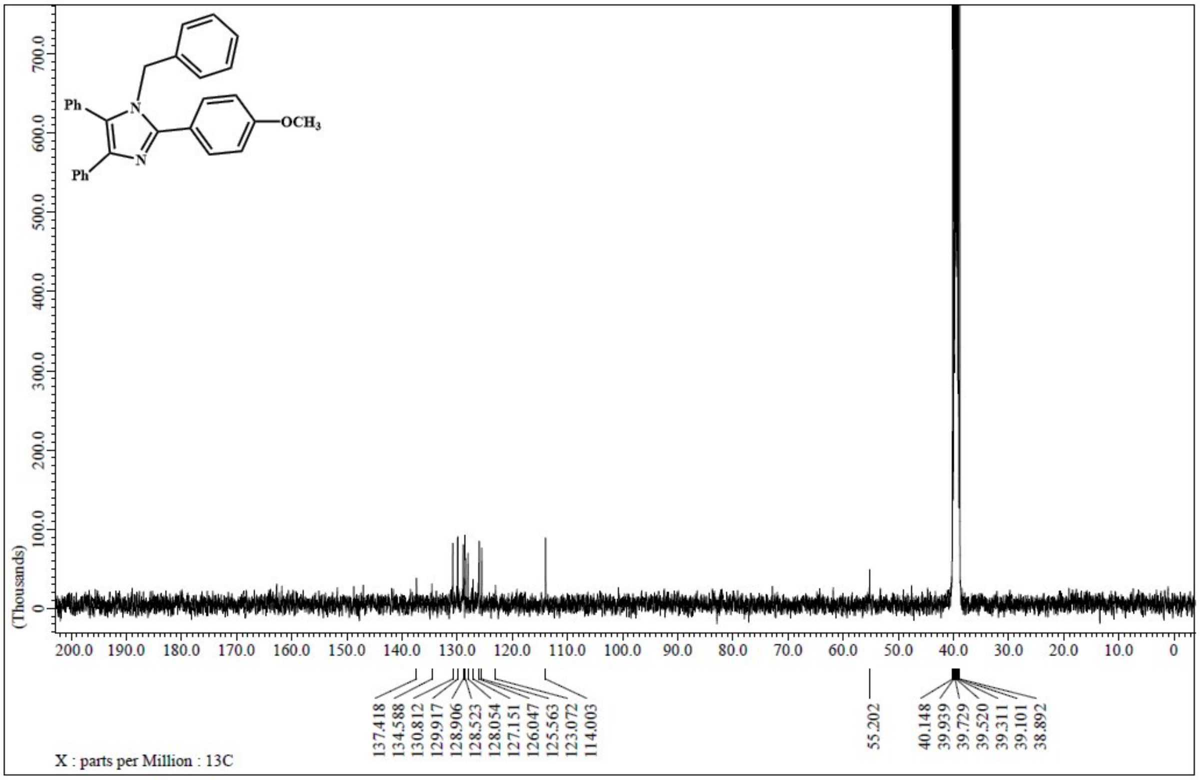

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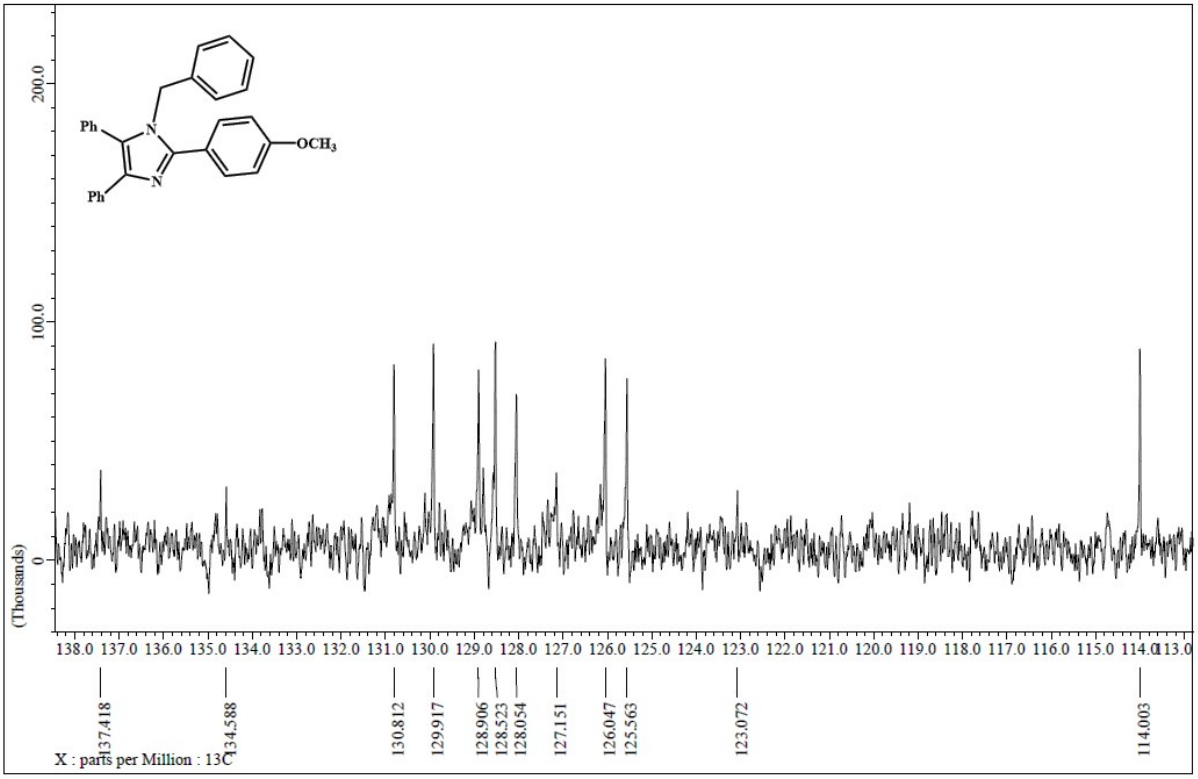

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