Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis, Characterization of Bridged Bis(amidinates) Lanthanide Amides and Their Application as Catalysts for Addition of Amines to Nitriles to Monosubstituted *N*-Arylamidines

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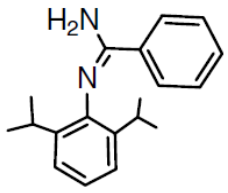
Supporting material

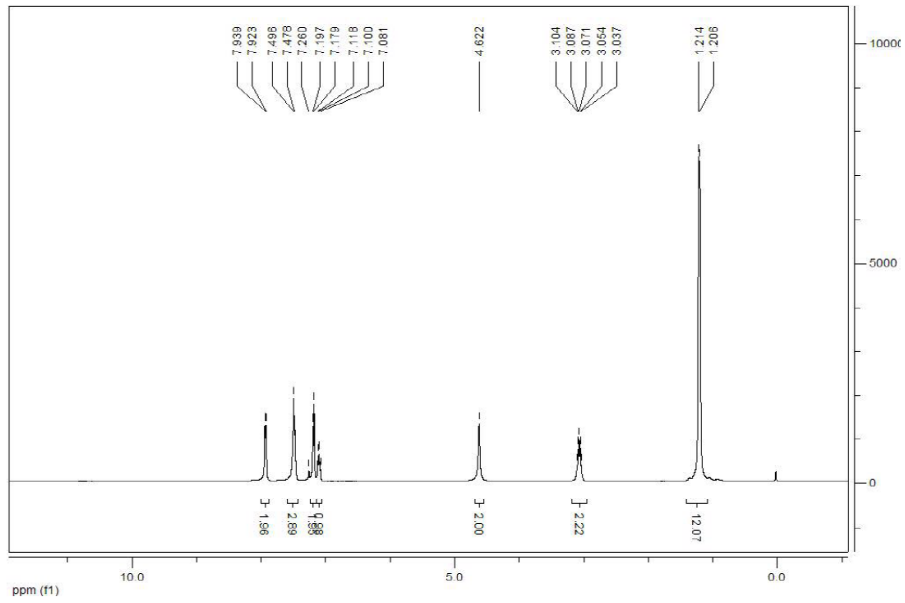
All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. All nitriles and amines were pre-dried, sublimed, recrystallized or redistilled before use. The IR spectra were recorded on a Magna-IR 550 spectrometer. Melting points were determined in sealed Ar-filled capillary tube, and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument.

Procedures: General procedure for the synthesis of amidines from reaction of amines with nitriles catalyzed by amide 1-7 and 9-10 (Table 3, entry 5 as an Example). A 30 mL of Schlenk tube under dried argon was charged with **5** (65 mg, 0.075 mmol). To the flask were added the benzonitrile (0.15 ml, 1.50 mmol), 2,6-diisopropylaniline (0.53 g, 3.00 mmol). The resulting mixture was stirred at 100 °C for 24 h. The product was isolated by distilling the reaction mixture under vacuum to remove unreacted starting materials. The residue was recrystallized from hexane to give compound in 90% yield.

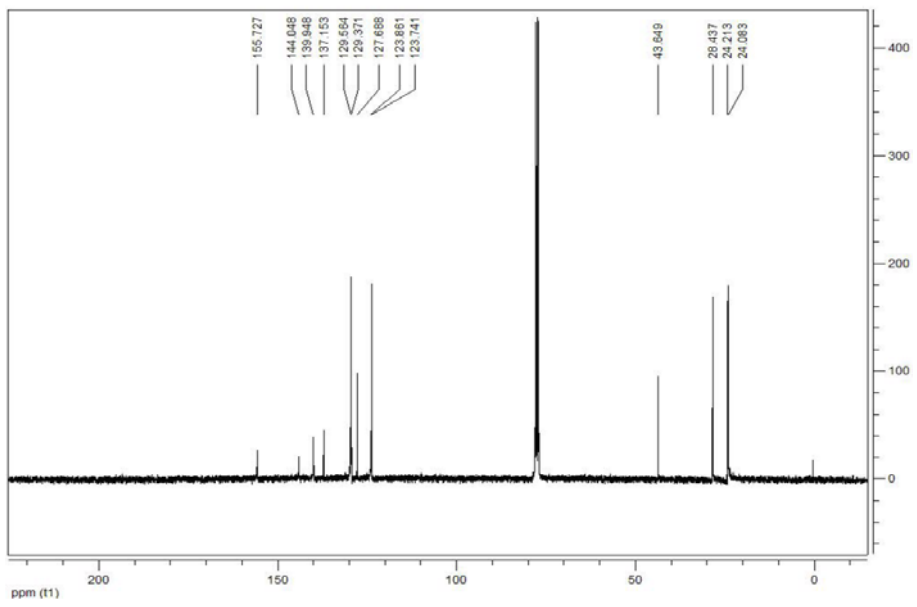
Analytical data: N'-(2,6-diisopropylphenyl)benamidine Compound was obtained following the procedure catalyzed by catalysts **1-7** and **9,** isolated as a white solid in 76, 86, 78, 72, 90, 65, 56 and 92% yields, respectively. Known compound.[] ^{1}H NMR ($CDCl_3$): δ = 7.92-7.94 (2H), 7.48-7.50 (3H), 7.18-7.20 (2H), 7.08-7.12 (1H), 4.62 (2H), 3.04-3.10 (2H), 1.21 (12H). ^{13}C NMR ($CDCl_3$): δ = 155.73, 144.05, 139.95, 137.15, 129.56, 129.37, 127.69, 123.86, 123.74, 43.65, 28.44, 24.21, 24.08.



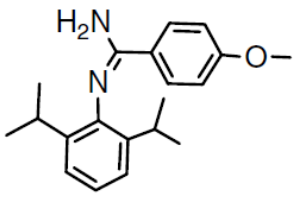
^{1}H NMR



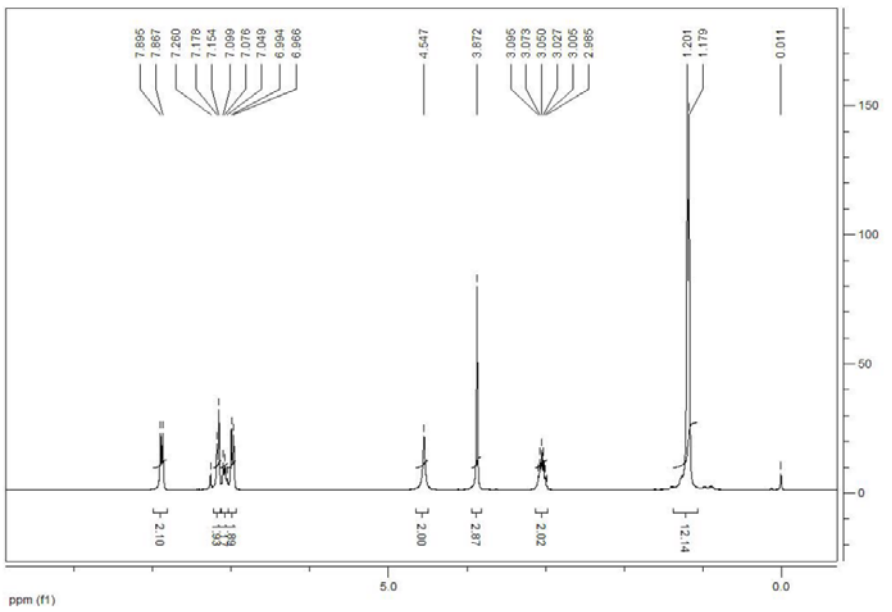
^{13}C NMR



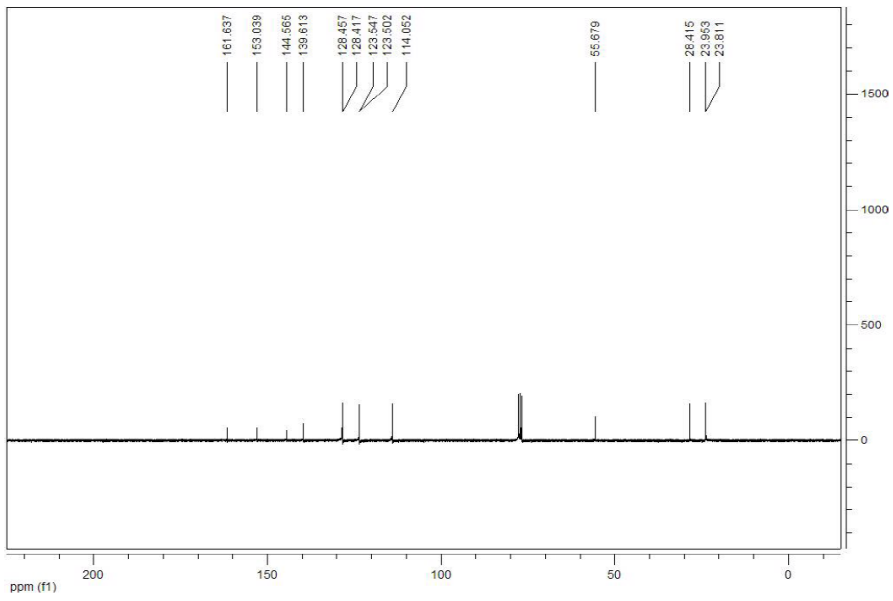
N'-(2,6-diisopropylphenyl)-4-methoxybenamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 93% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 7.87-7.90 (2H), 7.15-7.18 (2H), 7.08-7.10 (1H), 6.97-6.99(2H), 4.55 (2H), 3.87 (3H), 2.99-3.10 (2H), 1.18-1.20 (12H). ^{13}C NMR ($CDCl_3$): δ = 161.64, 153.04, 144.57, 139.61, 128.46, 128.42, 123.55, 123.50, 114.05, 55.68, 28.42, 23.95, 23.81.



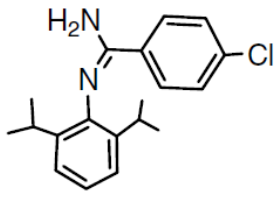
^{1}H NMR



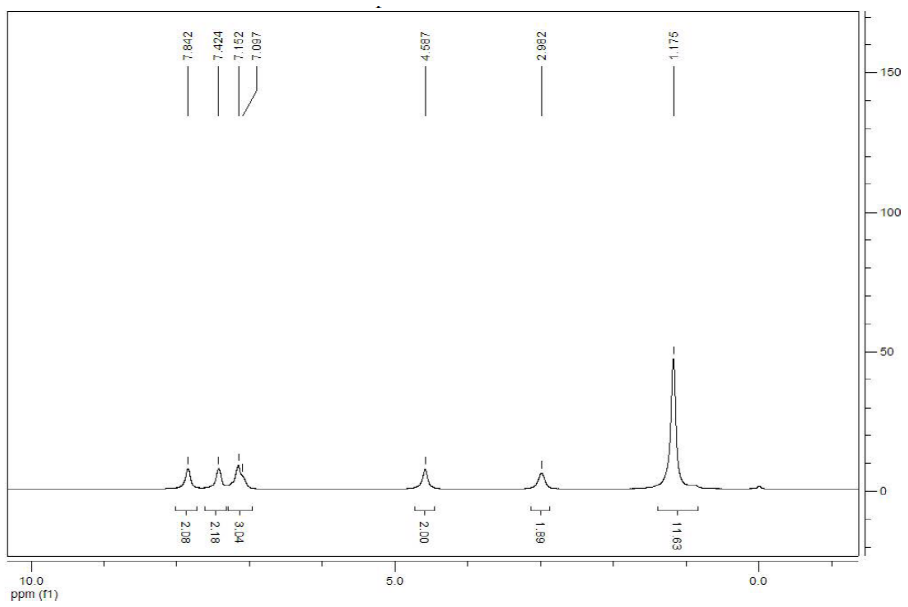
^{13}C NMR



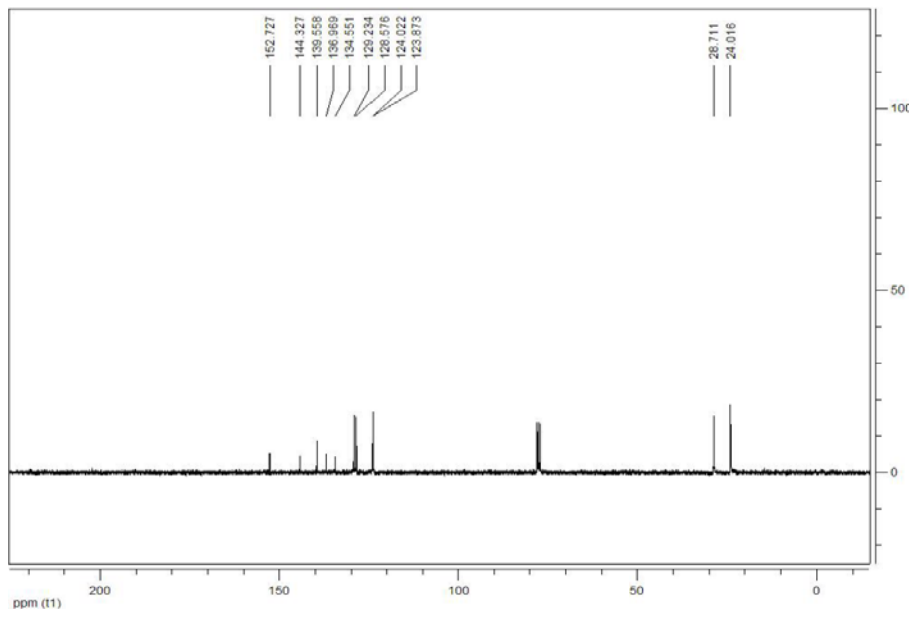
4-cloro-N' -(2,6-diisopropylphenyl)benamidine Compound was obtained following the procedure catalyzed by amides **5** and isolated as white solid in 86% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 7.84 (2H), 7.42 (2H), 7.10-7.15 (3H), 4.59 (2H), 2.98 (2H), 1.18 (12H). ^{13}C NMR ($CDCl_3$): δ = 152.73, 144.33, 139.56, 136.97, 134.55, 129.23, 128.58, 124.02, 123.87, 28.71, 24.02.



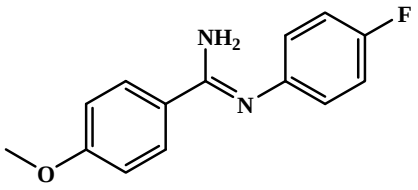
^{1}H NMR



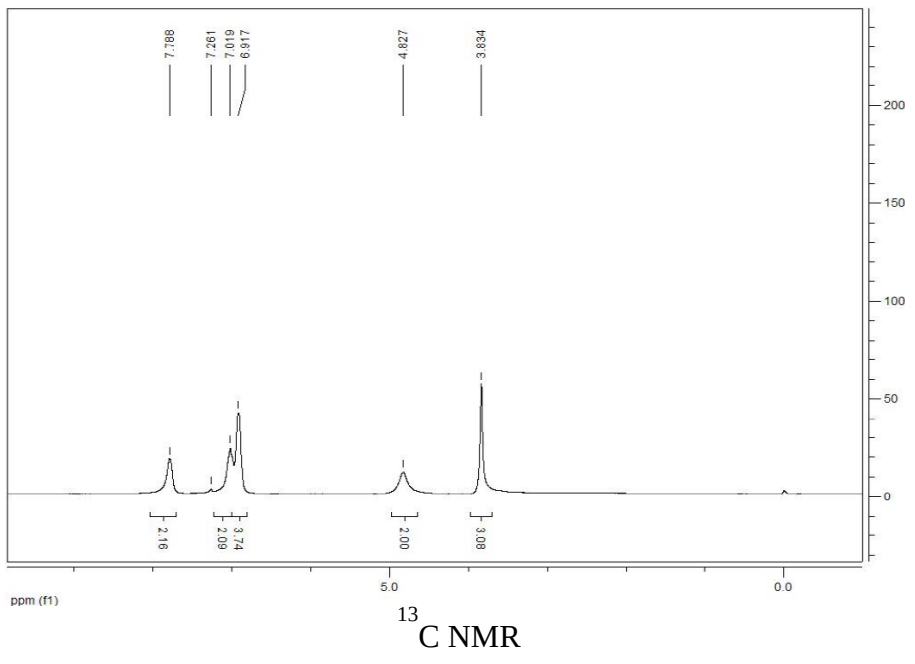
^{13}C NMR



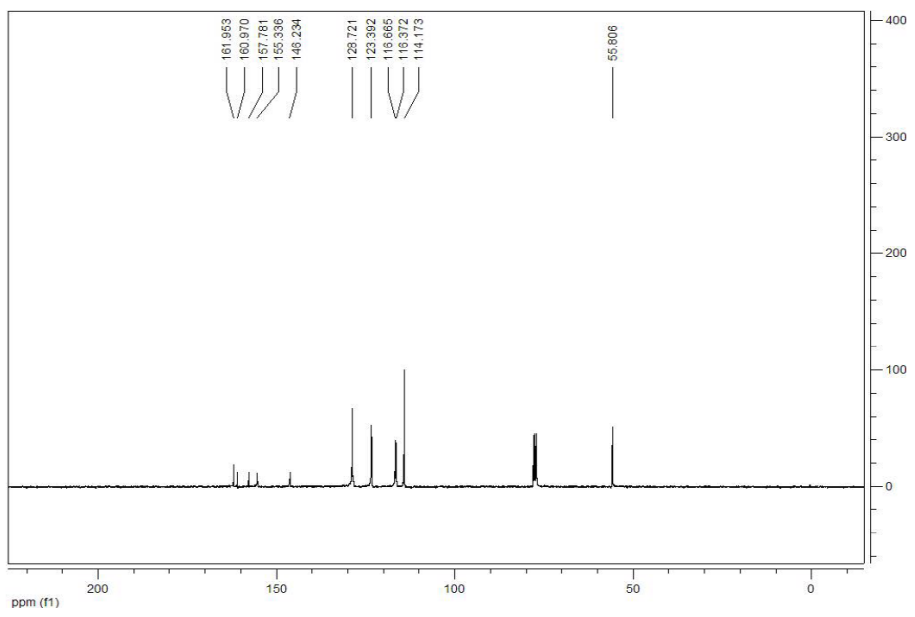
N'-(4-flurophenyl)-4-methoxylbenamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 98% yield. Known compound.[1] ^{1}HNMR ($CDCl_3$): δ = 7.79 (2H), 7.02 (2H), 6.92 (4H), 4.83 (2H), 3.83 (3H). ^{13}C NMR ($CDCl_3$): δ = 161.95, 160.97, 157.78, 155.34, 146.23, 128.72, 123.39, 116.67, 116.37, 114.17, 55.81.



^{1}H NMR



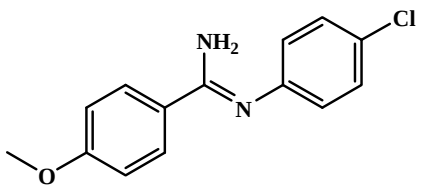
^{13}C NMR



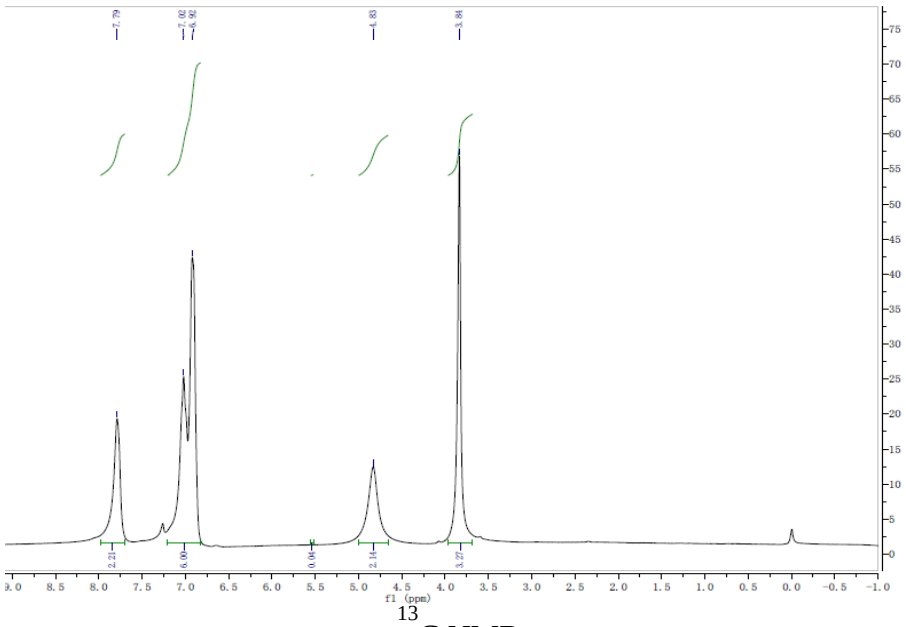
N'-(4-clorophenyl)-4-methoxylbenamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 93% yield.

Mp: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (2H), 7.46 – 7.38 (3H), 7.20 (2H), 6.98 (2H), 4.74 (3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 161.26, 160.28, 157.09, 154.60, 145.53, 127.71, 122.70, 115.98, 115.68, 113.49, 55.12. Anal. Calcd for

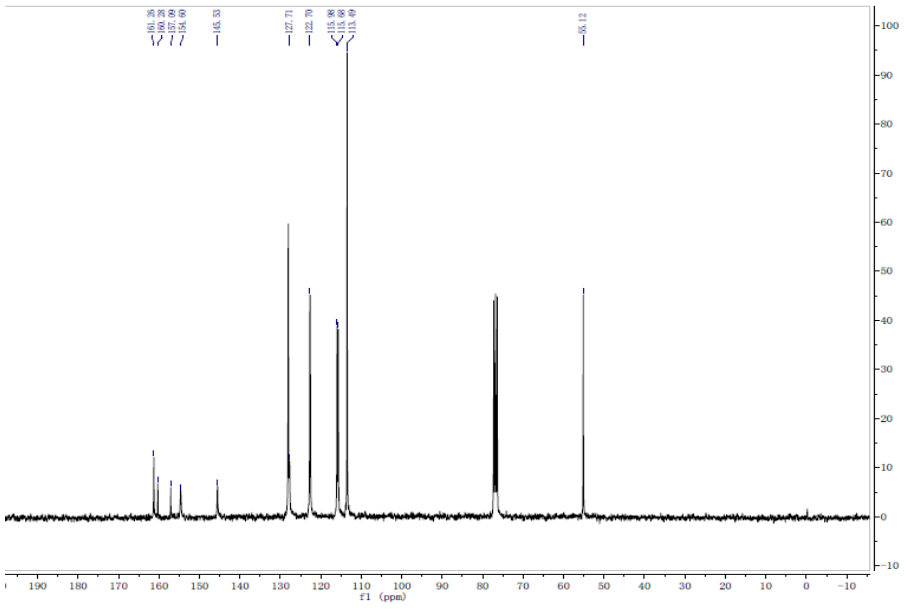
$C_{14}H_{13}ClN_2O$ (260.07): C, 64.49; H, 5.03; N, 10.74. Found: C,64.35; H, 4.92; N, 10.51.



^{1}H NMR

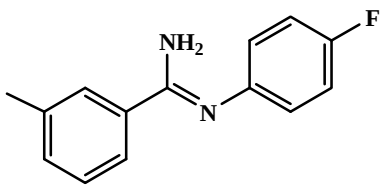


^{13}C NMR

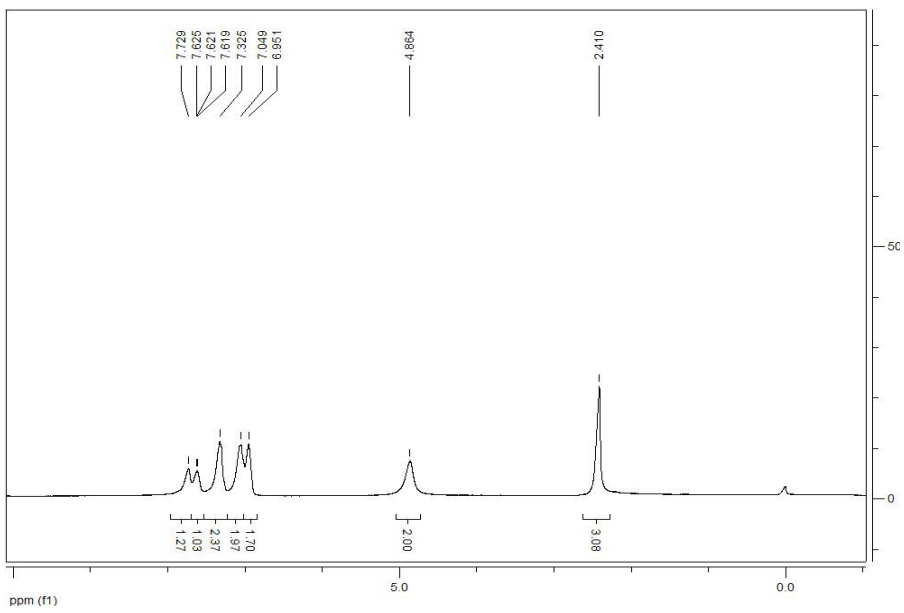


N'-(4-flurophenyl)-3-methylbenamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 96% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 7.73 (1H), 7.62-7.63 (1H), 7.33 (2H), 7.04 (2H),

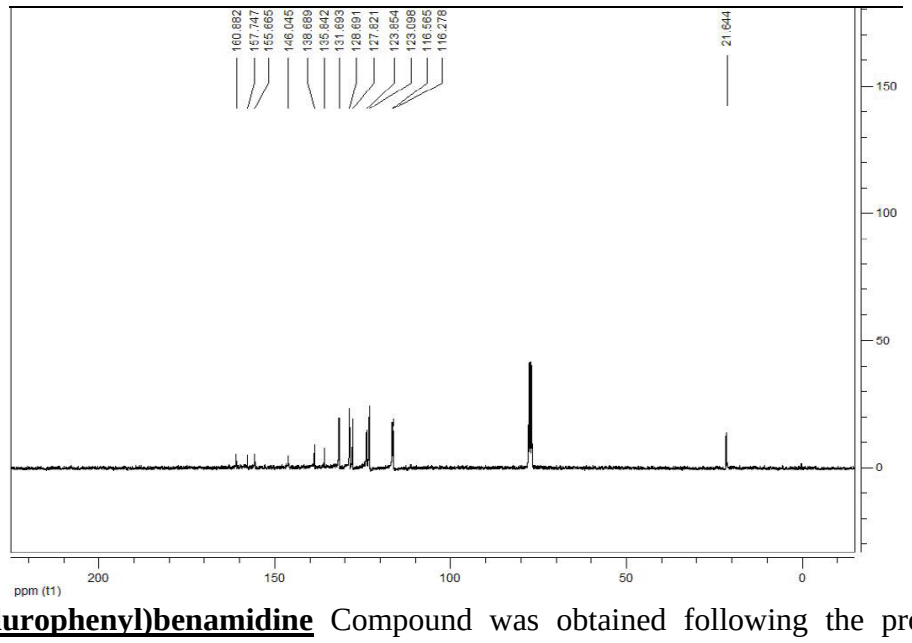
6.95 (2H), 4.86 (2H), 2.41 (3H). ^{13}C NMR (CDCl3): δ = 160.88, 157.75, 155.67, 146.05, 138.69, 135.84, 131.69, 128.69, 127.82, 123.85, 123.10, 116.57, 116.28, 21.64.



^{1}H NMR

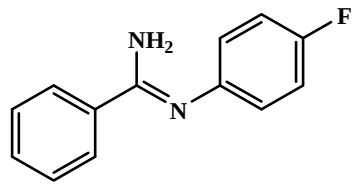


^{13}C NMR

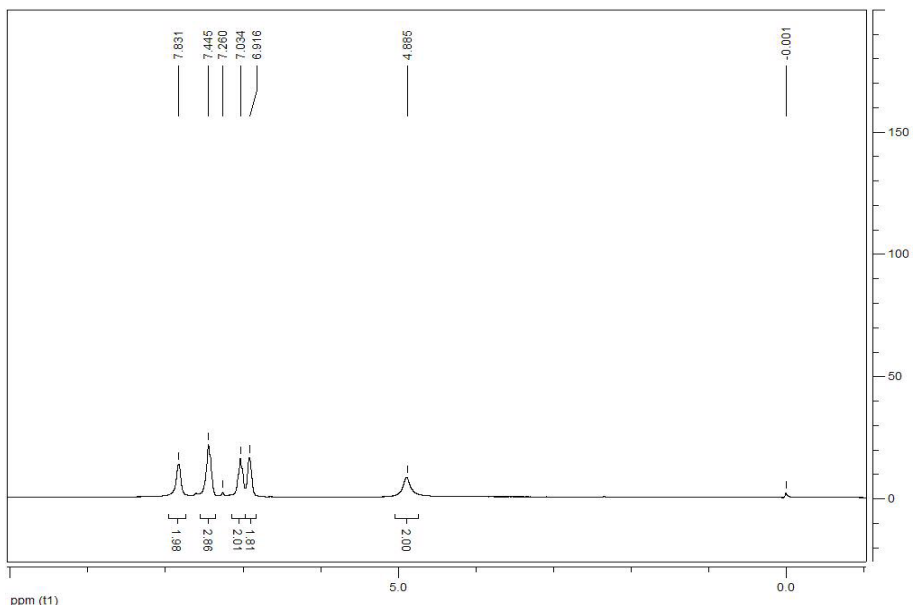


N'-(4-flurophenyl)benamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 98% yield. Known compound.[1] ^{1}HNMR ($CDCl_3$): δ = 7.83 (2H), 7.45 (3H), 7.03 (2H), 6.92 (2H), 4.89 (2H). ^{13}C NMR ($CDCl_3$): δ = 161.04, 157.84, 155.72, 146.06, 136.06, 131.07, 128.97,

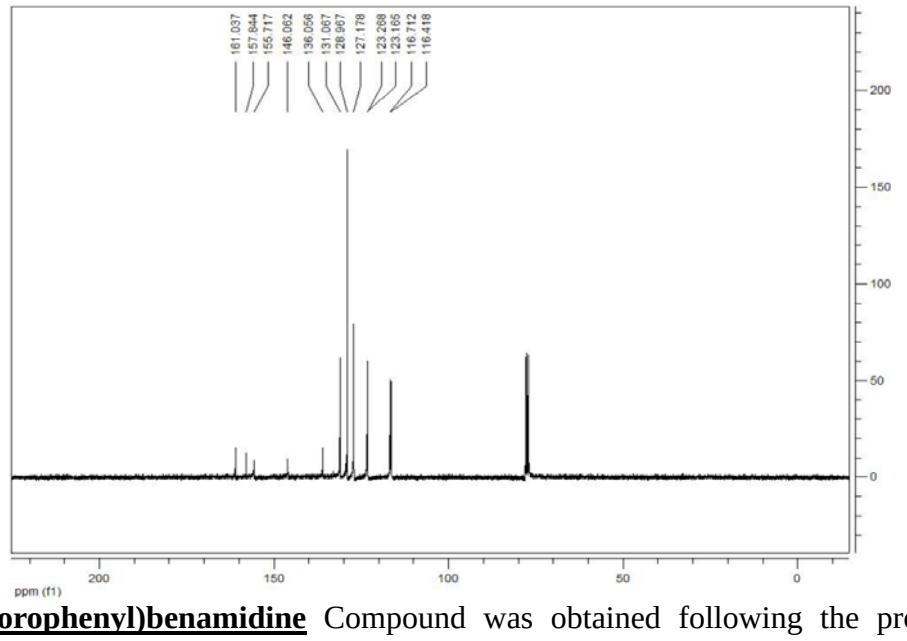
127.18, 123.27, 123.17, 116.71, 116.42.



^{1}H NMR

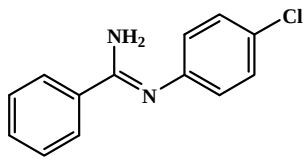


^{13}C NMR

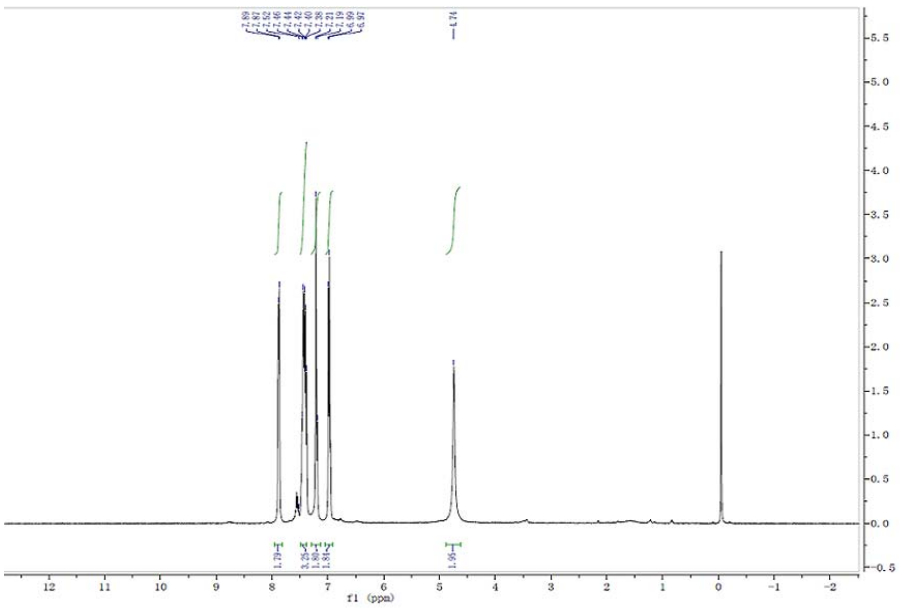


N'-(4-clorophenyl)benamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 96% yield. Mp: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (2H), 7.46 – 7.38 (3H), 7.20 (2H), 6.98 (2H), 4.74 (2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 164.20, 136.77, 133.11, 131.46, 130.80, 129.53, 129.22, 128.39, 127.52, 124.63, 123.81. Anal. Calcd for $C_{13}H_{11}ClN_2$ (230.06):

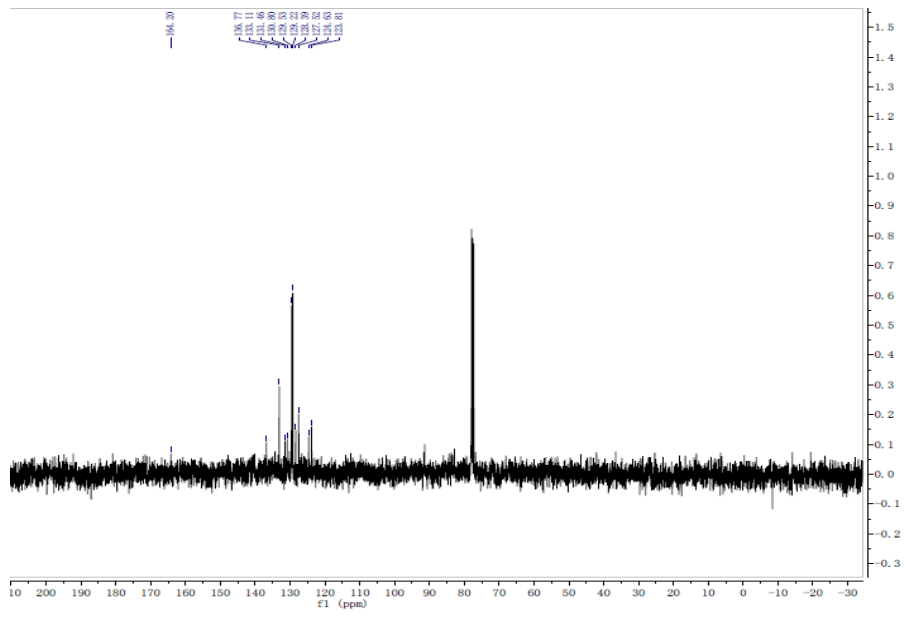
C, 67.68; H, 4.81; N, 12.14 Found: C,68.17; H, 4.79; N, 12.31.



^{1}H NMR

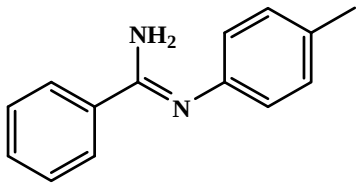


^{13}C NMR

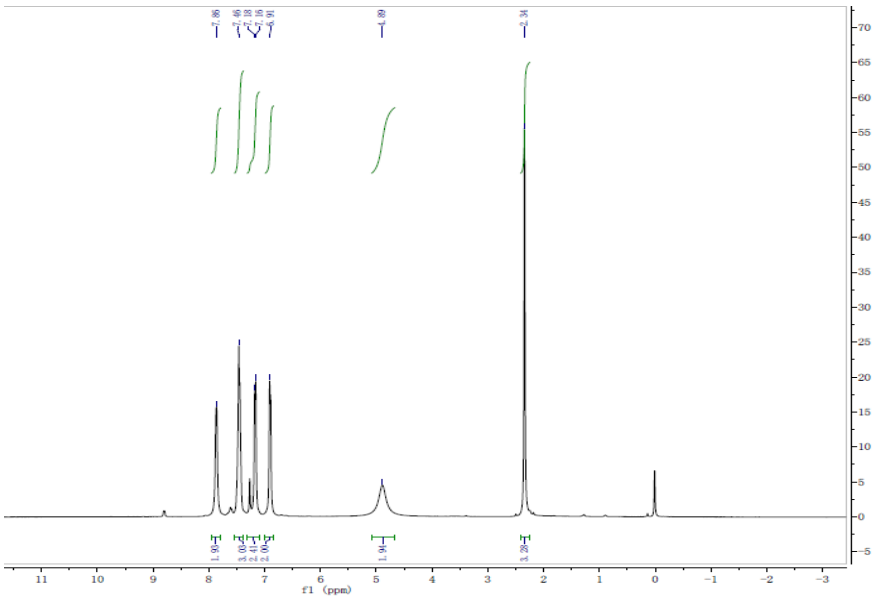


N'-(4-methyphenyl)benamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 94% yield. Mp: 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (2H), 7.45 (3H), 7.32 – 7.09 (2H), 6.90 (2H),

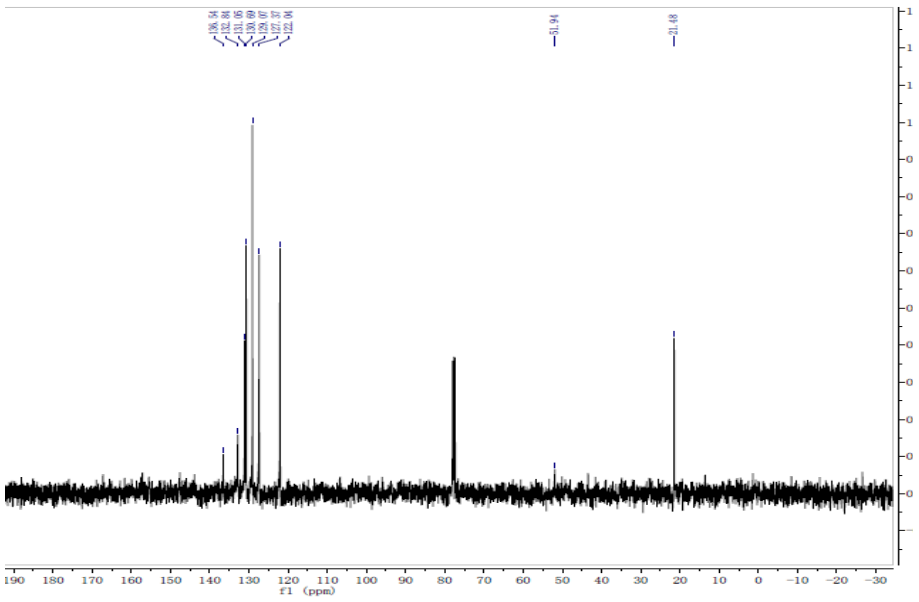
4.89 (2H), 2.34 (3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 136.54, 132.84, 131.05, 130.69, 129.07, 127.37, 122.04, 51.94, 21.48. Anal. Calcd for $C_{14}H_{14}N_2$ (210.12): C, 79.97; H, 6.71; N, 13.32. Found: C,79.39; H, 6.25; N, 13.34.



^{1}H NMR

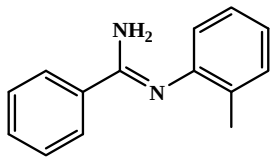


^{13}C NMR

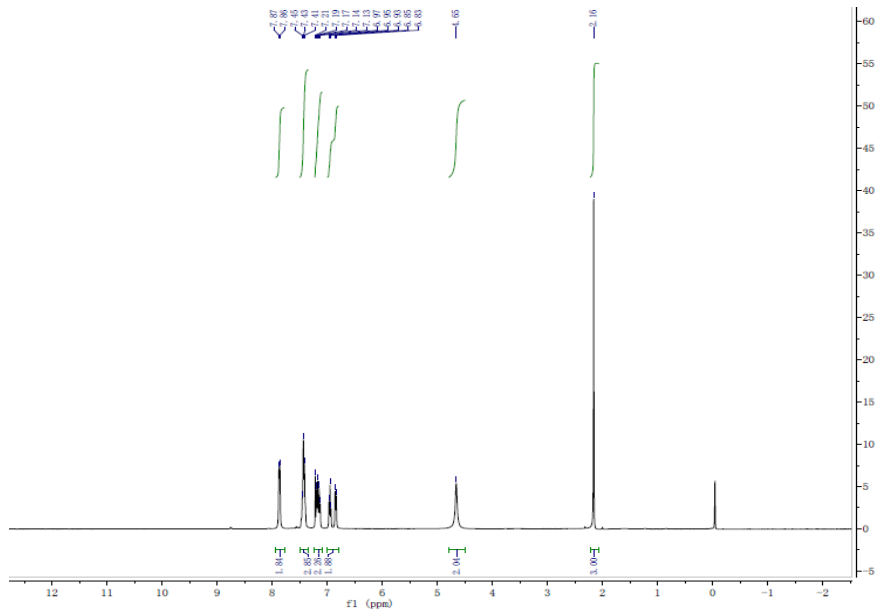


N'-(2-methyphenyl)benamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 93% yield. Mp: 126-128 °C.

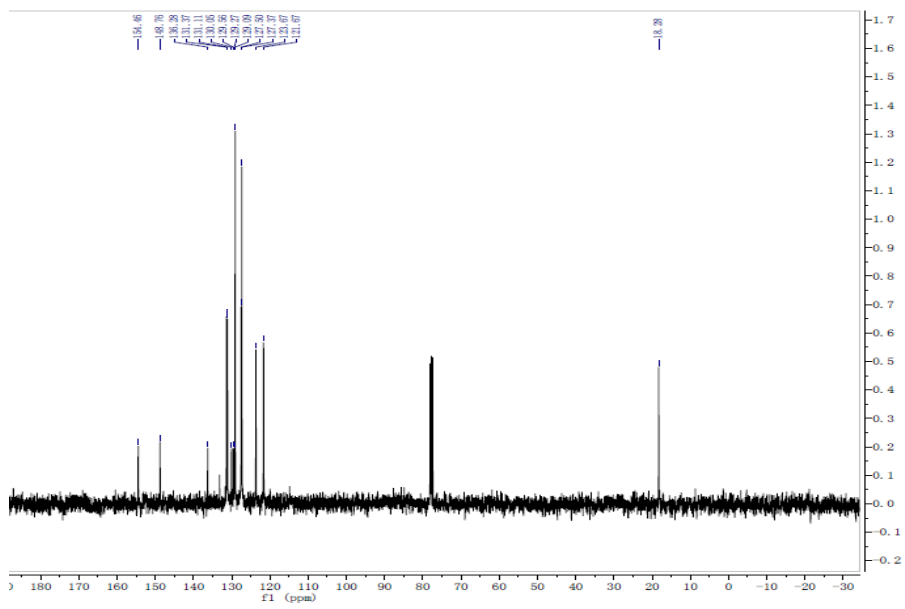
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (2H), 7.43 (3H), 7.23 – 7.09 (2H), 6.99 – 6.79 (2H), 4.65 (2H), 2.16 (3H). ^{13}C NMR (400 MHz,) δ = 154.46, 148.76, 136.28, 131.37, 131.11, 130.05, 129.56, 129.27, 129.09, 127.50, 127.37, 123.67, 121.67, 18.28. Anal. Calcd for $C_{14}H_{14}N_2$ (210.12): C, 79.97; H, 6.71; N, 13.32. Found: C,79.84; H, 6.58; N, 13.52.



^{1}H NMR

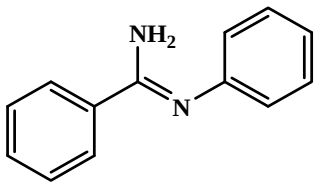


^{13}C NMR

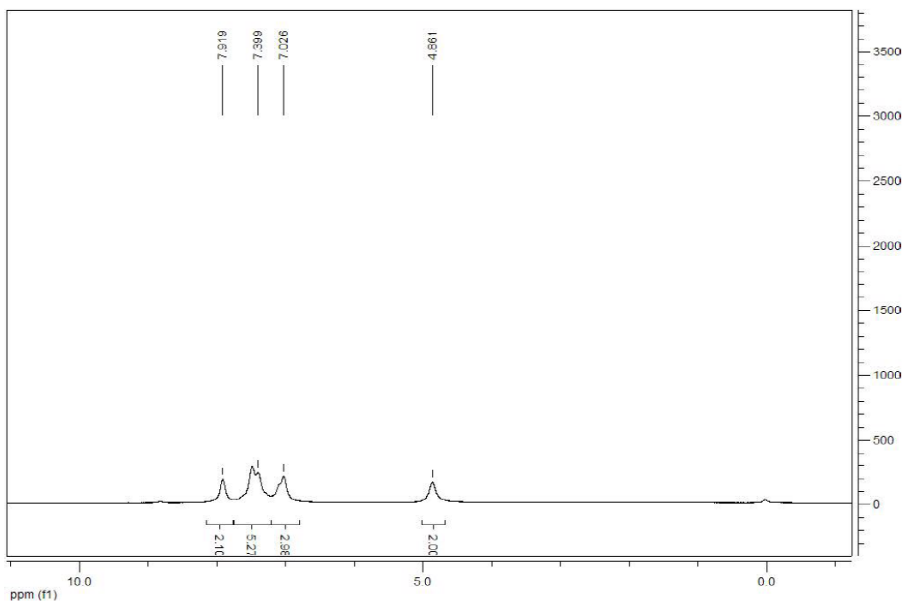


N'-Phenyl-benzamidine Compound was obtained following the above procedure

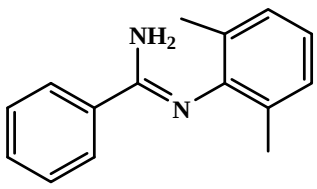
catalyzed by catalyst **5** and isolated as a white solid in a 95% yield. Known compound.[2] Mp: 114-115 °C (lit[]115°C). ^{1}HNMR ($CDCl_3$): δ = 7.92 (2H), 7.40 (5H), 7.02 (3H), 4.86 (2H).



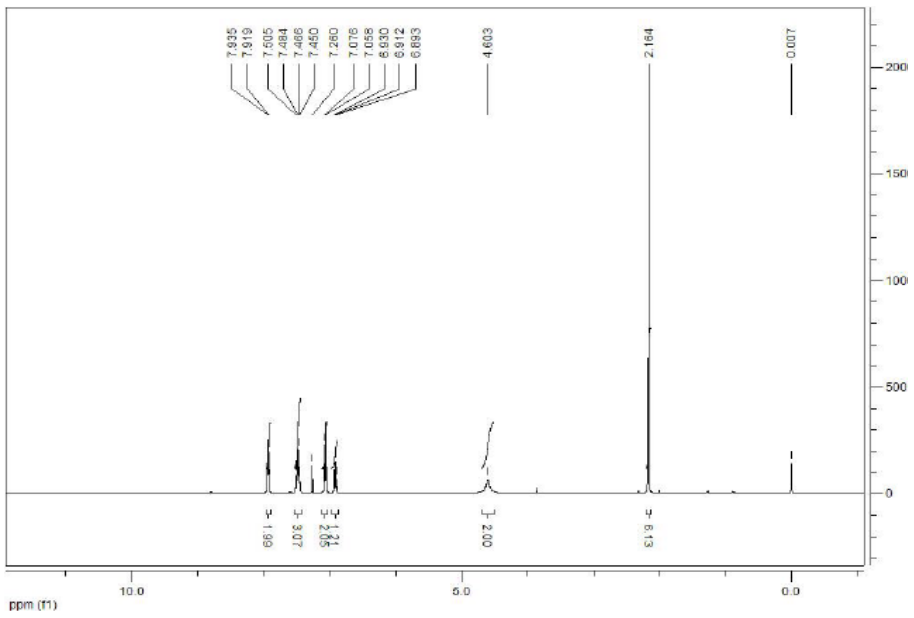
^{1}H NMR



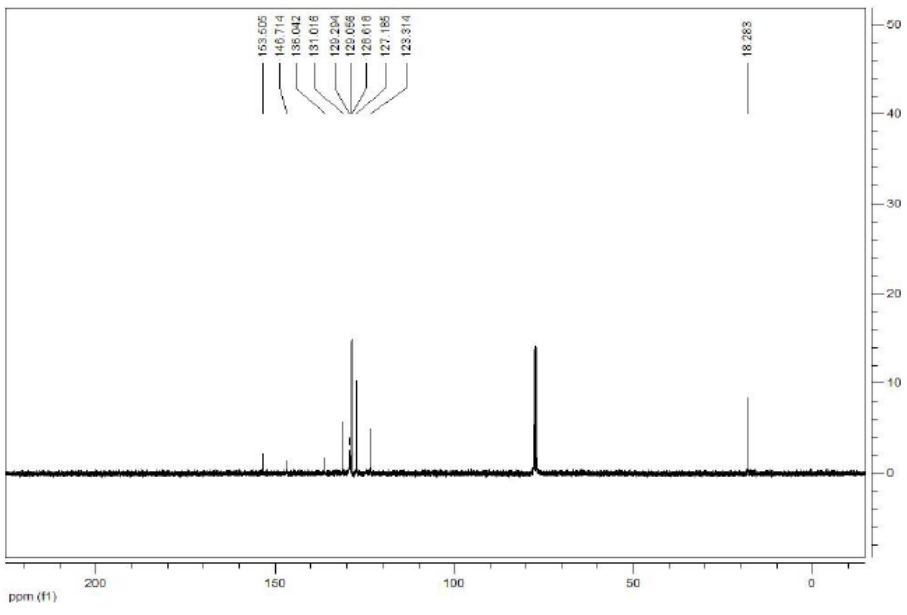
N'-(2,6-dimethylphenyl)benamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 92% yield. Known compound.[3] Mp: 104-106 °C (lit.[] 102-105). ^{1}H NMR ($CDCl_3$): δ = 7.92-7.94 (2H), 7.45-7.51 (3H), 7.06-7.08 (2H), 6.89-6.93 (1H), 4.60 (2H), 2.16 (6H). ^{13}C NMR ($CDCl_3$): δ = 153.51, 146.71, 136.04, 131.02, 129.29, 129.06, 128.62, 127.19, 123.31, 18.28. HRMS (ESI): m/z calcd for $C_{15}H_{16}N_2$: 224.1313, found: 224.1303.



^{1}H NMR

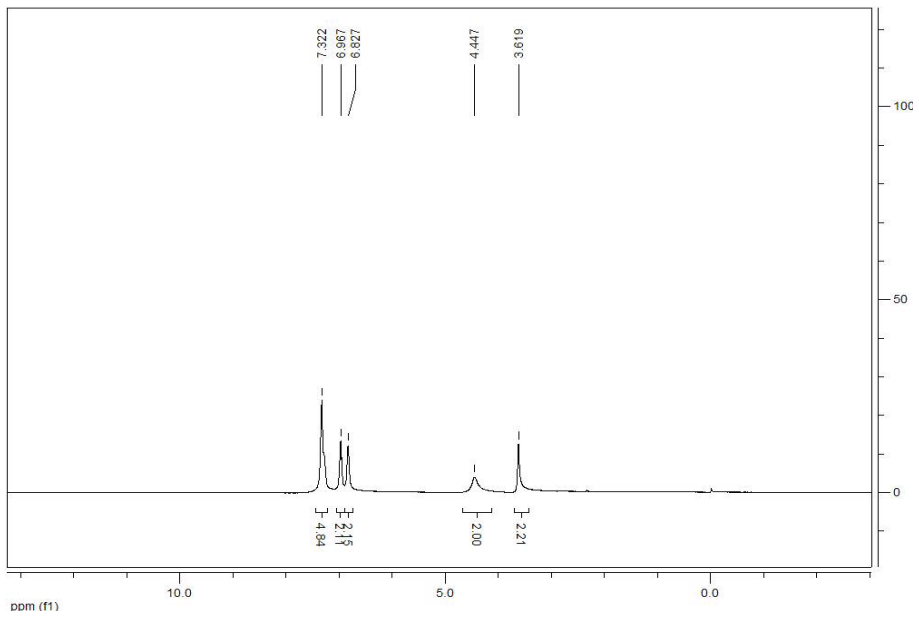


^{13}C NMR

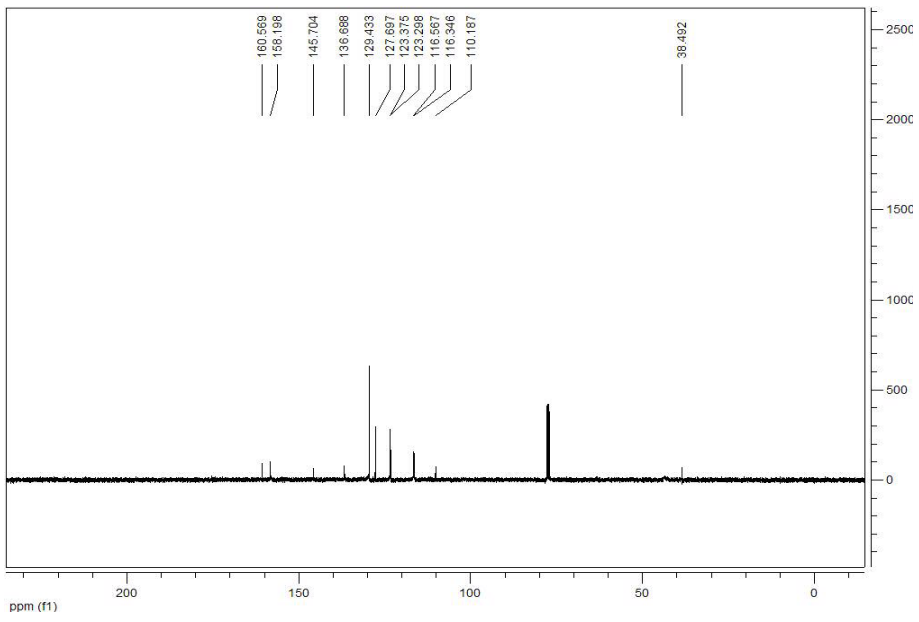


N'-(4-flurophenyl)-2-phenylacetamidine Compound was obtained following the above procedure catalyzed by catalysts **5** and isolated as a white solid in a 89% yield. Known compound.[1] ^{1}H NMR ($CDCl_3$): δ = 7.32 (5H), 6.97 (2H), 6.83 (2H), 4.45 (2H), 3.62 (2H). ^{13}C NMR ($CDCl_3$): δ = 160.57, 158.20, 145.70, 136.69, 129.43, 127.70, 123.38, 123.30, 116.57, 116.35, 110.19, 38.49.

^{1}H NMR

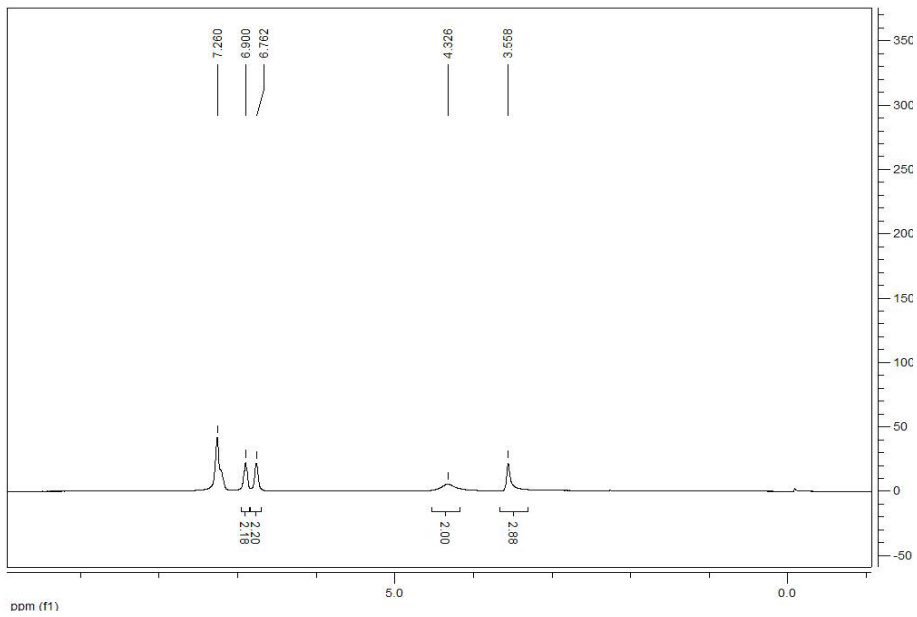


^{13}C NMR

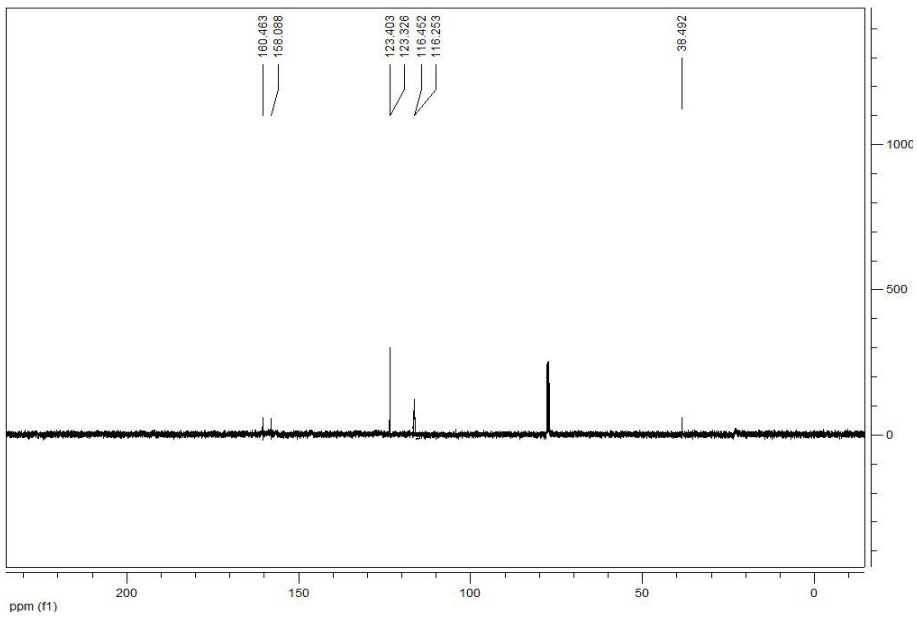


N'-(4-fluorophenyl)acetamidine Compound was obtained following the procedure catalyzed by catalyst **5** and isolated as a white solid in a 76% yield. Known compound.[1] ^{1}HNMR ($CDCl_3$): δ = 6.90 (2H), 6.76 (2H), 4.33 (2H), 3.56 (3H). ^{13}CNMR ($CDCl_3$): δ = 160.46, 158.09, 123.40, 123.33, 116.45, 116.25, 38.49.

^{1}H NMR



^{13}C NMR



Reference

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(3) Gilchrist, T. L.; Christopher, J. M.; Rees, C. W. *J. Chem. Soc. Perkin Trans. 1*. **1979**, 1871.