

Supporting Information

Construction of Stable Metal-Organic Framework Platforms Embedding *N*-Heterocyclic Carbene Metal Complexes for Selective Catalysis

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Table of Contents

1. Experimental procedures for ligand synthesis-----	S3-S7
2. Experimental procedures for construction of MOFs -----	S7-S8
3. Crystal structures of Cu-NHC MOF and Au-NHC MOF-----	S9
4. Analysis of Digested Solution of Cu-NHC MOFs and Au-NHC MOF by ICP-OES-----	S10
5. Nitrogen sorption isotherms of MOFs -----	S11
6. Recycle experiments and ICP spectroscopic evaluations -----	S12-S18
7. Experimental details of catalyzed reactions -----	S19-S30
8. Single crystal X-ray structure determination-----	S31-S34
9. ^1H and ^{13}C NMR spectra-----	S35-S77

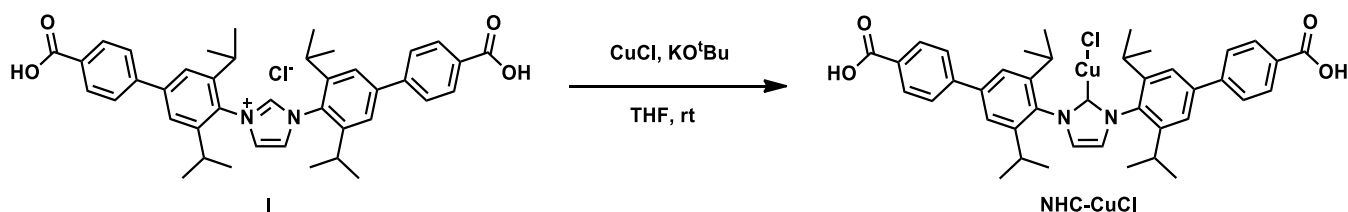
Materials

Without additional notes, all reagents were commercially available and used without further purification. DCM was distilled over CaH_2 , and THF was distilled over sodium and benzophenone. DMF were purified by solvent purification system using alumina column. *N*-methyl-2-pyrrolidone (NMP), *p*-xylene and methanol were purchased from Sigma-Aldrich, and directly used without further purification.

1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl) copper(I) chloride (IPrCuCl), 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl) copper(I) bromide (IPrCuBr), 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl) copper(I) iodide (IPrCuI), and 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl) gold(I) chloride (IPrAuCl) were synthesized as reported previously.^{1,2}

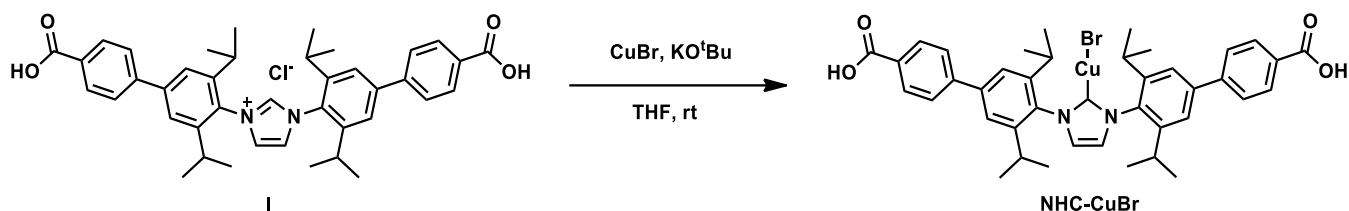
Experimental procedures for ligand synthesis

1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) chloride (NHC-CuCl)



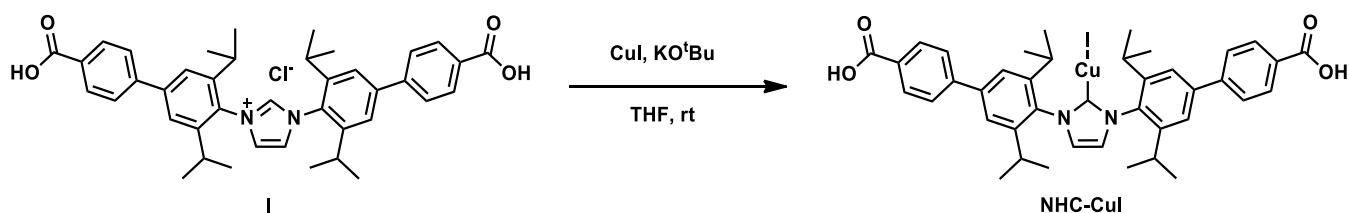
Precursor **I** was prepared by the method from the previous literature.³ A flask was charged with Precursor **I** (100 mg, 0.15 mmol), potassium tert-butoxide (60.7 mg, 0.54 mmol) and copper(I) chloride (22.3 mg, 0.23 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 54 mg of **NHC-CuCl** (48% yield). ^1H NMR (400 MHz, CD_3OD): δ 8.07-8.05 (d, 4H), 7.69-7.66 (m, 6H), 7.62 (s, 4H), 2.75-2.67 (sept, 4H), 1.40-1.37 (d, 12H), 1.35-1.33 (d, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 175.10, 147.61, 144.36, 143.56, 138.69, 135.54, 130.98, 127.59, 125.63, 124.09, 30.22, 25.14, 24.16; Anal. Calcd. for $\text{C}_{41}\text{H}_{44}\text{N}_2\text{O}_4\text{CuCl}$: C, 67.66; H, 6.09; N, 3.85. Found: C, 67.59; H, 5.91; N, 3.90.

1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) bromide (NHC-CuBr)



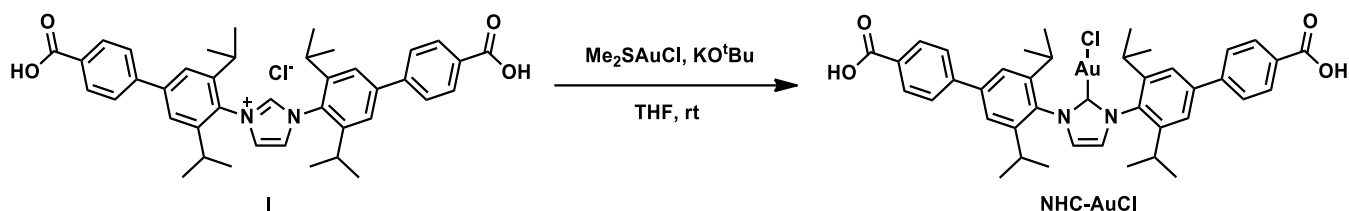
A flask was charged with precursor **I** (100 mg, 0.15 mmol), potassium tert-butoxide (60.7 mg, 0.54 mmol) and copper(I) bromide (32.3 mg, 0.23 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 62 mg of **NHC-CuBr** (53% yield). ^1H NMR (400 MHz, CD_3OD): δ 8.08-8.06 (d, 4H), 7.70-7.65 (m, 6H), 7.62 (s, 4H), 2.75-2.68 (sept, 4H), 1.39-1.37 (d, 12H), 1.35-1.33 (d, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 175.13, 147.59, 144.30, 143.61, 138.63, 135.47, 130.96, 127.63, 125.56, 124.05, 30.18, 25.17, 24.17; Anal. Calcd. for $\text{C}_{41}\text{H}_{44}\text{N}_2\text{O}_4\text{CuBr}$: C, 63.77; H, 5.74; N, 3.63. Found: C, 63.87; H, 5.56; N, 3.30.

1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) iodide (NHC-CuI)



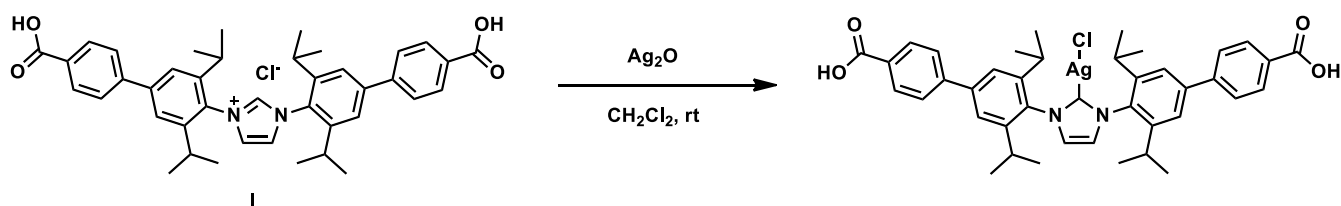
A flask was charged with precursor **I** (100 mg, 0.15 mmol), potassium tert-butoxide (60.7 mg, 0.54 mmol) and copper(I) iodide (42.9 mg, 0.23 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 58 mg of **NHC-CuI** (47% yield). ^1H NMR (400 MHz, CD_3OD): δ 8.08-8.06 (d, 4H), 7.65-7.62 (m, 6H), 7.62 (s, 4H), 2.75-2.69 (sept, 4H), 1.40-1.38 (d, 12H), 1.35-1.33 (d, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 175.15, 147.57, 144.30, 143.64, 138.61, 135.40, 130.96, 127.64, 125.43, 124.03, 30.18, 25.23, 24.19; Anal. Calcd. for $\text{C}_{41}\text{H}_{44}\text{N}_2\text{O}_4\text{CuI}$: C, 60.11; H, 5.41; N, 3.42. Found: C, 60.03; H, 5.53; N, 3.32.

1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl gold(I) chloride (NHC-AuCl)



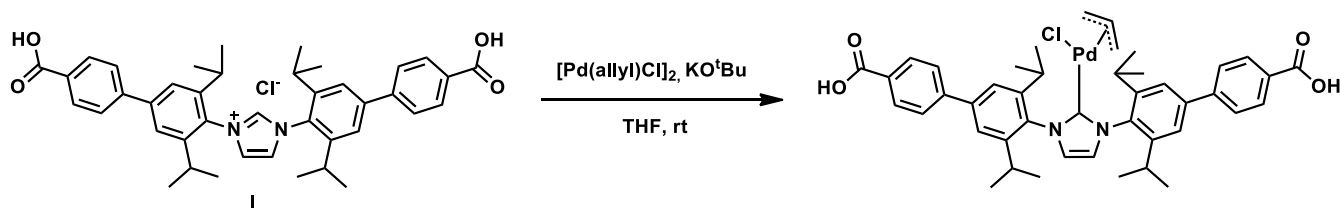
A flask was charged with precursor **I** (100 mg, 0.15 mmol), potassium tert-butoxide (60.7 mg, 0.54 mmol) and dimethylsulfide gold(I) chloride (66.4 mg, 0.23 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 67 mg of **NHC-AuCl** (52% yield). ^1H NMR (400 MHz, CD_3OD): δ 8.08-8.06 (d, 4H), 7.74-7.68 (m, 6H), 7.62 (s, 4H), 2.74-2.70 (sept, 4H), 1.44-1.42 (d, 12H), 1.34-1.33 (d, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 175.11, 147.60, 144.52, 143.58, 138.66, 135.08, 130.98, 127.63, 125.61, 124.15, 30.28, 24.76, 24.33; Anal. Calcd. for $\text{C}_{41}\text{H}_{44}\text{N}_2\text{O}_4\text{AuCl}$: C, 57.18; H, 5.15; N, 3.25. Found: C, 57.10; H, 5.27; N, 3.18.

(1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl)silver(I) chloride



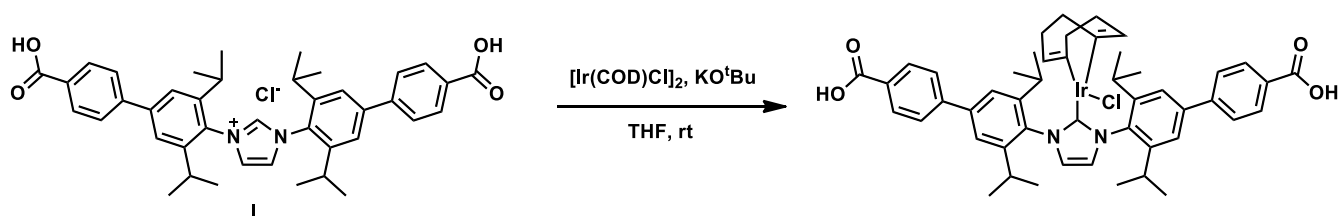
A flask was charged with precursor **I** (50 mg, 0.075 mmol) and silver oxide (10 mg, 0.045 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The crude material was washed with water and recrystallized from methanol to give 30 mg of desired complex (52% yield). ^1H NMR (400 MHz, CD_3OD): δ 8.35 (s, 2H), 8.10-8.08 (d, 4H), 7.75 (s, 4H), 7.72-7.69 (d, 4H), 2.56 (sept, 4H), 1.43-1.41 (d, 12H), 1.36-1.34 (d, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 174.79, 147.10, 146.14, 142.69, 139.09, 131.06, 130.81, 127.70, 124.63, 30.66, 24.76, 23.87.

Allyl(1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl)Chloropalladium(II)



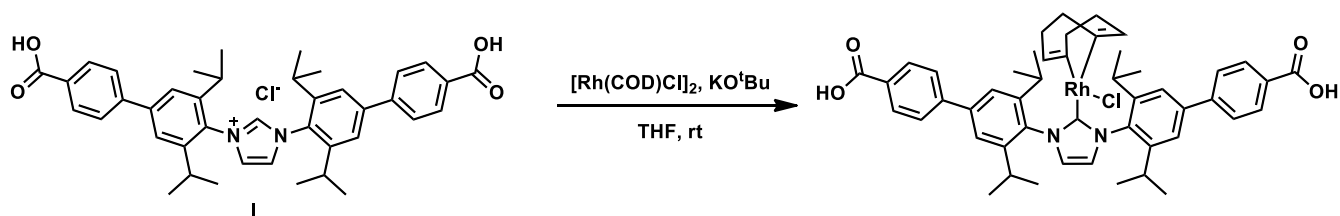
A flask was charged with precursor **I** (50 mg, 0.075 mmol), potassium tert-butoxide (60.7 mg, 0.27 mmol) and Allylpalladium(II) chloride dimer (17 mg, 0.045 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 33 mg of desired complex (53% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.09-8.06 (d, 4H), 7.69-7.66 (d, 4H), 7.63 (s, 2H), 7.59 (s, 4H), 3.86-3.83 (d, 1H), 3.28-3.26 (m, 1H), 3.21-3.17 (m, 2H), 2.98-2.91 (m, 2H), 2.84-2.81 (d, 1H), 1.83-1.80 (d, 1H), 1.50-1.43 (dd, 12H), 1.31-1.28 (d, 6H), 1.22-1.20 (d, 6H); ¹³C NMR (100 MHz, CD₃OD): δ 175.20, 147.94, 143.82, 143.65, 138.49, 136.85, 130.93, 127.70, 127.50, 126.52, 123.74, 116.06, 73.59, 30.03, 26.74, 26.12, 24.76, 23.35, 23.23.

[(IPr)(CO₂H)₂IrCl(COD)]



A flask was charged with precursor **I** (50 mg, 0.075 mmol), potassium tert-butoxide (60.7 mg, 0.27 mmol) and Bis(1,5-cyclooctadiene)diiridium(I) dichloride (30 mg, 0.045 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 33 mg of desired complex (45% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.09-8.06 (d, 4H), 7.71-7.68 (d, 4H), 7.60 (s, 4H), 7.46 (s, 2H), 4.15-4.12 (m, 2H), 3.49-4.42 (m, 2H), 3.13-3.11 (m, 2H), 2.78 (br, 2H), 1.79-1.70 (m, 2H), 1.64-1.59 (m, 2H), 1.50-1.42 (m, 12H), 1.40-1.24 (m, 7H), 1.21-1.20 (d, 12H); ¹³C NMR (100 MHz, CD₃OD): δ 175.24, 144.01, 143.55, 138.41, 137.17, 130.95, 127.49, 126.64, 83.41, 53.33, 34.41, 30.33, 29.62, 26.74, 24.76, 23.88.

[(IPr)(CO₂H)₂RhCl(COD)]



A flask was charged with precursor **I** (50 mg, 0.075 mmol), potassium tert-butoxide (60.7 mg, 0.27 mmol) and Chloro(1,5-cyclooctadiene)rhodium(I) dimer (22 mg, 0.045 mmol). To this flask, dry tetrahydrofuran (THF) was added and the reaction mixture was stirred for 48 h under a nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was evaporated and acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol to give 31 mg of desired complex (47% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.10-8.07 (d, 4H), 7.73-7.70 (d, 4H), 7.65 (s, 4H), 7.46 (s, 2H), 4.53-4.43

(m, 2H), 3.67-3.60 (m, 2H), 3.49-3.47 (m, 2H), 2.69-2.61 (m, 2H), 2.54-2.42 (m, 2H), 1.91-1.87 (m, 2H), 1.78-1.73 (m, 2H), 1.59-1.40 (m, 18H), 1.35-1.32 (d, 1H), 1.20-1.18 (d, 12H); ^{13}C NMR (100 MHz, CD_3OD): δ 175.26, 144.01, 143.66, 138.44, 137.36, 130.97, 127.70, 127.53, 126.94, 97.05, 69.95, 69.81, 33.59, 30.29, 29.16, 26.85

Experimental procedures for construction of MOFs

MOF_{CuCl}

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.16 mmol, 49 mg), **NHC-CuCl** (0.041 mmol, 30 mg) were added to 4-mL vial with mixed solvent of *N*-methyl-pyrrolidone (1 mL) and *p*-xylene (2 mL). The vial was sealed and placed in a preheated oven at 80 °C. After 72 h, block shaped crystals were obtained. The crystals were washed with DMF, followed by exchange solvent to THF. The crystals dried under vacuum to afford 28 mg of product as white crystals (75% yield). Anal. Calcd for $\text{C}_{128.25}\text{H}_{139.25}\text{N}_{9.75}\text{O}_{21.25}\text{Zn}_4\text{Cu}_3\text{Cl}_3 \cdot \{\text{Zn}_4\text{L}_3(\text{NO}_3)_2(\text{C}_3\text{H}_7\text{NO})_{1.75}(\text{H}_2\text{O})_{0.5}\}$ C, 56.72; H, 5.17; N, 5.03. Found: C, 56.58; H, 5.12; N, 5.04.

MOF_{CuBr}

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol, 46 mg), **NHC-CuBr** (0.039 mmol, 30 mg) were added to 4-mL vial with mixed solvent of *N*-methyl-pyrrolidone (1 mL) and *p*-xylene (2 mL). The vial was sealed and placed in a preheated oven at 80 °C. After 72 h, block shaped crystals were obtained. The crystals were washed with DMF, followed by exchange solvent to THF. The crystals dried under vacuum to afford 30 mg of product as white crystals (82% yield). Anal. Calcd for $\text{C}_{126}\text{H}_{134.5}\text{N}_9\text{O}_{20.75}\text{Zn}_4\text{Cu}_3\text{Br}_3 \cdot \{\text{Zn}_4\text{L}_3(\text{NO}_3)_2(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})_{0.75}\}$ C, 54.07; H, 4.84; N, 4.50. Found: C, 54.12; H, 4.92; N, 4.59.

MOF_{CuI}

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 mmol, 44 mg), **NHC-CuI** (0.037 mmol, 30 mg) were added to 4-mL vial with mixed solvent of *N*-methyl-pyrrolidone (1 mL) and *p*-xylene (2 mL). The vial was sealed and placed in a preheated oven at 80 °C. After 72 h, block shaped crystals were obtained. The crystals were washed with DMF, followed by exchange solvent to THF. The crystals dried under vacuum to afford 29 mg of product as white crystals (77% yield). Anal. Calcd for $\text{C}_{130.5}\text{H}_{144.5}\text{N}_{10.5}\text{O}_{22}\text{Zn}_4\text{Cu}_3\text{I}_3 \cdot \{\text{Zn}_4\text{L}_3(\text{NO}_3)_2(\text{C}_3\text{H}_7\text{NO})_{2.5}(\text{H}_2\text{O})_{0.5}\}$ C, 51.47; H, 4.78; N, 4.83. Found: C, 51.45; H, 4.59; N, 4.77.

MOF_{AuCl}

Zn(NO₃)₂·6H₂O (0.14 mmol, 42 mg), **NHC-AuCl** (0.035 mmol, 30 mg) were added to 4-mL vial with mixed solvent of *N*-methyl-pyrrolidone (1 mL) and *p*-xylene (2 mL). The vial was sealed and placed in a preheated oven at 80 °C. After 72 h, block shaped crystals were obtained. The crystals were washed with DMF, followed by exchange solvent to THF. The crystals dried under vacuum to afford 26 mg of product as white crystals (73% yield). Anal. Calcd for C₁₂₉H₁₄₂N₁₀O₂₂Zn₄Au₃Cl₃: {Zn₄L₃(NO₃)₂(C₃H₇NO)(H₂O)} C, 49.29; H, 4.55; N, 4.46. Found: C, 49.13; H, 4.61; N, 4.38.

References

1. Santoro, O.; Collado, A.; Slawin, A. M. Z.; Nolan, S. P.; Cazin, C. S. J. A general synthetic route to [Cu(X)(NHC)] (NHC = N-heterocyclic carbene, X = Cl, Br, I) complexes. *Chem. Commun.* **2013**, 49, 10483-10485.
2. Collado, A.; Gómez-Suárez, A.; Martin, A. R.; Slawin, A. M. Z.; Nolan, S. P. Straightforward synthesis of [Au(NHC)X] (NHC = N-heterocyclic carbene, X = Cl, Br, I) complexes. *Chem. Commun.*, **2013**, 49, 5541-5543.
3. Kim, H.; Kim, H.; Kim, K.; Lee, E. Structural Control of Metal–Organic Framework Bearing N-Heterocyclic Imidazolium Cation and Generation of Highly Stable Porous Structure. *Inorg. Chem.* **2019**, 58, 6619-6627.

Crystal structures of Cu-NHC MOF and Au-NHC MOF

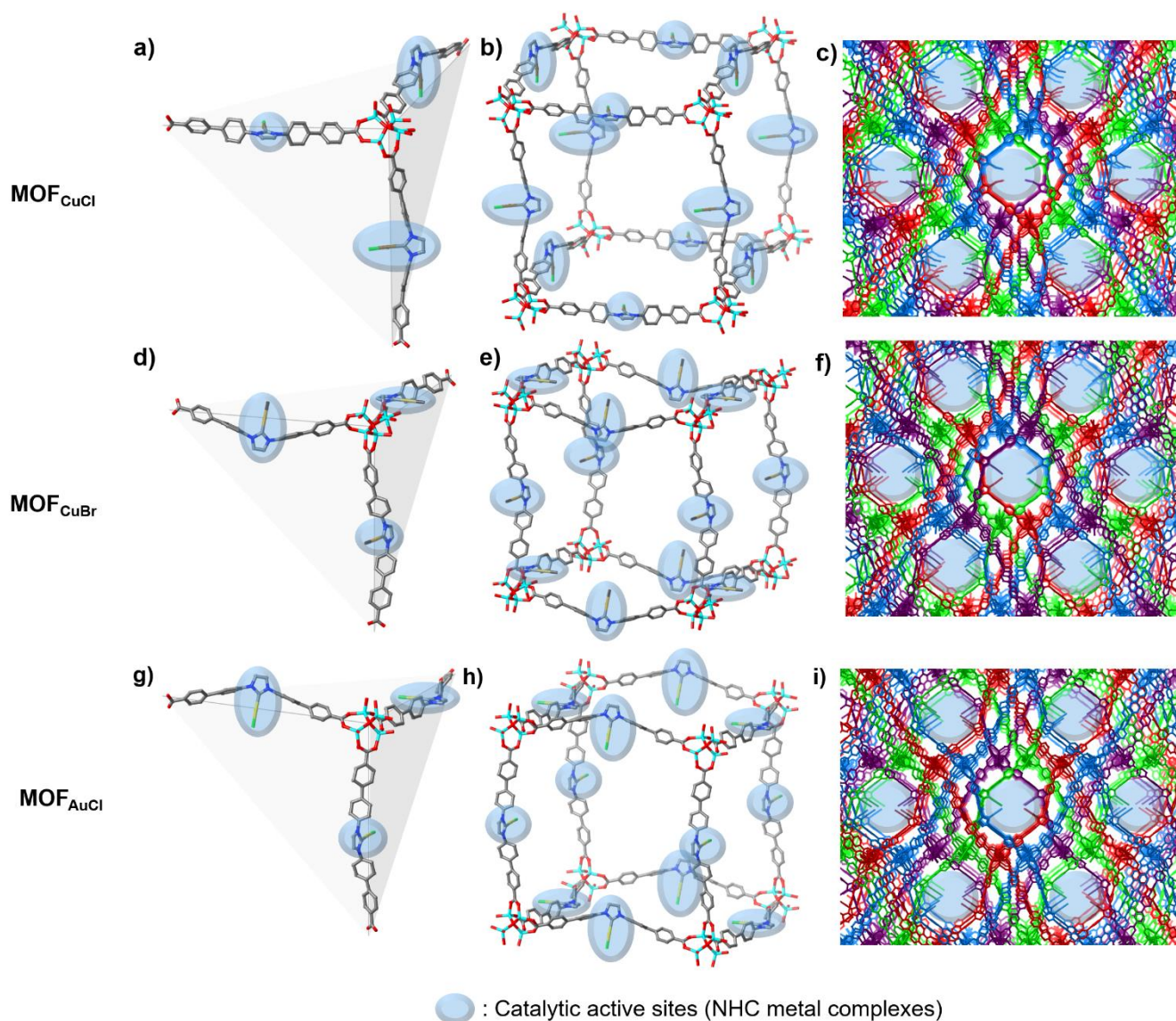


Figure S1. Single crystal X-ray structures of copper(I) chloride, copper(I) bromide, and gold(I) chloride bounded Zn MOFs. (a) coordination environment, (b) single set of cubic network, and (c) perspective view of 4-fold interpenetrated network of CuCl bounded Zn MOF. (d) coordination environment, (e) single set of cubic network, and (f) perspective view of 4-fold interpenetrated network of CuBr bounded Zn MOF. (g) coordination environment, (h) single set of cubic network, and (i) perspective view of 4-fold interpenetrated network of AuCl bounded Zn MOF. (C: gray, N: blue, O: red, Zn: cyan, Cu: brown, Au: yellow, Cl: light green, Br: dark brown. Hydrogen atoms and isopropyl substituents are omitted for clarity.)

Analysis of Digested Solution of Cu-NHC MOFs and Au-NHC MOF by ICP-OES

As-synthesized Cu-NHC MOFs and Au-NHC MOFs were soaked in THF for 3 days and evacuated by heating to 100 °C under a high vacuum (10^{-2} Pa) for overnight to remove residual solvents in MOFs.

The activated MOFs (MOF_{CuCl} (21 mg, C₁₂₃H₁₂₆N₈O₁₉Zn₄Cu₃Cl₃: {Zn₄L₃(NO₃)₂}), MOF_{CuBr} (20 mg, C₁₂₃H₁₂₆N₈O₁₉Zn₄Cu₃Br₃: {Zn₄L₃(NO₃)₂}), MOF_{CuI} (20 mg, C₁₂₃H₁₂₆N₈O₁₉Zn₄Cu₃I₃: {Zn₄L₃(NO₃)₂}), MOF_{AuCl} (14 mg, C₁₂₃H₁₂₆N₈O₁₉Zn₄Au₃Cl₃: {Zn₄L₃(NO₃)₂})) were dissolved in 5 mL of 1 M HCl. To digested solution, 35 mL of 1% aqueous solution of nitric acid was added for dilution. The resulting solution was evaluated by inductively coupled plasma optical emission spectrometer (ICP-OES) for Cu, Au, and Zn contents.

Table S1. Compositional analysis of Cu-NHC MOFs and Au-NHC MOF by ICP-OES.

	Formula	Calculated (ppm)		Observed (ppm)	
MOF _{CuCl}	C ₁₂₃ H ₁₂₆ N ₈ O ₁₉ Zn ₄ Cu ₃ Cl ₃ {Zn ₄ L ₃ (NO ₃) ₂ }	Cu: 38.81	Zn: 53.24	Cu: 38.72	Zn: 53.05
MOF _{CuBr}	C ₁₂₃ H ₁₂₆ N ₈ O ₁₉ Zn ₄ Cu ₃ Br ₃ {Zn ₄ L ₃ (NO ₃) ₂ }	Cu: 35.15	Zn: 48.21	Cu: 35.35	Zn: 48.68
MOF _{CuI}	C ₁₂₃ H ₁₂₆ N ₈ O ₁₉ Zn ₄ Cu ₃ I ₃ {Zn ₄ L ₃ (NO ₃) ₂ }	Cu: 33.41	Zn: 45.83	Cu: 33.71	Zn: 45.85
MOF _{AuCl}	C ₁₂₃ H ₁₂₆ N ₈ O ₁₉ Zn ₄ Au ₃ Cl ₃ {Zn ₄ L ₃ (NO ₃) ₂ }	Au: 69.42	Zn: 30.72	Au: 69.79	Zn: 31.03

Nitrogen sorption isotherms of MOFs

Nitrogen sorption isotherms were measured with a Autosorp-iQ volumetric adsorption equipment. Typically, as-synthesized materials (~30 mg) was soaked in THF for 3 days in order to remove residual solvents in the frameworks and evacuated by heating to 100 °C under a high vacuum (10^{-2} Pa) for overnight. Nitrogen isotherm was collected at 77 K. BET surface areas of MOF_{CuCl} , MOF_{CuBr} , MOF_{CuI} and MOF_{AuCl} are 1070 m^2/g , 1002 m^2/g , 958 m^2/g and 984 m^2/g , respectively.

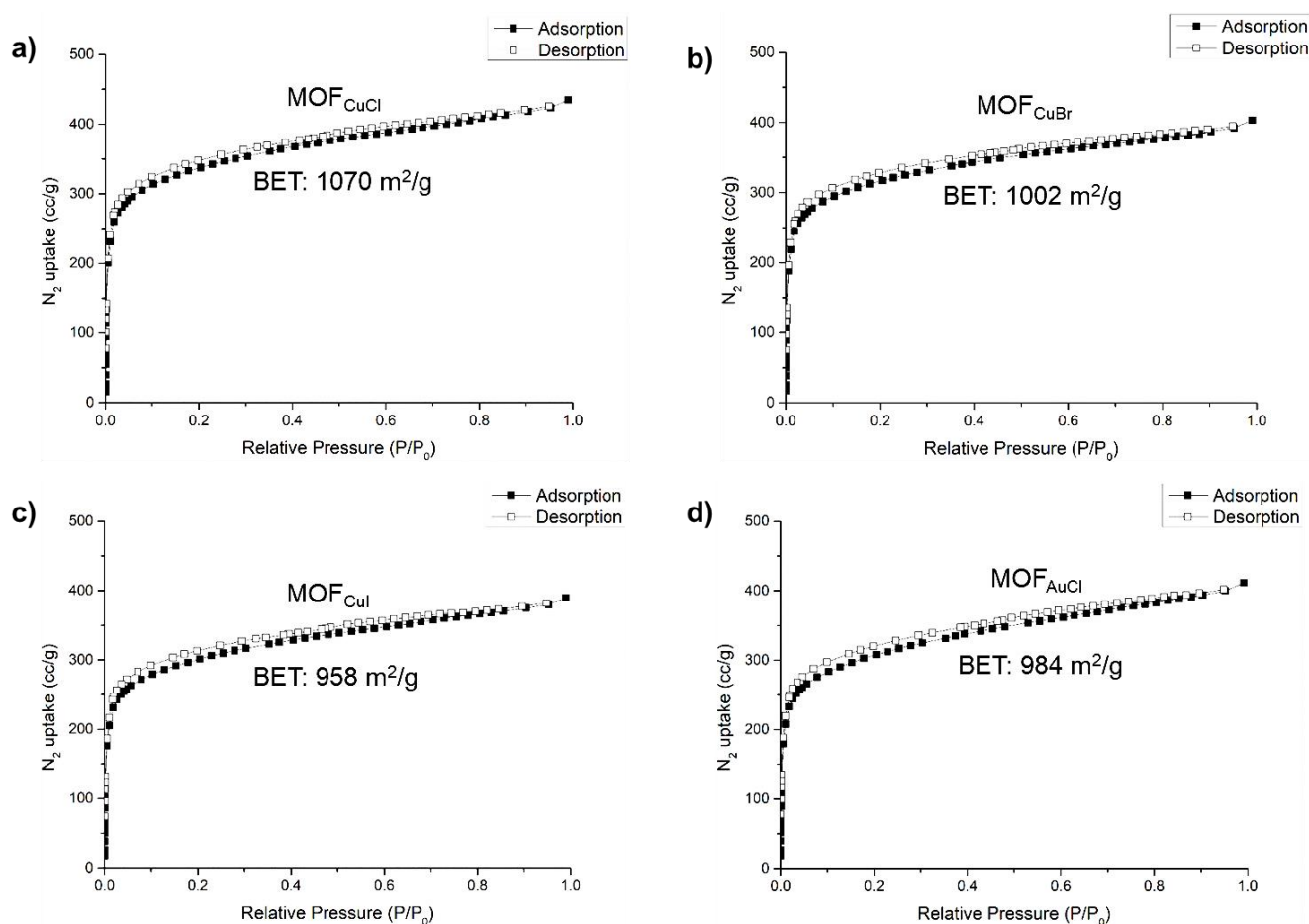
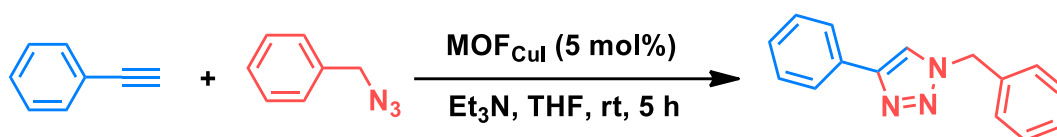


Figure S2. N_2 sorption isotherms of (a) MOF_{CuCl} , (b) MOF_{CuBr} , (c) MOF_{CuI} , (d) MOF_{AuCl} at 77 K. (open symbols: desorption, closed symbols: adsorption)

Recycle experiments and ICP spectroscopic evaluations

1. Cu-catalyzed azide-alkyne cycloaddition

Recycle Experiment in CuAAC



To THF (1.2 mL) in a vessel was added MOF_{CuI} (51 mg, 0.054 mmol, 5 mol%), phenylacetylene (118 μL , 1.07 mmol, 1 eq), TEA (180 μL , 1.30 mmol, 1.2 eq) under N_2 atmosphere, and then, benzyl azide (163 μL , 1.30 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature for 5 h. The yield of the reaction was determined by ^1H NMR (400 MHz) spectroscopy using CH_2Br_2 as an internal standard in CDCl_3 . After each cycle, MOF_{CuI} was separated by filtration, washed with DMF and THF and dried under high vacuum for 16 h, then reused in a freshly made reaction mixture.

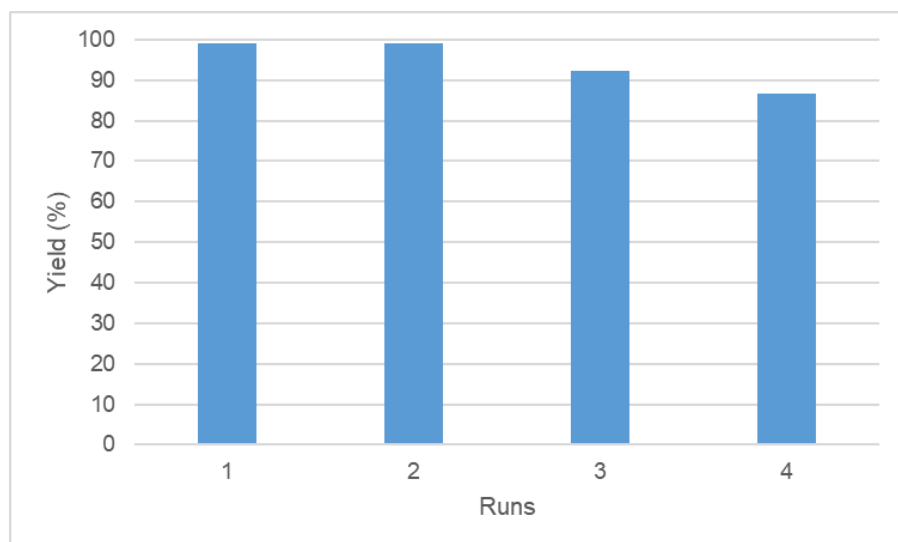


Figure S3. Recycling experiments of MOF_{CuI} in Cu-catalyzed azide-alkyne cycloaddition reaction.

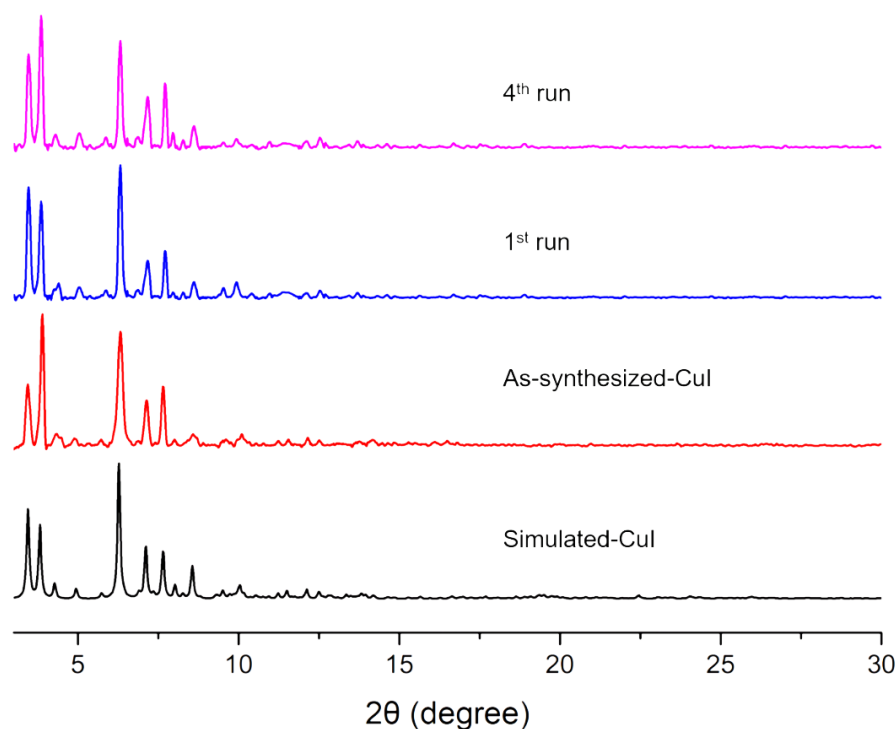


Figure S4. Powder X-ray diffraction (PXRD) profiles of as-synthesized MOF_{CuI} (red), after Cu-catalyzed azide-alkyne cycloaddition reaction between phenylacetylene and benzyl azide (blue) and after 4th run (magenta).

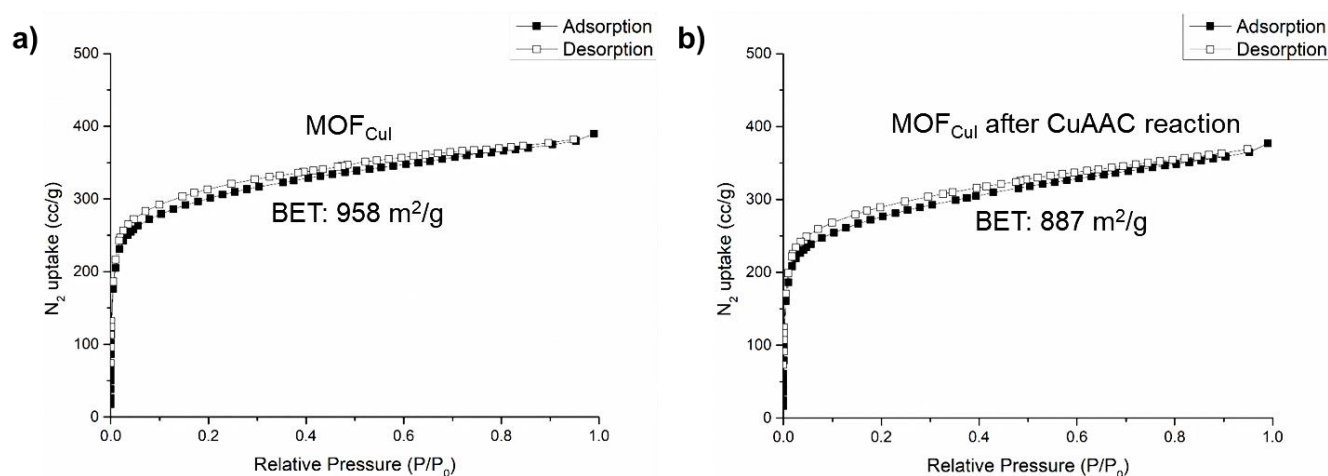


Figure S5. N_2 sorption isotherms of (a) as-synthesized MOF_{CuI} , (b) after 4th run of Cu-catalyzed azide-alkyne cycloaddition reaction between phenylacetylene and benzyl azide.

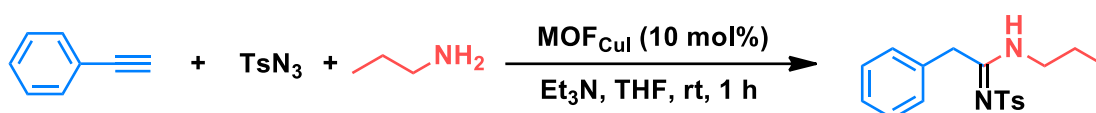
ICP spectrometric evaluation of metal loss in CuAAC

To THF (1.2 mL) in a vessel was added MOF_{CuI} (51 mg, 0.054 mmol, 5 mol%), phenylacetylene (118 μL , 1.07 mmol, 1 eq), TEA (180 μL , 1.30 mmol, 1.2 eq) under N_2 atmosphere, and then, benzyl azide (163 μL , 1.30 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature. After 5 h, the mixture was passed through a pad of celite, and washed by THF. The combined organic solvent was removed under reduced pressure. The remaining solid mixture was

dissolved in 5 mL of 1% aqueous solution (use doubly distilled water) of nitric acid by sonication. The resulting solution was then evaluated by inductively coupled plasma optical emission spectrometer (ICP-OES) for Cu and Zn contents. The Cu and Zn contents were measured in ppm based on calibration curves obtained with a series of calibration standard solutions doped with different amount of Cu and Zn. The quantity of Cu lost and Zn lost from CuI MOF was calculated to be 0.08% (0.572 ppm) of total Cu and 0.06% (0.515 ppm) of total Zn, respectively.

2. Cu-catalyzed multicomponent reaction

Recycle Experiment in MCR



To THF (1.3 mL) in a vessel was added MOF_{CuI} (65 mg, 0.075 mmol, 10 mol%), phenylacetylene (75 μ L, 0.68 mmol, 1 eq), propylamine (75 μ L, 0.83 mmol, 1.2 eq), TEA (113 μ L, 0.83 mmol, 1.2 eq) under N₂ atmosphere, and then, tosyl azide (126 μ L, 0.83 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature for 1 h. The yield of the reaction was determined by ¹H NMR (400 MHz) spectroscopy using CH₂Br₂ as an internal standard in CDCl₃. After each cycle, CuI MOF was separated by filtration, washed with DMF and THF and dried under high vacuum for 16 h, then reused in a freshly made reaction mixture.

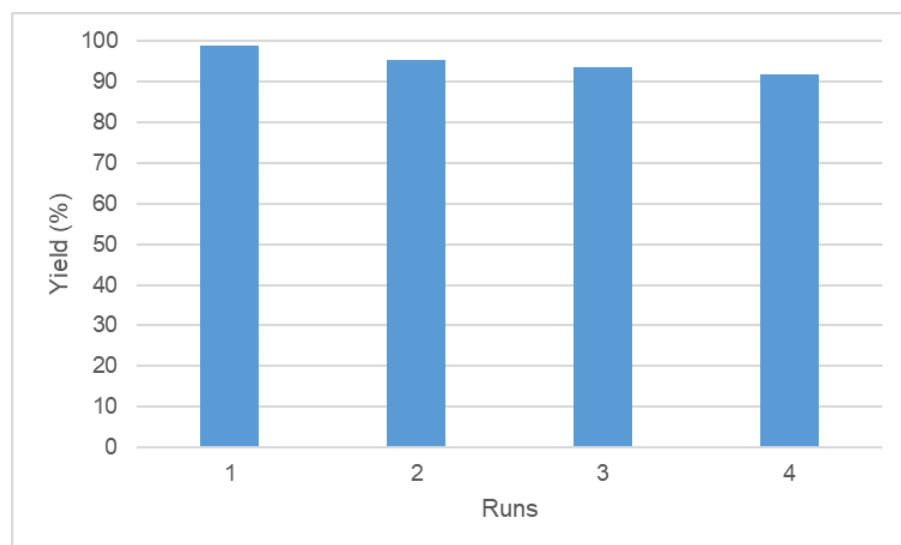


Figure S6. Recycling experiments of MOF_{CuI} in multicomponent reaction.

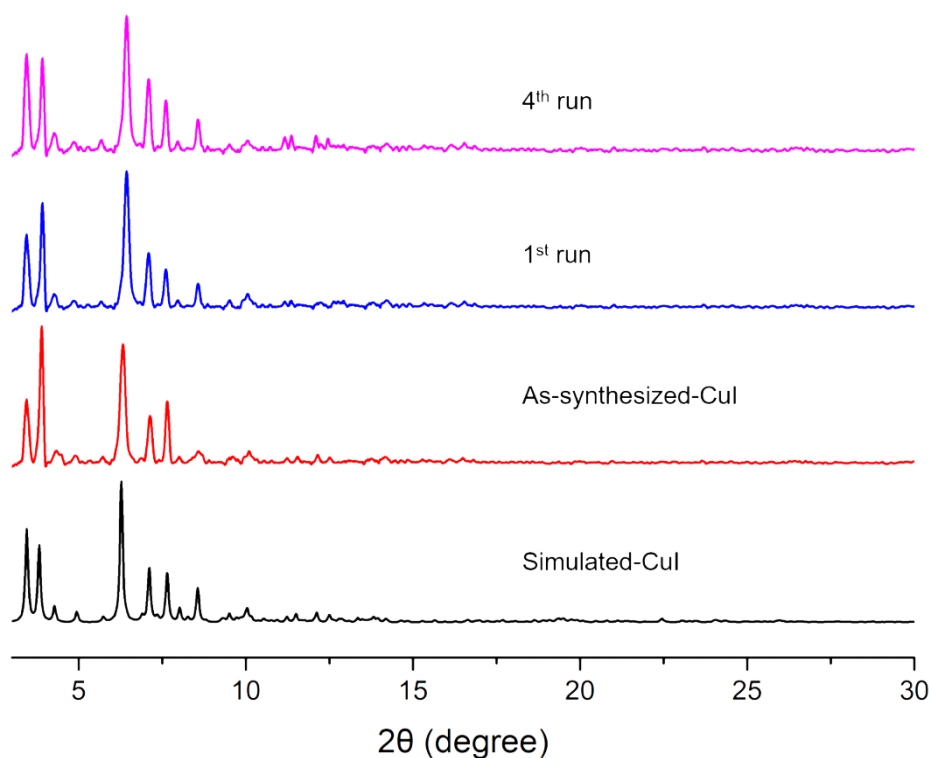


Figure S7. Powder X-ray diffraction (PXRD) profiles of as-synthesized MOF_{CuI} (red), after multicomponent reaction between phenylacetylene, tosyl azide and propylamine (blue) and after 4th run (magenta).

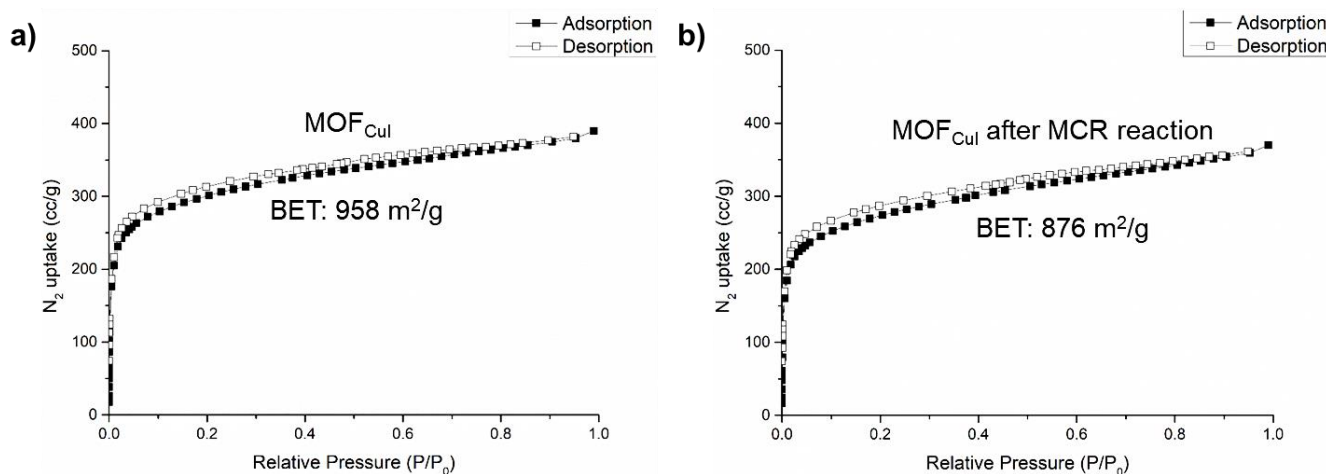


Figure S8. N_2 sorption isotherms of (a) as-synthesized MOF_{CuI} , (b) after 4th run of multicomponent reaction between phenylacetylene, tosyl azide and propylamine.

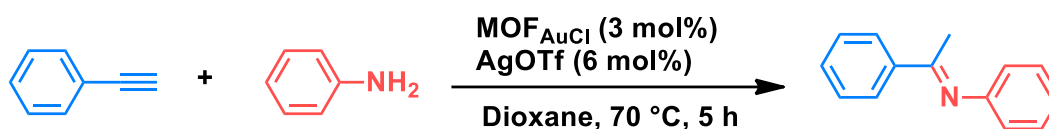
ICP spectrometric evaluation of metal loss in MCR

To THF (1.3 mL) in a vessel was added MOF_{CuI} (65 mg, 0.075 mmol, 10 mol%), phenylacetylene (75 μL , 0.68 mmol, 1 eq), propylamine (75 μL , 0.83 mmol, 1.2 eq), TEA (113 μL , 0.83 mmol, 1.2 eq) under N_2 atmosphere, and then, tosyl azide (126 μL , 0.83 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature. After 1 h, the mixture was passed through a pad of celite, and washed by THF. The combined organic solvent was removed under reduced pressure. The

remaining solid mixture was dissolved in 5 mL of 1% aqueous solution (use doubly distilled water) of nitric acid by sonication. The resulting solution was then evaluated by inductively coupled plasma optical emission spectrometer (ICP-OES) for Cu and Zn contents. The Cu and Zn contents were measured in ppm based on calibration curves obtained with a series of calibration standard solutions doped with different amount of Cu and Zn. The quantity of Cu lost and Zn lost from CuI MOF was calculated to be 0.08% (0.731 ppm) of total Cu and 0.04% (0.509 ppm) of total Zn, respectively.

3. Au-catalyzed hydroamination

Recycle Experiment in hydroamination



To dioxane (2.2 mL) in a vessel was added MOF_{AuCl} (34 mg, 0.034 mmol, 3 mol%), AgOTf (19 mg, 0.069 mmol, 6 mol%), phenylacetylene (126 μL , 1.14 mmol, 1 eq) under N_2 atmosphere, and then, aniline (114 μL , 1.38 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at 70 $^{\circ}\text{C}$ for 5 h. The yield of the reaction was determined by ^1H NMR (400 MHz) spectroscopy using CH_2Br_2 as an internal standard in CDCl_3 . After each cycle, CuI MOF was separated by filtration, washed with DMF and THF and dried under high vacuum for 16 h, then reused in a freshly made reaction mixture.

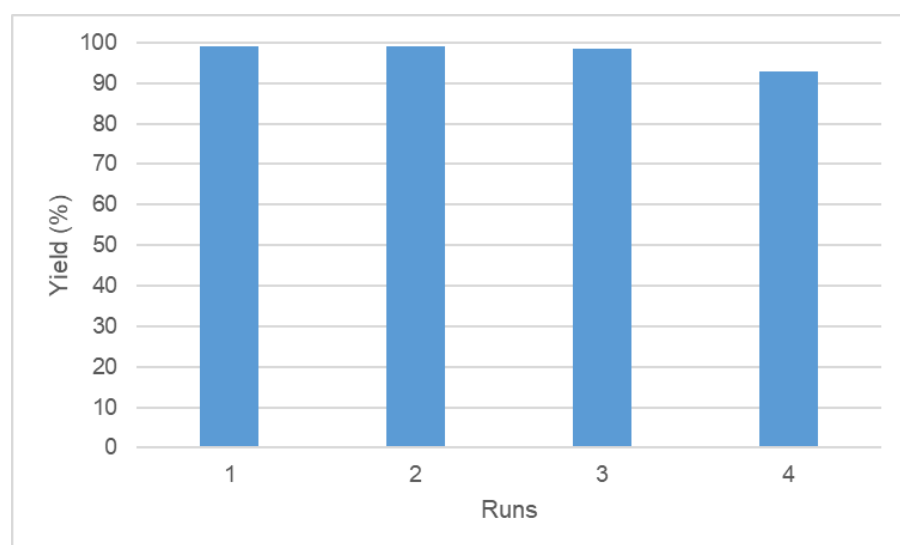


Figure S9. Recycling experiments of MOF_{AuCl} in hydroamination reaction.

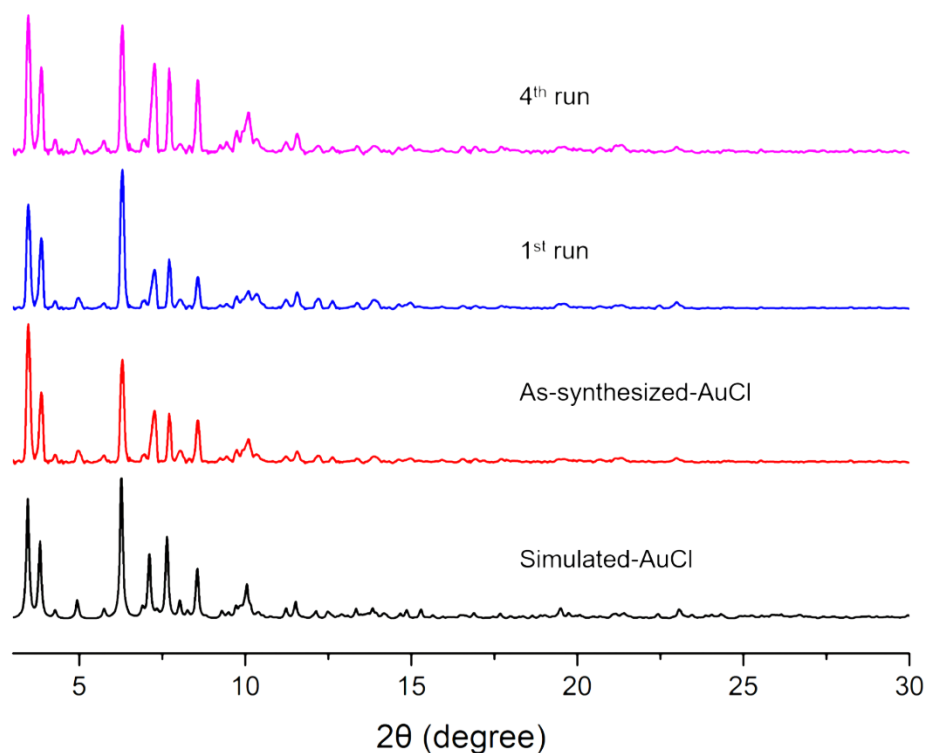


Figure S10. Powder X-ray diffraction (PXRD) profiles of as-synthesized MOF_{AuCl} (red), after hydroamination reaction between phenylacetylene and aniline (blue) and after 4th run (magenta).

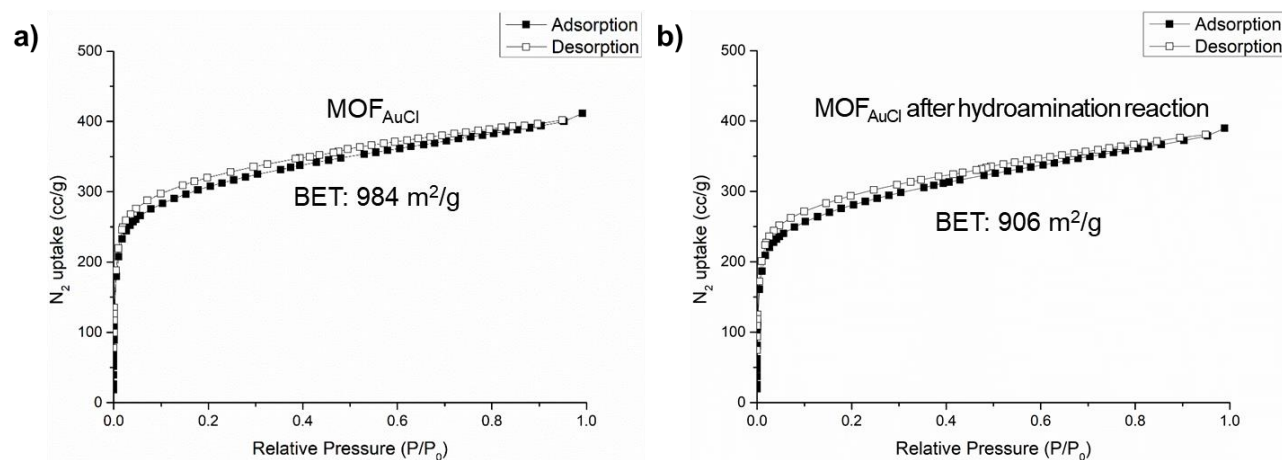


Figure S11. N₂ sorption isotherms of (a) as-synthesized MOF_{AuCl}, (b) after 4th run of hydroamination reaction between phenylacetylene and aniline.

ICP spectrometric evaluation of metal loss in hydroamination

To dioxane (2.2 mL) in a vessel was added MOF_{AuCl} (34 mg, 0.034 mmol, 3 mol%), AgOTf (19 mg, 0.069 mmol, 6 mol%), phenylacetylene (126 μ L, 1.14 mmol, 1 eq) under N₂ atmosphere, and then, aniline (114 μ L, 1.38 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at 70 $^{\circ}$ C for 5 h. After 5 h, the mixture was passed through a pad of celite, and washed by THF. The combined organic solvent was removed under reduced pressure. The remaining solid mixture was dissolved in 5

mL of 1% aqueous solution (use doubly distilled water) of nitric acid by sonication. The resulting solution was then evaluated by inductively coupled plasma optical emission spectrometer (ICP-OES) for Au and Zn contents. The Au and Zn contents were measured in ppm based on calibration curves obtained with a series of calibration standard solutions doped MOF_{AuCl} with different amount of Au and Zn. The quantity of Au lost and Zn lost from was calculated to be 0.05% (0.728 ppm) of total Au and 0.08% (0.504 ppm) of total Zn, respectively.

Experimental details of catalyzed reactions

1. Cu-catalyzed azide-alkyne cycloaddition

Caution! Organic azides are potentially-explosive substances that can and will decompose with the slightest input of energy from external sources (heat, light, pressure).

Typical procedure (A, heterogeneous catalyst): To THF (0.1 mL) in a vessel was added MOF_{CuI} (4.3 mg, 4.6 μmol, 5 mol%), alkyne (0.091 mmol, 1 eq), TEA (15.2 μL, 0.11 mmol, 1.2 eq) under N₂ atmosphere, and then, azide (0.11 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature for 5 h. The crude compound was isolated by silica column chromatography.

Typical procedure (B, homogeneous catalyst): To THF (0.1 mL) in a vessel was added IPrCuI (Iodo[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I)) (2.6 mg, 4.6 μmol, 5 mol%), alkyne (0.091 mmol, 1 eq), TEA (15.2 μL, 0.11 mmol, 1.2 eq) under N₂ atmosphere, and then, azide (0.11 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature for 5 h. The crude compound was isolated by silica column chromatography.

1-benzyl-4-phenyl-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (5:1, R_f: 0.21) to afford **1** as white solid (**A**: 40 mg, 95% yield, **B**: 43 mg, 99% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.83 (d, 2H), 7.71 (s, 1H), 7.44-7.32 (m, 8H), 5.61 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 148.20, 134.78, 130.61, 129.15, 128.83, 128.76, 128.17, 128.06, 125.72, 119.66, 54.19. These spectroscopic data are consistent with those previously reported in the literature.⁴

1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (5:1, R_f: 0.11) to afford **2** as yellow solid (47 mg, 93% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.28-8.26 (d, 2H), 7.85-7.84 (d, 2H), 7.83 (s, 1H), 7.48-7.33 (m, 5H), 5.73 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 148.78, 148.18, 141.86, 130.18, 129.02, 128.67, 128.61, 125.85, 124.42, 119.90, 53.28. These spectroscopic data are consistent with those previously reported in the literature.⁶

1-(4-methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, R_f : 0.44) to afford **3** as yellow solid (44 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.80 (dd, 2H), 7.64 (s, 2H), 7.43-7.28 (m, 4H), 6.95-6.92 (d, 2H), 5.53 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.99, 148.10, 130.69, 129.70, 128.83, 128.15, 126.72, 125.72, 119.44, 114.55, 55.38, 53.79. These spectroscopic data are consistent with those previously reported in the literature.⁸

1-benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, R_f : 0.32) to afford **4** as yellow solid (46 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.30-8.28 (d, 2H), 8.00-7.98 (d, 2H), 7.81 (s, 1H), 7.44-7.32 (m, 5H), 5.63 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.45, 146.44, 137.00, 134.30, 129.43, 129.20, 128.33, 126.25, 124.40, 121.33, 54.66. These spectroscopic data are consistent with those previously reported in the literature.⁵

1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, R_f : 0.35) to afford **5** as yellow solid (42 mg, 90% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.76-7.73 (d, 2H), 7.59 (s, 1H), 7.42-7.32 (m, 5H), 6.96-6.94 (d, 2H), 5.59 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.69, 148.17, 134.91, 129.20, 128.80, 128.12, 127.09, 123.41, 118.82, 114.30, 55.39, 54.25. These spectroscopic data are consistent with those previously reported in the literature.⁵

1-([1,1'-biphenyl]-4-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, R_f : 0.40) to afford **6** as yellow solid (**A**: 35 mg, 61% yield, **B**: 48 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.85-7.82 (d, 2H), 7.73 (s, 1H), 7.65-7.57 (m, 4H), 7.49-7.32 (m, 8H), 5.65 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.51, 141.96, 140.36, 133.71, 130.67, 129.02, 128.67, 128.33, 128.00, 127.83, 127.25, 125.85, 119.72, 54.12. These spectroscopic data are consistent with those previously reported in the literature.⁹

4-([1,1'-biphenyl]-4-yl)-1-benzyl-1*H*-1,2,3-triazole

The reaction mixture was stirred at room temperature for 5 h. The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, R_f : 0.42) to afford **7** as yellow solid (**A**: 11 mg, 20% yield, **B**: 41 mg, 73%). ^1H NMR (400 MHz, CDCl_3): δ 7.92 (s, 2H), 7.68-7.63 (m, 4H), 7.48-7.25 (m, 9H), 5.62 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 141.08, 140.73, 134.77, 129.32, 129.00, 128.96, 128.29, 127.69, 127.59, 127.12, 126.11, 54.73. These spectroscopic data are consistent with those previously reported in the literature.⁷

1-(naphthalen-1-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, *R*_f: 0.47) to afford **8** as yellow solid (**A**: 22 mg, 43% yield, **B**: 39 mg, 76% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.05-8.02(m, 1H), 7.96-7.91(m, 2H), 7.77 (s, 2H), 7.58-7.50 (m, 5H), 7.40-7.30 (m, 3H), 6.05 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 148.00, 133.95, 131.19, 130.55, 130.05, 129.97, 138.96, 128.76, 128.11, 127.80, 127.34, 126.46, 125.66, 125.41, 122.93, 119.60, 52.36. These spectroscopic data are consistent with those previously reported in the literature.⁸

1-benzyl-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (5:1, *R*_f: 0.37) to afford **25** as yellow solid (35 mg, 93% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.95 (d, 2H), 7.80 (s, 1H), 7.69-7.67 (d, 2H), 7.44-7.32 (m, 5H), 5.62 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 146.95, 134.53, 134.13, 130.57, 130.25, 129.93, 129.60, 129.35, 129.05, 128.24, 125.94, 125.88, 125.84, 125.56, 124.31, 122.86, 120.41, 54.47. These spectroscopic data are consistent with those previously reported in the literature.⁶

1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (5:1, *R*_f: 0.15) to afford **26** as yellow solid (41 mg, 91% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.72-7.71 (d, 2H), 7.66 (s, 1H), 7.42-7.3 (m, 5H), 7.24-7.22 (d, 2H), 5.59 (s, 2H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.48, 138.07, 134.87, 129.57, 129.21, 128.82, 128.14, 127.90, 125.68, 119.35, 54.30, 21.35. These spectroscopic data are consistent with those previously reported in the literature.⁵

1-(4-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (3:1, *R*_f: 0.23) to afford **27** as white solid (43 mg, 94% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.11-7.78 (m, 2H), 7.43 (s, 2H), 7.37-7.33 (m, 1H), 7.22(s, 4H), 5.55 (s, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.16, 138.74, 131.75, 130.69, 129.84, 128.83, 128.17, 128.15, 125.74, 119.52, 54.05, 21.22. These spectroscopic data are consistent with those previously reported in the literature.⁸

4-phenyl-1-(4-(trifluoromethyl)benzyl)-1*H*-1,2,3-triazole

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (5:1, *R_f*: 0.21) to afford **28** as yellow solid (52 mg, 94% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.85-7.84 (m, 2H), 7.72 (s, 1H), 7.69-7.66 (d, 2H), 7.45-7.33(m, 5H), 5.68 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 148.61, 138.80, 131.53, 131.21, 130.88, 130.56, 130.42, 128.95, 128.42, 128.25, 126.22, 126.18, 126.14, 126.11, 125.78, 122.52, 119.81, 53.59. These spectroscopic data are consistent with those previously reported in the literature.⁶

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2. Cu-catalyzed multicomponent reaction

Typical procedure (A, heterogeneous catalyst): To THF (0.18 mL) in a vessel was added MOF_{CuI} (8.7 mg, 9.1 μ mol, 10 mol%), alkyne (0.091 mmol, 1 eq), amine (0.11 mmol, 1.2 eq), TEA (15.2 μ L, 0.11 mmol, 1.2 eq) under N₂ atmosphere, and then, sulfonyl azide (0.11 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature for 1 h. The crude compound was isolated by silica column chromatography.

Typical procedure (B, homogeneous catalyst): To THF (0.18 mL) in a vessel was added IPrCuI (Iodo[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I)) (5.3 mg, 9.1 μ mol, 10 mol%), alkyne (0.091 mmol, 1 eq), amine (0.11 mmol, 1.2 eq), TEA (15.2 μ L, 0.11 mmol, 1.2 eq) under N₂ atmosphere, and then, sulfonyl azide (0.11 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at room temperature for 1 h. The crude compound was isolated by silica column chromatography.

2-phenyl-*N*-propyl-*N*-tosylacetimidamide

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f: 0.38) to afford **9** as white solid (**A**: 56 mg, 93% yield, **B**: 60 mg, 99% yield, a mixture of two isomers with a ratio 1:5, which is tentatively assigned as Z/E of the generated imino C=N double bond). ¹H NMR (400 MHz, CDCl₃): δ 7.88-7.85 (d, 2H), 7.41-7.32 (m, 3H), 7.29-7.26 (d, 2H), 7.22-7.19 (dd, 2H), 5.17 (br, 1H), 4.29 (s, 2H), 3.21 (m, 2H), 2.42 (s, 3H), 1.43-1.36 (m, 2H), 0.76 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.69, 143.44, 142.19, 140.89, 139.40, 133.18, 130.20, 129.71, 129.48, 129.26, 128.21, 126.48, 126.41, 43.73, 39.78, 21.60, 11.20; HRMS (FAB) *m/z* calcd. for C₁₈H₂₂N₂O₂SNa [*M*+Na]⁺ : 353.1300, found: 353.1297.

2-(4-nitrophenyl)-*N*-propyl-*N*-tosylacetimidamide

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f: 0.17) to afford **10** as white solid (56 mg, 93% yield, a mixture of two isomers with a ratio 1:2, which is tentatively assigned as Z/E of the generated imino C=N double bond). ¹H NMR (400 MHz, CDCl₃): δ 8.26-8.23 (d, 2H), 7.85-7.83 (d, 2H), 7.48-7.45 (d, 2H), 7.36-7.33 (d, 2H), 5.10 (br, 1H), 4.44 (s, 2H), 3.28-3.23 (m, 2H), 2.44 (s, 3H), 1.51-1.49 (m, 2H), 0.83 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.63, 147.13, 142.49, 141.81, 140.44, 130.30, 129.52, 129.46, 129.20, 126.20, 126.06, 123.92, 44.02, 39.10, 21.56, 21.43, 11.33, 11.03; HRMS (FAB) *m/z* calcd. for C₁₈H₂₁N₃O₄SNa [*M*+Na]⁺ : 398.1151, found: 398.1148.

2-(4-methoxyphenyl)-*N*-propyl-*N*-tosylacetimidamide

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f : 0.29) to afford **11** as white solid (54 mg, 85% yield, a mixture of two isomers with a ratio 1:6, which is tentatively assigned as Z/E of the generated imino C=N double bond). ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.88 (d, 2H), 7.31-7.29 (d, 2H), 7.15-7.12 (d, 2H), 6.93-6.91 (d, 2H), 5.24 (br, 1H), 4.24 (s, 2H), 3.83 (s, 3H), 3.24-3.18 (m, 2H), 2.44 (s, 3H), 1.46-1.39 (m, 2H), 0.79 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.18, 159.52, 142.15, 141.04, 131.46, 129.77, 129.50, 129.27, 126.46, 124.80, 114.94, 55.42, 43.71, 39.02, 21.68, 21.59, 11.27; HRMS (FAB) m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_3\text{SNa}$ [$M+\text{Na}$] $^+$: 383.1405, found: 383.1403.

***N,N*-diisopropyl-2-phenyl-*N*-tosylacetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f : 0.40) to afford **12** as white solid (**A**: 12 mg, 18% yield, **B**: 66 mg, 97% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.86-7.83 (d, 2H), 7.32-7.19 (m, 7H), 4.43 (s, 2H), 4.02 (sept, 1H), 2.41 (s, 3H), 1.41-1.40 (d, 6H), 0.92-0.88 (d, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.47, 141.61, 134.97, 129.08, 128.86, 128.03, 126.77, 126.25, 50.47, 48.07, 38.73, 21.48, 19.86. These spectroscopic data are consistent with those previously reported in the literature.¹⁰

***N*-benzyl-2-phenyl-*N*-tosylacetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (1:1, R_f : 0.55) to afford **13** as white solid (**A**: 26 mg, 37% yield, **B**: 64 mg, 93% yield, a mixture of two isomers with a ratio 1:8, which is tentatively assigned as Z/E of the generated imino C=N double bond). ^1H NMR (400 MHz, CDCl_3): δ 7.86-7.83 (d, 2H), 7.41-7.33 (m, 3H), 7.30-7.21 (m, 6H), 7.09-7.06 (m, 2H), 5.49 (br, 1H), 4.43 (d, 2H), 4.38 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.47, 142.23, 140.72, 136.49, 133.07, 130.10, 129.21, 128.77, 128.19, 127.78, 127.60, 126.42, 46.95, 39.74, 21.54. These spectroscopic data are consistent with those previously reported in the literature.¹⁰

***N*-methyl-*N*,2-diphenyl-*N*-tosylacetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (1:1, R_f : 0.59) to afford **14** as white solid (**A**: 6 mg, 8% yield, **B**: 63 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.91-7.89 (d, 2H), 7.32-7.20 (m, 5H), 7.12-7.09 (m, 3H), 6.84-6.78 (dd, 4H), 4.27 (s, 2H), 3.35 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.48, 142.66, 142.10, 141.15, 134.76, 129.54, 129.18, 128.27, 127.31, 126.49, 126.45, 41.18, 37.73, 21.53. These spectroscopic data are consistent with those previously reported in the literature.¹⁰

2-phenyl-*N*-propyl-*N*-((2,4,6-triisopropylphenyl)sulfonyl)acetimidamide

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f : 0.67) to afford **15** as white solid (**A**: 9 mg, 11% yield, **B**: 73 mg, 91% yield, a mixture of two isomers with a ratio 1:7, which is tentatively assigned as Z/E of the generated imino C=N double bond). ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.34 (m, 3H), 7.20-7.12 (m, 4H), 5.04 (br, 1H), 4.48 (sept, 1H), 4.16 (s, 2H), 3.21 (sept, 1H), 2.93 (sept, 1H), 1.43-1.36 (m, 4H), 1.29-1.27 (dd, 18H), 0.76 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.93, 151.65, 149.25, 136.80, 133.37, 130.12, 129.46, 128.90, 128.36, 128.15, 123.34, 53.53, 43.53, 34.19, 29.55, 24.86, 24.81, 23.76, 21.66, 11.15; HRMS (FAB) m/z calcd. for $\text{C}_{26}\text{H}_{39}\text{N}_2\text{O}_2\text{S}$ [$M+H$] $^+$: 443.2732, found: 443.2731.

***N*-(naphthalen-1-yl)-2-phenyl-*N*-tosylacetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f : 0.42) to afford **16** as white solid (**A**: 2 mg, 2% yield, **B**: 57 mg, 76% yield, a mixture of two isomers with a ratio 1:4, which is tentatively assigned as Z/E of the generated imino C=N double bond). ^1H NMR (400 MHz, CDCl_3): δ 10.06 (br, 1H), 7.95-7.88 (q, 4H), 7.68-7.65 (d, 1H), 7.56-7.50 (t, 1H), 7.49-7.46 (d, 1H), 7.43-7.39 (t, 1H), 7.37-7.34 (d, 2H), 7.16-7.14 (d, 1H), 7.08-7.05 (d, 1H), 7.01-6.99 (t, 2H), 6.75-6.72 (d, 2H), 3.49 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.26, 143.30, 139.28, 134.44, 134.24, 132.41, 129.56, 129.39, 128.82, 128.45, 128.31, 127.64, 127.04, 127.01, 126.73, 125.92, 125.20, 122.10, 40.71, 21.72; HRMS (FAB) m/z calcd. for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_2\text{SNa}$ [$M+\text{Na}$] $^+$: 437.1300, found: 437.1297.

***N*-propyl-2-(p-tolyl)-*N*-tosylacetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f : 0.35) to afford **29** as white solid (53 mg, 89% yield, a mixture of two isomers with a ratio 1:6, which is tentatively assigned as Z/E of the generated imino C=N double bond). ^1H NMR (400 MHz, CDCl_3): δ 7.91-7.88 (d, 2H), 7.32-7.30 (d, 2H), 7.21-7.19 (d, 2H), 7.11-7.08 (d, 2H), 5.23 (br, 1H), 4.26 (s, 2H), 3.23-3.18 (m, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 1.45-1.39 (m, 2H), 0.78 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.04, 143.65, 142.18, 141.02, 139.29, 138.14, 130.25, 130.21, 129.82, 129.29, 126.57, 126.48, 43.74, 39.48, 21.68, 21.63, 21.24, 11.26; HRMS (FAB) m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2\text{SNa}$ [$M+\text{Na}$] $^+$: 367.1456, found: 367.1454.

***N*-isopropyl-2-phenyl-*N*-tosylacetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (1:1, R_f : 0.45) to afford **30** as white solid (**A**: 23 mg, 39% yield, **B**: 56 mg, 94% yield, a mixture of two isomers with a ratio 1:6, which is tentatively assigned as Z/E of the generated imino C=N double bond). ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.87 (d, 2H), 7.43-7.34 (m, 3H), 7.31-7.28 (dd, 2H), 7.22-7.20 (dd, 2H), 4.97 (br, 1H), 4.29 (s, 2H), 4.12 (sept, 1H), 2.44 (s, 3H), 1.03 (d, 6H); ^{13}C NMR (100 MHz, CDCl_3):

δ 165.49, 142.06, 140.96, 133.28, 129.96 129.37, 129.19, 128.03, 126.30, 43.92, 39.68, 21.63, 21.50. These spectroscopic data are consistent with those previously reported in the literature.¹⁰

***N*-propyl-*N*-tosyl-2-(4-(trifluoromethyl)phenyl)acetimidamide**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (2:1, R_f : 0.53) to afford **31** as white solid (54 mg, 90% yield, a mixture of two isomers with a ratio 1:3 which is tentatively assigned as Z/E of the generated imino C=N double bond). ¹H NMR (400 MHz, CDCl₃): δ 7.87-7.85 (d, 2H), 7.70-7.64 (d, 2H), 7.40-7.37 (d, 2H), 7.30 (s, 2H) 5.08 (br, 1H), 4.40 (s, 2H), 3.27-3.22 (m, 2H), 2.44 (s, 3H), 1.49-1.43 (m, 2H), 0.81 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.29, 142.40, 140.69, 137.73, 137.72, 130.35, 129.45, 129.30, 128.92, 126.39, 126.36, 126.33, 126.29, 126.25, 125.90, 125.86, 125.82, 43.96, 39.51, 21.72, 21.72, 11.31; HRMS (FAB) m/z calcd. for C₁₉H₂₁F₃N₂O₂SNa [$M+Na$]⁺ : 421.1174, found: 421.1171.

References

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3. Au-catalyzed hydroamination

Typical procedure (A, heterogeneous catalyst): To dioxane (0.18 mL) in a vessel was added MOF_{AuCl} (2.7 mg, 2.7 μmol , 3 mol%), AgOTf (1.5 mg, 5.5 μmol , 6 mol%), alkyne (0.091 mmol, 1 eq) under N_2 atmosphere, and then, aniline (0.11 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at 70 °C for 5 h. The crude compound was isolated by silica column chromatography.

Typical procedure (B, homogeneous catalyst): To dioxane (0.18 mL) in a vessel was added IPrAuCl (Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]silver(I)) (1.7 mg, 2.7 μmol , 3 mol%), AgOTf (1.5 mg, 5.5 μmol , 6 mol%), alkyne (0.091 mmol, 1 eq) under N_2 atmosphere, and then, aniline (0.11 mmol, 1.2 eq) was added slowly to the above vessel. The reaction mixture was stirred at 70 °C for 5 h. The crude compound was isolated by silica column chromatography.

N-(1-phenylethylidene)aniline

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.44) to afford **17** as yellow solid (**A**: 33 mg, 93% yield, **B**: 35 mg, 99% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.03-8.00 (m, 2H), 7.51-7.37 (m, 5H), 7.15-7.10 (m, 1H), 6.85-6.83 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.59, 151.82, 139.62, 130.59, 129.08, 128.49, 127.30, 123.33, 119.50, 17.49. These spectroscopic data are consistent with those previously reported in the literature.¹¹

4-nitro-*N*-(1-phenylethylidene)aniline

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.21) to afford **18** as yellow solid (39 mg, 91% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.27-8.25 (d, 2H), 8.00-7.99 (d, 2H), 7.52-7.49 (m, 3H), 6.92-6.89 (d, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.40, 157.89, 143.85, 138.36, 131.40, 128.67, 127.50, 125.26, 119.70, 18.00. These spectroscopic data are consistent with those previously reported in the literature.¹⁴

4-methoxy-*N*-(1-phenylethylidene)aniline

The reaction mixture was stirred at room temperature for 5 h. The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.24) to afford **19** as yellow solid (25 mg, 62% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.01-7.98 (m, 2H), 7.48-7.46 (m, 3H), 6.96-6.93 (d, 2H), 6.80-6.78 (d, 2H), 3.84 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.88, 156.08, 144.84, 139.83, 130.45, 128.45, 127.23, 120.88, 114.36, 55.58, 17.42. These spectroscopic data are consistent with those previously reported in the literature.¹³

***N*-(1-(4-nitrophenyl)ethylidene)aniline**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.23) to afford **20** as white solid (10 mg, 32% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.33-8.30 (d, 2H), 8.17-8.15 (d, 2H) 7.42-7.38 (m, 2H), 7.18-7.13 (m, 1H), 6.84-6.81 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.81, 150.90, 149.12, 145.08, 129.25, 128.30, 124.11, 123.70, 119.22, 17.66. These spectroscopic data are consistent with those previously reported in the literature.¹²

***N*-(1-(4-methoxyphenyl)ethylidene)aniline**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.26) to afford **21** as yellow solid (33 mg, 94% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.93-7.90 (d, 2H), 7.39-7.34 (t, 2H) 7.12-7.08 (m, 1H), 7.13-7.10 (t, 1H), 6.99-6.97 (m, 2H), 3.89 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.70, 161.69, 151.92, 132.28, 129.03, 128.98, 123.17, 119.76, 113.73, 55.51, 17.29. These spectroscopic data are consistent with those previously reported in the literature.¹³

4-(*tert*-butyl)-*N*-(1-phenylethylidene)aniline

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.42) to afford **22** as yellow solid (**A**: 11 mg, 24% yield, **B**: 44 mg, 96% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.03-7.99 (m, 2H), 7.48-7.46 (m, 3H), 7.42-7.39 (d, 2H), 6.80-6.76 (d, 2H), 2.29 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.43, 149.03, 146.15, 139.79, 130.47, 128.46, 127.30, 125.85, 119.23, 34.42, 31.65, 17.50. These spectroscopic data are consistent with those previously reported in the literature.¹³

2,6-diisopropyl-*N*-(1-phenylethylidene)aniline

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.56) to afford **23** as yellow solid (**A**: 11 mg, 21% yield, **B**: 45 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3): δ 8.08-8.06 (m, 2H), 7.52-7.50 (m, 3H), 7.19-7.08 (m, 3H), 2.78 (sept, 2H), 2.13 (s, 3H), 1.17 (t, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.93, 146.86, 139.26, 136.24, 130.52, 128.54, 127.27, 123.45, 123.08, 28.35, 23.27, 23.08, 18.22. These spectroscopic data are consistent with those previously reported in the literature.¹⁵

***N*-(1-phenylethylidene)naphthalen-1-amine**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f : 0.38) to afford **24** as yellow solid (**A**: 9 mg, 20% yield, **B**: 43 mg, 97% yield). ^1H NMR (400

MHz, CDCl₃): δ 8.18-8.16 (m, 2H), 7.91-7.89 (d, 1H), 7.84-7.81 (dd, 1H), 7.66-7.63 (d, 1H), 7.60-7.42 (m, 6H), 6.84 (dd, 1H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.66, 148.03, 139.36, 134.34, 130.83, 128.60, 128.11, 127.46, 126.24, 126.02, 125.54, 123.71, 123.41, 113.65, 17.83. These spectroscopic data are consistent with those previously reported in the literature.¹⁴

***N*-(1-(*p*-tolyl)ethylidene)aniline**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f: 0.48) to afford **32** as yellow solid (30 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.93-7.90 (d, 2H), 7.39-7.35 (t, 2H) 7.29-7.27 (t, 2H), 7.13-7.10 (t, 1H), 6.86-6.84 (d, 2H), 2.44 (s, 3H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.06, 151.29, 141.20, 136.57, 129.26, 129.11, 127.47, 123.55, 119.88, 21.54, 17.57. These spectroscopic data are consistent with those previously reported in the literature.¹³

***N*-(1-(4-(trifluoromethyl)phenyl)ethylidene)aniline**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f: 0.36) to afford **33** as yellow solid (17 mg, 53% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.12-8.10 (d, 2H), 7.74-7.71 (d, 2H) 7.42-7.38 (m, 2H), 7.17-7.12 (m, 1H), 6.84-6.81 (m, 2H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.48, 151.22, 142.75, 132.43, 132.11, 129.20, 127.69, 125.53, 125.49, 125.45, 125.42, 123.82, 119.34, 17.58. These spectroscopic data are consistent with those previously reported in the literature.¹²

***N*-(1-phenylethylidene)-4-(trifluoromethyl)aniline**

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f: 0.40) to afford **34** as yellow solid (43 mg, 90% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.01-8.00 (d, 2H), 7.64-7.62 (d, 2H), 7.51-7.47 (m, 3H), 6.92-6.90 (d, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.62, 154.69, 138.84, 131.17, 128.64, 127.47, 126.49, 126.46, 126.42, 126.38, 125.97, 125.79, 125.47, 123.27, 119.67, 17.79. These spectroscopic data are consistent with those previously reported in the literature.¹⁴

4-methyl-*N*-(1-phenylethylidene)aniline

The crude compound was isolated by silica column chromatography eluting with hexane/ethyl acetate (20:1, R_f: 0.24) to afford **35** as yellow solid (30 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.01-7.98 (m, 2H), 7.49-7.45 (m, 3H), 7.19-7.17 (d, 2H), 6.75-6.73 (d, 2H), 2.38 (s, 3H), 2.27(s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.85, 148.96, 139.69, 132.86, 130.57, 129.65, 128.49, 127.33, 119.61, 21.00, 17.49. These spectroscopic data are consistent with those previously reported in the literature.¹³

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Single crystal X-ray structure determination

Summary of crystal data and structure refinement for MOF_{CuCl}

Empirical formula	C ₁₂₃ H ₁₂₆ Cl ₃ Cu ₃ N ₇ O ₁₆ Zn ₄
Formula weight	2516.75
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 31.2209(16) Å α = 90°. b = 46.176(3) Å β = 101.183(2)°. c = 28.6618(16) Å γ = 90°.
Volume	40536(4) Å ³
Z	8
Density (calculated)	0.825 Mg/m ³
Absorption coefficient	0.852 mm ⁻¹
F(000)	10392
Crystal size	0.300 x 0.300 x 0.200 mm ³
Theta range for data collection	0.987 to 24.849°.
Index ranges	-36 ≤ h ≤ 31, -45 ≤ k ≤ 54, -33 ≤ l ≤ 33
Reflections collected	173590
Independent reflections	34821 [R(int) = 0.0581]
Completeness to theta = 24.849°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.848 and 0.754
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	34821 / 1296 / 1405
Goodness-of-fit on F ²	1.024
Final R indices [I > 2σ(I)]	R ₁ = 0.0936, wR ₂ = 0.2622
R indices (all data)	R ₁ = 0.1419, wR ₂ = 0.3130
Largest diff. peak and hole	1.239 and -1.601 e.Å ⁻³

Summary of crystal data and structure refinement for MOF_{CuBr}

Empirical formula	C ₁₂₆ H ₁₃₂ Br ₃ Cu ₃ N ₇ O ₁₅ Zn ₄
Formula weight	2676.21
Temperature	100(2) K
Wavelength	0.70000 Å

Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 31.173(6) Å	$\alpha = 90^\circ$.
	b = 45.755(9) Å	$\beta = 99.98(3)^\circ$.
	c = 28.545(6) Å	$\gamma = 90^\circ$.
Volume	40098(14) Å ³	
Z	8	
Density (calculated)	0.887 Mg/m ³	
Absorption coefficient	1.326 mm ⁻¹	
F(000)	10952	
Crystal size	0.200 x 0.200 x 0.200 mm ³	
Theta range for data collection	1.427 to 24.941°.	
Index ranges	-37 ≤ h ≤ 37, -55 ≤ k ≤ 53, -34 ≤ l ≤ 34	
Reflections collected	64931	
Independent reflections	36032 [R(int) = 0.0526]	
Completeness to theta = 24.835°	98.1 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.839	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	36032 / 1303 / 1424	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2sigma(I)]	R ₁ = 0.1136, wR ₂ = 0.3243	
R indices (all data)	R ₁ = 0.1682, wR ₂ = 0.3494	
Largest diff. peak and hole	1.196 and -1.284 e.Å ⁻³	

Summary of crystal data and structure refinement for MOF_{CuI}

Empirical formula	C ₁₂₃ H ₁₂₆ Cu ₃ I ₃ N ₇ O ₁₆ Zn ₄		
Formula weight	2791.10		
Temperature	100(2) K		
Wavelength	0.70000 Å		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 31.335(6) Å	α= 90°.	
	b = 46.201(9) Å	β= 101.00(3)°.	
	c = 28.670(6) Å	γ= 90°.	
Volume	40743(15) Å ³		
Z	8		
Density (calculated)	0.910 Mg/m ³		
Absorption coefficient	1.157 mm ⁻¹		

F(000)	11256
Crystal size	0.300 x 0.300 x 0.200 mm ³
Theta range for data collection	1.456 to 29.866°.
Index ranges	-44≤h≤44, -65≤k≤65, -40≤l≤40
Reflections collected	112334
Independent reflections	60369 [R(int) = 0.0475]
Completeness to theta = 24.835°	98.4 %
Absorption correction	Empirical
Max. and min. transmission	1.000 and 0.875
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	60369 / 1224 / 1425
Goodness-of-fit on F ²	1.020
Final R indices [I>2sigma(I)]	R ₁ = 0.1282, wR ₂ = 0.3383
R indices (all data)	R ₁ = 0.1657, wR ₂ = 0.3546
Largest diff. peak and hole	1.519 and -2.238 e.Å ⁻³

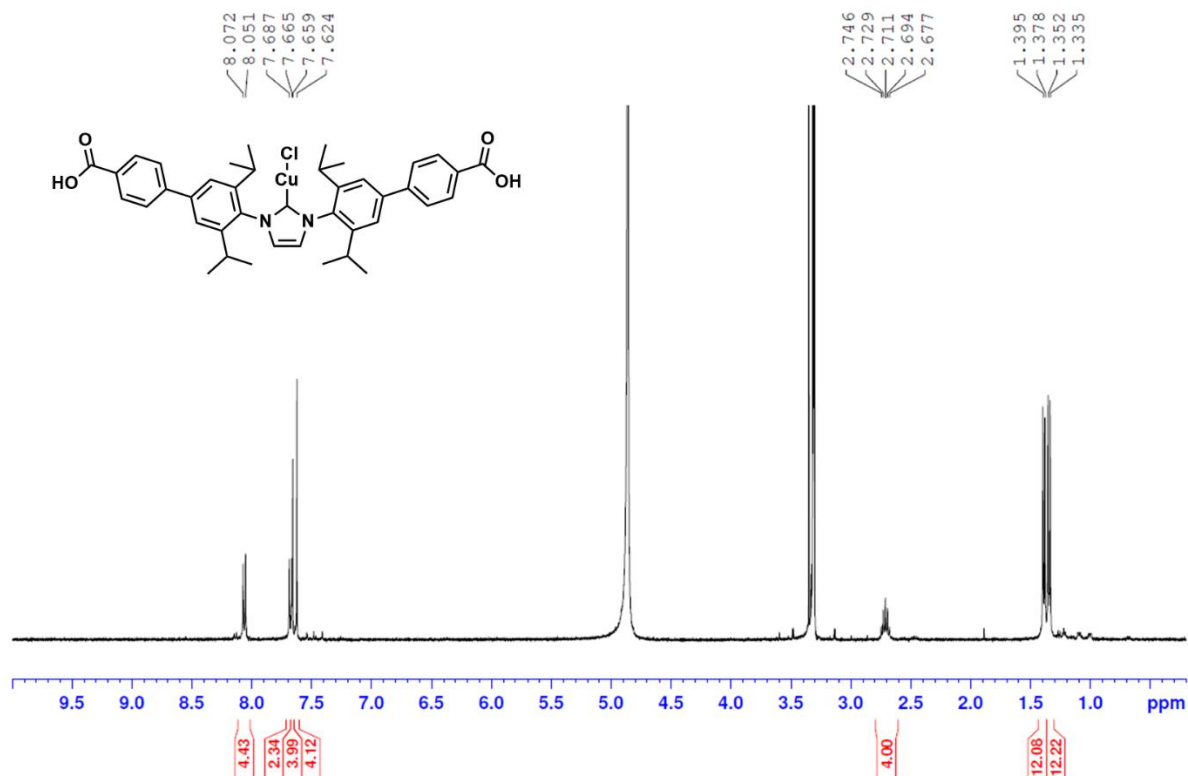
Summary of crystal data and structure refinement for MOF_{AuCl}

Empirical formula	C ₁₂₃ H ₁₂₄ Au ₃ Cl ₃ N ₇ O ₁₆ Zn ₄	
Formula weight	2915.01	
Temperature	100(2) K	
Wavelength	0.70000 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 31.303(6) Å	α = 90°.
	b = 46.242(9) Å	β = 101.08(3)°.
	c = 28.703(6) Å	γ = 90°.
Volume	40773(15) Å ³	
Z	8	
Density (calculated)	0.950 Mg/m ³	
Absorption coefficient	2.496 mm ⁻¹	
F(000)	11576	
Crystal size	0.200 x 0.200 x 0.200 mm ³	
Theta range for data collection	1.456 to 29.873°.	
Index ranges	-44≤h≤44, -64≤k≤65, -40≤l≤40	
Reflections collected	115768	
Independent reflections	61044 [R(int) = 0.0276]	
Completeness to theta = 24.835°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.805	

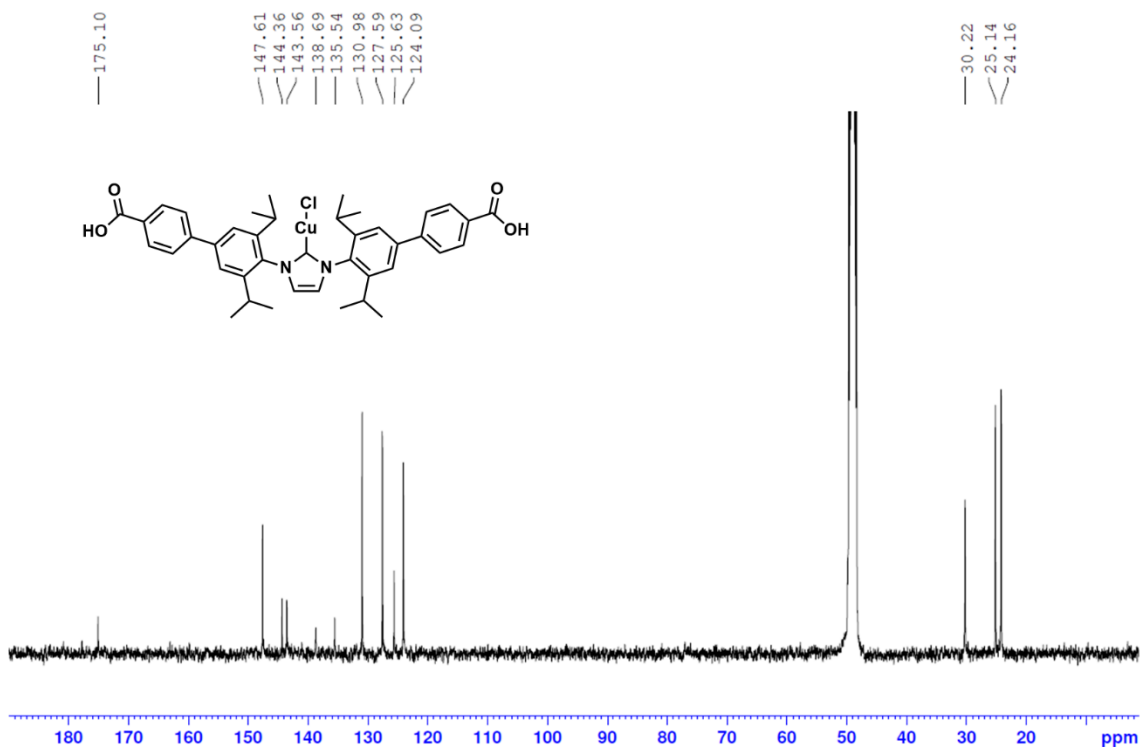
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	61044 / 1453 / 1405
Goodness-of-fit on F^2	1.119
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0921$, $wR_2 = 0.2908$
R indices (all data)	$R_1 = 0.1053$, $wR_2 = 0.3056$
Largest diff. peak and hole	2.388 and -4.858 e.Å ⁻³

^1H and ^{13}C NMR spectra

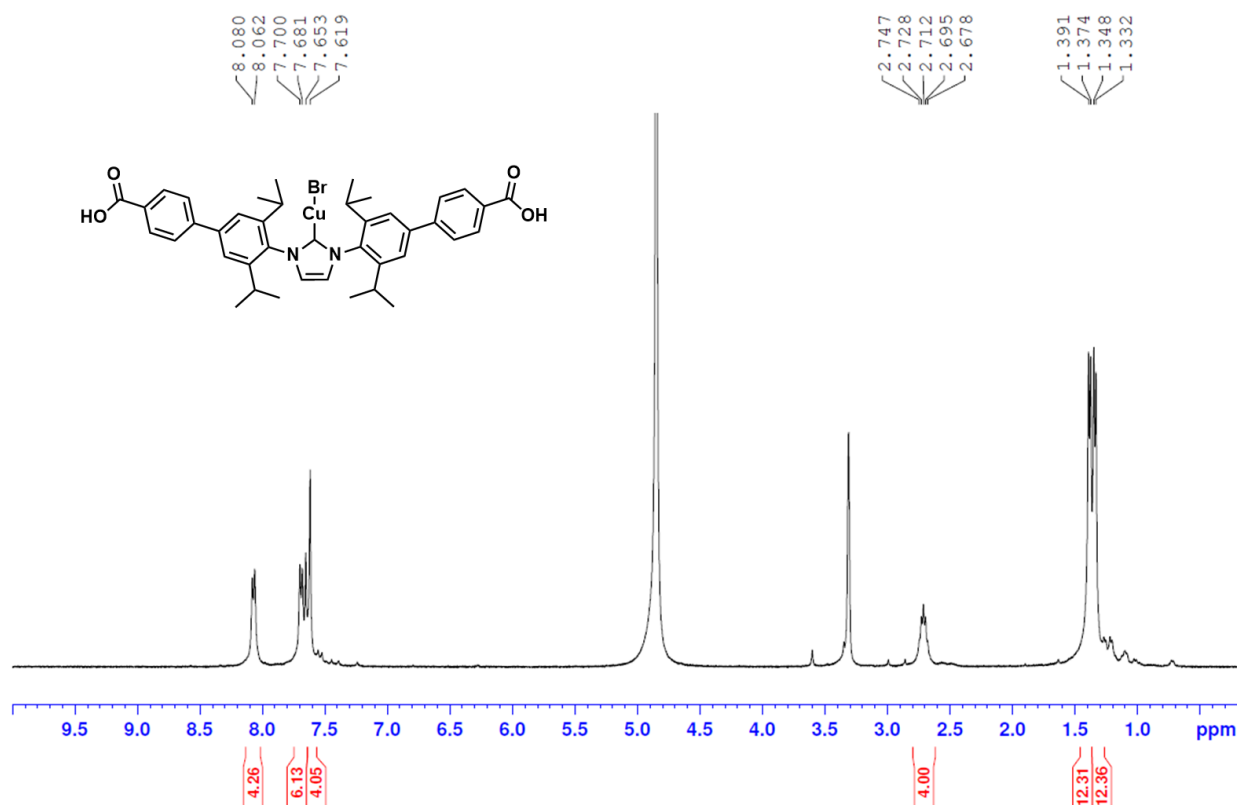
^1H NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) chloride (NHC-CuCl)



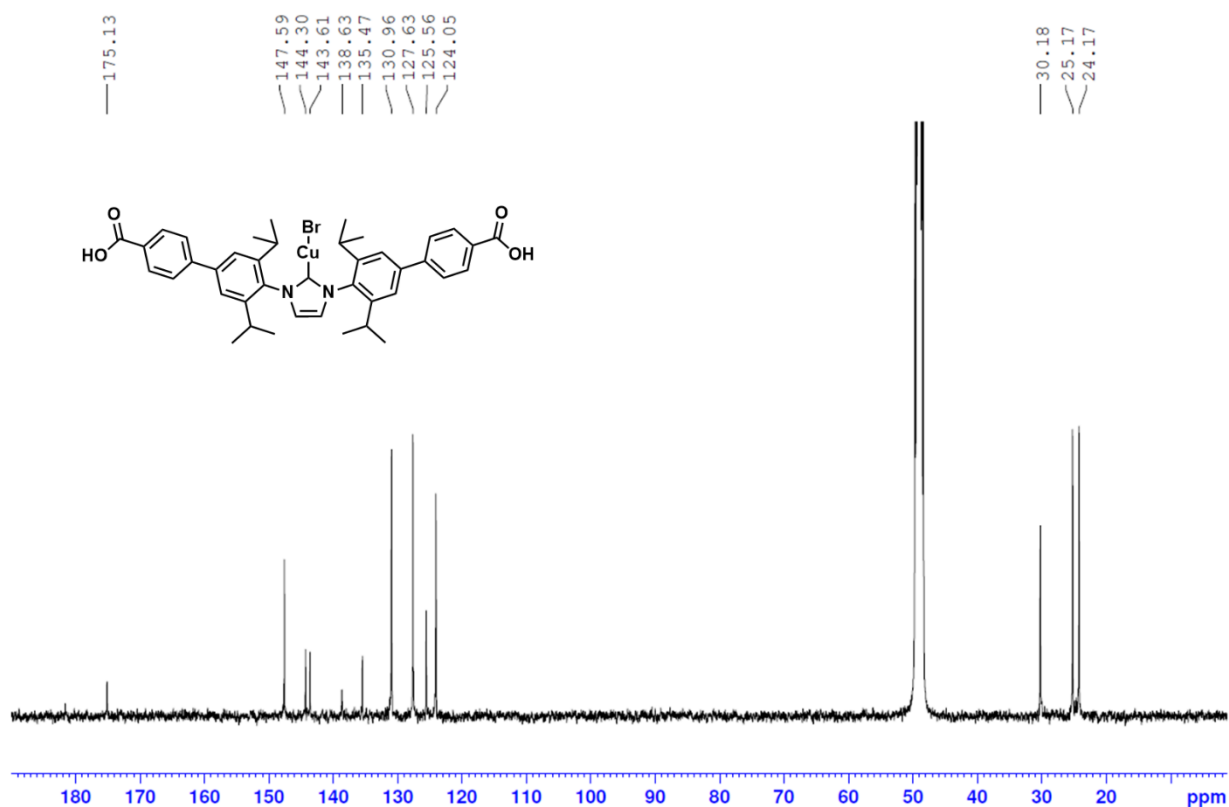
^{13}C NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) chloride (NHC-CuCl)



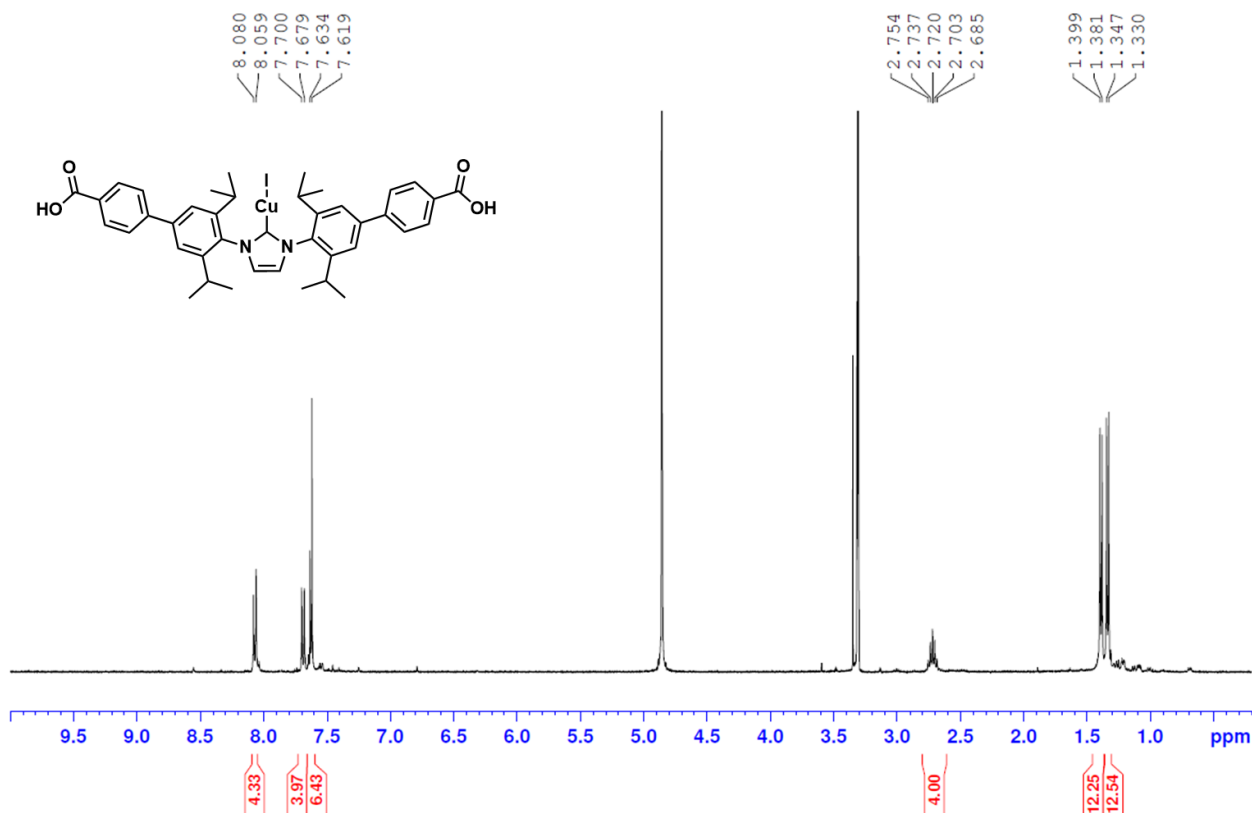
^1H NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) bromide (NHC-CuBr)



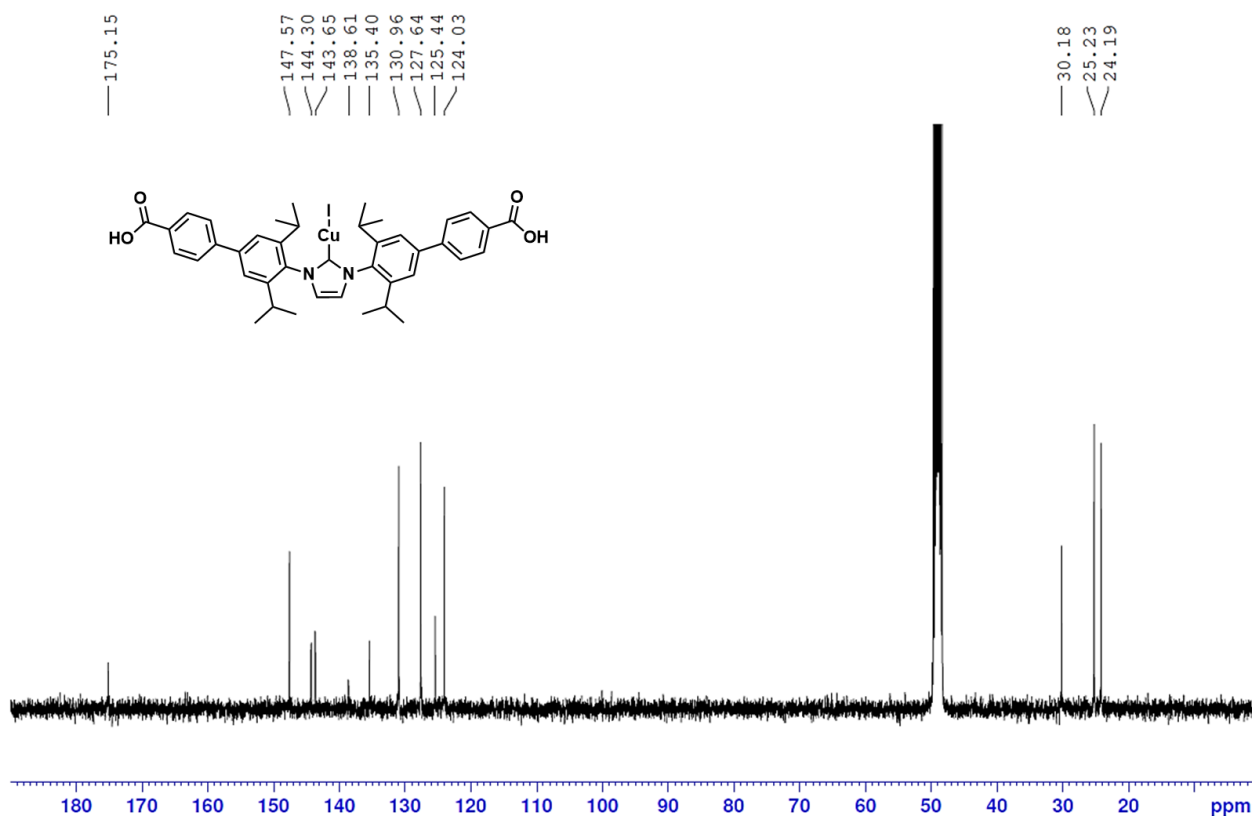
^{13}C NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) bromide (NHC-CuBr)



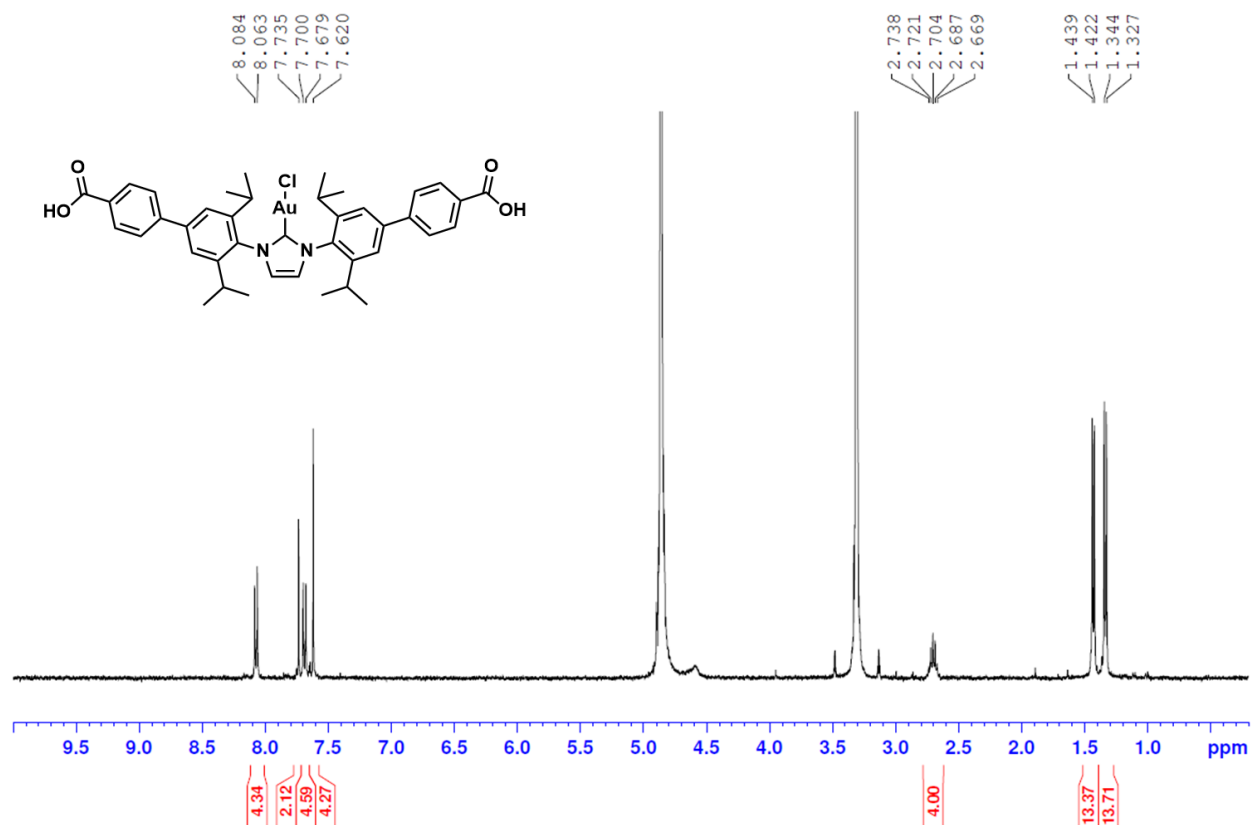
^1H NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) iodide (NHC-CuI)



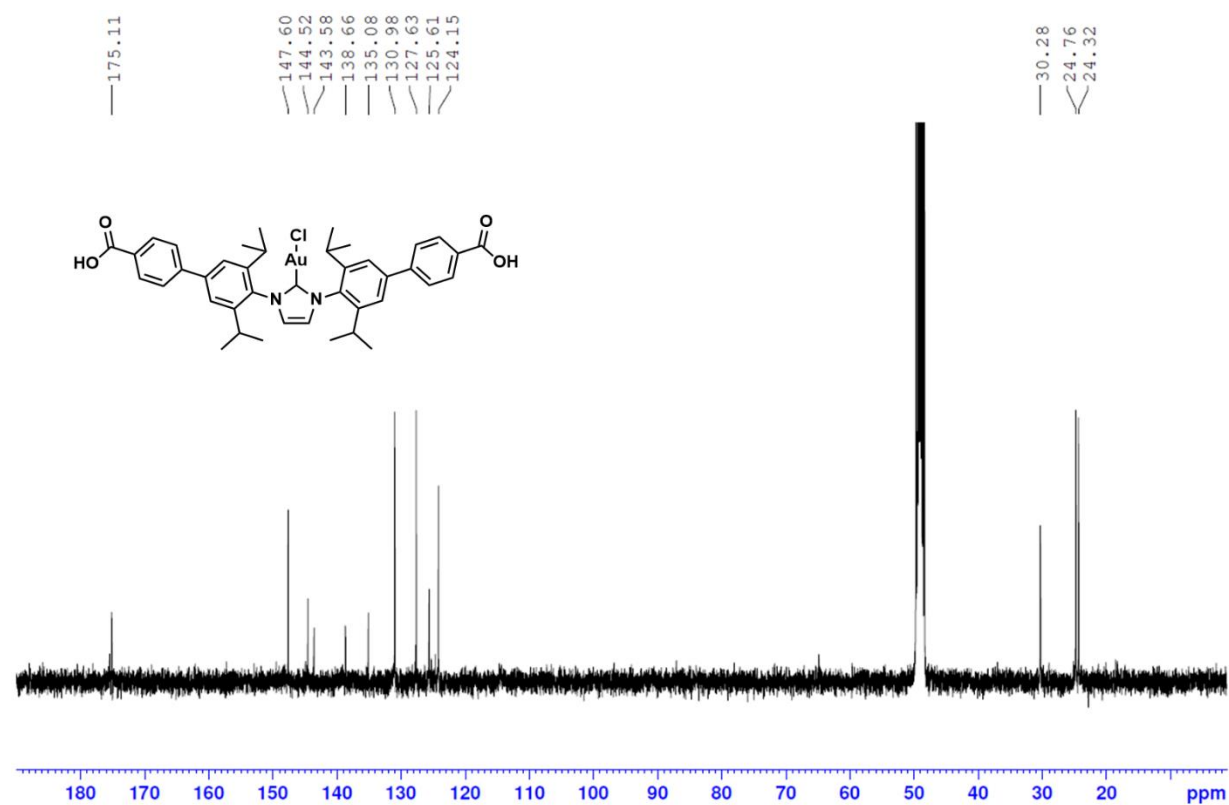
^{13}C NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) iodide (NHC-CuI)



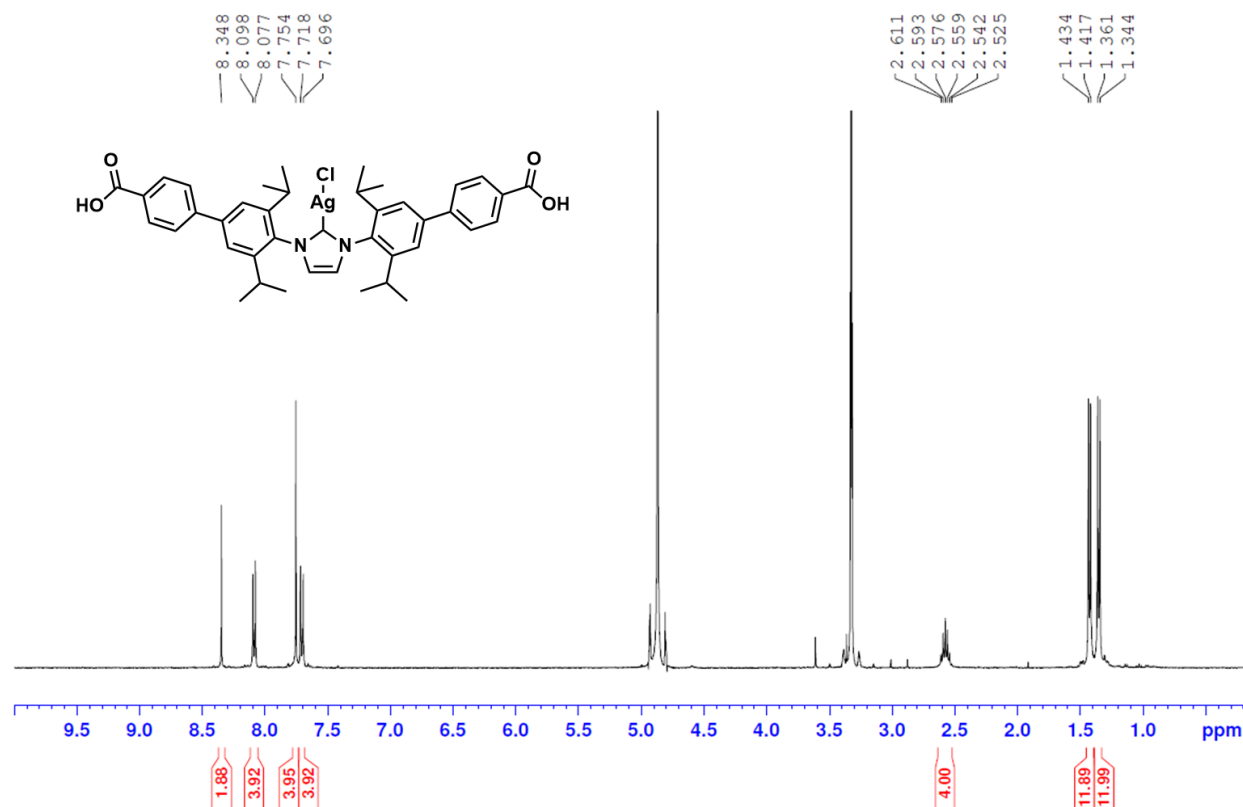
¹H NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl gold(I) chloride (NHC-AuCl)



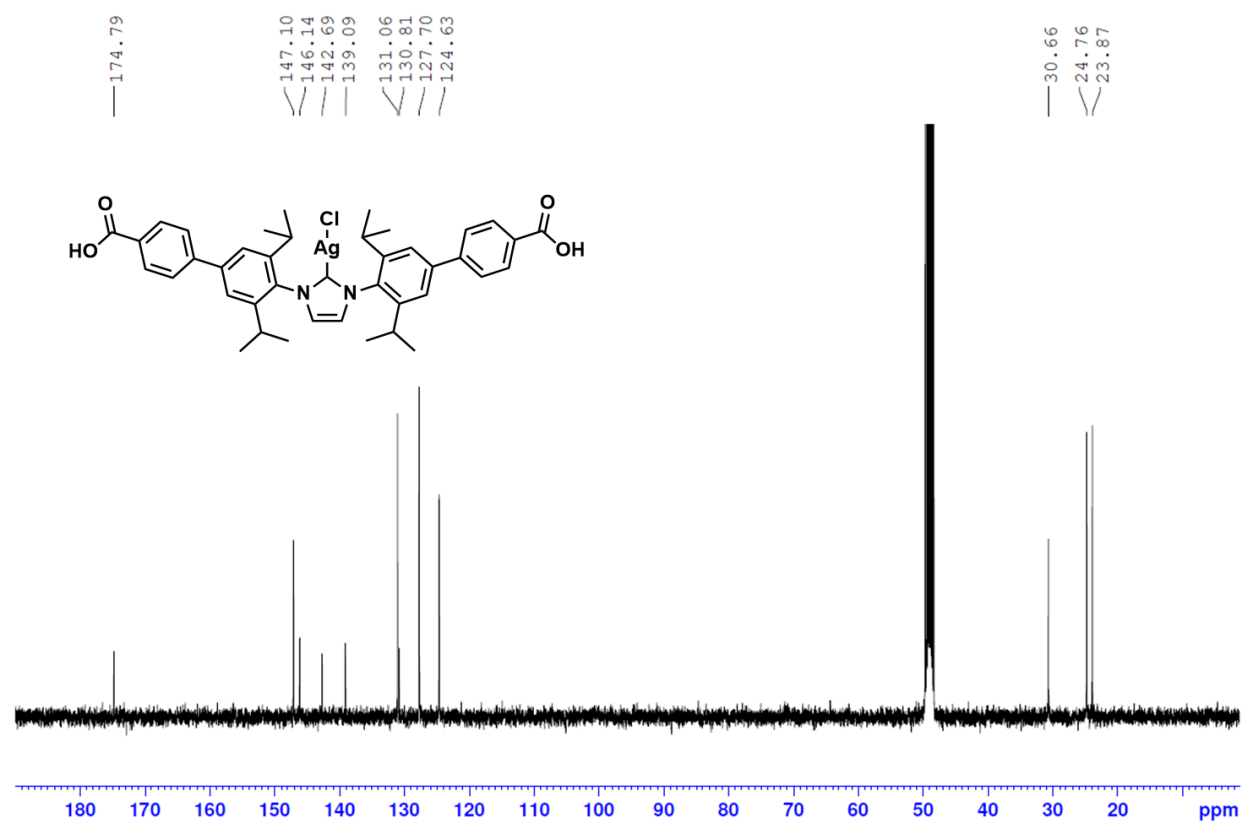
¹³C NMR spectrum of 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl gold(I) chloride (NHC-AuCl)



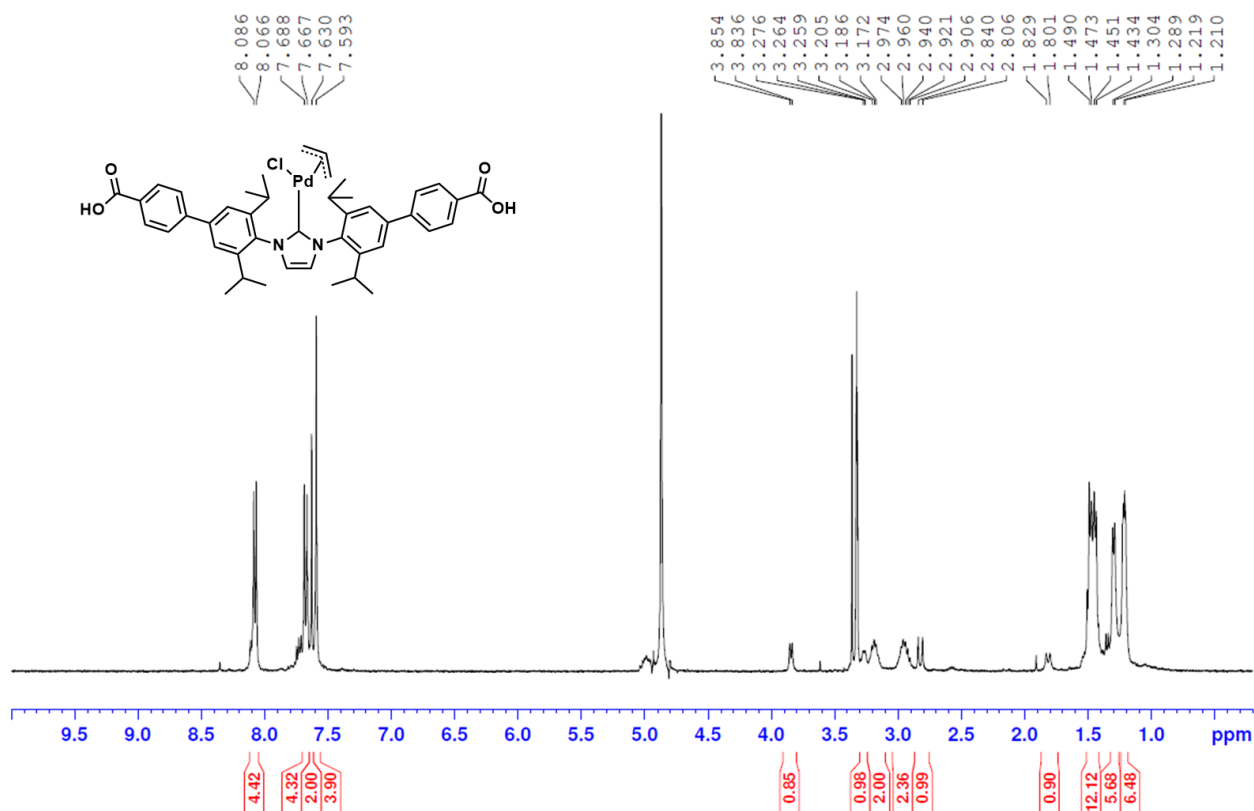
¹H NMR spectrum of (1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl)silver(I) chloride



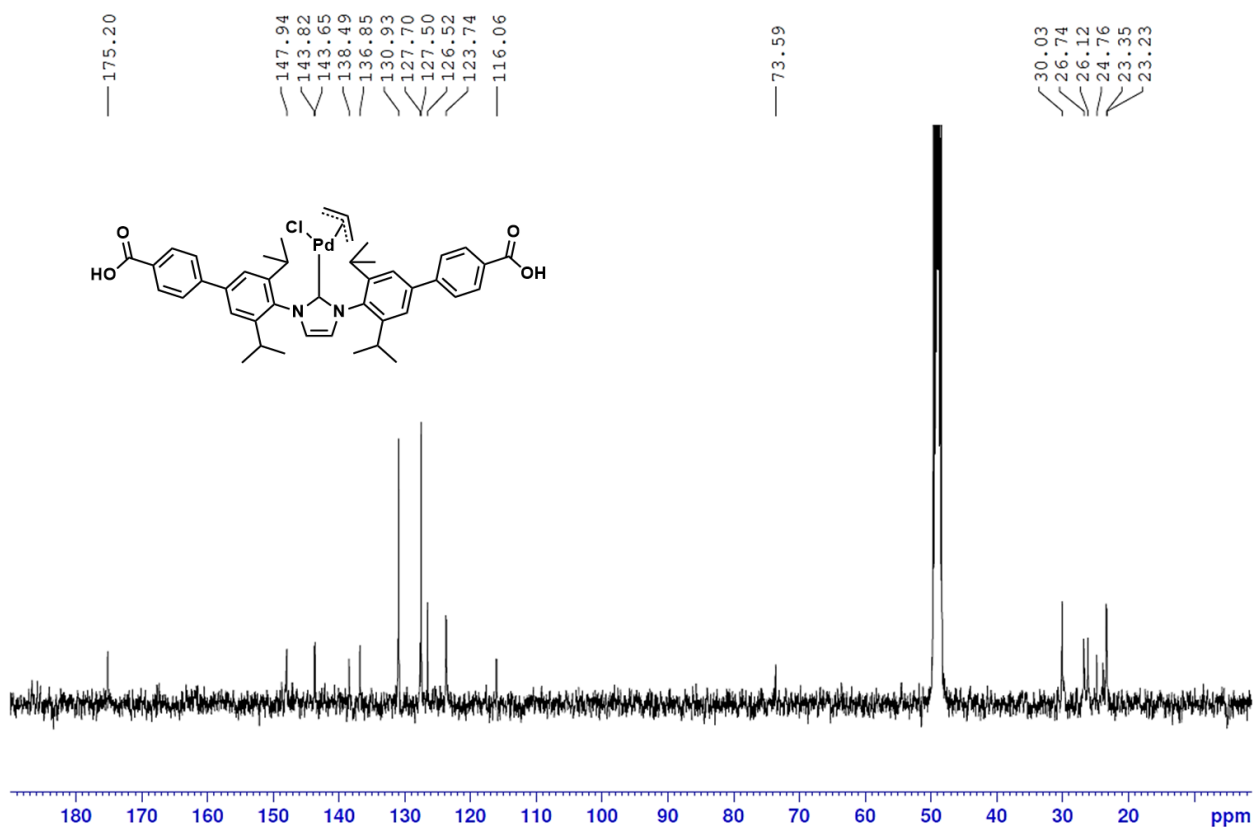
¹³C NMR spectrum of (1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl)silver(I) chloride



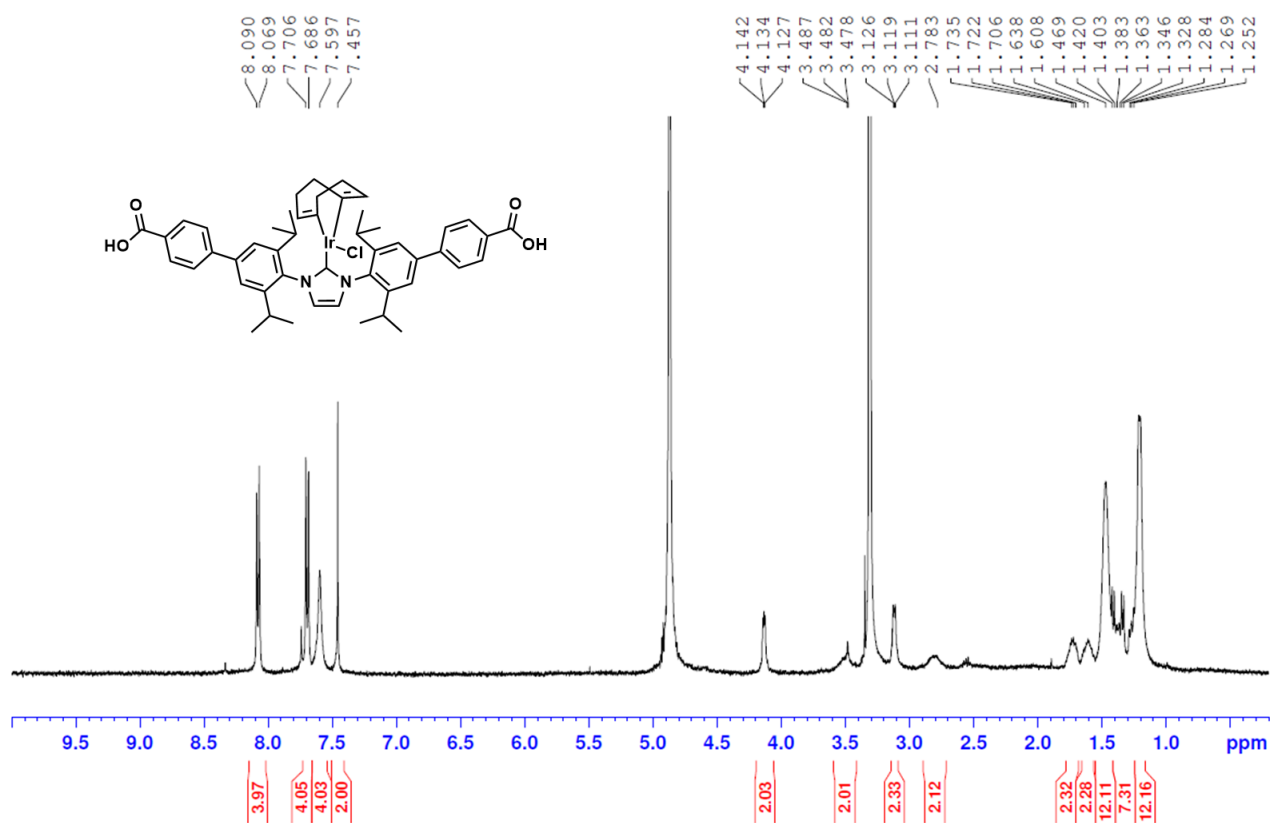
¹H NMR spectrum of Allyl(1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl)Chloropalladium(II)



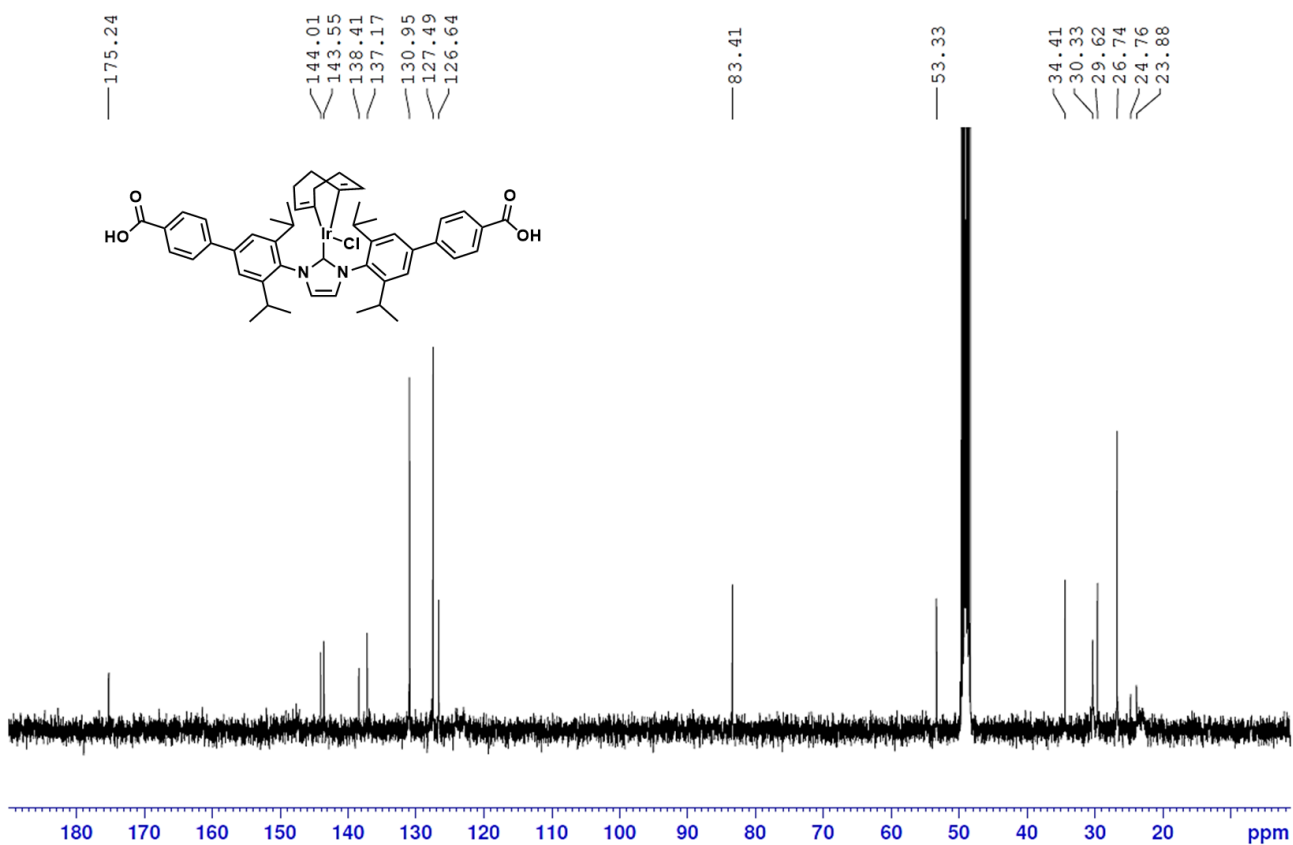
¹³C NMR spectrum of Allyl(1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl)Chloropalladium(II)



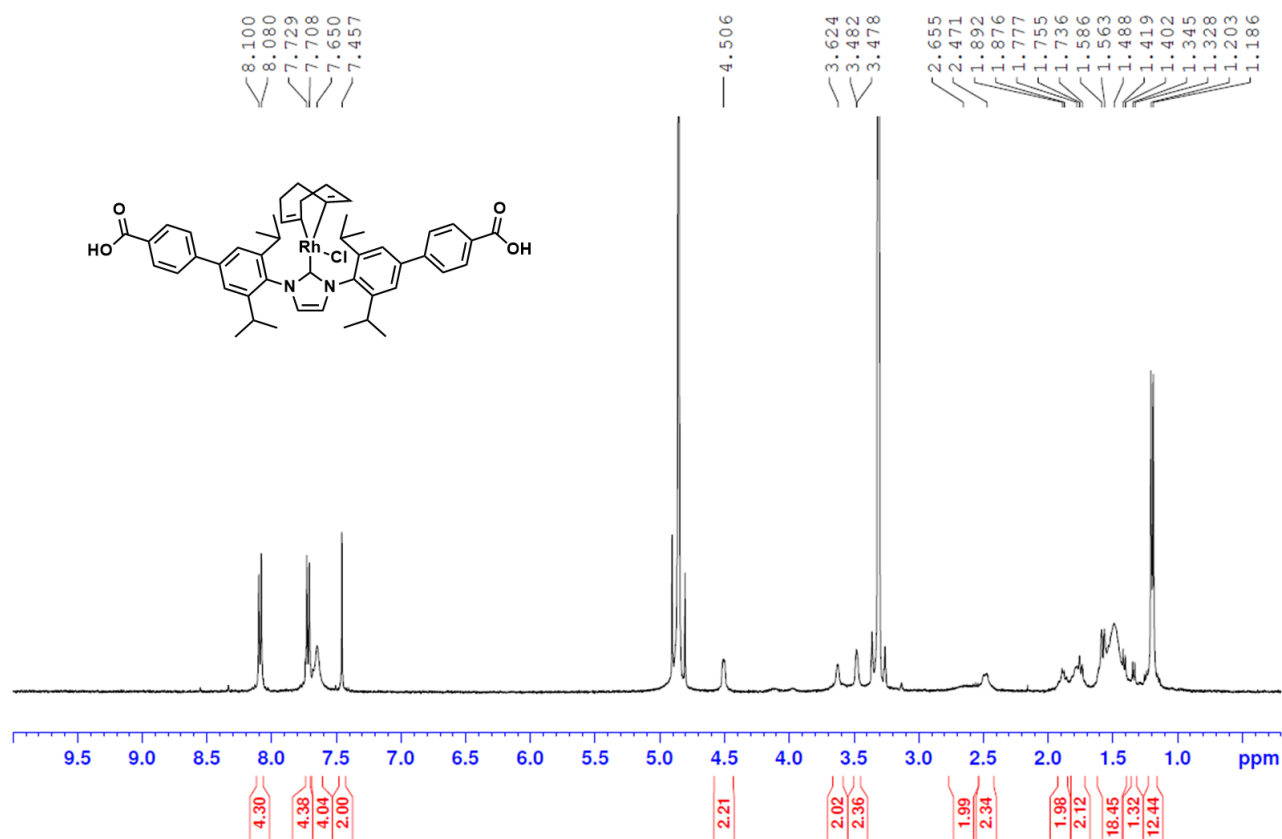
^1H NMR spectrum of $[(\text{IPr})(\text{CO}_2\text{H})_2\text{IrCl}(\text{COD})]$



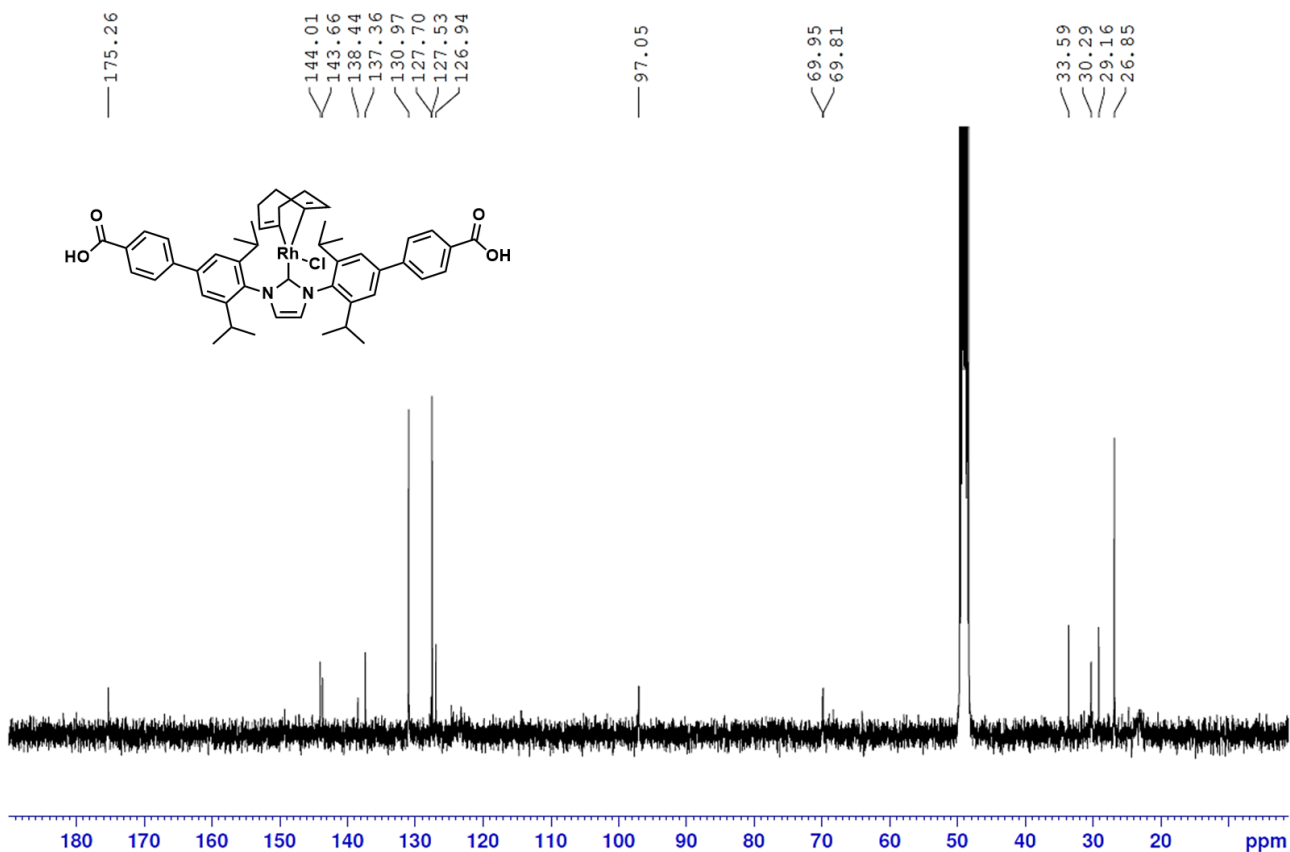
^{13}C NMR spectrum of $[(\text{IPr})(\text{CO}_2\text{H})_2\text{IrCl}(\text{COD})]$



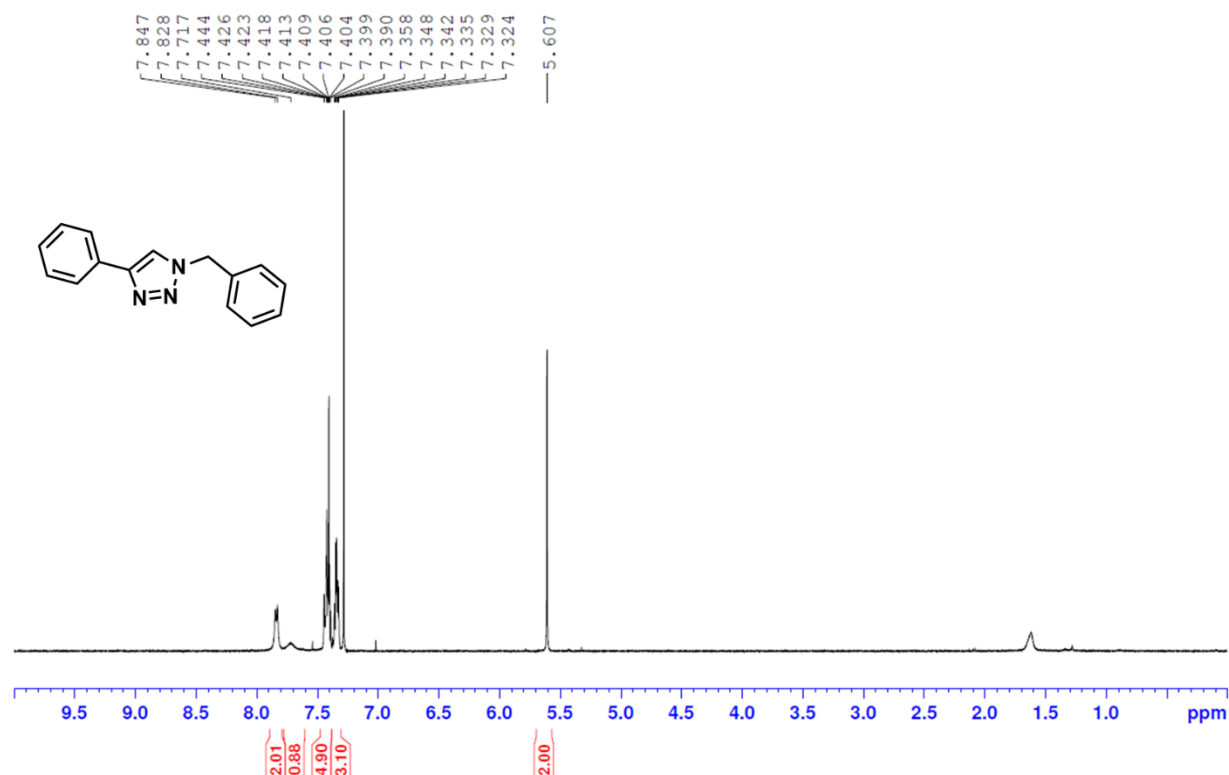
^1H NMR spectrum of $[(\text{IPr})(\text{CO}_2\text{H})_2\text{IrCl}(\text{COD})]$



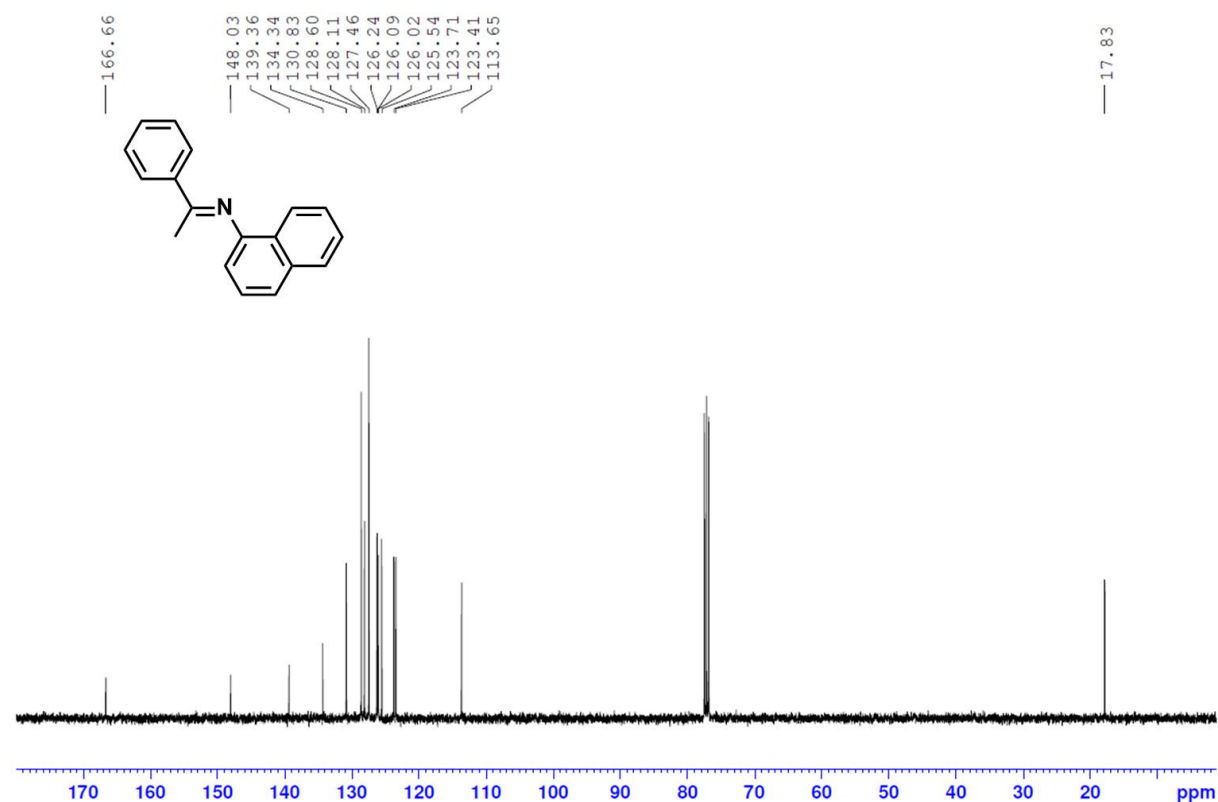
^{13}C NMR spectrum of $[(\text{IPr})(\text{CO}_2\text{H})_2\text{IrCl}(\text{COD})]$



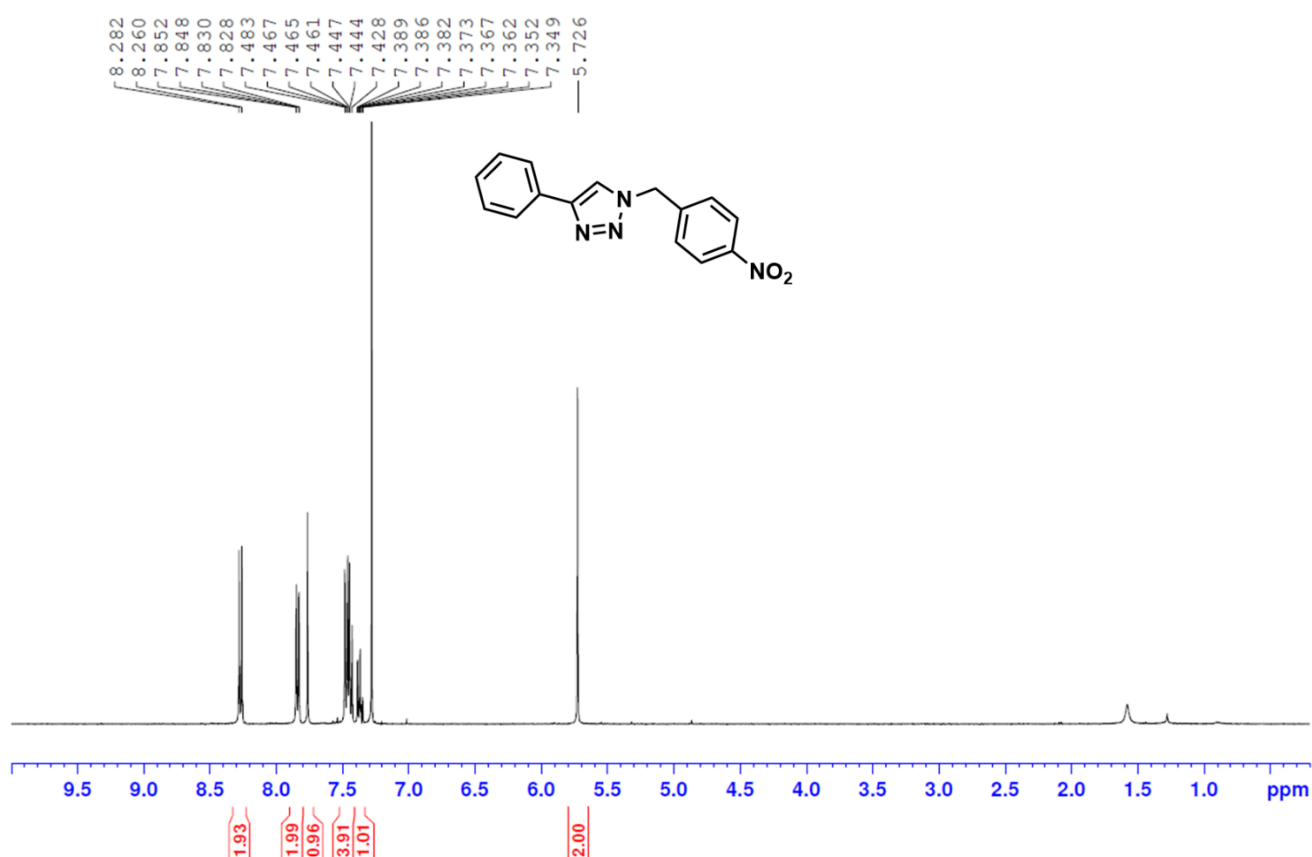
¹H NMR spectrum of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole



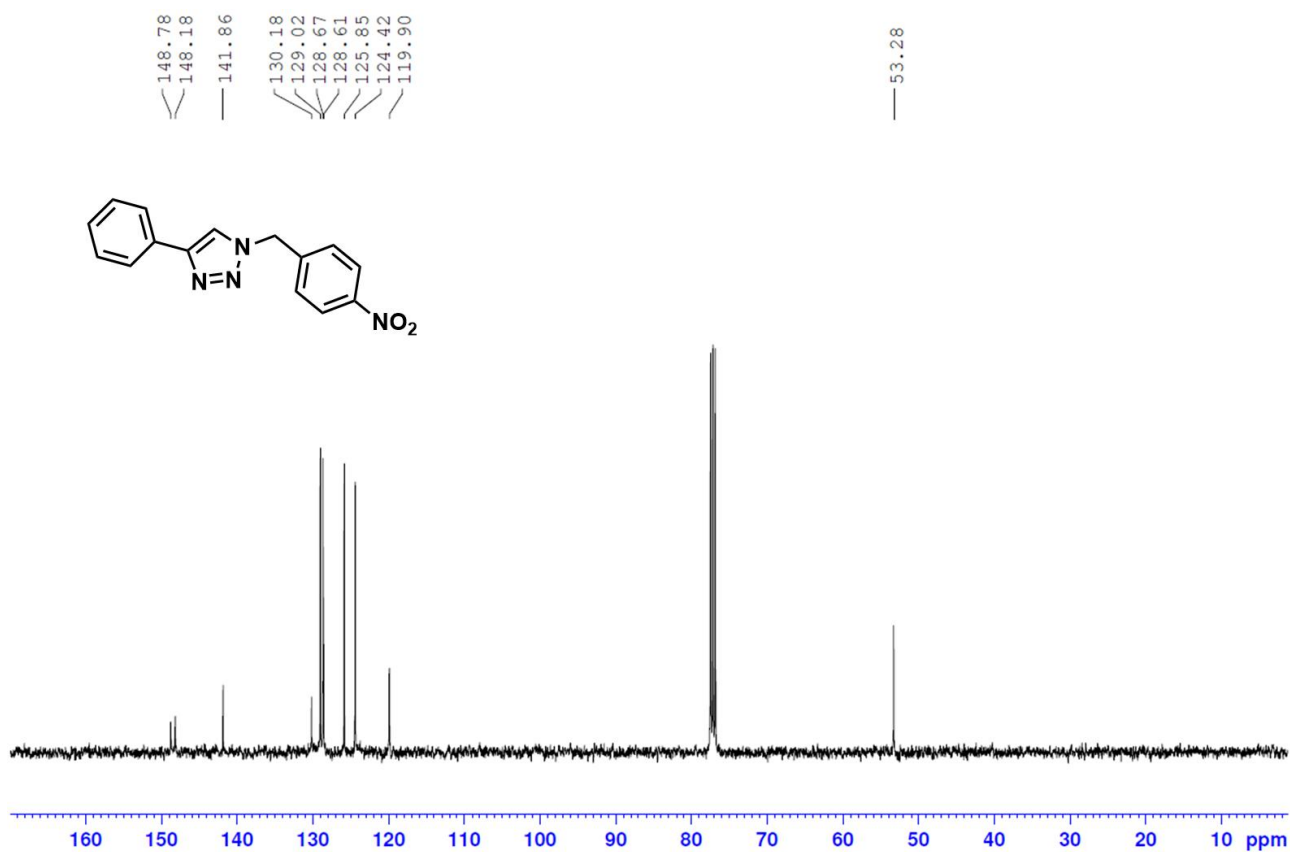
¹³C NMR spectrum of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole



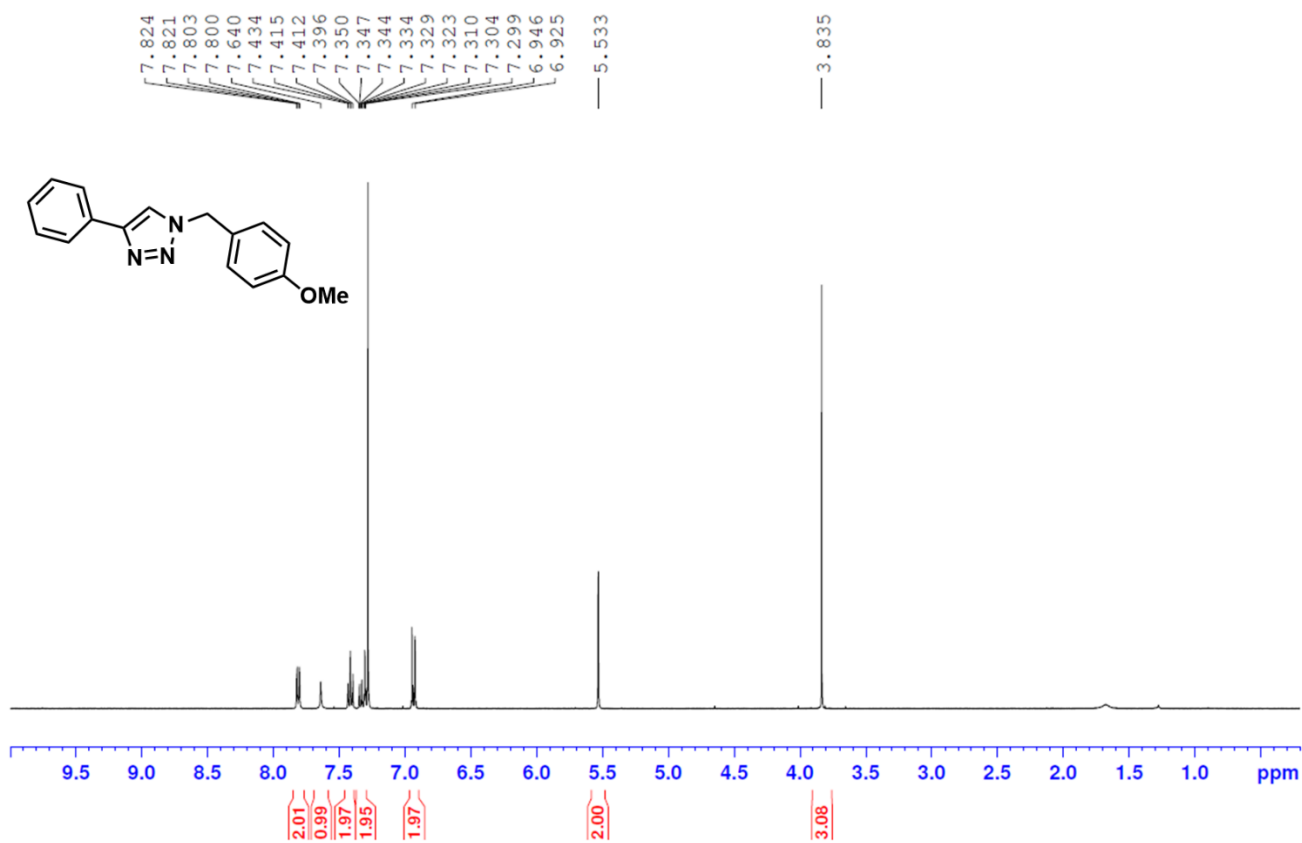
¹H NMR spectrum of 1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole



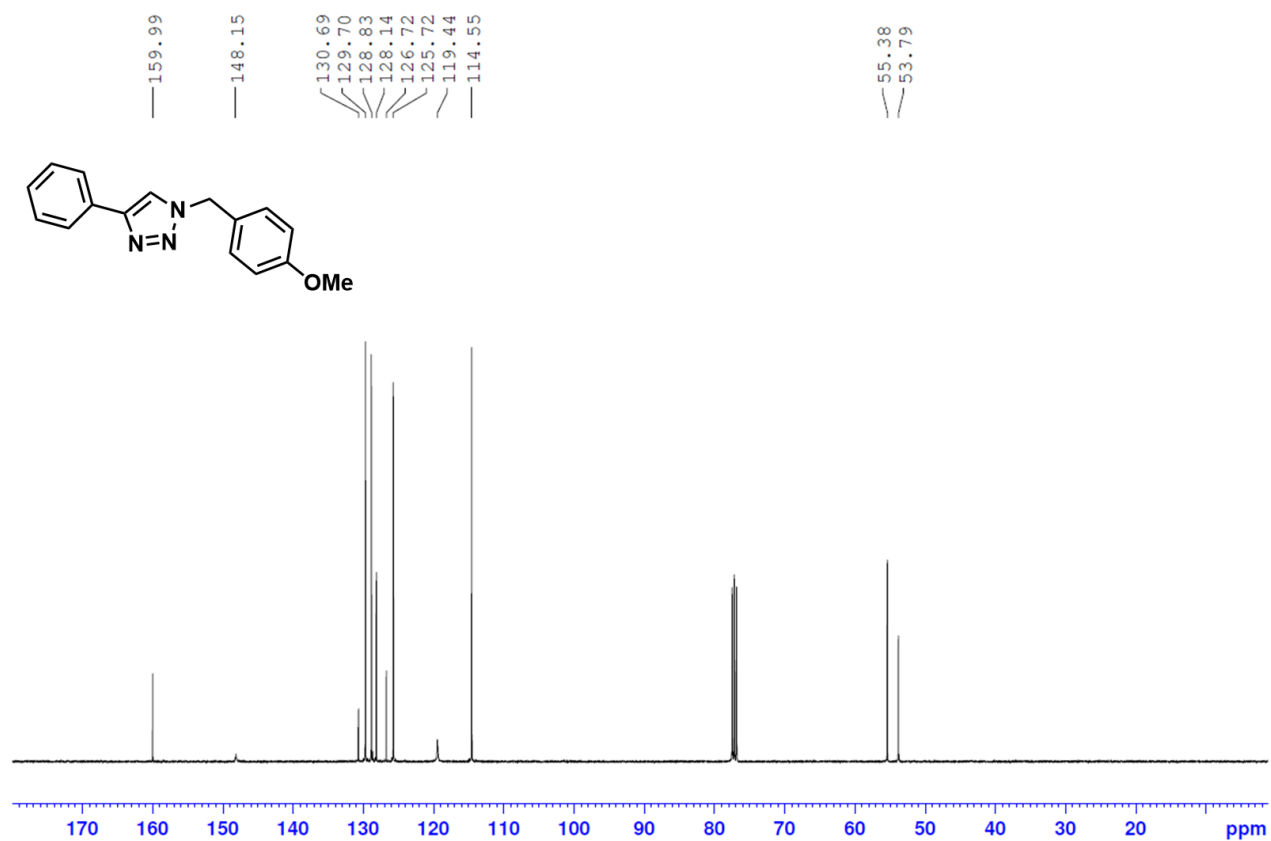
¹³C NMR spectrum of 1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole



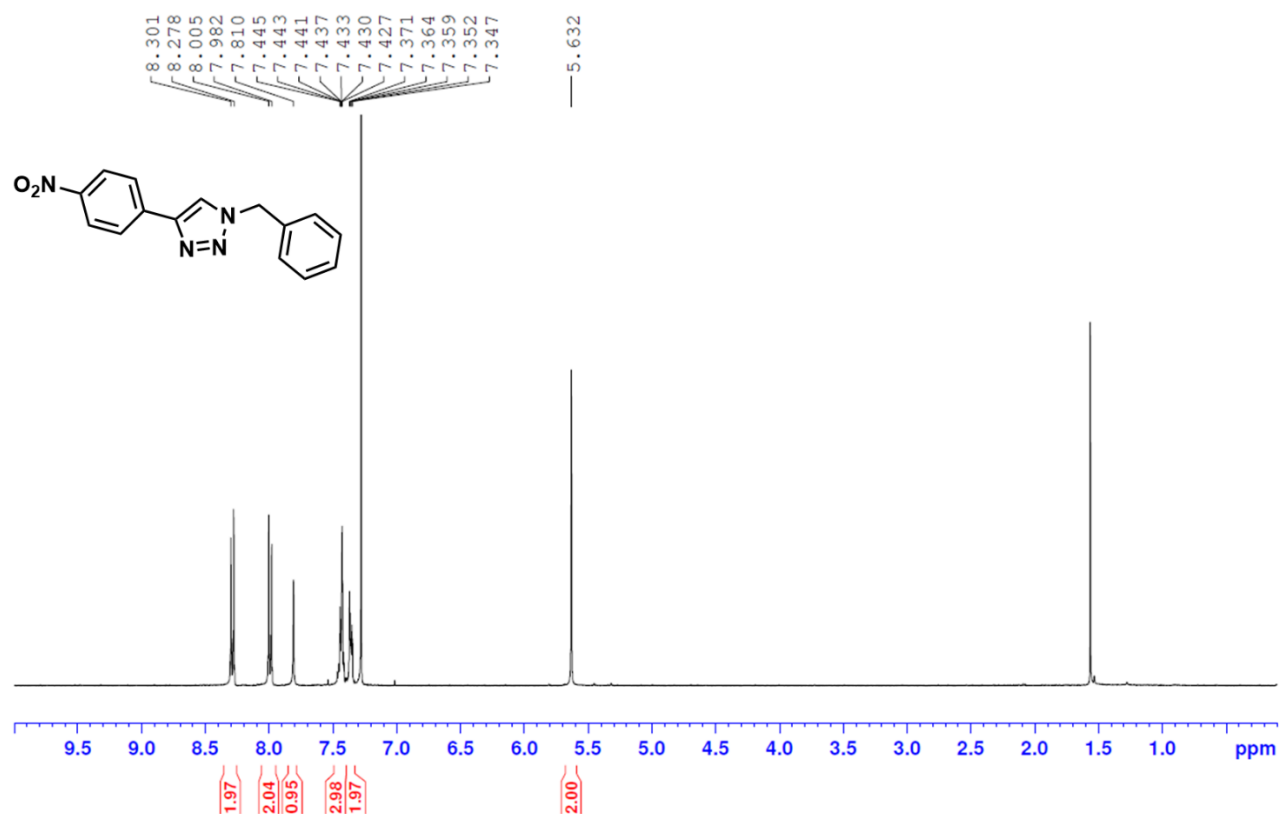
¹H NMR spectrum of 1-(4-methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole



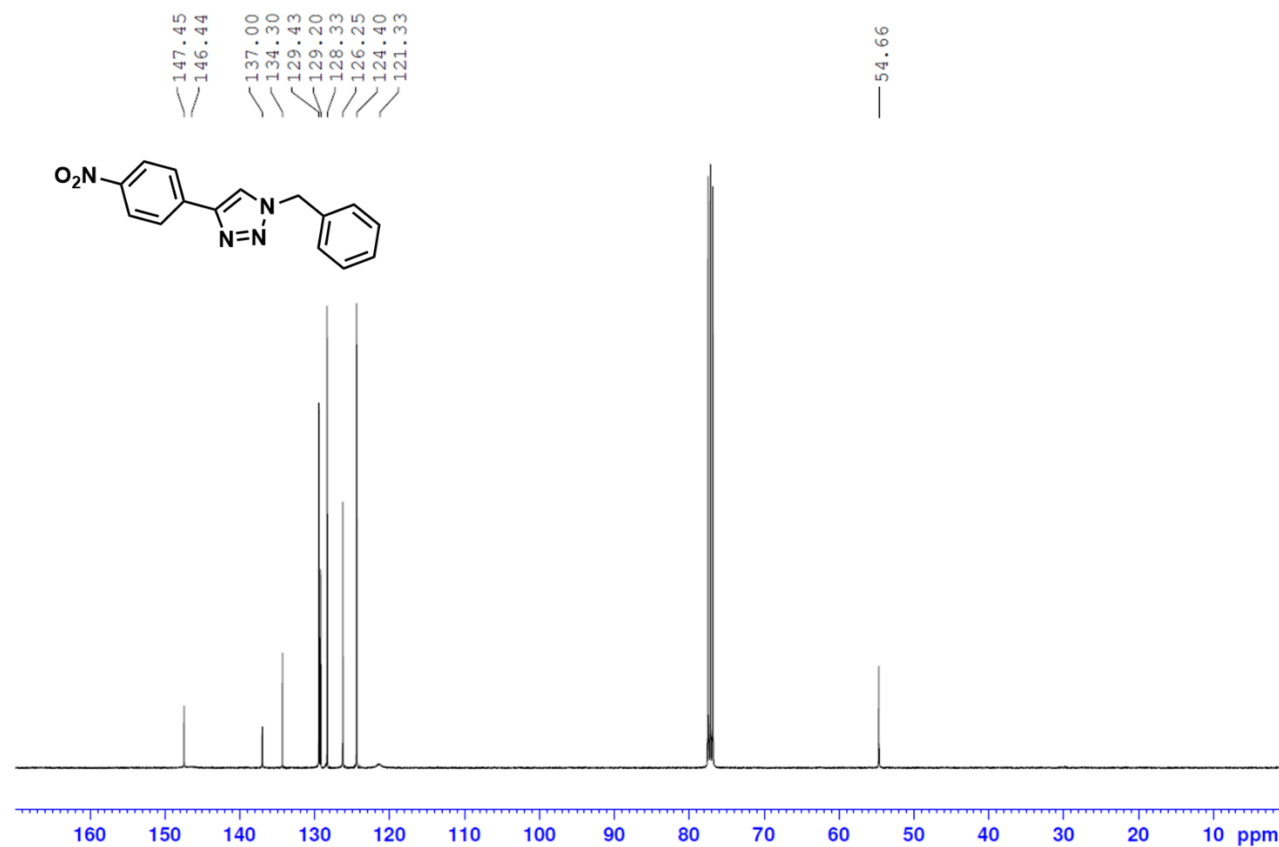
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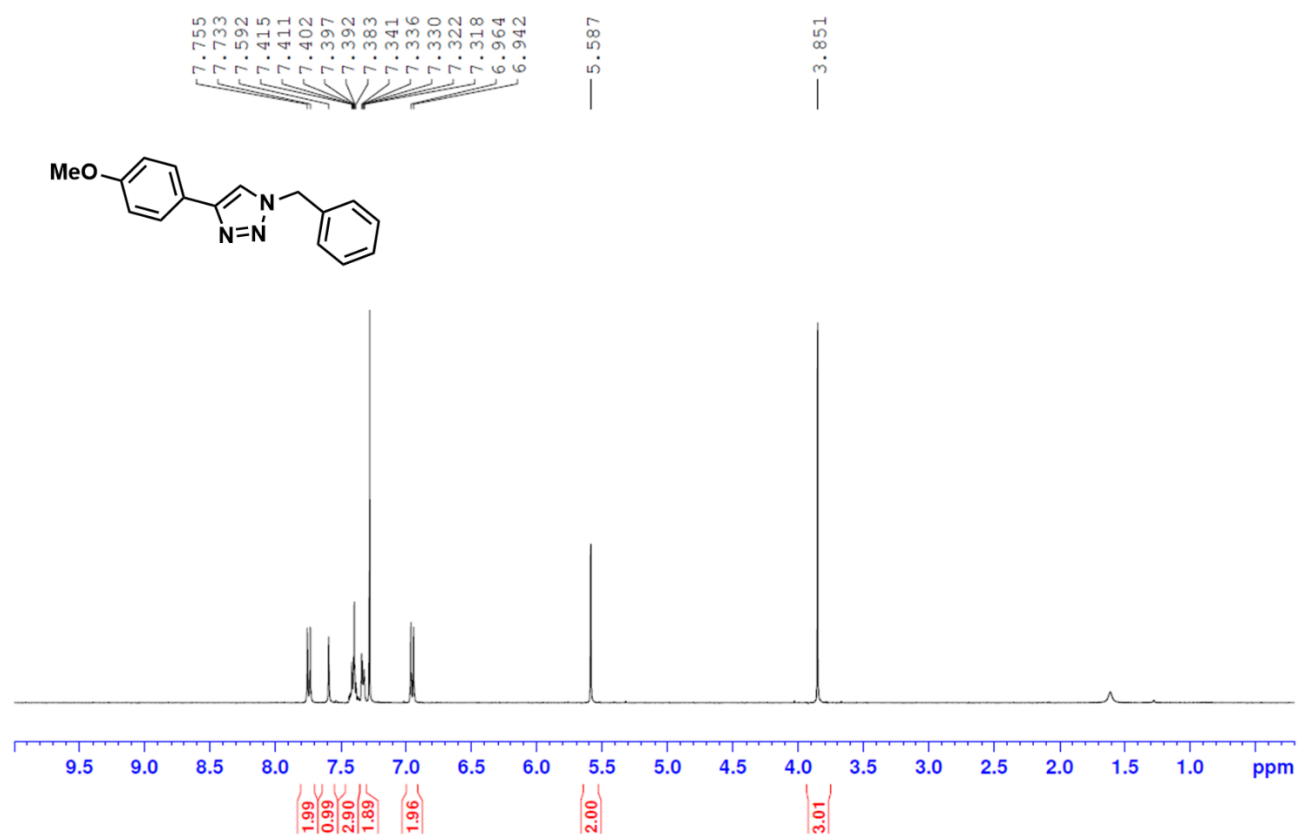
¹H NMR spectrum of 1-benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole



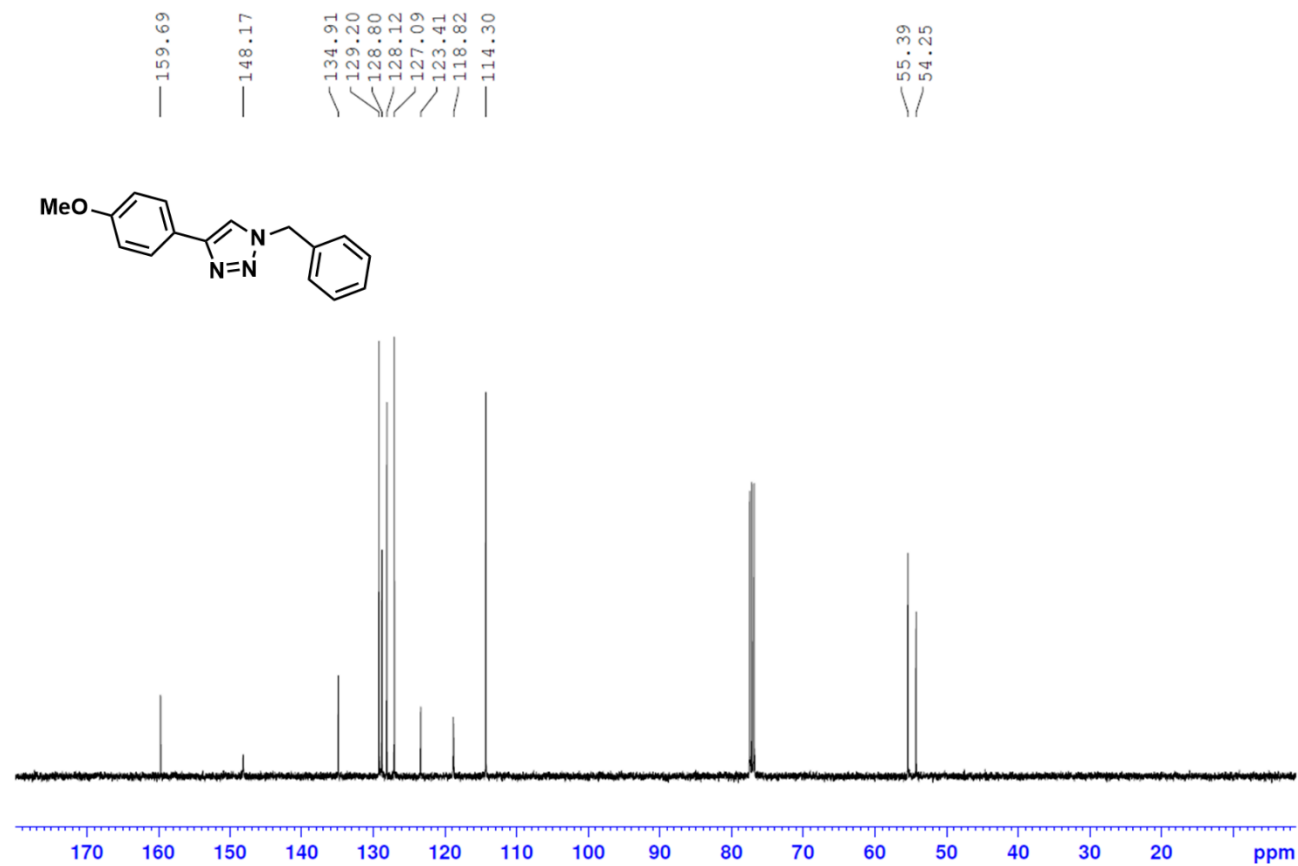
¹³C NMR spectrum of 1-benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole



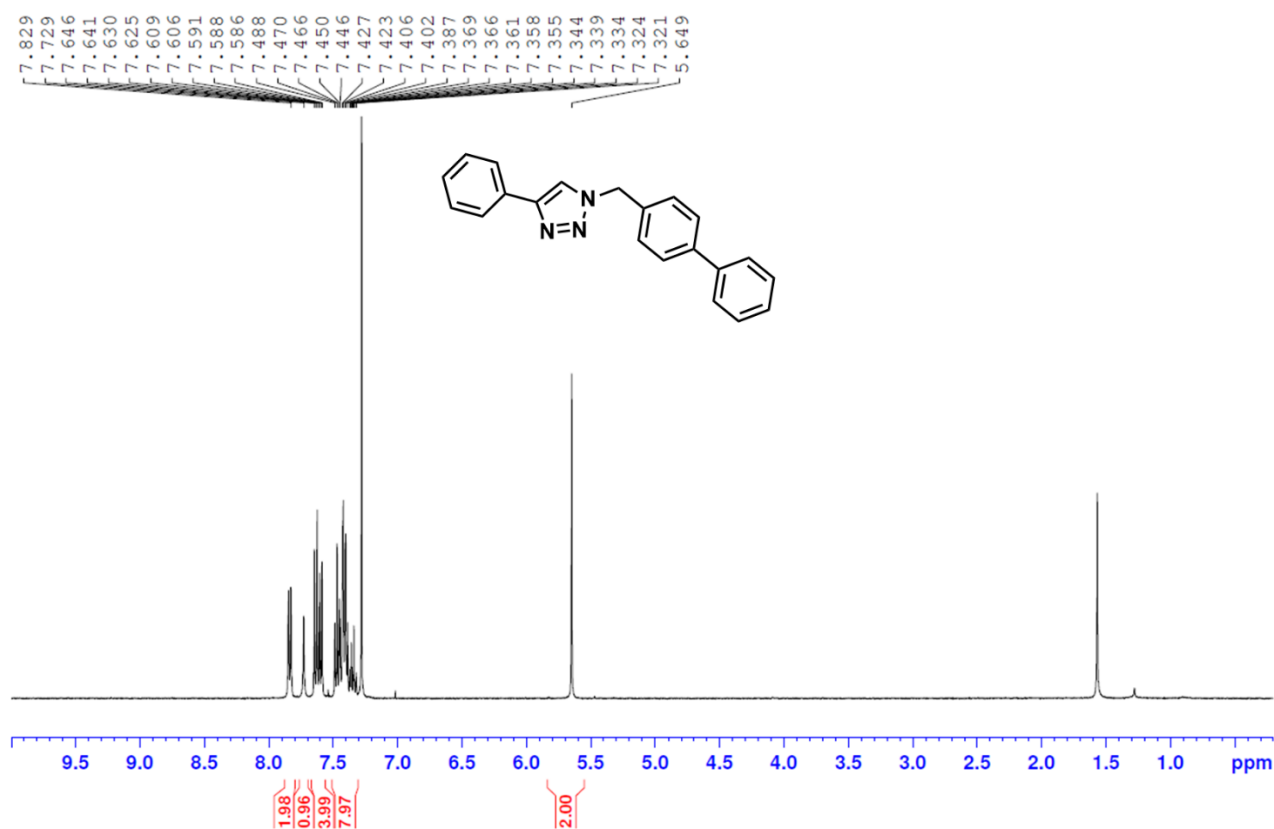
¹H NMR spectrum of 1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole



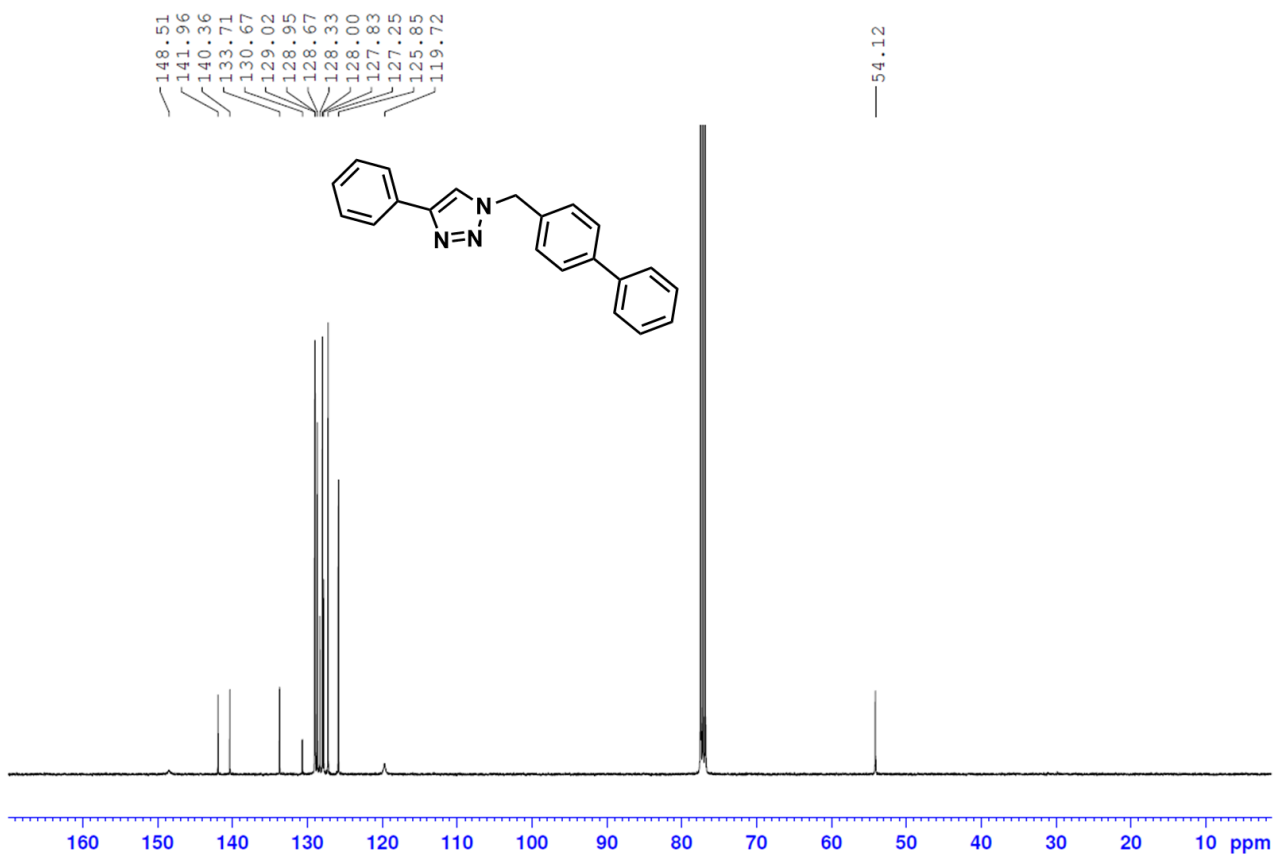
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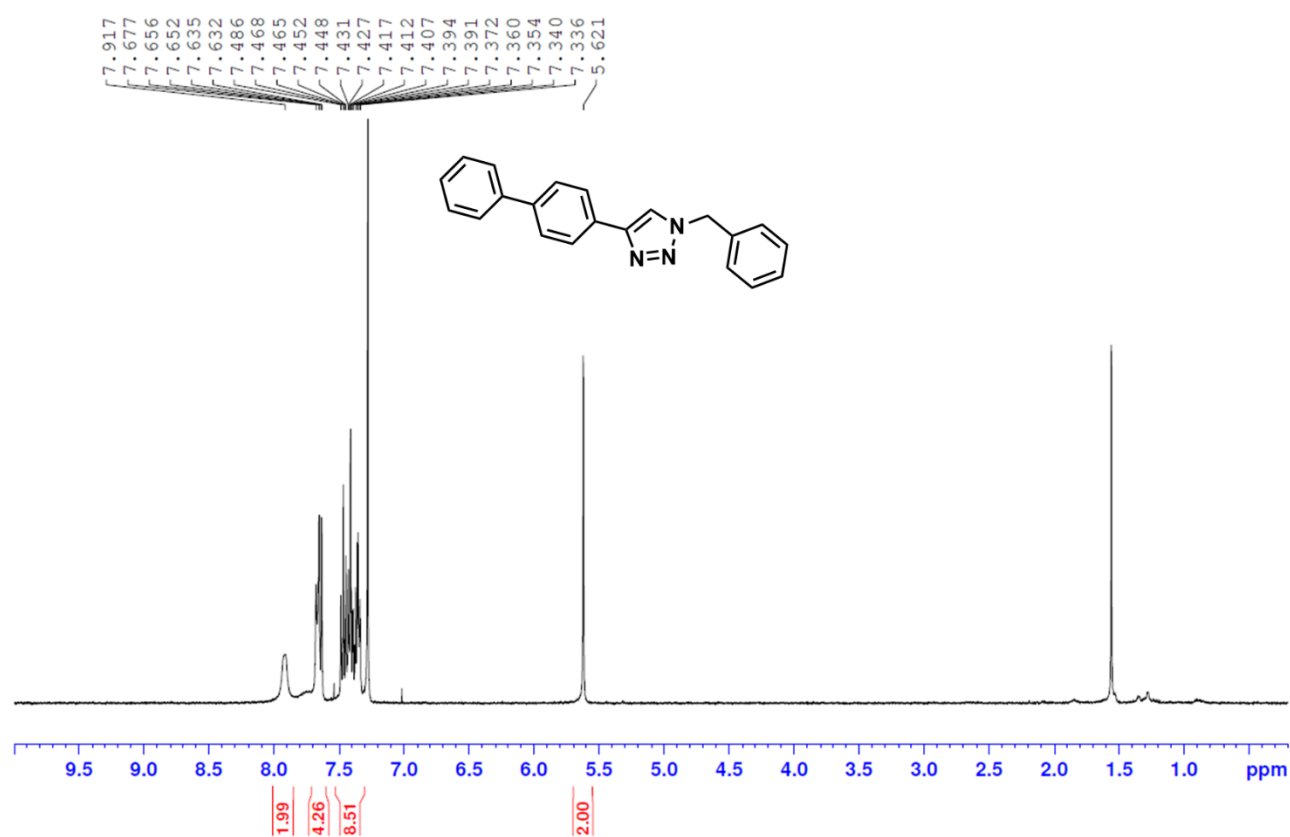
¹H NMR spectrum of 1-([1,1'-biphenyl]-4-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole



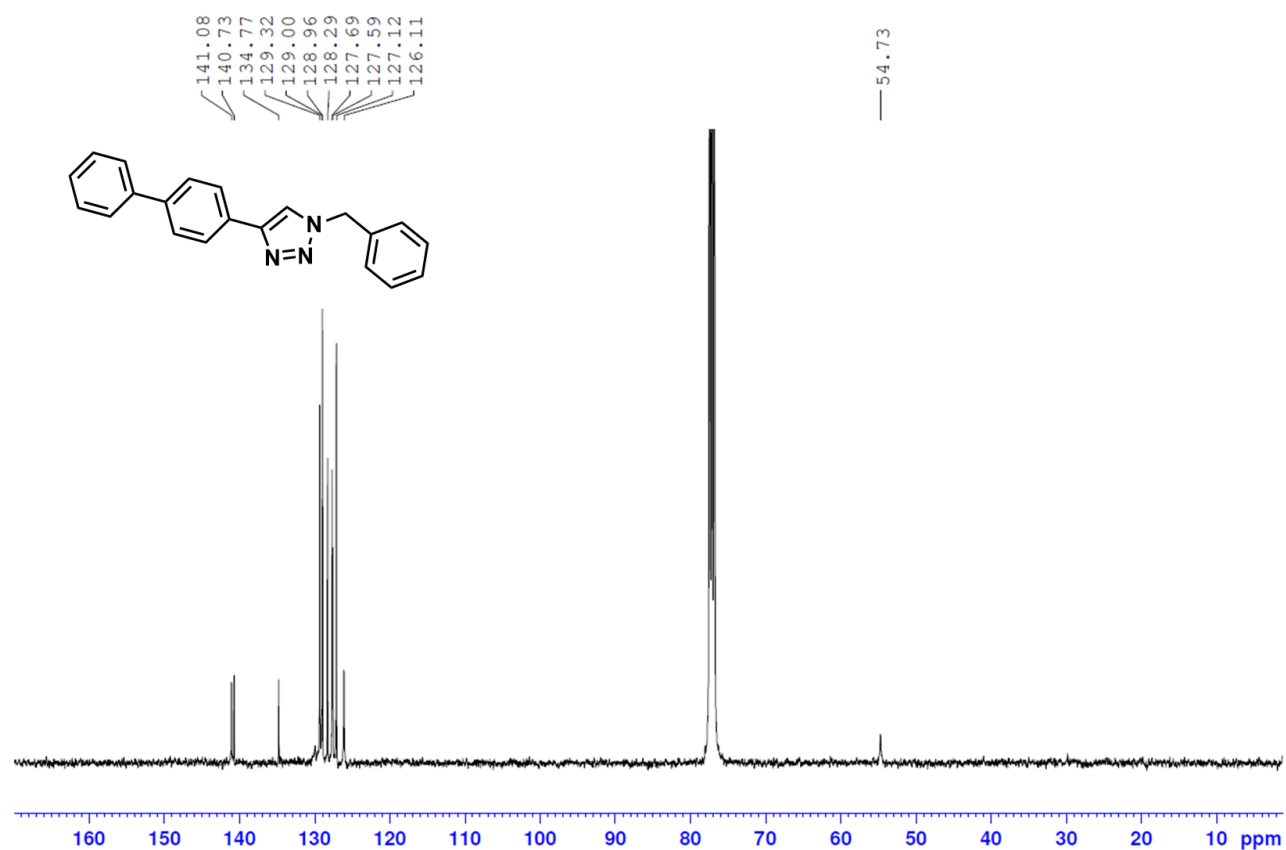
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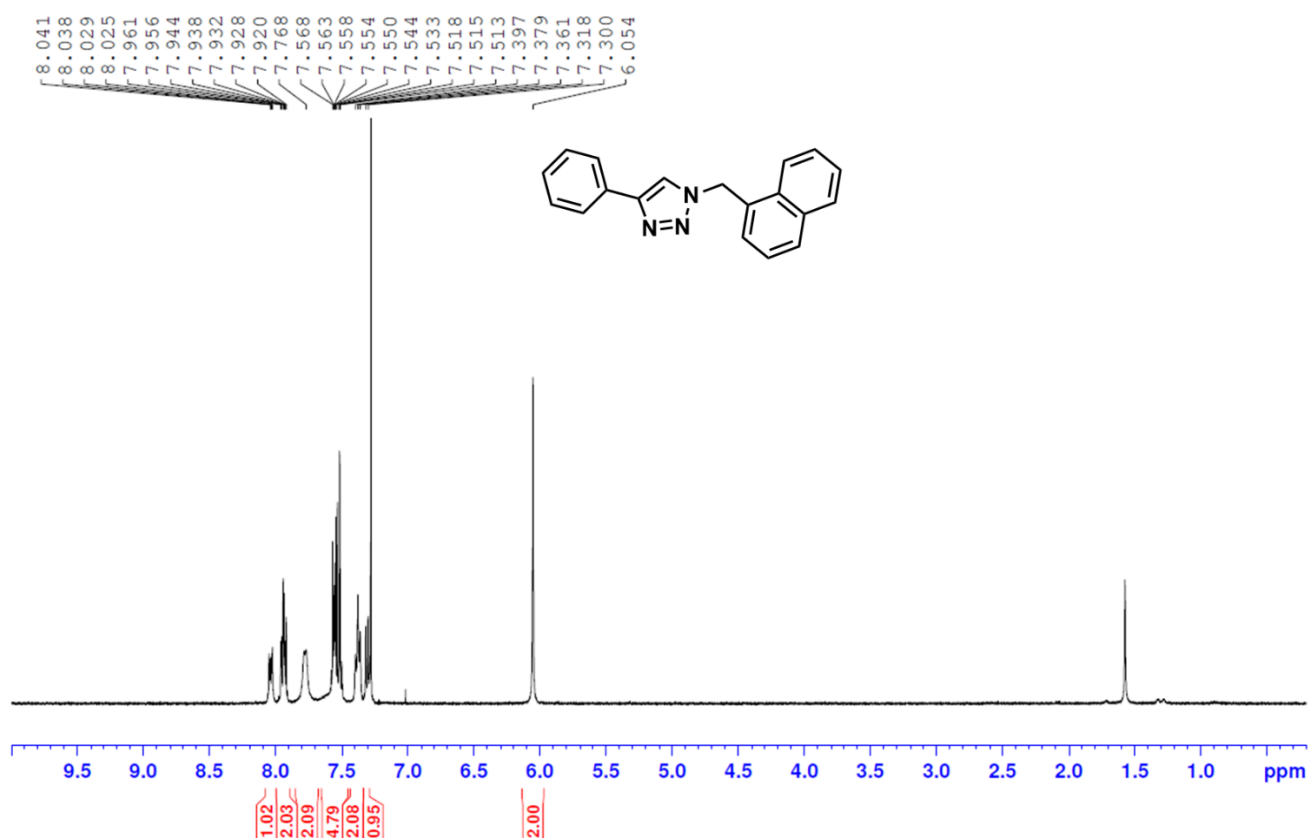
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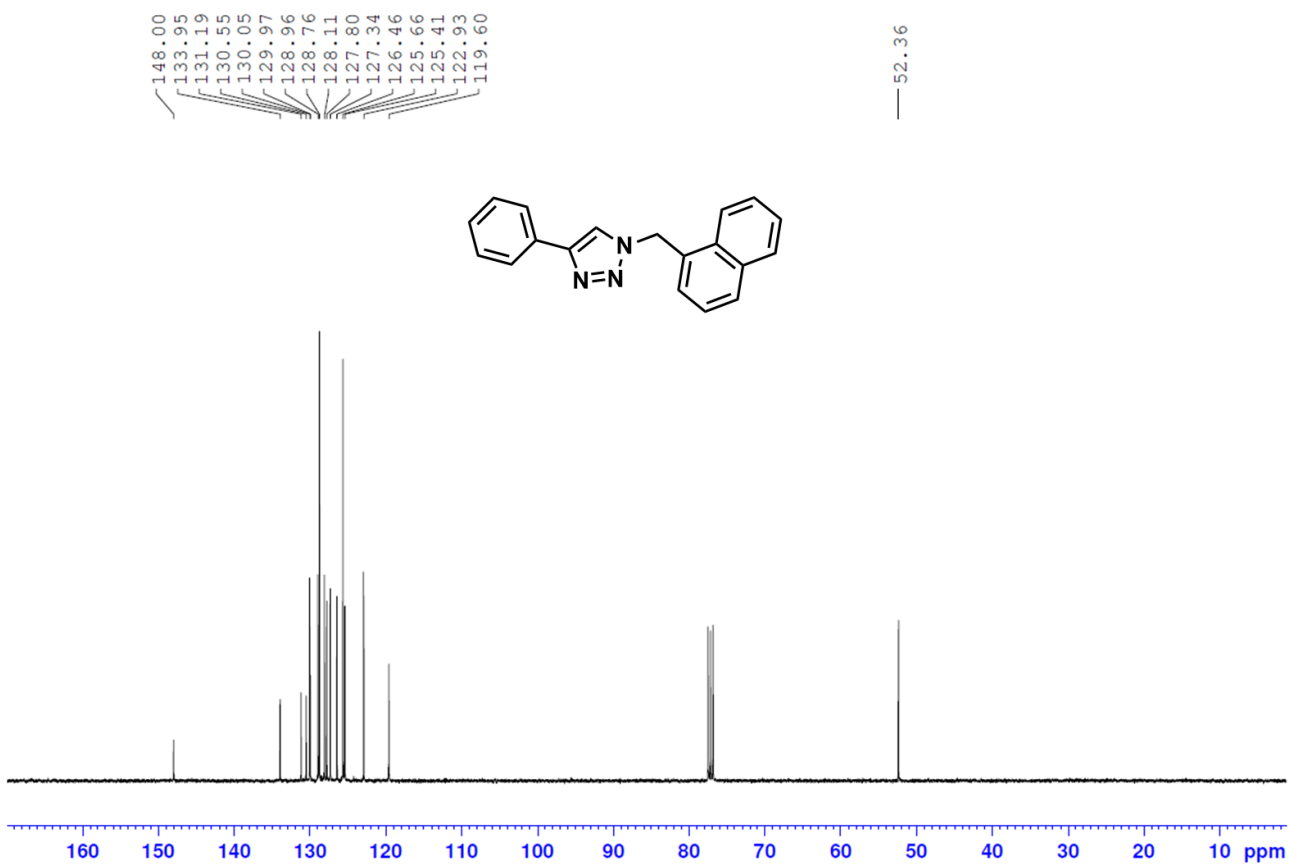
¹³C NMR spectrum of 4-([1,1'-biphenyl]-4-yl)-1-benzyl-1*H*-1,2,3-triazole



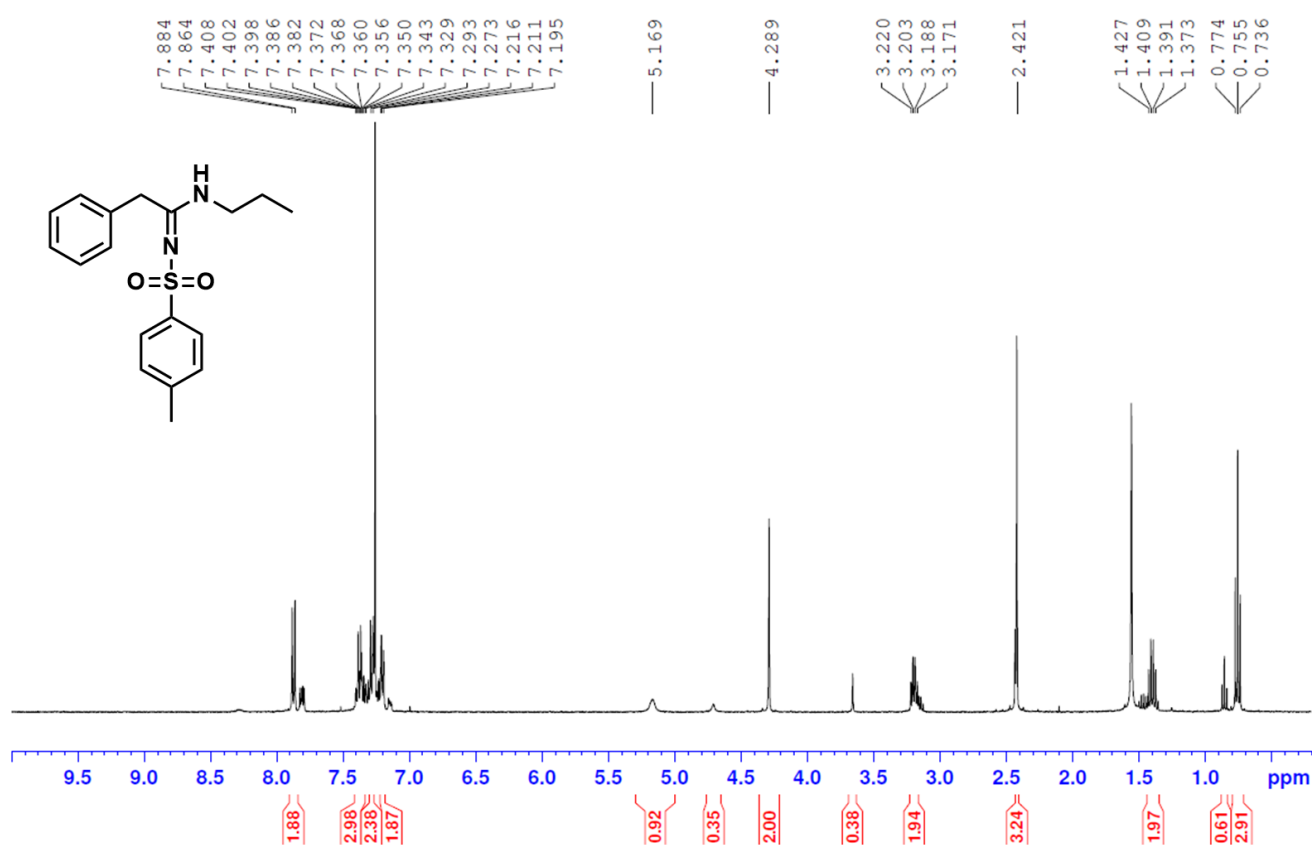
¹H NMR spectrum of 1-(naphthalen-1-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole



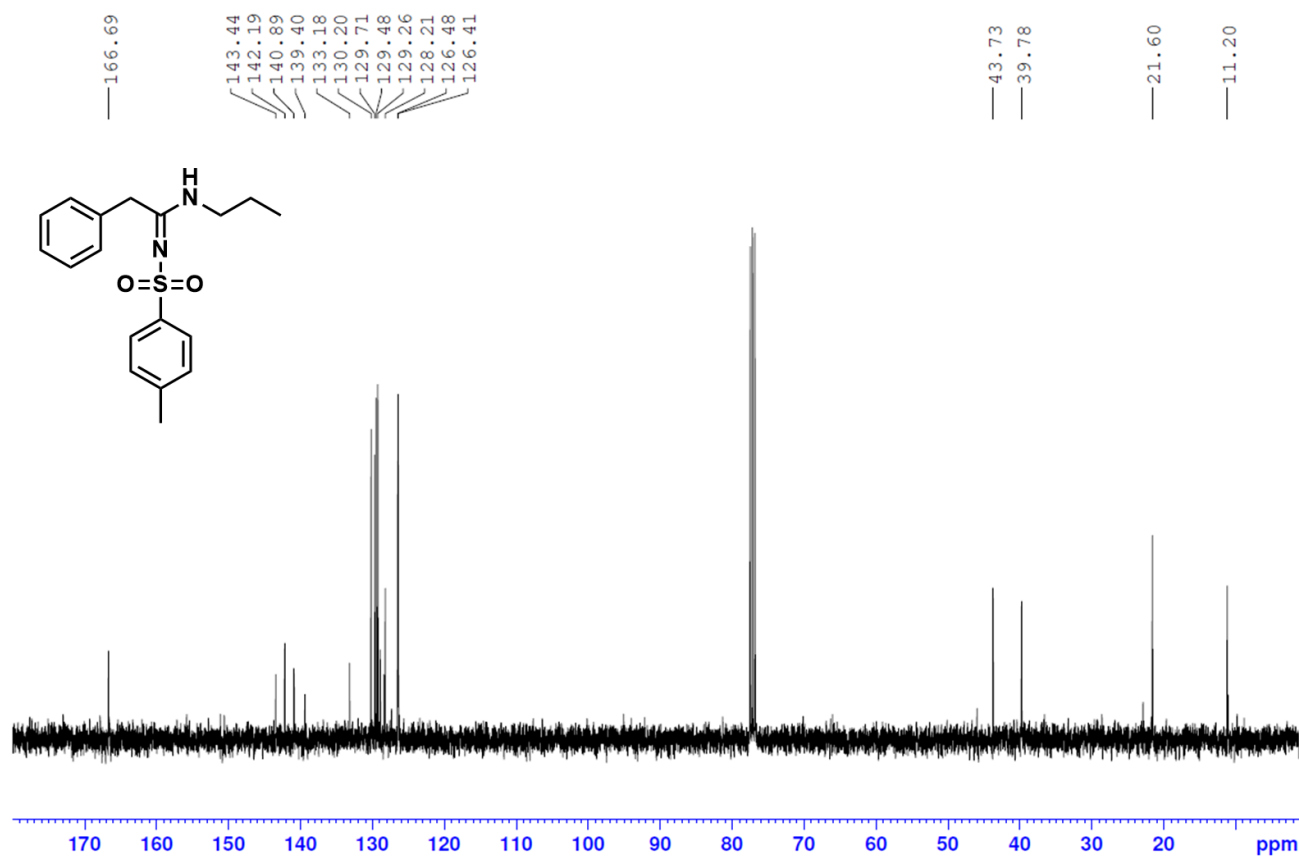
¹³C NMR spectrum of 1-(naphthalen-1-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole



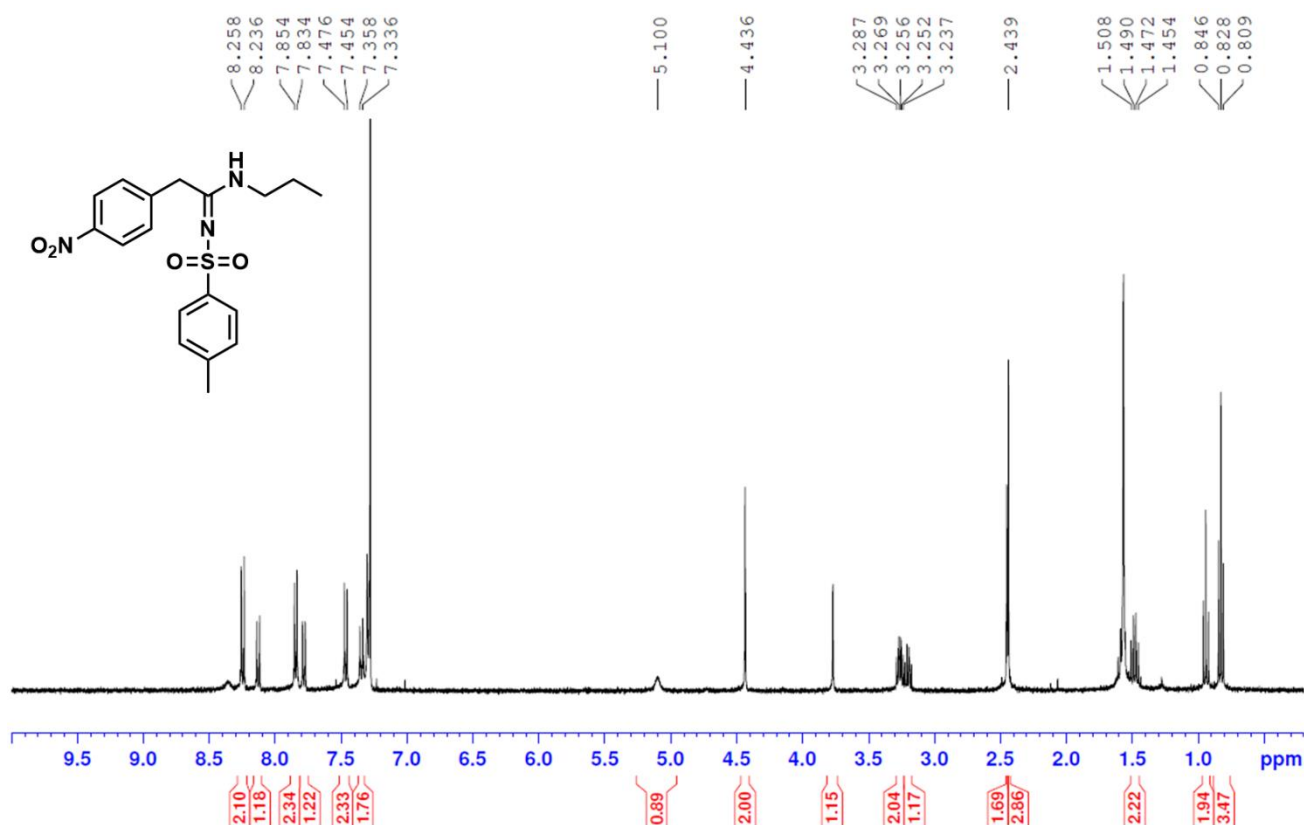
¹H NMR spectrum of 2-phenyl-*N*-propyl-*N*-tosylacetimidamide



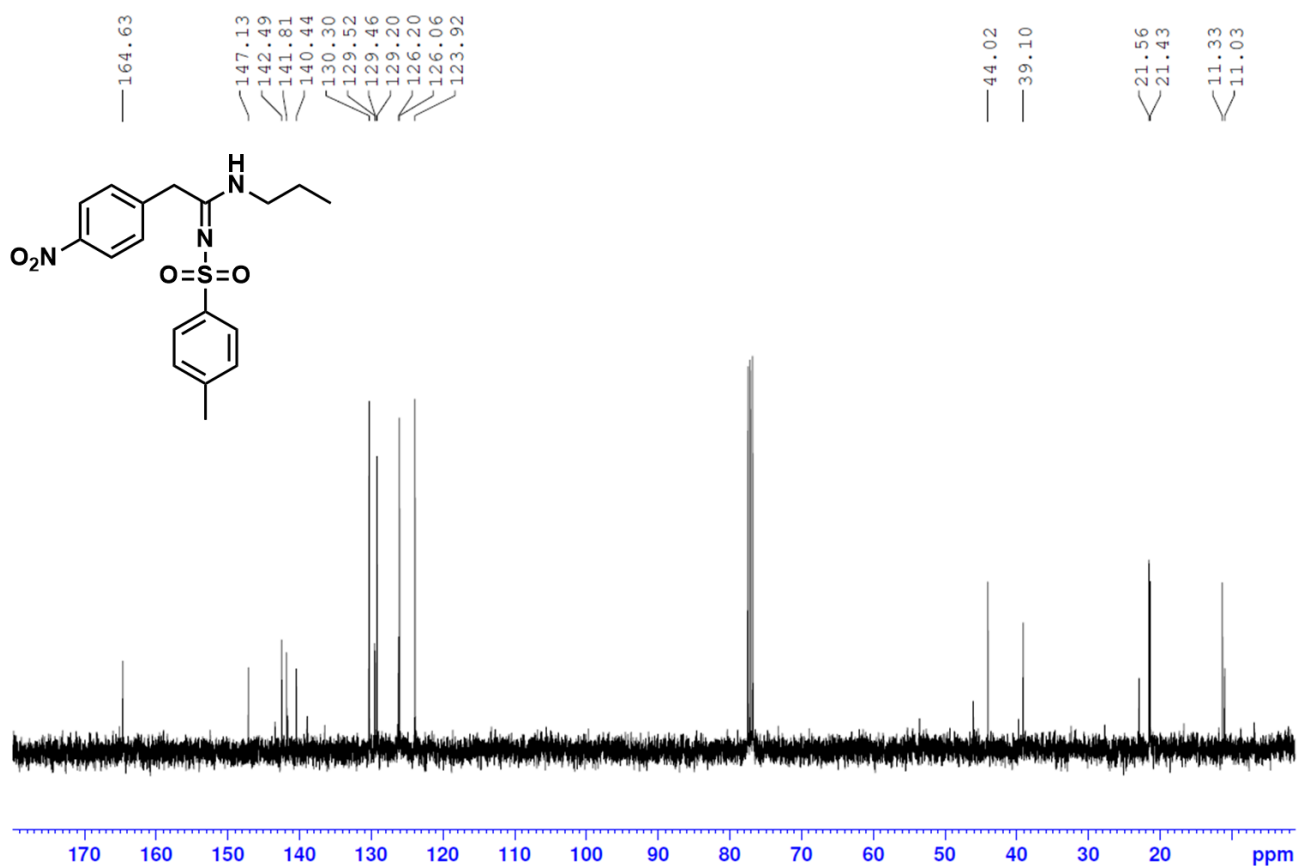
¹³C NMR spectrum of 2-phenyl-*N*-propyl-*N*-tosylacetimidamide



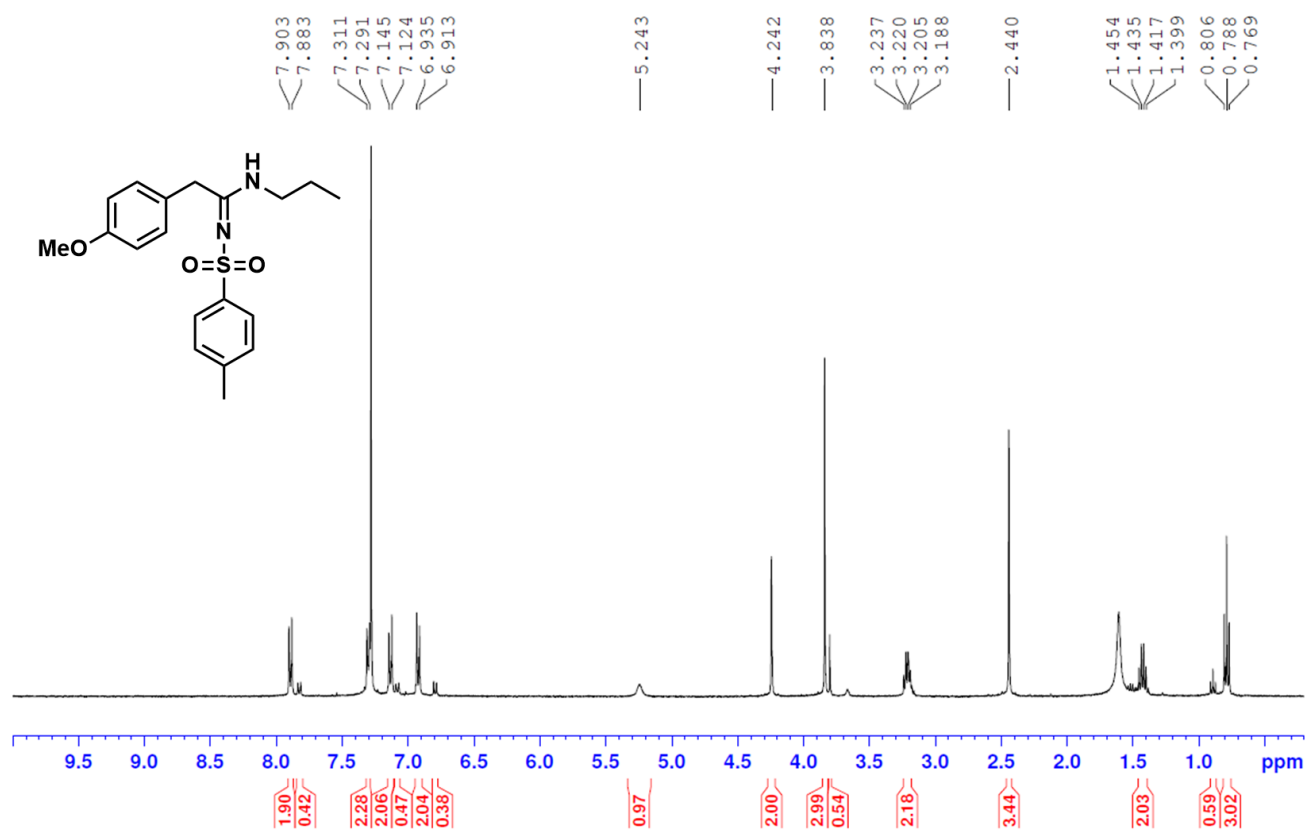
¹H NMR spectrum of 2-(4-nitrophenyl)-*N*-propyl-*N*-tosylacetimidamide



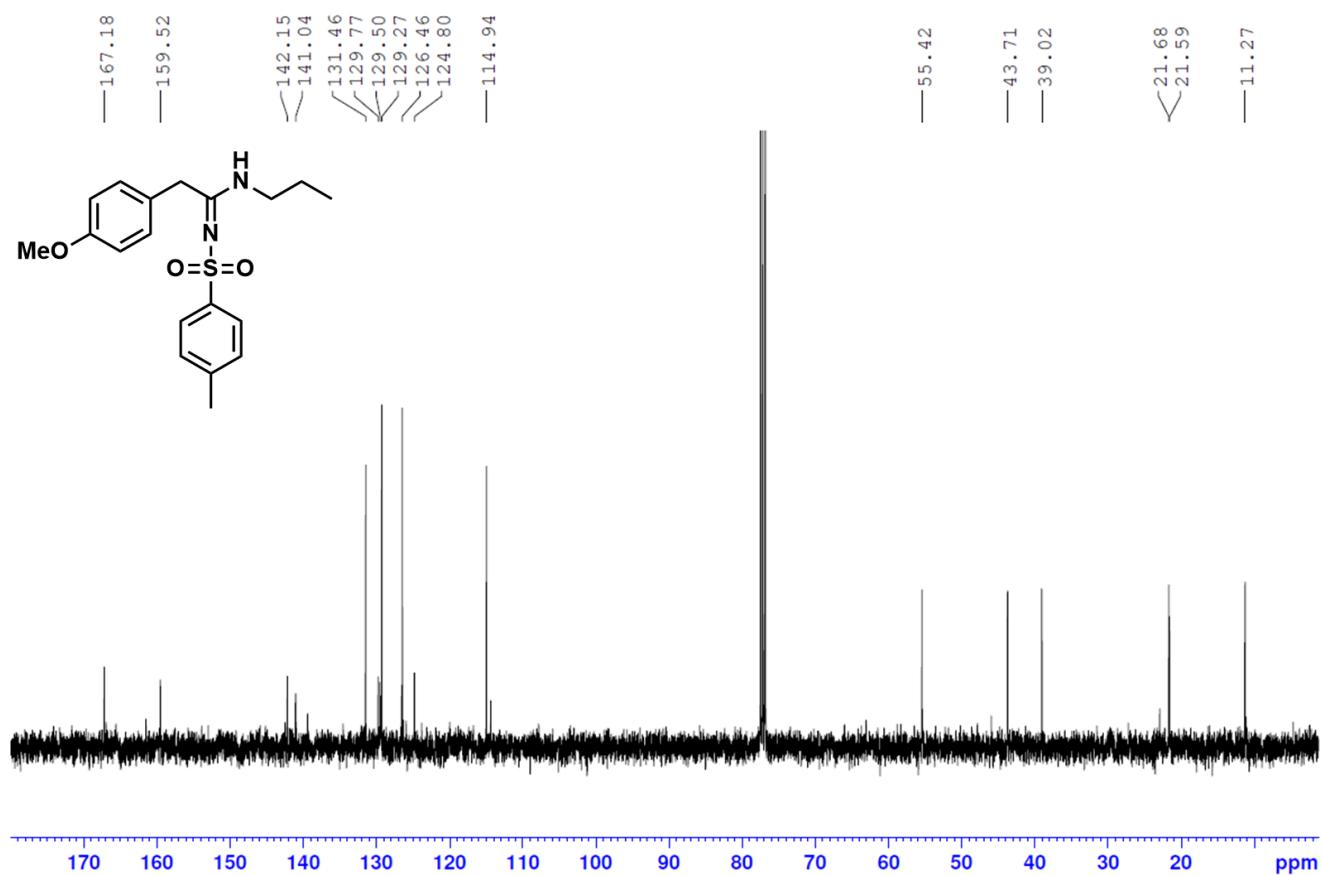
¹³C NMR spectrum of 2-(4-nitrophenyl)-*N*-propyl-*N*-tosylacetimidamide



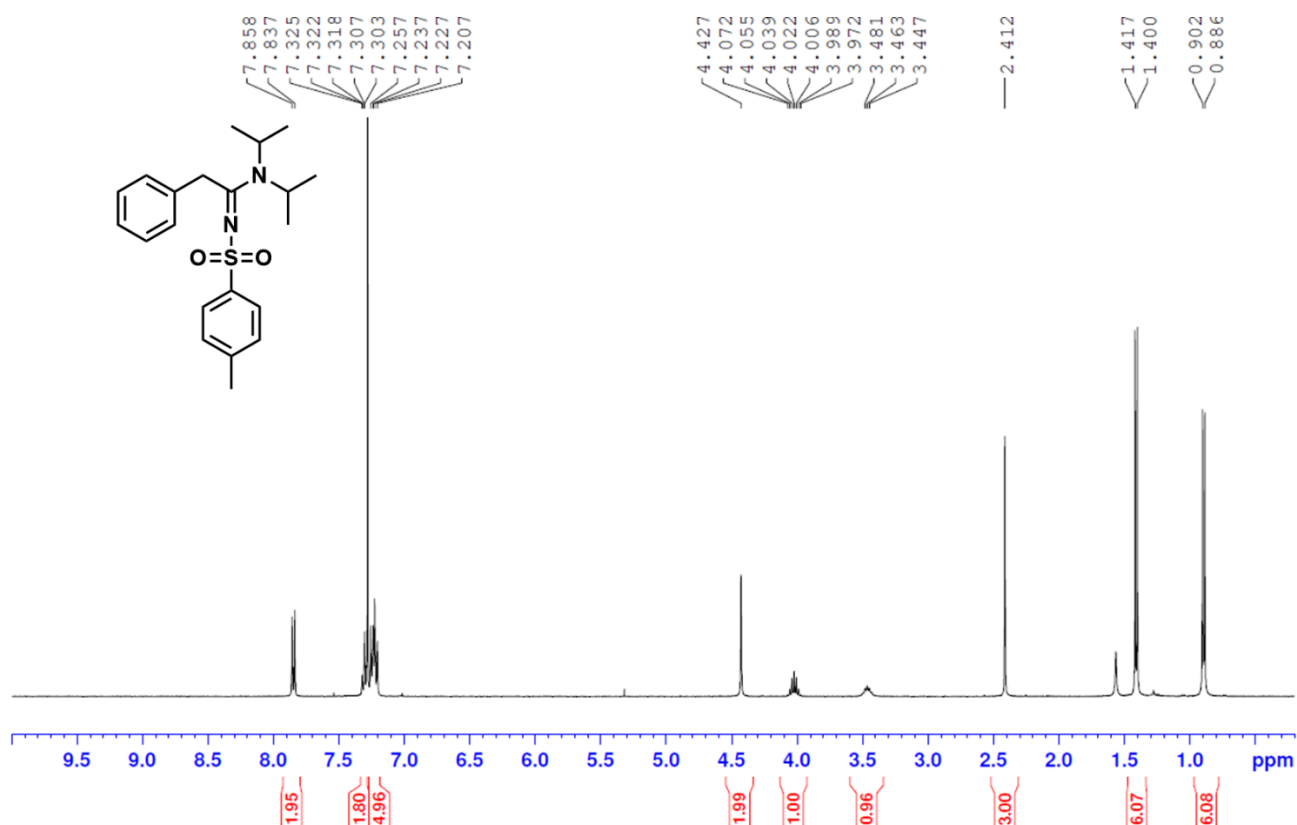
¹H NMR spectrum of 2-(4-methoxyphenyl)-*N*-propyl-*N'*-tosylacetimidamide



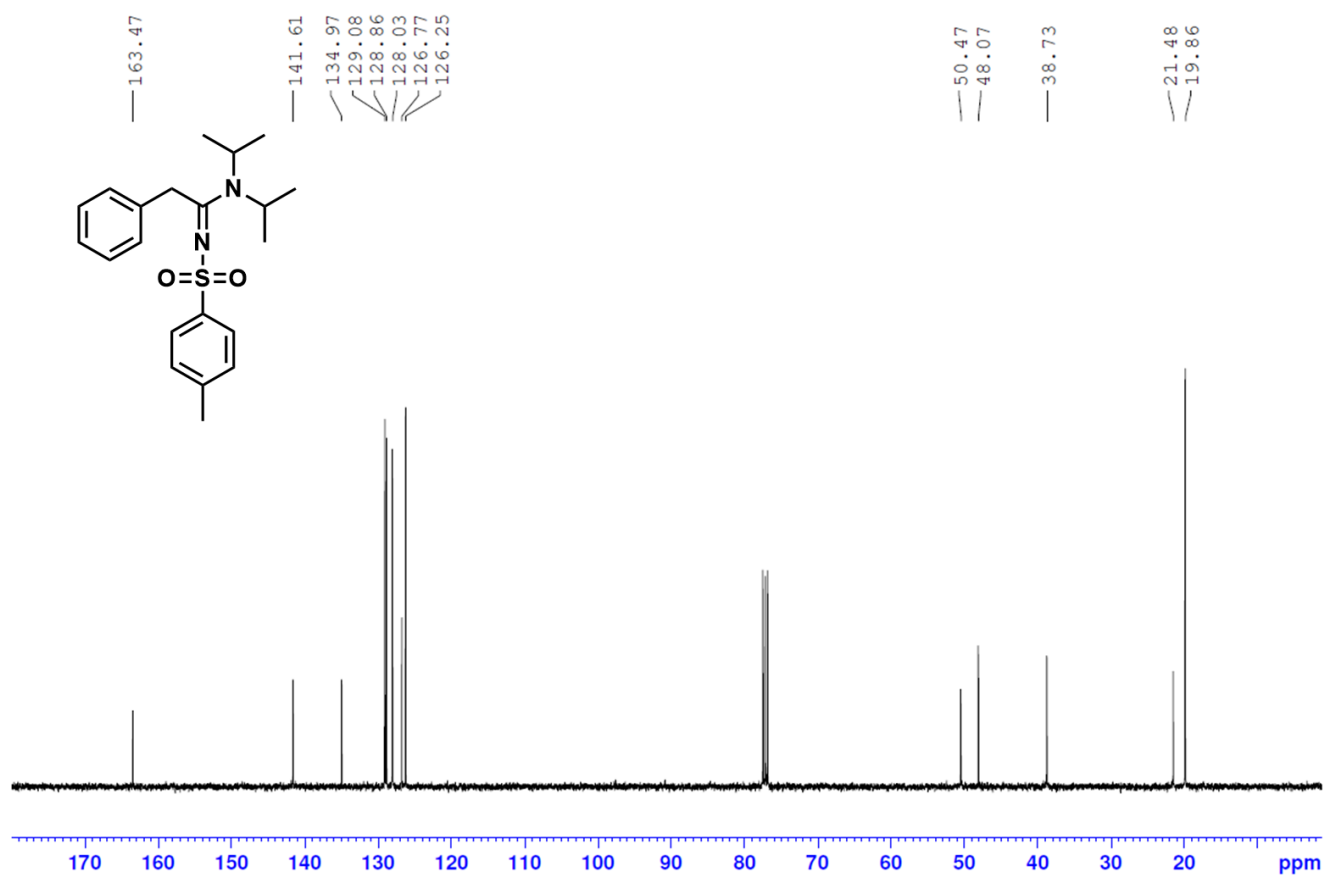
¹³C NMR spectrum of 2-(4-methoxyphenyl)-*N*-propyl-*N'*-tosylacetimidamide



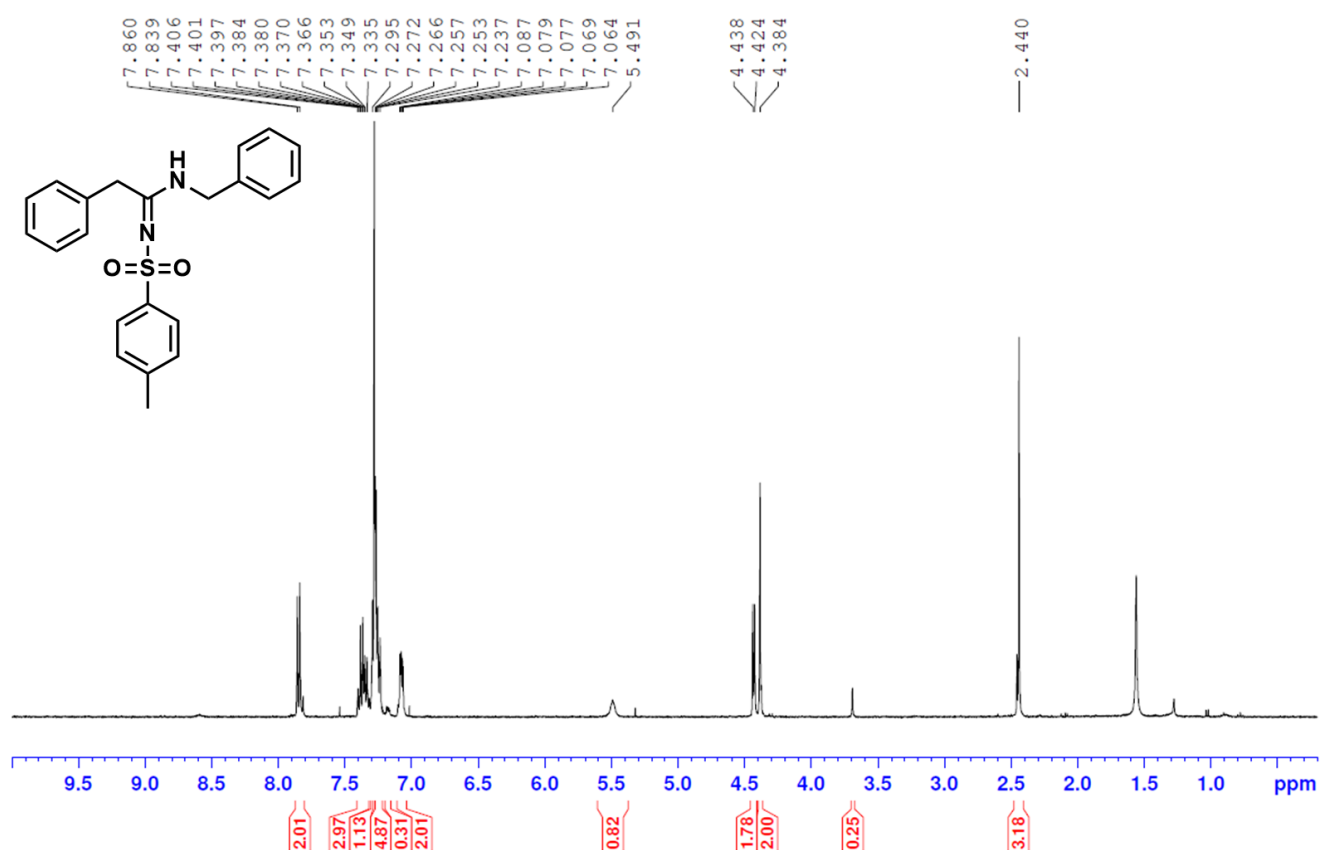
¹H NMR spectrum of *N,N*-diisopropyl-2-phenyl-*N'*-tosylacetimidamide



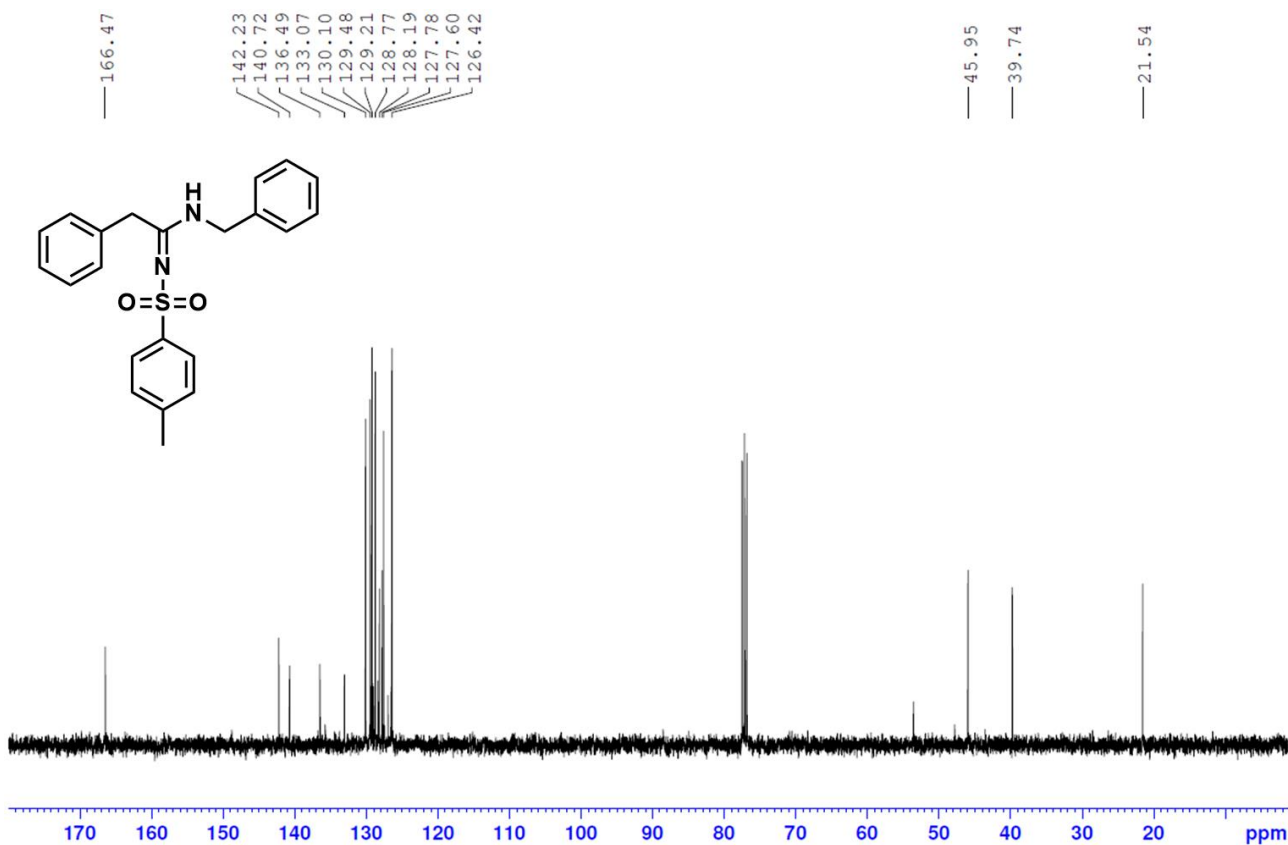
¹³C NMR spectrum of *N,N*-diisopropyl-2-phenyl-*N'*-tosylacetimidamide



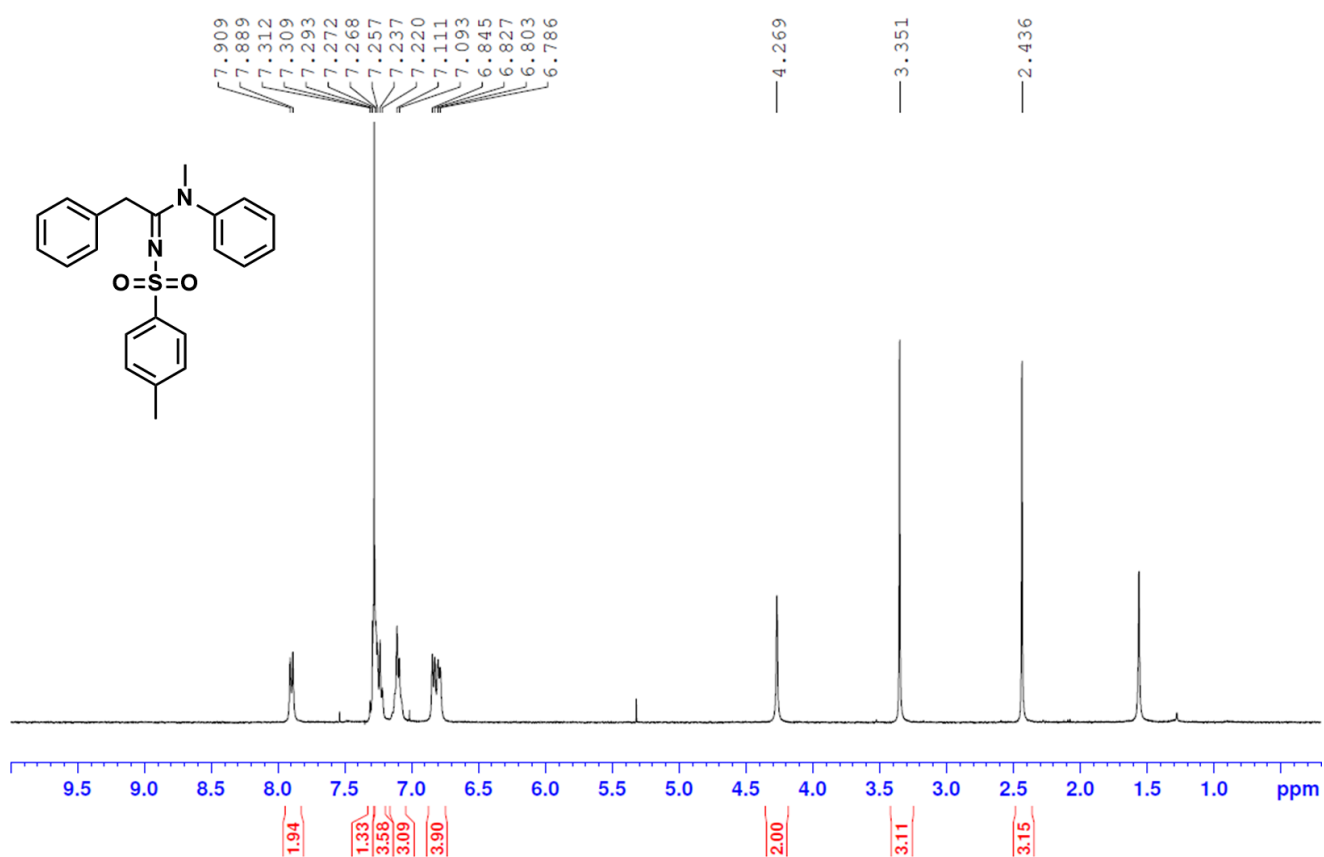
¹H NMR spectrum of *N*-benzyl-2-phenyl-*N*-tosylacetimidamide



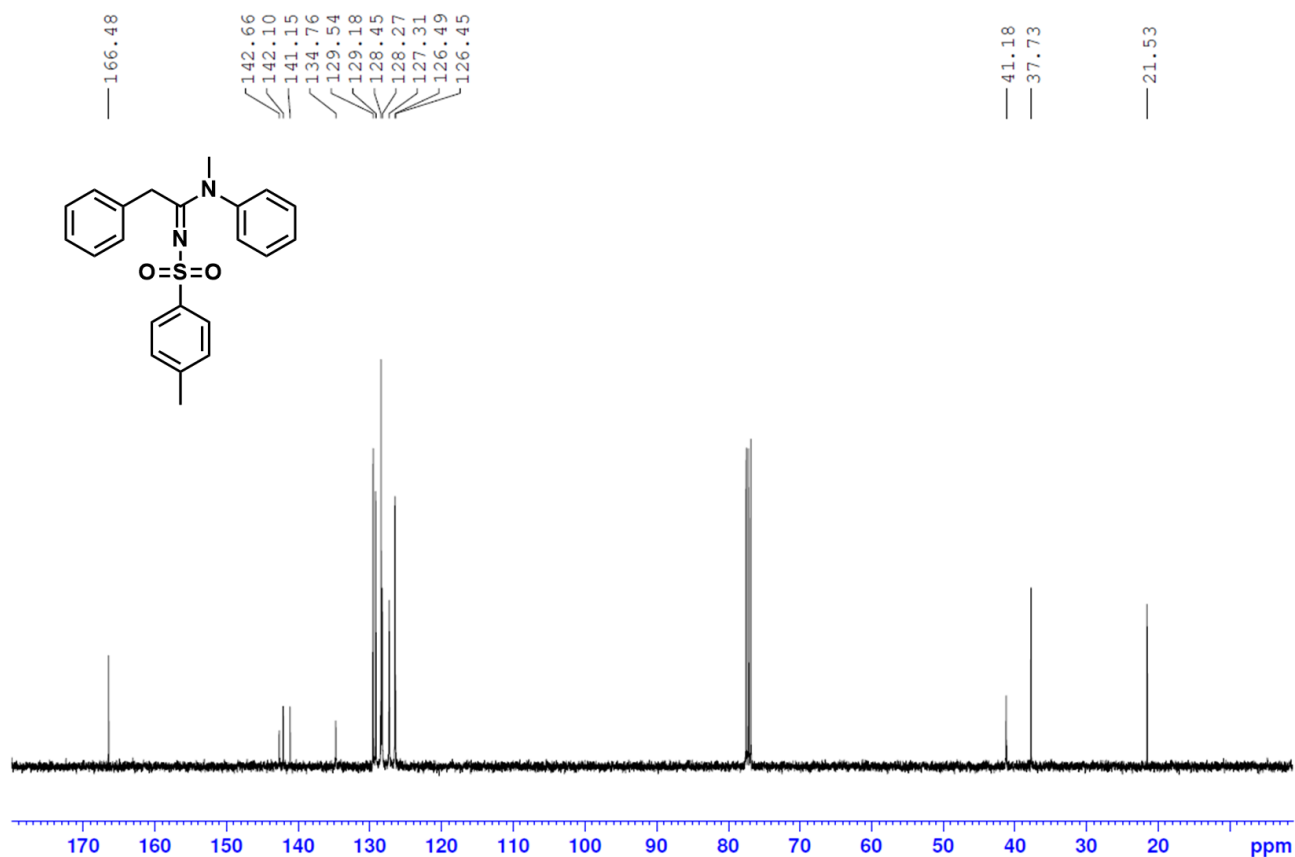
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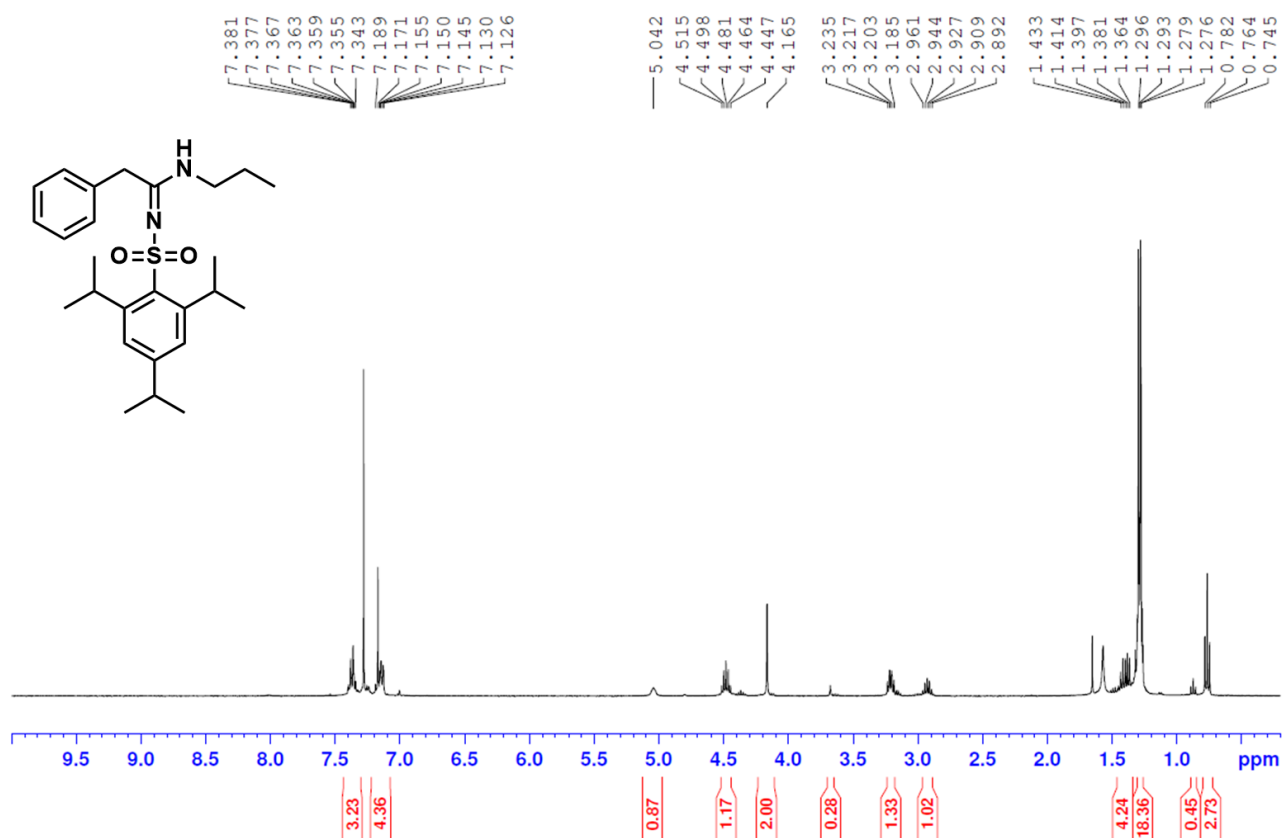
¹H NMR spectrum of *N*-methyl-*N*,2-diphenyl-*N'*-tosylacetimidamide



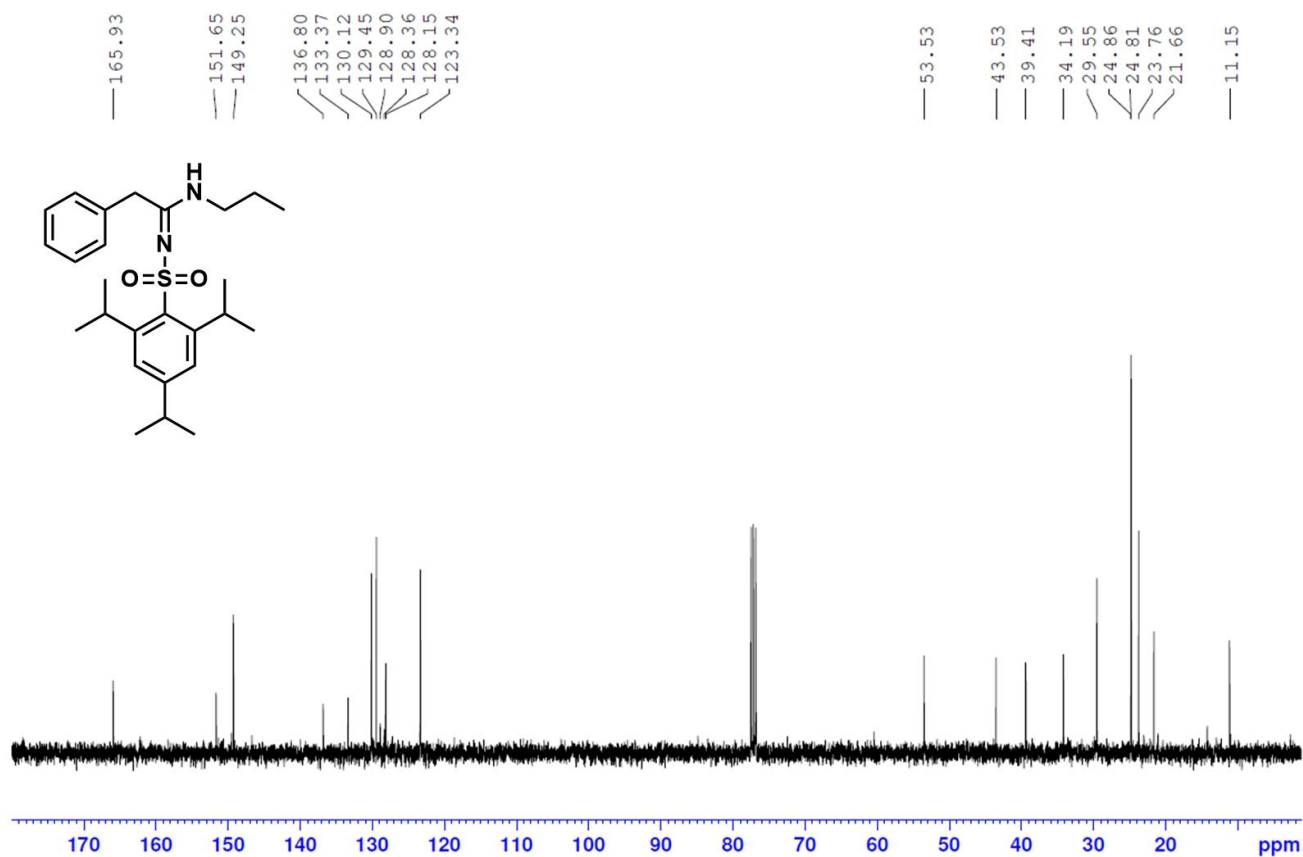
¹³C NMR spectrum of *N*-methyl-*N*,2-diphenyl-*N'*-tosylacetimidamide



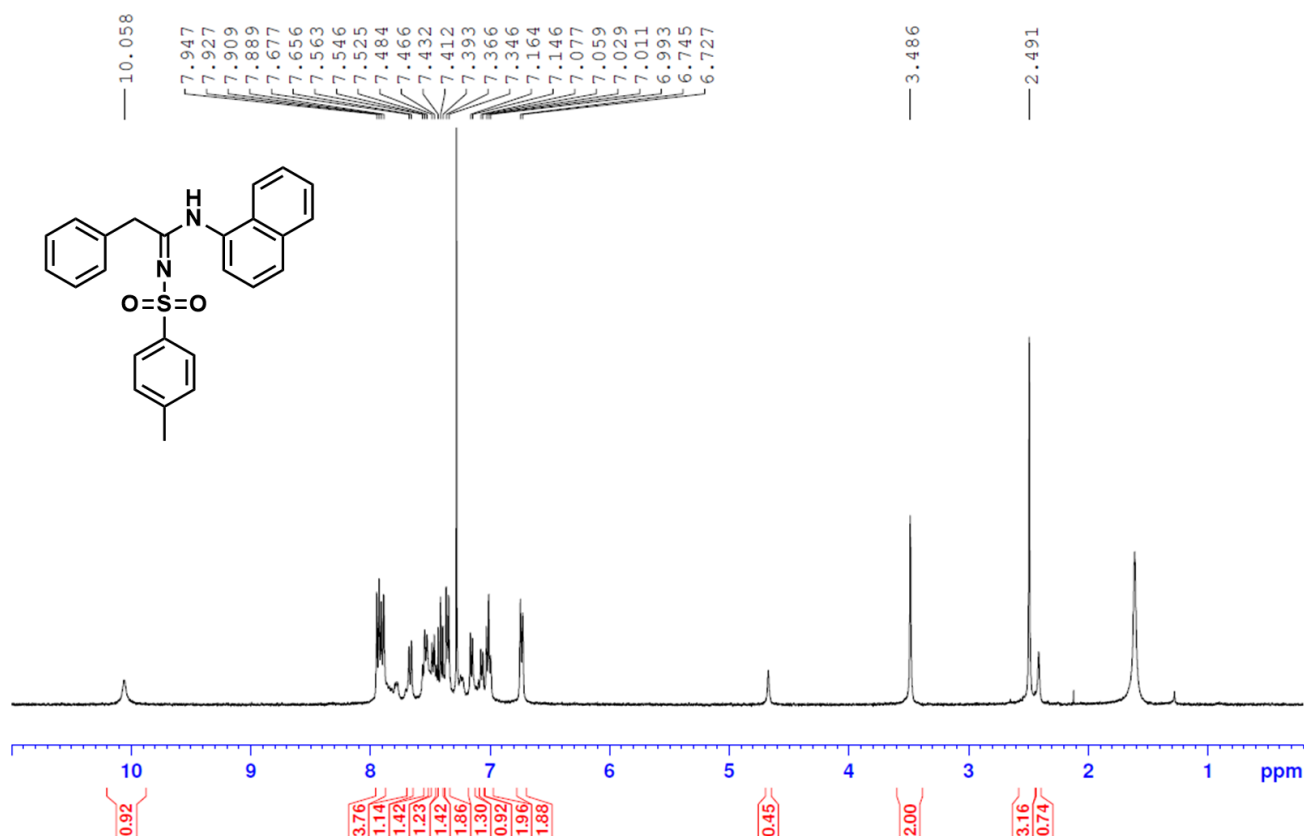
¹H NMR spectrum of 2-phenyl-*N*-propyl-*N*-((2,4,6-triisopropylphenyl)sulfonyl)acetimidamide



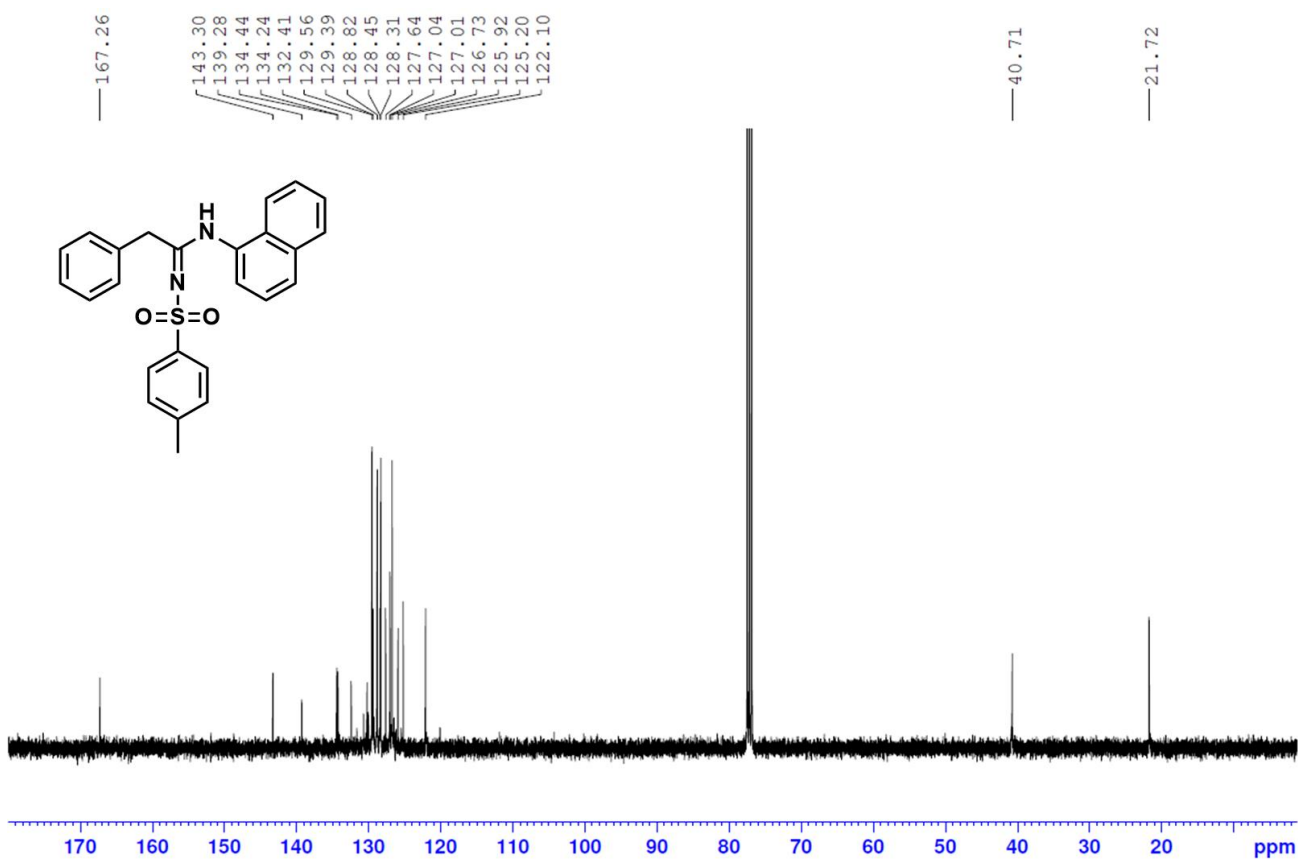
¹³C NMR spectrum of 2-phenyl-*N*-propyl-*N*-((2,4,6-triisopropylphenyl)sulfonyl)acetimidamide



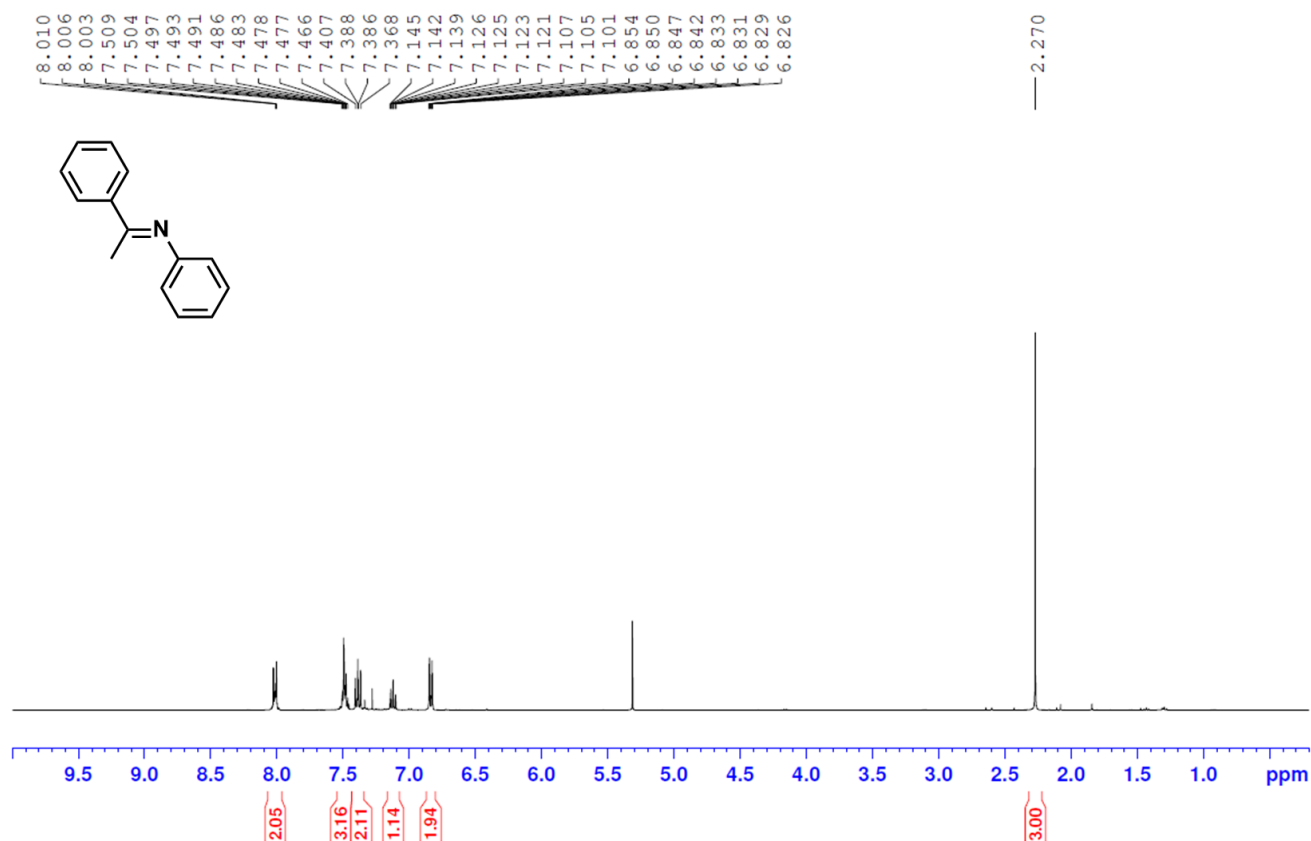
¹H NMR spectrum of *N*-(naphthalen-1-yl)-2-phenyl-*N*'-tosylacetimidamide



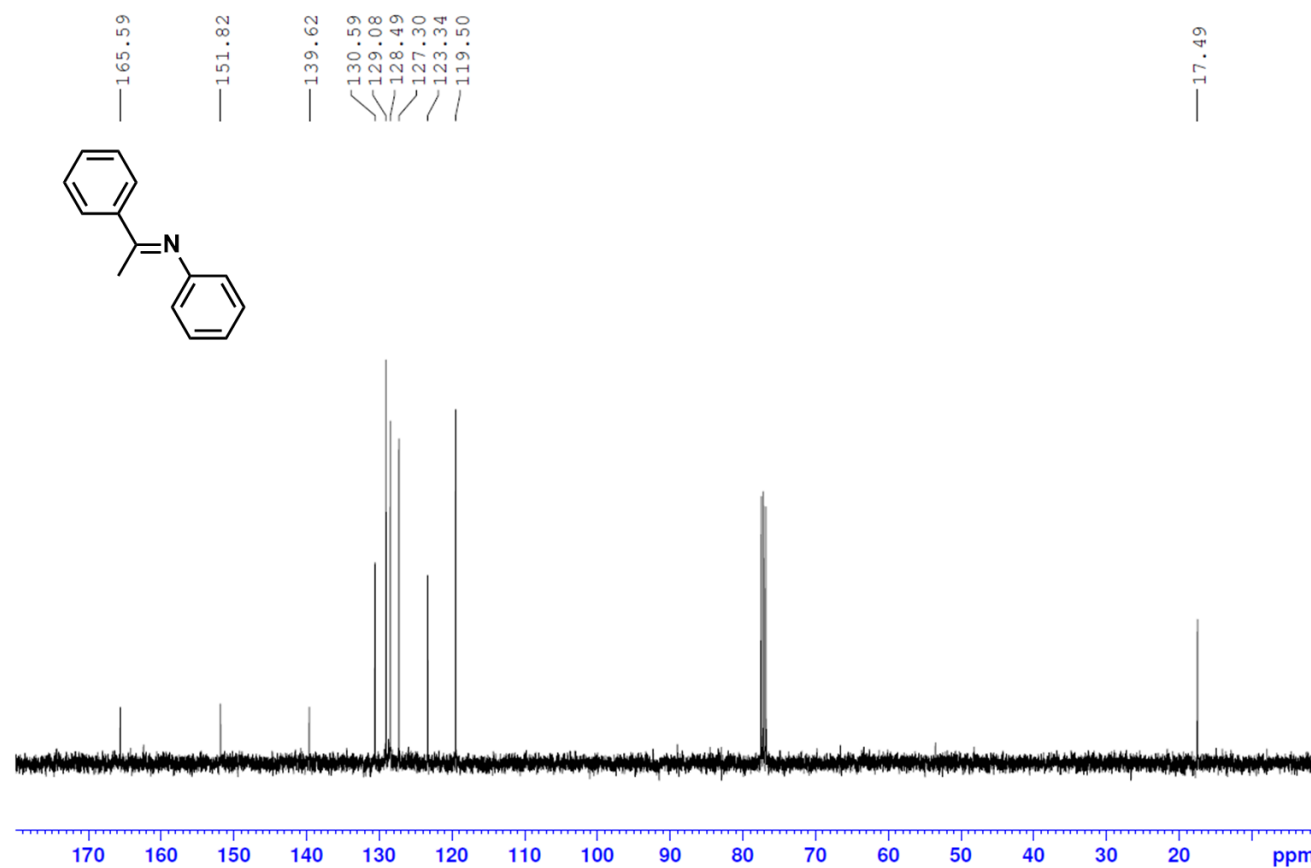
¹³C NMR spectrum of *N*-(naphthalen-1-yl)-2-phenyl-*N*'-tosylacetimidamide



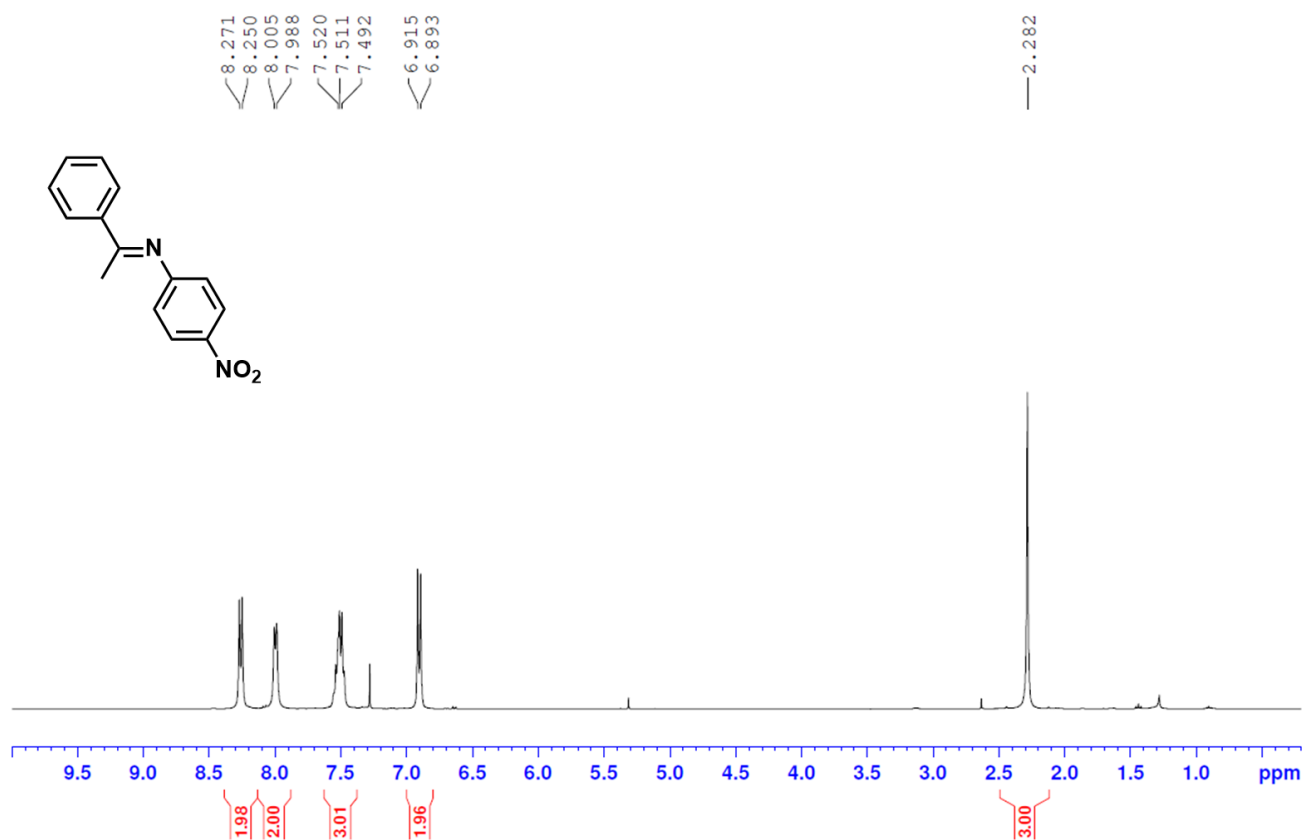
¹H NMR spectrum of *N*-(1-phenylethylidene)aniline



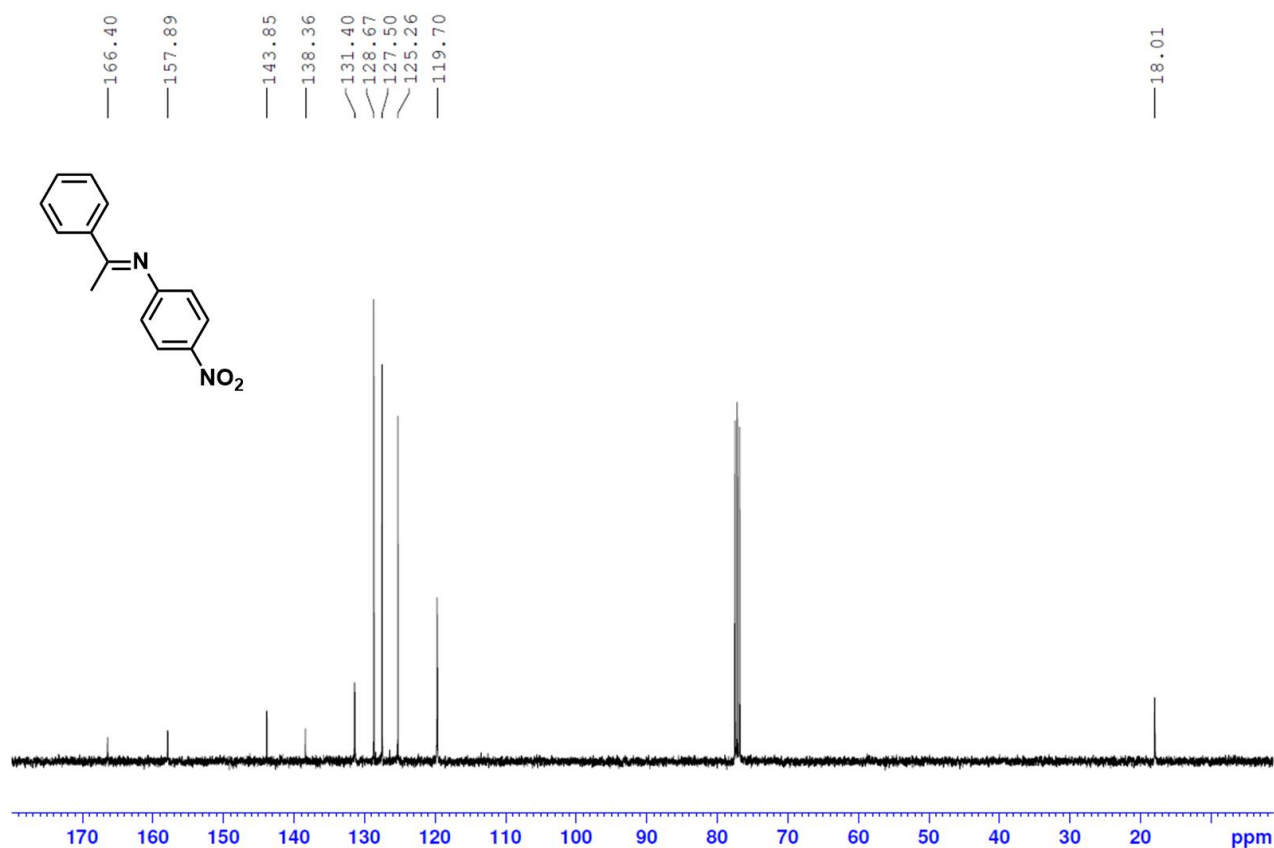
¹³C NMR spectrum of *N*-(1-phenylethylidene)aniline



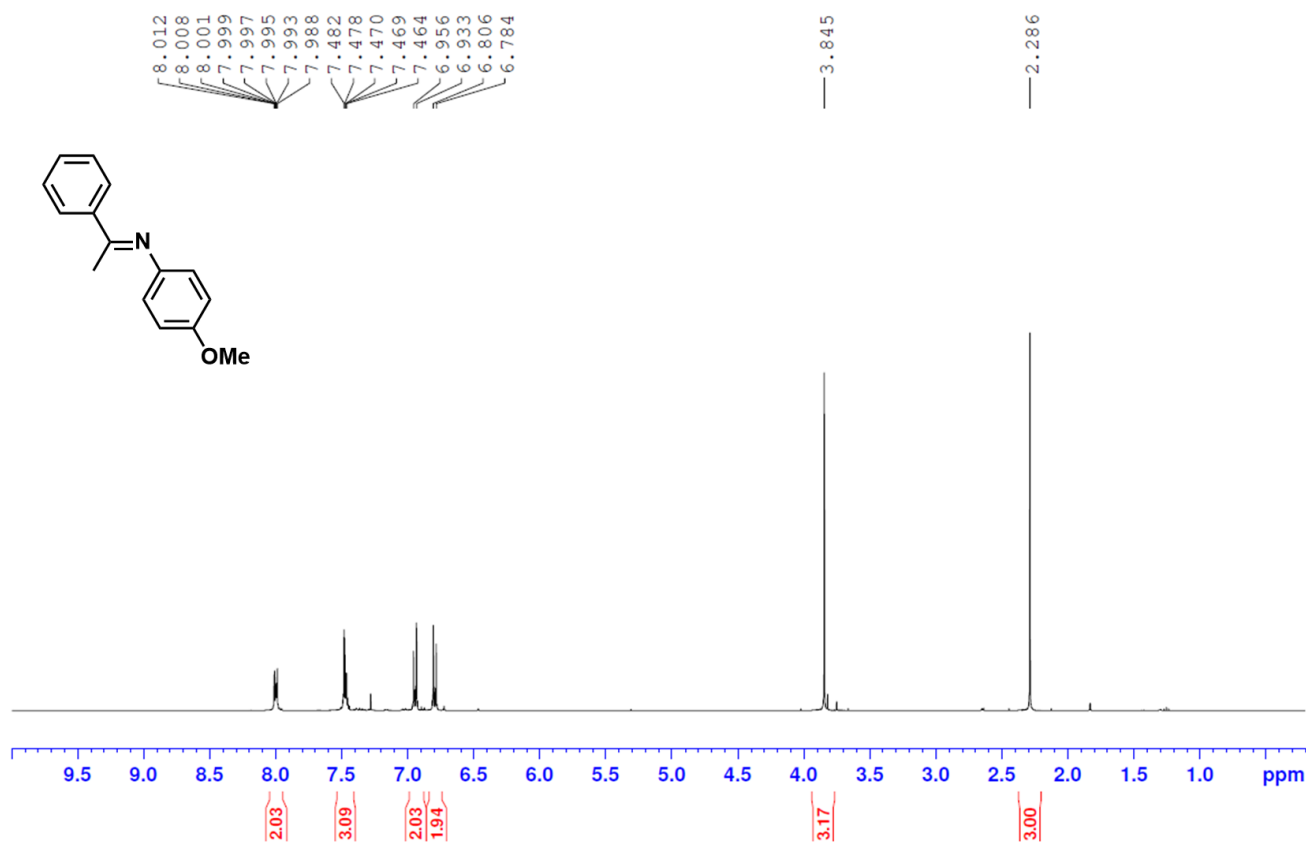
¹H NMR spectrum of 4-nitro-*N*-(1-phenylethylidene)aniline



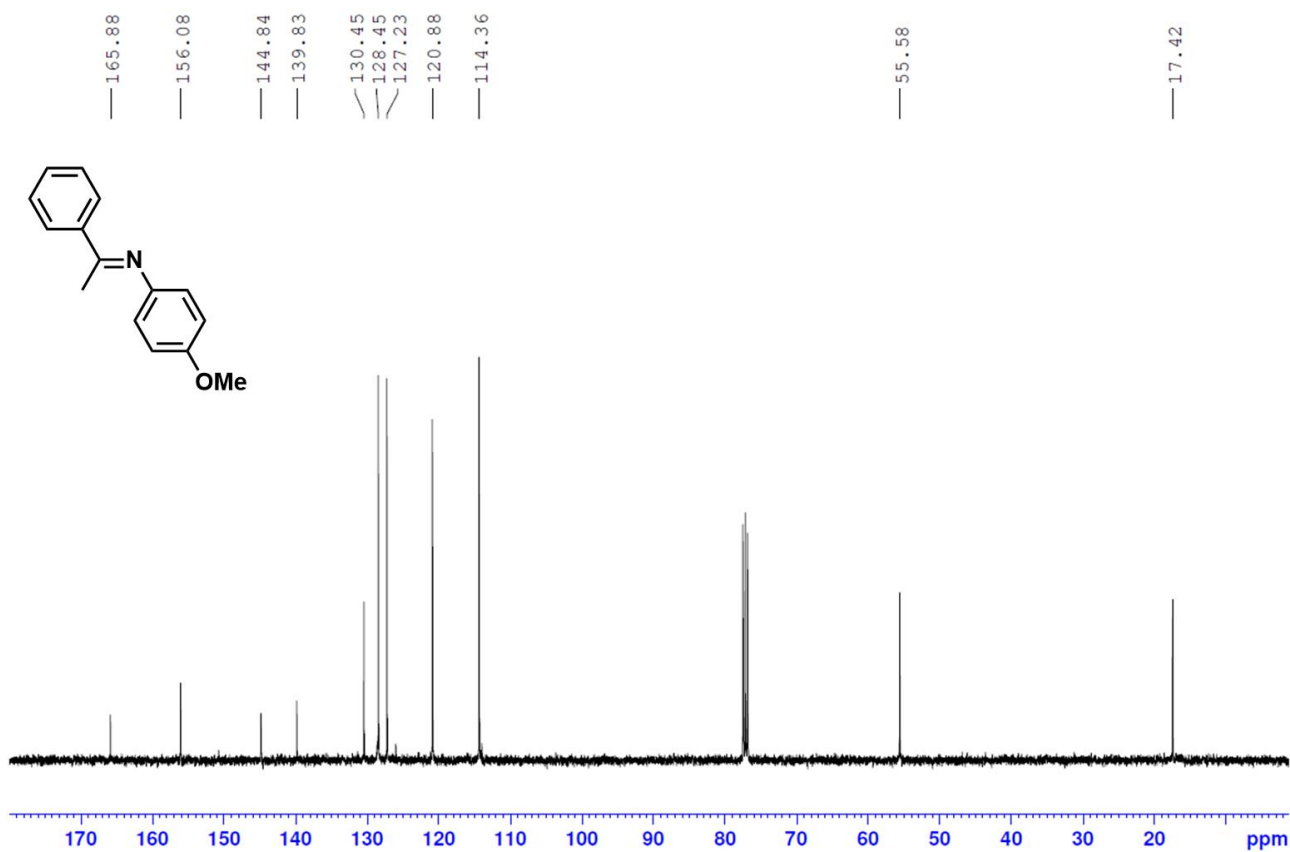
¹³C NMR spectrum of 4-nitro-*N*-(1-phenylethylidene)aniline



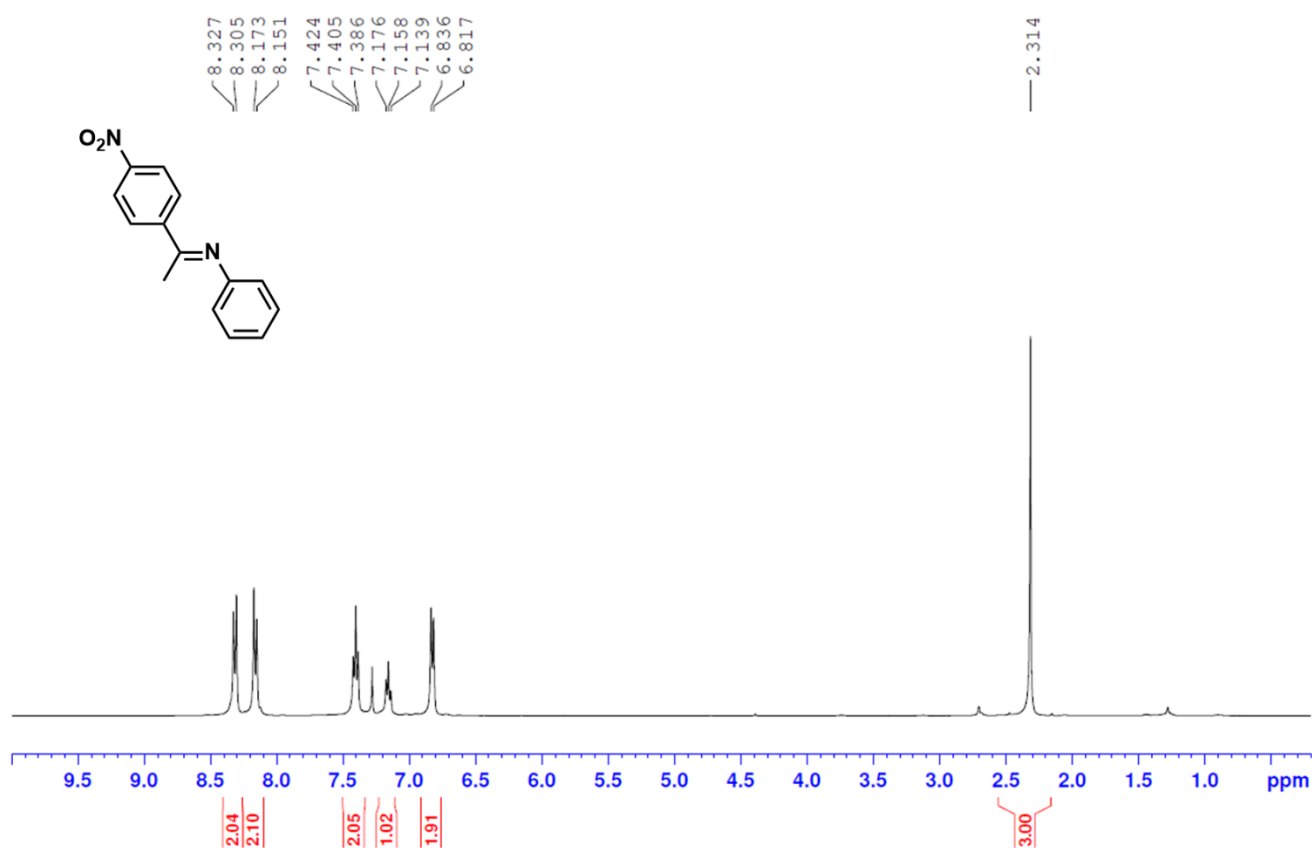
¹H NMR spectrum of 4-methoxy-*N*-(1-phenylethylidene)aniline



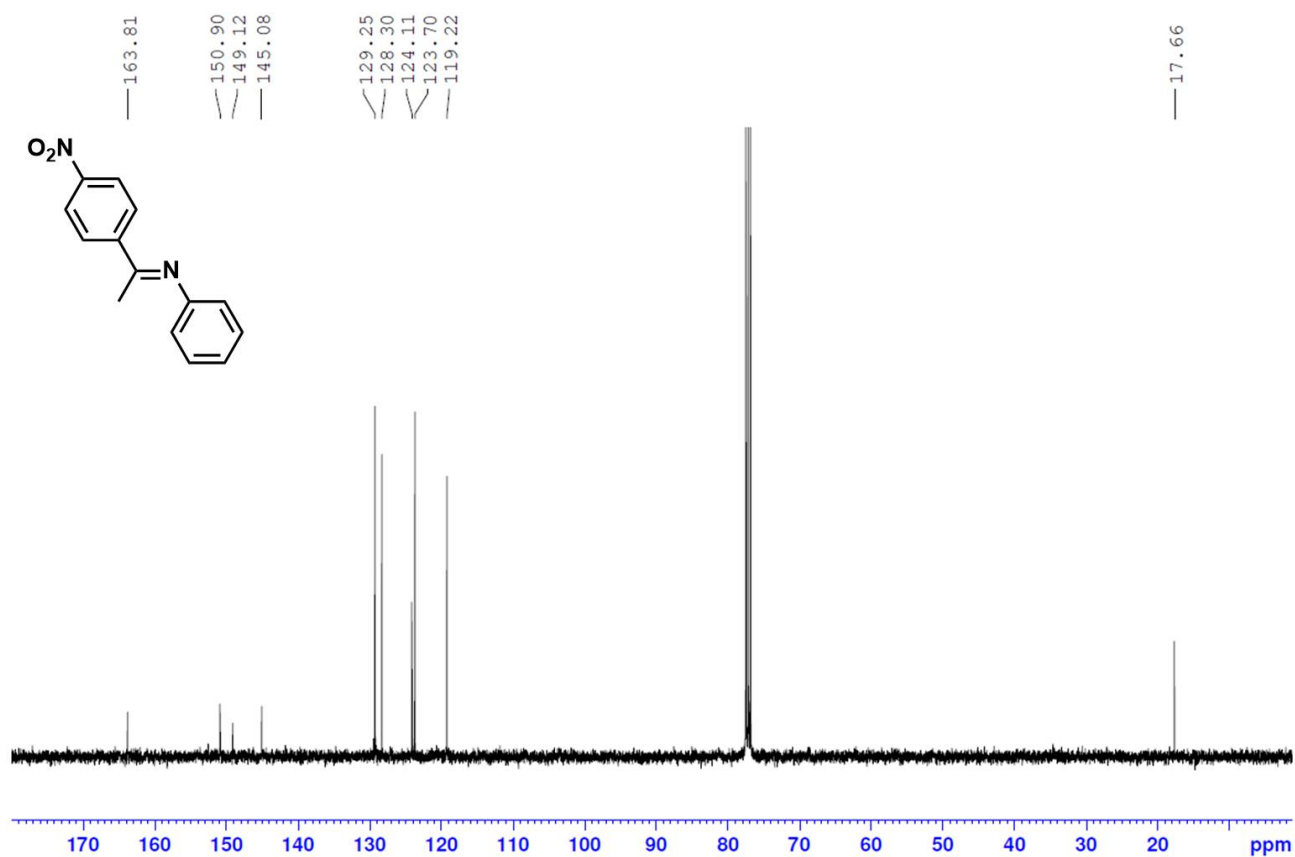
¹³C NMR spectrum of 4-methoxy-*N*-(1-phenylethylidene)aniline



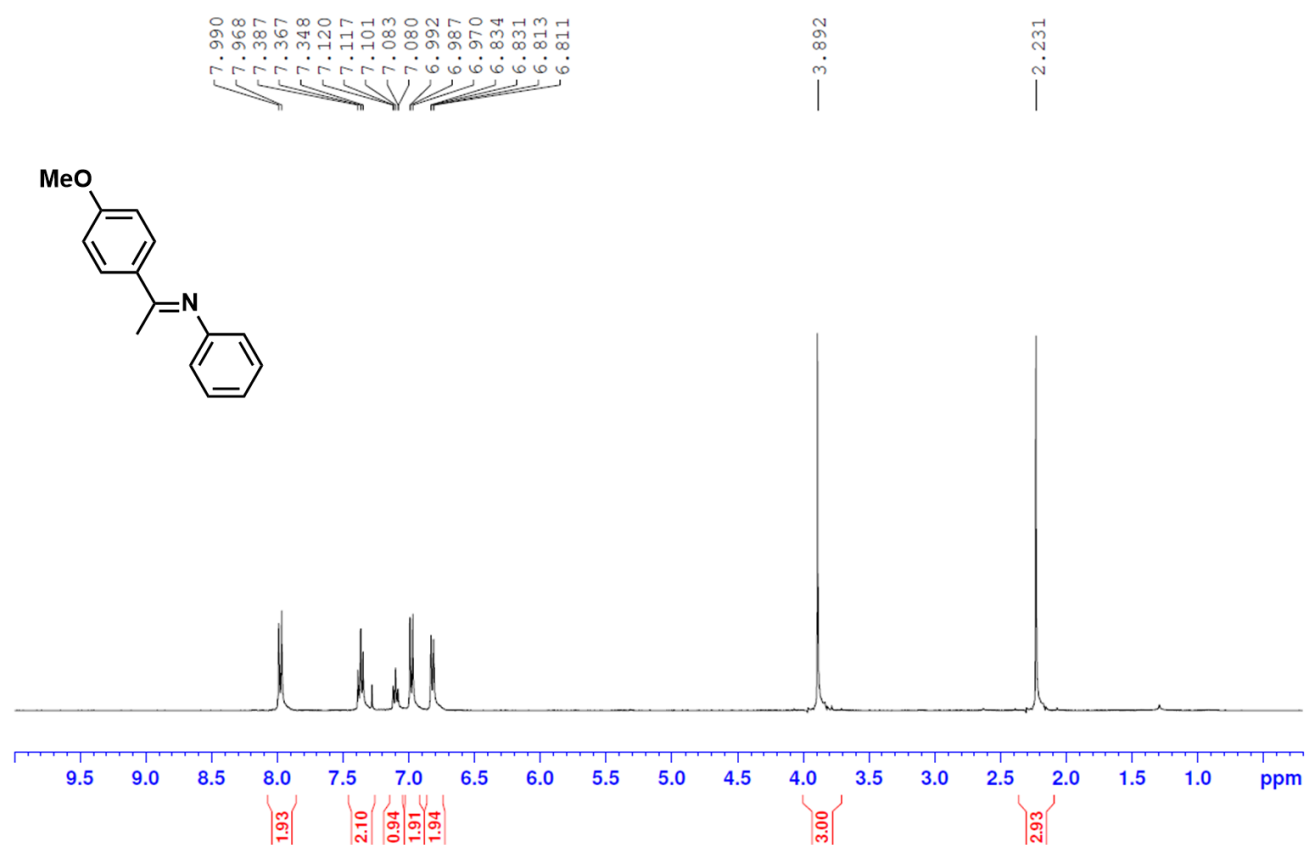
¹H NMR spectrum of *N*-(1-(4-nitrophenyl)ethylidene)aniline



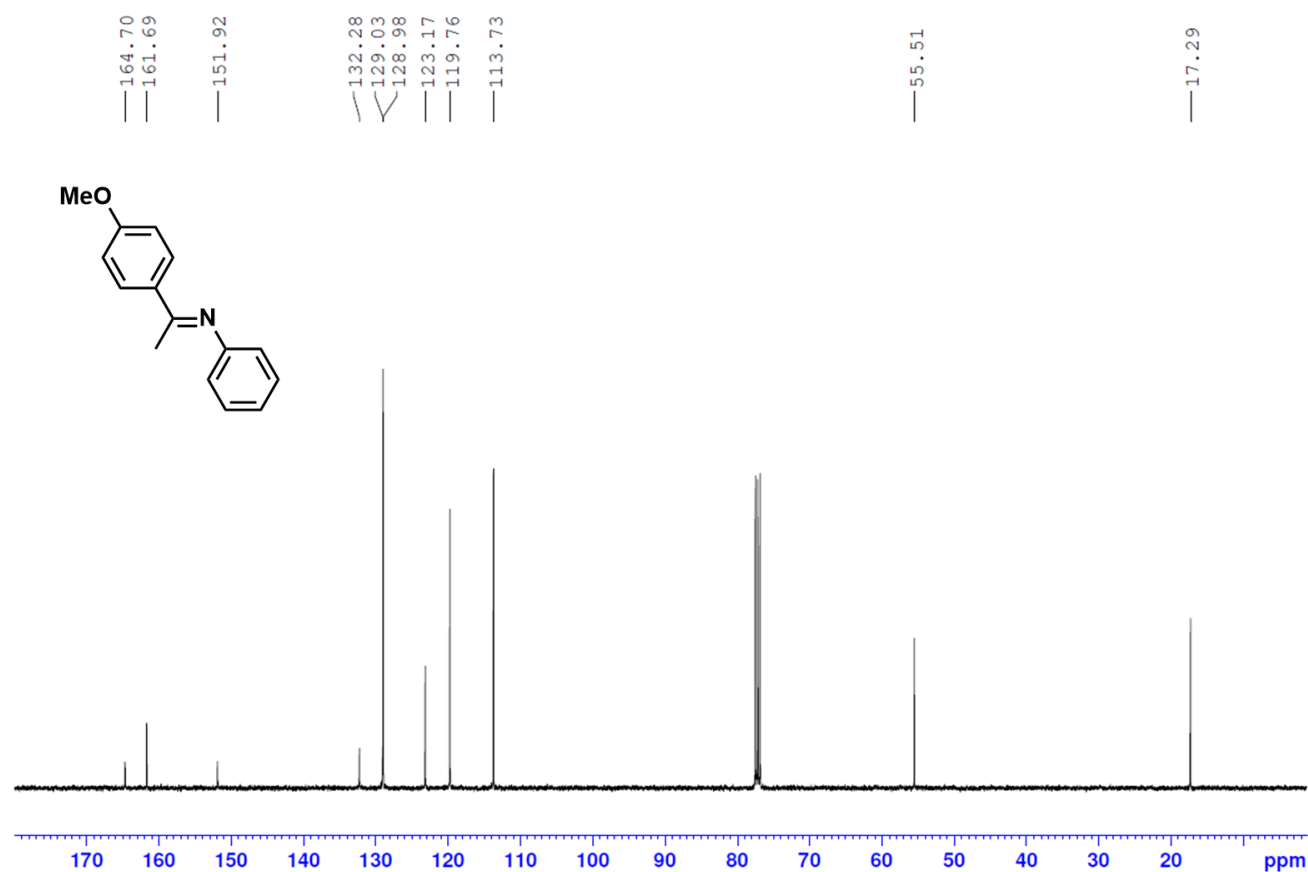
¹³C NMR spectrum of *N*-(1-(4-nitrophenyl)ethylidene)aniline



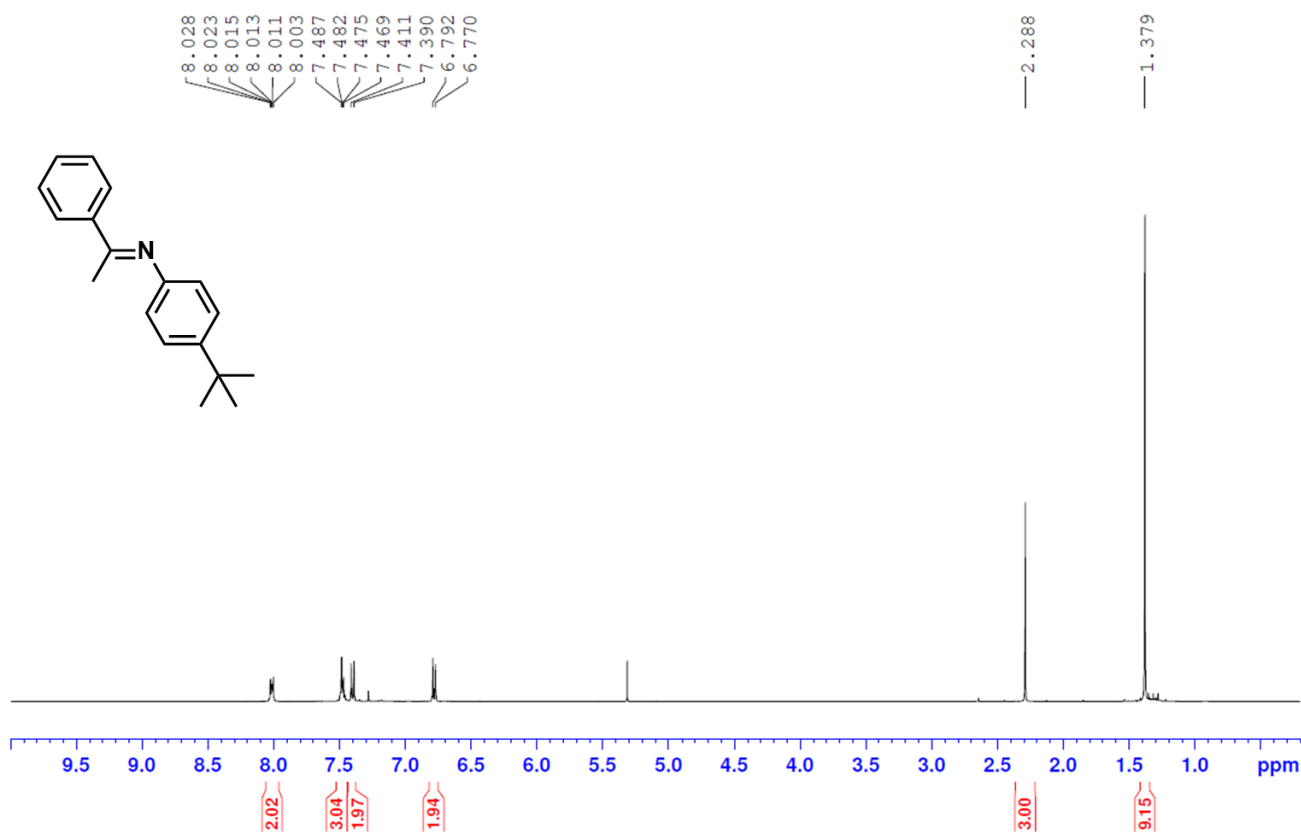
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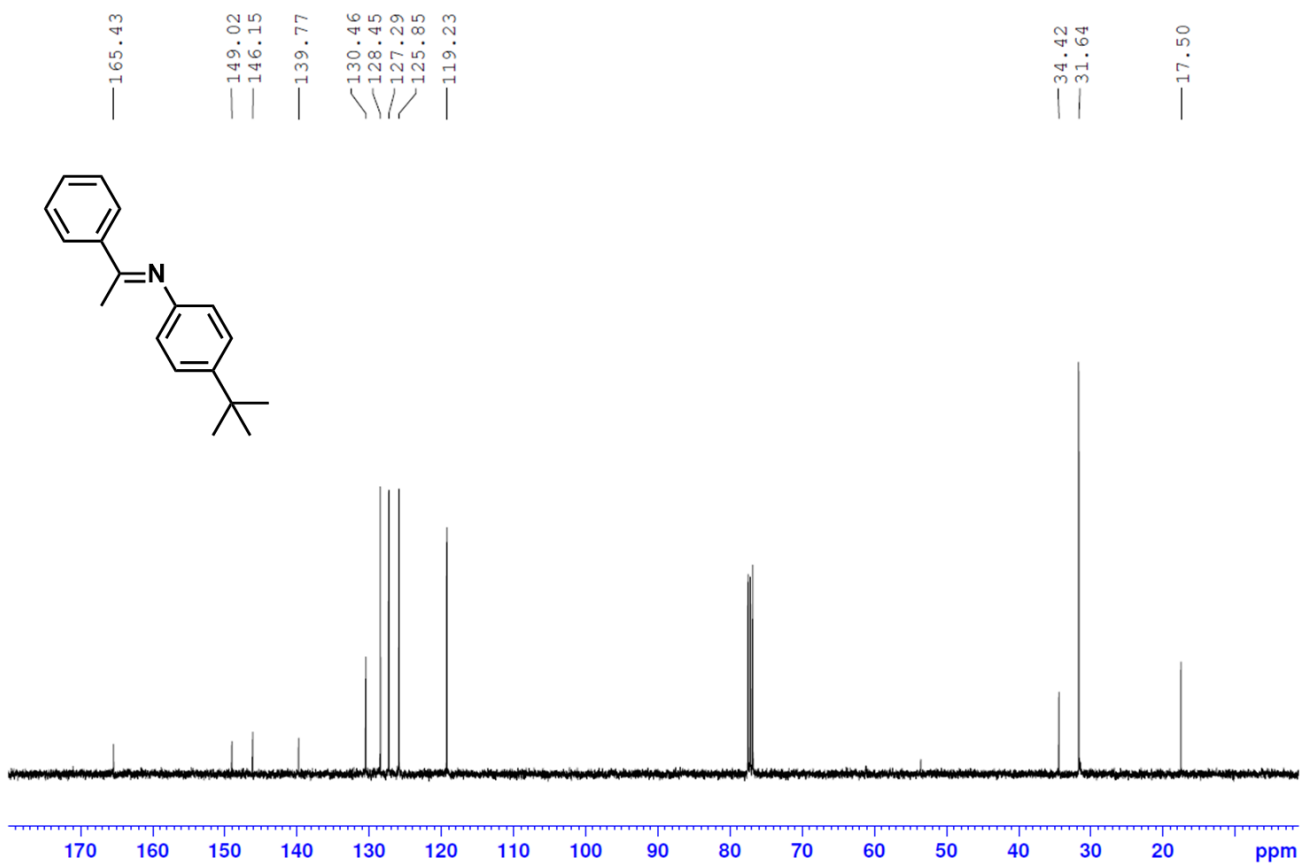
¹³C NMR spectrum of *N*-(1-(4-methoxyphenyl)ethylidene)aniline



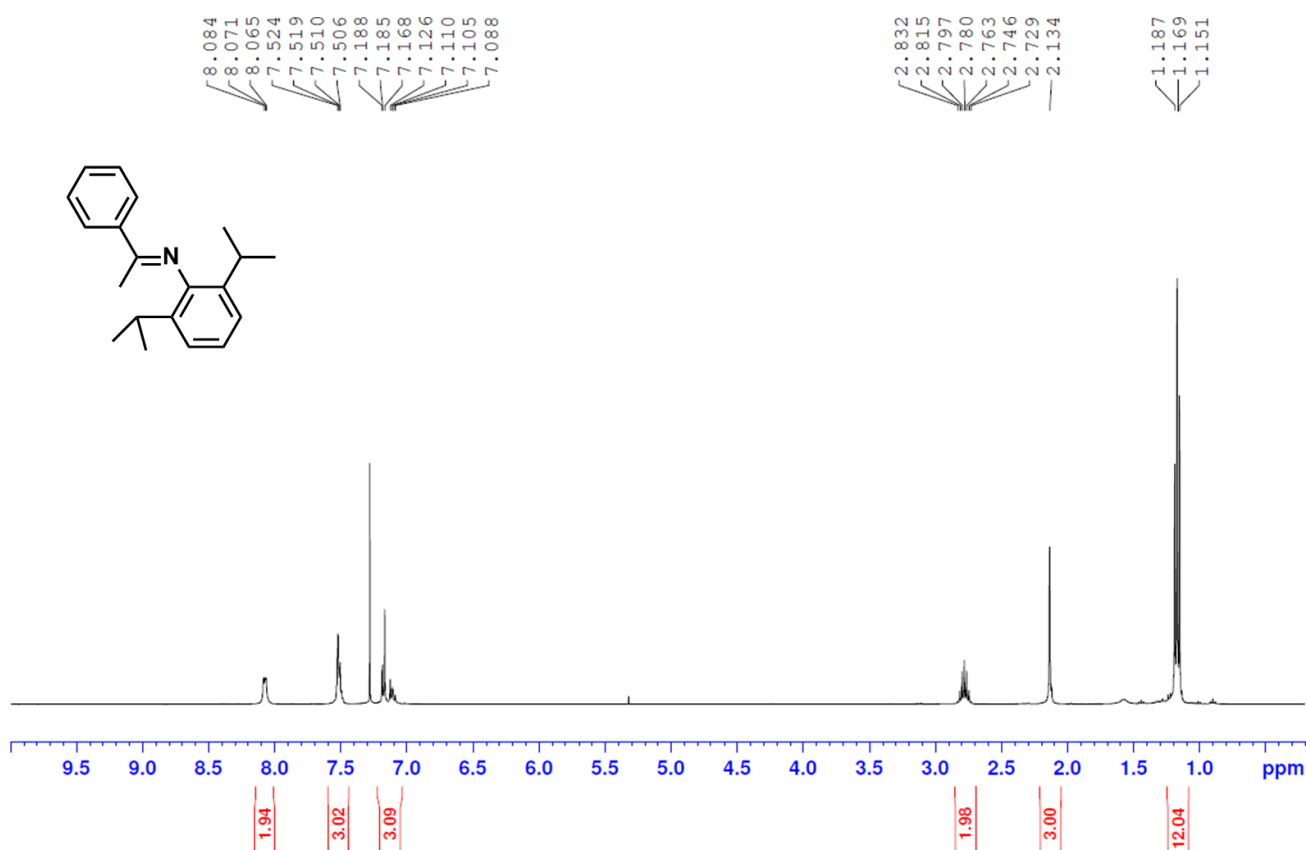
¹H NMR spectrum of 4-(*tert*-butyl)-*N*-(1-phenylethylidene)aniline



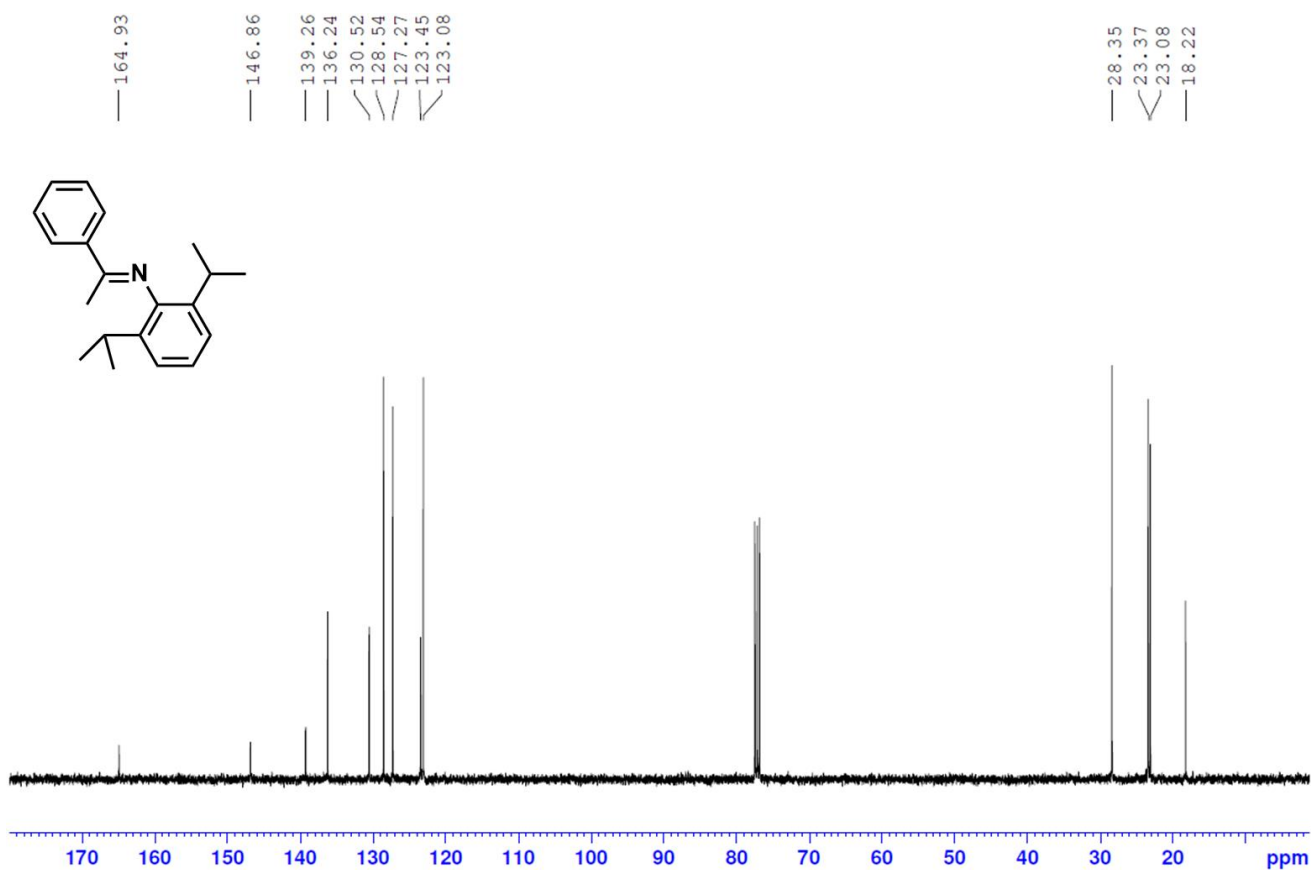
¹³C NMR spectrum of 4-(*tert*-butyl)-*N*-(1-phenylethylidene)aniline



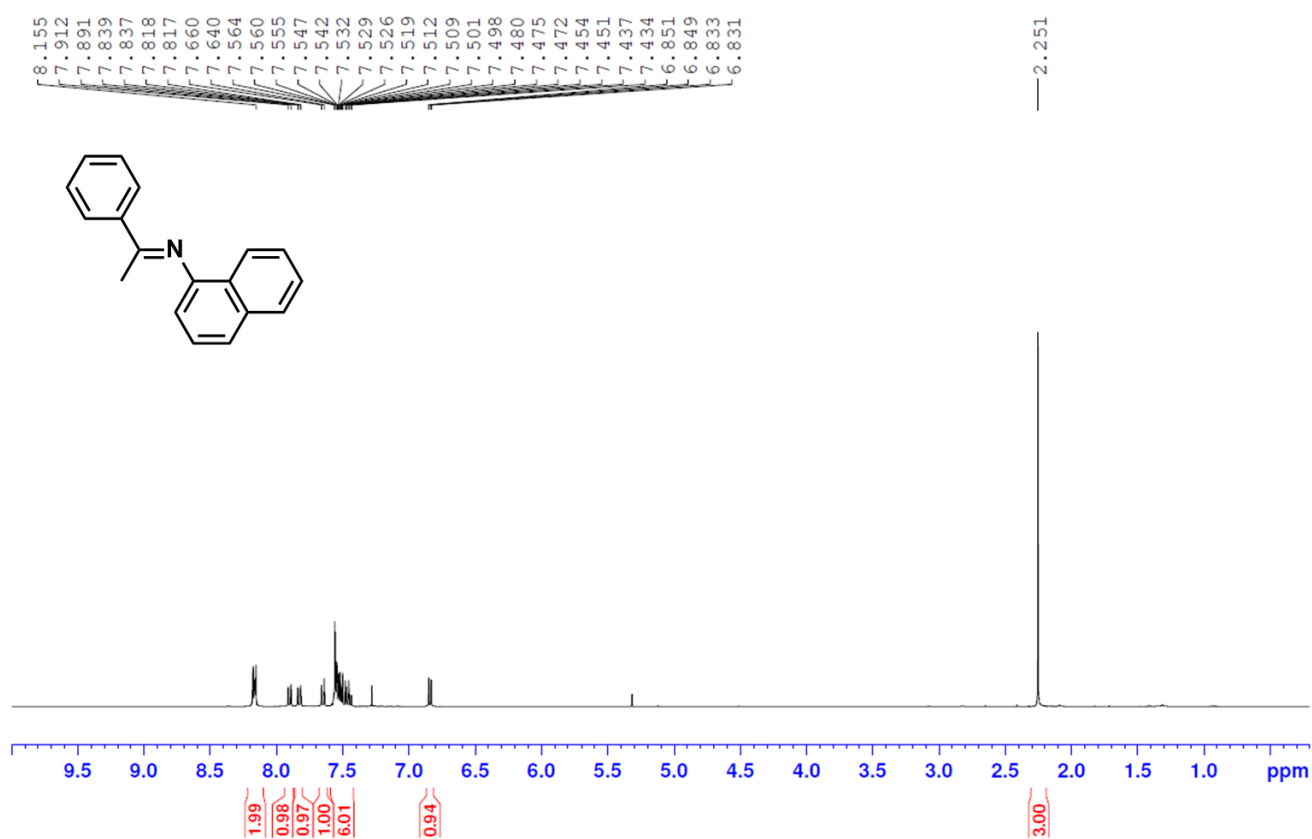
¹H NMR spectrum of 2,6-diisopropyl-*N*-(1-phenylethylidene)aniline



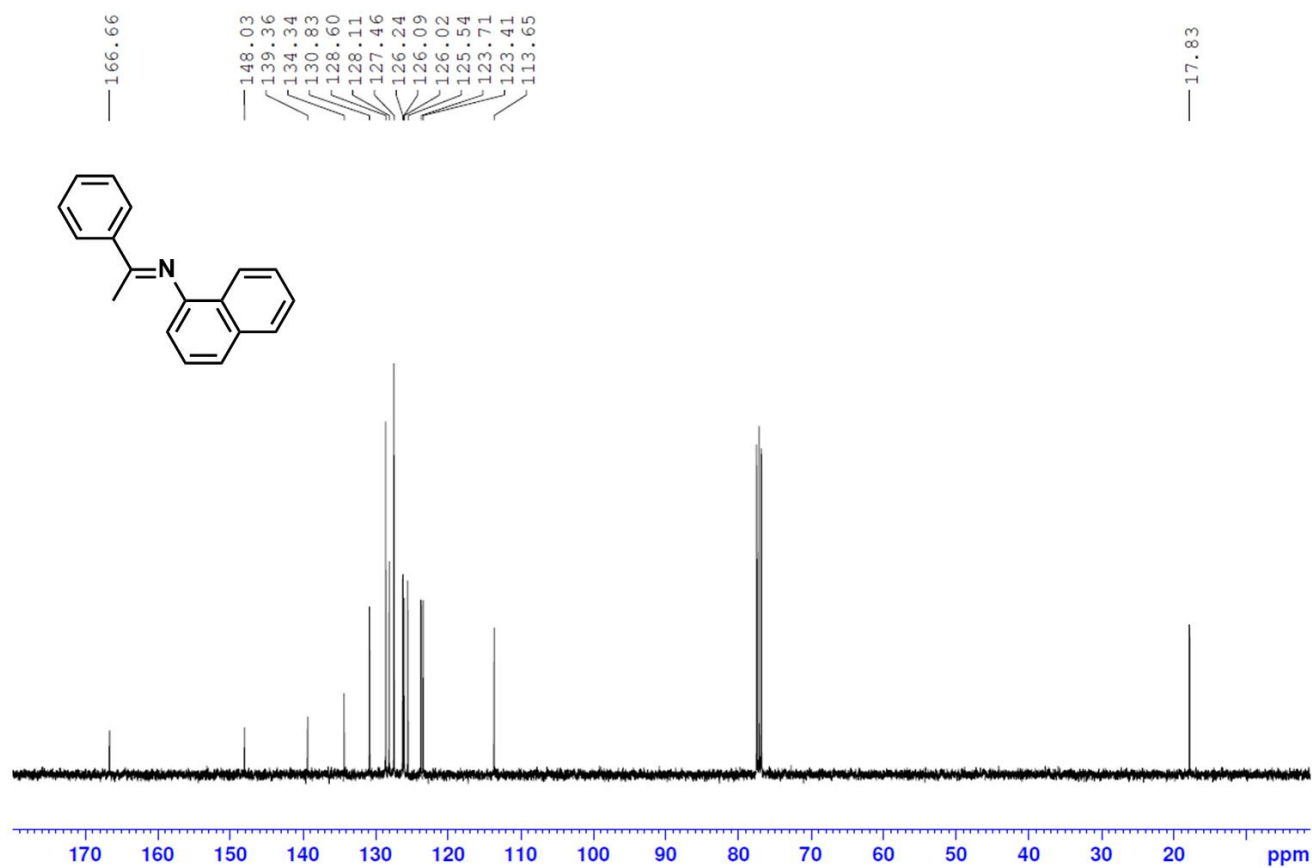
¹³C NMR spectrum of 2,6-diisopropyl-*N*-(1-phenylethylidene)aniline



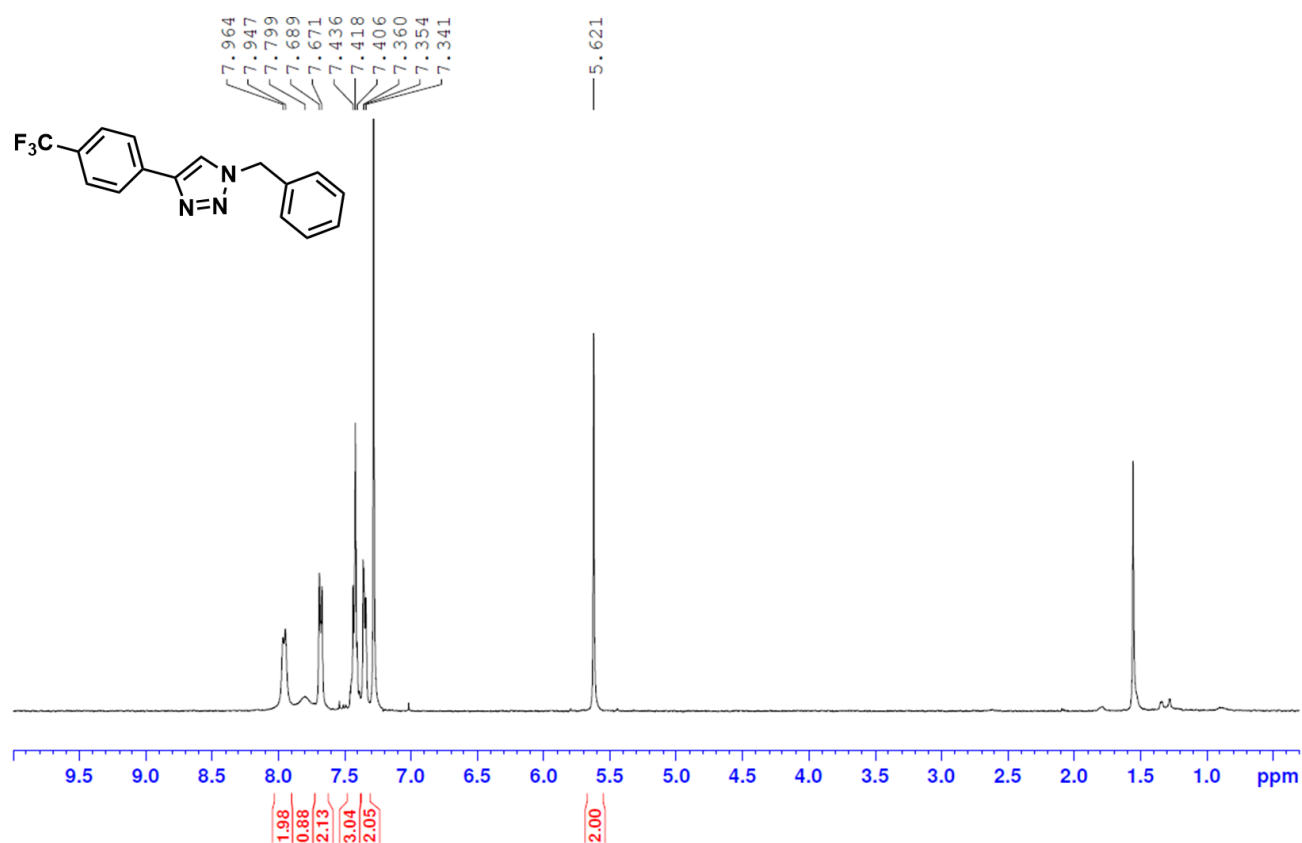
¹H NMR spectrum of *N*-(1-phenylethylidene)naphthalen-1-amine



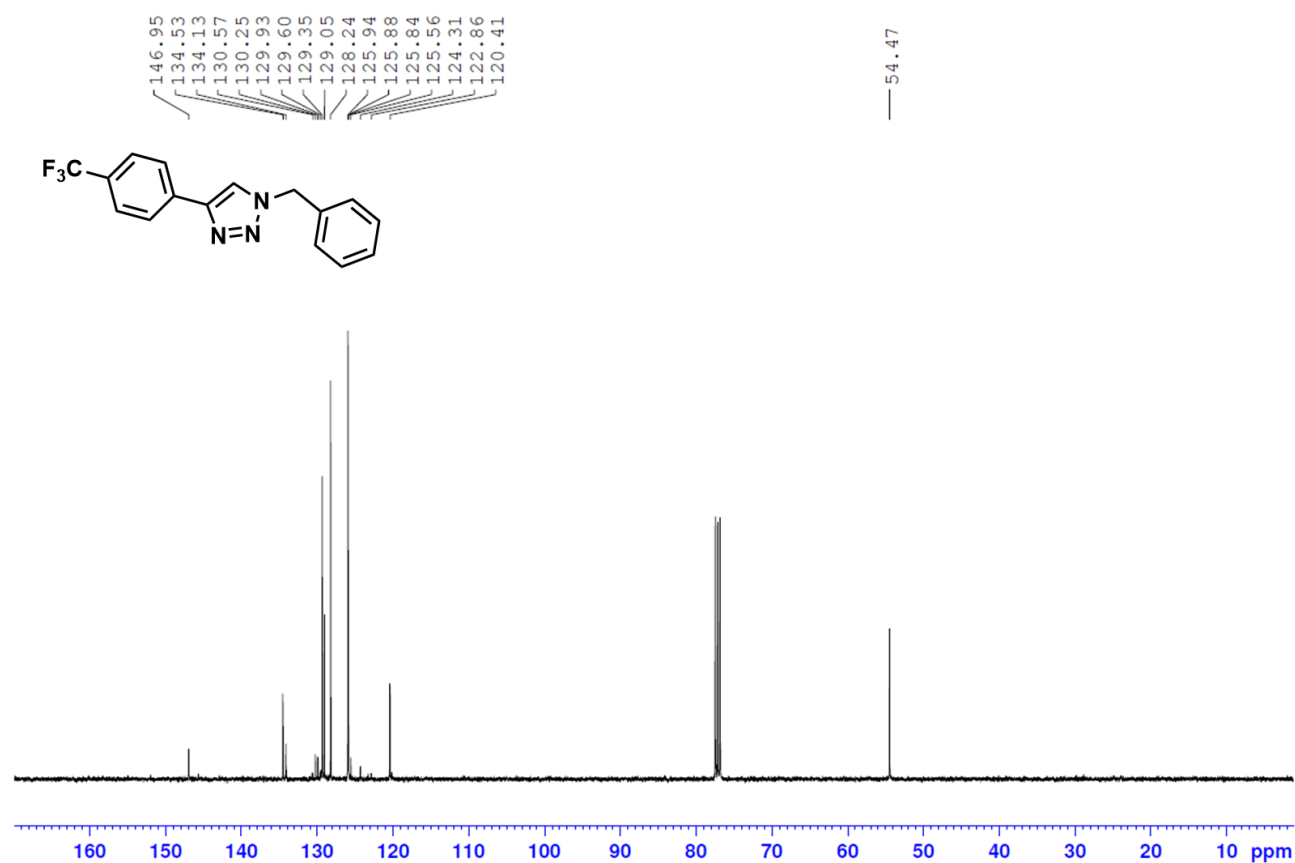
¹³C NMR spectrum of *N*-(1-phenylethylidene)naphthalen-1-amine



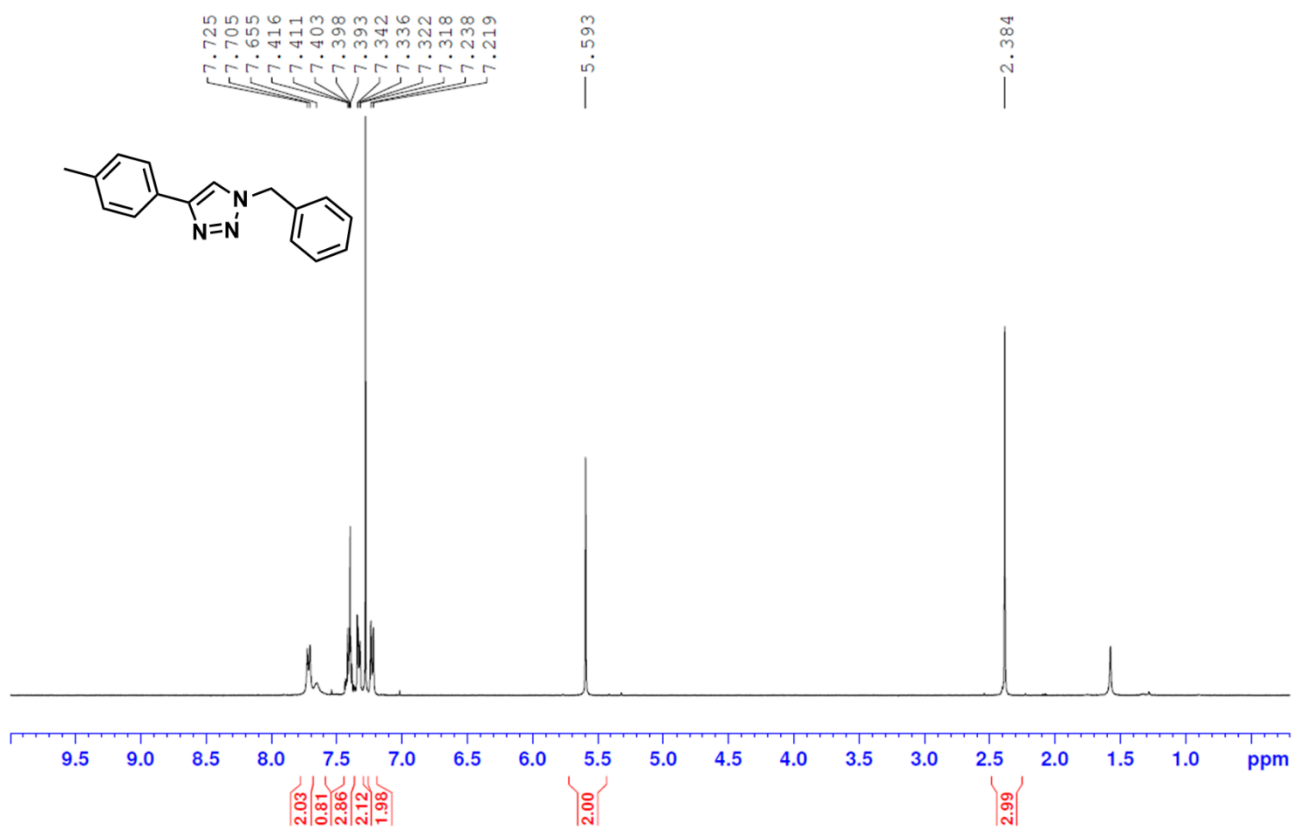
¹H NMR spectrum of 1-benzyl-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole



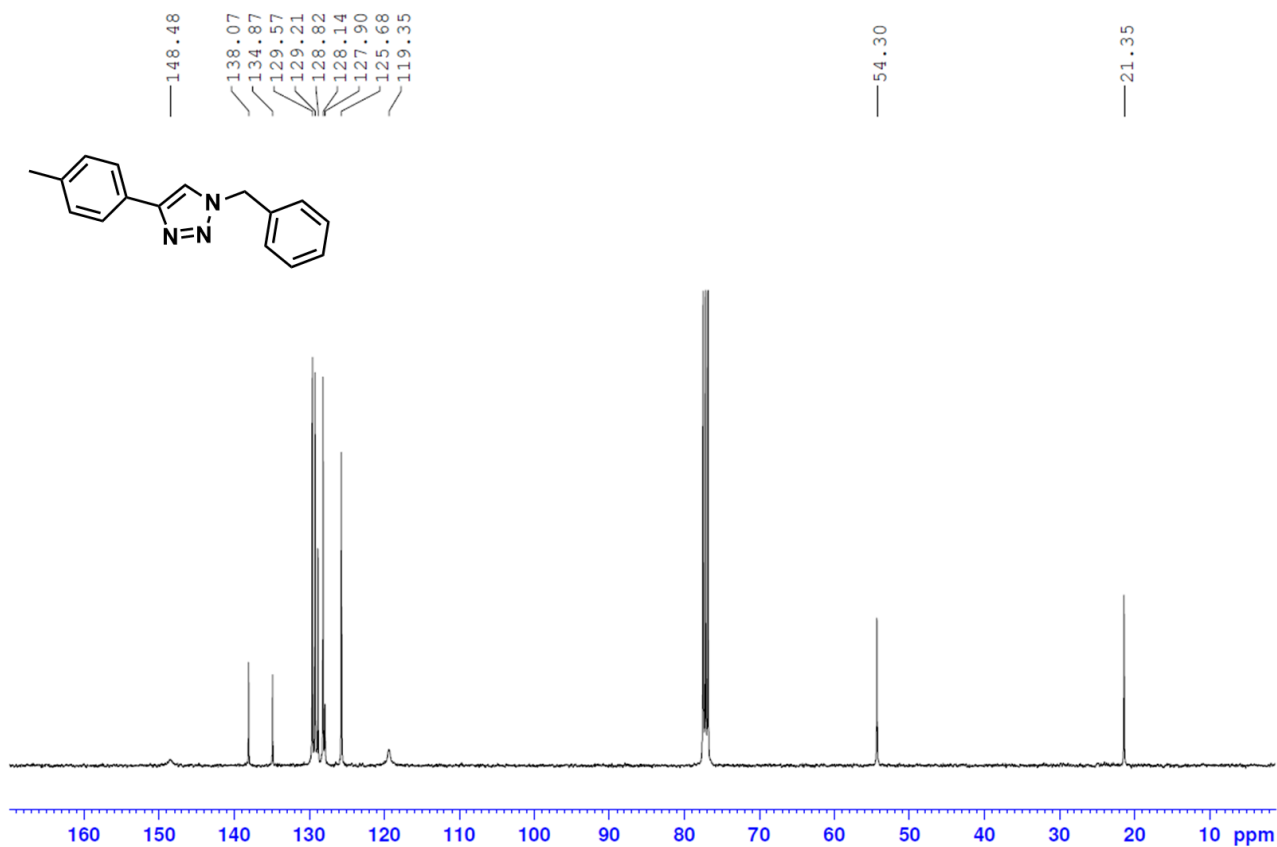
¹³C NMR spectrum of 1-benzyl-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole



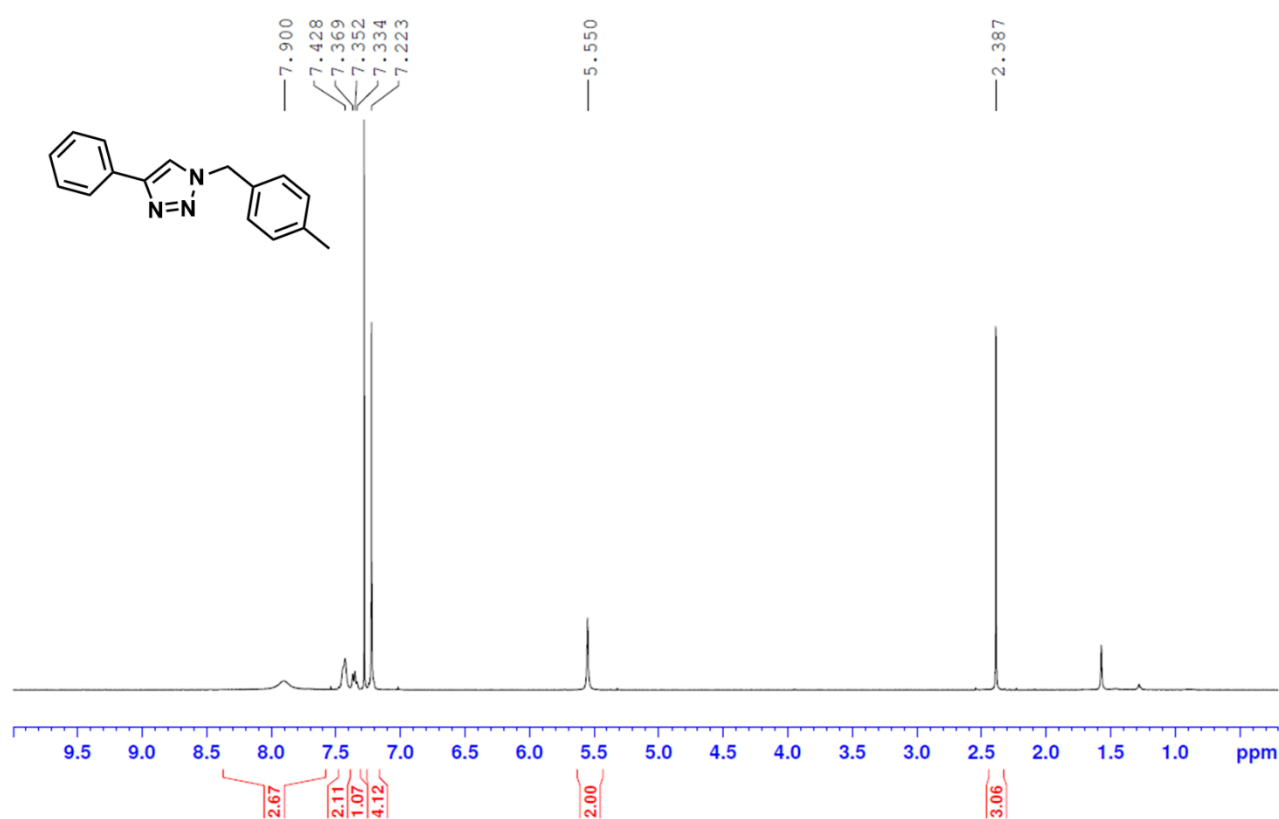
¹H NMR spectrum of 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole



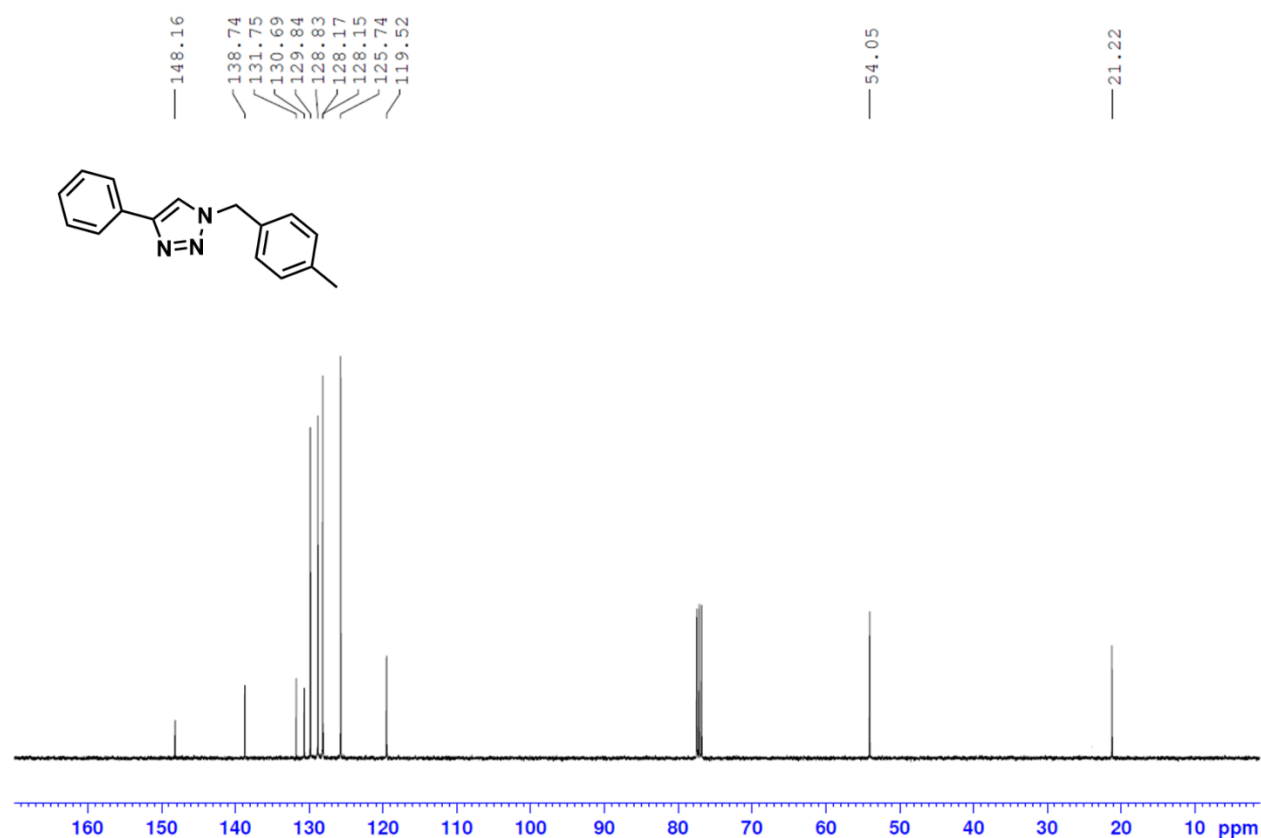
¹³C NMR spectrum of 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole



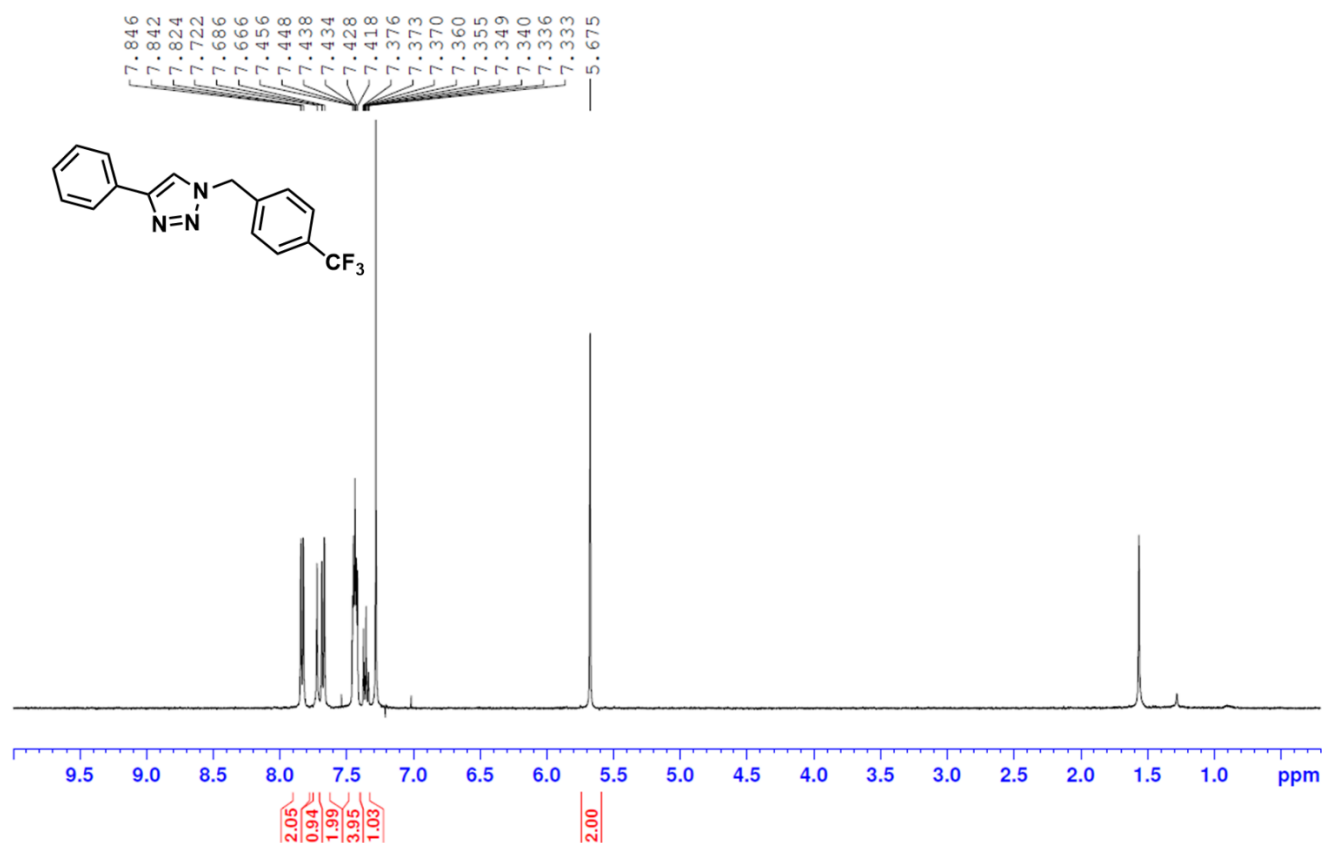
¹H NMR spectrum of 1-(4-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole



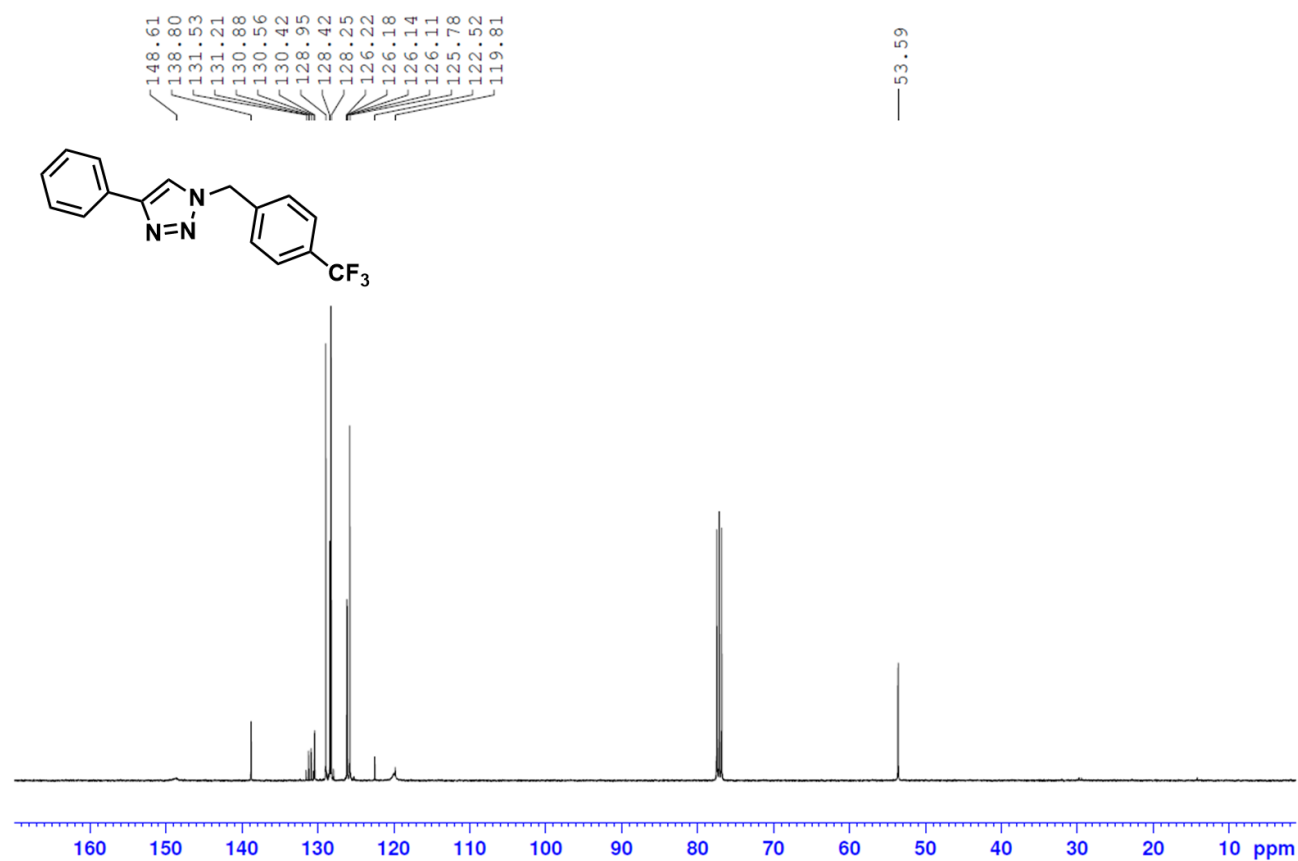
¹³C NMR spectrum of 1-(4-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole



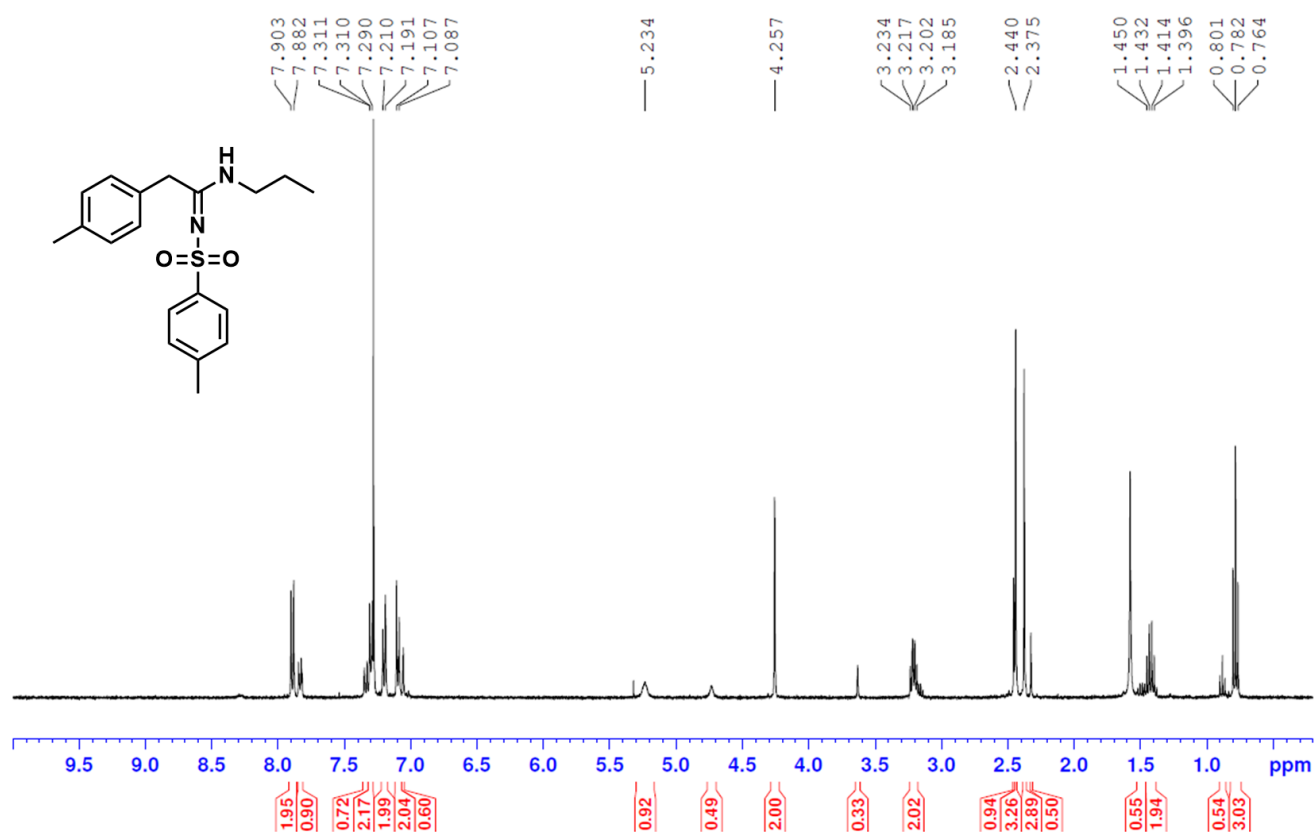
¹H NMR spectrum of 4-phenyl-1-(4-(trifluoromethyl)benzyl)-1*H*-1,2,3-triazole



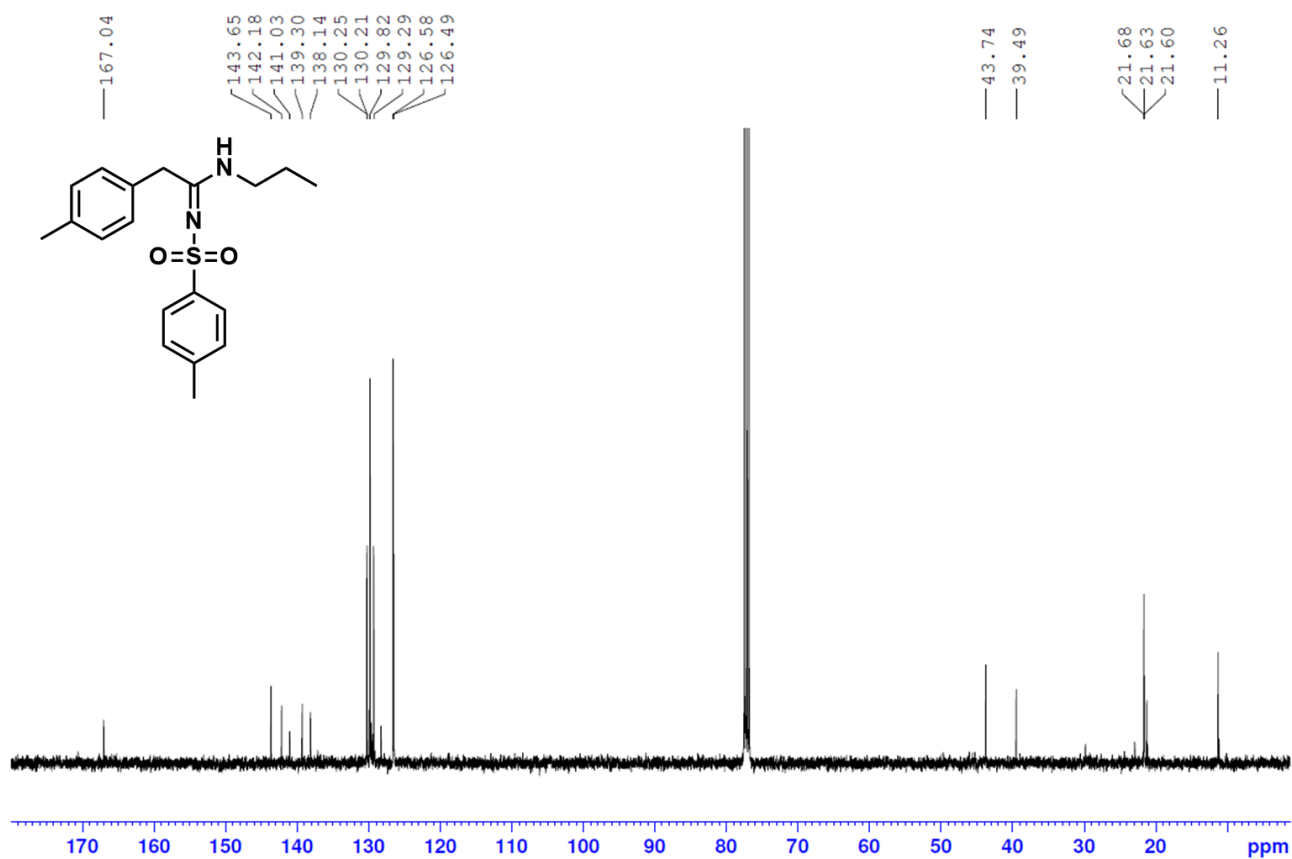
¹³C NMR spectrum of 4-phenyl-1-(4-(trifluoromethyl)benzyl)-1*H*-1,2,3-triazole



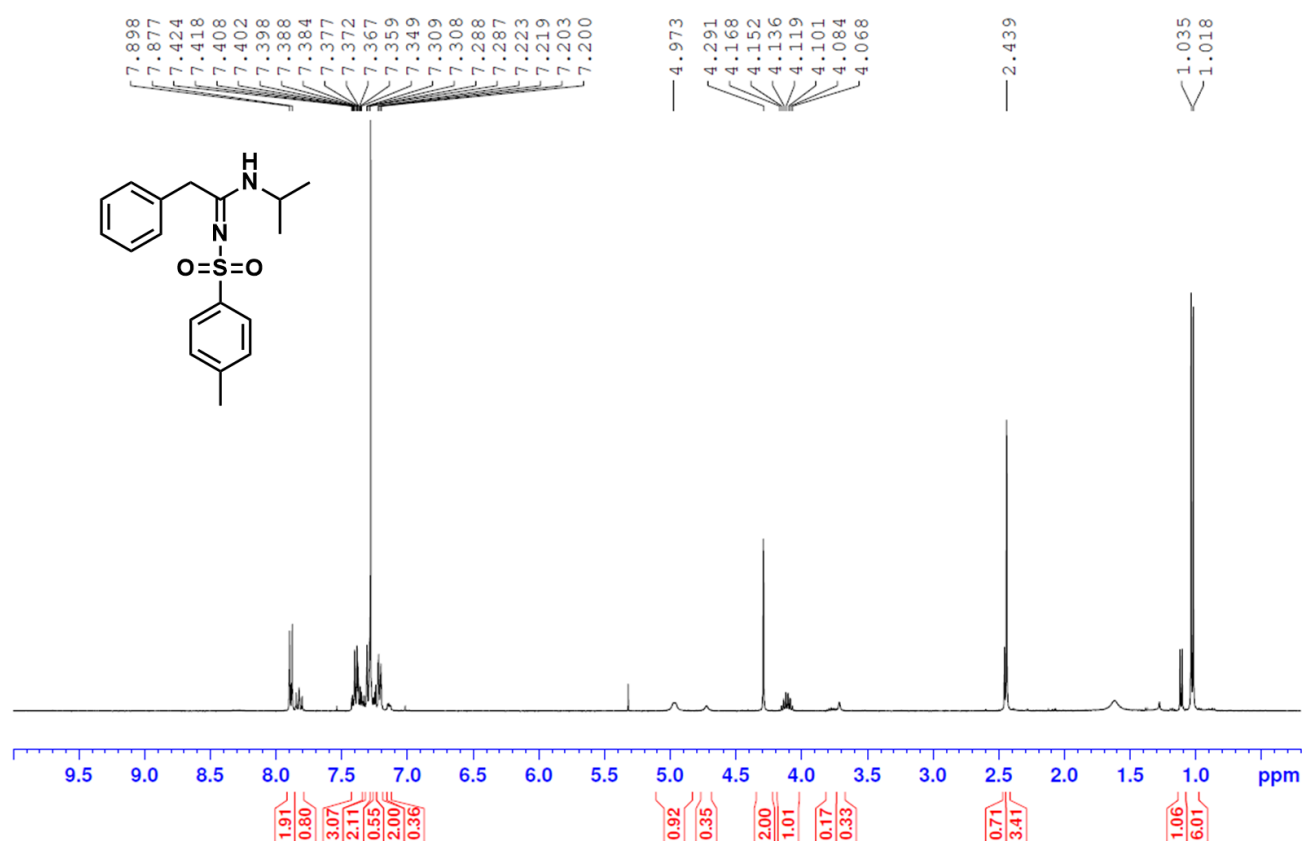
¹H NMR spectrum of *N*-propyl-2-(*p*-tolyl)-*N'*-tosylacetimidamide



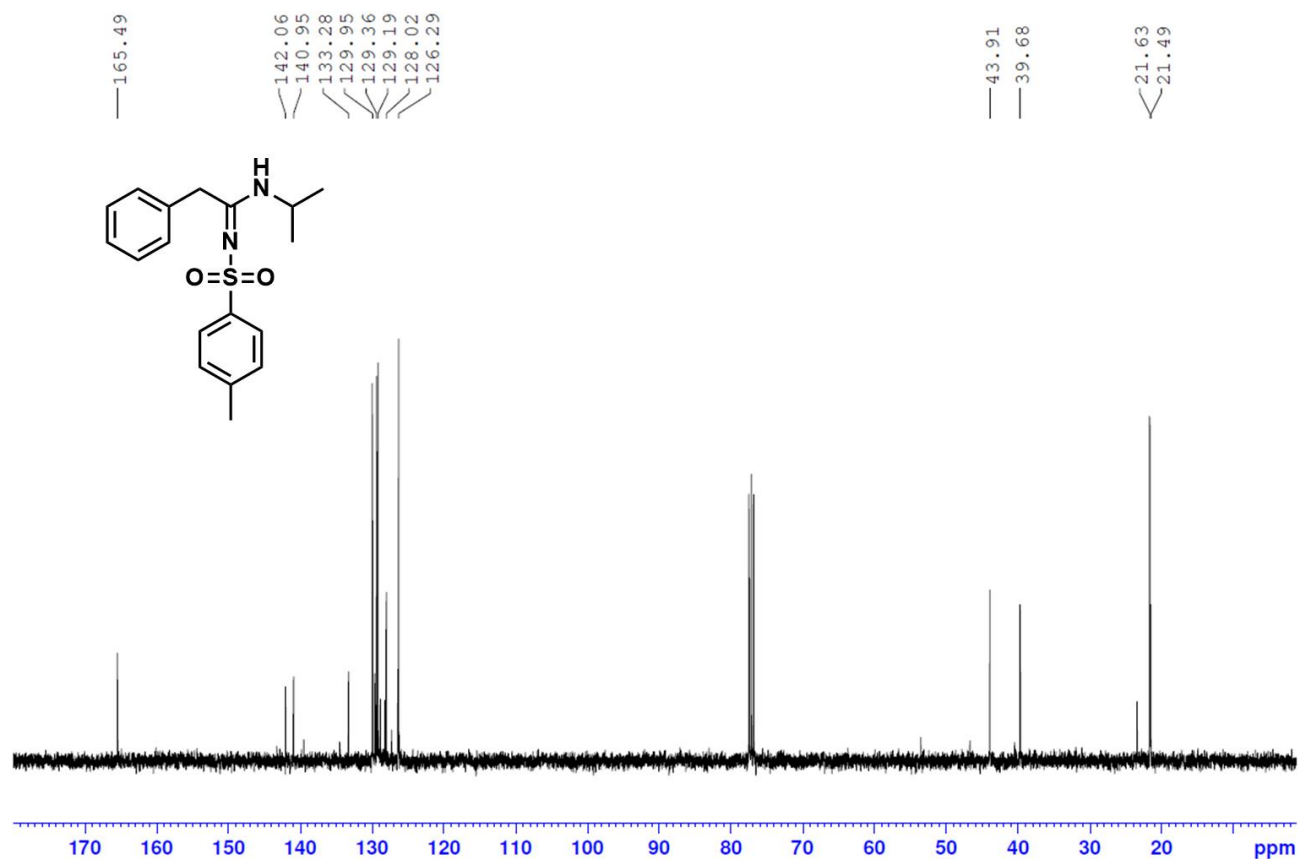
¹³C NMR spectrum of *N*-propyl-2-(*p*-tolyl)-*N'*-tosylacetimidamide



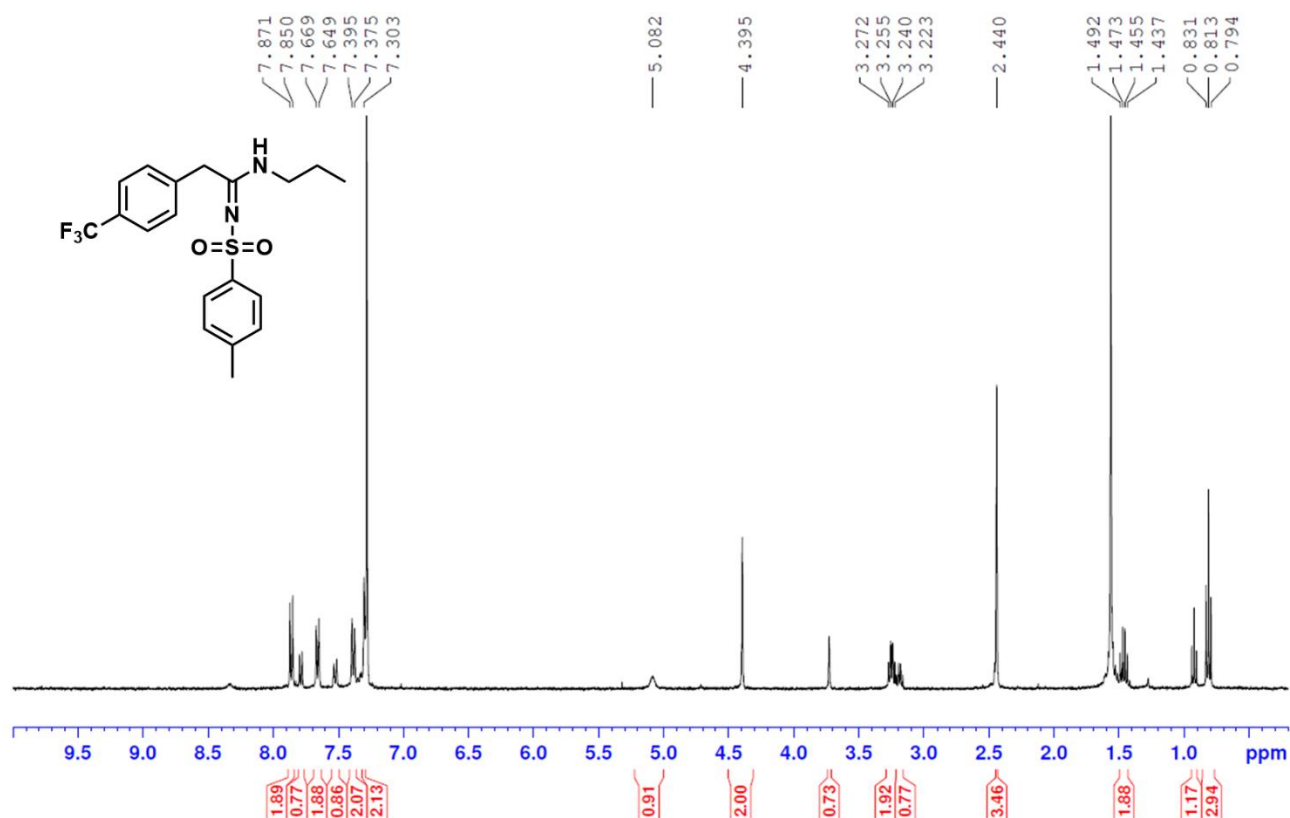
¹H NMR spectrum of *N*-isopropyl-2-phenyl-*N*-tosylacetimidamide



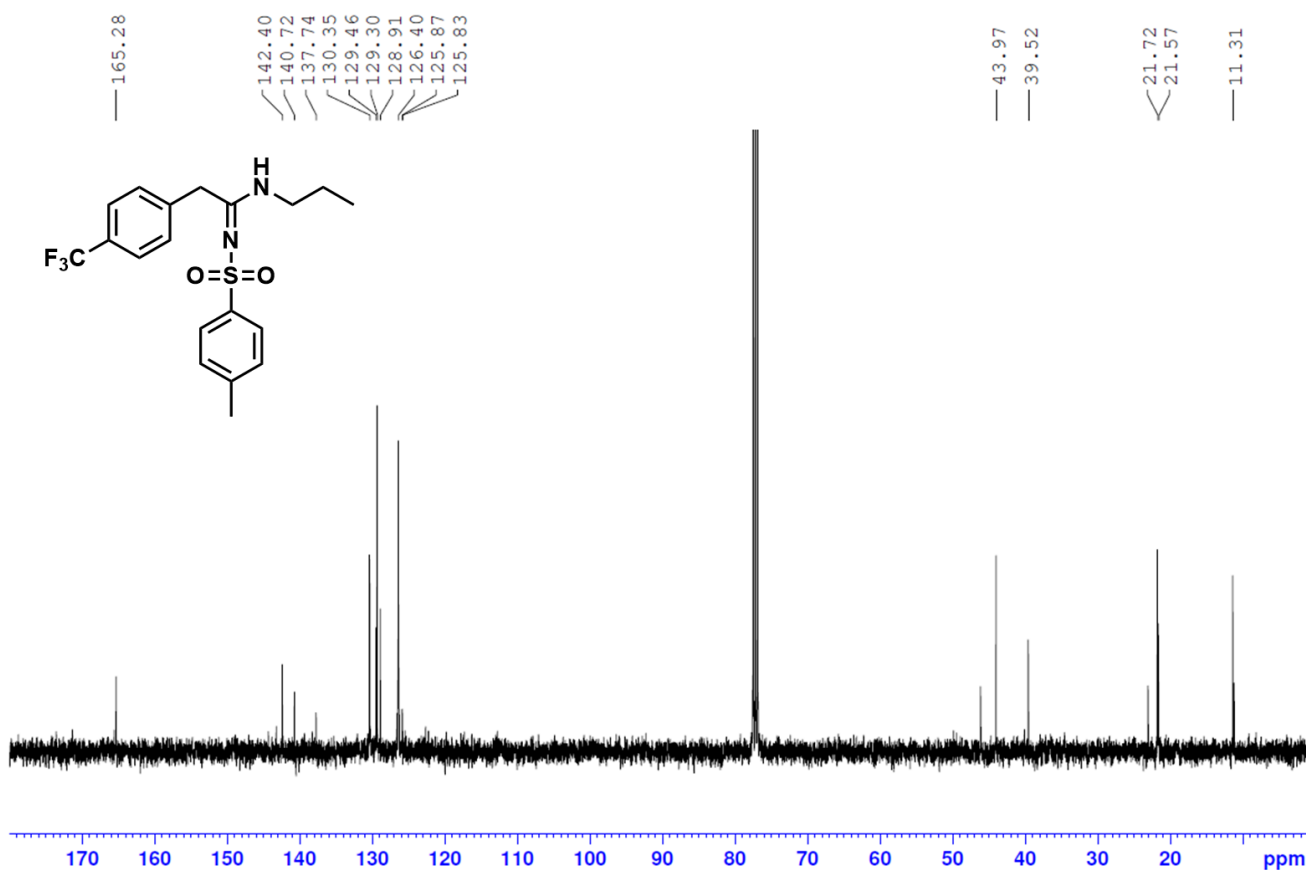
¹³C NMR spectrum of *N*-isopropyl-2-phenyl-*N*-tosylacetimidamide



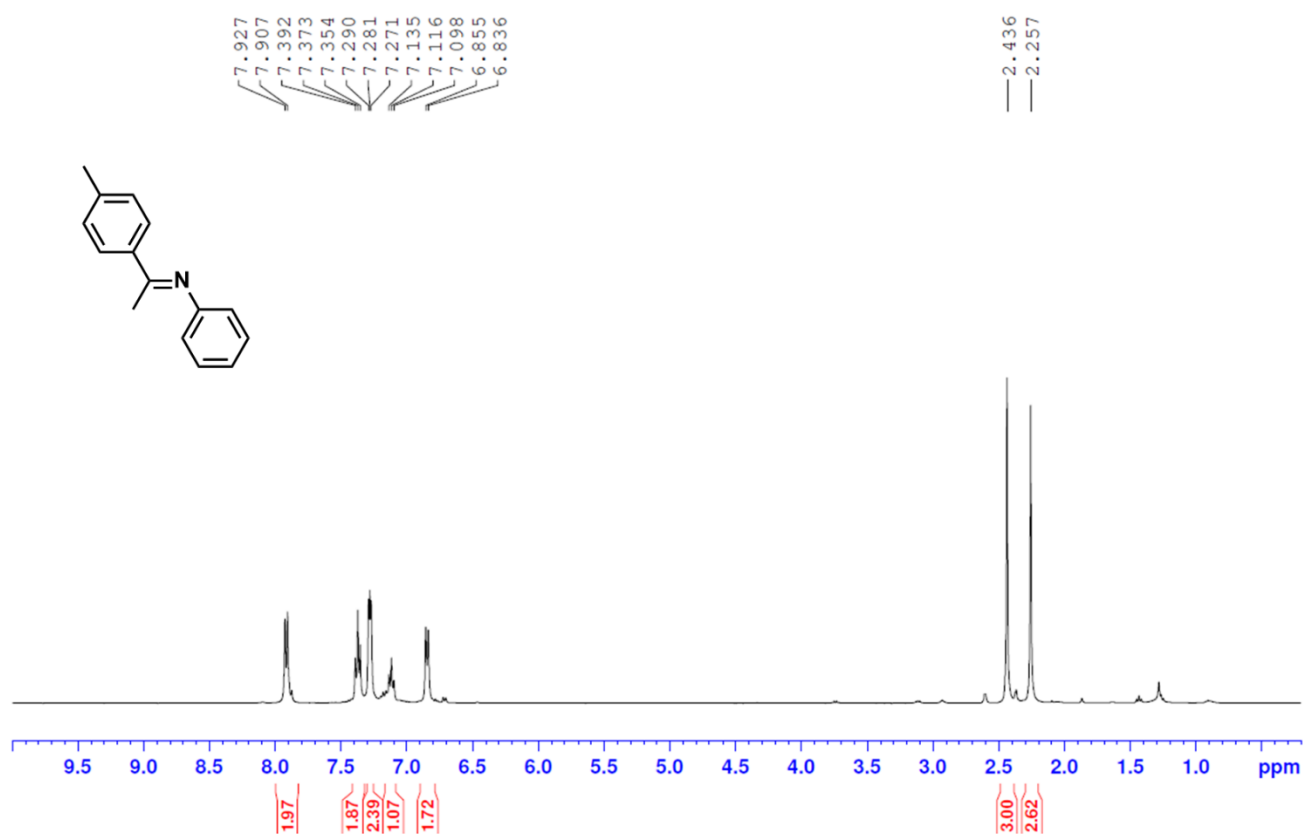
¹H NMR spectrum of *N*-propyl-*N*-tosyl-2-(4-(trifluoromethyl)phenyl)acetimidamide



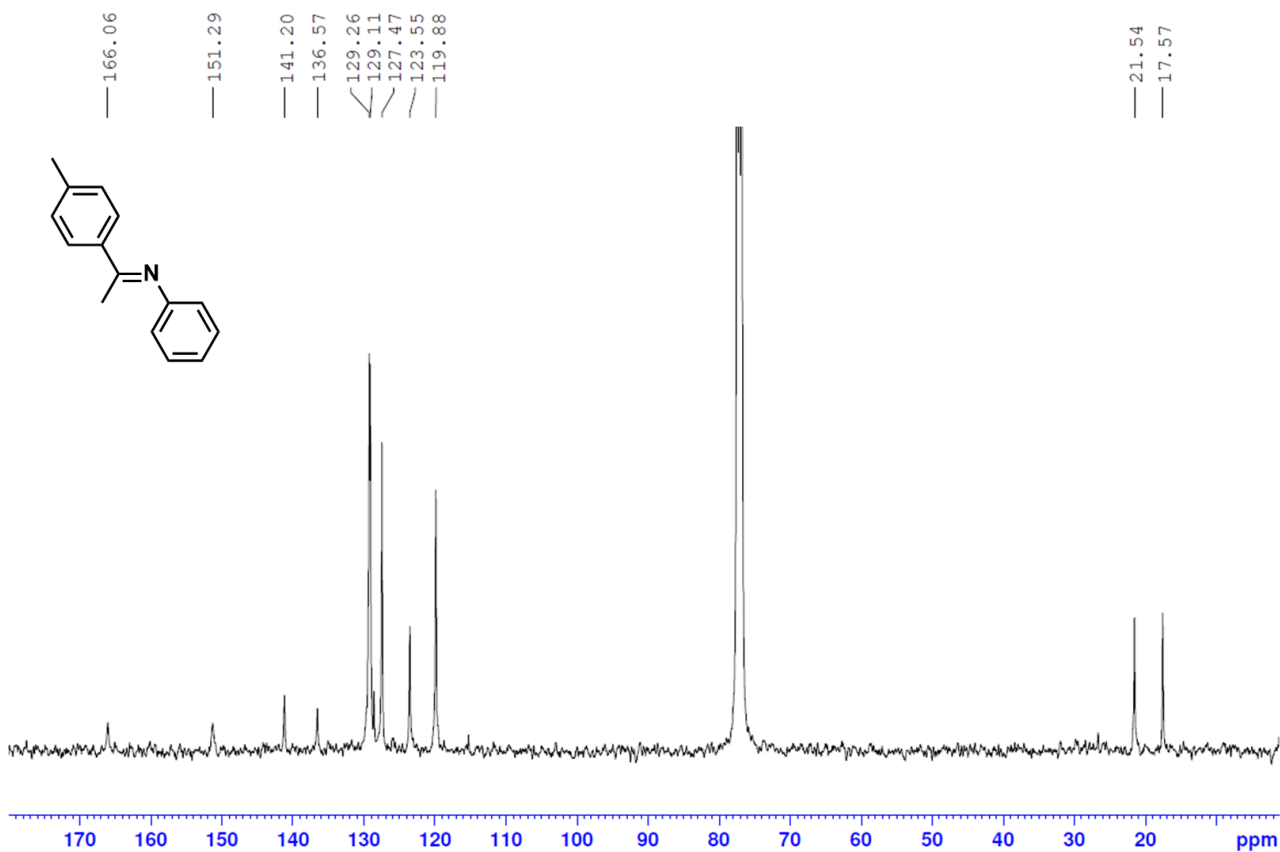
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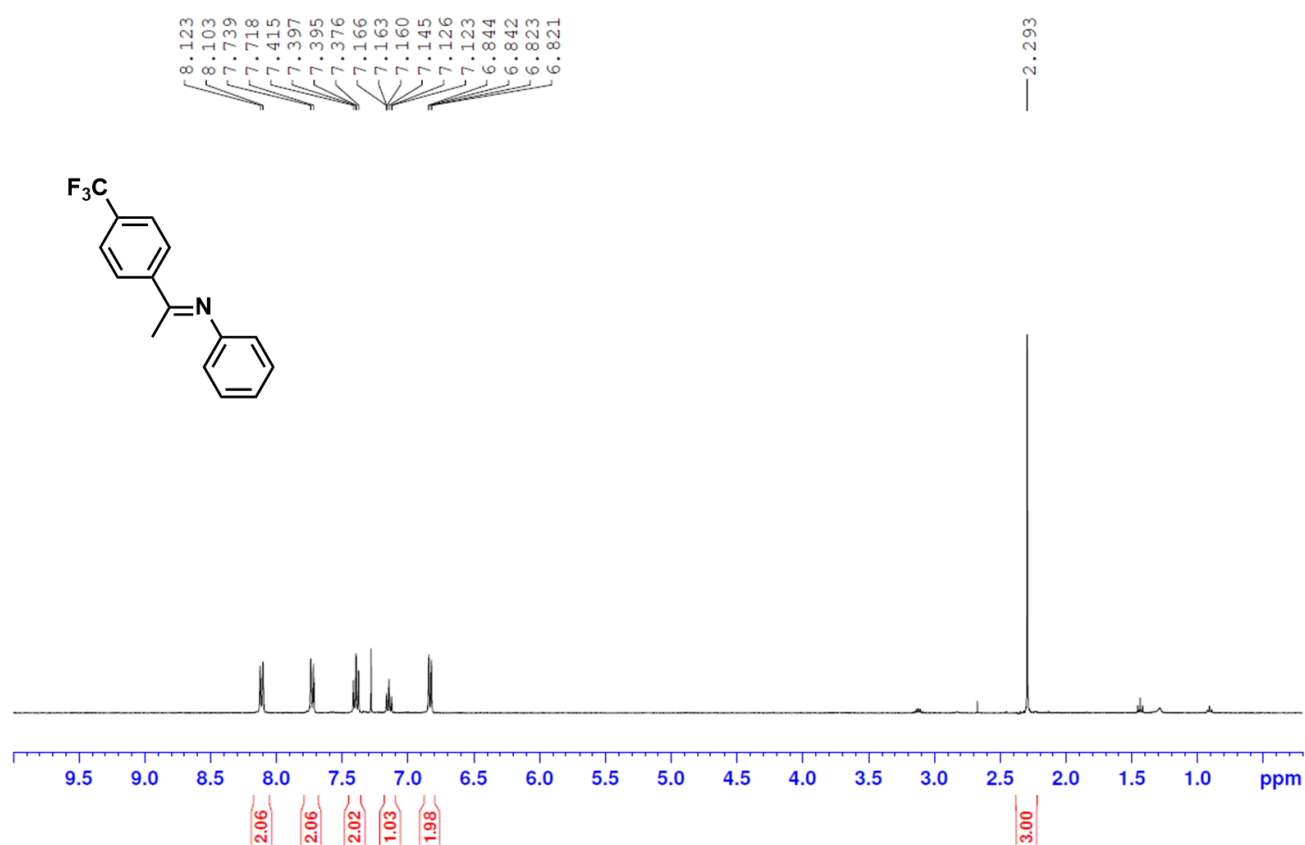
¹H NMR spectrum of *N*-(1-(*p*-tolyl)ethylidene)aniline



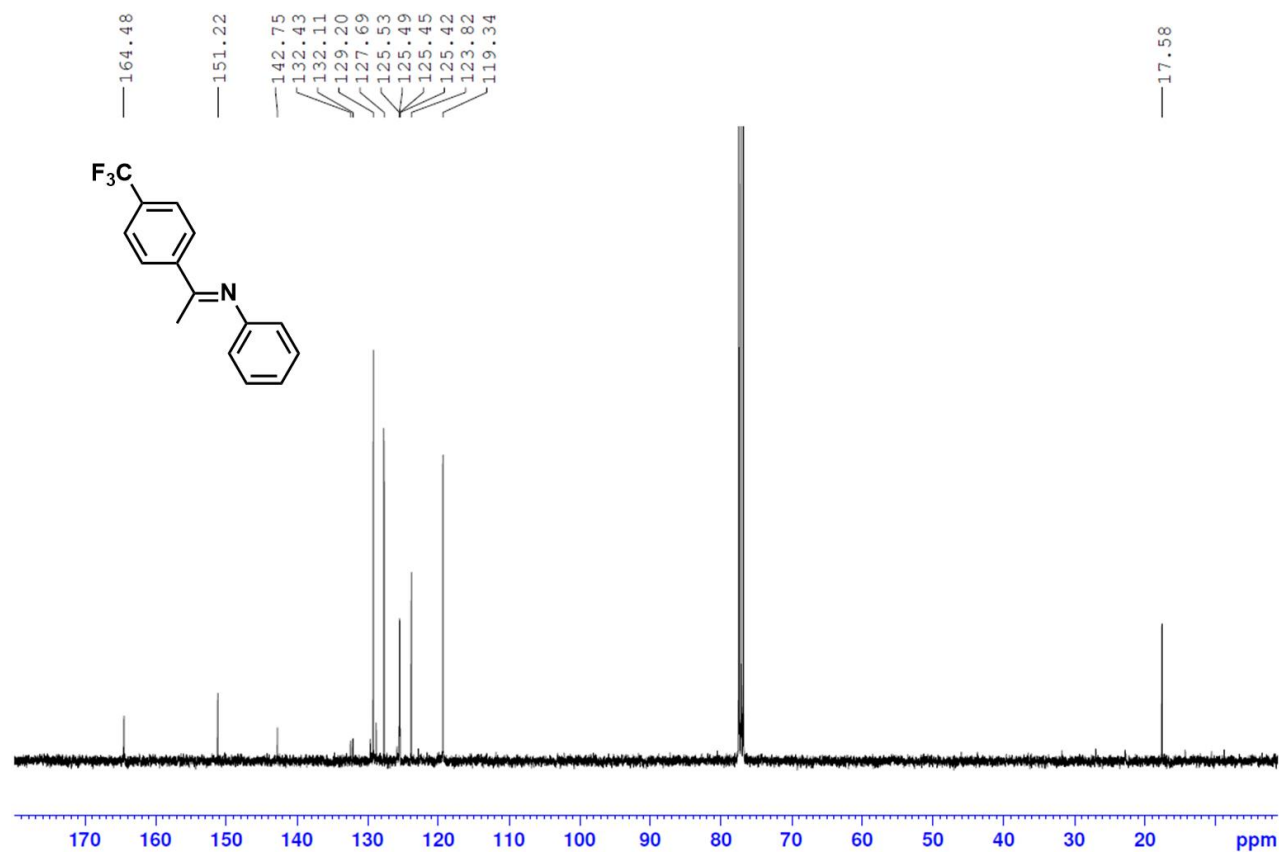
¹³C NMR spectrum of *N*-(1-(*p*-tolyl)ethylidene)aniline



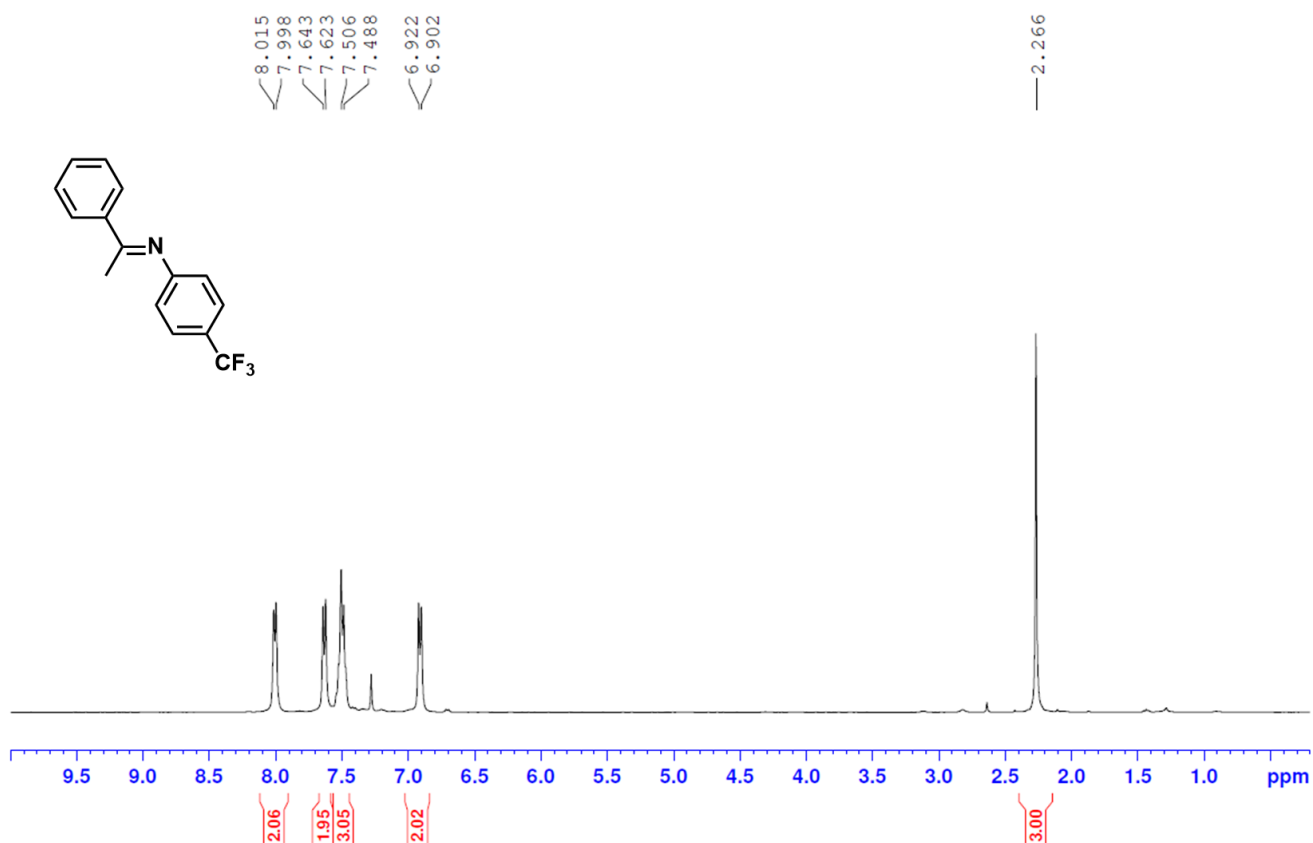
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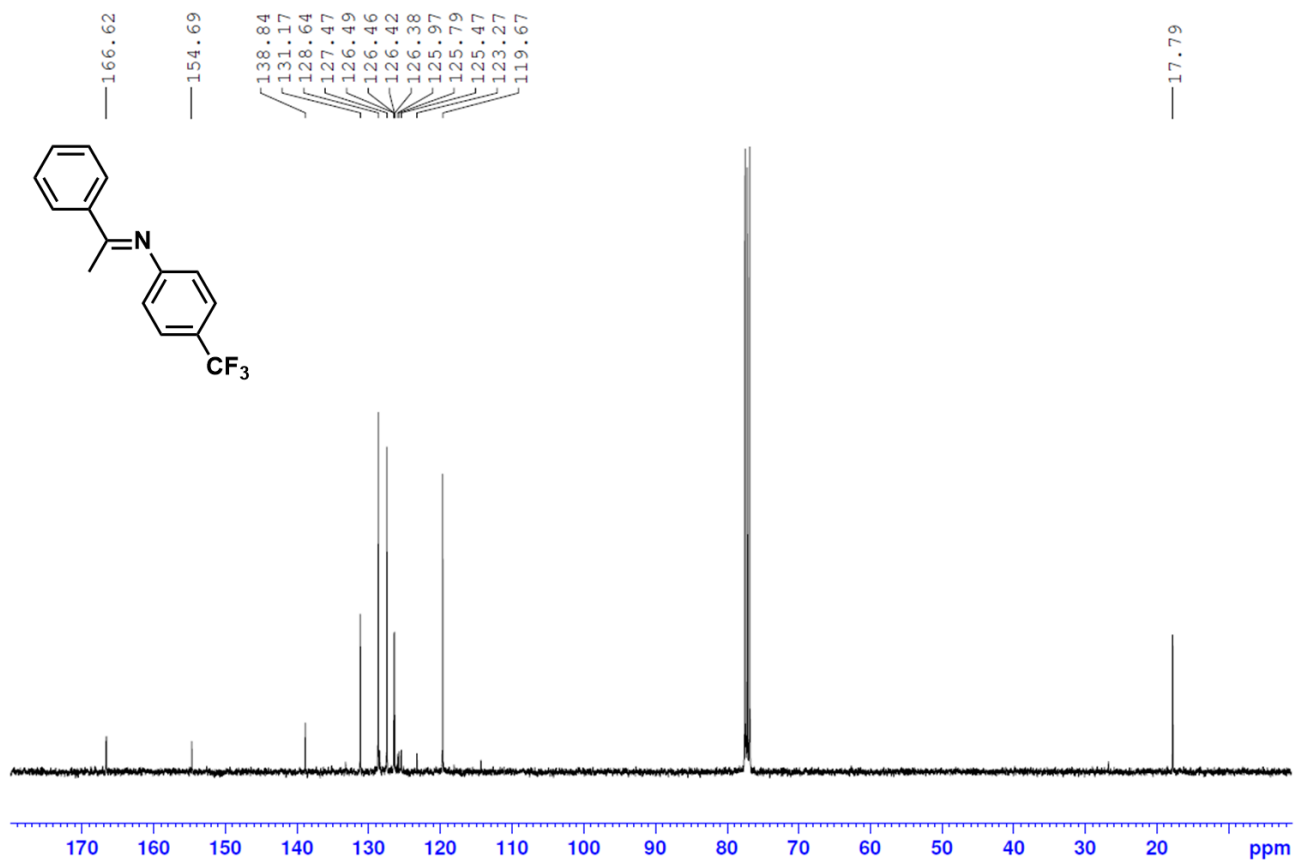
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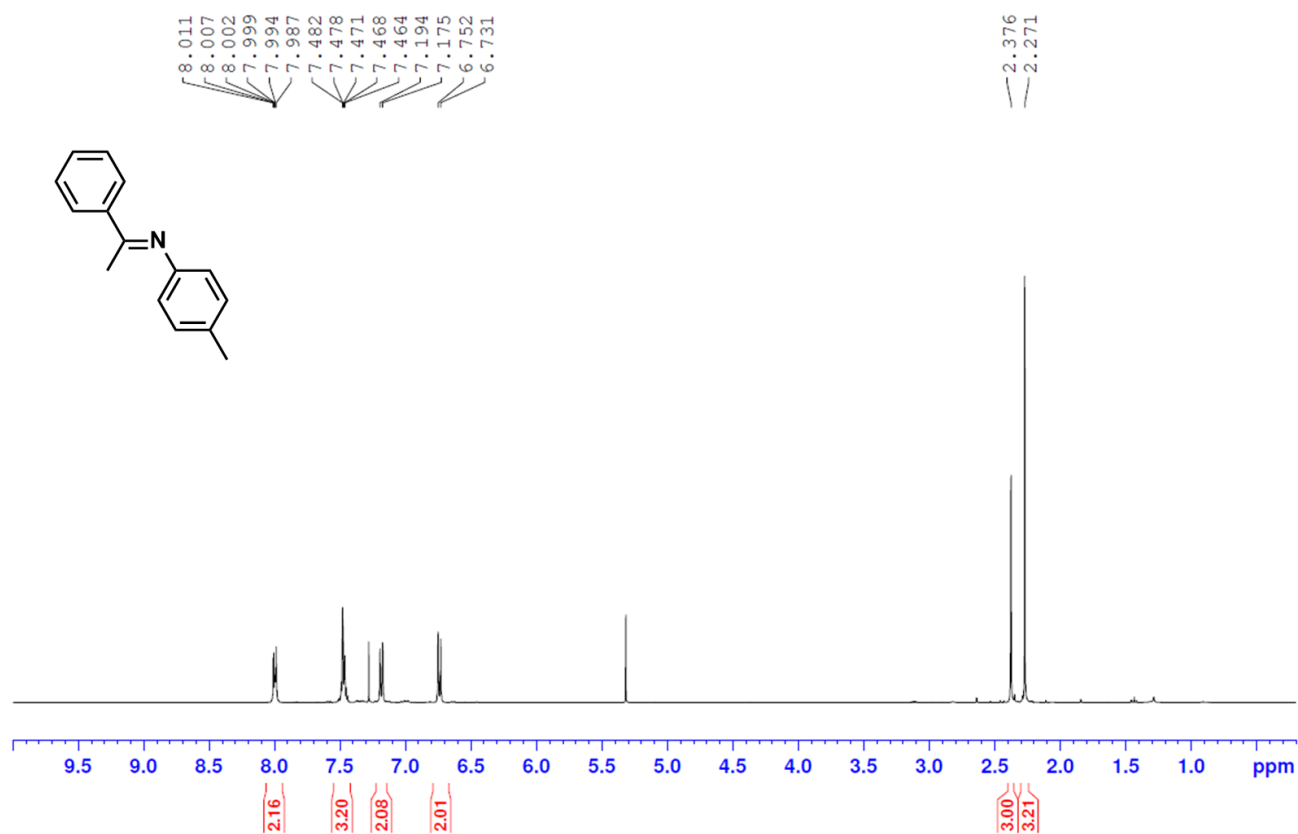
¹H NMR spectrum of *N*-(1-phenylethylidene)-4-(trifluoromethyl)aniline



¹³C NMR spectrum of *N*-(1-phenylethylidene)-4-(trifluoromethyl)aniline



¹H NMR spectrum of 4-methyl-*N*-(1-phenylethylidene)aniline



¹³C NMR spectrum of 4-methyl-*N*-(1-phenylethylidene)aniline

