

Supporting Information

Simultaneous N2 and N3 Coordination of *Inverse* Triazolyl-Pyridine Ligands in Ag(I) Complexes: Synthesis, Structure, and Application in A3 Coupling Reaction to Propargylamine in Solvent free and Low Catalyst Loading

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Materials

All the experiments were conducted under an ambient condition only if specifically stated to the use of an inert atmosphere. All the chemicals and solvents were used as received from the suppliers without further purification. Reagents, 2-bromopyridine (99%), propargyl bromide (87%), p-cresol (99%) were purchased from Spectrochem, India. Solvents hexane, ethyl acetate was purchased from Finar limited company. The A3 coupling reactions were performed in an ambient atmosphere to 70 °C. For inert atmosphere reactions, acetonitrile was dried using conventional method and was distilled before use. Normal (particle size: 100–200 mesh) and flash (particle size: 230–400 mesh) silica gels were used for column chromatography, and they were purchased from Qualigens-TM (India), Spectrochem (India), and Rankem (India). To monitor the progress of chemical reactions, TLC plates covered with silica gel (Kiesel 60-F254, Merck (India)) were utilized. UV light was the visualizing agent that was used for TLC. All the solvents were dried and concentrated using BUCHI's Rotavapor R-210. The supplied analytical-grade solvents, such as MeOH and EtOH, were all utilized without any previous purification. The chemicals and reagents acquired from Sigma Aldrich Chemicals Company (USA), TCI (India) Pvt. Ltd., Merck (India), and/or Spectrochem (India), were utilized as received. Deuterated solvent CDCl₃ and DMSO-d₆ were used to record the NMR spectrum of the synthesized compounds.

Instrumentation

Nuclear magnetic resonance spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz for ¹H NMR and 101 MHz for ¹³C{¹H} NMR respectively. Tetramethyl silane (TMS) (0.00 ppm) was used as a reference internal solvent to record ¹H and ¹³C{¹H} NMR spectra for all the compounds. During analysis of ¹H NMR spectra proton peak for CDCl₃ was fixed at 7.246

ppm and the carbon peak was fixed at 77.0 ppm. ^1H NMR patterns of chemical shifts were characterized in parts per million (ppm). The terms singlet (s), doublet (d), double of doublet (dd), triplet (t), and multiplet (m) were used to describe peak splitting patterns. The coupling constant (J) values are given in Hertz (Hz). The Xevo G2-SQ-ToF (Waters, USA) was used to examine high-resolution electron impact mass spectra (HR-EIMS), which are compatible with ACQUITY UPLC[®] and nano ACQUITY UPLC[®] systems. The melting point of ligand and complex were determined on an analog melting point apparatus. The Bruker single crystal X-ray diffractometer was used to determine the crystallography study of Ag-complexes.

Ligand Synthesis and characterization

Synthesis of 2-((4-((p-tolyloxy) methyl)-1H-1,2,3-triazol-1-yl) methyl)pyridine (tmtmp) (2)

The ligand 2-((4-((p-tolyloxy) methyl)-1H-1,2,3-triazol-1-yl)methyl)pyridine was synthesized by stirring at room temperature in a round-bottom flask on a magnetic stirrer. In a round bottom flask (0.146 g, 1.00 mmol) 1-(ethynyloxy)-4-methylbenzene solution was made in methanol to which (0.147g, 1.1 mmol) 2-(azidomethyl)pyridine was added. $\text{Cu}(\text{OAc})_2$ (2 mol%) was added to the solution and the resulting solution was stirred for 24h. After the reaction had reached completion, the workup was done with water (10 mL) and ethyl acetate (3×20 mL). Then, the combined organic layers were dried using anhydrous Na_2SO_4 , filtered, and then concentrated under reduced pressure to afford the crude residue that was further purified utilizing column chromatography on silica gel (100–200 mesh) (99:1 - Chloroform/MeOH). The solvent was removed under reduced pressure and off-white crystalline solid of product was obtained. Yield – 73% (0.280g), based on 1-(ethynyloxy)-4-methylbenzene. Mp: 92-94 °C. ^1H NMR (400 MHz, Chloroform- d): δ 8.58 (s, 1H), 7.73-7.62 (m, 2H), 7.24 – 7.18 (m, 2H), 7.01 – 6.99 (m, 2H), 6.80 (dd, $J = 8.8, 3.2$ Hz, 2H), 5.58 (s, 2H), 5.10 (s, 2H), 2.20 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, Chloroform- d): δ 156.2, 154.4, 137.4, 130.6, 130.0, 123.6, 114.7, 62.2, 55.9, 20.6. HRMS (ESI⁺) m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}$ ($[\text{M} + \text{H}]^+$) 281.1397; found 281.1398. IR ν_{max} (cm^{-1}): 3132 (m, $\text{C}_{\text{sp}2}\text{-H}$ stretch.), 3087 (w, triazole)¹, 2917

(m, C_{sp3}-H stretch.), 1611 (w, C=C_{sp2} stretch.), 1473 (m, C_{sp3}-H stretch.), 1242 (s, C_{sp3}-O stretch.), 814 (s, C=C_{sp2} bend)². Elemental analysis for C₁₆H₁₆N₄O: found: C, 69.05; H, 5.72; N, 18.54. Calculated: C, 68.55; H, 5.75; N, 19.19.

Synthesis of 2-(4-((p-tolyloxy)methyl)-1H-1,2,3-triazol-1-yl)pyridine (tmtp) (3)

The ligand 2-((4-((p-tolyloxy)methyl)-1H-1,2,3-triazol-1-yl))pyridine was synthesized by refluxing in a round-bottom flask on oil bath at 60 °C. In a round bottom flask (0.146 g, 1 mmol) 1-(ethynyloxy)-4-methylbenzene solution was made in chloroform to which (0.132 g, 1.1 mmol) 2-azidopyridine was added followed by (0.258 g, 2 mmol) DIPEA. CuBr (0.028 g, 0.2 mmol) was added as a catalyst to the solution and the resulting solution was refluxed for 6h. After the reaction had reached completion, the reaction mixture was cooled to room temperature and then the workup was done with water (10 mL) and dichloromethane (3 × 20 mL). Then, the combined organic layers were dried using anhydrous Na₂SO₄, filtered, and then concentrated under reduced pressure to afford the crude residue that was further purified utilizing column chromatography on silica gel (100–200 mesh) (70:30 – Hexane /EtOAc). The solvent was removed under reduced pressure and brown needle shaped crystalline solid product was obtained. Yield – 75% (0.199 g), based on 1-(ethynyloxy)-4-methylbenzene. Mp: 126-128 °C. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.57 (s, 1H), 8.43 – 8.42 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.29 – 7.26 (m, 1H), 7.02 (dd, *J* = 8.8, 0.8 Hz, 2H), 6.85 (dd, *J* = 6.4, 2.4 Hz, 2H), 5.21 (d, *J* = 0.8 Hz, 2H), 2.21 (s, 3H); ¹³C {¹H} NMR (101 MHz, Chloroform-*d*): δ 156.1, 149.1, 148.6, 144.9, 139.3, 130.7, 130.1, 123.8, 120.4, 114.8, 114.0, 62.0, 20.6. HRMS (ESI⁺) *m/z* calcd. for C₁₅H₁₄N₄O ([M + H]⁺) 267.1241; found 267.1229. IR *v*_{max} (cm⁻¹): 3135 (w, C_{sp2}-H stretch.), 3090 (w, triazole)¹, 2915 (w, C_{sp3}-H stretch.), 1240 (s, C_{sp3}-O stretch.), 817 (s, C=C_{sp2} bend.)² Elemental analysis for C₁₅H₁₄N₄O: found: C, 68.25; H, 5.20; N, 20.85. Calculated: C, 67.65; H, 5.30; N, 21.04.

Synthesis of compound and characterization

Compound 4

For the synthesis of compound **4** the tmtmp ligand (0.280 g, 1 mmol) solution was made in methanol (1 ml) in a 50 ml round bottom flask and to it methanolic solution of AgNO₃ (0.171 g, 1.01 mmol) was added dropwise. The round bottom flask was covered with foil paper due to the light sensitivity of the complex and was stirred at room temperature for 12h. After the completion of the reaction, the reaction mixture was filtered using a Buchner funnel. A white solid was obtained as product which was dried and kept in dark. Yield – 61% (0.593 g), based on ligand (tmtmp). Mp: 178-180 °C. ¹H NMR (400 MHz, Acetonitrile-*d*₃): δ 8.47 – 8.45 (m, 2H), 7.95 (s, 2H), 7.76 – 7.72 (m, 2H), 7.29 – 7.26 (m, 4H), 7.01 (dd, *J* = 9.2, 0.8 Hz, 4H), 6.80 – 6.77 (m, 4H), 5.60 (s, 4H), 5.02 (s, 4H), 2.17 (s, 6H); ¹³C {¹H} NMR (101 MHz, Acetonitrile-*d*₃): δ 156.2, 154.5, 150.2, 144.2, 137.9, 130.5, 130.00, 125.00, 123.8, 122.0, 114.7, 61.3, 55.4, 19.5. HRMS (ESI⁺) *m/z* calcd. for [M-2NO₃]²⁺ = 387.0370; found 387.0366. IR *v*_{max} (cm⁻¹): 3133 (m, C_{sp2}-H stretch.), 3088 (m, triazole) 2919 (m, C_{sp3}-H stretch.), 1378 (s, N=O stretch.), 1242 (s, C_{sp3}-O stretch), 816 (m, C=C_{sp2} bend)². Elemental analysis for C₃₂H₃₂Ag₂N₁₀O₈: Satisfactory elemental analysis data was not obtained despite several attempts.

Compound 5

For the synthesis of compound **5** the (ttmp) ligand (0.266 g, 1 mmol) solution was made in methanol (1 ml) in a 50 ml round bottom flask and to it methanolic solution of AgNO₃ (0.171 g, 1.01 mmol) was added dropwise. The round bottom flask was covered with foil paper due to the light sensitivity of the complex and was stirred at room temperature for 12h. After the completion of the reaction, the reaction mixture was filtered using a Buchner funnel. A white solid was obtained as product which was dried and kept in dark. Yield – 58% (0.561 g), based on ligand (ttmp). Mp: 210-213 °C. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.61 (s, 2H), 8.46 (ddd, *J* = 4.8,

2.0, 0.8 Hz, 2H), 8.05-8.03 (2H), 7.97 – 7.93 (m, 2H), 7.40 - 7.37 (m, 2H), 7.04 (dd, $J = 8.8, 0.8$ Hz, 4H), 6.88 – 6.84 (m, 4H), 5.14 (s, 4H), 2.10 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Acetonitrile- d_3): δ 155.8, 148.6, 144.2, 139.4, 130.2, 129.6, 123.9, 120.7, 114.4, 113.5, 60.9, 19.2. HRMS (ESI $^+$) m/z calcd. for $[\text{M}-2\text{NO}_3]^{2+} = 373.0213$; found 373.0207. IR ν_{max} (cm^{-1}): 3138 (w, $\text{C}_{\text{sp}2}\text{-H}$ stretch.), 3087 (w, triazole) 1 , 1587 (m, $\text{N}=\text{O}$ stretch.), 1240 (s, $\text{C}_{\text{sp}3}\text{-O}$ stretch.), 817 (s, $\text{C}=\text{C}_{\text{sp}2}$ bend.) 2 . Elemental analysis for $\text{C}_{30}\text{H}_{28}\text{Ag}_2\text{N}_{10}\text{O}_8$: Satisfactory elemental analysis data was not obtained despite several attempts.

X-ray crystallography

2-D polymeric structure of complex 4

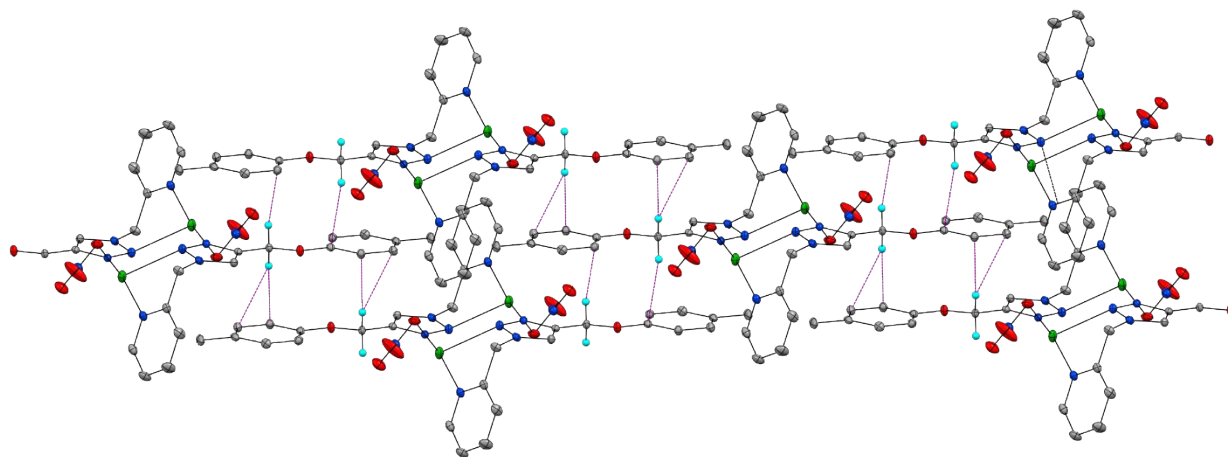
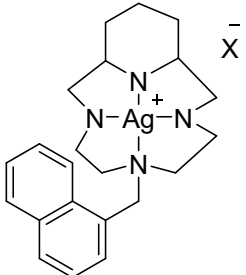
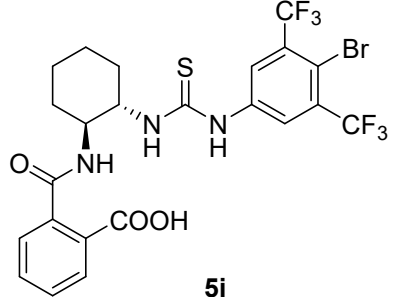
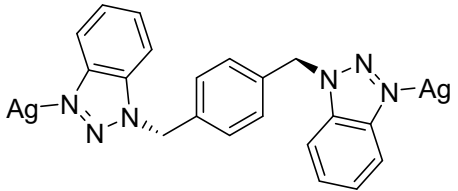
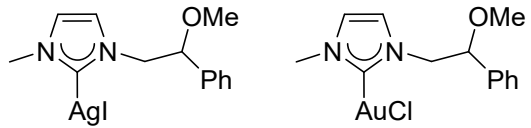
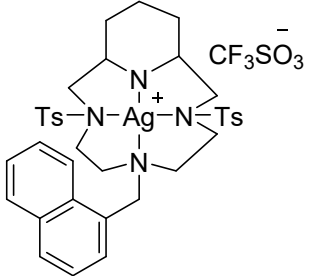


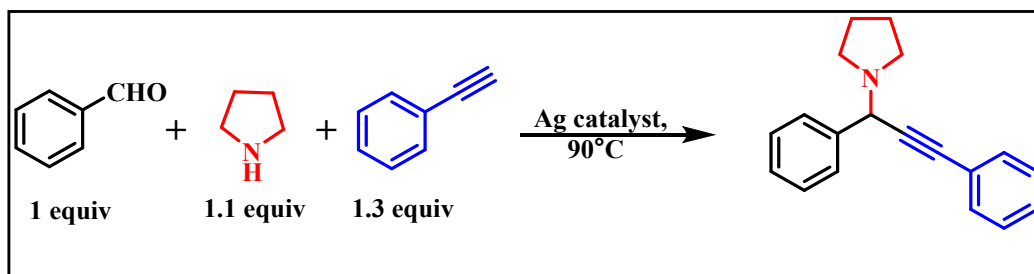
Fig. S1 C-H $\cdots\pi$ interaction to generate 2D polymeric structure of complex 4

Comparison table with respect to previous work [Table 1]

Catalyst	Reaction conditions	References
	[catalyst: 3.0 mol%; time: 4.5 h; MW; Toluene; 150 °C]	3
<p>CuI with 5j</p>  <p>5j</p>	[CuI: 4 mol%, 5j : 3.0 mol%; time: 12 h; 5 Å MS; DCM; 0 °C]	4
[Ag(IPr) ₂]PF ₆	[catalyst: 3.0 mol%; time: 1 h; MW; MeOH; 110 °C]	5
Ag-metalloligand based polymer	[catalyst: 1.0 mol%; time: 1 h; neat; 80 °C]	6
	[catalyst: (0.5- 2 mol%); time:12 h; iPrOH; 90 °C]	7
Inorganic-Organic hybrid Ag-polyoxometalates	[catalyst: 0.5 mol%; time:6 h; ACN; RT]	8
	[catalyst: 3 mol%; time:6 h; 80 °C; Au-NHC catalyst most effective]	9
	[catalyst: 5 mol%; time:5 h; DES; 60 °C]	10
Ag-nanoparticle Zr-based Metal organic framework	[catalyst: 20 mg; time:6 h; ACN; 80 °C]	11
Ag-nanoparticle Cu-based Metal organic framework	[catalyst: 75 mg; time:1 h; EtOH; 80 °C]	12

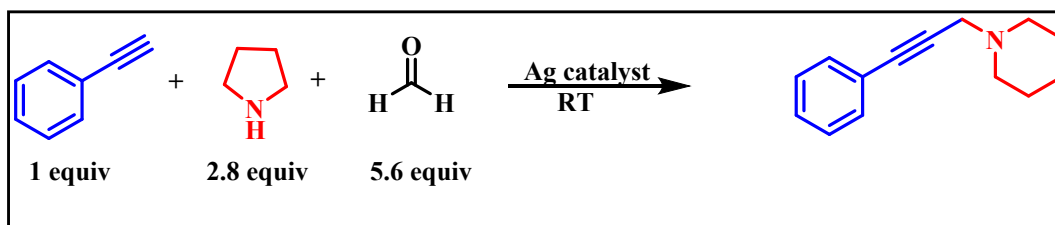
General catalytic protocol for synthesis of propargyl amines

Procedure 1



A mixture of aldehyde (1 mmol), amine (1.1 mmol), alkyne (1.3 mmol), Ag catalyst (catalyst 4, 0.25 mol%) was placed in a sealed tube in the absence of solvent and the reaction mixture was heated at 70°C for 5h. The reaction mixture was cooled to room temperature and then the workup was done with water (10 mL) and ethyl acetate (3 × 20 mL). Then, the combined organic layers were dried using anhydrous Na₂SO₄, filtered, and then concentrated under reduced pressure to afford the crude residue that was further purified utilizing column chromatography on silica gel (100–200 mesh) (99:1 to 95:5 - Hexane/EtOAc). The solvent was removed under reduced pressure and products were obtained as pale-yellow oily liquids. In good yield of about 81 – 98%.

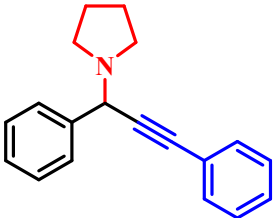
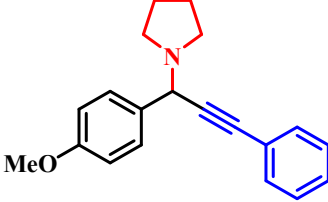
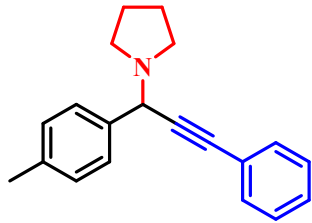
Procedure 2

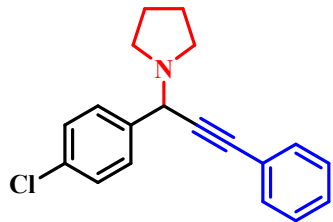
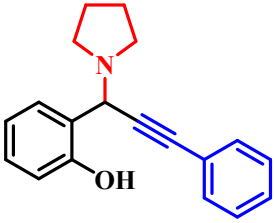
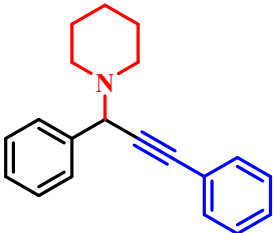
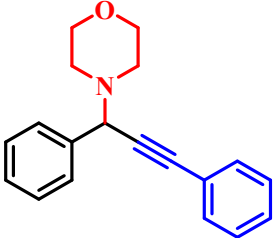


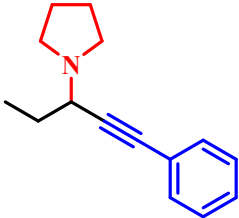
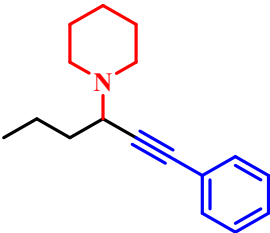
A mixture of aldehyde (1 mmol), amine (2.8 mmol), alkyne (5.6 mmol), Ag catalyst (catalyst 4, 0.25 mol%) was placed in a sealed tube in the absence of solvent and the reaction mixture was stirred at room temperature for 2h. The workup was done with water (10 mL) and ethyl acetate (3 × 20 mL). Then, the combined organic layers were dried using anhydrous Na₂SO₄, filtered, and

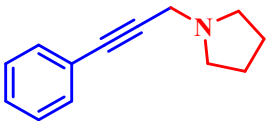
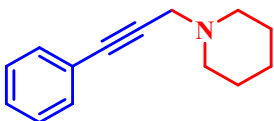
then concentrated under reduced pressure to afford the crude residue that was further purified utilizing column chromatography on silica gel (100–200 mesh) (99:1 to 95:5 - Hexane/EtOAc). The solvent was removed under reduced pressure and propargylamines were obtained as pale-yellow oily liquid.

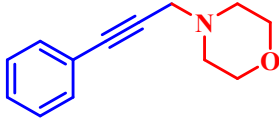
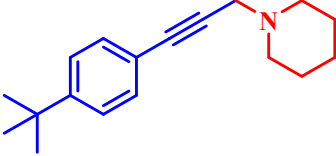
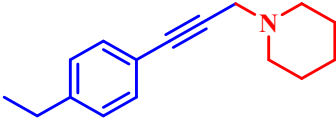
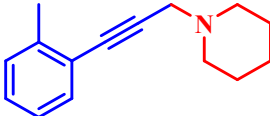
Characterization data for A3 coupling products

S.No	Substrate	Data analysis
9aaa		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9aaa in 95% (0.248g) yield as a according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.55 – 7.53 (m, 2H), 7.42 – 7.40 (m, 2H), 7.30 – 7.21 (m, 6H), 4.84 (s, 1H), 2.66 – 2.63 (m, 4H), 1.75 – 1.71 (m, 4H). Spectral data are in good agreement with literature values ^{3,7} .
9baa		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9baa in 93% (0.271g) yield as an according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.48 (d, <i>J</i> = 8.4 Hz, 2H), 7.42 – 7.40 (m, 2H), 7.25 – 7.22 (m, 3H), 6.81 (d, <i>J</i> = 8.8 Hz, 2H), 4.89 (s, 1H), 3.72 (s, 3H), 2.75 – 2.69 (m, 4H), 1.78 – 1.74 (m, 4H). Spectral data are in good agreement with literature values ⁷ .
9caa		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9caa in 91% (0.250g) yield as a according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.42 – 7.39 (m, 4H), 7.23 – 7.22 (m, 3H), 7.09 – 7.07 (m, 2H), 4.79 (s, 1H), 2.65 – 2.61 (m, 4H), 2.27 (s, 3H), 1.74 – 1.70 (m, 4H).

		Spectral data are in good agreement with literature values ⁷ .
9daa		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9daa in 87% (0.258g) yield as a according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.47 (dd, <i>J</i> = 6.4, 2 Hz, 2H), 7.42 – 7.39 (m, 2H), 7.26 – 7.23 (m, 5H), 4.80 (s, 1H), 2.62 – 2.58 (m, 4H), 1.75 – 1.68 (m, 4H). Spectral data are in good agreement with literature values ⁷ .
9eaa		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9eaa in 81% (0.225g) yield as a according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.49 – 7.45 (m, 3H), 7.32 – 7.27 (m, 4H), 7.17 – 7.14 (m, 1H), 6.84 – 6.79 (m, 2H), 5.30 (s, 1H), 2.89 – 2.79 (m, 4H), 1.86 – 1.82 (m, 4H). Spectral data are in good agreement with literature values ⁷ .
9aba		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9aba in 84% (0.231g) yield as a according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.68-7.65 (m, 2H), 7.55 – 7.52 (m, 2H), 7.43 – 7.30 (m, 6H), 4.83 (s, 1H), 2.60-2.58 (m, 4H), 1.64-1.59 (m, 4H), 1.49-1.44 (m, 2H). Spectral data are in good agreement with literature values ^{13,14} .
9aca		The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9aca in 86% (0.239g) yield as a according to the general procedure A . ¹ H NMR (400 MHz, Chloroform- <i>d</i>) δ 7.58 (d, <i>J</i> = 6.8 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.32 – 7.24 (m, 6H), 4.75 (s, 1H), 3.70 – 3.66 (m, 4H), 2.60 – 2.58 (m, 4H). Spectral data are in good agreement with literature values ¹⁵ .

9faa		<p>The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9faa in 89% (0.190g) yield as a according to the general procedure A.</p> <p>¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.37 – 7.35 (m, 2H), 7.23 – 7.21 (m, 3H), 3.55-3.51 (m, 1H), 2.73 – 2.62 (m, 4H), 1.76 – 1.67 (m, 6H), 1.04 – 1.00 (m, 3H). Spectral data are in good agreement with literature values¹⁶.</p>
9gba		<p>The reaction of aromatic aldehyde (1 mmol), alicyclic secondary amine (1.1 mmol) and phenyl acetylene (1.3 mmol) and Ag catalyst (0.25 mol %) at 90°C for 5 h can afford compound 9gba in 86% (0.208g) yield as a according to the general procedure A.</p> <p>¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.38 – 7.36 (m, 2H), 7.24 – 7.22 (m, 3H), 3.51 – 3.48 (m, 1H), 2.71 – 2.66 (m, 2H), 2.51 – 2.47 (m, 2H), 1.71 – 1.64 (m, 3H), 1.60 – 1.49 (m, 4H), 1.44 – 1.37 (m, 3H), 0.92 – 0.88 (m, 3H). Spectral data are in good agreement with literature values¹⁵.</p>

S.No		
13aaa		<p>The reaction of phenyl acetylene (1 mmol), alicyclic secondary amine (2.8 mmol), formaldehyde (5.6) and Ag catalyst (0.25 mol %) at RT for 5 h can afford compound 13aaa in 98% (0.181g) yield as a according to the general procedure B.</p> <p>¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.37 – 7.34 (m, 2H), 7.22 – 7.20 (m, 3H), 3.56 (s, 2H), 2.64 – 2.61 (m, 4H), 1.78 – 1.74 (m, 4H). Spectral data are in good agreement with literature values¹⁷.</p>
13aba		<p>The reaction of phenyl acetylene (1 mmol), alicyclic secondary amine (2.8 mmol), formaldehyde (5.6) and Ag catalyst (0.25 mol %) at RT for 5 h can afford compound 13aba in 96% (0.191g) yield as a according to the general procedure B.</p> <p>¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.36 – 7.34 (m, 2H), 7.20 – 7.18 (m, 3H), 3.39 (s, 2H), 2.49 (s, 4H), 1.56 (m, 4H), 1.36 (s, 2H). Spectral data are in good agreement with literature values⁸.</p>

<p>13aca</p>		<p>The reaction of phenyl acetylene (1 mmol), alicyclic secondary amine (2.8 mmol), formaldehyde (5.6) and Ag catalyst (0.25 mol %) at RT for 5 h can afford compound 13aca in 95% (0.191g) yield as a according to the general procedure B. ¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.38 – 7.35 (m, 2H), 7.24 – 7.22 (m, 3H), 3.71 – 3.69 (m, 4H), 3.44 (s, 2H), 2.59 – 2.57 (m, 4H). Spectral data are in good agreement with literature values⁸.</p>
<p>13bba</p>		<p>The reaction of phenyl acetylene (1 mmol), alicyclic secondary amine (2.8 mmol), formaldehyde (5.6) and Ag catalyst (0.25 mol %) at RT for 5 h can afford compound 13bba in 95% (0.248g) yield as a according to the general procedure B. ¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.31 – 7.29 (m, 2H), 7.25 – 7.22 (m, 2H), 3.40 (s, 2H), 2.50 (s, 4H), 1.60 – 1.54 (m, 4H), 1.37 (d, <i>J</i> = 5.6 Hz, 2H), 1.22 (s, 9H). Spectral data are in good agreement with literature values^{18,19}.</p>
<p>13cba</p>		<p>The reaction of phenyl acetylene (1 mmol), alicyclic secondary amine (2.8 mmol), formaldehyde (5.6) and Ag catalyst (0.25 mol %) at RT for 5 h can afford compound 13cba in 98% (0.223g) yield as a according to the general procedure B. ¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.28 (d, <i>J</i> = 8.4 Hz, 2H), 7.04 (d, <i>J</i> = 8.0 Hz, 2H), 3.41 (s, 2H), 2.58 – 2.52 (m, 6H), 1.61 – 1.53 (m, 4H), 1.40 - 1.34 (m, 2H), 1.16 – 1.11 (m, 3H). Spectral data are in good agreement with literature values⁸.</p>
<p>13dba</p>		<p>The reaction of phenyl acetylene (1 mmol), alicyclic secondary amine (2.8 mmol), formaldehyde (5.6) and Ag catalyst (0.25 mol %) at RT for 5 h can afford compound 13dba in 91% (0.194g) yield as a according to the general procedure B. ¹H NMR (400 MHz, Chloroform-<i>d</i>) δ 7.33 (d, <i>J</i> = 7.6 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.07 – 7.03 (m, 1H), 3.55 (s, 2H), 2.60 (s, 4H), 2.36 (s, 3H), 1.66 – 1.60 (m, 4H), 1.41 – 1.38 (m, 2H). Spectral data are in good agreement with literature values²⁰.</p>

Spectral data of Ligands, catalyst and A3 coupling product

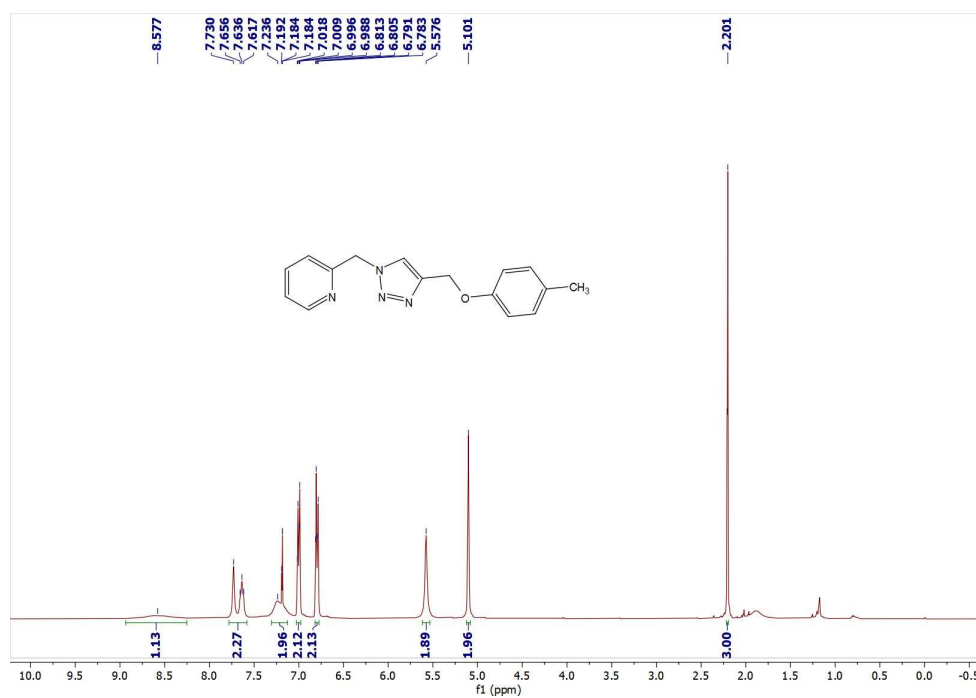


Fig. S2 ¹H NMR spectrum of **2** in CDCl₃ (400 MHz)

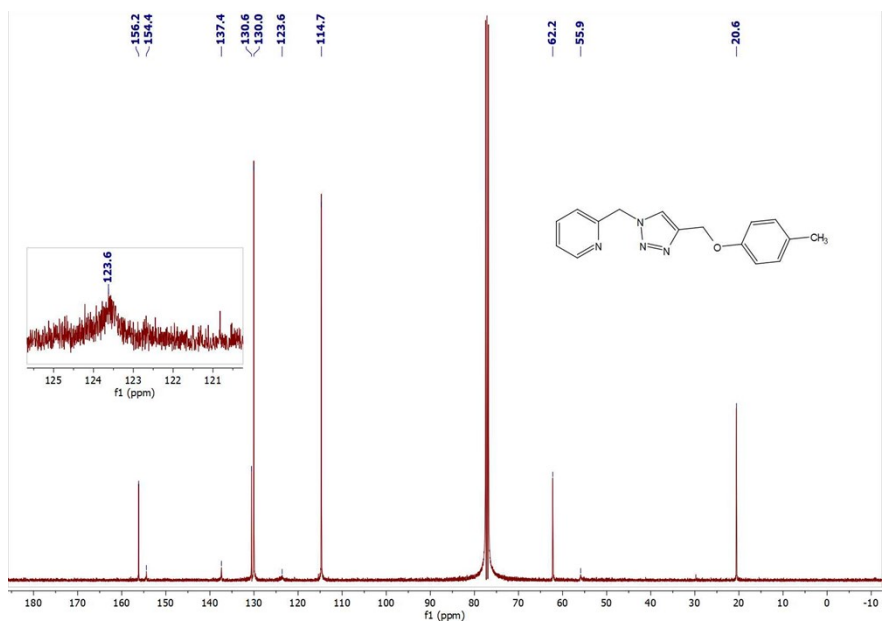


Fig. S3 ^{13}C NMR spectrum of **2** in CDCl_3 (101 MHz)

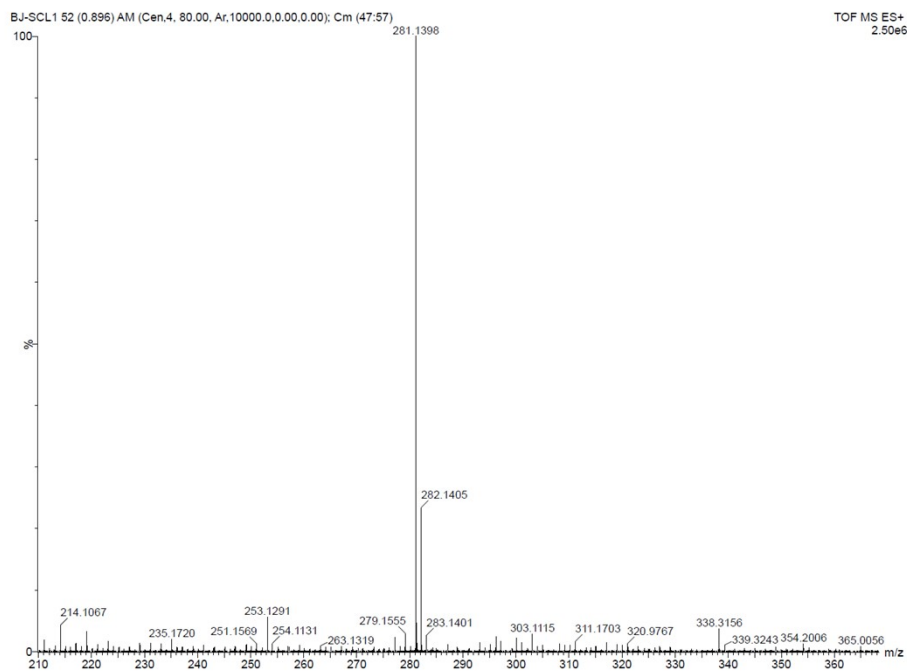


Fig. S4 ESI mass spectrum of **2**

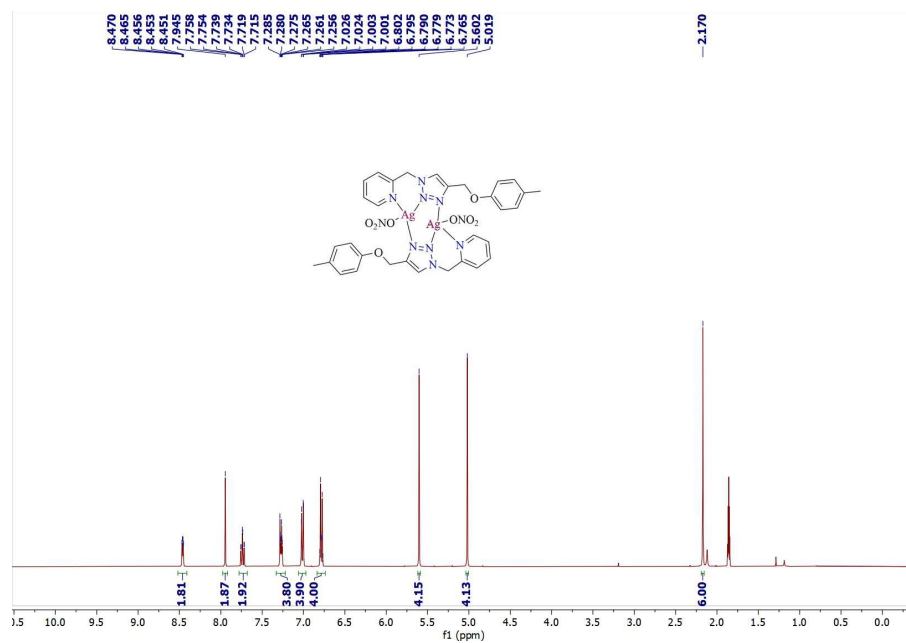


Fig. S5 ^1H NMR spectrum of 4 in Acetonitrile- d_3 (400 MHz)

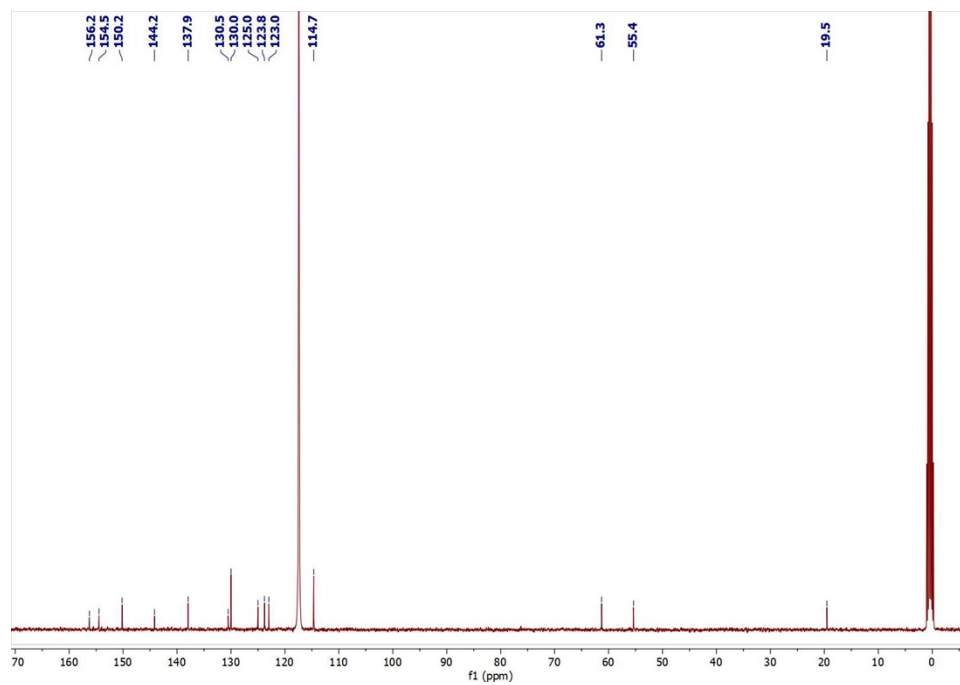


Fig. S6 ^{13}C NMR spectrum of 4 in Acetonitrile- d_3 (101 MHz)

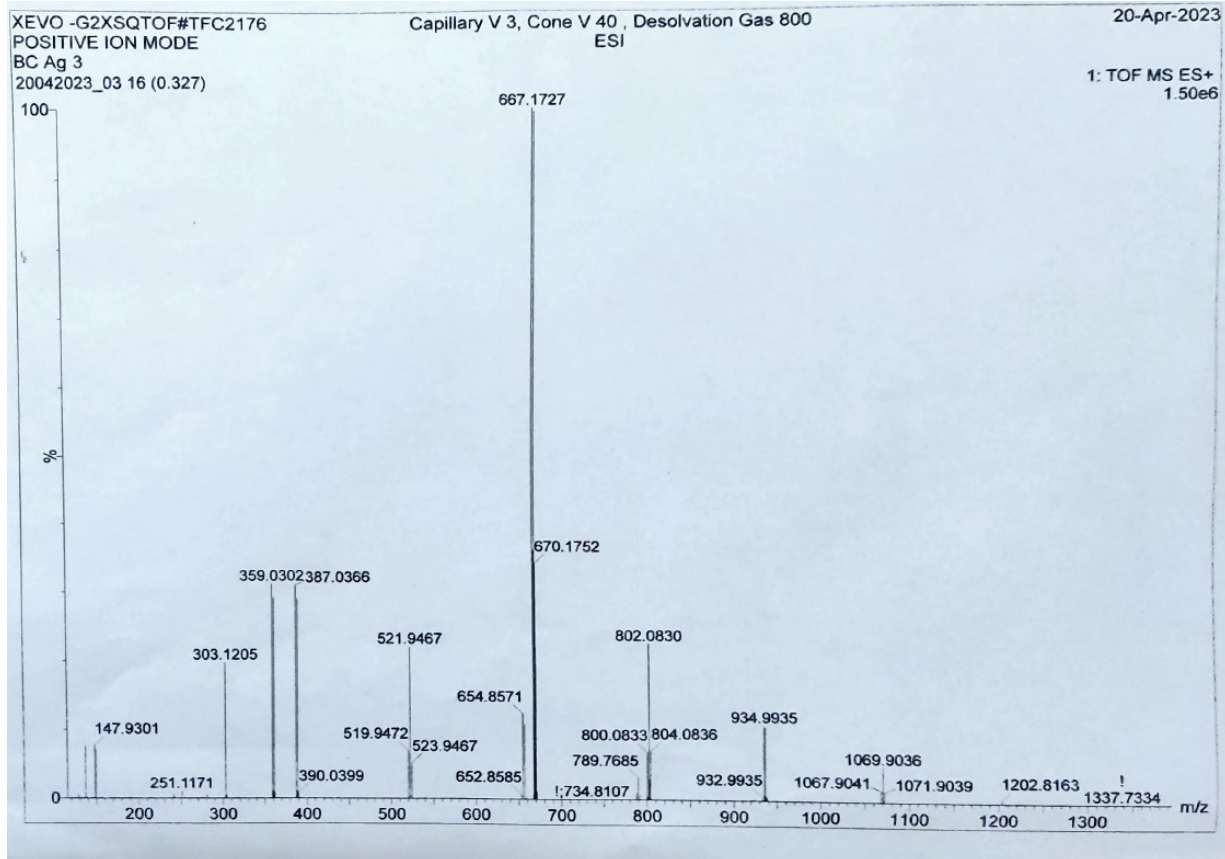


Fig. S7 ESI mass spectrum of 4

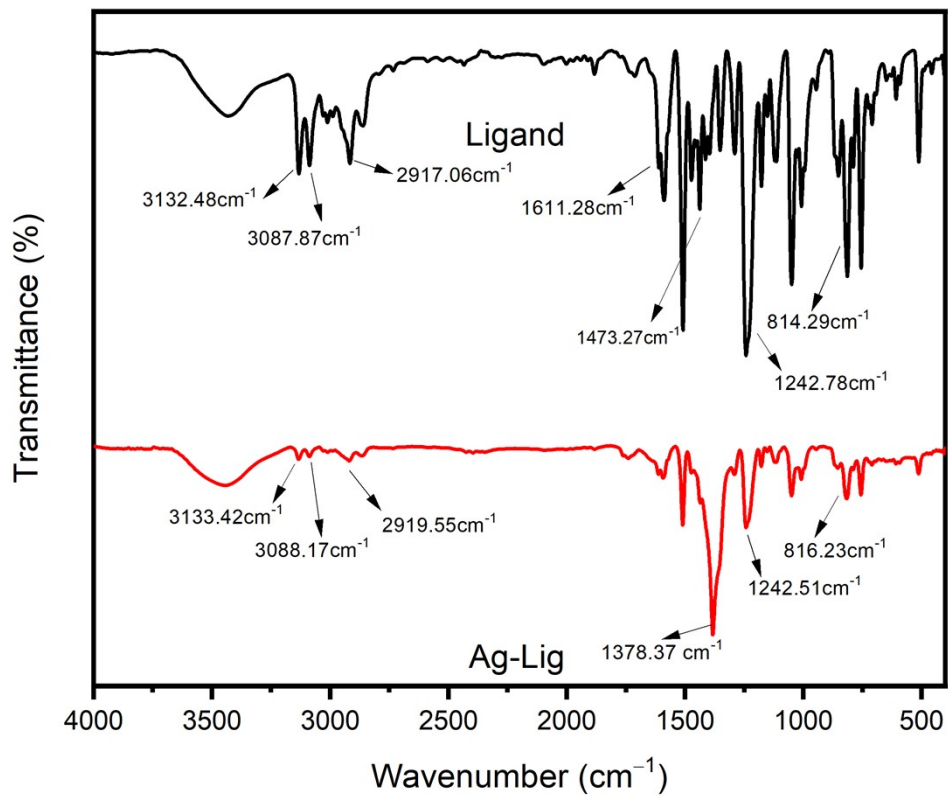


Fig. S8 FT-IR spectrum of ligand **2** and catalyst **4**

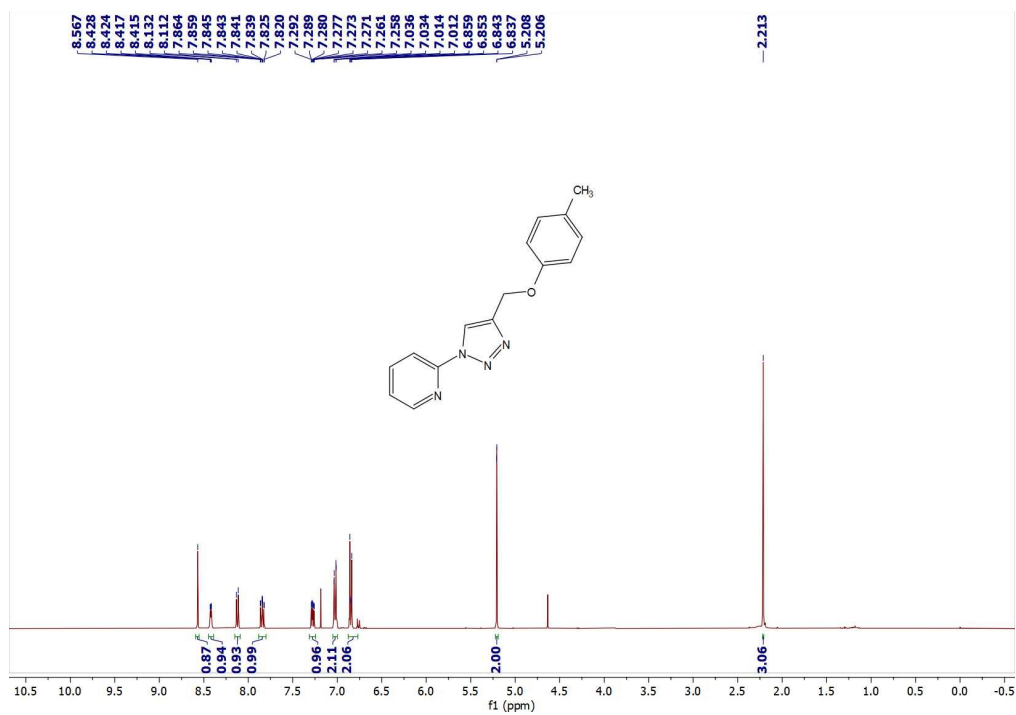


Fig. S9 ^1H NMR spectrum of **3** in CDCl_3 (400 MHz)

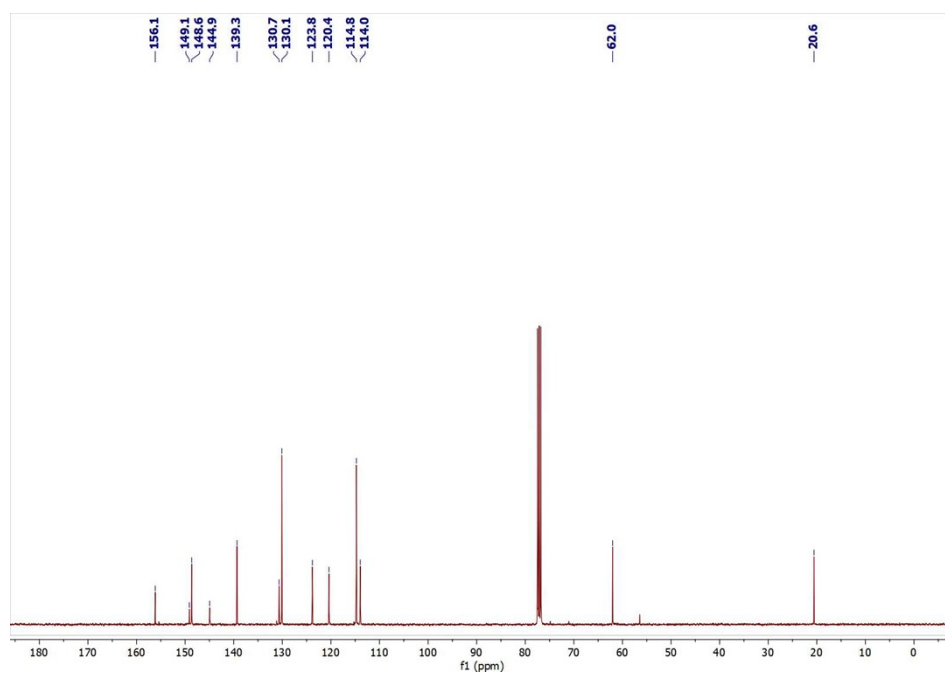


Fig. S10 ^{13}C NMR spectrum of **3** in CDCl_3 (101 MHz)

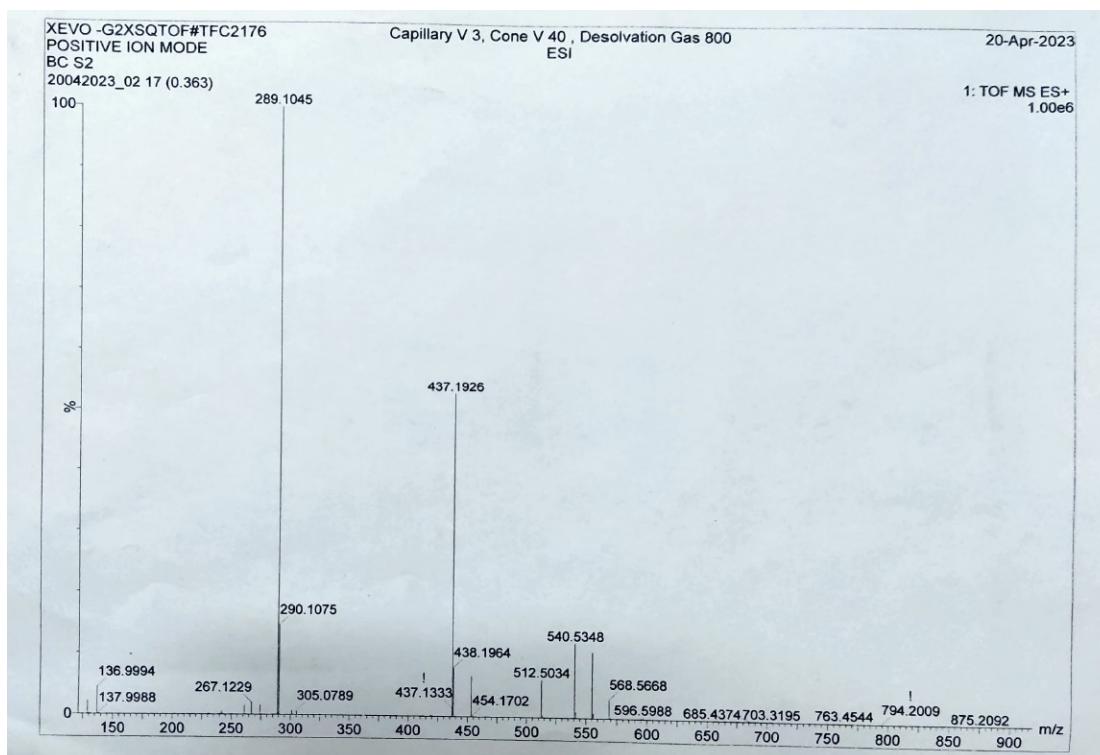


Fig. S11 ESI mass spectrum of **3**

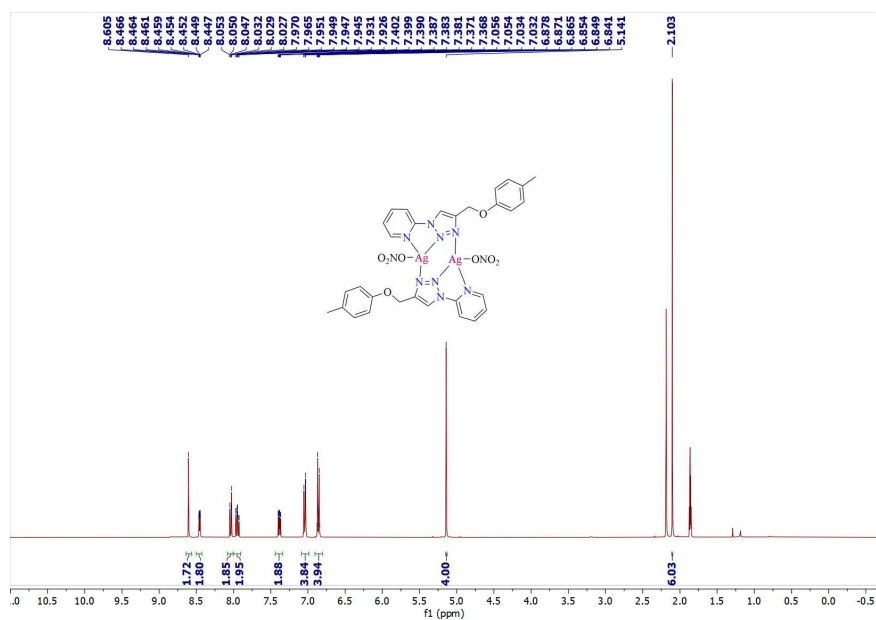


Fig. S12 ^1H NMR spectrum of **5** in Acetonitrile- d_3 (400 MHz)

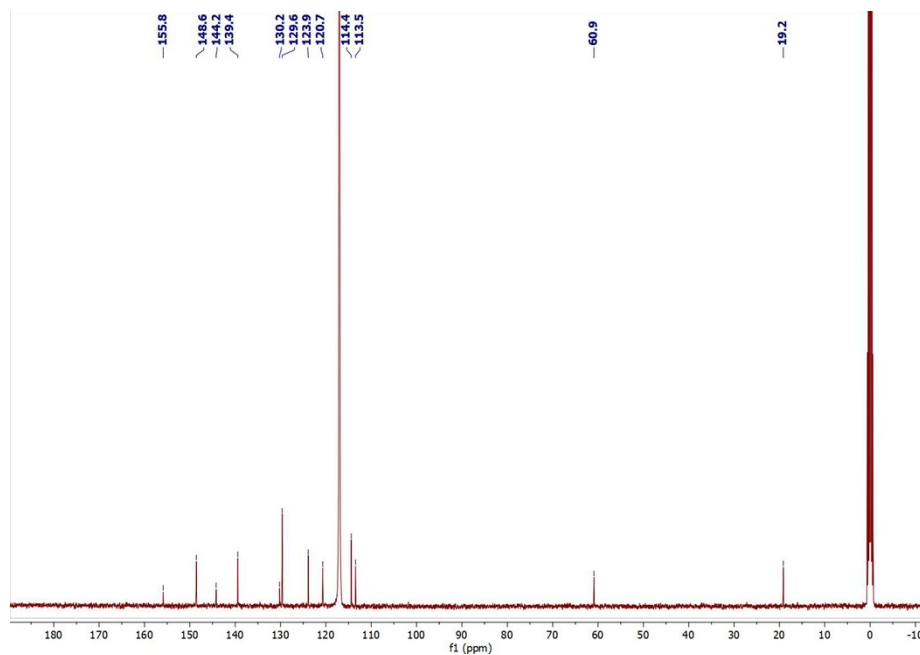


Fig. S13 ^{13}C NMR spectrum of **5** in Acetonitrile- d_3 (101 MHz)

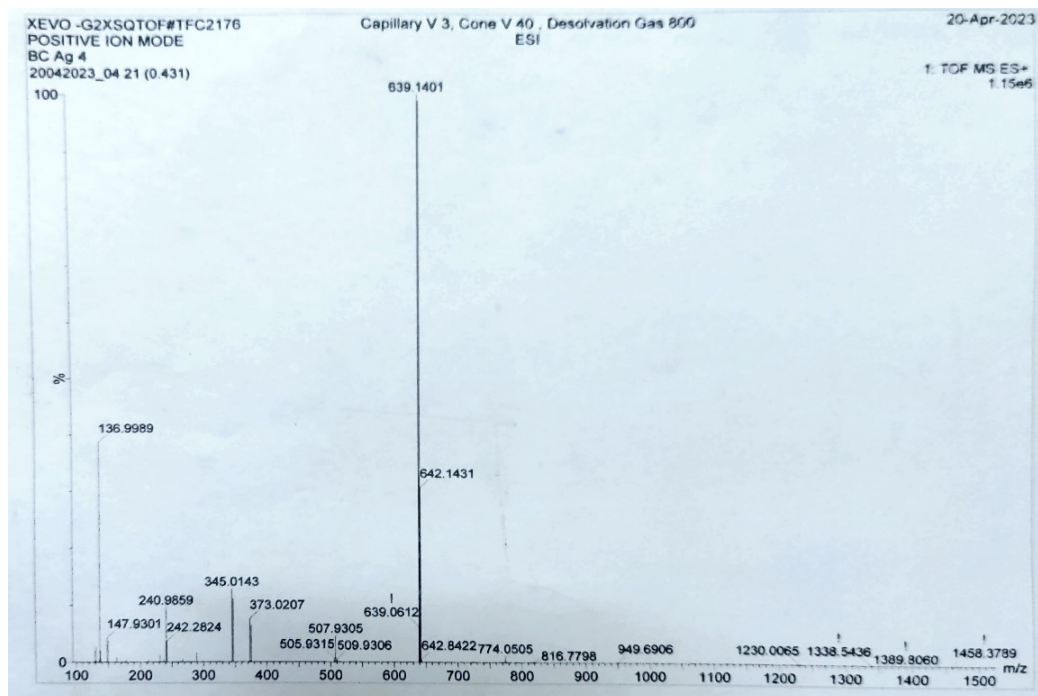


Fig. S14 ESI mass spectrum of **5**

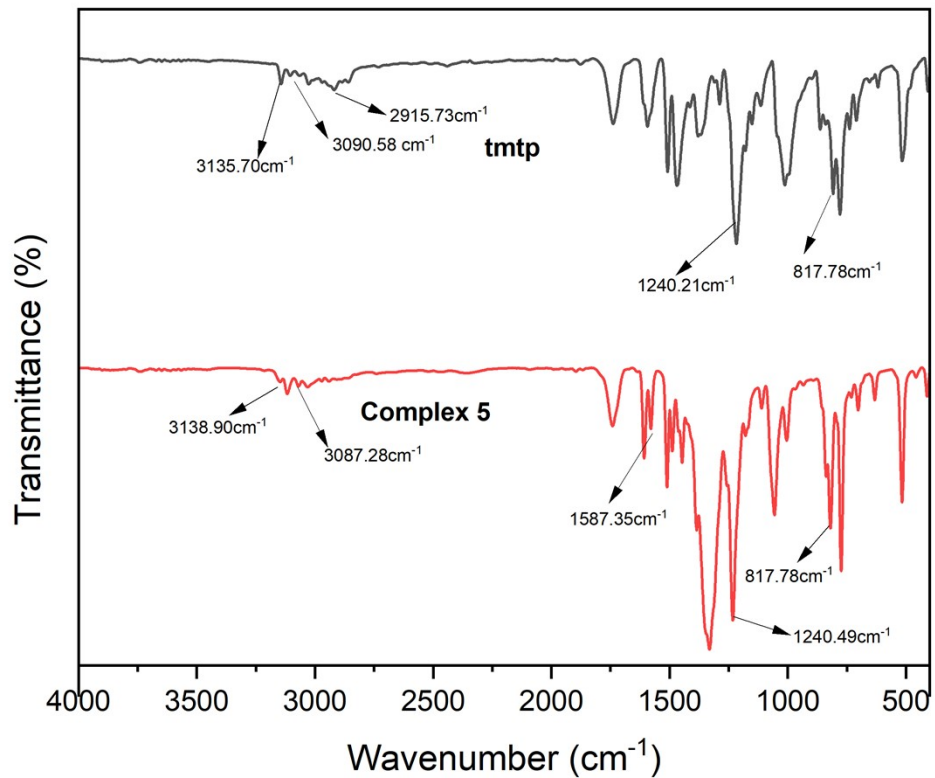


Fig. S15 FT-IR spectrum of ligand **3** and catalyst **5**

Characterization data of A3 coupling product 9aaa-9gba and 13aaa-13dba.

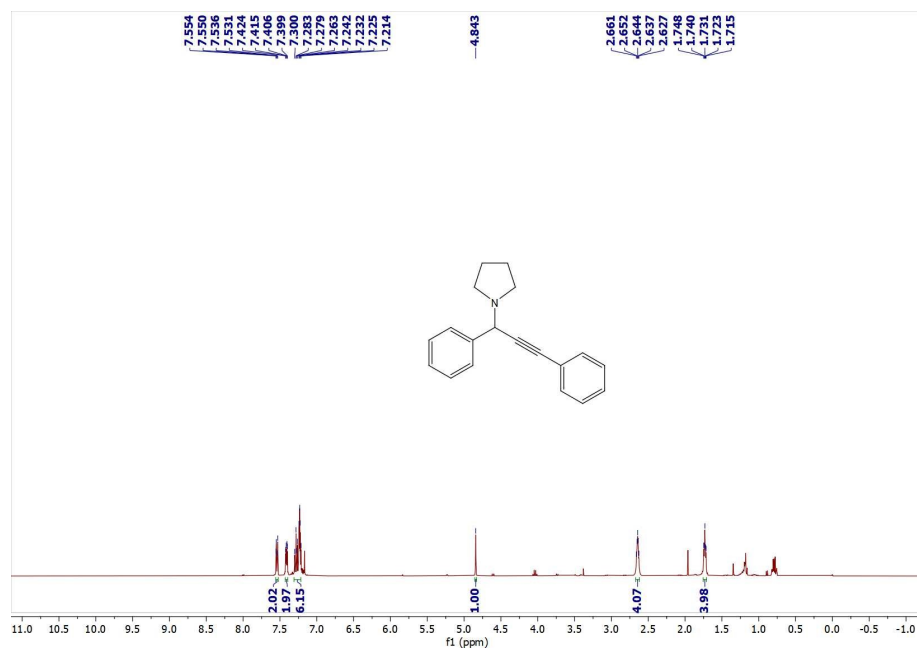


Fig. S16 ¹H NMR spectrum of 9aaa in CDCl₃ (400 MHz)

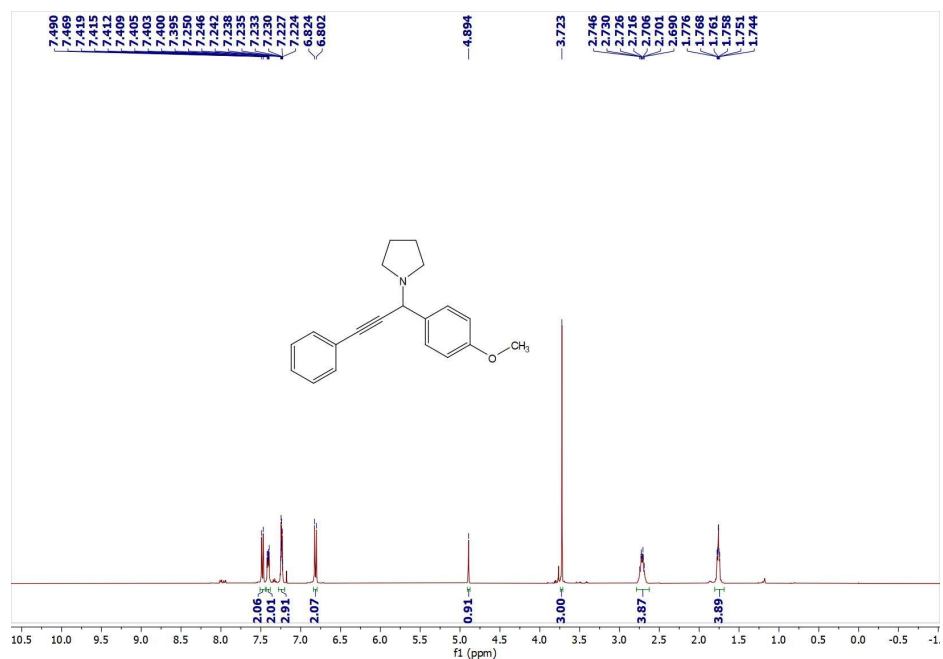


Fig. S17 ^1H NMR spectrum of **9baa** in CDCl_3 (400 MHz)

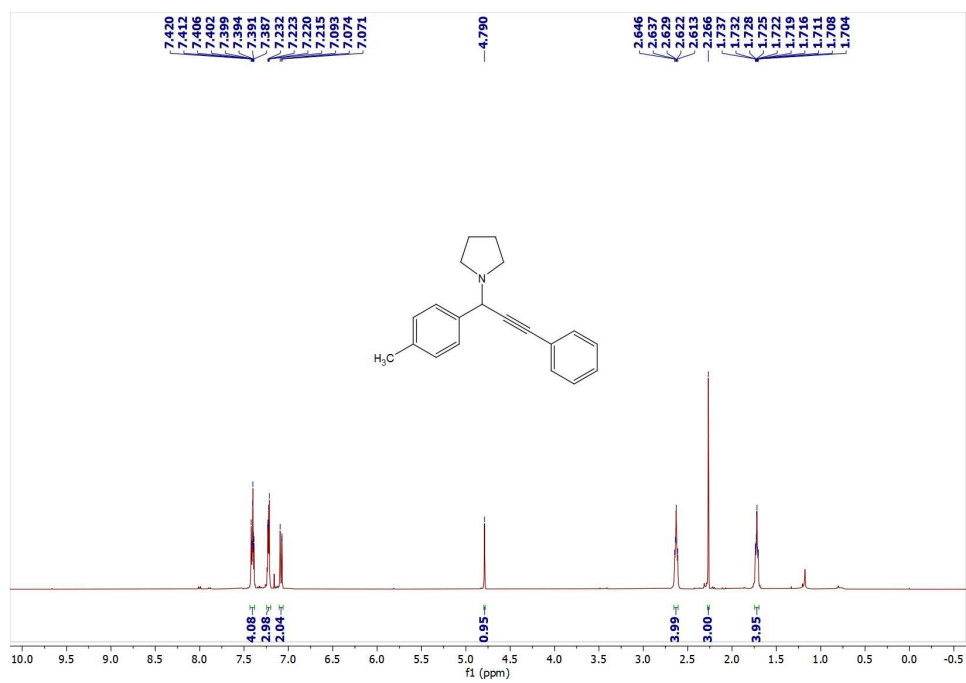


Fig. S18 ^1H NMR spectrum of **9caa** in CDCl_3 (400 MHz)

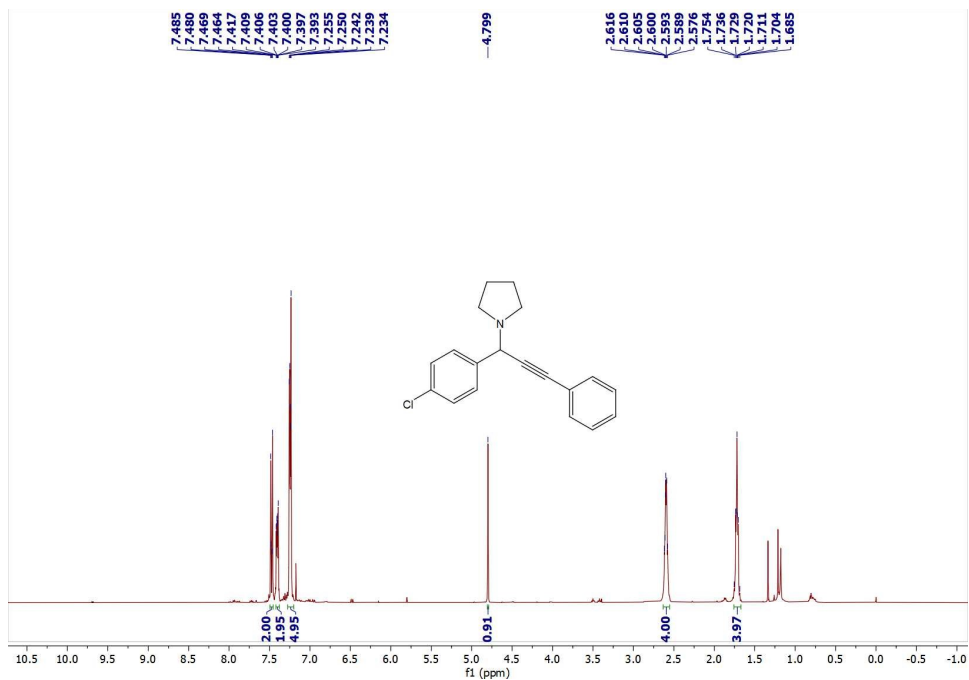


Fig. S19 ¹H NMR spectrum of **9daa** in CDCl₃ (400 MHz)

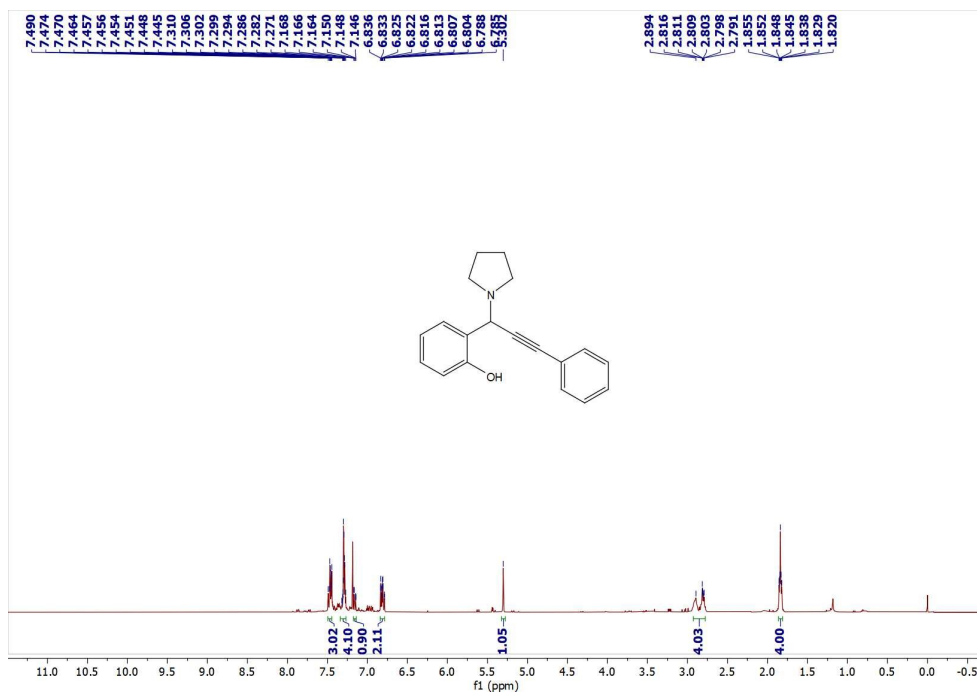


Fig. S20 ¹H NMR spectrum of **9eaa** in CDCl₃ (400 MHz)

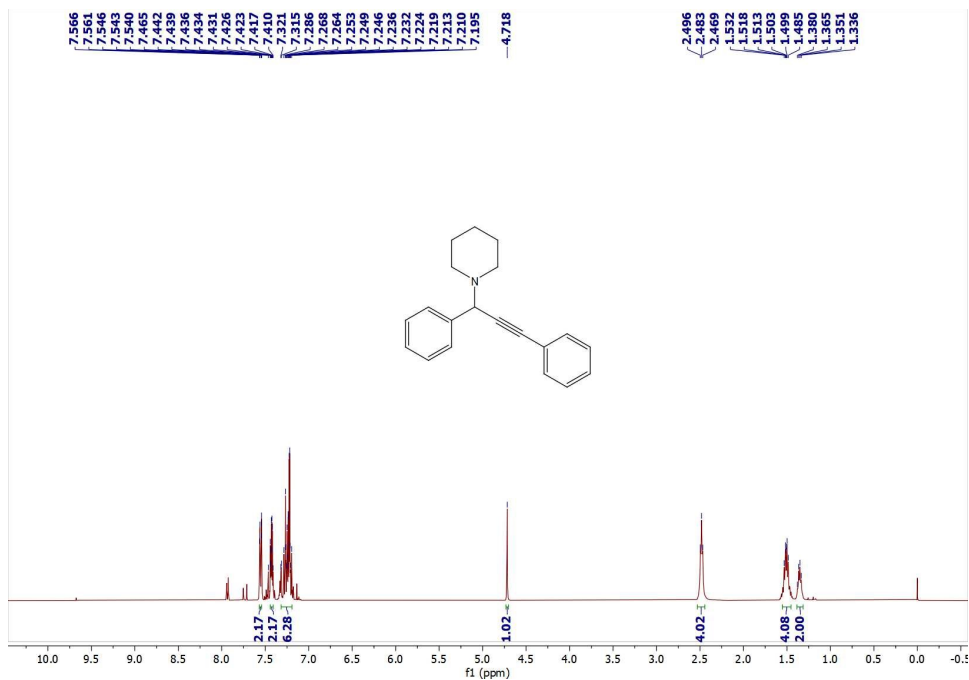


Fig. S21 ¹H NMR spectrum of **9aba** in CDCl₃ (400 MHz)

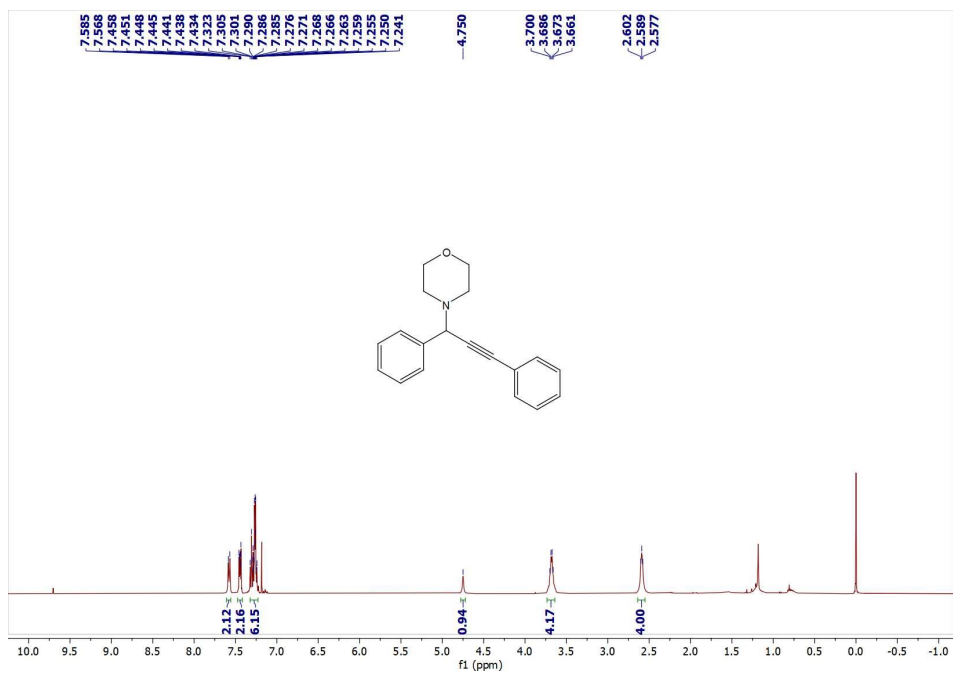


Fig. S22 ¹H NMR spectrum of **9aca** in CDCl₃ (400 MHz)

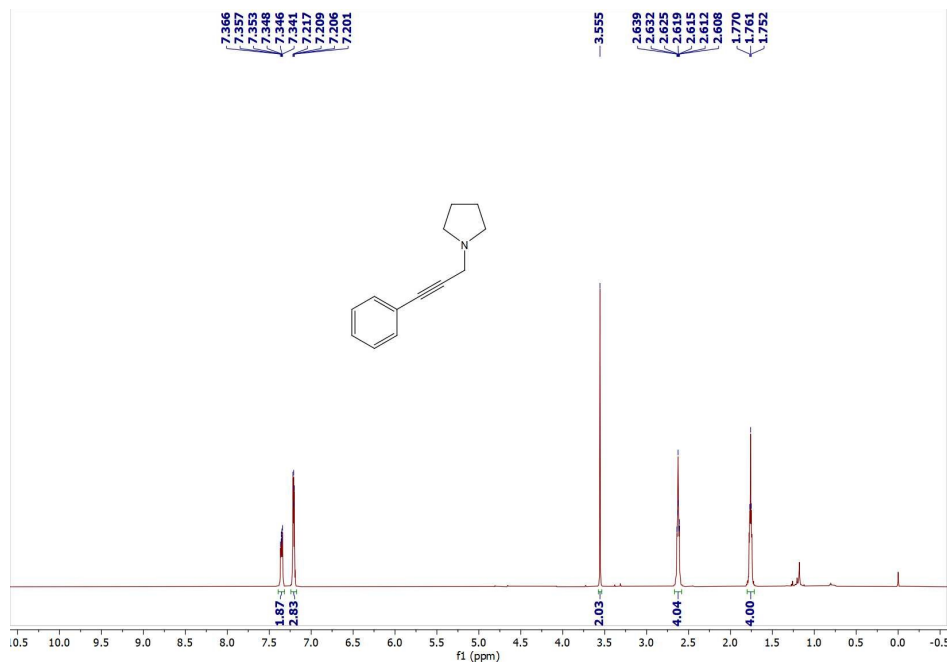


Fig. S25 ^1H NMR spectrum of **13aaa** in CDCl_3 (400 MHz)

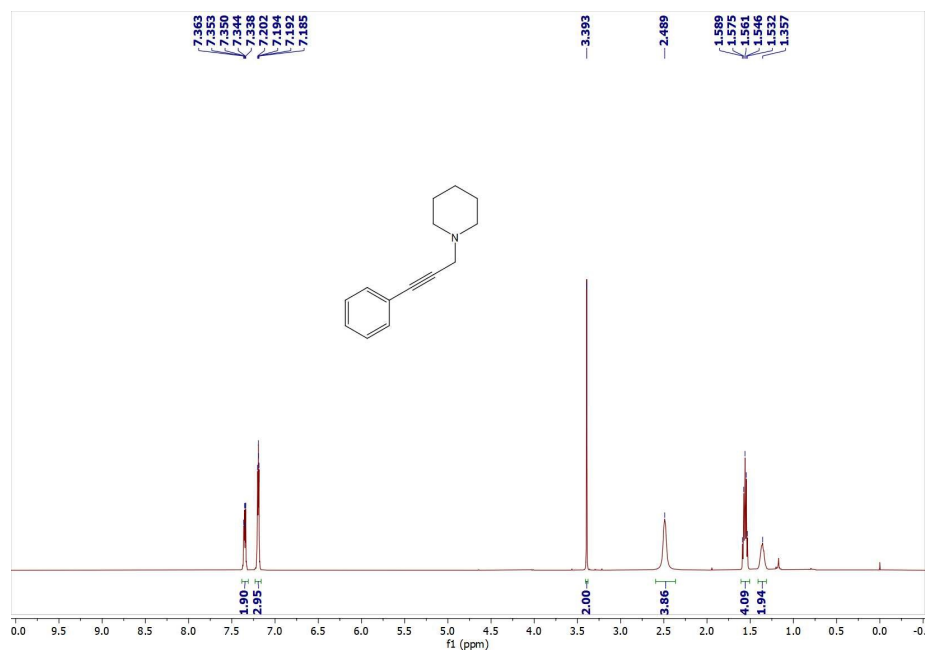


Fig. S26 ^1H NMR spectrum of **13aba** in CDCl_3 (400 MHz)

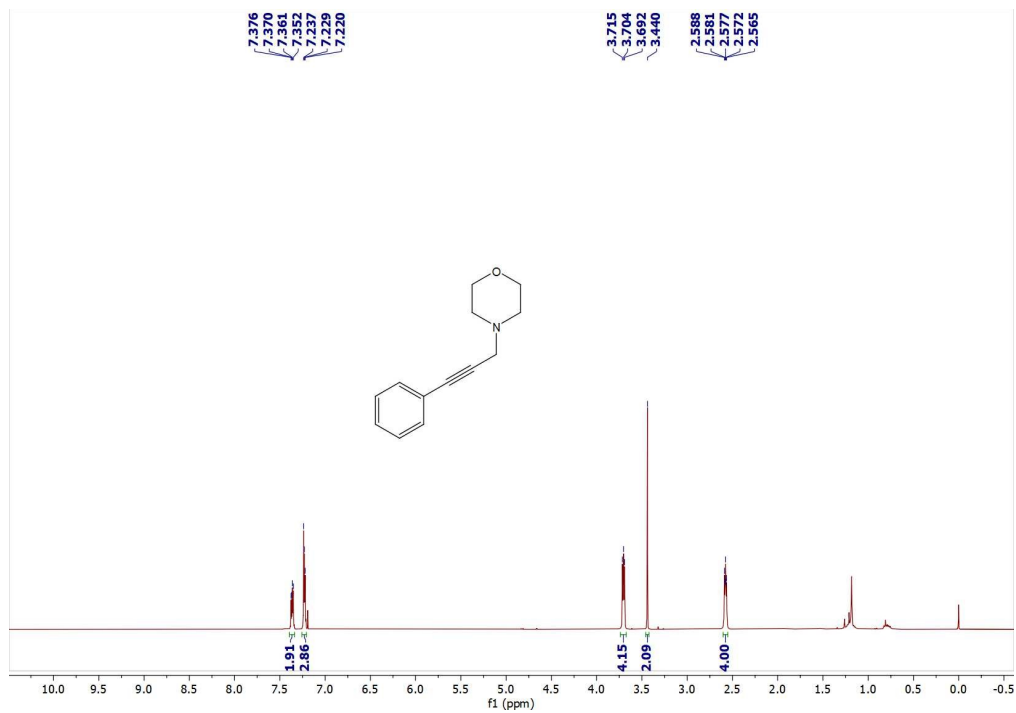


Fig. S27 ¹H NMR spectrum of **13aca** in CDCl₃ (400 MHz)

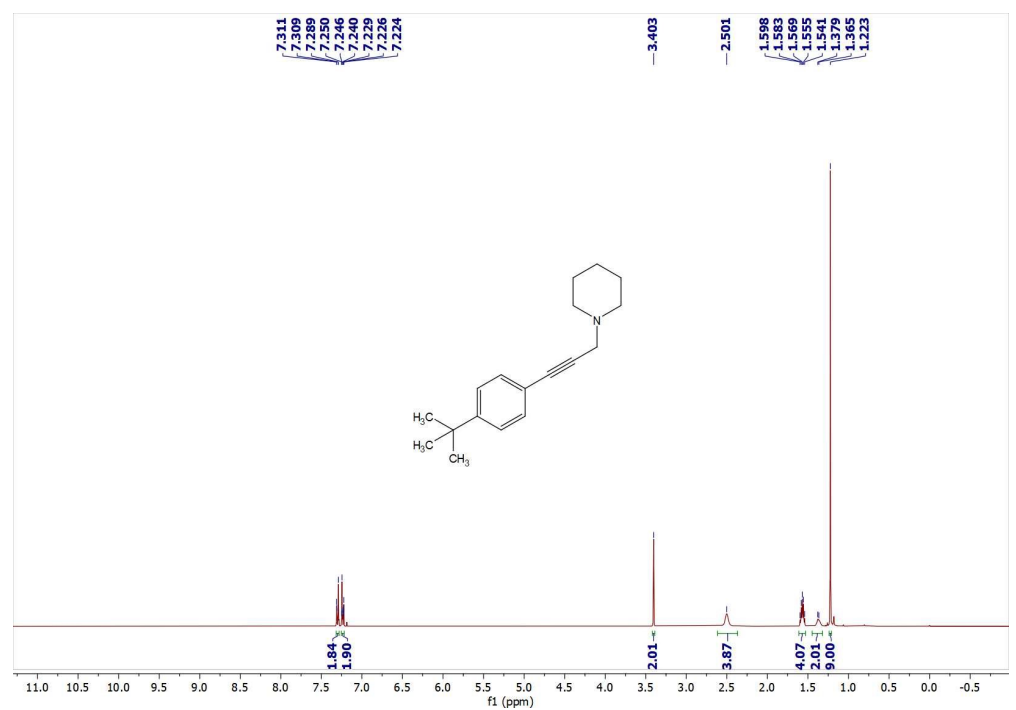


Fig. S28 ¹H NMR spectrum of **13bba** in CDCl₃ (400 MHz)

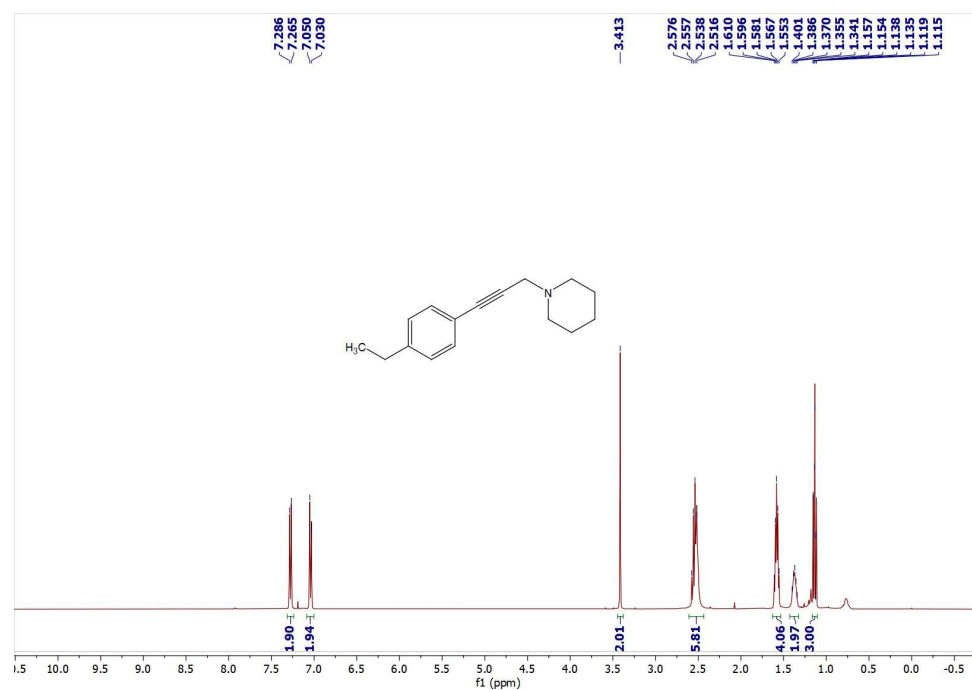


Fig. S29 ^1H NMR spectrum of **13ba** in CDCl_3 (400 MHz)

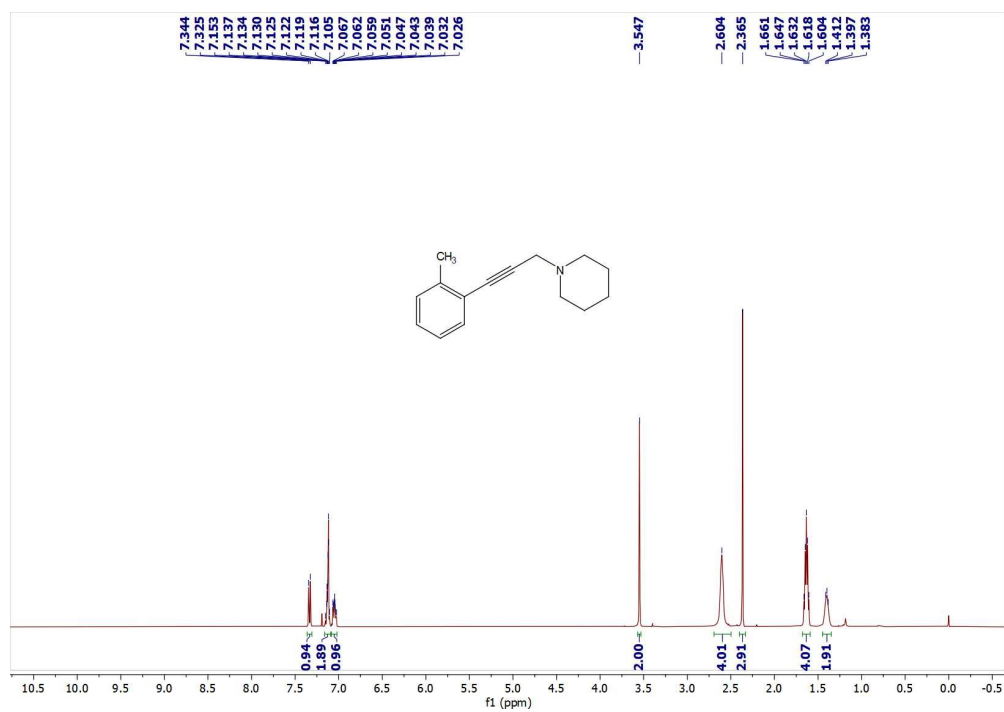


Fig. S30 ^1H NMR spectrum of **13dba** in CDCl_3 (400 MHz)

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