Supplementary Information (SI) for Green Chemistry.
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# Supplementary Information

## Synergistic Au–Pd catalysis of Sonogashira Couplings of Terminal Alkynes with Aryl Iodides in water

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## 1. General information

All starting materials were purchased from commercial sources. Reaction temperatures were controlled by an IKA RCT basic magnetic stirrer with a temperature probe. $^1$H NMR and $^{13}$C NMR were recorded on a 400 MHz Bruker spectrometer (400 MHz for $^1$H NMR and 101 MHz for $^{13}$C NMR). The high-resolution mass spectra (HRMS) data were measured on a Agilent G6230B High-Resolution Time-of-Flight Mass Spectrometer. The crystallographic parameters were measured using a D8 VENTURE X-ray single-crystal diffractometer manufactured by Bruker AXS Ltd. The ICP data were obtained using an inductively coupled plasma emission spectrometer manufactured by PerkinElmer. Isolated yields were calculated as the mass ratio of the purified product to the theoretical yield (based on the limiting substrate, typically aryl halide).

## 2. Preparation of a stock solution

The catalyst solution was prepared by dissolving 5.1 mg of tetrakis(triphenylphosphine)palladium(0) [Pd(PPh$_3$)$_4$] in 25 mL of dichloromethane (DCM). This stock solution is suitable for subsequent reactions (fresh preparation and immediate use are required for the stock solution). For a catalyst loading of 0.01 mol%, 250 μL of this stock solution was used per 0.4 mmol of the reaction substrate. The catalyst was transferred by adding the stock solution to the reactor, followed by vacuum evaporation of DCM.

## 3. Preparation procedure of gold complexes

### 3.1 Synthesis of the ligand

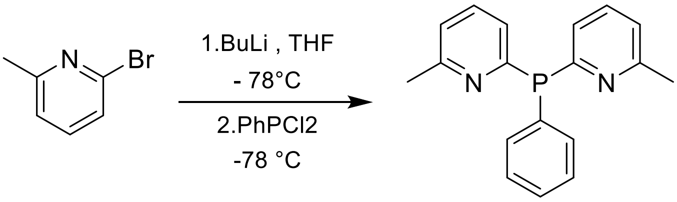


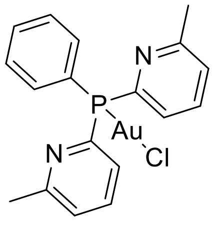
**Figure S1.** Synthesis of Ligand L$_1$

In a flame-dried Schlenk tube under an argon atmosphere, n-butyllithium (8 mL of a 2.5 M solution in hexane, 20 mmol) was added, and the reaction mixture was cooled to -78 ℃. Subsequently, a solution of 2-bromo-6-methylpyridine (3.4 g, 20 mmol) in tetrahydrofuran (THF, 8 mL) was added, and the reaction mixture was stirred at -78 ℃ for 4 hours. At -78 ℃, a solution of P,P-dichlorophenylphosphine (1.4 mL, 10 mmol) in tetrahydrofuran (12 mL) was added dropwise, and stirring was continued at this temperature for 2 hours. The reaction mixture was then slowly warmed to room temperature and quenched with water. After extraction with ethyl acetate (EA), column chromatography was performed using a mixed eluent of petroleum ether (PE) and ethyl acetate (EA) at a volume ratio of 5:1 (PE:EA = 5:1). Following vacuum drying, the pure product 2,2'-(phenylphosphanediyl)di-6-methylpyridine [P(2-Mepy)$_2$Ph] was obtained as a white solid (2.1 g, 7.3 mmol, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47-7.32 (m, 7H), 7.04 (d, $J$ = 7.8 Hz, 2H), 6.91 (d, $J$ = 7.6 Hz, 2H), 2.56 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3, 158.9, 135.9, 134.8, 129.2, 128.6 , 125.2, 122.1, 24.6. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ -4.43.

## 3.2 Synthesis of gold complexes

The entire reaction was carried out under nitrogen atmosphere in the dark. To a dichloromethane solution of chloro(dimethyl sulfide)gold(I) (0.3 mmol, 0.0884 g) was added an equimolar amount of phosphine ligand L$_1$ (0.3 mmol, 0.0876 g), and the mixture was stirred at room temperature for 90 minutes. After completion of the reaction, the solution was concentrated to 3 mL under reduced pressure by rotary evaporation, and 15 mL of n-hexane was added. After standing for 5 h, white needle-like crystals precipitated. The product was dried under vacuum to afford the target product.

**[P(2-Mepy)$_2$Ph]AuCl (L$_2$AuCl)**

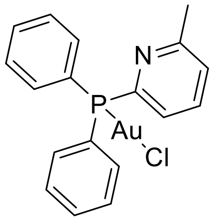


The pure product [AuCl(2,2'-(phenylphosphanediyl)di-6-methylpyridine)] was obtained as a white solid (146.7 mg, 0.28 mmol, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$)

$\delta$ 8.01-7.93 (m, 2H), 7.65-7.57 (m, 4H), 7.56-7.44 (m, 3H), 7.19-7.15 (m, 2H), 2.52 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 160.1 (d, *J* = 17.3 Hz), 153.1 (d, *J* = 88.7 Hz), 136.3 (d, *J* = 10.4 Hz), 135.7 (d, *J* = 13.6 Hz), 132.1 (d, *J* = 2.7 Hz), 128.8 (d, *J* = 11.9 Hz), 127.8 (d, *J* = 28.9 Hz), 124.9 (d, *J* = 2.5 Hz), 24.6 (s). $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 30.82.

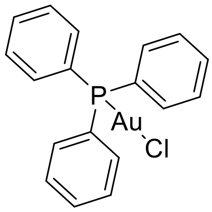
The synthesis procedures for other gold complexes were analogous to that of $L_1$AuCl.

**[P(2-Mepy)Ph$_2$]AuCl (L$_2$AuCl)**



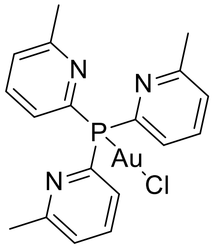
White powder (106.7 mg, yield 75%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.70 (dt, *J* = 14.6, 7.4 Hz, 6H), 7.53-7.42 (m, 6H), 7.23 (d, *J* = 7.6 Hz, 1H), 2.56 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 160.5 (d, *J* = 16 Hz), 152.6 (d, *J* = 85 Hz), 136.7 (d, *J* = 11 Hz), 134.6 (d, *J* = 13 Hz), 131.9 (d, *J* = 3 Hz), 129.0 (d, *J* = 34 Hz), 129.0 (d, *J* = 12 Hz), 128.4 (d, *J* = 3 Hz), 125.3 (d, *J* = 2 Hz), 24.6 (s). $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 31.37.

**(PPh$_3$)AuCl (L$_3$AuCl)**



White powder (123.2 mg, yield 83%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47 (t, *J* = 6.7 Hz, 6H), 7.45-7.37 (m, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 134.2 (d, *J* = 13.7 Hz), 132.0 (d, *J* = 2.7 Hz), 129.3 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 62.3 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 33.22.

**[P(2-Mepy)$_3$]AuCl (L$_4$AuCl)**



White powder (102.0 mg, yield 63%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77 (td, $J = 7.7$ Hz, $J = 4.2$ Hz, 3H), 7.59 (dd, $J = 7.6$ Hz, $J = 5.6$ Hz, 3H), 7.39 (dd, $J = 8.2$ Hz, $J = 2.9$ Hz, 3H), 2.54 (s, 9H). $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 31.92.

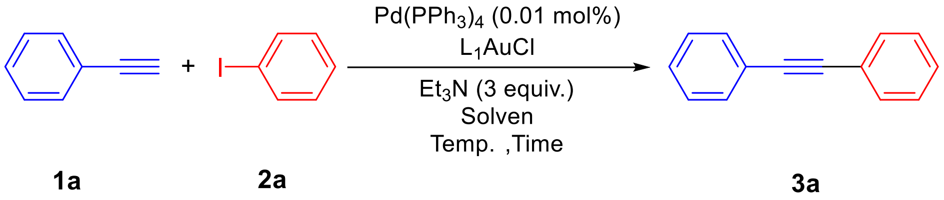
## 4. General procedure for Sonogashira couplings

An aliquot of the aforementioned stock solution was taken, and the required volume of the catalyst solution was added to an oven-dried 25 mL Schlenk tube preloaded with a Teflon-coated magnetic stir bar, followed by sealing of the tube opening. The dichloromethane (DCM) in the solution was removed under reduced pressure (ca. 20 min). Then, the gold complex (LAuCl), aryl halide **2** (0.4 mmol), 0.4 mmol terminal alkyne **1** , and 1.2 mmol triethylamine ($Et_3N$) were added to the reaction tube. Subsequently, 3 mL of water was introduced. The reaction tube was then placed in an oil bath and stirred at a rotation speed of 1000–1500 rpm at 120 °C for 30 min.

After the reaction was completed, the Schlenk tube was removed from the oil bath and allowed to cool to room temperature. The product was isolated via one of the following methods: suction filtration, decantation of the aqueous layer, or addition of 400 μL of ethyl acetate to the Schlenk tube followed by brief stirring. Stirring was stopped, and after phase separation, the organic layer was removed using a pipette. The organic layer was dried over anhydrous sodium sulfate ($Na_2SO_4$). The organic solvent was removed under vacuum to afford the crude product, which was further purified by silica gel column chromatography to yield the target products **3a-3s**.

## 5. Supplementary information for conditions screening

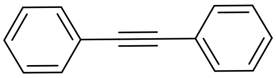
**Table S1.** Screening of reaction conditions



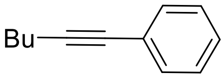
| Entry[a] | Temp.(°C) | Co-catalyst | Time | Solvent | Yield[b](%) |
|---|---|---|---|---|---|
| 1 | 100 | $L_1$AuCl (10mol%) | 12 h | $H_2O$ | 32 |
| 2 | 80 | $L_1$AuCl (10mol%) | 12 h | $H_2O$ | 20 |
| 3 | 40 | $L_1$AuCl (10mol%) | 12 h | $H_2O$ | 3 |
| 4 | 120 | $L_1$AuCl (7mol%) | 12 h | $H_2O$ | 99 |
| 5 | 120 | $L_1$AuCl (5mol%) | 12 h | $H_2O$ | 99 |
| 6 | 120 | $L_1$AuCl (2mol%) | 6 h | $H_2O$ | 99 |
| 7 | 120 | $L_1$AuCl (2mol%) | 1 h | $H_2O$ | 99 |
| 8 | 120 | $L_1$AuCl (2mol%) | 30 min | $H_2O$ | 99 |
| 9 | 120 | $L_1$AuCl (2mol%) | 10 min | $H_2O$ | 71 |
| 10 | 120 | $L_1$AuCl (2mol%) | 30 min | MeCN | 35 |
| 11 | 100 | $L_1$AuCl (2mol%) | 30 min | MeCN | 25 |
| 12 | 120 | $L_2$AuCl (2mol%) | 30 min | $H_2O$ | 37 |
| 13 | 120 | $L_3$AuCl (2mol%) | 30 min | $H_2O$ | 87 |
| 14 | 120 | $L_4$AuCl (2mol%) | 30 min | $H_2O$ | 48 |

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), $Pd(PPh_3)_4$ (0.01 mol%), Co-catalyst, $Et_3N$ (1.2 mmol) at 120 °C in $H_2O$ (3 mL) under ambient air conditions for 12 h. [b] Isolated yields.

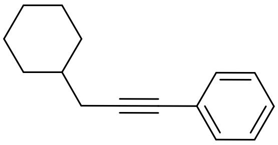
## 6. Characterization data of all products



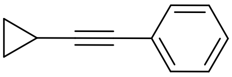
**1,2-diphenylethyne (3a)**[2] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White acicular crystal (70.6 mg, 99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57-7.47 (m, 4H), 7.35-7.22 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.7, 128.4, 128.31, 123.29, 89.4.



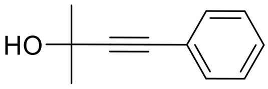
**(hex-1-yn-1-yl)benzene (3b)**[3] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. Pale yellow liquid (60.7mg, 96%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48-7.34 (m, 2H), 7.32-7.19 (m, 3H), 2.40 (t, $J$ = 7.0 Hz, 2H), 1.62-1.44 (m, 4H), 0.94 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.6, 128.2, 127.5, 124.2, 90.4, 80.6, 30.9, 22.1, 19.2, 13.7.



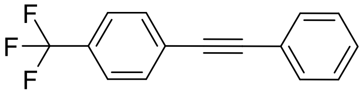
**(3-cyclohexylprop-1-yn-1-yl)benzene (3c)**[4] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. Pale yellow liquid (78.5mg, 99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.34 (m, 2H), 7.28-7.21 (m, 3H), 2.28 (d, $J$ = 6.7 Hz, 2H), 1.88-1.83 (m, 2H), 1.76-1.69 (m, 2H), 1.59-1.48 (m, 1H), 1.36-0.96 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.6, 128.2, 127.5, 124.2, 89.4, 81.5, 37.6, 32.8, 27.3, 26.4, 26.2.



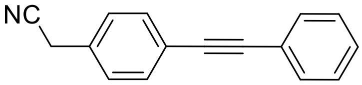
**(cyclopropylethynyl)benzene (3d)**[5] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. Colorless transparent liquid (56.3mg, 99%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30-7.27 (m, 2H), 7.18-7.14 (m, 3H), 1.39-1.32 (m, 1H), 0.78 – 0.66 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.4, 128.0, 127.3, 123.8, 93.2, 75.6, 8.4, -0.0.



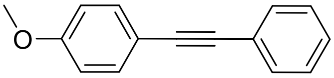
**2-methyl-4-phenylbut-3-yn-2-ol (3e)**[6] The product was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (PE/EA = 10:1, v/v). White solid (35.9mg, 56%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.39 (m, 2H), 7.33-7.25 (m, 3H), 1.62 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.7, 128.3, 128.3, 122.8, 93.9, 82.1, 65.6, 31.5.



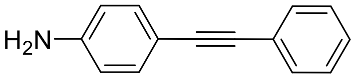
**1-(phenylethynyl)-4-(trifluoromethyl)benzene (3f)**[2] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White solid (96.6mg, 91%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62-7.57 (m, 4H), 7.56-7.50 (m, 2H), 7.38-7.30 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.9, 131.8, 129.9 (q, $J$ = 32.7 Hz), 128.9, 128.5, 127.2 (q, $J$ = 32.7 Hz), 125.4 (q, $J$ = 3.8 Hz), 121.4 (d, $J$ = 272.1 Hz), 91.8, 88.0.



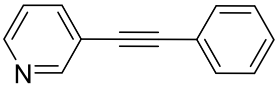
**2-(4-(phenylethynyl)phenyl)acetonitrile (3g)**[7] The product was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (PE/EA = 10:1, v/v). White solid (80.8mg, 93%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.49 (m, 4H), 7.36-7.21 (m, 5H), 3.70 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 132.8, 132.3, 131.7, 130.0, 128.5, 128.04, 123.2, 123.0, 117.6, 90.3, 88.6, 23.5.



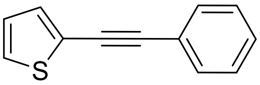
**1-methoxy-4-(phenylethynyl)benzene (3h)**[8] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White solid (81.6mg, 98%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56-7.49 (m, 2H), 7.35-7.30 (m, 3H), 7.29-7.21 (m, 1H), 7.14-7.11 (m, 1H), 7.06-7.05 (m, 1H), 6.89-6.86 (m, 1H), 3.78 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 159.6, 131.7, 129.5, 128.5, 128.4, 124.3, 116.4, 115.0, 89.4, 89.3, 55.3.



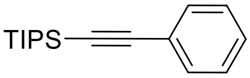
**4-(phenylethynyl)aniline (3i)**[9] The product was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (PE/EA = 5:1, v/v). White solid (71.9mg, 93%). $^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.52-7.46 (d, *J* = 7.3 Hz, 2H), 7.36-7.25 (m, 5H), 6.60-6.56 (m, 2H), 3.76 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 146.7, 133.1, 131.4, 128.4, 127.8, 124.0, 114.9, 112.5, 90.4, 87.5.



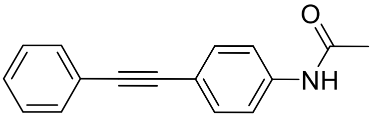
**3-(phenylethynyl)pyridine (3j)**[2] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White solid (70.3mg, 98%). $^1$H NMR (400 MHz, $CDCl_3$) *δ* 8.76 (s, 1H), 8.54-8.51 (m, 1H), 7.78 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.56-7.51 (m, 2H), 7.37-7.32 (m, 3H), 7.25 (dd, *J* = 7.6, 5.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 152.3, 148.6, 138.4, 131.7, 128.8, 128.5, 123.0, 122.5, 120.5, 92.7, 86.0.



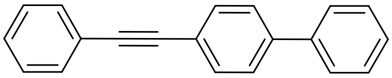
**2-(phenylethynyl)thiophene (3k)**[6] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White solid (70.8mg, 96%). $^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.52-7.47 (m, 2H), 7.35-7.22 (m, 5H), 6.96-7.98 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 132.0, 131.5, 128.52, 128.47, 127.4, 127.2, 123.4, 123.0, 93.2, 82.8.



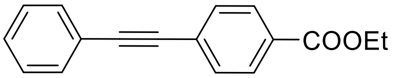
**Triisopropyl(phenylethynyl)silane (3l)**[10] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White solid (102.4mg, 99%). $^1$H NMR (400 MHz, $CDCl_3$) *δ* 7.50-7.43 (m, 2H), 7.30-7.23 (m, 3H), 1.13-1.09 (m, 16H), 1.09-1.07 (m, 5H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 132.1, 128.3, 128.2, 123.7, 107.2, 90.4, 18.7, 11.4.



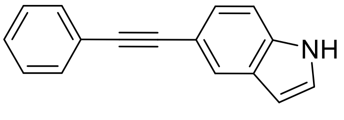
**N-(4-(phenylethynyl)phenyl)acetamide (3n)**[11] The product was purified by column chromatography on silica gel, eluting with ethyl acetate (EA). White solid (93.2mg, 99%). $^{1}$H NMR (400 MHz, DMSO) $\delta$ 10.15 (s, 1H), 7.71-7.64 (m, 2H), 7.55-7.46 (m, 4H), 7.41-7.38 (m, 3H), 2.08 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 169.1, 140.2, 132.5, 131.7, 129.2, 129.0, 123.0, 119.4, 116.9, 90.0, 89.0, 24.5.



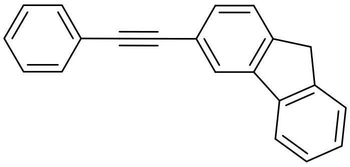
**4-(phenylethynyl)-1,1'-biphenyl (3o)**[8] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White solid (92.6mg, 91%). $^{1}$H NMR (400 MHz, DMSO) $\delta$ 7.79-7.70 (m, 4H), 7.68-7.62 (m, 2H), 7.62-7.55 (m, 2H), 7.55-7.35 (m, 6H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 140.7, 139.6, 132.5, 131.9, 129.5, 129.31, 129.27, 128.4, 127.4, 127.1, 122.8, 121.8, 90.6, 89.7.



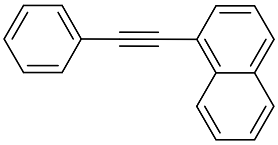
**Ethyl 4-(phenylethynyl)benzoate (3p)**[12] The product was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (PE/EA = 5:1, v/v). White acicular crystal (86.1 mg, 86%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.08-7.99 (m, 2H), 7.59-7.50 (m, 4H), 7.35-7.32 (m, 3H), 4.37 (q, $J$ = 7.1 Hz, 2H), 1.38 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 166.1, 131.8, 131.5, 129.9, 129.5, 128.8, 128.5, 127.9, 122.8, 92.3, 88.8, 61.2, 14.4.



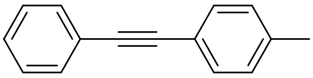
**5-(phenylethynyl)-1H-indole (3q)**[9] The product was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (PE/EA = 5:1, v/v). White acicular crystal (80.8 mg, 93%). $^1$H NMR (400 MHz, DMSO) $\delta$ 11.38 (s, 1H), 7.84 (s, 1H), 7.58-7.55 (m, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 2.8 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.38 (dt, *J* = 6.9, 2.5 Hz, 2H), 7.33-7.30 (m, 1H), 6.51 (t, *J* = 2.6 Hz, 1H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 136.2, 131.6 129.1, 128.5, 128.2, 127.1, 124.9, 124.4, 123.8, 113.0, 112.4, 101.9, 92.2, 87.2.



**3-(phenylethynyl)-9H-fluorene (3r)**[7] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White acicular crystal (98.0 mg, 92%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73-7.66 (m, 3H), 7.54-7.52 (m, 3H), 7.49-7.47 (m, 1H), 7.37-7.26 (m, 6H), 3.83 (s, 2H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 138.9, 138.6, 137.2, 136.4, 127.0, 125.9, 123.7, 123.51, 123.49, 122.5, 122.3, 120.4, 118.9, 116.6, 115.5, 115.1, 85.6, 84.8, 32.1.

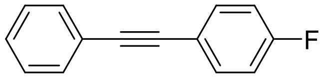


**1-(phenylethynyl)naphthalene (3s)**[2] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White acicular crystal (43.8 mg, 48%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.45 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 9.2 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.67-7.61 (m, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.50 (t, *J* = 6.8 Hz, 1H), 7.42 (t, *J* = 8.3 Hz, 1H), 7.40-7.30 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 133.34, 133.28, 131.7, 130.4, 128.8, 128.50, 128.45, 128.4, 126.8, 126.5, 126.3, 125.3, 123.5, 121.0, 94.4, 87.6.



**1-methyl-4-(phenylethynyl)benzene (3t)**[2] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White acicular crystal (6.7 mg, 10%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 (d, *J* = 7.3, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 6.5 Hz, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR

(101 MHz, $CDCl_3$) $\delta$ 138.4, 131.6, 131.5, 129.2, 128.4, 128.1, 123.5,120.2, 89.8, 88.7, 21.6.



**1-fluoro-4-(phenylethynyl)benzene (3u)**[2] The product was isolated by column chromatography on silica gel using petroleum ether (PE) as the eluent. White acicular crystal (20.0 mg, 29%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53-7.50 (m, 4H), 7.36-7.32 (m, 3H), 7.04 (t, $J$ = 8.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.6 (d, $J$ = 249.6 Hz), 133.6 (d, $J$ = 8.4 Hz), 131.6, 128.5 (d, $J$ = 4.2 Hz), 123.2, 119.4 (d, $J$ = 3.5 Hz), 115.8, 115.6, 89.2, 88.4.

## 7. Catalytic mechanism analysis

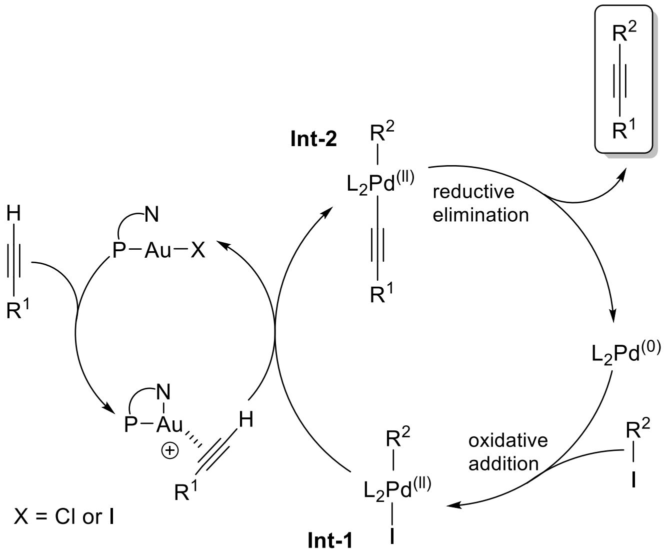


**Figure S2.** Proposed mechanism.

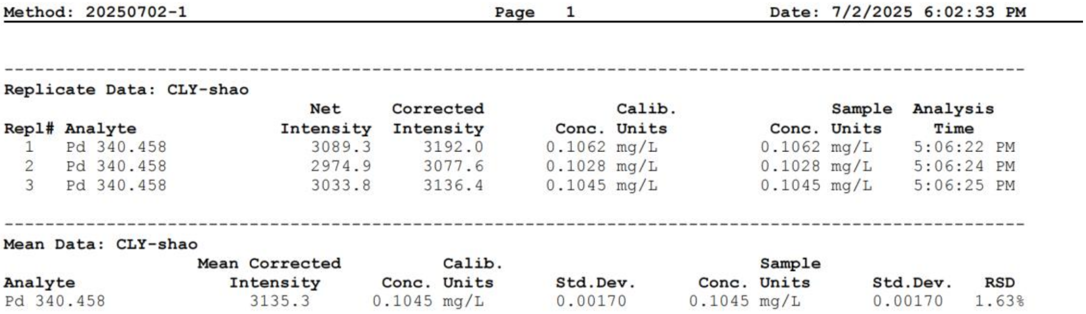
On the basis of the experimental results described above and previous reports on Sonogashira coupling reactions[13], a plausible reaction mechanism for the target palladium/gold co-catalyzed coupling process is depicted in Figure S2. The mechanism proceeds through a typical catalytic cycle involving four key steps: oxidative addition, alkyne activation, transmetallation, and reductive elimination, with the synergistic effect of Pd(0) catalyst, Au(I) co-catalyst and base ensuring the smooth progress of the reaction.

First, the active palladium(0) (Pd(0)) species, which is in situ generated via the reduction of a palladium precatalyst, undergoes an oxidative addition with the carbon-iodine (C-I) bond of iodobenzene. This step serves as the critical rate-determining step of the Sonogashira reaction, where the Pd(0) center inserts into the electrophilic C-I bond to form a square-planar arylpalladium(II) intermediate (**Int-1**), in which both the aryl group and iodide ligand are coordinated to the palladium center. Meanwhile, the terminal alkyne substrate is activated by the Au(I) complex. The Au(I) species coordinates with the π-system of the alkyne triple bond, a process that not only enhances the electrophilicity of the alkynyl carbon but also weakens the C-H bond of the terminal alkyne.[14]

Subsequently, the arylpalladium(II) intermediate (**Int-1**) undergoes a transmetallation reaction with the gold-alkynyl intermediate. In this step, the alkynyl group on the gold complex is transferred to the Pd(II) center, yielding a new palladium(II) intermediate (**Int-2**) coordinated with both aryl and alkynyl ligands; at the same time, the Au(I) complex is released and regenerated to re-participate in the next cycle of alkyne activation.

Finally, the intermediate **Int-2** undergoes reductive elimination, which is the final step for the formation of the coupling product. The aryl and alkynyl ligands on the Pd(II) center undergo reductive elimination to form the C($sp^2$)–C(sp) triple bond in the target Sonogashira coupling product (arylalkyne). Simultaneously, the Pd(II) center is reduced back to Pd(0), completing the palladium catalytic cycle, and the active Pd(0) species can be recycled for the next round of catalytic reactions.

## 8. Determination of palladium content in the reaction solution



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Method: 20250702-1                          Page   1               Date: 7/2/2025 6:02:33 PM

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Replicate Data: CLY-shao
                               Net      Corrected           Calib.             Sample  Analysis
Repl# Analyte               Intensity  Intensity      Conc. Units          Conc. Units     Time
  1    Pd 340.458              3089.3     3192.0     0.1062 mg/L          0.1062 mg/L    5:06:22 PM
  2    Pd 340.458              2974.9     3077.6     0.1028 mg/L          0.1028 mg/L    5:06:24 PM
  3    Pd 340.458              3033.8     3136.4     0.1045 mg/L          0.1045 mg/L    5:06:25 PM

-----------------------------------------------------------------------------------------------
Mean Data: CLY-shao
                       Mean Corrected         Calib.                           Sample
Analyte                    Intensity     Conc. Units        Std.Dev.       Conc. Units       Std.Dev.   RSD
Pd 340.458                  3135.3      0.1045 mg/L         0.00170        0.1045 mg/L       0.00170   1.63%
```

**Figure S3.** Result report for palladium (Pd) content determination via ICP

Sample Preparation: An aliquot of 625 μL of the stock solution was measured, and the required volume of the catalyst solution was added to an oven-dried 25 mL Schlenk tube followed by sealing of the tube opening. Dichloromethane (DCM) in the solution was removed by rotary evaporation under reduced pressure (ca. 20 min). The gold complex (LAuCl), aryl halide 2 (1.0 mmol), 1.0 mmol terminal alkyne 1, and 3.0 mmol triethylamine ($Et_3N$) were sequentially added to the reaction tube, followed by the addition of 1 mL of digestion solution. The solution was diluted to the mark in a 1 mL volumetric flask and then heated for digestion until it became clear and transparent.

# 9. Investigation on electrostatic potential and aqueous stability of gold(I) complexes

## 9.1 Investigation on electrostatic potential of gold(I) complexes

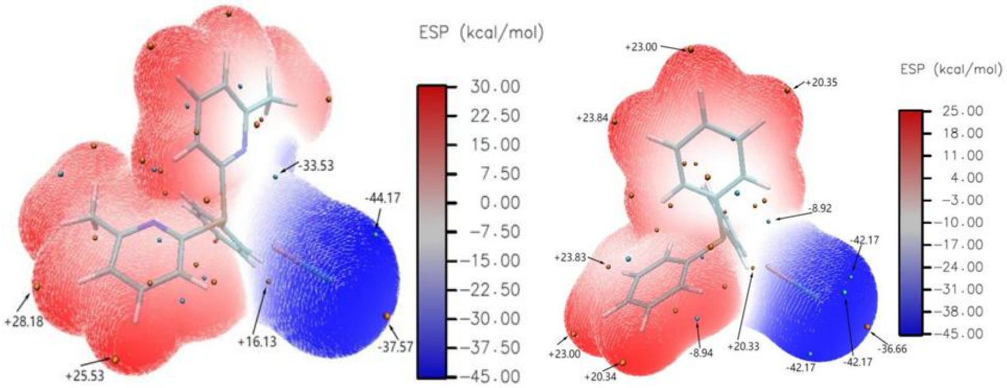


**Figure S4.** Investigation on electrostatic potential of gold complexes.

**Table S2.** Investigation on electrostatic potential of gold complexes.[15]

| | All (Ang^2) | Positive area (Ang^2) | Negative area (Ang^2) | Minimal value (kcal/mol) | Positive average (kcal/mol) | Negative average (kcal/mol) |
|---|---|---|---|---|---|---|
| $L_1$ | 14.66855 | 0.00000 | 14.66855 | -32.93714759 | Not a number | -19.63650 |
| $PPh_3$ | 12.64439 | 0.00000 | 12.64439 | -29.07102518 | Not a number | -18.49225 |

## 9.2 Aqueous stability investigation of $L_1AuCl$ complex

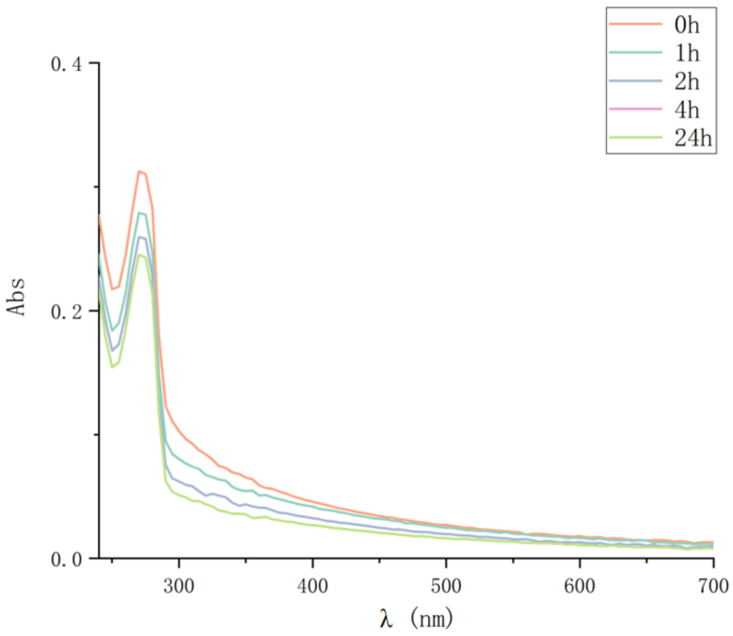
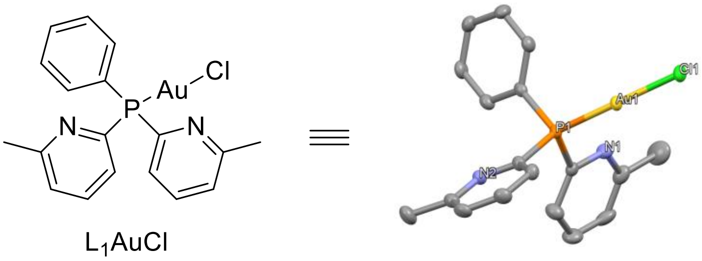


**Figure S5.** Stability test of $L_1AuCl$ in aqueous phase

We evaluated the stability of the gold complex in an aqueous environment. $L_1AuCl$ was dissolved in water at a concentration of 3 mM, and its stability was monitored continuously over 24 hours using UV-Vis spectrophotometry under alkaline conditions. As shown in Figure S5, spectral scans revealed no significant changes in the absorbance curves during the 24-hour period. Although a decrease in the intensity of characteristic absorption peaks was observed, this reduction was attributed to the precipitation of the complex over time. Comprehensive analysis indicates that $L_1AuCl$ exhibits good stability in alkaline aqueous solution, with no significant evidence of ligand dissociation or hydration reactions.

## 9.3 X-ray Crystal Structure of $L_1AuCl$

The structure of $L_1AuCl$ was determined based on single-crystal X-ray analysis. The detail procedure was shown as following: The $L_1AuCl$ solid was dissolved in DCM (5 mL) in glovebox. Then, the solvent was allowed to slowly evaporated into the atmosphere. The crystals of $L_1AuCl$ were grown from solution, which is suitable for X-ray diffraction analysis.



$L_1AuCl$

**Figure S6.** X-ray structure of $L_1AuCl$; hydrogen atoms are omitted for clarity

CCDC No. 2525465 ($L_1AuCl$) contains the supplementary crystallographic data for this paper. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data request/cif.

**Table S3.** Crystal data and structure refinement for $L_1AuCl$.

| | | |
|---|---|---|
| CCDC number | 2525465 | |
| Empirical formula | $C_{18} H_{17} Au Cl N_2 P$ | |
| Formula weight | 524.72 | |
| Temperature | 120.00 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 11.0461(8) Å | $\alpha$= 90° |
| | b = 19.0641(14) Å | $\beta$= 100.353(2)° |
| | c = 8.7989(6) Å | $\gamma$ = 90° |
| Volume | 1822.7(2) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.912 Mg/m$^3$ | |
| Absorption coefficient | 8.305 mm$^{-1}$ | |
| F(000) | 1000 | |
| Crystal size | 0.13 x 0.12 x 0.11 mm$^3$ | |
| Theta range for data collection | 2.584 to 28.144°. | |
| Index ranges | -14<=h<=14, -25<=k<=0, -11<=l<=11 | |

| | |
|---|---|
| Reflections collected | 8627 |
| Independent reflections | 4450 [R(int) = 0.0336] |
| Completeness to theta = 25.242° | 99.3 % |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4450 / 0 / 210 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indices [I>2sigma(I)] | R1 = 0.0296, wR2 = 0.0652 |
| R indices (all data) | R1 = 0.0382, wR2 = 0.0678 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.981 and -0.666 e.$Å^{-3}$ |

## 10. Transmission electron microscopy (TEM) image

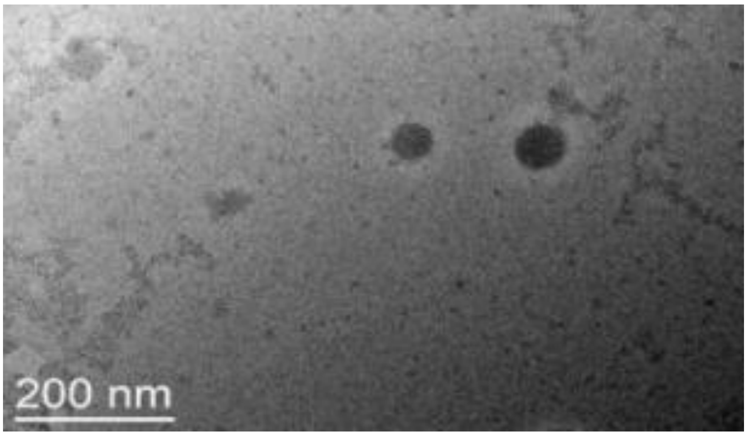


**Figure S7.** TEM image of the recovered gold nanoparticles after the reaction cycle.

## 11. Reusability experiments and control experiments

### 11.1 Catalyst reusability[16]

The initial reaction was set up according to the general procedure. A typical operation is as follows: 250 µL of palladium complex solution was added to the reaction system, followed by evaporation of the organic solvent. Subsequently, phenylethyne (0.4 mmol), iodobenzene (0.4 mmol) and triethylamine (1.2 mmol) were added to a 25 mL reaction vial, along with 3 mL of water. The reaction vial was placed in a reaction block preheated to 120 °C, and the reaction mixture was vigorously stirred with a magnetic stirrer under ambient atmosphere. After 30 minutes of reaction, fresh substrates were added to conduct the next cycle of the reaction. The isolated product yields are as follows: 1st run (66%), 2nd run (52%).

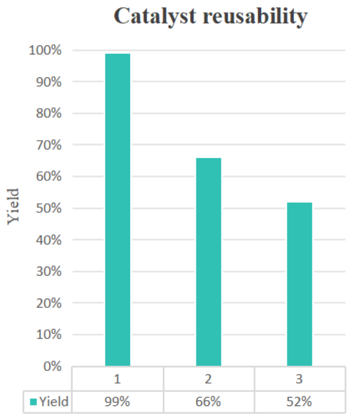


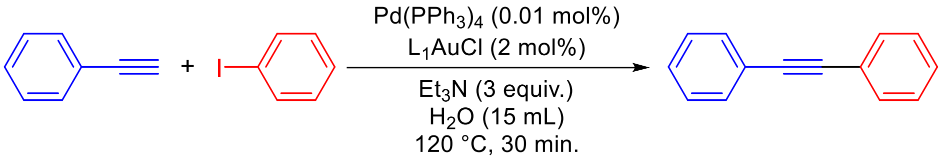
**Figure S8.** Catalyst reusability

## 11.2 Solvent reusability[16]

The initial reaction was set up according to the general procedure. A typical operation is as follows: First, 250 μL of a pre-prepared solution of the palladium complex in DCM was added to a 25 mL reaction vial. The DCM was then removed under reduced pressure. Subsequently, phenylacetylene (0.4 mmol), iodobenzene (0.4 mmol), triethylamine (1.2 mmol), and water (3 mL) were added. The vial was placed in a reaction block preheated to 120 °C, and the mixture was vigorously stirred with a magnetic stirrer under ambient atmosphere. After 30 minutes, ethyl acetate was added, and the two phases were separated using a separatory funnel. The organic phase was dried over anhydrous $MgSO_4$, and the target product was obtained via rotary evaporation followed by column chromatography. The separated aqueous phase was used directly in the next run without further treatment. For the next cycle, the entire procedure was repeated exactly as described for the first run, without additional water. The isolated product yields are as follows: 1st run (99%), 2nd run (99%), 3rd run (98%).

## 11.3 Control experiment

**Table S4.** Control experiment with the addition of surfactant.[a,b]



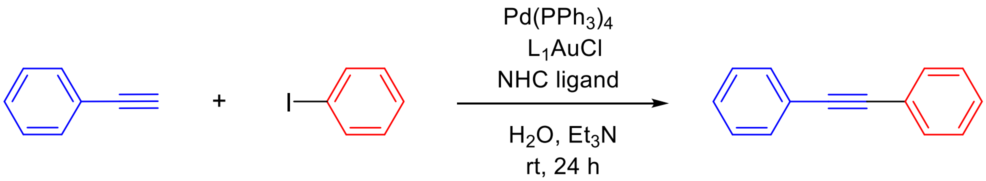
**1a** **2a** **3a**

| Entry | Dodecyltrimethylammonium Bromide | yield/% |
|---|---|---|
| 1 | none | 99 |
| 2 | 8mM | 71 |

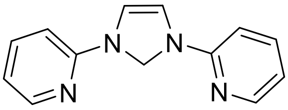
[a] **1a** (0.4 mmol), **2a** (0.4 mmol), $Pd(PPh_3)_4$ (0.01 mol%), $L_1AuCl$ (2 mol%), $Et_3N$ (1.2 mmol) at 120 °C in $H_2O$ (3 mL) under ambient air conditions for 30 minutes. [b]Isolated yields.

## 11.4 Further optimization attempts of the reaction system: addition of NHC ligand

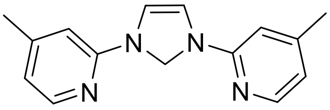
**Table S5.** Control experiment with the addition of NHC ligand.[a,b]



**1a** **2a** **3a**



**NHC-1**



**NHC-2**

| Entry | NHC ligand | Yield (%) |
|---|---|---|
| 1 | NHC-1 | 43 |
| 2 | NHC-2 | 28 |

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), Pd cat. (0.01 mol%), $L_1AuCl$ (2 mol%), NHC ligand (1 mol%), $Et_3N$ (1.2 mmol) at room temperature in $H_2O$ (3 mL) under ambient air conditions for 24 h. [b]Isolated yields.

Two pyridine-functionalized NHCs (NHC-1 and NHC-2) were successfully synthesized by ourselves, and were used as the ligand in the coupling reactions, respectively. According to the ref.[17], the reaction of 1a and 2a was conducted in the presence of $Pd(PPh_3)_4$ and $L_1AuCl$ as catalysts in $H_2O$ under room temperature for 24 h using NHC-1 and NHC-2 as additive ligand, respectively. The terminal product 3a was obtained in the yields of 43% and 28%, respectively.

**1,3-di(pyridin-2-yl)-2,3-dihydro-1H-imidazole (NHC-1)** The product was purified by recrystallization. Brown powder (82.1 mg, 74%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 12.60 (s, 1H), 9.34 (d, $J$ = 8.3 Hz, 2H), 8.57 (d, $J$ = 3.0 Hz, 2H), 8.51 (s, 2H), 8.16 (t, $J$ = 7.9 Hz, 2H), 7.53 (dd, $J$ = 7.5, 4.8 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 148.9, 145.8, 141.0, 125.7, 119.1, 116.3.

**1,3-bis(4-methylpyridin-2-yl)-2,3-dihydro-1H-imidazole (NHC-2)** The product was purified by recrystallization. Brown powder (61.0 mg, 49%).$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 12.30 (s, 1H), 9.14 (s, 2H), 8.48 (s, 1H), 8.39 (d, $J$ = 5.0 Hz, 2H), 7.31 (d, $J$ = 5.1 Hz, 2H), 2.64 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 153.5, 148.3, 145.8, 132.9, 126.7, 119.1, 116.5, 21.4.

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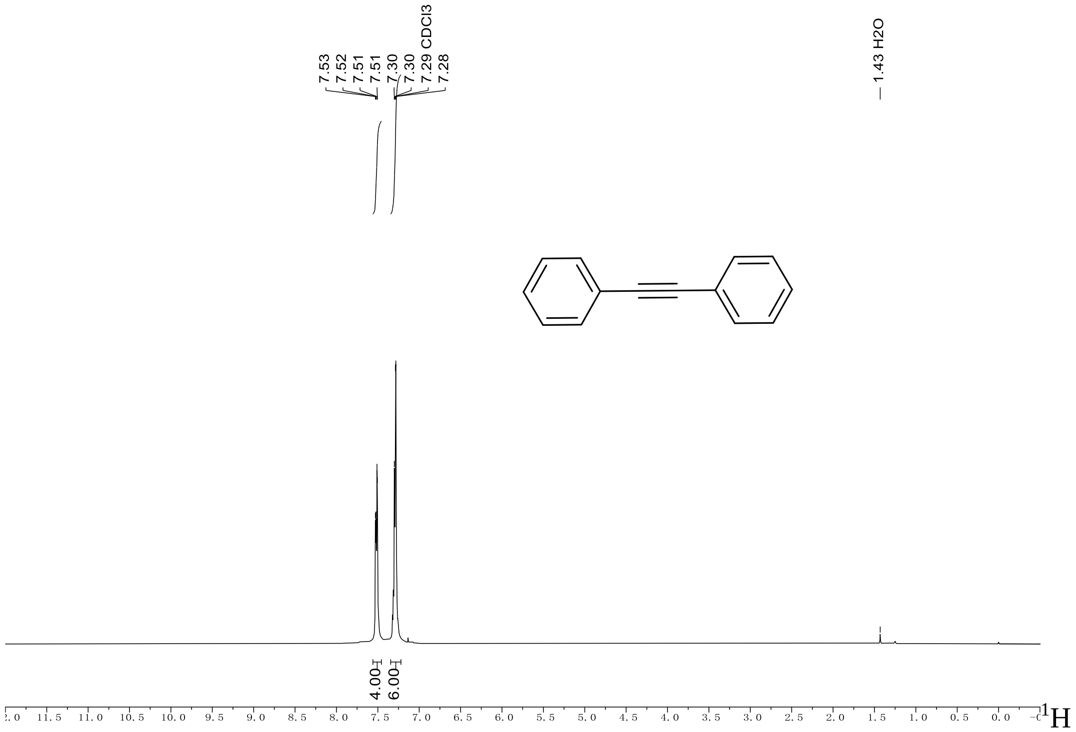
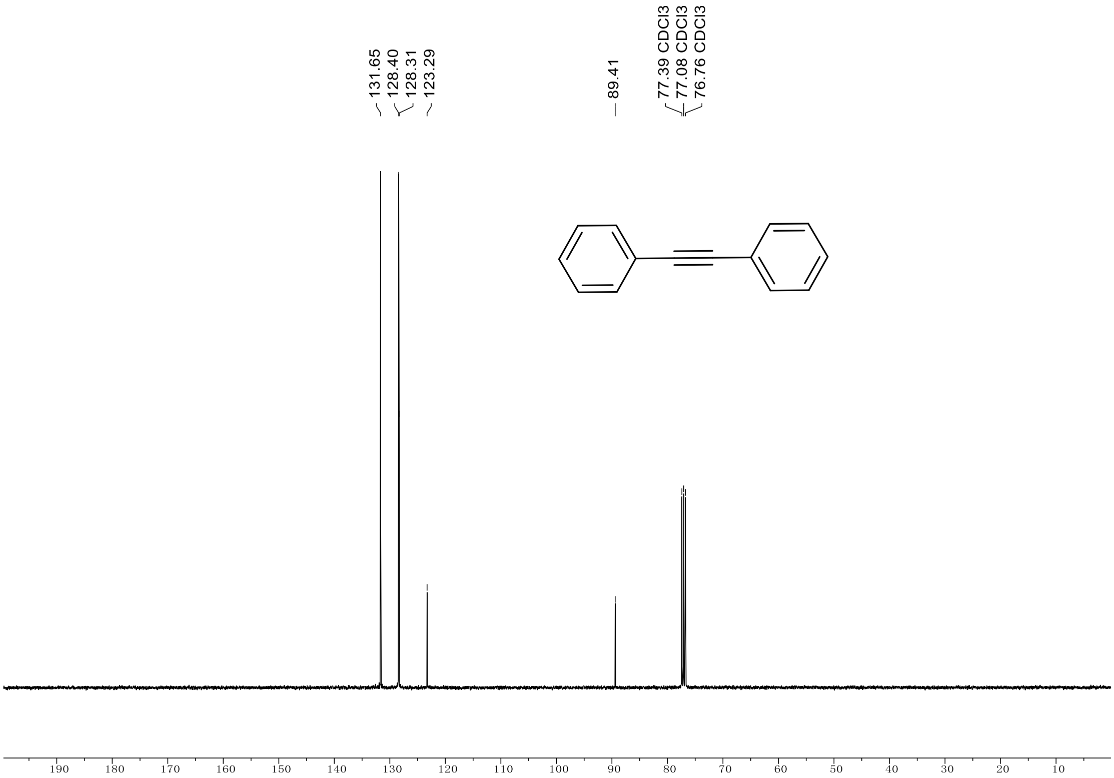
# 13. The NMR spectra of all products

## 1,2-diphenylethyne (3a)

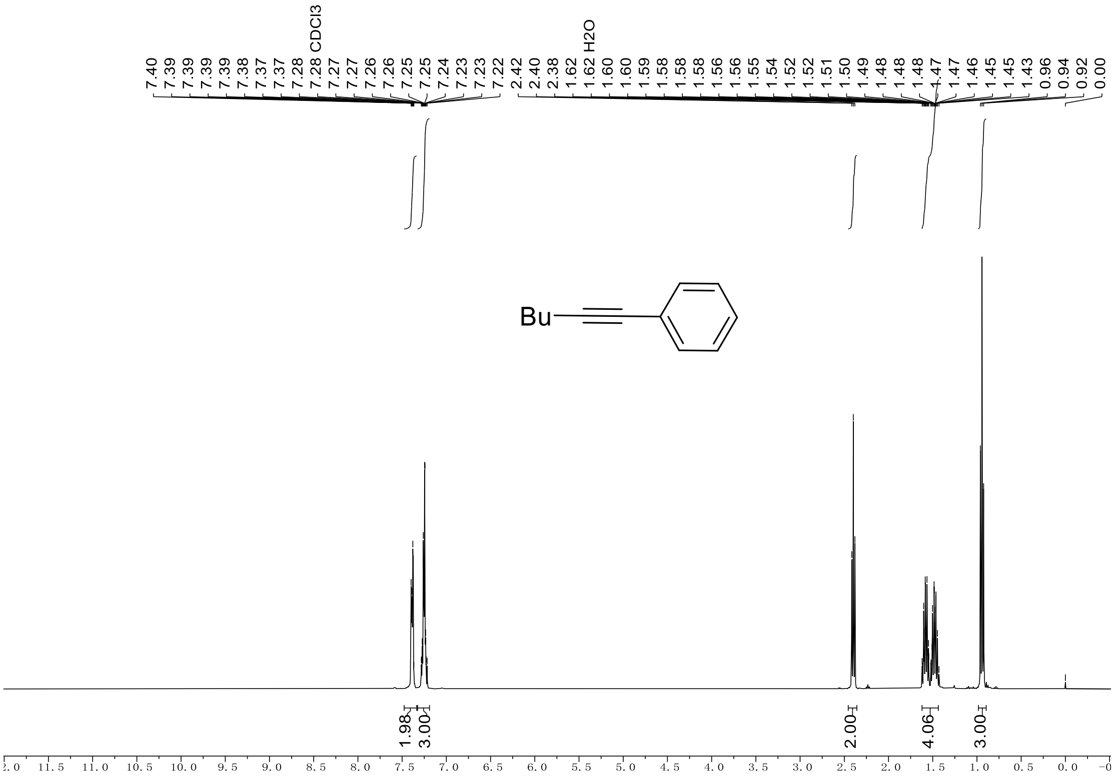


NMR (400 MHz, $CDCl_3$) of **3a**

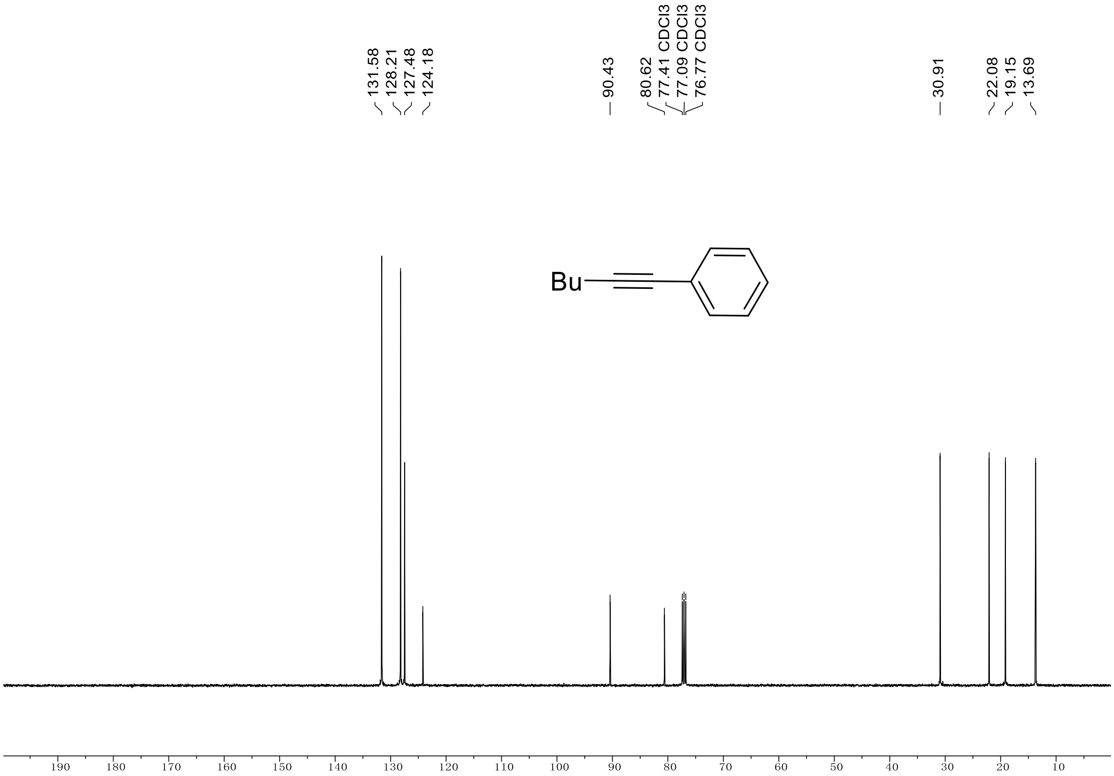


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3a**

# (hex-1-yn-1-yl)benzene (3b)

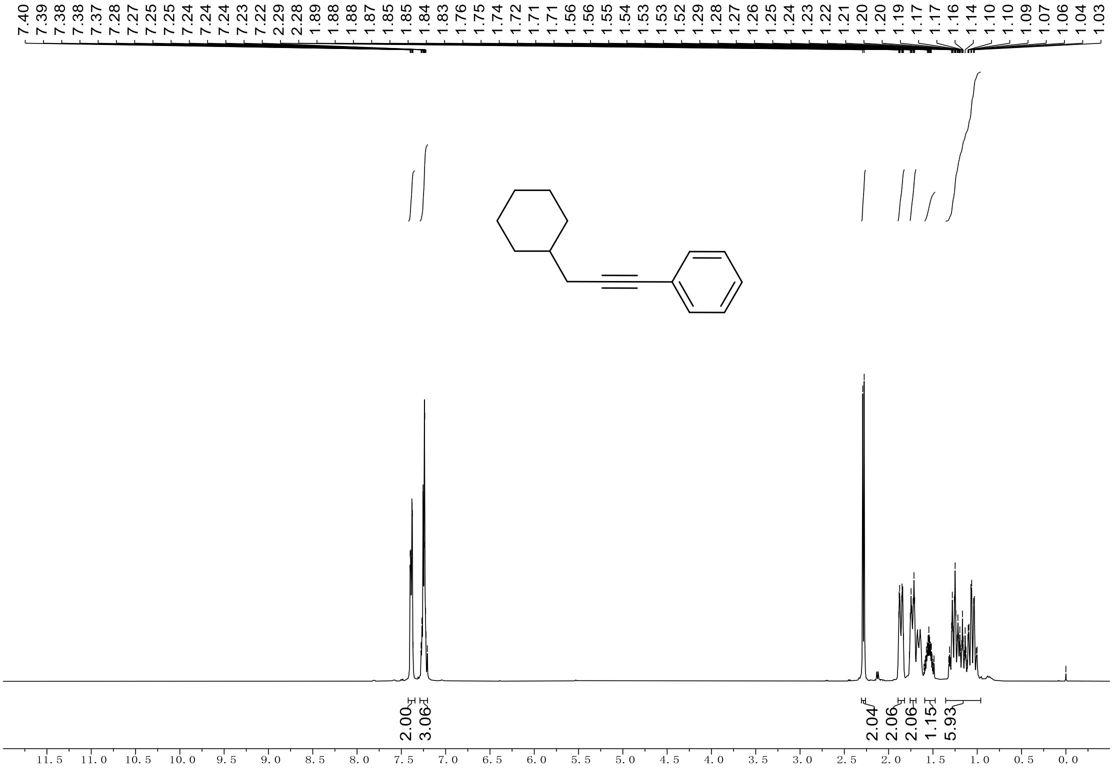


$^1$H NMR (400 MHz, CDCl$_3$) of **3b**

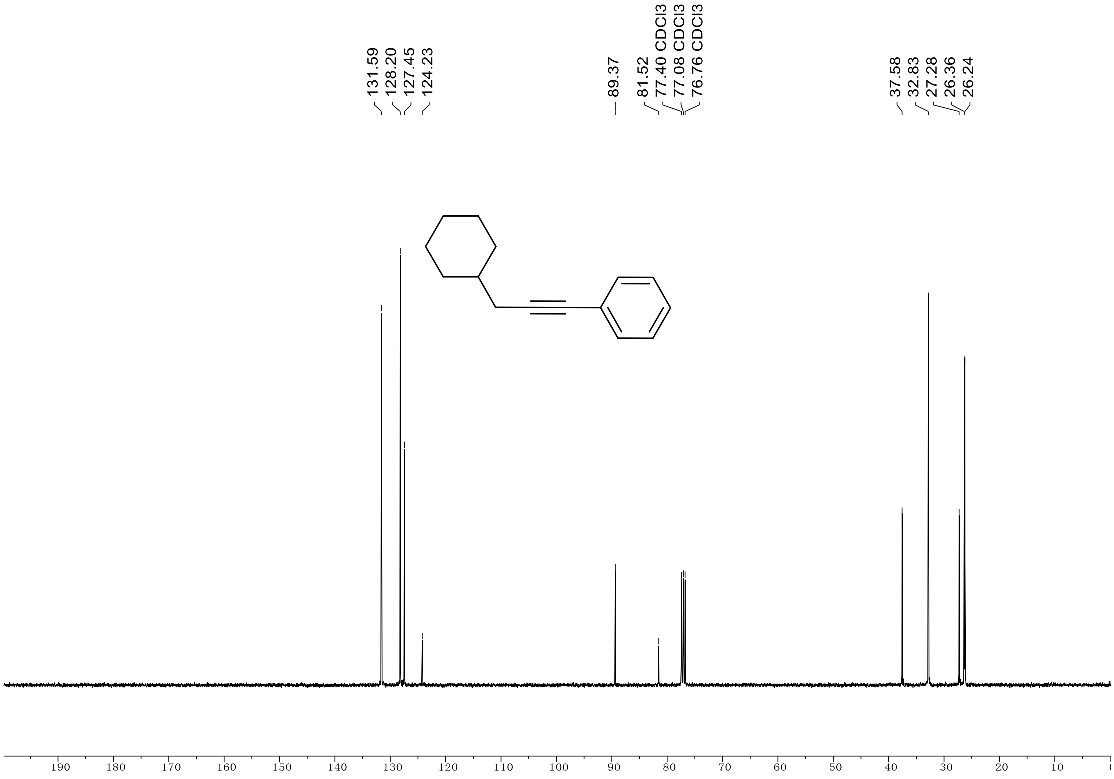


$^{13}$C NMR (101 MHz, CDCl$_3$) of **3b**

# (3-cyclohexylprop-1-yn-1-yl)benzene (3c)

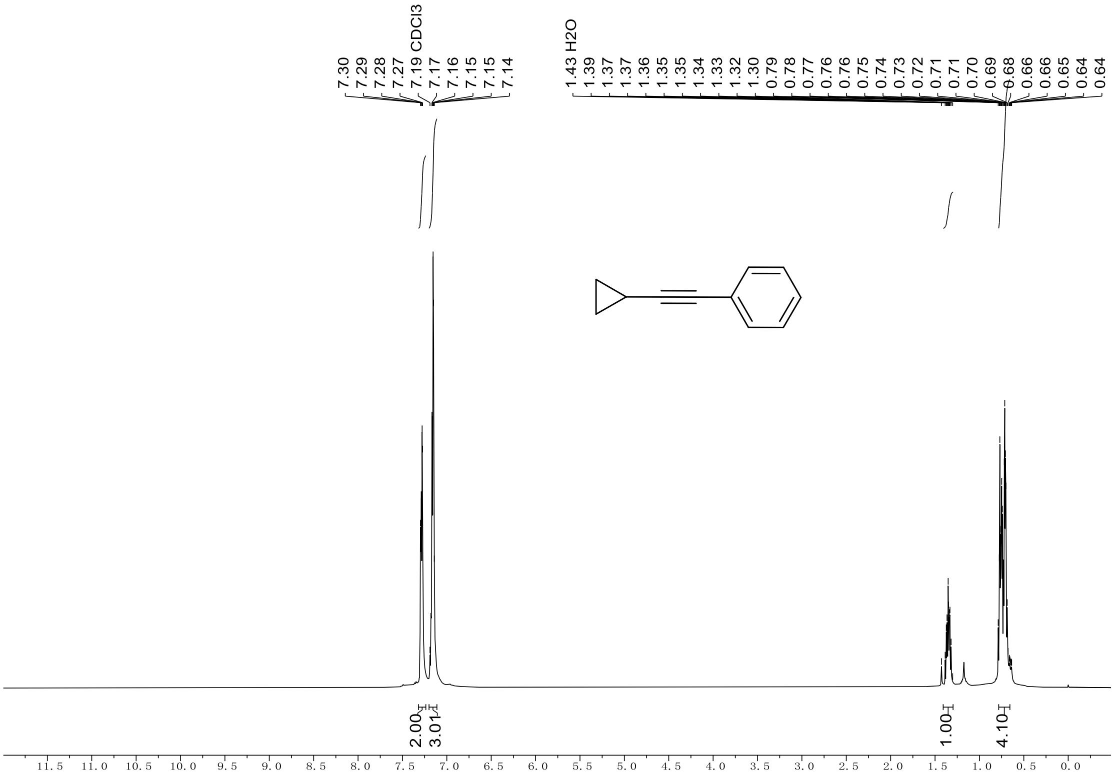


$^1$H NMR (400 MHz, $CDCl_3$) of **3c**

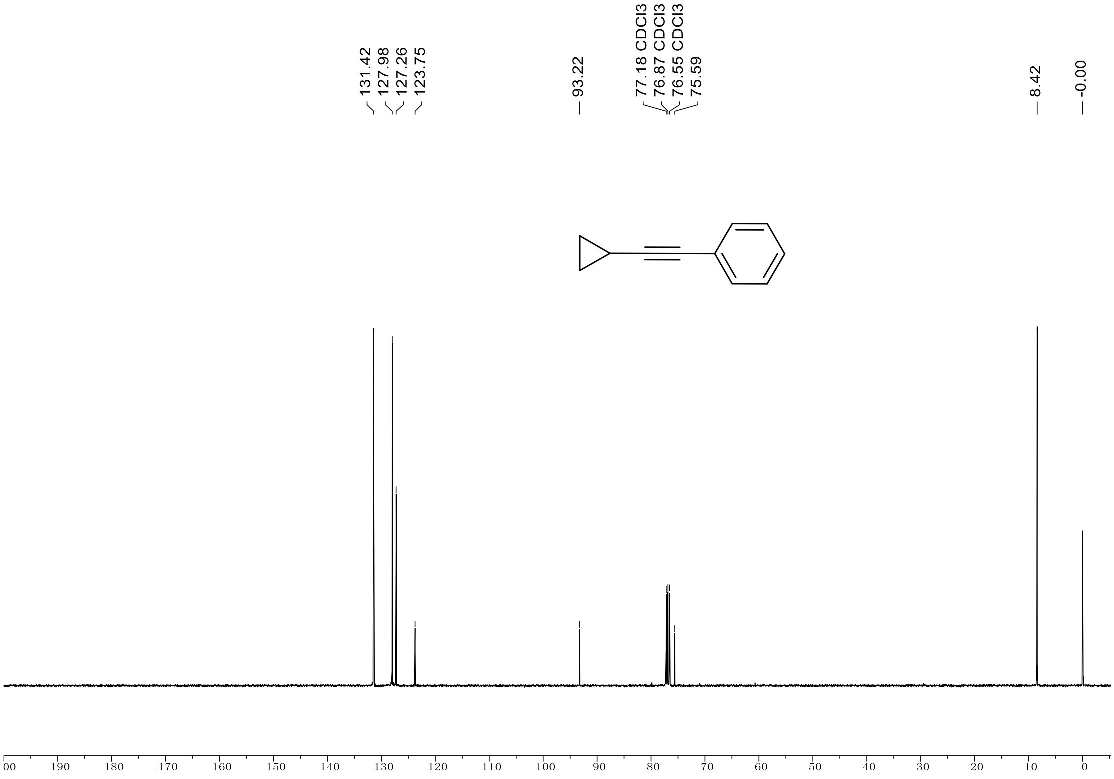


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3c**

# (cyclopropylethynyl)benzene (3d)

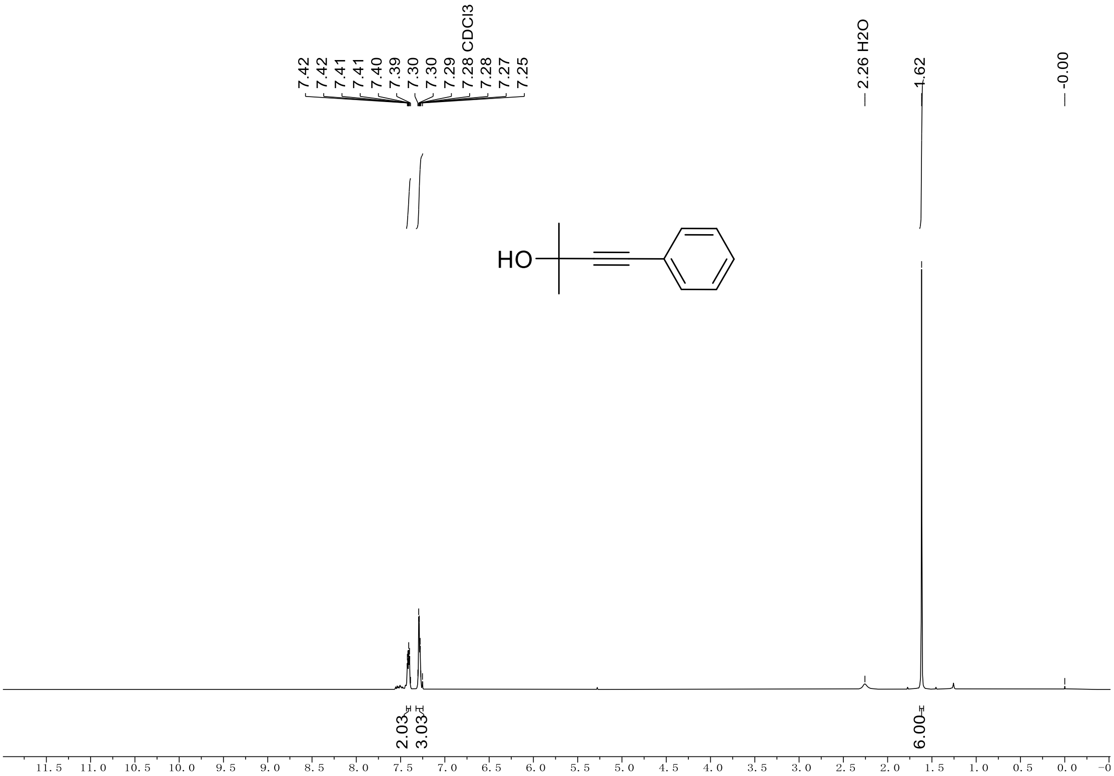


$^{1}$H NMR (400 MHz, $CDCl_3$) of **3d**

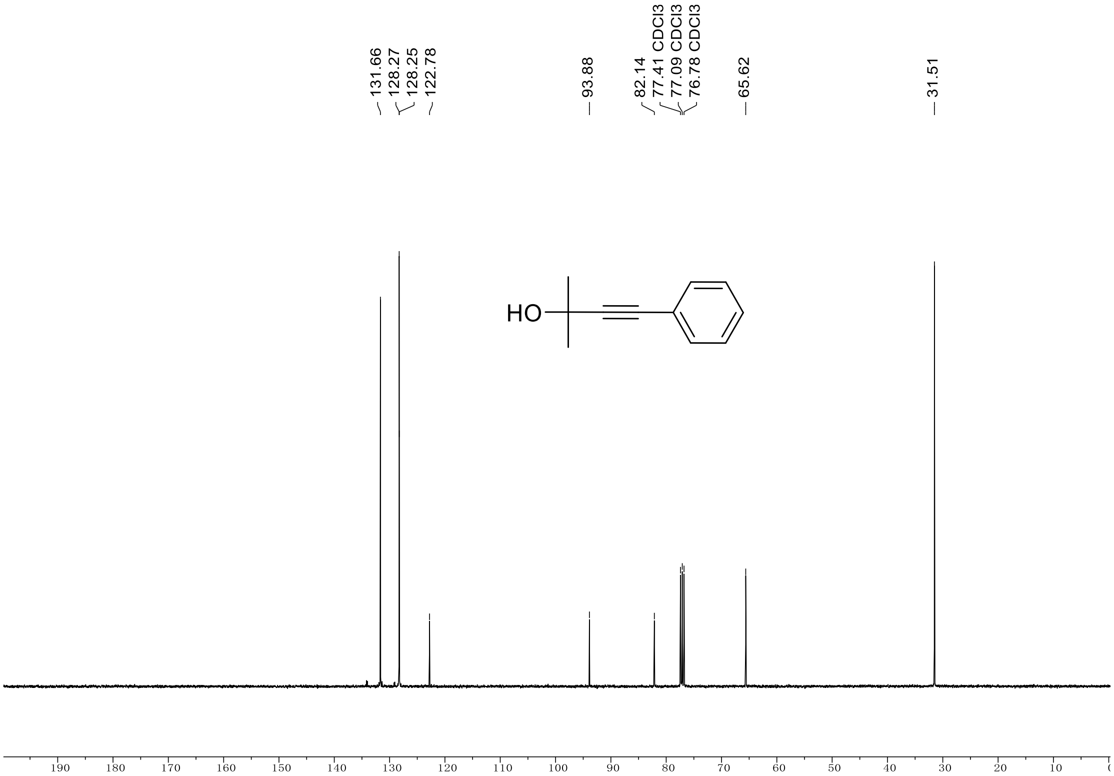


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3d**

# 2-methyl-4-phenylbut-3-yn-2-ol (3e)

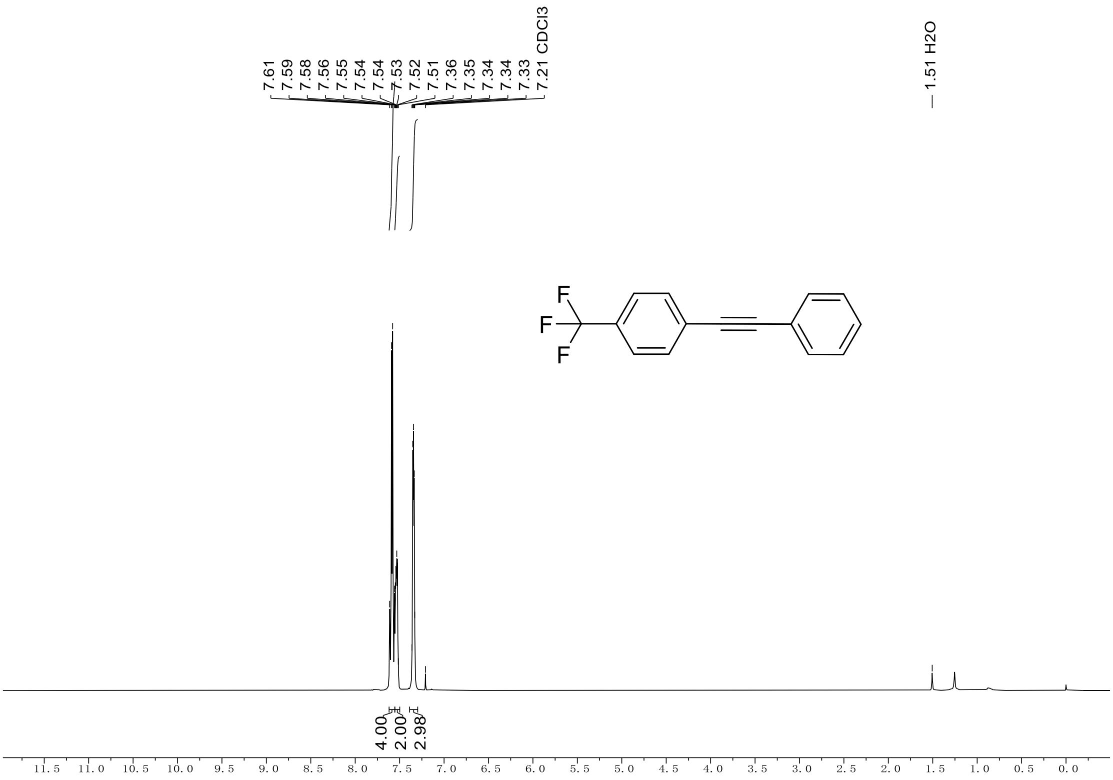


$^1$H NMR (400 MHz, $CDCl_3$) of **3e**

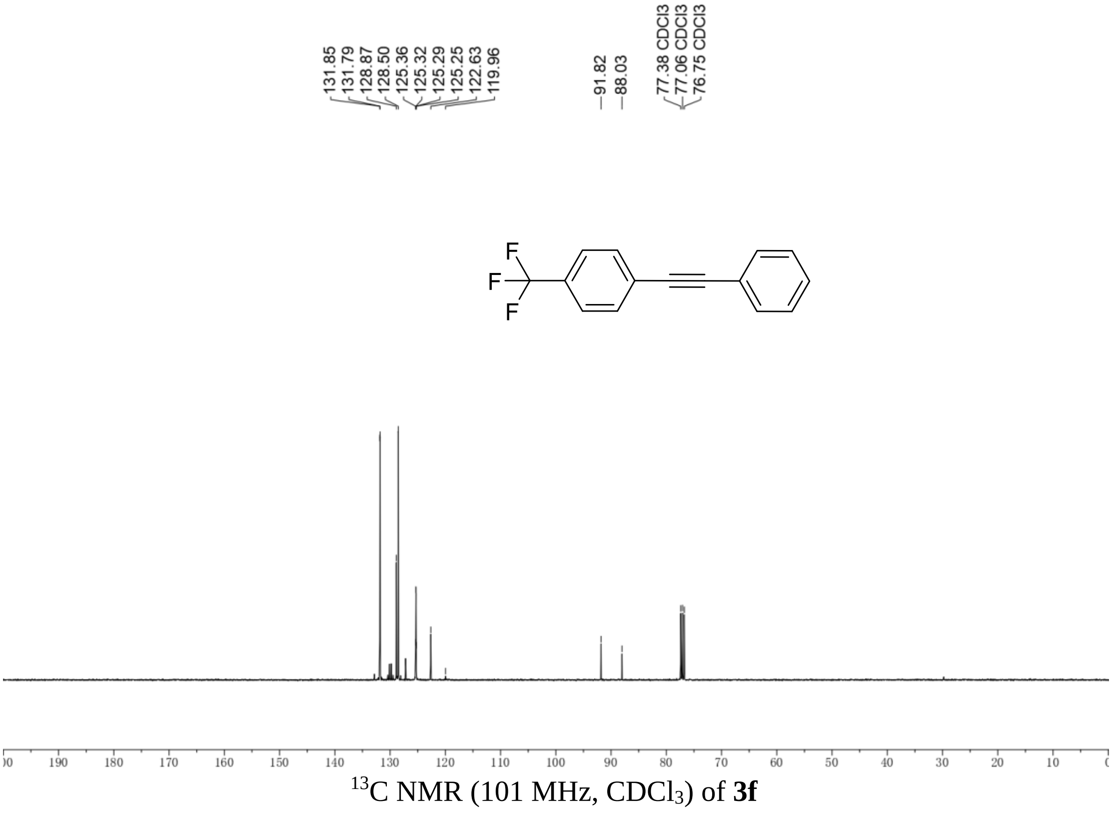


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3e**

# 1-(phenylethynyl)-4-(trifluoromethyl)benzene (3f)

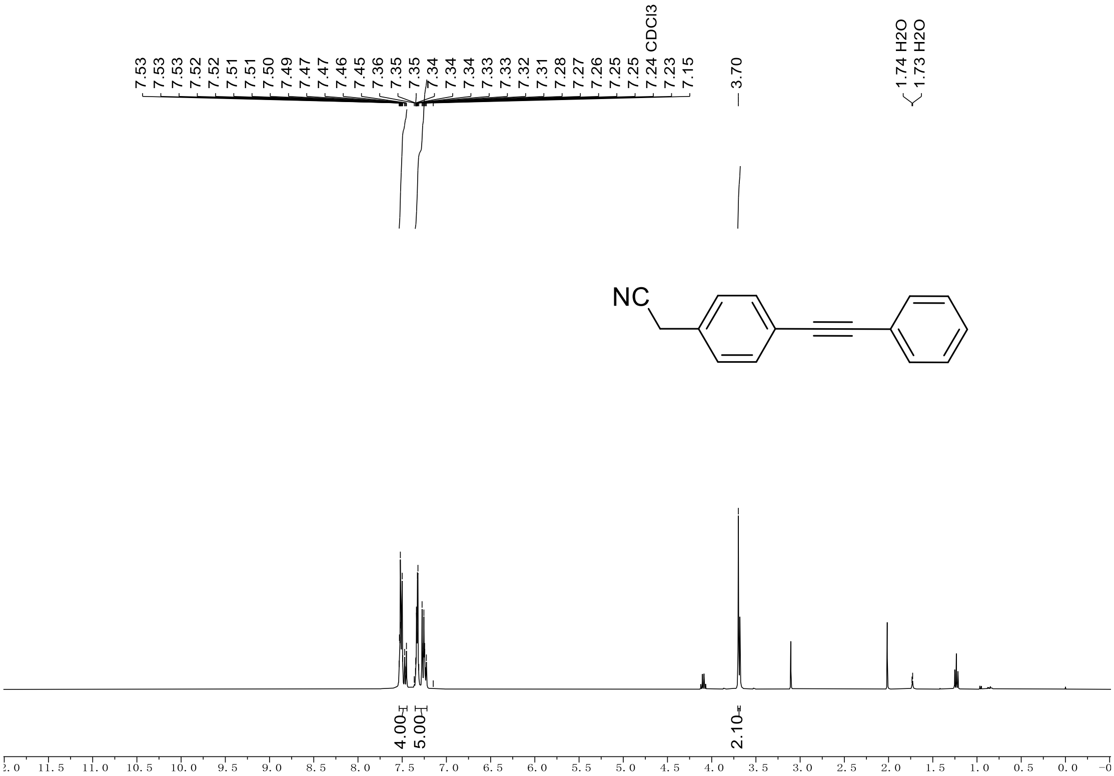


$^1$H NMR (400 MHz, CDCl$_3$) of **3f**

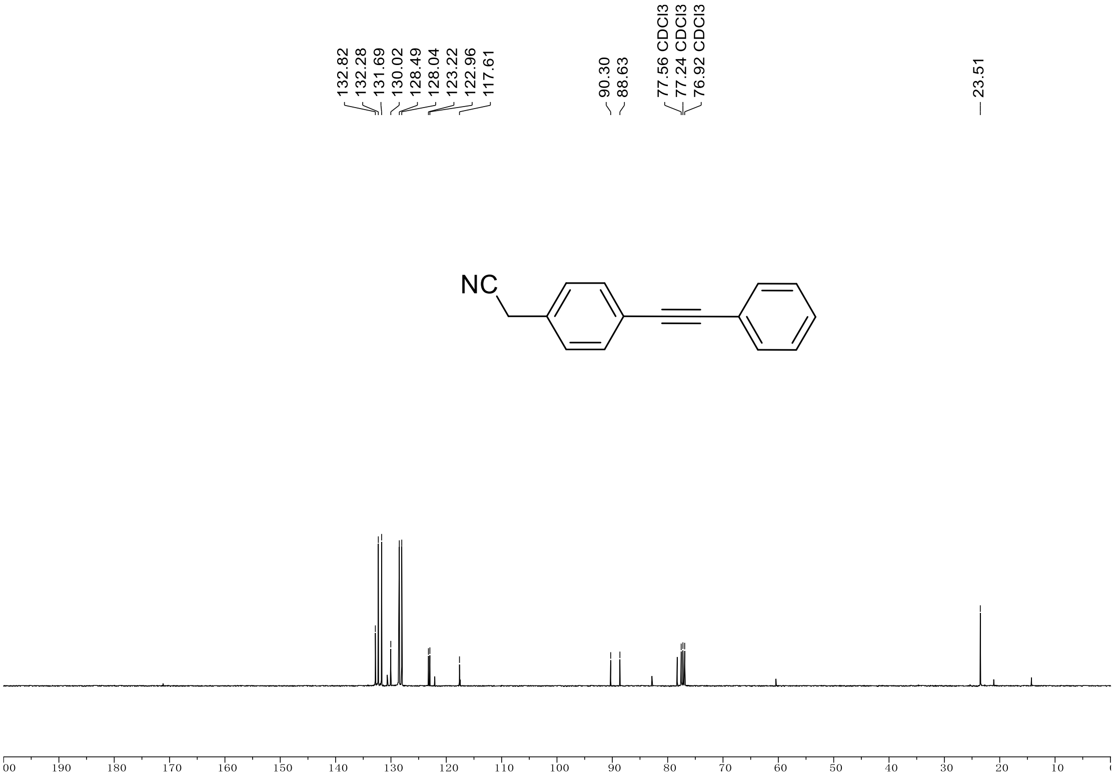


$^{13}$C NMR (101 MHz, CDCl$_3$) of **3f**

# 2-(4-(phenylethynyl)phenyl)acetonitrile (3g)

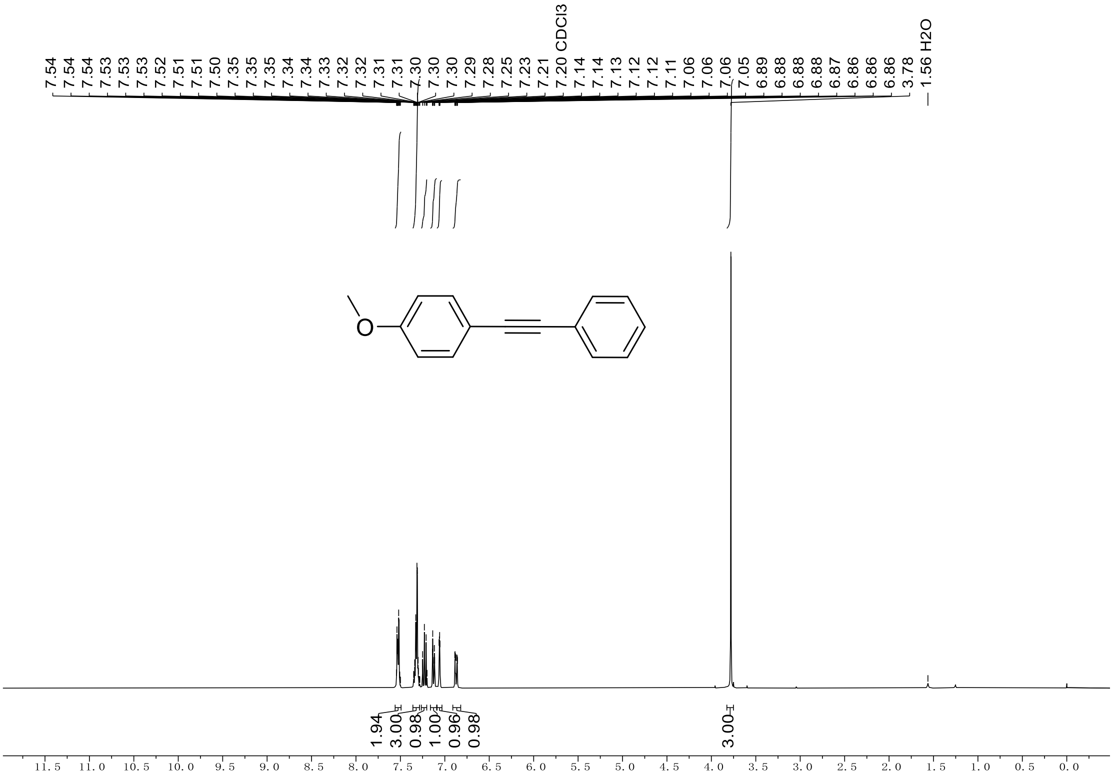


$^1$H NMR (400 MHz, $CDCl_3$) of **3g**

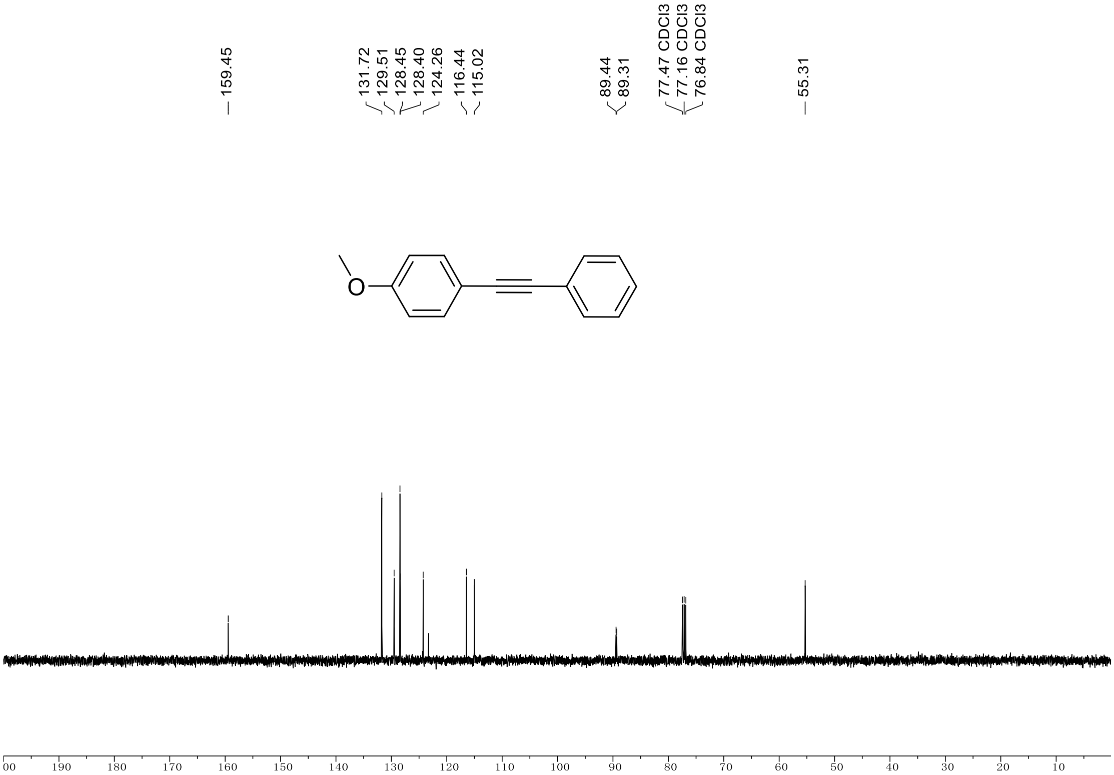


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3g**

# 1-methoxy-4-(phenylethynyl)benzene (3h)

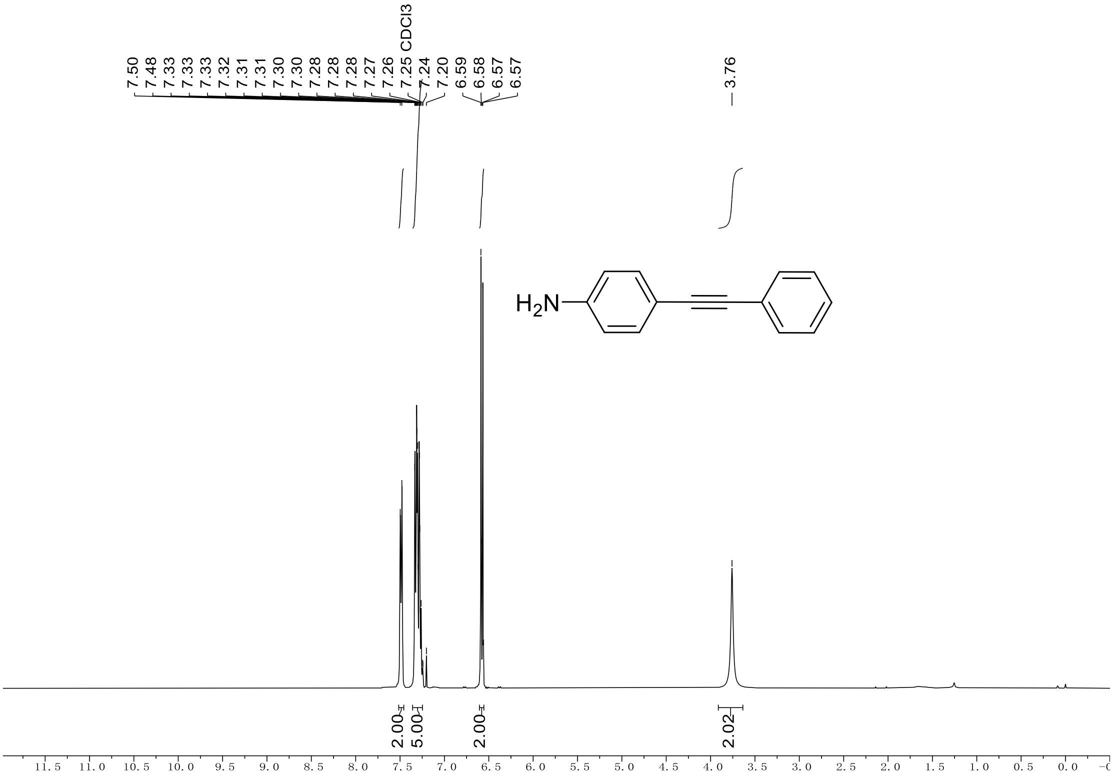


$^1$H NMR (400 MHz, $CDCl_3$) of **3h**

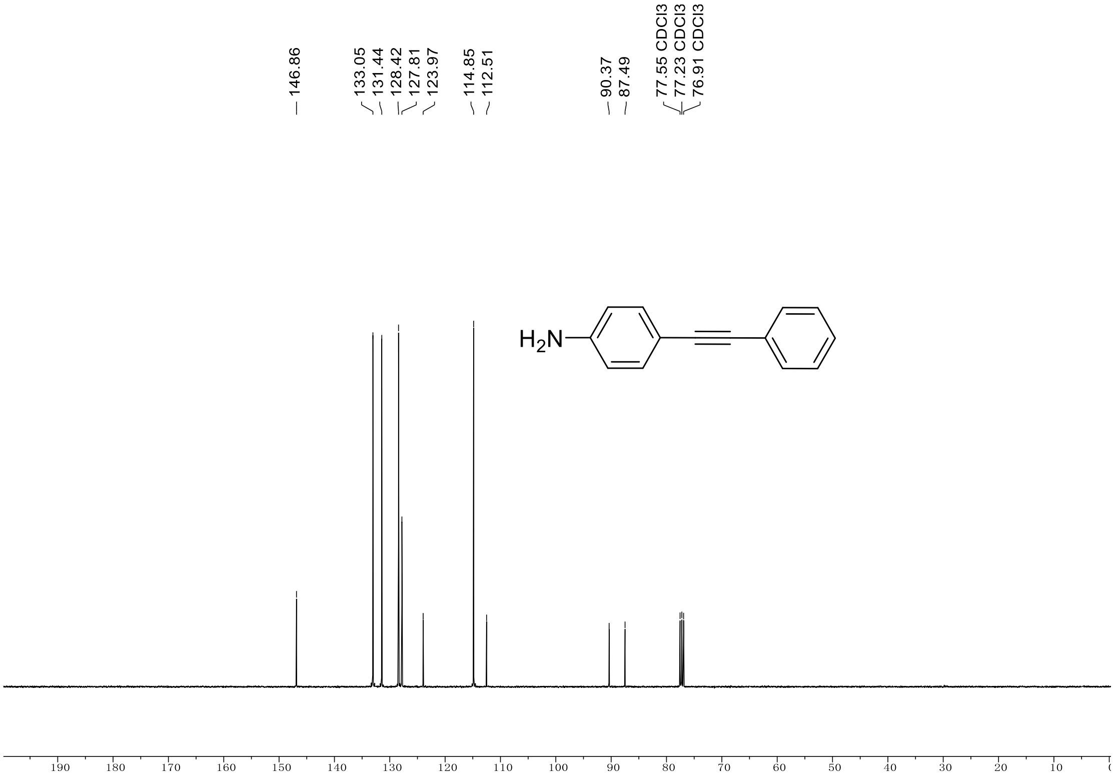


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3h**

# 4-(phenylethynyl)aniline (3i)

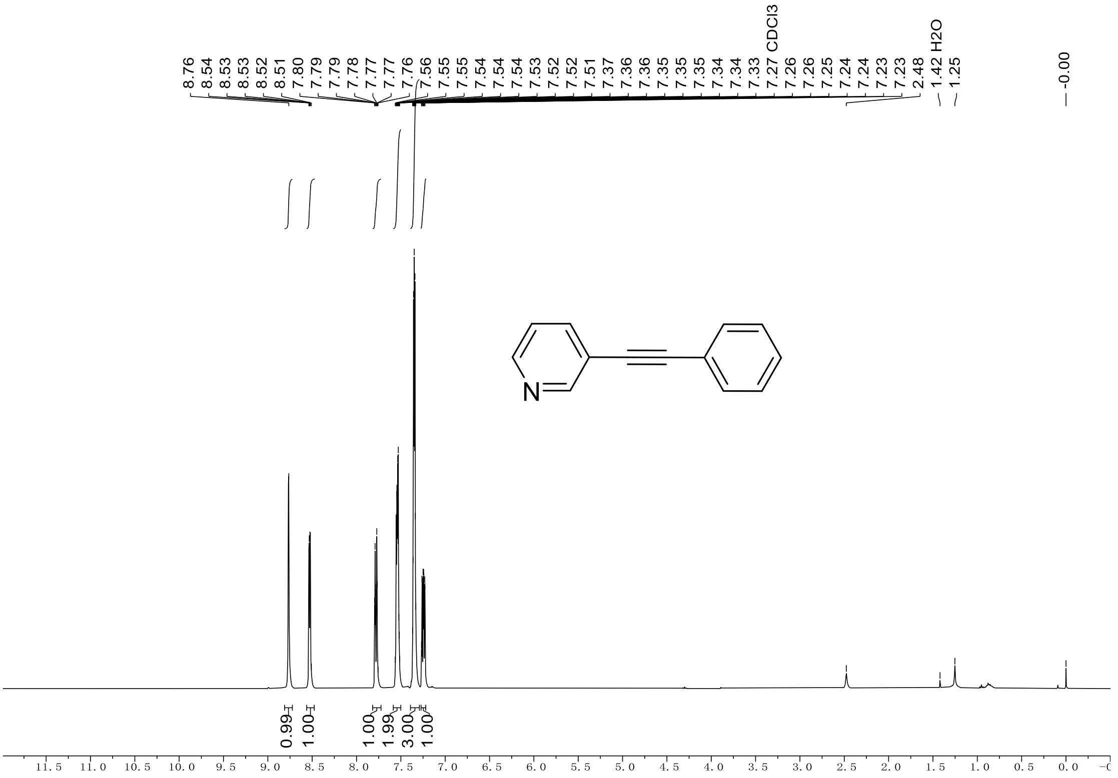


$^1$H NMR (400 MHz, CDCl$_3$) of **3i**

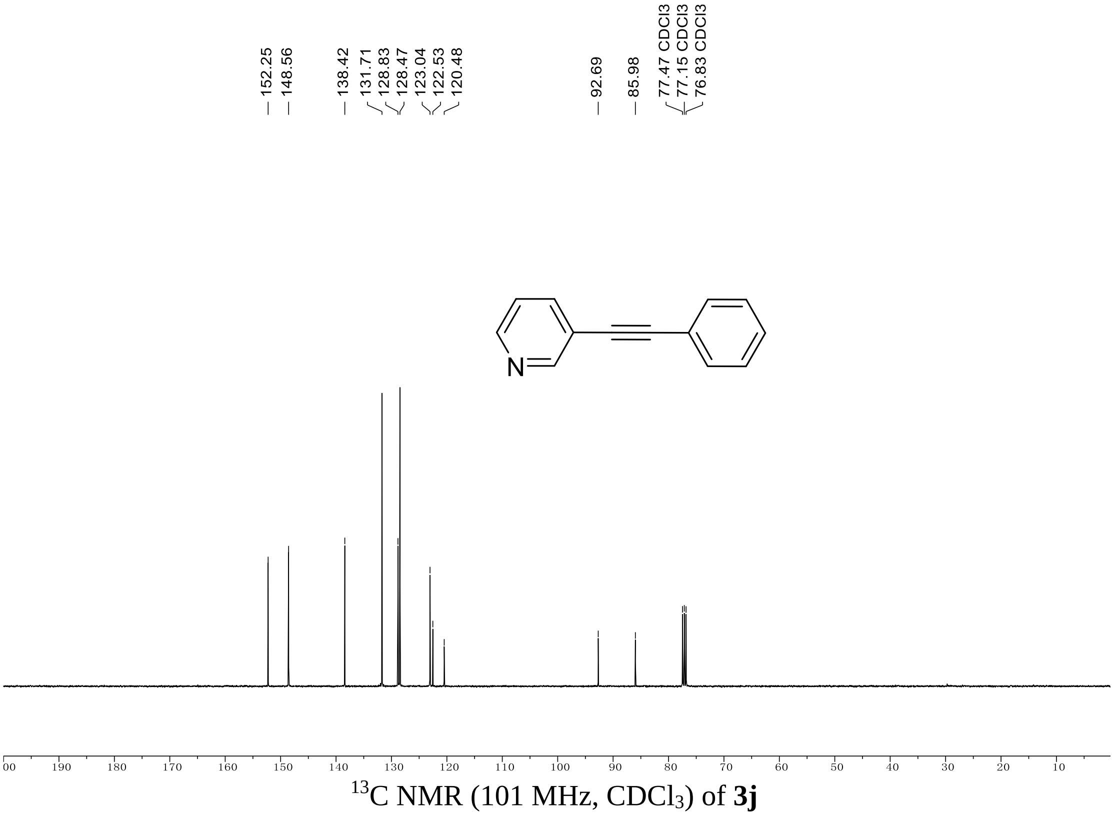


$^{13}$C NMR (101 MHz, CDCl$_3$) of **3i**

# 3-(phenylethynyl)pyridine (3j)



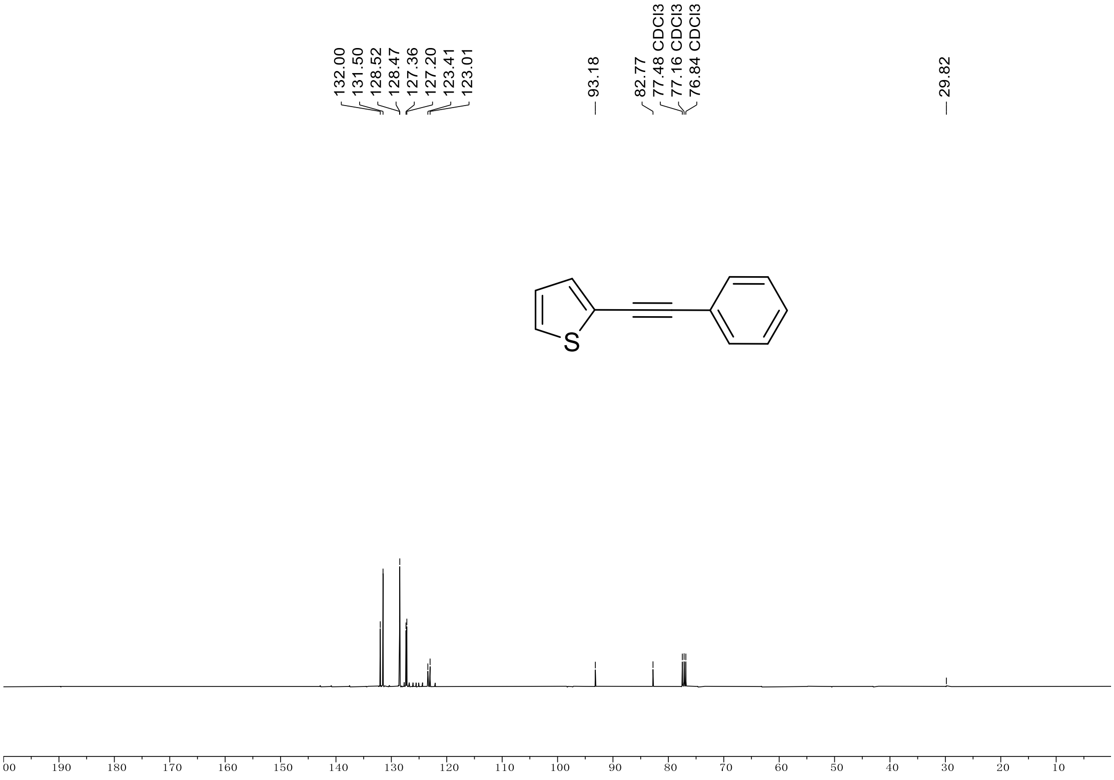
$^1$H NMR (400 MHz, CDCl$_3$) of **3j**



$^{13}$C NMR (101 MHz, CDCl$_3$) of **3j**

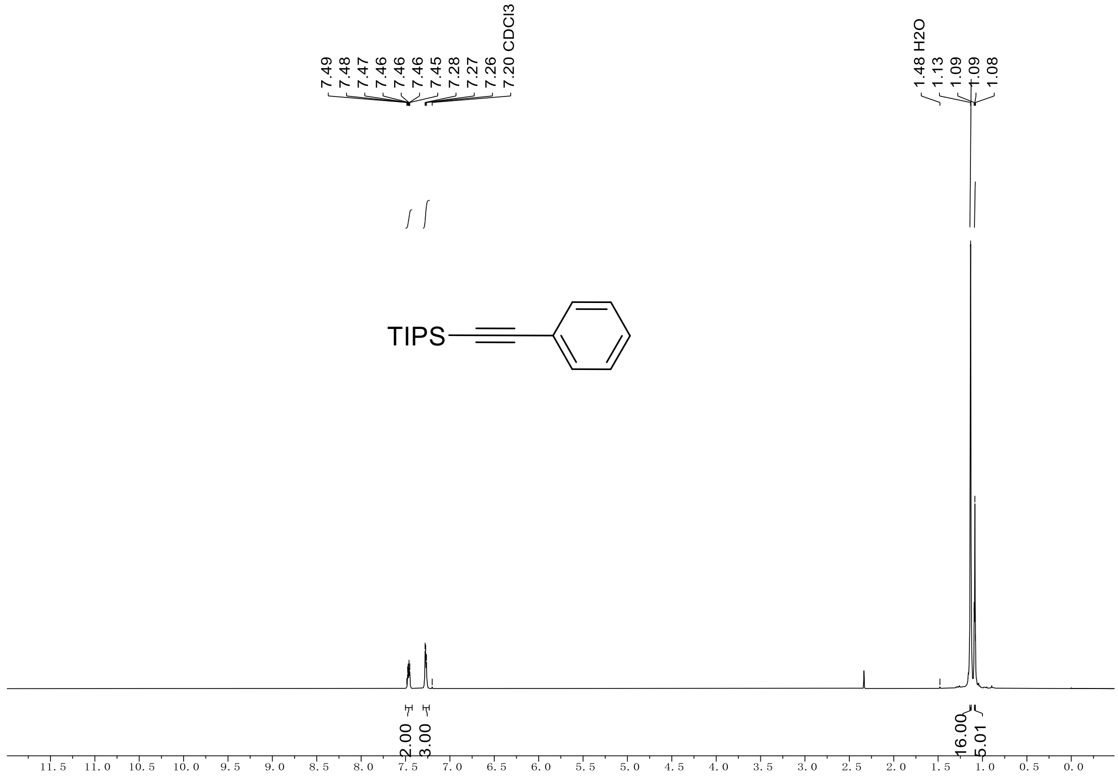
## 2-(phenylethynyl)thiophene (3k)

$^1$H NMR (400 MHz, $CDCl_3$) of **3k**

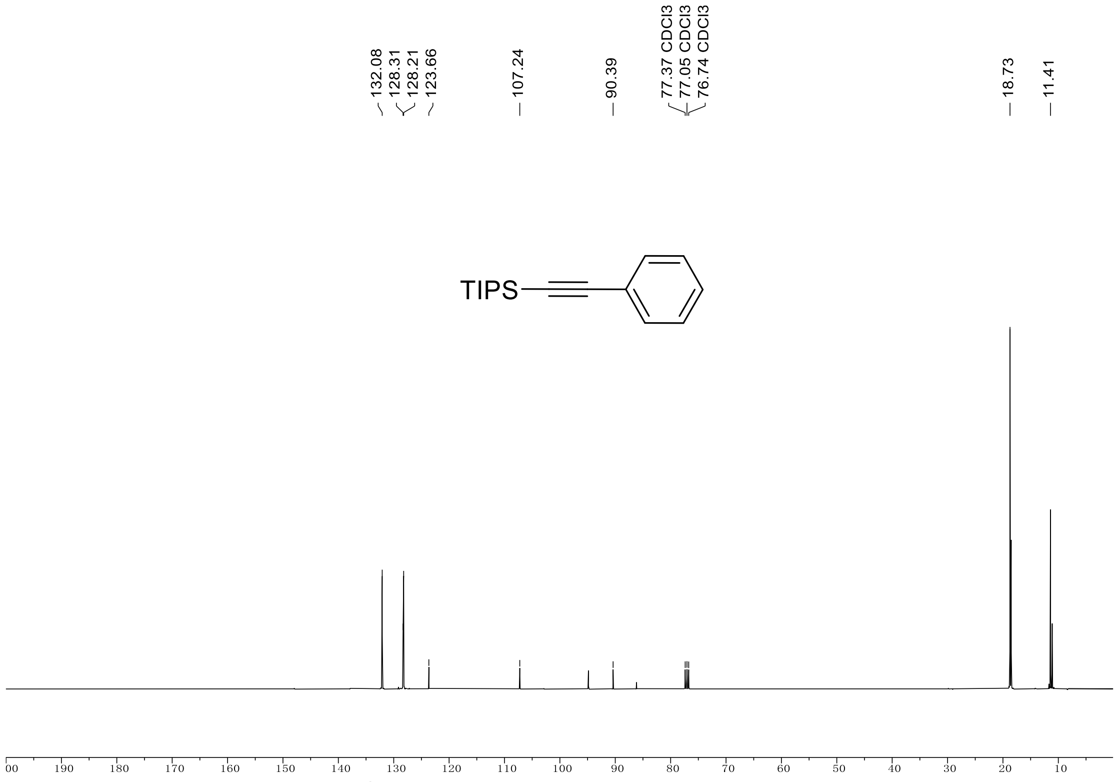


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3k**

# Triisopropyl(phenylethynyl)silane (3l)

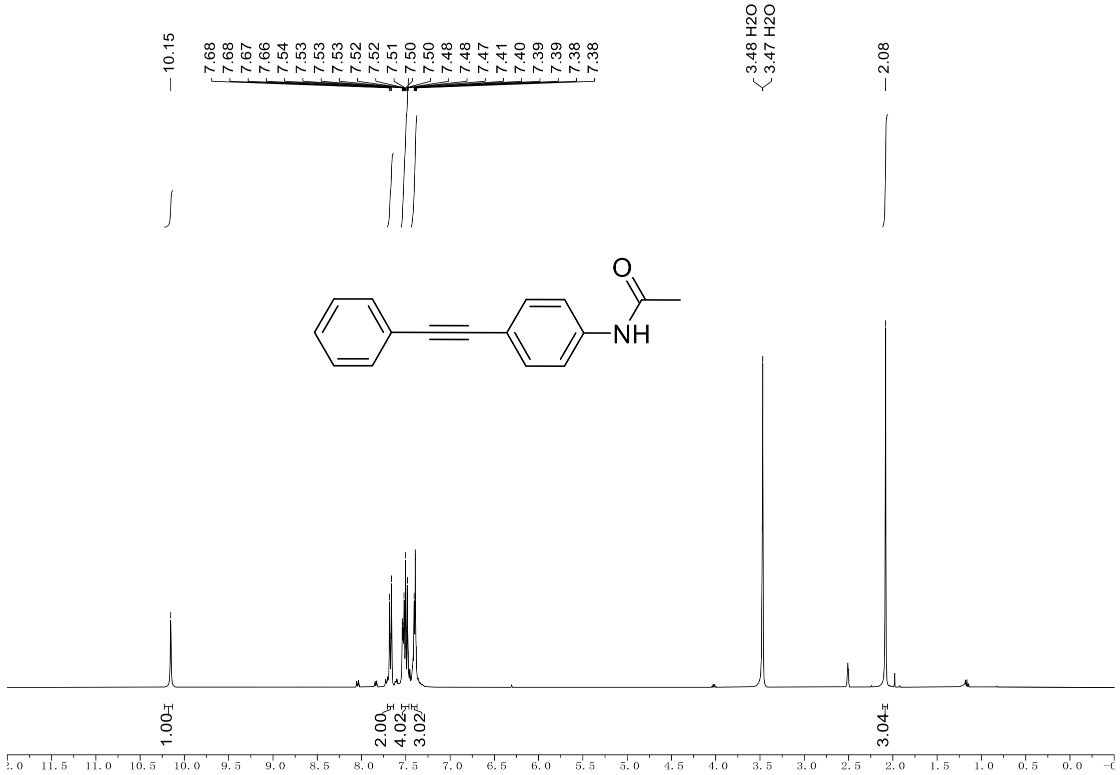


$^1$H NMR (400 MHz, $CDCl_3$) of **3l**

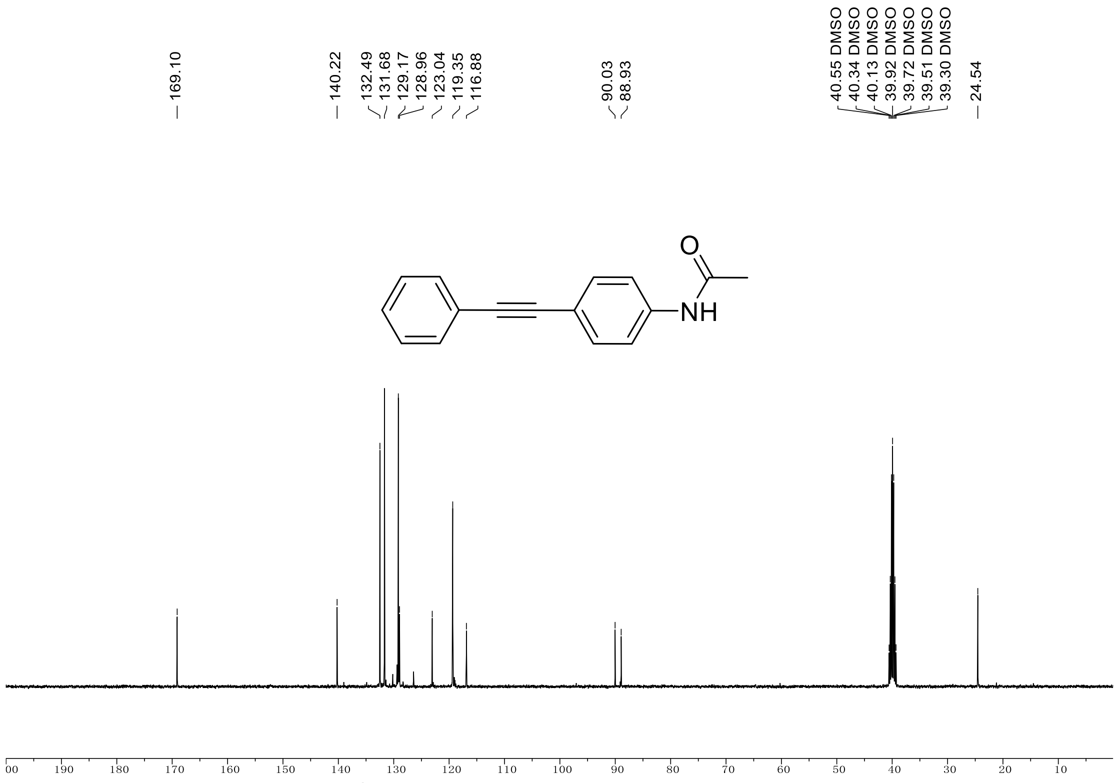


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3l**

# N-(4-(phenylethynyl)phenyl)acetamide (3n)

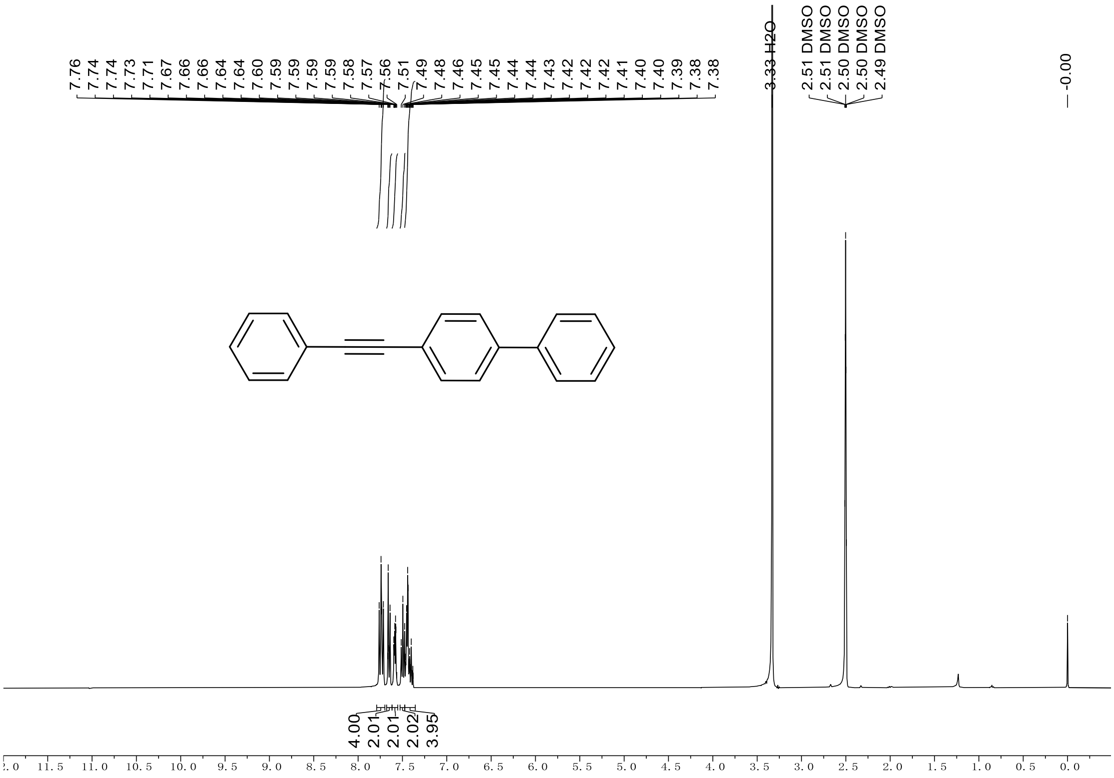


$^{1}$H NMR (400 MHz, DMSO) of **3n**

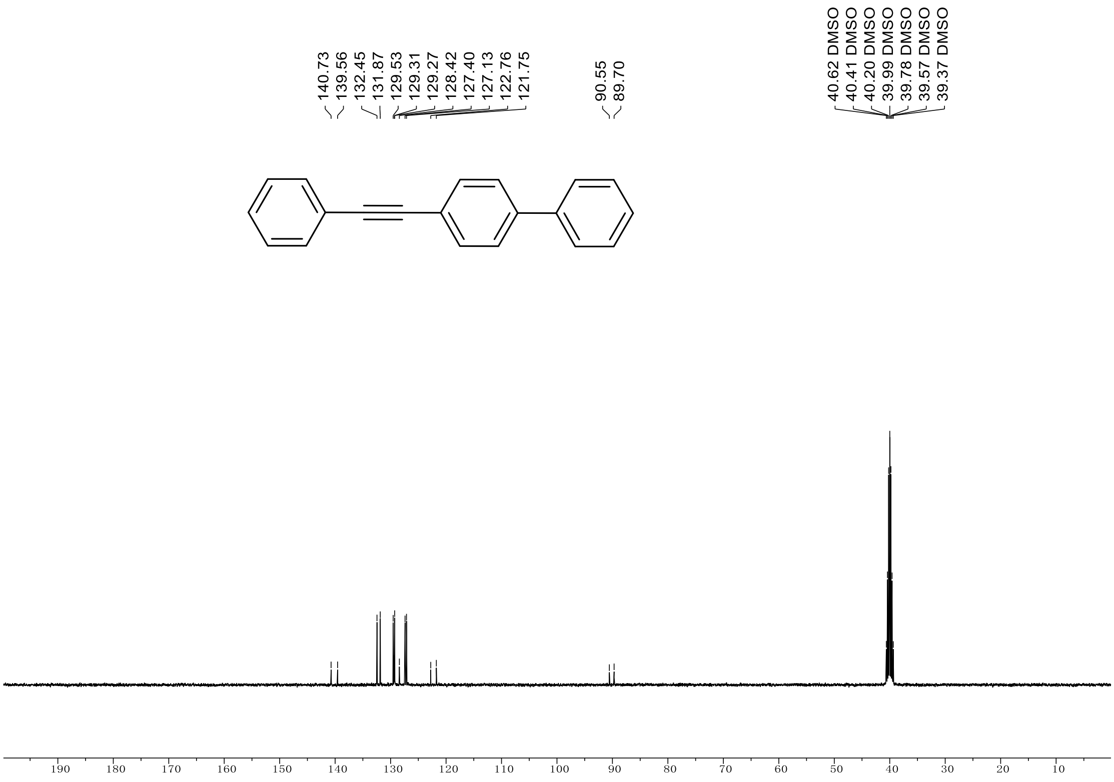


$^{13}$C NMR (101 MHz, DMSO) of **3n**

**4-(phenylethynyl)-1,1'-biphenyl (3o)**

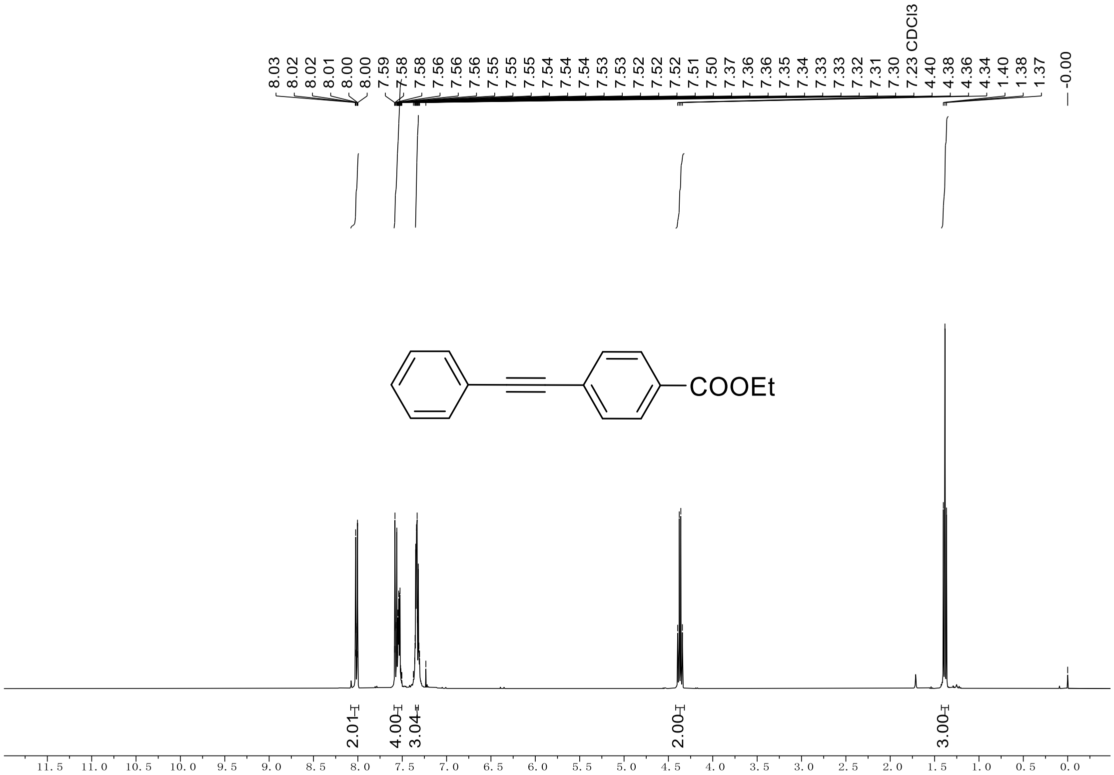


$^{1}$H NMR (400 MHz, DMSO) of **3o**

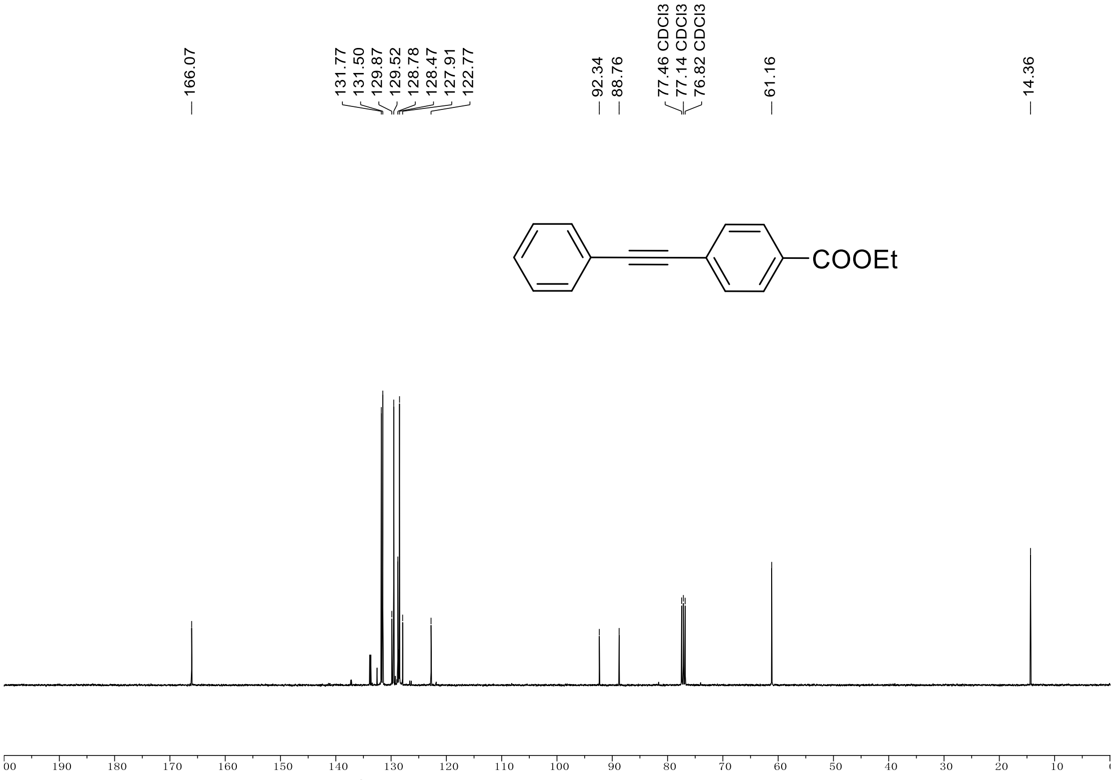


$^{13}$C NMR (101 MHz, DMSO) of **3o**

# Ethyl 4-(phenylethynyl)benzoate (3p)

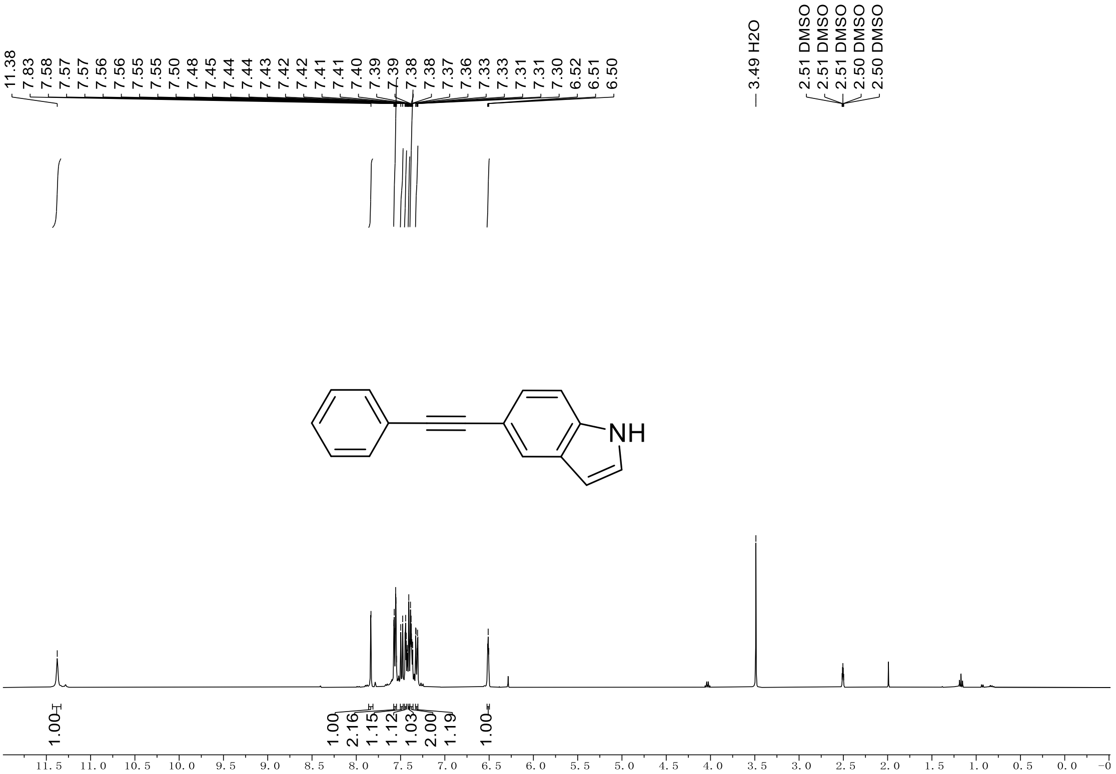


$^{1}$H NMR (400 MHz, CDCl$_3$) of **3p**

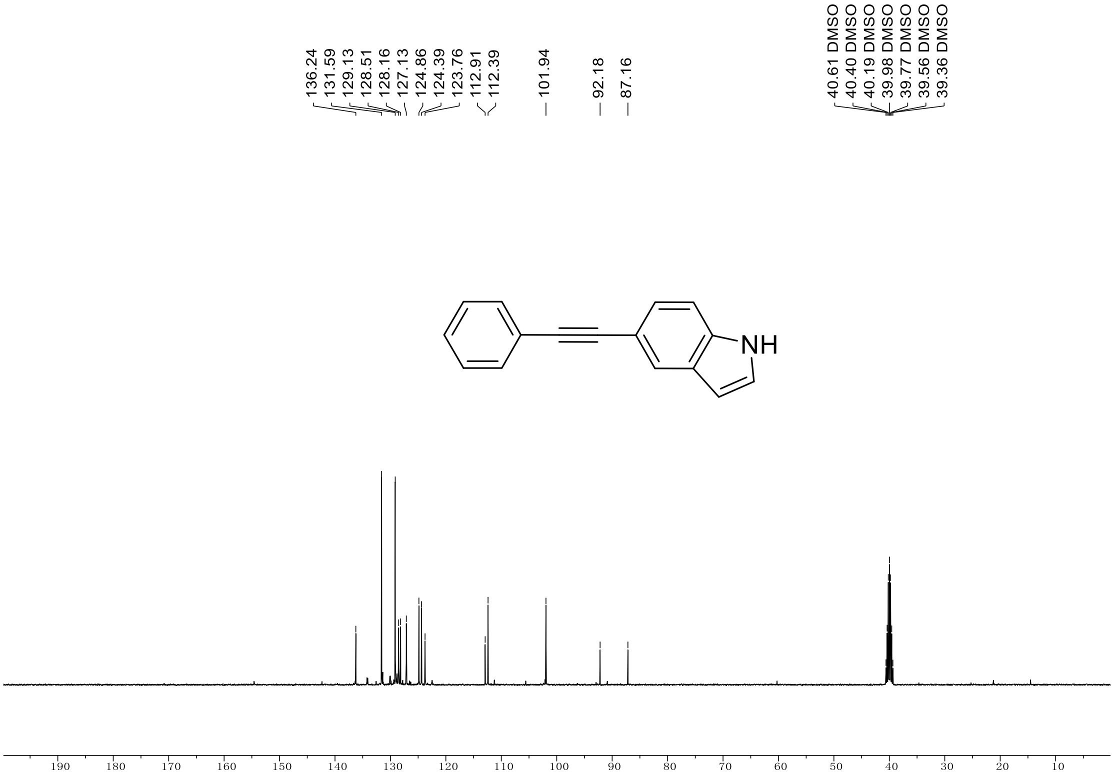


$^{13}$C NMR (101 MHz, CDCl$_3$) of **3p**

# 5-(phenylethynyl)-1H-indole (3q)

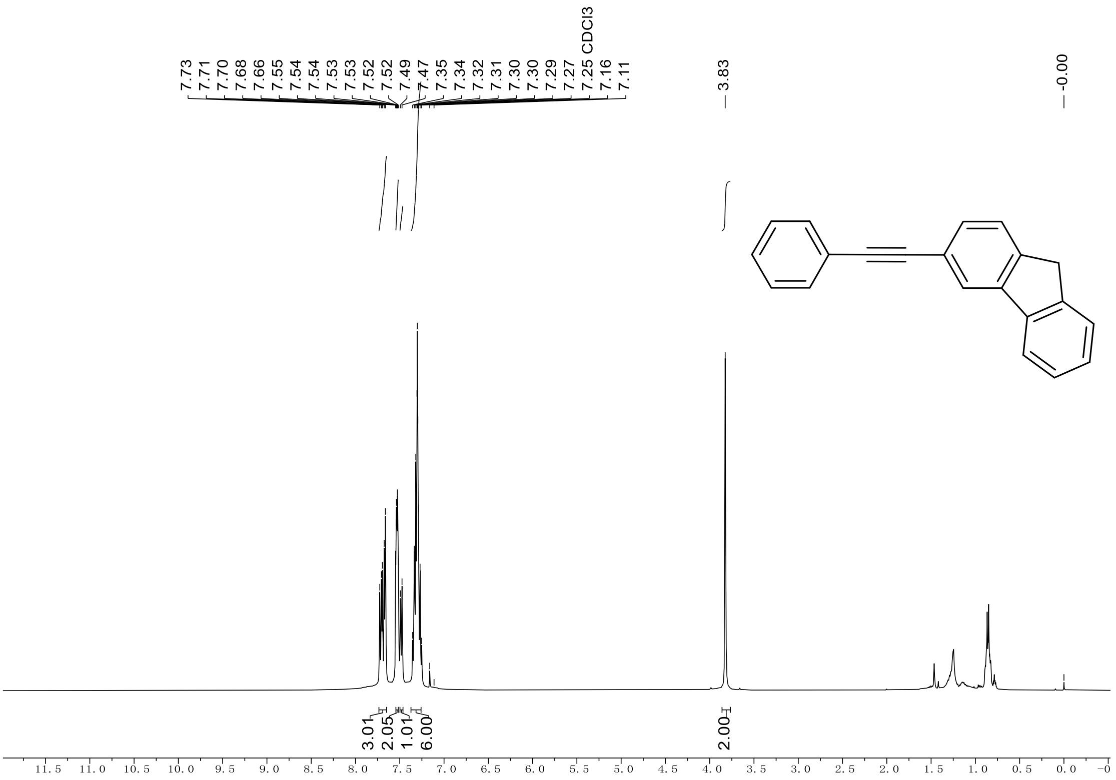


$^{1}$H NMR (400 MHz, DMSO) of **3q**

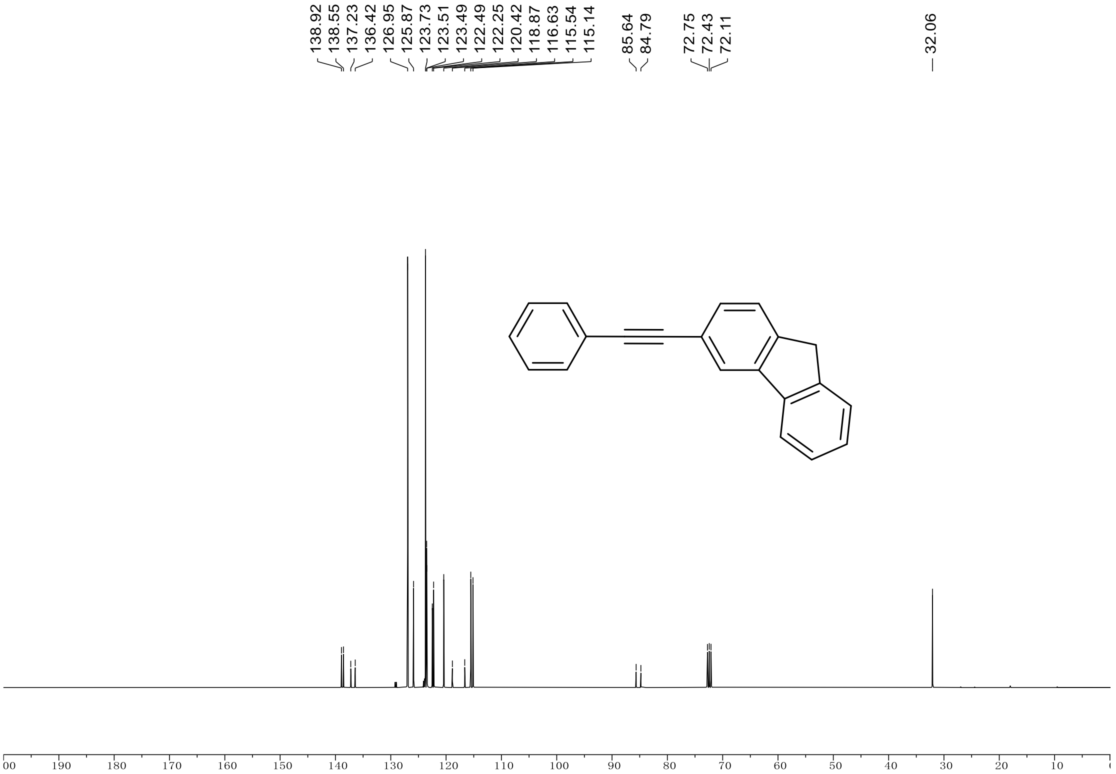


$^{13}$C NMR (101 MHz, DMSO) of **3q**

# 3-(phenylethynyl)-9H-fluorene (3r)

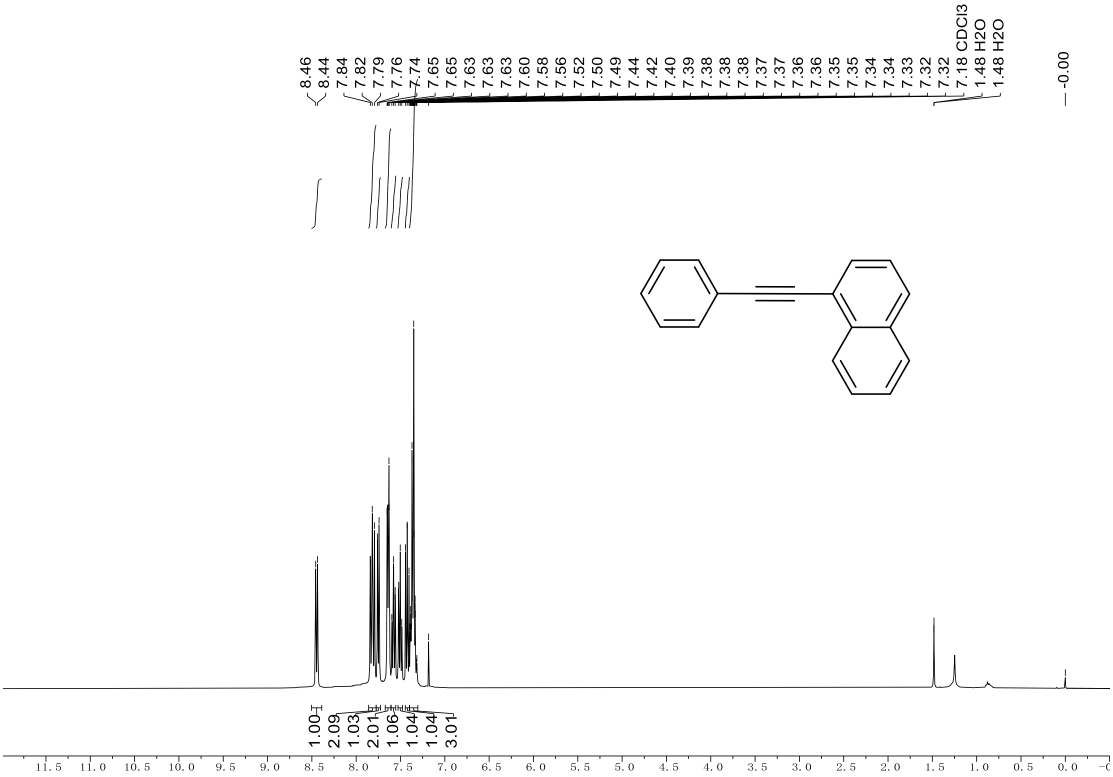


$^1$H NMR (400 MHz, $CDCl_3$) of **3r**

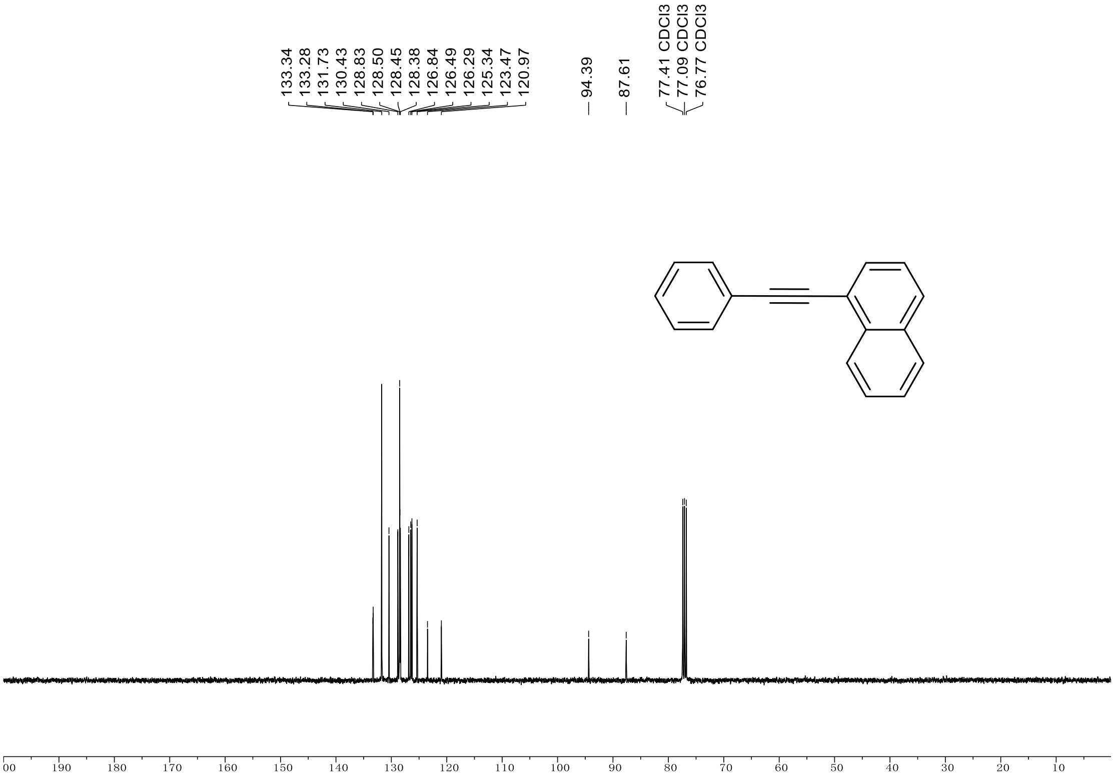


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3r**

# 1-(phenylethynyl)naphthalene (3s)

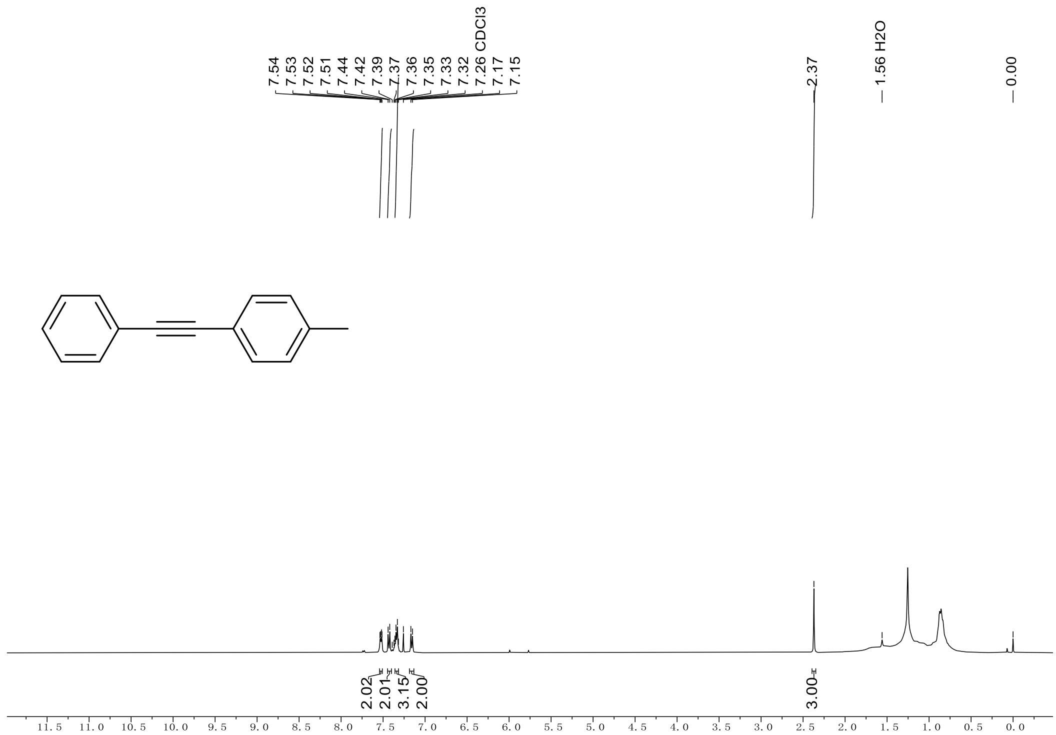


$^1$H NMR (400 MHz, $CDCl_3$) of **3s**

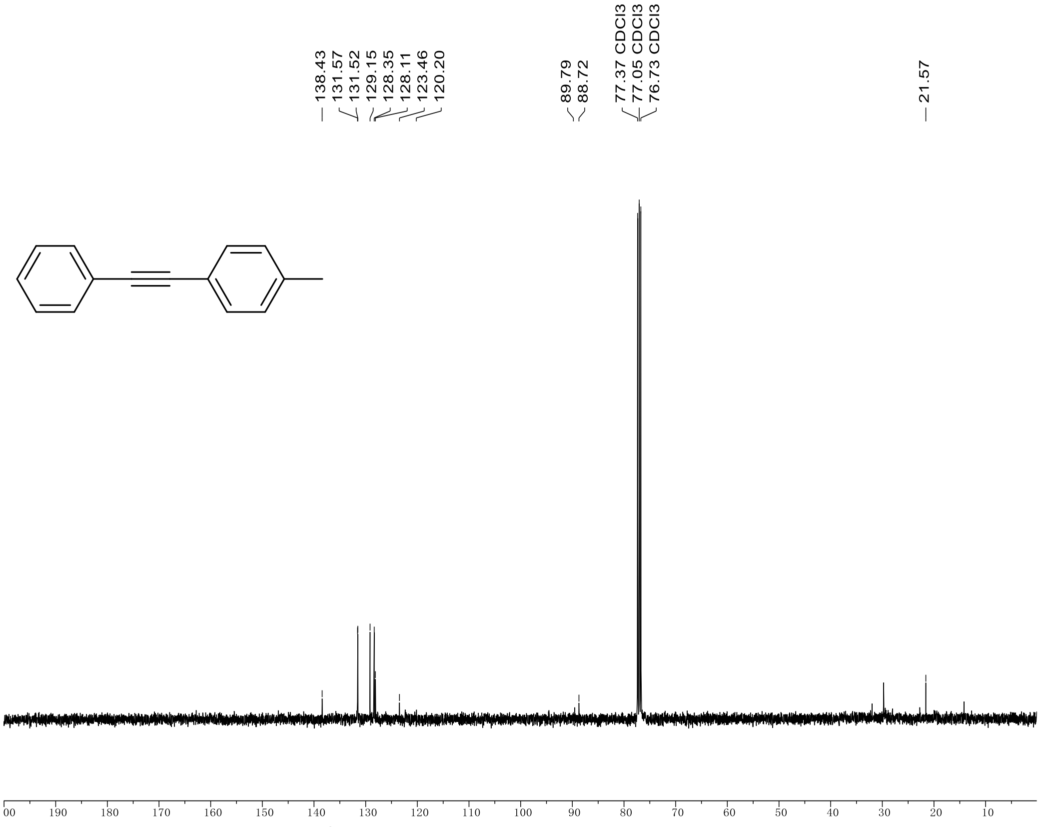


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3s**

# 1-methyl-4-(phenylethynyl)benzene (3t)



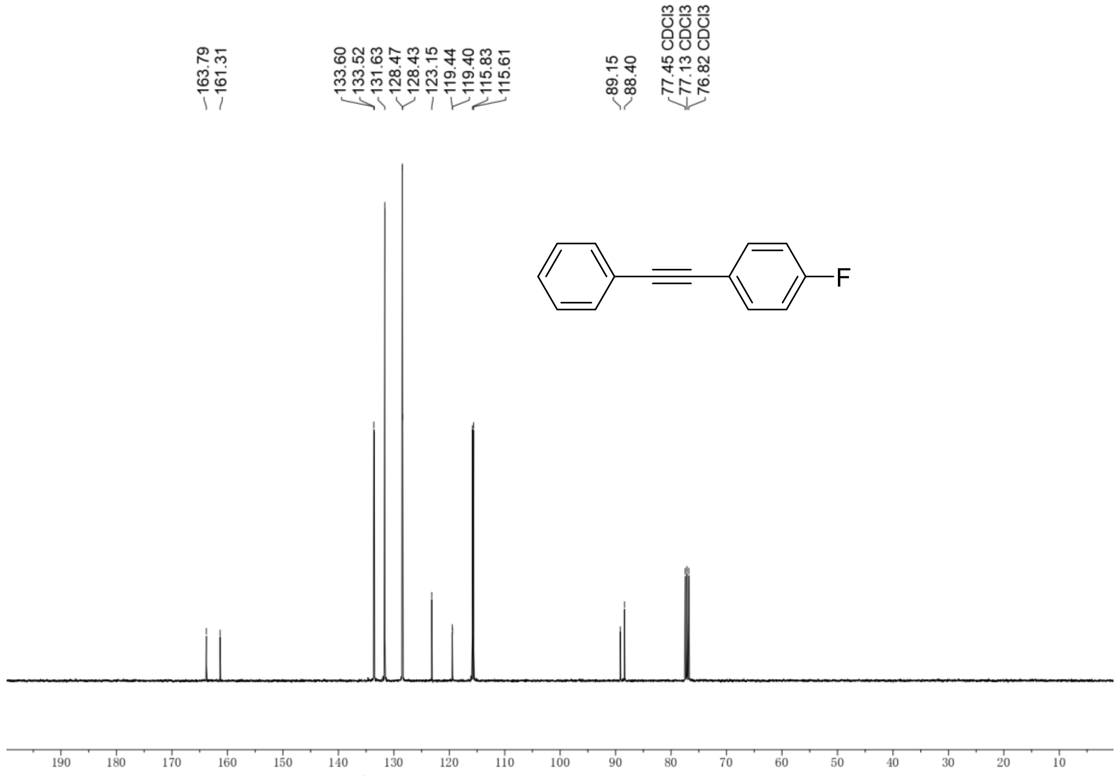
$^{1}$H NMR (400 MHz, CDCl$_3$) of **3t**



$^{13}$C NMR (101 MHz, CDCl$_3$) of **3t**

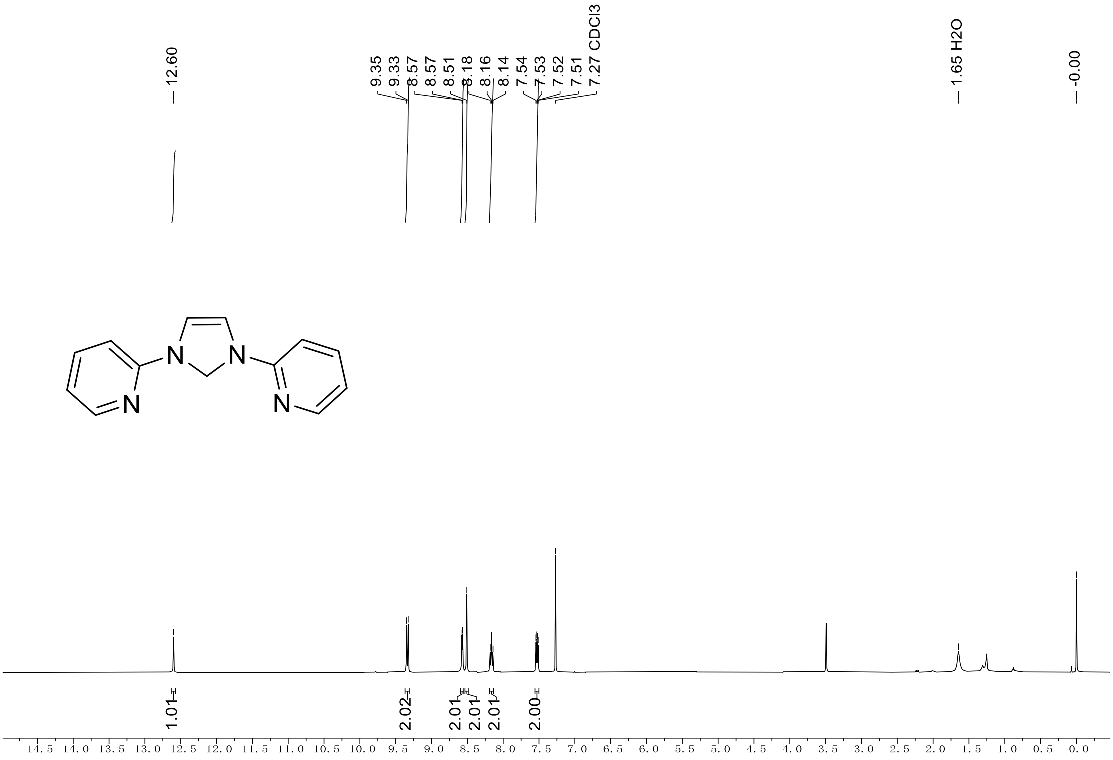
## 1-fluoro-4-(phenylethynyl)benzene (3u)

$^{1}$H NMR (400 MHz, $CDCl_3$) of **3u**

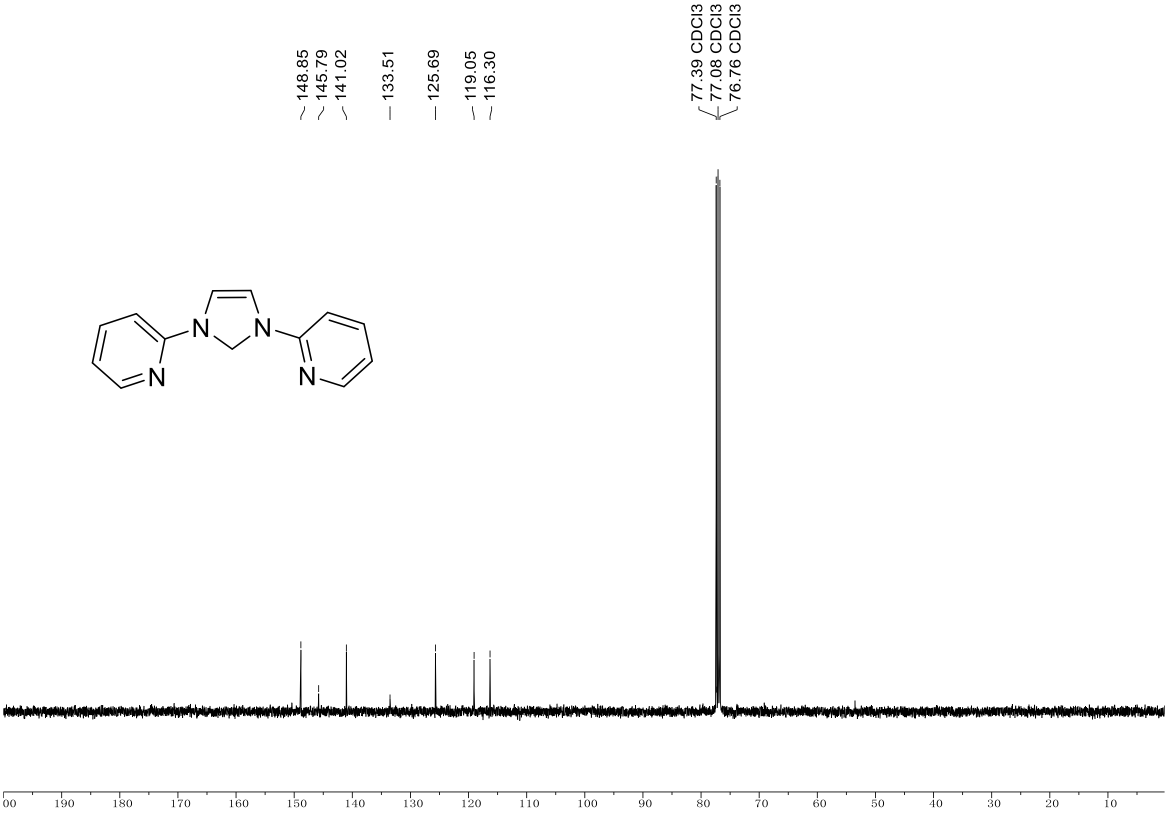


$^{13}$C NMR (101 MHz, $CDCl_3$) of **3u**

# 1,3-di(pyridin-2-yl)-2,3-dihydro-1H-imidazole (NHC-1)

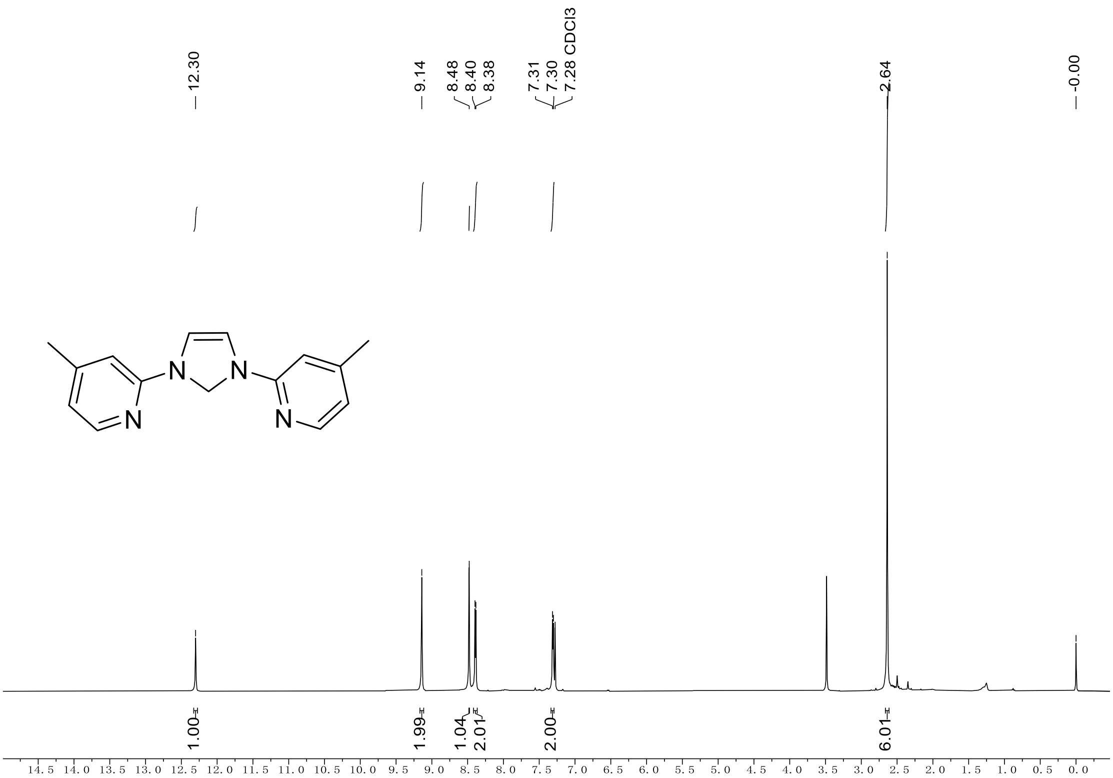


$^1$H NMR (400 MHz, $CDCl_3$) of **NHC-1**

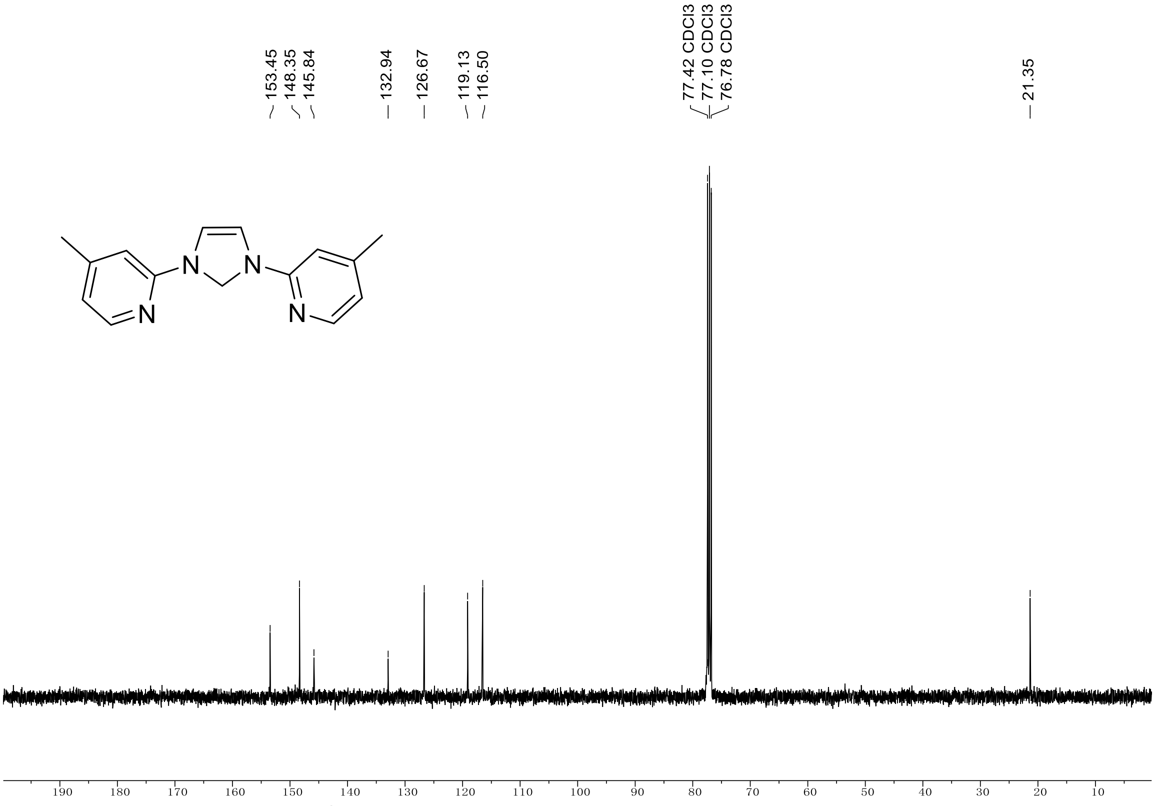


$^{13}$C NMR (101 MHz, $CDCl_3$) of **NHC-1**

## 1,3-bis(4-methylpyridin-2-yl)-2,3-dihydro-1H-imidazole (NHC-2)

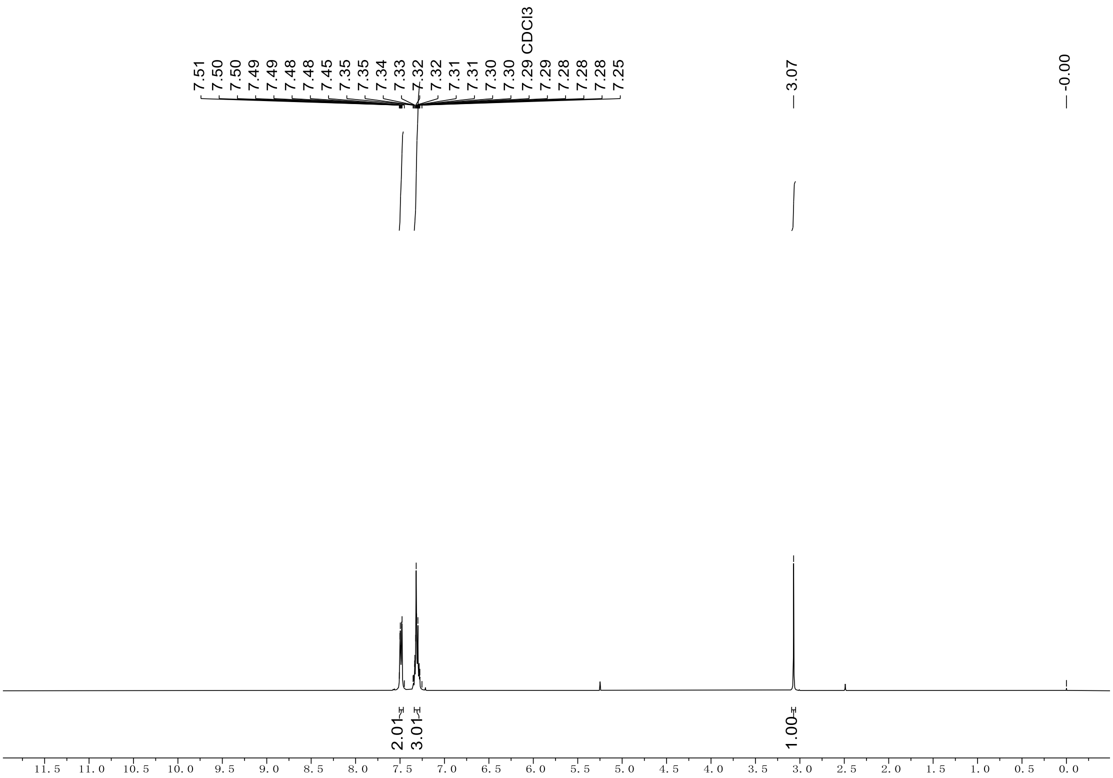


$^{1}$H NMR (400 MHz, CDCl$_3$) of **NHC-2**

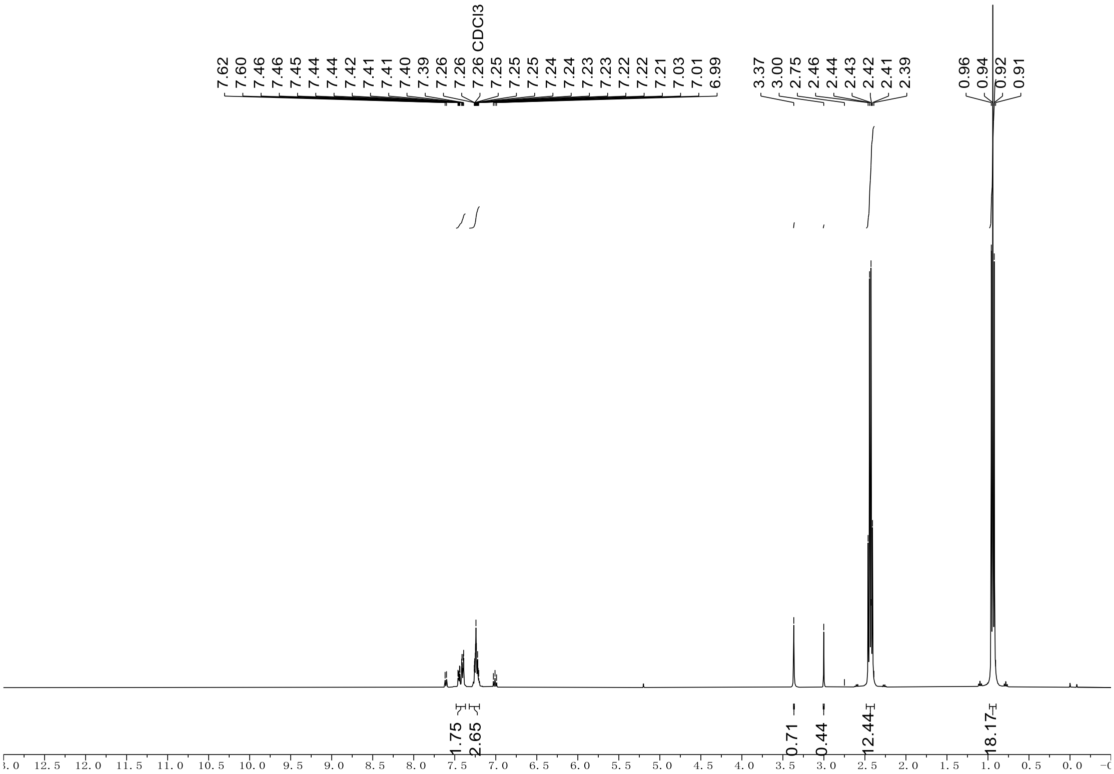


$^{13}$C NMR (101 MHz, CDCl$_3$) of **NHC-2**

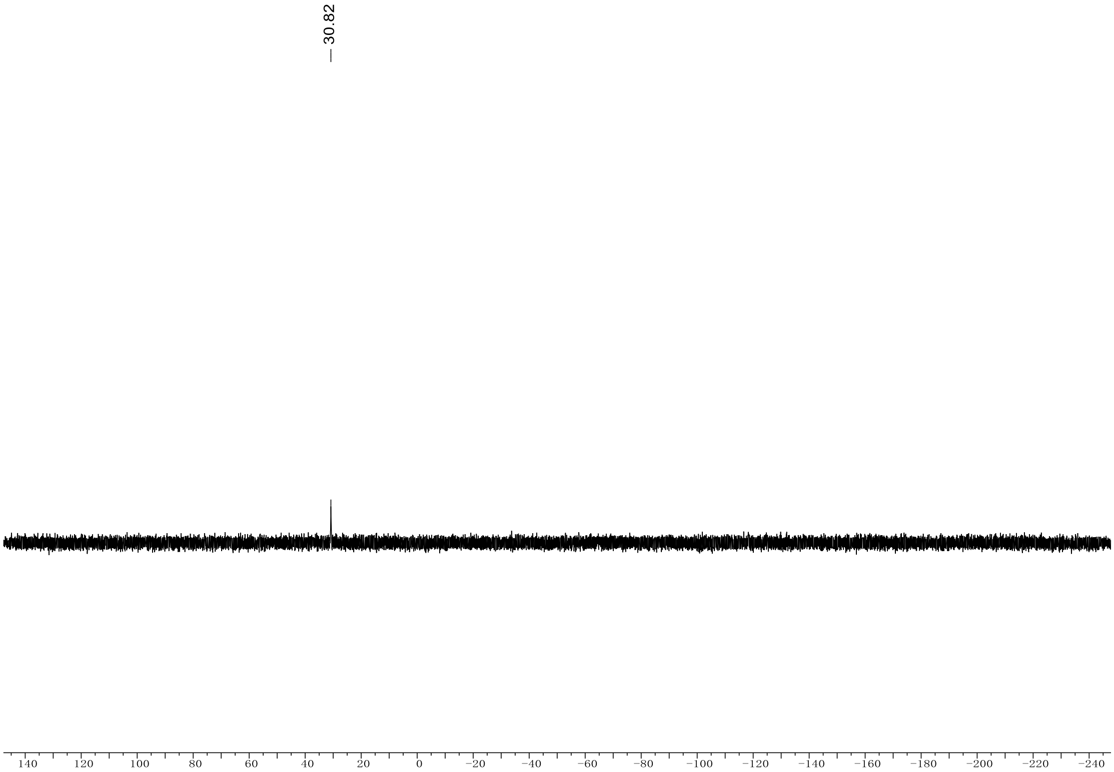
# In situ NMR



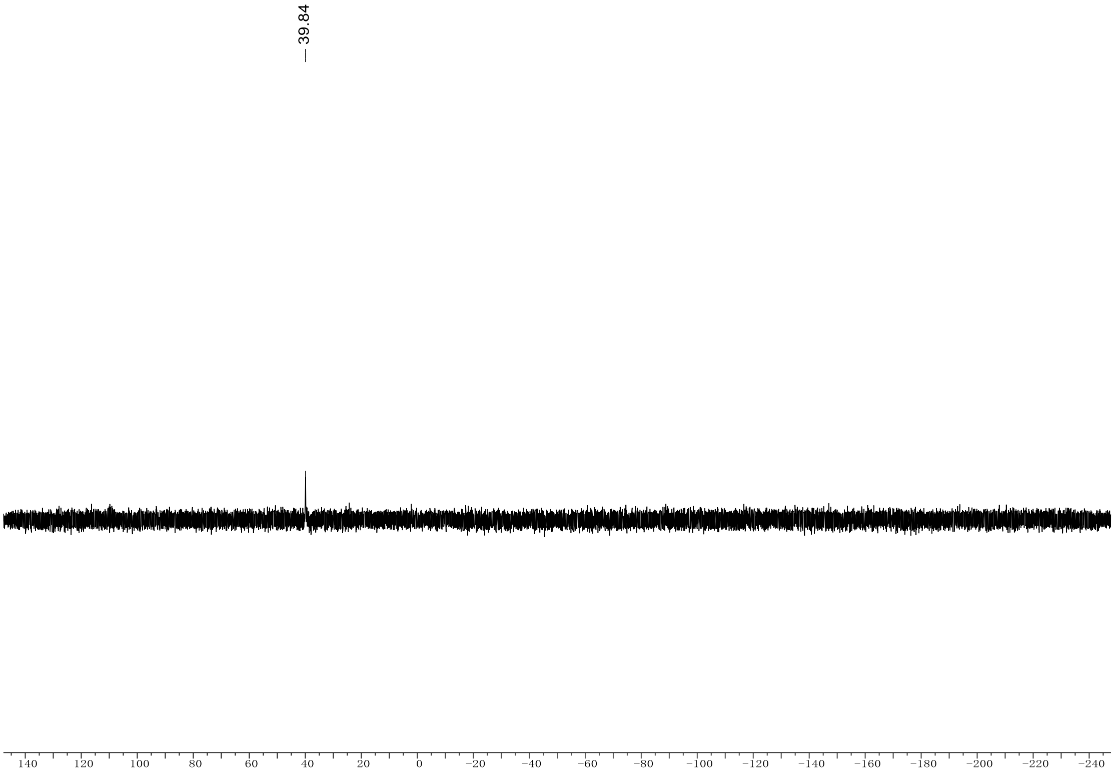
$^1$H NMR (400 MHz, CDCl$_3$) of **1a**



$^1$H NMR (400 MHz, CDCl$_3$) of **Reaction mixture**



$^{31}P$ NMR (162 MHz, $CDCl_3$) of **$L_1$AuCl**



$^{31}P$ NMR (162 MHz, $CDCl_3$) of **Reaction mixture**