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SUPPLEMENTARY MATERIAL

Thermoregulated aqueous biphasic catalysis of Sonogashira reactions

Xiaohua Zhao [a,*], Xiang Liu [b], Ming Lu [b,*]

[a] ***School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China***

[b] ***School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China***

****Email: zhao12_19@163.com; liuxiang8868@126.com***

Contents

Experimental Section

All the chemicals were from commercial sources and used without any pretreatment. All reagents were of analytical grade. 1H NMR spectra were recorded on a Bruker 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. All the products were known compounds and characterized by comparing their 1H NMR and MS spectral data (see supporting information) with those reported in the literature.

Typical procedure for the preparation of thermoregulated ligand (PEG-DAIL[BF4])

The thermoregulated ligand (PEG-DAIL[BF4]) was prepared according to the reference reported by our group [25]. 1H NMR (D2O): δ (ppm) 2.15 (t, 4H, J= 7 Hz, 2×CH2), 2.77 (m, 4H, 2×CH2), 3.45-3.66 (m, 90.3H, (OCH2CH2)n), 3.74 (4H, 2×CH2), 4.21-4.30 (8H, 4×NCH2), 7.41 (s, 4H, 4×CH), 8.71 (s, 2H, 2×CH); 13C NMR (D2O): δ (ppm) 25.2, 47.7, 47.9, 49.1, 68.6, 68.7, 69.6, 122.3, 123.1, 136.0; IR (cm−1): 3849, 3400, 3020, 2883, 1732, 1591, 1456, 1431, 1377, 1122, 1109, 972, 883, 798, 677, 577.

General conditions for Sonogashira reactions

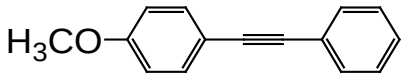
A solution of Pd(OAc)2 (0.34 mg, 0.0015 mmol) and ligand PEG-DAIL[BF4] (4.5 mg, 0.003 mmol) in deoxygenated H2O (2 mL) was stirred at room temperature for 30 min in air. Et3N (1 mmol, 101 mg), aryl halide (0.5 mmol), and terminal alkyne (0.75 mmol) were then successively added. The reaction mixture was heated in an oil bath with magnetic stirring. After cooling to room temperature, the reaction mixture was added to brine (15 mL) and extracted three times with diethyl ether (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by short column chromatography on a silica gel.

Catalyst Recycling for the Sonogashira Reaction:

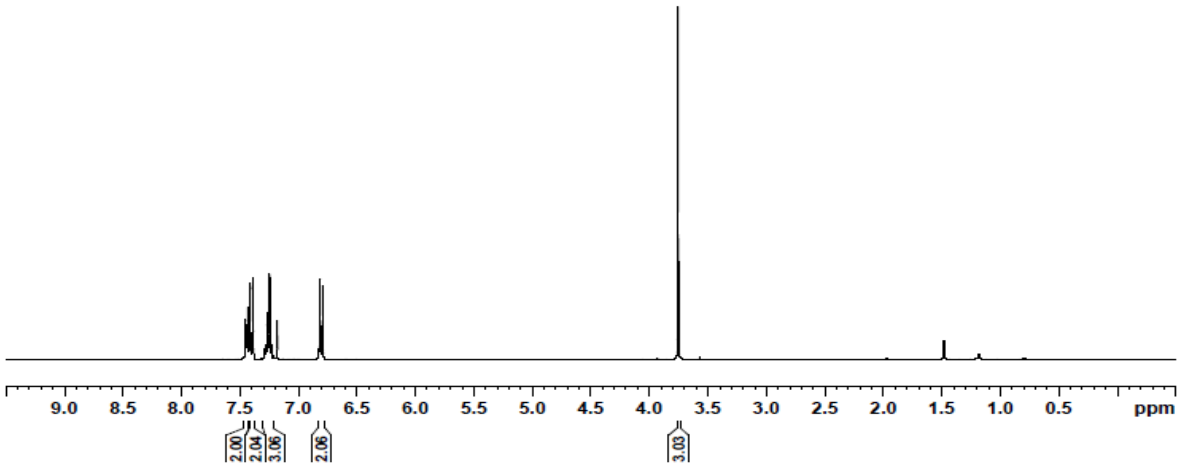
When the reaction was completed, the reaction mixture was cooled to room temperature and extracted with ethyl ether (2 mL). Et3N (1 mmol, 101 mg), bromobenzene (0.5 mmol) and phenylacetylene (0.75 mmol) were added to the aqueous phase that was separated from the previous catalytic run , and reacted at 80 °C.

Characterization Data of the Products

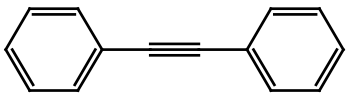
1-Methoxy-4-(phenylethynyl)benzene (Table 2, entry 1, 7, ref 1)



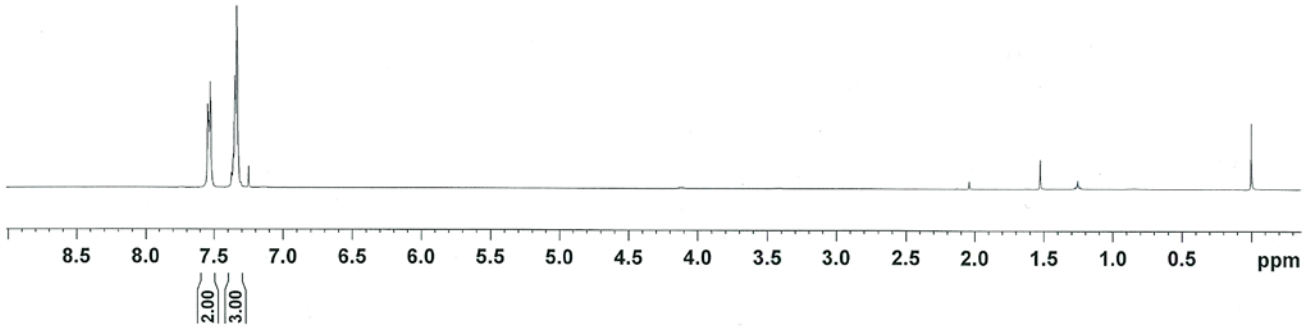
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.26 (m, 3H), 6.80 (d, *J* = 8.8 Hz 2H), 3.75 (s, 3H). **CAS Number: 7380-78-1**.



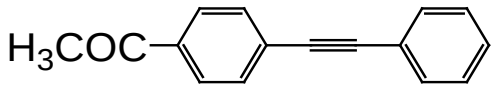
Diphenylacetylene (Table 2, entry 2, ref 1)



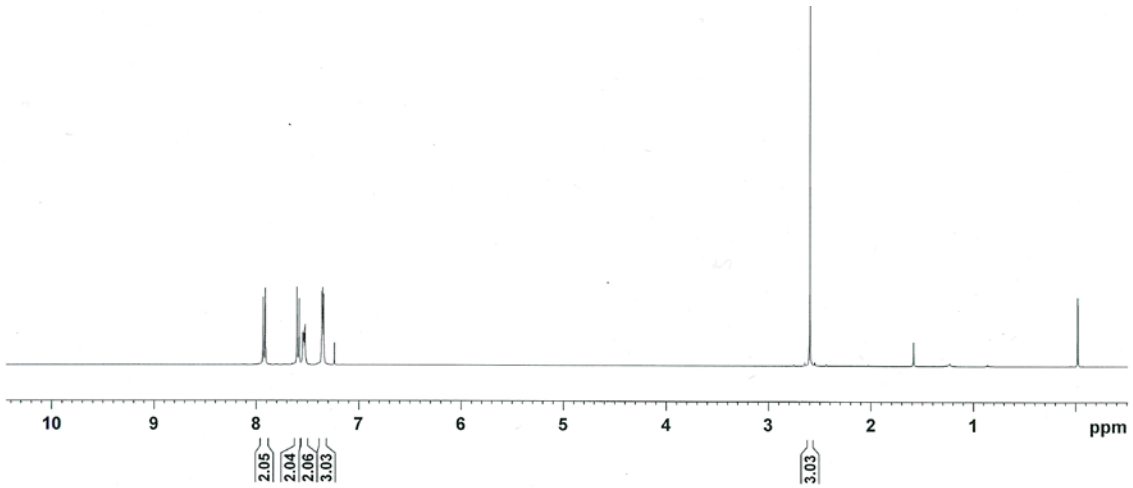
1H NMR (400MHz, CDCl3): δ 7.60 (m, 4H), 7.35 (m, 6H). **CAS Number: 501-65-5.**



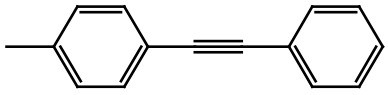
4-(Phenylethynyl)acetophenone (Table 2, entry 3, 13, ref 1)



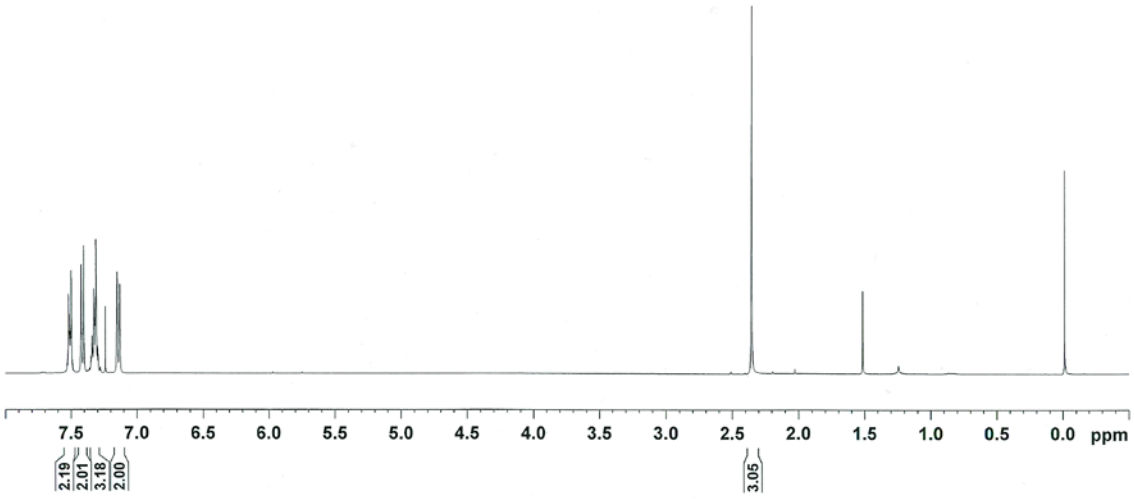
1H NMR (400 MHz, CDCl3): δ 7.92 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.53 (m, 2H), 7.35 (m, 3H), 2.59 (s, 3H). **CAS Number: 1942-31-0**.



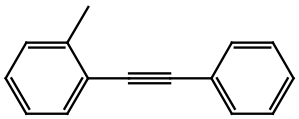
1-Methyl-4-(phenylethynyl)benzene (Table 2, entry 4, ref 1)



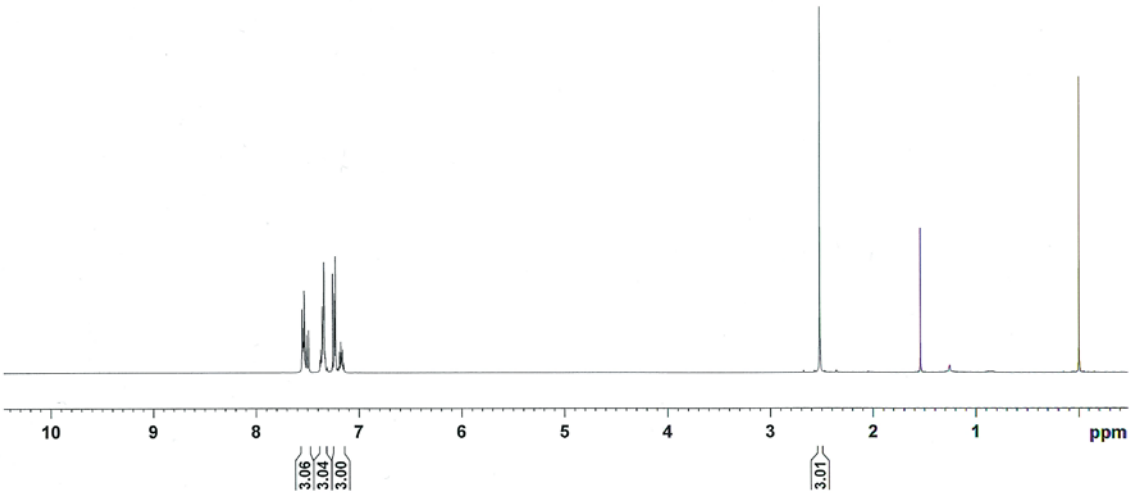
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H), 7.41 (d, *J* = 8.4 Hz), 7.32 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H). **CAS Number: 3287-02-3**.



1-Methyl-2-(phenylethynyl)benzene (Table 2, entry 5, ref 1)

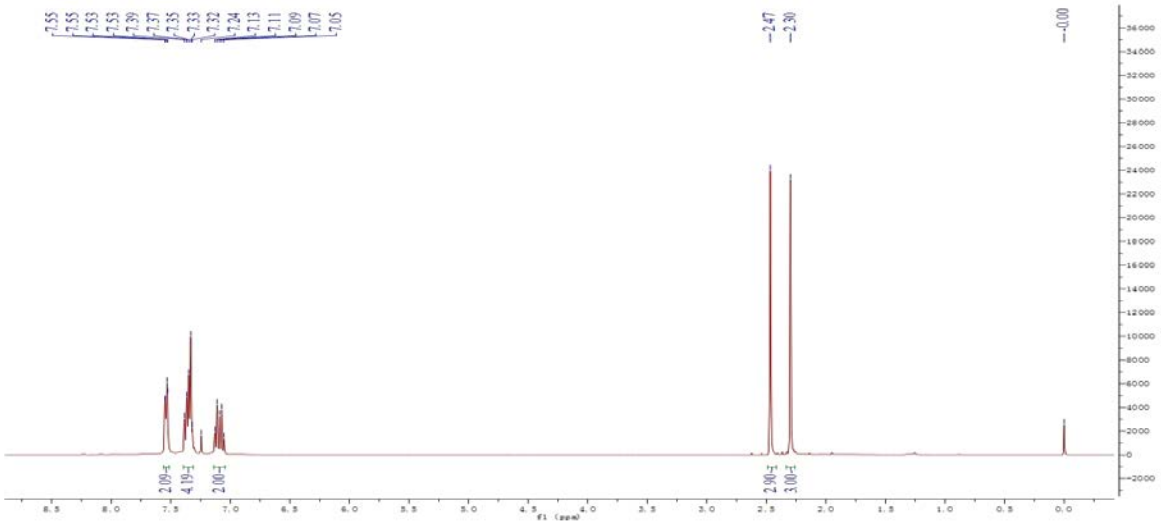


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.55 (m, 3H), 7.32-7.38 (m, 3H), 7.14-7.25 (m, 3H), 2.52 (s, 3H). **CAS Number: 14309-60-5**.

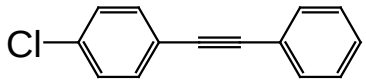


1,2-dimethyl-3-(phenylethynyl)benzene (Table 2, entry 6, ref 2)

1H NMR (400 MHz, CDCl3) δ 7.54 (dd, J = 7.7, 1.7 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.09 (dt, J = 15.0, 7.4 Hz, 2H), 2.47 (s, 3H), 2.30 (s, 3H).**CAS Number: 1262044-52-9**.

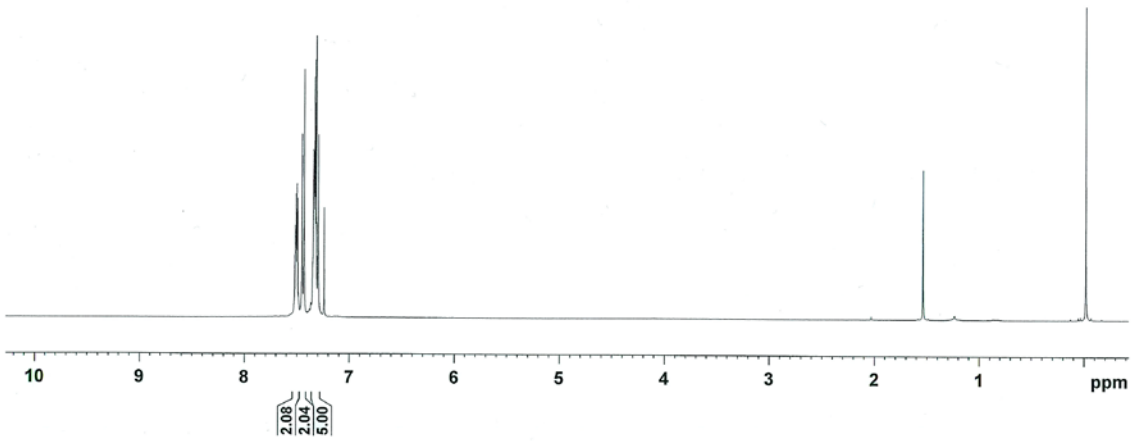


1-Chloro-4-(phenylethynyl)benzene (Table 2, entry 8, ref 1)

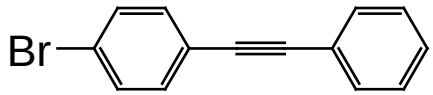


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.43 (m, 2H), 7.31 (m, 5H).

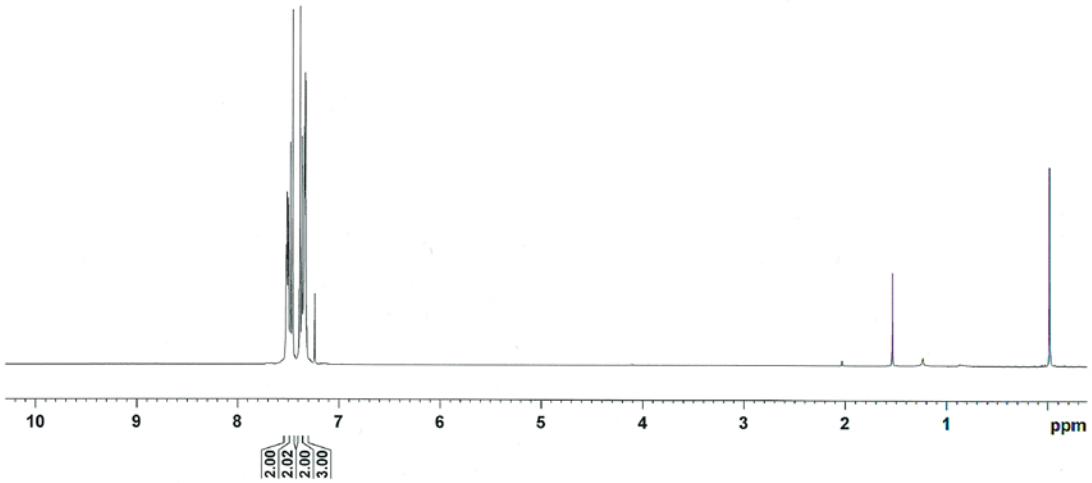
CAS Number: 5172-02-1.



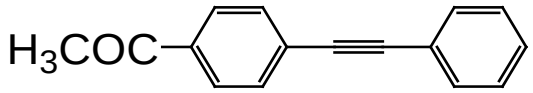
1-Bromo-4-(phenylethynyl)benzene (Table 2, entry 9, ref 1)



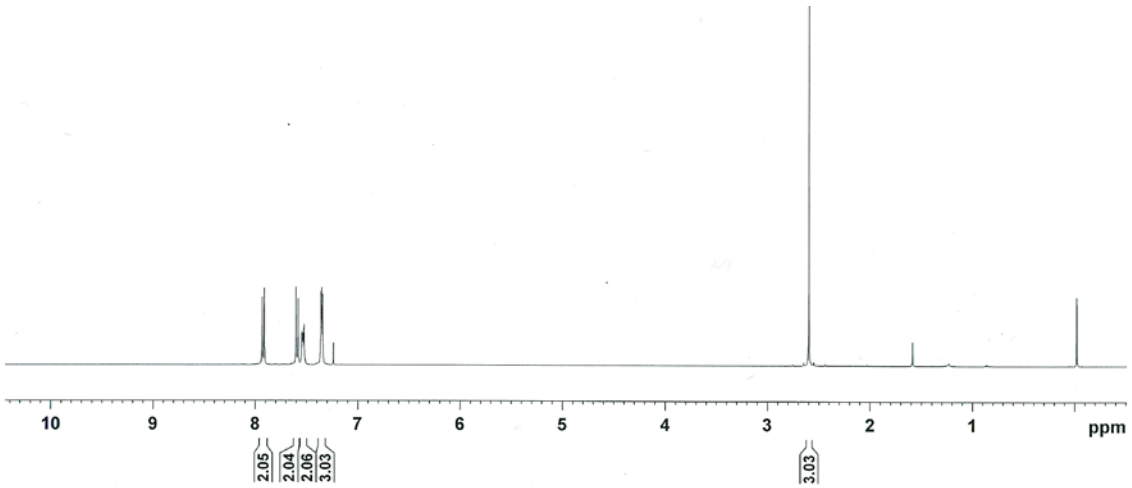
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.52 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.31-7.42 (m, 3H). **CAS Number: 13667-12-4**.



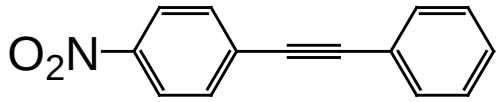
4-(Phenylethynyl)acetophenone (Table 2, entry 10, ref 1)



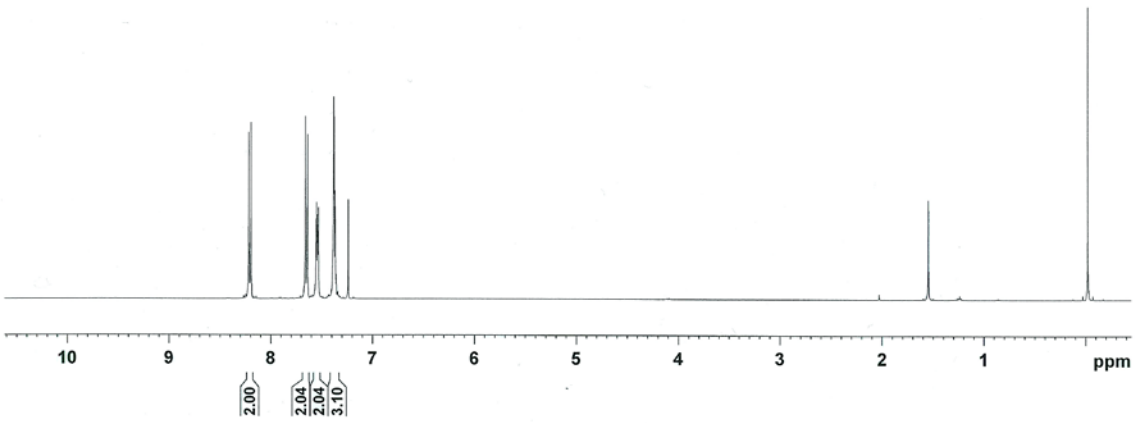
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.53 (m, 2H), 7.35 (m, 3H), 2.59 (s, 3H). **CAS Number: 1942-31-0.**



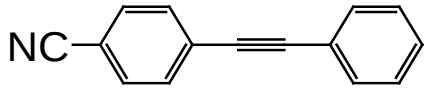
1-Nitro-4-(phenylethynyl)benzene (Table 2, entry 11 and 17, ref 1)



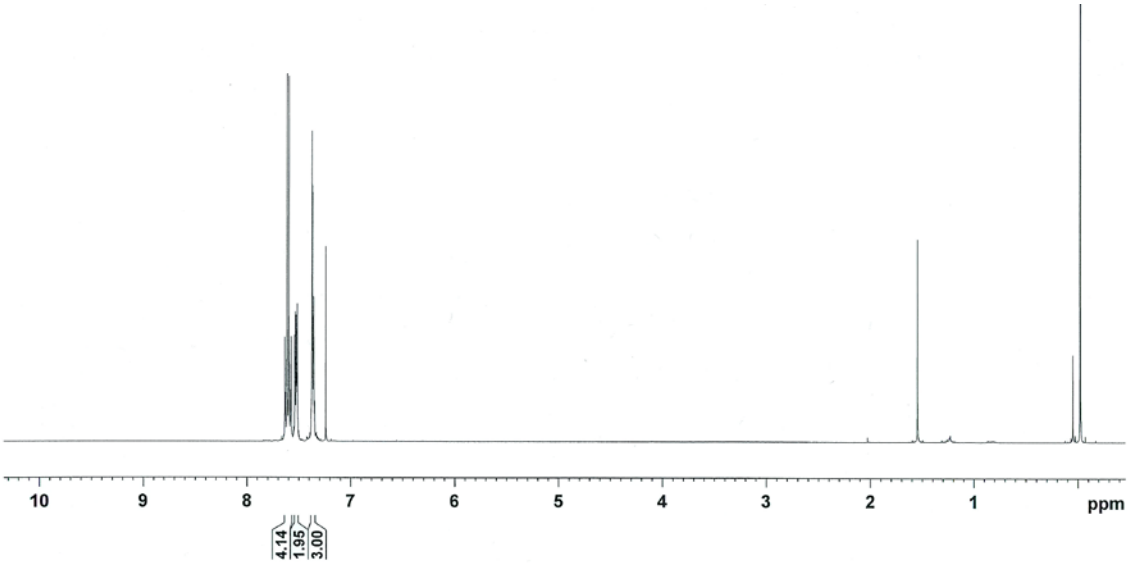
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.53 (m, 2H), 7.37 (m, 2H). **CAS Number: 1942-30-9.**



4-(Phenylethynyl)benzonitrile (Table 2, entry 12, ref 1)

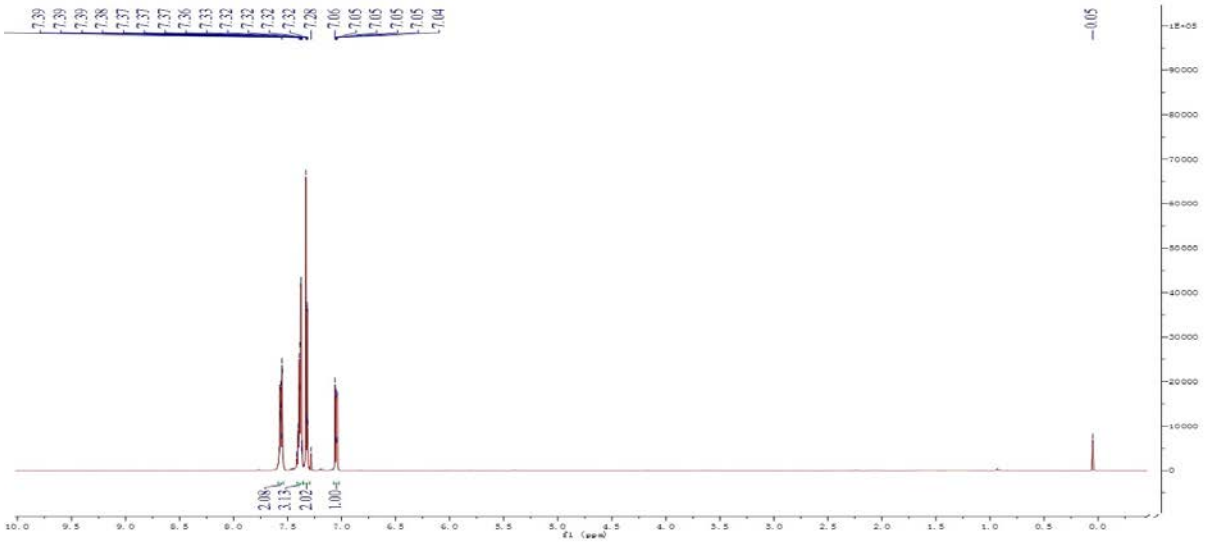


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (m, 4H), 7.53 (m, 2H), 7.36 (m, 3H). **CAS Number: 29822-79-5.**

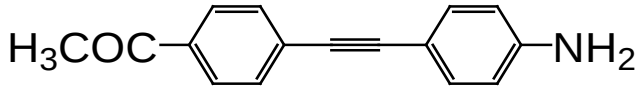


2-(phenylethynyl)thiophene (Table 2, entry 14, ref 2)

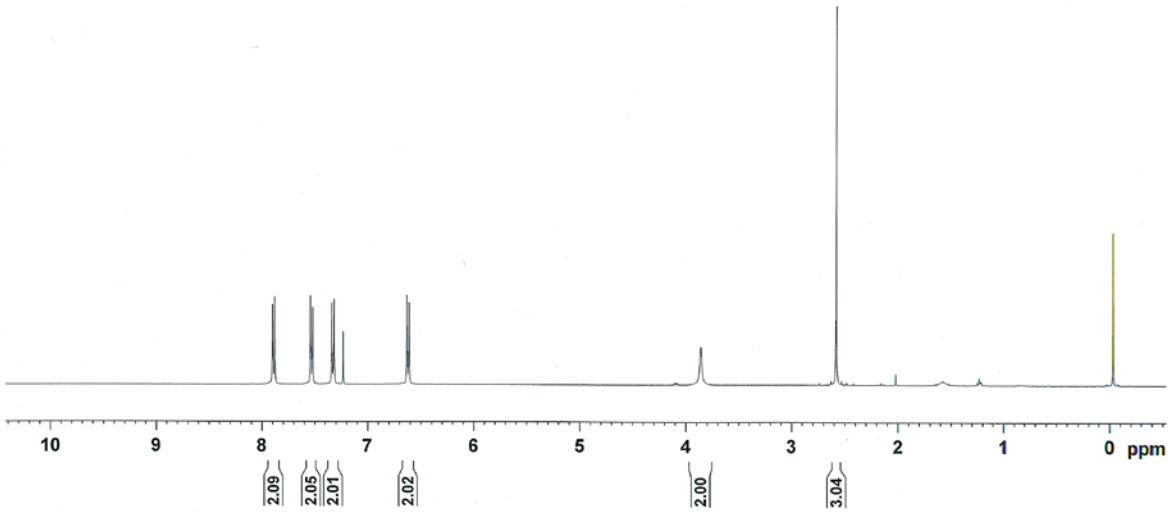
1H NMR (400 MHz, CDCl3) δ 7.59 -7.54 (m, 2H), 7.41-7.36 (m, 3H), 7.35-7.30 (m, 2H), 7.07-7.02 (m, 1H). **CAS Number: 4805-17-8.**



4-((4-Aminophenyl)ethynyl)acetophenone (Table 2, entry 15, ref 1)

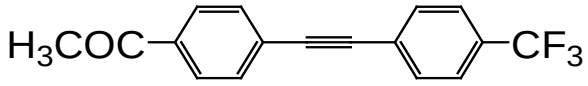


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 3.86 (bs, 2H), 2.58 (s, 3H). **CAS Number: 123770-68-3.**



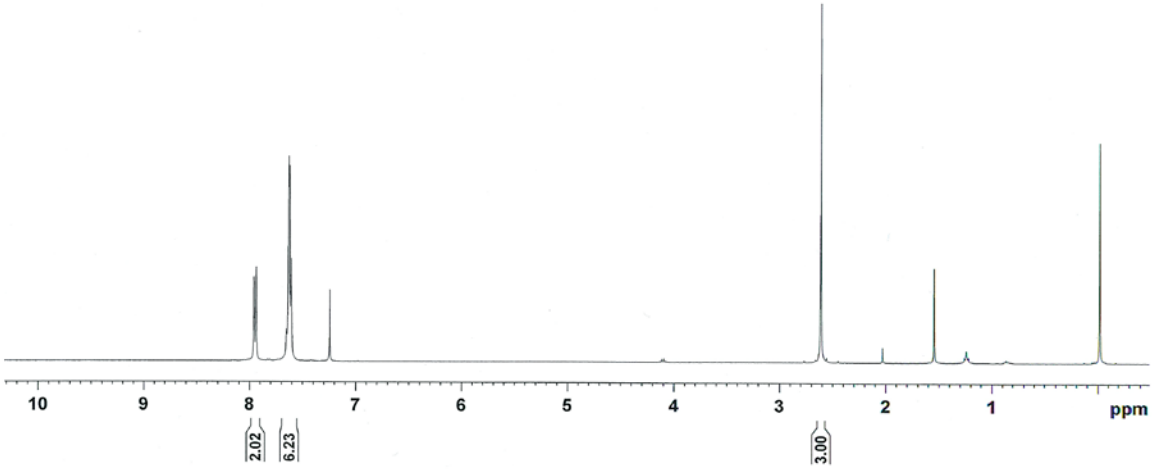
4-((4-Trifluoromethylphenyl)ethynyl)acetophenone

(Table 2, entry 16, ref 1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.62 (m, 6H), 2.61 (s, 3H).

CAS Number: 863922-21-8.



References

1. Y. Lee, M. C. Hong, H. Ahn, J. Yu, H. Rhee, J. Organomet. Chem., 2014, 769, 80-93.

2. H. F. Lu, L. Wang, F. F. Yang, R. Z. Wu, W. Shen, RSC Adv., 2014, 4, 30447-30452.