Supporting information for

Highly stable bidentate thiol-protected Ag_5Cu_4 nanoclusters: A Stable Catalyst for Enhanced Knoevenagel Condensation

Yan Nong,‡[a] Juefei Dai,‡[a] Chao Yang,‡*[a] Haifeng Su,[b] Chengcheng Feng,[a] Chuanhua Shi,[a] Zhixun Zhang,[a] Xianyong Yu,[c] Xueji Zhang*[a] and Huayan Yang*[a]

[a]Shenzhen Key Laboratory of Nano-Biosensing Technology, School of Biomedical Engineering, Shenzhen University Medical School，Shenzhen University，Shenzhen 518060, China.
[b]College of chemistry and chemical Engineering, Xiamen University, Xiamen University, Xiamen 361000, China.
[c]Key Laboratory of Theoretical Organic Chemistry and Functional Molecules, Ministry of Education, Hunan University of Science and Technology, Xiangtan 411100, China.
‡These authors contributed to this work equally.
Corresponding authors: E-mail addresses: yanghuayan@szu.edu.cn (Prof. Huayan Yang); zhangxueji@szu.edu.cn (Prof. Xueji Zhang), yangchao@szu.edu.cn (Dr. Chao Yang)

Experimental Details

Reagents: Silver nitrate ($AgNO_3$, 99%), Purchase from Xilong Scientific; copper nitrate trihydrate (Cu $(NO_3)_2·3H_2O$, 99%), purchase from Adamas Pharmaceuticals, Inc; 3,4,5,6-tetrafluoro-1,2-phenyldithiol ($H_2SSC_6F_4$, 99%), triphenylphosphine(PPh_3, 99%), 3,5-Bis(trifluoromethyl)thiophenol ($HSPh(CF_3)_2$, 98%), tetraphenylphosphine bromide (PPh_4Br, 99%), (2*S*,3*S*)-(-)-2,3-bis(diphenylphosphine)butane [(2*S*,3*S*)-(-) dppb, 99%], (2*R*,3*R*)-(-)-2,3-bis(diphenylphosphine)butane [(2*R*,3*R*)-(-) dppb, 99%], sodium borohydride ($NaBH_4$, 99%), purchase from Bide Pharmatech Co., Ltd; triethylamine (NEt_3, 99%), purchase from McKinley Corporation; benzaldehyde (98%), 4-methylbenzaldehyde (98%), 4-(Trifluoromethyl)benzaldehyde (99%), 4-Chlorobenzaldehyde (98%), 2-Methoxybenzaldehyde (98%), 3-Methoxybenzaldehyde (98%), 4-Methoxybenzaldehyde (98%), 4-Pyridinecarboxaldehyde (98%), 3-Furaldehyde (98%), 3-Thiophenecarboxaldehyde (98%), Cinnamaldehyde(98%), 3-Phenylpropionaldehyde (98%), Cyclopropanecarboxaldehyde (98%), Malononitrile(98%) purchase from Adamas Pharmaceuticals, Inc; deionized water (H_2O, homemade); All reagents without further processing, use directly.

Instruments: The X-ray single crystal diffractometer used was Brooke D8 VENTURE X-ray single crystal diffractometer, the UV visible absorption spectrometer used was Shimadzu UV-2550 spectrophotometer, the circular dichroism spectrometer used was Chirascan spectrometer, the field emission transmission electron microscope used was JEOL F200, the nuclear magnetic resonance used was AVANCE NEO 400MHz, the infrared absorption spectrum used was Fourier transform infrared spectrometer Nicolet AVATAR FT-IR330, and the double spherical aberration corrected transmission electron microscope used was Titan Themis G2.

Synthesis of {$Ag_5Cu_4(SSPhF_4)_6(PPh_4)_2[Cu[(2S,3S)\text{-dppb}]_2]$}: Ag_5Cu_4 was synthesized by a one-pot method. First, a mixture of $AgNO_3$ (50 mg, 0.29 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (75 mg, 0.31 mmol) in methanol and dichloromethane was added to a reaction flask at 0 °C. Then PPh_4Br (50 mg, 0.23 mmol), (2*S*,3*S*)-(-) dppb (30 mg, 0.07 mmol) and $H_2SSC_6F_4$ (75 mg, 0.35 mmol) in dichloromethane solution were added with stirring. After stirring for 20 minutes, NEt_3 (80 μL) and fresh $NaBH_4$ (5.3 mmol/ 2 mL H_2O) solution were added and the reaction was allowed to develop for 12 hours at 0 °C in the dark. After the reaction, the organic phase was collected, washed several times with deionised water and then diffused with n-hexane/dichloromethane at room temperature. Yellow rod-shaped crystals were obtained after 2 days (45% yield, base Ag).

Synthesis of {$Ag_5Cu_4(SSPhF_4)_6(PPh_4)_2[Cu[(2R,3R)\text{-dppb}]_2]$}: The procedure was same as {$Ag_5Cu_4(SSC_6F_4)_6(PPh_4)_3[Cu[(2S,3S)\text{-Dppb}]_2]$} with the replacement of (2*S*,3*S*)-dppb into (2*R*,3*R*)-Dppb (48% yield, base Ag).

Synthesis of [$Cu_5(SSPhF_4)_4(PPh_4)_2$]: The procedure was same as {$Ag_5Cu_4(SSC_6F_4)_6(PPh_4)_3[Cu[(2S,3S)\text{-dppb}]_2]$} with the exception of $AgNO_3$. After 7 days, purple rod-shaped crystals were obtained (10% yield, base Cu).

Synthesis of [$Ag_{14}(SPh(CF_3)_2)_{12}(PPh_3)_4(DMF)_4$]: The synthesis of Ag_{14} is based on Zheng.[1] Ag_{14} was synthesized using a one-pot method. First, a mixture of $AgNO_3$ (50 mg, 0.29 mmol) in N,N-dimethylformamide and dichloromethane was added to a reaction flask at room temperature. Then, PPh_3 (50 mg, 0.19 mmol) and $HSPh(CF_3)_2$ (37.5 μL, 0.22 mmol) in dichloromethane solution were added with stirring. After stirring for 10 minutes, NEt_3 (80 μL) and fresh $NaBH_4$ (5.3 mmol/2 mL H_2O) solution were added, and the reaction was allowed to stand at room temperature for 10 hours. At the end of the reaction, the organic phase was collected, washed several times with deionised water, then 20 μL DMF were added to the organic phase and diffused with n-hexane/dichloromethane at 4 °C. After 14 days, yellow rod-shaped crystals were obtained.

Synthesis of {$Cu[(2S,3S)\text{-dppb}]_2$}: The synthesis of {$Cu[(2S,3S)\text{-dppb}]_2$} is based on Allan H.[2] (2*S*,3*S*)-dppb (853 mg, 2 mmol) and 20 mL anhydrous ethanol were added to a 100 mL round bottom flask at room temperature. $CuCl_2$ (67.25 mg, 0.5 mmol) was added while stirring, and the reaction lasted for 24 hours. After the reaction was completed, it was washed 3-5 times with anhydrous ethanol and ether, filtered and dried to obtain a white solid for later use.

Synthesis of {Cu[(2*R*,3*R*)-dppb]$_2$}: Same as {Cu[(2*S*,3*S*)-dppb]$_2$} with the replacement of (2*S*,3*S*)-dppb into (2*R*,3*R*)-dppb.

Synthesis of Ag$_5$Cu$_4$@ carbon black: Carbon black (50 mg) and dichloromethane 8 mL were added to a 20 mL round bottom flask at room temperature, with addition of {Ag$_5$Cu$_4$(SSPhF$_4$)$_6$(PPh$_4$)$_3$[Cu[(2*S*,3*S*)-dppb]$_2$]} (5 mg, 10%) and stirred for 1 hour. After the reaction was completed, centrifuged at 5000 rpm for 3 minutes, poured out the clear liquid, washed 3-5 times with dichloromethane and anhydrous ethanol, and then filtered and dried for later use.

Single Crystal Analysis for all compounds: The diffraction data of all compounds were collected on the Bruke D8 Venture. X-ray single crystal diffractometer with Mo Kα radiation (λ = 0.7107 Å) at 100 K. The structure was solved and refined using Full-matrix least-squares based on F2 with program SHELXT and SHELXL within Olex2.

Crystallographic data for {Ag$_5$Cu$_4$(SSPhF$_4$)$_6$(PPh$_4$)$_3$[Cu[(2*S*, 3*S*)- dppb]$_2$]}. Yellow rod-shaped crystals, 0.25 × 0.10 × 0.07 mm, space group *P*1(1), *a* = 14.1667(9) Å, *b* = 15.8384(10) Å, *c* = 18.0867(11) Å, *α*=90.711(2)°, *β*=97.321(2)°, *γ*=110.931(2)°, *V*=3752.20(41) Å3, *Z* = 1, Mo Kα, *T* = 100 K, R_{int} = 0.0644. Final R_1=7.53%, wR_2=0.1979.

Crystallographic data for {Ag$_5$Cu$_4$(SSPhF$_4$)$_6$(PPh$_4$)$_3$[Cu[(2*R*, 3*R*)- dppb]$_2$]}. Yellow rod-shaped crystals, 0.30 × 0.15 × 0.1 mm, space group *P*1(1), *a*=14.1112(19) Å *b*=15.576(2) Å *c*=21.554(3) Å *α*=96.620(3)°, *β*=104.668(4)°, *γ*=111.928(3)°, *V*=4133.7(10) Å3, *Z*=1, Mo Kα, *T* = 100 K, R_{int} = 7.84%. Final R_1=8.84%, wR_2=23.08%.

Crystallographic data for [Cu$_5$(SSPhF$_4$)$_4$(PPh$_4$)$_2$]. Purple rod-shaped crystals, 0.23 × 0.18 × 0.11 mm, *P*121/c1(14), *a*=20.991(4) Å, *b*=18.312(2) Å, *c*=18.503(3) Å, *α*=90°, *β*=100.873(5)°, *γ*=90°, *V*=6984.63(190) Å3, *Z*=4, Mo Kα, *T* = 100 K, R_{int} = 15.31%, Final R_1=9.59%, wR_2=31.25%

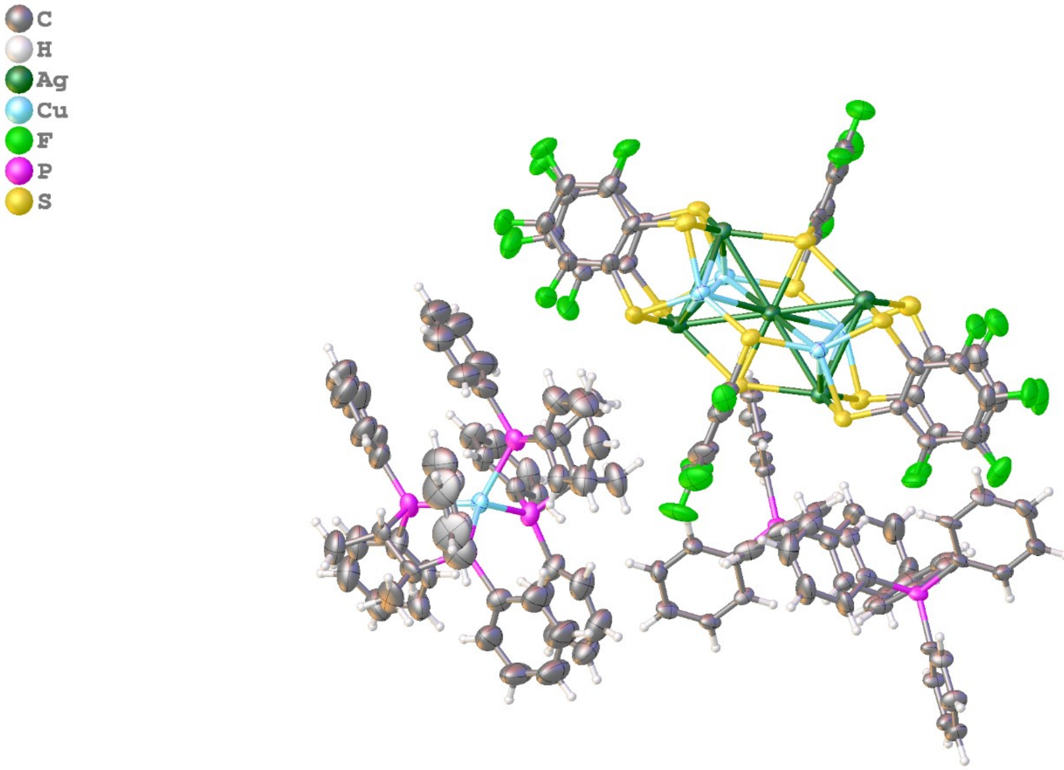


Fig. S1 The ADPs crystal structure of {$[Ag_5Cu_4(SSPhF_4)_6]\cdot[2PPh_4^+\ [Cu(2S,3S)\text{-dppp}]_2]$}. All hydrogen atoms are omitted for clarity. Color legend: Ag: green; Cu: blue; S: yellow; F: light green; P: purple; C: gray.

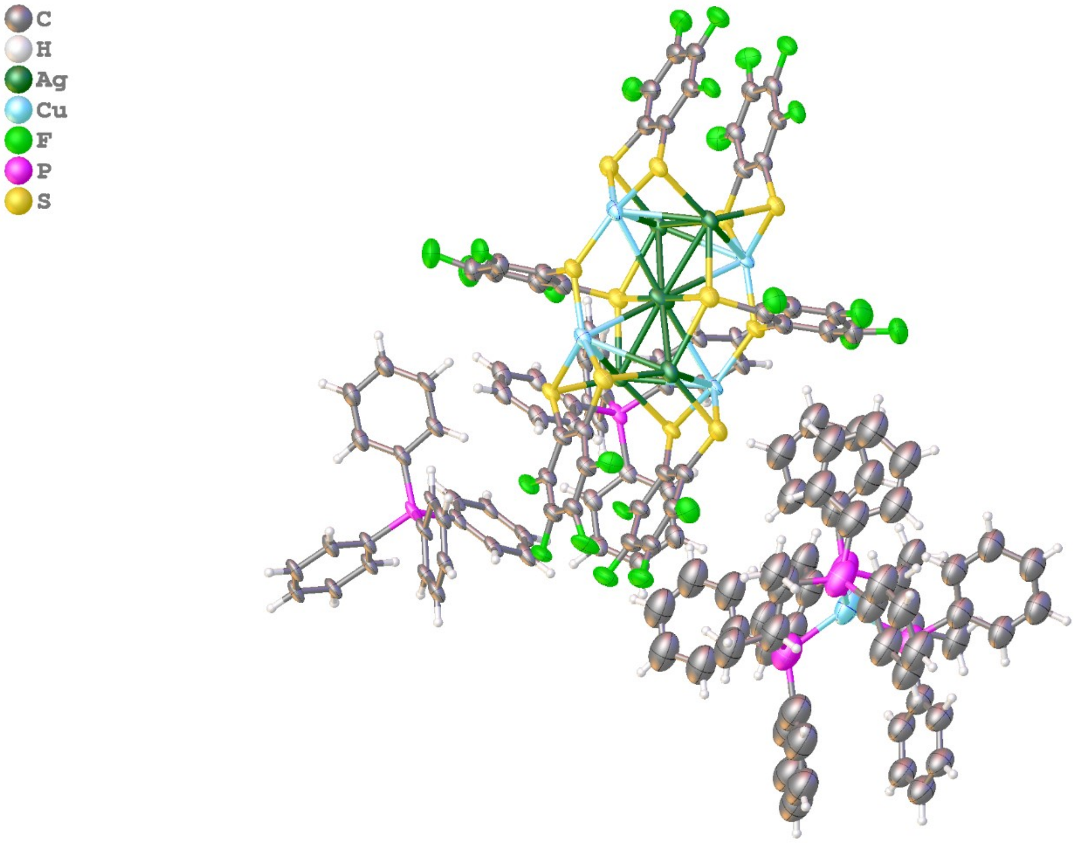


Fig. S2 The ADPs crystal structure of $\{[Ag_5Cu_4(SSPhF_4)_6]\cdot[2PPh_4^+\ [Cu(2R,3R)\text{-dppp}]_2]\}$. All hydrogen atoms are omitted for clarity. Color legend: Ag: green; Cu: blue; S: yellow; F: light green; P: purple; C: gray.

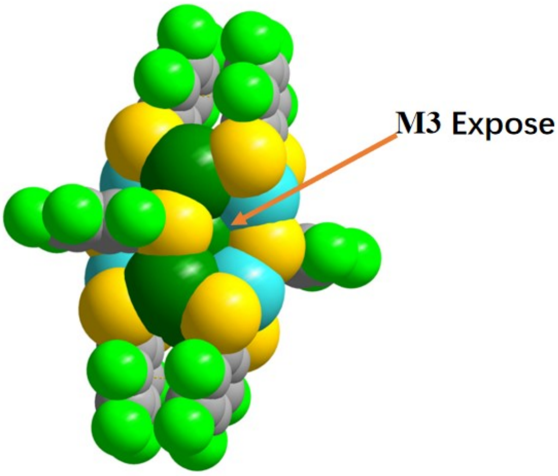


Fig. S3 The spacefilled structure of $(Ag_5Cu_4)^{3-}$, showing that the inner core M3 surface is exposed and that this M3 surface is catalytically reactive. Color legend: Cu: blue; S: yellow; F: light green; P: purple; C: gray.

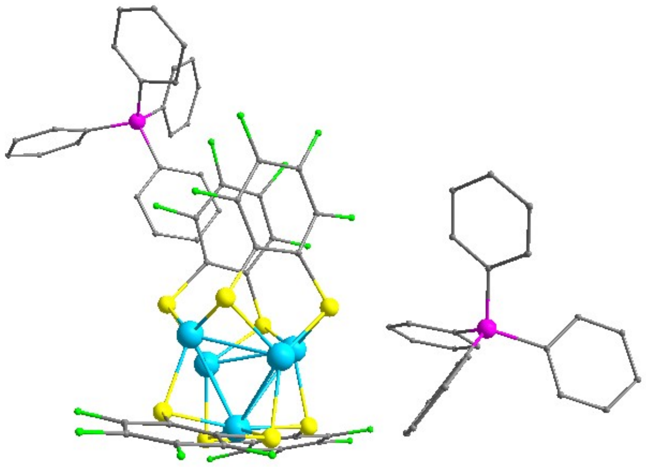


Fig. S4 The whole crystal structure of [$Cu_5(SSPhF_4)_4\cdot(2PPh_4^+)$]. All hydrogen atoms are omitted for clarity. Color legend: Cu: blue; S: yellow; F: light green; P: Purple; C: gray.

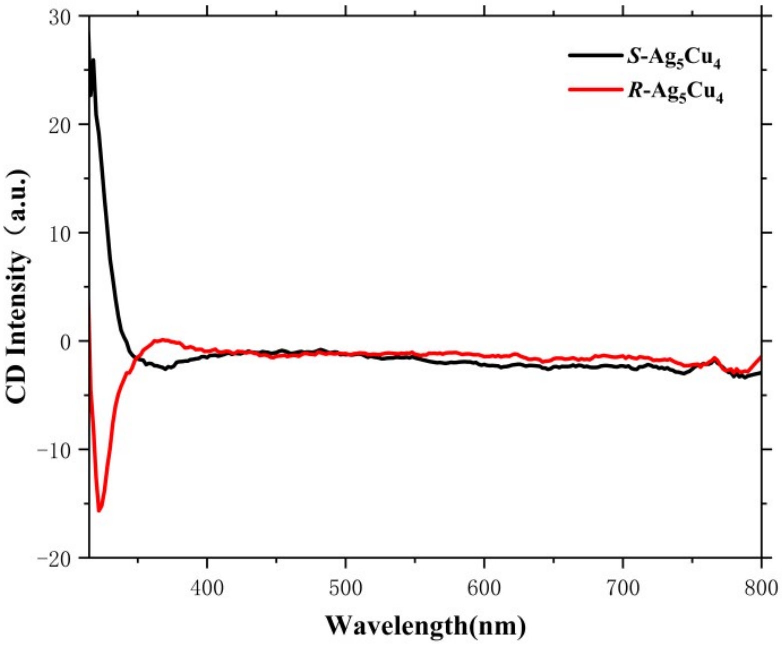


Fig. S5 The circular dichroism spectrogram of the dichloromethane solution of [$Ag_5Cu_4(SSC_6F_4)^-$]-[$2PPh_4^+$+Cu(chiral-dppb)] crystals, which shows only a pair of absorption peaks at 350 nm belonging to the Cu(2*S*,3*S*-Dppb)$_2$ / Cu(2*R*,3*R*-dppb)$_2$ complex, proves that $(Ag_5Cu_4)^{3-}$ has no chirality.

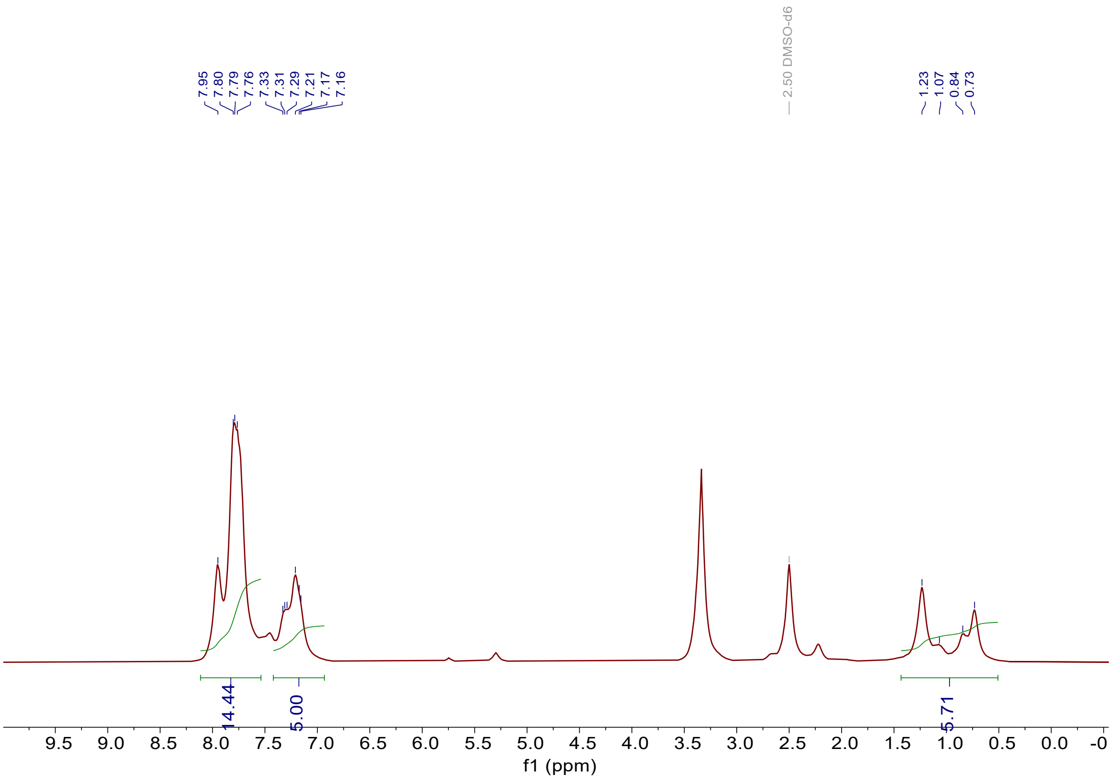


Fig. S6 ^{1}H NMR spectrum of {[$Ag_5Cu_4(SSPhF_4)_6$]·[2PPh_4^+ [Cu (2*S*, 3*S*)-dppp]$_2$] } in DMSO-*d*6.

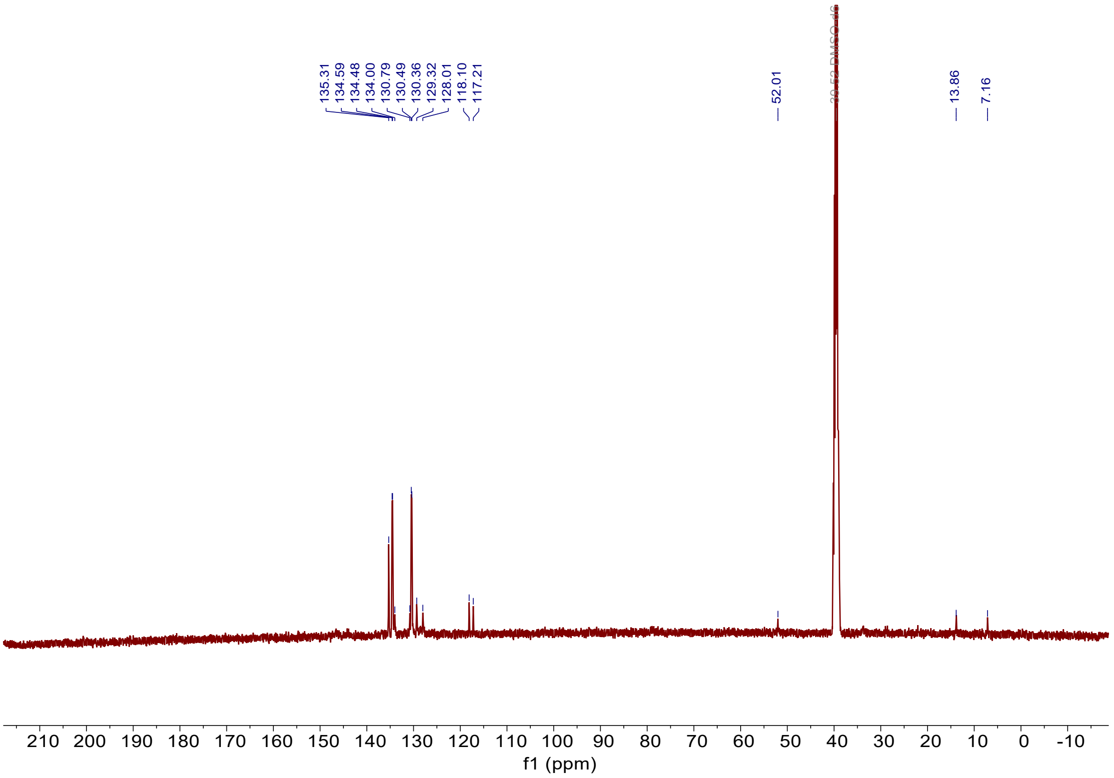


Fig. S7 ^{13}C NMR spectrum of {[$Ag_5Cu_4(SSPhF_4)_6$]·[2PPh_4^+ [Cu (2*S*, 3*S*)-dppp]$_2$] } in DMSO-*d*6.

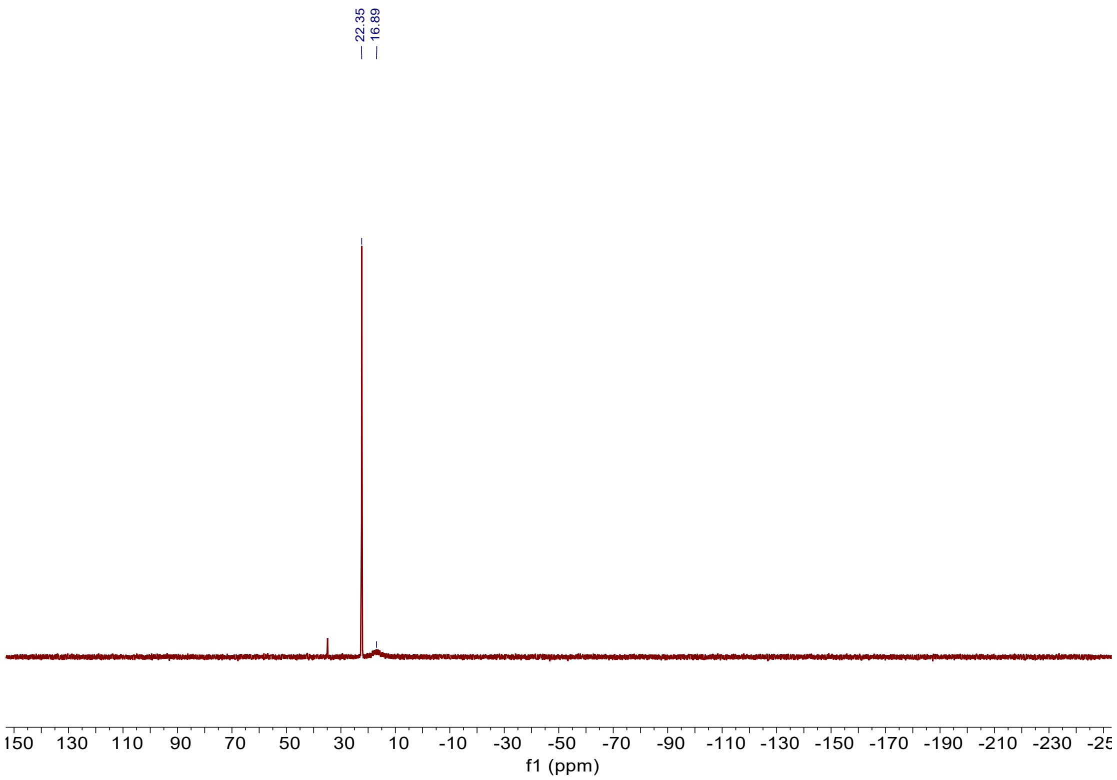


Fig. S8 ^{31}P NMR spectrum of {$[Ag_5Cu_4(SSPhF_4)_6]\cdot[2PPh_4^+$ [Cu (2*S*, 3*S*)-dppp$]_2]$ } in DMSO-*d*6.

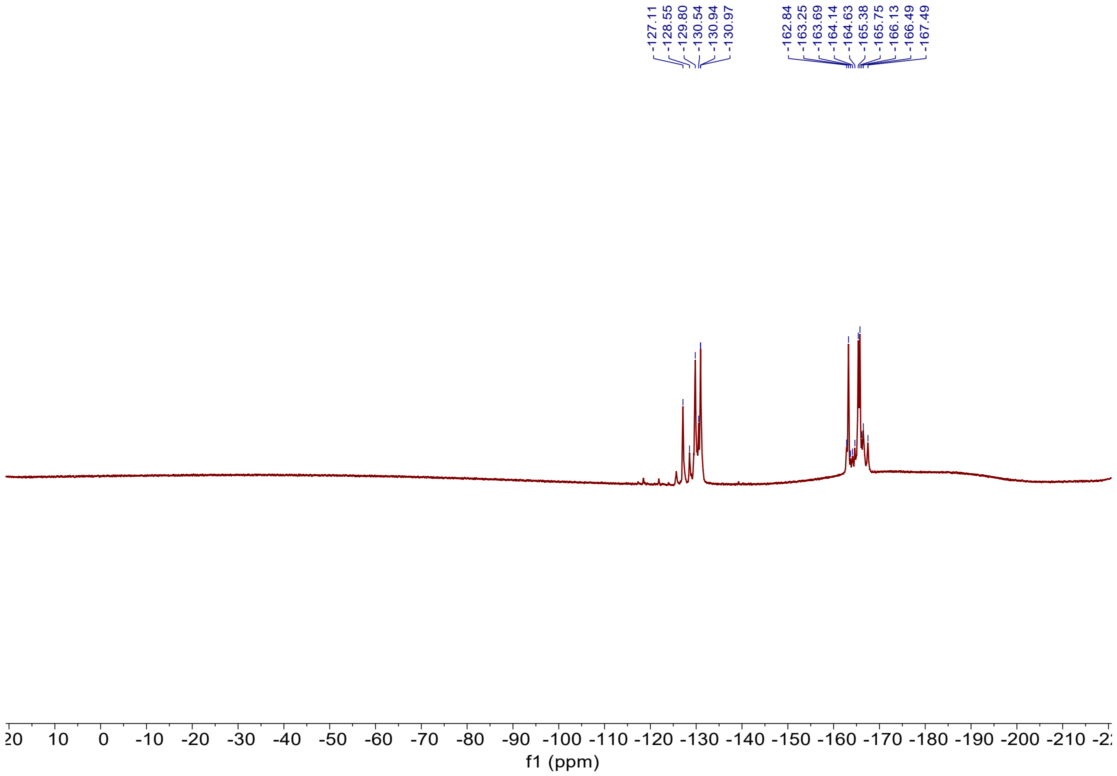


Fig. S9 ^{19}F NMR spectrum of {$[Ag_5Cu_4(SSPhF_4)_6]\cdot[2PPh_4^+$ [Cu (2*S*, 3*S*)-dppp$]_2]$ } in DMSO-*d*6.

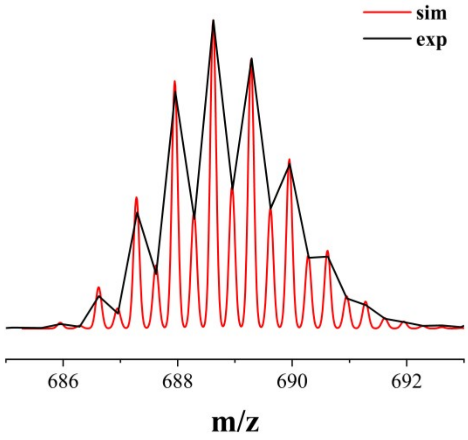


Fig. S10 ESI-mass spectrum of $Ag_5Cu_4^{3-}$.

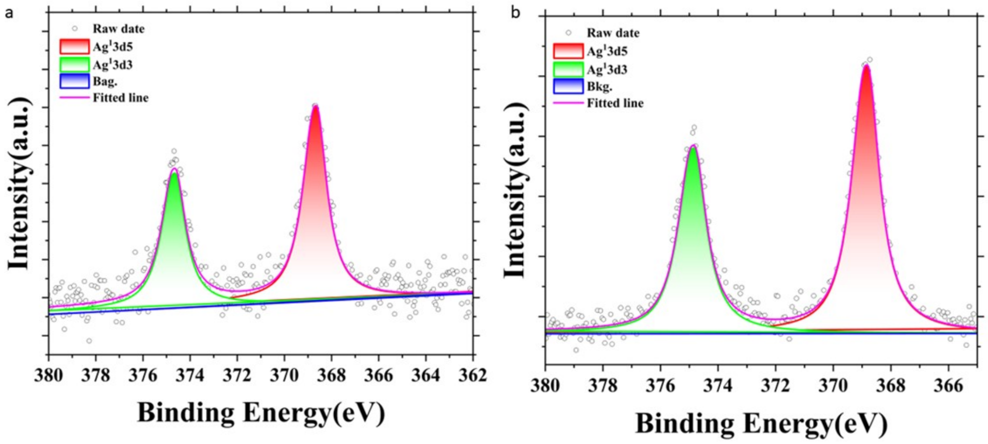


Fig. S11 XPS patterns of the Ag_5Cu_4@carbon black catalyst before and after the catalytic reaction of Ag.

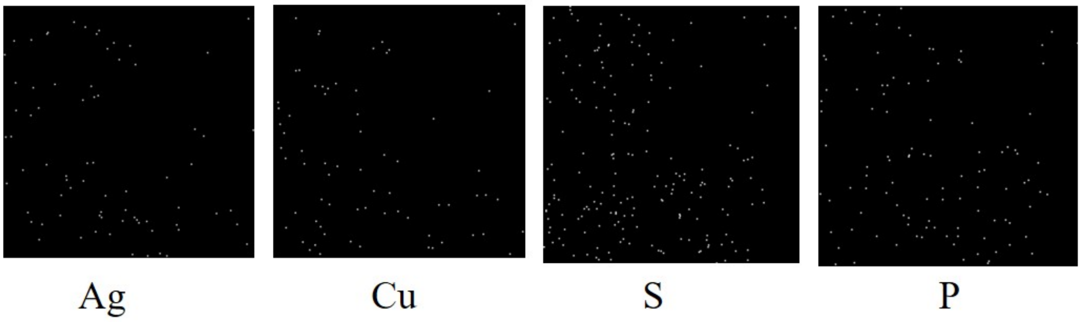


Fig. S12 AC-TEM Mapping images of Ag_5Cu_4@carbon black.

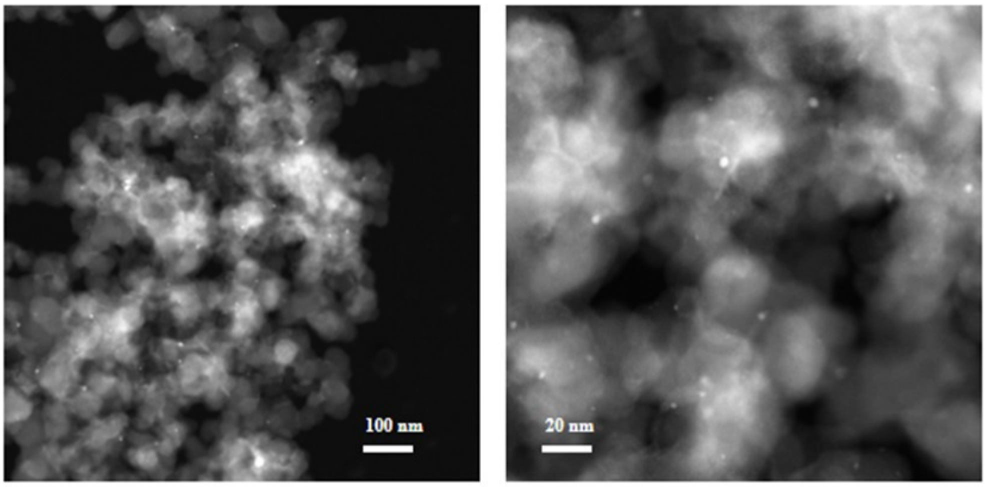


Fig. S13 Electron micrographs of Ag_5Cu_4@carbon black catalyst before and after six reaction cycles. The electron micrographs show that there is no obvious detachment and agglomeration of nanoparticles before and after six cycles of reaction, indicating that the catalyst is stable.

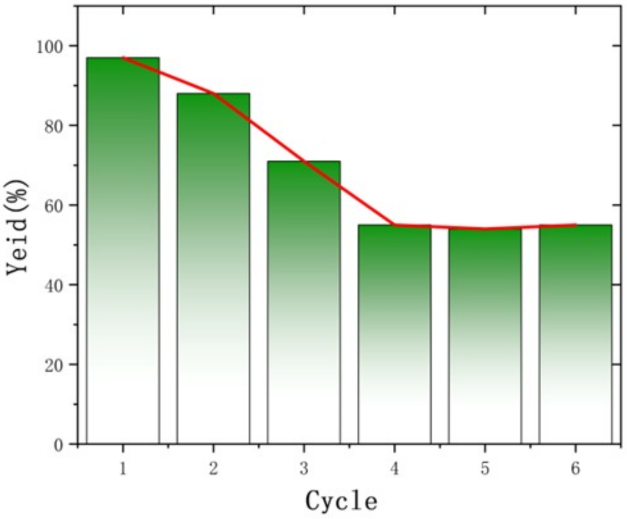


Fig. S14 Ag_5Cu_4@ carbon black catalyst stability experiments. From the figure it can be seen that in the first three catalytic cycle reactions the catalytic product difference rate remained stable after a small decrease. It can be assumed that a small amount of Ag_5Cu_4 nanoclusters were dislodged by physical stirring during the first three cycles, and then the catalytic efficiency remained unchanged in the last three cycle experiments after the physical state of the catalyst was stabilised. Therefore, we believe that the catalyst has good stability.

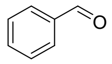
Table S1. ICP data of $Ag_5Cu_4(SSPhF_4)_6PPh_4Cu[(2S,3S)\text{-}Dpppb)_2]$

Element	Concentration (ppb)	Element ratio
Ag	194.138	1
Cu	137.220	1.2

Table S2. Catalytic yield of Ag_5Cu_4 on different carriers

Catalyst	Loading rate (wt%)	Catalytic yield (%)
Ag_5Cu_4@ carbon black	10	97
Ag_5Cu_4@ carbon black	5	70
Ag_5Cu_4@ carbon black	1	30
Ag_5Cu_4@ carbon nanotubes	10	65
Ag_5Cu_4@carbon spheres	10	50
Ag_5Cu_4@ monolayer graphene	＜1	NP
Ag_5Cu_4@ Multilayer graphene	＜1	32
Ag_5Cu_4@SiO_2	＜0.5	-
Ag_5Cu_4@TiO_2	＜0.5	-
Ag_5Cu_4@CeO_2	＜0.5	-

Substrates **1a-1m**, and **2a** were purchased from commercial sources and used without further purification.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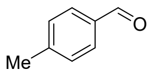
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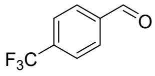
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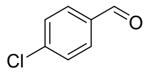
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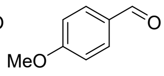
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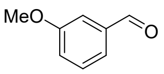
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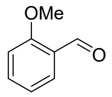
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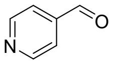
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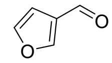
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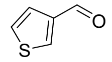
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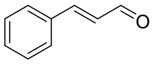
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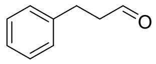
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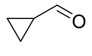
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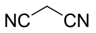
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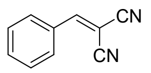
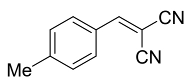
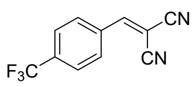

3a

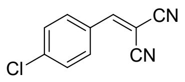
2-benzylidenemalononitrile (**3a**) was prepared as a white solid (purification by flash column chromatography: 10% EA in PE, 97% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.78 (s, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H).


3b

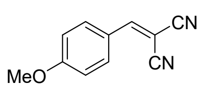
2-(4-methylbenzylidene)malononitrile (**3b**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 2.46 (s, 3H).


3c

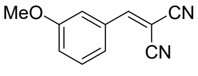
2-(4-(trifluoromethyl)benzylidene)malononitrile (**3c**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 2H).


3d

2-(4-chlorobenzylidene)malononitrile (**3d**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.73 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H).

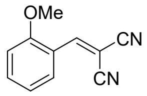

3e

2-(4-methoxybenzylidene)malononitrile (**3e**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.65 (s, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H).



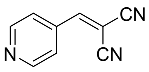
3f

2-(3-methoxybenzylidene)malononitrile (**3f**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 (s, 1H), 7.51 – 7.37 (m, 3H), 7.17 (dt, *J* = 7.5, 2.4 Hz, 1H), 3.86 (s, 3H).



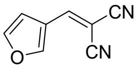
3g

2-(2-methoxybenzylidene)malononitrile (**3g**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (s, 1H), 8.18 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.4, 1.6 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.99 (dd, *J* = 8.5, 1.0 Hz, 1H), 3.93 (s, 3H).



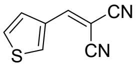
3h

2-(pyridin-4-ylmethylene)malononitrile (**3h**) was prepared as a red solid (purification by flash column chromatography). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.85 (d, *J* = 6.3 Hz, 2H), 7.80 (s, 1H), 7.66 (d, *J* = 6.2 Hz, 2H).



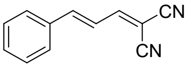
3i

2-(furan-3-ylmethylene)malononitrile (**3i**) was prepared as a red solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (t, *J* = 1.2 Hz, 1H), 7.70 (s, 1H), 7.59 (s, 1H), 7.19 (d, *J* = 2.0 Hz, 1H).



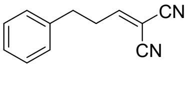
3j

2-(thiophen-3-ylmethylene)malononitrile (**3j**) was prepared as a red solid (purification by flash column chromatography). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.84 – 7.68 (m, 2H), 7.50 (dd, *J* = 5.2, 2.9 Hz, 1H).



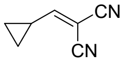
3k

(*E*)-2-(3-phenylallylidene)malononitrile (**3k**) was prepared as a yellow solid (purification by flash column). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.68 – 7.59 (m, 3H), 7.54 – 7.45 (m, 3H), 7.35 – 7.27 (m, 2H).



3l

2-(3-phenylpropylidene)malononitrile (**3l**) was prepared as a white solid (purification by flash column). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (q, *J* = 7.3 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 3.03 – 2.87 (m, 4H).

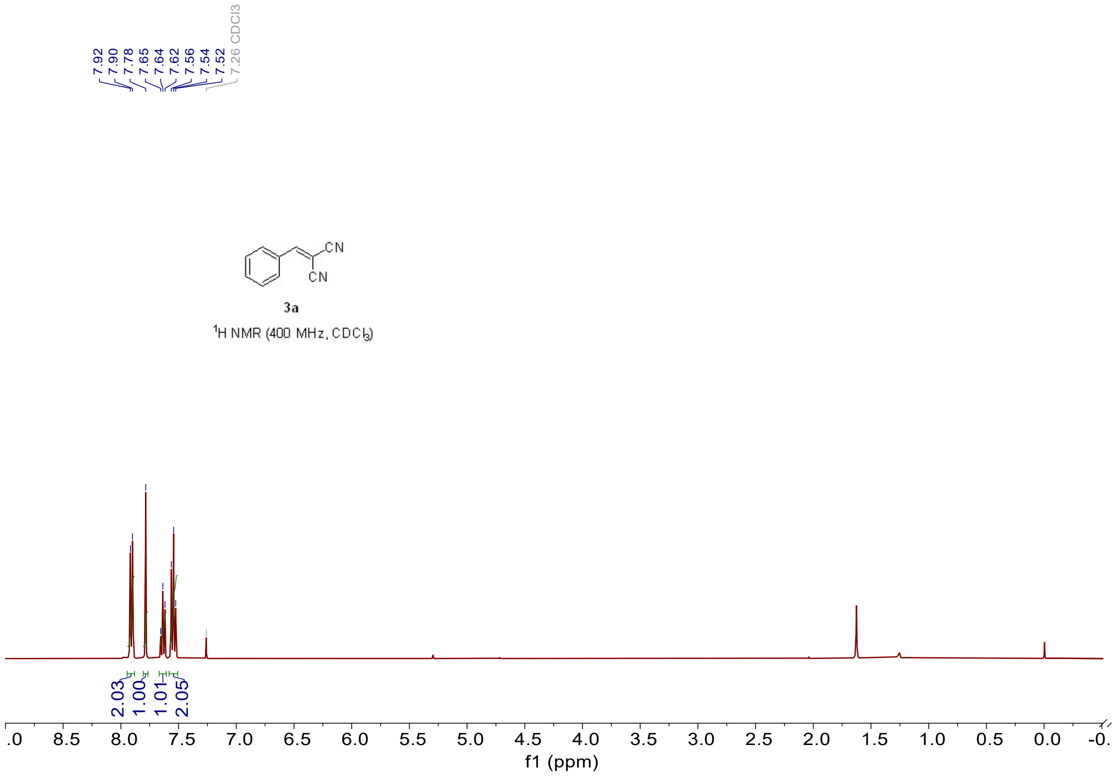


3m

2-(cyclopropylmethylene)malononitrile (**3m**) was prepared as a white solid (purification by flash column chromatography). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.63 (d, J = 11.3 Hz, 1H), 2.24 – 2.05 (m, 1H), 1.52 – 1.37 (m, 2H), 1.14 – 0.99 (m, 2H).

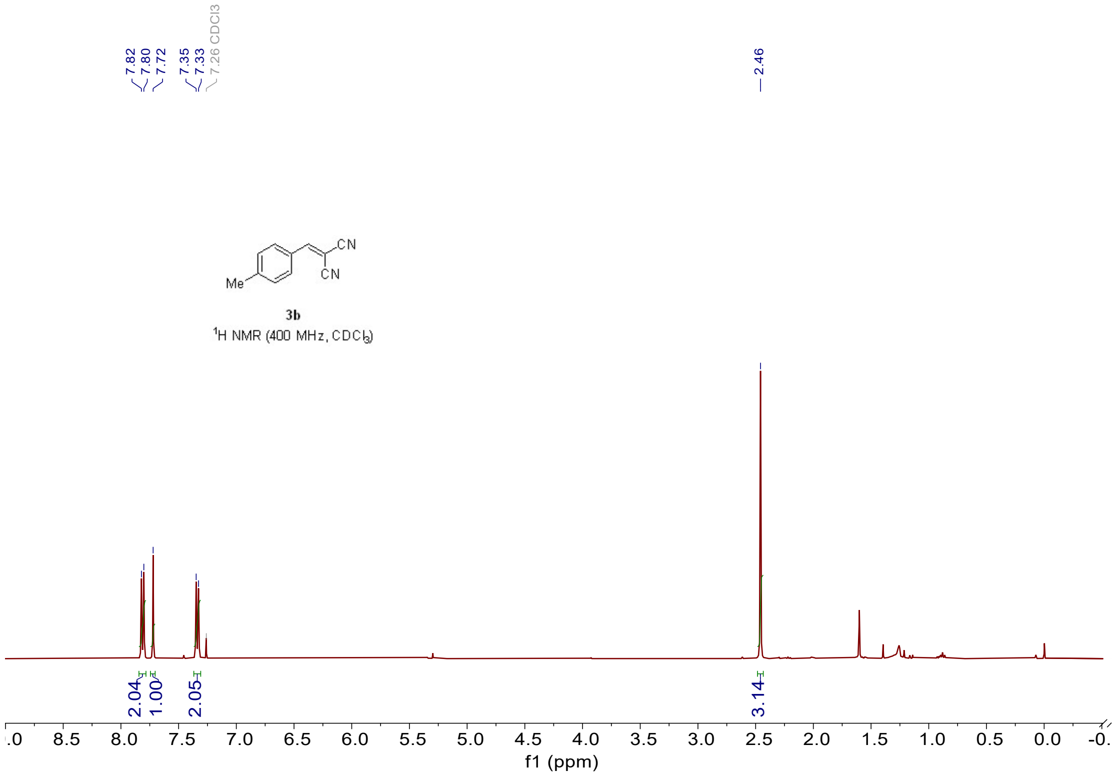
References

1. G. Deng, S. Malola, P. Yuan, X. Liu, B. K. Teo, H. Häkkinen and N. Zheng, *Angewandte Chemie International Edition*, 2021, **60**, 12897-12903.
2. C. di Nicola, C. Pettinari, M. Ricciutelli, B. W. Skelton, N. Somers and A. H. White, *Inorganica Chimica Acta*, 2005, **358**, 4003-4008.



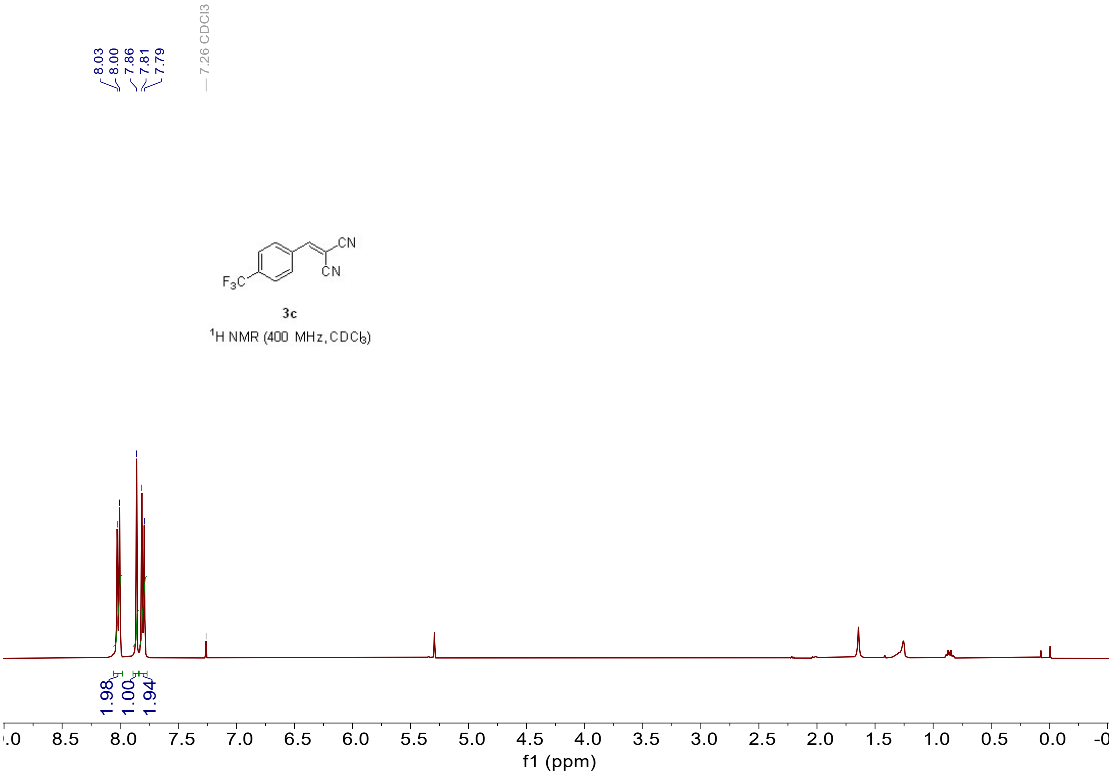
3a

^{1}H NMR (400 MHz, CDCl$_3$)



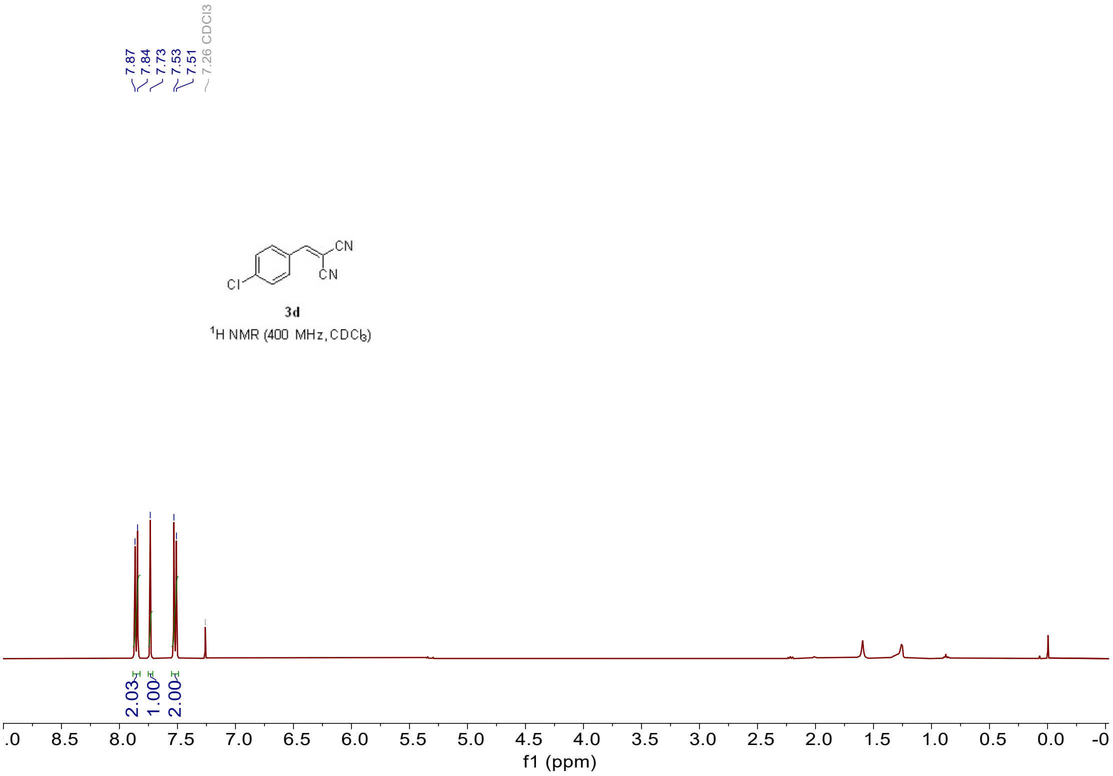
3b

^{1}H NMR (400 MHz, CDCl$_3$)



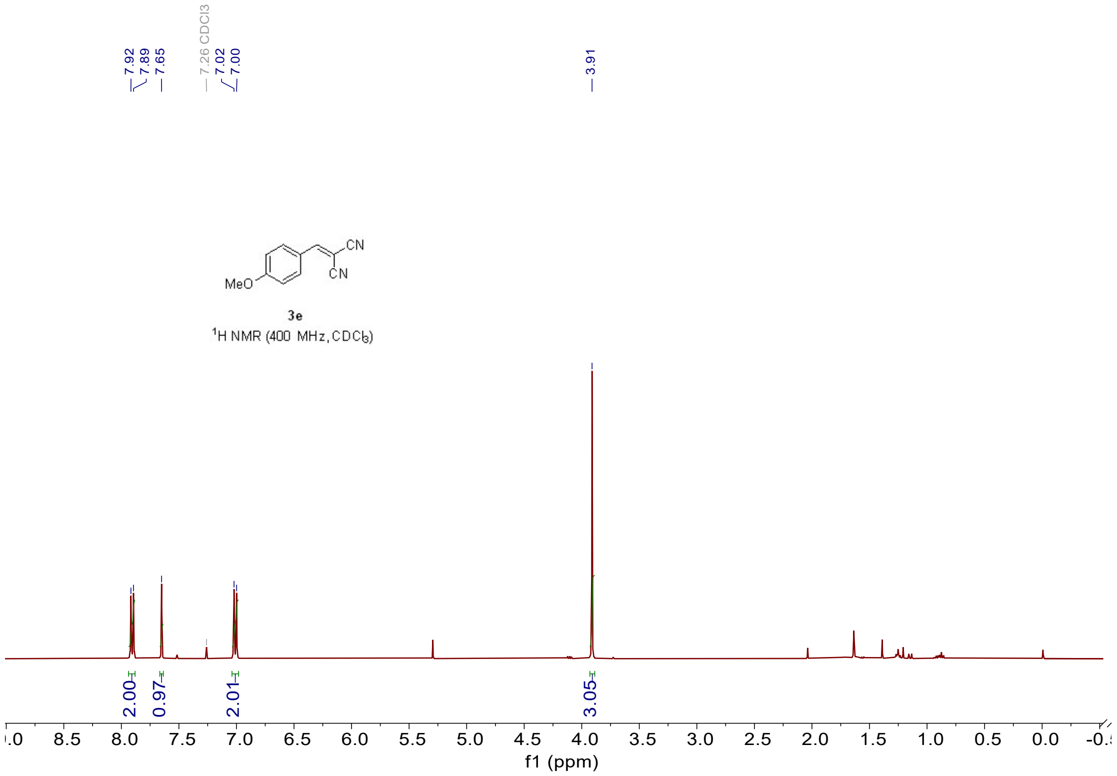
3c

^{1}H NMR (400 MHz, $CDCl_3$)



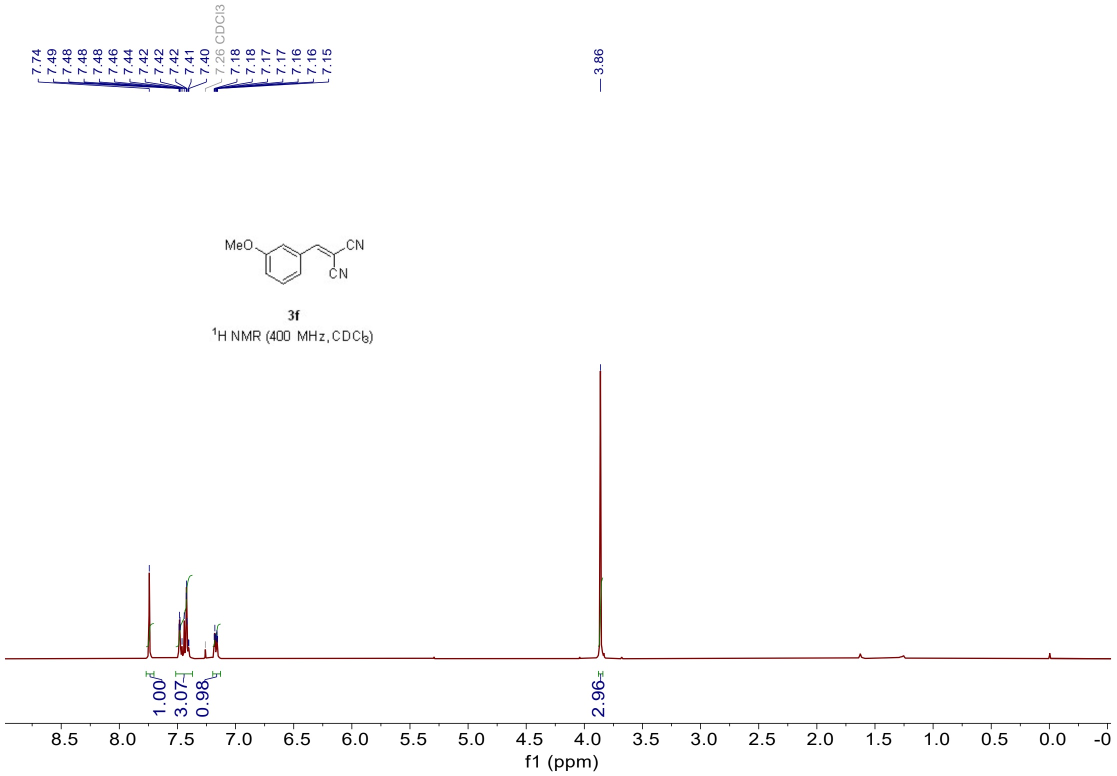
3d

^{1}H NMR (400 MHz, $CDCl_3$)



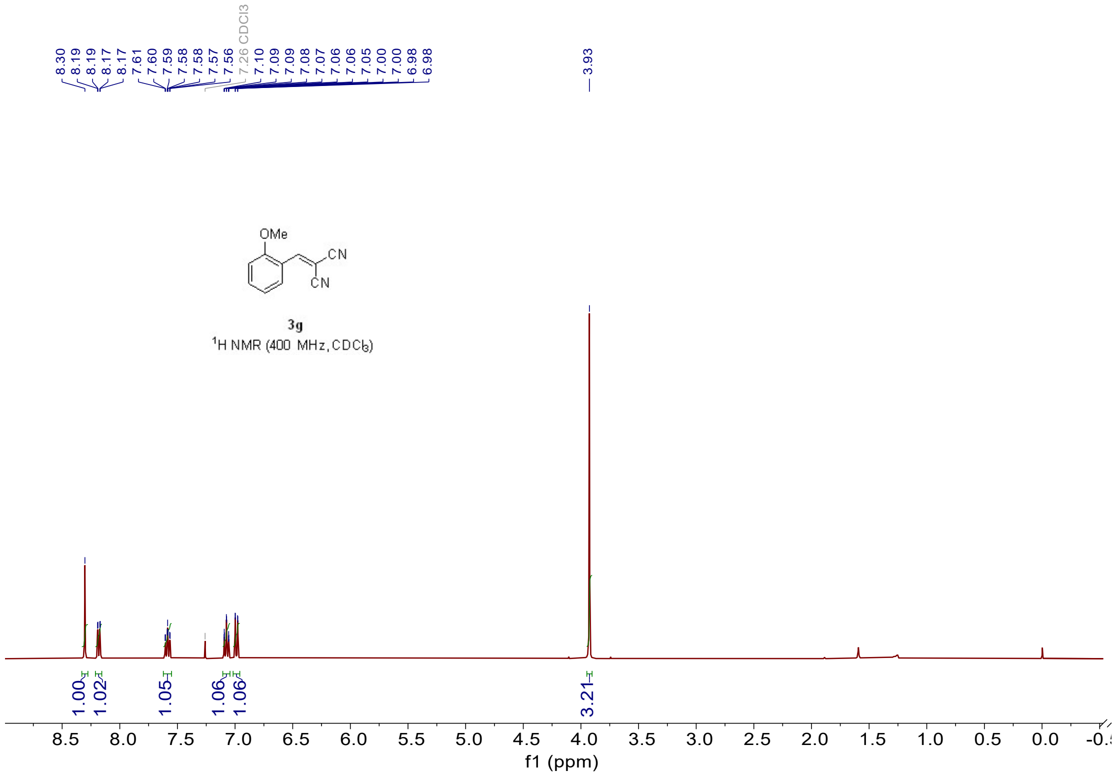
3e

^{1}H NMR (400 MHz, $CDCl_3$)



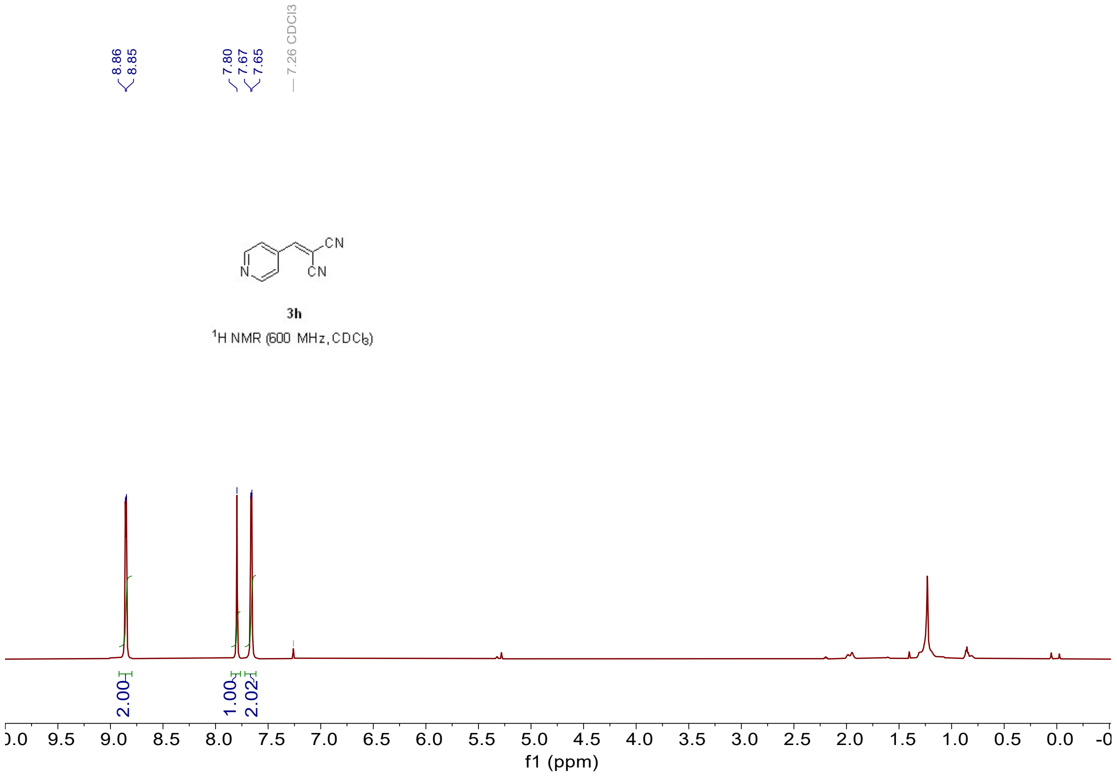
3f

^{1}H NMR (400 MHz, $CDCl_3$)



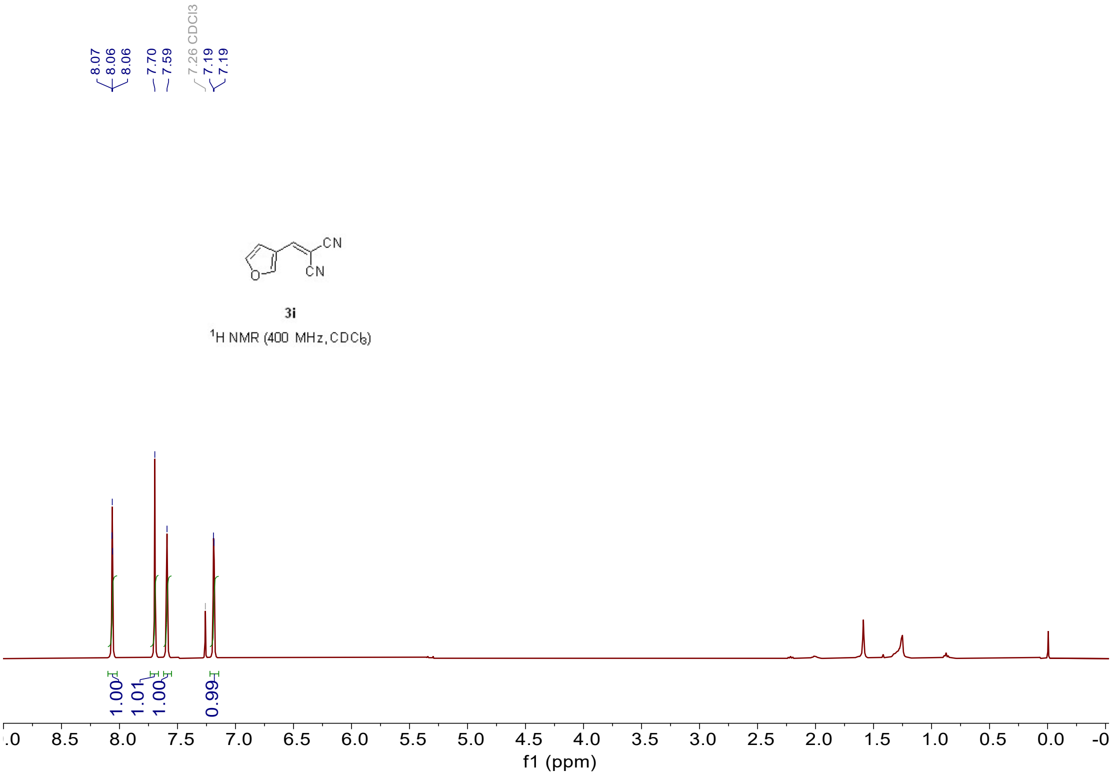
3g

^{1}H NMR (400 MHz, CDCl$_3$)

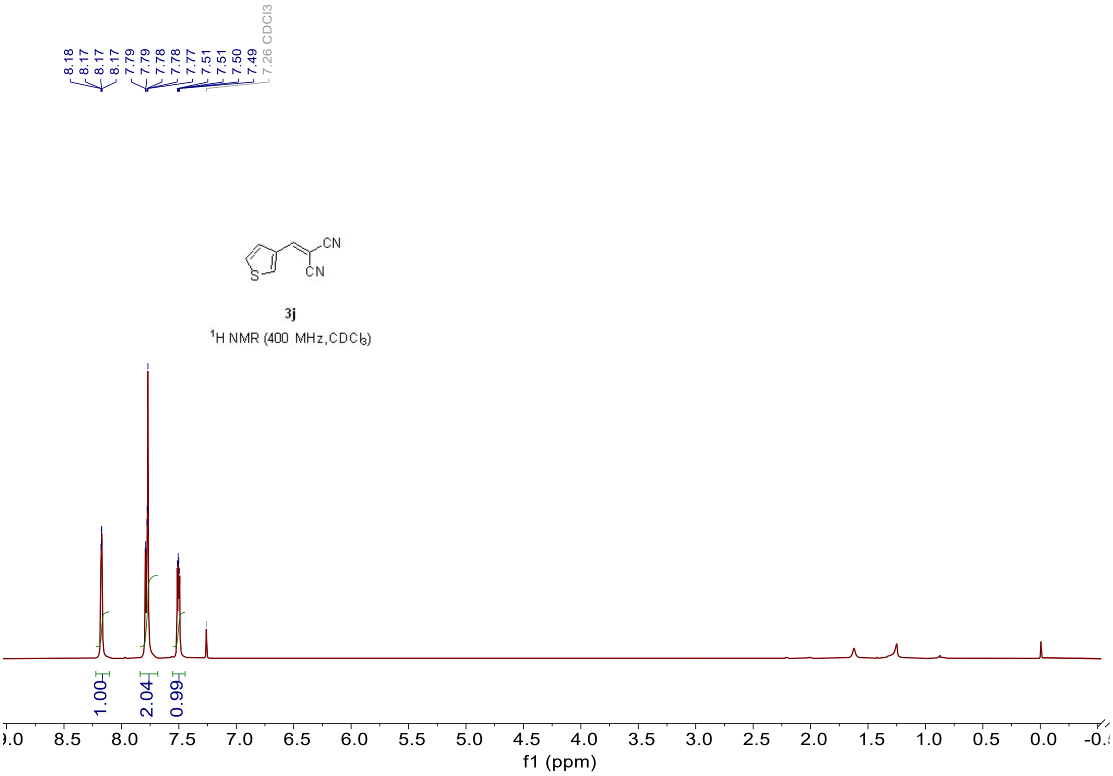


3h

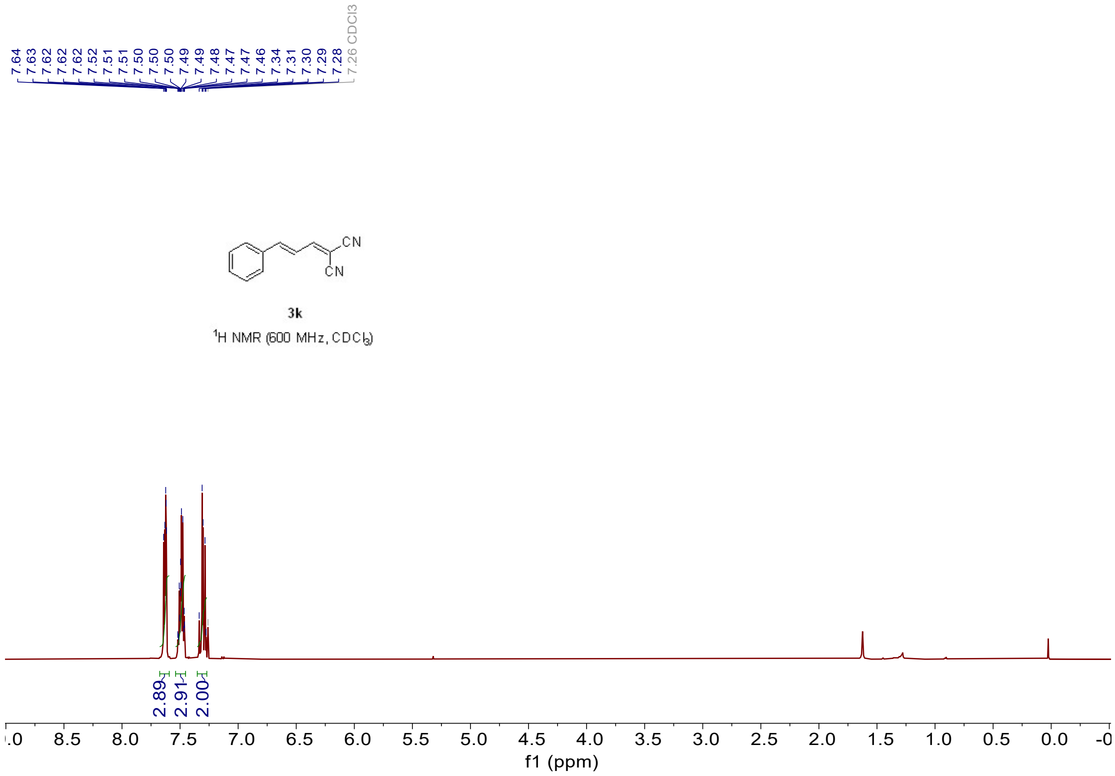
^{1}H NMR (600 MHz, CDCl$_3$)


3i

^1H NMR (400 MHz, $CDCl_3$)

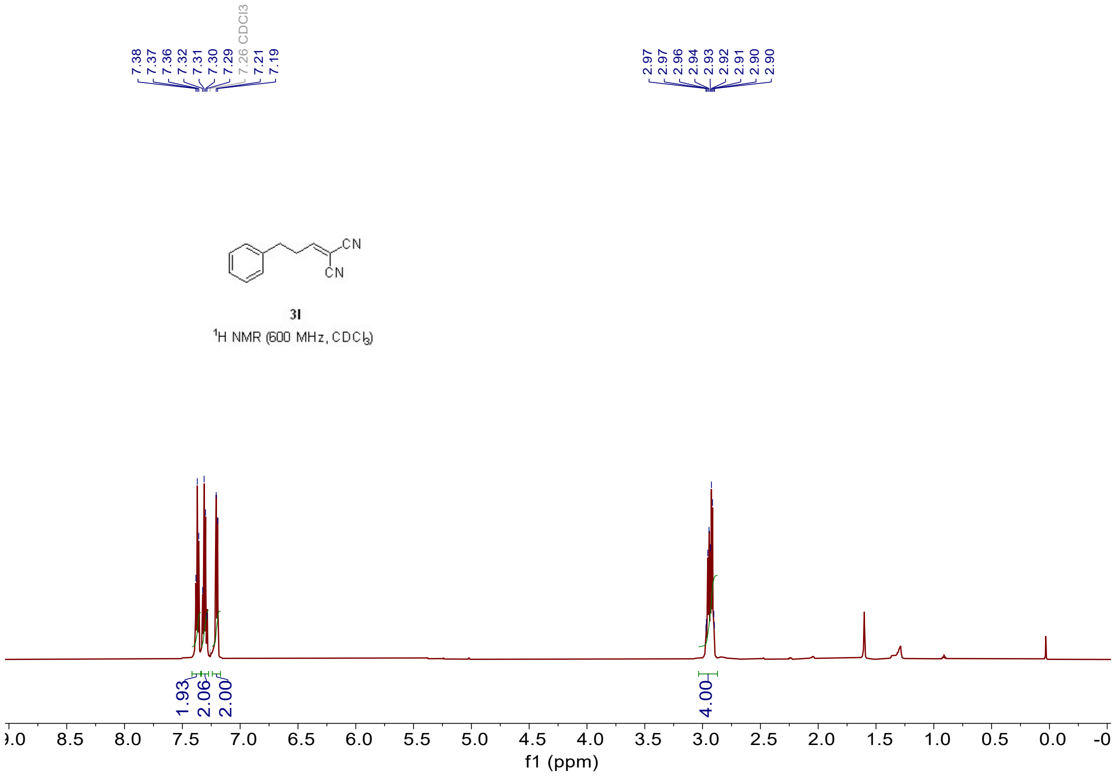

3j

^1H NMR (400 MHz, $CDCl_3$)



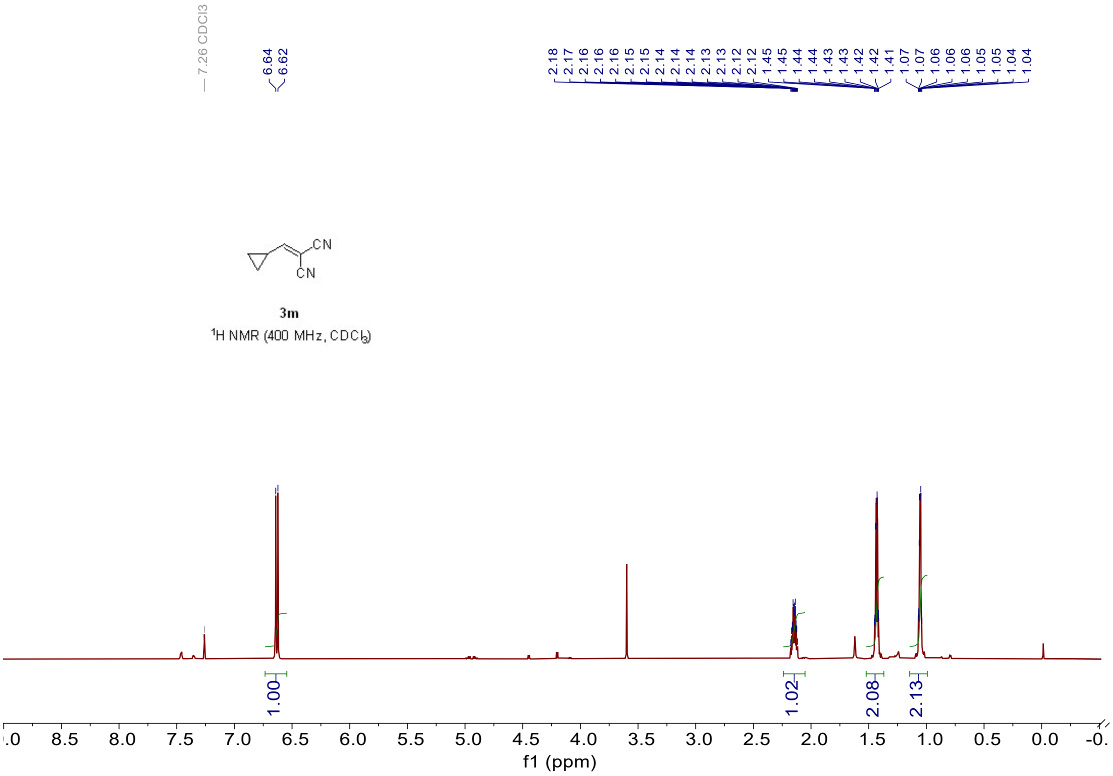
3k

^{1}H NMR (600 MHz, CDCl$_3$)



3l

^{1}H NMR (600 MHz, CDCl$_3$)



3m

^{1}H NMR (400 MHz, $CDCl_3$)