Mechanism of Copper(I)-Catalyzed 5-Iodo-1,2,3-triazole Formation From Azide and Terminal Alkyne

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Supporting Information

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1) Additional Figures

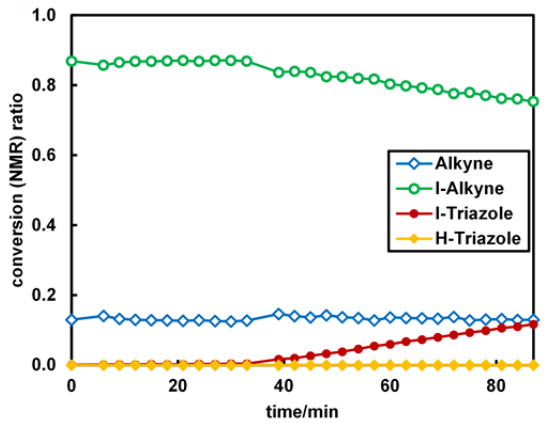

Figure S1. The non-chelating benzyl azide reacted much slower than 2-picolyl azide under the same conditions. The reaction components were dissolved in CD_3CN (0.5 mL) in the following order: TEA (20 mM), DCM (2.5 mM, internal standard), LiI (40 mM), alkyne **3** (10 mM, blue open diamonds), and $Cu(ClO_4)_2{\cdot}6H_2O$ (20 mM). Benzyl azide (10 mM, not shown) was added after the first spectrum was taken. Iodoalkyne (green open circles) formation was instantaneous before the addition of benzyl azide. TBTA (1.0 mM) was added at the 36-min mark, which prompted the production of iodotriazole product (garnet filled circles). No protiotriazole (solid gold diamonds) was observed.

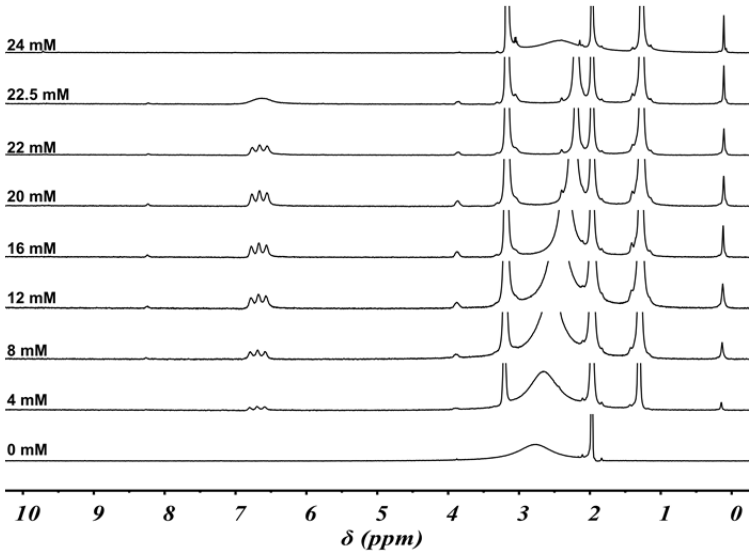

Figure S2. The origin of the broad triplet at 6.7-6.9 ppm, which acts as an indication of a condition detrimental to iodotriazole formation. ^1H NMR (CD_3CN, 500 MHz) spectra of $Cu(ClO_4)_2{\cdot}6H_2O$ (10 mM) in the presence of TEA (concentrations marked on the left margin).

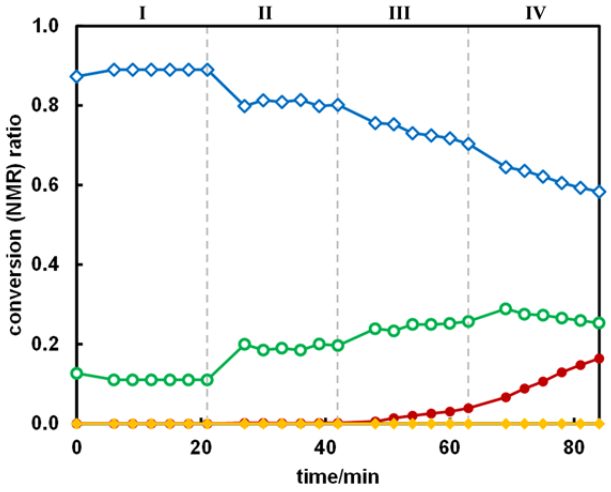

Figure S3. The effect of LiI on the outcome of the reaction (selected ^{1}H NMR spectra are shown in Figure 7). The conversion ratio, calculated based on the formulas in the caption of Figure 5, of alkyne **3** (blue open diamonds), iodoalkyne **4** (green open circles), and iodotriazole **6** (garnet filled circles). Initial concentrations: alkyne **3** (10 mM), LiI (20 mM), $Cu(ClO_4)_2{\cdot}6H_2O$ (20 mM), and TEA (20 mM). Azide **1** (10 mM, not shown) was added after the first datum point was taken. [LiI] was increased to 36, 50, 62 mM at the end of sections I, II, and III, respectively. The side product protiotriazole (gold filled diamonds) was not observed in this experiment.

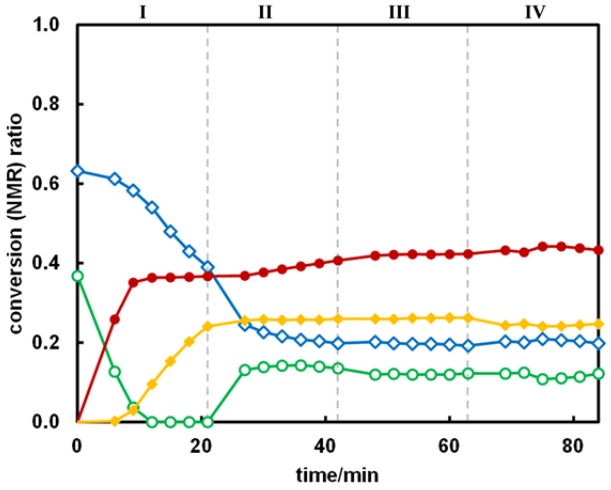

Figure S4. The effect of $Cu(ClO_4)_2{\cdot}6H_2O$ on the outcome of the reaction. The conversion ratio, calculated based on the formulas in the caption of Figure 5, of alkyne **3** (blue open diamonds), iodoalkyne **4** (green open circles), iodotriazole **6** (garnet filled circles), and protiotriazole **7** (gold filled diamonds). Initial concentrations: alkyne **3** (10 mM), LiI (40 mM), $Cu(ClO_4)_2{\cdot}6H_2O$ (5 mM), and TEA (15 mM). Azide **1** (10 mM, not shown) was added after the first datum point was taken. [$Cu(ClO_4)_2{\cdot}6H_2O$] was increased to 10, 14, 18 mM at the end of sections I, II, and III, respectively.

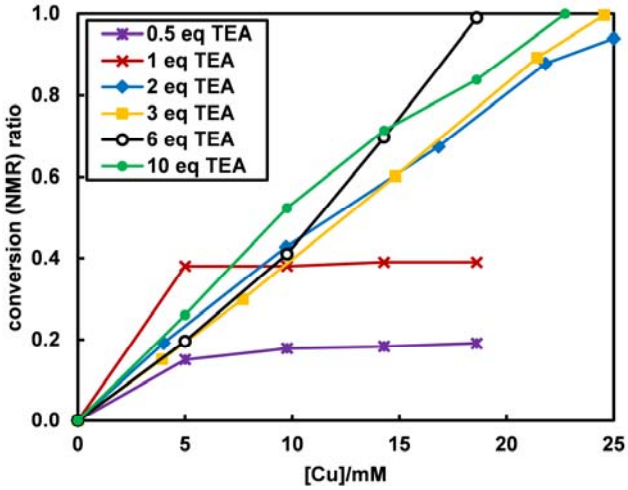

Figure S5. The effects of $Cu(ClO_4)_2{\cdot}6H_2O$ and TEA on iodoalkyne (**4**) formation. Concentrations: alkyne **3** (10 mM), LiI (40 mM), $Cu(ClO_4)_2{\cdot}6H_2O$ (0-25 mM), and TEA (5 mM purple stars, 10 mM garnet crosses, 20 mM blue diamonds, 30 mM gold squares, 60 mM black open circles, 100 mM green filled circles).

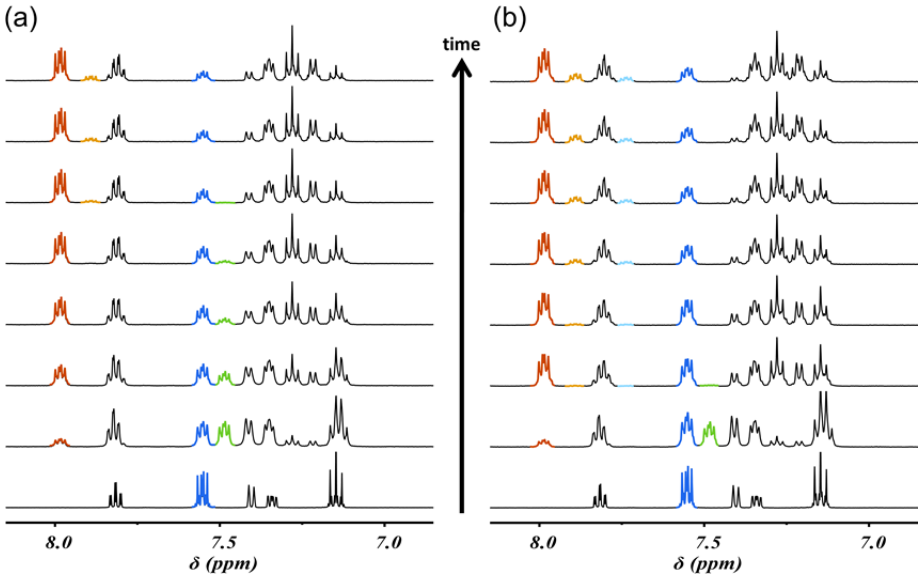

Figure S6. ^{1}H NMR spectra over time of the reaction shown in (a) Figure 10a, alkyne **3** (blue), iodoalkyne **4** (green), iodotriazole **6** (garnet), and protiotriazole **7** (gold); (b) Figure 10c; allyl iodide (25 µL, 200 mM) was included in the initial mixture and the corresponding allyltriazole (light blue) was observed. The first spectra (the bottom ones in 'a' and 'b') were taken before $Cu(ClO_4)_2{\cdot}6H_2O$ was added to initiate the reaction.

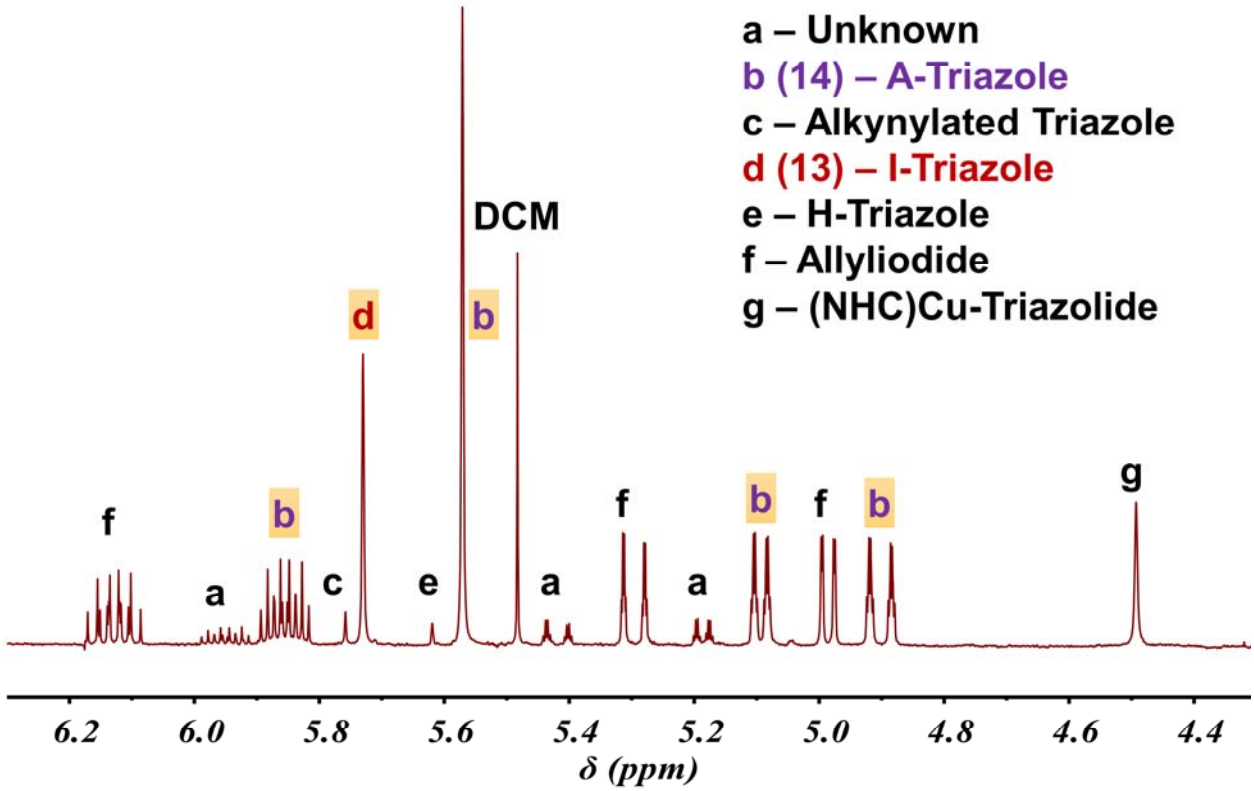

Figure S7. A section of the ^{1}H NMR spectrum of the reaction mixture ([Cu^{I}(NHC)(triazolide)] **12** (10 mM), iodoalkyne **4** (10 mM), and allyl iodide (10 mM) in CD_3CN with 12.5 (v/v)% THF at rt) taken at the 3-h point. The time course data is shown in Figure 11 in the text. Seven species (a-g) were observed.

2) ^{1}H and ^{13}C NMR Spectra of New Compounds

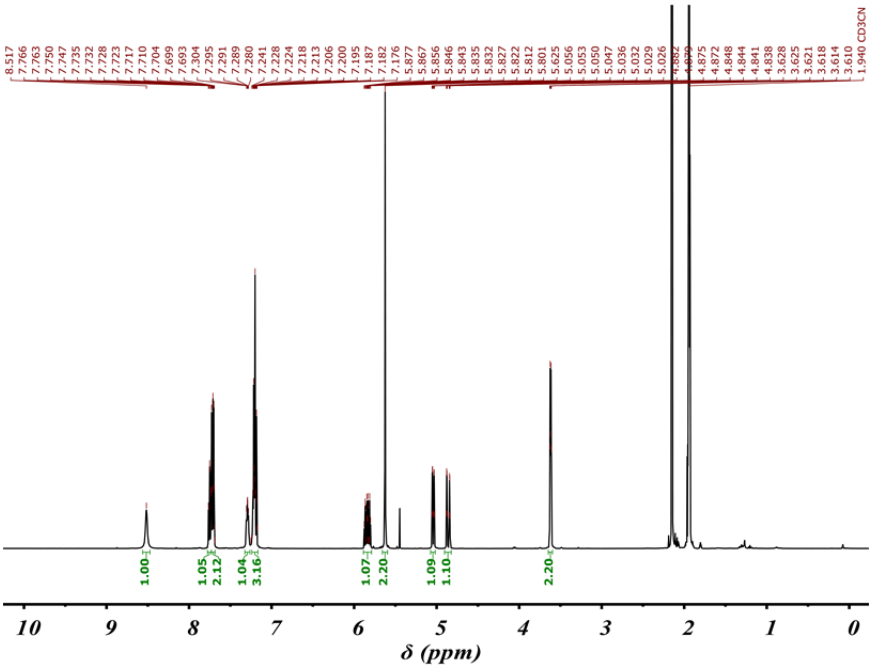

Figure S8. ^{1}H NMR (CD_3CN, 500 MHz) spectrum of compound **11.**

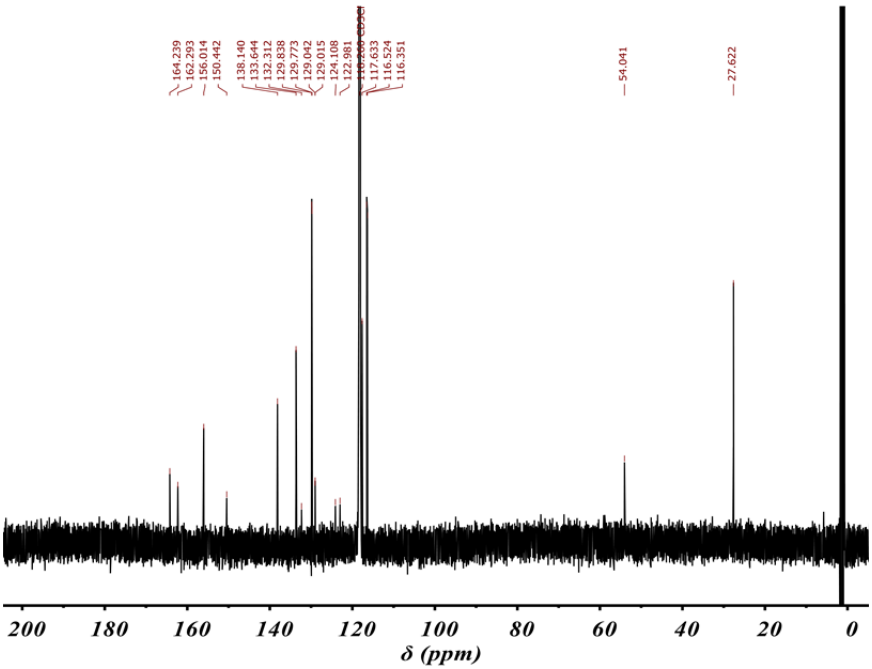

Figure S9. ^{13}C NMR (CD_3CN, 125 MHz) spectrum of compound **11.**

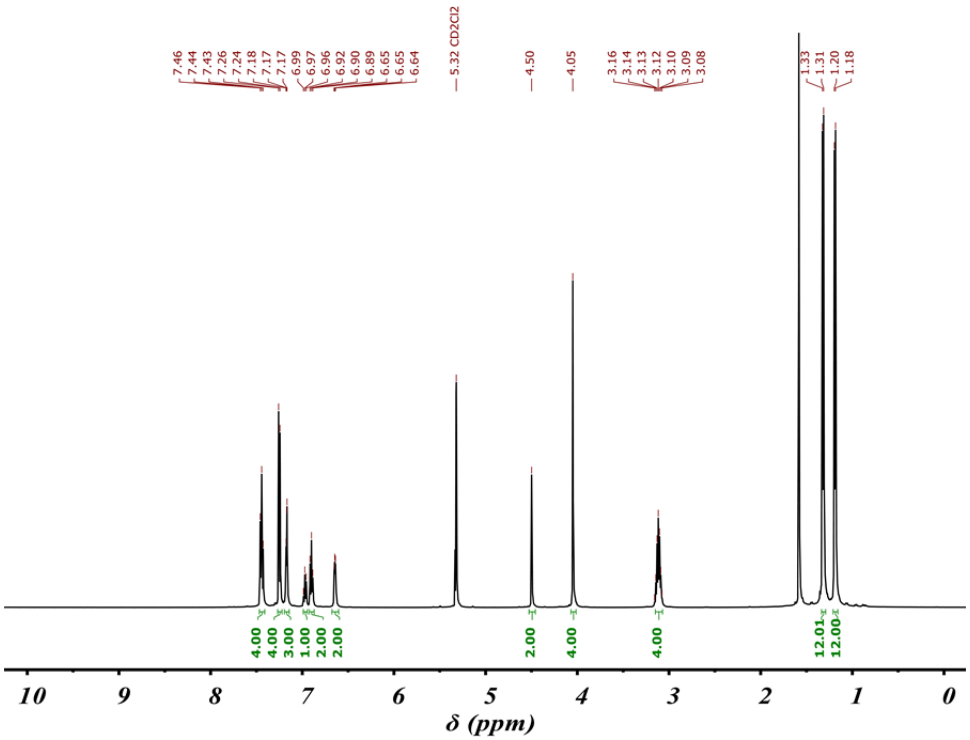

Figure S10. ^{1}H NMR (CD_2Cl_2, 500 MHz) spectrum of compound **12.**

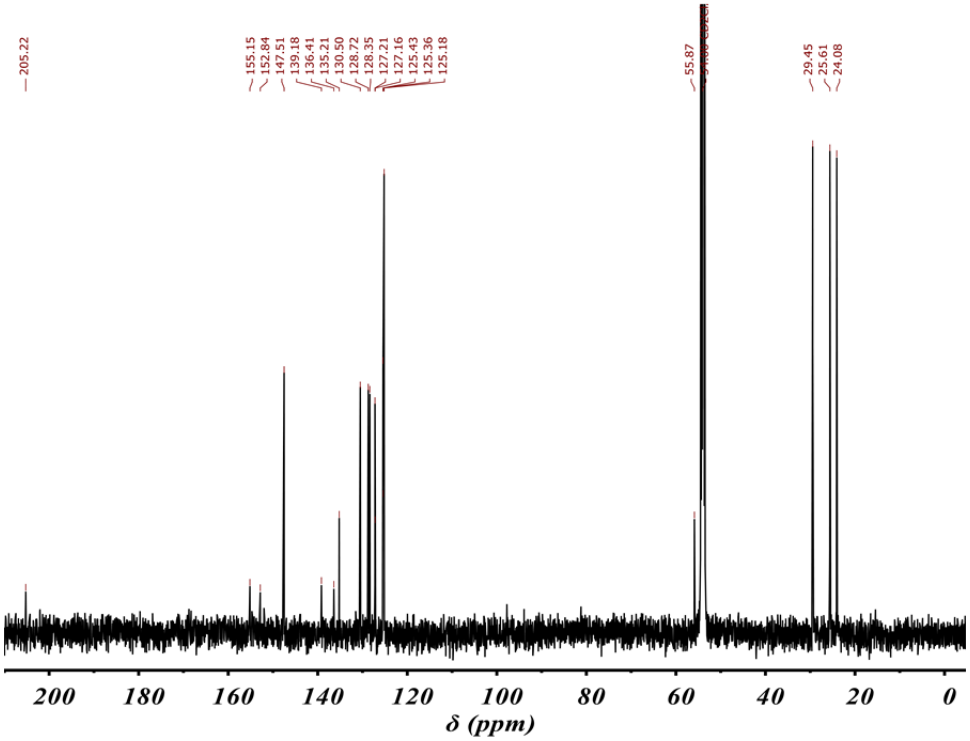

Figure S11. ^{13}C NMR (CD_2Cl_2, 125 MHz) spectrum of compound **12.**

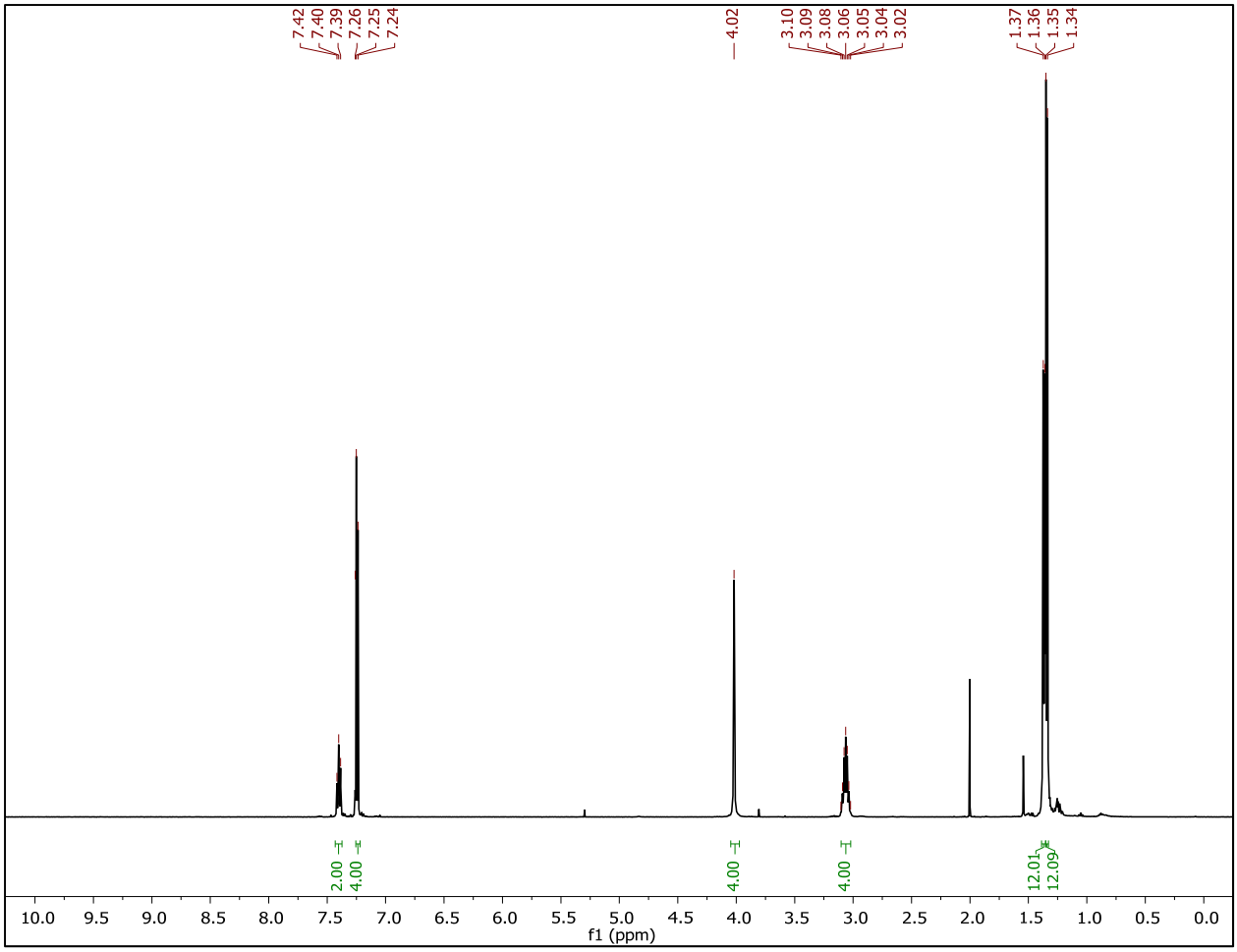

Figure S12. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **17.**

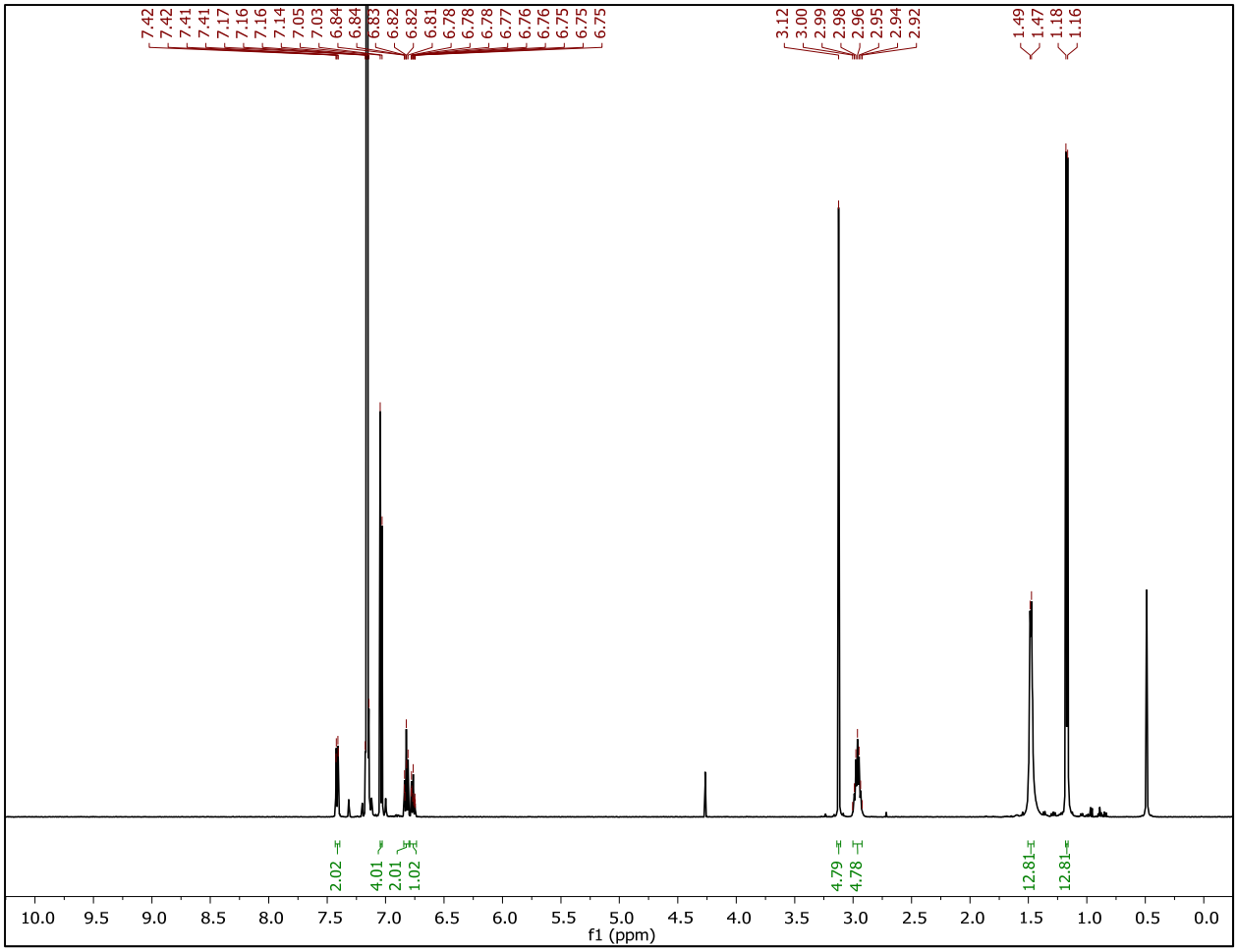

Figure S13. ^{1}H NMR (C_6D_6, 500 MHz) spectrum of compound **18.**