

## Ultrasound Assisted Nitratobis(triphenyl phosphine) Copper(I) Catalyzed Conjugate Addition of Alkyl or Aryl Bromides to $\alpha,\beta$ -Unsaturated Cyanoester

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The  $\alpha,\beta$ -unsaturated cyanoester was obtained from *p*-methoxy benzaldehyde and ethyl cyano acetate by reported method. The conjugated addition products were synthesized from alkyl or aryl bromides and  $\alpha,\beta$ -unsaturated cyanoester in the presence of 10 mol % Cu(I) catalyst in high yields within 17-21 min under ultrasound irradiation.

**Keywords:** Conjugate addition, Cyanoester, Cu(I) catalyst, Bromides, Ultrasound irradiation.

### INTRODUCTION

Ultrasound irradiation was first time introduced by Loomis and Richards [1]. Ultrasound mediated conjugate addition reaction in aqueous medium was developed by Luche and co-workers [2,3]. Ultrasound has increasingly been used in organic synthesis in the last three decades. Ultra sonication has been used to enhance reaction rates for a large number of classical organic reactions [4]. In Michael reaction, a conjugate addition reaction of nucleophiles to unsaturated carbonyl compounds requires basic or acidic conditions [5].

The sonochemical addition of alkyl halides to  $\alpha,\beta$ -unsaturated carbonyl compounds and nitriles in the presence of zinc-copper couple in aqueous medium has been developed. Organozinc reagents are very important in organometallic chemistry for the formation the products and transmetalation [6-9]. The organozinc halides undergo transmetalation by transition metal salt or complex such as copper, palladium, nickel, cadmium, etc. [10-13]. The conjugate addition of *n*-butyl and phenyl manganese bromide to *trans*-cinnamaldehyde and allylic bisacetate has been reported [14]. A conjugate addition of nucleophiles and indole to unsaturated carbonyl compounds in acidic or basic or Lewis acid catalyst were developed [15,16]. Recently, different varieties of catalysts such as ZnCl<sub>4</sub> [17], SnCl<sub>2</sub>·2H<sub>2</sub>O [18], NaAuCl<sub>2</sub>·2H<sub>2</sub>O [19], CeCl<sub>3</sub>·7H<sub>2</sub>O-NaI on silica gel [20], Pd(OAc)<sub>2</sub>

in CH<sub>3</sub>CN [21], InBr<sub>3</sub> [22], GaI<sub>3</sub> [23], SmI<sub>3</sub> [24], AuCl<sub>3</sub> [25], Cu(OTf)<sub>2</sub> immobilized in ionic liquids [26] and Mg, THF, NH<sub>4</sub>Cl [27-29] are used in conjugate addition. Also, ultrasound-assisted aza-Michael reaction in water was carried out as a green solvent [30]. In previous work, conjugate addition products were synthesized from heterocyclic bromides and 1,1-diacetate using Cu (I) catalyst [31]. Most of the reported method suffer from the serious drawbacks such as involvement of expensive reagents, acidic conditions, longer reaction time, environmental pollution and moderate yields.

In the present work, we have synthesized different conjugated addition products from alkyl or aryl bromides and  $\alpha,\beta$ -unsaturated cyanoester in the presence of nitratobis(triphenyl phosphine) copper(I) catalyst at room temperature within 17-21 min under ultrasound irradiation.

### EXPERIMENTAL

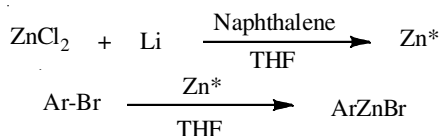
The boiling points were determined are uncorrected. IR spectra were determined on a Shimadzu Miracle 10 ATR instrument. NMR spectra were recorded on a Bruker 500 MHz spectrometer with CDCl<sub>3</sub> as the solvent and TMS as the internal standard. <sup>13</sup>C NMR spectra were recorded on Bruker 125 MHz spectrometer with CDCl<sub>3</sub> as the solvent. Column chromatography was conducted on silica gel 60 (70-230 mesh). Thin layer chromatography

graphy (TLC) was carried out on aluminum sheets precoated with silica gel. Ultrasound irradiation was performed in an ultrasonic cleaner with frequency of 33 KHz and a output power of 250 W. The reaction flasks were located in the maximum energy area of the cleaner.

#### Synthesis of nitratobis(triphenyl phosphine)copper(I):

Triphenyl phosphine (0.04 mol, 10.5 g) and  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (0.01 mol, 2.45 g) was added to 100 mL hot methanol. Immediately, Cu(II) dissolves and white suspension formed. This suspension was refluxed for 10 min and cooled to ambient temperature. After filtration, washed with ether, ethanol and dried. Recrystallization from methanol gave colourless solid. m.p. 232°C, soluble in DMF,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$  and THF. IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3047, 2924, 1538, 1479, 1464, 1384, 1295, 1096, 810, 741, 693.

**Preparation of Rieke zinc metal solution:** 100 mL two-neck RBF was flushed by nitrogen. In this flask, a mixture of 0.05 g lithium metal, 0.1 g naphthalene and 5 mL THF was stirred at room temperature to observed dark green colour solution. Then, 5 mL saturated solution of  $\text{ZnCl}_2$  in THF was added to above dark green colour solution by syringe and mixture was irradiated for 30 min. the black grey colour zinc metal solution observed in RBF (**Scheme-I**).



Scheme-I: Synthesis of Rieke zinc metal solution

**Preparation of alkyl or aryl zinc bromide and conjugate addition to  $\alpha,\beta$ -unsaturated cyanoester:** Saturated solution of LiCl (5 mL) in THF and 5 mmol alkyl or aryl bromide in 2 mL THF was added in zinc metal solution, then irradiated for 30 min, the formation of organozinc takes place, it was confirmed by TLC. Finally, 5 mmol cyanoester in 2 mL THF and 10 mol % Cu(I) catalyst were added in reaction mixture. The reaction mixture was sonicated for 15-25 min at room temperature. After completion of reaction, saturated  $\text{NH}_4\text{Cl}$  solution was added (2 x 5 mL). The solution extracted with diethyl ether, washed with brine solution (10 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The extract was then concentrated and the crude product was purified using column chromatography (silica gel, 80 % pet. ether/20 % EtOAc) to afford pure compound (**5a-i**). Products are easily identified by comparison of their spectroscopic data (**Scheme-II**).

#### Spectral data

##### Ethyl 2-cyano-3-(4-methoxy phenyl)-3-phenyl propanoate

(**5a**): Yellow liquid, m.f.  $\text{C}_{19}\text{H}_{19}\text{NO}_3$ , IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2971 (-C-H), 2240 (-CN), 1732 (-COO), 1591, 1514 (aromatic C=C), 1130 (-C-O).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.1 (t,  $\text{CH}_3$ ,

$J = 7.2$  Hz, 3H), 3.7 (s,  $\text{CH}_3$ ), 4.1 (q,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.2 (d, CH,  $J = 7$  Hz), 4.7 (d, CH,  $J = 7$  Hz), 6.8-7.4 (m, 9H, ArH).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 164.5, 158.1, 143.0, 135.5, 129.2, 128.2, 126.2, 166.8, 114.8, 60.8, 55.8, 40.8, 34.6, 14.1. Anal. Calcd. (found) % for  $\text{C}_{19}\text{H}_{19}\text{NO}_3$ : C, 73.77 (73.79); H, 6.19 (6.17); N, 4.53 (4.51); O, 15.52 (15.50).

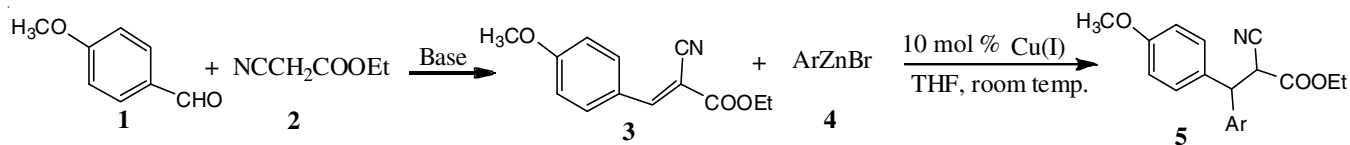
**Ethyl 2-cyano-3-(4-methoxy phenyl)-3-(pyridine-2-yl)propanoate (5b):** Yellow liquid, m.f.  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$ , IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2971 (-C-H), 2242 (-CN), 1733 (-COO), 1591, 1513, (aromatic C=C), 1110 (-C-O),  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.3 (t,  $\text{CH}_3$ ,  $J = 7.2$  Hz, 3H), 3.8 (s,  $\text{CH}_3$ ), 4.3 (q,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.4 (d, CH,  $J = 7$  Hz), 4.8 (d, CH,  $J = 7$  Hz), 6.9-8.4 (m, 8H, ArH).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 164.5, 163.4, 157.8, 148.3, 136.4, 132.5, 128.7, 122.9, 121.0, 116.8, 114.2, 60.8, 55.8, 40.8, 34.6, 14.1. Anal. Calcd. (found) % for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$ : C, 69.66 (69.64); H, 5.85 (5.87); N, 9.03 (9.00); O, 15.47 (15.49).

**Ethyl 2-cyano-3-(4-methoxyphenyl)-3-(thiophene-2-yl)propanoate (5c):** Yellow liquid, m.f.  $\text{C}_{17}\text{H}_{17}\text{NO}_3\text{S}$ , IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2978 (-C-H), 2242 (-CN), 1733 (-COO), 1589, 1512, (aromatic C=C), 1112 (-C-O).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.3 (t,  $\text{CH}_3$ ,  $J = 7.2$  Hz, 3H), 3.8 (s,  $\text{CH}_3$ ), 4.3 (q,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.4 (d, CH,  $J = 7$  Hz), 4.8 (d, CH,  $J = 7$  Hz), 6.8-7.4 (m, 7H, ArH).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 164.5, 157.8, 144.7, 132.5, 128.7, 127.0, 126.7, 125.5, 116.8, 114.2, 60.8, 55.8, 41.5, 35.3, 14.1. Anal. Calcd. (found) % for  $\text{C}_{17}\text{H}_{17}\text{NO}_3\text{S}$ : C, 64.74 (64.76); H, 5.43 (5.46); N, 4.44 (4.42); O, 15.22 (15.20); S, 10.17 (10.15).

**Ethyl 2-cyano-3-(1H-indol-5-yl)-3-(4-methoxyphenyl)propanoate (5d):** Yellow liquid, m.f.  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3$ , IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3383 (-NH) 2976 (-C-H), 2241 (-CN), 1732 (-COO), 1589, 1512, (aromatic C=C), 1112 (-C-O),  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.3 (t,  $\text{CH}_3$ ,  $J = 7.2$  Hz, 3H), 3.8 (s,  $\text{CH}_3$ ), 4.3 (q,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.4 (d, CH,  $J = 7$  Hz), 4.8 (d, CH,  $J = 7$  Hz), 6.9-8.0 (m, 9H, ArH), 9.9 (NH).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 164.5, 158.1, 141.2, 135.3, 133.0, 129.2, 128.7, 124.3, 119.8, 119.3, 116.8, 114.8, 111.6, 102.4, 60.8, 55.8, 40.8, 35.0, 14.1. Anal. Calcd. (found) % for  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3$ : C, 72.40 (72.43); H, 5.79 (5.77); N, 8.04 (8.02); O, 13.78 (13.80).

**Ethyl 2-cyano-3-(4-methoxy phenyl)-3-(pyrimidin-5-yl)propanoate (5e):** Yellow liquid, m.f.  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_3$ , IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2978 (-C-H), 2240 (-CN), 1733 (-COO), 1591, 1512, (aromatic C=C), 1114 (-C-O).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 1.3 (t,  $\text{CH}_3$ ,  $J = 7.2$  Hz, 3H), 3.8 (s,  $\text{CH}_3$ ), 4.3 (q,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 4.4 (d, CH,  $J = 7$  Hz), 4.8 (d, CH,  $J = 7$  Hz), 6.9-9.0 (m, 7H, ArH).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm:  $\delta$  163.0, 157.7, 154.3, 136.9, 133.9, 127.8, 116.1, 114.7, 62.3, 55.5, 40.3, 29.6, 14.1. Anal. Calcd. (found) % for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_3$ : C, 65.58 (65.56); H, 5.50 (5.48); N, 13.50 (13.52); O, 15.42 (15.40).

**Ethyl 2,4-dicyano-3-(4-methoxyphenyl)butanoate (5f):** Yellow liquid, m.f.  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$ , IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3010 (-C-H), 2238 (-CN), 1732 (-COO), 1589, 1512, (arom. C=C), 1174



Scheme-II: Synthesis of cyanoester

(-C-O). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm: 1.3 (t, CH<sub>3</sub>, *J* = 7.2 Hz, 3H), 3.0 (d, CH<sub>2</sub>), 3.8 (s, CH<sub>3</sub>), 4.3 (q, *J* = 7.2 Hz, CH<sub>2</sub>), 4.4 (dt, CH, *J* = 7 Hz), 4.7 (d, CH, *J* = 7 Hz), 6.9-7.9 (m, 4H, ArH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ ppm: 163.8, 154.4, 140.4, 127.8, 117.8, 116.0, 114.7, 62.4, 55.6, 40.6, 25.6, 21.61, 14.1. Anal. Calcd. (found) % for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 66.16 (66.18); H, 5.92 (5.90); N, 10.29 (10.26); O, 17.63 (17.62).

**Diethyl 2-cyano-3-(4-methoxyphenyl)pentanedioate (5g):** Pale Yellow liquid, m.f. C<sub>17</sub>H<sub>21</sub>NO<sub>5</sub>, IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 2980 (-C-H), 2239 (-CN), 1735 (-COO), 1591, 1512, (aromatic C=C), 1174 (-C-O). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm: 1.3 (t, CH<sub>3</sub>, *J* = 7.2 Hz, 6H), 2.6 (d, CH<sub>2</sub>), 3.8 (s, CH<sub>3</sub>), 4.2 (q, *J* = 7.2 Hz, CH<sub>2</sub>, 4H), 4.3 (dt, CH, *J* = 7 Hz), 4.8 (d, CH, *J* = 7 Hz), 6.9-7.3 (m, 4H, ArH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ ppm: 173.1, 164.5, 157.8, 129.9, 127.1, 116.8, 114.0, 61.3, 60.8, 55.8, 38.1, 35.8, 26.5, 14.1. Anal. Calcd. (found) % for C<sub>17</sub>H<sub>21</sub>NO<sub>5</sub>: C, 63.94 (63.93); H, 6.63 (6.65); N, 4.39 (4.40); O, 25.05 (25.07).

**Ethyl 2-cyano-3-(4-methoxyphenyl)-4-phenyl butanoate (5h):** Yellow liquid, m.f. C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>, IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 2976 (-C-H), 2241 (-CN), 1735 (-COO), 1591, 1512, (aromatic C=C), 1174 (-C-O). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm: 1.3 (t, CH<sub>3</sub>, *J* = 7.2 Hz, 3H), 2.7 (d, CH<sub>2</sub>), 3.8 (s, CH<sub>3</sub>), 4.2 (q, *J* = 7.2 Hz, CH<sub>2</sub>), 4.3 (dt, CH, *J* = 7 Hz), 4.8 (d, CH, *J* = 7 Hz), 6.9-7.4 (m, 9H, ArH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ ppm: 164.5, 157.8, 140.7, 138.0, 128.8, 128.1, 127.1, 126.0, 116.8, 114.0, 60.8, 55.8, 38.3, 38.2, 33.5, 14.1. Anal. Calcd. (found) % for C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>: C, 74.28 (74.30); H, 6.55 (6.53); N, 4.33 (4.35); O, 14.84 (14.82).

**Ethyl 2-cyano-3-(4-methoxyphenyl)-3-(5-nitrothiazol-2-yl)propanoate (5i):** Yellow liquid, m.f. C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S, IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 2980 (-C-H), 2238 (-CN), 1731 (-COO), 1589, 1511, (aromatic C=C), 1172 (-C-O). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ ppm: 1.3 (t, CH<sub>3</sub>, *J* = 7.2 Hz, 3H), 3.8 (s, CH<sub>3</sub>), 4.2 (q, *J* = 7.2 Hz, CH<sub>2</sub>), 4.3 (d, CH, *J* = 7 Hz), 4.8 (d, CH, *J* = 7 Hz), 6.9-9.0 (m, 5H, ArH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ ppm: 170.6, 164.5, 157.8, 151.1, 146.0, 132.5, 128.7, 116.8, 114.2, 60.8, 55.8, 40.5, 35.9, 14.1. Anal. Calcd. (found) % for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S: C, 53.18 (53.19); H, 4.18 (4.20); N, 11.63 (11.60); O, 22.14 (22.16); S, 8.87 (8.85).

## RESULTS AND DISCUSSION


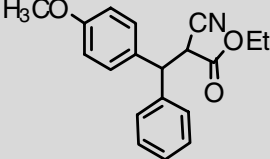

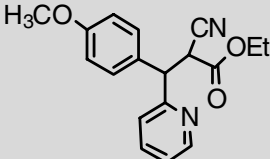

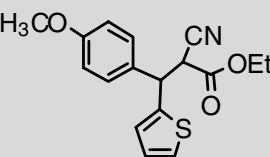
Table-1 shows the results obtained from using different reaction conditions for the synthesis of compound **5a**. In order to justify the significance of solvent in this process, the reaction was performed in the absence of catalyst where in the reaction failed to occur even at longer reaction time (Table-1, entry 1). The reaction was performed in the presence of catalyst and different solvents such as H<sub>2</sub>O, EtOH, DMF, DCM, where in the reaction failed to occur even at longer reaction time (Table-1, entry 2, 3, 4, 5, 6). In the presence of catalyst and CH<sub>3</sub>CN, the reaction occurred with isolated yield of compound **5a**, after 25 min of 29 % (Table-1, entry 8). Carrying out the reaction in the presence of catalyst and NMP (Table-1, entry 7) for 25 min led to a significant increase in the yield of compound **5a**. The reaction was then performed with catalyst such as THF and Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>, excellent yield (89 %) was obtained (Table-1, entry 9). It is also important to mention that when reactions were performed in H<sub>2</sub>O, EtOH, DMF, DCM, no product was found. From the results, catalyst such as Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> and THF was found to be optimum catalyst and solvent for this transformation.

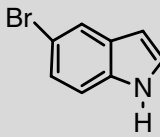
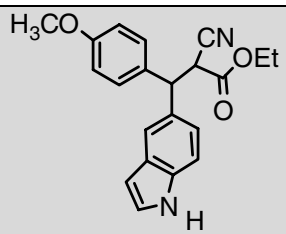
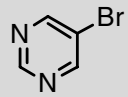
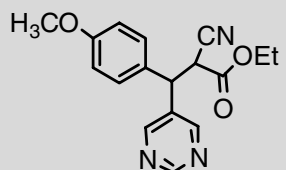
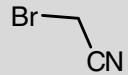
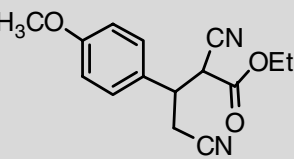
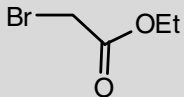
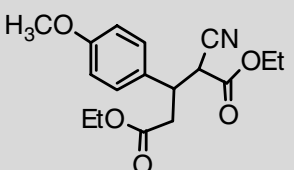
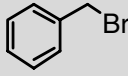
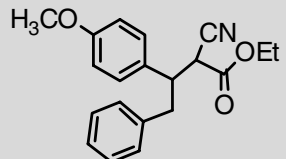
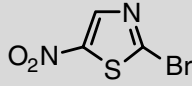
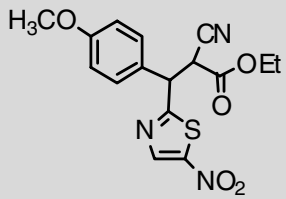
TABLE-1  
SCREENING OF SOLVENT FOR SYNTHESIS OF **5a**

Entry	Catalyst	Solvent	Time (min)	Yield (%)
1	Catalyst free	THF	30	–
2	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	H <sub>2</sub> O	30	–
3	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	MeOH	30	–
4	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	EtOH	30	–
5	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	DMF	30	–
6	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	DCM	30	–
7	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	NMP	25	48
8	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	CH <sub>3</sub> CN	25	29
9	Cu(PPh <sub>3</sub> ) <sub>2</sub> NO <sub>3</sub>	THF	20	89

From Table-2, In nitratobis(triphenyl phosphine)copper (I) [Cu(PPh<sub>3</sub>)<sub>2</sub>NO<sub>3</sub>] reaction proceeded smoothly under ultrasound irradiation and THF is efficient solvent for this synthesis

TABLE-2  
COPPER(I) CATALYZED CONJUGATE ADDITION OF ALKYL/ARYL ZINC BROMIDE TO  
α,β-UNSATURATED CYANOESTER UNDER ULTRASOUND IRRADIATION

Entry	Ar-Br	Product	Time (min)	Yield (%)
5a			20	89
5b			18	87
5c			21	86

5d			20	91
5e			17	88
5f			21	85
5g			17	91
5h			20	88
5i			19	87

of products. It is apparent that the reaction can be finished in shorter time to give excellent yield under ultrasound.

### Conclusion

In conclusion, we found that conjugated addition product were synthesized from alkyl or aryl bromides and cyanoester using  $\text{Cu}(\text{PPh}_3)_2\text{NO}_3$  as a catalyst under ultrasound irradiation to obtained excellent yields. The short reaction time, easy workup and high yields make this catalyst a more convenient alternative to the reported catalysts.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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