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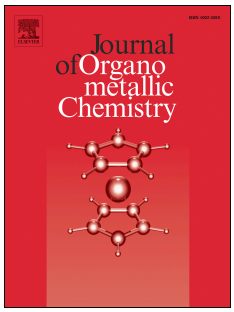

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Graphical abstract

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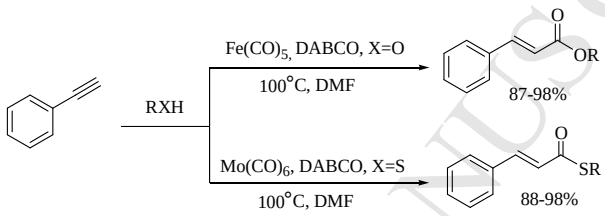

Regioselective hydrocarbonylation of phenylacetylene to α,β- unsaturated esters and thioesters with $Fe(CO)_5$ and $Mo(CO)_6$

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Abstract:A highly regioselective hydrocarbonylation of phenylacetylene with thiols and alcohols was developed using metal carbonyls/ diazabicyclo[2.2.2]octane (DABCO) system at 100 °C in DMF. The use of $Mo(CO)_6$ and thiols in the presence of DABCO was applied as an efficient Pd-free method for hydrothiocarbonylation of phenylacetylene into *trans*-α,β-cinamyl thioesters in excellent yields (88-98%). Similar reaction using $Fe(CO)_5$/ROH/DABCO system resulted into high yield synthesis of *trans*-α,β-cinamyl esters (87-98%). These reactions were conducted under mild reaction conditions without the need to use gaseous CO or any phosphine ligand and palladium catalyst.

Keywords: Hydroalkoxycarbonylation;Hydrothiocarbonylation; Phenylacetylene;$Fe(CO)_5$; $Mo(CO)_6$;diazabicyclo[2.2.2]octane (DABCO)

1. Introduction

Transition-metal catalyzed carbonylation is widely recognized as an important and attractive route for carbonyl-forming reactions in organic synthesis. In this regards, the oxidative carbonylation of terminal acetylenes is considered a practical approach for synthesis of α,β-unsaturated carboxylic acids and their derivatives [1,2]. Synthesis of cinnamic acid and its esters as important intermediates for the production of pharmaceuticals, fragrances, light-sensitive and electrically conductive materials and agrochemicals is still an important research subject [3]. For the first time, Reppe [4] reported the carbonylation of alkynes and alkenes in the presence of $Ni(CO)_4$ to produce unsaturated and saturated carboxylic acids and esters respectively. These reactions were performed under sever operating conditions (472–573 K and 10–100 MPa pressure) using reactor setup and the use of volatile and unstable material as catalyst. After that, various protocols for hydroesterification of alkyne were developed using CO as source of the carbonyl group in the presence of different catalytic systems such as $Pd(OAc)_2/PPh_3$/*p*-TsOH [5], $Pd(OAc)_2$/pyridine-2-carboxylic acid/PPh_3 [5], $Pd(OAc)_2$/dppb/H_2 [6], $Pd(OAc)_2$/dppb/BSA [7]. Recently, Mathur and co-workers [8] have reported the high yield synthesis of α,β-vinylester by the photochemical reaction of terminal acetylene with alcohols and gaseous carbon monoxide in the presence of iron pentacarbonyl as catalyst.

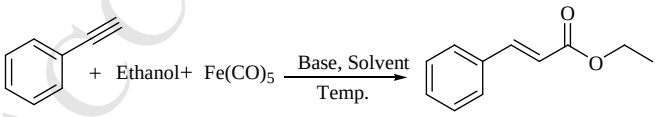
In comparison with hydroalkoxycarbonylation of terminal acetylenes with alcohols catalyzed by transition metals to give α,β- unsaturated esters, the reports on this reaction in the presence of thiols to give α,β- unsaturated thioesters are considerably less. The problem with this reaction in the presence of thiols is the poisoning of transition metal catalysts with organosulfure compounds. In this regard, a series of transition metal-catalyzed carbonylation–addition reactions of thiols to acetylenes in the presence of CO leading to α,β-unsaturated thioesters has been developed [9–12]. Later works on thiocarbonylation of acetylens have been performed using gaseous CO or CO/H_2 at high pressure of 3MPa to 600 psi at 110-120 ^oC [10, 11a, 12]. Apart from high pressure, these hydrocarbonylation reactions of alkynes, suffer from limitation of the use of CO as a highly lethal gas with a main concern of its handling [13]. In continuation of our recent work on the use of metal carbonyls as suitable source of CO gas in carbonylation reaction[14],

we now report an efficient Pd and phosphine-free method for the preparation of esters and thioesters of cinnamate from the reaction of phenylacetylene with alcohols and thiols using $Fe(CO)_5$ and $Mo(CO)_6$ as source of carbonyl group respectively.

2. Results and discussion

As mentioned above, the regioselective synthesis of *gem*- or *trans*-α,β-unsaturated esters have been achieved by direct carbonylation of phenylacetylene with alcohols in the presence of large amounts of gaseous carbon monoxide, catalyzed by transition metals in the presence of suitable ligands [1a]. In order to avoid using gaseous carbon monoxide, we decided to study the possibility of using metal carbonyls such as $Fe(CO)_5$, $W(CO)_6$, $Cr(CO)_6$, and $Mo(CO)_5$ for this important transformation. Initially, we selected iron pentacarbonyl as source of CO in the reaction with phenylacetylene as a model reaction. For the optimization of the reaction conditions, we first performed the hydroalkoxycarbonylation of phenylacetylene with ethanol in the presence of $Fe(CO)_5$ and the effect of different parameters were studied. In order to make easier and increase the possibility of CO releasing from $Fe(CO)_5$, we added some nitrogen compounds such as diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and *n*-Pr_3N. Initially, DBU was utilized to replace the CO group to form the DBU-iron carbonyl complex. The reaction was carried out at 100 °C in DMF as solvent and the desired product was obtained in moderate yield (Table 1, entry 1). Then DBU was substituted by DABCO and *n*-Pr_3N. The best result was obtained when we used DABCO as the complexing agent. Decreasing the amount of DABCO from three equimolar to two and one equimolar amount increased the reaction time from 0.5 h (Table 1, entry 3) to 2.5h and 6h respectively and also led to the production of side products (Table 1, entries 6,7). In the absence of DABCO, the performance of the reaction was not good and only 10% of the corresponding ester was obtained after 24h. We also studied the effect of different amount of alcohol on the progress of the reaction and observed that when the amount of ethanol was decreased from 4 to 2 and 1 equimolar, the reactions did not complete even after 12 h (Table 1, entries 3, 8, 9). The effect of other solvents such as diglyme, DMSO, xylene and toluene was also studied, but none of them were found to be as suitable as DMF. From this study, the result of entry 3 was found to be the optimum condition for this reaction. The effect of using catalytic amounts of $Fe(CO)_5$ was also investigated and observed that the reaction was not completed if its amount was reduced from 1.0 to 0.5 equivalent and nearly half of the starting material was recovered unchanged (Table 1, entry 14). Increasing the reaction temperature from 100 °C to 120°C did not have significant effect on the progress of the reaction.

Table 1. Optimization of different parameters for hydroalkoxycarbonylation of phenylacetylene.[a]



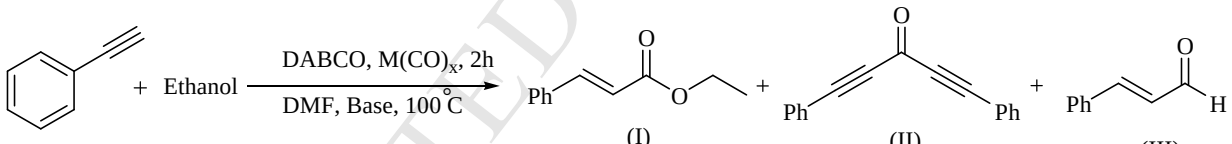
Entry	Base	Solvent	Temp. (° C)	Time (h)	Yield (%)[b]
1	DBU	DMF	100	2	47
2	*n*-Pr_3N	DMF	100	10	56
3	DABCO	DMF	100	0.5	95
4	*n*-Pr_3N	TBAB	110	3	52
5	DABCO	TBAB	110	3	70
6[c]	DABCO	DMF	100	2.5	75
7[c]	DABCO	DMF	100	6	65
8[d]	DABCO	DMF	100	12	25
9[d]	DABCO	DMF	100	12	40

10	K_2CO_3	DMF	100	2	60
11	NaOH	DMF	100	2	61
12	Cs_2CO_3	DMF	100	4	72
13	DABCO	DMSO	100	6	27
14	DABCO	diglyme	100	2.5	48
15	DABCO	toluene	Reflux	12	36
16	None	DMF	100	24	10
17	DABCO	xylene	100	24	Trace
18[e]	DABCO	DMF	100	10	10
19	DABCO	DMF	120	0.3	98

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Fe(CO)_5$, ethanol (4 mmol), Base (3 mmol), 2 mL of solvent.
[b] Isolated yield.
[c]The amount of DABCO are 2.0 and 1.0 mmol for entries 6 and 7 respectively.
[d]The amount of ethanol are 1.0 and 2.0 mmol for entries 8 and 9 respectively .
[e] The reaction was performed using 0.5 equivalent of $Fe(CO)_5$.

After optimizing the conditions for the reaction of phenylacetylene and ethanol with $Fe(CO)_5$, we then replaced $Fe(CO)_5$ with other metal carbonyls such as $W(CO)_6$, $Mo(CO)_6$ and $Cr(CO)_6$. The results of this study are shown in Table 2 (Entries 1-4). According to these results, the reaction in the presence of metal carbonyls other than $Fe(CO)_5$ did not give the desired carbonylated product (I). This reaction in the presence of $M(CO)_6$ [M=Cr, Mo, W] led to the formation of 1,5-diphenyl-1,4-pentadiyn-3-one (Table 2, product II) and when $Cr(CO)_6$ was used as CO source, small amounts of cinnamaldehyde was also formed. Moreover, when we investigated the hydroalkoxycarbonylation reaction of phenylacetylene in the presence of Pd(II), it was observed that the added catalyst doesn't have significant effect on the reaction time and yield% of the obtained product(Table 2, entry 5).

Table 2. Reaction of phenylacetylene with with ethanol in the presence of different metal carbonyls.[a]

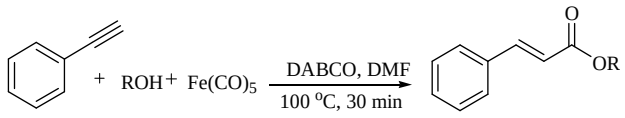


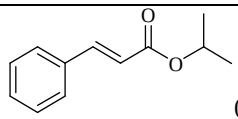
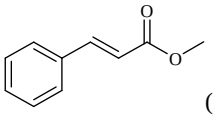
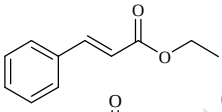
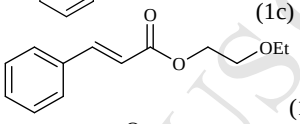
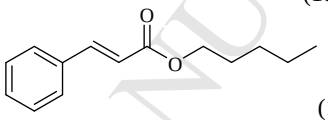
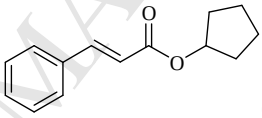
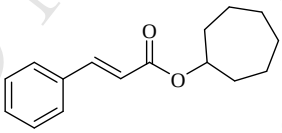
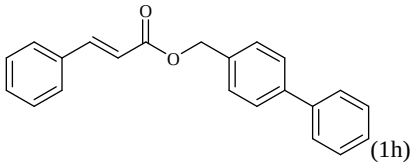
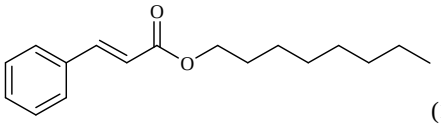
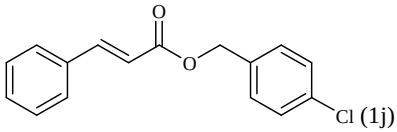
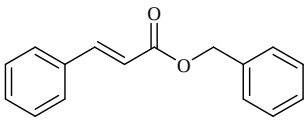
Entry	$M(CO)_x$	Catalyst/ Base	Isolated yield (%)
1	$Fe(CO)_5$	None/DABCO	95%[b] of I
2	$Mo(CO)_6$	None/DABCO	50% of II
3	$W(CO)_6$	None/DABCO -	35% of II
4	$Cr(CO)_6$	None/DABCO	55% of II+30% of III
5	$Fe(CO)_5$	$Pd(OAc)_2$/DABCO	94% of I

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $M(CO)_x$, 1.0 mmol of ethanol, 3.0 mmol of DABCO, 1.0 mmol of base and 2 mL of DMF at 100 °C.
[b] The reaction time is 30 min.

Having the optimized conditions, we then used different alcohols in the esterification reaction of phenylacetylene (Table 3). A wide range of alcohols including primary and secondary aliphatic alcohols reacted to give the desired product in high to excellent yields. The reaction of phenylacetylene and phenol derivatives did not proceed well to give the corresponding ester while the reaction with benzyl alcohol and 4-chlorobenzyl alcohol was performed completely and both reactions led to their corresponding vicinal α,β-vinylesters in excellent yields. The results of the carbonylation of phenylacetylene with different alcohols are summarized in Table 3. The obtained results of hydroalkoxycarbonylation of phenylacetylene with different alcohols showed excellent control of the regioselectivity for all of the products.

Table 3. Reaction of alcohols with phenylacetylene in the presence of iron pentacarbonyl.[a]



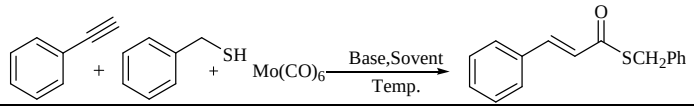
Entry	Alcohol	Product	Yield (%)[b]
1	$(CH_3)_2CHOH$	 (1a)	98
2	CH_3OH	 (1b)	96
3	CH_3CH_2OH	 (1c)	95
4	$EtO(CH_2)_2OH$	 (1d)	94
5	$CH_3(CH_2)_3CH_2OH$	 (1e)	95
6	$(CH_2)_4CHOH$	 (1f)	90
7	$(CH_2)_6CHOH$	 (1g)	90
8	4-biphenylCH_2OH	 (1h)	89
9	$CH_3(CH_2)_6CH_2OH$	 (1i)	96
10	4-Cl$PhCH_2OH$	 Cl (1j)	87
11	$PhCH_2OH$	 (1k)	90

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Fe(CO)_5$, 4.0 mmol of alcohol, 2.0 mmol of DABCO, and 2 mL of DMF at 100 °C.
[b] Isolated yield.

In continuation, we extended the applicability of this method for one-pot regioselective hydrothiocarbonylation of phenylacetylene. For this purpose, we selected the reaction of phenylacetylene

and benzyl mercaptan as a model reaction and studied the effect of different parameters such as the type and the amount of metal carbonyl, as well as the base as complexing agent, solvent and also temperature. The obtained results are shown in Table 4. Our observation showed that, the best result was obtained when the reaction was done with $Mo(CO)_6$ and DABCO in DMF at 100 °C.

Table 4. Optimization of different parameters for hydrothiocarbonylation reaction of phenylacetylene.[a]

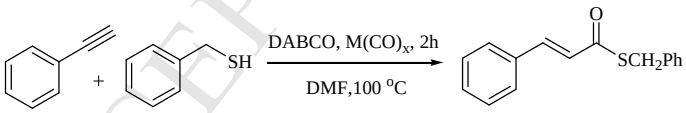


Entry	Base (mmol)	Solvent	Temp. (° C)	Time (h)	Yield[b] (%)
1	DBU	DMF	100	4	55
2	NBD	DMF	100	0.5	82
3	DABCO	DMF	100	15 min	92
4	*n*-Pr_3N	TBAB	100	8	52
5	DABCO	TBAB	100	6	70
6[c]	DABCO	DMF	100	45 min	92
7[c]	DABCO	DMF	100	2	60
8[d]	DABCO	DMF	100	2	45
9	DABCO	DMSO	100	6	35
10	DABCO	diglyme	100	3	45
11	DABCO	xylene	100	24	Trace
12	DABCO	toluene	reflux	24	Trace
13	DABCO	DMF	100	12	15[c]
14	DABCO	DMF	120	10 min	95

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Mo(CO)_6$, benzyl mercaptan (2.0 mmol), base (3.0 mmol), 2 mL of solvent.
[b] Isolated yield.
[c]The amount of DABCO are 2.0 and 1.0 mmol for entries 6 and 7 respectively.
[d]The amount of benzyl mercaptan is 1.0 mmol for entries 8.
[e] The reaction was performed using 0.5 equivalents of $Mo(CO)_6$.

As the obtained results show, similar reaction in the presence of other metal carbonyls, $M(CO)_6$ (M = Cr, W), and $Fe(CO)_5$ gave the desired product in lower yield (Table 5, Entries 2-4). For comparison, we also synthesized $Mo(CO)_5$DABCO complex and reacted it (one equimolar) with benzyl mercaptan under the optimized condition. The corresponding thioester was isolated in excellent yield (Table 5, Entry 5). This experiment shows that this complex can also be used as another solid source of generating CO for this transformation.

Table 5. Effect of different metal carbonyl in the reaction of phenylacetylene with benzyl mercaptan under the optimized condition.[a]

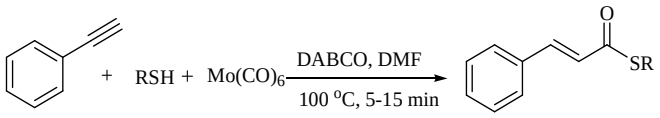


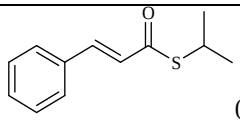
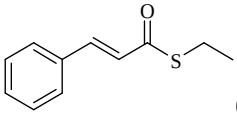
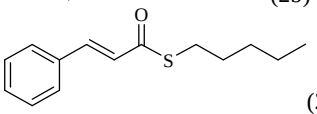
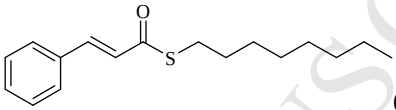
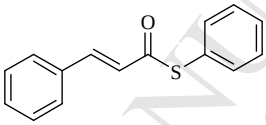
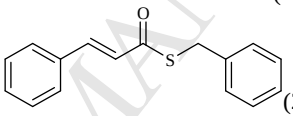
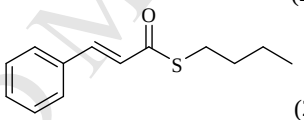
Entry	$M(CO)_x$	Isolated Yield(%)
1	$Mo(CO)_6$	92[b]
2	$Fe(CO)_5$	Trace
3	$W(CO)_6$	45
4	$Cr(CO)_6$	35
5	$Mo(CO)_5$DABCO	91[c]

[a]Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $M(CO)_x$, 2.0 mmol of benzyl mercaptan, 3.0 mmol of DABCO and 2 mL of DMF at 100 °C.
[b]The reaction time is 15 min.
[c] The reaction time is 60 min.

The optimized conditions were then applied for the thiocarbonylation of phenylacetylene with different alkyl- and aryl thiols. The results are summarized in Table 6. Hydrothiocarbonylation of phenylacetylene with alkyl thiols was found to be very fast and completed after 5 min. However, similar reaction of phenylacetylene with benzyl mercaptan and thiophenol were completed after 15 min.

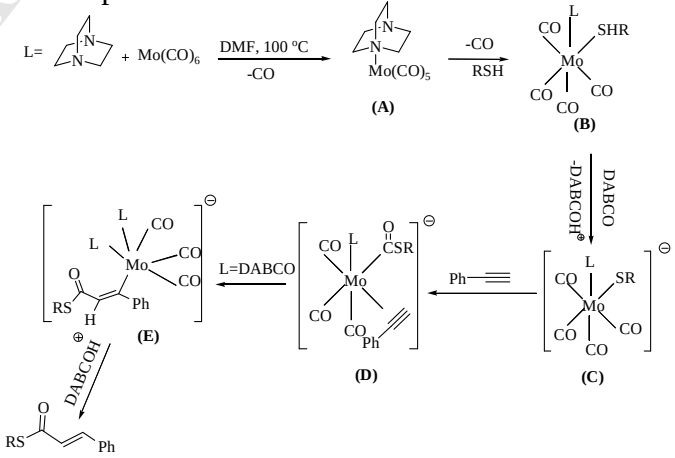
Table 6. Hydrothiocarbonylation of phenylacetylene with different thiols in the presence of $Mo(CO)_6$.[a]



Entry	Thiol	Product	Yield (%)[b]
1	$(CH_3)_2CHSH$	 (2a)	95
2	CH_3CH_2SH	 (2b)	98
3	$CH_3(CH_2)_3CH_2SH$	 (2c)	95
4	$CH_3(CH_2)_6CH_2SH$	 (2d)	95
5	PhSH	 (2e)	88[c]
6	$PhCH_2SH$	 (2f)	92[c]
7	$CH_3(CH_2)_2CH_2SH$	 (2g)	98

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Mo(CO)_6$, thiol (2.0 mmol), DABCO (2mmol), 2 mL of DMF.
[b] Isolated yield.
[c] The reaction was completed after 15 min.

The proposed mechanism was shown in Scheme 1.We suggest that a transient molybdenum carbonyl complex **(A)** can be resulted from the complexation of 1,4-diaza-bicyclo[2.2.2]octane (DABCO) with $Mo(CO)_6$ with rapid releasing of one CO. Then, the complex **B** is formed in the presence of nucleophile. Transfer of sulfide group to CO can then occur with the addition of phenylacetylene to give the intermediate **D**. In the next step, metal to ligand migration can produce the intermediate **E.** High regioselectivity of this method depends greatly to this step in which metal migrates to the terminal acetylenic carbon which is much less hindered. Finally, **E** is protonated through the reaction with BH^+ (B = DABCO) to generate the desired product.



Scheme 1. Mechanism of hydrothiocarbonylationof phenylacetylenein the presence of$Mo(CO)_6$ and DABCO

The obtained results from the reaction of $Mo(CO)_5$ DABCO complex with benzyl mercatptan (Table 5, Entry 5) can be considered as a support for the formation of the proposed intermediate complex (A) in this mechanism.

In conclusion, we introduced an efficient method for the carbonylation of phenylacetylene with alcohols and thiols in the presence of $Fe(CO)_5$/DABCO and $Mo(CO)_6$/DABCO system respectively. This method allows access to a wide range of α,β-cinamylesters and thioesters in excellent yields without the need for using any external gaseous CO. Overall, the hydroalkoxy and hydrothiocarbonylation reactions were occurred under atmospheric pressure at relatively mild reaction temperature and relatively short reaction times. The absence of any Pd catalyst and phosphine ligand can be considered as other advantages of this method.

3. Experimental

3.1. General

FTIR spectra were run on a Shimadzu FTIR-8300 spectrophotometer.^{1}H and C NMR spectra were recorded on a Brucker Avance DPX-250 spectrometer using tetramethylsilane (TMS) as internal standard in pure deuterated solvents. Chemical shifts are given in the δ scale in parts per million (ppm) and coupling constants (J) in hertz. Singlet (s), doublet (d), triplet (t) and multiplet (m) are recorded. The reaction monitoring was carried out on silica gel analytical sheets or by GC analysis using a 3-m length column packed with DC-200 stationary phase. Column chromatography was carried out on a column of silica gel 60 Merck (230-240 mesh) in glass columns (2 or 3 cm diameter) using 15-20 g of silica gel per 1 g of the crude mixture.

3.2. General procedure for hydroesterification of phenylacetylene with alcohols in the presence of $Fe(CO)_5$

A mixture of $Fe(CO)_5$ (1.0 mmol), phenylacetylene (1.0 mmol), alcohol (4.0 mmol) and DABCO (3.0 mmol) in DMF (3 mL) was heated at 100 °C. After completion of the reaction within 10-45 min, the reaction mixture was cooled down to room temperature. Water was then added and extracted with ethyl acetate (3 × 20 mL). Organic layer was dried over anhydrous Na_2SO_4. The crude organic mixture was then purified by column chromatography over silica gel using petroleum ether/ ethyl acetate = 20:1 to obtain the desired productin 85-98% (Table 3).

3.2.1. (E)-3-Phenyl-acrylic acid isopropyl ester (1a) [8]

^{1}H NMR (250 MHz, $CDCl_3$) δ= 7.68 (d, J= 16.2 Hz, 1H), 7.34-7.51(m, 5H), 6.32 (d, J= 16.2 Hz, 1H), 5.10 (m, 1H), 1.97 (d, J= 6.5 Hz, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ= 171.2, 144.3, 118.8, 134.5, 130.1, 128.8, 128.0, 67.87, 22.05.Anal.Calcd for $C_{12}H_{14}O_2$:C, 75.76; H, 7.42. Found: C, 75.88; H, 7.30.

3.2.2. (E)-3-Phenyl-acrylic acid methyl ester (1b) [15]

^{1}H NMR (250 MHz, $CDCl_3$) δ= 7.71 (d, J= 16.0 Hz, 1H), 7.21-7.43 (m, 5H), 6.45 (d, J= 16.0 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ= 171.2, 144.3, 134.5, 130.1, 128.8, 118.8, 51.7.Anal.Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.13; H, 6.18.

3.2.3.(E)-3-Phenyl acrylic acid ethyl ester (1c) [16]

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm)= 7.59 (d, J= 16.2 Hz, 1H), 7.31-7.46 (m, 5H), 6.34 (d, J= 16.2 Hz, 1H), 4.16 (q, 2H), 1.28 (t, J= 7.0 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ= 167.1, 144.7, 134.5, 130.1, 128.8, 126.6, 118.4, 60.6, 14.4. Anal.Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.91; H, 6.94.

3.2.4. (E)-3-Phenyl-acrylic acid 2-ethoxy-ethyl ester (1d)

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.64 (d, J= 16.0 Hz, 1H),7.29-7.47 (m, 5H), 6.42 (d, J= 16.0Hz, 1H), 4.27-4.31 (t, J= 4.5 Hz, J′= 5.0 Hz, 2H), 3.61-3.65(t, J= 5.0 Hz, 2H), 3.45-3.56 (q, 2H), 1.16 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ = 165.0, 142.8, 117.6, 134.9, 128.4, 127.7, 126.2, 69.6, 67.5, 62.7, 14.7.Anal.Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.74; H, 7.45.

3.2.5. (E)-3-Phenyl-acrylic acid pentyl ester (1e) [7]

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.61 (d, J= 16.0 Hz, 1H), 7.18-7.47 (m, 5H), 6.37 (d, J= 16.0Hz, 1H), 4.12 (t, J= 6.8 Hz, 2H), 1.58-1.66 (m, 2H), 1.25-1.34 (m, 2H), 1.18 (m,2H), 0.85 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ = 167.2, 144.8, 134.5, 130.1, 128.8, 118.4, 72.7, 30.0, 24.0, 21.8, 15.9.Anal.Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.14; H, 8.26.

3.2.6. (E)-3-Phenyl-acrylic acid cyclopentyl ester (1f)[17]

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.67 (d, J= 16.0 Hz, 1H), 7.26-7.55(m, 5H), 6.44 (d, J= 16.0 Hz, 1H), 4.84-4.93 (5H, m), 1.30-2.17 (m, 12H). ^{13}C NMR ($CDCl_3$) δ = 166.5, 144.2, 118.9, 134.5, 130.1, 128.8, 128.0, 72.7, 31.0, 21.0. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.84; H, 7.40.

3.2.7. (E)-3-Phenyl-acrylic acid cycloheptyl ester (1g) [18]

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.67 (d, J= 16.0 Hz, 1H), 7.26-7.55(m, 5H), 6.44 (d, J= 16.0 Hz, 1H), 4.84-4.93 (5H, m), 1.30-2.17 (m, 12H). ^{13}C NMR ($CDCl_3$) δ = 166.5, 144.2, 118.9, 134.5, 130.1, 128.8, 128.0, 72.7, 31.7, 23.8, 23.7.Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.42; H, 8.36.

3.2.8.(E)-3-Phenyl-acrylic acid biphenyl-4-ylmethyl ester (1h)

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.46 (d, J= 16.0 Hz, 1H), 7.27-7.39 (m, 14H), 6.42 (d, J= 16.0 Hz, 1H), 5.21 (s, 2H). ^{13}C NMR ($CDCl_3$) δ = 168.0, 145.4, 140.4, 139.6, 138.3, 135.8, 129.4, 129.0, 128.9, 128.4, 128.3, 128.0, 127.2, 117.1, 66.5.Anal.Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.05; H, 5.25.

3.2.9. (E)-3-Phenyl-acrylic acid octyl ester(1i) [18]

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.60 (d, J= 16.0 Hz, 1H), 7.25-7.47 (m, 5H), 6.31 (d, J= 16.0Hz, 1H), 4.10 (t, J= 6.8 Hz, 2H), 1.58-1.64 (m, 2H), 1.40-1.45 (m, 2H), 1.25-1.34 (m, 6H), 1.20 (m,2H), 0.88 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ = 167.1, 144.5, 134.5, 130.2, 128.8, 128.0, 118.3, 64.7, 31.8, 29.2, 29.1, 28.7,25.9, 22.6, 14.0.Anal.Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.63; H, 9.30.

3.2.10. (E)-3-Phenyl-acrylic acid 4-chloro-benzyl ester (1j) [19]

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.74 (d, J= 16.0 Hz, 1H), 7.29-7.52 (m, 9H), 6.48 (d, J= 16.0Hz, 1H), 5.21 (s, 2H).^{13}C NMR ($CDCl_3$) δ = 166.8, 145.2, 139.0, 134.9, 132.7, 129.1, 128.7, 128.4, 127.7, 126.2, 70.1.Anal.Calcd for $C_{16}H_{13}O_2$: C, 70.46; H, 4.80. Found: C, 70.63; H, 4.87.

3.2.11. (E)-3-Phenyl-acrylic acid benzyl ester (1k) [20]

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.64 (d, J= 16.0 Hz, 1H), 7.26-7.29 (m, 10H), 6.39 (d, J= 16.0 Hz, 1H), 5.16 (s, 2H). ^{13}C NMR ($CDCl_3$) δ= 166.8, 145.2, 136.1, 134.3, 130.4, 128.9, 128.6, 128.3, 128.2, 128.1, 117.9, 66.4. Anal.Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.75; H, 5.98.

3.3. General procedure for hydrothioesterification of phenylacetylene with thiols in the presence of $Mo(CO)_6$

A flask was charged with phenylacetylene (1.0 mmol), thiol (2.0 mmol), DABCO (1.0 mmol), $Mo(CO)_6$ (1.0 mmol) and 3 mL of DMF. The flask was then placed in an oil bath on a heater stirrer preset at 100 °C. After 5-15 min, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. After addition of water,the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was separated and dried by Na_2SO_4. Then, the solvent was removed by rotary evaporation under reduced pressure. The residue was purified by using column chromatography or preparative TLC (silica gel, eluant: *n*-hexane/ethyl acetate 20:1) to obtain the desired product in 88-98% (Table 6).

3.4. Preparation of $Mo(CO)_5$DABCO complex

A round bottom flask was charged with DABCO (5.38 g,16.0 mmol), THF (30 mL) and $Mo(CO)_6$ (1.06 g, 4.0 mmol). The mixture was refluxed for 5 h and then the solvent was evaporated under reduced pressure to dryness to yield a brown solid that was purified by *n*-hexane. Evaporation of all volatile materials under reduced pressure gave yellow crystals of the title compound (1.45 g; 84%). ^{1}H NMR data (250 MHz, $CHCl_3$): δ= 2.75 (t, J= 9.2 Hz, 6H), 3.04 (t, J= 9.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ= 47.3, 55.2, 204.0 (CO). IR ν_{max}/cm^{-1} =2047, 1960, 1929 and 1895 (CO); Anal. Calc. for $C_{11}H_{12}N_2O_5Mo$: C, 37.96; H, 3.45; N, 8.05; Found: C, 38.30%; H, 3.36%; N, 7.82%;

3.5. Typical procedure for hydrothiocarbonylation of phenylacetylene with penthane-1-thiol in the presence of $Mo(CO)_5$DABCO

To a round-bottom flask, phenylacetylene (1.0 mmol, 0.102 g), penthane-1-thiol (180 mg, 2.0 mmol), DABCO (3mmol, 0.336 g), $Mo(CO)_5$DABCO, (1 mmol, 0.432 g) and 3 mL of DMF were added. The flask was heated at 100 °C for 45 min and then cooled down to room temperature. The product was extracted with ethyl acetate (3 × 20 mL) from the aqueous layer, and dried over anhydrous Na_2SO_4. Then the crude organic mixture was purified by column chromatography over silica gel using petroleum ether/ ethyl acetate = 20:1 to obtain 3-phenyl-thioacrylic acid S-pentylester(0.223 g, 95%).

3.5.1. (E)-3-Phenyl-thioacrylic acid S-isopropyl ester (2a) [21]

^{1}H NMR (250 MHz, $CDCl_3$) δ7.52 (d, J= 16.0 Hz, 1H)**,** 7.31-7.40 (m, 5H); 6.38 (d, J= 16.2 Hz, 1H), 2.89 (m, 2H), 1.28 (d, J= 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 192.0, 145.8, 132.9, 129.0, 128.4, 128.0, 125.3, 30.0, 22.0.Anal.Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.95; H, 6.80.

3.5.2. (E)-3-Phenyl-thioacrylic acid S-ethyl ester (2b) [22]

^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.58 (d, J = 16.0 Hz,1H), 7.35-7.48 (m, 5H), 6.50 (d, J = 16.0 Hz, 1H), 2.91 (q, J = 7.5 Hz, 2H), 1.30 (t, J = 7.5 Hz, 3H); ^{13}C NMR($CDCl_3$) δ 193.9, 140.1, 130.4, 128.9,128.3, 127.8, 125.0, 23.3, 14.8.Anal.Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.54; H, 6.44.

3.5.3. (E)-3-Phenyl-thioacrylic acid S-pentyl ester (2c)

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.53 (d, J= 16.0 Hz, 1H), 7.23-7.47 (m, 5H), 6.64 (d, J= 16.0Hz, 1H), 2.93 (t, J= 7.5 Hz, 2H), 1.45-1.59 (m, 2H), 1.18-1.30 (m, 4H), 0.86 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 190.0, 140.1, 130.4, 128.8, 128.4, 128.0, 125.1, 31.9, 29.2, 28.3, 22.2, 13.9.Anal.Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.59; H, 7.90.

3.5.4. (E)-3-Phenyl-thioacrylic acid S-octyl ester (2d) [23]

^{1}H NMR (250 MHz, CDCl3) δ = 7.60 (d, J= 16.0 Hz, 1H), 7.30-7.47 (m, 5H), 6.78 (d, J= 16.0Hz, 1H), 2.98 (t, J= 7.5 Hz, 2H), 1.86-1.98 (m, 2H), 1.26-1.38 (m, 10H), 0.92 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 194.0, 148.8, 134.9, 128.4, 128.0, 127.8,125.1, 31.6, 29.9, 29.0, 28.9, 28.8, 22.9, 14.0.Anal.Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75. Found: C, 73.93; H, 8.56.

3.5.5.(E)- 3-Phenyl-thioacrylic acid S-phenyl ester (2e) [24]

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50 (d, J= 16.0 Hz, 1H)**,** 7.30-7.42 (m, 10H),6.41 (d, J= 16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ=194.2, 145.2, 136.0, 134.9, 129.5, 129.4, 129.2, 128.4, 127.7,127.1, 124.9. Anal.Calcd for $C_{15}H_{12}OS$: C,74.97; H, 5.03. Found: C, 74.75; H, 4.86.

3.5.6. (E)-3-Phenyl-thioacrylic acid S-benzyl ester(2f) [25]

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.54 (d, J= 16.0 Hz, 1H)**,** 7.26-7.36 (m, 10H), 6.39 (d, J= 16.0 Hz, 1H), 4.13 (s, 2H). ^{13}C NMR ($CDCl_3$) δ= 194.2, 145.2, 136.1, 134.3, 130.4, 129.4, 128.9, 128.6, 128.3, 128.2, 128.1, 37.4.Anal.Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.37; H, 5.64.

3.5.7. (E)-3-Phenyl-thioacrylic acid S-butyl ester (2g) [26]

^{1}H NMR (250 MHz, CDCl3) δ = 7.53 (d, J= 16.0 Hz, 1H), 7.23-7.47 (m, 5H), 6.64 (d, J= 16.0Hz, 1H), 2.93 (t, J= 7.5 Hz, 2H), 1.45-1.59 (m, 2H), 1.18-1.30 (m, 2H), 0.86 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 194.0, 148.8, 134.9, 128.4, 127.7, 125.6, 32.0, 30.3, 24.0, 15.9.Anal.Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.63; H, 7.50.

Acknowledgments

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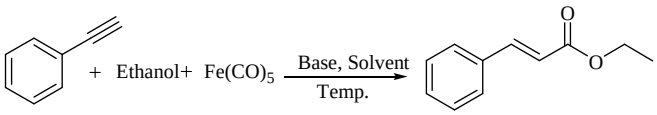
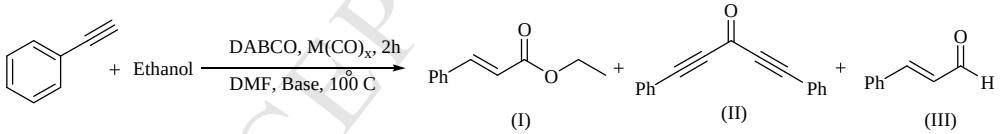
Table 1. Optimization of different parameters for hydroalkoxycarbonylation of phenylacetylene.[a]



Entry	Base	Solvent	Temp. (° C)	Time (h)	Yield (%)[b]
1	DBU	DMF	100	2	47
2	*n*-Pr_3N	DMF	100	10	56
3	DABCO	DMF	100	0.5	95
4	*n*-Pr_3N	TBAB	110	3	52
5	DABCO	TBAB	110	3	70
6[c]	DABCO	DMF	100	2.5	75
7[c]	DABCO	DMF	100	6	65
8[d]	DABCO	DMF	100	12	25
9[d]	DABCO	DMF	100	12	40
10	K_2CO_3	DMF	100	2	60
11	NaOH	DMF	100	2	61
12	Cs_2CO_3	DMF	100	4	72
13	DABCO	DMSO	100	6	27
14	DABCO	diglyme	100	2.5	48
15	DABCO	toluene	Reflux	12	36
16	None	DMF	100	24	10
17	DABCO	xylene	100	24	Trace
18[e]	DABCO	DMF	100	10	10
19	DABCO	DMF	120	0.3	98

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Fe(CO)_5$, ethanol (4 mmol), Base (3 mmol), 2 mL of solvent.
[b] Isolated yield.
[c]The amount of DABCO are 2.0 and 1.0 mmol for entries 6 and 7 respectively.
[d]The amount of ethanol are 1.0 and 2.0 mmol for entries 8 and 9 respectively.
[e] The reaction was performed using 0.5 equivalent of $Fe(CO)_5$.

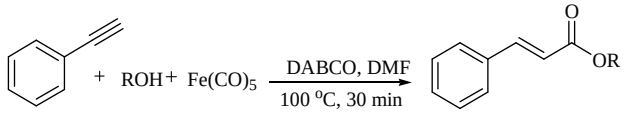
Table 2. Reaction of phenylacetylene with with ethanol in the presence of different metal carbonyls.[a]

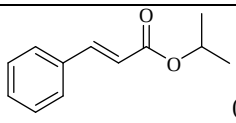
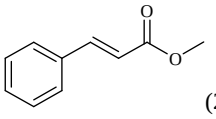
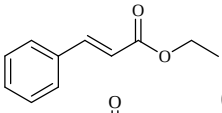
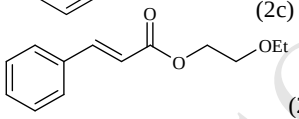
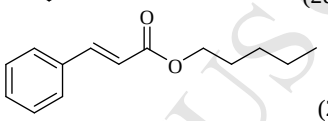
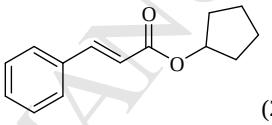
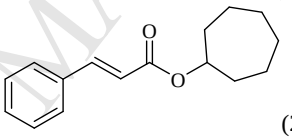
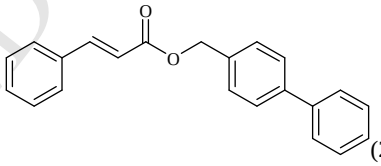
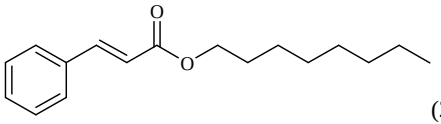
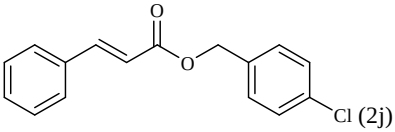
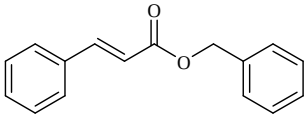


Entry	$M(CO)_x$	Catalyst/ Base	Isolated yield (%)
1	$Fe(CO)_5$	None/DABCO	95%[b] of I
2	$Mo(CO)_6$	None/DABCO	50% of II
3	$W(CO)_6$	None/DABCO -	35% of II
4	$Cr(CO)_6$	None/DABCO	55% of II+30% of III
5	$Fe(CO)_5$	$Pd(OAc)_2$/DABCO	94% of I

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $M(CO)_x$, 1.0 mmol of ethanol, 3.0 mmol of DABCO, 1.0 mmol of base and 2 mL of DMF at 100 °C.
[b] The reaction time is 30 min.

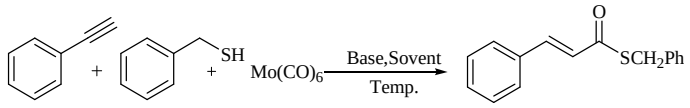
Table 3. Reaction of alcohols with phenylacetylene in the presence of iron pentacarbonyl.[a]



Entry	Alcohol	Product	Yield (%)[b]
1	$(CH_3)_2CHOH$ (1a)	 (2a)	98
2	CH_3OH (1b)	 (2b)	96
3	CH_3CH_2OH (1c)	 (2c)	95
4	$EtO(CH_2)_2OH$ (1e)	 (2d)	94
5	$CH_3(CH_2)_3CH_2OH$ (1f)	 (2e)	95
6	$(CH_2)_4CHOH$ (1h)	 (2f)	90
7	$(CH_2)_6CHOH$ (1i)	 (2g)	90
8	4-biphenylCH_2OH (1j)	 (2h)	89
9	$CH_3(CH_2)_6CH_2OH$ (1k)	 (2i)	96
10	4-Cl$PhCH_2OH$ (1l)	 (2j)	87
11	$PhCH_2OH$ (1m)	 (2k)	90

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Fe(CO)_5$, 4.0 mmol of alcohol, 2.0 mmol of DABCO, and 2 mL of DMF at 100 °C.
[b] Isolated yield.

Table 4. Optimization of different parameters for hydrothiocarbonylation reaction of phenylacetylene.[a]



Entry	Base (mmol)	Solvent	Temp. (° C)	Time (h)	Yield[b] (%)
1	DBU	DMF	100	4	55
2	NBD	DMF	100	0.5	82
3	DABCO	DMF	100	15 min	92
4	*n*-Pr_3N	TBAB	100	8	52
5	DABCO	TBAB	100	6	70
6[c]	DABCO	DMF	100	45 min	92
7[c]	DABCO	DMF	100	2	60
8[d]	DABCO	DMF	100	2	45
9	DABCO	DMSO	100	6	35
10	DABCO	diglyme	100	3	45
11	DABCO	xylene	100	24	Trace
12	DABCO	Toluene	reflux	24	Trace
13	DABCO	DMF	100	12	15[c]
14	DABCO	DMF	120	10 min	95

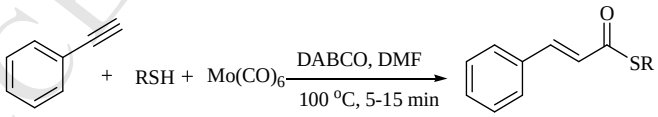
[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Mo(CO)_6$, benzyl mercaptan (2.0 mmol), base (3.0 mmol), 2 mL of solvent.
[b] Isolated yield.
[c]The amount of DABCO are 2.0 and 1.0 mmol for entries 6 and 7 respectively.
[d]The amount of benzyl mercaptane is 1.0 mmol for entries 8.
[e] The reaction was performed using 0.5 equivalents of $Mo(CO)_6$.

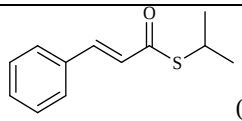
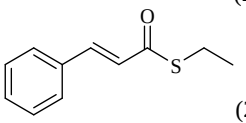
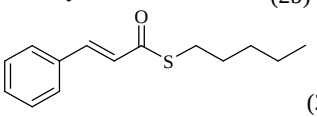
Table 5. Effect of different metal carbonyl in the reaction of phenylacetylene with benzyl mercaptan under the optimized condition.[a]

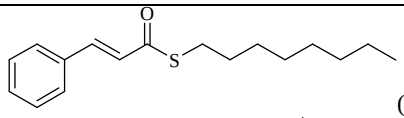
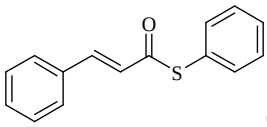
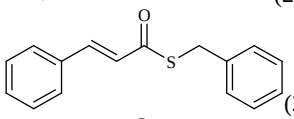
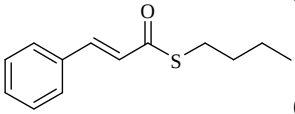
Entry	$M(CO)_x$	Isolated Yield(%)
1	$Mo(CO)_6$	92%[b]
2	$Fe(CO)_5$	trace
3	$W(CO)_6$	45%
4	$Cr(CO)_6$	35
5	$Mo(CO)_5$DABCO	91%[c]

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $M(CO)_x$, 2.0 mmol of benzyl mercaptan, 3.0 mmol of DABCO and 2 mL of DMF at 100 °C.
[b]The reaction time is 15 min.
[c] The reaction time is 60 min.

Table 6. Hydrothiocarbonylation of phenylacetylene with different thiols in the presence of $Mo(CO)_6$.[a]



Entry	Thiol	Product	Yield (%)[b]
1	$(CH_3)_2CHSH$	 (2a)	95
2	CH_3CH_2SH	 (2b)	98
3	$CH_3(CH_2)_3CH_2SH$	 (2c)	95

4	$CH_3(CH_2)_6CH_2SH$	 (2d)	95
5	PhSH	 (2e)	88[c]
6	$PhCH_2SH$	 (2f)	92[c]
7	$CH_3(CH_2)_2CH_2SH$	 (2g)	98

[a] Reaction conditions: 1.0 mmol of phenylacetylene, 1.0 mmol of $Mo(CO)_6$, benzyl mercaptan (2.0 mmol), DABCO (2mmol), 2 mL of DMF.
[b] Isolated yield.
[c] The reaction was completed after 15 min.

Research highlight

- The carbonylation of alkyne was performed by using metal carbonyl/DABCO system.
- α,β-Cinamylesters and thioesters was obtained in excellent yields.
- These reactions were carried out in the absence of Pd catalyst and phosphine ligand.