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FULL PAPER

Synthesis of Trisubstituted Acrylic Acids via Nickel-Catalyzed Carbomagnesiation of Alkynes and Carbon Dioxide Fixation

Chen-Hsun Hung, Rajagopal Santhoshkumar, Yu-Che Chang, and Chien-Hong Cheng*[a]

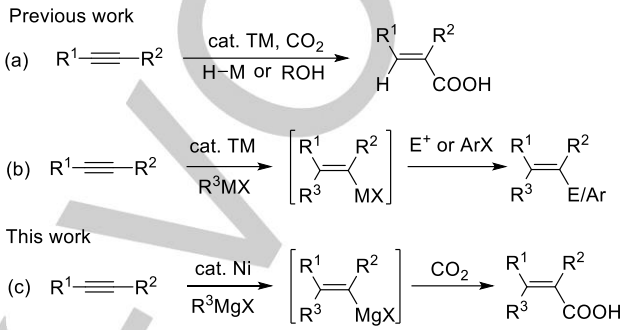
Dedication ((optional))

Abstract: A nickel-catalyzed synthesis of trisubstituted acrylic acids from alkynes, Grignard reagents, and CO_2 was demonstrated. The reaction proceeds through carbomagnesiation of the alkyne with Grignard reagent followed by carboxylation with CO_2 under mild reaction conditions in short time. Various unsymmetrical alkynes were transformed into the corresponding acid products in good yields with high stereoselectivity.

Introduction

Carbon dioxide (CO_2) is a benign, economical and stable one-carbon (C1) feedstock in organic synthesis.[1] However, since carbon dioxide is the end product of organic fuel after burning, and becomes the key molecule responsible for the present global warming, the fixation of CO_2 into useful organic compounds has attracted great attention in recent years.[2] As CO_2 is thermodynamically stable and kinetically inert but is electron-deficient, most of the methods developed to activate inert CO_2 requiring nucleophilic reagents under harsh reaction conditions. Thus, effective utilization of CO_2 with transition-metal catalysts is highly attractive.[3] Among the known methods, the reaction of CO_2 with alkynes such as hydrocarboxylation,[4] cyclization,[5] and carbocarboxylation[6,7] provides efficient routes to construct vinyl and cyclic carboxyl derivatives. In hydrocarboxylation, metal hydride or simple alcohol acts as a hydrogen source to afford unsaturated acrylic acids (Scheme 1a). These methodologies are beneficial in organic synthesis, however, the synthesis of trisubstituted acrylic acids has been rarely studied.[7]

In 1978, Jousseaume reported a nickel-catalyzed carbomagnesiation of alkynes to synthesize trisubstituted alkenes.[8] Recently, Hayashi[9] and others[10] developed a transition metal-catalyzed carbomagnesiation of alkynes using Grignard reagents to produce multi-substituted alkenes (Scheme 1b). Motivated by these results and our continued interest in the first-row transition metal-catalyzed reactions,[4h,11] we focused on the development of an appropriate carbometalation method to synthesize trisubstituted acrylic acids using CO_2. Herein, we wish to report the synthesis of trisubstituted acrylic acids via nickel-catalyzed carbomagnesiation and subsequent carboxylation reaction. During our preparation of this manuscript, Xi reported a similar Ni-catalyzed arylative carboxylation of alkynes with arylmagnesium reagents and CO_2.[12]



Scheme 1. Transformations of alkynes into alkenes and acrylic acids.

Results and Discussion

We initiated the studies using diphenylacetylene **1a** (0.20 mmol) and MeMgBr (0.30 mmol) in the presence of 10 mol% $NiBr_2$·glyme, and 20 mol% PPh_3 in THF at 60°C for 1 h. Then CO_2 gas was introduced to the reaction mixture at 25°C for 30 min to give carboxylation product **3aa** in 82% yield (Table 1, entry 1). Of the solvents examined, THF was found to be most effective; other solvents were much less effective (entries 2–7). Among the nickel catalysts tested, $NiBr_2$·diglyme (5 mol %) with PPh_3 (5 mol %) gave product **3aa** in 88% yield (entries 8–11). The use of bidentate ligands such as 1,10-phen, dppe, and bipy gave very low product yields (entries 12–14). The reaction is also sensitive to the temperature: lower product yield was observed with lower reaction temperature (entries 15–16).

Encouraged by these results, we started to explore the scope of alkynes **1a**-**m** for the nickel-catalyzed synthesis of trisubstituted acrylic acids (Scheme 2). Thus, treatment of symmetrical diaryl alkynes **1a**-**e** with **2a** proceeded well to provide products **3aa**-**ea** in moderate to excellent yields. The sterically-hindered *ortho*-substituted substrate **1f** afforded product **3fa** in 32% yield. However, *ortho*-methoxy substituted alkyne **1g** gave **3ga** in 83% yield plausibly due to the *ortho*-directing effect of the methoxy group.[13] Naphthyl substituted alkynes **1h**-**i** also furnished the corresponding acrylic acids **3ha**-**ia** in moderate yields. The reaction of alkyl(aryl)acetylenes **1j**-**m** with **2a** gave highly regioselective products **3ja**-**ma** in moderate yields. In addition, double alkyne insertion[14] was also found to give the corresponding 2,4-dienoic acids **3ja'**-**la'**. The relative yield of double insertion product decreases as the size of alkyl group increases probably owing to its steric effect of the alkyl group. The structure of **3ja'** was unambiguously confirmed by X-ray crystallography and NOE measurement (see Supporting Information for details).[15]

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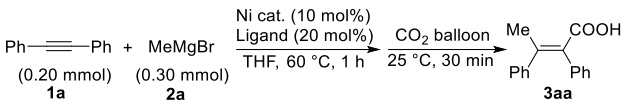
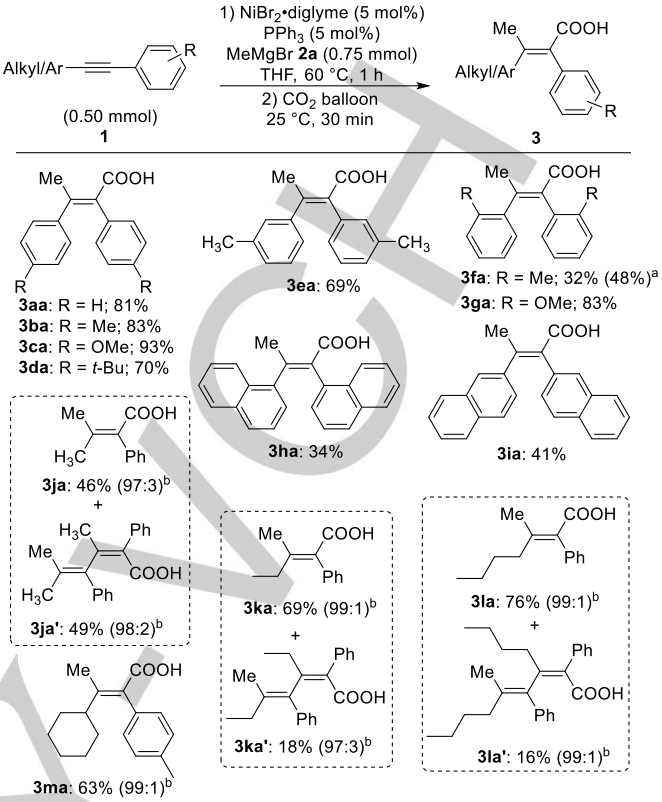
Table 1. Optimization of the reaction conditions[a,b]



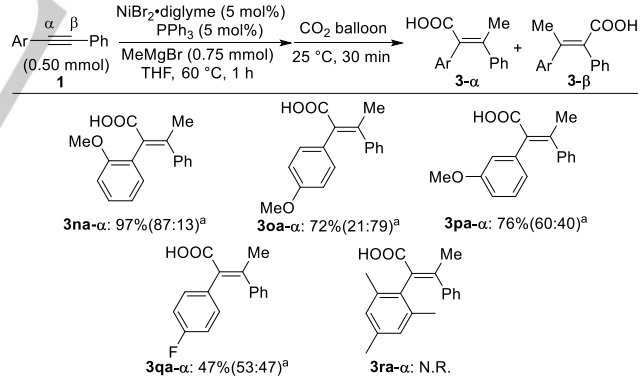
Entry	Catalyst	Ligand	Solvent	Yield (%)[b]
1	$NiBr_2$·glyme	PPh_3	THF	82[c]
2	$NiBr_2$·glyme	PPh_3	1,4-dioxane	11
3	$NiBr_2$·glyme	PPh_3	DME	3
4	$NiBr_2$·glyme	PPh_3	2-Me THF	12
5	$NiBr_2$·glyme	PPh_3	furan	trace
6	$NiBr_2$·glyme	PPh_3	DCE	54
7	$NiBr_2$·glyme	PPh_3	MeCN	4
8	$NiBr_2$·diglyme	PPh_3	THF	76[c]
9[d]	$NiBr_2$·diglyme	PPh_3	THF	88[c]
10[d]	$NiCl_2·6H_2O$	PPh_3	THF	68[c]
11[d]	$NiBr_2$	PPh_3	THF	trace
12[d]	$NiBr_2$·diglyme	1,10-phen	THF	59
13[d]	$NiBr_2$·diglyme	dppe	THF	trace
14[d]	$NiBr_2$·diglyme	bipy	THF	17[c]
15[e,d]	$NiBr_2$·diglyme	PPh_3	THF	20
16[f,d]	$NiBr_2$·diglyme	PPh_3	THF	10
17[g]	$NiBr_2$·diglyme	PPh_3	THF	81[c]

[a] Reactions were performed using **1a** (0.20 mmol), Ni cat. (0.020 mmol), ligand (0.040 mmol) and MeMgBr (3 M in 2-Me THF, 0.10 mL, 0.30 mmol) in THF (2.0 mL) at 60°C for 1 h, then CO_2 in a balloon was introduced to the mixture at 25 °C with stirring for 30 min. [b] Yields were determined by the ^{1}H NMR integration method using mesitylene as the internal standard. [c] Isolated yield. [d] Ni cat. (0.010 mmol) and PPh_3 (0.010 mmol) were used. [e] The reaction temperature is 40°C. [f] The reaction temperature is rt. [g] The reaction was performed using **1a** (0.50 mmol), $NiBr_2$·diglyme (0.025 mmol), PPh_3 (0.025 mmol) and MeMgBr (3 M in 2-Me THF, 0.25 mL, 0.75 mmol) in THF (2.0 mL) at 60°C for 1 h.

Next, we focused on unsymmetrical diarylalkynes **1n**-**r** to investigate the regioselectivity of the reaction (Scheme 3). In general, the *ortho*-directing effect,[13] electronic nature,[16] and steric effect of the unsymmetrical diarylalkynes would control the regioselectivity of the products. In this context, we observed that 2-methoxyphenyl substituted alkyne **1n** gave **3na**-**α** as the major isomer due to the *ortho*-directing effect of methoxy group. In contrast, the electronic donating nature of 4-methoxy substituted alkyne **1o** afforded mainly product **3oa**-**β**. Other substrates **1p** and **1q** gave **α** isomer as the major products in 76% and 47% yields, respectively. The favourable regioselectivity in the products form alkynes **1o**-**q** is plausibly due to electronic effect of the substituent on the phenyl group.[4h,16] Unfortunately, sterically-hindered alkyne **1r** did not give the expected product.



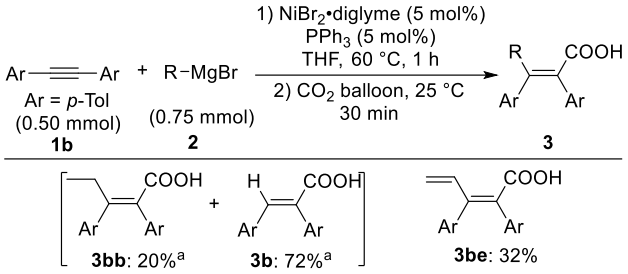
Scheme 2. The scope of alkynes. The reactions were performed using the conditions as in footnote g, Table 1. [a] TMEDA (0.025 mmol) instead of PPh_3. [b] Regioisomers were determined by ^{1}H NMR.



Scheme 3. The scope of unsymmetrical diarylalkynes. The reactions were performed using conditions as in footnote g, Table 1. [a] α:β ratio were determined by ^{1}H NMR.

To see the scope of Grignard reagents, we investigated different alkyl and vinyl Grignard reagents **2b**-**e** for the present catalytic reaction (Scheme 4). Thus, the reaction of **1b** with ethyl magnesium bromide (**2b**) afforded the desired product **3bb**, albeit in low yield. The competing *β*–hydride elimination gave hydrocarboxylation product **3b** in 72% yield and is the major reaction product. Similarly, *n*-hexyl and allyl magnesium bromides **2c**-**d** provided the hydrocarboxylation product **3b** in 67% and 36%

yields, respectively. Nevertheless, vinyl Grignard reagent **2e** furnished vinyl-substituted product **3be** in moderate yield.



Scheme 4. The scope of aliphatic Grignard reagents. The Reactions were performed using the conditions as in footnote g, Table 1. [a] PPh_3 (0.050 mmol).

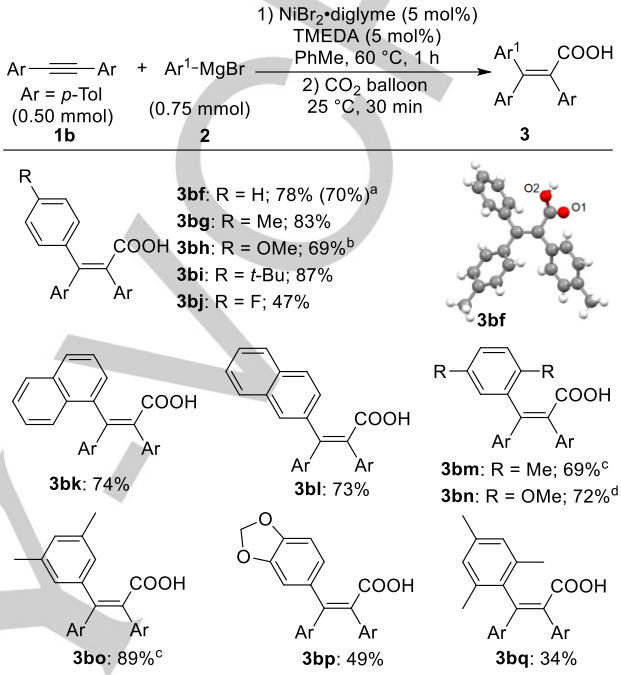
The present catalytic reaction was successfully extended to a variety of aryl Grignard reagents **2f-q** (Scheme 5). However, due to the low yield for the reaction of phenyl magnesium bromide (**2f**) with **1b** under the standard reaction conditions, we optimized the reaction conditions by introducing *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) to the nickel catalyst system in an attempt to improve the yield. Thus, treatment of **1b** with **2f** in the presence of $NiBr_2$·diglyme and TMEDA in toluene provided the triaryl-substituted acrylic acid **3bf** in 78% yield. In a similar manner, *para* substituted methyl, methoxy, *tert*-butyl, and fluoro phenyl Grignard reagents reacted smoothly with **1b** under the present reaction conditions to afford products **3bg**-**bj** in moderate to excellent yields. Naphthyl Grignard reagents **2k**-**l** were also suitable for the present reaction to give acrylic acids **3bk**-**bl** in 73–74% yields. Likewise, disubstituted aryl Grignard reagents **2m**-**p** delivered the desired products **3bm**-**bp** in 49–89% yields. Finally, sterically-hindered mesityl Grignard reagent **2q** also furnished the acrylic acid product **3bq** in 34% yield. It is noteworthy that the steric effect of alkynes influences the reaction more than that of the Grignard reagents.

The synthetic method was successfully applied to a gram-scale synthesis of products **3ba** and **3bf** in 85% and 92% yields, respectively (Scheme 6). In the reactions, a lower amount of the Grignard reagents were used. It is noteworthy that acrylic acid **3bf** could be converted to valuable coumarin derivative **4bf** via an iodine-catalyzed oxidative cyclization under sunlight (Scheme 7).[17]

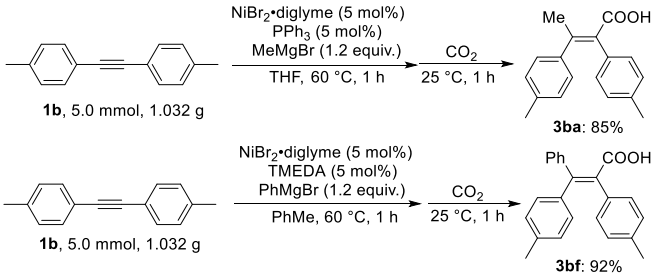
On the basis of literature reports,[4d,8,18] a plausible mechanism is proposed in Scheme 8 to account for the present reactions. The reaction is initiated by the reduction of Ni(II) to Ni(0) by the Grignard reagent. Transmetallation of the Grignard reagent with **I** to afford active nickel complex **II**, coordination of alkyne, followed by insertion into metal-carbon give **IV**. Then, transmetallation of the Grignard reagent with **IV** delivers **V** and regenerates **II** for the next cycle (path a). Alternatively, alkyne coordinates strongly to Ni(0) to form Ni complex **VI** with a formal oxidation state of (II). Subsequently, transmetallation with Grignard reagent and reductive elimination provide **V** (path b). Finally, addition of **V** to CO_2 and then protonation take place to provide the desired product **3**.

Conclusions

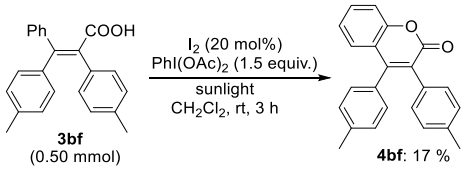
In conclusion, we have developed an efficient nickel-catalyzed carbomagnesiation and subsequent carboxylation reaction from alkynes, Grignard reagents, and CO_2 under mild reaction conditions in short reaction time. Various unsymmetrical alkynes were transformed into the corresponding acrylic acids in good yields with reasonable regioselectivity. *Ortho*-directing effect, electronic nature and steric effect of alkynes play a major role in the regioselectivity. The product, multi-substituted acrylic acid, could be converted into coumarin derivative for further applications.



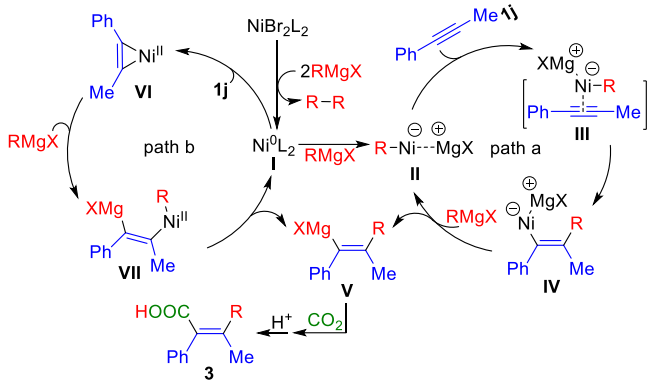
Scheme 5. Scope of aromatic Grignard reagents. Reactions were performed using **1b** (0.50 mmol), $NiBr_2$·diglyme (0.025 mmol), TMEDA (0.025 mmol) and ArMgBr (1 M in THF, 0.75 mL, 0.75 mmol) in PhMe (2.0 mL) at 60°C for 1 h, then CO_2 in a balloon was introduced to the mixture at 25 °C with stirring for 30 min, isolated yields. [a] Reaction without ligand. [b] PPh_3 (0.050 mmol) instead of TMEDA. [c] PPh_3 (0.025 mmol) instead of TMEDA. [d] THF (2.0 mL) was used as solvent.



Scheme 6. Gram-scale synthesis of trisubstituted acrylic acids.



Scheme 7. Synthesis of coumarin derivative.



Scheme 8. A plausible catalytic cycle.

Experimental Section

General procedure for the synthesis of acrylic acid 3: A Schlenk tube containing alkynes **1** (0.50 mmol), $NiBr_2$·diglyme (8.9 mg, 0.025 mmol) and PPh_3 (6.6 mg, 0.025 mmol) was evacuated and purged with nitrogen gas three times. Then dried THF (2.0 mL) and Grignard reagent (0.75 mmol) were added into the mixture in sequence. The reaction mixture was allowed to stir at 60 °C for 1 h. Next, the mixture was cooled to room temperature, nitrogen was removed by vacuum, and then CO_2 balloon was inserted. Later, the reaction stirred at 25°C for another 30 min. When the reaction was completed, the mixture was diluted with EtOAc, quenched with 20% $HCl_{(aq)}$ (2 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over $MgSO_4$, filtered through a Celite pad, and the solvents were removed in vacuum to give the crude product, which was purified by column chromatography using ethyl acetate/*n*-hexane system to afford multi-substituted acrylic acid **3**.

(*E*)-2,3-Diphenylbut-2-enoic acid (3aa): White solid; m.p. 185–187°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.80 (s, 1 H), 7.16–7.07 (m, 6 H), 7.04–7.02 (m, 2 H), 6.96–6.94 (m, 2 H), 2.26 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 170.2 (*C*O), 141.6 (C), 141.0 (C), 137.3 (C), 132.6 (C), 129.4 (2 *C*H), 128.2 (2 *C*H), 127.9 (2 *C*H), 127.7 (2 *C*H), 126.9 (*C*H), 126.6 (*C*H), 22.8 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{16}H_{14}O_2$ 238.0994, found 238.0987; IR (KBr): ṽ = 3417, 2962, 1673, 1589, 1403, 1272 cm^{-1}.

(*E*)-2,3-Di-*m*-tolylbut-2-enoic acid (3ea): White solid; m.p. 108–110°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.75 (s, 1 H), 7.03–6.95 (m, 2 H), 6.93–6.88 (m, 3 H), 6.82 (s, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.71 (d, *J* = 7.6 Hz, 1 H), 2.23 (s, 3 H), 2.14 (s, 3 H), 2.12 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 170.4 (*C*O), 141.5 (C), 140.2 (C), 137.1 (C), 136.9 (C), 136.6 (C), 132.5 (C), 129.7 (*C*H), 128.7 (*C*H), 127.7 (*C*H), 127.5 (*C*H), 127.5 (*C*H), 127.2 (*C*H), 126.7 (*C*H), 125.4 (*C*H), 22.8 (CH_3), 20.9 (CH_3), 20.8 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{18}H_{18}O_2$ 266.1307, found 266.1298; IR (KBr): ṽ = 3494, 2915, 1689, 1604, 1403, 1249 cm^{-1}.

3-Methyl-2-phenylbut-2-enoic acid (3ja): White solid; m.p. 158–160°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.32 (s, 1 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.25 (t, *J* = 7.2 Hz, 1 H), 7.13 (d, *J* = 6.8 Hz, 2 H), 2.03 (s, 3 H), 1.61 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 169.4 (*C*O), 141.7 (C), 138.2 (C), 130.7 (C), 129.1 (2 *C*H), 128.0 (2 *C*H), 126.7 (*C*H), 22.5 (CH_3), 22.2 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{11}H_{12}O_2$ 176.0837, found 176.0832; IR (KBr): ṽ = 3471, 1681, 1619, 1411, 1265, 1095 cm^{-1}.

(*Z*)-3,5-Dimethyl-2,4-diphenylhexa-2,4-dienoic acid (3ja'): White solid; m.p. 115–117°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.35 (s, 1 H), 7.42 (d, *J* = 6.8 Hz, 2 H), 7.39–7.29 (m, 5 H), 7.27–7.21 (m, 3 H), 1.85 (s, 3 H), 1.64 (s, 3 H), 1.49 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 169.9 (*C*O), 141.4 (C), 139.7 (C), 137.3 (C), 136.6 (C), 133.3 (C), 129.6 (2 *C*H), 129.0 (2 *C*H), 128.7 (C), 128.2 (2 *C*H), 127.8 (2 *C*H), 127.2 (*C*H), 126.5 (*C*H), 21.9 (CH_3), 21.5 (CH_3), 19.4 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{20}H_{20}O_2$ 292.1463, found 292.1458; IR (KBr): ṽ = 3694, 2985, 1689, 1596, 1403, 1295, 1072 cm^{-1}.

(*E*)-3-Cyclohexyl-2-(*p*-tolyl)but-2-enoic acid (3ma): White solid; m.p. 188–190°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.28 (s, 1 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 2.28 (s, 3 H), 2.15–2.09 (m, 1 H), 1.87 (s, 3 H), 1.61 (d, *J* = 13.2 Hz, 2 H), 1.51 (d, *J* = 12.4 Hz, 1 H), 1.40–1.27 (m, 4 H), 1.11–1.02 (m, 1 H), 0.96–0.87 (m, 2 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 170.0 (*C*O), 146.9 (C), 135.9 (C), 134.9 (C), 130.3 (C), 128.7 (2 *C*H), 128.6 (2 *C*H), 41.9 (*C*H), 29.8 (2 CH_2), 25.6 (2 CH_2), 25.3 (CH_2), 20.7 (CH_3), 15.2 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{17}H_{22}O_2$ 258.1620, found 258.1615; IR (KBr): ṽ = 2931, 2854, 1673, 1604, 1403, 1249, 933, 740 cm^{-1}.

(*E*)-2-(2-Methoxyphenyl)-3-phenylbut-2-enoic acid (3na-α): White solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.26 (s, 1 H), 7.10–7.02 (m, 4 H), 6.99–6.95 (m, 2 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 6.62 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1 H), 6.58–6.54 (m, 1 H), 3.67 (s, 3 H), 2.36 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 169.4 (*C*O), 157.2 (C), 146.4 (C), 142.9 (C), 131.9 (*C*H), 129.1 (C), 128.1 (C), 128.1 (*C*H), 127.7 (2 *C*H), 127.6 (2 *C*H), 126.8 (*C*H), 119.7 (*C*H), 110.6 (*C*H), 55.2 (CH_3), 22.6 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{17}H_{16}O_3$ 268.1099, found 268.1096.

(*E*)-3-(4-Methoxyphenyl)-2-phenylbut-2-enoic acid (3oa-β): White solid; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.72 (s, 1 H), 7.15–7.05 (m, 3 H), 6.97–6.94 (m, 4 H), 6.72–6.68 (m, 2 H), 3.65 (s, 3 H), 2.23 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 170.5 (*C*O), 158.1 (C), 140.5 (C), 137.7 (C), 133.5 (C), 132.0 (C), 129.6 (2 *C*H), 129.5 (2 *C*H), 127.8 (2 *C*H), 126.5 (*C*H), 113.3 (2 *C*H), 54.9 (CH_3), 22.8 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{17}H_{16}O_3$ 268.1099, found 268.1096.

(*E*)-2,3-Di-*p*-tolylpent-2-enoic acid (3bb): White solid; m.p. 188–191°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.68 (s, 1 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 2.58 (q, *J* = 7.2 Hz, 2 H), 2.20 (s, 3 H), 2.16 (s, 3 H), 0.87 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 170.6 (*C*O), 145.0 (C), 136.7 (C), 135.9 (C), 135.6 (C), 134.2 (C), 131.8 (C), 129.1 (2 *C*H), 128.7 (2 *C*H), 128.6 (2 *C*H), 128.3 (2 *C*H), 29.2 (CH_2), 20.6 (CH_3), 20.5 (CH_3), 12.7 (CH_3) ppm; HRMS (FD$^+$): calcd. for $C_{19}H_{20}O_2$ 280.1463, found 280.1462; IR (KBr): ṽ = 2969, 2869, 1681, 1596, 1511, 1403, 1272, 817, 725 cm^{-1}.

(*E*)-2,3-Di-*p*-tolylpenta-2,4-dienoic acid (3be): White solid; m.p. 158–161°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 13.05 (s, 1 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.99 (dd, *J* = 17.2 Hz, *J* = 10.8 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 5.34 (dd, *J* = 10.8 Hz, *J* = 1.6 Hz, 1 H), 4.84 (dd, *J* = 17.2 Hz, *J* = 1.6 Hz, 1 H), 2.23 (s, 3 H), 2.16 (s, 3 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 170.1 (*C*O), 140.1 (C), 136.6 (*C*H), 136.2 (C), 136.2 (C), 135.0 (C), 133.6 (C), 133.4 (C), 129.9 (2 *C*H), 128.9 (2 *C*H), 128.6 (2 *C*H), 128.3 (2 *C*H), 120.3 (CH_2), 20.7 (CH_3), 20.6 (CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{19}H_{18}O_2$ 278.1307, found 278.1295; IR (KBr): ṽ = 3463, 3023, 2923, 1689, 1504, 1403, 1265, 1025, 925, 817 cm^{-1}.

(*Z*)-3-(4-(*tert*-Butyl)phenyl)-2,3-di-*p*-tolylacrylic acid (3bi): White solid; m.p. 220–222°C; ^{1}H NMR (400 MHz, d_6-DMSO): δ = 12.59 (s, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.96 (d, *J* = 10.0 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.0 Hz, 2 H), 2.21 (s, 3 H), 2.20 (s, 3 H), 1.27 (s, 9 H) ppm; ^{13}C NMR (100 MHz, d_6-DMSO): δ = 171.1 (*C*O), 150.0 (C), 141.7 (C), 139.2 (C), 137.8 (C), 136.5 (C), 136.3 (C), 134.6 (C), 133.8 (C), 130.2 (2 *C*H), 129.1 (2 *C*H), 128.7 (2 *C*H), 128.6 (2 *C*H), 128.5 (2 *C*H), 124.8 (2 *C*H), 34.2 (C), 31.0 (3 CH_3), 20.6 (2 CH_3) ppm; HRMS (EI$^+$): calcd. for $C_{27}H_{28}O_2$ 384.2089, found 384.2079; IR (KBr): ṽ = 3694, 3023, 2954, 2869, 1689, 1589, 1511, 1403, 1272, 809 cm^{-1}.

3,4-di-*p*-tolyl-2*H*-chromen-2-one (4bf): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (td, *J* = 7.2 Hz, *J* = 1.6 Hz, 1 H), 7.38 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1 H), 7.21 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H), 7.14 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 7.01–6.95 (m, 6 H), 2.32 (s, 3 H), 2.24 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5 (*C*O), 153.1 (C), 151.3 (C), 138.0 (C), 137.2 (C), 131.6 (C), 131.1 (*C*H), 130.9 (C), 130.3 (2 *C*H), 129.2 (2 *C*H), 128.9 (2 *C*H), 128.4 (2 *C*H), 127.7 (*C*H), 126.8 (C), 123.9 (*C*H), 120.7 (C), 116.6 (*C*H), 21.2 (CH_3), 21.2 (CH_3) ppm; HRMS (FD$^+$): calcd. for $C_{23}H_{18}O_2$ 326.1307, found 326.1310.

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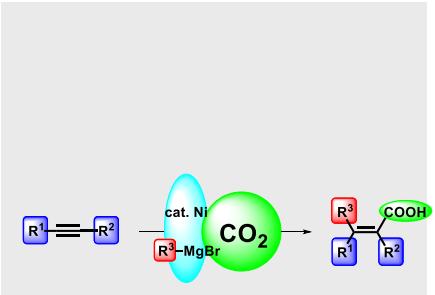
FULL PAPER

TOC

CO_2 must convert: The key molecule for the present global warming "CO_2" must be utilized wherever it applies. Herein, CO_2 is used for a nickel-catalyzed carbomagnesiation of alkynes to produce acrylic acids.



CO_2 Fixation

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Synthesis of Trisubstituted Acrylic Acids via Nickel-Catalyzed Carbomagnesiation of Alkynes and Carbon Dioxide Fixation