Trifluoromethyl-Radical-Mediated Carbonylation of Alkanes Leading to Ethynyl Ketones

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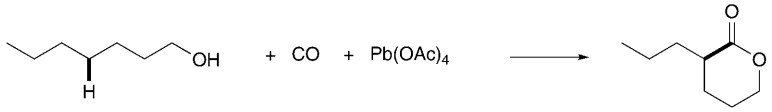
Dedicated to the memory of Professor *Hanns Fischer*

The carbonylation of alkanes **1** under radical-reaction conditions was examined by using ethynyl triflone **A** as the unimolecular chain-transfer (UMCT) reagent. Good to moderate yields of ethynyl ketones **2** were prepared by means of this three-component coupling reaction. Higher CO pressures as well as lower concentrations of triflone **A** improved the efficiency of the reaction over the direct addition, the latter leading to alkylated ethynes **3**. In contrast to the reaction with **A**, the reaction of cyclohexane (**1a**) with allyl triflone **B** (=ethyl 2-methylene-3-[(trifluoromethyl)sulfonyl]propanoate) in the presence of CO gave a mixture of carbonylation products, including **8a** formed from two molecules each of cyclohexane, CO, and allyl triflone **B**.

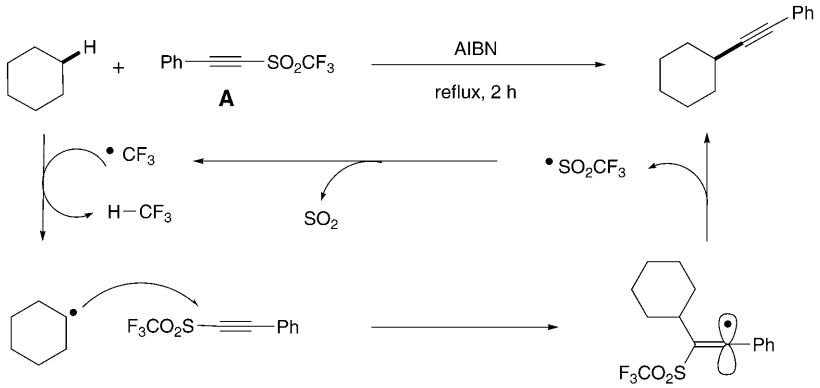
Introduction. – The carbonylation of unactivated C–H bonds is an important challenge in both transition-metal and radical chemistry, since both alkanes and carbon monoxide are potentially abundant and cheap feedstocks [1]. We previously reported that, in the presence of lead tetraacetate, the C–H bond at the δ position of saturated alcohols is carbonylated to give good yields of δ-lactones (*Scheme 1*) [2]. The key steps in the carbonylation reaction are a *Barton* 1,5-H shift [3] from C to O and a subsequent radical-carbonylation reaction [4].

Scheme 1



In general, the abstraction of a H-atom from the C–H bond of saturated hydrocarbons can be carried out with radicals that are capable of creating stronger σ-bonds, which include halogen radicals, alkoxy radicals, vinyl radicals, and aryl radicals [5]. *Fuchs* and co-workers previously reported that ethynyl triflones, such as phenylethynyl trifluoromethyl sulfone (**A**), can serve as unimolecular chain-transfer (UMCT) reagents [6], which are able to trap alkyl radicals with concurrent generation of (trifluoromethyl)sulfonyl radicals. Thus formed (trifluoromethyl)sulfonyl radicals undergo α-scission to give trifluoromethyl radicals, which in turn participate in the abstraction of

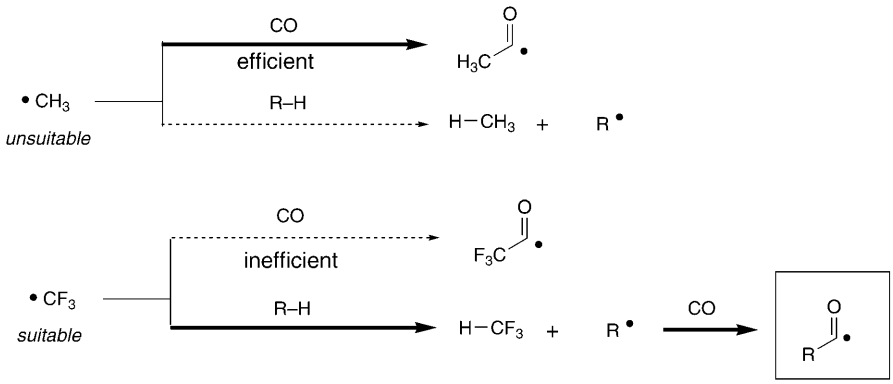
Scheme 2. *C–H Alkynylation by* Fuchs' *Acetylenic Triflone* **A** [7]



H-atoms from alkanes (*Scheme 2*; AIBN = 2,2′-azabis[2-methylpropanenitrile]) [7][8]. *Fuchs*, *Curran*, and co-workers demonstrated that an allyl triflone also serves as an efficient UMCT trap to produce substituted allylic compounds [9].

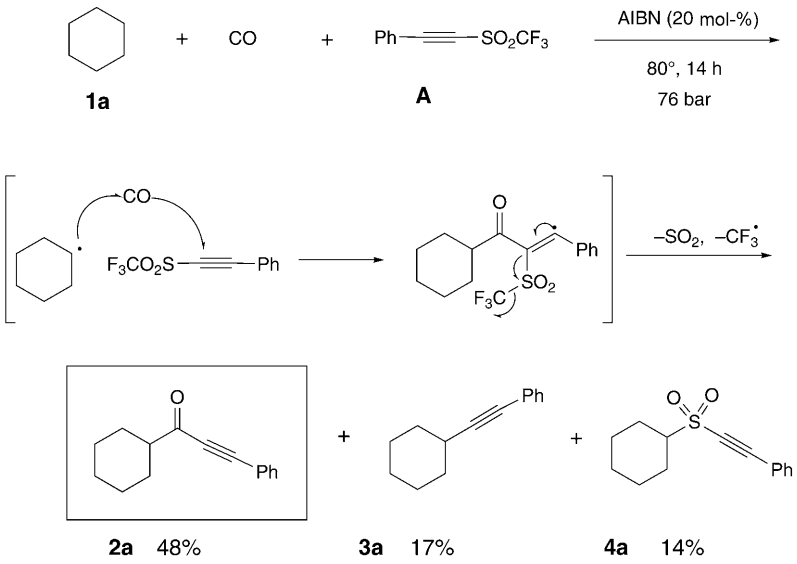
It is interesting to note that, in light of the C–H bond strength, both methyl and trifluoromethyl radicals have the potential to abstract a H-atom from a secondary or tertiary C–H bond of alkanes to create the corresponding alkyl radicals. However, the methyl radical exhibits nucleophilic characteristics, and this does not necessarily allow for a design of C–H activation chemistry based on the methyl radical. In our previous work, the methyl radical adds to CO to form an acetyl radical, but in contrast, perfluoroalkyl radicals do not undergo carbonylation [10]. Accordingly, we concluded that the above *Fuchs'* ethynyl triflone system which capitalized on the propensity of the trifluoromethyl radical might be a useful reagent, even in the case of radical carbonylation of saturated hydrocarbons (*Scheme 3*) [11]. In this article, we present the results of some direct carbonylation reactions of alkanes by means of phenylethynyl triflone **A** as the UMCT reagent.

Scheme 3. *Suitability of Trifluoromethyl Radical for the C–H Carbonylation Reaction*



Results and Discussions. – We carried out the reaction of cyclohexane (**1a**) (used as both solvent and reagent) under 76 bar of CO pressure in the presence of ethynyl triflone **A** at 80° (bath temperature) for 14 h (*Scheme 4*). After chromatography (silica gel), we isolated the anticipated ethynyl ketone **2a** in 48% yield. The reaction also gave ethynylcyclohexane **3a**, and cyclohexyl ethynyl sulfone **4a** as by-products. The former is produced *via* the direct addition of a cyclohexyl radical to **A**, whereas the latter is produced *via* the trapping of sulfur dioxide by the cyclohexyl radical [12], followed by reaction with **A**.

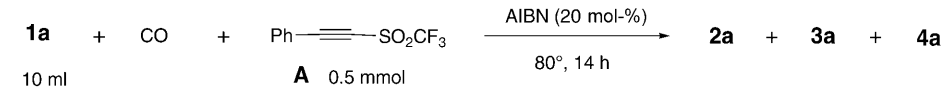
Scheme 4



The formation of the direct addition product **3a** indicated that this competing reaction is quite rapid at the CO concentration employed. As expected, the use of higher CO pressures resulted in increased yields of ethynyl ketone **2a** (*Table 1*). A high dilution was also effective in improving the yield of **2a** (*Entries 3* and *4*). On the other hand, to suppress the undesirable formation of sulfone **4a**, aqueous potassium carbonate solution was added to trap SO_2. This simple protocol turned out to be quite useful in eliminating the production of **4a** (*Entries 2–4*).

We then tested the reaction conditions with a variety of alkanes, and the results are summarized in *Table 2*. The carbonylation of cyclopentane (**1b**) also worked well, giving the corresponding ethynyl ketone **2b** in 58% yield along with 14% of ethyne **3b**. Cycloheptane (**1c**) gave a 1:1 mixture of **2c** and **3c** (*Table 2*, *Entry 4*), and cyclododecane (**1e**) furnished the corresponding ethynyl ketone **2e** in 44% yield besides 21% of **3e**. On the other hand, the carbonylation of cyclooctane (**1d**) gave the corresponding ethynyl ketone **2d** in only 28% yield, and the direct alkynylation product **3d** was the major product (*Entry 5*). Thus, in the cases of cycloalkanes, ring size affects the efficiency of the carbonylation. Three acyclic alkanes, pentane (**1f**), hexane (**1g**), and 2,3-dimethylbutane (**1h**), were also examined (*Entries 7–9*). In the case of pentane

Table 1. *Reaction of* **1a** *with* **A** *under High Pressures of CO*



Entry	[**A**] [**M**]	CO [bar]	Additive	Yield[a]) [%]		
				2a	**3a**	**4a**
1	0.05	109	none	51	14	16
2	0.05	113	K_2CO_3(aq)[b])	54	10	0
3	0.025[c])	108	K_2CO_3(aq)[b])	63	10	0
4	0.025[c])	142	K_2CO_3(aq)[b])	64	9	0

[a]) Isolated yield. [b]) K_2CO_3 (0.45 mmol) and H_2O (1 ml). [c]) Cyclohexane, 20 ml.

(**1f**), a mixture of two carbonylation products **2f** and **2f′**, arising by reaction at different methylene C-atoms, were formed in 39% total yield. Their ratio was 29:71, which reflects the number of methylene units in the substrate (*Entry 7*). Similarly, hexane (**1g**) gave a 43:57 mixture of ethynyl ketones **3g** and **3g′** in 43% total yield (*Entry 8*). In the case of 2,3-dimethylbutane (**1h**), the three carbonylation products **2h**, **2h′**, and **2i** were formed, albeit in low yields (*Entry 9*). The formation of **2i** may be ascribed to the carbonylation of the isopropyl radical, which may arise from the initially formed primary alkyl radical *via* β-fragmentation. In these cases, carbonylation occurred most efficiently at the secondary C-atoms. This is due to the less efficient carbonylation of tertiary alkyl radicals and less efficient generation of primary alkyl radicals in the present system.

To get some insight into the unusual reactivity of the cyclooctyl radical (*Entry 5*), we carried out the *Fuchs* reaction, which serves as the background reaction in our system, with a mixture of the four cycloalkanes **1a**–**d** (*Scheme 5*). When 50 mmol of each of the cycloalkanes were mixed and allowed to react with **A** in the presence of AIBN, we obtained a mixture **3b**/**3a**/**3c**/**3d** in the ratio of 9:13:30:48. This ratio was adjusted to 13:15:30:42, when the number of methylene units is taken into account. The *Fuchs* reaction of cyclooctane (**1d**) appears to be exceptionally efficient. We then carried out radical formylation reactions of bromocycloalkanes, which gave the corresponding aldehydes **5b**/**5a**/**5c**/**5d** in the ratio 18:29:28:25 (*Scheme 6*). The carbonylation efficiency of bromocyclooctane was not necessarily low, compared with other bromocycloalkanes. Based on the above findings, we conclude that the unusually low efficiency of cyclooctane (**1d**) with respect to carbonylation can be ascribed to the rapid addition of the cyclooctyl radical to the ethynyl triflone **A**, although the reason for this is not clear at this stage.

Finally we examined the carbonylation of cyclohexane (**1a**) in the presence of an allyl triflone, *i.e.*, ethyl 2-methylene-3-[(trifluoromethyl)sulfonyl]propanoate (**B**) [9]. The reaction proceeded, but was somewhat messy, since the product mixture contained at least three carbonylation products, **6a**, **7a**, and **8a** (*Scheme 7*). Unsaturated-ketone derivative **6a**, an expected product, was formed in low yield, while isomer **7a**, obtained by isomerization of the alkene moiety of **6a**, was also formed. We also isolated the six-component coupling product **8a**, which is composed of two molecules of cyclohexane,

Table 2. *Radical Carbonylation of Alkanes* **1** *with Ethynyl Triflone* **A**[a)]

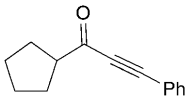
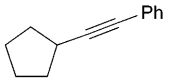
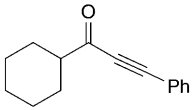
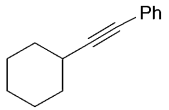
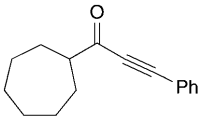
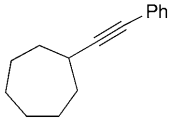
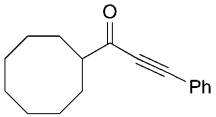
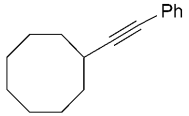
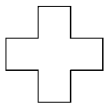
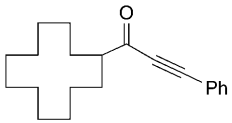
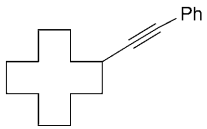
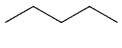
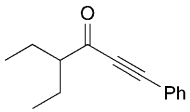
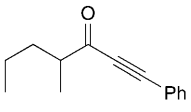
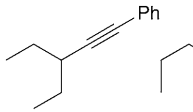
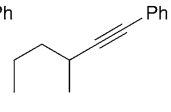
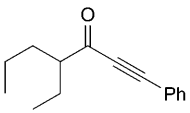
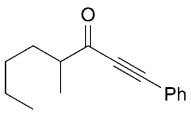
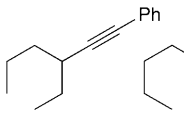
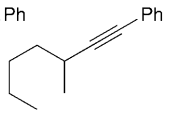
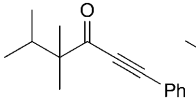
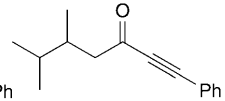
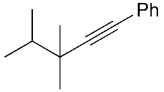
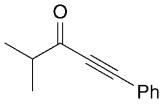
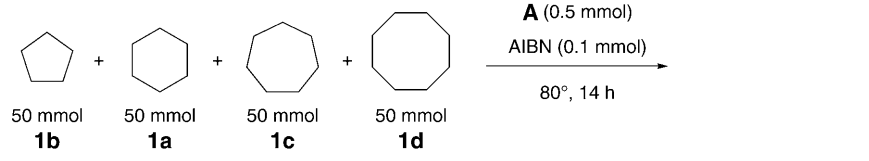
Entry	Alkane **1**	Ethynyl ketone **2**	Yield[b)] [%] of **2**	Ethyne **3**	Yield [%] of **3**
1	 **1b**	 **2b**	58	 **3b**	14
2	 **1a**	 **2a**	64	 **3a**	9
3[c])			68		8
4	 **1c**	 **2c**	41	 **3c**	41
5	 **1d**	 **2d**	28	 **3d**	51
6[d])	 **1e**	 **2e**	44	 **3e**	21

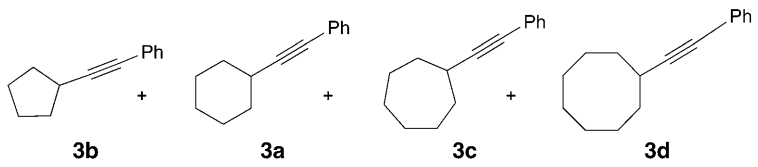
Table 2 (cont.)

Entry	Alkane **1**	Ethynyl ketone **2**	Yield[b]) [%] of **2**	Ethyne **3**	Yield [%] of **3**
7	 **1f**	 **2f**  **2f'**	39 (29:71)[e])	 **3f**  **3f'**	16 (32:68)[e])
8	 **1g**	 **2g**  **2g'**	43 (43:57)[e])	 **3g**  **3g'**	20 (43:57)[e])
9	 **1h**	 **2h**  **2h'**	4 (66:34)[e])	 **3h**	49
		 **2i**	2		

[a]) General conditions: [**A**] = 0.025M, **A** (0.5 mmol), CO (142 bar), K_2CO_3 (0.45 mmol), H_2O (1 ml). [b]) Yields after chromatography (silica gel). [c]) 1,2-Dichloroethane (10 ml), **1a** (6.5 ml, 60 mmol), **A** (0.5 mmol), CO (132 bar), K_2CO_3 (0.45 mmol), H_2O (1 ml). [d]) 1,2-Dichloroethane (12 ml), **1e** (10 g, 60 mmol), **A** (0.5 mmol), CO (147 bar). [e]) Ratio estimated by ^{1}H-NMR.

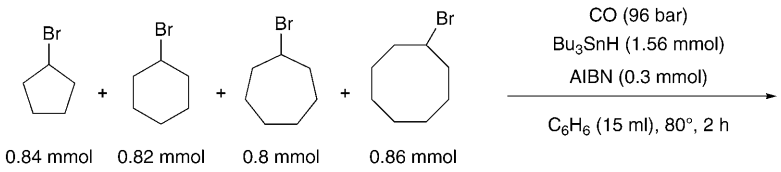
Scheme 5

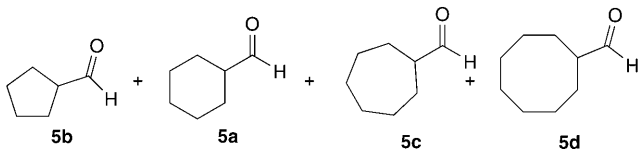




	3b	3a	3c	3d
relative yield	9%	13%	30%	48%
per CH_2	13%	15%	30%	42%

Scheme 6



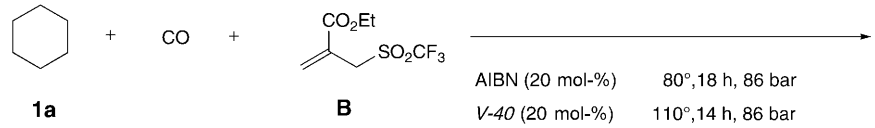


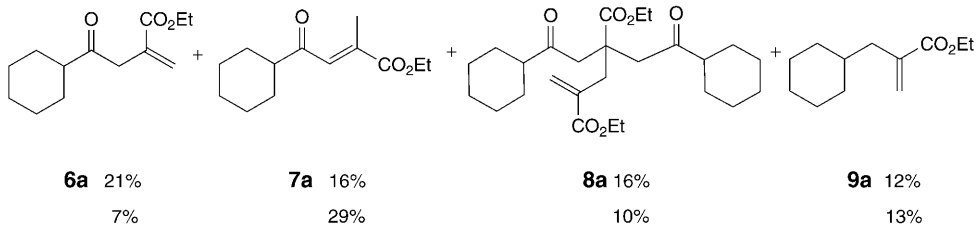
	5b	5a	5c	5d
relative yield	18%	29%	28%	25%

two molecules of CO, and two molecules of allyl triflone **B**. This suggests that the initially formed **6a** served as an acyl radical acceptor, thus leading to a somewhat complex reaction system (*Scheme 8*).

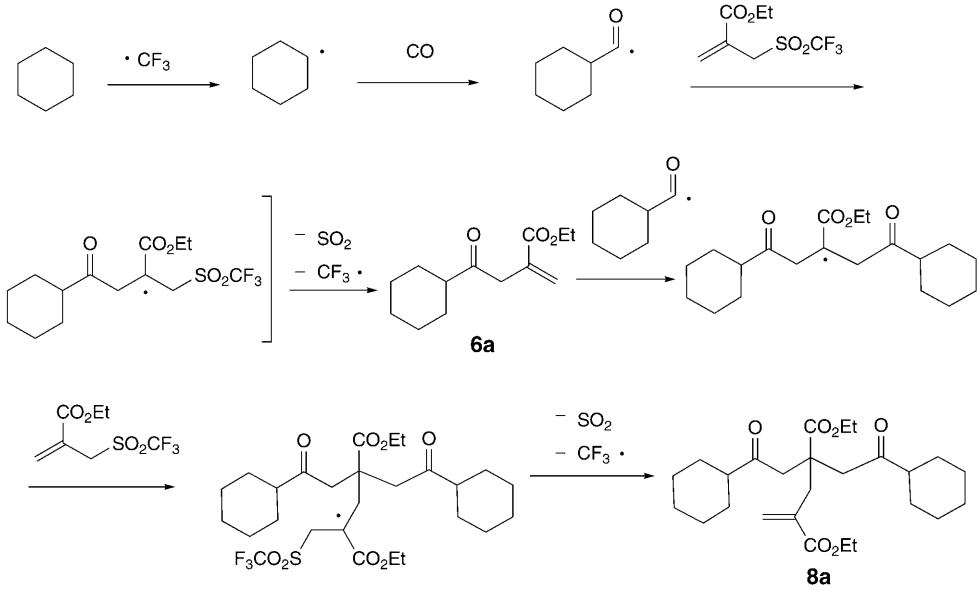
Conclusions. – The carbonylation of cyclic and acyclic alkanes under radical-reaction conditions was studied by using phenylethynyl triflone **A** as a UMCT reagent. With the exception of cyclooctane, cyclic alkanes were carbonylated to give good to moderate yields of ethynyl ketones. High CO pressures as well as lower concentrations are necessary to compete with the rapid background reaction. In the case of acyclic alkanes, the carbonylation was most efficient at secondary C-atoms, due to the less efficient carbonylation of tertiary alkyl radicals and the less efficient generation of primary alkyl radicals. The three-component reaction of cyclohexane with allyl triflone **B** in the presence of CO also proceeded, however, double-bond isomerization and further multi-component coupling reactions of the initially formed unsaturated ketone occurred as side-reaction pathways.

Scheme 7





Scheme 8. *Radical Carbonylation of Cyclohexane* (**1a**) *with Allyl Triflone* **B**



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Experimental Part

1. *General.* Ethynyl triflone **A** [7][13] and allyl triflone **B** [9][14] were prepared according to the methods described in the literature. Flash chromatography (FC): silica gel (*Nacalai Tesque Int.* silica gel *60*, 230–400 mesh). Prep. HPLC: *LC-908* chromatograph (*Japan Analytical Industry Co., Ltd.*);

GPC columns (*Jaigel-1H*+*Jaigel-2H* columns), $CHCl_3$ as eluent. Anal. GC: *Shimadzu-GC-18A* gas chromatographe; flame-ionization detector; fused capillary column. IR Spectra: *Shimadzu-FTIR-8400* spectrometer; in cm^{-1}. ^{1}H-NMR Spectra: *Jeol-JMN-500* (500 MHz) spectrometer; $CDCl_3$ solns.; chemical shifts δ in ppm downfield from internal $SiMe_4$ (=0.00 ppm), J in Hz. ^{13}C-NMR Spectra: *Jeol-JMN-ECP-500* (125 MHz) spectrometer; solvent peak as reference at 77.00 ppm. HR-MS and MS: *Jeol-MS700* spectrometer; in *m*/*z* (rel. %).

2. *Carbonylation of Cycloalkanes: General Procedure.* A magnetic stirring bar, AIBN (=2,2′-azobis-[isobutyronitrile]; 16.7 mg, 0.10 mmol), K_2CO_3 (62.7 mg, 0.45 mmol), ethynyl triflone **A** (115.3 mg, 0.49 mmol), cyclohexane (20 ml), and H_2O (1 ml) were placed in a 50-ml stainless-steel autoclave. The autoclave was closed, purged with carbon monoxide (3×), cooled to −40°, pressurized with 81 bar of CO, and then warmed to r.t. (CO pressure 142 bar) and heated to 80° (CO pressure 148 bar). The autoclave was heated at 80° for 14 h. Excess CO was discharged at r.t. The mixture was extracted with Et_2O, the combined extract washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*, and the residue purified by FC (silica gel, gradient hexane → hexane/AcOEt 5:1): **2a**, which contained a small amount of 2,2-dimethyl-4-phenylbut-3-ynenitrile, and **3a** (7.8 mg, 9%). Further purification of **2a** by prep. HPLC ($CHCl_3$) gave 66.8 mg (64%) of pure **2a**.

1-Cyclohexyl-3-phenylprop-2-yn-1-one (**2a**) [15]. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.20–1.36 (*m*, 3 H, CH_2); 1.45–1.52 (*m*, 2 H, CH_2); 1.62–1.68 (br., 1 H, CH_2); 1.75–1.82 (br., 2 H, CH_2); 2.00–2.05 (br., 2 H, CH_2); 2.44–2.52 (*m*, COCH); 7.32–7.46 (*m*, 3 arom. H); 7.53–7.62 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.50; 25.90; 28.40; 52.38; 87.31; 91.40; 120.25; 128.64; 130.67; 133.08; 191.48.

(Phenylethynyl)cyclohexane (**3a**) [7]. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.30–1.40 (*m*, 3 H, CH_2); 1.50–1.60 (*m*, 3 H, CH_2); 1.70–1.80 (br., 2 H, CH_2); 1.83–1.94 (*m*, 2 H, CH_2); 2.57–2.61 (*m*, CH); 7.23–7.30 (*m*, 3 arom. H); 7.39–7.42 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.01; 26.03; 29.75; 32.81; 80.59; 94.54; 124.21; 127.43; 128.24; 131.69.

[(Cyclohexylsulfonyl)ethynyl]benzene (**4a**). IR (neat): 1143, 1321, 2183. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.15–1.27 (*m*, 1 H, CH_2); 1.28–1.39 (*m*, 2 H, CH_2); 1.52–1.65 (*m*, 2 H, CH_2); 1.70–1.79 (*m*, 1 H, CH_2); 1.90–2.00 (*m*, 2 H, CH_2); 2.30–2.38 (*m*, 2 H, CH_2); 3.03 (*tt*, J=12.15, 3.43, CH); 7.38–7.42 (*m*, 2 arom. H); 7.48–7.52 (*m*, 1 arom. H); 7.57–7.60 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.03; 25.11; 25.59; 65.29; 81.92; 93.14; 117.90; 128.89; 131.68; 132.94. EI-MS: 248 (0.1, M^+), 54 (30), 55 (100), 67 (65), 81 (41), 82 (32), 83 (44), 102 (78), 167 (25). HR-EI-MS: 248.0875 ($C_{14}H_{16}SO$, M^+; calc. 248.0871).

1-Cyclopentyl-3-phenylprop-2-yn-1-one (**2b**). IR (neat): 1666, 2201. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.60–1.76 (*m*, 4 H, CH_2); 1.90–2.04 (*m*, 4 H, CH_2); 3.03 (*quint.*, J=6.30, COCH); 7.36–7.46 (*m*, 3 arom. H); 7.54–7.58 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 26.09; 29.22; 53.89; 87.37; 91.21; 120.26; 128.70; 130.66; 133.09; 191.16. EI-MS: 198 (6, M^+), 75 (11), 102 (24), 129 (100), 130 (19). HR-EI-MS: 198.1033 ($C_{14}H_{14}O^+$, M^+; calc. 198.1045).

(Phenylethynyl)cyclopentane (**3b**) [7]. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.54–1.64 (*m*, 2 H, CH_2); 1.66–1.81 (*m*, 4 H, CH_2); 1.95–2.02 (*m*, 2 H, CH_2); 2.81 (*quint.*, J=7.55, CH); 7.22–7.28 (*m*, 3 arom. H); 7.36–7.39 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.14; 30.90; 34.00; 80.13; 94.67; 124.23; 127.46; 128.24; 131.64.

1-Cycloheptyl-3-phenylprop-2-yn-1-one (**2c**). IR (neat): 1695, 2198. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.50–1.65 (*m*, 6 H, CH_2); 1.70–1.80 (*m*, 4 H, CH_2); 2.02–2.10 (*m*, 2 H, CH_2); 2.69 (*sept.*, J=4.58, CH); 7.34–7.40 (*m*, 2 arom. H); 7.42–7.46 (*m*, 1 arom. H); 7.55–7.60 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 26.49; 28.54; 29.82; 54.20; 87.43; 91.20; 120.30; 128.66; 130.62; 133.07; 191.86. EI-MS: 227 (12, $[M+H]^+$), 55 (63), 77 (31), 165 (100), 167 (34). HR-EI-MS: 227.1427 ($C_{16}H_{18}O^+$, M^+; calc. 227.1436).

(Phenylethynyl)cycloheptane (**3c**) [7]. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.50–1.80 (*m*, 8 H, CH_2); 1.85–1.93 (*m*, 2 H, CH_2); 1.95–2.20 (*m*, 1 H, CH_2); 2.10–2.18 (*m*, 1 H, CH_2); 2.80 (*sept.*, J=4.01, CH); 7.21–7.34 (*m*, 2 arom. H); 7.37–7.40 (*m*, 2 arom. H); 7.43–7.48 (*m*, 1 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.72; 28.01; 31.75; 34.78; 80.88; 95.27; 124.32; 127.44; 128.19; 131.60.

1-Cyclooctyl-3-phenylprop-2-yn-1-one (**2d**). IR (neat): 1667, 2199. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.50–1.65 (*m*, 8 H, CH_2); 1.70–1.80 (*m*, 4 H, CH_2); 2.00–2.08 (*m*, 2 H, CH_2); 2.72 (*sept.*, J=4.58, COCH); 7.36–7.39 (*m*, 2 arom. H); 7.42–7.50 (*m*, 1 arom. H); 7.55–7.58 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 25.43; 26.28; 26.80; 27.91; 52.92; 87.50; 91.07; 120.12; 128.69; 130.62; 133.09;

192.10. EI-MS: 240 (1, M^+), 55 (49), 67 (17), 69 (55), 75 (18), 102 (41), 129 (100), 130 (19), 165 (15). HR-EI-MS: 240.1511 ($C_{17}H_{20}O^+$, M^+; calc. 240.1514).

(Phenylethynyl)cyclooctane (**3d**). IR (neat): 1448, 2198. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.50–1.61 (*m*, 8 H, CH_2); 1.72–1.83 (*m*, 4 H, CH_2); 1.90–1.98 (*m*, 2 H, CH_2); 2.79 (*sept.*, J = 4.13, CH); 7.23–7.28 (*m*, 3 arom. H); 7.37–7.38 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 23.66; 25.55; 27.54; 30.91; 31.72; 80.59; 95.50; 124.34; 127.43; 128.24; 131.67. EI-MS: 212 (212, M^+), 91 (66), 115 (75), 129 (100), 141 (69), 155 (64). HR-EI-MS: 212.1561 ($C_{16}H_{20}^+$, M^+; calc. 212.1565).

1-Cyclododecyl-3-phenylprop-2-yn-1-one (**2e**). IR (neat): 1665, 2199. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.31–1.49 (*m*, 18 H, CH_2); 1.66–1.73 (*m*, 2 H, CH_2); 1.76–1.83 (*m*, 2 H, CH_2); 2.72–2.78 (*m*, COCH); 7.37–7.41 (*m*, 2 arom. H); 7.43–7.47 (*m*, 1 arom. H); 7.56–7.59 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.35; 23.40; 23.44; 23.54; 23.74; 23.83; 25.03; 25.90; 49.85; 87.47; 90.88; 120.45; 128.53; 130.52; 132.96; 191.93. EI-MS: 296 (5, M^+), 55 (20), 69 (22), 102 (36), 129 (100), 130 (24). HR-EI-MS: 296.2139 ($C_{21}H_{28}O^+$, M^+; calc. 296.2140).

(Phenylethynyl)cyclododecane (**3e**). IR (neat): 1489, 2225. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.25–1.61 (*m*, 16 H, CH_2); 1.50–1.61 (*m*, 4 H, CH_2); 1.65–1.73 (*m*, 2 H, CH_2); 2.65–2.71 (*m*, CH); 7.22–7.28 (*m*, 3 arom. H); 7.37–7.40 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.20; 23.38; 23.45; 23.81; 23.88; 27.41; 29.91; 80.18; 94.93; 124.18; 127.32; 128.09; 131.56. EI-MS: 268 (28, M^+), 91 (51), 115 (56), 128 (63), 129 (100). HR-EI-MS: 268.2193 ($C_{20}H_{28}^+$, M^+; calc. 268.2191).

4-Ethyl-1-phenylhex-1-yn-3-one (**2f**) *and 4-Methyl-1-phenylhept-1-yn-3-one* (**2f′**). Ratio **2f**/**2f′** 29 : 71. IR (neat): 2199, 1667. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.90–0.97 (*m*, 5.5 H, Me); 1.23 (*d*, J = 6.85, 3 H, Me); 1.34–1.54 (*m*, 2.5 H, CH_2); 1.59–1.68 (*m*, 1.1 H, CH_2); 1.77–1.88 (*m*, 1.4 H, CH_2); 2.42–2.48 (*m*, 0.4 H, COCH); 2.67 (*sext.*, J = 5.95, 1.0 H, COCH); 7.31–7.47 (*m*, 4.2 H, Ph); 7.57–7.59 (*m*, 2.8 H, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.66; 14.06; 16.01; 20.26; 24.16; 35.05; 48.36; 57.70; 86.95; 87.04; 91.00; 91.33; 128.59; 130.59; 133.02; 133.07; 192.31. EI-MS: 200 (7, M^+), 172 (22), 158 (39), 129 (100), 102 (76), 75 (100). HR-EI-MS: 200.1201 ($C_{14}H_{16}O^+$, M^+; calc. 200.1200).

(3-Ethylpent-1-ynyl)benzene (**3f**) *and 1-(3-Methylhex-1-ynyl)benzene* (**3f′**). Ratio **3f**/**3f′** 32 : 68. IR (neat): 2232. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.94 (*t*, J = 6.9, 3.0 H, Me); 1.06 (*t*, J = 7.35, 2.7 H, Me); 1.24 (*d*, J = 7.35, 3 H, Me); 1.40–1.63 (*m*, 5.8 H, CH_2); 2.37–2.45 (*m*, 0.46 H, CH); 2.65 (*sext.*, J = 5.5, 1 H, CH); 7.24–7.30 (*m*, 4 H, Ph); 7.37–7.42 (*m*, 2.9 H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): 11.98; 14.03; 20.69; 21.14; 26.36; 27.85; 35.79; 39.28; 80.71; 81.97; 93.58; 94.91; 124.20; 127.45; 128.20; 131.60. EI-MS: 172 (58, M^+), 157 (56), 143 (87), 129 (100), 83 (90). HR-EI-MS: 172.1252 ($C_{13}H_{16}^+$, M^+; calc. 172.1248).

4-Ethyl-1-phenylhept-1-yn-3-one (**2g**) *and 4-Methyl-1-phenyloct-1-yn-3-one* (**2g′**). Ratio **2g**/**2g′** 43 : 57. IR (neat): 2200, 1670. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.78–0.92 (*m*, 7.5 H, Me); 1.14 (*d*, J = 7.1, 3 H, Me); 1.20–1.35 (*m*, 6.1 H, CH_2); 1.40–1.60 (*m*, 2.1 H, CH_2); 1.64–1.82 (*m*, 2.3 H, CH_2); 2.42–2.49 (*m*, 0.75 H, COCH); 2.53–2.64 (*m*, 1.0 H, COCH); 7.25–7.40 (*m*, 5.3 H, Ph); 7.47–7.55 (*m*, 3.5 H, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.66; 13.89, 14.12; 16.00; 20.43; 22.64; 24.62; 29.19; 32.57; 33.34; 48.54; 55.98; 128.57; 130.56; 132.99; 133.04; 192.29; 192.34. EI-MS: 214 (6, M^+), 186 (11), 172 (48), 158 (49), 129 (100), 102 (39), 75 (21). HR-EI-MS: 214.1358 ($C_{15}H_{18}O^+$, M^+; calc. 214.1356).

(3-Ethylhex-1-ynyl)benzene (**3g**) *and (3-Methylhept-1-ynyl)benzene* (**3g′**) [16]. Ratio **3g**/**3g′** 43 : 57. IR (neat): 2228. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90–0.97 (*m*, 5.3 H, Me); 1.06 (*t*, J = 7.32, 2.3 H, Me); 1.24 (*d*, J = 6.84, 3.0 H, CH_2); 1.25–1.62 (*m*, 10.5 H, CH_2); 2.44–2.54 (*m*, 0.8 H, CH); 2.58–2.66 (*m*, 1 H, CH); 7.25–7.32 (*m*, 5.3 H, Ph); 7.37–7.43 (*m*, 3.5 H, Ph). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.88; 14.04; 14.68; 20.67; 21.11; 22.56; 26.49; 28.16; 29.65; 33.77; 36.72; 36.99; 41.59; 80.61; 81.73; 93.66; 94.89; 124.11; 124.22; 127.34; 127.38; 128.13; 131.55; 131.56. EI-MS: 186 (34, M^+), 157 (47), 129 (100), 83 (77). HR-EI-MS: 186.1409 ($C_{14}H_{18}^+$, M^+; calc. 186.1412).

4,4,5-Trimethyl-1-phenylhex-1-yn-3-one (**2h**). IR (neat): 1666, 2199. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*d*, J = 7.08, 2 Me); 1.16 (*s*, 2 Me); 2.25 (*sept.*, J = 4.55, Me_2CH); 7.35–7.47 (*m*, 3 arom. H); 7.56–7.60 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 8.57; 17.54; 20.18; 33.97; 51.47; 86.49; 91.58; 120.35; 128.57; 130.47; 132.95; 194.80. EI-MS: 214 (12, M^+), 84 (20), 85 (61), 102 (26), 129 (100), 130 (31), 143 (30), 199 (27). HR-EI-MS: 214.1353 ($C_{15}H_{18}O^+$, M^+; calc. 214.1358).

5,6-Dimethyl-1-phenylhept-1-yn-3-one (**2h′**). IR (neat): 1669, 2203. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88–0.97 (*m*, 3 Me); 1.62–1.70 (*m*, CH); 2.10–2.16 (*m*, CH); 2.43 (*dd*, J = 15.36, 9.00, 1 H, $COCH_2$);

2.70 (*dd*, *J* = 15.12, 4.88, 1 H, $COCH_2$); 7.37–7.48 (*m*, 3 arom. H); 7.55–7.60 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.91; 18.37; 19.81; 32.18; 35.42; 50.29; 88.09; 90.39; 120.07; 128.60; 130.63; 133.03; 188.49. EI-MS: 214 (8, M^+), 75 (17), 102 (90), 129 (100), 130 (25), 144 (93), 171 (29), 172 (22), 199 (42). HR-EI-MS: 214.1358 ($C_{15}H_{18}O^+$, M^+; calc. 214.1358).

4-Methyl-1-phenylpent-1-yn-3-one (**2i**) [15]. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.26 (*d*, *J* = 6.9, 2 Me); 2.75 (*sept*., *J* = 6.9, COCH); 7.30–7.40 (*m*, 2 arom. H); 7.43–7.47 (*m*, 1 arom. H); 7.50–7.59 (*m*, 2 arom. H).

(3,3,4-Trimethylpent-1-ynyl)benzene (**3h**) [7]. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.02 (*d* , *J* = 6.4, Me_2CH); 1.24 (*s*, Me_2C); 1.63 (*sept*., *J* = 6.9, Me_2CH); 7.20–7.30 (*m*, 3 arom. H); 7.36–7.41 (*m*, 2 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.36; 18.42; 26.94; 26.98; 35.46; 37.81; 80.86; 96.82; 124.26; 127.25; 128.10; 131.57.

3. *Reaction of Ethynyl Triflone* **A** *with a Mixture of Cycloalkanes.* A mixture of AIBN (16.5 mg, 0.10 mmol), ethynyl triflone **A** (117.6 mg, 0.50 mmol), cyclopentane (4.7 ml, 50 mmol), cyclohexane (5.4 ml, 50 mmol), cycloheptane (6.1 ml, 50 mmol), and cyclooctane (6.7 ml, 50 mmol) was stirred for 14 h at 85°. After cooling to r.t., the solvent was evaporated. The residue was purified by FC (silica gel, hexane → hexane/Et_2O 1 : 1): **3b**/**3a**/**3c**/**3d** (69.4 mg) 9 : 13 : 30 : 48. This ratio was determined by GC analysis.

4. *Formylation of a Mixture of Bromocycloalkanes.* A mixture of AIBN (51.7 mg, 0.31 mmol), tributylstannane (452.6 mg, 1.56 mmol), bromocyclopentane (125.6 mg, 0.84 mmol), bromocyclohexane (134.4 mg, 0.82 mmol), bromocycloheptane (141.8 mg, 0.80 mmol), bromocyclooctane (164.2 mg, 0.86 mmol), and benzene (15 ml) was placed in a 50-ml stainless-steel autoclave (stirring bar). The autoclave was closed, purged with carbon monoxide (3×), pressurized with 96 bar of CO, and then heated to 80° for 2 h. Excess CO was discharged at r.t. The residue was purified by FC (silica gel, hexane → hexane/Et_2O 10 : 1): **5b**/**5a**/**5c**/**5d** 18 : 29 : 28 : 25 and tributylstannanes. The ratio was determined by GC analysis.

5. *Carbonylation of Cyclohexane in the Presence of Allyl Triflone* ***B****. V-40* (= 2,2′-azobis[cyclohexanecarbonitrile]; 16.4 mg, 0.10 mmol), cyclohexane (30 ml), and allyl triflone **B** (119.5 mg, 0.49 mmol) were placed in a 100-ml stainless steel autoclave (stirring bar). The autoclave was closed, purged with carbon monoxide (3×), pressurized with 86 bar of CO and then heated to 110° for 14 h. Excess CO was discharged at r.t. The cyclohexane was evaporated and the oily residue (132.7 mg) purified by FC (silica gel, hexane/AcOEt: 50 : 1 → 15 : 1, then MeOH): **9a** (12.8 mg, 13%), **7a** (31.6 mg, 29%), **6a** (16.5 mg, 7%), and **8a** (11.3 mg, 10%).

α-Methylene-γ-oxocyclohexanebutanoic Acid Ethyl Ester (**6a**). IR (neat): 1757. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.24–1.40 (*m*, 8 H, CH_2, Me); 1.60–1.70 (*m*, 1 H, CH_2); 1.76–1.80 (*m*, 2 H, CH_2); 1.86–1.89 (*m*, 2 H, CH_2); 2.42 (*tt*, *J* = 11.45, 3.2, COCH); 3.43 (*s*, $COCH_2$); 4.17 (*q*, *J* = 7.18, CO_2CH_2); 5.58 (*s*, 1 H, C=CH_2); 6.32 (*s*, 1 H, C=CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.21; 25.69; 25.91; 28.72; 43.79; 50.77; 60.99; 128.35; 134.80; 166.44; 210.39. EI-MS: 224 (9, M^+), 55 (100), 67 (27), 68 (20), 69 (24), 83 (56), 85 (50), 113 (86), 114 (27), 141 (54), 178 (24). HR-EI-MS: 224.1405 ($C_{13}H_{20}O_3^+$, M^+; calc. 224.1412).

*(2*E*)-4-Cyclohexyl-2-methyl-4-oxobut-2-enoic Acid Ethyl Ester* (**7a**). The (2*E*) configuration was determined by comparison of the chemical shift of the olefinic proton with that of a related compound [17]. IR (neat): 1691, 1720. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.17–1.38 (*m*, 8 H, CH_2, Me); 1.65–1.68 (*m*, 1 H, CH_2); 1.77–1.90 (*m*, 4 H, CH_2); 2.17 (*s*, 3 H, Me); 2.44 (*m*, COCH); 4.25 (*q*, *J* = 7.02, CO_2CH_2); 7.13 (*s*, C=CH). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.22; 14.42; 25.63; 25.87; 28.13; 51.88; 61.58; 131.94; 140.92; 167.76; 205.15. EI-MS: 224 (21, M^+), 55 (47), 83 (100), 85 (63), 113 (56), 141 (45), 178 (30). HR-EI-MS: 224.1404 ($C_{13}H_{20}O_3^+$, M^+; calc. 224.1412).

2,2-Bis(2-cyclohexyl-2-oxoethyl)-4-methylenepentanedioic Acid Diethyl Ester (**8a**). IR (neat): 1712. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.10–1.30 (*m*, 16 H, CH_2, Me); 1.65–1.68 (*m*, 2 H, CH_2); 1.70–1.80 (*m*, 8 H, CH_2); 2.64 (br., 2 H, COCH); 2.78 (*s*, C=CH_2); 3.11 (*s*, 4 H, $COCH_2$); 3.99 (*q*, *J* = 6.95, 2 H, CO_2CH_2); 4.11 (*q*, *J* = 7.35, 2 H, CO_2CH_2); 5.44 (*s*, 1 H, C=CH_2); 6.17 (*s*, 1 H, C=CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$): 13.86; 14.08; 25.56; 25.75; 28.50; 37.69; 43.21; 45.22; 51.09; 60.66; 60.79; 128.34; 136.76; 166.85; 174.39; 213.09. EI-MS: 448 (3, M^+), 55 (52), 69 (28), 81 (20), 111 (33). HR-EI-MS: 448.2834 ($C_{26}H_{40}O_6^+$, M^+; calc. 448.2825).

α-Methylenecyclohexanepropanoic Acid Ethyl Ester (**9a**) [18]. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.08–1.31 (*m*, 8 H, CH_2, Me); 1.39–1.48 (*m*, 1 H, CH_2); 1.59–1.74 (*m*, 5 H, CH_2); 2.18 (*d*, *J* = 7.30, 2 H, CH_2=CCH_2); 4.19 (*q*, *J* = 7.18, CO_2CH_2); 5.45 (*s*, 1 H, C=CH_2); 6.13 (*s*, 1 H, C=CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.26; 26.30; 26.57; 33.13; 36.72; 39.96; 60.52; 125.38; 139.56; 167.55.

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