Indirect Electroreductive Sequential Radical Reaction Catalyzed by a Ni(II) Complex. One-Step Preparation of Functionalized (Methylene)cyclopentanes

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Substituted (methylene)cyclopentanes were prepared by one-step reaction at room temperature from butynyl iodides and activated olefins by sequencing of free radical addition and cyclization reactions. The reactions, which were conducted by indirect electroreduction catalyzed by a nickel(II) complex, proceeded with modest selectivity for formation of the *Z*(methylene)cyclopentanes.

Key words sequential radical reaction; catalytic electroreduction; nickel(II) complex; (methylene)cyclopentane; butynyl iodide

An important advantage of radical reactions is that sequential reactions can be accomplished in a single step. Most synthetic applications of sequential radical reactions have utilized the tin hydride method to achieve serial cyclizations by successive intra- and intramolecular radical reactions, so-called tandem radical cyclization.[1] Quite a few examples of sequential reactions including an intermolecular radical addition,[2] particularly those involving relatively slow addition reactions of the intermediate radical prior to intramolecular cyclization, have been reported.[2d–h] Usually such sequential reactions have been conducted using a large excess of radical acceptors, around 10 eq or more of olefins, and/or by keeping the concentration of the tin hydride as low as possible.[2d–g] Undesired side reactions of the final radicals, such as addition of the final radicals to olefins, have been prevented by introducing radical stabilizing groups into the final radicals[2e,g] or by the steric hindrance around the final vinyl radicals.[2d,f] In related sequential reactions conducted by other methods, such as the iodine atom transfer method[3] or the thiohydroxamate ester method,[4] the undesired side reactions of the final radicals have been avoided by rapid iodine transfer to the final radicals or by rapid β-elimination of the final radicals,[4b,c] respectively.

We have shown that nickel(II) complexes catalyze electroreductive generation of alkyl and vinyl radicals from various halides is a useful synthetic alternative to the tin hydride method, and is particularly useful for the intermolecular addition of alkyl radicals to olefins because of the absence of an overt hydrogen atom donor such as Sn-H in the system.[5b] It was also shown that the hydrogen atom transfer from solvent to alkyl radicals is not so fast as to prevent the final radicals from undergoing undesired side reactions such as coupling[5a] or disproportionation,[5d] while that to vinyl radicals is fast enough to give the products in good yield.[5a,6]

These results suggest that this electroreductive method for radical generation could control the course of sequential radical reactions outlined in Chart 1, where the reaction is terminated by rapid hydrogen transfers to vinyl radicals from the solvent after the relatively slow addition of intermediate radicals **1'** to olefins and cyclization of **2'**.[7]

In this work, we wish to show that this approach is available as a direct and mild method for construction of functionalized rings which possess a double bond that permits further functionalization, such as cleavage to ketones. Preliminary experiments using 1-iodo-3-butyne and methylacrylate, constant currents from 1 to 10 mA (current density = 1 to 10 mA cm^{-2}) and four nickel(II) complexes exhibiting redox couples at -0.7, -0.96, -1.10, and -1.38 V *vs.* saturated calomel electrode

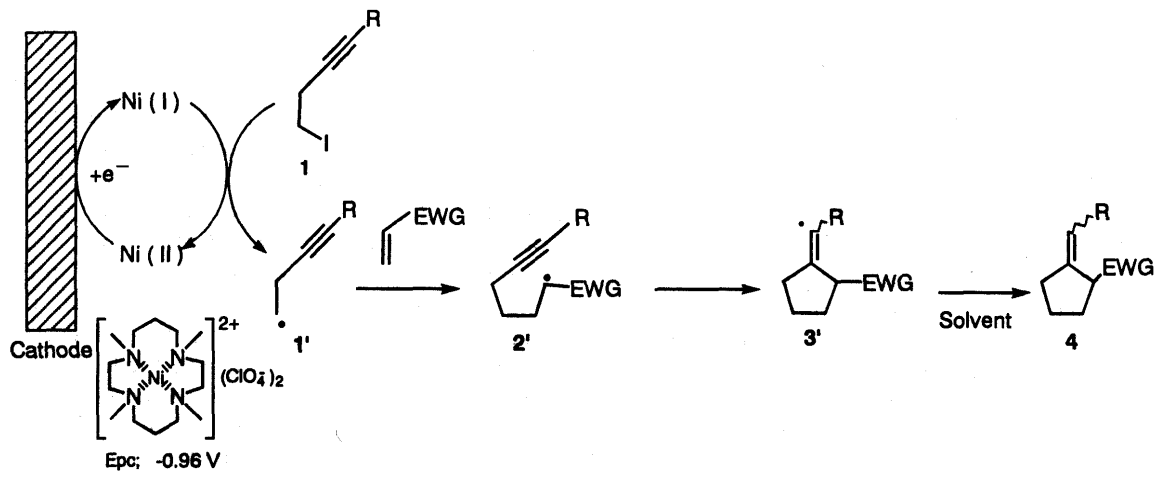

Chart 1

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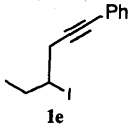
Table 1. Ni(II)(tmc)$(ClO_4)_2$ Catalysed Electroreductive Cycloaddition Reaction of Butynyl Iodides with Activated Olefins[a]

Run	Iodide (R)	Olefin	Procedure	2	Product Yield (%)[b] 3	4 (E:Z)	5 (E:Z)[c]
	H (1a)	CO_2Me		2a	3a	4a	5a
1			A	0	16	5	5 (1:5)
1′			B	0	[d]	16	0
	Ph (1b)	CO_2Me		2b	3b	4b	5b
2			A	21	4	11 (3:11)	38 (1:5)
2′			A′[e]	45	Trace	20	0
2″			B	45	Trace	23 (1:4)	Trace
	Ph (1b)	CO_2Me		2b	3c	4c	5c
3			A	9	0	23 (1:4)	10 (1:1)[f]
3′			B	[d]	[d]	41 (1:7)	0
	Ph (1b)	CN		2b	3d	4d	5d
4			A[g]	22	5	37 (7:13)	9 (1:2)
4′			B	[d]	5	30 (1:1)	0
	Ph (1b)	CN		2b	3e	4e	5e
5			A	33	35	8 (4:11)	0
5′			B	[d]	[d]	30 (2:5)	0
	Ph (1b)	CO_2Bn		2b	3f	4f	5f
6			A	9	0	23 (1:4)	26 (1:15)
6′			B	[d]	[d]	41 (1:4)	Trace
	Ph (1b)	COMe		2b	3g	4g	5g
7			A	12	14	15 (1:2)	17 (Z-only)
7′			B	[d]	[d]	35 (1:3)	4 (Z only)
	Ph (1b)	CO_2Me		2b	3h	4h	5h
8			A	45	Trace	19 (2:11)	0
8′			B	[d]	[d]	9 (z only)[h]	0
	$SiMe_3$ (1c)	CO_2Me		2c	3i	4i	5i
9			A	0	19	10 (1:3)	15 (1:2)
9′			B	0	[d]	33 (1:2)	Trace
	CH_3 (1d)	CO_2Me		2d	3j	4j	5j
10			A	0	14	10[i]	8[i]
10′			B	[d]	[d]	32[i]	Trace
	1e[j]	CO_2Me		2e	3k	4k	5k
11			A	[d]	7	21 (4:9)	51 (1:2)
11′			B	[d]	0	62 (3:8)	Trace

a) For conditions, see text. b) Isolated yield based on the iodides in procedure A, or the olefins in procedure B. c) The isomer that has a structure wherein a vinyl hydrogen of Z-4 is substituted by an olefin is indicated as Z-5. d) Detected but not determined. e) Electrolysis in the presence of 2 eq of Ph_2PH. f) Mixture of diastereoisomers. g) Electrolyzed in dimethylformamide. h) *trans*-Isomer. i) Single isomer about the double bond. The E/Z stereochemistry has not been determined. j) 4-Iodo-1-phenyl-1-hexyne (1e).



1e

(SCE),[8] indicated that the electroreductions with the nickel(II) complexes exhibiting peak potential at more negative potentials than *ca.* −1.10 V *vs.* SCE afforded the adduct, methyl 1-hepynate, but not the cyclized products.[9] The use of a nickel complex, nickel(II)(tmc)$(ClO_4)_2$ (Epc; −0.96 V *vs.* SCE) and a constant current of 3 mA (current density = 3 mA cm^{-2}) was found to be most favorable for formation of the cyclised products. Typical electroreductions were carried out by two procedures A or B, using 10 ml of dimethyl sulfoxide (DMSO) containing the iodide (1 or 2 mmol), the activated olefin (3 or 1 mmol), tetraethylammonium perchlorate (TEAP) (1 mmol) and Ni(tmc)$(ClO_4)_2$ (0.05 eq based on the iodide), a constant current of 3 mA (current density = *ca.* 3 mA cm^{-2}), a graphite cathode and a zinc anode in an undivided cell at ambient temperature under an inert gas until electricity amounting 1.04 F/mol based on the iodide was consumed: in procedure A, 1 mmol of the iodide and 3 mmol of the olefin were used; and in procedure B, 2 mmol of the iodide and 1 mmol of the olefin were used. The results are shown in Table 1. Procedure A provided the undesired product **5** (**a**—**k**) as a separable (**5b** and **5f**) or inseparable (other **5** than **5b** and **5f**) stereoisomeric mixture of *E* and *Z* isomers along with the desired product **4** (**a**—**k**), the simple reduction product **2** (**a**—**e**) and the adduct product **3** (**a**—**k**), though this procedure gave the higher total yields of cyclopentane derivatives in some cases (runs 2, 4, and 6). Procedure B provided **4** (**a**—**k**) as almost the sole cyclized product in modest yield as a separable (**4d** and **4e**) or inseparable mixture of *E* and *Z* isomers (other **4**

than **4d** and **4e**) with modest selectivity for formation of *Z*-**4**, along with the simple reduction product **2** and a trace of the adduct product **3**. The major isomer of **4** was tentatively assigned as *Z* based on the deshielding effect of the phenyl group on the *cis* allylic proton (**4b, d, f, g, h, k**) and/or the shielding effect of the phenyl group on protons of the acetyl (**4g**) or methyl group in the ester (**4b, c, h**) at the *cis* allylic position. The stereochemistry of *Z*-**4b** was confirmed by the ^1H–^1H correlation spectroscopy (COSY) spectrum of the *E*/*Z* mixture of **4b**, showing a cross-peak between phenyl protons and methyl protons in the major isomer. The stereochemistry of products from 1,5-ring closure of 2(4)- or 3-substituted 5-hexenyl radical is considered to reflect the conformations in the transition state; those containing the substituents in the pseudo-equatorial position will be predominant.[10] This suggests that 1,5-ring closure of 2(4)-methyl-5-hexenyl radical would afford a mixture in which the *trans*-stereoisomer predominates, whereas the 3-substituted radical would give a similar mixture containing mainly the *cis*-product. If this hypothesis holds for 1,5-ring closure of 1,2- or 1,3-disubstituted 5-hexynyl radicals, *trans*-**4h**, *cis*-**4k** and *cis*-**5k** would be the major stereoisomers in reactions of runs 8′, 11 and 11′, respectively. Nuclear Overhauser effect (NOE) difference spectroscopy showed compound *Z*-**4h** to have a *trans* stereochemistry (see the experimental section). The *cis*/*trans* stereochemistry of **4k** and **5k** has not been assigned, since the *E* and *Z* isomers of these compounds could not be obtained separately. As for *E*/*Z* nomenclature of **5**, the isomer in which the vinyl hydrogen of *Z*-**4** is substituted by an olefin is indicated as *Z*-**5**. The compound *E*/*Z*-**5c**, which possesses two chiral centers, was obtained as a mixture of the diastereoisomers. The product derived *via* 6-*endo* mode of cyclization could not be detected from both procedures A or B. The electrolysis conducted by procedure A in the presence of 2 eq of a hydrogen donor, diphenyl phosphine (Ph_2PH) (procedure A, run 2′) also gave the desired product **4b** as the sole cyclized product, but in a slightly lower yield than that by procedure B. As shown by the yields of the cyclized product **4**, the stabilizing effect of the phenyl group of the butynyl iodide on the final radical **3′** seems to play an important role in the cyclization of the adduct radicals **2′**. The addition of the 1-phenyl-1-butynyl radical to a substituted olefin, methyl crotonate (runs 8 and 8′), seems to be slower than that to terminal olefins as shown by the larger yield of the simple reduction product, 1-phenyl-1-butyne. The addition of a secondary alkyl radical to a terminal olefin, methylacrylate, proceeded smoothly (runs 11 and 11′).[5b] The modest selectivity for formation of the thermodynamically less stable *Z*-**4** and *Z*-**5** might suggest that the transfer of a hydrogen atom or an olefin to the alkenyl radical **3′** occurs preferentially from the less hindered side of the radical,[11] in other words, the formation of *E* and *Z* substituted cyclopentanes **4** and **5** is kinetically controlled. In contrast with the result of electroreductive cyclization of α-iodoamides,[5e] which provided iodinated pyrrolidinones as the sole cyclized product, the present electroreduction of 3-butynyl iodides did not afford the iodinated product. This might be attributed to the fact that alkyl iodides, 3-butynyl iodides are not good iodine atom donor compared to α-iodoamides,[12] and so at room temperature hydrogen transfer to the final vinyl radical **3′** from the solvent DMSO and/or electron transfer from nickel(I)(tmc) to 3-butynyl iodide are much more rapid than iodine atom transfer from 3-butynyl iodide to the final radical **3′**.

In summary, the present sequential reactions conducted by the electroreductive method of radical generation appear to afford a direct and mild method for construction of functionalized rings, although the yields are inherently modest (30—60%) in this type of sequential reaction.

Experimental

Instrumentation NMR spectra were taken on a JEOL EX-270, JEOL GX-500 or Varian VXR-200 instrument. The *J*-values are given in hertz (Hz). IR spectra were taken on a JASCO VALOR III instrument. Cyclic voltammetry was performed with a three-electrode system employing a linear scanning unit (Huso Electrochemical System HECS 321B) equipped with a potentiostat (Hokuto Denko PS-55B). Constant current electrolysis was carried out with a potentio-galvanostat (Hokuto Denko HA 105S), and the quantity of electricity was recorded with a coulometer (Hokuto Denko HF-201).

Materials **4-Iodo-1-butyne (1a)** Compound **1a** was prepared by a literature method[13] with small modifications. Purification of the crude product by distillation yielded **1a** (68%), bp 58 °C/68 mm (lit.[12] 61 °C/80 mm).

4-Iodo-1-phenyl-1-butyne (1b) Compound **1b** was prepared based on the literature,[14] as follows. Triphenyl phosphine (13.5 g, 51.3 mmol) and hexamethylphosphoric triamide (HMPA) (12.3 g, 68.4 mmol) were successively added dropwise to iodine in dry ether (120 ml) under nitrogen gas. 1-Phenyl-1-butyn-4-ol (5 g, 34.2 mmol) in dry ether was added to the mixture at 0 °C. After having being stirred for 6 h at 0 °C the reaction mixture was diluted with saturated aqueous (sat. aq.) $NaHCO_3$ and extracted with ether. The extract was washed successively with 5% aq. Na_2SO_3, 1 N aqueous (aq.) H_2SO_4 and sat. aq. $NaHCO_3$. Purification of the crude product by silica gel column chromatography yielded **1b** as an oil (8.09 g, 86%). ^1H-NMR (200 MHz, $CDCl_3$) δ: 2.99 (2H, t, J=7.2, $CH_2C{\equiv}C$), 3.12 (2H, t, J=7.4, CH_2I), 7.30 (3H, m, ArH), 7.42 (2H, m, ArH).

4-Iodo-1-(trimethylsilyl)-1-butyne (1c) Compound **1c** was prepared by literature method[14] from 4-butyn-1-ol. A colorless oil (33%); ^1H-NMR (200 MHz, $CDCl_3$) δ: 0.16 (9H, s, 3 × Me), 2.78 (2H, t, J=7.5, $CH_2C{\equiv}C$), 3.21 (2H, t, J=7.5, CH_2I).

5-Iodo-2-pentyne (1d) Compound **1d** was prepared in a similarly to **1a**, from 3-pentyn-1-ol. Purification of the crude product by distillation yielded **1d** as a colorless oil (95%), bp 66 °C/20 mm.

4-Iodo-1-phenyl-1-hexyne (1e) Compound **1e** was prepared by literature method[15] as follows. BuLi (23.1 ml of 1.6 M in hexane) was added to phenylacetylene (3.77 g, 37 mmol) in tetrahyrofuran (THF) (60 ml) at −78 °C under nitrogen. The mixture was stirred for 30 min, then $BF_3{\cdot}Et_2O$ (3.3 ml) was added dropwise. After 30 min, 1,2-butylene oxide (1.78 g, 24.6 mmol) in THF (15 ml) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C, then diluted with sat. aq. NH_4Cl and extracted with Et_2O. Evaporation of the Et_2O gave the crude product, 1-phenyl-1-hexyn-4-ol as oil (2.41 g, 60%). Triethylamine (1.53 g, 15.1 mmol) and methansulfonyl chloride (1.73 g, 15.1 mmol) were added successively to 1-phenyl-1-hexen-4-ol (2.17 g, 12.2 mmol) in methylene chloride (50 ml). The reaction mixture was stirred for 3 h, then diluted with sat. aq. NH_4Cl and extracted with methylene chloride. NaI (3.63 g, 24.2 mmol) was added to the crude 4-mesylated-1-phenyl-1-hexyne in acetone (80 ml) under nitrogen. The mixture was heated under reflux for 48 h, then the acetone was evaporated off. The residue was diluted with sat. aq. NH_4Cl (60 ml) and extracted by Et_2O. Purification of the crude product by silica gel column chromatography provided **1e** as a colorless oil (2.37 g, 68%).

Constant Current Electrolysis Electroreductions were carried out by procedure A or B using 10 ml of DMSO containing TEAP (1 mmol) in an undivided cell, with the iodide (1 mmol) and the activated olefin (3 mmol) in procedure A or the iodide (2 mmol) and the activated olefin (1 mmol) in procedure B, and $Ni(tmc)(ClO_4)_2$ (0.05 mmol), at a constant current of 3 mA (current density *ca.* 3 mA cm^{-2}), between a graphite

cathode and a zinc anode at ambient temperature under an inert gas until electricity amounting to 1.04 F/mol based on the iodide was consumed. The products were extracted with diethyl ether from the electrolyte, after dilution with sat. aq. NH_4Cl, and separated by column chromatography (silica gel). The major isomer was tentatively assigned as *Z* based on the deshielding effect of the phenyl group on the *cis* allylic proton (**4b, d, f, g, h, k**) and/or the shielding effect of the phenyl group on the methyl protons in the acetyl group (**4g**), or the methyl protons in ester at the *cis* allylic position (**4b, c, h**). The stereochemistry of the major product **4b** was confirmed as *Z* by ^1H–^1H COSY examination of an *E*/*Z* mixture of **4b**, showing a cross-peak between the phenyl protons and major methyl protons . The stereochemistry of **5** was tentatively assigned in a similar way, applied to **4**. The *E*/*Z* ratios were determined by ^1H-NMR integration of singlet methyl or benzyl protons. The *cis*/*trans* stereochemistry of *Z*-**4h** was assigned by means of NOE difference spectroscopy. Good elemental analyses of some of **4** and **5** were not obtained since they decomposed on standing, probably through autoxidation or polymerization. Spectra data and analytical results of the products are as follows.

1-Phenyl-1-butyne (2b) An oil. IR ν_{max}^{KBr} cm^{-1}: 2238 (C≡C), 1599, 1491 (phenyl ring). ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.15 (3H, t, J=7.9, Me), 2.34 (2H, q, J=7.4, CH_2), 7.16—7.35 (5H, m. ArH).

Methyl 6-Heptynate (3a) An oil. IR ν_{max}^{KBr} cm^{-1}: 1738 (CO). ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.50—1.83 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.22 (2H, td, J=7, 3, CH_2C), 2.35 (2H, t, J=7.3, CH_2CO), 3.68 (3H, s, MeO).

Methyl 7-Phenyl-6-heptynate (3b) An oil. IR ν_{max}^{KBr} cm^{-1}: 1738 (CO). ^1H-NMR (200 MHz, $CDCl_3$) δ: 161—1.90 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.34—2.47 (4H, m, $C\underline{H}_2CH_2CH_2C\underline{H}_2$), 3.68 (3H, s, MeO), 7.22—7.42 (5H, m, ArH).

7-Phenyl-6-heptynenitrile (3d) An oil. IR ν_{max}^{KBr} cm^{-1}: 1489, 1599 (phenyl ring), 2200 (CN). ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.68—1.95 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.20—2.52 (4H, m, $C\underline{H}_2CH_2CH_2C\underline{H}_2$), 7.24—7.44 (5H, m, ArH).

2-Methyl-7-phenyl-heptynenitrile (3e) IR ν_{max}^{KBr} cm^{-1}: 1506, 1599 (phenyl ring), 2237 (CN). ^1H-NMR (200 MHz, $CDCl_3$) 1.32 (3H, d, J=7, $\underline{Me}CH$), 1.64—1.88 (4H, m, $C\underline{H}_2C\underline{H}_2CH$), 2.44 (2H, m, CH_2C), 2.68 (1H, m, $MeC\underline{H}$), 7.20—7.44 (5H, m, ArH).

8-Phenyl-7-octyn-2-one (3g) IR ν_{max}^{KBr} cm^{-1}: 1599 (phenyl ring), 1719 (CO). ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.5—2.4 (4H, m, $CH_2C\underline{H}_2$-$C\underline{H}_2CH_2$), 2.35 (3H, s, MeCO), 2.38—2.58 (4H, m, $C\underline{H}_2CH_2CH_2C\underline{H}_2$), 7.22—7.45 (5H, m, ArH).

Methyl 7-Trimethylsilyl-6-heptynate (3i) An oil. IR ν_{max}^{KBr} cm^{-1}: 1742 (CO), 2174 (C≡C). ^1H-NMR (200 MHz, $CDCl_3$) δ: 0.144 (9H, s, 3 × MeSi), 1.46—1.82 (4H, m, $CH_2C\underline{H}_2C\underline{H}_2CH_2$), 2.21—2.38 (4H, m, $C\underline{H}_2CH_2CH_2C\underline{H}_2$) and 3.68 (3H, s, MeO).

Methyl 7-Methyl-6-heptynate (3j) An oil. IR ν_{max}^{KBr} cm^{-1}: 1736 (CO). ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.43—2.05 (4H, m, CCH_2CH_2), 1.76 (3H, t, J=3, MeC≡C), 2.15 (2H, m, CH_2C=), 2.33 (2H, t, J=6.7, CH_2CO), 3.66 (3H, s, MeO).

Methyl 4-Ethyl-7-phenyl-6-heptynate (3k) An oil. IR ν_{max}^{KBr} cm^{-1}: 1603 (phenyl ring), 1728 (CO). ^1H-NMR (200 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7.3, $\underline{Me}CH_2$), 1.22—1.60 (5H, m, CH_2CHCH_2), 2.52—2.72 (2H, m, CH_2CO), 3.05—3.25 (2H, m, CH_2C), 3.93 (3H, s, MeO), 7.30—7.50 (5H, m, ArH).

Methyl 2-(Methylene)cyclopentanecarboxylate (4a) An oil. IR ν_{max}^{KBr} cm^{-1}: 1651 (C=CH_2), 1738 (CO). ^1H-NMR (^1H–^1H COSY) (500 MHz, $CDCl_3$) δ: 1.58—2.13 (4H, m, CH_2CH_2), 2.38 (2H, m, CH_2C=), 3.34 (1H, t, J=6, CHCO), 3.74 (3H, s, MeCO), 5.04 (1H, d, J=10, C$\underline{H}$H=), 5.06 (1H, d, J=10, CH$\underline{H}$=).

(*E*)- and (*Z*)-Methyl 2-(Benzylidene)cyclopentanecarboxylate (4b) Inseparable 3/11 and 1/4 mixtures of *E* and *Z* isomers from procedures A and B, respectively. Oils. Found: C, 77.49; H, 7.52. *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1433 (CH_2), 1732 (CO). *E* isomer ^1H-NMR (^1H–^1H COSY) (500 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 1.69 (1H, m, $CH_2C\underline{H}HCH_2$, overlapped with *Z* isomer), 1.88 (1H, m, $CH_2CH\underline{H}CH_2$, overlapped with that of the *Z* isomer), 1.95—2.14 (2H, m, $C\underline{H}_2CH$, overlapped with those of the *Z* isomer), 2.51 (1H, m, $CH\underline{H}C$=C, overlapped with that of the *Z* isomer), 2.68 (1H, m, $CH\underline{H}C$=C, overlapped with *Z* isomer), 3.50 (3H, m, CHCO), 3.70 (3H, s, OMe), 6.50 (1H, m, HC=C, overlapped with that of the *Z* isomer), 7.16—7.39 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 3.54 (3H, s, MeO), 3.70 (1H, m, CHCO) (the peaks of the other twelve protons overlapped with those of *E* isomer). ^{13}C NMR δ_C (67.8 MHz, $CDCl_3$, *E*/*Z* mixture): 23.65, 32.51 and 35.37 (CH_2), 46.96 ($\underline{C}HCO$), 51.68 ($\underline{C}H_3CO$), 123.74, 124.33, 126.32, 128.10, 128.25, and 128.89 (CH=$\underline{C}$ and aromatic CH), 137.48 and 143.20 (Cq), 174.88 (CO).

(*E*)- and (*Z*)-Methyl 2-(Benzylidene)-1-methylcyclopentanecarboxylate (4c) Inseparable 1/7 and 1/4 mixtures of *E* and *Z* isomers from procedures A and B, respectively. Oils. Found: C, 78.46; H, 8.30. *Anal.* Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1458 (CH_2) and 1732 (CO). *E* isomer ^1H-NMR (270 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 1.43 (3H, s, MeC), 1.66—2.24 (4H, m, CH_2CH_2C overlapped with those of the *Z* isomer), 2.68—2.78 (2H, m, CH_2C=), 3.68 (3H, s, MeO), 6.37 (1H, t, J=2.5, CH=C), 7.02—7.62 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 1.28 (3H, s, MeC), 3.45 (3H, s, MeO), 6.48 (1H, s, CH=C) (the peaks of other six protons overlapped with those of the *E* isomer). ^{13}C-NMR (67.8 MHz, $CDCl_3$, *E*/*Z* mixture): 22.61 and 51.54 (CH_3), 23.20, 36.05 and 43.14 (CH_2), 123.06, 126.36, 127.92, 128.27, and 128.37 (CH and aromatic CH), 131.50, 137.57 and 148.86 (Cq), 177.47 (CO).

(*E*)- and (*Z*)-2-(Benzylidene)-1-cyclopentanecarbonitrile (4d) Inseparable 7/13 and 1/1 mixtures of *E* and *Z* isomers from procedures A and B, respectively. A part of the *Z* isomer was isolated from the product of procedure A. Oils. Found: C, 85.16; H, 7.75; N, 6.92. *Anal.* Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1447 (CH_2), 2236 (C≡N). *E* isomer ^1H-NMR (200 MHz, $CDCl_3$, (*E*/*Z* mixture) δ: 1.80—2.72 (6H, m, 3 × CH_2, overlapped with those of the *Z* isomer), 3.57 (1H, t, J=7.6, CHCN), 6.58 (1H, s, CH=C), 7.24—7.39 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer (500 MHz, $CDCl_3$) δ: [1.81 (1H, m), 1.91—2.05 (2H, m), 2.20 (1H, m) $C\underline{H}_2C\underline{H}_2CH$], 2.53 (1H, m, $C\underline{H}HC$=), 2.70 (1H, m, $CH\underline{H}C$=), 3.66 (1H, m, CHCN), 6.58 (1H, s, CH=C), 7.24—7.39 (5H, m, ArH) (the peaks of the other six protons overlapped with those of the *E* isomer).

(*E*)- and (*Z*)-2-(Benzylidene)-1-methylcyclopentanecarbonitrile (4e) A separable 4/11 mixture of *E* and *Z* isomers from procedure A and an inseparable 2/5 mixture of *E* and *Z* isomers from procedure B. Oils. *E* isomer IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1447 (CH_2), 2228 (CN). ^1H-NMR (200 MHz, $CDCl_3$) δ: 1.57 (3H, s, Me), 1.75—2.35 (4H, m, CH_2CH_2C), 2.66—2.84 (2H, m, CH_2C=), 6.62 (1H, t, J=2.4, CH=C), 7.18—7.45 (5H, m, ArH); *Z* isomer (200 MHz, $CDCl_3$) δ: 1.30 (3H, s, Me), 1.74—2.50 (4H, m, CH_2CH_2C), 2.50—2.82 (2H, m, CH_2C=), 6.65 (1H, s, CH=C), 7.18—7.45 (5H, m, ArH). ^{13}C-NMR (67.8 MHz, $CDCl_3$, *Z* isomer): 25.82 (CH_3), 23.69, 30.33 and 31.30 (CH_2), 124.73, 127.08, 128.36, 128.48 (CH and aromatic CH), 133.80 and 136.90 (Cq).

(*E*)- and (*Z*)-Benzyl 2-(Benzylidene)cyclopentanecarboxylate (4f) Inseparable 1/4 mixture of *E* and *Z* isomer from both procedures A and B as determined by ^1H-NMR integration of benzyl protons. Oils. Found: C, 82.36; H, 6.99. *Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90). IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1456 (CH_2), 1732 (CO). *E* isomer ^1H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 1.59—2.19 (4H, m, $C\underline{H}_2C\underline{H}_2CH$, overlapped with those of the *Z*-isomer), 2.42—2.82 (2H, m, CH_2C=), 3.57 (1H, t, J=4.7, CHCO), 5.17 and 5.19 (2H, s, CH_2Ph), 6.50 (1H, s, CH=C), 7.11—7.38 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 3.76 (1H, t, J=4.7, CHCO), 5.00 and 5.01 (2H, s, CH_2Ph) (the peaks of the other twelve protons overlapped with those of the *E* isomer).

(*E*)- and (*Z*)-2-Acetyl(benzylidene)cyclopentane (4g) Inseparable 1/2 and 1/3 mixtures of *E* and *Z* isomers from procedures A and B, respectively. Oils. Found: C, 83.70; H, 8.36. *Anal.* Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1447 (CH_2), 1705 (CO). ^1H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 2.21 (3H, s, MeCO), 1.58—2.27 (4H, m, $C\underline{H}_2C\underline{H}_2CH$, overlapped with those of the *Z* isomer), 2.53—2.71 (2H, m, CH_2C=, overlapped with those of the *Z* isomer), 3.58 (1H, t, J=6.2, CHCO), 6.37 (1H, dd, J=2.4, 2.0, CH=C), 7.12—7.38 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 1.99 (3H, s, MeCO), 3.82 (1H, t, J=8.2, CHCO), 6.56 (1H, d, J=2.0, CH=C) (the peaks of the other eleven protons overlapped with those of the *E* isomer).

(*E*)- and (*Z*)-Methyl 5-Methyl-2-(benzylidene)cyclopentanecarboxylate (4h) An inseparable 2/11 mixture of *E* and *Z* isomers from procedure A and *Z* isomer only from procedure B. Oils. ^1H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 1.08 (3H, d, J=8, $\underline{Me}CH$), 1.30—2.64 (5H, m, CH_2CH_2CH , overlapped with *Z* isomer), 2.64 (2H, m, CH_2C=, overlapped with those of the *Z* isomer), 3.10 (1H, d, J=8.7, CHCO), 3.78 (3H, s, MeO), 6.40 (1H, s, CH=C), 7.15—7.34 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer (^1H–^1H COSY) (500 MHz, $CDCl_3$) δ: 1.10 (3H, d, J=8, $\underline{Me}CH$), 1.35 (1H, m, $C\underline{H}HCH$), 2.0 (1H, m, $CH\underline{H}CH$), 2.34 (1H, m, $C\underline{H}Me$), 2.57 (1H, m, $C\underline{H}HC$=),

2.70 (1H, m, CHHC=), 3.22 (1H, d, J=8.7, CHCO), 6.51 (1H, s, CH=C), 7.06—7.44 (5H, m, ArH). NOE difference spectroscopy: when the signal due to the 1-H proton was irradiated, no effect was observed at the 5-H proton.

(*E*)- and (*Z*)-Methyl 2-[(Trimethylsilyl)methylidene]cyclopentanecarboxylate (4i) Inseparable 1/3 and 1/2 mixtures of *E* and *Z* isomers from procedures A and B, respectively, the *E*/*Z* ratio was tentatively determined based on the trend that the *Z* isomer is formed predominantly. Oils. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1736 (CO). ^{1}H-NMR (270 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 0.103 (9H, s, Me_3Si), 1.62—2.62 (6H, m, 3×CH_2, overlapped with those of the *Z* isomer), 3.32 (1H, t, *J*=8.2, CHCO), 3.72 (3H, s, MeO), 5.52 (1H, s, CH=C); *Z* isomer δ: 0.096 (9H, s, Me_3Si), 3.46 (1H, t, *J*=8.0, CHCO), 3.69 (3H, s, MeO), 5.59 (1H, s, CH=C) (the peaks of other six protons overlapped with those of *E* isomer).

(*E*) and (*Z*)-Methyl (2-Ethylene)cyclopentanecarboxylate (4j) Inseparable mixture of *E* and *Z* isomers from both procedures A and B, oils, (methoxy singlets of both *E*- and *Z*-**4j** exhibit ^{1}H-NMR resonances too close together to determine the exact *E*/*Z* ratio). IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1674 (C=CH), 1736 (CO). ^{1}H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 1.4—2.2 (6H, m, 3×CH_2), 1.80 (3H, m, MeCH), 3.29 and 3.44 (1H, m, CHCO), 3.675 and 3.68 (3H, s, MeO), 5.49 (1H, m, CH=C).

(*E*)- and (*Z*)-Methyl 4-Ethyl-2-(benzylidene)cyclopentanecarboxylate (4k) Inseparable mixtures of 4/9 and 3/8 *E* and *Z* isomer from procedures A and B, respectively. Oils. Found: C, 78.50; H, 8.59. *Anal.* Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. IR ν_{max}^{KBr} (*E*/*Z* isomer) cm^{-1}: 1456 (CH_2), 1775 (CO). Assignment of ^{1}H-NMR signals was referred to that of *Z*-**4h**; (270 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 3.56 (3H, s, MeO), 3.71 (1H, m, CHCO), 6.43 (1H, s, CH=C) (the peaks of the other protons overlapped with those of the *Z* isomer); ^{1}H-NMR (270 MHz, $CDCl_3$) *Z* isomer δ: 0.98 (3H, t, *J*=6, Me), 1.17—1.92 (3H, m, $CHCH_2Me$ and CHHCHCO overlapped with those of the *E* isomer), 2.15 (1H, m, CHHCH overlapped with that of the *E* isomer), 236 (1H, m, CHEt overlapped with that of the *E* isomer), 2.63 (1H, dd, *J*=15.8, 6.6, CHHC=, overlapped that of the *E* isomer), 2.82 (1H, m, CHHC=, overlapped with that of the *E* isomer) 3.48 (3H, s, MeO), 3.74 (1H, m, CHCO), 6.48 (1H, s, CH=C), 7.13—7.72 (5H, m, ArH overlapped with those of the *E* isomer). ^{13}C-NMR (67.8 MHz, $CDCl_3$, *E*/*Z* mixture): 12.76 and 51.79 (CH_3), 27.89, 38.36 and 42.41 (CH_2), 40.54, 46.97 and 133.71 (CH), 124.40, 126.36, 127.49, 127.92 and 127.96 (aromatic CH), 138.72 and 140.74 (Cq), 175.08 (CO).

(*E*)- and (*Z*)-Methyl 4-[(2-Methoxycarbonyl)cyclopentylidene]butyrate (5a) Products **5** were obtained only through proecedure A, as an inseparable 1/5 mixture of *E* and *Z* isomers. An oil. *E* isomer IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1655 (C=CH_2), 1738 (CO). ^{1}H-NMR (270 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 1.49—2.49 (10H, 5×CH_2, overlapped with those of the *Z* isomer), 3.46 (1H, t, CHCO), 3.66 (6H, s, MeCO), 5.48 (1H, m, CH=C); *Z* iosmer δ: 3.30 (1H, t, CHCO), 3.68 (6H, s, MeO), 5.36 (1H, m, CH=C) (the peaks of other ten protons overlapped with those of the *E* isomer). ^{13}C-NMR (67.8 MHz, $CDCl_3$, *E*/*Z* isomer): 24.42, 24.93, 27.84, 29.62 and 33.64 (CH_2), 49.17 and 51.43 (CH_3O), 118.76, 121.31 and 122.26 (CH), 142.46 (Cq), 173.57 and 174.90 (CO).

(*E*)- and (*Z*)-Methyl 4-[2-(Methoxycarbonyl)cyclopentylidene]-4-phenylbutyrate (5b) An inseparable 1/5 mixture of *E* and *Z* isomers. An oil. Found: C, 71.40; H, 7.34. *Anal.* Calcd for $C_{17}H_{22}O_4$: C, 71.50; H, 7.33. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1499 and 1600 (phenyl ring), 1736 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 1.61—2.85 (10H, m, 5×CH_2, overlapped with those of the *Z* isomer), 3.26 (1H, m, CHCO) , 3.58 (3H, s, $MeCO_2CH$), 3.72 (3H, s, $MeCO_2CH_2$), 7.03—7.35 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 3.30 (3H, s, $MeCO_2CH$), 3.60 (3H, s, $MeCO_2CH_2$), 3.68 (1H, m, CHCO) and (the peaks of the other ten protons overlapped with those of the *E* isomer). ^{13}C-NMR (67.8 MHz, $CDCl_3$, *E*/*Z* mixture) *Z* isomer δ: 24.94, 30.42, 30.87, 32.23 and 32.32 (CH_2), 48.21 and 51.14 (CH_3CO), 51.14 (CHCO), 128.01, 128.12, 128.27, and 128.45 (aromatic CH), 133.93, 141.29 and 141.60 (Cq), 173.46 and 175.40 (CO).

(*E*)- and (*Z*)-Methyl 4-[(2-Methoxycarbonyl-2-methyl)cyclopentylidene]-2-methyl-4-phenylbutyrate (5c) An inseparable 1/1 mixture of *E* and *Z* isomers. An oil. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1506 and 1599 (phenyl ring), 1738 and 1784 (CO). ^{1}H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 1.11 (3H, s, MeCCO), 1.16 (3H, d, MeCHCO), 1.58—2.72 (9H, m, 4×CH_2 and CH, overlapped with those of the *Z* isomer), 3.41 (3H, s, MeOCOC), 3.61 (3H, s, MeOCOCH, overlapped with those of the *Z* isomer), 7.00—7.28 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 1.00 (3H, s, MeCCO), 1.13 (3H, d, MeCHCO), 3.37 (3H, s, MeOCOC) (the peaks of the other twelve protons overlapped with those of *E* isomer). ^{13}C-NMR (67.8 MHz, $CDCl_3$, *E*/*Z* mixture): 16.44, 23.56, 51.38 and 52.17 (CH_3), 23.43, 32.33, 41.19 and 42.72 (CH_2) 37.50, 126.70, 127.67 and 129.18 (CH), 131.66, 140.74 and 145.31 (Cq), 176.94 and 177.56 (CO).

(*E*)- and (*Z*)-1-Cyano-3-[(2-cycano)cyclopentylidene]-3-phenylpropane (5d) An inseparable 1/2 mixture of *E* and *Z* isomers. An oil. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1500 and 1600 (phenyl ring), 2200 (CN). ^{1}H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 1.80—2.94 (10H, m, 5×CH_2, overlapped with those of the *Z* isomer), 3.33 (1H, t, CH), 7.10—7.42 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 3.80 (1H, t, *J*=6.4, CH) (the peaks other fifteen protons overlapped with those of the *E* isomer).

(*E*)-Benzyl 4-[(2-Benzyloxycarbonyl)cyclopentylidene]-4-phenylbutyrate (*E*-5f) An oil. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.64—2.86 (10H, m, $CH_2CH_2CH_2$ and $COCH_2CH_2$), 3.31 (1H, t, *J*=4.8, CHCO), 4.66 (1H, d, *J*=12.3, $CHCO_2CHH$), 4.82 (1H, d, *J*=12.3, $CHCO_2CHH$), 5.09 (2H, s, CH_2OCOCH_2), 6.96—7.45 (15H, m, 3×ArH).

(*Z*)-Benzyl 4-[(2-Benzyloxycarbonyl)cyclopentylidene]-4-phenylbutyrate, (*Z*-5f) An oil. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.40—2.30 (8H, m, $CH_2CH_2CH_2C$= and $COCH_2CH_2$), 2.69 (2H, m, CH_2CH_2C=C), 3.71 (1H, t, *J*=4.8, CHCO), 4.99 (2H, s, $CH_2CO_2CH_2$), 5.08 (1H, d, *J*=2.4, $CHCO_2CHH$), 5.19 (1H, d, *J*=12.4, $CHCO_2HH$), 7.08—7.35 (15H, m, 3×ArH). ^{13}C-NMR (67.8 MHz, $CDCl_3$): 25.21, 29.69, 30.33, 31.52, 32.37, 66.01 and 66.36 (CH_2), 47.52 (CHCO), 126.59, 127.89, 127.98, 128.09, 128.16, 128.28, 128.36 and 128.43 (aromatic CH), 131.14, 136.01, 136.14, 139.10 and 141.76 (Cq), 172.94 and 174.88 (CO).

(*Z*)-5-[(2-Acetyl)cyclopentylidene]-5-phenylpentan-2-one (*Z*-5g) An oil. *Z* isomer only from both procedures A and B. IR ν_{max}^{KBr} cm^{-1}: 1497 and 1600 (phenyl ring), 1716 (CO). ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.60—2.73 (10H, m, 5×CH_2), 2.06 (3H, s, MeCOCH), 2.18 (3H, s, $MeCOCH_2$), 3.44 (1H, m, CHCO), 6.98—7.40 (5H, m, ArH).

(*E*)- and (*Z*)-Methyl 4-[(2-Methoxycarbonyl)cyclopentylidene]-4-trimethylsilylbutyrate (5i) Inseparable 1/2 mixture of *E* and *Z* isomers as determined by ^{1}H-NMR integration of Me_3Si protons. An oil. ^{1}H-NMR (500 MHz, $CDCl_3$) *E* isomer δ: 0.13 (9H, s, Me_3Si), 1.48—2.53 (10H, m, 5×CH_2, overlapped with those of the *Z* isomer), 3.52 (1H, d, *J*=7.0, CHCO, overlapped with those of *Z* isomer), 3.65 (6H, s, 2×MeO); *Z* isomer δ: 0.09 (9H, s, Me_3Si), 3.63 (3H, s, $MeCO_2CH$), 3.65 (3H, s, $MeCO_2CH_2$) (the peaks of other eleven protons overlapped with those of the *E* isomer).

(*E*)- or (*Z*)-Methyl 4-[(2-Methoxycarbonyl)cyclopentylidene]valerate (5j) An oil. The compound **5j** appeared to be a single isomer from ^{1}H-NMR spectrum, but the stereochemistry has not been determined. IR ν_{max}^{KBr} (*E* or *Z*) cm^{-1}: 660 (C=C), 1732 and 1770 (CO). ^{1}H-NMR (200 MHz, $CDCl_3$, *E* or *Z*) δ: 1.54—2.53 (10H, m, 5×CH_2), 1.63 (3H, m, MeC=), 3.42 (1H, t, *J*=6.3, CHCO), 3.68 (3H, s, MeO), 3.70 (3H, s, MeO).

(*E*)- and (*Z*)-Methyl 4-[(2-Methoxycarbonyl-4-ethyl)cyclopentylidene]-4-phenylbutyrate (5k) An inseparable 1/2 mixture of *E* and *Z* isomers. An oil. IR ν_{max}^{KBr} (*E*/*Z* mixture) cm^{-1}: 1738 (CO). ^{1}H-NMR (200 MHz, $CDCl_3$, *E*/*Z* mixture) *E* isomer δ: 0.88—0.98 (3H, m, $MeCH_2$, overlapped with *Z* isomer), 1.22—2.82 (9H, m, CH_2CH_2CO, $CHCH_2CH$, CH_2Me and $CHCH_2$), 2.52—2.85 (2H, m, CH_2C=), 3.37 (3H, s, $MeCO_2CH$), 3.61 (3H, s, $MeCO_2CH_2$, overlapped with those of *Z* isomer), 3.66 (1H, m, CHCO), 7.0—7.33 (5H, m, ArH, overlapped with those of the *Z* isomer); *Z* isomer δ: 3.15 (3H, s, $MeCO_2CH$), 3.73 (1H, d, CHCO) (the peaks of other 22 protons overlapped with those of the *E* isomer). ^{13}C-NMR (67.8 MHz, *E*/*Z* mixture): 12.58, 51.21 and 51.75 (CH_3), 27.59, 32.02, 32.11, 37.83, and 38.38 (CH_2), 41.26 and 48.52 (CH), 126.13, 127.48, 127.69, 127.75, 127.98, and 128.48 (aromatic CH), 133.71, 138.72 and 140.74 (Cq), 173. 40 and 175.33 (CO).

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9) The amounts of electicities consumed (F/mol) in the electroreductive addition of alkyl radicals to activated olefins were around two, which indicates that the final radical stabilized by the electron withdrawing group was reduced to the corresponding carbanion at the applied potential (−1.35 V *vs.* SCE).[5b]

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