

Radical Addition of α-Halo Ester to Homoallylic Gallium or Indium Species: Formation of Cyclopropane Derivatives

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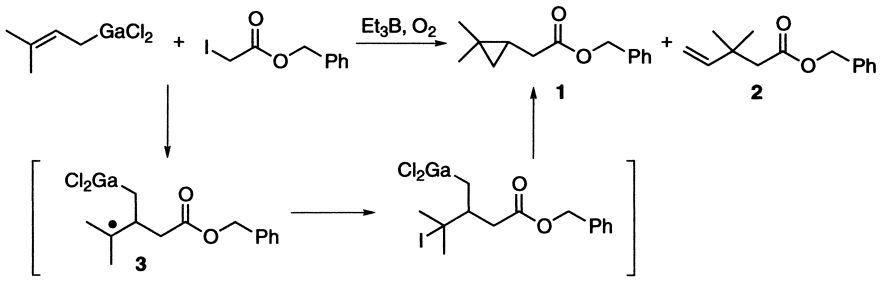
Treatment of benzyl bromoacetate with 3-butenylgallium dichloride in ether in the presence of a catalytic amount of Et_3B as a radical initiator provided benzyl 3-cyclopropylpropanoate in 64% yield via a radical addition–substitution sequence. The use of 3-butenylindium dichloride in place of the gallium reagent also afforded the same product in good yield.

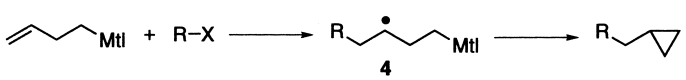
We have recently reported radical allylation of α-iodo esters with allylic gallium reagents.[1] During the course of our study, we found the formation of cyclopropylacetate **1**, in addition to the expected prenylated product **2**, when we employed prenylgallium dichloride as the allylating reagent (Scheme 1). The cyclopropane formation was observed only in the reaction with prenylgallium. This cyclopropane derivative was probably derived from a radical intermediate **3**. This unexpected result prompted us to examine whether the reaction of α-halo esters with homoallylmetal reagents could proceed to provide an efficient and mild route to cyclopropanes via a radical intermediate **4** (Scheme 2).[2] Herein we wish to report that homoallylgallium and homoallylindium species are effective reagents for the formation of cyclopropane derivatives from α-halo esters by way of a radical pathway.[3]

Treatment of α-halo esters and amides with homoallylgallium **5**, prepared from $GaCl_3$ and 3-butenylmagnesium bromide,[4] in the presence of Et_3B[5,6] provided the corresponding 3-cyclopropylpropanoate derivatives **7** in good yields.[7] The reaction of α-halo ketones was also examined. The results are summarized in Table 1.

Several comments are worth noting. (1) The reaction of benzyl iodoacetate (**6a**) with 3-butenylgallium dichloride in the presence of Et_3B (20 mol%) for 3 h gave benzyl 3-cyclopropylpropanoate (**7a**) in 79% yield. In contrast, **7a** was obtained in only 19% yield without Et_3B after prolonged reaction time (12 h) (entry 2). Moreover, no observable reaction proceeded in the presence of a radical scavenger such as TEMPO (entry 3). These facts suggest that the reaction proceeds via a radical process. (2) α-Halo amides provided the corresponding 3-cyclopropylpropanamides in moderate yields upon treatment with 3-butenylgallium dichloride **5** under the same reaction conditions (entries 10–16). Meantime, α-halo ketones afforded the adducts in poor yields except the case with phenacyl iodide (**6n**) (entries 17–20). (3) Not only primary halides but also secondary halides afforded the corresponding cyclopropane derivatives in 39–70% yields in cases of α-halo esters and amides (entry 5, 7, 9, 11, 13, and 15). However, a tertiary halide, benzyl 2-bromo-2-methylpropanoate (**6e**), provided the 3-cyclopropyl-2,2-dimethylpropanoate (**7e**) in only 22% yield (entry 8). (4) Although we have reported that the addition of water in the radical allylation with allylgalliums facilitated the

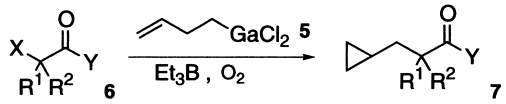


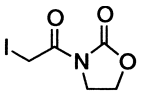
Scheme 1.



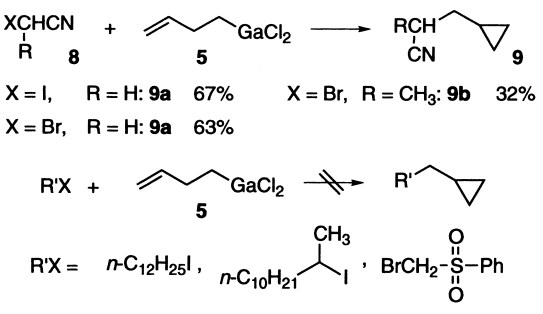
Scheme 2.

Table 1. Reaction of α-Halo Carbonyl Compounds with 3-Butenylgallium Dichloride

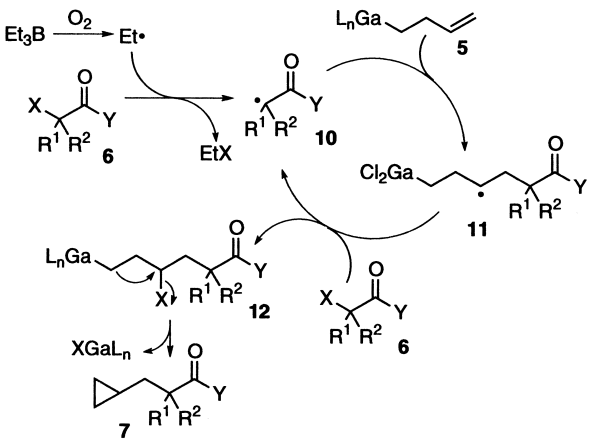


Entry	R^1	R^2	X	Y		Equiv of Et_3B	time/h		yield/%
1	H	H	I	OBn	**6a**	0.2	3	**7a**	79
2	H	H	I	OBn	**6a**	0	12	**7a**	19
3[a)]	H	H	I	OBn	**6a**	0.2	12	**7a**	0
4[b)]	H	H	I	OBn	**6a**	0.2	12	**7a**	<10
5	Me	H	I	OBn	**6b**	0.2	5	**7b**	70
6	H	H	Br	OBn	**6c**	0.5	10	**7c** (= **7a**)	64
7	Me	H	Br	OBn	**6d**	1.0	19	**7d** (= **7b**)	56
8	Me	Me	Br	OBn	**6e**	1.0	16	**7e**	22
9					**6f**	0.5	12	**7f**	64
10	H	H	I	NHBn	**6g**	0.5	4	**7g**	48
11	Me	H	I	NHBn	**6h**	0.5	13	**7h**	42
12	H	H	I	NEt_2	**6i**	0.5	13	**7i**	65
13	Me	H	I	NEt_2	**6j**	0.5	9	**7j**	40
14	H	H	Br	NEt_2	**6k**	0.5	15	**7k** (= **7i**)	40
15	Me	H	Br	NEt_2	**6l**	1.0	17	**7l** (= **7j**)	39
16					**6m**	0.5	13	**7m**	57
17	H	H	I	Ph	**6n**	0.2	4	**7n**	60
18	H	H	Br	Ph	**6o**	0.5	6	**7o** (= **7n**)	32
19	*n*-C_6H_{13}	H	I	Me	**6p**	0.5	3	**7p**	20
20	*n*-C_8H_{17}	H	Br	Me	**6q**	1.0	11	**7q**	27

a) The reaction was carried out in the presence of TEMPO(2,2,6,6-tetramethyl-1-piperidinyloxy) (0.1 mmol).
b) The reaction was carried out in the presence of water (1.0 mL).



Scheme 3.



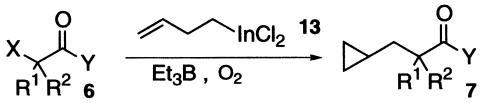
Scheme 4.

reaction, water proved to lower the yields of the adducts in this cyclopropane formation reaction (entry 4).

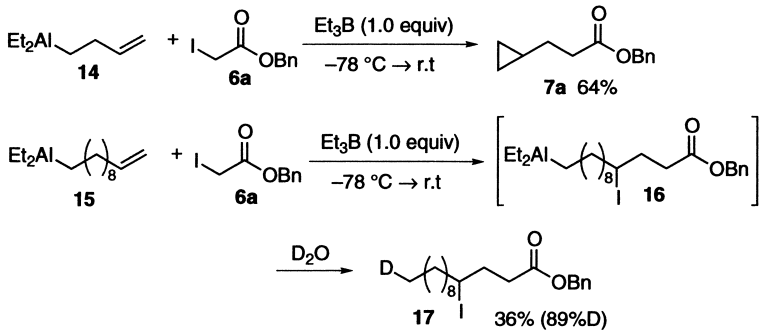
Whereas α-haloacetonitriles **8** provided the corresponding 3-cyclopropylpropanenitriles **9**, bromomethyl phenyl sulfone, 1-iodododecane, and 2-iodododecane afforded no trace of the corresponding cyclopropane derivatives upon treatment with 3-butenylgallium dichloride **5** (Scheme 3).

We assume the following reaction mechanism (Scheme 4). Initially, an ethyl radical, produced by the action of O_2 on Et_3B, abstracts halogen from an α-halo carbonyl compound **6** to give a carbon radical **10**. The radical **10** adds to the terminal carbon atom of the alkenyl moiety of the 3-butenyl group to afford **11**. The radical **11** then abstracts halogen from a second molecule of the α-halo carbonyl compound **6** to provide the atom transfer radical addition product **12** with concurrent regeneration of **10**.[8] Finally, an ionic intramolecular attack of the alkylgallium species on carbon bearing halogen furnishes cyclopropane derivatives **7**. The direct formation of cyclopro-

Table 2. Reaction of α-Halo Esters and α-Halo Ketones with 3-Butenylindium Dichloride



Entry	R^1	R^2	X	Y		Equiv of Et_3B	time/h		yield/%
1	H	H	I	OBn	**6a**	0.5	3	**7a**	65
2	H	H	I	OBn	**6a**	0	12	**7a**	19
3	Me	H	I	OBn	**6b**	0.5	10	**7b**	63
4	H	H	Br	OBn	**6c**	0.5	8	**7a**	65
5	Me	H	Br	OBn	**6d**	0.5	10	**7b**	50
6	Me	Me	Br	OBn	**6e**	0.5	10	**7e**	trace
7					**6f**	0.5	11	**7f**	71
8	H	H	I	Ph	**6n**	0.2	5	**7n**	55
9	n-C_6H_{13}	H	Br	CH_3	**6r**	0.5	4	**7r** (= **7p**)	23



Scheme 5.

pane compound **7** from **12** via the elimination of gallium(II) might be an alternative pathway.[9] In this case, low valent gallium(II) would abstract halogen from the starting α-halo compound **6** to regenerate the carbon radical **10**.[10]

The use of homoallylindium dichloride **13** in place of homoallylgallium dichloride **5** gave the same cyclopropane derivatives **7** upon treatment with α-halo carbonyl compounds **6** in the presence of Et_3B. 3-Butenylmagnesium bromide was added to a solution of indium trichloride in ether at 25 °C.[11] α-Halo ester **6** and Et_3B were added to the resulting indium reagent, and the mixture was stirred for several hours in the presence of air, which was introduced via a syringe. After aqueous workup, concentration followed by silica-gel column purification provided the corresponding cyclopropane derivative **7**. Table 2 summarizes the results of the cyclopropane formation reaction with homoallylindium **13**. Again, the addition of triethylborane is necessary for the successful reaction (entry 2). A similar reaction mechanism is also probable, as in the case of the reaction with the homoallylic gallium reagent. Although there are exceptions, homoallylgallium **5** affords the cyclopropane derivatives in somewhat better yields than homoallylindium **13**.

Homoallylaluminum **14**, derived from 3-butenylmagnesium bromide and Et_2AlCl, can also undergo the same type of the cyclopropane formation, although the reaction required a stoichiometric amount of Et_3B (Scheme 5). The Et_3B-induced reaction of 10-undecenylaluminum **15** with benzyl iodoacetate (**6a**) provided the radical addition product **17** in 36% yield with 89% of deuterium incorporation after deuteriolysis.[12] These results indicate that the carbon radical derived from benzyl iodoacetate can attack at the terminal carbon atom of the olefin moiety in the aluminum reagents.

In conclusion, we have developed the cyclopropane formation reaction with homoallylgallium and homoallylindium via an atom-transfer radical process. In this reaction, homoallylmetal reagents act as a cyclopropylmethylating reagent toward carbon-centered radicals. Radical addition to organometallics is limited to organosilanes and organostannanes,[13] which have relatively unreactive carbon–metal bonds. In this article, we have demonstrated that carbon radicals can add to the olefin moiety of organogalliums and organoindiums, which undergo the subsequent intramolecular substitution reaction to form a cyclopropane ring. Consequently, this reaction is a new entry of the radical reaction with a reactive organometallic compound as a radical acceptor.

Experimental

^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts are given in δ value with tetramethylsi-

lane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was freshly distilled from sodium benzophenone ketyl before use. Et_3B was purchased from Aldrich Chemicals and was diluted to prepare a 1.0 M hexane solution, which was stored under argon.

General Procedure for Cyclopropane Formation with Homoallylgallium. A solution of $GaCl_3$ (1.0 mL, 1.0 M hexane solution, 1.0 mmol) was diluted with ether (2 mL), then 3-butenylmagnesium bromide (1.25 mL, 0.86 M ether solution, 1.0 mmol) was introduced dropwise via a syringe. After the mixture was stirred for 20 min, benzyl bromoacetate (115 mg, 0.5 mmol) and Et_3B (0.25 mL, 1.0 M hexane solution, 0.25 mmol) were sequentially added. After the addition of air (10 mL) via a syringe, the mixture was stirred for 10 h. The mixture was then poured into water and extracted with ethyl acetate (20 mL×3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The residual oil was purified by silica-gel column chromatography to provide benzyl 3-cyclopropylpropanoate (**7a**, 65 mg) in 64% yield.

General Procedure for Cyclopropane Formation with Homoallylindium. To a solution of $InCl_3$ (221 mg, 1.0 mmol) in ether (2 mL), 3-butenylmagnesium bromide (1.25 mL, 0.86 M ether solution, 1.0 mmol) was added dropwise via a syringe. After the mixture was stirred for 20 min, benzyl bromoacetate (115 mg, 0.5 mmol) and Et_3B (0.25 mL, 1.0 M hexane solution, 0.25 mmol) were sequentially added. After the addition of air (10 mL) via a syringe, the mixture was stirred for 9 h. The mixture was then poured into water and extracted with ethyl acetate (20 mL×3). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The residual oil was purified by silica-gel column chromatography to provide benzyl 3-cyclopropylpropanoate (**7a**, 67 mg) in 65% yield.

Characterization Data. Benzyl 3-Cyclopropylpropanoate (7a): IR (neat) 3354, 3076, 2999, 2928, 1688, 1597, 1448, 1358, 1277, 1205, 1016, 941, 902, 741, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (m, 2H), 0.42 (m, 2H), 0.71 (m, 1H), 1.56 (dt, J = 7.2, 7.5 Hz, 2H), 2.46 (t, J = 7.5 Hz, 2H), 5.13 (s, 2H), 7.32–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 4.23, 10.33, 29.97, 34.34, 66.02, 128.20, 128.23, 128.58, 136.20, 173.64. HRMS calcd for $C_{13}H_{16}O_2$ (*m*/*z*) 204.1150, found 204.1144.

Benzyl 3-Cyclopropyl-2-methylpropanoate (7b): IR (neat) 3076, 3034, 2974, 2934, 1732, 1498, 1456, 1379, 1352, 1252, 1150, 1018, 968, 825, 798, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (m, 2H), 0.38 (m, 2H), 0.66 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H), 1.37 (m, 1H), 1.54 (m, 1H), 2.59 (qt, J = 6.9, 6.9 Hz, 1H), 5.10 (s, 2H), 7.30–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 4.12 (2C), 8.75, 16.88, 38.68, 40.07, 65.98, 126.16 (2C), 128.59, 136.34, 176.79. Found: C, 77.09; H, 8.53%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

Benzyl 3-Cyclopropyl-2,2-dimethylpropanoate (7e): IR (neat) 3078, 3034, 2972, 2930, 1728, 1499, 1472, 1454, 1319, 1229, 1146, 1018, 978, 912, 735, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (m, 2H), 0.38 (m, 2H), 0.62 (m, 1H), 1.25 (s, 6H), 1.49 (d, J = 6.9 Hz, 2H), 5.12 (s, 2H), 7.30–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 4.21, 6.82, 25.14, 43.06, 45.46, 66.00, 127.93, 128.05, 128.56, 136.48, 178.07. HRMS calcd for $C_{15}H_{20}O_2$ (*m*/*z*) 232.1463, found 232.1466.

2-(Cyclopropylmethyl)butanolide (7f): IR (neat) 3078, 3001, 2914, 1771, 1456, 1375, 1217, 1175, 1142, 1022, 953, 829, 790, 702, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (m, 2H), 0.46 (m, 2H), 0.72 (m, 1H), 1.43 (m, 1H), 1.65 (m, 1H), 2.04 (m, 1H), 2.42 (m, 1H), 2.60 (m, 1H), 4.17 (m, 1H), 4.32 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 4.01, 4.55, 8.67, 28.39, 34.95, 39.66, 66.57, 179.60. HRMS calcd for $C_8H_{12}O_2$ (*m*/*z*) 140.0837, found 140.0843.

***N*-Benzyl-3-cyclopropylpropanamide (7g):** IR (neat) 3302, 3076, 2924, 2855, 1638, 1551, 1454, 1377, 1016, 822, 729, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (m, 2H), 0.39 (m, 2H), 0.67 (m, 1H), 1.54 (dt, J = 7.2, 7.5 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 4.20 (d, J = 5.7 Hz, 2H), 5.74 (bs, 1H), 7.24–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 4.29, 10.47, 30.68, 36.79, 43.56, 127.58, 127.94, 128.79, 138.49, 172.94. HRMS calcd for $C_{13}H_{17}ON$ (*m*/*z*) 203.1310, found 203.1310.

***N*-Benzyl-3-cyclopropyl-2-methylpropanamide (7h):** IR (neat) 3290, 3276, 2966, 2927, 1645, 1549, 1454, 1358, 1254, 1227, 1016, 893, 822, 797, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (m, 2H), 0.40 (m, 2H), 0.66 (m, 1H), 1.19 (d, J = 6.9 Hz, 3H), 1.30 (dt, J = 7.2, 5.7 Hz, 1H), 1.62 (dt, J = 7.2, 5.7 Hz, 1H), 2.30 (qt, J = 6.9, 7.2 Hz, 1H), 4.45 (d, J = 5.7 Hz, 2H), 5.72 (bs, 1H), 7.26–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 4.33, 9.08, 17.73, 39.23, 42.16, 43.49, 127.57, 127.94, 128.79, 138.59, 176.47. HRMS calcd for $C_{14}H_{19}ON$ (*m*/*z*) 217.1467, found 217.1458.

3-Cyclopropyl-*N*,*N*-diethylpropanamide (7i): IR (neat) 3476, 3076, 2974, 2934, 1626, 1433, 1381, 1364, 1275, 1244, 1146, 1097, 1015, 947, 822, 797 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (m, 2H), 0.39 (m, 2H), 0.69 (m, 1H), 1.08 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H), 1.52 (dt, J = 7.5, 7.2 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 3.30 (q, J = 7.2 Hz, 2H), 3.34 (q, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 4.35, 10.59, 12.96, 14.26, 30.58, 32.99, 39.94, 41.88, 172.31. HRMS calcd for $C_{10}H_{19}ON$ (*m*/*z*) 169.1467, found 169.1466.

3-Cyclopropyl-*N*,*N*-diethyl-2-methylpropanamide (7j): IR (neat) 3076, 2974, 2932, 2874, 1639, 1466, 1431, 1381, 1261, 1221, 1130, 1016, 824, 789, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (m, 2H), 0.36 (m, 2H), 0.61 (m, 1H), 1.08 (t, J = 6.9 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 1.60–1.70 (m, 2H), 1.17 (t, J = 6.9 Hz, 3H), 2.75 (dq, J = 6.9, 6.9 Hz, 1H), 3.21–3.55 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 4.24, 4.55, 9.23, 12.97, 14.83, 18.20, 36.00, 39.58, 40.33, 41.82, 176.20. HRMS calcd for $C_{11}H_{21}ON$ (*m*/*z*) 183.1623, found 183.1628.

(3-Cyclopropylpropanoyl)-2-oxazolidinone (7m): IR (neat) 3078, 3001, 2924, 1778, 1693, 1479, 1393, 1279, 1227, 1105, 1040, 1015, 962, 903, 824, 760, 696, 619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (m, 2H), 0.40 (m, 2H), 0.74 (m, 1H), 1.53 (dt, J = 7.2, 7.5 Hz, 2H), 3.00 (t, J = 7.5 Hz, 2H), 3.99 (t, J = 8.1 Hz, 2H), 4.38 (t, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 4.40, 10.30, 29.39, 35.13, 42.44, 61.94, 153.66, 173.60. Found: C, 58.70; H, 7.27%. Calcd for $C_9H_{13}O_3N$: C, 59.00; H, 7.15%.

3-Cyclopropyl-1-phenyl-1-propanone (7n): IR (neat) 3076, 3034, 3001, 2927, 1738, 1498, 1454, 1379, 1352, 1259, 1169, 1016, 908, 822, 736, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (m, 2H), 0.44 (m, 2H), 0.76 (m, 1H), 1.64 (dt, J = 7.2, 7.2 Hz, 2H), 3.08 (t, J = 7.2 Hz, 2H), 7.46 (t, J = 8.1 Hz, 2H), 7.55 (t, J = 8.1 Hz, 1H), 7.97 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 4.47, 10.58, 29.46, 38.61, 128.15, 128.62, 132.95, 137.26, 200.69. HRMS calcd for $C_{12}H_{14}O$ (*m*/*z*) 174.1045, found 174.1046.

3-(Cyclopropylmethyl)-2-nonanone (7p): IR (neat) 3078, 3001, 2957, 2930, 2857, 1713, 1462, 1352, 1252, 1167, 1016, 824

cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.10 (m, 2H), 0.40 (m, 2H), 0.59 (m, 1H), 0.84 (t, J = 6.6 Hz, 3H), 1.12–1.32 (m, 9H), 1.32–1.62 (m, 3H), 2.13 (s, 3H), 2.56 (tt, J = 6.0, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 4.44, 4.74, 9.07, 13.92, 22.47, 27.29, 29.31, 29.40, 31.56, 31.70, 36.91, 53.53, 213.68. HRMS calcd for $C_{13}H_{24}O$ (*m/z*) 196.1827, found 196.1828.

3-(Cyclopropylmethyl)-2-undecanone (7q): IR (neat) 3078, 2926, 2855, 1715, 1458, 1429, 1352, 1165, 1016, 825, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (m, 2H), 0.39 (m, 2H), 0.60 (m, 1H), 0.85 (t, J = 6.6 Hz, 3H), 1.18–1.32 (m, 13H), 1.36–1.61 (m, 3H), 2.14 (s, 3H), 2.56 (tt, J = 6.0, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 4.45, 4.75, 9.08, 13.98, 22.55, 27.34, 29.15, 29.32, 29.41, 29.66, 31.72, 31.76, 36.91, 53.54, 213.72. HRMS calcd for $C_{15}H_{28}O$ (*m/z*) 224.2140, found 224.2147.

3-Cyclopropylpropanenitrile (9a): IR (neat) 3080, 3005, 2930, 2862, 2247, 1641, 1450, 1427, 1319, 1249, 1051, 1020, 945, 914, 870, 827, 743, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (m, 2H), 0.51 (m, 2H), 0.80 (m, 1H), 1.54 (dt, J = 7.2, 7.5 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 4.31, 10.08, 17.30, 30.46, 119.90. HRMS calcd for C_6H_9N (*m/z*) 95.0735, found 95.0738.

3-Cyclopropyl-2-methylpropanenitrile (9b): IR (neat) 3082, 2930, 2856, 2243, 1639, 1462, 1381, 1198, 1088, 1020, 970, 914, 827, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (m, 2H), 0.51 (m, 2H), 0.82 (m, 1H), 1.32 (d, J = 7.2 Hz, 3H), 1.31–1.43 (m, 1H), 1.52–1.62 (m, 1H), 2.68 (qd, J = 7.2, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 4.13, 4.46, 8.49, 17.78, 25.87, 38.85, 123.28. HRMS calcd for $C_7H_{11}N$ (*m/z*) 109.0891, found 109.0887.

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