Efficient Allylation of Active Ketones Promoted by *p*-Nitrobenzoic Acid

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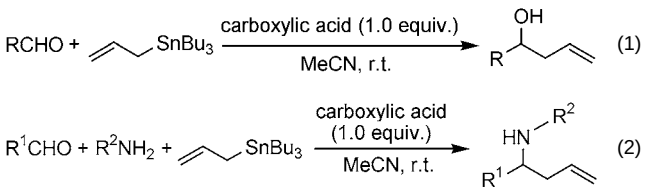
A general and practical method of allylation of carbonyl compounds promoted by *p*-nitrobenzoic acid under mild reaction condition has been developed. *p*-Nitrobenzoic acid can be easily recovered after workup by aqueous HCl.

Keywords allylic compounds, α-keton esters, trifluoro-phenylethanones, allylation, allyltributyltin, *p*-nitrobenzoic acid

Introduction

The allylation of carbonyl compounds, using allyltin reagents, as a very important method to synthesize synthetically useful homoallylic alcohols, has been a subject of extensive investigation during the past years. Generally, this type of allylation with allyltin reagents should be carried out in the presence of Lewis acids or other catalysts.[1,2] Recently, we have found that carboxylic acids are efficient promoters for the allylation of aldehydes and imines under mild reaction conditions.[3] But under the same reaction conditions, it is difficult for the carboxylic acids to promote the allylation of ketones (Scheme 1).[3a] α-Keton esters and other active ketones are important intermediates in organic synthesis.[4] In order to extend the scope of the allylation mediated by carboxylic acids, herein, we would like to report an efficient allylation of some active ketones with tributylallyltin by using *p*-nitrobenzoic acid as a promoter.

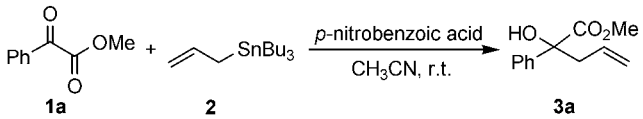
Scheme 1



Results and discussion

In the former studies, we have found that *p*-nitrobenzoic acid is the best promoter for the allylation of aldehydes due to its appropriate acidity and solubility in acetonitrile. Therefore, we initially used *p*-nitrobenzoic acid as a promoter to investigate the allylation of α-keton esters. As shown in the Table 1, when 1.0 equiv. of *p*-nitrobenzoic acid was used as a promoter, the allylation of ethyl benzoylformate (**1a**) could provide the corresponding homoallylic alcohol **3a** in 61% yield after 22 h at room temperature. The yields were increasing along with the increase of the amount of promoter and tin reagent. Excellent yield (93%, Table 1, Entry 3) was obtained when excess of *p*-nitrobenzoic acid and tributylallyltin was used.

Table 1 The optimization of reaction conditions of allylation of active ketones



1a **2** **3a**

Entry	**1a**/**2**/*p*-nitrobenzoic acid	Time/h	Yield[a]/%
1	1.0/1.1/1.0 (equiv.)	22	61
2	1.0/1.2/1.0 (equiv.)	49	80
3	1.0/1.4/1.4 (equiv.)	48	93[b]

[a] Determined by ^{1}H NMR. [b] Isolated yield.

The scope of the *p*-nitrobenzoic acid-mediated allylation of active ketones was evaluated. The results are summarized in Table 2. It is clearly that the allylation of most aromatic α-keton esters could proceed smoothly and afforded moderate to excellent yields. For examples, if the aromatic ring of α-keton ester was substituted with

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electron-withdrawing groups, the allylations resulted in high yields of the corresponding homoallylic alcohols (Table 2, Entries 4 and 5). The low yield provided by α-keton ester **1b** may be due to the steric hindrance of the 2-methyl group. In addition, only trace amount of allylation products was detected when aromatic α-keton ester, which was substituted with strong electron-donating group, such as methoxyl, was used as a substrate (Table 2, Entry 7). The allylation of aliphatic α-keton ester also gave only trace amount product even after 48 h (Table 2, Entry 10). Finally, another kind of active ketone, trifluoromethyl ketone, was examined. As shown in Table 2, the allylation of various trifluoromethyl ketones promoted by *p*-nitrobenzoic acid provided very high yields of the desired products (Table 2, Entries 11—14).

At this time, the exact process of the allylation of active ketone compounds promoted by *p*-nitrobenzoic acid is not very clear. Based on the results of our experiments,[3b] a possible mechanism is proposed. The active ketone compounds (**1**) were activated by *p*-nitrobenzoic acid through hydrogen bonding, the resulting electrophile intermediate **I** could attack **2** on C_1 (adjoining tin atom) involving a six-centered cyclic transition state **II**, the products **3** are obtained.

In summary, we have successfully extended the carboxylic acids-mediated allylation to active ketones. After extensively studies, we found that the allylation of α-keton esters and trifluoromethyl ketones promoted by *p*-nitrobenzoic acid proceeded smoothly under mild reaction conditions and gave the corresponding homoallylic alcohols in good to excellent yields. A possible mechanism for the allylation was discussed.

Experimental

General information

All solvents were distilled prior to use except where noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates visualized with UV light and/or by staining with I_2. Flash column chromatography was performed on silica gel H (10—40 mesh). NMR spectra were recorded on Varian Mercury 300 and/or Unity 400 MHz instruments. Chemical shifts (δ) are relative to TMS. IR spectra were recorded on a Nicolet 320 Avatar FT-IR spectrometer. Mass spectra (MS) were measured with an HP-5989A spectrometer. High resolution mass spectra (HRMS) were recorded on a Finnigan MAT-95 mass spectrometer.

Typical procedure for the allylation of carbonyl compounds

To a suspension of *p*-nitrobenzoic acid (46.8 mg, 0.28 mmol) in acetonitrile (0.5 mL) were added

Scheme 2 Proposed mechanism for the allylation promoted by *p*-nitrobenzoic acid

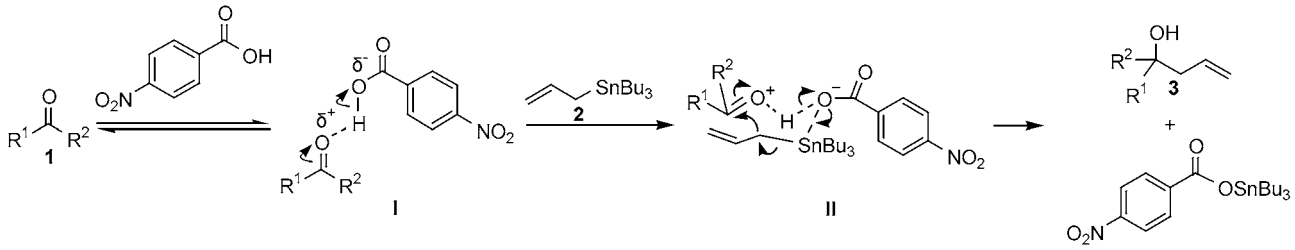
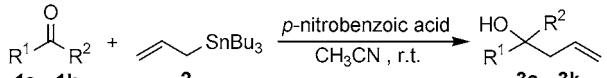
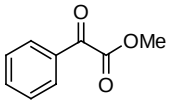
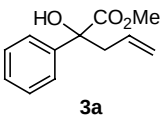
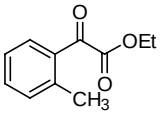
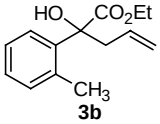
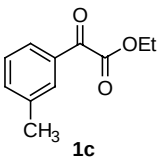
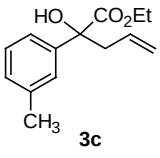


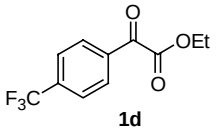
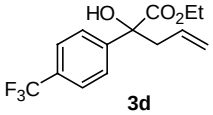
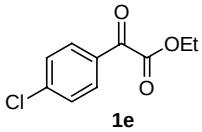
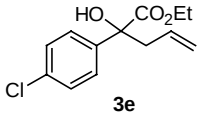
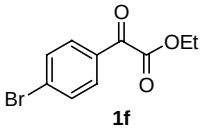
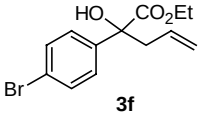
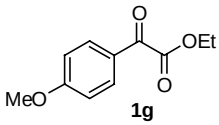
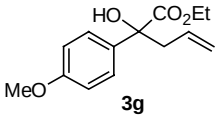
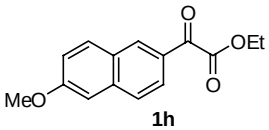
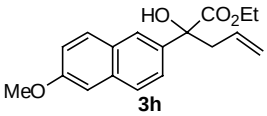
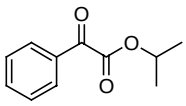
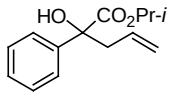
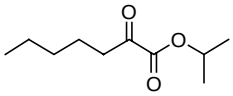
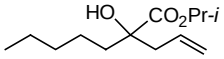
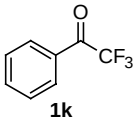
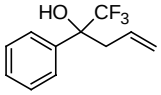
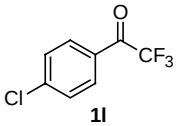
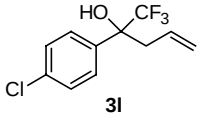
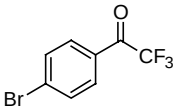
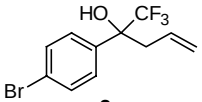
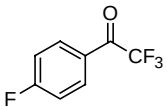
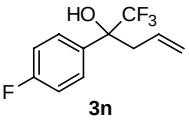
Table 2 The scope of the allylation of active ketones mediated by *p*-nitrobenzoic acid



R^2 = CO_2Me; CO_2Et; CO_2Pr-*i*; CF_3

Entry	Active ketone	Product	Yield/%	Ref.
1	 **1a**	 **3a**	93	5a
2	 **1b**	 **3b**	68	—
3	 **1c**	 **3c**	90	—

Continued

Entry	Active ketone	Product	Yield/%	Ref.
4	 **1d**	 **3d**	96	—
5	 **1e**	 **3e**	95	—
6	 **1f**	 **3f**	92	—
7	 **1g**	 **3g**	trace	—
8	 **1h**	 **3h**	83	—
9	 **1i**	 **3i**	92	—
10	 **1j**	 **3j**	trace	—
11	 **1k**	 **3k**	97	5d
12	 **1l**	 **3l**	99	—
13	 **1m**	 **3m**	95	—
14	 **1n**	 **3n**	89	—

successively carbonyl compound (**1a**) (32.8 mg, 0.2 mmol) and allyltributyltin (92.7 mg, 0.28 mmol) at room temperature. After being stirred for 48 h, the reaction was quenched with NaOH (1 mol/L, 2 mL), then extracted with CH_2Cl_2 (5 mL×3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to furnish the crude product, which was purified by silica gel chromatography (typical eluent: petroleum ether/EtOAc, V∶V=14∶1) to afford product **3a** (38 mg, 93%). The aqueous layer was acidified with 1 mol/L HCl. The white precipitate was filtered and washed with ice water to afford the *p*-nitrobenzoic acid.

Methyl 2-hydroxy-2-phenylpent-4-enoate (3a)[4a] Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.73—3.01 (m, 2H), 3.71 (s, 1H), 3.77 (s, 3H), 5.11—5.20 (m, 2H), 5.72—5.83 (m, 1H), 7.29—7.38 (m, 2H), 7.58—7.61 (m, 2H); IR (KBr, film) v: 3512, 3076, 2954, 2924, 1736, 1641, 1494, 1448, 1438, 1232, 1145, 1071, 922, 733 cm^{-1}.

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Ethyl 2-hydroxy-2-*o*-tolylpent-4-enoate (3b) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.18—1.25 (m, 3H), 2.35 (s, 3H), 2.98—3.03 (m, 2H), 3.62 (s, 1H), 4.11—4.29 (m, 2H), 5.18—5.23 (m, 2H), 5.80—5.89 (m, 1H), 7.13—7.24 (m, 3H), 7.45—7.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.01, 20.65, 43.13, 62.18, 77.92, 119.60, 125.62, 126.25, 128.06, 132.16, 132.24, 137.31, 138.67, 175.17; IR (KBr, film) *v*: 3512, 3077, 2980, 2936, 1728, 1641, 1459, 1263, 1227, 1178, 1139, 1080, 1033, 920, 742 cm^{-1}; LRMS (ESI) *m*/*z*: 257.1 [M + Na$^+$]; HRMS calcd for $C_{14}H_{18}O_3Na$ 257.1148, found 257.1148.

Ethyl 2-hydroxy-2-*m*-tolylpent-4-enoate (3c) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.06 (t, J=7.1 Hz, 3H), 2.28 (s, 3H), 2.63 (dd, J=1.5, 5.5 Hz, 1H), 2.85 (dd, J=7.7, 6.4 Hz, 1H), 3.66 (s, 1H), 4.07—4.21 (m, 2H), 5.03—5.13 (m, 2H), 5.66—5.79 (m, 1H), 7.00 (d, J=7.5 Hz, 2H), 7.13—7.18 (m, 1H), 7.29 (m, J=7.9, 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.07, 21.54, 44.13, 62.34, 77.93, 119.11, 122.61, 126.14, 128.11, 128.50, 132.52, 137.86, 141.49, 174.62; IR (KBr, film) *v*: 3512, 3076, 2981, 2924, 1726, 1641, 1606, 1223, 1085, 1036, 920, 698 cm^{-1}; LRMS (ESI) *m*/*z*: 252.1 (M+ NH_4^+); HRMS calcd for $C_{14}H_{18}O_3Na$ 257.1148, found 257.1148.

Ethyl 2-hydroxy-2-(4-(trifluoromethyl)phenyl)-pent-4-enoate (3d) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.26 (t, J=7.1 Hz, 3H), 2.71 (dd, J=6.4, 7.7 Hz, 1H), 2.93 (dd, J=7.6, 6.5 Hz, 1H), 3.88 (s, 1H), 4.17—4.32 (m, 2H), 5.13—5.20 (m, 2H), 5.73—5.79 (m, 1H), 7.60 (d, J=8.4 Hz, 2H), 7.75 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.03, 44.39, 62.83, 77.79, 119.68, 125.08, 125.12, 125.18, 125.22, 126.17, 131.76, 145.32, 145.34, 173.93; IR (KBr, film) *v*: 3507, 3081, 2984, 2939, 1729, 1642, 1618, 1412, 1328, 1265, 1231, 1167, 1127, 1070, 1018, 846 cm^{-1}; LRMS (ESI) *m*/*z*: 311.2 (M+Na^+); HRMS calcd for $C_{15}H_{15}F_3O_3^+$ 289.1043, found 289.1046

Ethyl 2-(4-chlorophenyl)-2-hydroxypent-4-enoate (3e) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24 (t, J=7.4 Hz, 3H), 2.68 (dd, J=6.8, 7.5 Hz, 1H), 2.88 (dd, J=7.8, 6.2 Hz, 1H), 3.80 (s, 1H), 4.15—4.30 (m, 2H), 5.12—5.19 (m, 2H), 5.72—5.83 (m, 1H), 7.29—7.33 (m, 2H), 7.53—7.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.06, 29.68, 44.27, 62.63, 77.59, 119.46, 127.16, 128.34, 132.00, 133.79, 139.98, 174.22; IR (KBr, film) *v*: 3510, 3078, 2982, 2926, 2854, 1727, 1641, 1491, 1228, 1189, 1146, 1093, 1014, 921, 831 cm^{-1}; LRMS (ESI) *m*/*z*: 272.1 (M+ NH_4^+); HRMS calcd for $C_{13}H_{15}O_3Na^+$ 277.0605, found 277.0601.

Ethyl 2-(4-bromophenyl)-2-hydroxypent-4-enoate (3f) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.26 (t, J=7.7 Hz, 3H), 2.70 (dd, J=6.5, 7.7 Hz, 1H), 2.90 (dd, J=7.2, 6.9 Hz, 1H), 3.84 (s, 1H), 4.17—4.31 (m, 2H), 5.14—5.21 (m, 2H), 5.72—5.86 (m, 1H), 7.47—7.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.13, 44.24, 62.76, 77.62, 119.62, 122.00, 127.53, 131.34, 131.98, 140.45, 174.20; IR (KBr, film) *v*: 3504, 3078, 2981, 2936, 1728, 1641, 1589, 1486, 1396, 1279, 1228, 1146, 1076, 1010, 921, 828 cm^{-1}; HRMS calcd for $C_{13}H_{15}O_3BrNa^+$ 321.0112, found 321.0096.

Ethyl 2-hydroxy-2-(6-methoxynaphthalen-2-yl)-pent-4-enoate (3h) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24 (t, J=6.9 Hz, 3H), 2.83 (dd, J=6.5, 6.7 Hz, 1H), 3.03 (dd, J=7.7, 6.2 Hz, 1H), 3.90 (s, 3H), 4.14—4.33 (m, 2H), 5.13—5.23 (m, 2H), 5.78—5.91 (m, 1H), 7.12—7.25 (m, 2H), 7.66—7.76 (m, 3H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.17, 44.10, 55.35, 62.54, 78.01, 105.44, 119.07, 119.36, 124.21, 124.49, 126.68, 128.53, 129.90, 132.48, 134.02, 136.55, 158.01, 174.73; IR (KBr, film) *v*: 3501, 3075, 2980, 2937, 2907, 2840, 1727, 1634, 1605, 1484, 1390, 1267, 1221, 1169, 1092, 1032, 854 cm^{-1}; LRMS (ESI) *m*/*z*: 318.0 (M + NH_4^+); HRMS calcd for $C_{18}H_{20}O_4Na$ 323.1267, found 323.1253.

Isopropyl 2-hydroxy-2-phenylpent-4-enoate (3i) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.18 (d, J=5.8 Hz, 3H), 1.25 (d, J=6.7 Hz, 3H), 2.70 (dd, J=6.4, 5.7 Hz, 1H), 2.91 (dd, J=6.8, 6.5 Hz, 1H), 3.81 (s, 1H), 5.00—5.20 (m, 3H), 5.74—5.85 (m, 1H), 7.25—7.37 (m, 3H), 7.59—7.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.49, 21.71, 44.16, 70.43, 77.75, 119.08, 125.51, 127.67, 128.16, 132.44, 141.69, 174.13; IR (KBr, film) *v*: 3511, 3076, 2982, 2934, 1724, 1641, 1449, 1376, 1266, 1232, 1105, 1070, 916, 733, 698 cm^{-1}; LRMS (ESI) *m*/*z*: 252.2 (M+ NH_4^+); HRMS calcd for $C_{14}H_{18}O_3Na^+$ 257.1159, found 257.1148.

1,1,1-Trifluoro-2-phenylpent-4-en-2-ol (3k)[4d] Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.65 (s, 1H), 2.80—2.88 (m, 1H), 2.94—3.02 (m, 1H), 5.18—5.27 (m, 2H), 5.51—5.57 (m, 1H), 7.34—7.43 (m, 3H), 7.55—7.58 (m, 2H); ^{19}F NMR ($CDCl_3$, 300 MHz) δ: −79.16 (s, CF_3); IR (KBr, film) *v*: 3551, 3067, 3033, 2984, 2929, 1643, 1498, 1450, 1271, 1163, 1073, 996, 929, 767, 714 cm^{-1}.

2-(4-Chlorophenyl)-1,1,1-trifluorpent-4-en-2-ol (3l) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.70 (s, 1H), 2.78—2.97 (m, 2H), 5.20—5.27 (m, 2H), 5.46—5.61 (m, 1H), 7.34—7.38 (m, 2H), 7.49—7.52 (m, 2H); ^{19}F NMR ($CDCl_3$, 300 MHz) δ: −79.28 (s, CF_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 40.24, 75.78 (s_{CH}, q_{CF}, $^2J_{CF}$=28.2 Hz, COH), 122.21, 125.13 (s_{CH}, q_{CF}, $^1J_{CF}$= 283.8 Hz, CF_3), 128.03, 128.55, 129.96, 134.72, 135.41; IR (KBr, film) *v*: 3545, 3083, 2927, 1643, 1599, 1495, 1269, 1231, 1164, 1097, 1014, 942, 824, 735 cm^{-1}; LRMS (EI) *m*/*z*: 211, 209, 141, 139, 111, 77, 69, 51, 41. Anal. calcd for $C_{11}H_{10}ClF_3O$: C 52.71, H 4.02; found C 52.66, H 4.08.

2-(4-Bromophenyl)-1,1,1-trifluorpent-4-en-2-ol (3m) Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.68 (s, 1H), 2.78—2.97 (m, 2H), 5.21—5.27 (m, 2H), 5.47—5.61 (m, 1H), 7.42—7.46 (m, 2H), 7.51—7.56 (m, 2 H); ^{19}F NMR ($CDCl_3$, 300 MHz) δ: −79.25 (s, CF_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 40.22, 75.65 (s_{CH}, q_{CF}, $^2J_{CF}$=28.2 Hz, COH), 122.30, 122.97, 125.04 (s_{CH}, q_{CF}, $^1J_{CF}$ = 283.8 Hz, CF_3), 128.33, 129.93, 131.53,

135.95; IR (KBr, film) *v*: 3544, 3083, 2923, 2850, 1643, 1593, 1491, 1399, 1269, 1231, 1163, 1076, 1010, 942, 820, 734 cm^{-1}; LRMS (EI) *m*/*z*: 255, 253, 185, 183, 157, 155, 77, 69, 51, 41; LRMS (ESI) *m*/*z*: 318 [M+Na^+], 279, 277. Anal. calcd for $C_{11}H_{10}BrF_3O$: C 44.77, H 3.42; found C 44.85, H, 3.39.

1,1,1-Trifluoro-2-(4-fluorophenyl)pent-4-en-2-ol (3n) ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.66 (s, 1H), 2.79—2.94 (m, 2H), 5.22—5.28 (m, 2H), 5.50—5.57 (m, 1H), 7.05—7.11 (m, 2H), 7.52—7.57 (m, 2H); ^{19}F NMR ($CDCl_3$, 300 MHz) δ: −79.44 (s, CF_3), −113.71 (s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 40.35, 75.56 (s_{CH}, q_{CF}, $^2J_{CF}$=28.2 Hz, COH), 115.27 (d_{CF}, $^2J_{CF}$=21.4 Hz), 122.18, 125.04 (q_{CF}, $^1J_{CF}$=283.8 Hz, CF_3), 128.48 (d_{CF}, $^3J_{CF}$=8.2 Hz), 130.11, 132.65 (d_{CF}, $^4J_{CF}$=3.1 Hz), 162.84 (d_{CF}, $^1J_{CF}$=245.9 Hz); IR (KBr, film) *v*: 3565, 2919, 2849, 1606, 1513, 1271, 1237, 1163, 1093, 1015, 996, 940, 834, 738 cm^{-1}; LRMS (EI) *m*/*z*: 193, 123, 95, 69, 57, 41. Anal. calcd for $C_{11}H_{10}F_4O$: C 56.41, H 4.30; found C 56.46, H 4.25.

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