Cobalt-Catalyzed Allylzincations of Internal Alkynes

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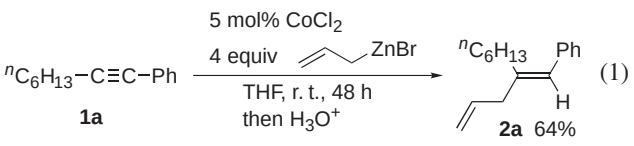
Cobalt salts such as cobalt(II) chloride catalyze allylzincation reactions of 1-aryl-1-alkynes. The allylzincations proceed in a *syn* fashion to form 2-allyl-1-aryl-1-alkenylzinc species. Other internal alkynes such as 6-dodecyne or 2-nonyn-1-ol are much less reactive than 1-aryl-1-alkynes.

Due to the importance of allylic groups, allylmetalation reactions of alkynes and alkenes represent powerful methods for the construction of complex organic molecules.[1] Among them, allylzincation reactions of internal alkynes are rather difficult processes.[1f,2] We have been interested in allylation reactions under cobalt catalysis.[3] Here, we report cobalt-catalyzed allylzincation reactions of internal alkynes.[4]

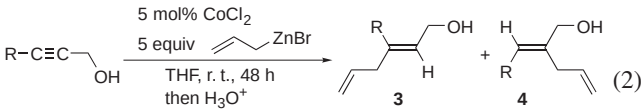
Results and Discussion

As a model substrate, 1-phenyl-1-octyne (**1a**) was subjected to various conditions for cobalt-catalyzed allylzincation reaction (Eq. 1). Treatment of **1a** with 4 equiv of allylzinc bromide in the presence of 5 mol % of cobalt(II) chloride in THF at room temperature for 48 h provided the corresponding allylated product **2a** in 64% yield. No traces of regio- or stereoisomers were obtained. The formation of 2-allyl-1-aryl-1-alkenylzinc species was confirmed by quantitative deuterium incorporation upon quenching with deuterated hydrochloric acid. THF was chosen as the solvent. Other solvents such as toluene, hexane, and Et_2O resulted in a slight decrease of the yield of **2a**. Cobalt(II) bromide, (8-quinolinolato)cobalt(II), and acetylacetonatocobalt(III) also catalyzed the reaction to provide **2a** in 64, 59, and 53% yields, respectively. Cobalt(II) fluoride did not promote the allylzincation reaction. In the presence of a phosphine ligand, the yield of **2a** was significantly decreased (13% with 5 mol % of PPh_3). The reaction did not go to completion when the reaction was carried out for 24 h (53% yield). A smaller amount, 3.0 equiv for instance, of allylzinc bromide also furnished a 56% yield of **2a**. The use of 10 equiv of allylzinc bromide slightly increased the yield of **2a** to 73%. Reaction at 40 °C gave rise to a lower conversion of **1a** (43% recovery) and 30% of **2a** was obtained, probably because the cobalt catalyst lost its activity upon heating. In the absence of a cobalt(II) catalyst, the reaction did not occur and the starting material remained untouched. It is noteworthy that the use of allylmagnesium bromide instead of allylzinc bromide resulted in no conversion of **1a**.



(1)

A variety of internal alkynes were subjected to the cobalt-catalyzed allylzincation reaction (Table 1). An electron-donating substituent on the aromatic ring rendered the reaction less efficient (Entry 1). On the other hand, 1-aryl-1-alkynes having electron-withdrawing groups underwent the allylzincation to yield the corresponding products in high yields (Entries 2–5). Unfortunately, an attempted allylzincation reaction of 1,2-diphenylacetylene (**1g**) provided the desired product **2g** in only 41% yield (Entry 6). The allylzincation reaction of 6-dodecyne (**1h**) and the homopropargyl methyl ether **1i** afforded the corresponding products in only 18 and 34% yields, respectively (Entries 7 and 8). The allylzincation reaction of 3-phenyl-2-propyn-1-ol (**1j**) gave a mixture of the allylzincation products **3a** and **4a**, albeit the yield was low (Eq. 2). The formation of **4a** was often observed in the previous allylmetalation reactions.[1a,5] Similarly, a mixture of **3b** and **4b** was formed in the reaction of 2-nonyn-1-ol (**1k**).



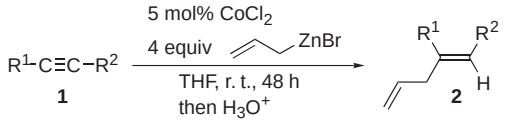
(2)

1j : R = Ph
1k : R = $^nC_6H_{13}$

from **1j** : 37% yield (**3a/4a** = 87:13)
from **1k**: 24% yield (**3b/4b** = 89:11)

The reaction of **1f** with substituted allylic zinc reagents was studied. 2-Methyl-2-propenylzinc bromide reacted with **1f**

Table 1. Cobalt-Catalyzed Allylzincation Reactions of Internal Alkynes



Entry	**1**	R^1	R^2	Yield of **2**/%
1	**1b**	$^nC_6H_{13}$	4-MeO-C_6H_4	**2b**, 51
2	**1c**	$^nC_6H_{13}$	4-Cl-C_6H_4	**2c**, 67
3	**1d**	$^nC_6H_{13}$	4-F-C_6H_4	**2d**, 70
4	**1e**	$^nC_6H_{13}$	4-CF_3-C_6H_4	**2e**, 73
5	**1f**	$^nC_6H_{13}$	3,5-$(CF_3)_2$-C_6H_3	**2f**, 73
6	**1g**	Ph	Ph	**2g**, 41
7	**1h**	$^nC_5H_{11}$	$^nC_5H_{11}$	**2h**, 18
8	**1i**	$^nC_6H_{13}$	CH_2CH_2OMe	**2i**, 34

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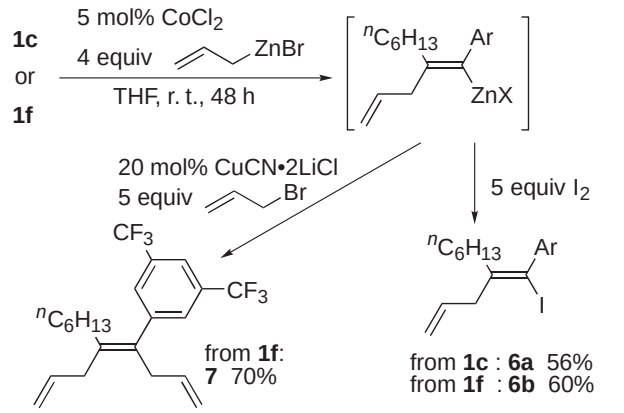
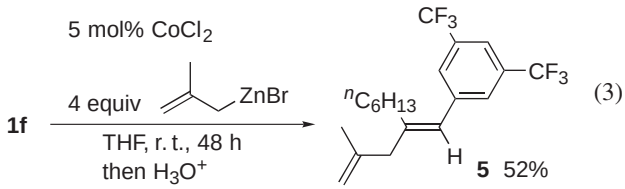


Scheme 1. Reactions of alkenylzinc intermediates.

under catalysis of $CoCl_2$ to afford **5** in 52% yield (Eq. 3). An attempt to use a 2-butenylzinc reagent resulted in the formation of a complex mixture.



(3)

The intermediary alkenylzinc compounds obtained by the allylzincation reaction reacted with electrophiles (Scheme 1). The cobalt-catalyzed allylzincations of **1c** and **1f** followed by the addition of iodine provided the corresponding tetrasubstituted alkenes **6** in moderate yields. Copper(I) cyanide mediated a carbon–carbon bond formation reaction with allyl bromide.

In conclusion, cobalt salts such as cobalt(II) chloride proved to catalyze the allylzincation reaction of 1-aryl-1-alkynes efficiently. The cobalt catalysis did not efficiently promote the allylzincation reactions of other internal alkynes such as 6-dodecyne and propargylic alcohols.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. ^{2}H NMR (46 MHz) spectra were measured on a Varian Mercury 300 spectrometer in $CHCl_3$ with 1,1,2,2-tetrachloroethane-d_2 as an internal standard. IR spectra were determined on a Shimadzu FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 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 and ether were purchased from Kanto Chemical Co., stored under nitrogen, and used as provided. The starting materials **1** were prepared by the conventional Sonogashira coupling reaction or were commercially available. Allylic zinc reagents were prepared and titrated according to the literature.[3a]

Typical Procedure for the Cobalt-Catalyzed Allylzincation of Internal Alkynes. The synthesis of **7** is representative. Cobalt(II) chloride (3.2 mg, 0.025 mmol) was placed in a 20 mL reaction flask under argon. A solution of **1f** (161 mg, 0.50 mmol in 1 mL of THF) was added to the reaction flask. A solution of allylzinc bromide (1.50 mL, 1.34 M THF solution, 2.0 mmol) was added at room temperature. The mixture was stirred for 48 h at room temperature. Allyl bromide (0.22 mL, 2.5 mmol) and CuCN•2LiCl (0.1 mL, 1.0 M THF solution, 0.1 mmol) were then added. The resulting mixture was stirred for an additional 3 h. The mixture was poured into 1 M hydrochloric acid. The organic compounds were extracted with ether three times. The combined organic part was dried and concentrated in vacuo. Chromatographic purification on silica gel afforded **7** (142 mg, 0.35 mmol) in 70% yield.

Characterization Data: The spectral data of the products **2g**,[6] **2i**,[7] **3a**,[8] **3b**,[7] and **4a**[9] can be found in the literature. The stereochemistry of **2a**[6,9,10] and **2h**[11] was determined by comparison with their closely related analogues. The stereochemistry of **2b**–**2f** are tentatively assigned compared to that of **2a**.

1-[3,5-Bis(trifluoromethyl)phenyl]-1-octyne (1f): IR (neat) 2936, 2862, 2232, 1464, 1385, 1279, 1234, 1180, 1138, 1106, 896, 848, 701, 684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, $J = 7.5$ Hz, 3H), 1.31–1.35 (m, 4H), 1.42–1.48 (m, 2H), 1.62 (tt, $J = 7.5$, 7.5 Hz, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 7.74 (s, 1H), 7.81 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 19.34, 22.53, 28.34, 28.62, 31.31, 78.05, 94.65, 120.83 (m), 123.02 (q, $J = 271.5$ Hz), 126.39, 131.47 (m), 131.66 (q, $J = 33.4$ Hz); Found: C, 59.63; H, 5.02%. Calcd for $C_{16}H_{16}F_6$: C, 59.63; H, 5.00%.

(*E*)-2-Hexyl-1-phenyl-1,4-pentadiene (2a): IR (neat) 2956, 2927, 2857, 1466, 995, 913, 748, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, $J = 7.0$ Hz, 3H), 1.22–1.31 (m, 6H), 1.44–1.50 (m, 2H), 2.22 (t, $J = 6.0$ Hz, 2H), 2.91 (d, $J = 7.0$ Hz, 2H), 5.07–5.14 (m, 2H), 5.88 (ddt, $J = 17.0$, 10.0, 7.0 Hz, 1H), 6.28 (s, 1H), 7.17–7.21 (m, 3H), 7.29–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.60, 28.10, 29.38, 30.83, 31.62, 41.73, 116.25, 125.82, 125.94, 128.03, 128.56, 136.70, 138.41, 141.95; Found: C, 89.54; H, 10.67%. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59%.

(*E*)-2-Hexyl-1-(4-methoxyphenyl)-1,4-pentadiene (2b): IR (neat) 2955, 2929, 1609, 1511, 1464, 1249, 1176, 1039, 911 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, $J = 7.5$ Hz, 3H), 1.21–1.34 (m, 6H), 1.44–1.51 (m, 2H), 2.22 (t, $J = 8.0$ Hz, 2H), 2.90 (d, $J = 6.5$ Hz, 2H), 3.82 (s, 3H), 5.08–5.15 (m, 2H), 5.89 (ddt, $J = 17.5$, 10.0, 6.5 Hz, 1H), 6.23 (s, 1H), 6.87 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.62, 28.10, 29.43, 30.81, 31.65, 41.83, 55.20, 113.44, 116.10, 125.22, 129.65, 130.97, 136.88, 140.59, 157.75; Found: C, 83.45; H, 9.98%. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14%.

(*E*)-1-(4-Chlorophenyl)-2-hexyl-1,4-pentadiene (2c): IR (neat) 2958, 2927, 2857, 1490, 1093, 1015, 914 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, $J = 7.5$ Hz, 3H), 1.21–1.31 (m, 6H), 1.42–1.48 (m, 2H), 2.18 (t, $J = 8.0$ Hz, 2H), 2.90 (dd, $J = 7.0$, 1.5 Hz, 2H), 5.08–5.14 (m, 2H), 5.86 (ddt, $J = 17.0$, 10.0, 7.0 Hz, 1H), 6.21 (s, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.59, 28.01, 29.34, 30.82, 31.59, 41.67, 116.48, 124.63, 128.17, 129.86, 131.60, 136.40, 136.84, 142.81; Found: C, 77.96; H, 8.81%. Calcd for $C_{17}H_{23}Cl$: C, 77.69; H, 8.82%.

(*E*)-1-(4-Fluorophenyl)-2-hexyl-1,4-pentadiene (2d): IR (neat) 2928, 2858, 1603, 1505, 1229, 1156, 913, 837, 823 cm^{-1};

^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.20–1.32 (m, 6H), 1.42–1.48 (m, 2H), 2.18 (t, J = 8.5 Hz, 2H), 2.89 (dd, J = 7.0, 1.5 Hz, 2H), 5.07–5.14 (m, 2H), 5.87 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 6.22 (s, 1H), 6.97–7.02 (m, 2H), 7.13–7.16 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.27, 22.80, 28.23, 29.55, 30.92, 31.80, 41.81, 115.05 (d, J = 21.0 Hz), 116.56, 124.92, 130.24 (d, J = 7.6 Hz), 134.58 (d, J = 3.4 Hz), 136.76, 142.19, 161.37 (d, J = 243.4 Hz); Found: C, 82.76; H, 9.42%. Calcd for $C_{17}H_{23}F$: C, 82.88; H, 9.41%.

(*E*)-2-Hexyl-1-[4-(trifluoromethyl)phenyl]-1,4-pentadiene (2e): IR (neat) 2930, 1615, 1326, 1165, 1127, 1069, 1017 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.20–1.33 (m, 6H), 1.44–1.50 (m, 2H), 2.20 (t, J = 8.0 Hz, 2H), 2.93 (dt, J = 6.0, 1.0 Hz, 2H), 5.10–5.16 (m, 2H), 5.88 (ddt, J = 17.0, 10.5, 6.0 Hz, 1H), 6.28 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.22, 22.81, 28.26, 29.54, 31.13, 31.81, 41.90, 116.89, 124.58 (q, J = 270.0 Hz), 124.89, 125.14–125.23 (m), 128.20 (q, J = 32.0 Hz), 128.99, 136.37, 142.32, 144.51; Found: C, 72.81; H, 7.68%. Calcd for $C_{18}H_{23}F_3$: C, 72.95; H, 7.82%.

(*E*)-1-[3,5-Bis(trifluoromethyl)phenyl]-2-hexyl-1,4-pentadiene (2f): IR (neat) 2932, 2861, 1387, 1368, 1279, 1177, 1138, 918, 897, 708, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.23–1.33 (m, 6H), 1.48–1.54 (m, 2H), 2.19 (t, J = 8.0 Hz, 2H), 2.96 (dd, J = 7.5, 1.5 Hz, 2H), 5.14–5.18 (m, 2H), 5.84–5.92 (m, 1H), 6.31 (s, 1H), 7.64 (s, 2H), 7.71 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.53, 28.06, 29.20, 31.02, 31.49, 41.59, 117.19, 119.65 (m), 123.14, 123.42 (q, J = 271.6 Hz), 128.54 (m), 131.29 (q, J = 33.0 Hz), 135.62, 140.30, 146.17; Found: C, 62.90; H, 6.11%. Calcd for $C_{19}H_{22}F_6$: C, 62.63; H, 6.09%.

(*E*)-4-Pentyl-1,4-decadiene (2h): IR (neat) 2958, 2927, 2858, 1467, 994, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7.5 Hz, 6H), 1.16–1.31 (m, 12H), 1.49–1.94 (m, 4H), 2.65 (d, J = 7.0 Hz, 2H), 4.91–4.97 (m, 2H), 5.07 (t, J = 7.0 Hz, 1H), 5.72 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 14.09, 22.59, 22.60, 27.77, 27.95, 29.74, 30.00, 31.62, 31.90, 41.52, 115.34, 126.14, 137.57, 137.70; HRMS(EI) Found: 208.2194. Calcd for $C_{15}H_{28}$: 208.2192 [M^+].

(*E*)-1-Deuterio-2-hexyl-1-phenyl-1,4-pentadiene (2a-*d*): IR (neat) 2956, 2926, 2857, 1494, 1467, 1443, 995, 913, 754, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.22–1.32 (m, 6H), 1.46–1.50 (m, 2H), 2.22 (t, J = 9.0 Hz, 2H), 2.91 (d, J = 7.0 Hz, 2H), 5.08–5.14 (m, 2H), 5.89 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 7.17–7.22 (m, 3H), 7.29–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.60, 28.09, 29.38, 30.82, 31.63, 41.71, 116.24, 125.48 (t, J = 22.9 Hz), 125.94, 128.03, 128.56, 136.70, 138.33, 141.85; ^{2}H NMR ($CHCl_3$) δ 6.32 (br). Found: C, 89.21; H and D, 10.73%. Calcd for $C_{17}H_{23}D$: C, 89.02; H and D, 10.99%.

(*E*)-1-[3,5-Bis(trifluoromethyl)phenyl]-2-hexyl-4-methyl-1,4-pentadiene (5): IR (neat) 2960, 2932, 1387, 1365, 1279, 1174, 1138, 896, 705, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.5 Hz, 3H), 1.22–1.32 (m, 6H), 1.46–1.55 (m, 2H), 1.74 (s, 3H), 2.15 (t, J = 8.0 Hz, 2H), 2.91 (s, 2H), 4.82 (s, 1H), 4.90 (s, 1H), 6.33 (s, 1H), 7.64 (s, 2H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.15, 22.18, 22.73, 28.31, 29.45, 30.66, 31.68, 46.47, 113.49, 119.83–119.89 (m), 123.64 (q, J = 271.5 Hz), 124.14, 128.70, 131.53 (q, J = 33.0 Hz), 140.47, 143.17, 145.76; Found: C, 63.74; H, 6.47%. Calcd for $C_{20}H_{24}F_6$: C, 63.48; H, 6.39%.

1-(4-Chlorophenyl)-2-hexyl-1-iodo-1,4-pentadiene (6a): IR (neat) 2955, 2926, 2857, 1486, 1091, 1016, 914, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.5 Hz, 3H), 1.09–1.13 (m, 4H), 1.18–1.23 (m, 2H), 1.29–1.34 (m, 2H), 2.02 (t, J = 8.0 Hz, 2H), 3.18 (dt, J = 6.5, 1.5 Hz, 2H), 5.13–5.16 (m, 1H), 5.18–5.22 (m, 1H), 5.84 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 7.14 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.45, 28.26, 28.88, 31.36, 32.28, 45.38, 95.28, 116.65, 128.38, 129.90, 133.17, 134.09, 143.20, 146.29; HRMS (FAB) Found: 388.0459. Calcd for $C_{17}H_{22}{}^{35}ClI$: 388.0455 [M^+].

(*Z*)-1-[3,5-Bis(trifluoromethyl)phenyl]-2-hexyl-1-iodo-1,4-pentadiene (6b): IR (neat) 2930, 1376, 1278, 1178, 1140, 917, 684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.5 Hz, 3H), 1.09 (m, 4H), 1.18–1.21 (m, 2H), 1.34–1.37 (m, 2H), 1.99 (t, J = 7.0 Hz, 2H), 3.22 (d, J = 9.5 Hz, 2H), 5.18–5.26 (m, 2H), 5.85 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 7.65 (s, 2H), 7.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.08, 22.53, 28.45, 29.00, 31.47, 32.74, 45.53, 91.97, 117.47, 121.44, 123.26 (q, J = 271.1 Hz), 129.07, 131.80 (q, J = 33.4 Hz), 133.69, 146.62, 148.90; HRMS (FAB) Found: 490.0593. Calcd for $C_{19}H_{21}F_6I$: 490.0592 [M^+].

(*E*)-4-[3,5-Bis(trifluoromethyl)phenyl]-5-hexyl-1,4,7-octatriene (7): IR (neat) 2960, 2930, 2860, 1383, 1278, 1177, 1138, 992, 916, 897, 847, 711, 683, 684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7.0 Hz, 3H), 1.09–1.14 (m, 4H), 1.18–1.22 (m, 2H), 1.30–1.36 (m, 2H), 1.82 (t, J = 8.0 Hz, 2H), 2.99 (dt, J = 6.0, 1.5 Hz, 2H), 3.11 (d, J = 6.0 Hz, 2H), 4.93–5.01 (m, 2H), 5.09–5.16 (m, 2H), 5.69 (ddt, J = 17.0, 10.0, 6.0 Hz, 1H), 5.85 (ddt, J = 17.5, 10.0, 6.0 Hz, 1H), 7.55 (s, 2H), 7.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.08, 22.63, 28.74, 29.36, 31.66, 33.30, 35.78, 38.79, 116.04, 116.44, 120.25–120.43 (m), 123.68 (q, J = 271.1 Hz), 126.94, 129.35–129.37 (m), 131.44 (q, J = 32.9 Hz), 135.00, 135.92, 138.33, 145.70; Found: C, 65.10; H, 6.52%. Calcd for $C_{22}H_{26}F_6$: C, 65.34; H, 6.48%.

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