Experimental

Hexakis(methyl)ester (2). To a solution of 1,3,5-tris (bromomethyl)benzene (1.75 g, 4.90 mmol) and dimethyl 5-hydroxyisophthalate (3.09 g, 14.7 mmol) in 20 mL of DMF were added Cs_2CO_3 (9.55 g, 29.3 mmol) and n-Bu_4NI (185 mg, 0.50 mmol). The mixture was stirred at 50 ℃ for 3 days and poured into 200 mL of water. The resulting mixture was extracted three times with $CHCl_3$. The combined organic extracts were washed three times with water and then with brine. Drying ($MgSO_4$) and solvent removal were followed by trituration with ether to give a white solid (3.23 g, 89% yield).

IR (KBr) 2950, 1730, 1600, 1430, 1335, 1245, 1120, 1055, 1050, 880 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 3.90 (s, 18H, $ArCO_2CH_3$), 5.20 (s, 6H, Ar'CH_2OAr), 7.52 (s, 3H, Ar'H), 7.84 (s, 6H, ArH_a), 8.30 (s, 3 H, ArH_b).

Hexakisacid (3). To a solution of **2** (1.56 g, 2.10 mmol) in 200 mL of THF-methanol-water (v/v, 3 : 1 : 1) was added dropwise 25 mL of 1 N aqueous NaOH solution (25 mmol). The resulting solution was stirred at room temperature and concentrated to 1/5 of the original volume. The residue was diluted with 50 mL of water and treated with $BaCl_2$ (dihydrate, 2.97 g, 12.1 mmol). After the mixture had been stirred for 1 h at room temperature, the white barium salt was filtered. The dried barium salt was dissolved in water and acidified with 3 N aqueous HCl solution (pH 2-3). The resulting acid was filtered to give a white solid (1.22 g, 88% yield).

IR (KBr) 3100, 1700, 1600, 1420, 1270, 1130, 1070, 890 cm^{-1}; ^1H NMR (80 MHz, DMSO-d_6) δ 5.30 (s, 6H, Ar'CH_2OAr), 7.62 (s, 3H, Ar'H), 7.80 (s, 6H, ArH_a), 8.18 (s, 3H, ArH_b).

Hexakis(pentafluorophenyl)ester (4). To a solution of **3** (74 mg, 0.11 mmol) in 3 mL of dry DMF was added pentafluorophenol (138 mg, 0.75 mmol) followed by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (140 mg, 0.73 mmol). The solution was stirred at room temperature for 24 h. Solvent removal followed by chromatographic purification (silica gel, CH_2Cl_2) produced the desired product **4** (48 mg, 26% yield) as a white solid.

IR (neat) 1765, 1595, 1520, 1340, 1300, 1190, 1145, 1090, 1000 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 5.31 (s, 6H, Ar'CH_2 OAr), 7.66 (s, 3H, Ar'H), 8.08 (s, 6H, ArH_a), 8.61 (s, 3H, ArH_b).

C_3 receptor (1a). A solution of the active ester **4** (95 mg, 0.057 mmol) in 10 mL of dry THF and a solution of (1R,2R)-1,2-diaminocyclohexane (21 mg, 0.18 mmol) in 10 mL of dry THF were separately added with sirring to 200 mL of dry THF at room temperature over 12 h *via* syringe pumps. After the solution was stirred for an additional 12 h, the solvent was evaporated and 30 mL of 1 N aqueous HCl solution was added. The mixture was extracted three times with 30 mL of 4% MeOH/$CHCl_3$. The combined ogranic extracts were washed successively with saturated $NaHCO_3$ solution and brine. Drying ($MgSO_4$) followed by chromatographic purification (silica gel, 10% MeOH/CH_2Cl_2) furnished the macrotricycle **1a** (14 mg, 27% yield) as a white solid.

IR (KBr) 3427, 3292, 2980, 1645, 1595, 1540, 1265, 1100, 1030, 805 cm^{-1}; ^1H NMR (2% $CD_3OD/CDCl_3$, 500 MHz) δ 1.23-2.07 (m, 24H, aliphatic CH_2's), 3.69 (br, 3H, CH_eNH), 4.03 (dt, J=3.7, 11.4 Hz, 3H, CH_fNH), 5.16 (s, 6H, ArCH_2 OAr'), 7.11 (s, 3H, ArH), 7.34 (s, 3H, ArH), 7.56 (s, 3H, ArH), 7.63 (s, 3H, ArH); ^{13}C NMR (2% $CD_3OD/CDCl_3$, 125 MHz) δ 24.5, 25.0, 31.3, 32.0, 52.5, 56.0, 67.9, 116.6, 118.2, 118.8, 128.5, 133.4, 136.6, 156.8, 166.5; MS (FAB, glycerol) m/z 896 (M+1).

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Trialkylsilyl Triflate Promoted Conjugate Addition of Alkynylcuprates to α,β-Enones

Sunggak Kim*, Joo Hyeon Park, and Sang Yong Jon

Department of Chemistry,
Korea Advanced Institute of Science and Technology,
Taejon 305-701, Korea

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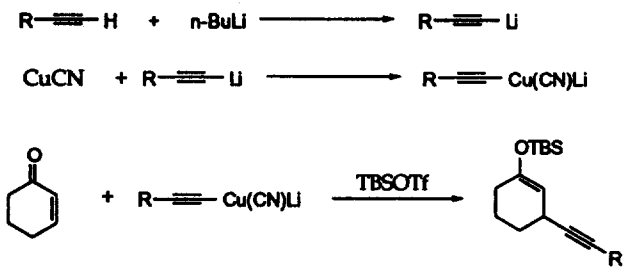
Organocuprates are the most commonly used reagents for 1,4-addition of alkyl and alkenyl groups to α,β-enones.[1] However, they cannot be employed in alkynylation reactions due to their inability to transfer alkynyl groups.[2] Therefore, the conjugate addition of alkynyl groups to α,β-enones has been a synthetic challenge. Dialkylalkynylalanes undergo 1,4-addition reactions with α,β-enones to give β-alkynyl ketones.[3]



Scheme 1.

This reaction is known to be complicated by the concurrent formation of significant amounts of 1,2-addition products and is also restricted to α,β-enones which can achieve s-*cis*-conformation. Alkynylboron derivatives have been utilized for the same purpose.[4] As for alkynylalanes, the cisoid ketones react to give the 1,4-addition products. The transoid enones do not react in a desired manner, indicating the intramolecular delivery of the alkynyl group through a six-membered transition state. Conjugate addition of a terminal alkynyl group has been also successfully achieved using diethylalkynylalane and nickel as a catalyst.[5]

In connection with our research on trialkylsilyl triflate promoted conjugate addition reactions to α,β-enones, we have reported that the conjugate addition of alkynyl groups to α,β-enones can be achieved by alkynylzinc reagents[6] and by lithium trimethylalkynylaluminates[7] using *t*-butyldimethylsilyl triflate (TBSOTf) as a promoter. We have found that TBSOTf is an efficient promoter for conjugate addition of monoalkylcuprates to α,β-enones. Very recently, only one example of iodotrimethylsilane promoted conjugate addition of pentynylcopper-lithium iodide to 2-cyclopenten-1-one has been recently reported.[8] This report prompts us to disclose our findings concerning the scope and limitations of the present method.

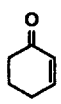
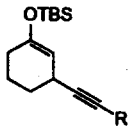
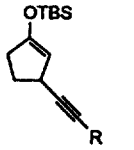
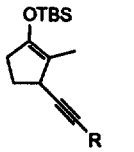
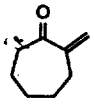
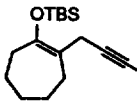
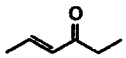
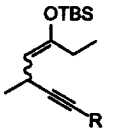
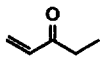
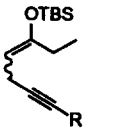
Monoalkynylcuprates were prepared from the reaction of lithium acetylides with copper(I) cyanide as shown in Scheme 1. Alkynylcuprates did not react with α,β-enones at room temperature. However, conjugate addition of the alkynylcuprates to α,β-enones proceeded cleanly and rapidly in the presence of TBSOTf at −78 ℃ within 30 min. When TMSOTf was used instead of TBSOTf, the conjugate addition product was partially hydrolyzed during isolation. Since TBS enol ethers are much more stable than TMS enol ethers to hydrolysis, remaining reactions were carried out using TBSOTf as a promoter. The present method is based on two features. (i) an initial complexation of carbonyl groups by TBSOTf and (ii) a preferential 1,4-addition of alkynyl groups to α,β-enones.

When lithium 1-hexynylcyanocuprate was treated with 2-cyclohexen-1-one using TBSOTf as a promoter in diethyl ether at −78 ℃ (Method A), the conjugate addition product was isolated in 89% yield. It is noteworthy that the reaction of alkynylcuprates did not react with highly reactive TBSOTf under the present conditions. Similar results were obtained with 2-cyclopenten-1-one and 2-methyl-2-cyclopenten-1-one. Lithium 2-phenylethynylcyanocuprate and lithium trimethylsilylethynylcyanocuprate could be utilized without any problems.

However, the present method reaches a limit with *exo*-methylenocycloheptanone and acyclic enones. When a solution of *exo*-methylenocycloheptanone and TBSOTf in ether at −78 ℃ was treated with lithium 2-phenylethynylcyanocuprate, 1,2-addition product was isolated in 16% yield along with 1,4-addition product (60%) as a major product. Similar results were also obtained with acyclic enones. In order to obviate the problem of 1,2-addition of alkynylcuprates to α,β-enones, we have examined the solvent effects because the success of conjugate addition is dependent very much on the solvent.[9] Among several solvents tested in this study, ether-*p*-dioxane (5 : 1) gave the best result without yielding 1,2-addition product.[10] We conceived that the addition of *p*-dioxane would not only reduce the reactivity of organocuprates but also alter the mode of the reaction by complexation between lithium cation and *p*-dioxane. Using ether-*p*-dioxane (5 : 1) (Method B), alkynylcuprates underwent conjugate addition to *exo*-methylenocycloheptanone and acyclic enones as shown in Table 1.

Finally, the present method failed with β,β-disubstituted α,β-enones like 3-methyl-2-cyclohexen-1-one and α,β-unsaturated esters like methyl crotonate. When 3-methyl-2-cyclohexen-1-one was treated with TBSOTf and lithium butynylcyanocuprate in diethyl ether at −78 ℃ for 1 h, a mixture of silyl enol ethers was produced due to deprotonation by lithium butynylcyanocuprate. So far the nickel-catalyzed con-

Table 1. Conjugate Addition of Organocuprates to α,β-Enones

Enone	Method	Product	Yield, %
	A		1: R=*n*-Bu 89
	A		2: =TMS 88
	A		3: =Ph 84
	A		4: R=*n*-Bu 93
	A		5: =TMS 84
	A		6: =Ph 87
	A		7: R=TMS 78
	B		75
	A		8: =Ph 75
	B		68
	A		9: R=TMS 72(5)[a]
	B		76
	A		10: =Ph 60(16)[a]
	B		66
	B		11: R=*n*-Bu 82(77/27)[b]
	B		12: =TMS 80(20/1)[b]
	B		13: =Ph 73(22/3)[b]
	B		14: R=*n*-Bu 64(13/20)[b]
	B		15: =TMS 72(11/8)[b]
	B		16: =Ph 68(3/2)[b]

[a]The isolated yield of 1,2-addition product. [b]E/Z isomer ratio.

jugate addition of alkynyl units from dialkylaluminum acetylides to β,β-disubstituted α,β-enones would be the method of choice.

In conclusion, the present procedure seems to be one of the most efficient methods to achieve alkynyl 1,4-addition to β-monosubstituted α,β-enones in view of the easy preparation of alkynylcyanocuprates and the good yield. The formation of silyl enol ethers as products should be beneficial because subsequent α-functionalization can be effected if desired.

Experimental

Preparation of 1-*tert*-Butyldimethylsilyloxy-3-hex-1-ynylcyclohexene (1). (Method A). A solution of 1-butyne (60 mg, 0.72 mmol) in ethyl ether (4 mL) was treated at −78 ℃ with n-butyllithium in hexane (1.5 M, 0.48 mL, 0.72 mmol) and stirred at −78 ℃ for 30 min. The solution of lithium butynylide was added *via* cannula to a suspension of CuCN (70 mg, 0.78 mmol) at −78 ℃ in ethyl ether (4 mL). The organocuprate formation was typically completed within 30 min. The resulting heterogeneous mixture was added *via* cannula to 2-cyclohexen-1-one (56 mg, 0.60 mmol) and *tert*-butyldimethylsilyl triflate (185 mg, 0.70 mmol) at −78 ℃ in ethyl ether (5 mL). The reaction mixture was stirred at −78 ℃ for 30 min, quenched with saturated potassium carbonate (10 mL), and extracted three times with diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered through silica gel, and concentrated under reduced pressure. The residure was purified by column chromatography on silica gel using ethyl acetate/hexane (1/20) as an eluent to afford 1-*tert*-butyldimethylsilyloxy-3-hex-1-ynylcyclohexene (**1**) (182 mg, 89%) as colorless oil. ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 4.72 (d, J=3.66, 1H), 3.00(br, 1H), 2.12-2.04 (m, 2H), 1.93-1.89 (m, 2H), 1.82-1.35 (m, 8H), 0.92-0.85 (m, 12H), 0.11 (d, J=2.41, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 150.99, 105.89, 83.99, 79.71, 31.56, 29.99, 29.96, 27.17, 26.19, 22.26, 21.40, 18.91, 18.46, 14.12, −3.90, −3.96.

Preparation of (*E*)-(5-*tert*-butyldimethylsilyloxy-3-methylhept-4-en-1-ynyl)-benzne (13). (Method B). A solution of phenylacetylene (74 mg, 0.72 mmol) in ethyl ether (3 mL) at −78 ℃ was treated with n-butyllithium (1.5 M, 0.50 mL, 0.75 mmol) in hexane and stirred at −78 ℃ for 30 min. The solution of lithium phenylacetylide was added *via* cannula to a suspension of CuCN (70 mg, 0.78 mmol) at −78 ℃ in ethyl ether (3 mL). Then, dry dioxane (2 mL) was added *via* syringe at −20 ℃ and the resulting heterogeneous mixture was stirred for 30 min at −20 ℃. The resulting heterogeneous mixture was added *via* cannula to a solution of 4-hexen-3-one (58 mg, 0.60 mmol) and *tert*-butyldimethylsilyl triflate (190 mg, 0.72 mmol) at −78 ℃ in ethyl ether (4 mL). The reaction mixture was stirred at −78 ℃ for 30 min, quenched with saturated potassium carbonate (10 mL), and extracted three times with ethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered through silica gel, and concentrated under reduced pressure. The residure was purified by column chromatography on silica gel using ethyl acetate/hexane (1/20) as an eluent to afford (*E*)-(5-*tert*-butyldimethylsilyloxy-3-methylhept-4-en-1-ynyl)benzne (138 mg, 73%) as colorless oil. ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 7.31-7.13 (m, 5H), 4.52 (d, J=9.12, 1H), 3.37-3.24 (m, 1H), 2.11 (q, J=7.47, 2H), 1.28 (d, J=6.93, 3H), 1.06 (t, J=7.43, 3H), 0.89 (s, 9H), 0.15 (d, J=2.93, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 153.44, 131.64, 128.00, 127.28, 124.38, 109.04, 93.72, 80.33, 25.99, 25.06, 24.77, 23.23, 18.32, 12.06, −4.18.

Spectral data (^{1}H NMR and ^{13}C NMR) of the products are as follows.

1-*tert*-Butyldimethylsilyloxy-3-trimethylsilanylethynylcyclohexene (2). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 4.72 (d, J=3.81, 1H), 3.05 (br, 1H), 1.92-1.90 (m, 2H), 1.84-1.54 (m, 4H), 0.89 (s, 9H), 0.12 (s, 9H), 0.10 (s, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 151.61, 110.72, 104.69, 83.74, 29.93, 29.36, 28.09, 26.19, 21.25, 18.46, 0.71, −3.92.

(3-*tert*-Butyldimethylsilyloxycyclohex-2-enylethynyl benzene (3). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 7.04-7.23 (m, 5H), 4.74-4.76 (m, 1H), 3.19 (br, 1H), 1.87 (br, 2H), 1.55-1.82 (m, 4H), 0.82 (s, 9H), 0.04 (d, 6H, J=2.8 Hz); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 151.70, 131.94, 128.24, 127.53, 124.66, 104.88, 93.39, 80.84, 30.02, 29.59, 27.76, 26.18, 21.38, 18.47, −3.88.

1-*tert*-Butyldimethylsilyloxy-3-hex-1-ynylcyclopentene (4). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 4.39 (br, 1H), 3.22 (br, 1H), 2.20-1.95 (m, 5H), 1.80-1.65 (m, 1H), 1.35-1.26 (m, 4H), 0.84-0.81 (m, 12H), 0.04 (d, J=4.04, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 155.85, 104.43, 84.35, 80.07, 33.33, 32.88, 31.52, 30.35, 26.13, 22.27, 18.96, 18.50, 14.12, −4.21.

1-*tert*-Butyldimethylsilyloxy-3-trimethylsilanylethynyl-cyclopentene (5). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 4.41 (br, 1H), 3.31-3.27 (m, 1H), 2.23-2.01 (m, 3H), 1.84-1.75 (m, 1H), 0.81 (s, 9H), 0.04 (d, J=4.64, 6H), 0.00 (s, 9H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 156.49, 111.12, 103.43, 84.01, 33.76, 33.29, 29.85, 26.13, 18.51, 0.71, −4.17, −4.20.

(3-*tert*-Butyldimethylsilyloxycyclopent-2-enylethynyl)-benzene (6). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 7.32-7.27 (m, 2H), 7.18-7.13 (m, 3H), 4.59 (br, 1H), 3.59 (br, 1H), 2.32-2.19 (m, 3H), 2.10-1.92 (m, 1H), 0.92 (s, 9H), 0.15 (d, J=3.93, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 156.28, 131.65, 128.00, 127.26, 124.48, 103.31, 93.59, 80.89, 33.24, 33.14, 29.82, 25.90, 18.30, −4.39.

1-*tert*-Butyldimethylsilyloxy-2-methyl-3-trimethylsilanyl-ethynylcyclopentene (7). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 3.11 (br, 1H), 2.21-1.98 (m, 3H), 1.78-1.71 (m, 1H), 1.47 (s, 3H), 0.83 (s, 9H), 0.03 (s, 9H), 0.00 (d, J=2.01, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 147.96, 112.70, 110.28, 84.93, 37.75, 32.81, 28.49, 26.13, 18.49, 10.79, 0.75, -3.50.

(3-*tert*-Butyldimethylsilyloxy-2-methyl-cyclopent-2-enyl-ethynyl)benzene (8). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 7.33-7.28 (m, 2H), 7.19-7.13 (m, 3H), 3.42-3.40 (m, 1H), 2.29-2.15 (m, 3H), 2.08-1.91 (m, 1H), 1.64 (s, 3H), 0.92 (s, 9H), 0.11 (d, J=1.74, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 147.97, 131.93, 128.23, 127.49, 124.71, 113.01, 92.97, 81.98, 37.44, 32.89, 28.71, 26.14, 18.52, 10.99, −3.47.

1-*tert*-Butyldimethylsilyloxy-2-(3-trimethylsilanylprop-2-ynyl)cycloheptene (9). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 2.83 (s, 2H), 2.17-2.12 (m, 2H), 2.09-2.03 (m, 2H), 1.61-1.57 (m, 2H), 1.51-1.45 (m, 4H), 0.87 (s, 9H), 0.05 (s, 15H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 149.51, 115.24, 106.39, 83.82, 35.44, 32.09, 30.38, 27.31, 26.34, 25.62, 22.99, 18.55, 0.69, −3.43.

1-*tert*-Butyldimethylsilyloxy-2-(3-phenylpro-2-ynyl) cycloheptene (10). ^{1}H NMR : (7% C_6D_6 in CCl_4) δ 7.25-7.07 (m, 5H), 3.04 (s, 2H), 2.19-2.11 (m, 4H), 1.62-1.48 (m,

6H), 0.88 (s, 9H), 0.08 (s, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 149.56, 131.87, 128.25, 127.39, 124.90, 115.59, 89.07, 80.54, 35.48, 32.08, 30.51, 27.38, 26.35, 25.66, 22.51, 18.58, −3.39.

3-*tert*-Butyldimethylsilyloxy-5-methylundec-3-en-6-yne (11). ^1H NMR : (7% C_6D_6 in CCl_4) δ 4.33 (d, J=9.26, 1H), 3.02-2.94 (m, 1H), 2.00-1.89 (m, 4H), 1.33-1.28 (m, 4H), 1.03 (d, J=6.83, 3H), 0.92 (t, J=7.34, 3H), 0.82-0.76 (m, 12H), 0.02 (d, J=2.16, 6H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 152.86, 110.24, 84.65, 79.53, 31.50, 26.25, 25.14, 24.43, 23.87, 22.23, 18.89, 18.55, 14.11, 12.28, −3.95, −4.00.

(*E*)-5-*tert*-Butyldimethylsilyloxy-3-methyl-1-trimethyl-silanylhept-4-en-1-yne (12). ^1H NMR : (7% C_6D_6 in CCl_4) δ 4.33 (d, J=9.11, 1H), 3.10-2.91 (m, 1H), 1.95 (q, J=7.47, 2H), 1.08 (d, J=6.95, 3H), 0.93 (t, J=7.44, 3H), 0.83 (s, 9H), 0.00 (ds, 15H); ^{13}C NMR : (7% C_6D_6 in CCl_4) δ 153.66, 111.32, 109.14, 83.45, 26.24, 25.33, 23.23, 18.56, 12.17, 0.67, −3.93, −4.00.

3-*tert*-Butyldimethylsilyloxyundec-3-en-6-yne (14). ^1H NMR : (7% C_6D_6 in CCl_4) δ 4.42-4.31 (m, 1H), 2.73-2.60 (m, 2H), 2.02-1.90 (m, 4H), 1.40-1.32 (m, 4H), 0.95 (dt, 3H), 0.89-0.79 (m, 12H), 0.05 (ds, 6H).

5-*tert*-Butyldimethylsilyloxy-1-trimethylsilanylhept-4-en-1-yne (15). ^1H NMR : (7% C_6D_6 in CCl_4) δ 4.39-4.31 (m, 1H), 2.78-2.65 (m, 2H), 1.92 (dq, 2H), 0.92 (dt, 3H), 0.84 (ds, 9H), 0.02 (ds, 15H).

(5-*tert*-Butyldimethylsilyloxyhept-4-en-1-ynyl)benzene (16). ^1H NMR : (7% C_6D_6 in CCl_4) δ 7.28-7.20 (m, 2H), 7.15-7.10 (m, 3H), 4.59-4.51 (m, 1H), 2.95 (dd, J=7.37, 2H), 2.11 (dq, 2H), 1.00 (dt, 3H), 0.89 (ds, 9H), 0.09 (ds, 6H).

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