Notes

Tin-free Radical Acylation Reactions Using Alkyl Allyl Sulfones as Radical Precursors

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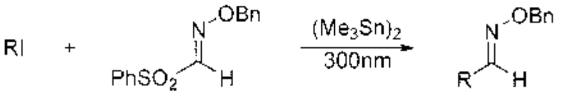
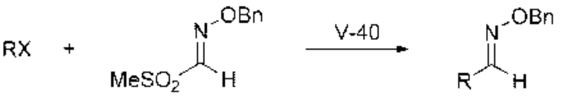
Tin-free radical reactions have attracted a great deal of attention in recent years.[1] To obviate the problem of using highly toxic organotin compounds, several approaches have been developed and include fluorous[2] or polymer-supported organotins,[3] organosilyl substitutes,[4] and thiocarbonyl and organosulfone derivatives.[5] The organosulfone-mediated approach is very effective for allylation,[6] vinylation,[7] and azidation.[8] However, the reported methods did not work well with primary alkyl iodides and xanthates due to inefficient iodine atom and xanthate group transfers, respectively. We reported a highly efficient indirect approach for a radical acylation using phenylsulfonyl oxime ether under tin-mediated conditions (eq. 1)[9] and also developed tin-free acylation approach using methanesulfonyl oxime ether, in which primary alkyl iodides and xanthates caused the same problem due to a small energy difference between a methyl radical and a primary alkyl radical (eq. 2).[10]



(1)



(2)

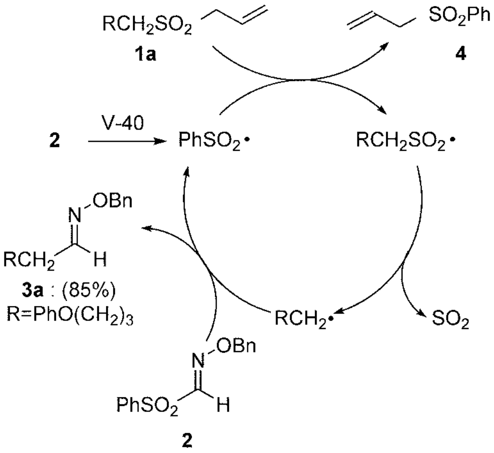
X= iodide, xanthate

In connection with our continuing effort to develop intermolecular radical reactions under tin-free conditions, we recently reported new tin-free carbon-carbon bond forming reactions using alkyl allyl sulfones as radical precursors.[11] This newly developed approach could be successfully applied to allylation, vinylation, and cyanation reactions. Although *S*-alkoxycarbonyl dithiocarbonate has been known to be a precursor of primary alkyl radicals from alcohols, it can not be applied to carbon-carbon bond formations due to a rapid formation of the corresponding xanthates.[12] However, the use of alkyl allyl sulfones was turned out to be exceedingly effective and reliable for the generation of primary alkyl radicals under tin-free conditions and for the formation of carbon-carbon bonds.

We have studied radical reaction of phenylsulfonyl oxime ethers **2** and **5** using alkyl allyl sulfones as radical precursors and found that alkyl allyl sulfones are highly efficient and reliable radical precursors for the radical reaction of phenyl sulfonyl oxime ethers.

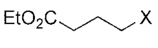
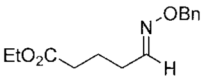
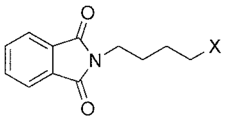
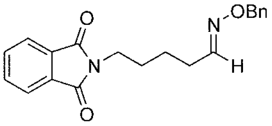
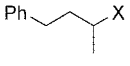
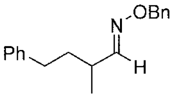
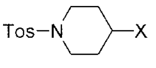
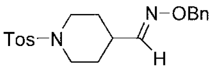
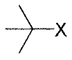
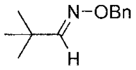
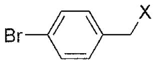
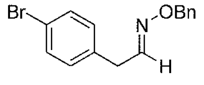
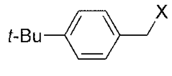
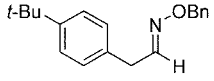
As shown in Scheme 1, the addition of a phenylsulfonyl radical onto alkyl allyl sulfone **1a** would produce an alkylsulfonyl radical along with phenyl allyl sulfone **4**. Although the alkylsulfonyl radical can add to **1a** and **4**, the former is a degenerate process and the latter produces the phenylsulfonyl radical. Thus, they do not interfere with the desired process. Since the addition of an alkyl radical onto **4** and **1a** is relatively slow,[13] the alkyl radical should preferentially add to phenylsulfonyl oxime ether **2** along with regeneration of the phenylsulfonyl radical for propagation of a radical chain reaction.

Since thermal decomposition of primary alkyl sulfonyl radicals into primary alkyl radicals and SO_2 requires heating around 100 °C, the reaction of **1a** with **2** (1.5 equiv) was carried out in the presence of V-40 (1,1'-azobis(cyclohexane-



Scheme 1. Pathways for radical acylation of alkyl allyl sulfone **1a** with phenyl sulfonyl oxime ether **2**.

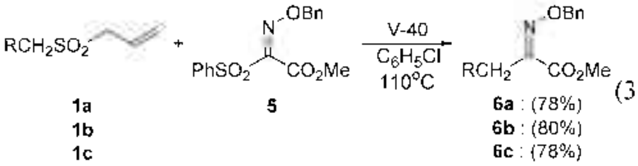
Table 1. Tin-free Radical Acylation using Alkyl Allyl Sulfones[a]

Substrate ($X = SO_2CH_2CH{=}CH_2$)	Product	Yield[b]
 **1b**	 **3b**	86%
 **1c**	 **3c**	86%
 **1d**	 **3d**	98%
 **1e**	 **3e**	98%
 **1f**	 **3f**	95%
 **1g**	 **3g**	97%
 **1h**	 **3h**	95%

[a] The reaction carried out using V-40 in chlorobenzene at 110 °C for 4-6 h. [b] The yields refer to the isolated yields.

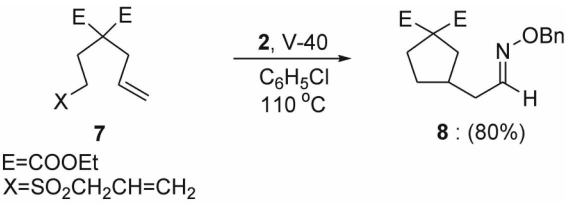
1-carbonitrile)) (0.2 equiv) as initiator in chlorobenzene at 110 °C and was complete within 6 h, yielding the desired oxime ether **3a** in 85% yield, indicating clean generation of the primary alkyl radical under tin-free condition. The remaining reactions were carried out in chlorobenzene at 110 °C for 4-6 h. However, it is noteworthy that the reaction temperature might be lowered to some extent along with the use of AIBN as initiator when secondary, tertiary alkyl, and benzyl allyl sulfones are employed because those sulfones can undergo thermal decomposition at lower temperature. As shown in Table 1, the present method worked well with primary, secondary and sterically bulky tertiary alkyl allyl sulfones along with benzyl allyl sulfones.

The present method can be further applied to the preparation of α-oxime ester **6**, a synthetic equivalent of an α-keto ester, by using phenylsulfonyl methoxy carbonyl oxime ether **5** (eq. 3). The reactions were performed under the similar conditions and afforded **6** in good yields, showing efficiency of the alkyl allyl sulfone as radical precursor.



(3)

Finally, when tandem radical reaction involving cyclization and acylation sequence was briefly studied with **7**, the reaction worked well, yielding **8** in 80% yield (eq. 4).



(4)

In conclusion, we have demonstrated the successful tin-free radical acylation using alkyl allyl sulfones as useful and reliable source of primary alkyl radicals under tin-free conditions.

Experimental Section

General. All reagents were purchased from Aldrich Co. and Wako Co. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometers. The chemical shifts in $CDCl_3$ or benzene-d_6 reported in δ (ppm) relative to $CDCl_3$ or Me_4Si as an internal reference. IR spectra were measured on a BOMEM MB-100 Fourier Transform spectrometer. High resolution mass spectra were obtained on a VG AUTOSPEC Ultma GC/MS system using direct insertion probe (DIP) and electron impact (EI) (70 eV) method. Flash chromatography was carried out on Merck silica 60 (230-400 mesh ASTM).

Typical procedure for tin-free radical acylation: A solution of 4-phenoxybutyl allyl sulfone **1a** (51 mg, 0.2 mmol), *O*-benzyl-1-(benzenesulfonyl)formaldoxime **2** (83 mg, 0.3 mmol) and V-40 (10 mg, 0.04 mmol) in chlorobenzene (1mL) was degassed with nitrogen for 10 min and then the solution was heated at 110 °C under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was separated by a silica gel column chromatography using ethyl acetate and *n*-hexane (1 : 5) as eluant to give oxime ether **3a** (48 mg, 85%, $E : Z = 1.4 : 1$).

***O*-Benzyl-5-phenoxy-pentanaldoxime (3a).** MW: $C_{18}H_{21}NO_2$ = 283.36; $E : Z = 1.4 : 1$ (from ^{1}H NMR ratio); ^{1}H NMR ($CDCl_3$, 400 MHz) *E*: δ 1.65-1.71 (m, 2H), 1.77-1.84 (m, 2H), 2.24-2.29 (m, 2H), 3.94 (t, J = 6.1 Hz, 2H), 5.05 (s, 2H), 6.86-6.93 (m, 3H), 7.24-7.35 (m, 7H), 7.46 (t, J = 6.1 Hz, 1H); *Z*: δ 1.65-1.71 (m, 2H), 1.77-1.84 (m, 2H), 2.42-2.47 (m, 2H), 3.94 (t, J = 6.1 Hz, 2H), 5.10 (s, 2H), 6.70 (t, J = 5.5 Hz, 1H), 6.86-6.93 (m, 3H), 7.24-7.35 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.8, 23.2, 25.5, 28.6, 28.9, 29.2, 67.1, 67.2, 75.6, 75.7, 114.4, 120.6, 127.7, 127.8, 128.0, 128.2, 128.4, 129.4, 137.6, 138.0, 151.0, 151.9, 158.9; IR (polymer) 2919, 2866, 1601, 1497, 1246, 754, 693 cm^{-1}; HRMS (M^+) calcd for $C_{18}H_{21}NO_2$: 283.1572, found 283.1573.

5-Benzyloxyimino-pentanoic acid ethyl ester (3b). MW: $C_{14}H_{19}NO_3$ = 249.31; $E : Z = 1.4 : 1$ (from ^{1}H NMR ratio);

^{1}H NMR (CDCl$_3$, 400 MHz) *E*: δ 1.23 (td, J = 7.2 Hz, 3.4 Hz, 3H), 1.78-1.83 (m, 2H), 2.19-2.23 (m, 2H), 2.31 (t, J = 7.5 Hz, 2H), 4.11 (qd, J = 7.2 Hz, 2.3 Hz, 2H), 5.03 (s, 2H), 7.24-7.34 (m, 5H), 7.42 (t, J = 6.1 Hz, 1H); *Z*: δ 1.23 (td, J = 7.2 Hz, 3.4 Hz, 3H), 1.78-1.83 (m, 2H), 2.31 (t, J = 7.5 Hz, 2H), 2.38-2.40 (m, 2H), 4.11 (qd, J = 7.2 Hz, 2.3 Hz, 2H), 5.08 (s, 2H), 6.66 (t, J = 5.5 Hz, 1H), 7.24-7.34 (m, 5H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 14.2, 21.5, 21.8, 25.2, 28.9, 33.4, 33.7, 60.3, 75.6, 75.8, 127.7, 127.8.127.9, 128.2, 128.3, 137.6, 137.9, 150.2, 151.1, 173.0 (2C); IR (polymer) 2983, 2934, 2870, 1736, 1455, 1374, 1249, 1163, 1024, 927, 754, 700 cm^{-1}; HRMS (M$^+$) calcd for $C_{14}H_{19}NO_3$: 249.1365, found 249.1368.

_O_-Benzyl-5-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-pentanaldoxime (3c). MW: $C_{20}H_{20}N_2O_3$ = 336.38; *E* : *Z* = 1.4 : 1 (from ^{1}H NMR ratio); ^{1}H NMR (CDCl$_3$, 400 MHz) *E*: δ 1.47-1.56 (m, 2H), 1.65-1.72 (m, 2H), 2.19-2.24 (m, 2H), 3.67 (td, J = 7.1 Hz, 2.3 Hz, 2H), 5.00 (s, 2H), 7.21-7.87 (m, 9H), 7.40 (t, J = 6.1 Hz, 1H); *Z*: δ 1.47-1.56 (m, 2H), 1.65-1.72 (m, 2H), 2.37-2.42 (m, 2H), 3.67 (td, J = 7.1 Hz, 2.3 Hz, 2H), 5.06 (s, 2H), 6.64 (t, J = 5.5 Hz, 1H), 7.21-7.87 (m, 9H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 23.5, 23.9, 25.3, 28.0, 28.3, 29.0, 37.5, 75.5, 75.7, 123.2, 127.7 (2C), 127.9, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 130.8, 132.1, 133.9, 137.6, 150.6, 151.6, 168.3; IR (polymer) 2941, 1773, 1714, 1448, 1398, 1321, 1148, 1087, 724, 626, 533 cm^{-1}; HRMS (M$^+$) calcd for $C_{20}H_{20}N_2O_3$: 336.1474, found 336.1478.

_O_-Benzyl-2-methyl-4-phenyl-butyraldoxime (3d). MW: $C_{18}H_{21}NO$ = 267.37; *E* : *Z* = 2.8 : 1 (from ^{1}H NMR ratio); ^{1}H NMR (CDCl$_3$, 400 MHz) *E*: δ 1.09 (d, J = 6.9 Hz, 3H), 1.65-1.76 (m, 2H), 2.34-2.43 (m, 1H), 2.58 (td, J = 8.7 Hz, 1.8Hz, 2H), 5.06 (s, 2H), 7.11-7.38 (m, 11H); *Z*: δ 1.05 (d, J = 6.8 Hz, 3H), 1.65-1.76 (m, 2H), 2.58 (td, J = 8.7 Hz, 1.8 Hz, 2H), 3.10-3.20 (m, 1H), 5.09 (s, 2H), 6.52 (d, J = 7.7 Hz, 1H), 7.11-7.38 (m, 10H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 17.6, 18.3, 30.1, 33.3, 33.6, 34.0, 36.4, 36.5, 75.6, 75.7, 125.8, 127.7, 127.8, 127.9, 128.3 (3C), 128.4 (2C), 137.7, 141.9, 155.4, 156.7; IR (polymer) 2964, 2947, 1706, 1658, 1497, 1456, 1050, 924, 751, 700 cm^{-1}; HRMS (M$^+$) calcd for $C_{18}H_{21}NO$ = 267.1623, found 267.1630.

_O_-Benzyl-1-(toluene-4-sulfonyl)-piperidine-4-carbaldoxime (3e). MW: $C_{20}H_{24}N_2O_3S$ = 372.48; *E* : *Z* = 2.5 : 1 (from ^{1}H NMR ratio); ^{1}H NMR (CDCl$_3$, 400 MHz) *E*: δ 1.47-1.65 (m, 2H), 1.78-1.82 (m, 2H), 2.09-2.18 (m, 1H), 2.27-2.38 (m, 2H), 2.41 (s, 3H), 4.99 (s, 2H), 7.24-7.87 (m, 10H); *Z*: δ 1.47-1.65 (m, 2H), 1.78-1.82 (m, 2H), 2.27-2.38 (m, 2H), 2.40 (s, 3H), 2.75-2.85 (m, 1H), 5.02 (s, 2H), 6.45 (d, J = 6.8 Hz, 1H), 7.24-7.87 (m, 9H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 21.5, 28.0, 28.7, 32.0, 35.8, 45.5 (2C), 75.8, 75.9, 127.6, 127.7, 127.9, 128.0, 128.3 (2C), 128.5, 128.6, 128.8, 130.8, 133.2, 137.3, 143.5, 152.5, 153.3; IR (polymer) 2926, 2848, 1598, 1449, 1354, 1320, 1167, 1148, 1088, 931, 728, 690, 550 cm^{-1}; HRMS (M$^+$) calcd for $C_{20}H_{24}N_2O_3S$ = 372.1508, found 372.1524.

(_E_)-_O_-Benzyl-2,2-dimethyl-1-propanaldoxime (3f). MW: $C_{12}H_{17}NO$ = 191.27; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.08 (s, 9H), 5.03 (s, 2H), 7.25-7.36 (m, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 27.6, 33.6, 75.6, 127.8, 128.3, 128.4, 137.7, 158.7; IR (polymer) 2963, 2869, 1476, 1366, 1027 cm^{-1}; HRMS (M+) calcd for $C_{12}H_{17}NO$: 191.1310, found 191.1323.

_O_-Benzyl-1-(4-bromo-benzyl)-formaldoxime (3g). MW: $C_{15}H_{14}BrNO$ = 304.18; *E* : *Z* = 1.1 : 1 (from ^{1}H NMR ratio); ^{1}H NMR (CDCl$_3$, 400 MHz) *E*: δ 3.45 (d, J = 6.4 Hz, 2H), 5.08 (s, 2H), 7.02-7.06 (m, 2H), 7.27-7.43 (m, 7H), 7.48 (t, J = 6.5 Hz, 1H); *Z*: δ 3.65 (d, J = 5.4 Hz, 2H), 5.15 (s, 2H), 6.79 (t, J = 5.4 Hz, 1H), 7.02-7.06 (m, 2H), 7.32-7.43 (m, 7H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 31.9, 35.3, 75.8, 76.1, 120.5, 120.7, 127.9 (2C), 128.1, 128.2, 128.4, 130.5 (2C), 131.7, 131.8, 135.3, 135.7, 137.5, 137.7, 149.0, 149.4; IR (polymer) 3035, 2939, 1702, 1653, 1560, 1489, 1456, 1368, 1073, 1014, 700 cm^{-1}; HRMS (M$^+$) calcd for $C_{15}H_{14}BrNO$: 303.0259, found 303.0264.

_O_-Benzyl-1-(4-_t_-butyl-benzyl)-formaldoxime (3h). MW: $C_{19}H_{23}NO$ = 281.39; *E* : *Z* = 1.1 : 1 (from ^{1}H NMR ratio); ^{1}H NMR (CDCl$_3$, 400 MHz) *E*: δ 1.31 (s, 9H), 3.49 (d, J = 6.5 Hz, 2H), 5.10 (s, 2H), 7.11-7.14 (m, 2H), 7.32-7.38 (m, 7H), 7.54 (t, J = 6.5 Hz, 1H); *Z*: δ 1.31 (s, 9H), 3.70 (d, J = 5.3 Hz, 2H), 5.17 (s, 2H), 6.86 (t, J = 5.3 Hz, 1H), 7.11-7.14 (m, 2H), 7.32-7.38 (m, 7H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 31.3, 32.0, 34.4, 35.3, 75.6, 75.9, 125.6, 127.8, 128.0, 128.2, 128.4 (3C), 133.2, 133.7, 137.7, 137.9, 149.5, 149.7, 150.0, 150.5; IR (polymer) 2962, 2868, 1510, 1457, 1365, 1093, 1019, 836, 736, 699 cm^{-1}; HRMS (M$^+$) calcd for $C_{19}H_{23}NO$: 281.1780, found 281.1781.

2-Benzyloxyimino-6-phenoxy-hexanoic acid methyl ester (6a). MW: $C_{20}H_{23}NO_4$ = 341.40; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.66-1.78 (m, 4H), 2.66 (t, J = 7.5 Hz, 2H), 3.83 (s, 3H), 3.90 (t, J = 6.0 Hz, 2H), 5.27 (s, 2H), 6.81-6.92 (m, 3H), 7.22-7.35 (m, 7H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 22.6, 25.3, 29.0, 52.7, 67.2, 77.7, 114.5, 120.5, 128.2 (2C), 128.5, 129.4, 136.5, 152.7, 159.0, 164.1; IR (polymer) 2953, 2873, 1722, 1601, 1497, 1245, 755, 694 cm^{-1}; HRMS (M$^+$) calcd for $C_{20}H_{23}NO_4$ = 341.1627, found 341.1637.

2-Benzyloxyimino-hexanedioic acid 6-ethyl ester 1-methyl ester (6b). MW: $C_{16}H_{21}NO_5$ = 307.34; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.19 (t, J = 7.1 Hz, 3H), 1.78-1.86 (m, 2H), 2.27 (t, J = 7.5 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 3.82 (s, 3H), 4.06 (q, J = 7.1Hz, 2H), 5.26 (s, 2H), 7.28-7.33 (m, 5H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 14.2, 21.3, 24.9, 33.8, 52.7, 60.3, 77.7, 128.2, 128.5, 136.4, 152.1, 163.9, 172.9; IR (polymer) 2959, 1739, 1723, 1462, 1377, 1215, 1124, 1021, 700 cm^{-1}; HRMS (M$^+$) calcd for $C_{16}H_{21}NO_5$ = 307.1420, found 307.1424.

2-Benzyloxyimino-6-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-hexanoic acid methyl ester (6c). MW: $C_{22}H_{22}N_2O_5$ = 394.42; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.51-1.67 (m, 4H), 2.62 (t, J = 7.5 Hz, 2H), 3.63 (t, J = 7.1 Hz, 2H), 3.81 (s, 3H), 5.25 (s, 2H), 7.26-7.82 (m, 9H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 23.4, 25.1, 28.3, 37.6, 52.7, 77.6, 123.2, 128.1, 128.2, 128.4, 129.0, 132.1, 133.8, 152.4, 164.0, 168.3; IR (polymer) 2960, 1773, 1709, 1398, 1164, 859, 722 cm^{-1}; HRMS (M$^+$) calcd for $C_{22}H_{22}N_2O_5$ = 394.1529, found 394.1524.

3-(2-Benzyloxyimino-ethyl)-cyclopentane-1,1-dicarboxylic acid diethyl ester (8). MW: $C_{20}H_{27}NO_5$ = 361.43; *E* : *Z*

= 1.4 : 1 (from ^{1}H NMR ratio); ^{1}H NMR ($CDCl_3$, 400 MHz) *E*: δ 1.22 (t, J = 7.1Hz, 6H), 1.26-1.38 (m, 1H), 1.73-1.79 (m, 1H), 1.85-1.92 (m, 1H), 2.10-2.17 (m, 2H), 2.20-2.32 (m, 2H), 2.40-2.48 (m, 2H), 4.15 (q, J = 7.1 Hz, 4H), 5.03 (s, 2H), 7.27-7.40 (m, 5H), 7.41 (t, J = 6.0 Hz, 1H); *Z*: δ 1.21 (t, J = 7.1Hz, 6H), 1.26-1.38 (m, 1H), 1.73-1.79 (m, 1H), 1.85-1.92 (m, 1H), 2.10-2.17 (m, 2H), 2.20-2.32 (m, 2H), 2.40-2.48 (m, 2H), 4.15 (q, J = 7.1 Hz, 4H), 5.08 (s, 2H), 6.68 (t, J = 5.5 Hz, 1H), 7.27-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 30.9, 31.7, 31.9, 33.6, 33.7, 34.7, 37.0, 37.4, 40.1, 40.3, 60.0 (2C), 61.3, 75.6, 75.7, 127.8, 127.9, 128.2, 128.3, 128.8, 137.7, 138.0, 150.0, 150.6, 172.4 (2C); IR (polymer) 2985, 2941, 1730, 1477, 1368, 1267, 1157, 1048, 700 cm^{-1}; HRMS (M$^+$) calcd for $C_{20}H_{27}NO_5$: 361.1889, found 361.1892.

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