Direct use of allylic alcohols in allylation of sulfonylimidates

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Electronic Supplementary Information

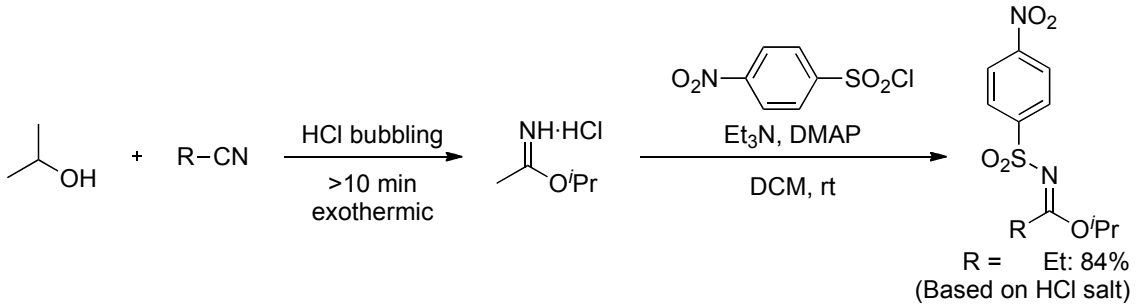
<General>

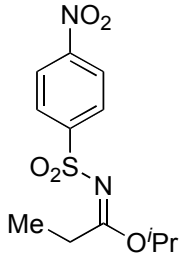
Melting points are uncorrected. 1H and 13C NMR spectra were recorded on a JEOL JNM-ECX-400, JNM-ECX-500 and JNM-ECX-600 spectrometer in $CDCl_3$ unless otherwise noted. Tetramethylsilane served as an internal standard ($\delta = 0$) for ^1H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. IR spectra were measured on a JASCO FT/IR-610 spectrometer. Column chromatography was conducted on Silica gel60 (Merck) and preparative thin-layer chromatography was carried out using Wakogel B-5F. All the reactions were carried out under argon atmosphere in dried glasswares. All the solvents were dried and distilled by standard procedures. All the desiccants were dried at 200 °C under reduced pressure, and kept in an Ar box. All the sulfonylimidates were prepared according to the reported method[1]. All the allylic alcohols except **1d** and **1f** were purchased from TCI and used as received.

[1] J. S. B. Kan, R. Matsubara, F. Berthiol, S. Kobayashi, *Chem. Commun.* **2008**, 6354.

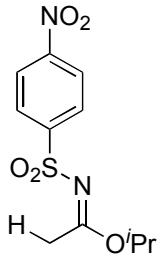
<Sulfonylimidates>

HCl gas was bubbled into a mixture of isopropyl alcohol (400 mmol) and alkyl nitrile (440 mmol) for 10-20 min (The reaction was not cooled though the reaction was a little exothermic). After the completion of the HCl bubbling, the mixture was left for 2 h under Ar atmosphere. Removal of all the volatiles by evaporation gave imidate HCl salt, which was further purified by washing with dry Et_2O. Et_3N (13.8 mL, 99 mmol, 3 equiv), 4-nitrobenzenesulfonyl chloride (7.24 g, 33 mmol, 1 equiv), and DMAP (399 mg, 3.3 mmol, 10 mol%) were added to a solution of the imidate HCl salt (5.0 g, 33 mmol, 1 equiv) in dichloromethane (100 mL) at rt. The reaction mixture was stirred until 4-nitrobenzenesulfonyl chloride was consumed (20-40 h). The mixture was poured into water, and extracted with DCM. The organics were dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvents afforded the crude product, which was purified by column chromatography on SiO_2 and recrystallized from hexane/EtOAc to give pure sulfonylimidate.

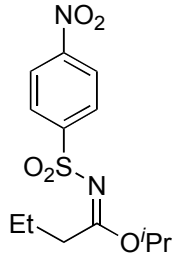




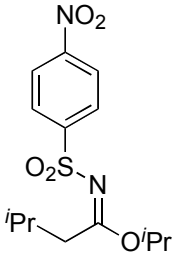
Isopropyl *N*-(4-nitrobenzenesulfonyl)propionimidate: Slightly yellow rod crystal. Mp. 70-71 °C; ^{1}H NMR ($CDCl_3$) δ = 8.35 (d, 2H, *J* = 9.2 Hz), 8.12 (d, 2H, *J* = 9.2 Hz), 5.00 (septet, 1H, *J* = 6.3 Hz), 2.98 (q, 2H, *J* = 8.0 Hz), 1.27 (t, 3H, *J* = 8.0 Hz), 1.26 (d, 6H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.5, 149.8, 147.6, 127.8, 124.1, 72.9, 28.6, 21.1, 10.2; IR (KBr) 3021, 2987, 1579, 1532, 1350, 1308, 1216, 1158, 1094 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{12}H_{17}N_2O_5S$ $[M+H]^+$, 301.0858. Found 301.0871.



Isopropyl *N*-(4-nitrobenzenesulfonyl)acetimidate: Slightly yellow rod crystal. Mp. 73-74 °C; ^{1}H NMR ($CDCl_3$) δ = 8.34 (d, 2H, *J* = 8.7 Hz), 8.11 (d, 2H, *J* = 8.7 Hz), 5.02 (septet, 1H, *J* = 6.2 Hz), 2.51 (s, 3H), 1.23 (d, 6H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 174.1, 147.5, 127.9, 124.1, 73.1, 21.6, 21.2; IR (KBr) 3105, 2985, 1591, 1529, 1350, 1304, 1157, 1096, 1041 cm^{-1}; HRMS (DART) Exact mass calcd for $C_{11}H_{15}N_2O_5S$ $[M+H]^+$, 287.0702. Found 287.0687.



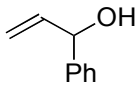
Isopropyl *N*-(4-nitrobenzenesulfonyl)butyrimidate: Slightly yellow rod crystal. Mp. 49-50 °C; ^{1}H NMR ($CDCl_3$) δ = 8.35 (d, 2H, *J* = 8.6 Hz), 8.12 (d, 2H, *J* = 8.6 Hz), 5.00 (septet, 1H, *J* = 6.3 Hz), 2.88 (t, 2H, *J* = 7.5 Hz), 1.77 (tq, 2H, *J* = 8.0, 8.0 Hz), 1.26 (d, 6H, *J* = 6.3 Hz), 1.02 (t, 3H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 176.7, 149.8, 147.7, 127.8, 124.0, 72.8, 36.6, 21.2, 19.6, 13.7; IR (KBr) 2972, 2938, 1582, 1530, 1349, 1311, 1160, 1093 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{13}H_{19}N_2O_5S$ $[M+H]^+$, 315.1015. Found 315.1028.



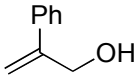
Isopropyl 3-methyl-*N*-(4-nitrobenzenesulfonyl)butyrimidate: White rod crystal. Mp. 79-80 °C; ^{1}H NMR ($CDCl_3$) δ =8.36 (d, 2H, *J* = 9.1 Hz), 8.10 (d, 2H, *J* = 9.1 Hz), 4.99 (septet, 1H, *J* = 6.2 Hz), 2.77 (d, 2H, *J* = 7.4 Hz), 2.24 (app septet, 1H, *J* = 6.8 Hz), 1.23 (d, 6H, *J* = 6.3 Hz), 0.99 (d, 6H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 176.0, 149.7, 147.8, 127.8, 124.0, 72.8, 43.2, 26.9, 22.3, 21.2; IR (KBr) 2961, 1597, 1534, 1370, 1305, 1158, 1091 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{14}H_{21}N_2O_5S$ $[M+H]^+$, 329.1171. Found 329.1173.

<Allylic alcohols>

Allylic alcohols **1d** and **1f** were prepared according to the reported method[2]. Both were obtained as colorless oil and freshly distilled by Kugelrohr before use.



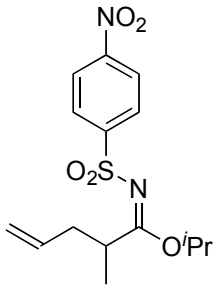
1-Phenylprop-2-en-1-ol[2] (1d): ^{1}H NMR ($CDCl_3$) δ = 7.37-7.30 (m, 5H), 6.06 (ddd, 1H, *J* = 16.4, 10.3, 6.0 Hz), 5.35 (dd, 1H, *J* = 16.4, 1.5 Hz), 5.19-5.15 (m, 2H), 3.18 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ = 142.5, 140.1, 128.4, 127.6, 126.2, 114.9, 75.1.



2-Phenylprop-2-en-1-ol[2] (1f): ^{1}H NMR ($CDCl_3$) δ = 7.44-7.24 (m, 5H), 5,46 (s, 1H), 5.34 (s, 1H), 4.53 (s, 2H), 1.57 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 147.4, 138.6, 128.6, 127.9, 126.1, 112.7, 65.1.

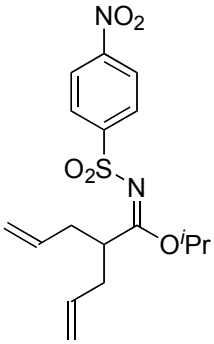
<General procedure of allylation reactions of sulfonylimidates>

In an Ar box, sulfonylimidate **2a** (90 mg, 0.3 mmol, 1 equiv), As_2O_3 (3.7 mg, 0.018 mmol, 6 mol%), $Pd(PPh_3)_4$ (13.7 mg, 0.012 mmol, 4 mol%) and MS 3A (50 mg) were combined in a capped vial, then the vial was taken out of the Ar box. Dioxane (0.5 mL), and allylic alcohol (31 μL, 0.45 mmol, 1.5 equiv) were added. The mixture was stirred at the indicated temperature and then quenched by passing through a silica gel pad (washed with hexane/EtOAc = 5/1). After removal of the solvents, purification of the crude productperformed by preparative TLC afforded the desired allylated sulfonylimidates **3a** (86%).

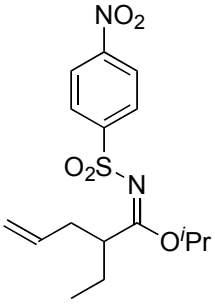


Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (3a): Slightly yellow solid. Mp. 69-70 °C; ^{1}H NMR ($CDCl_3$) δ = 8.35 (d, 2H, *J* = 9.2 Hz), 8.12 (d, 2H, *J* = 9.2 Hz), 5.70-5.81 (m, 1H), 5.08 (dd, 1H, *J* = 17.1, 1.0 Hz), 5.05 (dd, 1H, *J* = 10.2, 1.0 Hz), 4.97 (septet, 1H, *J* = 6.3 Hz), 3.71-3.63 (m, 1H), 2.42-2.48 (m, 1H), 2.22-2.27(m, 1H), 1.22-1.27 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 179.0, 149.7, 147.8, 134.6, 127.8, 124.0, 117.4, 72.6, 39.2, 38.1, 21.1, 21.0, 17.5; IR (KBr) 3111, 3075, 2984, 2935, 1585, 1529, 1460, 1354, 1305, 1215, 1157, 1092; HRMS (DART) Exact mass calcd for $C_{15}H_{21}N_2O_5S$ $[M+H]^+$, 341.1171. Found 341.1181.

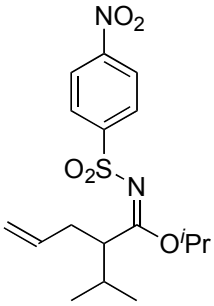
[2] (a) S. Jautze, R. Peters, *Angew. Chem. Int. Ed.* **2008**, *47*, 9284. (b) T. Ohmura, K. Masuda, I. Takase, M. Suginome, *J. Am. Chem. Soc.* **2009**, *131*, 16624. (c) J. J. Gajewski, K. R. Gee, J. Jurayj, *J. Org. Chem.* **1990**, *55*, 1813.



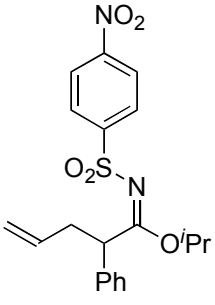
Isopropyl 2-allyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (3b): Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 8.35 (d, 2H, *J* = 8.5 Hz), 8.12 (d, 2H, *J* = 8.5 Hz), 5.79 (ddd, 2H, *J* = 17.0, 10.1, 7.4 Hz), 5.08 (d, 2H, *J* = 17.0 Hz), 5.06 (d, 2H, *J* = 10.1 Hz), 4.98 (septet, 1H, *J* = 6.2 Hz), 3.76 (quintet, 1H, *J* = 6.5), 2.41-2.37 (m, 4H), 1.23 (d, 6H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.5, 149.8, 147.9, 134.5, 127.9, 124.1, 117.6, 72.7, 44.0, 36.6, 21.2; IR (neat) 3080, 2985, 2931, 1585, 1307, 1222, 1158, 1099; HRMS (DART) Exact mass calcd for $C_{17}H_{23}N_2O_5S$ $[M+H]^+$, 367.1328. Found 367.1330.



Isopropyl 2-ethyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (3c): White solid. Mp. 38-40 °C; ^{1}H NMR ($CDCl_3$) δ = 8.33 (d, 2H, *J* = 9.2 Hz), 8.10 (d, 2H, *J* = 9.2 Hz), 5.77 (ddt, 1H, *J* = 17.2, 9.7, 6.9 Hz), 4.94-5.07 (m, 3H), 3.56 (app quint, 1H, *J* = 7.5 Hz), 2.28-2.40 (m, 2H), 1.57-1.73 (m, 2H), 1.23 (d, 3H, *J* = 6.3 Hz), 1.21 (d, 3H, *J* = 6.3 Hz), 0.95 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 178.2, 149.6, 147.8, 134.7, 127.7, 123.9, 117.2, 72.4, 46.0, 36.8, 25.5, 21.1, 21.0, 11.5; IR (KBr) 2980, 2936, 1583, 1531, 1465, 1350, 1307, 1245, 1160, 1091 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{16}H_{23}N_2O_5S$ $[M+H]^+$, 355.1328. Found 355.1324.

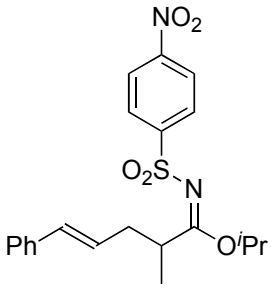


Isopropyl 2-isopropyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (3d): Slightly yellow oil; ^{1}H NMR ($CDCl_3$) δ = 8.27 (d, 2H, *J* = 9.2 Hz), 8.03 (d, 2H, *J* = 9.2 Hz), 5.68-5.78 (m, 1H), 4.86-5.00 (m, 3H), 3.34 (ddd, 1H, *J* = 10.3, 8.6, 4.6 Hz), 2.40-2.47 (m, 1H), 2.17-2.25 (m, 1H), 1.82-1.92 (m, 1H), 1.17 (d, 3H, *J* = 6.3 Hz), 1.14 (d, 3H, *J* = 6.3 Hz), 0.96 (d, 3H, *J* = 6.9 Hz), 0.92 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.8, 149.7, 148.0, 135.0, 127.7, 123.9, 117.0, 72.4, 51.0, 34.9, 30.9, 21.2, 21.0, 20.9, 19.8; IR (neat) 2968, 1579, 1532, 1467, 1350, 1306, 1159, 1093 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{17}H_{25}N_2O_5S$ $[M+H]^+$, 369.1484. Found 369.1476.

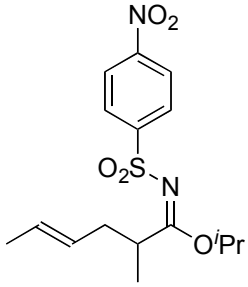


Isopropyl 2-phenyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (3e): Slightly yellow oil. ^{1}H NMR ($CDCl_3$) δ = 8.28 (d, 2H, *J* = 8.9 Hz), 8.03 (d, 2H, *J* = 8.9 Hz), 7.45 (d, 2H *J* = 8.2 Hz), 7.32 (dd, 2H, *J* = 8.2, 7.6 Hz), 7.27 (t, 1H, *J* = 7.6 Hz), 5.82-5.75 (m, 1H), 5.14 (d, 1H, *J* = 17.2 Hz), 5.06 (d, 1H, *J* = 10.3 Hz), 5.01 (septet, 1H, *J* = 6.2 Hz), 4.94 (dd, 1H, *J* = 9.3, 6.2 Hz), 2.88-2.82 (m, 1H), 2.64-2.59 (m, 1H), 1.29 (d, 3H, *J* = 6.2Hz), 1.19 (d, 3H, *J* = 6.2Hz); ^{13}C NMR ($CDCl_3$) δ = 175.0, 149.7, 147.6, 137.2, 134.3, 128.6, 128.4, 127.7,

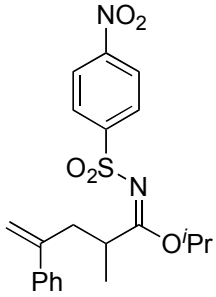
127.6, 123.9, 17.6, 73.2, 49.5, 37.9, 21.0, 20.9; IR (neat) 3105, 3074, 3033, 2983, 2938, 2871, 1577, 1529, 1348, 1305, 1158, 1093; HRMS (DART) Exact mass calcd for $C_{20}H_{23}N_2O_5S$ $[M+H]^+$, 403.1328. Found 403.1322.



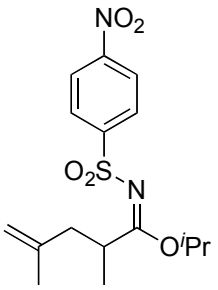
Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)-5-phenylpent-4-enimidate (3fa): Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 8.22 (d, 2H, *J* = 8.7 Hz), 8.04 (d, 2H, *J* = 8.7 Hz), 7.30-7.21 (m, 5H), 6.40 (d, 1H, *J* = 16.0 Hz), 6.15 (ddd, 1H, *J* = 16.1, 7.2, 7.4 Hz), 5.00 (septet, 1H, *J* = 6.4 Hz), 3.85-3.76 (m, 1H), 2.58 (ddd, 1H, *J* = 7.4, 9.0, 13.3 Hz), 2.42 (ddd, 1H, *J* = 7.2, 4.8, 13.3 Hz), 1.31 (d, 3H, *J* = 6.9 Hz), 1.26 (d, 3H, *J* = 6.4 Hz), 1.21 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.9, 142.3, 137.2, 132.3, 132.1, 128.7, 128.5, 127.1, 126.7, 126.4, 126.1, 71.9, 38.7, 37.5, 21.3, 21.1, 17.5; IR (neat) 2983, 2933, 1578, 1530, 1457, 1349, 1305, 1159, 1090 cm^{-1}; HRMS (DART) Exact mass calcd for $C_{21}H_{25}N_2O_5S$ $[M+H]^+$, 417.1484. Found 417.1489.



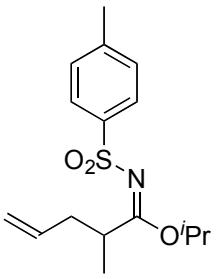
Isopropyl 2-methyl-N-(4-nitrobenzenesulfonyl)hex-4-enimidate (3ga): obtained as a mixture with isopropyl 2,3-dimethyl-N-(4-nitrobenzenesulfonyl)pent-4-enimidate (**3gb**); ^{1}H NMR ($CDCl_3$) δ = 8.36 (d, 2H, *J* = 8.9 Hz), 8.12 (d, 2H, *J* = 8.9 Hz), 5.52-5.45 (m, 1H), 5.36 (dt, 1H, *J* = 15.6, 7.0 Hz), 5.03-4.93 (m, 1H), 2.40-2.34 (m, 1H), 2.20-2.14 (m, 1H), 1.63 (d, 3H, *J* = 6.0 Hz), 1.25-1.22 (m, 6H); ^{13}C NMR ($CDCl_3$) δ = 179.4, 127.8, 124.0, 72.5, 39.6, 37.0, 21.0, 17.8, 17.2, 15.5. Indistinguishable peaks are below. δ = 149.8, 148.0, 127.1, 44.7, 41.7, 21.1, 20.9, 17.5, 16.2.; IR (neat) 3114, 2982, 1935, 1585, 1458, 1304, 1155, 1085; HRMS (DART) Exact mass calcd for $C_{16}H_{23}N_2O_5S$ $[M+H]^+$, 355.1328. Found 355.1319.



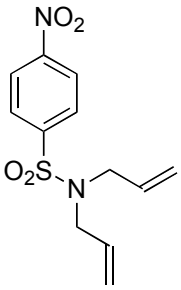
Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)-4-phenylpent-4-enimidate (3h): Slightly yellow solid. Mp. 61-62 °C; ^{1}H NMR ($CDCl_3$) δ = 8.22 (d, 2H, *J* = 8.5 Hz), 7.96 (d, 2H, *J* = 8.5 Hz), 7.34-7.15 (m, 5H), 5.27 (s, 1H), 5.10 (s, 1H), 4.92-4.84 (m, 1H), 3.70-3.63 (m, 1H), 2.94 (dd, 1H, *J* = 14.5, 8.0 Hz), 2.51 (dd, 1H, *J* = 14.5, 7.0 Hz), 1.16-1.11 (m. 9H); ^{13}C NMR ($CDCl_3$) 178.8, 149.6, 147.7, 145.1, 140.3, 128.3, 127.7, 126.2, 123.9, 114.7, 72.7, 38.6, 38.0, 20.9(3), 20.9(0), 17.6; IR (KBr) 3111, 2982, 2934, 1806, 1575, 1455, 1312, 1222, 1156, 1097; HRMS (DART) Exact mass calcd for $C_{21}H_{25}N_2O_5S$ $[M+H]^+$, 417.1484. Found 417.1481.



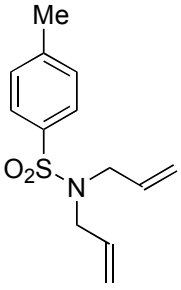
Isopropyl 2,4-dimethyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (3i): White solid. Mp. 56-57 °C; ^{1}H NMR ($CDCl_3$) δ = 8.36 (br d, 2H, *J* = 8.7 Hz), 8.13 (br d, 2H, *J* = 8.7 Hz), 5.01-4.96 (m, 1H), 4.80 (s, 1H), 4.77 (s, 1H), 3.80-3.76 (m, 1H), 2.48 (dd, 1H, *J* = 13.6, 7.9 Hz), 2,12 (dd, 1H, *J* = 13.6, 7.0 Hz), 1.78 (s, 3H), 1.27-1.22 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 179.2, 149.8, 147.9, 142.3, 127.8, 124.0, 112.8, 72.6, 52.9, 41.8, 37.8, 22.2, 21.0, 17.7; IR (KBr) 3109, 2982, 1948, 1811, 1567, 1456, 1308, 1156; HRMS (DART) Exact mass calcd for $C_{16}H_{23}N_2O_5S$ $[M+H]^+$, 355.1328. Found 355.1299.



Isopropyl 2-methyl-*N*-(4-toluenesulfonyl)pent-4-enimidate: Obtained as a mixture with N,N-diallyl-4-toluenesulfonylamine (X = Me); ^{1}H NMR ($CDCl_3$) δ = 7.63 (d, 2H, *J* = 8.5 Hz), 7.21 (d, 2H, *J* = 8.5 Hz), 5.68-5.60 (m, 1H), 4.99-4.92 (m, 3H), 3.66-3.59 (m, 1H), 2.37-3.30 (m, 3H), 2.13-2.10 (m, 1H), 1.18-1.12 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 177.7, 129.2, 127.1, 117.0, 71.6, 38.1, 38.0, 21.1, 21.0, 17.3. Indistinguishable peaks are below. δ = 143.1, 142.8, 139.7, 134.9; IR (neat) 3421, 2981, 2933, 1591, 1457, 1382, 1346, 1304, 1156, 1091; HRMS (DART) Exact mass calcd for $C_{13}H_{18}NO_2S$ $[M+H]^+$, 252.1058. Found 252.1056.



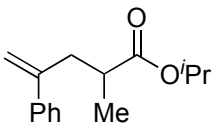
***N*,*N*-diallyl-(4-nitrobenzene)sulfonylamine:** White solid. Mp. 61.2-61.9 °C; ^{1}H NMR ($CDCl_3$) δ = 8.28 (d, 2H, *J* = 8.5 Hz), 7.94 (d, 2H, *J* = 8.5 Hz), 5.57-5.49 (m, 2H), 5.12-5.08 (m, 4H), 3.80 (d, 4H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 149.9, 146.4, 131.7, 128.3, 124.3, 119.6, 49.3; IR (KBr) 3109, 3086, 3072, 3039, 3014, 2984, 2863, 1955, 1862, 1820, 1643, 1605, 1526, 1347, 1160, 1089, 1055; HRMS (DART) Exact mass calcd for $C_{12}H_{15}N_2O_4S$ $[M+H]^+$,283.0753. Found 283.0753.



***N*,*N*-Diallyl-4-toluenesulfonylamine:** Obtained as a mixture with isopropyl 2-methyl-N-(4-toluenesulfonyl)pent-4-enimidate; ^{1}H NMR ($CDCl_3$) δ = 7.74 (d, 2H, *J* = 7.9 Hz), 7.22 (d, 2H, *J* = 7.9 Hz), 5.58-5.50 (m, 2H), 5.08-5.05 (m, 4H), 3.73 (d, 4H, *J* = 6.2 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 132.6, 129.6, 126.5, 118.8, 49.3, 21.4. Indistinguishable peaks are below. δ = 143.1, 142.8, 139.7, 134.9; IR (neat) 3421, 2981, 2933, 1591, 1457, 1382, 1346, 1304, 1156, 1091; HRMS (DART) Exact mass calcd for $C_{16}H_{24}NO_2S$ $[M+H]^+$, 310.1478. Found 310.1474.

<One-pot allylation-hydrolysis>

In an Ar box, sulfonylimidate **2a** (90 mg, 0.3 mmol, 1 equiv), As_2O_3 (3.7 mg, 0.018 mmol, 6 mol%), $Pd(PPh_3)_4$ (13.7 mg, 0.012 mmol, 4 mol%) and MS 3A (50 mg) were combined in a capped vial, then the vial was taken out of the Ar box. Dioxane (0.5 mL), and allylic alcohol **1f** (80 mg, 0.60 mmol, 2.0 equiv) were added, and the mixture was stirred at 90 °C for 6 h. After the reaction, dioxane (14.5 ml) and pH 10 buffer ($NaOH/Na_2CO_3$, 15 ml) were added and then the reaction mixture was stirred at 40 °C for 44 h. The mixture was extracted with dichloromethane and the organic extract was dried over sodium sulfate, and then concentrated in vacuo. After purification by preparative TLC (Hexane/EtOAc = 9/1), the desired ester **11** was obtained (82%).



Isopropyl 2-methyl-4-phenylpent-4-enate (11): Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 7.32-7.18 (m, 5H), 5.28 (d, 1H, *J* = 1.1 Hz), 5.09 (d, 1H, *J* = 1.1 Hz), 4.97 (septet, 1H, *J* = 6.2 Hz), 2.92-2.87 (m, 1H), 2.46-2.40 (m, 2H), 1.20 (d, 3H, *J* = 6.2 Hz), 1.19 (d, 3H, *J* = 6.2 Hz), 1.11 (d, 3H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 175.7, 146.1, 140.6, 128.3, 127.5, 126.3, 114.4, 67.4, 39.4, 38.1, 21.8, 21.7, 16.7; IR (neat) 2979, 1730, 1629, 1495, 1455, 1376, 1273, 1176, 1109, 1037; HRMS (DART) Exact mass calcd for $C_{15}H_{21}O_2$ $[M+H]^+$, 233.1542. Found 233.1550.