Supplementary Material (ESI) for Chemical Communications

Catalytic Direct-Type Substitution Reaction of α-alkyl Enolates: A Pd/Brønsted Base-Catalyzed Approach to the Decarboxylative Allylation of Sulfonylimidates

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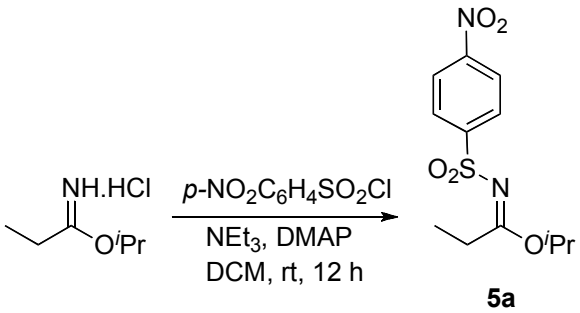
Electronic Supplementary Information

Experimental details and physical data of products.

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECX-500 or a JNM-ECX-600 spectrometer in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS, δ = 0 ppm) or $CDCl_3$ (δ = 7.26 ppm) served as internal standard for ^{1}H NMR, and $CDCl_3$ (δ = 77.0 ppm) was used as internal standard for ^{13}C NMR. IR spectra were measured on a JASCO FT/IR-610 spectrometer and only the strongest/structurally important peaks are listed (ν_{max}, cm^{-1}). Column chromatography was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography was carried out using Wakogel B-5F. All air and moisture sensitive reactions were carried out under argon atmosphere in dried glassware. All solvents were dried and distilled by standard procedures. Imidate hydrochloride salts were prepared as previously reported.[1] All allyl carbonates were prepared from the corresponding alcohols according to standard method for carbonate formation.[2] (*E*)-3-(pyridin-3-yl)prop-2-en-1-ol was prepared from Horner-Wadsworth-Emmons reaction of nicotinaldehyde and subsequent DIBALH reduction.[2] (*E*)-isopropyl 4-hydroxybut-2-enoate was prepared by borane reduction of (*E*)-4-isopropoxy-4-

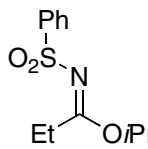
oxobut-2-enoic acid.[3] (*E*)-4-(*tert*-butyldimethylsilyloxy)but-2-en-1-ol was prepared by TBS protection of (*E*)-isopropyl 4-hydroxybut-2-enoate and subsequent DIBALH reduction.

(I) Representative procedure for the syntheses of sulfonylimidates.

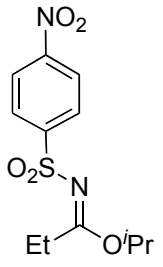


5a

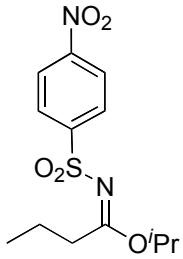
To a solution of isopropyl propionimidate hydrochloride salt (3.00 g, 19.8 mmol) in DCM (50 mL) was added Et_3N (6.0 mL, 43.6 mmol) dropwise at 0 ^oC. The resulting white suspension was stirred vigorously, and 4-nitrobenzenesulfonyl chloride (4.39 g, 19.8 mmol) and DMAP (243 mg, 1.98 mmol) were added. After stirring at room temperature for 12 h, the reaction mixture was quenched with $NaHCO_3$ and extracted with DCM. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (4:1 hexane/acetone) and recrystallisation (hexane/DCM) afforded the desired imidate **5a** as white crystals (4.26 g, 14.2 mmol, 72%).



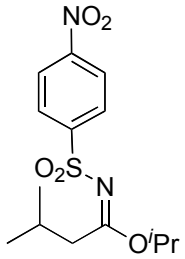
Isopropyl *N*-(benzenesulfonyl)propionimidate (2): ^1H NMR ($CDCl_3$) δ = 8.06-8.09 (m, 2H), 7.60-7.64 (m, 3H), 4.70 (septet, 1H, J = 6.3 Hz), 2.88 (qd, 2H, J = 7.3, 1.7 Hz), 1.05 (td, 3H, J = 7.3, 1.2 Hz), 0.83 (d, 6H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 176.0, 143.6, 132.0, 128.8, 126.9, 71.6, 28.2, 20.9, 10.4; IR (neat) 3055, 2988, 1506, 1448, 1308, 1265, 1157, 1093, 896, 740, 705, 634, 459, 445, 413 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{12}H_{18}NO_3S$ $[M+H]^+$, 256.1007. Found 256.1010.



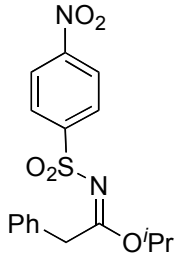
Isopropyl *N*-(4-nitrobenzenesulfonyl)propionimidate (5a): Mp. 70-71 ^{o}C; ^{1}H NMR ($CDCl_3$) δ = 8.35 (br d, 2H, J = 9.2 Hz), 8.12 (br d, 2H, J = 9.2 Hz), 5.00 (septet, 1H, J = 6.3 Hz), 2.98 (q, 2H, J = 8.0 Hz), 1.27 (t, 3H, J = 8.0 Hz), 1.26 (d, 6H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.5, 149.8, 147.6, 127.8, 124.1, 72.9, 28.6, 21.1, 10.2; IR (neat) 3021, 2987, 1579, 1532, 1350, 1308, 1216, 1158, 1094 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{12}H_{16}N_2O_5S$ $[M+H]^+$, 301.0858. Found 301.0871.



Isopropyl *N*-(4-nitrobenzenesulfonyl)butyrimidate (5b): Mp. 49-50 ^{o}C; ^{1}H NMR ($CDCl_3$) δ = 8.35 (br d, 2H, J = 8.6 Hz), 8.12 (br 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 (neat) 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.

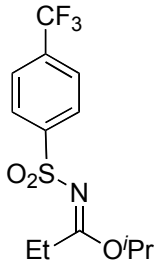


Isopropyl *N*-(4-nitrobenzenesulfonyl)-3-methylbutanimidate (5c): Mp. 79-80 ^{o}C; ^{1}H NMR ($CDCl_3$) δ =8.36 (br d, 2H, J = 9.2 Hz), 8.12 (br d, 2H, J = 9.2 Hz), 5.00 (septet, 1H, J = 6.3 Hz), 2.79 (d, 2H, J = 7.4 Hz), 2.26 (app septet, 1H, J = 7.0 Hz), 1.25 (d, 6H, J = 6.3 Hz), 1.02 (d, 3H, J = 7.0 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 (neat) 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.

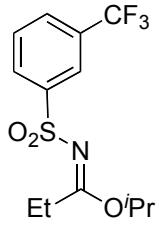


Isopropyl *N*-(4-nitrobenzenesulfonyl)-2-phenylacetimidate (5d): Mp. 92-93 ^{o}C; ^{1}H NMR ($CDCl_3$) δ = 8.32 (br d, 2H, J = 9.2 Hz), 8.07 (br d, 2H, J = 9.2 Hz), 7.25-7.40 (m, 5H), 5.01 (septet, 1H, J = 6.3

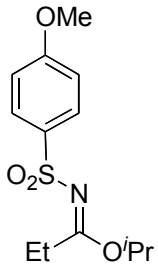
Hz), 4.22 (s, 2H), 1.20 (d, 6H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 173.8, 149.8, 147.3, 133.1, 129.3, 128.6, 127.8, 127.4, 124.0, 73.4, 40.4, 21.0; IR (neat) 3020, 1580, 1532, 1351, 1308, 1216, 1158, 1093 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{17}H_{19}N_2O_5S$ $[M+H]^+$, 363.1015. Found 363.1015.



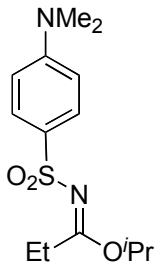
Isopropyl *N*-(4-trifluoromethylbenzenesulfonyl)propionimidate (6): ^{1}H NMR ($CDCl_3$) δ = 8.06 (br d, 2H, J = 8.6 Hz), 7.76 (br d, 2H, J = 8.6 Hz), 5.00 (septet, 1H, J = 6.3 Hz), 2.91 (q, 2H, J = 7.5 Hz), 1.21-1.24 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 177.1, 145.5, 126.9, 125.8, 125.8, 72.5, 28.3, 21.0, 10.1; IR (neat) 2987, 2946, 1593, 1323, 1163, 1097, 1064 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{13}H_{17}F_3NO_3S$ $[M+H]^+$, 324.0881. Found 324.0871.



Isopropyl *N*-(3-trifluoromethylbenzenesulfonyl)propionimidate (7): ^{1}H NMR ($CDCl_3$) δ = 8.21 (s, 1H), 8.13 (br d, 1H, J = 8.0 Hz), 7.81 (br d, 1H, J = 8.0 Hz), 7.65 (dd, 1H, J = 8.0, 8.0 Hz), 5.00 (septet, 1H, J = 6.3 Hz), 2.92 (q, 2H, J = 7.5 Hz), 1.22-1.27 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 177.1, 143.3, 129.7, 129.5, 128.9, 128.8, 123.6, 72.6, 28.3, 21.1, 10.1; IR (neat) 2986, 2946, 1595, 1328, 1159, 1105, 1072 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{13}H_{17}F_3NO_3S$ $[M+H]^+$, 324.0881. Found 324.0873.

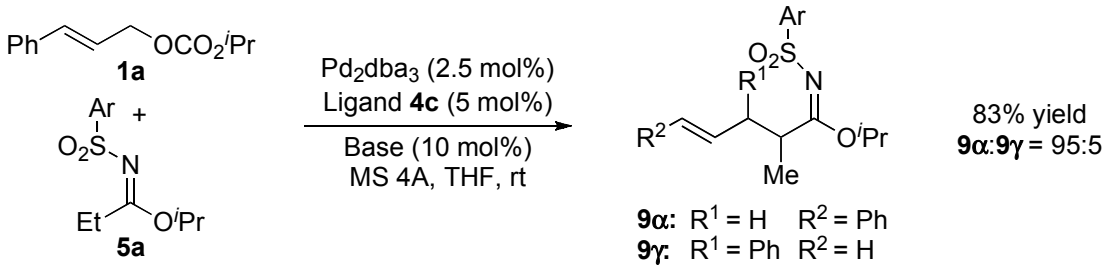


Isopropyl *N*-(4-methoxybenzenesulfonyl)propionimidate (8): Mp. 25-26 °C; ^{1}H NMR ($CDCl_3$) δ = 7.86 (br d, 2H, J = 9.2 Hz), 6.96 (br d, 2H, J = 9.2 Hz), 5.03 (septet, 1H, J = 6.3 Hz), 3.86 (s, 3H), 2.88 (q, 2H, J = 8.0 Hz), 1.23 (d, 6H, J = 6.3 Hz), 1.21 (t, 3H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 176.1, 162.5, 134.2, 128.5, 113.8, 71.8, 55.5, 27.8, 21.2, 10.2; IR (neat) 2983, 2944, 1597, 1313, 1259, 1154, 1095 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{13}H_{20}NO_4S$ $[M+H]^+$, 286.1113. Found 286.1106.

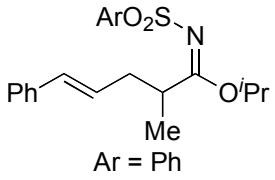


Isopropyl *N*-(4-dimethylaminobenzenesulfonyl)propionimidate (11): Mp. 98-99 °C; ^{1}H NMR ($CDCl_3$) δ = 7.74 (dq, 2H, *J* = 9.2, 2.3 Hz), 6.66 (dq, 2H, *J* = 9.2, 2.3 Hz), 5.04 (septet, 1H, *J* = 6.3 Hz), 3.03 (d, 6H, *J* = 2.3 Hz), 2.85 (qd, 2H, *J* = 7.4, 2.3 Hz), 1.22 (overlapping d, 6H, *J* = 6.3 Hz), 1.18 (td, 3H, *J* = 7.4, 2.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 175.4, 152.5, 128.1, 128.0, 110.6, 71.4, 40.1, 27.4, 21.2, 10.2; IR (neat) 2982, 2923, 1589, 1368, 1308, 1146, 1088 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{14}H_{23}N_2O_3S$ $[M+H]^+$, 299.1429. Found 299.1444.

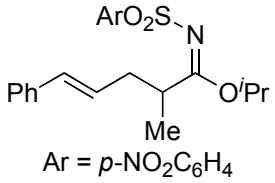
(II) Representative procedure for allylation reaction.



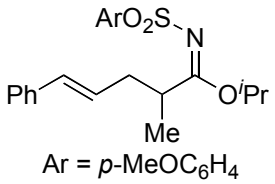
To a prestirred, degassed solution of Pd_2dba_3 (6.9 mg, 7.5 μmol), ligand **4c** (10.3 mg, 15 μmol) and MS 4A (50 mg) in dry THF (1.5 ml) was successively added a solution of cinnamyl carbonate **1a** (99.1 mg, 0.45 mmol) in THF (0.4 ml), imidate **5a** (90.3 mg, 0.3 mmol) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 4.6 mg, 0.03 mmol) in THF (100 μl) and the mixture was stirred at room temperature. Upon complete consumption of the imidate starting material, the resulting orange solution was diluted with acetone (1 ml), filtered and concentrated *in vacuo*. The ratio of regioisomers was determined by ^{1}H NMR of the crude products (α:γ 95:5). Purification by preparative TLC eluting with hexane/acetone (4:1) afforded the allylation adduct (103.8 mg, 0.25 mmol, 83%).



(*E*)-Isopropyl *N*-(benzenesulfonyl)-2-methyl-5-phenyl pent-4-enimidate (3α): ^{1}H NMR ($CDCl_3$) δ = 7.90 (br d, 2H, *J* = 7.5 Hz), 7.51 (tt, 1H, *J* = 7.5, 1.2 Hz), 7.43 (br t, 2H, *J* = 7.5 Hz), 7.26-7.32 (m, 4H), 7.19-7.23 (m, 1H), 6.40 (d, 1H, *J* = 16.1 Hz), 6.13 (dt, 1H, *J* = 16.1, 7.4 Hz), 5.03 (septet, 1H, *J* = 6.3 Hz), 3.80-3.84 (m, 1H), 2.53-2.57 (m, 1H), 2.37-2.41 (m, 1H), 1.26 (d, 3H, *J* = 6.9 Hz), 1.24 (d, 3H, *J* = 6.3 Hz), 1.19 (d, 3H, *J* = 6.3 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) 2981, 2933, 2357, 1593, 1447, 1304, 1156, 1090 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{21}H_{26}NO_3S$ $[M+H]^+$, 372.1633. Found 372.1634.



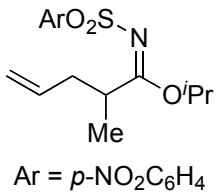
(*E*)- Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)-5-phenylpent-4-enimidate (9α): ^{1}H NMR ($CDCl_3$) δ = 8.13 (dt, 2H, *J* = 9.0, 2.1 Hz), 7.95 (dt, 2H, *J* = 9.0, 2.1 Hz), 6.31 (d, 1H, *J* = 15.9 Hz), 6.09-6.03 (m, 1H), 4.90 (septet, 1H, *J* = 6.5 Hz), 3.72 (td, 1H, *J* = 7.5, 6.0 Hz), 2.46-2.52 (m, 1H), 2.32-2.37 (m, 1H), 1.23 (d, 3H, *J* = 6.5 Hz), 1.18 (d, 3H, *J* = 6.5 Hz), 1.13 (d, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 178.8, 149.6, 147.6, 137.0, 132.4, 128.5, 127.7, 127.3, 126.3, 126.0, 123.9, 72.6, 39.4, 37.6, 39.4, 37.6, 21.2, 21.0, 17.6; IR (neat) 2983, 2933, 2363, 1578, 1530, 1457, 1349, 1305, 1159, 1090 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{21}H_{25}N_2O_5S$ $[M+H]^+$, 417.1484. Found 417.1489.



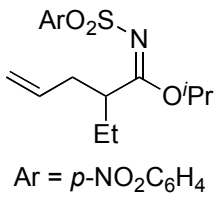
(*E*)-Isopropyl *N*-(4-methoxybenzenesulfonyl)-2-methyl-5-phenylpent-4-enimidate (8pα): ^{1}H NMR[†] ($CDCl_3$) δ = 7.74 (br d, 2H, *J* = 9.2 Hz), 7.11-7.25 (m, 5H), 6.80 (br d, 2H, *J* = 9.2 Hz), 6.40* (d, 1H, *J* = 16.0 Hz), 6.31 (d, 1H, *J* = 16.1 Hz), 6.10* (dt, 1H, *J* = 16.0, 7.5 Hz), 6.03 (dt, 1H, *J* = 16.1, 7.5 Hz), 4.95 (septet, 1H,

[†] Reported as an inseparable mixture of α (major) and γ (minor) regioisomers. Asterisk indicated data corresponded to the γ regioisomer.

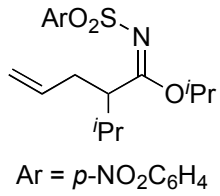
J = 6.3 Hz), 3.72-3.80 (m, 4H), 2.86* (dd, 1H, *J* = 14.3, 7.5 Hz), 2.44-2.50 (m, 1H), 2.26-2.31 (m, 1H), 1.18 (d, 3H, *J* = 6.3 Hz), 1.16 (d, 3H, *J* = 6.3 Hz), 1.11 (d, 3H, *J* = 6.3 Hz), 1.09* (d, 3H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.4, 162.4, 137.3, 134.3, 132.2, 128.5, 128.4, 127.1, 126.8, 126.1, 113.8, 71.6, 55.5, 38.4, 37.5, 21.3, 21.1, 17.5; IR (neat) 2980, 2938, 2361, 1595, 1498, 1458, 1296, 1258, 1152, 1091 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{22}H_{28}NO_4S$ $[M+H]^+$, 402.1739. Found 402.1728.



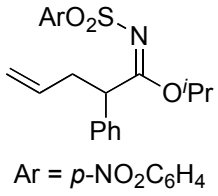
Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (9ab): MP. 69-70 °C; ^{1}H NMR ($CDCl_3$) δ = 8.35 (br d, 2H, *J* = 9.2 Hz), 8.12 (br d, 2H, *J* = 9.2 Hz), 5.70-5.81 (m, 1H), 5.08 (d, 1H, *J* = 20.6 Hz), 5.05 (br d, 1H, *J* = 14.9 Hz), 4.97 (septet, 1H, *J* = 6.3 Hz), 3.66 (qt, 1H, *J* = 7.5, 6.9 Hz), 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 (neat) 2982, 2933, 1581, 1532, 1458, 1350, 1298, 1157, 1089 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{15}H_{21}N_2O_5S$ $[M+H]^+$, 341.1171. Found 341.1181.



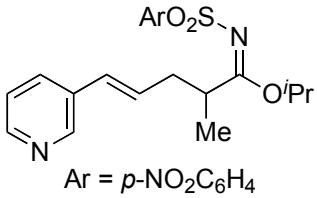
Isopropyl 2-ethyl-*N*-(4-nitrobenzenesulfonyl)pent-4-enimidate (9bb): ^{1}H NMR ($CDCl_3$) δ = 8.33 (br d, 2H, *J* = 9.2 Hz), 8.10 (br d, 2H, *J* = 9.2 Hz), 5.77 (ddt, 1H, *J* = 17.2, 9.7, 6.9 Hz), 4.94-5.07 (m, 3H), 3.56 (app quint, 1H, *J* = 7.5 Hz), 2.28-2.40 (m, 2H), 1.57-1.73 (m, 2H), 1.23 (d, 3H, *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 (neat) 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 (9cb): ^{1}H NMR ($CDCl_3$) δ = 8.27 (br d, 2H, *J* = 9.2 Hz), 8.03 (br 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.

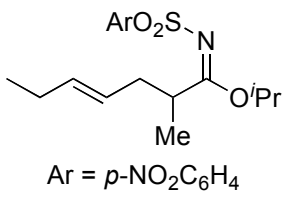


Isopropyl *N*-(4-nitrobenzenesulfonyl)-2-phenylpent-4-enimidate (9db): ^{1}H NMR ($CDCl_3$) δ = 8.28 (br d, 2H, *J* = 9.2 Hz), 8.02 (br d, 2H, *J* = 9.2 Hz), 7.44 (br d, 2H, *J* = 7.5 Hz), 7.25-7.34 (m, 3H), 5.74-5.82 (m, 1H), 5.13 (br d, 1H, *J* = 17.2 Hz), 5.06 (br d, 1H, *J* = 10.9 Hz), 4.99 (septet, 1H, *J* = 6.3 Hz), 4.93 (dd, 1H, *J* = 9.2, 6.3 Hz), 2.81-2.88 (m, 1H), 2.58-2.64 (m, 1H), 1.29 (d, 3H, *J* = 6.3 Hz), 1.18 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ = 175.1, 149.7, 149.7, 147.6, 137.2, 134.3, 128.6, 128.4, 127.8, 123.9, 117.7, 73.3, 49.6, 38.0, 21.1, 21.0; IR (neat) 2983, 2938, 1577, 1531, 1350, 1306, 1159, 1093 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{20}H_{23}N_2O_5S$ $[M+H]^+$, 403.1328. Found 403.1317.

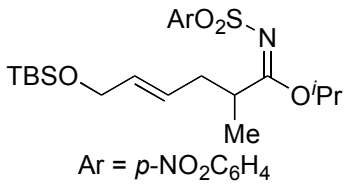


(*E*)-Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)-5-(pyridin-3-yl)pent-4-enimidate (9ac): ^{1}H NMR ($CDCl_3$) δ = 8.53 (br s, 1H), 8.46 (br d, 1H, *J* = 5.2 Hz), 8.30 (br d, 2H, *J* = 9.2 Hz), 8.08 (br d, 2H, *J* = 9.2 Hz), 7.67 (br d, 1H, *J* = 8.6 Hz), 7.23 (dd, 1H, *J* = 8.6, 5.2 Hz), 6.42 (d, 1H, *J* = 16.0 Hz), 6.27 (dt, 1H, *J* = 16.0, 8.6 Hz), 4.98 (septet, 1H, *J* = 6.3 Hz), 3.78-3.85 (m, 1H), 2.63 (app dt, 1H, *J* = 14.3, 8.6 Hz), 2.47 (app dt, 1H, *J* = 14.3, 8.6 Hz), 1.33 (d, 3H, *J* = 6.9 Hz), 1.26 (d, 3H, *J* = 6.3 Hz), 1.21 (d, 3H, *J* = 6.3 H); ^{13}C NMR ($CDCl_3$) δ = 178.5, 149.7, 148.5, 148.1, 147.6, 132.6, 132.5, 128.9, 128.9, 127.8, 124.0, 123.5, 72.7, 39.5,

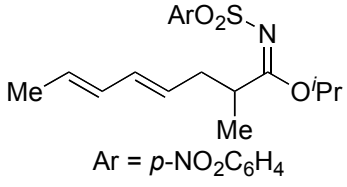
37.6, 21.2, 21.1, 17.5; IR (neat) 2983, 2918, 2362, 1716, 1578, 1530, 1351, 1305, 1158, 1091 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{20}H_{24}N_3O_5S$ $[M+H]^+$, 418.1437. Found 418.1451.



(*E*)-Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)hept-4-enimidate (9ad): ^1H NMR ($CDCl_3$) δ = 8.34 (br d, 2H, *J* = 9.2 Hz), 8.10 (br d, 2H, *J* = 9.2 Hz), 5.50 (br dt, 1H, *J* = 15.5, 6.3 Hz), 5.33 (br dt, 1H, *J* = 15.5, 8.0 Hz), 4.96 (septet, 1H, *J* = 6.3 Hz), 3.60 (qt, 1H, *J* = 7.5, 6.9 Hz), 2.36 (app dt, 1H, *J* = 13.7, 6.9 Hz), 2.16 (app dt, 1H, *J* = 13.7, 6.9 Hz), 1.97 (app quint, 2H, *J* = 7.5 Hz), 1.20-1.25 (m, 9H), 0.93 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 179.3, 149.7, 147.9, 135.2, 127.7, 124.9, 124.0, 72.4, 39.6, 37.0, 25.5, 21.1, 21.0, 17.3, 13.7; IR (neat) 2981, 2935, 1582, 1531, 1459, 1350, 1307, 1160, 1091 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{17}H_{25}N_2O_5S$ $[M+H]^+$, 369.1484. Found 369.1480.

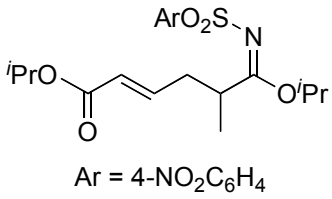


(*E*)-Isopropyl 6-(*tert*-butyldimethylsilyloxy)-2-methyl-*N*-(4-nitrobenzenesulfonyl)hex-4-enimidate (9ae): ^1H NMR ($CDCl_3$) δ = 8.33 (br d, 2H, *J* = 9.2 Hz), 8.10 (br d, 2H, *J* = 9.2 Hz), 4.94-5.56 (m, 2H), 4.95 (septet, 1H, *J* = 6.3 Hz), 4.09 (br s, 2H), 3.63 (qt, 1H, *J* = 7.5, 6.9 Hz), 2.36-2.47 (m, 1H), 2.18-2.25 (m, 1H), 1.18-1.26 (m, 9H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 179.0, 149.7, 147.8, 132.4, 127.8, 126.4, 124.0, 72.6, 63.5, 39.4, 36.5, 25.9, 21.1, 21.0, 18.4, 17.4; IR (neat) 2930, 2857, 1583, 1531, 1463, 1350, 1308, 1255, 1160, 1092 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{22}H_{37}N_2O_6SSi$ $[M+H]^+$, 485.2142. Found 485.2153.

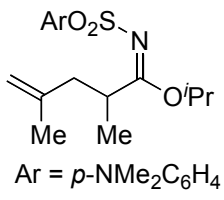


(4*E*,6*E*)-Isopropyl 2-methyl-*N*-(4-nitrobenzenesulfonyl)octa-4,6-dienimidate (9af):

^{1}H NMR[†] ($CDCl_3$) δ = 8.32 (br d, 2H, *J* = 9.2 Hz), 8.10 (br d, 2H, *J* = 9.2 Hz), 5.89-6.02 (m, 2H), 5.77* (ddd, 1H, *J* = 17.2, 10.3, 8.6 Hz), 5.57 (dq, 1H, *J* = 14.3, 6.9 Hz), 5.41 (dt, 1H, *J* = 14.3, 6.9 Hz), 5.28* (ddq, 1H, *J* = 15.5, 8.6, 1.7 Hz), 4.98 (septet, 1H, *J* = 6.3 Hz), 3.59-3.68 (m, 1H), 3.48-3.55* (m, 1H), 2.88* (app quint, 1H, *J* = 9.1 Hz), 2.38-2.46 (m, 1H), 2.19-2.27 (m, 1H), 1.71 (d, 3H, *J* = 6.9 Hz), 1.18-1.26 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 179.1, 178.6, 149.7, 147.8, 138.7, 133.1, 131.0, 130.0, 128.3, 128.0, 127.8, 127.8, 126.8, 124.0, 115.5, 72.6, 51.2, 43.5, 39.5, 37.0, 21.2, 21.0, 18.0, 17.4, 15.9; IR (neat) 2983, 2936, 1578, 1531, 1457, 1160, 1091 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{18}H_{25}N_2O_5S$ $[M+H]^+$, 381.1484. Found 381.1474.



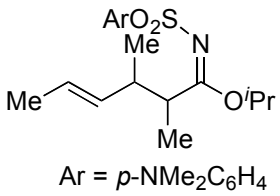
(*E*)-Isopropyl 5-isopropoxycarbonyl-2-methyl-*N*-(4-nitrobenzenesulfonyl)hex-2-enimidate (9ag): ^{1}H NMR ($CDCl_3$) δ = 8.34 (br d, 2H, *J* = 9.2 Hz), 8.11 (br d, 2H, *J* = 9.2 Hz), 6.84 (dt, 1H, *J* = 16.1, 7.5 Hz), 5.84 (dt, 1H, *J* = 16.1, 1.8 Hz), 5.04 (septet, 1H, *J* = 6.3 Hz), 5.03 (septet, 1H, *J* = 6.3 Hz), 3.77 (qt, 1H, *J* = 7.5, 6.9 Hz), 2.58 (dddd, 1H, *J* = 14.9, 7.5, 6.9, 1.8 Hz), 2.40 (dddd, 1H, *J* = 14.9, 7.5, 6.9, 1.8 Hz), 1.20-1.30 (m, 15H); ^{13}C NMR ($CDCl_3$) δ = 177.7, 165.5, 149.8, 147.5, 143.8, 127.8, 124.4, 124.1, 73.0, 67.6, 38.4, 36.0, 21.8, 21.0, 21.0, 17.4; IR (neat) 2982, 2938, 1714, 1656, 1583, 1531, 1465, 1351, 1307, 1160, 1107 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{19}H_{27}N_2O_7S$ $[M+H]^+$, 427.1539. Found 427.1550.



Isopropyl 2,4-dimethyl-*N*-(4-dimethylaminobenzenesulfonyl) pent-4-enimidate (9ai): 52-53 °C; ^{1}H NMR ($CDCl_3$) δ = 7.72 (br d, 2H, *J* = 9.2 Hz), 6.64 (br d, 2H, *J* = 9.2 Hz), 5.01 (septet, 1H, *J* = 6.3 Hz), 4.72 (d, 2H, *J* = 13.2 Hz), 3.81 (qt, 1H, *J* = 7.5, 6.9

[†] Reported as an inseparable mixture of α (major) and γ (minor) regioisomers. Asterisk indicated data corresponded to the γ regioisomer.

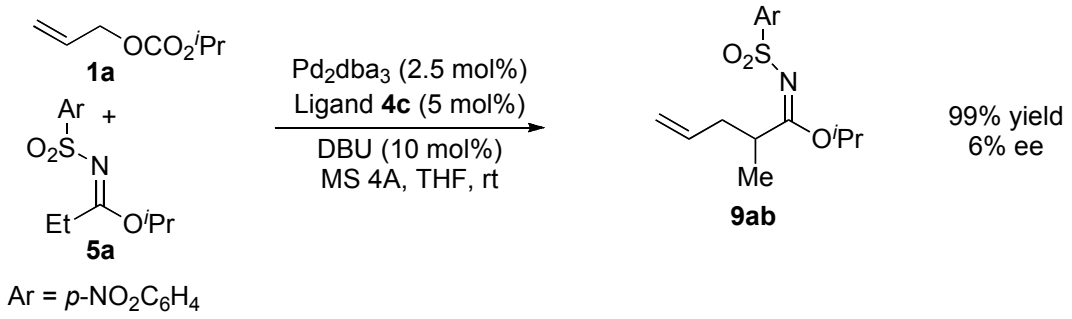
Hz), 3.00 (s, 3H), 2.39 (dd, 1H, J = 14.3, 8.0 Hz), 2.04 (dd, 1H, J = 14.3, 8.0 Hz), 1.73 (s, 3H), 1.19 (overlapping d, 6H, J = 6.3 Hz), 1.13 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ =176.7, 152.4, 142.5, 128.3, 128.0, 112.4, 110.5, 71.0, 41.7, 40.0, 36.1, 22.1, 21.0, 17.4; IR (neat) 2981, 2935, 1714, 1595, 1518, 1448, 1370, 1300, 1221, 1149, 1093 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{18}H_{29}N_2O_3S$ $[M+H]^+$, 353.1899. Found 353.1903.



(*E*)-Isopropyl 2,3-dimethyl-*N*-(4-dimethylaminobenzenesulfonyl) hex-4-enimidate (9aj): ^{1}H NMR[†] ($CDCl_3$) δ = 7.65-7.68 (m, 2H), 6.59 (br d, 2H, J = 7.5 Hz), 5.37* (dq, 1H, J = 12.6, 5.8 Hz), 5.26 (dq, 1H, J = 12.6, 5.8 Hz), 5.13* (ddq, 1H, J = 12.6, 7.5, 1.2 Hz), 5.06 (ddq, 1H, J = 12.6, 7.5, 1.2 Hz), 4.99* (septet, 1H, J = 5.2 Hz), 4.96 (septet, 1H, J = 5.2 Hz), 3.34-3.38 (m, 1H), 3.26-3.31* (m, 1H), 2.95 (s, 6H), 2.19-2.23 (m, 1H), 1.59* (dd, 3H, J = 5.2, 1.2 Hz), 1.45 (dd, 3H, J = 5.8, 1.2 Hz), 1.15* (d, 3H, J = 6.3 Hz), 1.14* (d, 3H, J = 6.3 Hz), 1.13 (d, 3H, J = 5.2 Hz), 1.09 (d, 3H, J = 5.2 Hz), 1.05 (d, 3H, J = 5.7 Hz), 1.00* (d, 3H, J = 5.6 Hz), 0.90 (d, 3H, J = 5.2 Hz), 0.84* (d, 3H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 177.3, 177.1, 152.4, 134.4, 133.9, 128.5, 128.4, 128.2, 125.8, 124.8, 110.6, 70.8, 43.4, 43.2, 40.6, 40.5, 40.0, 21.2, 21.1, 21.0, 19.3, 18.0, 17.8, 17.6, 16.3, 15.5; IR (neat) 2980, 2935, 1596, 1517, 1451, 1371, 1294, 1229, 1147, 1092 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{19}H_{31}N_2O_3S$ $[M+H]^+$, 367.2055. Found 367.2054.

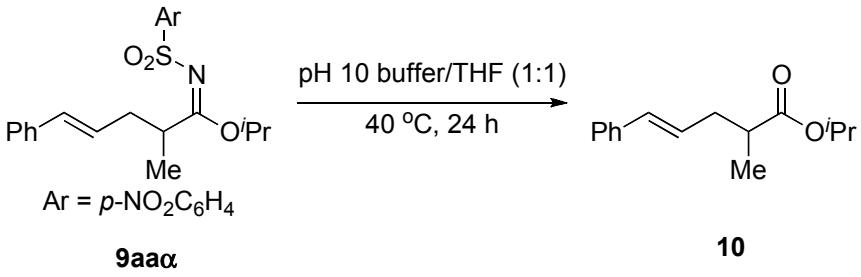
[†] Reported as an inseparable mixture of diastereomers. Asterisk indicated data corresponded to the minor diastereomer.

(III) Enantioselectivity of the allylation reaction of sulfonylimidate 5a with allyl carbonate 1a

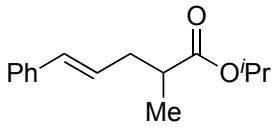


(IV) Procedure for the hydrolysis of sulfonylimidate 9aaα to ester 10.

In addition to the procedure previously reported for the conversion of sulfonylimidates to the corresponding esters,[1] it was found that the desired transformation could also be achieved in excellent yield upon mild hydrolysis as shown below:



To sulfonylimidate **9aaα** (20 mg, 0.048 mmol) was added THF (10 ml), pH 10 buffer (10 ml), and the solution was stirred at 40 ^{o}C for 24 h until no starting material remained. After evaporation of THF, the crude mixture was extracted with ether, and the combined organic layer washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by preparative TLC eluting with hexane/acetone (4:1) afforded ester **10** as a colourless oil (11.0 mg, 0.047 mmol, 99%).



(*E*)-propyl 2-methyl-5-phenylpent-4-enoate (10): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.18-7.26 (m, 4H), 7.12 (br t, 1H, *J* = 7.4 Hz), 6.34 (d, 1H, *J* = 16.1 Hz), 6.08 (dt, 1H, *J* = 16.1, 7.5 Hz), 4.93 (septet, 1H, *J* = 6.9 Hz), 2.44-2.51 (m, 2H), 2.23-2.30 (m, 1H), 1.10-1.17 (m, 9H); ^{13}C NMR ($CDCl_3$) δ = 175.6, 137.4, 132.0, 128.5, 127.3, 127.1, 126.0, 67.4, 39.8, 37.1, 21.8, 16.7; IR (neat) 2979, 2933, 1728, 1457, 1375, 1173, 1108 cm^{-1}; HRMS (APCI) Exact mass calcd for $C_{15}H_{21}O_2$ $[M+H]^+$, 233.1542. Found 233.1544.

References

1. Matsubara, R.; Berthiol, F.; Kobayashi, S. *J. Am. Chem. Soc.* **2008**, *130*, 1804.
2. Welter, C.; Moreno, R. M.; Streiff, S.; Helmchen, G. *Org. Biomol. Chem.* **2005**, *3*, 3266.
3. Kende, A. S.; Fludzinski, P. *Org. Syn.* **1986**, *64*, 104.