Si-Free Enolate Claisen Rearrangements of Enamido Substrates

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Supporting Information

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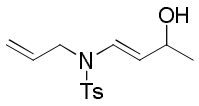
General Experimental Information

Reactions were conducted in flame dried vessels using anhydrous solvents and under an inert atmosphere of nitrogen. In all cases, solvents were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. All reagents were purchased from commercial suppliers: Acros Organics, Alfa Aesar, Sigma Aldrich or Novabiochem and used without purification. Triethylamine and chlorotrimethylsilane (over 10 % quinoline) were freshly distilled prior to use. All distilled materials were stored under nitrogen at 4 $^{\circ}$C or less. All reactions were monitored by thin layer chromatography (TLC) using pre-coated MN Alugram Sil G/UV_{254} silica gel 60 aluminium backed plates. Plates were developed using UV light followed by a chemical dip, usually $KMnO_4$ and gentle heating. Flash chromatography was performed on chromatography grade, silica 60Å particle size 35-70 micron from Fisher Scientific using the solvent system as stated. Compounds purified through preparative HPLC were subjected to the 'Waters Autopurification LC System'.

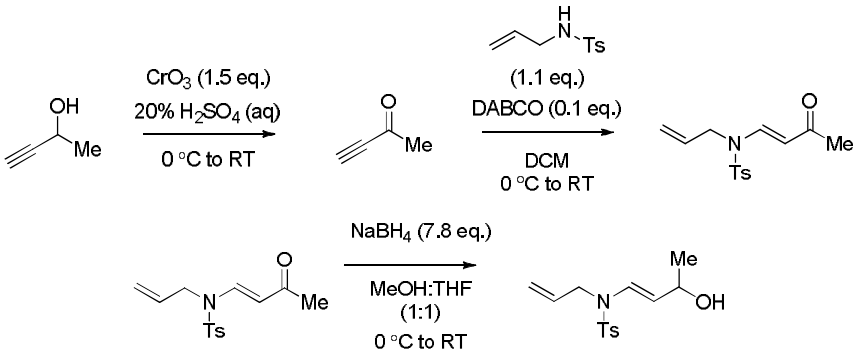
^{1}H and ^{13}C were performed on a Brüker Avance 250 (250 MHz), Brüker Avance 300 (300 MHz), Brüker Avance 400 (400 MHz) and Brüker Avance 500 (500 MHz) as stated. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) (δ = 0.00). Coupling constants are reported in Hertz (Hz) and signal multiplicity is denoted as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), quartet of triplets (qt), triplet of doublets (td), multiplet (m), quintet (quin) and broad (br). Mass spectroscopy was performed on a Brüker µTOF using electrospray ionisation (ESI) in either positive or negative ionisation as stated. Infra-red spectroscopy was carried out using a Perkin Elmer Spectrum RX FT-IR system with KBr plates, using a thin film.

Experimental Procedures

(E)-*N*-Allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide (5e)



5e



To a solution of Cr(VI)O_3 (10.3 g, 103 mmol, 1.5 eq.) in 20% H_2SO_4 (180 ml) at 0 ^oC under a nitrogen atmosphere was added a solution of 3-butyn-2-ol (5.00 g, 71.3 mmol, 1.0 eq.) in 20% H_2SO_4 (180 ml) by dropwise addition. The reaction mixture was stirred at 0 ^oC for 12 hours and a colour change from orange to green was noted, saturated aqueous sodium bicarbonate was added and the organics were extracted with DCM (3 × 450 mL) and dried over $MgSO_4$. The crude butynone was chilled to 0 ^oC then *N*-allyl-4-methylbenzenesulfonamide 15.0 g, 78.4 mmol, 1.1 eq.) and DABCO (0.80 g, 7.13 mmol, 0.1 eq.) were added. The reaction mixture was allowed to stir for 12 hours whilst slowly warming to room temperature and a colour change from a clear to a deep maroon solution was noted. The reaction mixture was washed with 5% NaOH (3 × 500 ml), brine and then the organics were dried over $MgSO_4$ and concentrated *in vacuo* to give a red oil which was subjected to flash column chromatography (25% EtOAc/Petrol 40-60^o) to give the desired *(E)*-*N*-allyl-4-methyl-N-(3-oxobut-1-enyl)benzenesulfonamide **327** (10.5 g, 53%) as well as the –(*Z*) (0.79 g, 4%) as a brown oil in both cases.

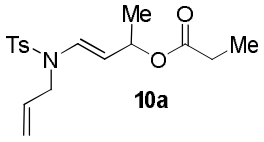
(*E*) product- FTIR (film/cm^{-1}) υ_{max}: 3082(s), 2980(s), 2879(s), 1682(s), 1586(s); ^{1}H NMR (250MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.44 (s, 3H), 4.07 (dt, 2H, *J* = 5.24, 1.59 Hz), 5.13 (dm, 1H, *J* = 9.2 Hz), 5.19

(m, 1H), 5.48 (d, 1H, *J* = 14.3 Hz), 5.56 (ddt, 1H, *J* = 17.2, 10.6, 5.3 Hz), 7.34 (m, 2H), 7.71 (m, 2H), 8.03 (d, 1H, *J* = 14.3 Hz); ^{13}C NMR (250MHz, $CDCl_3$) δ 21.7, 27.6, 48.3, 109.0, 118.9, 127.3, 129.9, 130.2, 135.3, 141.2, 145.1, 196.6; HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{18}NO_3S$ 280.1007, found 280.0990 $(M+H)^+$.

(*Z*) product- FTIR (film/cm^{-1}) υ_{max}: 3100(s), 2925(s), 1679(s), 1595(s); ^{1}H NMR (250MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.33 (s, 3H), 4.41 (dt, 2H, *J* = 5.7, 1.3 Hz,), 4.86 (dq, 1H, J = 29.0, 1.5 Hz), 4.91 (dq, 1H, *J* = 22.3, 1.4 Hz), 5.21 (ddq, 1H, *J* = 17.9, 10.3, 5.6 Hz), 5.35 (d, 1H, J = 10.3 Hz), 6.71 (d, 1H, *J* = 10.4 Hz), 7.23 (m, 2H), 7.62 (m, 2H); ^{13}C NMR (250MHz, $CDCl_3$) δ: 21.5, 30.9, 49.67, 108.5, 118.4, 127.2, 130.0, 131.3, 133.3, 135.6, 144.7, 196.2; HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{18}NO_3S$ 280.1007, found 280.0990 $(M+H)^+$. Formation of the minor *Z*-ene-sulfonamide was not observed on subsequent repeats of this reaction and yields in the order of 60% were obtained.

To a solution of *(E)-N*-allyl-4-methyl-*N*-(3-oxobut-1-enyl)benzenesulfonamide (1.00 g, 3.58 mmol, 1.0 eq.) in THF/MeOH (1:1, 40 mL) at 0 $^{\circ}$C was added $NaBH_4$ (1.03 g, 27.8 mmol, 7.8 eq.) by portionwise addition. The reaction mixture was allowed to stir whilst slowly warming to RT over 12 hours and then was poured onto sat. NaCl (100 mL) and extracted with DCM (3 × 100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give *(E)-N*-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** as a colourless oil (1.00 g, 100%). FTIR (film/cm^{-1}) υ_{max}: 3392 (bs), 3086 (s), 2971(s), 2925 (s), 2871(s), 1708 (s), 1657 (s), 1597 (s); ^{1}H NMR (250MHz, $CDCl_3$) δ 1.27 (d, 3H), 2.42 (s, 3H), 4.00 (dt, 2H, *J* = 5.2, 1.6 Hz), 4.32 (m, 1H), 4.87 (dd, 1H, *J* = 14.2, 7.5Hz), 5.18 (dm, 2H, *J* = 9.9Hz), 5.32 (ddt, 1H, *J* = 17.4, 10.3, 5.2 Hz), 6.89 (d, 1H, *J* = 14.2 Hz), 7.30 (m, 2H), 7.67 (m, 2H); ^{13}C NMR (250MHz, $CDCl_3$) δ 21.9, 24.4, 48.5, 68.1, 115.3, 118.3, 127.4, 127.5, 130.2, 131.9, 136.6, 144.3; HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{19}NNaO_3S$ 304.0983, found 304.0978 $(M+Na)^+$.

(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl propionate (10a)

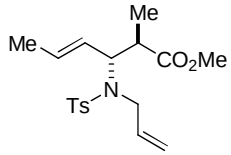


10a

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), propionic acid (0.22 mL, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (10 mL) were combined according to

general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl propionate **10a** as a yellow oil (0.40 g, 84%). FTIR (film/cm^{-1}) υ_{max}: 3082 (m), 3039 (m), 2980 (m), 2931 (m), 2861 (m), 1727 (s), 1656 (s), 1597 (s); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 1.10 (t, 3H, *J* = 7.6 Hz, C*H*$_3$CH$_2$-), 1.29 (d, 3H, *J* = 6.6 Hz, C*H*$_3$CH(CH-)O-), 2.25 (q, 2H, *J* = 7.6 Hz, CH$_3$C*H*$_2$-), 2.45 (s, 3H, -C$_6$H$_4$C*H*$_3$), 3.96 (qd, 2H, *J* = 15.0, 5.4 Hz, -NC*H*$_2$CHCH$_2$), 4.80 (dd, 1H, *J* = 14.2, 6.6 Hz, -NCHC*H*-), 5.09–5.17 (m, 2H, C*H*$_2$CHCH$_2$N-), 5.34 (app. quin, 1H, *J* = 6.6 Hz, CH$_3$C*H*(CH-)O-), 5.79 (ddt, 1H, *J* = 17.0, 10.3, 5.4 Hz, -NCH$_2$C*H*CH$_2$), 6.96 (d, 1H, *J* = 14.2 Hz, -NC*H*CH-), 7.29 (app. d, 2H, *J* = 7.6 Hz, Ar*H* Ts), 7.65 (d, 2H, *J* = 7.6 Hz, Ar*H* Ts) ; ^{13}C NMR (125 MHz, $(CDCl_3)$ δ: 9.1, 21.0, 21.5, 27.9, 48.0, 69.8, 110.1, 117.9, 127.0, 129.5, 129.8, 131.3, 136.1, 143.9, 173.6; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{27}NNaO_4S$ 436.1558, found 436.1679 $(M+Na)^+$.

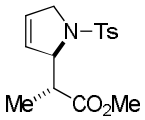
(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-methylhex-4-enoate (11a)



11a

LiHMDS (1M in toluene, 1.34 mL, 1.34 mmol), triethylamine (1.81 mL, 13.4 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl propionate **10a** (0.10 g, 0.30 mmol) in THF (1 mL) was combined according to general procedure 4 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*anti*-*E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-methylhex-4-enoate **11a** as a white solid (0.06 g, 55%, d.r. >25:1). M.p. 88–90 ˚C; FTIR (film/cm^{-1}) υ_{max}: 2966 (m), 2916 (m), 1735 (s), 165s (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.06 (d, 3H, *J* = 6.9 Hz), 1.51 (dd, 3H, *J* = 6.4, 1.5 Hz), 2.39 (3H, s), 3.02 (ddt, 2H, *J* = 10.1, 7.8, 6.9 Hz), 2.83 (s, 3H), 3.69–3.85 (s, 2H), 4.27 (app. t, 1H, *J* = 10.1 Hz), 5.07–5.18 (m, 2H), 5.41 (ddq, 1H, *J* = 15.1, 10.1, 1.5 Hz), 5.55 (dq, 1H, *J* = 15.1, 6.4 Hz), 5.71 (ddt, 1H, *J* = 17.3, 10.2, 6.5 Hz), 7.26 (app. d, 2H, *J* = 8.2 Hz), 7.69 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 15.6, 17.7, 21.4, 43.4, 49.4, 51.7, 64.1, 117.6, 126.2, 127.7, 129.1, 132.1, 135.3, 137.8, 142.9, 175.0; HRMS (ESI, +ve) *m/z* calcd. for $C_{18}H_{25}NO_4S$ 352.1582, found 352.1577 $(M+H)^+$.

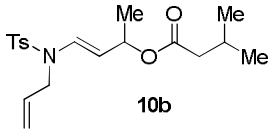
Methyl 2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)propanoate (13a)



13a

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-methylhex-4-enoate **11a** (0.02 g, 0.05 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time: 6 hours). Purification was achieved by the reported procedure to yield the methyl 2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)propanoate **13a** as a white solid (0.01 g, 79%). M.p. 95–97 ˚C; FTIR (film/cm^{-1}) υ_{max}: 2960 (m), 2928 (m), 2878 (m), 1730 (s), 1597 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.12 (d, 3H, *J* = 7.1 Hz), 2.44 (s, 3H), 3.31 (qd, 1H, *J* = 7.13, 3.96 Hz), 3.72 (s, 3H), 4.06–4.19 (m, 2H), 4.84–4.89 (m, 1H), 5.55 (app dq, 1H, *J* = 5.5, 2.2 Hz), 5.72 (app. dq, 1H, *J* = 5.5, 2.2 Hz), 7.33 (app. d, 2H, *J* = 8.1 Hz), 7.74 (app. d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 10.1, 21.5, 43.9, 51.8, 56.1, 67.9, 126.5, 126.8, 127.4, 129.8, 134.1, 143.6, 174.5; HRMS (ESI, +ve) *m/z* calcd. for $C_{15}H_{20}NO_4S$ 310.113, found 310.1108 $(M+H)^+$.

(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 3-methylbutanoate (10b)

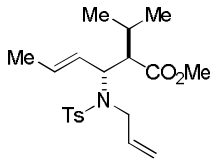


10b

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), isovaleric acid (0.31 mL, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (10 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 3-methylbutanoate **335** as a yellow oil (0.45 g, 87%). FTIR (film/cm^{-1}) υ_{max}: 2960 (m), 2931 (m), 1725 (s), 1655 (s), 1597 (m); ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 0.92–0.96 (m, 6H), 1.32 (d, 3H, *J* = 6.6 Hz), 2.01–2.10 (m, 1H), 2.14 (d, 2H, *J* = 6.7 Hz), 2.44 (s, 3H), 3.94–4.06 (m, 2H), 4.83 (dd, 1H, *J* = 14.1, 6.6 Hz), 5.15 (d, 1H, *J* = 11.0 Hz), 5.18 (d, 1H, *J* = 17.6 Hz), 5.38 (app. quin, 1H, *J* = 6.6 Hz), 5.64 (ddt, 1H, *J* = 17.6, 11.0, 6.3 Hz), 7.02 (d, 1H, *J* = 14.1 Hz), 7.35 (app. d, 2H, *J* = 7.7 Hz), 7.69 (app. d, 2H, *J* = 7.7 Hz); ^{13}C NMR

(125 MHz, CD_2Cl_2) δ: 20.8, 21.2, 22.1, 25.7, 43.6, 47.9, 69.6, 110.2, 117.5, 126.9, 129.6, 129.8, 131.4, 136.0, 144.1, 172.0; HRMS (ESI, +ve) *m/z* calcd. for $C_{19}H_{27}NNaO_4S$ 388.1558, found 388.1567 $(M+Na)^+$.

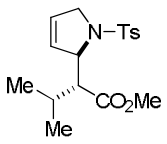
(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-isopropylhex-4-enoate (11b)



11b

LiHMDS (1M in toluene, 2.47 mL, 2.47 mmol), triethylamine (3.42 mL, 24.7 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 3-methylbutanoate **10b** (0.20 g, 0.55 mmol) in THF (2 mL) was combined according to general procedure 4 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*anti*-*E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-isopropylhex-4-enoate **11b** as a white solid (0.14 g, 65%, d.r. >25:1). M.p. 105–107 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3082 (m), 3021 (m), 2985 (m), 2958 (m), 1730 (s), 1655 (m), 1615 (m), 1597 (m), 1509 (m); ^{1}H NMR (400 MHz, CD_3Cl) δ: 0.90 (d, 3H, *J* = 6.7 Hz), 0.99 (d, 3H, *J* = 6.7 Hz), 1.67 (d, 3H, *J* = 5.8 Hz), 1.78–1.94 (1H, m), 2.43 (s, 3H), 3.08 (dd, 2H, *J* = 11.3, 2.7 Hz), 3.65 (s, 3H), 3.67–3.86 (m, 2H), 4.45 (app. t, 1H, *J* = 11.3 Hz), 5.07–5.28 (m, 1H), 5.48–5.80 (m, 1H), 7.27 (app. d, 2H, *J* = 8.1 Hz), 7.72 (app. d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, CD_3Cl) δ: 16.0, 17.8, 21.4, 21.9, 27.6, 51.1, 54.2, 61.9, 117.8, 126.9, 127.9, 129.1, 131.5, 135.2, 137.9, 142.9, 172.8; HRMS (ESI, +ve) *m/z* calcd. for $C_{20}H_{30}NO_4S$ 380.1895, found 380.1900 $(M+H)^+$.

Methyl 3-methyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)butanoate (13b)

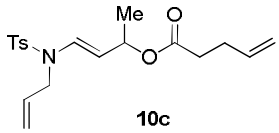


13b

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-isopropylhex-4-enoate **11b** (0.05 g, 0.13 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time: 13 hours). Purification was achieved by the reported procedure to yield the methyl 3-

methyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)butanoate **13b** as an amorphous white solid (0.04 g, 86%). FTIR (film/cm^{-1}) υ_{max}: 2994 (m), 2956 (m), 2878 (m), 1727 (s), 1598 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 0.86 (d, 3H, *J* = 6.0 Hz), 1.10 (d, 3H, *J* = 6.0 Hz), 1.96–2.06 (m, 1H), 2.42 (s, 3H), 3.03 (app. t, 1H, *J* = 6.0 Hz), 3.72 (s, 3H), 4.08–4.18 (m, 2H), 4.68–4.73 (m, 1H), 5.66 (app. dq, 1H, *J* = 6.4, 2.1 Hz), 5.86 (app. dq, 1H, *J* = 6.4, 2.1 Hz), 7.31 (app. d, 2H, *J* = 8.1 Hz), 7.70 (app. d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 20.0, 21.5, 22.7, 26.3, 51.2, 56.0, 67.6, 125.5, 127.5, 128.5, 129.7, 134.0, 143.6, 173.9; HRMS (ESI, +ve) *m/z* calcd. for $C_{17}H_{24}NO_4S$ 338.1426, found 338.1426 $(M+H)^+$.

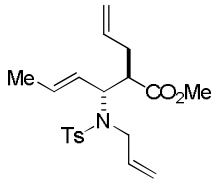
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl pent-4-enoate (10c)



10c

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), penteneoic acid (0.28 g, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl pent-4-enoate **10c** as a yellow oil (0.51 g, 99%). FTIR (film/cm^{-1}) υ_{max}: 3054 (m), 2981 (m), 2918 (m), 1718 (s), 1655 (s), 1597 (m); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 1.28 (d, 3H, *J* = 6.8 Hz), 2.29–2.37 (m, 4H), 2.44 (s, 3H), 3.98–4.11 (m, 2H), 4.90 (dd, 1H, *J* = 14.4, 6.7 Hz), 4.94 (dd, 1H, *J* = 10.1, 1.2 Hz), 5.04 (dd, 1H, *J* = 17.1, 1.4 Hz), 5.13 (dd, 1H, *J* = 10.1, 1.2 Hz), 5.21 (dd, 1H, *J* = 17.1, 1.2 Hz), 5.35 (app. quin, 1H, *J* = 6.8 Hz), 5.66 (ddt, 1H, *J* = 17.1, 10.1, 5.4 Hz), 5.78–5.92 (m, 1H), 7.01 (d, 1H, *J* = 14.4 Hz), 7.44 (app. d, 2H, *J* = 8.2 Hz), 7.74 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) *δ*: 20.4, 20.5, 33.4, 34.0, 47.6, 69.7, 110.3, 114.7, 117.1, 127.0, 129.7, 129.8, 131.8, 136.3, 137.0, 144.1, 171.4; HRMS (ESI, +ve) *m/z* calcd. for $C_{19}H_{25}NNaO_4S$ 386.1402, found 386.1480 $(M+Na)^+$.

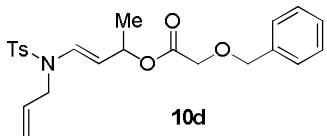
(*anti*-*E*)-Methyl 2-allyl-3-(*N*-allyl-4-methylphenylsulfonamido)hex-4-enoate (11c)



11c

LiHMDS (1M in toluene, 2.48 mL, 2.48 mmol), triethylamine (3.43 mL, 24.80 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl pent-4-enoate **10c** (0.20 g, 0.55 mmol) in THF (2 mL) was combined according to general procedure 4 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*anti*-*E*)-methyl 2-allyl-3-(*N*-allyl-4-methylphenylsulfonamido)hex-4-enoate **11c** as a yellow oil (0.15 g, 70%, d.r. 10:1). FTIR (film/cm^{-1}) υ_{max}: 3012 (m), 2983 (m), 2934 (m), 1729 (s), 1655 (s), 1616 9 (s), 1596 (s), 1509 (m); ^{1}H NMR (400 MHz, CD_3Cl) δ: 1.66 (d, 3H, *J* = 6.3 Hz), 2.12–2.29 (2H, m), 2.43 (s, 3H), 3.08 (td, 1H, *J* = 10.6, 4.5 Hz), 3.66 (s, 3H), 3.74 (dd, 1H, *J* = 15.8, 6.7 Hz), 3.83 (dd, 1H, *J* = 16.0, 6.7 Hz), 4.33 (app. t, 1H, *J* = 10.6 Hz), 4.98–5.22 (m, 4H), 5.48 (dd, 1H, *J* = 15.5, 9.9 Hz), 5.60 (dq, 1H, *J* = 14.2, 6.3 Hz), 5.65–5.77 (m, 2H), 7.28 (app. d, 2H, *J* = 8.1 Hz), 7.73 (app. d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.8, 21.4, 34.9, 49.4, 49.5, 51.5, 63.2, 117.1, 117.8, 126.4, 127.8, 129.2, 132.4, 134.5, 135.1, 137.7, 143.0, 173.6; HRMS (ESI, +ve) *m/z* calcd. for $C_{20}H_{28}NO_4S$ 378.1739, found 378.1699 $(M+H)^+$.

Benzyloxy-acetic acid 3-[allyl-(toluene-4-sulfonyl)-amino]-1-methyl-allyl ester (10d)

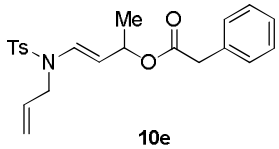


10d

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), benzyloxyacetic acid (0.41 mL, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford benzyloxy-acetic acid 3-[allyl-(toluene-4-sulfonyl)-amino]-1-methyl-allyl ester **10d** as a yellow oil (0.54 g, 87%). FTIR (film/cm^{-1}) υ_{max}: 3051 (m), 2971 (m), 2934 (m), 1744 (s), 1655 (s),

1597 (m); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 1.32 (d, 3H, *J* = 6.8 Hz), 2.40 (s, 3H), 3.98–4.15 (m, 4H), 4.60 (s, 2H), 4.93 (dd, 1H, *J* = 14.3, 6.8 Hz), 4.93 (dq, 1H, *J* = 10.5, 1.4 Hz), 5.21 (dq, 1H, *J* = 17.2, 1.5 Hz), 5.46 (app. quin, 1H, *J* = 6.8 Hz), 5.65 (ddt, 1H, *J* = 17.2, 10.5, 5.2 Hz), 7.08 (d, 1H, *J* = 14.3 Hz), 7.28–7.43 (m, 7H), 7.74 (app. d, 2H, *J* = 8.1 Hz); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) *δ*: 20.4, 20.5, 47.6, 67.3, 70.5, 72.6, 109.9,117.1, 127.0, 127.5, 127.7, 128.2, 129.8, 130.2, 131.7, 136.3, 138.1, 144.1, 169.3; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{27}NNaO_5S$ 452.1508, found 452.1543 $(M+Na)^+$.

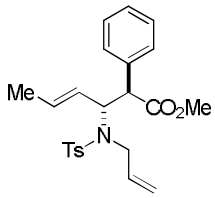
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate (10e)



10e

EDCi (0.68 g, 3.55 mmol) in DCM (100 mL), triethylamine (0.49 mL, 3.55 mmol), DMAP (0.02 g, 0.18 mmol), phenylacetic acid (0.48 g, 3.55 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.50 g, 1.78 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate **10e** as a yellow oil (0.70 g, 98%). FTIR (film/cm^{-1}) υ_{max}: 3051 (m), 2977 (m), 2922 (m), 1727 (s), 1655 (s), 1597 (m); ^{1}H NMR (250 MHz, $(CD_3)_2CO$) δ: 1.29 (d, 3H, *J* = 6.5 Hz, CH_3CH(CH-)O-), 2.40 (s, 3H, $CH_3C_6H_4$-), 3.60 (s, 2H, -$CH_2C_6H_5$), 3.93–4.10 (m, 2H, -NCH_2CHCH_2), 4.88 (dd, 1H, *J* = 14.2, 6.5 Hz, -NC*H*CH-), 5.05–5.24 (m, 2H, -NCH_2CHCH_2), 5.37 (app quin, 1H, *J* = 6.5 Hz, CH_3C*H*(CH-)O-), 5.62 (ddt, 1H, *J* = 17.3, 10.4, 5.2 Hz, -NCH_2C*H*CH_2), 7.03 (d, 1H, *J* = 14.2 Hz, -NC*H*CH-), 7.23–7.37 (m, 5H, $CH_2C_6H_5$), 7.39 (app. d, 2H, *J* = 8.3 Hz, Ar*H*), 7.71 (app. d, 2H, *J* = 8.3 Hz, Ar*H*); ^{13}C NMR (100 MHz, CD_3Cl) *δ*: 20.9, 21.5, 41.7, 48.0, 70.7, 109.7, 117.9, 127.0 (x2), 128.5, 129.2, 129.8 (x2), 131.2, 134.2, 136.1, 143.9, 170.7; HRMS (ESI, +ve) *m/z* calcd. for $C_{22}H_{25}NNaO_4S_1$ 422.1411, found 422.1375 $(M+Na)^+$.

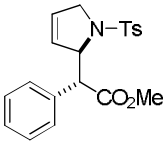
(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate (11d)



11d

LiHMDS (1M in toluene, 0.63 mL, 0.63 mmol), TMSCl (0.19 mL, 2.91 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate **10e** (0.10 g, 0.48 mmol) in THF (1 mL) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*anti*-*E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate **11d** as a white solid (0.06 g, 57%, d.r. >25:1). M.p. 103–104 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3032 (m), 2950 (m), 2855 (m), 1734 (s), 1668 (w), 1598 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.28 (d, 3H, *J* = 4.8 Hz, C*H*$_3$CH-), 2.33 (s, 3H, C*H*$_3$C$_6$H$_4$-), 3.55 (s, 3H, -CO$_2$C*H*$_3$), 3.62–3.87 (m, 2H, -NC*H*$_2$CHCH$_2$), 4.19 (d, 1H, *J* = 11.2 Hz, -C*H*CO$_2$CH$_3$), 4.68 (dd, 1H, *J* = 11.2, 7.4 Hz, -NC*H*(CH-)CH-), 4.99–5.30 (m, 4H, C*H*$_2$C*H*CH$_2$N(Ts)CH(CH-)CHC*H*CH$_3$), 5.63 (ddt, 1H, *J* = 17.0, 10.3, 6.5 Hz, -NCH(CH-)C*H*-), 7.08–7.30 (m, 7H, Ar*H*), 7.65 (app. d, 2H, *J* = 8.2 Hz, ArH Ts); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.6, 21.4, 50.1, 52.0, 55.7, 63.7, 118.1, 125.9, 127.7, 127.8, 128.5, 128.9, 129.2, 131.8, 134.9, 135.8, 137.8, 143.1, 172.5; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{28}NO_4S$ 414.1739, found 414.1734 $(M+H)^+$.

Methyl 2-phenyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13c)

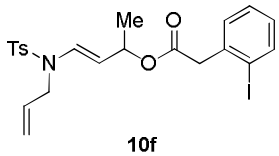


13c

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate **11d** (0.10 g, 0.24 mmol), catalytic Grubbs I and DCM (10 mL) were combined according to general procedure 6 (reaction time: 13 hours). Purification was achieved by the reported procedure to yield the methyl 2-phenyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **13c** as a white solid (0.08 g, 92%). M.p. 98–100 ˚C. FTIR (film/cm^{-1}) υ_{max}: 3024 (m), 2950 (m), 2931 (m), 1730 (s), 1657 (m), 1615 (m), 1596

(m), 1510 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.43 (s, 3H), 3.39–3.45 (m, 1H), 3.73 (s, 3H), 3.85 (app. dq, 1H, *J* = 15.2, 2.1 Hz), 4.48 (d, 1H, *J* = 4.4 Hz), 5.06–5.06 (m, 1H), 5.43 (app. dq, 1H *J* = 6.4, 2.0 Hz), 5.80 (app. dq, 1H *J* = 6.4, 2.0 Hz), 7.23–7.30 (m, 5H), 7.32 (app. d, 2H, *J* = 8.2 Hz), 7.73 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.5, 52.0, 55.5, 56.2, 68.3, 129.9, 127.3 (x2), 127.6, 127.8, 129.8, 130.0, 134.0, 134.3, 143.6, 172.9; HRMS (ESI, +ve) *m/z* calcd. for $C_{20}H_{22}NO_4S$ 372.1269, found 372.1238 $(M+H)^+$.

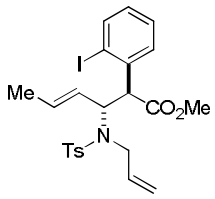
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2-iodophenyl)acetate (10f)



10f

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 2-Iodo phenylacetic acid (0.74 g, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2-iodophenyl)acetate **10f** as a yellow oil (0.64 g, 86%). FTIR (film/cm^{-1}) υ_{max}: 2978 (m), 2922 (m), 1727 (s), 1655 (s), 1596 (w); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 1.31 (d, 3H, *J* = 6.6 Hz), 2.44 (s, 3H), 3.77 (app. d, 2H), 3.97–4.08 (m, 2H), 4.91 (dd, 1H, *J* = 14.2, 6.6 Hz), 5.12 (app. dq, 1H, *J* = 10.4, 1.4 Hz), 5.20 (app. dq, 1H, *J* = 17.3, 1.7 Hz), 5.39 (app. quin, 1H, *J* = 6.6 Hz), 5.65 (ddt, 1H, *J* = 17.3, 10.4, 5.0 Hz), 7.00–7.08 (m, 2H), 7.35–7.43 (m, 4H), 7.72 (app. d, 2H, *J* = 8.2 Hz), 7.88 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) *δ*: 20.4, 20.5, 46.0, 47.6, 70.6, 100.6, 109.9, 117.1, 127.0, 128.4, 128.8, 129.8, 129.9, 131.0, 131.8, 136.4, 138.5, 139.2, 144.0, 169.0; HRMS (ESI, +ve) *m/z* calcd. for $C_{22}H_{24}INNaO_4S$ 548.0368, found 548.0407 $(M+Na)^+$.

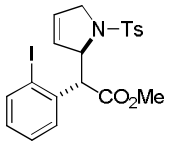
(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(2-iodophenyl) hex-4-enoate (11e)



11e

LiHMDS (1M in toluene, 0.34 mL, 0.34 mmol), TMSCl (0.10 mL, 1.57 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2-iodophenyl)acetate **10f** (0.07 g, 0.26 mmol) in THF (0.7 mL) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*anti*-*E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(2-iodophenyl)hex-4-enoate **11e** as a white solid (0.05 g, 67%, d.r. >25:1). M.p. 97–99 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3179 (w), 2953 (m), 2922 (m), 1734 (s), 1597 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.35 (d, 3H, *J* = 6.5 Hz), 2.41 (s, 3H), 3.63 (s, 3H), 3.83 (app. d, 1H, *J* = 17.3, 6.7 Hz), 3.93 (app. d, 1H, *J* = 17.3, 6.7 Hz), 4.75 (d, 1H, *J* = 11.7 Hz), 4.91 (d, 1H, *J* = 11.7 Hz), 5.14–5.23 (m, 2H), 5.25–5.37 (m, 2H), 5.79 (ddt, 1H, *J* = 17.0, 10.8, 6.7 Hz), 6.92 (app. t, 1H, *J* = 7.9 Hz), 7.26 (app. d, 2H, *J* = 8.7 Hz), 7.27–7.33 (m, 1H), 7.51 (app d, 1H, *J* = 7.9 Hz), 7.74 (app. d, 2H, *J* = 8.7 Hz), 7.82 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.6, 21.4, 49.2, 52.2, 57.8, 64.2, 118.1, 124.7, 127.9, 128.5, 128.9, 129.0, 129.2, 129.3, 132.1, 135.0, 137.7, 138.9, 139.6, 143.1, 171.8; HRMS (ESI, +ve) *m/z* calcd. for $C_{25}H_{32}NO_6S$ 474.1950, found 474.1948 $(M+H)^+$.

Methyl 2-(2-iodophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13d)

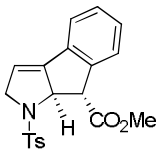


13d

anti-(*E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(2-iodophenyl)hex-4-enoate **11e** (0.09 g, 0.17 mmol), catalytic Grubbs I and toluene (5 mL) were combined according to general procedure 7 (reaction time : 5 hours). Purification was achieved by the reported procedure to yield the methyl 2-(2-iodophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **13d** as a white solid (0.04 g, 51%).

M.p. 186–188 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3026 (m), 2952 (m), 2878 (m), 1728 (s), 1597 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.42 (s, 3H), 3.66–3.75 (m, 1H), 3.75 (s, 3H), 3.97 (app. dq, 1H *J* = 15.7, 1.9 Hz), 4.78 (d, 1H, *J* = 5.6 Hz), 5.19–5.24 (m, 1H), 5.50–5.59 (m, 2H), 6.95 (app. t, 1H, *J* = 7.4 Hz), 7.24–7.34 (m, 4H), 7.73 (app. d, 2H, *J* = 8.3 Hz), 7.89 (app. d, 1H, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.5, 52.3, 55.5, 59.9, 68.7, 127.5, 127.6 (x2), 127.7, 129.1, 129.7, 129.9, 134.2, 136.3, 138.0, 140.2, 143.6, 172.2; HRMS (ESI, +ve) *m/z* calcd. for $C_{22}H_{21}INO_4S$ 498.0235, found 498.0259 $(M+H)^+$.

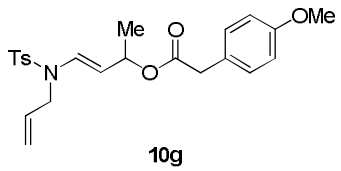
anti-methyl 1-tosyl-1,2,8,8a-tetrahydroindeno[2,1-b]pyrrole-8-carboxylate 14



14

To a solution of $Pd(OAc)_2$ (3.00 mg, 0.01 mmol, 0.2 eq.), PPh_3 (3.67 mg, 0.01 mmol, 0.2 eq.), Ag_2CO_3 (29.1 mg, 0.11 mmol, 1.5 eq.) in MeCN was added methyl 2-(2-iodophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **11e** (35.0 mg, 0.07 mmol, 1.0 eq.). The reaction mixture was refluxed for 4 hours and then concentrated *in vacuo* and subjected to flash column chromatography using ethyl acetate/petroleum ether 40-60˚ (20:80) to yield *anti*-methyl 1-tosyl-1,2,8,8a-tetrahydroindeno[2,1-b]pyrrole-8-carboxylate **14** as an amorphous clear solid (22.0 mg, 84%). FTIR (film/cm^{-1}) υ_{max}: 2958 (m), 2919 (m), 2849 (m), 1734 (s), 1597 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.47 (s, 3H, -$C_6H_4CH_3$), 3.80 (s, 3H, -CO_2CH_3), 4.92 (br. d, 1H, *J* = 9.5 Hz, -NCH*H*CH-), 4.63 (br. s, 1H, -C*H*CO_2CH_3), 4.90 (dd, 1H, *J* = 9.5, 2.0 Hz, -NCH*H*CH-), 5.31 (app. dd, 1H, *J* = 4.1, 2.8 Hz, -NC*H*(CH-)CH-), 6.36 (app. dd, 1H, *J* = 4.1, 2.8 Hz, -NCH_2CH-), 7.10–7.15 (m, 1H, Ar*H*), 7.23–7.27 (m, 2H, Ar*H*), 7.36 (app. d, 2H, *J* = 8.2 Hz, Ar*H*, Ts), 7.45–7.51 (m, 1H, Ar*H*), 7.75 (app. d, 2H, *J* = 8.2 Hz, Ar*H*, Ts); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.6, 52.5, 54.5, 58.3, 66.1, 112.9, 125.1, 126.1, 127.8, 127.9, 128.6, 129.9, 130.5, 132.9, 137.8, 142.9, 144.2, 172.3; HRMS (ESI, +ve) *m/z* calcd. for $C_{20}H_{20}N_1O_4S_1$ 370.1148, found 370.1113 $(M+H)^+$.

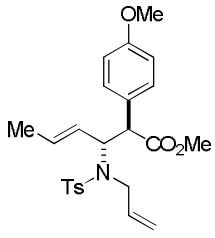
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-methoxyphenyl)acetate (10g)



10g

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 4-methoxy phenylacetic acid (0.47 g, 2.81 mmol) and (E)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-methoxyphenyl)acetate **10g** as a yellow oil (0.54 g, 81%). FTIR (film/cm^{-1}) υ_{max}: 2978 (m), 2943 (m), 1726 (s), 1655 (s), 1613 (m), 1597 (w); ^{1}H NMR (250 MHz, $(CD_3)_2CO$) δ: 1.27 (d, 3H, *J* = 6.5 Hz), 2.42 (s, 3H), 3.50 (2H, s), 3.77 (s, 3H), 3.92–4.05 (m, 2H), 4.86 (dd, 1H, *J* = 14.1, 6.5 Hz), 5.09 (dd, 1H, *J* = 10.7, 1.5 Hz), 5.16 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.37 (app. quin, 1H, *J* = 6.5 Hz), 5.59 (ddt, 1H, *J* = 17.1, 10.7, 5.4 Hz), 6.85 (d, 2H, *J* = 8.5 Hz), 6.99 (d, 1H, *J* = 14.1 Hz), 7.17 (app. d, 2H, *J* = 8.3 Hz), 7.37 (app. d, 2H, *J* = 8.2 Hz), 7.68 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ: 21.3, 21.4, 41.0, 48.4, 55.4, 71.0, 111.0, 114.5, 118.0, 127.4, 127.8, 127.9, 130.7, 131.0, 132.6, 137.2, 144.9, 159.6, 171.3; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{27}NNaO_5S_1$ 452.1508, found 452.1463 $(M+Na)^+$.

(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(4-methoxyphenyl)hex-4-enoate (11f)

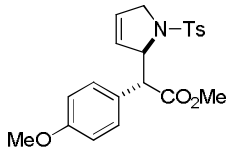


11f

LiHMDS (1M in toluene, 1.16 mL, 1.16 mmol), TMSCl (0.35 mL, 5.35 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-methoxyphenyl)acetate **10g** (0.20 g, 0.89 mmol) in THF (2 mL) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment

with diazomethane and purification by flash chromatography afforded (*anti-E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(4-methoxyphenyl)hex-4-enoate **11f** as a white solid (0.15 g, 73%, d.r. >25:1). M.p. 109–110 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3039 (w), 2952 (m), 2919 (m), 1734 (s), 1670 (w), 1608 (m), 1598 (m), 1522 (m), 1512 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.39 (d, 3H, *J* = 4.5 Hz), 2.41 (s, 3H), 3.62 (s, 3H), 3.77 (s, 3H), 3.75–3.88 (m, 2H), 4.21 (d, 1H, *J* = 11.5 Hz), 4.73 (dd, 1H, *J* = 11.5, 7.44 Hz), 5.12 (app. d, 1H, *J* = 10.3 Hz), 5.20 (app d, 1H, *J* = 17.1 Hz), 5.23–5.33 (m, 2H), 5.70 (ddt, 1H, *J* = 17.1, 10.3, 6.5 Hz), 6.81 (app. d, 2H, *J* = 8.7 Hz), 7.22 (app. d, 2H, *J* = 8.7 Hz), 7.26 (app. d, 2H, *J* = 8.4 Hz), 7.73 (app. d, 2H, *J* = 8.4 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.6, 21.4, 50.0, 51.9, 54.9, 55.1, 63.6, 113.9, 118.0, 126.0, 127.8 (x2), 129.2, 129.9, 131.7, 134.9, 137.9, 143.0, 159.0, 172.8; HRMS (ESI, +ve) *m/z* calcd. for $C_{24}H_{30}NO_5S$ 444.1844, found 444.1857 $(M+H)^+$.

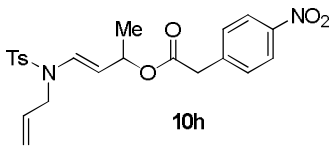
Methyl 2-(4-methoxyphenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13e)



13e

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(4-methoxyphenyl)hex-4-enoate **11f** (0.05 g, 0.11 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time: 13 hours). Purification was achieved by the reported procedure to yield the methyl 2-(4-methoxyphenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **13e** as a clear oil (0.04 g, 89%). FTIR (film/cm^{-1}) υ_{max}: 3035 (m), 2953 (m), 2884 (m), 1727 (s), 1597 (m), 1512 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.42 (s, 3H), 3.44 (ddt, 1H, *J* = 15.0, 5.4, 2.0 Hz), 3.72 (s, 3H), 3.79 (s, 3H), 3.85 (app. dq, 1H, *J* = 15.0, 2.0 Hz), 4.42 (d, 1H, *J* = 4.3 Hz), 4.97–5.02 (m, 1H), 5.44 (app. dq, 1H *J* = 6.4, 2.0 Hz), 5.80 (app. dq, 1H *J* = 6.4, 2.0 Hz), 6.82 (app. d, 2H, *J* = 8.6 Hz), 7.17 (app. d, 2H, *J* = 8.6 Hz), 7.31 (app. d, 2H, *J* = 8.6 Hz), 7.72 (app. d, 2H, *J* = 8.6 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.5, 52.0, 55.1, 55.4, 55.5, 68.4, 113.3, 126.0, 127.0, 127.3, 127.6, 129.8, 131.1, 134.4, 143.6, 158.8, 173.1; HRMS (ESI, +ve) *m/z* calcd. for $C_{21}H_{24}NO_5S$ 402.1375, found 402.1366 $(M+H)^+$.

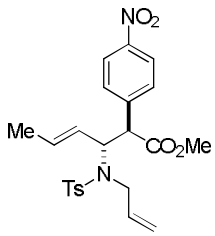
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-nitrophenyl)acetate (10h)



10h

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 4-nitrophenylacetic acid (0.51 g, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-nitrophenyl)acetate **10h** as an orange oil (0.54 g, 86%). FTIR (film/cm^{-1}) υ_{max}: 3018 (w), 2988 (m), 2967 (m), 1727 (s), 1698 (s), 1656 (m), 1599 (w), 1522 (m); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 1.29 (d, 3H, *J* = 6.7 Hz), 2.41 (s, 3H), 3.80 (2H, s), 3.95–4.05 (m, 2H), 4.87 (dd, 1H, *J* = 14.5, 6.7 Hz), 5.08 (dq, 1H, *J* = 10.7, 1.95 Hz), 5.15 (dq, 1H, *J* = 17.2, 1.3 Hz), 5.38 (app. quin, 1H, *J* = 6.7 Hz), 5.59 (ddt, 1H, *J* = 17.2, 10.7, 5.1 Hz), 7.00 (d, 1H, *J* = 14.5 Hz), 7.38 (app. d, 2H, *J* = 7.9 Hz), 7.57 (app. d, 2H, *J* = 8.7 Hz), 7.69 (app. d, 2H, *J* = 7.9 Hz), 8.18 (app. d, 2H, *J* = 8.7 Hz); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) *δ*: 20.3, 20.5, 40.6, 47.5, 70.9, 109.6, 117.1, 123.3, 126.9, 129.8, 130.1, 130.5, 131.6, 136.3, 142.5, 144.1, 147.0, 169.2; HRMS (ESI, +ve) *m/z* calcd. for $C_{44}H_{48}N_4NaO_{12}S_2$ 911.2613, found 911.2604 $(2M+Na)^+$.

(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(4-nitrophenyl)hex-4-enoate (11g)

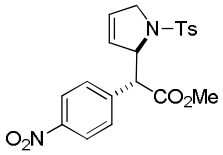


11g

LiHMDS (1M in toluene, 1.13 mL, 1.13 mmol), TMSCl (0.34 mL, 5.22 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-nitrophenyl)acetate **10h** (0.20 g, 0.87 mmol) in THF (2 mL) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography, recrystallisation and a two subsequent recrystallisations of the mother liquor afforded (*anti*-*E*)-methyl 3-(*N*-allyl-4-

methylphenylsulfonamido)-2-(4-nitrophenyl)hex-4-enoate **11g** as an off white solid (0.10 g, 53%, d.r. 20:1). M.p. 128–130 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3018 (w), 2988 (m), 2952 (m) 2925 (m), 1736 (s), 1669 (w), 1598 (m), 1521 (s); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.38 (dd, 3H, *J* = 6.2, 1.0 Hz), 2.42 (s, 3H), 3.69 (s, 3H), 3.78 (dd, 1H, *J* = 16.0, 6.8 Hz), 3.86 (dd, 1H, *J* = 16.0, 6.8 Hz), 4.49 (d, 1H, *J* = 11.2 Hz), 4.69 (app. t, 1H, *J* = 11.2 Hz), 5.17 (app. d, 1H, *J* = 10.2 Hz), 5.23 (app. d, 1H, *J* = 17.0 Hz), 5.20–5.38 (m, 2H), 5.69 (ddt, 1H, *J* = 17.0, 10.2, 6.8 Hz), 7.28 (app. d, 2H, *J* = 8.2 Hz), 7.51 (app. d, 2H, *J* = 8.2 Hz), 7.73 (app. d, 2H, *J* = 8.2 Hz), 8.16 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.5, 21.4, 50.5, 52.5, 55.6, 63.8, 118.6, 123.7, 125.4, 127.8, 129.3, 129.9, 132.9, 134.5, 137.5, 143.2, 143.4, 147.4, 171.5; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{26}N_2O_6S$ 481.1409, found 481.1715 $(M+Na)^+$.

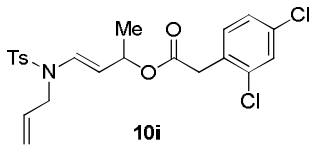
Methyl 2-(4-nitrophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13f)



13f

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(4-nitrophenyl)hex-4-enoate **11g** (0.03 g, 0.07 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time : 13 hours). Purification was achieved by the reported procedure to yield the methyl 2-(4-nitrophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **13f** as an off white solid (0.03 g, 96%). M.p. 178–180 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3030 (m), 2954 (m), 1732 (s), 1599 (s), 1521 (s); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.44 (s, 3H), 3.34–3.42 (m, 1H), 3.76 (s, 3H), 3.84 (app. d, 1H, *J* = 15.6 Hz), 4.69 (d, 1H, *J* = 4.2 Hz), 5.03–5.09 (m, 1H), 5.48–5.54 (m, 1H), 5.80–5.85 (m, 1H), 7.34 (app. d, 2H, *J* = 8.1 Hz), 7.45 (app. d, 2H, *J* = 8.4 Hz), 7.72 (app. d, 2H, *J* = 8.1 Hz), 8.16 (app. d, 2H, *J* = 8.4 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.5, 52.4, 55.6, 55.7, 68.2, 122.8, 126.7, 127.4, 127.8, 129.9, 131.2, 133.7, 141.5, 144.0, 147.3, 171.6; HRMS (ESI, +ve) *m/z* calcd. for $C_{20}H_{21}N_2O_6S$ 417.1120, found 417.1123 $(M+H)^+$.

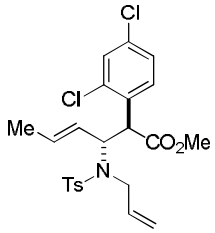
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2,4-dichlorophenyl)acetate (10i)



10i

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 2,4-dichlorophenylacetic acid (0.58 g, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2,4-dichlorophenyl)acetate **10i** as a yellow oil (0.55 g, 82%). FTIR (film/cm^{-1}) υ_{max}: 3091 (m), 2978 (m), 2937 (m), 1729 (s), 1655 (s), 1614 (s), 1591 (s), 1509 (s); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 1.29 (d, 3H, *J* = 6.7 Hz), 2.44 (s, 3H), 3.76 (2H, s), 3.97–4.07 (m, 2H), 4.89 (dd, 1H, *J* = 14.2, 6.7 Hz), 5.12 (app d, 1H, *J* = 10.3 Hz), 5.19 (app d, 1H, *J* = 17.2 Hz), 5.38 (app. quin, 1H, *J* = 6.7 Hz), 5.63 (ddt, 1H, *J* = 17.2, 10.3, 5.1 Hz), 7.01 (d, 1H, *J* = 14.2 Hz), 7.32–7.47 (m, 4H), 7.50 (d, 1H, *J* = 1.9 Hz), 7.71 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) *δ*: 20.4, 20.5, 38.4, 47.6, 70.8, 109.7, 117.1, 126.9, 127.2, 128.7, 129.8, 129.9, 131.7, 132.2, 133.0, 133.1, 135.1, 136.4, 144.0, 168.7; HRMS (ESI, +ve) *m/z* calcd. for $C_{22}H_{23}Cl_2N_1NaO_4S_1$ 490.0617, found 490.0614 $(M+Na)^+$.

(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate (11h)

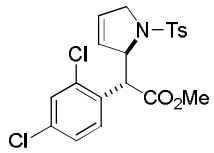


11h

LiHMDS (1M in toluene, 1.07 mL, 1.07 mmol), TMSCl (0.33 mL, 4.94 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2,4-dichlorophenyl)acetate **10i** (0.20 g, 0.82 mmol) in THF (2 mL) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*anti*-*E*)-methyl 3-(*N*-allyl-4-

methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate **11h** as a yellow oil (0.14 g, 68%, d.r. >25:1). FTIR (film/cm^{-1}) υ_{max}: 3034 (w), 2950 (m), 2919 (m), 1736 (s), 1669 (m), 1598 (m), 1523 (m), 1512 (m); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.37 (d, 3H, *J* = 5.8 Hz), 2.41 (s, 3H), 3.65 (s, 3H), 3.80 (dd, 1H, *J* = 15.9, 6.9 Hz), 3.92 (dd, 1H, *J* = 15.9, 6.9 Hz), 4.79 (dd, 1H, *J* = 11.5, 8.6 Hz), 4.90 (d, 1H, *J* = 11.5 Hz), 5.15 (app. d, 1H, *J* = 10.2 Hz), 5.18–5.33 (m, 3H), 5.71 (ddt, 1H, *J* = 16.9, 10.3, 6.9 Hz), 7.21 (dd, 2H, *J* = 8.3, 2.3 Hz), 7.26 (app. d, 2H, *J* = 8.2 Hz), 7.36 (d, 1H, *J* = 2.3 Hz), 7.51 (d, 1H, *J* = 8.3 Hz), 7.72 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.6, 21.4, 49.5, 49.6, 52.3, 63.9, 118.2, 124.7, 127.4, 127.8, 129.2, 129.3, 130.3, 132.4, 132.5, 133.9, 134.9, 135.2, 137.6, 143.2, 171.5; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{26}Cl_2NO_4S$ 482.0959, found 482.0971 $(M+H)^+$.

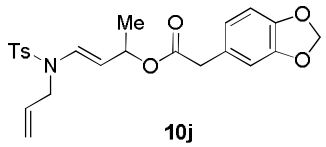
Methyl 2-(2,4-dichlorophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13g)



13g

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate **11h** (0.04 g, 0.08 mmol), catalytic Grubbs I and toluene (5 mL) were combined according to general procedure 7 (reaction time : 5 hours). Purification was achieved by the reported procedure to yield the methyl 2-(2,4-dichlorophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **13g** as a white solid (0.03 g, 83%). M.p. 147–148 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3039 (m), 2953 (m), 2931 (m), 2876 (m), 1734 (s), 1589 (m), 1542 (w), 1524 (w); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.43 (s, 3H), 3.52 (ddt, 1H, *J* = 15.4, 5.2, 2.2 Hz), 3.74 (s, 3H), 3.84 (app. dq, 1H, *J* = 15.4, 2.2 Hz), 4.83 (d, 1H, *J* = 4.5 Hz), 5.14–5.23 (m, 1H), 5.50 (app. dq, 1H *J* = 6.3, 2.2 Hz), 5.79 (app. dq, 1H *J* = 6.3, 2.2 Hz), 7.21 (d, 1H, *J* = 2.1 Hz), 7.29–7.36 (m, 3H), 7.38 (app. d, 1H, *J* = 2.1 Hz), 7.72 (app. d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.5, 52.3, 53.2, 55.4, 68.5, 126.6, 127.0, 127.2, 127.4, 129.7, 129.8, 131.1, 133.4, 133.9, 134.0, 135.7, 143.8, 171.8; HRMS (ESI, +ve) *m/z* calcd. for $C_{20}H_{20}Cl_2NO_5S$ 440.0490, found 440.0686 $(M+H)^+$.

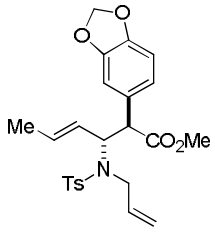
(*E*)-4-(*N*-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate (10j)



10j

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39l, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 3,4-methylenedioxyphenylacetic acid (0.51 g, 2.81 mmol) and (*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **5e** (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate **10j** as a yellow oil (0.54 g, 86%). FTIR (film/cm^{-1}) υ_{max}: 3049 (m), 2916 (m), 1729 (s), 1655 (s), 1503 (s); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.30 (d, 3H, *J* = 6.6 Hz), 2.41 (s, 3H), 3.46 (2H, s), 3.89–4.01 (m, 2H), 4.76 (dd, 1H, *J* = 14.3, 6.6 Hz), 5.10 (app. d, 1H, *J* = 10.3 Hz), 5.10 (app. d, 1H, *J* = 17.0 Hz), 5.32 (app. quin, 1H, *J* = 6.6 Hz), 5.50 (ddt, 1H, *J* = 17.0, 10.3, 5.3 Hz), 5.91 (s, 2H), 6.65–6.75 (m, 3H), 6.97 (d, 1H, *J* = 14.3 Hz), 7.26 (app. d, 2H, *J* = 7.8 Hz), 7.63 (app. d, 2H, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 20.9, 21.5, 30.9, 41.2, 47.9, 70.6, 100.9, 108.2, 109.6 (x2), 117.8, 122.2, 127.0, 127.1, 127.7, 129.7, 129.8, 131.2, 136.0, 143.9, 146.6, 147.7, 170.7; HRMS (ESI, +ve) *m/z* calcd. for $C_{23}H_{25}NNaO_6S$ 466.1300, found 466.1295 $(M+Na)^+$.

(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(benzo[d][1,3]dioxol-5-yl)hex-4-enoate (11i)

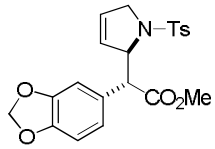


11i

LiHMDS (1M in toluene, 0.55 mL, 0.55 mmol), TMSCl (0.17 mL, 2.53 mmol) and (*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate **10j** (0.10 g, 0.42 mmol) in THF (1 mL) was combined according to general procedure 3 (reaction time : 75 minutes).

Treatment with diazomethane and purification by flash chromatography afforded (*anti-E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(benzo[d][1,3]dioxol-5-yl)hex-4-enoate **11i** as a white solid (0.06 g, 55%, d.r. >25:1). M.p. 119–121 ˚C; FTIR (film/cm^{-1}) υ_{max}: 3020 (w), 2952 (m), 2928 (m), 1733 (s), 1597 (m), 1504 (s); ^{1}H NMR (500 MHz, CD_3Cl) δ: 1.42 (d, 3H, *J* = 4.8 Hz), 2.41 (s, 3H), 3.17 (s, 3H), 3.77 (dd, 1H, *J* = 16.0, 6.9 Hz), 3.84 (dd, 1H, *J* = 16.0, 6.9 Hz), 4.19 (d, 1H, *J* = 11.3 Hz), 4.66 (dd, 1H, *J* = 11.3 Hz), 5.13 (app. d, 1H, *J* = 10.1 Hz), 5.20 (app. d, 1H, *J* = 17.1 Hz), 5.27–5.35 (m, 2H), 5.69 (ddt, 1H, *J* = 17.1, 10.1, 6.9 Hz), 5.92–5.95 (m, 2H), 6.68–6.77 (m, 2H), 6.85 (d, 1H, *J* = 1.7 Hz), 7.26 (app. d, 2H, *J* = 8.3 Hz), 7.72 (app. d, 2H, *J* = 8.3 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 17.7, 21.4, 50.2, 52.0, 55.3, 63.6, 101.0, 108.1, 108.8, 118.1, 122.6, 125.9, 127.8, 129.2, 129.5, 131.8, 134.8, 137.8, 143.1, 147.0, 147.8, 172.6; HRMS (ESI, +ve) *m/z* calcd. for $C_{24}H_{28}NO_6S$ 458.1637, found 458.1649 $(M+H)^+$.

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13h

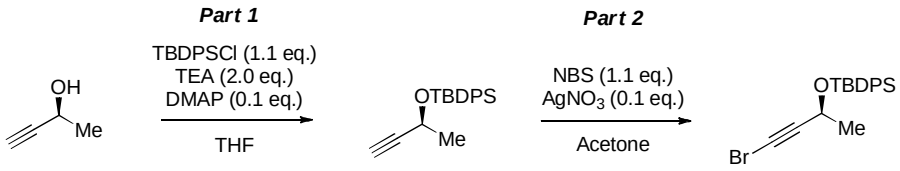


13h

anti-(*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-(benzo[d][1,3]dioxol-5-yl)hex-4-enoate **11i** (0.05 g, 0.11 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time : 5 hours). Purification was achieved by the reported procedure to yield methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate **13h** as a white solid (0.04 g, 89%). M.p. 134–136 ˚C; FTIR (film/cm^{-1}) υ_{max}: 2994 (m), 2946 (m), 2909 (m), 1728 (s), 1598 (m), 1504 (s); ^{1}H NMR (500 MHz, CD_3Cl) δ: 2.43 (s, 3H), 3.56 (app. ddt, 1H, *J* = 15.0, 5.3, 2.0 Hz), 3.73 (s, 3H), 3.89 (app. dq, 1H, *J* = 15.0, 2.4 Hz), 4.38 (d, 1H, *J* = 4.4 Hz), 4.95–4.99 (m, 1H), 5.49 (app. dq, 1H, *J* = 6.3, 2.1 Hz), 5.77 (app. dq, 1H, *J* = 6.3, 2.1 Hz), 5.94 (app. d, 2H, *J* = 4.7 Hz), 6.70–6.76 (m, 3H), 7.32 (app. d, 2H, *J* = 8.5 Hz), 7.72 (app. d, 2H, *J* = 8.9 Hz); ^{13}C NMR (125 MHz, CD_3Cl) *δ*: 21.5, 52.1, 55.6, 55.8, 68.3, 101.0, 107.9, 110.1, 123.7, 127.0, 127.3, 127.6 (x2), 129.8, 134.2, 143.7, 146.9, 147.0, 172.9; HRMS (ESI, +ve) *m/z* calcd. for $C_{21}H_{22}NO_6S$ 416.1167, found 416.1168 $(M+H)^+$.

Chirality Transfer Study – Synthesis and Rearrangement of (*S*)-10e

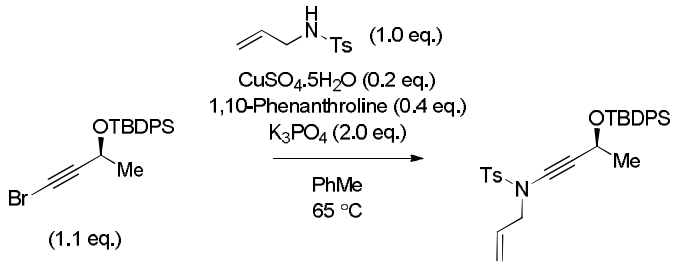
(*S*)-(4-Bromobut-3-yn-2-yloxy)(*tert*-butyl)diphenylsilane



Part 1 - To a stirred solution of 3-butyn-2-ol (15.0 g, 214 mmol, 1.0 eq.) in THF (200 mL) was added DMAP (2.61 g, 21.4 mmol, 0.1 eq.), TEA (59.1 mL, 428 mmol, 2.0 eq.) and TBDPSCl (64.7 g, 235, 1.1 eq.). The reaction mixture was stirred for 15 hours and then poured onto saturated ammonium chloride (200 mL). The organics were extracted with heptane (3 × 200 mL), concentrated *in vacuo* and the crude product was subjected to flash column chromatography (0-5% EtOAc/Petrol 40-60^{o}) to give (but-3-yn-2-yloxy)(*tert*-butyl)diphenylsilane as a clear oil (66.0 g, 100%). $[\alpha]_D^{20}$ = +65 .0 (*c* 1, DCM); Other data as previously reported.

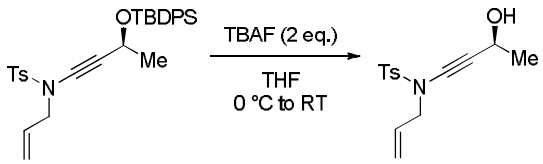
Part 2 - To a stirred solution of but-3-yn-2-yloxy)(*tert*-butyl)diphenylsilane (66.0 g, 214 mmol, 1.0 eq.) in acetone (200 mL) was added NBS (41.9 g, 235 mmol, 1.1 eq.) and silver nitrate (3.63 g, 21.4 mmol, 0.1 eq.). The reaction mixture was stirred for 15 hours and then poured onto saturated sodium chloride (100 mL). The organics were extracted with diethyl ether (3 × 200 mL), dried over magnesium sulphate and concentrated *in vacuo* to yield a yellow oil which was triturated with heptane and the insolubilities were filtered off and the mother liquor was concentrated in vacuo to yield (4-bromobut-3-yn-2-yloxy)(*tert*-butyl)diphenylsilane as an orange oil (65.0 g, 78%). $[\alpha]_D^{20}$ = +10.3 (*c* 1, DCM); Other data as previously reported.

(*S*)-*N*-Allyl-*N*-(3-(*tert*-butyldiphenylsilyloxy)but-1-ynyl)-4-methylbenzenesulfonamide



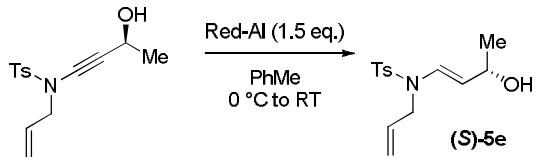
To a solution of *N*-allyl-4-methylbenzenesulfonamide (2.46 g, 11.6 mmol, 1.0 eq.) in toluene (200 mL) was added (*S*)-(4-bromobut-3-yn-2-yloxy)(*tert*-butyl)diphenylsilane (5.00 g, 12.9 mmol, 1.1 eq.), $CuSO_4.5H_2O$ (0.58 g, 2.34 mmol, 0.2 eq.), 1,10-phenanthroline (0.84 g, 4.68 mmol, 0.4 eq.) and finely ground K_3PO_4 (4.97 g, 23.2 mmol, 2 eq.). The reaction mixture was allowed to stir at 65 ^oC for 48 hours, after which was concentrated *in vacuo* and subjected to flash column chromatography (5-10% EtOAc/Petrol 40-60^o) to give (*S*)-*N*-allyl-*N*-(3-(*tert*-butyldiphenylsilyloxy)but-1-ynyl)-4-methylbenzenesulfonamide as a colourless oil (5.05 g, 83%). $[\alpha]_D^{20}$ = +20.0 (*c* 1, DCM); FTIR (film/cm^{-1}) υ_{max}: 3036 (m), 3105 (m), 2961 (m), 2932 (m), 1681 (m), 1647 (m), 1619 (s), 1582 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.06 (s, 9H), 1.41 (d, 3H, *J* = 6.4 Hz), 2.44 (s, 3H), 3.79 (ddt, 1H, *J* = 14.6, 6.3, 1.3 Hz), 3.85 (ddt, 1H, *J* = 14.6, 6.3, 1.3 Hz), 4.61 (app. quin, 1H, *J* = 6.4 Hz), 5.11–5.17 (m, 2H), 5.62 (ddt, 1H, *J* = 17.3, 10.2, 6.3 Hz), 7.28–7.46 (m, 7H), 7.66–7.72 (m, 4H), 7.72–7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.1, 21.6, 25.3, 26.5, 26.8, 54.0, 60.1, 73.2, 119.6, 127.4, 127.6, 127.8, 129.6, 131.0, 133.7, 134.8, 135.7, 135.9, 144.4; HRMS (ESI, +ve) *m/z* calcd. for $C_{30}H_{35}NNaO_3SSi$ 540.2005, found 540.2209 $(M+Na)^+$.

_N_-Allyl-_N_-(3-hydroxy-but-1-ynyl)-4-methyl-benzenesulfonamide



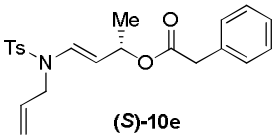
To a solution of *N*-allyl-*N*-(3-(*tert*-butyldiphenylsilyloxy)but-1-ynyl)-4-methylbenzenesulfonamide (3.72 g, 7.20 mmol, 1.0 eq.) in THF (200 mL) at 0 ^oC was added TBAF (1M soln. in THF, 14.4 mL, 14.4 mmol, 2.0 eq.). The reaction mixture was allowed to stir for 2 hours whilst slowly warming to RT, until complete by TLC, followed by concentration in vacuo and subjection to flash column chromatography (10% EtOAc/Petrol 40-60^o) to give *N*-allyl-*N*-(3-hydroxy-but-1-ynyl)-4-methyl-benzenesulfonamide as a faint yellow oil (1.40 g, 70%). $[\alpha]_D^{20}$ = -38.0 (*c* 1, DCM); FTIR (film/cm^{-1}) υ_{max}: 2978 (m), 2929 (m), 1697 (m), 1596 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (d, 3H, *J* = 6.6 Hz), 2.03 (d, 1H, *J* = 5.2 Hz), 2.49 (s, 3H), 3.93–4.04 (m, 2H), 4.67 (app quin, 1H, *J* = 6.6 Hz), 5.22–5.31 (m, 4H), 5.71 (ddt, 1H, *J* = 17.1, 10.2, 6.4 Hz), 7.39 (d, 2H, *J* = 8.3 Hz), 7.83 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 24.4, 26.5, 54.1, 58.5, 73.1, 120.0, 127.7, 129.7, 130.8, 134.6, 144.8; HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{18}NO_3S$ 280.1007, found 280.1004 $(M+H)^+$.

(*S*)-(*E*)-*N*-Allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide



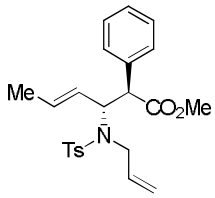
To a solution of (*S*)-*(E)*-*N*-allyl-4-methyl-*N*-(3-oxobut-1-enyl)benzenesulfonamide (0.10 g, 0.36 mmol, 1.0 eq.) in toluene (5 mL) at 0 ^{o}C was added Red-Al (0.11 µl, 0.53 mmol, 1.5 eq.) by portionwise addition. The reaction mixture was allowed to stir whilst slowly warming to RT over 4 hours and then was quenched by the addition of Na2SO4.10H_2O. After the solution cleared the reaction mixture was filtered through celite and concentrated in vacuo to yield (*S*)-(*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide as a colourless oil (0.07 g, 76%). $[\alpha]_D^{20}$ = -11.0 (*c* 1, DCM); Other data as previously reported for racemic compound.

(*S*,*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate ((*S*)-10e)



EDCi (0.68 g, 3.55 mmol) in DCM (100 mL), triethylamine (0.49 mL, 3.55 mmol), DMAP (0.02 g, 0.18 mmol), phenylacetic acid (0.48 g, 3.55 mmol) and (*S*)-(*E*)-*N*-allyl-*N*-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide **(S)-5e** 0.50 g, 1.78 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (*S*,*E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate **(*S*)-10e** as a yellow oil (0.53 g, 74%); $[\alpha]_D^{20}$ = -8.0 (*c* 1, DCM). All data as previously recorded for racemic compound.

(*2R,3R,E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate ((*2R,3S*)-11d)

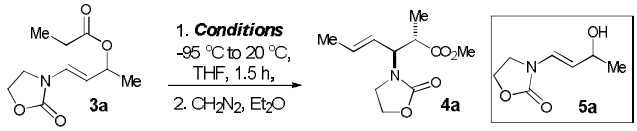


(2R,3R)-11d

LiHMDS (1M in toluene, 0.63 ml, 0.63 mmol), TMSCl (0.19 ml, 2.91 mmol) and (*S,E*)-4-(*N*-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate **(*S*)-10e** (0.10 g, 0.48 mmol) in THF (1 ml) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (*2R,3R,E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate **(*S*)-11d** as a white solid (0.08 g, 71%, d.r. >25:1). M.p. 105–107 ˚C; $[\alpha]_D^{20}$ = -15.0 (*c* 1, DCM). All other data as previously recorded for racemic compound.

Initial optimisation Attemtpts

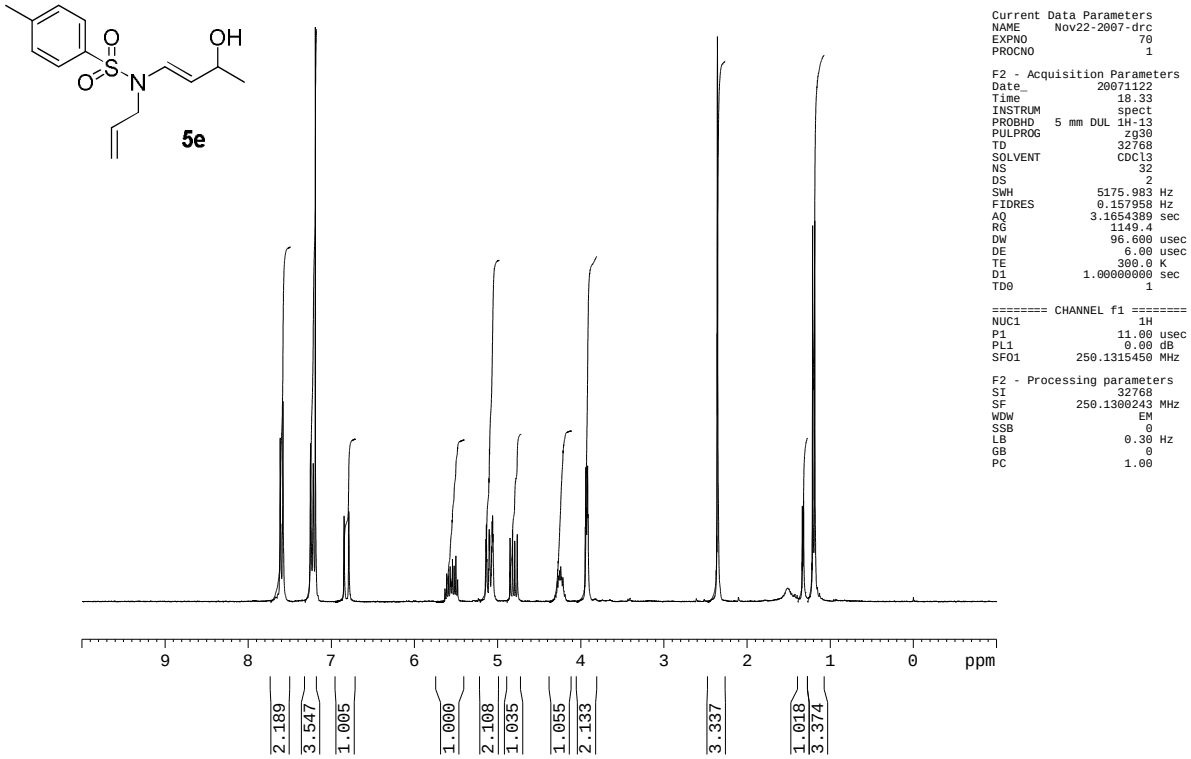
Table 1 Propionate Diastereoselectivity Explorations

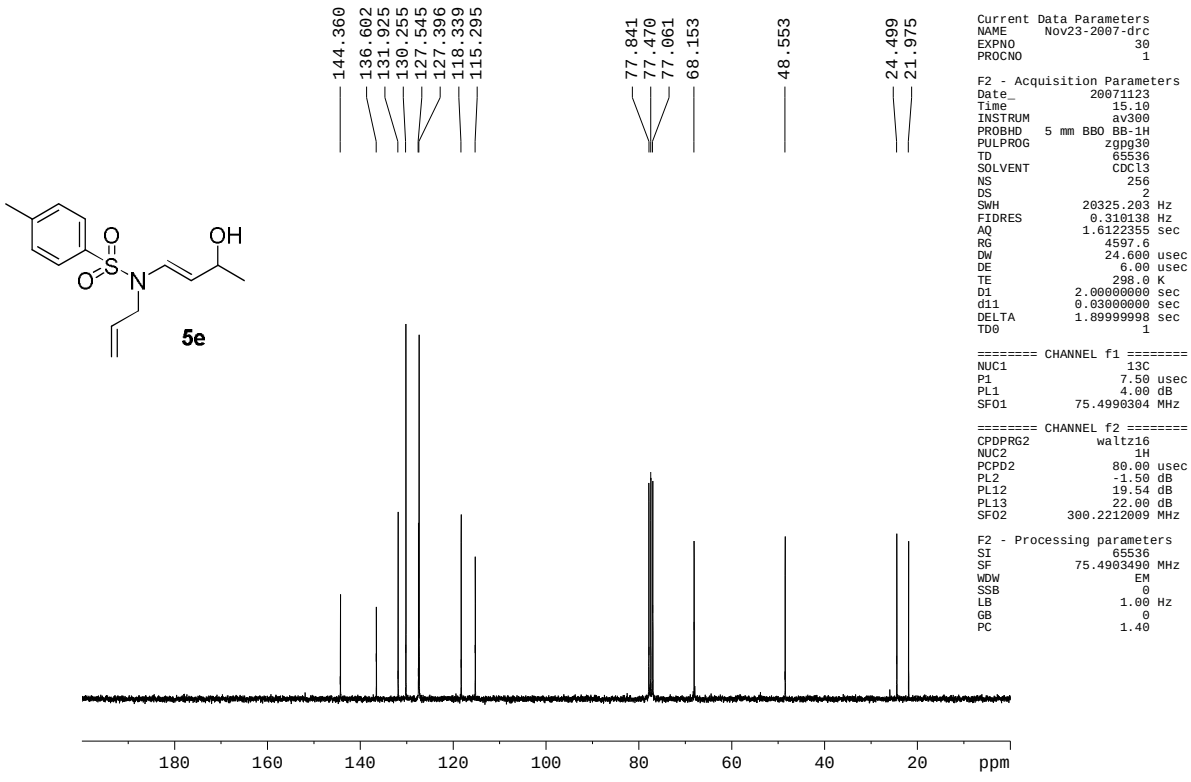


Entry	Conditions	Yield **4a** (%)	dr[a]
1	LiHMDS (1.3 equiv), Me_3SiCl, (1.3 equiv)	72	2:1
2	LiHMDS (1.3 equiv), Me_3SiCl (6 equiv)	70	2:1
3	NaHMDS (1.3 equiv), Me_3SiCl (1.3 equiv)	0[b]	-
4	KHMDS (1.3 equiv), Me_3SiCl (1.3 equiv)	0[c]	-
5	$MgHMDS_2$ (1.3 equiv), Me_3SiCl (1.3 equiv)	0[c]	-
6	LDA (1.3 equiv), Me_3SiCl (1.3 equiv)	0[c]	-
7	Et_3N (1.5 equiv), TIPSOTf (1.1 equiv)[d]	0[c]	-
8	LDA (1.5 equiv), HMPA (5 equiv)$ClP(O)(OEt)_2$ (1.5 equiv)[e]	0[c]	-
9	LiHMDS (1.3 equiv), HMPA (23%), Me_3SiCl (1.3 equiv) [f]	0[c]	-
10	LiHMDS (1.3 equiv), HMPA (23%), Me_3SiCl (1.3 equiv)[g]	0[b]	-

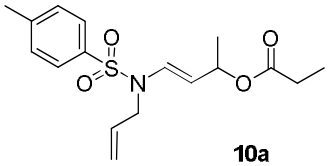
[a] *anti/syn*, measured by ^1H NMR analysis of crude reaction mixtures. [b] Allylic alcohol **5a** recovered (99%). [c] Intractable mixture. [d] In CH_2Cl_2 at 20 °C. [e] Reaction conducted -78 °C→-10 °C and quenched with MeOH. [f] Quenched with 1:1 1M HCl(aq.)/brine. [g] Quenched with MeOH..

NMR Spectra





WH4-063-A1



10a

BRUKER

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Current Data Parameters
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EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20081107
Time              14.25
INSTRUM           spect
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PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                45.2
DW               48.400 usec
DE                6.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.50 usec
PL1              -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
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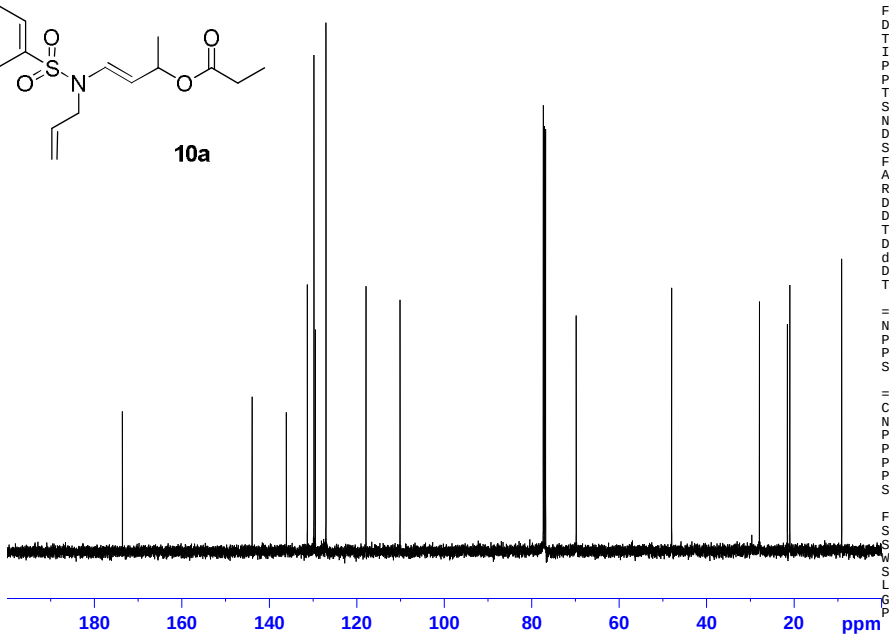
10a



BRUKER

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Current Data Parameters
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EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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Time              14.20
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PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  65
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 362
DW               16.800 usec
DE                6.00 usec
TE               298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                7.50 usec
PL1               0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL12              17.98 dB
PL13              20.00 dB
PL2               -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
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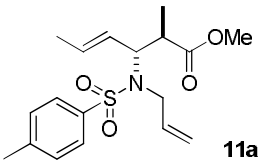
WH9-097-B1



11a

Current Data Parameters
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PROCNO 1

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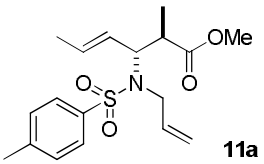
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 362
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



11a

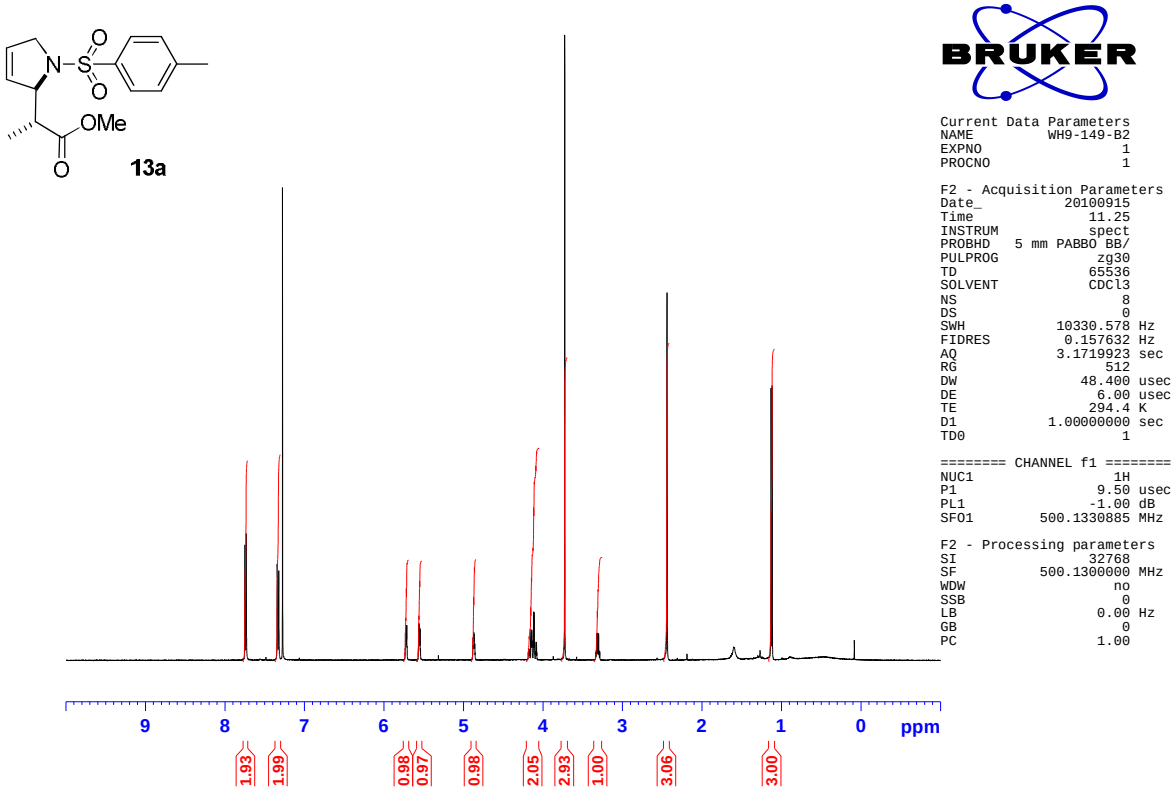
Current Data Parameters
NAME WH9-097-B1
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100906
Time 13.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

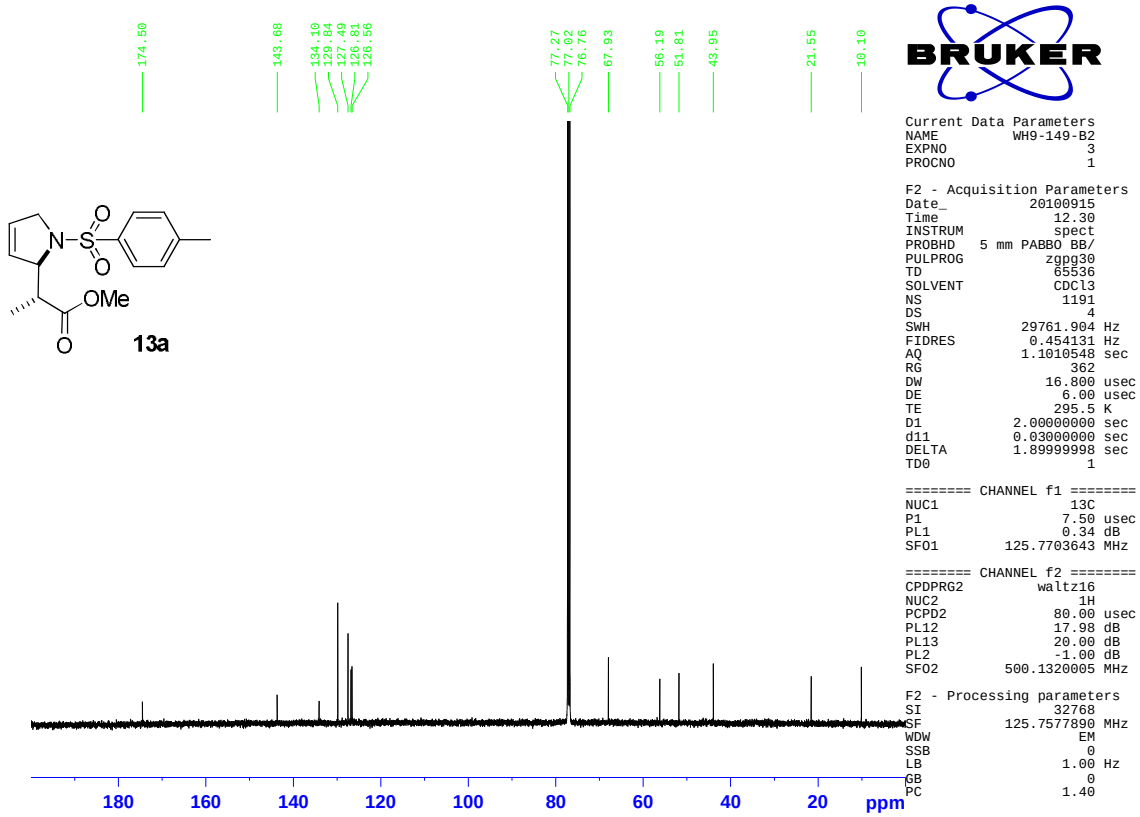
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz

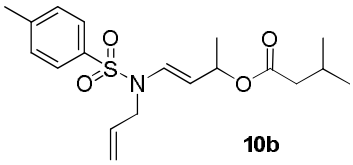
F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



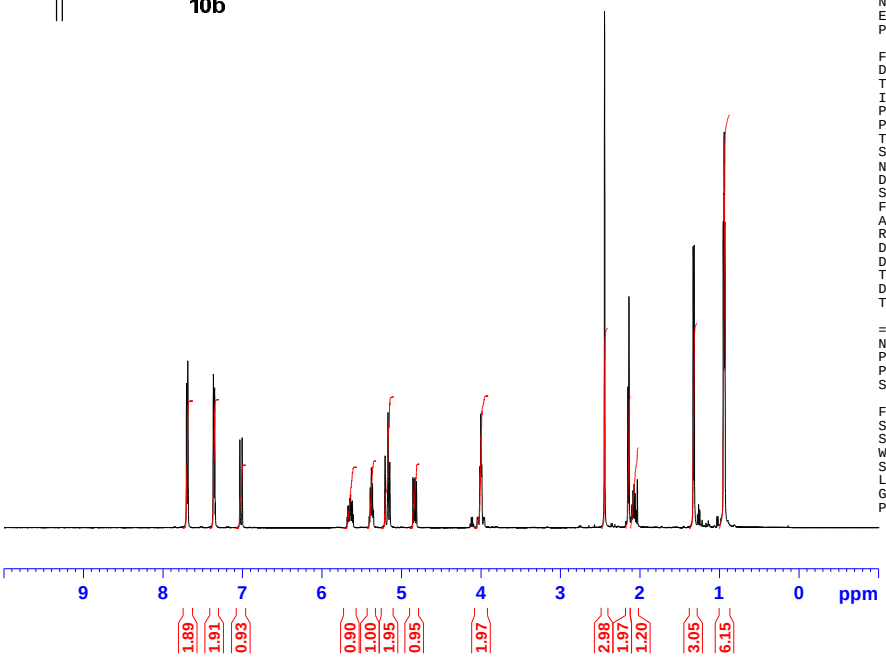

```
Current Data Parameters
NAME          WH9-149-B2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100915
Time               11.25
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   512
DW                48.400 usec
DE                 6.00 usec
TE                294.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```




```
Current Data Parameters
NAME          WH9-149-B2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100915
Time               12.30
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1191
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                295.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2               -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

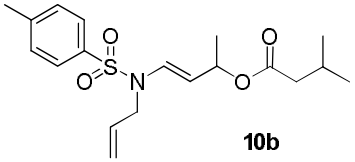


10b

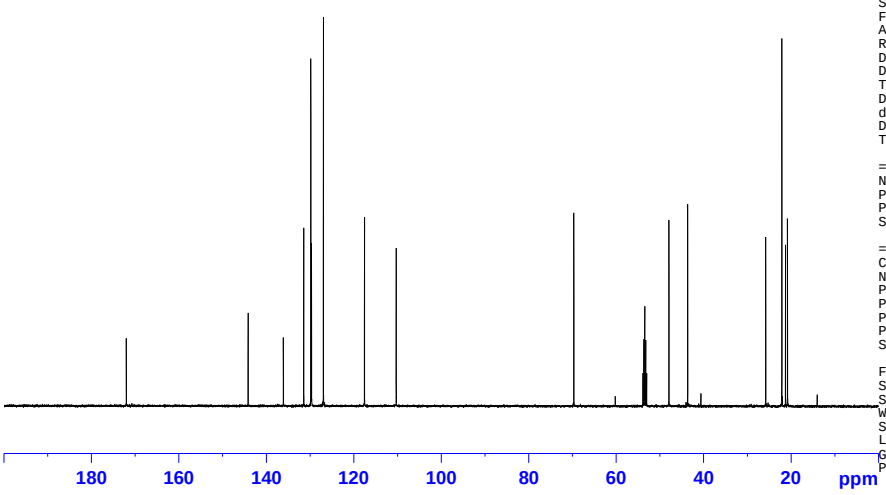


BRUKER

```
Current Data Parameters
NAME          WH9-043-B1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100820
Time               15.57
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT           CD2Cl2
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                  22.6
DW                48.400 usec
DE                 6.00 usec
TE                294.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```

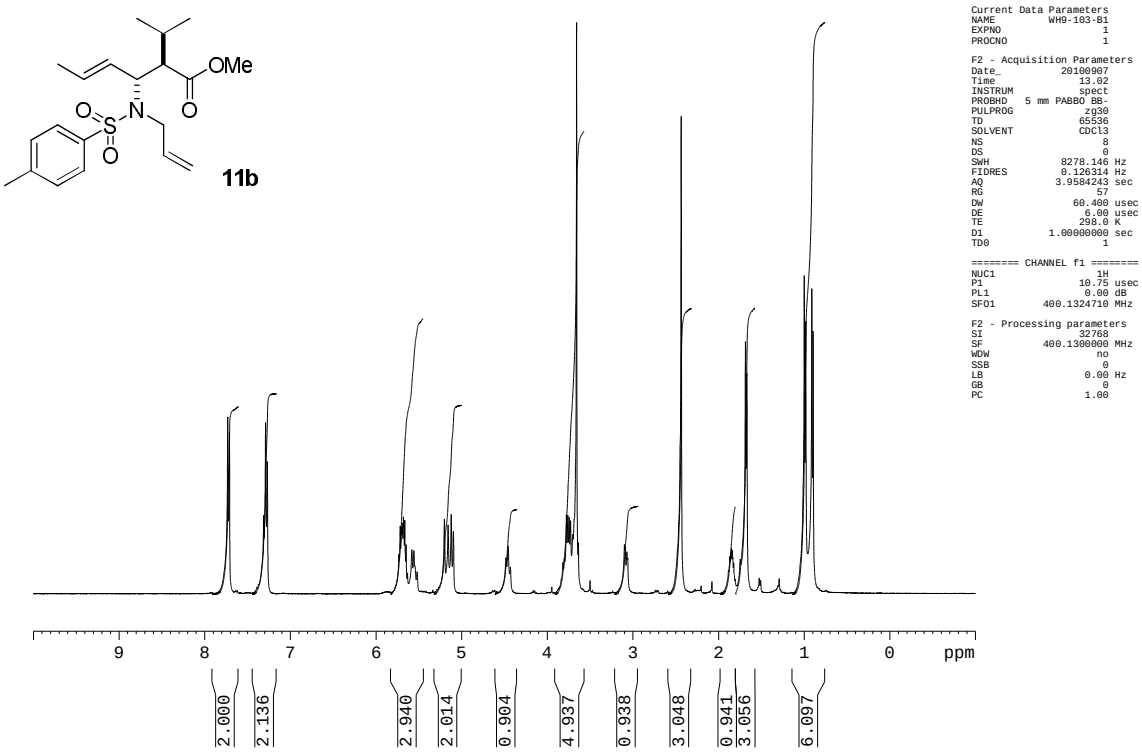


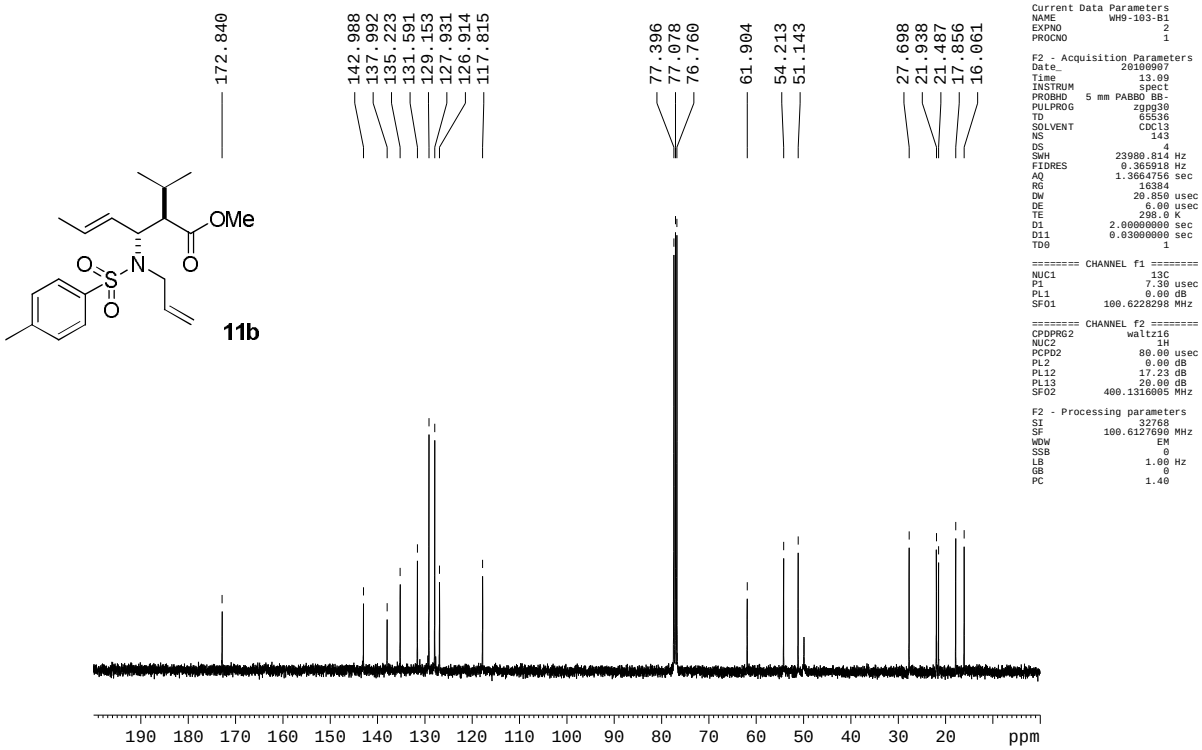
10b

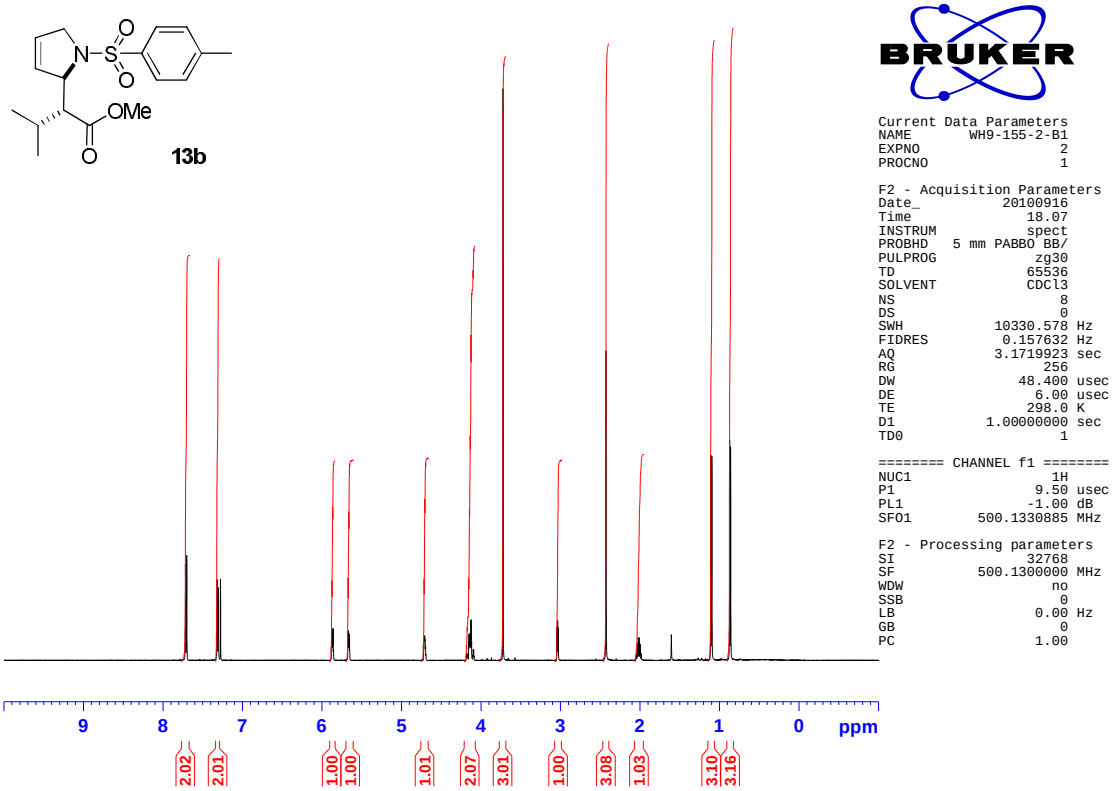


BRUKER

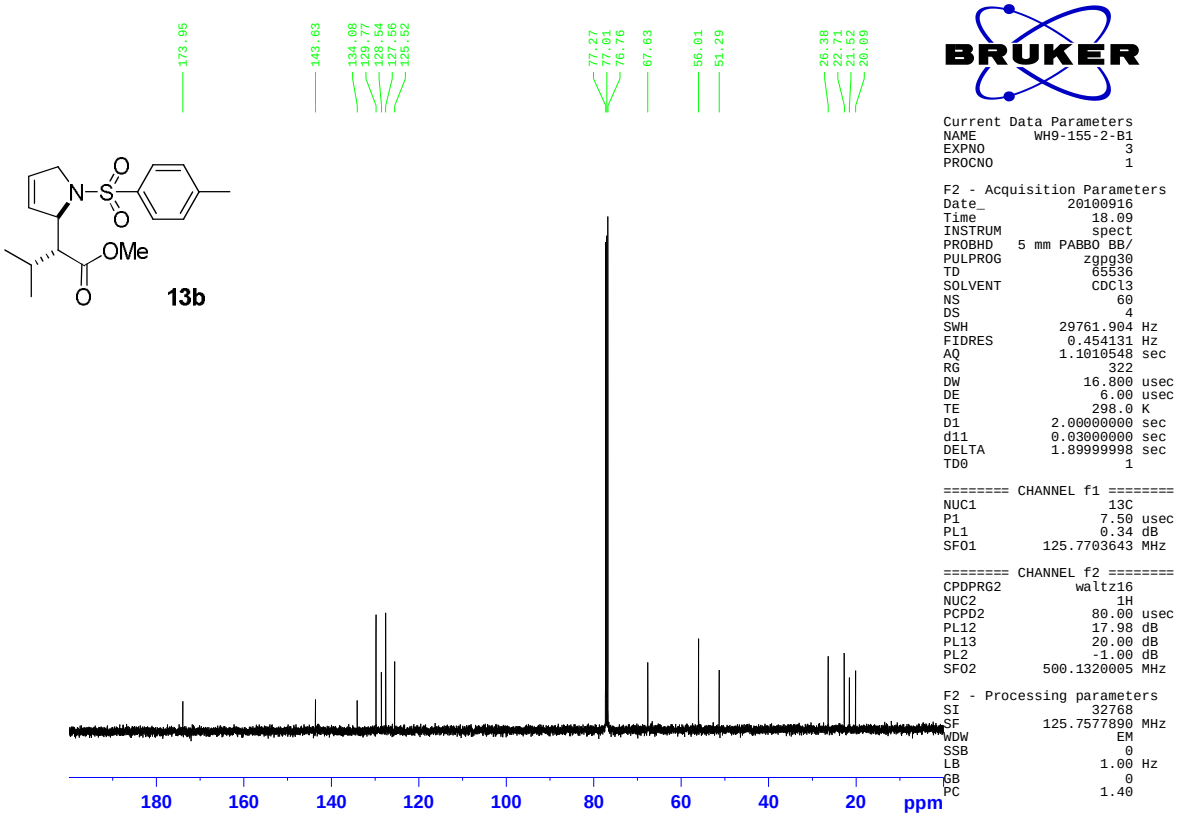
```
Current Data Parameters
NAME          WH9-043-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100820
Time               16.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                    93
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                295.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2               -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```



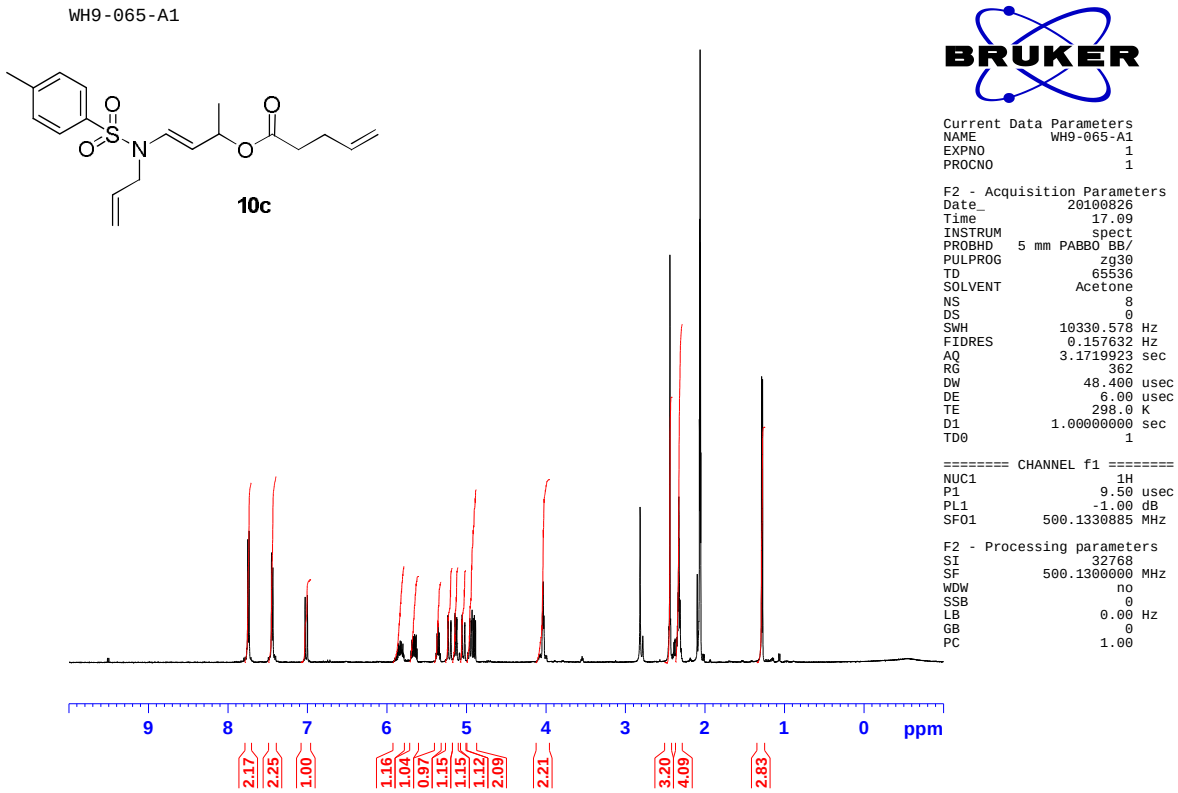




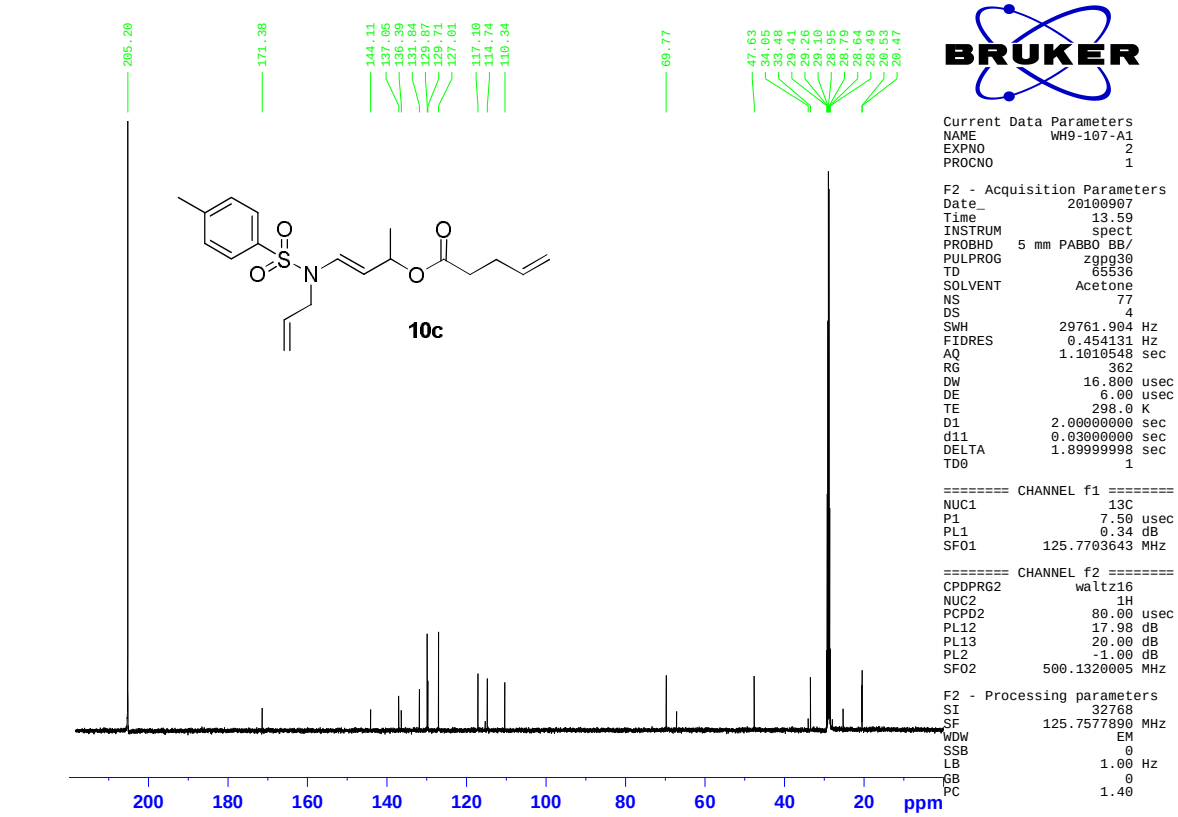

```
Current Data Parameters
NAME       WH9-155-2-B1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100916
Time              18.07
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                 256
DW              48.400 usec
DE               6.00 usec
TE              298.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               9.50 usec
PL1             -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                 1.00
```



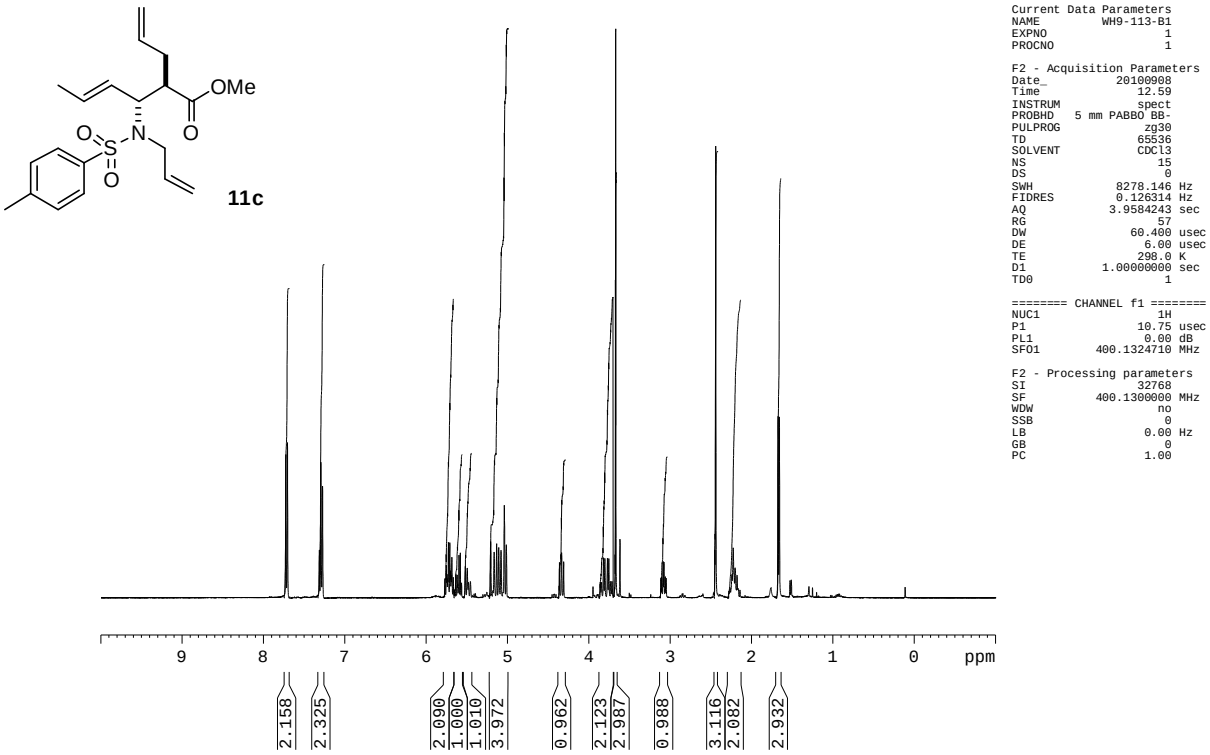

```
Current Data Parameters
NAME       WH9-155-2-B1
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20100916
Time              18.09
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  60
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 322
DW              16.800 usec
DE               6.00 usec
TE              298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               7.50 usec
PL1              0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL12             17.98 dB
PL13             20.00 dB
PL2              -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                 1.40
```

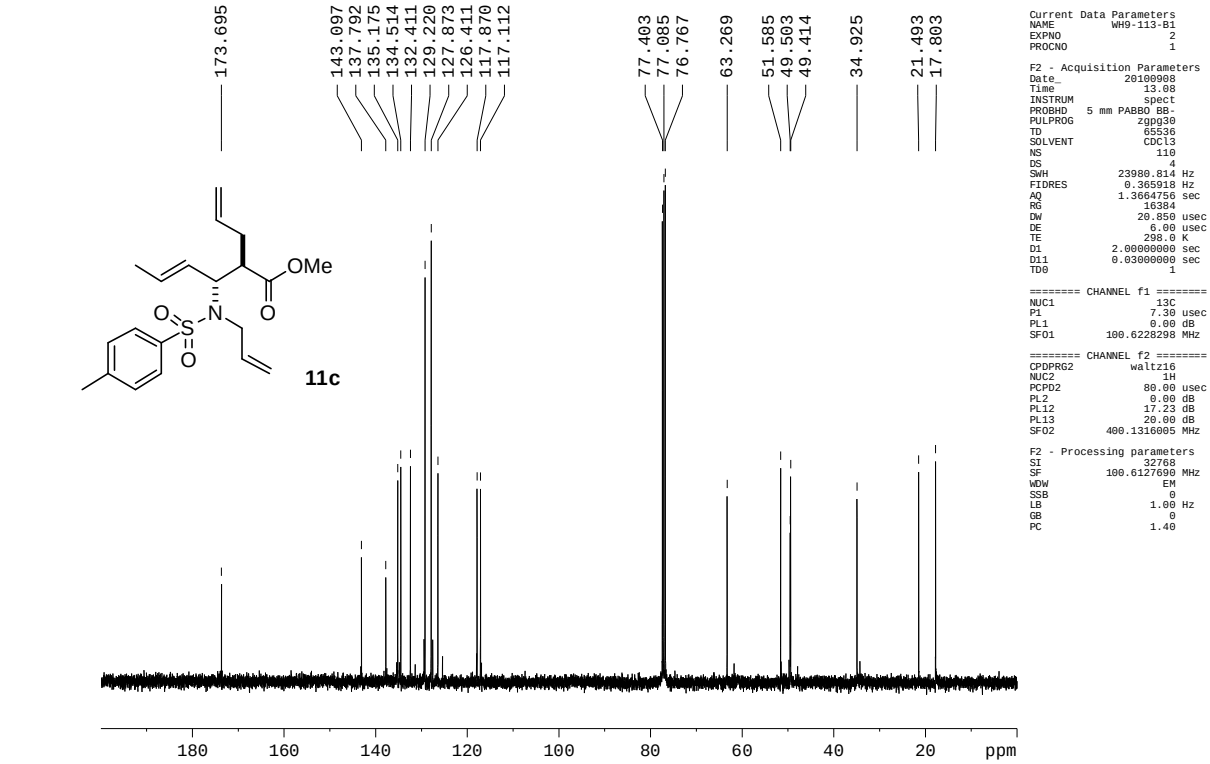


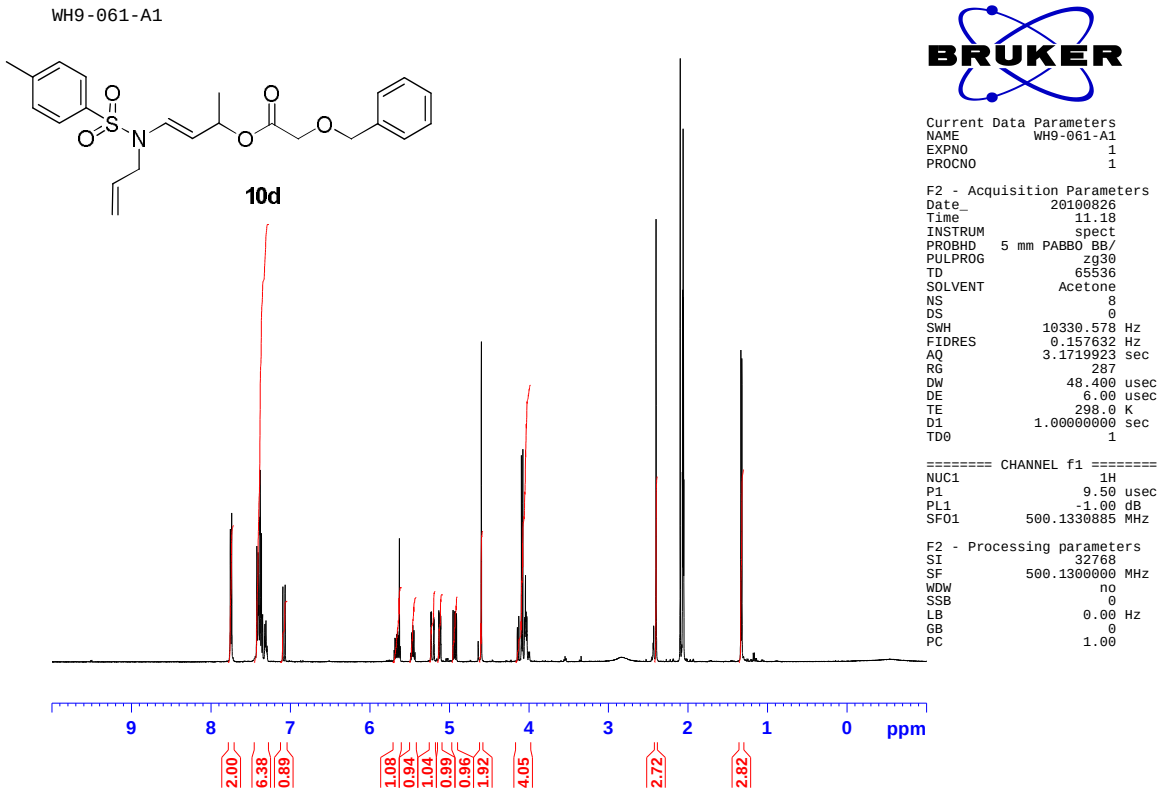

```
Current Data Parameters
NAME          WH9-065-A1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20100826
Time              17.09
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT         Acetone
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                  362
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.50 usec
PL1              -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```



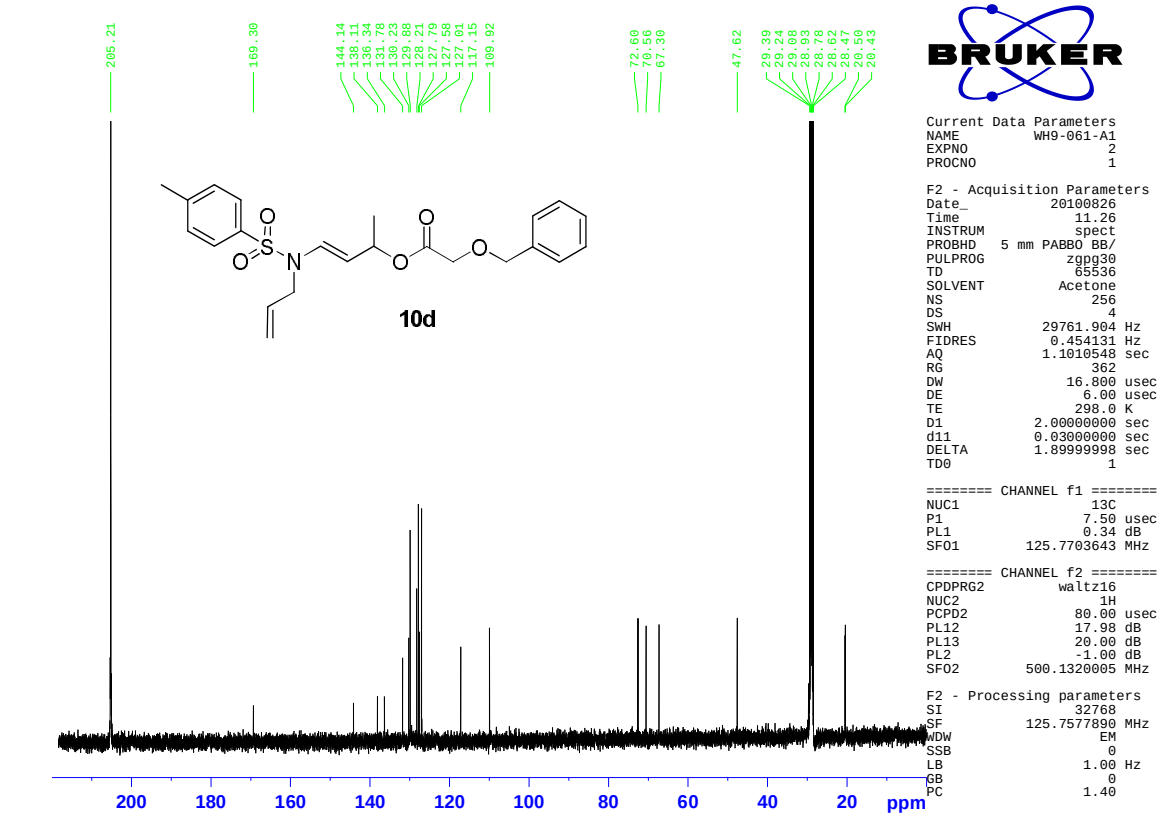

```
Current Data Parameters
NAME          WH9-107-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20100907
Time              13.59
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT         Acetone
NS                   77
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                  362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                7.50 usec
PL1               0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL12              17.98 dB
PL13              20.00 dB
PL2               -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



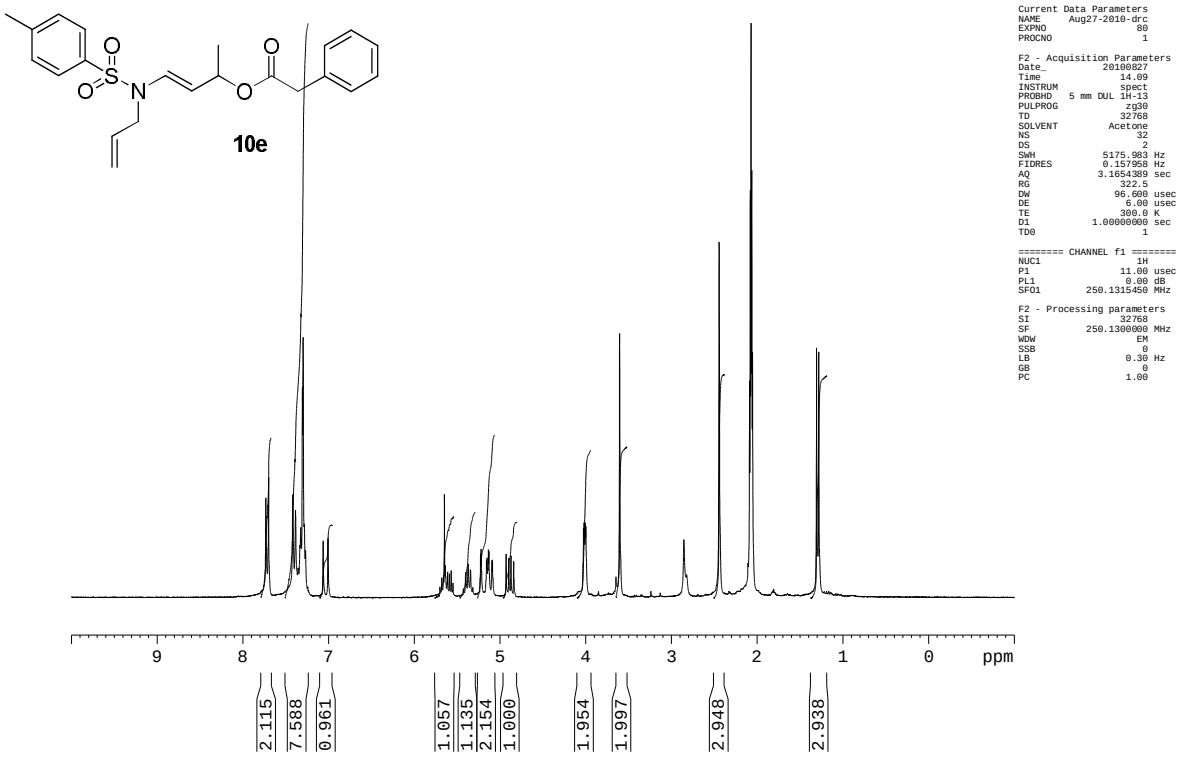


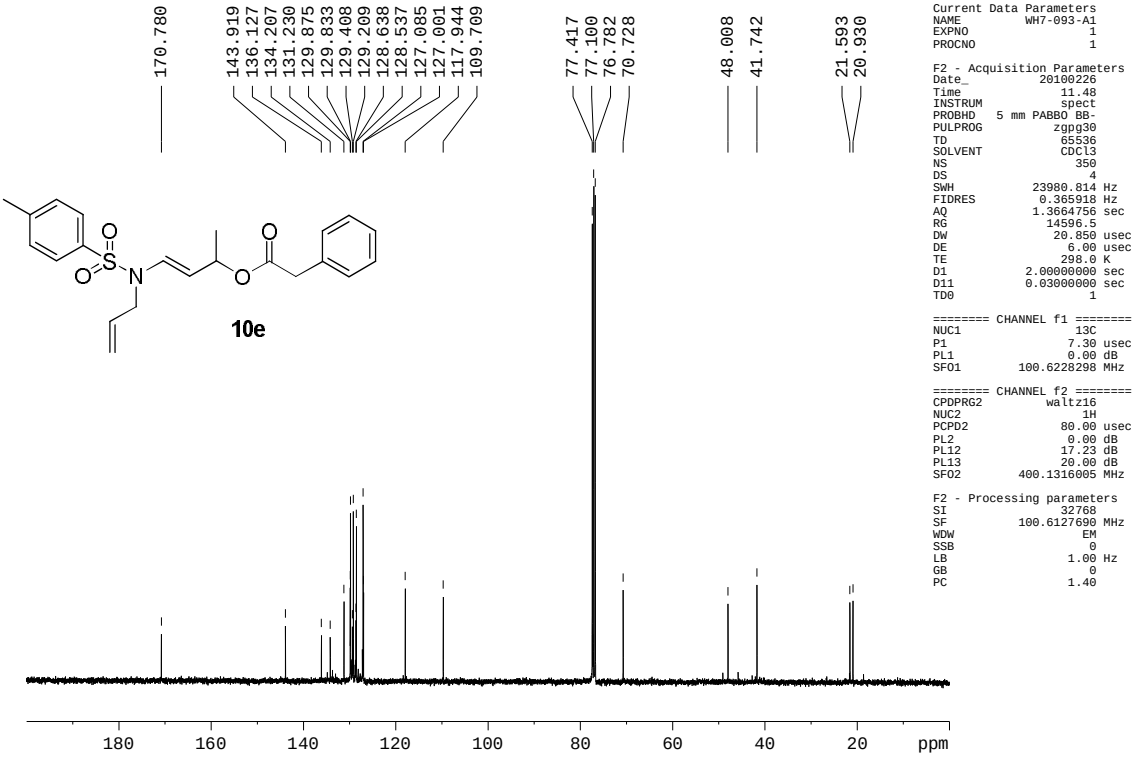


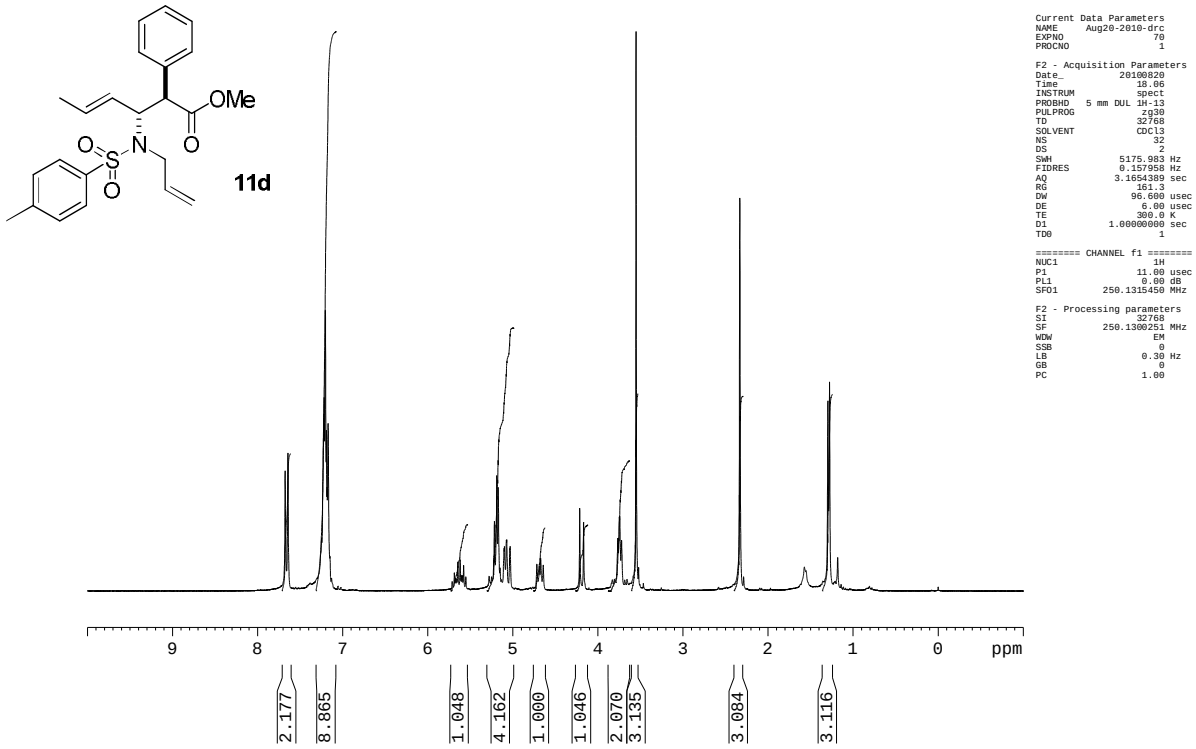

```
Current Data Parameters
NAME          WH9-061-A1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               11.18
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                   287
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PL1                -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



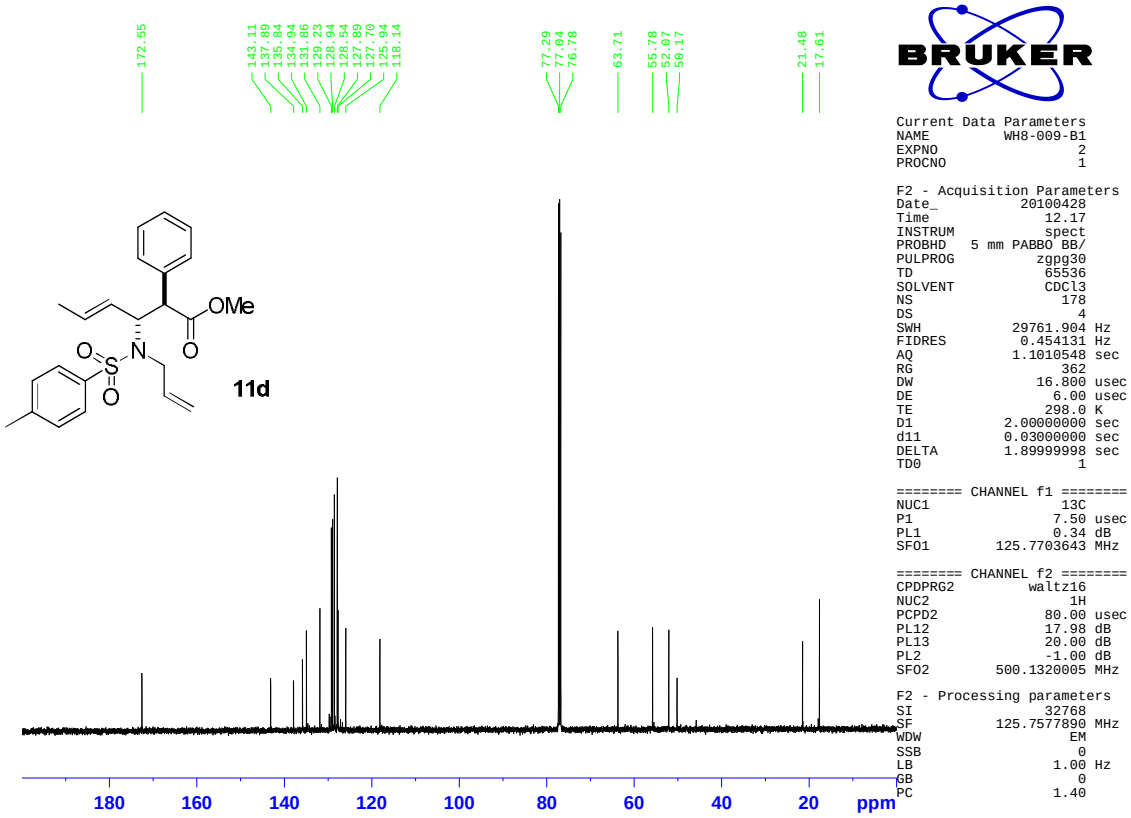

```
Current Data Parameters
NAME          WH9-061-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               11.26
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                   256
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.50 usec
PL1                 0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2                -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


10e
Current Data Parameters
NAME Aug27-2010-drc
EXPNO 80
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100827
Time 14.09
INSTRUM spect
PROBHD 5 mm DUL 1H-13
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 32
DS 2
SWH 5175.983 Hz
FIDRES 0.157958 Hz
AQ 3.1654389 sec
RG 322.5
DW 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 0.00 dB
SFO1 250.1315450 MHz
F2 - Processing parameters
SI 32768
SF 250.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 0 ppm
2.115 7.588 0.961 1.057 1.135 2.154 1.000 1.954 1.997 2.948 2.938

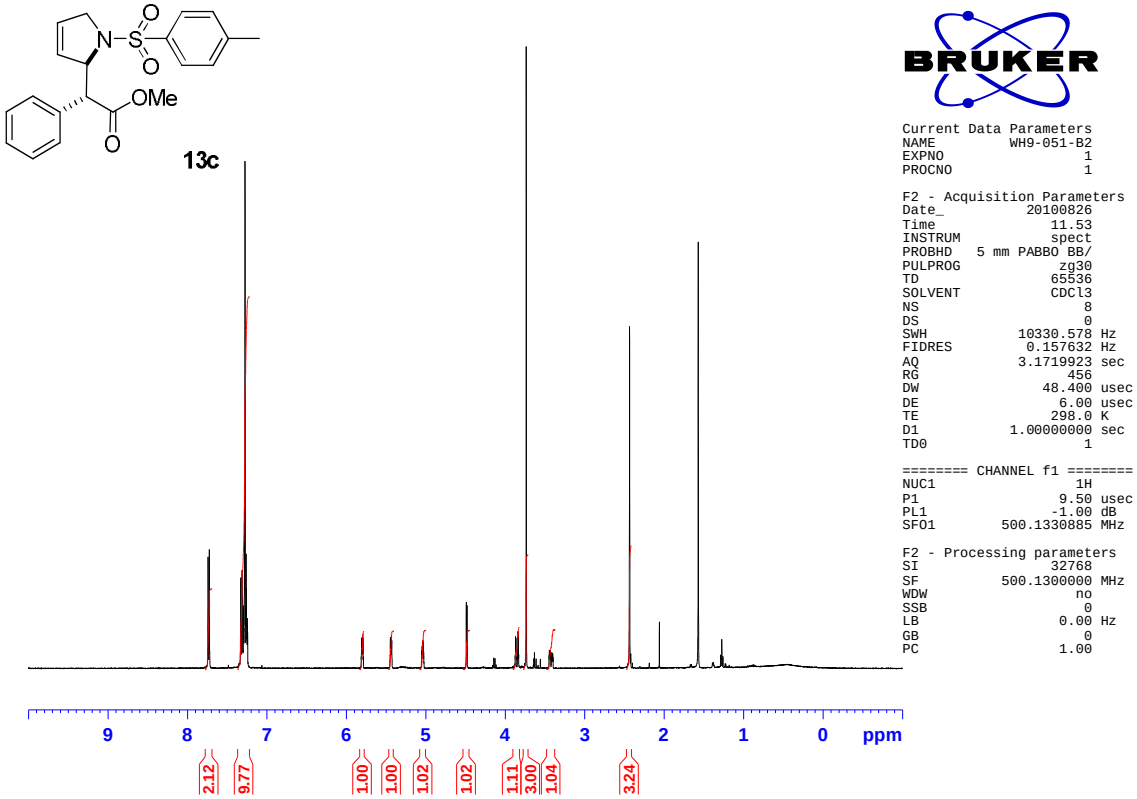

170.780
143.919 136.127 134.207 131.230 129.875 129.833 129.408 129.209 128.638 128.537 127.085 127.001 117.944 109.709
77.417 77.100 76.782 70.728
48.008 41.742
21.593 20.930
10e
Current Data Parameters
NAME WH7-093-A1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100226
Time 11.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 350
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 14596.5
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.30 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 160 140 120 100 80 60 40 20 ppm



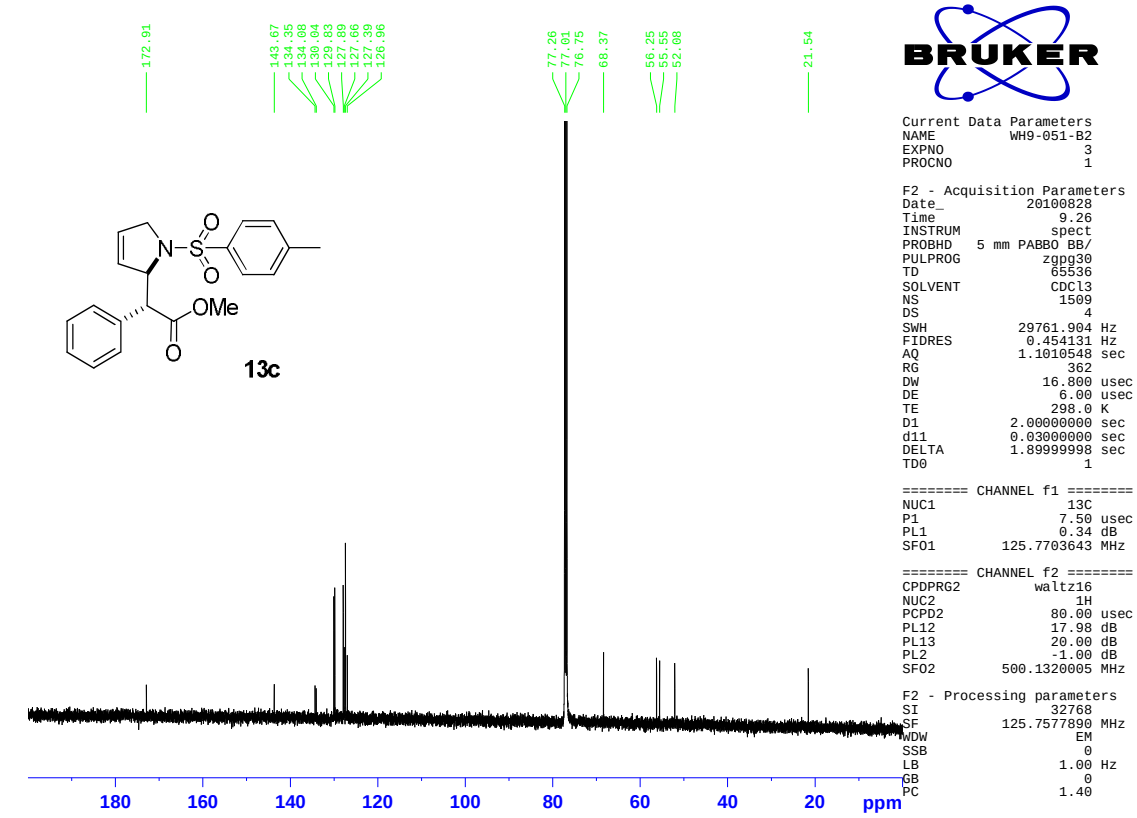

```
Current Data Parameters
NAME      Aug20-2010-drc
EXPNO                70
PROCNO                1

F2 - Acquisition Parameters
Date_          20100820
Time              18.06
INSTRUM           spect
PROBHD   5 mm DUL 1H-13
PULPROG           zg30
TD               32768
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           5175.983 Hz
FIDRES        0.157958 Hz
AQ            3.1654389 sec
RG                161.3
DW               96.600 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.00 usec
PL1                0.00 dB
SFO1        250.1315450 MHz

F2 - Processing parameters
SI                32768
SF          250.1300251 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



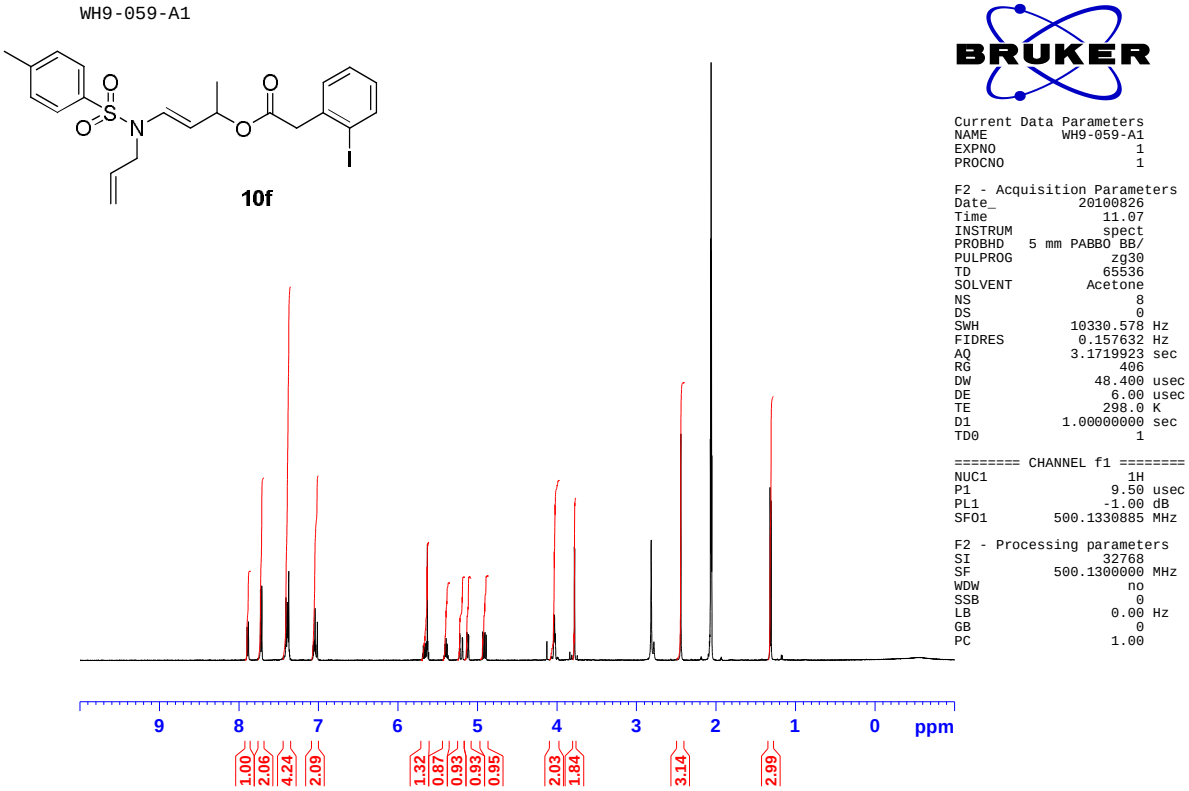

```
Current Data Parameters
NAME          WH8-009-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20100428
Time              12.17
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  178
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                  362
DW               16.800 usec
DE                6.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                7.50 usec
PL1               0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            80.00 usec
PL12              17.98 dB
PL13              20.00 dB
PL2               -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



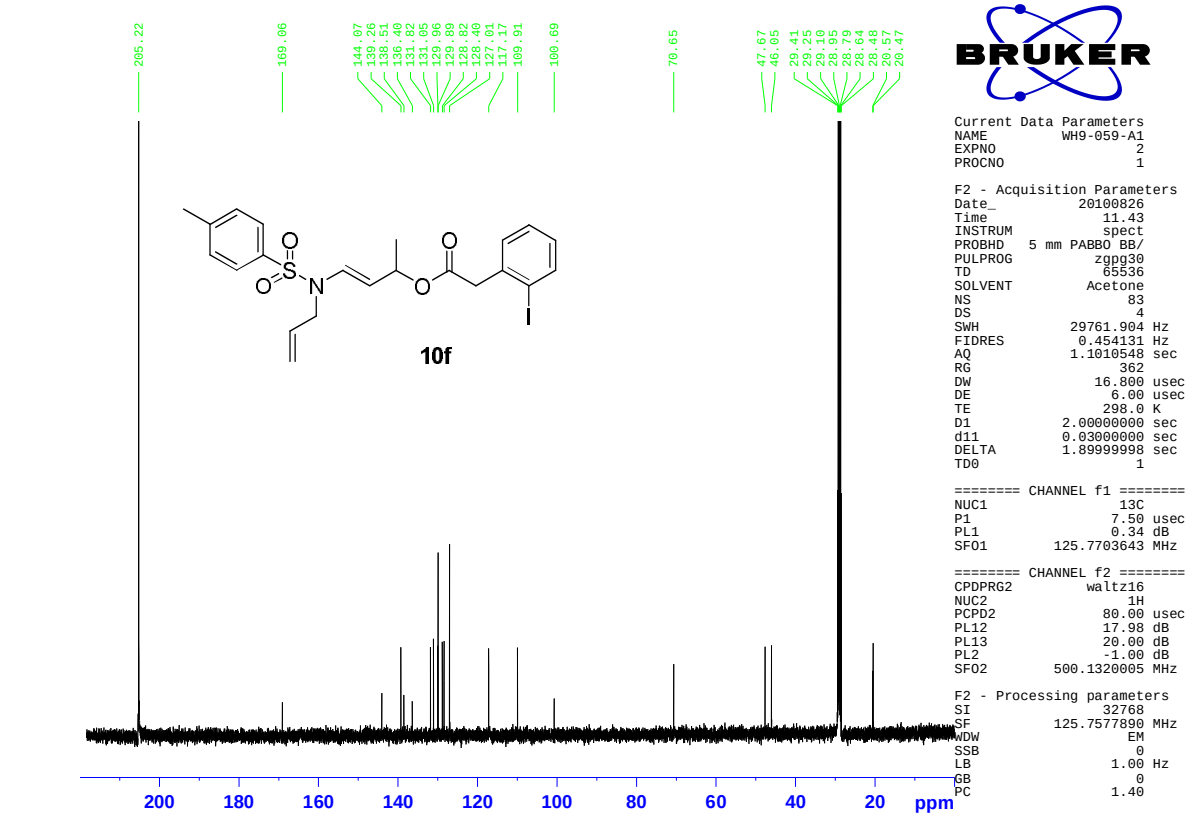

```
Current Data Parameters
NAME          WH9-051-B2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               11.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   456
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```




```
Current Data Parameters
NAME          WH9-051-B2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100828
Time                9.26
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1509
DS                     4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2                -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

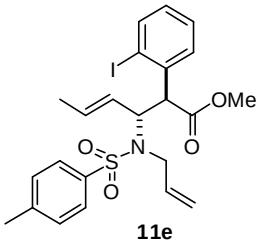



```
Current Data Parameters
NAME          WH9-059-A1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               11.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   406
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```



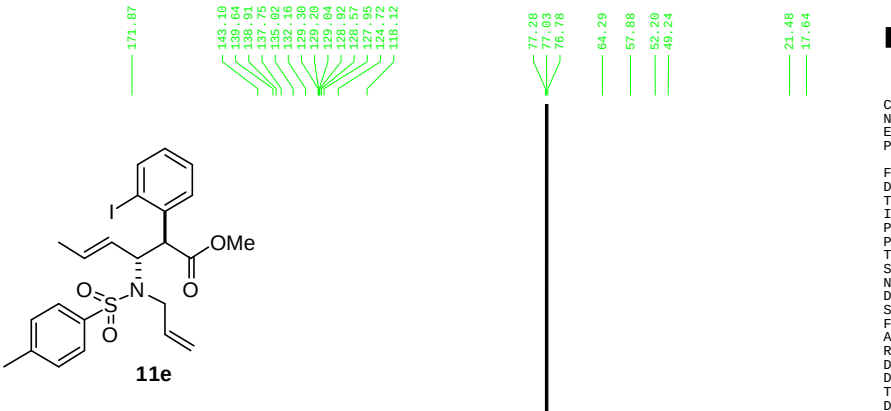

```
Current Data Parameters
NAME          WH9-059-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               11.43
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT          Acetone
NS                    83
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2                -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

WH9-099-B1

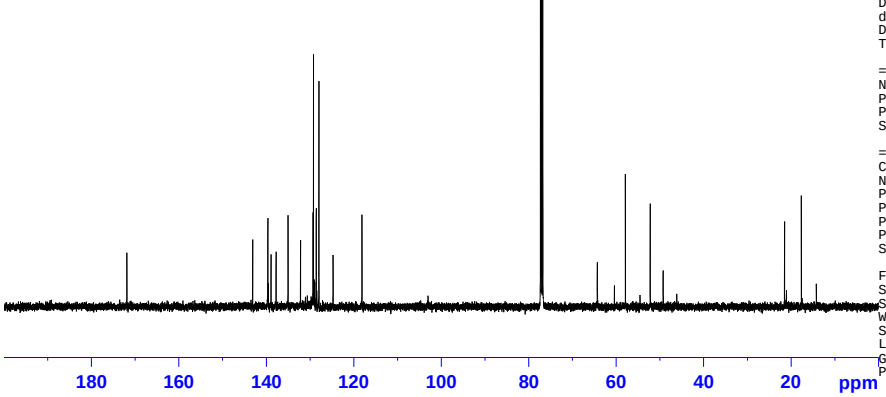


11e


```
Current Data Parameters
NAME          WH9-099-B1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100906
Time               11.22
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   181
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```

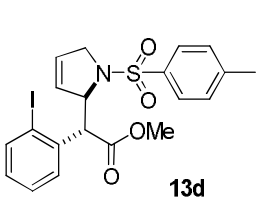


11e




```
Current Data Parameters
NAME          WH9-099-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100906
Time               11.31
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2               -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

WH9-145-2-C1

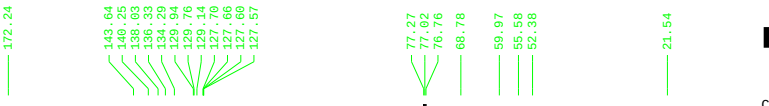


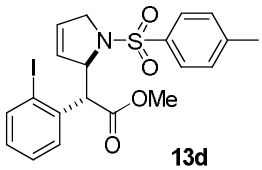
Current Data Parameters
NAME WH9-145-2-C1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100916
Time 11.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 362
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00





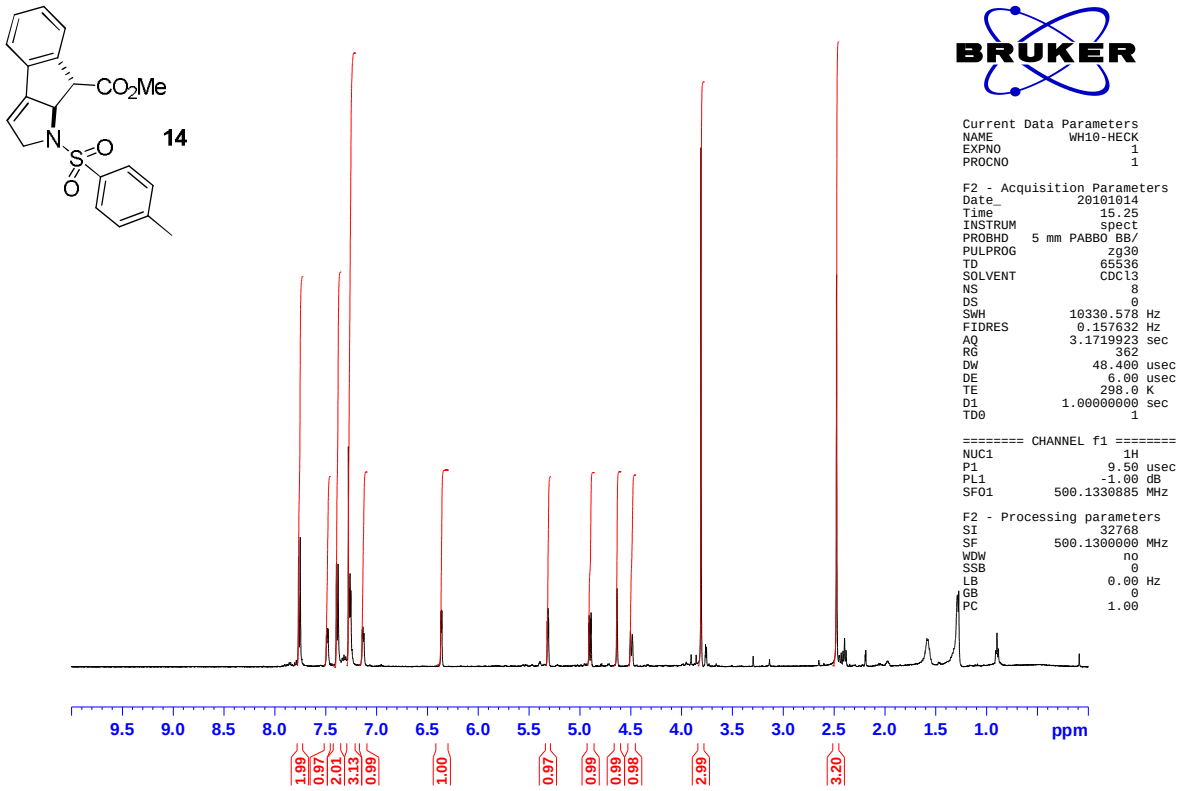
Current Data Parameters
NAME WH9-145-2-C1
EXPNO 2
PROCNO 1

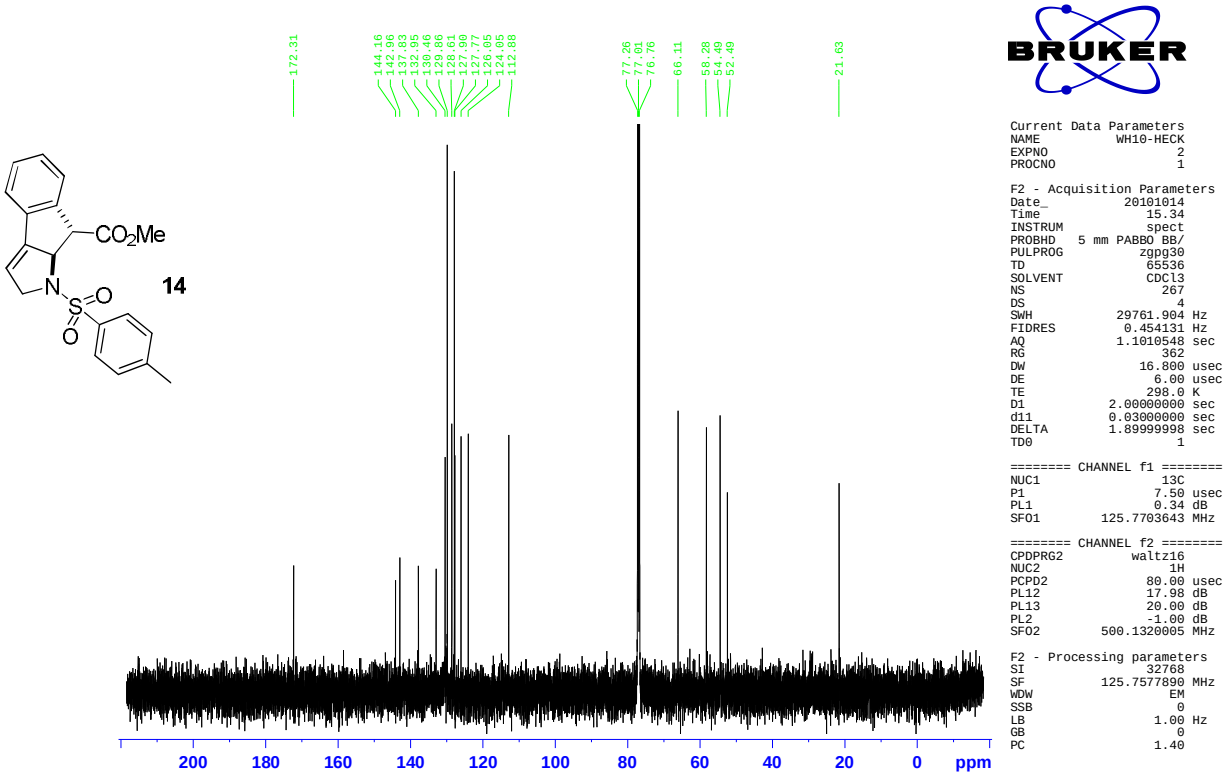
F2 - Acquisition Parameters
Date_ 20100916
Time 11.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 575
DW 16.800 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

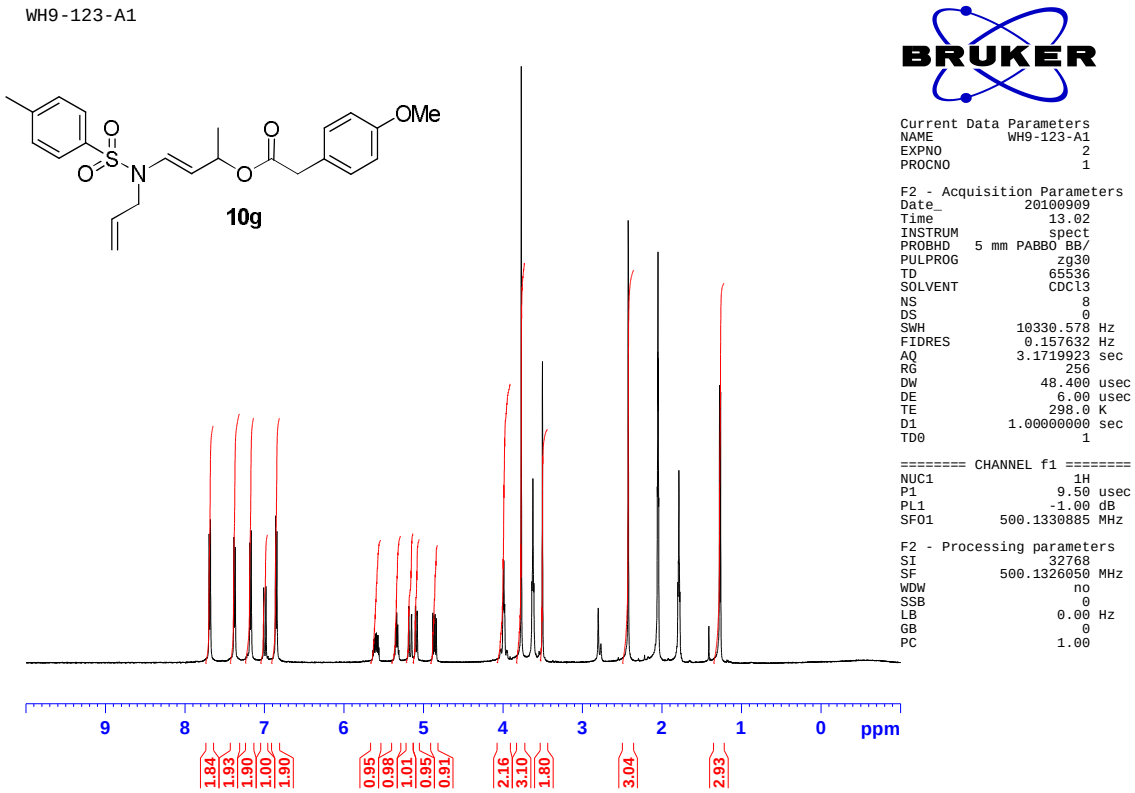
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz

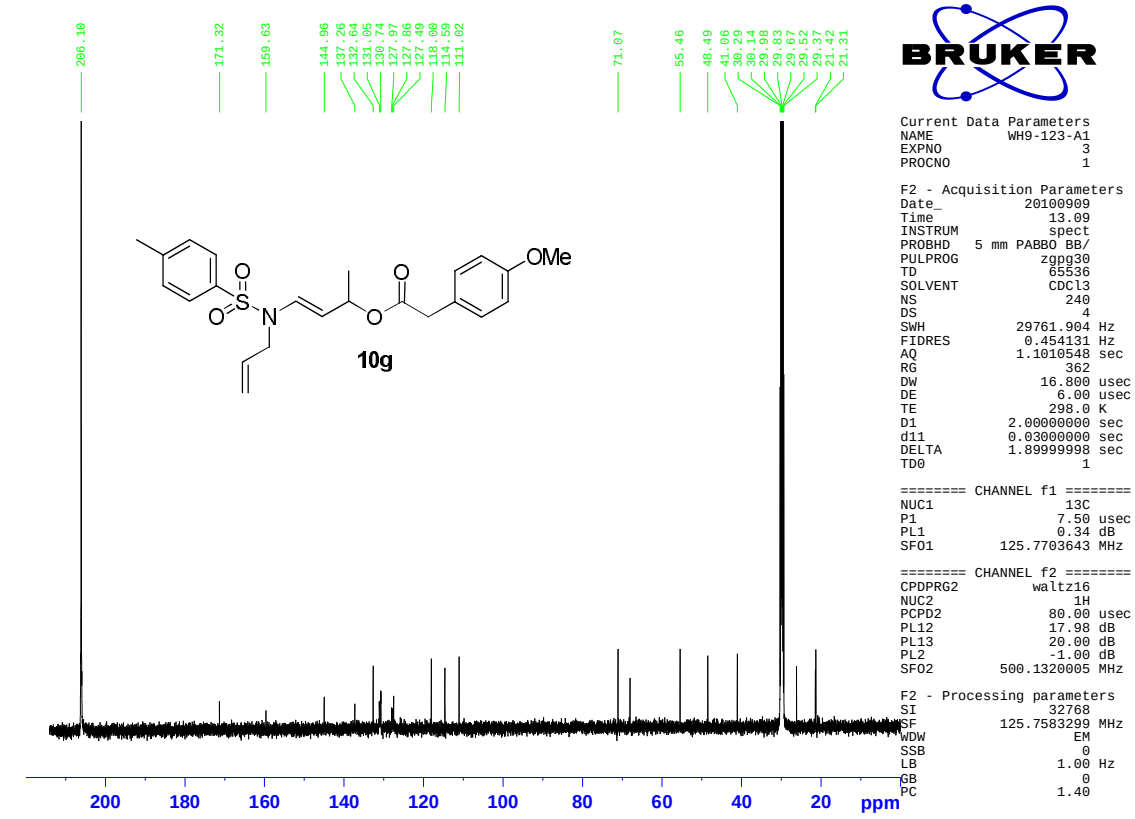
F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


CO2Me
N
S
O
O
14
BRUKER
Current Data Parameters
NAME WH10-HECK
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101014
Time 15.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 362
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99 0.97 2.01 3.13 0.99 1.00 0.97 0.99 0.99 0.98 2.99 3.20

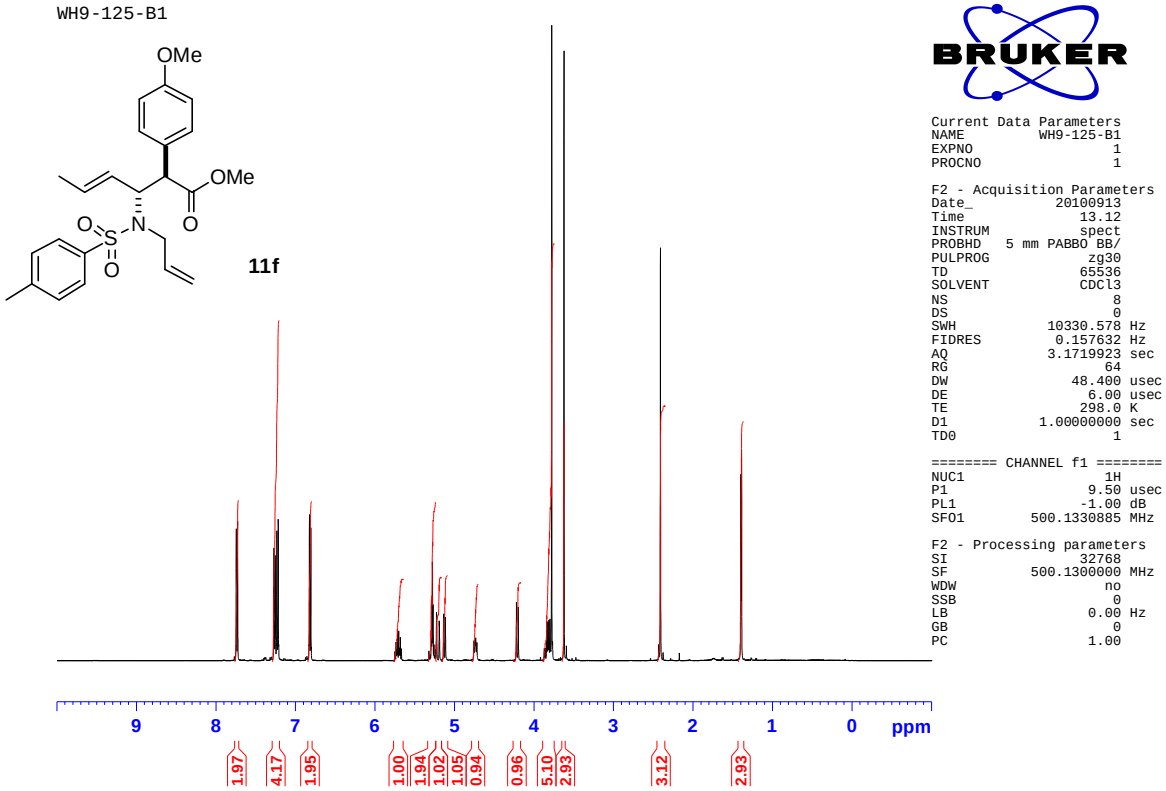

172.31
144.16
142.96
137.83
132.95
130.46
128.86
128.61
128.50
127.77
126.05
124.05
112.88
77.26
77.01
76.76
66.11
58.28
54.49
52.49
21.63
CO2Me
N
S
O
O
14
BRUKER
Current Data Parameters
NAME WH10-HECK
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101014
Time 15.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 267
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm



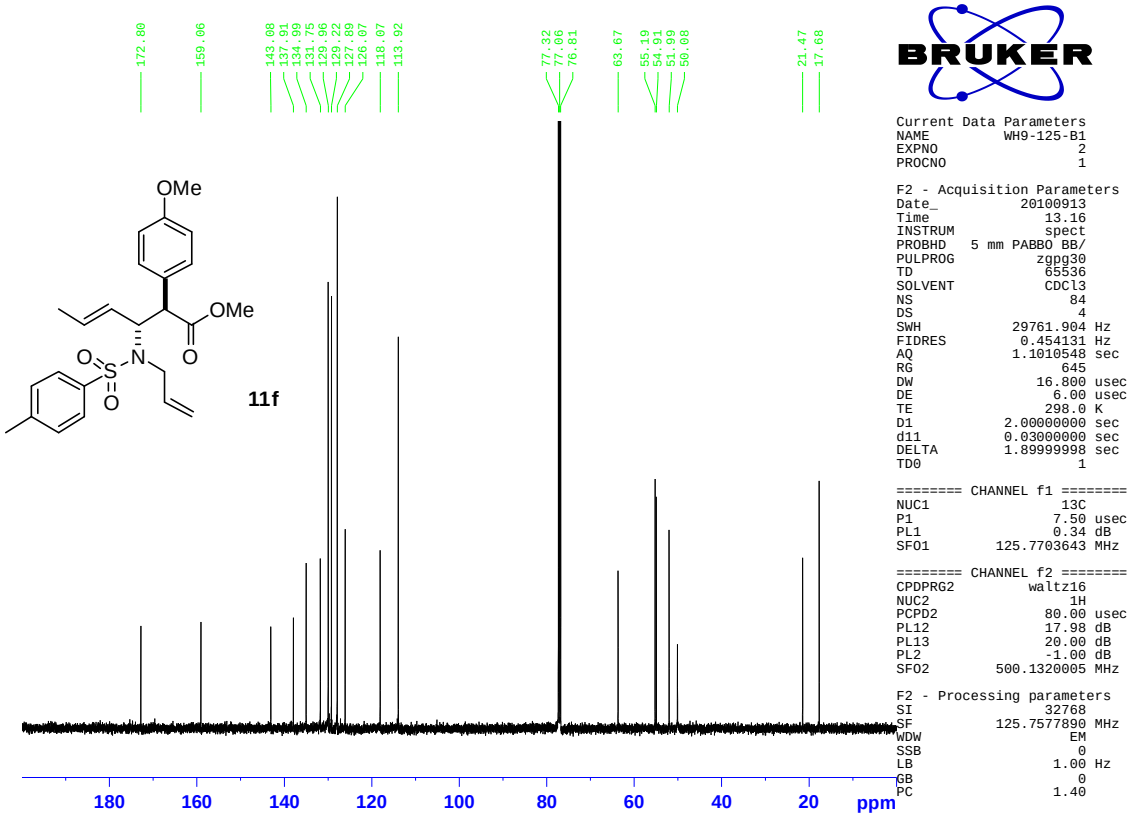

```
Current Data Parameters
NAME          WH9-123-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100909
Time               13.02
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   256
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1326050 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```



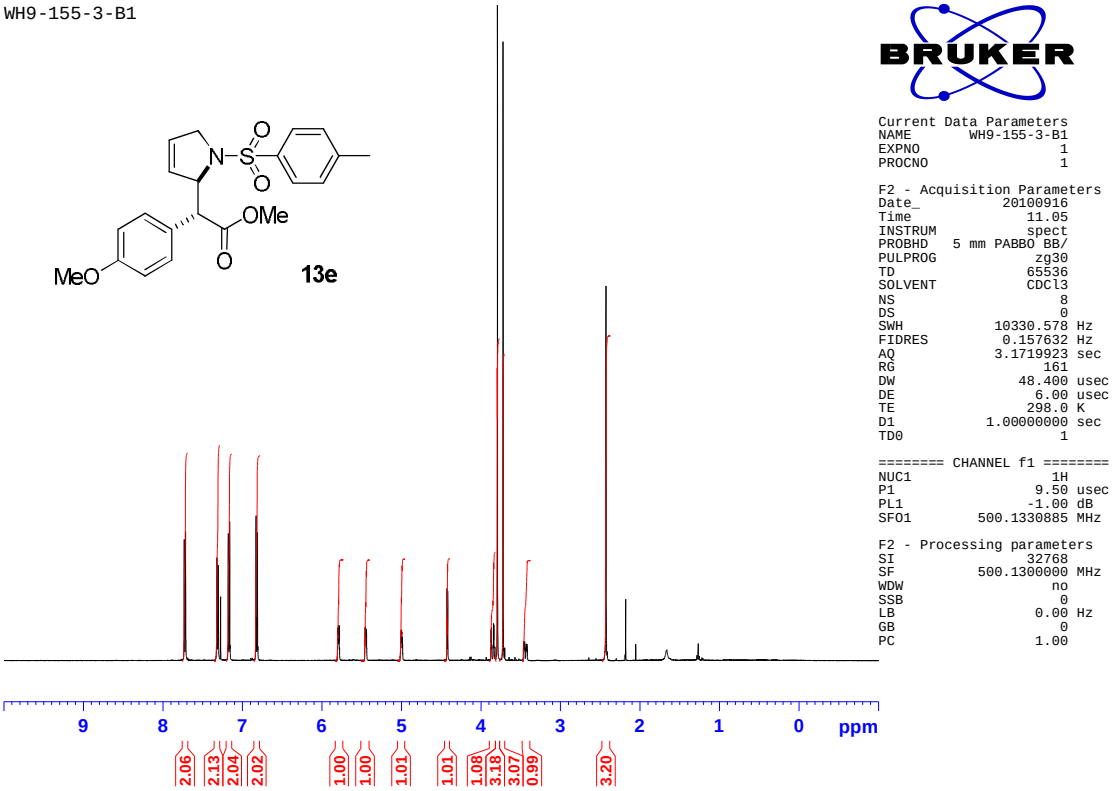

```
Current Data Parameters
NAME          WH9-123-A1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100909
Time               13.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   240
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2               -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF          125.7583299 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```



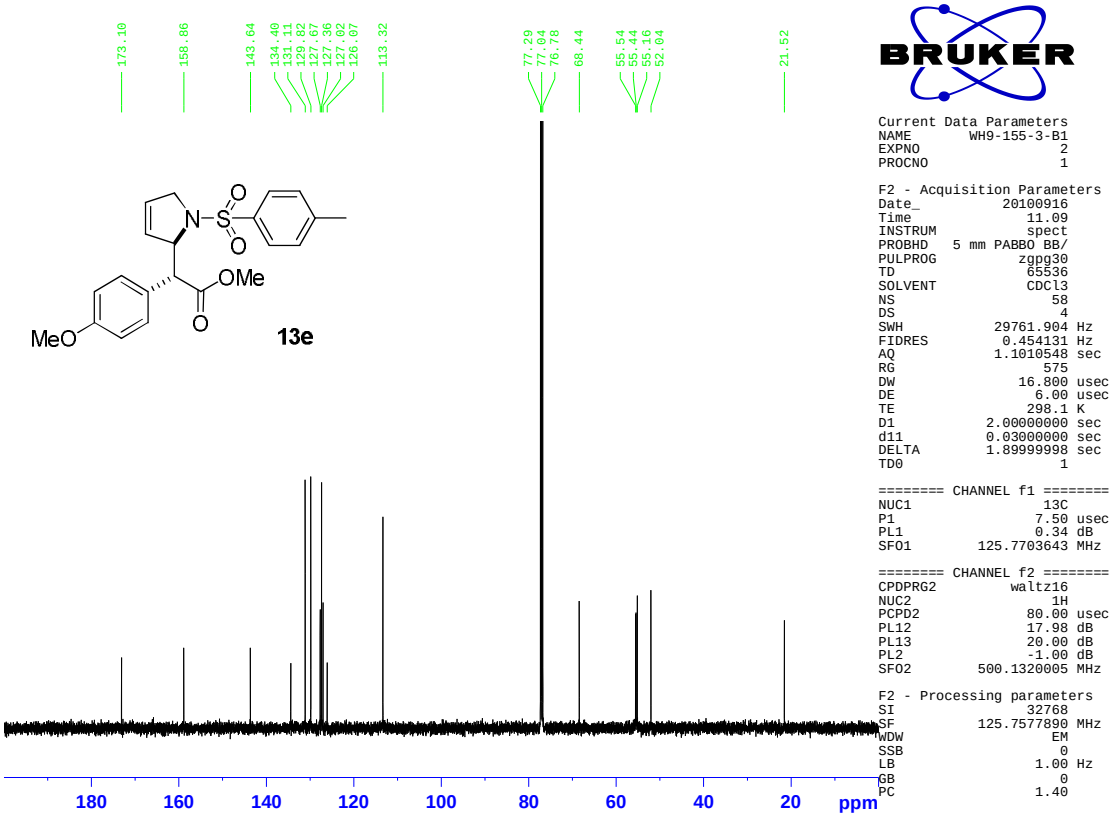

```
Current Data Parameters
NAME          WH9-125-B1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100913
Time               13.12
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                    64
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```



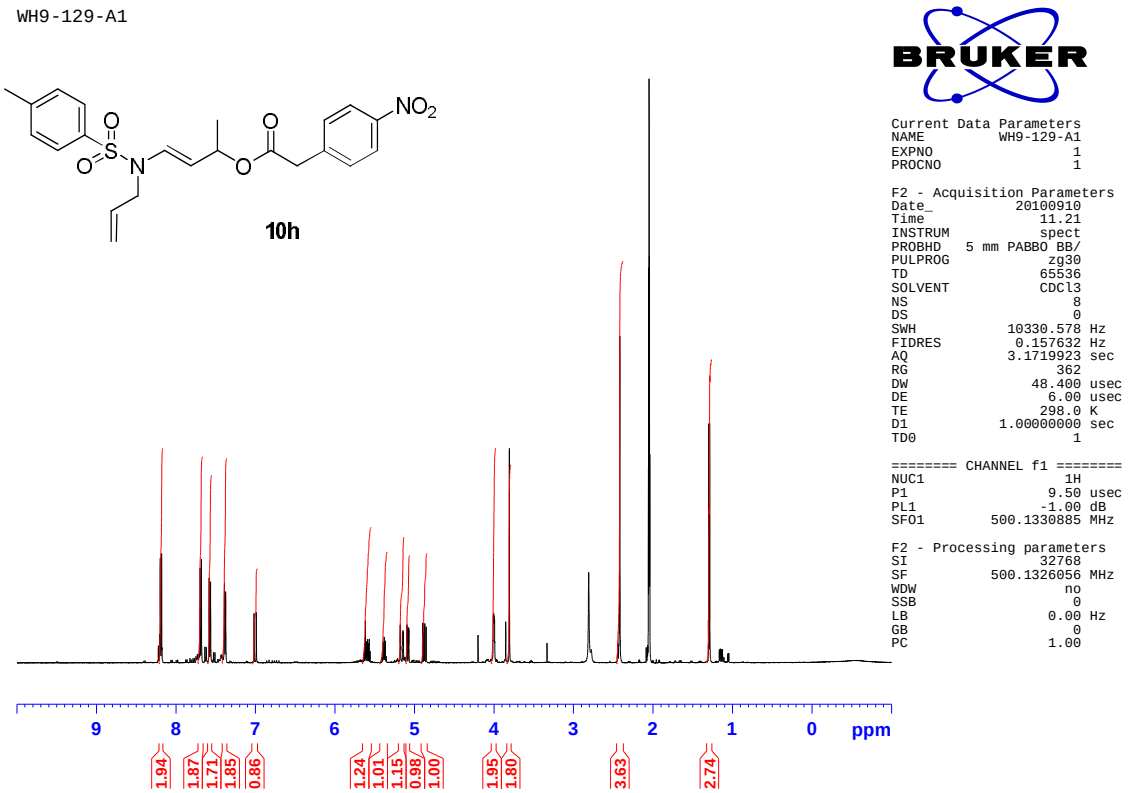

```
Current Data Parameters
NAME          WH9-125-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100913
Time               13.16
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    84
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   645
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2               -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

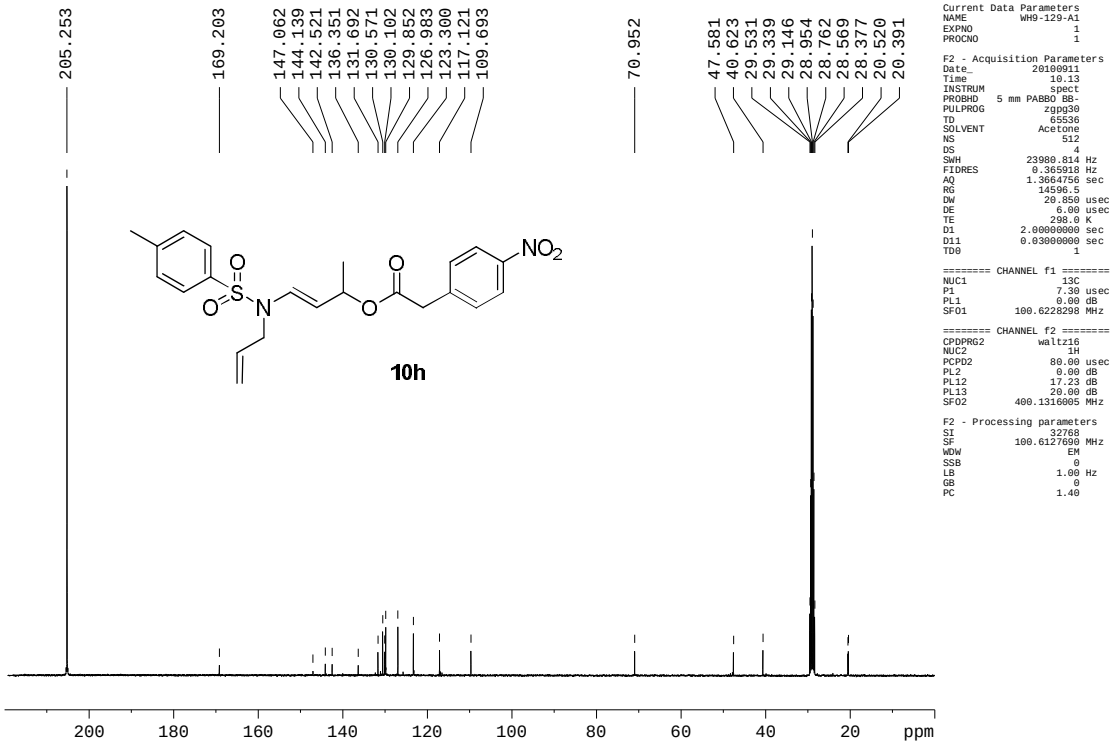



```
Current Data Parameters
NAME       WH9-155-3-B1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100916
Time               11.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                  161
DW               48.400 usec
DE                6.00 usec
TE               298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                9.50 usec
PL1              -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                1.00
```

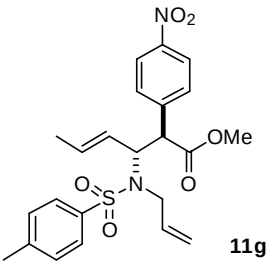



```
Current Data Parameters
NAME       WH9-155-3-B1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100916
Time               11.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   58
DS                    4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                  575
DW               16.800 usec
DE                6.00 usec
TE               298.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                7.50 usec
PL1               0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            80.00 usec
PL12             17.98 dB
PL13             20.00 dB
PL2              -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```


WH9-129-A1
10h
Current Data Parameters
NAME WH9-129-A1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100910
Time 11.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 362
DW 48.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1326056 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
9 8 7 6 5 4 3 2 1 0 ppm
1.94 1.87 1.71 1.85 0.86 1.24 1.01 1.15 0.98 1.00 1.95 1.80 3.63 2.74

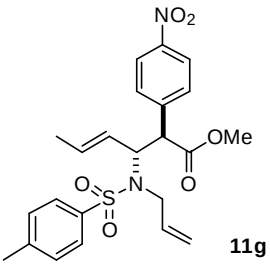

205.253
169.203
147.062
144.139
142.521
136.351
131.692
130.571
130.102
129.852
126.983
123.300
117.121
109.693
70.952
47.581
40.623
29.531
29.339
29.146
28.954
28.762
28.569
28.377
20.520
20.391
10h
Current Data Parameters
NAME WH9-129-A1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100911
Time 10.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 512
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 14596.5
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.30 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 17.23 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 ppm

WH9-p-Nitro R



11g

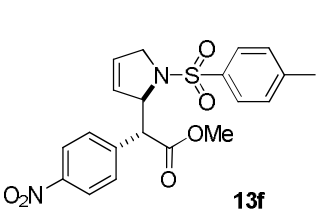

```
Current Data Parameters
NAME      WH9-p-Nitro R
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20100919
Time              11.07
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   5
DS                   0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                 256
DW              48.400 usec
DE               6.00 usec
TE              298.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               9.50 usec
PL1             -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB               0.00 Hz
GB                    0
PC                 1.00
```



11g


```
Current Data Parameters
NAME      WH9-p-Nitro R
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20100919
Time              11.09
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS                 139
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 362
DW              16.800 usec
DE               6.00 usec
TE              298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1               7.50 usec
PL1              0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL12             17.98 dB
PL13             20.00 dB
PL2              -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB               1.00 Hz
GB                    0
PC                 1.40
```

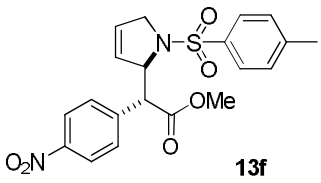
WH9-175-B1



13f

BRUKER

```
Current Data Parameters
NAME          WH9-175-B1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100922
Time               13.00
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   256
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```

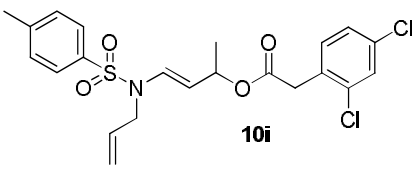


13f

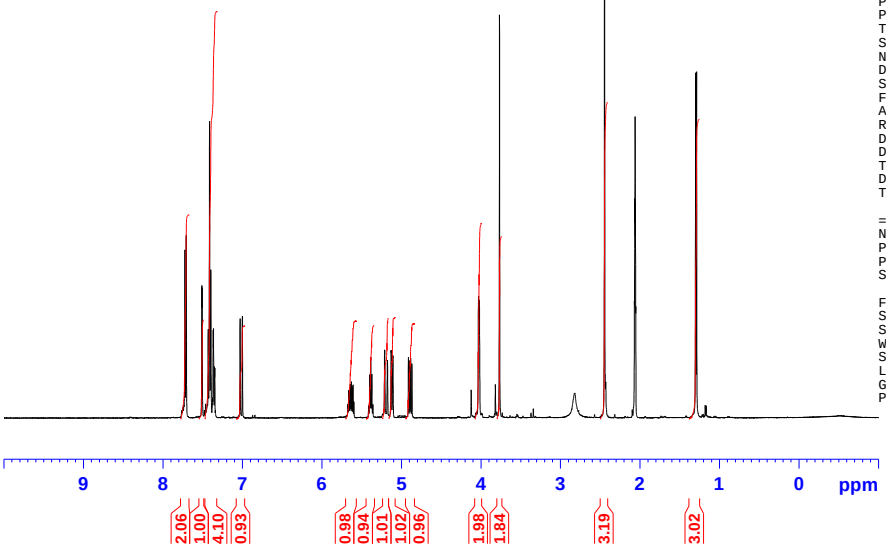
BRUKER

```
Current Data Parameters
NAME          WH9-175-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100922
Time               13.06
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    75
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   812
DW                16.800 usec
DE                 6.00 usec
TE                298.1 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2               -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

WH9-137-A1

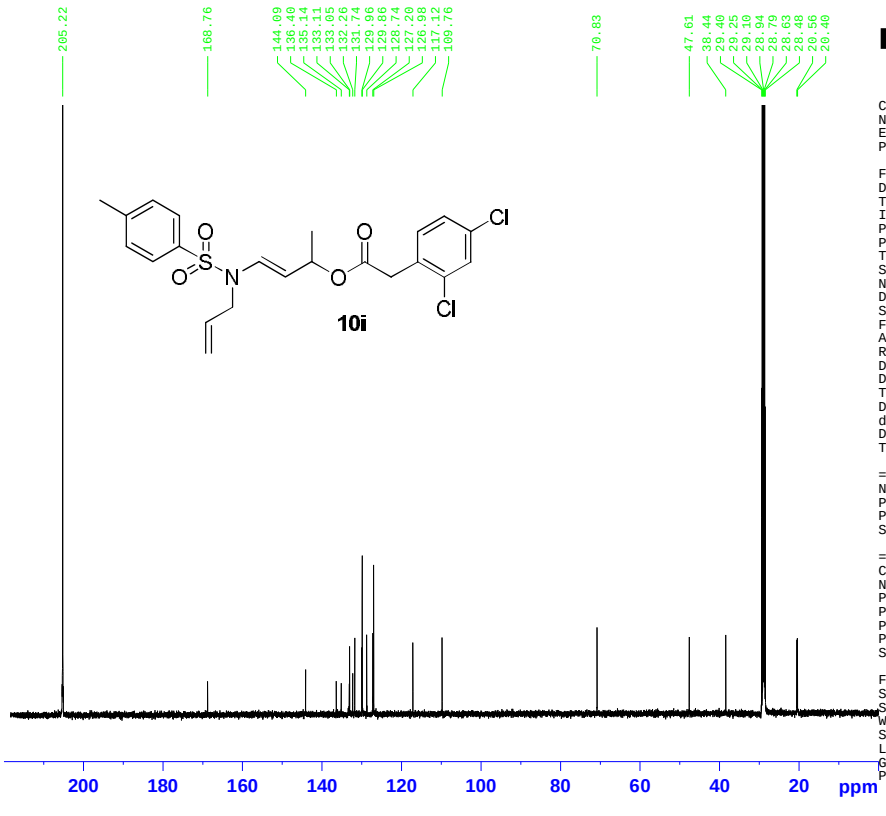


10i



BRUKER

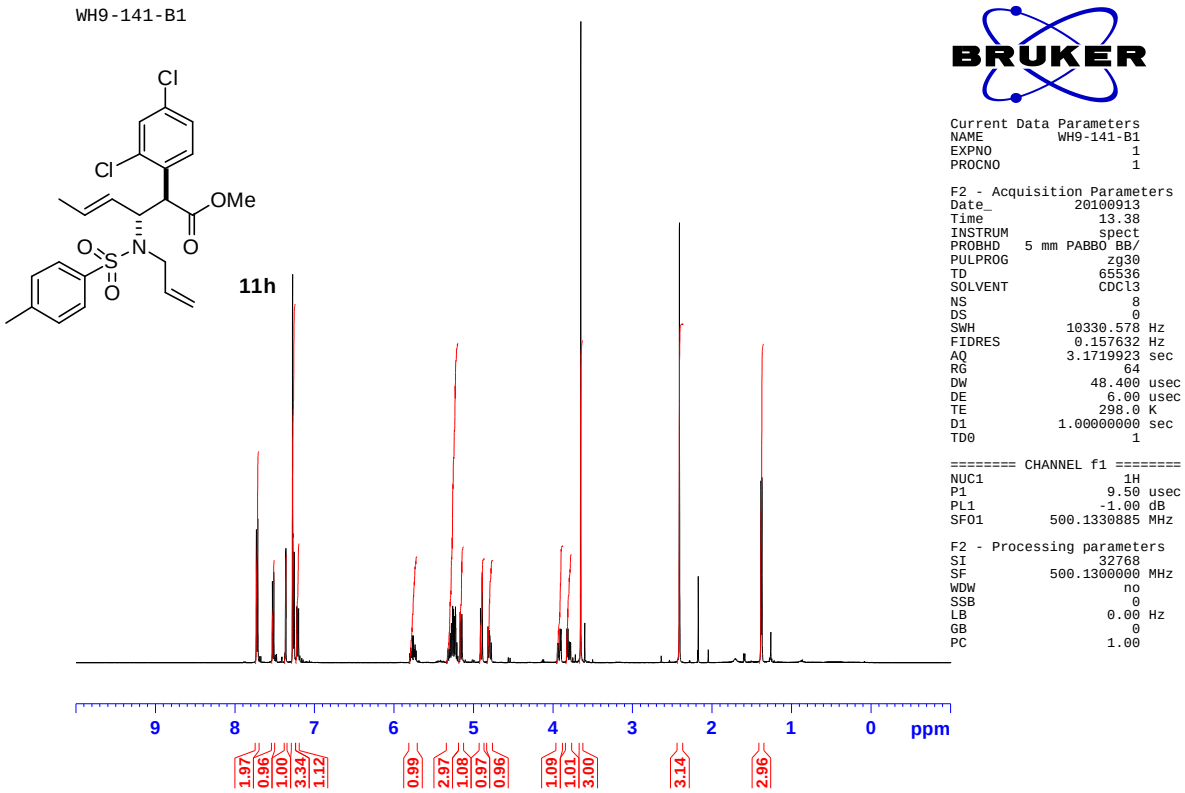
```
Current Data Parameters
NAME          WH9-137-A1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100911
Time               11.10
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                   228
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PL1                -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF            500.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



10i

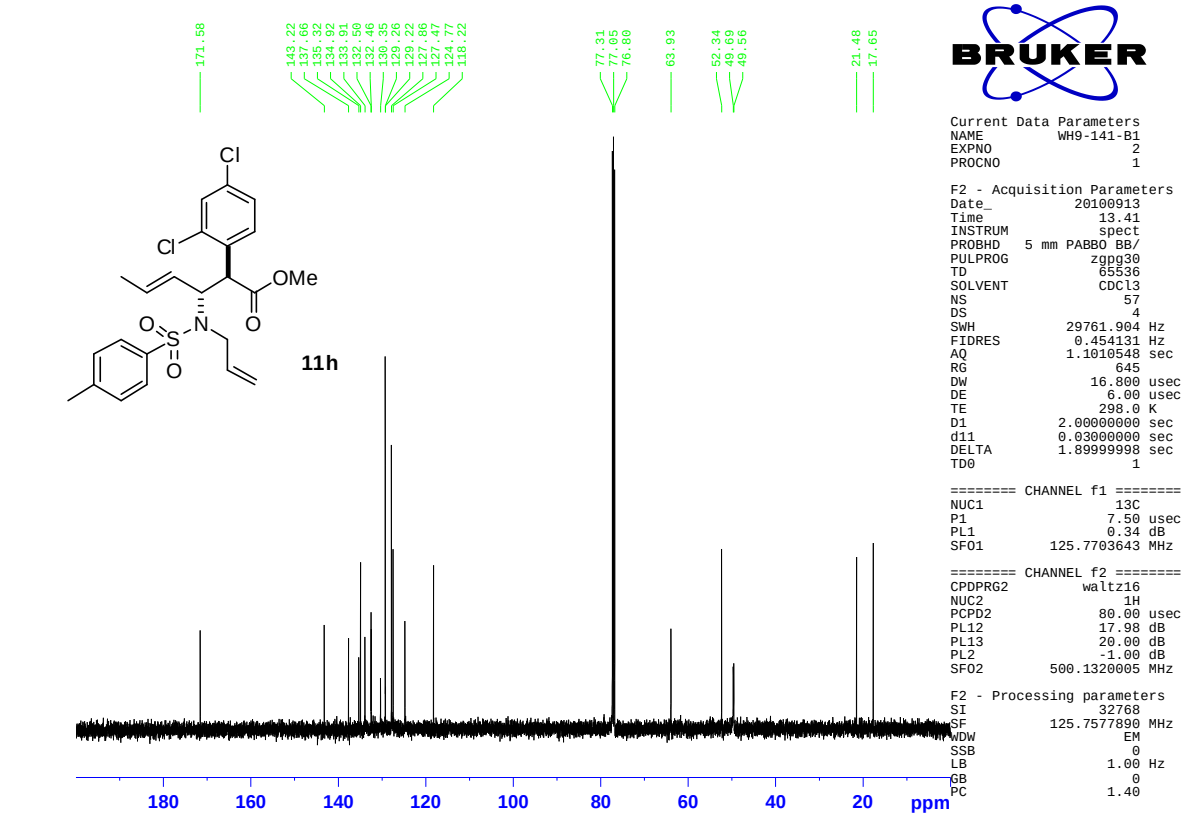
BRUKER

```
Current Data Parameters
NAME          WH9-137-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100911
Time               11.25
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT          Acetone
NS                   256
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                   575
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.50 usec
PL1                 0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2                -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF            125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



BRUKER

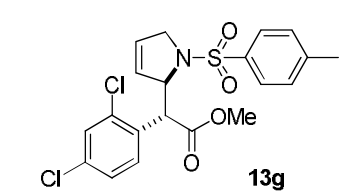
```
Current Data Parameters
NAME          WH9-141-B1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100913
Time               13.38
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                    64
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```



BRUKER

```
Current Data Parameters
NAME          WH9-141-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100913
Time               13.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    57
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   645
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.50 usec
PL1                0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL12              17.98 dB
PL13              20.00 dB
PL2               -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

WH9-157-1-B1

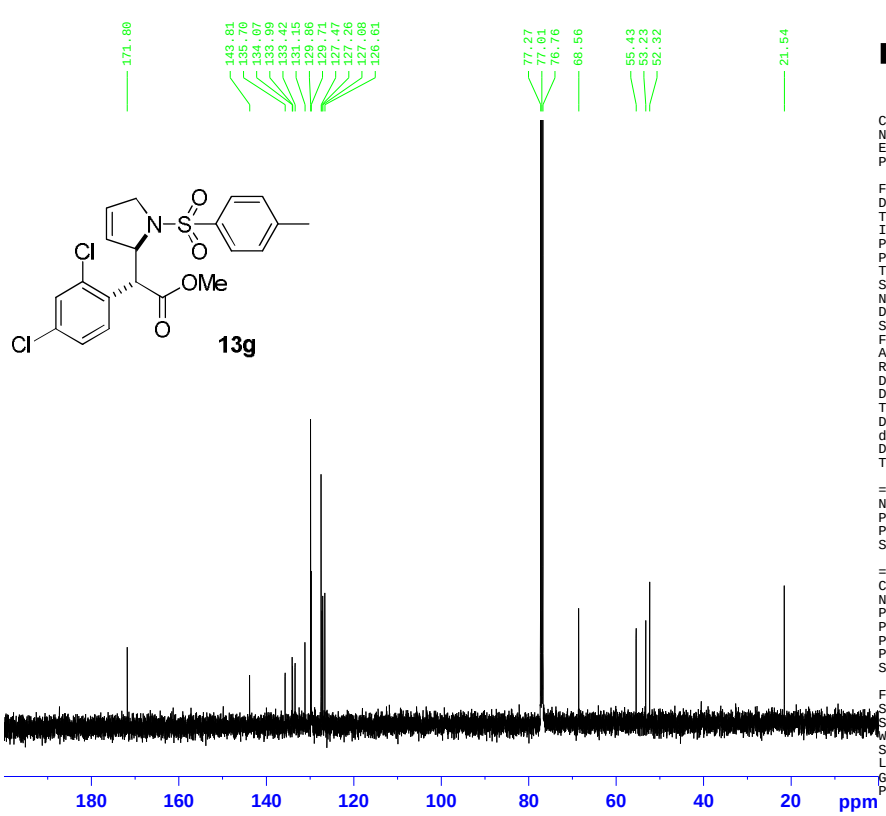


13g

BRUKER

```
Current Data Parameters
NAME       WH9-157-1-B1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100918
Time              11.26
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                  228
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

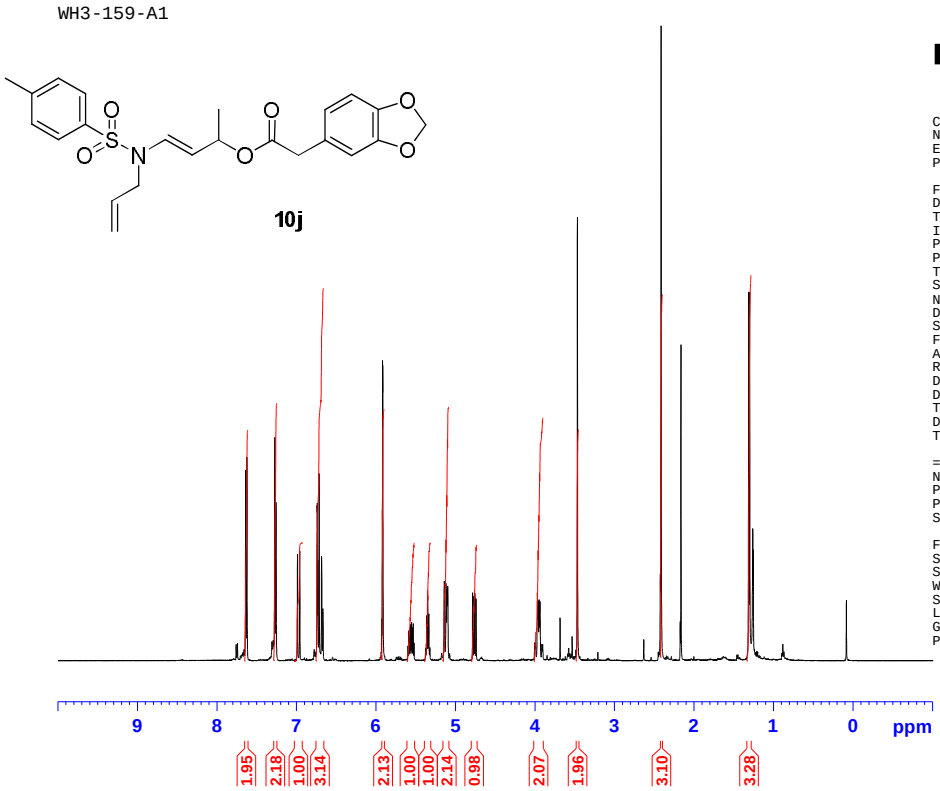
WH9-157-1-B1



13g

BRUKER

```
Current Data Parameters
NAME       WH9-157-1-B1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100918
Time              11.29
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  133
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                  362
DW                16.800 usec
DE                 6.00 usec
TE                297.9 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 7.50 usec
PL1                0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL12              17.98 dB
PL13              20.00 dB
PL2               -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

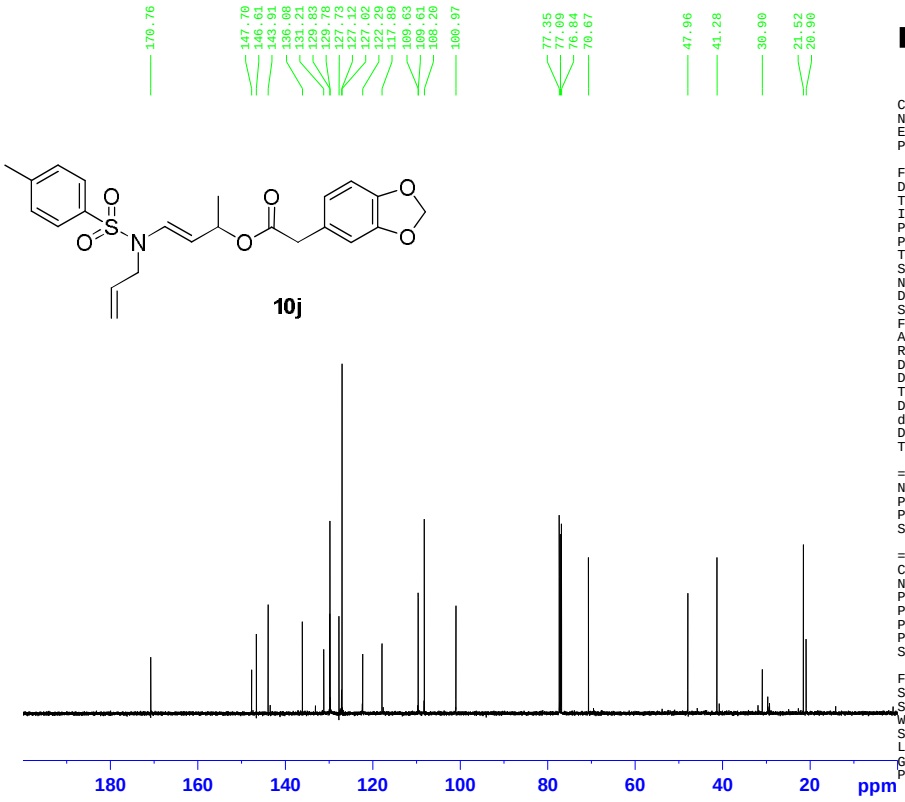


Current Data Parameters
NAME WH3-159-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080912
Time 14.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 45.2
DW 48.400 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -1.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



Current Data Parameters
NAME WH3-159-A1
EXPNO 2
PROCNO 1

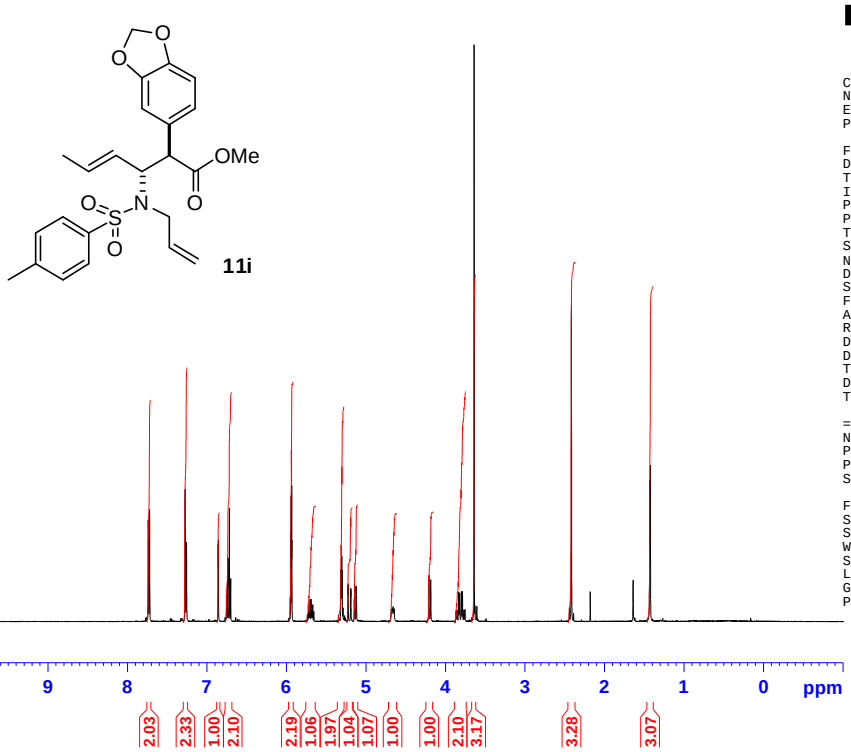
F2 - Acquisition Parameters
Date_ 20080912
Time 15.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 362
DW 16.800 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 0.34 dB
SFO1 125.7703643 MHz

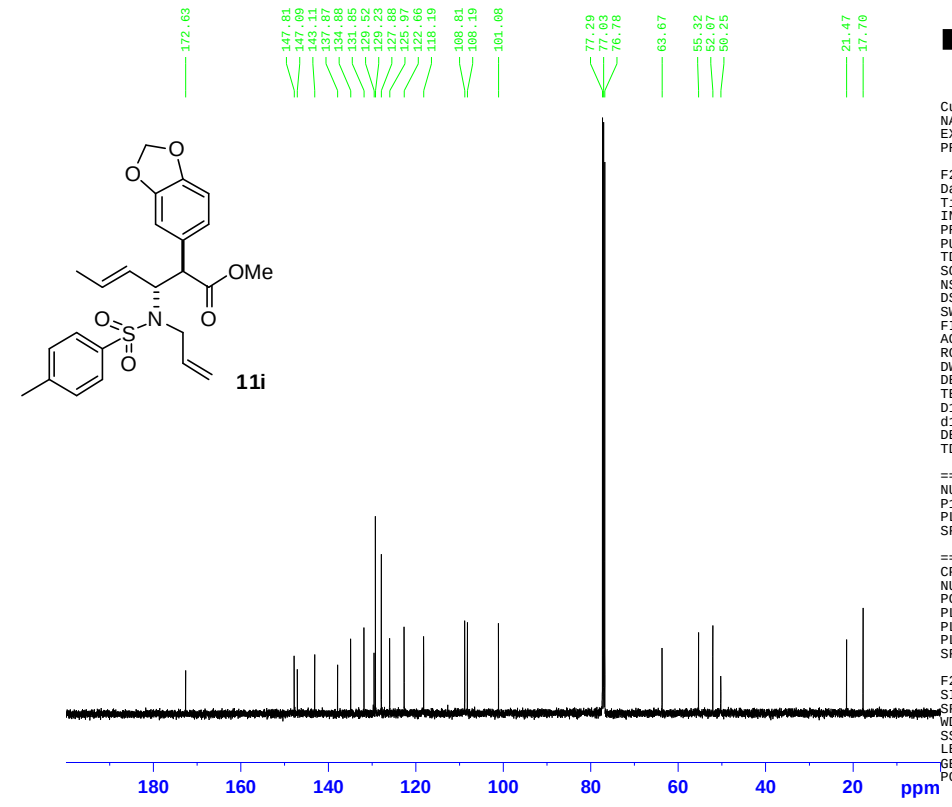
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 17.98 dB
PL13 20.00 dB
PL2 -1.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

WH9-101-B1

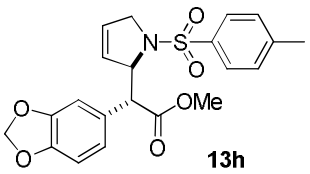



```
Current Data Parameters
NAME          WH9-101-B1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100906
Time               11.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                   161
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1         500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300000 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                  1.00
```



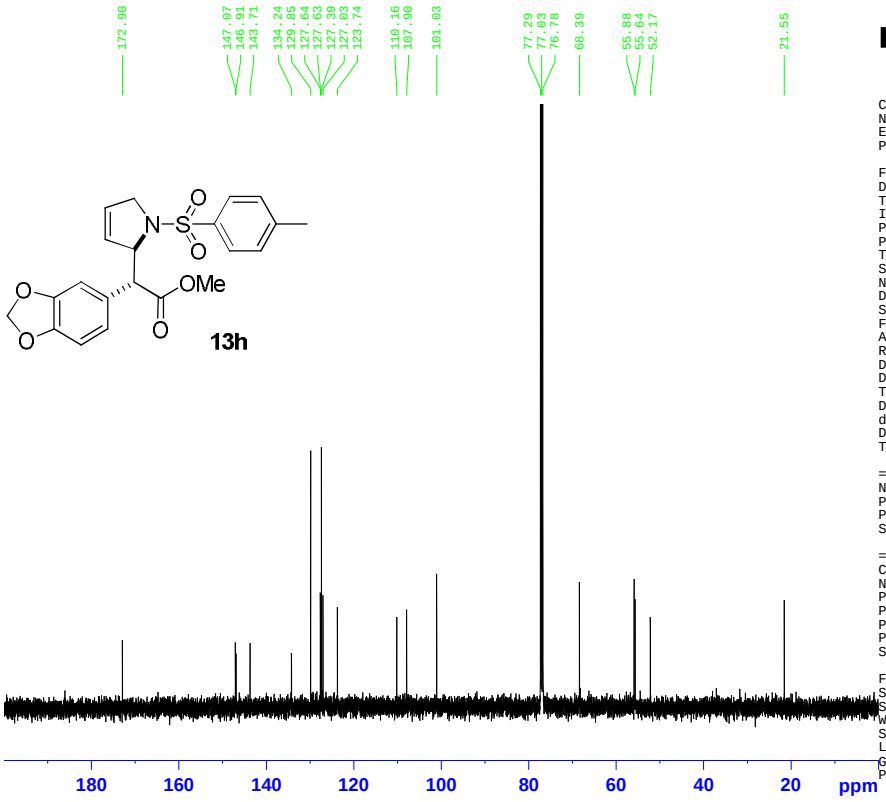

```
Current Data Parameters
NAME          WH9-101-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100906
Time               11.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    99
DS                     4
SWH            29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010548 sec
RG                   362
DW                16.800 usec
DE                 6.00 usec
TE                298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 7.50 usec
PL1                0.34 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               17.98 dB
PL13               20.00 dB
PL2                -1.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

WH9-145-3-B2



13h


```
Current Data Parameters
NAME       WH9-145-3-B2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100915
Time              11.09
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719923 sec
RG                 256
DW              48.400 usec
DE               6.00 usec
TE              294.3 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               9.50 usec
PL1             -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB               0.00 Hz
GB                    0
PC                 1.00
```

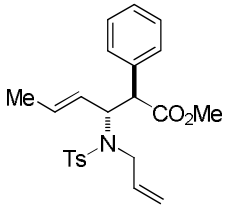


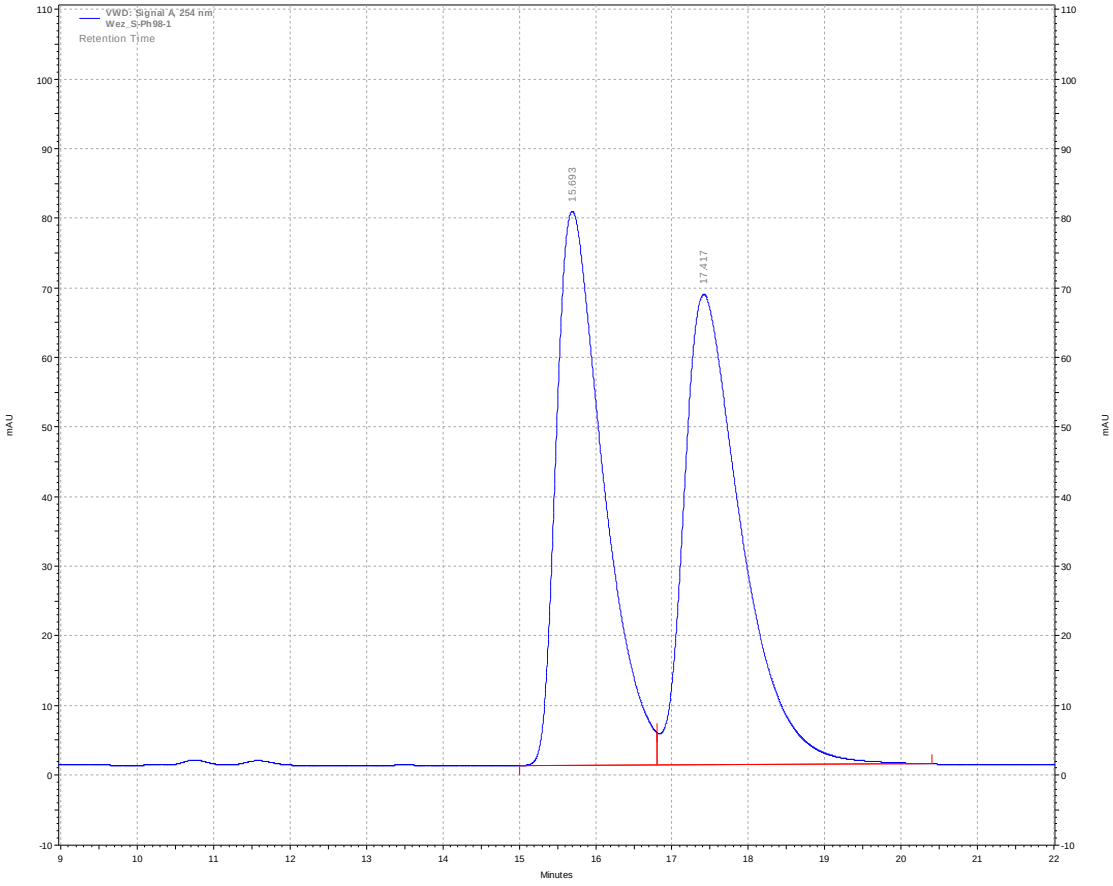
13h

```
Current Data Parameters
NAME       WH9-145-3-B2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100915
Time              11.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  96
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                 362
DW              16.800 usec
DE               6.00 usec
TE              295.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               7.50 usec
PL1              0.34 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           80.00 usec
PL12            17.98 dB
PL13            20.00 dB
PL2             -1.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB               1.00 Hz
GB                    0
PC                 1.40
```

HPLC Data

(*anti*-*E*)-Methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate (*rac*-11d)



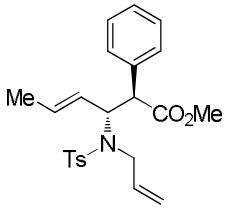


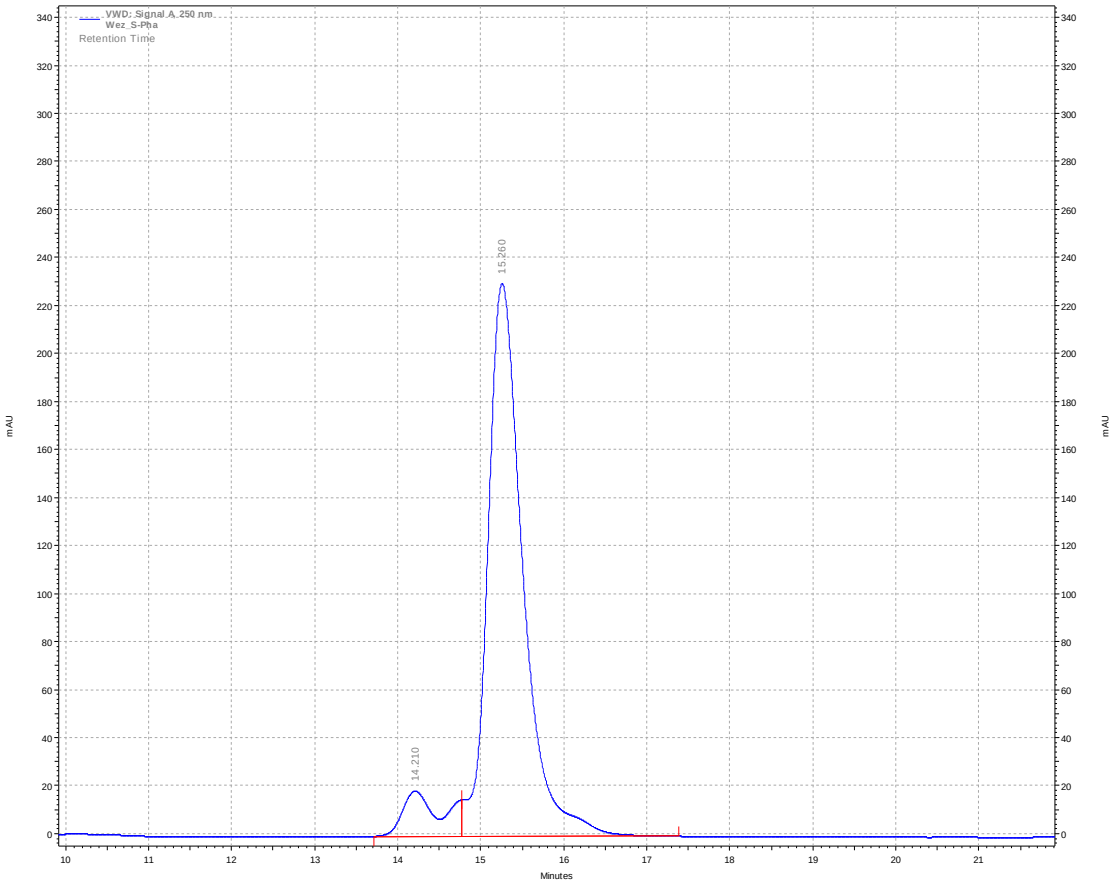
VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %	Height	Height %
15.693	57182044	49.13	1335586	54.09
17.417	59210450	50.87	1133646	45.91
Totals	116392494	100.00	2469232	100.00

(*2R,3R,E*)-methyl 3-(*N*-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate

(*S*)-(*2R,3R*-11d)





VWD: Signal A, 250 nm
Results

Retention Time	Area	Area %	Height	Height %
14.210	10037774	8.15	316073	7.56
15.260	113118091	91.85	3863316	92.44
Totals	123155865	100.00	4179389	100.00