Supporting Information

Asymmetric Rh(I)-Catalyzed Addition of MIDA Boronates to *N*-*tert*-Butanesulfinyl Aldimines: Development and Comparison to Trifluoroborates

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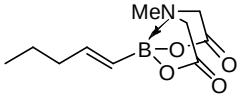
1. General methods. All catalytic alkenylation reactions were assembled in a nitrogen-filled inert atmosphere box and carried out in microvials using PTFE stir-vanes and capped with mini-inert seals and blue nylon caps. The reaction vials were heated in a custom-made aluminum heating block drilled to fit the vials, and the temperature was maintained by placing the block on a stirrer/hot plate with a thermistor controller. Flash column chromatography was carried out either with Merck 60 230-240 mesh silica gel, or using a Biotage SP Flash Purification System with Flash+ 3 cartridges. Diastereoselectivity determinations were performed on products prior to purification using a silica normal phase column (Microsorb Si 100 A packing). ^{1}H NMR resonances are referenced to the residual solvent peak ($CDCl_3$, 7.26 ppm; acetone-d_6, 2.05 ppm), ^{13}C NMR resonances are referenced to the residual solvent peak ($CDCl_3$, 77.23 ppm; acetone-d_6, 29.84 ppm), and ^{19}F resonances are referenced to $CFCl_3$ (0 ppm). Chemical shifts are reported in ppm, and coupling constants are reported in Hz.

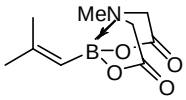
2. General materials. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without purification. 1,4-Dioxane, *N*,*N*-dimethylformamide (DMF), and CH_2Cl_2 were dried over alumina under a N_2 atmosphere prior to use. Triethylamine was distilled under N_2 over CaH_2 prior to use. All liquid reagents and solvents were thoroughly degassed using three freeze-pump-thaw cycles prior to introduction to the inert atmosphere box. Hydroxy(1,5-cyclooctadiene)rhodium(I) dimer and 1,2-bis(diphenylphosphino)benzene (dppbenz) were purchased from Strem. Potassium trifluoroborates **1a**[1], **1b**[2], and **1c-e**[1] were synthesized according to the literature procedures. *N*-sulfinyl imines **2a-b**[3], **2c**[4], **2d**[5], **2e**[6], **2f**[7], **2g**[8]. were synthesized according to the literature procedures. ^{1}H-NMR data of these compounds corresponded to the previously reported data. The preparation of sulfinamides **3a-d** and **3f-k** by the Rh(I)-catalyzed addition of trifluoroborates was previously reported.[1]

3. Synthesis of MIDA boronates.

General procedure for the synthesis of MIDA boronates (Procedure A). This procedure was adapted from Burke.[9] To a round-bottom flask equipped with a stir bar was added the appropriate boronic acid (1 equiv), *N*-methyliminodiacetic acid (1.05 equiv), and 10:1 toluene:DMSO (0.02 M). The flask was fitted with a Dean-Stark trap and the Dean-Stark trap was fitted with a reflux condenser. The stirred mixture was heated to reflux with azeotropic removal of water for 18 h. The toluene (40 ºC, 30 mm Hg) and DMSO (40 ºC, 0.050 mm Hg) were removed *in vacuo*. The resulting residue was adsorbed onto Celite *in vacuo* from an acetone suspension and the resulting powder was subjected to column chromatography (0-20% MeCN/Et_2O).



(*E*)-1-Pentenyl MIDA boronate (4a). Procedure A was followed using commercially available (*E*)-1-pentenylboronic acid (500 mg, 4.38 mmol), *N*-methyliminodiacetic acid (677 mg, 4.60 mmol), toluene (200 mL), and DMSO (20 mL) to afford 821 mg (83%) of **4a** as a white solid. IR 2957, 1748, 1643, 1461, 1289, 1119, 998, 856 cm^{-1}. ^1H NMR (600 MHz, acetone-d_6): δ 0.89 (t, 3H, J = 7.4), 1.42 (sextet, 2H, J = 7.4), 2.06-2.11 (m, 2H), 2.97 (s, 3H), 3.98 (d, 2H, J = 16.9), 4.17 (d, 2H, J = 16.9), 5.47 (dt, J = 17.6, 1.5), 6.08 (dt, J = 17.6, 6.5). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.6, 38.2, 47.3, 62.1, 126.8 (br), 145.7, 169.1. HRMS-ESI (m/z): $[MH]^+$ calcd for $C_{10}H_{17}NO_4B$, 226.1251; found, 226.1248.



2,2-Dimethylethenyl MIDA boronate (4b). Dimethylethenylboronic acid was prepared immediately prior to conversion to the MIDA boronate. To a solution of trimethylborate (1.77 mL, 15.6 mmol) in THF (2.5 mL) cooled to -78 ºC, was added 2-methyl-1-propenylmagnesium bromide (25.0 mL, 0.5 M in THF, 12.5 mmol) over 30 min using an addition funnel. The reaction mixture was stirred at -78 ºC for 15 min and then warmed to room temperature with stirring for 1 h. After cooling the reaction mixture to 0 ºC, a 30% aqueous HCl solution (17.5 mL) was added, and the mixture was stirred for 1 h at 0 ºC and then 30 min at room temperature. The reaction mixture was extracted with Et_2O (3 x 25 mL). The combined organic layers

were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to ~ 10 mL. To avoid decomposition of the boronic acid, it is important to avoid concentrating to dryness. Toluene (562 mL) and DMSO (62.5 mL) were then added, and the remaining Et_2O was removed (15 ºC, 30 mm Hg). *N*-methyliminodiacetic acid (1.93 g, 13.1 mmol) was added to the toluene/DMSO solution containing the crude 2,2-dimethylethenyl boronic acid and procedure A was followed to afford 1.81 g (68%, 2 steps) of **4b** as a white solid. IR 3010, 1743, 1647, 1450, 1288, 1140, 982, 867 cm^{-1}. ^1H NMR (600 MHz, acetone-d_6): δ 1.78 (d, 3H, J = 1.0), 1.81 (d, 3H, J = 1.3), 2.99 (s, 3H), 3.98 (d, 2H, J = 16.8), 4.15 (d, 2H, J = 16.8), 5.05-5.08 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.1, 29.7, 47.0, 62.3, 121.1 (br), 149.6, 169.1. HRMS-ESI (m/z): $[MH]^+$ calcd for $C_9H_{15}NO_4B$, 212.1092; found, 212.1089.

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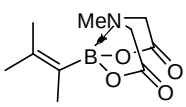
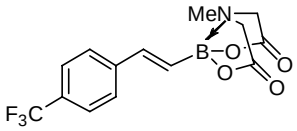


3-Methyl-2-buten-2-yl MIDA boronate (4c). Procedure A was followed using commercially available 3-methyl-2-buten-2-ylboronic acid (304 mg, 2.67 mmol), *N*-methyliminodiacetic acid (412 mg, 2.80 mmol), toluene (120 mL), and DMSO (12 mL) to afford 56 mg (9%) of **4c** as a white solid. IR 2914, 1743, 1627, 1454, 1335, 1284, 1156, 1022, 980, 859 cm^{-1}. ^1H NMR (500 MHz, acetone-d_6): δ 1.58 (s, 3H), 1.74 (s, 3H), 1.82 (s, 3H), 2.95 (s, 3H), 4.02 (d, 2H, J = 17.0), 4.20 (d, 2H, J = 17.0). ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.1, 23.0, 23.7, 47.3, 63.4, 124.7 (br), 142.3, 169.2. HRMS-ESI (m/z): $[MNa]^+$ calcd for $C_{10}H_{16}NO_4BNa$, 248.1065; found, 248.1062.



(*E*)-2-[4-(Trifluoromethyl)phenyl] MIDA boronate (4e). Procedure A was followed using commercially available (*E*)-2-[4-(trifluoromethyl)phenyl]vinylboronic acid (398 mg, 1.84 mmol), *N*-methyliminodiacetic acid (284 mg, 1.93 mmol), toluene (184 mL), and DMSO (18.4 mL) to afford 570 mg (95%) of **4e** as a white solid. IR 3010, 1754, 1326, 1116, 1065, 993, 851 cm^{-1}. ^1H NMR (600 MHz, acetone-d_6): δ 3.09 (s, 3H), 4.13 (d, 2H, J = 16.9), 4.31 (d, 2H, J = 16.9), 6.57 (d, 1H, J = 18.2), 7.05 (d, 1H, J = 18.2), 7.68 (d, 2H, J = 8.3), 7.74 (d, 2H, J = 8.3). ^{13}C NMR (150 MHz, $CDCl_3$): δ 47.5, 62.5, 125.4 (q, J = 270), 126.3 (q, J = 4.5), 128.0, 129.5 (br), 129.8 (q, J = 31.5), 141.3, 143.0, 169.1. ^{19}F

NMR (376 MHz, acetone-d_6): δ -62.2 (s, 3F). HRMS-FAB (m/z): $[MH]^+$ calcd for $C_{14}H_{14}F_3NO_4B$, 328.0968; found, 328.0970.

4. General procedures for the addition of alkenyl trifluoroborates or MIDA boronates to *N-tert*-butanesulfinyl imines.

General procedure for the addition of trifluoroborates to *N-tert*-butanesulfinyl imines (Procedure B). The Rh(I)-catalyzed addition of trifluoroborates was carried out according to the previously reported procedure[1]: Reactions were set up in an inert atmosphere box. Hydroxy(1,5-cyclooctadiene)rhodium(I) dimer (2.9 mg, 0.0063 mmol, 0.025 equiv) was dissolved in DMF (0.2 mL, 1.25 M or 0.4 mL, 0.62 M), and the resulting solution was added to a vial containing 1,2-bis(diphenylphosphino)benzene (5.6 mg, 0.013 mmol, 0.050 equiv). The mixture of catalyst and ligand was then added to a vial containing a stir-vane and the appropriate potassium alkenyltrifluoroborate (0.300-500 mmol, 1.2-2.0 equiv). To the mixture of catalyst, ligand, and trifluoroborate was added the appropriate sulfinyl imine (0.250 mmol, 1.0 equiv) dissolved in DMF (0.2 mL, 1.25 M or 0.4 mL, 0.62 M), followed by water (0.6 mL, 0.42 M or 1.2 mL, 0.21 M), and triethylamine (0.070 mL, 0.50 mmol, 2.0 equiv). The reaction vial was capped, removed from the inert atmosphere box, and placed in a heating block on the benchtop with stirring. The reaction mixture was heated to 60 °C and stirred for 20 h. Upon heating and stirring, the reaction mixture becomes biphasic with globules of starting imine/product in the reaction medium. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL). The organic layer was washed with brine (10 mL) and the aqueous layer was back-extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The products were isolated by silica gel chromatography using EtOAc/hexanes mixtures and were visualized with PMA stain.

General procedure for the addition of MIDA boronates to *N-tert*-butanesulfinyl imines (Procedure C and D).

Procedure C- inert atmosphere box procedure: Reactions were set up in an inert atmosphere box. Hydroxy(1,5-cyclooctadiene)rhodium(I) dimer (2.9 mg, 0.0063 mmol, 0.025 equiv) was dissolved in dioxane (0.4 mL, 0.62 M), and the resulting solution was added to a vial containing 1,2-bis(diphenylphosphino)benzene (5.6 mg, 0.013 mmol, 0.050 equiv). The mixture of catalyst and ligand was then added to a vial containing a stir-vane and the appropriate MIDA boronate (0.300-0.500 mmol, 1.2-2.0 equiv). To the mixture of catalyst, ligand, and MIDA boronate was added the appropriate sulfinyl imine (0.250 mmol, 1.0 equiv) dissolved in dioxane (0.4 mL, 0.62 M), followed by water (1.2 mL, 0.21 M), and K_3PO_4 (106 mg, 0.500 mmol, 2.0 equiv). The reaction vial was capped, removed from the inert atmosphere box, and placed in a heating block on the benchtop with stirring. The reaction mixture was heated to 60 °C and stirred for 20 h. Upon heating and stirring, the reaction mixture becomes biphasic with globules of starting imine/product in the reaction medium. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL). The organic layer was washed with brine (10 mL), and the aqueous layer was back-extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The products were isolated by silica gel chromatography using EtOAc/hexanes mixtures and were visualized with PMA stain.

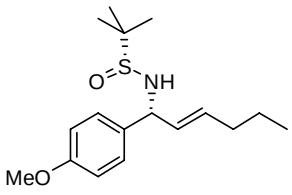
Procedure D- Schlenk-line procedure: Reactions were set up in a fumehood using Schlenk technique. The appropriate sulfinyl imine (0.250 mmol, 1.0 equiv) was added to a 2 mL single neck round-bottom flask fitted with a rubber septum, which was subjected to three cycles of evacuation and refilling with nitrogen gas via an inlet needle. Water (1.2 mL) and K_3PO_4 (106 mg, 0.500 mmol, 2.0 equiv) were added to a separate 5 mL single neck round-bottom flask fitted with a rubber septum, which was subjected to three cycles of evacuation and refilling with nitrogen gas via an inlet needle. A 5-mL Schlenk tube equipped with a vacuum adaptor, septum and stir bar, was charged with hydroxy(1,5-cyclooctadiene)rhodium(I) dimer (2.9 mg, 0.0063 mmol, 0.025 equiv) and 1,2-bis(diphenylphosphino)benzene (5.6 mg, 0.013 mmol, 0.050 equiv). After evacuating and refilling the flask with N_2 gas (3x), freshly distilled dioxane (0.3 mL) was added by gas-tight syringe. The catalyst and ligand were stirred under N_2 atmosphere for 2 min, and then the septum was removed and the MIDA boronate (0.500 mmol, 2.0

equiv) was added while maintaining a strong N_2 gas flow. The mixture of catalyst, ligand, and MIDA boronate was stirred under a N_2 atmosphere until the solution was homogenous. Then the sulfinyl imine dissolved in dioxane (0.5 mL) followed by the aqueous K_3PO_4 solution were added by cannula. The Schlenk tube was capped, and the reaction mixture was heating in a 60 °C oil bath with stirring for 20 h whereupon the reaction mixture becomes biphasic with globules of starting imine/product in the reaction medium. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL). The organic layer was washed with brine (10 mL), and the aqueous layer was back-extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The products were isolated by silica gel chromatography using EtOAc/hexanes mixtures and were visualized with PMA stain.

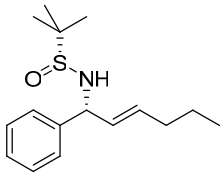
5. General procedure for diastereoselectivity determination.

General procedure for preparing authentic mixture of *N*-sulfinyl allylic amine diastereomers for diastereoselectivity determination. The authentic mixture of diastereomers were prepared according to literature procedure[10]: The *N*-sulfinyl amine (1.0 equiv) dissolved in CH_2Cl_2 (0.16 M) in an oven-dried vial equipped with a Teflon coated stir bar under nitrogen was placed in an ambient water bath. 4 M HCl in dioxane (2.2 equiv) was added dropwise to this solution, and the reaction mixture was stirred at rt for 0.5-1 h. NEt_3 (2.4 equiv) was then added dropwise and the resulting mixture was stirred at rt for 1 h. The reaction mixture was diluted with EtOAc and washed successively with 1 N $NaHSO_4$, saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to provide an authentic mixture of *N*-sulfinyl amine diastereomers. The extractive isolation provided analytically pure material. Separation conditions for the mixture of authentic diastereomers were then established by HPLC in hexanes/EtOH or hexanes/iPrOH. The dr was determined for the crude products and was confirmed by coinjections with the authentic mixture of diastereomers.

6. Additions of boron reagents to *N*-*tert*-butanesulfinyl imines.



(R_S)-*N*-((*R*,*E*)-1-(4-methoxyphenyl)hex-2-enyl)-2-methylpropanesulfinamide (3a). Procedure C was followed using sulfinyl imine **2a** (59.8 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 65.6 mg (85% yield, 99:1 dr) of **3a** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 17.8 min, t_{major} = 23.0 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



(R_S)-*N*-((*R*,*E*)-1-(phenyl)hex-2-enyl)-2-methylpropanesulfinamide (3b)

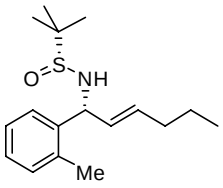
- Procedure B was followed using sulfinyl imine **2b** (52.3 mg, 0.250 mmol) and trifluoroborate **1a** (52.8 mg, 0.300 mmol) in 2:3 DMF:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 52.5 mg (75% yield, 99:1 dr) of **3b** as a pale yellow oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 210 nm): t_{minor} = 10.6 min, t_{major} = 12.5 min). ^{1}H NMR and HPLC data corresponded to previously reported data.[1]

- Procedure C was followed using sulfinyl imine **2b** (52.3 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 68.4 mg (98% yield, 99:1 dr) of **3b** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 210 nm): t_{minor} = 10.6 min, t_{major} = 12.5 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]

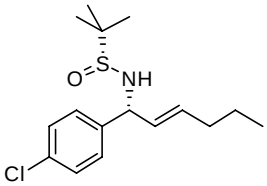
- Procedure C was followed using sulfinyl imine **2b** (52.3 mg, 0.250 mmol) and MIDA boronate **4a** (67.5 mg, 0.300 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The

reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 67.0 mg (96% yield, 99:1 dr) of **3b** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 210 nm): t_{minor} = 10.7 min, t_{major} = 12.5 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]

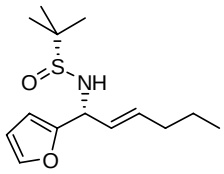
- Procedure D was followed using sulfinyl imine **2b** (52.3 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 64.2 mg (92% yield, 99:1 dr) of **3b** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 210 nm): t_{minor} = 10.4 min, t_{major} = 12.2 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



(R_S)-*N*-((*R*,*E*)-1-(2-methylphenyl)hex-2-enyl)-2-methylpropanesulfinamide (3c). Procedure C was followed using sulfinyl imine **3c** (55.8 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 72.7 mg (99% yield, >99:1 dr) of **3c** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 99:1, 1.0 mL/min, λ = 210 nm): t_{minor} = 20.5 min, t_{major} = 22.2 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



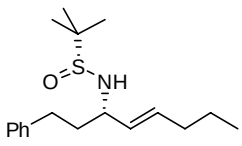
(R_S)-*N*-((*R*,*E*)-1-(4-chlorophenyl)hex-2-enyl)-2-methylpropanesulfinamide (3d). Procedure C was followed using sulfinyl imine **2d** (60.9 mg, 0.250 mmol) and MIDA boronate **1a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 76.6 mg (98% yield, 99:1 dr) of **3d** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 222 nm): t_{minor} = 30.3 min, t_{major} = 31.5 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



(R_S)-*N*-((*R*,*E*)-1-(furan-2-yl)hex-2-enyl)-2-methylpropanesulfinamide (3e).

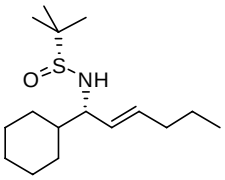
- Procedure B was followed using sulfinyl imine **2e** (49.8 mg, 0.250 mmol) and trifluoroborate **1a** (88 mg, 0.50 mmol) in 2:3 DMF:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 25.1 mg (37% yield, 98:2 dr) of **3e** as a pale yellow oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 16.1 min, t_{major} = 21.1 min). IR 3196, 2958, 1459, 1363, 1060, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J* = 7.4), 1.20 (s, 9H), 1.41 (sextet, 2H, *J* = 7.4), 2.05 (app q, 2H, *J* = 6.9), 3.56 (d, 1H, *J* = 3.4), 4.95 (dd, 1H, *J* = 3.4, 7.7), 5.53 (ddt, 1H, *J* = 7.7, 15.3, 1.4), 5.77 (dt, 1H, *J* = 15.3, 6.7), 6.20 (d, 1H, *J* = 3.2), 6.30 (dd, 1H, *J* = 3.2, 1.8), 7.36 (d, 1H, *J* = 1.8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.8, 22.2, 22.7, 34.4, 55.1, 55.8, 106.9, 110.4, 127.3, 135.7, 142.4, 154.4. HRMS-ESI (m/z): $[MH]^+$ calcd for $C_{14}H_{24}NO_2S$, 270.1526; found, 270.1522.

- Procedure C was followed using sulfinyl imine **2e** (49.8 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 47.5 mg (71% yield, 98:2 dr) of **3e** as a pale yellow oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 17.0 min, t_{major} = 22.3 min. ^1H NMR and HPLC data corresponded to data reported for Procedure B (vide supra).

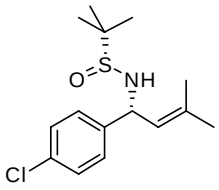


(R_S)-*N*-((*S*,*E*)-1-phenyloct-4-en-3-yl)-2-methylpropanesulfinamide (3f). Procedure C was followed using sulfinyl imine **2f** (59.4 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 60.5 mg (79% yield, 99:1 dr) of **3f** as a pale yellow oil. HPLC (silica column,

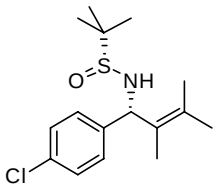
hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 10.6 min, t_{major} = 12.2 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



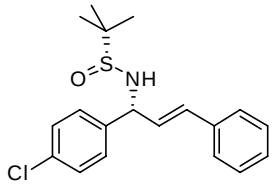
(R_S)-*N*-((*S*,*E*)-1-cyclohex-2-enyl)-2-methylpropanesulfinamide (3g). Procedure C was followed using sulfinyl imine **3g** (53.9 mg, 0.250 mmol) and MIDA boronate **4a** (113 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 14.9 mg (21% yield, 98:2 dr) of **3g** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 18.0 min, t_{major} = 25.2 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



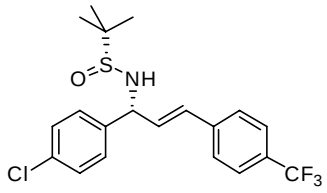
(R_S)-*N*-((*R*)-1-(4-chlorophenyl)-3-methylbut-2-enyl)-2-methylpropanesulfinamide (3h). Procedure C was followed using sulfinyl imine **1d (**60.9 mg, 0.250 mmol) and MIDA boronate **4b** (106 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 69.6 mg (93% yield, 98:2 dr) of **3h** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{major} = 14.4 min, t_{minor} = 16.4 min. ^{1}H NMR and HPLC data corresponded to previously reported data.[1]



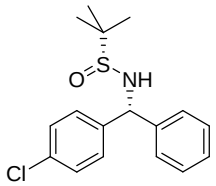
(R_S)-*N*-((*S*)-1-(4-chlorophenyl)-2,3-dimethylbut-2-enyl)-2-methylpropanesulfinamide (3i). Procedure C was followed using sulfinyl imine **3d** (29.3 mg, 0.250 mmol), MIDA boronate **4c** (54.0 mg, 0.500 mmol), $[Rh(OH)(cod)]_2$ (1.4 mg, 0.0030 mmol), dppbenz (2.7 mg, 0.006 mmol), and K_3PO_4 (50.9 mg, 0.240 mmol) in 2:3 dioxane:H_2O (0.4:.6 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 31.9 mg (85% yield, 99.5:0.5 dr) of **3i** as a pale yellow oil. HPLC (silica column, hexanes:*i*PrOH 99:1, 1.0 mL/min, λ = 210 nm): t_{major} = 22.6 min, t_{minor} = 24.5 min. ^{1}H NMR and HPLC corresponded to previously reported data.[1]



(R_S)-*N*-((*R*,*E*)-1-(4-chlorophenyl)-3-phenylallyl)-2-methylpropanesulfinamide (3j). Procedure C was followed using sulfinyl imine **3d** (60.9 mg, 0.250 mmol) and commercially available (*E*)-styryl MIDA boronate **4d** (130 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 79.0 mg (91% yield, 99:1 dr) of **3j** as a pale yellow oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 222 nm): t_{minor} = 14.4 min, t_{major} = 16.2 min. ^{1}H NMR and HPLC corresponded to previously reported data.[1]



(R_S)-*N*-((*R*,*E*)-1-(4-chlorophenyl)-3-(4-(trifluoro)phenyl)allyl)-2-methylpropanesulfinamide (3k). Procedure C was followed using sulfinyl imine **3d** (60.9 mg, 0.250 mmol) and MIDA boronate **4e** (164 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 10-80% EtOAc/CH_2Cl_2) afforded 14.5 mg (14% yield, 99:1 dr) of **xx** as a pale yellow oil. HPLC (silica column, hexanes:*i*PrOH 97:3, 1.0 mL/min, λ = 254 nm): t_{minor} = 12.6 min, t_{major} = 17.1 min. ^{1}H NMR and HPLC corresponded to previously reported data.[1]

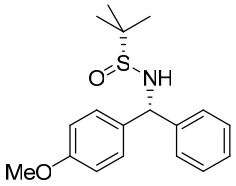


(R_S)-*N*-((*R*)-1-(4-chlorophenyl)-1-phenylmethyl)-2-methylpropanesulfinamide (3l).

- Procedure B was followed using sulfinyl imine **2d** (60.9 mg, 0.250 mmol) and commercially available trifluoroborate **1f** (92 mg, 0.50 mmol) in 2:3 DMF:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 67.5 mg (84% yield, 96:4 dr) of **3l** as a pale yellow solid. HPLC (silica column, hexanes:*i*PrOH 99:1, 1.0 mL/min, λ = 222

nm): t_{major} = 24.3 min, t_{minor} = 31.9 min). ^{1}H NMR data corresponded to previously reported data for the enantiomer.[11]

- Procedure C was followed using sulfinyl imine **2d** (60.9 mg, 0.250 mmol) and commercially available MIDA boronate **4f** (117 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 78.1 mg (97% yield, 98:2 dr) of **3l** as a pale yellow solid. HPLC (silica column, hexanes:*i*PrOH 99:1, 1.0 mL/min, λ = 222 nm): t_{major} = 24.2 min, t_{minor} = 31.8 min. ^{1}H NMR corresponded to previously reported data for the enantiomer.[11]



(R_S)-*N*-((*R*)-1-(4-methoxyphenyl)-1-phenylmethyl)-2-methylpropanesulfinamide (3m).

- Procedure B was followed using sulfinyl imine **2a** (59.8 mg, 0.250 mmol) and commercially available trifluoroborate **1f** (92 mg, 0.50 mmol) in 2:3 DMF:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 40.0 mg (50% yield, 94:6 dr) of **3m** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 222 nm): t_{minor} = 20.4 min, t_{major} = 22.1 min). ^{1}H NMR data corresponded to previously reported data for the enantiomer.[11]

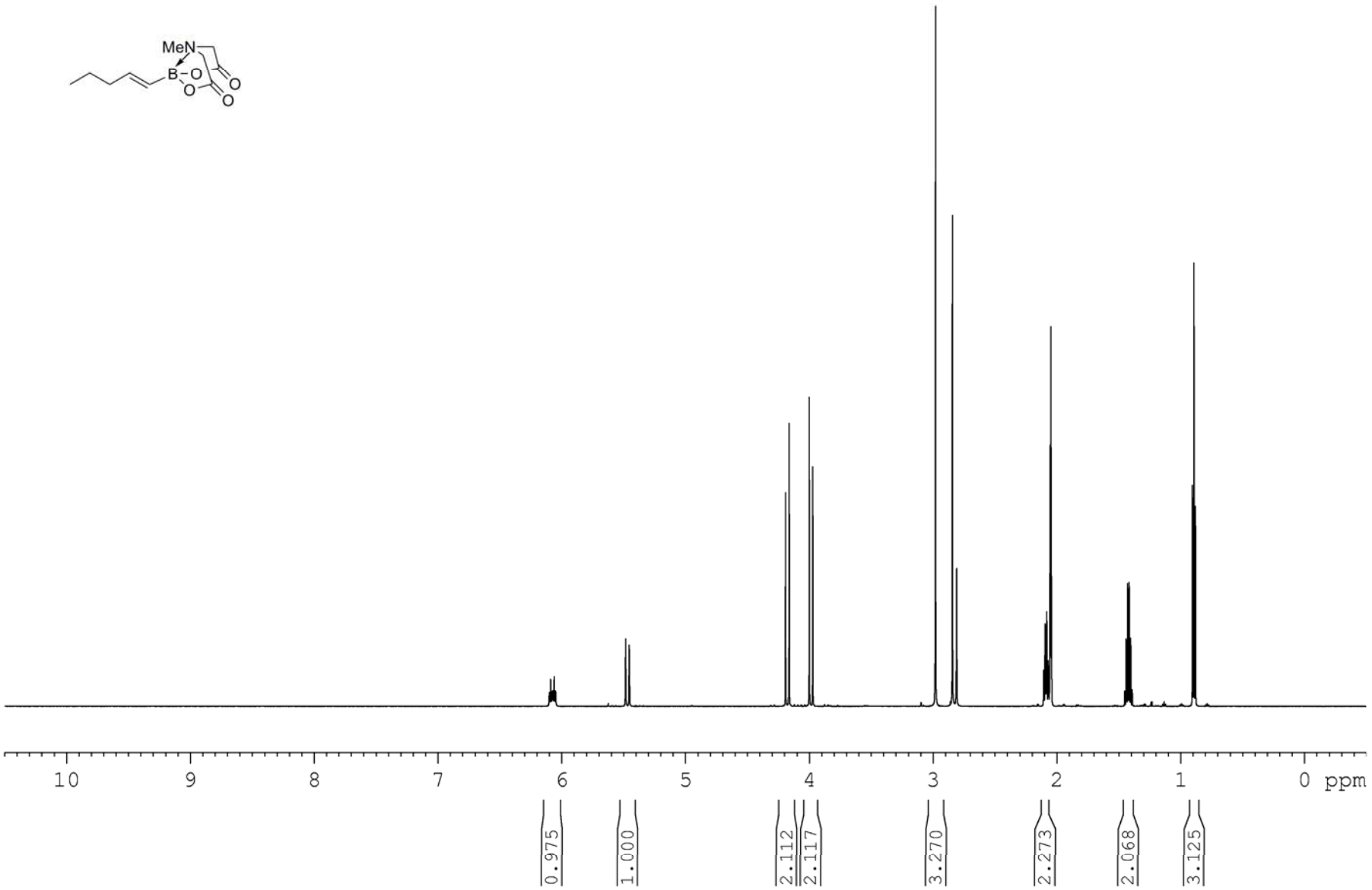
- Procedure C was followed using sulfinyl imine **2a** (59.8 mg, 0.250 mmol) and commercially available MIDA boronate **4f** (117 mg, 0.500 mmol) in 2:3 dioxane:H_2O (0.8:1.2 mL). The reaction mixture was stirred for 20 h. Column chromatography (Biotage Flash+ cartridge, 12-100% EtOAc/hexanes) afforded 70.6 mg (89% yield, 98:2 dr) of **xx** as a colorless oil. HPLC (silica column, hexanes:*i*PrOH 98:2, 1.0 mL/min, λ = 222 nm): t_{minor} = 20.4 min, t_{major} = 22.0 min. ^{1}H NMR data corresponded to previously reported data for the enantiomer.[11]

7. References

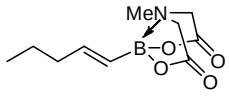
(1) Brak, K.; Ellman, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 3850.
(2) Brak, K.; Ellman, J. A. *Org. Lett.* **2010**, *12*, submitted.
(3) Liu, G.; Cogan, D. A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. *J. Org. Chem.* **1999**, *64*, 1278.
(4) Maji, M. S.; Frohlich, R.; Studer, A. *Org. Lett.* **2008**, *10*, 1847.
(5) Plobeck, N.; Powell, D. *Tetrahedron: Asymmetry* **2002**, *13*, 303.
(6) Owens, T. D.; Souers, A. J.; Ellman, J. A. *J. Org. Chem.* **2003**, *68*, 3.
(7) Schenkel, L. B.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 3621.
(8) Staas, D. D.; Savage, K. L.; Homnick, C. F.; Tsou, N. N.; Ball, R. G. *J. Org. Chem.* **2002**, *67*, 8276.
(9) Knapp, D. M.; Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 6961.
(10) Brak, K.; Barrett, K. T.; Ellman, J. A. *J. Org. Chem.* **2009**, *74*, 3606.
(11) Bolshan, Y.; Batey, R. A. *Org. Lett.* **2005**, *7*, 1481.

8. NMR spectra

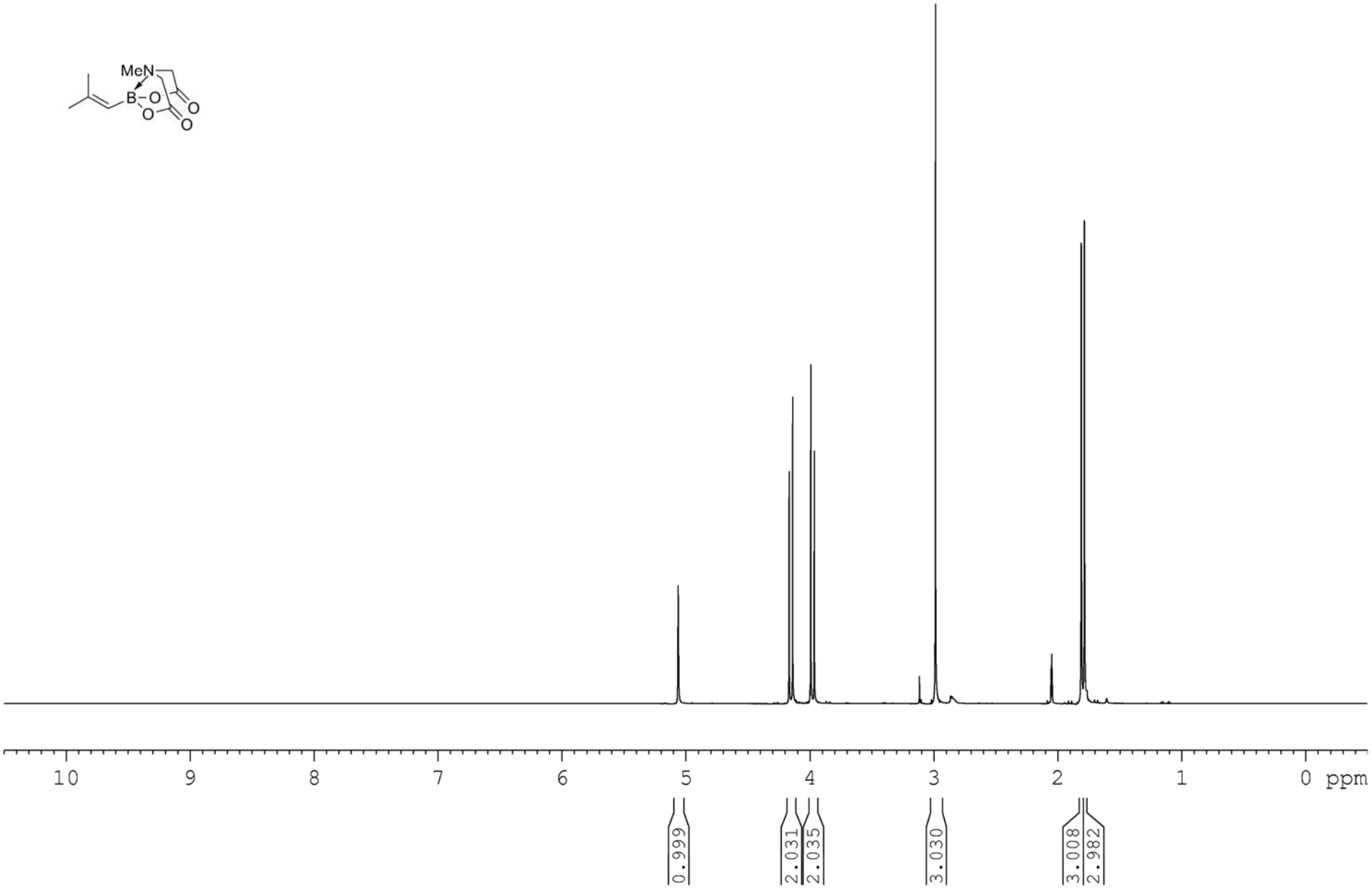
MIDA boronate **4a** ^{1}H-NMR (600 MHz, acetone-d_6):



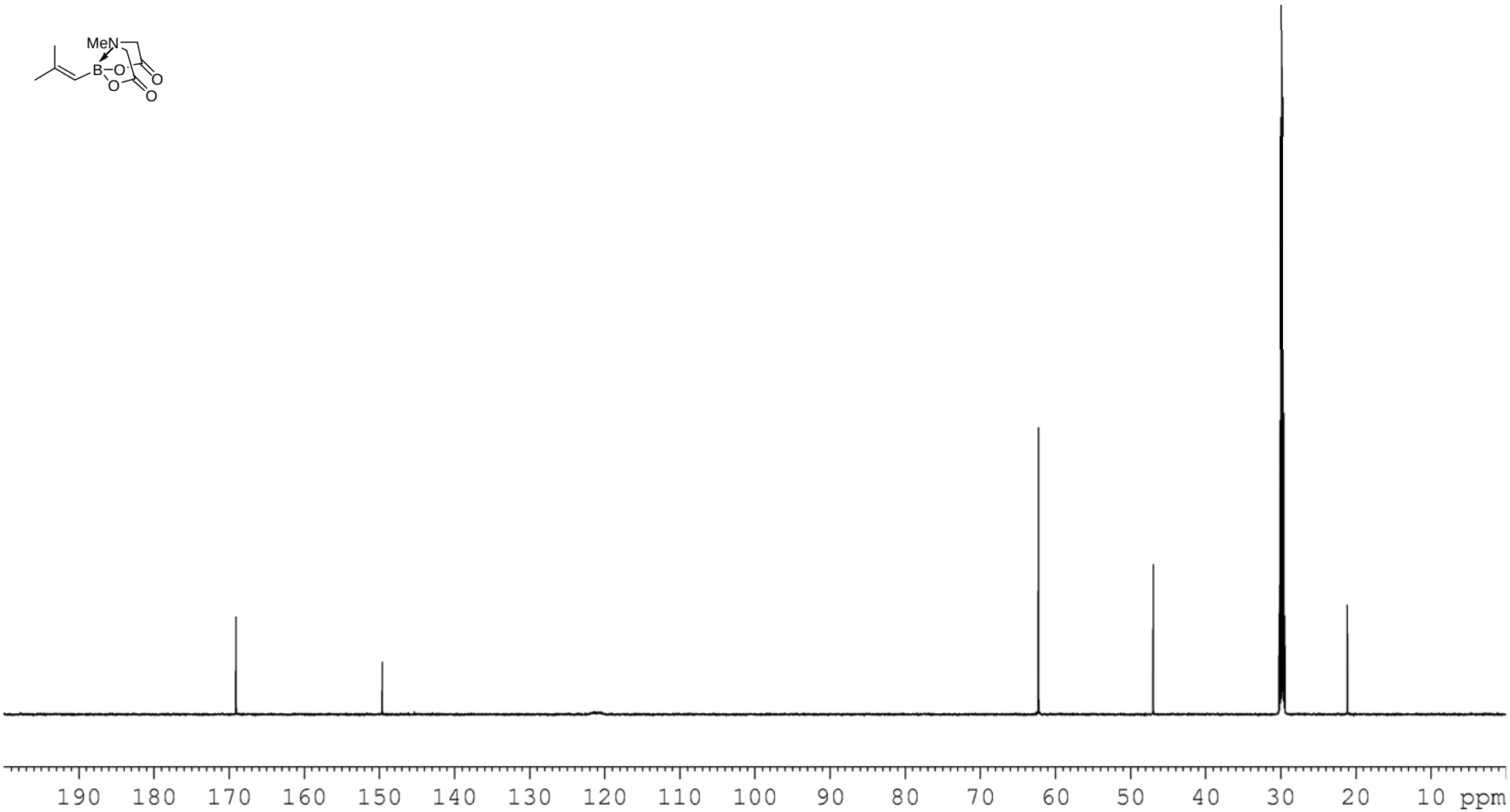
MIDA boronate **4a** ^{13}C-NMR (150 MHz, $CDCl_3$):



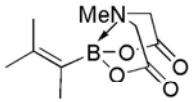
MIDA boronate **4b** ^{1}H-NMR (600 MHz, acetone-d_6):



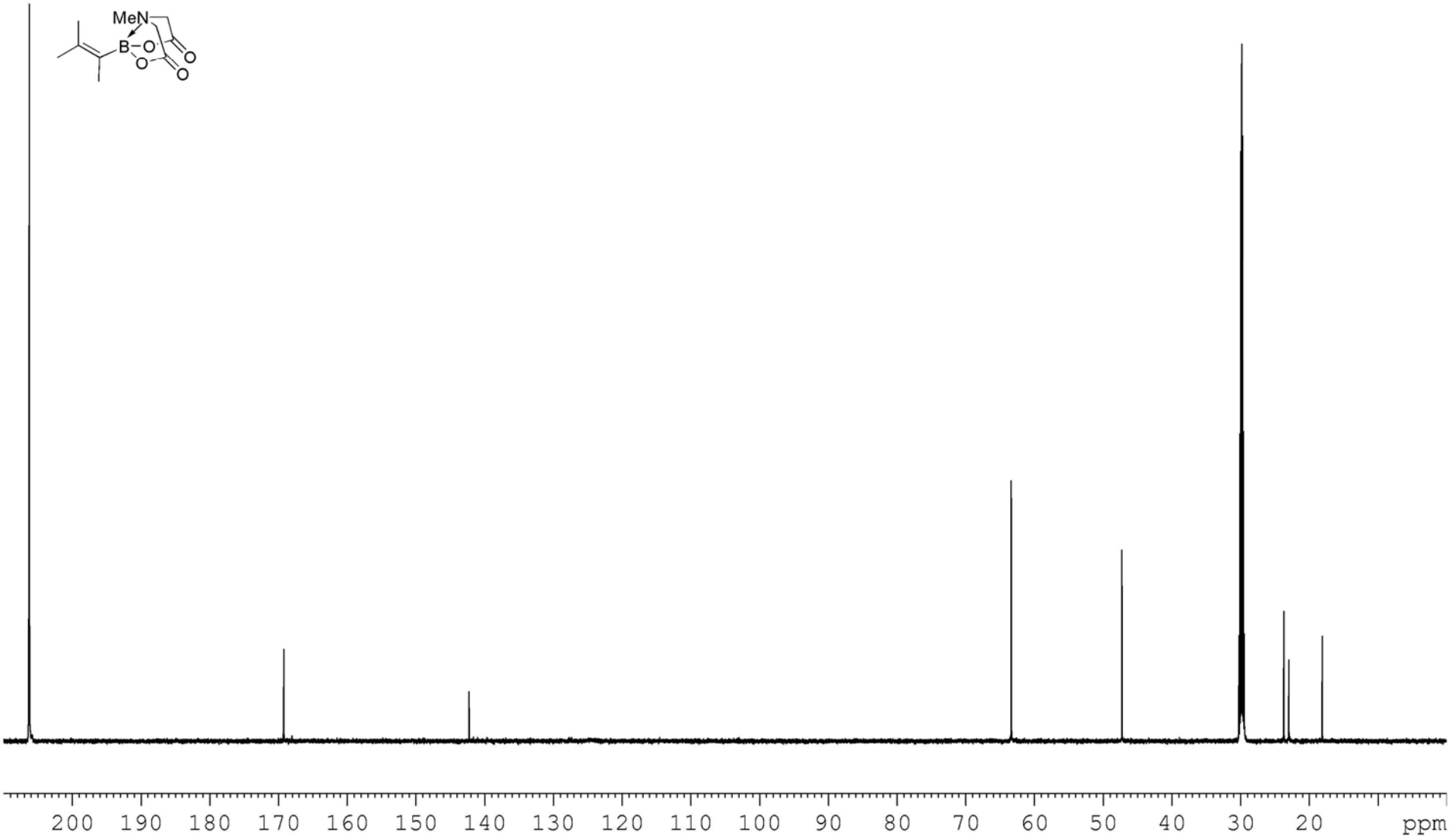
MIDA boronate **4b** ^{13}C-NMR (150 MHz, acetone-d_6):



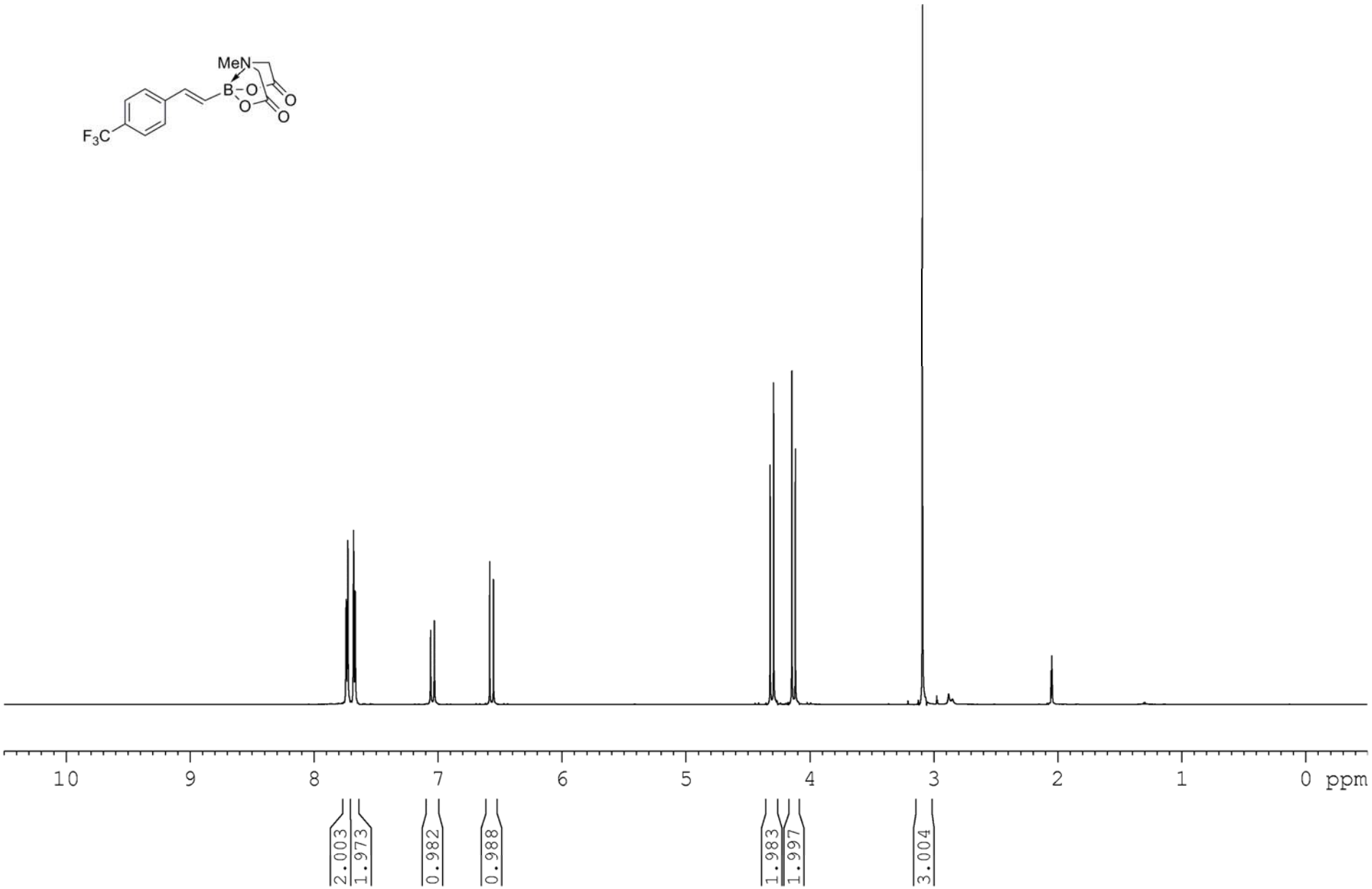
MIDA boronate **4c** ^{1}H-NMR (500 MHz, acetone-d_6):



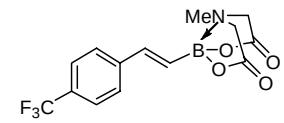
MIDA boronate **4c** ^{13}C-NMR (150 MHz, acetone-d_6):



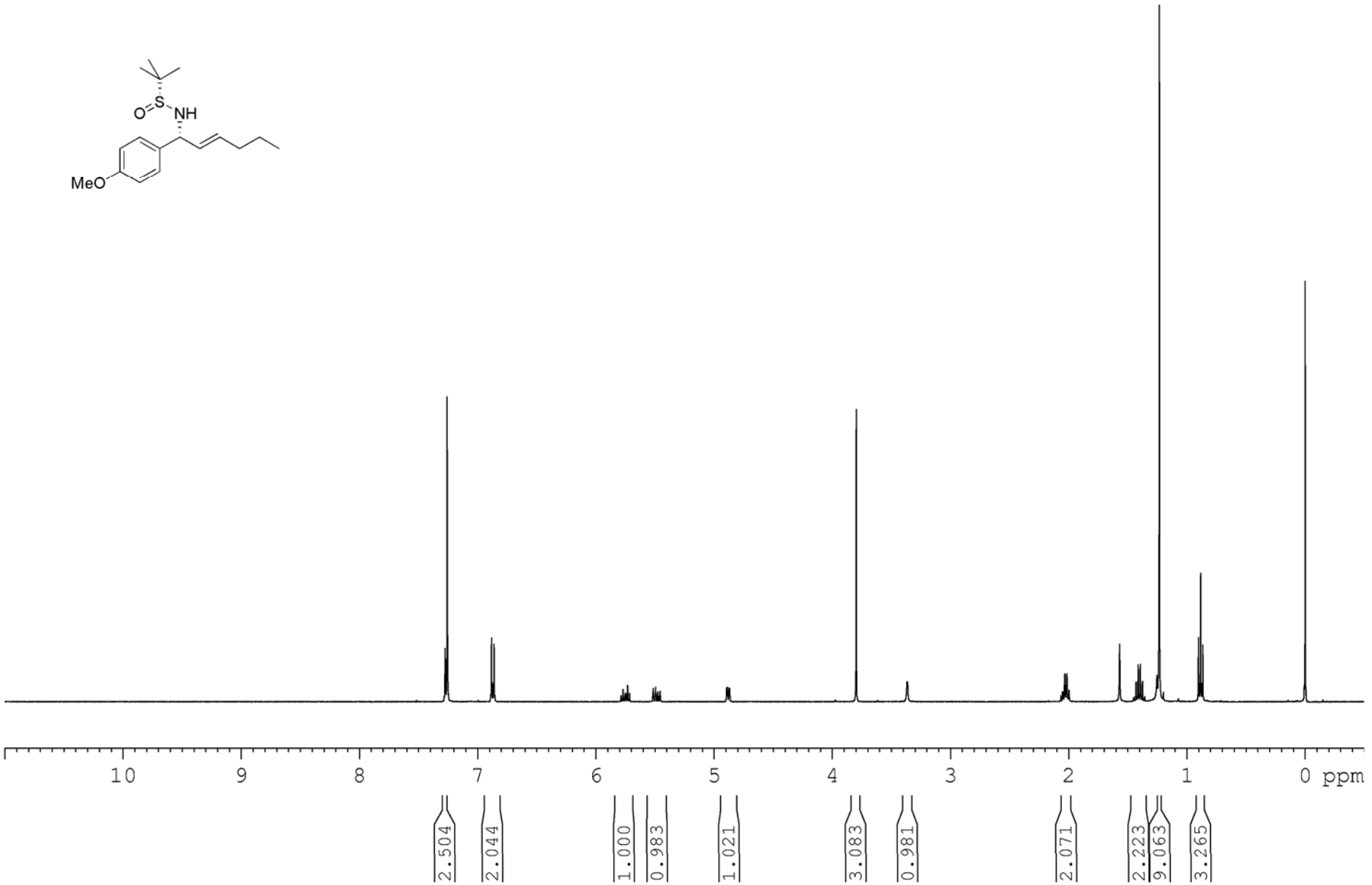
MIDA boronate **4e** ^{1}H-NMR (600 MHz, acetone-d_6):



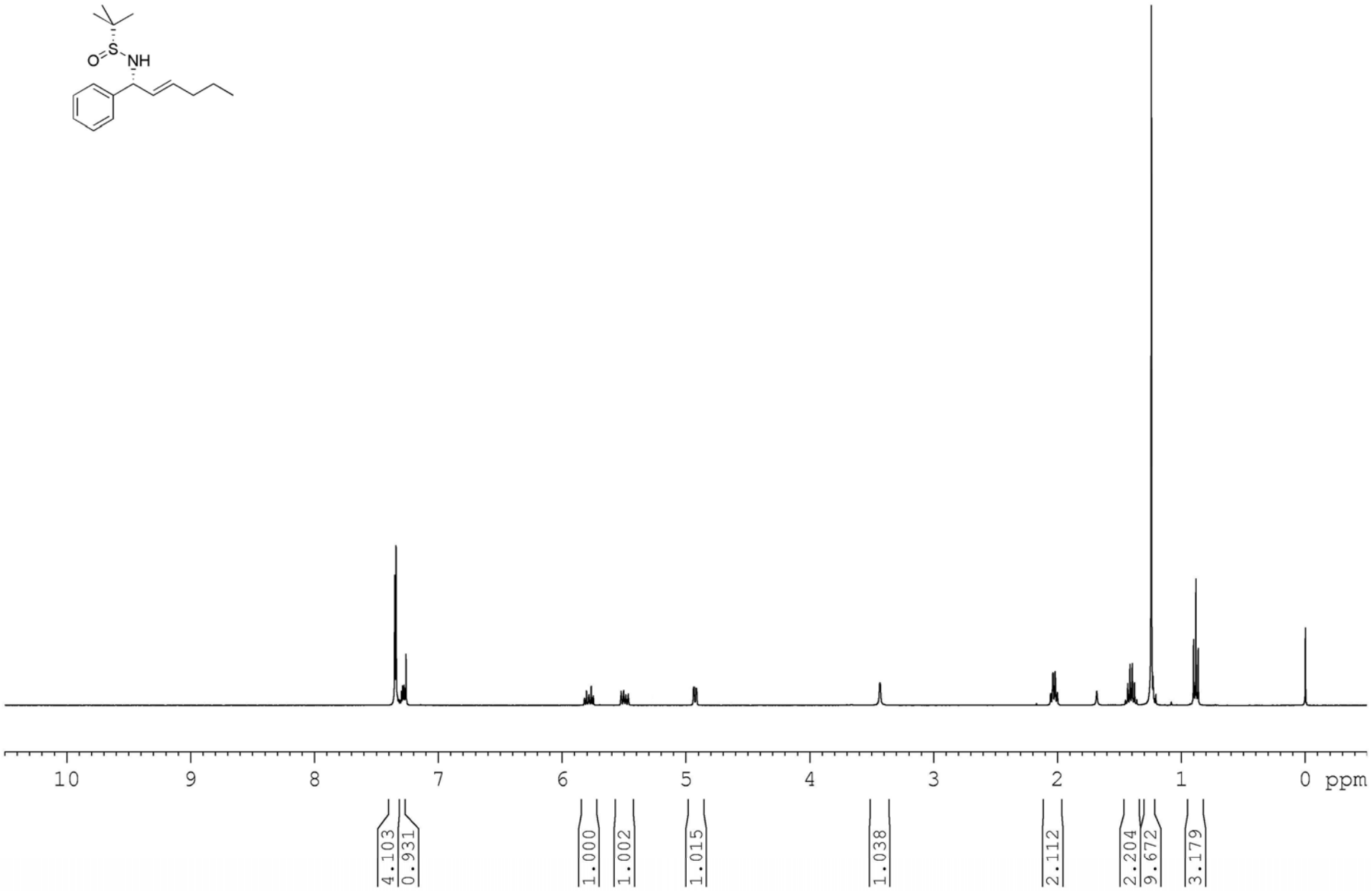
MIDA boronate **4e** ^{13}C-NMR (150 MHz, acetone-d_6):



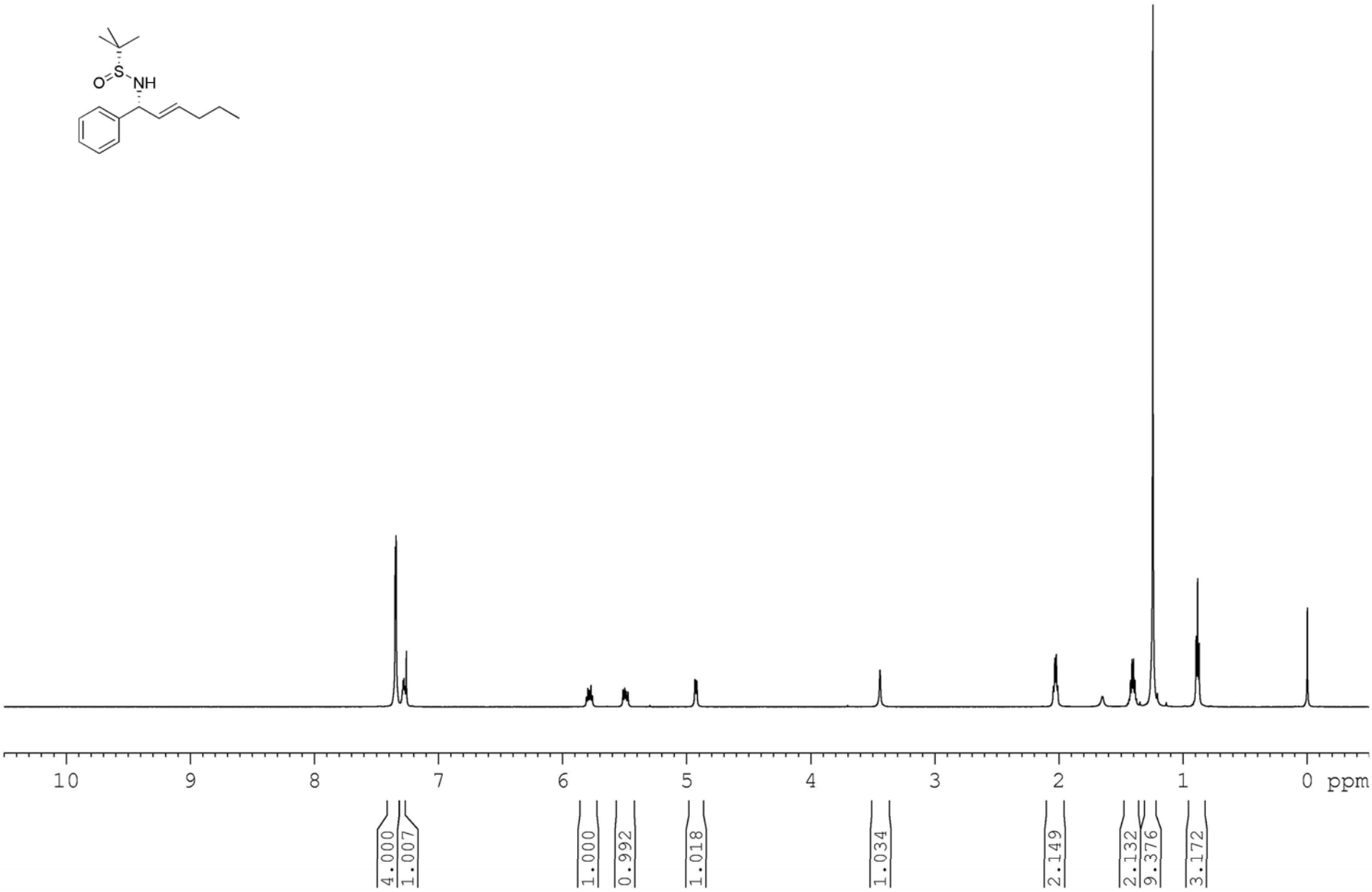
Sulfinamide **3a** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure C):



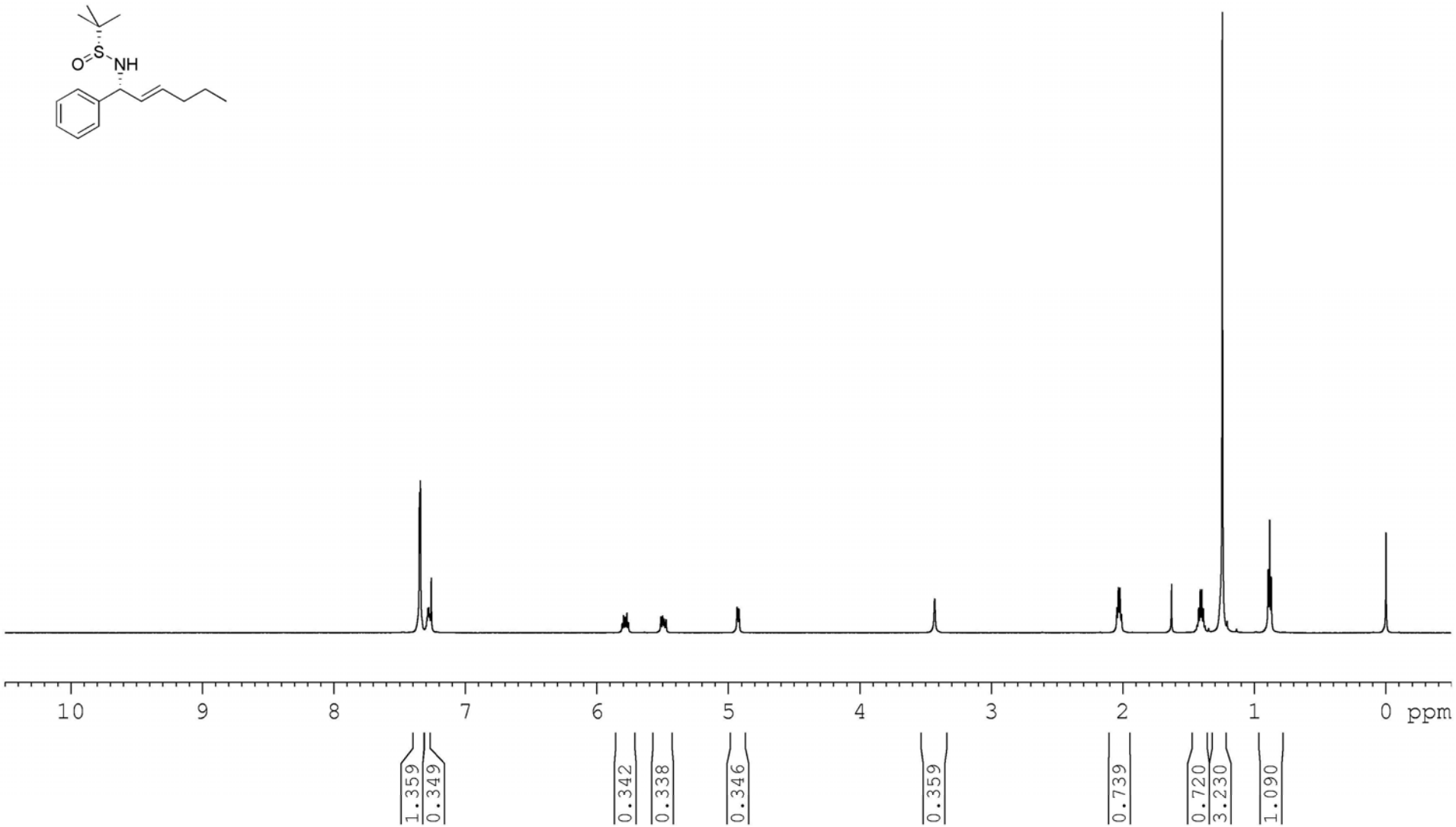
Sulfinamide **3b** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure B with 1.2 equiv):



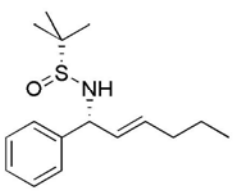
Sulfinamide **3b** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C with 2 equiv):



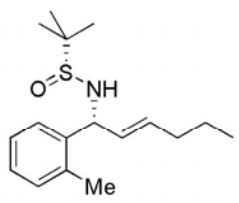
Sulfinamide **3b** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C with 1.2 equiv):



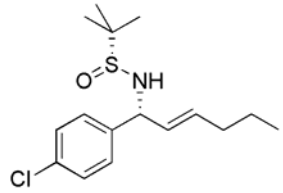
Sulfinamide **3b** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure D):



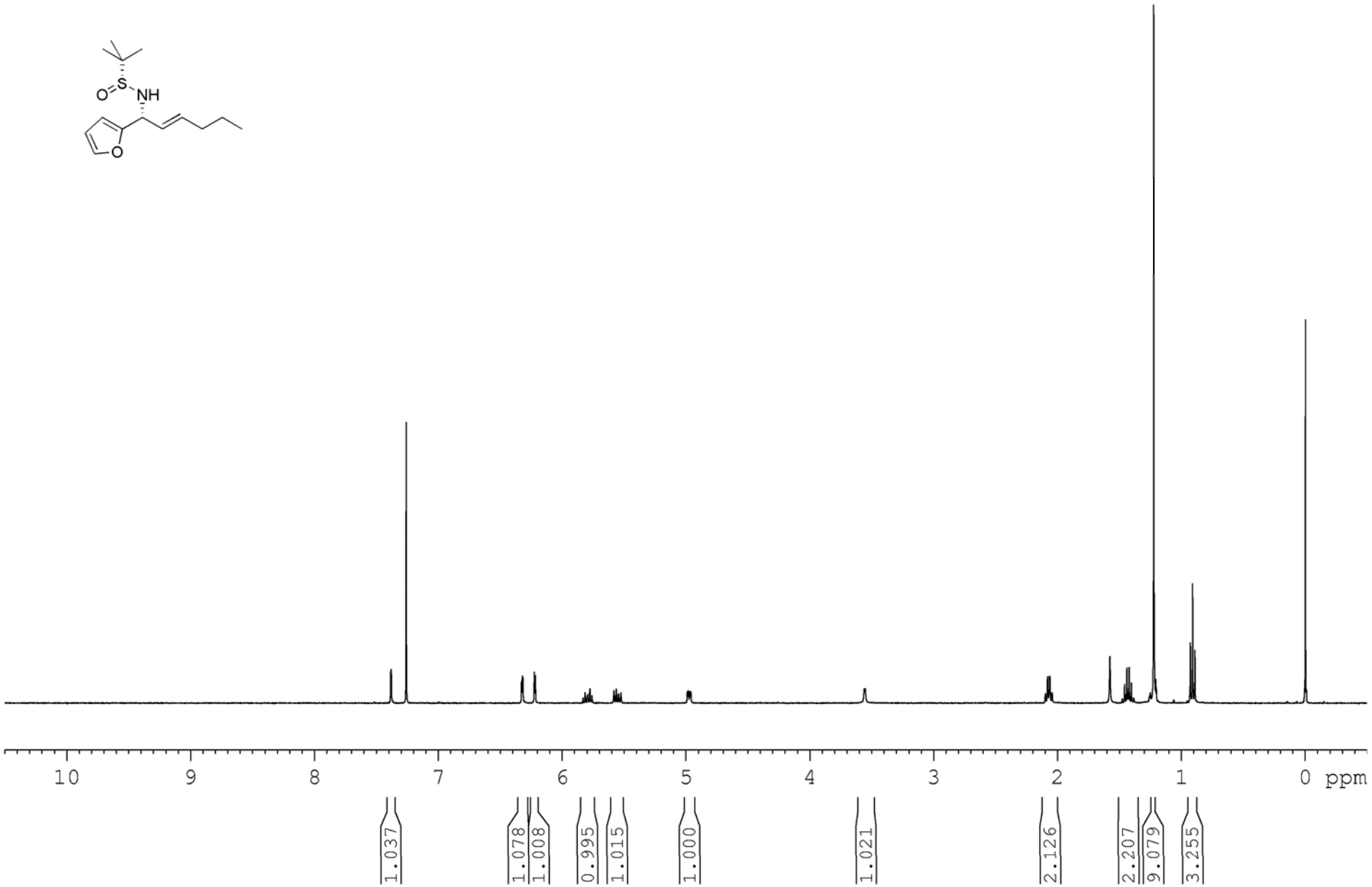
Sulfinamide **3c** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C):



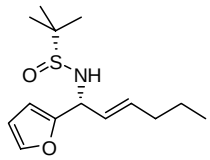
Sulfinamide **3d** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure C):



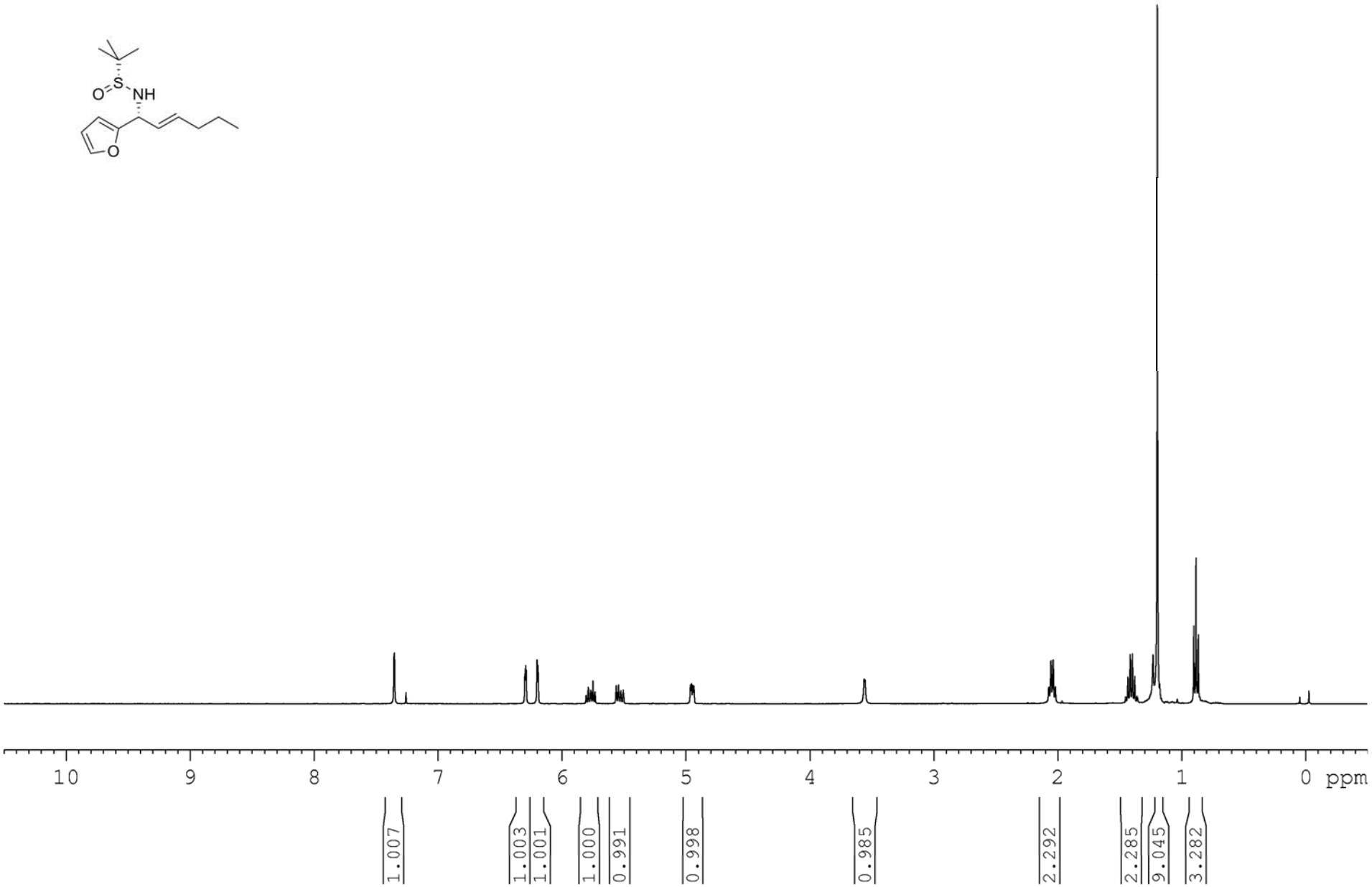
Sulfinamide **3e** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure B):



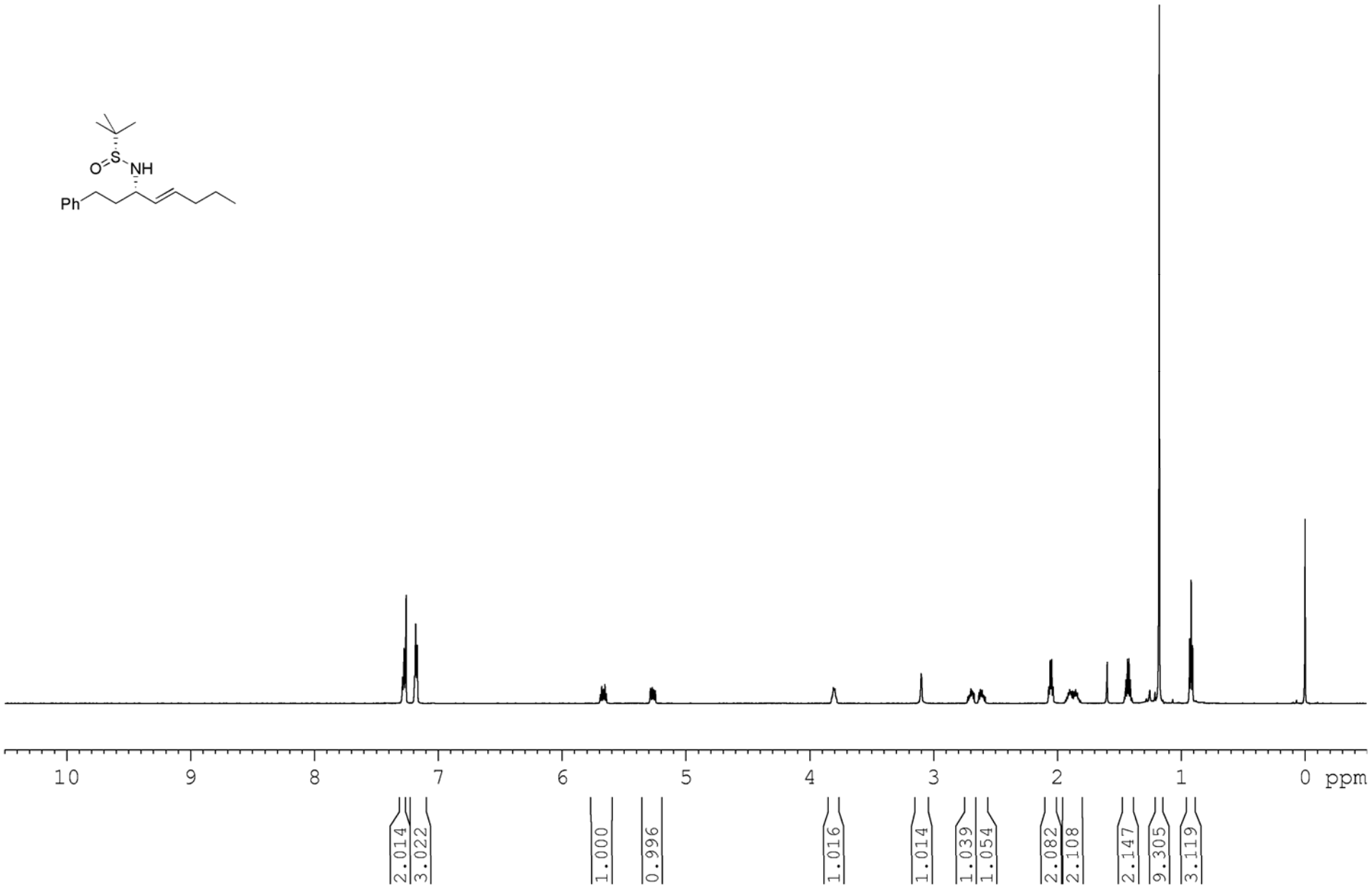
Sulfinamide **3e** ^{13}C-NMR (100 MHz, $CDCl_3$; Procedure B):



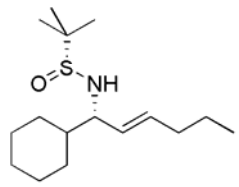
Sulfinamide **3e** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure C):



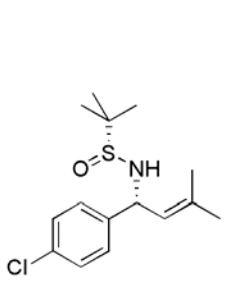
Sulfinamide **3f** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C):



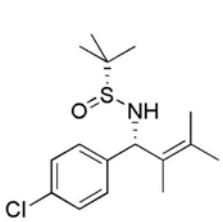
Sulfinamide **3g** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C):



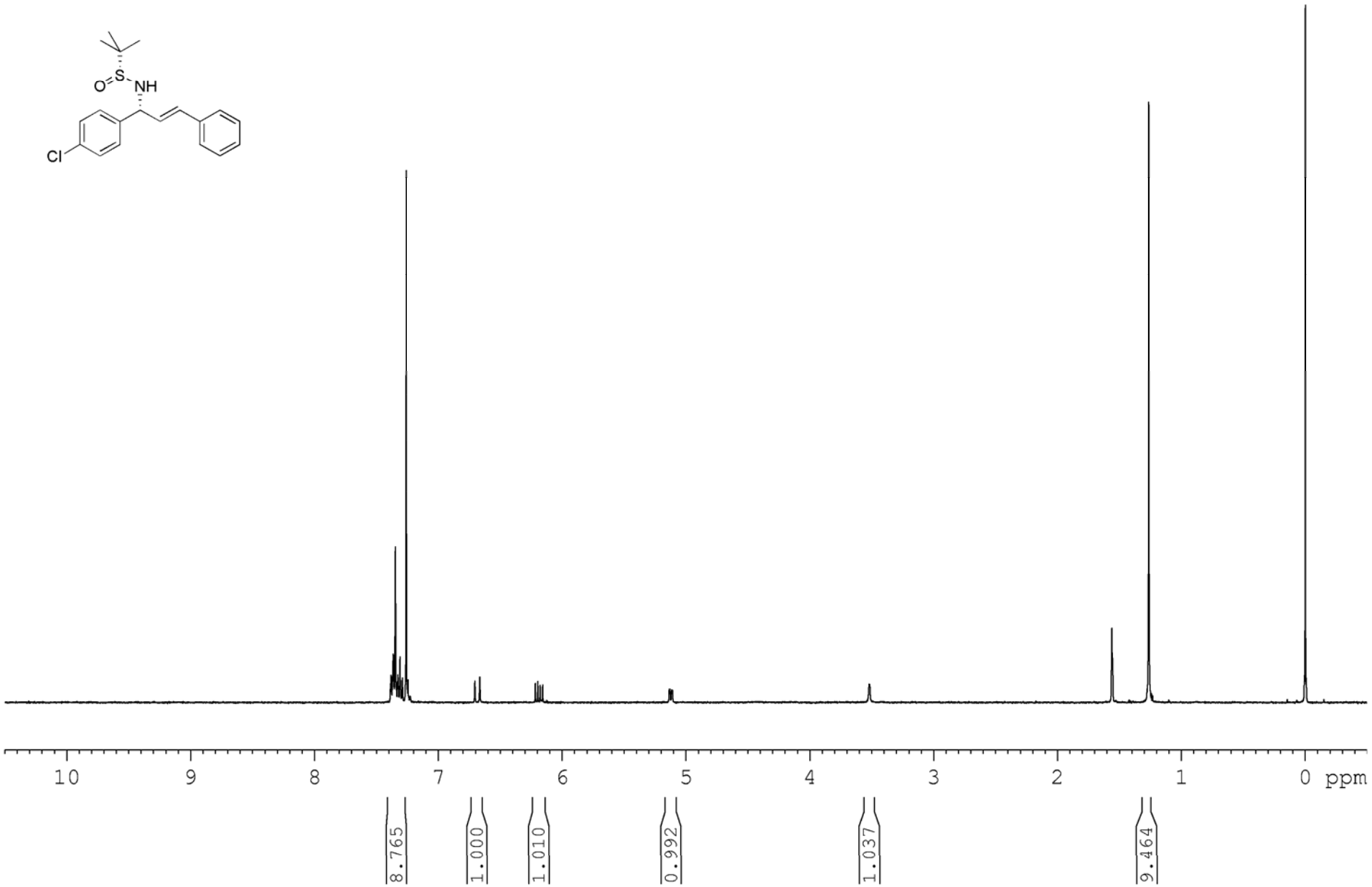
Sulfinamide **3h** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C):



Sulfinamide **3i** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C):



Sulfinamide **3j** ^{1}H-NMR (600 MHz, $CDCl_3$; Procedure C):



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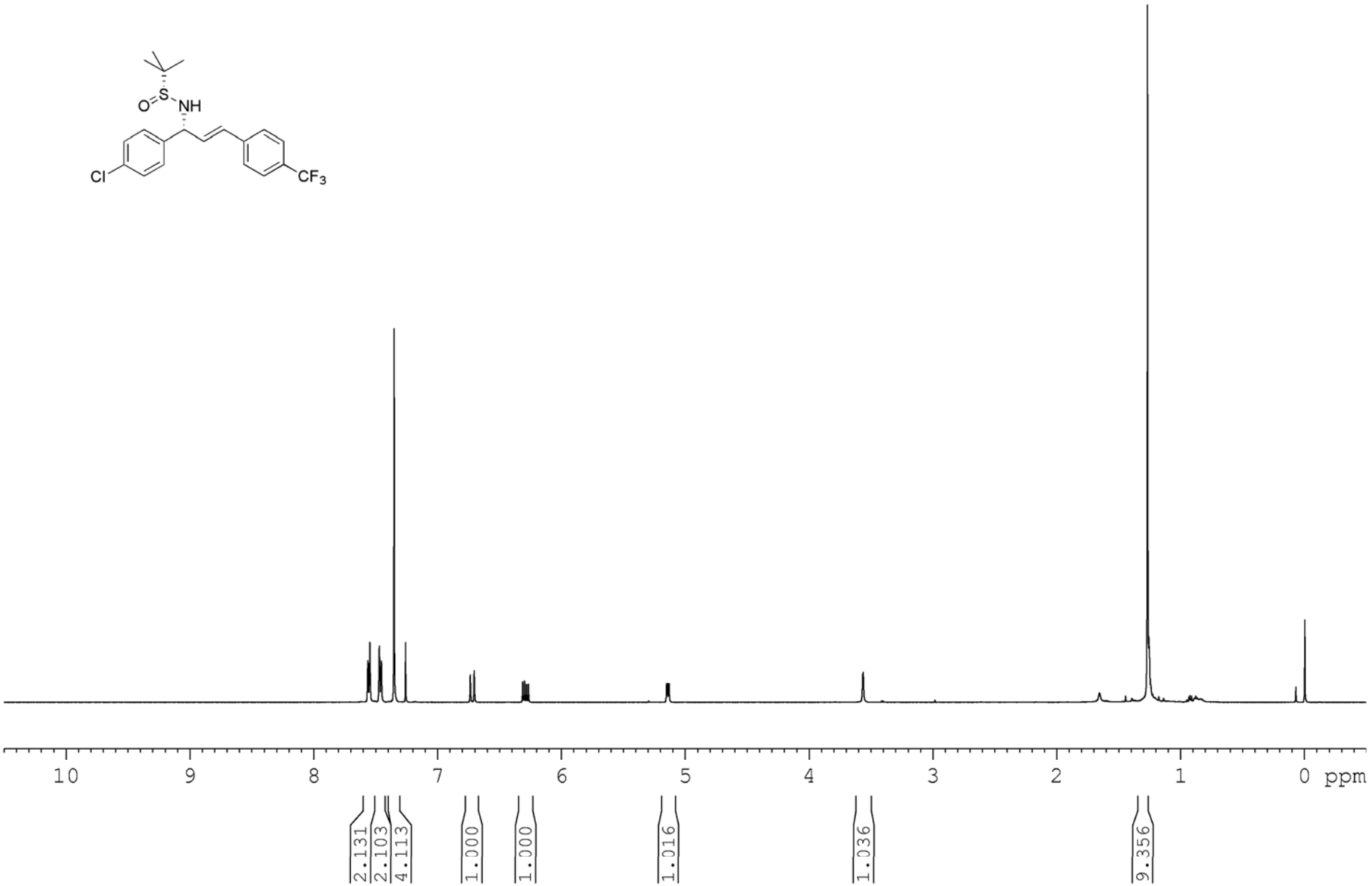
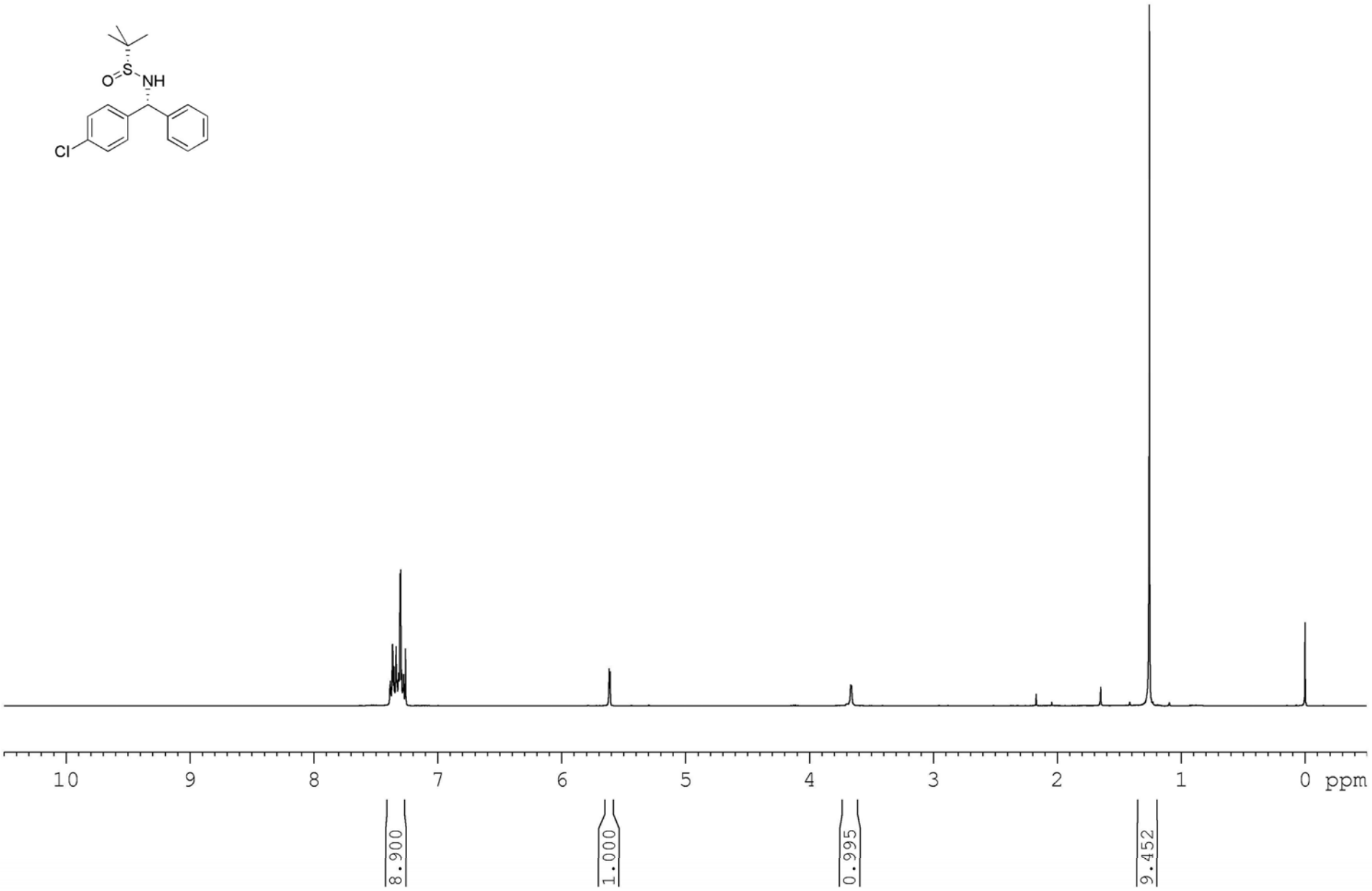
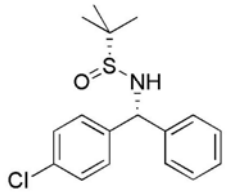


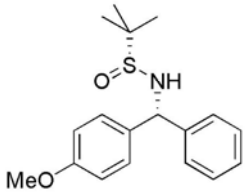
Sulfinamide **3l** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure B):



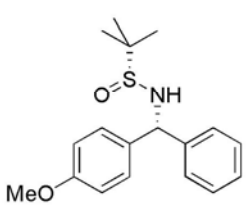
Sulfinamide **3l** ^{1}H-NMR (500 MHz, $CDCl_3$; Procedure C):



Sulfinamide **3m** ^{1}H-NMR (400 MHz, $CDCl_3$; Procedure B):

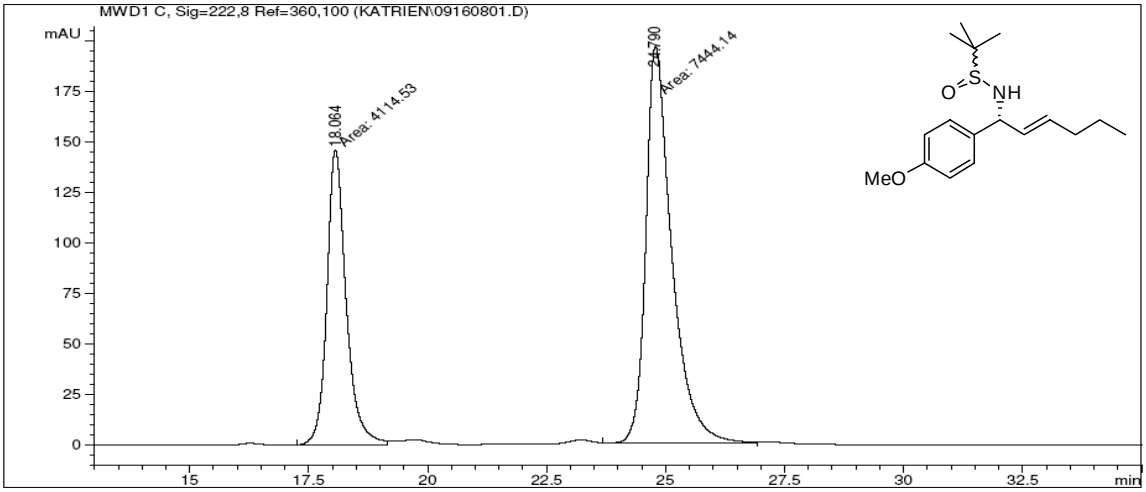


Sulfinamide **3m** ^{1}H-NMR (500 MHz, $CDCl_3$; Procedure C):



9. HPLC traces

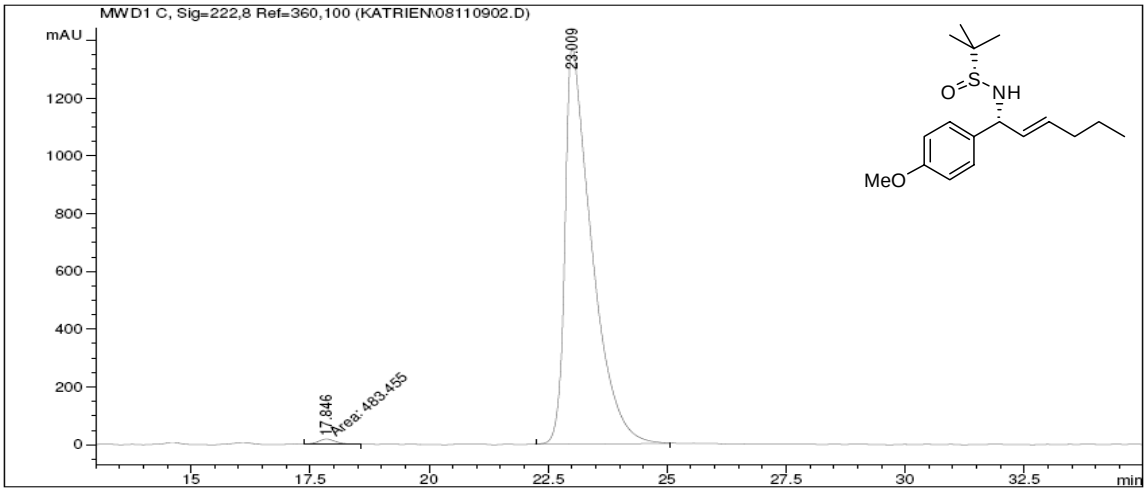
Sulfinamide **3a** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.064	MM	0.4690	4114.53223	146.22235	35.5969
2	24.790	MM	0.6311	7444.13574	196.58430	64.4031
Totals :				1.15587e4	342.80666	

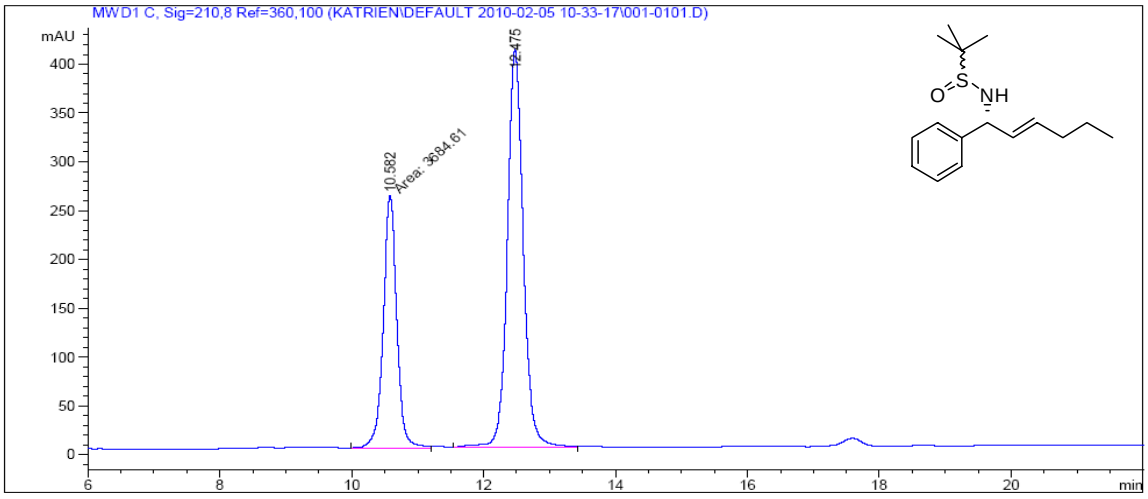
Sulfinamide **3a** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.846	MM	0.4402	483.45477	18.30606	0.8921
2	23.009	BB	0.5447	5.37113e4	1372.13489	99.1079
Totals :				5.41947e4	1390.44094	

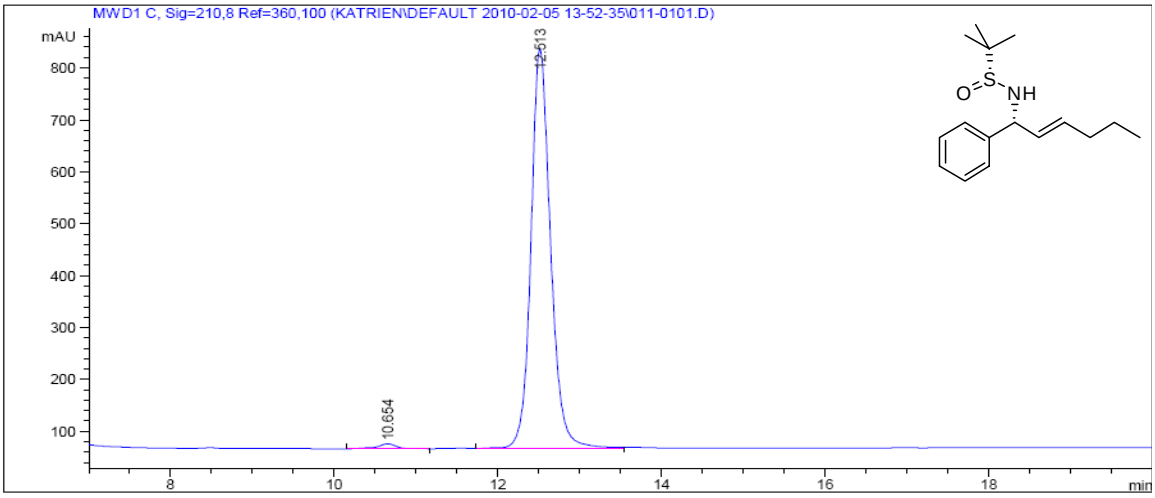
Sulfinamide **3b** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.582	MM	0.2376	3684.60693	258.44226	35.0102
2	12.475	BV	0.2534	6839.76953	408.27560	64.9898
Totals :				1.05244e4	666.71786	

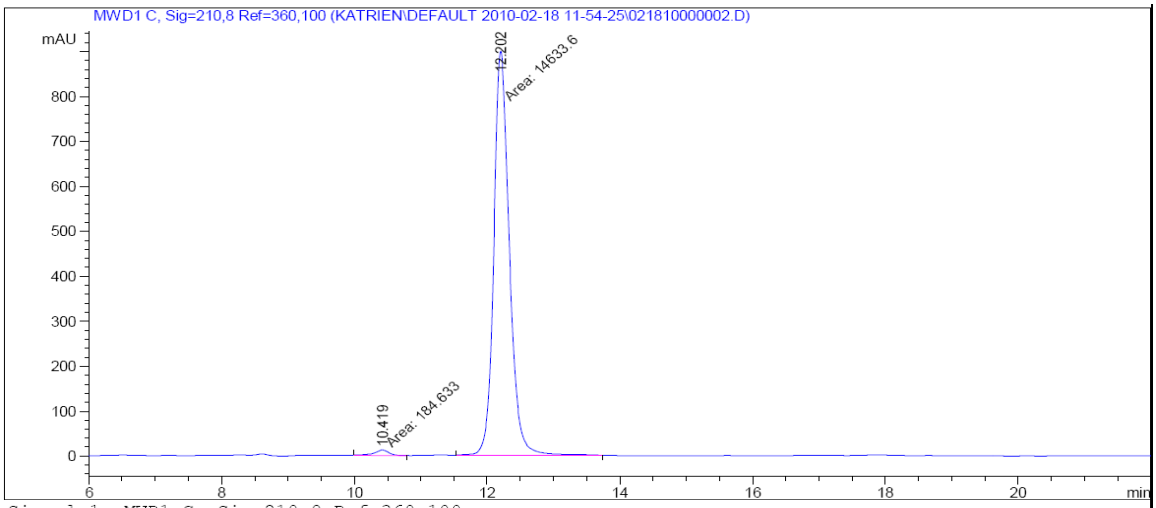
Sulfinamide **3b** HPLC trace (Procedure C with 2 equiv MIDA boronate):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.654	BB	0.2373	150.07744	9.34597	1.1533
2	12.513	VB	0.2528	1.28628e4	770.55206	98.8467
Totals :				1.30129e4	779.89803	

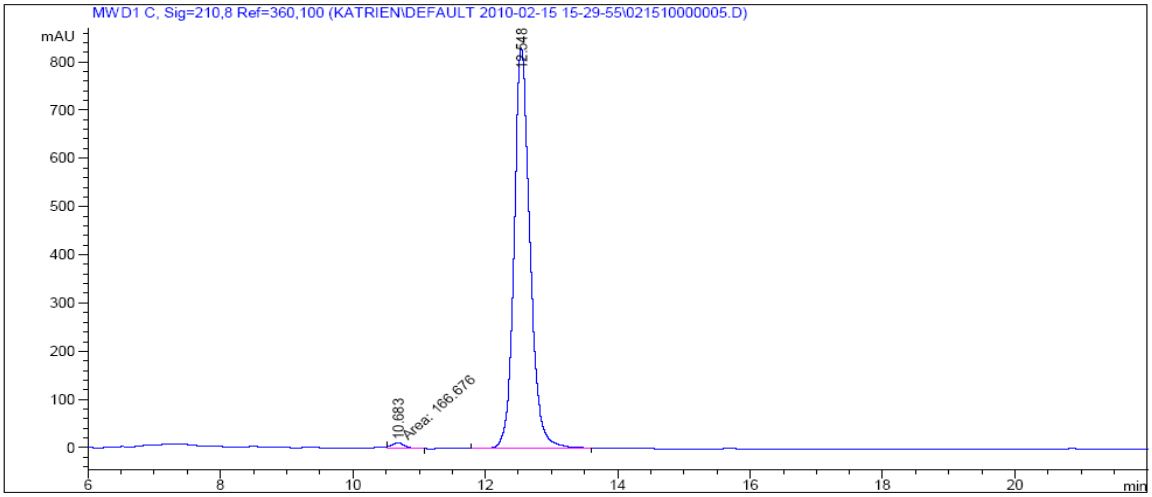
Sulfinamide **3b** HPLC trace (Procedure D):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.419	MM	0.2563	184.63289	12.00535	1.2460
2	12.202	MM	0.2713	1.46336e4	898.92535	98.7540
Totals :				1.48182e4	910.93070	

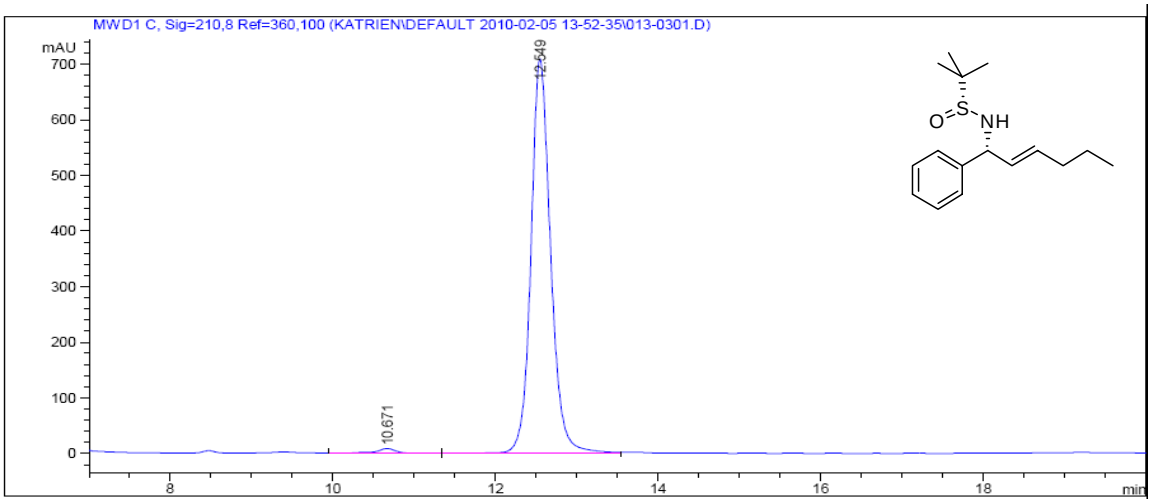
Sulfinamide **3b** HPLC trace (Procedure B with 1.2 equiv trifluoroborate):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.683	MM	0.2429	166.67638	11.43609	1.1919
2	12.548	VB	0.2522	1.38169e4	830.06158	98.8081
Totals :				1.39836e4	841.49767	

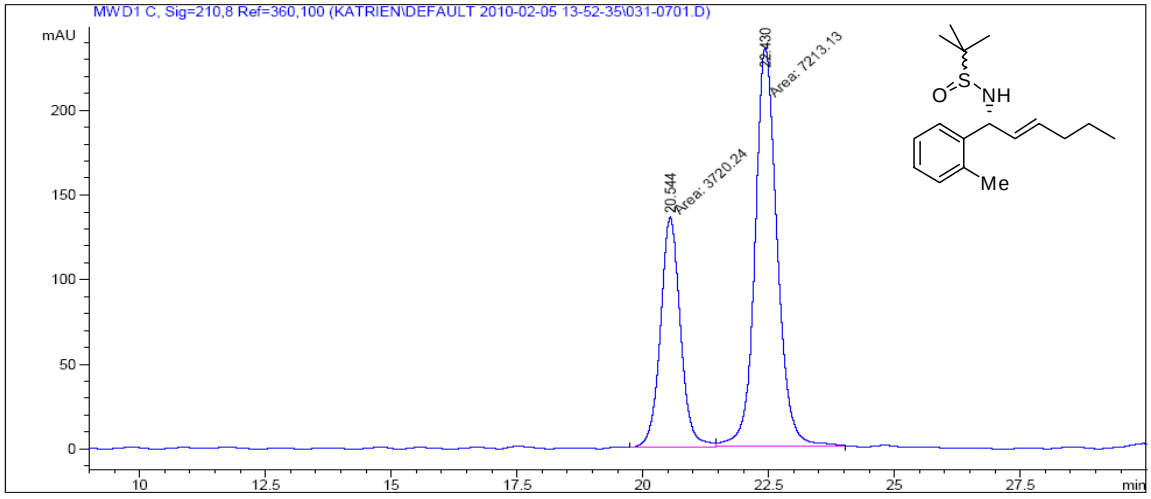
Sulfinamide **3b** HPLC trace (Procedure C with 1.2 equiv MIDA boronate):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.671	VV	0.2489	143.05196	8.30821	1.1871
2	12.549	VV	0.2562	1.19071e4	707.92548	98.8129
Totals :				1.20502e4	716.23369	

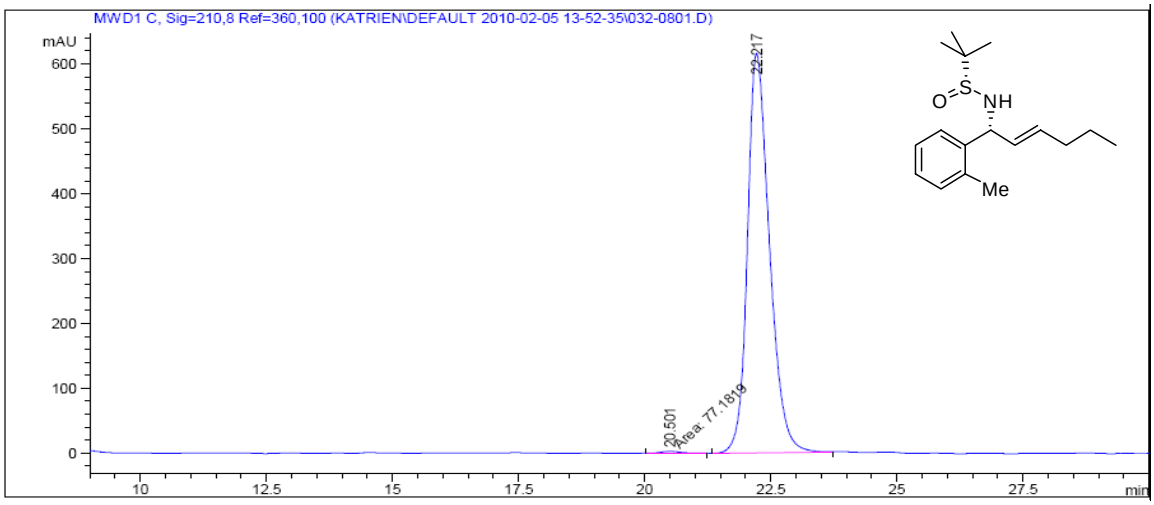
Sulfinamide **3c** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.544	MF	0.4569	3720.24243	135.69612	34.0265
2	22.430	FM	0.5103	7213.13379	235.60440	65.9735
Totals :				1.09334e4	371.30052	

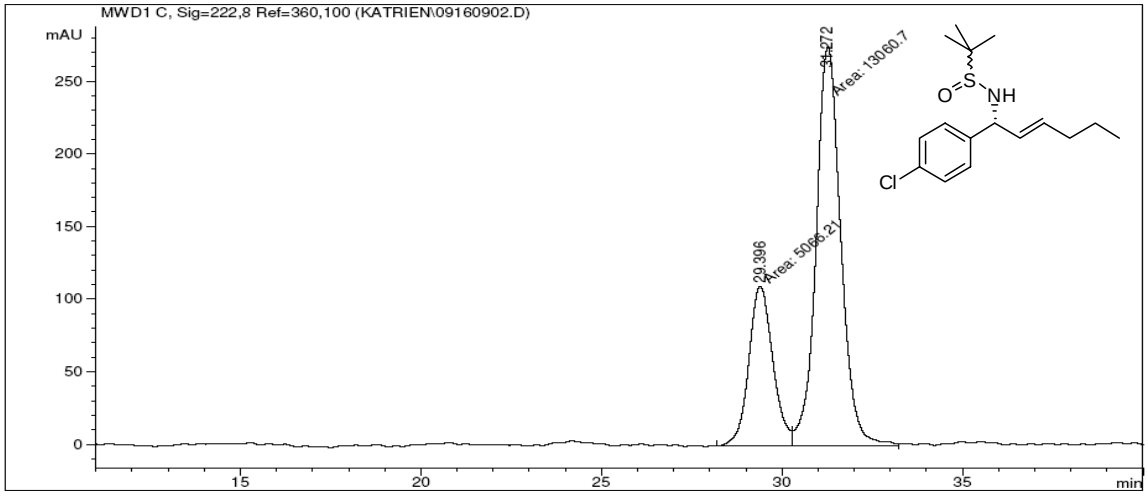
Sulfinamide **3c** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.501	MM	0.4626	77.18195	2.78043	0.4117
2	22.217	VB	0.4598	1.86685e4	615.59662	99.5883
Totals :				1.87457e4	618.37705	

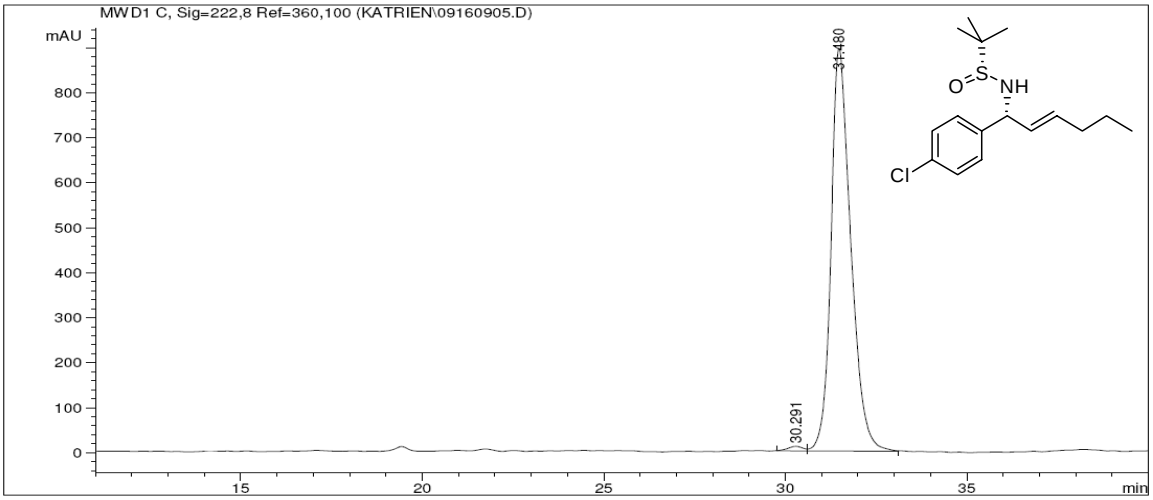
Sulfinamide **3d** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.396	MF	0.7707	5066.20947	109.56258	27.9485
2	31.272	FM	0.7943	1.30607e4	274.03549	72.0515
Totals :				1.81270e4	383.59807	

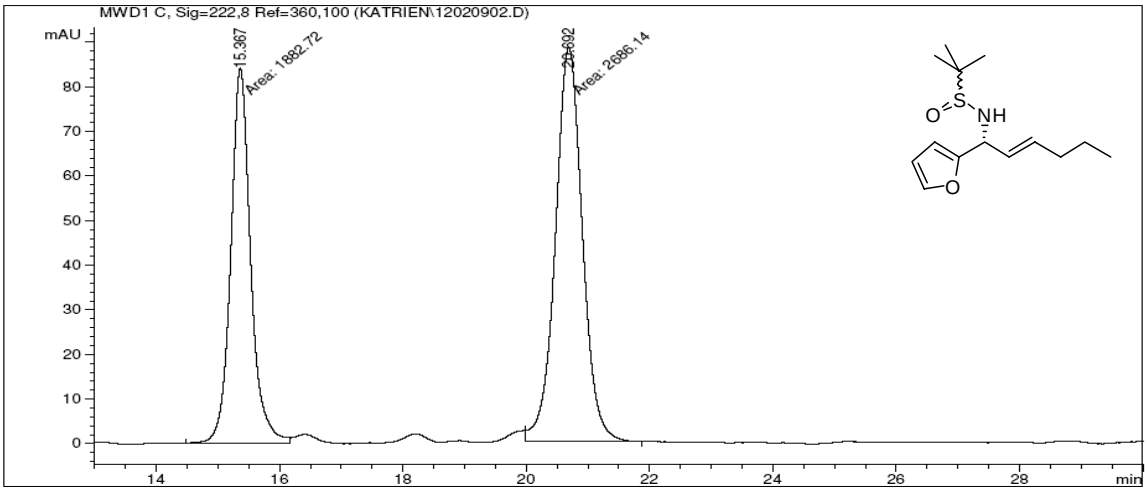
Sulfinamide **3d** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.291	BV	0.4386	299.46173	10.19693	0.8748
2	31.480	VB	0.5599	3.39319e4	895.88983	99.1252
Totals :				3.42314e4	906.08676	

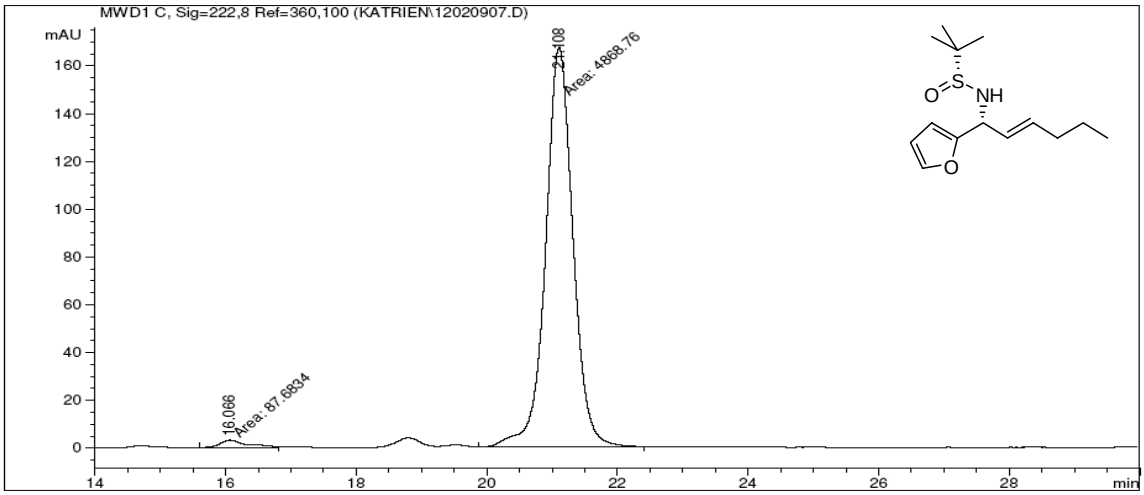
Sulfinamide **3e** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.367	MM	0.3737	1882.71558	83.96080	41.2076
2	20.692	MM	0.5063	2686.13647	88.41515	58.7924
Totals :				4568.85205	172.37595	

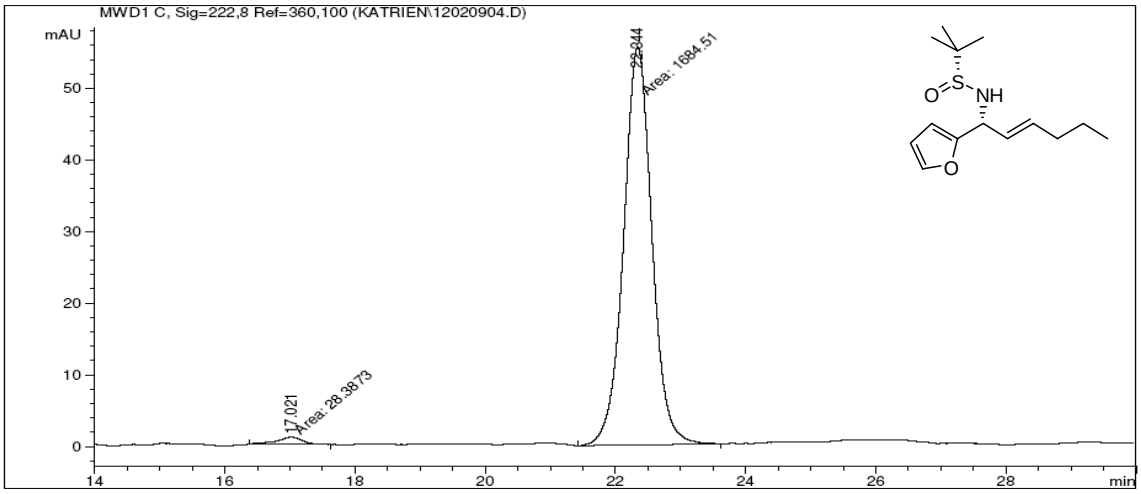
Sulfinamide **3e** HPLC trace (Procedure B):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.066	MM	0.4756	87.68341	3.07262	1.7691
2	21.108	MM	0.4857	4868.76025	167.07237	98.2309
Totals :				4956.44366	170.14499	

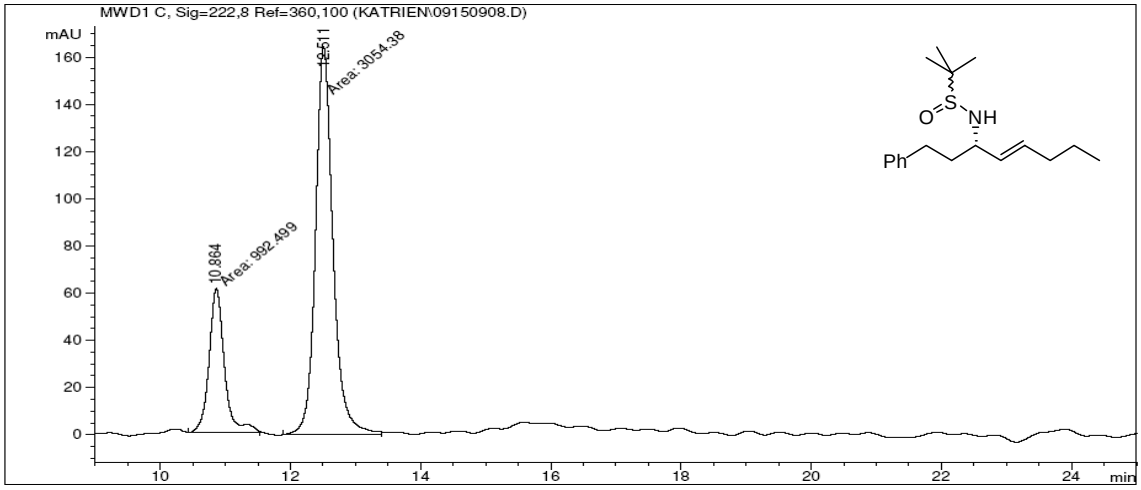
Sulfinamide **3e** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.021	MM	0.4640	28.38732	1.01965	1.6573
2	22.344	MM	0.5057	1684.50610	55.51943	98.3427
Totals :				1712.89342	56.53908	

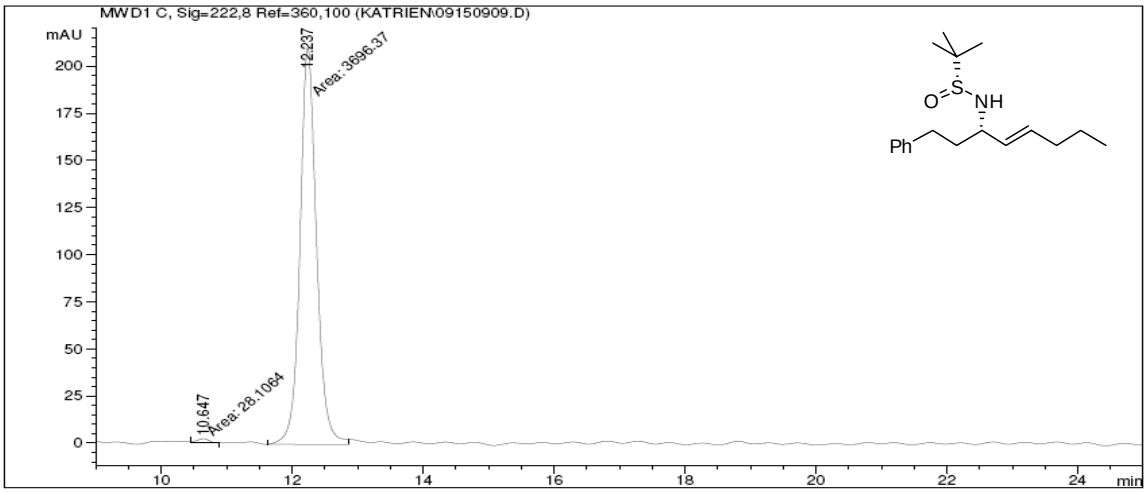
Sulfinamide **3f** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.864	MM	0.2715	992.49872	60.92955	24.5251
2	12.511	MM	0.3100	3054.37549	164.23750	75.4749
Totals :				4046.87421	225.16705	

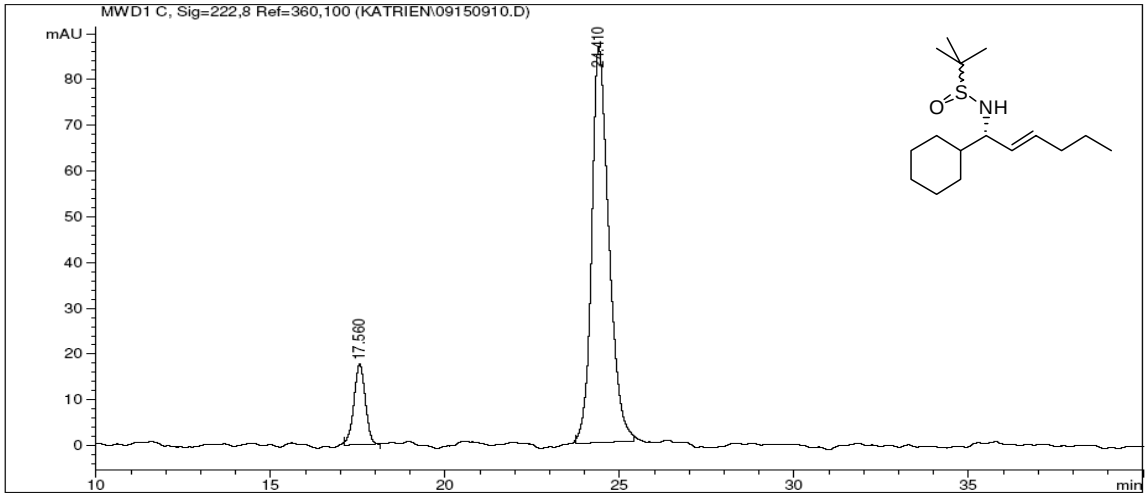
Sulfinamide **3f** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.647	MM	0.2200	28.10642	2.12884	0.7546
2	12.237	MM	0.2927	3696.36572	210.49593	99.2454
Totals :				3724.47215	212.62476	

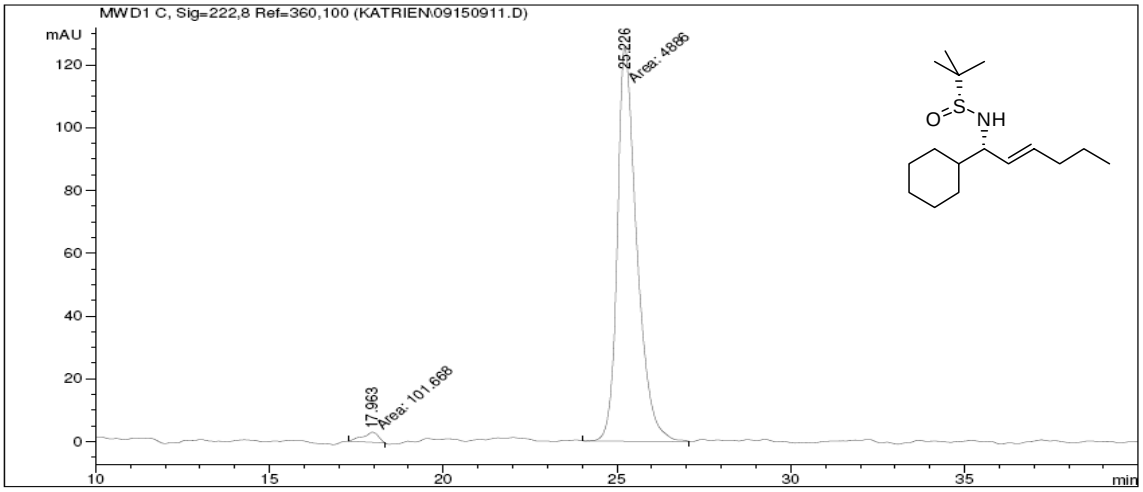
Sulfinamide **3g** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.560	BP	0.3499	398.36917	17.61201	11.8414
2	24.410	BB	0.5161	2965.83594	86.47298	88.1586
Totals :				3364.20511	104.08500	

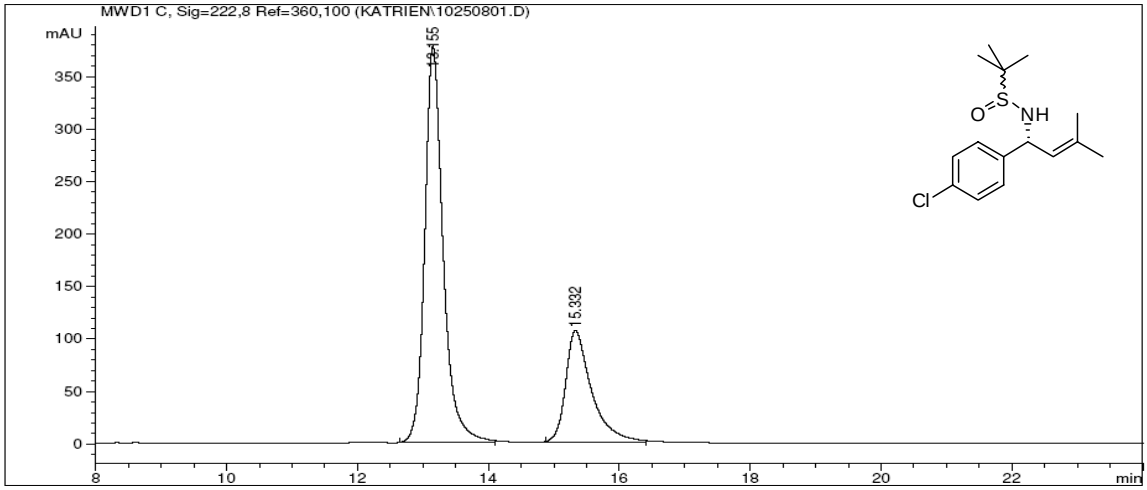
Sulfinamide **3g** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.963	MM	0.5260	101.66827	3.22121	2.0384
2	25.226	MM	0.6496	4886.00195	125.35416	97.9616
Totals :				4987.67023	128.57538	

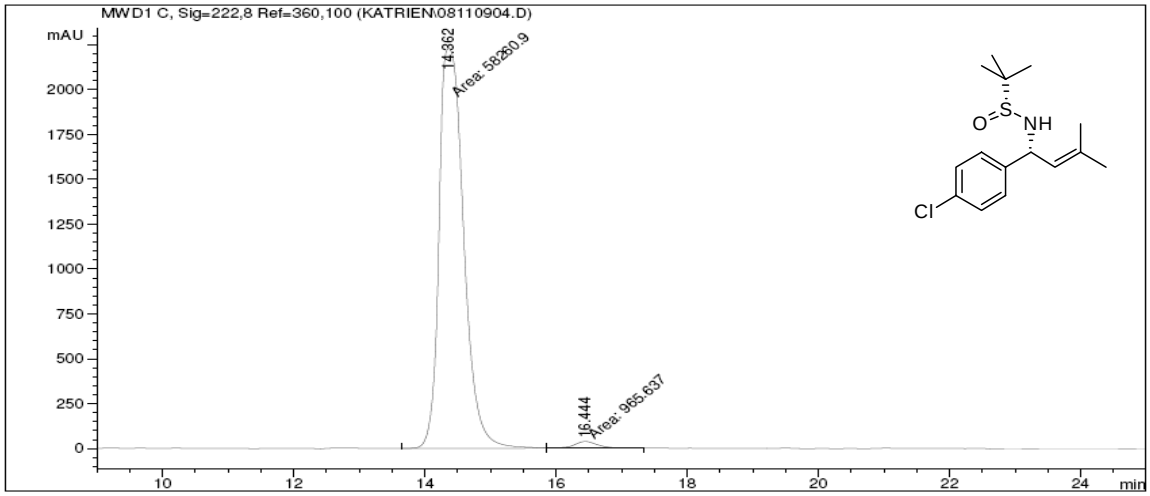
Sulfinamide **3h** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.155	BB	0.2905	7324.51758	377.26117	71.6785
2	15.332	BB	0.3994	2894.05396	106.36273	28.3215
Totals :				1.02186e4	483.62390	

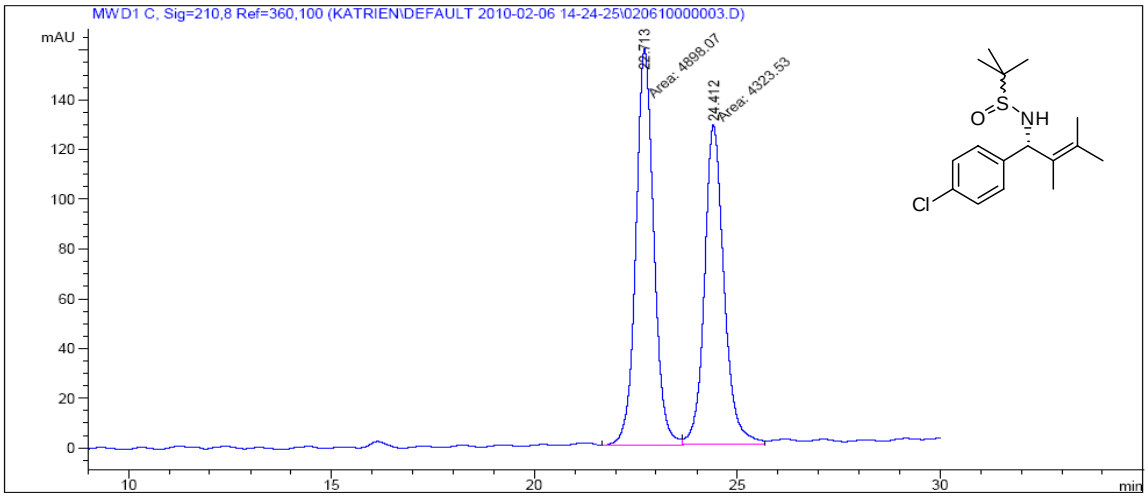
Sulfinamide **3h** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.362	MF	0.4354	5.82609e4	2229.92505	98.3696
2	16.444	FM	0.4273	965.63721	37.66351	1.6304
Totals :				5.92266e4	2267.58856	

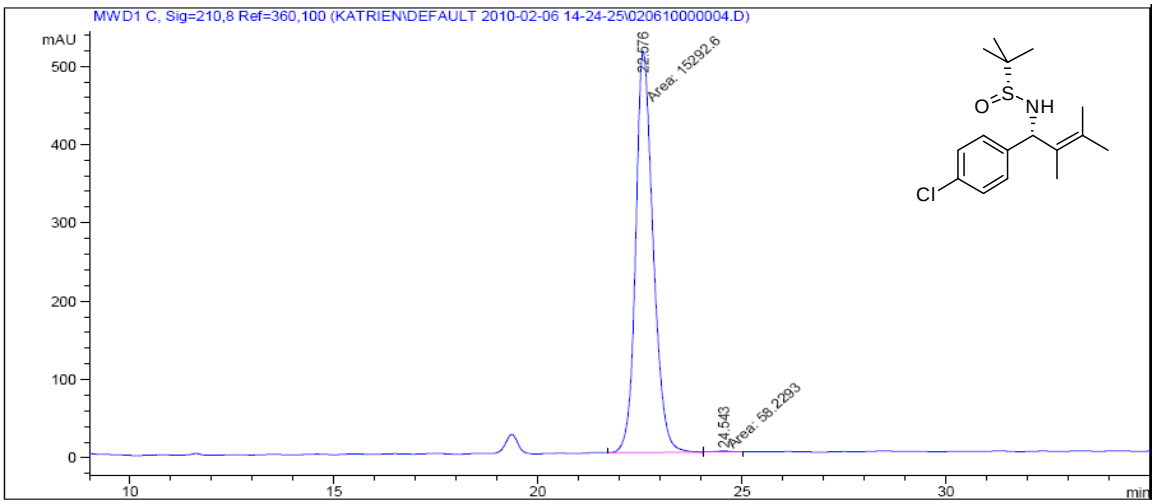
Sulfinamide **3i** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.713	MF	0.5124	4898.07373	159.32303	53.1152
2	24.412	FM	0.5603	4323.53271	128.60434	46.8848
Totals :				9221.60645	287.92737	

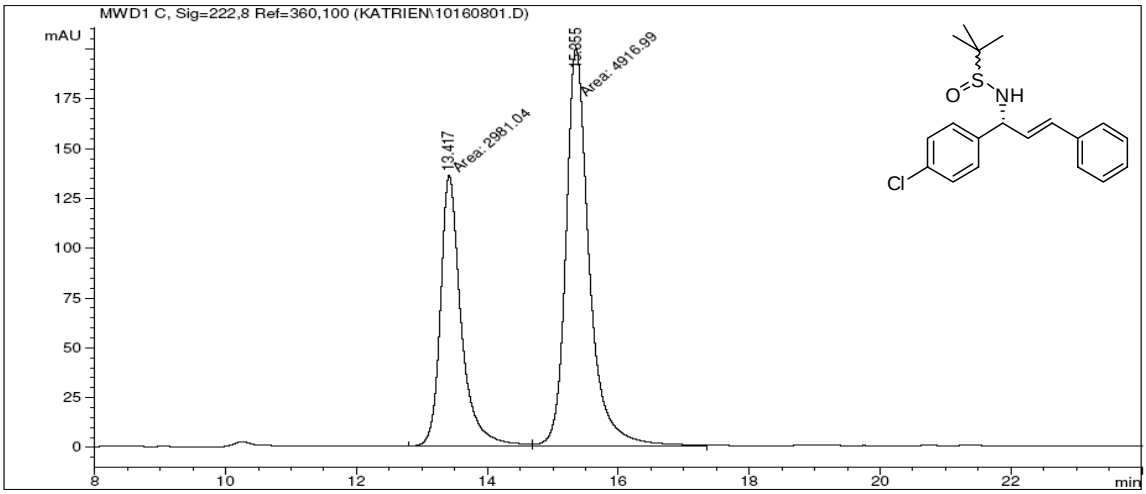
Sulfinamide **3i** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.576	MF	0.4975	1.52926e4	512.27216	99.6207
2	24.543	FM	0.5934	58.22931	1.63547	0.3793
Totals :				1.53508e4	513.90763	

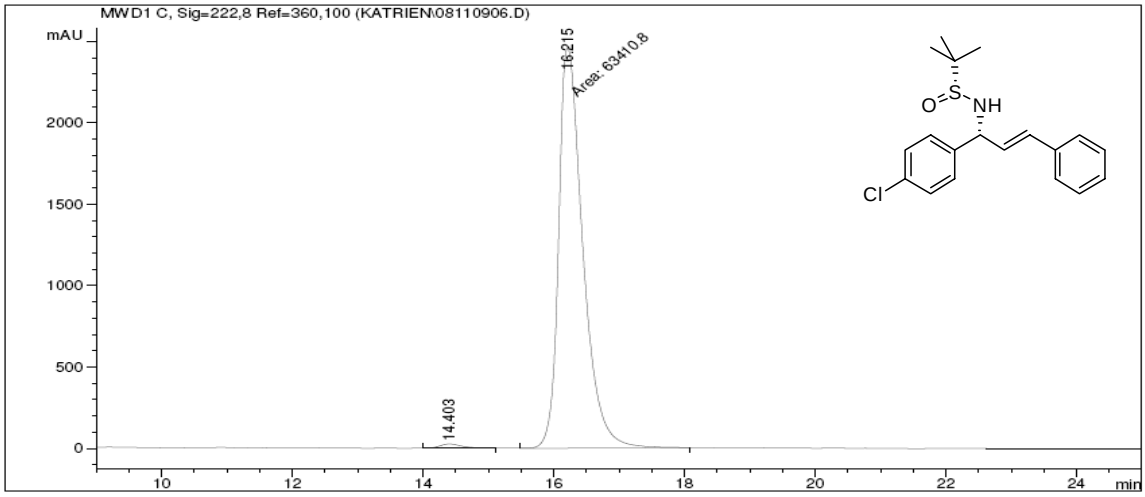
Sulfinamide **3j** HPLC trace (authentic mixture):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.417	MF	0.3655	2981.04102	135.92772	37.7441
2	15.355	FM	0.4102	4916.99170	199.79172	62.2559
Totals :				7898.03271	335.71944	

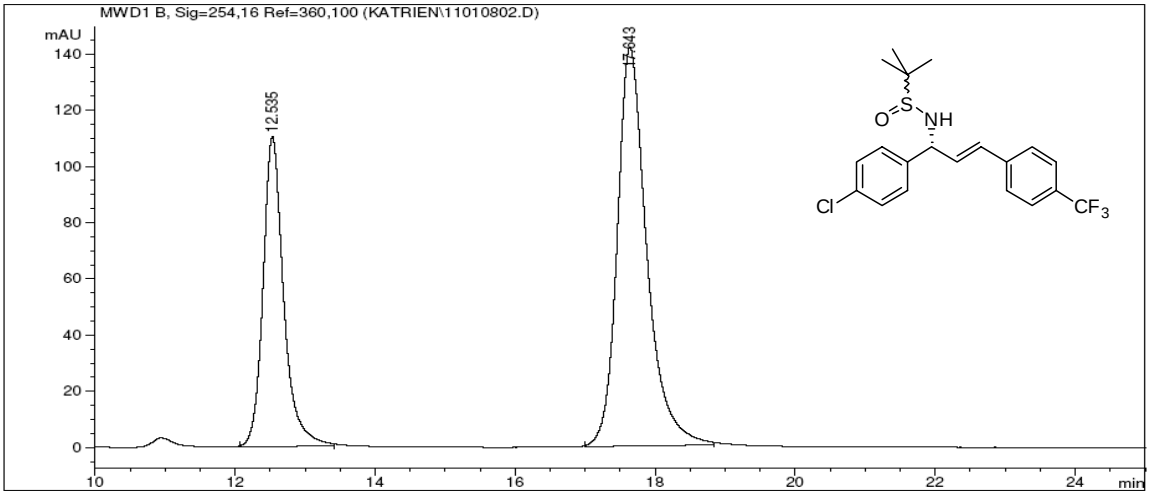
Sulfinamide **3j** HPLC trace (Procedure C):



Signal 1: MWD1 C, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.403	BB	0.3538	637.36499	27.15765	0.9951
2	16.215	MM	0.4299	6.34108e4	2458.24072	99.0049
Totals :				6.40482e4	2485.39837	

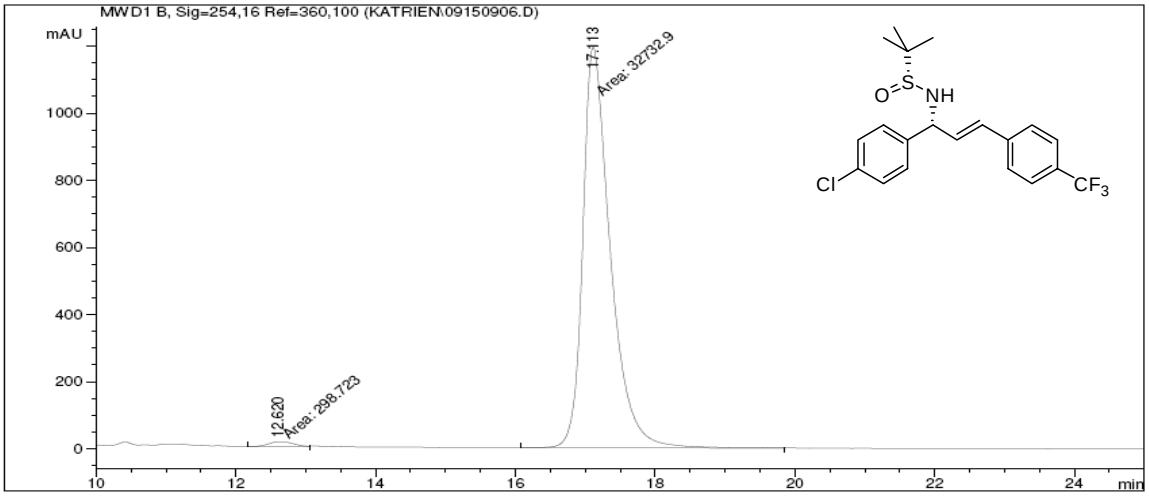
Sulfinamide **3k** HPLC trace (authentic mixture):



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.535	BB	0.3064	2254.21338	110.31187	35.0973
2	17.643	BB	0.4389	4168.54590	141.84659	64.9027
Totals :				6422.75928	252.15846	

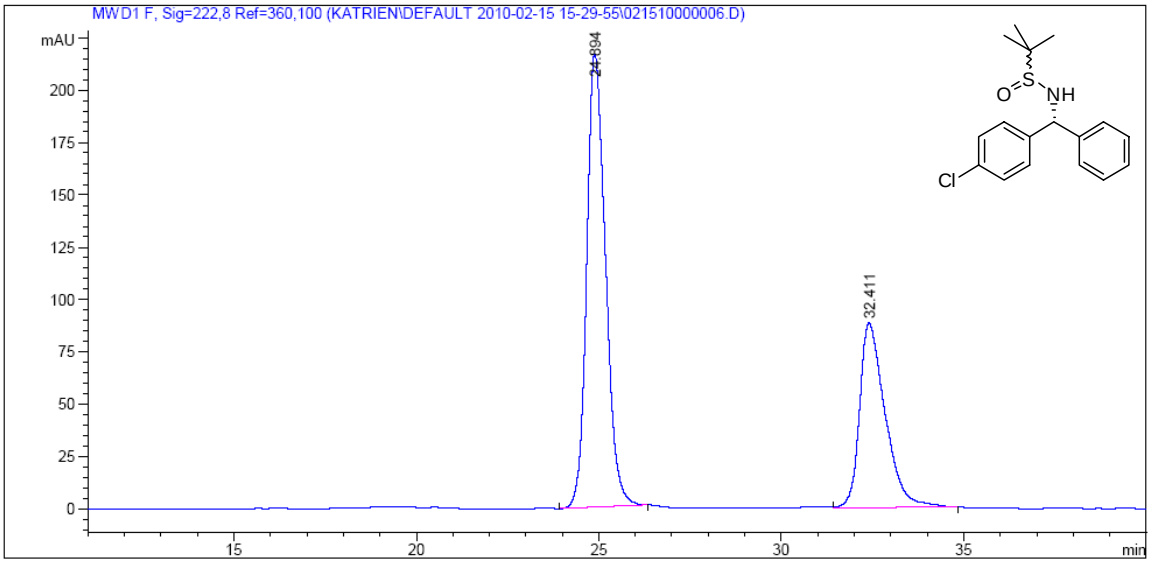
Sulfinamide **3k** HPLC trace (Procedure C):



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.620	MM	0.3867	298.72287	12.87463	0.9044
2	17.113	MM	0.4569	3.27329e4	1194.11389	99.0956
Totals :				3.30316e4	1206.98852	

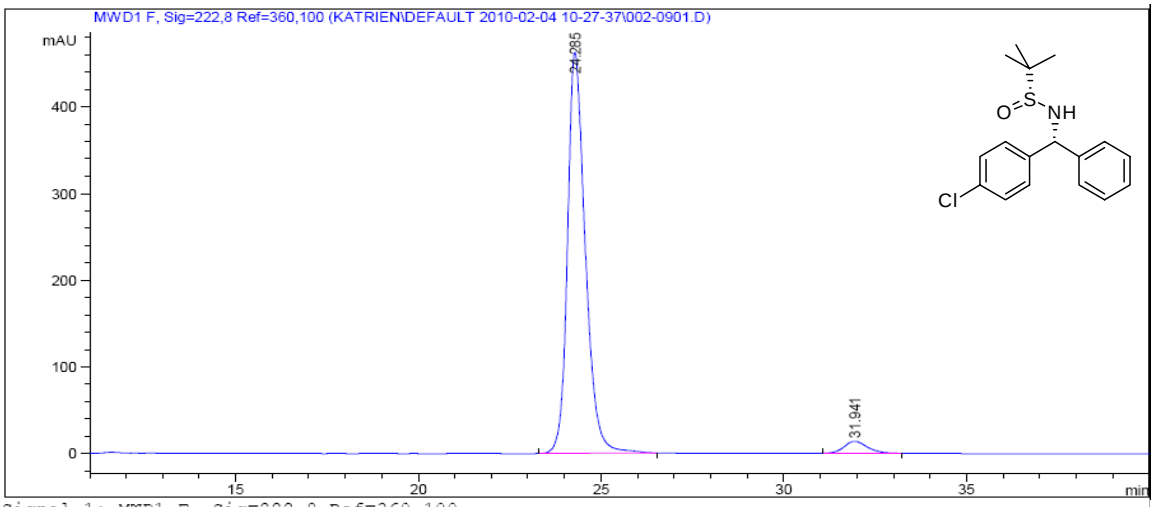
Sulfinamide **3l** HPLC trace (authentic mixture):



Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.894	VB	0.5362	7714.71729	216.27905	64.2262
2	32.411	BB	0.7193	4297.06592	88.06334	35.7738
Totals :				1.20118e4	304.34239	

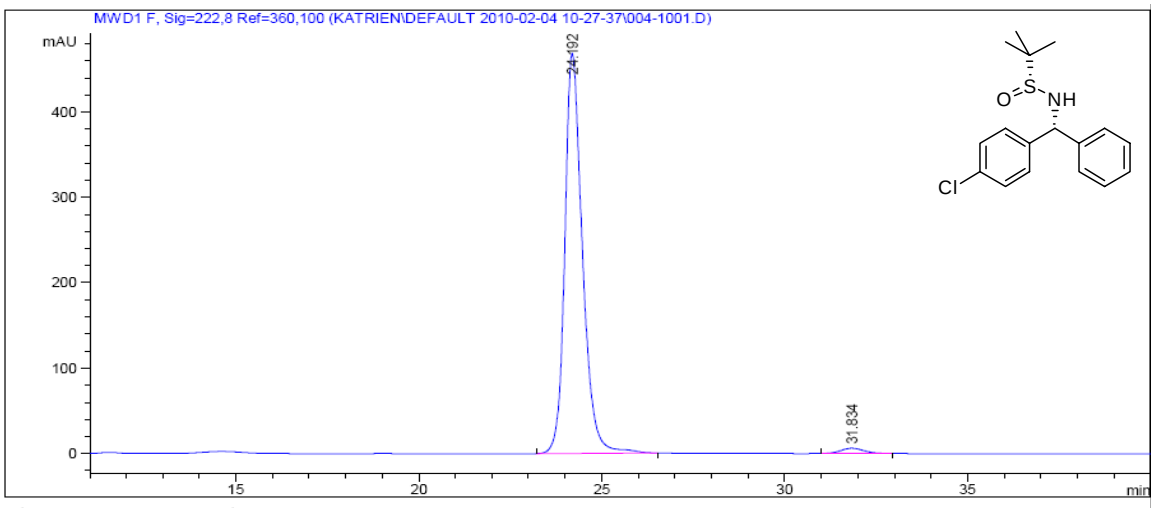
Sulfinamide **3l** HPLC trace (Procedure B):



Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.285	BB	0.5116	1.56910e4	462.69238	96.1982
2	31.941	BB	0.6706	620.11517	13.94967	3.8018
Totals :				1.63111e4	476.64205	

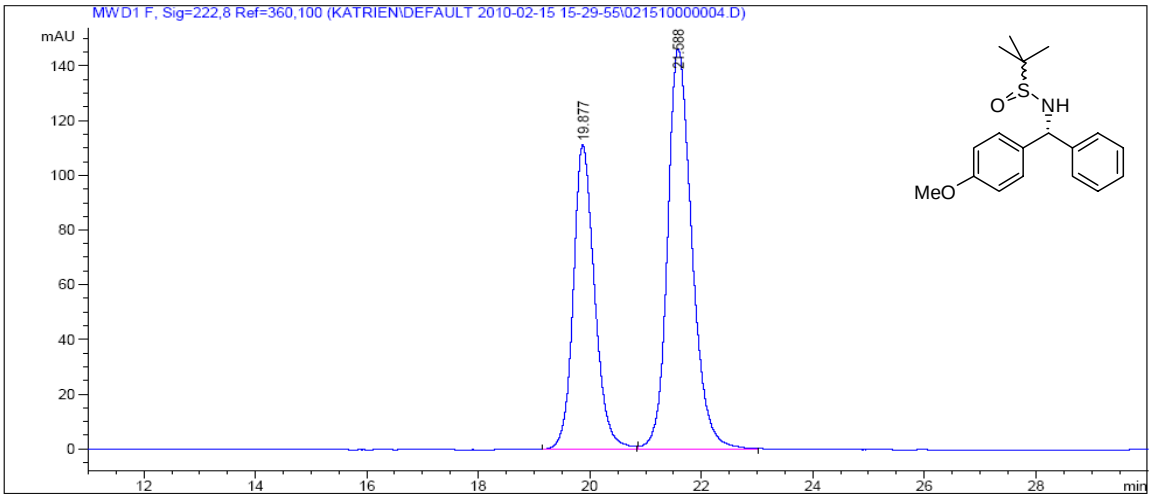
Sulfinamide **3l** HPLC trace (Procedure C):



Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.192	BB	0.5054	1.57145e4	468.36545	98.2828
2	31.834	BB	0.6642	274.57281	6.20586	1.7172
Totals :				1.59891e4	474.57131	

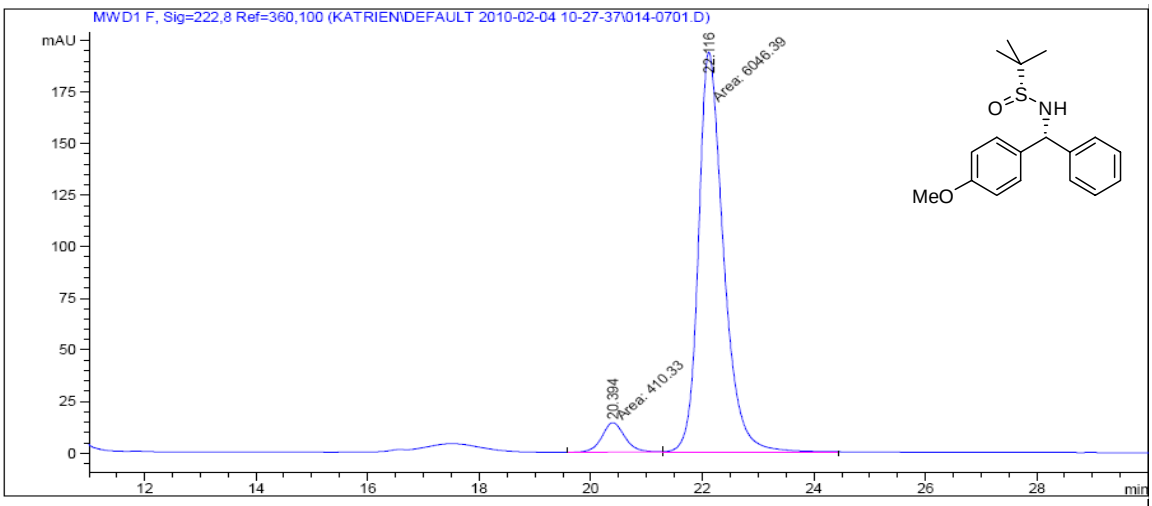
Sulfinamide **3m** HPLC trace (authentic mixture):



Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.877	BB	0.4011	2947.53223	111.24980	39.9609
2	21.588	BB	0.4630	4428.51367	146.37581	60.0391
Totals :				7376.04590	257.62561	

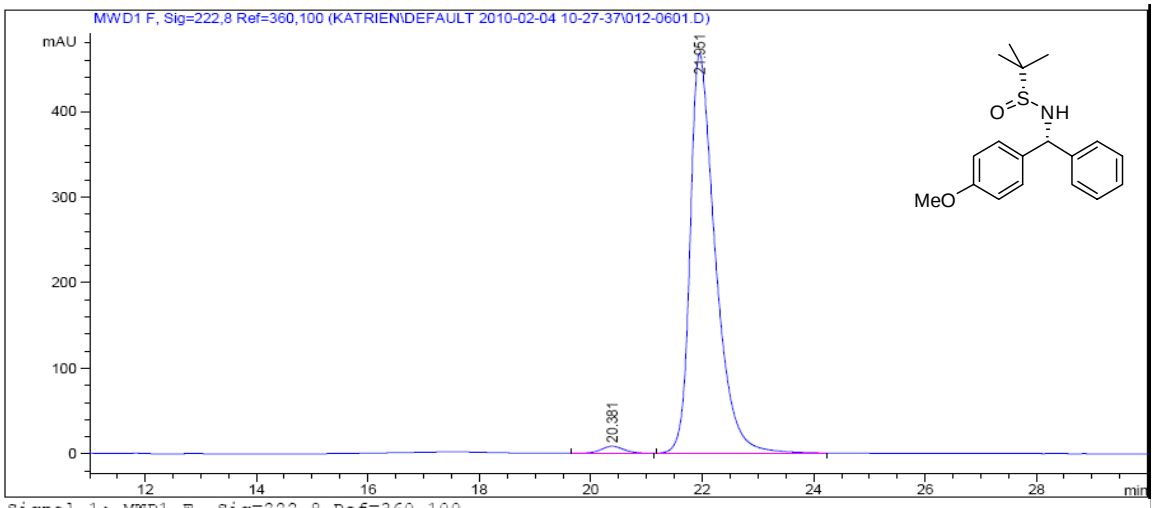
Sulfinamide **3m** HPLC trace (Procedure B):



Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.394	MF	0.4780	410.32986	14.30641	6.3551
2	22.116	FM	0.5200	6046.39014	193.80782	93.6449
Totals :				6456.72000	208.11422	

Sulfinamide **3m** HPLC trace (Procedure C):



Signal 1: MWD1 F, Sig=222,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.381	VB	0.4371	240.80142	8.33266	1.6111
2	21.951	BB	0.4712	1.47059e4	467.21802	98.3889
Totals :				1.49467e4	475.55068	