Supplementary Information

“*anti*-Aminoallylation of Aldehydes *via* Ruthenium Catalyzed Reductive Transfer Hydrogenative Coupling of Sulfonamido-Allenes: 1,2-Aminoalcohols”

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General Experimental Details. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred *via* oven-dried syringe. Reaction tubes were oven-dried and cooled under a stream of argon. Reactions tubes were purchased from Fischer Scientific (catalog number 14-959-35C). Tetrahydrofuran was obtained from solvent delivery system (Innovative Technology Inc. Ps-MD-5). $RuBr(CO)_3(\eta^3\text{-}C_3H_5)$ was prepared according to the literature procedure.[1] Cy_3P was used as received from Strem Chemicals. Anhydrous isopropanol was used as received from Acros. *tert*-Butyl allene was prepared according to the literature procedure.[2] Aldehydes were purified by distillation or recrystallisation immediately prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still.[3] Solvents for chromatography are listed as volume/volume ratios. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+H]^+$ or a suitable fragment ion. Melting points were obtained on a Thomas-Hoover Unimelt apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Gemini (400 MHz or 300MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini 300 (75 MHz) or 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling.

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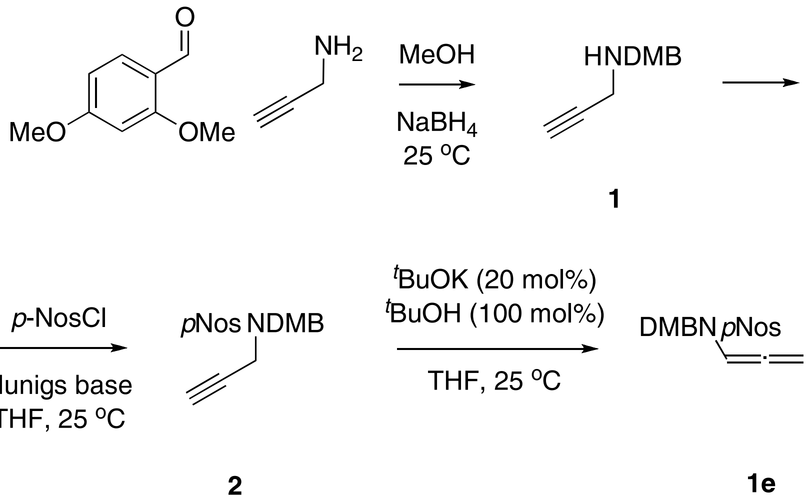
[1] Sbrana, G.; Braca, G.; Piacenti, F.; Pino, P. *J. Organometal. Chem.* **1968**, *13*, 240

[2] Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes Methods and Techniques;* Elsevier Publishing Co.: Amsterdam, 2004; pp 244-245

[3] Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923

General Procedure for the Preparation of Allene 1e



2,4-Dimethoxybenzyl Protection:

To a stirred solution of 2,4-dimethoxybenzaldehyde (100 mol%) in dry MeOH (0.3 M) under nitrogen at 25 °C was added propargyl amine (120 mol%). The resulting mixture was allowed to stir for 3.5 hours at ambient temperature, at which point the mixture was cooled to 0 °C using an ice bath. Sodium borohydride (200 mol%) was added portion wise over 10 min. The ice batch was removed and the reaction mixture was allowed to warm to ambient temperature and was allowed to stir for 3 hours, at which point saturated solution of NH_4Cl (aq.) was added to the reaction mixture drop-wise. The mixture was transferred to a separatory funnel. The organic layer was separated. The aqueous layer was extracted twice with EtOAc and the combined organic layers were dried (Mg_2SO_4), filtered and the filtrate was concentrated *in vacuo* to furnish an oily residue that was purified by flash column chromatography (SiO_2, 30% EtOAc/hexanes).

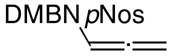
p-Nitrobenzenesulfonamide Protection:

To a stirred solution of compound **1** (100 mol%) in dry THF (0.4 M) under nitrogen at 25 °C was added *N*,*N*-diisopropylethylamine (160 mol%). The resulting mixture was cooled to 0 °C using an ice bath and a solution of *p*-nitrophenylsulfonyl chloride (130 mol%) in dry THF (0.4 M) was added dropwise over 5 min. The ice bath was removed and the reaction mixture was allowed to warm to ambient temperature and was allowed to stir for 14 hours. Water was added drop-wise to the reaction mixture. The reaction mixture was transferred to a separatory funnel. The organic layer was separated. The aqueous layer was extracted three times with EtOAc and the combined organic layers were washed with aqueous HCl (3 N), dried (Mg_2SO_4), filtered and the filtrate was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 10% EtOAc/toluene).

Preparation of Allene **1e**:

To a stirred solution of compound **2** (3.0 g, 7.7 mmol, 100 mol%) in dry THF (38.5 mL, 0.2 M with respect to **2**) under nitrogen at 25 °C was added *t*-BuOH (0.736 mL, 7.7 mmol, 100 mol%) followed by drop-wise addition of 1.0M *t*-BuOK in THF (1.54 mL, 1.54 mmol, 20 mol%). The resulting reaction mixture was stirred until the complete consumption of **2** was observed, as determined by TLC analysis. The reaction mixture was filtered through a pad of Celite, concentrated *in vacuo* and purified by flash column chromatography (SiO_2: toluene) to furnish the title compound (2.28 g, 76%) as a yellow solid. Allene **1e** was recrystallized from DCM/hexanes (1:3) at -4 °C.

N-(2,4-dimethoxybenzyl)-4-nitro-*N*-(propa-1,2-dienyl)benzenesulfonamide (1e)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.80 (t, *J* = 6.0 Hz, 1H), 6.40 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 5.15 (d, *J* = 6.0 Hz, 2H), 4.34 (s, 2H), 3.78 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 160.5, 157.7, 150.0, 144.2, 129.1, 128.3, 115.6, 104.0, 99.6, 98.1, 88.0, 55.3, 55.1, 45.0.

HRMS (CI): Calcd. for $C_{18}H_{19}N_2O_6S$ (M+1): 391.0964, Found: 391.0965

FTIR (neat): 1588, 1532, 1505, 1348, 1212, 1170, 1118, 1033, 862 cm^{-1}.

M.P. 113 – 115 °C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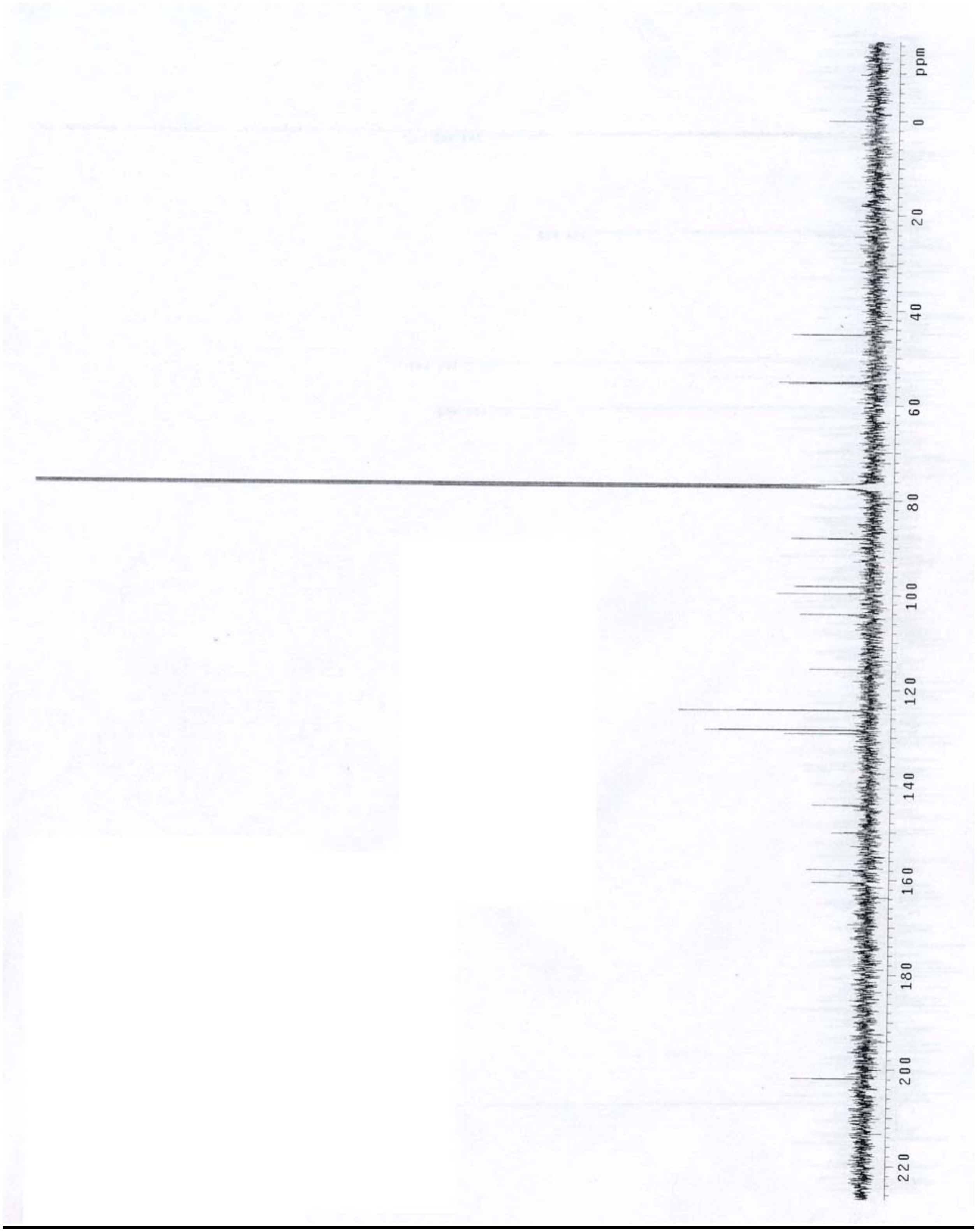
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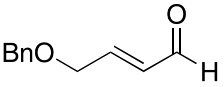
Preparation of Aldehyde **2i**:



To a stirred solution of *cis*-1,4-dibenzyloxy-2-butene (1.00g, 3.7 mmol, 100 mol%) in dry DCM (37 mL, 0.1 M with respect to *cis*-1,4-dibenzyloxy-2-butene) under nitrogen at 25 ^{o}C was added acrolein (0.75 mL, 11.1 mmol, 300 mol%). Grubbs second generation catalyst (0.158 g, 0.185 mmol, 5 mol%) was added and reaction was allowed to stir until complete consumption of *cis*-1,4-dibenzyloxy-2-butene was observed, as determined by TLC analysis. The reaction mixture was filtered through a pad of Celite, concentrated *in vacuo* and purified by flash column chromatography (SiO_2, 20% EtOAc/Hex) to furnish the title compound (1.30 g) as a colorless oil in 99% yield. *The spectroscopic properties of this compound were consistent with the data available in the literature.* [4]

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (d, *J* = 7.8 Hz, 1H), 7.40-7.30 (m, 5H), 6.87 (dt, *J* = 15.9, 6.0 Hz, 1H,), 6.42 (ddt, *J* = 15.9, 7.8, 1.8 Hz, 1H), 4.61 (s, 2H), 4.31 (dd, *J* = 6.0, 1.8 Hz, 2H)

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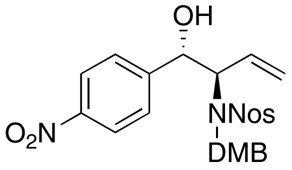
[4] Fournier, J.; Mathieu, S.; Charette, A.. *J. Am. Chem. Soc.* **2005**, *127* (38), 13140–1314.

<u>General Procedure</u> for the Coupling of Allenamide to Aldehydes: To a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar was added $RuBr(CO)_3(\eta^3\text{-}C_3H_5)$ (3.1 mg, 0.01 mmol, 5 mol%) and Cy_3P (8.4 mg, 0.03 mmol, 15 mol%). Aldehyde (0.200 mmol, 100 mol%) and allene (0.300 mmol, 150 mol%) were added and the tube was sealed with a rubber septum and purged with argon. THF (0.2 mL, 1.0 M concentration with respect to aldehyde) and isopropanol (61 μL, 0.800 mmol, 400 mol%) were added and the rubber septum was quickly replaced with a screw cap. The mixture was heated at 100 °C (oil bath temperature) for the time stated. The reaction mixture was then concentrated *in vacuo* and purified by flash column chromatography (SiO_2) under the conditions noted to furnish the corresponding product of *anti*-aminoallylation.

N-(2,4-dimethoxybenzyl)-*N*-(1-hydroxy-1-(4-nitrophenyl)but-3-en-2-yl)-4-nitrobenzenesulfonamide (3a)



In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 14 hours, at which point the mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 25% EtOAc/cyclohexane) to furnish the title compound (99 mg) as a yellow solid in 91% yield. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from chloroform.

<u>^{1}H NMR</u> (400 MHz, DMSO): δ 8.25 (d, *J* = 9.0 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2 H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* =8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 6.29 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.91 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.86 (d, *J* = 5.2 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 17.6 Hz, 1H), 4.95 (d, *J* = 6.8 Hz, 1H), 4.31 (s, 2H), 4.24 (dd, *J* = 7.2, 6.8 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H).

<u>^{1}H NMR</u> (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.39 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.07 (ddd, *J* = 17.2, 104, 7.2 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.20 (d, *J* = 5.2 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.32 (d, *J* = 14.7 Hz, 1H), 4.25 – 4.24 (m, 1H), 4.25 (d, *J* = 14.7 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.89 (s, 1H).

<u>^{13}C NMR</u> (100 MHz, DMSO): δ 160.9, 158.9, 151.2, 150.0, 147.2, 146.6, 132.8, 131.8, 131.9, 129.4, 128.6, 124.8, 123.5, 121.6, 116.6, 105.2, 98.5, 74.4, 67.3, 55.8, 45.1.

<u>HRMS</u> (EI): Calcd. for $C_{25}H_{24}N_3O_9S$ (M-1) : 542.1239, Found : 542.1238

<u>FTIR</u> (neat): 3521, 3108, 2940, 2896, 2359, 1609, 1587, 1510, 1421, 1310, 1269, 1158 cm^{-1}.

<u>M.P.</u> 191-194 °C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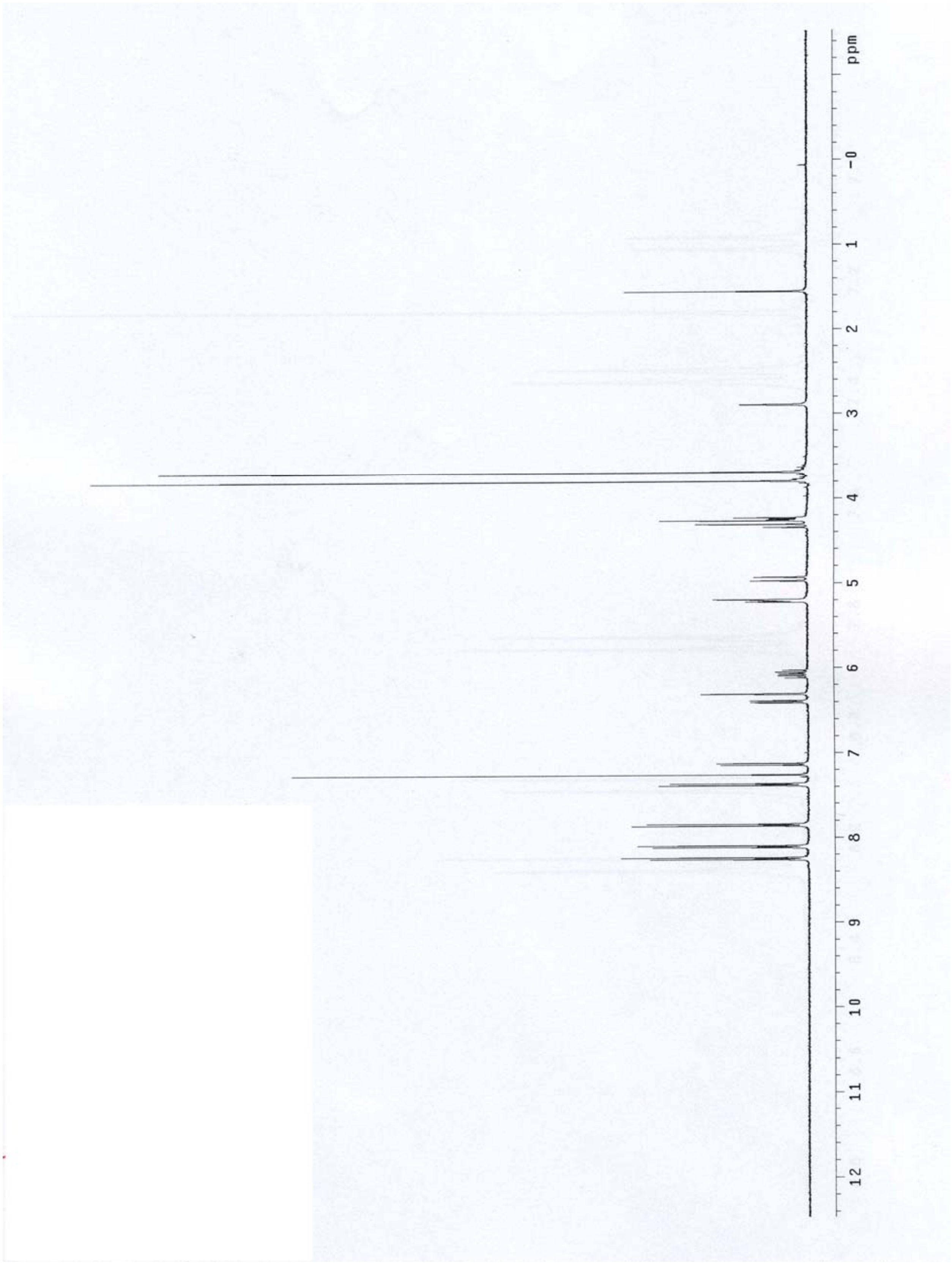
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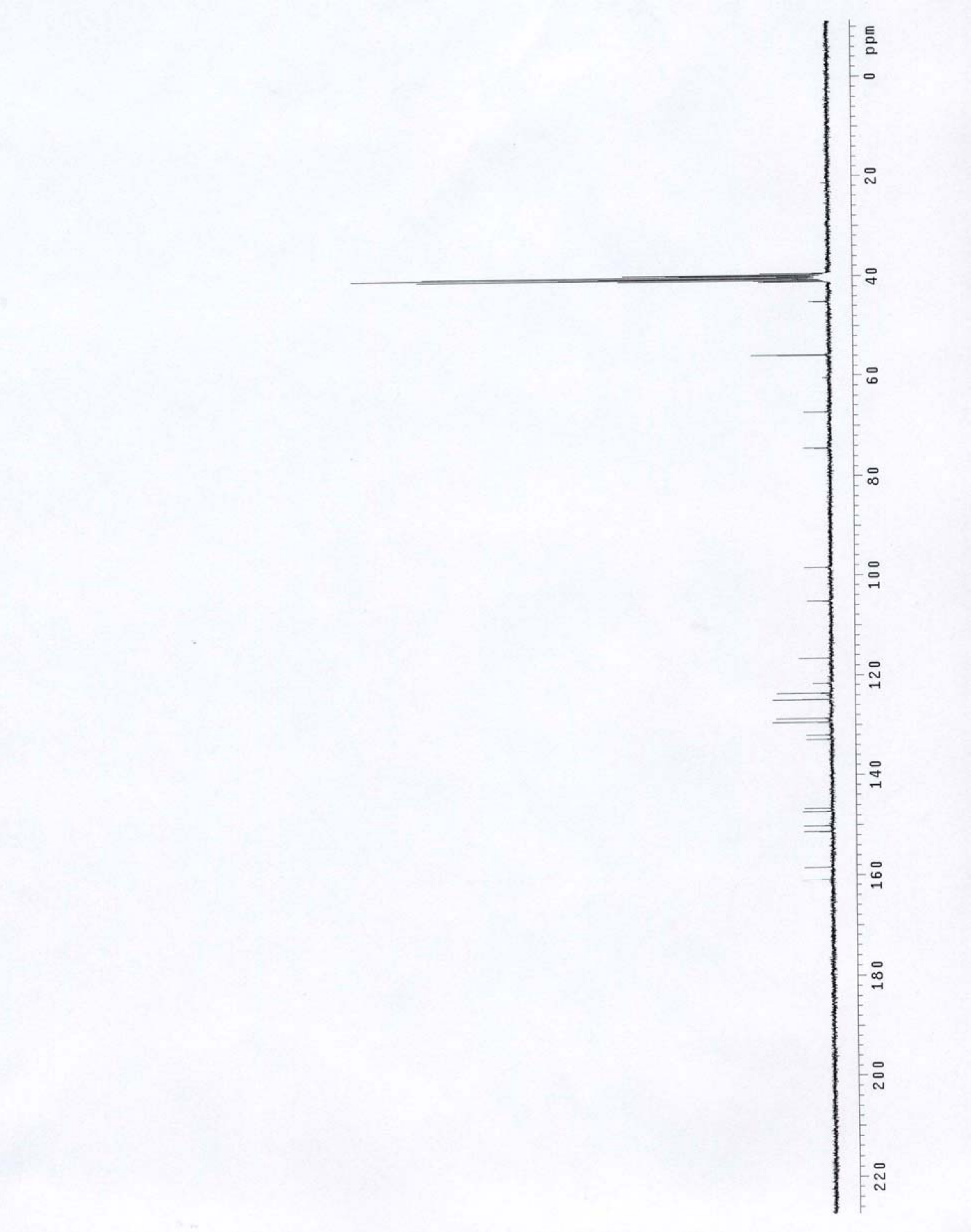
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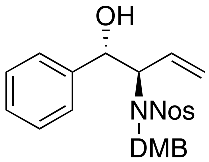
N-(2,4-dimethoxybenzyl)-*N*-(1-hydroxy-1-phenylbut-3-en-2-yl)-4-nitrobenzenesulfonamide (3b)



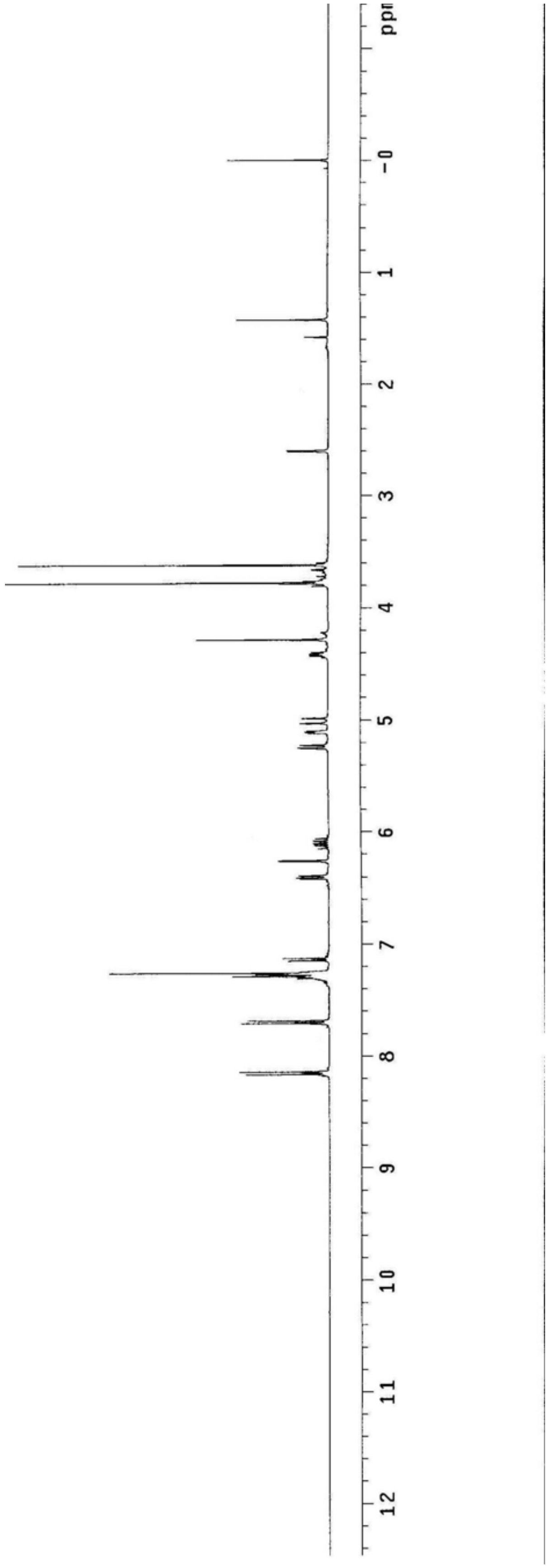
In a modification of the general procedure employing 200 mol% of allene **1e** (0.4 mmol), the reaction was allowed to stir at 100 °C for 16 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 0-25% EtOAc/cyclohexane) to furnish the title compound (70 mg) as a yellow oil in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.22 – 7.29 (m, 5H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.40 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 6.10 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H) 5.23 (d, *J* = 10.4 Hz, 1H), 5.10 (dd, *J* = 5.2, 2.4 Hz, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.41 (dd, *J* = 6.8, 5.2 Hz, 1H), 4.28 (s, 2H), 3.78 (s, 3H), 3.62 (s, 3H), 2.60 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 158.4, 149.7, 147.0, 140.9, 132.3, 131.4, 128.8, 128.5, 128.1, 127.0, 123.8, 122.3, 116.1, 104.7, 98.4, 76.2, 68.4, 55.7, 55.3, 46.4.

HRMS (EI): Calcd. for $C_{25}H_{26}N_2O_7SNa$ (M+23): 521.1348, Found: 521.1353

FTIR (neat) – 3530, 2937, 2361, 1612, 1529, 1509, 1349, 1295, 1209, 1160, 1132, 1107, 1090, 1036 cm^{-1}.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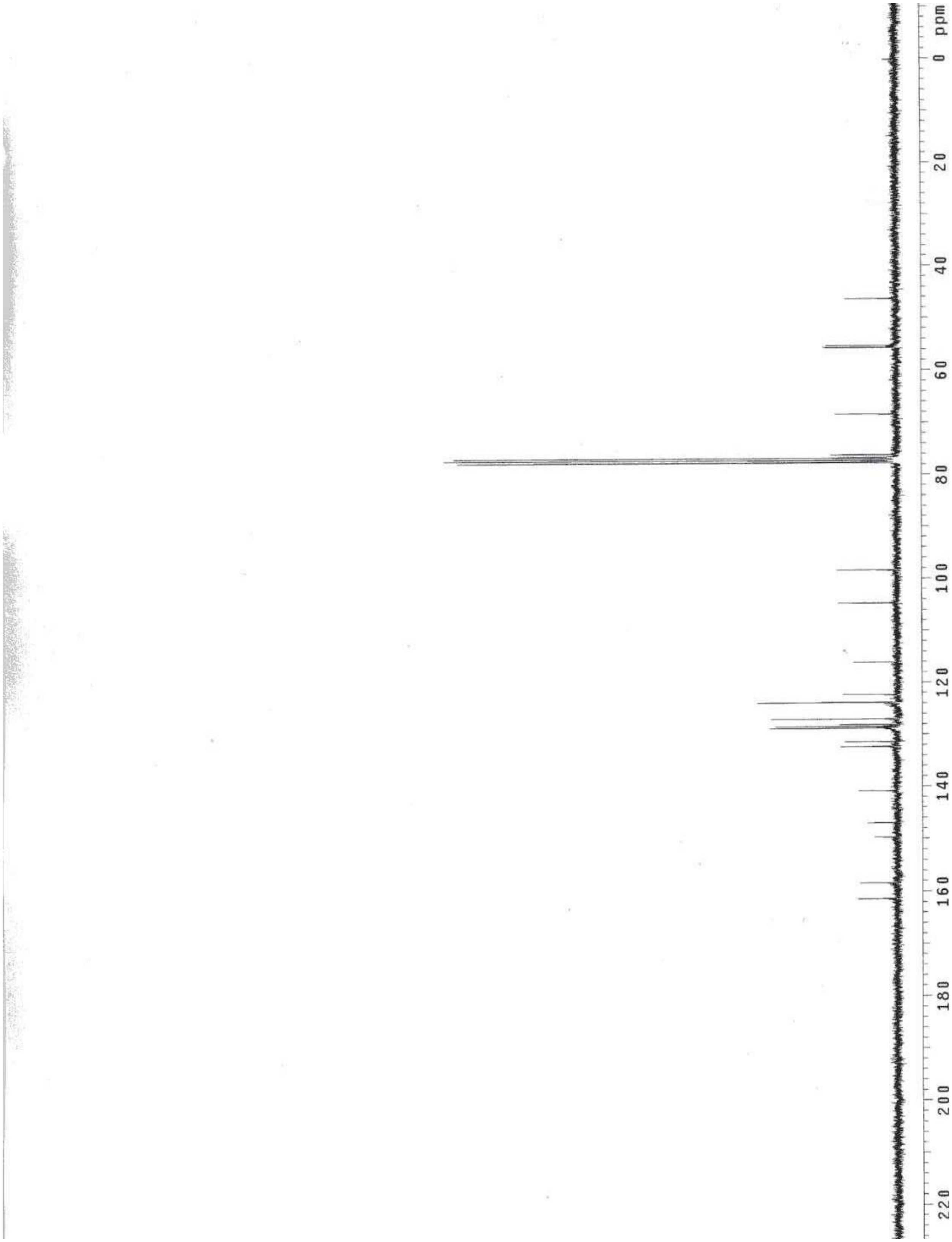
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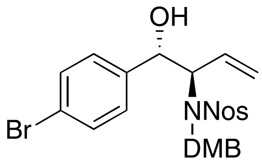
N-(1-(4-bromophenyl)-1-hydroxybut-3-en-2-yl)-*N*-(2,4-dimethoxybenzyl)-4-nitrobenzenesulfonamide (3c)



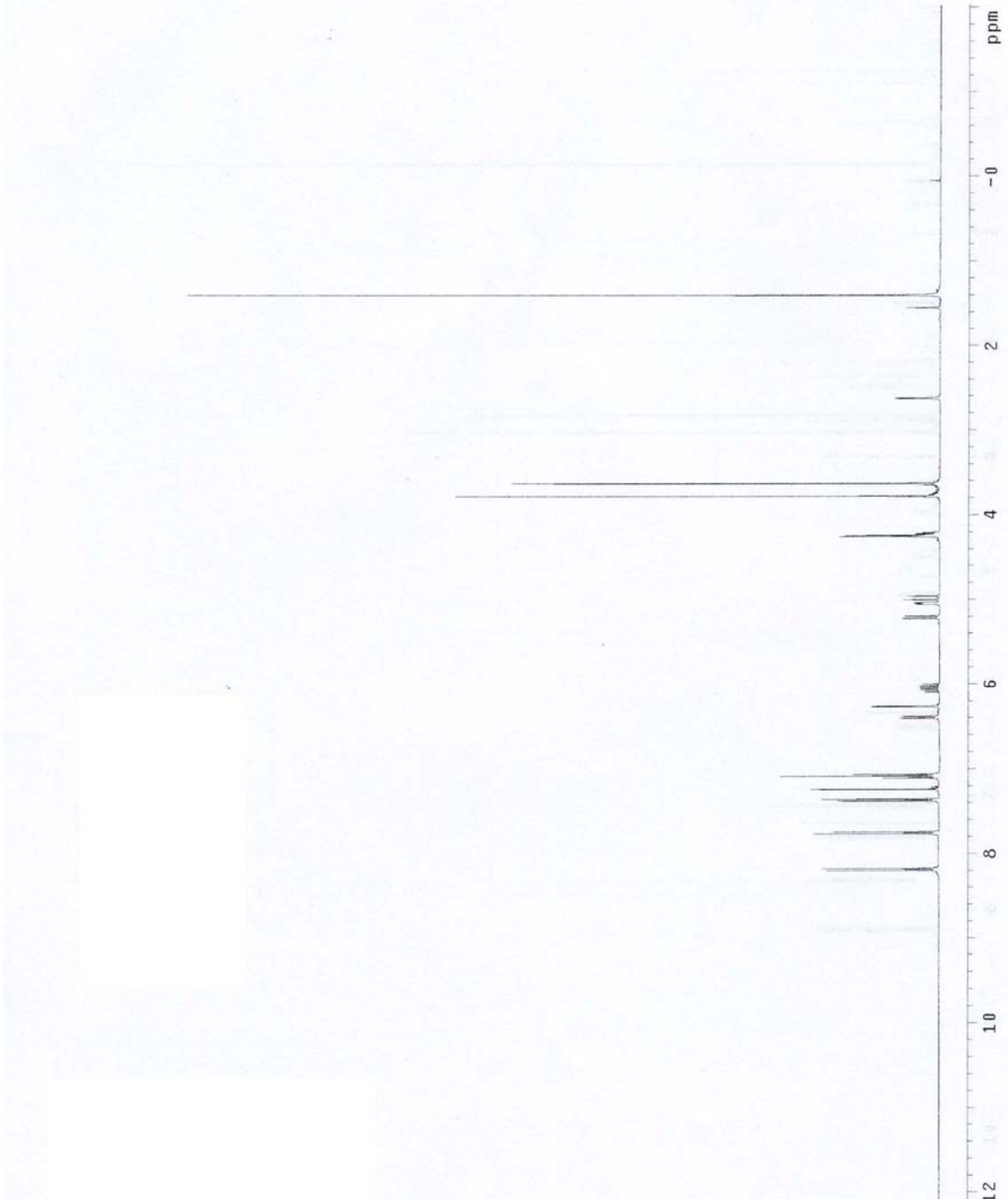
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 14 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 25% EtOAc/cyclohexane) to furnish the title compound (89 mg) as a brown foam in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.08 (m, 3H), 6.39 (d, *J* = 8.4 Hz, 1H), 6.26 (d, *J* = 2.3 Hz, 1H), 6.05 (ddd, *J* = 17.2, 102, 7.0 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.04 (dd, *J* = 5.1, 2.6 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 4.22 (m, 3H), 3.78 (s, 3H), 3.63 (s, 3H), 2.62 (d, *J* = 2.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 158.1, 149.6, 146.5, 139.6, 132.1, 131.2, 130.6, 128.5, 128.4, 123.7, 122.5, 121.6, 115.5, 104.6, 98.2, 75.4, 68.2, 55.4, 55.1, 46.1.

HRMS (EI): Calcd. for $C_{25}H_{25}N_2O_7SBrNa$ (M+23): 599.0468 Found: 599.0458

FTIR (neat): 3509, 2938, 2359, 1733, 1611, 1588, 1464, 1348, 1209, 1158, 1010 cm^{-1}.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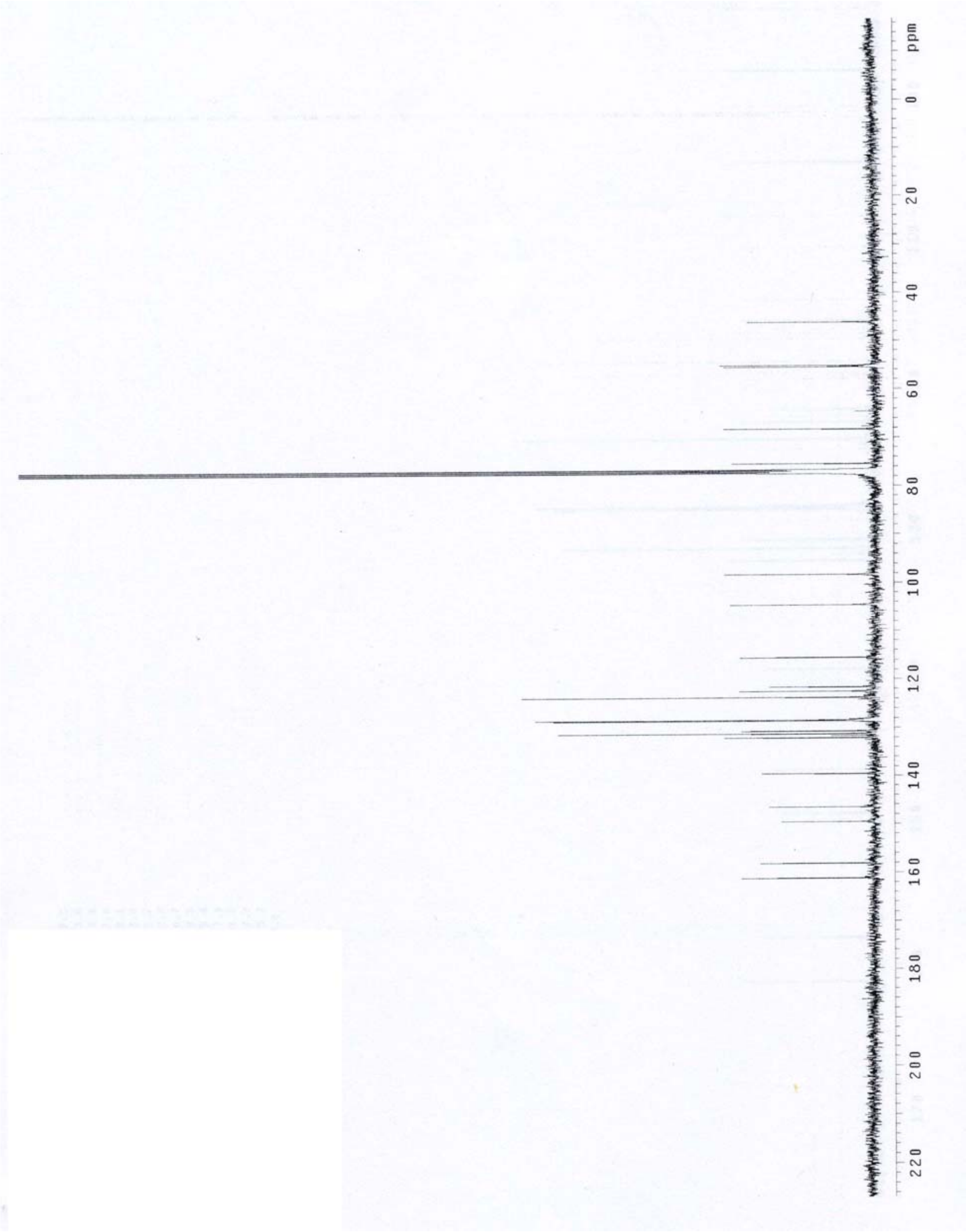
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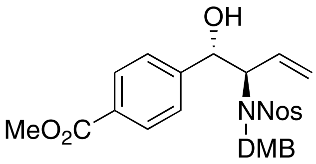
Methyl 4-(2-(*N*-(2,4-dimethoxybenzyl)-4-nitrophenylsulfonamido)-1-hydroxybut-3-enyl)benzoate (3d)



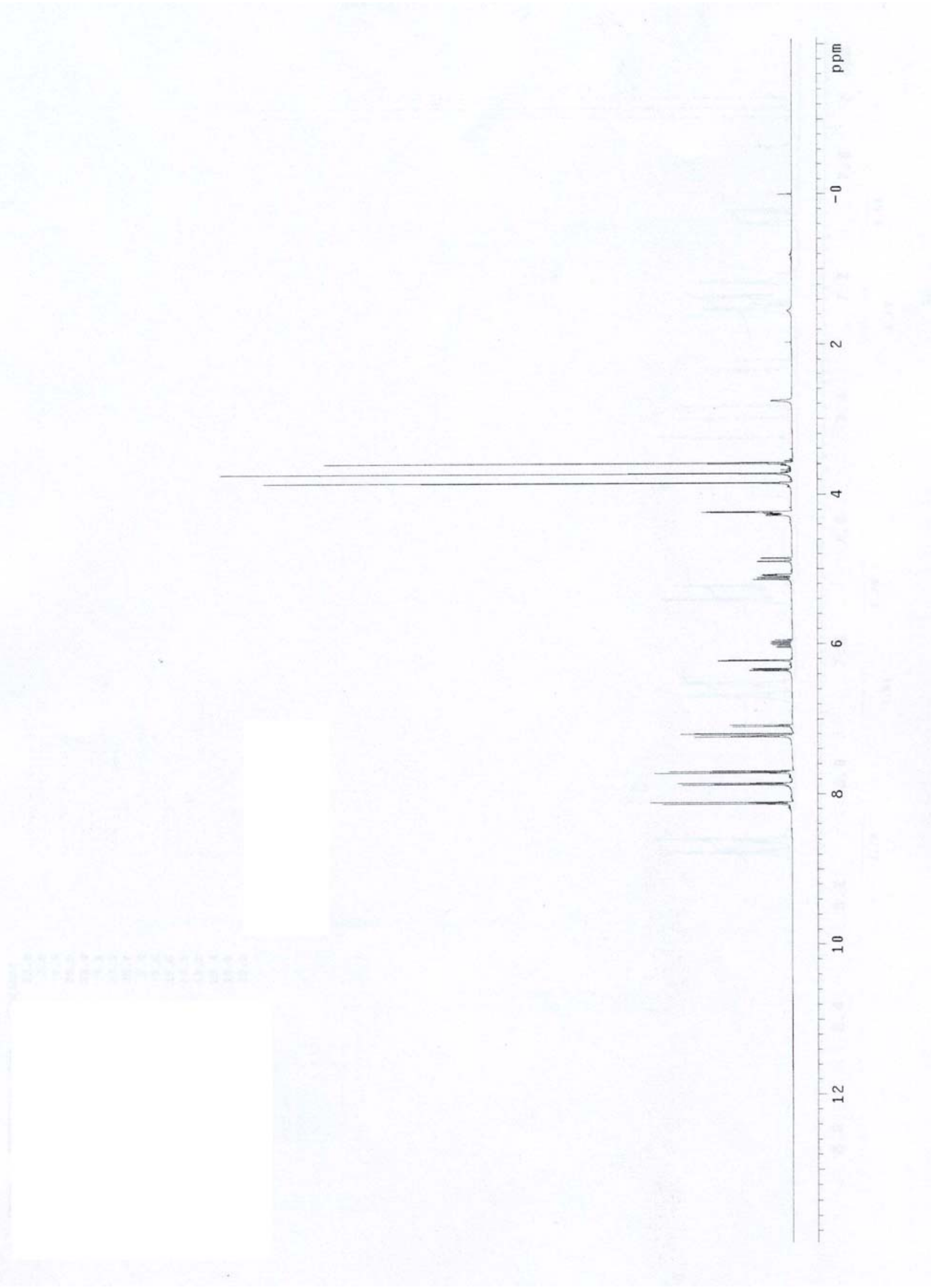
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 14 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 30% EtOAc/cyclohexane) to furnish the title compound (105 mg) as a yellow oil in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.34 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 5.99 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 5.08 (d, *J* = 4.7 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 4.26 (dd, *J* = 6.8, 4.7 Hz, 1H), 4.23 (s, 1H), 4.22 (s, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 3.58 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 161.2, 158.1, 149.5, 146.5, 145.7, 132.0, 130.4, 129.5, 129.4, 128.5, 126.6, 123.7, 122.5, 115.6, 104.6, 98.2, 75.8, 68.3, 55.4, 55.2, 52.1, 46.1.

HRMS (EI): Calcd. for $C_{27}H_{27}N_2O_9S$ (M-1): 555.1434, Found: 555.1443.

FTIR (neat): 3502, 2952, 2360, 1720, 1588, 1437, 1348, 1209, 1108 cm^{-1}.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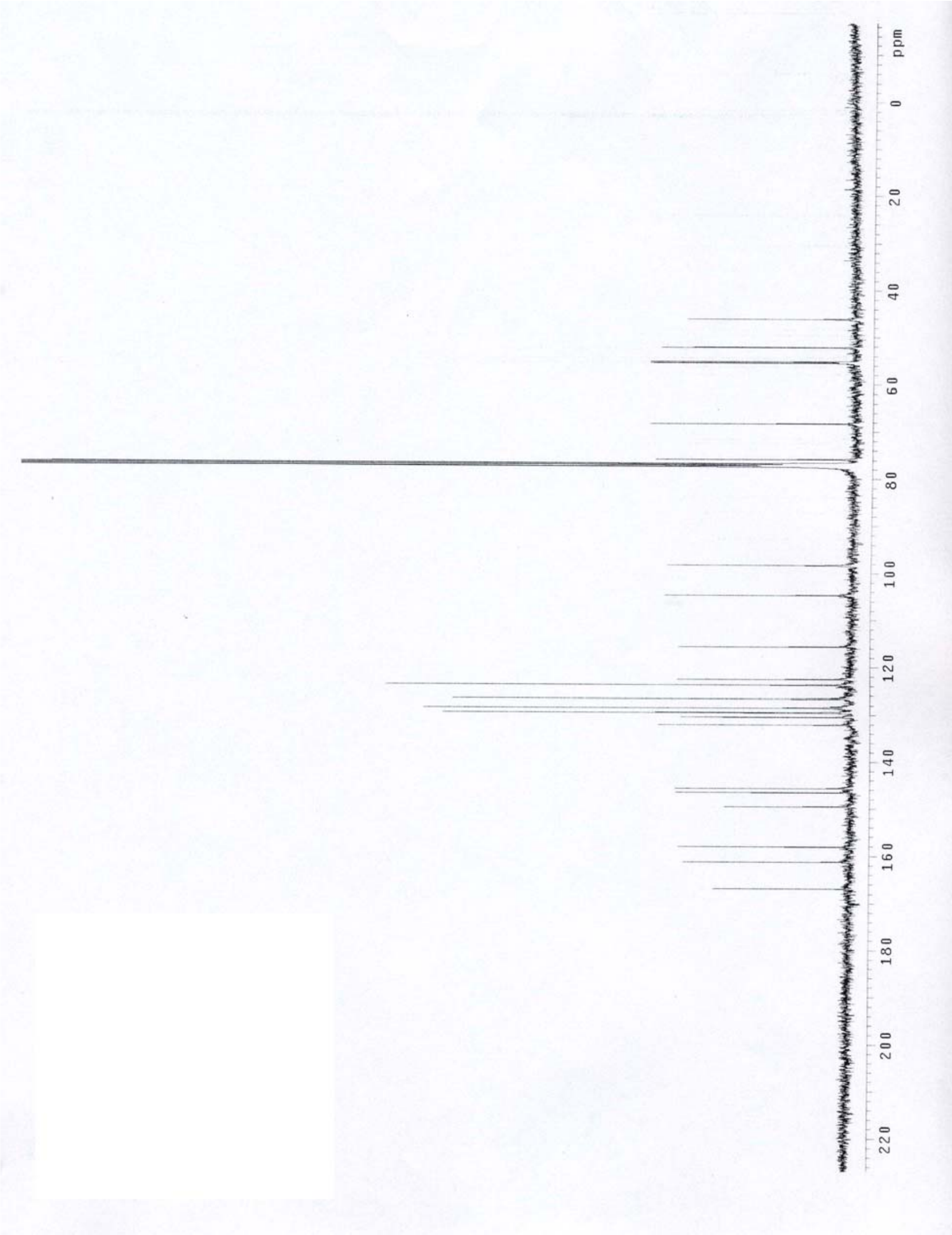
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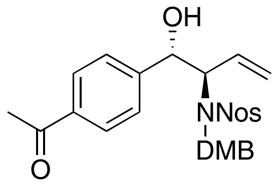
N-(1-(4-acetylphenyl)-1-hydroxybut-3-en-2-yl)-*N*-(2,4-dimethoxybenzyl)-4-nitrobenzenesulfonamide (3e)



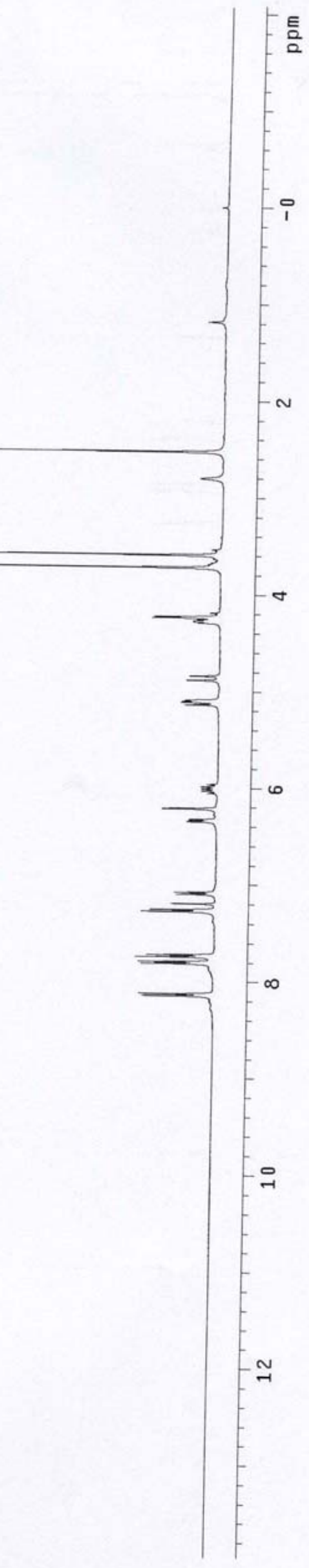
In accordance with the general procedure, the reaction was allowed to stir at 100 ^{o}C for 14 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 30% EtOAc/cyclohexane) to furnish the title compound (80 mg) as a yellow oil in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* =8.6 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 638 (d, *J* =8.4 Hz, 1H), 6.26 (s, 1H), 6.05 (dd, *J* = 17.6, 10.2 Hz, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 4.3 Hz, 1H), 4.91 (d, *J* = 17.6 Hz, 1H), 4.28 (m, 3H), 3.78 (s, 3H), 3.64 (s, 3H), 2.85 (s, 1H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 161.2, 158.1, 149.5, 146.5, 145.8, 136.5, 132.0, 130.2, 128.5, 128.2, 126.7, 123.7, 122.6, 115.6, 104.7, 98.2, 75.9, 68.3, 55.4, 55.2, 46.2, 26.2.

HRMS (EI): Calcd. for $C_{27}H_{27}N_2O_8S$ (M-1): 539.1487, Found: 539.1439

FTIR (neat): 3485, 3105, 2935, 2361, 1678, 1508, 1455, 1348, 1269, 1160 cm^{-1}.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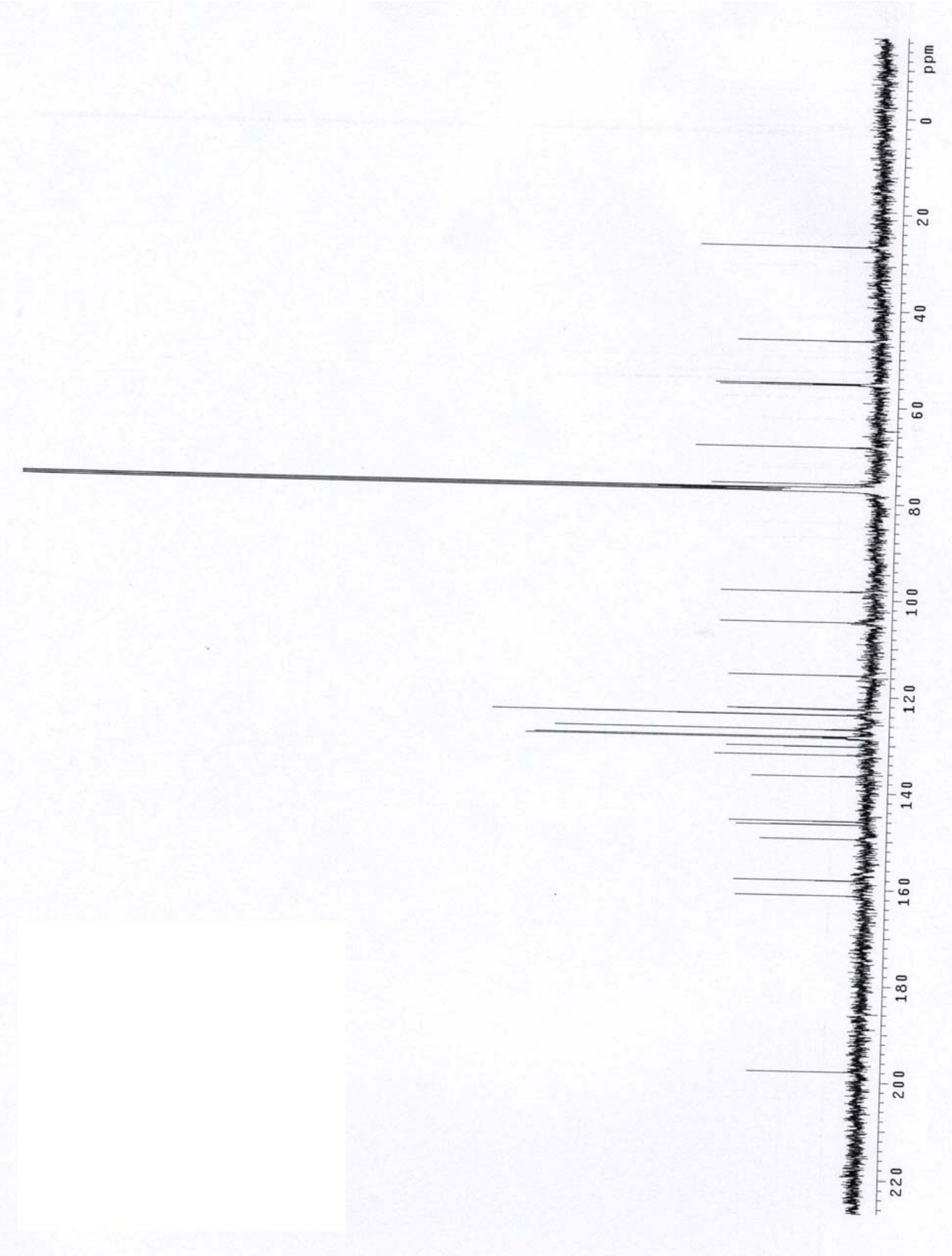
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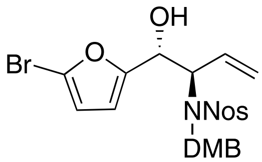
N-(1-(5-bromofuran-2-yl)-1-hydroxybut-3-en-2-yl)-*N*-(2,4-dimethoxybenzyl)-4-nitrobenzenesulfonamide (3f)



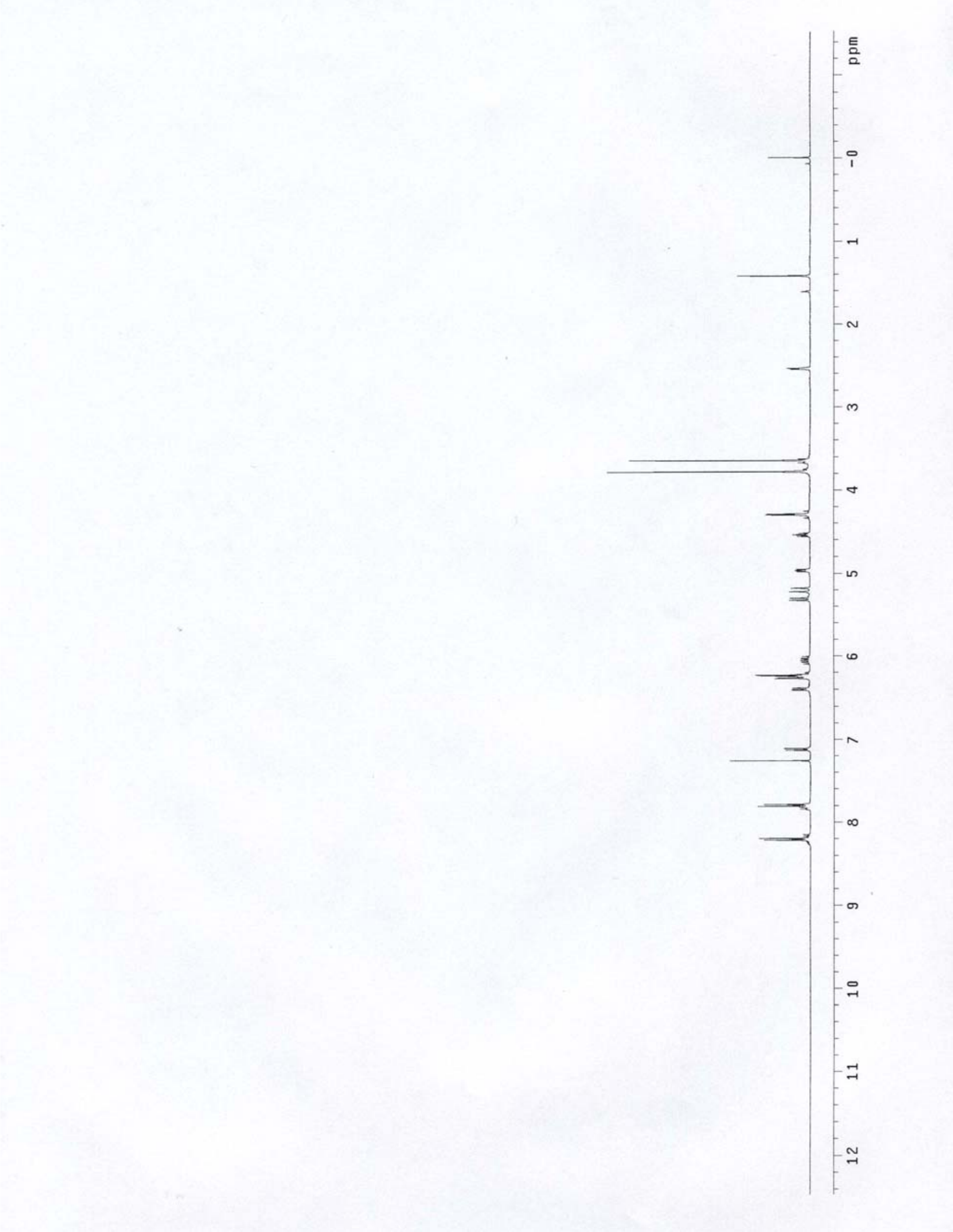
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 14 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 35% EtOAc/cyclohexane) to furnish the title compound (102 mg) as a orange oil in 74% yield.

<u>^{1}H NMR</u> (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 9.2 Hz, 2H), 7.80 (d, *J* = 9.2 Hz, 2H), 7.12 (d, *J* = 8.4, 2.4 Hz, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 6.25 – 6.22 (m, 2H), 6.05 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 4.96 (dd, *J* = 7.2, 4.4 Hz, 1H), 4.54 (t, *J* = 7.2 Hz, 1H), 4.30 (s, 1H), 4.29 (s, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 2.57 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 158.3, 155.3, 149.8, 146.8, 132.5, 131.8, 128.8, 123.9, 122.6, 121.6, 115.7, 112.4, 111.2, 104.7, 98.4, 69.3, 65.5, 55.6, 55.4, 45.9.

HRMS (EI): Calcd. for $C_{23}H_{23}N_2O_8SBrNa$ (M+23): 589.0249, Found: 589.0250.

FTIR (neat): 3503, 2939, 2361, 1611, 1588, 1464, 1293, 1158, 1034 cm^{-1}.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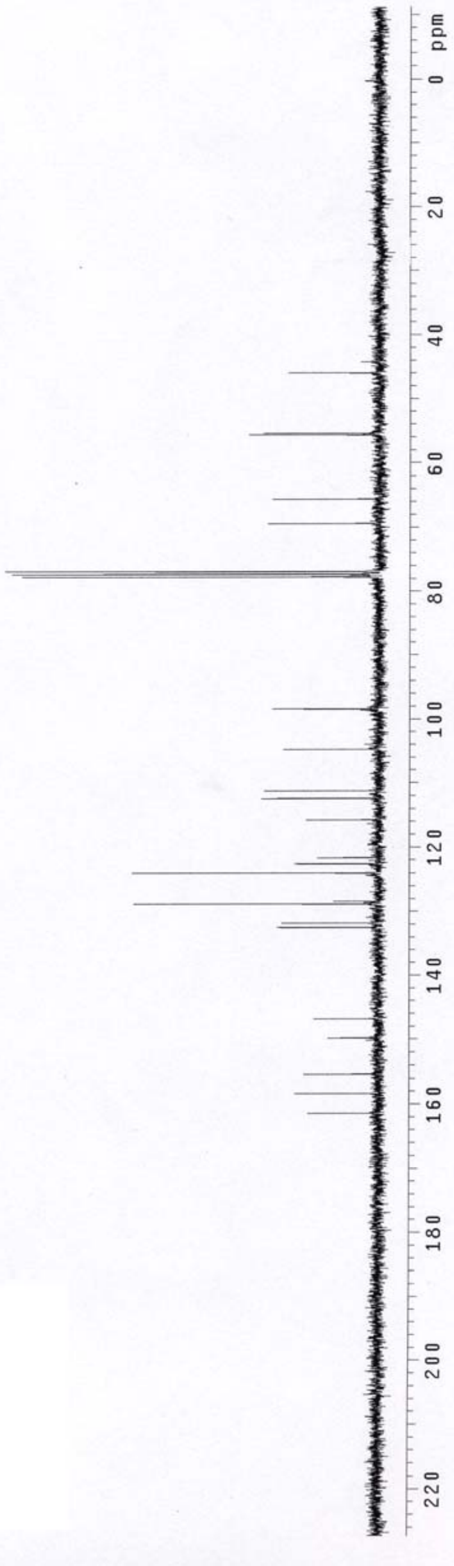
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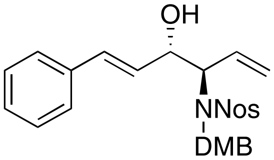
(*E*)-*N*-(2,4-dimethoxybenzyl)-*N*-(4-hydroxy-6-phenylhexa-1,5-dien-3-yl)-4-nitrobenzenesulfonamide (3g)



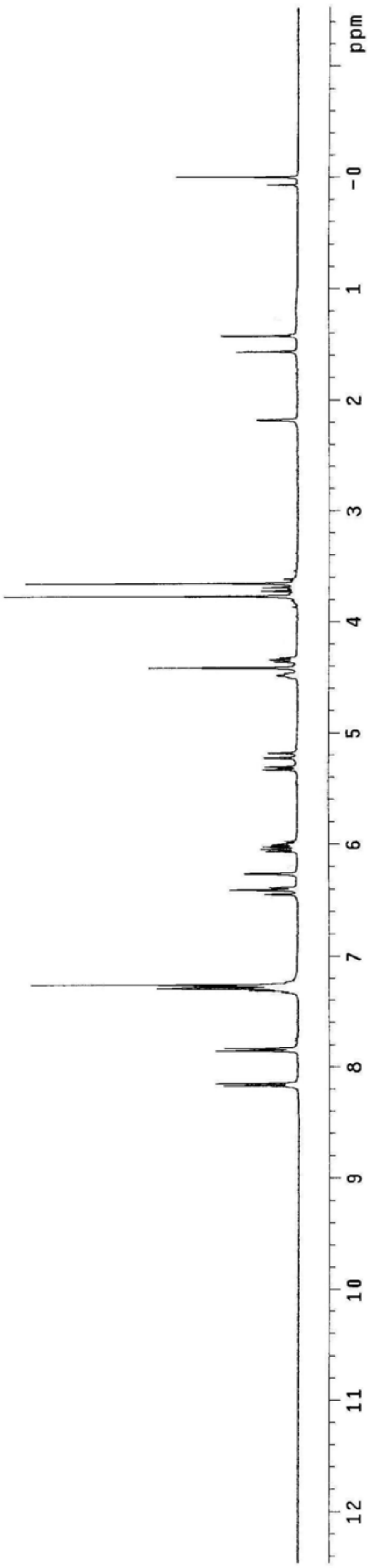
In a modification of the general procedure employing 200 mol% of allene **1e** (0.4 mmol), the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 0-25% EtOAc/cyclohexane) to furnish the title compound (64 mg) as a yellow oil in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.35 (m, 6H), 6.40 (m, 2H), 6.26 (d, *J* = 2.0 Hz, 1H), 6.02 (m, 2H), 5.31 (d, *J* = 10.4 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 4.48 (m, 1H), 4.42 (s, 2H), 4.34 (t, *J* = 7.2 Hz, 1H), 3.77 (d, *J* = .8 Hz, 3H), 3.66 (s, 3H), 2.18 (d, *J* = 3.2 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 158.1, 149.5, 146.7, 136.4, 132.7, 132.4, 132.0, 128.6, 128.5, 128.3, 128.0, 126.6, 123.7, 121.9, 116.0, 104.5, 98.1, 73.7, 66.4, 55.4, 55.1, 44.9.

HRMS (EI): Calcd. for $C_{27}H_{29}N_2O_7S$ (M+1): 525.1688, Found: 525.1690

FTIR (neat): 3530, 2937, 2361, 1611, 1588, 1529, 1509, 1456, 1349, 1295, 1209, 1160, 1132, 1107, 1090, 1036, 735, 686 cm^{-1}.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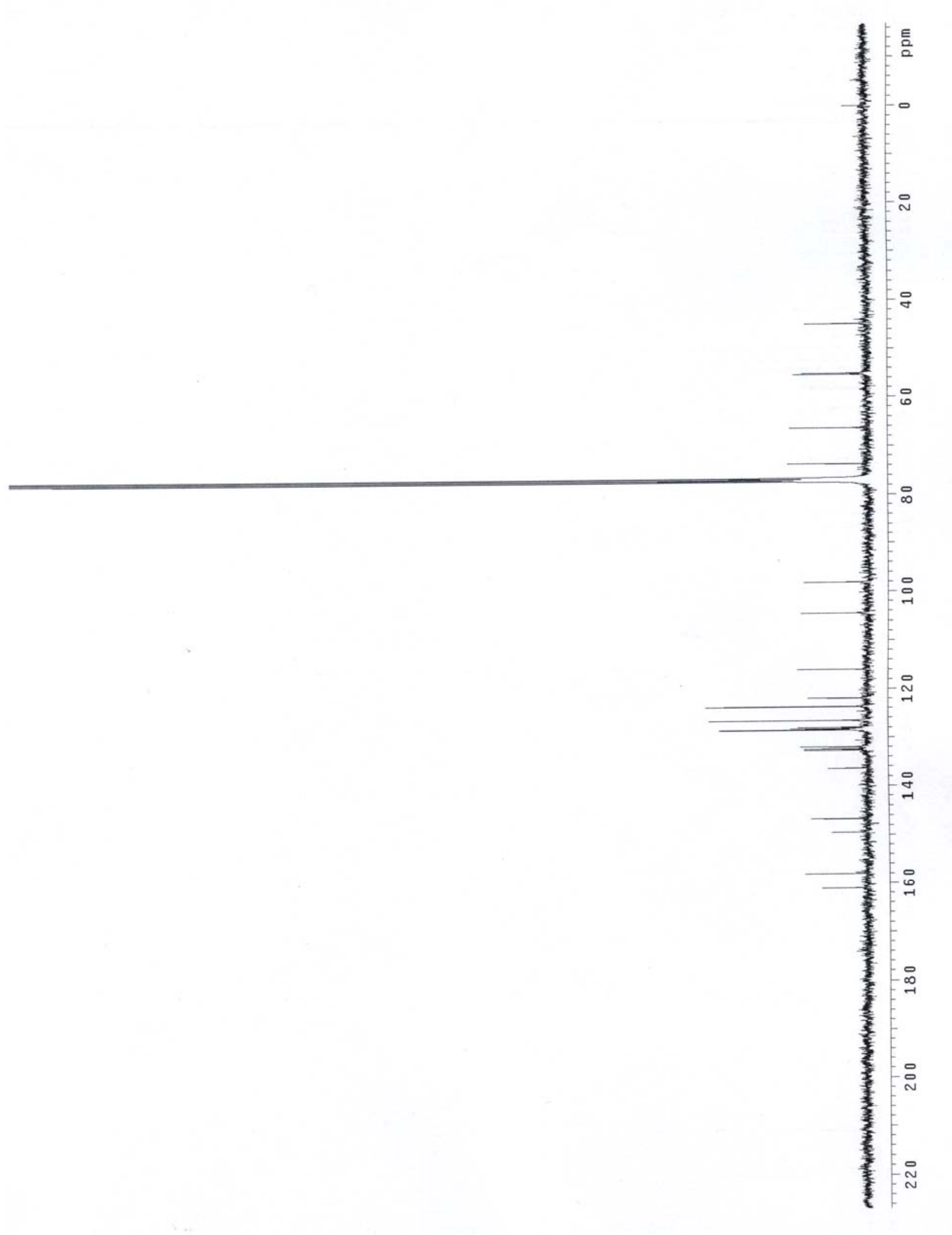
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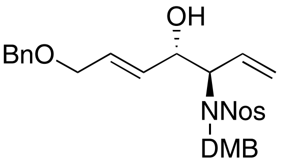
(*E*)-*N*-(7-(benzyloxy)-4-hydroxyhepta-1,5-dien-3-yl)-*N*-(2,4-dimethoxybenzyl)-4-nitrobenzenesulfonamide (3h)



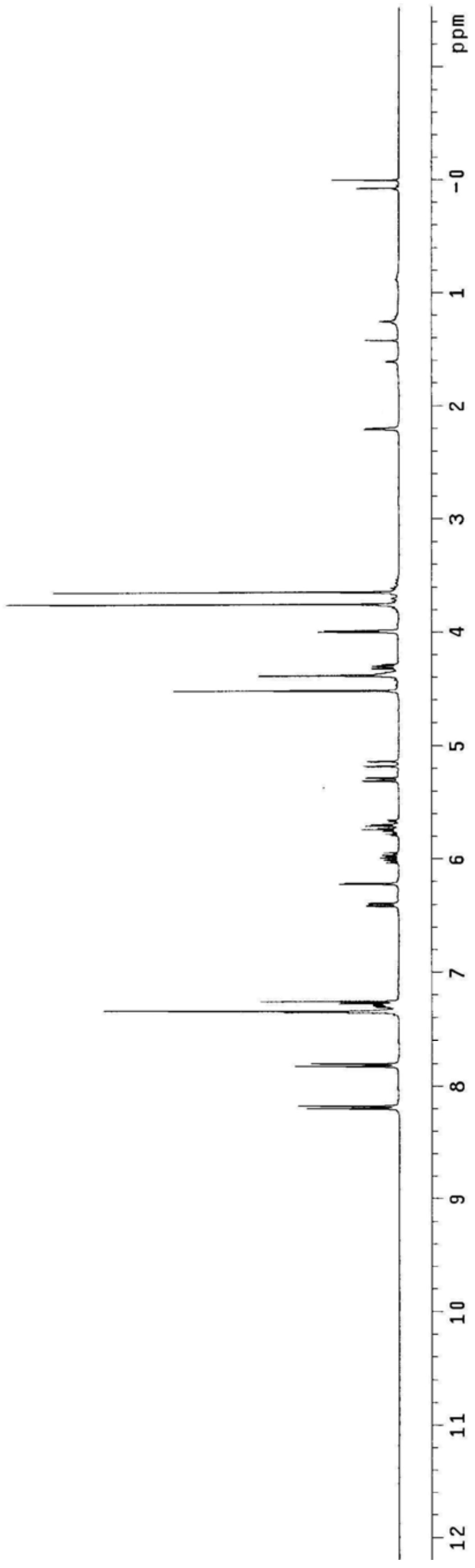
In a modification of the general procedure employing 200 mol% of allene **1e** (0.4 mmol), the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 0-30% EtOAc/cyclohexane) to furnish the title compound (70 mg) as a yellow oil in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.35 (m, 3H), 7.27 – 7.32 (m, 3H), 6.40 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 5.99 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.71 (m, 2H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 4.52 (s, 2H), 4.39 (s, 2H), 4.37 (m, 1H), 4.30 (m, 1H), 3.99 (d, *J* = 5.2 Hz, 2H), 3.75 (s, 3H), 3.64 (s, 3H), 2.20 (d, *J* = 3.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 158.3, 149.7, 147.0, 138.5, 132.5, 131.9, 131.7, 130.2, 128.7, 128.6, 128.0, 127.9, 123.9, 122.1, 116.1, 104.7, 98.2, 73.6, 72.5, 70.1, 66.4, 55.6, 55.3, 45.4.

HRMS (CI): Calcd. for $C_{29}H_{32}N_2O_8S$ (M+1): 568.1879, Found: 568.1874

FTIR (neat): 3530, 2936, 2361, 1611, 1529, 1509, 1349, 1295, 1209, 1160, 1107, 1090, 1036, 736 cm^{-1}.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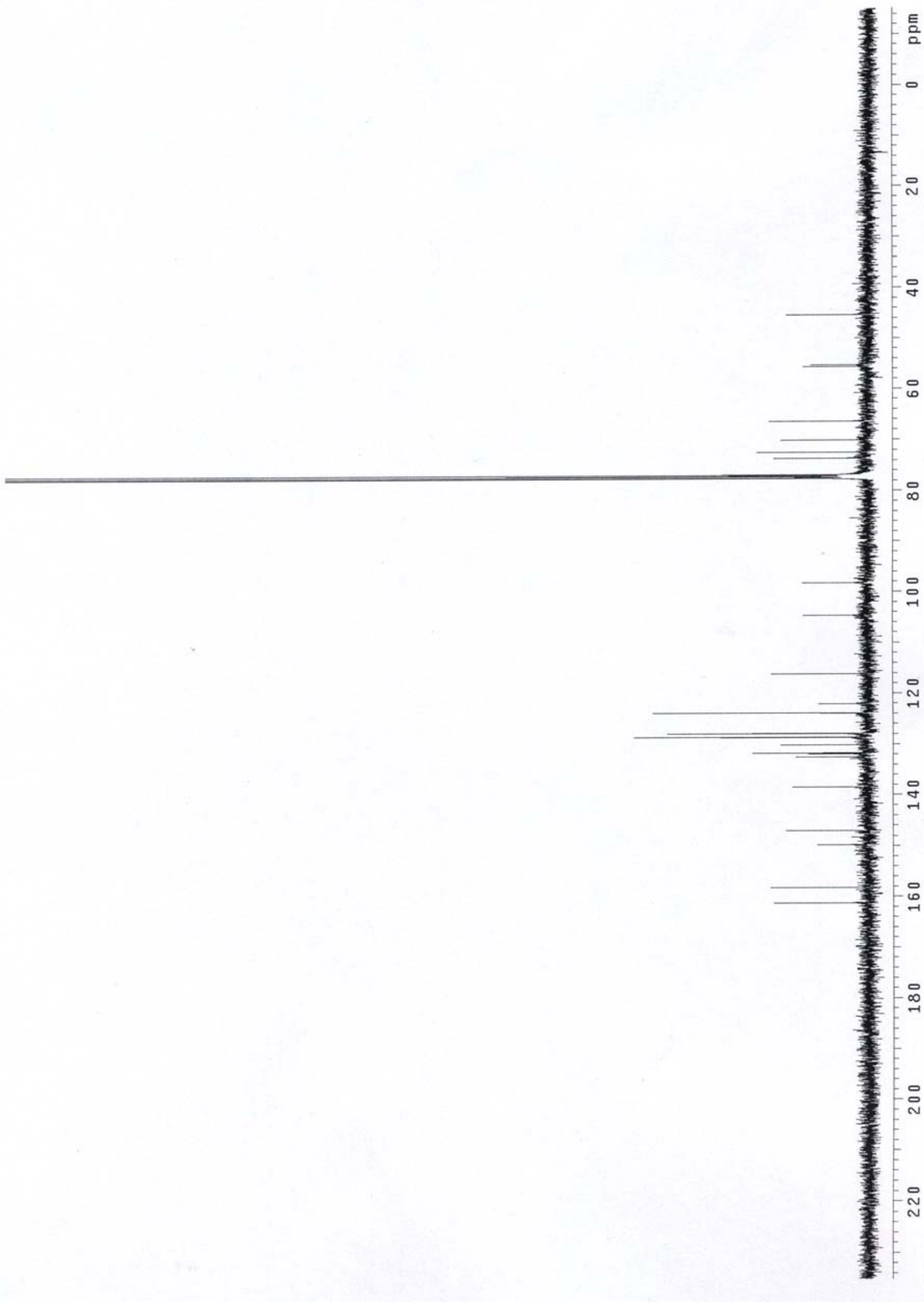
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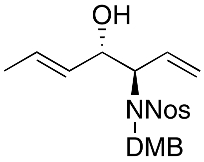
(*E*)-*N*-(2,4-dimethoxybenzyl)-*N*-(4-hydroxyhepta-1,5-dien-3-yl)-4-nitrobenzenesulfonamide (3i)



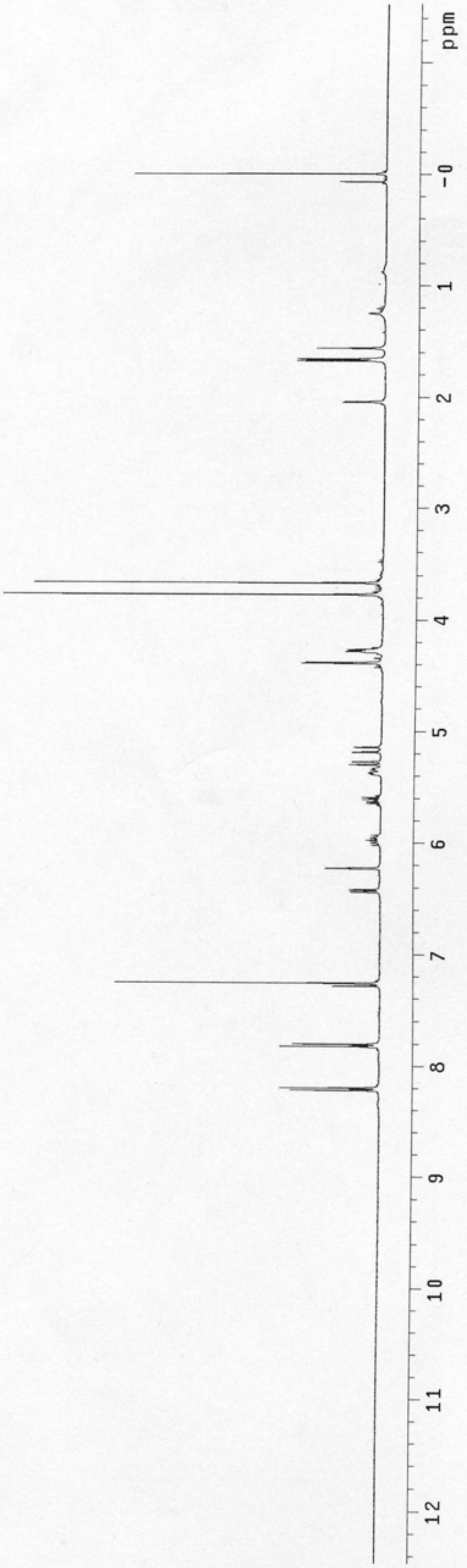
In a modification of the general procedure employing 200 mol% of allene **1e** (0.4 mmol), the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 20% EtOAc/cyclohexane) to furnish the title compound (54 mg) as a yellow oil in 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.42 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.23 (d, *J* = 2.4 Hz, 1H), 5.97 (ddd, *J* = 17.2, 10.4, 6.8 Hz 1H), 5.62 (ddd, *J* = 13.2, 6.8, 1.2 Hz 1H), 5.36 (dd, *J* = 6.8, 1.2 Hz, 1H), 5.28 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 4.38 (d, *J* = 3.6 Hz, 2H), 4.27 (m, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 2.04 (d, *J* = 2.8 Hz, 1H), 1.66 (dd, *J* = 6.8, 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 158.0, 149.5, 147.0, 132.3, 132.0, 130.1, 129.7, 128.4, 123.6, 121.6, 116.1, 104.4, 97.9, 74.1, 66.4, 55.4, 55.1, 45.1, 17.9.

HRMS (EI): Calcd. for $C_{22}H_{26}N_2O_7SNa$ (M+23): 485.1356, Found: 485.1353.

FTIR (neat): 3530, 3102, 2938, 2359, 1612, 1587, 1529, 1509, 1349, 1295, 1210, 1159, 1133, 1090, 1036, 855, 735, 686 cm^{-1}.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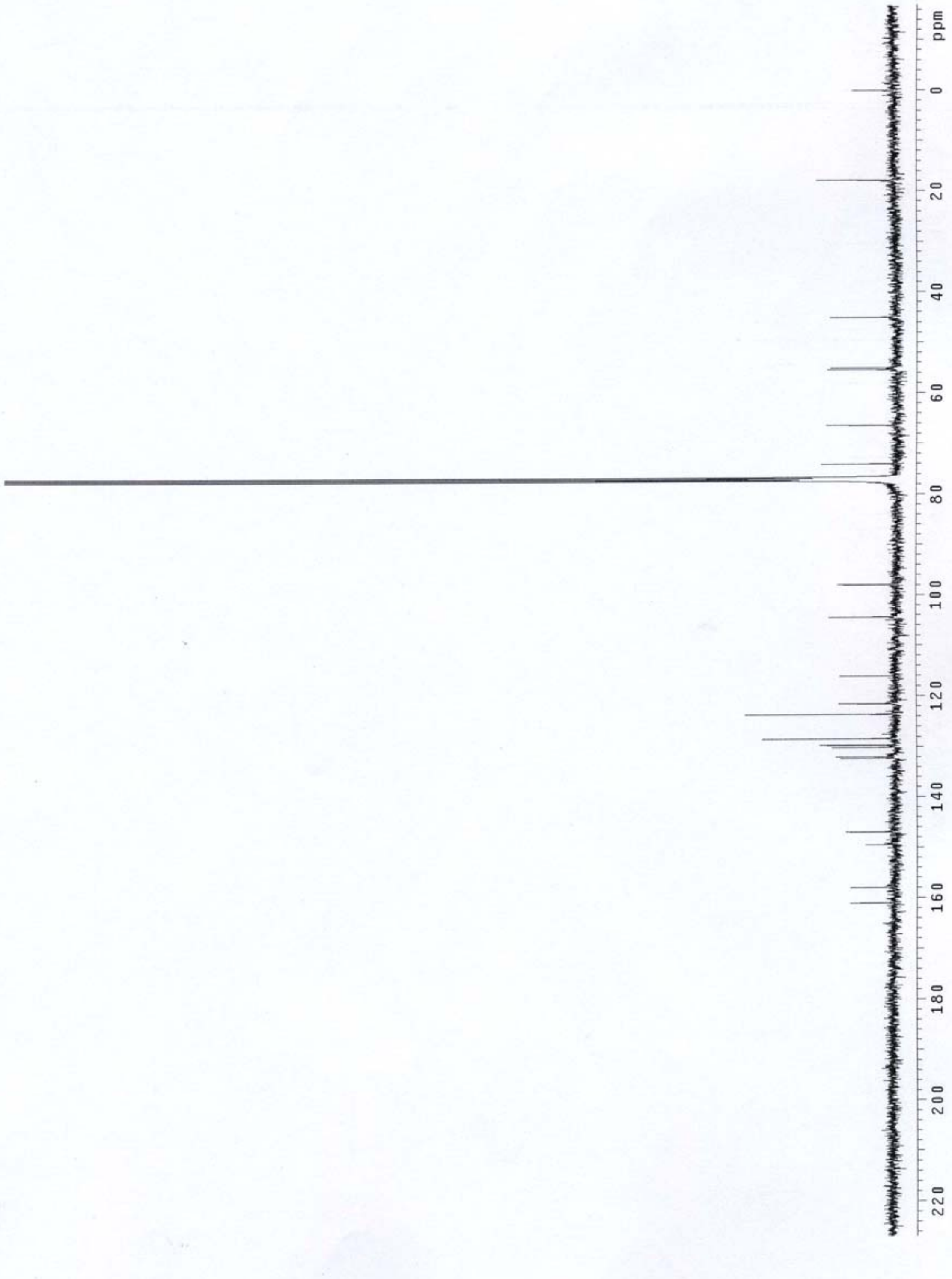
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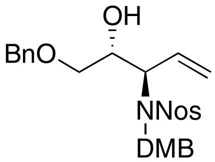
N-(5-(benzyloxy)-4-hydroxypent-1-en-3-yl)-*N*-(2,4-dimethoxybenzyl)-4-nitrobenzenesulfonamide (3j)



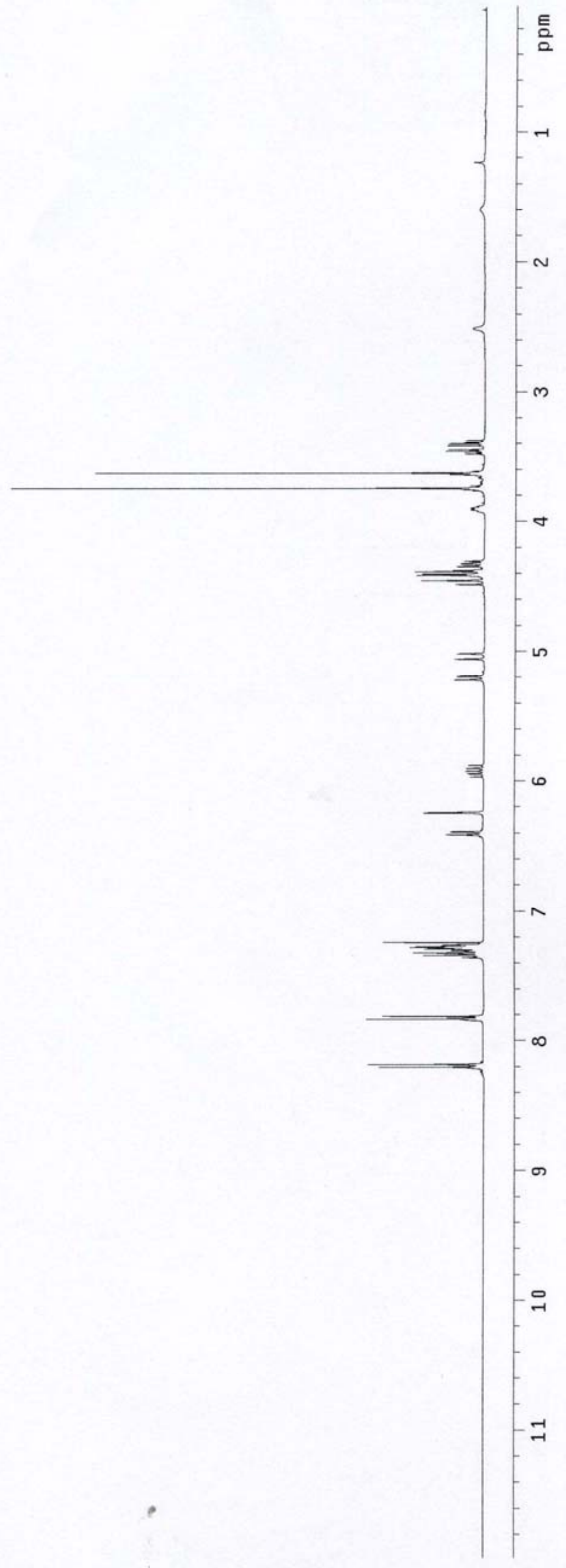
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 14 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 35% EtOAc/cyclohexane) to furnish the title compound (83 mg) as a yellow foam in 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9/0 Hz, 2H), 7.34 – 7.27 (m, 6H), 6.4 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.24 (d, *J* = 2.3 Hz, 1H), 5.92 (ddd, *J* = 17.2, 10.4, 6.6 Hz, 1H), 5.2 (d, *J* = 10.4 Hz, 1H), 5.04 (d, *J* = 17.2 Hz, 1H), 4.39 (m, 5H), 3.90 (m, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 3.46 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.39 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.51 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 158.0, 149.6, 146.6, 137.8, 132.0, 131.8, 128.5, 128.4, 127.8, 127.8, 123.9, 121.5, 116.2, 104.5, 98.1, 73.3, 71.0, 70.9, 63.1, 55.4, 55.1, 44.6.

HRMS (EI): Calcd. for $C_{27}H_{30}N_2O_8SNa$ (M+23): 565.1614, Found: 565.1615.

FTIR (neat) – 3507, 2939, 1733, 1587, 1529, 1421, 1372, 1243, 1130, 1038 cm^{-1}.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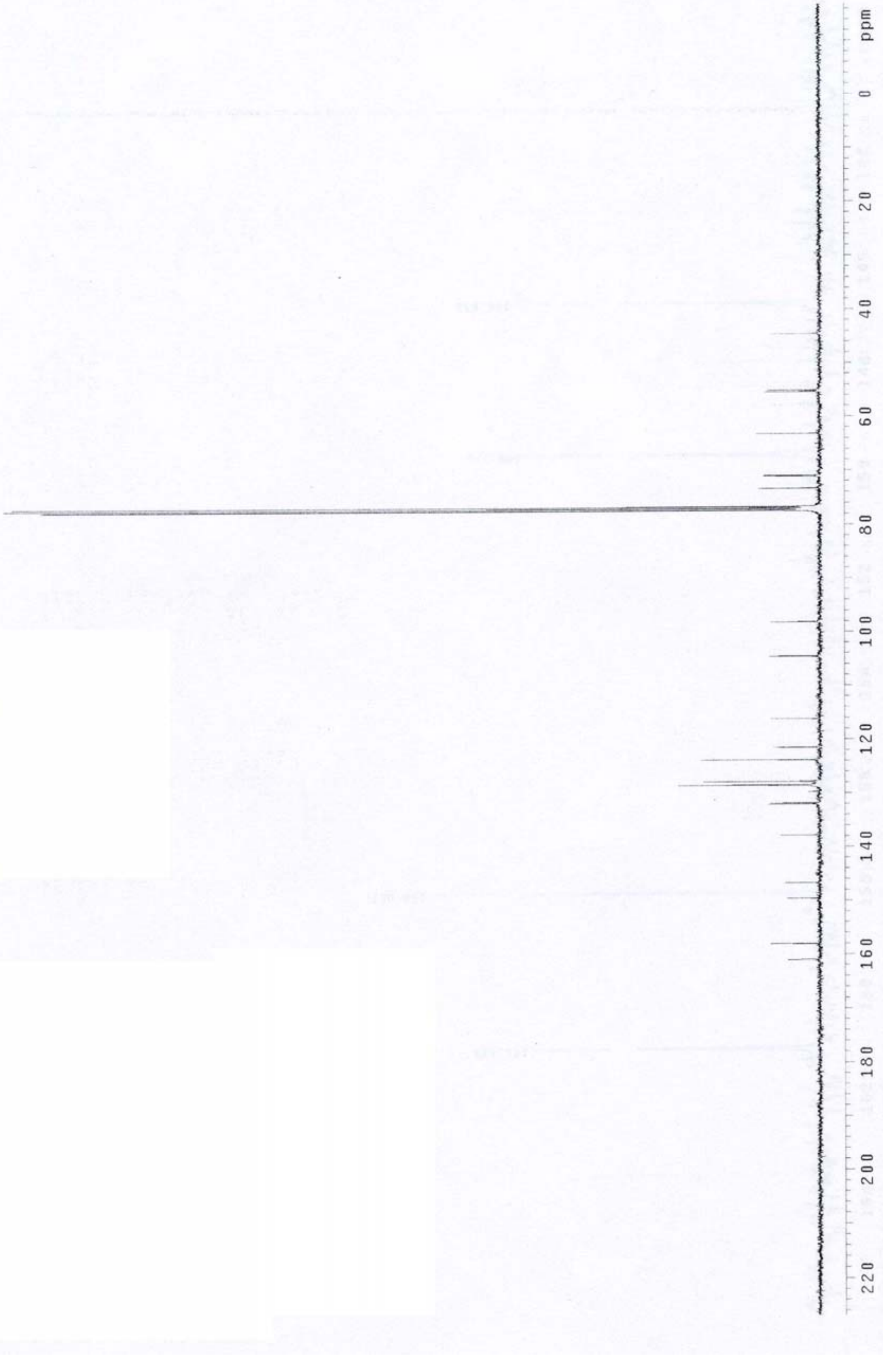
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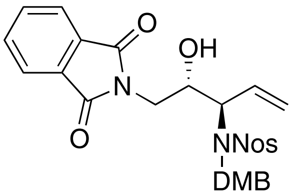
N-(2,4-dimethoxybenzyl)-*N*-(5-(1,3-dioxoisoindolin-2-yl)-4-hydroxypent-1-en-3-yl)-4-nitrobenzenesulfonamide (3k)



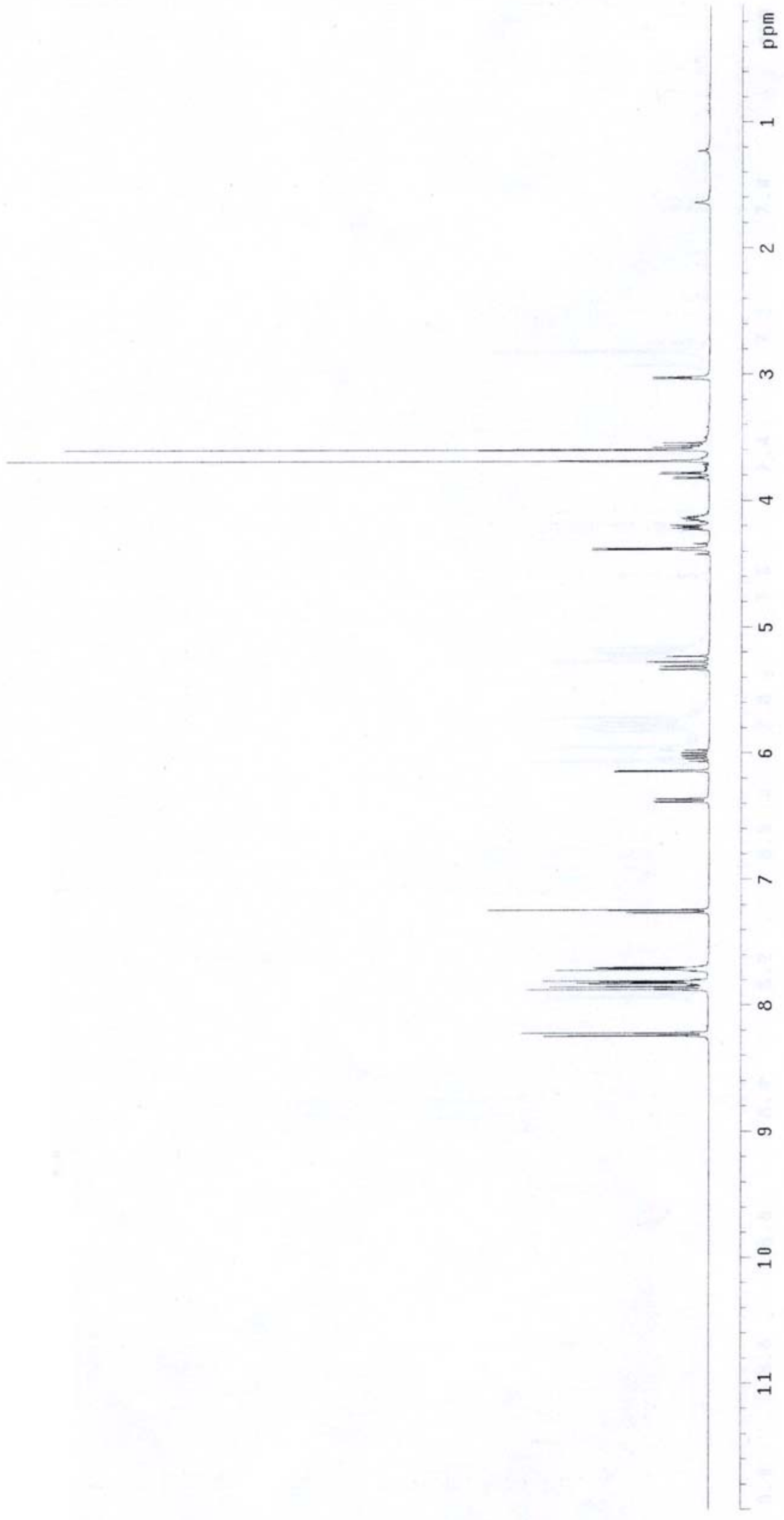
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 14 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 35% EtOAc/cyclohexane) to furnish the title compound (99 mg) as a white foam in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.81 (d, *J* = 5.5 Hz, 1H), 7.71 (d, *J* = 5.7 Hz, 1H), 7.70 (d, *J* = 5.5 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 6.38 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.14 (d, *J* = 2.3 Hz, 1H), 6.02 (ddd, *J* = 16.6, 10.4, 6.8 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 5.25 (d, *J* = 16.6 Hz, 1H), 4.38 (d, *J* = 3.7 Hz, 2H), 4.19 (dd, *J* = 6.8, 5.1 Hz, 1H), 4.13 (m, 1H), 3.80 (dd, *J* = 14.3, 4.5 Hz, 1H), 3.69 (s, 3H), 3.60 (s, 3H), 3.57 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.02 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 161.0, 158.0, 149.6, 146.4, 134.1, 132.1, 131.8, 130.6, 128.6, 123.8, 123.4, 122.6, 115.5, 104.5, 98.1, 71.5, 64.3, 55.3, 55.1, 45.1, 41.9.

HRMS (EI): Calcd. for $C_{28}H_{27}N_3O_9SNa$ (M+23): 604.1361, Found: 604.1360.

FTIR (neat) – 3506, 2940, 2360, 1771, 1611, 1529, 1348, 1158, 1035 cm^{-1}.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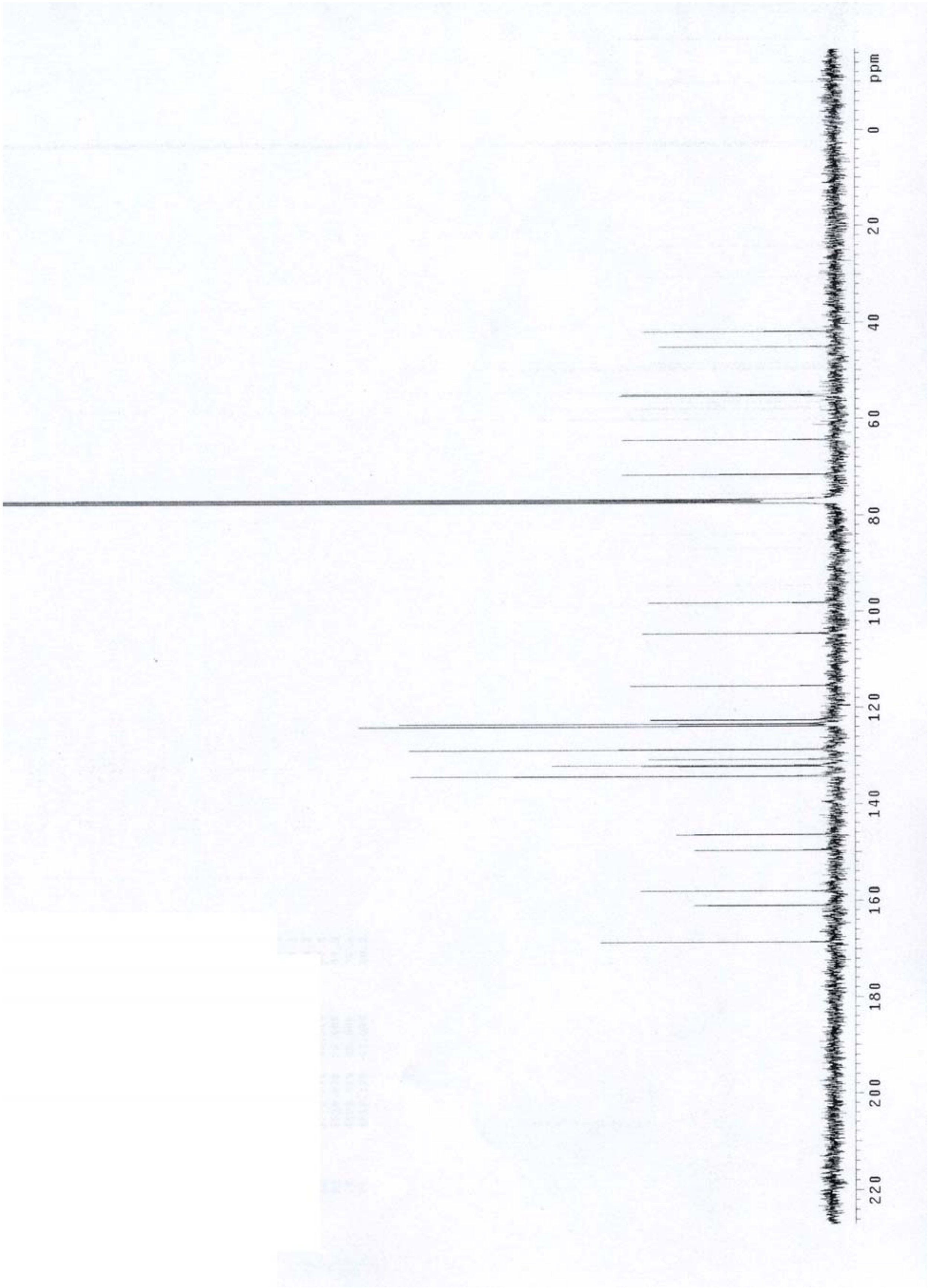
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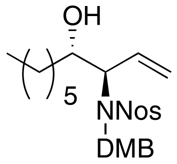
N-(2,4-dimethoxybenzyl)-*N*-(4-hydroxydec-1-en-3-yl)-4-nitrobenzenesulfonamide (3l)



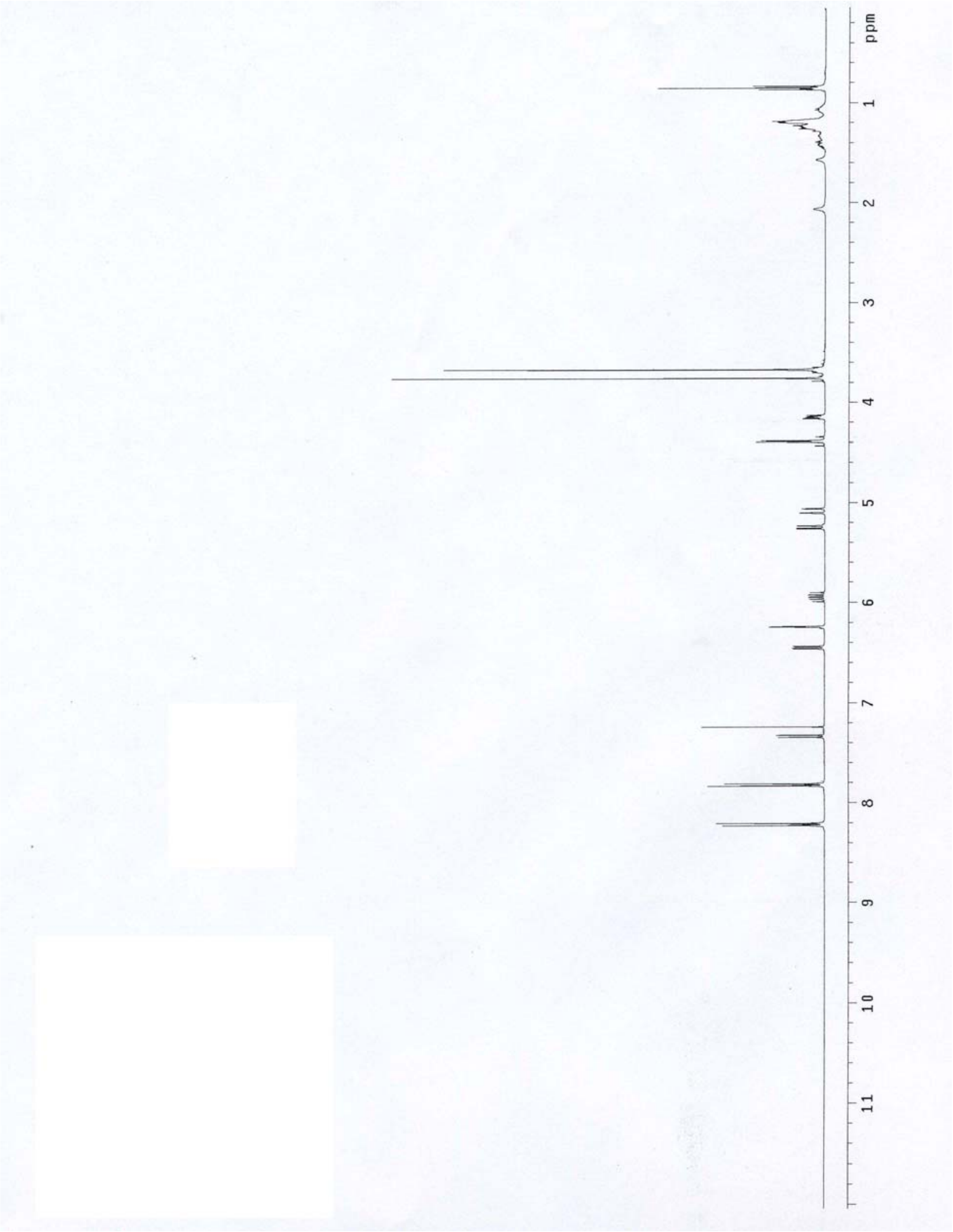
In a modification of the general procedure employing 200 mol% of allene **1e** (0.4 mmol), the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 20% EtOAc/cyclohexane) to furnish the title compound (70 mg) as a yellow oil in 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.44 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.23 (d, *J* = 2.6 Hz, 1H), 5.94 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.39 (s, 1H), 4.38 (s, 1H), 4.15 (q, *J* = 4.7 Hz, H), 3.76 (s, 3H), 3.67 (s, 4H), 2.06 (s, 1H), 1.45 – 1.02 (m, 10H), 0.85 (t, *J* = 6.8Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 157.9, 149.5, 146.8, 131.9, 131.3, 128.4, 123.7, 122.0, 116.2, 104.6, 98.1, 73.3, 66.4, 55.4, 55.2, 44.6, 33.8, 31.8, 29.2, 25.7, 22.6, 14.1.

HRMS (EI): Calcd. for $C_{25}H_{34}N_2O_7SNa$ (M+23): 529.1972, Found: 529.1979

FTIR (neat): 3541, 2928, 2856, 1611, 1400, 1347, 1293, 1158, 1131, 1035 cm^{-1}.



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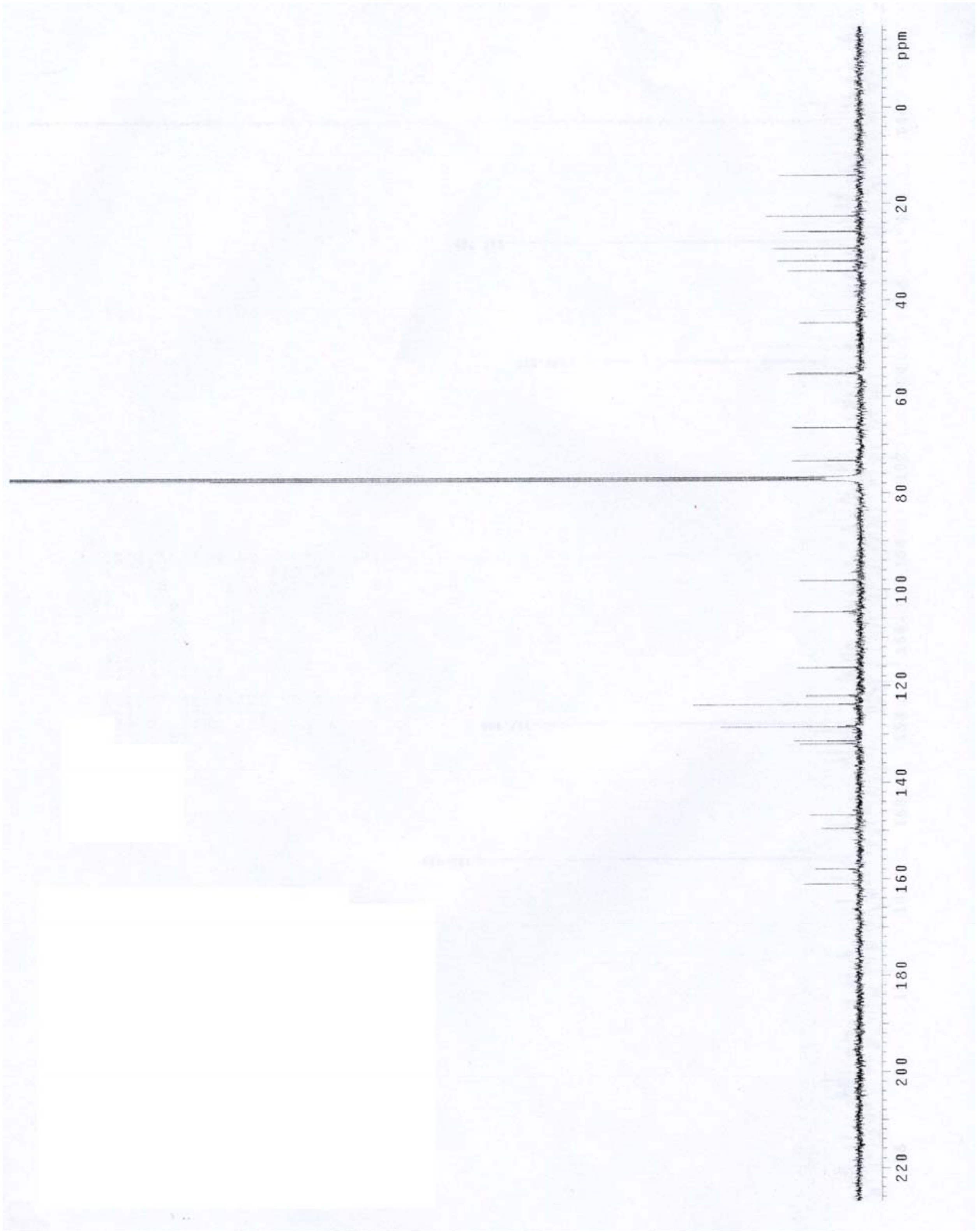
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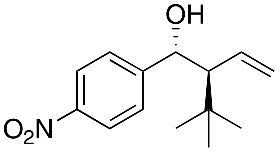
2-*tert*-Butyl-1-(4-nitrophenyl)but-3-en-1-ol



In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 5% EtOAc/cyclohexane) to furnish the title compound (40 mg) as a yellow oil in 80% yield. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from hexanes.

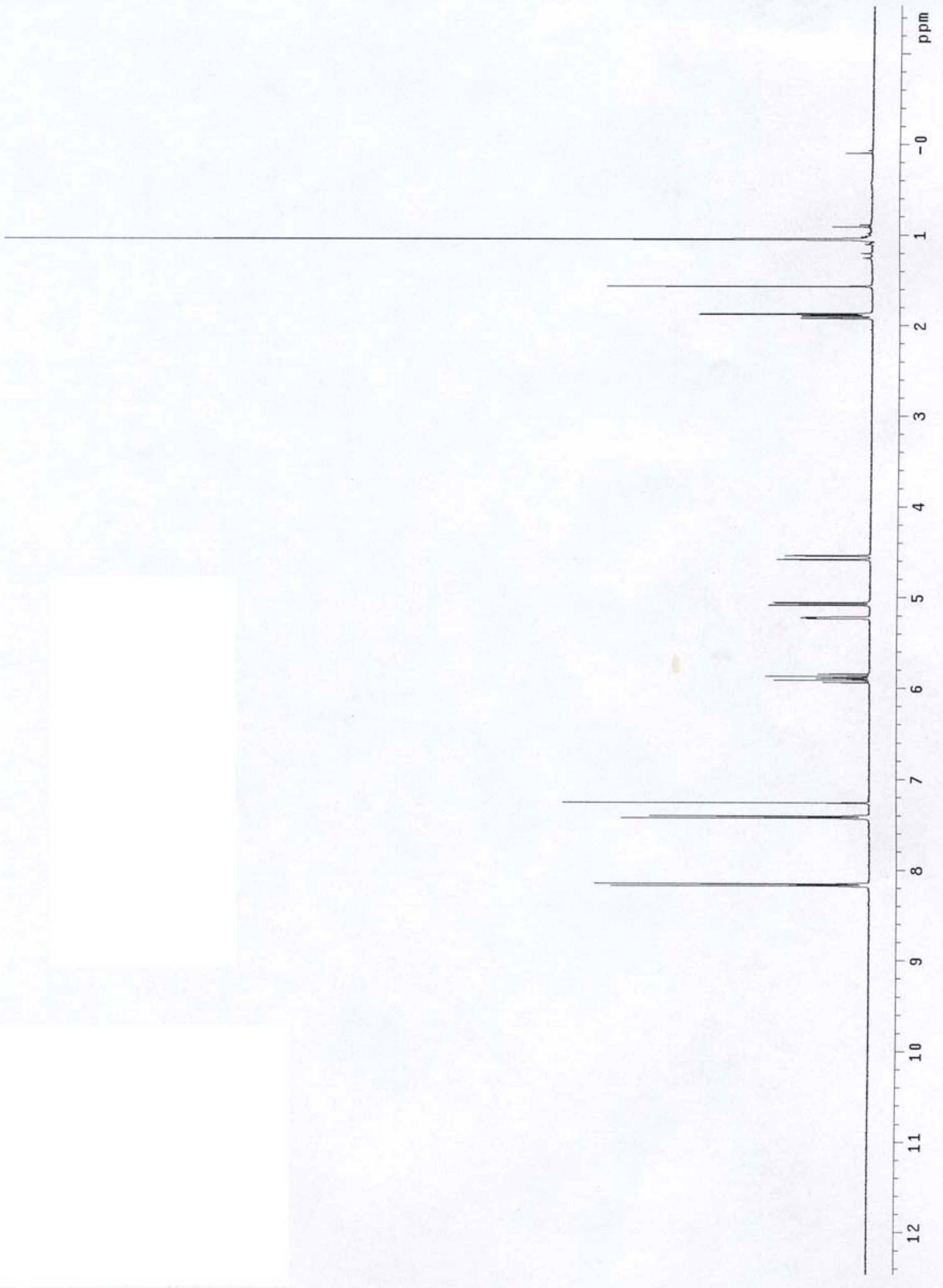
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 5.89 (dt, *J* = 17.2, 10.2 Hz, 1H), 5.09 – 5.06 (m, 1H), 4.58 (d, *J* = 10.2 Hz, 1H), 4.54 (d, *J* = 17.2 Hz, 1H), 1.90 (d, *J* =7.8 Hz, 1H), 1.86 (d, *J* = 4.2 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 146.8, 132.8, 126.7, 123.2, 119.9, 72.8, 62.1, 33.2, 28.7.

HRMS (CI): Calcd. for $C_{14}H_{20}NO_3$ (M+1): 250.1443, Found: 250.1447

FTIR (neat) – 3536, 2949, 1596, 1363, 1341, 1231, 1107, 1025 cm^{-1}.

M.P. 143 – 147 °C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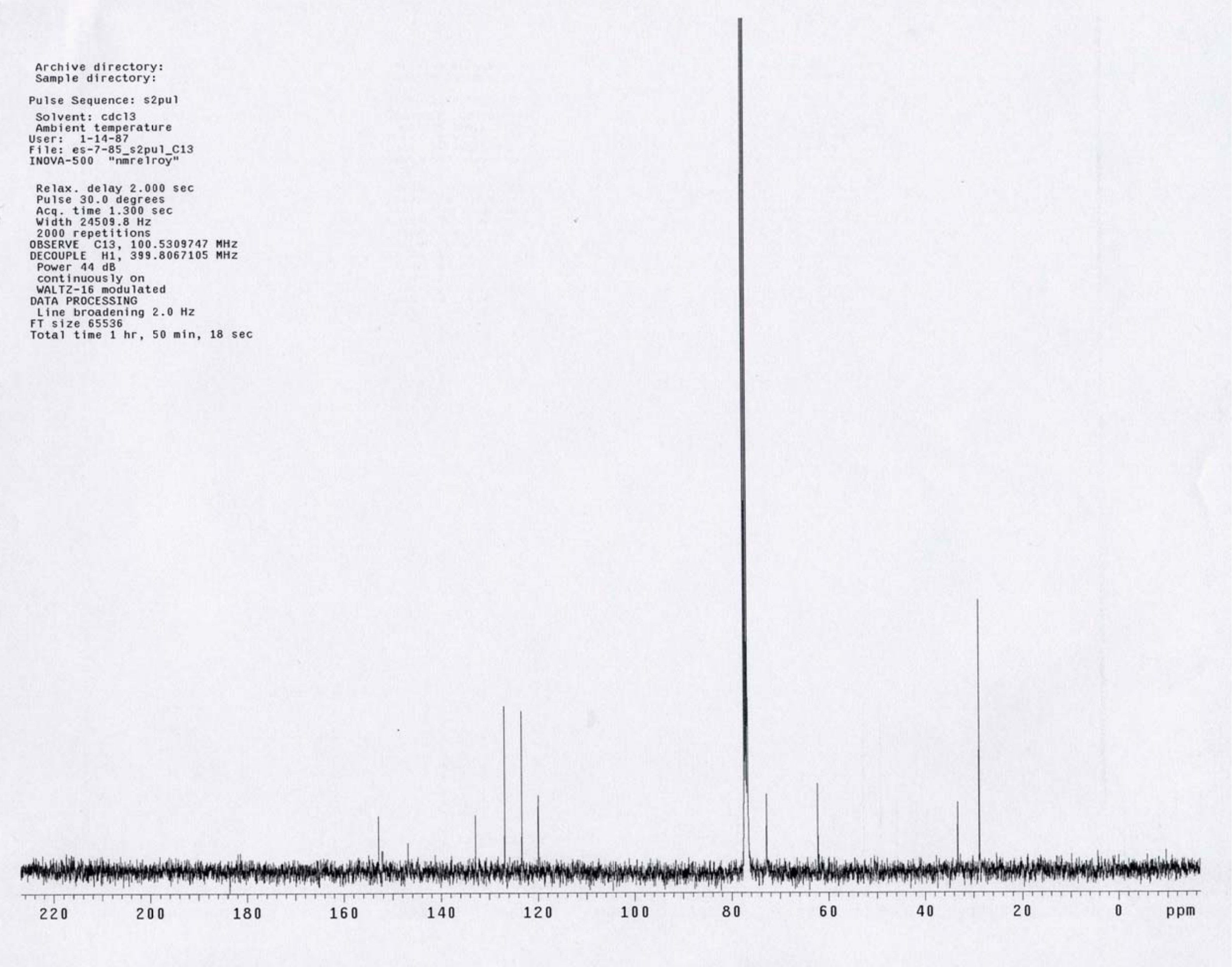

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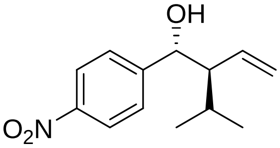
(1R,2R)-2-isopropyl-1-(4-nitrophenyl)but-3-en-1-ol



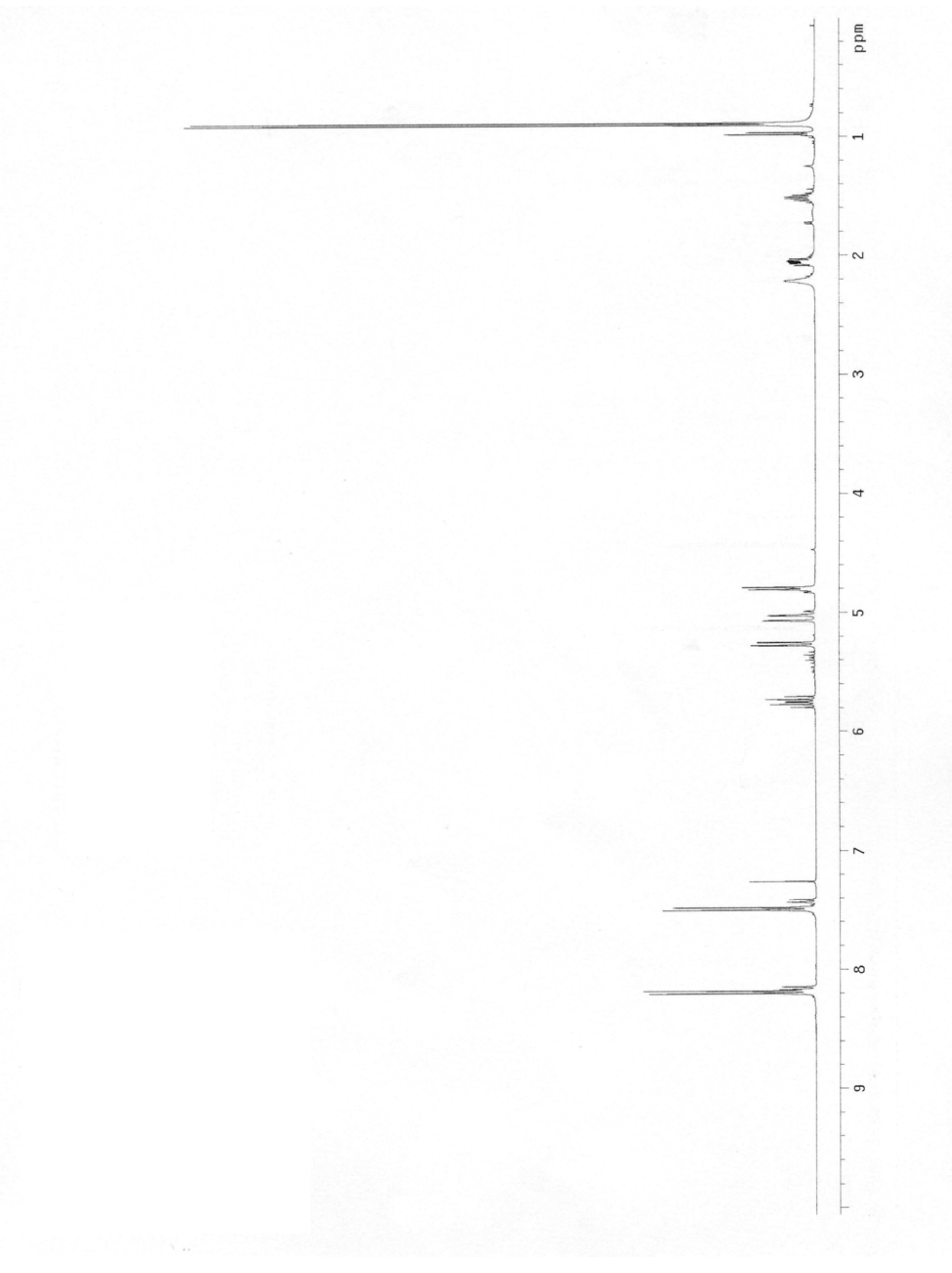
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 5% EtOAc/cyclohexane) to furnish the title compound (37 mg, 6:1 d.r *A:B*) as a yellow oil in 79% yield.

<u>^{1}H NMR</u> (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H *of A*), 8.17 (d, *J* = 8.8 Hz, 2H *of B*), 7.49 (d, *J* = 8.8 Hz, 2H *of A*), 7.42 (d, *J* = 8.8 Hz, 2H *of B*), 5.75 (dt, *J* = 17.0, 10.2 Hz, 1H *of A*), 5.38 (dt, *J* = 17.0, 10.3 Hz, 1H *of B*), 5.26 (dd, *J* = 10.2, 2.0 Hz, 1H *of A*), 5.05 (dd, *J* = 17.2, 2.0 Hz, 1H *of A*), 5.00 (dd, *J* = 10.2, 2.0 Hz, 1H *of B*), 4.79 (d, *J* = 7.0 Hz, 1H *of A*), 4.83 – 4.79 (m, 2H *of B*), 2.23 – 2.15 (m, 2H), 2.08 – 1.92 (m, 2H), 1.69 -1.56 (m, 1H *of B*), 1.54 – 1.41 (m, 1H *of A*), 0.97 (d, *J* = 6.7 Hz, 6H *of B*), 0.89 (d, *J* = 6.7 Hz, 6H *of A*).

<u>^{13}C NMR</u> (100 MHz, $CDCl_3$): δ 150.7, 150.6, 147.3, 147.2, 134.6, 134.2, 127.7, 127.5, 127.7, 127.5, 123.5, 123.3, 120.9, 119.5, 73.9, 73.6, 59.2, 58.2, 27.7, 27.0, 21.7, 21.6, 18.2, 17.7.

<u>HRMS</u> (CI): Calcd. for $C_{13}H_{18}NO_3$ (M+1): 236.1287, Found: 236.1292

<u>FTIR</u> (neat) – 3448, 2959, 1604, 1516, 1345, 1231, 1108, 856 cm^{-1}.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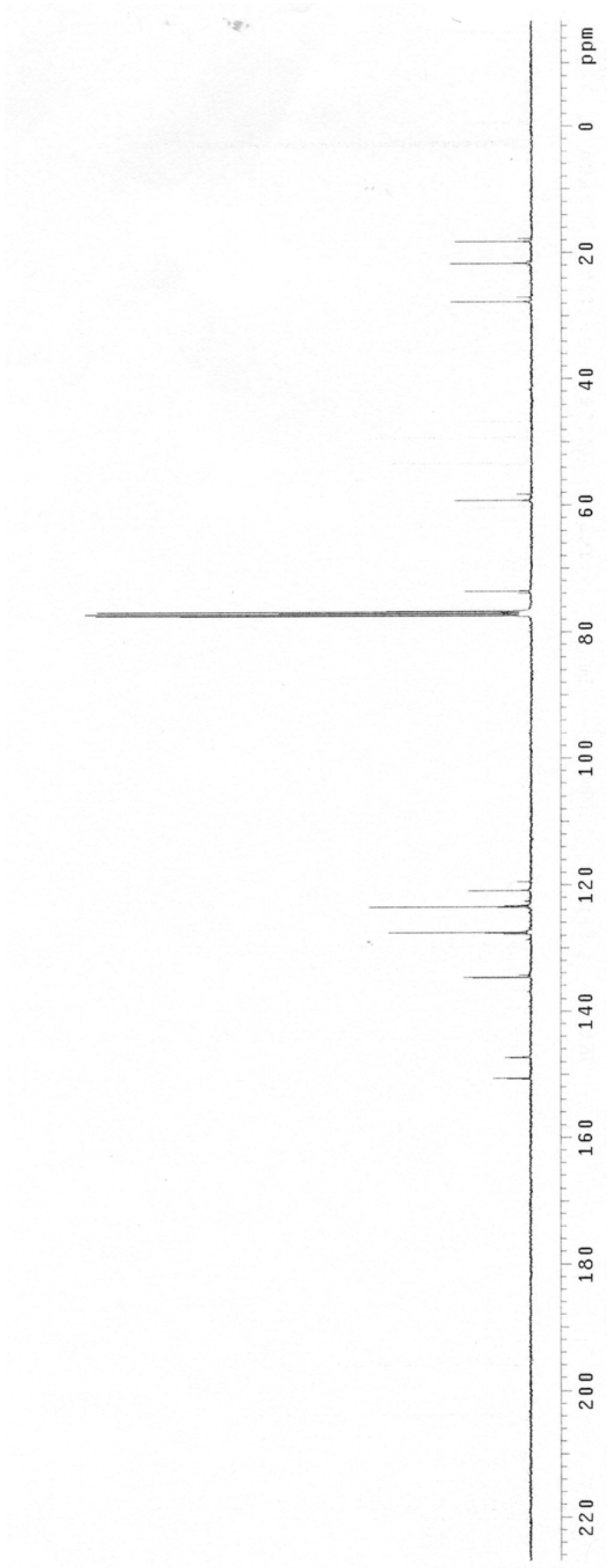
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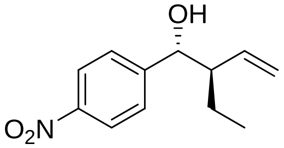
(1*R*,2*R*)-2-ethyl-1-(4-nitrophenyl)but-3-en-1-ol



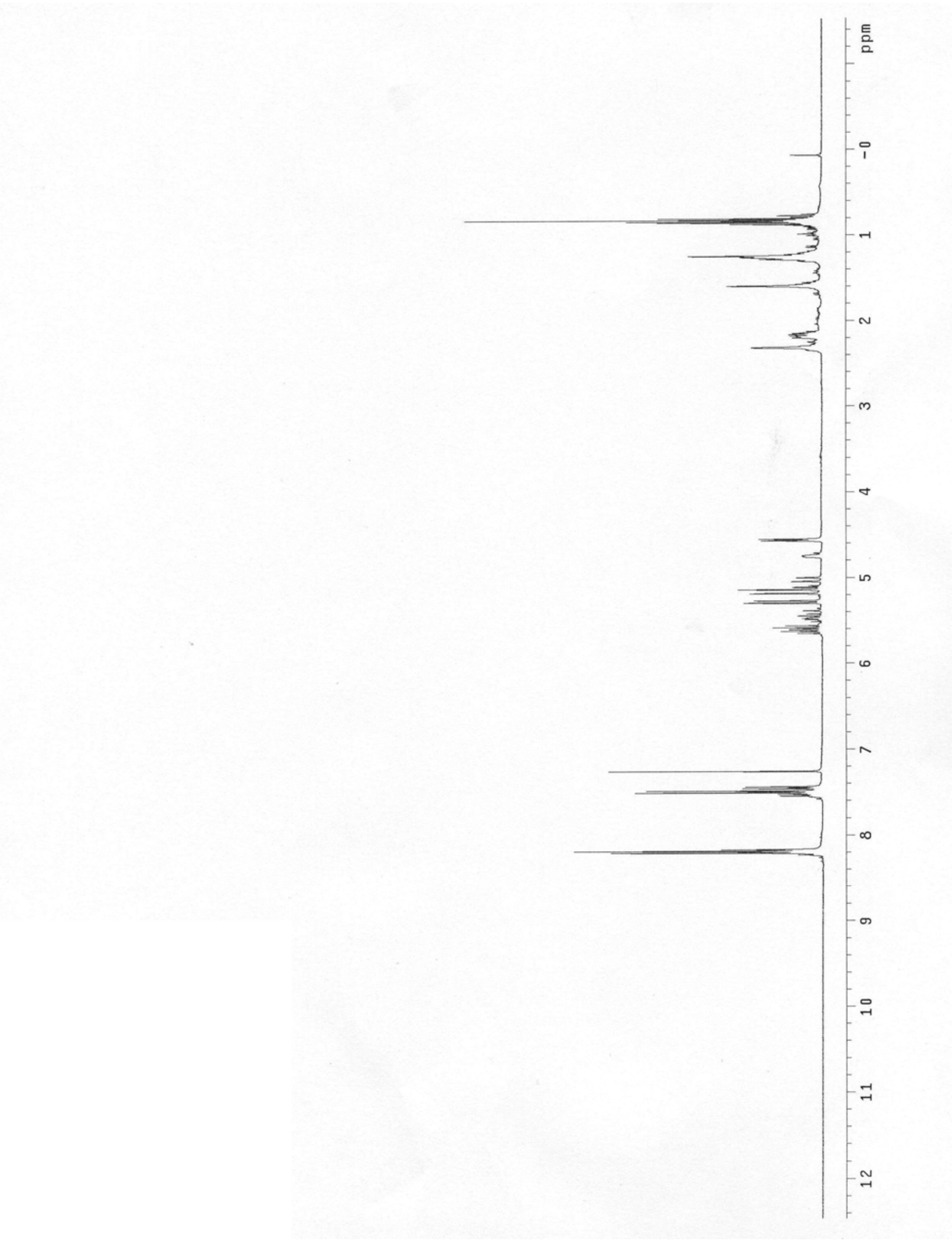
In accordance with the general procedure, the reaction was allowed to stir at 100 °C for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 5% EtOAc/cyclohexane) to furnish the title compound (33 mg, 2:1 d.r *A:B*) as a yellow oil in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H *of A*), 8.17 (d, *J* = 8.8 Hz, 2H *of B*), 7.49 (d, *J* = 8.8 Hz, 2H *of A*), 7.44 (d, *J* = 8.8 Hz, 2H *of B*), 5.61 (dt, *J* 17.2, 10.2 Hz, 1H *of A*), 5.52 – 5.39 (m, 1H *of B*), 5.28 (d, *J* = 10.2 Hz, 1H *of A*), 5.16 (d, *J* =17.2 Hz, 1H *of A*), 5.14 – 5.09 (m, 1H *of B*), 5.02 (d, *J* = 17.2 Hz, 1H *of B*), 4.75 – 4.72 (m, 1H *of B*), 4.56 (d, *J* = 7.2 Hz, 1H *of A*), 2.35 – 2.27 (m, 2H), 2.24 – 2.19 (m, 2H), 1.31 – 1.18 (m, 4H), 0.85 – 0.77 (m, 6H).

^{13}CNMR(100MHz,$CDCl_3$):δ 150.1, 150.0, 147.4, 147.2, 137.7, 137.3, 127.7, 127.5, 123.4, 123.2 , 120.0, 118.5, 75.9, 75.6, 54.7, 53.3, 23.4, 22.2.

HRMS (CI): Calcd. for $C_{12}H_{16}NO_3$ (M+1): 222.1130, Found: 222.1128

FTIR (neat) – 3421, 2964, 2931, 2875, 1604, 1518, 1346, 1040, 1108, 854 cm^{-1}.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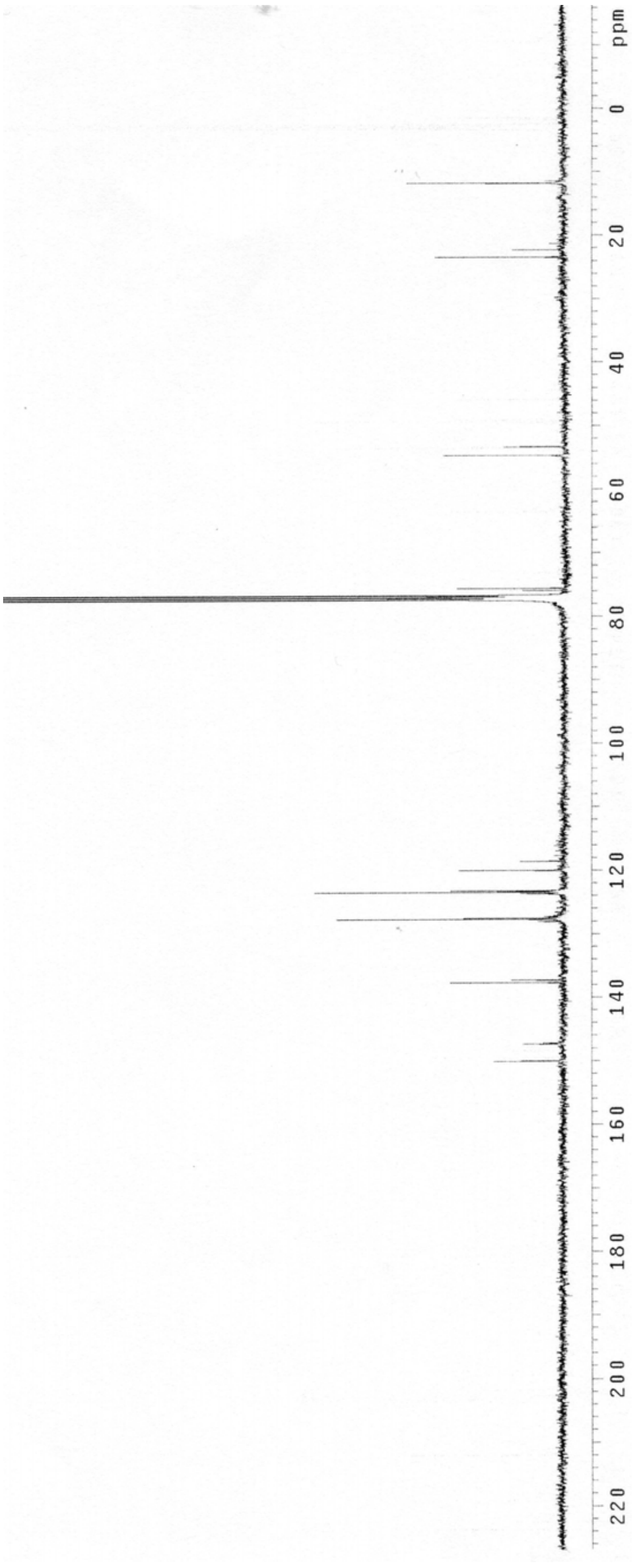

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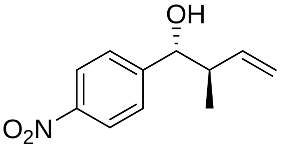
2-Methyl-1-(4-nitrophenyl)but-3-en-1-ol



In a modification of the general procedure to a re-sealable pressure tube (13 x 100 mm) equipped with magnetic stir bar was added RuBr(CO)$_3$(η^3-C$_3$H$_5$) (6.2 mg, 0.02 mmol, 5 mol%) and Cy$_3$P (16.8 mg, 0.06 mmol, 15 mol%). Aldehyde (0.400 mmol, 100 mol%) was added and the tube was sealed with a rubber septum and purged with argon. THF (0.4 mL, 1.0 M concentration with respect to aldehyde) and isopropanol (122 μL, 1.600 mmol, 400 mol%) were added. 1,2-butadiene (48 μL, 0.600 mmol, 150 mol%) was condensed into a 1 dram vial at -78 °C and quickly transferred via syringe to the reaction tube. The rubber septum was quickly replaced with a screw cap and the mixture was heated at 100 °C (oil bath temperature) for 18 hours, at which point the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO$_2$: 10% EtOAc / Hexane) to furnish the title compound (70 mg, 2:1 d.r *A:B*) as a yellow oil in 85% yield. *The spectroscopic properties of this compound were consistent with the data available in the literature.*[5]

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19-8.16 (m, 4H), 7.49-7.45 (m, 4H), 5.80-5.67 (m, 2H), 5.21-5.04 (m, 4H), 4.76-4.74 (m, 1H *of B*), 4.49 (dd, J = 7.2, 2.2 Hz, 1H *of A*), 2.60-2.56 (m, 1H *of B*), 2.47-2.41 (m, 1H *of A*), 2.30 (d, J = 2.2 Hz, 1H *of A*), 2.11 (d, J = 3.4 Hz, 1H *of B*), 0.94 (d, J = 6.8 Hz, 3H *of B*), 0.91 (d, J = 6.8 Hz, 3H *of A*)

^{13}C NMR (100 MHz, CDCl$_3$): δ 149.8, 149.7, 146.3, 146.2, 139.3, 139.2, 127.6, 127.2, 123.4, 123.3, 118.0, 116.7, 76.8, 76.0, 46.6, 44.6, 16.3, 13.2.

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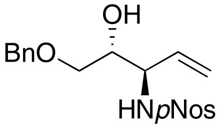
[5] Jiang, S.; Agoston, E. G.; Chen, T.; Cabal, M.-P.; Turos. E. *Organometallics* **1995**, *14*, 4697.

N-(5-(benzyloxy)-4-hydroxypent-1-en-3-yl)-4-nitrobenzenesulfonamide (4)



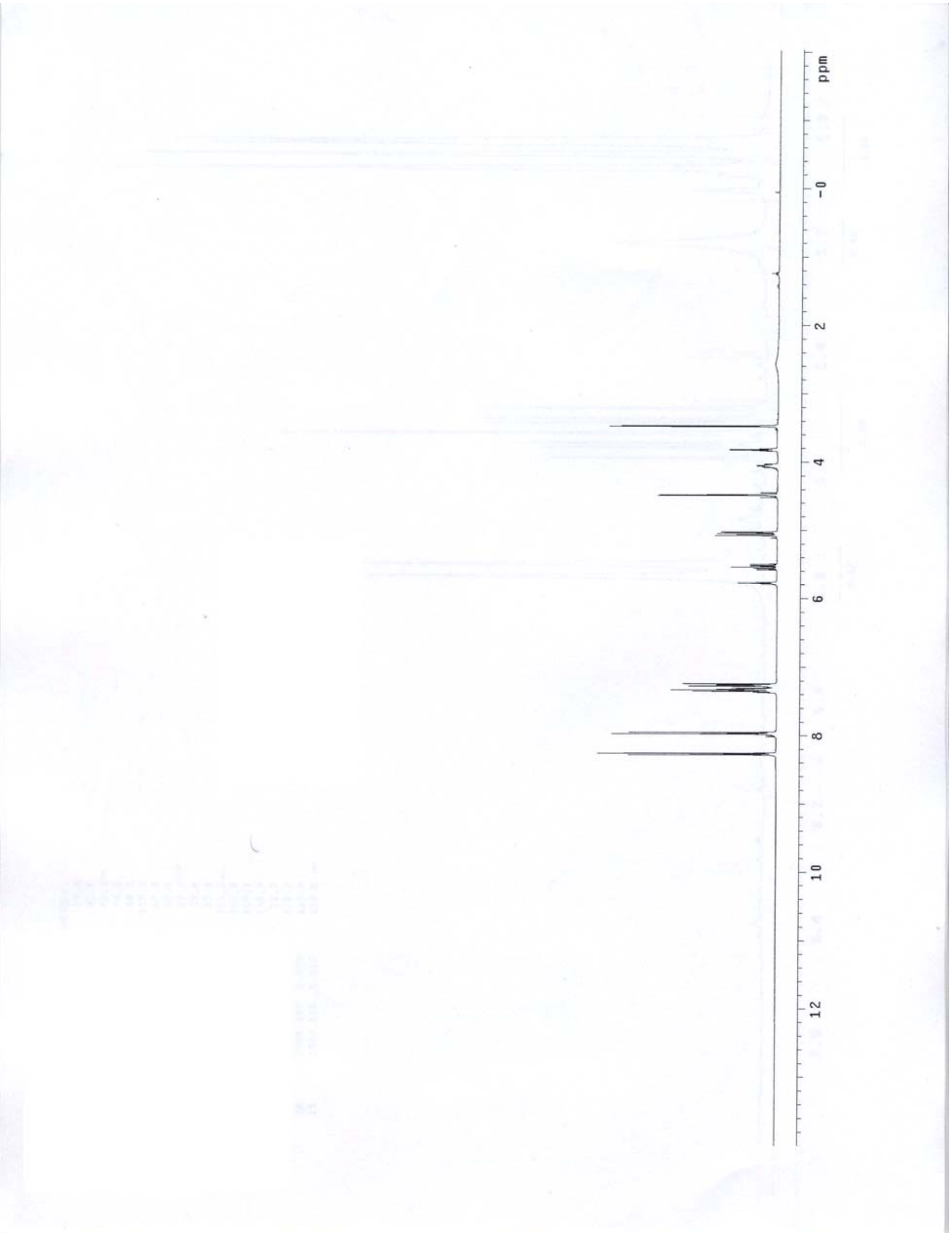
To a stirred solution of **3j** (0.682 g, 1.257 mmol, 100 mol%) in dry toluene/anisole (2:1, 0.3 M with respect to **3j**) under nitrogen at 25 ^{o}C was added trifluoroacetic acid (3.27 ml, 43.995 mmol, 3500 mol%). The reaction mixture was heated at 45 ^{o}C for 45 min., at which point the reaction mixture was allowed to cool to ambient temperature and saturated $NaHCO_3$ (aq.) was added. The reaction mixture was transferred to a separatory funnel and the organic layer was separated. The aqueous layer was extracted three times with EtOAc. The combined organic layers were dried (Mg_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2: 40% EtOAc/hexanes) to furnish the title compound (0.438 g) as yellow oil in 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.37 – 7.27 (m, 5H), 5.77 (d, *J* = 8.4 Hz, 1H), 5.53 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.05 (m, 2H), 4.84 (s, 1H), 4.47 (s, 1H), 4.08 – 4.03 (m, 1H), 3.81 (q, *J* = 4.3 Hz, 1H), 3.47 (d, *J* = 4.7 Hz, 2H), 2.56 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.8, 137.1, 132.8, 128.4, 128.2, 127.8, 124.4, 124.1, 118.9, 73.7, 71.4, 70.9, 59.5.

HRMS (CI): Calcd. for $C_{18}H_{21}N_2O_6S$ (M+1): 393.1122, Found: 393.1120.

FTIR (neat): 3511, 3289, 2988, 2360, 1606, 1529, 1453, 1349, 1207, 1165 cm^{-1}.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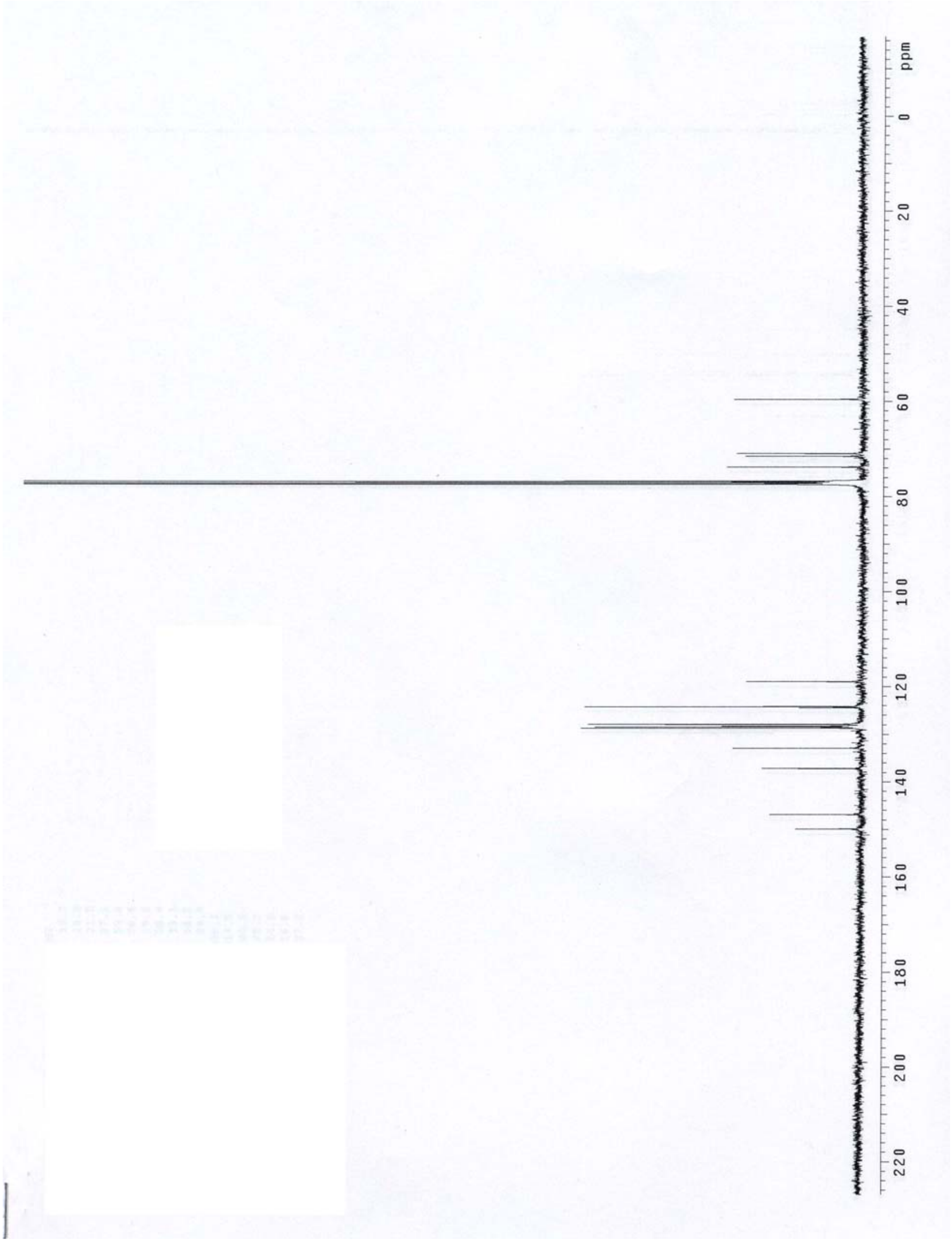
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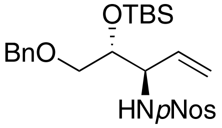
N-(5-(benzyloxy)-4-(*tert*-butyldimethylsilyloxy)pent-1-en-3-yl)-4-nitrobenzenesulfonamide (5)



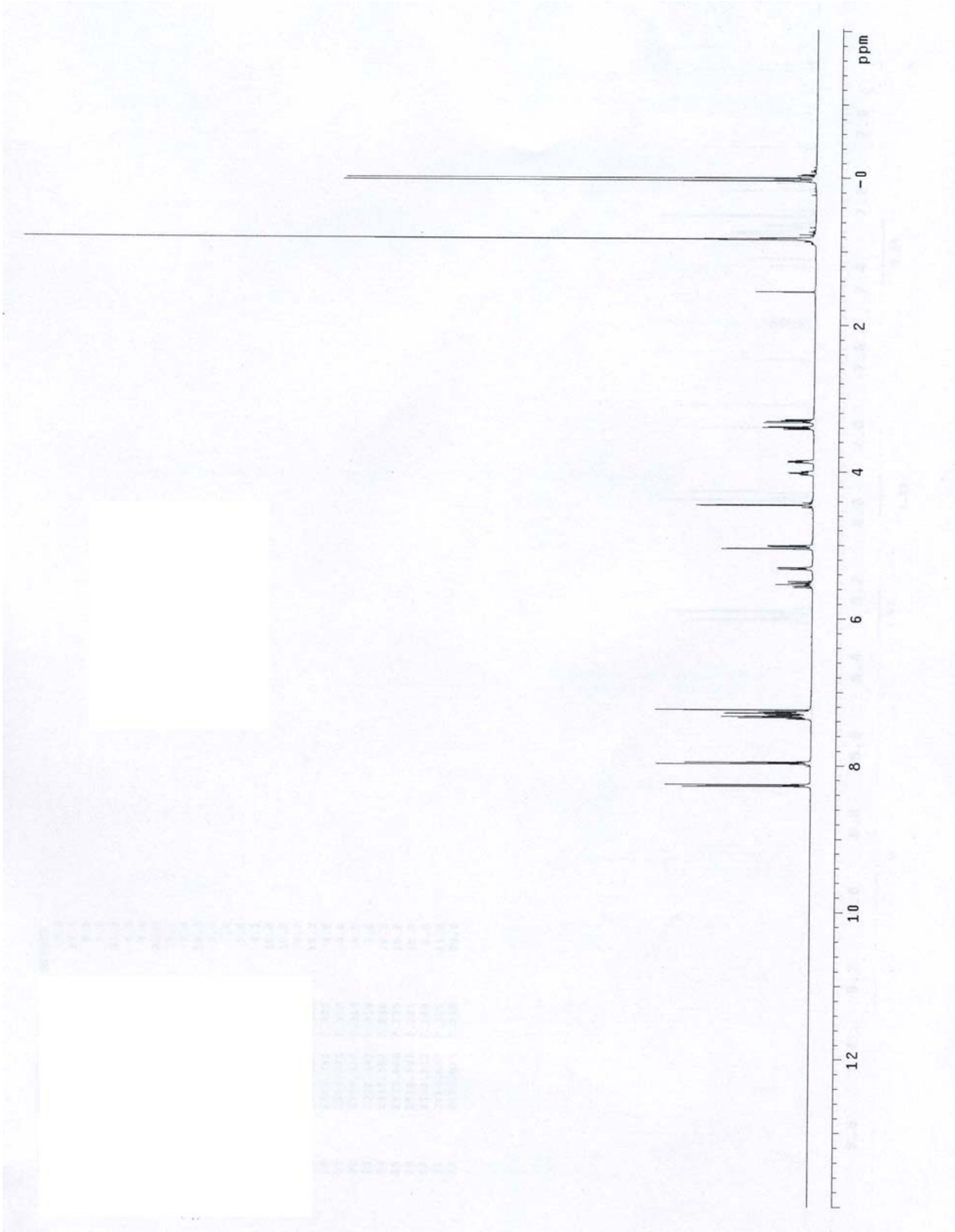
To a stirred solution of compound **4** (0.400 g, 1.02 mmol, 100 mol%) in dry DCM (0.3 M with respect to **4**) under nitrogen at 0 °C was added 2,6-lutidine (0.355 ml, 3.06 mmol, 300 mol%) followed by a drop-wise addition of TBSOTf (0.398 ml, 1.734 mmol, 170 mol%). The mixture was allow to warm to ambient temperature and was allowed to stir until complete consumption of **4** was observed, as determined by TLC analysis. Saturated $NaHCO_3$ (aq.) was added drop-wise. The mixture was transferred to a separatory funnel and the organic layer was separated. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with aqueous HCl (1N), dried (Mg_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 10% EtOAc/hexanes) to furnish the title compound (0.454 g) as yellow oil in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.37 7.27 (m, 5H), 5.53 (ddd, *J* = 17.6, 9.8, 7.6 Hz, 1H), 5.31 (d, *J* = 8.0 Hz, 1H), 5.05 – 5.00 (m, 2H), 4.45 (s, 1H), 4.45 (s, 1H), 4.01 (ddd, *J* =7.8, 6.3, 4.7 Hz, 1H), 3.88 – 3.84 (m, 1H), 3.40 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.31 (dd, *J* = 9.8, 6.3 Hz, 1H), 0.83 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 147.1, 137.5, 133.1, 128.5, 128.4, 127.9, 127.7, 124.1, 118.9, 73.5, 72.9, 71.2, 60.1, 25.7, 18.1, -4.49, -4.92.

HRMS (CI): Calcd. for $C_{24}H_{35}N_2O_6SSi$ (M+1): 507.1985, Found: 507.1992.

FTIR (neat): 3364, 2929, 2856, 1530, 1349, 1163, 1092, 1023 cm^{-1}.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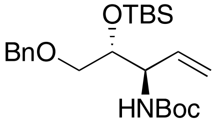
tert-Butyl 5-(benzyloxy)-4-(_tert_-butyldimethylsilyloxy)pent-1-en-3-ylcarbamate (4a)



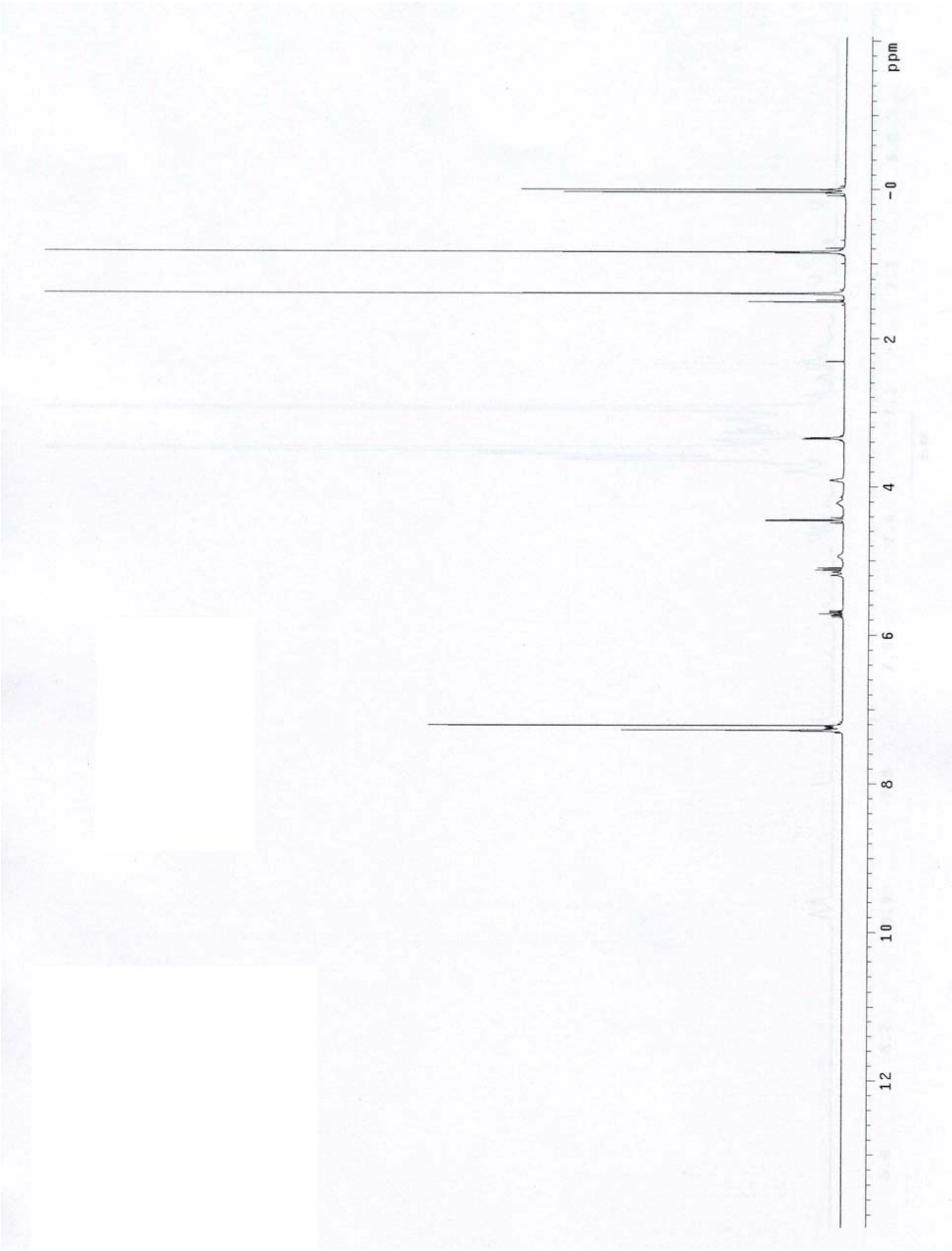
To a stirred solution of compound **5** (0.400 g, 0.8 mmol, 100 mol%) in dry MeCN (0.15 M with respect to **5**) under nitrogen at 25 °C was added thiophenol (0.286 ml, 2.8 mmol, 350 mol%) followed by addition of Cs_2CO_3 (1.04 g, 3.2 mmol, 400 mol%). The mixture heated at 50 °C and was allowed to stir until complete consumption of **5** was observed, as determined by TLC analysis. The solution was allowed to cool to ambient temperature, at which point Boc_2O (0.209 g, 0.96 mmol, 120 mol%) was added in one portion. After 1 hour another portion of Boc_2O (0.174 g, 0.8 mmol, 100 mol%) was added and the reaction mixture was allowed to stir for 2 hours at ambient temperature. Saturated NH_4Cl (aq.) was added dropwise and the mixture was transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried (Mg_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2: 5% EtOAc/hexanes) to furnish the title compound (0.269 g) as yellow oil in 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.21 (m, 5H), 5.71 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 4.95 (m, 1H), 4.45 (s, 1H), 4.44 (s, 1H), 4.21 – 4.14 (m, 1H), 3.93 – 3.89 (m, 1H), 3.37 – 3.30 (m, 2H), 1.39 (s, 9H), 0.84 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 138.6, 132.2, 128.3, 127.6, 127.6, 117.3, 73.2, 4, 72.8, 72.1, 56.0, 28.4, 25.8, -4.4, -5.0.

HRMS (CI): Calcd. for $C_{23}H_{40}NO_4Si$ (M+1): 422.2727, Found: 422.2729

FTIR (neat): 2929, 2857, 2359, 1716, 1495, 1365, 1168, 1004 cm^{-1}.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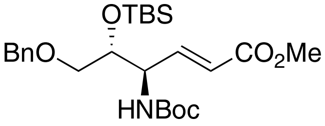
(*E*)-Methyl 6-(benzyloxy)-4-(*tert*-butoxycarbonylamino)-5-(*tert*-butyldimethylsilyloxy)hex-2-enoate (4c)



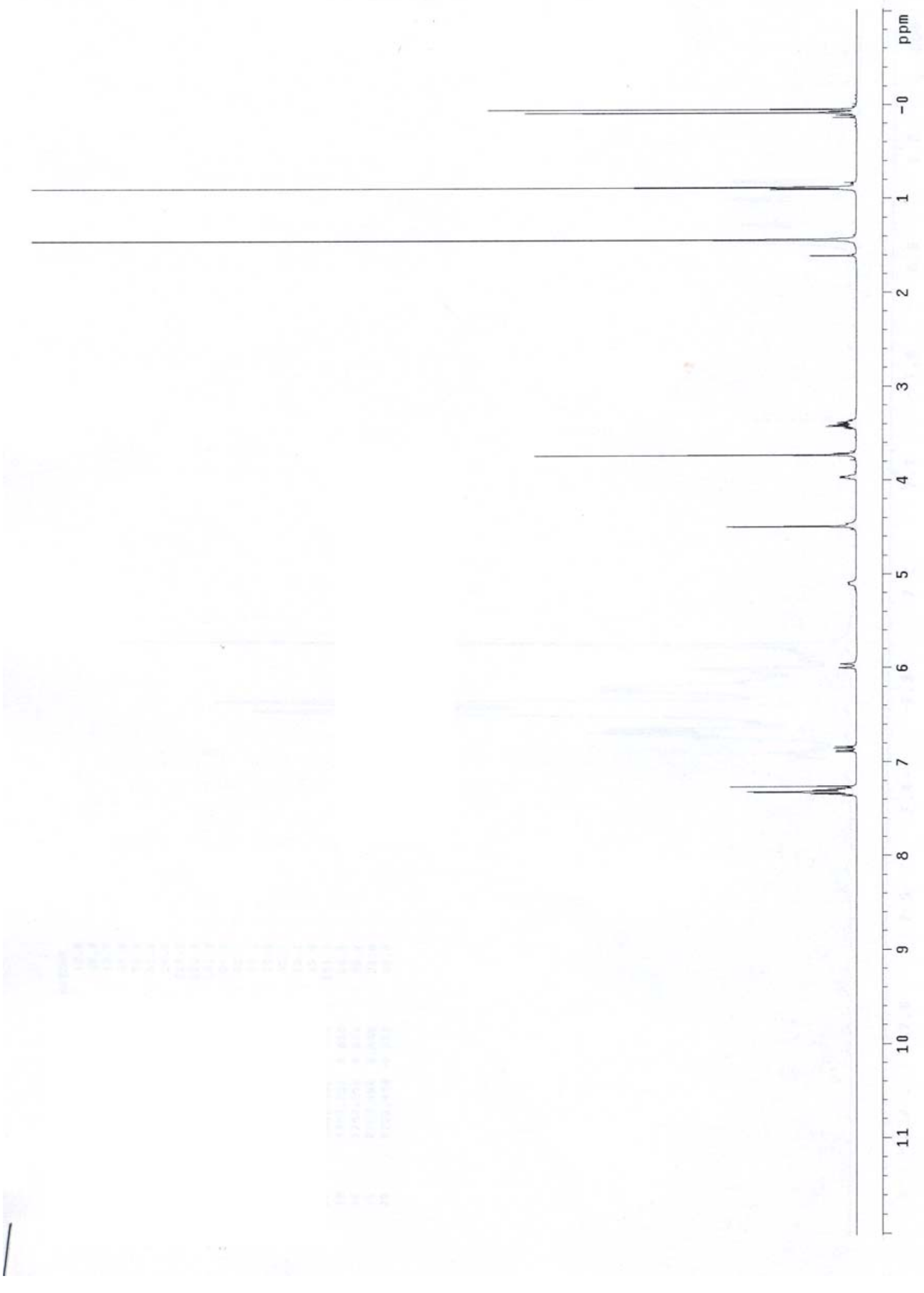
To a stirred solution of compound **4a** (50 mg, 0.12 mmol, 100 mol%) in dry DCM (0.1 M with respect to **4a**) under nitrogen at 25 °C was added methyl acrylate (49 μl, 0.54 mmol, 450 mol%). The reaction mixture heated at 40 °C and the Grubbs-Hoveyda II catalyst (3.7 mg, 0.006 mmol, 5 mol%) was added in a single portion. The reaction mixture was stirred until the complete consumption of **4a** was observed, as determined by TLC analysis. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: 10% EtOAc/hexanes) to furnish the title compound (52 mg) as yellow oil in 91% yield as a 20:1 ratio of *E/Z* olefin isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 -7.27 (m, 5H), 6.86 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.98 (d, *J* = 15.8 Hz, 1H), 5.09 (d, *J* = 8.2 Hz, 1H), 4.49 (s, 2H), 3.98 – 3.94 (m, 1H), 3.73 (s, 3H), 3.45 – 3.56 (m, 2H), 1.43 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 155.0, 144.4, 137.7, 128.4, 127.7, 122.5, 79.6, 73.5, 72.7, 71.8, 54.6, 51.6, 28.3, 25.7, 18.1, -4.5, -5.1.

HRMS (CI): Calcd. for $C_{25}H_{42}NO_6Si$ (M+1): 480.2781, Found: 480.2781

FTIR (neat): 2929, 2360, 1709, 1496, 1366, 1253, 1165, 907 cm^{-1}.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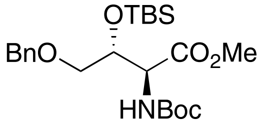
Methyl 4-(benzyloxy)-2-(*tert*-butoxycarbonylamino)-3-(*tert*-butyl dimethyl silyloxy)butanoate (4b)



To a stirred solution of compound **4a** (50 mg, 0.12 mmol, 100 mol%) in MeCN:CCl_4:H_2O (1:1:1.5, 0.1 M with respect to **4a**) was added $NaIO_4$ (128 mg, 0.6 mmol, 500 mol%) followed by $RuCl_3{\cdot}6H_2O$ (1.6 mg, 0.006 mmol, 5 mol%). The reaction mixture was allowed to stir until complete consumption of **4a** was observed, as determined by TLC analysis. The reaction mixture was diluted with DCM, filtered through celite and transferred to a separatory funnel. The organic layer was separated and The aqueous layer was extracted three times with DCM. The combined organic layers were dried (Mg_2SO_4), filtered and the filtrate was concentrated *in vacuo.* The residue was dissolved in $CHCl_3$:MeOH (2:1, 0.2 M with respect to **4a**) and 2M solution of $TMSCH_2N_2$ in ether (240 μl, 0.24 mmol, 200 mol%) was added. After conversion to the methyl ester was complete, as determined by TLC analysis, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (SiO_2, 10% EtOAc/hexanes) to furnish the title compound (36 mg) as yellow oil in 67% yield over two steps.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 -7.27 (m, 5H), 5.38 (d, *J* = 8.0 Hz, 1H), 4.56 -4.47 (m, 3H), 4.19 – 4.18(m, 1H), 3.67 (s, 3H), 3.56 (dd, *J* = 6.0, 4.0 Hz, 1H), 3.46 (dd, *J* = 5.6, 4.0 Hz, 1H), 1.44 (s, 9H), 0.85 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 155.1, 137.9, 128.3, 127.7, 127.6, 79.7, 73.4, 72.3, 71.7, 56.8, 28.3, 25.6, 18.0, -4.6, -5.1

HRMS (CI): Calcd. for $C_{23}H_{40}NO_6Si$ (M+1): 454.2625, Found: 454.2625.

FTIR (neat): 2930, 2359, 1709, 1497, 1367, 1164, 906 cm^{-1}.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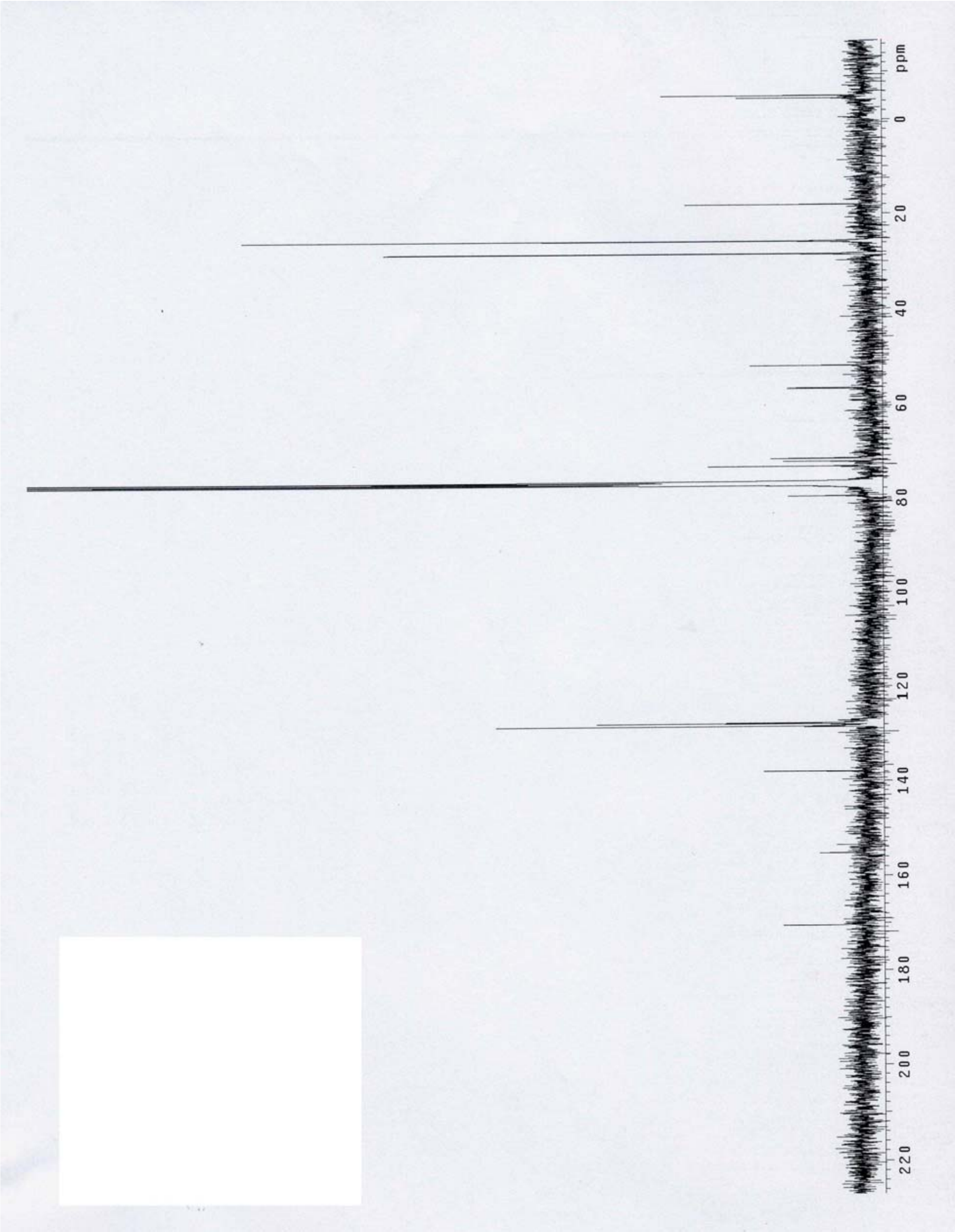
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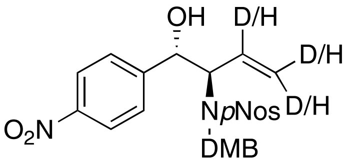
100
120
140
160
180
200
220

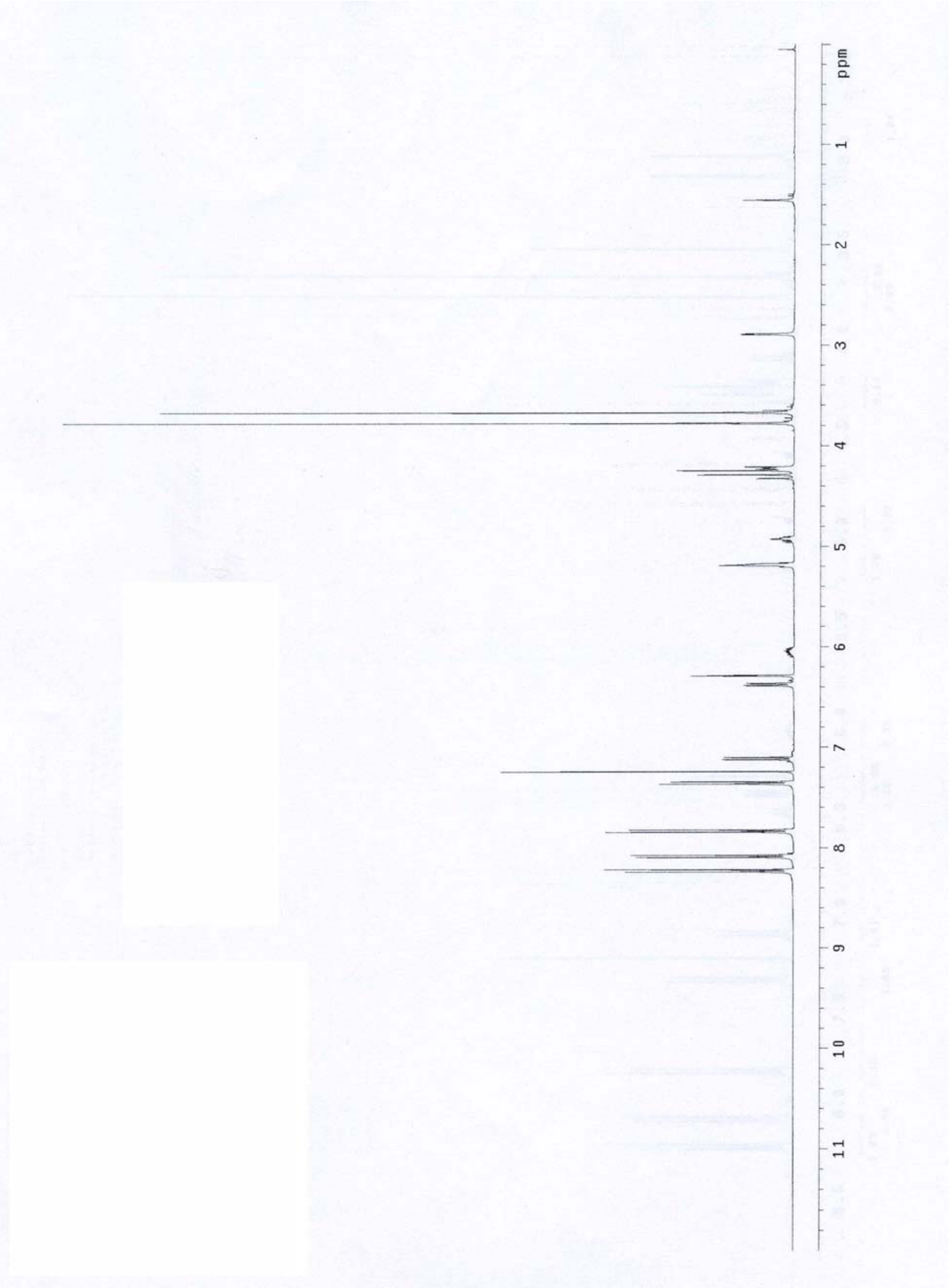
Deuterium Labeling (*deuterio*-3a)



The same procedure used for the preparation of **3a** was used for the preparation of *deuterio*-**3a**, withstanding the substitution of d_8-isopropanol for isopropanol.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.39 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.09 – 6.01 (m, 0.71H), 5.20 – 5.16 (m, 1.93H), 4.95 – 4.90 (m, 0.91H), 4.32 (d, *J* = 14.7 Hz, 1H), 4.25 – 4.24 (m, 1H), 4.25 (d, *J* = 14.7 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.89 (s, 1H).

^{2}H NMR (77 MHz, $CHCl_3$): δ 6.09 (s, 0.29 ^{2}H), 5.22 (s, 0.07 ^{2}H), 4.97 (s, 0.09 ^{2}H).


ppm
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4
5
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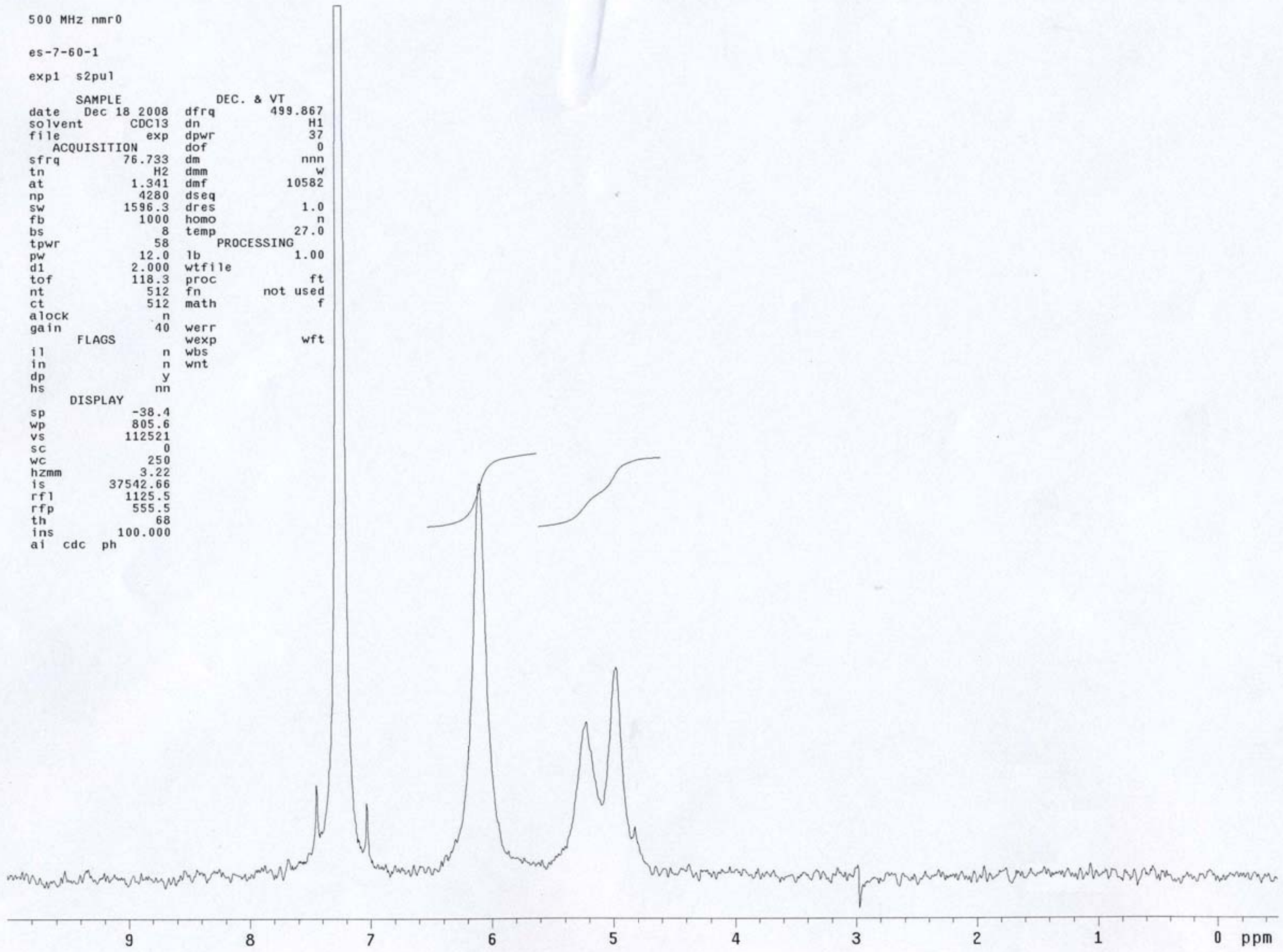
8
9
10
11



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500 MHz nmr0

es-7-60-1

exp1  s2pul

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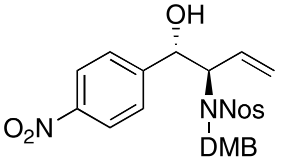
solvent      CDC13  dn               H1
file           exp  dpwr             37
   ACQUISITION      dof               0
sfrq        76.733  dm              nnn
tn              H2  dmm               w
at           1.341  dmf           10582
np            4280  dseq
sw          1596.3  dres            1.0
fb            1000  homo              n
bs               8  temp           27.0
tpwr            58      PROCESSING
pw            12.0  lb             1.00
d1           2.000  wtfile
tof          118.3  proc             ft
nt             512  fn         not used
ct             512  math              f
alock            n
gain            40  werr
      FLAGS         wexp            wft
il               n  wbs
in               n  wnt
dp               y
hs              nn
     DISPLAY
sp           -38.4
wp           805.6
vs          112521
sc               0
wc             250
hzmm          3.22
is        37542.66
rfl         1125.5
rfp          555.5
th              68
ins        100.000
ai  cdc  ph
```

X-Ray Crystolographic Data for 3a



X-ray Experimental.

Table 1. Crystallographic Data for **3a**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms of **3a**.

Table 3. Bond Lengths (Å) and Angles (^{o}) for the non-hydrogen atoms of **3a**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **3a**.

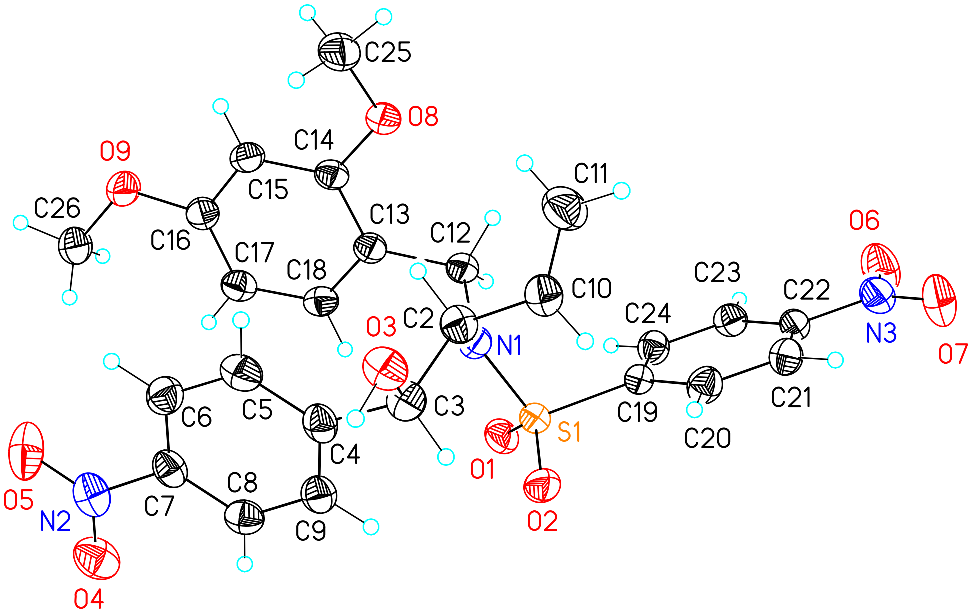
Table 5. Fractional coordinates and isotropic thermal parameters (Å^2) for the hydrogen atoms of **3a**.

Table 6. Torsion Angles (^{o}) for the non-hydrogen atoms of **3a**.

Table 7. H-Bond Lengths (Å) and Angles (^{o}) for **3a**.

Figure 1. View of **3a** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 1. View of **3a** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for $C_{25}H_{25}N_3O_9S$ –$CHCl_3$: Crystals grew as clusters of large colorless prisms by slow evaporation from chloroform. The data crystal was cut from a much larger crystal and had approximate dimensions; 0.25 x 0.20 x 0.15 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKa radiation (l = 0.71073Å). A total of 215 frames of data were collected using w-scans with a scan range of 2° and a counting time of 56 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydroxyl group hydrogen atom, H3O, was observed in a ΔF map and refined with isotropic displacement parameters. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(s(F_o))^2 + (0.0421*P)^2 + (3.3612*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.132, with R(F) equal to 0.0545 and a goodness of fit, S, = 1.06. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[4] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, torsion angles, H-bonding interactions, figures and lists of observed and calculated structure factors are located in tables 1 through 8.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. J. Appl. Cryst. 32, 115-119.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_W(F^2) = \{Sw(|F_o|^2 - |F_c|^2)^2/Sw(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = S(|F_o| - |F_c|)/S|F_o|\}$ for reflections with $F_o > 4(s(F_o))$.
$S = [Sw(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 3a.

Empirical formula	C26 H26 Cl3 N3 O9 S	
Formula weight	662.91	
Temperature	153(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 18.2859(7) Å	a= 90°.
	b = 11.0179(5) Å	b= 108.605(2)°.
	c = 14.8299(6) Å	g = 90°.
Volume	2831.7(2) $Å^3$	
Z	4	
Density (calculated)	1.555 Mg/m^3	
Absorption coefficient	0.457 mm^{-1}	
F(000)	1368	
Crystal size	0.25 x 0.20 x 0.15 mm	
Theta range for data collection	2.19 to 27.50°.	
Index ranges	-23<=h<=23, -12<=k<=14, -19<=l<=19	
Reflections collected	11485	
Independent reflections	6469 [R(int) = 0.0301]	
Completeness to theta = 27.50°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6469 / 0 / 385	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1146	
R indices (all data)	R1 = 0.0988, wR2 = 0.1321	
Largest diff. peak and hole	0.643 and -0.680 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	7402(1)	3809(1)	6030(1)	28(1)
O1	6679(1)	3368(2)	5414(2)	36(1)
O2	7624(1)	3582(2)	7031(1)	38(1)
O3	7982(1)	7145(2)	8068(2)	37(1)
O4	3912(1)	6185(2)	6780(2)	48(1)
O5	4076(1)	8091(2)	6574(2)	56(1)
O6	9573(1)	1174(2)	3762(2)	56(1)
O7	10421(1)	1320(2)	5157(2)	53(1)
O8	7473(1)	8233(2)	4694(1)	31(1)
O9	4839(1)	9286(2)	4044(2)	38(1)
N1	7395(1)	5271(2)	5891(2)	26(1)
N2	4318(1)	7054(3)	6731(2)	38(1)
N3	9774(2)	1476(2)	4601(2)	39(1)
C2	7832(2)	6145(3)	6625(2)	32(1)
C3	7552(2)	6178(3)	7487(2)	35(1)
C4	6689(2)	6405(3)	7228(2)	31(1)
C5	6391(2)	7581(3)	7052(2)	36(1)
C6	5613(2)	7808(3)	6869(2)	35(1)
C7	5140(2)	6824(3)	6870(2)	31(1)
C8	5413(2)	5653(3)	7029(2)	33(1)
C9	6188(2)	5454(3)	7197(2)	33(1)
C10	8692(2)	6001(3)	6875(2)	35(1)
C11	9102(2)	6665(3)	6483(2)	46(1)
C12	7200(2)	5728(3)	4900(2)	29(1)
C13	6576(2)	6683(2)	4702(2)	26(1)
C14	6716(2)	7912(2)	4592(2)	26(1)
C15	6126(2)	8754(3)	4386(2)	29(1)
C16	5379(2)	8383(3)	4285(2)	29(1)
C17	5221(2)	7178(3)	4416(2)	31(1)

C18	5825(2)	6351(3)	4621(2)	29(1)
C19	8120(2)	3138(2)	5607(2)	26(1)
C20	8863(2)	2978(3)	6223(2)	33(1)
C21	9408(2)	2429(3)	5894(2)	33(1)
C22	9193(2)	2060(2)	4960(2)	30(1)
C23	8457(2)	2208(3)	4336(2)	30(1)
C24	7910(2)	2750(2)	4671(2)	30(1)
C25	7670(2)	9494(3)	4858(2)	39(1)
C26	4078(2)	8977(3)	4026(2)	40(1)
Cl1A	9148(1)	5217(1)	4144(1)	55(1)
Cl2A	7884(1)	4448(1)	2520(1)	71(1)
Cl3A	9290(1)	5281(1)	2248(1)	61(1)
C1A	8668(2)	5435(3)	2926(2)	44(1)

Table 3. Bond lengths [Å] and angles [°] for 3a.

S1-O1	1.430(2)	C10-H10	0.95
S1-O2	1.431(2)	C11-H11A	0.95
S1-N1	1.624(2)	C11-H11B	0.95
S1-C19	1.786(3)	C12-C13	1.511(4)
O3-C3	1.436(4)	C12-H12A	0.99
O3-H3O	0.90(4)	C12-H12B	0.99
O4-N2	1.228(3)	C13-C18	1.388(4)
O5-N2	1.221(3)	C13-C14	1.398(4)
O6-N3	1.226(3)	C14-C15	1.381(4)
O7-N3	1.220(3)	C15-C16	1.388(4)
O8-C14	1.390(3)	C15-H15	0.95
O8-C25	1.437(3)	C16-C17	1.386(4)
O9-C16	1.367(3)	C17-C18	1.389(4)
O9-C26	1.426(3)	C17-H17	0.95
N1-C2	1.482(4)	C18-H18	0.95
N1-C12	1.485(3)	C19-C24	1.386(4)
N2-C7	1.472(4)	C19-C20	1.386(4)
N3-C22	1.477(4)	C20-C21	1.380(4)
C2-C10	1.504(4)	C20-H20	0.95
C2-C3	1.522(4)	C21-C22	1.375(4)
C2-H2	1.0000	C21-H21	0.95
C3-C4	1.520(4)	C22-C23	1.378(4)
C3-H3	1.0000	C23-C24	1.385(4)
C4-C9	1.384(4)	C23-H23	0.95
C4-C5	1.398(4)	C24-H24	0.95
C5-C6	1.383(4)	C25-H25A	0.98
C5-H5	0.95	C25-H25B	0.98
C6-C7	1.387(4)	C25-H25C	0.98
C6-H6	0.95	C26-H26A	0.98
C7-C8	1.377(4)	C26-H26B	0.98
C8-C9	1.375(4)	C26-H26C	0.98
C8-H8	0.95	Cl1A-C1A	1.754(3)
C9-H9	0.95	Cl2A-C1A	1.747(3)
C10-C11	1.309(4)	Cl3A-C1A	1.750(3)

C1A-H1A	1.00		
O1-S1-O2	120.19(13)	C6-C5-H5	119.3
O1-S1-N1	106.67(12)	C4-C5-H5	119.3
O2-S1-N1	107.08(12)	C5-C6-C7	117.4(3)
O1-S1-C19	105.53(12)	C5-C6-H6	121.3
O2-S1-C19	107.15(12)	C7-C6-H6	121.3
N1-S1-C19	110.04(12)	C8-C7-C6	122.7(3)
C3-O3-H3O	105(2)	C8-C7-N2	118.9(3)
C14-O8-C25	116.8(2)	C6-C7-N2	118.3(3)
C16-O9-C26	116.8(2)	C9-C8-C7	118.5(3)
C2-N1-C12	114.1(2)	C9-C8-H8	120.8
C2-N1-S1	124.80(18)	C7-C8-H8	120.8
C12-N1-S1	116.92(18)	C8-C9-C4	121.2(3)
O5-N2-O4	123.4(3)	C8-C9-H9	119.4
O5-N2-C7	118.7(3)	C4-C9-H9	119.4
O4-N2-C7	117.9(3)	C11-C10-C2	122.2(3)
O7-N3-O6	124.0(3)	C11-C10-H10	118.9
O7-N3-C22	118.2(3)	C2-C10-H10	118.9
O6-N3-C22	117.8(3)	C10-C11-H11A	120.0
N1-C2-C10	112.9(2)	C10-C11-H11B	120.0
N1-C2-C3	112.7(2)	H11A-C11-H11B	120.0
C10-C2-C3	113.6(2)	N1-C12-C13	110.9(2)
N1-C2-H2	105.6	N1-C12-H12A	109.5
C10-C2-H2	105.6	C13-C12-H12A	109.5
C3-C2-H2	105.6	N1-C12-H12B	109.5
O3-C3-C4	110.7(2)	C13-C12-H12B	109.5
O3-C3-C2	104.7(2)	H12A-C12-H12B	108.1
C4-C3-C2	113.0(2)	C18-C13-C14	117.3(3)
O3-C3-H3	109.4	C18-C13-C12	119.9(2)
C4-C3-H3	109.4	C14-C13-C12	122.8(2)
C2-C3-H3	109.4	C15-C14-O8	122.3(2)
C9-C4-C5	118.7(3)	C15-C14-C13	121.1(3)
C9-C4-C3	120.4(3)	O8-C14-C13	116.6(2)
C5-C4-C3	120.8(3)	C14-C15-C16	119.9(3)
C6-C5-C4	121.4(3)	C14-C15-H15	120.1

C16-C15-H15	120.1	C22-C23-H23	120.9
O9-C16-C17	124.6(3)	C24-C23-H23	120.9
O9-C16-C15	114.7(2)	C23-C24-C19	119.5(3)
C17-C16-C15	120.7(3)	C23-C24-H24	120.3
C16-C17-C18	118.1(3)	C19-C24-H24	120.3
C16-C17-H17	120.9	O8-C25-H25A	109.5
C18-C17-H17	120.9	O8-C25-H25B	109.5
C13-C18-C17	122.8(3)	H25A-C25-H25B	109.5
C13-C18-H18	118.6	O8-C25-H25C	109.5
C17-C18-H18	118.6	H25A-C25-H25C	109.5
C24-C19-C20	121.4(2)	H25B-C25-H25C	109.5
C24-C19-S1	118.7(2)	O9-C26-H26A	109.5
C20-C19-S1	119.8(2)	O9-C26-H26B	109.5
C21-C20-C19	119.3(3)	H26A-C26-H26B	109.5
C21-C20-H20	120.4	O9-C26-H26C	109.5
C19-C20-H20	120.4	H26A-C26-H26C	109.5
C22-C21-C20	118.7(3)	H26B-C26-H26C	109.5
C22-C21-H21	120.6	Cl2A-C1A-Cl3A	110.70(19)
C20-C21-H21	120.6	Cl2A-C1A-Cl1A	110.82(18)
C21-C22-C23	122.9(3)	Cl3A-C1A-Cl1A	112.05(18)
C21-C22-N3	119.0(3)	Cl2A-C1A-H1A	107.7
C23-C22-N3	118.1(3)	Cl3A-C1A-H1A	107.7
C22-C23-C24	118.2(3)	Cl1A-C1A-H1A	107.7

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 3a. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	30(1)	27(1)	31(1)	4(1)	15(1)	3(1)
O1	31(1)	32(1)	50(1)	-1(1)	20(1)	-3(1)
O2	50(1)	36(1)	33(1)	9(1)	21(1)	12(1)
O3	39(1)	40(1)	32(1)	-7(1)	12(1)	-6(1)
O4	34(1)	64(2)	46(1)	1(1)	12(1)	-7(1)
O5	38(1)	49(2)	76(2)	-15(1)	13(1)	10(1)
O6	53(2)	74(2)	50(2)	-12(1)	27(1)	11(1)
O7	33(1)	68(2)	59(2)	-5(1)	15(1)	12(1)
O8	28(1)	28(1)	38(1)	3(1)	13(1)	-2(1)
O9	29(1)	35(1)	49(1)	10(1)	13(1)	6(1)
N1	30(1)	26(1)	23(1)	0(1)	8(1)	2(1)
N2	31(1)	48(2)	32(1)	-9(1)	7(1)	1(1)
N3	38(2)	39(2)	46(2)	0(1)	21(1)	2(1)
C2	30(2)	33(2)	33(2)	-2(1)	9(1)	-2(1)
C3	35(2)	35(2)	35(2)	0(1)	11(1)	0(1)
C4	33(2)	37(2)	25(1)	-4(1)	11(1)	4(1)
C5	37(2)	38(2)	36(2)	-2(1)	16(1)	-7(1)
C6	41(2)	33(2)	32(2)	-1(1)	13(1)	3(1)
C7	28(2)	40(2)	26(2)	-3(1)	10(1)	1(1)
C8	37(2)	34(2)	27(2)	-3(1)	11(1)	-5(1)
C9	36(2)	33(2)	31(2)	-3(1)	14(1)	1(1)
C10	32(2)	39(2)	33(2)	-1(1)	10(1)	2(1)
C11	34(2)	57(2)	49(2)	6(2)	14(2)	-2(2)
C12	33(2)	28(1)	28(2)	3(1)	15(1)	2(1)
C13	30(2)	29(1)	20(1)	1(1)	9(1)	1(1)
C14	28(1)	30(2)	22(1)	2(1)	9(1)	-1(1)
C15	32(2)	25(1)	29(2)	3(1)	11(1)	-2(1)
C16	30(2)	32(2)	24(1)	3(1)	8(1)	3(1)
C17	28(2)	35(2)	30(2)	3(1)	9(1)	-3(1)
C18	34(2)	28(2)	26(1)	1(1)	11(1)	-3(1)
C19	27(1)	24(1)	30(2)	4(1)	13(1)	3(1)

C20	36(2)	33(2)	28(2)	1(1)	8(1)	5(1)
C21	28(2)	35(2)	33(2)	2(1)	7(1)	3(1)
C22	28(2)	25(1)	40(2)	2(1)	17(1)	1(1)
C23	35(2)	30(2)	27(2)	-2(1)	12(1)	0(1)
C24	26(2)	30(2)	32(2)	-1(1)	7(1)	1(1)
C25	35(2)	36(2)	48(2)	-3(1)	15(2)	-8(1)
C26	29(2)	41(2)	51(2)	8(2)	14(1)	7(1)
Cl1A	52(1)	66(1)	44(1)	3(1)	10(1)	-15(1)
Cl2A	55(1)	89(1)	57(1)	17(1)	-1(1)	-28(1)
Cl3A	53(1)	78(1)	56(1)	-1(1)	25(1)	4(1)
C1A	42(2)	44(2)	49(2)	4(2)	19(2)	1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3a.

	x	y	z	U(eq)
H2	7712	6965	6324	38
H3	7684	5393	7841	42
H5	6729	8238	7058	43
H6	5410	8607	6748	42
H8	5074	4997	7022	39
H9	6382	4648	7293	39
H10	8946	5409	7333	42
H11A	8857	7262	6024	55
H11B	9644	6550	6658	55
H12A	7022	5045	4449	34
H12B	7667	6080	4801	34
H15	6232	9586	4313	34
H17	4713	6924	4368	37
H18	5720	5523	4708	35
H20	8997	3243	6865	39
H21	9920	2309	6304	39
H23	8328	1946	3694	37
H24	7396	2854	4261	36
H25A	8225	9599	4977	59
H25B	7535	9777	5412	59
H25C	7383	9967	4297	59
H26A	3749	9700	3874	60
H26B	4093	8664	4650	60
H26C	3867	8353	3541	60
H1A	8462	6283	2840	52
H3O	7840(20)	7130(30)	8600(30)	60(11)

Table 6. Torsion angles [°] for 3a.

O1-S1-N1-C2	152.5(2)	C2-N1-C12-C13	-72.3(3)
O2-S1-N1-C2	22.6(2)	S1-N1-C12-C13	129.4(2)
C19-S1-N1-C2	-93.5(2)	N1-C12-C13-C18	-71.1(3)
O1-S1-N1-C12	-51.8(2)	N1-C12-C13-C14	109.1(3)
O2-S1-N1-C12	178.32(19)	C25-O8-C14-C15	18.0(4)
C19-S1-N1-C12	62.2(2)	C25-O8-C14-C13	-162.4(2)
C12-N1-C2-C10	-91.5(3)	C18-C13-C14-C15	-1.6(4)
S1-N1-C2-C10	64.7(3)	C12-C13-C14-C15	178.2(2)
C12-N1-C2-C3	138.1(2)	C18-C13-C14-O8	178.8(2)
S1-N1-C2-C3	-65.6(3)	C12-C13-C14-O8	-1.4(4)
N1-C2-C3-O3	-174.4(2)	O8-C14-C15-C16	179.6(2)
C10-C2-C3-O3	55.6(3)	C13-C14-C15-C16	0.0(4)
N1-C2-C3-C4	-53.8(3)	C26-O9-C16-C17	6.7(4)
C10-C2-C3-C4	176.3(2)	C26-O9-C16-C15	-173.9(2)
O3-C3-C4-C9	-141.7(3)	C14-C15-C16-O9	-177.5(2)
C2-C3-C4-C9	101.1(3)	C14-C15-C16-C17	1.9(4)
O3-C3-C4-C5	35.9(4)	O9-C16-C17-C18	177.3(2)
C2-C3-C4-C5	-81.3(3)	C15-C16-C17-C18	-2.0(4)
C9-C4-C5-C6	1.4(4)	C14-C13-C18-C17	1.5(4)
C3-C4-C5-C6	-176.2(3)	C12-C13-C18-C17	-178.4(2)
C4-C5-C6-C7	0.2(4)	C16-C17-C18-C13	0.3(4)
C5-C6-C7-C8	-1.1(4)	O1-S1-C19-C24	23.0(2)
C5-C6-C7-N2	176.6(2)	O2-S1-C19-C24	152.2(2)
O5-N2-C7-C8	-178.7(3)	N1-S1-C19-C24	-91.7(2)
O4-N2-C7-C8	1.3(4)	O1-S1-C19-C20	-154.9(2)
O5-N2-C7-C6	3.5(4)	O2-S1-C19-C20	-25.7(3)
O4-N2-C7-C6	-176.5(3)	N1-S1-C19-C20	90.4(2)
C6-C7-C8-C9	0.3(4)	C24-C19-C20-C21	0.5(4)
N2-C7-C8-C9	-177.4(2)	S1-C19-C20-C21	178.3(2)
C7-C8-C9-C4	1.4(4)	C19-C20-C21-C22	0.1(4)
C5-C4-C9-C8	-2.2(4)	C20-C21-C22-C23	-0.3(4)
C3-C4-C9-C8	175.5(3)	C20-C21-C22-N3	179.8(3)
N1-C2-C10-C11	95.9(4)	O7-N3-C22-C21	1.5(4)
C3-C2-C10-C11	-134.2(3)	O6-N3-C22-C21	-178.7(3)

O7-N3-C22-C23	-178.4(3)
O6-N3-C22-C23	1.3(4)
C21-C22-C23-C24	-0.3(4)
N3-C22-C23-C24	179.7(2)
C22-C23-C24-C19	0.9(4)
C20-C19-C24-C23	-1.0(4)
S1-C19-C24-C23	-178.9(2)

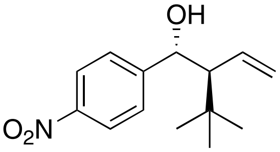
Table 7. Hydrogen bonds for 3a [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O3-H3O...O8#1	0.90(4)	1.99(4)	2.878(3)	169(3)
C1A-H1A...O3#2	1.00	2.02	2.983(4)	161.1

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z+1/2 #2 x,-y+3/2,z-1/2

X-Ray Crystolographic Data for 3m



Crystallographic Material for **3m**.

Table 1. Crystallographic Data for **1**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms of **1**.

Table 3. Bond Lengths (Å) and Angles (^{o}) for the non-hydrogen atoms of **3m**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **3m**.

Table 5. Fractional coordinates and isotropic thermal parameters (Å^2) for the hydrogen atoms of **3m**.

Table 6. Torsion Angles (^{o}) for the non-hydrogen atoms of **3m**.

Table 7. H-Bond Lengths (Å) and Angles (^{o}) for **3m**.

Figure 1. View of molecule 1 of **3m** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 2. View of molecule 2 of **3m** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 1. View of molecule 1 of **3m** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

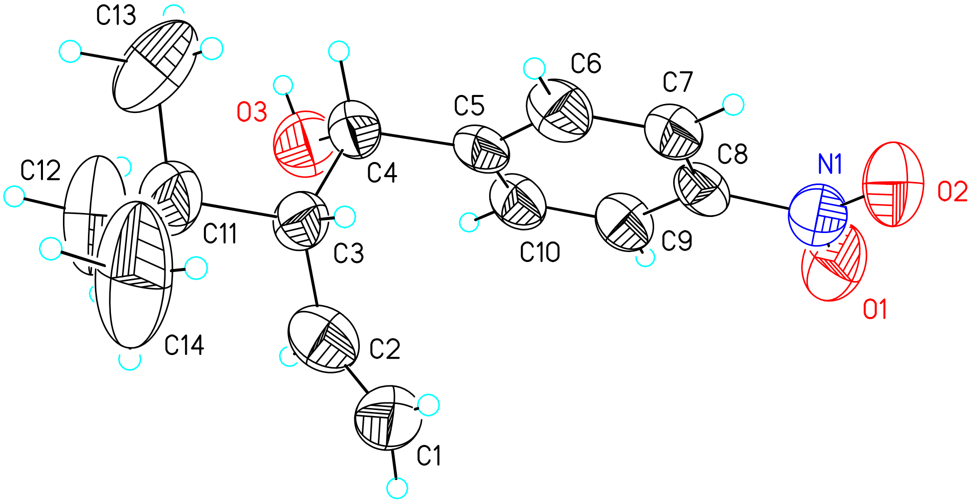


Figure 2. View of molecule 2 of **3m** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

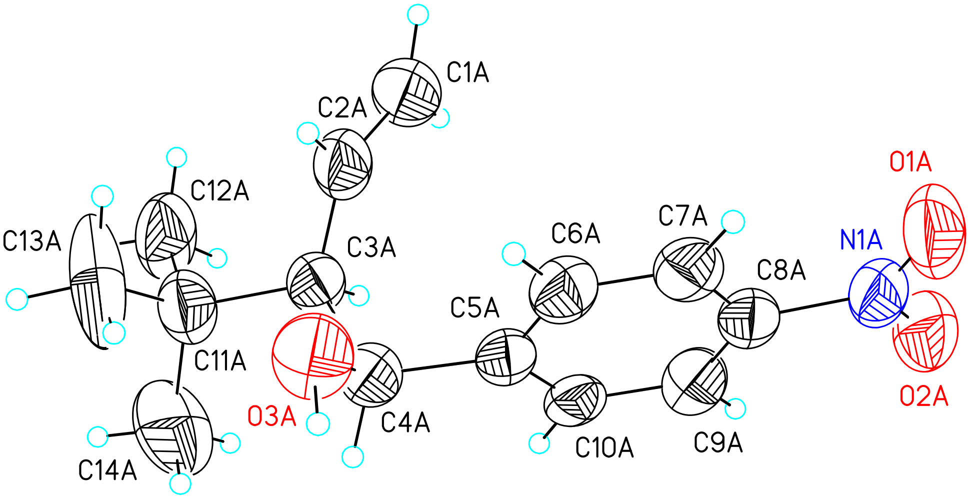


Table 1. Crystal data and structure refinement for 3m.

Empirical formula	C14 H19 N O3	
Formula weight	249.30	
Temperature	153(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 15.7991(12) Å	a= 90°.
	b = 8.3868(9) Å	b= 90°.
	c = 21.179(2) Å	g = 90°.
Volume	2806.2(5) Å^3	
Z	8	
Density (calculated)	1.180 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	1072	
Crystal size	0.49 x 0.18 x 0.06 mm	
Theta range for data collection	1.92 to 25.00°.	
Index ranges	-18<=h<=18, -9<=k<=9, -25<=l<=25	
Reflections collected	4662	
Independent reflections	2541 [R(int) = 0.0561]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2541 / 1 / 333	
Goodness-of-fit on F^2	1.200	
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.1909	
R indices (all data)	R1 = 0.1580, wR2 = 0.2199	
Absolute structure parameter	2(4)	
Largest diff. peak and hole	0.630 and -0.190 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	3377(4)	6051(9)	4891(4)	84(2)
O2	3363(4)	6171(8)	5903(4)	80(2)
O3	-267(4)	1709(8)	4810(4)	74(2)
N1	3072(5)	5724(8)	5399(5)	57(2)
C1	1827(6)	-921(11)	5222(8)	100(5)
C2	1040(6)	-609(11)	5102(5)	69(3)
C3	405(5)	0(9)	5572(5)	49(3)
C4	122(5)	1709(10)	5441(5)	55(2)
C5	889(5)	2853(9)	5417(5)	51(2)
C6	1232(6)	3393(11)	5992(5)	58(2)
C7	1933(5)	4353(10)	5981(5)	55(2)
C8	2299(5)	4747(9)	5413(5)	48(2)
C9	1961(5)	4229(10)	4854(4)	54(2)
C10	1253(6)	3294(10)	4859(4)	54(2)
C11	-326(6)	-1184(12)	5705(6)	77(3)
C12	-826(8)	-1620(16)	5140(6)	120(5)
C13	-934(7)	-425(19)	6206(7)	124(5)
C14	31(8)	-2587(16)	6024(8)	146(6)
O1A	4043(5)	6017(8)	3460(4)	91(2)
O2A	4091(4)	6029(9)	2439(4)	90(2)
O3A	7689(4)	1775(8)	3707(3)	78(2)
N1A	4373(5)	5642(9)	2958(6)	72(2)
C1A	5632(6)	-971(11)	3281(6)	75(3)
C2A	6420(6)	-567(11)	3402(5)	65(3)
C3A	7064(5)	-56(9)	2969(5)	53(3)
C4A	7327(5)	1716(10)	3086(4)	56(2)
C5A	6559(5)	2798(9)	3045(5)	50(2)
C6A	6136(6)	3275(10)	3585(5)	58(2)
C7A	5440(6)	4219(10)	3570(5)	57(2)

C8A	5142(5)	4667(10)	2971(5)	55(3)
C9A	5519(6)	4246(11)	2422(5)	61(3)
C10A	6247(5)	3314(9)	2475(5)	53(2)
C11A	7828(5)	-1227(11)	2885(6)	69(3)
C12A	7475(7)	-2788(10)	2611(6)	93(4)
C13A	8294(8)	-1497(18)	3501(6)	126(6)
C14A	8448(7)	-599(17)	2399(6)	107(4)

Table 3. Bond lengths [Å] and angles [°] for 3m.

O1-N1	1.211(10)	C14-H14D	0.98
O2-N1	1.220(10)	C14-H14E	0.98
O3-C4	1.471(11)	C14-H14F	0.98
O3-H3O	0.84	O1A-N1A	1.225(11)
N1-C8	1.471(11)	O2A-N1A	1.231(11)
C1-C2	1.297(13)	O3A-C4A	1.435(10)
C1-H1A	0.95	O3A-H3OA	0.84
C1-H1B	0.95	N1A-C8A	1.464(12)
C2-C3	1.503(13)	C1A-C2A	1.315(12)
C2-H2	0.95	C1A-H1A1	0.95
C3-C4	1.527(11)	C1A-H1A2	0.95
C3-C11	1.549(12)	C2A-C3A	1.436(13)
C3-H3	1.00	C2A-H2A	0.95
C4-C5	1.547(11)	C3A-C4A	1.563(11)
C4-H4	1.00	C3A-C11A	1.566(11)
C5-C10	1.365(12)	C3A-H3A	1.00
C5-C6	1.408(13)	C4A-C5A	1.518(11)
C6-C7	1.369(12)	C4A-H4A	1.00
C6-H6	0.95	C5A-C10A	1.375(12)
C7-C8	1.375(13)	C5A-C6A	1.384(12)
C7-H7	0.95	C6A-C7A	1.355(12)
C8-C9	1.370(12)	C6A-H6A	0.95
C9-C10	1.367(12)	C7A-C8A	1.404(13)
C9-H9	0.95	C7A-H7A	0.95
C10-H10	0.95	C8A-C9A	1.354(13)
C11-C14	1.469(15)	C9A-C10A	1.395(12)
C11-C12	1.481(16)	C9A-H9A	0.95
C11-C13	1.566(16)	C10A-H10A	0.95
C12-H12A	0.98	C11A-C14A	1.515(16)
C12-H12B	0.98	C11A-C13A	1.515(16)
C12-H12C	0.98	C11A-C12A	1.537(13)
C13-H13D	0.98	C12A-H12D	0.98
C13-H13E	0.98	C12A-H12E	0.98
C13-H13F	0.98	C12A-H12F	0.98

C13A-H13A	0.98	C14A-H14A	0.98
C13A-H13B	0.98	C14A-H14B	0.98
C13A-H13C	0.98	C14A-H14C	0.98

C4-O3-H3O	109.5	C9-C8-N1	118.9(9)
O1-N1-O2	123.9(8)	C7-C8-N1	120.0(9)
O1-N1-C8	118.3(9)	C10-C9-C8	119.6(9)
O2-N1-C8	117.8(9)	C10-C9-H9	120.2
C2-C1-H1A	120.0	C8-C9-H9	120.2
C2-C1-H1B	120.0	C5-C10-C9	120.4(8)
H1A-C1-H1B	120.0	C5-C10-H10	119.8
C1-C2-C3	125.3(12)	C9-C10-H10	119.8
C1-C2-H2	117.3	C14-C11-C12	112.2(10)
C3-C2-H2	117.3	C14-C11-C3	108.1(8)
C2-C3-C4	113.2(8)	C12-C11-C3	114.1(9)
C2-C3-C11	113.6(8)	C14-C11-C13	104.5(12)
C4-C3-C11	114.6(7)	C12-C11-C13	108.8(10)
C2-C3-H3	104.7	C3-C11-C13	108.7(9)
C4-C3-H3	104.7	C11-C12-H12A	109.5
C11-C3-H3	104.7	C11-C12-H12B	109.5
O3-C4-C3	106.7(7)	H12A-C12-H12B	109.5
O3-C4-C5	107.3(8)	C11-C12-H12C	109.5
C3-C4-C5	111.0(6)	H12A-C12-H12C	109.5
O3-C4-H4	110.6	H12B-C12-H12C	109.5
C3-C4-H4	110.6	C11-C13-H13D	109.5
C5-C4-H4	110.6	C11-C13-H13E	109.5
C10-C5-C6	120.0(7)	H13D-C13-H13E	109.5
C10-C5-C4	121.8(9)	C11-C13-H13F	109.5
C6-C5-C4	118.2(9)	H13D-C13-H13F	109.5
C7-C6-C5	119.0(9)	H13E-C13-H13F	109.5
C7-C6-H6	120.5	C11-C14-H14D	109.5
C5-C6-H6	120.5	C11-C14-H14E	109.5
C6-C7-C8	119.8(9)	H14D-C14-H14E	109.5
C6-C7-H7	120.1	C11-C14-H14F	109.5
C8-C7-H7	120.1	H14D-C14-H14F	109.5
C9-C8-C7	121.1(7)	H14E-C14-H14F	109.5

C4A-O3A-H3OA	109.5	C9A-C8A-N1A	119.6(10)
O1A-N1A-O2A	123.6(9)	C7A-C8A-N1A	116.4(10)
O1A-N1A-C8A	118.7(11)	C8A-C9A-C10A	116.1(9)
O2A-N1A-C8A	117.7(10)	C8A-C9A-H9A	121.9
C2A-C1A-H1A1	120.0	C10A-C9A-H9A	122.0
C2A-C1A-H1A2	120.0	C5A-C10A-C9A	122.9(9)
H1A1-C1A-H1A2	120.0	C5A-C10A-H10A	118.6
C1A-C2A-C3A	128.6(11)	C9A-C10A-H10A	118.6
C1A-C2A-H2A	115.7	C14A-C11A-C13A	108.8(9)
C3A-C2A-H2A	115.7	C14A-C11A-C12A	105.9(10)
C2A-C3A-C4A	111.8(8)	C13A-C11A-C12A	111.9(10)
C2A-C3A-C11A	115.6(8)	C14A-C11A-C3A	111.0(8)
C4A-C3A-C11A	114.2(7)	C13A-C11A-C3A	111.7(9)
C2A-C3A-H3A	104.6	C12A-C11A-C3A	107.3(7)
C4A-C3A-H3A	104.6	C11A-C12A-H12D	109.5
C11A-C3A-H3A	104.6	C11A-C12A-H12E	109.5
O3A-C4A-C5A	110.5(7)	H12D-C12A-H12E	109.5
O3A-C4A-C3A	106.5(7)	C11A-C12A-H12F	109.5
C5A-C4A-C3A	110.3(6)	H12D-C12A-H12F	109.5
O3A-C4A-H4A	109.8	H12E-C12A-H12F	109.5
C5A-C4A-H4A	109.8	C11A-C13A-H13A	109.5
C3A-C4A-H4A	109.8	C11A-C13A-H13B	109.5
C10A-C5A-C6A	117.5(7)	H13A-C13A-H13B	109.5
C10A-C5A-C4A	121.7(9)	C11A-C13A-H13C	109.5
C6A-C5A-C4A	120.8(8)	H13A-C13A-H13C	109.5
C7A-C6A-C5A	122.7(9)	H13B-C13A-H13C	109.5
C7A-C6A-H6A	118.6	C11A-C14A-H14A	109.5
C5A-C6A-H6A	118.6	C11A-C14A-H14B	109.5
C6A-C7A-C8A	116.8(9)	H14A-C14A-H14B	109.5
C6A-C7A-H7A	121.6	C11A-C14A-H14C	109.5
C8A-C7A-H7A	121.6	H14A-C14A-H14C	109.5
C9A-C8A-C7A	123.9(8)	H14B-C14A-H14C	109.5

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 3m. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	74(5)	81(5)	97(6)	20(4)	10(4)	-23(4)
O2	76(4)	76(5)	87(5)	6(4)	-4(4)	-27(4)
O3	60(4)	63(4)	98(5)	2(4)	-14(4)	7(3)
N1	54(5)	42(4)	75(5)	9(5)	-10(5)	4(4)
C1	58(6)	56(6)	186(15)	-14(7)	4(8)	6(5)
C2	81(7)	50(6)	77(7)	5(6)	-1(6)	5(6)
C3	45(5)	39(6)	62(6)	9(4)	5(5)	-1(4)
C4	45(5)	46(5)	75(6)	-12(5)	-7(5)	-2(4)
C5	49(5)	31(4)	72(6)	-9(5)	-3(5)	9(4)
C6	71(6)	54(6)	50(6)	-6(5)	2(5)	0(5)
C7	50(5)	43(5)	73(7)	-12(5)	-3(5)	4(5)
C8	58(6)	29(4)	56(5)	-1(5)	-3(5)	3(4)
C9	66(6)	45(5)	52(6)	0(4)	0(5)	-1(5)
C10	63(6)	38(5)	59(6)	-2(4)	1(5)	0(4)
C11	58(6)	52(6)	120(10)	13(6)	2(7)	-2(5)
C12	113(10)	134(11)	112(10)	26(9)	-30(9)	-67(9)
C13	85(8)	148(13)	140(13)	6(11)	58(9)	-28(9)
C14	145(12)	127(11)	165(14)	90(11)	-41(12)	-64(10)
O1A	77(5)	66(5)	130(7)	-16(5)	7(5)	23(4)
O2A	59(4)	81(5)	131(7)	22(5)	-14(5)	15(4)
O3A	74(5)	68(4)	92(5)	-11(4)	-21(4)	-9(4)
N1A	53(5)	42(4)	120(9)	5(6)	3(6)	2(4)
C1A	56(6)	69(7)	100(8)	8(6)	-5(6)	-8(5)
C2A	55(6)	46(5)	95(8)	2(6)	-3(6)	4(5)
C3A	49(5)	42(5)	68(7)	-3(5)	-1(5)	0(4)
C4A	51(5)	53(5)	63(6)	3(5)	-5(5)	-3(4)
C5A	43(4)	32(4)	73(6)	-1(5)	-5(5)	-10(4)
C6A	62(6)	46(5)	66(7)	1(5)	-1(5)	-2(5)
C7A	60(6)	40(5)	72(7)	-8(5)	7(5)	-9(5)
C8A	43(5)	40(5)	82(8)	2(5)	-6(6)	-9(4)
C9A	66(6)	53(6)	65(6)	2(5)	-9(5)	-2(5)

C10A	58(6)	32(4)	67(6)	0(4)	14(5)	-6(4)
C11A	55(5)	61(6)	92(8)	-6(6)	-3(6)	11(5)
C12A	83(6)	52(5)	143(10)	-12(6)	-14(8)	18(6)
C13A	104(9)	173(14)	101(10)	-21(9)	-28(8)	90(10)
C14A	90(9)	131(10)	101(10)	-27(9)	29(8)	33(9)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for 3m.

	x	y	z	U(eq)
H3O	-715	2249	4818	110
H1A	2044	-768	5636	120
H1B	2187	-1304	4897	120
H2	848	-778	4682	83
H3	724	64	5979	59
H4	-295	2069	5767	66
H6	981	3096	6382	70
H7	2166	4745	6364	67
H9	2218	4519	4464	65
H10	1012	2948	4471	64
H12A	-458	-2152	4832	179
H12B	-1066	-655	4950	179
H12C	-1285	-2343	5262	179
H13D	-1355	-1216	6338	186
H13E	-1222	498	6021	186
H13F	-605	-81	6574	186
H14D	-429	-3242	6194	218
H14E	400	-2239	6369	218
H14F	360	-3215	5720	218
H3OA	8016	2563	3733	117
H1A1	5427	-944	2859	90
H1A2	5268	-1289	3614	90
H2A	6584	-620	3833	78
H3A	6779	-45	2548	64
H4A	7758	2049	2766	67
H6A	6341	2926	3984	69
H7A	5167	4561	3946	69
H9A	5301	4567	2024	73

H10A	6539	3023	2100	63
H12D	7937	-3557	2559	139
H12E	7213	-2577	2200	139
H12F	7051	-3228	2900	139
H13A	7910	-1989	3808	189
H13B	8495	-473	3666	189
H13C	8778	-2203	3428	189
H14A	8882	-1408	2316	161
H14B	8718	371	2560	161
H14C	8146	-355	2007	161

Table 6. Torsion angles [°] for 3m.

C1-C2-C3-C4	111.8(11)
C1-C2-C3-C11	-115.2(11)
C2-C3-C4-O3	60.2(9)
C11-C3-C4-O3	-72.3(10)
C2-C3-C4-C5	-56.3(11)
C11-C3-C4-C5	171.2(9)
O3-C4-C5-C10	-19.0(10)
C3-C4-C5-C10	97.2(10)
O3-C4-C5-C6	163.4(7)
C3-C4-C5-C6	-80.4(10)
C10-C5-C6-C7	-0.3(12)
C4-C5-C6-C7	177.3(7)
C5-C6-C7-C8	-1.3(12)
C6-C7-C8-C9	1.7(12)
C6-C7-C8-N1	-177.5(7)
O1-N1-C8-C9	0.8(11)
O2-N1-C8-C9	-179.9(8)
O1-N1-C8-C7	-179.9(8)
O2-N1-C8-C7	-0.6(11)
C7-C8-C9-C10	-0.5(12)
N1-C8-C9-C10	178.7(7)
C6-C5-C10-C9	1.5(12)
C4-C5-C10-C9	-176.1(7)
C8-C9-C10-C5	-1.1(13)
C2-C3-C11-C14	66.4(13)
C4-C3-C11-C14	-161.3(11)
C2-C3-C11-C12	-59.2(12)
C4-C3-C11-C12	73.1(12)
C2-C3-C11-C13	179.2(10)
C4-C3-C11-C13	-48.5(13)
C1A-C2A-C3A-C4A	114.0(11)
C1A-C2A-C3A-C11A	-113.0(11)
C2A-C3A-C4A-O3A	63.6(9)
C11A-C3A-C4A-O3A	-70.1(10)
C2A-C3A-C4A-C5A	-56.4(11)
C11A-C3A-C4A-C5A	169.9(9)
O3A-C4A-C5A-C10A	160.9(7)
C3A-C4A-C5A-C10A	-81.5(10)
O3A-C4A-C5A-C6A	-20.4(10)
C3A-C4A-C5A-C6A	97.1(9)
C10A-C5A-C6A-C7A	-0.3(12)
C4A-C5A-C6A-C7A	-178.9(7)
C5A-C6A-C7A-C8A	1.9(13)
C6A-C7A-C8A-C9A	-1.8(13)
C6A-C7A-C8A-N1A	178.0(7)
O1A-N1A-C8A-C9A	-179.7(9)
O2A-N1A-C8A-C9A	0.9(13)
O1A-N1A-C8A-C7A	0.6(12)
O2A-N1A-C8A-C7A	-178.9(8)
C7A-C8A-C9A-C10A	-0.1(13)
N1A-C8A-C9A-C10A	-179.8(7)
C6A-C5A-C10A-C9A	-1.8(11)
C4A-C5A-C10A-C9A	176.9(7)
C8A-C9A-C10A-C5A	2.0(13)
C2A-C3A-C11A-C14A	177.6(10)
C4A-C3A-C11A-C14A	-50.6(12)
C2A-C3A-C11A-C13A	-60.7(12)
C4A-C3A-C11A-C13A	71.1(12)
C2A-C3A-C11A-C12A	62.3(12)
C4A-C3A-C11A-C12A	-165.9(9)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 3m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O3-H3O...O1#1	0.84	2.03	2.854(9)	167.4
O3A-H3OA...O1A#2	0.84	2.09	2.876(10)	154.8

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,-y+1,z #2 x+1/2,-y+1,z