Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

# Alcohols as Alkylating Agents in the Cation-Induced Formation of Nitrogen Heterocycles

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## General Experimental Details

*Reagents, solvents and techniques:* All reactions were performed under an inert atmosphere with constant magnetic stirring, unless otherwise stated, using clean, oven dried glassware. Reagents and solvents were obtained from commercial supplies and were used without further purification. All inert gases were sourced from the University of Oxford's internal supplies and dried through $CaCl_2$ drying columns. Anhydrous solvents were obtained from the University of Oxford internal solvent system and dried by passing through alumina columns, manufactured by Innovative Technology Inc. PS-400-7. Temperatures of −78 °C and 0 °C were achieved with a $CO_2$(s)/acetone bath and ice/water bath respectively. Where a reaction was required to stay at 0 °C for 48 h a Thermo Scientific EK90 Immersion Cooler with Flex Probe and isopropanol bath was used.

*Chromatography:* Reactions were monitored by TLC using aluminium backed silica gel plates (Merck Kieselgel 60 PF254) with the appropriate solvent system and were visualised using UV fluorescence (254 nm) and developed with potassium permanganate, phosphomolybdic acid or vanillin. Flash column chromatography was performed on silica gel (60 Å, 230-400 mesh) under a positive pressure of nitrogen and the required eluent.

*NMR Spectroscopy:* $^{1}$H and $^{13}$C NMR samples were run on a Bruker AVIIIHD 400 MHz spectrometer, where required COSY and HSQC spectra were used to assign NMR spectra. In addition, Bruker AVIIIHD 500 MHz and Bruker NEO 600 MHz spectrometers were used to obtain NOESY and HMBC data where required. All NMR spectra were recorded at ambient temperature. Chemical shifts (δ) are recorded in parts per million (ppm). The residual protic solvent signal(s) acted as the internal reference for $^{1}$H NMR spectra [$CDCl_3$ (δ 7.26) or MeOH-d4 (δ 3.31)], and the deuterated solvent signal acted as the internal reference for $^{13}$C NMR spectra [$CDCl_3$ (δ 77.16), MeOH-d4 (δ 49.0)]. All diastereomeric ratio values were based on the crude NMR unless otherwise stated.

*Mass Spectroscopy:* Mass spectra were obtained through the University of Oxford mass spectrometry service by electrospray ionisation (ESI) using a Bruker Daltonics microTOF spectrometer. The m/z values were all recorded in Daltons to four decimal places, the mass found was compared to the mass calculated from the monoisotopic molecular formula.

*Infrared Spectroscopy:* Infrared spectra were obtained using a Bruker Tensor 27 FT-IR spectrometer equipped with a diamond ATR module. Absorption maxima ($\nu_{max}$) are quoted in wavenumbers ($cm^{-1}$).

*Melting Points:* Melting points were obtained using Griffin melting point apparatus.

*Optical Rotations:* Optical rotations were recorded on a Schmidt Haensch Unipol L2000 polarimeter in a cell with a path length of 1 dm (using the sodium D line, 589 nm). Concentrations are reported in g/100 mL. Temperatures are reported in °C.

*Chiral normal phase HPLC:* Chiral normal phase HPLC was performed on an Agilent 1260 Series HPLC unit equipped with UV-vis diode-array detector, fitted with the appropriate Daicel Chiralpak column (dimensions: 0.46 cm ø × 25 cm) along with the corresponding guard column (0.4 cm ø × 1 cm). Wavelengths (λ) are reported in nm, retention times (tR) are reported in minutes and solvent flow rates are reported in mL $min^{-1}$.

# Experimental Procedures and Data

## General Procedures

### General Procedure A: Wittig

According to the procedure of *Maryanoff.*[1] To a solution of (3-carboxypropyl)triphenyl-phosphonium bromide (1.2 equiv.) in anhydrous THF (2.0 mL/mmol) was added NaHMDS (2.0 M in THF, 2.4 equiv.) dropwise at 0 °C and left to stir for 30 min. The solution was cooled to –78 °C before addition of aldehyde (1.0 equiv.) dropwise. The reaction mixture was left to warm to rt over 16 h. The solution was diluted with EtOAc and water and the layers separated. The aqueous layer was acidified to pH 1 with 1.0 M HCl before extracting with EtOAc. The combined organic layers were washed with 1.0 M HCl and dried over $MgSO_4$ before concentrating *in vacuo* and purifying by FCC.

### General Procedure B: Curtius rearrangement and amine protection sequence

To a solution of acid (1.0 equiv.) in PhMe (4.0 mL/mmol) was added $Et_3N$ (1.5 equiv.) followed by dropwise addition of diphenylphosphoryl azide (DPPA) (1.5 equiv.) before heating to 85 °C for 2 h. The solution was cooled to rt before the addition of THF (4.0 mL/mmol) and aq. NaOH (2.0 M, 2 mL/mmol) and the reaction was left to stir vigorously for 16 h. The solution was diluted with EtOAc and water and the layers separated. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1.0 M NaOH and dried over $MgSO_4$ before concentrating *in vacuo.* The crude amine was re-dissolved in $CH_2Cl_2$ (5.0 mL/mmol) and $Et_3N$ added (1.25 equiv.). The solution was cooled to 0 °C before addition of the appropriate sulfonamide (as a solution) or chloroformate (1.25 equiv.). The reaction mixture was left to warm up to rt and stirred for 16 h. The reaction mixture was diluted with $CH_2Cl_2$ and water. The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo* and purifying by FCC.

### General Procedure C: Ru-catalysed metathesis

To a solution of the appropriate Ru catalyst (1.5 mol%) in anhydrous solvent (4 mL/mmol, previously degassed by bubbling through Ar for 30 min.) was added the alkene components in solution (1.0 mL/mmol) and the mixture heated at reflux. The reaction was monitored by TLC until completion, before the solvent was removed *in vacuo* and the crude material purified by FCC.

### General Procedure D: Mitsunobu reaction

To a solution of alcohol (1.0 equiv.), $Ph_3P$ (1.5 equiv.) and nucleophile (1.2 equiv.) in THF (3.0 mL/mmol) was added diisopropyl azodicarboxylate (1.3 equiv.) dropwise at 0 °C before allowing to warm to rt. After 16 h the solvent was removed *in vacuo* before purifying by FCC.

### General Procedure E: Boc deprotection

To a solution of carbamate (1.0 equiv.) in $CH_2Cl_2$ (3.0 mL/mmol) was added trifluoroacetic acid (5.0 equiv.) dropwise at 0 °C. The reaction was monitored by TLC until completion before addition of aq. $NaHCO_3$. The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo* and using crude in the following reaction.

**General Procedure F: Carboxylic acid reduction**

To a suspension of $LiAlH_4$ (1.2 equiv.) in anhydrous THF (1.0 mL/mmol) was added a solution of acid (1.0 equiv.) in THF dropwise at 0 °C and left to stir for 3 h. The solution was quenched using a Fieser workup before concentrating *in vacuo* and purifying by FCC.

**General Procedure G: Mesylate formation**

To a solution of alcohol (1.0 equiv.) in anhydrous $CH_2Cl_2$ (5.0 mL/mmol) was added triethylamine (1.5 equiv.) before cooling to 0 °C. Methanesulfonic anhydride (1.2 equiv.) was added portionwise before warming to rt. The reaction mixture was left to stir for 3 h before addition of 0.5 M HCl (4.5 mL/mmol). The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine, dried over $MgSO_4$ before concentrating *in vacuo* and purifying by FCC.

**General Procedure H: $S_N2$**

A suspension of sulfonamide (1.5 equiv.) and potassium hydroxide (1.5 equiv.) in DMF (10 mL/mmol) was stirred at 100 °C for 30 min before dropwise addition of mesylate (1.0 equiv.) in DMF. The reaction mixture was left to stir at 100 °C for 1 h before cooling to rt and diluting with water. The aqueous layer was extracted with $Et_2O$ and the organic layer washed with water and brine before drying over $Na_2SO_4$, concentrating *in vacuo* and purifying by FCC.

**General Procedure I: Amide formation**

To a solution of carboxylic acid (1.0 equiv.) in anhydrous $CH_2Cl_2$ (2 mL/mmol) was added oxalyl chloride (1.2 equiv.) dropwise at 0 °C followed by DMF (2 drops) and left to warm up to rt. After 45 min, 80% of the solvent was removed in vacuo before re-dissolving in $CH_2Cl_2$ (2 mL/mmol). Aq. ammonia (28% in $H_2O$, 4.0 mL/mmol) was added portionwise at 0 °C and left to warm up to rt and stirred for 16 h. The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo*. The crude amide was recrystallised from hot EtOAc.

**General Procedure J: Amide reduction and protection sequence**

To a solution of amide (1.0 equiv.) in anhydrous THF (3.0 mL/mmol) was added $LiAlH_4$ (1.0 M in THF, 1.5 equiv.) dropwise at 0 °C and left to warm up to rt and stirred for 16 h. The solution was diluted with $Et_2O$ and cooled to 0 °C before subsequent addition of $H_2O$ (1.0 mL/g of $LiAlH_4$), aq. NaOH (15 wt%, 1.0 mL/g of $LiAlH_4$) and $H_2O$ (3.0 mL/g of $LiAlH_4$). The solution was warmed to rt and stirred for 15 min before addition of anhydrous $MgSO_4$, after a further 15 min the solid was removed by filtration before concentrating *in vacuo*. The crude amine was used directly in the following protection reaction. To a solution of amine (1.0 equiv.) in anhydrous $CH_2Cl_2$ (5.0 mL/mmol) was added triethylamine (1.25 equiv.). The solution was cooled to 0 °C before addition of the appropriate sulfonamide (as a solution) or chloroformate (1.25 equiv.). The reaction mixture was left to warm up to rt and stirred for 16 h. The reaction mixture was diluted with $CH_2Cl_2$ and water. The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo* and purifying by FCC.

*Modification for low molecular weight amines*: Following the Fieser workup, before concentrating in vacuo, the solution was cooled to 0 °C and HCl (2.0 M in $Et_2O$, 1.25 equiv.) was added dropwise and stirred for 15 min. The hydrochloride salt of the amine was then used directly in the following protection reaction. To a solution of hydrochloride salt of the amine (1.0 equiv.) in anhydrous $CH_2Cl_2$ (5.0 mL/mmol) at 0 °C was added triethylamine (3.0 equiv.) dropwise and left to stir for 30 min before addition of methylchloroformate (1.25 equiv.) dropwise. The normal procedure was then followed.

**General Procedure K: Cyclisation**

To a microwave vial charged with a stirrer bar was added the appropriately protected amine (1.0 equiv.), alcohol (1.0 equiv.) and HFIP (10 mL/mmol) under argon. A solution of $Ti(O^iPr)_4$ in HFIP (30 mol%) was added and the reaction stirred at the given temperature for the given period of time. The reaction mixture was concentrated *in vacuo* and purified by FCC.

**General Procedure L: *ortho*-Ns removal**

To a solution of pyrrolidine (1.0 equiv.) in anhydrous DMF (1.0 mL/mmol) under Ar was added LiOH (4.0 equiv.) and mercaptoacetic acid (2.0 equiv.) before stirring at rt for 16 h. The solution was diluted with EtOAc and water and the layers separated. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine and dried over $Na_2SO_4$ before concentrating *in vacuo* and purifying by FCC.

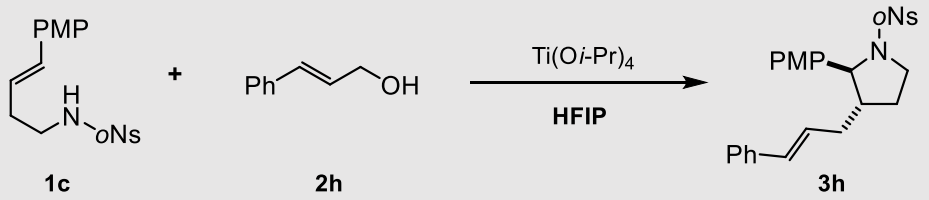
**General Procedure M: Methyl carbamate removal**

To a solution of cyclised product (1.0 equiv.) in $CHCl_3$ (25 mL/mmol) was added trimethylsilyl iodide (3.0 equiv.) before heating to 55 °C for 2 h. The reaction mixture was concentrated *in vacuo* and purified by FCC.

*Modification for piperidines containing alkenes:* Isoprene (10.0 equiv.) was added before heating to 55 °C.

## Extended Optimisation Tables

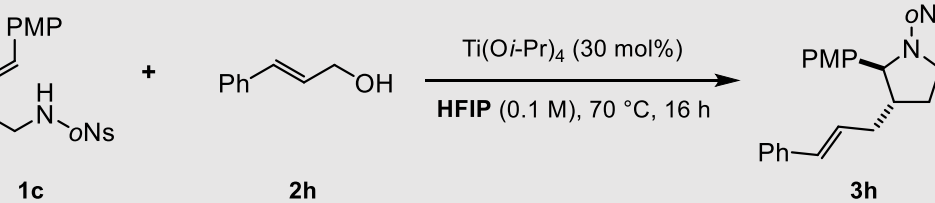
Additional condition screening




| Entry | **1c**:**2h** | Ti(O$^i$Pr)$_4$ / mol% | Temp / ˚C | Time / h | Concentration/ M | Yield **3h** / % | Recovered / % | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | **1c** | **2h** |
| 1 | 1:1 | 30 | 70 | 16 | 0.1 | 58 | 42 | 0 |
| 2 | 1:1 | 20 | 70 | 16 | 0.1 | 43 | - | - |
| 3 | 1:1 | 10 | 70 | 16 | 0.1 | 38 | - | - |
| 4 | 1:2 | 30 | 70 | 16 | 0.1 | 40 | 37 | 37 |
| 5 | 1:1 | 30 | 40 | 16 | 0.1 | 31 | 68 | 35 |
| 6 | 1:1 | 30 | 70 | 16 | 0.05 | 54 | 46 | 0 |
| 7 | 1:1 | 30 | 40 | 36 | 0.1 | 40 | 60 | 5 |
| 8 | 1:2 | 30 | 70 | 36 | 0.1 | 43 | 57 | 33 |
| 9 | 1:2 | 30 | 95 | 16 | 0.1 | 52 | 48 | 33 |
| 10 | 1:2 | 50 | 70 | 16 | 0.1 | 58 | 41 | 0 |
| 11[†] | 1:2 | 50 | 70 | 16 | 0.1 | 43 | 57 | 5 |

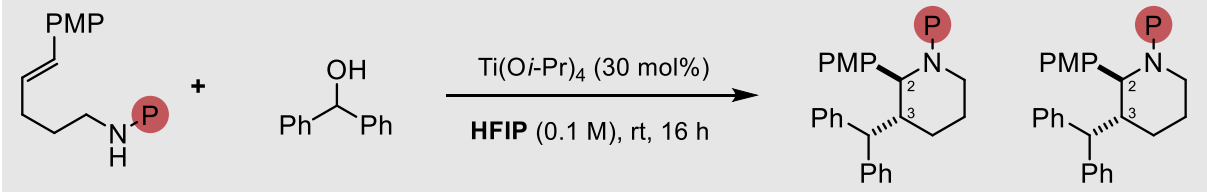
[†]1 equiv. of **2h** was added after 6 h.

HFIP source




| Entry | **HFIP** source | Yield **3h** / % | Recovered **1c** / % | Recovered **2h** / % |
|---|---|---|---|---|
| 1 | Commercial bottle | 58 | 42 | 0 |
| 2 | Commercial bottle with additional 20 equiv. $H_2O$ | 58 | 42 | 0 |
| 3 | Distilled | 57 | 42 | 0 |
| 4 | Degassed | 58 | 42 | 0 |
| 5 | Distilled and degassed | 58 | 42 | 0 |

Piperidine protecting group screen



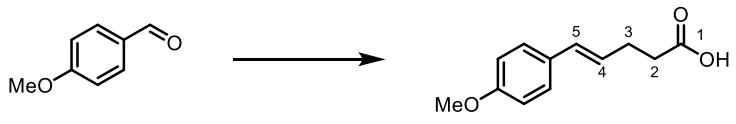

**4** (1.0 equiv.) **2a** (1.0 equiv.) **5**

| P = | **Ts** | **Ms** | ***o*Ns** | ***p*Ns** | **Cbz** | **$CO_2Me$** |
|---|---|---|---|---|---|---|
| Yield **5** / % | 95 | 64 | 84 | 88 | 86 | 98 |
| d.r (C2-C3) | 5:1 | 2:1 | 1:2 | 3:1 | >20:1 | >20:1 |

## Experimental Procedures

Preparation of Nucleophiles

**(S1): (*E*)-5-(4-Methoxyphenyl)pent-4-enoic acid**

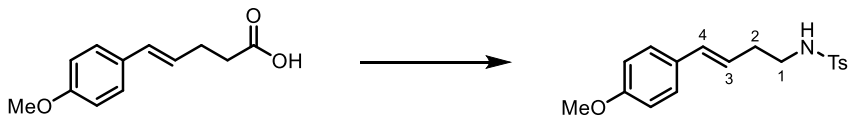



**S1**

Prepared by **General Procedure A** using 4-methoxybenzaldehyde (1.22 mL, 10.0 mmol), (3-carboxypropyl)triphenylphosphonium bromide (5.15 g, 12.0 mmol), NaHMDS (2.0 M in THF, 12.0 mL, 24.0 mmol). Flash column chromatography (50% $Et_2O$ – pentane + 1% acetic acid) afforded **S1** as a crystalline white solid (1.65 g, 80%).

Data for **S1**: **$R_f$** 0.54 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$)** 7.27 (2H, d, *J* = 8.5 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.39 (1H, d, *J* = 15.8 Hz, C5-H), 6.07 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 3.80 (3H, s, OMe), 2.69 – 2.45 (4H, m, 2 × C2-$H_2$ + 2 × C3-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.2 (C Ar), 130.7 (C5), 130.3 (C Ar), 127.4 (C4), 126.0 (2 × C Ar), 114.1 (2 × C Ar), 55.5 (OMe), 33.9 (C2), 28.1 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[1]

**(1a): (3*E*)-*N*-[4-(4-Methoxyphenyl)but-3-en-1-yl]-4-methylbenzenesulfonamide**

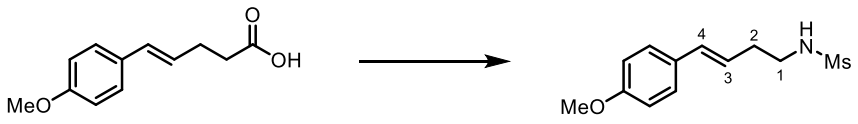



**S1** **1a**

Prepared by **General Procedure B** using **S1** (1.00 g, 4.85 mmol), $Et_3N$ (1.00 mL, 7.28 mmol) and DPPA (1.50 mL, 7.28 mmol). Crude amine was then subjected to $Et_3N$ (0.84 mL, 6.08 mmol) and 4-toluenesulfonyl chloride (1.16 g, 6.08 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **1a** as a white solid (1.08 g, 67%).

Data for **1a**: **$R_f$** 0.50 (70% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.74 (2H, d, *J* = 8.7 Hz, Ar), 7.29 (2H, d, *J* = 8.7 Hz, Ar), 7.21 (2H, d, *J* = 8.7 Hz, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.30 (1H, d, *J* = 15.8 Hz, C4-H), 5.82 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 4.41 (1H, t, *J* = 6.5 Hz, *N*H), 3.81 (3H, s, OMe), 3.09 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.43 (3H, s, TsMe), 2.34 (2H, qd, *J* = 6.5, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.3 (2 × C Ar), 143.6 (2 × C Ar), 132.9 (C4), 129.9 (2 × C Ar), 127.4 (2 × C Ar), 127.3 (2 × C Ar), 123.3 (C3), 114.1 (2 × C Ar), 55.5 (OMe), 42.8 (C1), 33.1 (C-2), 21.7 (TsMe). *The spectroscopic properties were consistent with the data available in the literature.*[2]

**(1b): (*E*)-*N*-(4-(4-Methoxyphenyl)but-3-en-1-yl)methanesulfonamide**

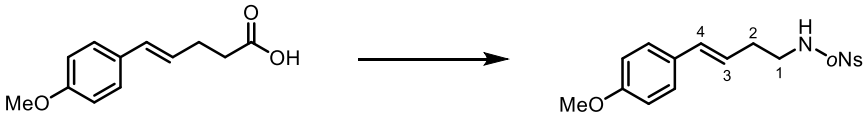



**S1** **1b**

Prepared by **General Procedure B** using **S1** (500 mg, 2.43 mmol), $Et_3N$ (0.50 mL, 3.6 mmol) and DPPA (0.78 mL, 3.6 mmol). Crude amine was then subjected to $Et_3N$ (0.420 mL, 3.04 mmol) and methanesulfonyl chloride (0.24 mL, 3.04 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **1b** as a white solid (382 mg, 56 %).

Data for **1b**: $\mathbf{R_f}$ 0.50 (60% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.28 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.43 (1H, d, *J* = 15.8 Hz, C4-H), 5.97 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 4.50 (1H, t, *J* = 6.5 Hz, *N*H), 3.80 (3H, s, OMe), 3.09 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.94 (3H, s, $SO_2Me$), 2.46 (2H, qd, *J* = 6.5, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.3 (C Ar), 132.9 (C4), 129.7 (C Ar), 127.4 (2 × C Ar), 123.3 (C3), 114.1 (2 × C Ar), 55.4 (OMe), 42.9 (C1), 40.5 ($SO_2Me$), 33.7 (C2). **HRMS** (ESI): calculated for $C_{12}H_{17}NO_3SNa$ $[M+Na]^+$ requires *m/z* 278.0827, found *m/z* 278.0821. **IR** (film) $\nu_{max}$ : 3283, 2980, 2360, 1576, 1511, 1313 $cm^{-1}$. **mp** (97 – 99 °C, EtOAc).

**(1c): (3*E*)-*N*-[4-(4-Methoxyphenyl)but-3-en-1-yl]-2-nitrobenzenesulfonamide**

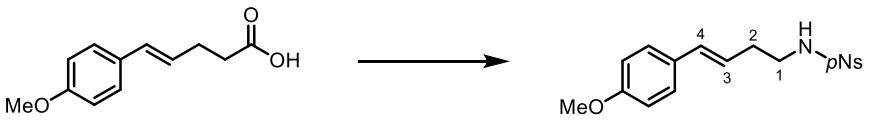



**S1** **1c**

Prepared by **General Procedure B** using **S1** (1.00 g, 4.85 mmol), $Et_3N$ (1.00 mL, 7.28 mmol) and DPPA (1.50 mL, 7.28 mmol). Crude amine was then subjected to $Et_3N$ (0.84 mL, 6.08 mmol) and 2-nitrobenzenesulfonyl chloride (1.35 g, 6.08 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **1c** as a white solid (1.30 mg, 68%).

Data for **1c**: $\mathbf{R_f}$ 0.22 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.15 – 8.11 (1H, m, Ar), 7.79 – 7.63 (3H, m, Ar), 7.17 (2H, d, *J* = 8.6 Hz, Ar), 6.81 (2H, d, *J* = 8.8 Hz, Ar), 6.29 (1H, dt, *J* = 15.8, 1.5 Hz, C4-H), 5.82 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 5.39 (1H, t, *J* = 5.9 Hz, *N*H), 3.80 (3H, s, OMe), 3.27 (2H, td, *J* = 6.7, 5.9 Hz, C1-$H_2$), 2.40 (2H, qd, *J* = 6.7, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.3 (C Ar), 134.0 (C Ar), 133.5 (C Ar), 133.0 (C Ar), 132.9 (C4), 131.1 (C Ar), 129.6 (C Ar), 127.4 (2 × C Ar), 125.5 (C Ar), 122.9 (C3), 114.1 (2 × C Ar), 55.4 (OMe), 43.7 (C1), 33.3 (C2). **HRMS** (ESI): calculated for $C_{17}H_{18}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 385.0829, found *m/z* 385.0826. **IR** (film) $\nu_{max}$ : 2981, 2360, 1521, 1441, 1342, 1126, 969 $cm^{-1}$. **mp** (111 – 113 °C, EtOAc).

**(1d): (3*E*)-*N*-[4-(4-Methoxyphenyl)but-3-en-1-yl]-4-nitrobenzenesulfonamide**

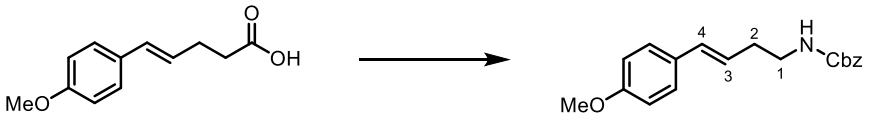



**S1** **1d**

Prepared by **General Procedure B** using **S1** (1.00 g, 4.85 mmol), $Et_3N$ (1.00 mL, 7.28 mmol) and DPPA (1.50 mL, 7.28 mmol). Crude amine was then subjected to $Et_3N$ (0.84 mL, 6.08 mmol) and 4-nitrobenzenesulfonyl chloride (1.35 g, 6.08 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **1d** as a white solid (1.35 mg, 71%).

Data for **1d**: **$R_f$** 0.23 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.28 (2H, d, *J* = 8.8 Hz, Ar), 8.01 (2H, d, *J* = 8.8 Hz, Ar), 7.17 (2H, d, *J* = 8.8 Hz, Ar), 6.82 (2H, d, *J* = 8.8 Hz, Ar), 6.30 (1H, d, *J* = 15.8 Hz, C4-H), 5.76 (1H, dt, *J* = 15.8, 7.2 Hz, C3-H), 4.70 (1H, t, *J* = 6.0 Hz, *N*H), 3.18 (2H, q, *J* = 6.3 Hz, C1-$H_2$), 2.37 (tdd, *J* = 7.6, 6.5, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.5 (C Ar), 150.1 (C Ar), 146.1 (C Ar), 133.3 (C4), 129.4 (C Ar), 128.4 (2 × C Ar), 127.4 (2 × C Ar), 124.5 (2 × C Ar), 122.7 (C3), 114.2 (2 × C Ar), 55.5 (OMe), 43.0 (C1), 33.3 (C2). **HRMS** (ESI): calculated for $C_{17}H_{18}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 385.0829, found *m/z* 385.0826. **IR** (film) $\nu_{max}$ : 3294, 1667, 1529, 1521, 1348, 1248, 1092, 918 $cm^{-1}$. **mp** (104 – 106 °C, EtOAc).

**(1e): Benzyl (*E*)-(4-(4-methoxyphenyl)but-3-en-1-yl)carbamate**

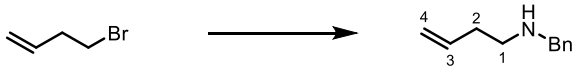



**S1** **1e**

Prepared by **General Procedure B** using **S1** (500 mg, 2.43 mmol), $Et_3N$ (0.50 mL, 3.6 mmol) and DPPA (0.78 mL, 3.6 mmol). Crude amine was then subjected to $Et_3N$ (0.420 mL, 3.04 mmol) and benzyl chloroformate (0.43 mL, 3.6 mmol). Flash column chromatography (20% EtOAc – pentane) afforded **1e** as a white solid (614 mg, 75%).

Data for **1e**: **$R_f$** 0.28 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.38 – 7.30 (5H, m, Ar), 7.28 – 7.24 (2H, m, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.39 (1H, d, *J* = 16.0 Hz, C4-H), 5.99 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 5.10 (2H, s, $CH_2Ph$), 4.83 (1H, *br*.s, *N*H), 3.80 (3H, s, OMe), 3.34 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.40 (2H, q, *J* = 6.8 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.1 (C Ar), 156.5 (CO), 136.7 (C Ar), 132.0 (C Ar), 130.1 (C Ar), 128.7 (2 × C Ar), 128.3 (C4), 128.2 (2 × C Ar), 127.4 (2 × C Ar), 124.5 (C3), 114.1 (2 × C Ar), 66.8 ($CH_2Ph$), 55.4 (OMe), 40.8 (C1), 33.4 (C2). **HRMS** (ESI): calculated for $C_{19}H_{21}NO_3Na$ $[M+Na]^+$ requires *m/z* 334.1414, found *m/z* 334.1411. **IR** (film) $\nu_{max}$ : 2981, 2360, 1713, 1511, 1247, 907, 730, 650 $cm^{-1}$. **mp** (117 – 119 °C, EtOAc).

**(S2): *N*-Benzylbut-3-en-1-amine**

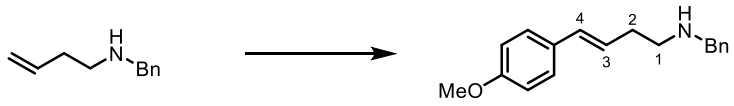



**S2**

To a solution of benzylamine (4.00 mL, 37.1 mmol, 5.00 equiv.) and 4-bromo-1-butene (0.75 mL, 7.4 mmol, 1.0 equiv.) in EtOH (5 mL) was added NaI (110 mg, 0.74 mmol, 0.10 equiv.), before heating to reflux for 4 h. The reaction mixture was cooled to rt and the solvent removed *in vacuo*. The residue was dissolved in $CH_2Cl_2$ and 1.0 M aq. KOH added. The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (gradient elution 20% → 100% EtOAc – pentane) afforded **S2** as a colourless oil (780 mg, 65%).

Data for S2: **$R_f$** 0.20 (60% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.29 – 7.34 (4H, m, Ar), 7.23 – 7.27 (1H, m, Ar), 5.79 (1H, ddt, *J* = 17.1, 10.2, 6.9 Hz, C3-H), 4.99 – 5.13 (2H, m, C4-$H_2$), 3.80 (2H, s, $CH_2Ph$), 2.71 (2H, t, *J* = 6.9 Hz, C1-$H_2$), 2.29 (2H, qt, J = 6.9, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 140.5 (C Ar), 136.6 (C3), 128.5 (2 × C Ar), 128.2 (2 × C Ar), 127.0 (C Ar), 116.5 (C4), 54.1 ($CH_2Ph$), 48.4 (C1), 34.4 (C2). *The spectroscopic properties were consistent with the data available in the literature.*[3]

**(1f): (3*E*)-*N*-Benzyl-4-(4-methoxyphenyl)but-3-en-1-amine**

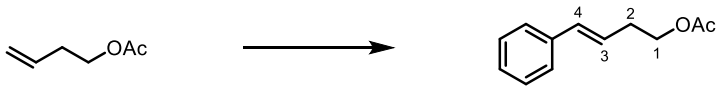



**S2** **1f**

To a solution of **S2** (254 mg, 1.56 mmol, 1.00 equiv.) in $Et_2O$ (1.70 mL) was added trifluoroacetic acid (0.24 mL, 1.7 mmol, 1.1 equiv.) dropwise at 0 ˚C. After stirring for 2 h at rt water was added and the layers separated. The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with brine and dried over $Na_2SO_4$ before concentrating *in vacuo*. The crude material was then subjected to **General Procedure C** using 4-methoxystyrene (290 mg, 2.16 mmol) and Grubbs II (14 mg, 0.016 mmol) in PhMe at 100 ˚C. The solvent was removed *in vacuo* before being re-dissolved in MeOH (4 mL) and water (0.5 mL). KOH (123 mg, 2.16 mmol) was added and the reaction mixture heated to reflux for 2 h. The reaction mixture was diluted with EtOAc and water and the layers separated. The aqueous later was extracted with EtOAc and the combined organic layers were washed with brine and dried over $Na_2SO_4$ before concentrating *in vacuo*. Flash column chromatography (gradient elution 20% → 50% EtOAc – pentane) afforded **1f** as a colourless oil (130 mg, 43%).

Data for **1f**: $\mathbf{R_f}$ 0.50 (40% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.22 – 7.37 (7H, m, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.39 (1H, d, *J* = 15.8 Hz, C4-H), 6.02 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 3.84 (2H, s, $CH_2Ph$), 3.80 (3H, s, OMe), 2.78 (2H, t, *J* = 6.9 Hz, C1-$H_2$), 2.45 (2H, qd, *J* = 7.0, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 158.9 (C Ar), 139.2 (C Ar), 131.2 (C4), 130.3 (C Ar), 128.5 (2 × C Ar), 128.4 (2 × C Ar), 127.2 (C Ar), 127.1 (2 × C Ar), 125.5 (C3), 113.9 (2 × C Ar), 55.3 (OMe), 53.6 ($CH_2Ph$), 48.5 (C1), 33.1 (C2). **HRMS (ESI):** calculated for $C_{18}H_{22}NO$ $[M+H]^+$ requires m/z 268.1701, found m/z 268.1695. **IR** (film) $\nu_{max}$: 2980, 1606, 1576, 1509, 1453, 1245 $cm^{-1}$.

**(S3): (3*E*)-4-Phenylbut-3-en-1-yl acetate**

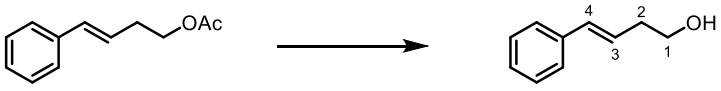



**S3**

Prepared according to **General Procedure C** using but-3-en-1-yl acetate (1.00 g, 8.76 mmol), styrene (456 mg, 4.38 mmol) and Grubbs II (56 mg, 0.066 mmol) at reflux in $CH_2Cl_2$. Flash column chromatography (5% → 8% $Et_2O$ – pentane) afforded **S3** as a white solid (494 mg, 59%).

Data for **S3**: $\mathbf{R_f}$ 0.50 (20% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.28 – 7.38 (4H, m, Ar), 7.19 – 7.25 (1H, m, Ar), 6.48 (1H, d, *J* = 15.9 Hz, C4-H), 6.18 (1H, dt, *J* = 15.9, 7.0 Hz, C3-H), 4.20 (2H, t, *J* = 6.7 Hz, C1-$H_2$), 2.55 (2H, qd, *J* = 6.8, 1.5 Hz, C2-$H_2$), 2.06 (3H, s, C(O)Me). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 171.1 (CO), 137.3 (C Ar), 132.4 (C4), 128.6 (2 × C Ar), 127.3 (C Ar), 126.1 (2 × C Ar), 125.6 (C3), 63.8 (C1), 32.4 (C2), 21.0 (C(O)Me). *The spectroscopic properties were consistent with the data available in the literature.*[4]

**(S4): (3*E*)-4-Phenylbut-3-en-1-ol**



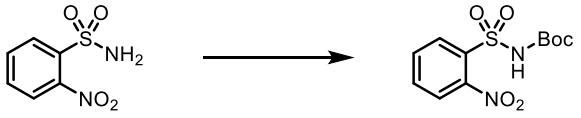

**S3** **S4**

To a solution of **S3** (541 mg, 2.85 mmol) in MeOH (30 mL) was added $K_2CO_3$ (1.97 g, 14.3 mmol, 5.0 equiv.) at 0 °C. The reaction was monitored by TLC until completion and the solid removed by filtration before concentrating *in vacuo*. Flash column chromatography (20% → 50% $Et_2O$ – pentane) afforded **S4** as a colourless oil (369 mg, 87%).

Data for **S4**: $\mathbf{R_f}$ 0.40 (75% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.28 – 7.39 (4H, m, Ar), 7.19 – 7.25 (1H, m, Ar), 6.51 (1H, d, *J* = 15.8 Hz, C4-H), 6.21 (1H, dt, *J* = 15.9, 7.1 Hz, C3-H), 3.73 – 3.81 (2H, m, C1-$H_2$), 2.47 – 2.53 (2H, m, C2-$H_2$), 1.47 (1H, *br.* s, *O*H). **$^{13}$C NMR (100 MHz, $CDCl_3$)**

**δ** 137.2 (C Ar), 132.9 (C4), 128.6 (2 × C Ar), 127.3 (C Ar), 126.3 (C3), 126.1 (2 × C Ar), 62.0 (C1), 36.4 (C2). *The spectroscopic properties were consistent with the data available in the literature.*[5]

**(S5): *tert*-Butyl [(2-nitrophenyl)sulfonyl]carbamate**

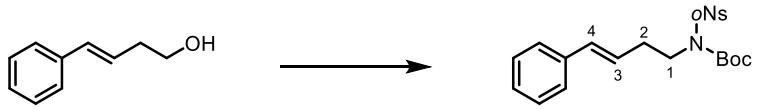



**S5**

To a solution of 2-nitrobenzene sulfonamide (1.00 g, 4.95 mmol, 1.00 equiv.), DMAP (640 mg, 0.50 mmol, 0.1 equiv.), in $CH_2Cl_2$ (10 mL) was added Et3N (0.83 mL, 5.95 mmol, 1.20 equiv.) followed by di-tert-butyl decarbonate (1.10 g, 4.95 mmol, 1.00 equiv.) at 0 °C. The mixture was stirred at rt for 8 h before concentrating *in vacuo* and re-dissolving in EtOAc. The solution was washed with 1.0 M HCl before drying over $Na_2SO_4$ and concentrating *in vacuo*. Recrystallisation from hot hexane afforded **S5** as a crystalline white solid (1.34 g, 80%).

Data for **S5**: **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.31 – 8.36 (1H, m, Ar), 7.83 – 7.88 (1H, m, Ar), 7.74 – 7.82 (2H, m, Ar), 1.43 (9H, s, C(C**H**$_3$)$_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 148.8 (C(O)), 148.2 (C Ar), 134.8 (C Ar), 133.4 (C Ar), 132.6 (C Ar), 132.2 (C Ar), 125.2 (C Ar), 84.9 (**C**(CH$_3$)$_3$), 28.0 (C(**C**H$_3$)$_3$). *The spectroscopic properties were consistent with the data available in the literature.*[6]

**(S6): *tert*-Butyl (3*E*)-[(2-nitrophenyl)sulfonyl](4-phenylbut-3-en-1-yl)carbamate**

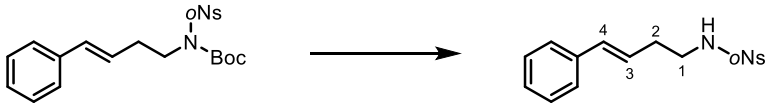



**S4** **S6**

Prepared by **General Procedure D** using alcohol **S4** (201 mg, 1.36 mmol), **S5** (442 mg, 1.63 mmol), triphenylphosphine (535 mg, 2.04 mmol) and DIAD (359 mg, 1.77 mmol). Flash column chromatography (15% → 25% $Et_2O$ – pentane) afforded **S6** as a colourless oil (474 mg, 80%).

Data for **S6**: **$R_f$** 0.50 (60% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.27 – 8.33 (1H, m, Ar), 7.68 – 7.76 (3H, m, Ar), 7.33 – 7.39 (2H, m, Ar), 7.26 – 7.32 (2H, m, Ar), 7.17 – 7.23 (1H, m, Ar), 6.52 (1H, d, *J* = 15.8 Hz, C4-H), 6.21 (1H, dt, *J* = 15.8, 7.3 Hz, C3-H), 3.88 – 3.96 (2H, m, C1-H$_2$), 2.66 (2H, qd, *J* = 7.3, 1.4 Hz, C2-H$_2$), 1.33 (9H, s, C(C**H**$_3$)$_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 150.5 (CO), 147.8 (C Ar), 137.5 (C Ar), 134.2 (C Ar), 133.8 (C Ar), 133.4 (C Ar), 133.0 (C4), 131.8 (C Ar), 128.6 (2 × C Ar), 127.3 (C Ar), 126.4 (2 × C Ar), 126.0 (C3), 124.5 (C Ar), 85.1 (**C**(CH$_3$)$_3$), 47.7 (C1), 34.1 (C2), 28.0 (C(**C**H$_3$)$_3$). **HRMS** (ESI): calculated for $C_{21}H_{25}N_2O_6SN$ $[M+H]^+$ requires *m/z* 433.1729, found *m/z* 433.1734. **IR** (film) $\nu_{max}$: 2980, 2888, 1731, 1542, 1369, 1152cm$^{-1}$.

**(1g): (3*E*)-2-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide**

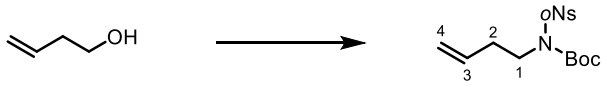



**S6** **1g**

Prepared by **General Procedure E** using **S6** (454 mg, 1.05 mmol) and TFA (0.40 mL, 5.26 mmol). Flash column chromatography (10% → 40% $Et_2O$ – pentane) afforded **1g** as a colourless oil (312 mg, 85%).

Data for **1g**: **$R_f$** 0.40 (40% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.13 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 7.75 (1H, dd, *J* = 7.7, 1.6 Hz, Ar), 7.62 – 7.72 (2H, m, Ar), 7.18 – 7.30 (5H, m, Ar), 6.36 (1H, d, *J* = 15.8 Hz, C4-H), 5.99 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 5.43 (1H, t, *J* = 6.5 Hz, *N*H), 3.29 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.43 (qd, *J* = 7.1, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 147.9 (C Ar), 136.8 (C Ar), 133.8 (C Ar), 133.5 (C4), 133.4 (C Ar), 132.8 (C Ar), 130.9 (C Ar), 128.6 (2 × C Ar), 127.6 (C Ar), 126.2 (2 × CH Ar), 125.4 (C Ar), 125.3 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[7]

**(S7): *tert*-Butyl but-3-en-1-yl[(2-nitrophenyl)sulfonyl]carbamate**

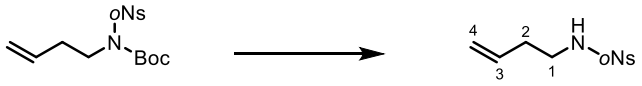



**S7**

Prepared by **General Procedure D** using but-3-en-1-ol (150 mg, 2.08 mmol), **S5** (755 mg, 2.50 mmol), triphenylphosphine (709 mg, 2.70 mmol) and DIAD (630 mg, 3.12 mmol). Flash column chromatography (15% → 25% EtOAc – pentane) afforded **S7** as a colourless oil (740 mg, 99%).

Data for **S7**: **$R_f$** 0.50 (60% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.27 – 8.32 (1H, m, Ar), 7.69 – 7.76 (3H, m, Ar), 5.82 (1H, ddt, *J* = 17.2, 10.2, 7.0 Hz, C3-H), 5.07 – 5.19 (2H, m, C4-$H_2$), 3.79 – 3.86 (2H, m, C1-$H_2$), 2.50 (2H, qd, *J* = 7.1, 1.3 Hz, C2-$H_2$), 1.36 (9H, s, C(C**$H_3$**)$_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 150.5 (CO), 147.8 (C Ar), 134.3 (C3), 134.2 (C Ar), 133.7 (C Ar), 133.5 (C Ar), 131.8 (C Ar), 124.5 (C Ar), 117.9 (C4), 85.1 (**C**$(CH_3)_3$), 47.5 (C1), 34.8 (C2), 28.0 (C(**C**$H_3$)$_3$). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) $\nu_{max}$: 2980, 1721, 1607, 1510, 1348, 1246 $cm^{-1}$.

**(S8): *N*-(but-3-en-1-yl)-2-nitrobenzenesulfonamide**

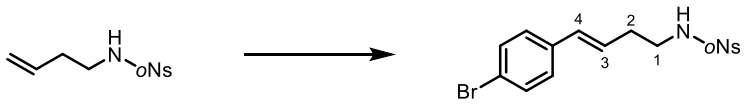



**S7** **S8**

Prepared by **General Procedure E** using **S7** (720 mg, 2.02 mmol) and TFA (0.77 mL, 10 mmol). Flash column chromatography (10% → 40% $Et_2O$ – pentane) afforded **S8** as a colourless oil (535 mg, 85%).

Data for **S8**: **$R_f$** 0.40 (70% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.11 – 8.16 (1H, m, Ar), 7.84 – 7.89 (1H, m, Ar), 7.71 – 7.77 (2H, m, Ar), 5.66 (1H, ddt, *J* = 17.1, 10.3, 6.9 Hz, C3-H), 5.34 (1H, t, *J* = 6.5 Hz, *N*H), 5.00 – 5.10 (2H, m, C4-$H_2$), 3.18 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.28 (qt, *J* = 6.5, 1.3 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, CDCl3) δ** 134.0 (C Ar), 133.9 (C3), 133.7 (2 × C Ar), 132.9 (C Ar), 131.2 (C Ar), 125.5 (C Ar), 118.5 (C4), 43.0 (C1), 33.8 (C2). *The spectroscopic properties were consistent with the data available in the literature.*[8]

**(1h): (3*E*)-*N*-[4-(4-Bromophenyl)but-3-en-1-yl]-2-nitrobenzenesulfonamide**

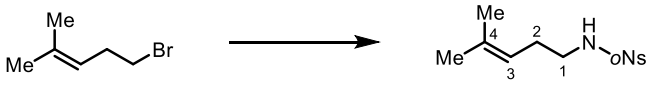



**S8** **1h**

Prepared by **General Procedure C** using **S8** (104 mg, 0.407 mmol), 1-bromo-4-vinylbenzene (0.11 mL, 0.814 mmol) and Grubbs II (5 mg, 0.06 mmol) in PhMe at 100 ˚C. Flash column chromatography (15% → 25% $Et_2O$ – pentane) afforded **1h** as a colourless oil (53 mg, 31%).

Data for **1h**: **$R_f$** 0.45 (40% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.14 (1H, dd, *J* = 7.6, 1.7 Hz, Ar), 7.79 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 7.65 – 7.74 (2H, m, Ar), 7.40 (2H, d, *J* = 8.5 Hz, Ar), 7.11 (2H, d, *J* = 8.5 Hz, Ar), 6.31 (1H, d, *J* = 15.9 Hz, C4-H), 6.00 (1H, dt, *J* = 15.8, 7.1 Hz, C3-H), 5.37 (1H, t, *J* = 6.5 Hz, *N*H), 3.28 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.43 (2H, qd, *J* = 6.5, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 135.8 (C Ar), 134.0 (2 × C Ar), 133.6 (C Ar), 132.9 (C Ar), 132.5 (C4), 131.8 (2 × C Ar), 131.1 (C Ar), 127.8 (2 × C Ar), 126.2 (C3), 125.6 (C Ar), 121.4 (C Ar), 43.4 (C1), 33.3 (C2). **HRMS** (ESI): calculated for $C_{16}H_{15}N_2O_4SBrNa$ $[M+Na]^+$ requires *m/z* 432.9834, found *m/z* 432.9828. **IR** (film) $\nu_{max}$: 3334, 2980, 2888, 2360, 1536, 1382 $cm^{-1}$.

**(1i): *N*-(4-Methylpent-3-en-1-yl)-2-nitrobenzenesulfonamide**

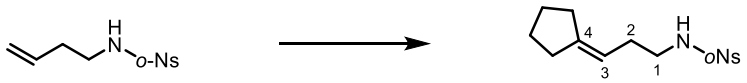



**1i**

A solution of 5-bromo-2-methylpent-2-ene (500 mg, 3.00 mmol, 1.10 equiv.), 2-nitrobenzenesulfonamide (553 mg, 2.74 mg, 1.00 equiv.), $K_2CO_3$ (755 mg, 5.47 mmol, 2.00 equiv.) in acetone (3 mL) was heated to 60 °C for 16 h. The reaction mixture was filtered through a plug of Celite, washed with EtOAc and concentrated *in vacuo*. Flash column chromatography (10% → 15% $Et_2O$ – pentane) afforded **1i** as a colourless oil (107 mg, 14%).

Data for **1i**: **$R_f$** 0.40 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.11 – 8.15 (1H, m, Ar), 7.84 – 7.89 (1H, m, Ar), 7.70 – 7.77 (2H, m, Ar), 5.28 (1H, t, *J* = 6.6 Hz, *N*H), 4.94 (1H, tp, *J* = 7.4, 1.5 Hz, C3-H), 3.10 (2H, q, *J* = 6.6 Hz, C1-$H_2$), 2.22 (2H, q, *J* = 7.0 Hz, C2-$H_2$), 1.66 (3H, s, Me), 1.56 (3H, s, Me). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 148.2 (C Ar), 136.2 (C4), 134.0 (C Ar), 133.6 (C Ar), 132.9 (C Ar), 131.2 (C Ar), 125.5 (C Ar), 119.5 (C3), 43.8 (C1), 28.2 (C2), 25.9 (Me), 18.0 (Me). **HRMS** (ESI): calculated for $C_{12}H_{16}N_2O_4SNa$ $[M+Na]^+$ requires *m/z* 307.0728, found *m/z* 307.0722. **IR** (film) $\nu_{max}$: 3341, 2980, 1538, 1408, 1338, 1162 $cm^{-1}$.

**(1j): *N*-(3-Cyclopentylidenepropyl)-2-nitrobenzenesulfonamide**

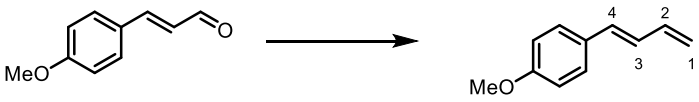



**S8** **1j**

Prepared by **General Procedure C** using **S8** (625 mg, 2.44 mmol), methylenecyclopentane (1.00 g, 12.2 mmol) and Grubbs II (31 mg, 0.036 mmol) in $CH_2Cl_2$ at rt for 72 h. Flash column chromatography (10% → 15% EtOAc – pentane) afforded **1j** as a colourless oil (134 mg, 18%).

Data for **1j**: **$R_f$** 0.40 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.10 – 8.15 (1H, m, Ar), 7.83 – 7.88 (1H, m, Ar), 7.70 – 7.76 (2H, m, Ar), 5.30 (1H, t, *J* = 6.4 Hz, *N*H), 5.05 (1H, tt, *J* = 7.3, 2.3 Hz, C3-H), 3.11 (2H, q, *J* = 6.4 Hz, C1-$H_2$), 2.06 – 2.24 (7H, m, C2-$H_2$ + C-H cyclopentyl + 2 × $CH_2$ cyclopentyl), 1.51 – 1.68 (5H, m, C-H cyclopentyl + 2 × C-$H_2$ cyclopentyl). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 148.2 (C Ar), 134.0 (C Ar), 133.6 (C Ar), 132.9 (C Ar), 131.3 (C4), 131.2 (C Ar), 125.5 (C Ar), 114.9 (C3), 43.7 (C1), 33.8 ($CH_2$ cyclopentyl), 29.8 ($CH_2$ cyclopentyl), 29.0 ($CH_2$ cyclopentyl), 26.4 and 26.3 ($CH_2$ cyclopentyl + C2). **HRMS** (ESI): calculated for $C_{14}H_{18}N_2O_4SNa$ $[M+Na]^+$ requires *m/z* 333.09, found *m/z* 333.09. **IR** (film) $\nu_{max}$: 3341, 2980, 2888, 1538, 1340, 1163 $cm^{-1}$.

**(S9): (*E*)-1-(Buta-1,3-dien-1-yl)-4-methoxybenzene**

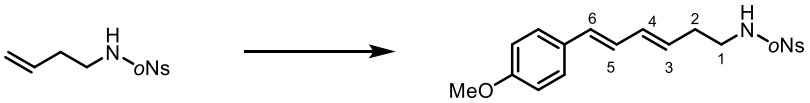



**S9**

*Prepared according to the procedure reported by Doye et. al.*[9] To suspension of methyltriphenylphosphonium bromide (8.57 g, 24.0 mmol) in THF (100 mL) was added *n*-butyllithium (2.5 M in hexanes, 9.60 mL, 24.0 mmol) dropwise at 0 °C. After stirring at 0 °C for 1.5 h 4-methoxy-cinnamaldehyde (3.24 g, 20.0 mmol) in THF (20 mL) was added slowly and allowed to warm up to rt. After 1 h, silica gel (10 g) and hexane (150 mL) was added. After stirring for 15 minutes the solid was removed by filtration and the filtrate concentrated *in vacuo*. Flash column chromatography (100% pentane) afforded **S9** as a crystalline white solid (2.34 g, 73%).

Data for **S9**: $\mathbf{R_f}$ 0.80 (5% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.25 (2H, d, *J* = 8.7 Hz, Ar), 6.77 (2H, d, *J* = 8.8 Hz, Ar), 6.67 – 6.54 (1H, m, C4-H), 6.49 – 6.34 (2H, m, C2-H + C3-H), 5.21 (1H, ddd, *J* = 16.9, 1.8, 0.9 Hz, C1-$H_A$), 5.12 – 4.96 (1H, m, C1-$H_B$), 3.68 (s, 3H, OMe). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.5 (C Ar), 137.6 (C2), 132.6 (C3), 130.1 (C Ar), 127.8 (C4), 127.8 (2 × C Ar), 116.5 (C1), 114.2 (2 × C Ar), 55.3 (OMe). *The spectroscopic properties were consistent with the data available in the literature.*[9]

**(1k): *N*-[(3*E*,5*E*)-6-(4-Methoxyphenyl)hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide and *N*-[(3*E*,5*Z*)-6-(4-Methoxyphenyl)hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide**




**S8** **1k**

*E,E : E,Z*
6:1

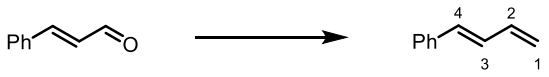
Prepared by **General Procedure C** using **S8** (95 mg, 0.37 mmol), **S9** (118 mg, 0.738 mmol) and Grubbs I (15 mg, 0.019 mmol, 5 mol%) in PhMe at 40 °C for 16 h. Flash column chromatography (20% → 35% EtOAc – pentane) afforded **1k** as a partially separable 6:1 mixture of ***E,E*-1k** and ***E,Z*-1k**; ***E,E*-1k** was isolated as a yellow oil (15 mg, 15%) and a 4:1 mixture of ***E,Z*-1k** + ***E,E*-1k** was isolated as a yellow oil (39 mg, 36%).

Data for ***E,E*-1k**: $\mathbf{R_f}$ 0.50 (40% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.14 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 7.83 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 7.67 – 7.76 (2H, m, Ar), 7.28 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.47 (1H, dd, *J* = 15.6, 9.9 Hz, C5-H), 6.36 (1H, d, *J* = 15.6 Hz, C6-H), 6.14 (1H, ddt, *J* = 14.8, 9.9, 1.3 Hz, C4-H), 5.52 (1H, dt, *J* = 14.8, 6.8 Hz, C3-H), 5.37 (1H, t, *J* = 6.8 Hz,

*N*H), 3.81 (3H, s, OMe), 3.23 (2H, q, *J* = 6.8 Hz, C1-$H_2$), 2.35 (2H, qd, *J* = 6.8, 1.3 Hz, C2-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.4 (C Ar), 134.3 (C4), 134.2 (2 × C Ar), 133.6 (C Ar), 132.9 (C Ar), 131.6 (C6), 131.1 (C Ar), 130.1 (C Ar), 128.1 (C3), 127.7 (2 × C Ar), 126.4 (C5), 125.6 (C Ar), 114.2 (2 × C Ar), 55.4 (OMe), 43.6 (C1), 33.1 (C2). **HRMS** (EI): calculated for $C_{19}H_{20}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 411.0991, found *m/z* 411.0986. **IR** (film) $\nu_{max}$: 3349, 2980, 2888, 1541, 1428, 1163 $cm^{-1}$.

Partial data for ***E,Z*-1k** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.14 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 7.83 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 7.60 – 7.79 (2H, m, Ar), 7.30 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.69 (1H, ddd, *J* = 15.4, 11.1, 1.2 Hz, C5-H), 6.13 (1H, d, *J* = 15.4 Hz, C6-H), 6.15 – 6.23 (1H, m, C4-H), 5.43 (1H, d, *J* = 6.4 Hz, *N*H), 5.28 (1H, dt, *J* = 10.7, 7.7 Hz, C3-H), 3.82 (3H, s, OMe), 3.19-3.26 (2H, m, C1-$H_2$), 2.50 (2H, qd, *J* = 6.9, 1.5 Hz, C2-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.6 (C Ar), 148.1 (C Ar), 134.1 (C Ar), 133.71 (C Ar), 133.66 (C Ar), 132.5 (C4), 131.6 (C6), 131.1 (C Ar), 130.0 (C Ar), 127.9 (2 × C Ar), 125.6 (C Ar), 125.5 (C3), 121.4 (C5), 114.2 (2 × C Ar), 55.5 (OMe), 43.7 (C1), 28.4 (C2).

**(S10): (3*E*)-Buta-1,3-dien-1-ylbenzene**

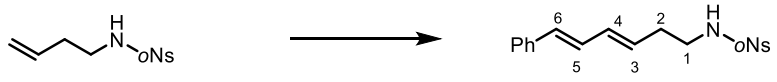



**S10**

To suspension of methyltriphenylphosphonium bromide (6.13 g, 17.5 mmol) in THF (55 mL) was added *n*-butyllithium (2.5 M in hexanes, 8.00 mL, 15.9 mmol) dropwise at 0 °C. After stirring at 0 °C for 1.5 h cinnamaldehyde (2.00 mL, 15.9 mmol) in THF (5 mL) was added slowly and allowed to warm up to rt. After 1 h, silica gel (10 g) and hexane (150 mL) was added. After stirring for 15 minutes the solid was removed by filtration and the filtrate concentrated *in vacuo*. Flash column chromatography (0% → 5% $Et_2O$ – pentane) afforded **S10** as a crystalline white solid (817 mg, 41%).

Data for **S10**: **$R_f$** 0.50 (10% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.38 – 7.44 (2H, m, Ar), 7.29 – 7.36 (2H, m, Ar), 7.20 – 7.27 (1H, m, Ar), 6.80 (1H, dd, *J* = 15.7, 10.5 Hz, C3-H), 6.58 (1H, d, *J* = 15.7 Hz, C4-H), 6.52 (1H, dt, *J* = 16.9, 10.5 Hz, C2-H), 5.35 (1H, d, *J* = 16.9 Hz, C1-$H_A$), 5.19 (1H, d, *J* = 10.5 Hz, C1-$H_B$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 137.3 (C2), 137.3 (C Ar), 133.0 (C4), 129.8 (C3), 128.7 (2 × C Ar), 127.8 (C Ar), 126.6 (2 × C Ar), 117.8 (C1). *The spectroscopic properties were consistent with the data available in the literature.*[10]

**(1l): *N*-[(3*E*,5*E*)-6-Phenyl-hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide and *N*-[(3*E*,5*Z*)-6-Phenyl-hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide**




**S8** **1l**

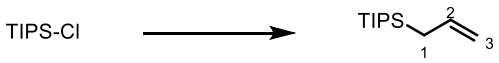
*E,E* : *E,Z*
5:1

Prepared by **General Procedure C** using sulfonamide **S8** (228 mg, 0.969 mmol), **S10** (259 mg, 1.94 mmol) and Grubbs I (40 mg, 0.048 mmol, 5 mol%) in PhMe at 40 °C for 16 h. Flash column chromatography (10% → 35% EtOAc – pentane) afforded **1l** as a partially separable 5:1 mixture of ***E,E*-1l** and ***E,Z*-1l**; ***E,E*-1l** was isolated as a yellow oil (45 mg, 13%) and a 3.5:1 mixture of ***E,Z*-1l** + ***E,E*-1l** was isolated as a yellow oil (147 mg, 43%).

Data for ***E,E*-1l**: $\mathbf{R_f}$ 0.40 (40% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.15 (1H, dd, *J* = 7.6, 1.7 Hz, Ar), 7.84 (1H, dd, *J* = 7.7, 1.6 Hz, Ar), 7.67 – 7.82 (2H, m, Ar), 7.28 – 7.38 (4H, m, Ar), 7.19 – 7.24 (1H, m, Ar), 6.60 (1H, dd, *J* = 15.7, 10.4 Hz, C5-H), 6.42 (1H, d, *J* = 15.7 Hz, C6-H), 6.17 (1H, ddt, *J* = 15.2, 10.4, 1.4 Hz, C4-H), 5.59 (1H, dt, *J* = 15.2, 6.4 Hz, C3-H), 5.36 (1H, t, *J* = 6.4 Hz, *N*H), 3.24 (q, *J* = 6.4 Hz, C1-$H_2$), 2.37 (2H, qd, *J* = 6.4, 1.4 Hz, C2-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 137.2 (C Ar), 134.1 (C Ar), 134.1 (C4), 133.6 (C Ar), 132.9 (C Ar), 132.1 (C6), 131.2 (C Ar), 129.4 (C3), 128.8 (2 × C Ar), 128.3 (C5), 127.7 (C Ar), 126.5 (2 × C Ar), 125.6 (C Ar), 43.5 (C1), 33.1 (C2)**. HRMS** (ESI): calculated for $C_{18}H_{19}N_2O_4SNa$ $[M+H]^+$ requires *m/z* 359.1060, found *m/z* 359.1063. **IR** (film) $\nu_{max}$: 3304, 2980, 2888, 1382, 1251, 1158 $cm^{-1}$.

Partial data for ***E,Z*-1l** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.15 (1H, dd, *J* = 7.6, 1.7 Hz, Ar), 7.68 – 7.78 (2H, m, Ar), 7.61 – 7.66 (1H, m, Ar), 7.28 – 7.38 (4H, m, Ar), 7.19 – 7.24 (1H, m, Ar), 6.82 (1H, ddd, *J* = 15.5, 11.1, 1.2 Hz, C5-H), 6.53 (1H, d, *J* = 15.5 Hz, C6-H), 6.20 – 6.26 (1H, m, C4-H), 5.36 (1H, dt, *J* = 10.8, 7.7 Hz, C3-H), 3.23 – 3.26 (2H, m, C1-$H_2$), 2.52 (2H, qd, *J* = 6.9, 1.5 Hz, C2-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 137.2 (C Ar), 134.2 (C6), 134.2 (C Ar), 133.7 (C Ar), 132.9 (2 × C Ar), 132.3 (C4), 131.1 (C Ar), 129.4 (C Ar), 128.8 (2 × C Ar), 128.0 (C Ar), 126.7 (C3), 126.7 (2 × C Ar), 123.4 (C5), 43.7 (C1), 28.5 (C2).

**(S11): Allyltriisopropylsilane**



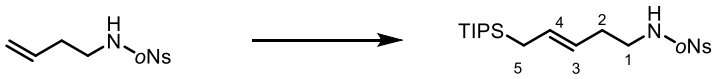

**S11**

To a solution of triisopropylsilyl chloride (1.10 mL, 5.21 mmol) in anhydrous THF (1.5 mL) was added allylmagnesium bromide (1.0 M in $Et_2O$, 7.3 mL, 7.3 mmol) at 0 °C. After warming to rt, the reaction

mixture was heated to reflux for 16 h. The reaction was cooled to 0 °C before addition of aq. $NH_4Cl$. The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (0% → 5% $Et_2O$ – pentane) afforded **S11** as a colourless oil (1.02 g, 99%).

Data for **S11**: $\mathbf{R_f}$ 0.40 (2% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 5.88 (1H, ddt, *J* = 16.9, 10.0, 8.1 Hz, C2-H), 4.76 – 4.97 (2H, m, C3-$H_2$), 1.64 (2H, d, *J* = 8.1 Hz, C1-$H_2$), 1.06 (18H, s, 6 × CH(C**H**$_3$)$_2$), 1.03 – 1.08 (3H, m, 3 × C**H**$(CH_3)_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 136.4 (C2), 112.9 (C3), 18.8 (6 × CH(**C**$H_3)_2$), 11.2 (3 × **C**H$(CH_3)_2$). *The spectroscopic properties were consistent with the data available in the literature.*[11]

**(1m): (3*E*)-2-Nitro-*N*-[5-(triisopropylsilyl)pent-3-en-1-yl]benzenesulfonamide and (3*Z*)-2-Nitro-*N*-[5-(triisopropylsilyl)pent-3-en-1-yl]benzenesulfonamide**




**S8** **1m** *E*:*Z* 4:1

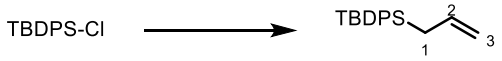
Prepared by **General Procedure C** using **S8** (511 mg, 2.00 mmol), **S11** (790 mg, 4.00 mmol) and Grubbs II (25 mg, 0.030 mmol) in PhMe at 100 °C for 16 h. Flash column chromatography (20% → 35% EtOAc – pentane) afforded **1m** as an inseparable 4:1 mixture of ***E*-1m** and ***Z*-1m** as a yellow oil (770 mg, 90%).

Data for ***E*-1m** (from the mixture): **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.11 – 8.16 (1H, m, Ar), 7.83 – 7.88 (1H, m, Ar), 7.70 – 7.76 (2H, m, Ar), 5.51 (1H, dtt, *J* = 15.3, 8.1, 1.3 Hz, C4-H), 5.29 (1H, t, *J* = 5.9 Hz, *N*H), 5.13 (1H, dtt, *J* = 15.3, 6.9, 1.3 Hz, C3-H), 3.10 (2H, td, *J* = 6.9, 5.9 Hz, C1-$H_2$), 2.18 (2H, qd, *J* = 6.9, 1.2 Hz, C2-$H_2$), 1.52 (2H, dd, *J* = 8.1, 1.3 Hz, C5-$H_2$), 1.01 (18H, s, 6 × CH(C**H**$_3$)$_2$), 0.97 – 1.04 (3H, m, 3 × C**H**$(CH_3)_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 148.3 (C Ar), 134.1 (C Ar), 133.58 (C Ar), 132.8 (C Ar), 132.0 (C4), 131.2 (C Ar), 125.5 (C Ar), 123.3 (C3), 43.8 (C1), 33.0 (C2), 18.8 (6 × CH(**C**$H_3)_2$), 15.7 (C-5), 11.1 (3 × **C**H$(CH_3)_2$).

Partial data for ***Z*-1m** (from the mixture): **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.11 – 8.16 (1H, m, Ar), 7.83 – 7.88 (1H, m, Ar), 7.70 – 7.76 (2H, m, Ar), 5.50 – 5.58 (1H, m, C3-H), 5.63 (1H, dtt, *J* = 10.2, 8.6, 1.6 Hz, C4-H), 5.34 (1H, d, *J* = 5.9 Hz, *N*H), 5.00 – 5.08 (1H, m, C3-H), 3.14 (1H, td, *J* = 6.9, 5.9 Hz, C1-$H_2$), 2.29 (2H, qd, *J* = 6.9, 1.6 Hz, C2-$H_2$), 1.52 (2H, dd, *J* = 8.6, 1.3 Hz, C5-$H_2$), 1.01 (18H, s, 6 × CH(C**H**$_3$)$_2$), 0.97 – 1.04 (3H, m, 3 × C**H**$(CH_3)_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 148.3 (C Ar), 134.1 (C Ar), 133.6 (C Ar), 132.9 (C Ar), 131.3 (C Ar), 130.9 (C4), 125.51 (C Ar), 121.7 (C3), 43.8 (C1), 27.4 (C2), 18.8 (6 × CH(**C**$H_3)_2$), 11.2 (C5 + 3 × **C**H$(CH_3)_2$).

Data for both ***E*-1m** and ***Z*-1m**: $\mathbf{R_f}$ 0.30 (45% $Et_2O$ – pentane). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) $\nu_{max}$: 3347, 2980, 2888, 1540, 1382, 1164 $cm^{-1}$.

**(S12): Allyl(*tert*-butyl)diphenylsilane**

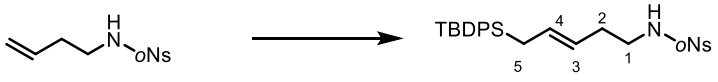



**S12**

To a solution of *tert*-butylchlorodiphenylsilane (1.00 mL, 3.91 mmol) in anhydrous THF (2.3 mL) was added allylmagnesium bromide (1.0 M in $Et_2O$, 4.3 mL, 4.3 mmol) at 0 °C. After warming to rt, the reaction mixture was left to stir for 16 h. The reaction was cooled to 0 °C before addition of aq. $NH_4Cl$. The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (0% → 5% $Et_2O$ – pentane) afforded **S12** as a colourless oil (458 mg, 42%).

Data for **S12**: $\mathbf{R_f}$ 0.40 (2% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.59 – 7.65 (4H, m, Ar), 7.32 – 7.43 (6H, m, Ar), 5.79 (1H, ddt, *J* = 17.0, 10.0, 7.9 Hz, C2-H), 4.92 (1H, dq, *J* = 17.0, 1.6 Hz, C3-$H_A$), 4.81 (1H, ddt, *J* = 10.0, 2.1, 1.2 Hz, C3-$H_B$), 2.20 (2H, dt, *J* = 7.9, 1.3 Hz, C1-$H_2$), 1.08 (9H, s, C(C$\mathbf{H_3}$)$_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 136.2 (4 × C Ar), 134.8 (2 × C Ar), 134.6 (C2), 129.2 (2 × C Ar), 127.7 (4 × C Ar), 114.6 (C3), 28.0 (C1), 18.9 (C(**C**$H_3$)$_3$), 18.6 (**C**($CH_3$)$_3$). *The spectroscopic properties were consistent with the data available in the literature.*[12]

**(1n): (3*E*)-2-Nitro-*N*-[5-(*tert*-butyldiphenylsilyl)pent-3-en-1-yl]benzenesulfonamide and (3*Z*)-2-Nitro-*N*-[5-(*tert*-butyldiphenylsilyl)pent-3-en-1-yl]benzenesulfonamide**




**S8** **1n** *E*:*Z* 3:1

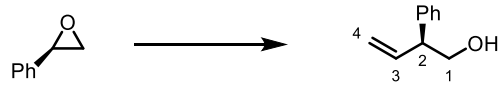
Prepared by **General Procedure C** using **S8** (177 mg, 0.691 mmol), **S12** (387 mg, 1.38 mmol) and Grubbs II (9.0 mg, 0.010 mmol) in PhMe at 100 °C for 16 h. Flash column chromatography (15% → 25% EtOAc – pentane) afforded **1n** as a partially separable 3:1 mixture of ***E*-1n** and ***Z*-1n**; a 16:1 mixture of ***E*-1n** + ***Z*-1n** was isolated as a yellow oil (18 mg, 1%) and a 3:1 mixture of ***E*-1n** + ***Z*-1n** was isolated as a yellow oil (285 mg, 85%).

Data for ***E*-1n**: $\mathbf{R_f}$ 0.50 (60% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.03 – 8.08 (1H, m, Ar), 7.78 – 7.82 (1H, m, Ar), 7.65 – 7.71 (2H, m, Ar), 7.52 – 7.58 (4H, m, Ar), 7.30 – 7.41 (6H, m, Ar), 5.37 (1H, dt, *J* = 15.4, 7.8 Hz, C4-H), 5.10 (1H, t, *J* = 6.5 Hz, *N*H), 5.05 (1H, dt, *J* = 15.4, 7.0 Hz, C3-H), 2.93 (2H, q, *J* = 6.5 Hz, C1-$H_2$), 2.07 (2H, d, *J* = 7.8 Hz, C5-$H_2$), 2.01 (2H, q, *J* = 7.0 Hz, C2-$H_2$), 1.02

(9H, s, C(C**H**$_3$)$_3$). **$^{13}$C NMR (100 MHz, CDCl$_3$) δ** 136.1 (4 × C Ar), 134.4 (3 × C Ar), 133.9 (C Ar), 133.5 (C Ar), 132.8 (C Ar), 131.2 (C Ar), 130.3 (C4), 129.3 (2 × C Ar), 127.7 (4 × C Ar), 125.4 (C Ar), 125.2 (C3), 45.8 (C1), 32.9 (C2), 28.0 (C(**C**H$_3$)$_3$), 18.5 (**C**(CH$_3$)$_3$), 17.1 (C5). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) $\nu_{max}$: 3347, 2980, 2888, 1539, 1426, 1163 cm$^{-1}$.

Partial data for ***Z*-1n** (from the mixture): **$^1$H NMR (400 MHz, CDCl$_3$) δ** 8.06 – 8.09 (1H, m, Ar), 7.82 – 7.86 (1H, m, Ar), 7.70 – 7.75 (2H, m, Ar), 7.52 – 7.58 (4H, m, Ar), 7.30 – 7.41 (6H, m, Ar), 5.51 – 5.61 (1H, m, C4-H), 5.13 (1H, t, *J* = 6.5 Hz, *N*H), 4.93 – 5.01 (1H, m, C3-H), 2.85 (2H, td, *J* = 7.0, 5.9 Hz, C1-H$_2$), 1.90-2.04 (4H, m, 1 × C2-H$_2$ + 1 × C5-H$_2$), 1.05 (9H, s, 3 × C(C**H$_3$**)$_3$). **$^{13}$C NMR (100 MHz, CDCl$_3$) δ** 136.2 (4 × C Ar), 134.4 (3 × C Ar), 133.9 (C Ar), 133.5 (C Ar), 132.8 (C Ar), 131.2 (C Ar), 129.4 (2 × Ar + C4), 127.7 (4 × C Ar), 125.4 (C Ar), 123.3 (C3), 43.5 (C1), 27.95 (C(**C**H$_3$)$_3$), 27.4 (C2), 18.5 (**C**(CH$_3$)$_3$), 12.9 (C5).

**((+)-S13): (+)-(*S*)-2-Phenylbut-3-en-1-ol**



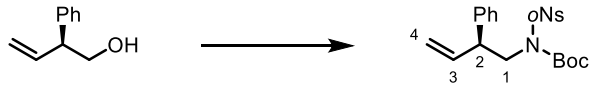

**(+)-S13**

To a solution of (*R*)-phenyloxirane (1.00 g, 8.33 mmol, 1.00 equiv.) and [Cu(COD)Cl]$_2$ (172 mg, 0.415 mmol) in THF (12 mL) at – 78 °C was added vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol). The reaction was allowed to warm to rt and stirred for 6 h before addition of aq. NH$_4$Cl and dilution with EtOAc. The aqueous later was extracted with EtOAc and the combined organic layers were washed with brine and dried over MgSO$_4$ before concentrating *in vacuo*. Flash column chromatography (15% → 20% Et$_2$O – pentane) afforded **(+)-S13** as a colourless oil (650 mg, 53%).

Data for **(+)-S13**: **R$_f$** 0.40 (40% Et$_2$O – pentane). **[α]$_D^{25}$** = +62.1 (0.01 g/mL, CHCl$_3$). **$^1$H NMR (400 MHz, CDCl$_3$) δ** 7.20 – 7.37 (2H, m, Ar), 7.20 – 7.27 (3H, m, Ar), 6.00 (1H, ddd, *J* = 17.6, 10.4, 7.7 Hz, C3-H), 5.15 – 5.23 (2H, m, C4-H$_2$), 3.81 (2H, t, *J* = 6.0 Hz, C1-H$_2$), 3.52 (1H, q, *J* = 7.3 Hz, C2-H), 1.57 (1H, *br*. s, *O*H). **$^{13}$C NMR (100 MHz, CDCl$_3$) δ** 140.7 (C Ar), 138.3 (C3), 128.9 (2 × C Ar), 128.1 (2 × C Ar), 127.1 (C Ar), 117.2 (C4), 66.2 (C1), 52.6 (C2). *The spectroscopic properties were consistent with the data available in the literature.*[13]

Racemic **(±)-S13** was made *via* the same procedure without using [Cu(COD)Cl]$_2$ (55%).

**((–)-S14): (–)-*tert*-Butyl (2*S*)-[(2-nitrophenyl)sulfonyl](2-phenylbut-3-en-1-yl)carbamate**



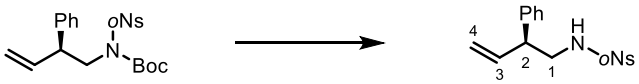

**(–)-S13** **(–)-S14**

Prepared by **General Procedure D** using **(–)-S13** (652 mg, 4.41 mmol), **S5** (1.60 g, 5.29 mmol), triphenylphosphine (1.73 g, 6.61 mmol) and DIAD (1.15 g, 5.73 mmol). Flash column chromatography (5% → 25% $Et_2O$ – pentane) afforded **(–)-S14** as a colourless oil (1.53 g, 81%).

Data for **(–)-S14**: **$R_f$** 0.30 (50% $Et_2O$ – pentane). **$[\alpha]_D^{25}$** = –0.164 (*c* = 10.0, $CHCl_3$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.24 – 8.28 (1H, m, Ar), 7.68 – 7.75 (3H, m, Ar), 7.29 – 7.37 (4H, m, Ar), 7.23 – 7.27 (1H, m, Ar), 6.11 (1H, ddd, *J* = 17.1, 10.2, 8.7 Hz, C3-H), 5.18 – 5.27 (4H, m, C4-$H_2$), 4.10 (1H, dd, *J* = 14.6, 9.2 Hz, C1-$H_A$), 4.01 (1H, dd, *J* = 14.6, 6.6 Hz, C1-$H_B$), 3.78 – 3.86 (1H, m, C2-H), 1.32 (9H, s, 3 × C(C**$H_3$**)$_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 150.4 (CO), 147.7 (C Ar), 140.9 (C Ar), 138.1 (C3), 134.2 (C Ar), 133.8 (C Ar), 133.7 (C Ar), 131.8 (C Ar), 128.8 (2 × C Ar), 128.2 (2 × C Ar), 127.2 (C Ar), 124.5 (C Ar), 117.7 (C4), 85.1 (**C**($CH_3$)$_3$), 52.7 (C1), 50.8 (C2), 27.9 (C(**C**$H_3$)$_3$). **HRMS** (ESI): calculated for $C_{21}H_{24}N_2O_6SNa$ $[M+Na]^+$ requires *m/z* 455.1253, found *m/z* 455.1239. **IR** (film) $\nu_{max}$: 2980, 2888, 2360, 1728, 1541, 1365 $cm^{-1}$.

Racemic **(±)-S14** was made *via* the same procedure using **(±)-S13** (55%).

**((+)-S15): (+)-(2*S*)-2-Nitro-*N*-(2-phenylbut-3-en-1-yl)benzenesulfonamide**



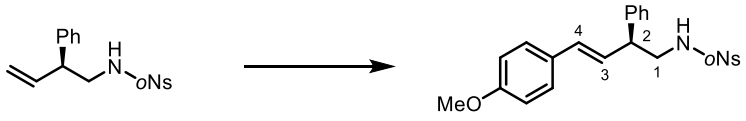

**(–)-S14** **(+)-S15**

Prepared by **General Procedure E** using **(–)-S14** (320 mg, 0.744 mmol) and TFA (0.29 mL, 3.72 mmol). Flash column chromatography (15% → 50% EtOAc – pentane) afforded **(+)-S15** as a colourless oil (240 mg, 97%).

Data for **(+)-S15**: **$R_f$** 0.40 (70% $Et_2O$ – pentane). **$[\alpha]_D^{25}$** = +0.182 (*c* = 10.0, $CHCl_3$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.09 – 8.13 (1H, m, Ar), 7.81 – 7.86 (1H, m, Ar), 7.70 – 7.76 (2H, m, Ar), 7.19 – 7.28 (3H, m, Ar), 7.05 – 7.09 (2H, m, Ar), 5.89 (1H, ddd, *J* = 17.5, 10.3, 7.5 Hz, C3-H), 5.34 (1H, t, *J* = 6.5 Hz, *N*H), 5.06 – 5.20 (2H, m, C4-$H_2$), 3.49 (1H, q, *J* = 7.5 Hz, C2-H), 3.37 – 3.43 (2H, m, C1-$H_2$). **$^{13}$C NMR (100 MHz, CDCl3) δ** 148.1 (C Ar), 139.9 (C Ar), 137.7 (C3), 133.9 (C Ar), 133.7 (C Ar), 133.0 (C Ar), 131.1 (C Ar), 129.1 (2 × C Ar), 127.7 (2 × C Ar), 127.5 (C Ar), 125.6 (C Ar), 117.6 (C4), 49.5 (C1), 48.0 (C2). **HRMS** (ESI): calculated for $C_{16}H_{17}N_2O_4S$ $[M+H]^+$ requires *m/z* 333.0909, found *m/z* 333.0909. **IR** (film) $\nu_{max}$: 3360, 2980, 2888, 2360, 1738, 1545 $cm^{-1}$.

Racemic (**±)-S15** was made *via* the same procedure using (**±)-S14** (81%).

**((–)-1o): (–)-(2*S*,3*E*)-*N*-[4-(4-Methoxyphenyl)-2-phenylbut-3-en-1-yl]-2-nitrobenzenesulfonamide**



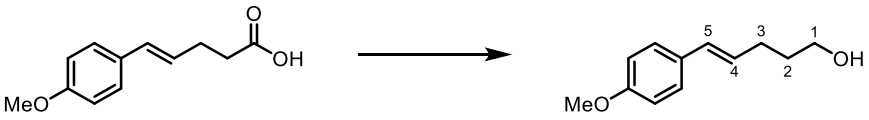

**(+)-S15** **1o**

Prepared by **General Procedure C** using **(+)-S15** (73 mg, 0.23 mmol), 4-methoxystyrene (61 mg, 0.45 mmol) and Grubbs II (3 mg, 0.03 mmol) in PhMe at 100 ˚C. Flash column chromatography (15% → 50% $Et_2O$ – pentane) afforded **(–)-1o** as a colourless oil (55 mg, 56%).

Data for **(–)-1o**: **$R_f$** 0.50 (75% $Et_2O$ – pentane). **$[\alpha]_D^{25}$** = –0.153 (*c* = 10.0, $CHCl_3$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.10 – 8.14 (1H, m, Ar), 7.65 – 7.79 (3H, m, Ar), 7.24 – 7.30 (2H, m, Ar), 7.17 – 7.24 (3H, m, Ar), 7.11 – 7.16 (2H, m, Ar), 6.81 (2H, d, *J* = 8.7 Hz, Ar), 6.34 (1H, d, *J* = 15.8 Hz, C4-H), 6.05 (1H, dd, *J* = 15.9, 7.9 Hz, C3-H), 5.40 (1H, t, *J* = 5.9 Hz, *N*H), 3.80 (OMe), 3.63 (1H, q, *J* = 7.6 Hz, C2-H), 3.47-3.52 (1H, m, C1-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.5 (C Ar), 148.0 (C Ar), 140.4 (C Ar), 134.0 (C Ar), 133.5 (C Ar), 132.9 (C Ar), 132.1 (C4), 131.0 (C Ar), 129.4 (C Ar), 129.1 (2 × C Ar), 127.7 (2 × C Ar), 127.6 (2 × C Ar), 127.5 (C Ar), 126.8 (C3), 125.6 (C Ar), 114.1 (2 × C Ar), 55.4 (OMe), 49.0 (C2), 48.6 (C1)**. HRMS** (ESI): calculated for $C_{23}H_{22}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 461.1147, found *m/z* 461.1147. **IR** (film) $\nu_{max}$: 3344, 2980, 2888, 1576, 1510, 1163 $cm^{-1}$.

Racemic (**±)-1o** was made *via* the same procedure using (**±)-S15** (56%).

**(S16): (*E*)-5-(4-Methoxyphenyl)pent-4-en-1-ol**

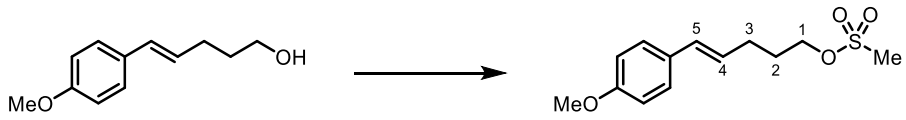



**S1** **S16**

Prepared by **General Procedure F** using **S1** (1.00 g, 4.85 mmol) and $LiAlH_4$ (1.0 M in THF, 6.0 mL, 6.0 mmol). Flash column chromatography (50% $Et_2O$ – pentane) afforded **S16** as a crystalline white solid (750 mg, 80%).

Data for **S16**: **$R_f$** 0.45 (50% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.27 (2H, d, *J* = 8.6 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.36 (1H, d, *J* = 15.7 Hz, C5-H), 6.09 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 3.80 (3H, s, OMe), 3.70 (2H, t, *J* = 6.5 Hz, C1-$H_2$), 2.29 (2H, qd, *J* = 7.1, 1.5 Hz, C3-$H_2$), 1.82 – 1.65 (2H, m, C2-$H_2$), 1.58 – 1.56 (1H, m, *O*H). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 158.9 (C Ar), 130.6 (C Ar), 129.9 (C5), 128.0 (C4), 127.2 (2 × C Ar), 114.1 (2 × C Ar), 62.6 (C1), 55.4 (OMe), 32.5 (C2), 29.4 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[14]

**(S17): (*E*)-5-(4-Methoxyphenyl)pent-4-en-1-yl methanesulfonate**

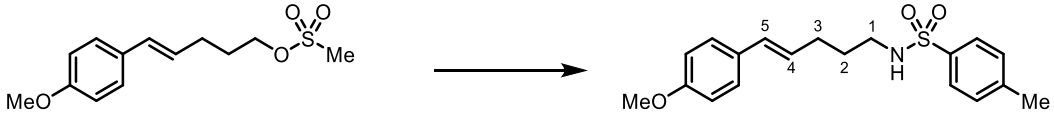



**S16** **S17**

Prepared by **General Procedure G** using **S16** (711 mg, 3.70 mmol), triethylamine (0.77 mL, 5.6 mmol) and methanesulfonic anhydride (805 mg, 4.62 mmol). Flash column chromatography (30% $Et_2O$ – pentane) afforded **S17** as a crystalline white solid (730 mg, 73%).

Data for **S17**: **$R_f$** 0.42 (50% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.27 (2H, d, *J* = 8.9 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.38 (1H, d, *J* = 15.8 Hz, C5-H), 6.02 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 4.28 (2H, t, *J* = 6.4 Hz, C1-$H_2$), 3.80 (3H, s, OMe), 3.00 (3H, s, $SO_2Me$), 2.33 (2H, *app.* qd, *J* = 7.3, 1.5 Hz, C3-$H_2$), 1.93 (2H, *app.* dq, *J* = 7.8, 6.5 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.1 (C Ar), 131.0 (C5), 130.2 (C Ar), 127.3 (2 × C Ar), 126.2 (C4), 114.1 (2 × C Ar), 69.4 (C1), 55.4 (OMe), 37.5 ($SO_2Me$), 29.0 (C2), 28.9 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[15]

**(4-Ts): (*E*)-*N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)-4-methylbenzenesulfonamide**

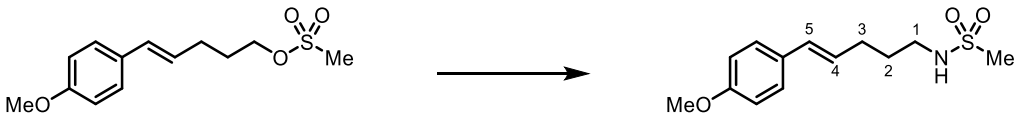



**S17** **4-Ts**

Prepared by **General Procedure H** using **S17** (100 mg, 0.370 mmol), *p*-toluenesulfonamide (94 mg, 0.55 mmol) and potassium hydroxide (31 mg, 0.55 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4-Ts** as a white solid (82 mg, 64%).

Data for **4-Ts**: **$R_f$** 0.29 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$)** 7.75 (2H, d, *J* = 8.3 Hz, Ar), 7.28 (2H, d, *J* = 7.9 Hz, Ar), 7.22 (2H, d, *J* = 8.6 Hz, Ar), 6.82 (2H, d, *J* = 8.7 Hz, Ar), 6.26 (1H, d, *J* = 15.8 Hz, C5-H), 5.93 (1H, dt, *J* = 15.8, 6.9 Hz, C4-H), 4.71 (1H, t, *J* = 6.2 Hz, *N*H), 3.80 (3H, s, OMe), 3.03 – 2.93 (2H, m, C1-$H_2$), 2.41 (3H, s, TsMe), 2.17 (2H, *app.* qd, *J* = 7.1, 1.5 Hz, C3-$H_2$), 1.63 (2H, p, *J* = 7.1 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.0 (C Ar), 143.5 (C Ar), 137.1 (C Ar), 130.4 (C5), 130.3 (C Ar), 129.8 (2 × C Ar), 127.2 (2 × C Ar), 127.2 (2 × C Ar), 126.8 (C4), 114.0 (2 × C Ar), 55.4 (OMe), 42.7 (C1), 29.9 (C3), 29.4 (C2), 21.6 (TsMe). *The spectroscopic properties were consistent with those reported in the literature.*[16]

**(4-Ms): (*E*)-*N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)methanesulfonamide**

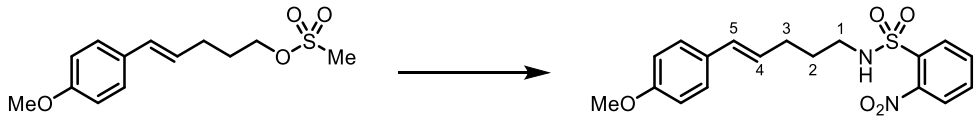


**S17** **4-Ms**

Prepared by **General Procedure H** using **S17** (100 mg, 0.370 mmol), methanesulfonamide (53 mg, 0.55 mmol) and potassium hydroxide (31 mg, 0.55 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4-Ms** as a white solid (53 mg, 53%).

Data for **4-Ms**: $\mathbf{R_f}$ 0.31 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.28 (2H, d, *J* = 8.8 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.37 (1H, d, *J* = 15.8 Hz, C5-H), 6.03 (1H, dt, *J* = 15.7, 7.0 Hz, C4-H), 4.40 (1H, t, *J* = 6.3 Hz, *N*H), 3.81 (3H, s, OMe), 3.19 (2H, q, *J* = 6.8 Hz, C1-$H_2$), 2.96 (s, 3H, $SO_2Me$), 2.34 – 2.23 (2H, m, C3-$H_2$), 1.76 (p, *J* = 7.2 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 158.9 (C Ar), 130.5 (C Ar), 130.2 (C5), 127.1 (2 × C Ar), 126.6 (C4), 114.0 (2 × C Ar), 55.3 (OMe), 42.8 (C1), 40.4 ($SO_2Me$), 29.9 (C3), 29.9 (C2). **HRMS** (ESI): calculated for $C_{13}H_{19}O_3NNaS$ $[M+Na]^+$ requires m/z 292.0978, found m/z 292.0978. **IR** (film) $\nu_{max}$: 3239, 2940, 2360, 1511, 1302, 1247, 1161, 1140, 1063, 1024 $cm^{-1}$. **mp** (90 – 92 °C, EtOAc).

**(4-*o*Ns): (*E*)-*N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)-2-nitrobenzenesulfonamide**

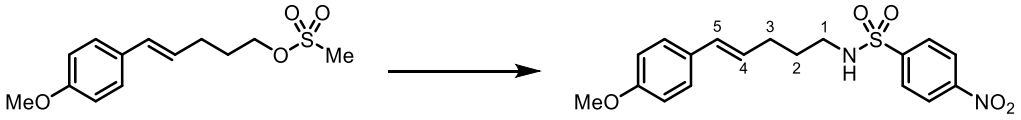


**S17** **4-*o*Ns**

Prepared by **General Procedure H** using **S17** (200 mg, 0.740 mmol), 2-nitrobenzenesulfonamide (224 mg, 1.11 mmol) and potassium hydroxide (62 mg, 1.1 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4-*o*Ns** as a white solid (169 mg, 61%).

Data for **4-*o*Ns**: $\mathbf{R_f}$ 0.21 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.21 – 7.99 (1H, m, Ar), 7.88 – 7.79 (1H, m, Ar), 7.77 – 7.62 (2H, m, Ar), 7.22 (2H, d, *J* = 8.6 Hz, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.29 (1H, d, *J* = 15.9 Hz, C5-H), 5.94 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 5.30 (1H, t, *J* = 6.1 Hz, *N*H), 3.80 (3H, s, OMe), 3.15 (2H, td, *J* = 7.0, 6.1 Hz, C1-$H_2$), 2.23 (2H, *app.* qd, *J* = 7.1, 1.5 Hz, C3-$H_2$), 1.71 (2H, p, *J* = 7.1 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.0 (C Ar), 133.6 (C Ar), 132.9 (C Ar), 131.2 (C Ar), 130.7 (C5), 130.2 (C Ar), 127.2 (2 × C Ar), 126.5 (C4), 125.5 (C Ar), 114.1 (2 × C Ar), 55.4 (OMe), 43.3 (C1), 29.9 (C3), 29.4 (C2). **HRMS** (ESI): calculated for $C_{18}H_{21}O_5NS$ $[M+H]^+$ requires m/z 377.1166, found m/z 377.1170. **IR** (film) $\nu_{max}$: 3265, 2981, 2361, 2341, 1670, 1606, 1539, 1510, 1464, 1440, 1363, 1336, 1298, 1247, 1163 $cm^{-1}$. **mp** (86 – 88 °C, EtOAc).

**(4-*p*Ns): (*E*)-*N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)-4-nitrobenzenesulfonamide**

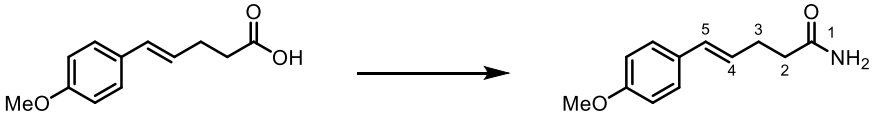



**S17** **4-*p*Ns**

Prepared by **General Procedure H** using **S17** (250 mg, 0.920 mmol), 4-nitrobenzenesulfonamide (281 mg, 1.39 mmol) and potassium hydroxide (78 mg, 1.4 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4-*p*Ns** as a white solid (308 mg, 89%).

Data for **4-*p*Ns**: **$R_f$** 0.21 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.38 – 8.28 (2H, m, Ar), 8.08 – 7.99 (2H, m, Ar), 7.26 – 7.17 (2H, m, Ar), 6.90 – 6.79 (2H, m, Ar), 6.27 (1H, d, *J* = 15.7 Hz, C5-H), 5.92 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 4.58 (1H, t, *J* = 6.1 Hz, *N*H), 3.81 (3H, s, OMe), 3.07 (2H, q, *J* = 6.7 Hz, C1-$H_2$), 2.21 (2H, *app.* qd, *J* = 7.1, 1.4 Hz, C3-$H_2$), 1.68 (2H, p, *J* = 7.1 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 146.1 (C Ar), 130.9 (C5), 130.0 (C Ar), 128.4 (2 × C Ar), 127.2 (2 × C Ar), 126.2 (C4), 124.5 (2 × C Ar), 114.2 (2 × C Ar), 55.5 (OMe), 42.9 (C1), 29.9 (C3), 29.4 (C2). *The spectroscopic properties were consistent with the data available in the literature.*[17]

**(S18): (*E*)-5-(4-Methoxyphenyl)pent-4-enamide**




**S1** **S18**

Prepared by **General Procedure I** using **S1** (1.67 g, 8.10 mmol) and oxalyl chloride (0.81 mL, 9.6 mmol). Recrystallisation from hot EtOAc afforded **S18** as a crystalline white solid (784 mg, 47%).

Data for **S18**: **$R_f$** 0.65 (5% MeOH – $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.27 (2H, d, *J* = 8.8 Hz, Ar), 6.83 (2H, d, *J* = 8.8 Hz, Ar), 6.40 (1H, d, *J* = 15.9 Hz, C5-H), 6.07 (1H, dt, *J* = 15.8, 6.9 Hz, C4-H), 5.50 (2H, *br.* s, $NH_2$), 3.80 (3H, s, OMe), 2.53 (2H, *app.* q, *J* = 6.6, C3-$H_2$), 2.45 – 2.32 (2H, m, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 174.7 (C1), 159.1 (C Ar), 130.7 (C5), 130.2 (C Ar), 127.3 (C4), 126.4 (2 × C Ar), 114.1 (2 × C Ar), 55.4 (OMe), 35.8 (C2), 28.8 (C3). **HRMS** (ESI): calculated for $C_{12}H_{16}ON$ $[M+H]^+$ requires m/z 206.1176, found m/z 206.1176. **IR** (film) $\nu_{max}$: 3386, 3191, 1648, 1604, 1510, 1440, 1282, 1174, 1029, 968, 847, 807 $cm^{-1}$. **mp** (165 – 167 °C, EtOAc).

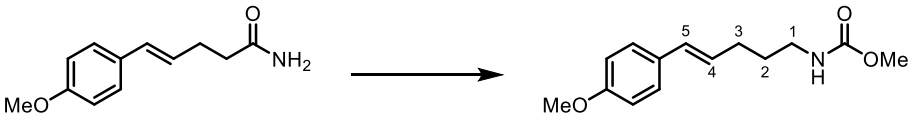
**(4-Cbz): Benzyl (*E*)-(5-(4-methoxyphenyl)pent-4-en-1-yl)carbamate**


**S18** **4-Cbz**

Prepared by **General Procedure J** using **S8** (120 mg, 0.600 mmol) and $LiAlH_4$ (33 mg, 0.90 mmol). Crude amine (80 mg, 0.42 mmol), triethylamine (0.07 mL, 0.5 mmol) and benzyl chloroformate (0.07 mL, 0.5 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4-Cbz** as a white solid (107 mg, 73%).

Data for **4-Cbz**: **$R_f$** 0.30 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.43 – 7.20 (5H, m, Ar), 7.28 – 7.19 (2H, m, Ar), 6.83 (2H, d, *J* = 8.8 Hz, Ar), 6.34 (1H, d, *J* = 15.8 Hz, C5-H), 6.04 (1H, dt, *J* = 15.5, 6.9 Hz, C4-H), 5.10 (2H, s, $CH_2Ph$), 4.77 (1H, *br*. s, *N*H), 3.80 (3H, s, OMe), 3.25 (2H, q, *J* = 6.7 Hz, C1-$H_2$), 2.31 – 2.15 (2H, m, C3-$H_2$), 1.68 (2H, p, *J* = 7.2 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 158.9 (C6), 136.8 (C Ar), 130.5 (C Ar), 130.1 (C5), 128.7 (2 × C Ar), 128.3 (C Ar), 128.3 (2 × C Ar), 127.5 (C Ar), 127.2 (2 × C Ar), 114.1 (2 × C Ar), 66.8 ($CH_2Ph$), 55.4 (OMe), 40.8 (C1), 30.3 (C2), 29.9 (C3). **HRMS** (ESI): calculated for $C_{20}H_{23}O_3NNa$ $[M+Na]^+$ requires m/z 348.1570, found m/z 348.1570. **IR** (film) $\nu_{max}$: 3328, 2970, 2359, 1686, 1542, 1510, 1247, 1231, 1175, 1143 $cm^{-1}$. **mp** (68 – 70 °C, EtOAc).

**(4a): Methyl (*E*)-(5-(4-methoxyphenyl)pent-4-en-1-yl)carbamate**



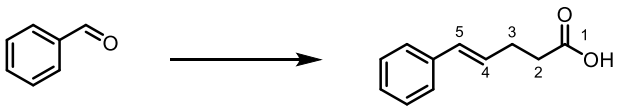

**S18** **4a**

Prepared by **General Procedure J** using **S18** (726 mg, 3.54 mmol) and $LiAlH_4$ (201 mg, 3.51 mmol). Crude amine (411 mg, 2.15 mmol), triethylamine (0.37 mL, 2.7 mmol) and methyl chloroformate (0.21 mL, 2.7 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4a** as a white solid (418 mg, 78%).

Data for **4a**: **$R_f$** 0.16 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.26 (2H, d, *J* = 8.6 Hz, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.34 (1H, d, *J* = 15.8 Hz, C5-H), 6.04 (1H, dt, *J* = 15.8, 6.9 Hz, C4-H), 4.69 (1H, *br*. s, *N*H), 3.80 (3H, s, OMe), 3.66 (3H, s, OMe), 3.23 (2H, q, *J* = 6.8 Hz, C1-$H_2$), 2.28 – 2.17 (2H, m, C3-$H_2$), 1.67 (2H, p, *J* = 7.2 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 158.6 (CO), 130.5 (C Ar), 130.1 (C5), 127.5 (C4), 127.2 (2 × C Ar), 114.1 (2 × C Ar), 55.4 (OMe), 52.2 (OMe), 40.8 (C1), 30.3 (C3), 29.9 (C2). **HRMS** (ESI): calculated for $C_{14}H_{19}O_3NNa$ $[M+Na]^+$ requires m/z 272.1257,

found m/z 272.1526. **IR** (film) $\nu_{max}$: 3327, 2929, 1688, 1607, 2545, 1511, 1271, 1251, 1176, 1030 $cm^{-1}$. **mp** (74 – 76 °C, EtOAc).

**(S19): (*E*)-5-Phenylpent-4-enoic acid**

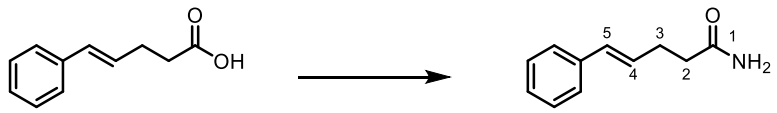



**S19**

Prepared by **General Procedure A** using benzaldehyde (1.38 mL, 13.6 mmol), (3-carboxypropyl)triphenylphosphonium bromide (7.00 g, 16.3 mmol), NaHMDS (2.0 M in THF, 16.3 mL, 32.6 mmol). Flash column chromatography (80% $Et_2O$ – pentane + 1% acetic acid) followed by trituration with ice cold hexane (3 × 10 mL) afforded **S19** as a crystalline white solid (1.52 g, 63%).

Data for **S19**: **$R_f$** 0.54 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.39 – 7.28 (4H, m, Ar), 7.22 (1H, m, Ar), 6.46 (1H, d, *J* = 16.0 Hz, C5-H), 6.24 (1H, m, C4-H), 2.61-2.49 (4H, m, C2-$H_2$ + C3-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 179.2 (C1) 137.3 (C Ar), 131.2 (C5), 128.5 (2 × C Ar), 128.0 (C4), 127.2 (2 × C Ar), 126.1 (C Ar), 33.8 (C2), 27.9 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[18]

**(S20): (*E*)-5-Phenylpent-4-enamide**

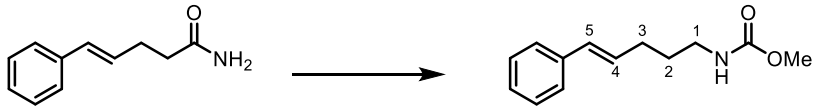



**S19** **S20**

Prepared by **General Procedure I** using **S19** (500 mg, 2.84 mmol) and oxalyl chloride (0.29 mL, 3.4 mmol). Recrystallisation from hot EtOAc afforded **S20** as a crystalline white solid (350 mg, 70%).

Data for **S20**: **$R_f$** 0.59 (10% MeOH – $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.26 (4H, m, Ar), 7.24 – 7.17 (1H, m, Ar), 6.46 (1H, dt, *J* = 15.7, 1.5 Hz, C5-H), 6.22 (1H, dt, *J* = 15.8, 6.9 Hz, C4-H), 5.50 (2H, *br*. s, *N*$H_2$), 2.75 – 2.52 (2H, m, C3-$H_2$), 2.47 – 2.34 (2H, m, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 174.8 (C1), 137.4 (C Ar), 131.3 (C5), 128.7 (C4 + 2 × C Ar), 127.3 (C Ar), 126.2 (2 × C Ar), 35.6 (C2), 28.8 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[16]

**(4b): Methyl (*E*)-(5-phenylpent-4-en-1-yl)carbamate**

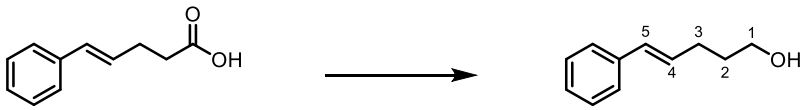



**S20** **4b**

Prepared by **General Procedure J** using **S20** (300 mg, 1.71 mmol) and $LiAlH_4$ (97 mg, 2.6 mmol). Crude amine (270 mg, 1.67 mmol), triethylamine (0.29 mL, 2.1 mmol) and methyl chloroformate (0.16 mL, 2.1 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4b** as a yellow oil (112 mg, 30%).

Data for **4b**: **$R_f$** 0.43 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.37 – 7.25 (4H, m, Ar), 7.24 – 7.17 (1H, m, Ar), 6.41 (1H, d, *J* = 15.8, C5-H), 6.19 (1H, dt, *J* = 15.8, 6.9 Hz, C4-H), 4.85 (1H, *br*. s, *N*H), 3.66 (3H, s, C7-$H_3$), 3.23 (2H, q, *J* = 6.8 Hz, C1-$H_2$), 2.33 – 2.08 (2H, m, C3-$H_2$), 1.68 (2H, p, *J* = 7.3 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 157.2 (C6), 137.6 (C Ar), 130.6 (C5), 129.6 (C4), 128.6 (2 × C Ar), 127.1 (C Ar), 126.0 (2 × C Ar), 52.1 (C7), 40.7 (C1), 30.2 (C3), 29.7 (C2). **HRMS** (ESI): calculated for $C_{13}H_{18}O_2N$ $[M+H]^+$ requires m/z 220.1332, found m/z 220.1333. **IR** (film) $\nu_{max}$: 3650, 3338, 3959, 3024, 2981, 2889, 2360, 2339, 1699, 1531, 1253, 966 $cm^{-1}$.

**(S21): (*E*)-5-Phenylpent-4-en-1-ol**

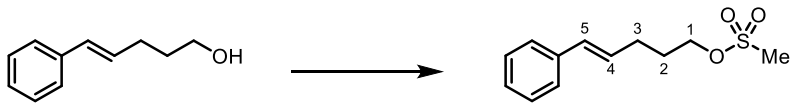



**S19** **S21**

Prepared by **General Procedure F** using **S19** (1.00 g, 5.67 mmol) and $LiAlH_4$ (1.0 M $LiAlH_4$ in THF, 6.8 mL, 6.8 mmol). Flash column chromatography (50% $Et_2O$ – pentane) afforded **S21** as a colourless liquid (799 mg, 87%).

Data for **S21**: **$R_f$** 0.45 (50% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.40 – 7.28 (4H, m, Ar), 7.22 (1H, m, 1H, Ar), 6.44 (1H, d, *J* = 15.7 Hz, C5-H), 6.25 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 3.71 (2H, t, *J* = 6.5 Hz, C1-$H_2$), 2.40 – 2.24 (2H, m, C3-$H_2$), 1.76 (2H, *app*. dq, *J* = 9.5, 6.5 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 137.6 (C Ar), 130.3 (C5), 130.0 (C4), 128.4 (2 × C Ar), 126.9 (2 × C Ar), 125.9 (Ar), 62.28 (C1), 32.2 (C2), 29.3 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[19]

**(S22): (*E*)-5-Phenylpent-4-en-1-yl methanesulfonate**

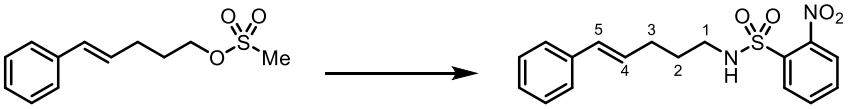



**S21** **S22**

Prepared by **General Procedure G** using **S21** (500 mg, 3.08 mmol), triethylamine (0.64 mL, 4.6 mmol) and methanesulfonic anhydride (644 mg, 3.70 mmol). Flash column chromatography (30% $Et_2O$ – pentane) afforded **S22** as a colourless liquid (600 mg, 81%).

Data for **S22**: **$R_f$** 0.42 (50% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.40 – 7.28 (4H, m, Ar), 7.22 (1H, m, Ar), 6.45 (1H, d, *J* = 15.8 Hz, C5-H), 6.18 (1H, dt, *J* = 15.8, 7.0 Hz, C4-H), 4.28 (2H, t, *J* = 6.4 Hz, C1-$H_2$), 3.00 (3H, s, $SO_2Me$) 2.36 (2H, dt, *J* = 7.3, 7.0 Hz, C3-$H_2$), 1.99 – 1.89 (2H, m, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 137.2 (C Ar), 131.4 (C5), 128.5 (2 × C Ar), 128.2 (2 × C Ar), 127.2 (C4), 126.0 (C Ar), 69.2 (C1), 37.3 ($SO_2Me$), 28.7 (C2), 28.7 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[15]

**(4b-Ns): (*E*)-2-Nitro-*N*-(5-phenylpent-4-en-1-yl)benzenesulfonamide**

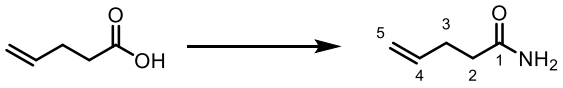



**S22** **4b-Ns**

Prepared by **General Procedure H** using **S22** (1.20 g, 5.00 mmol), 2-nitrobenzenesulfonamide (1.52 g, 7.50 mmol) and potassium hydroxide (421 mg, 7.50 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4b-Ns** as a white solid (902 mg, 52%).

Data for **4b-Ns**: **$R_f$** 0.21 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.12 (1H, m, Ar), 7.82 (1H, m, Ar), 7.76 – 7.67 (2H, m, Ar), 7.31 – 7.27 (4H, m, Ar), 7.21 (1H, m, Ar), 6.35 (1H, d, *J* = 15.7 Hz , C5-H), 6.10 (1H, dt, *J* = 15.7, 7.0 Hz, C4-H), 5.32 (1H, t, *J* = 6.1 Hz, *N*H), 3.16 (2H, q, *J* = 6.1, 5.5 Hz, C1-$H_2$), 2.26 (2H, *app*. qd, *J* = 7.1, 1.5 Hz, C3-$H_2$), 1.73 (2H, p, *J* = 7.0 Hz, C2-$H_2$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 148.1 (C Ar), 137.3 (C Ar), 133.7 (C Ar), 133.5 (C Ar), 132.7 (C Ar), 131.2 (C5), 131.0 (C Ar), 128.6 (C4), 128.5 (2 × C Ar), 127.1 (C Ar), 126.0 (2 × C Ar), 125.3 (C Ar), 43.1 (C1), 29.7 (C3), 29.1 (C2). **HRMS** (ESI): calculated for $C_{17}H_{19}O_4N_2S$ $[M+H]^+$ requires m/z 347.1060, found m/z 347.1062. **IR** (film) $\nu_{max}$: 3344, 3025, 2925, 1538, 1412, 1342, 1165, 740 $cm^{-1}$. **mp** (92 – 94 °C, EtOAc).

**(S23): Pent-4-enamide**

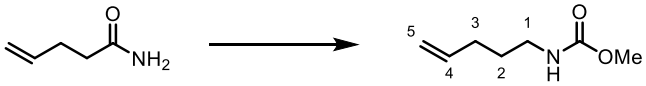


**S23**

Prepared by **General Procedure I** using pent-4-enoic acid (2.04 mL, 20.0 mmol) and oxalyl chloride (2.04 mL, 24.0 mmol). Recrystallisation from hot EtOAc afforded **S23** as a crystalline white solid (780 mg, 39%).

Data for **S23**: **$R_f$** 0.62 (10% MeOH – $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 6.13 – 5.42 (2H, *br*. s, *N*$H_2$), 5.83 (1H, *app*. dddd, *J* = 16.6, 12.4, 8.0, 5.1 Hz, C4-H), 5.17 – 4.90 (2H, m, C5-$H_2$), 2.43 – 2.26 (4H, m, 2 × C2-$H_2$ + 2 × C3-$H_2$).**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 175.3 (C1), 137.0 (C4), 115.8 (C5), 35.1 (C2), 29.4 (C3). *The spectroscopic properties were consistent with the data available in the literature.*[20]

**(S24): Methyl pent-4-en-1-ylcarbamate**

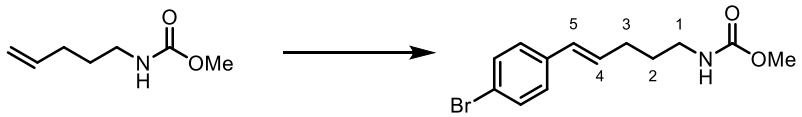


**S23** **S24**

Prepared by **General Procedure J** *(with modification)* using **S23** (1.00 g, 10.0 mmol) and $LiAlH_4$ (574 mg, 15.0 mmol). Crude amine hydrochloride salt (787 mg, 6.47 mmol), triethylamine (2.71 mL, 19.4 mmol) and methyl chloroformate (0.63 mL, 8.1 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **S24** as a colourless oil (450 mg, 31%).

Data for **S24**: **$R_f$** 0.50 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.76 (1H, ddt, *J* = 16.9, 10.2, 6.6 Hz, C4-H), 5.00 (1H, dq, *J* = 17.1, 1.7 Hz, C5-$H_A$), 4.95 (1H, dq, *J* = 10.2, 1.4 Hz, C5-$H_B$), 4.82 (1H, *br*. s, *N*H), 3.62 (3H, s, OMe), 3.15 (2H, q, *J* = 6.8 Hz, C1-$H_2$), 2.05 (2H, td, *J* = 8.0, 6.0 Hz, C3-$H_2$), 1.57 (2H, p, *J* = 7.3 Hz, C2-$H_2$).**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 157.2 (CO), 137.8 (C4), 115.2 (C5), 52.0 (OMe), 40.6 (C1), 31.0 (C3), 29.2 (C2). **HRMS** (ESI): calculated for $C_7H_{14}O_2N$ $[M+H]^+$ requires m/z 144.1019, found m/z 144.1018. **IR** (film) $\nu_{max}$: 3649, 3331, 3078, 2980, 2359, 2342, 1697, 1536, 1449, 1256 $cm^{-1}$.

**(4c): Methyl (*E*)-(5-(4-bromophenyl)pent-4-en-1-yl)carbamate**




**S24** **4c**

Prepared by **General Procedure C** using **S24** (200 mg, 1.40 mmol), 4-bromostyrene (0.37 mL, 2.80 mmol), Grubbs II (58 mg, 0.070 mmol) in PhMe (5 mL). Flash column chromatography (gradient elution 0% → 15% EtOAc – pentane) followed by recrystallisation from hot EtOAc afforded **4c** as a white solid (91 mg, 22%).

Data for **4c**: **$R_f$** 0.38 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.48 – 7.34 (2H, m, Ar), 7.25 – 7.06 (2H, m, Ar), 6.34 (1H, d, *J* = 15.8 Hz, C5-H), 6.18 (1H, dt, *J* = 15.9, 6.8 Hz, C4-H), 4.69 (1H, *br*. s, *N*H), 3.66 (3H, s, OMe), 3.23 (2H, q, *J* = 6.8 Hz, C1-$H_2$), 2.40 – 2.10 (2H, m, C3-$H_2$), 1.68 (2H, p, *J* = 7.3 Hz, C2-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 157.2 (CO), 136.6 (C Ar), 131.7 (2 × C Ar), 130.6 (C5), 129.6 (C4), 127.6 (2 × C Ar), 120.8 (C Ar), 52.2 (OMe), 40.7 (C1), 30.3 (C3), 29.7 (C2). **HRMS** (ESI): calculated for $C_{13}H_{17}O_2N^{78}BrNa$ $[M+Na]^+$ requires m/z 336.0206, found m/z 336.0205. **IR** (film) $\nu_{max}$: 3650, 3338, 2981, 2886, 2360, 2336, 1690, 1538, 1487, 1461 $cm^{-1}$. **mp** (78 – 80 °C, EtOAc).

**(4d): Methyl ((4*E*,6*E*)-7-(4-methoxyphenyl)hepta-4,6-dien-1-yl)carbamate**

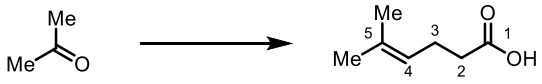

**S24** **4d**

Prepared by **General Procedure C** using **S24** (400 mg, 2.86 mmol), **S9** (918 mg, 5.73 mmol), Grubbs I (115 mg, 0.140 mmol) in PhMe (12 mL) at 100 °C. Flash column chromatography (gradient elution 0% → 15% EtOAc – pentane) followed by recrystallisation from hot EtOAc afforded **4d** as a crystalline white solid (125 mg, 16%).

Data for **4d**: **$R_f$** 0.43 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.31 (2H, d, *J* = 8.7 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.61 (1H, dd, *J* = 15.7, 10.3 Hz, C6-H), 6.40 (1H, d, *J* = 15.7 Hz, C7-H), 6.19 (1H, dd, *J* = 14.0, 10.3 Hz, C5-H), 5.73 (1H, dt, *J* = 14.7, 7.0 Hz, C4-H), 4.69 (1H, *br*. s, *N*H), 3.80 (3H, s, OMe), 3.66 (3H, s, OMe), 3.21 (2H, q, *J* = 7.0 Hz, C1-$H_2$), 2.17 (2H, td, *J* = 7.3, 1.5 Hz, C3-$H_2$), 1.63 (2H, p, *J* = 7.3 Hz, C2-$H_2$).**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.2 (CO), 133.0 (C4), 131.6 (C5), 130.5 (C Ar), 130.3 (C7), 127.5 (2 × C Ar), 127.2 (C6), 114.2 (2 × C Ar), 55.4 (OMe), 52.1 (OMe), 40.7 (C1), 30.1 (C3), 29.8 (C2). **HRMS** (ESI): calculated for $C_{16}H_{22}O_3N$ $[M+H]^+$ requires

m/z 276.1594, found m/z 276.1596. **IR** (film) $\nu_{max}$: 3331, 3015, 2363, 1692, 1602, 1552, 1510, 1284, 1254, 1030, 985, 834 $cm^{-1}$. **mp** (105 – 107 °C, EtOAc).

**(S25): 5-Methylhex-4-enoic acid**

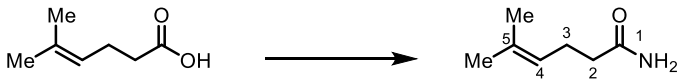



**S25**

Prepared by **General Procedure A** using acetone (0.73 mL, 10 mmol), (3-carboxypropyl)triphenylphosphonium bromide (5.15 g, 12.0 mmol), NaHMDS (2.0 M in THF, 12.0 mL, 24.0 mmol). Flash column chromatography (80% $Et_2O$/pentane + 1% acetic acid) afforded **S25** as a yellow oil (903 mg, 70%).

Data for **S25**: **$R_f$** 0.54 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 5.01 (1H, m, C4-H), 2.44 – 2.13 (4H, m, 2 × C2-$H_2$ + 2 × C3-$H_2$), 1.60 (3H, d, *J* = 1.3 Hz, Me), 1.53 (3H, d, *J* = 1.3 Hz, Me). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 179.2 (C1), 133.6 (C5), 122.2 (C4), 34.3 (C2), 25.8 (C3), 23.5 (Me), 17.8 (Me). *The spectroscopic properties were consistent with the data available in the literature.*[21]

**(S26): 5-Methylhex-4-enamide**

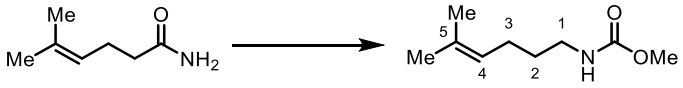



**S25** **S26**

Prepared by **General Procedure I** using **S25** (500 mg, 3.90 mmol) and oxalyl chloride (0.40 mL, 4.70 mmol). Recrystallisation from hot EtOAc afforded **S26** as a crystalline white solid (418 mg, 84%).

Data for **S26**: **$R_f$** 0.54 (10% MeOH, $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 6.08 (1H, *br*. s, *N*H), 5.69 (1H, *br*. s, *N*H), 5.15 – 5.05 (1H, m, C4-H), 2.33 – 2.25 (2H, m, C3-$H_2$), 2.25 – 2.19 (2H, m, C2-$H_2$), 1.67 (3H, s, Me), 1.60 (3H, s, Me). **$^{13}$C NMR (100 MHz, $CDCl_3$)** 175.9 (C1), 133.5 (C5), 122.8 (C4), 36.1 (C2), 25.9 (Me), 24.3 (C3), 17.9 (Me). **HRMS** (ESI): calculated for $C_7H_{14}ON$ $[M+H]^+$ requires m/z 128.1070, found m/z 128.1070. **IR** (film) $\nu_{max}$: 3366, 3186, 2969, 1678, 1657, 1452, 1411, 1318, 952, 817 $cm^{-1}$. **mp** (87 – 89 °C, EtOAc).

**(4e): Methyl (5-methylhex-4-en-1-yl) carbamate**



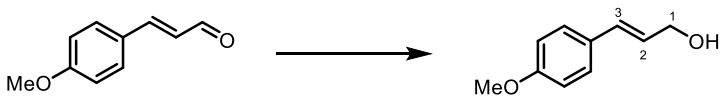

**S26** **4e**

Prepared by **General Procedure J** *(with modification)* using **S26** (300 mg, 2.37 mmol) and $LiAlH_4$ (574 mg, 3.56 mmol). Crude amine hydrochloride salt (208 mg, 1.39 mmol), triethylamine (0.58 mL, 4.2 mmol) and methyl chloroformate (0.13 mL, 1.7 mmol). Flash column chromatography (25% EtOAc – pentane) afforded **4e** as a colourless oil (90 mg, 27%).

Data for **4e**: $\mathbf{R_f}$ 0.38 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.07 (1H, *app.* dddd, *J* = 7.2, 5.7, 2.9, 1.5 Hz, C4-H), 4.73 (1H, *br.* s, *N*H), 3.63 (3H, s, C8-$H_3$), 3.14 (2H, q, *J* = 6.7 Hz, C1-$H_2$), 1.99 (2H, q, *J* = 7.4 Hz, C3-$H_2$), 1.66 (3H, s, Me), 1.58 (3H, s, Me), 1.51 (2H, p, *J* = 7.4 Hz, C2-$H_2$).**$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 157.2 (C7), 132.4 (C4), 123.6 (C5), 52.0 (C8), 40.8 (C1), 30.1 (C3), 25.8 (Me), 25.3 (C2), 17.8 (Me). **HRMS** (ESI): calculated for $C_9H_{17}O_2N$ $[M+H]^+$ requires m/z 172.1332, found m/z 172.1335. **IR** (film) $\nu_{max}$: 3112, 1698, 1536, 1525, 1449, 1380, 1262, 1193, 1145, 779 $cm^{-1}$.

Preparation of Electrophiles

**(2d): (2*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol**

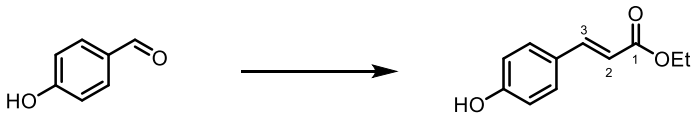



**2d**

To a solution of 4-methoxycinnamaldehyde (4.80 g, 29.6 mmol) in MeOH (56 mL) under Ar was added $NaBH_4$ (840 mg, 17.8 mmol) portionwise at 0 °C. The reaction mixture was warmed to rt after 30 min at 0 °C. After an additional 1 h at rt the reaction was quenched with aq. $NH_4Cl$. The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with brine and dried over $MgSO_4$ before concentrating *in vacuo*. Recrystallisation from $Et_2O$ afforded **2d** as a white solid (4.85 g, 98%).

Data for **2d**: **$R_f$** 0.50 (80% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.32 (2H, d, *J* = 8.7 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 6.56 (1H, d, *J* = 15.9 Hz, C3-H), 6.24 (1H, dt, *J* = 15.8, 6.0 Hz, C2-H), 4.29 (2H, dd, *J* = 5.9, 1.2 Hz, C1-$H_2$), 3.81 (3H, s, OMe), 1.53 (1H, *br*. s, *O*H). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.5 (C Ar), 131.1 (C3), 129.6 (C Ar), 127.8 (2 × C Ar), 126.4 (C2), 114.2 (2 × C Ar), 64.1 (C1), 55.43 (OMe). *The spectroscopic properties were consistent with the data available in the literature.*[22]

**(S27): Ethyl (*E*)-3-(4-hydroxyphenyl)acrylate**

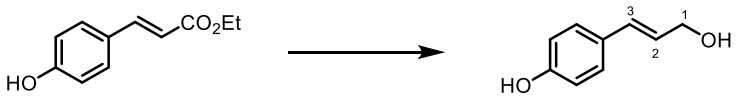



**S27**

To a solution of 4-hydroxybenzaldehyde (305 mg, 2.50 mmol) in $CH_2Cl_2$ (2.5 mL) was added ethyl(triphenylphosphoranylidene)acetate (1.34 g, 3.75 mmol) and stirred for 16 h. Consumption of aldehyde was monitored by TLC and upon completetion the solvent was removed *in vacuo*. Flash column chromatography (10% → 20% EtOAc – pentane) afforded **S27** as a white solid (364 mg, 76%).

Data for **S27**: **$R_f$** 0.50 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.63 (1H, d, *J* = 16.0 Hz, C3-H), 7.50 – 7.35 (2H, m, Ar), 6.94 – 6.78 (2H, m, Ar), 6.30 (1H, d, *J* = 15.9 Hz, C2-H), 4.26 (2H, q, *J* = 7.1 Hz, C**$H_2$**$CH_3$), 1.34 (3H, t, *J* = 7.1 Hz, $CH_2$C**$H_3$**). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 166.8 (CO), 158.1 (C Ar), 144.9 (C3), 130.1 (2 × C Ar), 127.2 (C Ar), 116.0 (2 × C Ar), 115.5 (C2), 60.8 (**C**$H_2CH_3$), 14.5 ($CH_2$**C**$H_3$). *The spectroscopic properties were consistent with the data available in the literature.*[23]

**(2i): (*E*)-4-(3-Hydroxyprop-1-en-1-yl)phenol**

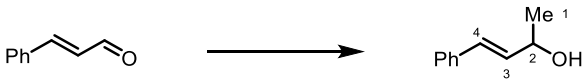



**S27** **2i**

To a solution of **S27** (200 mg, 1.04 mmol) in $CH_2Cl_2$ (6.5 mL) was added DIBALH (1.0 M in $CH_2Cl_2$, 3.60 mL, 3.64 mmol) dropwise at -78 ˚C before warming to rt. After 1 h the solution was cooled to -78 ˚C and aq. sat. Rochelle salts (3.5 mL) were added before warming to rt. To solution was stirred vigorously for 2 h before diluted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers washed with brine and dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (10% → 35% EtOAc – pentane) afforded **2i** as a white solid (135 mg, 90%).

Data for **2i**: **$R_f$** 0.27 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, DMSO) δ** 9.44 (1H, s, *O*H), 7.22 (2H, d, *J* = 8.6 Hz, Ar), 6.70 (2H, d, *J* = 8.6 Hz, Ar), 6.42 (1H, dt, *J* = 16.0, 1.7 Hz, C3-H), 6.12 (1H, dt, *J* = 15.9, 5.4 Hz, C2-H), 4.06 (2H, td, *J* = 5.5, 1.6 Hz, C1-$H_2$). **$^{13}$C NMR (101 MHz, DMSO) δ** 156.8 (C Ar), 128.7 (C3), 127.9 (C Ar), 127.4 (2 × C Ar), 127.2 (C2), 115.4 (2 × C Ar), 61.73 (C1). *The spectroscopic properties were consistent with the data available in the literature.*[24]

**(2m): (±)-(*E*)-4-Phenylbut-3-en-2-ol**

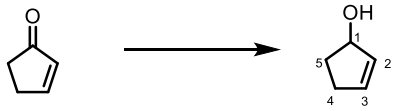



**2m**

To a solution of cinamaldehyde (1.26 mL, 10.0 mmol) in THF (15 mL) was added MeMgBr (3.0 M in $Et2_O$, 3.7 mL, 11 mmol) dropwise at 0 °C. After 30 min at 0 °C the reaction was warmed to rt and quenched with sat. aq. $NH_4Cl$ (10 mL). The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with brine, dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (50% $Et_2O$ – pentane) afforded **2m** as a colourless oil (1.39 g, 94%).

Data for **2m**: **$R_f$** 0.30 (80% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, CDCl3) δ** 7.36 – 7.41 (2H, m, Ar), 7.29 – 7.35 (2H, m, Ar), 7.21 – 7.27 (1H, m, Ar), 6.57 (1H, d, *J* = 15.8 Hz, C4-H), 6.27 (1H, dd, *J* = 15.9, 6.4 Hz, C3-H), 4.44 – 4.55 (1H, m, C2-H), 1.66 (1H, *br*. s, *O*H), 1.38 (3H, d, *J* = 6.4 Hz, C1-$H_3$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 136.8 (C Ar), 133.7 (C3), 129.5 (C4), 128.7 (2 × C Ar), 127.8 (C Ar), 126.6 (2 × C Ar), 69.1 (C2), 23.5 (C1). *The spectroscopic properties were consistent with the data available in the literature.*[25]

**(2o): (±)-Cyclopent-2-en-1-ol**

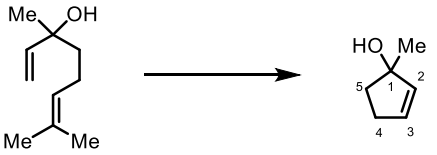



**2o**

To a solution of cerium trichloride (976 mg, 3.96 mmol) in MeOH (10 mL) was added cyclopent-2-enone (0.50 mL, 6.0 mmol). After 5 min, sodium borohydride (454 mg, 12.0 mmol) was added portionwise before stirring at rt for 15 min. $H_2O$ was added until a clear solution was observed, the aqueous later was extracted with Et2O and the combined organic layers were washed with brine, dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (20% $Et_2O$ – pentane) afforded **2o** as a colourless oil (368 mg, 73%).

Data for **2o**: **$R_f$** 0.45 (50% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 5.93 – 5.99 (1H, m, C3-H), 5.78 – 5.84 (1H, m, C2-H), 4.82-4.88 (1H, m, C1-H), 2.49 (1H, ddt, *J* = 16.5, 10.9, 5.4 Hz, C4-$H_A$), 2.17 – 2.31 (2H, m, 1 × C4-$H_B$ + 1 × C5-$H_A$), 1.95 (1H, *br*. s, *O*H), 1.61 – 1.76 (1H, m, C5-$H_B$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 135.2 (C3), 133.4 (C2), 77.6 (C1), 33.3 (C5), 31.1 (C4). *The spectroscopic properties were consistent with the data available in the literature.*[25]

**(2p): (±)-1-Methylcyclopent-2-en-1-ol**

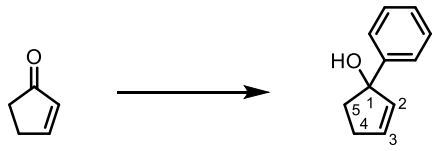



**2p**

Prepared according to **General Procedure C** using linalool (500 mg, 3.23 mmol) and Grubbs I (133 mg, 0.161 mmol) at rt in $CHCl_3$. Flash column chromatography (20% → 50% $Et_2O$ – pentane) afforded **2p** as a yellow oil (250 mg, 79%).

Data for **2p**: **$R_f$** 0.40 (80% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 5.81 (1H, dt, *J* = 5.4, 2.3 Hz, C3-H), 5.69 (1H, dt, *J* = 5.4, 2.3 Hz, C2-H), 2.48 (1H, m, C4-$H_A$), 2.30 (1H, m, C4-$H_B$), 1.96 (1H, ddd, *J* = 13.4, 8.1, 4.8 Hz, C5-$H_A$), 1.89 (1H, ddd, *J* = 13.4, 8.1, 4.8 Hz, C5-$H_B$), 1.37 (3H, s, Me). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 138.0 (C2), 132.8 (C3), 83.6 (C1), 39.8 (C5), 31.2 (C4), 27.6 (Me). *The spectroscopic properties were consistent with the data available in the literature.*[25]

**(2q): (±)-1-Phenylcyclopent-2-en-1-ol**



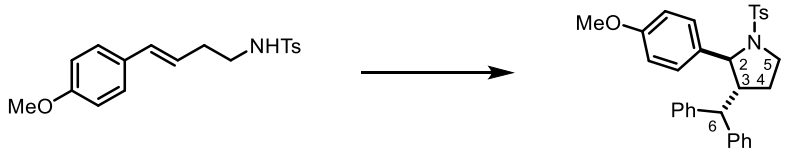

**2q**

To a solution of bromobenzene (0.63 mL, 6.0 mmol) in THF (30 mL) was added *n*-butyllithium (2.5 M in hexanes, 2.08 mL, 5.20 mmol) dropwise at -78 °C. After stirring at -78 °C for 30 min cyclopent-2-enone (0.34 mL, 4.0 mmol) in THF (5 mL) was added slowly. After 1 h stirring at -78 °C $H_2O$ was added and allowed to warm to rt. The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with brine, dried over $MgSO_4$ before concentrating *in vacuo*. Flash column chromatography (20% $Et_2O$ – pentane) afforded **2q** as a white solid (0.564 g, 88%).

Data for **2q**: **$R_f$** 0.45 (30% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.43 – 7.47 (2H, m, Ar), 7.32 – 7.38 (2H, m, Ar), 7.23 – 7.28 (1H, m, Ar), 6.12 (1H, dt, *J* = 5.6, 2.4 Hz, C3-H), 5.88 (1H, dt, *J* = 5.5, 2.2 Hz, C2-H), 2.60 – 2.70 (1H, m, C4-$H_A$), 2.43 – 2.52 (1H, m, C4-$H_B$), 2.24 – 2.29 (2H, m, C5-$H_2$), 1.98 (1H, *br*. s, *O*H). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 147.0 (C Ar), 136.6 (C2), 134.9 (C3), 128.2 (2 × C Ar), 126.8 (C Ar), 124.9 (2 × C Ar), 87.0 (C1), 42.0 (C5), 31.5 (C4). *The spectroscopic properties were consistent with the data available in the literature.*[25]

Cyclisations

**(3a): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-tosylpyrrolidine**

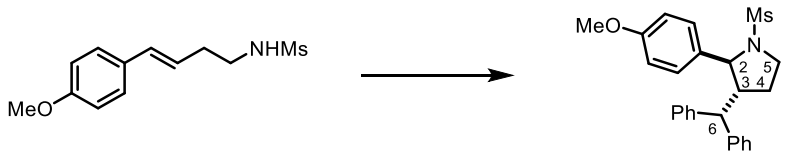



**1a** **3a**

Prepared according to **General Procedure K** using **1a** (27 mg, 0.082 mmol) and benzhydrol (15 mg, 0.082 mmol). Flash column chromatography (gradient elution 20% → 25% $Et_2O$ – pentane) afforded **3a** as a colourless oil (26 mg, 64%).

Data for **3a**: **$R_f$** 0.50 (60% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.67 (2H, d, *J* = 8.3 Hz, Ar), 7.35 (2H, d, *J* = 8.3 Hz, Ar), 7.23 – 7.27 (2H, m, Ar), 7.17 – 7.22 (3H, m, Ar), 7.07 – 7.14 (1H, m, Ar), 7.05 (2H, d, *J* = 8.4 Hz, Ar), 6.98 (2H, d, *J* = 8.4 Hz, Ar), 6.95 (2H, d, *J* = 8.7 Hz, Ar), 6.77 (2H, d, *J* = 8.7 Hz, Ar), 4.47 (1H, d, *J* = 2.0 Hz, C2-H), 3.78 (3H, s, OMe), 3.67 – 3.73 (1H, m, C5-$H_A$), 3.52 (1H, td, *J* = 10.0, 6.7 Hz, C5-$H_B$), 3.20 (1H, d, *J* = 12.1 Hz, C6-H), 2.93 (1H, ddt, *J* = 12.1, 6.6, 2.0 Hz, C3-H), 2.52 (3H, s, TsMe), 2.03 – 2.12 (1H, m, C4-$H_A$), 1.52 (1H, ddt, *J* = 13.2, 6.7, 2.3 Hz, C4-$H_B$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 158.6 (C Ar), 143.4 (C Ar), 143.0 (C Ar), 142.8 (C Ar), 135.7 (C Ar), 135.6 (C Ar), 129.8 (2 × C Ar), 128.82 (2 × C Ar), 128.75 (2 × C Ar), 128.5 (2 × C Ar), 127.8 (4 × C Ar), 127.1 (2 × C Ar), 126.9 (C Ar), 126.7 (C Ar), 113.8 (2 × C Ar), 66.4 (C2), 55.4 (OMe), 54.0 (C6), 52.9 (C3), 47.5 (C5), 26.9 (C4), 21.7 (TsMe). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H. **HRMS** (ESI): calculated for $C_{31}H_{32}NO_3S$ $[M+H]^+$ requires *m/z* 498.2103, found *m/z* 498.2097. **IR** (film) $\nu_{max}$: 3649, 2980, 2888, 1611, 1511, 1159 $cm^{-1}$.

**(3b): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-(methylsulfonyl)pyrrolidine**



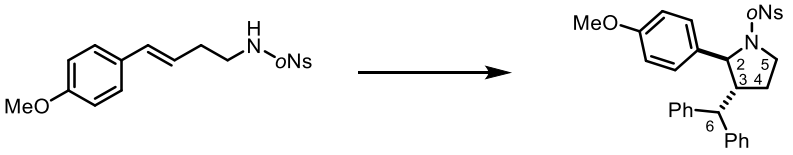

**1b** **3b**

Prepared according to **General Procedure K** using **1a** (22 mg, 0.086 mmol) and benzhydrol (16 mg, 0.086 mmol). Flash column chromatography (gradient elution 40% → 45% $Et_2O$ – pentane) afforded **3b** as a colourless oil (19.5 mg, 43%).

Data for **3b**: **$R_f$** 0.30 (80% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.15 – 7.32 (10H, m, Ar), 6.94 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 4.61 (1H, d, *J* = 2.4 Hz, C2-H), 3.87 (1H, d,

*J* = 11.9 Hz, C6-H), 3.74 – 3.81 (1H, m, C5-$H_A$), 3.78 (3H, s, OMe), 3.61 (1H, ddd, *J* = 9.6, 8.0, 3.6 Hz, C5-$H_B$), 3.06 (1H, ddt, *J* = 11.9, 6.5, 3.0 Hz, C3-H), 2.62 (3H, s, $SO_2Me$), 1.10 – 1.21 (1H, m, C4-$H_A$), 1.75 (1H, ddt, *J* = 13.5, 6.5, 3.5 Hz, C4-$H_B$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 158.8 (C Ar),143.1 (C Ar), 143.0 (C Ar), 135.0 (C Ar), 129.0 (2 × C Ar), 128.9 (2 × C Ar), 128.4 (2 × C Ar), 128.0 (2 × C Ar), 127.4 (2 × C Ar), 127.0 (C Ar), 126.8 (C Ar), 114.0 (2 × C Ar), 66.2 (C2), 55.4 (OMe), 54.7 (C6), 53.1 (C3), 47.3 (C5), 39.3 ($SO_2Me$), 27.9 (C4). **HRMS** (ESI): calculated for $C_{25}H_{27}NO_3SNa$ $[M+Na]^+$ requires *m/z* 444.1609, found *m/z* 444.1602. **IR** (film) $\nu_{max}$: 2980, 1511, 1493, 1452, 1247, 1175 $cm^{-1}$.

**(3c): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**




**1c** **3c**

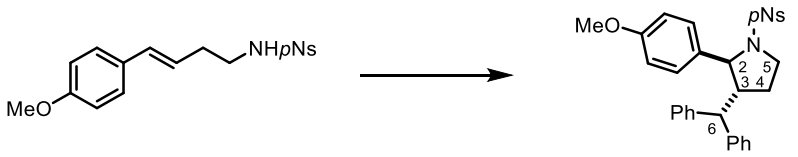
Prepared according to **General Procedure K** using **1c** (40 mg, 0.11 mmol) and benzhydrol (20 mg, 0.11 mmol). Flash column chromatography (gradient elution 15% → 25% $Et_2O$ – pentane) afforded **3c** as a colourless oil (58 mg, 99%).

Data for **3c**: **$R_f$** 0.30 (50% $Et_2O$ – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.47 – 7.55 (2H, m, Ar), 7.34 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.19 – 7.28 (6H, m, Ar), 7.06 – 7.18 (6H, m, Ar), 6.74 (2H, d, *J* = 8.7 Hz, Ar), 6.52 (2H, d, *J* = 8.7 Hz, Ar), 4.65 (1H, d, *J* = 3.6 Hz, C2-H), 3.97 (1H, dt, *J* = 10.2, 7.4 Hz, C5-$H_A$), 3.88 (1H, ddd, *J* = 10.2, 7.7, 5.0 Hz, C5-$H_B$), 3.79 (1H, d, *J* = 11.5 Hz, C6-H), 3.70 (3H, s, OMe), 3.05 (1H, m, C3-H), 3.01 – 3.09 (1H, m, C4-$H_A$), 1.72 (1h, ddt, *J* = 12.3, 7.2, 5.0 Hz, C4-$H_B$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 158.7 (C Ar), 147.7 (C Ar), 143.0 (C Ar), 142.9 (C Ar), 133.8 (C Ar), 133.6 (C Ar), 132.8 (C Ar), 131.2 (C Ar), 131.1 (C Ar), 128.9 (2 × C Ar),128.8 (2 × C Ar), 128.3 (2 × C Ar), 127.9 (2 × C Ar), 127.7 (2 × C Ar), 126.8 (C Ar), 126.8 (C Ar), 123.6 (C Ar), 113.6 (2 × C Ar), 67.0 (C2). 55.4 (OMe), 54.9 (C6), 53.6 (C3), 48.6 (C5), 28.3 (C4). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) $\nu_{max}$: 2980, 1542, 1511, 1493, 1371, 1161 $cm^{-1}$.

*Gram scale reaction:*

To a solution of **1c** (906 mg, 2.50 mmol) in HFIP (25 mL) was added benzhydrol (461 mg, 2.50 mmol) before addition of $Ti(O^iPr)_4$ (0.22 mL, 30 mol%). Following stirring at rt for 16 h the solvent was removed *in vacuo*. Flash column chromatography (gradient elution 15% → 25% $Et_2O$ – pentane) afforded **3c** as a colourless oil (1.25 g, 95%).

**(3d): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(4-nitrophenyl)sulfonyl]-pyrrolidine**

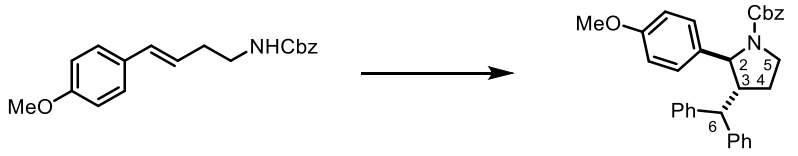



**1d** **3d**

Prepared according to **General Procedure K** using **1d** (36 mg, 0.10 mmol) and benzhydrol (18 mg, 0.10 mmol). Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3d** as a colourless oil (47 mg, 89%).

Data for **3c**: $\mathbf{R_f}$ 0.30 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.21 (2H, d, *J* = 8.8 Hz, Ar), 7.71 (2H, d, *J* = 8.8 Hz, Ar), 7.23 (4H, m, Ar), 7.20 – 7.17 (1H, m, Ar), 7.17 – 7.11 (3H, m, Ar), 7.09 – 7.01 (2H, m, Ar), 6.76 (2H, d, *J* = 8.6 Hz, Ar), 6.65 (2H, d, *J* = 8.7 Hz, Ar), 4.57 (1H, d, *J* = 2.7 Hz, C2-H), 3.75 (3H, s, OMe), 3.74 – 3.69 (1H, m, C5-$H_A$), 3.66 (1H, ddd, *J* = 9.6, 8.0, 4.1 Hz, C5-$H_B$), 3.49 (1H, d, *J* = 11.8 Hz, C6-H), 3.07 – 2.94 (1H, m, C3-H), 2.14 (1H, dtd, *J* = 13.1, 8.3, 6.7 Hz, C4-$H_A$), 1.68 (ddt, *J* = 13.2, 7.3, 3.9 Hz, C4-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.9 (C Ar), 149.8 (C Ar), 145.1 (C Ar), 142.7 (C Ar), 142.6 (C Ar), 134.2 (C Ar), 128.9 (2 × C Ar), 128.9 (2 × C Ar), 128.4 (2 × C Ar), 128.3 (2 × C Ar), 127.8 (2 × C Ar), 127.5 (2 × C Ar), 127.1 (C Ar), 126.9 (C Ar), 124.1 (2 × C Ar), 113.8 (2 × C Ar), 67.0 (C2), 55.4 (OMe), 54.7 (C6), 52.9 (C3), 47.8 (C5), 27.8 (C4). **HRMS** (ESI): calculated for $C_{30}H_{28}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 551.1611, found *m/z* 551.1611. **IR** (film) $\nu_{max}$: 2913, 2360, 1530, 1513, 1350, 1249, 1164, 1104 $cm^{-1}$.

**(3e): (±)-Benzyl (2*S*,3*R*)-3-benzhydryl-2-(4-methoxyphenyl)pyrrolidine-1-carboxylate**



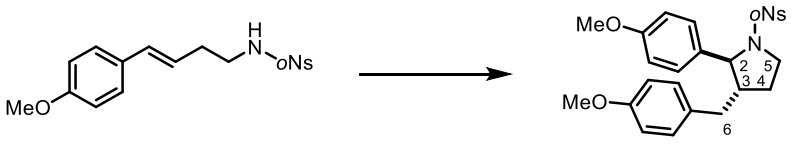

**1e** **3e**

Prepared according to **General Procedure K** using **1e** (31 mg, 0.10 mmol) and benzhydrol (18 mg, 0.10 mmol). Flash column chromatography (gradient elution 10% → 15% EtOAc – pentane) afforded **3e** as a colourless oil (37 mg, 77%).

Data for **3e,** 1.75:1 mixture of rotamers *A:B*: $\mathbf{R_f}$ 0.45 (30% EtOAc – pentane). **$^1$H NMR (600 MHz, $CDCl_3$) δ** 7.41 – 7.23 (10H, m, Ar), 7.22 – 7.12 (4H, m, Ar), 6.93 – 6.82 (3H, m, Ar), 6.80 – 6.74 (2H, m, Ar), 5.13 (1H, q, *J* = 12.4 Hz, $CH_2$Ph, *B*), 5.05 – 4.95 (1H, m, $CH_2$Ph, *A*), 4.73 (1H, *br.* s, C2-H, *B*), 4.68 (1H, *br.* s, C2-H, *A*), 3.78 (3H, s, OMe, *A*+*B*), 3.85 – 3.61 (3H, m, C5-$H_2$ + C6-H, *A*+*B*), 3.02 –

2.96 (1H, m, C3-H, *A*+*B*), 2.04 (1H, dq, *J* = 15.8, 9.3 Hz, C4-$H_A$, *A*+*B*), 1.67 – 1.59 (1H, m, C4-$H_B$). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 158.5, 155.4, 154.8, 143.7, 143.5, 143.5, 143.3, 137.1, 137.1, 136.1, 135.7, 129.0, 128.8, 128.8, 128.6, 128.6, 128.4, 128.3, 128.3, 128.0, 128.0, 127.6, 127.3, 126.8, 126.7, 126.6, 126.6, 113.9, 113.8, 66.9 ($CH_2$Ph, *B*), 66.5 ($CH_2$Ph, *A*), 64.8 (C2, *B*), 64.3 (C2, *A)*, 55.4 (OMe, *A*), 55.4 (OMe, *B*), 54.7 (C6, *B*), 54.5 (C6, *A*), 52.5 (C3, *A*), 51.7 (C3, *B*), 45.8 (C5, *A*), 45.6 (C5, *B*), 26.9 (C4, *B*), 25.7 (C4, *A*). **HRMS** (ESI): calculated for $C_{32}H_{32}NO_3$ $[M+H]^+$ requires *m/z* 478.2377, found *m/z* 478.2376. **IR** (film) $\nu_{max}$: 2953, 2361, 1698, 1512, 1451, 1411, 1351, 1247 $cm^{-1}$.

**(3g): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl)-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**

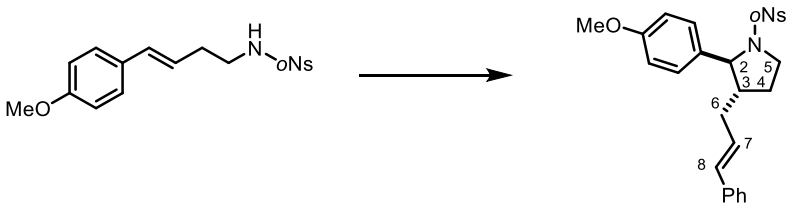



**1c** **3g**

Prepared according to **General Procedure K** using **1c** (40 mg, 0.11 mmol) and 4-methoxybenzyl alcohol (15 mg, 0.11 mmol). Flash column chromatography (gradient elution 15% → 25% EtOAc – pentane) afforded **3g** as a colourless oil (53 mg, 99%).

Data for **3g: $R_f$** 0.45 (40% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.45 – 7.53 (2H, m, Ar), 7.24 – 7.27 (1H, m, Ar), 7.18 – 7.23 (1H, m, Ar), 7.00 (2H, d, *J* = 8.6 Hz, Ar), 6.95 (2H, d, *J* = 8.6 Hz, Ar), 6.78 (2H, d, *J* = 8.6 Hz, Ar), 6.60 (2H, d, *J* = 8.6 Hz, Ar), 4.48 (1H, d, *J* = 7.4 Hz, C2-H), 4.05 (1H, ddd, *J* = 11.9, 8.9, 3.5 Hz, C5-$H_A$), 3.77 (3H, s, OMe), 3.71 – 3.76 (1H, m, C5-$H_B$), 3.73 (3H, s, OMe), 2.69 (1H, dd, *J* = 13.4, 5.2 Hz, C6-$H_A$), 2.45 (1H, dd, *J* = 13.5, 9.2 Hz, C6-$H_B$), 2.32-2.41 (1H, m, C3-H), 2.00 (1H, dtd, *J* = 12.2, 6.1, 3.6 Hz, C4-$H_A$), 1.71 (1H, dq, *J* = 12.3, 8.9 Hz, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 158.2 (C Ar), 147.5 (C Ar), 134.1 (C Ar), 132.6 (CH Ar), 132.1 (C Ar), 131.5 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.9 (2 × C Ar), 128.7 (2 × C Ar), 123.6 (C Ar), 114.0 (2 × C Ar), 113.7 (2 × C Ar), 68.5 (C2), 55.40 (OMe), 55.37 (OMe), 52.3 (C3), 49.4 (C5), 37.0 (C6), 30.3 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-$H_A$, between C2-H and C6-$H_B$. **HRMS** (ESI): calculated for $C_{25}H_{27}N_2O_5S$ $[M+H]^+$ requires *m/z* 483.1590, found *m/z* 483.1585. **IR** (film) $\nu_{max}$: 2980, 2890, 1514, 1510, 1244 $cm^{-1}$.

**(3h): (±)-(2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

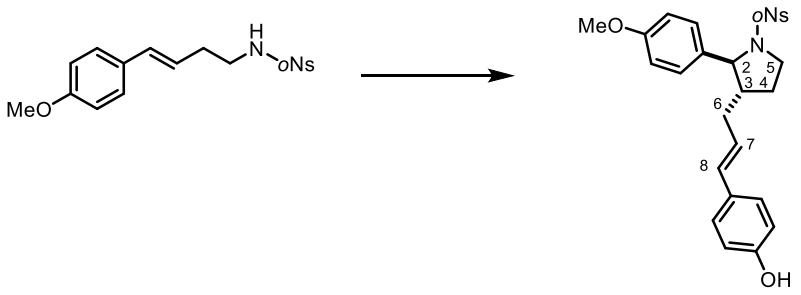



**1c** **3h**

Prepared according to **General Procedure K** using **1c** (30 mg, 0.083 mmol) and cinnamyl alcohol (11 mg, 0.083 mmol) at 70 ˚C. Flash column chromatography (gradient elution 10% → 25% EtOAc – pentane) afforded **3h** as a colourless oil (23 mg, 58%).

Data for **3h**: **$R_f$** 0.30 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.51 (1H, dd, *J* = 7.9, 1.4 Hz, Ar), 7.43 – 7.48 (1H, m, Ar), 7.23 – 7.29 (5H, m, Ar), 7.16 – 7.22 (2H, m, Ar), 7.05 (2H, d, *J* = 8.7 Hz, Ar), 6.60 (2H, d, *J* = 8.7 Hz, Ar), 6.35 (1H, d, *J* = 15.8 Hz, C8-H), 6.03 (1H, dt, *J* = 15.8, 7.1 Hz, C7-H), 4.49 (1H, d, *J* = 7.5 Hz, C2-H), 4.08 (1H, ddd, *J* = 10.9, 7.9, 3.1 Hz, C5-$H_A$), 3.75 – 3.82 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.32 – 2.39 (1H, m, C6-$H_A$), 2.26 – 2.32 (1H, m, C3-H), 2.14 – 2.23 (2H, m, C4-$H_A$ + C6-$H_B$), 1.75 (1H, dtd, *J* = 12.3, 9.5, 7.9 Hz, C4-$H_B$). **$^{13}$C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 147.5 (C Ar), 137.3 (C Ar), 134.1 (C Ar), 132.6 (C Ar), 132.3 (C Ar + C8), 132.1 (C Ar), 131.1 (C Ar), 130.9 (C Ar), 128.9 (2 × C Ar), 128.6 (2 × C Ar), 127.4 (C7), 126.2 (2 × C Ar), 123.6 (C Ar), 113.8 (2 × C Ar), 68.7 (C2), 55.4 (OMe), 50.4 (C3), 49.6 (C5), 35.3 (C4), 30.6 (C6). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-$H_B$, between C2-H and C7-H. **HRMS** (ESI): calculated for $C_{26}H_{27}N_2O_5S$ $[M+H]^+$ requires *m/z* 479.1641, found *m/z* 479.1636. **IR** (film) $\nu_{max}$: 2980, 1541, 1511, 1371, 1289, 1159 $cm^{-1}$.

**(3i): (±)-4-((*E*)-3-((2*S*,3*S*)-2-(4-Methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)pyrrolidin-3-yl)prop-1-en-1-yl)phenol**

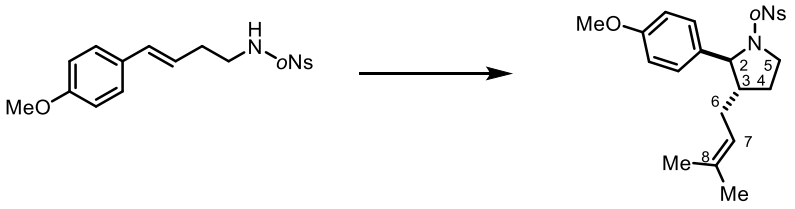



**1c** **3i**

Prepared according to **General Procedure K** using **1c** (18 mg, 0.050 mmol) and **2i** (7.5 mg, 0.050 mmol) at 70 ˚C. Flash column chromatography (gradient elution 10% → 30% EtOAc – pentane) afforded **3i** as a colourless oil (12 mg, 49%).

Data for **3i**: **$R_f$** 0.42 (40% EtOAc – pentane). **$^1$H NMR (600 MHz, $CDCl_3$) δ** 7.51 (1H, dd, *J* = 7.9, 1.3 Hz, Ar), 7.46 (1H, ddd, *J* = 7.9, 7.3, 1.4 Hz, Ar), 7.25 (1H, d, *J* = 8.9 Hz, Ar), 7.19 (1H, ddd, *J* = 8.0, 7.4, 1.4 Hz, Ar), 7.14 (2H, d, *J* = 8.6 Hz, Ar), 7.05 (2H, d, *J* = 8.7 Hz, Ar), 6.74 (2H, d, *J* = 8.6 Hz, Ar), 6.60 (2H, d, *J* = 8.7 Hz, Ar), 6.27 (1H, dd, *J* = 15.8, 1.6 Hz, C8-H), 5.87 (1H, dt, *J* = 15.7, 7.1 Hz, C7-H), 4.78 (1H, *br*. s, *O*H), 4.48 (1H, d, *J* = 7.5 Hz, C2-H), 4.07 (1H, ddd, *J* = 10.8, 8.0, 3.2 Hz, C5-$H_A$), 3.78 (1H, ddd, *J* = 10.4, 9.5, 6.3 Hz, C5-$H_B$), 3.72 (3H, s, OMe), 2.36 – 2.24 (2H, m, C3-H + C6-$H_A$), 2.20 – 2.12 (2H, m, C5-$H_A$ + C6-$H_B$), 1.74 (1H, dtd, *J* = 12.4, 9.5, 8.0 Hz, C5-$H_B$). **$^{13}$C NMR (151 MHz, $CDCl_3$) δ** 159.2 (C Ar), 155.0 (C Ar), 147.5 (C Ar), 134.2 (C Ar), 132.6 (C Ar), 132.2 (C Ar), 131.6 (C8), 131.1 (C Ar), 131.0 (C Ar), 130.4 (C Ar), 128.9 (2 × C Ar), 127.5 (2 × C Ar), 125.2 (C7), 123.6 (C Ar), 115.5 (2 × C Ar), 113.8 (2 × C Ar), 68.7 (C2), 55.4 (OMe), 50.5 (C3), 49.6 (C5), 35.3 (C6), 30.6 (C4). **NOESY- 2D (600 MHz, $CDCl_3$)**: between C2-H and C6-$H_B$, between C2-H and C7-H. **HRMS** (ESI): calculated for $C_{26}H_{27}N_2O_6S$ $[M+H]^+$ requires *m/z* 495.1584, found *m/z* 495.1585. **IR** (film) $\nu_{max}$: 2923, 2852, 1611, 1542, 1513, 1371, 1247, 1160 $cm^{-1}$.

**(3j): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-pent-3-en-2-yl]-pyrrolidine**

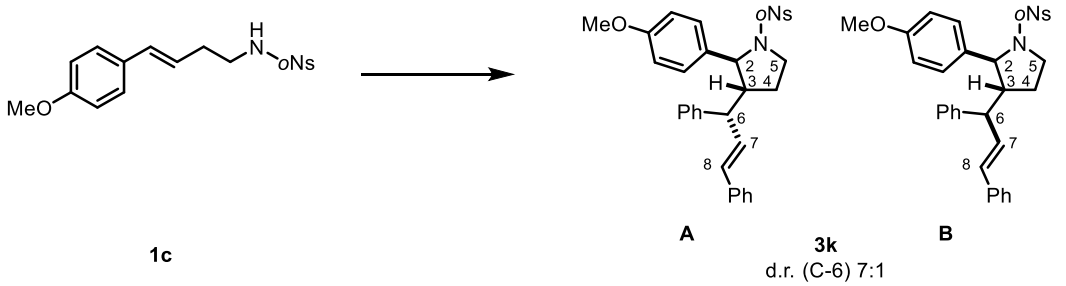



**1c** **3j**

Prepared according to **General Procedure K** using **1c** (40 mg, 0.11 mmol) and 3-methyl-2-buten-1-ol (19 mg, 0.22 mmol, 2.0 equiv.) at 70 ˚C. Flash column chromatography (gradient elution 10% → 15% EtOAc – pentane) afforded **3j** as a colourless oil (15 mg, 32%).

Data for **3j: $R_f$** 0.50 (35% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.50 (1H, dd, *J* = 8.0, 1.5 Hz, Ar), 7.43 – 7.48 (1H, m, Ar), 7.24 (1H, dd, *J* = 8.0, 1.5 Hz, Ar), 7.16 – 7.20 (1H, m, Ar), 7.03 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (2H, d, *J* = 8.7 Hz, Ar), 5.00 (1H, t, *J* = 7.2 Hz, C7-H), 4.42 (1H, d, *J* = 7.6 Hz, C2-H), 4.04 (1H, ddd, *J* = 10.6, 7.9, 3.1 Hz, C5-$H_A$), 3.72 – 3.80 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.13 – 2.19 (1H, m, C3-H), 2.05 – 2.13 (2H, m, C4-$H_A$ + C6-$H_A$), 1.95 (1H, dt, *J* = 15.0, 7.9 Hz, C6-$H_B$), 1.65 – 1.72 (1H, m, C4-$H_B$), 1.64 (3H, s, Me), 1.51 (3H, s, Me). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 147.5 (C Ar), 134.2 (C Ar), 133.8 (C Ar), 132.5 (C Ar), 132.4 (C8), 131.0 (C Ar), 130.9 (C Ar), 128.8 (2 × C Ar), 123.6 (C Ar), 131.3 (C7), 113.6 (2 × C Ar), 68.8 (C2), 55.4 (OMe), 50.8 (C3), 49.6 (C5), 30.4 (C4), 29.9 (C6), 25.9 (Me), 18.0 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-$H_B$, between C2-H and C7-H. **HRMS** (ESI): calculated for $C_{22}H_{27}N_2O_5S$ $[M+H]^+$ requires *m/z* 431.1641, found *m/z* 431.1634. **IR** (film) $\nu_{max}$: 2980, 2888, 2360, 1541, 1462, 1159, 1127 $cm^{-1}$.

**(3k): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine and (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine**



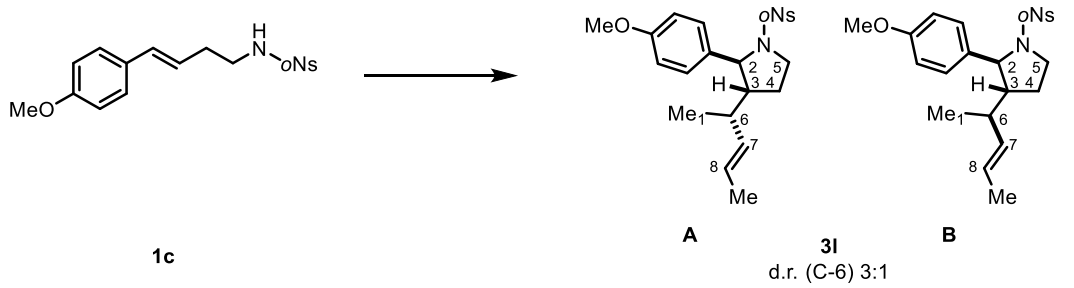

Prepared according to **General Procedure K** using **1c** (40 mg, 0.11 mmol) and *trans*-1,3-diphenyl-2-propen-1-ol (23 mg, 0.11 mmol) at 0 ˚C for 48 h. Flash column chromatography (gradient elution 25% → 30% EtOAc – pentane) afforded **3j** as an inseparable 7:1 mixture of diastereomers as a colourless oil (61 mg, 99%).

Data for **3k-A** (from the mixture): **$^{1}$H NMR (500 MHz, $CDCl_3$) δ** 7.43 – 7.52 (2H, m, Ar), 7.13 – 7.33 (12H, m, Ar), 7.02 (2H, d, *J* = 8.7 Hz, Ar), 6.55 (2H, d, *J* = 8.7 Hz, Ar), 6.37 (1H, d, *J* = 15.8 Hz, C8-H), 6.04 (1H, dd, *J* = 15.8, 9.3 Hz, C7-H), 4.84 (1H, d, *J* = 5.7 Hz, C2-H), 3.97 (1H, ddd, *J* = 10.3, 7.5, 5.2 Hz, C5-$H_A$), 3.81 (1H, dt, *J* = 10.3, 7.5 Hz, C5-$H_B$), 3.70 (3H, s, OMe), 3.39 (1H, t, *J* = 9.8 Hz, C6-H), 2.64 – 2.71 (1H, m, C3-H), 1.89 – 1.97 (1H, m, C4-$H_A$), 1.67 (1H, dq, *J* = 12.7, 7.5 Hz, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.9 (C Ar), 147.5 (C Ar), 142.4 (C Ar), 137.0 (C Ar), 133.9 (C Ar), 133.2 (C Ar), 132.6 (C Ar), 132.2 (C7), 131.06 (C8), 130.97 (2 × C Ar), 129.1 (2 × C Ar), 129.0 (2 × C Ar), 128.5 (2 × C Ar), 127.7 (2 × C Ar), 127.5 (C Ar), 126.94 (C Ar), 126.42 (2 × C Ar), 123.5 (C Ar), 113.7 (2 × C Ar), 67.2 (C2), 55.4 (OMe), 55.0 (C3), 53.5 (C6), 49.2 (C5), 29.1 (C4). **NOESY-2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H, between C2-H and C8-H.

Partial data for **3k-B** (from the mixture): **$^{1}$H NMR (500 MHz, $CDCl_3$) δ** 7.43 – 7.52 (2H, m, Ar), 7.13 – 7.33 (10H, m, Ar), 7.07 (2H, d, *J* = 6.9 Hz, Ar), 6.76 (2H, d, *J* = 8.7 Hz, Ar), 6.53 (2H, d, *J* = 8.7 Hz, Ar), 6.45 (1H, d, *J* = 15.7 Hz, C8-H), 6.29 (1H, dd, *J* = 15.7, 9.3 Hz, C7-H), 4.59 (1H, d, *J* = 5.3 Hz, C2-H), 4.04 (1H, ddd, *J* = 10.2, 7.4, 6.0 Hz, C5-$H_A$), 3.83 – 3.89 (1H, m, C5-$H_B$), 3.70 (3H, s, OMe), 3.38 (1H, d, *J* = 6.0 Hz, C6-H), 2.60 – 2.65 (1H, m, C3-H), 2.12 – 2.20 (1H, m, C4-$H_A$), 1.99 – 2.07 (1H, m, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 147.6 (C Ar), 142.4 (C Ar), 137.0 (C Ar), 133.7 (C Ar), 133.1 (C Ar), 132.7 (C Ar), 132.0 (C8), 131.09 (C Ar), 130.3 (C7), 128.8 (2 × C Ar), 128.7 (2 × C Ar), 128.0 (2 × C Ar), 128.0 (2 × C Ar), 127.6 (C Ar), 126.9 (C Ar), 126.4 (C Ar), 126.4 (2 × C Ar), 123.5 (C Ar), 113.6 (2 × C Ar), 66.5 (C2), 55.4 (OMe), 54.8 (C3), 51.5 (C6), 48.9 (C5), 27.7 (C4).

Data for **3k:** $\mathbf{R_f}$ 0.50 (35% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{32}H_{30}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 577.1773, found *m/z* 577.1764. **IR** (film) $\nu_{max}$: 2980, 2888, 1541, 1511, 1372, 1159 $cm^{-1}$.

**(3l): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-pent-3-en-2-yl]-pyrrolidine and (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-pent-3-en-2-yl]pyrrolidine**



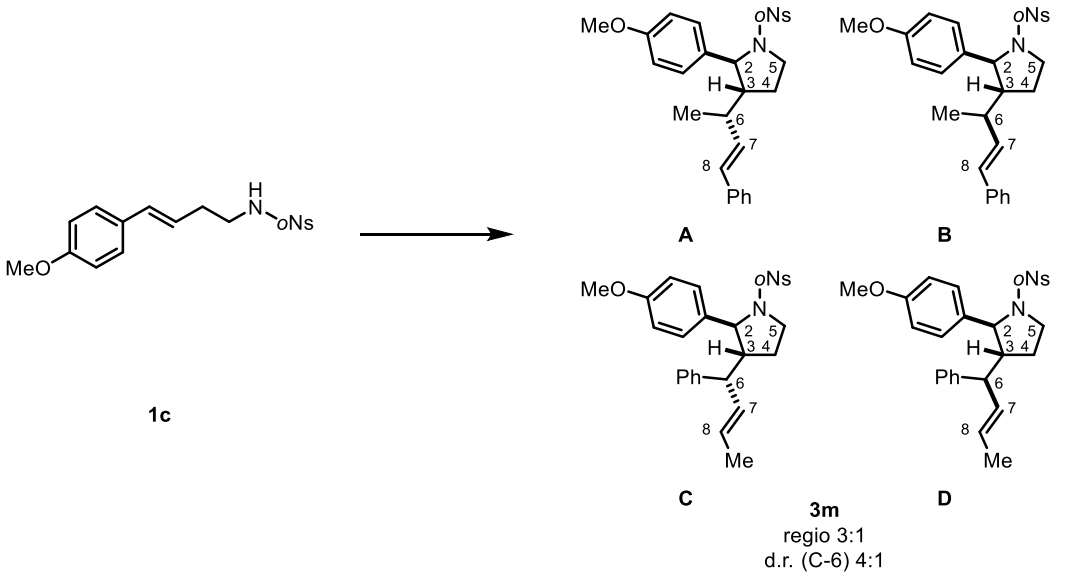

Prepared according to **General Procedure K** using **1c** (40 mg, 0.11 mmol) and 3-penten-2-ol (19 mg, 0.22 mmol, 2.0 equiv.) at 0 ˚C for 48 h. Flash column chromatography (gradient elution 10% → 15% EtOAc – pentane) afforded **3l** as an inseparable 3:1 mixture of diastereomers as a colourless oil (47 mg, 99%).

Data for **3l-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.51 (2H, m, Ar), 7.16 – 7.24 (2H, m, Ar), 6.99 (2H, d, *J* = 8.7 Hz, Ar), 6.57 (2H, d, *J* = 8.7 Hz, Ar), 5.32 (1H, dq, *J* = 15.1, 6.3 Hz, C8-H), 4.98 – 5.05 (1H, m, C7-H), 4.61 (1H, d, *J* = 5.8 Hz, C2-H), 3.98 (1H, ddd, *J* = 10.6, 7.6, 3.3 Hz, C5-$H_A$), 3.76 (1H, ddd, *J* = 10.3, 9.2, 6.1 Hz, C5-$H_B$), 3.71 (3H, s, OMe), 2.04 – 2.14 (3H, m, C4-$H_A$ + C6-H), 1.71 – 1.81(1H, m, C4-$H_B$), 1.53 (3H, dd, *J* = 6.4, 1.7 Hz, $Me_2$), 0.93 (3H, d, *J* = 6.3 Hz, $Me_1$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 147.4 (C Ar), 135.5 (C7), 134.2 (C Ar), 133.5 (C Ar), 132.4 (C Ar), 130.9 (C Ar), 130.9 (C Ar), 129.2 (2 × C Ar), 124.9 (C8), 123.5 (C Ar), 113.4 (2 × C Ar), 67.0 (C2), 55.5 (C3), 55.4 (OMe), 49.6 (C5), 39.7 (C6), 28.6 (C4), 18.6 ($Me_1$), 17.8 ($Me_2$). **NOESY--2D (500 MHz, $CDCl_3$)**: between C2-H and $Me_1$, between C2-H and C7-H, between C2-H and C8-H.

Partial data for **3l-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.51 (2H, m, Ar), 7.16 – 7.24 (2H, m, Ar), 7.04 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (2H, d, *J* = 8.7 Hz, Ar), 5.43 (1H, dq, *J* = 15.2, 6.3 Hz, C8-H), 5.23 – 5.28 (1H, m, C7-H), 4.54 (1H, d, *J* = 7.8 Hz, C2-H), 3.95 – 4.02 (1H, m, C5-$H_A$), 3.73 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.04 – 2.14 (2H, m, C3-H + C6-H), 1.97 (1H, dtd, *J* = 12.1, 6.0, 2.9 Hz, C4-$H_A$), 1.71 – 1.81(1H, m, C4-$H_B$), 1.67 (3H, dd, *J* = 6.3, 1.6 Hz, $Me_2$), 0.92 (3H, d, *J* = 6.4 Hz, $Me_1$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 134.17 (C Ar), 134.15 (C Ar), 132.7 (C7), 132.5 (C Ar), 132.5 (C Ar), 130.9 (C Ar), 130.9 (C Ar), 129.0 (2 × C Ar), 126.7 (C8), 123.5 (C Ar), 113.7 (2 × C Ar), 66.8 (C2), 55.6 (OMe), 55.4 (C3), 49.5 (C5), 37.0 (C6), 26.8 (C4), 20.2 ($Me_1$), 18.2 ($Me_2$). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and $Me_1$, between C2-H and C7-H, between C2-H and C8-H.

Data for **3l**: $\mathbf{R_f}$ 0.40 (30% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{22}H_{27}N_2O_5S$ $[M+H]^+$ requires *m/z* 431.1641, found *m/z* 431.1637. **IR** (film) $\nu_{max}$: 2980, 2888, 1541, 1511, 1372, 1159 $cm^{-1}$.

**(3m): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine, (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine, (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-1-phenylbut-2-en-1-yl]pyrrolidine, (±)-(2*S*,3*R*)-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-1-phenylbut-2-en-1-yl]pyrrolidine**




Prepared according to **General Procedure K** using **1c** (40 mg, 0.11 mmol) and **2m** (16.5 mg, 0.22 mmol) at 0 ˚C for 48 h. Flash column chromatography (gradient elution 15% → 25% EtOAc – pentane) afforded **3m** as an inseparable 9:3:3:1 mixture of diastereomers as a colourless oil (53 mg, 99%).

Data for **3m-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.00 – 7.52 (9H, m, Ar), 6.97 (2H, d, *J* = 8.7 Hz, Ar), 6.49 (2H, d, *J* = 8.7 Hz, Ar), 6.30 (1H, d, *J* = 15.8 Hz, C8-H), 5.72 (1H, dd, *J* = 15.8, 8.8 Hz, C7-H), 4.66 (1H, d, *J* = 7.3 Hz, C2-H), 4.00 – 4.10 (1H, m, C5-$H_A$), 3.75 – 3.84 (1H, m, C5-$H_B$), 3.68 (3H, s, OMe), 2.29 – 2.41 (1H, m, C6-H), 2.20 – 2.29 (1H, m, C3-H), 2.10 – 2.20 (1H, m, C4-$H_A$), 1.75 – 1.85 (1H, m, C4-$H_B$), 1.08 (3H, d, *J* = 6.7 Hz, Me). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 137.2 (C Ar), 134.6 (C7), 134.2 (C Ar), 132.7 (C Ar), 132.4 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.5 (C8), 129.5 (2 × C Ar), 128.8 (C Ar), 128.8 (C Ar), 128.5 (2 × C Ar), 126.2 (2 × C Ar), 123.5 (C Ar), 113.6 (2 × C Ar), 67.3 (C2), 55.8 (C3), 55.4 (OMe), 49.7 (C5), 40.8 (C6), 29.2 (C4), 19.9 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H, between C2-H and Me.

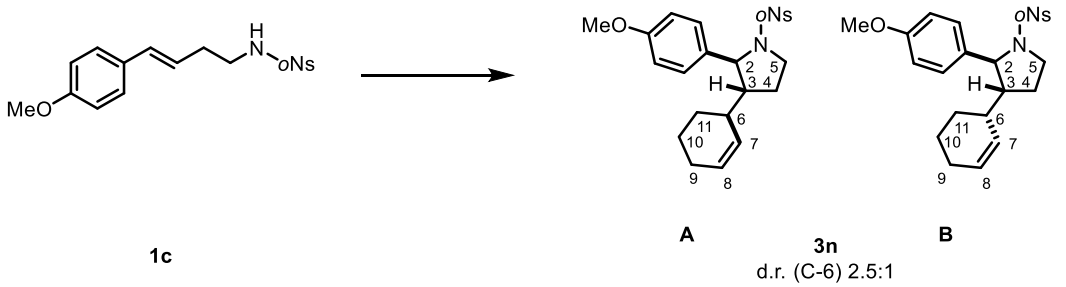
Partial data for **3m-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.00 – 7.52 (13H, m, Ar), 6.36 (1H, d, *J* = 15.8 Hz, C8-H), 6.02 (1H, dd, *J* = 15.8, 8.8 Hz, C7-H), 4.60 (1H, d, *J* = 8.0 Hz, C2-H),

3.99 – 4.05 (1H, m, C5-$H_A$), 3.75 – 3.84 (1H, m, C5-$H_B$), 3.74 (3H, s, OMe), 2.29 – 2.41 (1H, m, C6-H), 2.20 – 2.29 (1H, m, C3-H), 2.00 – 2.09 (1H, m, C4-$H_A$), 1.75 – 1.85 (1H, m, C4-$H_B$), 1.06 (3H, d, *J* = 6.7 Hz, Me). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 147.6 (C Ar), 143.2 (C Ar), 133.9 (C Ar), 133.77 (C Ar), 131.7 (C7), 131.1 (C8), 128.65 (2 × C Ar), 128.5 (C Ar), 127.5 (C Ar), 127.2 (2 × C Ar), 126.7 (C Ar), 126.3 (2 × C Ar), 126.2 (C Ar), 123.5 (C Ar), 113.8 (2 × C Ar), 66.8 (C2), 55.7 (C3), 55.39 (OMe), 49.5 (C5), 37.8 (C6), 27.2 (C4), 19.9 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H, between C2-H and Me.

Characteristic data for **3m-C** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.00 – 7.52 (11H, m, Ar), 6.65 (2H, d, *J* = 8.7 Hz, Ar), 5.30 – 5.44 (2H, m, C7-H + C8-H), 4.80 (1H, d, *J* = 5.1 Hz, C2-H), 3.74 – 3.97 (2H, m, C5-$H_2$), 3.74 (3H, s, OMe), 3.08 – 3.16 (1H, m, C6-H), 2.43 – 2.53 (1H, m, C3-H), 1.86 – 1.92 (1H, m, C4-$H_A$), 1.60 – 1.53 (4H, m, C4-$H_B$ + Me). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 131.4 (C7), 126.8 (C8), 66.9 (C2), 55.4 (OMe), 54.7 (C3), 52.8 (C6), 49.0 (C5), 28.5 (C4), 17.9 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H.

Data for **3m: $R_f$** 0.50 (40% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{27}H_{29}N_2O_5S$ $[M+H]^+$ requires *m/z* 493.1797, found *m/z* 493.1792. **IR** (film) $\nu_{max}$: 2980, 2888, 1541, 1511, 1372, 1247 $cm^{-1}$.

**(3n): (±)-(2*S*,3*R*)-3-[(1'*R*)-Cyclohex-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*S*,3*R*)-3-[(1'*S*)-Cyclohex-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**




Prepared according to **General Procedure K** using **1c** (30 mg, 0.083 mmol) and 2-cyclohexen-1-ol (8.0 mg, 0.083 mmol) at 70 ˚C. Flash column chromatography (gradient elution 10% → 15% EtOAc – pentane) afforded **3n** as an inseparable 2.5:1 mixture of diastereomers as a colourless oil (21.5 mg, 58%).

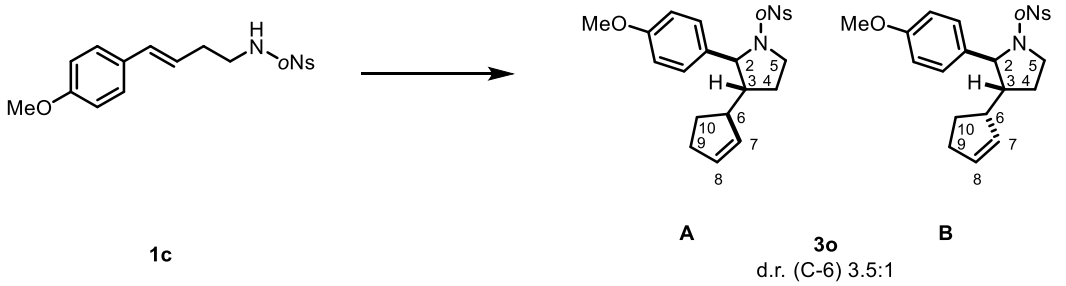
Data for **3n-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.51 (2H, m, Ar), 7.14 – 7.23 (2H, m, Ar), 7.05 (2H, d, *J* = 8.7 Hz, Ar), 6.58 (2H, d, *J* = 8.7 Hz, Ar), 5.74 – 5.80 (1H, m, C8-H), 5.60 (1H, dd, *J* = 10.5, 2.3 Hz, C7-H), 4.65 (1H, d, *J* = 8.1 Hz, C2-H), 4.00 – 4.08 (1H, m, C5-$H_A$), 3.72 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.17 – 2.25 (1H, m, C3-H), 2.10 – 2.17 (1H, m, C6-H), 2.06 (1H, dtd, *J* = 12.6, 6.3, 2.7 Hz, C4-$H_A$), 1.88 – 1.96 (2H, m, C9-$H_2$), 1.76 – 1.86 (1H, m, C4-$H_B$), 1.59 – 1.65 (1H, m, C11-$H_A$), 1.36 – 1.48 (2H, m, C10-$H_2$), 1.15 – 1.29 (1H, m, C11-$H_B$). **$^{13}$C NMR**

**(125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 147.4 (C Ar), 134.3 (C Ar), 133.0 (C Ar), 132.4 (C Ar), 131.1 (C Ar), 130.9 (C Ar), 129.8 (C8), 129.1 (2 × C Ar), 127.6 (C7), 123.5 (C Ar), 113.7 (2 × C Ar), 66.5 (C2), 55.4 (OMe), 54.9 (C3), 49.8 (C5), 36.1 (C6), 28.6 (C9), 27.9 (C4), 25.3 (C11), 21.8 (C10). **NOESY--2D (500 MHz, $CDCl_3$)**: between C2-H and C7-H.

Partial data for **3n-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.51 (2H, m, Ar), 7.16 – 7.23 (2H, m, Ar), 7.06 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (2H, d, *J* = 8.7 Hz, Ar), 5.62 – 5.66 (1H, m, C8-H), 5.39 (1H, dd, *J* = 10.2, 2.3 Hz, C7-H), 4.67 (1H, d, *J* = 8.4 Hz, C2-H), 4.00 – 4.08 (1H, m, C5-$H_A$), 3.72 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.17 – 2.25 (1H, m, C3-H), 2.10 – 2.17 (1H, m, C6-H), 2.00 (1H, dtd, *J* = 12.4, 6.6, 3.2 Hz, C4-$H_A$), 1.88 – 1.96 (2H, m, C9-$H_2$), 1.76 – 1.86 (1H, m, C4-$H_B$), 1.68 – 1.76 (2H, m, C10-$H_A$ + C11-$H_A$), 1.59 – 1.65 (1H, m, C10-$H_B$), 1.15 – 1.29 (1H, m, C11-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 147.4 (C Ar), 134.3 (C Ar), 133.0 (C Ar), 132.4 (C Ar), 130.9 (C Ar), 130.9 (C Ar), 129.6 (C7), 129.1 (2  C Ar), 128.7 (C8), 123.5 (C Ar), 113.7 (2 × C Ar), 66.5 (C2), 55.4 (OMe), 54.8 (C3), 49.5 (C5), 36.3 (C6), 27.8 (C4), 25.8 (C9), 25.2 (C11), 21.9 (C10). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C7-H.

Data for **3n**: **$R_f$** 0.40 (35% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{23}H_{27}N_2O_5S$ $[M+H]^+$ requires *m/z* 443.1641, found *m/z* 443.1635. **IR** (film) $\nu_{max}$: 2980, 1541, 1512, 1370, 1159 $cm^{-1}$.

**(3o): (±)-(2*S*,3*R*)-3-[(1'*R*)-Cyclopent-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*S*,3*R*)-3-[(1'*S*)-Cyclopent-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**




Prepared according to **General Procedure K** using **1c** (30 mg, 0.083 mmol) and **3o** (14 mg, 0.17 mmol, 2.0 equiv.). Flash column chromatography (gradient elution 15% → 20% EtOAc – pentane) afforded **3o** as an inseparable 3.5:1 mixture of diastereomers as a colourless oil (33 mg, 93%).

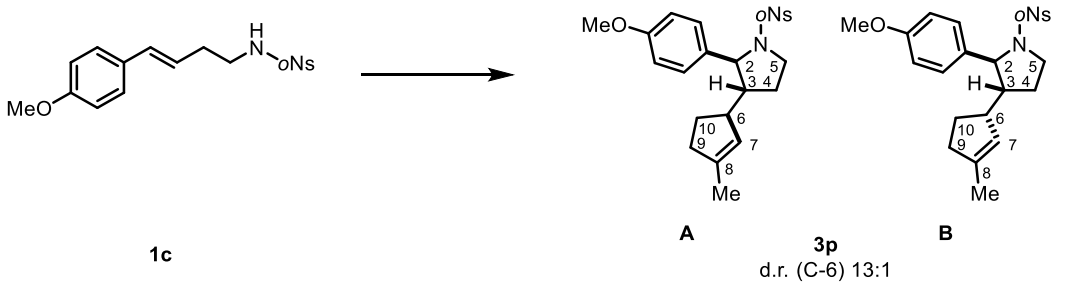
Data for **3o-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.49 (1H, dd, *J* = 7.9, 1.4 Hz, Ar), 7.42 – 7.46 (1H, m, Ar), 7.15 – 7.23 (2H, m, Ar), 7.05 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (2H, d, *J* = 8.7 Hz, Ar), 5.77 – 5.81 (1H, m, C8-H), 5.61 – 5.64 (1H, m, C7-H), 4.57 (1H, d, *J* = 7.9 Hz, C2-H), 4.03 (1H, ddd, *J* = 10.6, 7.9, 3.0 Hz, C5-$H_A$), 3.72 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.66 – 2.74 (1H, m, C3-H), 2.14 – 2.28 (3H, m, C6-H + C9-$H_2$), 2.02 – 2.10 (1H, m, C4-$H_A$), 1.83 – 1.91 (1H, m, C10-$H_A$), 1.71 – 1.81 (1H, m, C4-$H_B$), 1.23 – 1.33 (1H, m, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.1

(C Ar), 147.4 (C Ar), 134.2 (C Ar), 132.9 (C8), 132.8 (C Ar), 132.5 (C Ar), 131.5 (C7), 130.9 (C Ar), 130.9 (C Ar), 129.0 (2 × C Ar), 123.5 (C Ar), 113.6 (2 × C Ar), 67.9 (C2), 55.4 (OMe), 55.0 (C6), 49.6 (C5), 47.0 (C3), 32.2 (C9), 28.7 (C10), 28.5 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C7-H.

Data for **3o-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.49 (1H, dd, *J* = 7.9, 1.4 Hz, Ar), 7.42 – 7.46 (1H, m, Ar), 7.15 – 7.23 (2H, m, Ar), 7.06 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (2H, d, *J* = 8.7 Hz, Ar), 5.65 – 5.69 (1H, m, C8-H), 5.41 – 5.45 (1H, m, C7-H), 4.58 (1H, d, *J* = 8.1 Hz, C2-H), 3.99 – 4.05 (1H, m, C5-$H_A$), 3.72 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.66 – 2.74 (1H, m, C3-H), 2.14 – 2.28 (3H, m, C6-H + C9-$H_2$), 2.02 – 2.10 (1H, m, C4-$H_A$), 1.94 – 2.01 (1H, m, C10-$H_A$), 1.71 – 1.81 (1H, m, C4-$H_B$), 1.48 (1H, ddt, *J* = 13.2, 8.9, 6.8 Hz, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 147.4 (C Ar), 132.8 (C Ar), 132.8 (C Ar), 132.5 (C7), 132.5 (C Ar), 132.0 (C8), 130.9 (C Ar), 130.9 (C Ar), 129.0 (2 × C Ar), 123.6 (C Ar), 113.7 (2 × C Ar), 67.7 (C2), 55.4 (OMe), 54.7 (C6), 49.4 (C5), 46.8 (C3), 32.1 (C9), 28.5 (C4), 26.8 (C10). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C7-H.

Data for **3o**: **$R_f$** 0.40 (35% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{22}H_{25}N_2O_5S$ $[M+H]^+$ requires *m/z* 429.1484, found *m/z* 429.1476. **IR** (film) $\nu_{max}$: 2980, 2890, 1541, 1511, 1371, 1159 $cm^{-1}$.

**(3p): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*R*)-3-methylcyclopent-2-en-1-yl]-1-[(2-nitrophenyl)-sulfonyl]pyrrolidine and (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*S*)-3-methylcyclopent-2-en-1-yl]-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**




Prepared according to **General Procedure K** using **1c** (30 mg, 0.083 mmol) and **2p** (16 mg, 0.17 mmol, 2.0 equiv.). Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3p** as an inseparable 13:1 mixture of diastereomers as a colourless oil (13 mg, 36%).

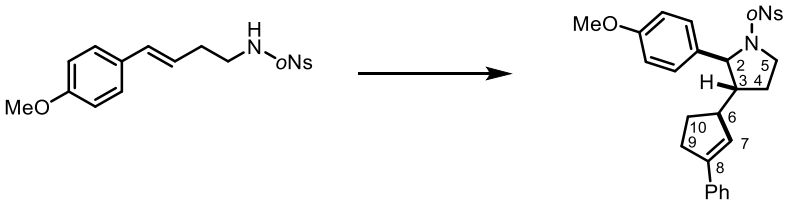
Data for **3p-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.51 (2H, m, Ar), 7.16 – 7.23 (2H, m, Ar), 7.04 (2H, d, *J* = 8.7 Hz, Ar), 6.58 (2H, d, *J* = 8.7 Hz, Ar), 5.20 – 5.24 (1H, m, C7-H), 4.54 (1H, d, *J* = 7.9 Hz, C2-H), 4.03 (1H, ddd, *J* = 10.7, 8.0, 3.0 Hz, C5-$H_A$), 3.73 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.62 – 2.72 (1H, m, C6-H), 2.10 – 2.20 (3H, m, C3-H + C9-$H_2$), 2.05 (1H, dtd, *J* = 12.5, 6.2, 3.1 Hz, C4-$H_A$), 1.86 – 1.94 (1H, m, C10-$H_A$), 1.76 (dtd, J = 12.3, 9.8, 8.0 Hz, C4-$H_B$), 1.69 (1H, s, Me), 1.29 – 1.37 (1H, m, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 147.5 (C Ar), 142.8 (C Ar), 134.3 (C Ar), 133.0 (C8), 132.4 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.1

(2 × C Ar), 125.3 (C7), 123.5 (C Ar), 113.6 (2 × C Ar), 67.6 (C2), 55.4 (C3 + OMe), 49.7 (C5), 47.1 (C6), 36.6 (C9), 29.5 (C10), 28.5 (C4), 16.8 (Me).

Partial data for **3p-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.51 (2H, m, Ar), 7.16 – 7.23 (2H, m, Ar), 7.04 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (2H, d, *J* = 8.7 Hz, Ar), 5.03 – 5.07 (1H, m, C7-H), 4.57 (1H, d, *J* = 7.9 Hz, C2-H), 4.00 – 4.05 (1H, m, C5-$H_A$), 3.73 – 3.79 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 2.62 – 2.72 (1H, m, C6-H), 2.10 – 2.20 (3H, m, C3-H + C9-$H_2$), 2.02 – 2.08 (1H, m, C4-$H_A$), 1.97 – 2.00 (1H, m, C10-$H_A$), 1.72 – 1.81 (1H, m, C4-$H_B$), 1.64 (1H, s, Me), 1.29 – 1.37 (1H, m, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 147.5 (C Ar), 141.9 (C Ar), 134.3 (C Ar), 133.0 (C8), 132.4 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.0 (2 × C Ar), 126.3 (C7), 123.5 (C Ar), 113.7 (2 × C Ar), 67.7 (C2), 55.4 (OMe), 54.7 (C3), 49.4 (C5), 46.9 (C6), 36.4 (C9), 28.4 (C10), 27.7 (C4), 16.8 (Me).

Data for **3p**: **$R_f$** 0.50 (25% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{23}H_{27}N_2O_5S$ $[M+H]^+$ requires *m/z* 443.1641, found *m/z* 443.1635. **IR** (film) $\nu_{max}$: 2980, 2889, 1543, 1512, 1374, 1249 $cm^{-1}$.

**(3q): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl)-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**



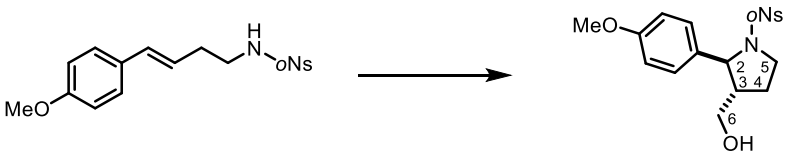

**1c** **3q**

Prepared according to **General Procedure K** using **1c** (31 mg, 0.086 mmol) and **2q** (14 mg, 0.086 mmol) at 0 °C for 48 h. Flash column chromatography (gradient elution 15% → 20% EtOAc – pentane) afforded **3q** as a colourless oil (43 mg, 99%).

Data for **3q: $R_f$** 0.40 (35% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.53 (1H, dd, *J* = 7.9, 1.4 Hz, Ar), 7.45 – 7.50 (1H, m, Ar), 7.38 – 7.42 (2H, m, Ar), 7.31 – 7.36 (2H, m, Ar), 7.24 – 7.28 (2H, m, Ar), 7.19 – 7.23 (1H, m, Ar), 7.10 (2H, d, *J* = 8.7 Hz, Ar), 6.62 (2H, d, *J* = 8.7 Hz, Ar), 6.07 (1H, q, *J* = 2.0 Hz, C7-H), 4.67 (1H, d, *J* = 8.0 Hz, C2-H), 4.09 (1H, ddd, *J* = 10.7, 8.0, 2.9 Hz, C5-$H_A$), 3.79 – 3.85 (1H, m, C5-$H_B$), 3.75 (3H, s, OMe), 2.93 – 3.00 (1H, m, C6-H), 2.61 – 2.72 (2H, m, C9-$H_2$), 2.35 (1H, ddt, *J* = 10.1, 8.0, 6.5 Hz, C3-H), 2.13 – 2.19 (1H, m, C4-$H_A$), 2.09 (1H, ddt, *J* = 13.2, 8.4, 4.2 Hz, C10-$H_A$), 1.82 – 1.91 (1H, m, C4-$H_B$), 1.54 (1H, ddt, *J* = 13.3, 8.6, 6.9 Hz, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 147.4 (C Ar), 144.2 (C Ar), 136.2 (C Ar), 134.2 (C Ar), 132.9 (C8), 132.5 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.1 (2 × C Ar), 128.4 (C Ar), 127.5 (C7), 126.5 (2 × C Ar), 125.8 (C Ar), 123.6 (2 × C Ar), 113.7 (2 × C Ar), 67.8 (C2), 55.4 (OMe), 55.1 (C3), 49.7 (C5), 47.6

(C6), 32.9 (C9), 28.8 (C10), 28.7 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H, between C2-H and C10-$H_A$, between C2-H and C10-$H_B$. **HRMS** (ESI): calculated for $C_{28}H_{29}N_2O_5S$ $[M+H]^+$ requires *m/z* 505.1797, found *m/z* 505.1792. **IR** (film) $\nu_{max}$: 2980, 2889, 1729, 1514, 1369, 1150 $cm^{-1}$.

**(3r): (±)-{(2*S*,3*S*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidin-3-yl}methanol**

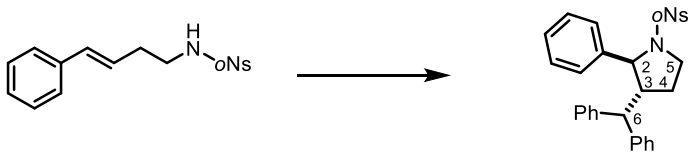



**1c** **3r**

Prepared according to **General Procedure K** using **1c** (26 mg, 0.071 mmol) and paraformaldehyde (43 mg, 1.43 mmol, 20 equiv.) at 0 °C for 48 h. Flash column chromatography (gradient elution 20% → 30% EtOAc – pentane) afforded **3r** as a colourless oil (20 mg, 74%).

Data for **3r: $R_f$** 0.20 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.46 – 7.53 (2H, m, Ar), 7.34 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.22 – 7.27 (1H, m, Ar), 7.07 (2H, d, *J* = 8.7 Hz, Ar), 6.62 (2H, d, *J* = 8.7 Hz, Ar), 4.70 (1H, d, *J* = 6.9 Hz, C2-H), 3.99 (1H, ddd, *J* = 10.3, 8.0, 4.2 Hz, C5-$H_A$), 3.76 – 3.84 (1H, m, C5-$H_B$), 3.72 (3H, s, OMe), 3.59 – 3.64 (1H, m, C6-$H_A$), 3.53 – 3.59 (1H, m, C6-$H_B$), 2.33 – 2.41 (1H, m, C3-H), 2.10 – 2.19 (1H, m, C4-$H_A$), 1.85 (1H, dq, *J* = 12.5, 8.4 Hz, C4-$H_B$), 1.60 (1H, *br*. s, *O*H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 147.5 (C Ar), 133.8 (C Ar), 132.8 (C Ar), 132.6 (C Ar), 131.1 (C Ar), 131.1 (C Ar), 128.5 (2 × C Ar), 123.7 (C Ar), 113.8 (2 × C Ar), 65.7 (C2), 63.0 (C6), 55.4 (OMe), 52.3 (C3), 49.4 (C5), 27.7 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-$H_A$, between C2-H and C6-$H_B$. **HRMS** (ESI): calculated for $C_{18}H_{20}N_2O_6SNa$ $[M+Na]^+$ requires *m/z* 415.0940, found *m/z* 415.0925. **IR** (film) $\nu_{max}$: 3649, 2980, 2888, 2360, 1382, 1154 $cm^{-1}$.

**(3s): (±)-(2*S*,3*R*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-2-phenylpyrrolidine**

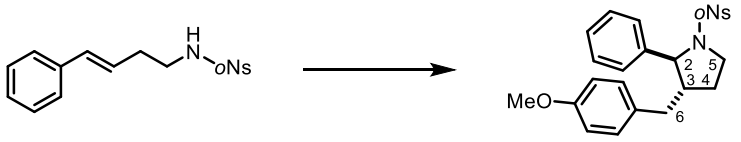



**1g** **3s**

Prepared according to **General Procedure K** using **1g** (41 mg, 0.12 mmol) and benzhydrol (23.5 mg, 0.12 mmol). Flash column chromatography (gradient elution 8% → 16% EtOAc – pentane) afforded **3s** as a colourless oil (61 mg, 99%).

Data for **3s: $R_f$** 0.50 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.46 – 7.53 (2H, m, Ar), 7.34 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.22 – 7.27 (4H, m, Ar), 7.08 – 7.21 (7H, m, Ar), 6.97 – 7.04 (3H, m, Ar), 6.80 – 6.84 (2H, m, Ar), 4.71 (1H, d, *J* = 3.2 Hz, C2-H), 3.99 (1H, dt, *J* = 10.1, 7.6 Hz, C5-$H_A$), 3.91 (1H, ddd, *J* = 10.1, 7.8, 4.7 Hz, C5-$H_B$), 3.80 (1H, d, *J* = 11.7 Hz, C6-H), 3.04 – 3.12 (1H, m, C3-H), 2.08 – 2.17 (1H, m, C4-$H_A$), 1.69 – 1.73 (1H, m, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 147.7 (C Ar), 142.9 (C Ar), 142.9 (C Ar), 141.6 (C Ar), 133.3 (C Ar), 133.0 (C Ar), 131.149 (CH9 Ar), 131.1 (C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.3 (2 × C Ar), 128.2 (2 × C Ar), 127.9 (2 × C Ar), 127.1 (C Ar), 126.8 (C Ar), 126.8 (C Ar), 126.4 (2 × C Ar), 123.6 (C Ar), 67.3 (C2), 54.8 (C6), 53.6 (C3), 48.6 (C5), 28.0 (C4). **HRMS** (ESI): calculated for $C_{29}H_{27}N_2O_4S$ $[M+H]^+$ requires *m/z* 499.1692, found *m/z* 499.1684. **IR** (film) $\nu_{max}$: 2980, 2890, 2360, 1710, 1542, 1164 $cm^{-1}$.

**(3t): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-1-[(2-nitrophenyl)sulfonyl]-2-phenylpyrrolidine**



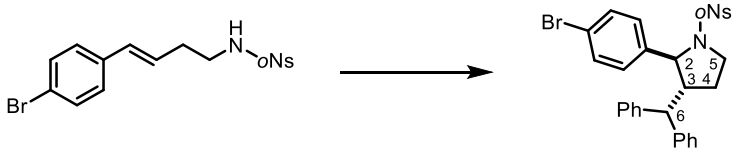

**1g** **3t**

Prepared according to **General Procedure K** using **1g** (72 mg, 0.22 mmol) and 4-methoxybenzyl alcohol (31 mg, 0.22 mmol). Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3t** as a colourless oil 86 mg, 85%).

Data for **3t: $R_f$** 0.50 (35% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.51 (1H, dd, *J* = 8.0, 1.5 Hz, Ar), 7.43 – 7.48 (1H, m, Ar), 7.26 (1H, dd, *J* = 8.0, 1.5 Hz, Ar) 7.14 – 7.20 (1H, m, Ar), 7.04 – 7.10 (5H, m, Ar), 6.96 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 4.56 (1H, d, *J* = 6.8 Hz, C2-H), 4.06 (1H, ddd, *J* = 10.3, 7.7, 4.1 Hz, C5-$H_A$), 3.77 – 3.82 (1H, m, C5-$H_B$), 3.77 (OMe), 2.71 (1H, dd, *J* = 13.3, 5.5 Hz, C6-$H_A$), 2.48 (1H, dd, *J* = 13.3, 9.0 Hz, C6-$H_B$), 2.35 – 2.43 (1H,

m, C3-H), 1.97 – 2.06 (1H, m, C4-$H_A$), 1.72 (1H, dq, *J* = 12.3, 7.7 Hz, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.2 (C Ar), 147.5 (C Ar), 140.4 (C Ar), 133.8 (C Ar), 132.8 (C Ar), 131.4 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.9 (2 × C Ar), 128.3 (2 × C Ar), 127.6 (C Ar), 127.3 (2 × C Ar), 123.6 (C Ar), 114.0 (2 × C Ar), 68.8 (C2), 55.3 (OMe), 52.4 (C3), 49.5 (C5), 37.1 (C6), 30.2 (C4). **HRMS** (ESI): calculated for $C_{24}H_{24}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 475.1304, found *m/z* 475.1295. **IR** (film) $\nu_{max}$: 3029, 2918, 1710, 1542, 1359, 1161 $cm^{-1}$.

**(3u): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-bromophenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

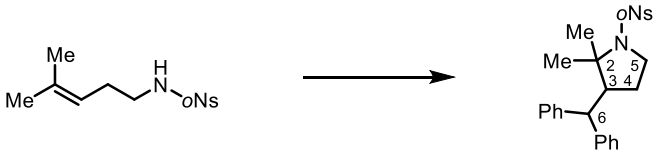



**1h** **3u**

Prepared according to **General Procedure K** using **1h** (15.5 mg, 0.038 mmol) and benzhydrol (7.0 mg, 0.038 mmol). Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3u** as a colourless oil (19 mg, 87%).

Data for **3u: $R_f$** 0.40 (25% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.52 – 7.58 (2H, m, Ar), 7.33 – 7.37 (1H, m, Ar), 7.21 – 7.29 (5H, m, Ar), 7.12 – 7.19 (4H, m, Ar), 7.05 – 7.10 (4H, m, Ar), 6.67 (2H, d, *J* = 8.4 Hz, Ar), 4.64 (1H, d, *J* = 3.8 Hz, C2-H), 3.98 (1H, dt, *J* = 10.2, 7.4 Hz, C5-$H_A$), 3.88 (1H, ddd, *J* = 10.2, 7.6, 5.2 Hz, C5-$H_B$), 3.79 (1H, d, *J* = 11.7 Hz, C6-H), 3.02 – 3.09 (1H, m, C3-H), 2.05 – 2.14 (1H, m, C4-$H_A$), 1.74 (1H, ddt, *J* = 12.6, 7.2, 5.4 Hz, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 147.7 (C Ar), 142.7 (C Ar), 142.7 (C Ar), 140.8 (C Ar), 133.3 (C Ar), 133.1 (C Ar), 131.3 (C Ar), 131.2 (2 × C Ar), 131.1 (C Ar), 129.0 (2 × C Ar), 128.8 (2 × C Ar), 128.4 (2 × C Ar), 128.3 (2 × C Ar), 127.8 (2 × C Ar), 127.0 (C Ar), 126.9 (C Ar), 123.7 (C Ar), 121.0 (C Ar), 67.0 (C2), 55.2 (C6), 53.8 (C3), 48.9 (C5), 28.6 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H. **HRMS** (ESI): calculated for $C_{29}H_{26}N_2O_4SBr$ $[M+H]^+$ requires *m/z* 577.0797, found *m/z* 577.0791. **IR** (film) $\nu_{max}$: 2922, 1709, 1543, 1359, 1163, 1221 $cm^{-1}$.

**(3v): (±)-3-Benzhydryl-2,2-dimethyl-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**




**1i** **3v**

Prepared according to **General Procedure K** using **1i** (29 mg, 0.10 mmol) and benzhydrol (19 mg, 0.10 mmol). Flash column chromatography (gradient elution 15% → 20% EtOAc – pentane) afforded **3v** as a colourless oil (43 mg, 93%).

Data for **3v: $R_f$** 0.30 (35% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.01 (1H, dd, *J* = 7.6, 1.7 Hz, Ar), 7.59 – 7.67 (2H, m, Ar), 7.57 (1H, dd, *J* = 7.1, 2.1 Hz, Ar), 7.30 – 7.35 (4H, m, Ar), 7.20 – 7.29 (4H, m, Ar), 7.10 – 7.17 (2H, m, Ar), 3.74 (1H, d, *J* = 11.5 Hz, C6-H), 3.56 (1H, td, *J* = 9.6, 2.1 Hz, C5-$H_A$), 3.33 (td, *J* = 9.6, 7.7 Hz, C5-$H_B$), 2.94 (1H, td, *J* = 11.5, 6.5 Hz, C3-H), 1.71 – 1.79 (1H, m, C4-$H_A$), 1.55 (3H, s, Me), 1.48 – 1.58 (1H, m, C4-$H_B$), 1.40 (3H, s, Me). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 148.3 (C Ar), 144.1 (C Ar), 142.8 (C Ar), 135.8 (C Ar), 133.3 (C Ar), 131.5 (C Ar), 130.4 (C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.3 (2 × C Ar), 127.8 (2 × C Ar), 126.9 (C Ar), 126.7 (C Ar), 123.9 (C Ar), 68.6 (C2), 53.9 (C6), 53.4 (C3), 47.0 (C5), 28.5 (C4), 27.5 (Me), 22.2 (Me). **HRMS** (ESI): calculated for $C_{25}H_{26}N_2O_4SNa$ $[M+Na]^+$ requires *m/z* 473.1511, found *m/z* 473.1506. **IR** (film) $\nu_{max}$: 2980, 1542, 1370, 1337, 1216, 1159 $cm^{-1}$.

**(3w): (±)- 4-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-1-azaspiro[4.4]nonane**

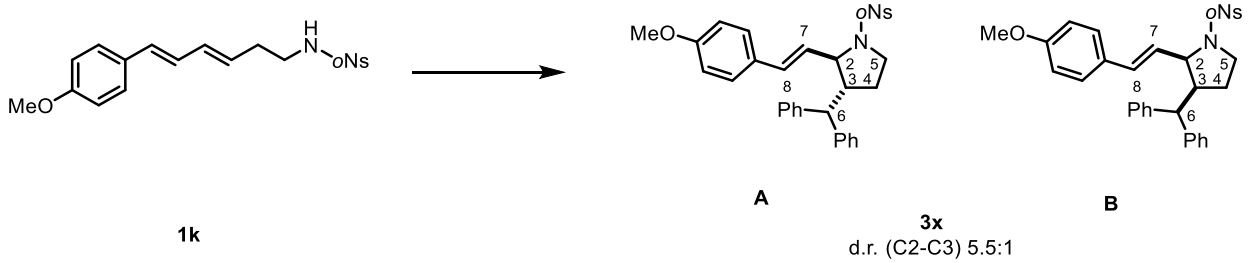

**1j** **3w**

Prepared according to **General Procedure K** using **1j** (32.5 mg, 0.11 mmol) and benzhydrol (19 mg, 0.11 mmol). Flash column chromatography (gradient elution 15% → 25% EtOAc – pentane) afforded **3w** as a colourless oil (50 mg, 99%).

Data for **3w: $R_f$** 0.30 (30% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.00 – 8.05 (1H, m, Ar), 7.62 – 7.70 (3H, m, Ar), 7.33 – 7.37 (2H, m, Ar), 7.19 – 7.28 (6H, m, Ar), 7.09 – 7.16 (2H, m, Ar), 3.87 (1H, d, *J* = 10.5 Hz, C6-H), 3.41 (1H, ddd, *J* = 9.9, 8.8, 5.3 Hz, C5-$H_A$), 3.34 (1H, ddd, *J* = 9.9, 8.3, 6.7 Hz, C5-$H_B$), 3.07 (1H, ddd, *J* = 10.5, 8.5, 6.3 Hz, C3-H), 2.00 – 2.11 (2H, m, 2 × C-H), 1.90 (1H, ddd, *J* = 13.5, 8.3, 5.3 Hz, C4-$H_A$), 1.74 – 1.84 (1H, m, C-H), 1.65 – 1.74 (1H, m, C-H), 1.51 – 1.64

(3H, m, 3 × C-H), 1.42 – 1.50 (1H, m, C4-$H_B$), 1.17 – 1.29 (1H, m, C-H), 1.00 – 1.10 (1H, m, C-H). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 149.7 (C Ar), 144.6 (C Ar), 144.1 (C Ar), 135.4 (C Ar), 133.4 (C Ar), 131.7 (C Ar), 130.3 (C Ar), 128.8 (2 × C Ar), 128.8 (2 × C Ar), 128.0 (2 × C Ar), 128.0 (2 × C Ar), 126.6 (C Ar), 126.5 (C Ar), 124.3 (C Ar), 80.1 (C2), 52.7 (C6), 51.5 (C3), 47.1 (C5), 36.6 ($CH_2$), 33.3 ($CH_2$), 28.2 (C4), 25.0 ($CH_2$), 24.3 ($CH_2$). **HRMS** (ESI): calculated for $C_{27}H_{28}N_2O_4SNa$ $[M+Na]^+$ requires *m/z* 499.1667, found *m/z* 499.1660. **IR** (film) $\nu_{max}$: 2980, 2888, 1710, 1541, 1371, 1159 $cm^{-1}$.

**(3x): (±)-(2*R*,3*R*)-3-Benzhydryl-2-[(1'*E*)-4-methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*R*,3*S*)-3-Benzhydryl-2-[(1'*E*)-4-methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine**

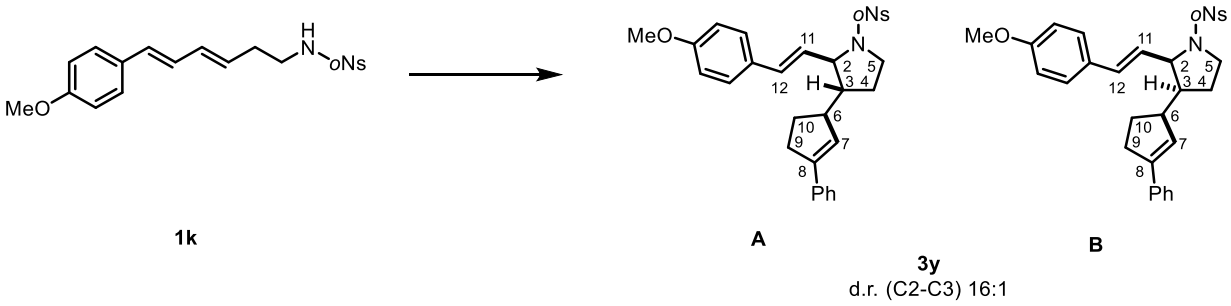



Prepared according to **General Procedure K** using **1k** (15 mg, 0.040 mmol) and benzhydrol (7 mg, 0.040 mmol). Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3w** as a partially separable 5.5:1 mixture of diastereomers, **3x-A** was isolated as a colourless oil (3 mg, 15%) and a 4.5:1 mixture of **3x-A** + **3x-B** was isolated as a colourless oil (17 mg, 78%).

Data for **3x-A: $R_f$** 0.45 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.83 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.55 (1H, dd, *J* = 8.0, 1.4 Hz, Ar), 7.47 – 7.52 (1H, m, Ar), 7.31 – 7.36 (1H, m, Ar), 7.22 – 7.29 (4H, m, Ar), 7.14 – 7.21 (5H, m, Ar), 7.06 – 7.11 (1H, m, Ar), 6.94 (2H, d, *J* = 8.7 Hz, Ar), 6.74 (2H, d, *J* = 8.7 Hz, Ar), 5.92 (1H, d, *J* = 15.7 Hz, C8-H), 5.57 (1H, dd, *J* = 15.7, 7.8 Hz, C7-H), 4.27 (1H, dd, *J* = 7.8, 3.6 Hz, C2-H), 3.87 (1H, dt, *J* = 10.2, 7.2 Hz, C5-$H_A$), 3.79 (OMe), 3.75 (1H, d, *J* = 11.5 Hz, C6-H), 3.62 (1H, ddd, *J* = 10.2, 7.2, 5.7 Hz, C5-$H_B$), 2.92 – 3.00 (1H, m, C3-H), 2.07 (1H, dq, *J* = 13.8, 7.2 Hz, C4-$H_A$), 1.61 – 1.69 (1H, m, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.4 (C Ar), 148.1 (C Ar), 143.1 (C Ar), 142.9 (C Ar), 134.2 (C Ar), 133.1 (C Ar), 131.7 (C Ar), 131.4 (C Ar), 131.4 (C8), 129.1 (C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.3 (2 × C Ar), 128.0 (2 × C Ar), 127.7 (2 × C Ar), 126.9 (C Ar), 126.8 (C Ar), 125.9 (C7), 123.8 (C Ar), 113.8 (2 × C Ar), 66.3 (C2), 55.4 (OMe), 54.5 (C6), 50.5 (C3), 48.0 (C5), 28.9 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C3-H and C7-H, between C3-H and C8-H. **HRMS** (ESI): calculated for $C_{32}H_{30}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 577.1773, found *m/z* 577.1761. **IR** (film) $\nu_{max}$: 2980, 2888, 2360, 1381, 1251, 1158 $cm^{-1}$.

Data for **3x-B** (from the mixture): **$R_f$** 0.40 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.93 – 7.97 (1H, m, Ar), 7.43 – 7.49 (2H, m, Ar), 7.08 – 7.39 (11H, m, Ar), 7.02 (2H, d, *J* = 8.7 Hz, Ar), 6.82 (2H, d, *J* = 8.7 Hz, Ar), 5.84 (1H, d, *J* = 15.7 Hz, C8-H), 5.71 (1H, dd, *J* = 15.7, 7.8 Hz, C7-H), 4.65 (1H, t, *J* = 7.4 Hz, C2-H), 3.83 (OMe), 3.74 – 3.79 (1H, m, C5-$H_A$), 3.62 – 3.64 (1H, m, C6-H), 3.48 (1H, td, *J* = 10.2, 7.2 Hz, C5-$H_A$), 3.17 – 3.27 (1H, m, C3-H), 1.75 – 1.89 (1H, m, C4-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.4 (C Ar), 148.2 (C Ar), 143.5 (C Ar), 142.4 (C Ar), 133.3 (C Ar), 133.3 (C8), 131.7 (C Ar), 131.3 (C Ar), 129.0 (2 × C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.1 (2 × C Ar), 127.8 (2 × C Ar), 127.7 (C Ar + 2 × C Ar), 126.7 (C Ar), 123.8 (C Ar), 121.8 (C7), 114.0 (2 × C Ar), 64.1 (C2), 55.4 (OMe), 53.0 (C6), 48.5 (C3), 47.5 (C5), 29.3 (C4).

**(3y): (±)-(2*R*,3*R*)-2-[(1'*E*)-4-Methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-3-[(1''*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine and (±)-(2*R*,3*S*)-2-[(1'*E*)-4-Methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-3-[(1''*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**



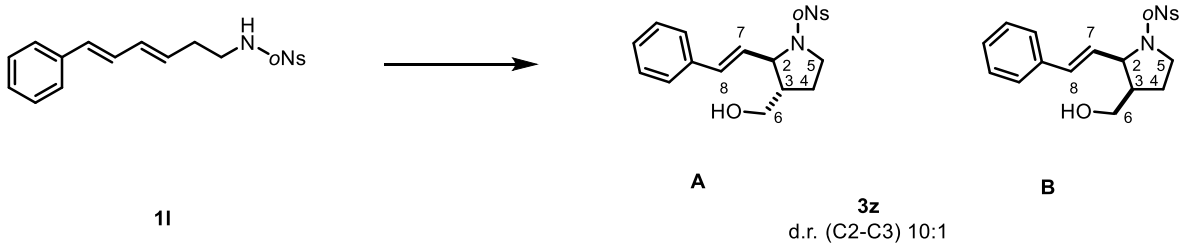

Prepared according to **General Procedure K** using **1k** (13 mg, 0.032 mmol) and **2q** (5.0 mg, 0.032 mmol) at 0 °C for 48 h. Flash column chromatography (gradient elution 15% → 25% EtOAc – pentane) afforded **3y-A** as a colourless oil (15 mg, 86%). (Note the d.r. was determined *via* $^1$H NMR integration of the crude mixture).

Data for **3y-A**: **$R_f$** 0.45 (35% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.91 (1H, dd, *J* = 8.0, 1.4 Hz, Ar), 7.55 (1H, dd, *J* = 7.9, 1.3 Hz, Ar), 7.45 – 7.50 (1H, m, Ar), 7.37 – 7.41 (2H, m, Ar), 7.28 – 7.33 (3H, m, Ar), 7.20 – 7.25 (1H, m, Ar), 7.04 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 6.40 (1H, d, *J* = 15.7 Hz, C12-H), 6.07 (1H, q, *J* = 2.0 Hz, C7-H), 5.61 (1H, dd, *J* = 15.7, 8.7 Hz, C11-H), 4.26 (1H, t, *J* = 8.7 Hz, C2-H), 3.95 (1H, ddd, *J* = 10.8, 6.3, 3.1 Hz, C5-$H_A$), 3.80 (OMe), 3.53 (td, *J* = 9.9, 6.3 Hz, C5-$H_B$), 2.93 – 3.00 (1H, m, C6-H), 2.61 – 2.75 (2H, m, C9-$H_2$), 2.18 – 2.23 (1H, m, C10-$H_A$), 2.10 – 2.17 (1H, m, C3-H), 2.02 – 2.09 (1H, m, C4-$H_A$), 1.73 – 1.82 (1H, m, C4-$H_B$), 1.66 – 1.73 (1H, m, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.6 (C Ar), 148.0 (C Ar), 144.2 (C Ar), 136.2 (C Ar), 135.0 (C Ar), 133.2 (C12), 132.9 (C Ar), 131.6 (C Ar), 131.4 (C Ar), 128.9 (C8), 128.5 (2 × C Ar), 127.8 (2 × C Ar), 127.5 (C Ar), 126.5 (C7), 126.2 (C11), 125.8 (2 × C Ar), 123.8 (C Ar), 113.9 (2 × C Ar), 67.0 (C2), 55.4 (OMe), 51.9 (C3), 48.9 (C5), 47.4 (C6), 32.9 (C9), 29.0 (C10), 28.4 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H. **HRMS**

(ESI): calculated for $C_{30}H_{30}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 533.1773, found *m/z* 533.1765. **IR** (film) $\nu_{max}$: 2980, 2889, 2360, 1461, 1381, 1251 $cm^{-1}$.

Data for **3y-B:** not isolated after flash column chromatography.

**(3z): (±)-{(2*R*,3*S*)-1-[(2-Nitrophenyl)sulfonyl]-2-[(1'*E*)-styryl]pyrrolidin-3-yl}methanol and (±)-{(2*R*,3*R*)-1-[(2-Nitrophenyl)sulfonyl]-2-[(1'*E*)-styryl]pyrrolidin-3-yl}methanol**



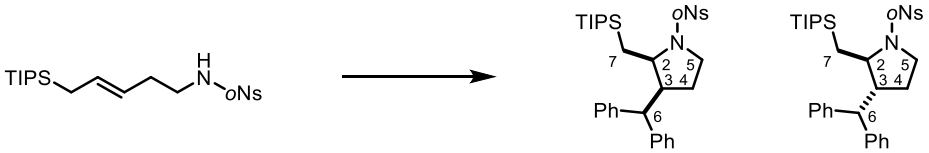

Prepared according to **General Procedure K** using **1l** (9.5 mg, 0.026 mmol) and paraformaldehyde (16 mg, 0.53 mmol, 20.0 equiv.). Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3z** as an inseparable 10:1 mixture of diastereomers as a colourless oil (3 mg, 20%).

Data for **3z-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.94 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.57 (1H, dd, *J* = 7.9, 1.3 Hz, Ar), 7.51 (1H, td, *J* = 7.7, 1.4 Hz, Ar), 7.39 (1H, td, *J* = 7.7, 1.4 Hz, Ar), 7.27 – 7.21 (3H, m, Ar), 7.17 – 7.12 (2H, m, Ar), 6.47 (1H, d, *J* = 15.8 Hz, C8-H), 5.85 (1H, dd, *J* = 15.8, 8.1 Hz, C7-H), 4.36 (1H, dd, *J* = 8.1, 6.2 Hz, C2-H), 3.88 (1H, ddd, *J* = 10.3, 8.0, 4.6 Hz, C5-$H_A$), 3.55 – 3.68 (3H, m, C5-$H_B$ + C6-$H_2$), 2.28 (1H, dp, *J* = 7.9, 6.2 Hz, C3-H), 2.12 (1H, dtd, *J* = 11.5, 6.9, 4.6 Hz, C4-$H_A$), 1.83 (1H, dq, *J* = 12.6, 8.0 Hz, C4-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 148.1 (C Ar), 136.0 (C Ar), 134.3 (C Ar), 133.2 (C8), 133.2 (C Ar), 131.6 (C Ar), 131.5 (C Ar), 128.6 (2 × C Ar), 128.1 (C7), 128.0 (C Ar), 126.6 (2 × C Ar), 123.9 (C Ar), 64.6 (C2), 62.8 (C6), 48.8 (C3), 48.6 (C5), 27.3 (C4).

Partial data for **3z-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.96 – 8.00 (1H, m, Ar), 7.49 – 7.53 (1H, m, Ar), 7.42 – 7.46 (1H, m, Ar), 7.17 – 7.27 (6H, m, Ar), 6.48 (1H, d, *J* = 15.9 Hz, C8-H), 5.93 (1H, dd, *J* = 15.8, 8.3 Hz, C7-H), 4.73 (1H, t, *J* = 8.0 Hz, C2-H), 3.84 – 3.90 (1H, m, C5-$H_A$), 3.74 – 3.81 (2H, m, C5-$H_B$ + C6-$H_A$), 3.55 – 3.68 (1H, m, C6-$H_B$), 2.54 – 2.63 (1H, m, C3-H), 2.06 – 2.16 (1H, m, C4-$H_A$), 1.77 – 1.88 (1H, m, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 148.1 (C Ar), 136.0 (C Ar), 134.3 (C Ar), 133.6 (C Ar), 133.4 (C8), 131.6 (C Ar), 131.4 (C Ar), 128.7 (2 × C Ar), 128.2 (C7), 128.0 (C Ar), 126.7 (2 × C Ar), 124.8 (C Ar), 63.8 (C2), 62.1 (C6), 48.8 (C3), 46.5 (C5), 26.9 (C4).

Data for **3z**: **$R_f$** 0.50 (30% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{19}H_{20}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 411.0991, found *m/z* 411.0985. **IR** (film) $\nu_{max}$: 3658, 2980, 2888, 1738, 1542, 1378 $cm^{-1}$.

**(3aa): (±)-(2*S*,3*S*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)methyl]-pyrrolidine and (±)-(2*S*,3*R*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)-methyl]pyrrolidine**




**1m**
*E:Z*
4:1

**3aa**
d.r. (C2-C3) 4:1

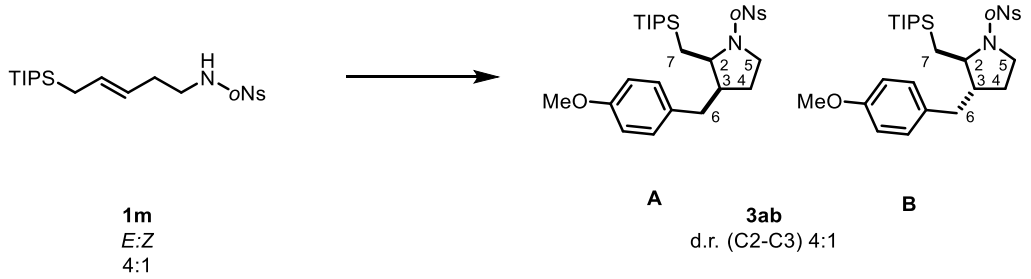
Prepared according to **General Procedure K** using **1m** (22 mg, 0.052 mmol) and benzhydrol (16 mg, 0.053 mmol) at 0 °C for 16 h. Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3aa** as a separable 4:1 mixture of diastereomers as a colourless oil (31 mg, 99%).

Data for **3aa-A**: $\mathbf{R_f}$ 0.40 (50% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.02 (1H, dd, *J* = 7.7, 1.6 Hz, Ar), 7.73 – 7.82 (2H, m, Ar), 7.68 (1H, dd, *J* = 7.7, 1.6 Hz, Ar), 7.24 – 7.29 (2H, m, Ar), 7.14 – 7.20 (5H, m, Ar), 7.05 – 7.12 (3H, m, Ar), 4.22 (1H, ddd, *J* = 12.6, 5.8, 2.0 Hz, C2-H), 3.71 – 3.77 (1H, m, C5-$H_A$), 3.70 (1H, d, *J* = 11.7 Hz, C6-H), 3.52 (1H, ddd, *J* = 12.9, 8.7, 4.7 Hz, C5-$H_B$), 2.43 – 2.52 (1H, m, C3-H), 1.68 – 1.78 (2H, m, C4-$H_2$), 1.11 (3H, hept, *J* = 7.5 Hz, 3 × C**H**$(CH_3)_2$), 0.95 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 0.82 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 0.76 – 0.80 (1H, m, C7-$H_A$), 0.69 (1H, dd, *J* = 14.8, 2.0 Hz, C7-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 148.8 (C Ar), 143.6 (C Ar), 142.6 (C Ar), 133.7 (C Ar), 132.7 (C Ar), 131.6 (C Ar), 131.3 (C Ar), 129.1 (2 × C Ar), 128.8 (2 × C Ar), 127.9 (2 × C Ar), 127.4 (2 × C Ar), 127.0 (C Ar), 126.6 (C Ar), 124.1 (C Ar), 60.4 (C2), 53.7 (C6), 49.0 (C3), 46.6 (C5), 28.3 (C4), 19.3 (3 × CH(**C**$H_3$)$_2$), 19.0 (3 × CH(**C**$H_3$)$_2$), 11.6 (3 × **C**H$(CH_3)_2$), 7.6 (C7). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C3-H, between C6-H and C7-$H_A$, between C6-H and C7-$H_B$. **HRMS** (ESI): calculated for $C_{33}H_{44}N_2O_4SSiNa$ $[M+Na]^+$ requires *m/z* 615.2689, found *m/z* 615.2678. **IR** (film) $\nu_{max}$: 2980, 2889, 1544, 1371, 1163, 1127 $cm^{-1}$.

Data for **3aa-B**: $\mathbf{R_f}$ 0.50 (50% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.09 (1H, dd, *J* = 7.8, 1.4 Hz, Ar), 7.65 – 7.77 (2H, m, Ar), 7.25 – 7.30 (3H, m, Ar), 7.21 – 7.24 (2H, m, Ar), 7.15 – 7.20 (1H, m, Ar), 7.05 – 7.14 (3H, m, Ar), 6.92 – 6.96 (2H, m, Ar), 3.97 (1H, dd, *J* = 12.1, 2.8 Hz, C2-H), 3.63 – 3.69 (1H, m, C5-$H_A$), 3.62 (1H, d, *J* = 11.8 Hz, C6-H), 3.51 (td, *J* = 9.6, 1.9 Hz, C5-$H_B$), 2.71 (1H, dd, *J* = 11.9, 6.2 Hz, C3-H), 2.16 – 2.27 (1H, m, C4-$H_A$), 1.77 – 1.85 (1H, m, C4-$H_B$), 1.06 (1H, dd, *J* = 15.0, 2.8 Hz, C7-$H_A$), 0.96 – 1.03 (1H, m, C7-$H_B$), 0.94 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 0.82 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 0.64 (3H, hept, *J* = 7.5 Hz, 3 × C**H**$(CH_3)_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 148.4 (C Ar), 143.2 (C Ar), 143.0 (C Ar), 134.5 (C Ar), 133.4 (C Ar), 131.7 (C Ar), 131.5 (C Ar), 128.9 (2 × C Ar), 128.7 (2 × C Ar), 128.6 (2 × C Ar), 128.4 (2 × C Ar), 126.7 (C Ar), 126.7 (C Ar), 124.3 (C Ar), 61.6 (C2), 53.0 (C6), 49.7 (C3), 45.6 (C5), 27.2 (C4), 19.2 (3 × CH(**C**$H_3$)$_2$), 18.9

(3 × CH(**C**H$_3$)$_2$), 16.7 (C7), 11.5 (3 × **C**H(CH$_3$)$_2$). **NOESY- 2D (500 MHz, CDCl$_3$)**: between C2-H and C6-H. **HRMS** (ESI): calculated for $C_{33}H_{44}N_2O_4SSiNa$ $[M+Na]^+$ requires *m/z* 615.2689, found *m/z* 615.2677. **IR** (film) $\nu_{max}$: 2980, 2889, 1544, 1371, 1163, 1127 cm$^{-1}$.

**(3ab): (±)-(2*S*,3*R*)-3-(4-Methoxybenzyl)-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)methyl]-pyrrolidine and (±)-(2*S*,3*S*)-3-(4-methoxybenzyl)-1-[(2-nitrophenyl)sulfonyl]-2-[(triiso-propylsilyl)methyl]pyrrolidine**




**1m**
*E:Z*
4:1

**3ab**
d.r. (C2-C3) 4:1

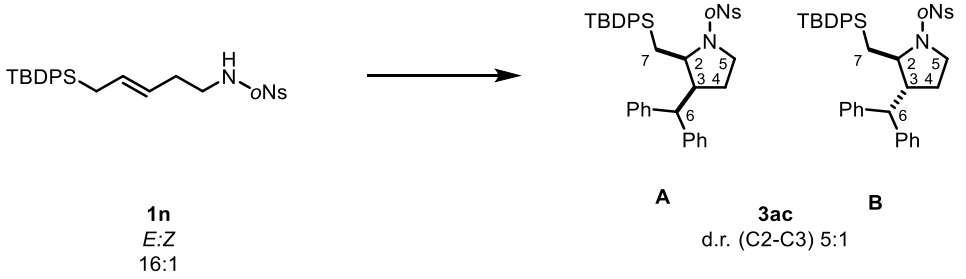
Prepared according to **General Procedure K** using **1m** (27 mg, 0.063 mmol) and 4-methoxybenzyl alcohol (9.0 mg, 0.063 mmol) at 0 °C for 16 h. Flash column chromatography (gradient elution 20% → 35% EtOAc – pentane) afforded **3ab** as a separable 4:1 mixture of diastereomers as a colourless oil (34.5 mg, 99%).

Data for **3ab-A**: **R$_f$** 0.50 (60% EtOAc – pentane). **$^1$H NMR (500 MHz, CDCl$_3$) δ** 7.99 (1H, dd, *J* = 7.7, 1.6 Hz, Ar), 7.62 – 7.71 (2H, m, Ar), 7.60 (1H, dd, *J* = 7.6, 1.6 Hz, Ar), 6.95 (2H, d, *J* = 8.7 Hz, Ar), 6.80 (2H, d, *J* = 8.7 Hz, Ar), 4.24 (1H, dt, *J* = 8.6, 5.9 Hz, C2-H), 3.78 (OMe), 3.68 (1H, ddd, *J* = 11.7, 9.0, 5.9 Hz, C5-H$_A$), 3.47 (1H, ddd, *J* = 11.7, 8.6, 5.8 Hz, C5-H$_B$), 2.65 (1H, dd, *J* = 14.0, 6.2 Hz, C6-H$_A$), 2.46 (1H, dd, *J* = 14.0, 6.9 Hz, C6-H$_B$), 2.02 – 2.10 (1H, m, C3-H), 1.75 – 1.84 (1H, m, C4-H$_A$), 1.69 (1H, dtd, *J* = 12.7, 8.6, 5.8 Hz, C4-H$_B$), 1.17 (3H, hept, *J* = 7.5 Hz, 3 × C**H**(CH$_3$)$_2$), 1.05 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 1.02 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 0.87 (1H, dd, *J* = 14.8, 8.6 Hz, C7-H$_A$), 0.75 (1H, dd, *J* = 14.8, 5.9 Hz, C7-H$_B$). **$^{13}$C NMR (125 MHz, CDCl$_3$) δ** 158.2 (C Ar), 148.5 (C Ar), 133.6 (C Ar), 133.5 (C Ar), 131.9 (C Ar), 131.4 (C Ar), 131.1 (C Ar), 129.6 (2 × C Ar), 124.1 (C Ar), 114.1 (2 × C Ar), 62.0 (C2), 55.4 (OMe), 46.5 (C5), 45.5 (C3), 34.2 (C6), 28.1 (C4), 19.2 (3 × CH(**C**H$_3$)$_2$), 19.1 (3 × CH(**C**H$_3$)$_2$), 11.7 (3 × C**H**(CH$_3$)$_2$), 9.2 (CC-7). **NOESY- 2D (500 MHz, CDCl$_3$)**: between C2-H and C6-H, between C3-H$_A$ and C7-H$_B$, between C6-H$_B$ and C7-H$_B$. **HRMS** (ESI): calculated for $C_{28}H_{43}N_2O_5SSi$ $[M+H]^+$ requires *m/z* 547.2662, found *m/z* 547.2654. **IR** (film) $\nu_{max}$: 2980, 2866, 1544, 1545, 1512, 1372 cm$^{-1}$.

Data for **3ab-B**: **R$_f$** 0.45 (60% EtOAc – pentane). **$^1$H NMR (500 MHz, CDCl$_3$) δ** 8.07-8.11 (1H, m, Ar), 7.66 – 7.71 (2H, m, Ar), 7.60 – 7.64 (1H, m, Ar), 6.88 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 4.05 (1H, dd, *J* = 12.7, 2.5 Hz, C2-H), 3.77 (OMe), 3.53 – 3.59 (2H, m, C5-H$_2$), 2.45 – 2.51 (1H, m, C6-H$_A$), 2.06 – 2.17 (3H, m, C3-H + C4-H$_A$ + C6-H$_B$), 1.69 – 1.76 (1H, m, C4-H$_B$), 1.04 – 1.13 (2H, m, C7-H$_2$), 0.99 (9H, d, *J* = 7.4 Hz, 3 × CH(C**H$_3$**)$_2$), 0.97 (9H, d, *J* = 7.4 Hz,

3 × CH(C**H**$_3$)$_2$), 0.86 (3H, hept, *J* = 7.5 Hz, 3 × C**H**(CH$_3$)$_2$). **$^{13}$C NMR (125 MHz, CDCl$_3$) δ** 158.3 (C Ar), 148.4 (C Ar), 133.4 (C Ar), 133.4 (C Ar), 131.7 (C Ar),131.4 (C Ar), 131.0 (C Ar), 130.1 (2 × C Ar), 124.2 (C Ar), 114.0 (2 × C Ar), 63.8 (C2), 55.4 (OMe), 46.8 (C3), 45.7 (C5), 37.8 (C6), 27.6 (C4), 19.0 (3 × CH(**C**H$_3$)$_2$), 18.9 (3 × CH(**C**H$_3$)$_2$), 18.0 (C7), 11.4 (3 × **C**H(CH$_3$)$_2$). **HRMS** (ESI): calculated for $C_{28}H_{43}N_2O_5SSi$ $[M+H]^+$ requires *m/z* 547.2662, found *m/z* 547.2654. **IR** (film) $\nu_{max}$: 2980, 2866, 1544, 1545, 1512, 1372 cm$^{-1}$.

**(3ac): (±)-(2*S*,3*S*)-3-Benzhydryl-2-[(*tert*-butyldiphenylsilyl)methyl]-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*S*,3*R*)-3-Benzhydryl-2-[(*tert*-butyldiphenylsilyl)methyl]-1-[(2-nitrophenyl)-sulfonyl]pyrrolidine**



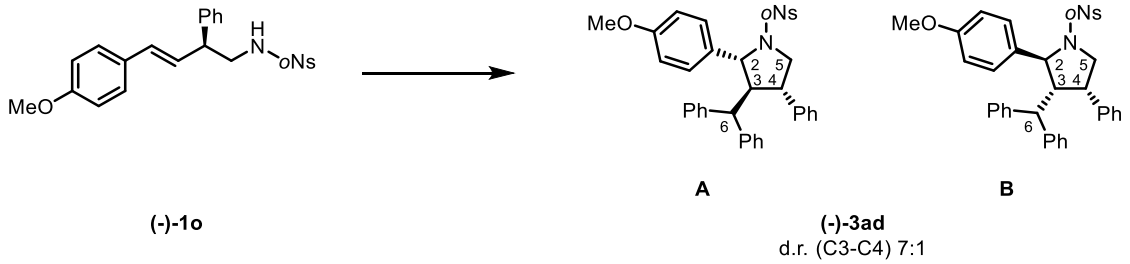

Prepared according to **General Procedure K** using **1n** (114 mg, 0.225 mmol) and benzhydrol (42 mg, 0.225 mmol) at 0 °C for 16 h. Flash column chromatography (gradient elution 6% → 10% EtOAc – pentane) afforded **3ac** as a separable 5:1 mixture of diastereomers as a colourless oil (150 mg, 99%).

Data for **3ac-A**: **R$_f$** 0.45 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, CDCl$_3$) δ** 7.51 – 7.60 (3H, m, Ar), 7.45 – 7.48 (1H, m, Ar), 7.15 – 7.40 (17H, m, Ar), 6.94 – 6.98 (2H, m, Ar), 6.65 – 6.68 (1H, m, Ar), 4.11 (1H, ddd, *J* = 12.2, 5.9, 2.0 Hz, C2-H), 3.86 (1H, d, *J* = 12.0 Hz, C6-H), 3.81 – 3.89 (1H, m, C5-H$_A$), 3.52 (1H, ddd, *J* = 13.0, 9.4, 3.8 Hz, C5-H$_B$), 2.65 – 2.76 (1H, m, C3-H), 1.78 – 1.93 (1H, m, C4-H$_2$), 1.45 (1H, dd, *J* = 15.1, 12.2 Hz, C7-H$_A$), 1.34 (1H, dd, *J* = 15.2, 2.1 Hz, C7-H$_B$). 0.83 (9H, s, 3 × C(C**H**$_3$)$_3$). **$^{13}$C NMR (125 MHz, CDCl$_3$) δ** 147.2 (C Ar), 143.4 (C Ar), 142.9 (C Ar), 136.03 (2 × C Ar), 136.02 (C Ar), 135.9 (2 × C Ar), 133.5 (C Ar), 132.9 (C Ar), 132.7 (C Ar), 131.9 (C Ar), 131.3 (C Ar), 129.3 (2 × C Ar), 129.0 (C Ar), 128.9 (2 × C Ar), 128.7 (C Ar), 128.0 (2 × C Ar), 127.8 (2 × C Ar), 127.4 (2 × C Ar), 127.3 (2 × C Ar), 127.0 (C Ar), 126.8 (C Ar), 123.9 (C Ar), 59.5 (C2), 53.7 (C6), 49.5 (C3), 46.9 (C5), 28.3 (C4), 27.5 (3 × C(**C**H$_3$)$_3$), 18.6 (**C**(CH$_3$)$_3$), 7.0 (C7). **NOESY-2D (500 MHz, CDCl$_3$)**: between C2-H and C3-H, between C6-H and C7-H$_A$, between C6-H and C7-H$_B$. **HRMS** (ESI): calculated for $C_{40}H_{42}N_2O_4SSiNa$ $[M+Na]^+$ requires *m/z* 697.2532, found *m/z* 697.2521. **IR** (film) $\nu_{max}$: 2980, 2360, 1543, 1372, 1164, 1126 cm$^{-1}$.

Data for **3ac-B**: **R$_f$** 0.50 (30% EtOAc – pentane). **$^1$H NMR (500 MHz, CDCl$_3$) δ** 7.11 – 7.15 (2H, m, Ar), 7.61 – 7.67 (2H, m, Ar), 7.48 – 7.56 (3H, m, Ar), 7.35 – 7.45 (4H, m, Ar), 7.22 – 7.31 (3H, m, Ar), 7.07 – 7.13 (2H, m, Ar), 7.02 – 7.07 (1H, m, Ar), 6.80 – 6.86 (1H, m, Ar), 6.74 – 6.79 (2H, m, Ar), 6.58 – 6.64 (2H, m, Ar), 6.01 – 6.06 (2H, m, Ar), 3.71 – 3.74 (1H, m, C2-H), 3.67 – 3.71 (1H, m,

C5-$H_A$), 3.58 (1H, td, *J* = 9.6, 1.6 Hz, C5-$H_B$), 3.19 (1H, d, *J* = 12.0 Hz, C6-H), 2.64 (1H, dd, *J* = 12.1, 6.0 Hz, C3-H), 2.07 – 2.19 (1H, m, C4-$H_A$), 1.87 (1H, dd, *J* = 15.1, 2.2 Hz, C7-$H_A$), 1.61 (1H, dd, *J* = 15.1, 11.9 Hz, C7-$H_B$), 1.49 – 1.56 (1H, m, C4-$H_B$), 0.93 (9H, s, 3 × C(C**H**$_3$)$_3$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 148.1 (C Ar), 143.5 (C Ar), 142.5 (C Ar), 136.4 (C Ar), 136.4 (C Ar), 134.9 (C Ar), 133.6 (C Ar), 133.0 (C Ar), 132.8 (C Ar), 131.8 (C Ar), 131.6 (C Ar), 129.7 (C Ar), 129.1 (C Ar), 128.6 (2 × C Ar), 128.3 (2 × C Ar), 128.0 (2 × C Ar), 127.9 (2 × C Ar), 127.7 (2 × C Ar), 127.7 (2 × C Ar), 126.4 (C Ar), 126.0 (C Ar), 123.8 (C Ar), 60.7 (C2), 52.8 (C6), 48.3 (C3), 45.5 (C5), 27.6 (3 × C(**C**H$_3$)$_3$), 26.6 (C4), 18.4 (C7), 18.2 (3 × **C**(CH$_3$)$_3$). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H. **HRMS** (ESI): calculated for $C_{40}H_{42}N_2O_4SSiNa$ $[M+Na]^+$ requires *m/z* 697.2532, found *m/z* 697.2521. **IR** (film) $\nu_{max}$: 2980, 2360, 1543, 1372, 1164, 1126 $cm^{-1}$.

**((–)-3ad): (–)-(2*R*,3*R*,4*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenylpyrrolidine and (–)-(2*S*,3*S*,4*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenylpyrrolidine**



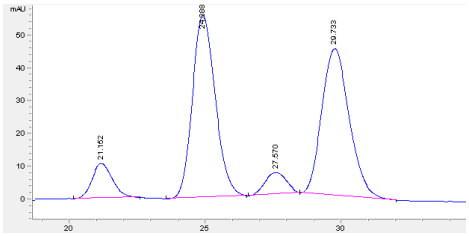

**(-)-1o** **A** **B** **(-)-3ad** d.r. (C3-C4) 7:1

Prepared according to **General Procedure K** using **(–)-1o** (9.5 mg, 0.022 mmol) and benzhydrol (4.0 mg, 0.022 mmol) at 0 °C for 48 h. Flash column chromatography (gradient elution 15% → 25% EtOAc – pentane) afforded **(–)-3ad** as an inseparable 7:1 mixture of diastereomers as a colourless oil (30 mg, 99%, 99% *ee*).

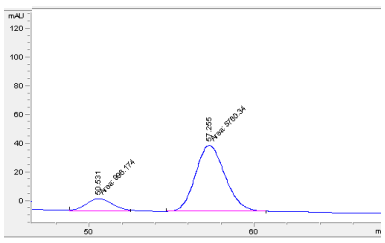
Data for **(–)-3ad-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.51 (1H, dd, *J* = 7.9, 1.4 Hz, Ar), 7.43 – 7.48 (1H, m, Ar), 7.00 – 7.24 (8H, m, Ar), 6.86 – 7.00 (6H, m, Ar), 6.72 – 6.85 (3H, m, Ar), 6.62 (2H, d, *J* = 8.6 Hz, Ar), 6.45 (2H, d, *J* = 8.6 Hz, Ar), 4.85 (1H, d, *J* = 5.9 Hz, C2-H), 4.35 (1H, dd, *J* = 10.8, 8.7 Hz, C5-$H_A$), 4.01 (1H, d, *J* = 10.4 Hz, C6-H), 3.86 – 3.93 (1H, m, C5-$H_B$), 3.70 (OMe), 3.43 – 3.51 (1H, m, C3-H), 3.26 (1H, q, *J* = 8.7 Hz, C4-H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.7 (C Ar), 147.6 (C Ar), 142.5 (C Ar), 141.6 (C Ar), 140.6 (C Ar), 134.0 (C Ar), 133.8 (C Ar), 132.6 (C Ar), 131.1 (C Ar), 131.1 (C Ar), 128.7 (2 × C Ar), 128.6 (2 × C Ar), 128.5 (2 × C Ar), 128.5 (2 × C Ar), 128.4 (2 × C Ar), 128.2 (2 × C Ar), 128.0 (2 × C Ar), 126.8 (C Ar), 126.5 (C Ar), 126.4 (C Ar), 123.6 (C Ar), 113.6 (2 × C Ar), 68.7 (C2), 61.0 (C3), 58.8 (C6), 57.9 (C5), 55.4 (OMe), 51.0 (C4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C4-H, between C2-H and C6-H, between C4-H and C6-H.

Partial data for **(–)-3ad-B** (from the mixture): **$^{1}$H NMR (500 MHz, $CDCl_3$) δ** 7.43 – 7.48 (1H, m, Ar), 7.32 – 7.37 (1H, m, Ar), 7.00 – 7.24 (8H, m, Ar), 6.86 – 7.00 (6H, m, Ar), 6.72 – 6.85 (3H, m, Ar), 6.54 (2H, d, *J* = 8.6 Hz, Ar), 6.18 (2H, d, *J* = 8.6 Hz, Ar), 4.84 (1H, d, *J* = 12.7 Hz, C2-H), 4.37 – 4.40 (1H, m, C5-$H_A$), 4.17 – 4.22 (1H, m, C5-$H_B$), 3.74 – 3.79 (1H, m, C3-H), 3.62 (OMe), 3.43 – 3.51 (2H, m, C4-H + C6-H). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.3 (C Ar), 146.6 (C Ar), 142.8 (C Ar), 142.0 (C Ar), 140.2 (C Ar), 134.0 (C Ar), 133.8 (C Ar), 132.0 (C Ar), 131.1 (C Ar), 130.8 (C Ar), 129.0 (2 × C Ar), 128.6 (2 × C Ar), 128.5 (4 × C Ar), 128.3 (2 × C Ar), 128.1 (2 × C Ar), 127.9 (2 × C Ar), 127.2 (C Ar), 126.6 (C Ar), 126.4 (C Ar), 123.4 (C Ar), 113.2 (2 × C Ar), 67.4 (C2), 57.2 (C3), 56.4 (C5), 55.4 (OMe), 53.5 (C6), 46.3 (C4). *The stereochemistry of the minor isomer was not proven.*

Data for **(–)-3ad**: **$R_f$** 0.40 (30% EtOAc – pentane). **[α]$_D^{25}$** (of the mixture) = –0.159 (*c* = 10.0, $CHCl_3$). **HRMS** (ESI): calculated for $C_{36}H_{33}N_2O_5S$ $[M+H]^+$ requires *m/z* 605.2110, found *m/z* 605.2100. **IR** (film) $\nu_{max}$: 2980, 2889, 2360, 1542, 1372, 1162 $cm^{-1}$. **Chiral HPLC** (Chiralpak IC with guard, 20% IPA, 80% hexane, 1.0 mL/min, 25 ˚C, λ = 210 nm, 10 μL injection).



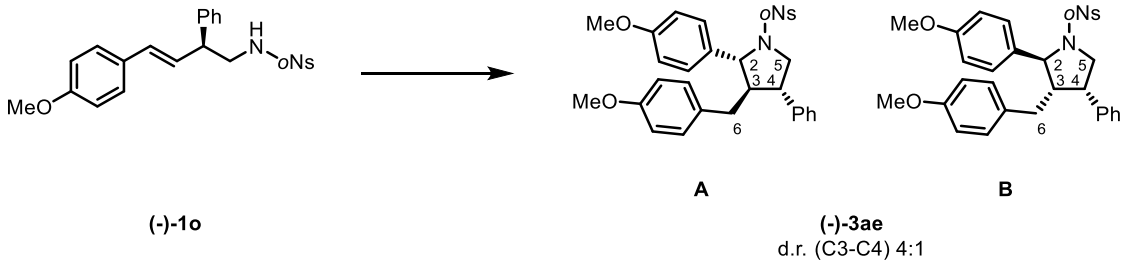

| # | Time | Type | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|---|
| 1 | 3.313 | BV | 38.8 | 7.4 | 0.0795 | 0.518 | 1.625 |
| 2 | 3.424 | VB | 144 | 26.9 | 0.0784 | 1.924 | 0.742 |
| 3 | 21.152 | BB | 556.8 | 10.6 | 0.7797 | 7.437 | 0.797 |
| 4 | 24.888 | BB | 3250.6 | 55.5 | 0.8991 | 43.417 | 0.821 |
| 5 | 27.57 | BB | 361.3 | 6.6 | 0.7638 | 4.826 | 1.052 |
| 6 | 29.733 | BB | 3135.2 | 44.7 | 1.08 | 41.877 | 0.826 |




| # | Time | Type | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|---|
| 1 | 50.531 | MM | 996.2 | 8.7 | 1.9054 | 14.744 | 0.908 |
| 2 | 57.255 | MM | 5760.3 | 45.7 | 2.0997 | 85.256 | 0.864 |

Racemic **(±)-3ad** was made *via* the same procedure using **(±)-1o** (99%, 7:1 d.r.).

**((–)-3ae): (–)-(2*R*,3*R*,4*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenylpyrrolidine and (–)-(2*S*,3*S*,4*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenylpyrrolidine**




**(-)-1o**

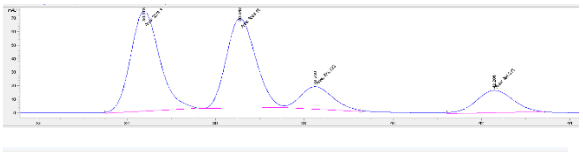
**(-)-3ae**
d.r. (C3-C4) 4:1

Prepared according to **General Procedure K** using **(–)-1o** (38.5 mg, 0.088 mmol) and 4-methoxybenzyl alcohol (12 mg, 0.088 mmol) at 0 °C for 48 h. Flash column chromatography (gradient elution 10% → 30% EtOAc – pentane) afforded **(–)-3ae** as an inseparable 4:1 mixture of diastereomers as a colourless oil (39.5 mg, 80%, 99% *ee*).

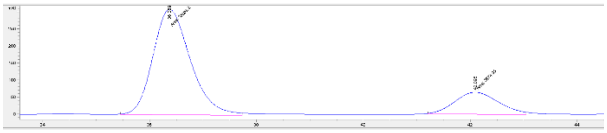
Data for **(–)-3ae-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.49 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.40 – 7.45 (1H, m, Ar), 7.30 – 7.36 (2H, m, Ar), 7.24 – 7.30 (3H, m, Ar), 7.08 – 7.15 (2H, m, Ar), 7.06 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 6.64 (2H, d, *J* = 8.7 Hz, Ar), 6.56 (2H, d, *J* = 8.6 Hz, Ar), 4.62 (1H, d, *J* = 9.6 Hz, C2-H), 4.32 (1H, dd, *J* = 10.7, 7.8 Hz, C5-$H_A$), 3.74 (3H, s, OMe), 3.73 (3H, s, OMe), 3.67 – 3.71 (1H, m, C5-$H_B$), 3.12 (1H, td, *J* = 11.4, 7.8 Hz, C4-H), 2.79 (1H, ddt, *J* = 11.4, 9.6, 5.5 Hz, C3-H), 2.59 (1H, d, *J* = 5.5 Hz, C6-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 158.2 (C Ar), 147.3 (C Ar), 138.2 (C Ar), 134.5 (C Ar), 132.4 (C Ar), 131.6 (C Ar), 130.9 (2 × C Ar), 130.8 (2 × C Ar), 129.5 (2 × C Ar), 129.5 (C Ar), 129.0 (C Ar), 128.2 (2 × C Ar), 127.5 (C Ar), 123.6 (C Ar), 113.7 (2 × C Ar), 113.7 (2 × C Ar), 67.7 (C2), 57.0 (C5), 56.3 (C3), 55.5 (OMe), 55.4 (OMe), 48.5 (C4), 33.8 (C6). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C4-H, between C2-H and C6-$H_2$, between C4-H and C6-$H_2$.

Partial data for **(–)-3ae-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.45 – 7.49 (1H, m, Ar), 7.40 – 7.45 (1H, m, Ar), 7.30 – 7.36 (2H, m, Ar), 7.24 – 7.30 (3H, m, Ar), 7.17 – 7.21 (2H, m, Ar), 6.95 (2H, d, *J* = 8.7 Hz, Ar), 6.89 (2H, d, *J* = 8.7 Hz, Ar), 6.69 – 6.73 (2H, m, Ar), 6.52 (2H, d, *J* = 8.7 Hz, Ar), 4.54 (1H, d, *J* = 9.8 Hz, C2-H), 4.27 (1H, dd, *J* = 10.6, 7.8 Hz, C5-$H_A$), 3.82 (3H, s, OMe), 3.79 (3H, s, OMe), 3.66 – 3.70 (1H, m, C5-$H_B$), 3.04 (1H, td, *J* = 11.4, 7.8 Hz, C4-H), 2.68 – 2.74 (1H, m, C3-H), 2.44 – 2.49 (2H, m, C6-$H_2$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.21 (C Ar), 158.0 (C Ar), 155.9 (C Ar), 143.6 (C Ar), 133.0 (C Ar), 132.3 (C Ar), 131.7 (C Ar), 130.9 (2 × C Ar), 130.3 (2 × C Ar), 130.0 (C Ar), 129.6 (2 × C Ar), 129.0 (2 × C Ar), 128.2 (2 × C Ar), 127.4 (C Ar), 123.5 (C Ar), 114.0 (2 × C Ar), 113.6 (2 × C Ar), 67.1 (C2), 57.0 (C5), 56.0 (C3), 55.6 (OMe), 55.4 (OMe), 47.8 (C4), 33.0 (C6). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C6-$H_2$,

Data for **(–)-3ae**: $\mathbf{R_f}$ 0.40 (30% EtOAc – pentane). $\mathbf{[\alpha]_D^{25}}$ (of the mixture) = –3.15 (*c* = 10.0, $CHCl_3$). **HRMS** (ESI): calculated for $C_{31}H_{30}N_2O_6SNa$ $[M+Na]^+$ requires *m/z* 581.1722, found *m/z* 581.1715. **IR** (film) $\nu_{max}$: 2921, 1711, 1611, 1542, 1511, 1464 $cm^{-1}$. **Chiral HPLC** (Chiralpak IA with guard, 5% IPA, 95% hexane, 1.0 mL/min, 25 ˚C, λ = 210 nm, 10 μL injection).



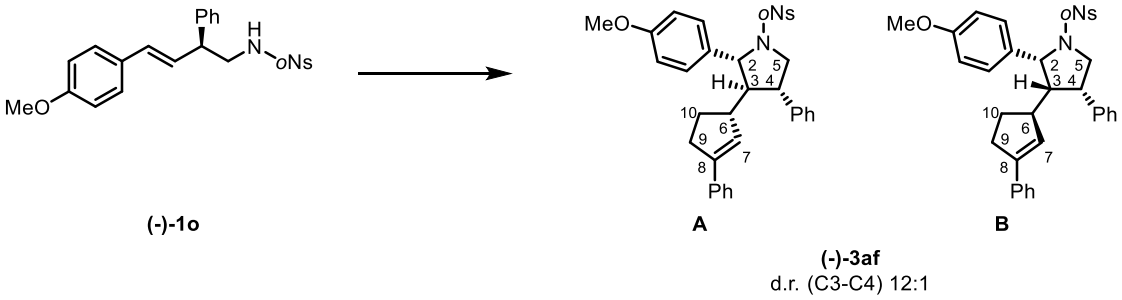
| # | Time | Type | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|---|
| 1 | 34.378 | MM | 3376.3 | 73.8 | 0.7626 | 40.696 | 0.851 |
| 2 | 36.543 | MM | 3053.2 | 66.2 | 0.7688 | 36.801 | 0.842 |
| 3 | 38.25 | MM | 872.7 | 16.8 | 0.8642 | 10.519 | 0.76 |
| 4 | 42.286 | MM | 994.3 | 16.7 | 0.9905 | 11.985 | 0.954 |



| # | Time | Type | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|---|
| 1 | 36.369 | MM | 15262.2 | 310.8 | 0.8185 | 79.752 | 0.783 |
| 2 | 42.095 | MM | 3874.9 | 66.2 | 0.9756 | 20.248 | 0.864 |

Racemic **(±)-3ae** was made *via* the same procedure using **(±)-1o** (99%, 4:1 d.r.).

**((–)-3af): (–)-(2*R*,3*R*,4*S*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenyl-3-[(1'*S*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine and (–)-(2*S*,3*S*,4*S*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenyl-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**




Prepared according to **General Procedure K** using **(–)-1o** (9.0 mg, 0.020 mmol) and **2q** (3.0 mg, 0.020 mmol) at 0 °C for 48 h. Flash column chromatography (gradient elution 15% → 25% EtOAc – pentane) afforded **(–)-3af** as an inseparable 12:1 mixture of diastereomers as a colourless oil (9.5 mg, 83%, 99% *ee*).

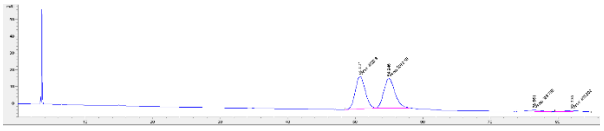
Data for **(–)-3af-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.48 – 7.52 (1H, m, Ar), 7.39 – 7.46 (2H, m, Ar), 7.06 – 7.39 (13H, m, Ar), 6.56 (2H, d, *J* = 8.7 Hz, Ar), 5.55 (1H, q, *J* = 2.3 Hz, C7-H), 4.80 (1H, d, *J* = 9.1 Hz, C2-H), 4.39 (1H, dd, *J* = 10.7, 7.6 Hz, C5-$H_A$), 3.82 – 3.90 (1H, m, C5-$H_B$), 3.73 (OMe), 3.26 (1H, td, *J* = 11.4, 7.5 Hz, C4-H), 2.97 – 3.04 (1H, m, C6-H), 2.81 (1H, ddd, *J* = 11.4, 9.1, 4.4 Hz, C3-H), 2.46 – 2.62 (2H, m, C10-$H_2$), 2.02 (1H, dtd, *J* = 13.3, 9.0, 4.4 Hz, C9-$H_A$), 1.54 – 1.66 (1H, m, C9-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 147.4 (C Ar), 142.6 (C Ar), 139.0 (C Ar), 136.2 (C Ar), 134.5 (C Ar), 133.1 (C8), 132.4 (C Ar), 131.0 (C Ar), 130.9 (C Ar), 129.7 (2 × C Ar), 129.0 (2 × C Ar), 128.3 (2 × C Ar), 128.1 (2 × C Ar), 127.7 (C Ar), 127.6 (C7), 127.3 (C Ar), 125.8 (2 × C Ar), 123.6 (C Ar), 113.7 (2 × C Ar), 66.7 (C2), 60.2 (C3), 57.1 (C5), 55.5 (OMe), 48.3 (C4), 45.9 (C3), 32.7 (C10), 26.0 (C9). **NOESY- 2D (500 MHz, $CDCl_3$)**: between C2-H and C4-H,

between C2-H and C6-H, between C4-H and C7-H, between C4-H and C9-$H_A$, between C4-H and C6-H, between C4-H and C7-H, between C4-H and C9-$H_B$.

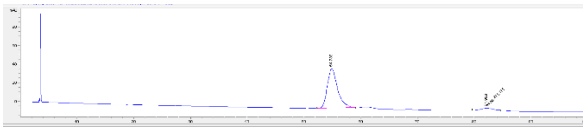
**(–)-3af-B** *could not be assigned due to low intensity of signals in* $^{1}H$ *and* $^{13}C$ *spectra; the stereochemistry is not proven.*

Data for **(–)-3af**: $\mathbf{R_f}$ 0.50 (35% EtOAc – pentane). $[\alpha]_D^{25}$ (of the mixture) = –3.12 (*c* = 10.0, $CHCl_3$). **HRMS** (ESI): calculated for $C_{34}H_{32}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 603.1930, found *m/z* 603.1917. **IR** (film) $\nu_{max}$: 2980, 2889, 1738, 1542, 1372, 1250 $cm^{-1}$.

**Chiral HPLC** (Chiralpak IC with guard, 10% IPA, 90% hexane, 1.0 mL/min, 25 ˚C, λ = 210 nm, 10 μL injection).



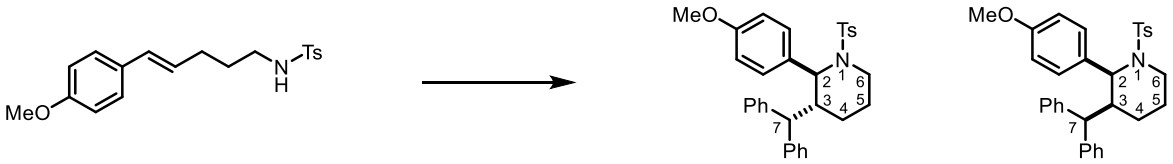
| # | Time | Type | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|---|
| 1 | 50.661 | MM | 2023.8 | 19.5 | 1.7296 | 45.165 | 0.877 |
| 2 | 54.946 | MM | 2072.6 | 17.8 | 1.9456 | 46.254 | 0.8 |
| 3 | 76.551 | MM | 183.7 | 9.8E-1 | 3.1093 | 4.100 | 1.026 |
| 4 | 82.135 | MM | 200.8 | 9.8E-1 | 3.4311 | 4.481 | 0.85 |



| # | Time | Type | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|---|
| 1 | 54.738 | BB | 5363 | 42.3 | 1.8075 | 91.924 | 0.711 |
| 2 | 81.999 | MM | 471.2 | 2.8 | 2.8347 | 8.076 | 0.833 |

Racemic **(±)-3af** was made *via* the same procedure using **(±)-1o** (99%, 12:1 d.r.).

**(5-Ts): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-tosylpiperidine and (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-tosylpiperidine**




Prepared according to **General Procedure K** using **4-Ts** (14 mg, 0.040 mmol) and benzhydrol (7.5 mg, 0.040 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5-Ts** as an inseparable 5:1 mixture of diastereomers as a colourless oil (20 mg, 95%).

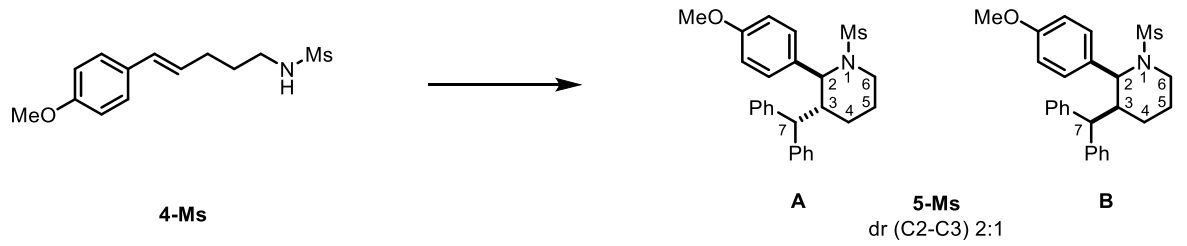
Data for **5-Ts-A** (from the mixture): **$^{1}$H NMR (500 MHz, $CDCl_3$) δ** 7.50 (2H, d, *J* = 8.3 Hz, Ar), 7.45 – 7.39 (2H, m, Ar), 7.33 (2H, t, *J* = 7.7 Hz, Ar), 7.30 – 7.17 (8H, m, Ar), 7.04 – 6.95 (2H, m, Ar), 6.73 (2H, d, *J* = 8.7 Hz, Ar), 5.07 (1H, *br.* s, C2-H), 4.24 (1H, d, *J* = 11.9 Hz, C7-H), 3.93 (1H, dd, *J* = 13.2, 5.0 Hz, C6-$H_A$), 3.77 (3H, s, OMe), 3.15 (1H, td, *J* = 13.1, 3.4 Hz, C6-$H_B$), 3.02 – 2.96 (1H, m, C3-H), 2.41 (3H, s, TsMe), 1.93 – 1.69 (1H, m, C5-$H_A$), 1.52 (1H, tt, *J* = 13.8, 4.0 Hz, C4-$H_A$), 1.42 – 1.34 (1H, m, C4-$H_B$), 1.34 – 1.28 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 143.6 (C Ar), 142.8 (C Ar), 138.0 (C Ar), 132.7 (C Ar), 131.6 (C Ar), 129.4 (2 × C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.3 (2 × C Ar), 128.2 (2 × C Ar), 128.2 (2 × C Ar), 127.3 (2 × C Ar), 126.8

(C Ar), 126.4 (C Ar), 113.8 (2 × C Ar), 57.4 (C1), 55.4 (OMe), 52.1 (C7), 42.2 (C6), 41.9 (C3), 21.6 (TsMe), 20.4 (C4), 19.7 (C5).

Partial data for **5-Ts-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.08 – 7.04 (2H, m, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 6.61 (2H, d, *J* = 8.7 Hz, Ar), 5.04 (1H, d, *J* = 5.4 Hz, C2-H), 3.85 – 3.80 (1H, m, C6-$H_A$), 3.80 (3H, s, OMe), 3.11 – 3.05 (1H, m, C6-$H_B$), 2.88 – 2.79 (1H, m, C3-H), 2.33 (3H, s, TsMe), 1.73 – 1.68 (1H, m, C5-$H_A$), 1.62 (1H, td, *J* = 13.2, 3.8 Hz, C4-$H_A$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 159.1 (C Ar), 143.5 (C Ar), 142.4 (C Ar), 142.0 (C Ar), 137.0 (C Ar), 129.4 (C Ar), 129.0 (2 × C Ar), 128.7 (2 × C Ar), 128.4 (2 × C Ar), 128.0 (C Ar), 127.3 (2 × C Ar), 126.7 (C Ar), 113.2 (2 × C Ar), 58.1 (C2), 55.3 (OMe), 55.2 (C7), 43.3 (C3), 41.1 (C6), 25.3 (C5), 23.4 (C4), 21.5 (TsMe).

Data for **5-Ts**: **$R_f$** 0.52 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{32}H_{33}O_3SNNa$ $[M+Na]^+$ requires m/z 534.2073, found m/z 534.2069. **IR** (film) $\nu_{max}$: 3671, 3649, 3026, 2981, 2972, 2889, 2359, 2339, 1512, 1382 $cm^{-1}$.

**(5-Ms): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-(methylsulfonyl)piperidine and (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-(methylsulfonyl)piperidine**




Prepared according to **General Procedure K** using **4-Ms** (28 mg, 0.10 mmol) and benzhydrol (18 mg, 0.10 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5-Ms** as an inseparable 2:1 mixture of diastereomers as a colourless oil (28 mg, 64%).

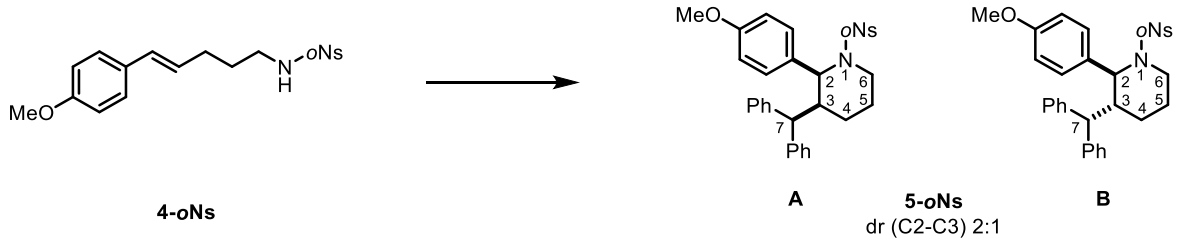
Data for **5-Ms-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.49 – 7.44 (2H, d, *J* = 8.7 Hz, Ar), 7.39 – 7.14 (10H, m, Ar), 6.88 (2H, d, *J* = 8.7 Hz, 2H), 4.91 (1H, s, C2-H), 4.32 (1H, d, *J* = 11.9 Hz, C7-H), 3.87 (1H, dd, *J* = 13.1, 5.3 Hz, C6-$H_A$), 3.80 (3H, s, OMe), 3.28 (1H, td, *J* = 12.8, 3.4 Hz, C6-$H_B$), 2.99 – 2.94 (1H, m, C3-H), 2.62 (3H, s, $SO_2Me$), 1.98 – 1.91 (1H, m, C5-$H_A$), 1.72 – 1.65 (1H, m, C4-$H_A$), 1.60 – 1.53 (1H, m, C4-$H_B$), 1.50 – 1.41 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.8 (C Ar), 143.5 (C Ar), 143.3 (C Ar), 131.9 (C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.5 (2 × C Ar), 128.3 (2 × C Ar), 128.1 (2 × C Ar), 126.9 (C Ar), 126.5 (C Ar), 114.2 (2 × C Ar), 57.3 (C2), 55.4 (OMe), 52.5 (C7), 42.0 (C6), 41.8 (C3), 39.5 ($SO_2Me$), 20.4 (C4), 19.9 (C5).

Partial data for **5-Ms-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.08 – 7.04 (2H, m, Ar), 6.97 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 4.99 (1H, d, *J* = 5.5 Hz, C2-H), 3.82 (3H, s, OMe), 3.83 – 3.79 (1H, m, C7-H), 3.74 – 3.68 (1H, m, C6-$H_A$), 3.16 (1H, td, *J* = 12.4, 3.0 Hz, C6-$H_B$),

3.02 – 2.99 (1H, m, C3-H), 2.06 (3H, s, OMe), 1.91 – 1.83 (1H, m, C5-$H_A$), 1.83 – 1.74 (2H, m, C4-$H_A$ + C5-$H_B$), 1.63 – 1.59 (1H, m, C4-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 159.4 (C Ar), 143.4 (C Ar), 141.8 (C Ar), 132.8 (C Ar), 129.0 (2 × C Ar), 128.7 (2 × C Ar), 128.5 (2 × C Ar), 128.3 (2 × C Ar), 128.0 (2 × C Ar), 126.7 (C Ar), 126.5 (C Ar), 113.7 (2 × C Ar), 58.3 (C2), 55.6 (OMe), 55.3 (C7), 43.5 (C6), 40.6, 37.3 ($SO_2Me$), 25.5 (C4), 23.8 (C5).

Data for **5-Ms**: **$R_f$** 0.32 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{26}H_{26}O_3SNNa$ $[M+Na]^+$ requires m/z 458.1760, found m/z 458.1756. **IR** (film) $\nu_{max}$: 3026, 2935, 1609, 1512, 1451, 1333, 1251, 1151, 1031 $cm^{-1}$.

**(5-*o*Ns): (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine and (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine**



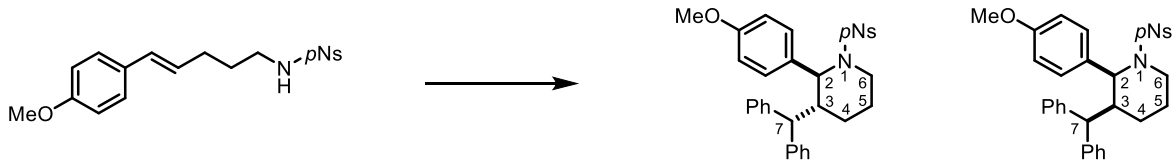

Prepared according to **General Procedure K** using **4-*o*Ns** (30 mg, 0.080 mmol) and benzhydrol (14 mg, 0.080 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5-*o*Ns** as a separable 2:1 mixture of diastereomers as a colourless oil (37 mg, 84%).

Data for **5-*o*Ns-A**: **$R_f$** 0.45 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.64 – 7.62 (1H, m, Ar), 7.58 – 7.54 (2H, m, Ar), 7.43 (1H, ddd, *J* = 7.9, 5.4, 3.4 Hz, Ar), 7.29 – 7.22 (3H, m, Ar), 7.20 – 7.16 (5H, m, Ar), 7.13 – 7.08 (3H, m, Ar), 6.89 – 6.85 (2H, m, Ar), 5.01 (1H, d, *J* = 5.5 Hz, C2-H), 3.79 (3H, s, OMe), 3.75 (1H, d, *J* = 2.4 Hz C6-$H_A$), 3.40 (1H, td, *J* = 13.1, 3.2 Hz, C6-$H_B$), 3.19 (1H, d, *J* = 11.9 Hz, C7-H), 2.94 (1H, app. qd, *J* = 7.0, 6.4, 4.4 Hz, C3-H), 1.89 – 1.86 (1H, m, C5-$H_A$), 1.73 – 1.69 (2H, m, C4-$H_A$ + C5-$H_B$), 1.50 (1H, tt, *J* = 9.9, 2.7 Hz, C4-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 159.2 (C Ar), 148.0 (C Ar), 143.3 (C Ar), 141.9 (C Ar), 133.8 (C Ar), 133.1 (C Ar), 131.4 (3 × C Ar), 131.0 (C Ar), 129.3 (C Ar), 128.8 (2 × C Ar), 128.7 (2 × C Ar), 128.4 (2 × C Ar), 128.0 (2 × C Ar), 126.7 (C Ar), 126.5 (C Ar), 124.3 (C Ar), 113.4 (2 × C Ar), 58.5 (C2), 55.3 (OMe), 55.3 (C7), 43.2 (C3), 41.4 (C6), 25.5 (C5), 23.5 (C4). **HRMS** (ESI): calculated for $C_{31}H_{30}O_5SN_2Na$ $[M+Na]^+$ requires m/z 565.1768, found m/z 565.1766. **IR** (film) $\nu_{max}$: 2981, 2361, 2341, 1609, 1542, 1512, 1494, 1453, 1372, 1341 $cm^{-1}$.

Data for **5-*o*Ns-B**: **$R_f$** 0.49 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.62 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.54 (1H, td, *J* = 7.7, 1.4 Hz, Ar), 7.42 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.30 – 7.20 (11H, m, Ar), 7.19 – 7.16 (1H, m, Ar), 7.14 – 7.11 (3H, m, Ar), 6.77 – 6.75 (2H, m, Ar), 4.96 (1H, *br*. s, C2-H), 4.25 (1H, d, *J* = 11.8 Hz, C7-H), 4.20 (1H, dd, *J* = 13.6, 5.1 Hz, C6-$H_A$), 3.75 (3H, s, OMe),

3.48 (1H, td, *J* = 13.0, 3.3 Hz, C6-$H_B$), 3.03 (1H, *app.* d, *J* = 11.6 Hz, C3-H), 1.94 (1H, dtd, *J* = 14.5, 11.7, 10.5, 6.9 Hz, C4-$H_A$), 1.52 – 1.44 (1H, m, C5-$H_A$), 1.44 – 1.36 (2H, m, C4-$H_B$ + C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.5 (C Ar), 143.5 (C Ar), 143.4 (C Ar), 134.3 (C Ar), 133.0 (C Ar), 131.9 (C Ar), 131.7 (2 × C Ar), 131.7 (C Ar), 128.9 (C Ar), 128.9 (2 × C Ar), 128.2 (2 × C Ar), 128.2 (2 × C Ar), 128.0 (2 × C Ar), 126.6 (C Ar), 126.5 (C Ar), 123.9 (C Ar), 113.9 (2 × C Ar), 58.1 (C2), 55.4 (OMe), 51.7 (C7), 43.6 (C6), 42.5 (C2), 20.5 (C5), 19.9 (C4). **HRMS** (ESI): calculated for $C_{31}H_{30}O_5SN_2Na$ $[M+Na]^+$ requires m/z 565.1768, found m/z 565.1764. **IR** (film) $\nu_{max}$: 2981, 2361, 2341, 1609, 1542, 1512, 1494, 1453, 1372, 1341 $cm^{-1}$.

**(5-*p*Ns): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine and (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine**



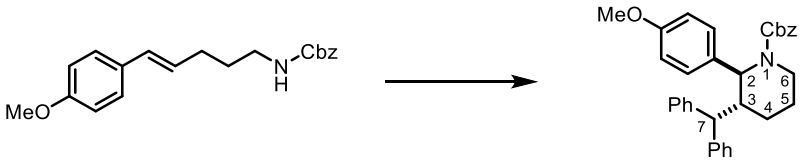

Prepared according to **General Procedure K** using **4-*p*Ns** (15 mg, 0.040 mmol) and benzhydrol (7.5 mg, 0.040 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5-*p*Ns** as an inseparable 3:1 mixture of diastereomers as a colourless oil (19 mg, 88%).

Data for **5-*p*Ns-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.11 (2H, d, *J* = 8.9 Hz, Ar), 7.63 (2H, d, *J* = 8.8 Hz, Ar), 7.47 – 7.32 (5H, m, Ar), 7.32 – 7.07 (5H, m, Ar), 6.91 – 6.77 (2H, m, Ar), 6.72 – 6.61 (2H, m, Ar), 5.03 (1H, *br.* s, C2-H), 4.25 (1H, d, *J* = 11.9 Hz, C7-H), 4.03 (1H, dd, *J* = 12.8, 5.3 Hz, C6-$H_A$), 3.73 (3H, s, OMe), 3.20 (1H, td, *J* = 12.8, 3.3 Hz, C6-$H_B$), 2.91 (1H, dt, *J* = 12.5, 3.2 Hz, C3-H), 1.98 – 1.81 (1H, m, C5-$H_A$), 1.70 – 1.51 (1H, m, C4-$H_A$), 1.51 – 1.38 (2H, m, C4-$H_B$ + C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.8 (C Ar), 149.6 (C Ar), 145.9 (C Ar), 143.3 (C Ar), 143.0 (C Ar), 132.2 (C Ar), 129.0 (2 × C Ar), 129.0 (2 × C Ar), 128.4 (2 × C Ar), 128.3 (2 × C Ar), 128.2 (2 × C Ar), 128.1 (2 × C Ar), 127.1 (C Ar), 126.6 (C Ar), 123.8 (2 × C Ar), 113.9 (2 × C Ar), 58.0 (C2), 55.4 (OMe), 52.2 (C7), 42.7 (C3), 42.6 (C6), 19.9 (C4), 19.6 (C5).

Partial data for **5-*p*Ns-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.98 – 7.92 (2H, m, Ar), 7.40 (2H, d, *J* = 8.8 Hz, Ar), 6.59 – 6.50 (2H, m, Ar), 5.11 (1H, d, *J* = 5.4 Hz, C2-H), 3.95 – 3.86 (1H, m, C6-$H_A$), 3.75 (3H, s, OMe), 3.13 – 3.04 (2H, m, 1 × C6-$H_B$ + 1 × C7-H). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 159.5 (C Ar), 149.3 (C Ar), 145.2 (C Ar), 143.2 (C Ar), 141.7 (C Ar), 131.5 (2 × C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.6 (C Ar), 128.3 (2 × C Ar), 128.0 (2 × C Ar), 126.9 (C Ar), 126.6 (C Ar), 123.4 (2 × C Ar), 113.2 (2 × C Ar), 58.7 (C2), 55.4 (OMe), 55.1 (C7), 43.7 (C3), 41.8 (C6), 25.5 (C5), 23.0 (C4).

Data for **5-*p*Ns**: $\mathbf{R_f}$ 0.54 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{31}H_{30}O_5SN_2Na$ $[M+Na]^+$ requires m/z 565.1768, found m/z 565.1764. **IR** (film) $\nu_{max}$: 3649, 3104, 3062, 3026, 2981, 2889, 2360, 2342, 1528, 1512 $cm^{-1}$.

**(5-Cbz): (±)-Benzyl (2*S*,3*R*)-3-benzhydryl-2-(4-methoxyphenyl)piperidine-1-carboxylate**

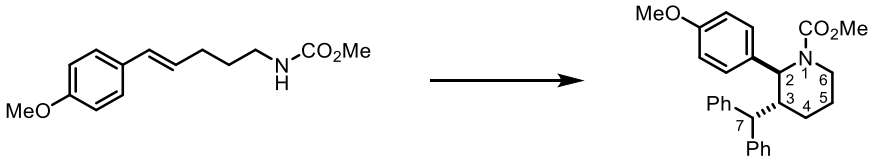



**4-Cbz** **5-Cbz**

Prepared according to **General Procedure K** using **4-Cbz** (13 mg, 0.040 mmol) and benzhydrol (7.5 mg, 0.040 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5-Cbz** as a colourless oil (17 mg, 86%).

Data for **5-Cbz**: $\mathbf{R_f}$ 0.39 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.42 – 7.05 (16H, m, Ar), 6.87 (2H, d, *J* = 8.8 Hz, Ar), 5.26 (1H, s, C2-H), 5.16 – 4.90 (2H, m, $CH_2Ph$), 4.32 – 4.14 (2H, m, C6-$H_A$ + C7-H), 3.79 (3H, s, OMe), 3.22 (1H, ddt, *J* = 12.1, 4.3, 2.2 Hz, C3-H), 2.90 (1H, td, *J* = 13.2, 3.5 Hz, C6-$H_B$), 1.84 – 1.72 (1H, m, C5-$H_A$), 1.63 – 1.50 (1H, m, C4-$H_A$), 1.46 – 1.39 (1H, m, C4-$H_B$), 1.30 – 1.22 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 144.0 (C Ar), 143.6 (C Ar), 132.1 (C Ar), 128.9 (2 × C Ar), 128.9 (2 × C Ar), 128.4 (2 × C Ar), 128.1 (2 × C Ar), 127.9 (2 × C Ar), 127.8 (2 × C Ar), 127.5 (2 × C Ar), 127.1 (2 × C Ar), 126.6 (2 × C Ar), 126.5 (2 × C Ar), 114.2 (2 × C Ar), 67.2 ($CH_2Ph$), 55.4 (OMe), 55.1 (C2), 52.3 (C7), 40.2 (C6), 39.4 (C3), 21.0 (C4), 19.7 (C5). *A signal corresponding to C(O) was not observed.* **HRMS** (ESI): calculated for $C_{33}H_{34}O_3N$ $[M+H]^+$ requires m/z 492.2533, found m/z 492.2533. **IR** (film) $\nu_{max}$: 3028, 2947, 2360, 1691, 1511, 1423, 1245, 1127, 1035, 732 $cm^{-1}$.

**(5a): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-2-(4-methoxyphenyl)piperidine-1-carboxylate**



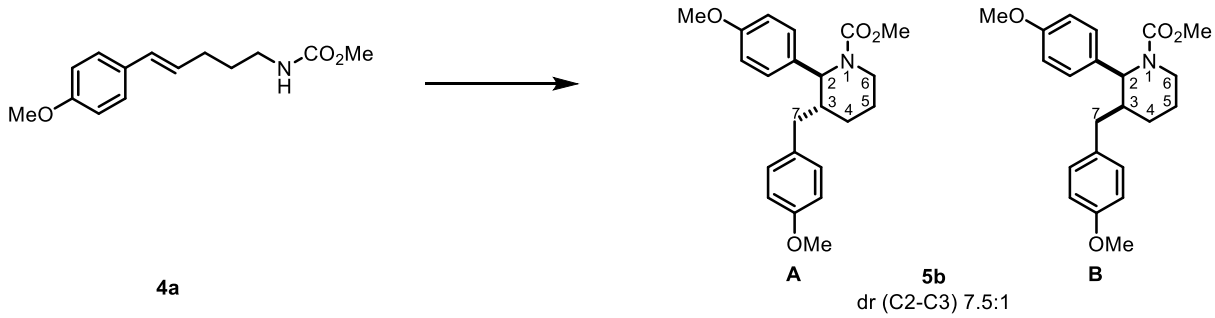

**4a** **5a**

Prepared according to **General Procedure K** using **4a** (25 mg, 0.10 mmol) and benzhydrol (19 mg, 0.10 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5a** as a colourless oil (40 mg, 98%).

Data for **5a**: $\mathbf{R_f}$ 0.37 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.43 – 7.36 (4H, m, Ar), 7.28 (4H, dt, *J* = 10.1, 7.7 Hz, Ar), 7.22 – 7.09 (4H, m, Ar), 6.91 – 6.86 (2H, m, Ar), 5.15 – 5.11 (1H,

*br*. s, C2-H), 4.23 (1H, *br*. s, C6-$H_A$), 4.19 (1H, d, *J* = 11.9 Hz, C7-H), 3.79 (3H, s, OMe), 3.56 (3H, s, OMe), 3.20 (1H, ddt, *J* = 11.8, 4.2, 2.2 Hz, C3-H), 2.88 (1H, td, *J* = 13.2, 3.5 Hz, C6-$H_B$), 1.85 – 1.67 (1H, m, C5-$H_A$), 1.55 (1H, tt, *J* = 13.7, 4.2 Hz, C4-$H_A$), 1.46 – 1.37 (1H, m, C4-$H_B$), 1.29 – 1.21 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 157.5 (CO), 144.2 (C Ar), 143.5 (C Ar), 132.0 (C Ar), 128.9 (2 × C Ar), 128.8 (2 × C Ar), 128.1 (2 × C Ar), 128.0 (2 × C Ar), 127.4 (2 × C Ar), 126.7 (C Ar), 126.5 (C Ar), 114.2 (2 × C Ar), 55.4 (OMe), 55.0 (C2), 52.5 (C7), 52.4 (OMe), 40.0 (C6), 39.8 (C3), 21.0 (C4), 19.7 (C5). **HRMS** (ESI): calculated for $C_{27}H_{30}O_3N$ $[M+H]^+$ requires m/z 416.2220, found m/z 416.2222. **IR** (film) $\nu_{max}$: 2950, 2360, 1694, 1511, 1446, 1348, 1249, 1179, 1141, 706 $cm^{-1}$.

**(5b): (±)-Methyl (2*S*,3*R*)-3-(4-methoxybenzyl)-2-(4-methoxyphenyl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*S*)-3-(4-methoxybenzyl)-2-(4-methoxyphenyl)piperidine-1-carboxylate**



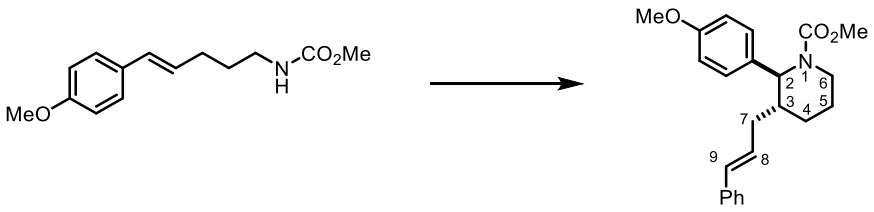

Prepared according to **General Procedure K** using **4a** (25 mg, 0.10 mmol) and 4-methoxybenzyl alcohol (14 mg, 0.10 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5b** a**s** an inseparable 7.5:1 mixture of diastereomers as a colourless oil (27 mg, 74%).

Data for **5b-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.19 – 7.13 (2H, m, Ar), 7.13 – 7.06 (2H, m, Ar), 6.88 – 6.82 (4H, m, Ar), 5.17 (1H, *br*. s, C2-H), 4.18 – 4.10 (1H, m, C6-$H_A$), 3.79 (3H, s, OMe), 3.78 (3H, s, OMe), 3.76 (3H, s, OMe), 2.88 – 2.82 (2H, m, C6-$H_B$ + C7-$H_A$), 2.70 (1H, dd, *J* = 13.7, 7.0 Hz, C7-$H_B$), 2.53 (1H, tq, *J* = 6.8, 3.2 Hz, C3-H), 1.81 (1H, qt, *J* = 13.0, 4.6 Hz, C5-$H_A$), 1.68 – 1.58 (1H, m, C4-$H_A$), 1.52 – 1.44 (1H, m, C4-$H_B$), 1.41 – 1.33 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 158.1 (C Ar), 157.5 (CO), 132.9 (C Ar), 132.1 (C Ar), 130.2 (2 × C Ar), 127.7 (2 × C Ar), 114.1 (2 × C Ar), 113.9 (2 × C Ar), 56.3 (C2), 55.4 (OMe), 55.4 (OMe), 52.9 (OMe), 40.1 (C6), 38.3 (C3), 37.3 (C7), 23.4 (C4), 20.3 (C5).

Partial data for **5b-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.01 – 6.89 (2H, d, *J* = 8.7 Hz, Ar), 6.78 (2H, d, *J* = 8.7 Hz, Ar), 3.81 (3H, s, OMe), 3.78 (3H, s, OMe), 3.63 (3H, s, OMe), 3.14 (1H, td, *J* = 13.4, 3.3 Hz, C6-$H_A$), 2.45 (1H, m, C7-$H_A$), 2.25 – 2.04 (2H, m, C3-H + C7-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.8 (C Ar), 158.0 (C Ar), 132.2 (C Ar), 130.1 (2 × C Ar), 113.8 (2 × C Ar), 113.6 (2 × C Ar), 55.4 (OMe), 55.3 (OMe), 52.6 (OMe), 41.9 (C6), 39.3 (C3).

Data for **5b**: $\mathbf{R_f}$ 0.30 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{22}H_{27}O_4NNa$ $[M+Na]^+$ requires m/z 392.1832, found m/z 392.1832. **IR** (film) $\nu_{max}$: 2938, 1694, 1611, 1511, 1443, 1408, 1247, 1179, 1125, 1037 $cm^{-1}$.

**(5c): (±)-Methyl (2*S*,3*R*)-3-cinnamyl-2-(4-methoxyphenyl)piperidine-1-carboxylate**

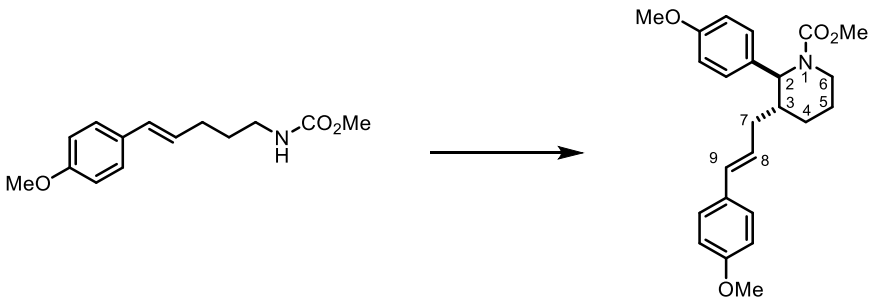



**4a** **5c**

Prepared according to **General Procedure K** using **4a** (21 mg, 0.080 mmol) and cinnamyl alcohol (11 mg, 0.080 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5c** as a colourless oil (15 mg, 51%).

Data for **5c**: $\mathbf{R_f}$ 0.57 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.41 – 7.33 (2H, m, Ar), 7.31 – 7.28 (2H, m, Ar), 7.23 – 7.18 (1H, m, Ar), 7.18 – 7.14 (2H, m, Ar), 6.91 – 6.83 (2H, m, Ar), 6.46 (1H, d, *J* = 15.8 Hz, C9-H), 6.27 (1H, dt, *J* = 15.7, 7.2 Hz, C8-H), 5.24 (1H, *br*. s, C2-H), 4.18 – 4.05 (1H, m, C6-$H_A$), 3.80 (3H, s, OMe), 3.75 (3H, s, OMe), 2.84 (1H, td, *J* = 12.9, 3.5 Hz, C6-$H_B$), 2.52 (1H, dtd, *J* = 13.1, 7.2, 1.3 Hz, C7-$H_A$), 2.45 (1H, dq, *J* = 7.0, 3.1 Hz, C3-H), 2.38 (1H, dtd, *J* = 13.9, 7.0, 1.3 Hz, C7-$H_B$), 1.76 (1H, dt, *J* = 12.7, 4.5 Hz, C5-$H_A$), 1.69 (1H, tt, *J* = 12.9, 3.8 Hz, C4-$H_A$), 1.60 – 1.52 (1H, m, C4-$H_B$), 1.43 – 1.33 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 157.5 (CO), 137.7 (C Ar), 132.2 (C9), 132.0 (C Ar), 128.8 (C8), 128.7 (2 × C Ar), 127.8 (2 × C Ar), 127.2 (2 × C Ar), 126.2 (2 × C Ar), 114.1 (2 × C Ar), 56.7 (C2), 55.4 (OMe), 52.9 (COMe), 40.0 (C6), 36.1 (C3), 35.5 (C7), 23.4 (C4), 20.2 (C5). **HRMS** (ESI): calculated for $C_{23}H_{27}O_3NNa$ $[M+Na]^+$ requires m/z 388.1883, found m/z 388.1884. **IR** (film) $\nu_{max}$: 3649, 2981, 2360, 2342, 1693, 1511, 1443, 1407, 1248, 1178 $cm^{-1}$.

**(5d): (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*E*)-3-(4-methoxyphenyl)allyl)piperidine-1-carboxylate**

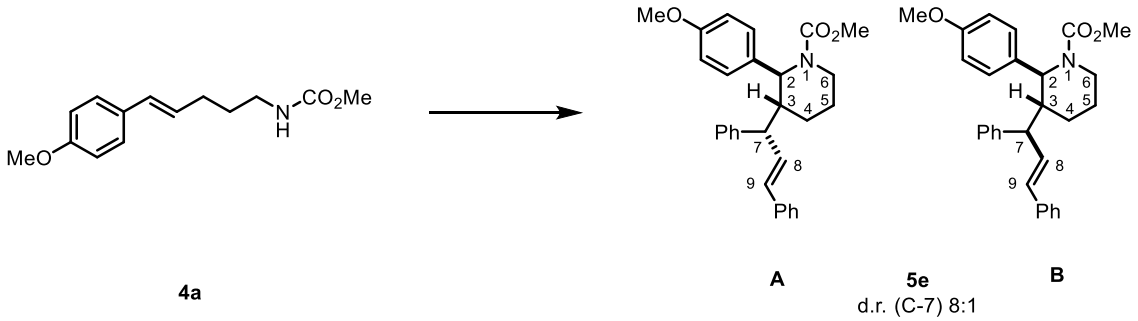



**4a** **5d**

Prepared according to **General Procedure K** using **4a** (10.5 mg, 0.040 mmol) and **2d** (6.5 mg, 0.040 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5d** as a colourless oil (8 mg, 51%).

Data for **5d**: $\mathbf{R_f}$ 0.48 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.31 – 7.27 (2H, m, Ar), 7.20 – 7.11 (2H, m, Ar), 6.90 – 6.86 (2H, m, Ar), 6.86 – 6.81 (2H, m, Ar), 6.40 (1H, d, *J* = 15.7 Hz, C9-H), 6.11 (1H, dt, *J* = 15.6, 7.2 Hz, C8-H), 5.23 (1H, *br*. s, C2-H), 4.11 (1H, d, *J* = 13.1 Hz, C6-$H_A$), 3.80 (3H, s, OMe), 3.80 (3.80, s, OMe), 3.75 (3H, s, OMe), 2.83 (1H, td, *J* = 13.0, 3.5 Hz, C6-$H_B$), 2.49 (1H, dtd, *J* = 13.0, 7.2, 1.3 Hz, C7-$H_A$), 2.42 (1H, tq, *J* = 6.6, 3.0 Hz, C3-H), 2.38 – 2.31 (1H, m, C7-$H_B$), 1.81 – 1.62 (2H, m, C4-$H_A$ + C5-$H_A$), 1.57 – 1.52 (1H, m, C4-$H_B$), 1.42 – 1.33 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 159.0 (C Ar), 158.4 (C Ar), 157.5 (CO), 132.1 (C Ar), 131.5 (C9), 130.5 (C Ar), 127.8 (2 × C Ar), 127.3 (2 × C Ar), 126.6 (C8), 114.0 (2 × C Ar), 114.1 (2 × C Ar), 56.7 (C2), 55.5 (OMe), 55.4 (OMe), 52.9 (OMe), 40.0 (C6), 36.2 (C3), 35.4 (C7), 23.4 (C4), 20.2 (C5). **HRMS** (ESI): calculated for $C_{24}H_{29}O_4NNa$ $[M+Na]^+$ requires m/z 418.1989, found m/z 418.1984. **IR** (film) $\nu_{max}$: 3649, 2981, 2971, 2837, 2359, 2342, 1694, 1510, 1443, 1407 $cm^{-1}$.

**(5e): (±)-Methyl (2*S*,3*R*)-3-((*S*,*E*)-1,3-diphenylallyl)-2-(4-methoxyphenyl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-3-((*R*,*E*)-1,3-diphenylallyl)-2-(4-methoxyphenyl)-piperidine-1-carboxylate**



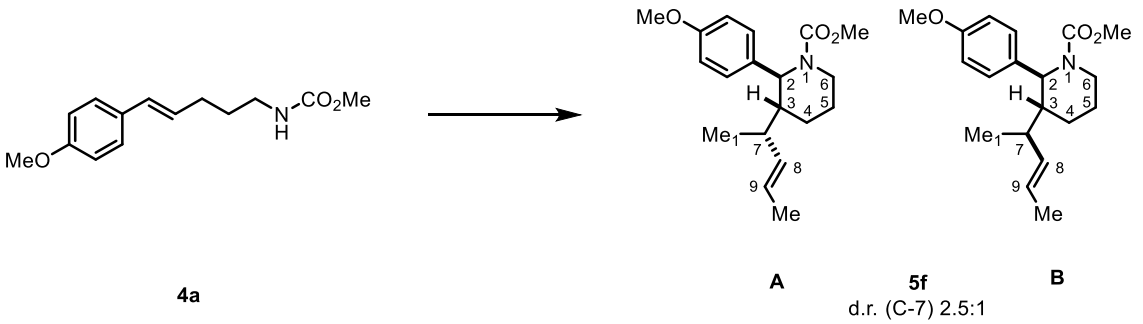

Prepared according to **General Procedure K** using **4a** (25 mg, 0.10 mmol) and (*E*)-1,3-diphenyl-2-propen-1-ol (21 mg, 0.10 mmol) at rt. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5e** a**s** an inseparable 8:1 mixture of diastereomers as a colourless oil (38 mg, 85%).

Data for **5e-A** (from the mixture): **$^1$H NMR (500 MHz, CDCl$_3$) δ** 7.39 – 7.29 (6H, m, Ar), 7.28 – 7.22 (3H, m, Ar), 7.19 – 7.15 (3H, m, Ar), 6.89 (2H, d, *J* = 8.8 Hz, Ar), 6.49 (1H, d, *J* = 15.6 Hz, C9-H), 6.37 (1H, dd, *J* = 15.7, 9.4 Hz, C8-H), 5.61 (1H, s, C2-H), 4.21 (1H, d, *J* = 14.0 Hz, C6-H$_A$), 3.80 (3H, s, OMe), 3.72 (3H, s, OMe), 3.67 (1H, d, *J* = 16.4 Hz, C7-H), 2.86 (1H, td, *J* = 13.2, 3.3 Hz, C6-H$_B$), 2.69 (1H, dp, *J* = 11.2, 2.2 Hz, C3-H), 1.71 (1H, dt, *J* = 13.0, 4.3 Hz, C5-H$_A$), 1.46 (1H, tt, *J* = 14.6, 4.2 Hz, C4-H$_A$), 1.30 – 1.16 (2H, m, C4-H$_B$ + C5-H$_B$). **$^{13}$C NMR (126 MHz, CDCl$_3$) δ** 158.4 (C Ar), 157.6 (CO), 143.0 (C Ar), 137.4 (C Ar), 132.9 (C8), 132.1 (C9), 129.1 (2 × C Ar), 128.6 (2 × C Ar), 127.9 (2 × C Ar), 127.6 (2 × C Ar), 127.4 (C Ar), 127.4 (C Ar), 126.6 (C Ar), 126.3 (2 × C Ar), 114.2 (2 × C Ar), 55.5 (OMe), 54.9 (C2), 52.9 (OMe), 50.3 (C7), 40.7 (C3), 39.9 (C6), 20.8 (C4), 20.0 (C5).

Partial data for **5e-B** (from the mixture): **$^1$H NMR (500 MHz, CDCl$_3$) δ** 7.11 – 7.01 (2H, m, Ar), 6.86 – 6.82 (2H, m, Ar), 4.99 (1H, *br*. s, C2-H), 3.78 (3H, s, OMe), 2.92 (1H, td, *J* = 13.1, 3.5 Hz, C6-H$_B$), 2.73 (1H, d, *J* = 11.6 Hz, C3-H), 1.85 (1H, m, C5-H$_A$), 1.36 (1H, d, *J* = 13.0 Hz, C5-H$_B$).**$^{13}$C NMR (126 MHz, CDCl$_3$) δ** 158.4 (C Ar), 143. (C Ar), 132.2 (C9), 132.0 (C8), 130.6 (C Ar), 128.9 (2 × C Ar), 128.6 (2 × C Ar), 128.1 (2 × C Ar), 126.8 (C Ar), 126.3 (2 × C Ar), 114.1 (2 × C Ar), 55.4 (OMe), 54.6 (C7), 52.6 (OMe), 41.2 (C3), 21.4 (C4, 19.5 (C5).

Data for **5e**: **R$_f$** 0.52 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{29}H_{31}O_3NNa$ $[M+Na]^+$ requires m/z 464.2196, found m/z 464.2195. **IR** (film) $\nu_{max}$: 3649, 3059, 3025, 2981, 2954, 2836, 2358, 2338, 2246, 1691 cm$^{-1}$.

**(5f): (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*S*,*E*)-pent-3-en-2-yl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*R*,*E*)-pent-3-en-2-yl)piperidine-1-carboxylate**



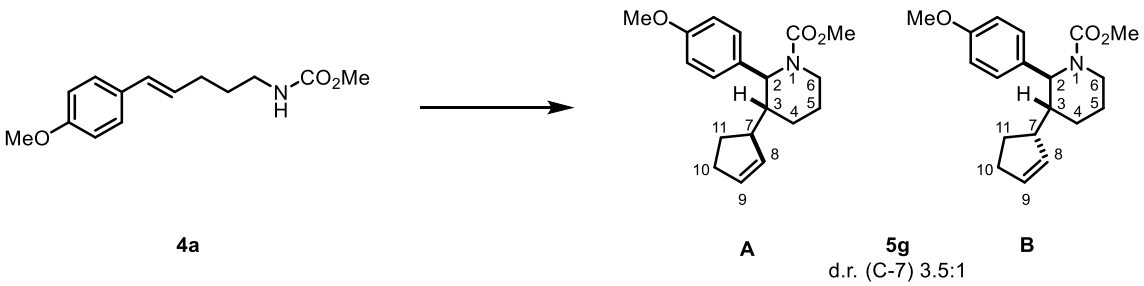

Prepared according to **General Procedure K** using **4a** (10 mg, 0.040 mmol) and 3-penten-2-ol (7 mg, 0.08 mmol, 2.0 equiv.) at 0 °C for 48 h. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5f** a**s** an inseparable 2.5:1 mixture of diastereomers as a colourless oil (12 mg, 95%).

Data for **5f-A** (from the mixture): **$^{1}$H NMR (500 MHz, $CDCl_3$) δ** 7.11 (2H, d, *J* = 8.9 Hz, Ar), 6.87 (2H, d, *J* = 8.8 Hz, Ar), 5.46 (1H, ddq, *J* = 15.0, 8.6, 6.3 Hz, C9-H), 5.36 (1H, *br*. s, C2-H), 5.31 (1H, ddd, *J* = 15.1, 8.8, 1.6 Hz, C8-H), 4.15 – 4.08 (1H, m, C6-$H_A$), 3.80 (3H, s, OMe), 3.70 (3H, s, OMe), 2.89 – 2.80 (1H, m, C6-$H_B$), 2.39 – 2.27 (1H, m, C7-H), 1.95 – 1.88 (1H, m, C3-H), 1.66 (3H, dd, *J* = 6.5, 1.6 Hz, $Me_2$), 1.69 – 1.57 (2H, m, C4-$H_A$ + C5-$H_A$), 1.55 – 1.44 (1H, m, C4-$H_B$), 1.38 – 1.30 (1H, m, C5-$H_B$), 1.01 (3H, d, *J* = 6.7 Hz, $Me_1$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.3 (C Ar), 157.4 (CO), 136.4 (C8), 132.7 (C Ar), 127.6 (2 × C Ar), 125.8 (C9), 114.1 (2 × C Ar), 55.5 (OMe), 55.4 (C2), 52.7 (OMe), 41.4 (C3), 40.1 (C6), 36.5 (C7), 20.6 (C4), 20.3 (C5), 18.5 ($Me_1$), 18.2 ($Me_2$).

Partial data for **5f-B** (from the mixture): **$^{1}$H NMR (500 MHz, $CDCl_3$) δ** 7.15 (2H, d, *J* = 8.9 Hz, Ar), 6.88 (2H, d, *J* = 9.0 Hz, Ar), 4.08 – 4.02 (1H, m, C6-$H_A$), 3.80 (3H, s, OMe), 3.73 (3H, s, OMe), 1.12 (3H, d, *J* = 6.6 Hz, $Me_1$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.3 (C Ar), 157.4 (CO), 135.5 (C8), 132.5 (C Ar), 127.8 (2 × C Ar), 124.4 (C9), 55.4 (OMe), 54.9 (C2), 52.9 (OMe), 41.4 (C3), 39.8 (C6), 36.6 (C7), 21.5 (C4), 20.5 ($Me_1$), 20.1 (C5), 18.1 ($Me_2$).

Data for **5f**: **$R_f$** 0.46 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{19}H_{28}O_3N$ $[M+H]^+$ requires m/z 318.2064, found m/z 318.2066. **IR** (film) $\nu_{max}$: 3735, 3649, 2980, 2971, 2338, 4697, 1512, 1444, 1407, 1262 $cm^{-1}$.

**(5g): (±)-Methyl (2*S*,3*R*)-3-((*R*)-cyclopent-2-en-1-yl)-2-(4-methoxyphenyl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-3-((*S*)-cyclopent-2-en-1-yl)-2-(4-methoxyphenyl)-piperidine-1-carboxylate**



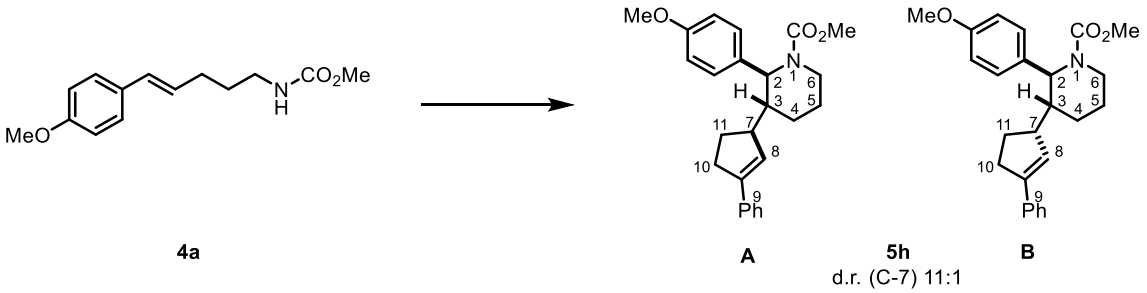

Prepared according to **General Procedure K** using **4a** (10 mg, 0.040 mmol) and **2o** (13 mg, 0.08 mmol, 2.0 equiv.) at 0 °C for 48 h. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5g** as an inseparable 3.5:1 mixture of diastereomers as a colourless oil (12 mg, 95%).

Data for **5g-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.14 (2H, d, *J* = 8.9 Hz, Ar), 6.88 (2H, d, *J* = 8.7 Hz, Ar), 5.83 (1H, dt, *J* = 6.4, 2.2 Hz, C8-H), 5.78 (1H, dq, *J* = 5.9, 2.1 Hz, C9-H), 5.31 (1H, s, C2-H), 4.14 – 4.04 (1H, m, C6-$H_A$), 3.80 (3H, s, OMe), 3.74 (3H, s, OMe), 3.07 – 2.96 (1H, m, C7-H), 2.86 (1H, td, *J* = 13.1, 3.5 Hz, C6-$H_B$), 2.45 – 2.38 (1H, m, C10-$H_A$), 2.38 – 2.30 (1H, m, C10-$H_B$), 2.25 (1H, ddd, *J* = 12.6, 8.3, 4.0 Hz, C11-$H_A$), 2.07 – 1.97 (1H, m, C3-H), 1.79 – 1.73 (1H, m, C5-$H_A$), 1.72 – 1.66 (1H, m, C4-$H_A$), 1.66 – 1.53 (2H, m, 1 × C4-$H_B$ + 1 × C11-$H_B$), 1.36 (1H, ddd, *J* = 12.9, 5.2, 2.9 Hz, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 157.5 (CO), 132.6 (C9), 132.2 (C8), 132.0 (C Ar), 127.7 (2 × C Ar), 114.1 (2 × C Ar), 56.3 (C2), 55.4 (OMe), 52.9 (COMe), 45.3 (C7), 41.9 (C3), 40.1 (C6), 32.2 (C10), 30.2 (C11), 22.2 (C4), 20.4 (C5).

Partial data for **5g-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 5.92 (1H, dq, *J* = 6.1, 2.1 Hz, C8-H), 5.82 – 5.80 (1H, m, C9-H), 5.42 (1H, d, *J* = 2.3 Hz, C2-H), 3.73 (3H, s, OMe), 2.09 – 2.05 (1H, m, C3-H), 1.51 – 1.45 (1H, m, C4-H). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 157.4 (CO), 134.0 (C8), 131.6 (C9), 127.8 (2 × C Ar), 114.1 (2 × C Ar), 56.2 (C2), 45.3 (C7), 41.3 (C3), 40.0 (C6), 32.3 (C10), 29.9 (C11), 21.7 (C4), 20.3 (C3).

Data for **5g**: **$R_f$** 0.43 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{19}H_{26}O_3N$ $[M+H]^+$ requires m/z 316.1907, found m/z 316.1910. **IR** (film) $\nu_{max}$: 3735, 3649, 3050, 2981, 2971, 2954, 2868, 2380, 2341, 1697 $cm^{-1}$.

**(5h): (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*R*)-3-phenylcyclopent-2-en-1-yl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*S*)-3-phenylcyclopent-2-en-1-yl)-piperidine-1-carboxylate**



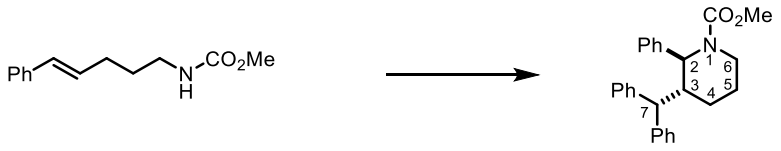

Prepared according to **General Procedure K** using **4a** (25 mg, 0.10 mmol) and **2q** (16 mg, 0.10 mmol). Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5h** a**s** an inseparable 11:1 mixture of diastereomers as a yellow oil (39 mg, 96%).

Data for **5h-A** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.51 – 7.43 (2H, m, Ar), 7.38 – 7.28 (2H, m, Ar), 7.28 – 7.21 (1H, m, Ar), 7.21 – 7.10 (2H, m, Ar), 6.93 – 6.84 (2H, m, Ar), 6.24 (1H, d, *J* = 2.0 Hz, C8-H), 5.36 (1H, s, C2-H), 4.21 – 4.06 (1H, m, C6-$H_A$), 3.81 (3H, s, OMe), 3.77 (3H, s, OMe), 3.23 – 3.14 (1H, m, C7-H), 2.89 (1H, td, *J* = 12.9, 3.5 Hz, C6-$H_B$), 2.84 – 2.80 (1H, m, C11-$H_A$), 2.77 – 2.70 (1H, m, C11-$H_B$), 2.43 (1H, dtd, *J* = 12.6, 8.5, 4.1 Hz, C10-$H_A$), 2.17 – 2.13 (1H, m, C3-H), 1.89 – 1.70 (3H, m, C4-$H_A$ + C5-$H_A$ + C10-$H_B$), 1.68 – 1.64 (1H, m, C4-$H_B$), 1.46 – 1.36 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.4 (C Ar), 157.5 (CO), 143.4 (C Ar), 136.7 (C Ar), 132.1 (C9), 128.5 (2 × C Ar), 127.7 (2 × C Ar), 127.6 (C8), 127.3 (C Ar), 125.8 (2 × C Ar), 114.1 (2 × C Ar), 56.1 (C2), 55.4 (OMe), 52.9 (OMe), 45.9 (C7), 41.9 (C3), 40.1 (C6), 32.7 (C11), 30.5 (C10), 22.3 (C4), 20.5 (C5).

Characteristic signals for **5h-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 6.37 (1H, s, C8-H), 5.52 (1H, s, C2-H), 3.74 (3H, s, OMe).

Data for **5h**: **$R_f$** 0.59 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{25}H_{29}O_3NNa$ $[M+Na]^+$ requires m/z 414.2040, found m/z 414.2040. **IR** (film) $\nu_{max}$: 2946, 1695, 1612, 1511, 1445, 1408, 1345, 1250, 1179, 1122 $cm^{-1}$.

**(5i): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-2-phenylpiperidine-1-carboxylate**

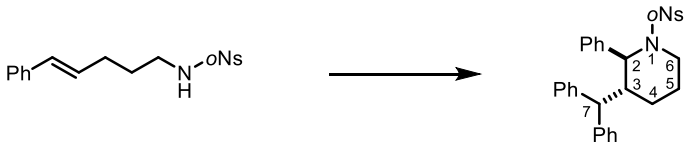


**4b** **5i**

Prepared according to **General Procedure K** using **4b** (18 mg, 0.08 mmol) and benzhydrol (15 mg, 0.08 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5i** as a colourless oil (20 mg, 65%).

Data for **5i**: **$R_f$** 0.42 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.41 (4H, ddd, *J* = 8.1, 4.8, 1.4 Hz, Ar), 7.35 (2H, dd, *J* = 8.5, 6.6 Hz, Ar), 7.32 – 7.26 (4H, m, Ar), 7.25 – 7.20 (3H, m, Ar), 7.20 – 7.12 (2H, m, Ar), 5.18 (1H, s, C2-H), 4.27 (1H, *br.* s, C6-$H_A$), 4.20 (1H, d, *J* = 12.0 Hz, C7-H), 3.54 (3H, *br.* s, OMe), 3.25 (1H, ddt, *J* = 12.2, 4.3, 2.1 Hz, C3-H), 2.96 – 2.77 (1H, m, C6-$H_B$), 1.78 (1H, d, *J* = 13.3 Hz, C5-$H_A$), 1.52 (1H, tt, *J* = 13.5, 4.1 Hz, C4-$H_A$), 1.47 – 1.39 (1H, m, C4-$H_B$), 1.29 – 1.21 (2H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 157.6 (CO), 144.1 (C Ar), 143.4 (C Ar), 140.2 (C Ar), 128.9 (2 × C Ar), 128.9 (2 × C Ar), 128.9 (2 × C Ar), 128.1 (2 × C Ar), 128.0 (2 × C Ar), 126.8 (C Ar), 126.7 (C Ar), 126.5 (C Ar), 126.3 (2 × C Ar), 55.5 (C2), 52.4 (OMe), 52.5 (C7), 40.1 (C6), 39.9 (C3), 21.0 (C4), 19.6 (C5). **HRMS** (ESI): calculated for $C_{26}H_{28}O_2N$ $[M+H]^+$ requires m/z 386.2115, found m/z 386.2118. **IR** (film) $\nu_{max}$: 2948, 1696, 1599, 1494, 1446, 1408, 1348, 1266, 1191, 1132 $cm^{-1}$.

**(5i-Ns): (±)-(2*S*,3*R*)-3-Benzhydryl-1-((2-nitrophenyl)sulfonyl)-2-phenylpiperidine**



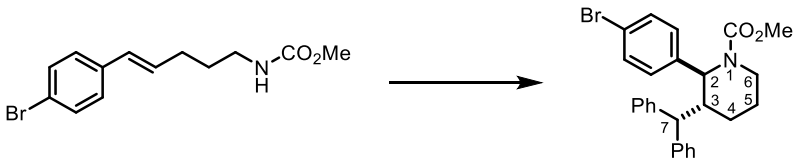
**4b-Ns** **5i-Ns**

Prepared according to **General Procedure K** using **4bNs** (28 mg, 0.08 mmol) and benzhydrol (15 mg, 0.08 mmol) in 3:1 HFIP:$CH_2Cl_2$. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5i-Ns** as a white solid (31 mg, 69%).

Data for **5i-Ns**: **$R_f$** 0.23 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.60 (1H, dd, *J* = 8.0, 1.5 Hz, Ar), 7.52 (1H, td, *J* = 7.5, 1.5 Hz, Ar), 7.42 (1H, dd, *J* = 8.0, 1.5 Hz, Ar), 7.36 – 7.07 (15H, m, Ar), 5.02 (1H, s, C2-H), 4.36 – 4.20 (2H, m, C6-$H_A$ + C7-H), 3.53 (1H, td, *J* = 13.0, 3.0 Hz, C6-$H_B$), 3.09 – 3.05 (1H, m, C3-H), 1.98 – 1.95 (1H, m, C5-$H_A$), 1.51 – 1.45 (1H, m, C4-$H_A$), 1.45 – 1.35 (2H, m, C4-$H_B$ + C5-$H_B$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 147.8 (C Ar), 143.5 (C Ar), 143.4 (C Ar), 140.1

(C Ar), 134.2 (C Ar), 133.0 (C Ar), 131.7 (C Ar), 131.7 (C Ar), 129.0 (2 × C Ar) 128.9 (2 × C Ar), 128.5 (2 × C Ar), 128.3 (2 × C Ar), 128.1 (2 × C Ar), 126.9 (C Ar), 126.8 (2 × C Ar), 126.6 (C Ar), 126.5 (C Ar), 123.9 (C Ar), 58.5 (C2), 51.9 (C7), 43.8 (C6), 42.7 (C3), 20.5 (C4), 19.7 (C5). **HRMS** (ESI): calculated for $C_{30}H_{32}O_4SN_2Na$ $[M+Na]^+$ requires m/z 535.1658, found m/z 535.1660. **IR** (film) $\nu_{max}$: 2980, 2925, 1542, 1379, 1346, 1164, 1134, 942, 759, 706 $cm^{-1}$.

**(5j): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-2-(4-bromophenyl)piperidine-1-carboxylate**

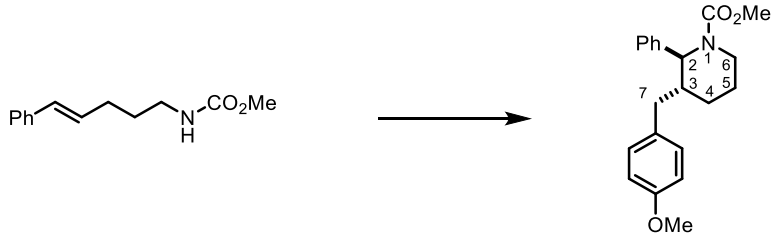



**4c** **5j**

Prepared according to **General Procedure K** using **4c** (12 mg, 0.040 mmol) and benzhydrol (7.5 mg, 0.08 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 15% EtOAc – pentane) afforded **5j** as a colourless oil (12 mg, 65%).

Data for **5j**: $\mathbf{R_f}$ 0.44 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$)** 7.46 (2H, d, *J* = 8.6 Hz, Ar), 7.42 – 7.35 (4H, m, Ar), 7.29 (4H, td, *J* = 7.7, 5.8 Hz, Ar), 7.20 – 7.13 (2H, m, Ar), 7.09 (2H, d, *J* = 7.5 Hz, Ar), 5.11 (1H, *br*. s, C2-H), 4.25 (1H, *br*. s, C6-$H_A$), 4.17 (1H, d, *J* = 12.0 Hz, C7-H), 3.58 (3H, *br*. s, OMe), 3.17 (1H, ddt, *J* = 12.1, 4.0, 2.2 Hz, C3-H), 2.93 – 2.76 (1H, m, C6-$H_B$), 1.84 – 1.69 (1H, m, C5-$H_A$), 1.49 – 1.41 (2H, m, C4-$H_2$), 1.29 – 1.22 (1H, m, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 157.4 (CO), 143.9 (C Ar), 143.1 (C Ar), 139.4 (C Ar), 131.9 (2 × C Ar), 129.0 (2 × C Ar), 128.9 (2 × C Ar), 128.2 (2 × C Ar), 128.1 (2 × C Ar), 128.0 (2 × C Ar), 126.8 (C Ar), 126.6 (C Ar), 120.6 (C Ar), 55.2 (C2), 52.7 (OMe), 52.4 (C7), 40.0 (C3 + C6), 21.0 (C4), 19.5 (C6). **HRMS** (ESI): calculated for $C_{26}H_{27}O_2N^{78}Br$ $[M+H]^+$ requires m/z 464.1220, found m/z 464.1220. **IR** (film) $\nu_{max}$: 2949, 1694, 1489, 1445, 1410, 1347, 1262, 1191, 1131, 1075 $cm^{-1}$.

**(5k): (±)-Methyl (2*S*,3*R*)-3-(4-methoxybenzyl)-2-phenylpiperidine-1-carboxylate**

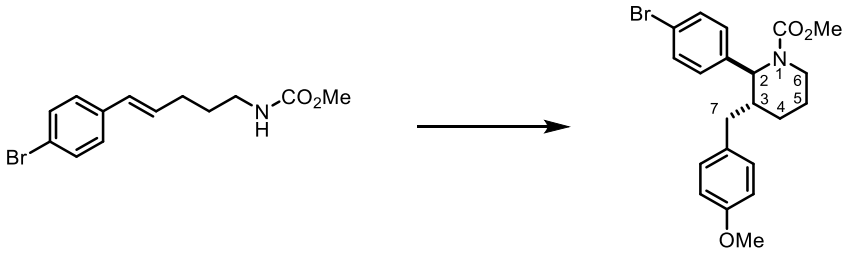



**4b** **5k**

Prepared according to **General Procedure K** using **4b** (9 mg, 0.04 mmol) and 4-methoxybenzyl alcohol (5.5 mg, 0.040 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 15% EtOAc – pentane) afforded **5k** as a colourless oil (10 mg, 74%).

Data for **5k**: **$R_f$** 0.33 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.32 (2H, t, *J* = 7.7 Hz, Ar), 7.24 – 7.12 (5H, m, Ar), 6.85 (2H, d, *J* = 8.6 Hz, Ar), 5.22 (1H, s, C2-H), 4.22 – 4.12 (1H, m, C6-$H_A$), 3.79 (3H, s, OMe), 3.77 (3H, s, OMe), 2.93 – 2.80 (2H, m, C6-$H_B$ + C7-$H_A$), 2.72 (1H, dd, *J* = 13.7, 6.8 Hz, C7-$H_B$), 2.59 (1H, q, *J* = 6.8, 5.0 Hz, C3-H), 1.82 (1H, tdt, *J* = 13.0, 9.2, 4.6 Hz, C5-$H_A$), 1.69 – 1.55 (1H, m, C4-$H_A$), 1.49 (1H, dd, *J* = 13.5, 3.6 Hz, C4-$H_B$), 1.38 (1H, dq, *J* = 13.3, 3.4 Hz, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.1 (C Ar), 157.6 (C8), 140.2 (C Ar), 132.9 (C Ar), 130.2 (2 × C Ar), 128.7 (2 × C Ar), 126.7 (C Ar), 126.6 (2 × C Ar), 114.0 (2 × C Ar), 56.7 (C2), 55.4 (OMe), 52.9 (C9), 40.4 (C6), 38.4 (C3), 37.3 (C7), 23.5 (C4), 20.2 (C5). **HRMS** (ESI): calculated for $C_{21}H_{25}O_3N$ $[M+H]^+$ requires m/z 340.1907, found m/z 340.1908. **IR** (film) $\nu_{max}$: 2942, 1697, 1512, 1445, 1408, 1247, 1179, 1126, 1035, 807 $cm^{-1}$.

**(5l): (±)-Methyl (2*S*,3*R*)-2-(4-bromophenyl)-3-(4-methoxybenzyl)piperidine-1-carboxylate**



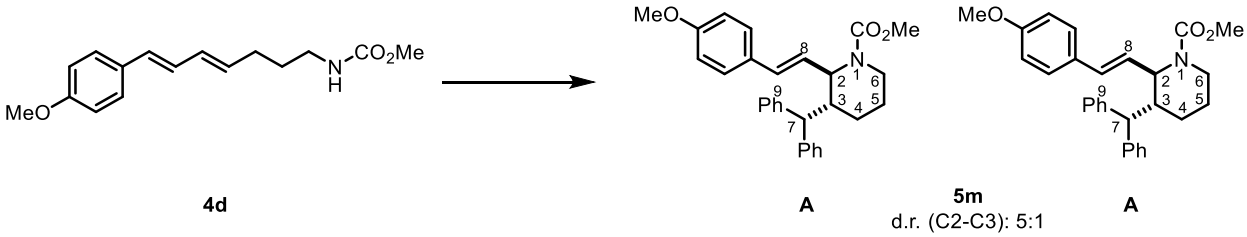

**4c** **5l**

Prepared according to **General Procedure K** using **4c** (12 mg, 0.04 mmol) and 4-methoxybenzyl alcohol (5.5 mg, 0.040 mmol) at 70 °C. Flash column chromatography (gradient elution 0% → 15% EtOAc – pentane) afforded **5l** as a colourless oil (10 mg, 60%).

Data for **5l**: **$R_f$** 0.33 (20% EtOAc – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.43 (2H, d, *J* = 8.6 Hz, Ar), 7.15 (2H, d, *J* = 8.6 Hz, Ar), 7.04 (2H, d, *J* = 8.6 Hz, Ar), 6.85 (2H, d, *J* = 8.6 Hz, Ar), 5.15 (1H,

*br*. s, C2-H), 4.21 – 4.12 (1H, m, C6-$H_A$), 3.79 (3H, s, OMe), 3.76 (3H, s, OMe), 2.86 – 2.80 (2H, m, C6-$H_B$ + C7-$H_A$), 2.69 (1H, dd, *J* = 13.8, 6.8 Hz, C7-$H_B$), 2.56 – 2.43 (1H, m, C3-H), 1.88 – 1.73 (1H, m, C5-$H_A$), 1.57 (1H, tdd, *J* = 12.9, 8.7, 4.4 Hz, C4-$H_A$), 1.52 – 1.46 (1H, m, C4-$H_B$), 1.39 (1H, dd, *J* = 13.5, 3.7 Hz, C5-$H_B$). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 158.2 (C Ar), 157.4 (CO), 139.4 (C Ar), 132.6 (C Ar), 131.8 (2 × C Ar), 130.2 (2 × C Ar), 128.5 (2 × C Ar), 120.6 (C Ar), 114.0 (2 × C Ar), 56.4 (C2), 55.4 (OMe), 53.0 (OMe), 40.3 (C6), 38.5 (C3), 37.3 (C7), 23.4 (C4), 20.1 (C5). **HRMS** (ESI): calculated for $C_{21}H_{25}O_3N^{79}Br$ $[M+H]^+$ requires m/z 418.1012, found m/z 418.1012. **IR** (film) $\nu_{max}$: 2941, 1696, 1512, 1488, 1443, 1409, 1247, 1179, 1127, 1037 $cm^{-1}$.

**(5m): (±)-Methyl (2*R*,3*R*)-3-benzhydryl-2-((*E*)-4-methoxystyryl)piperidine-1-carboxylate and (±)-Methyl (2*R*,3*S*)-3-benzhydryl-2-((*E*)-4-methoxystyryl)piperidine-1-carboxylate**




Prepared according to **General Procedure K** using **4d** (10 mg, 0.040 mmol) and benzhydrol (7.5 mg, 0.040 mmol) at 0 °C for 48 h. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5m** as a colourless oil (12 mg, 65%).

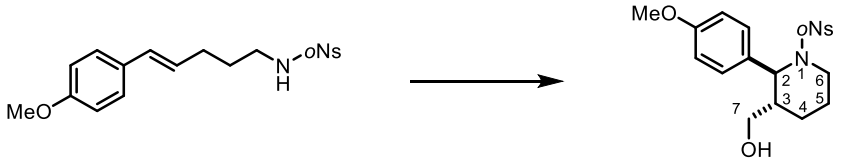
Characteristic data for **5m-A,** 1.5:1 mixture of rotamers *A:B* (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.35 – 7.11 (12H, m, Ar), 6.92 – 6.85 (2H, m, Ar), 6.24 (1H, dt, *J* = 16.2, 8.2 Hz, C8-H, *A*+*B*), 5.99 (1H, d, *J* = 15.7 Hz, C9-H, *A*), 5.91 (1H, d, *J* = 15.7 Hz, C9-H, *B*), 4.93 (1H, *br*. s, C2-H, *A*), 4.75 (1H, *br*. s, C2-H, *B*), 4.17 – 4.07 (1H, m, C6-$H_A$, *A*), 4.01 – 3.94 (1H, m, C6-$H_A$, *B*), 3.83 (3H, s, OMe), 3.67 (1H, s, OMe, *A*), 3.64 (1H, s, OMe, *B*), 3.54 (1H, *br*. s, C7-H, *A*), 3.52 (1H, *br*. s, C7-H, *B*), 3.01 (1H, *ap*. q, *J* = 13.7 Hz, C6-$H_B$, *A*+*B*), 2.64 – 2.52 (1H, m, C3-H, *A*+*B*), 1.78 – 1.62 (1H, m, C5-$H_A$, *A*+*B*), 1.55 – 1.40 (2H, m, C4-$H_A$ + C5-$H_B$, *A*+*B*), 1.40 – 1.29 (1H, m, C4-$H_B$, *A*+*B*). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 156.0 (CO, *A*+*B*), 134.6 (C9, *A*), 133.9 (C9, *B*), 119.6 (C8, *B*), 119.1 (C8, *A*), 55.8 (C2, *A*+*B*), 55.6 (C7, *A*+*B*), 55.5 (OMe, *A*), 55.4 (OMe, *B*), 52.8 (OMe, *B*), 52.6 (OMe, *A*), 43.4 (C3, *B*), 43.0 (C3, *A*), 40.0 (C6, *A*), 39.7 (C6, *B*), 26.0 (C5, *A*), 25.7 (C5, *B*), 24.9 (C4, *A*), 24.8 (C4, *B*).

Characteristic data for **5m-B** (from the mixture): **$^1$H NMR (500 MHz, $CDCl_3$) δ** 6.11 (1H, dd, *J* = 4.9 Hz, C9-H), 4.74 (1H, *br*. s, C2-H), 4.13 (1H, d, *J* = 12.1 Hz, C8-H), 3.83 (3H, s, OMe), 2.72 (1H, *ap*. d, *J* = 12.2 Hz, C3-H). **$^{13}$C NMR (126 MHz, $CDCl_3$) δ** 156.4 (CO), 129.9 (C9), 129.8 (C8), 55.4 (OMe), 54.3 (OMe), 52.1 (C7), 41.8 (C3).

Data for **5m**: $\mathbf{R}_f$ 0.33 (20% EtOAc – pentane). **HRMS** (ESI): calculated for $C_{29}H_{31}O_3NNa$ $[M+Na]^+$ requires m/z 464.2196, found m/z 464.2193. **IR** (film) $\nu_{max}$: 3027, 2953, 2858, 1695, 1607, 1511, 1445, 1250, 1032, 706 $cm^{-1}$. Aromatic signals for **5m-A+B** (from the mixture): **$^{13}$C NMR (126 MHz, $CDCl_3$)**

**δ** 159.4, 159.3, 143.8, 143.7, 143.4, 142.5, 142.2, 128.9, 128.8, 128.8, 128.4, 128.1, 128.1, 127.8, 127.7, 127.6, 126.6, 126.6, 126.4, 126.4, 114.2, 114.1, 114.1.

**(5n'): 2-(4-Methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidin-3-yl)methanol**



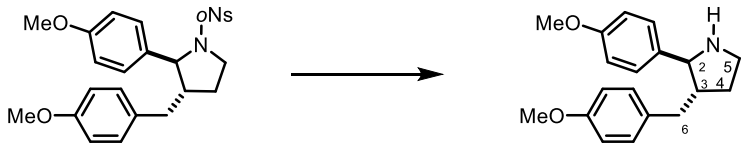

**4-*o*Ns** **5nNs**

Prepared according to **General Procedure K** using **4-*o*Ns** (30 mg, 0.080 mmol) and paraformaldehyde (48 mg, 1.6 mmol, 20.0 equiv.) at 0 °C for 48 h. Flash column chromatography (gradient elution 0% → 25% EtOAc – pentane) afforded **5n-Ns** as a colourless oil (19 mg, 61%).

Data for **5n-Ns**: **$R_f$** 0.23 (20% EtOAc – pentane). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 7.90 – 7.80 (1H, m, Ar), 7.70 – 7.61 (2H, m, Ar), 7.50 (1H, ddd, *J* = 7.9, 6.5, 2.3 Hz, Ar), 7.06 (2H, d, *J* = 9.0 Hz, Ar), 6.69 (2H, d, *J* = 8.8 Hz, Ar), 5.18 (1H, d, *J* = 3.0 Hz, C2-H), 4.02 – 3.90 (2H, m, C6-$H_A$ + C7-$H_A$), 3.73 (3H, s, OMe), 3.60 (1H, ddd, *J* = 11.5, 6.5, 5.2 Hz, C7-$H_B$), 3.37 (1H, ddd, *J* = 13.7, 11.8, 3.2 Hz, C6-$H_B$), 2.42 (1H, dt, *J* = 8.7, 4.6 Hz, C3-H), 2.20 (1H, t, *J* = 6.2 Hz, *O*H), 1.76 (1H, dddd, *J* = 16.2, 11.9, 8.5, 4.6 Hz, C5-$H_A$), 1.64 (1H, ddt, J = 13.3, 9.9, 4.7 Hz, C5-$H_B$), 1.58 – 1.43 (2H, m, C4-$H_2$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 158.6 (C Ar), 147.5 (C Ar), 134.5 (C Ar), 133.3 (C Ar), 131.9 (C Ar), 130.9 (C Ar), 129.9 (C Ar), 128.1 (2 × C Ar), 124.1 (C Ar), 114.0 (2 × C Ar), 62.6 (C7), 56.7 (C2), 55.4 (OMe), 43.3 (C6), 40.2 (C3), 21.7 (C4), 21.3 (C5). **HRMS** (ESI): calculated for $C_{19}H_{23}O_6N_2S$ $[M+H]^+$ requires m/z 407.1271, found m/z 407.1271. **IR** (film) $\nu_{max}$: 3423, 2936, 1612, 1584, 1542, 1513, 1463, 1441, 1371, 1250 $cm^{-1}$.

Product Derivatisations

**(6a): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)pyrrolidine**

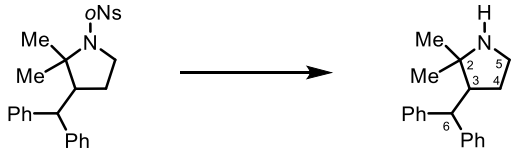



**3g** **6a**

Prepared according to **General Procedure L** using **3g** (34 mg, 0.070 mmol), LiOH (7.0 mg, 0.28 mmol) and thioglycolic acid (0.0097 mL, 0.14 mmol). Flash column chromatography (gradient elution 10% → 15% MeOH – $CH_2Cl_2$) afforded **6a** as a colourless oil (15 mg, 70%).

Data for **6a**: **$R_f$** 0.30 (15% MeOH – $CH_2Cl_2$). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.36 (2H, d, *J* = 8.7 Hz, Ar), 6.95 (2H, d, *J* = 8.7 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 6.77 (2H, d, *J* = 8.7 Hz, Ar), 3.85 (1H, d, *J* = 9.9 Hz, C2-H), 3.79 (3H, s, OMe), 3.77 (3H, s, OMe), 3.19 (1H, dt, *J* = 11.7, 8.2 Hz, C5-$H_A$), 3.05 (1H, td, *J* = 11.7, 10.4, 3.9 Hz, C5-$H_B$), 2.69 (1H, dd, *J* = 13.6, 4.1 Hz, C6-$H_A$), 2.40-2.49 (1H, m, C3-H), 2.36 (1H, dd, *J* = 13.5, 9.6 Hz, C6-$H_B$), 1.95-2.04 (1H, m, C4-$H_A$), 1.59-1.69 (1H, m, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 160.0 (C Ar), 158.3 (C Ar), 131.4 (C Ar), 129.9 (3 × C Ar), 129.5 (2 × C Ar), 114.4 (2 × C Ar), 114.0 (2 × C Ar), 67.6 (C2), 55.4 (OMe), 55.4 (OMe), 47.7 (C3), 44.2 (C5), 36.8 (C6), 30.3 (C4). **HRMS** (ESI): calculated for $C_{19}H_{24}O_2N$ $[M+H]^+$ requires *m/z* 298.1807, found *m/z* 298.1801. **IR** (film) $\nu_{max}$: 2980,2888, 2360, 1738, 1612, 1512 $cm^{-1}$.

**(6b): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)pyrrolidine**



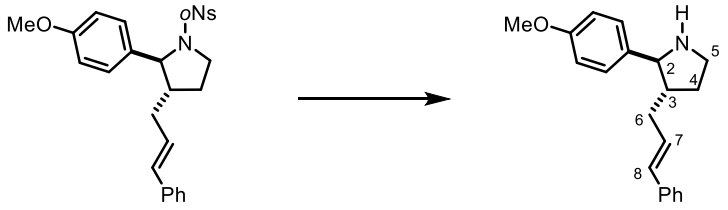

**3v** **6b**

Prepared according to **General Procedure L** using **3v** (42 mg, 0.093 mmol), LiOH (7.0 mg, 0.28 mmol) and thioglycolic acid (0.0097 mL, 0.14 mmol). Flash column chromatography (gradient elution 5% → 10% MeOH – $CH_2Cl_2$) afforded **6b** as a colourless oil (15 mg, 70%).

Data for **6b**: **$R_f$** 0.40 (15% MeOH – $CH_2Cl_2$). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.33 – 7.38 (4H, m, Ar), 7.20 – 7.26 (4H, m, Ar), 7.09 – 7.16 (2H, m, Ar), 3.68 (1H, d, *J* = 11.7 Hz, C6-H), 2.87 (1H, dd, *J* = 8.4, 6.4 Hz, C5-$H_2$), 2.66 (1H, ddd, *J* = 11.7, 10.7, 8.4 Hz, C3-H), 1.85 (1H, ddt, *J* = 13.0, 8.4, 6.4 Hz, C4-$H_A$), 1.46 (1H, ddt, *J* = 13.2, 10.7, 8.4 Hz, C4-$H_B$), 1.05 (3H, s, Me), 0.70 (3H, s, Me). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 145.7 (C Ar), 144.3 (C Ar), 128.7 (2 × C Ar), 128.6 (2 × C Ar), 128.3 (2 × C Ar), 127.8 (2 × C Ar), 126.5 (C Ar), 126.2 (C Ar), 60.6 (C2), 55.1 (C6), 52.7 (C3), 42.3 (C5), 33.2 (C4),

29.7 (Me), 22.3 (Me). **HRMS** (ESl): calculated for $C_{19}H_{23}N$ $[M+H]^+$ requires *m/z* 266.1909, found *m/z* 266.1904. **IR** (film) $\nu_{max}$: 2980, 2886, 2360, 1738, 1451, 1380 $cm^{-1}$.

**(6c): (±)- (2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)pyrrolidine**

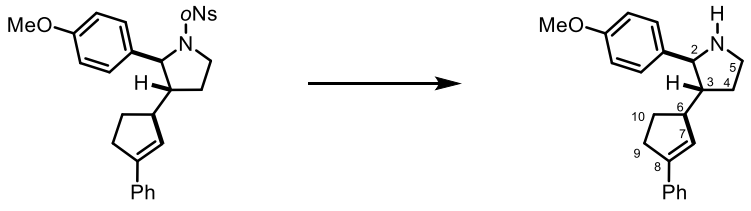



**3h** **6c**

Prepared according to **General Procedure L** using **3h** (43 mg, 0.089 mmol), LiOH (8.5 mg, 0.36 mmol) and thioglycolic acid (0.012 mL, 0.18 mmol). Flash column chromatography (gradient elution 3% → 6% MeOH – $CH_2Cl_2$) afforded **6c** as a colourless oil (18 mg, 67%).

Data for **6c**: $\mathbf{R_f}$ 0.40 (20% MeOH – $CH_2Cl_2$). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.23 – 7.31 (6H, m, Ar), 7.15 – 7.21 (1H, m, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 6.36 (1H, dt, *J* = 15.7, 1.4 Hz, C8-H), 6.11 (1H, dt, *J* = 15.8, 7.1 Hz, C7-H), 3.80 (3H, s, OMe), 3.67 (1H, d, *J* = 8.0 Hz, C2-H), 3.22 (1H, ddd, *J* = 10.1, 7.5, 6.1 Hz, C5-$H_A$), 3.07 (1H, ddd, *J* = 10.1, 8.5, 5.4 Hz, C5-$H_B$), 2.38 (1H, dddd, *J* = 13.5, 6.6, 4.8, 1.4 Hz, C6-$H_A$), 2.10 – 2.21 (2H, m, 1 × C4-$H_A$ + 1 × C6-$H_B$), 2.03 – 2.10 (1H, m, C3-H), 1.64 (1H, dddd, *J* = 11.8, 8.5, 7.5, 6.1 Hz, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 158.9 (C Ar), 137.8 (C Ar), 135.8 (C Ar), 131.0 (C-8), 129.3 (C7), 128.6 (2 × C Ar), 128.5 (2 × C Ar), 127.0 (C Ar), 126.1 (2 × Ar), 114.0 (2 × C Ar), 68.3 (C2), 55.4 (OMe), 47.7 (C3), 46.0 (C5), 36.5 (C6), 32.0 (C4). **HRMS** (ESl): calculated for $C_{20}H_{24}ON$ $[M+H]^+$ requires *m/z* 294.1858, found *m/z* 294.1852. **IR** (film) $\nu_{max}$: 2980, 2360, 1764, 1461, 1382, 1251 $cm^{-1}$.

**(6d): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**



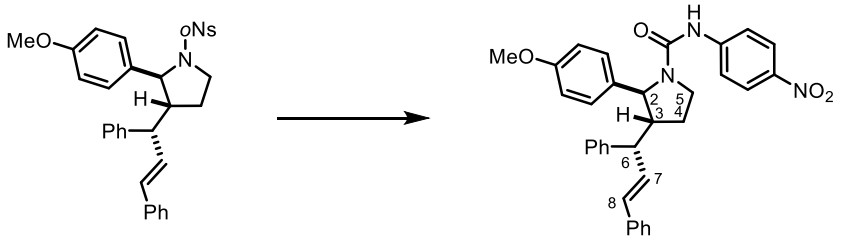

**3q** **6d**

Prepared according to **General Procedure L** using **3q** (27 mg, 0.053 mmol), LiOH (5.0 mg, 0.21 mmol) and thioglycolic acid (0.008 mL, 0.11 mmol). Flash column chromatography (gradient elution 1% → 15% MeOH – $CH_2Cl_2$) afforded **6d** as a colourless oil (10 mg, 60%).

Data for **6d**: $\mathbf{R_f}$ 0.40 (15% MeOH – $CH_2Cl_2$). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.37 – 7.40 (2H, m, Ar), 7.35-7.37 (4H, m, Ar), 7.20 – 7.24 (1H, m, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 3.89 (1H, d, *J* = 9.0 Hz,

C2-H), 3.79 (3H, s, OMe), 3.23 (1H, dt, *J* = 10.5, 7.3 Hz, C5-$H_A$), 3.03 (1H, ddd, *J* = 10.5, 8.9, 5.2 Hz, C5-$H_B$), 2.88 – 2.95 (1H, m, C6-H), 2.55 – 2.68 (2H, m, C9-$H_2$), 2.19 – 2.27 (1H, m, C3-H), 2.13 (1H, dtd, *J* = 12.6, 8.0, 5.2 Hz, C4-$H_A$), 1.98 – 2.06 (1H, m, C10-$H_A$), 1.75 (1H, dtd, *J* = 12.6, 8.9, 6.8 Hz, C4-$H_B$), 1.48 (1H, ddt, *J* = 13.0, 9.1, 7.1 Hz, C10-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 159.3 (C Ar), 143.9 (C Ar), 136.5 (C Ar), 129.1 (2 × C Ar), 128.4 (2 × C Ar + C8), 127.4 (C Ar), 127.2 (C7), 125.8 (2 × C Ar), 114.1 (2 × C Ar), 67.0 (C2), 55.4 (OMe), 51.6 (C3), 48.2 (C6), 45.5 (C5), 32.9 (C9), 29.2 and 29.1 (C4 + C10). **NOESY-2D (500 MHz, $CDCl_3$)**: between C2-H and C6-H, between C2-H and C7-H, between C2-H and C10-$H_A$. **HRMS** (ESl): calculated for $C_{22}H_{26}ON$ $[M+H]^+$ requires *m/z* 320.2014, found *m/z* 320.2007. **IR** (film) $\nu_{max}$: 2980, 2888, 2360, 1738, 1382, 1251 $cm^{-1}$.

**(3k'): (±)-(2*S*,3*R*)-3-((*S*,*E*)-1,3-Diphenylallyl)-2-(4-methoxyphenyl)-*N*-(4-nitrophenyl)-pyrrolidine-1-carboxamide**

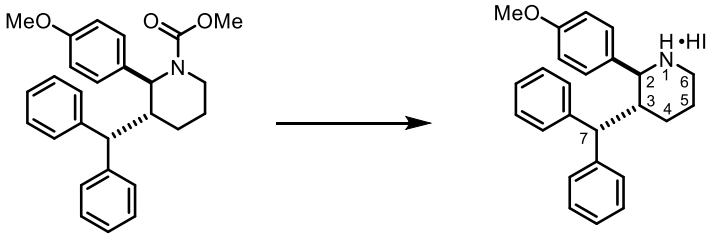



**3k** **3k'**

Prepared according to **General Procedure L** using **3k** (33 mg, 0.06 mmol), LiOH (4.5 mg, 0.18 mmol) and thioglycolic acid (0.008 mL, 0.088 mmol). The crude material was re-dissolved in $CH_2Cl_2$ (1 mL) and $Et_3N$ (0.01 mL, 0.07 mmol) and 4-nitrophenylisocyanate (12 mg, 0.073 mmol) added. After 16 h the solvent was removed *in vacuo*. Flash column chromatography (gradient elution 1% → 5% MeOH – $CH_2Cl_2$) afforded **3k'** as a yellow solid (25 mg, 78%).

Data for **3k'**: **$R_f$** 0.40 (5% MeOH – $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$) δ** 8.07 – 7.98 (3H, m, Ar), 7.36 – 7.14 (12H, m, Ar), 6.89 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (1H, d, *J* = 9.0 Hz, Ar), 6.51 (1H, d, *J* = 15.7 Hz, C8-H), 6.46 (1H, *br*. s, *N*H), 6.21 (1H, dd, *J* = 15.7, 9.3 Hz, C7-H), 4.76 – 4.64 (1H, *br*. s, C2-H), 3.89 (1H, dt, *J* = 11.0, 7.3 Hz, C5-$H_A$), 3.79 (3H, s, OMe), 3.74 – 3.65 (1H, m, C5-$H_B$), 3.44 (1H, t, *J* = 9.8 Hz, C6-H), 2.76 – 2.59 (1H, m, C3-H), 1.97 (1H, dq, *J* = 14.1, 7.2 Hz, C4-$H_A$), 1.61 (1H, ddt, *J* = 13.0, 7.4, 5.5 Hz, C4-$H_B$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 159.7 (C Ar), 153.2 (CO), 145.3 (C Ar), 142.4 (C Ar), 142.3 (C Ar), 136.8 (C Ar), 132.1 (C7), 131.4 (C8), 129.1 (2 × C Ar), 128.7 (2 × C Ar), 128.0 (C Ar), 127.8 (2 × C Ar), 127.2 (C Ar), 126.5 (2 × C Ar), 126.4 (2 × C Ar), 125.1 (2 × C Ar), 118.0 (2 × C Ar), 115.0 (2 × C Ar), 113.5 (C Ar), 65.1 (C2), 55.5 (OMe), 55.5 (C3), 53.3 (C6), 46.4 (C5), 27.0 (C4). **HRMS** (ESI): calculated for $C_{33}H_{32}N_3O_4$ $[M+H]^+$ requires *m/z* 534.2387, found *m/z* 534.2388. **IR** (film) $\nu_{max}$: 3655, 2981, 2918, 2850, 2361, 2341, 1380, 1250, 1137 $cm^{-1}$. **mp** (240 – 242 °C, EtOAc).

**(7a): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)piperidin-1-ium iodide**

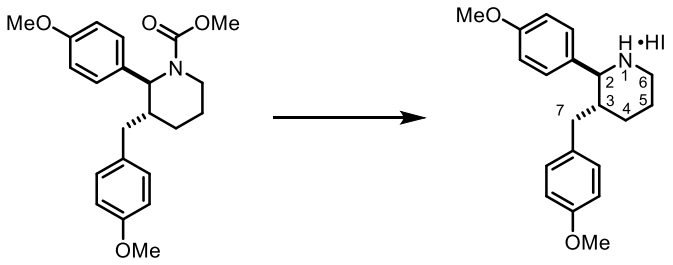



**5a** **7a**

Prepared according to **General Procedure M** using **5a** (37 mg, 0.089 mmol), trimethylsilyl iodide (0.038 mL, 0.27 mmol) in $CHCl_3$ (3.0 mL) at 55 °C for 2 h. Flash column chromatography (gradient elution 0% → 5% MeOH – $CH_2Cl_2$) afforded **7a** as an off white waxy solid (39 mg, 86%).

Data for **7a**: **$R_f$** 0.64 (10% MeOH – $CH_2Cl_2$). **$^1$H NMR (600 MHz, $CDCl_3$) δ** 8.75 – 8.41 (2H, m, Ar), 7.48 (2H, d, *J* = 8.2 Hz, Ar), 7.29 – 7.24 (3H, m, Ar), 7.22 (2H, t, *J* = 7.7 Hz, Ar), 7.17 – 7.12 (1H, m, Ar), 7.09 (2H, d, *J* = 8.3 Hz, Ar), 6.93 – 6.88 (2H, m, Ar), 6.87 – 6.79 (2H, m, Ar), 3.95 (1H, d, *J* = 3.7 Hz, C7-H), 3.77 (3H, s, OMe), 3.69 (1H, d, *J* = 11.2 Hz, C2-H), 3.17 (1H, tt, *J* = 11.5, 3.4 Hz, C3-H), 2.91 – 2.78 (1H, m, C6-$H_A$), 2.52 (1H, t, *J* = 12.7 Hz, C6-$H_B$), 2.18 – 2.00 (2H, m, C4-$H_A$ + C5-$H_A$), 1.72 (1H, dt, *J* = 14.5, 2.9 Hz, C5-$H_B$), 1.36 (1H, qd, *J* = 13.1, 3.5 Hz, C4-$H_B$). **$^{13}$C NMR (101 MHz, $CDCl_3$) δ** 160.0 (C Ar), 142.6 (C Ar), 140.4 (C Ar), 130.7 (C Ar), 130.6 (2 × C Ar), 128.4 (4 × C Ar), 128.2 (4 × C Ar), 127.0 (C Ar), 126.2 (C Ar), 114.4 (2 × C Ar), 64.7 (C7), 55.4 (OMe), 50.6 (C2), 46.0 (C6), 43.0 (C3), 26.4 (C5), 23.7 (C4). **NOESY-2D (600 MHz, $CDCl_3$)**: between C2-H and C6-$H_B$, between C2-H and C4-$H_B$, between C3-H and C5-$H_A$. **HRMS** (ESI): calculated for $C_{25}H_{28}ON$ $[M+H]^+$ requires m/z 358.2165, found m/z 358.2162. **IR** (film) $\nu_{max}$: 2981, 2930, 2360, 2341, 1611, 1515, 1451, 1255, 1181, 1302 $cm^{-1}$.

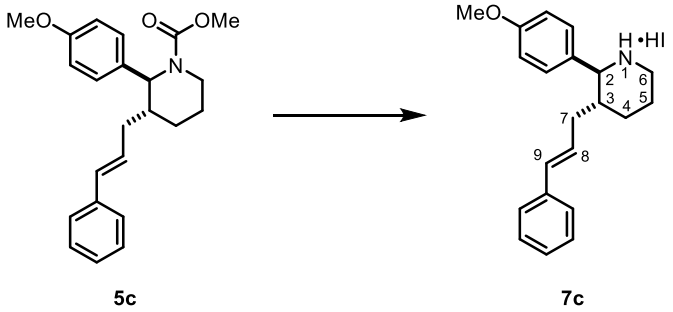
**(7b): (±)-(2*S*,3*R*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)piperidin-1-ium iodide**




Prepared according to **General Procedure M** using **5b** (38 mg, 0.10 mmol), trimethylsilyl iodide (0.044 mL, 0.30 mmol) in $CHCl_3$ (3.0 mL) at 55 °C for 2 h. Flash column chromatography (gradient elution 0% → 5% MeOH – $CH_2Cl_2$) afforded **7b** as an off white waxy solid (42 mg, 93%).

Data for **7b**: $\mathbf{R_f}$ 0.47 (10% MeOH – $CH_2Cl_2$). **$^1$H NMR (400 MHz, MeOD) δ** 7.47 (2H, d, *J* = 8.7 Hz, Ar), 7.06 (2H, d, *J* = 8.8 Hz, Ar), 6.92 (2H, d, *J* = 8.6 Hz, Ar), 6.79 (2H, d, *J* = 8.7 Hz, Ar), 3.93 (2H, d, *J* = 10.8 Hz, C2-H), 3.84 (3H, s, OMe), 3.74 (3H, s, OMe), 3.46 – 3.28 (1H, m, C6-$H_A$), 3.10 (1H, td, *J* = 12.9, 3.3 Hz, C6-$H_B$), 2.43 (1H, dd, *J* = 13.0, 2.8 Hz, C7-$H_A$), 2.26 – 2.04 (1H, m, C7-$H_B$), 1.99 – 1.83 (2H, m, 1 × C4-$H_A$ + 1 × C5-$H_A$), 1.74 (1H, qt, *J* = 14.2, 4.0 Hz, C4-$H_B$), 1.44 – 1.25 (1H, m, C5-$H_B$). **$^{13}$C NMR (101 MHz, MeOD) δ** 162.1 (C Ar), 159.7 (C Ar), 131.8 (C Ar), 131.1 (2 × C Ar), 130.7 (2 × C Ar), 129.0 (C Ar), 115.9 (2 × C Ar), 114.9 (2 × C Ar), 66.4 (C2), 55.9 (OMe), 55.7 (OMe), 46.6 (C6), 42.6 (C3), 38.6 (C7), 29.5 (C5), 23.8 (C4). **HRMS** (ESI): calculated for $C_{20}H_{26}O_2N$ $[M+H]^+$ requires m/z 312.1958, found m/z 312.1957. **IR** (film) $\nu_{max}$: 2935, 17096, 1692, 1676, 1586, 1513, 1349, 1363, 1247, 1198 $cm^{-1}$.

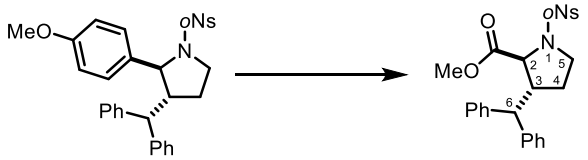
**(7c): (±)-(2*S*,3*R*)-3-Cinnamyl-2-(4-methoxyphenyl)piperidin-1-ium iodide**




Prepared according to **General Procedure M** using **5c** (46 mg, 0.13 mmol), trimethylsilyl iodide (0.050 mL, 0.39 mmol), isoprene (0.13 mL, 1.3 mmol) in $CHCl_3$ (3.0 mL) at 55 °C for 2 h. Flash column chromatography (gradient elution 0% → 5% MeOH – $CH_2Cl_2$) afforded **7c** as a white waxy solid (44 mg, 80%).

Data for **7c**: **$R_f$** 0.51 (10% MeOH – $CH_2Cl_2$). **$^1$H NMR (400 MHz, MeOD) δ** 7.44 (2H, d, *J* = 8.7 Hz, Ar), 7.31 – 7.22 (4H, m, Ar), 7.20 – 7.14 (1H, m, Ar), 7.04 (1H, d, *J* = 8.8 Hz, Ar), 6.20 (1H, d, *J* = 15.8 Hz, C9-H), 6.03 (1H, ddd, *J* = 15.7, 8.1, 6.5 Hz, C8-H), 3.98 (1H, d, *J* = 11.2 Hz, C2-H), 3.81 (3H, s, OMe), 3.39 (1H, ddd, *J* = 12.6, 3.9, 1.8 Hz, C6-$H_A$), 3.15 (1H, td, *J* = 13.0, 3.4 Hz, C6-$H_B$), 2.26 – 2.04 (3H, m, 1 × C3-H + 1 × C5-$H_A$ + 1 × C7-$H_A$), 2.04 – 1.93 (3H, m, 2 × C4-$H_2$ + 1 × C7-$H_B$), 1.93 – 1.82 (1H, m, C5-$H_B$). **$^{13}$C NMR (101 MHz, MeOD) δ** 162.3 (C Ar), 138.6 (C Ar), 134.0 (C9), 130.7 (2 × C Ar), 129.5 (2 × C Ar), 128.3 (C Ar), 128.2 (C Ar), 127.0 (2 × C Ar), 126.9 (C8), 115.9 (2 × C Ar), 66.0 (C2), 55.9 (OMe), 46.4 (C6), 40.7 (C3), 36.9 (C7), 29.8 (C5), 23.6 (C4). **HRMS** (ESI): calculated for $C_{21}H_{26}ON$ $[M+H]^+$ requires m/z 308.2009, found m/z 308.2012. **IR** (film) $\nu_{max}$: 3024, 2957, 2934, 2837, 2069, 1612, 1516, 1256, 1182, 1030, 968, 826, 746 $cm^{-1}$.

**(8): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-1-((2-nitrophenyl)sulfonyl)pyrrolidine-2-carboxylate**

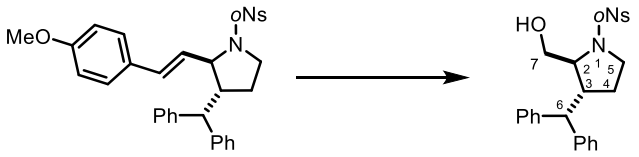



**3c** **8**

To a solution of **3c** (55 mg, 0.10 mmol) in a 2:2:3 mixture of $CCl_4$:MeCN:pH 7 buffer ($Na_2HPO_4$) (1.0 mL) was added $NaIO_4$ (445 mg, 2.08 mmol) at 0 °C. After 15 min $RuCl_3$ (1.0 mg, 5.0 mol%) was added and the reaction mixture allowed to warm up to rt before being stirred vigorously for 16 h. The reaction mixture was diluted with $Et_2O$ and 1.0 M HCl. The aqueous later was extracted with $Et_2O$ and the combined organic layers were washed with 1.0 M HCl and dried over $MgSO_4$ before concentrating *in vacuo.* The crude residue was re-dissolved in a 9:1 PhMe:MeOH mixture (1.0 mL) and trimethylsilyldiazomethane solution (2.0 M in $Et_2O$) was added dropwise until the yellow colour persisted. After 15 min the solvent was removed *in vacuo*. Flash column chromatography (gradient elution 10% → 25% EtOAc – pentane) afforded **8** as a colourless oil (25 mg, 52%).

Data for **8**: **$R_f$** 0.27 (30% EtOAc – pentane). **$^1$H NMR (600 MHz, $CDCl_3$) δ** 7.99 (1H, dd, *J* = 7.9, 1.4 Hz, Ar), 7.73 – 7.67 (1H, m, Ar), 7.67 – 7.58 (2H, m, Ar), 7.28 – 7.23 (6H, m, Ar), 7.22 – 7.15 (4H, m, Ar), 4.27 (1H, d, *J* = 2.4 Hz, C2-H), 3.83 (1H, dt, *J* = 9.4, 7.7 Hz, C5-$H_A$), 3.71 (1H, d, *J* = 12.0 Hz, C6-H), 3.70 – 3.63 (1H, m, C5-$H_B$), 3.52 (3H, s, OMe), 3.31 (1H, ddt, *J* = 12.2, 6.5, 3.0 Hz, C3-H), 2.07 (1H, dtd, *J* = 16.3, 8.2, 5.7 Hz, C4-$H_A$), 1.71 (1H, ddt, *J* = 12.6, 7.8, 4.1 Hz, C4-$H_B$). **$^{13}$C NMR (151 MHz, $CDCl_3$) δ** 172.2 (CO), 148.2 (C Ar), 142.6 (C Ar), 142.4 (C Ar), 133.6 (C Ar), 133.1 (C Ar), 131.8 (C Ar), 131.2 (C Ar), 129.0 (4 × C Ar), 128.1 (2 × C Ar), 128.0 (2 × C Ar), 127.1 (C Ar), 127.0 (C Ar), 124.2 (C Ar), 64.5 (C2), 54.1 (C6), 52.6 (OMe), 48.4 (C3), 47.6 (C5), 28.6 (C4). **HRMS** (ESI): calculated for $C_{25}H_{25}N_2O_6S$ $[M+H]^+$ requires *m/z* 481.1429, found *m/z* 481.1428. **IR** (film) $\nu_{max}$: 2981, 2361, 2312, 1745, 1544, 1453, 1372, 1215, 1032 $cm^{-1}$.

**(*trans*-9): (±)-2-{(2*S*,3*R*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]pyrrolidin-2-yl}methanol**

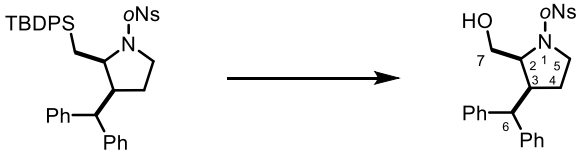



*trans*-**3x** *trans*-**9**

$O_3$ was bubbled through a solution of **3x** (26 mg, 0.048 mmol) in a 2:1 mixture of $CH_2Cl_2$:MeOH (0.5 mL) at -78 °C for 10 min (at which point a blue colour was observed) before bubbling with $O_2$ for a further 3 min and then $N_2$ for a further 3 min (at which point no blue colour was observed). $NaBH_4$ (0.5 mg, 0.1 mmol) was added and the reaction mixture left to warm to rt before concentrating *in vacuo.* Flash column chromatography (gradient elution 10% → 20% acetone – pentane) afforded *trans*-**9** as a colourless oil (10 mg, 45%).

Data for *trans*-**9**: **$R_f$** 0.30 (35% acetone – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 7.98 (1H, dd, *J* = 8.2, 1.4 Hz, Ar), 7.73 – 7.79 (1H, m, Ar), 7.62 – 7.68 (2H, m, Ar), 7.10 – 7.25 (8H, m, Ar), 7.00 – 7.05 (2H, m, Ar), 3.72 – 3.77 (1H, m, C5-$H_A$), 6.67 – 3.72 (1H, m, C2-H), 3.56 (1H, ddd, *J* = 11.5, 6.5, 4.6 Hz, C7-$H_A$), 3.44 – 3.51 (2H, m, 1 × C5-$H_B$ + 1 × C6-H), 3.36 –3.44 (1H, m, C7-$H_B$), 2.10 (1H, t, *J* = 6.5 Hz, *O*H), 1.98 – 2.07 (1H, m, C4-$H_A$), 1.49 – 1.57 (1H, m, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 143.0 (C Ar), 142.8 (C Ar), 134.0 (C Ar), 131.9 (C Ar), 131.8 (C Ar), 131.5 (C Ar), 129.0 (2 × C Ar), 128.9 (2 × C Ar), 128.1 (C Ar), 128.0 (2 × C Ar), 127.9 (2 × C Ar), 126.9 (C Ar), 126.8 (C Ar), 124.2 (C Ar), 65.5 (C2), 65.1 (C7), 54.6 (C6), 48.4 (C5), 45.7 (C3), 29.0 (C4). **HRMS** (ESI): calculated for $C_{24}H_{24}N_2O_5S$ $[M+H]^+$ requires *m/z* 475.1304, found *m/z* 475.1295. **IR** (film) $\nu_{max}$: 3026, 2934, 1705, 1543, 1371, 1335 $cm^{-1}$.

**(*cis*-9): (±)-2-{(2*S*,3*S*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]pyrrolidin-2-yl}methanol**



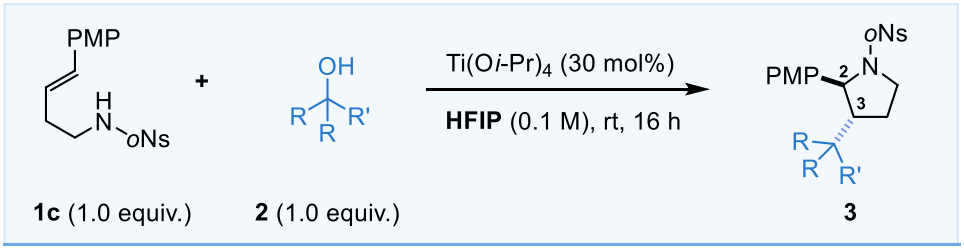

*cis*-**3ac** *cis*-**9**

To a solution of **3ac** (29 mg, 0.045 mmol) in anhydrous $CH_2Cl_2$ (0.45 mL) was added $BF_3$·2AcOH (0.03 mL, 0.22 mmol) before heating to reflux for 24 h. After cooling to rt aq. $NaHCO_3$ was added and the layers separated. The aqueous later was extracted with $CH_2Cl_2$ and the combined organic layers were washed with brine and dried over $Na_2SO_4$ before concentrating *in vacuo*. The crude material was re-dissolved in a 1:1 THF:MeOH mixture (0.60 mL) before addition of $NaHCO_3$ (4 mg, 0.05 mmol), KF (8.0 mg, 0.15 mmol) and $H_2O_2$ (30%, 0.42 mL, 0.44 mmol). The reaction mixture was heated to reflux for 6 h, cooled to rt and aq. $NaHCO_3$ added. The aqueous later was extracted with EtOAc and the

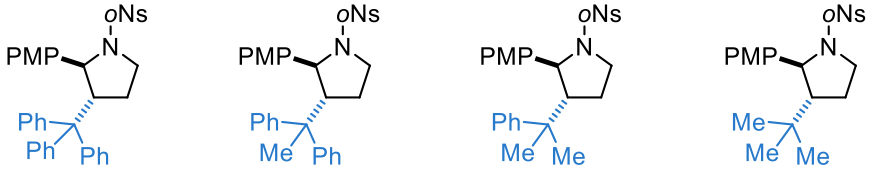
combined organic layers were washed with brine and dried over $Na_2SO_4$ before concentrating *in vacuo*. Flash column chromatography (gradient elution 10% → 20% acetone – pentane) afforded *cis*-**9** as a colourless oil (9 mg, 55%).

Data for *cis*-**9**: **$R_f$** 0.40 (35% acetone – pentane). **$^1$H NMR (500 MHz, $CDCl_3$) δ** 8.09 (1H, dd, *J* = 7.8, 1.5 Hz, Ar), 7.68 – 7.77 (2H, m, Ar), 7.67 (1H, dd, *J* = 7.8, 1.5 Hz, Ar), 7.34 – 7.38 (2H, m, Ar), 7.28 – 7.33 (2H, m, Ar), 7.17 – 7.22 (4H, m, Ar), 7.09 – 7.16 (2H, m, Ar), 4.08 (1H, dt, *J* = 7.4, 3.6 Hz, C2-H), 3.97 (1H, d, *J* = 11.9 Hz, C6-H), 3.65 (1H, ddd, *J* = 12.2, 5.3, 3.6 Hz, C7-$H_A$), 3.50 – 3.59 (2H, m, 1 × C7-$H_B$ + 1 × C5-$H_A$), 3.30 (1H, td, *J* = 10.0, 7.3 Hz, C5-$H_B$), 3.01 – 3.10 (1H, m, C3-H), 1.98 – 2.10 (1H, m, C4-$H_A$), 1.93 (1H, dd, *J* = 7.7, 5.3 Hz, *O*H), 1.62 (1H, dt, *J* = 13.1, 7.3 Hz, C4-$H_B$). **$^{13}$C NMR (125 MHz, $CDCl_3$) δ** 143.9 (C Ar), 142.5 (C Ar), 134.0 (2 × C Ar), 131.9 (2 × C Ar), 131.7 (C Ar), 129.2 (2 × C Ar), 128.8 (2 × C Ar), 127.6 (4 × C Ar), 127.0 (C Ar), 126.7 (C Ar), 124.3 (C Ar), 63.2 (C2), 62.4 (C7), 52.2 (C6), 47.7 (C5), 46.5 (C3), 30.4 (C4). **HRMS** (ESI): calculated for $C_{24}H_{24}N_2O_5S$ $[M+H]^+$ requires *m/z* 475.1304, found *m/z* 475.1295. **IR** (film) $\nu_{max}$: 3026, 2934, 1705, 1543, 1371, 1335 $cm^{-1}$.

Use of Tertiary Alcohols



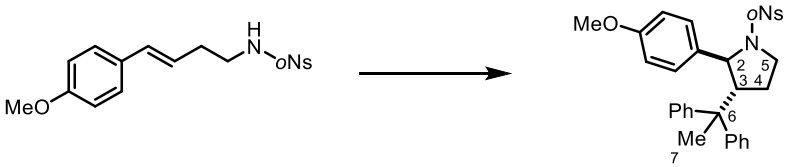

Tertiary alcohols were found to be partially compatible with the reaction conditions, however they gave diminished yields when compared to primary and secondary alcohols.




**3ag**, 0%; 0%[a] **3ah**, 0%; 13%[a] **3ai**, 33%[a] **3aj**, 0%, 0%[a]

[a] Performed at 70 °C

**(3ah): (±)-(2*S*,3*R*)-3-(1,1-Diphenylethyl)-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)-pyrrolidine**

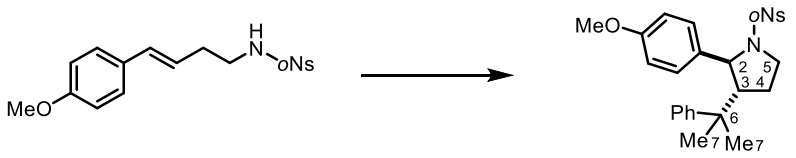



**1c** **3ah**

Prepared according to **General Procedure K** using **1c** (36 mg, 0.10 mmol) and 1,1-diphenylethanol (20 mg, 0.10 mmol) at 70 ˚C. Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3ah** as a colourless oil (7 mg, 13%).

Data for **3ah**: **$R_f$** 0.35 (30% EtOAc – pentane). **$^1$H NMR (600 MHz, $CDCl_3$) δ** 7.45 – 7.38 (2H, m, Ar), 7.25 – 7.23 (2H, m, Ar), 7.22 – 7.17 (4H, m, Ar), 7.18 – 7.13 (5H, m, Ar), 7.10 (1H, ddd, *J* = 8.3, 7.2, 1.5 Hz, Ar), 6.51 (2H, d, *J* = 8.7 Hz, Ar), 6.41 (2H, d, *J* = 8.7 Hz, Ar), 4.73 (1H, d, *J* = 3.8 Hz, C2-H), 3.94 (1H, ddd, *J* = 9.9, 8.8, 4.1 Hz, C5-$H_A$), 3.70 – 3.67 (1H, m, C5-$H_B$), 3.66 (3H, s, OMe), 3.27 (1H, dt, *J* = 8.3, 3.8 Hz, C3-H), 2.53 (1H, dq, *J* = 13.6, 8.7 Hz, C4-$H_A$), 2.16 (1H, ddt, *J* = 13.4, 8.0, 4.0 Hz, C4-$H_B$), 1.76 (3H, s, C7-$H_3$). **$^{13}$C NMR (151 MHz, $CDCl_3$) δ** 158.8 (C Ar), 147.8 (C Ar), 147.8 (C Ar), 147.7 (C Ar), 135.0 (C Ar), 134.0 (C Ar), 132.7 (C Ar), 131.3 (C Ar), 131.0 (C Ar), 128.6 (2 × C Ar), 128.5 (2 × C Ar), 128.2 (3 × C Ar), 128.0 (2 × C Ar), 126.5 (C Ar), 126.4 (C Ar), 123.6 (2 × C Ar), 113.7 (2 × C Ar), 65.5 (C2), 57.6 (C3), 55.6 (OMe), 50.4 (C5), 50.1 (C6), 28.0 (C4), 23.0 (C7). **HRMS** (ESI): calculated for $C_{31}H_{30}N_2O_5SNa$ $[M+Na]^+$ requires *m/z* 565.1768, found *m/z* 565.1768. **IR** (film) $\nu_{max}$: 2361, 1544, 1513, 1372, 1247, 1166, 1034, 912 $cm^{-1}$.

**(3ai): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)-3-(2-phenylpropan-2-yl)pyrrolidine**



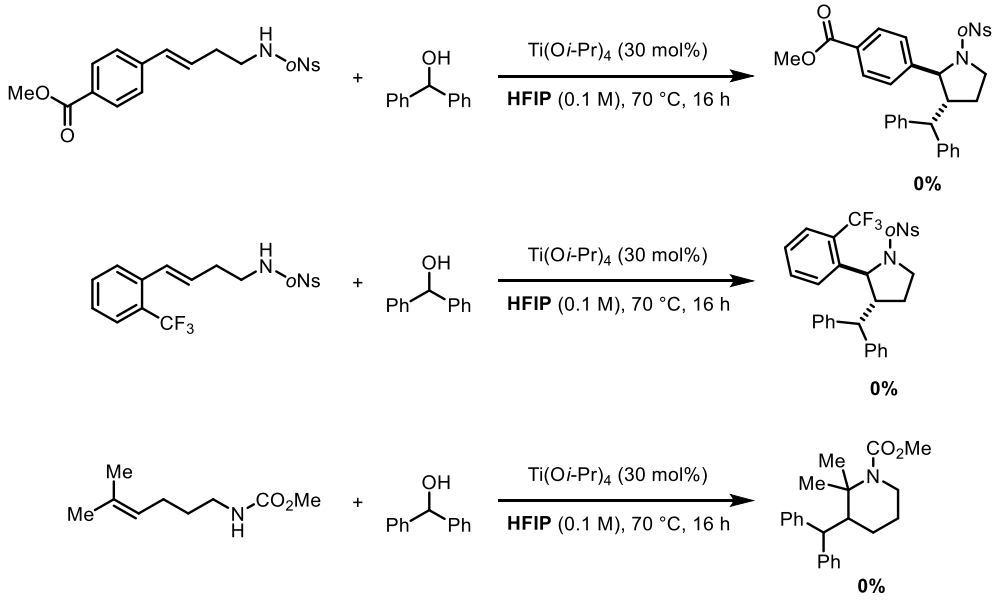

**1c** **3ai**

Prepared according to **General Procedure K** using **1c** (36 mg, 0.10 mmol) and 1-methyl-1-phenylethyl alcohol (13.5 mg, 0.10 mmol) at 70 ˚C. Flash column chromatography (gradient elution 10% → 20% EtOAc – pentane) afforded **3ai** as a colourless oil (16 mg, 33%).

Data for **3ai**: $\mathbf{R_f}$ 0.39 (30% EtOAc – pentane). **$^1$H NMR (600 MHz, $CDCl_3$) δ** 7.44 (1H, d, *J* = 7.6 Hz, Ar), 7.40 (1H, ddd, *J* = 7.9, 6.6, 2.3 Hz, Ar), 7.25 – 7.19 (4H, m, Ar), 7.16 – 7.09 (3H, m, Ar), 6.76 (2H, d, *J* = 8.5 Hz, Ar), 6.45 (2H, d, *J* = 8.5 Hz, Ar), 4.62 (1H, d, *J* = 6.6 Hz, C2-H), 3.89 (1H, ddd, *J* = 10.2, 7.8, 4.6 Hz, C5-$H_A$), 3.75 (1H, ddd, *J* = 10.1, 8.1, 7.0 Hz, C5-$H_B$), 3.68 (3H, s, OMe), 2.63 (1H, q, *J* = 7.5 Hz, C3-H), 1.98 – 1.90 (1H, m, C4-$H_A$), 1.90 – 1.85 (1H, m, C4-$H_B$), 1.31 (3H, s, C7-$H_3$), 1.27 (3H, s, C7-$H_3$). **$^{13}$C NMR (151 MHz, $CDCl_3$) δ** 158.7 (C Ar), 147.8 (C Ar), 147.4 (C Ar), 134.4 (C Ar), 134.2 (C Ar), 132.3 (C Ar), 130.9 (C Ar), 130.8 (C Ar), 128.7 (2 × C Ar), 128.3 (2 × C Ar), 126.3 (2 × C Ar), 126.2 (C Ar), 123.4 (C Ar), 113.5 (2 × C Ar), 65.1 (C2), 60.4 (C3), 55.4 (OMe), 49.8 (C5), 39.9 (C6), 27.4 (C4), 26.2 (C7), 25.9 (C7). **HRMS** (ESI): calculated for $C_{26}H_{29}N_2O_5S$ $[M+H]^+$ requires *m/z* 481.1792, found *m/z* 481.1794. **IR** (film) $\nu_{max}$: 2363, 1545, 1513, 1373, 1248, 1165, 1033, 765, 653 $cm^{-1}$.

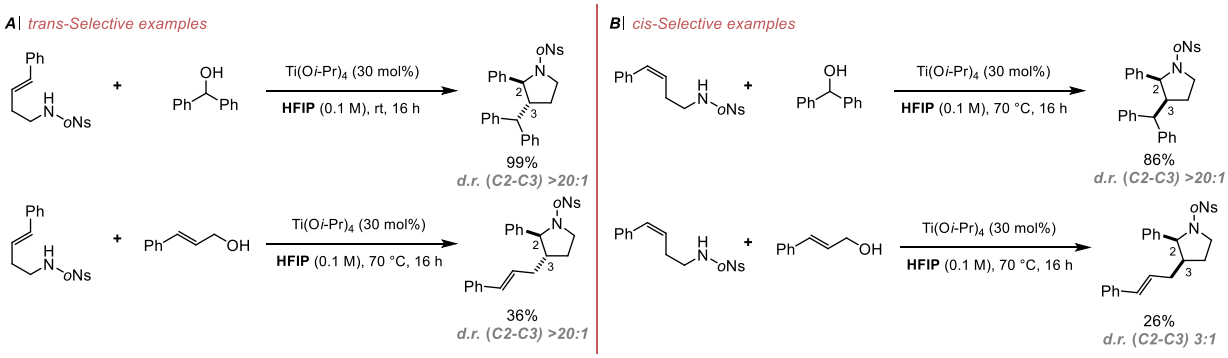
<u>Unreactive Nucleophiles</u>

Nucleophiles that were found to be unreactive with benzhydrol at elevated temperatures.



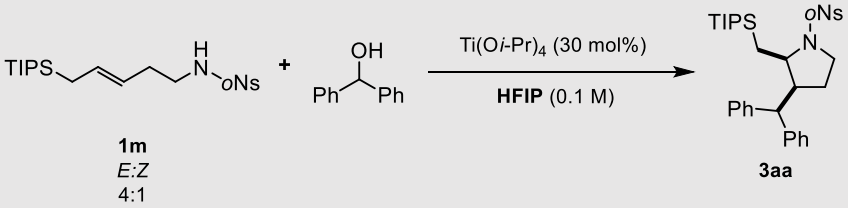
## Supporting document for mechanistic hypothesis

a) Influence of alkene geometry in a parent system




The role of the double bond geometry above shows that the *E* isomer gives exclusively the *trans* diastereomer with high stereoselectivity when reacted with benzhydrol and cinnamyl alcohol whereas the *Z* isomer leads to a major, but not exclusive, *cis* product when subjected to the same reaction suggesting a less stereoselective pathway.

b) Temperature experiments



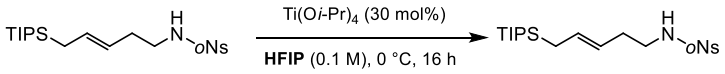

**1m**
*E:Z*
4:1

**3aa**

| Entry | Temp / ˚C | Time / h | Yield **3aa** / % | *trans:cis* |
|---|---|---|---|---|
| 1 | 0 | 16 | 99 | *1:4* |
| 2 | 70 | 16 | 99 | *1:2* |
| 3 | 70 | 24 | 99 | *1:1.4* |
| 4 | 70 | 40 | 99 | *1:1.1* |

Higher temperature experiments support the equilibration at high temperature between the *trans* and *cis* diastereomers of **3aa**, with the *cis*-diastereomer being the kinetic product whereas the *trans*-diastereomer is the thermodynamically more stable product.

c) Resubjection experiment



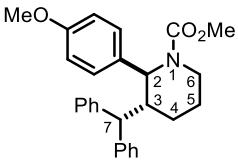

**1m**
*E:Z*
4:1

**1m**
*E:Z*
4:1

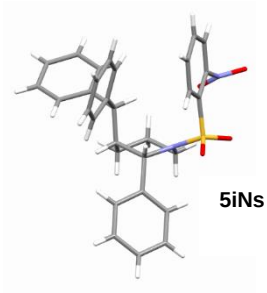
Finally, a control experiment confirmed that starting material **1m** was not simply being isomerised under the reaction conditions. Following 16 h at 0 ˚C the alkene geometry ratio was unchanged.

## Supporting document for structural assignment of piperidines

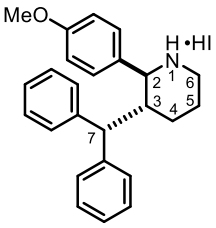
### Coupling constant analysis




**5a**



**5iNs**




**7a**

$J_{C2\text{-}C3}$ = 2.2 Hz

$J_{C3\text{-}C7}$ = 11.9 Hz

$J_{C3\text{-}C4ax}$ = 4.2 Hz

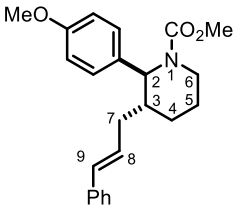
$J_{C3\text{-}C4eq}$ = 2.2 Hz

$J_{C2\text{-}C3}$ = 11.2 Hz

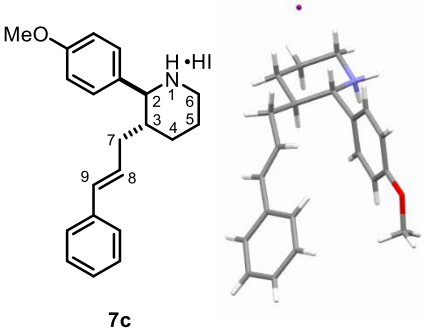
$J_{C3\text{-}C7}$ = 3.7 Hz

$J_{C3\text{-}C4ax}$ = 11.5 Hz

$J_{C3\text{-}C4eq}$ = 3.5 Hz




**5c**




**7c**

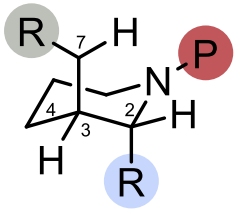
$J_{C2\text{-}C3}$ = 3.0 Hz

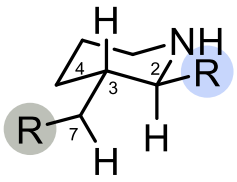
$J_{C3\text{-}C7}$ = 7.0 Hz

$J_{C3\text{-}C4ax}$ = 3.0 Hz

$J_{C3\text{-}C4eq}$ = 3.0 Hz

$J_{C2\text{-}C3}$ = 11.2 Hz

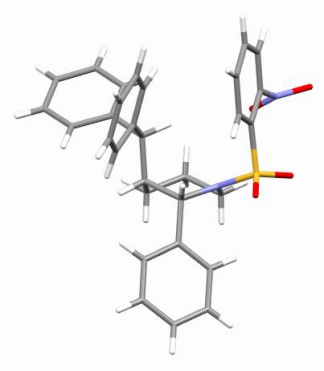


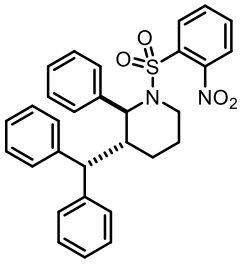



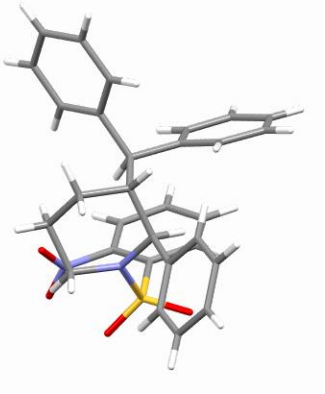

The relative stereochemistry of the piperidine products was corroborated through $^{1}$H *J* coupling analysis (see above for representative examples) which support the 2,3-substituents adopting a diaxial conformation (nOe correlations provide little support for this due to the spatial positions of the key protons); X-ray data is available for **5iNs** which supports the above conclusion. Following the removal of the methyl carbamate group the 2,3-substituents then adopt a diequatorial conformation, which can be corroborated through 1H *J* coupling analysis (see above for representative examples) along with nOe correlations for **7a** and X-ray data for **7c**.

## Crystallography

**X-ray Crystallographic data for (5iNs): (±)-(2*S*,3*R*)-3-Benzhydryl-1-((2-nitrophenyl)-sulfonyl)-2-phenylpiperidine, 7372**



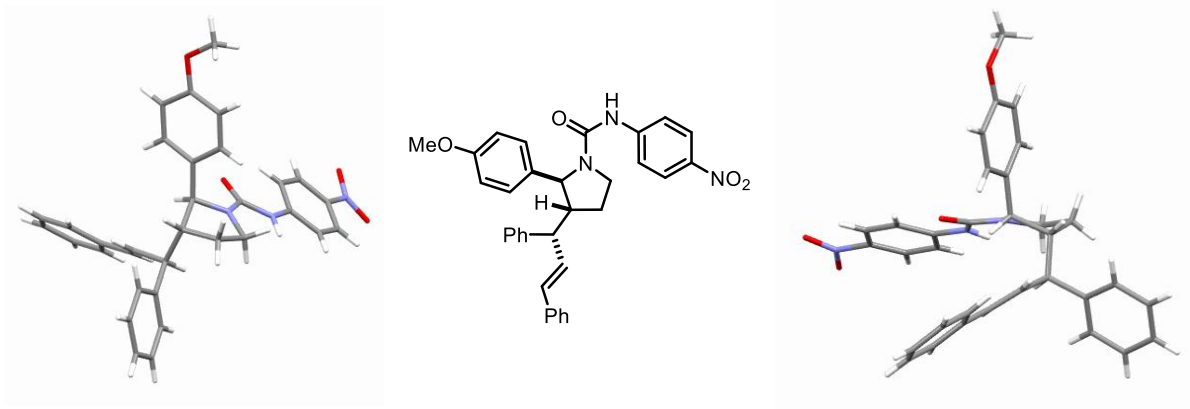


Crystals suitable for single crystal X-ray Crystallography were obtained *via* vapour diffusion of pentane into a solution of **5iNs** (10 mg) in EtOAc (0.5 mL).

| | | |
|---|---|---|
| Identification code | 7372 | |
| Empirical formula | C30 H28 N2 O4 S | |
| Formula weight | 512.63 | |
| Temperature | 150 K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 10.38990(10) Å | α= 90°. |
| | b = 23.2970(3) Å | β= 108.9135(16)°. |
| | c = 11.2415(2) Å | γ = 90°. |
| Volume | 2574.13(7) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.323 $Mg/m^3$ | |
| Absorption coefficient | 1.437 $mm^{-1}$ | |
| F(000) | 1080 | |
| Crystal size | 0.20 x 0.18 x 0.09 $mm^3$ | |
| Theta range for data collection | 3.795 to 76.114°. | |
| Index ranges | -12<=h<=9, -29<=k<=28, -13<=l<=14 | |
| Reflections collected | 13843 | |
| Independent reflections | 5310 [R(int) = 0.026] | |
| Completeness to theta = 73.831° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.88 and 0.85 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5310 / 0 / 334 | |
| Goodness-of-fit on $F^2$ | 0.9955 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0348, wR2 = 0.0885 | |
| R indices (all data) | R1 = 0.0393, wR2 = 0.0935 | |
| Largest diff. peak and hole | 0.43 and -0.45 $e.Å^{-3}$ | |

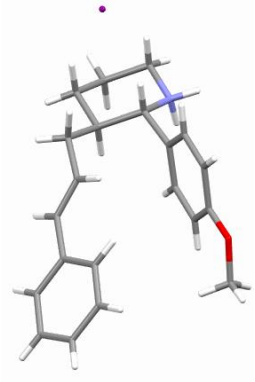
**X-ray Crystallographic data for (3k'): (±)-(2*S*,3*R*)-3-((*S*,*E*)-1,3-Diphenylallyl)-2-(4-methoxy-phenyl)-*N*-(4-nitrophenyl)-pyrro-lidine-1-carboxamide, 7493**

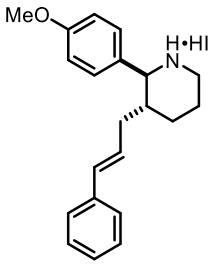


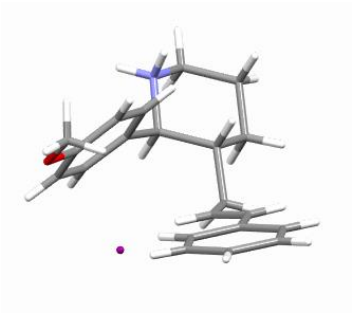

Crystals suitable for single crystal X-ray Crystallography were obtained *via* evaportation of a solution of **3k'** (18 mg) in heptane/EtOAc (0.5 mL).

| | | |
|---|---|---|
| Identification code | 7493 | |
| Empirical formula | C33 H31 N3 O4 | |
| Formula weight | 533.62 | |
| Temperature | 150 K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Orthorhombic | |
| Space group | P c a 21 | |
| Unit cell dimensions | a = 9.4987(7) Å | α= 90°. |
| | b = 14.7759(11) Å | β= 90°. |
| | c = 19.5458(13) Å | γ = 90°. |
| Volume | 2743.3(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.292 $Mg/m^3$ | |
| Absorption coefficient | 0.689 $mm^{-1}$ | |
| F(000) | 1127.993 | |
| Crystal size | 0.16 x 0.05 x 0.03 $mm^3$ | |
| Theta range for data collection | 4.524 to 76.720°. | |
| Index ranges | -11<=h<=11, -16<=k<=18, -21<=l<=24 | |
| Reflections collected | 16415 | |
| Independent reflections | 4936 [R(int) = 0.062] | |
| Completeness to theta = 73.831° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.98 and 0.94 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4932 / 1 / 362 | |
| Goodness-of-fit on $F^2$ | 1.0100 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0556, wR2 = 0.1306 | |
| R indices (all data) | R1 = 0.0845, wR2 = 0.1602 | |
| Largest diff. peak and hole | 0.19 and -0.15 $e.Å^{-3}$ | |

**X-ray Crystallographic data for (7c): (±)-(2*S*,3*R*)-3-Cinnamyl-2-(4-methoxyphenyl)piperidin-1-ium iodide, 7509**





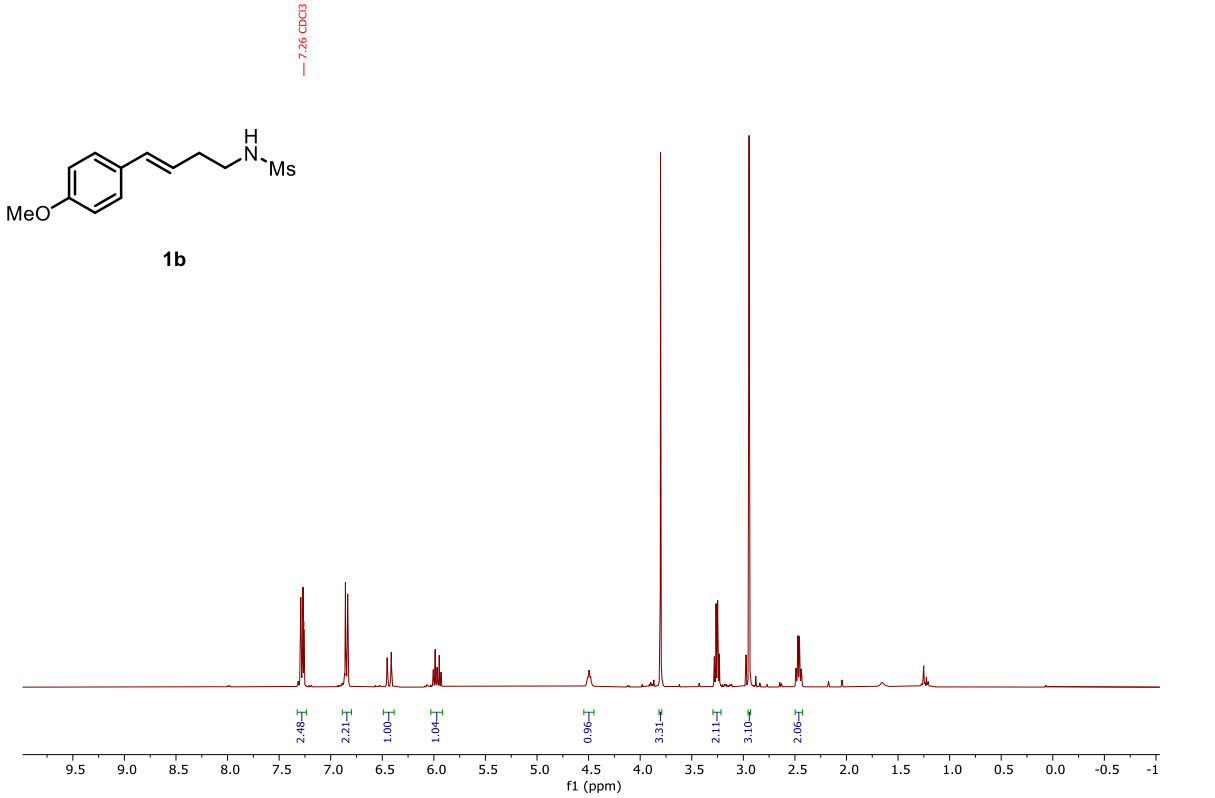



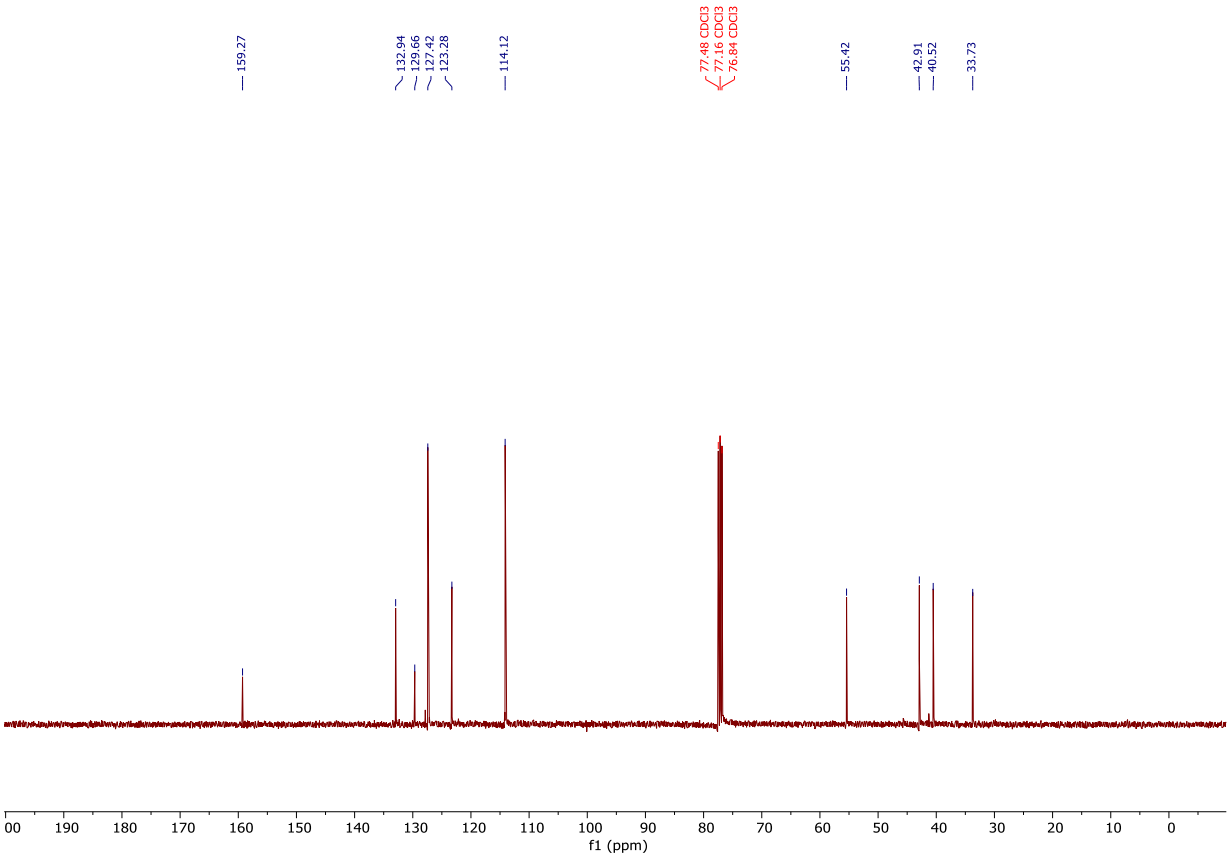
Crystals suitable for single crystal X-ray Crystallography were obtained *via* evaporation of **7c** (15 mg) in $CDCl_3$ (0.5 mL).

| | | |
|---|---|---|
| Identification code | 7509 | |
| Empirical formula | C21 H26 I N O | |
| Formula weight | 435.35 | |
| Temperature | 150 K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pccn | |
| Unit cell dimensions | a = 45.0554(5) Å | α= 90°. |
| | b = 10.23090(10) Å | β= 90°. |
| | c = 8.46320(10) Å | γ = 90°. |
| Volume | 3901.17(7) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.482 $Mg/m^3$ | |
| Absorption coefficient | 12.936 $mm^{-1}$ | |
| F(000) | 1760 | |
| Crystal size | 0.28 x 0.05 x 0.02 $mm^3$ | |
| Theta range for data collection | 3.925 to 76.529°. | |
| Index ranges | -56<=h<=56, -12<=k<=12, -10<=l<=10 | |
| Reflections collected | 95997 | |
| Independent reflections | 4096 [R(int) = 0.046] | |
| Completeness to theta = 76.529° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.77 and 0.07 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4095 / 0 / 217 | |
| Goodness-of-fit on $F^2$ | 0.9999 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0709, wR2 = 0.1669 | |
| R indices (all data) | R1 = 0.0718, wR2 = 0.1691 | |
| Largest diff. peak and hole | 2.68 and -0.38 $e.Å^{-3}$ | |

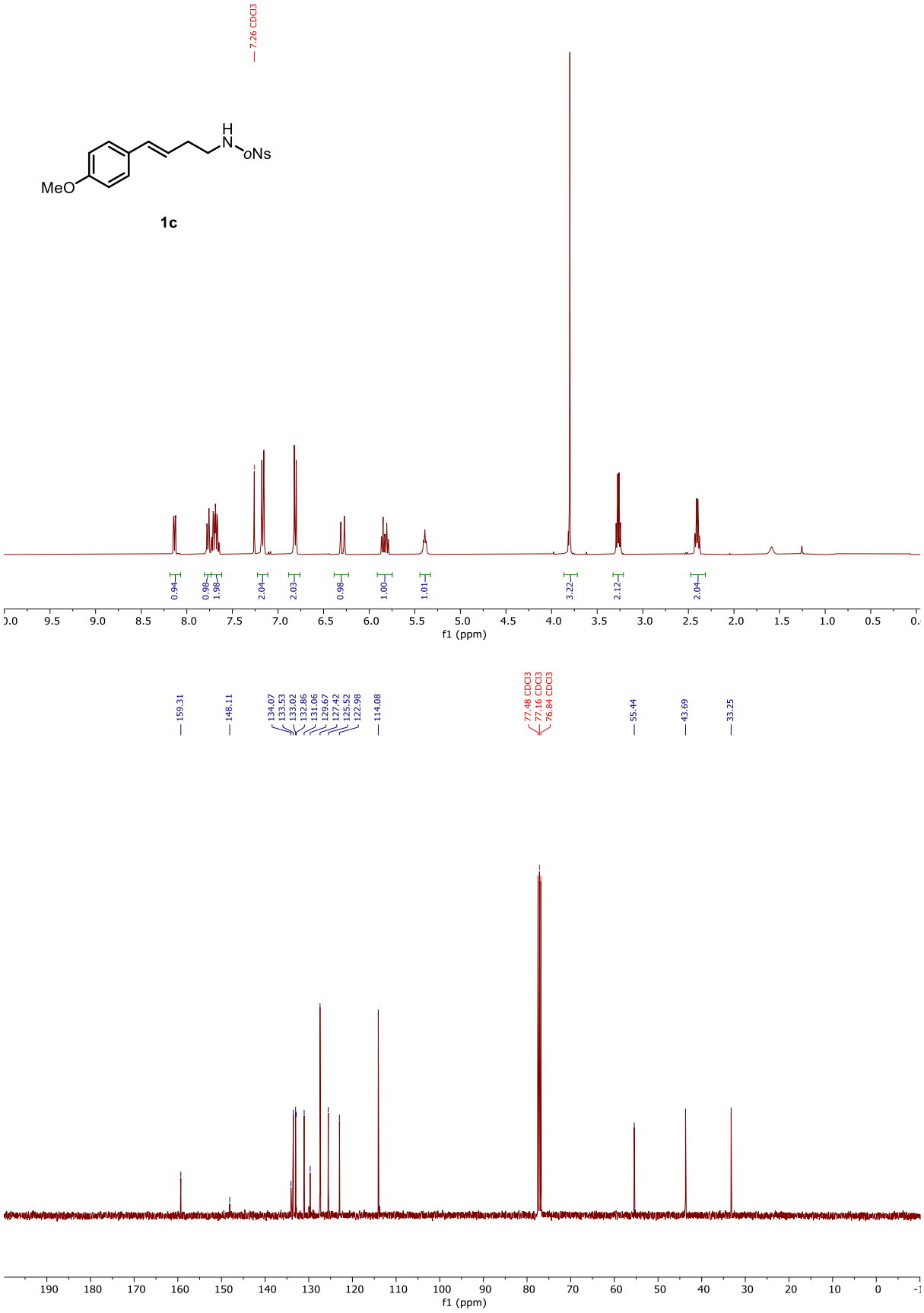
# Copies of $^{1}H$ & $^{13}C$ NMR spectra for novel compounds

## (1b): (*E*)-*N*-(4-(4-Methoxyphenyl)but-3-en-1-yl)methanesulfonamide

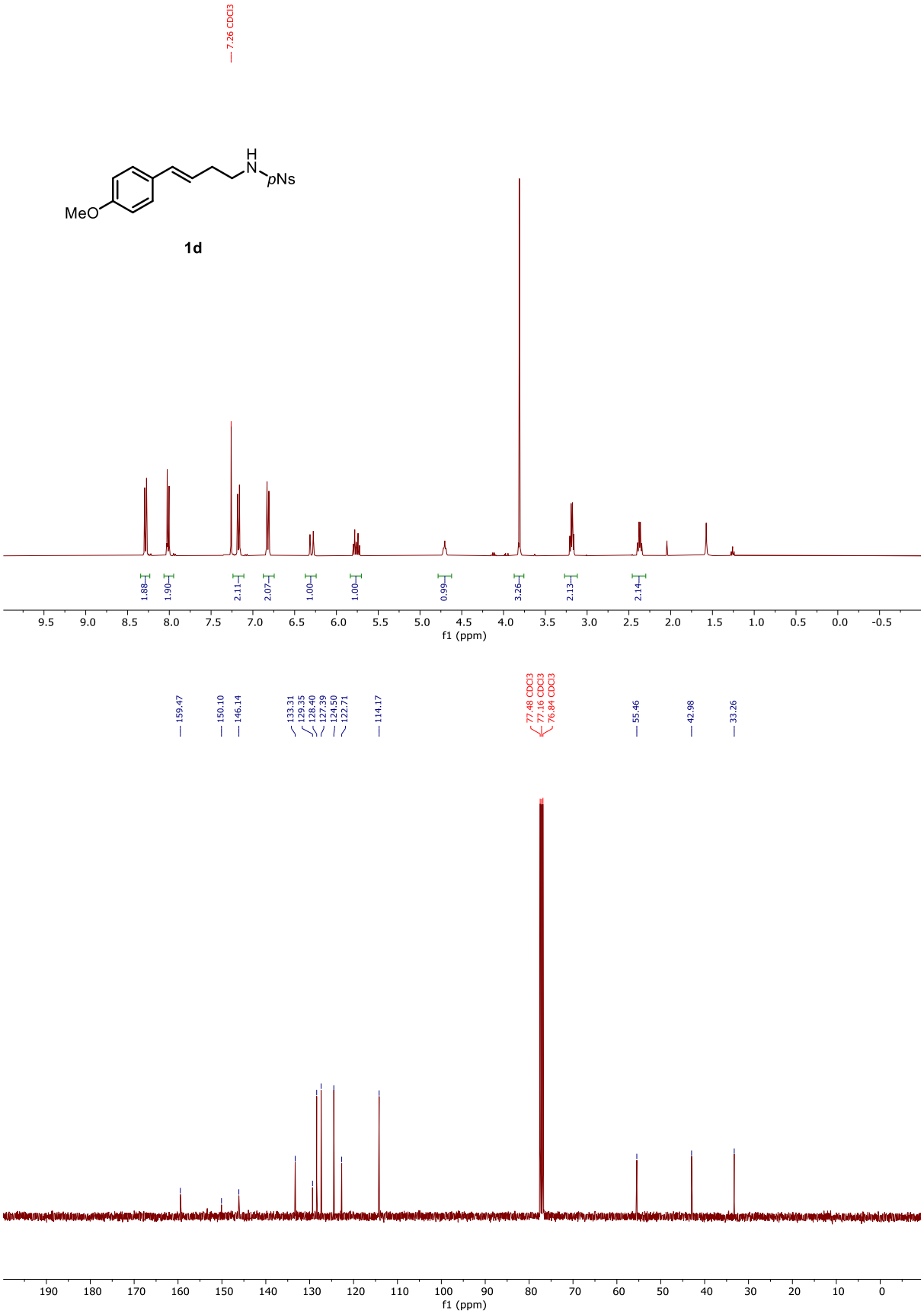


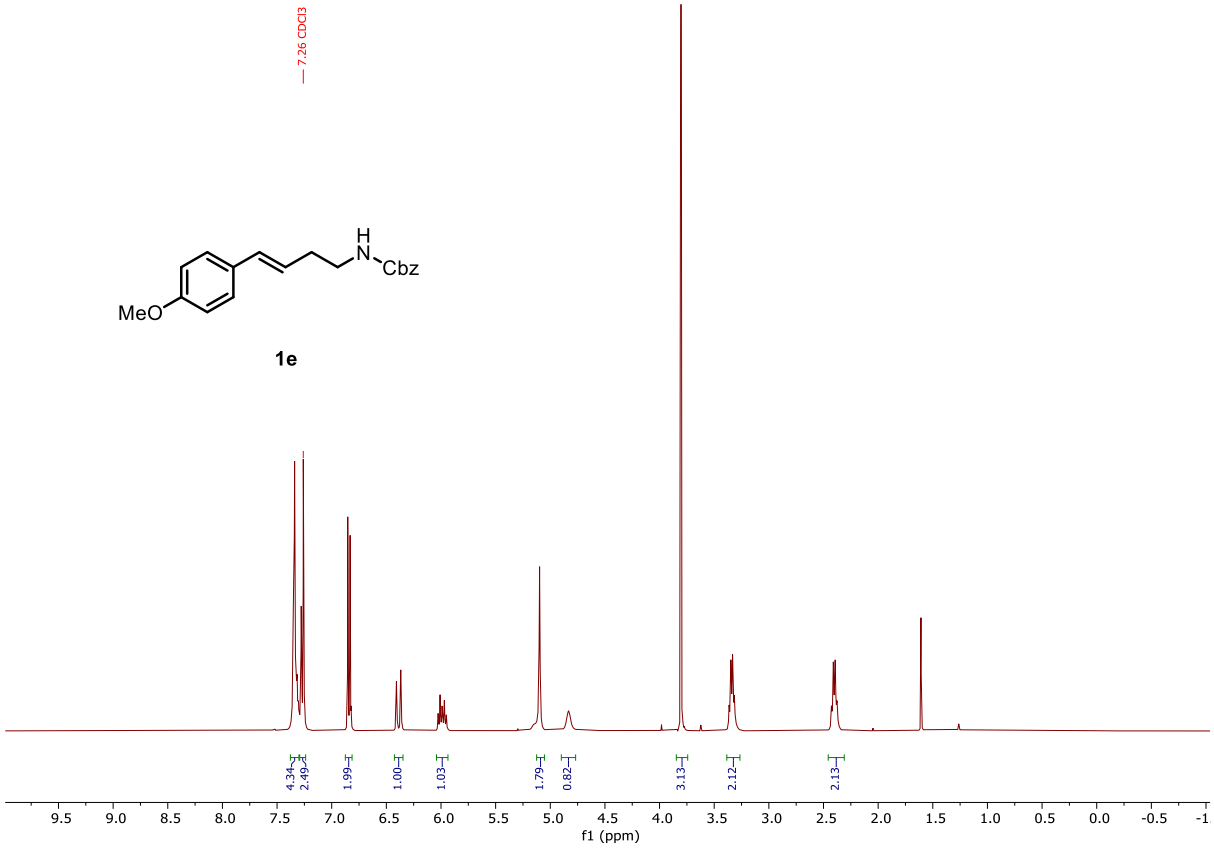
**(1c): (3*E*)-*N*-[4-(4-Methoxyphenyl)but-3-en-1-yl]-2-nitrobenzenesulfonamide**

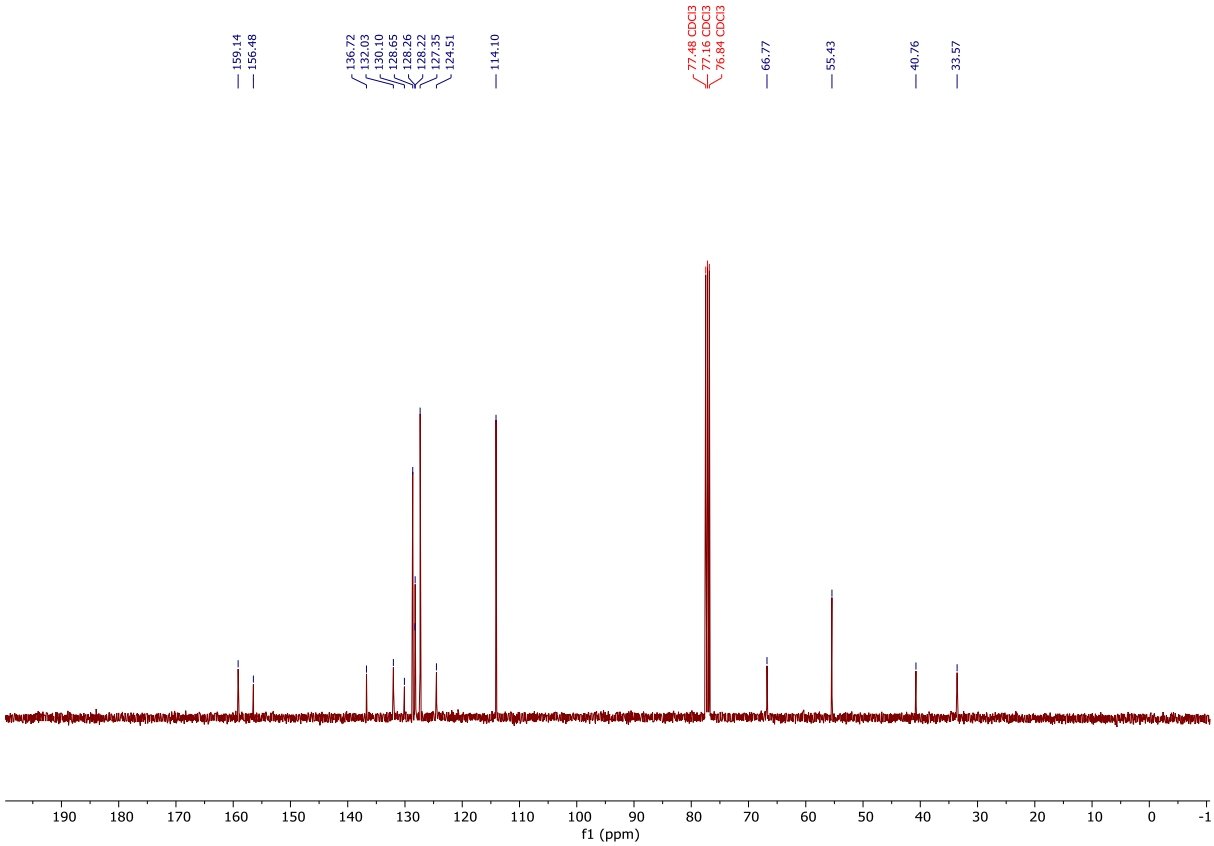


**(1d): (3*E*)-*N*-[4-(4-Methoxyphenyl)but-3-en-1-yl]-4-nitrobenzenesulfonamide**

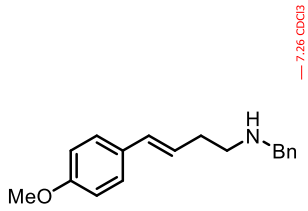


**(1e): Benzyl (*E*)-(4-(4-methoxyphenyl)but-3-en-1-yl)carbamate**

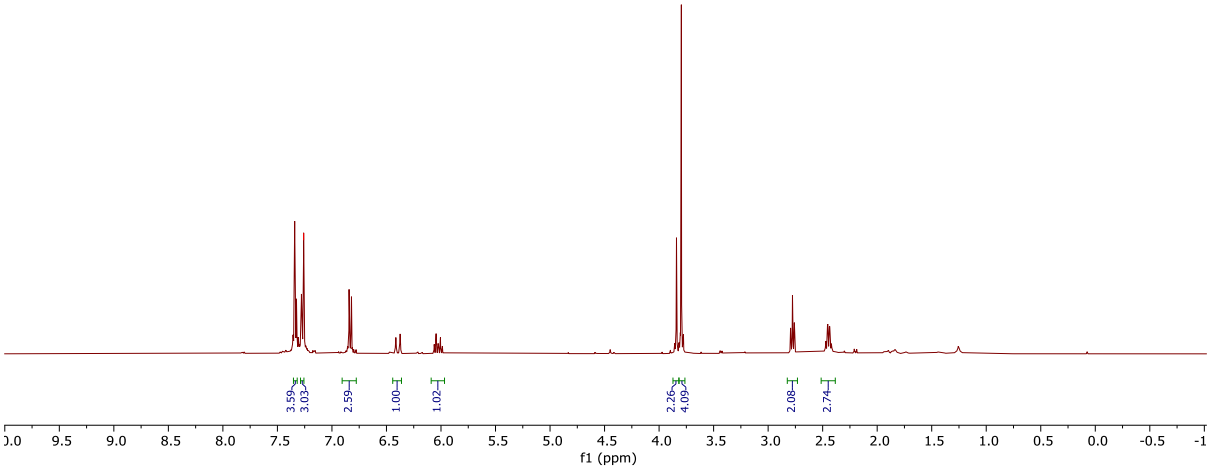


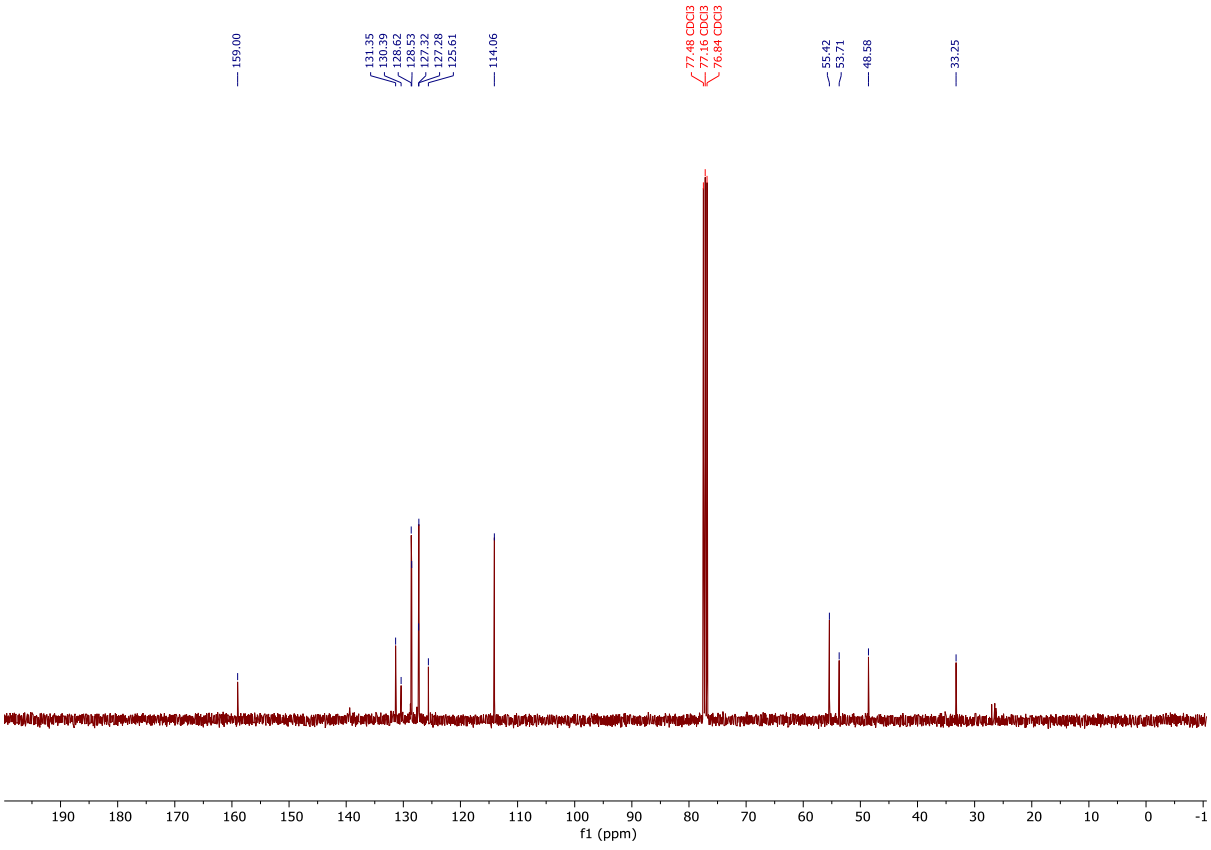



**(1f): (3*E*)-*N*-Benzyl-4-(4-methoxyphenyl)but-3-en-1-amine**

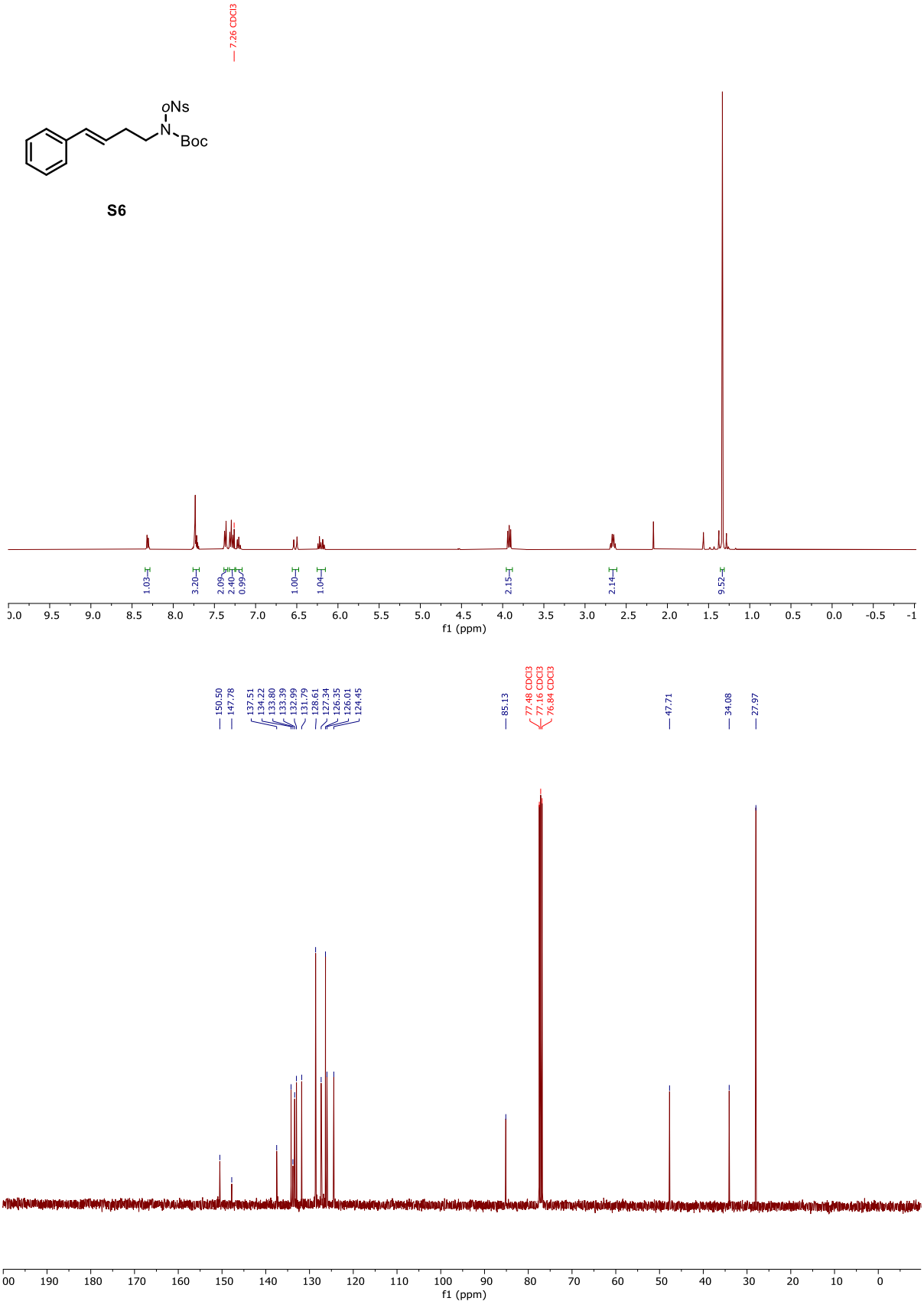



**1f**

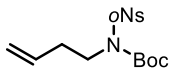


**(S6): *tert*-Butyl (3*E*)-[(2-nitrophenyl)sulfonyl](4-phenylbut-3-en-1-yl)carbamate**

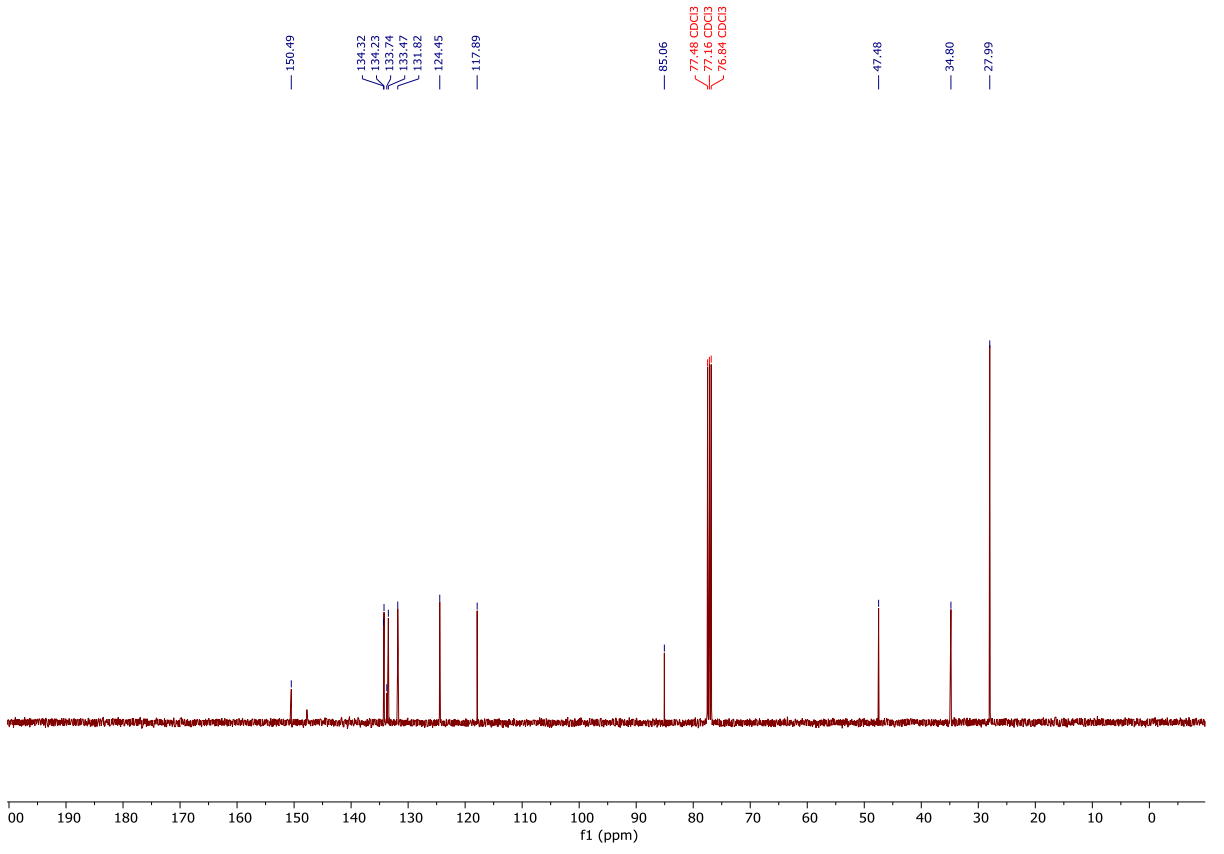


**(S7): *tert*-Butyl but-3-en-1-yl[(2-nitrophenyl)sulfonyl]carbamate**

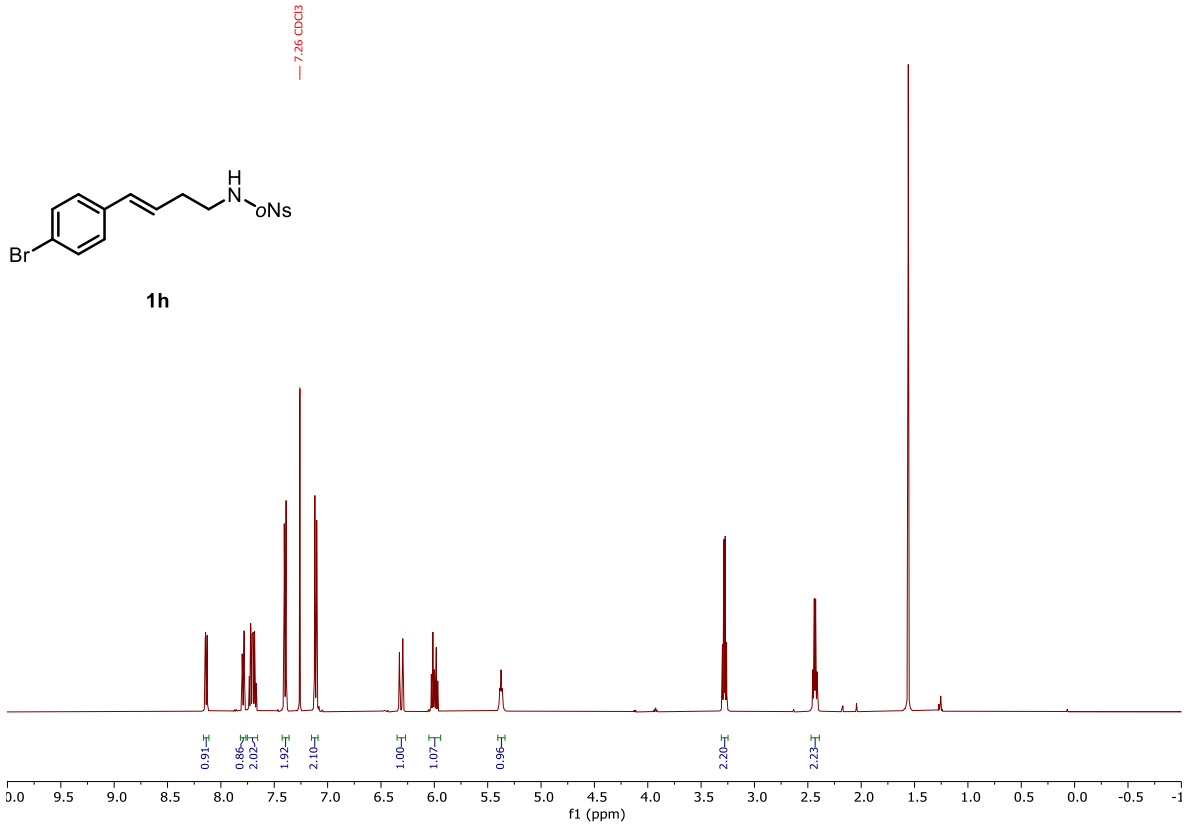


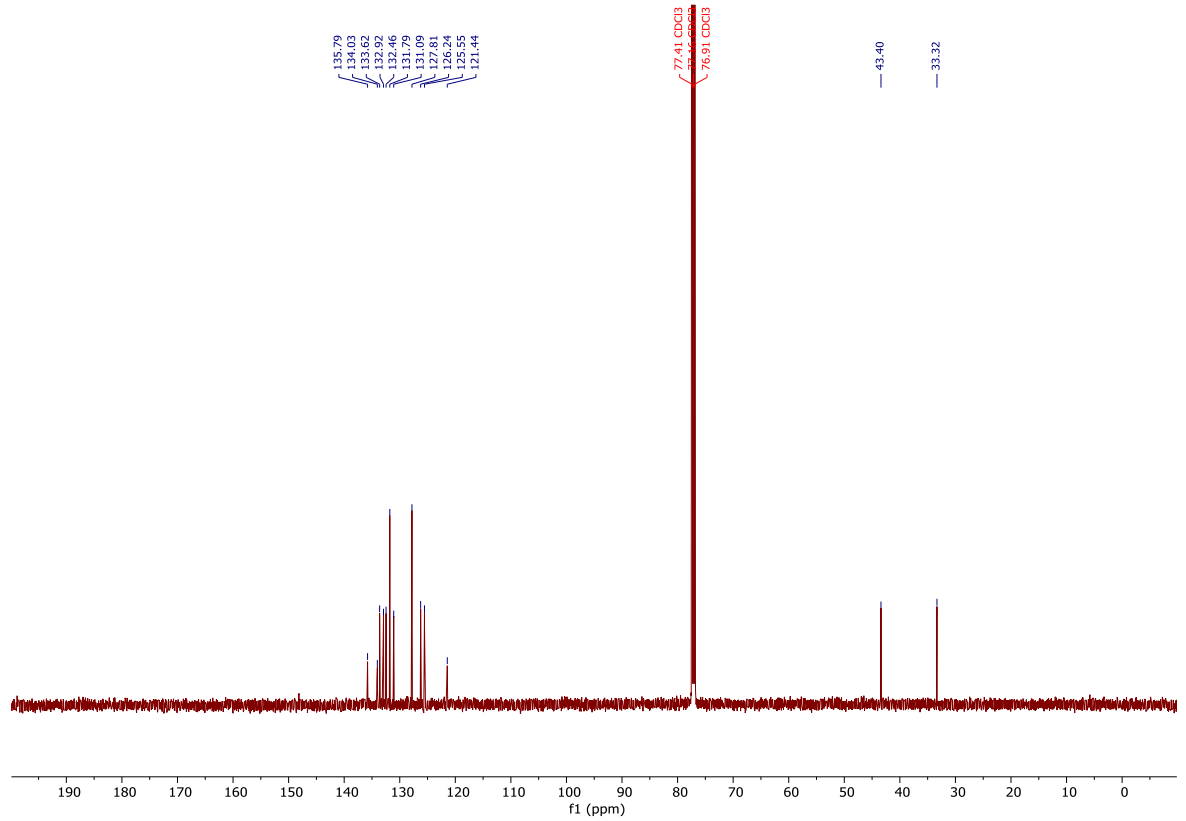

**S7**



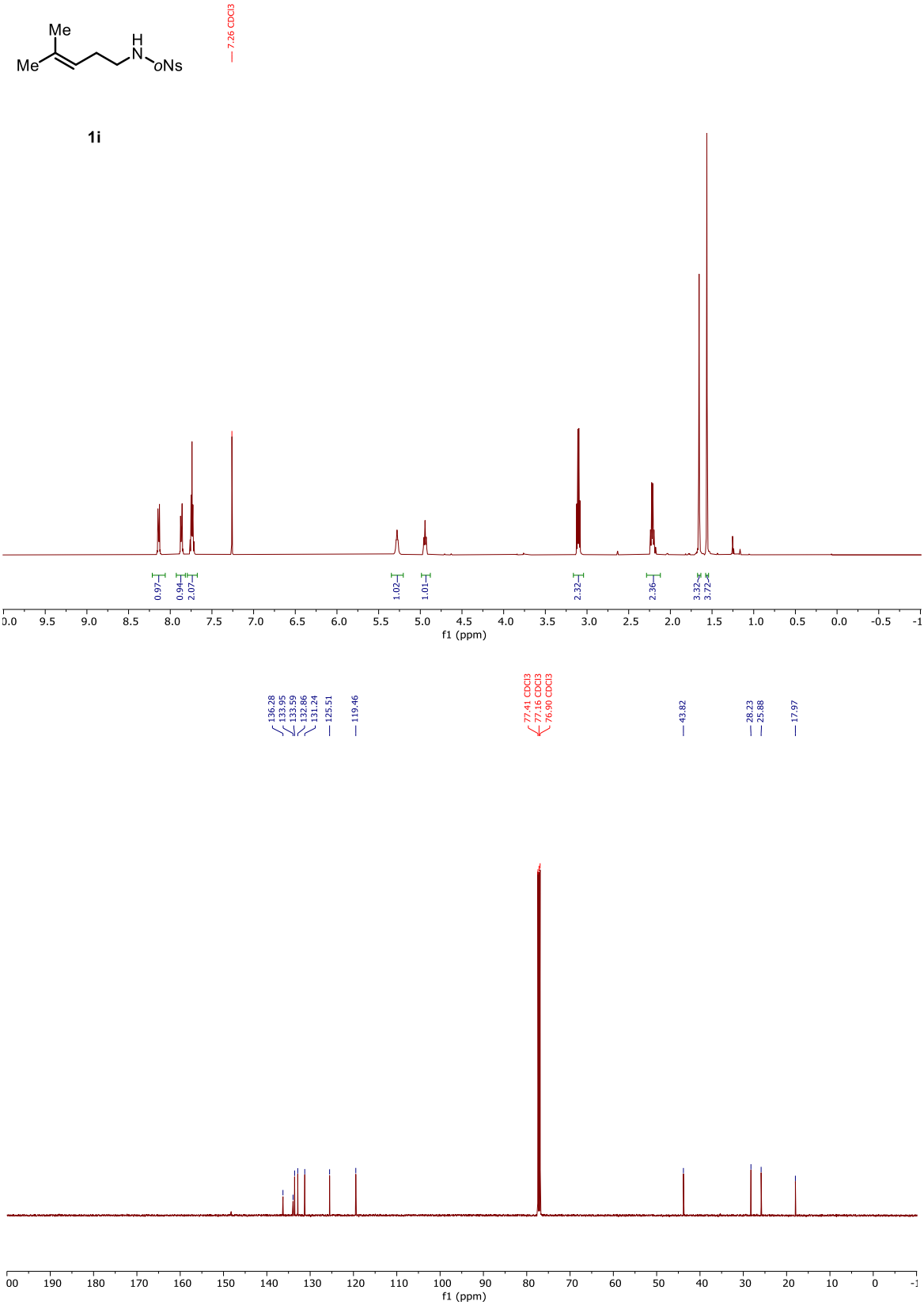



**(1h): (3*E*)-*N*-[4-(4-Bromophenyl)but-3-en-1-yl]-2-nitrobenzenesulfonamide**

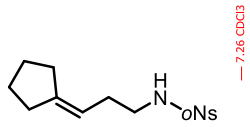


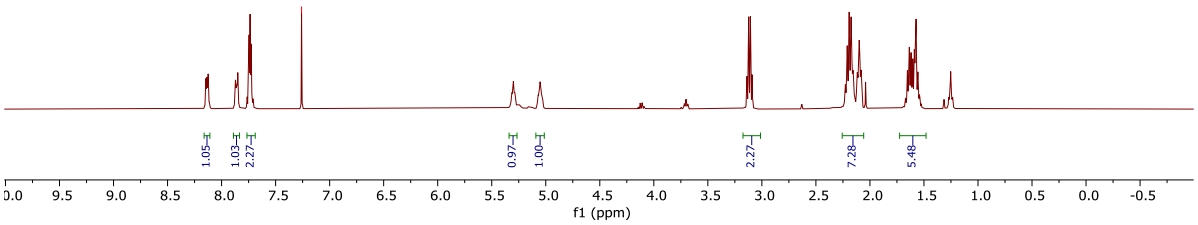
**(1i): *N*-(4-Methylpent-3-en-1-yl)-2-nitrobenzenesulfonamide**

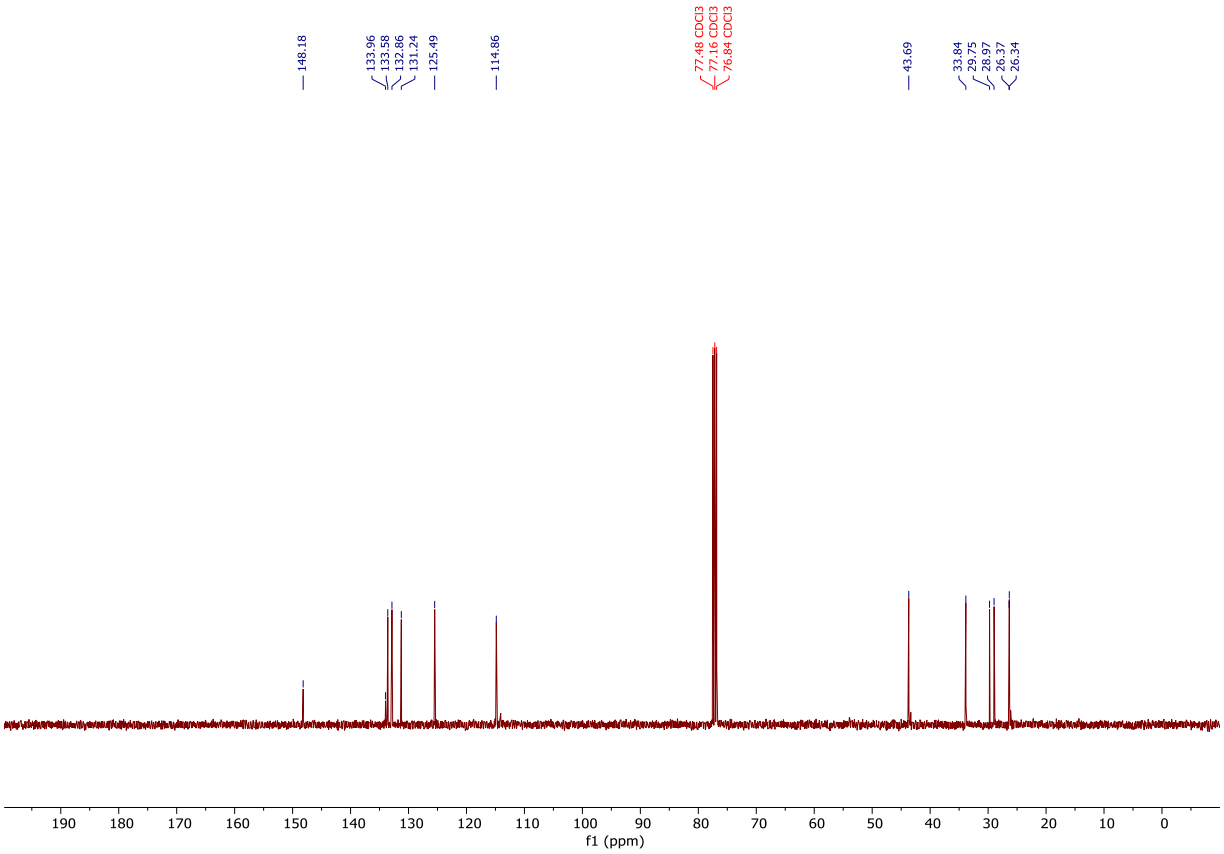


**(1j): *N*-(3-Cyclopentylidenepropyl)-2-nitrobenzenesulfonamide**

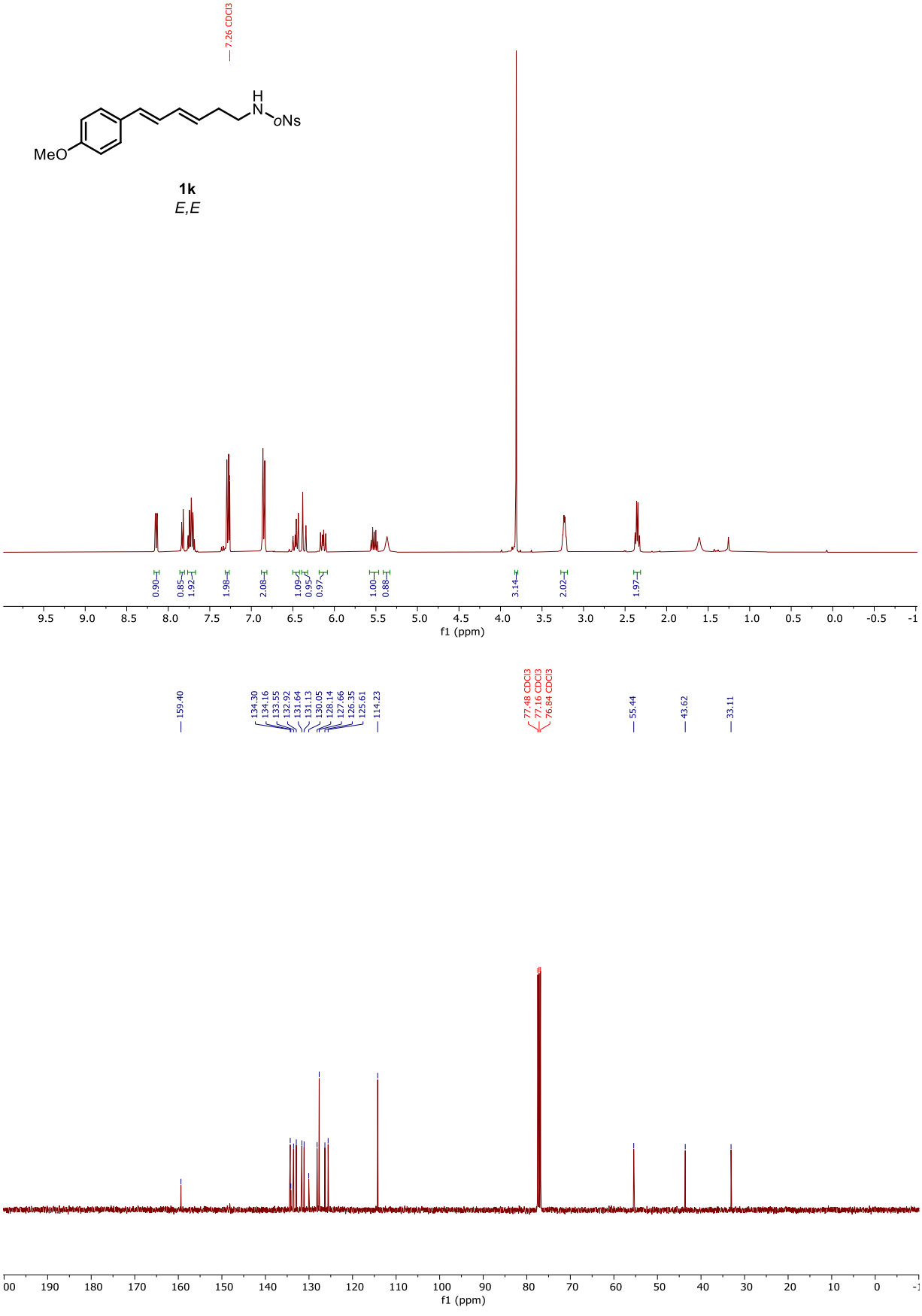



**1j**

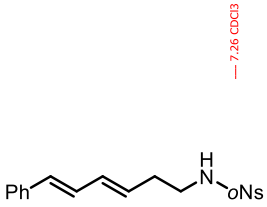


**(1k): *N*-[(3*E*,5*E*)-6-(4-Methoxyphenyl)hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide and *N*-[(3*E*,5*Z*)-6-(4-Methoxyphenyl)hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide**

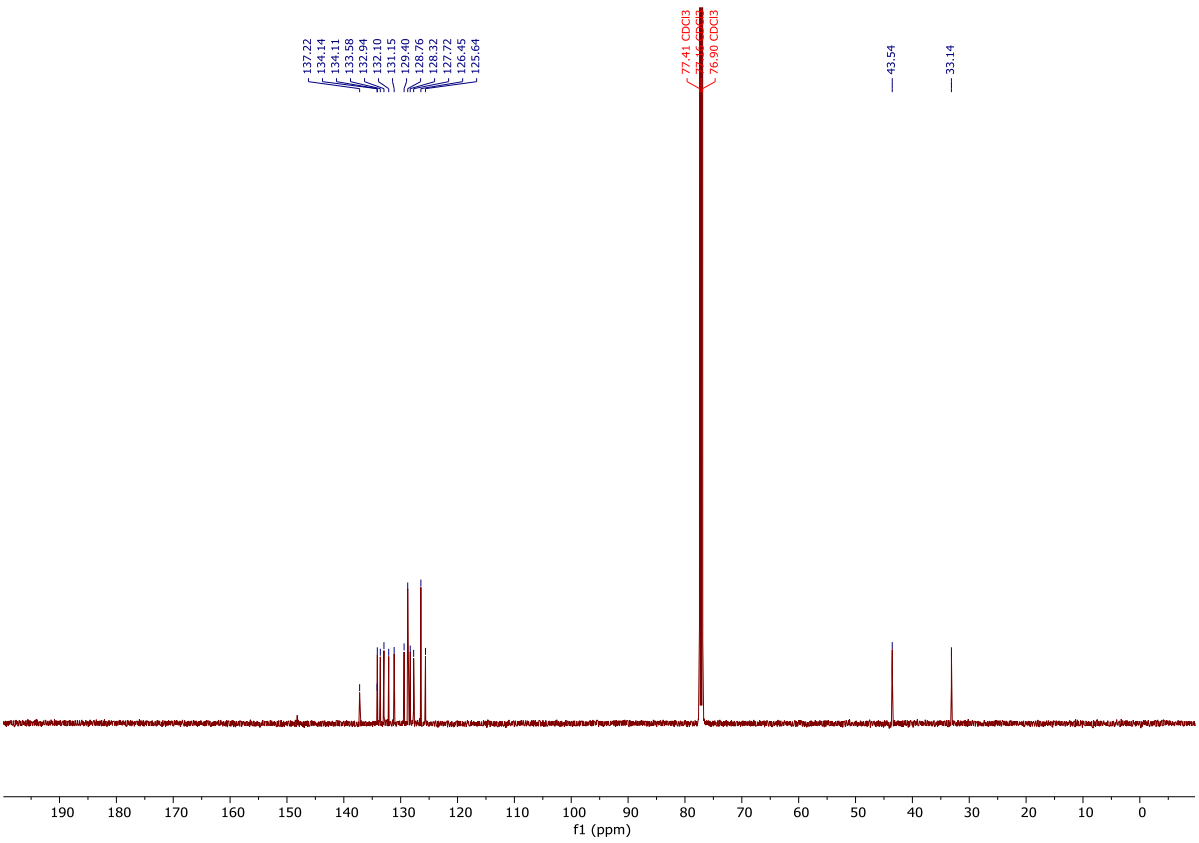


**(1l): *N*-[(3*E*,5*E*)-6-Phenyl-hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide and *N*-[(3*E*,5*Z*)-6-Phenyl-hexa-3,5-dien-1-yl]-2-nitrobenzenesulfonamide**

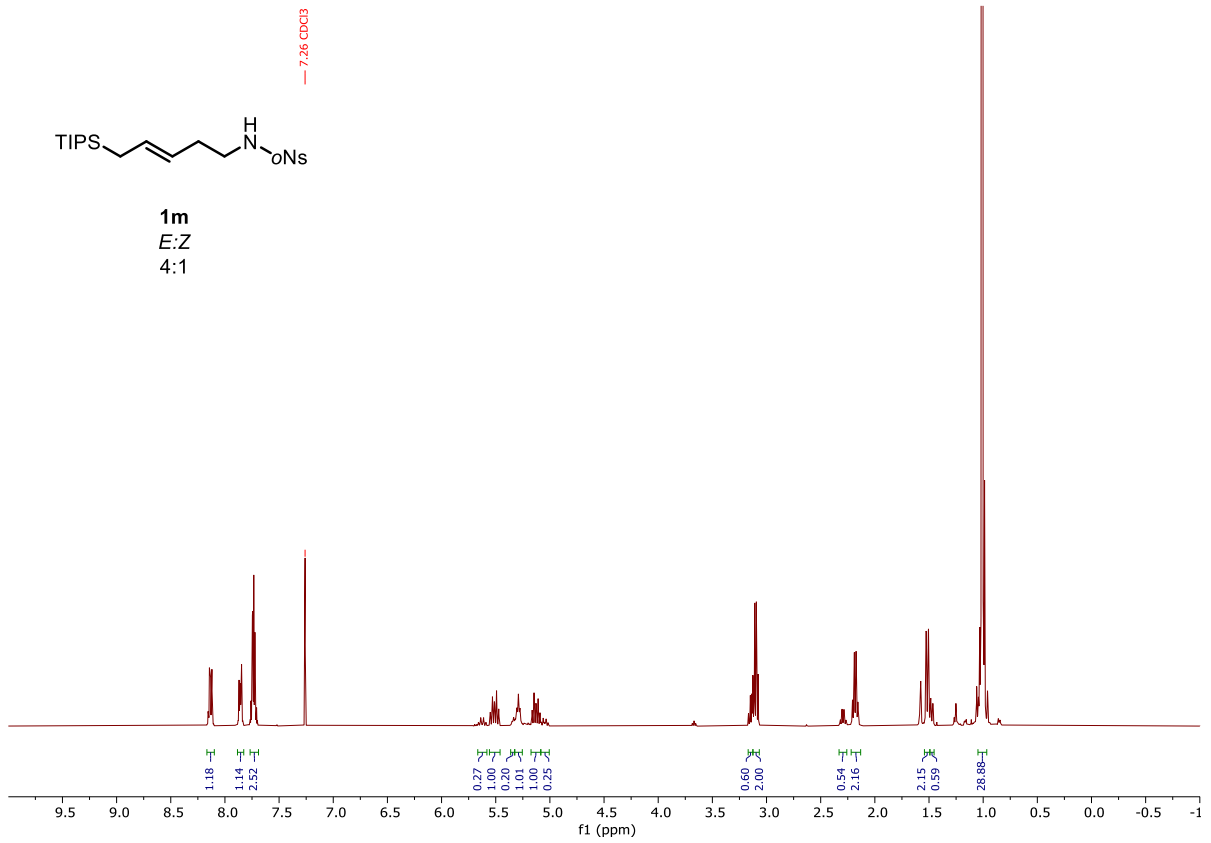


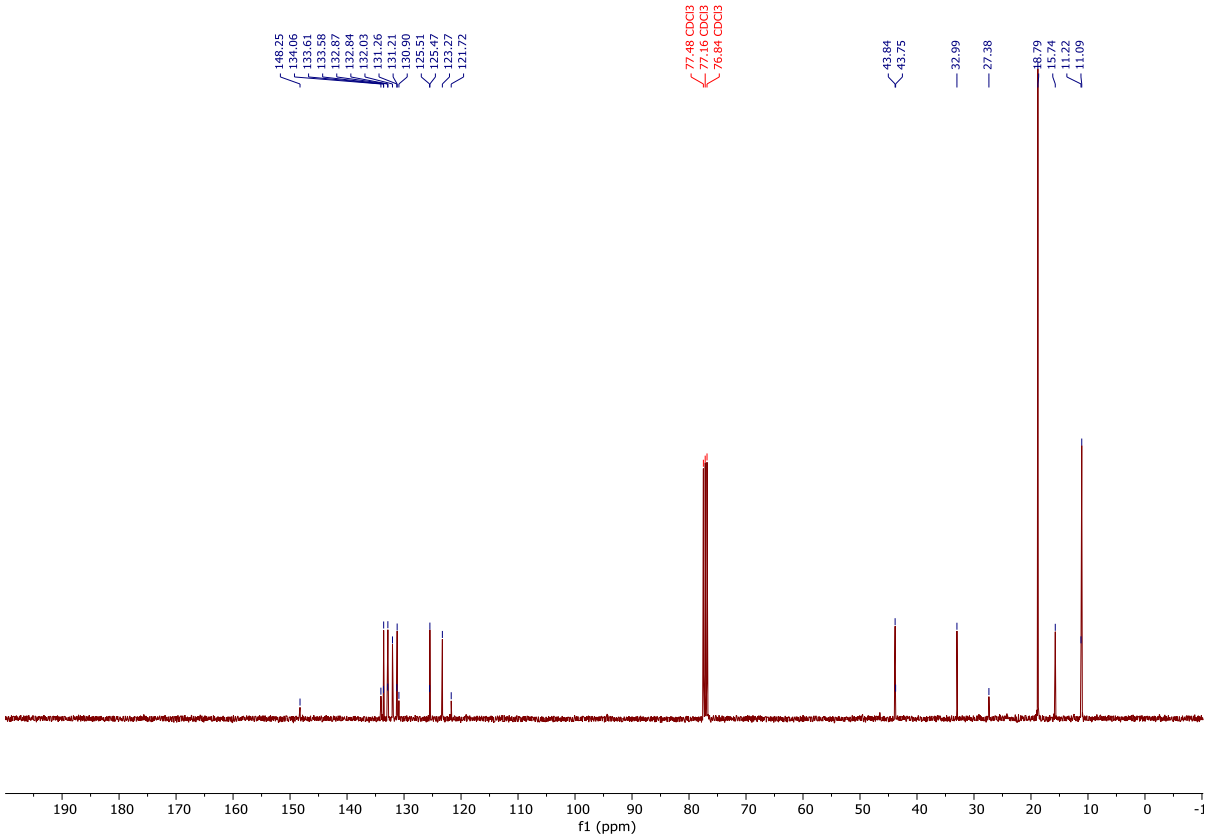

**1l**
*E,E*



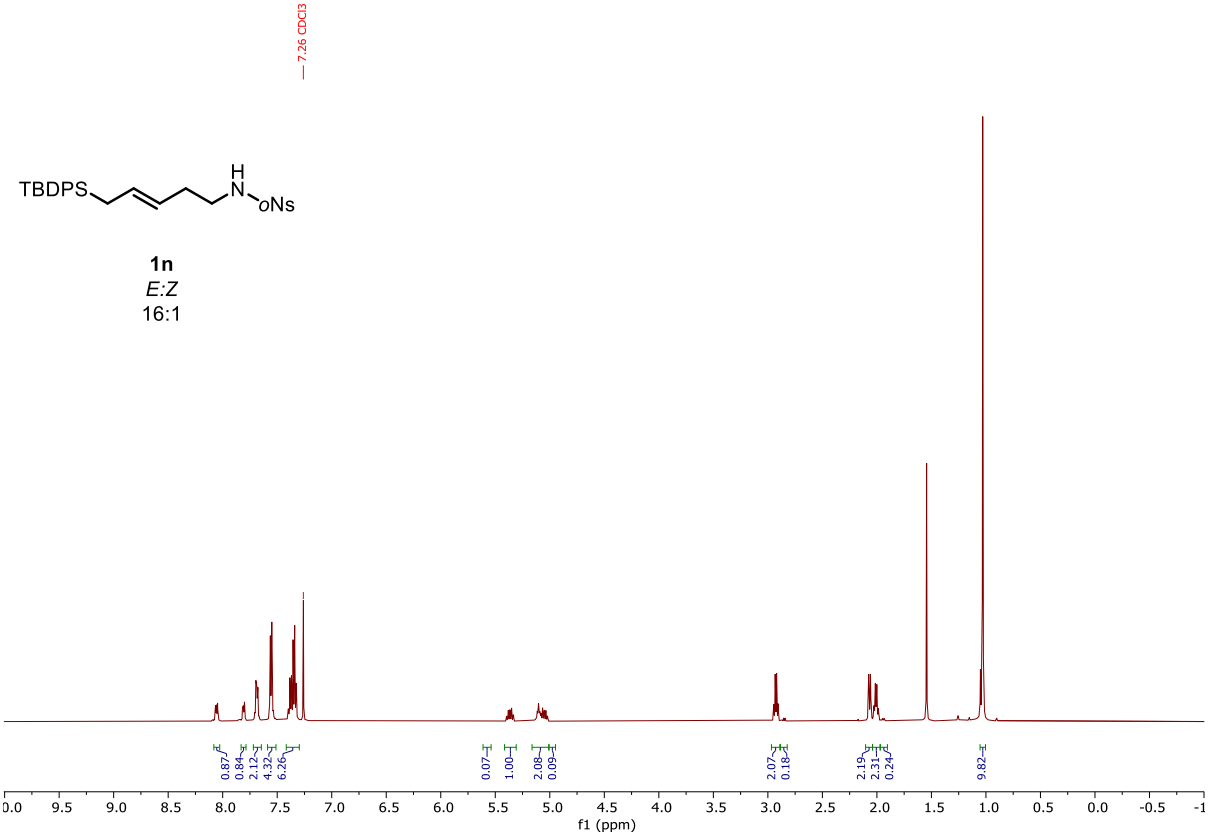



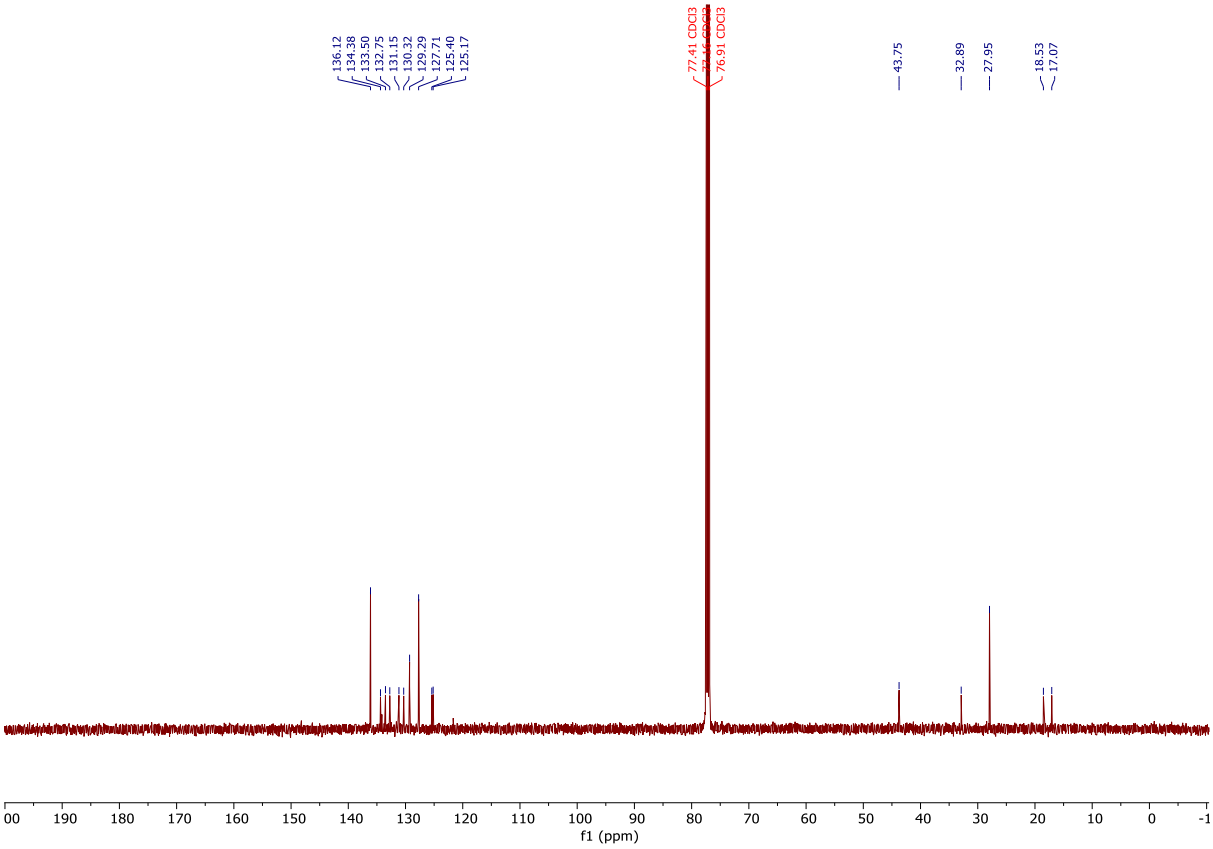
**(1m): (3*E*)-2-Nitro-*N*-[5-(triisopropylsilyl)pent-3-en-1-yl]benzenesulfonamide and (3*Z*)-2-Nitro-*N*-[5-(triisopropylsilyl)pent-3-en-1-yl]benzenesulfonamide**



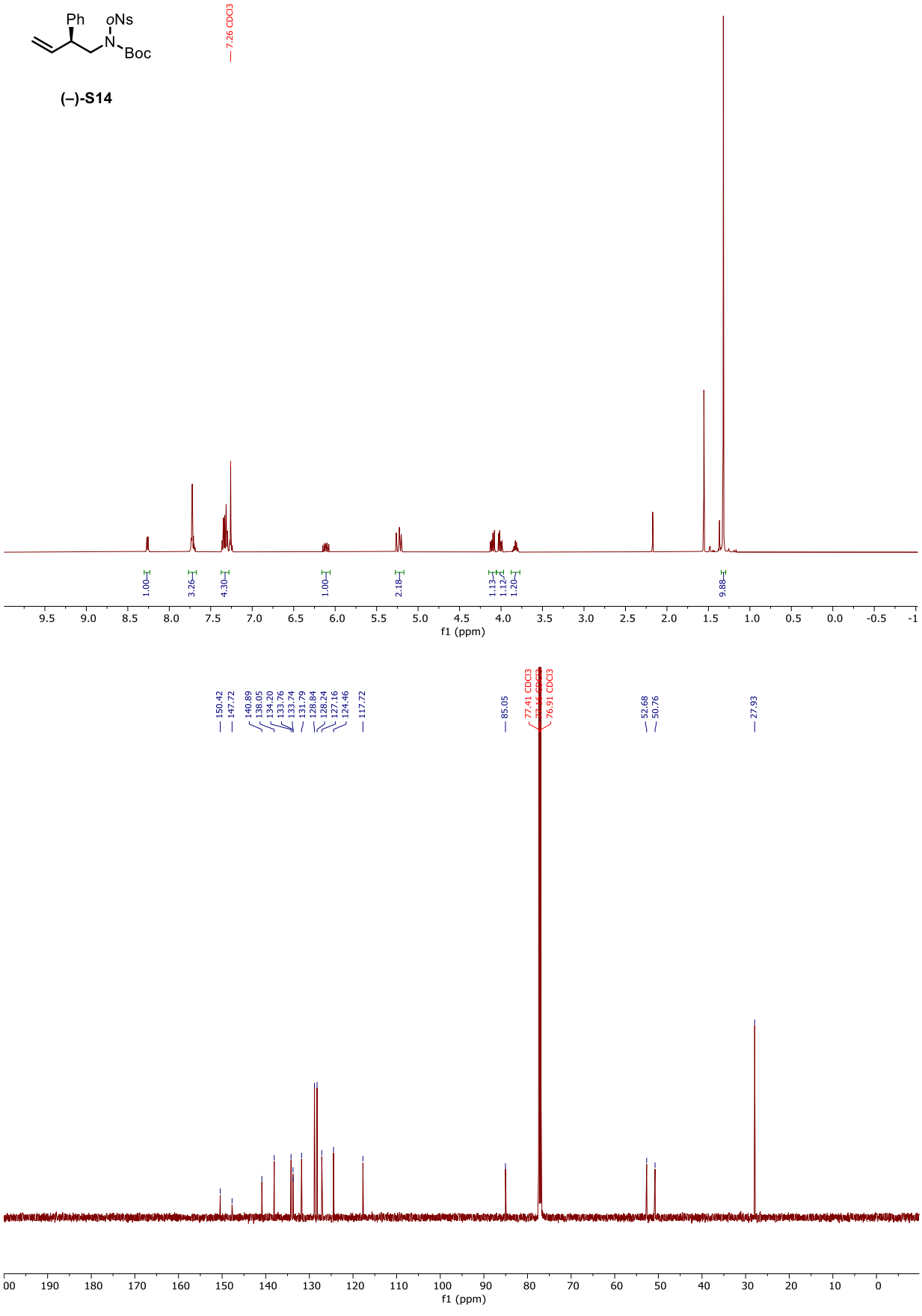



**(1n): (3*E*)-2-Nitro-*N*-[5-(*tert*-butyldiphenylsilyl)pent-3-en-1-yl]benzenesulfonamide and (3*Z*)-2-Nitro-*N*-[5-(*tert*-butyldiphenylsilyl)pent-3-en-1-yl]benzenesulfonamide**

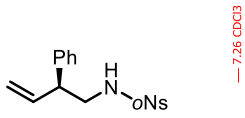


**((–)-S14): (–)-*tert*-Butyl (2*S*)-[(2-nitrophenyl)sulfonyl](2-phenylbut-3-en-1-yl)carbamate**

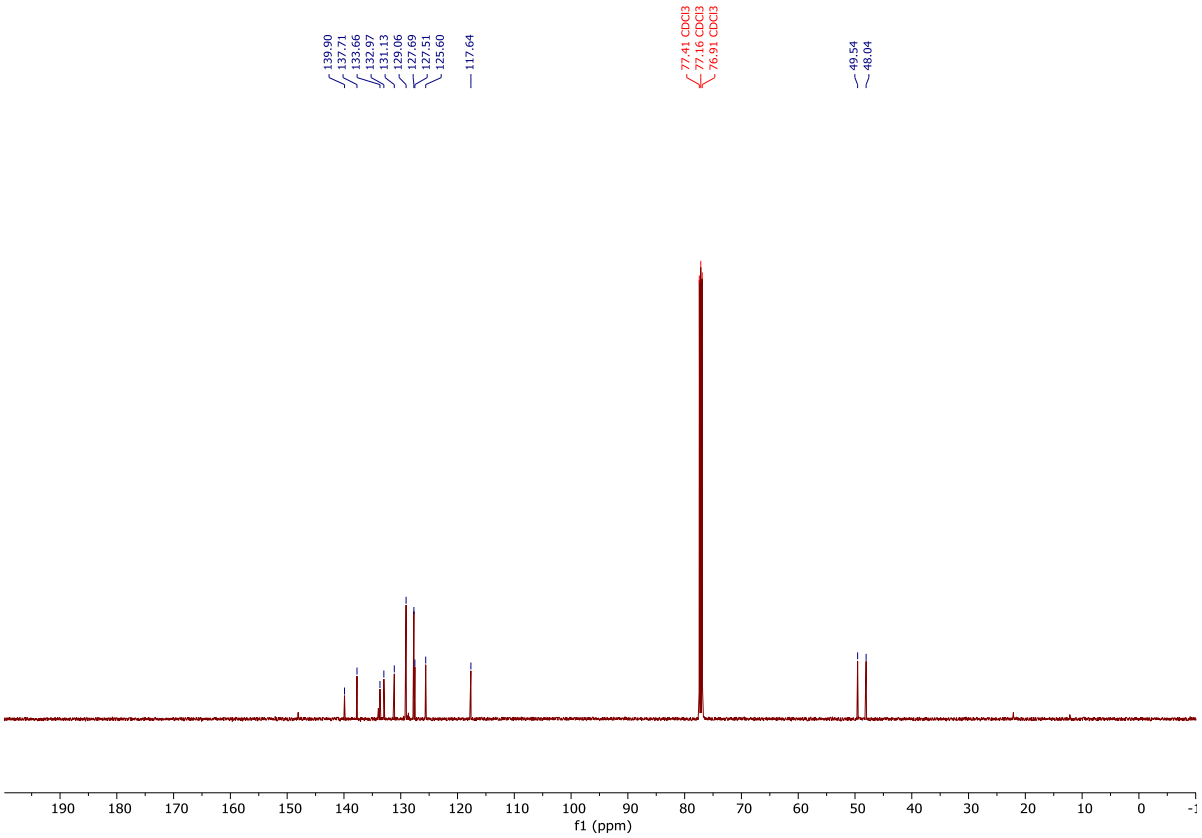


**((+)-S15): (+)-(2*S*)-2-Nitro-*N*-(2-phenylbut-3-en-1-yl)benzenesulfonamide**

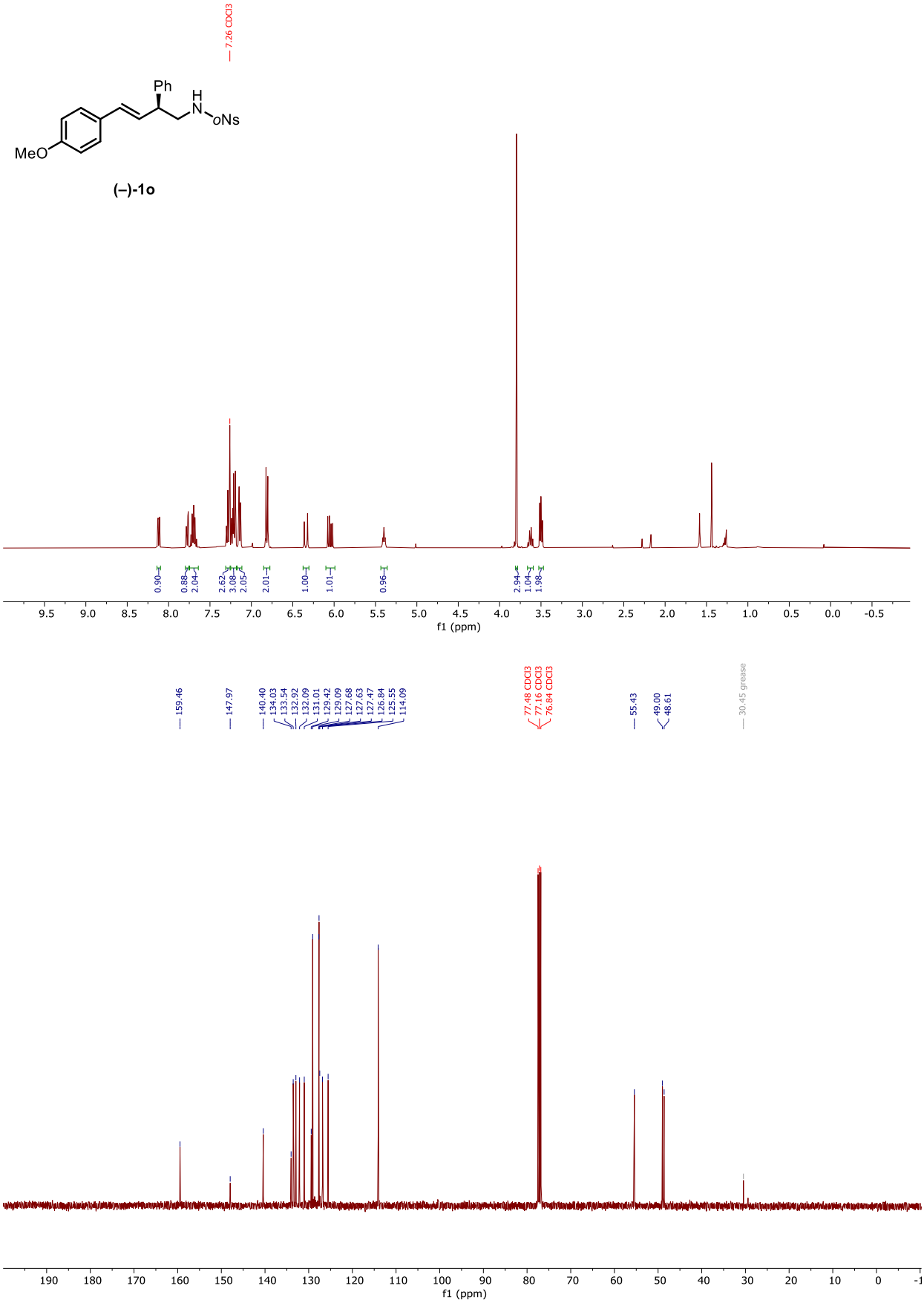



**(+)-S15**

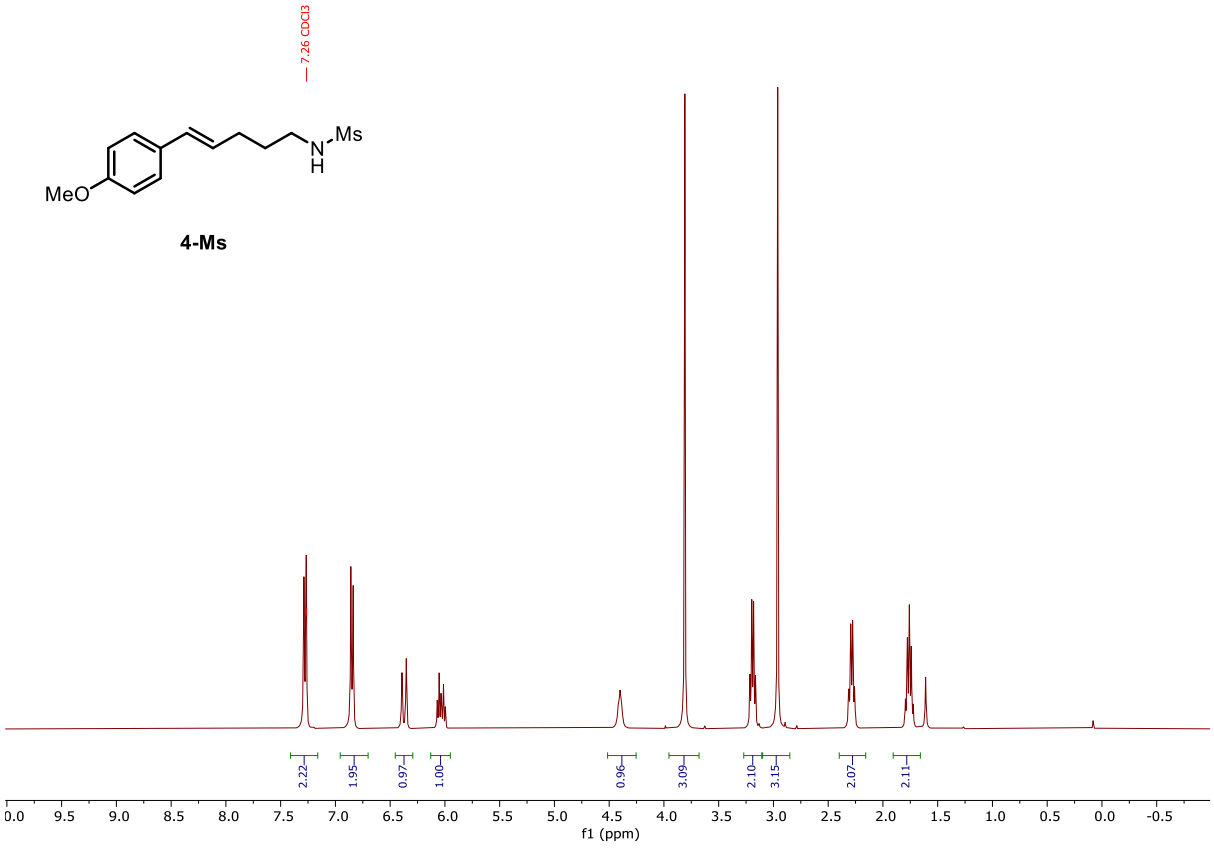


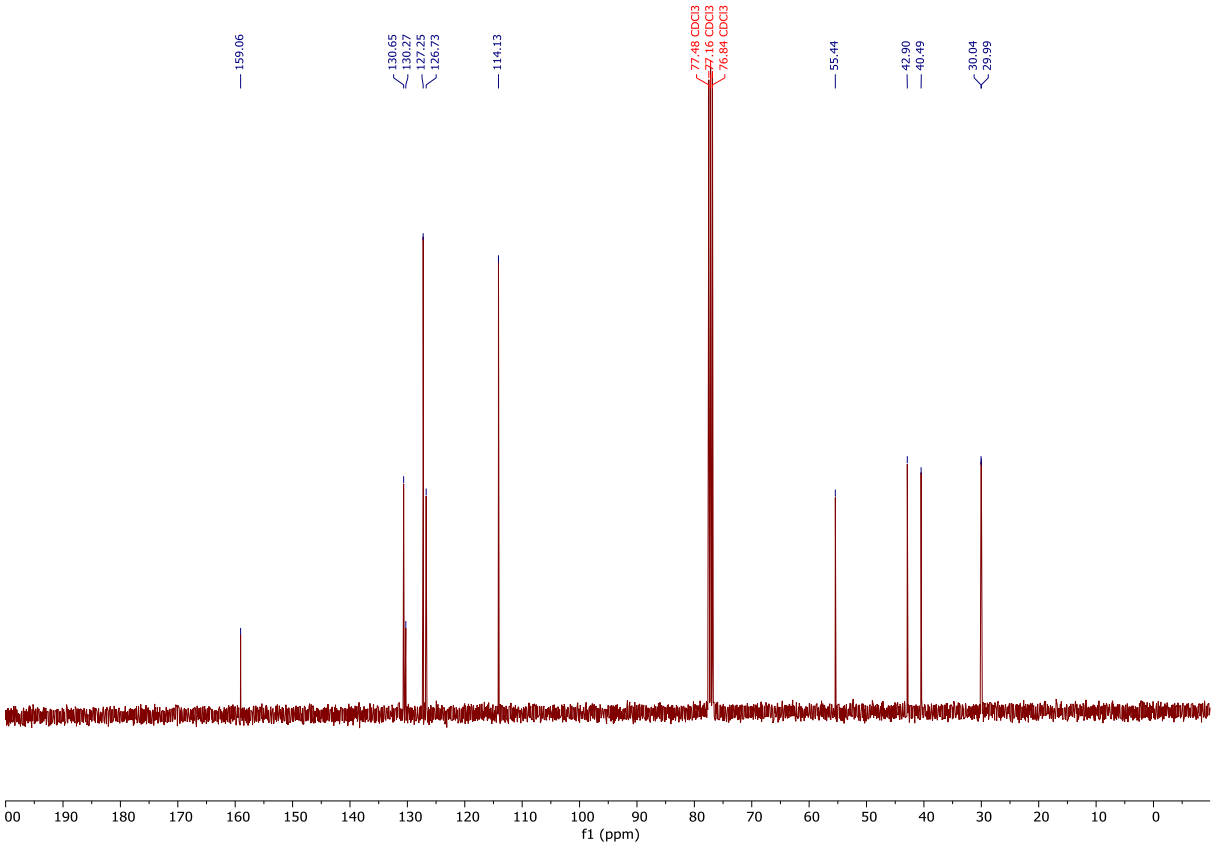



**((–)-1o): (–)-(2*S*,3*E*)-*N*-[4-(4-Methoxyphenyl)-2-phenylbut-3-en-1-yl]-2-nitrobenzenesulfonamide**

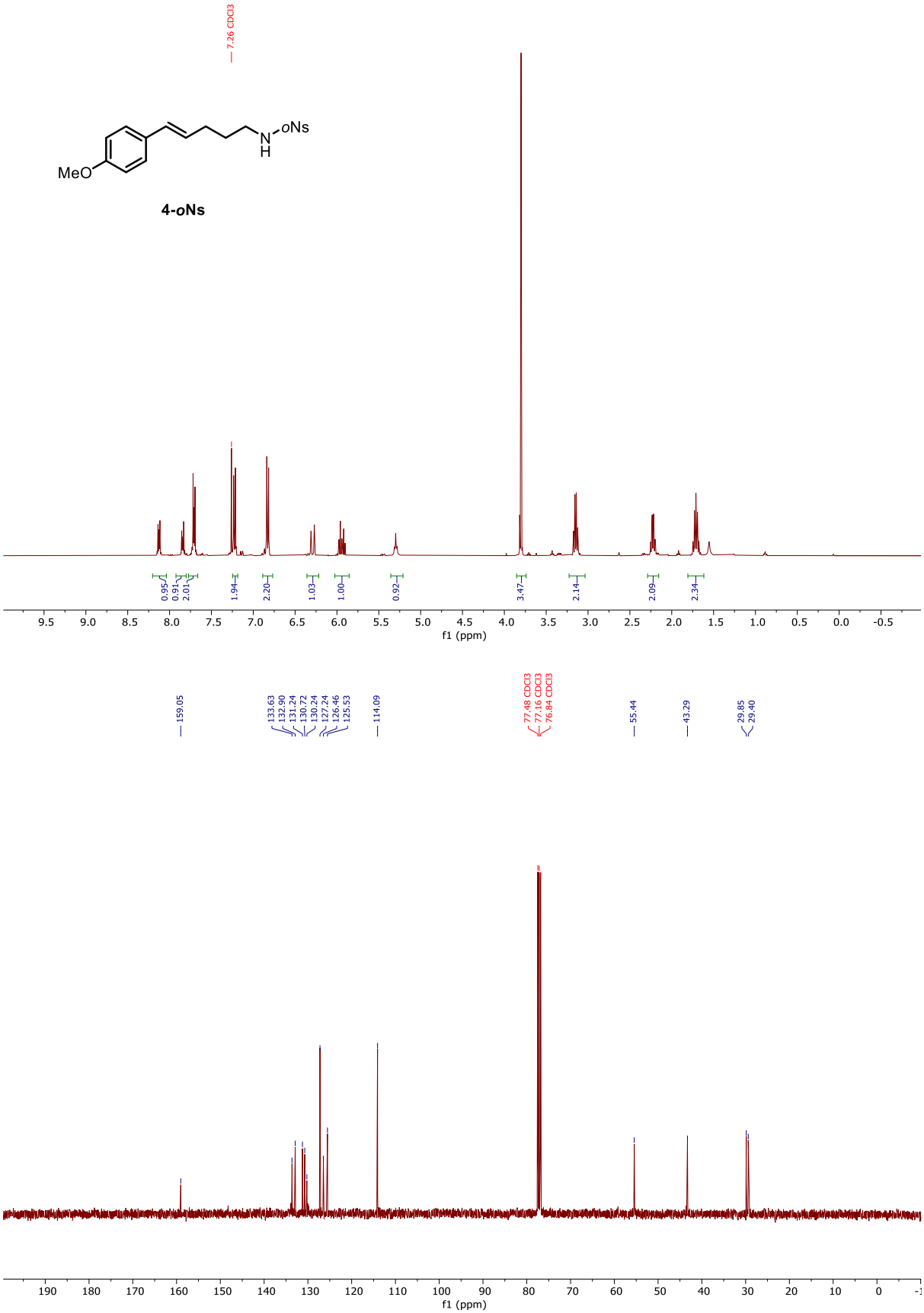


**(4-Ms): (*E*)-*N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)methanesulfonamide**

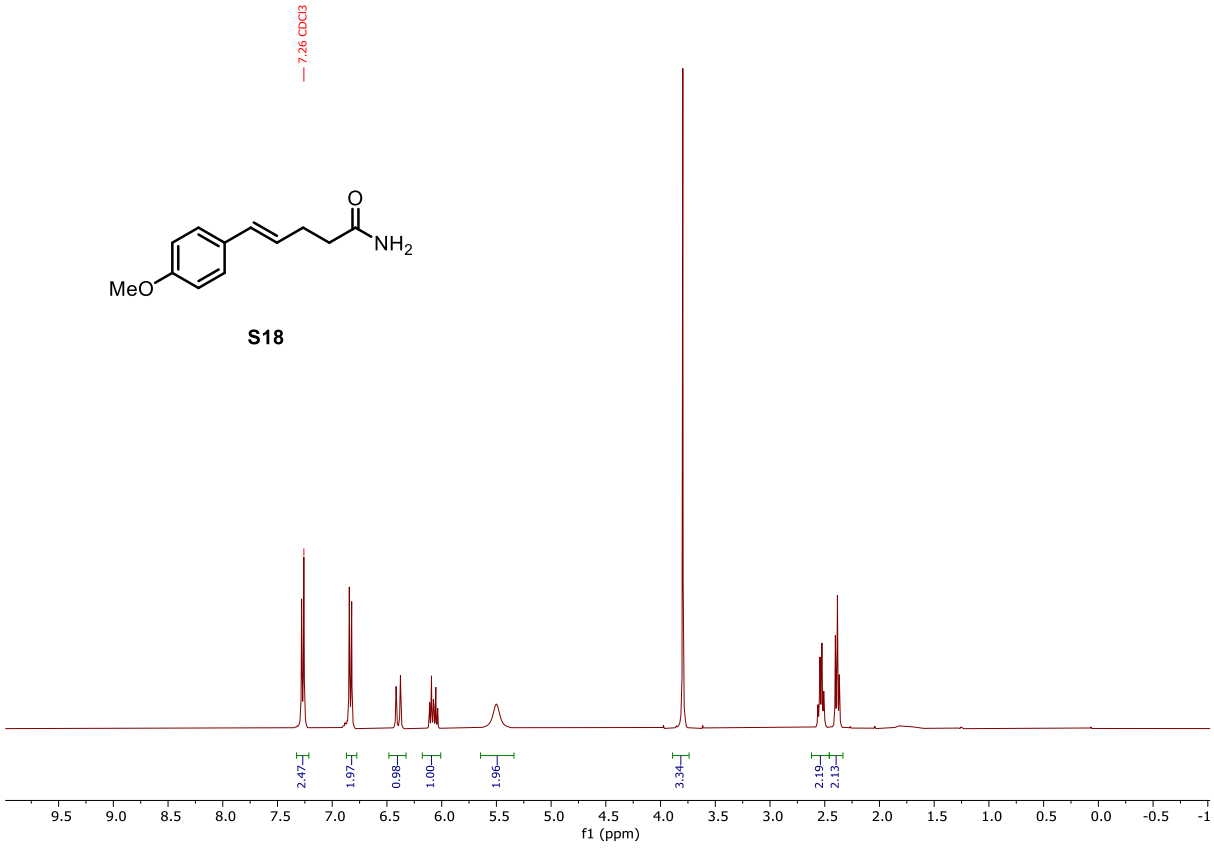


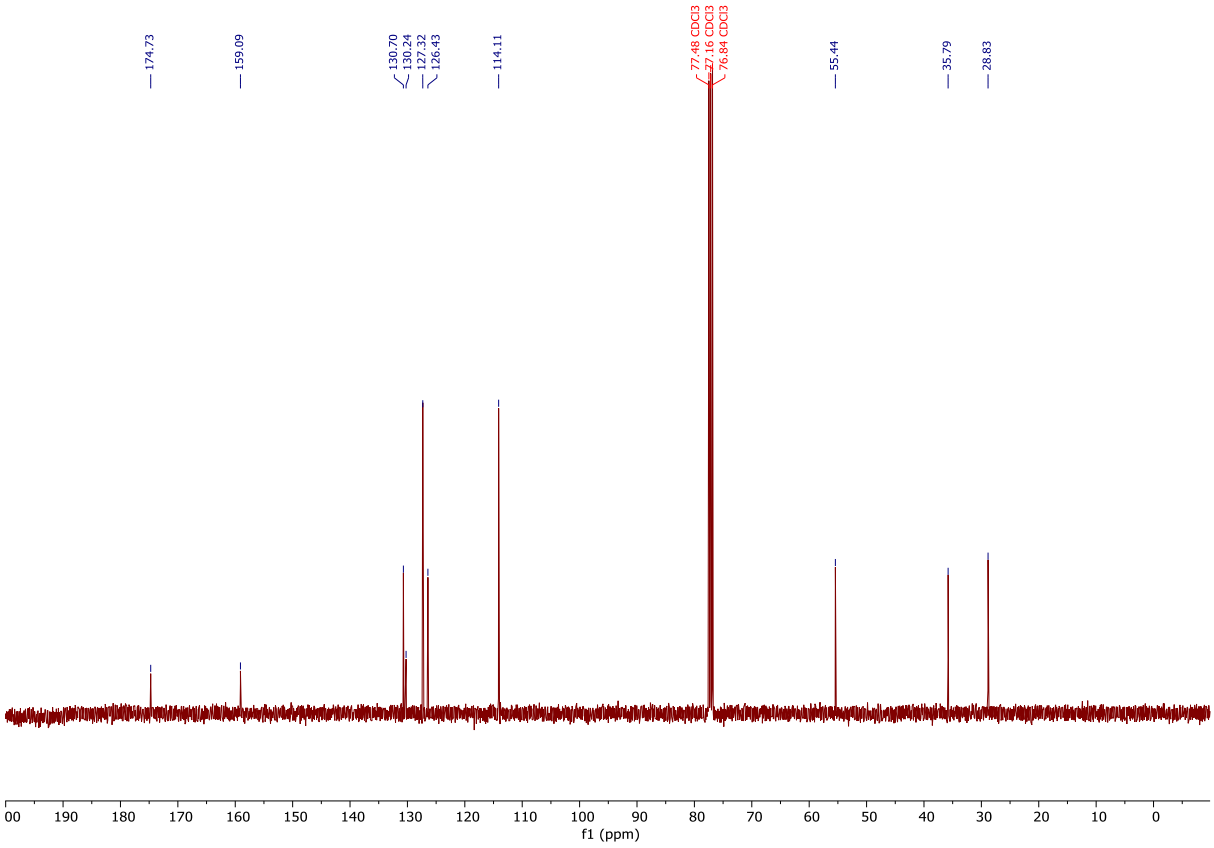



**(4-*o*Ns): (*E*)-*N*-(5-(4-Methoxyphenyl)pent-4-en-1-yl)-2-nitrobenzenesulfonamide**

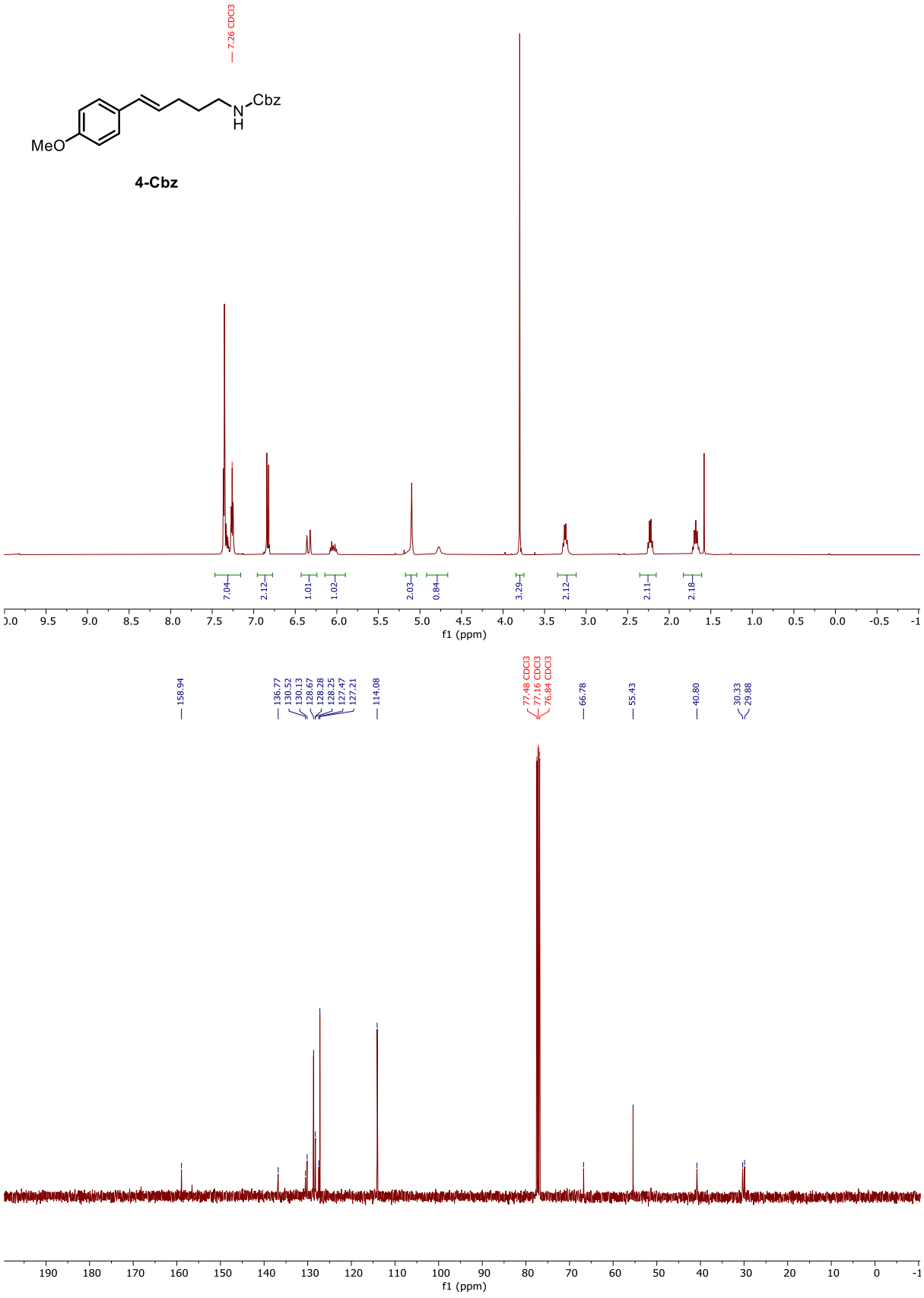


**(S18): (*E*)-5-(4-Methoxyphenyl)pent-4-enamide**

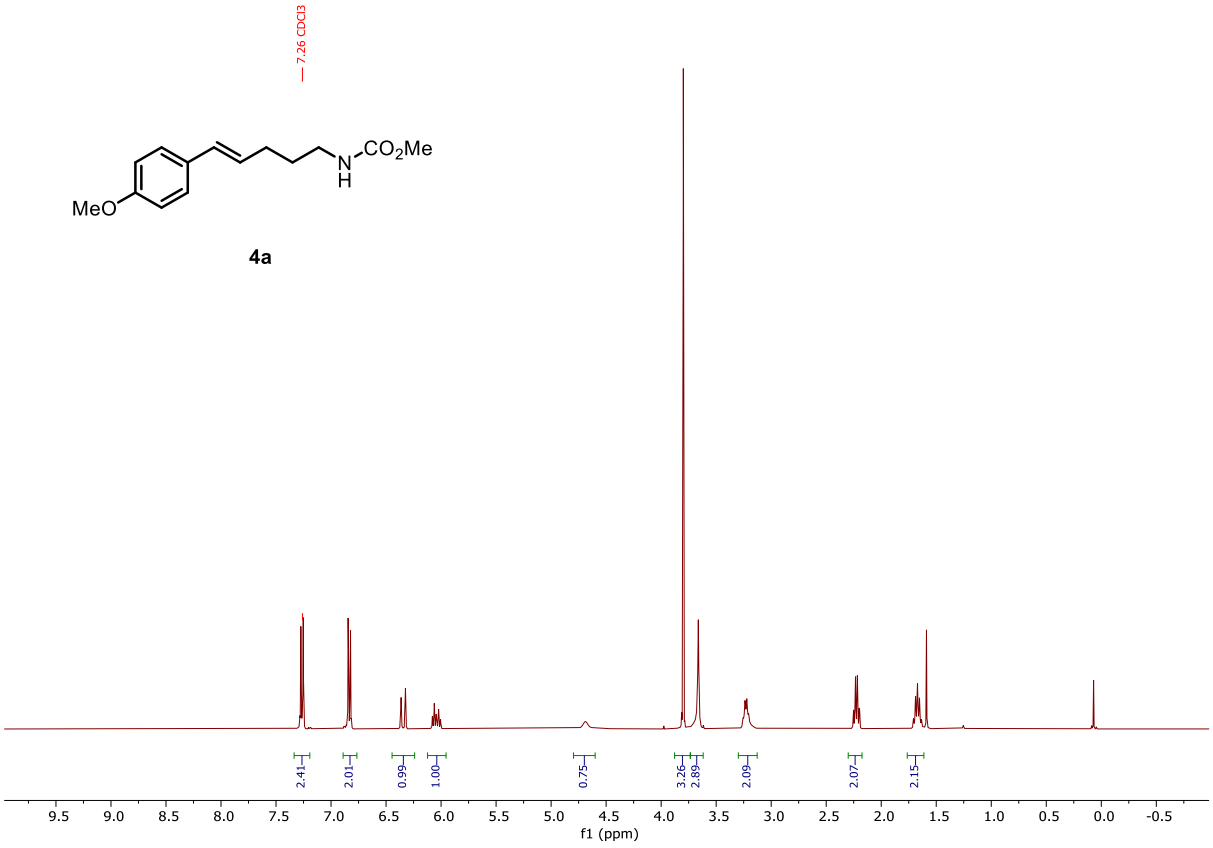


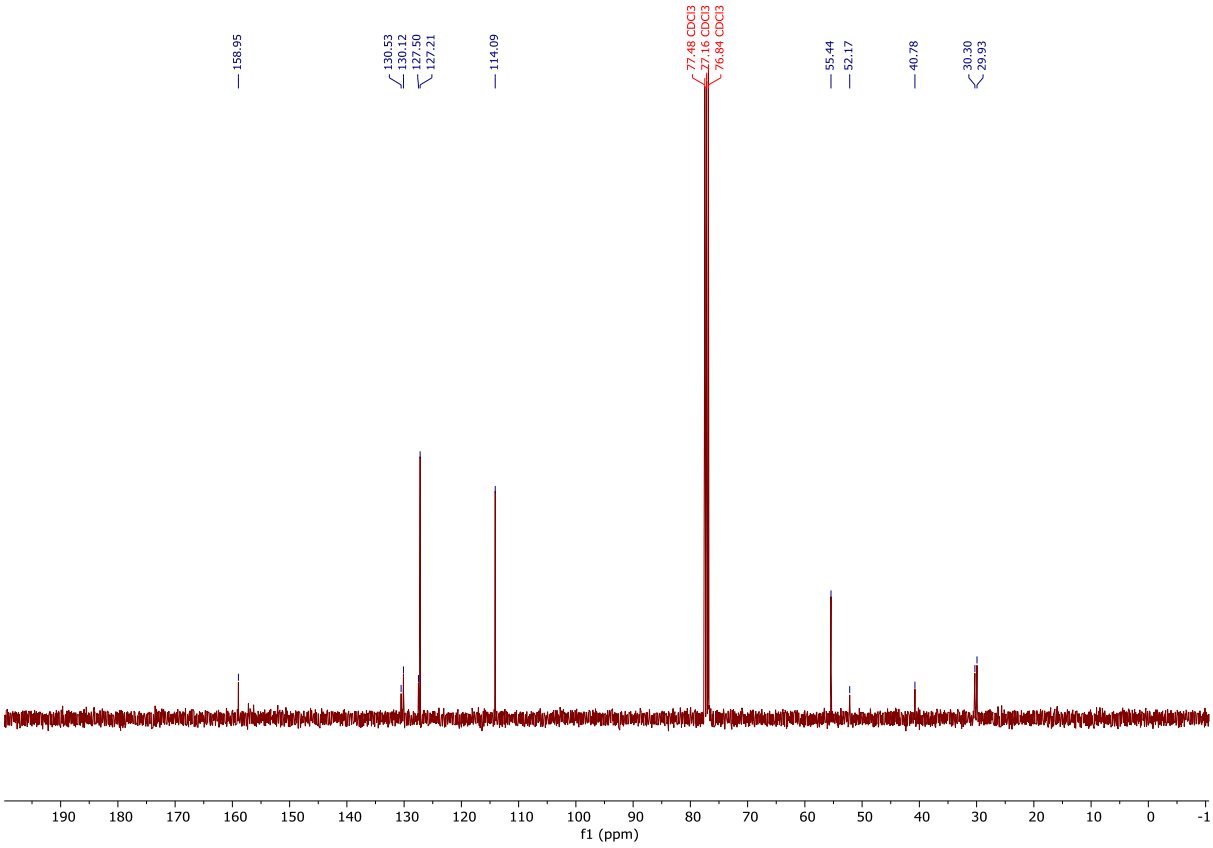
**(4-Cbz): Benzyl (*E*)-(5-(4-methoxyphenyl)pent-4-en-1-yl)carbamate**



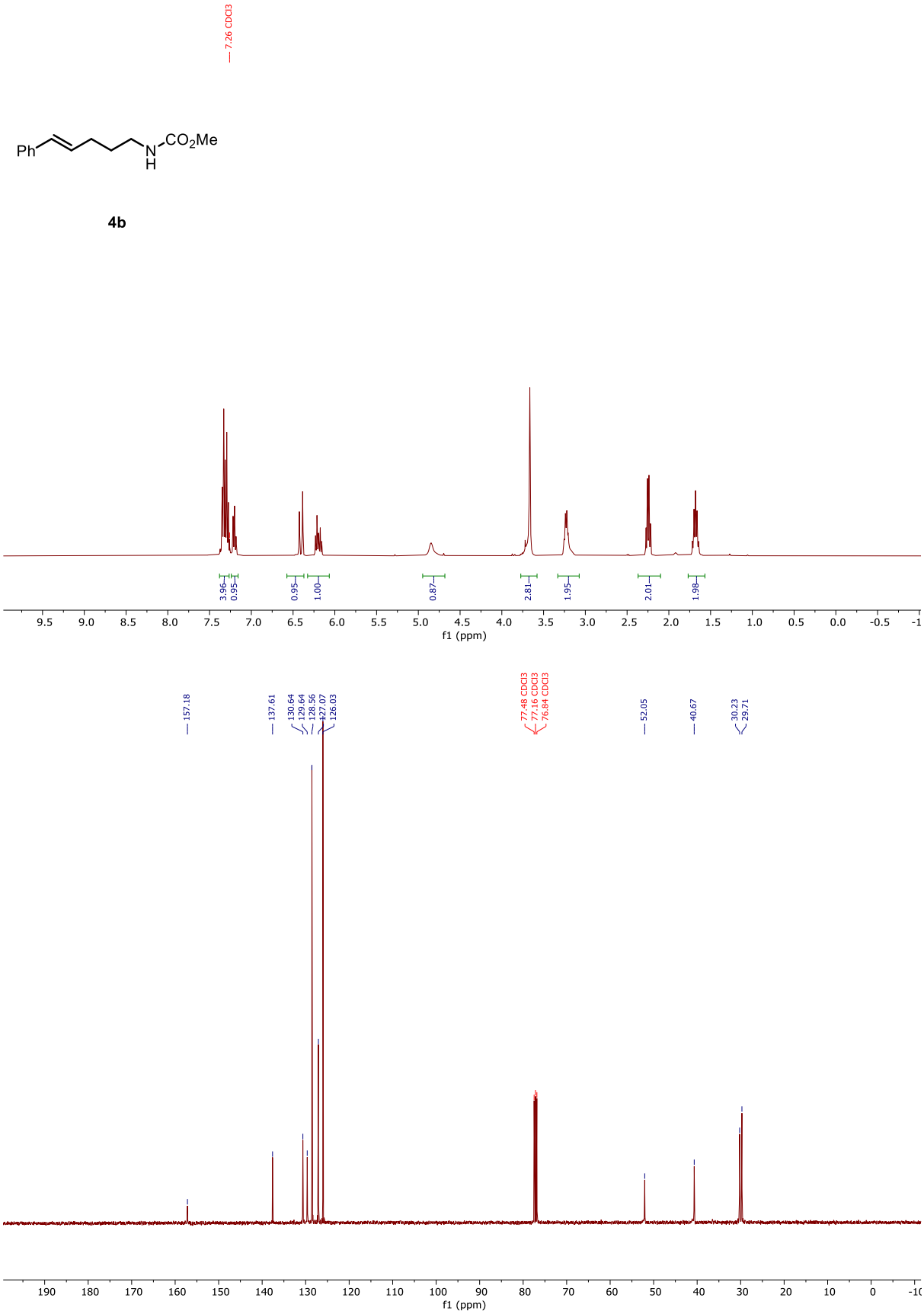
**(4a): Methyl (*E*)-(5-(4-methoxyphenyl)pent-4-en-1-yl)carbamate**




4a

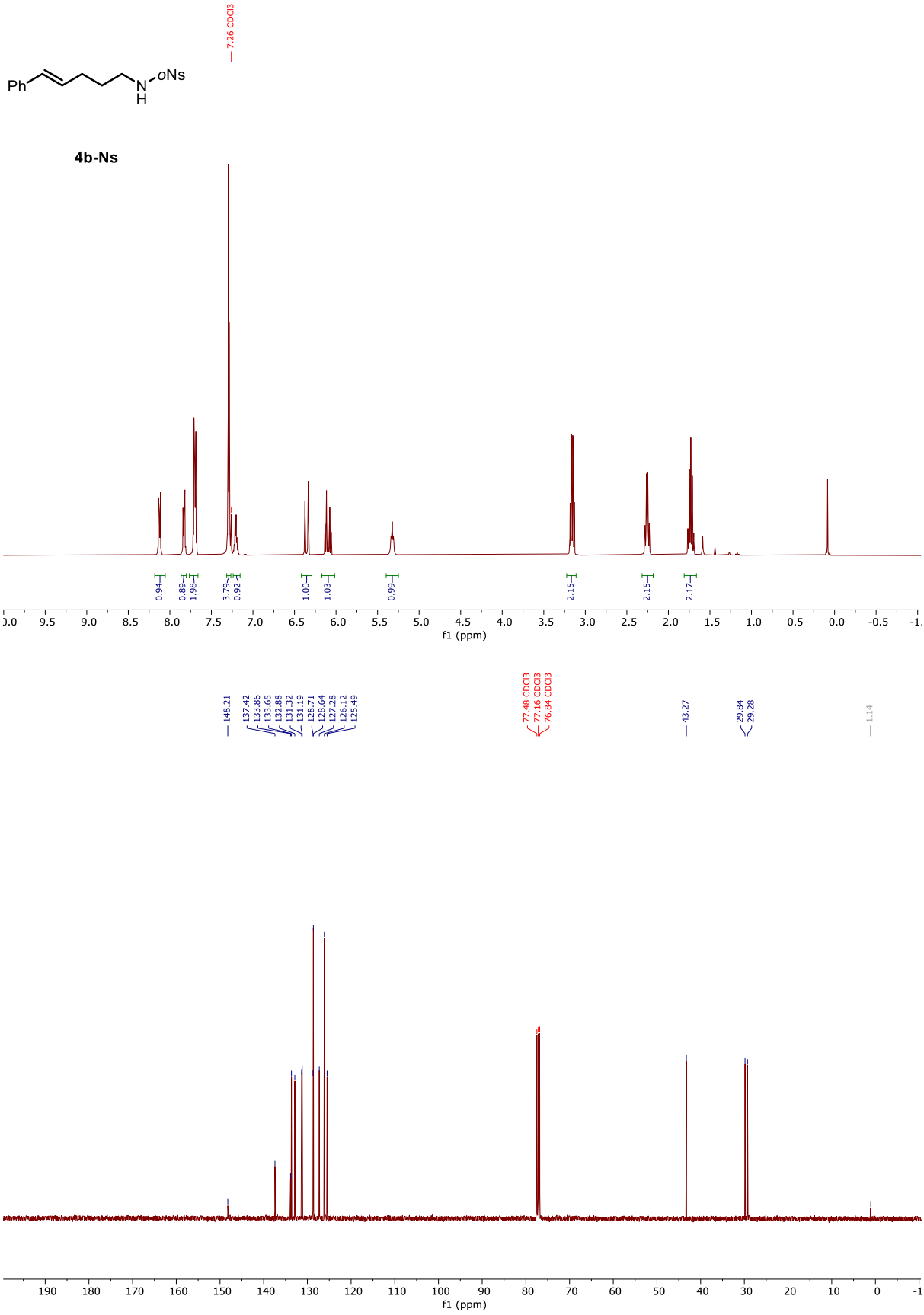


**(4b): Methyl (*E*)-(5-phenylpent-4-en-1-yl)carbamate**

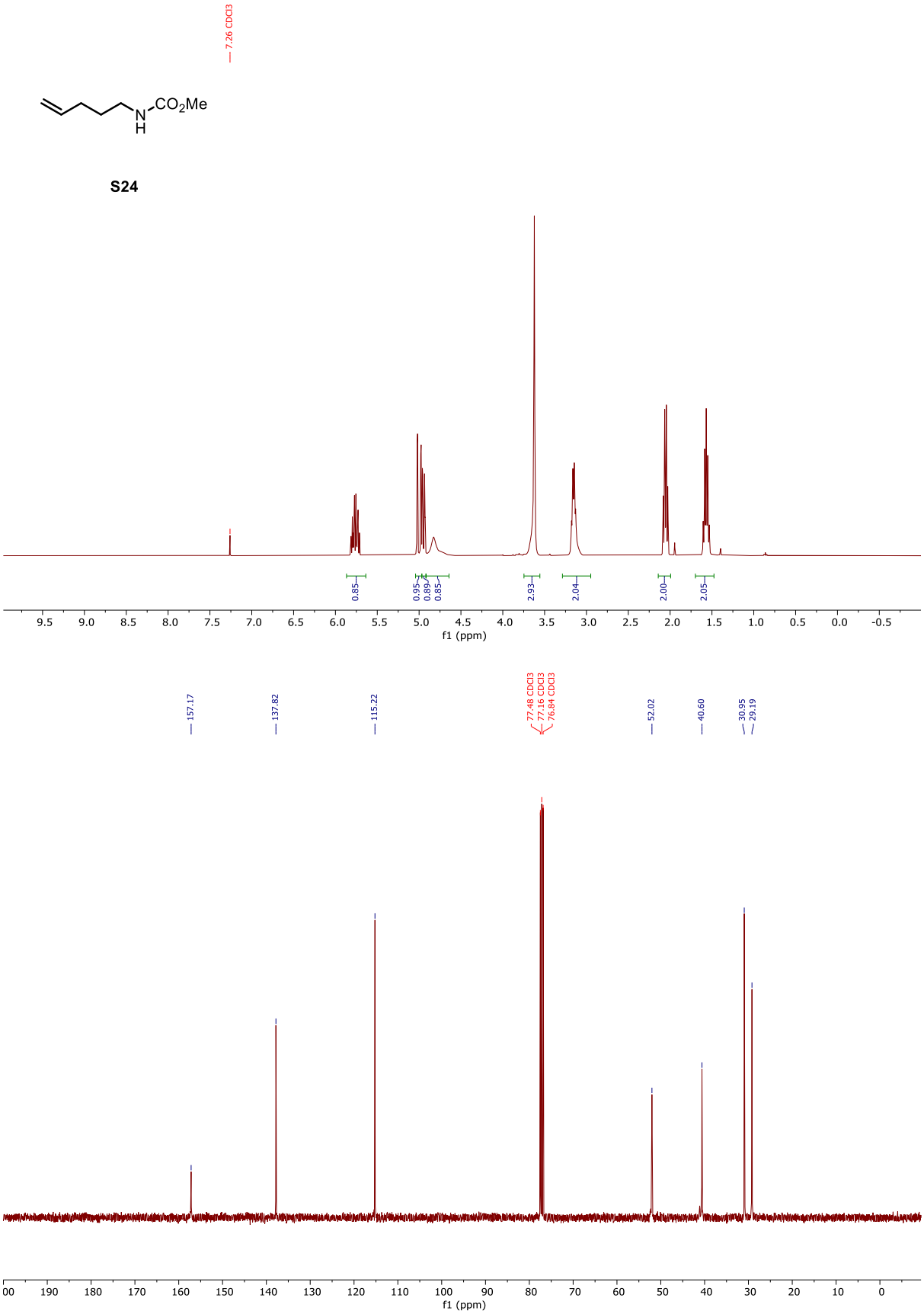



**4b**

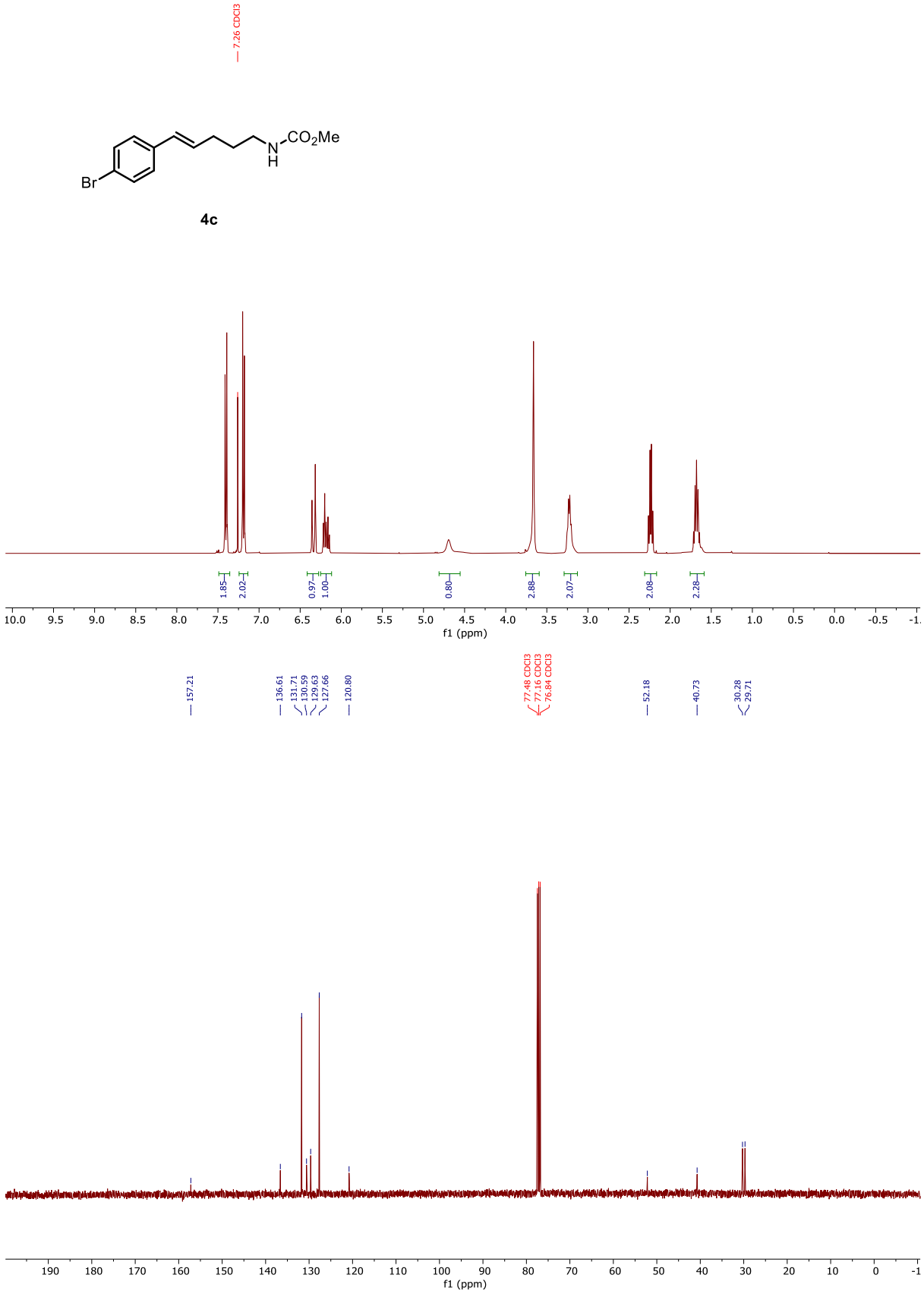
**(4b-Ns): (*E*)-2-Nitro-*N*-(5-phenylpent-4-en-1-yl)benzenesulfonamide**



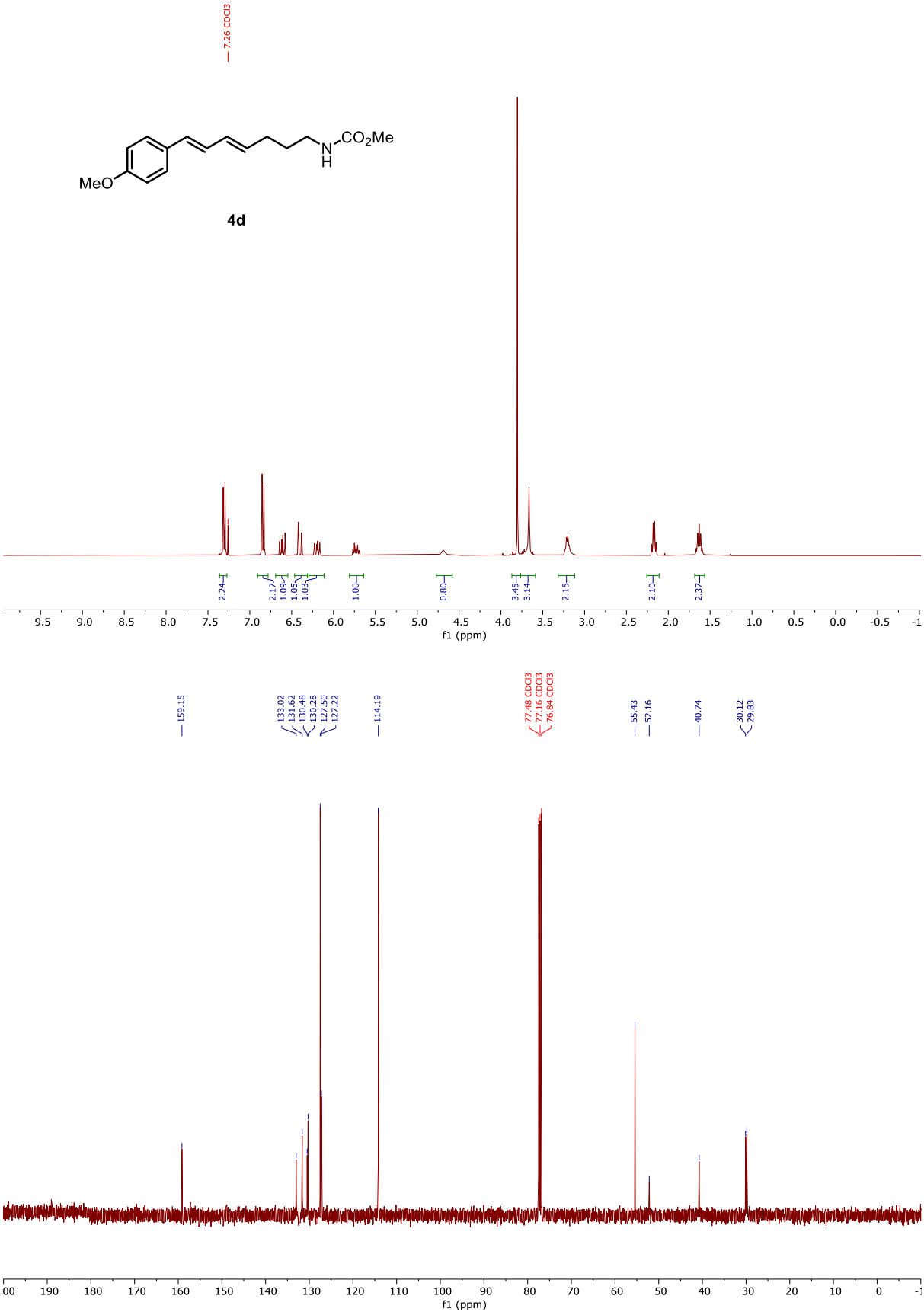
## (S24): Methyl pent-4-en-1-ylcarbamate



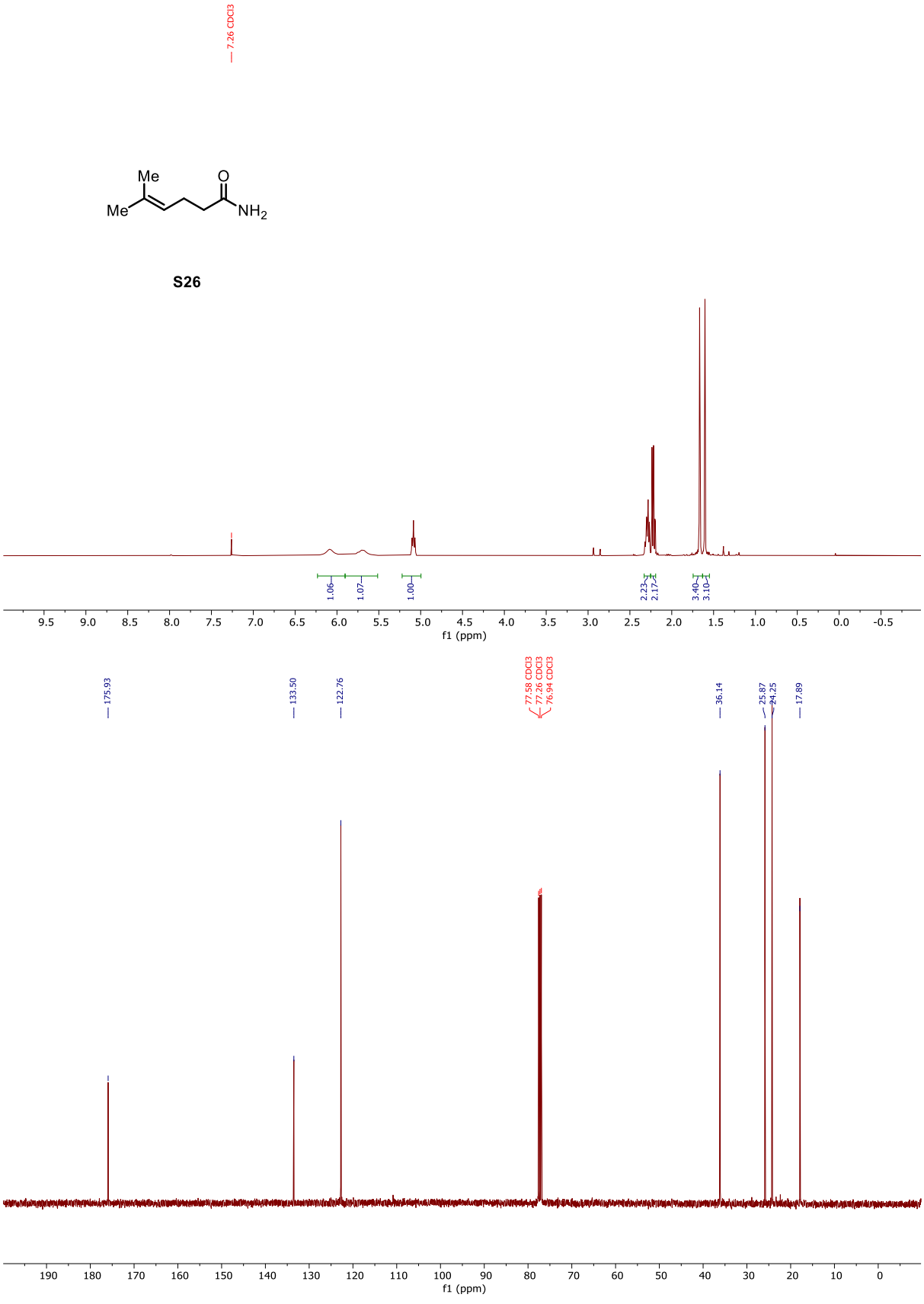
**(4c): Methyl (*E*)-(5-(4-bromophenyl)pent-4-en-1-yl)carbamate**



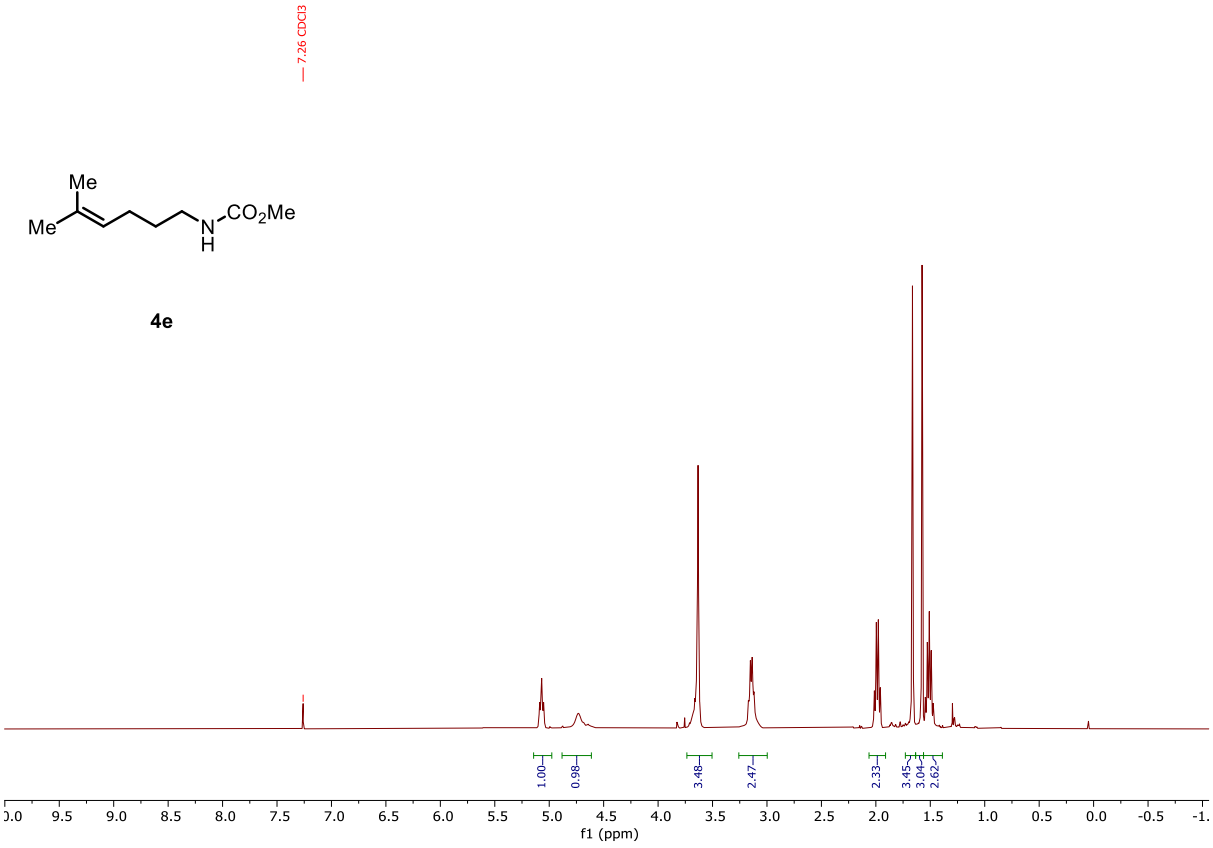
**(4d): Methyl ((4*E*,6*E*)-7-(4-methoxyphenyl)hepta-4,6-dien-1-yl)carbamate**



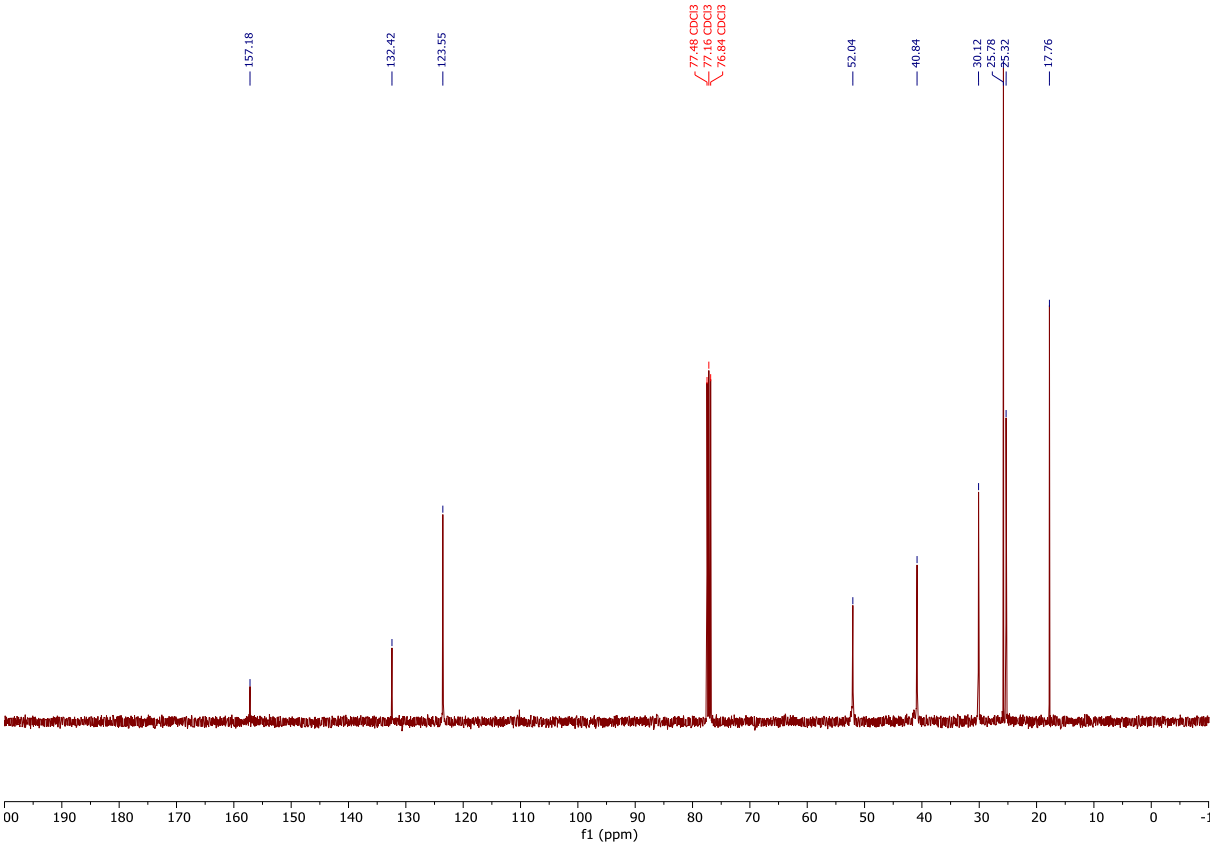
## (S26): 5-Methylhex-4-enamide



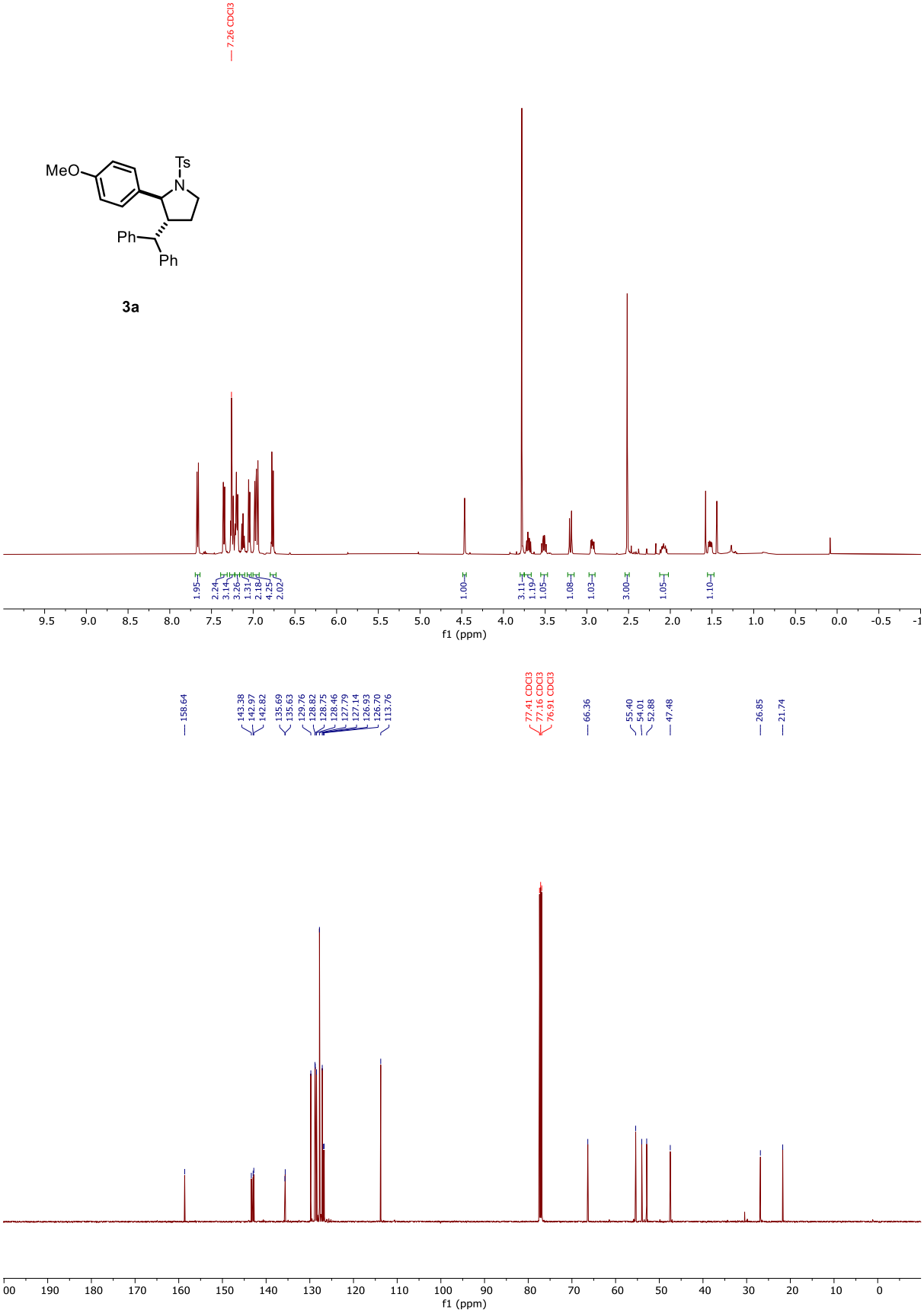
## (4e): Methyl (5-methylhex-4-en-1-yl) carbamate



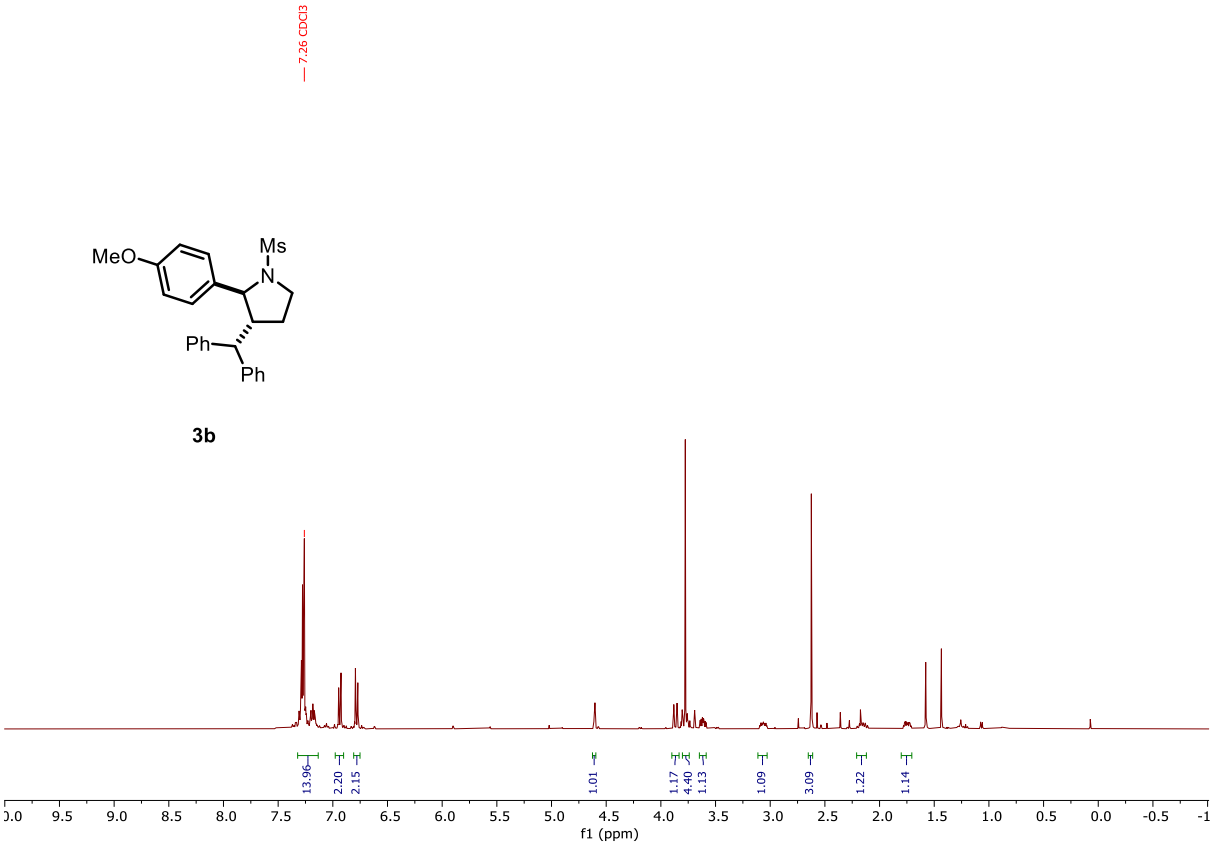

**4e**

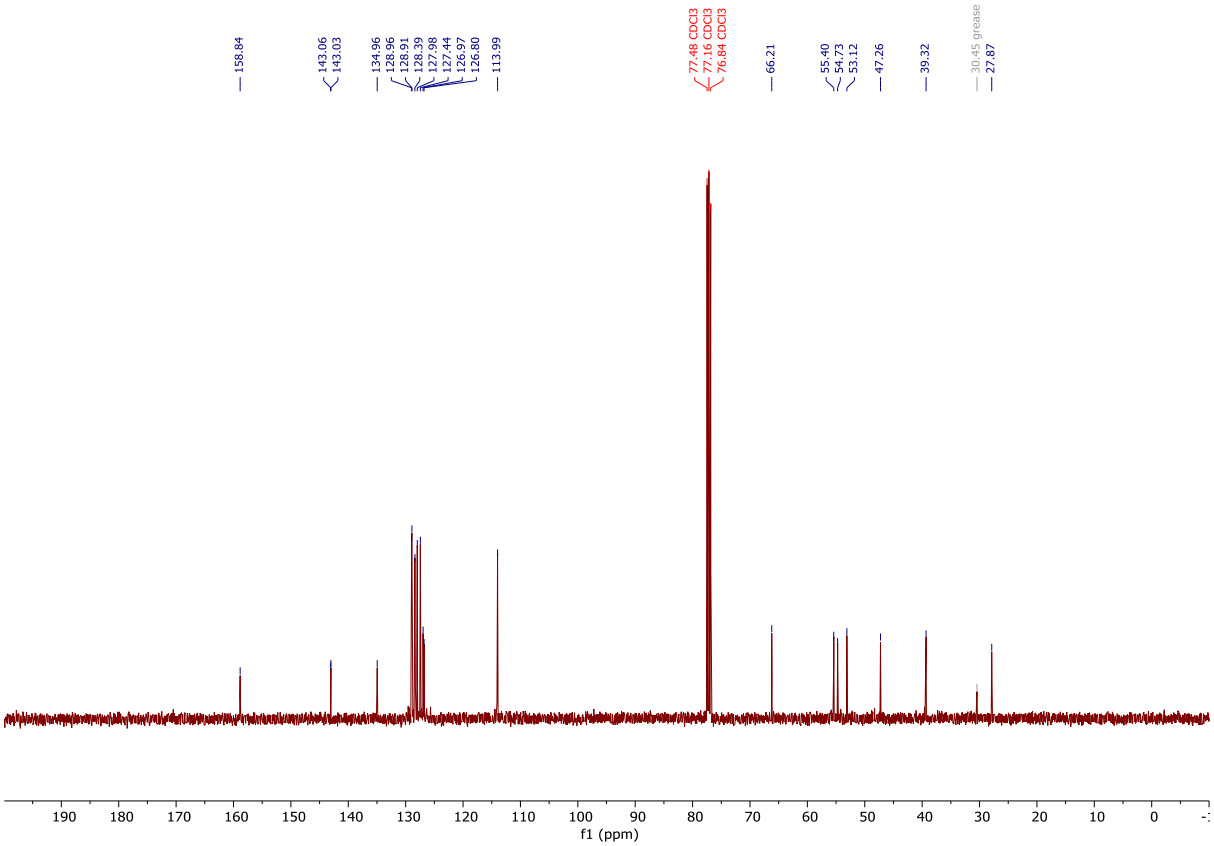


**(3a): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-tosylpyrrolidine**

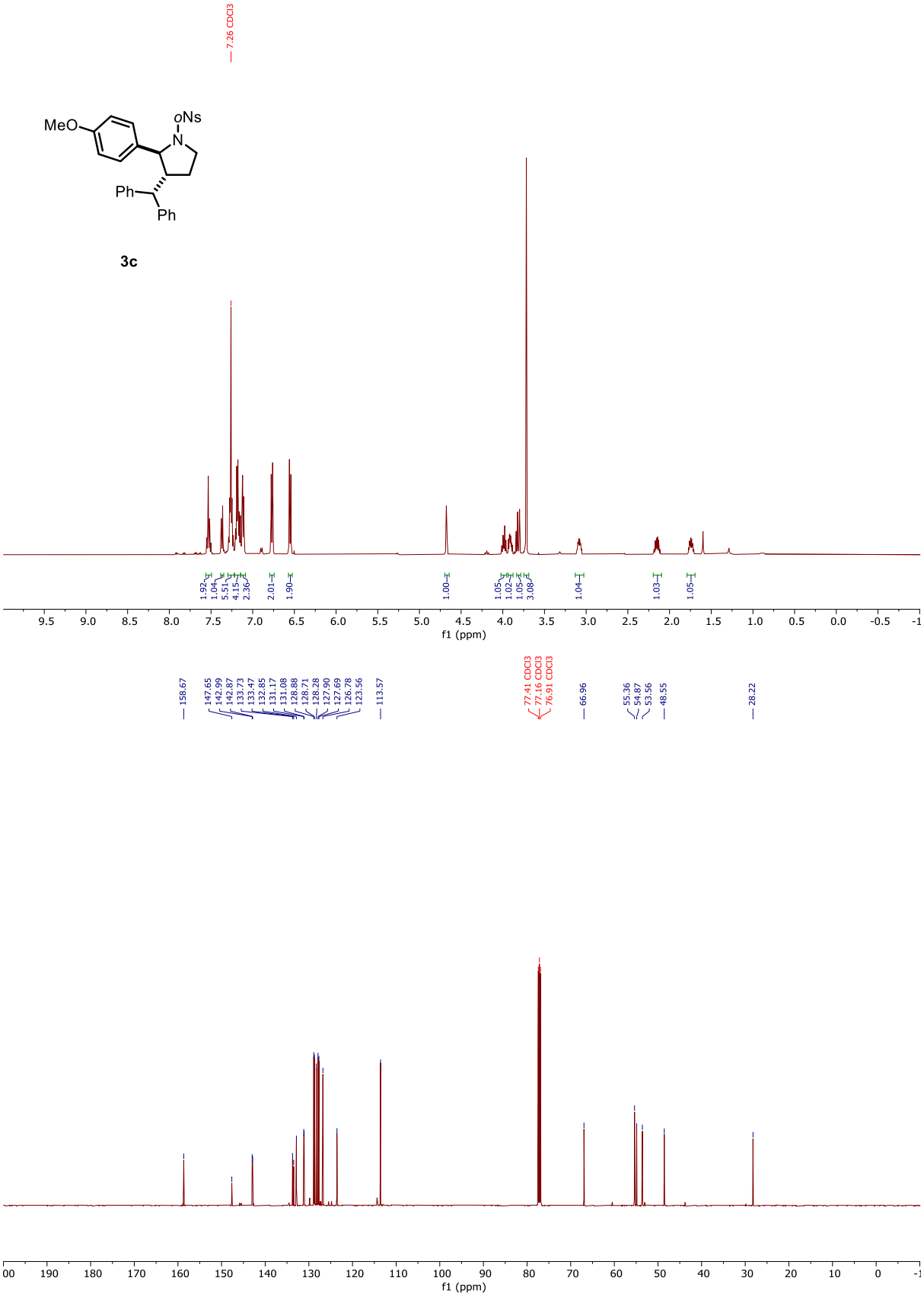


**(3b): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-(methylsulfonyl)pyrrolidine**

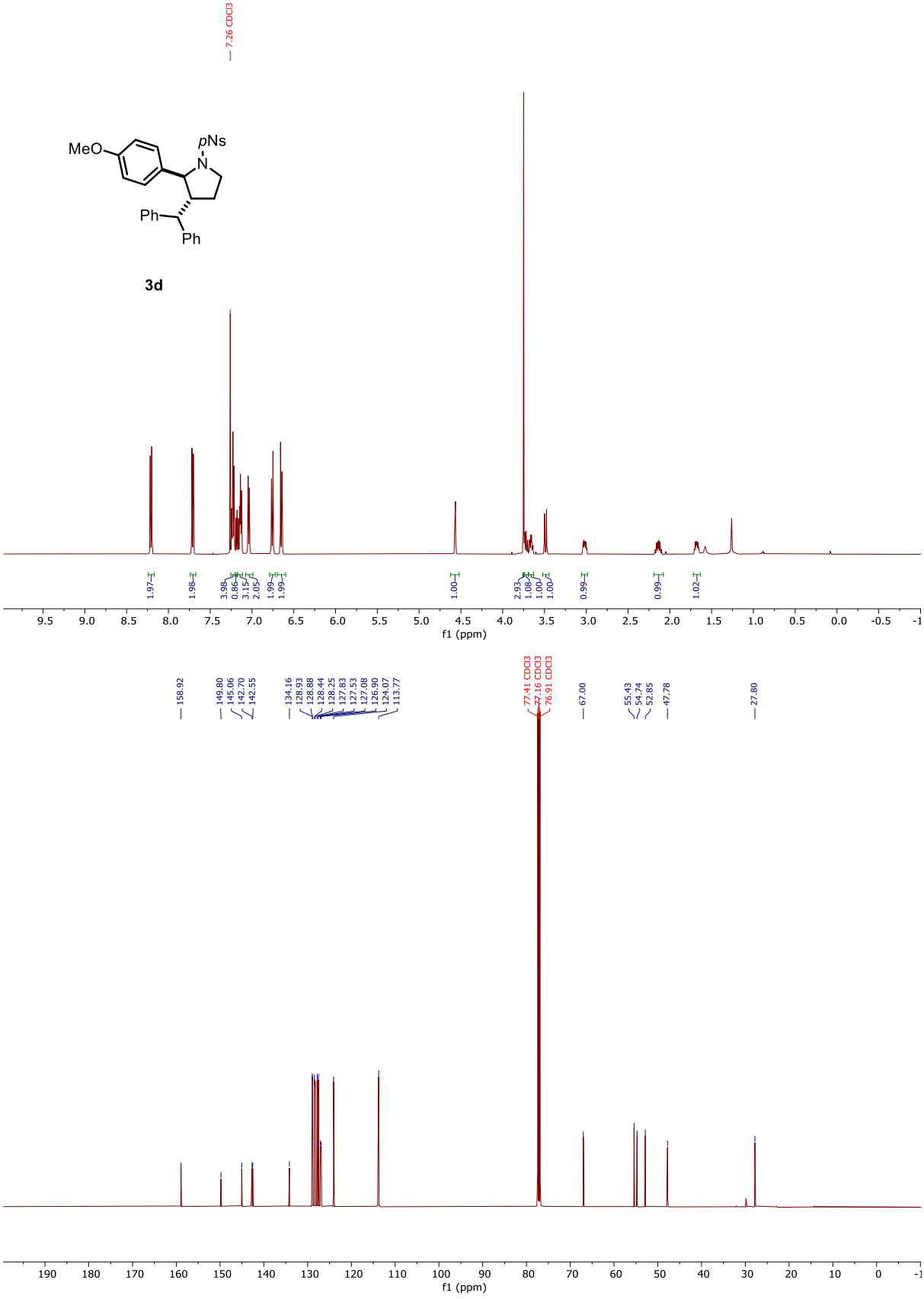


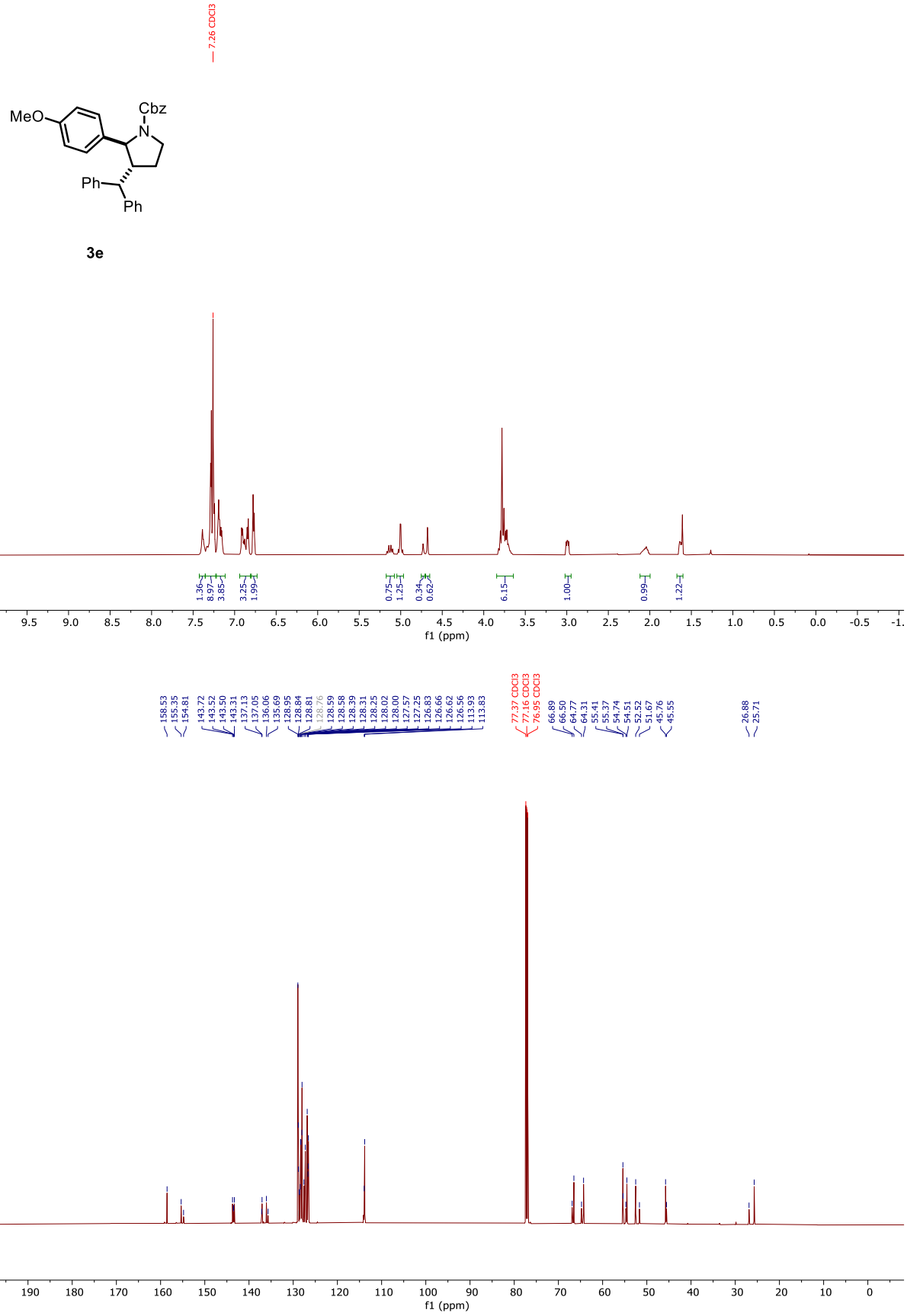
**(3c): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**



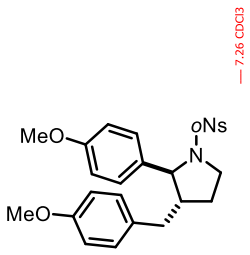
**(3d): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(4-nitrophenyl)sulfonyl]-pyrrolidine**



**(3e): (±)-Benzyl (2*S*,3*R*)-3-benzhydryl-2-(4-methoxyphenyl)pyrrolidine-1-carboxylate**

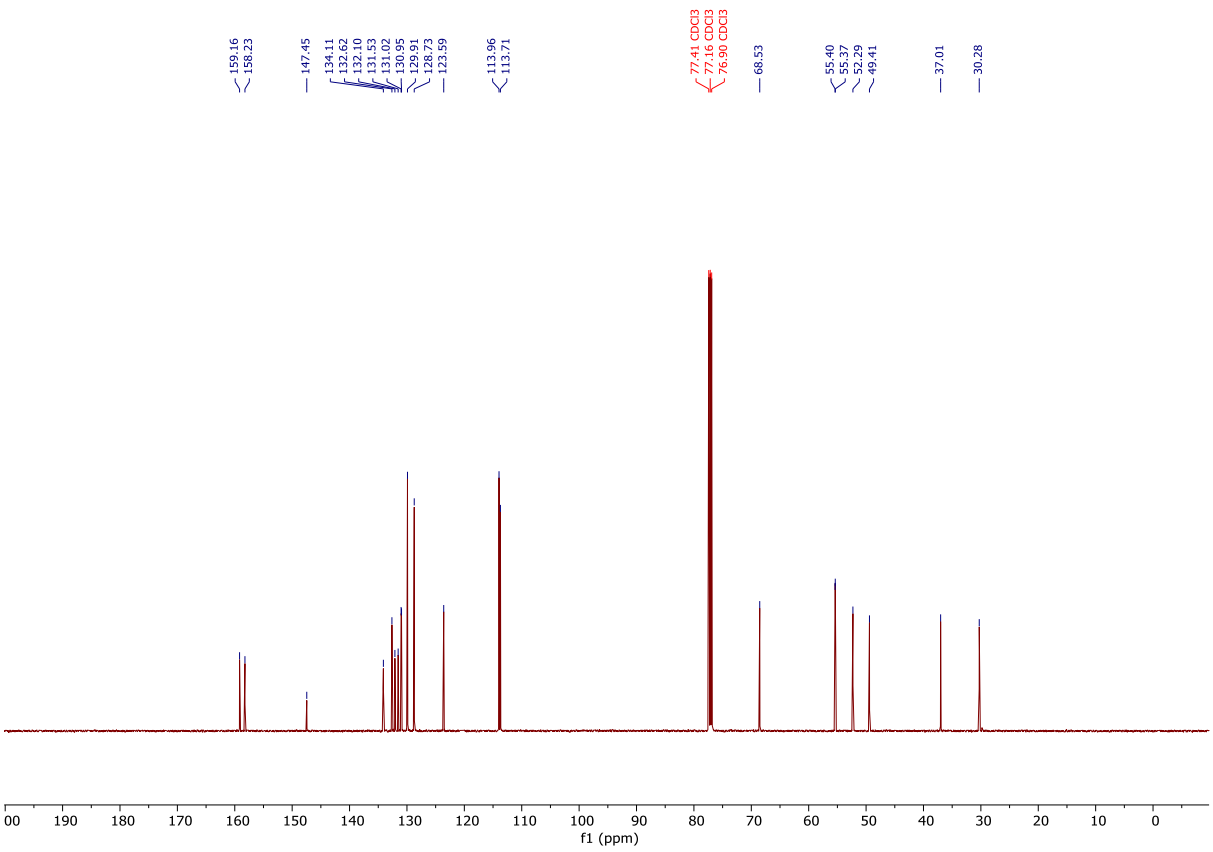


**(3g): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl)-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**

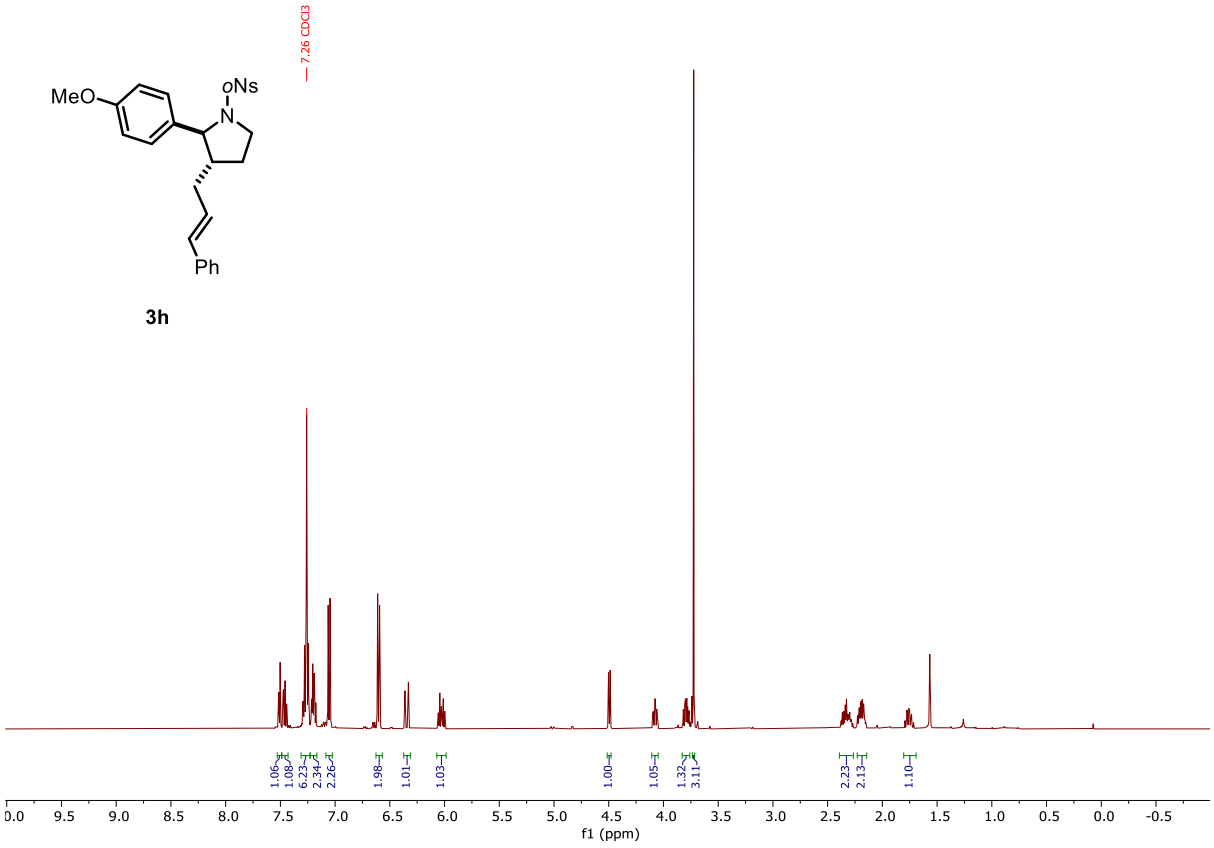



**3g**

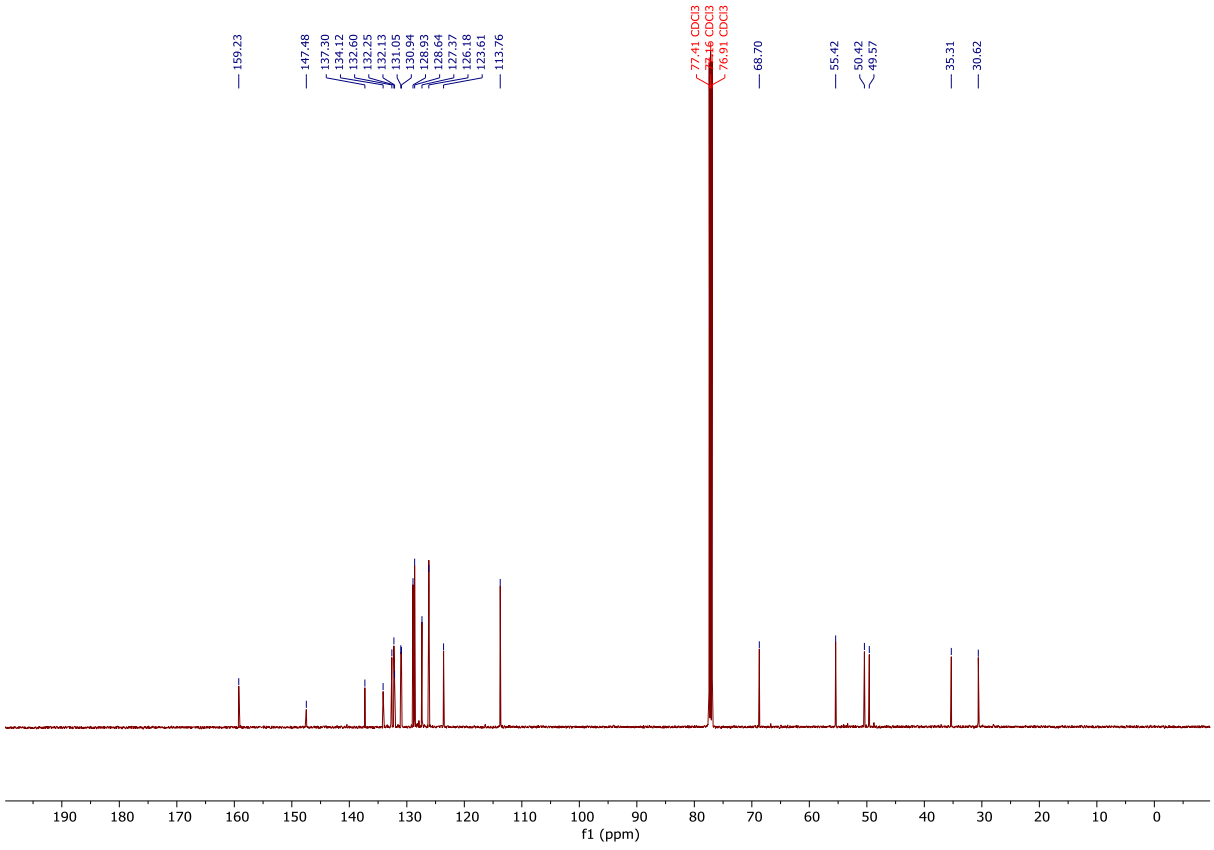


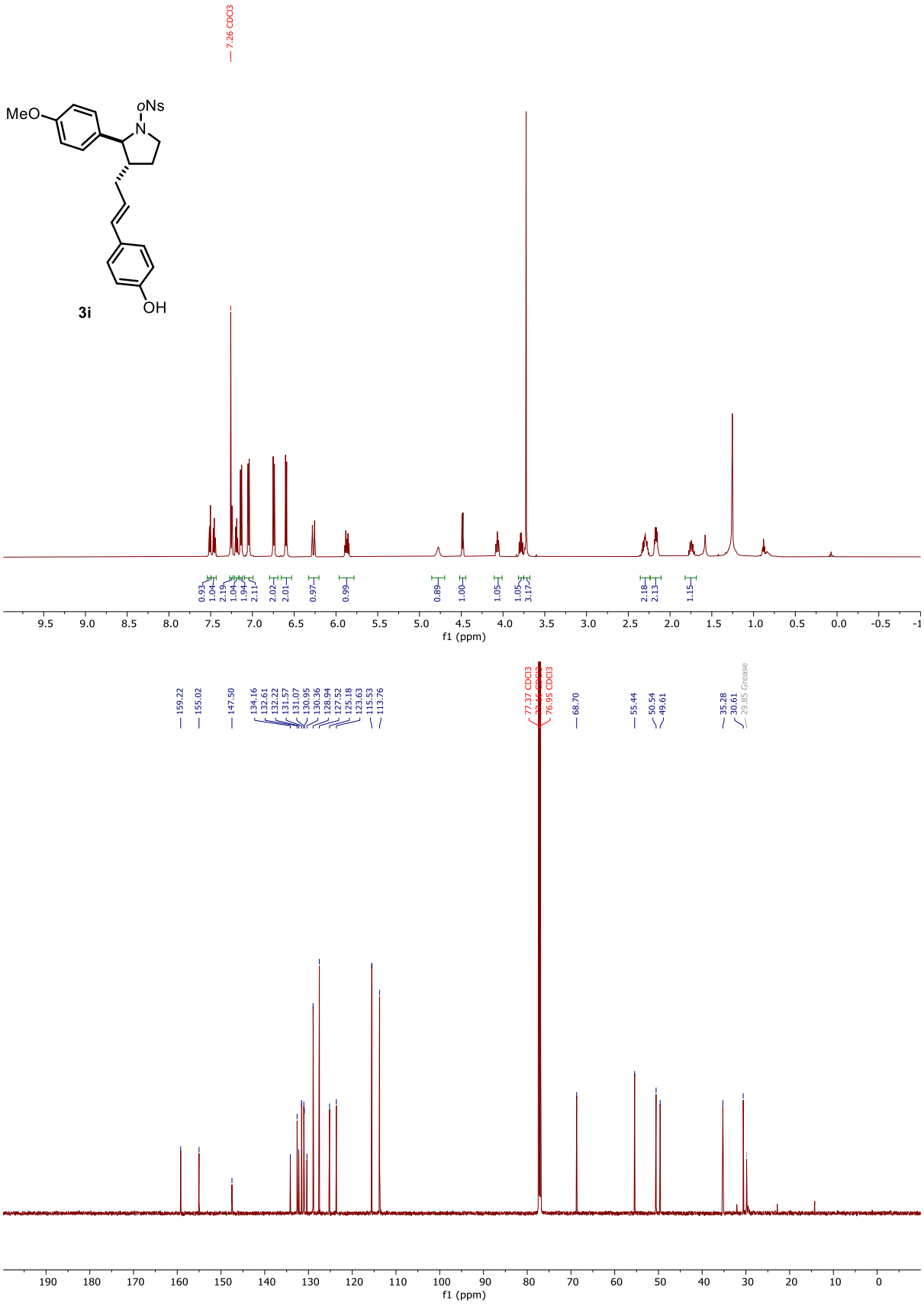
**(3h): (±)-(2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**



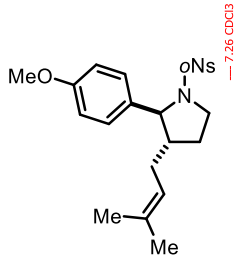

3h



**(3i): (±)-4-((*E*)-3-((2*S*,3*S*)-2-(4-Methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)pyrrolidin-3-yl)prop-1-en-1-yl)phenol**

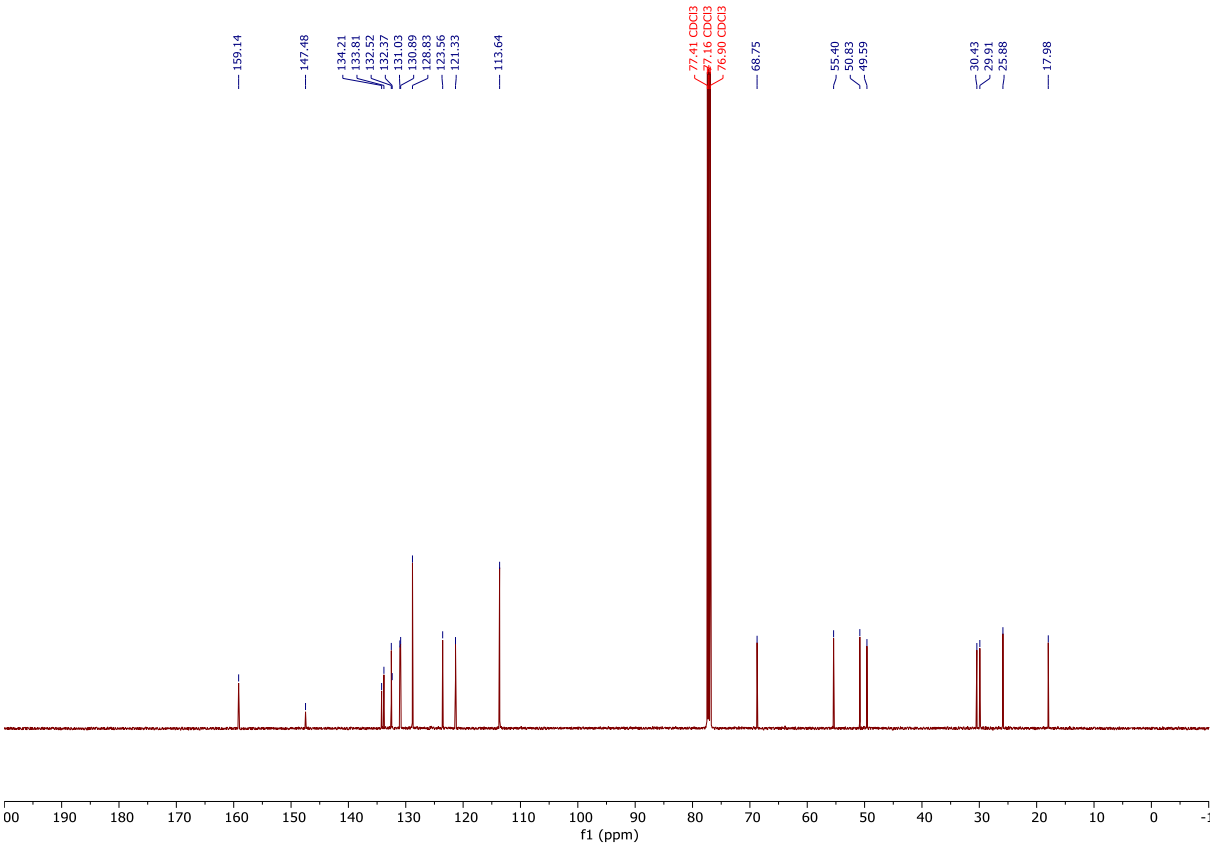


**(3j): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-pent-3-en-2-yl]-pyrrolidine**

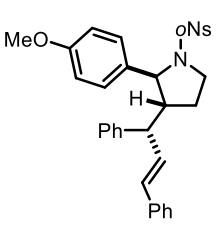



**3j**

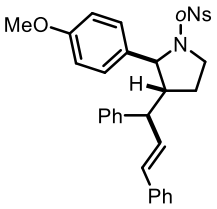


**(3k): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine and (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine**

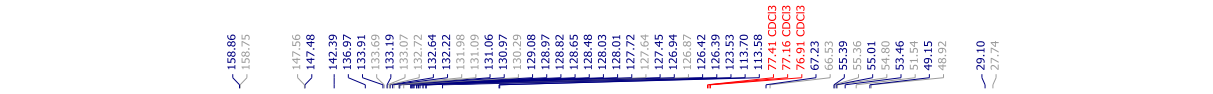


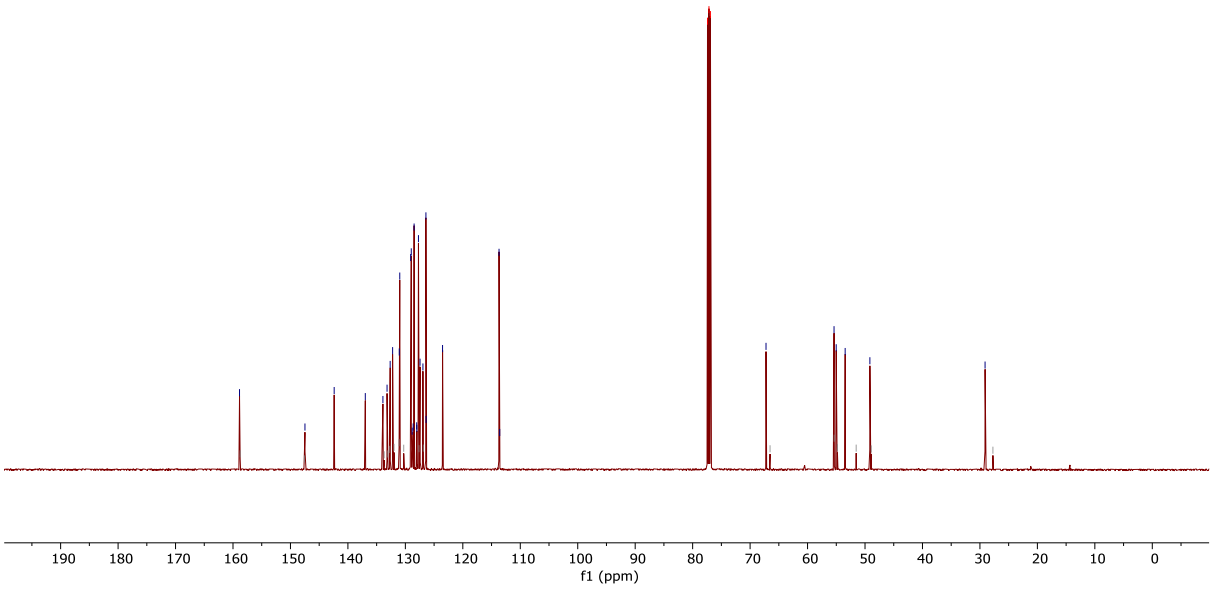

**3k**



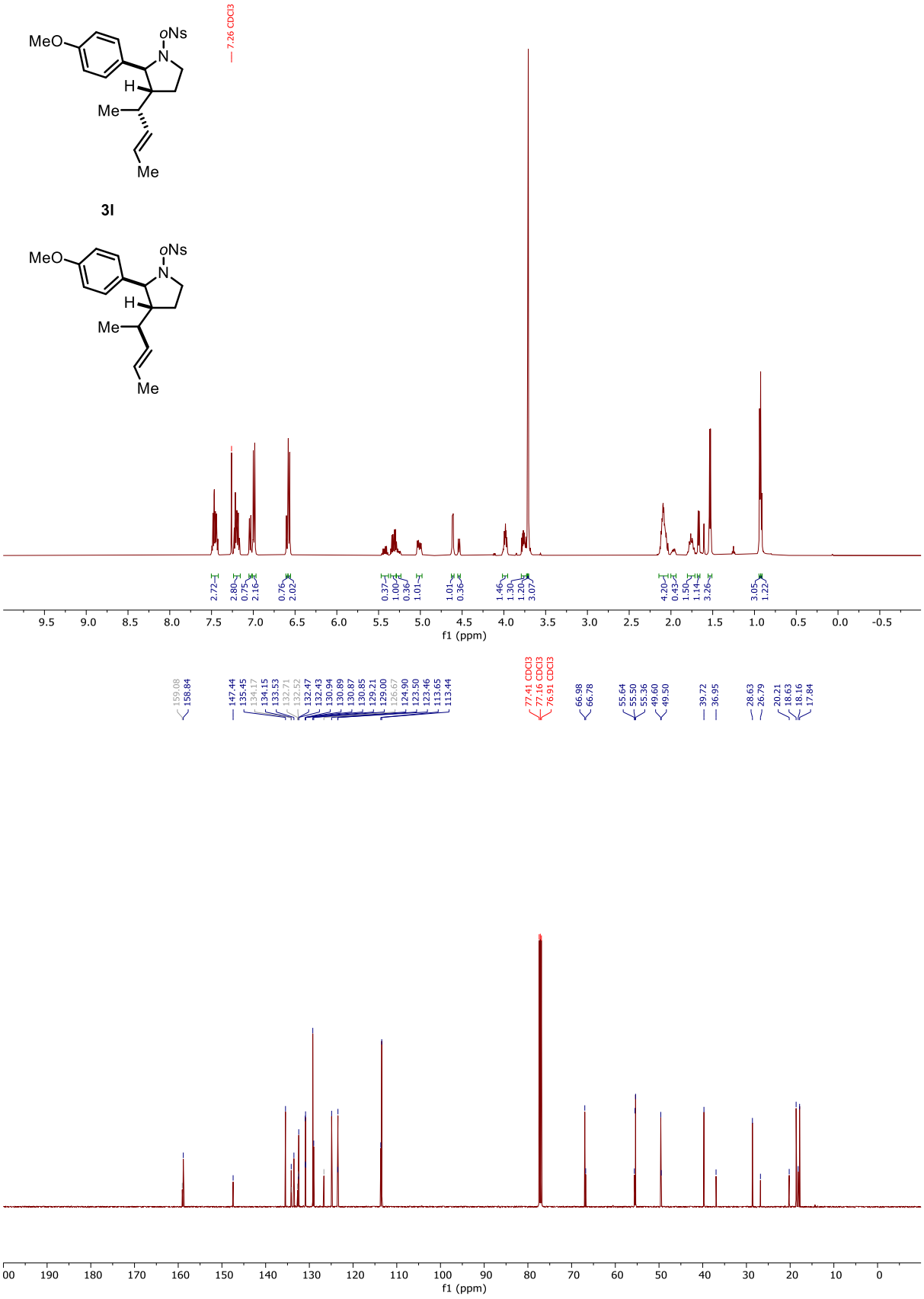




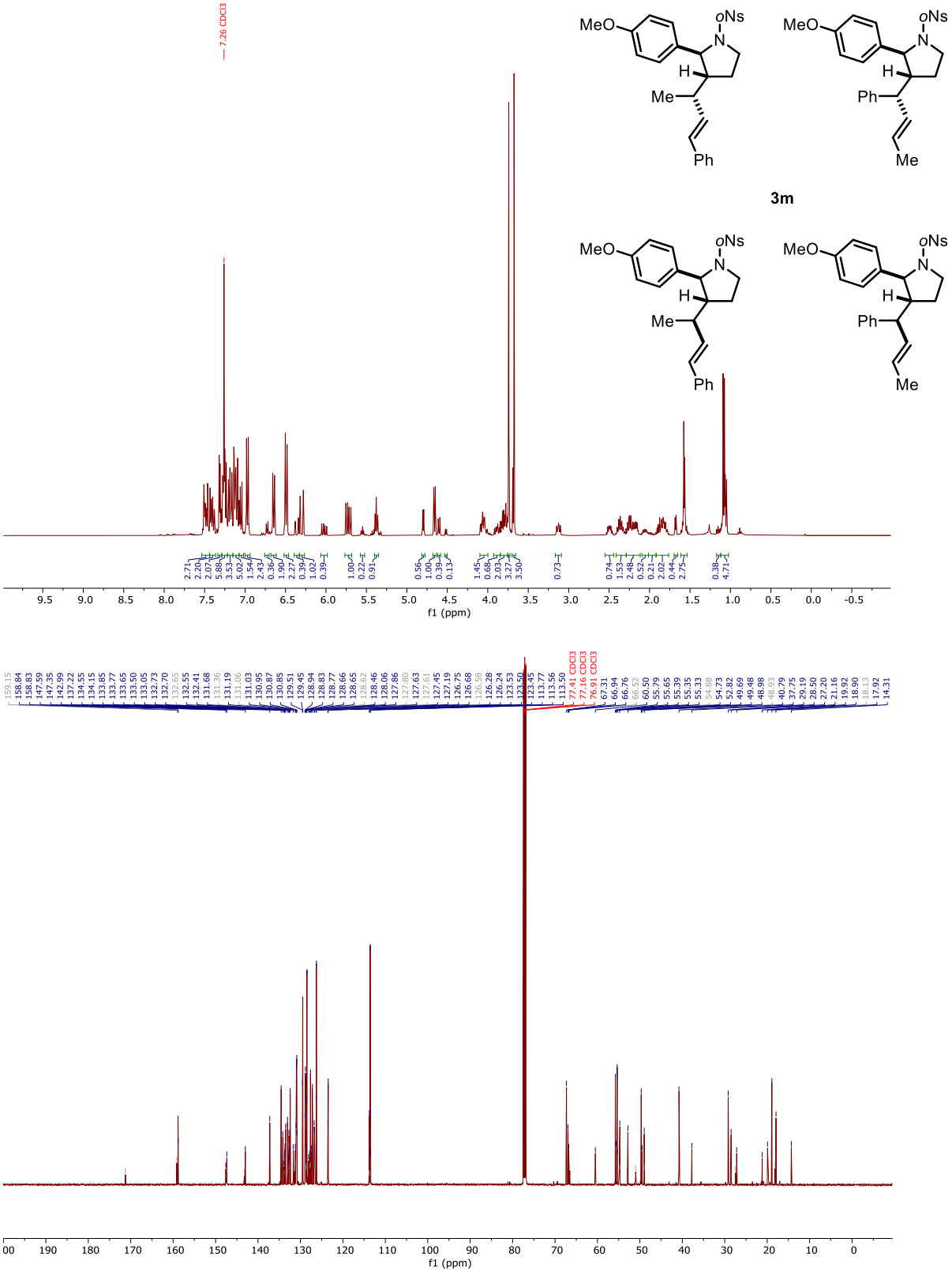


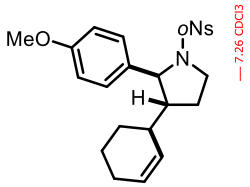
**(3l): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-pent-3-en-2-yl]-pyrrolidine and (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-pent-3-en-2-yl]pyrrolidine**



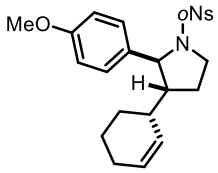
**(3m): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine, (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*R*,2'*E*)-4-phenylbut-3-en-2-yl]pyrrolidine, (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-3-[(1'*S*,2'*E*)-1-phenylbut-2-en-1-yl]pyrrolidine, (±)-(2*S*,3*R*)-2-(4-methoxyphenyl)-1-[(2-nitro-phenyl)sulfonyl]-3-[(1'*R*,2'*E*)-1-phenylbut-2-en-1-yl]pyrrolidine**



**(3n): (±)-(2*S*,3*R*)-3-[(1'*R*)-Cyclohex-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*S*,3*R*)-3-[(1'*S*)-Cyclohex-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

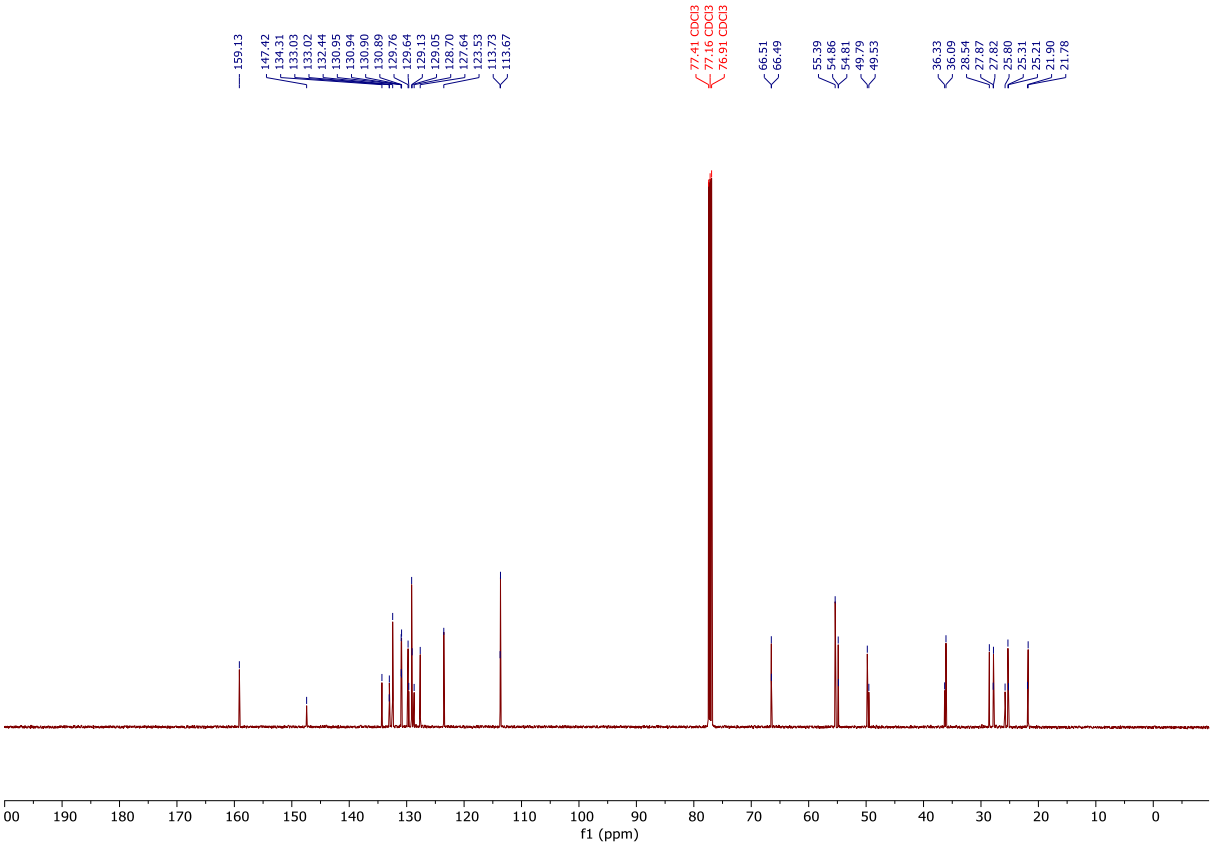



**3n**

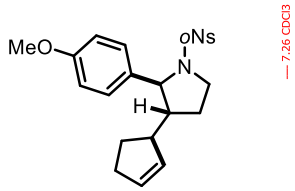




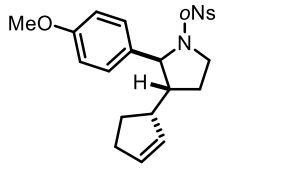




**(3o): (±)-(2*S*,3*R*)-3-[(1'*R*)-Cyclopent-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*S*,3*R*)-3-[(1'*S*)-Cyclopent-2-en-1-yl]-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

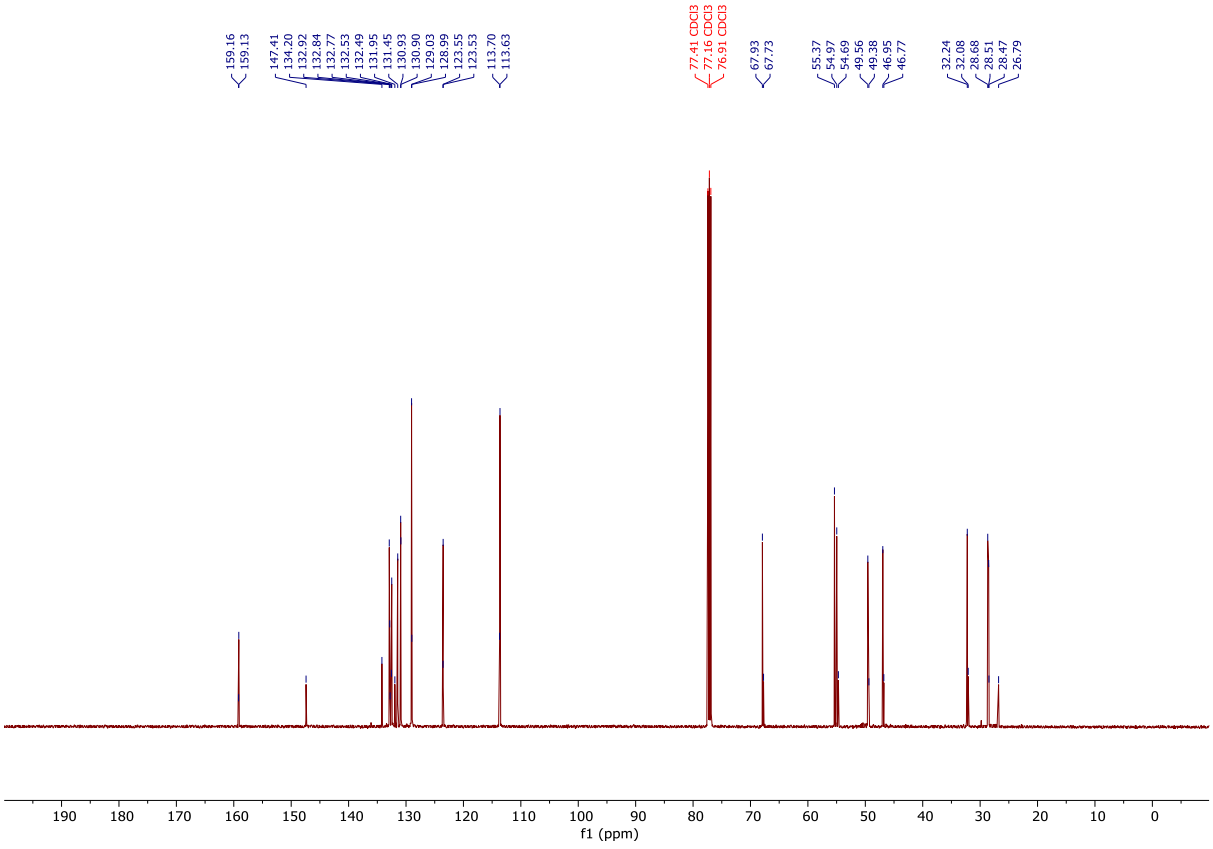



**3o**

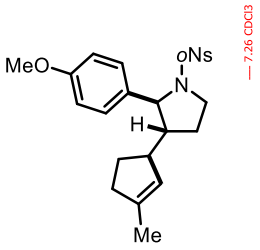




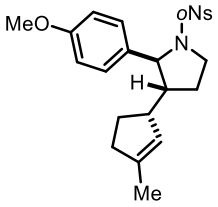




**(3p): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*R*)-3-methylcyclopent-2-en-1-yl]-1-[(2-nitrophenyl)-sulfonyl]pyrrolidine and (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*S*)-3-methylcyclopent-2-en-1-yl]-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

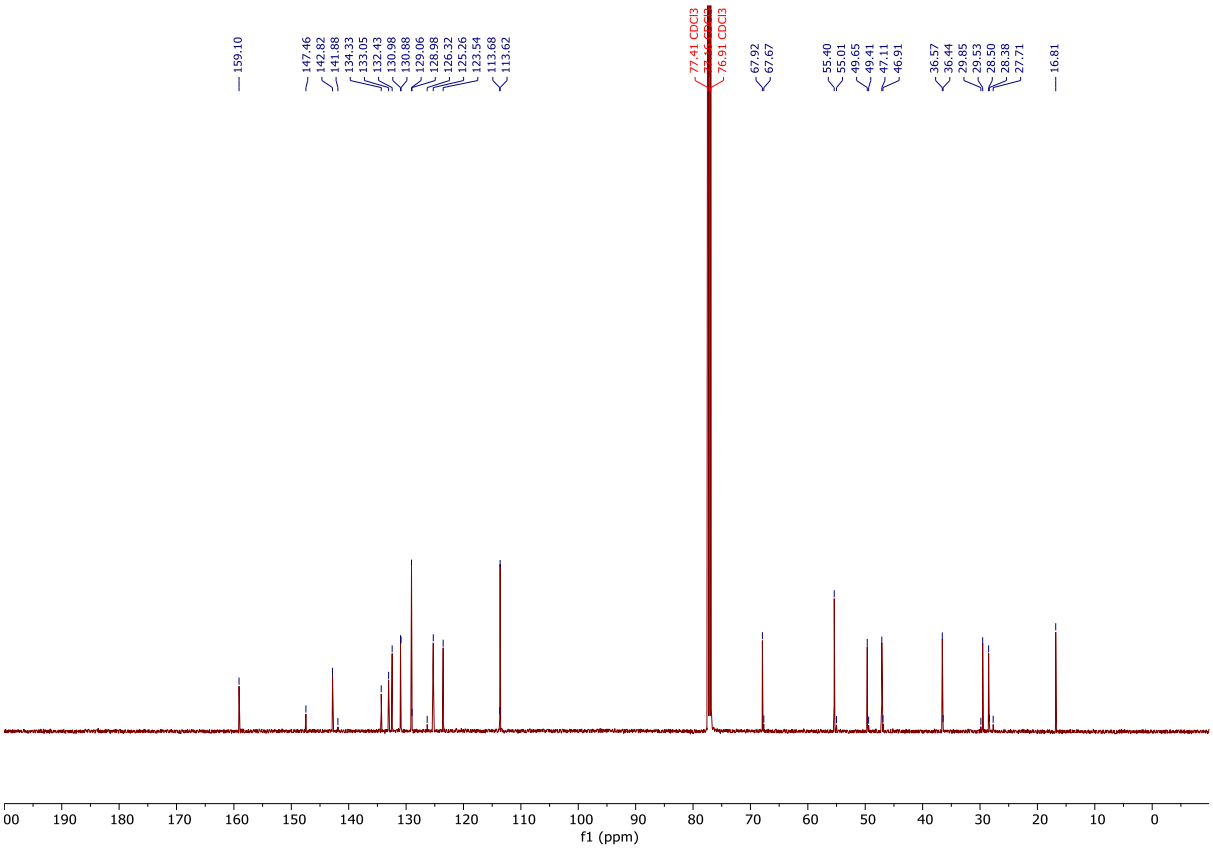



**3p**

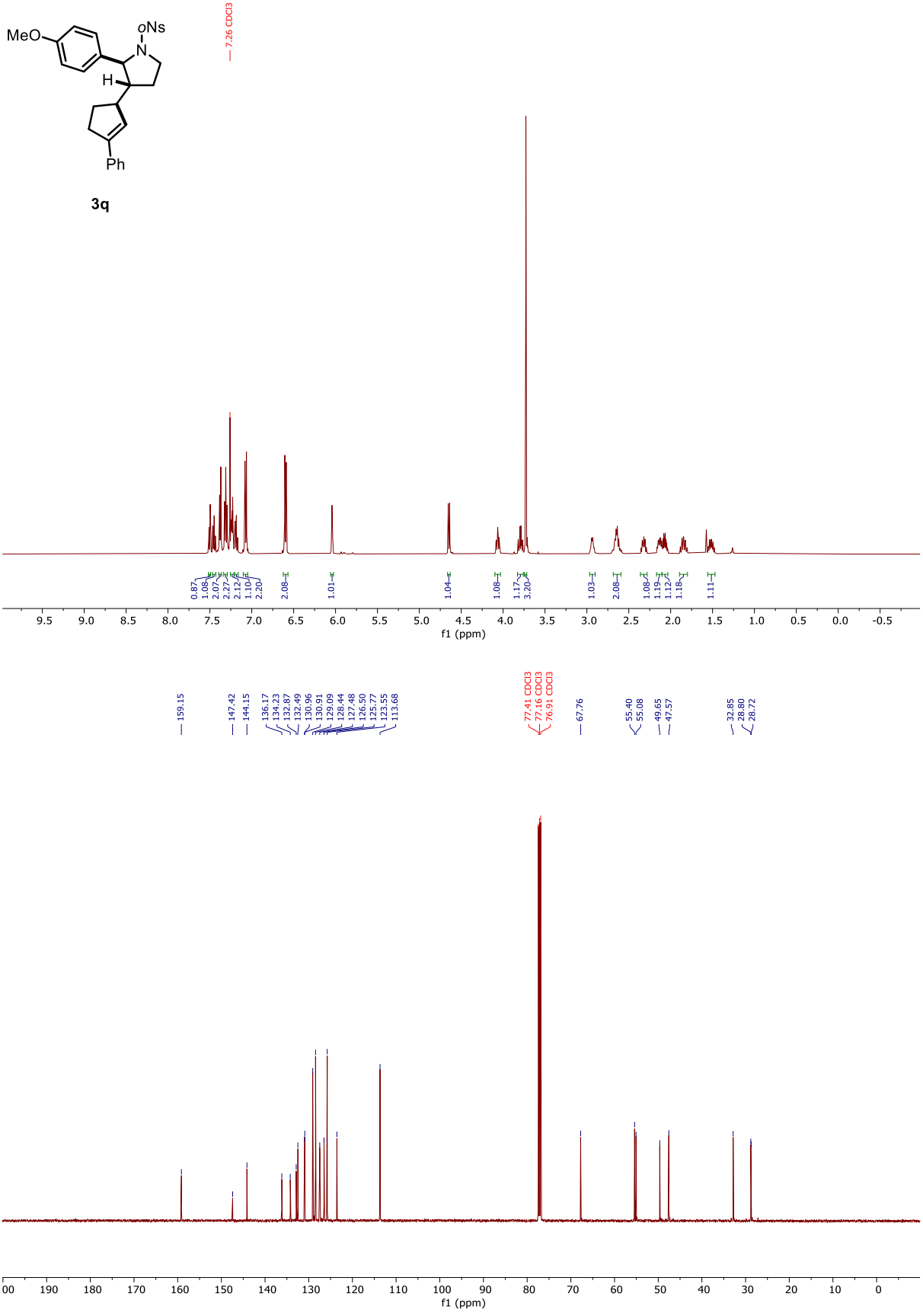




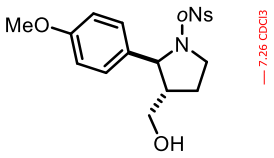




**(3q): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl)-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**

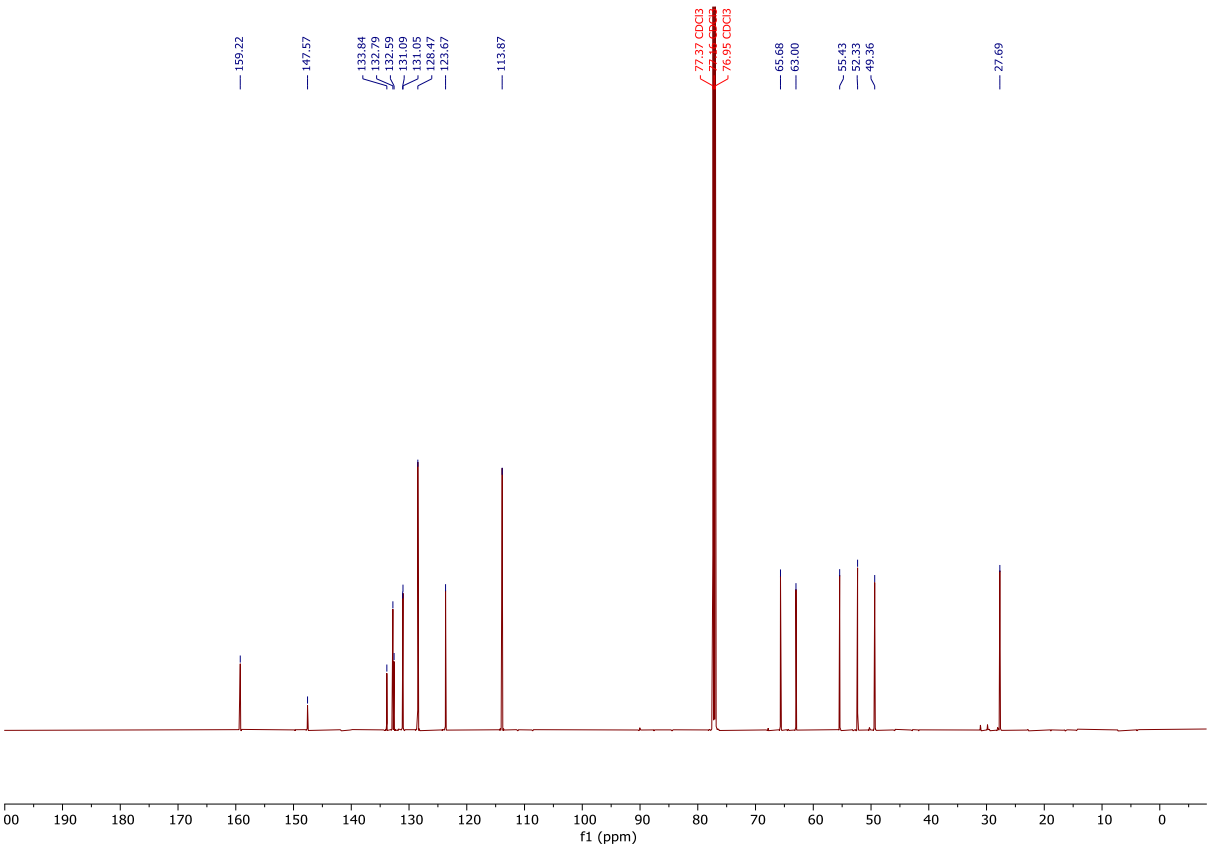


**(3r): (±)-{(2*S*,3*S*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidin-3-yl}methanol**

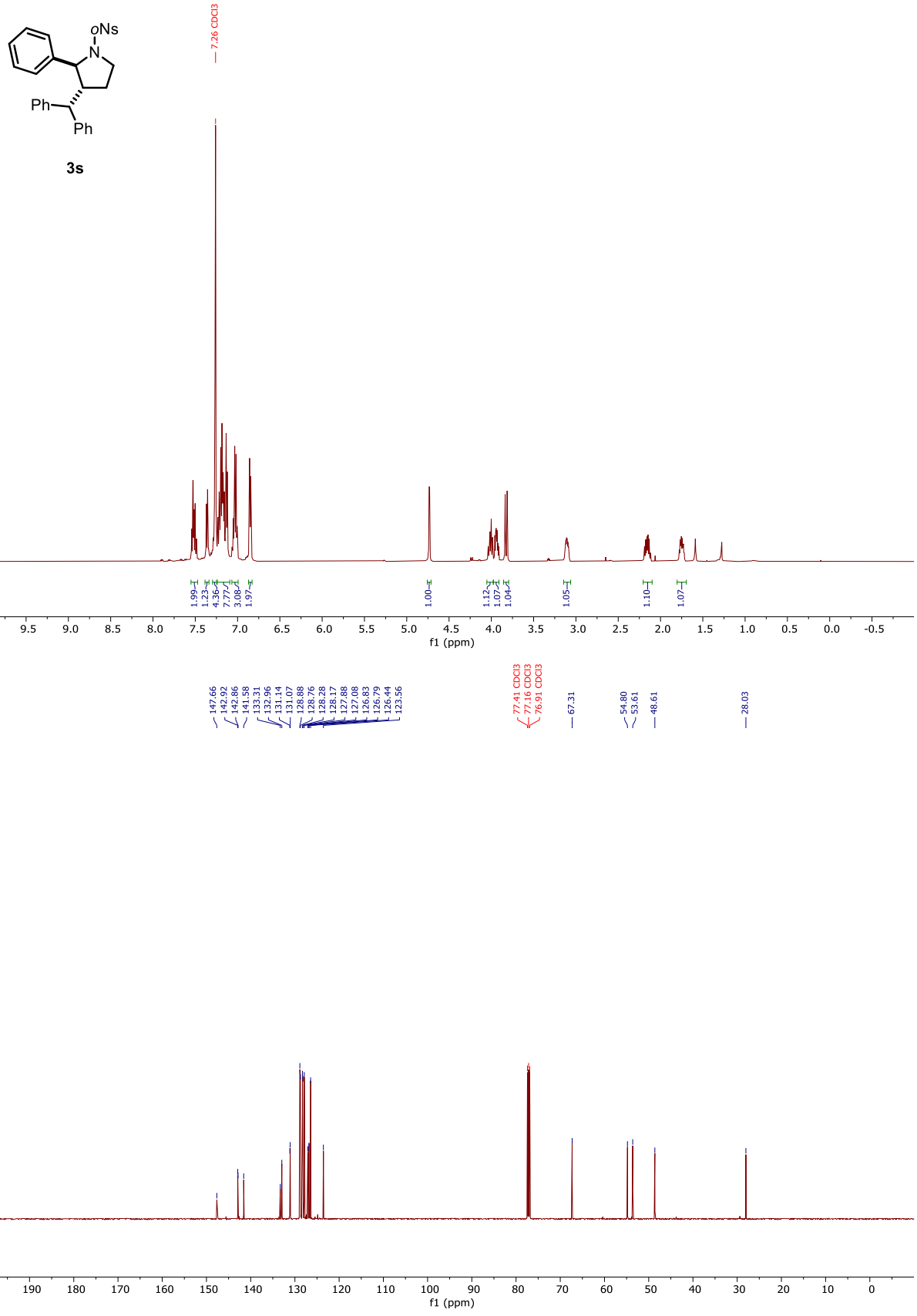



**3r**

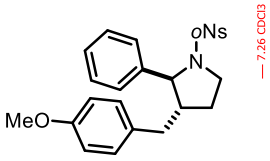


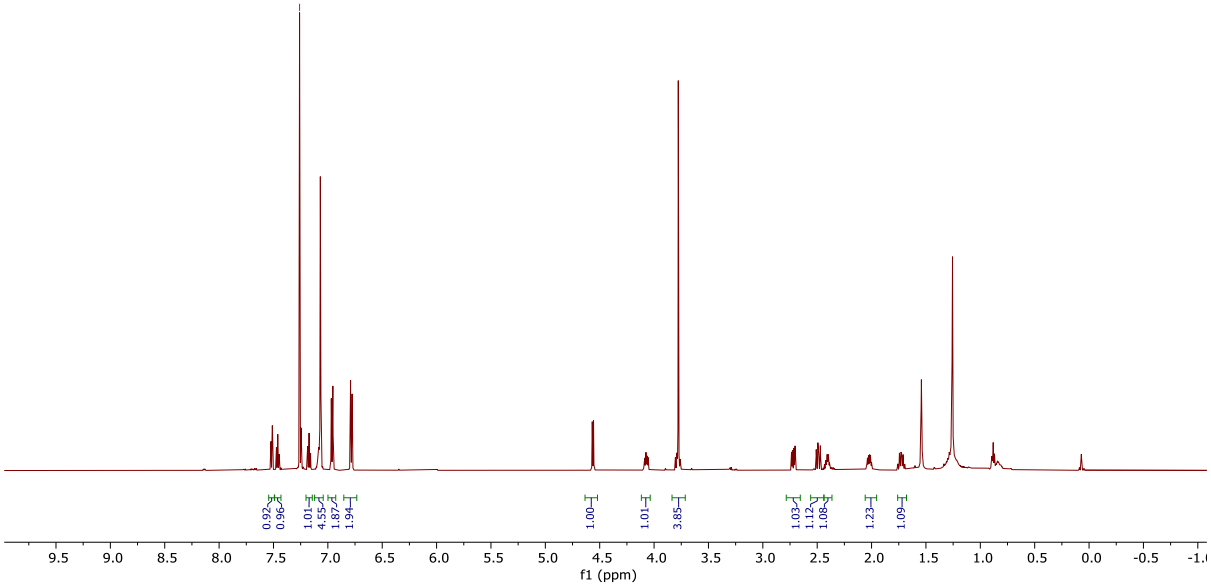
**(3s): (±)-(2*S*,3*R*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-2-phenylpyrrolidine**

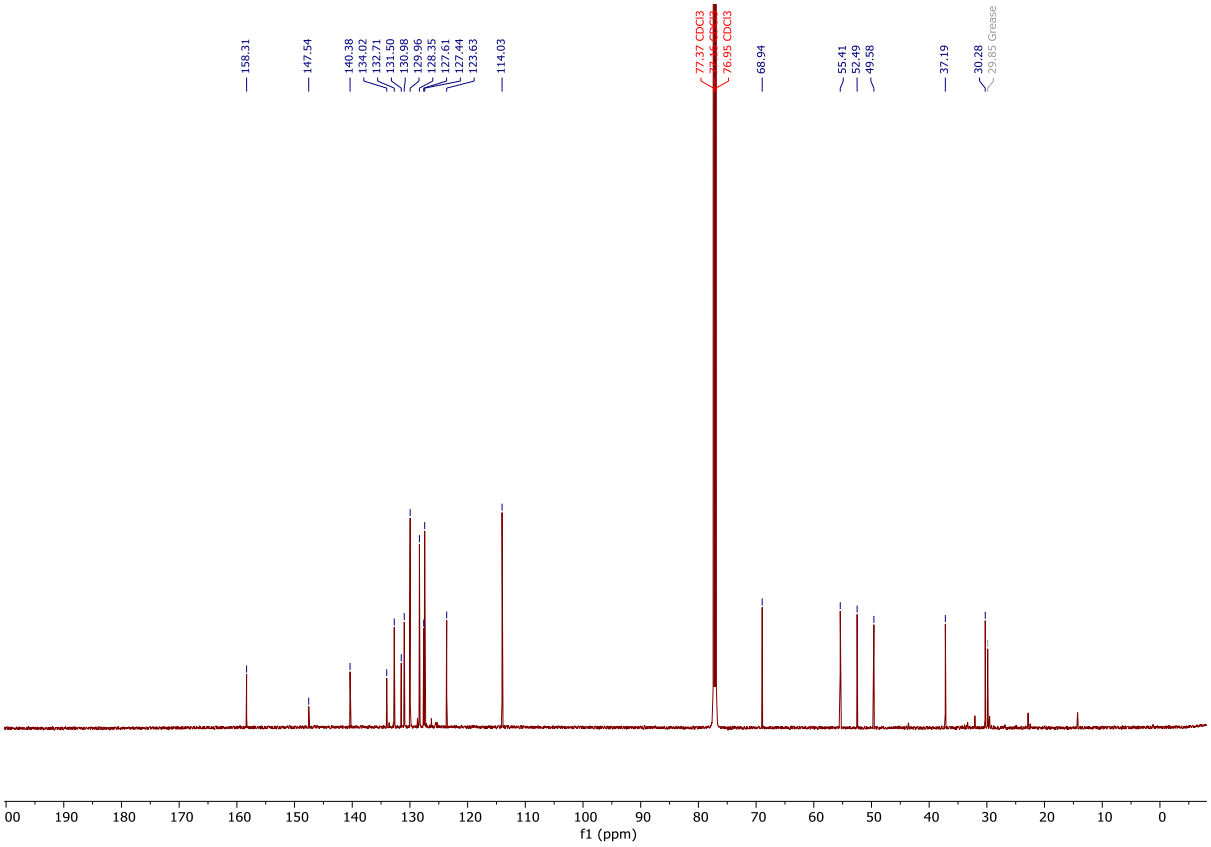


**(3t): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-1-[(2-nitrophenyl)sulfonyl]-2-phenylpyrrolidine**

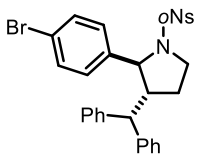



**3t**



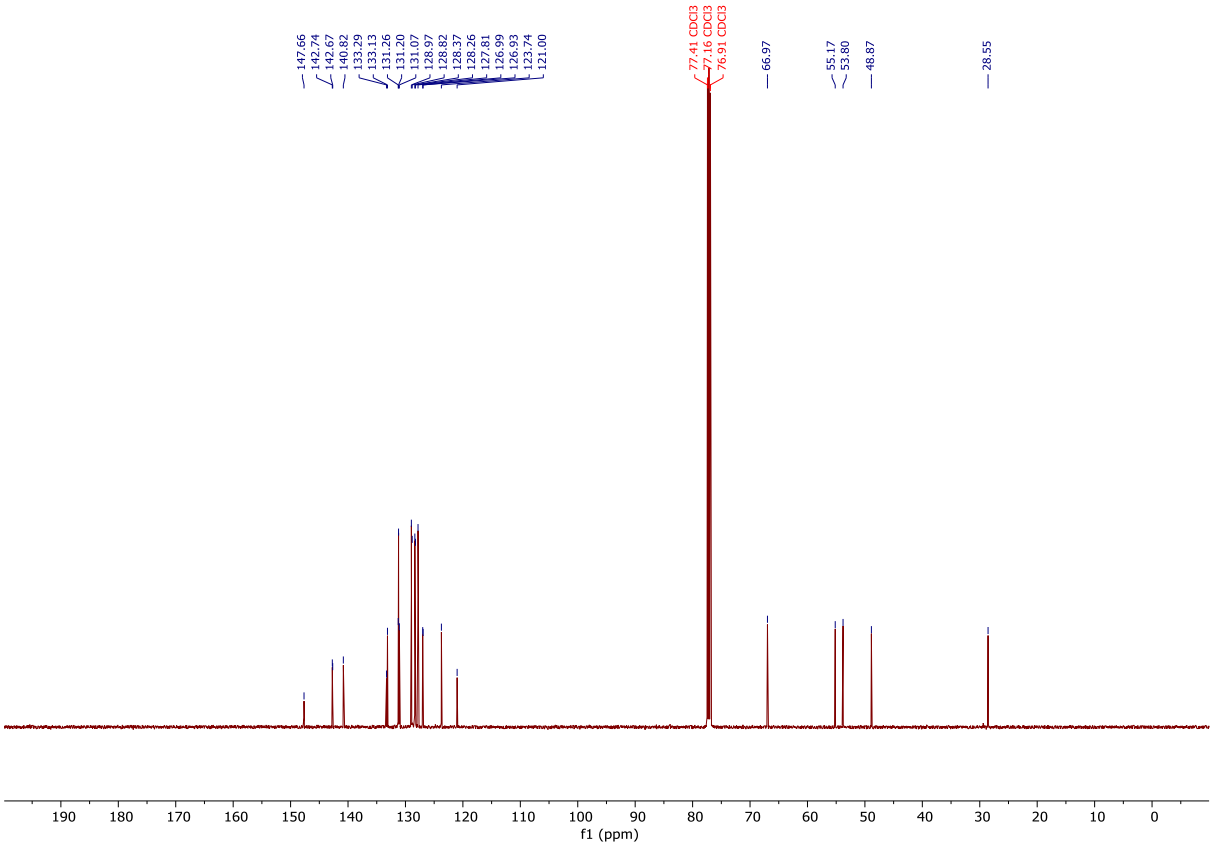



**(3u): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-bromophenyl)-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

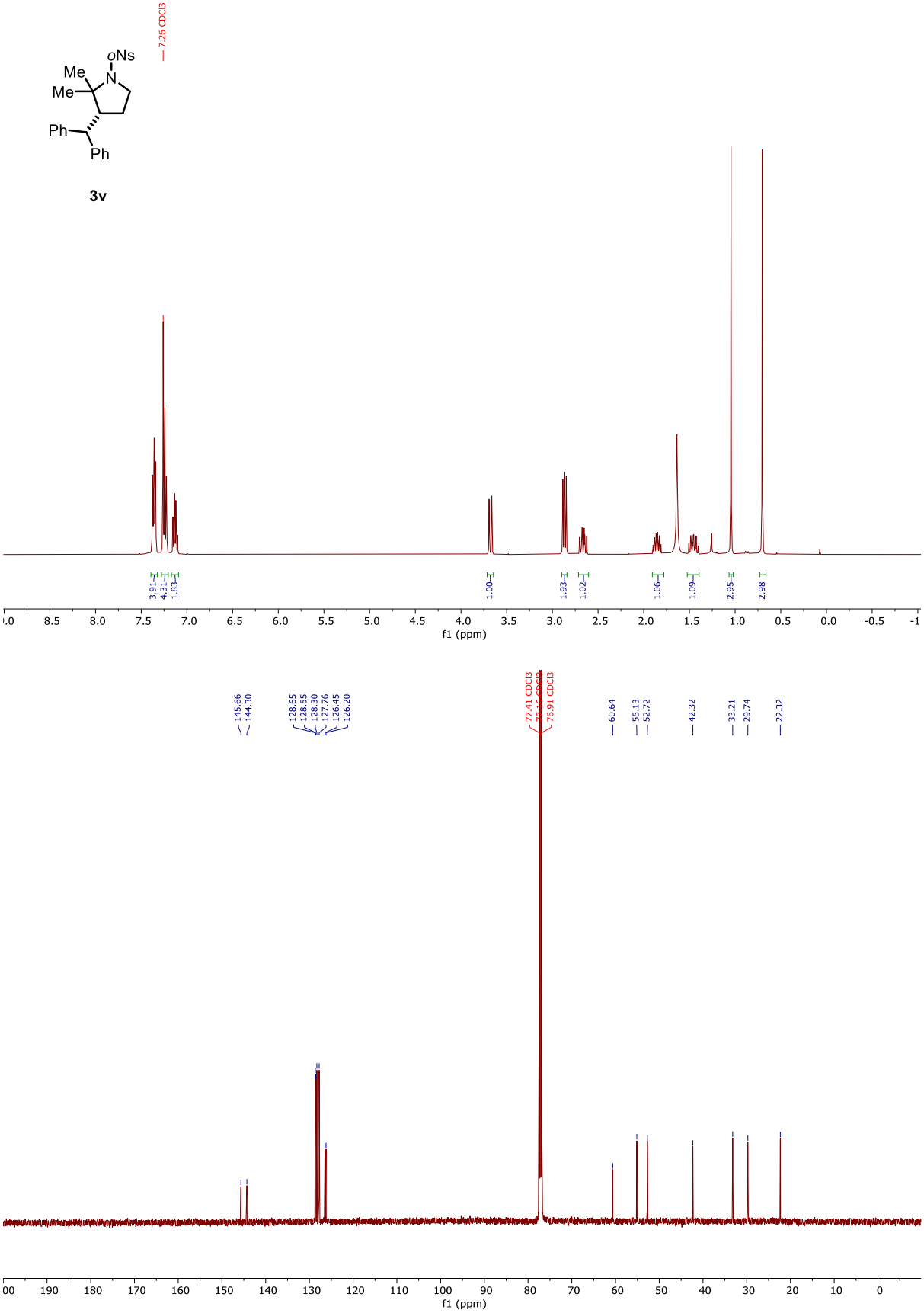



**3u**

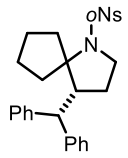


**(3v): (±)-3-Benzhydryl-2,2-dimethyl-1-[(2-nitrophenyl)sulfonyl]pyrrolidine**

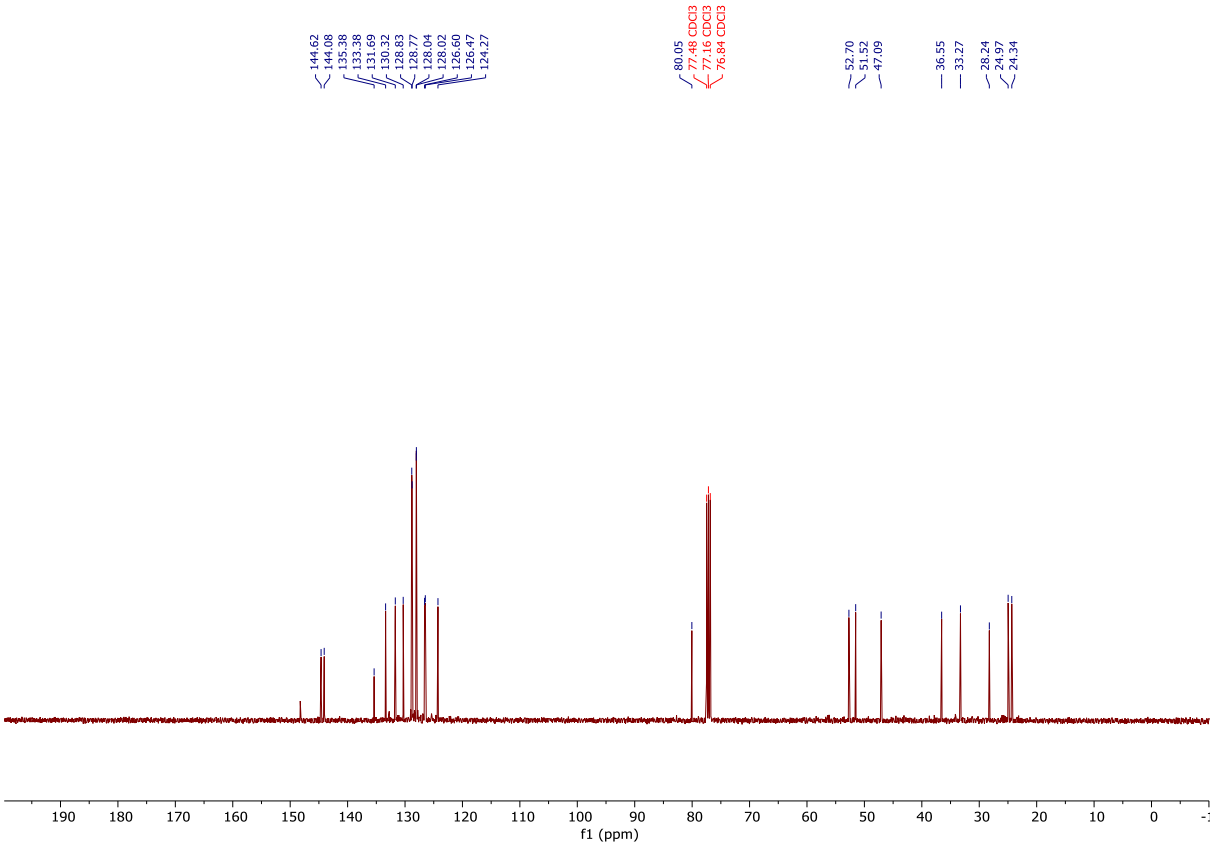


**(3w): (±)- 4-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-1-azaspiro[4.4]nonane**

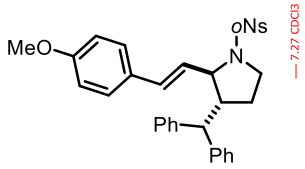



**3w**

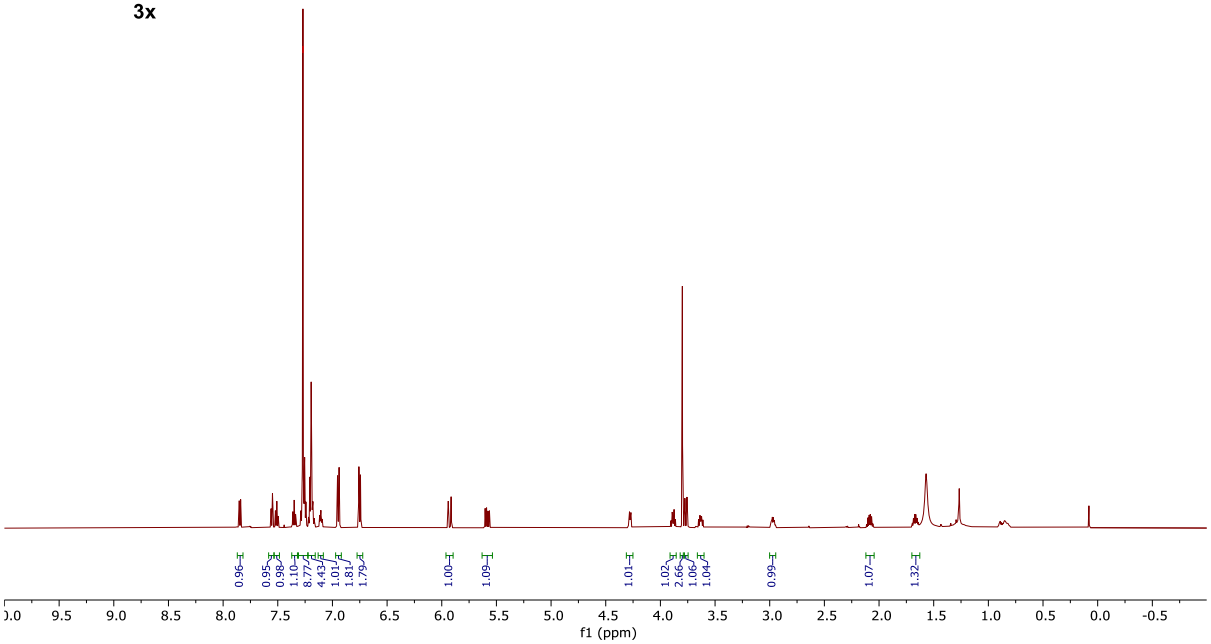


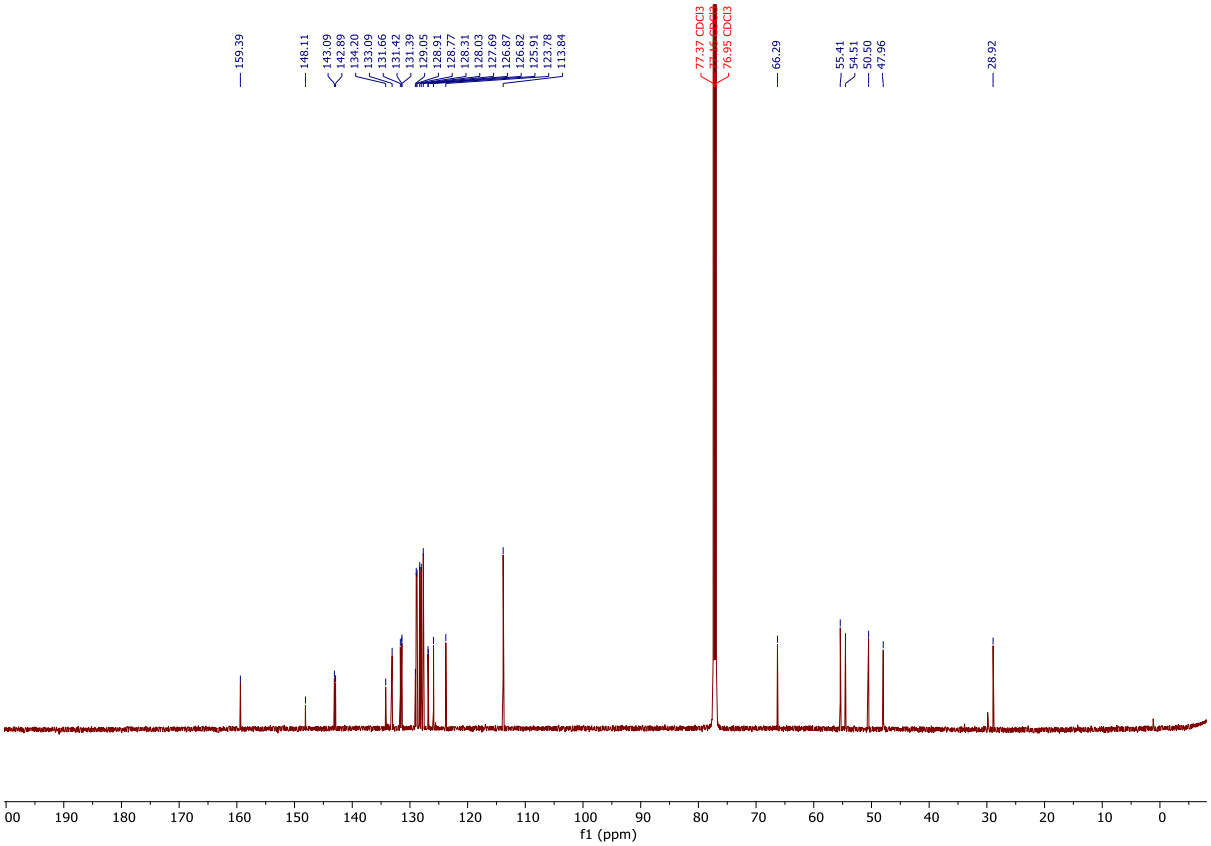



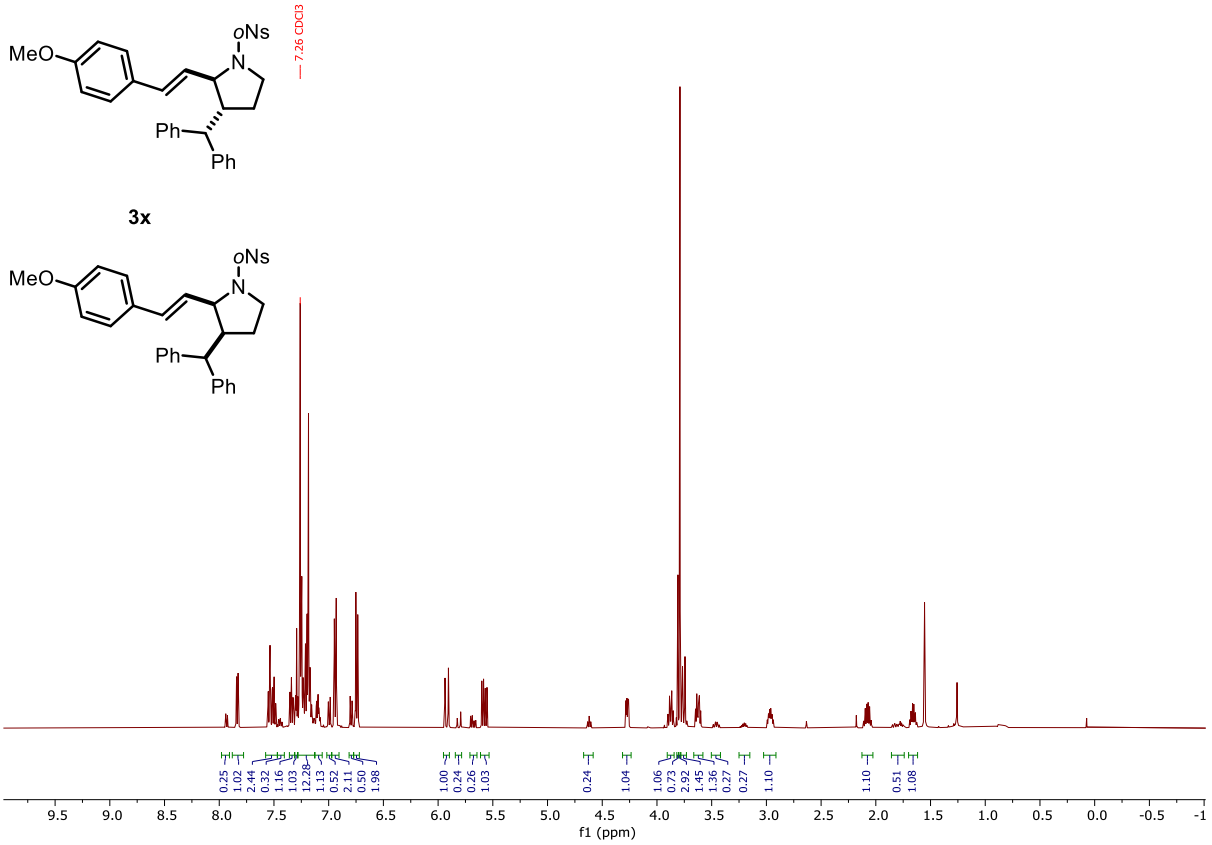
**(3x): (±)-(2*R*,3*R*)-3-Benzhydryl-2-[(1'*E*)-4-methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine and (±)-(2*R*,3*S*)-3-Benzhydryl-2-[(1'*E*)-4-methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-pyrrolidine**




**3x**

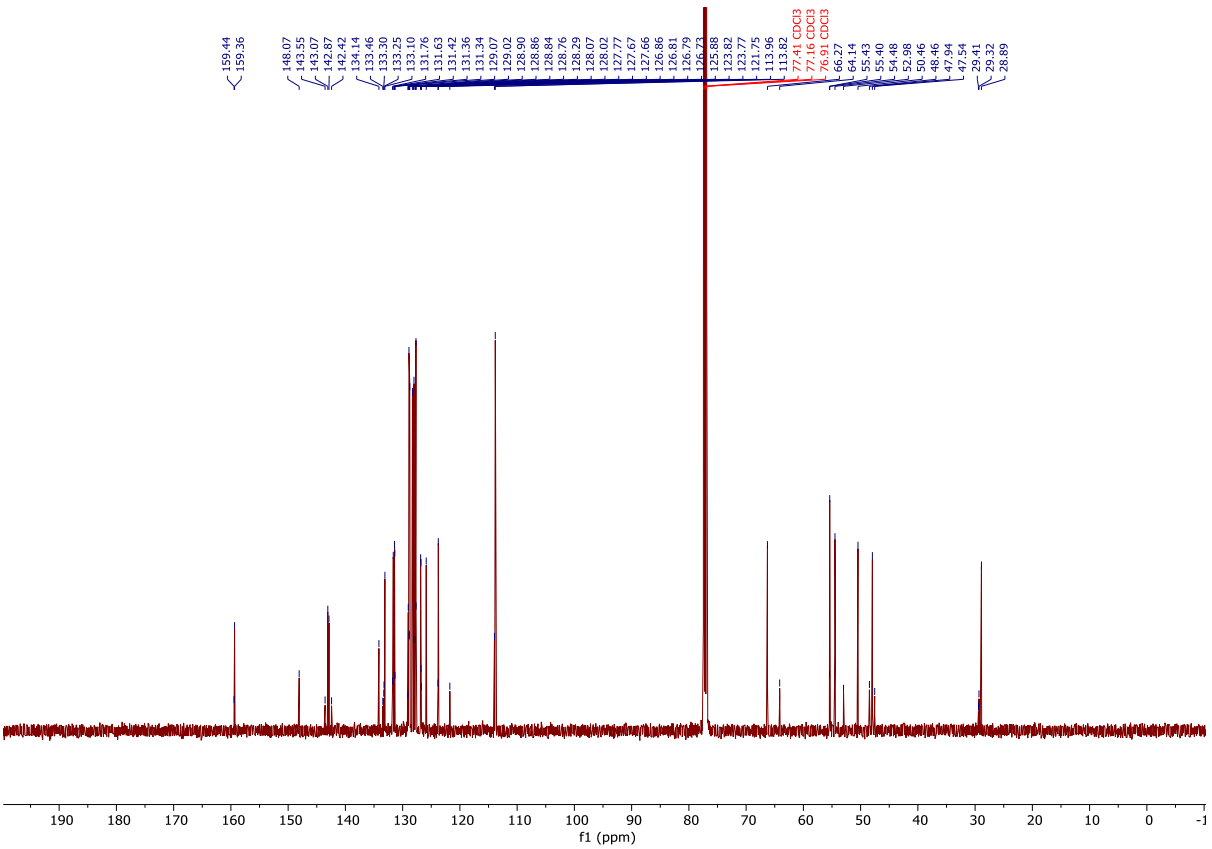


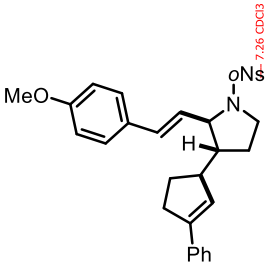

MeO
oNs
N
Ph
Ph
7.26 CDCl3
0.25
1.02
2.44
0.32
1.16
1.03
12.28
1.13
0.52
2.11
0.50
1.98
1.00
0.24
0.26
1.03
0.24
1.04
1.06
0.73
2.92
1.45
1.36
0.27
0.27
1.10
1.10
0.51
1.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

**3x**

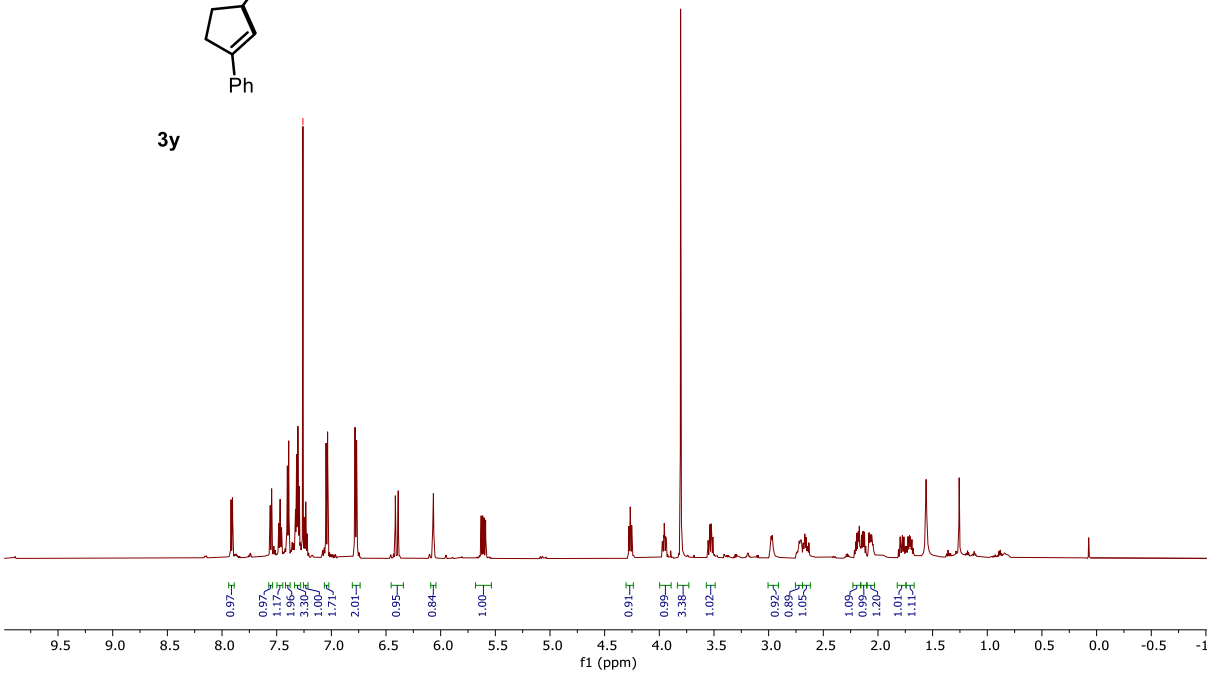

MeO
oNs
N
Ph
Ph

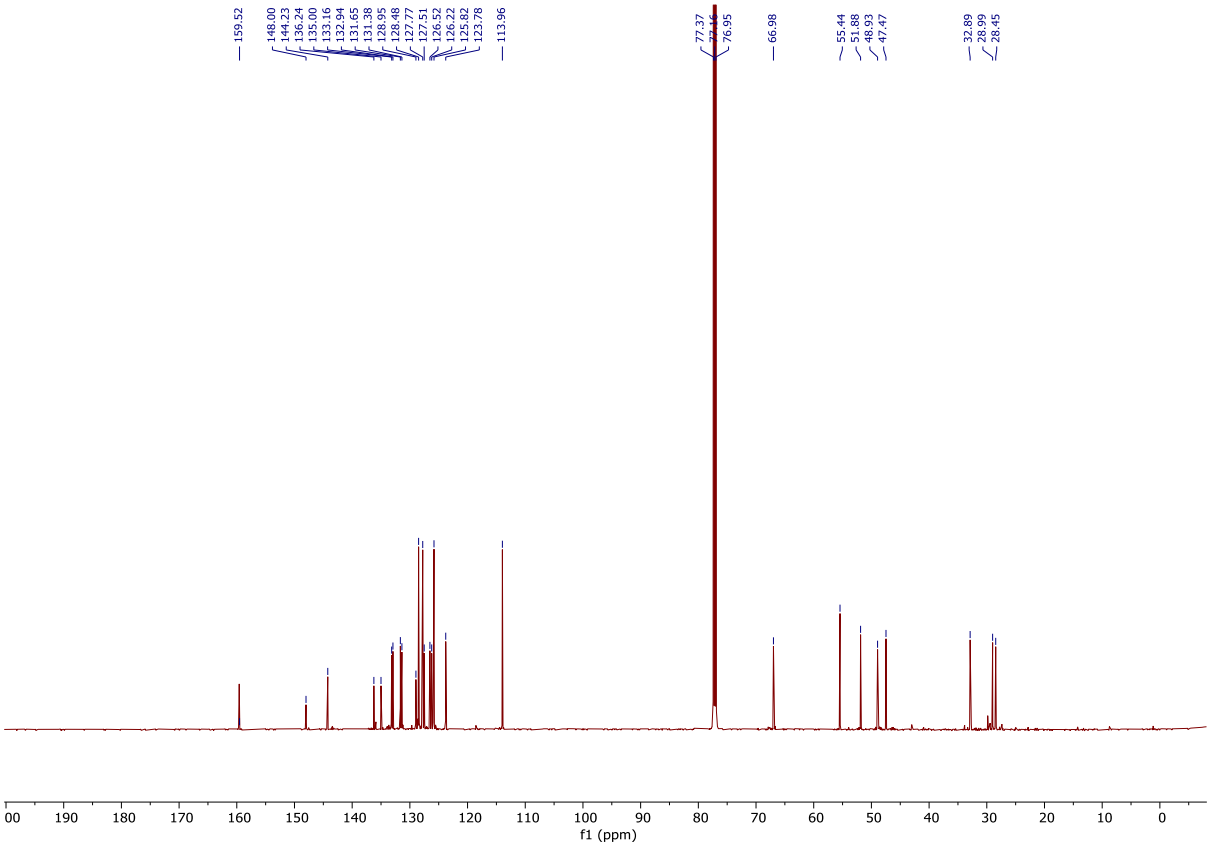

159.44
159.36
148.07
143.55
143.07
142.87
142.42
134.14
133.46
133.30
133.25
133.10
131.76
131.63
131.42
131.36
131.34
129.07
129.02
128.90
128.86
128.84
128.76
128.29
128.07
128.02
127.77
127.67
127.66
126.86
126.81
126.79
126.73
125.88
123.82
123.77
121.75
113.96
113.82
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.27
64.14
55.43
55.40
54.48
52.98
50.46
48.46
47.94
47.54
29.41
29.32
28.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

**(3y): (±)-(2*R*,3*R*)-2-[(1'*E*)-4-Methoxystyryl]-1-[(2-nitrophenyl)sulfonyl]-3-[(1''*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**

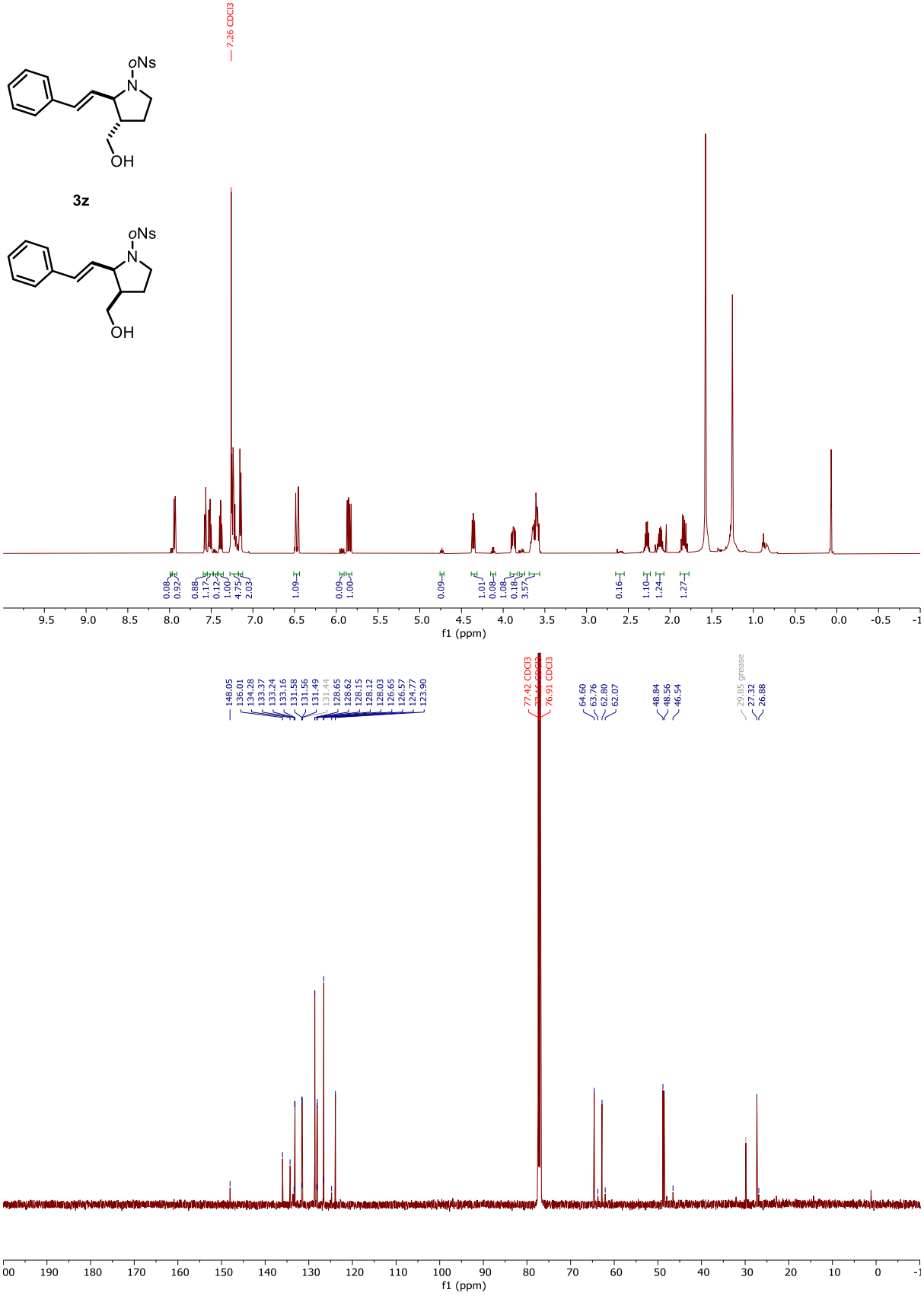



**3y**

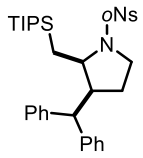


**(3z): (±)-{(2*R*,3*S*)-1-[(2-Nitrophenyl)sulfonyl]-2-[(1'*E*)-styryl]pyrrolidin-3-yl}methanol and (±)-{(2*R*,3*R*)-1-[(2-Nitrophenyl)sulfonyl]-2-[(1'*E*)-styryl]pyrrolidin-3-yl}methanol**

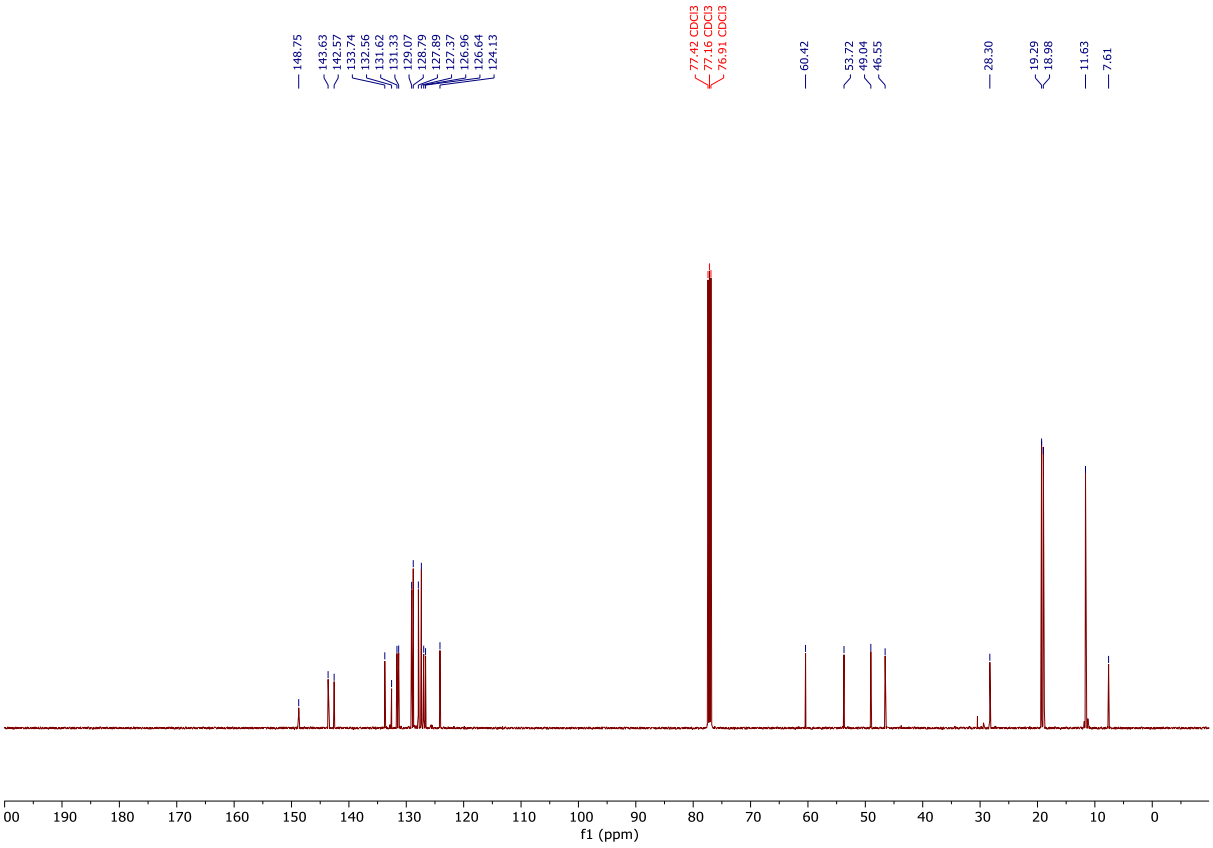


**(*cis*-3aa): (±)-(2*S*,3*S*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)methyl]-pyrrolidine**

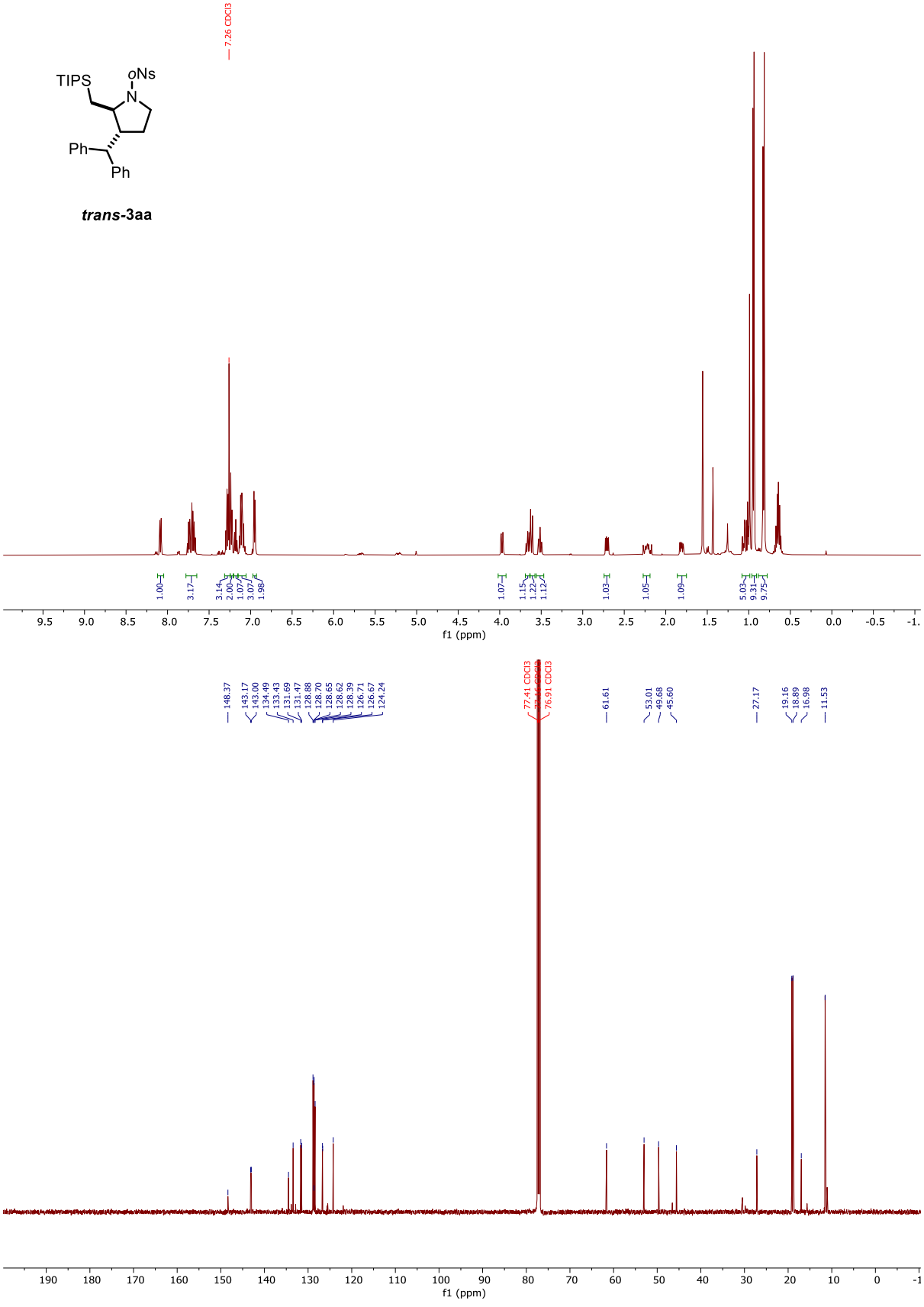



***cis*-3aa**

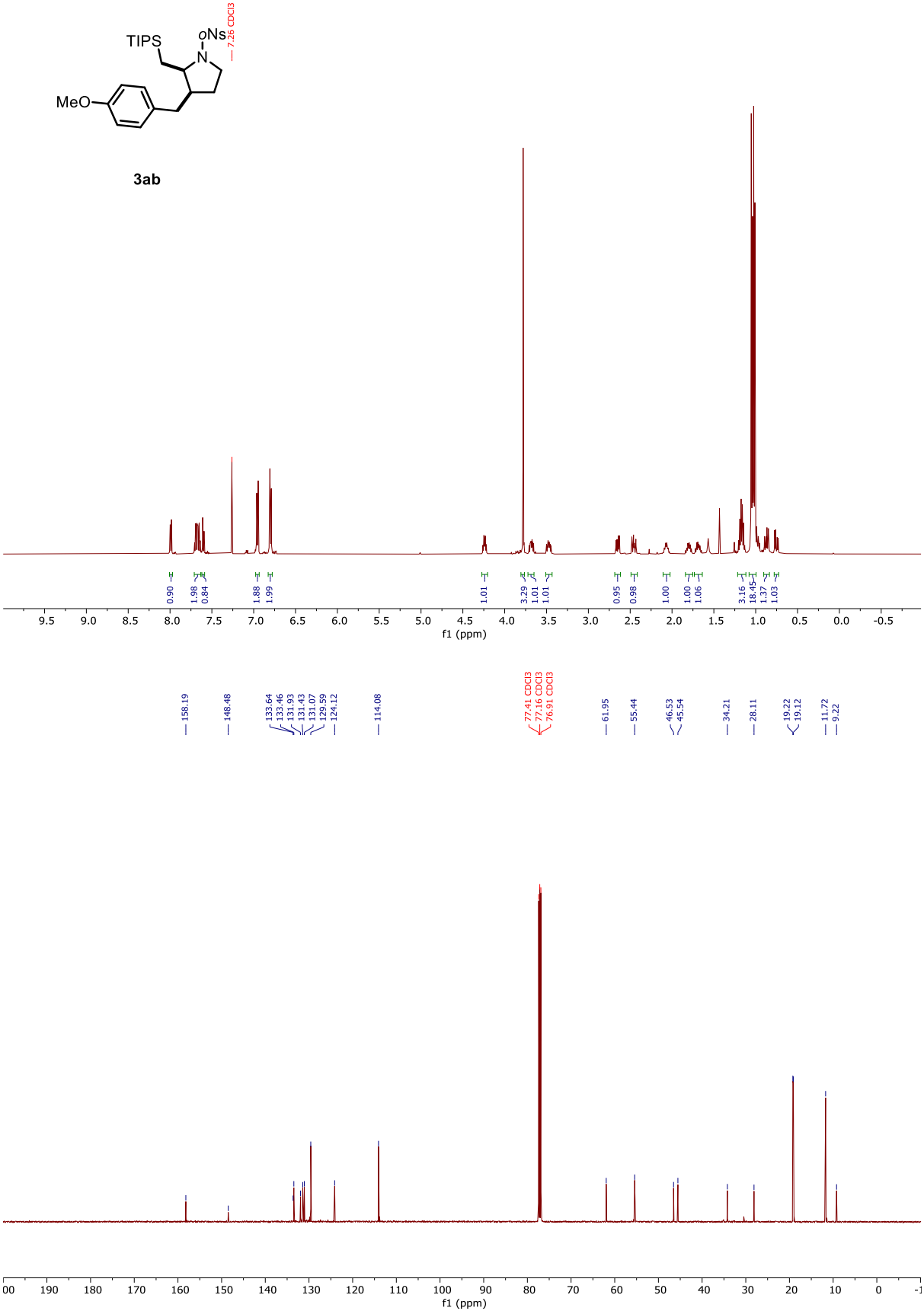


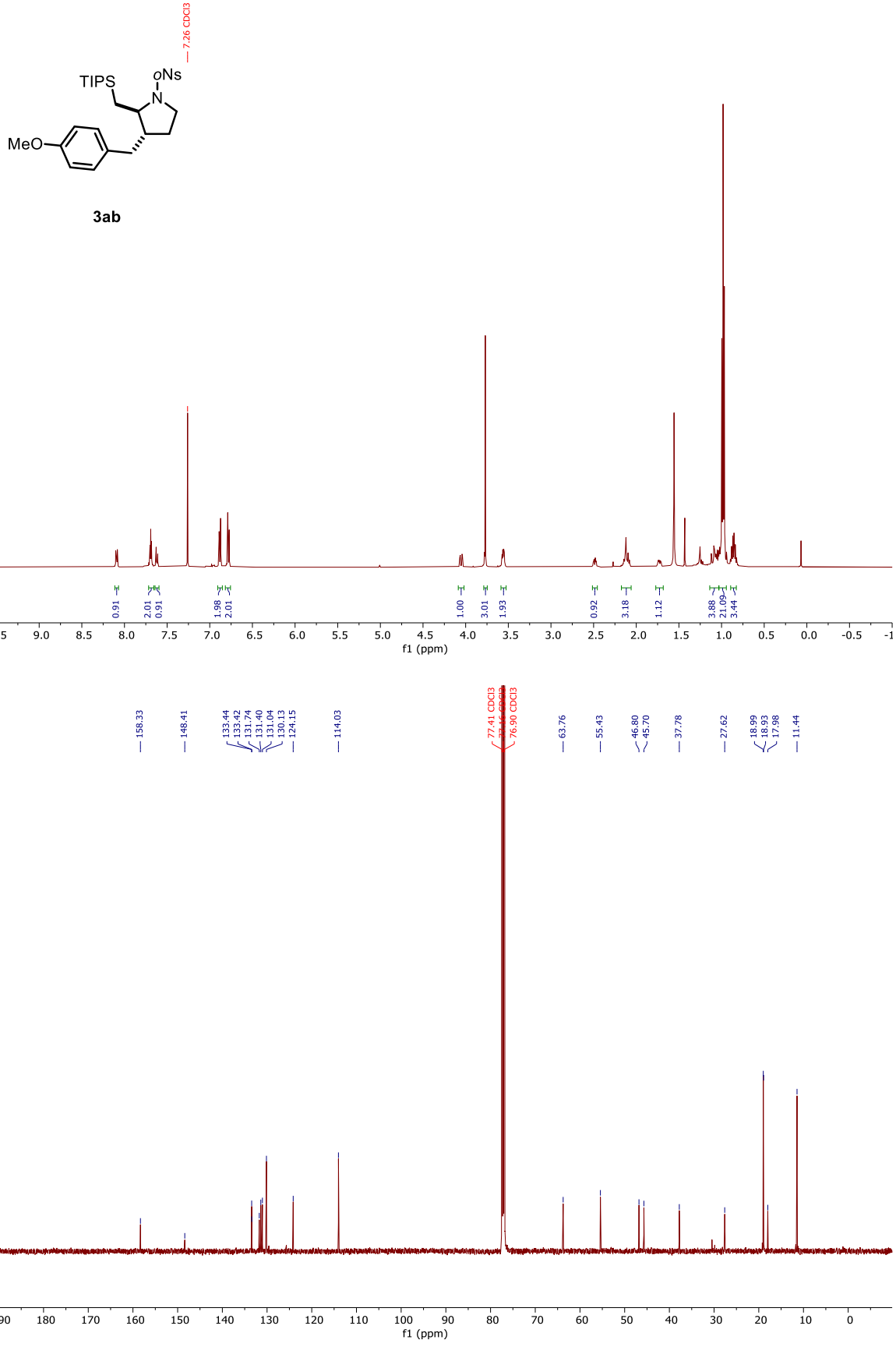
**(*trans*-3aa): (±)-(2*S*,3*R*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)methyl]-pyrrolidine**



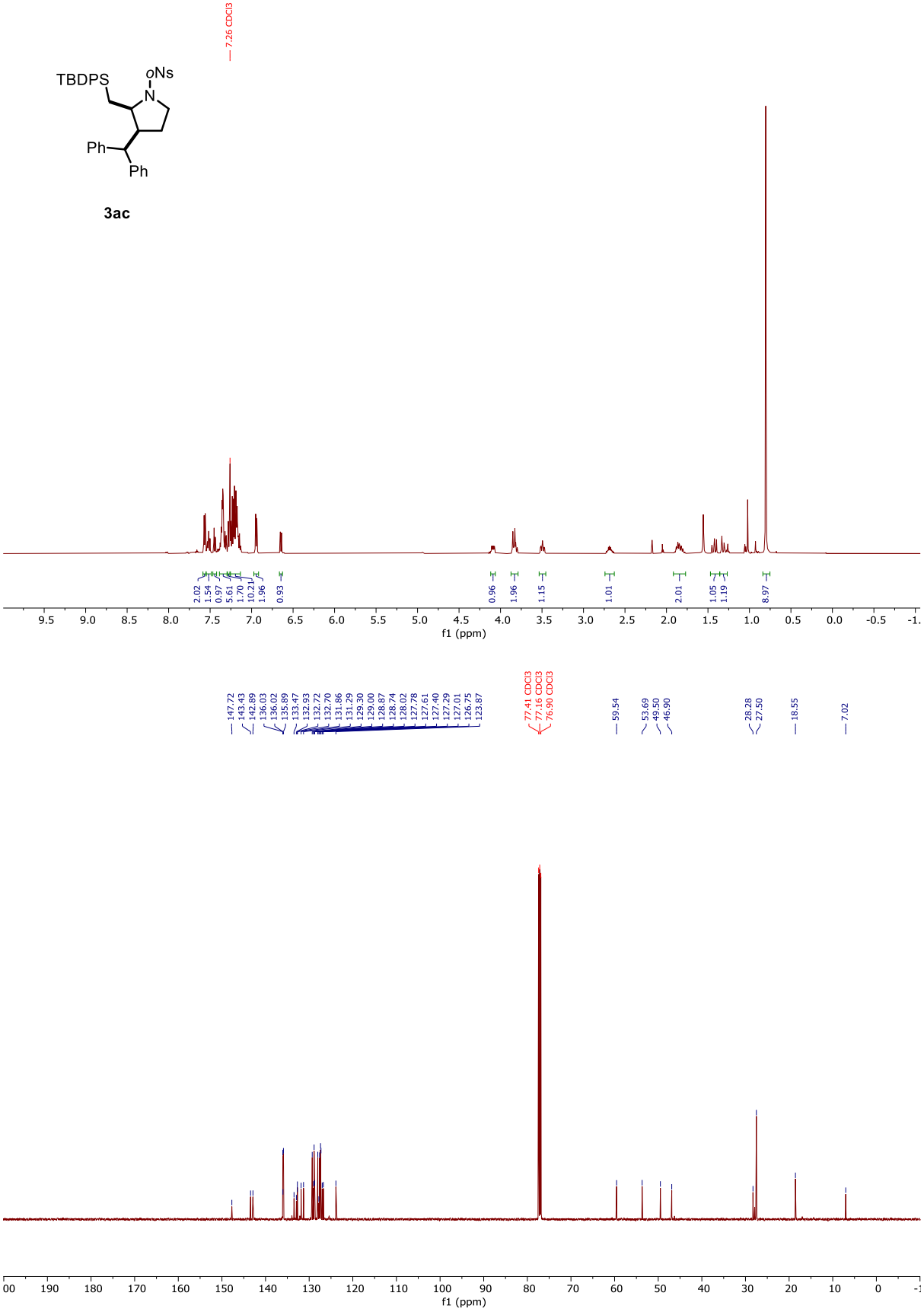
**(*cis*-3ab): (±)-(2*S*,3*R*)-3-(4-Methoxybenzyl)-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)-methyl]-pyrrolidine**



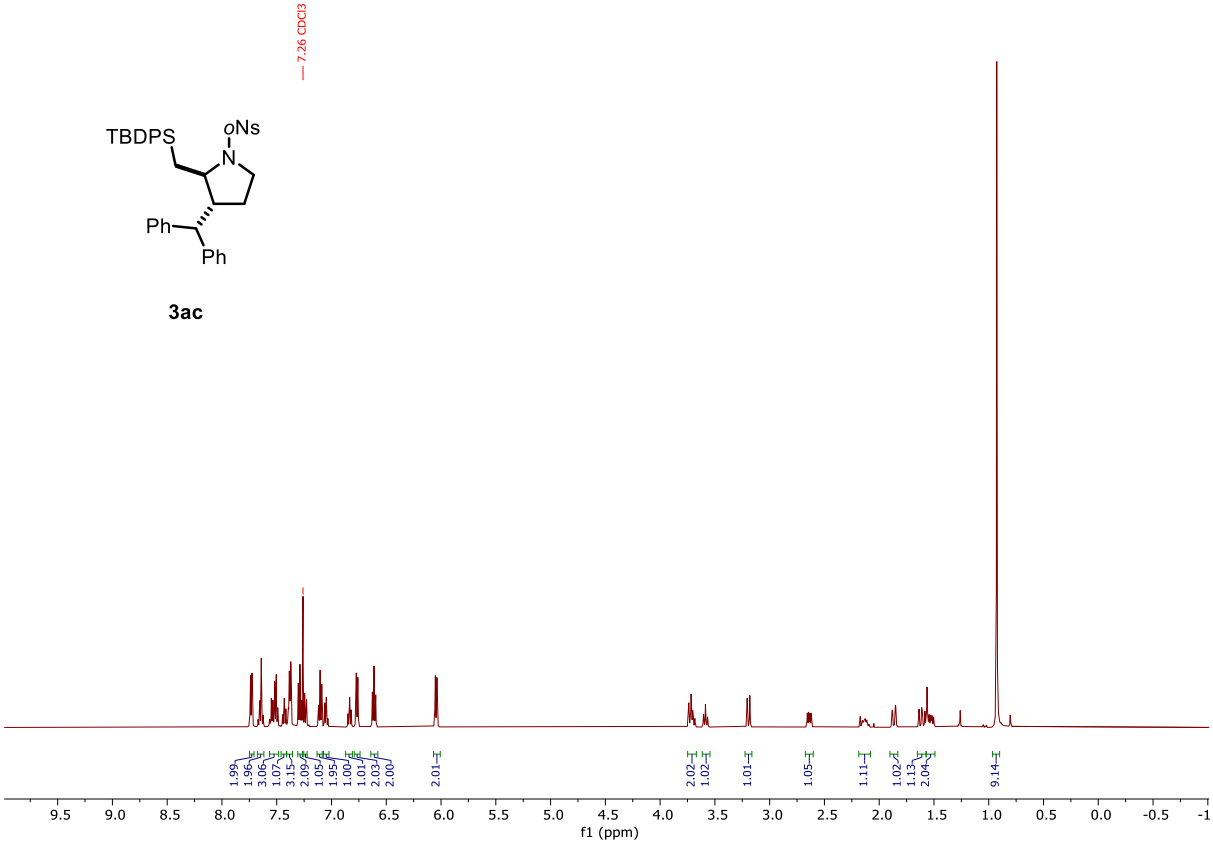
**(*trans*-3ab): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-1-[(2-nitrophenyl)sulfonyl]-2-[(triisopropylsilyl)-methyl]-pyrrolidine**

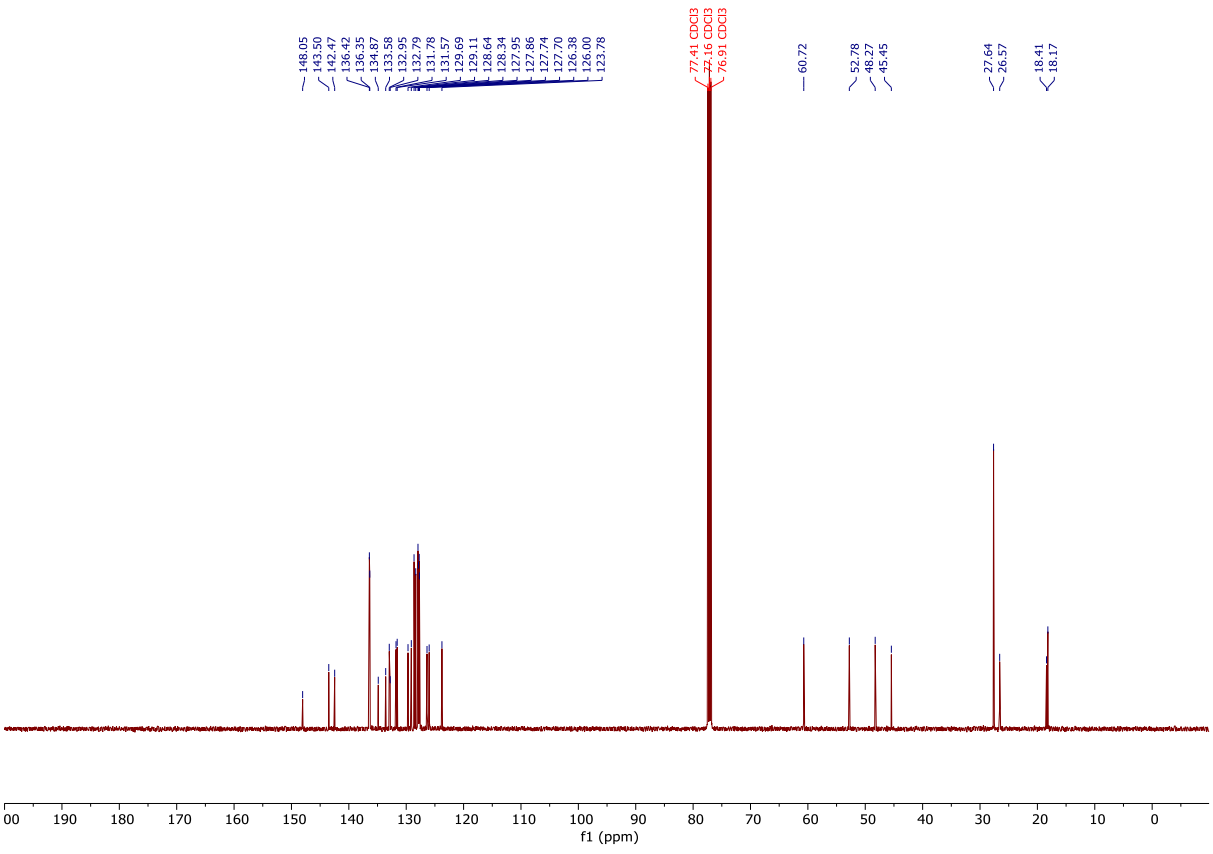


**(*cis*-3ac): (±)-(2*S*,3*S*)-3-Benzhydryl-2-[(*tert*-butyldiphenylsilyl)methyl]-1-[(2-nitrophenyl)-sulfonyl]-pyrrolidine**

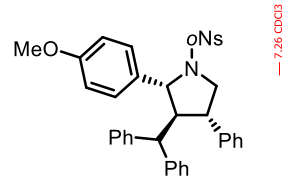


**(*trans*-3ac): (±)-(2*S*,3*R*)-3-Benzhydryl-2-[(*tert*-butyldiphenylsilyl)methyl]-1-[(2-nitrophenyl)-sulfonyl]-pyrrolidine**

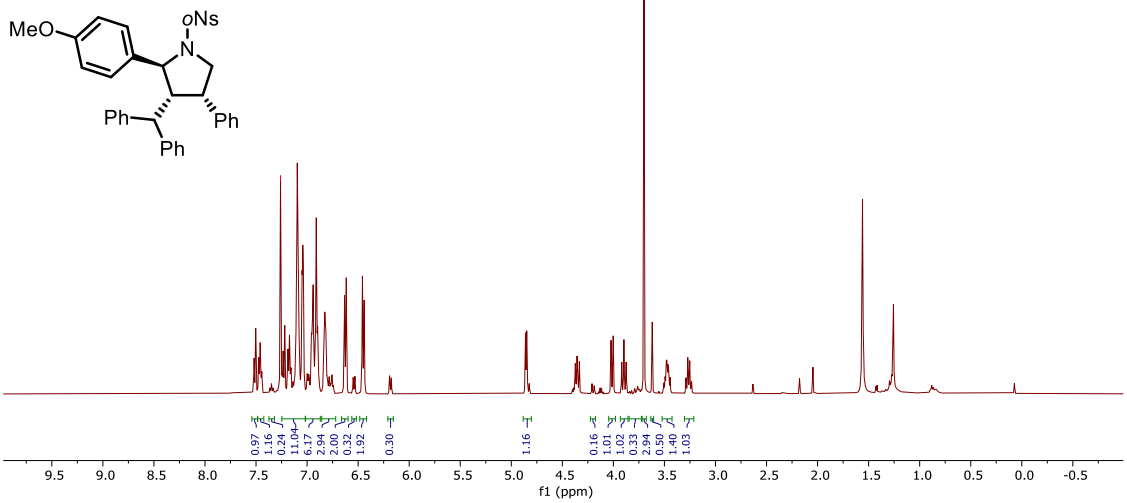


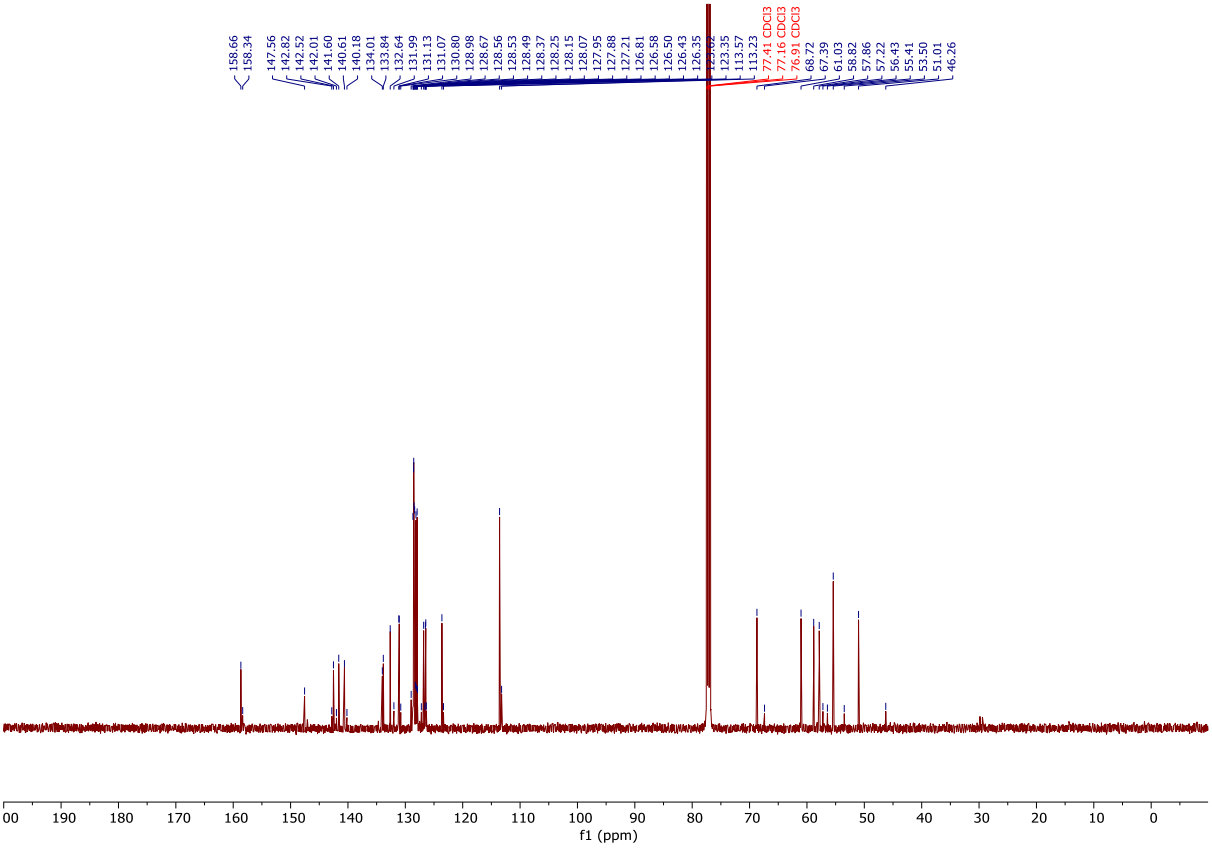



**((–)-3ad): (–)-(2*R*,3*R*,4*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenyl-pyrrolidine and (–)-(2*S*,3*S*,4*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-[(2-nitro-phenyl)sulfonyl]-4-phenylpyrrolidine**

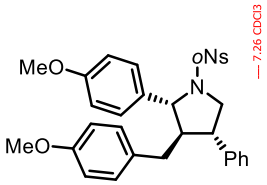



**(-)-3ad**

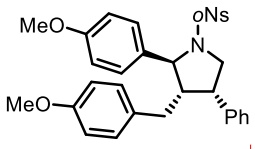


**((–)-3ae): (–)-(2*R*,3*R*,4*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenylpyrrolidine and (–)-(2*S*,3*S*,4*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenylpyrrolidine**

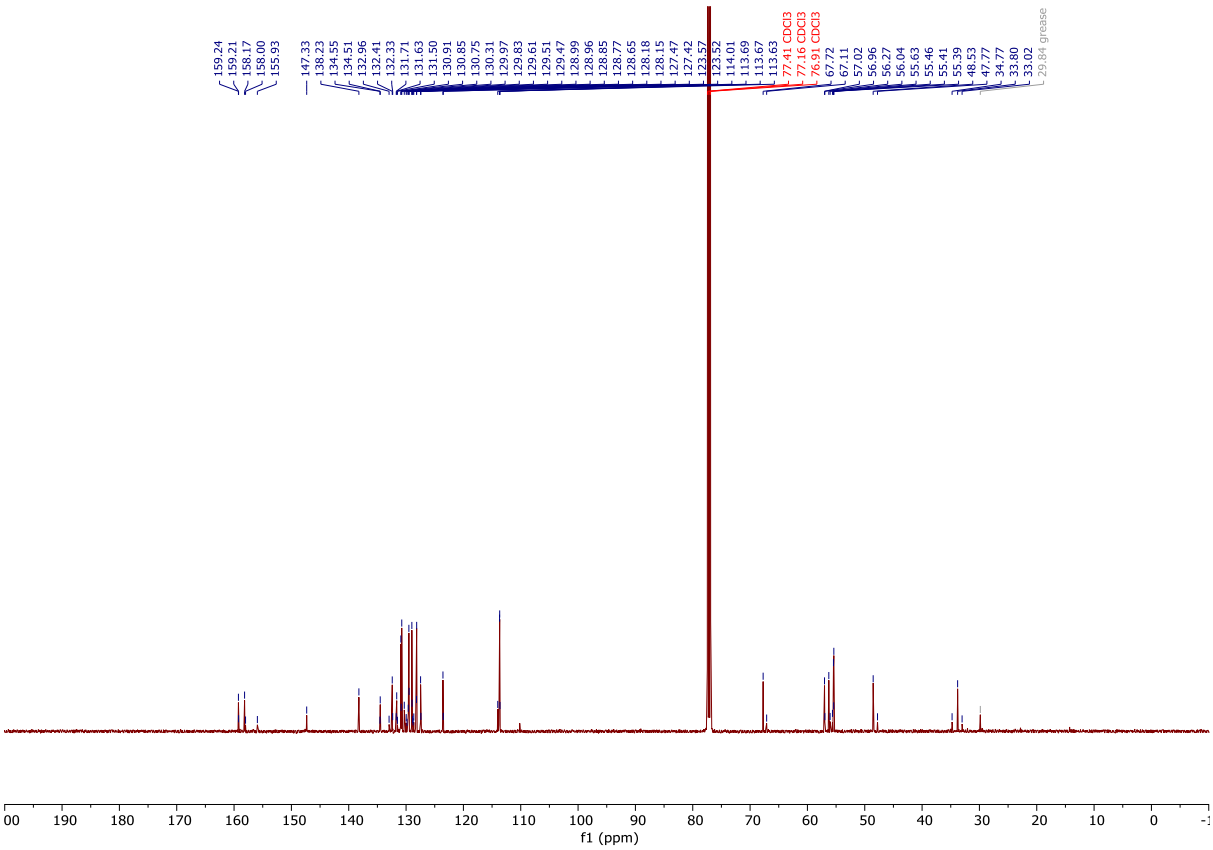



**(-)-3ae**

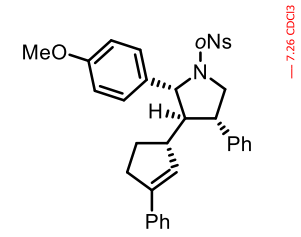




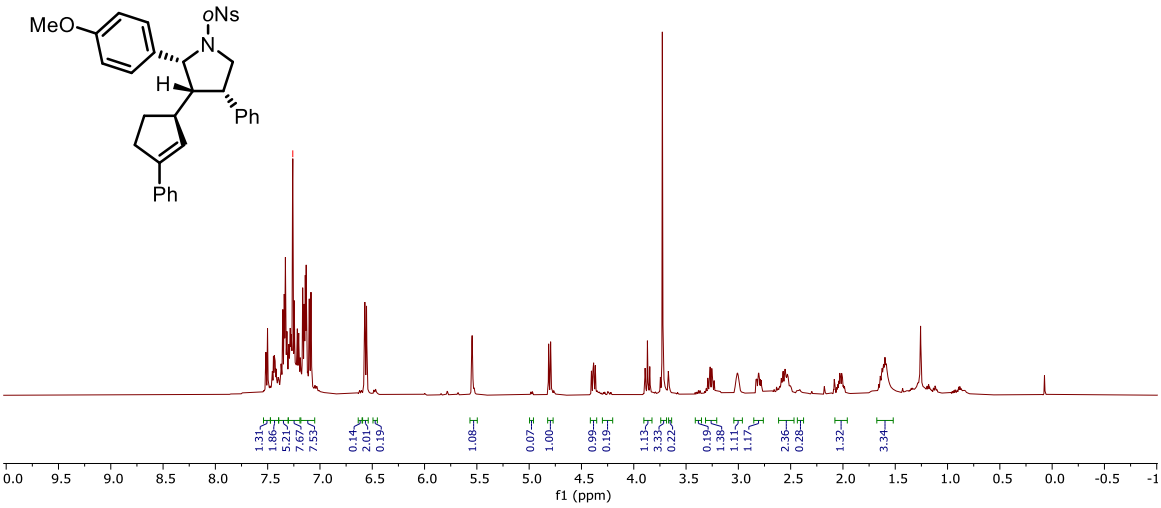


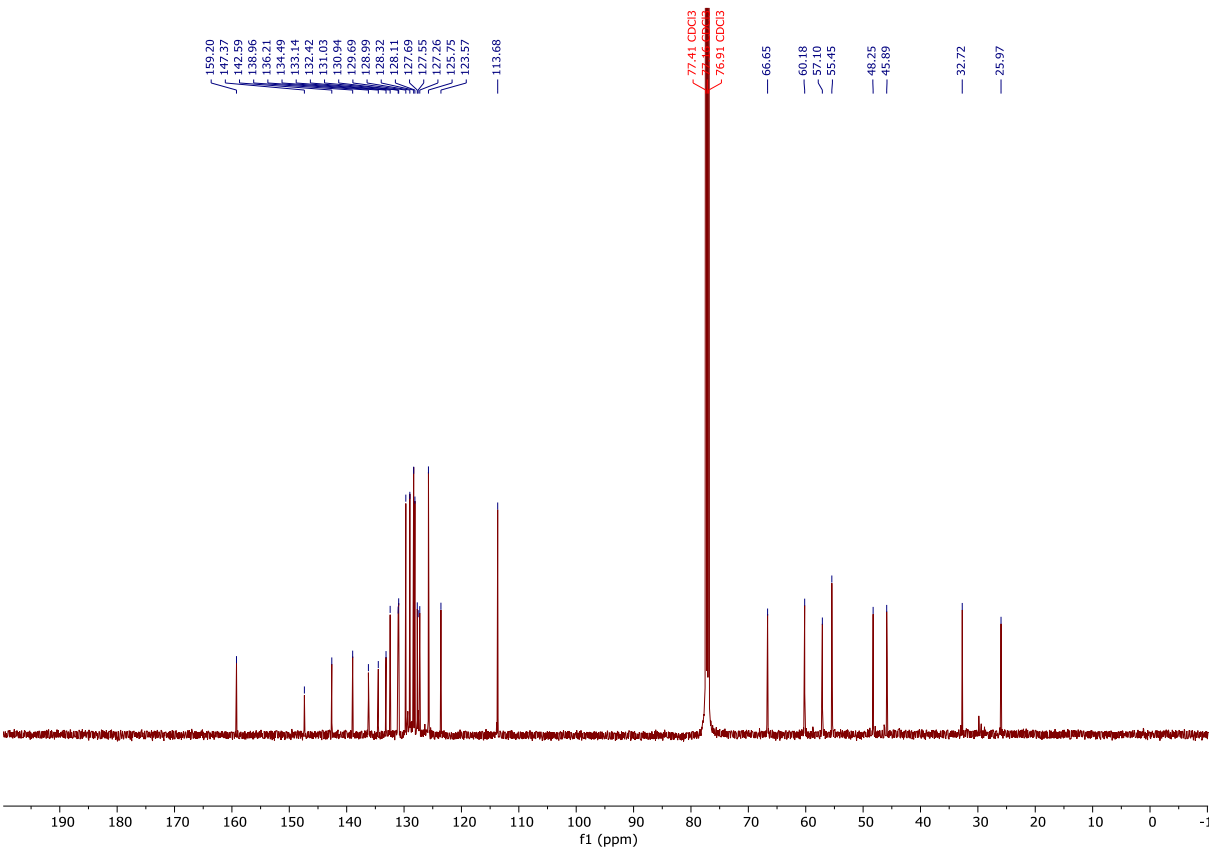


**((–)-3af): (–)-(2*R*,3*R*,4*S*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenyl-3-[(1'*S*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine and (–)-(2*S*,3*S*,4*S*)-2-(4-Methoxyphenyl)-1-[(2-nitrophenyl)sulfonyl]-4-phenyl-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**

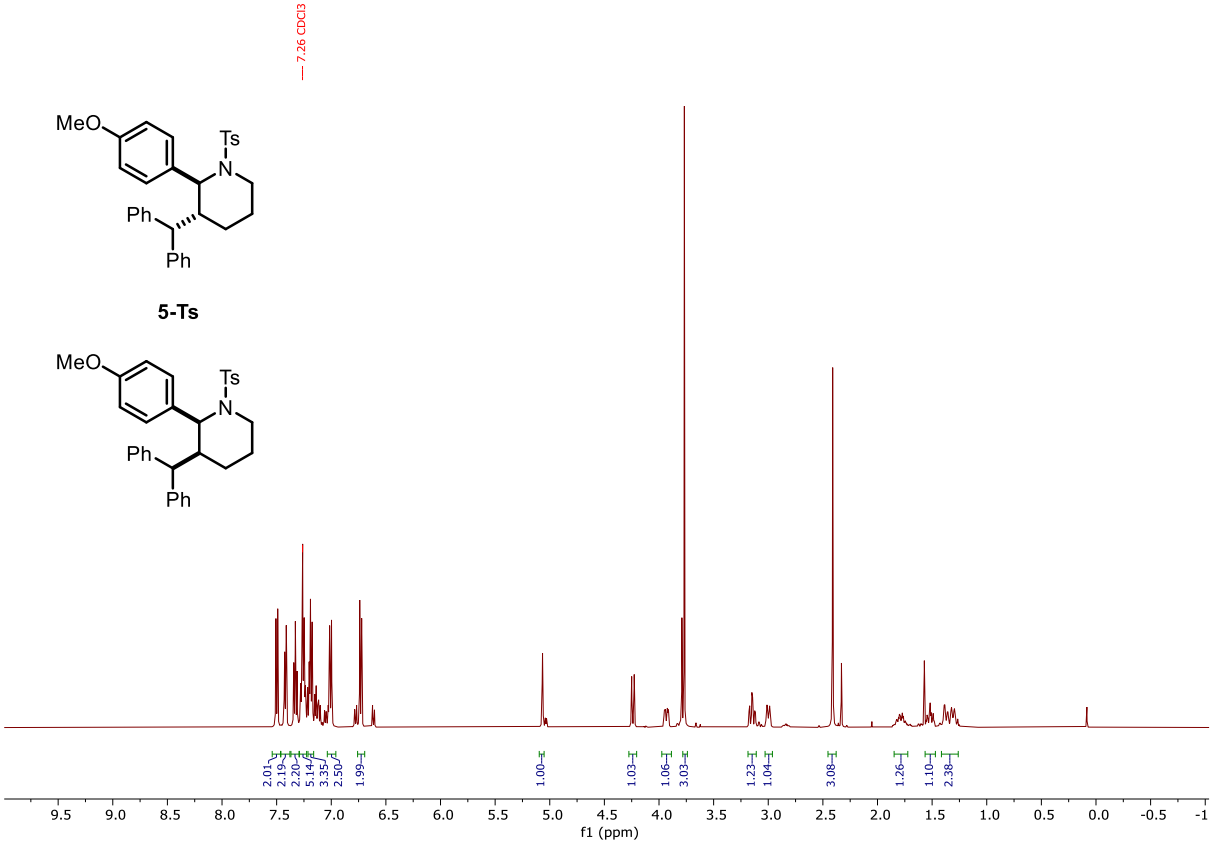


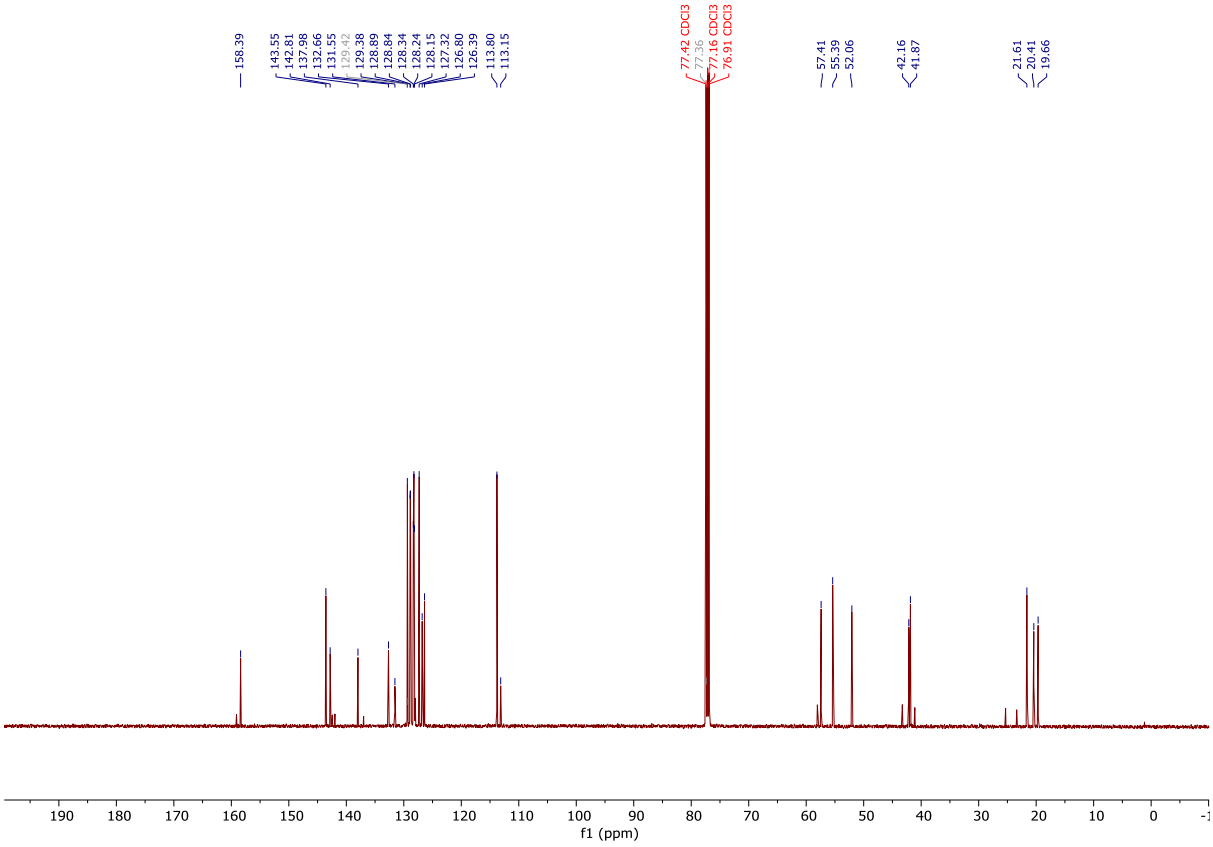

**(-)-3af**



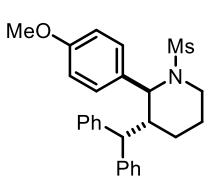



**(5-Ts): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-tosylpiperidine and (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-tosylpiperidine**

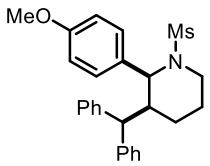


**(5-Ms): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-(methylsulfonyl)piperidine and (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-(methylsulfonyl)piperidine**

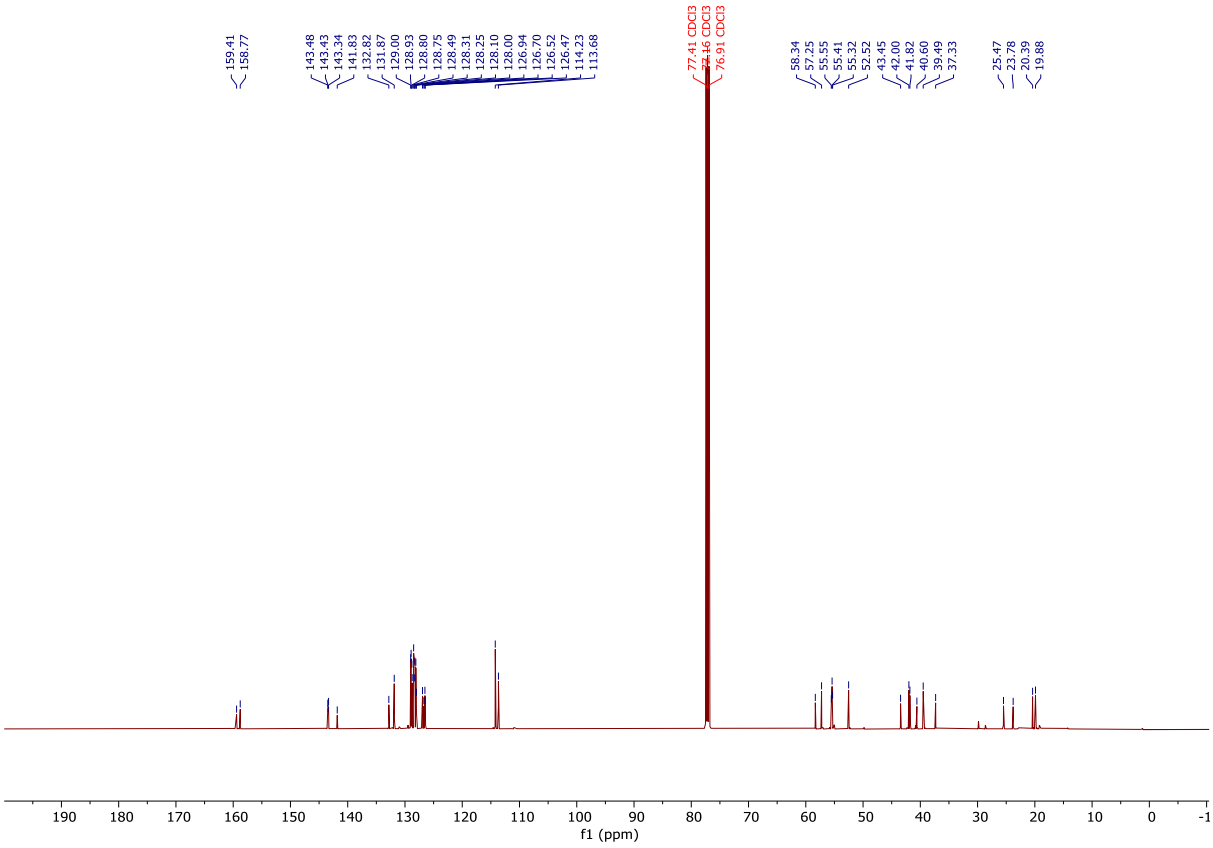



**5-Ms**

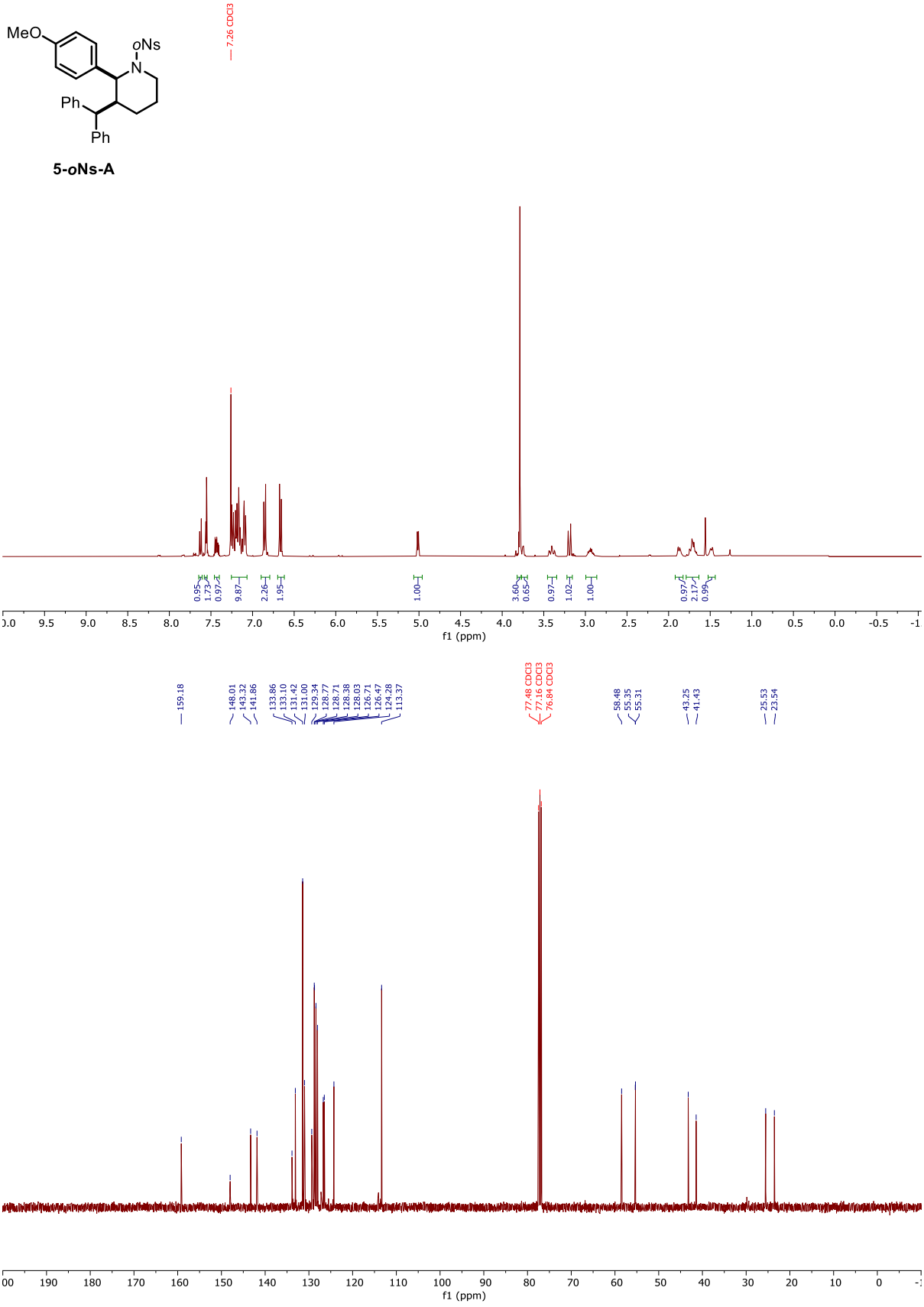




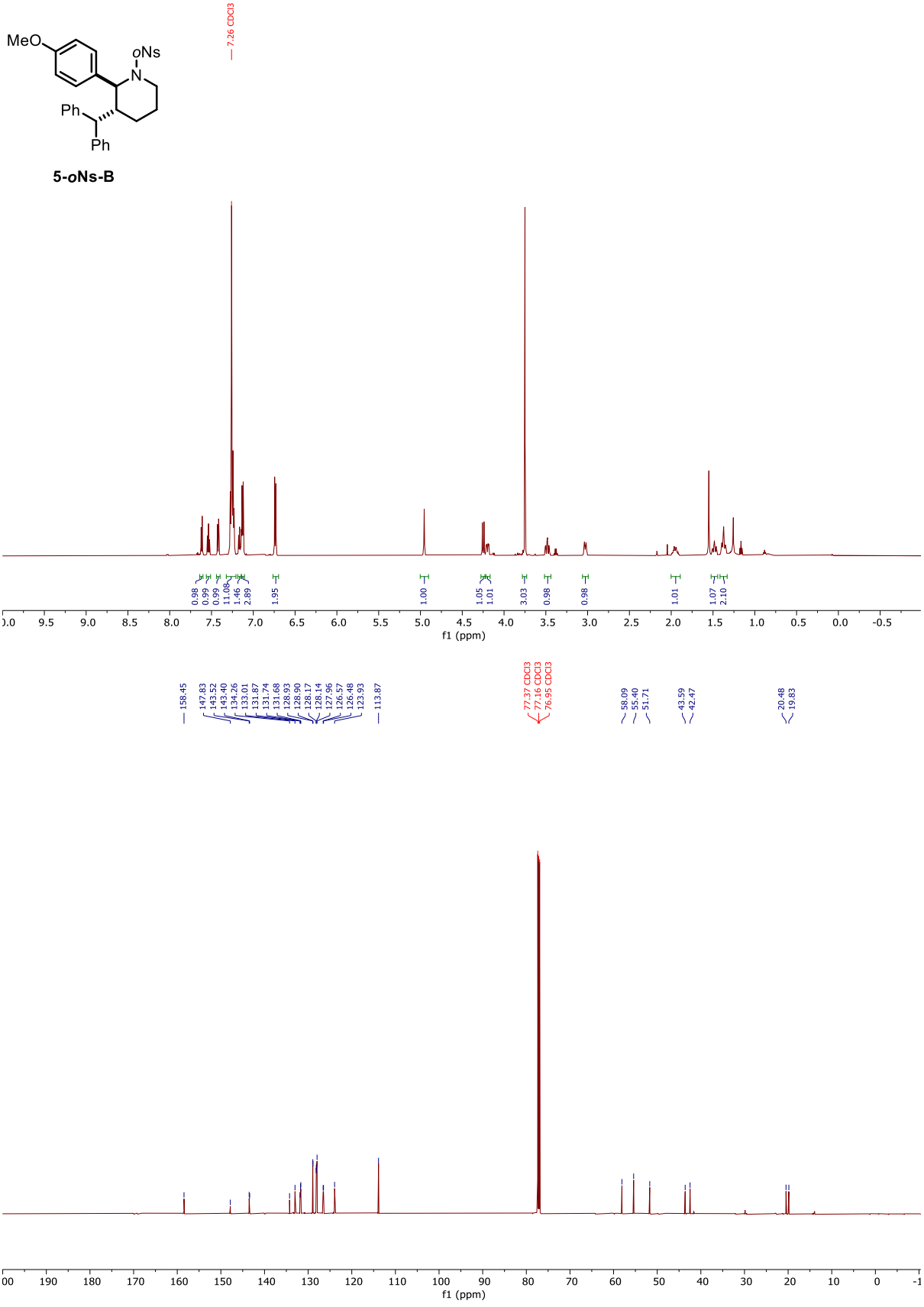




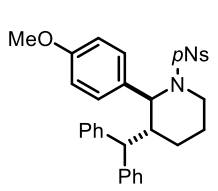
**(5-*o*Ns-A): (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine**



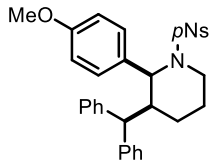
**(5-*o*Ns-B): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine**



**(5-*p*Ns): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine and (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidine**

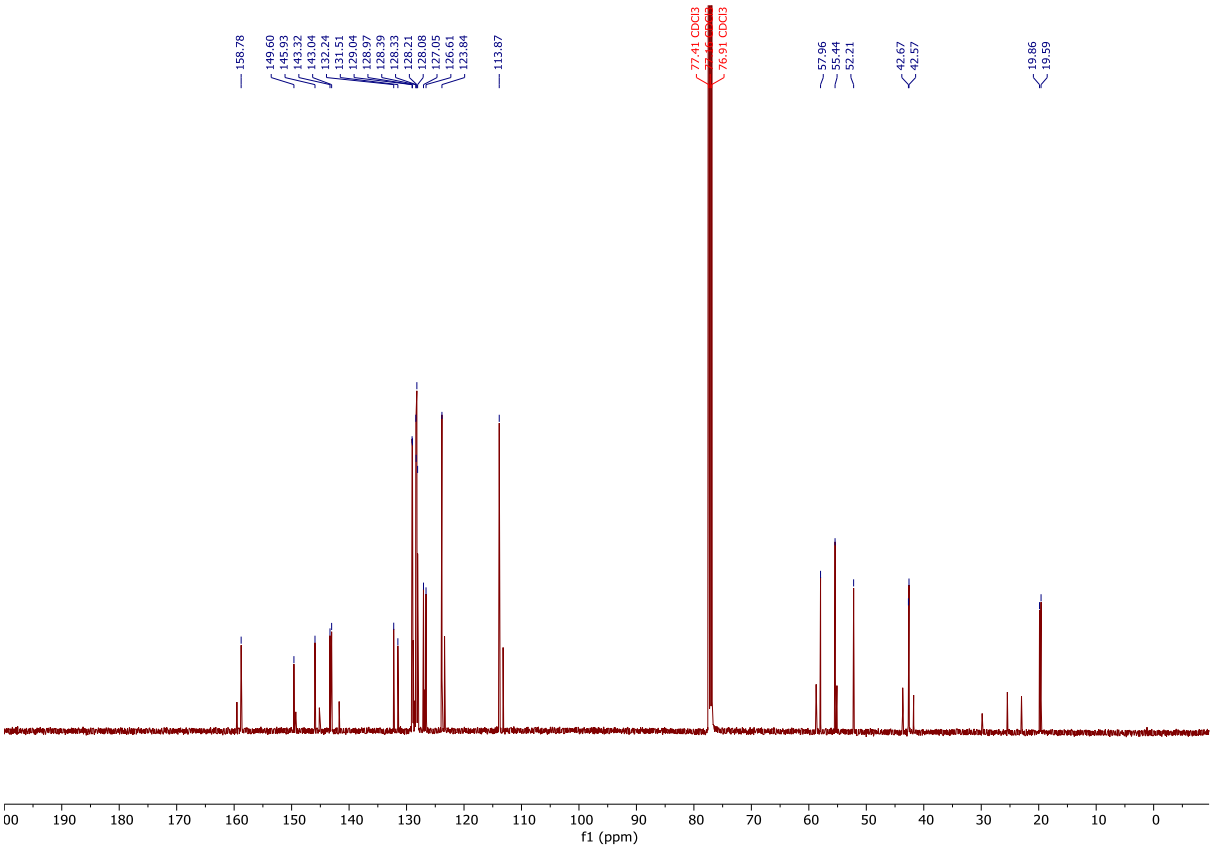



**5-*p*Ns**

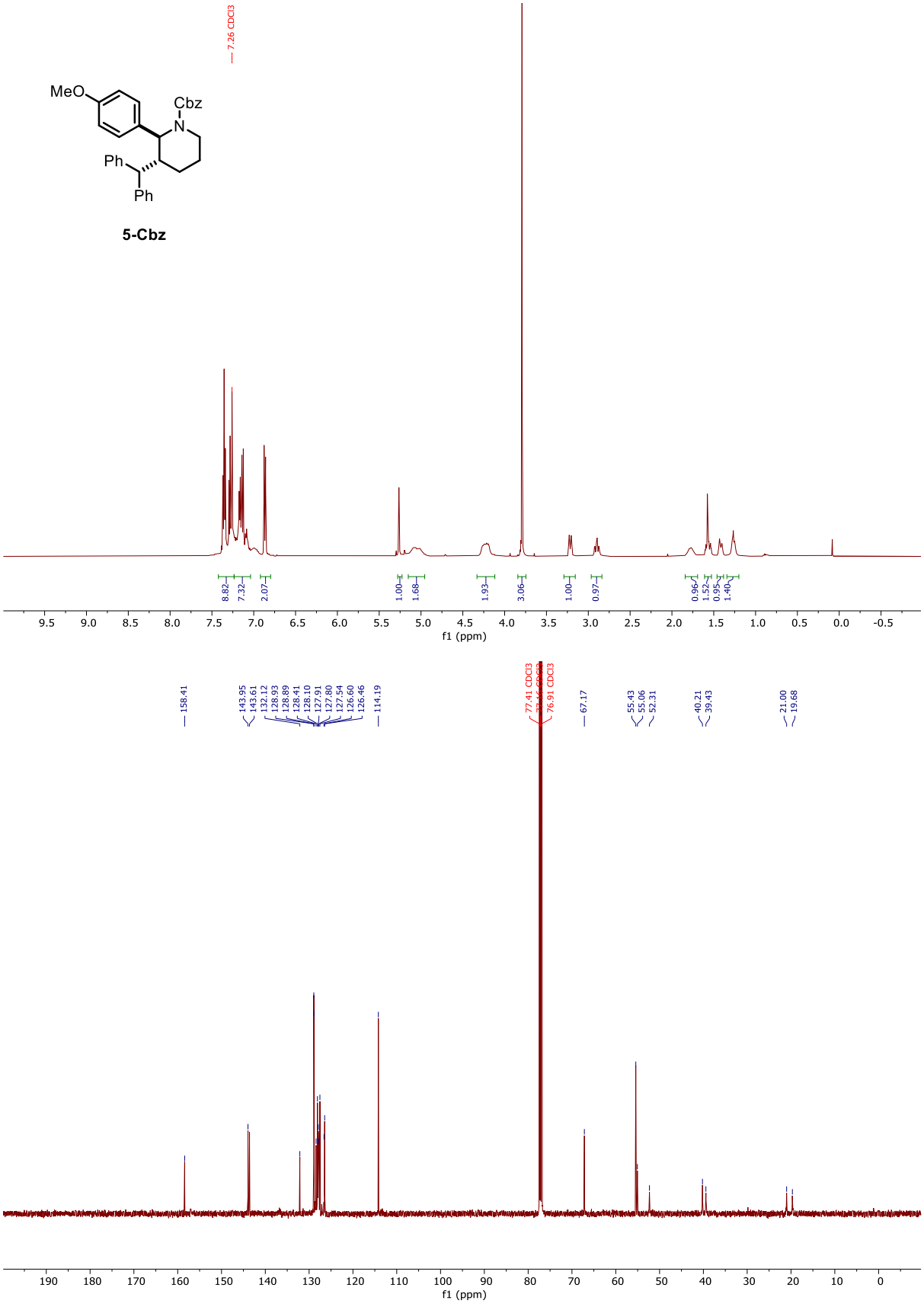




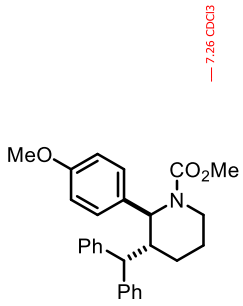




**(5-Cbz): (±)-Benzyl (2*S*,3*R*)-3-benzhydryl-2-(4-methoxyphenyl)piperidine-1-carboxylate**

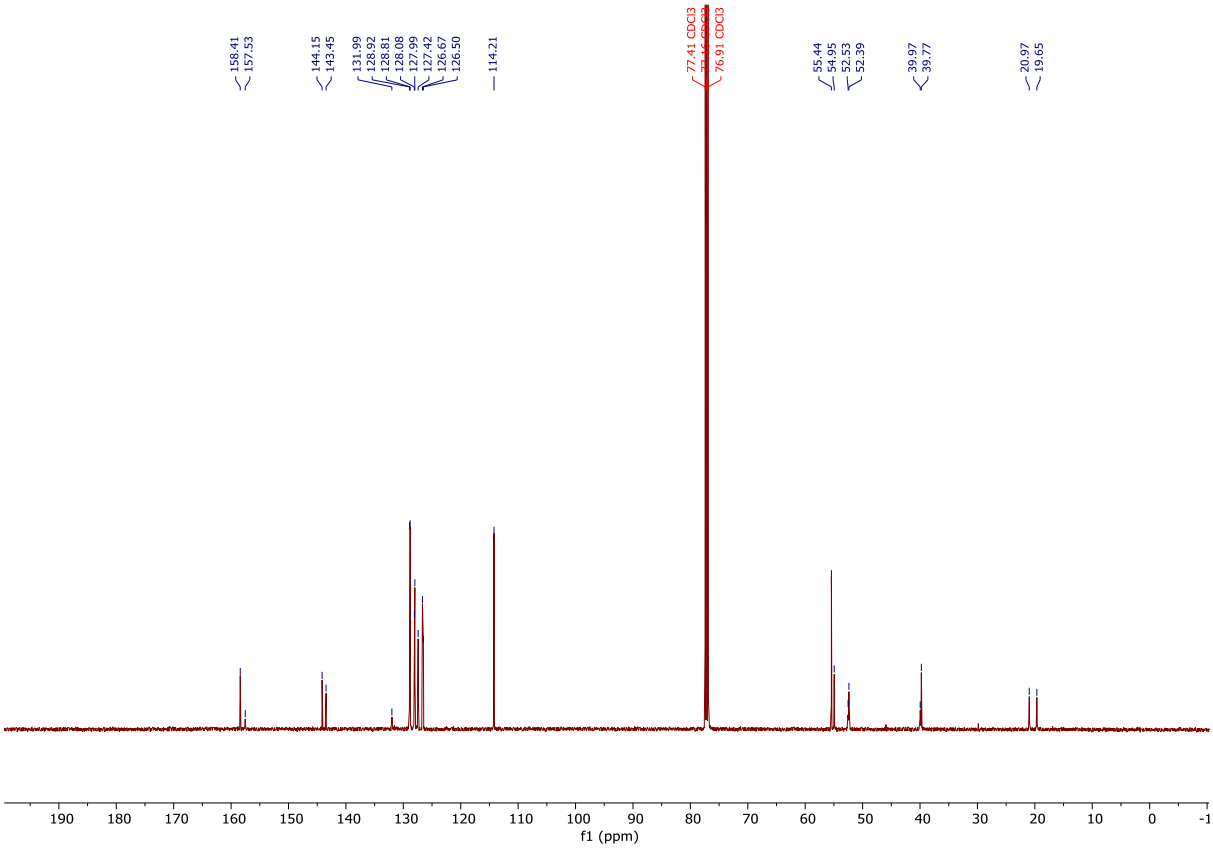


**(5a): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-2-(4-methoxyphenyl)piperidine-1-carboxylate**

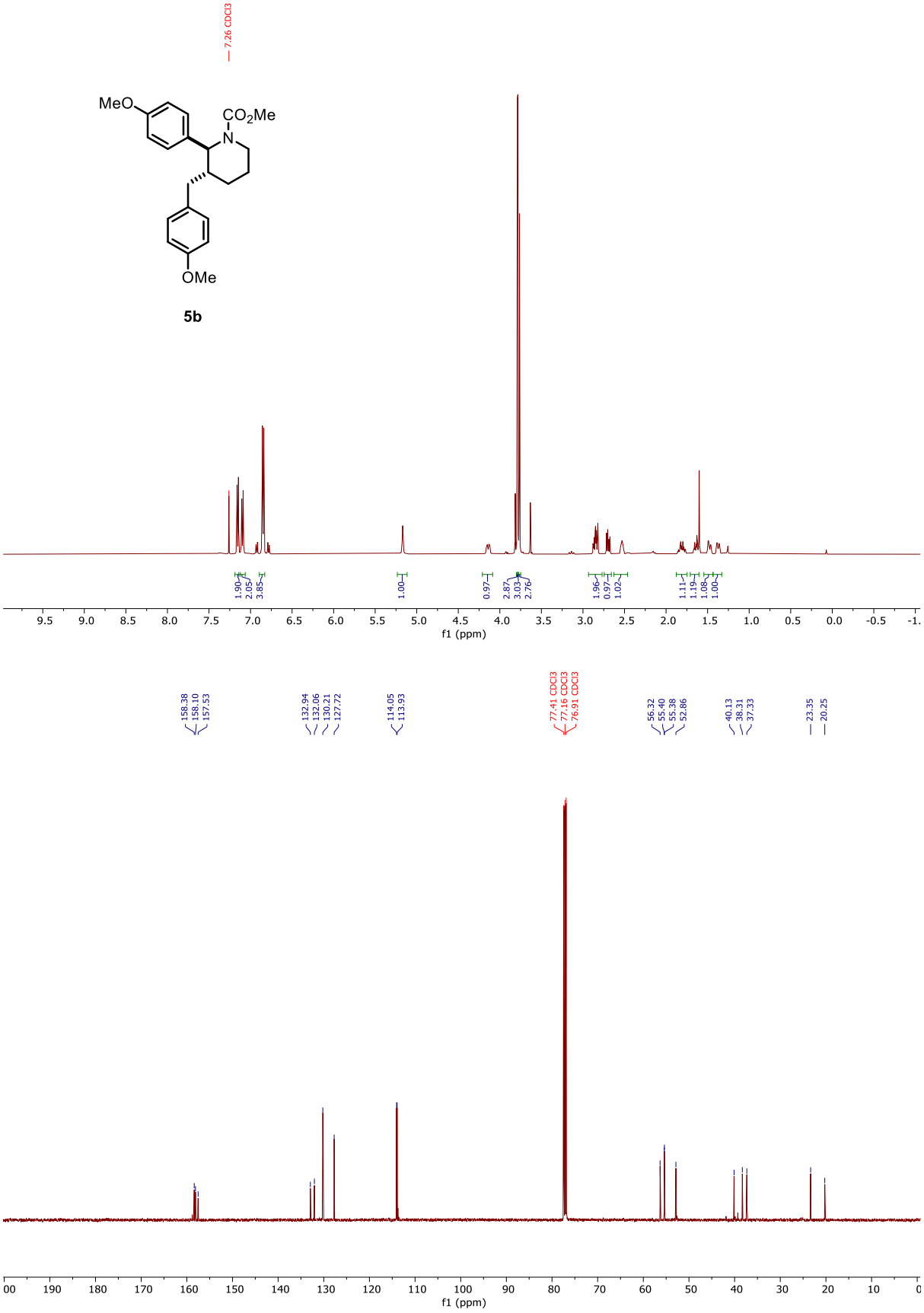



**5a**

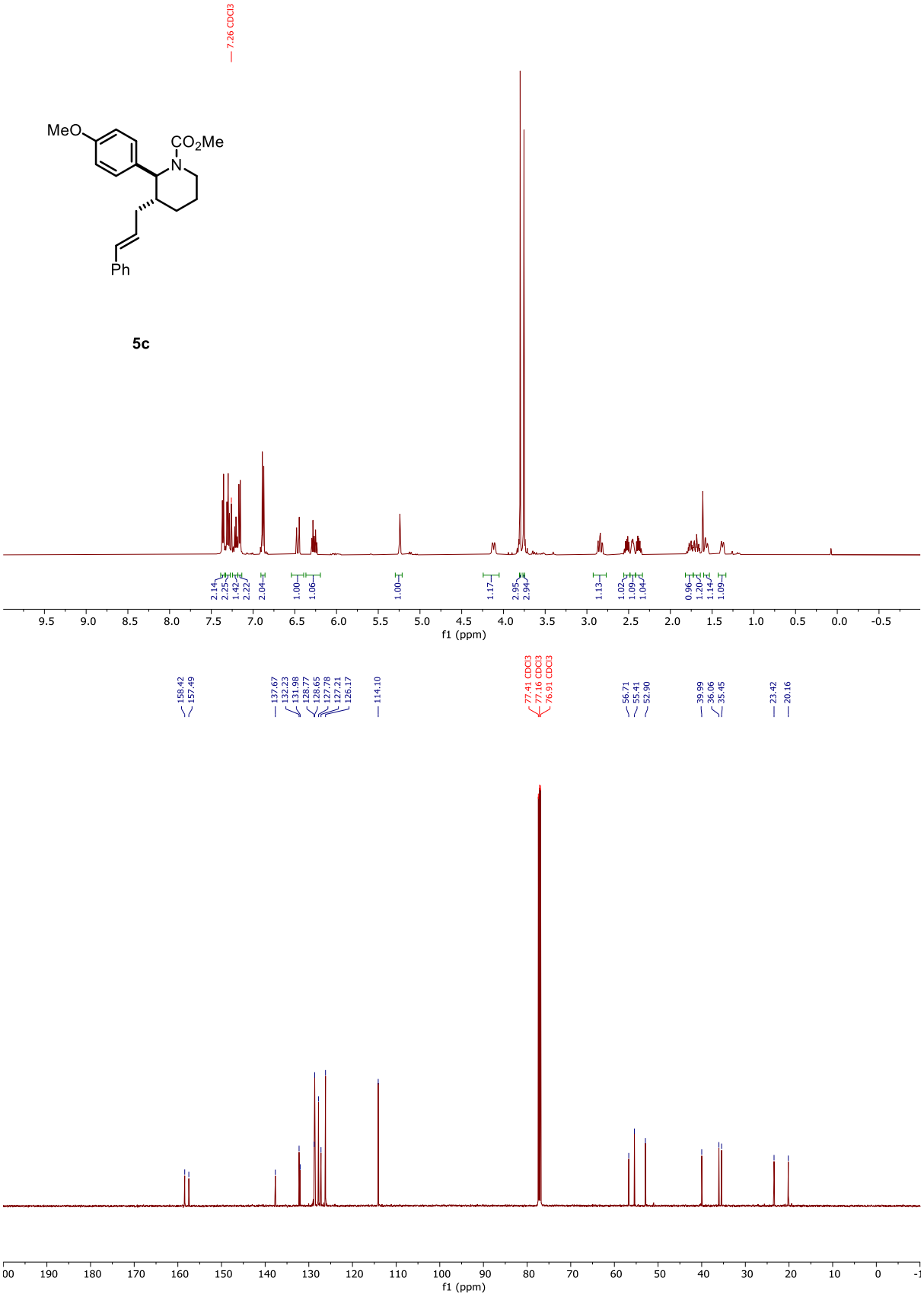


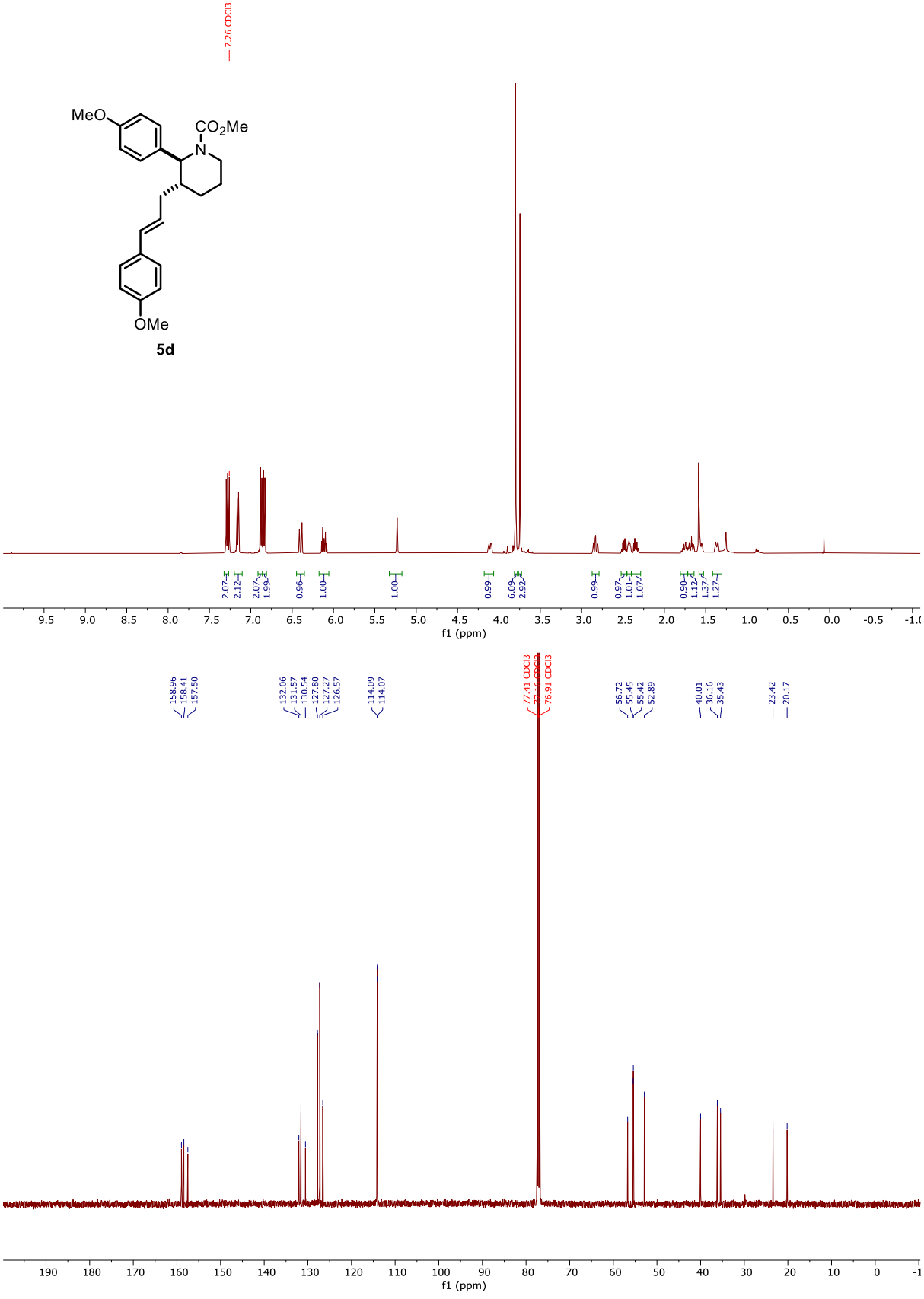
**(5b): (±)-Methyl (2*S*,3*R*)-3-(4-methoxybenzyl)-2-(4-methoxyphenyl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*S*)-3-(4-methoxybenzyl)-2-(4-methoxyphenyl)piperidine-1-carboxylate**



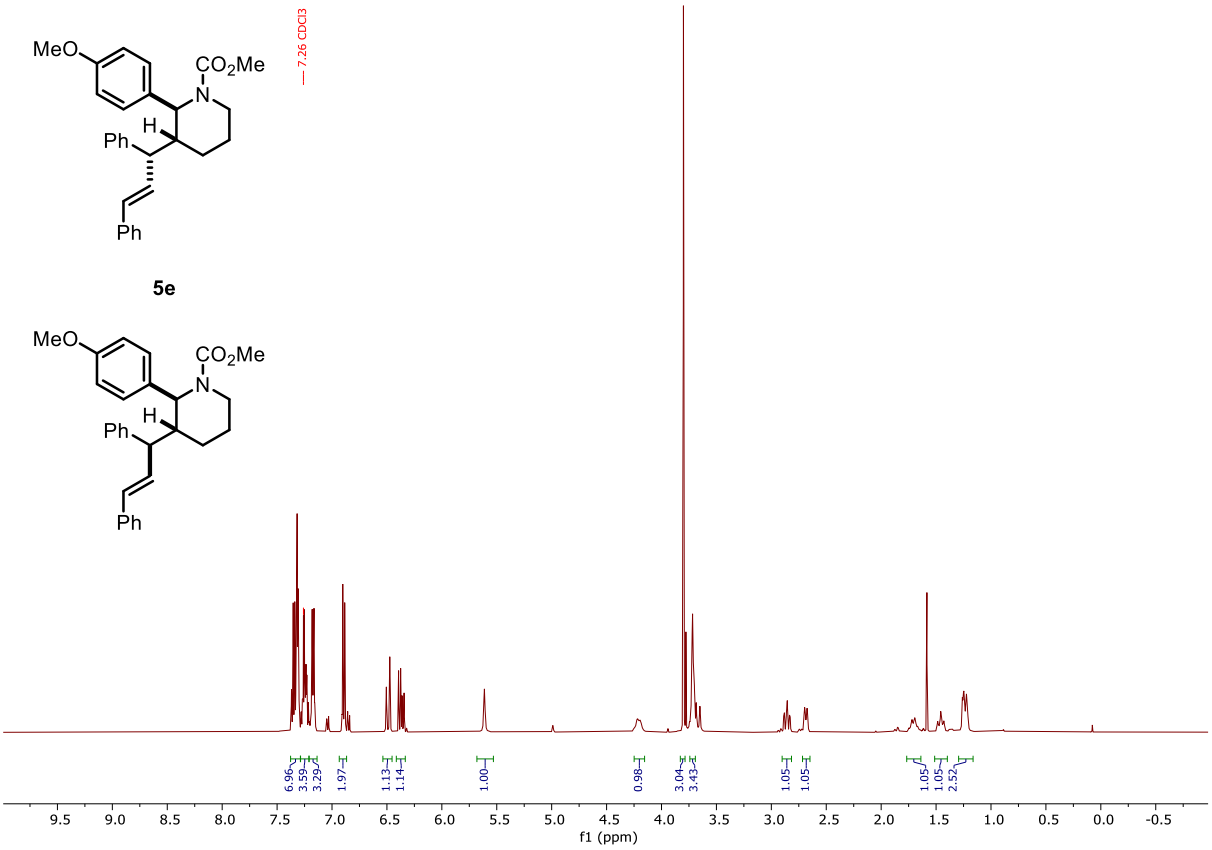
**(5c): (±)-Methyl (2*S*,3*R*)-3-cinnamyl-2-(4-methoxyphenyl)piperidine-1-carboxylate**



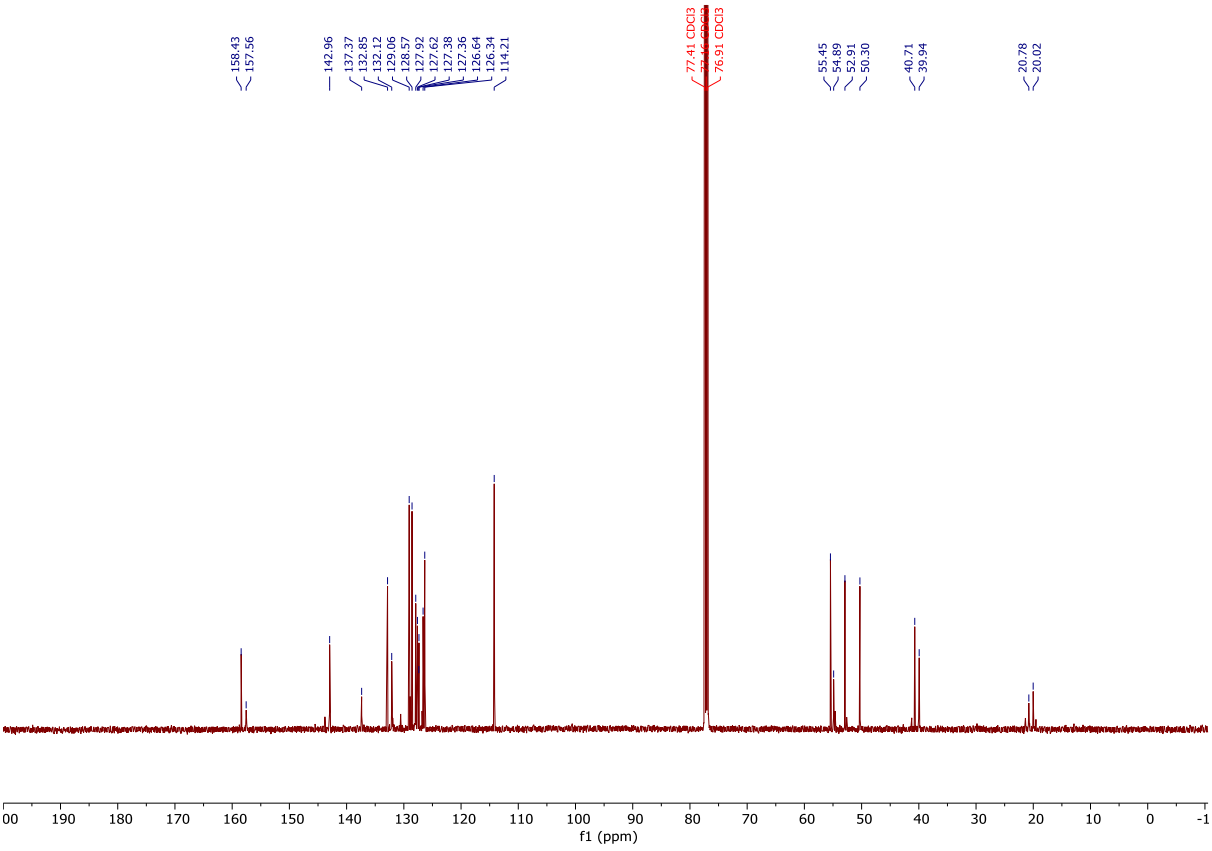
**(5d): (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*E*)-3-(4-methoxyphenyl)allyl)piperidine-1-carboxylate**



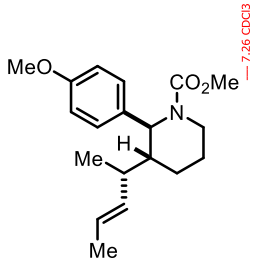
**(5e): (±)-Methyl (2*S*,3*R*)-3-((*S*,*E*)-1,3-diphenylallyl)-2-(4-methoxyphenyl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-3-((*R*,*E*)-1,3-diphenylallyl)-2-(4-methoxyphenyl)-piperidine-1-carboxylate**



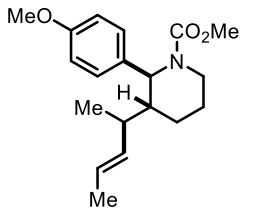

**5e**



**(5f): (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*S*,*E*)-pent-3-en-2-yl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*R*,*E*)-pent-3-en-2-yl)piperidine-1-carboxylate**

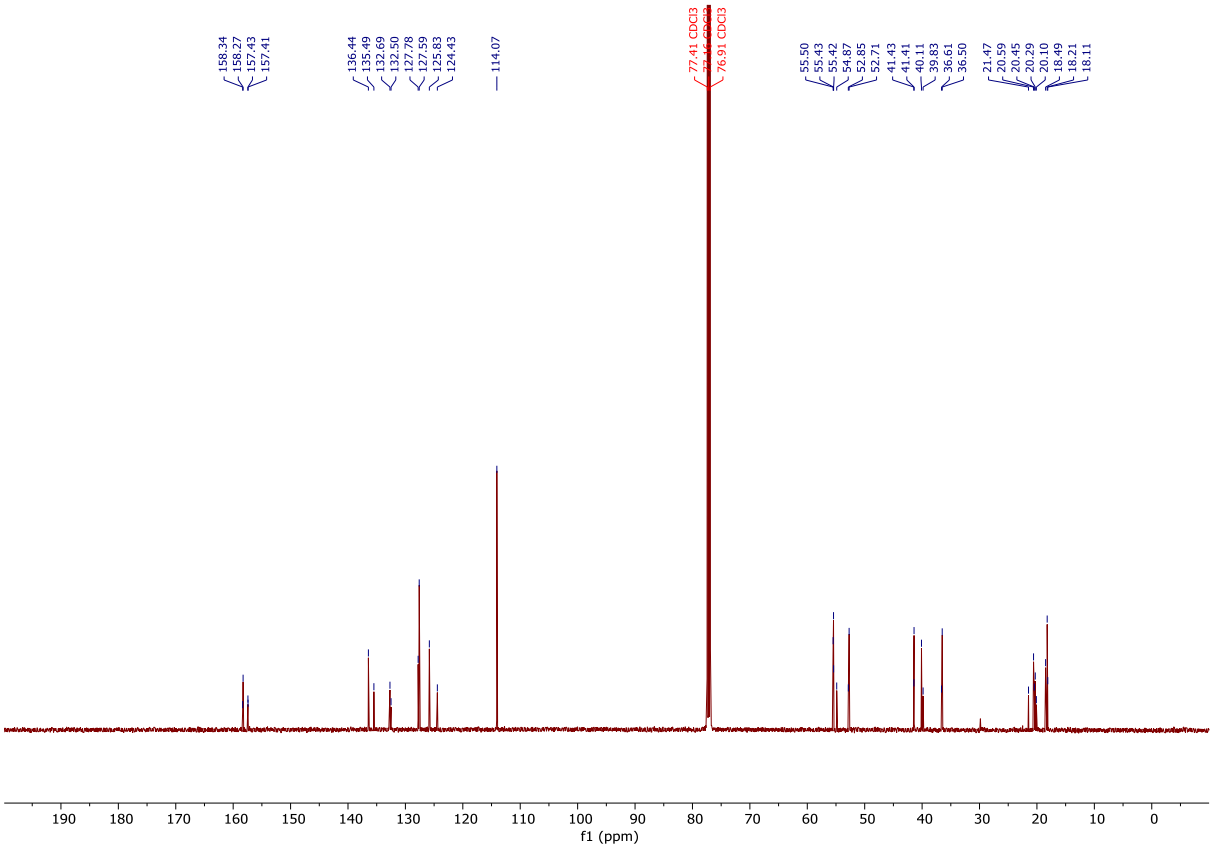



**5f**

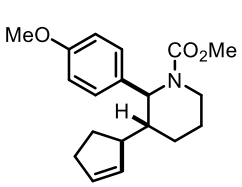




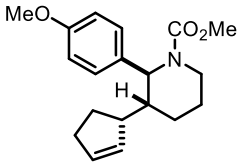




**(5g): (±)-Methyl (2*S*,3*R*)-3-((*R*)-cyclopent-2-en-1-yl)-2-(4-methoxyphenyl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-3-((*S*)-cyclopent-2-en-1-yl)-2-(4-methoxyphenyl)-piperidine-1-carboxylate**

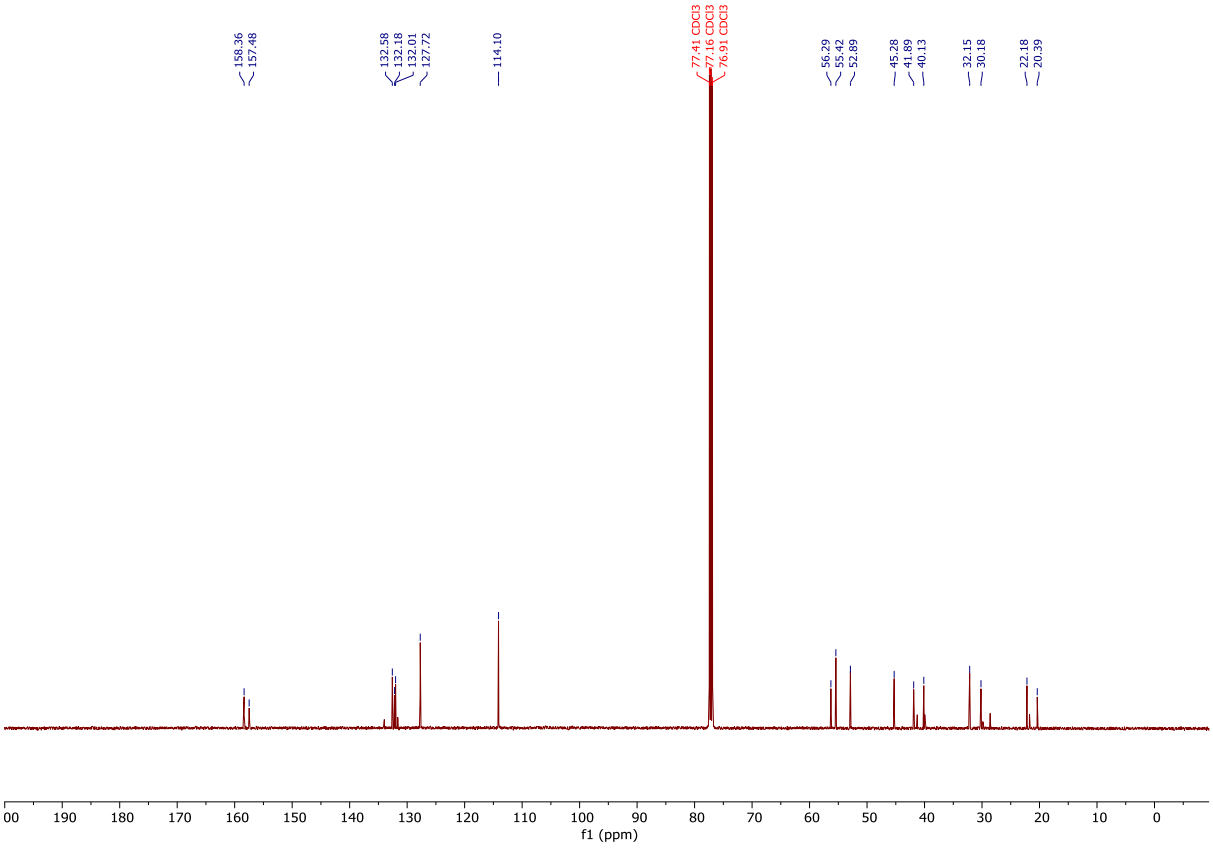



**5g**

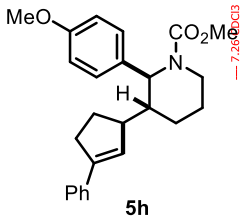




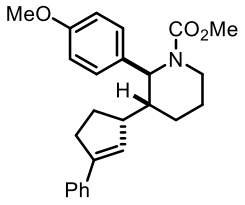




**(5h): (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*R*)-3-phenylcyclopent-2-en-1-yl)piperidine-1-carboxylate and (±)-Methyl (2*S*,3*R*)-2-(4-methoxyphenyl)-3-((*S*)-3-phenylcyclopent-2-en-1-yl)-piperidine-1-carboxylate**

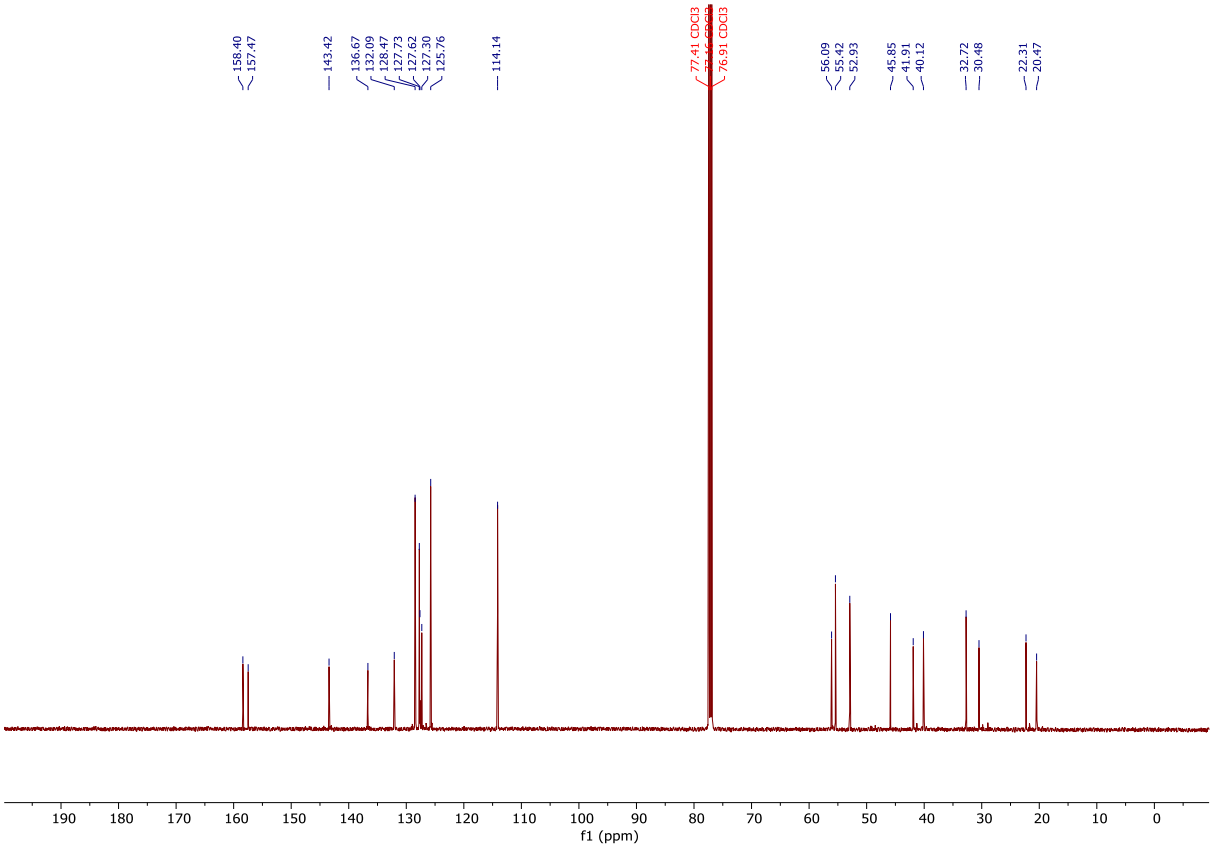



**5h**

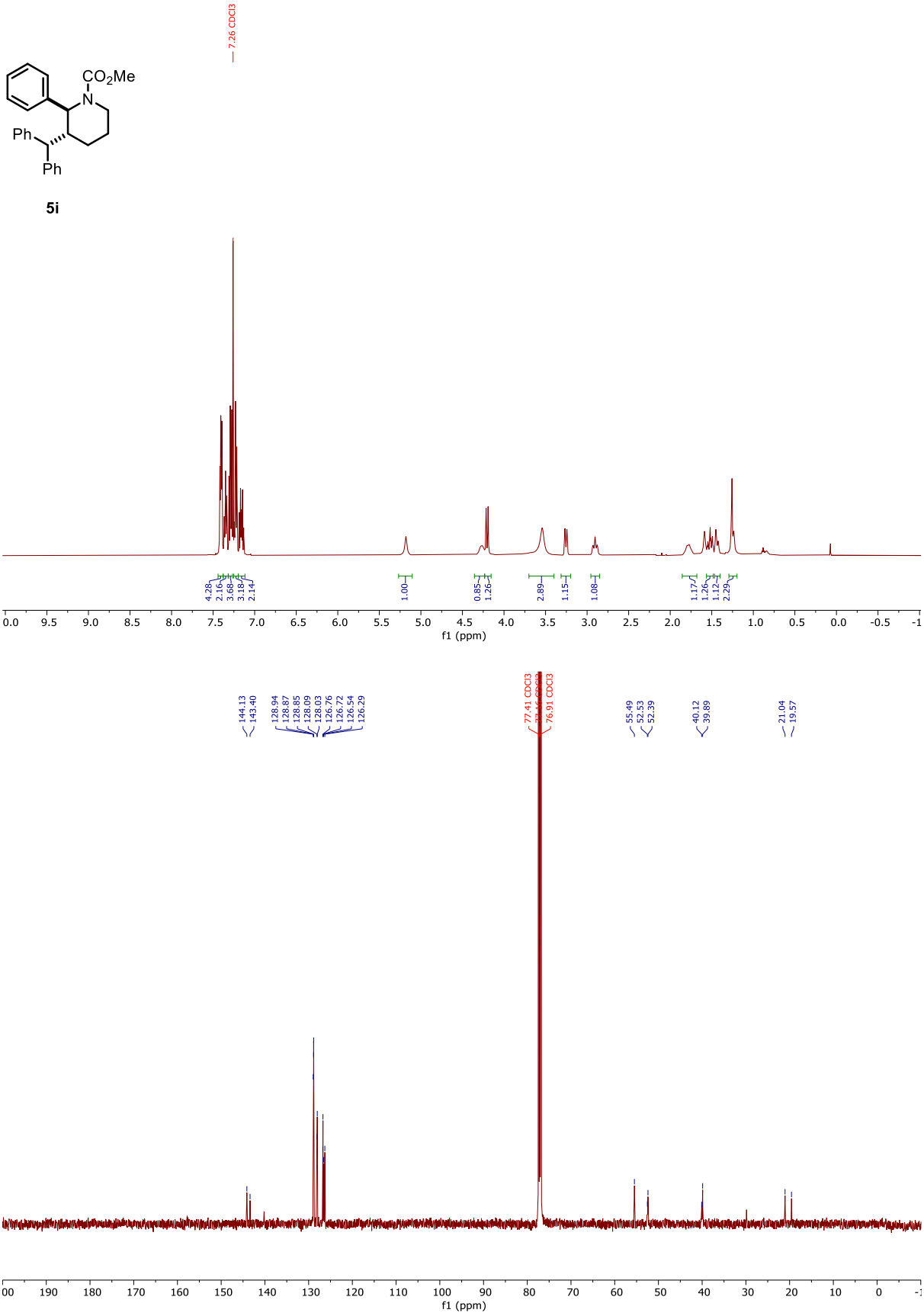




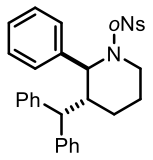




**(5i): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-2-phenylpiperidine-1-carboxylate**

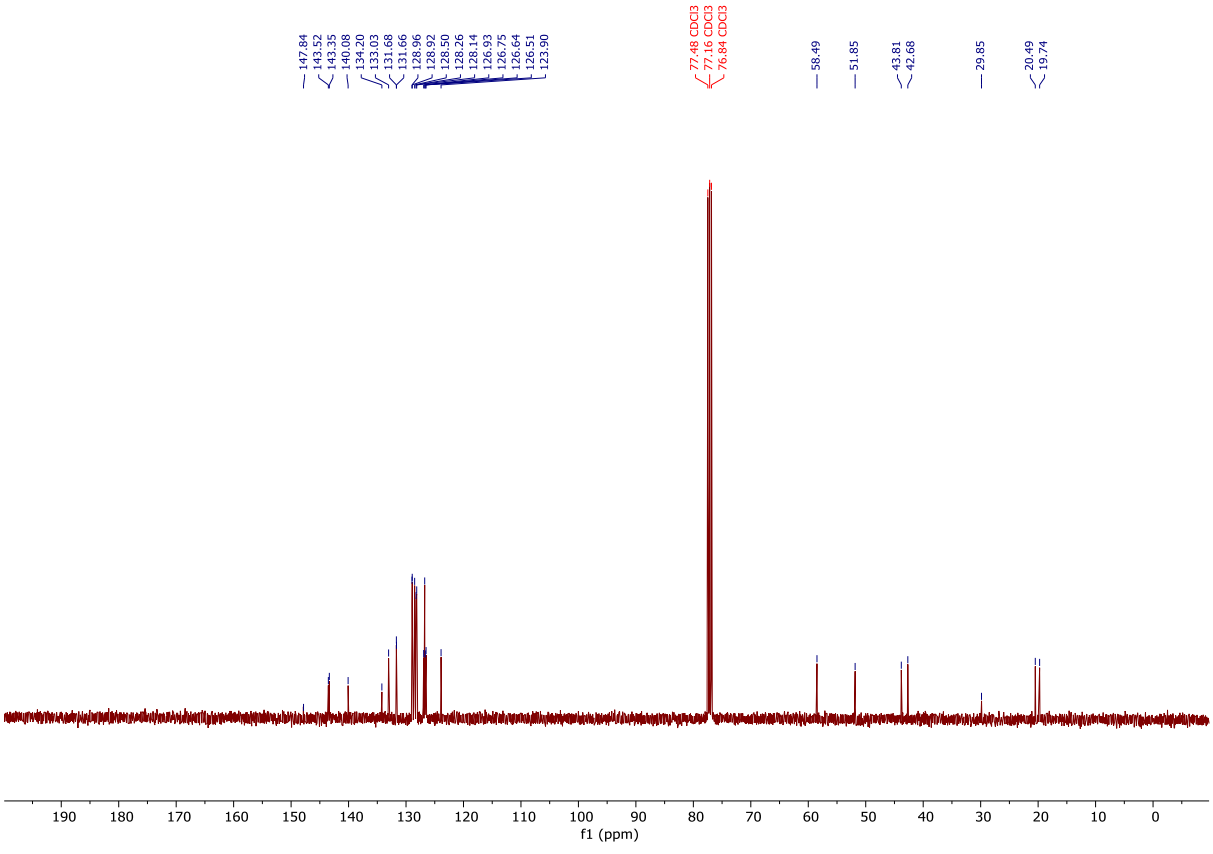


**(5i-Ns): (±)-(2*S*,3*R*)-3-Benzhydryl-1-((2-nitrophenyl)sulfonyl)-2-phenylpiperidine**

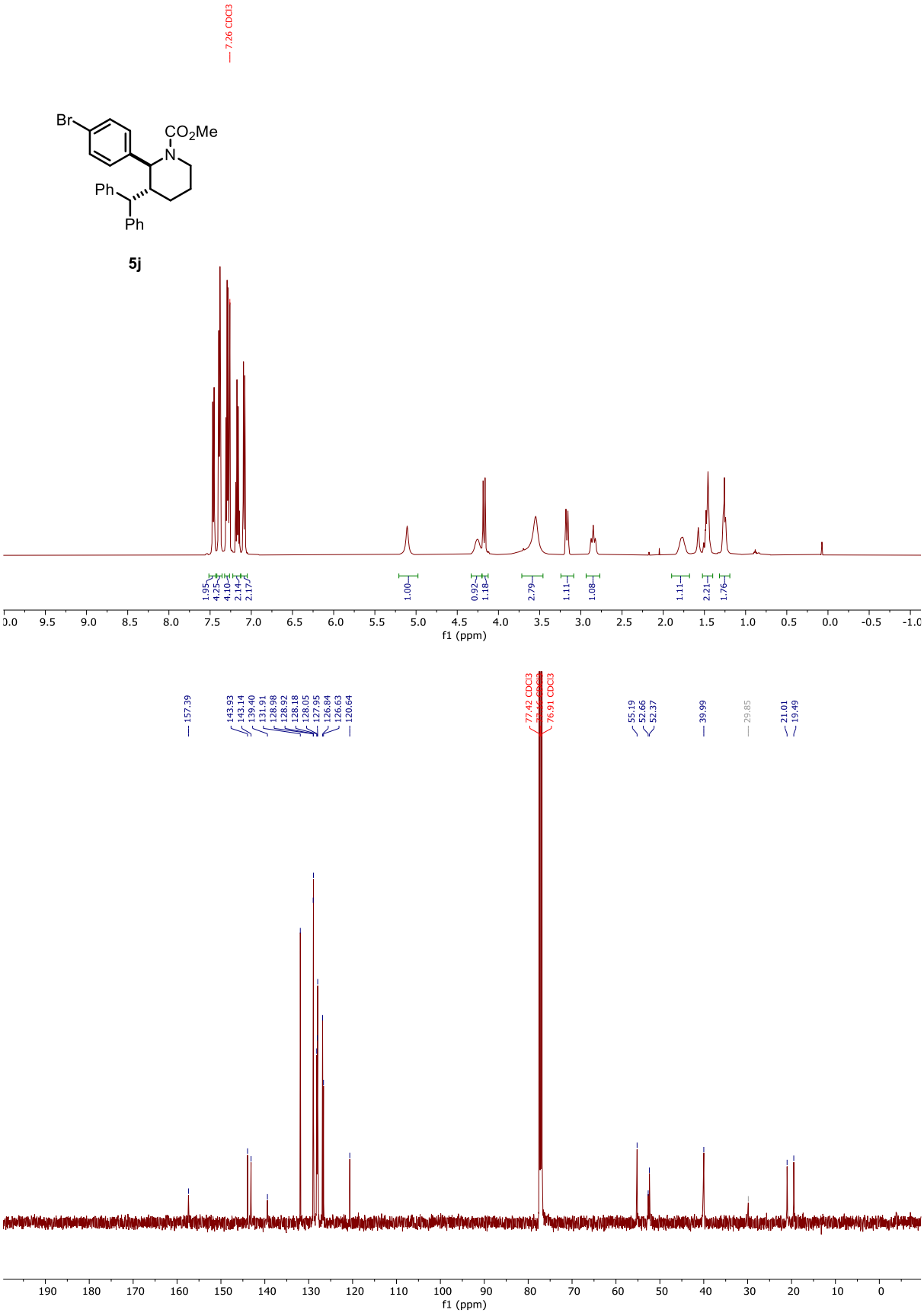



**5i-Ns**

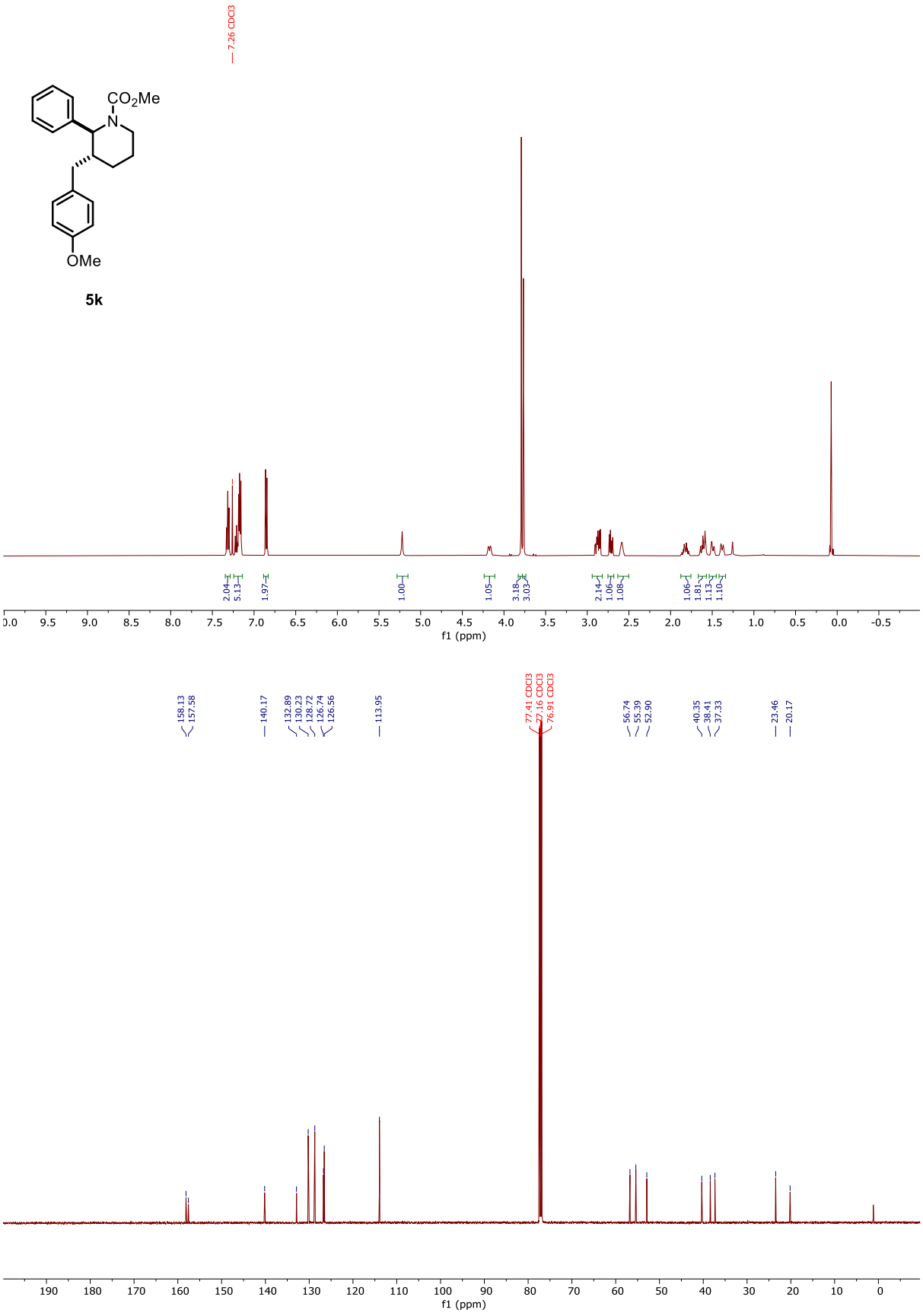


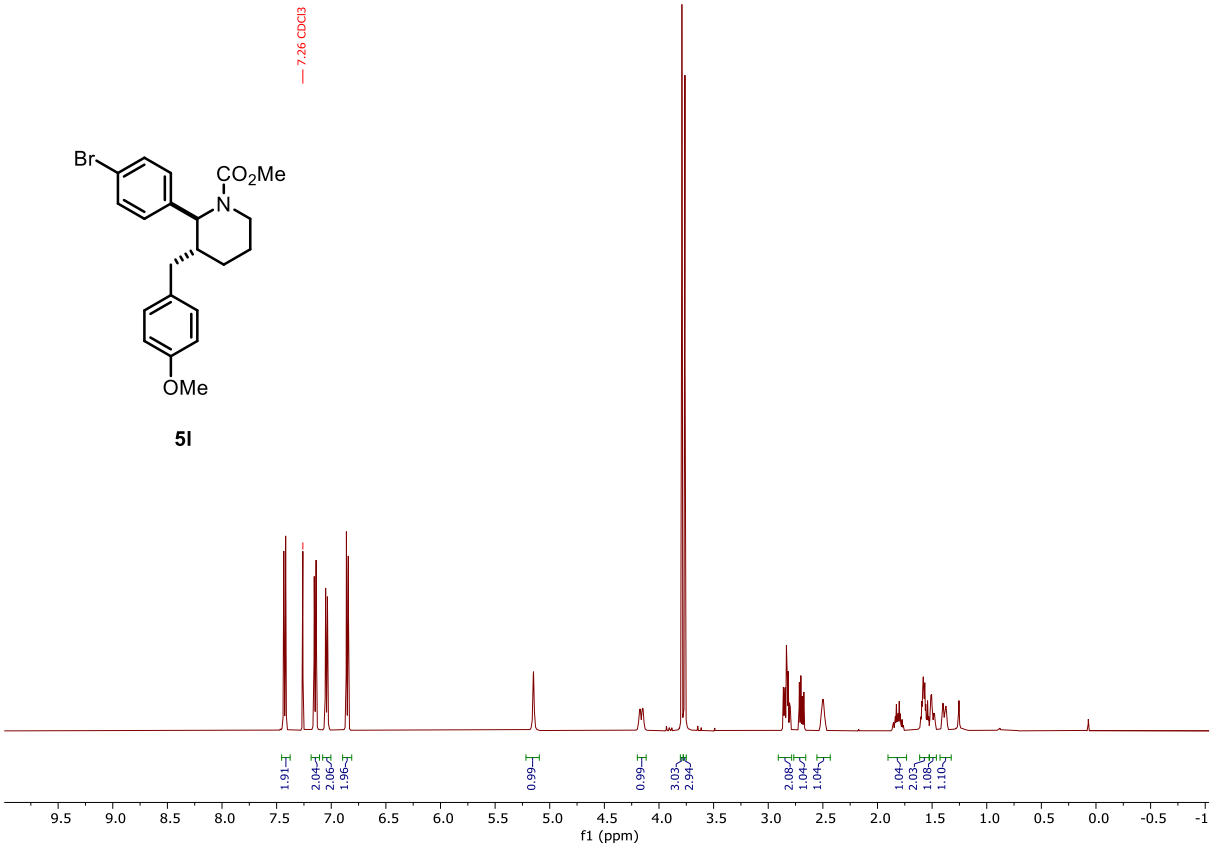
**(5j): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-2-(4-bromophenyl)piperidine-1-carboxylate**

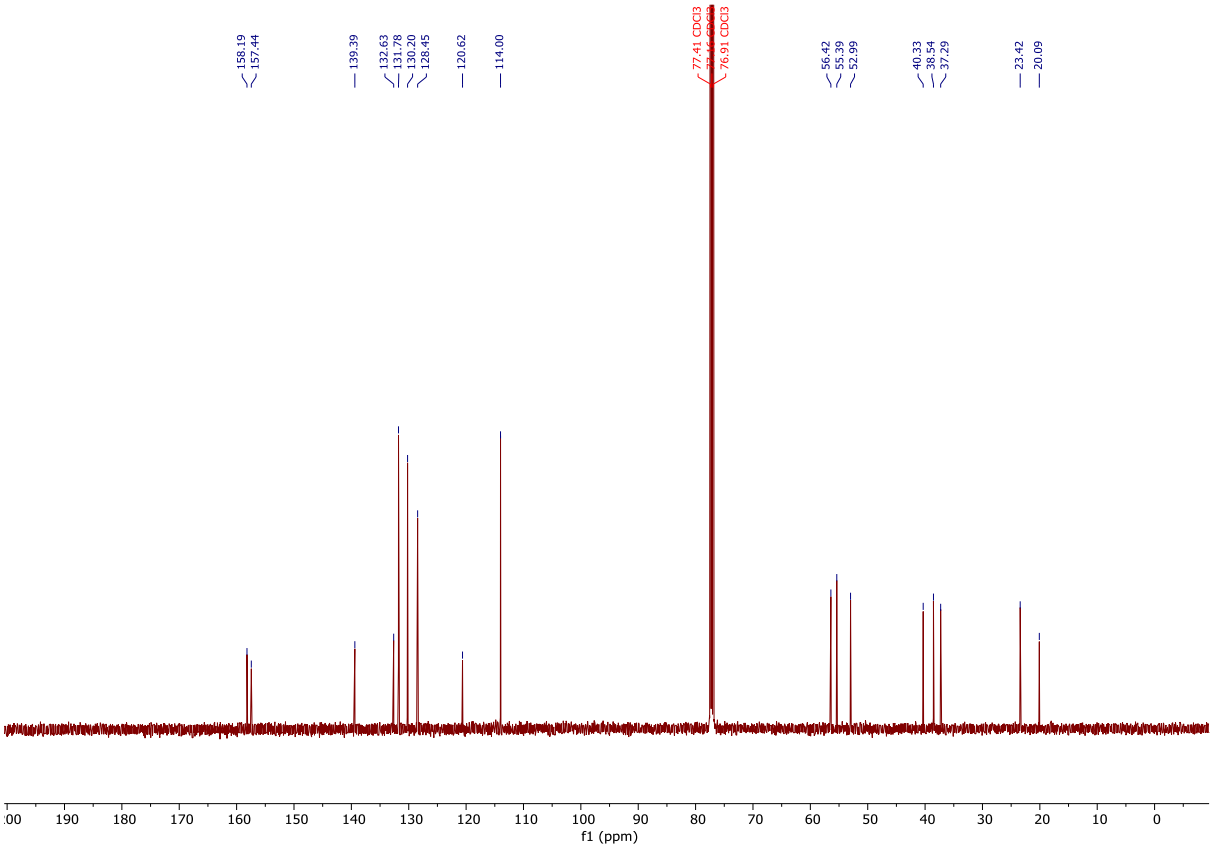


**(5k): (±)-Methyl (2*S*,3*R*)-3-(4-methoxybenzyl)-2-phenylpiperidine-1-carboxylate**

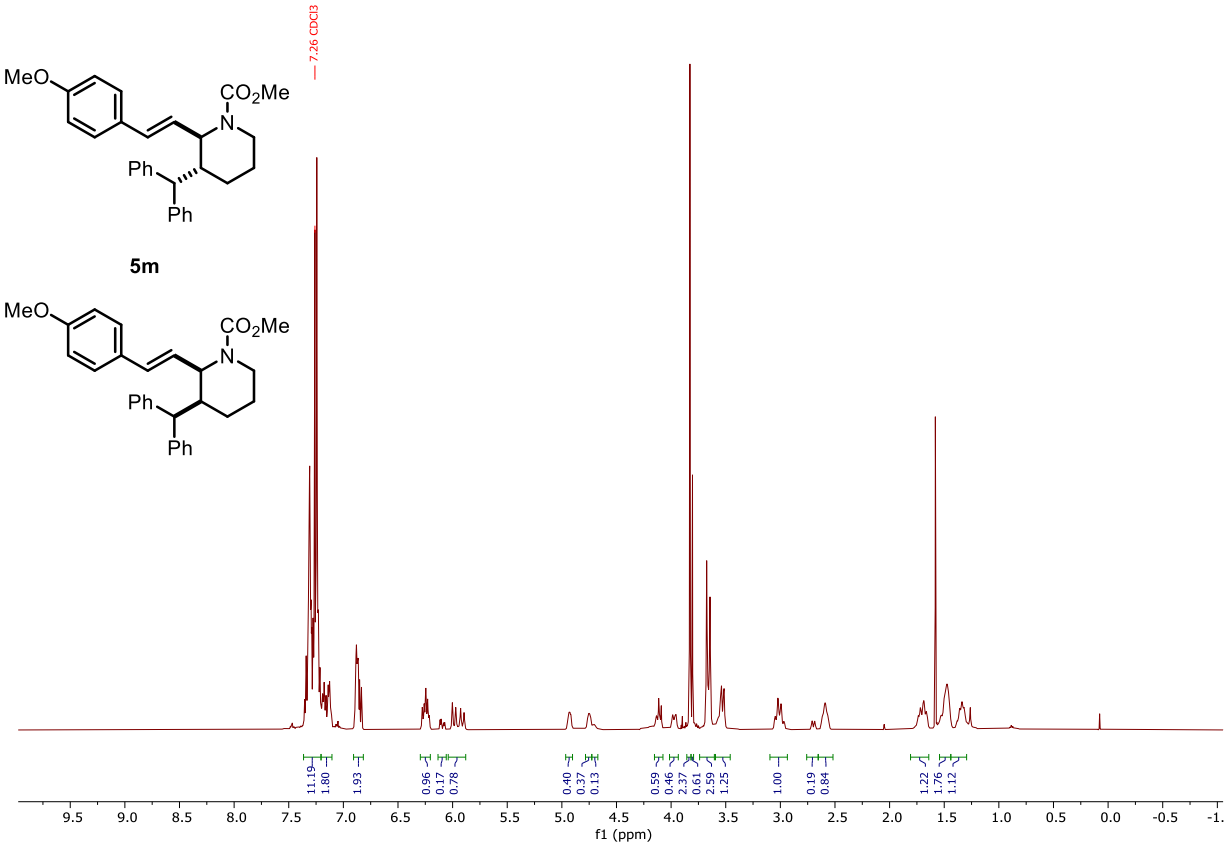


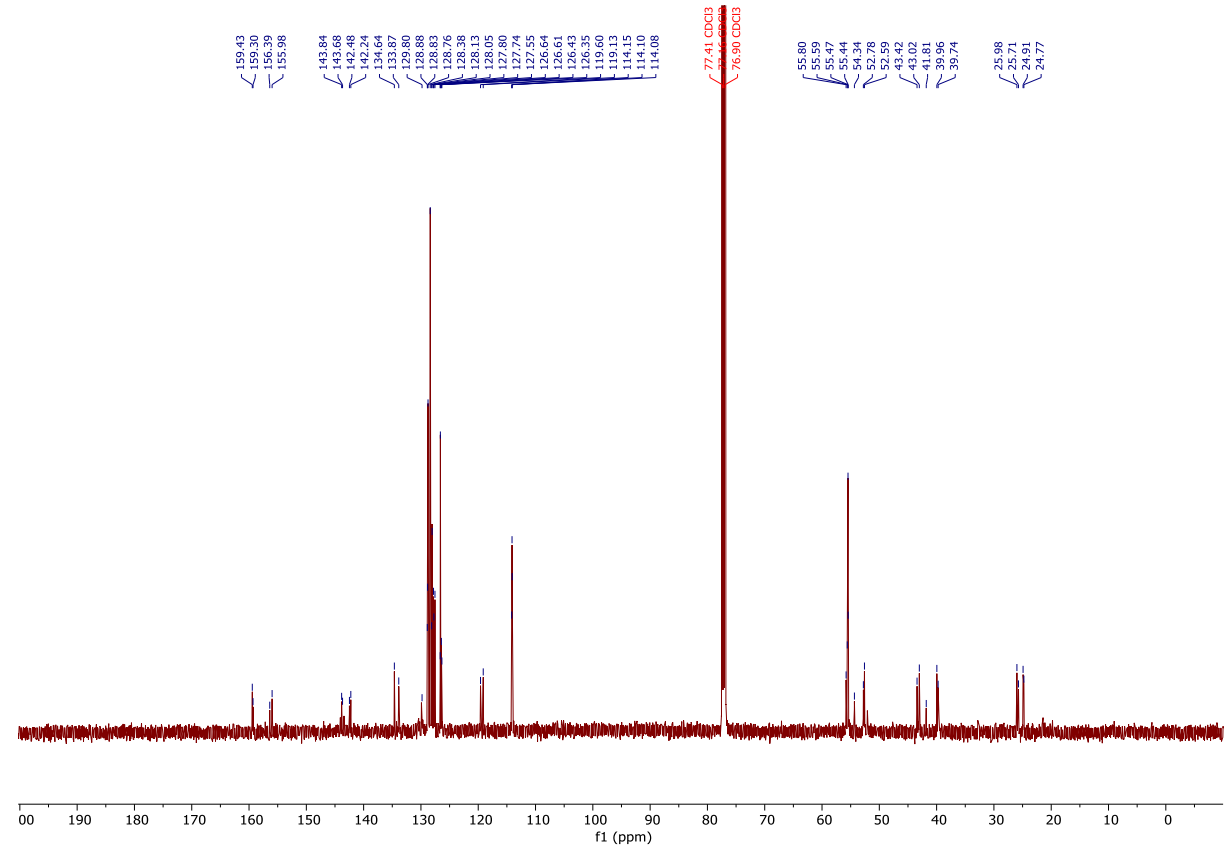
**(5l): (±)-Methyl (2*S*,3*R*)-2-(4-bromophenyl)-3-(4-methoxybenzyl)piperidine-1-carboxylate**



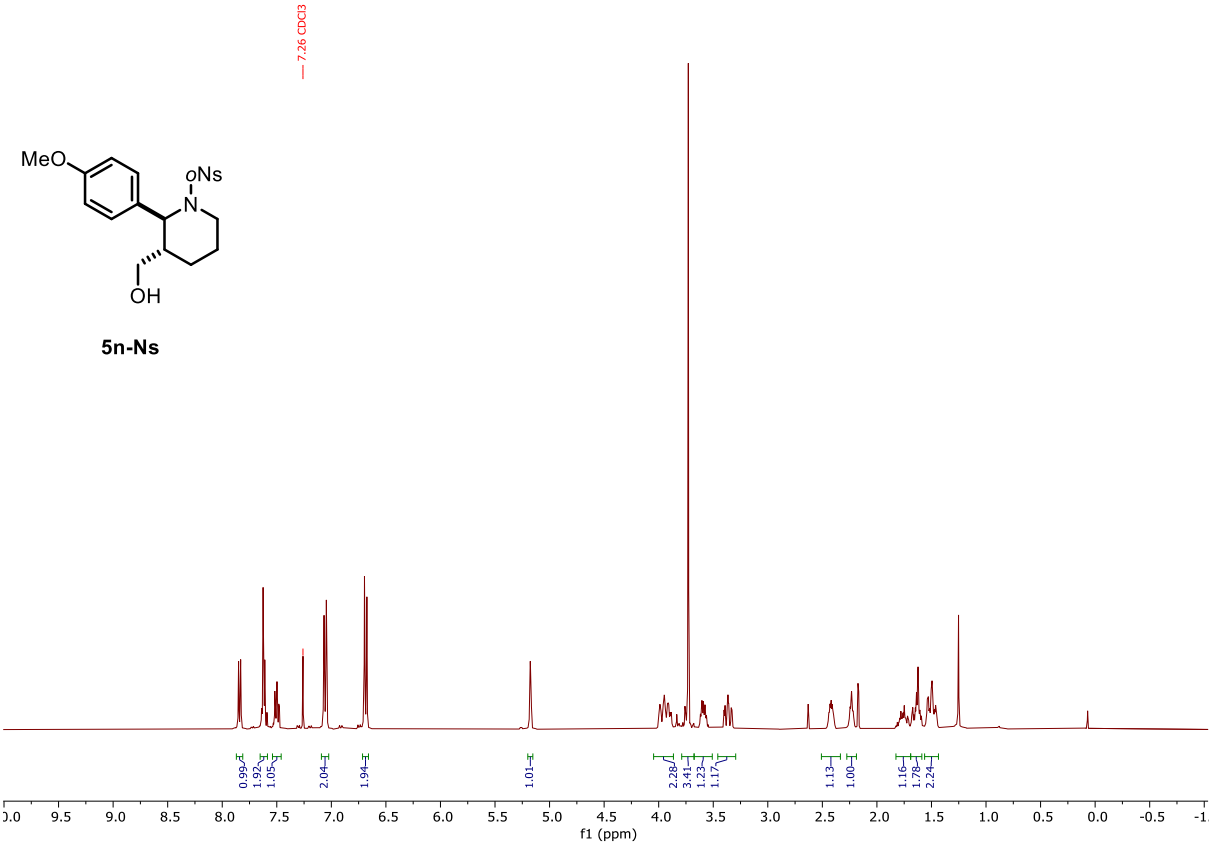



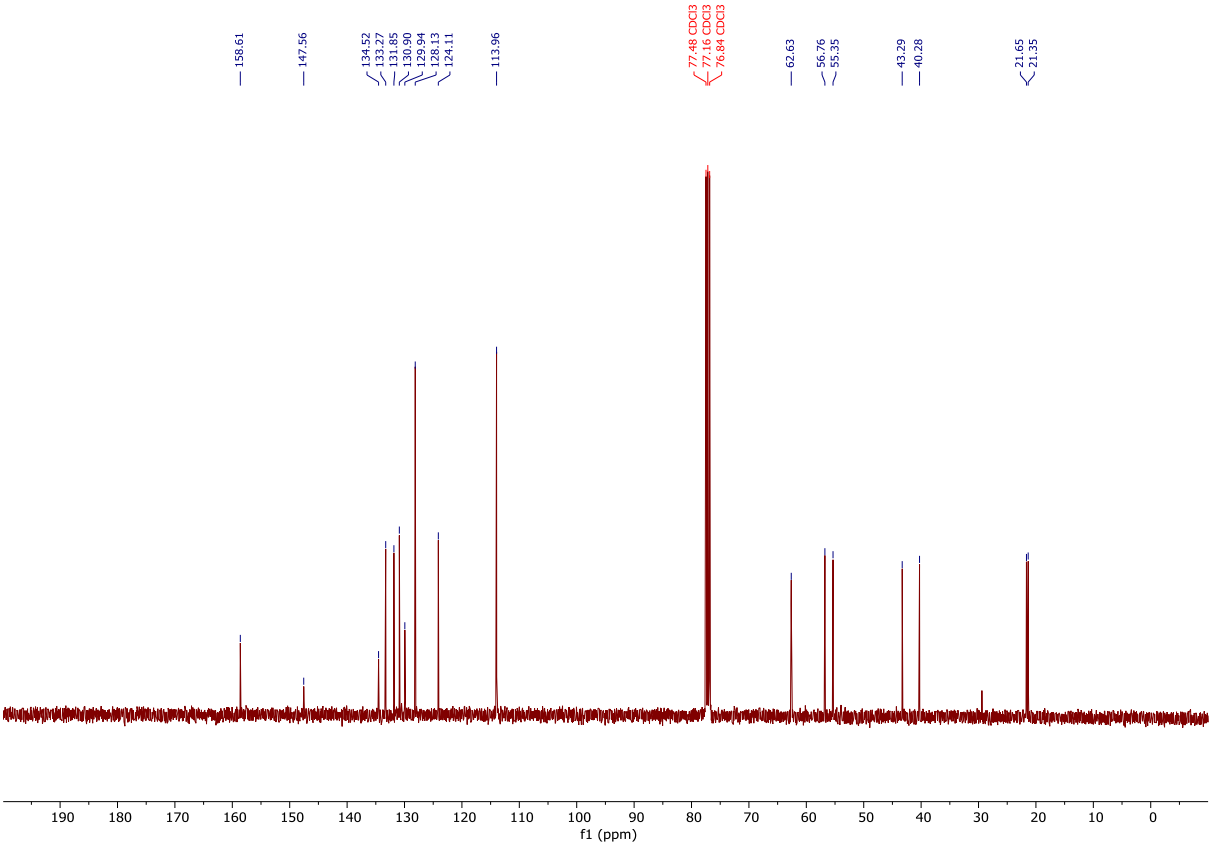
**(5m): (±)-Methyl (2*R*,3*R*)-3-benzhydryl-2-((*E*)-4-methoxystyryl)piperidine-1-carboxylate and (±)-methyl (2*R*,3*S*)-3-benzhydryl-2-((*E*)-4-methoxystyryl)piperidine-1-carboxylate**



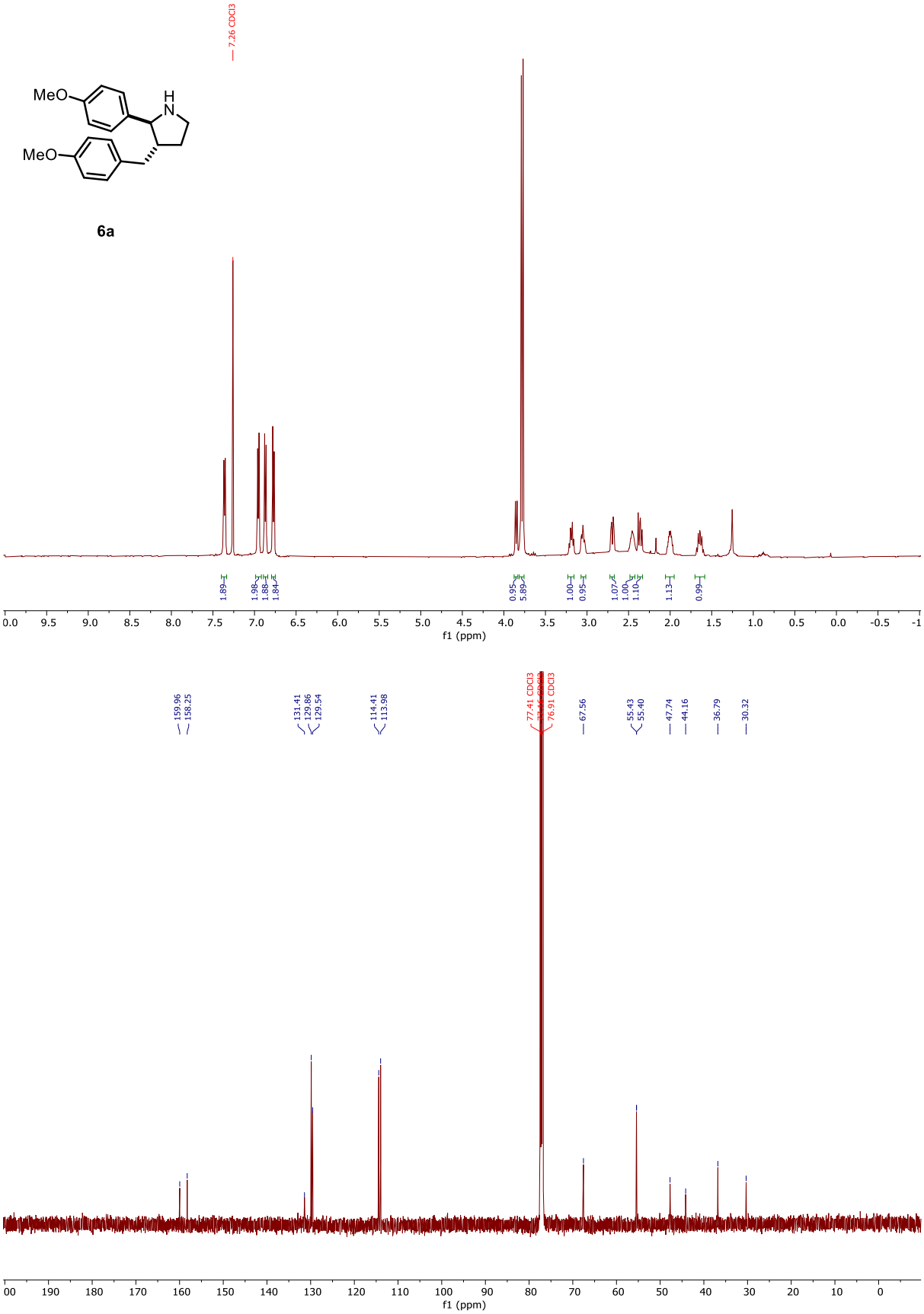



**(5n-Ns): 2-(4-Methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)piperidin-3-yl)methanol**

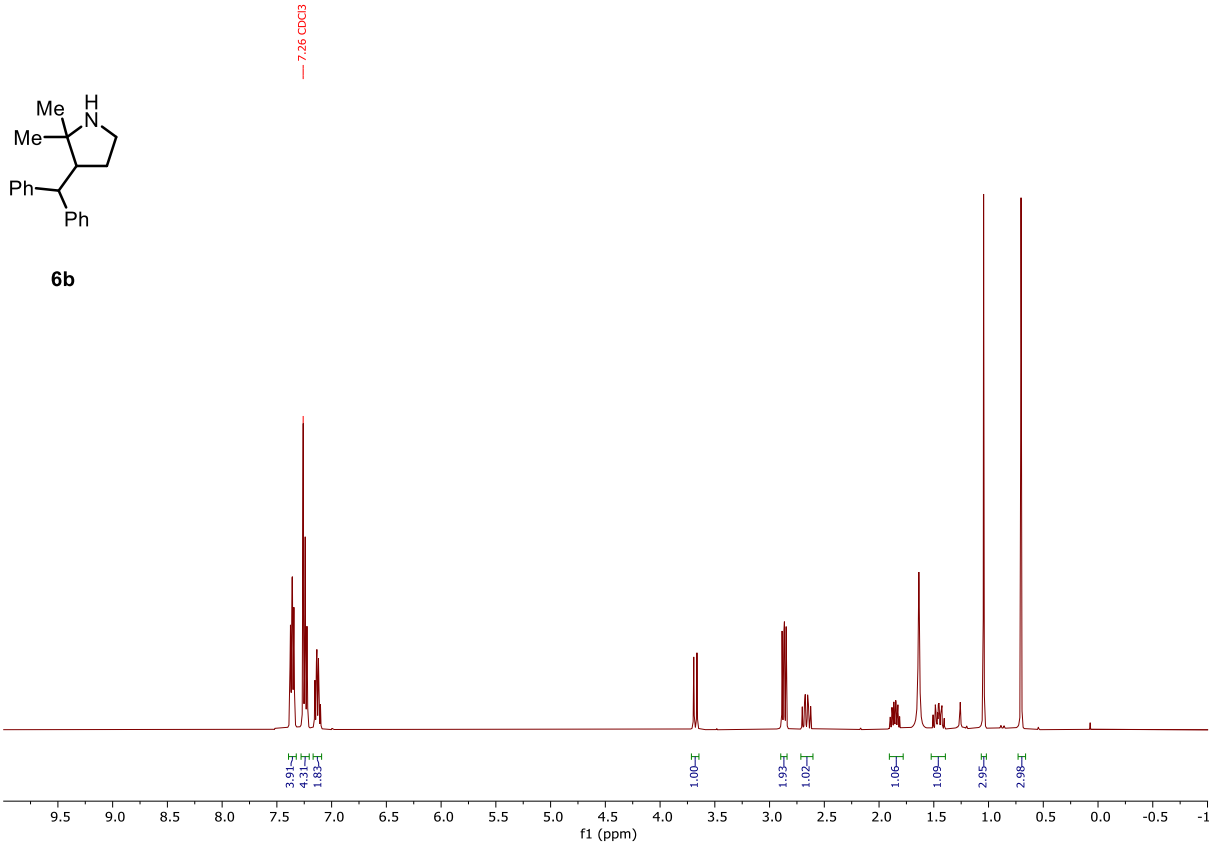


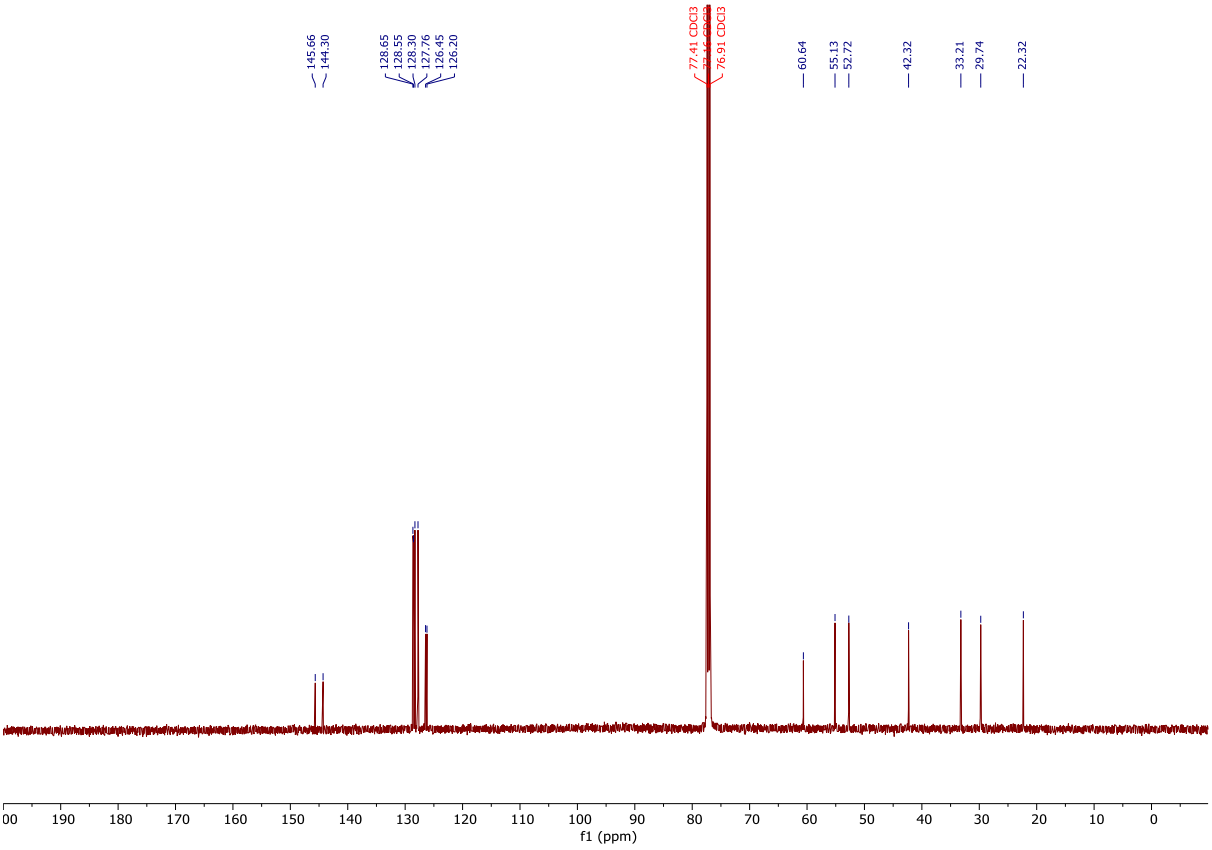
**(6a): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)pyrrolidine**



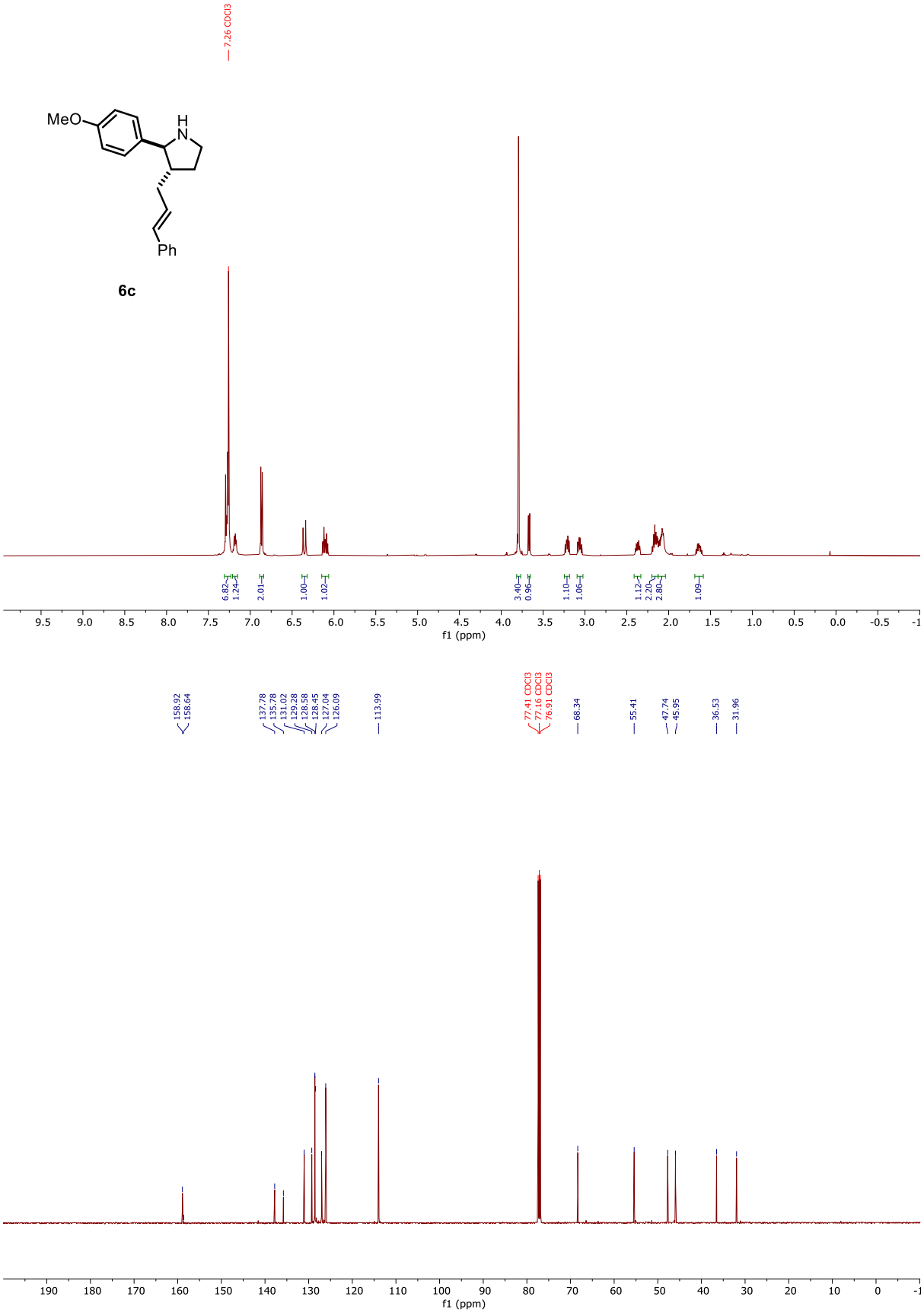
**(6b): (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)pyrrolidine**



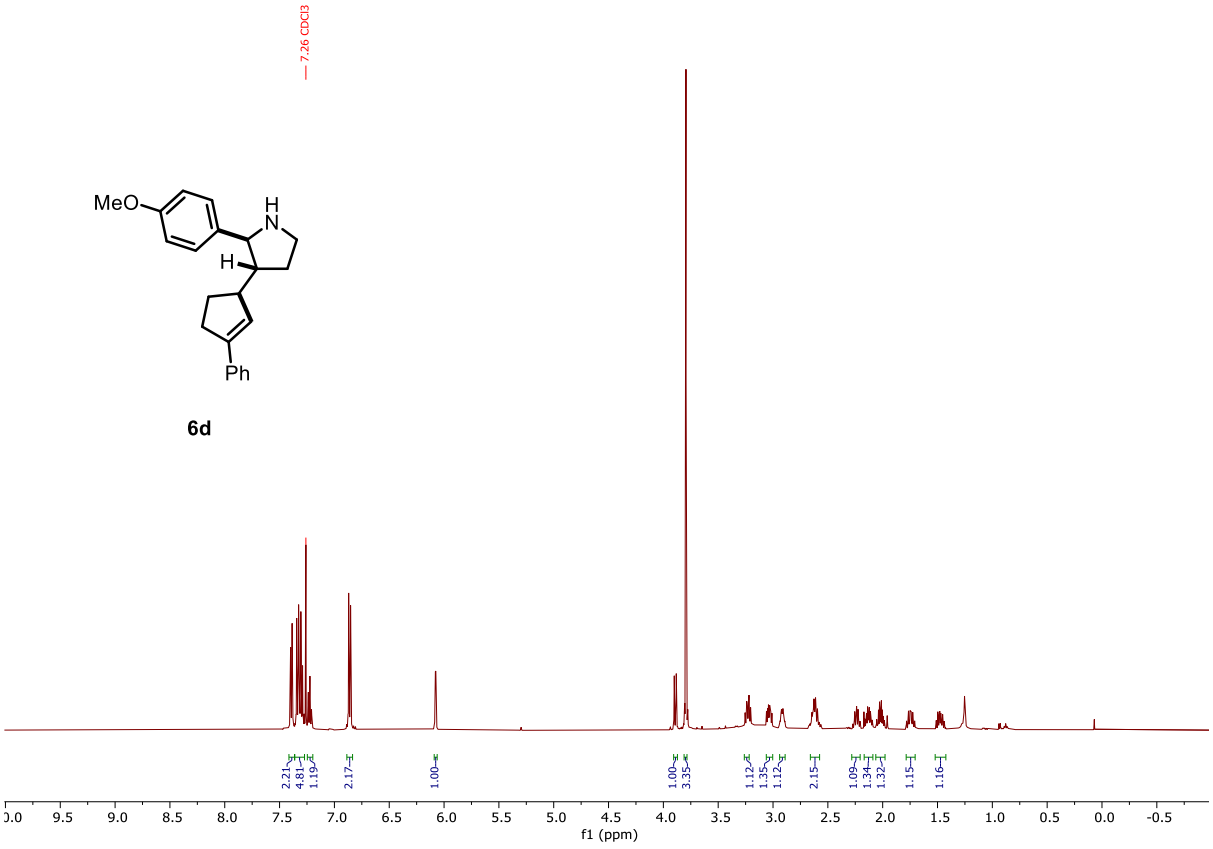

**6b**



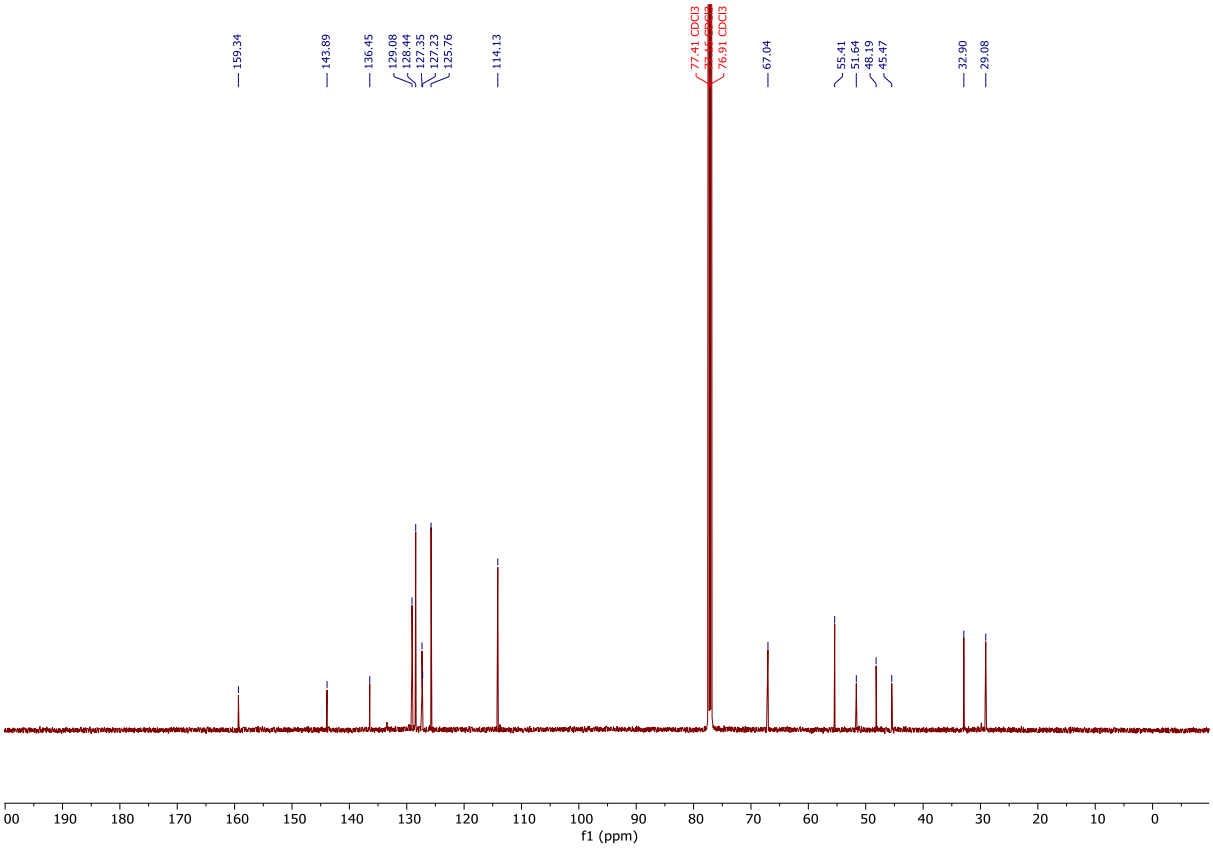
**(6c): (±)- (2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)pyrrolidine**



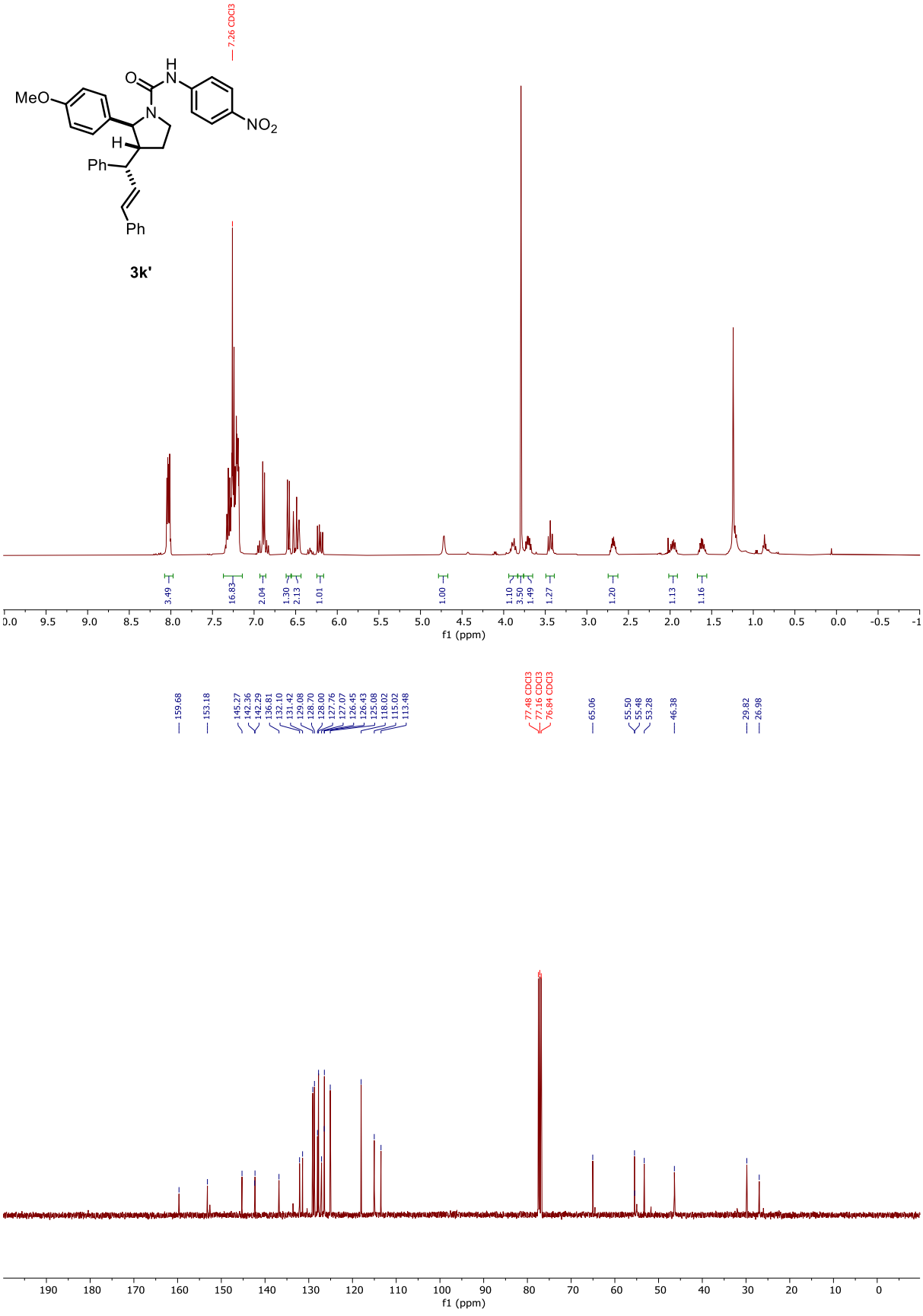
**(6d): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*R*)-3-phenylcyclopent-2-en-1-yl]pyrrolidine**



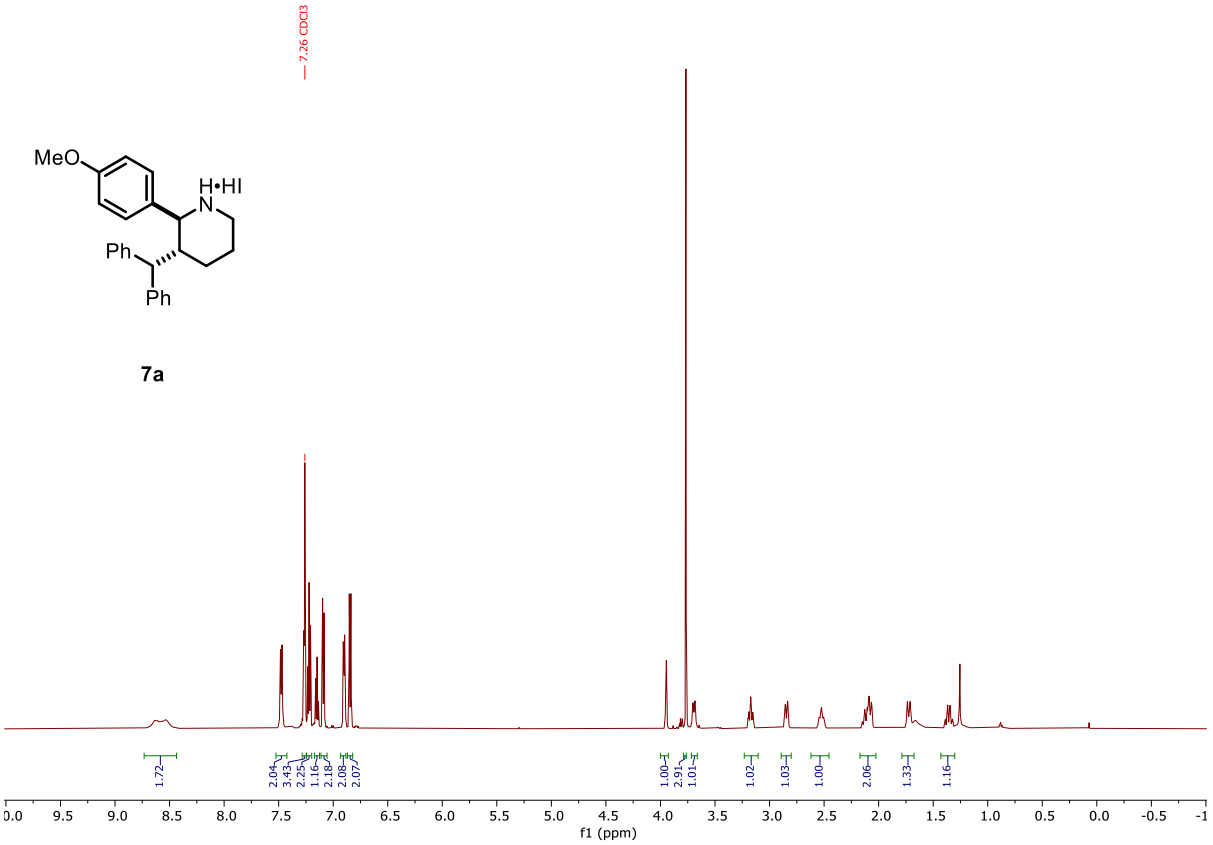

6d

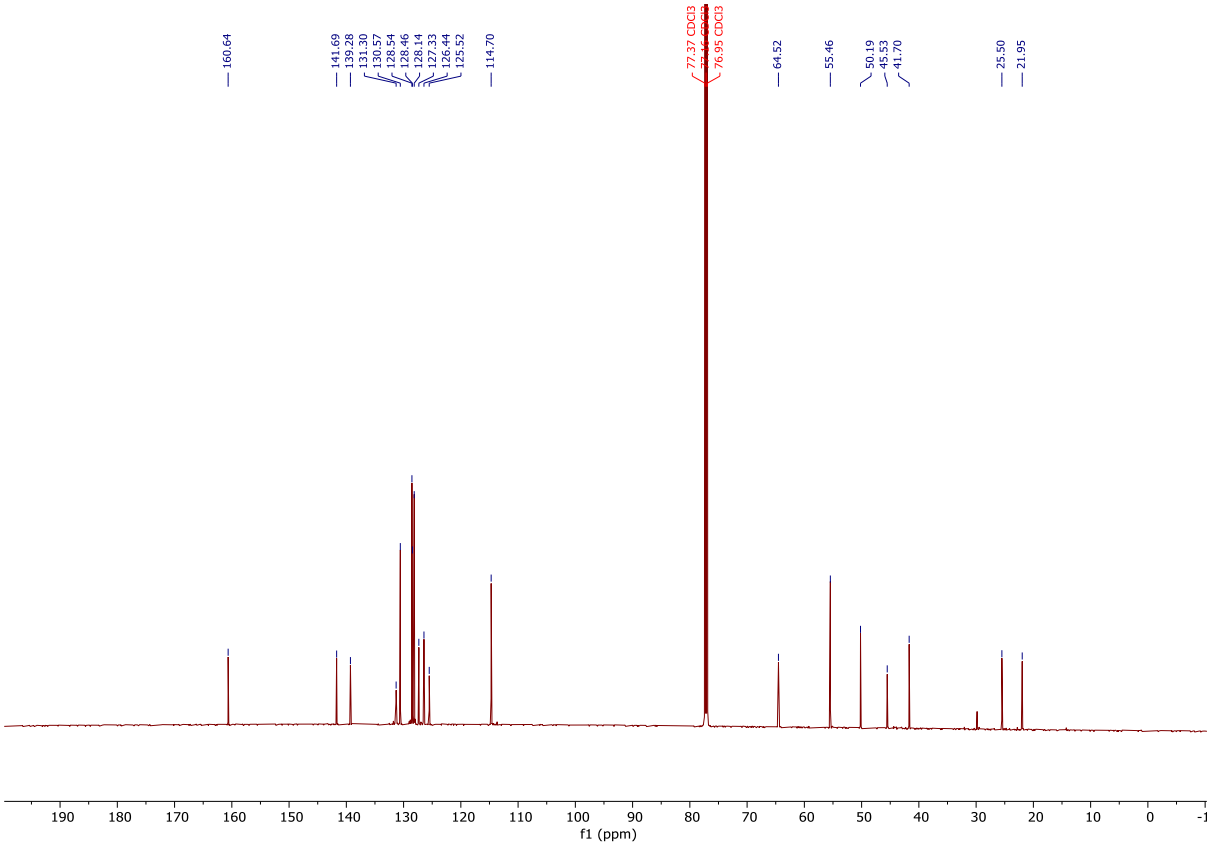


**(3k'): (±)-(2*S*,3*R*)-3-((*S*,*E*)-1,3-Diphenylallyl)-2-(4-methoxyphenyl)-*N*-(4-nitrophenyl)-pyrrolidine-1-carboxamide**

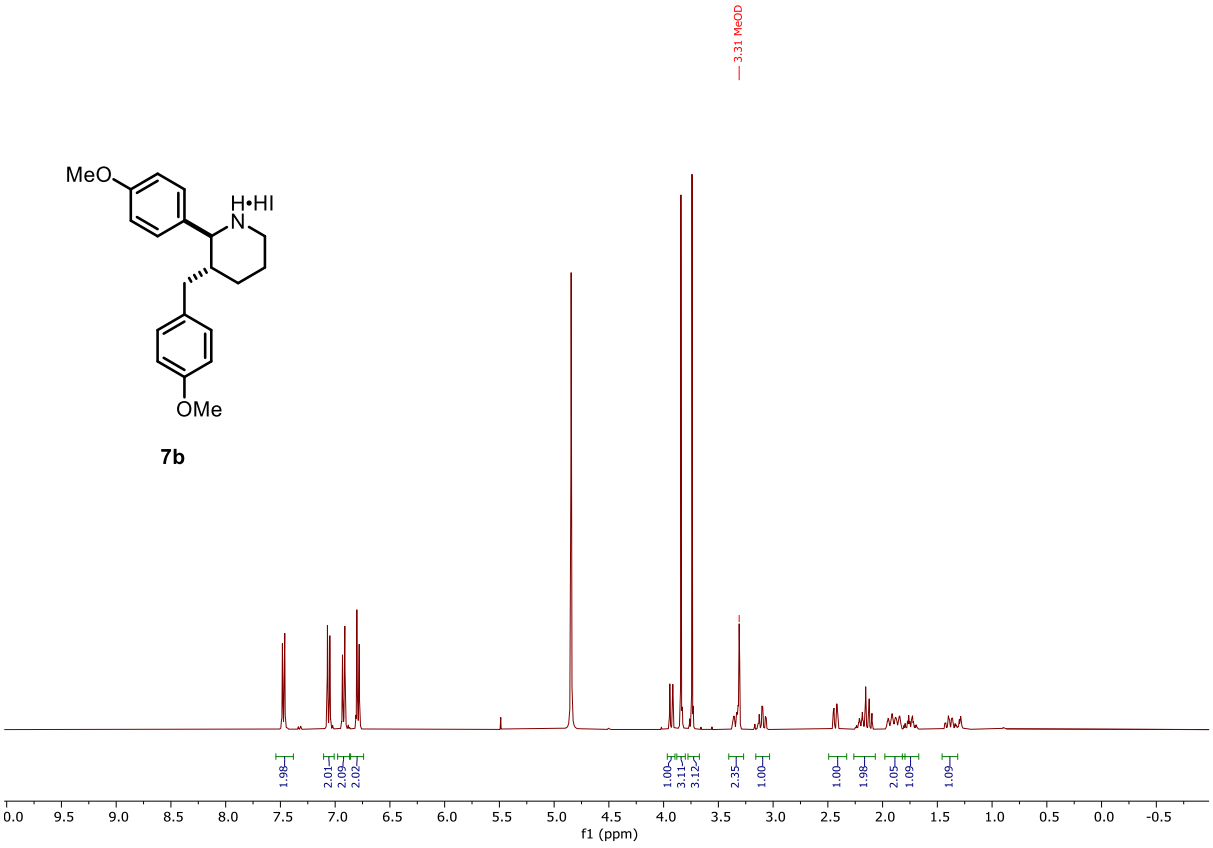


**(7a): (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)piperidin-1-ium iodide**

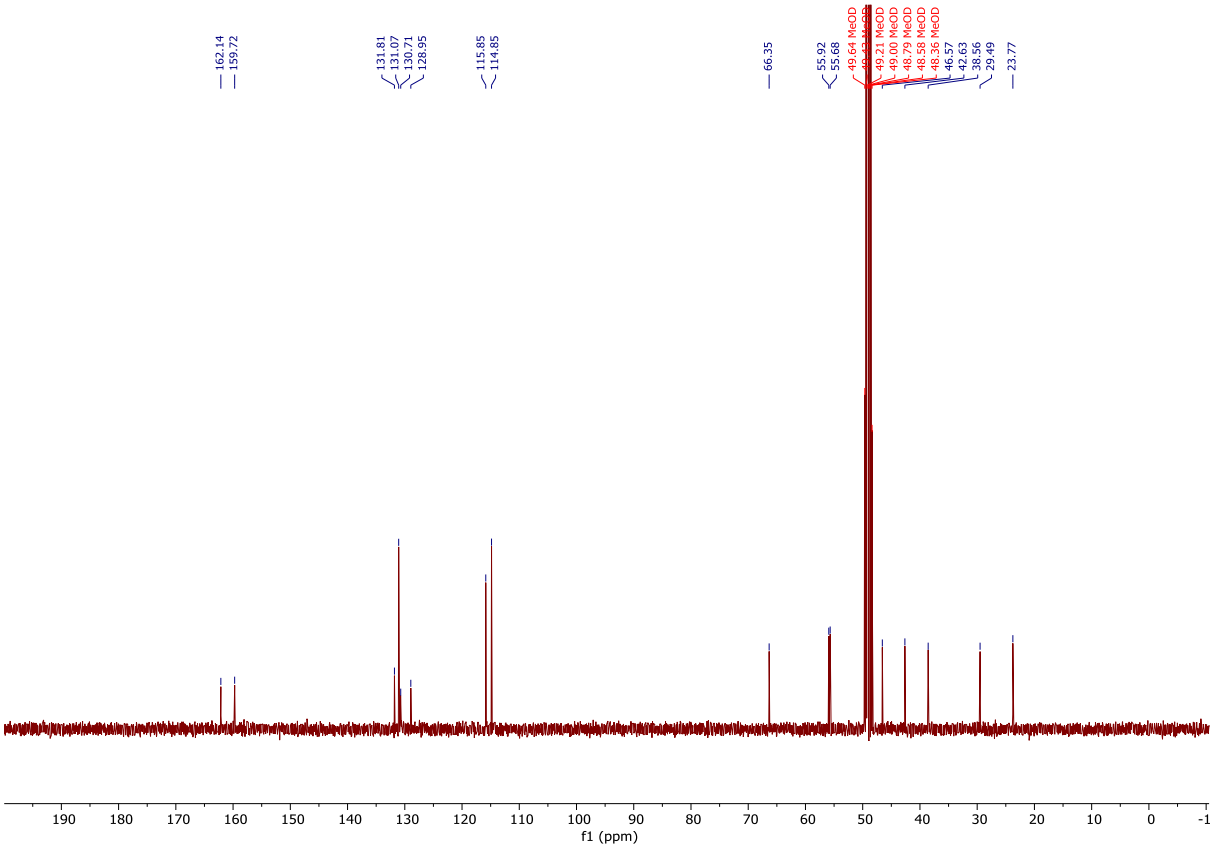


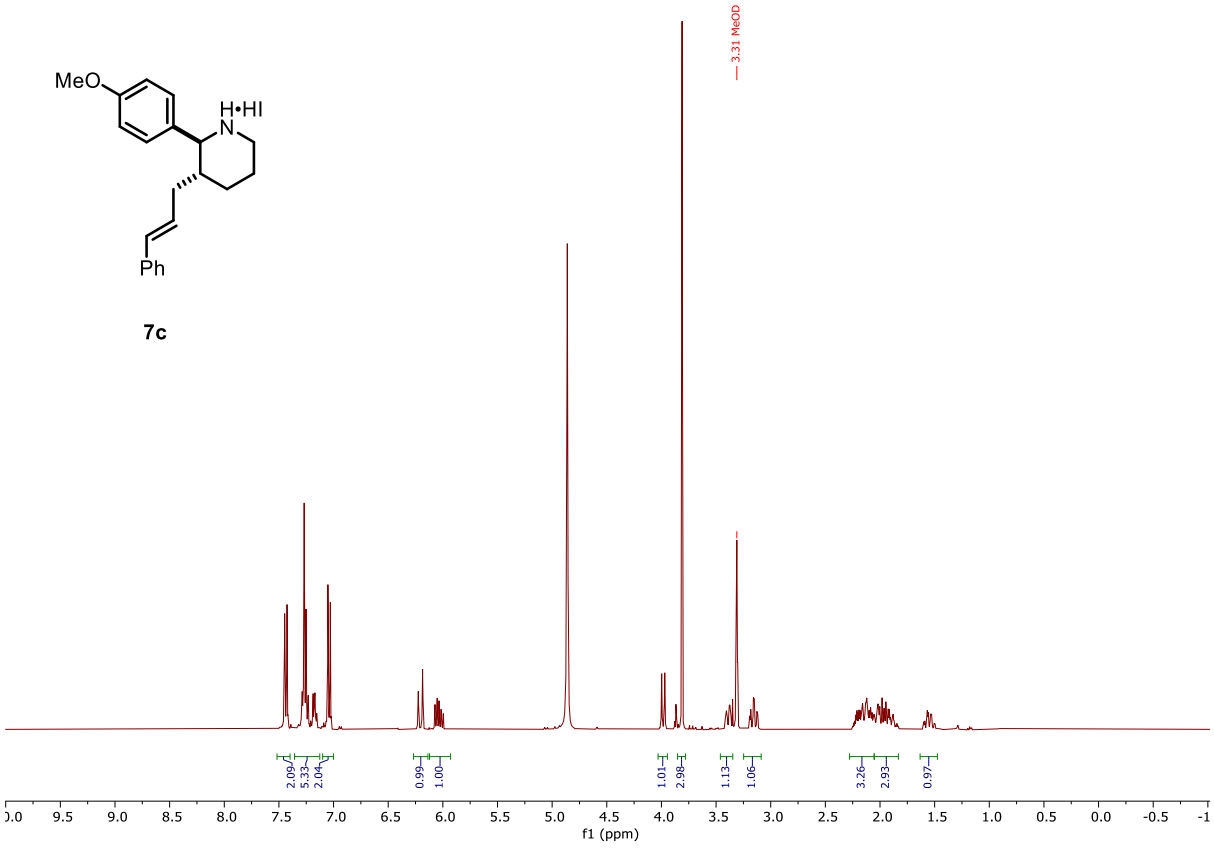
**(7b): (±)-(2*S*,3*R*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)piperidin-1-ium iodide**

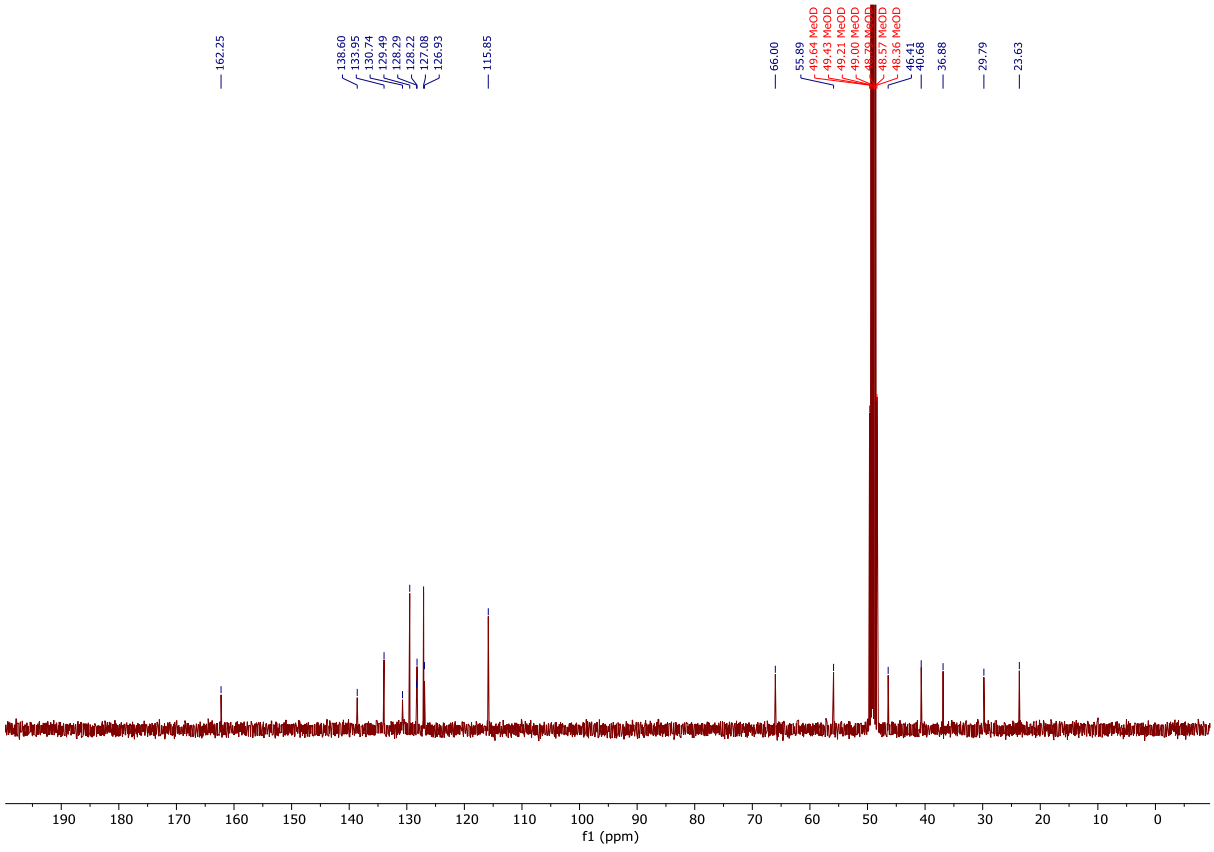



**7b**

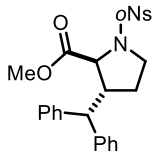


**(7c): (±)-(2*S*,3*R*)-3-Cinnamyl-2-(4-methoxyphenyl)piperidin-1-ium iodide**



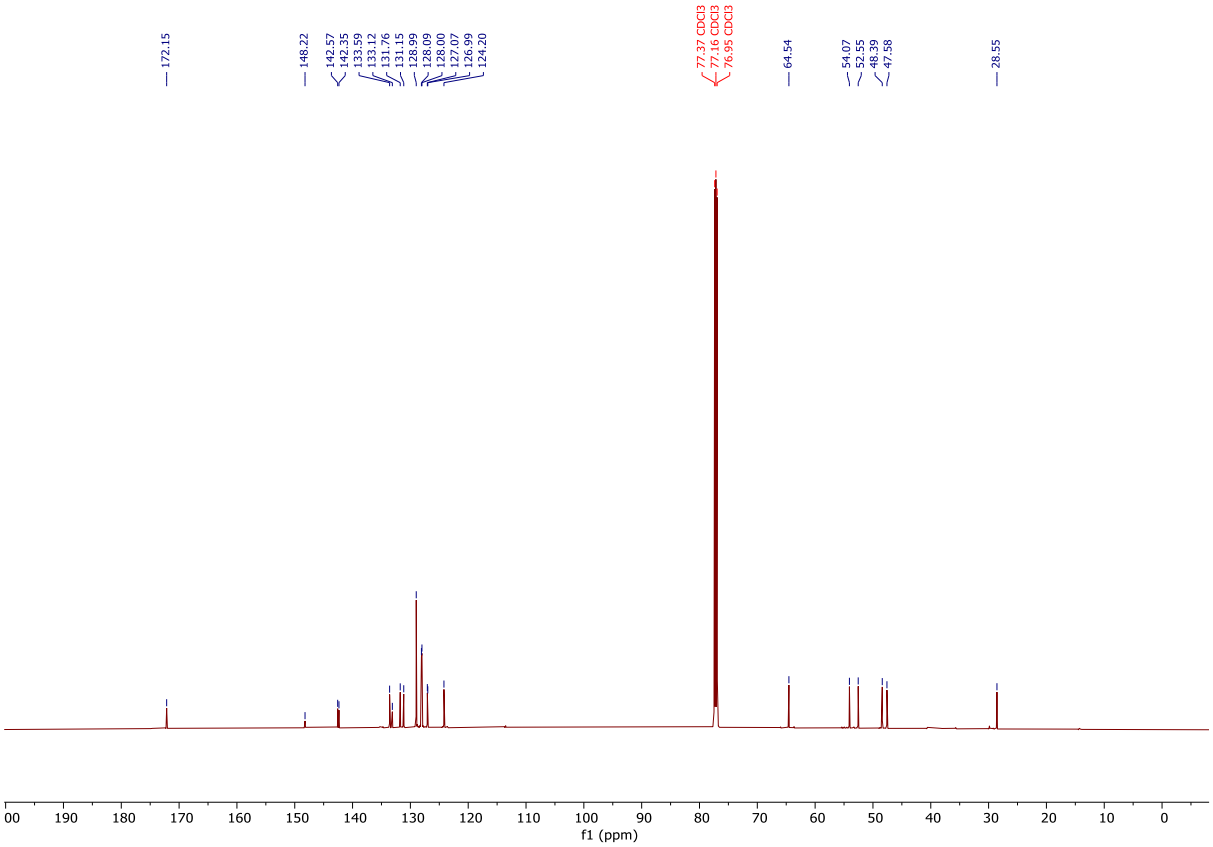



**(8): (±)-Methyl (2*S*,3*R*)-3-benzhydryl-1-((2-nitrophenyl)sulfonyl)pyrrolidine-2-carboxylate**

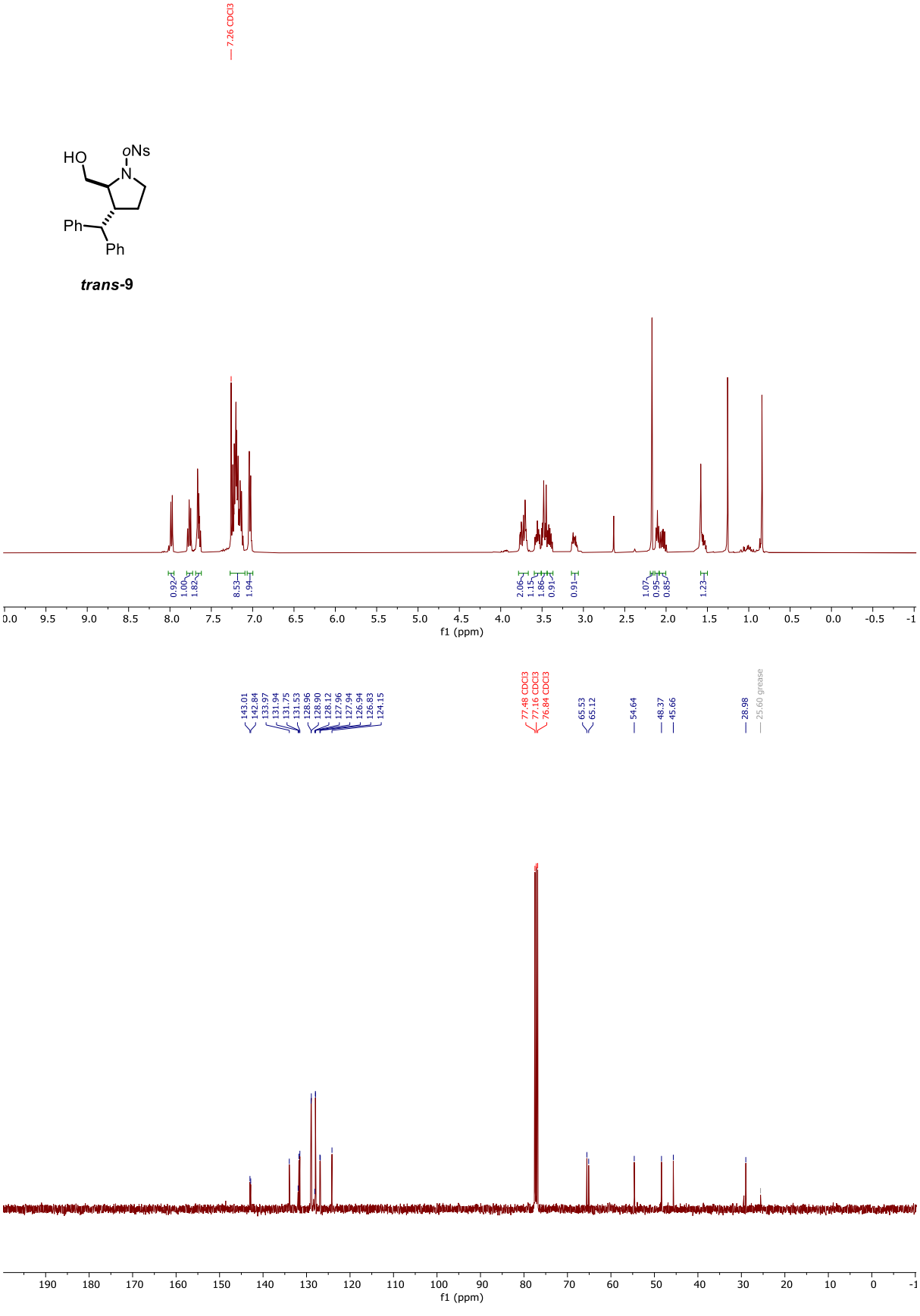



**8**

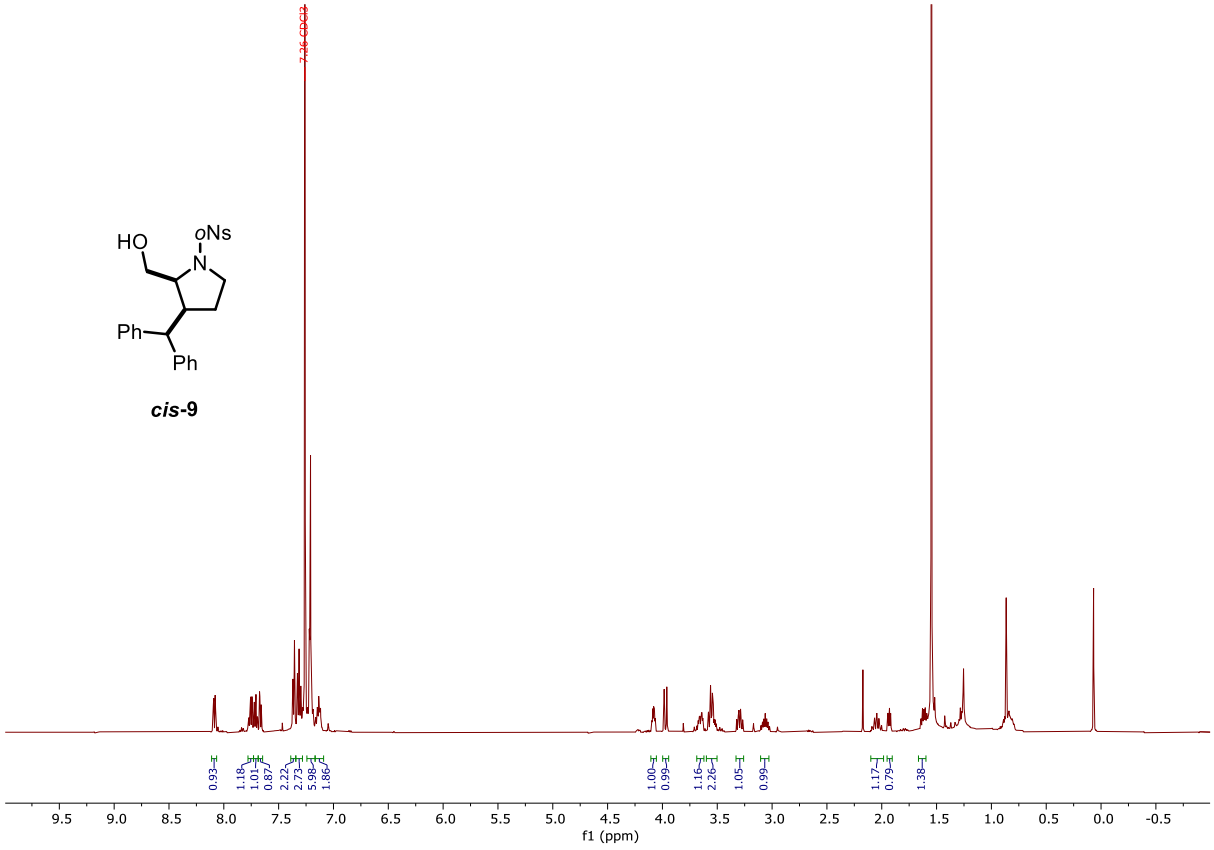


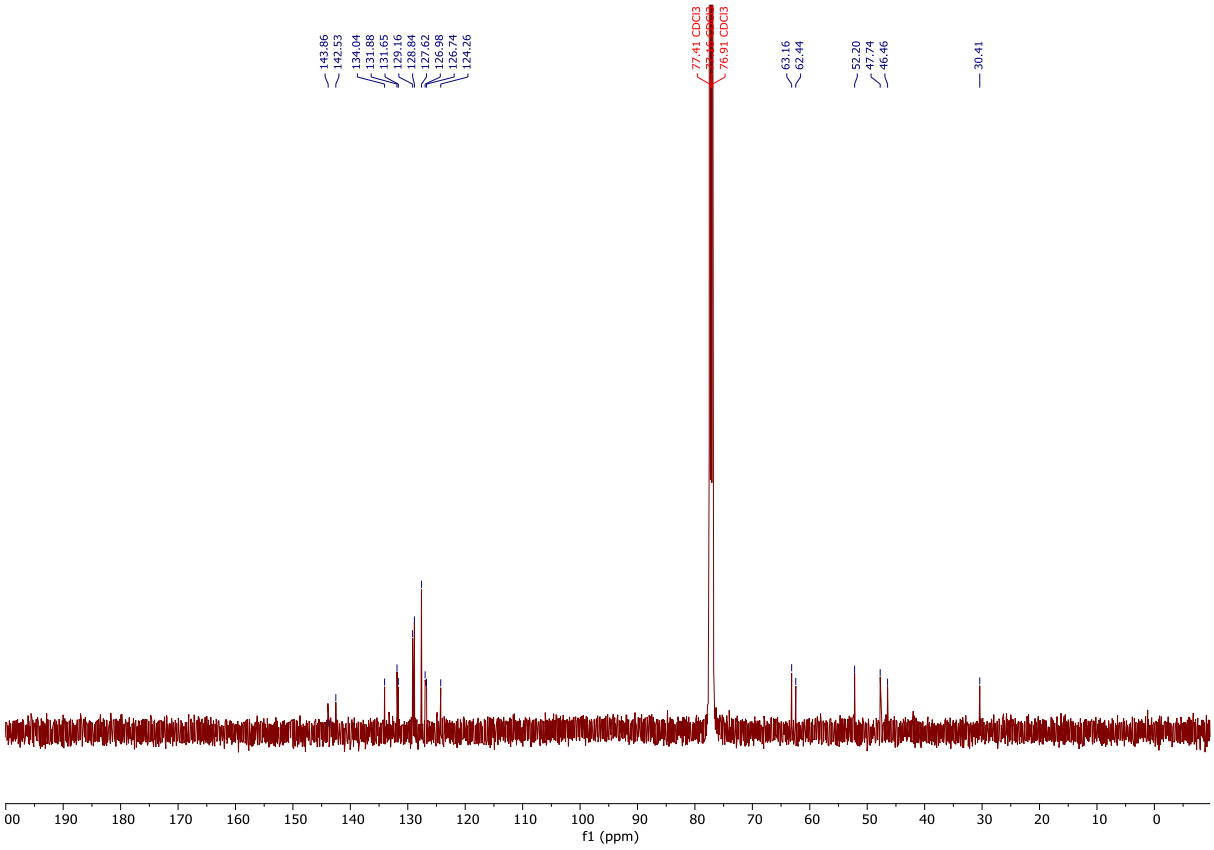



**(*trans*-9): (±)-2-{(2*S*,3*R*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]pyrrolidin-2-yl}methanol**

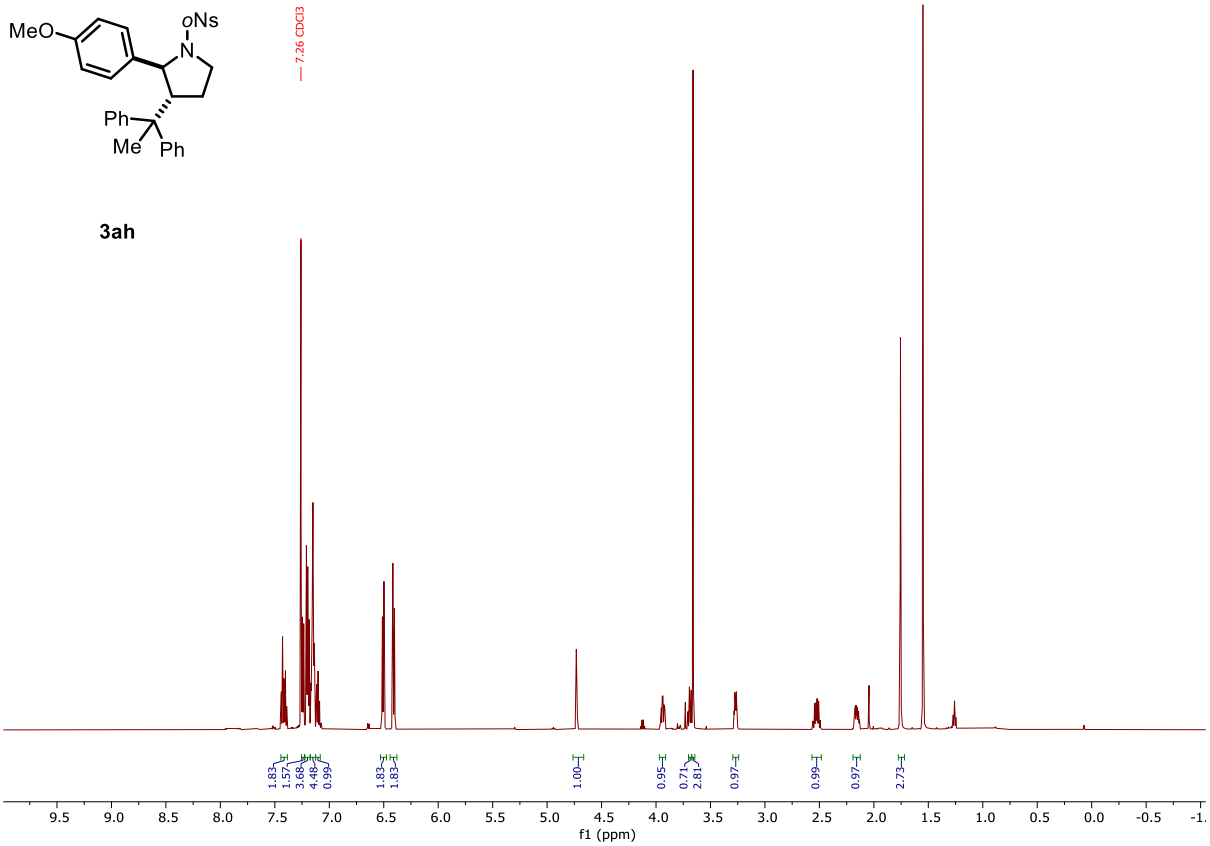


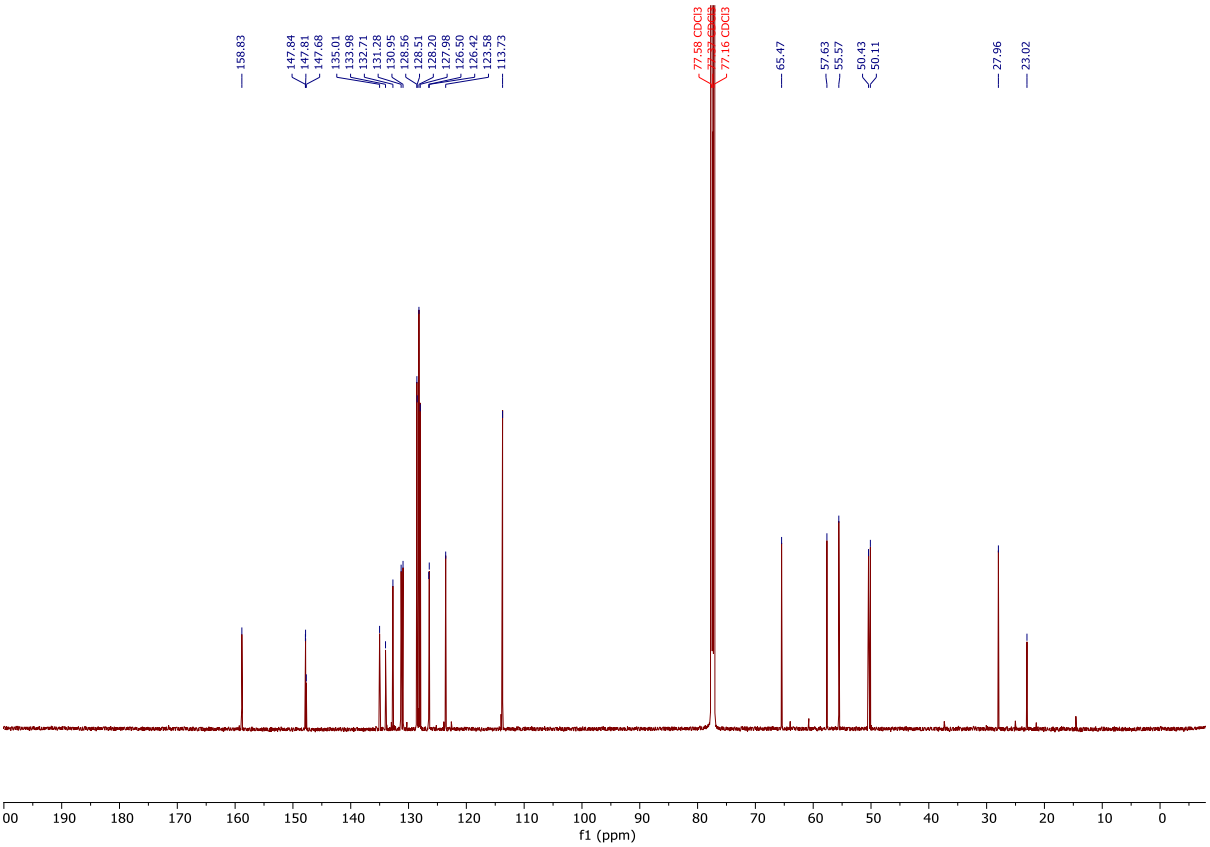
**(*cis*-9): (±)-2-{(2*S*,3*S*)-3-Benzhydryl-1-[(2-nitrophenyl)sulfonyl]pyrrolidin-2-yl}methanol**



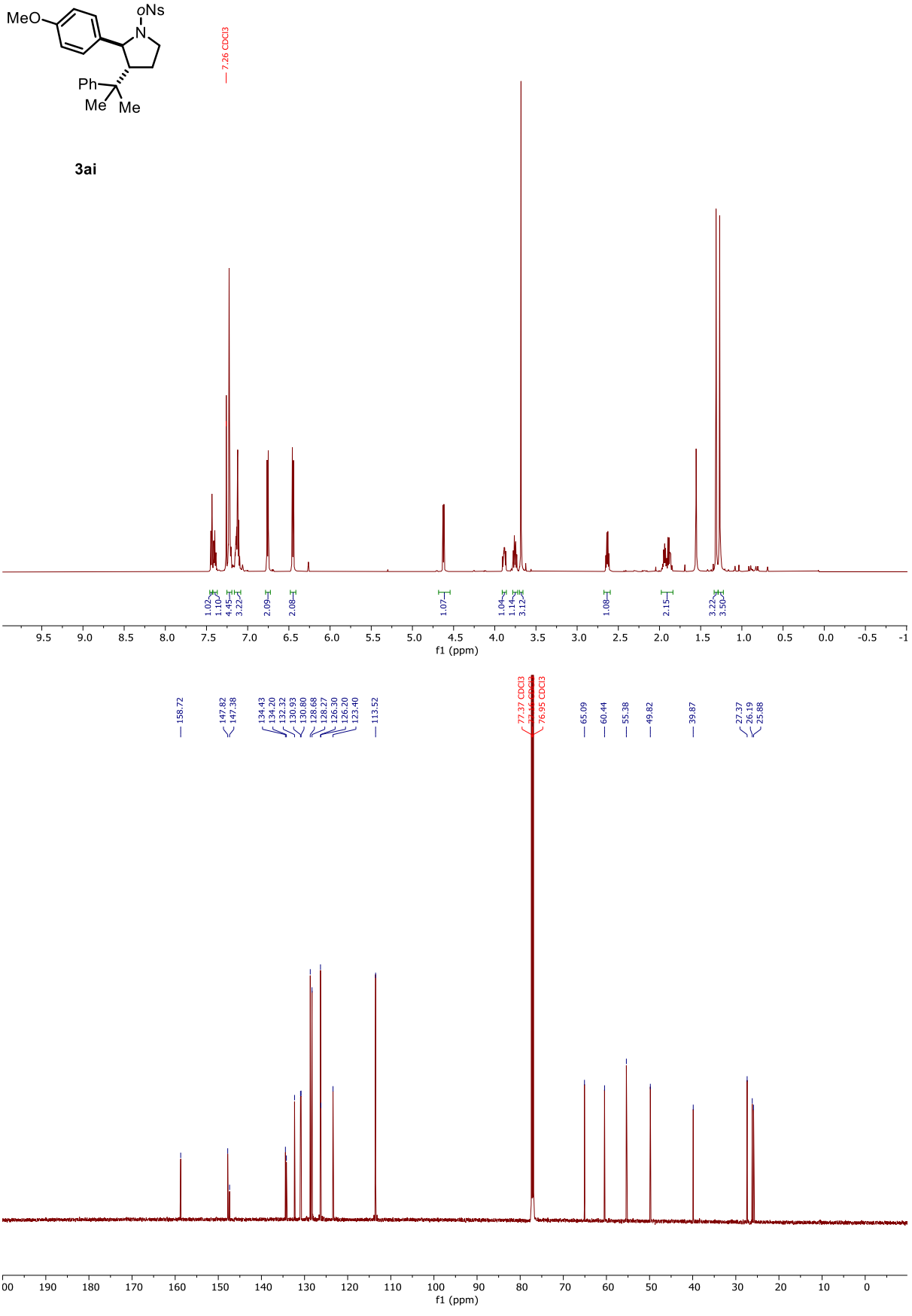



**(3ah): (±)-(2*S*,3*R*)-3-(1,1-Diphenylethyl)-2-(4-methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)-pyrrolidine**



**(3ai): (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-1-((2-nitrophenyl)sulfonyl)-3-(2-phenylpropan-2-yl)pyrrolidine**



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