Enantioselective Nickel-Catalyzed Michael Additions of 2-Acetylazaarenes to Nitroalkenes

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Supporting Information

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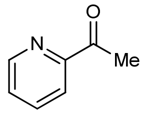
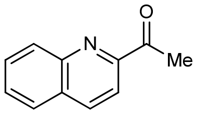
General Information

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen using oven-dried glassware. Solvents were dried and purified by passage through activated alumina columns using a solvent purification system. Unless specified otherwise, all other commercially available reagents were used as received. Microwave-assisted reactions were carried out in thick-walled glass vials using a Biotage Initiator. TLC analyses were performed on pre-coated Merck DF-Alufoilien $60F_{254}$ 0.2 mm plates, visualized by UV light at 254 nm, and subsequently developed using potassium permanganate, vanillin, *p*-anisaldehyde, or ceric ammonium molybdate solution as appropriate. Column chromatography was carried out using silica gel (Fisher Scientific 60 Å, particle size 35–70 μm) according to the method of Still and co-workers.[1] Melting points were recorded on a Gallenkamp or Griffin melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz or 500 MHz spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CHCl_3$ at 7.27 ppm, CD_3OD at 3.31 ppm, or DMSO-d_6 at 2.50 ppm).[2] Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), quin (quintet), sept (septet), app (apparent), br (broad), m (multiplet). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz or 500 MHz spectrometer. Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm, CD_3OD at 49.0 ppm, or DMSO-d_6 at 39.5 ppm).[2] Proton-decoupled ^{19}F NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of $CFCl_3$, using residual protonated solvent as internal standard ($CFCl_3$ at 376.38 MHz with respect to tetramethylsilane at 400.00 MHz).[3] Low resolution mass spectra were obtained by electrospray ionization (ESI) or electron impact (EI) of MeOH or CH_2Cl_2 solutions (*ca.* 1 mg/mL) with detection in the positive or negative ion mode as appropriate. High resolution mass spectra were recorded using nanoelectrospray ionization (NSI) or atmospheric pressure chemical ionization (APCI) techniques on a Finnigan MAT 900 XLT spectrometer, a Finnigan MAT 95XP spectrometer, or a Thermo Fisher LTQ Orbitrap XL spectrometer at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, or using electrospray ionization (ESI) or electron impact (EI) techniques on a Finnigan MAT 900 XLT spectrometer at the School of Chemistry, University of Edinburgh. Optical rotations were recorded on an Optical Activity POLAAR 20 polarimeter. Enantiomeric excesses were determined by chiral HPLC analysis performed on an Agilent 1100 or 1200 instrument using 4.6 × 250 mm columns. X-ray diffraction data were collected at 120 K on an Agilent SuperNova diffractometer using Mo Kα radiation at 0.71 Å and refined in SHELXTL.

Synthesis of 2-Acetylazaarenes


1a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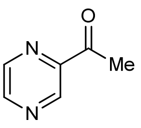
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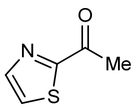
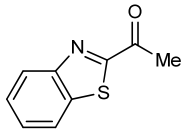

1d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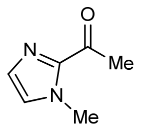
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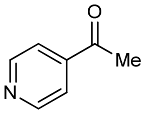
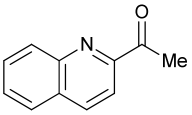
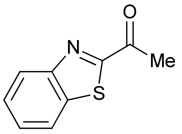

1g

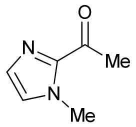
2-Acetylpyridine (**1a**) was purchased from Acros. 2-Acetylpyrazine (**1c**) and 2-acetylthiazole (**1d**) were purchased from Fluorochem. 4-Acetylpyridine (**1g**) was purchased from Fluka.



2-Acetylquinoline (**1b**) was prepared according to a previously reported procedure.[4] $R_f = 0.52$ (2:1 hexane/Et_2O). ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[5]

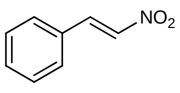


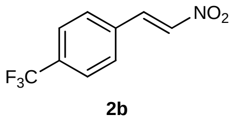
2-Acetylbenzothiazole (**1e**) was prepared according to a previously reported procedure.[6] $R_f = 0.52$ (2:1 hexane/Et_2O); IR (solid) 1682 (C=O), 1481, 1321, 1258, 1242, 932, 766, 735, 704, 621 cm^{-1}; LRMS (EI) *m*/*z* = 177.1 (M^+). ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[6]

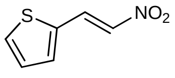


2-Acetyl-1-methylimidazole (**1f**) was prepared according to a previously reported procedure.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (1H, s, Ar**H**), 7.02 (1H, s, Ar**H**), 4.00 (3H, s, NC**H**$_3$), 2.66 (3H, s, O=CC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.6 (C), 143.2 (C), 129.0 (CH), 126.9 (CH), 36.2 (CH_3), 27.1 (CH_3). ^{1}H NMR data were consistent with those reported in the literature.[7]

Synthesis of Nitroalkenes


2a


2b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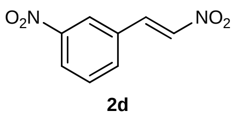
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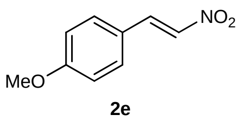
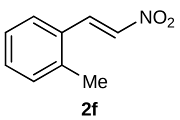
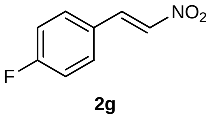
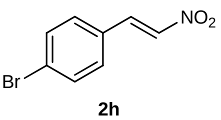
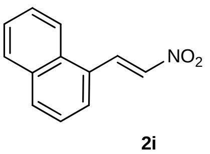
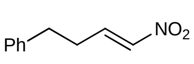

2e

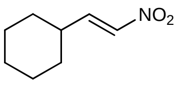

2f


2g


2h

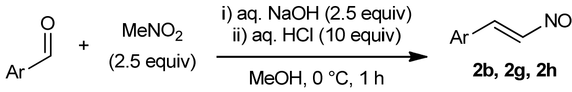

2i


2j

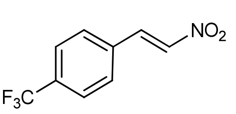

2k

(*E*)-β-Nitrostyrene (**2a**) and 4′-methoxynitrostyrene (**2e**) were purchased from Sigma-Aldrich. Nitroalkenes **2c**,[8] **2d**,[9] **2f**,[10] and **2i**[11] were prepared according to previously reported procedures.

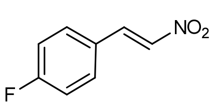
Synthesis of Aromatic Nitroalkenes: General Procedure A



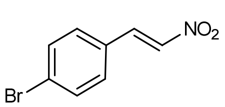
In a modification of a previously reported procedure for the synthesis of β-nitrostyrene (**2a**),[12] aqueous NaOH (10 M, 2.5 mL, 25 mmol) was added to a solution of the appropriate aldehyde (10.0 mmol) and $MeNO_2$ (1.34 mL, 25.0 mmol) in MeOH (100 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. Crushed ice was added until complete dissolution of any precipitate, and the mixture was poured into vigorously stirring aqueous HCl (5 M, 20 mL, 100 mmol) at 0 °C. The resulting precipitate was collected by filtration, washed with H_2O (2 × 100 mL) and dried *in vacuo* to afford the nitroalkenes **2**.



(*E*)-1-(2-Nitroethenyl)-4-(trifluoromethyl)benzene (2b).[13] The title compound was prepared according to General Procedure A from 4-(trifluoromethyl)benzaldehyde (1.74 g, 9.99 mmol) to afford a yellow solid which required no further purification (1.19 g, 55%). $R_f = 0.66$ (4:1 hexane/EtOAc); IR (solid) 1639, 1522 (NO_2), 1341, 1319, 1161, 1109, 1067, 966, 953, 824, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (1H, d, J = 13.7 Hz, C**H**=CHNO$_2$), 7.74–7.67 (4H, m, Ar**H**), 7.64 (1H, d, J = 13.7 Hz, CH=C**H**NO$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 138.8 (CH), 137.1 (CH), 133.5 (C), 133.3 (C, q, $^2J_{CF}$ = 33.0 Hz), 129.2 (2 × CH), 126.3 (2 × CH, q, $^3J_{CF}$ = 3.8 Hz), 123.5 (C, q, $^1J_{CF}$ = 272.5 Hz); ^{19}F NMR (376.3 Hz, $CDCl_3$) δ −63.2 (3F, s, C**F**$_3$); LRMS (EI) m/z = 217.0 (M^+). ^{1}H NMR data were consistent with those reported in the literature.[13]

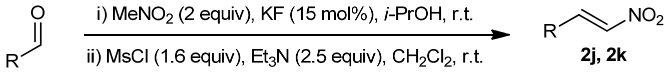


(*E*)-1-Fluoro-4-(2-nitroethenyl)benzene (2g).[14] The title compound was prepared according to General Procedure A from 4-fluorobenzaldehyde (1.24 g, 10.0 mmol) to afford short, fine yellow needles which required no further purification (1.20 g, 70%). $R_f = 0.48$ (4:1 hexane/Et_2O); IR (solid) 1636, 1593 (NO_2), 1499, 1339, 1263, 1229, 1163, 964, 826, 797 cm^{-1}; ^{19}F NMR (376.3 Hz, $CDCl_3$) δ −105.8 (1F, tt, $^3J_{HF}$ = 8.5, $^4J_{HF}$ = 5.5 Hz, Ar**F**). ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[14]

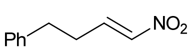


(*E*)-1-Bromo-4-(2-nitroethenyl)benzene (2h).[15] The title compound was prepared according to General Procedure A from 4-bromobenzaldehyde (1.85 g, 10.0 mmol) to afford a yellow solid which required no further purification (1.82 g, 73%). $R_f = 0.52$ (4:1 hexane/Et_2O); IR (solid) 1634, 1516 (NO_2), 1499, 1485, 1331, 1260, 1070, 966, 812, 743 cm^{-1}; LRMS (EI) m/z = 226.9 (M^+). ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[15]

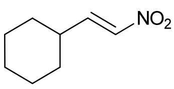
Synthesis of Aliphatic Nitroalkenes: General Procedure B



In a modification of a reported procedure,[16] KF (436 mg, 7.35 mmol) was added to a solution of the appropriate aldehyde (50 mmol) and $MeNO_2$ (5.4 mL, 101 mmol) in *i*-PrOH (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h, then diluted with H_2O (30 mL). The resulting solution was extracted with Et_2O (3 × 30 mL) and the combined organic extracts were washed with H_2O (30 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford the intermediate nitroaldols in quantitative yield.[17] In a modification of a second reported procedure,[18] Et_3N (17.5 mL, 125 mmol) was added dropwise to a solution of the crude nitroaldol (theoretically 50 mmol) and MsCl (5.8 mL, 75 mmol) in CH_2Cl_2 (200 mL) at 0 °C over 1 min. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. H_2O (100 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine (2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography afforded the nitroalkenes **2**.

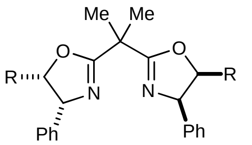


(*E*)-(4-Nitrobut-3-en-1-yl)benzene (2j).[18] The title compound was prepared according to General Procedure B from hydrocinnamaldehyde (6.9 mL, 49.8 mmol) and purified by column chromatography (8:1 hexane/Et_2O) to afford a yellow oil (5.91 g, 65%). R_f = 0.44 (8:1 hexane/Et_2O). ^1H and ^{13}C NMR data were consistent with those reported in the literature.[18]

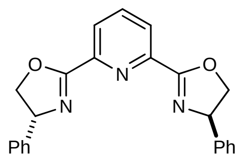


(*E*)-(2-Nitroethenyl)cyclohexane (2k).[16] The title compound was prepared according to General Procedure B from cyclohexanecarboxaldehyde (6.1 mL, 50.4 mmol) for a reaction time of 18 h and purified by column chromatography (10:1 hexane/Et_2O) to afford a yellow oil (6.43 g, 82%). R_f = 0.72 (4:1 hexane/Et_2O); IR (film) 2928, 2855, 1645, 1520 (NO_2), 1449, 1348, 959, 835, 731, 596 cm^{-1}; LRMS (EI) *m*/*z* = 156 ($[M+H]^+$). ^1H and ^{13}C NMR data were consistent with those reported in the literature.[16]

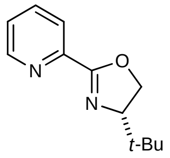
Synthesis of Ligands and Catalysts



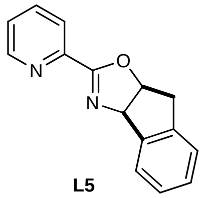
L1 R = Ph
L2 R = H



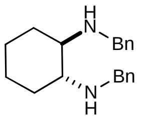
L3



L4

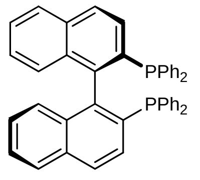


L5

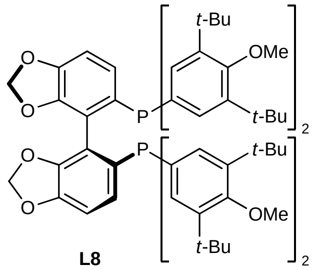


(racemate)

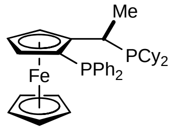
L6



L7



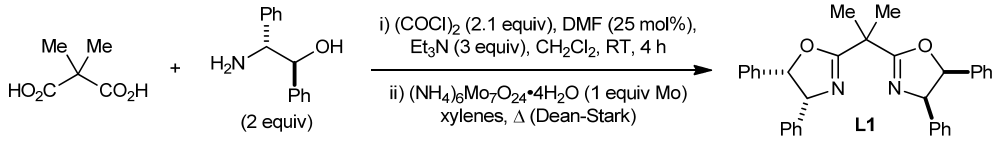
L8



L9

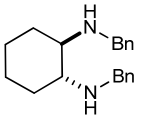
Ligands **L2** and **L3** were purchased from Aldrich. (*R*)-BINAP (**L7**) was purchased from Acros. (*S*)-DTBM-Segphos (**L8**) was obtained from Takasago. (*R*)-Josiphos SL-J001-1 (**L9**) was obtained from Solvias. Ligands **L4**[19] and **L5**[20] were prepared according to previously reported procedures.

2,2-*Bis*[(4*R*,5*S*)-4,5-diphenyl-4,5-dihydro-1,3-oxazol-2-yl]propane (L1)[21]



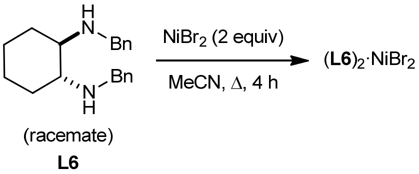
In a modification of a previously reported procedure,[21] a suspension of dimethylmalonic acid (661 mg, 5.00 mmol) and DMF (0.1 mL, 1.3 mmol) in CH_2Cl_2 (10 mL) at 0 °C was treated with oxalyl chloride (1.1 mL, 11 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then added by cannula transfer to a vigorously stirred mixture of (1*S*,2*R*)-2-amino-1,2-diphenylethanol (2.13 g, 9.99 mmol) and Et_3N (2.1 mL, 15 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h, then diluted with EtOAc (80 mL), washed with 1:1 brine/aqueous HCl (1 M) (3 × 50 mL) and brine (80 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the intermediate *bis*-amide in quantitative yield.[21] In a modification of a second previously reported procedure,[22] this *bis*-amide (theoretically 5 mmol) was suspended in xylenes (150 mL) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (884 mg, 0.715 mmol) was added. The mixture was heated at reflux using a Dean-Stark apparatus for 24 h. After cooling to room temperature, the mixture was concentrated to approximately 25 mL *in vacuo*, adsorbed onto silica (*ca.* 10 g) and concentrated *in vacuo*. Purification of the residue by column chromatography (0–16% acetone/hexane) followed by recrystallization from heptane afforded the title compound as fine white needles (1.28 g, 52%); $R_f = 0.61$ (3:2 hexane/acetone); IR (solid) 1674, 1689, 1450, 1319, 1140, 1119, 984, 741, 698, 567 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.05–7.00

(10H, m, Ar**H**), 6.99–6.95 (10 H, m, Ar**H**), 5.98 (2H, d, *J* = 10.1 Hz, 2 × OC**H**), 5.61 (2H, d, *J* = 10.2 Hz, 2 × NC**H**), 1.93 (6H, s, 2 × C**H**$_3$); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 170.4 (2 × C), 137.5 (2 × C), 136.2 (2 × C), 127.8 (4 × CH), 127.6 (4 × CH), 127.6 (4 × CH), 127.4 (2 × CH), 126.9 (2 × CH), 126.5 (4 × CH), 86.3 (2 × CH), 73.8 (2 × CH), 39.6 (C), 24.8 (2 × CH$_3$); LRMS (ESI) *m*/*z* = 487 ([M+H]$^+$). ^{1}H NMR data were consistent with those reported in the literature.[21]


(racemate)

(±)-*Trans*-*N*,*N*′-dibenzylcyclohexane-1,2-diamine (**L6**) was prepared according to a previously reported procedure.[23] R_f = 0.17 (4:1 hexane/EtOAc, plate pre-doped with 5% Et$_3$N/CH$_2$Cl$_2$). ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[23]

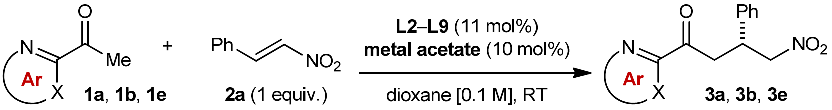
***Bis*-(*trans*-(*N*,*N*′-dibenzyl)cyclohexane-1,2-diamine)nickel (II) bromide [(L6)$_2$·NiBr$_2$]**[24]



According to a previously reported procedure for *bis*-[(*R*,*R*)-(*N*,*N*′-dibenzyl)cyclohexane-1,2-diamine]nickel (II) bromide,[24] a solution of NiBr$_2$ (1.09 g, 4.99 mmol) and (±)-*trans*-*N*,*N*′-dibenzylcyclohexane-1,2-diamine **L6** (3.68 g, 12.5 mmol) in MeCN (100 mL) was stirred at reflux for 4 h, allowed to cool to room temperature, and concentrated *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$ (100 mL) and filtered, and the filtrate was concentrated *in vacuo*. The residue was recrystallized from 1:1 MeCN/CH$_2$Cl$_2$ to afford the title compound as a pale blue powder (2.25 g, 56%). m.p (decomp.) 175–180 °C (1:1 MeCN/CH$_2$Cl$_2$); ^{1}H NMR (500 MHz, CD$_3$OD) δ 7.36–7.28 (16H, m, Ar**H**), 7.28–7.23 (4H, m, Ar**H**), 3.90 (4H, d, *J* = 13.0 Hz, 4 × NC**H**$_2$), 3.70 (4H, d, *J* = 13.0 Hz, 4 × NC**H**$_2$), 2.41–2.32 (4H, m, 4 × C**H**$_2$CHN), 2.19 (4H, dd, *J* = 10.6, 2.4 Hz, CH$_2$C**H**N), 1.81–1.71 (4H, m, 4 × C**H**$_2$CHN), 1.32–1.20 (4H, m, 2 × CH$_2$C**H**$_2$C**H**$_2$), 1.20–1.09 (4H, m, 2 × CH$_2$C**H**$_2$C**H**$_2$); ^{13}C NMR (125.8 MHz, CD$_3$OD) δ 137.3 (4 × C), 129.62 (8 × CH), 129.60 (8 × CH), 128.5 (4 × CH), 61.1 (4 × CH), 50.8 (4 × CH$_2$), 31.1 (4 × CH$_2$), 25.8 (4 × CH$_2$); LRMS (ESI) *m*/*z* = 807 ([M+H]$^+$).

Screening and Optimization

Initial Catalyst Screening: General Procedure C

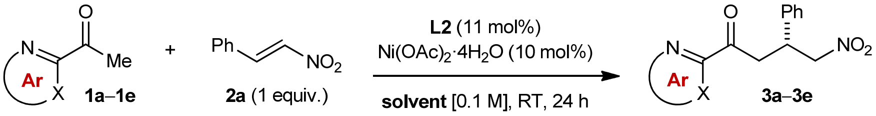


A 1 mL vial was charged with metal salt (0.010 mmol) and 3 Å molecular sieves (50 mg). A solution of the appropriate ligand (0.011 mmol) in dioxane (0.5 mL), a solution of the appropriate 2-acetylazaarene **1** (0.10 mmol) in dioxane (0.25 mL) and a solution of (*E*)-β-nitrostyrene (**2a**) (15 mg, 0.10 mmol) in dioxane (0.25 mL) were added, and the vial was sealed. The reaction mixture was stirred at room temperature for 24 h, then filtered through a plug of silica gel (*ca.* 1 cm), eluting with EtOAc (2 × 5 mL), and concentrated *in vacuo*.

Results

Each of $Ni(OAc)_2{\cdot}4H_2O$, AgOAc, $Pd(OAc)_2$, $Cu(OAc){\cdot}H_2O$, $Zn(OAc)_2{\cdot}2H_2O$ and $Mg(OAc)_2{\cdot}4H_2O$ was screened against each of ligands **L2**–**L5** and **L7**–**L9**. The only combinations that exhibited good catalytic activity (as determined by TLC analysis) were those of $Ni(OAc)_2{\cdot}4H_2O$ with **L2** (81–89% ee), **L3** (0–31% ee), **L4** (10–42% ee), or **L5** (2–40% ee). The crude products of the reactions with **L2** were analysed by ^{1}H NMR spectroscopy, which indicated 84–98% conversion into the desired products.

Solvent Screening: General Procedure D



A solution of $Ni(OAc)_2{\cdot}4H_2O$ (2.5 mg, 0.010 mmol), **L2** (3.7 mg, 0.011 mmol), the appropriate 2-acetylazaarene **1** (0.10 mmol) and (*E*)-β-nitrostyrene (**2a**) (15 mg, 0.10 mmol) in the appropriate solvent (1 mL) was stirred at room temperature for 24 h, then filtered through a plug of silica gel (*ca.* 1 cm), eluting with EtOAc (2 × 5 mL), and concentrated *in vacuo*.

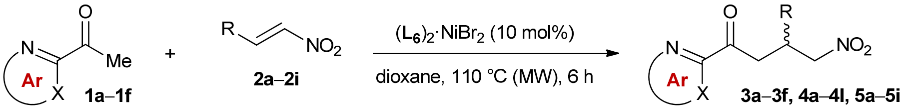
Results

i-PrOH gave the highest enantioselectivity (88–96% ee) and high conversion (90–98%). Other alcohols (MeOH, *n*-BuOH) and ethers (THF, Et_2O, *t*-BuOMe) gave comparable conversion (84–99%), but with generally lower levels of enantioselectivity (74–96% ee) which were highly variable across the substrate range. MeCN, toluene and chlorinated solvents (CH_2Cl_2, $CHCl_3$) gave lower conversion (64–75%).

Further Ligand Evaluation

On subsequent scaling up of the reaction, significant proportions of an undesired side product (not detected in screening) were observed. Based on NMR and LRMS analysis of isolated material, this was tentatively identified as a mixture of diastereomers and/or regioisomers corresponding to a 2:1 adduct of nitroalkene and azaarene. Attempts to suppress the second addition by varying the reaction temperature and/or concentration were unsuccessful. It was found that the more sterically congested ligand **L1**, when used in conjunction with a slight excess of the azaarene, gave much cleaner reactions with minimal side product formation (<5%). A significant acceleration of the reaction was also noted under these conditions, with no loss of enantioselectivity.

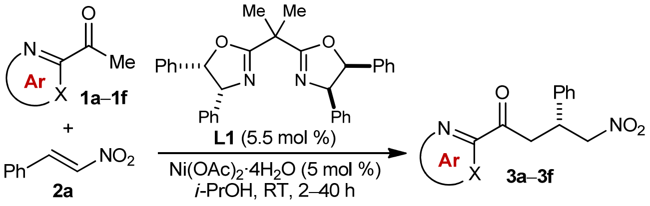
Racemic Conjugate Addition of 2-Acetylazaarenes to Nitroalkenes: General Procedure E



A solution of the appropriate 2-acetylazaarene **1** (0.12 mmol), the appropriate nitroalkene **2** (0.10 mmol) and (**L6**)$_2$·NiBr$_2$ (8 mg, 0.010 mmol) in dioxane (1 mL) was stirred under microwave irradiation at 110 °C for 6 h, then allowed to cool to room temperature. A small aliquot of the reaction mixture was purified by preparative TLC (hexane/EtOAc, hexane/Et$_2$O or Et$_2$O as appropriate) to afford an authentic racemic sample for HPLC analysis.

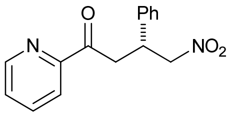
Enantioselective Ni-Catalyzed Michael Addition of 2-Acetylazaarenes to Nitroalkenes

Figure 1: General Procedure F

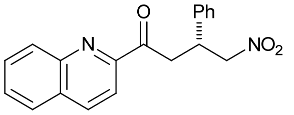


A suspension of Ni(OAc)$_2$·4H$_2$O (6.2 mg, 0.025 mmol) and ligand **L1** (13.4 mg, 0.0275 mmol) in *i*-PrOH (1 mL) was stirred at room temperature for 10 min. To the resulting solution was added a solution of the appropriate 2-acetylazaarene **1** (0.60 mmol) in *i*-PrOH (2 mL) followed by a solution of (*E*)-β-nitrostyrene (**2a**) (75 mg, 0.50 mmol) in *i*-PrOH (2 mL), and the reaction mixture was stirred at room temperature until complete consumption of the nitroalkene as indicated by TLC analysis. The reaction mixture was diluted with EtOAc (10 mL) and washed with brine (2 × 5 mL). The aqueous layers were extracted with EtOAc (5 mL) and the combined organic layers were dried

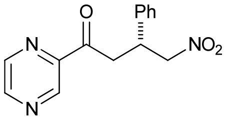
($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography afforded the nitroalkane **3**.



(*R*)-4-Nitro-3-phenyl-1-(pyridin-2-yl)butan-1-one (3a).[25] The title compound was prepared according to General Procedure F from 2-acetylpyridine (**1a**) (67 μL, 0.60 mmol) for a reaction time of 2 h and purified by column chromatography (1:1 hexane/Et_2O) to afford a white solid (116 mg, 86%). $[\alpha]_D^{20}$ +21.9 (*c* 0.53, $CHCl_3$); R_f = 0.23 (1:1 hexane/Et_2O); IR (solid) 2922, 1701 (C=O), 1545 (NO_2), 1435, 1366, 993, 766, 704, 631, 615, 557 cm^{-1}; HPLC (Chiralpak AS-H, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 31.0 min, t_r (major) = 36.7 min, 96% ee. ^1H and ^{13}C NMR data were consistent with those reported in the literature.[25]

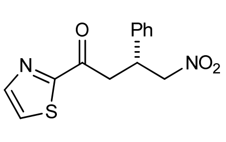


(*R*)-4-Nitro-3-phenyl-1-(quinolin-2-yl)butan-1-one (3b). The title compound was prepared according to General Procedure F from 2-acetylquinoline (**1b**) (103 mg, 0.60 mmol) for a reaction time of 21 h and purified by column chromatography (3:1 hexane/EtOAc) to afford a white solid (150 mg, 94%). m.p. 168–170 °C (hexane); $[\alpha]_D^{20}$ +57.5 (*c* 0.53, $CHCl_3$); R_f = 0.31 (3:1 hexane/EtOAc); IR (solid) 1693 (C=O), 1545 (NO_2), 1385, 1368, 1202, 974, 826, 754, 700, 561 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.21 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.07 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.88 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.81 (1H, ddd, *J* = 8.4, 6.9, 1.4 Hz, Ar**H**), 7.67 (1H, ddd, *J* = 8.1, 7.1, 1.1 Hz, Ar**H**), 7.40–7.31 (4H, m, Ar**H**), 7.30–7.23 (1H, m, Ar**H**), 4.86 (1H, dd, *J* = 12.4, 6.8 Hz, C**H**$_2$NO$_2$), 4.74 (1H, dd, *J* = 12.4, 8.2 Hz, C**H**$_2$NO$_2$), 4.33 (1H, app dq, *J* = 8.0, 7.0 Hz, CH$_2$C**H**), 4.03 (1H, dd, *J* = 17.9, 7.1 Hz, C**H**$_2$C=O), 3.80 (1H, dd, *J* = 17.9, 7.2 Hz, C**H**$_2$C=O); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 199.0 (C), 152.3 (C), 147.1 (C), 139.3 (C), 137.1 (CH), 130.5 (CH), 130.2 (CH), 129.7 (C), 129.0 (2 × CH), 128.8 (CH), 127.73 (CH), 127.68 (CH), 127.6 (2 × CH), 118.0 (CH), 79.9 (CH_2), 40.6 (CH_2), 39.6 (CH); HRMS (APCI) Exact mass calcd for $C_{19}H_{17}N_2O_3$ $[M+H]^+$: 321.1234, found 321.1234; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 25.7 min, t_r (major) = 31.3 min, 94% ee.

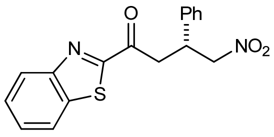


(*R*)-4-Nitro-3-phenyl-1-(pyrazin-2-yl)butan-1-one (3c). The title compound was prepared according to General Procedure F from 2-acetylpyrazine (**1c**) (79 mg, 0.60 mmol) for a reaction time of 2 h and purified by column chromatography (3:1 Et_2O/hexane) to afford a white solid (113 mg, 83%). m.p. 137–139 °C (hexane); $[\alpha]_D^{20}$ +11.0 (*c* 0.50, $CHCl_3$); R_f = 0.33 (3:1 Et_2O/hexane); IR (solid) 1703 (C=O), 1543

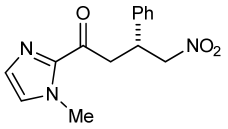
(NO_2), 1396, 1369, 1047, 1018, 989, 772, 704, 559 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (1H, br s, Ar**H**), 8.78 (1H, br s, Ar**H**), 8.64 (1H, br s, Ar**H**), 7.38–7.22 (5H, m, Ar**H**), 4.79 (1H, dd, *J* = 12.4, 7.2 Hz, C**H**$_2$NO$_2$), 4.70 (1H, dd, *J* = 12.4, 7.7 Hz, C**H**$_2$NO$_2$), 4.25 (1H, app quin, *J* = 7.3 Hz, CH$_2$C**H**), 3.83 (1H, dd, *J* = 18.3, 7.3 Hz, C**H**$_2$C=O), 3.61 (1H, dd, *J* = 18.3, 6.8 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.1 (C), 148.2 (CH), 146.9 (C), 143.7 (CH), 143.5 (CH), 138.8 (C), 129.0 (2 × CH), 127.9 (CH), 127.5 (2 × CH), 79.7 (CH_2), 40.8 (CH_2), 39.0 (CH); HRMS (APCI) Exact mass calcd for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1030, found 272.1028; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 42.5 min, t_r (major) = 44.7 min, 99% ee.



(*R*)-4-Nitro-3-phenyl-1-(1,3-thiazol-2-yl)butan-1-one (3d).[26] The title compound was prepared according to General Procedure F from 2-acetylthiazole (**1d**) (62 μL, 0.60 mmol) for a reaction time of 21 h and purified by column chromatography (2:1 hexane/Et_2O) to afford an off-white oil (118 mg, 75%). $[\alpha]_D^{20}$ +9.1 (*c* 0.50, $CHCl_3$); R_f = 0.25 (1:1 hexane/Et_2O); IR (film) 2922, 1686 (C=O), 1549 (NO_2), 1479, 1379, 1347, 783, 762, 700, 554 cm^{-1}; HPLC (Chiralpak IC, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 21.5 min, t_r (major) = 23.7 min, 97% ee. ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[26]

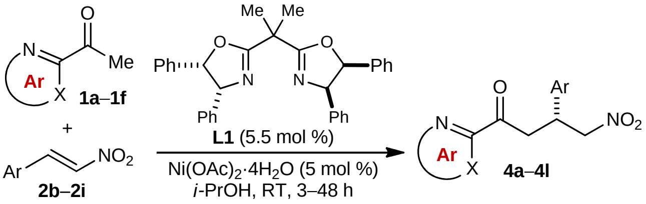


(*R*)-1-(1,3-Benzothiazol-2-yl)-4-nitro-3-phenylbutan-1-one (3e). The title compound was prepared according to General Procedure F from 2-acetylbenzothiazole (**1e**) (106 mg, 0.60 mmol) for a reaction time of 40 h and purified by column chromatography (2:1 hexane/Et_2O) to afford a white solid (105 mg, 64%). m.p. 159–161 °C (hexane); $[\alpha]_D^{20}$ +30.3 (*c* 0.55, $CHCl_3$); R_f = 0.27 (2:1 hexane/Et_2O); IR (solid) 2924, 1697 (C=O), 1543 (NO_2), 1476, 943, 762, 733, 718, 700, 554 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, ddd, *J* = 8.1, 1.3, 0.6 Hz, Ar**H**), 7.98 (1H, ddd, *J* = 7.8, 1.5, 0.7 Hz, Ar**H**), 7.62–7.58 (1H, m, Ar**H**), 7.57–7.53 (1H, m, Ar**H**), 7.36–7.31 (4H, m, Ar**H**), 7.30–7.25 (1H, m, Ar**H**), 4.83 (1H, dd, *J* = 12.6, 7.0 Hz, C**H**$_2$NO$_2$), 4.73 (1H, dd, *J* = 12.6, 7.9 Hz, C**H**$_2$NO$_2$), 4.31 (1H, app quin, *J* = 7.3 Hz, CH$_2$C**H**), 3.91 (1H, dd, *J* = 18.0, 7.3 Hz, C**H**$_2$C=O), 3.71 (1H, dd, *J* = 18.0, 7.0 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 192.1 (C), 165.4 (C), 153.4 (C), 138.5 (C), 137.3 (C), 129.1 (2 × CH), 128.0 (CH), 127.99 (CH), 127.5 (2 × CH), 127.2 (CH), 125.5 (CH), 122.5 (CH), 79.6 (CH_2), 41.6 (CH_2), 39.2 (CH); HRMS (APCI) Exact mass calcd for $C_{17}H_{15}N_2O_3S$ $[M+H]^+$: 327.0798, found 327.0795; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 34.7 min, t_r (major) = 38.4 min, 97% ee.



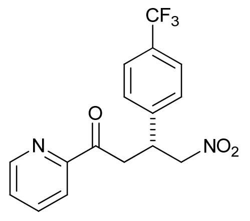
(*R*)-1-(1-Methyl-1*H*-imidazol-2-yl)-4-nitro-3-phenylbutan-1-one (3f).[27] The title compound was prepared according to General Procedure F from 2-acetyl-1-methylimidazole (**1f**) (75 mg, 0.60 mmol) for a reaction time of 40 h and purified by column chromatography (2:1 CH_2Cl_2/Et_2O) to afford a white oil (122 mg, 85%). $[\alpha]_D^{20}$ +17.8 (*c* 0.51, $CHCl_3$); R_f = 0.53 (2:1 CH_2Cl_2/Et_2O); IR (film) 2924, 1678 (C=O), 1541 (NO_2), 1408, 1155, 972, 781, 766, 702, 556 cm^{-1}; ^{1}H NMR 500 MHz, $CDCl_3$) δ 7.35–7.28 (4H, m, Ar**H**), 7.27–7.22 (1H, m, Ar**H**), 7.13 (1H, d, J = 0.8 Hz, Ar**H**), 7.03 (1H, s, Ar**H**), 4.75 (1H, dd, J = 12.5, 6.8 Hz, C**H**$_2$NO$_2$), 4.66 (1H, dd, J = 12.5, 8.3 Hz, C**H**$_2$NO$_2$), 4.22 (1H, app dq, J = 8.3, 7.1 Hz, CH$_2$C**H**), 3.95 (3H, s, C**H**$_3$), 3.74 (1H, dd, J = 17.4, 7.2 Hz, C**H**$_2$C=O), 3.52 (1H, dd, J = 17.4, 7.2 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 189.1 (C), 142.6 (C), 139.0 (C), 129.3 (CH), 128.9 (2 × CH), 127.7 (CH), 127.6 (2 × CH), 127.3 (CH), 79.9 (CH_2), 41.9 (CH_2), 39.3 (CH), 36.1 (CH_3); HRMS (APCI) Exact mass calcd for $C_{14}H_{16}N_3O_3$ $[M+H]^+$: 274.1186, found 274.1187; HPLC (Chiracel OD-H, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 21.5 min, t_r (minor) = 24.5 min, 97% ee. ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[27]

Figure 2: General Procedure G

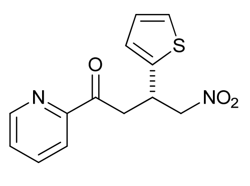


A suspension of $Ni(OAc)_2 \cdot 4H_2O$ (6.2 mg, 0.025 mmol) and ligand **L1** (13.4 mg, 0.0275 mmol) in *i*-PrOH (1 mL) was stirred at room temperature for 10 min. To the resulting solution was added a solution of the appropriate 2-acetylazaarene **1** (0.60 mmol) in *i*-PrOH (2 mL) followed by a solution of the appropriate nitroalkene **2** in *i*-PrOH (2 mL)* and the mixture was stirred at room temperature until complete consumption of the nitroalkene as indicated by TLC analysis. The reaction mixture was diluted with EtOAc (10 mL) and washed with brine (2 × 5 mL). The aqueous layers were extracted with EtOAc (5 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography afforded the nitroalkane **4**.

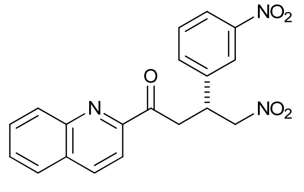
* (Poorly soluble 2-acetylazaarenes and nitroalkenes were added solid or neat and rinsed in with the equivalent volume of *i*-PrOH.)



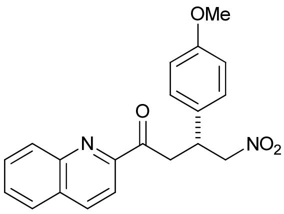
(*R*)-4-Nitro-1-(pyridin-2-yl)-3-[4-(trifluoromethyl)phenyl]butan-1-one (4a). The title compound was prepared according to General Procedure G from 4-acetylpyridine (**1a**) (67 µL, 0.60 mmol) and (*E*)-1-(2-nitroethenyl)-4-(trifluoromethyl)benzene (**2b**) (109 mg, 0.50 mmol) for a reaction time of 18 h and purified by column chromatography (0–20% EtOAc/hexane) to afford a white solid (161 mg, 73%); m.p. 87–89 °C (9:1 hexane/EtOH); $[\alpha]_D^{20}$ +34.0 (*c* 1.24, $CHCl_3$); R_f = 0.46 (1:1 EtOAc/hexane); IR (solid) 1697 (C=O), 1549 (NO_2), 1321, 1157, 1113, 1065, 991, 841, 772, 606 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (1H, ddd, *J* = 4.8, 1.6, 0.9 Hz, Ar**H**), 8.00 (1H, dt, *J* = 7.9, 1.0 Hz, Ar**H**), 7.85 (1H, td, *J* = 7.7, 1.7 Hz, Ar**H**), 7.60 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.51 (1H, ddd, *J* = 7.6, 4.8, 1.2 Hz, Ar**H**), 7.46 (2H, d, *J* = 8.2 Hz, Ar**H**), 4.83 (1H, dd, *J* = 12.7, 6.5 Hz, $C\mathbf{H}_2NO_2$), 4.71 (1H, dd, *J* = 12.7, 8.6 Hz, $C\mathbf{H}_2NO_2$), 4.33 (1H, dq, *J* = 8.1, 6.9 Hz, $CH_2C\mathbf{H}$), 3.86 (1H, dd, *J* = 18.3, 7.3 Hz, $C\mathbf{H}_2C{=}O$), 3.65 (1H, dd, *J* = 18.3, 6.9 Hz, $C\mathbf{H}_2C{=}O$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.1 (C), 152.5 (C), 149.0 (CH), 143.3 (C), 137.2 (CH), 131.1 (C, q, $^2J_{CF}$ = 33.7 Hz), 128.1 (2 × CH), 127.7 (CH), 125.9 (2 × CH, q, $^3J_{CF}$ = 3.8 Hz), 123.9 (C, $^1J_{CF}$ = 272.0 Hz), 122.0 (CH), 79.3 (CH_2), 40.5 (CH_2), 39.0 (CH); HRMS (ESI) Exact mass calcd for $C_{16}H_{13}F_3N_2O_3$ $[M]^+$: 338.0873, found 338.0871; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 254 nm, 25 °C) t_r (minor) = 18.6 min, t_r (major) = 23.2 min, 92% ee.



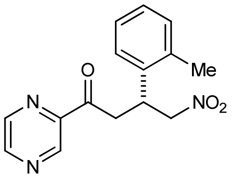
(*S*)-4-Nitro-1-(pyridin-2-yl)-3-(thiophen-2-yl)butan-1-one (4b).[25] The title compound was prepared according to General Procedure G from 2-acetylpyridine (**1a**) (67 µL, 0.60 mmol) and (*E*)-β-(2-thienyl)nitroethene (**2c**) (78 mg, 0.50 mmol) for a reaction time of 5 h and purified by column chromatography (CH_2Cl_2) to afford a white solid (70 mg, 51%). m.p. 54–58 °C (hexane); $[\alpha]_D^{20}$ +29.7 (*c* 0.56, $CHCl_3$); R_f = 0.35 (CH_2Cl_2); IR (solid) 1701 (C=O), 1547 (NO_2), 1435, 1362, 1275, 1252, 1053, 1032, 993, 772 cm^{-1}; HPLC (Chiralpak AS-H, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 39.0 min, t_r (major) = 44.3 min, 93% ee. ^1H and ^{13}C NMR data were consistent with those reported in the literature.[25]



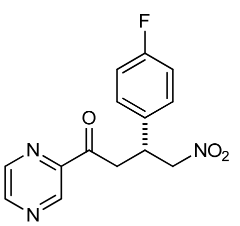
(*R*)-4-Nitro-3-(3-nitrophenyl)-1-(quinolin-2-yl)butan-1-one (4c). The title compound was prepared according to General Procedure G from 2-acetylquinoline (**1b**) (103 mg, 0.60 mmol) and (*E*)-3,β-dinitrostyrene (**2d**) (97 mg, 0.50 mmol) for a reaction time of 24 h and purified by column chromatography (0–30% Et_2O/hexane) to afford a yellow oil (113 mg, 62%). $[\alpha]_D^{20}$ +52.1 (*c* 1.10, $CHCl_3$); R_f = 0.31 (1:1 hexane/Et_2O); IR (solid) 1697 (C=O), 1549, 1531 (NO_2), 1350, 1204, 827, 804, 731, 689 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.29 (1H, t, *J* = 2.1 Hz, Ar**H**), 8.28 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.21 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.13 (1H, ddd, *J* = 8.3, 2.1, 1.0 Hz, Ar**H**), 8.06 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.88 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.82 (1H, ddd, *J* = 8.5, 7.0, 1.1 Hz, Ar**H**), 7.74 (1H, dt, *J* = 7.7, 1.4 Hz, Ar**H**), 7.68 (1H, ddd, *J* = 8.1, 7.0, 1.0 Hz, Ar**H**), 7.53 (1H, app t, *J* = 8.0 Hz, Ar**H**), 4.92 (1H, dd, *J* = 12.9, 6.2 Hz, C**H**$_2$NO$_2$), 4.80 (1H, dd, *J* = 12.9, 8.9 Hz, C**H**$_2$NO$_2$), 4.45 (1H, dq, *J* = 8.7, 6.9 Hz, CH$_2$C**H**), 4.08 (1H, dd, *J* = 18.0, 7.4 Hz, C**H**$_2$C=O), 3.83 (1H, dd, *J* = 18.0, 6.8 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 198.3 (C), 151.9 (C), 147.1 (C), 141.5 (C), 137.3 (CH), 134.3 (CH), 130.5 (CH), 130.4 (CH), 129.9 (CH), 129.8 (C), 129.0 (CH), 127.7 (CH), 122.9 (CH), 122.5 (CH), 117.9 (CH), 79.2 (CH$_2$), 40.3 (CH$_2$), 39.2 (CH); HRMS (ESI) Exact mass calcd for $C_{19}H_{15}N_3O_5$ [M+H]$^+$: 365.1006, found 365.1017; HPLC (Chiralpak IA-3, 10% *i*-PrOH/hexane, 1.5 mL/min, 280 nm, 25 °C) t_r (minor) = 26.5 min, t_r (major) = 29.5 min, 99% ee.



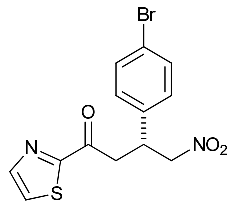
(*R*)-3-(4-Methoxyphenyl)-4-nitro-1-(quinolin-2-yl)butan-1-one (4d). The title compound was prepared according to General Procedure G from 2-acetylquinoline (**1b**) (103 mg, 0.60 mmol) and (*E*)-4-methoxy-β-nitrostyrene (**2e**) (90 mg, 0.50 mmol) for a reaction time of 48 h and purified by column chromatography (2:1 hexane/Et$_2$O) to afford a white solid (172 mg, >95%). m.p. 146–148 °C (hexane); $[\alpha]_D^{20}$ +59.1 (*c* 0.97, CHCl$_3$); R_f = 0.26 (2:1 hexane/Et$_2$O); IR (solid) 1694 (C=O), 1545 (NO$_2$), 1514, 1254, 1179, 1036, 833, 787, 756, 565 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.27 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.21 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.07 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.88 (1H, dd, *J* = 8.2, 1.4 Hz, Ar**H**), 7.81 (1H, ddd, *J* = 8.4, 6.9, 1.4 Hz, Ar**H**), 7.67 (1H, ddd, *J* = 8.1, 6.9, 1.1 Hz, Ar**H**), 7.30–7.25 (2H, m, Ar**H**), 6.87–6.84 (2H, m, Ar**H**), 4.83 (1H, dd, *J* = 12.3, 6.8 Hz, C**H**$_2$NO$_2$), 4.70 (1H, dd, *J* = 12.3, 8.3 Hz, C**H**$_2$NO$_2$), 4.28 (1H, app dq, *J* = 7.8, 6.9 Hz, CH$_2$C**H**), 4.00 (1H, dd, *J* = 17.7, 7.3 Hz, C**H**$_2$C=O), 3.78 (3H, s, C**H**$_3$), 3.76 (1H, dd, *J* = 17.7, 7.1 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 199.1 (C), 159.0 (C), 152.3 (C), 147.1 (C), 137.1 (CH), 131.2 (C), 130.5 (CH), 130.2 (CH), 129.7 (C), 128.8 (CH), 128.6 (2 × CH), 127.7 (CH), 118.0 (CH), 114.3 (2 × CH), 80.2 (CH$_2$), 55.2 (CH$_3$), 40.7 (CH$_2$), 38.9 (CH$_2$); HRMS (ESI) Exact mass calcd for $C_{20}H_{18}N_2O_4Na$ [M+H]$^+$: 373.1159, found 373.1158; HPLC (Chiralpak AD-H, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 20.6 min, t_r (major) = 24.9 min, 95% ee.



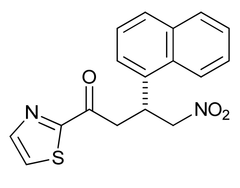
(*R*)-3-(2-Methylphenyl)-4-nitro-1-(pyrazin-2-yl)butan-1-one (4e). The title compound was prepared according to General Procedure G from 2-acetylpyrazine (**1c**) (73 mg, 0.60 mmol) and (*E*)-2-methyl-β-nitrostyrene (**2f**) (82 mg, 0.50 mmol) for a reaction time of 48 h and purified by column chromatography (1:1 hexane/Et_2O) to afford off-white oil (113 mg, 79%). $[\alpha]_D^{20}$ +30.6 (*c* 1.10, $CHCl_3$); R_f = 0.17 (1:1 hexane/Et_2O); IR (film) 1695 (C=O), 1543 (NO_2), 1377, 1360, 1271, 1016, 978, 768, 756, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (1H, br s, Ar**H**), 8.77 (1H, br s, Ar**H**), 8.63 (1H, br s, Ar**H**), 7.23–7.18 (2H, m, Ar**H**), 7.17–7.14 (2H, m, Ar**H**), 4.73 (1H, dd, *J* = 12.6, 7.7 Hz, C**H**$_2$NO$_2$), 4.66 (1H, dd, *J* = 12.6, 7.3 Hz, C**H**$_2$NO$_2$), 4.55 (1H, app quin, *J* = 7.3 Hz, CH$_2$C**H**), 3.86 (1H, dd, *J* = 18.2, 7.5 Hz, C**H**$_2$C=O), 3.56 (1H, dd, *J* = 18.1, 6.6 Hz, C**H**$_2$C=O), 2.51 (3H, s, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 198.2 (C), 148.2 (CH), 146.9 (CH), 143.6 (CH), 143.5 (C), 137.0 (C), 136.5 (C), 131.1 (CH), 127.6 (CH), 126.6 (CH), 125.5 (CH), 79.2 (CH_2), 40.8 (CH_2), 34.2 (CH), 19.5 (CH_3); HRMS (ESI) Exact mass calcd for $C_{15}H_{15}N_3O_3Na$ $[M+Na]^+$: 308.1006, found 308.1008; HPLC (Chiralpak AS-H, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 30.7 min, t_r (major) = 50.8 min, 98% ee.



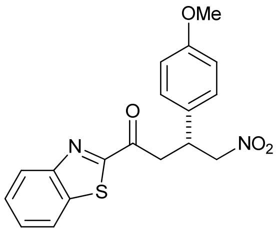
(*R*)-3-(4-Fluorophenyl)-4-nitro-1-(pyrazin-2-yl)butan-1-one (4f). The title compound was prepared according to General Procedure G from 2-acetylpyrazine (**1c**) (73 mg, 0.60 mmol) and (*E*)-4-fluoro-β-nitrostyrene (**2g**) (84 mg, 0.50 mmol) for a reaction time of 3 h and purified by column chromatography (2:1 Et_2O/hexane) to afford a white solid (144 mg, 91%). m.p. 118–119 °C (hexane); $[\alpha]_D^{20}$ +33.7 (*c* 0.80, $CHCl_3$); R_f = 0.15 (2:1 Et_2O/hexane); IR (solid) 1695 (C=O), 1541 (NO_2), 1512, 1377, 1238, 1163, 1018, 862, 833, 772 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (1H, d, *J* = 1.5 Hz, Ar**H**), 8.79 (1H, d, *J* = 2.3 Hz, Ar**H**), 8.64 (1H, dd, *J* = 2.3, 1.5 Hz, Ar**H**), 7.33–7.26 (2H, m, Ar**H**), 7.08–6.99 (2H, m, Ar**H**), 4.77 (1H, dd, *J* = 12.5, 6.9 Hz, C**H**$_2$NO$_2$), 4.67 (1H, dd, *J* = 12.5, 8.0 Hz, C**H**$_2$NO$_2$), 4.25 (1H, app quin, *J* = 7.2 Hz, CH$_2$C**H**), 3.80 (1H, dd, *J* = 18.3, 7.5 Hz, C**H**$_2$C=O), 3.58 (1H, dd, *J* = 18.3, 6.8 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 197.9 (C), 162.2 (C, d, $^1J_{CF}$ = 246.9 Hz), 148.3 (CH), 146.8 (C), 143.7 (CH), 143.5 (CH), 134.5 (C, d, $^4J_{CF}$ = 3.3 Hz), 129.2 (2 × CH, d, $^3J_{CF}$ = 8.1 Hz), 116.0 (2 × CH, d, $^2J_{CF}$ = 21.5 Hz), 79.7 (CH_2), 40.8 (CH_2), 38.4 (CH); ^{19}F NMR (376.3 Hz, $CDCl_3$) δ −114.0 (1F, tt, $^3J_{HF}$ = 8.5, $^4J_{HF}$ = 5.2 Hz, Ar**F**); HRMS (EI) Exact mass calcd for $C_{14}H_{12}FN_3O_3$ $[M]^+$: 289.0857, found 289.0858; HPLC (Chiralpak AD-H, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 20.1 min, t_r (major) = 23.6 min, 97% ee.



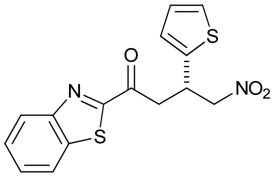
(*R*)-3-(4-Bromophenyl)-4-nitro-1-(1,3-thiazol-2-yl)butan-1-one (4g). The title compound was prepared according to General Procedure G from 2-acetylthiazole (**1d**) (62 μL, 0.60 mmol) and (*E*)-4-bromo-β-nitrostyrene (**2h**) (114 mg, 0.50 mmol) for a reaction time of 4 h and purified by column chromatography (4:1 hexane/acetone) to afford a colorless glass (156 mg, 88%); m.p. 52–54 °C (1:1 MeOH/hexane); $[\alpha]_D^{20}$ −12.1 (*c* 1.00, $CHCl_3$); R_f = 0.24 (1:1 hexane/Et_2O); IR (solid) 1682 (C=O), 1543 (NO_2), 1479, 1377, 1011, 951, 826, 762, 750, 714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (1H, d, *J* = 3.0 Hz, Ar**H**), 7.72 (1H, d, *J* = 3.0 Hz, Ar**H**), 7.48–7.45 (2H, m, Ar**H**), 7.22–7.17 (2H, m, Ar**H**), 4.77 (1H, dd, *J* = 12.6, 6.6 Hz, C**H**$_2$NO$_2$), 4.67 (1H, dd, *J* = 12.6, 8.2 Hz, C**H**$_2$NO$_2$), 4.24 (1H, app quin, *J* = 7.3 Hz, CH$_2$C**H**), 3.75 (1H, dd, *J* = 17.7, 7.6 Hz, C**H**$_2$C=O), 3.55 (1H, dd, *J* = 17.7, 6.8 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.2 (C), 166.0 (C), 144.9 (CH), 137.5 (C), 132.2 (2 × CH), 129.2 (2 × CH), 127.0 (CH), 121.9 (C), 79.2 (CH_2), 41.2 (CH_2), 38.7 (CH); HRMS (EI) Exact mass calcd for $C_{13}H_{11}BrN_2O_3S$ $[M]^+$: 353.9668, found 353.9669; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 30.1 min, t_r (major) = 32.4 min, 97% ee.



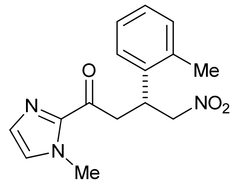
(*R*)-3-(Naphthalen-1-yl)-4-nitro-1-(1,3-thiazol-2-yl)butan-1-one (4h). The title compound was prepared according to General Procedure G from 2-acetylthiazole (**1d**) (62 μL, 0.60 mmol) and (E)-1-(2-nitroethenyl)naphthalene (**2i**) (100 mg, 0.50 mmol) for a reaction time of 24 h and purified by column chromatography (4:1 hexane/EtOAc) to afford an off-white oil (116 mg, 71%). $[\alpha]_D^{20}$ +31.8 (c 0.96, CHCl3); R_f = 0.12 (4:1 hexane/EtOAc); IR (film) 1684 (C=O), 1549 (NO_2), 1479, 1379, 1231, 1063, 945, 878, 777, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.02 (1H, d, *J* = 3.0 Hz, Ar**H**), 7.88 (1H, dd, *J* = 8.1, 1.4 Hz, Ar**H**), 7.79 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.69 (1H, d, *J* = 3.0 Hz, Ar**H**), 7.63 (1H, ddd, *J* = 8.5, 6.9, 1.4 Hz, Ar**H**), 7.54 (1H, ddd, *J* = 8.1, 6.9, 1.0 Hz, Ar**H**), 7.47 (1H, dd, *J* = 7.1, 1.3 Hz, Ar**H**), 7.44 (1H, app q, *J* = 7.7 Hz, Ar**H**), 5.22 (1H, app quin, *J* = 7.0 Hz, CH$_2$C**H**), 4.89 (1H, dd, *J* = 12.7, 6.6 Hz, C**H**$_2$NO$_2$), 4.86 (1H, dd, *J* = 12.7, 7.7 Hz, C**H**$_2$NO$_2$), 3.96 (1H, dd, *J* = 17.8, 6.8 Hz, C**H**$_2$C=O), 3.78 (1H, dd, *J* = 17.8, 7.3 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.8 (C), 166.2 (C), 144.9 (CH), 134.6 (C), 134.2 (C), 131.0 (C), 129.2 (CH), 128.6 (CH), 127.0 (CH), 126.8 (CH), 126.1 (CH), 125.3 (CH), 123.8 (br, CH), 122.4 (CH), 79.0 (CH_2), 41.5 (CH_2), 33.6 (br, CH); HRMS (ESI) Exact mass calcd for $C_{17}H_{15}N_2O_3S$ $[M+H]^+$: 327.0798, found 327.0797; HPLC (Chiralpak IC, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 22.5 min, t_r (minor) = 25.4 min, 97% ee.



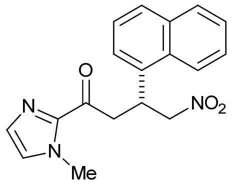
(*R*)-1-(1,3-Benzothiazol-2-yl)-3-(4-methoxyphenyl)-4-nitrobutan-1-one (4i). The title compound was prepared according to General Procedure G from 2-acetylbenzothiazole (**1e**) (106 mg, 0.60 mmol) and (*E*)-4-methoxy-β-nitrostyrene (**2e**) (90 mg, 0.50 mmol) for a reaction time of 24 h and purified by column chromatography (0–20% EtOAc/hexane) to afford an off-white solid (157 mg, 88%). m.p. 126–127 °C (hexane); $[\alpha]^{20}_{\mathrm{D}}$ +36.4 (*c* 1.00, $CHCl_3$); R_f = 0.37 (3:1 hexane/EtOAc); IR (solid) 1694 (C=O), 1545 (NO_2), 1514, 1476, 1252, 1177, 1032, 945, 840, 766 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, d, *J* = 8.2 Hz, Ar**H**), 7.98 (1H, d, *J* = 7.9 Hz, Ar**H**), 7.60 (ddd, *J* = 7.9, 7.4, 1.0 Hz, Ar**H**), 7.55 (ddd, *J* = 8.2, 7.4, 1.0 Hz, Ar**H**), 7.25 (2H, d, *J* = 8.6 Hz, Ar**H**), 6.86 (2H, d, *J* = 8.6 Hz, Ar**H**), 4.79 (1H, dd, *J* = 12.4, 6.9 Hz, C**H**$_2NO_2$), 4.69 (1H, dd, *J* = 12.4, 8.0 Hz, C**H**$_2NO_2$), 4.26 (1H, app quin, *J* = 7.3 Hz, CH_2C**H**), 3.87 (1H, dd, *J* = 17.8, 7.6 Hz, C**H**$_2$C=O), 3.77 (3H, s, C**H**$_3$), 3.66 (1H, dd, *J* = 17.8, 6.8 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 192.2 (C), 165.5 (C), 159.2 (C), 153.4 (C), 137.3 (C), 130.4 (C), 128.6 (2 × CH), 128.0 (CH), 127.2 (CH), 125.5 (CH), 122.5 (CH), 114.4 (2 × CH), 79.8 (CH_2), 55.2 (CH_3), 41.7 (CH_2), 38.6 (CH); HRMS (ESI) Exact mass calcd for $C_{18}H_{16}N_2O_4SNa$ $[M+H]^+$: 379.0723, found 379.0728; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 51.6 min, t_r (major) = 54.3 min, 97% ee.



(*S*)-1-(1,3-Benzothiazol-2-yl)-4-nitro-3-(thiophen-2-yl)butan-1-one (4j). The title compound was prepared according to General Procedure G from 2-acetylbenzothiazole (**1e**) (106 mg, 0.60 mmol) and (*E*)-β-(2-thienyl)nitroethene (**2c**) (78 mg, 0.50 mmol) for a reaction time of 48 h and purified by column chromatography (2:1 hexane/Et_2O) to afford a white solid (146 mg, 88%). m.p. 102–105 °C (hexane); $[\alpha]^{20}_{\mathrm{D}}$ +33.0 (*c* 1.10, $CHCl_3$); R_f = 0.28 (2:1 hexane/Et_2O); IR (solid) 1690 (C=O), 1549 (NO_2), 1477, 1385, 1215, 1180, 393, 762, 718, 602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (1H, ddd, *J* = 8.3, 1.3, 0.6 Hz, Ar**H**), 8.00 (1H, ddd, *J* = 7.9, 1.3, 0.6 Hz, Ar**H**), 7.62 (1H, ddd, *J* = 8.3, 7.3, 1.4 Hz, Ar**H**), 7.57 (1H, ddd, *J* = 7.9, 7.3, 1.3 Hz, Ar**H**), 7.23 (1H, dd, *J* = 5.1, 1.1 Hz, Ar**H**), 7.03 (1H, dd, *J* = 3.5, 1.1 Hz, Ar**H**), 6.96 (1H, dd, *J* = 5.1, 3.5 Hz, Ar**H**), 4.86 (1H, dd, *J* = 12.7, 6.8 Hz, C**H**$_2NO_2$), 4.77 (1H, dd, *J* = 12.7, 7.6 Hz, C**H**$_2NO_2$), 4.65 (1H, app quin, *J* = 7.1 Hz, CH_2C**H**), 3.96 (1H, dd, *J* = 18.0, 7.2 Hz, C**H**$_2$C=O), 3.77 (1H, dd, *J* = 18.0, 6.7 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 191.7 (C), 165.2 (C), 153.3 (C), 141.2 (C), 137.3 (C), 128.0 (CH), 127.2 (CH), 127.1 (CH), 125.8 (CH), 125.6 (CH), 124.9 (CH), 122.5 (CH), 79.8 (CH_2), 42.4 (CH_2), 34.6 (CH); HRMS (ESI) Exact mass calcd for $C_{15}H_{12}N_2O_3S_2Na$ $[M+Na]^+$: 355.0182, found 355.0190; HPLC (Chiralpak IC, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 21.1 min, t_r (major) = 23.8 min, 97% ee.

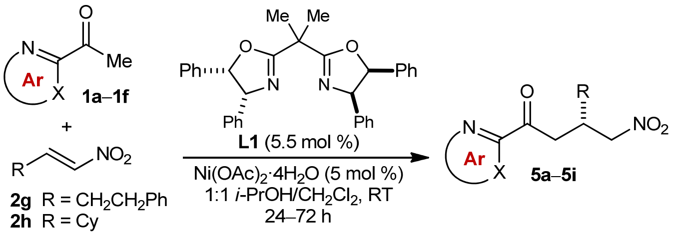


(*R*)-1-(1-Methyl-1*H*-imidazol-2-yl)-3-(2-methylphenyl)-4-nitrobutan-1-one (4k). The title compound was prepared according to General Procedure G from 2-acetyl-1-methylimidazole (**1f**) (75 mg, 0.60 mmol) and (*E*)-2-methyl-β-nitrostyrene (**2f**) (82 mg, 0.50 mmol) for a reaction time of 24 h and purified by column chromatography (0–10% EtOAc/CH_2Cl_2) to afford an off-white oil (109 mg, 76%). $[\alpha]_D^{20}$ +24.3 (*c* 1.10, $CHCl_3$); $R_f = 0.34$ (3:1 Et_2O/hexane); IR (film) 1672 (C=O), 1548 (NO_2), 1464, 1406, 1377, 1290, 997, 914, 764, 727 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26–7.24 (1H, m, Ar**H**), 7.19–7.14 (4H, m, Ar**H**), 7.03 (1H, s, Ar**H**), 4.72 (1H, dd, *J* = 12.6, 7.4 Hz, C**H**$_2$NO$_2$), 4.64 (1H, dd, *J* = 12.6, 7.7 Hz, C**H**$_2$NO$_2$), 4.52 (1H, app quin, *J* = 7.3 Hz, CH$_2$C**H**), 3.95 (3H, s, NC**H**$_3$), 3.74 (1H, dd, *J* = 17.3, 7.3 Hz, C**H**$_2$C=O), 3.50 (1H, dd, *J* = 17.3, 7.2 Hz, C**H**$_2$C=O), 2.49 (3H, s, ArC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 189.1 (C), 142.3 (C), 137.2 (C), 136.4 (C), 131.0 (CH), 128.9 (CH), 127.4 (CH), 127.3 (CH), 126.6 (CH), 125.7 (CH), 79.3 (CH_2), 42.3 (CH_2), 36.2 (CH_3), 34.5 (CH), 19.5 (CH_3); HRMS (ESI) Exact mass calcd for $C_{15}H_{17}N_3O_3$ $[M+H]^+$: 288.1343, found 288.1350; HPLC (Chiracel OD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 38.7 min, t_r (minor) = 50.6 min, 95% ee.

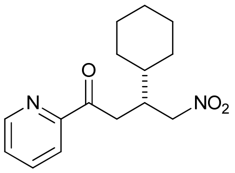


(*R*)-1-(1-Methyl-1*H*-imidazol-2-yl)-3-(naphthalen-1-yl)-4-nitrobutan-1-one (4l). The title compound was prepared according to General Procedure G from 2-acetyl-1-methylimidazole (**1f**) (75 mg, 0.60 mmol) and (*E*)-1-(2-nitroethenyl)naphthalene (**2i**) (100 mg, 0.50 mmol for a reaction time of 16 h and purified by column chromatography (0–20% acetone/hexane) to afford a colorless oil (133 mg, 82%). $[\alpha]_D^{20}$ +94.3 (*c* 1.30, $CHCl_3$); $R_f = 0.40$ (Et_2O); IR (film) 1672 (C=O), 1549 (NO_2), 1408, 1377, 914, 799, 777, 752, 704, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (1H, d, *J* = 8.6 Hz, Ar**H**), 7.88 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.78 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.61 (1H, ddd, *J* = 8.4, 6.8, 1.3 Hz, Ar**H**), 7.53 (1H, ddd, *J* = 7.9, 7.0, 0.8 Hz, Ar**H**), 7.49 (1H, d, *J* = 6.5 Hz, Ar**H**), 7.43 (1H, dd, *J* = 8.0, 7.4 Hz, Ar**H**), 7.15 (1H, d, *J* = 0.8 Hz, Ar**H**), 7.02 (1H, s, Ar**H**), 5.18 (1H, app quin, *J* = 7.0 Hz, CH$_2$C**H**), 4.85 (1H, dd, *J* = 12.8, 6.7 Hz, C**H**$_2$NO$_2$), 4.81 (1H, dd, *J* = 12.8, 7.9 Hz, C**H**$_2$NO$_2$), 3.93 (1H, dd, *J* = 17.4, 6.8 Hz, C**H**$_2$C=O), 3.91 (3H, s, C**H**$_3$), 3.70 (1H, dd, *J* = 17.4, 7.4 Hz, C**H**$_2$C=O); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 189.2 (C), 142.6 (C), 134.9 (C), 134.1 (C), 131.1 (C), 129.3 (CH), 129.1 (CH), 128.4 (CH), 127.3 (CH), 126.8 (CH), 126.0 (CH), 125.3 (2 × CH), 122.5 (CH), 79.3 (CH_2), 42.0 (CH_2), 36.1 (CH_3), 33.7 (br, CH); HRMS (EI) Exact mass calcd for $C_{18}H_{18}N_3O_3$ $[M]^+$: 323.1264, found 323.1262; HPLC (Chiralpak IC, 20% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 17.0 min, t_r (minor) = 19.7 min, 97% ee.

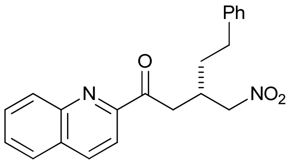
Figure 3: General Procedure H



A solution of Ni(OAc)$_2$·4H$_2$O (6.2 mg, 0.025 mmol) and ligand **L1** (13.4 mg, 0.0275 mmol) in *i*-PrOH (0.5 mL) was stirred at room temperature for 30 min. To the resulting solution was added a solution of the appropriate 2-acetylazaarene **1** (0.60 mmol) and the appropriate nitroalkene **2** (0.50 mmol) in CH$_2$Cl$_2$ (0.5 mL), and the reaction mixture was stirred until complete consumption of the nitroalkene as indicated by TLC analysis. The reaction mixture was diluted with CH$_2$Cl$_2$ (10 mL) and washed with brine (2 × 5 mL), dried (MgSO$_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography afforded the nitroalkane **4**.

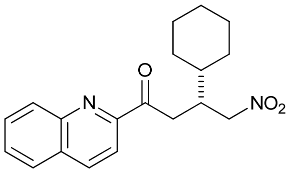


(*R*)-3-Cyclohexyl-4-nitro-1-(pyridin-2-yl)butan-1-one (5a). The title compound was prepared according to General Procedure H from 2-acetylpyridine (**1a**) (67 µL, 0.60 mmol) and (*E*)-(2-nitroethenyl)cyclohexane (**2k**) (78 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (5% acetone/hexane) to afford a colorless oil (95 mg, 69%). $[\alpha]_D^{20}$ −3.9 (*c* 1.00, CHCl$_3$); R_f = 0.34 (4:1 hexane/acetone); IR (film) 2920, 2851, 1699 (C=O), 1545 (NO$_2$), 1435, 1377, 1215, 995, 768, 687, 619 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.68 (1H, ddd, *J* = 4.7, 1.6, 0.9 Hz, Ar**H**), 8.05 (1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 7.86 (1H, td, *J* = 7.7, 1.7 Hz, Ar**H**), 7.50 (1H, ddd, *J* = 7.5, 4.8, 1.1 Hz, Ar**H**), 4.54 (1H, dd, *J* = 12.3, 6.6 Hz, C**H**$_2$NO$_2$), 4.51 (1H, dd, *J* = 12.3, 6.7 Hz, C**H**$_2$NO$_2$), 3.48 (1H, dd, *J* = 18.3, 5.0 Hz, C**H**$_2$C=O), 3.27 (1H, dd, *J* = 18.3, 7.9 Hz, C**H**$_2$C=O), 2.90–2.83 (1H, m, C**H**CH$_2$NO$_2$), 1.81–1.72 (4H, m, C**H**(C**H**$_2$)$_5$), 1.71–1.64 (1H, m, C**H**(C**H**$_2$)$_5$), 1.56–1.48 (1H, m, C**H**(C**H**$_2$)$_5$), 1.30–1.19 (2H, m, C**H**(C**H**$_2$)$_5$), 1.19–1.11 (1H, m, C**H**(C**H**$_2$)$_5$), 1.11–1.03 (2H, m, C**H**(C**H**$_2$)$_5$); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 200.0 (C), 153.0 (C), 148.9 (CH), 137.0 (CH), 127.4 (CH), 121.9 (CH), 77.3 (CH$_2$), 39.2 (CH), 38.3 (CH), 36.6 (CH$_2$), 30.0 (CH$_2$), 29.4 (CH$_2$), 26.4 (CH$_2$), 26.3 (CH$_2$), 26.3 (CH$_2$); HRMS (EI) Exact mass calcd for C$_{15}$H$_{20}$N$_2$O$_3$ [M]$^+$: 276.1468, found 276.1469; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 230 nm, 25 °C) t_r (major) = 21.4 min, t_r (minor) = 24.9 min, 65% ee.

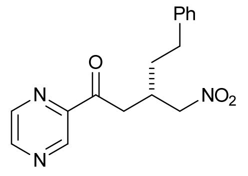


(*S*)-3-(Nitromethyl)-5-phenyl-1-(quinolin-2-yl)pentan-1-one (5b). The title compound was prepared according to General Procedure H from 2-acetylquinoline (**1b**) (103 mg, 0.60 mmol) and (*E*)-4-(nitrobut-3-en-1-

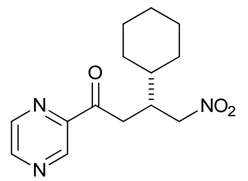
yl)benzene (**2j**) (89 mg, 0.50 mmol) for a reaction time of 24 h and purified by column chromatography (0–10% Et_2O/hexane) to afford an off-white oil (121 mg, 68%). $[\alpha]_D^{20}$ +32.1 (*c* 1.40, $CHCl_3$); R_f = 0.31 (4:1 hexane/Et_2O); IR (film) 1697 (C=O), 1549 (NO_2), 1369, 1204, 1113, 999, 831, 791, 748, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (1H, d, *J* = 8.6 Hz, Ar**H**), 8.22 (1H, dd, *J* = 8.5, 1.1 Hz, Ar**H**), 8.13 (1H, d, *J* = 8.6 Hz, Ar**H**), 7.90 (1H, dd, *J* = 8.2, 1.3 Hz, Ar**H**), 7.82 (1H, ddd, *J* = 8.5, 6.9, 1.3 Hz, Ar**H**), 7.68 (1H, ddd, *J* = 8.2, 6.9, 1.1 Hz, Ar**H**), 7.32–7.25 (2H, m, Ar**H**), 7.23–7.16 (3H, m, Ar**H**), 4.67 (1H, dd, *J* = 12.1, 6.1 Hz, C**H**$_2NO_2$), 4.60 (1H, dd, *J* = 12.1, 6.2 Hz, C**H**$_2NO_2$), 3.66 (1H, dd, *J* = 17.9, 6.1 Hz, C**H**$_2$C=O), 3.61 (1H, dd, *J* = 17.9, 6.8 Hz, C**H**$_2$C=O), 3.01 (1H, app sept, *J* = 6.5 Hz, C**H**CH_2NO_2), 2.80 (2H, td, *J* = 7.3, 1.7 Hz, PhC**H**$_2$), 1.94–1.86 (2H, m, PhCH_2C**H**$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 200.2 (C), 152.5 (C), 147.1 (C), 141.0 (C), 137.1 (CH), 130.5 (CH), 130.2 (CH), 129.7 (C), 128.8 (CH), 128.5 (2 × CH), 128.3 (2 × CH), 127.7 (CH), 126.1 (CH), 118.0 (CH), 78.8 (CH_2), 38.7 (CH_2), 33.6 (CH_2), 33.4 (CH), 32.9 (CH_2); HRMS (EI) Exact mass calcd for $C_{21}H_{20}N_2O_3$ $[M]^+$: 348.1468, found 348.1464; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 18.0 min, t_r (major) = 20.6 min, 80% ee.



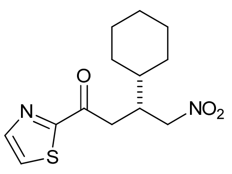
(*R*)-3-Cyclohexyl-4-nitro-1-(quinolin-2-yl)butan-1-one (5c). The title compound was prepared according to General Procedure H from 2-acetylquinoline (**1b**) (103 mg, 0.60 mmol) and (*E*)-(2-nitroethenyl)cyclohexane (**2k**) (78 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (5% acetone/hexane) to afford a white solid (124 mg, 76%). m.p. 94–97 °C (hexane); $[\alpha]_D^{20}$ +17.9 (*c* 0.60, $CHCl_3$); R_f = 0.30 (4:1 hexane/Et_2O); IR (solid) 2924, 2855, 1697 (C=O), 1545 (NO_2), 1375, 982, 943, 827, 781, 770, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.28 (1H, d, *J* = 8.7 Hz, Ar**H**), 8.14 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.91 (1H, dd, *J* = 8.1, 1.3 Hz, Ar**H**), 7.83 (1H, ddd, *J* = 8.7, 7.1, 1.3 Hz, Ar**H**), 7.69 (1H, ddd, *J* = 8.1, 7.1, 1.1 Hz, Ar**H**), 4.58 (2H, app d, *J* = 6.8 Hz, C**H**$_2NO_2$), 3.69 (1H, dd, *J* = 17.8, 5.2 Hz, C**H**$_2$C=O), 3.45 (1H, dd, *J* = 17.8 7.6 Hz, C**H**$_2$C=O), 2.94 (1H, app dtd, *J* = 7.6, 6.8, 5.2 Hz, C**H**CH_2NO_2), 1.86–1.76 (4H, m, C**H**(C**H**$_2$)$_5$), 1.74–1.51 (2H, m, C**H**(C**H**$_2$)$_5$), 1.34–1.07 (5H, m, C**H**(C**H**$_2$)$_5$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 200.6 (C), 152.5 (C), 147.1 (C), 137.1 (CH), 130.5 (CH), 130.1 (CH), 129.7 (C), 128.7 (CH), 127.7 (CH), 118.1 (CH), 77.4 (CH_2), 39.3 (CH), 38.7 (CH), 36.5 (CH_2), 30.1 (CH_2), 29.4 (CH_2), 26.4 (CH_2), 26.4 (CH_2), 26.3 (CH_2); HRMS (EI) Exact mass calcd for $C_{19}H_{22}N_2O_3$ $[M]^+$: 326.1625, found 326.1623; HPLC (Chiralpak AD-H, 5% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 14.9 min, t_r (major) = 16.8 min, 78% ee.



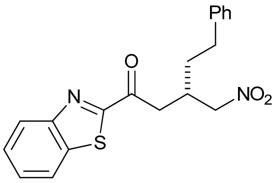
(*S*)-3-(Nitromethyl)-5-phenyl-1-(pyrazin-2-yl)pentan-1-one (5d). The title compound was prepared according to General Procedure H from 2-acetylpyrazine (**1c**) (73 mg, 0.60 mmol) and (*E*)-4-(nitrobut-3-en-1-yl)benzene (**2j**) (89 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (0–20% Et_2O/hexane) to afford an off-white oil (136 mg, 86%). $[\alpha]_D^{20}$ +5.4 (*c* 1.10, $CHCl_3$); $R_f = 0.19$ (1:1 hexane/Et_2O); IR (film) 2924, 1695 (C=O), 1545 (NO_2) 1381, 1364, 1053, 1018, 997, 837, 745, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.25 (1H, br s, Ar**H**), 8.80 (1H, br s, Ar**H**), 8.65 (1H, br s, Ar**H**), 7.35–7.26 (2H, m, Ar**H**), 7.25–7.18 (3H, m, Ar**H**), 4.61 (1H, dd, *J* = 12.1, 6.1 Hz, $C\mathbf{H}_2NO_2$), 4.57 (1H, dd, *J* = 12.1, 5.8 Hz, $C\mathbf{H}_2NO_2$), 3.46 (1H, dd, *J* = 18.6, 7.2 Hz, $C\mathbf{H}_2C{=}O$), 3.39 (1H, dd, *J* = 18.6, 5.7 Hz, $C\mathbf{H}_2C{=}O$), 2.94 (1H, app dq, *J* = 12.1, 6.1 Hz, $C\mathbf{H}CH_2NO_2$), 2.75 (2H, app dd, *J* = 9.3, 6.8 Hz, $PhC\mathbf{H}_2$), 1.86 (2H, app dtd, *J* = 9.3, 6.8, 0.7 Hz, $PhCH_2C\mathbf{H}_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 199.2 (C), 148.2 (CH), 147.1 (C), 143.60 (CH), 143.56 (CH), 140.7 (C), 128.6 (2 × CH), 128.3 (2 × CH), 126.2 (CH), 78.4 (CH_2), 39.1 (CH_2), 33.4 (CH_2), 32.9 (CH_2), 32.8 (CH); HRMS (EI) Exact mass calcd for $C_{16}H_{17}N_3O_3$ $[M]^+$: 299.1264, found 299.1262; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 29.1 min, t_r (major) = 34.8 min, 69% ee.



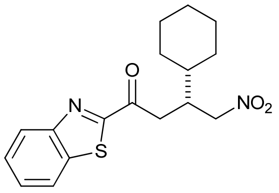
(*R*)-3-Cyclohexyl-4-nitro-1-(pyrazin-2-yl)butan-1-one (5e). The title compound was prepared according to General Procedure H from 2-acetylpyrazine (**1c**) (74 mg, 0.60 mmol) and (*E*)-(2-nitroethenyl)cyclohexane (**2k**) (78 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (0–10% acetone/hexane) to afford a yellow oil (86 mg, 62%). $[\alpha]_D^{20}$ −28.3 (*c* 1.00, $CHCl_3$); $R_f = 0.36$ (3:1 hexane/acetone); IR (film) 2920, 2851, 1697 (C=O), 1545 (NO_2), 1398, 1373, 1350, 1167, 1016, 999, 839, 716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 (1H, br s, Ar**H**), 8.80 (1H, br s, Ar**H**), 8.66 (1H, br s, Ar**H**), 4.55 (1H, dd, *J* = 12.3, 6.2 Hz, $C\mathbf{H}_2NO_2$), 4.52 (1H, dd, *J* = 12.3, 6.9 Hz, $C\mathbf{H}_2NO_2$), 3.44 (1H, dd, *J* = 18.4, 5.2 Hz, $C\mathbf{H}_2C{=}O$), 3.27 (1H, dd, *J* = 18.4, 7.6 Hz, $C\mathbf{H}_2C{=}O$), 2.90–2.80 (1H, m, $C\mathbf{H}CH_2NO_2$), 1.82–1.74 (4H, m, $C\mathbf{H}(C\mathbf{H}_2)_5$), 1.74–1.65 (1H, m, $C\mathbf{H}(C\mathbf{H}_2)_5$), 1.56–1.48 (1H, m, $C\mathbf{H}(C\mathbf{H}_2)_5$), 1.32–1.18 (2H, m, $C\mathbf{H}(C\mathbf{H}_2)_5$), 1.14 (1H, dt, *J* = 12.1, 3.1 Hz, $C\mathbf{H}(C\mathbf{H}_2)_5$), 1.11–1.00 (2H, m, $C\mathbf{H}(C\mathbf{H}_2)_5$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 199.5 (C), 148.1 (C), 147.2 (C), 143.7 (CH), 143.5 (CH), 77.3 (CH_2), 39.2 (CH), 38.1 (CH), 36.8 (CH_2), 30.0 (CH_2), 29.5 (CH_2), 26.29 (CH_2), 26.26 (CH_2), 26.20 (CH_2); HRMS (ESI) Exact mass calcd for $C_{14}H_{20}N_3O_3$ $[M+H]^+$: 278.1499, found 278.1503; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 17.0 min, t_r (major) = 20.0 min, 67% ee.



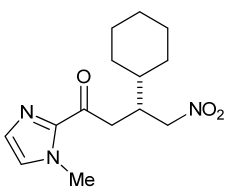
(*R*)-3-Cyclohexyl-4-nitro-1-(1,3-thiazol-2-yl)butan-1-one (5f). The title compound was prepared according to General Procedure H from 2-acetylthiazole (**1d**) (62 µL, 0.60 mmol) and (*E*)-(2-nitroethenyl)cyclohexane (**2k**) (78 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (0–5% acetone/hexane) to afford a colorless oil (126 mg, 89%). $[\alpha]_D^{20}$ +4.5 (*c* 0.90, $CHCl_3$); R_f = 0.33 (4:1: hexane/acetone); IR (film) 2924, 2853, 1684 (C=O), 1547 (NO_2), 1385, 1225, 962, 945, 772, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (1H, d, *J* = 3.0 Hz, Ar**H**), 7.71 (1H, d, *J* = 3.0 Hz, Ar**H**), 4.55 (1H, *J* = 12.4, 6.5 Hz, C**H**$_2$NO$_2$), 4.52 (1H, dd, *J* = 12.4, 6.8 Hz, C**H**$_2$NO$_2$), 3.42 (1H, dd, *J* = 18.0, 5.1 Hz, C**H**$_2$C=O), 3.23 (1H, dd, *J* = 18.0, 7.8 Hz, C**H**$_2$C=O), 2.90–2.82 (1H, m, C**H**CH$_2$NO$_2$), 1.81–1.71 (4H, m, C**H**(C**H**$_2$)$_5$), 1.71–1.64 (1H, m, C**H**(C**H**$_2$)$_5$), 1.56–1.48 (1H, m, C**H**(C**H**$_2$)$_5$), 1.30–1.18 (2H, m, C**H**(C**H**$_2$)$_5$), 1.19–1.11 (1H, C**H**(C**H**$_2$)$_5$), 1.11–1.02 (2H, m, C**H**(C**H**$_2$)$_5$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 192.1 (C), 166.6 (C), 144.8 (CH), 126.7 (CH), 77.1 (CH_2), 39.2 (CH), 38.3 (CH), 37.4 (CH_2), 30.0 (CH_2), 29.4 (CH_2), 26.29 (CH_2), 26.25 (CH_2), 26.20 (CH_2); HRMS (EI) Exact mass calcd for $C_{13}H_{18}N_2O_3S$ $[M]^+$: 282.1033, found 282.1032; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 21.1 min, t_r (minor) = 27.7 min, 70% ee.



(*S*)-1-(1,3-Benzothiazol-2-yl)-3-(nitromethyl)-5-phenylpentan-1-one (5g). The title compound was prepared according to General Procedure H from 2-acetylbenzothiazole (**1e**) (106 mg, 0.60 mmol) and (*E*)-4-(nitrobut-3-en-1-yl)benzene (**2j**) (89 mg, 0.50 mmol) for a reaction time of 24 h and purified by column chromatography (0–10% Et_2O/hexane) to afford a white solid (86 mg, 51%). m.p. 109–111 °C (hexane); $[\alpha]_D^{20}$ +28.0 (*c* 0.90, $CHCl_3$); R_f = 0.29 (4:1 hexane/Et_2O); IR (solid) 1686 (C=O), 1545 (NO_2), 1483, 1204, 932, 901, 758, 743, 731, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (1H, dd, *J* = 7.9, 1.3 Hz, Ar**H**), 8.01 (1H, dd, *J* = 7.8, 1.4 Hz, Ar**H**), 7.61 (1H, ddd, *J* = 8.3, 7.2, 1.3 Hz, Ar**H**), 7.57 (1H, ddd, *J* = 7.9, 7.2, 1.3 Hz, Ar**H**), 7.33–7.24 (2H, m, Ar**H**), 7.23–7.17 (3H, m, Ar**H**), 4.64 (1H, dd, *J* = 12.3, 6.1 Hz, C**H**$_2$NO$_2$), 4.59 (1H, dd, *J* = 12.3, 6.0 Hz, C**H**$_2$NO$_2$), 3.55 (1H, dd, *J* = 18.2, 7.0 Hz, C**H**$_2$C=O), 3.51 (1H, dd, *J* = 18.2, 6.0 Hz, C**H**$_2$C=O), 2.97 (1H, m, C**H**CH$_2$NO$_2$), 2.80–2.75 (2H, m, PhC**H**$_2$), 1.92–1.85 (2H, m, PhCH$_2$C**H**$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 193.3 (C), 165.6 (C), 153.4 (C), 140.6 (C), 137.3 (C), 128.6 (2 × CH), 128.3 (2 × CH), 128.0 (CH), 127.2 (CH), 126.2 (CH), 125.6 (CH), 122.5 (CH), 78.3 (CH_2), 39.8 (CH_2), 33.3 (CH_2), 33.0 (CH), 32.8 (CH_2); HRMS (EI) Exact mass calcd for $C_{19}H_{19}N_2O_3S$ $[M]^+$: 354.1033, found 354.1033; HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 18.0 min, t_r (major) = 21.1 min, 82% ee.

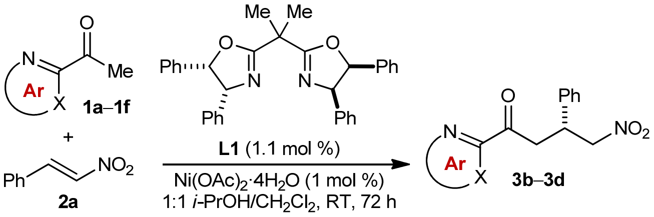


(*R*)-1-(1,3-Benzothiazol-2-yl)-3-cyclohexyl-4-nitrobutan-1-one (5h). The title compound was prepared according to General Procedure H from 2-acetylbenzothiazole (**1e**) (106 mg, 0.60 mmol) and (*E*)-(2-nitroethenyl)cyclohexane (**2k**) (78 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (0-3% acetone/hexane) to afford a colorless oil (80 mg, 48%). $[\alpha]_{\mathrm{D}}^{20}$ +8.6 (*c* 0.90, CHCl$_3$); R_f = 0.34 (4:1 hexane/Et$_2$O); IR (solid) 2922, 1694 (C=O), 1549 (NO$_2$) 1479, 1375, 1211, 937, 874, 758, 731 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.20 (1H, ddd, *J* = 8.3, 1.3, 0.6 Hz, Ar**H**), 8.00 (1H, ddd, *J* = 8.1, 1.3, 0.6 Hz, Ar**H**), 7.60 (1H, ddd, *J* = 8.1, 7.2, 1.3 Hz, Ar**H**), 7.55 (1H, ddd, *J* = 8.3, 7.2, 1.3 Hz, Ar**H**), 4.58 (1H, dd, *J* = 15.1, 6.6 Hz, C**H**$_2$NO$_2$), 4.55 (1H, dd, *J* = 15.1, 6.6 Hz, C**H**$_2$NO$_2$), 3.54 (1H, dd, *J* = 18.2, 5.3 Hz, C**H**$_2$C=O), 3.36 (1H, dd, *J* = 18.2, 7.6 Hz, C**H**$_2$C=O), 2.91 (1H, app qt, *J* = 6.6, 5.5 Hz, C**H**CH$_2$NO$_2$), 1.86–1.73 (4H, m, C**H**(C**H**$_2$)$_5$), 1.72–1.65 (1H, m, C**H**(C**H**$_2$)$_5$), 1.55 (1H, tdt, *J* = 11.5, 5.3, 3.0 Hz, C**H**(C**H**$_2$)$_5$), 1.32–1.20 (2H, m, C**H**(C**H**$_2$)$_5$), 1.20–1.13 (1H, m, C**H**(C**H**$_2$)$_5$), 1.13–1.03 (2H, m, C**H**(C**H**$_2$)$_5$); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 193.6 (C), 165.8 (C), 153.4 (C), 137.3 (C), 127.9 (CH), 127.1 (CH), 125.5 (CH), 122.5 (CH), 77.1 (CH$_2$), 39.2 (CH), 38.3 (CH), 37.6 (CH$_2$), 30.0 (CH$_2$), 29.5 (CH$_2$), 26.29 (CH$_2$), 26.26 (CH$_2$), 26.19 (CH$_2$); HRMS (EI) Exact mass calcd for C$_{17}$H$_{20}$N$_2$O$_3$S [M]$^+$: 332.1189, found 332.1130; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 19.9 min, t_r (minor) = 23.6 min, 78% ee.

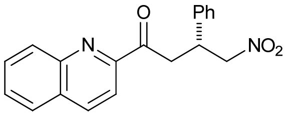


(*R*)-3-Cyclohexyl-1-(1-methyl-1H-imidazol-2-yl)-4-nitrobutan-1-one (5i). The title compound was prepared according to General Procedure H from 2-acetylthiazole (**1d**) (62 μL, 0.60 mmol) and (*E*)-(2-nitroethenyl)cyclohexane (**2k**) (78 mg, 0.50 mmol) for a reaction time of 72 h and purified by column chromatography (4:1 Et$_2$O/hexane) to afford a colorless oil (75 mg, 54%). $[\alpha]_{\mathrm{D}}^{20}$ +8.2 (*c* 1.00, CHCl$_3$); R_f = 0.35 (4:1 Et$_2$O/hexane); IR (film) 2924, 2853, 1672 (C=O), 1547 (NO$_2$), 1406, 1383, 997, 914, 773, 692 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.14 (1H, d, *J* = 0.5 Hz, Ar**H**), 7.05 (1H, br s, Ar**H**), 4.50 (1H, dd, *J* = 12.4, 6.8 Hz, C**H**$_2$NO$_2$), 4.47 (1H, dd, *J* = 12.4, 6.8 Hz, C**H**$_2$NO$_2$), 4.00 (3H, s, C**H**$_3$), 3.37 (1H, dd, *J* = 17.6, 4.8 Hz, C**H**$_2$C=O), 3.14 (1H, dd, *J* = 17.6, 8.3 Hz, C**H**$_2$C=O), 2.88–2.80 (1H, m, C**H**CH$_2$NO$_2$), 1.80–1.70 (4H, m, C**H**(C**H**$_2$)$_5$), 1.69–1.65 (1H, m, C**H**(C**H**$_2$)$_5$), 1.53–1.44 (1H, m, C**H**(C**H**$_2$)$_5$), 1.29–1.17 (2H, m, C**H**(C**H**$_2$)$_5$), 1.13 (1H, dt, *J* = 12.6, 3.1 Hz, C**H**(C**H**$_2$)$_5$), 1.07 (2H, ddd, *J* = 15.7, 11.2, 3.4 Hz, C**H**(C**H**$_2$)$_5$); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 190.8 (C), 142.7 (C), 129.2 (CH), 127.3 (CH), 77.4 (CH$_2$), 39.4 (CH), 38.3 (CH), 37.9 (CH$_2$), 36.2 (CH$_3$), 30.0 (CH$_2$), 29.1 (CH$_2$), 26.4 (CH$_2$), 26.3 (CH$_2$), 26.2 (CH$_2$); HRMS (EI) Exact mass calcd for C$_{14}$H$_{21}$N$_3$O$_3$ [M]$^+$: 279.1577, found 279.1575; HPLC (Chiralpak IC, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (major) = 26.9 min, t_r (minor) = 36.4 min, 67% ee.

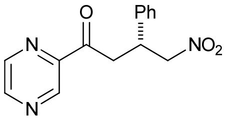
Larger-Scale Enantioselective Michael Addition of 2-Acetylazaarenes to Nitroalkenes: General Procedure I



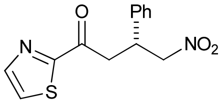
A solution of $Ni(OAc)_2 \cdot 4H_2O$ (24.8 mg, 0.100 mmol) and ligand **L1** (53.5 mg, 0.110 mmol) in *i*-PrOH (10 mL) was stirred at room temperature for 30 min. To the resulting solution was added a solution of the appropriate 2-acetylazaarene **1** (12.0 mmol) and (*E*)-β-nitrostyrene (**2a**) (1.49 g, 9.99 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature until complete consumption of the nitroalkene as indicated by TLC analysis, and then concentrated *in vacuo*. Purification of the residue by column chromatography afforded the nitroalkane **3**.



(*R*)-4-Nitro-3-phenyl-1-(quinolin-2-yl)butan-1-one (3b). The title compound was prepared according to General Procedure I from 2-acetylquinoline (**1b**) (2.05 g, 12.0 mmol) for a reaction time of 72 h. After concentration *in vacuo*, the crude residue was washed with Et_2O (3 × 25 mL) and dried *in vacuo* to afford short, fine white needles which required no further purification (2.59 g, 81%). HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = *ca.* 21.8 min, t_r (major) = 26.0 min, 99% ee. ^{1}H and ^{13}C NMR data were consistent with those reported above.



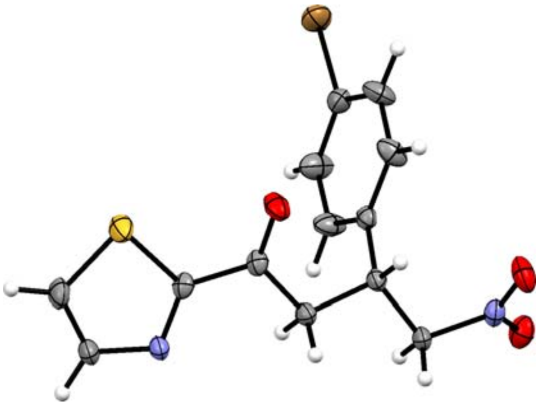
(*R*)-4-Nitro-3-phenyl-1-(pyrazin-2-yl)butan-1-one (3c). The title compound was prepared according to General Procedure I from 2-acetylpyrazine (**1c**) (1.47 g, 12.0 mmol) for a reaction time of 72 h and purified by column chromatography (hexane → Et_2O) to afford a white solid (1.80 g, 66%). HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C), t_r (minor) = 36.2 min, t_r (major) = 39.4 min, 95% ee. ^{1}H and ^{13}C NMR data were consistent with those reported above.

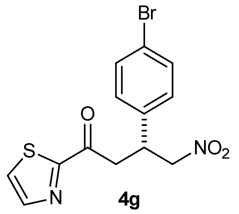


(*R*)-4-Nitro-3-phenyl-1-(1,3-thiazol-2-yl)butan-1-one (3d).[26] The title compound was prepared according to General Procedure I from 2-acetylthiazole (**1d**) (1.24 mL, 12.0 mmol) for a reaction time of 72 h and purified by column chromatography (0–20% acetone/hexane) to afford a pale yellow oil (2.20 g, 77%). HPLC (Chiralpak AD-H, 10% *i*-PrOH/hexane, 0.8 mL/min, 280 nm, 25 °C) t_r (minor) = 18.0 min, t_r (major) = 19.5 min, 96% ee. ^{1}H and ^{13}C NMR data were consistent with those reported in the literature.[26]

Determination of Absolute Configurations

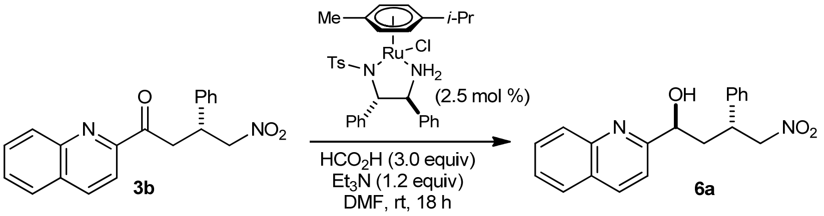
Recrystallization of **4g** from 1:1 hexane/MeOH afforded large, colorless cuboidal crystals (>99% ee) suitable for X-ray crystallography, which allowed determination of the absolute configuration (displacement ellipsoids shown at the 50% probability level). The absolute configurations of the remaining Michael addition products were assigned by analogy.





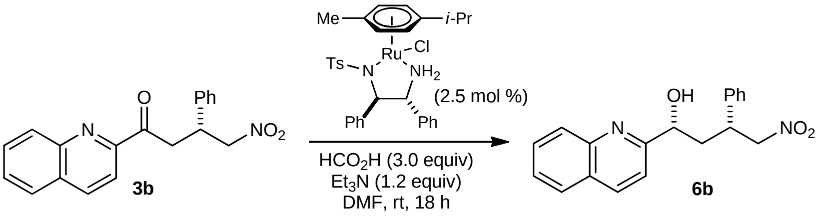
Asymmetric Transfer Hydrogenation of Michael Product 3b

(1*S*,3*R*)-4-Nitro-3-phenyl-1-(quinolin-2-yl)butan-1-ol (6a)



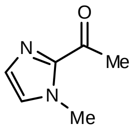
In a modification of a previously reported procedure for the reduction of other acylazaarenes,[28] to a solution of (*R*)-4-nitro-3-phenyl-1-(quinolin-2-yl)butan-1-one (**3b**) (160 mg, 0.50 mmol) and RuCl[(*S*,*S*)-TsDPEN](*p*-cymene)[29] (8.0 mg, 0.013 mmol) in DMF (2.5 mL) was added a mixture of HCO_2H (108 µL, 1.51 mmol) and Et_3N (84 µL, 0.60 mmol). The reaction mixture was stirred at room temperature, open to the air, for 18 h, then quenched carefully with MeOH (0.25 mL) and stirred for 5 min. The mixture was diluted with Et_2O (10 mL) and washed with saturated aqueous $NaHCO_3$ solution (2 × 10 mL), H_2O (5 × 10 mL), and brine (10 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo* to leave *the alcohol* **6a** as a yellow solid which required no further purification (154 mg, >95%, >19:1 dr by ^1H NMR spectroscopy). m.p. 133–135 °C (EtOAc/hexane); $[\alpha]_D^{20}$ +18.5 (*c* 1.08, $CHCl_3$); $R_f = 0.50$ (1:1 hexane/EtOAc); IR (solid) 3370 (OH), 2922, 1547 (NO_2), 1414, 1377, 1177, 1074, 1012, 833, 762, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (1H, d, *J* = 8.5 Hz, Ar**H**), 8.09 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.83 (1H, dd, *J* = 8.2, 1.1 Hz, Ar**H**), 7.75 (1H, ddd, *J* = 8.4, 7.0, 1.4 Hz, Ar**H**), 7.57 (1H, ddd, *J* = 8.1, 7.0, 1.1 Hz, Ar**H**), 7.46–7.36 (4H, m, Ar**H**), 7.36–7.29 (1H, m, Ar**H**), 7.19 (1H, d, *J* = 8.5 Hz, Ar**H**), 5.00 (1H, br s, O**H**), 4.81 (1H, dd, *J* = 12.4, 7.0 Hz, C**H**$_2$NO$_2$), 4.66 (2H, app dd, *J* = 12.4, 8.7 Hz, C**H**$_2$NO$_2$ and C**H**OH), 4.10 (1H, dddd, *J* = 9.9, 8.7, 7.0, 4.9 Hz, C**H**CH$_2$NO$_2$), 2.25 (1H, ddd, *J* = 13.8, 9.9, 2.3 Hz, C**H**$_2$CHOH), 1.95 (1H, ddd, *J* = 13.8, 10.6, 4.9 Hz, C**H**$_2$CHOH); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 161.0 (C), 146.1 (C), 139.1 (C), 137.5 (CH), 130.2 (CH), 129.1 (2 × CH), 128.5 (CH), 127.85 (CH), 127.81 (2 × CH), 127.63 (CH), 127.55 (C), 126.8 (CH), 118.0 (CH), 80.8 (CH$_2$), 70.1 (CH), 42.5 (CH$_2$), 41.8 (CH); HRMS (ESI) Exact mass calcd for $C_{19}H_{19}O_3N_2$ [M+H]$^+$: 323.1390, found 323.1392.

(1*R*,3*R*)-4-Nitro-3-phenyl-1-(quinolin-2-yl)butan-1-ol (6b)

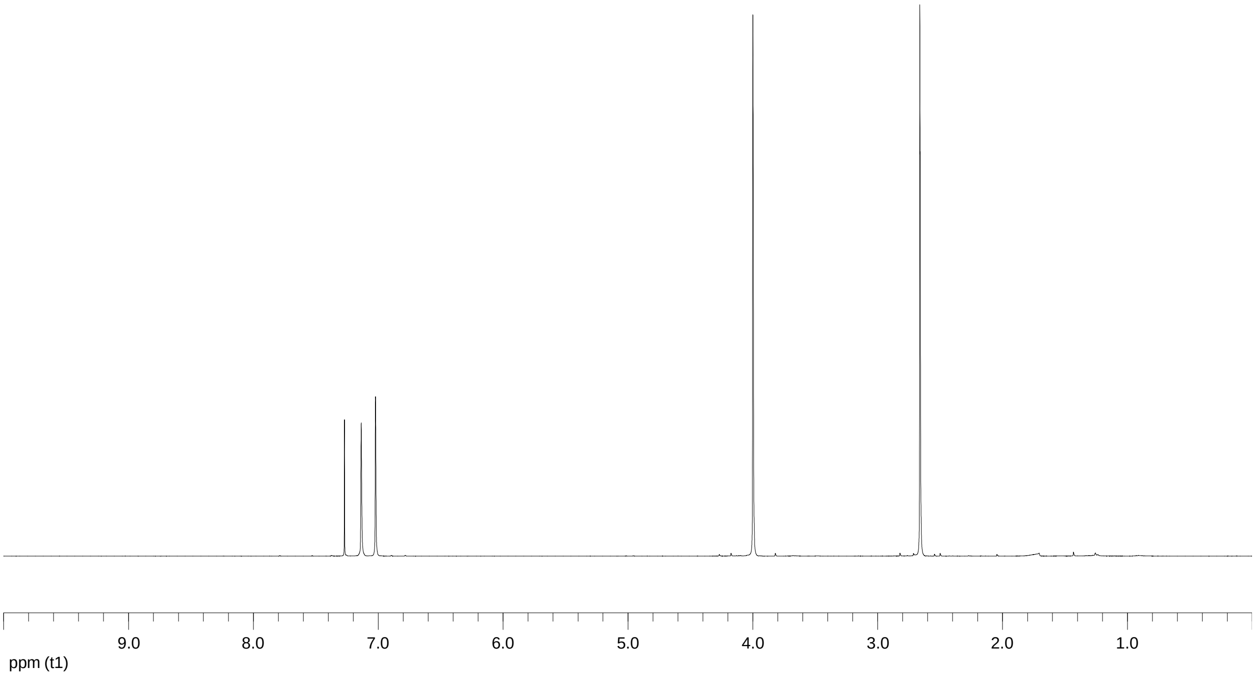


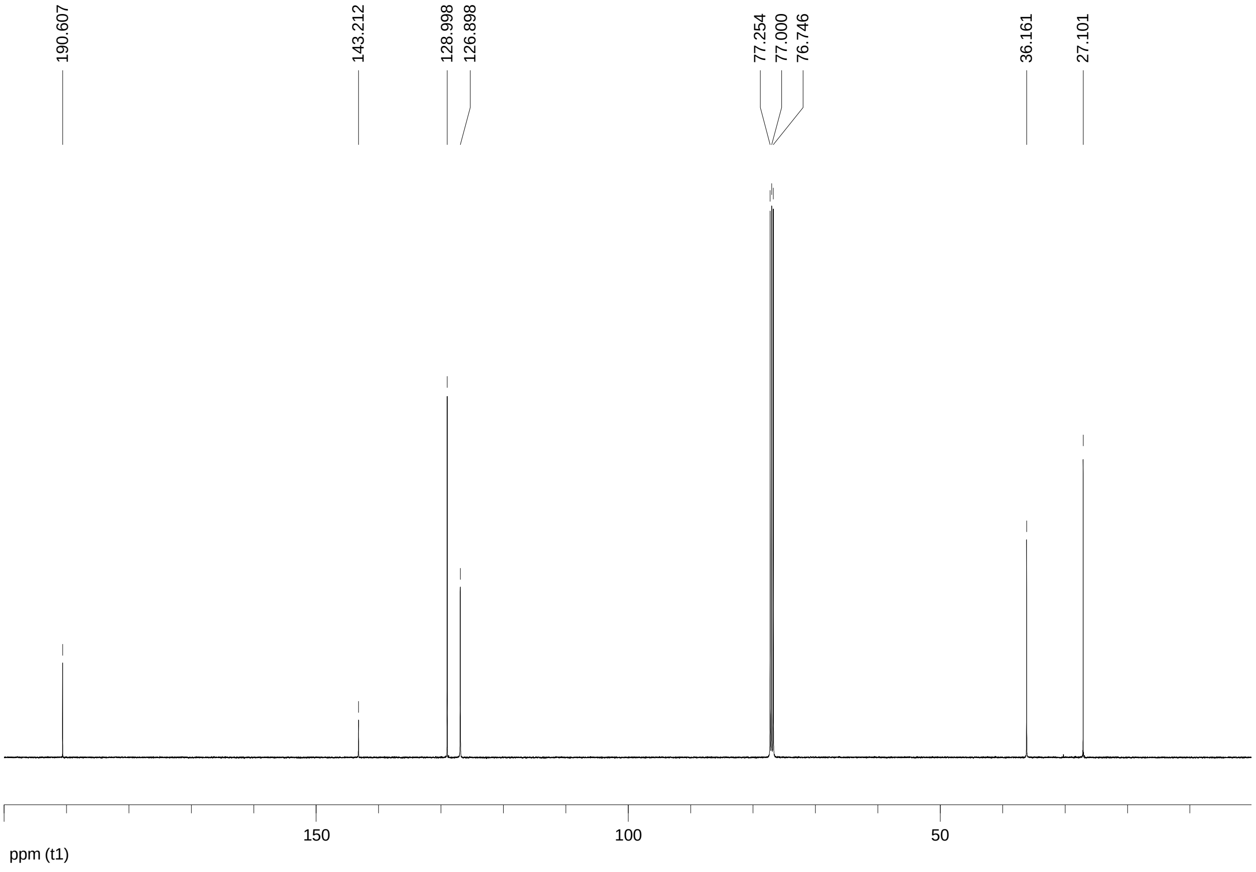
In a modification of a previously reported procedure for the reduction of other acylazaarenes,[28] to a solution of (*R*)-4-nitro-3-phenyl-1-(quinolin-2-yl)butan-1-one (**3b**) (160 mg, 0.50 mmol) and RuCl[(*R*,*R*)-TsDPEN](*p*-cymene)[29] (8.0 mg, 0.013 mmol) in DMF (2.5 mL) was added a mixture of HCO$_2$H (108 μL, 1.51 mmol) and Et$_3$N (84 μL, 0.60 mmol). The reaction mixture was stirred at room temperature, open to the air, for 18 h, then quenched carefully with MeOH (0.25 mL) and stirred for 5 min. The mixture was diluted with Et$_2$O (10 mL) and washed with saturated aqueous NaHCO$_3$ solution (2 × 10 mL), H$_2$O (5 × 10 mL), and brine (10 mL). The organic layer was dried (Na$_2$SO$_4$), filtered, and concentrated *in vacuo* to leave *the alcohol* **6a** as a yellow oil which required no further purification (157 mg, >95%, >19:1 dr by ^{1}H NMR spectroscopy). $[\alpha]_D^{20}$ −82.9 (*c* 1.11, CHCl$_3$); R_f = 0.42 (1:1 hexane/EtOAc); IR (film) 3063 (br, OH), 2361, 2342, 1545 (NO$_2$), 1504, 1379, 1063, 831, 754, 698 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.07 (1H, dd, *J* = 8.4, 1.4 Hz, Ar**H**), 7.81 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.75 (1H, ddd, *J* = 8.4, 6.9, 1.4 Hz, Ar**H**), 7.56 (1H, ddd, *J* = 8.1, 6.9, 1.1 Hz, Ar**H**), 7.25–7.20 (2H, m, Ar**H**), 7.20–7.19 (1H, m, Ar**H**), 7.18–7.15 (3H, m, Ar**H**), 5.10 (1H, br s, O**H**), 4.96 (1H, dd, *J* = 7.4, 4.3 Hz, C**H**OH), 4.90 (1H, dd, *J* = 12.6, 6.0 Hz, C**H**$_2$NO$_2$), 4.82 (1H, dd, *J* = 12.6, 9.0 Hz, C**H**$_2$NO$_2$), 3.78 (1H, app dq, *J* = 9.0, 6.0 Hz, C**H**CH$_2$NO$_2$), 2.41 (1H, ddd, *J* = 14.3, 7.2, 4.3 Hz, C**H**$_2$CHOH), 2.21 (1H, ddd, *J* = 14.3, 7.5, 6.0 Hz, C**H**$_2$CHOH); ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 160.4 (C), 146.4 (C), 139.7 (C), 137.0 (CH), 130.0 (CH), 128.8 (2 × CH), 128.7 (CH), 127.6 (CH), 127.5 (C and 2 × CH), 127.4 (CH), 126.6 (CH), 118.1 (CH), 79.9 (CH$_2$), 70.2 (CH), 41.2 (CH$_2$), 40.4 (CH); HRMS (ESI) Exact mass calcd for $C_{19}H_{19}O_3N_2$ [M+H]$^+$: 323.1390, found 323.1393.

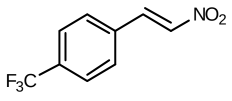
NMR Spectra



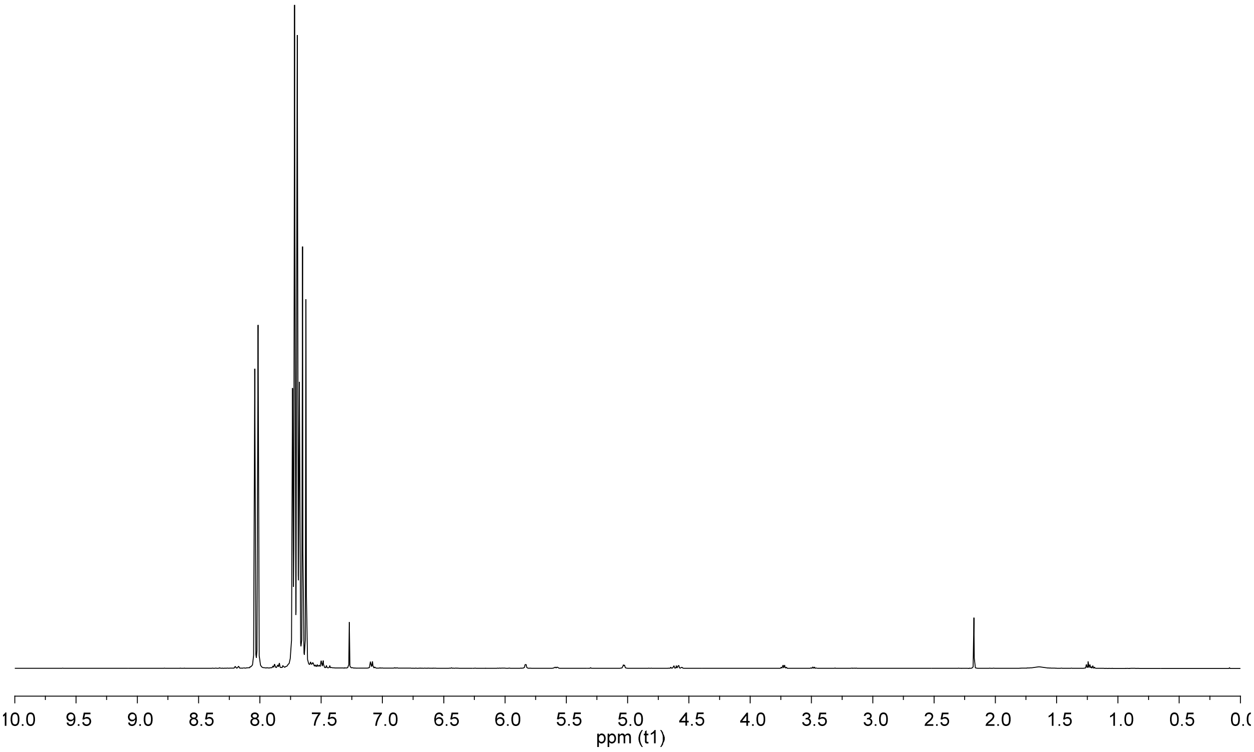
1f






NO$_2$
F$_3$C

2b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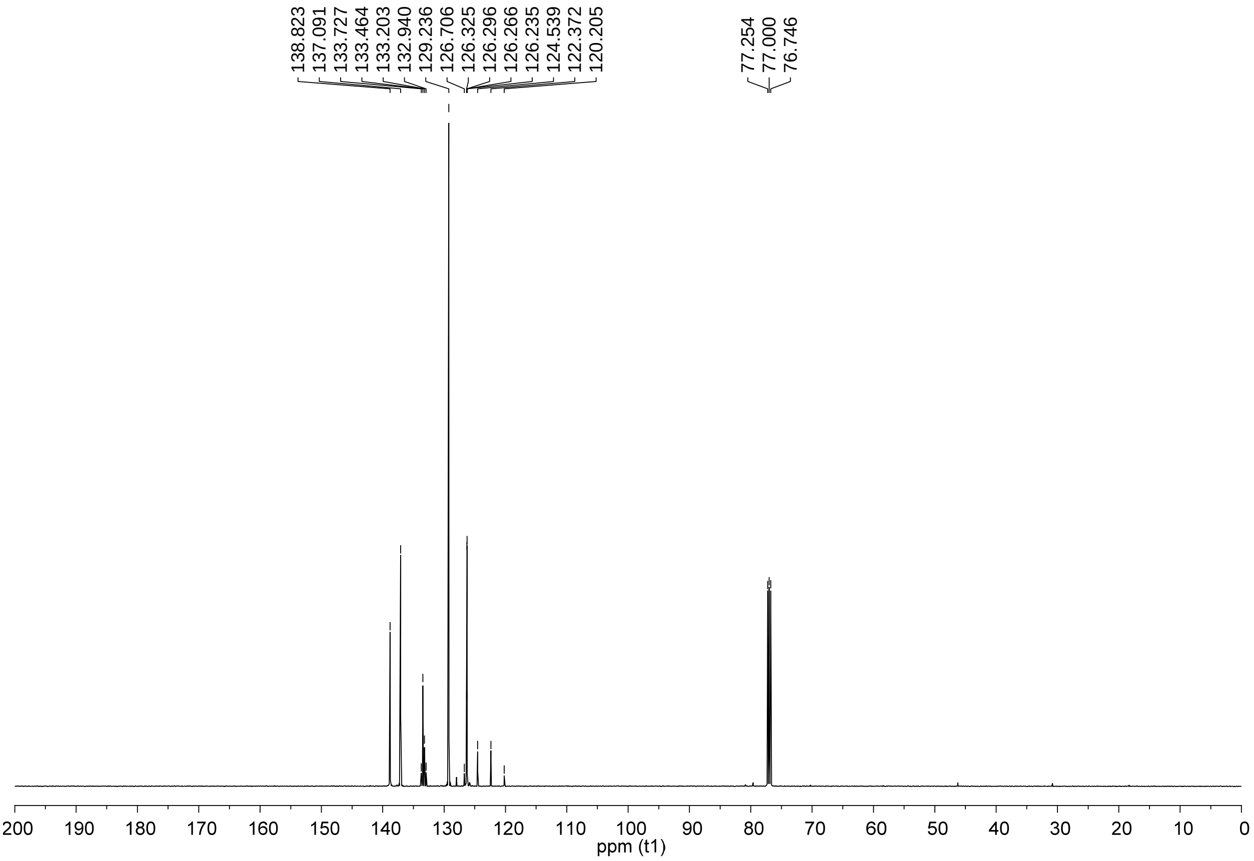
ppm (t1)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126.235
124.539
122.372
120.205
77.254
77.000
76.746
200
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180
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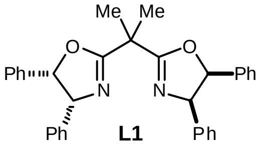
ppm (t1)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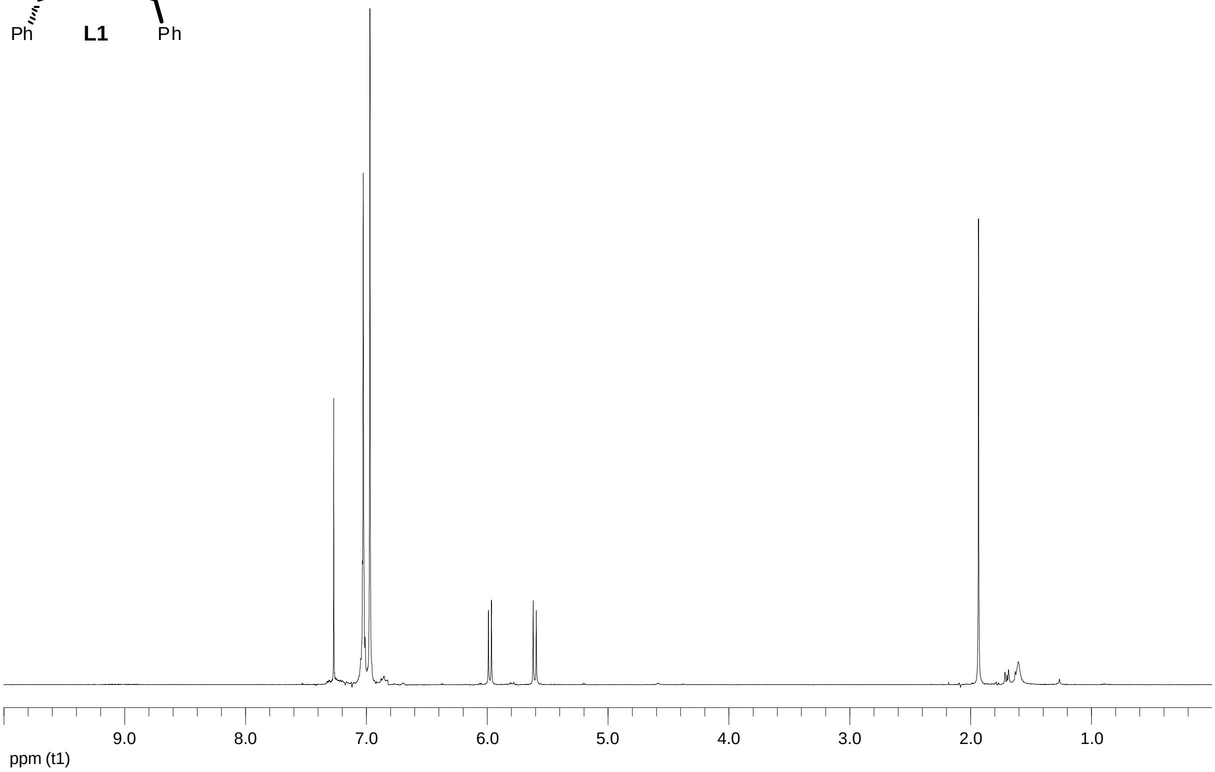
Me
O
O
N
N
Ph
Ph
Ph
Ph

L1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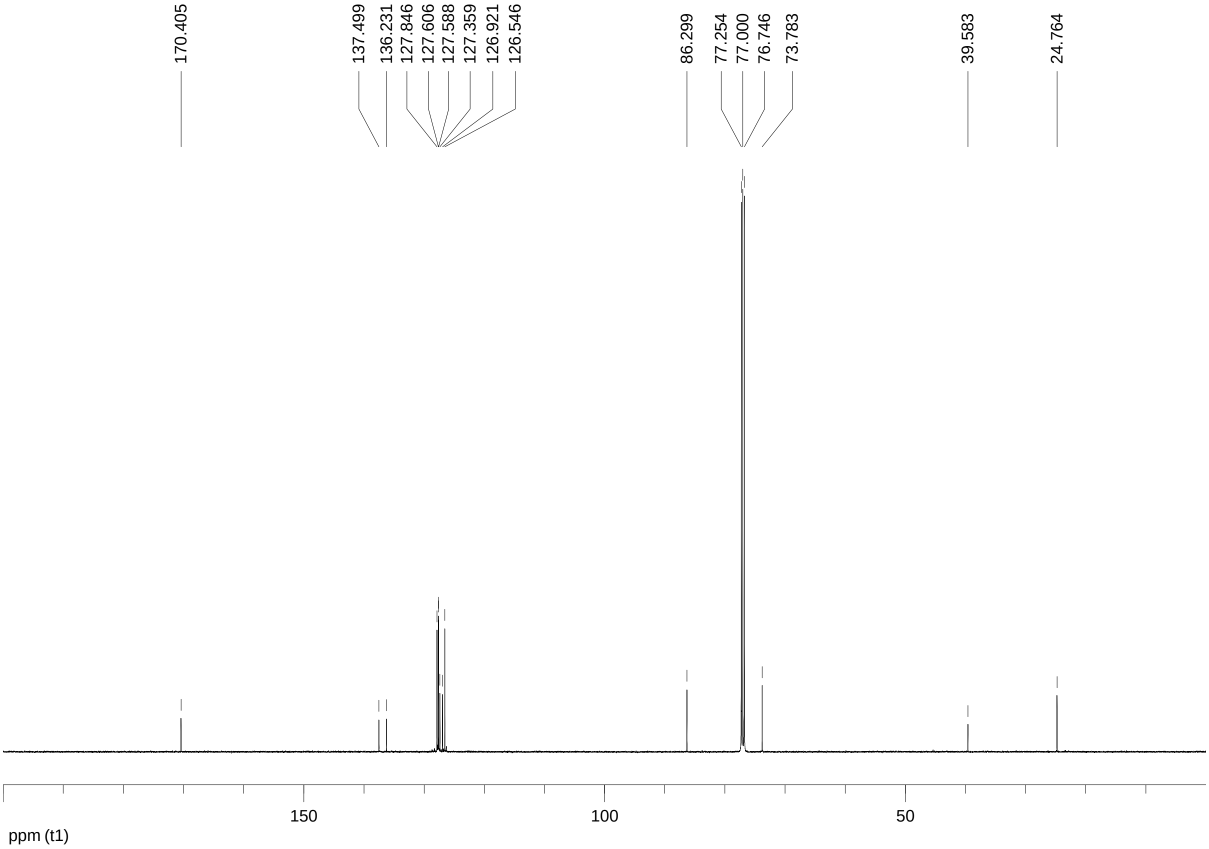
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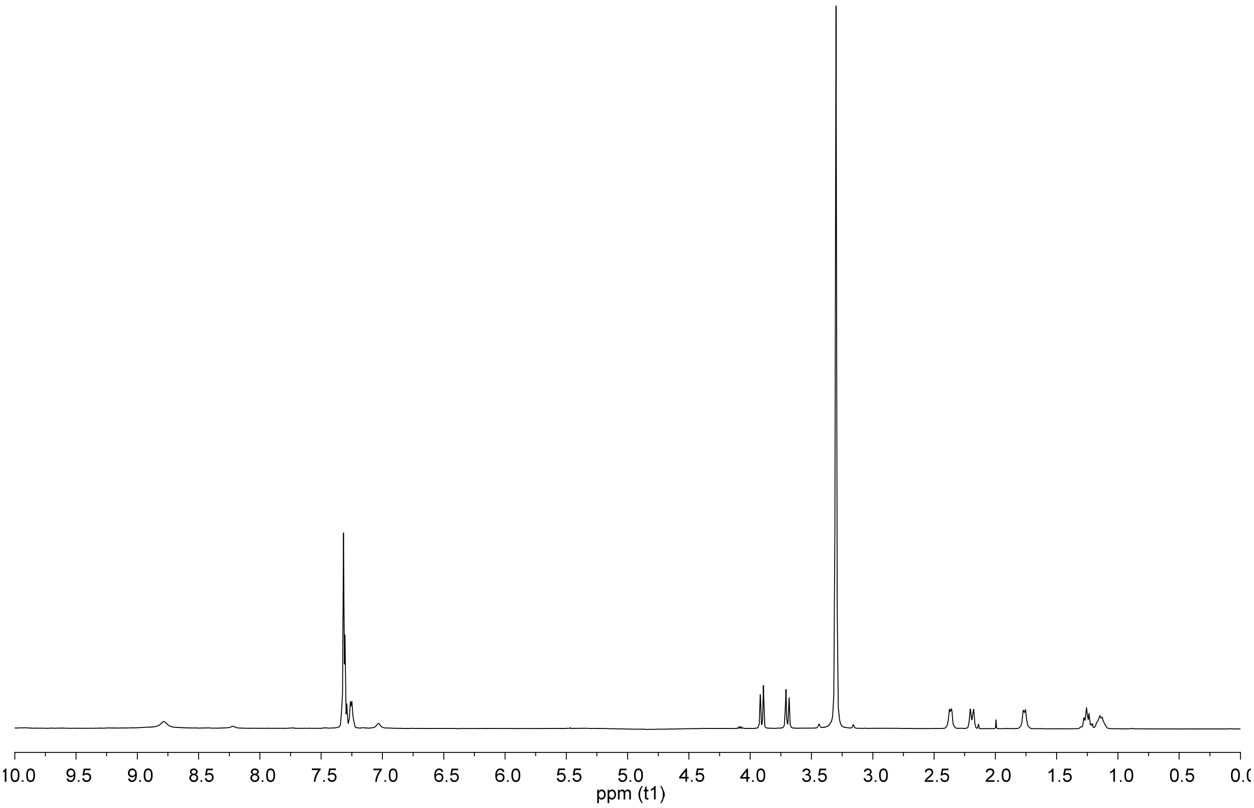
(**L6**)$_2$·NiBr$_2$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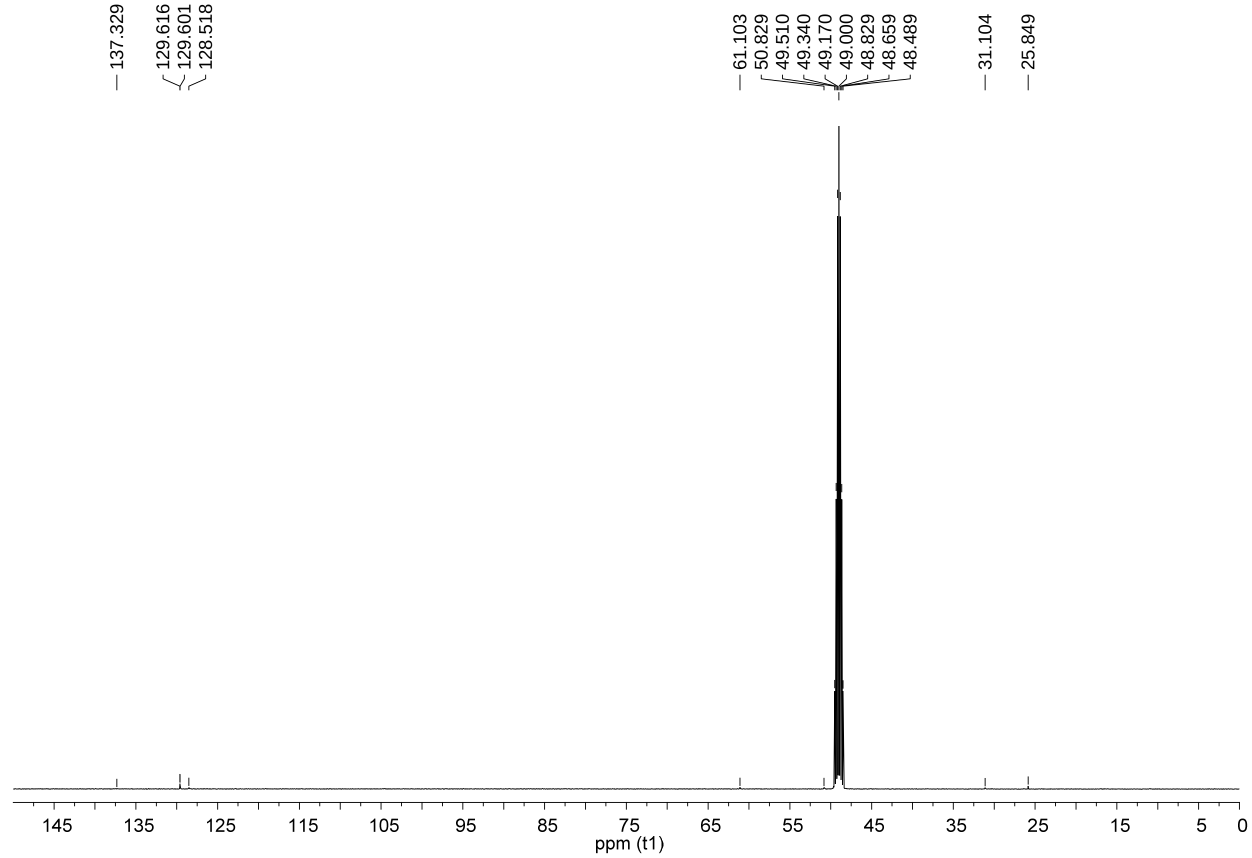
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31.104
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125
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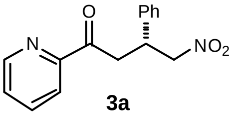
ppm (t1)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Ph
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NO2

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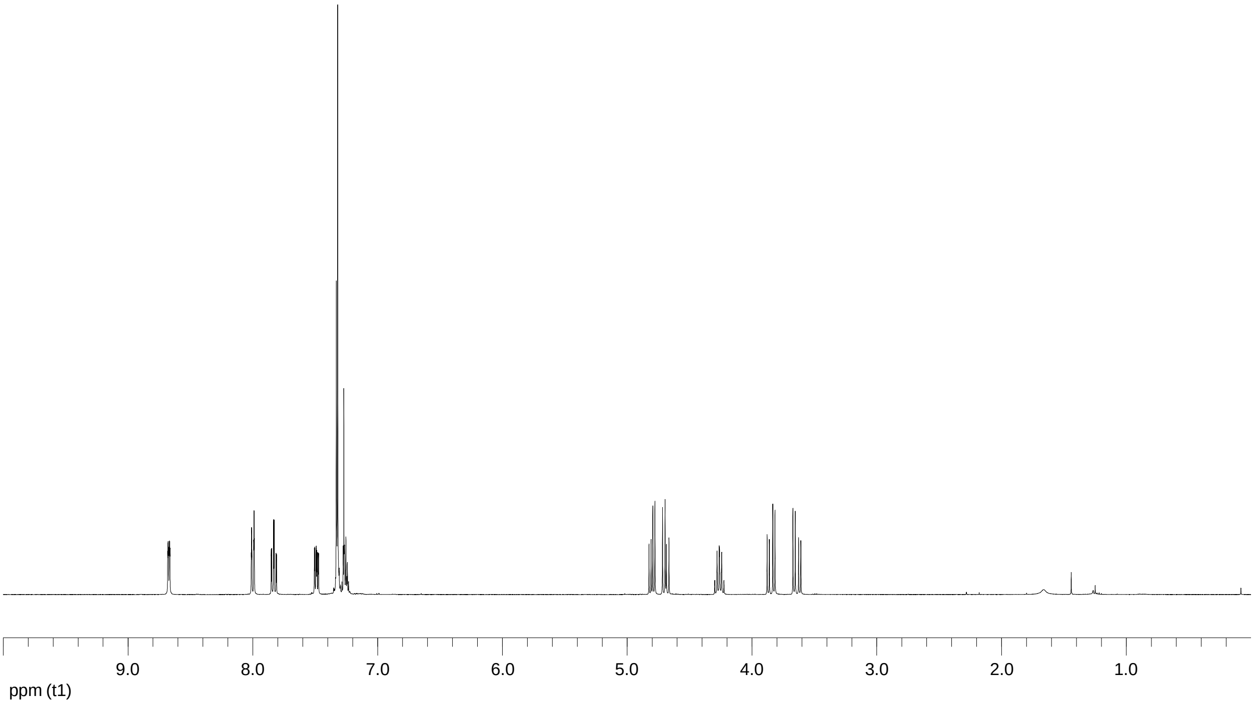
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2.0
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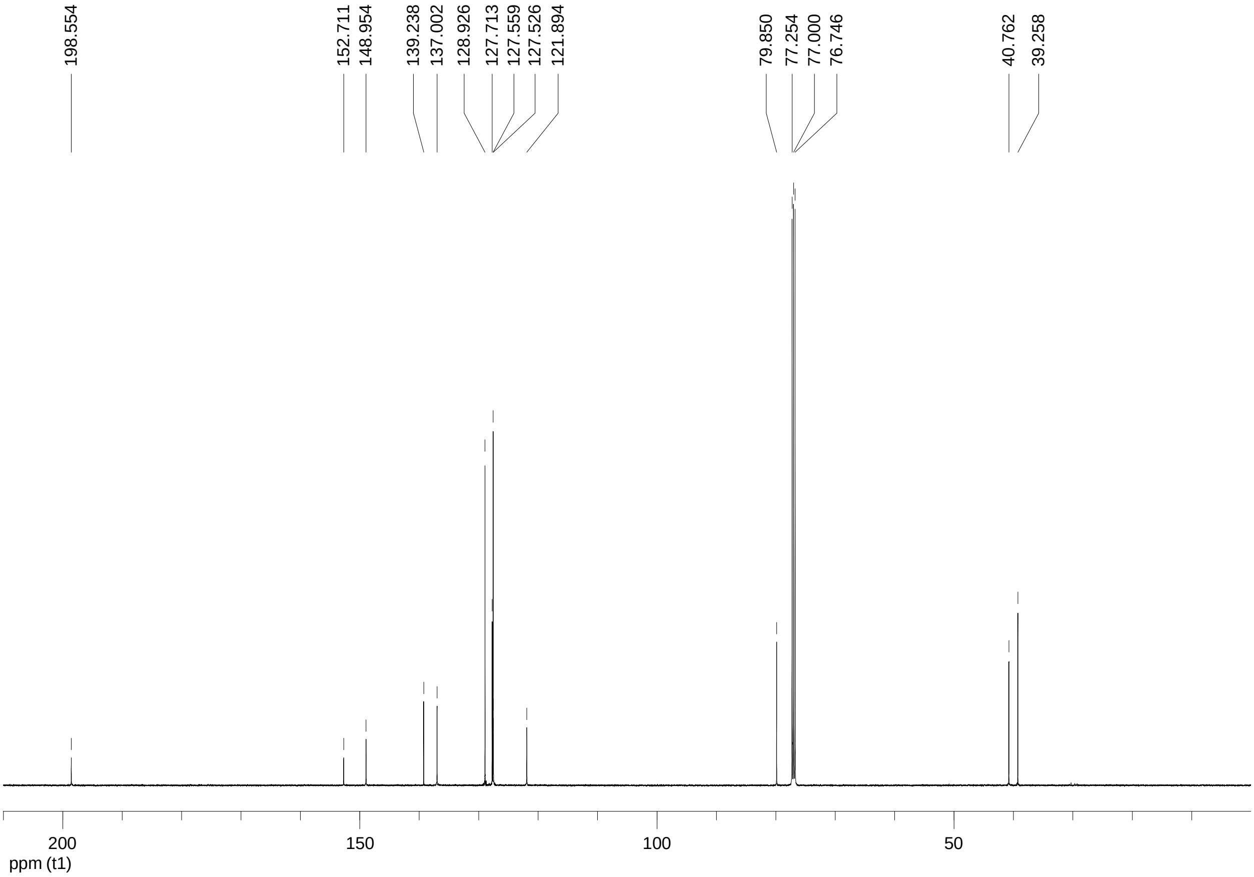
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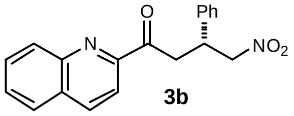
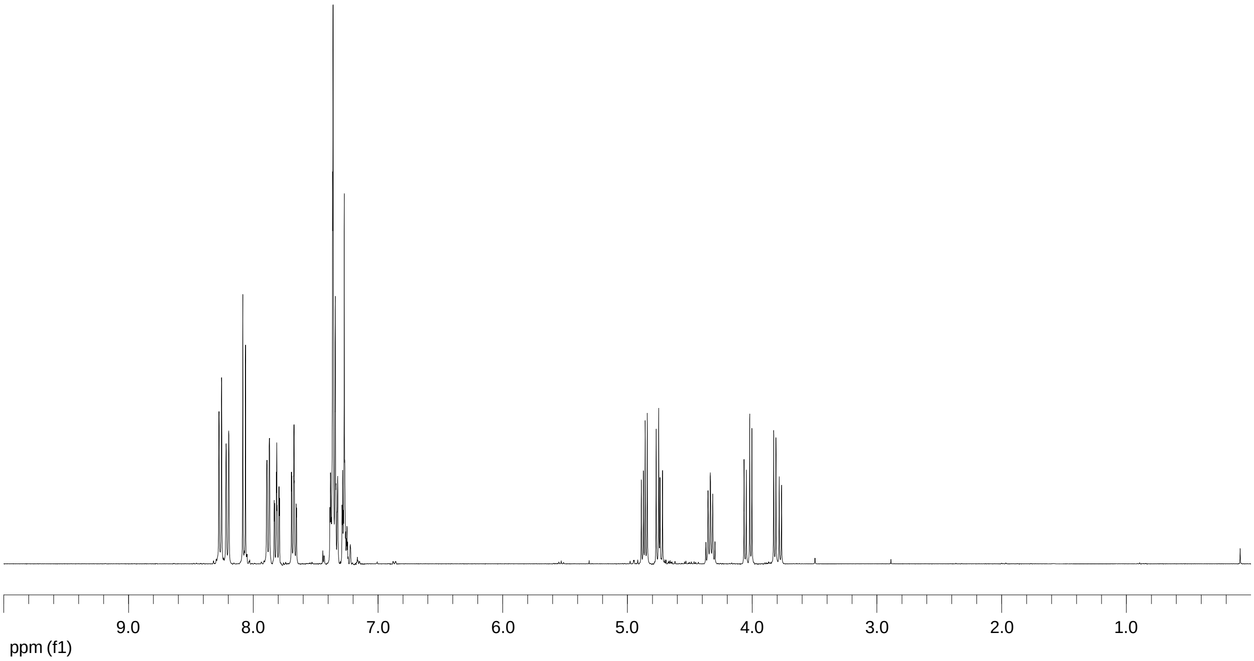
ppm (t1)


O
Ph
N
NO2

3b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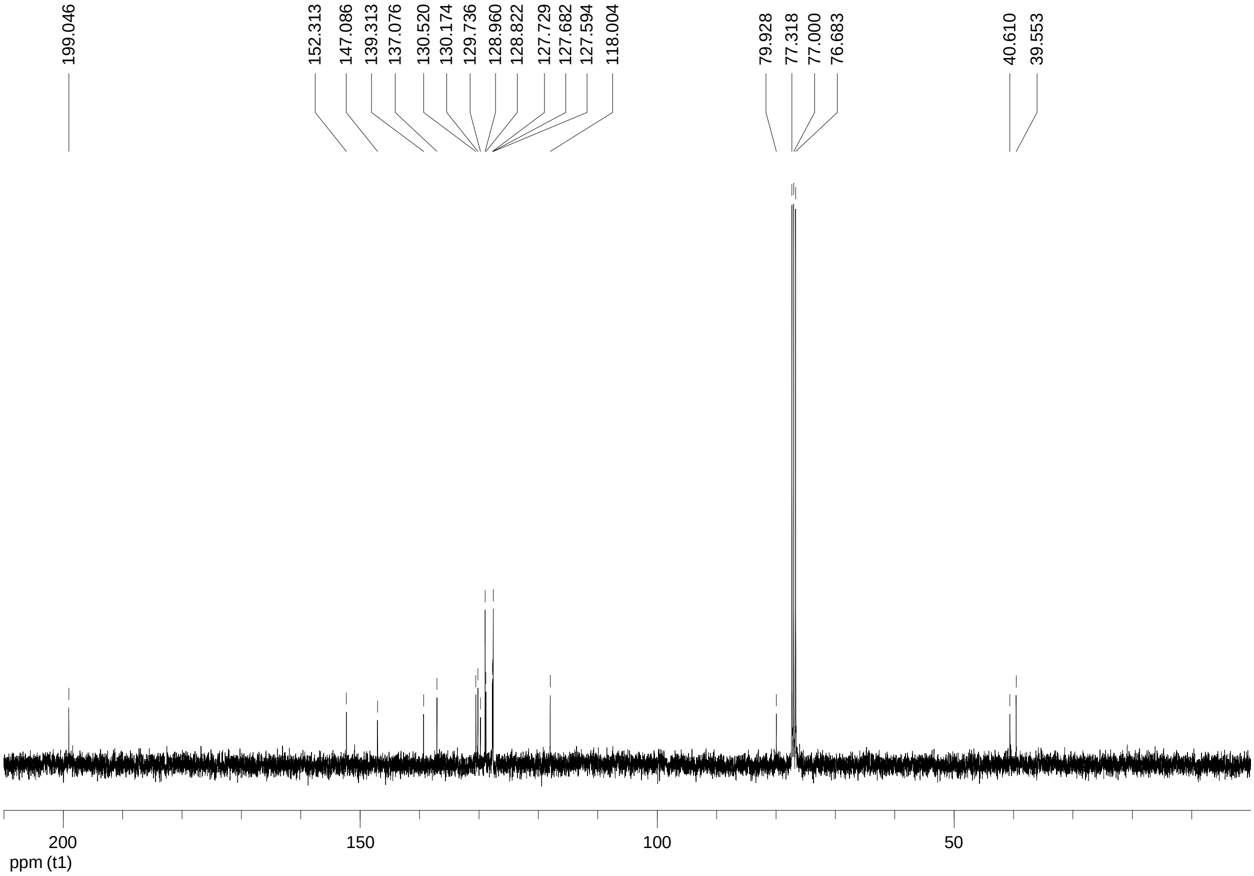
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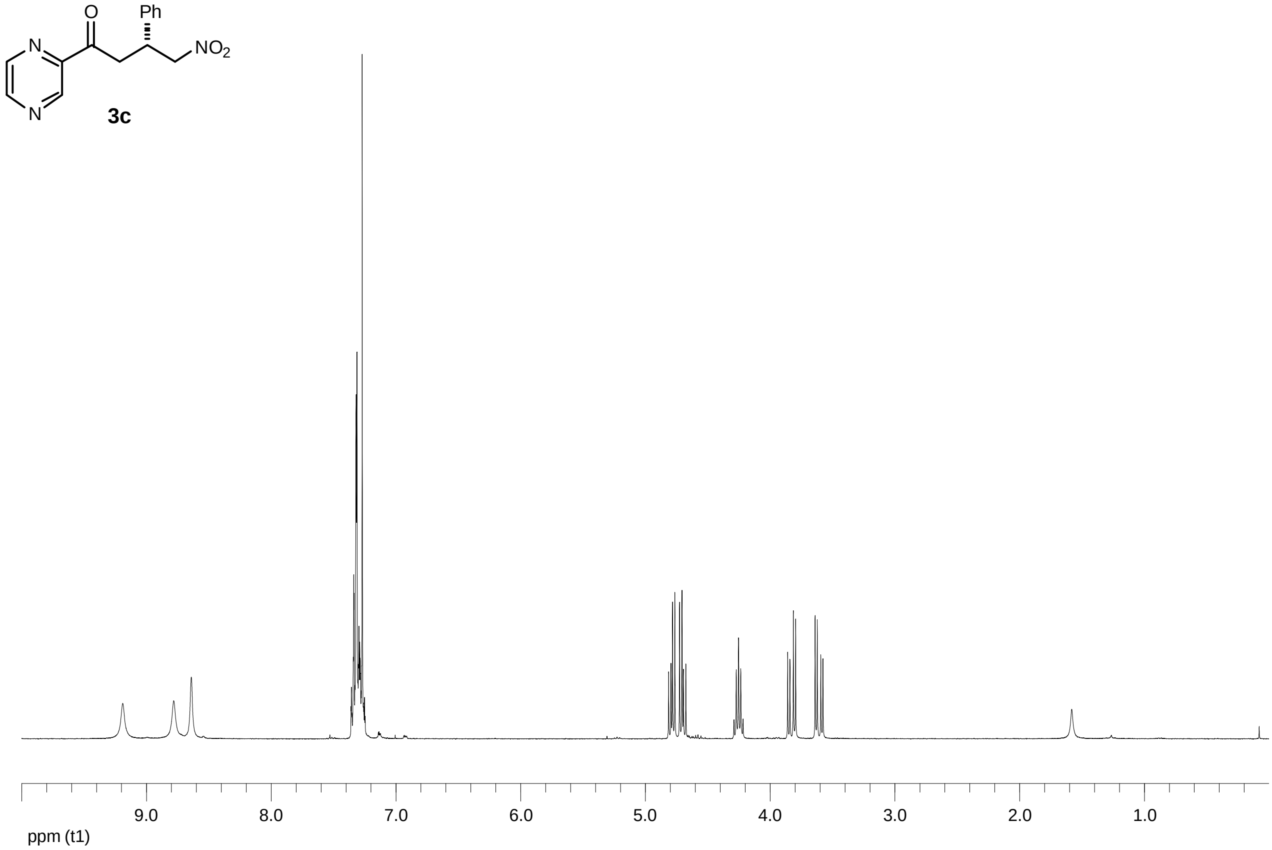
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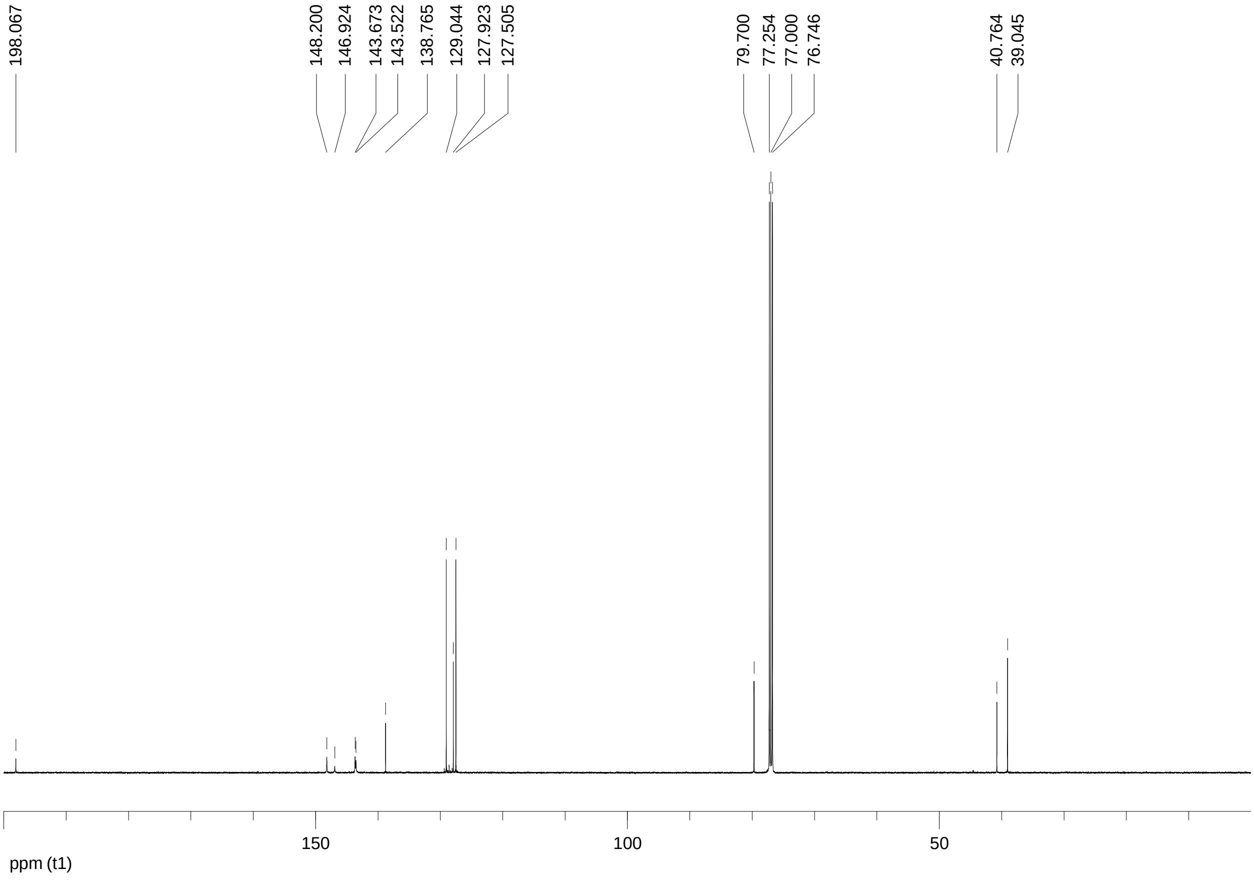
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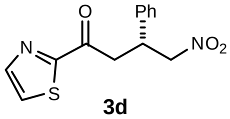
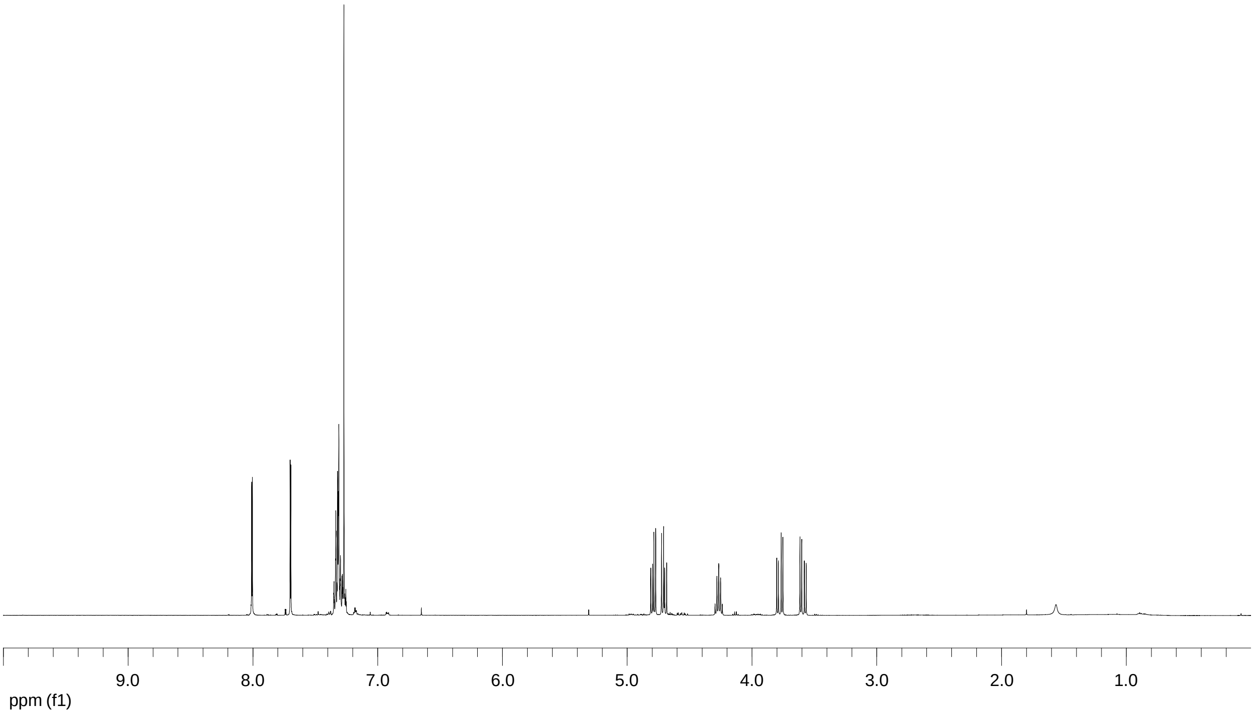


3d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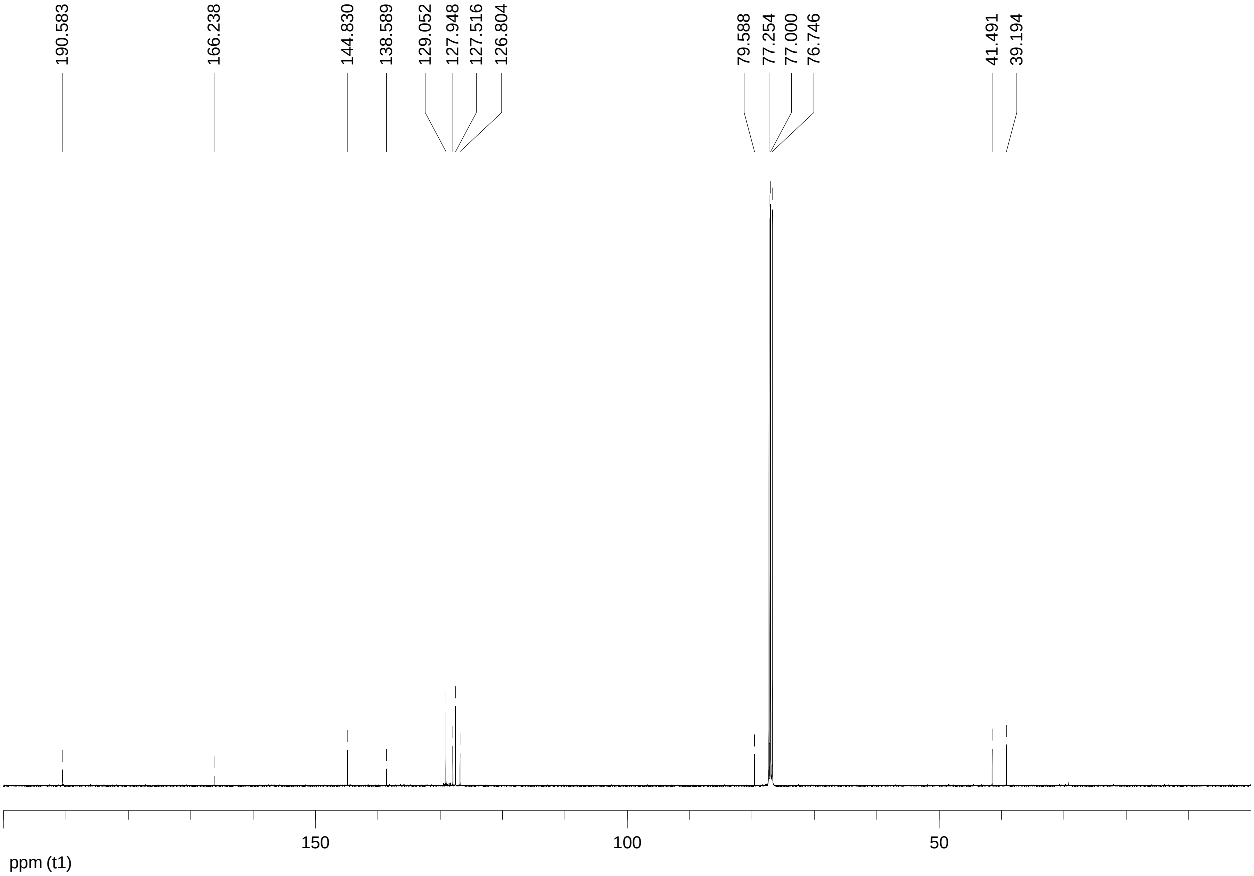
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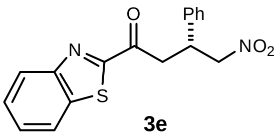
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NO2

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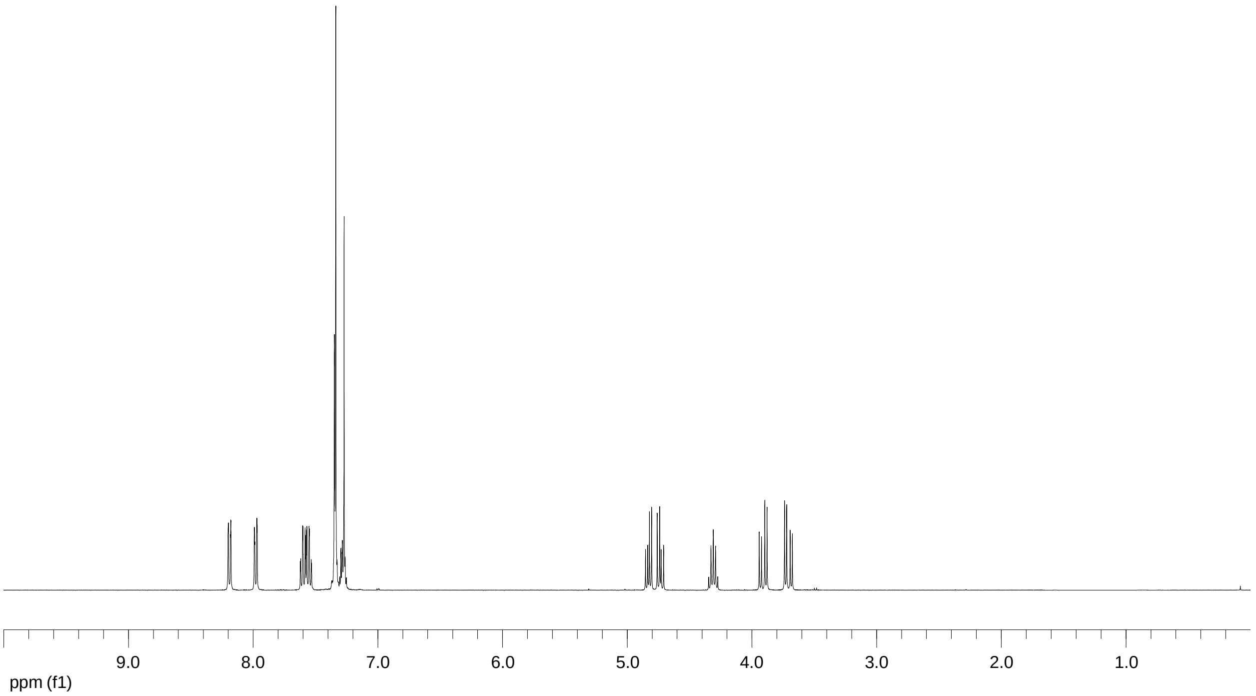
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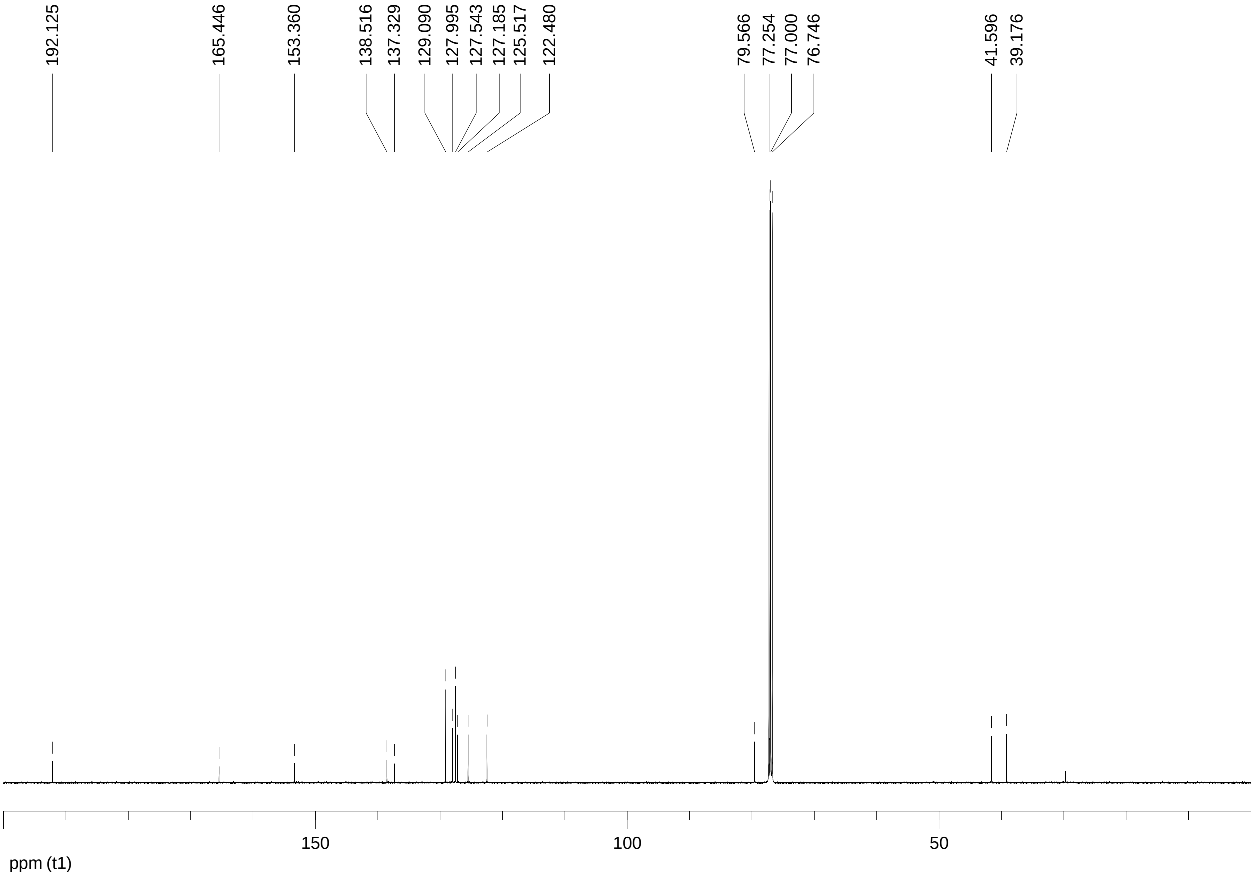
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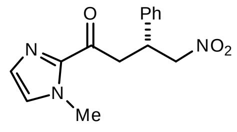
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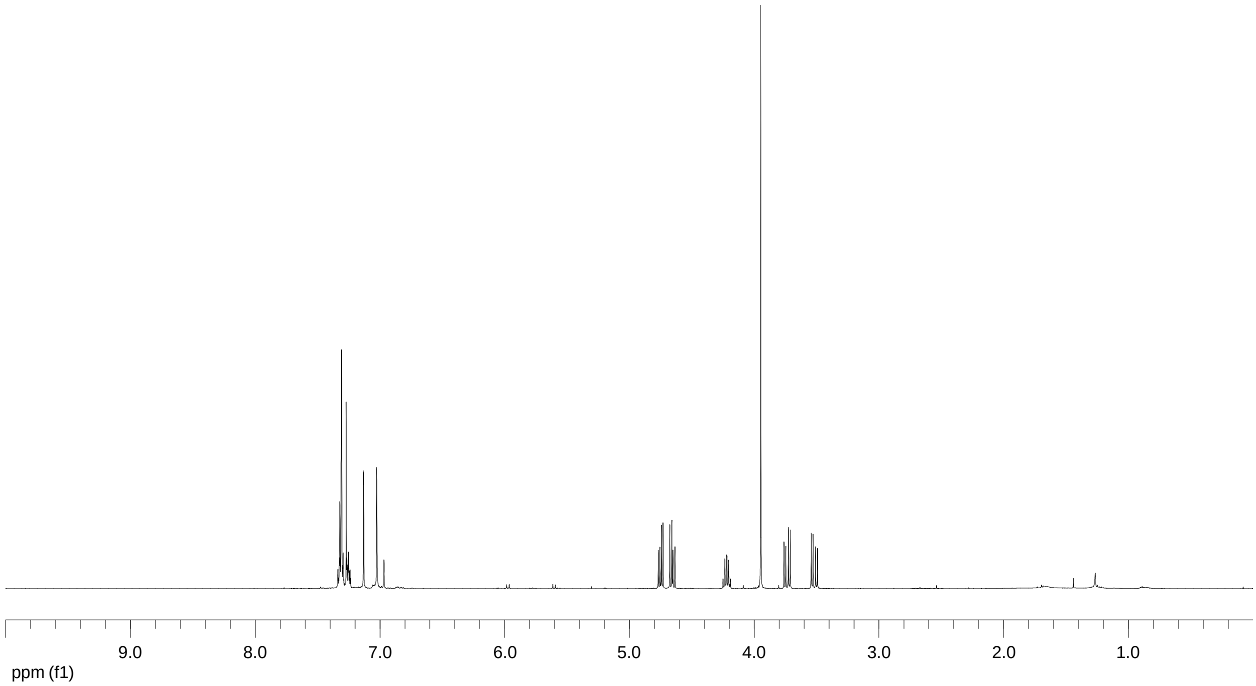
Me

3f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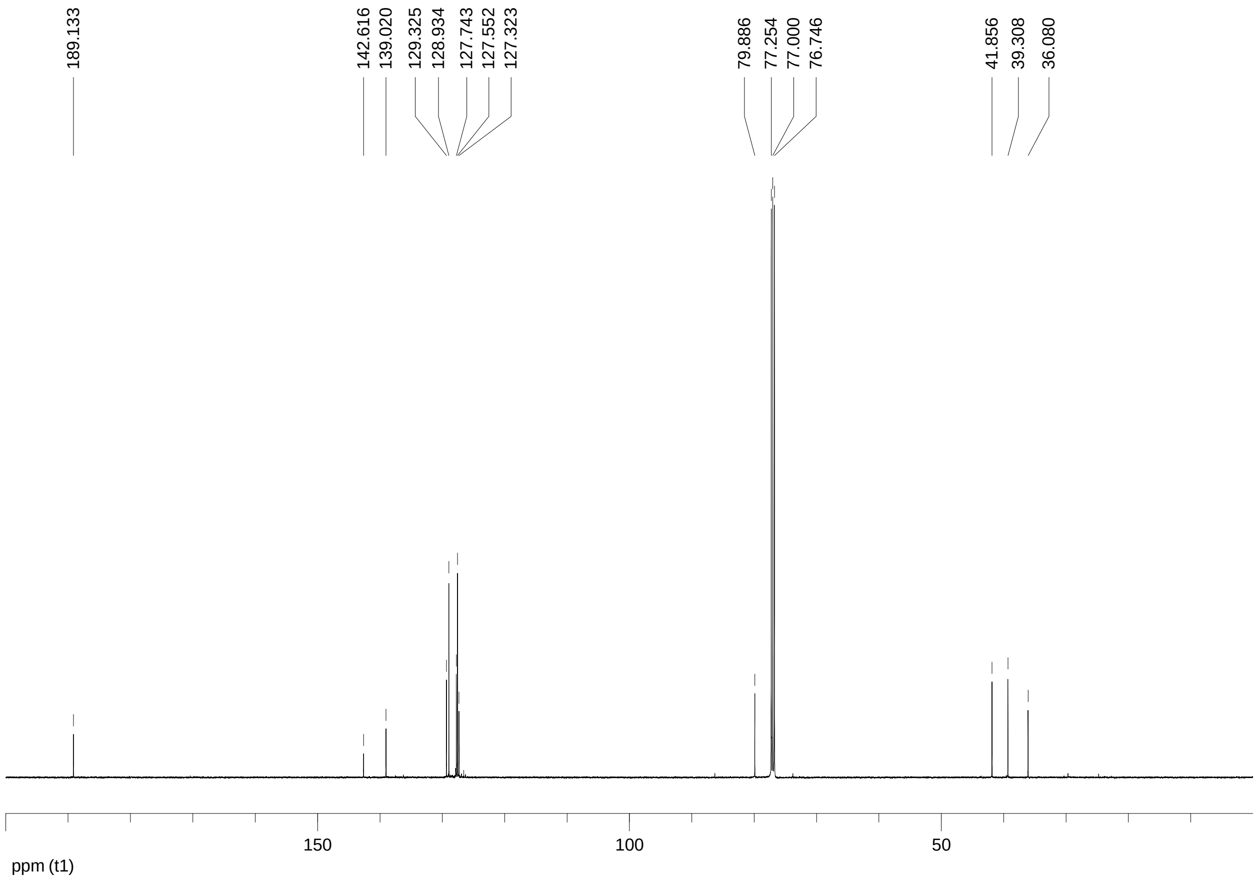
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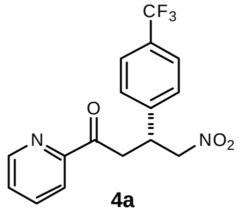
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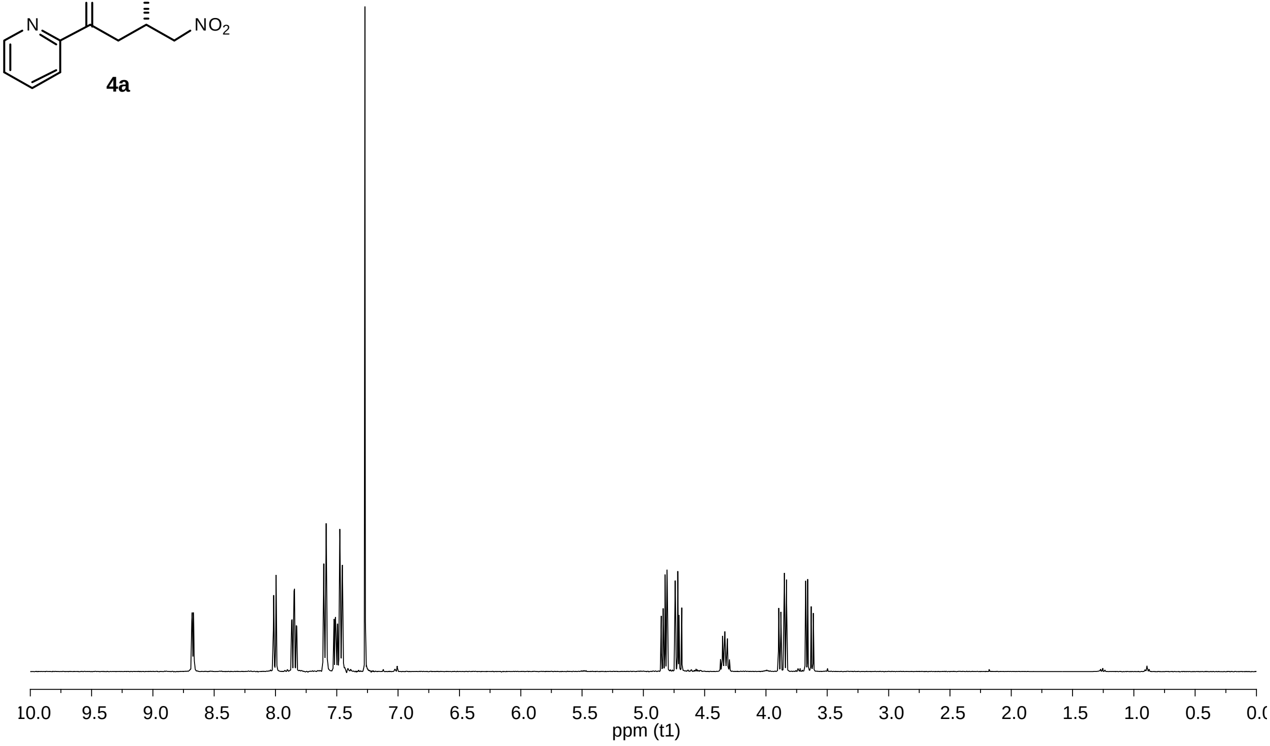
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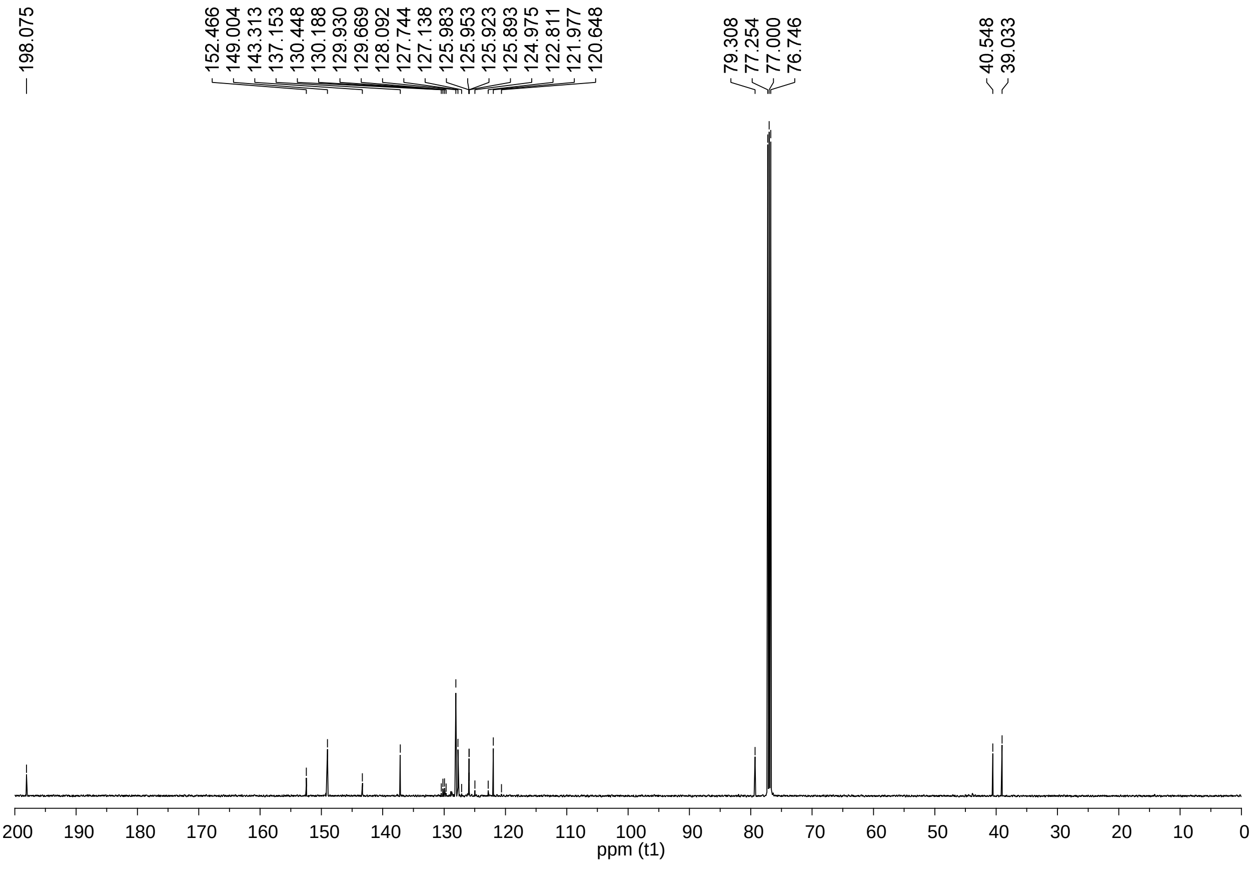
ppm (t1)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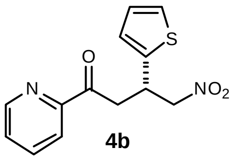
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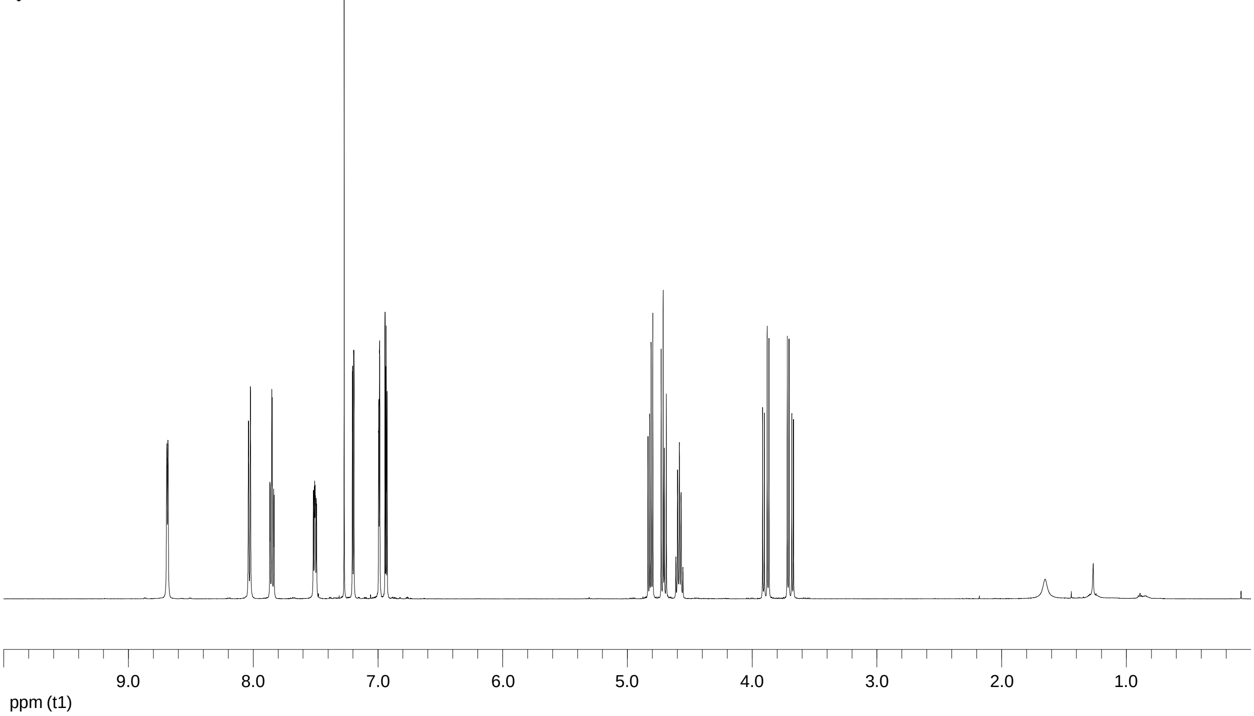
S
NO2

4b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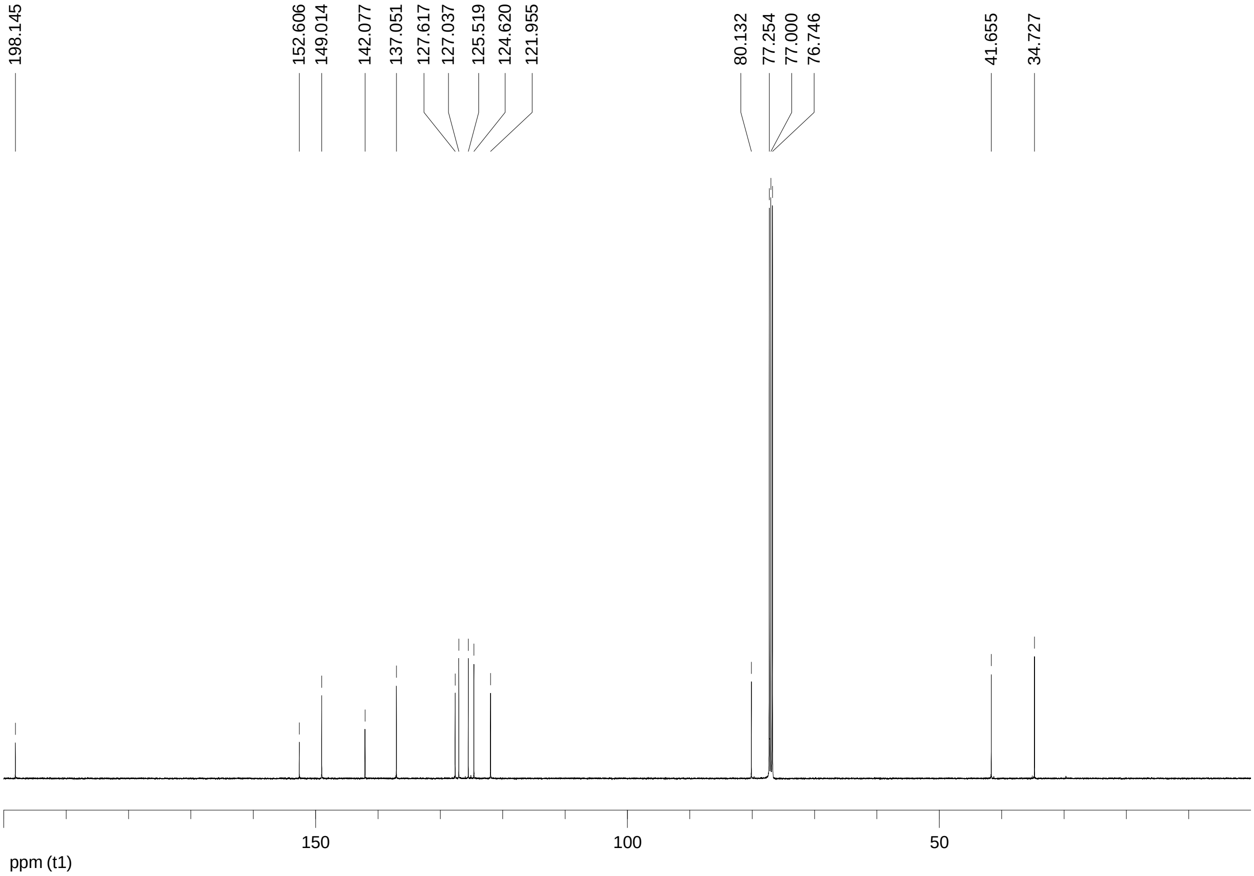
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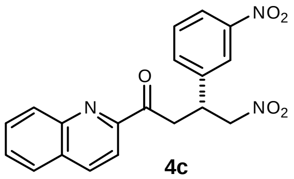
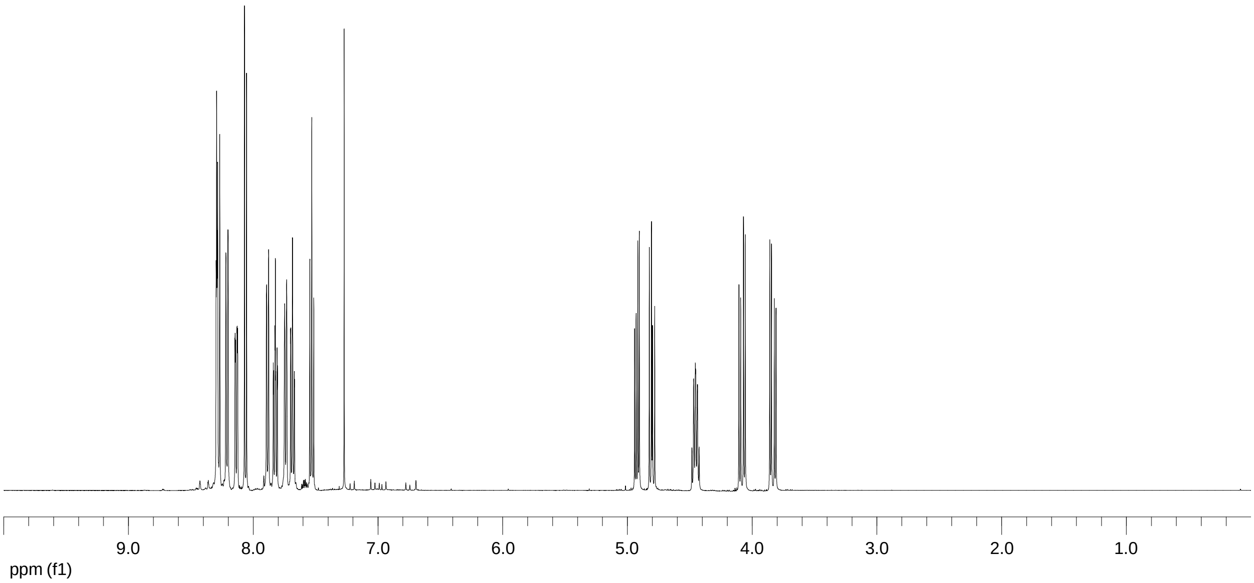
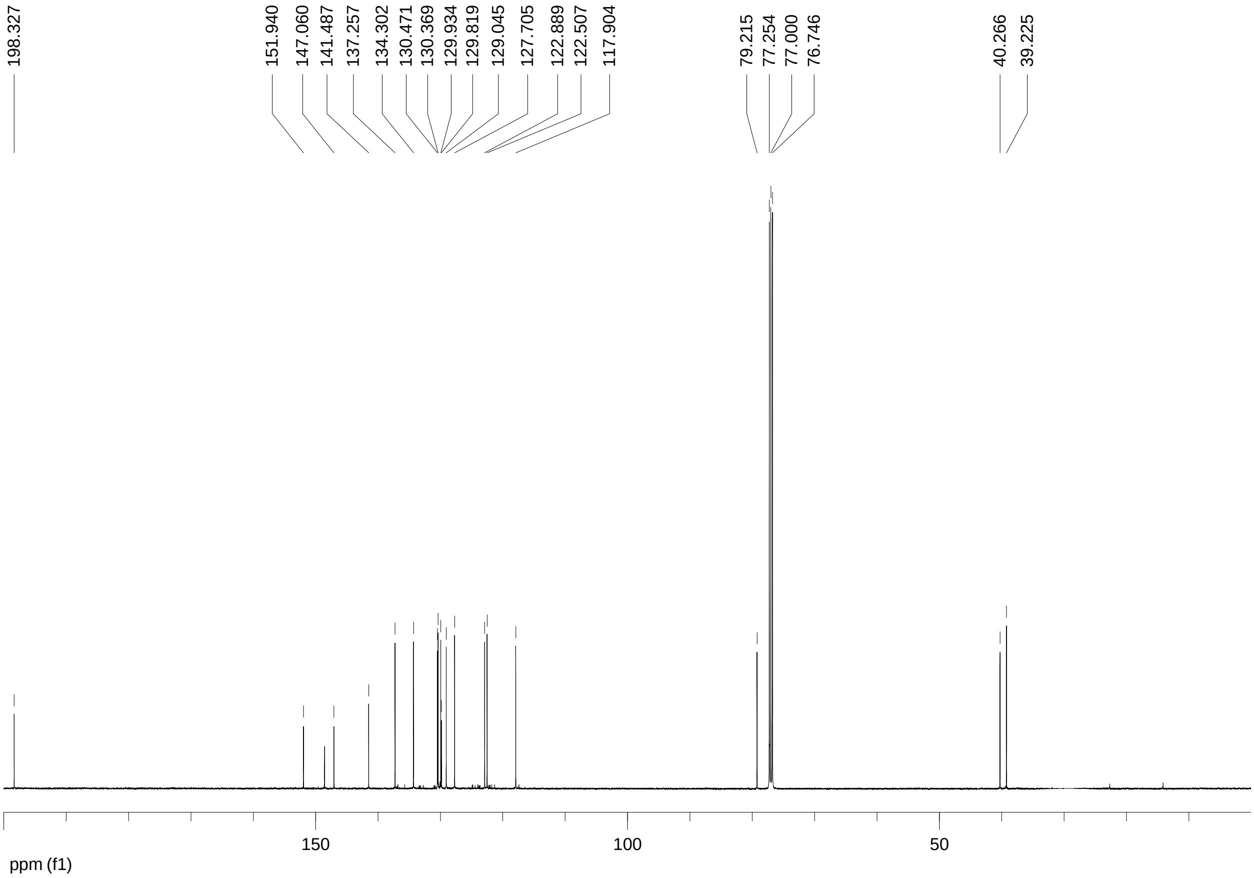
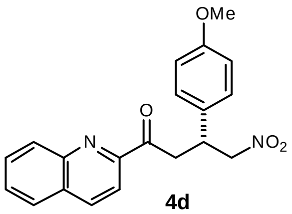

NO2
O
N
NO2

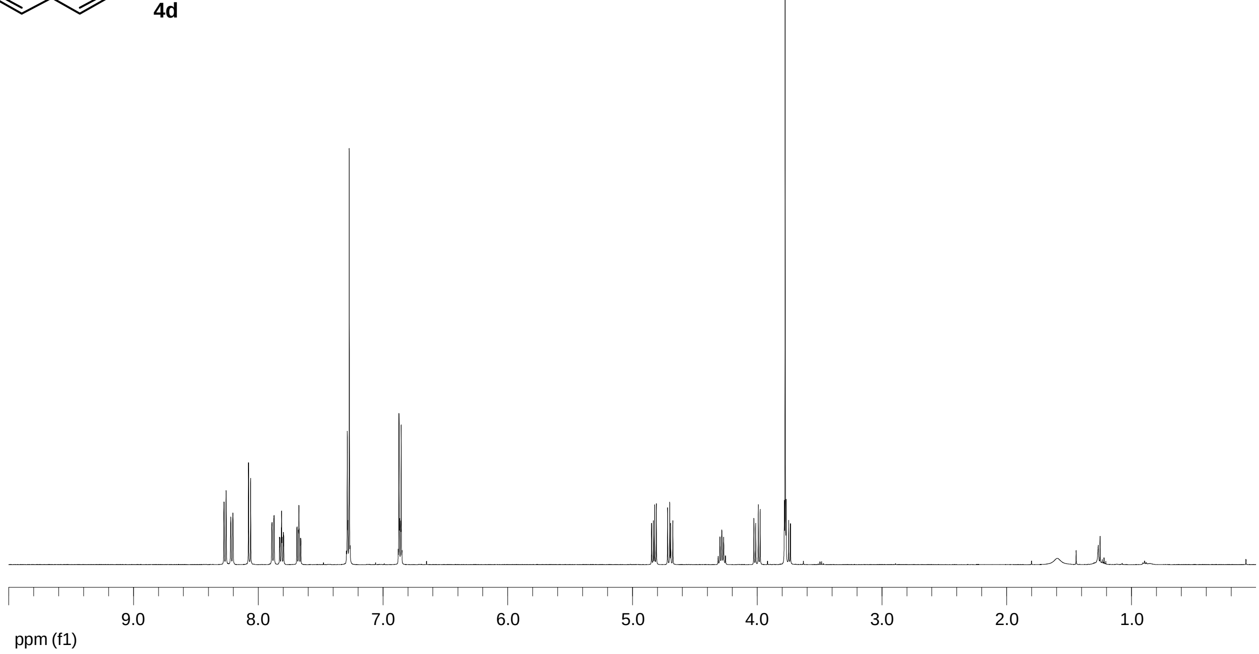
4c

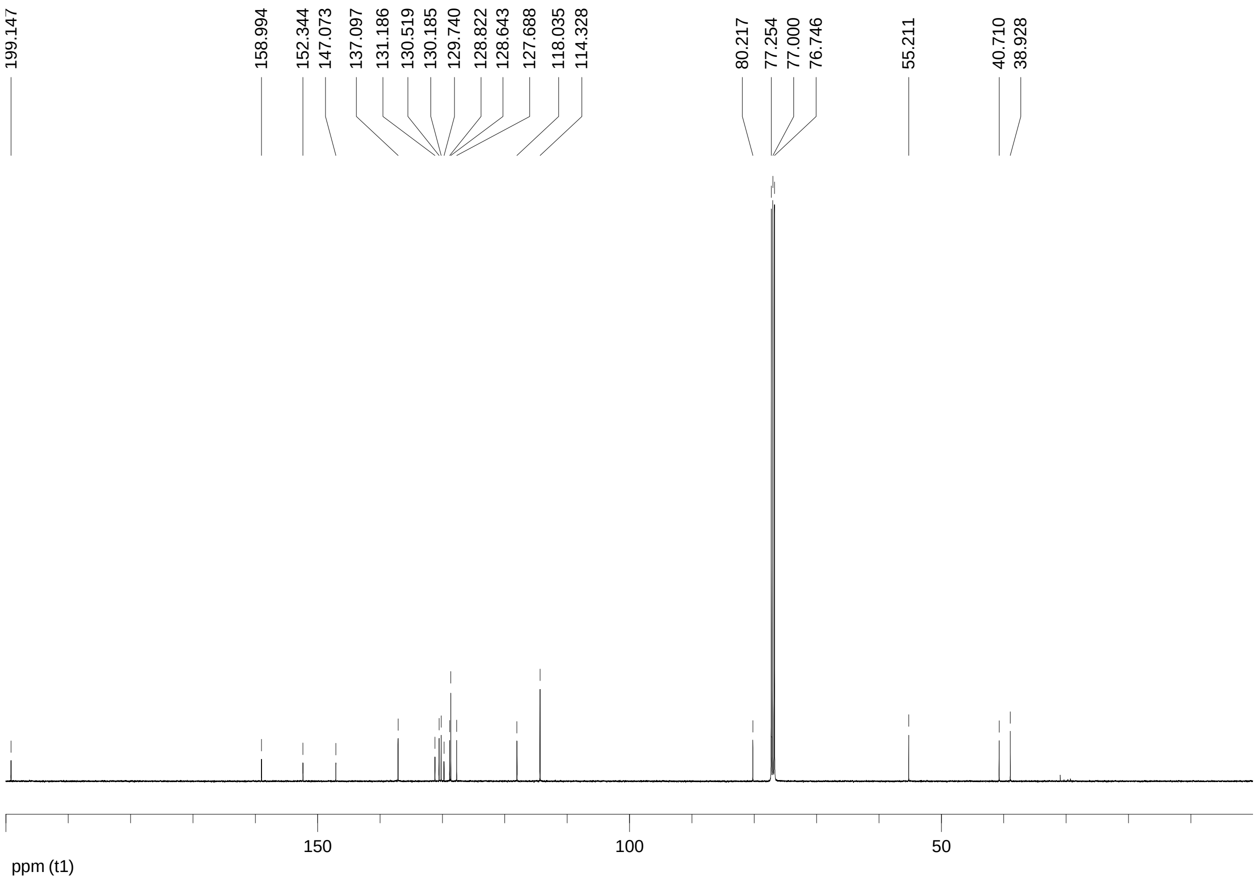

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

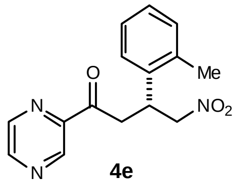

198.327
151.940
147.060
141.487
137.257
134.302
130.471
130.369
129.934
129.819
129.045
127.705
122.889
122.507
117.904
79.215
77.254
77.000
76.746
40.266
39.225
150
100
50
ppm (f1)


OMe
O
N
NO2

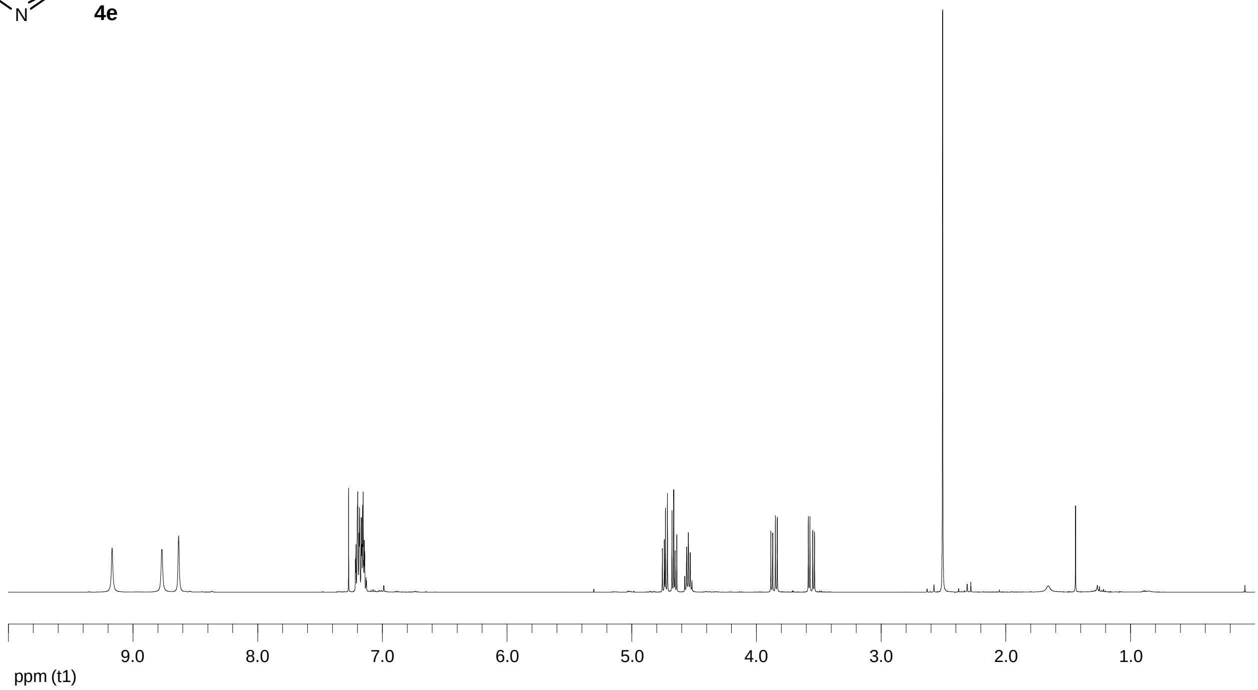
4d

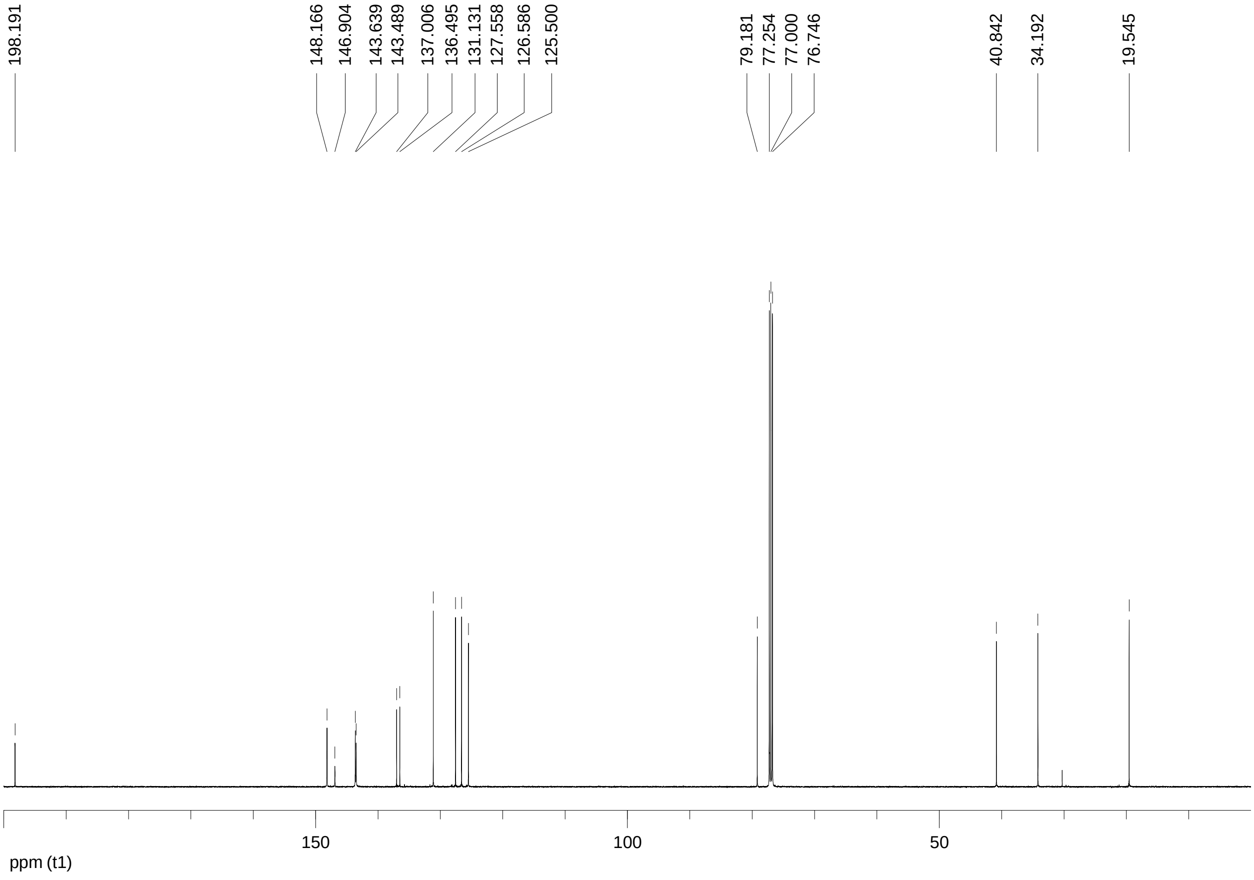

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

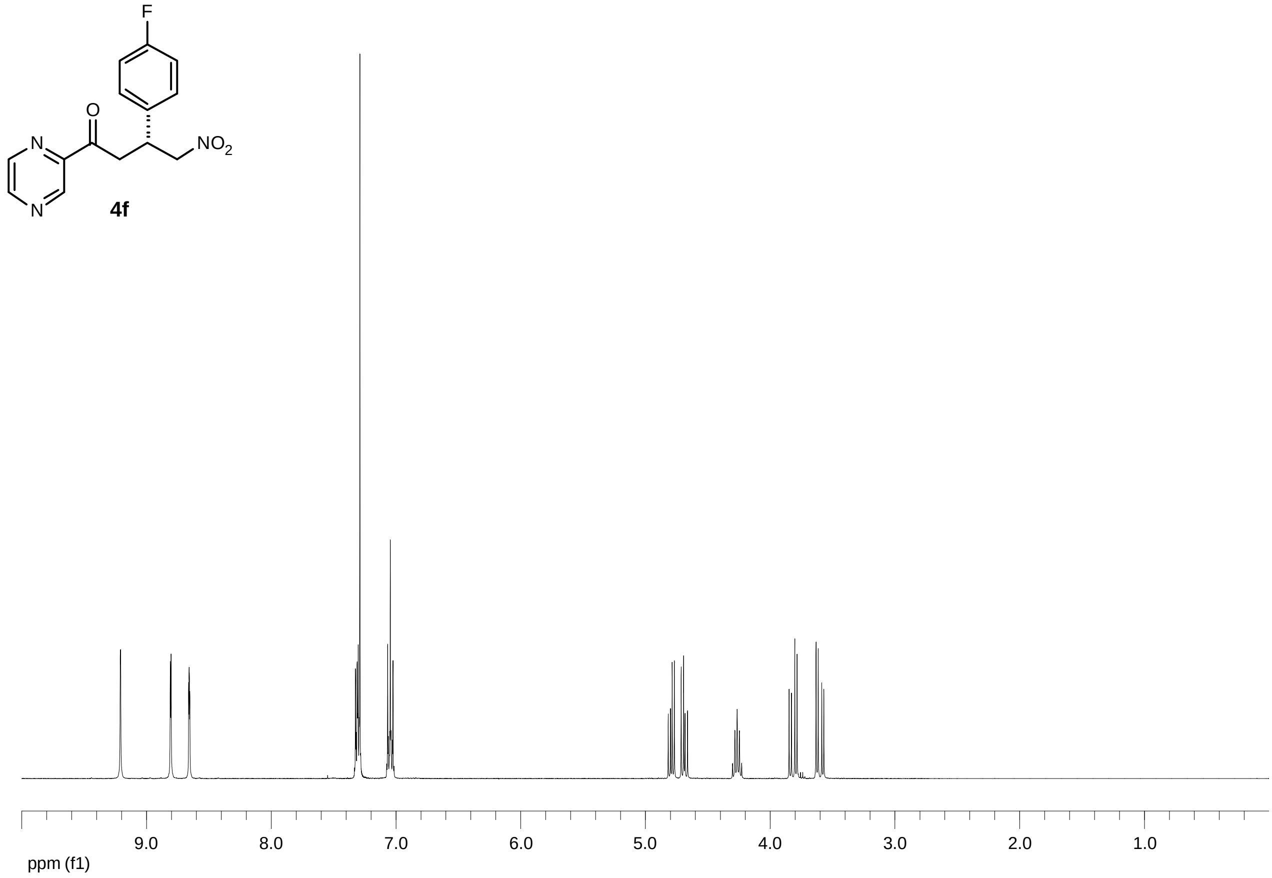

199.147
158.994
152.344
147.073
137.097
131.186
130.519
130.185
129.740
128.822
128.643
127.688
118.035
114.328
80.217
77.254
77.000
76.746
55.211
40.710
38.928
150
100
50
ppm (t1)


O
Me
N
NO2
N

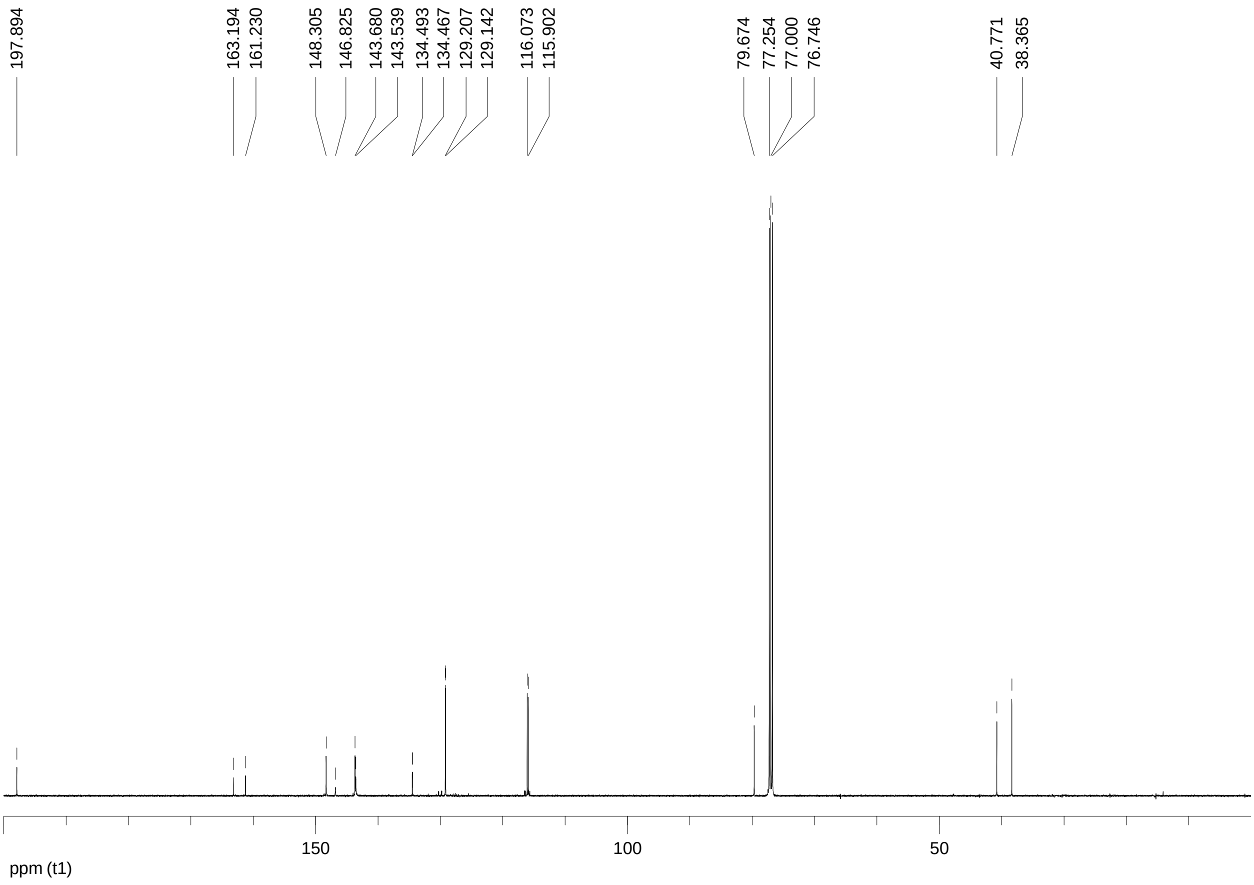
4e

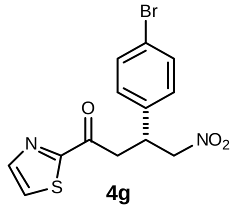

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


198.191
148.166
146.904
143.639
143.489
137.006
136.495
131.131
127.558
126.586
125.500
79.181
77.254
77.000
76.746
40.842
34.192
19.545
150
100
50
ppm (t1)

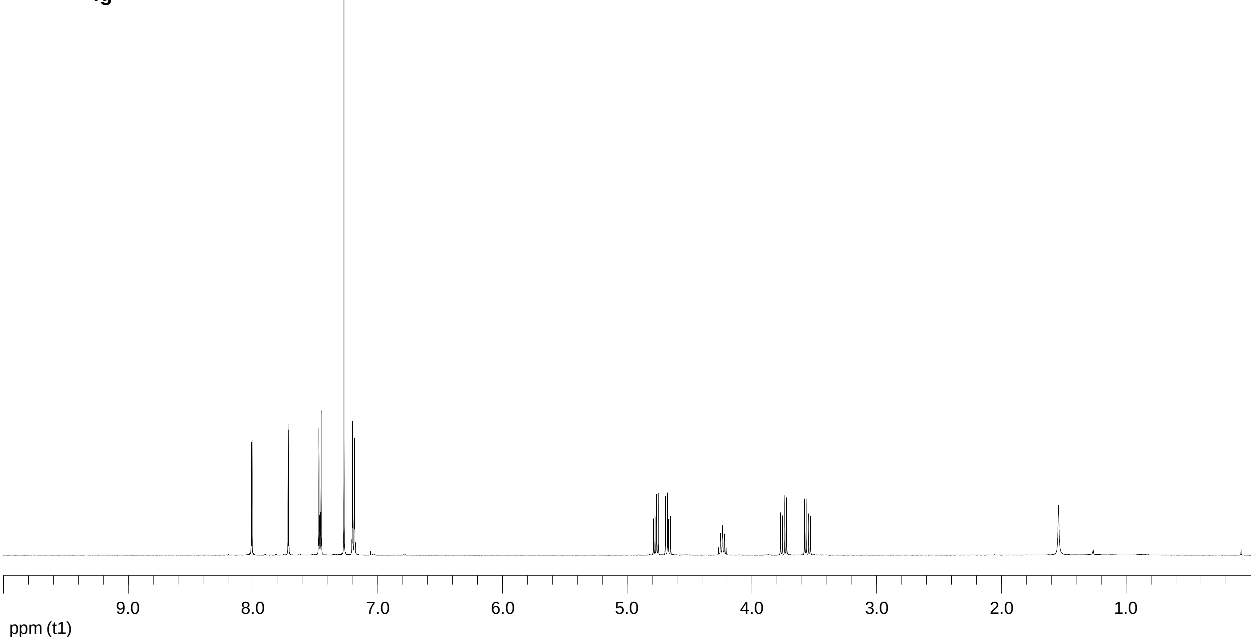


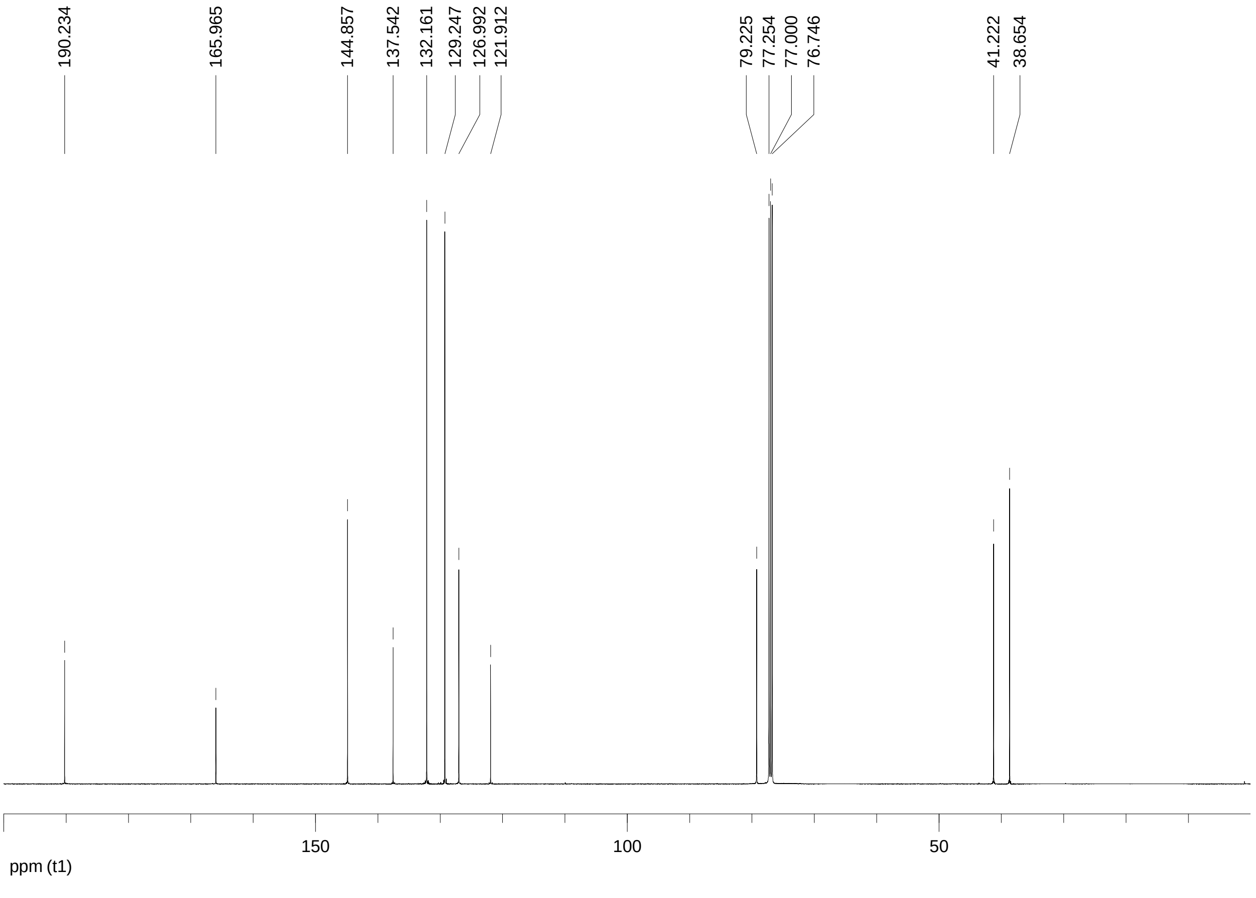
4f
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

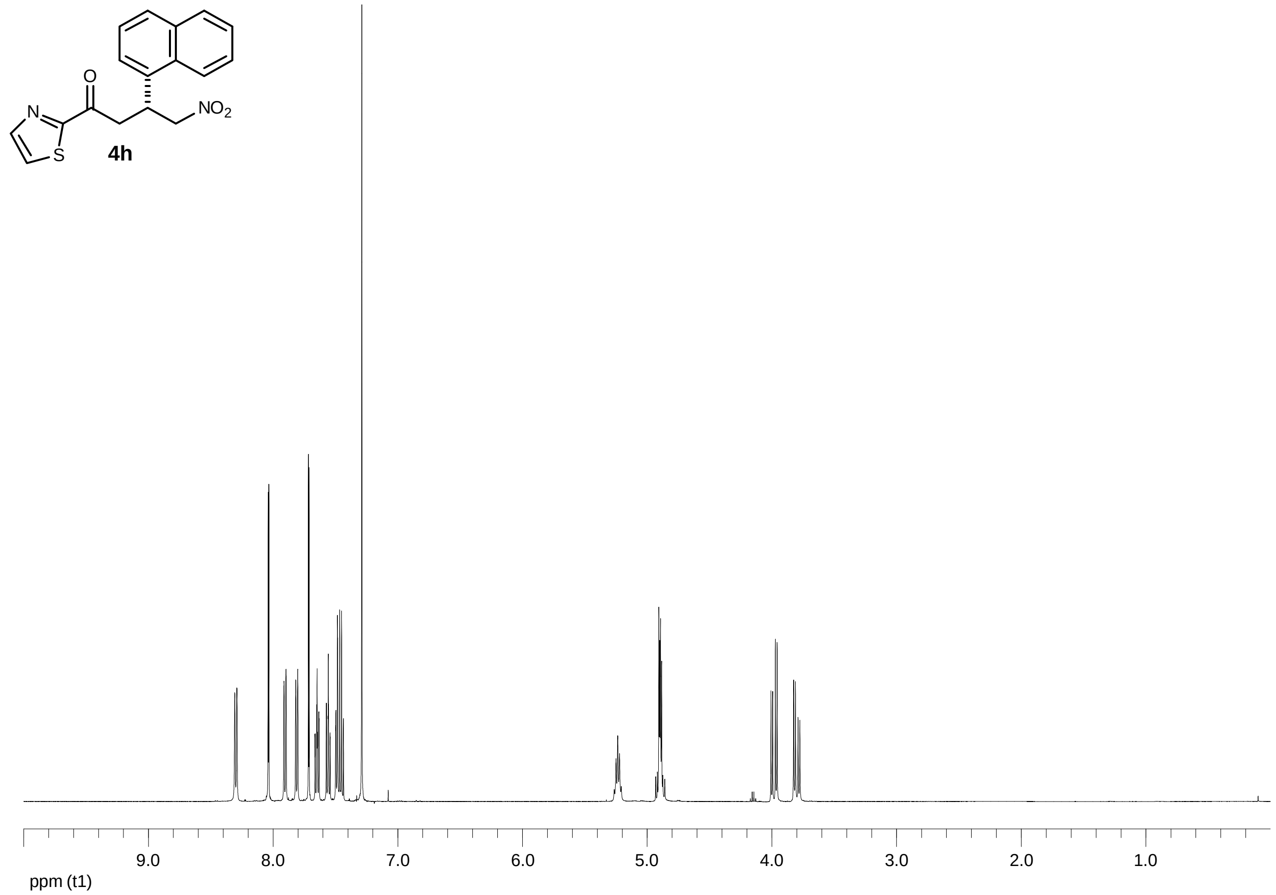

197.894
163.194
161.230
148.305
146.825
143.680
143.539
134.493
134.467
129.207
129.142
116.073
115.902
79.674
77.254
77.000
76.746
40.771
38.365
150
100
50
ppm (t1)

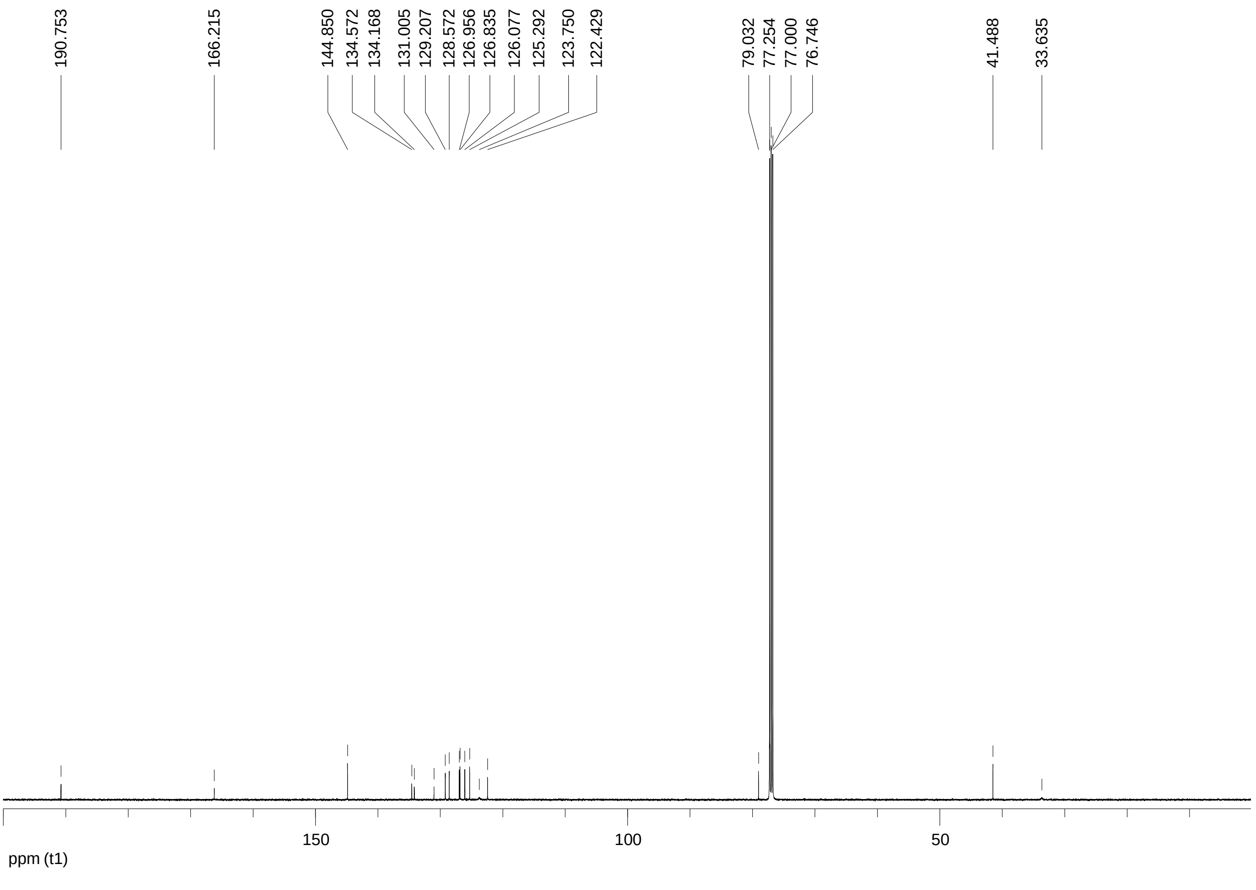

Br
O
N
S
NO2

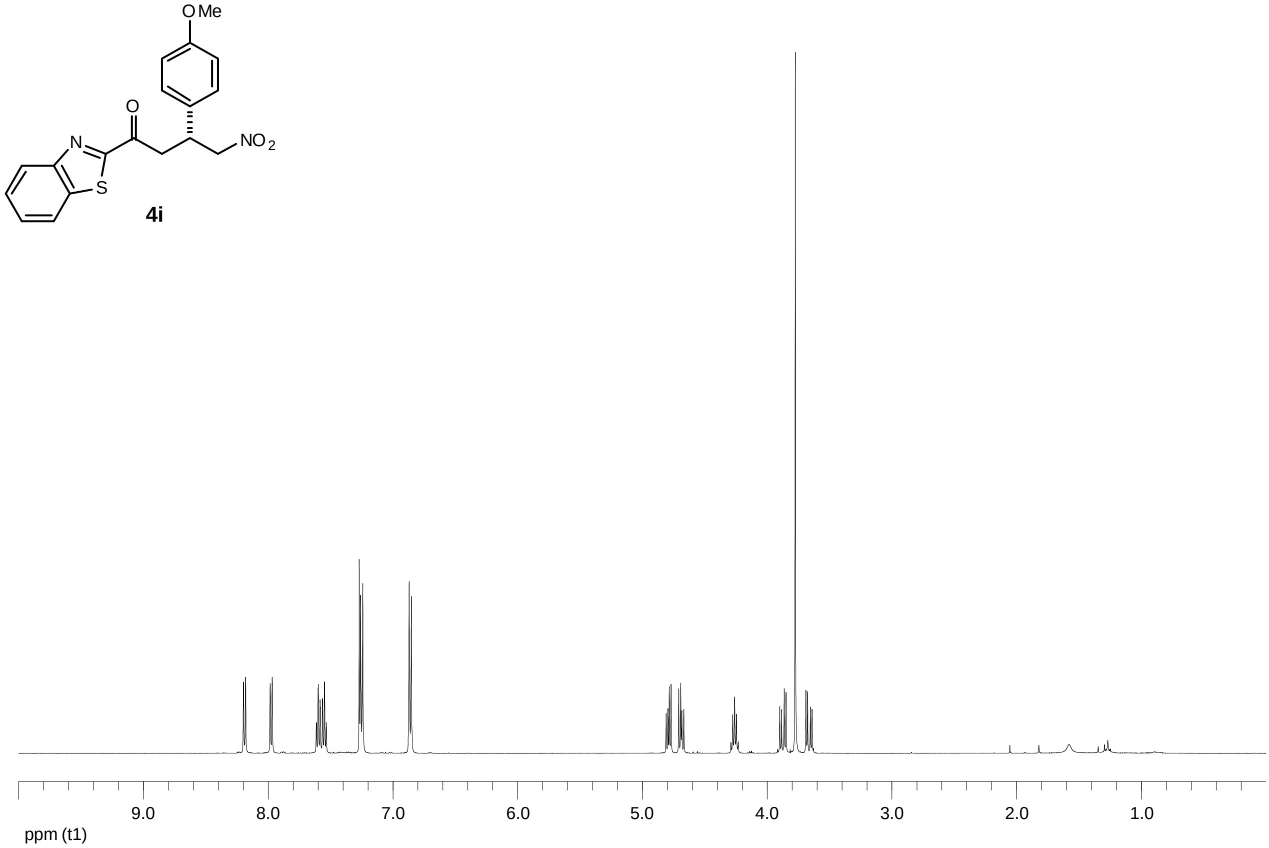
4g


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


190.234
165.965
144.857
137.542
132.161
129.247
126.992
121.912
79.225
77.254
77.000
76.746
41.222
38.654
150
100
50
ppm (t1)

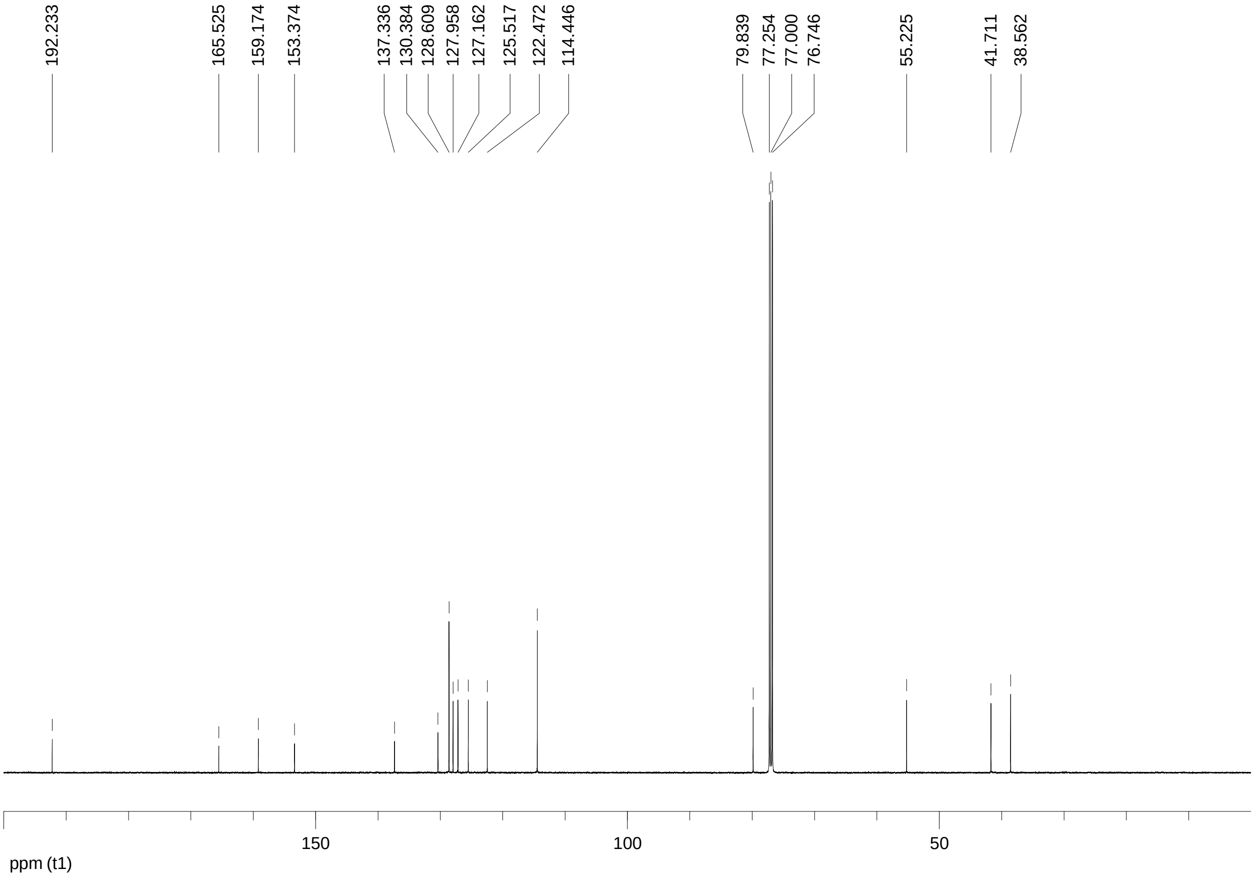

O
N
S
NO2
4h
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


190.753
166.215
144.850
134.572
134.168
131.005
129.207
128.572
126.956
126.835
126.077
125.292
123.750
122.429
79.032
77.254
77.000
76.746
41.488
33.635
150
100
50
ppm (t1)

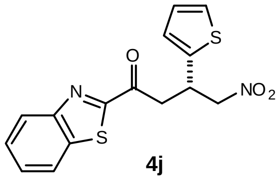


4i

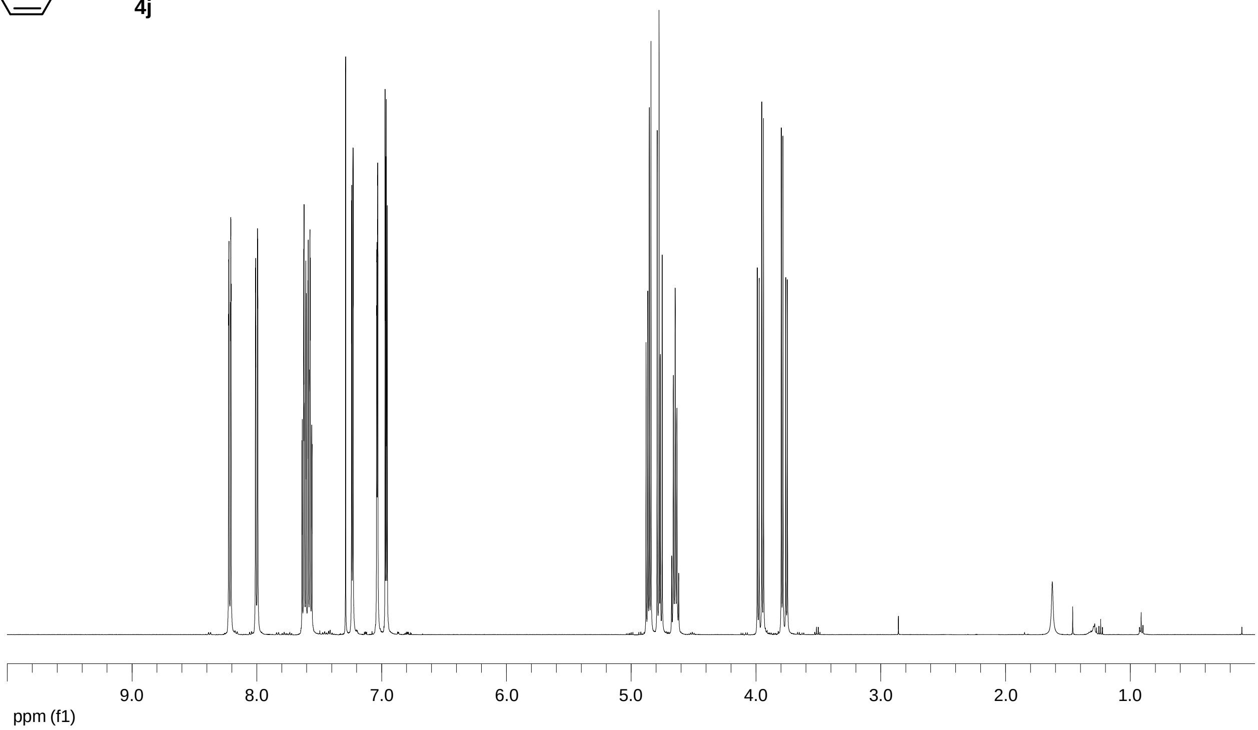
OMe
O
N
S
NO2
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

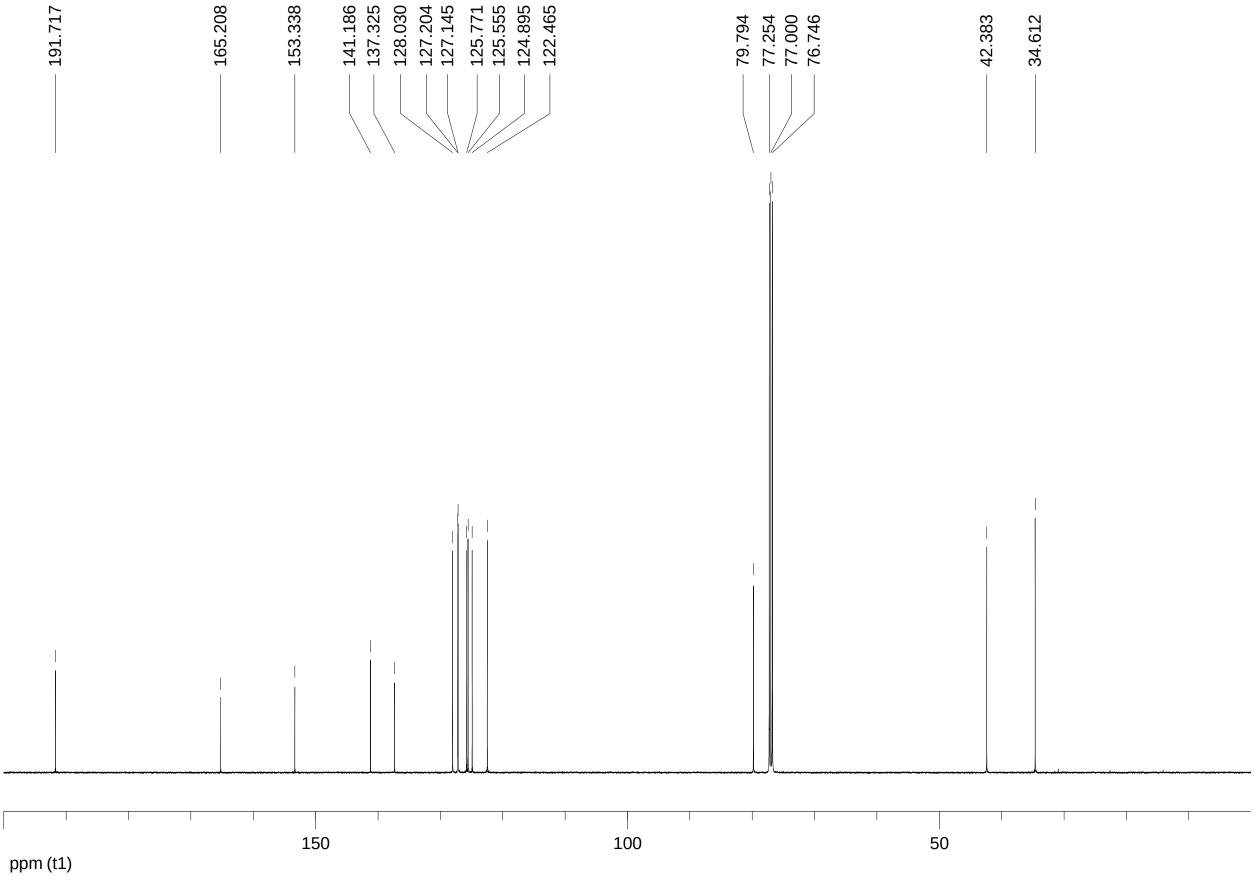


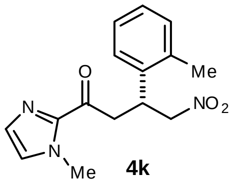
192.233
165.525
159.174
153.374
137.336
130.384
128.609
127.958
127.162
125.517
122.472
114.446
79.839
77.254
77.000
76.746
55.225
41.711
38.562
150
100
50
ppm (t1)


O
N
S
S
NO2

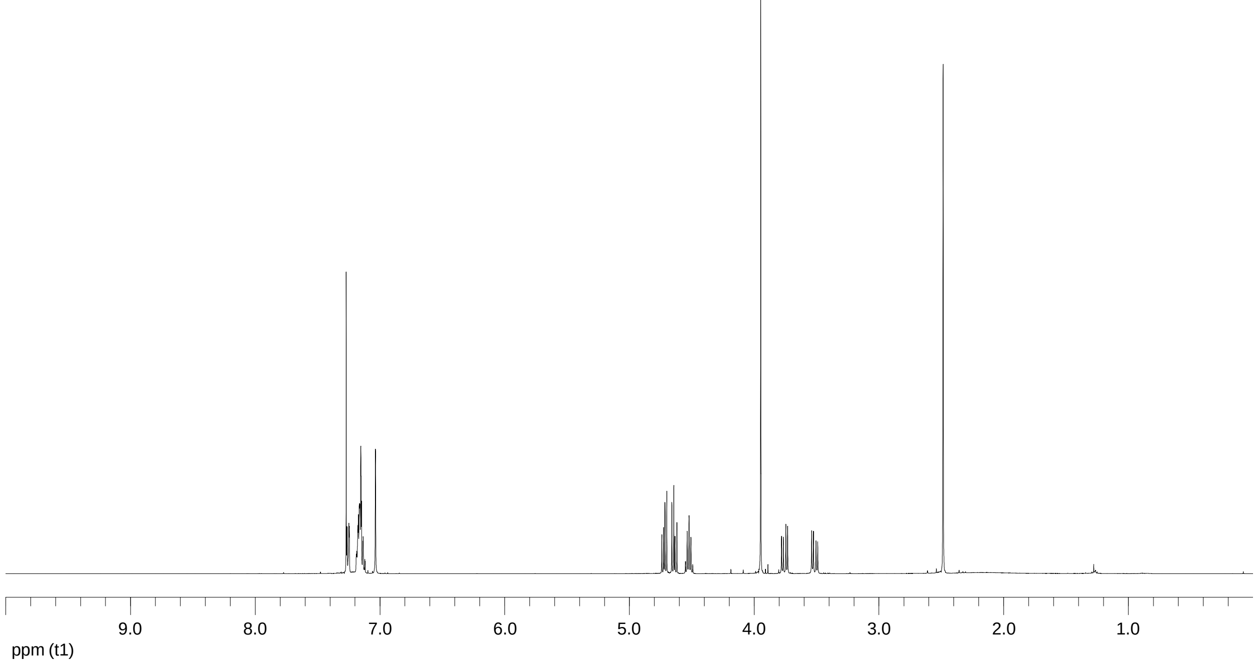
4j

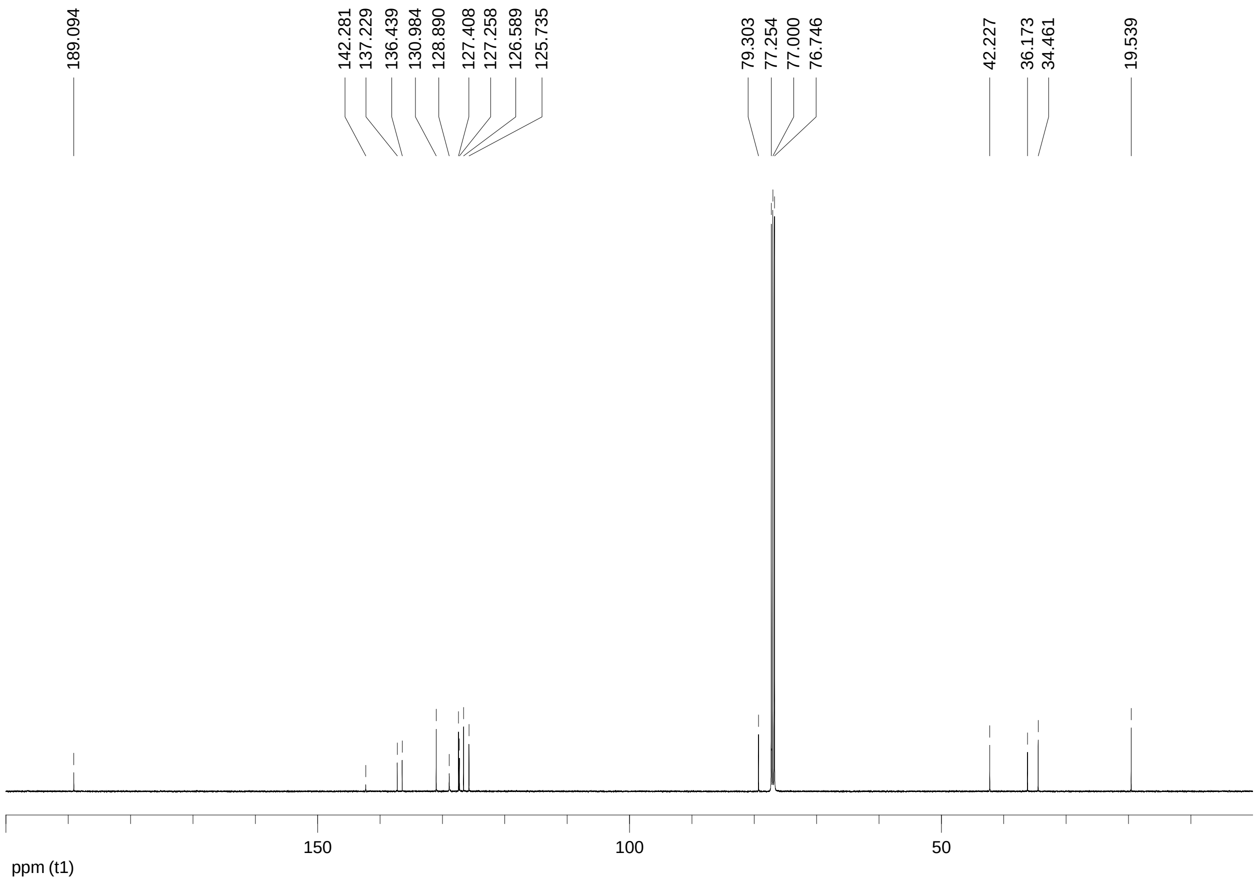

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

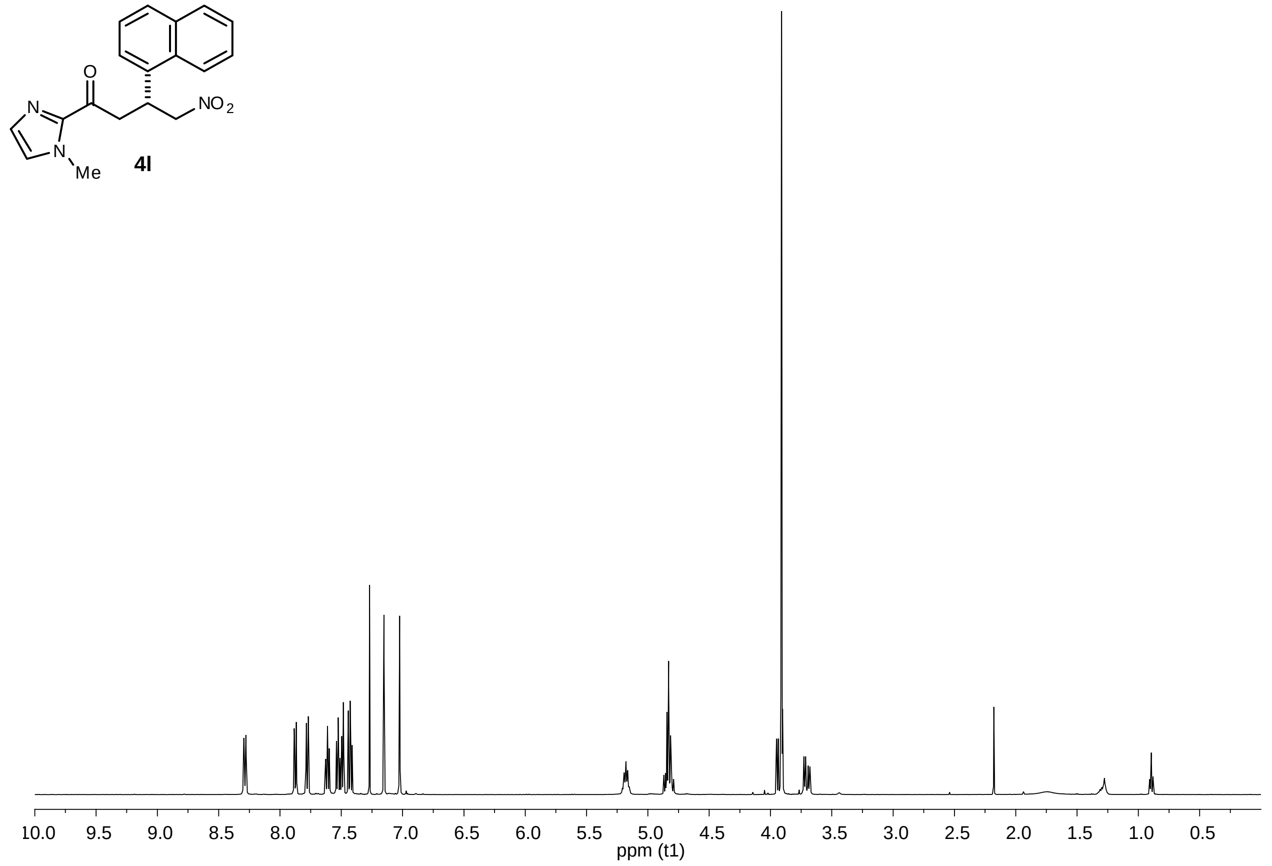

191.717
165.208
153.338
141.186
137.325
128.030
127.204
127.145
125.771
125.555
124.895
122.465
79.794
77.254
77.000
76.746
42.383
34.612
150
100
50
ppm (t1)

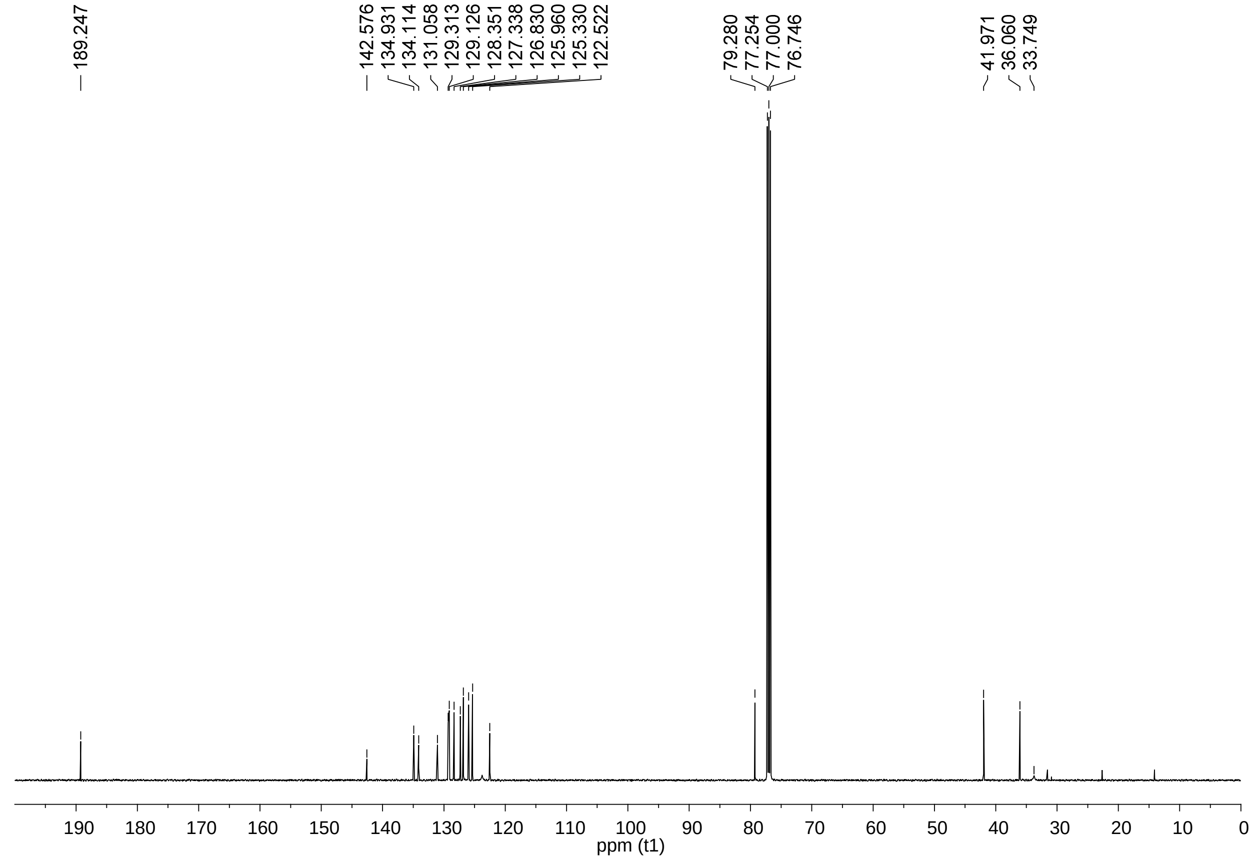

O
N
N
Me
Me
NO2

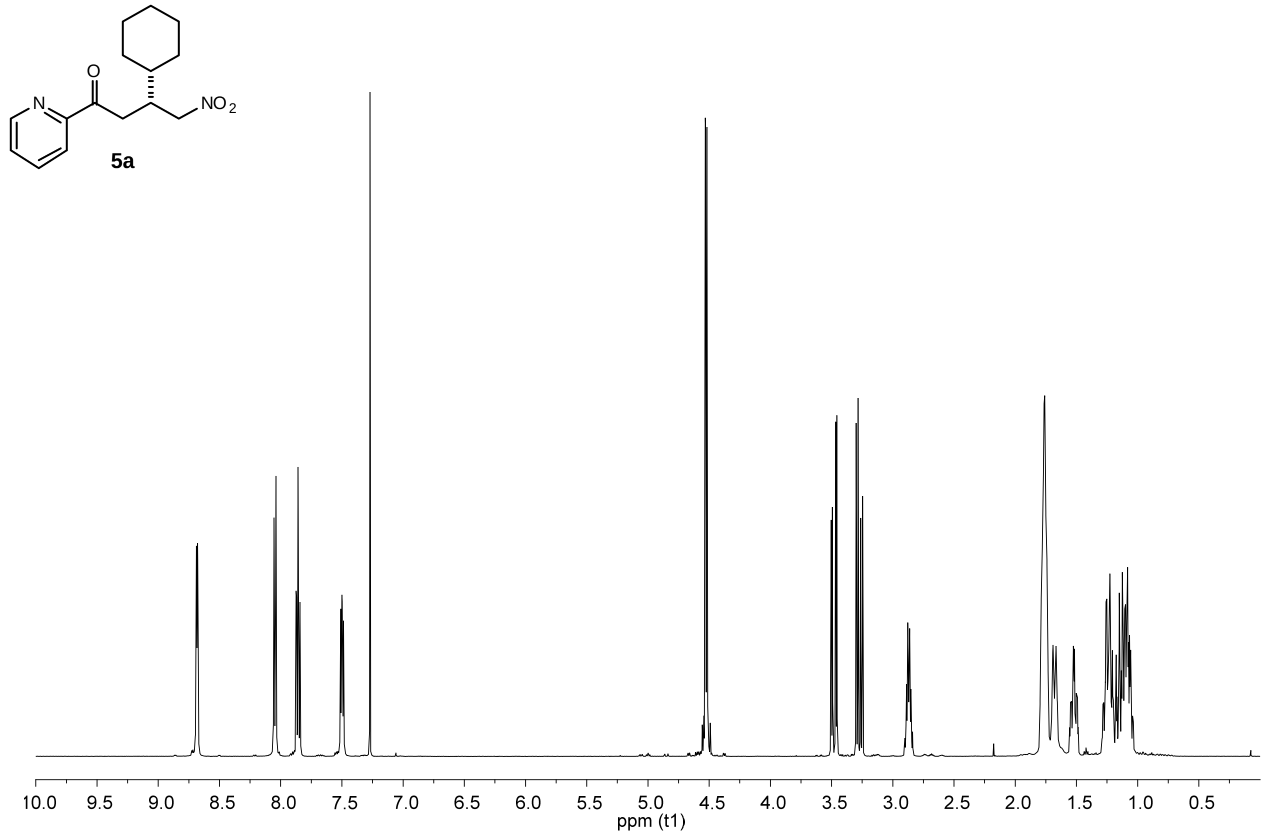
4k


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

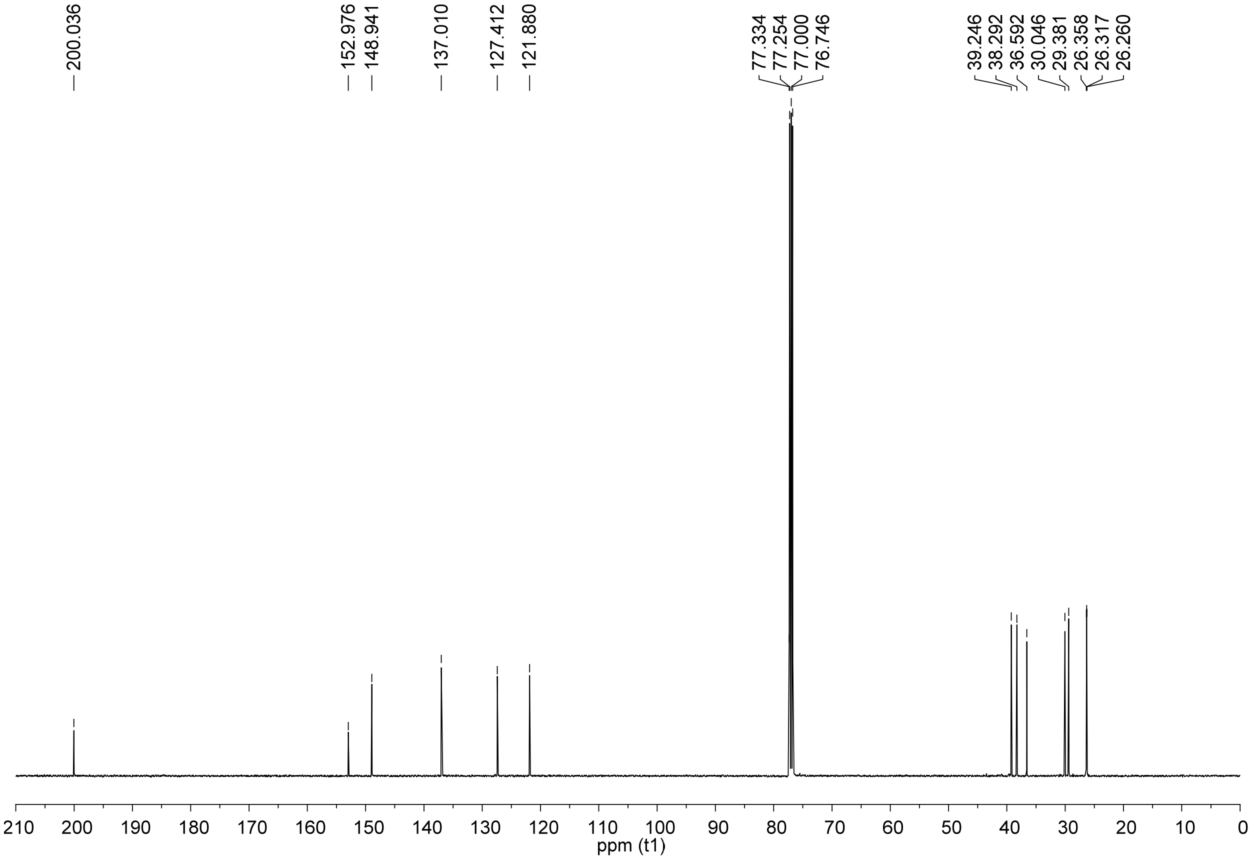

189.094
142.281
137.229
136.439
130.984
128.890
127.408
127.258
126.589
125.735
79.303
77.254
77.000
76.746
42.227
36.173
34.461
19.539
150
100
50
ppm (t1)

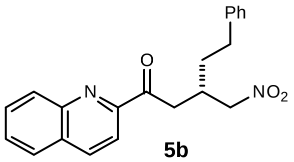

4l
O
N
N
Me
NO2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)


189.247
142.576
134.931
134.114
131.058
129.313
129.126
128.351
127.338
126.830
125.960
125.330
122.522
79.280
77.254
77.000
76.746
41.971
36.060
33.749
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

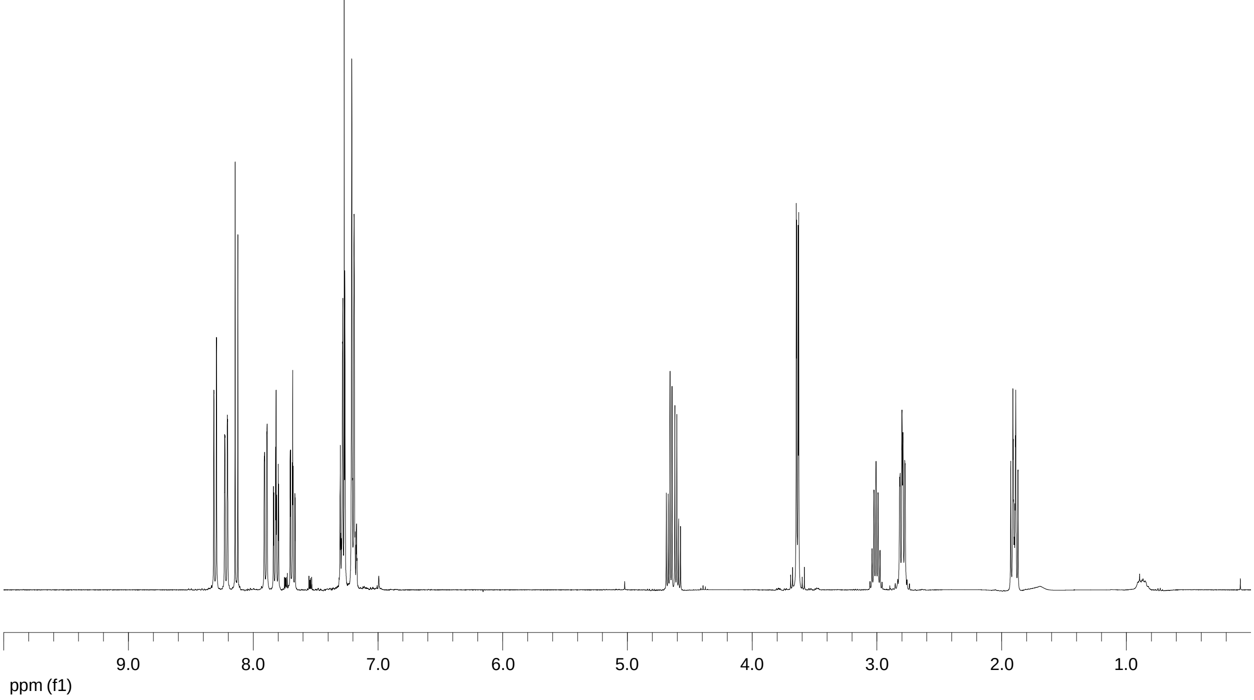

O
N
NO2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)

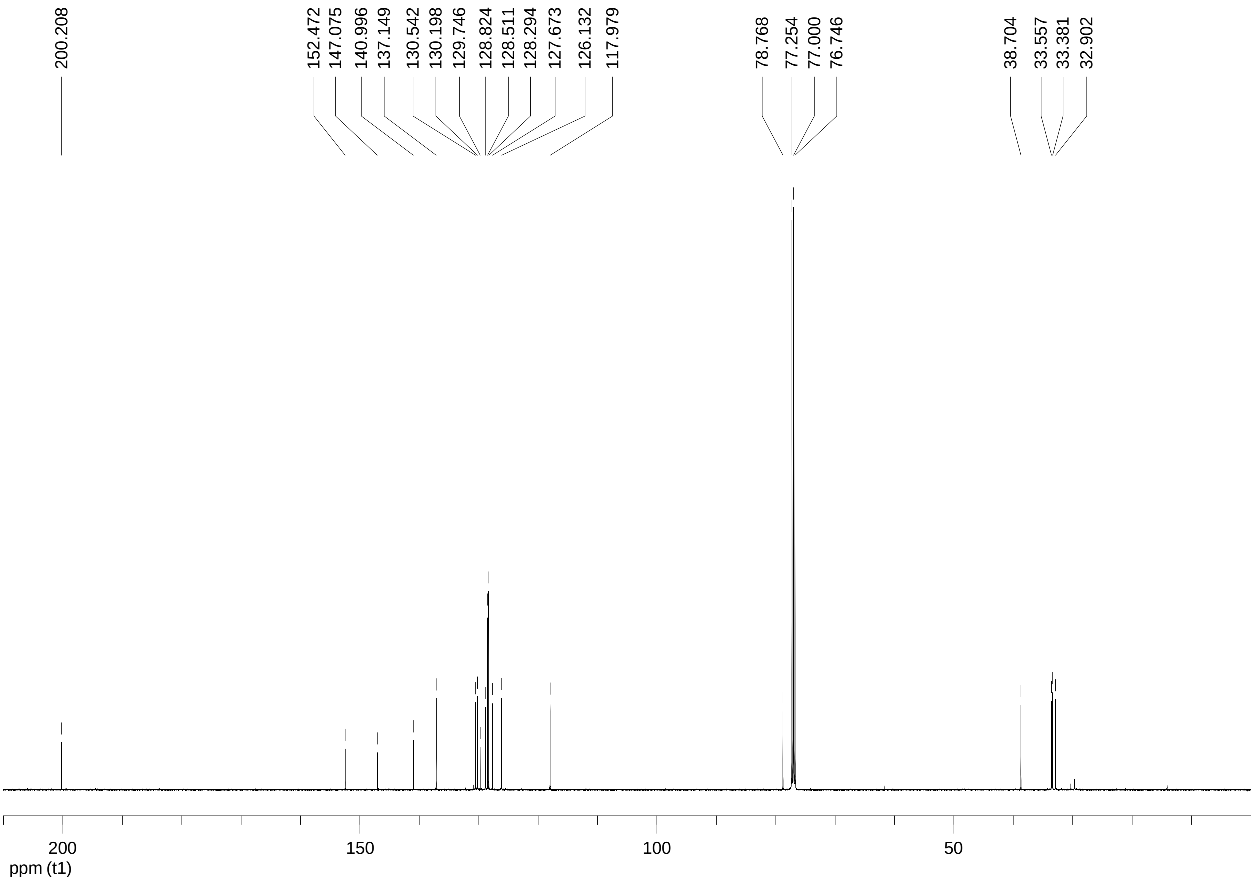
5a

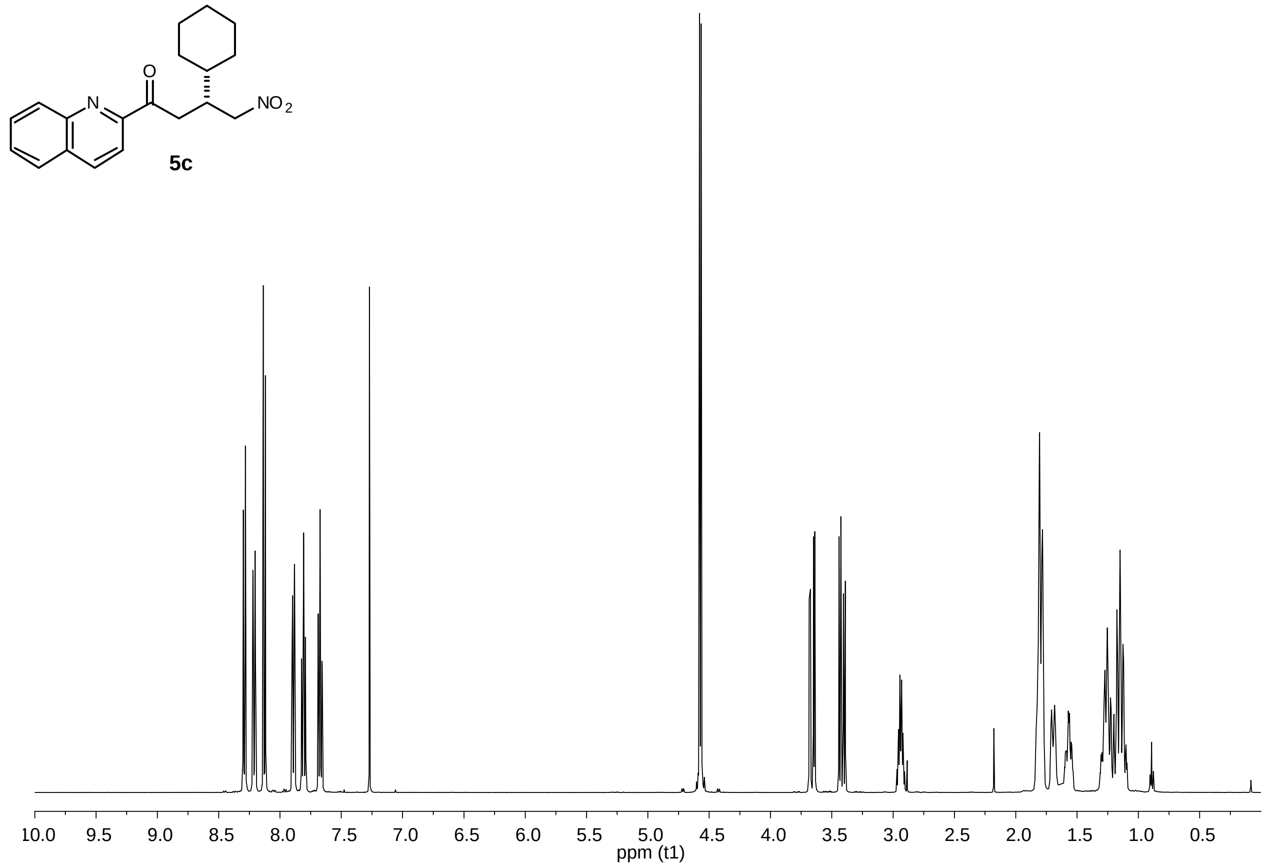

200.036
152.976
148.941
137.010
127.412
121.880
77.334
77.254
77.000
76.746
39.246
38.292
36.592
30.046
29.381
26.358
26.317
26.260
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


Ph
O
N
NO2

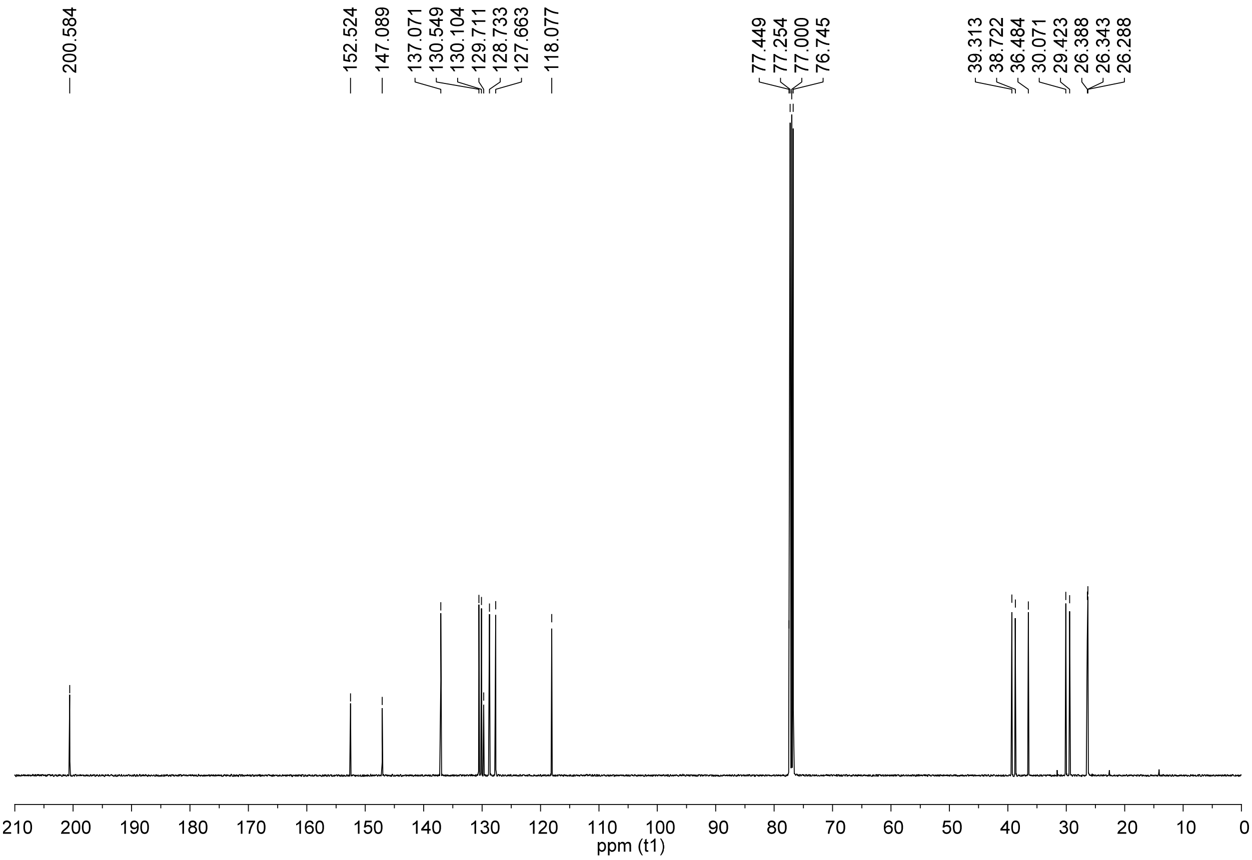
5b

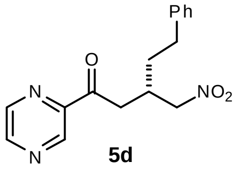

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


200.208
152.472
147.075
140.996
137.149
130.542
130.198
129.746
128.824
128.511
128.294
127.673
126.132
117.979
78.768
77.254
77.000
76.746
38.704
33.557
33.381
32.902
200
150
100
50
ppm (t1)

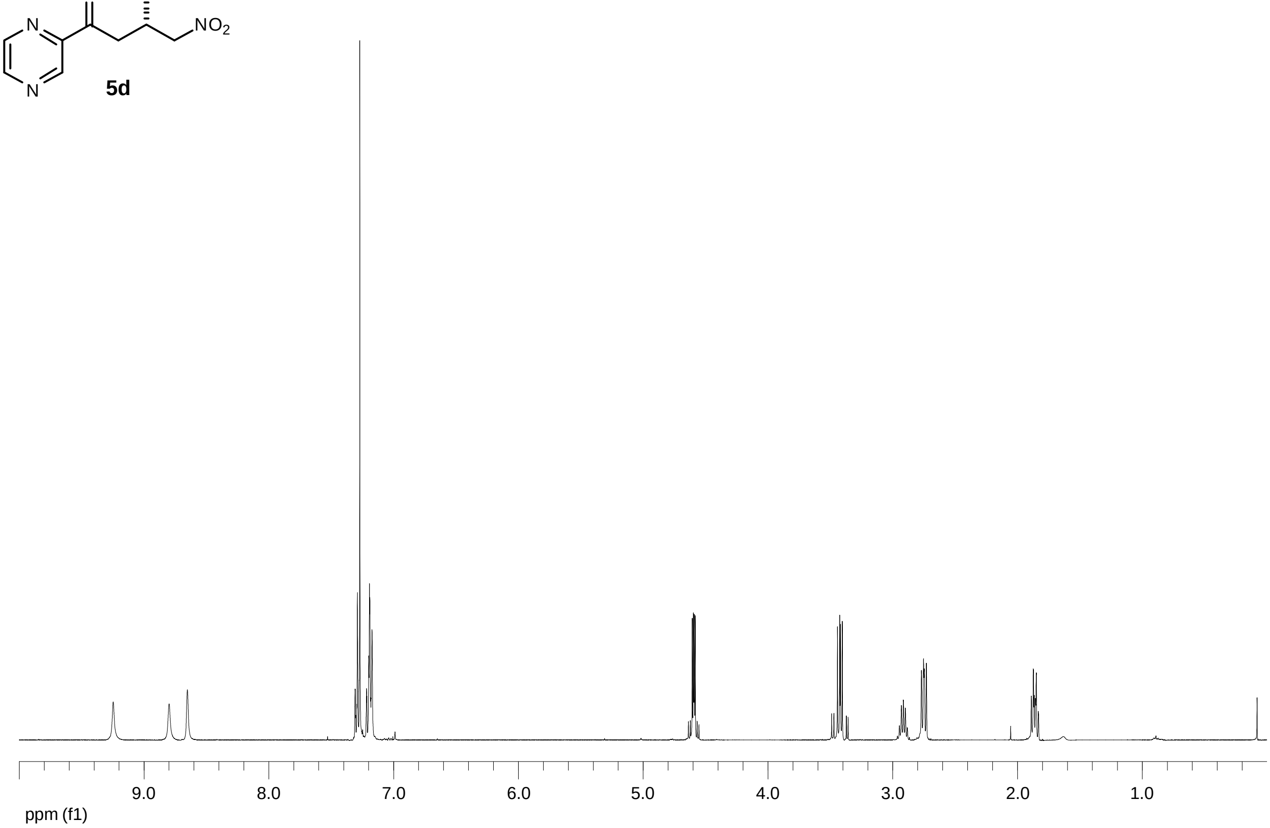

5c

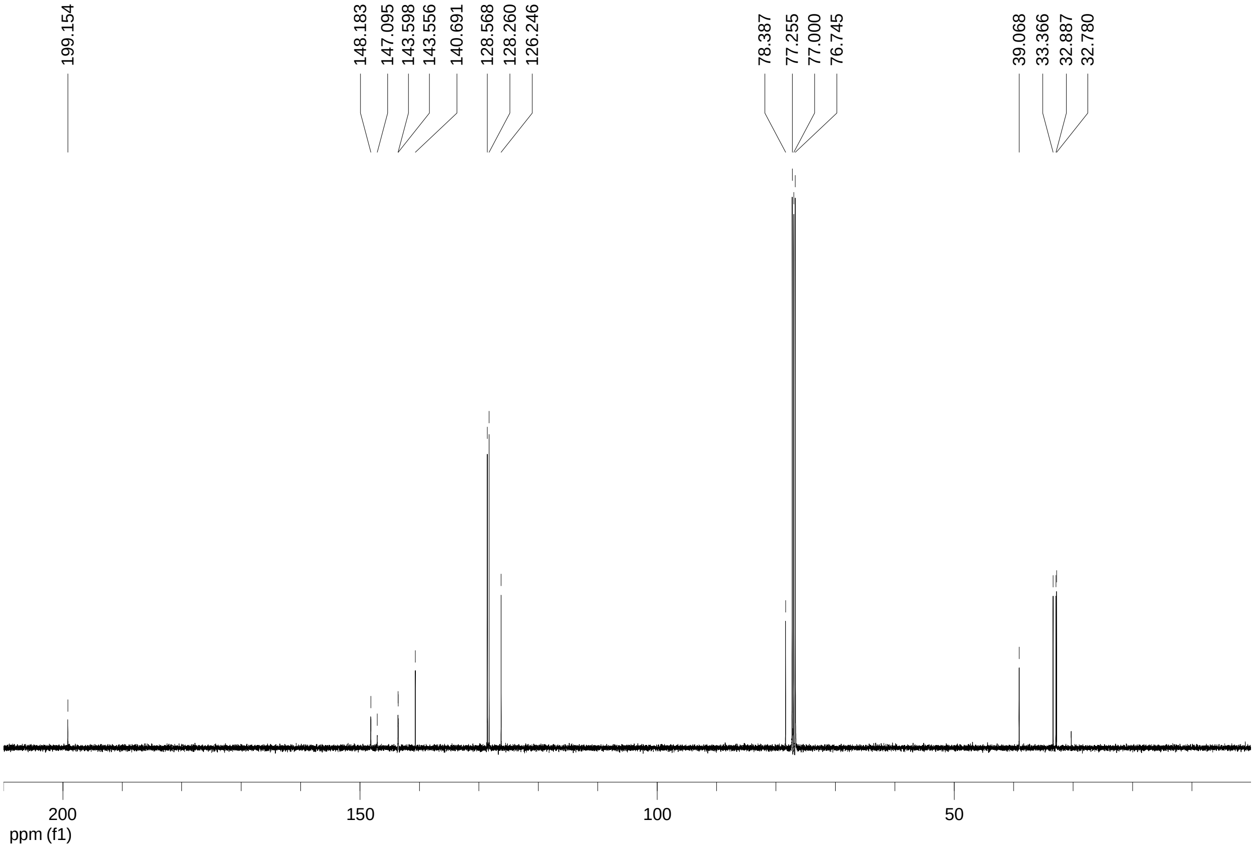
O
N
NO2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)

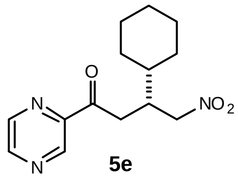

200.584
152.524
147.089
137.071
130.549
130.104
129.711
128.733
127.663
118.077
77.449
77.254
77.000
76.745
39.313
38.722
36.484
30.071
29.423
26.388
26.343
26.288
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


Ph
O
N
N
NO2

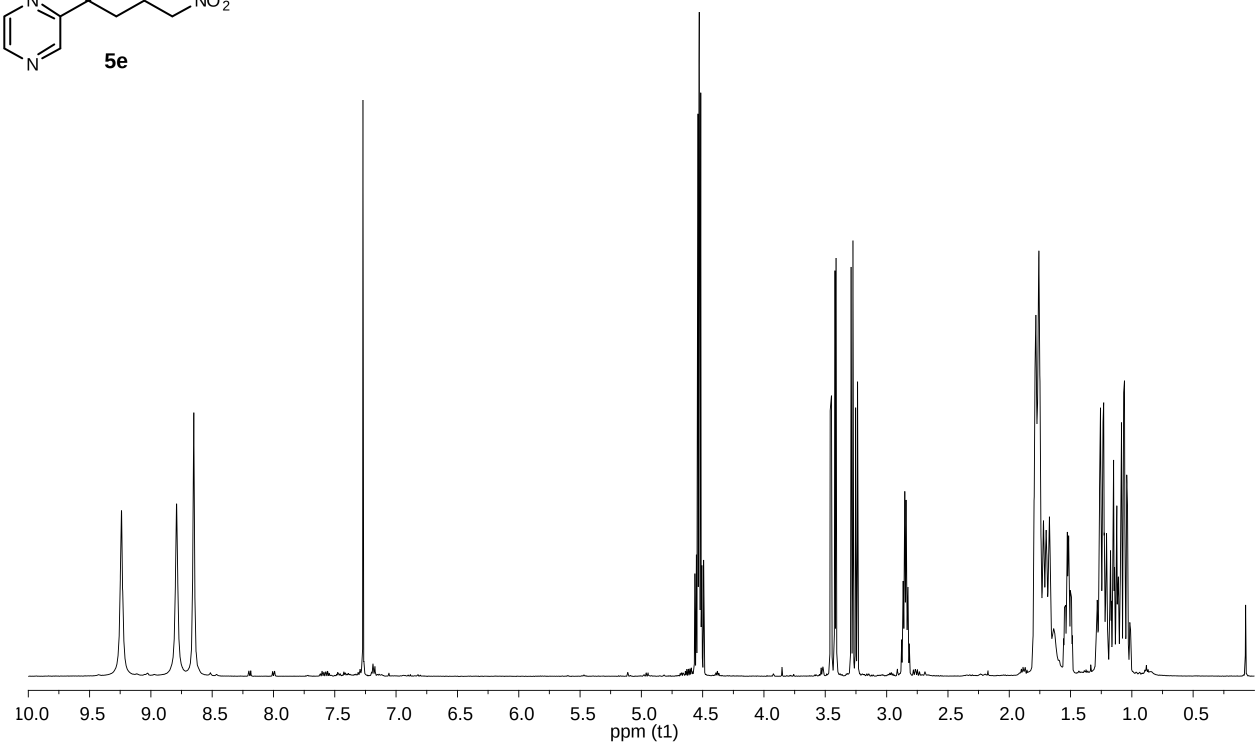
5d

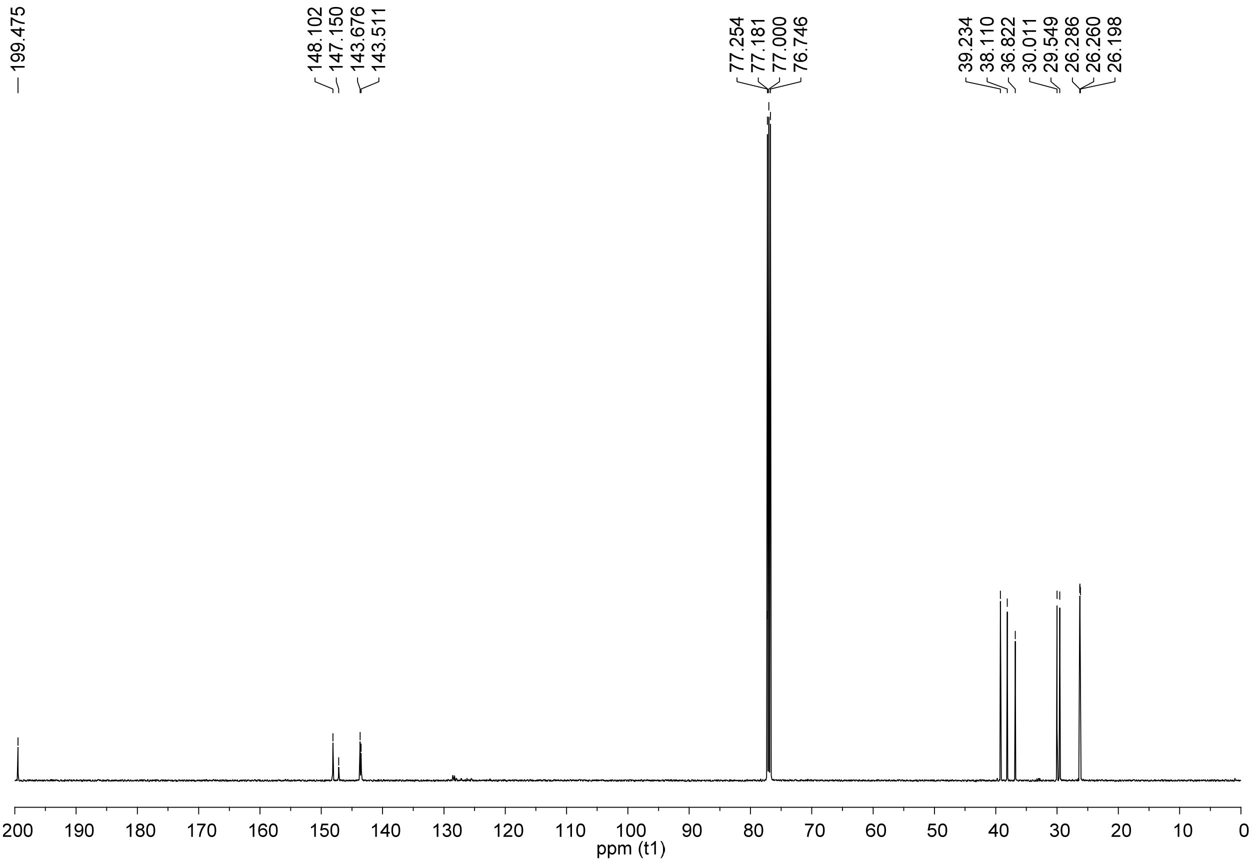

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

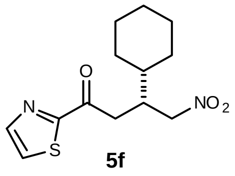

199.154
148.183
147.095
143.598
143.556
140.691
128.568
128.260
126.246
78.387
77.255
77.000
76.745
39.068
33.366
32.887
32.780
200
150
100
50
ppm (f1)


O
N
N
NO2

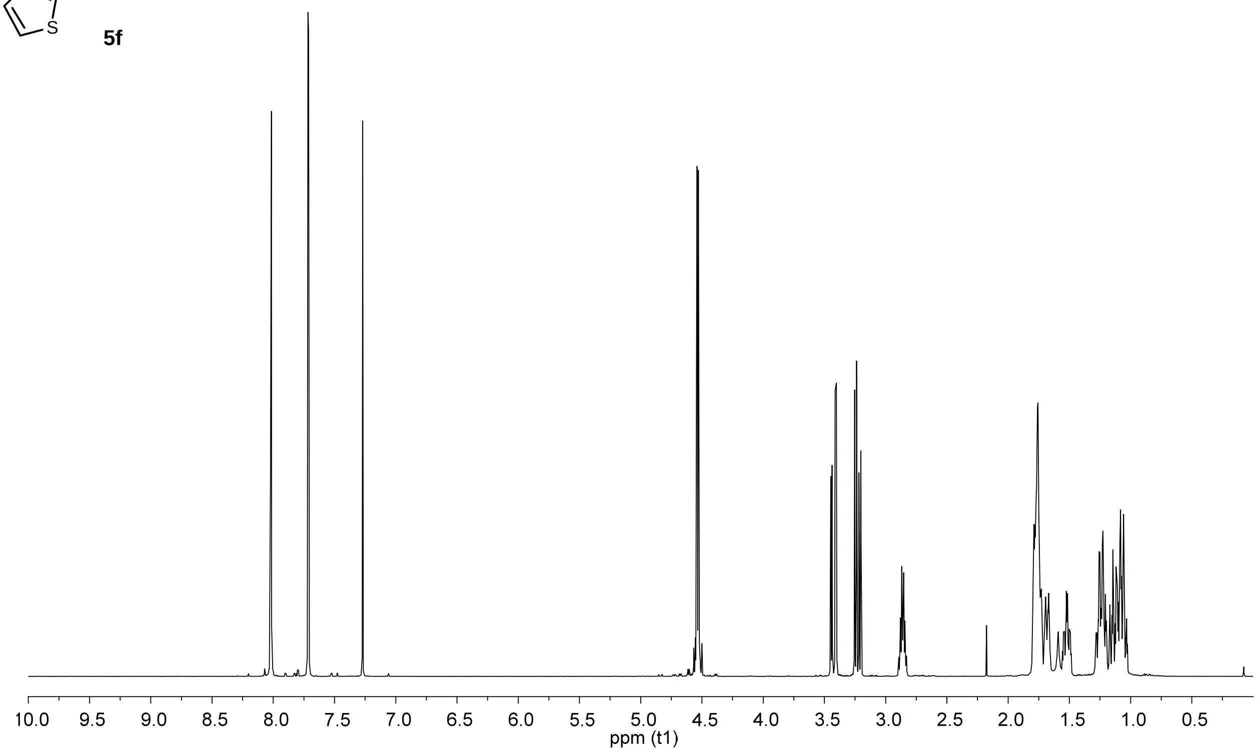
5e

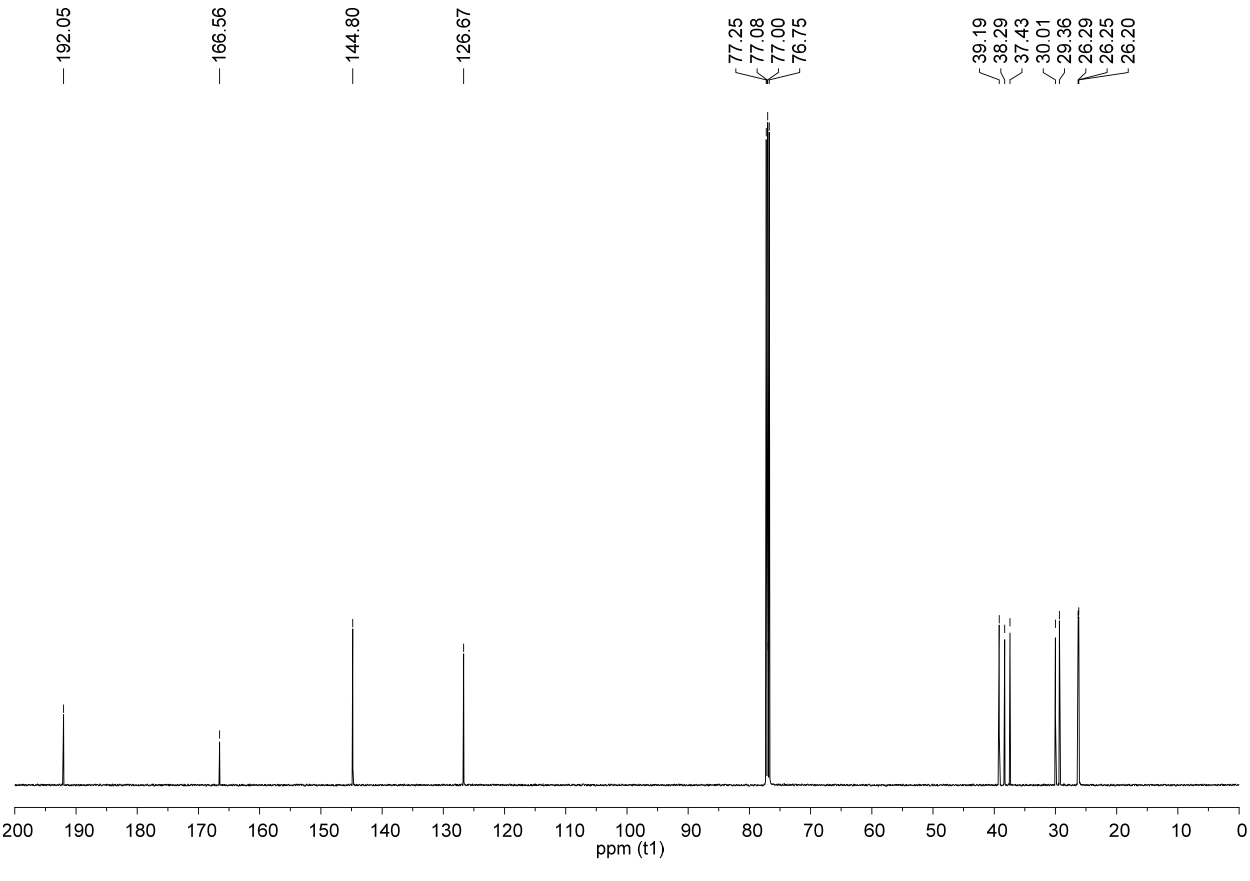

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)

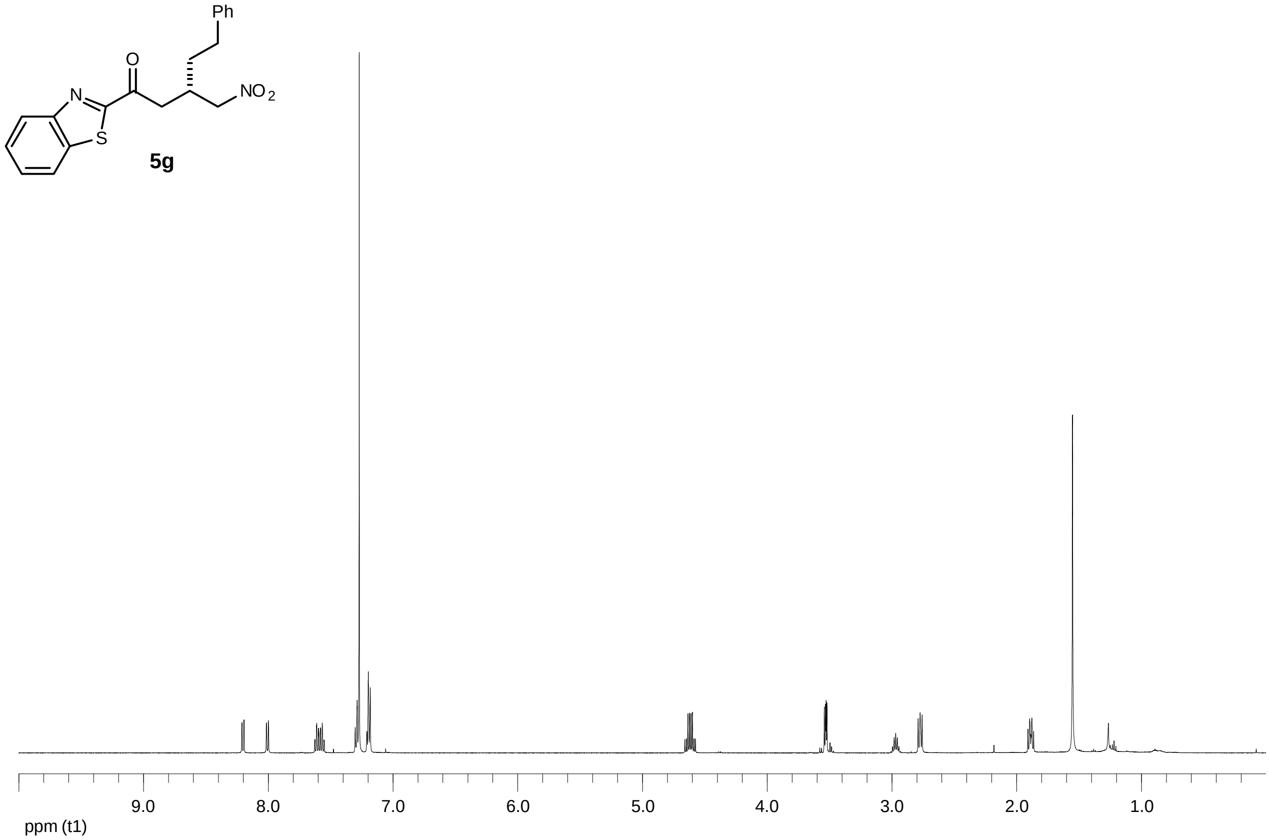

199.475
148.102
147.150
143.676
143.511
77.254
77.181
77.000
76.746
39.234
38.110
36.822
30.011
29.549
26.286
26.260
26.198
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


O
N
S
NO2

5f

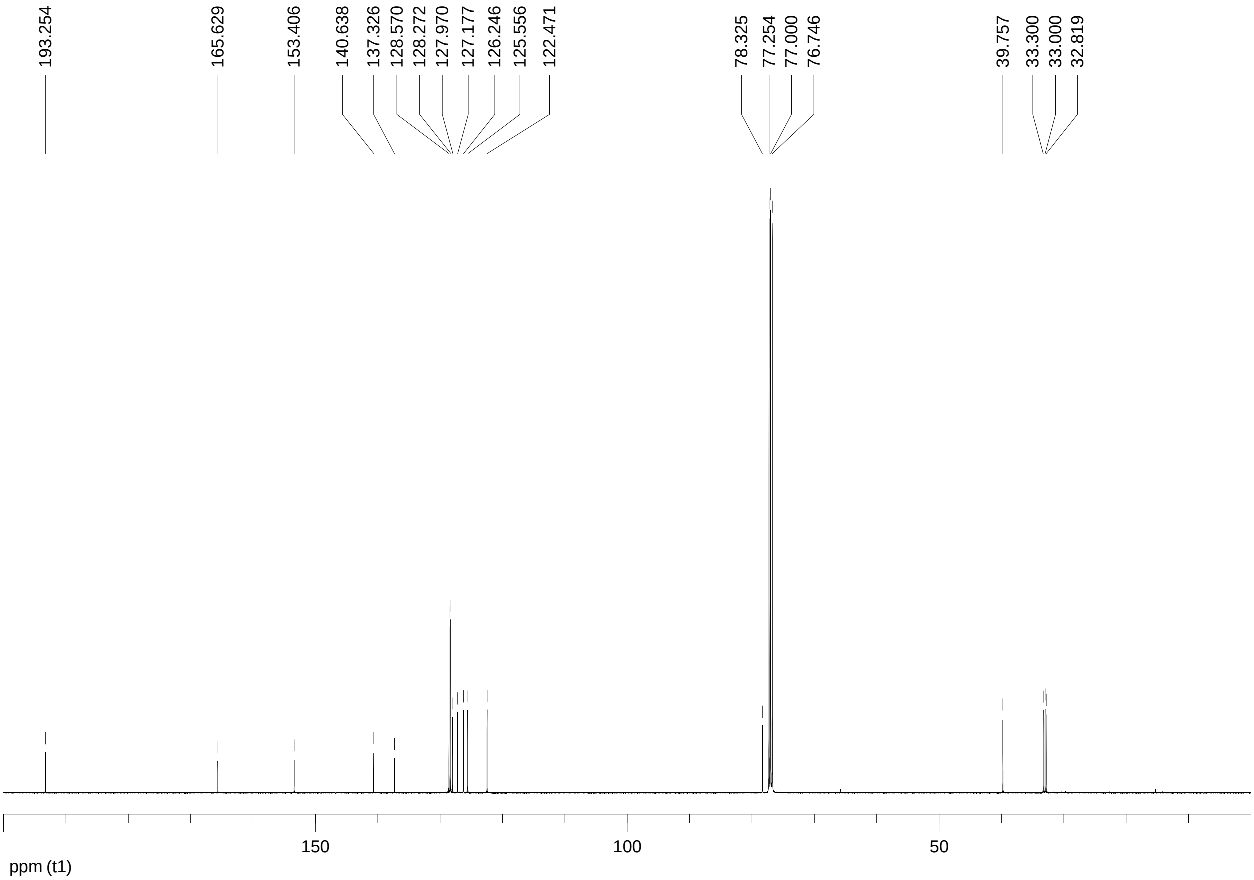

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)

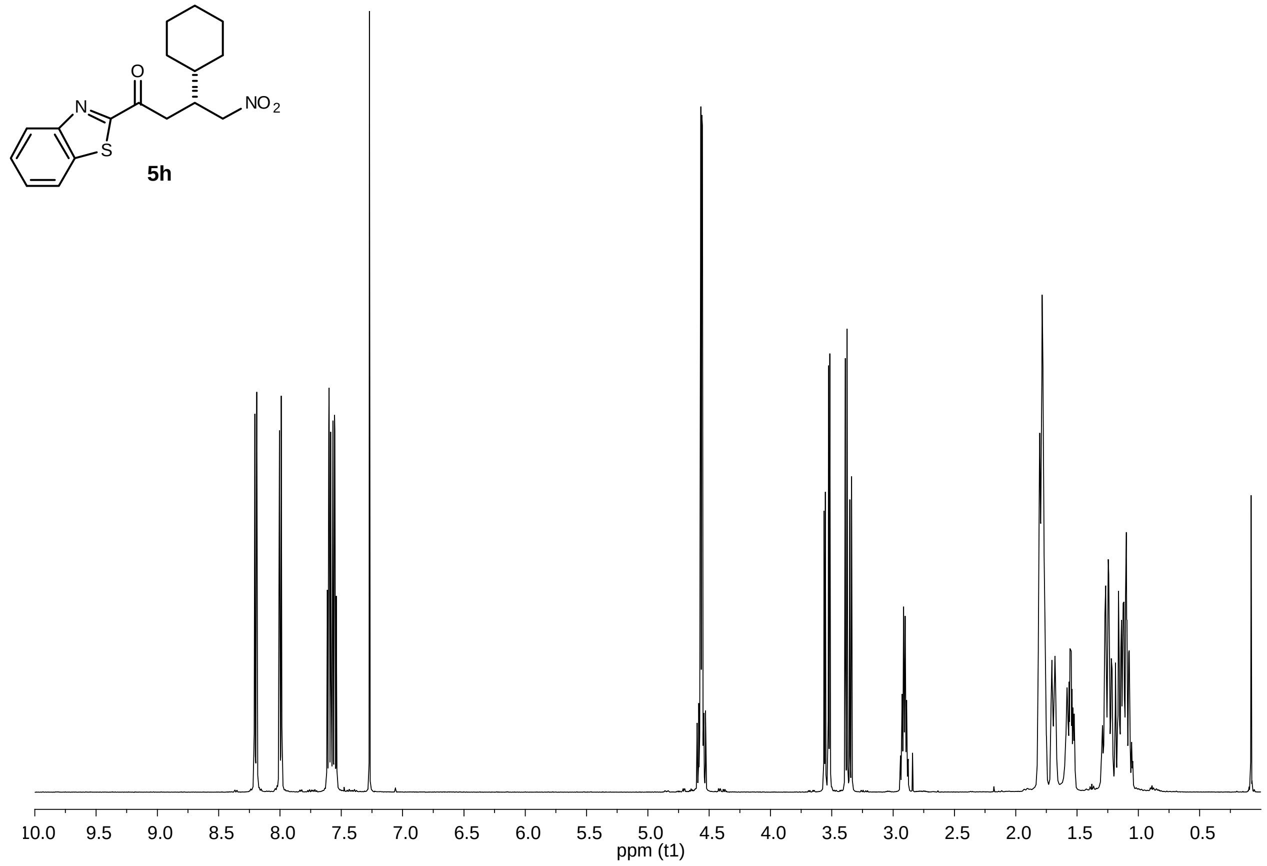

192.05
166.56
144.80
126.67
77.25
77.08
77.00
76.75
39.19
38.29
37.43
30.01
29.36
26.29
26.25
26.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


Ph
O
N
S
NO2

5g

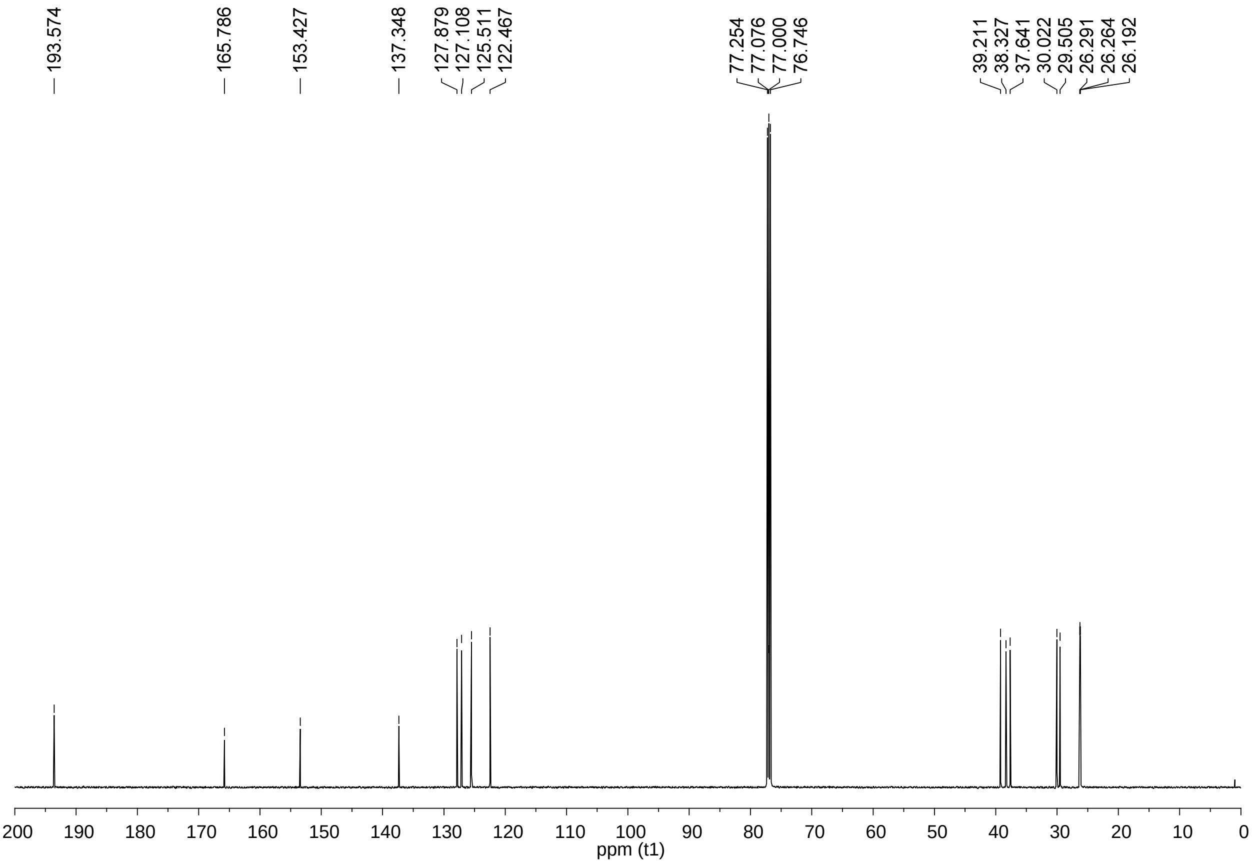
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


193.254
165.629
153.406
140.638
137.326
128.570
128.272
127.970
127.177
126.246
125.556
122.471
78.325
77.254
77.000
76.746
39.757
33.300
33.000
32.819
150
100
50
ppm (t1)

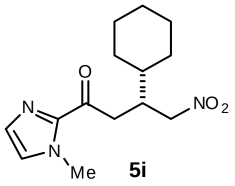


5h

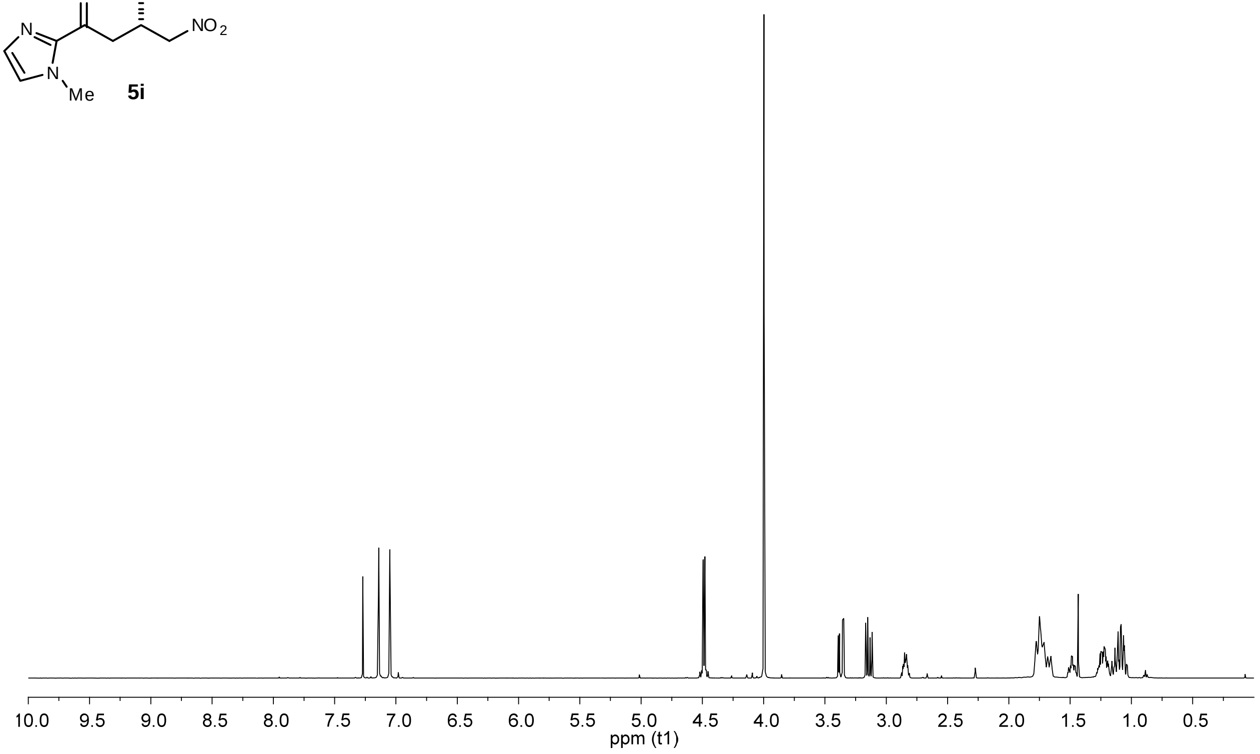
O
N
S
NO2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)

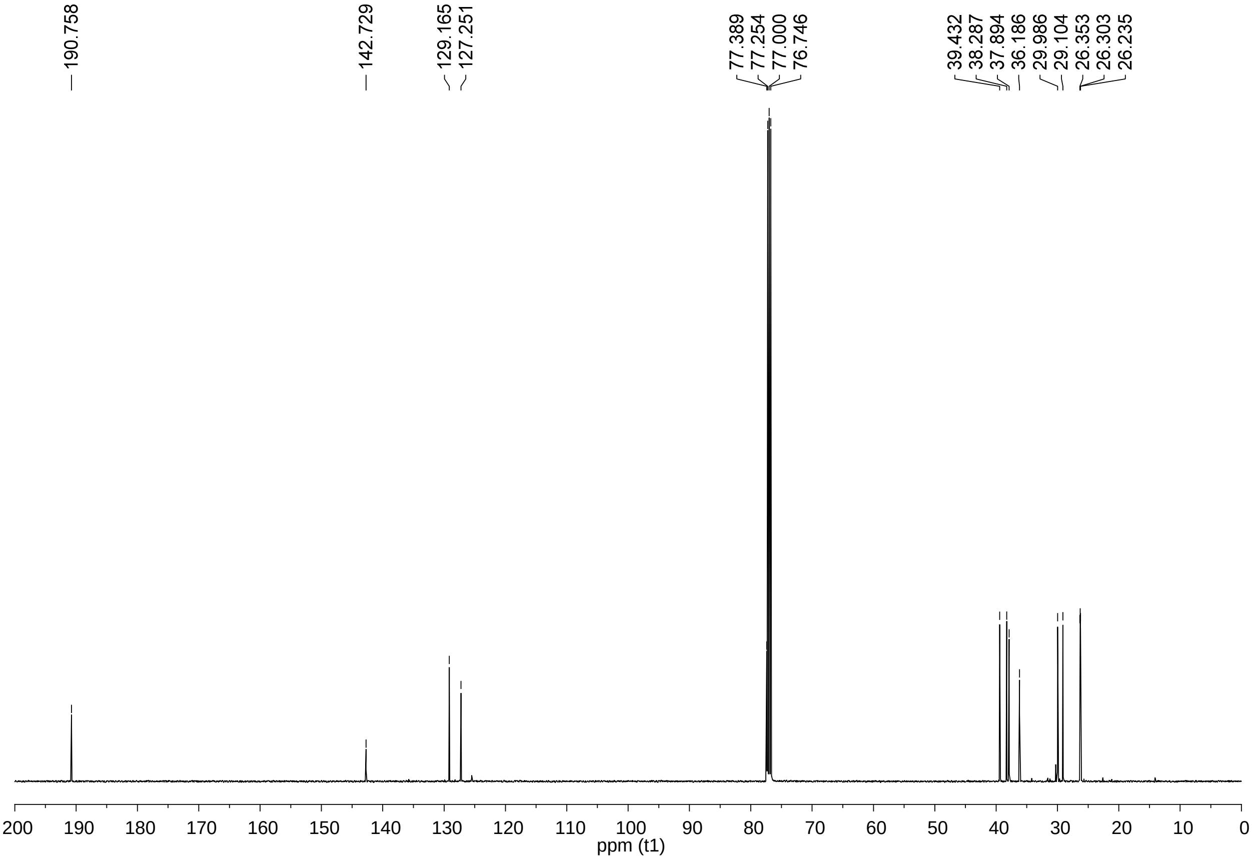


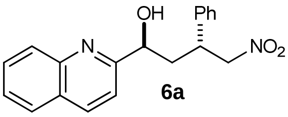
193.574
165.786
153.427
137.348
127.879
127.108
125.511
122.467
77.254
77.076
77.000
76.746
39.211
38.327
37.641
30.022
29.505
26.291
26.264
26.192
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


O
N
N
Me
NO2

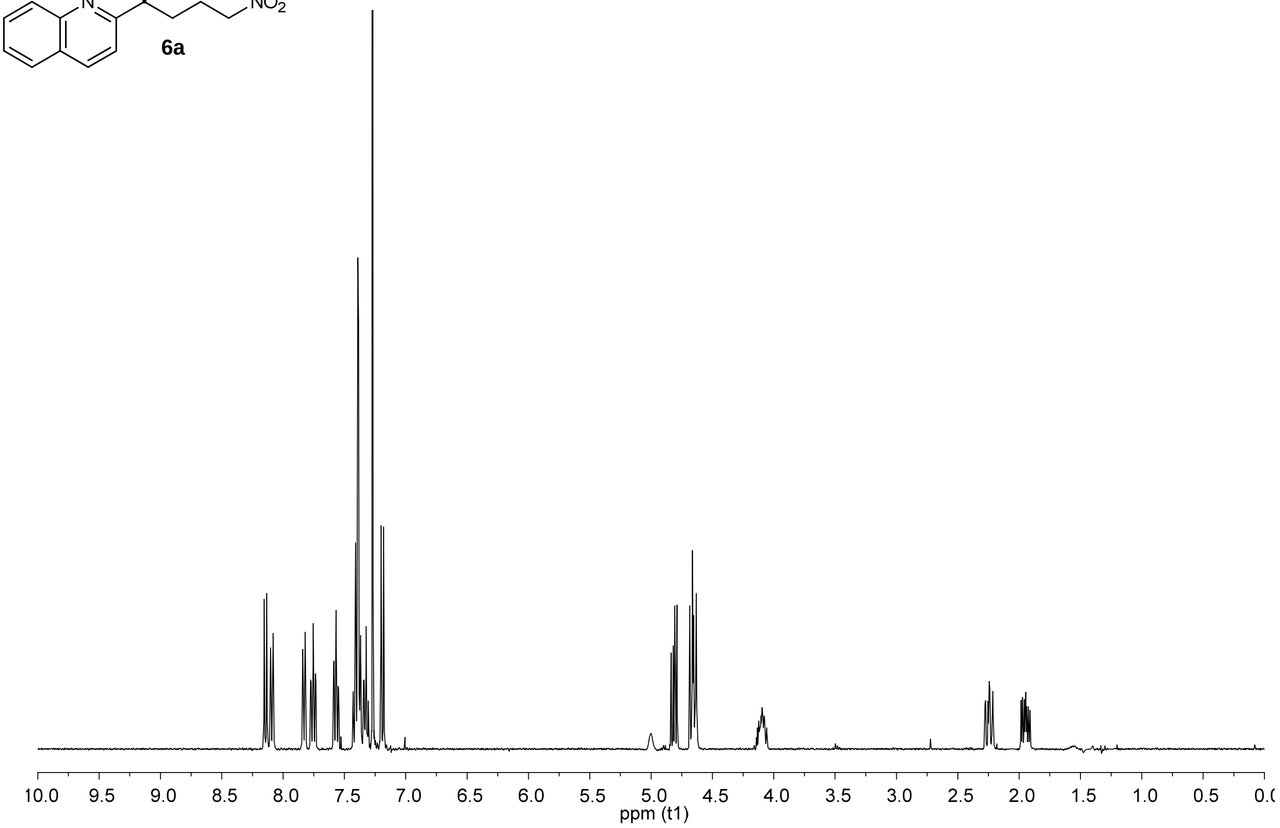
5i

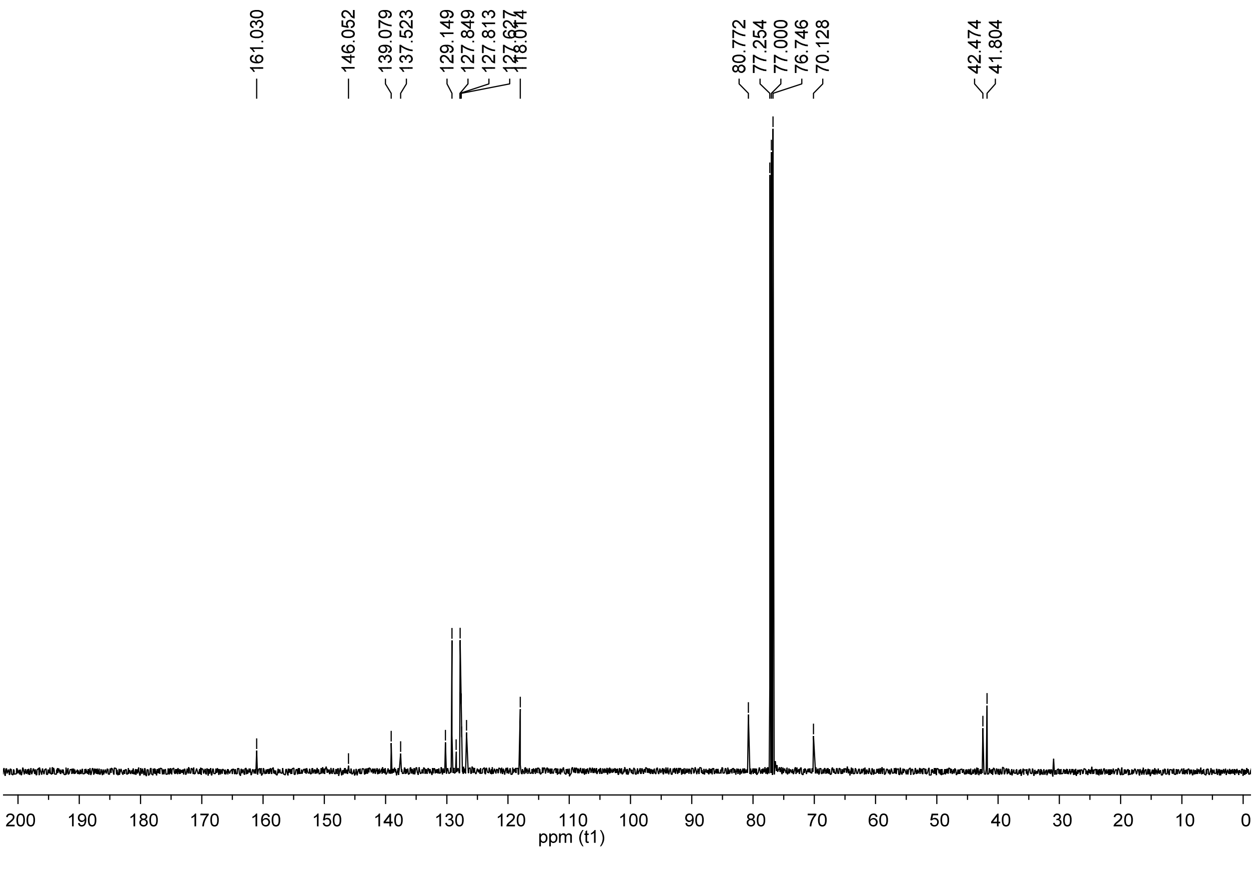

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm (t1)

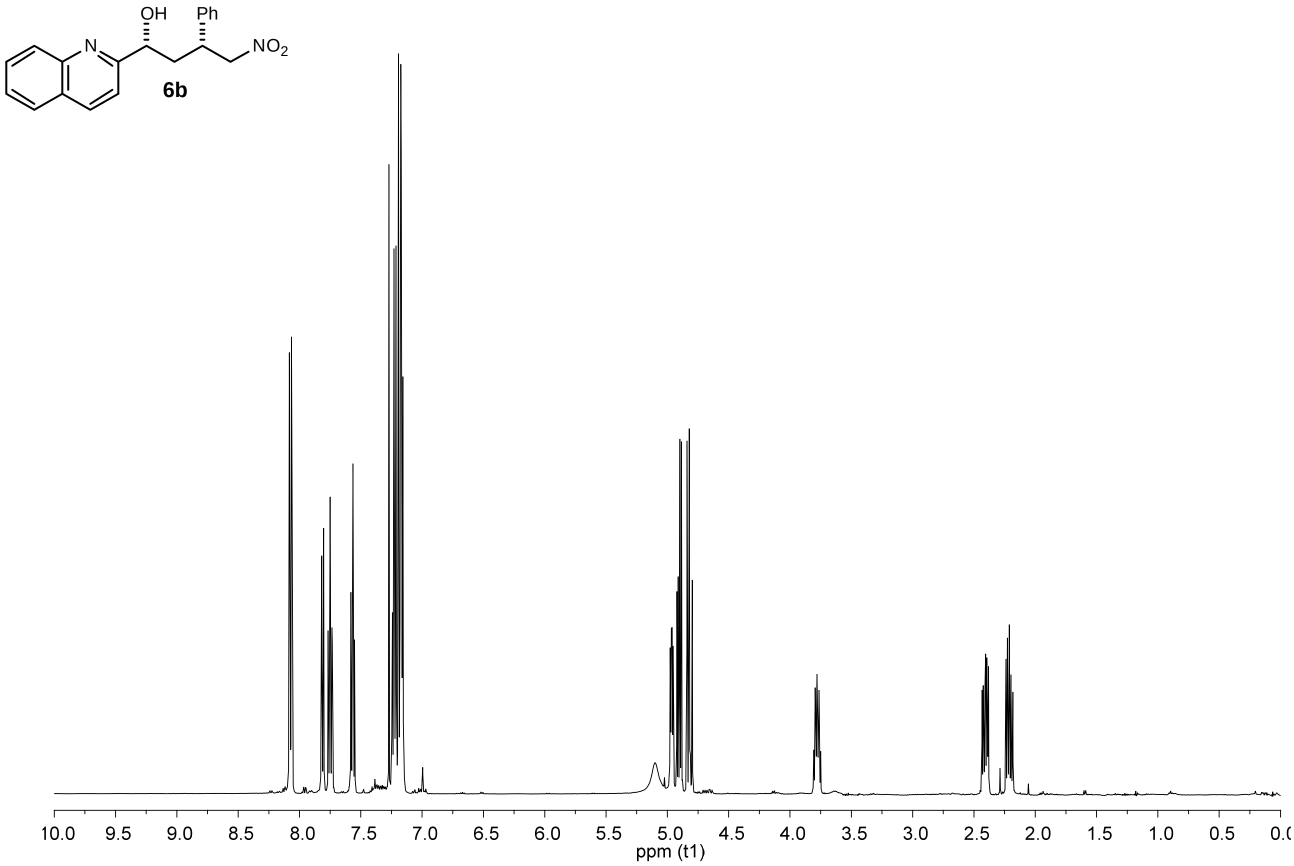

190.758
142.729
129.165
127.251
77.389
77.254
77.000
76.746
39.432
38.287
37.894
36.186
29.986
29.104
26.353
26.303
26.235
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

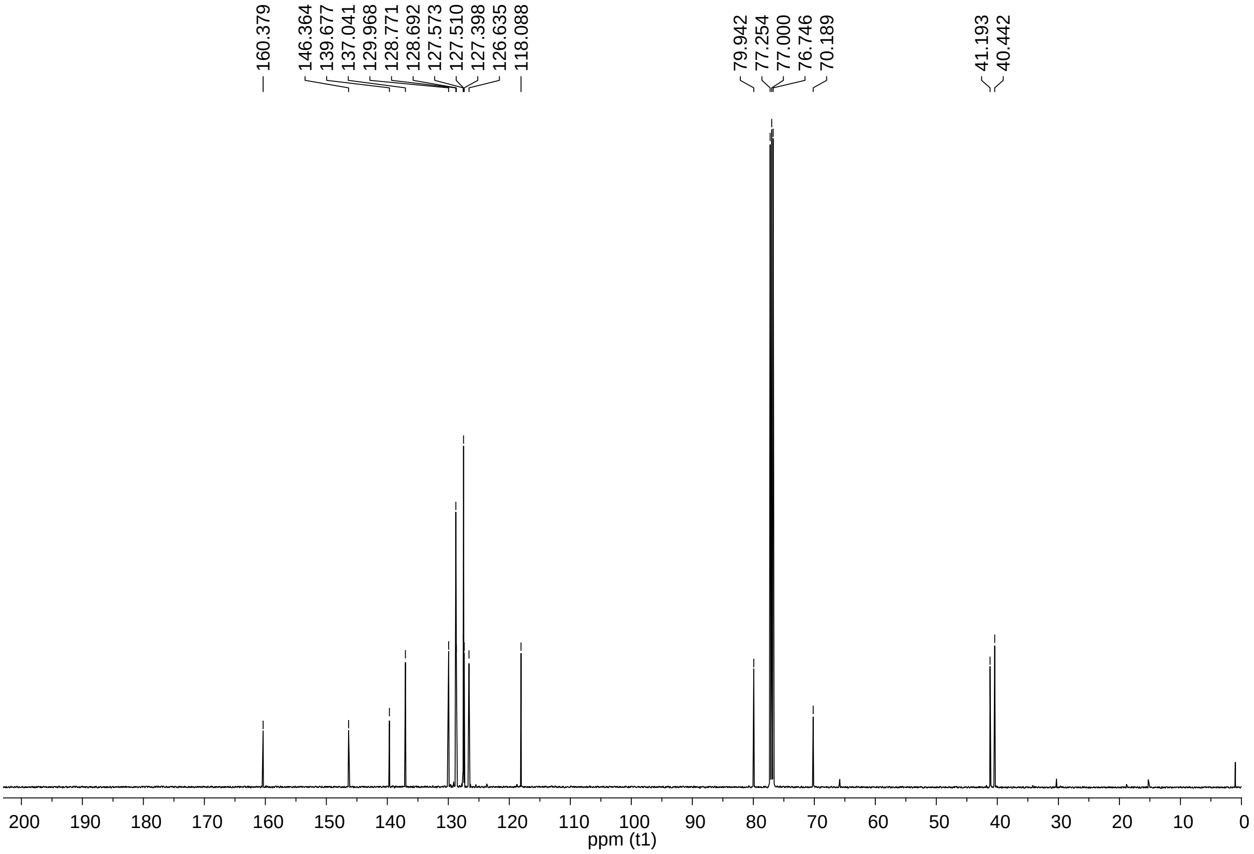

OH
Ph
N
NO2

6a

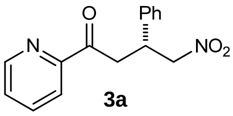

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm (t1)


161.030
146.052
139.079
137.523
129.149
127.849
127.813
127.627
118.014
80.772
77.254
77.000
76.746
70.128
42.474
41.804
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


OH
Ph
N
NO2
6b
10.0
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.(
ppm (t1)

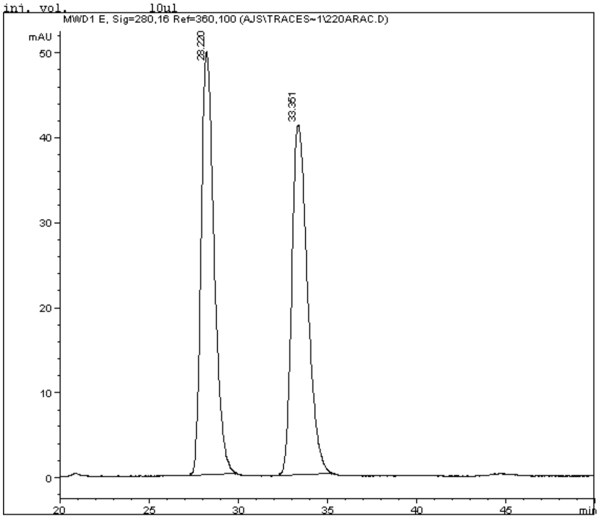

160.379
146.364
139.677
137.041
129.968
128.771
128.692
127.573
127.510
127.398
126.635
118.088
79.942
77.254
77.000
76.746
70.189
41.193
40.442
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

HPLC Traces



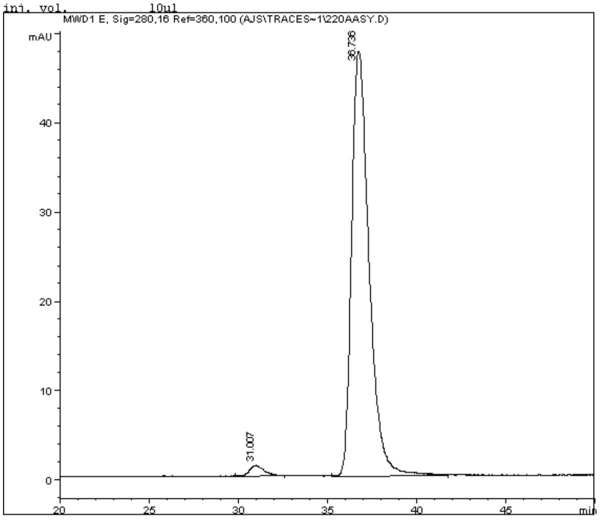
3a

```
Data File name:                                  C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                    ASH8020A.M
data acquired by:   Hon Wai Lam
on:                 07/06/2012
location:           Vial 3
Sample:             AJS03-172a-Z1
inj. vol.           10ul
```

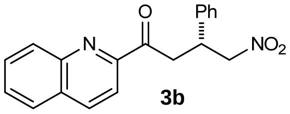


```
Meas. R Area %   Width  Symmetr
-------------------------------
 28.220  49.976   0.740   0.686
 33.351  50.024   0.881   0.650
-------------------------------
```

```
Data File name:                                  C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                    ASH8020.M
data acquired by:   Hon Wai Lam
on:                 16/03/2012
location:           Vial 8
Sample:             AJS04-220a-B1
inj. vol.           10ul
```

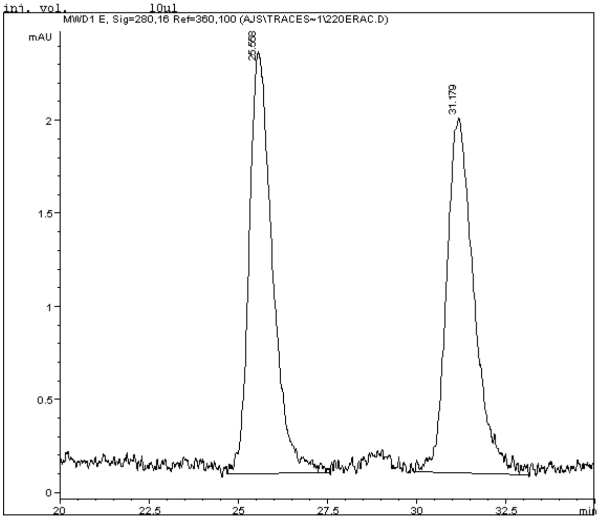


```
Meas. R Area %   Width  Symmetr
-------------------------------
 31.007   2.121   0.980   0.840
 36.736  97.879   1.136   0.641
-------------------------------
```



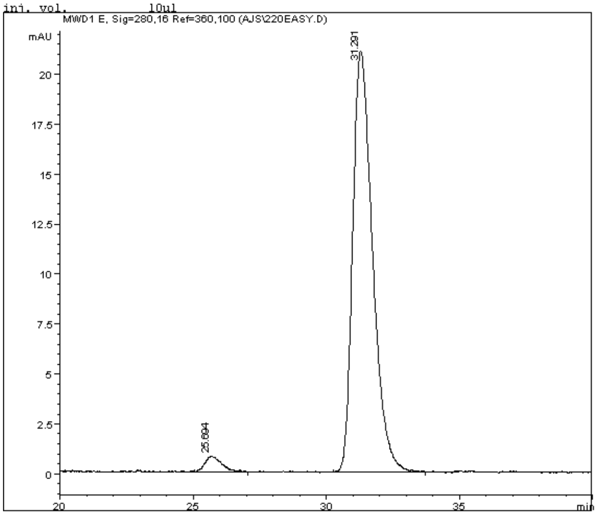
3b

```
Data File name:                                  C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                    ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 08/06/2012
location:           Vial 11
Sample:             AJS03-183a-B1
inj. vol.           10ul
```

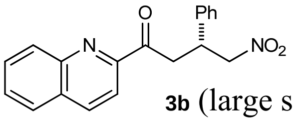


```
Meas. R Area %   Width  Symmetr
-------------------------------
 25.558  50.140   0.755   0.629
 31.179  49.860   0.893   0.770
-------------------------------
```

```
Data File name:                                  C:\HPCHEM\1\DATA\AJS\220EASY.D
Method name:                    ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 08/06/2012
location:           Vial 12
Sample:             AJS04-220e-B1
inj. vol.           10ul
```

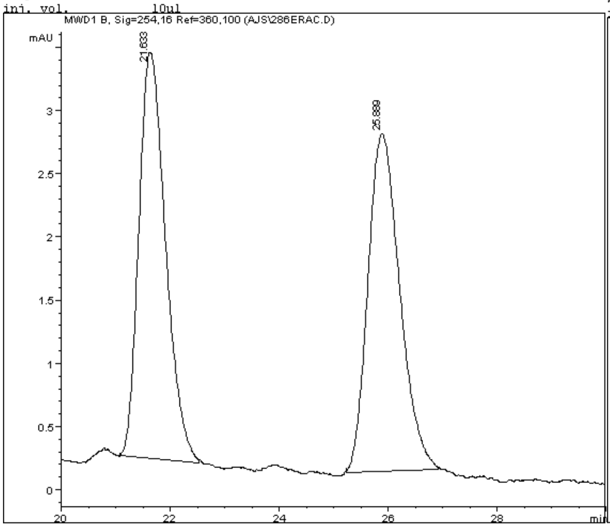


```
Meas. R Area %   Width  Symmetr
-------------------------------
 25.694   3.167   0.740   0.587
 31.291  96.833   0.862   0.639
-------------------------------
```



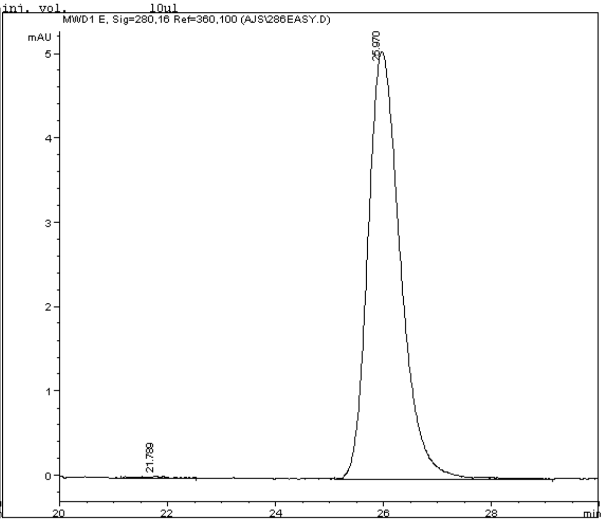
3b (large scale)

```
Data File name:                                C:\HPCHEM\1\DATA\AJS\286ERAC.D
Method name:                     ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 93
Sample:             AJS03-183a-Z1
inj. vol.           10ul
```

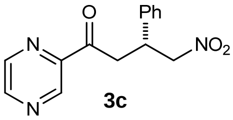


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.633  50.215   0.481   0.692
 25.889  49.785   0.507   0.752
-------------------------------
```

```
Data File name:                                C:\HPCHEM\1\DATA\AJS\286EASY.D
Method name:                     ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 94
Sample:             AJS04-286e-B1
inj. vol.           10ul
```

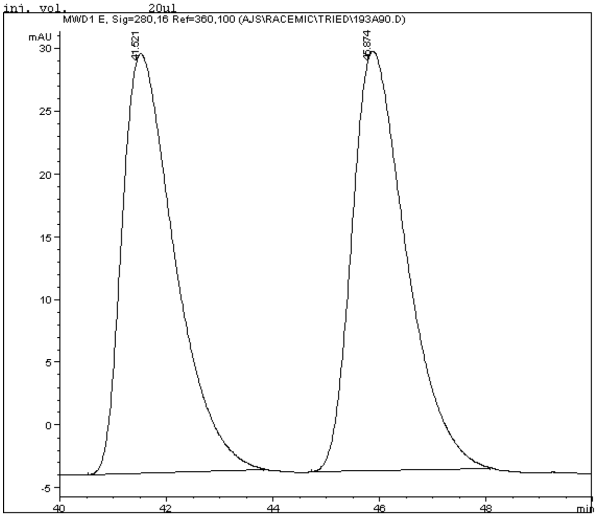


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.789   0.491   0.723   1.108
 25.970  99.509   0.702   0.715
-------------------------------
```



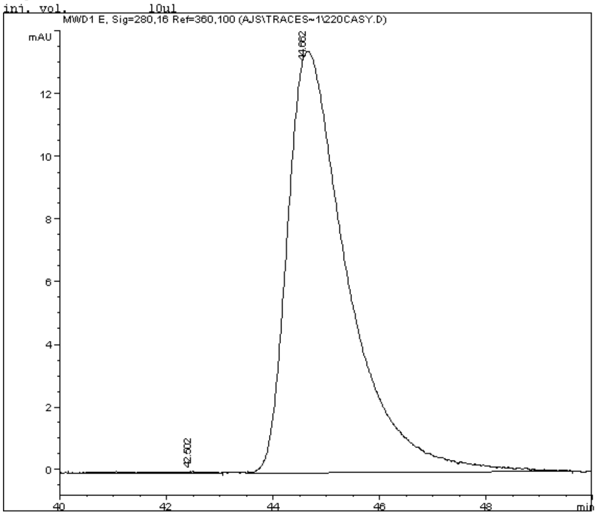
3c

```
Data File name:                               C:\HPCHEM\1\DATA\AJS\RACEMIC\TRIE->
Method name:                     ADH9010.M
data acquired by:   Alison
on:                 23/01/2012
location:           Vial 8
Sample:             AJS03-193-Z1
inj. vol.           20ul
```

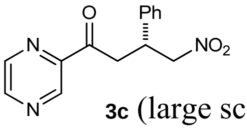


```
Meas. R Area %   Width  Symmetr
-------------------------------
 41.521  49.205   0.991   0.520
 45.874  50.795   1.048   0.593
-------------------------------
```

```
Data File name:                                C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                     ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 21/03/2012
location:           Vial 10
Sample:             AJS04-220c-A2
inj. vol.           10ul
```

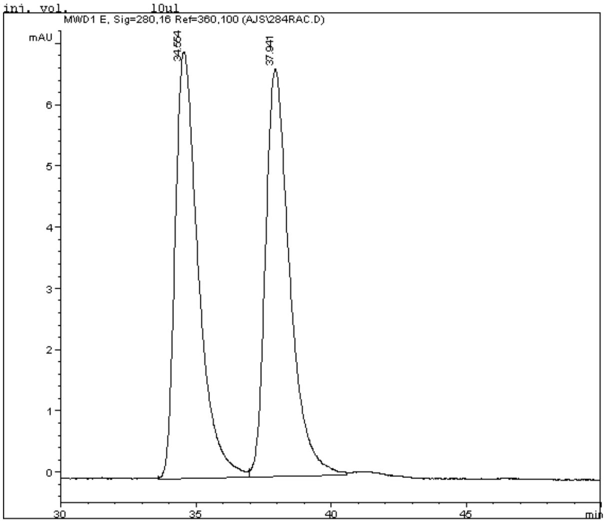


```
Meas. R Area %   Width  Symmetr
-------------------------------
 42.502   0.483   1.285   4.098
 44.662  99.517   1.305   0.507
-------------------------------
```



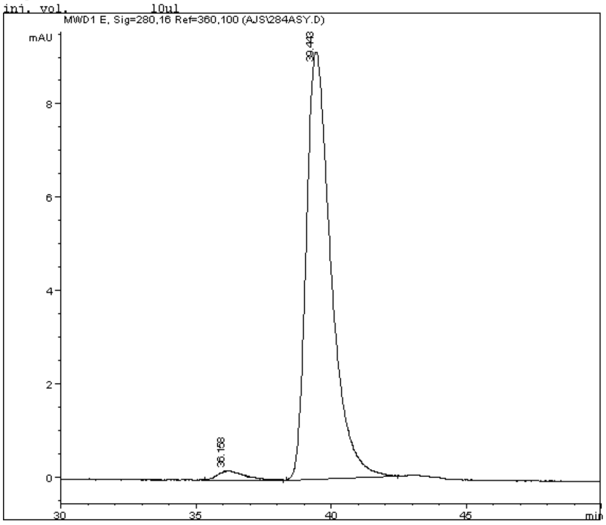
3c (large scale)

```
Data File name:                            C:\HPCHEM\1\DATA\AJS\284RAC.D
Method name:                  ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 11
Sample:             AJS03-193-Z1
inj. vol.           10ul
```

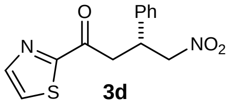


```
Meas. R Area %   Width  Symmetr
-------------------------------
 34.554  50.196   0.993   0.562
 37.941  49.804   1.034   0.649
-------------------------------
```

```
Data File name:                            C:\HPCHEM\1\DATA\AJS\284ASY.D
Method name:                  ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 12
Sample:             AJS04-284-B1
inj. vol.           10ul
```

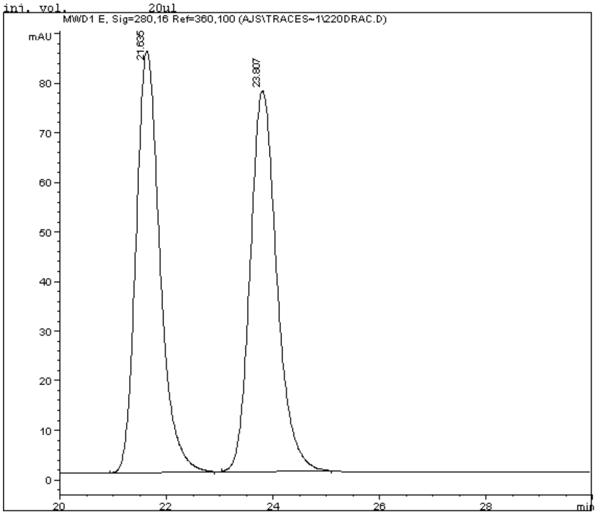


```
Meas. R Area %   Width  Symmetr
-------------------------------
 36.158   2.295   1.153   0.529
 39.443  97.705   1.056   0.623
-------------------------------
```



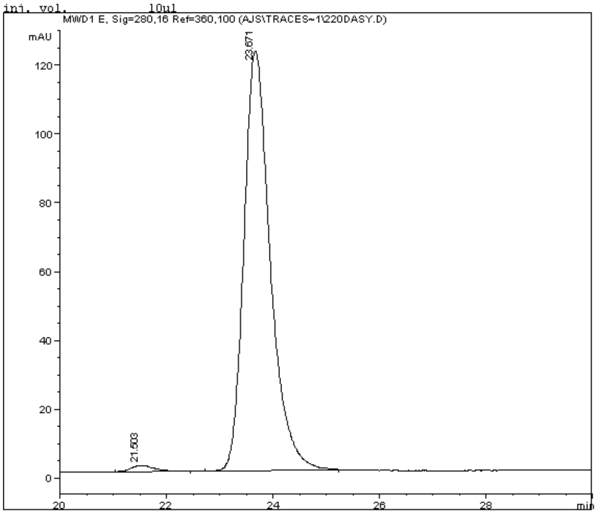
3d

```
Data File name:                            C:\HPCHEM\1\DATA\AJS\TRACES~1\    ->
Method name:                  IC8020.M
data acquired by:   Alison
on:                 23/01/2012
location:           Vial 9
Sample:             AJS03-194-Z1
inj. vol.           20ul
```

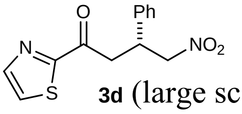


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.635  49.860   0.478   0.780
 23.807  50.140   0.532   0.816
-------------------------------
```

```
Data File name:                            C:\HPCHEM\1\DATA\AJS\TRACES~1\    ->
Method name:                  IC8020AS.M
data acquired by:   Hon Wai Lam
on:                 28/03/2012
location:           Vial 10
Sample:             AJS04-220d-B1
inj. vol.           10ul
```

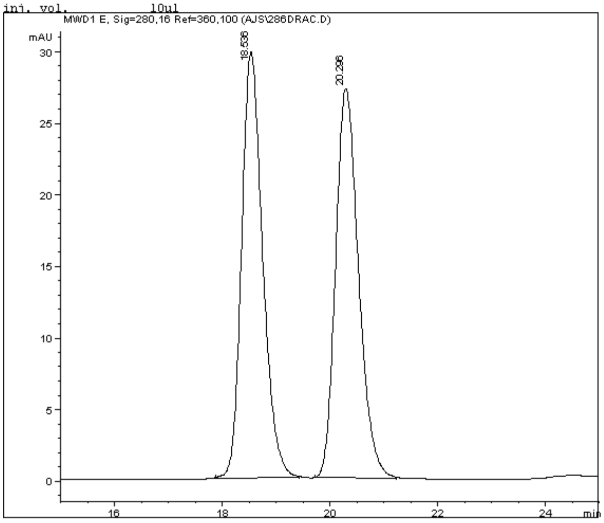


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.503   1.345   0.385   0.599
 23.671  98.655   0.523   0.720
-------------------------------
```



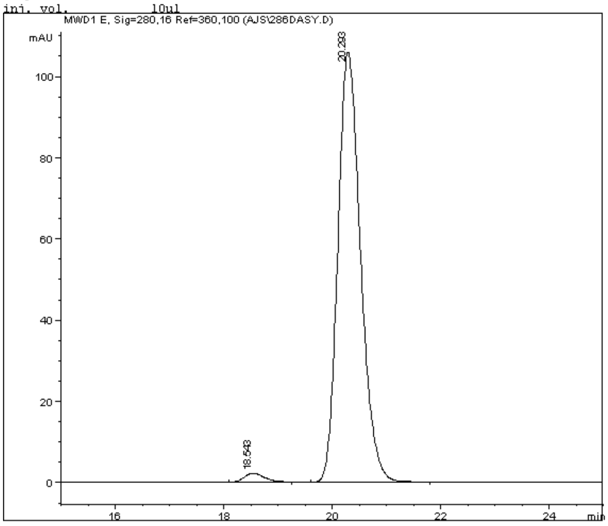
3d (large scale)

```
Data File name:                               C:\HPCHEM\1\DATA\AJS\286DRAC.D
Method name:                IC8020AS.M
data acquired by:    Hon Wai Lam
on:                  23/11/2012
location:            Vial 13
Sample:              AJS03-194-Z1
inj. vol.            10ul
```

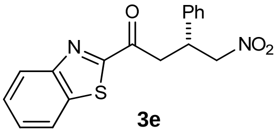


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.536  50.140   0.414   0.757
 20.296  49.860   0.454   0.765
-------------------------------
```

```
Data File name:                               C:\HPCHEM\1\DATA\AJS\286DASY.D
Method name:                IC8020AS.M
data acquired by:    Hon Wai Lam
on:                  23/11/2012
location:            Vial 14
Sample:              AJS04-286d-B1
inj. vol.            10ul
```

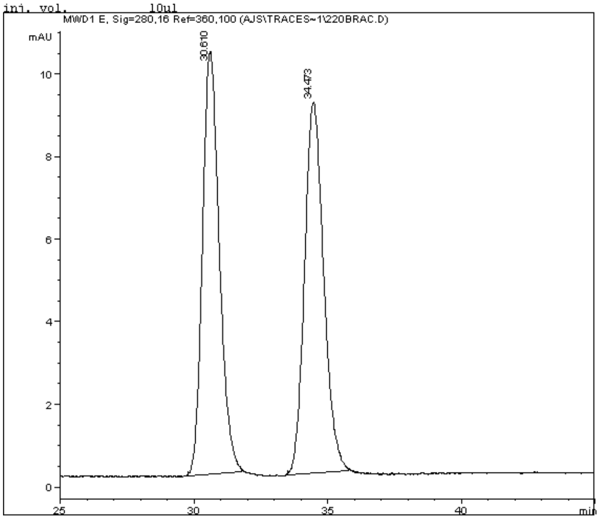


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.543   2.012   0.459   0.724
 20.293  97.988   0.484   0.786
-------------------------------
```



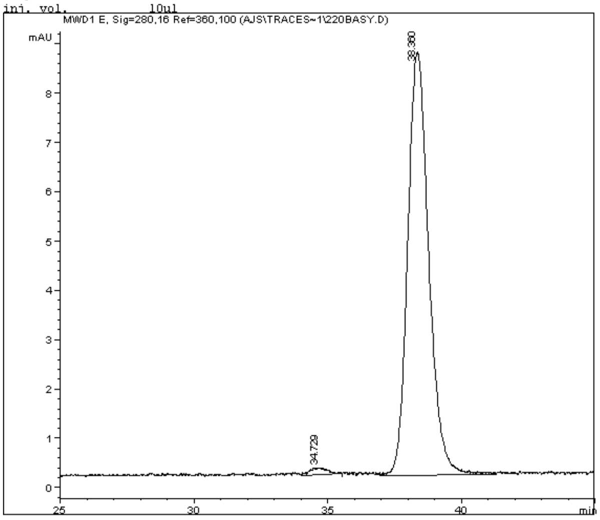
3e

```
Data File name:                               C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                IC9010.M
data acquired by:    Alison
on:                  01/02/2012
location:            Vial 43
Sample:              AJS03-196-Z1
inj. vol.            10ul
```

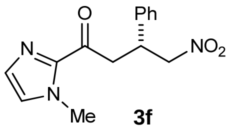


```
Meas. R Area %   Width  Symmetr
-------------------------------
 30.610  50.058   0.648   0.789
 34.473  49.942   0.700   0.839
-------------------------------
```

```
Data File name:                               C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                IC9010.M
data acquired by:    Hon Wai Lam
on:                  20/03/2012
location:            Vial 6
Sample:              AJS04-220b-B1
inj. vol.            10ul
```

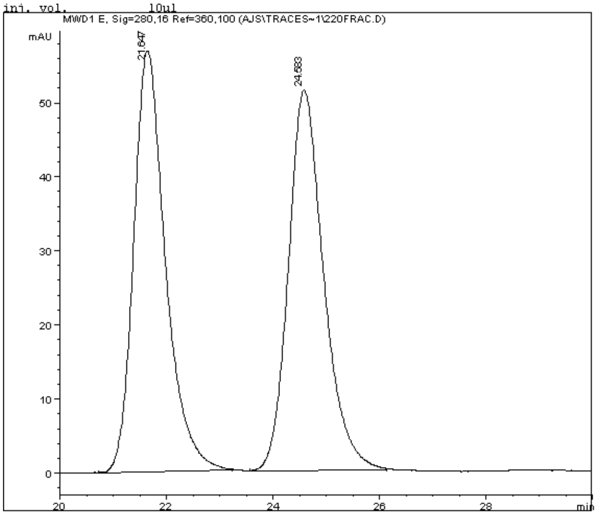


```
Meas. R Area %   Width  Symmetr
-------------------------------
 34.729   1.356   0.769   1.242
 38.360  98.644   0.910   0.824
-------------------------------
```



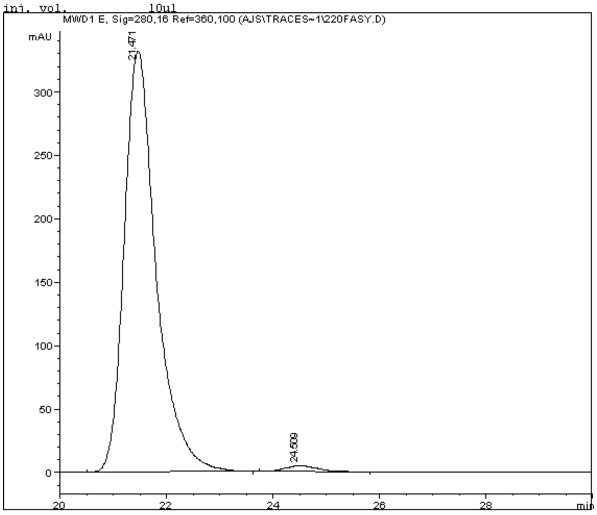
3f

```
Data File name:                                    C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                        ODH8020L.M
data acquired by:   Hon Wai Lam
on:                 12/05/2012
location:           Vial 6
Sample:             AJS04-207-Z1
inj. vol.           10ul
```

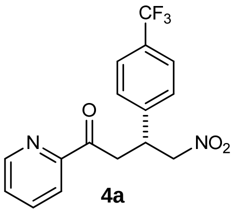


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.647  49.994   0.624   0.720
 24.583  50.006   0.683   0.760
-------------------------------
```

```
Data File name:                                    C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                        ODH8020L.M
data acquired by:   Hon Wai Lam
on:                 12/05/2012
location:           Vial 16
Sample:             AJS04-220f-B1
inj. vol.           10ul
```

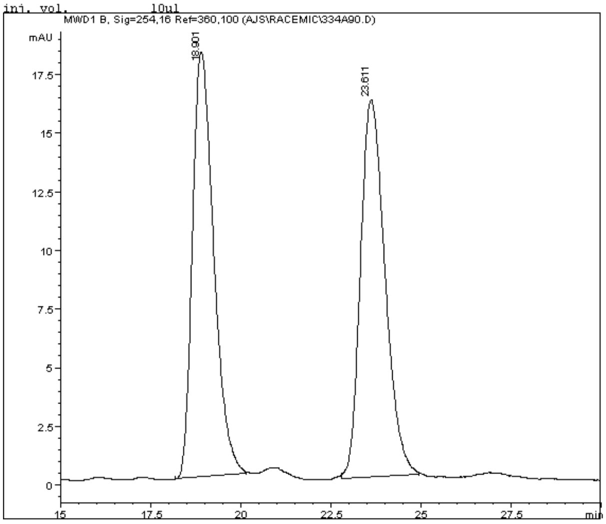


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.471  98.537   0.629   0.707
 24.509   1.463   0.536   0.783
-------------------------------
```



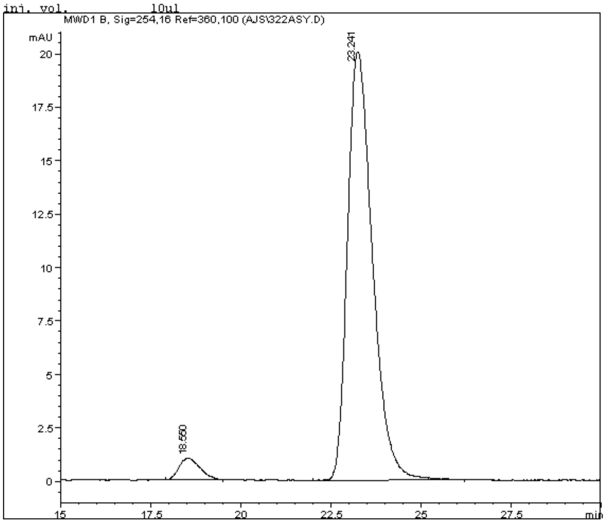
4a

```
Data File name:                                    C:\HPCHEM\1\DATA\AJS\RACEMIC\    ->
Method name:                        ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 21/02/2013
location:           Vial 1
Sample:             AJS05-334-X6
inj. vol.           10ul
```

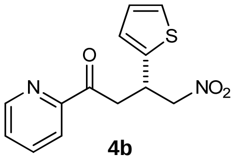


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.901  49.339   0.624   0.666
 23.611  50.661   0.699   0.730
-------------------------------
```

```
Data File name:                                    C:\HPCHEM\1\DATA\AJS\322ASY.D
Method name:                        ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/02/2013
location:           Vial 1
Sample:             AJS05-322-B1
inj. vol.           10ul
```

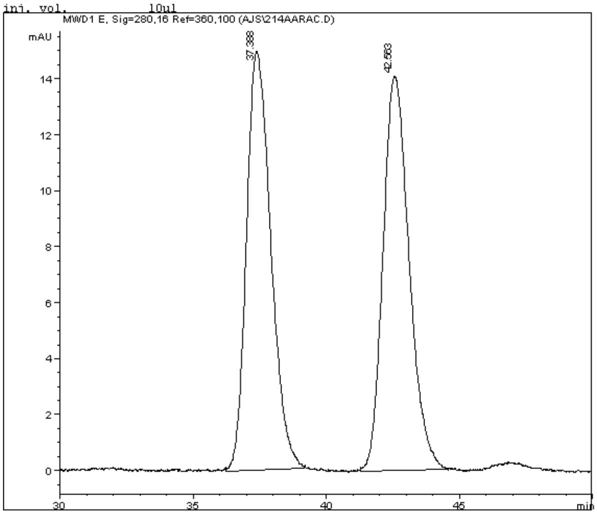


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.550   4.042   0.680   0.805
 23.241  95.958   0.806   0.674
-------------------------------
```



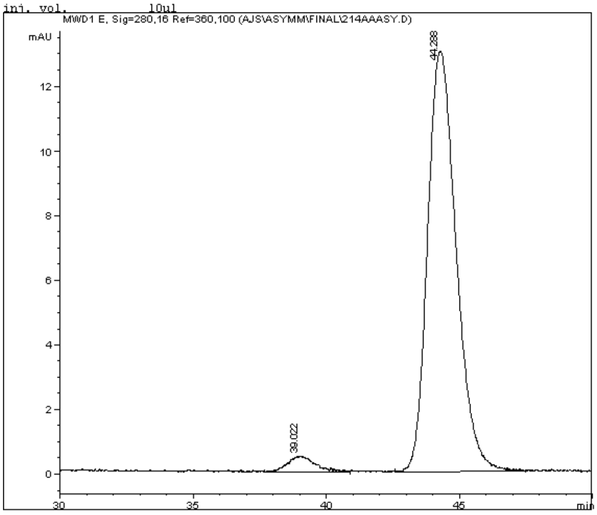
4b

```
Data File name:                                   C:\HPCHEM\1\DATA\AJS\214AARAC.D
Method name:                        ASH8020A.M
data acquired by:   Hon Wai Lam
on:                 07/06/2012
location:           Vial 9
Sample:             AJS04-216aa-Z1
inj. vol.           10ul
```

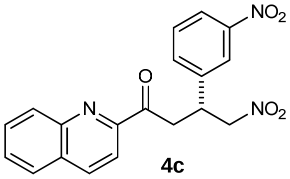


```
Meas. R Area %   Width  Symmetr
-------------------------------
 37.388  49.792   0.785   0.679
 42.563  50.208   0.808   0.754
-------------------------------
```

```
Data File name:                                   C:\HPCHEM\1\DATA\AJS\ASYMM\FINAL\->
Method name:                        ASH8020A.M
data acquired by:   Hon Wai Lam
on:                 02/04/2012
location:           Vial 14
Sample:             AJS04-214aa-Z1
inj. vol.           10ul
```

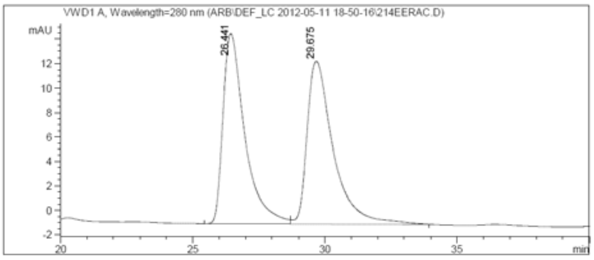


```
Meas. R Area %   Width  Symmetr
-------------------------------
 39.022   3.713   1.231   0.833
 44.288  96.287   1.243   0.781
-------------------------------
```



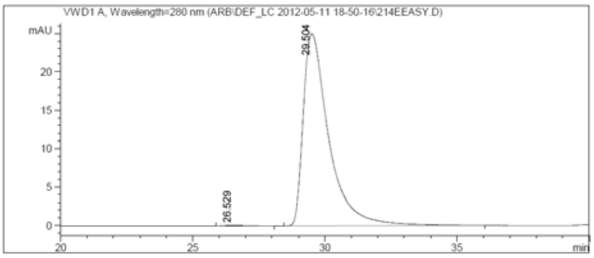
4c

```
data acquired by:  Alan
on:                5/11/2012
location:          Vial 61
```

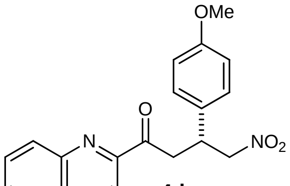


```
 Meas. R     Area %     Width      Symmetr.
--------------------------------------------
26.441      49.313          0.960       0.532
29.675      50.687          1.153       0.516
--------------------------------------------
```

```
data acquired by:  Alan
on:                5/11/2012
location:          Vial 62
```

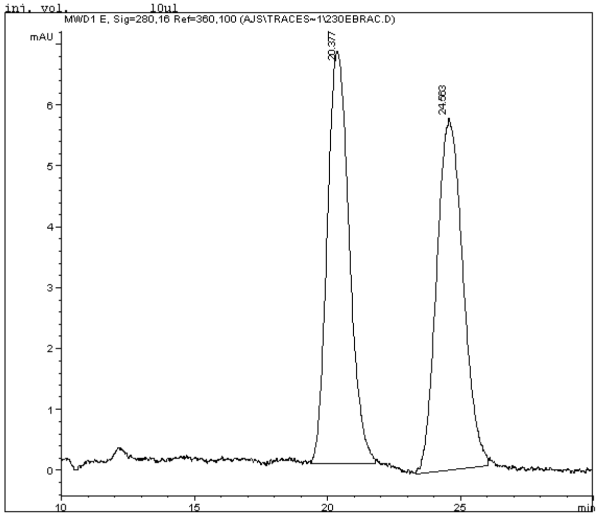


```
 Meas. R     Area %     Width      Symmetr.
--------------------------------------------
26.529      0.272           0.896       0.706
29.504      99.728          1.126       0.479
--------------------------------------------
```



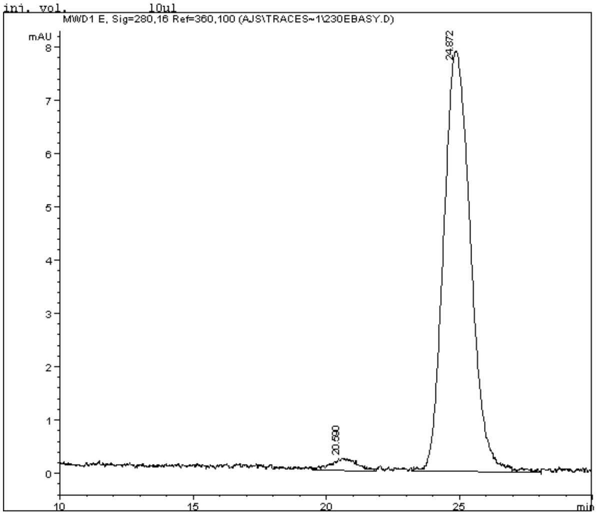
4d

```
Data File name:                             C:\HPCHEM\1\DATA\AJS\TRACES~1\    ->
Method name:                   ADH8020L.M
data acquired by:    Hon Wai Lam
on:                  17/05/2012
location:            Vial 9
Sample:              AJS04-231eb-X16
inj. vol.            10ul
```

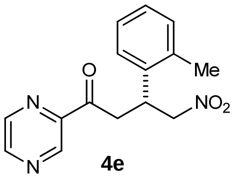


```
Meas. R Area %   Width  Symmetr
-------------------------------
 20.377  49.569  0.692   0.821
 24.563  50.431  0.813   0.838
-------------------------------
```

```
Data File name:                             C:\HPCHEM\1\DATA\AJS\TRACES~1\    ->
Method name:                   ADH8020L.M
data acquired by:    Hon Wai Lam
on:                  17/05/2012
location:            Vial 3
Sample:              AJS04-230eb-B1
inj. vol.            10ul
```

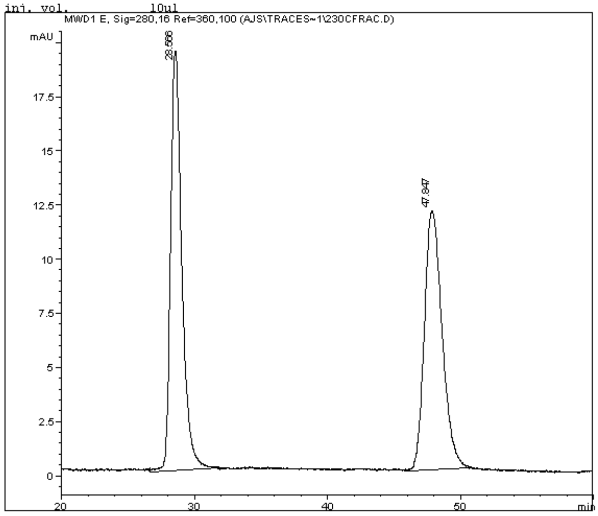


```
Meas. R Area %   Width  Symmetr
-------------------------------
 20.590   2.716  1.140   0.746
 24.872  97.284  1.170   0.817
-------------------------------
```



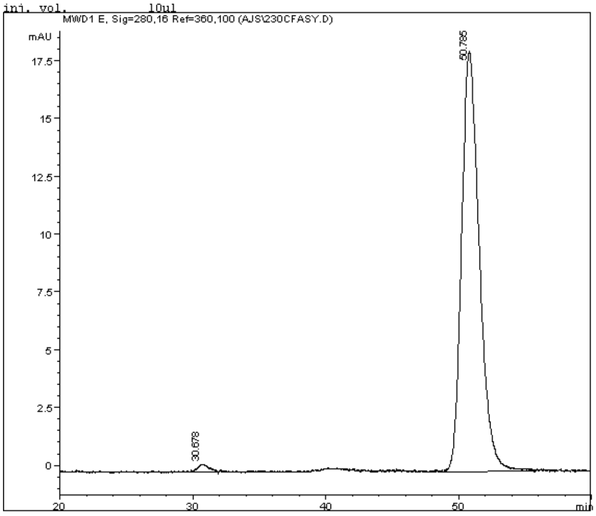
4e

```
Data File name:                             C:\HPCHEM\1\DATA\AJS\TRACES~1\    ->
Method name:                   ASH8020A.M
data acquired by:    Hon Wai Lam
on:                  17/05/2012
location:            Vial 8
Sample:              AJS04-231cf-X48
inj. vol.            10ul
```

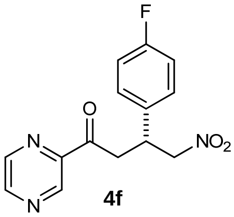


```
Meas. R Area %   Width  Symmetr
-------------------------------
 28.566  50.696  0.976   0.678
 47.847  49.304  1.094   0.706
-------------------------------
```

```
Data File name:                             C:\HPCHEM\1\DATA\AJS\230CFASY.D
Method name:                   ASH8020A.M
data acquired by:    Hon Wai Lam
on:                  07/06/2012
location:            Vial 2
Sample:              AJS04-230cf-B1
inj. vol.            10ul
```

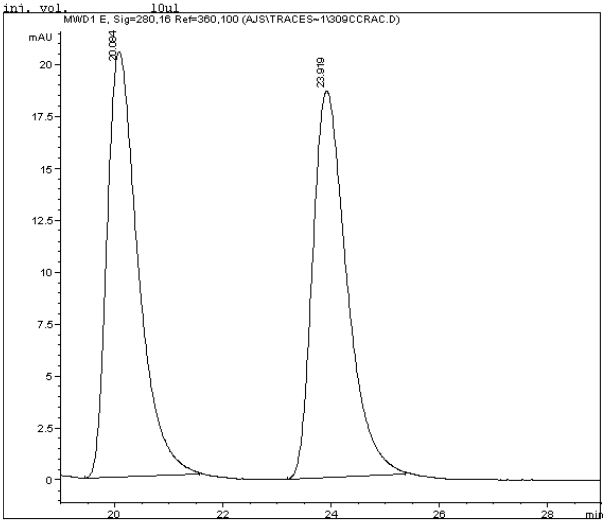


```
Meas. R Area %   Width  Symmetr
-------------------------------
 30.678   1.105  0.957   0.535
 50.785  98.895  1.546   0.708
-------------------------------
```



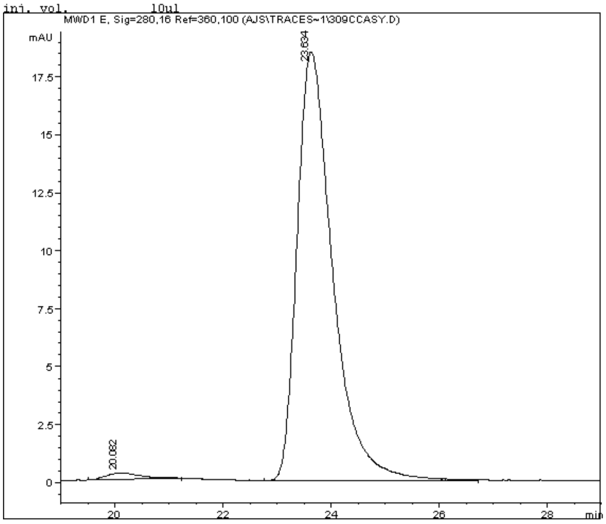
4f

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                  ADH8020L.M
data acquired by:   Alan
on:                 08/01/2013
location:           Vial 1
Sample:             AJS05-311-X18
inj. vol.           10ul
```

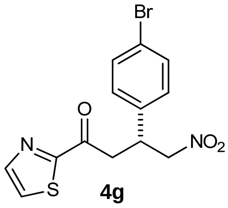


```
Meas. R Area %   Width  Symmetr
-------------------------------
 20.084  50.056   0.599   0.582
 23.919  49.944   0.663   0.646
-------------------------------
```

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                  ADH8020L.M
data acquired by:   Alan
on:                 08/01/2013
location:           Vial 2
Sample:             AJS05-309cc-Z1
inj. vol.           10ul
```

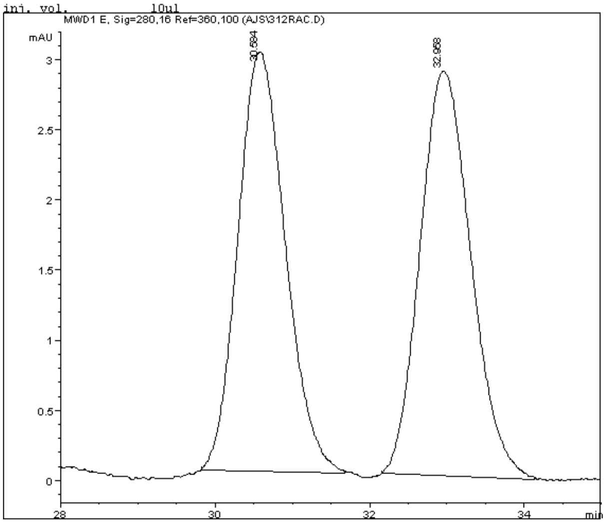


```
Meas. R Area %   Width  Symmetr
-------------------------------
 20.082   1.447   0.769   0.605
 23.634  98.553   0.764   0.627
-------------------------------
```



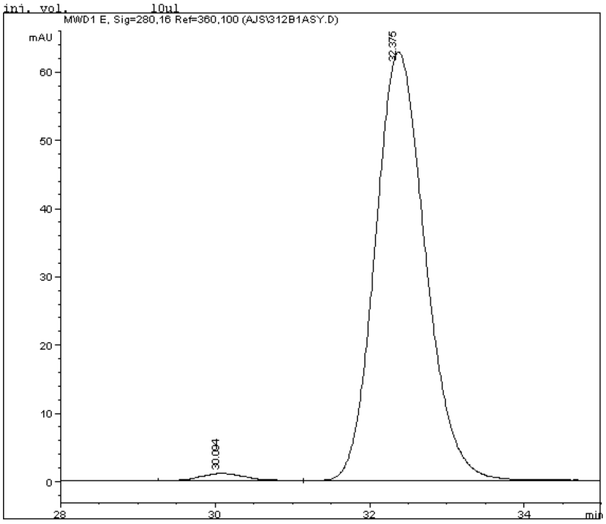
4g

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\312RAC.D
Method name:                  IC9010AS.M
data acquired by:   Alan
on:                 16/01/2013
location:           Vial 91
Sample:             AJS04-231dh-X16
inj. vol.           10ul
```

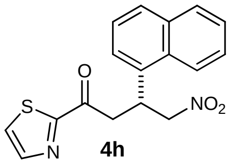


```
Meas. R Area %   Width  Symmetr
-------------------------------
 30.584  49.170   0.539   0.851
 32.958  50.830   0.567   0.818
-------------------------------
```

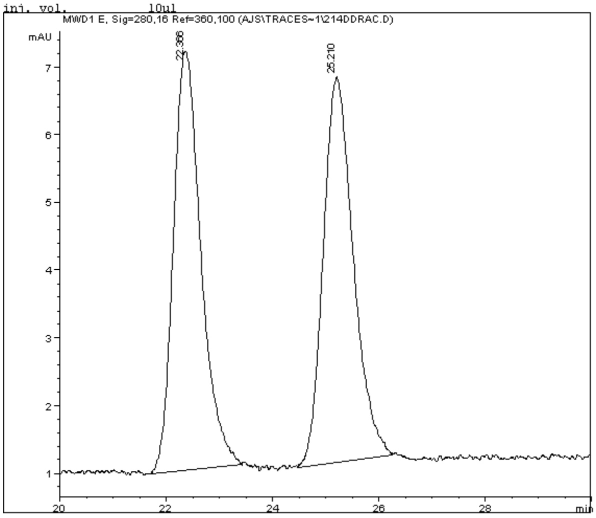
```
Data File name:                        C:\HPCHEM\1\DATA\AJS\312B1ASY.D
Method name:                  IC9010AS.M
data acquired by:   Alan
on:                 16/01/2013
location:           Vial 92
Sample:             AJS05-312-B1
inj. vol.           10ul
```



```
Meas. R Area %   Width  Symmetr
-------------------------------
 30.094   1.575   0.702   0.911
 32.375  98.425   0.751   0.848
-------------------------------
```

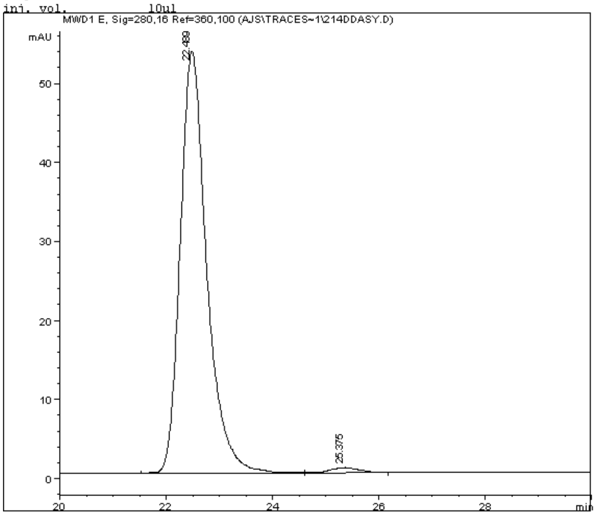

4h

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                   IC8020AS.M
data acquired by:   Hon Wai Lam
on:                 14/05/2012
location:           Vial 23
Sample:             AJS04-216dd-Z1
inj. vol.           10ul
```

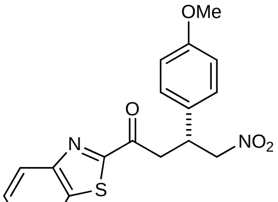


```
Meas. R Area %   Width  Symmetr
------------------------------
 22.366  49.995   0.434   0.767
 25.210  50.005   0.473   0.788
------------------------------
```

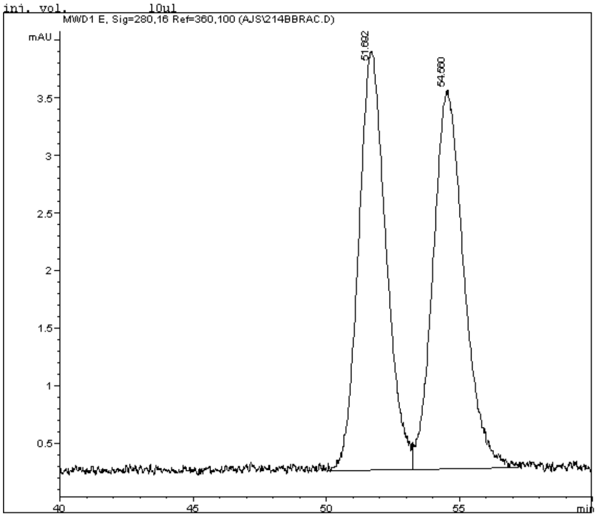
```
Data File name:                              C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                   IC8020AS.M
data acquired by:   Hon Wai Lam
on:                 14/05/2012
location:           Vial 33
Sample:             AJS04-214dd-C1
inj. vol.           10ul
```



```
Meas. R Area %   Width  Symmetr
------------------------------
 22.489  98.503   0.575   0.761
 25.375   1.497   0.669   0.989
------------------------------
```

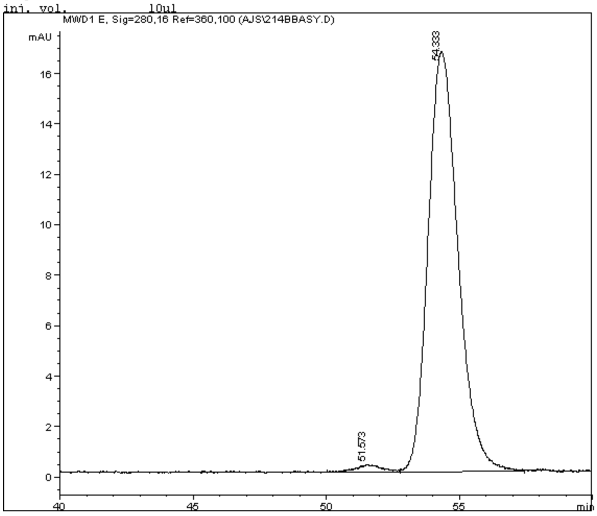

4i

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\214BBRAC.D
Method name:                   IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 08/06/2012
location:           Vial 5
Sample:             AJS04-216bb-Z1
inj. vol.           10ul
```

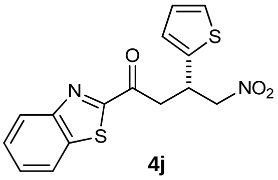


```
Meas. R Area %   Width  Symmetr
------------------------------
 51.692  49.722   1.198   0.837
 54.560  50.278   1.341   0.858
------------------------------
```

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\214BBASY.D
Method name:                   IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 08/06/2012
location:           Vial 6
Sample:             AJS04-214bb-B1
inj. vol.           10ul
```

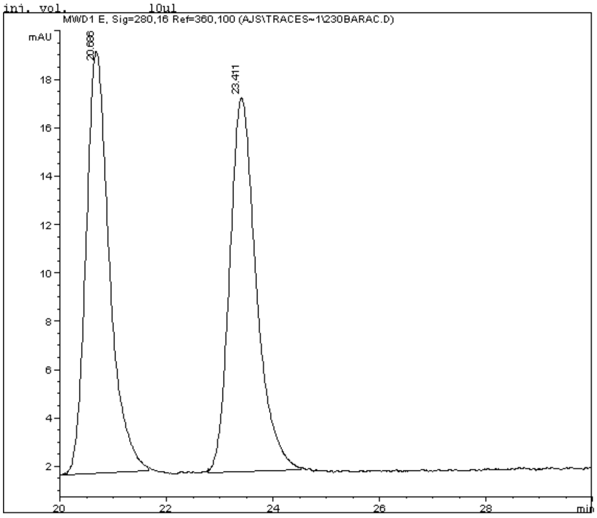


```
Meas. R Area %   Width  Symmetr
------------------------------
 51.573   1.536   1.188   0.959
 54.333  98.464   1.299   0.800
------------------------------
```



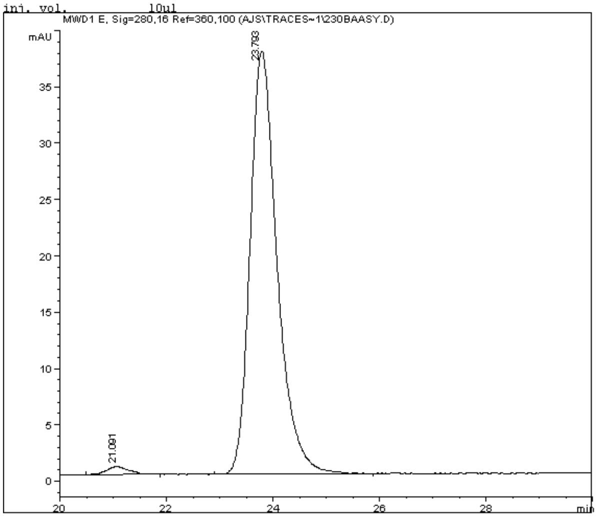
4j

```
Data File name:                          C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                 IC8020AS.M
data acquired by:   Hon Wai Lam
on:                 15/05/2012
location:           Vial 7
Sample:             AJS04-231ba-X16
inj. vol.           10ul
```

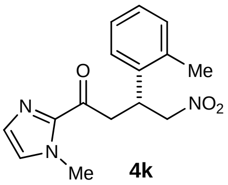


```
Meas. R Area %   Width  Symmetr
-------------------------------
 20.686  49.861   0.455   0.733
 23.411  50.139   0.494   0.755
-------------------------------
```

```
Data File name:                          C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                 IC8020AS.M
data acquired by:   Hon Wai Lam
on:                 17/05/2012
location:           Vial 4
Sample:             AJS04-230ba-B1
inj. vol.           10ul
```

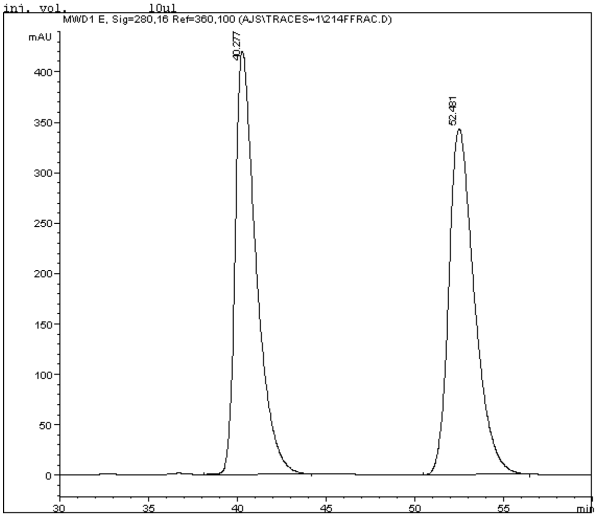


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.091   1.639   0.516   0.889
 23.793  98.361   0.588   0.740
-------------------------------
```



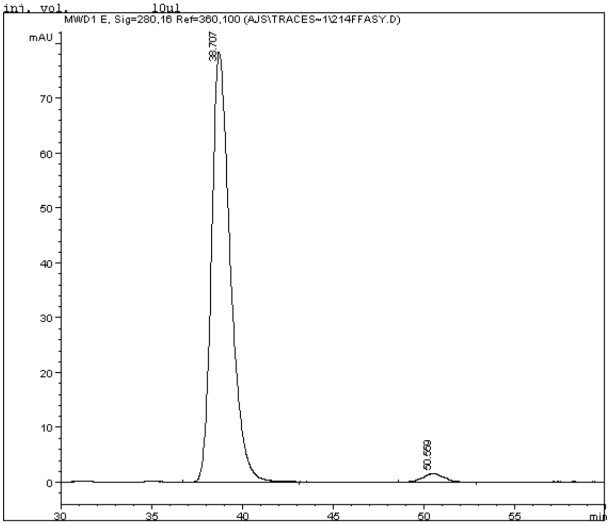
4k

```
Data File name:                          C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                 ODH9010L.M
data acquired by:   Hon Wai Lam
on:                 29/03/2012
location:           Vial 60
Sample:             AJS04-216ff-Z1
inj. vol.           10ul
```

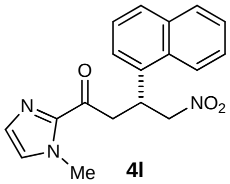


```
Meas. R Area %   Width  Symmetr
-------------------------------
 40.277  50.028   1.172   0.484
 52.481  49.972   1.436   0.639
-------------------------------
```

```
Data File name:                          C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                 ODH9010L.M
data acquired by:   Hon Wai Lam
on:                 17/05/2012
location:           Vial 6
Sample:             AJS04-214ff-C1
inj. vol.           10ul
```

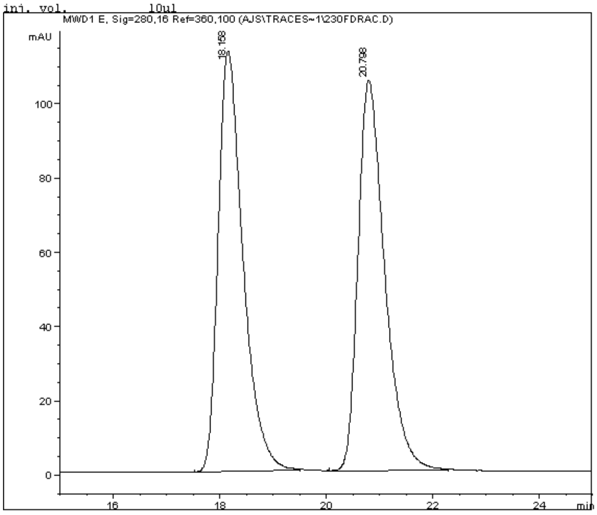


```
Meas. R Area %   Width  Symmetr
--------------------------------
 38.707  97.625   1.199   0.000
 50.559   2.375   1.449   1.062
--------------------------------
```



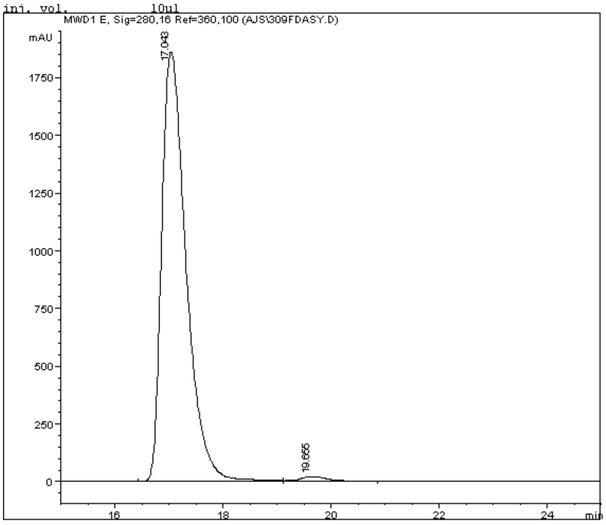
4l

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                 IC8020AS.M
data acquired by:   Hon Wai Lam
on:                 25/05/2012
location:           Vial 10
Sample:             AJS04-231fd-Z2
inj. vol.           10ul
```

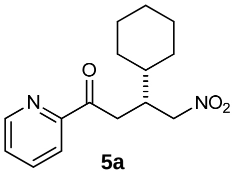


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.158  50.108   0.487   0.616
 20.798  49.892   0.532   0.629
-------------------------------
```

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\309FDASY.D
Method name:                 IC8020AS.M
data acquired by:   Alain
on:                 21/12/2012
location:           Vial 4
Sample:             AJS05-309fd-Z1
inj. vol.           10ul
```

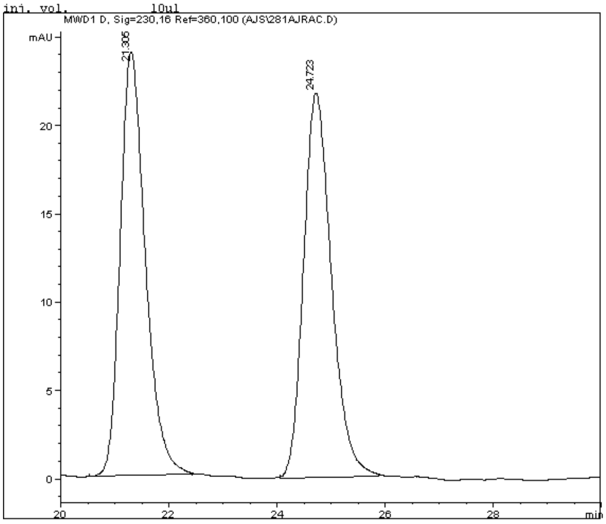


```
Meas. R Area %   Width  Symmetr
-------------------------------
 17.043  98.693   0.482   0.571
 19.655   1.307   0.544   0.773
-------------------------------
```



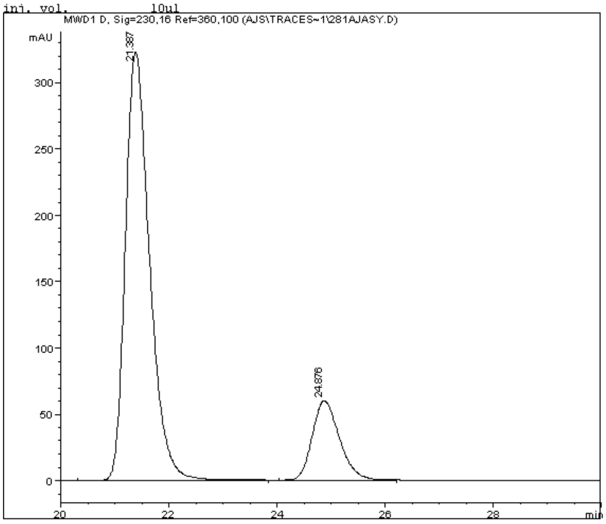
5a

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\281AJRAC.D
Method name:                 IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 21/11/2012
location:           Vial 95
Sample:             AJS04-283aj-Z2
inj. vol.           10ul
```

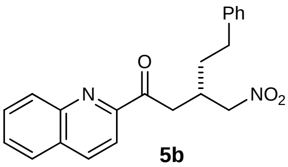


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.305  50.029   0.488   0.728
 24.723  49.971   0.539   0.761
-------------------------------
```

```
Data File name:                        C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:                 IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 21/11/2012
location:           Vial 96
Sample:             AJS04-281aj-B1
inj. vol.           10ul
```

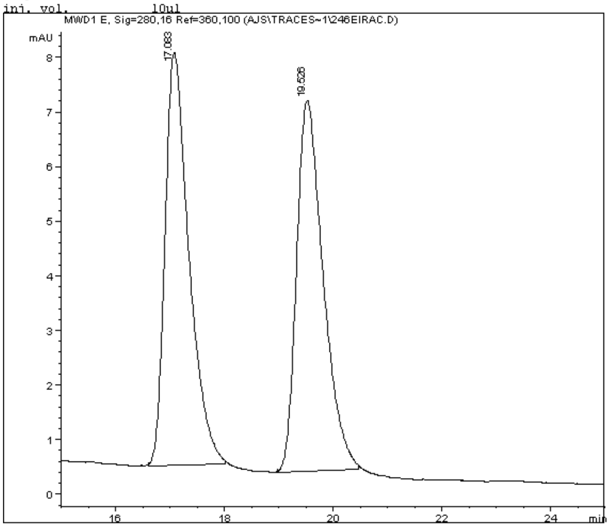


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.387  82.587   0.519   0.692
 24.876  17.413   0.588   0.768
-------------------------------
```



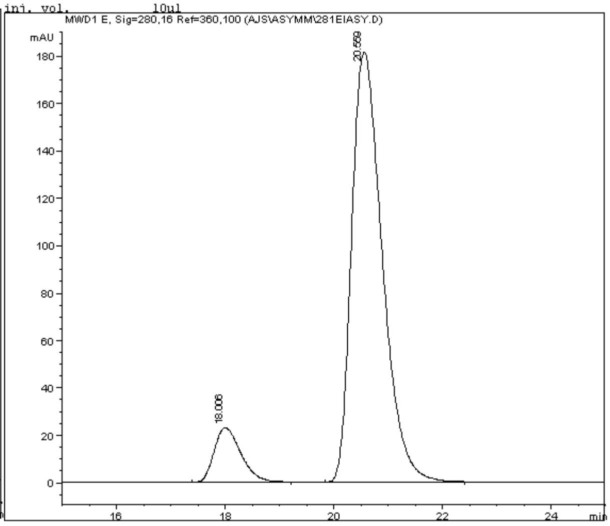
5b

```
Data File name:                      C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:              ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 03/08/2012
location:           Vial 4
Sample:             AJS04-249ei-TOP
inj. vol.           10ul
```

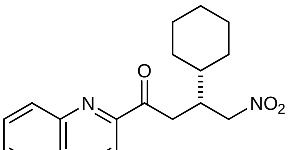


```
Meas. R Area %   Width  Symmetr
-------------------------------
 17.083  50.102   0.444   0.585
 19.526  49.898   0.499   0.629
-------------------------------
```

```
Data File name:                      C:\HPCHEM\1\DATA\AJS\ASYMM\      ->
Method name:              ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 17/11/2012
location:           Vial 97
Sample:             AJS04-281ei-B1
inj. vol.           10ul
```

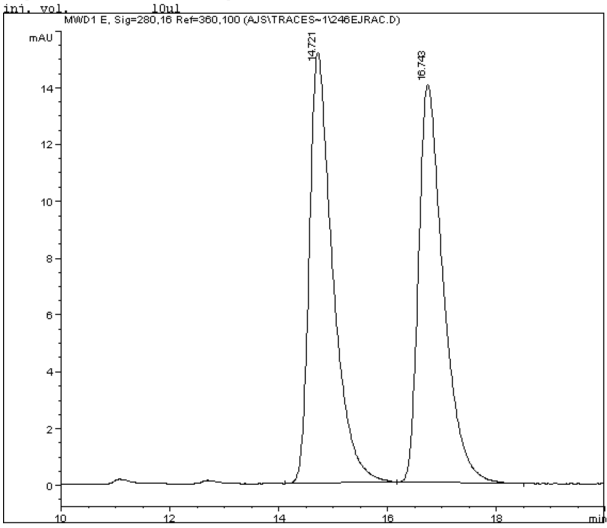


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.006  10.069   0.530   0.678
 20.559  89.931   0.605   0.644
-------------------------------
```



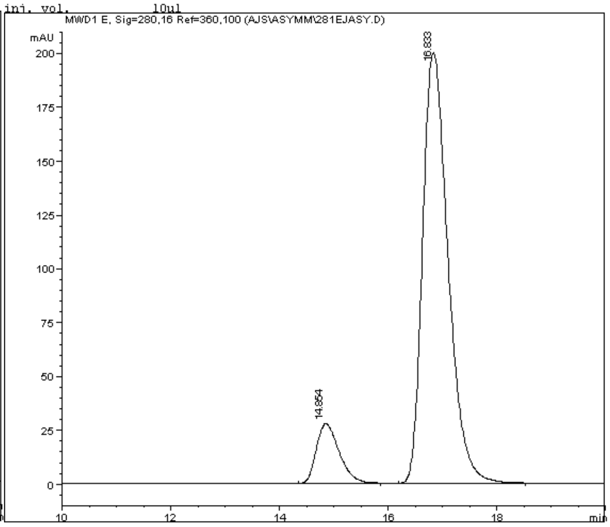
5c

```
Data File name:                      C:\HPCHEM\1\DATA\AJS\TRACES~1\   ->
Method name:              ADH9505L.M
data acquired by:   Hon Wai Lam
on:                 15/08/2012
location:           Vial 5
Sample:             AJS04-249ej-F3
inj. vol.           10ul
```

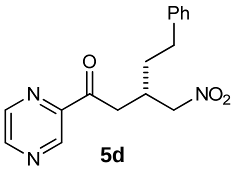


```
Meas. R Area %   Width  Symmetr
-------------------------------
 14.721  50.553   0.497   0.547
 16.743  49.447   0.527   0.573
-------------------------------
```

```
Data File name:                      C:\HPCHEM\1\DATA\AJS\ASYMM\      ->
Method name:              ADH9505L.M
data acquired by:   Hon Wai Lam
on:                 17/11/2012
location:           Vial 98
Sample:             AJS04-281ej-B1
inj. vol.           10ul
```

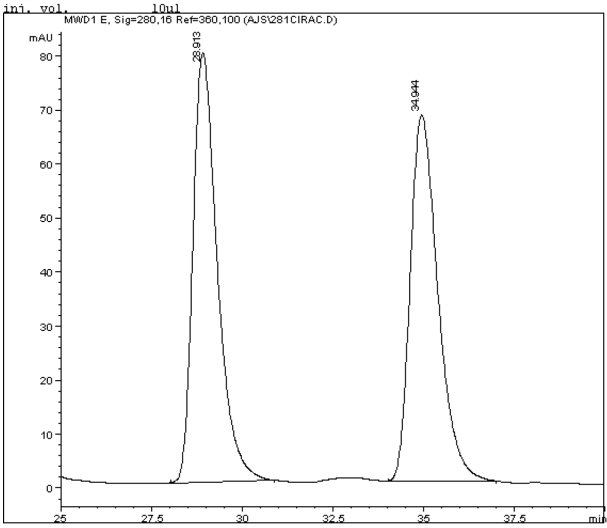


```
Meas. R Area %   Width  Symmetr
-------------------------------
 14.854  11.116   0.450   0.667
 16.833  88.884   0.501   0.682
-------------------------------
```



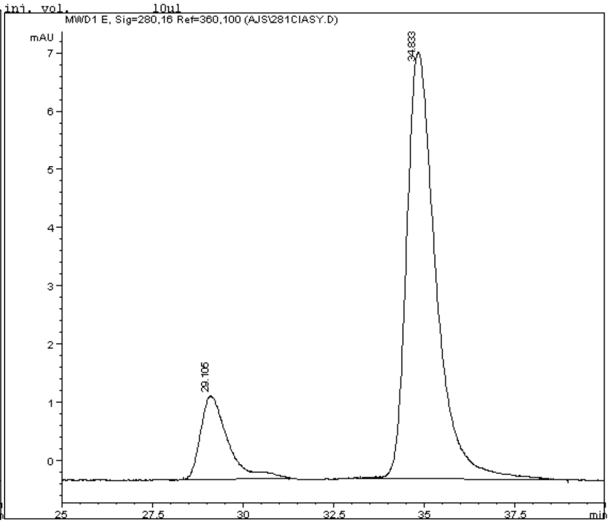
5d

```
Data File name:                           C:\HPCHEM\1\DATA\AJS\281CIRAC.D
Method name:                ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 89
Sample:             AJS04-249ci-X6
inj. vol.           10ul
```

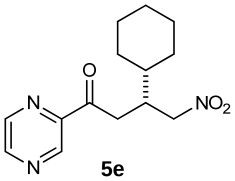


```
Meas. R Area %   Width  Symmetr
------------------------------
 28.913  50.745   0.706   0.636
 34.944  49.255   0.806   0.657
------------------------------
```

```
Data File name:                           C:\HPCHEM\1\DATA\AJS\281CIASY.D
Method name:                ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 90
Sample:             AJS04-281ci-B1
inj. vol.           10ul
```

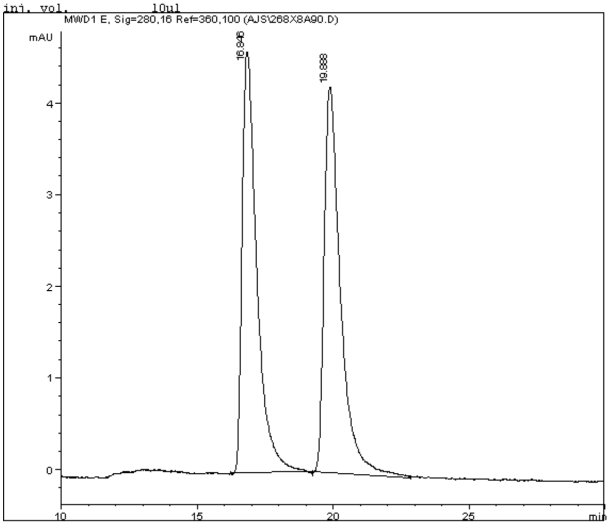


```
Meas. R Area %   Width  Symmetr
------------------------------
 29.105  15.406   0.876   0.567
 34.833  84.594   0.935   0.635
------------------------------
```



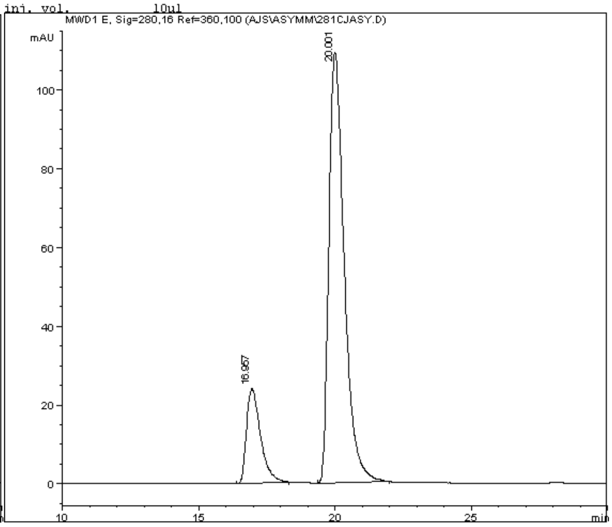
5e

```
Data File name:                           C:\HPCHEM\1\DATA\AJS\268X8A90.D
Method name:                ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 18/09/2012
location:           Vial 5
Sample:             AJS04-268-X8
inj. vol.           10ul
```

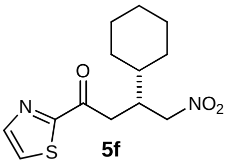


```
Meas. R Area %   Width  Symmetr
------------------------------
 16.846  49.545   0.626   0.499
 19.888  50.455   0.696   0.526
------------------------------
```

```
Data File name:                           C:\HPCHEM\1\DATA\AJS\ASYMM\      ->
Method name:                ADH9010L.M
data acquired by:   Hon Wai Lam
on:                 17/11/2012
location:           Vial 95
Sample:             AJS04-281cj-B1
inj. vol.           10ul
```

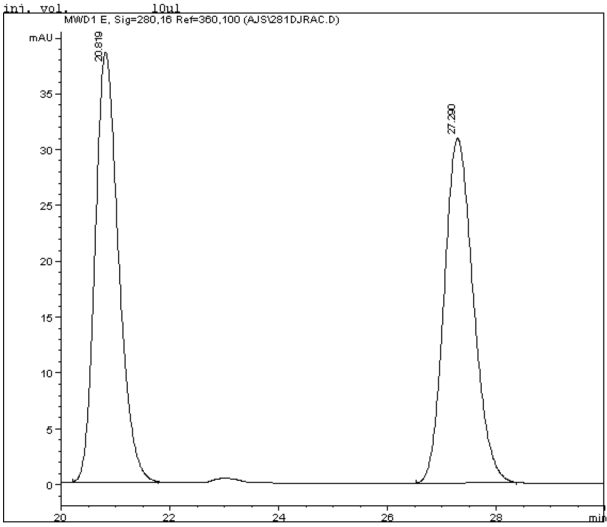


```
Meas. R Area %   Width  Symmetr
------------------------------
 16.957  16.715   0.548   0.570
 20.001  83.285   0.604   0.600
------------------------------
```



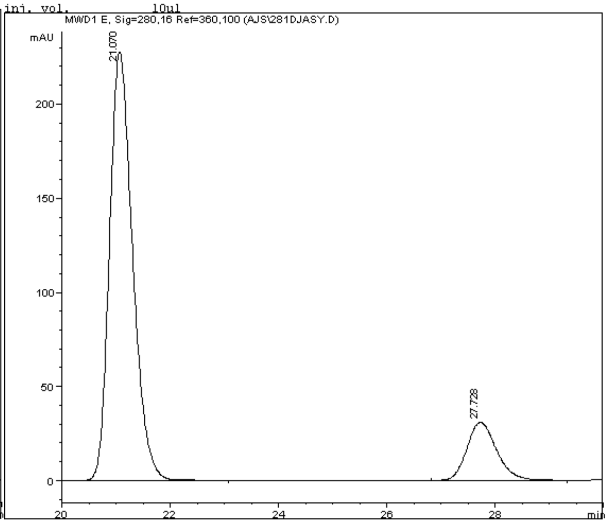
5f

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\281DJRAC.D
Method name:                  IC9010AS.M
data acquired by:    Hon Wai Lam
on:                  21/11/2012
location:            Vial 97
Sample:              AJS04-283dj-Z1
inj. vol.            10ul
```

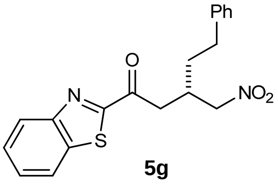


```
Meas. R Area %   Width  Symmetr
-------------------------------
 20.819  50.006   0.458   0.757
 27.290  49.994   0.576   0.816
-------------------------------
```

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\281DJASY.D
Method name:                  IC9010AS.M
data acquired by:    Hon Wai Lam
on:                  22/11/2012
location:            Vial 98
Sample:              AJS04-281dj-B1
inj. vol.            10ul
```

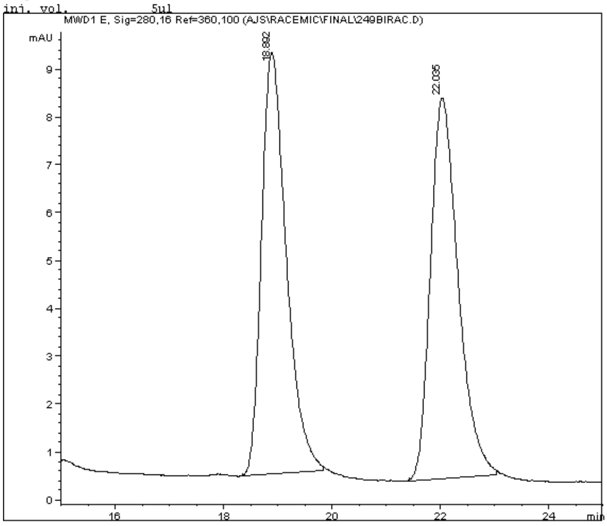


```
Meas. R Area %   Width  Symmetr
-------------------------------
 21.070  85.058   0.493   0.751
 27.728  14.942   0.636   0.806
-------------------------------
```



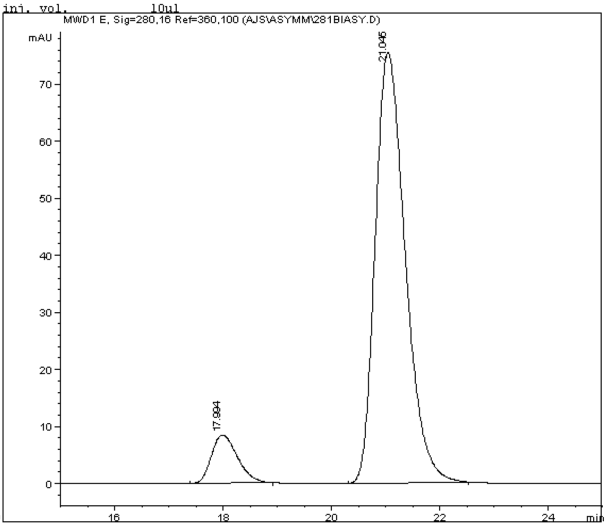
5g

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\RACEMIC\FINA->
Method name:                  ADH9010.M
data acquired by:    Hon Wai Lam
on:                  30/07/2012
location:            Vial 1
Sample:              AJS04-249bi-TOP
inj. vol.            5ul
```

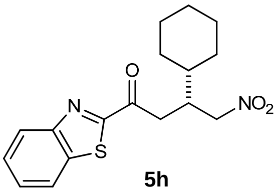


```
Meas. R Area %   Width  Symmetr
-------------------------------
 18.892  49.873   0.477   0.663
 22.035  50.127   0.522   0.698
-------------------------------
```

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\ASYMM\      ->
Method name:                  ADH9010L.M
data acquired by:    Hon Wai Lam
on:                  17/11/2012
location:            Vial 92
Sample:              AJS04-281bi-B1
inj. vol.            10ul
```

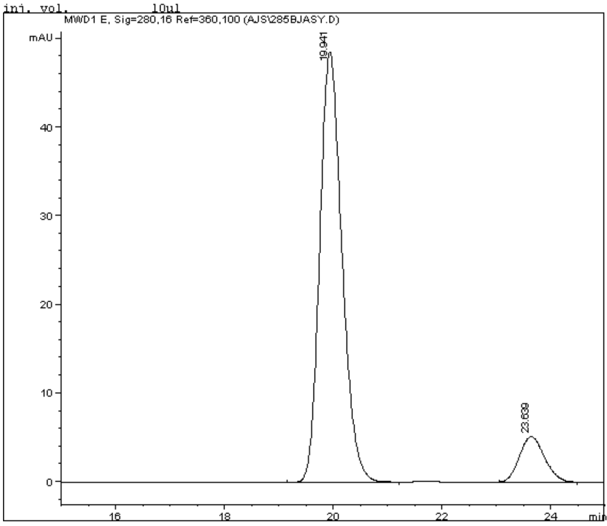


```
Meas. R Area %   Width  Symmetr
-------------------------------
 17.994   8.985   0.514   0.711
 21.045  91.015   0.597   0.699
-------------------------------
```



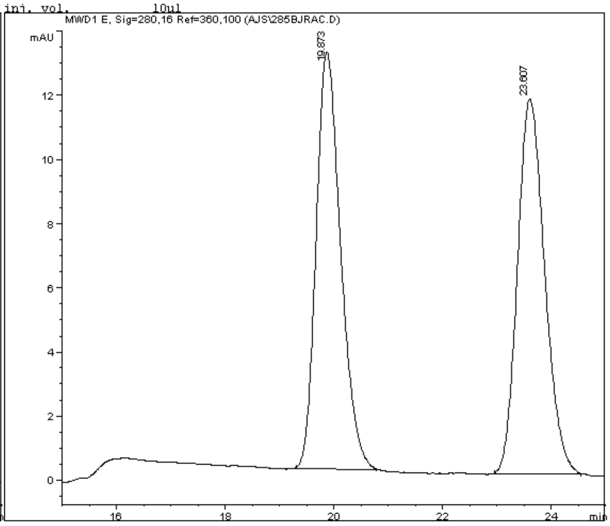
5h

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\285BJASY.D
Method name:                 IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 23/11/2012
location:           Vial 16
Sample:             AJS04-285bj-B1
inj. vol.           10ul
```

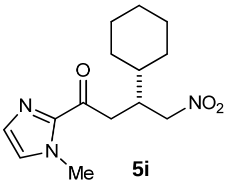


```
Meas. R Area %   Width  Symmetr
-------------------------------
 19.941  89.103   0.474   0.799
 23.639  10.897   0.482   0.836
-------------------------------
```

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\285BJRAC.D
Method name:                 IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 23/11/2012
location:           Vial 15
Sample:             AJS04-249bj-Z1
inj. vol.           10ul
```

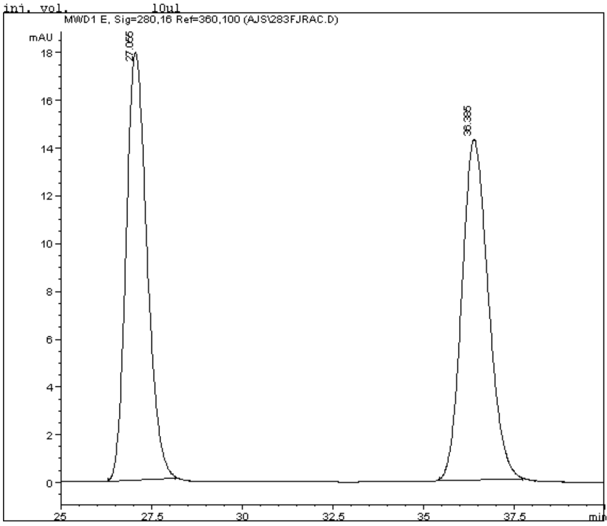


```
Meas. R Area %   Width  Symmetr
-------------------------------
 19.873  50.032   0.472   0.737
 23.607  49.968   0.534   0.797
-------------------------------
```



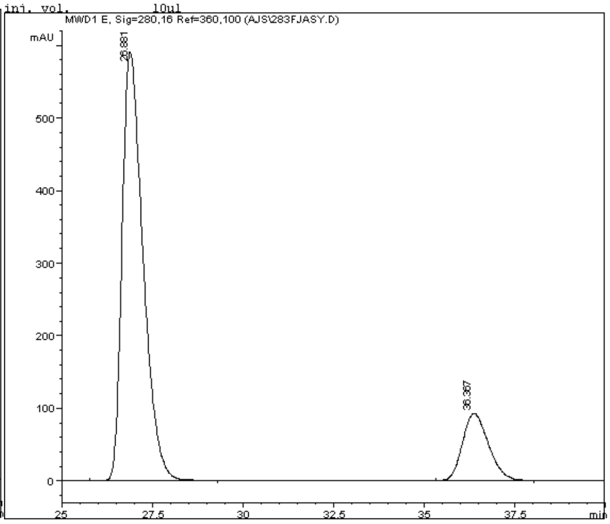
5i

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\283FJRAC.D
Method name:                 IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 99
Sample:             AJS04-283fj-Z1
inj. vol.           10ul
```



```
Meas. R Area %   Width  Symmetr
-------------------------------
 27.055  49.901   0.608   0.779
 36.385  50.099   0.765   0.817
-------------------------------
```

```
Data File name:                              C:\HPCHEM\1\DATA\AJS\283FJASY.D
Method name:                 IC9010AS.M
data acquired by:   Hon Wai Lam
on:                 22/11/2012
location:           Vial 100
Sample:             AJS04-281fj-B1
inj. vol.           10ul
```



```
Meas. R Area %   Width  Symmetr
-------------------------------
 26.881  83.555   0.668   0.597
 36.367  16.445   0.783   0.754
-------------------------------
```

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