# Supporting Information for

# Chiral Anthranilic Pyrrolidine as Custom-made Amine Catalyst for Enantioselective Michael Reaction of Nitroalkenes with Carbonyl Compounds

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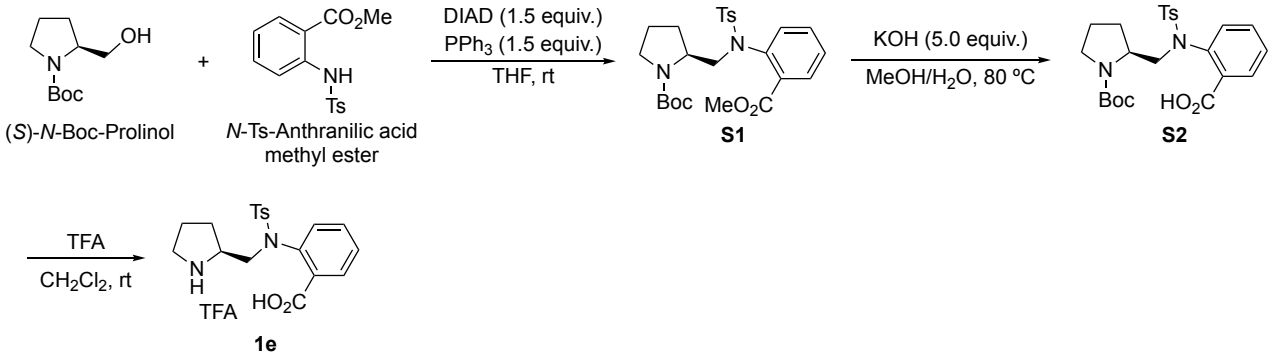
**1. General Methods.** $^{1}H$ NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. $^{13}C$ NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.0 ppm). High-resolution mass spectra were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Infrared (IR) spectra were recorded on a JASCO FT/IR 4100 spectrometer. Single crystal X-ray diffraction data were collected at 173K on a Bruker SMART APEX II ultra CCD diffractometer with Cu Kα (λ = 1.54178) radiation and graphite monochromator. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. silica gel 60N, Prod. No. 37560-84; Merck silica gel 60, Prod. No. 1.09385.9929). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. In experiments that required dry solvents such as DMSO and *i*-PrOH were distilled in prior to use.

**2. Procedure for Synthesis of Chiral Anthranilic Pyrrolidine Catalyst (1).**

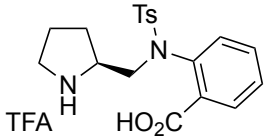
**< Synthesis of Chiral Anthranilic Pyrrolidine Acid (1e) >**




To a solution of *N*-Boc-Prolinol (2.01g, 10.0 mmol) and *N*-Ts-anthranilic acid methyl ester (3.05 g, 10.0 mmol) and $PPh_3$ (3.93 g, 15.0 mmol) in THF (50 mL) was added DIAD (in toluene 1.9 M, 7.89 mL, 15.0 mmol) at 0 ºC. The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was concentrated reduced pressure, and the crude product was purified by column chromatography (eluent: hexane/AcOEt = 5/1) to give the desired product **S1** (4.86 g, >99% yield).

To a solution of **S1** (4.86 g, 10.0 mmol) in MeOH (25 mL) and $H_2O$ (25 mL) was added KOH (2.81 g, 50.0 mmol) at room temperature. The reaction mixture was stirred under reflux conditions at 80 ºC for 18 h. The reaction mixture was washed with $Et_2O$ (15 mL×5). The aqueous layer was acidified with 1*N* HCl aqueous solution until pH to 1. The product was extracted with AcOEt (15 mL × 3). The organic phase was dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure to give the desired product **S2** (4.72 g, >99% yield).

To a solution of **S2** (1.80 g, 3.79 mmol) in $CH_2Cl_2$ (38 mL) was added TFA (11 mL) at room temperature. The reaction mixture was stirred room temperature for 15 h. The volatile solvents were removed under reduced pressure. $Et_2O$ was added, then the precipitated solid was washed with $Et_2O$ (20 mL) to give the desired product **1e** (1.65 g, 89% yield).




**(*S*)-2-((4-Methyl-*N*-(pyrrolidin-2-ylmethyl)phenyl)sulfonamido)benzoic acid TFA salt (1e):** White solid, mp 180.0-180.5 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.71 (brs, 1H), 10.16 (brs, 0.6H), 9.57 (brs, 0.4H), 9.01 (brs, 0.6H), 8.79 (brs, 0.4H), 8.30-8.11 (m, 1H), 7.63-7.42 (m, 4H), 7.37-7.28 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 0.4H), 6.80-6.68 (m, 0.6H), 4.96-4.81 (m, 0.6H), 4.76-4.63 (m, 0.4H), 4.10-3.95 (m, 0.4H), 3.95-3.73 (m, 1H), 3.64 (d, *J* = 16.0 Hz, 0.4H), 3.58-3.31 (m, 1.6H), 3.44 (d, *J* = 16.0 Hz, 0.6H), 2.44 (s, 3H), 2.28-2.12 (m, 0.6H), 2.12-1.76 (m, 2.6H), 1.73-1.58 (m, 0.4H), 1.38-1.22 (m, 0.4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.5 and 144.1 (rotamers), 140.5, 137.9, 134.9 and 134.1 (rotamers), 133.1 and 132.9 (rotamers), 132.7 (2C), 130.0 and 129.9 (rotamers) (2C), 129.0 and 128.5 (rotamers), 127.9 and 127.6 (rotamers) (2C),

127.5 and 126.0 (rotamers), 59.5 and 59.3 (rotamers), 51.1 and 48.2 (rotamers), 45.4 and 45.1 (rotamers), 26.9 and 25.5 (rotamers), 22.9 and 22.2 (rotamers), 21.5. IR (neat) 2978, 2931, 2781, 1700, 1666, 1409, 1346, 1269, 1180, 1162, 1130 $cm^{-1}$. HRMS (ESI) *m/z*: $[M+H–TFA]^+$ calcd for $C_{19}H_{23}N_2O_4S$ 375.1373, found 375.1364. $[\alpha]_D^{20} = 4.3$ (*c* 1.1, $CHCl_3$, >99% ee (*S*)).

**Crystal data of 1e:** Recrystallization of **1e** was carried out by slow evaporation from $Et_2O$ and MeOH solution at room temperature. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2098360. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

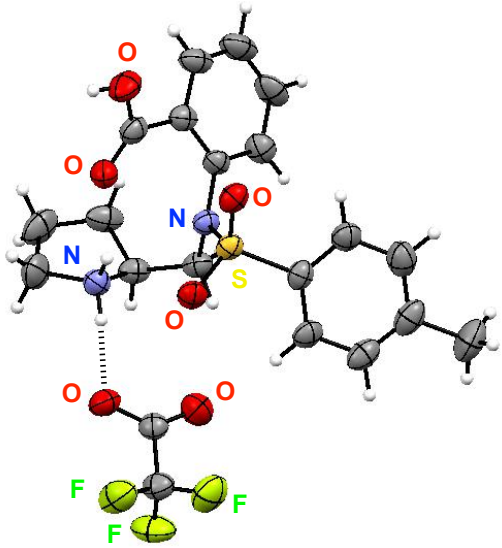
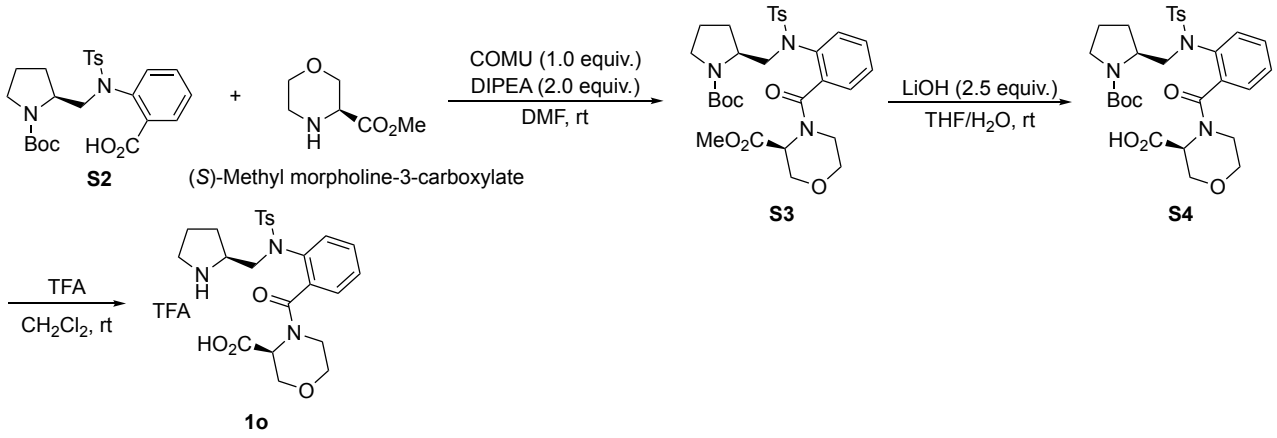



**Figure S1.** ORTEP drawing of **1e**. The ellipsoids correspond to 50% probability.

| | |
|---|---|
| Formula | $C_{21}H_{23}F_3N_2O_6S$ |
| Formula Weight | 488.47 |
| Temperature | 123 K |
| Wavelength | 1.54178 Å |
| Crystal System | Monoclinic |
| Space Group | P 1 21 1 |
| Unit Cell Dimensions | *a* = 16.1768(16) Å α = 90.00 º |
| | *b* = 7.6356(7) Å β = 92.555(4) º |
| | *c* = 18.1963(17) Å γ = 90.00 º |
| Volume | 2245.4(4) $Å^3$ |
| Z Value | 4 |
| Calculated Density | 1.445 g $cm^{-3}$ |
| Absorption coeficiente | 1.877 $mm^{-1}$ |
| F(000) | 1016 |

| | |
|---|---|
| Crystal size | 0.20×0.10×0.05 $mm^3$ |
| Theta Range for Data Collection | 2.430-68.706º |
| Index Ranges | $-19 \le h \le 19$, $-9 \le k \le 9$, $-21 \le l \le 21$ |
| Reflections Collected | 27043 |
| Independent Reflections | 7981 [R(int) = 0.0266] |
| Completeness to Theta = 68.706º | 98.5% |
| Refinement Method | Full-matrix least-squares on $F^2$ |
| Data/ Restraints/ Parameters | 7981/1/644 |
| Goodness-of-Fit on $F^2$ | 1.050 |
| Final R Indices [I>2sigma(I)] | $R_1 = 0.0547$ and $wR_2 = 0.1526$ |
| R Indices (All Data) | $R_1 = 0.0560$ and $wR_2 = 0.1544$ |
| Largest Diff. Peak and Hole | 0.651 and –0.315 $e^-/ Å^3$ |
| Flack x | 0.055(6) |

**< Synthesis of Chiral Anthranilic Pyrrolidine Peptide-like Catalyst (1o) >**

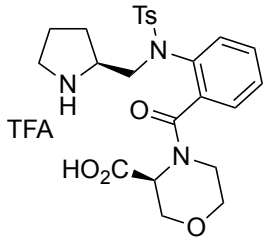



To a solution of **S2** (985.9 mg, 2.08 mmol) and DIPEA (361.8 μL, 2.08 mmol) in DMF (10 mL) was added COMU (889.7 mg, 2.08 mmol) at 0 ºC, the mixture was stirred at 0 ºC for 10 min. Then, (*S*)-methyl morpholine-3-carboxylate (301.6 mg, 2.08 mmol) and DIPEA (361.8 μL, 2.08 mmol) was added to the mixture at 0 ºC, the mixture was stirred at 0 ºC for 1 h. The reaction mixture was stirred at room temperature for 18 h. $H_2O$ (5 mL) was added to the mixture, and the product was extracted with AcOEt (15 mL × 3). The organic phase was washed with saturated $NaHCO_3$ aqueous solution, 1*N* HCl aqueous solution, and brine, and dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluent: hexane/AcOEt = 3/2) to give the desired product **S3** (967.8 mg, 77% yield).

To a solution of **S3** (967.8 mg, 1.61 mmol) in THF (8 mL) and $H_2O$ (8mL) was added LiOH

(96.3 mg, 4.02 mmol) at room temperature. The reaction mixture was stirred room temperature for 18 h. The reaction mixture was washed with $Et_2O$ (15 mL×3). The aqueous layer was acidified with 1*N* HCl aqueous solution until pH to 1. The product was extracted with AcOEt (15 mL × 3). The organic phase was dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure to give the desired product **S4** (708.4 mg, 75% yield).

To a solution of **S4** (708.4 mg, 1.21 mmol) in $CH_2Cl_2$ (12 mL) was added TFA (3 mL) at room temperature. The reaction mixture was stirred room temperature for 18 h. The volatile solvents were removed under reduced pressure. $Et_2O$ was added, then the precipitated solid was washed with $Et_2O$ (20 mL) to give the desired product **1o** (550.8 mg, 76% yield).



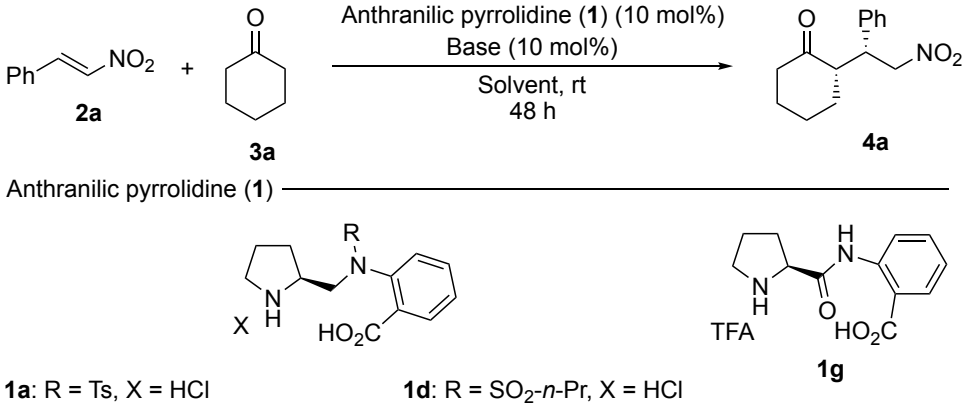

**(*S*)-4-(2-((4-Methyl-*N*-(((*S*)-pyrrolidin-2-yl)methyl)phenyl)sulfonamido)benzoyl)morpholine-3-carboxylic acid TFA salt (1o):** White solid, mp 146.5-147.0 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 11.25 (brs, 1H), 10.16 (brs, 0.7H), 9.54 (brs, 1H), 9.46 (brs, 0.3 H), 7.57-7.29 (m, 7H), 6.75 (d, *J* = 8.0 Hz, 0.7H), 6.70 (d, *J* = 7.2 Hz, 0.3H), 5.23 (s, 0.7H), 4.60 (d, *J* = 12.8 Hz, 0.3H), 4.51 (d, *J* = 12.0 Hz, 0.7H), 4.28 (d, *J* = 11.6 Hz, 0.3H), 4.24-4.04 (m, 1.3H), 4.04-3.35 (m, 7.4H), 3.35-3.13 (m, 1.3H), 2.46 (s, 3H), 2.36-1.92 (m, 3.3H), 1.92-1.74 (m, 0.7H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.7 and 170.8 (rotamers), 170.4 and 169.5 (rotamers), 161.4, 144.9 and 144.7 (rotamers), 137.25 and 137.19 (rotamers), 136.2 and 135.5 (rotamers), 133.7 and 133.1 (rotamers), 131.4 and 131.1 (rotamers), 129.8 (2C), 128.9 and 128.8 (rotamers), 128.3 and 127.7 (rotamers), 128.2 and 127.4 (rotamers), 127.8 (2C), 67.7 and 67.3 (rotamers), 66.3 and 66.1 (rotamers), 63.1 and 58.9 (rotamers), 52.2 and 50.1 (rotamers), 45.9 and 44.2 (rotamers), 44.7 and 39.6 (rotamers), 26.5 and 25.5 (rotamers), 22.0 and 21.7 (rotamers), 21.5. IR (neat) 2986, 2947, 1720, 1681, 1619, 1459, 1393, 1349, 1307, 1166, 1133, 1118 $cm^{-1}$. HRMS (ESI) *m/z*: $[M+H-TFA]^+$ calcd for $C_{24}H_{30}N_3O_6S$ 488.1850, found 488.1844. $[\alpha]_D^{20} = -52.9$ (*c* 1.1, $CHCl_3$, >99% ee (*S*)).

## 3. Procedure for Enantioselective Michael Reaction of Nitroalkenes (2) with Cyclic Ketones (3) Using Anthranilic Pyrrolidine Catalyst (1e) (Scheme 2 and Scheme 3).

To a solution of catalyst **1e** (12.2 mg, 0.025 mmol) in *i*-PrOH (250 μL) was added 2,6-lutidine (2.9

μL, 0.025 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 10 min. Then, *trans*-β-nitrostyrene (**2a**) (37.3 mg, 0.25 mmol) and cyclohexanone (**3a**) (259.1 μL, 2.5 mmol) was added to the mixture at room temperature, and the mixture was stirred at room temperature for 48 h. Saturated $NaHCO_3$ aqueous solution (5 mL) was added to the mixture, and the product was extracted with AcOEt (15 mL × 3). The organic phase was washed with brine and dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluent: hexane/AcOEt = 5/1) to give the desired product **4a** (61.5 mg, >99% yield, dr = 93:7, 96% ee).

**Table S1.** Screening for chiral anthranilic pyrrolidine catalyst (**1**) for enantioselective Michael reaction of β-nitrostyrene (**2a**) with cyclohexanone (**3a**).



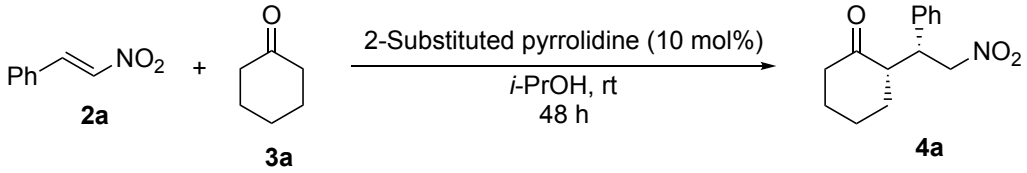

**1a**: R = Ts, X = HCl
**1b**: R = $SO_2$-1-Naphthyl, X = HCl
**1c**: R = $SO_2$-1-Naphthyl, X = $HBPh_4$
**1d**: R = $SO_2$-*n*-Pr, X = HCl
**1e**: R = Ts, X = TFA
**1f**: R = $SO_2$-*n*-Pr, X = TFA

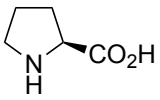
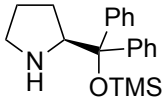
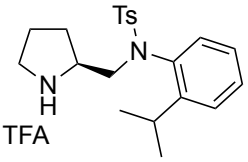
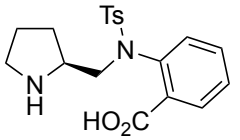
| Entry | Cat | Base | Solvent | Yield (%) | Dr | Ee (%)[a] |
|---|---|---|---|---|---|---|
| 1 | **1a** | NMM[b] | *i*-PrOH | 70 | 92:8 | 93 |
| 2 | **1a** | Pyridine | *i*-PrOH | 39 | 96:4 | 95 |
| 3 | **1a** | 2,6-Lutidine | *i*-PrOH | 90 | 96:4 | 95 |
| 4 | **1a** | 2,6-Lutidine | DMSO | 58 | 88:12 | 93 |
| 5 | **1b** | 2,6-Lutidine | *i*-PrOH | 72 | 97:3 | 96 |
| 6 | **1c** | 2,6-Lutidine | *i*-PrOH | 78 | 97:3 | 96 |
| 7 | **1d** | 2,6-Lutidine | *i*-PrOH | 38 | 96:4 | 93 |
| 8 | **1e** | 2,6-Lutidine | *i*-PrOH | >99 | 93:7 | 96 |
| 9 | **1f** | 2,6-Lutidine | *i*-PrOH | 80 | 96:4 | 91 |
| 10 | **1g** | 2,6-Lutidine | *i*-PrOH | >99 | 92:8 | 58 |
| 11[c] | **1e** | 2,6-Lutidine | *i*-PrOH | 84 | 96:4 | 94 |
| 12 | **1e** | - | *i*-PrOH | 64 | 97:3 | 95 |

[a]Numbers indicate ee of *syn*-product as the major diastereomer. [b]NMM=*N*-methylmorpholine. [c]2,6-Lutidine

(20 mol%) was used.

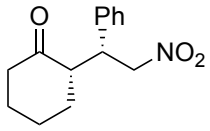
**Table S2.** Other chiral 2-substituted pyrrolidine catalyst for enantioselective Michael reaction of β-nitrostyrene (**2a**) with cyclohexanone (**3a**).



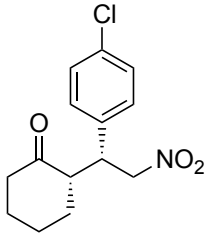

| 2-Substituted pyrrolidine, Yield (%), Dr, and Ee (%) | | | | |
|---|---|---|---|---|
|  |  |  |  | |
| L-Proline | Prolinol | Prolinol + 4-$NO_2$-$C_6H_4CO_2H$ (10 mol%) | Aniline-type pyrrolidine + 2,6-Lutidine (10 mol%) | Salt-free anthranilic pyrrolidine |
| 97% yield[a] | 3% | 7% | 98% yield | 22% yield |
| dr = 92:8 | - | - | dr = 97:3 | dr = 94:6 |
| 25% ee | - | - | 94% ee | 91% ee |

[a] For 24 h

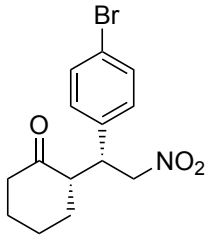
[a] The reaction was carried out for 24 h.



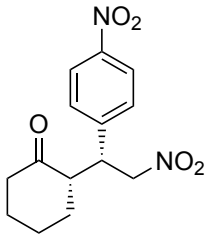

**(*S*)-2-((*R*)-2-Nitro-1-phenylethyl)cyclohexan-1-one (4a):**[1] >99% yield, 61.5 mg, White solid, mp 132.5-133.0 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H), 7.29-7.24 (m, 1H), 7.19-7.14 (m, 2H), 4.94 (dd, *J* = 12.6, 4.6 Hz, 1H), 4.63 (dd, *J* = 12.6, 10.1 Hz, 1H), 4.63 (td, *J* = 10.1, 4.6 Hz, 1H), 2.74-2.64 (m, 1H), 2.52-2.44 (m, 1H), 2.44-2.34 (m, 1H), 2.14-2.03 (m, 1H), 1.83-1.50 (m, 4H), 1.30-1.17 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 212.0, 137.7, 128.9 (2C), 128.1 (2C), 127.8, 78.9, 52.5, 43.9, 42.7, 33.2, 28.5, 25.0. IR (neat) 2955, 1696, 1550, 1385, 1129, 1013 $cm^{-1}$. $[\alpha]_D^{20}$ = –29.3 (*c* 1.1, $CHCl_3$, 93% ee (*S,R*)). HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 75/25, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 9.3 min (minor, *R,S*), 13.4 min (major, *S,R*).




**(*S*)-2-((*R*)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexan-1-one (4b):**[1] 90% yield, 63.1 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.15-7.09 (m, 2H), 4.93 (dd, *J* = 12.7, 4.6 Hz, 1H), 4.60 (dd, *J* = 12.7, 10.1 Hz, 1H), 3.76 (td, *J* = 10.1, 4.6 Hz, 1H), 2.70-2.60 (m, 1H), 2.52-2.44 (m, 1H), 2.44-2.32 (m, 1H), 2.15-2.04 (m, 1H), 1.86-1.50 (m, 4H), 1.30-1.16 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.5, 136.2, 133.6, 129.5 (2C), 129.1 (2C), 78.6, 52.4, 43.3, 42.7, 33.1, 28.4, 25.0. IR (neat) 2947, 1697, 1553, 1386, 1131, 1099, 1013 $cm^{-1}$. HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 17.2 min (minor, *R,S*), 29.8 min (major, *S,R*).

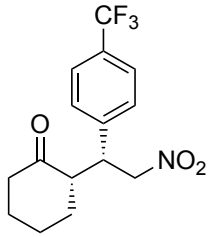



**(*S*)-2-((*R*)-1-(4-Bromophenyl)-2-nitroethyl)cyclohexan-1-one (4c):**[1] 94% yield, 77.0 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2H), 7.09-7.04 (m, 2H), 4.93 (dd, *J* = 12.8, 4.6 Hz, 1H), 4.60 (dd, *J* = 12.8, 10.2 Hz, 1H), 3.75 (td, *J* = 10.2, 4.6 Hz, 1H), 2.65 (dddd, *J* = 10.7, 10.0, 5.3, 0.9 Hz, 1H), 2.52-2.44 (m, 1H), 2.43-2.32 (m, 1H), 2.15-2.04 (m, 1H), 1.85-1.51 (m, 4H), 1.29-1.17 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.5, 136.8, 132.1 (2C), 129.9 (2C), 121.7, 78.5, 52.3, 43.4, 42.7, 33.1, 28.4, 25.0. IR (neat) 2931, 1696, 1552, 1387, 1130, 1074, 1011 $cm^{-1}$. HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 17.0 min (minor, *R,S*), 29.4 min (major, *S,R*).

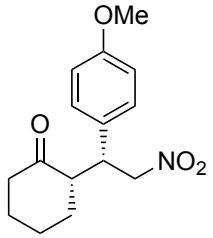



**(*S*)-2-((*R*)-2-Nitro-1-(4-nitrophenyl)ethyl)cyclohexan-1-one (4d):**[2] 79% yield, 57.7 mg, Yellow solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25-8.17 (m, 2H), 7.45-7.36 (m, 2H), 5.00 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.70 (dd, *J* = 13.2, 10.2 Hz, 1H), 3.94 (td, *J* = 10.2, 4.8 Hz, 1H), 2.77-2.67 (m, 1H),

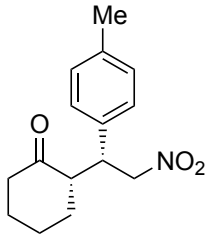
2.55-2.46 (m, 1H), 2.46-2.34 (m, 1H), 2.18-2.08 (m, 1H), 1.87-1.78 (m, 1H), 1.75-1.56 (m, 3H), 1.34-1.18 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 210.8, 147.4, 145.5, 129.3 (2C), 124.0 (2C), 77.9, 52.1, 43.7, 42.7, 33.1, 28.2, 25.0. IR (neat) 2943, 1705, 1550, 1518, 1345, 1130, 1015 $cm^{-1}$. HPLC analysis; Daicel Chiralpack AD-H, Hexane/*i*-PrOH = 75/25, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 13.3 min (minor, *R,S*), 27.9 min (major, *S,R*).



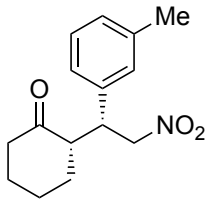

**(*S*)-2-((*R*)-2-Nitro-1-(4-(trifluoromethyl)phenyl)ethyl)cyclohexan-1-one (4e):**[3] 90% yield, 70.9 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.97 (dd, *J* = 13.0, 4.6 Hz, 1H), 4.67 (dd, *J* = 13.0, 10.1 Hz, 1H), 3.86 (td, *J* = 10.1, 4.6 Hz, 1H), 2.70 (dddd, *J* = 12.7, 9.8, 5.2, 0.9 Hz, 1H), 2.53-2.45 (m, 1H), 2.44-2.33 (m, 1H), 2.16-2.06 (m, 1H), 1.86-1.76 (m, 1H), 1.76-1.51 (m, 3H), 1.31-1.18 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.3, 142.0, 130.0 (q, $J_{C–F}$ = 33.3 Hz), 128.7 (2C), 125.9 (q, $J_{C–F}$ = 2.9 Hz, 2C), 123.9 (q, $J_{C–F}$ = 276.6 Hz), 78.3, 52.3, 43.7, 42.7, 33.2, 28.4, 25.1. $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.6. IR (neat) 2961, 1697, 1555, 1329, 1115, 1017 $cm^{-1}$. HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 11.4 min (minor, *R,S*), 19.2 min (major, *S,R*).



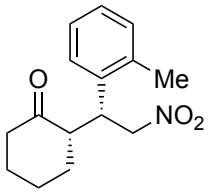

**(*S*)-2-((*R*)-1-(4-Methoxyphenyl)-2-nitroethyl)cyclohexan-1-one (4f):**[1] 94% yield, 65.4 mg, White solid, mp 148.0-148.5 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.11-7.05 (m, 2H), 6.88-6.82 (m, 2H), 4.91 (dd, *J* = 12.6, 4.8 Hz, 1H), 4.59 (dd, *J* = 12.6, 10.1 Hz, 1H), 3.78 (s, 3H), 3.71 (td, *J* = 10.1, 4.8 Hz, 1H), 2.70-2.59 (m, 1H), 2.52-2.43 (m, 1H), 2.43-2.33 (m, 1H), 2.13-2.02 (m, 1H), 1.84-1.50 (m, 4H), 1.30-1.17 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 212.1, 159.0, 129.5, 129.1 (2C), 114.3 (2C), 79.1, 55.2, 52.7, 43.2, 42.7, 33.1, 28.5, 25.0. IR (neat) 2953, 1699, 1551, 1390, 1255, 1130, 1026 $cm^{-1}$. $[\alpha]_D^{20}$ = –21.5 (*c* 1.1, $CHCl_3$, 94% ee (*S*)). HPLC analysis; Daicel Chiralpack AD-H, Hexane/*i*-PrOH = 75/25, flow rate = 0.7 mL/min, 210 nm, $t_R$ = 10.3 min (minor, *R,S*), 12.2 min (major, *S,R*).




**(*S*)-2-((*R*)-2-Nitro-1-(*p*-tolyl)ethyl)cyclohexan-1-one (4g):**[1] 96% yield, 62.7 mg, White solid, mp 130.0-130.5 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.15-7.09 (m, 2H), 7.07-7.02 (m, 2H), 4.92 (dd, *J* = 12.6, 4.6 Hz, 1H), 4.61 (dd, *J* = 12.6, 10.1 Hz, 1H), 3.72 (td, *J* = 10.1, 4.6 Hz, 1H), 2.71-2.62 (m, 1H), 2.51-2.44 (m, 1H), 2.44-2.33 (m, 1H), 2.31 (s, 3H), 2.12-2.03 (m, 1H), 1.83-1.50 (m, 4H), 1.30-1.17 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 212.1, 137.4, 134.5, 129.6 (2C), 128.0 (2C), 79.0, 52.5, 43.6, 42.7, 33.2, 28.5, 25.0, 21.1. IR (neat) 2949, 1697, 1551, 1386, 1130, 1015 cm$^{-1}$. $[\alpha]_D^{20}$ = –30.0 (*c* 1.1, $CHCl_3$, 97% ee (*S*)). HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 11.7 min (minor, *R,S*), 20.5 min (major, *S,R*).

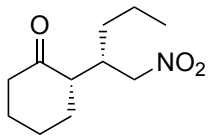



**(*S*)-2-((*R*)-2-Nitro-1-(*m*-tolyl)ethyl)cyclohexan-1-one (4h):**[4] 87% yield, 56.6 mg, White solid, mp 98.0-98.5 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 1H), 7.10-7.02 (m, 1H), 6.98-6.92 (m, 2H), 4.93 (dd, *J* = 12.8, 4.6 Hz, 1H), 4.62 (dd, *J* = 12.8, 10.1 Hz, 1H), 3.71 (td, *J* = 10.1, 4.6 Hz, 1H), 2.72-2.62 (m, 1H), 2.52-2.44 (m, 1H), 2.44-2.34 (m, 1H), 2.33 (s, 3H), 2.14-2.02 (m, 1H), 1.83-1.50 (m, 4H), 1.31-1.17 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 212.1, 138.5, 137.6, 128.9, 128.7, 128.5, 125.0, 78.9, 52.5, 43.9, 42.7, 33.2, 28.5, 25.0, 21.4. IR (neat) 2950, 1699, 1550, 1384, 1130, 1015 cm$^{-1}$. $[\alpha]_D^{20}$ = –25.2 (*c* 1.1, $CHCl_3$, 94% ee (*S*)). HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 10.6 min (minor, *R,S*), 17.6 min (major, *S,R*).

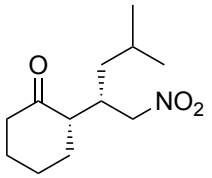



**(*S*)-2-((*R*)-2-Nitro-1-(*o*-tolyl)ethyl)cyclohexan-1-one (4i):**[4] 94% yield, 61.2 mg, White solid, mp

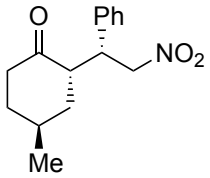
83.0-83.5 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 1H), 7.17-7.13 (m, 2H), 7.12-7.08 (m, 1H), 5.00 (dd, *J* = 12.8, 4.6 Hz, 1H), 4.61 (dd, *J* = 12.8, 10.6 Hz, 1H), 4.12 (td, *J* = 10.6, 4.6 Hz, 1H), 2.71-2.60 (m, 1H), 2.52-2.45 (m, 1H), 2.44-2.34 (m, 1H), 2.36 (s, 3H), 2.15-2.04 (m, 1H), 1.80-1.62 (m, 3H), 1.61-1.47 (m, 1H), 1.30-1.17 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 212.3, 137.4, 136.4, 131.0, 127.3, 126.7, 125.6, 78.7, 53.4, 42.9, 38.2, 32.9, 28.7, 25.3, 19.9. IR (neat) 2940, 1704, 1548, 1379, 1130 cm$^{-1}$. $[\alpha]_D^{20}$ = –33.3 (*c* 1.1, $CHCl_3$, 97% ee (*S*)). HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 10.3 min (minor, *R,S*), 10.8 min (major, *S,R*).



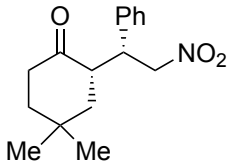

**(*S*)-2-((*S*)-1-Nitropentan-2-yl)cyclohexan-1-one (4j):** 90% yield, 47.8 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.56 (dd, *J* = 12.6, 6.2 Hz, 1H), 4.40 (dd, *J* = 12.6, 6.4 Hz, 1H), 2.65-2.54 (m, 1H), 2.54-2.45 (m, 1H), 2.45-2.37 (m, 1H), 2.37-2.22 (m, 1H), 2.17-2.03 (m, 2H), 2.01-1.88 (m, 1H), 1.77-1.57 (m, 2H), 1.57-1.20 (m, 5H), 0.92 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.3, 77.1, 51.3, 42.6, 37.0, 31.4, 30.2, 27.7, 25.2, 20.2, 14.0. IR (neat) 2958, 1707, 1547, 1381, 1124, 1018 cm$^{-1}$. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{11}H_{19}NNaO_3$ 236.1257, found 236.1259. HPLC analysis; Daicel Chiralpack AD-H, Hexane/*i*-PrOH = 75/25, flow rate = 0.7 mL/min, 214 nm, $t_R$ = 6.7 min (major, *S,R*), 7.4 min (minor, *R,S*). The absolute configuration of **4j** was assigned from that of **4m** by analogy of the HPLC analysis.



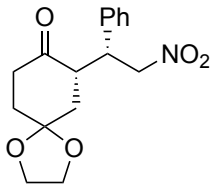

**(*S*)-2-((*S*)-4-Methyl-1-nitropentan-2-yl)cyclohexan-1-one (4k):**[5] 80% yield, 45.7 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.59 (dd, *J* = 12.8, 5.4 Hz, 1H), 4.38 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.69-2.58 (m, 1H), 2.56-2.47 (m, 1H), 2.44-2.26 (m, 2H), 2.18-2.05 (m, 2H), 2.01-1.88 (m, 1H), 1.76-1.42 (m, 4H), 1.30 (ddd, *J* = 14.0, 8.4, 5.2 Hz, 1H), 1.19 (ddd, *J* = 14.0, 9.0, 5.6 Hz, 1H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 211.2, 77.2, 51.5, 42.6, 38.5, 35.2, 30.2, 27.6, 25.5, 25.3, 23.1, 21.8. IR (neat) 2953, 1707, 1547, 1382, 1208, 1124, 1066 cm$^{-1}$. $[\alpha]_D^{20}$ = –39.7 (*c* 1.1, $CHCl_3$, 97% ee (*S*)). HPLC analysis; Daicel Chiralpack IA, Hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, 210 nm, $t_R$ = 11.6 min (major, *S,R*), 12.6 min (minor, *R,S*).




**(2*S*,4*S*)-4-Methyl-2-((*R*)-2-nitro-1-phenylethyl)cyclohexan-1-one (4l):**[2] 92% yield, 59.9 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.23 (m, 3H), 7.20-7.14 (m, 2H), 4.69 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.60 (dd, *J* = 13.2, 10.6 Hz, 1H), 3.80 (td, *J* = 10.6, 4.8 Hz, 1H), 2.77-2.68 (m, 1H), 2.54-2.46 (m, 2H), 2.12-1.94 (m, 2H), 1.69-1.58 (m, 1H), 1.52-1.36 (m, 2H), 0.97 (d, *J* = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 213.0, 137.2, 129.1 (2C), 128.01, 127.97 (2C), 79.1, 50.1, 44.1, 38.6, 37.8, 34.4, 26.5, 19.4. IR (neat) 2957, 1705, 1549, 1455, 1379, 1200, 1129 cm$^{-1}$. HPLC analysis; Daicel Chiralpack AS-H, Hexane/EtOH = 90/10, flow rate = 0.7 mL/min, 210 nm, $t_R$ = 13.1 min (minor, *R,S*), 19.4 min (major, *S,R*).

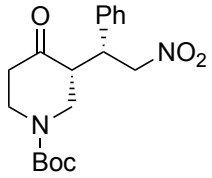



**(*S*)-4,4-Dimethyl-2-((*R*)-2-nitro-1-phenylethyl)cyclohexan-1-one (4m):**[2] 54% yield, 36.9 mg, White solid, mp 93.5-94.0 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.23 (m, 3H), 7.17-7.11 (m, 2H), 5.00 (dd, *J* = 12.6, 4.6 Hz, 1H), 4.63 (dd, *J* = 12.6, 9.8 Hz, 1H), 3.70 (td, *J* = 9.8, 4.6 Hz, 1H), 2.92-2.81 (m, 1H), 2.62-2.50 (m, 1H), 2.31 (ddd, *J* = 13.8, 4.8, 2.8 Hz, 1H), 1.80-1.70 (m, 1H), 1.64 (td, *J* = 14.0, 4.6 Hz, 1H), 1.37 (ddd, *J* = 13.8, 5.2, 3.4 Hz, 1H), 1.22 (t, *J* = 13.8 Hz, 1H), 1.13 (s, 3H), 0.88 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 212.6, 137.7, 128.9 (2C), 128.1 (2C), 127.7, 79.0, 47.6, 45.8, 43.8, 40.7, 39.1, 31.0 (2C), 24.3. IR (neat) 2957, 1707, 1549, 1431, 1377, 1122 cm$^{-1}$. $[\alpha]_D^{20}$ = –53.8 (*c* 1.0, $CHCl_3$, 93% ee (*S*)). HPLC analysis; Daicel Chiralpack AD-H, Hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 8.5 min (minor, *R,S*), 10.5 min (major, *S,R*).

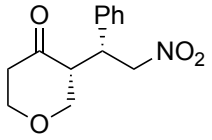



**(*S*)-7-((*R*)-2-Nitro-1-phenylethyl)-1,4-dioxaspiro[4.5]decan-8-one (4n):**[6] 89% yield, 68.1 mg, White solid, mp 129.0-129.5 ºC. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2H), 7.29-7.23 (m, 1H), 7.19-7.14 (m, 2H), 4.94 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.61 (dd, *J* = 12.8, 10.1 Hz, 1H), 4.01-3.78 (m, 5H), 3.11-3.01 (m, 1H), 2.76-2.64 (m, 1H), 4.46 (ddd, *J* = 14.2, 5.3, 3.4 Hz, 1H), 2.09-2.01 (m, 1H), 1.95 (td, *J* = 13.5, 5.2 Hz, 1H), 1.68 (ddd, *J* = 13.7, 5.7, 3.4 Hz, 1H), 1.55 (t, *J* = 13.5 Hz, 1H).

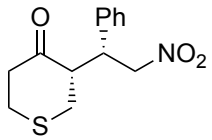
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 210.5, 137.3, 129.1 (2C), 128.3 (2C), 128.0, 107.1, 79.0, 64.9, 64.6, 48.2, 43.5, 39.4, 38.7, 35.1. IR (neat) 2954, 1719, 1545, 1381, 1119, 1045 $cm^{-1}$. $[\alpha]_D^{20} = -13.1$ (*c* 1.1, $CHCl_3$, 97% ee (*S*)). HPLC analysis; Daicel Chiralpack AS-H, Hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 16.3 min (minor, *R,S*), 27.1 min (major, *S,R*).




***tert*-butyl (*R*)-3-((*R*)-2-Nitro-1-phenylethyl)-4-oxopiperidine-1-carboxylate (4o):**[7] 85% yield, 74.3 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 3H), 7.23-7.16 (m, 2H), 4.94 (dd, *J* = 12.8, 4.4 Hz, 1H), 4.60 (dd, *J* = 12.8, 10.0 Hz, 1H), 4.37-4.08 (brs, 1H), 4.00-3.66 (m, 2H), 3.31-3.11 (m, 1H), 2.90-2.65 (m, 2H), 2.62-2.45 (m, 2H), 1.57-1.17 (m, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 208.4, 154.0, 136.3, 129.2 (2C), 128.2, 128.0 (2C), 80.7, 78.8, 51.9, 48.1, 44.2, 41.80, 41.75, 28.2 (3C). IR (neat) 2927, 1691, 1550, 1412, 1367, 1241, 1161 $cm^{-1}$. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 17.1 min (minor, *R,S*), 19.3 min (major, *S,R*).




**(*R*)-3-((*R*)-2-Nitro-1-phenylethyl)tetrahydro-4*H*-pyran-4-one (4p):**[1] 98% yield, 60.8 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.23 (m, 3H), 7.22-7.14 (m, 2H), 4.94 (dd, *J* = 12.9, 4.6 Hz, 1H), 4.65 (dd, *J* = 12.9, 10.3 Hz, 1H), 4.20-4.08 (m, 1H), 3.89-3.73 (m, 2H), 3.70 (ddd, *J* = 12.0, 5.6, 1.2 Hz, 1H), 3.27 (dd, *J* = 11.8, 9.1 Hz, 1H), 2.94-2.83 (m, 1H), 2.73-2.62 (m, 1H), 2.56 (dt, *J* = 14.2, 4.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 207.4, 136.2, 129.2 (2C), 128.3, 127.9 (2C), 78.7, 71.6, 69.0, 53.2, 43.0, 41.3. IR (neat) 2862, 1698, 1552, 1456, 1383, 1236, 1150, 1109 $cm^{-1}$. HPLC analysis; Daicel Chiralpack IA, Hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 14.7 min (minor, *R,S*), 25.6 min (major, *S,R*).

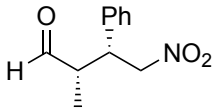



**(*S*)-3-((*R*)-2-Nitro-1-phenylethyl)tetrahydro-4*H*-thiopyran-4-one (4q):**[2] 85% yield, 56.2 mg, White solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.24 (m, 3H), 7.24-7.17 (m, 2H), 4.75 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.63 (dd, *J* = 12.8, 10.3 Hz, 1H), 3.98 (td, *J* = 10.3, 4.8 Hz, 1H), 3.11-3.01 (m,

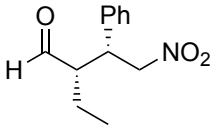
1H), 3.01-2.91 (m, 2H), 2.91-2.75 (m, 2H), 2.62 (ddd, $J$ = 14.2, 4.4, 1.8 Hz, 1H), 2.46 (dd, $J$ = 14.2, 9.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 209.5, 136.4, 129.3 (2C), 128.3, 128.1 (2C), 78.6, 54.9, 44.5, 43.4, 35.1, 31.6. IR (neat) 2900, 1702, 1545, 1427, 1380, 1291, 1112, 1080 $cm^{-1}$. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 254 nm, $t_R$ = 22.8 min (minor, *R,S*), 25.6 min (major, *S,R*).

**4. Procedure for Enantioselective Michael Reaction of Nitroalkenes (2) with Aldehydes (5) Using Anthranilic Pyrrolidine Peptide-like Catalyst (1o) (Table 2 and Scheme 4).**

To a solution of catalyst **1o** (15.0 mg, 0.025 mmol) in *i*-PrOH (250 μL) was added *N*,*N*-dimethylaniline (3.2 μL, 0.025 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 10 min. Then, *trans*-β-nitrostyrene (**2a**) (37.3 mg, 0.25 mmol) and propionaldehyde (**5a**) (180.4 μL, 2.5 mmol) was added to the mixture at 0 ºC, and the mixture was stirred at 0 ºC for 48 h. Saturated $NaHCO_3$ aqueous solution (5 mL) was added to the mixture, and the product was extracted with AcOEt (15 mL × 3). The organic phase was washed with brine and dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluent: hexane/AcOEt = 10/1) to give the desired product **6a** (45.1 mg, 87% yield, dr = 95:5, 93% ee).

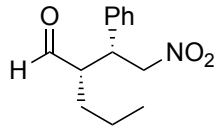



**(2*S*,3*R*)-2-Methyl-4-nitro-3-phenylbutanal (6a):**[1] 87% yield, 45.1 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.72 (d, $J$ = 1.6 Hz, 1H), 7.38-7.27 (m, 3H), 7.19-7.13 (m, 2H), 4.80 (dd, $J$ = 12.8, 5.6 Hz, 1H), 4.68 (dd, $J$ = 12.8, 9.6 Hz, 1H), 3.81 (td, $J$ = 9.6, 5.6 Hz, 1H), 2.87-2.71 (m, 1H), 1.01 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.2, 136.5, 129.1 (2C), 128.1, 128.0 (2C), 78.1, 48.4, 44.0, 12.1. IR (neat) 2924, 1722, 1549, 1455, 1379, 1097 $cm^{-1}$. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 26.6 min (major, *S,R*), 39.5 min (minor, *R,S*).

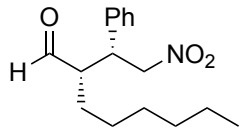



**(2*S*,3*R*)-2-Ethyl-4-nitro-3-phenylbutanal (6b):**[1] 93% yield, 51.4 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.72 (d, $J$ = 2.5 Hz, 1H), 7.38-7.27 (m, 3H), 7.21-7.15 (m, 2H), 4.72 (dd, $J$ = 12.8,

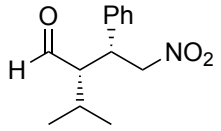
5.3 Hz, 1H), 4.63 (dd, *J* = 12.8, 9.8 Hz, 1H), 3.79 (td, *J* = 9.8, 5.3 Hz, 1H), 2.73-2.63 (m, 1H), 1.57-1.44 (m, 2H), 0.84 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.2, 136.7, 129.0 (2C), 128.1, 127.9 (2C), 78.5, 54.9, 42.6, 20.3, 10.6. IR (neat) 2967, 1717, 1550, 1379, 1203, 1089 cm$^{-1}$. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 0.7 mL/min, 210 nm, $t_R$ = 26.9 min (major, *S,R*), 33.6 min (minor, *R,S*).




**(*S*)-2-((*R*)-2-Nitro-1-phenylethyl)pentanal (6c):**[1] 92% yield, 53.9 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 3.2 Hz, 1H), 7.39-7.27 (m, 3H), 7.21-7.14 (m, 2H), 4.71 (dd, *J* = 13.2, 5.6 Hz, 1H), 4.64 (dd, *J* = 13.2, 9.6 Hz, 1H), 3.78 (td, *J* = 9.6, 5.6 Hz, 1H), 2.71 (tt, *J* = 9.6, 3.2 Hz, 1H), 1.55-1.43 (m, 1H), 1.43-1.24 (m, 2H), 1.24-1.09 (m, 1H), 0.80 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.2, 136.7, 129.1 (2C), 128.1, 127.9 (2C), 78.4, 53.7, 43.1, 29.4, 19.7, 13.9. IR (neat) 2921, 1720, 1551, 1456, 1379, 1090 cm$^{-1}$. $[\alpha]_D^{25}$ = –39.6 (*c* 1.0, $CHCl_3$, 90% ee (*S*)). HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 220 nm, $t_R$ = 15.9 min (major, *S,R*), 21.2 min (minor, *R,S*).

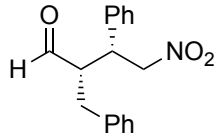



**(*S*)-2-((*R*)-2-Nitro-1-phenylethyl)octanal (6d):**[1] 97% yield, 67.4 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 3.2 Hz, 1H), 7.38-7.25 (m, 3H), 7.20-7.14 (m, 2H), 4.71 (dd, *J* = 13.0, 5.2 Hz, 1H), 4.64 (dd, *J* = 13.0, 10.0 Hz, 1H), 3.78 (td, *J* = 10.0, 5.2 Hz, 1H), 2.75-2.64 (m, 1H), 1.54-1.06 (m, 10H), 0.82 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.3, 136.7, 129.1 (2C), 128.1, 128.0 (2C), 78.4, 53.8, 43.0, 31.3, 29.0, 27.3, 26.3, 22.4, 13.9. IR (neat) 2925, 1719, 1552, 1455, 1379, 1092 cm$^{-1}$. $[\alpha]_D^{25}$ = –39.0 (*c* 1.0, $CHCl_3$, 85% ee (*S*)). HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 220 nm, $t_R$ = 13.2 min (major, *S,R*), 17.3 min (minor, *R,S*).

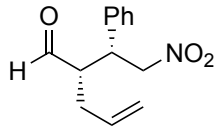



**(2*S*,3*R*)-2-Isopropyl-4-nitro-3-phenylbutanal (6e):**[1] >99% yield, 58.4 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.8 Hz, 1H), 7.38-7.25 (m, 3H), 7.23-7.16 (m, 2H), 4.67 (dd, *J* = 12.8, 4.4 Hz, 1H), 4.57 (dd, *J* = 12.8, 10.4 Hz, 1H), 3.90 (td, *J* = 10.4, 4.4 Hz, 1H), 2.78

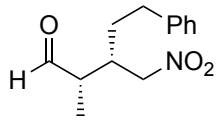
(ddd, $J$ = 10.4, 4.4, 2.8 Hz, 1H), 1.78-1.64 (m, 1H), 1.10 (d, $J$ = 7.4 Hz, 3H), 0.88 (d, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.4, 137.0, 129.1 (2C), 128.1, 127.9 (2C), 79.0, 58.7, 41.9, 27.9, 21.6, 16.9. IR (neat) 2921, 1715, 1550, 1455, 1378, 1089 cm$^{-1}$. $[\alpha]_D^{25}$ = –69.8 (*c* 1.0, $CHCl_3$, 91% ee (*S*)). HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 95/5, flow rate = 0.5 mL/min, 220 nm, $t_R$ = 27.4 min (minor, *R,S*), 28.9 min (major, *S,R*).




**(2*S*,3*R*)-2-Benzyl-4-nitro-3-phenylbutanal (6f):**[1] 93% yield, 65.6 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, $J$ = 2.0 Hz, 1H), 7.42-7.15 (m, 8H), 7.06-7.00 (m, 2H), 4.74 (dd, $J$ = 13.2, 6.4 Hz, 1H), 4.70 (dd, $J$ = 13.2, 8.6 Hz, 1H), 3.82 (td, $J$ = 8.6, 6.4 Hz, 1H), 3.16-3.07 (m, 1H), 2.80-2.70 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.0, 137.1, 136.6, 129.3 (2C), 128.8 (2C), 128.7 (2C), 128.3, 128.0 (2C), 126.9, 78.0, 55.3, 43.4, 34.2. IR (neat) 2922, 1721, 1550, 1454, 1378, 1090 cm$^{-1}$. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, 220 nm, $t_R$ = 37.4 min (major, *S,R*), 40.7 min (minor, *R,S*).

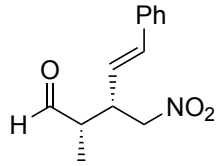



**(*S*)-2-((*R*)-2-Nitro-1-phenylethyl)pent-4-enal (6g):**[1] 87% yield, 50.9 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, $J$ = 2.4 Hz, 1H), 7.39-7.27 (m, 3H), 7.21-7.15 (m, 2H), 5.69-5.56 (m, 1H), 5.11-4.94 (m, 2H), 4.77 (dd, $J$ = 13.2, 5.2 Hz, 1H), 4.67 (dd, $J$ = 13.2, 10.0 Hz, 1H), 3.81 (td, $J$ = 10.0, 5.2 Hz, 1H), 2.90-2.81 (m, 1H), 2.27-2.18 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.7, 136.5, 132.9, 129.1 (2C), 128.2, 128.0 (2C), 118.8, 78.2, 52.9, 42.7, 31.7. IR (neat) 2920, 1722, 1550, 1454, 1379, 1089 cm$^{-1}$. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 220 nm, $t_R$ = 18.5 min (major, *S,R*), 25.7 min (minor, *R,S*).

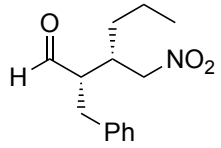



**(2*S*,3*S*)-2-Methyl-3-(nitromethyl)-5-phenylpentanal (6h):**[9] 96% yield, 56.4 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.32-7.27 (m, 2H), 7.25-7.18 (m, 1H), 7.18-7.12 (m, 2H), 4.54 (dd, $J$ = 12.8, 6.0 Hz, 1H), 4.44 (dd, $J$ = 12.8, 8.0 Hz, 1H), 2.85-2.74 (m, 1H), 2.74-2.53

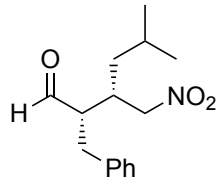
(m, 3H), 1.78 (q, $J$ = 7.6 Hz, 1H), 1.74-1.55 (m, 1H), 1.16 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.5, 140.4, 128.6 (2C), 128.2 (2C), 126.4, 76.7, 47.0, 36.7, 33.1, 30.2, 9.0. IR (neat) 2923, 1722, 1549, 1454, 1381, 1081 cm$^{-1}$. HPLC analysis; Daicel Chiralpack AD-H, Hexane/EtOH = 90/10, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 15.5 min (minor, *R,S*), 16.4 min (major, *S,R*).




**(2*S*,3*S*,*E*)-2-Methyl-3-(nitromethyl)-5-phenylpent-4-enal (6i):**[10] 90% yield, 52.3 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, $J$ = 0.8 Hz, 1H), 7.38-7.20 (m, 5H), 6.54 (d, $J$ = 16.0 Hz, 1H), 5.95 (dd, $J$ = 16.0, 9.6 Hz, 1H), 4.63-4.47 (m, 2H), 3.56-3.44 (m, 1H), 2.63-2.54 (m, 1H), 1.20 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.1, 135.8, 135.1, 128.6 (2C), 128.1, 126.4 (2C), 123.5, 77.5, 47.2, 41.8, 10.8. IR (neat) 2931, 1721, 1549, 1450, 1379, 1073 cm$^{-1}$. HPLC analysis; Daicel Chiralpack AD-H, Hexane/EtOH = 90/10, flow rate = 1.0 mL/min, 210 nm, $t_R$ = 15.5 min (minor, *R,S*), 16.4 min (major, *S,R*). The enantioselectivity of **6i** was determined after its derivatization to **6h**.

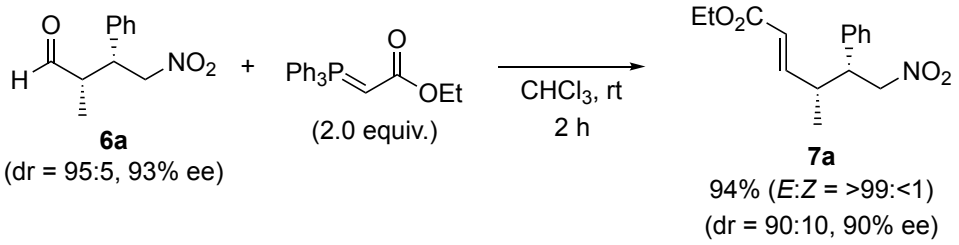



**(2*S*,3*S*)-2-Benzyl-3-(nitromethyl)hexanal (6j):**[11] >99% yield, 62.0 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.35-7.26 (m, 2H), 7.26-7.14 (m, 3H), 4.45 (dd, $J$ = 12.8, 6.8 Hz, 1H), 4.39 (dd, $J$ = 12.8, 6.8 Hz, 1H), 3.06 (dd, $J$ = 14.0, 8.8 Hz, 1H), 2.92-2.80 (m, 1H), 2.80-2.66 (m, 2H), 1.52-1.23 (m, 4H), 0.89 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.5, 138.3, 129.0 (2C), 128.9 (2C), 126.9, 77.5, 54.2, 36.8, 31.5, 31.4, 20.2, 13.9. IR (neat) 2930, 1721, 1549, 1454, 1381, 1079 cm$^{-1}$. HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{20}NO_3$ 250.1438; found 250.1439. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 220 nm, $t_R$ = 17.9 min (major, *S,R*), 19.6 min (minor, *R,S*).

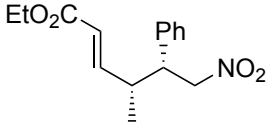


**(2*S*,3*S*)-2-Benzyl-5-methyl-3-(nitromethyl)hexanal (6k):** 92% yield, 60.4 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.35-7.28 (m, 2H), 7.26-7.17 (m, 3H), 4.45 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.40 (dd, *J* = 12.8, 7.2 Hz, 1H), 3.07 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.91-2.83 (m, 1H), 2.83-2.68 (m, 2H), 1.65-1.50 (m, 1H), 1.38-1.19 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.3, 138.2, 128.9 (2C), 128.8 (2C), 126.8, 76.97, 54.2, 38.2, 34.8, 31.3, 25.2, 22.4, 22.1. IR (neat) 2928, 1721, 1549, 1468, 1382, 1081 cm$^{-1}$. HRMS (APCI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{22}NO_3$ 264.1594; found 264.1595. HPLC analysis; Daicel Chiralpack OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, 220 nm, $t_R$ = 10.1 min (major, *S,R*), 11.3 min (minor, *R,S*). The absolute configuration of **6k** was assigned from that of **6j** by analogy of the HPLC analysis.

## 5. Transformation of chiral Michael reaction adduct (3a) into β-proline derivative (8a) (Scheme 7).

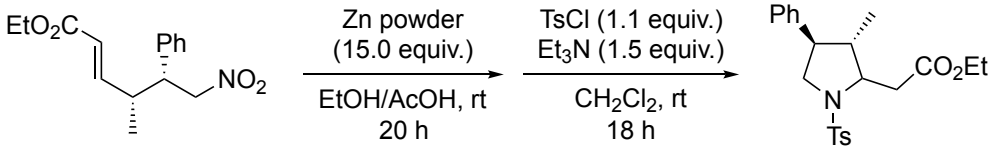



To a solution of **6a** (52.9 mg, 0.26 mmol) in $CHCl_3$ (750 μL) was added triphenylphosphonium ethoxycarbonylmethylylide (177.9 mg. 0.51 mmol), and the reaction mixture was stirred at room temperature for 2 h under argon atomosphere. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (eluent: hexane/AcOEt=10:1) to give the desired product **5** (66.5 mg, 94% yield (*E*: *Z* = >99:<1, dr = 90:10, 90% ee)).



**Ethyl (4*R*,5*R*,*E*)-4-methyl-6-nitro-5-phenylhex-2-enoate (7a):** 94% yield, 66.5 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 3H), 7.21-7.14 (m, 2H), 6.86 (dd, *J* = 16.0, 9.8 Hz, 1H), 5.92 (dd, *J* = 16.0, 0.4 Hz, 1H), 4.64 (dd, *J* = 13.2, 5.2 Hz, 1H), 4.57 (dd, *J* = 13.2, 10.4 Hz,

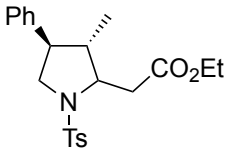
1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.37 (td, *J* = 10.4, 5.2 Hz, 1H), 2.68-2.55 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 149.8, 137.3, 128.8 (2C), 127.9 (2C), 127.9, 122.7, 79.1, 60.5, 48.9, 40.2, 18.1, 14.1. IR (neat) 2979, 1712, 1551, 1455, 1377, 1271, 1175, 1036 cm$^{-1}$. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{20}NO_4$ 278.1387; found 278.1385. HPLC analysis; Daicel Chiralpack AD-H, Hexane/EtOH = 90/10, flow rate = 1.0 mL/min, 230 nm, $t_R$ = 8.6 min (minor, *S,S*), 12.9 min (major, *R,R*).




**7a**
(dr = 90:10, 90% ee)

**8a**
68%
(dr = 87:6:5:2, 91% ee)

To a solution of **7a** (62.8 mg (dr = 90:10, 90% ee), 0.23 mmol) in EtOH (2.3 mL) and AcOH (518 μL) was added Zn powder (222.1 mg, 3.40 mmol) at –5 ºC, and the reaction mixture was stirred at room temperature for 20 h. The reaction mixture was filtered through Celite with EtOH and the organic layer was concentrated under reducecd pressure. The residue was cooled to –5 ºC and basified with 1N NaOH aqueous solution (5.0 mL) to pH 10, and the product was extracted with $CH_2Cl_2$ (10 mL × 3). The combined extracts was dried over $Na_2SO_4$. The organic phase concentrated under reduced pressure to give the crude product. To a solution of the crude product and $Et_3N$ (47.3 μL, 0.34 mmol) in $CH_2Cl_2$ (1.1 mL) was added TsCl (47.5 mg, 0.25 mmol) at room temperature, and then sttired at room temperature for 18 h. 1N HCl aqueous solution (10 mL) was added to the mixture, and the product was extracted with $CHCl_3$ (10 mL × 3). The organic products was washed with brine (10 mL) and dried over $Na_2SO_4$. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt=8:1) to give the desired product **8a** (61.5 mg, 68% yield (dr = 87:6:5:2), 91% ee).




**Ethyl 2-((3*S*,4*R*)-3-methyl-4-phenyl-1-tosylpyrrolidin-2-yl)acetate (8a):** 68% yield, 61.5 mg, Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31-7.25 (m, 2H), 7.25-7.18 (m, 1H), 7.12-7.06 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.76 (dd, *J* = 12.0, 7.6 Hz, 1H), 3.63 (ddd, *J* = 8.8, 6.8, 4.0 Hz, 1H), 3.46 (t, *J* = 12.0 Hz, 1H), 3.00 (dd, *J* = 16.4, 4.0 Hz, 1H), 2.81 (dd, *J* = 16.4, 6.8 Hz, 1H), 2.47 (s, 3H), 2.37-2.24 (m, 1H), 2.12 (td, *J* = 11.2, 7.6

Hz, 1H), 1.30 (t, $J$ = 7.2 Hz, 3H), 0.79 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.4, 143.8, 138.4, 134.8, 129.9 (2C), 128.8 (2C), 127.8 (2C), 127.6 (2C), 127.4, 63.9, 60.7, 55.4, 51.5, 47.0, 39.6, 21.7, 15.8, 14.3. IR (neat) 2963, 1730, 1454, 1344, 1289, 1161, 1092, 1030 $cm^{-1}$. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{28}NO_4S$ 402.1734; found 402.1733. HPLC analysis; Daicel Chiralpack OJ-H, Hexane/*i*-PrOH = 90/10, flow rate = 0.6 mL/min, 210 nm, $t_R$ = 31.0 min (minor), 34.9 min (major).

## 6. DFT Calculation Studies for Transition State of Enantioselective Michael Reaction of Nitroalkenes with Carbonyl compounds Using Chiral Pyrrolidyl Anthranilic Acid Catalyst

All calculation were performed with the Gaussian 16 package.[12] As a preliminary study, various TS models were explored at the B3LYP/6-311G* level according to the SCRF method based on PCM (i-PrOH). The promising TS models were further optimized at the M06-02X/6-31G* level according to the SCRF method based on PCM (i-PrOH). Frequency analyses were also carried out to identify the stationary points (TS: one imaginary frequency). Single-point energy calculations of the optimized structures were evaluated at the M06-02X/6-31G* level according to the SCRF method based on PCM (i-PrOH).

### < Transition State model of Enantioselective Michael Reaction of β-Nitrostyrene with Cyclohexanone using Catalyst 1e >

To identify the promising TS model for the enantioselective Michael reaction of β-nitrostyrene with cyclohexanone using catalyst **1e**, various TS models consisting of **1e**-enamine generated from catalyst **1e** and cyclohexanone, and β-nitrostyrene were explored based on previous studies and the results in Scheme 5. The energetically favored TS models (**TS-A**–**TS-H**) were identified at the B3LYP/6-311G** level according to the SCRF method based on PCM (*i*-PrOH). The TS models (**TS-A**–**TS-H**) were further optimized at the M06-02X/6-31G* level according to the SCRF method based on PCM (*i*-PrOH) to find the most energetically favored TS model (**TS-E**).

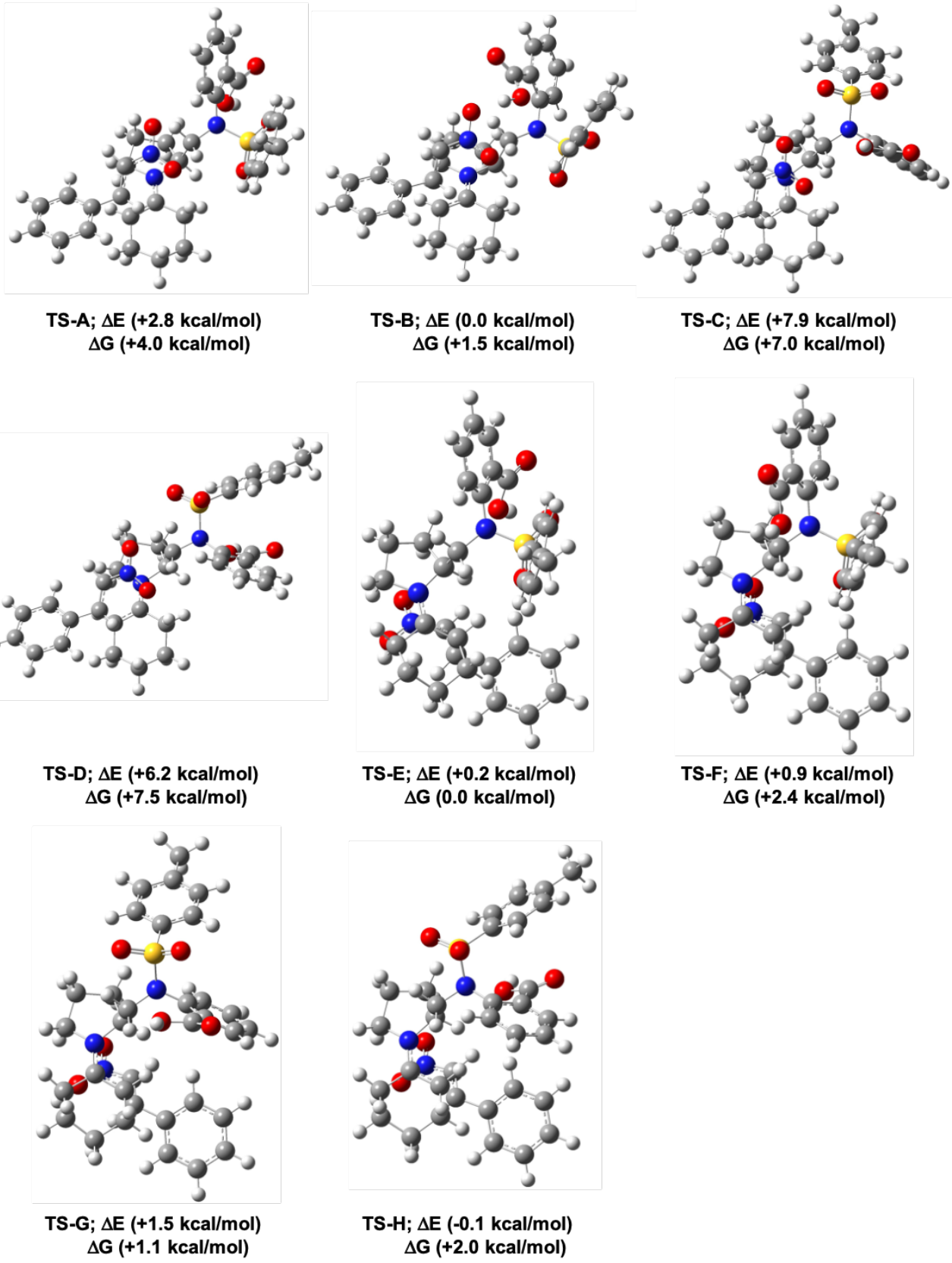



**Figure S2.** Optimized geometries for the transition states of Michael reaction of β-nitrostyrene with cyclohexanone using catalyst **1e**.

**TS-A**

M062X/6-31G*

E(RM062X) = -2292.656867 Hartree

EE+Thermal Free Energy of Correction = -2292.066382 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 1.446291 | -1.423335 | -0.997572 |
| 2 | 6 | 0 | 2.183867 | -0.416374 | -1.490816 |
| 3 | 6 | 0 | 3.573196 | -0.40759 | -1.326746 |
| 4 | 6 | 0 | 4.441044 | 0.546332 | -2.117814 |
| 5 | 6 | 0 | 3.716195 | 1.830724 | -2.513808 |
| 6 | 6 | 0 | 2.366568 | 1.490893 | -3.137433 |
| 7 | 6 | 0 | 1.482417 | 0.769867 | -2.119568 |
| 8 | 1 | 0 | 4.044989 | -1.355519 | -1.089606 |
| 9 | 1 | 0 | 5.349291 | 0.775448 | -1.549925 |
| 10 | 1 | 0 | 4.781324 | 0.035304 | -3.029049 |
| 11 | 1 | 0 | 3.555849 | 2.463684 | -1.630818 |
| 12 | 1 | 0 | 4.334424 | 2.405645 | -3.209254 |
| 13 | 1 | 0 | 1.851007 | 2.392954 | -3.479218 |
| 14 | 1 | 0 | 2.519634 | 0.852288 | -4.015889 |
| 15 | 1 | 0 | 1.23931 | 1.463102 | -1.305643 |
| 16 | 1 | 0 | 0.536603 | 0.464527 | -2.57502 |
| 17 | 6 | 0 | 2.049021 | -2.671388 | -0.492875 |
| 18 | 6 | 0 | 0.860014 | -3.427361 | 0.084065 |
| 19 | 6 | 0 | -0.259577 | -3.069655 | -0.895114 |
| 20 | 6 | 0 | -0.016869 | -1.586139 | -1.194709 |
| 21 | 1 | 0 | 2.819071 | -2.454507 | 0.245212 |
| 22 | 1 | 0 | 2.507901 | -3.21414 | -1.330754 |
| 23 | 1 | 0 | 0.638405 | -3.049243 | 1.088098 |
| 24 | 1 | 0 | 1.047276 | -4.499505 | 0.153413 |
| 25 | 1 | 0 | -1.268082 | -3.229727 | -0.50776 |
| 26 | 1 | 0 | -0.151618 | -3.655369 | -1.812814 |
| 27 | 1 | 0 | -0.294893 | -1.332807 | -2.218972 |
| 28 | 6 | 0 | -0.749827 | -0.676846 | -0.21038 |
| 29 | 1 | 0 | -0.505033 | -0.99509 | 0.804527 |
| 30 | 1 | 0 | -0.404206 | 0.357847 | -0.294126 |
| 31 | 6 | 0 | 3.690329 | 0.304369 | 0.74245 |
| 32 | 6 | 0 | 5.115151 | -0.037628 | 0.963819 |
| 33 | 6 | 0 | 6.081154 | 0.971605 | 0.87953 |
| 34 | 6 | 0 | 7.424591 | 0.69202 | 1.12004 |
| 35 | 6 | 0 | 7.820572 | -0.60275 | 1.442316 |
| 36 | 6 | 0 | 6.866236 | -1.617686 | 1.523815 |
| 37 | 6 | 0 | 5.526215 | -1.338004 | 1.286177 |
| 38 | 1 | 0 | 5.772053 | 1.983937 | 0.633241 |
| 39 | 1 | 0 | 8.15965 | 1.487373 | 1.054311 |
| 40 | 1 | 0 | 8.866673 | -0.823611 | 1.626475 |
| 41 | 1 | 0 | 7.168928 | -2.630215 | 1.769628 |
| 42 | 1 | 0 | 4.794639 | -2.13987 | 1.344648 |
| 43 | 6 | 0 | 2.729582 | -0.253436 | 1.582998 |
| 44 | 7 | 0 | 1.492786 | 0.336077 | 1.724026 |
| 45 | 8 | 0 | 0.693339 | -0.146132 | 2.55566 |
| 46 | 8 | 0 | 1.192131 | 1.341775 | 1.048578 |
| 47 | 1 | 0 | 3.493036 | 1.32282 | 0.418613 |
| 48 | 1 | 0 | 2.880491 | -1.109784 | 2.222551 |
| 49 | 7 | 0 | -2.211648 | -0.769573 | -0.364481 |
| 50 | 6 | 0 | -2.995627 | -0.995611 | 0.813144 |
| 51 | 6 | 0 | -2.614836 | -0.396432 | 2.018335 |
| 52 | 6 | 0 | -3.38977 | -0.565402 | 3.160832 |
| 53 | 6 | 0 | -4.570844 | -1.301131 | 3.105034 |
| 54 | 6 | 0 | -4.957521 | -1.885916 | 1.905709 |
| 55 | 6 | 0 | -4.170417 | -1.762899 | 0.758204 |
| 56 | 1 | 0 | -1.702739 | 0.193969 | 2.060128 |
| 57 | 1 | 0 | -3.07715 | -0.101932 | 4.090444 |
| 58 | 1 | 0 | -5.18555 | -1.420958 | 3.99018 |
| 59 | 1 | 0 | -5.872406 | -2.464125 | 1.837945 |
| 60 | 6 | 0 | -4.673043 | -2.484404 | -0.452825 |
| 61 | 8 | 0 | -5.846152 | -2.719255 | -0.63738 |
| 62 | 8 | 0 | -3.714625 | -2.929836 | -1.272557 |
| 63 | 1 | 0 | -4.158857 | -3.39213 | -2.001686 |
| 64 | 16 | 0 | -2.86296 | 0.332923 | -1.451806 |
| 65 | 8 | 0 | -4.271241 | -0.00315 | -1.612218 |
| 66 | 8 | 0 | -1.966549 | 0.337352 | -2.603108 |

| | | | | | |
|---|---|---|---|---|---|
| 67 | 6 | 0 | -2.755337 | 1.909734 | -0.654589 |
| 68 | 6 | 0 | -3.727647 | 2.258455 | 0.284813 |
| 69 | 6 | 0 | -3.594694 | 3.459902 | 0.966515 |
| 70 | 6 | 0 | -2.508765 | 4.312327 | 0.725854 |
| 71 | 6 | 0 | -1.553556 | 3.937079 | -0.222229 |
| 72 | 6 | 0 | -1.667436 | 2.737019 | -0.917322 |
| 73 | 1 | 0 | -4.572445 | 1.601565 | 0.467122 |
| 74 | 1 | 0 | -4.344838 | 3.745091 | 1.698199 |
| 75 | 1 | 0 | -0.710605 | 4.59155 | -0.421417 |
| 76 | 1 | 0 | -0.935475 | 2.450003 | -1.665506 |
| 77 | 6 | 0 | -2.39364 | 5.616649 | 1.468385 |
| 78 | 1 | 0 | -1.417491 | 6.078005 | 1.310271 |
| 79 | 1 | 0 | -2.538385 | 5.467357 | 2.541349 |
| 80 | 1 | 0 | -3.161116 | 6.319139 | 1.129549 |

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**TS-B**

M062X/6-31G*

E(RM062X) = -2292.661327 Hartree

EE+Thermal Free Energy of Correction = -2292.070424 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.466536 | -1.408552 | 1.106158 |
| 2 | 6 | 0 | -2.208051 | -0.393515 | 1.597417 |
| 3 | 6 | 0 | -3.580582 | -0.347415 | 1.374119 |
| 4 | 6 | 0 | -4.4711 | 0.613859 | 2.125829 |
| 5 | 6 | 0 | -3.737896 | 1.871315 | 2.586967 |
| 6 | 6 | 0 | -2.434924 | 1.482194 | 3.276529 |
| 7 | 6 | 0 | -1.50998 | 0.749815 | 2.303637 |
| 8 | 1 | 0 | -4.06612 | -1.254687 | 1.031143 |
| 9 | 1 | 0 | -5.337634 | 0.875011 | 1.508547 |
| 10 | 1 | 0 | -4.880125 | 0.097616 | 3.005667 |
| 11 | 1 | 0 | -3.512164 | 2.516994 | 1.727714 |
| 12 | 1 | 0 | -4.378591 | 2.449852 | 3.258767 |
| 13 | 1 | 0 | -1.915699 | 2.362702 | 3.665183 |
| 14 | 1 | 0 | -2.657243 | 0.833784 | 4.132968 |
| 15 | 1 | 0 | -1.169783 | 1.449177 | 1.530771 |
| 16 | 1 | 0 | -0.61462 | 0.400575 | 2.819002 |
| 17 | 6 | 0 | -2.093017 | -2.622129 | 0.552452 |
| 18 | 6 | 0 | -0.909349 | -3.500876 | 0.165339 |
| 19 | 6 | 0 | 0.121687 | -3.159485 | 1.243229 |
| 20 | 6 | 0 | -0.038042 | -1.646022 | 1.422335 |
| 21 | 1 | 0 | -2.73558 | -2.371321 | -0.291929 |
| 22 | 1 | 0 | -2.710381 | -3.095516 | 1.328274 |
| 23 | 1 | 0 | -0.544455 | -3.220207 | -0.827959 |
| 24 | 1 | 0 | -1.174635 | -4.558432 | 0.143084 |
| 25 | 1 | 0 | 1.147052 | -3.423497 | 0.971432 |
| 26 | 1 | 0 | -0.12788 | -3.673305 | 2.175958 |
| 27 | 1 | 0 | 0.18836 | -1.336969 | 2.443586 |
| 28 | 6 | 0 | 0.837017 | -0.856004 | 0.448884 |
| 29 | 1 | 0 | 0.715615 | -1.275769 | -0.552649 |
| 30 | 1 | 0 | 0.510376 | 0.186123 | 0.38536 |
| 31 | 6 | 0 | -3.534782 | 0.50937 | -0.732416 |
| 32 | 6 | 0 | -4.947179 | 0.200767 | -1.036835 |
| 33 | 6 | 0 | -5.902998 | 1.218255 | -0.930842 |
| 34 | 6 | 0 | -7.236051 | 0.976058 | -1.25404 |
| 35 | 6 | 0 | -7.631028 | -0.288508 | -1.680569 |
| 36 | 6 | 0 | -6.686898 | -1.311391 | -1.78398 |
| 37 | 6 | 0 | -5.356921 | -1.069531 | -1.465246 |
| 38 | 1 | 0 | -5.593633 | 2.207384 | -0.604076 |
| 39 | 1 | 0 | -7.963674 | 1.776493 | -1.171208 |
| 40 | 1 | 0 | -8.669553 | -0.480493 | -1.928709 |
| 41 | 1 | 0 | -6.990512 | -2.300472 | -2.110455 |
| 42 | 1 | 0 | -4.633194 | -1.876901 | -1.539868 |
| 43 | 6 | 0 | -2.533295 | -0.024658 | -1.528661 |
| 44 | 7 | 0 | -1.288807 | 0.565894 | -1.57426 |
| 45 | 8 | 0 | -0.480533 | 0.156697 | -2.443652 |
| 46 | 8 | 0 | -0.984107 | 1.493393 | -0.805622 |
| 47 | 1 | 0 | -3.334275 | 1.489322 | -0.308438 |
| 48 | 1 | 0 | -2.657439 | -0.827992 | -2.238589 |
| 49 | 7 | 0 | 2.258428 | -0.929974 | 0.823203 |
| 50 | 6 | 0 | 3.222963 | -1.632342 | 0.028858 |
| 51 | 6 | 0 | 4.065417 | -2.521969 | 0.703908 |
| 52 | 6 | 0 | 5.023718 | -3.260002 | 0.020768 |

| | | | | | |
|---|---|---|---|---|---|
| 53 | 6 | 0 | 5.132041 | -3.14871 | -1.363584 |
| 54 | 6 | 0 | 4.278236 | -2.293849 | -2.045781 |
| 55 | 6 | 0 | 3.338346 | -1.509445 | -1.369344 |
| 56 | 1 | 0 | 3.946465 | -2.622318 | 1.776058 |
| 57 | 1 | 0 | 5.66932 | -3.937505 | 0.569215 |
| 58 | 1 | 0 | 5.86586 | -3.733282 | -1.907281 |
| 59 | 1 | 0 | 4.325031 | -2.207296 | -3.12583 |
| 60 | 6 | 0 | 2.46294 | -0.657993 | -2.239536 |
| 61 | 16 | 0 | 2.813948 | 0.295753 | 1.820971 |
| 62 | 8 | 0 | 4.112638 | -0.1179 | 2.334019 |
| 63 | 8 | 0 | 1.717316 | 0.575741 | 2.74309 |
| 64 | 6 | 0 | 3.050506 | 1.71545 | 0.799065 |
| 65 | 8 | 0 | 2.174974 | -0.985139 | -3.371423 |
| 66 | 8 | 0 | 2.041346 | 0.464748 | -1.66784 |
| 67 | 1 | 0 | 1.19288 | 0.718993 | -2.105668 |
| 68 | 6 | 0 | 4.260412 | 1.859489 | 0.124588 |
| 69 | 6 | 0 | 4.402432 | 2.911054 | -0.77109 |
| 70 | 6 | 0 | 3.351846 | 3.805846 | -1.005323 |
| 71 | 6 | 0 | 2.148215 | 3.630419 | -0.314903 |
| 72 | 6 | 0 | 1.987214 | 2.588516 | 0.590314 |
| 73 | 6 | 0 | 3.526983 | 4.955315 | -1.961923 |
| 74 | 1 | 0 | 5.071798 | 1.162139 | 0.305645 |
| 75 | 1 | 0 | 5.341493 | 3.040074 | -1.301154 |
| 76 | 1 | 0 | 1.325672 | 4.317361 | -0.490612 |
| 77 | 1 | 0 | 1.05308 | 2.451285 | 1.125354 |
| 78 | 1 | 0 | 3.958262 | 5.819141 | -1.445846 |
| 79 | 1 | 0 | 2.569763 | 5.265859 | -2.385468 |
| 80 | 1 | 0 | 4.201057 | 4.688871 | -2.778785 |

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**TS-C**

M062X/6-31G*

E(RM062X) = -2292.648752 Hartree

EE+Thermal Free Energy of Correction = -2292.061607 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.44444 | -0.747165 | 0.99843 |
| 2 | 6 | 0 | -2.266303 | 0.257676 | 1.337276 |
| 3 | 6 | 0 | -3.64571 | 0.031237 | 1.456971 |
| 4 | 6 | 0 | -4.540089 | 1.061148 | 2.113854 |
| 5 | 6 | 0 | -4.011133 | 2.486117 | 1.973906 |
| 6 | 6 | 0 | -2.549591 | 2.533059 | 2.405335 |
| 7 | 6 | 0 | -1.698553 | 1.655303 | 1.487156 |
| 8 | 1 | 0 | -3.953105 | -0.9972 | 1.61749 |
| 9 | 1 | 0 | -5.552842 | 0.983399 | 1.704182 |
| 10 | 1 | 0 | -4.630877 | 0.819739 | 3.181736 |
| 11 | 1 | 0 | -4.091353 | 2.820887 | 0.931102 |
| 12 | 1 | 0 | -4.618211 | 3.168286 | 2.575927 |
| 13 | 1 | 0 | -2.161039 | 3.554774 | 2.378155 |
| 14 | 1 | 0 | -2.464508 | 2.180922 | 3.44061 |
| 15 | 1 | 0 | -1.662969 | 2.103575 | 0.488897 |
| 16 | 1 | 0 | -0.670326 | 1.610424 | 1.854993 |
| 17 | 6 | 0 | -1.875939 | -2.159393 | 0.996924 |
| 18 | 6 | 0 | -0.674446 | -2.885827 | 0.411162 |
| 19 | 6 | 0 | 0.4913 | -2.119507 | 1.035395 |
| 20 | 6 | 0 | 0.037744 | -0.657889 | 0.954733 |
| 21 | 1 | 0 | -2.782999 | -2.28528 | 0.41124 |
| 22 | 1 | 0 | -2.075581 | -2.475256 | 2.03048 |
| 23 | 1 | 0 | -0.672403 | -2.76914 | -0.678369 |
| 24 | 1 | 0 | -0.674627 | -3.949553 | 0.651166 |
| 25 | 1 | 0 | 1.442241 | -2.264469 | 0.519176 |
| 26 | 1 | 0 | 0.620539 | -2.418695 | 2.079726 |
| 27 | 1 | 0 | 0.396052 | -0.089481 | 1.818647 |
| 28 | 6 | 0 | 0.493054 | 0.023339 | -0.335973 |
| 29 | 1 | 0 | 0.2237 | -0.584096 | -1.202323 |
| 30 | 1 | 0 | 0.007179 | 0.989088 | -0.472807 |
| 31 | 6 | 0 | -4.246033 | 0.014393 | -0.604684 |
| 32 | 6 | 0 | -5.600239 | -0.564657 | -0.422983 |
| 33 | 6 | 0 | -6.716668 | 0.278407 | -0.457074 |
| 34 | 6 | 0 | -8.003406 | -0.239341 | -0.327012 |
| 35 | 6 | 0 | -8.190408 | -1.607858 | -0.154648 |
| 36 | 6 | 0 | -7.0839 | -2.456866 | -0.113019 |
| 37 | 6 | 0 | -5.800749 | -1.939781 | -0.244977 |
| 38 | 1 | 0 | -6.571992 | 1.346444 | -0.596275 |

| | | | | | |
|---|---|---|---|---|---|
| 39 | 1 | 0 | -8.857937 | 0.428486 | -0.359825 |
| 40 | 1 | 0 | -9.191371 | -2.012911 | -0.049574 |
| 41 | 1 | 0 | -7.222223 | -3.524013 | 0.026235 |
| 42 | 1 | 0 | -4.946772 | -2.611139 | -0.202737 |
| 43 | 6 | 0 | -3.349247 | -0.65191 | -1.440555 |
| 44 | 7 | 0 | -2.257974 | 0.009566 | -1.955813 |
| 45 | 8 | 0 | -1.505883 | -0.595118 | -2.748513 |
| 46 | 8 | 0 | -2.049923 | 1.201442 | -1.643932 |
| 47 | 1 | 0 | -4.202007 | 1.099384 | -0.647383 |
| 48 | 1 | 0 | -3.441387 | -1.675893 | -1.76933 |
| 49 | 7 | 0 | 1.949224 | 0.221753 | -0.323999 |
| 50 | 6 | 0 | 2.480215 | 1.365997 | 0.353343 |
| 51 | 6 | 0 | 2.603139 | 2.62654 | -0.25858 |
| 52 | 6 | 0 | 3.178482 | 3.676301 | 0.458459 |
| 53 | 6 | 0 | 3.600258 | 3.499279 | 1.772254 |
| 54 | 6 | 0 | 3.472317 | 2.253229 | 2.378079 |
| 55 | 6 | 0 | 2.928199 | 1.18971 | 1.662717 |
| 56 | 6 | 0 | 2.185869 | 2.940452 | -1.66258 |
| 57 | 1 | 0 | 3.285051 | 4.636357 | -0.034567 |
| 58 | 1 | 0 | 4.033677 | 4.330753 | 2.316915 |
| 59 | 1 | 0 | 3.808434 | 2.10153 | 3.397972 |
| 60 | 1 | 0 | 2.859688 | 0.197815 | 2.099415 |
| 61 | 16 | 0 | 2.92104 | -0.482228 | -1.47925 |
| 62 | 8 | 0 | 3.577265 | 0.553836 | -2.273578 |
| 63 | 8 | 0 | 2.11227 | -1.503699 | -2.135104 |
| 64 | 6 | 0 | 4.19503 | -1.279943 | -0.537461 |
| 65 | 8 | 0 | 2.695964 | 3.818554 | -2.319974 |
| 66 | 8 | 0 | 1.153909 | 2.212469 | -2.095777 |
| 67 | 1 | 0 | 0.956085 | 2.481244 | -3.00719 |
| 68 | 6 | 0 | 5.268699 | -0.524328 | -0.06806 |
| 69 | 6 | 0 | 6.24386 | -1.151566 | 0.69684 |
| 70 | 6 | 0 | 6.167607 | -2.519485 | 0.985272 |
| 71 | 6 | 0 | 5.086692 | -3.253049 | 0.487445 |
| 72 | 6 | 0 | 4.09584 | -2.642738 | -0.274743 |
| 73 | 6 | 0 | 7.250665 | -3.189923 | 1.787919 |
| 74 | 1 | 0 | 5.338661 | 0.532811 | -0.304016 |
| 75 | 1 | 0 | 7.082246 | -0.572596 | 1.072599 |
| 76 | 1 | 0 | 5.021663 | -4.316922 | 0.694345 |
| 77 | 1 | 0 | 3.2658 | -3.214466 | -0.676528 |
| 78 | 1 | 0 | 8.105166 | -3.431236 | 1.14782 |
| 79 | 1 | 0 | 6.894423 | -4.120248 | 2.234162 |
| 80 | 1 | 0 | 7.611495 | -2.535395 | 2.584494 |

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**TS-D**

M062X/6-31G*

E(RM062X) = -2292.651443 Hartree

EE+Thermal Free Energy of Correction = -2292.060731 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 1.663845 | -0.245807 | -1.396998 |
| 2 | 6 | 0 | 2.458642 | 0.830398 | -1.3535 |
| 3 | 6 | 0 | 3.853233 | 0.67344 | -1.321965 |
| 4 | 6 | 0 | 4.758212 | 1.871966 | -1.492599 |
| 5 | 6 | 0 | 4.110661 | 3.154073 | -0.975184 |
| 6 | 6 | 0 | 2.757348 | 3.336069 | -1.652085 |
| 7 | 6 | 0 | 1.801972 | 2.196326 | -1.290455 |
| 8 | 1 | 0 | 4.244093 | -0.265636 | -1.700397 |
| 9 | 1 | 0 | 5.710295 | 1.682991 | -0.984392 |
| 10 | 1 | 0 | 5.00887 | 2.00117 | -2.554407 |
| 11 | 1 | 0 | 3.964738 | 3.096481 | 0.111351 |
| 12 | 1 | 0 | 4.761799 | 4.010412 | -1.172575 |
| 13 | 1 | 0 | 2.295538 | 4.286309 | -1.370678 |
| 14 | 1 | 0 | 2.903809 | 3.359436 | -2.738775 |
| 15 | 1 | 0 | 1.401227 | 2.348629 | -0.284047 |
| 16 | 1 | 0 | 0.953869 | 2.207537 | -1.980418 |
| 17 | 6 | 0 | 2.170331 | -1.599084 | -1.691702 |
| 18 | 6 | 0 | 0.928281 | -2.491775 | -1.659898 |
| 19 | 6 | 0 | -0.208662 | -1.534858 | -2.028 |
| 20 | 6 | 0 | 0.187412 | -0.240411 | -1.324029 |
| 21 | 1 | 0 | 2.923547 | -1.889575 | -0.959717 |
| 22 | 1 | 0 | 2.640399 | -1.58755 | -2.683252 |
| 23 | 1 | 0 | 0.769489 | -2.893868 | -0.655195 |
| 24 | 1 | 0 | 1.021217 | -3.332157 | -2.348829 |

| | | | | | |
|---|---|---|---|---|---|
| 25 | 1 | 0 | -1.189284 | -1.876214 | -1.691608 |
| 26 | 1 | 0 | -0.243623 | -1.371322 | -3.109315 |
| 27 | 1 | 0 | -0.233843 | 0.63626 | -1.81882 |
| 28 | 6 | 0 | -0.178063 | -0.230539 | 0.157832 |
| 29 | 1 | 0 | 0.211471 | -1.131193 | 0.636577 |
| 30 | 1 | 0 | 0.295983 | 0.623807 | 0.643495 |
| 31 | 6 | 0 | 4.245564 | 0.093563 | 0.729423 |
| 32 | 6 | 0 | 5.518306 | -0.638801 | 0.516349 |
| 33 | 6 | 0 | 6.731284 | 0.034505 | 0.707 |
| 34 | 6 | 0 | 7.947716 | -0.625373 | 0.54762 |
| 35 | 6 | 0 | 7.970138 | -1.971026 | 0.193945 |
| 36 | 6 | 0 | 6.768413 | -2.655205 | 0.008288 |
| 37 | 6 | 0 | 5.555601 | -1.996356 | 0.168582 |
| 38 | 1 | 0 | 6.718532 | 1.07958 | 1.003389 |
| 39 | 1 | 0 | 8.876122 | -0.086115 | 0.704157 |
| 40 | 1 | 0 | 8.915988 | -2.486913 | 0.066416 |
| 41 | 1 | 0 | 6.776937 | -3.705802 | -0.262743 |
| 42 | 1 | 0 | 4.630911 | -2.547534 | 0.024667 |
| 43 | 6 | 0 | 3.197318 | -0.551145 | 1.388776 |
| 44 | 7 | 0 | 2.208567 | 0.204594 | 1.978517 |
| 45 | 8 | 0 | 1.366981 | -0.352153 | 2.711313 |
| 46 | 8 | 0 | 2.161048 | 1.436467 | 1.763181 |
| 47 | 1 | 0 | 4.354292 | 1.14752 | 0.967596 |
| 48 | 1 | 0 | 3.124989 | -1.610924 | 1.581406 |
| 49 | 7 | 0 | -1.631441 | -0.142554 | 0.35623 |
| 50 | 6 | 0 | -2.152525 | 1.167221 | 0.626942 |
| 51 | 6 | 0 | -1.671583 | 1.876537 | 1.730085 |
| 52 | 6 | 0 | -2.191043 | 3.129112 | 2.03691 |
| 53 | 6 | 0 | -3.21304 | 3.670168 | 1.258059 |
| 54 | 6 | 0 | -3.697979 | 2.963452 | 0.165077 |
| 55 | 6 | 0 | -3.161212 | 1.718683 | -0.175235 |
| 56 | 1 | 0 | -0.885696 | 1.429441 | 2.334403 |
| 57 | 1 | 0 | -1.808394 | 3.675497 | 2.892121 |
| 58 | 1 | 0 | -3.629694 | 4.641192 | 1.501862 |
| 59 | 1 | 0 | -4.493967 | 3.367496 | -0.450683 |
| 60 | 6 | 0 | -3.742175 | 1.063717 | -1.389856 |
| 61 | 16 | 0 | -2.334313 | -1.390632 | 1.232376 |
| 62 | 8 | 0 | -2.370399 | -1.087985 | 2.661795 |
| 63 | 8 | 0 | -1.661541 | -2.608963 | 0.787077 |
| 64 | 6 | 0 | -3.994442 | -1.371902 | 0.624579 |
| 65 | 8 | 0 | -4.886533 | 1.235612 | -1.745042 |
| 66 | 8 | 0 | -2.872875 | 0.326839 | -2.092492 |
| 67 | 1 | 0 | -3.357146 | -0.037403 | -2.851827 |
| 68 | 6 | 0 | -4.962346 | -0.6372 | 1.303645 |
| 69 | 6 | 0 | -6.246291 | -0.576217 | 0.775131 |
| 70 | 6 | 0 | -6.566038 | -1.235035 | -0.415858 |
| 71 | 6 | 0 | -5.576136 | -1.98512 | -1.062657 |
| 72 | 6 | 0 | -4.286896 | -2.056949 | -0.552667 |
| 73 | 6 | 0 | -7.940018 | -1.108721 | -1.015074 |
| 74 | 1 | 0 | -4.706541 | -0.122671 | 2.224209 |
| 75 | 1 | 0 | -7.010216 | -0.002552 | 1.290935 |
| 76 | 1 | 0 | -5.820714 | -2.5154 | -1.978128 |
| 77 | 1 | 0 | -3.516384 | -2.636713 | -1.05041 |
| 78 | 1 | 0 | -8.694989 | -0.936117 | -0.245549 |
| 79 | 1 | 0 | -8.211151 | -2.002874 | -1.580099 |
| 80 | 1 | 0 | -7.965614 | -0.258368 | -1.704518 |

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**TS-E**

M062X/6-31G*

E(RM062X) = -2292.660945 Hartree

EE+Thermal Free Energy of Correction = -2292.072746 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.591862 | -1.839368 | -2.928698 |
| 2 | 1 | 0 | -1.449307 | -1.383868 | -3.911099 |
| 3 | 6 | 0 | -0.282204 | -2.681447 | -1.083901 |
| 4 | 1 | 0 | 0.694568 | -3.024581 | -0.738169 |
| 5 | 6 | 0 | -0.474661 | -1.182473 | -0.862107 |
| 6 | 1 | 0 | -0.81239 | -0.960401 | 0.149924 |
| 7 | 7 | 0 | -1.50525 | -0.831355 | -1.856764 |
| 8 | 6 | 0 | -2.224861 | 0.30021 | -1.823302 |
| 9 | 6 | 0 | -2.305576 | 1.061114 | -0.64779 |
| 10 | 1 | 0 | -1.516963 | 0.934372 | 0.088278 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 6 | 0 | -3.020201 | 0.668063 | -3.059057 |
| 12 | 1 | 0 | -3.905238 | 0.026825 | -3.101381 |
| 13 | 1 | 0 | -2.41903 | 0.438613 | -3.943568 |
| 14 | 6 | 0 | -3.426989 | 2.142436 | -3.085004 |
| 15 | 1 | 0 | -2.548263 | 2.761453 | -3.30436 |
| 16 | 1 | 0 | -4.141117 | 2.299986 | -3.898002 |
| 17 | 6 | 0 | -4.010859 | 2.571924 | -1.743708 |
| 18 | 1 | 0 | -4.365556 | 3.605735 | -1.787733 |
| 19 | 1 | 0 | -4.880264 | 1.944781 | -1.505851 |
| 20 | 6 | 0 | -2.946144 | 2.430935 | -0.659074 |
| 21 | 1 | 0 | -2.168747 | 3.19106 | -0.820285 |
| 22 | 1 | 0 | -3.368519 | 2.640439 | 0.329737 |
| 23 | 1 | 0 | -2.590635 | -2.293279 | -2.895978 |
| 24 | 1 | 0 | -1.059799 | -3.224016 | -0.539809 |
| 25 | 6 | 0 | -0.489342 | -2.847586 | -2.59239 |
| 26 | 1 | 0 | 0.428083 | -2.604072 | -3.137088 |
| 27 | 1 | 0 | -0.780229 | -3.862597 | -2.865955 |
| 28 | 6 | 0 | -3.67036 | -0.181265 | 0.461648 |
| 29 | 1 | 0 | -4.515618 | 0.152705 | -0.133283 |
| 30 | 6 | 0 | -3.349193 | -1.533997 | 0.341069 |
| 31 | 1 | 0 | -2.757595 | -2.099258 | 1.046143 |
| 32 | 7 | 0 | -3.767237 | -2.251262 | -0.753451 |
| 33 | 8 | 0 | -4.450987 | -1.693358 | -1.639647 |
| 34 | 8 | 0 | -3.454803 | -3.457853 | -0.854188 |
| 35 | 6 | 0 | -3.524436 | 0.464502 | 1.788587 |
| 36 | 6 | 0 | -3.325927 | 1.668578 | 4.311952 |
| 37 | 6 | 0 | -4.53684 | 1.309832 | 2.256384 |
| 38 | 6 | 0 | -2.403376 | 0.240086 | 2.597242 |
| 39 | 6 | 0 | -2.305405 | 0.837912 | 3.848003 |
| 40 | 6 | 0 | -4.441173 | 1.904578 | 3.512346 |
| 41 | 1 | 0 | -5.406601 | 1.494423 | 1.631257 |
| 42 | 1 | 0 | -1.585467 | -0.376848 | 2.234161 |
| 43 | 1 | 0 | -1.425473 | 0.663139 | 4.458681 |
| 44 | 1 | 0 | -5.236809 | 2.553781 | 3.863011 |
| 45 | 1 | 0 | -3.246205 | 2.13586 | 5.287985 |
| 46 | 6 | 0 | 0.789594 | -0.354033 | -1.131682 |
| 47 | 1 | 0 | 0.527606 | 0.70715 | -1.206756 |
| 48 | 1 | 0 | 1.2453 | -0.641225 | -2.083658 |
| 49 | 7 | 0 | 1.769504 | -0.547614 | -0.059834 |
| 50 | 6 | 0 | 2.862502 | -1.448665 | -0.20921 |
| 51 | 6 | 0 | 3.109982 | -2.460897 | 0.733314 |
| 52 | 6 | 0 | 4.218535 | -3.292848 | 0.560795 |
| 53 | 6 | 0 | 5.049328 | -3.15855 | -0.545011 |
| 54 | 6 | 0 | 4.792555 | -2.162092 | -1.483228 |
| 55 | 6 | 0 | 3.714357 | -1.301681 | -1.305263 |
| 56 | 6 | 0 | 2.274916 | -2.728677 | 1.947284 |
| 57 | 1 | 0 | 4.406379 | -4.05596 | 1.307836 |
| 58 | 1 | 0 | 5.895054 | -3.825106 | -0.671222 |
| 59 | 1 | 0 | 5.440888 | -2.0395 | -2.344035 |
| 60 | 1 | 0 | 3.530288 | -0.495837 | -2.009291 |
| 61 | 16 | 0 | 1.821756 | 0.603141 | 1.13632 |
| 62 | 8 | 0 | 2.692791 | 0.088233 | 2.184281 |
| 63 | 8 | 0 | 0.438408 | 0.96669 | 1.42541 |
| 64 | 6 | 0 | 2.609066 | 2.00701 | 0.396055 |
| 65 | 8 | 0 | 2.710372 | -3.284651 | 2.929809 |
| 66 | 8 | 0 | 0.988386 | -2.371485 | 1.838582 |
| 67 | 1 | 0 | 0.555981 | -2.613861 | 2.673848 |
| 68 | 6 | 0 | 3.99862 | 2.005173 | 0.268146 |
| 69 | 6 | 0 | 4.610194 | 3.074185 | -0.37189 |
| 70 | 6 | 0 | 3.855901 | 4.138932 | -0.882772 |
| 71 | 6 | 0 | 2.46612 | 4.110194 | -0.74028 |
| 72 | 6 | 0 | 1.831838 | 3.047755 | -0.103083 |
| 73 | 6 | 0 | 4.540561 | 5.303239 | -1.547358 |
| 74 | 1 | 0 | 4.584429 | 1.186617 | 0.67428 |
| 75 | 1 | 0 | 5.691074 | 3.088209 | -0.475659 |
| 76 | 1 | 0 | 1.871396 | 4.930649 | -1.130057 |
| 77 | 1 | 0 | 0.753554 | 3.027431 | 0.019346 |
| 78 | 1 | 0 | 4.952641 | 5.982628 | -0.794644 |
| 79 | 1 | 0 | 3.844194 | 5.871535 | -2.166497 |
| 80 | 1 | 0 | 5.369887 | 4.965289 | -2.172967 |

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**TS-F**

M062X/6-31G*

E(RM062X) = -2292.659832 Hartree

EE+Thermal Free Energy of Correction = -2292.068942 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.666227 | -3.008585 | 1.653727 |
| 2 | 1 | 0 | 1.384403 | -3.036638 | 2.708565 |
| 3 | 6 | 0 | 0.616006 | -2.992608 | -0.520323 |
| 4 | 1 | 0 | -0.295868 | -3.181375 | -1.090533 |
| 5 | 6 | 0 | 0.700938 | -1.544775 | -0.042508 |
| 6 | 1 | 0 | 1.118359 | -0.888478 | -0.805485 |
| 7 | 7 | 0 | 1.602859 | -1.63512 | 1.122463 |
| 8 | 6 | 0 | 2.211446 | -0.577935 | 1.681295 |
| 9 | 6 | 0 | 2.338336 | 0.627675 | 0.977458 |
| 10 | 1 | 0 | 1.657962 | 0.799324 | 0.147946 |
| 11 | 6 | 0 | 2.849397 | -0.762177 | 3.042734 |
| 12 | 1 | 0 | 3.796427 | -1.29309 | 2.907511 |
| 13 | 1 | 0 | 2.208021 | -1.406627 | 3.650281 |
| 14 | 6 | 0 | 3.080703 | 0.56338 | 3.770524 |
| 15 | 1 | 0 | 2.11962 | 0.96485 | 4.115082 |
| 16 | 1 | 0 | 3.688677 | 0.378775 | 4.66055 |
| 17 | 6 | 0 | 3.742092 | 1.584057 | 2.850928 |
| 18 | 1 | 0 | 3.966009 | 2.50724 | 3.393297 |
| 19 | 1 | 0 | 4.699335 | 1.184891 | 2.490265 |
| 20 | 6 | 0 | 2.817729 | 1.881783 | 1.673164 |
| 21 | 1 | 0 | 1.94662 | 2.445522 | 2.036143 |
| 22 | 1 | 0 | 3.313323 | 2.53329 | 0.945401 |
| 23 | 1 | 0 | 2.698821 | -3.367757 | 1.558914 |
| 24 | 1 | 0 | 1.483213 | -3.212826 | -1.148187 |
| 25 | 6 | 0 | 0.695312 | -3.80462 | 0.776333 |
| 26 | 1 | 0 | -0.286854 | -3.866864 | 1.254076 |
| 27 | 1 | 0 | 1.05144 | -4.822251 | 0.610922 |
| 28 | 6 | 0 | 3.955946 | 0.049846 | -0.333704 |
| 29 | 1 | 0 | 4.682731 | 0.089074 | 0.472706 |
| 30 | 6 | 0 | 3.735294 | -1.214519 | -0.880279 |
| 31 | 1 | 0 | 3.284565 | -1.407848 | -1.842373 |
| 32 | 7 | 0 | 4.078671 | -2.344596 | -0.177324 |
| 33 | 8 | 0 | 4.609879 | -2.241142 | 0.950021 |
| 34 | 8 | 0 | 3.853727 | -3.469388 | -0.674563 |
| 35 | 6 | 0 | 3.930122 | 1.22814 | -1.232824 |
| 36 | 6 | 0 | 3.957855 | 3.447871 | -2.943909 |
| 37 | 6 | 0 | 4.914471 | 2.214423 | -1.103743 |
| 38 | 6 | 0 | 2.950709 | 1.374864 | -2.222803 |
| 39 | 6 | 0 | 2.964802 | 2.475919 | -3.070823 |
| 40 | 6 | 0 | 4.931468 | 3.315354 | -1.957216 |
| 41 | 1 | 0 | 5.673743 | 2.111315 | -0.3329 |
| 42 | 1 | 0 | 2.153147 | 0.642126 | -2.309114 |
| 43 | 1 | 0 | 2.193646 | 2.580559 | -3.827218 |
| 44 | 1 | 0 | 5.704114 | 4.069421 | -1.848044 |
| 45 | 1 | 0 | 3.96613 | 4.307743 | -3.605679 |
| 46 | 6 | 0 | -0.640483 | -0.968327 | 0.432813 |
| 47 | 1 | 0 | -0.476555 | -0.028887 | 0.971483 |
| 48 | 1 | 0 | -1.120405 | -1.651693 | 1.136691 |
| 49 | 7 | 0 | -1.573388 | -0.758308 | -0.683273 |
| 50 | 6 | 0 | -2.749317 | -1.562826 | -0.84721 |
| 51 | 6 | 0 | -2.782419 | -2.386843 | -1.974187 |
| 52 | 6 | 0 | -3.871032 | -3.210628 | -2.234704 |
| 53 | 6 | 0 | -4.957051 | -3.214359 | -1.364186 |
| 54 | 6 | 0 | -4.94796 | -2.37913 | -0.255838 |
| 55 | 6 | 0 | -3.861127 | -1.541925 | 0.02193 |
| 56 | 1 | 0 | -1.931392 | -2.359378 | -2.645604 |
| 57 | 1 | 0 | -3.867088 | -3.846167 | -3.113492 |
| 58 | 1 | 0 | -5.810429 | -3.85646 | -1.551399 |
| 59 | 1 | 0 | -5.794523 | -2.348421 | 0.420385 |
| 60 | 6 | 0 | -4.050962 | -0.662078 | 1.220389 |
| 61 | 16 | 0 | -1.506552 | 0.693312 | -1.496981 |
| 62 | 8 | 0 | -2.163747 | 0.496292 | -2.780706 |
| 63 | 8 | 0 | -0.111832 | 1.122162 | -1.43393 |
| 64 | 6 | 0 | -2.471878 | 1.828266 | -0.547761 |
| 65 | 8 | 0 | -5.132019 | -0.475811 | 1.732734 |
| 66 | 8 | 0 | -2.933461 | -0.105634 | 1.694056 |
| 67 | 1 | 0 | -3.186107 | 0.484207 | 2.423771 |
| 68 | 6 | 0 | -3.854885 | 1.839982 | -0.723873 |
| 69 | 6 | 0 | -4.631415 | 2.596212 | 0.144423 |
| 70 | 6 | 0 | -4.044667 | 3.337793 | 1.177696 |
| 71 | 6 | 0 | -2.652375 | 3.319562 | 1.315528 |
| 72 | 6 | 0 | -1.856591 | 2.564952 | 0.459775 |

| | | | | | |
|---|---|---|---|---|---|
| 73 | 6 | 0 | -4.901812 | 4.161906 | 2.100731 |
| 74 | 1 | 0 | -4.308021 | 1.262555 | -1.523481 |
| 75 | 1 | 0 | -5.710687 | 2.608135 | 0.025064 |
| 76 | 1 | 0 | -2.186631 | 3.900868 | 2.105537 |
| 77 | 1 | 0 | -0.776803 | 2.543809 | 0.568471 |
| 78 | 1 | 0 | -5.21002 | 5.089178 | 1.607808 |
| 79 | 1 | 0 | -4.361522 | 4.428824 | 3.010709 |
| 80 | 1 | 0 | -5.809202 | 3.620494 | 2.378314 |

**TS-G**

M062X/6-31G*

E(RM062X) = -2292.658556 Hartree

EE+Thermal Free Energy of Correction = -2292.071067 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.985565 | -3.437381 | 0.814033 |
| 2 | 1 | 0 | 1.104706 | -3.835729 | 1.82368 |
| 3 | 6 | 0 | -0.62814 | -2.231311 | -0.513311 |
| 4 | 1 | 0 | -1.667083 | -1.906343 | -0.613922 |
| 5 | 6 | 0 | 0.21966 | -1.201031 | 0.227771 |
| 6 | 1 | 0 | 0.602357 | -0.437044 | -0.450473 |
| 7 | 7 | 0 | 1.333582 | -2.005375 | 0.761403 |
| 8 | 6 | 0 | 2.486096 | -1.489444 | 1.213641 |
| 9 | 6 | 0 | 2.866434 | -0.181232 | 0.883157 |
| 10 | 1 | 0 | 2.083322 | 0.506208 | 0.578169 |
| 11 | 6 | 0 | 3.405071 | -2.400739 | 2.001126 |
| 12 | 1 | 0 | 3.900508 | -3.077486 | 1.298917 |
| 13 | 1 | 0 | 2.796879 | -3.021285 | 2.665303 |
| 14 | 6 | 0 | 4.439737 | -1.632877 | 2.825386 |
| 15 | 1 | 0 | 3.948409 | -1.168429 | 3.689112 |
| 16 | 1 | 0 | 5.176538 | -2.339438 | 3.217178 |
| 17 | 6 | 0 | 5.105926 | -0.543866 | 1.991834 |
| 18 | 1 | 0 | 5.891695 | -0.042899 | 2.564473 |
| 19 | 1 | 0 | 5.587451 | -0.996622 | 1.114942 |
| 20 | 6 | 0 | 4.054735 | 0.471733 | 1.551485 |
| 21 | 1 | 0 | 3.710361 | 1.03482 | 2.429863 |
| 22 | 1 | 0 | 4.490882 | 1.212228 | 0.872366 |
| 23 | 1 | 0 | 1.662446 | -3.979502 | 0.1411 |
| 24 | 1 | 0 | -0.206081 | -2.397342 | -1.508169 |
| 25 | 6 | 0 | -0.468723 | -3.495984 | 0.336704 |
| 26 | 1 | 0 | -1.151865 | -3.473685 | 1.191499 |
| 27 | 1 | 0 | -0.666624 | -4.408194 | -0.227362 |
| 28 | 6 | 0 | 3.484828 | -0.513684 | -1.16116 |
| 29 | 1 | 0 | 4.405668 | -0.991027 | -0.838785 |
| 30 | 6 | 0 | 2.58634 | -1.336699 | -1.838604 |
| 31 | 1 | 0 | 1.78272 | -0.994532 | -2.474117 |
| 32 | 7 | 0 | 2.663169 | -2.703704 | -1.706112 |
| 33 | 8 | 0 | 3.553135 | -3.210127 | -0.989751 |
| 34 | 8 | 0 | 1.83559 | -3.425251 | -2.302915 |
| 35 | 6 | 0 | 3.609143 | 0.903398 | -1.579138 |
| 36 | 6 | 0 | 3.914707 | 3.559226 | -2.425971 |
| 37 | 6 | 0 | 4.881815 | 1.473114 | -1.695949 |
| 38 | 6 | 0 | 2.488357 | 1.689366 | -1.877602 |
| 39 | 6 | 0 | 2.640734 | 3.004124 | -2.301074 |
| 40 | 6 | 0 | 5.034631 | 2.791171 | -2.120137 |
| 41 | 1 | 0 | 5.756143 | 0.872562 | -1.459618 |
| 42 | 1 | 0 | 1.487388 | 1.275842 | -1.768535 |
| 43 | 1 | 0 | 1.762169 | 3.599418 | -2.527815 |
| 44 | 1 | 0 | 6.029013 | 3.215987 | -2.209596 |
| 45 | 1 | 0 | 4.030665 | 4.586871 | -2.753977 |
| 46 | 6 | 0 | -0.504572 | -0.532541 | 1.404363 |
| 47 | 1 | 0 | 0.196543 | 0.074876 | 1.986391 |
| 48 | 1 | 0 | -0.920689 | -1.291329 | 2.06936 |
| 49 | 7 | 0 | -1.608036 | 0.308871 | 0.938031 |
| 50 | 6 | 0 | -1.327252 | 1.477184 | 0.161654 |
| 51 | 6 | 0 | -1.088903 | 2.735271 | 0.742819 |
| 52 | 6 | 0 | -0.861267 | 3.834526 | -0.086303 |
| 53 | 6 | 0 | -0.851613 | 3.697473 | -1.47042 |
| 54 | 6 | 0 | -1.089516 | 2.452081 | -2.04513 |
| 55 | 6 | 0 | -1.337102 | 1.350836 | -1.228473 |
| 56 | 6 | 0 | -1.119163 | 3.020064 | 2.212739 |
| 57 | 1 | 0 | -0.699428 | 4.801356 | 0.377052 |
| 58 | 1 | 0 | -0.671082 | 4.564072 | -2.097439 |

| | | | | | |
|---|---|---|---|---|---|
| 59 | 1 | 0 | -1.094006 | 2.336011 | -3.123724 |
| 60 | 1 | 0 | -1.55488 | 0.376786 | -1.657344 |
| 61 | 16 | 0 | -3.135785 | 0.176185 | 1.582823 |
| 62 | 8 | 0 | -3.604848 | 1.513082 | 1.932182 |
| 63 | 8 | 0 | -3.078765 | -0.874316 | 2.592698 |
| 64 | 6 | 0 | -4.137807 | -0.392204 | 0.235925 |
| 65 | 8 | 0 | -1.337095 | 4.122043 | 2.661171 |
| 66 | 8 | 0 | -0.835204 | 1.969832 | 2.990413 |
| 67 | 1 | 0 | -0.893336 | 2.268071 | 3.912773 |
| 68 | 6 | 0 | -4.669015 | 0.537227 | -0.654617 |
| 69 | 6 | 0 | -5.400338 | 0.07674 | -1.744158 |
| 70 | 6 | 0 | -5.60869 | -1.29122 | -1.947669 |
| 71 | 6 | 0 | -5.065387 | -2.199865 | -1.031878 |
| 72 | 6 | 0 | -4.328815 | -1.761189 | 0.061761 |
| 73 | 6 | 0 | -6.429169 | -1.779594 | -3.111603 |
| 74 | 1 | 0 | -4.51734 | 1.599016 | -0.490242 |
| 75 | 1 | 0 | -5.819376 | 0.791293 | -2.44611 |
| 76 | 1 | 0 | -5.224696 | -3.264217 | -1.176746 |
| 77 | 1 | 0 | -3.913599 | -2.463629 | 0.77751 |
| 78 | 1 | 0 | -6.054071 | -2.735244 | -3.484082 |
| 79 | 1 | 0 | -6.422627 | -1.057774 | -3.930547 |
| 80 | 1 | 0 | -7.469887 | -1.929316 | -2.807096 |

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**TS-H**

M062X/6-31G*

E(RM062X) = -2292.661126 Hartree

EE+Thermal Free Energy of Correction = -2292.069641 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.232289 | -3.376125 | -0.47531 |
| 2 | 1 | 0 | 2.601433 | -4.06024 | 0.291732 |
| 3 | 6 | 0 | 0.158551 | -2.397163 | -1.237178 |
| 4 | 1 | 0 | -0.93185 | -2.434773 | -1.192353 |
| 5 | 6 | 0 | 0.719793 | -1.494607 | -0.143364 |
| 6 | 1 | 0 | 0.74347 | -0.452071 | -0.45891 |
| 7 | 7 | 0 | 2.085122 | -2.009523 | 0.056815 |
| 8 | 6 | 0 | 3.050862 | -1.335776 | 0.695019 |
| 9 | 6 | 0 | 2.932267 | 0.045442 | 0.917015 |
| 10 | 1 | 0 | 1.932216 | 0.469186 | 0.914883 |
| 11 | 6 | 0 | 4.305642 | -2.094328 | 1.075448 |
| 12 | 1 | 0 | 4.897354 | -2.25562 | 0.169986 |
| 13 | 1 | 0 | 4.014356 | -3.082019 | 1.444713 |
| 14 | 6 | 0 | 5.137172 | -1.375478 | 2.139338 |
| 15 | 1 | 0 | 4.643461 | -1.46749 | 3.1145 |
| 16 | 1 | 0 | 6.108888 | -1.869565 | 2.22429 |
| 17 | 6 | 0 | 5.295038 | 0.103493 | 1.804379 |
| 18 | 1 | 0 | 5.948248 | 0.598091 | 2.528951 |
| 19 | 1 | 0 | 5.770838 | 0.207152 | 0.820171 |
| 20 | 6 | 0 | 3.922048 | 0.770678 | 1.799951 |
| 21 | 1 | 0 | 3.535021 | 0.801549 | 2.827864 |
| 22 | 1 | 0 | 3.99815 | 1.8147 | 1.477355 |
| 23 | 1 | 0 | 2.958342 | -3.34799 | -1.298234 |
| 24 | 1 | 0 | 0.468075 | -2.016956 | -2.214394 |
| 25 | 6 | 0 | 0.827258 | -3.747369 | -0.959462 |
| 26 | 1 | 0 | 0.28503 | -4.287416 | -0.177216 |
| 27 | 1 | 0 | 0.866769 | -4.386763 | -1.842341 |
| 28 | 6 | 0 | 3.328826 | 0.755986 | -1.076344 |
| 29 | 1 | 0 | 4.393916 | 0.579426 | -0.958063 |
| 30 | 6 | 0 | 2.694437 | -0.026457 | -2.042245 |
| 31 | 1 | 0 | 1.74041 | 0.195086 | -2.498418 |
| 32 | 7 | 0 | 3.25962 | -1.208823 | -2.454894 |
| 33 | 8 | 0 | 4.35462 | -1.575022 | -1.975102 |
| 34 | 8 | 0 | 2.667216 | -1.910136 | -3.303547 |
| 35 | 6 | 0 | 2.890914 | 2.161788 | -0.902094 |
| 36 | 6 | 0 | 2.132826 | 4.849125 | -0.640364 |
| 37 | 6 | 0 | 3.853925 | 3.161485 | -0.724382 |
| 38 | 6 | 0 | 1.537986 | 2.525863 | -0.931697 |
| 39 | 6 | 0 | 1.164255 | 3.858796 | -0.807099 |
| 40 | 6 | 0 | 3.478673 | 4.496732 | -0.596288 |
| 41 | 1 | 0 | 4.9051 | 2.886956 | -0.696765 |
| 42 | 1 | 0 | 0.772382 | 1.761021 | -1.051358 |
| 43 | 1 | 0 | 0.113586 | 4.127663 | -0.83798 |
| 44 | 1 | 0 | 4.238933 | 5.259477 | -0.463842 |

| | | | | | |
|---|---|---|---|---|---|
| 45 | 1 | 0 | 1.836858 | 5.888248 | -0.541873 |
| 46 | 6 | 0 | -0.060696 | -1.600045 | 1.171274 |
| 47 | 1 | 0 | 0.523453 | -1.181086 | 1.9979 |
| 48 | 1 | 0 | -0.268456 | -2.647184 | 1.399614 |
| 49 | 7 | 0 | -1.333239 | -0.875679 | 1.025871 |
| 50 | 6 | 0 | -1.326859 | 0.526854 | 1.336338 |
| 51 | 6 | 0 | -0.97827 | 0.941413 | 2.623284 |
| 52 | 6 | 0 | -1.015904 | 2.287854 | 2.969784 |
| 53 | 6 | 0 | -1.446415 | 3.232495 | 2.04123 |
| 54 | 6 | 0 | -1.819353 | 2.824422 | 0.766689 |
| 55 | 6 | 0 | -1.734813 | 1.481314 | 0.390489 |
| 56 | 1 | 0 | -0.700704 | 0.191745 | 3.357477 |
| 57 | 1 | 0 | -0.733593 | 2.593476 | 3.971281 |
| 58 | 1 | 0 | -1.497879 | 4.281628 | 2.310381 |
| 59 | 1 | 0 | -2.175869 | 3.541717 | 0.035036 |
| 60 | 6 | 0 | -2.113414 | 1.183834 | -1.027384 |
| 61 | 16 | 0 | -2.732762 | -1.7014 | 1.457407 |
| 62 | 8 | 0 | -3.099622 | -1.425347 | 2.84471 |
| 63 | 8 | 0 | -2.514786 | -3.085253 | 1.045065 |
| 64 | 6 | 0 | -3.94257 | -0.955038 | 0.407444 |
| 65 | 8 | 0 | -2.946336 | 1.815653 | -1.634894 |
| 66 | 8 | 0 | -1.386582 | 0.210441 | -1.592104 |
| 67 | 1 | 0 | -1.695891 | 0.10888 | -2.507831 |
| 68 | 6 | 0 | -4.713825 | 0.097422 | 0.892159 |
| 69 | 6 | 0 | -5.625768 | 0.704068 | 0.036499 |
| 70 | 6 | 0 | -5.769191 | 0.272522 | -1.28551 |
| 71 | 6 | 0 | -4.993214 | -0.802642 | -1.736346 |
| 72 | 6 | 0 | -4.074839 | -1.421072 | -0.89928 |
| 73 | 6 | 0 | -6.713025 | 0.97506 | -2.222562 |
| 74 | 1 | 0 | -4.59546 | 0.430104 | 1.91823 |
| 75 | 1 | 0 | -6.231662 | 1.528941 | 0.398602 |
| 76 | 1 | 0 | -5.110884 | -1.155586 | -2.756435 |
| 77 | 1 | 0 | -3.474143 | -2.256788 | -1.243283 |
| 78 | 1 | 0 | -6.17763 | 1.760583 | -2.766049 |
| 79 | 1 | 0 | -7.535096 | 1.445838 | -1.680065 |
| 80 | 1 | 0 | -7.127235 | 0.284692 | -2.960226 |

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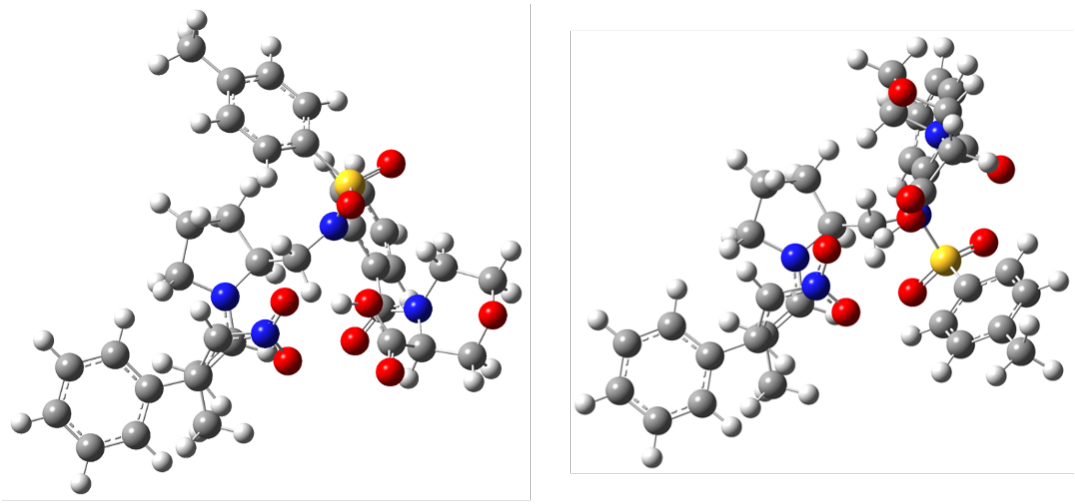
**< Transition State model of Enantioselective Michael Reaction of β-Nitrostyrene with Propionaldehyde using Catalyst 1o >**

To identify the promising TS model for the enantioselective Michael reaction of β-nitrostyrene with propionaldehyde using catalyst **1o**, various TS models consisting of **1o**-enamine generated from catalyst **1o** and propionaldehyde, and β-nitrostyrene were explored based on previous studies and the results in Scheme 5. The energetically favored TS models consisting by hydrogen bonding interaction between **1o**-enamine and β-nitrostyrene (**TS-I** and **TS-J**) were identified at the B3LYP/6-311G** level according to the SCRF method based on PCM (*i*-PrOH). The TS models (**TS-I** and **TS-J**) were further optimized at the M06-02X/6-31G* level according to the SCRF method based on PCM (*i*-PrOH) to find the most energetically favored TS model (**TS-I**).



TS-I; ΔE (0.0 kcal/mol)
ΔG (0.0 kcal/mol)

TS-J; ΔE (+2.1 kcal/mol)
ΔG (+1.4 kcal/mol)

**Figure S3.** Optimized geometries for the transition states of Michael reaction of β-nitrostyrene with propionaldehyde using catalyst **1o**.

**TS-I**

M062X/6-31G*

E(RM062X) = -2575.777237 Hartree

EE+Thermal Free Energy of Correction = -2575.132327 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 1.722545 | 0.612317 | 1.338128 |
| 2 | 6 | 0 | 2.521499 | 1.840668 | 1.258743 |
| 3 | 6 | 0 | 1.506738 | 2.882413 | 0.800786 |
| 4 | 6 | 0 | 0.223308 | 2.431054 | 1.50719 |
| 5 | 6 | 0 | 0.274544 | 0.901638 | 1.404426 |
| 6 | 6 | 0 | -0.392274 | 0.327231 | 0.156516 |
| 7 | 1 | 0 | 3.356423 | 1.703774 | 0.571005 |
| 8 | 1 | 0 | 2.92609 | 2.077371 | 2.252549 |
| 9 | 1 | 0 | 1.387101 | 2.829517 | -0.286245 |
| 10 | 1 | 0 | 1.804816 | 3.898484 | 1.062123 |
| 11 | 1 | 0 | -0.682745 | 2.843796 | 1.055948 |
| 12 | 1 | 0 | 0.248225 | 2.73241 | 2.558313 |
| 13 | 1 | 0 | -0.144101 | 0.415684 | 2.291764 |
| 14 | 1 | 0 | -0.003602 | 0.817878 | -0.740921 |
| 15 | 1 | 0 | -0.140768 | -0.731875 | 0.067586 |
| 16 | 6 | 0 | 2.235799 | -0.568531 | 1.689106 |
| 17 | 6 | 0 | 3.594062 | -0.81199 | 1.806633 |
| 18 | 6 | 0 | 4.068858 | -2.1253 | 2.364354 |
| 19 | 1 | 0 | 4.246349 | 0.046681 | 1.940153 |
| 20 | 1 | 0 | 4.114627 | -2.107946 | 3.458031 |
| 21 | 1 | 0 | 5.075019 | -2.363249 | 2.006546 |
| 22 | 1 | 0 | 3.398996 | -2.937149 | 2.065096 |
| 23 | 1 | 0 | 1.50681 | -1.370418 | 1.807012 |
| 24 | 7 | 0 | -1.854691 | 0.497943 | 0.186058 |
| 25 | 6 | 0 | -2.579035 | 0.255682 | 1.396421 |
| 26 | 6 | 0 | -2.634884 | -1.044367 | 1.90926 |
| 27 | 6 | 0 | -3.28535 | -1.283277 | 3.120211 |
| 28 | 6 | 0 | -3.909944 | -0.243715 | 3.801536 |
| 29 | 6 | 0 | -3.856399 | 1.050059 | 3.287957 |
| 30 | 6 | 0 | -3.177309 | 1.301026 | 2.100716 |
| 31 | 6 | 0 | -1.903026 | -2.187564 | 1.251983 |
| 32 | 1 | 0 | -3.307283 | -2.292829 | 3.518721 |
| 33 | 1 | 0 | -4.427181 | -0.441153 | 4.734 |
| 34 | 1 | 0 | -4.327244 | 1.86959 | 3.819795 |

| | | | | | |
|---|---|---|---|---|---|
| 35 | 1 | 0 | -3.100643 | 2.312445 | 1.716218 |
| 36 | 16 | 0 | -2.613124 | 1.165524 | -1.134901 |
| 37 | 8 | 0 | -4.044239 | 1.02303 | -0.899523 |
| 38 | 8 | 0 | -1.990382 | 0.600324 | -2.32357 |
| 39 | 6 | 0 | -2.213446 | 2.896013 | -1.135448 |
| 40 | 6 | 0 | -3.053967 | 3.797776 | -0.486336 |
| 41 | 6 | 0 | -2.677344 | 5.133584 | -0.411324 |
| 42 | 6 | 0 | -1.477541 | 5.578748 | -0.978417 |
| 43 | 6 | 0 | -0.666548 | 4.65533 | -1.646401 |
| 44 | 6 | 0 | -1.028251 | 3.315508 | -1.736454 |
| 45 | 6 | 0 | -1.088913 | 7.031228 | -0.908373 |
| 46 | 1 | 0 | -3.991832 | 3.456375 | -0.060153 |
| 47 | 1 | 0 | -3.326188 | 5.843953 | 0.092117 |
| 48 | 1 | 0 | 0.259333 | 4.989738 | -2.10519 |
| 49 | 1 | 0 | -0.408356 | 2.605486 | -2.275258 |
| 50 | 1 | 0 | -1.494494 | 7.505052 | -0.012296 |
| 51 | 1 | 0 | -1.480354 | 7.571493 | -1.776167 |
| 52 | 1 | 0 | -0.003418 | 7.149189 | -0.906803 |
| 53 | 8 | 0 | -0.801103 | -2.525508 | 1.679806 |
| 54 | 7 | 0 | -2.534966 | -2.843804 | 0.245671 |
| 55 | 6 | 0 | -1.790573 | -3.888233 | -0.442863 |
| 56 | 6 | 0 | -2.749045 | -4.930098 | -1.015121 |
| 57 | 8 | 0 | -3.748808 | -4.32057 | -1.805418 |
| 58 | 6 | 0 | -4.530852 | -3.439555 | -1.016257 |
| 59 | 6 | 0 | -3.67928 | -2.296215 | -0.487055 |
| 60 | 1 | 0 | -1.13047 | -4.368468 | 0.283637 |
| 61 | 1 | 0 | -2.190782 | -5.614308 | -1.655953 |
| 62 | 1 | 0 | -3.207883 | -5.492143 | -0.189488 |
| 63 | 1 | 0 | -5.322462 | -3.048755 | -1.657905 |
| 64 | 1 | 0 | -4.984962 | -3.991848 | -0.180187 |
| 65 | 1 | 0 | -3.309756 | -1.692198 | -1.324301 |
| 66 | 1 | 0 | -4.266316 | -1.657311 | 0.174177 |
| 67 | 6 | 0 | -0.867194 | -3.335563 | -1.533941 |
| 68 | 8 | 0 | -0.161936 | -4.067087 | -2.193812 |
| 69 | 8 | 0 | -0.936633 | -2.024547 | -1.647651 |
| 70 | 1 | 0 | -0.138305 | -1.639731 | -2.102761 |
| 71 | 6 | 0 | 4.176928 | -0.991534 | -0.339599 |
| 72 | 6 | 0 | 3.244781 | -0.419538 | -1.197114 |
| 73 | 7 | 0 | 2.059377 | -1.084942 | -1.386478 |
| 74 | 8 | 0 | 1.264848 | -0.683102 | -2.284236 |
| 75 | 8 | 0 | 1.783768 | -2.066819 | -0.676614 |
| 76 | 1 | 0 | 4.052681 | -2.055152 | -0.161499 |
| 77 | 1 | 0 | 3.361701 | 0.482049 | -1.77876 |
| 78 | 6 | 0 | 5.560811 | -0.481865 | -0.27258 |
| 79 | 6 | 0 | 6.603099 | -1.380776 | -0.011236 |
| 80 | 6 | 0 | 7.922871 | -0.941724 | 0.049451 |
| 81 | 6 | 0 | 8.220018 | 0.403452 | -0.150118 |
| 82 | 6 | 0 | 7.191202 | 1.306961 | -0.419041 |
| 83 | 6 | 0 | 5.874211 | 0.86929 | -0.479685 |
| 84 | 1 | 0 | 6.377215 | -2.434753 | 0.121769 |
| 85 | 1 | 0 | 8.717741 | -1.652803 | 0.248106 |
| 86 | 1 | 0 | 9.247448 | 0.748295 | -0.100798 |
| 87 | 1 | 0 | 7.416859 | 2.355695 | -0.580943 |
| 88 | 1 | 0 | 5.086377 | 1.585474 | -0.693717 |

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**TS-J**

M062X/6-31G*

E(RM062X) = -2575.773918 Hartree

EE+Thermal Free Energy of Correction = -2575.130046 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 1.945928 | -1.586286 | -0.88814 |
| 2 | 6 | 0 | 2.5566 | -2.72292 | -0.191939 |
| 3 | 6 | 0 | 1.352013 | -3.370913 | 0.478558 |
| 4 | 6 | 0 | 0.273352 | -3.24074 | -0.602578 |
| 5 | 6 | 0 | 0.519754 | -1.84456 | -1.203852 |
| 6 | 6 | 0 | -0.382755 | -0.747459 | -0.61979 |
| 7 | 1 | 0 | 3.319782 | -2.378878 | 0.505634 |
| 8 | 1 | 0 | 3.025934 | -3.398469 | -0.921276 |
| 9 | 1 | 0 | 1.078185 | -2.790598 | 1.36688 |
| 10 | 1 | 0 | 1.540042 | -4.402574 | 0.777125 |
| 11 | 1 | 0 | -0.742302 | -3.340223 | -0.212663 |
| 12 | 1 | 0 | 0.416955 | -4.008979 | -1.368083 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 1 | 0 | 0.402643 | -1.84196 | -2.291611 | 51 | 1 | 0 | -0.414762 | 6.237697 | 0.419213 |
| 14 | 1 | 0 | -0.680786 | -0.989699 | 0.403862 | 52 | 1 | 0 | -2.054252 | 5.914984 | 1.011277 |
| 15 | 1 | 0 | 0.156926 | 0.203118 | -0.562475 | 53 | 8 | 0 | -4.264898 | 0.697282 | -0.081896 |
| 16 | 6 | 0 | 2.644716 | -0.667695 | -1.564226 | 54 | 7 | 0 | -3.452606 | -0.514865 | 1.65683 |
| 17 | 6 | 0 | 4.020508 | -0.539537 | -1.52865 | 55 | 6 | 0 | -3.431578 | 0.646205 | 2.536745 |
| 18 | 6 | 0 | 4.706793 | 0.40988 | -2.471772 | 56 | 6 | 0 | -3.992068 | 0.262373 | 3.902123 |
| 19 | 1 | 0 | 4.594848 | -1.393387 | -1.179214 | 57 | 8 | 0 | -3.301625 | -0.85349 | 4.433121 |
| 20 | 1 | 0 | 4.969248 | -0.08229 | -3.413762 | 58 | 6 | 0 | -3.420176 | -1.981704 | 3.586039 |
| 21 | 1 | 0 | 5.637034 | 0.793166 | -2.041666 | 59 | 6 | 0 | -2.804394 | -1.694219 | 2.222604 |
| 22 | 1 | 0 | 4.061175 | 1.262067 | -2.704554 | 60 | 1 | 0 | -4.042475 | 1.426493 | 2.074223 |
| 23 | 1 | 0 | 2.035798 | 0.035528 | -2.133166 | 61 | 1 | 0 | -3.854903 | 1.086458 | 4.602232 |
| 24 | 7 | 0 | -1.602645 | -0.518786 | -1.403496 | 62 | 1 | 0 | -5.062415 | 0.035916 | 3.799625 |
| 25 | 6 | 0 | -2.597948 | -1.547395 | -1.486292 | 63 | 1 | 0 | -2.894423 | -2.804788 | 4.073448 |
| 26 | 6 | 0 | -3.646971 | -1.537218 | -0.562254 | 64 | 1 | 0 | -4.479131 | -2.252988 | 3.460119 |
| 27 | 6 | 0 | -4.589283 | -2.566017 | -0.572641 | 65 | 1 | 0 | -1.728312 | -1.499616 | 2.344367 |
| 28 | 6 | 0 | -4.495842 | -3.589459 | -1.511516 | 66 | 1 | 0 | -2.932434 | -2.547722 | 1.556839 |
| 29 | 6 | 0 | -3.461762 | -3.587407 | -2.445766 | 67 | 6 | 0 | -1.997209 | 1.18003 | 2.673084 |
| 30 | 6 | 0 | -2.512113 | -2.570947 | -2.430703 | 68 | 8 | 0 | -1.570917 | 1.679519 | 3.690206 |
| 31 | 6 | 0 | -3.803683 | -0.350819 | 0.353321 | 69 | 8 | 0 | -1.306688 | 1.028439 | 1.555556 |
| 32 | 1 | 0 | -5.399568 | -2.55646 | 0.150487 | 70 | 1 | 0 | -0.325191 | 1.092914 | 1.726632 |
| 33 | 1 | 0 | -5.233706 | -4.384333 | -1.517867 | 71 | 6 | 0 | 4.301182 | 0.489609 | 0.446046 |
| 34 | 1 | 0 | -3.390999 | -4.379369 | -3.183246 | 72 | 6 | 0 | 3.302323 | 0.133155 | 1.339387 |
| 35 | 1 | 0 | -1.699512 | -2.563806 | -3.151327 | 73 | 7 | 0 | 2.060114 | 0.695078 | 1.197705 |
| 36 | 16 | 0 | -1.460376 | 0.567744 | -2.662113 | 74 | 8 | 0 | 1.173443 | 0.416778 | 2.050754 |
| 37 | 8 | 0 | -2.671053 | 0.438496 | -3.462801 | 75 | 8 | 0 | 1.823338 | 1.4675 | 0.252198 |
| 38 | 8 | 0 | -0.152166 | 0.383608 | -3.297904 | 76 | 1 | 0 | 4.143739 | 1.414339 | -0.100669 |
| 39 | 6 | 0 | -1.439546 | 2.15287 | -1.87639 | 77 | 1 | 0 | 3.394098 | -0.556358 | 2.164588 |
| 40 | 6 | 0 | -2.653423 | 2.755636 | -1.547108 | 78 | 6 | 0 | 5.703183 | 0.104955 | 0.696202 |
| 41 | 6 | 0 | -2.630646 | 3.982455 | -0.900877 | 79 | 6 | 0 | 6.726142 | 0.994042 | 0.344149 |
| 42 | 6 | 0 | -1.418892 | 4.609442 | -0.577767 | 80 | 6 | 0 | 8.059019 | 0.674312 | 0.589846 |
| 43 | 6 | 0 | -0.22177 | 3.980472 | -0.924084 | 81 | 6 | 0 | 8.385519 | -0.541113 | 1.184299 |
| 44 | 6 | 0 | -0.221477 | 2.75302 | -1.580619 | 82 | 6 | 0 | 7.37377 | -1.436134 | 1.535934 |
| 45 | 6 | 0 | -1.422219 | 5.943847 | 0.119709 | 83 | 6 | 0 | 6.044104 | -1.116899 | 1.293819 |
| 46 | 1 | 0 | -3.587118 | 2.256233 | -1.775146 | 84 | 1 | 0 | 6.470728 | 1.948384 | -0.107484 |
| 47 | 1 | 0 | -3.567177 | 4.465758 | -0.637614 | 85 | 1 | 0 | 8.839892 | 1.376222 | 0.317183 |
| 48 | 1 | 0 | 0.724545 | 4.4517 | -0.67687 | 86 | 1 | 0 | 9.423581 | -0.793747 | 1.37286 |
| 49 | 1 | 0 | 0.709888 | 2.266809 | -1.848636 | 87 | 1 | 0 | 7.623959 | -2.386015 | 1.996338 |
| 50 | 1 | 0 | -1.822575 | 6.720936 | -0.538436 | 88 | 1 | 0 | 5.266743 | -1.826277 | 1.56423 |

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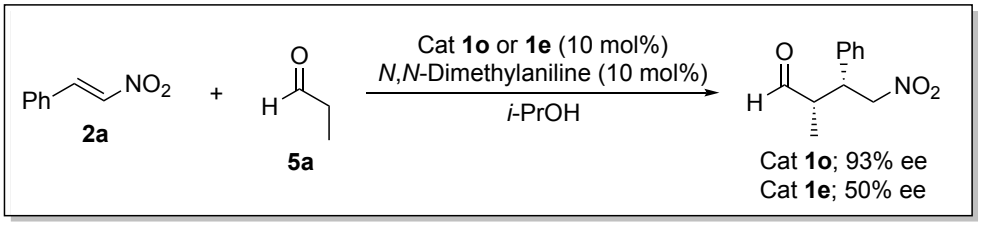
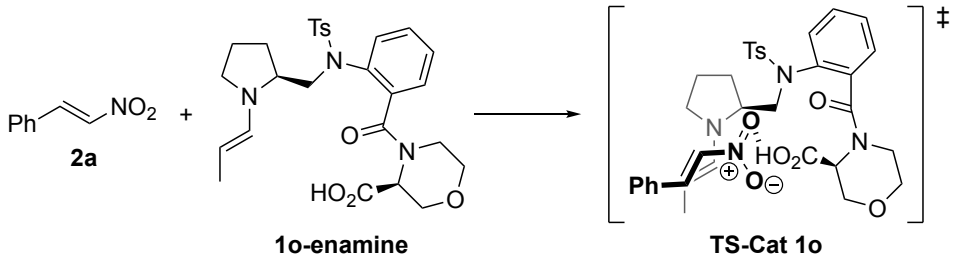
**< Distortion/Interaction Analysis of TS-Cat 1o and TS-Cat 1e >**

To support the origin of the enantioselectivity differences between Cat **1o** and Cat **1e** for Michael reaction of β-nitrostyrene with proionaldehyde, a flexibility of TS models was considered by distortion/interaction analysis at the M06-02X/6-31G* level according to the SCRF method based on PCM (i-PrOH).

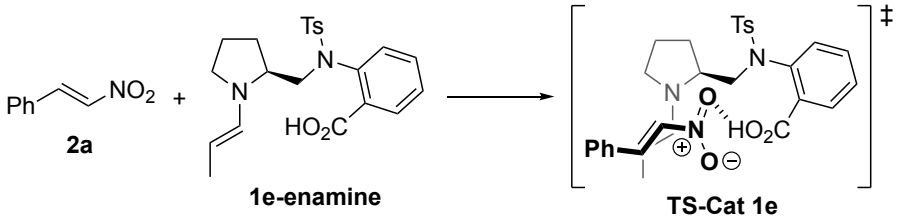
< Michael Reaction of β-Nitrostyrene (**2a**) with Propionaldehyde (**5a**) using Catalyst **1o** and **1e** >

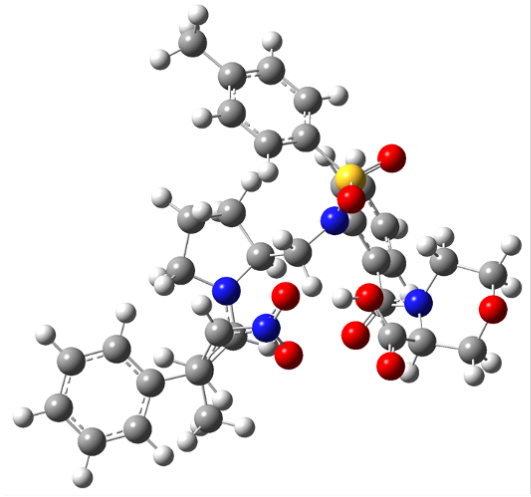



***< Distortion/Interaction Analysis of TS-Cat 1o >***

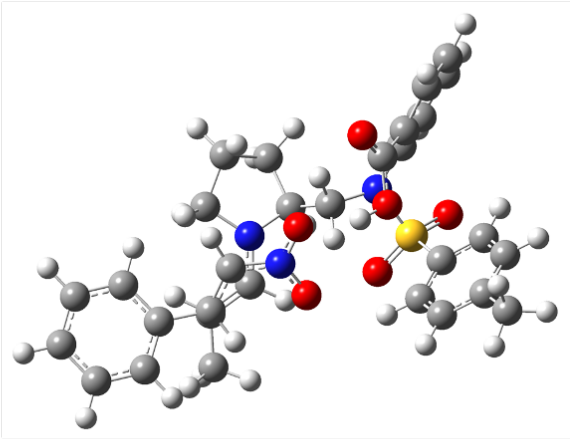



***< Distortion/Interaction Analysis of TS-Cat 1e >***





**TS-Cat 1o**
$E_{dist(enamine)}$ = 10.0 kcal/mol
$E_{dist(nitrostyrene)}$ = 11.3 kcal/mol
$E_{int}$ = 29.3 kcal/mol
ΔE‡ = -8.0 kcal/mol



**TS-Cat 1e**
$E_{dist(enamine)}$ = 11.2 kcal/mol
$E_{dist(nitrostyrene)}$ = 10.6 kcal/mol
$E_{int}$ = 27.9 kcal/mol
ΔE‡ = -6.1 kcal/mol

$$E_{int\text{-}TS\text{-}Cat\ 1o} - E_{int\text{-}TS\text{-}Cat\ 1e} = +1.4\ kcal/mol$$

**Figure S4.** Distortion/interaction analysis of the transition states of Michael reaction of β-nitrostyrene with propionaldehyde between catalyst **1o** and catalyst **1e**.

**β-Nitrostyrene (2a)**

M062X/6-31G*

E(RM062X) = -513.945300 Hartree

EE+Thermal Free Energy of Correction = -513.842351 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.783817 | 2.381159 | -0.017585 |
| 2 | 6 | 0 | -1.311713 | 1.012524 | -0.029229 |
| 3 | 6 | 0 | -0.000706 | 0.76384 | 0.019879 |
| 4 | 6 | 0 | 0.625782 | -0.55689 | 0.015675 |
| 5 | 6 | 0 | 2.024227 | -0.624202 | 0.072495 |
| 6 | 6 | 0 | 2.674655 | -1.853546 | 0.071417 |
| 7 | 6 | 0 | 1.932202 | -3.030029 | 0.013421 |
| 8 | 6 | 0 | 0.537871 | -2.974717 | -0.043504 |
| 9 | 6 | 0 | -0.112891 | -1.749352 | -0.042537 |
| 10 | 8 | 0 | -0.980764 | 3.300478 | 0.037393 |
| 11 | 8 | 0 | -2.996238 | 2.534391 | -0.06511 |
| 12 | 1 | 0 | -2.127164 | 0.306383 | -0.07963 |
| 13 | 1 | 0 | 0.662029 | 1.624501 | 0.067358 |
| 14 | 1 | 0 | 2.599434 | 0.295896 | 0.117628 |
| 15 | 1 | 0 | 3.757635 | -1.892325 | 0.115728 |
| 16 | 1 | 0 | 2.436127 | -3.990848 | 0.012404 |
| 17 | 1 | 0 | -0.040369 | -3.891261 | -0.088673 |
| 18 | 1 | 0 | -1.196789 | -1.721047 | -0.087128 |

**1o-enamine**

M062X/6-31G*

E(RM062X) = -2061.819190 Hartree

EE+Thermal Free Energy of Correction = -2061.307672 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 4.015601 | -1.97028 | 0.355154 |
| 2 | 6 | 0 | 4.371581 | -3.03473 | 1.280511 |
| 3 | 6 | 0 | 3.080326 | -3.255032 | 2.067781 |
| 4 | 6 | 0 | 1.998969 | -3.013046 | 1.008007 |
| 5 | 6 | 0 | 2.56682 | -1.856262 | 0.174884 |
| 6 | 6 | 0 | 2.109944 | -0.484482 | 0.682924 |
| 7 | 1 | 0 | 5.216583 | -2.736787 | 1.911268 |
| 8 | 1 | 0 | 4.670306 | -3.944309 | 0.732795 |
| 9 | 1 | 0 | 3.005803 | -2.517244 | 2.873617 |
| 10 | 1 | 0 | 3.02724 | -4.249076 | 2.515107 |
| 11 | 1 | 0 | 1.009067 | -2.778927 | 1.405935 |
| 12 | 1 | 0 | 1.898384 | -3.900281 | 0.374921 |
| 13 | 1 | 0 | 2.288854 | -1.940259 | -0.880846 |
| 14 | 1 | 0 | 2.190041 | -0.45373 | 1.772753 |
| 15 | 1 | 0 | 2.771047 | 0.297336 | 0.289598 |
| 16 | 6 | 0 | 4.875508 | -1.598247 | -0.659541 |
| 17 | 6 | 0 | 6.158797 | -1.965355 | -0.796361 |
| 18 | 6 | 0 | 7.031214 | -1.475929 | -1.91601 |
| 19 | 1 | 0 | 6.607375 | -2.636742 | -0.067804 |
| 20 | 1 | 0 | 7.428438 | -2.303768 | -2.514258 |
| 21 | 1 | 0 | 7.895774 | -0.912978 | -1.545449 |
| 22 | 1 | 0 | 6.471642 | -0.819044 | -2.588507 |
| 23 | 1 | 0 | 4.422855 | -0.923157 | -1.38737 |
| 24 | 7 | 0 | 0.702129 | -0.213491 | 0.324629 |
| 25 | 6 | 0 | -0.237291 | 0.084392 | 1.36693 |
| 26 | 6 | 0 | -1.503248 | -0.514664 | 1.36207 |
| 27 | 6 | 0 | -2.408924 | -0.200487 | 2.377945 |
| 28 | 6 | 0 | -2.064405 | 0.692757 | 3.388244 |
| 29 | 6 | 0 | -0.808644 | 1.293438 | 3.382948 |
| 30 | 6 | 0 | 0.096194 | 0.998893 | 2.368067 |
| 31 | 6 | 0 | -1.865254 | -1.605913 | 0.3853 |
| 32 | 1 | 0 | -3.383343 | -0.680788 | 2.379041 |
| 33 | 1 | 0 | -2.774414 | 0.916242 | 4.176936 |
| 34 | 1 | 0 | -0.534462 | 1.998987 | 4.159612 |
| 35 | 1 | 0 | 1.068197 | 1.483038 | 2.342709 |
| 36 | 16 | 0 | 0.486746 | 0.629862 | -1.10246 |
| 37 | 8 | 0 | -0.942983 | 0.594396 | -1.390988 |
| 38 | 8 | 0 | 1.448301 | 0.081793 | -2.05067 |
| 39 | 6 | 0 | 0.93531 | 2.309907 | -0.767505 |
| 40 | 6 | 0 | -0.002824 | 3.156999 | -0.176153 |
| 41 | 6 | 0 | 0.377493 | 4.452363 | 0.148559 |
| 42 | 6 | 0 | 1.675586 | 4.910604 | -0.108837 |
| 43 | 6 | 0 | 2.592909 | 4.039356 | -0.703915 |
| 44 | 6 | 0 | 2.233418 | 2.737511 | -1.036577 |
| 45 | 6 | 0 | 2.061903 | 6.327223 | 0.22251 |
| 46 | 1 | 0 | -1.011761 | 2.805655 | 0.015397 |
| 47 | 1 | 0 | -0.343696 | 5.122013 | 0.607482 |
| 48 | 1 | 0 | 3.600716 | 4.38493 | -0.912796 |
| 49 | 1 | 0 | 2.939203 | 2.065605 | -1.513886 |
| 50 | 1 | 0 | 1.742254 | 7.004837 | -0.575486 |
| 51 | 1 | 0 | 3.143306 | 6.427016 | 0.332133 |
| 52 | 1 | 0 | 1.583614 | 6.658796 | 1.146749 |
| 53 | 8 | 0 | -1.196761 | -2.631068 | 0.335655 |
| 54 | 7 | 0 | -3.009778 | -1.444726 | -0.338665 |
| 55 | 6 | 0 | -3.728776 | -0.195089 | -0.495469 |
| 56 | 6 | 0 | -3.973965 | 0.080225 | -1.987739 |
| 57 | 8 | 0 | -4.624225 | -1.015088 | -2.597259 |
| 58 | 6 | 0 | -3.794769 | -2.166078 | -2.541241 |
| 59 | 6 | 0 | -3.552116 | -2.572654 | -1.096777 |
| 60 | 1 | 0 | -3.132154 | 0.630056 | -0.097036 |
| 61 | 1 | 0 | -4.617543 | 0.952663 | -2.104665 |
| 62 | 1 | 0 | -3.002444 | 0.266957 | -2.459892 |
| 63 | 1 | 0 | -4.31293 | -2.962685 | -3.078564 |
| 64 | 1 | 0 | -2.836814 | -1.957386 | -3.039729 |
| 65 | 1 | 0 | -4.49855 | -2.876454 | -0.635805 |
| 66 | 1 | 0 | -2.839651 | -3.393692 | -1.033488 |
| 67 | 6 | 0 | -5.047043 | -0.238205 | 0.275023 |
| 68 | 8 | 0 | -5.393065 | -1.126875 | 1.015984 |
| 69 | 8 | 0 | -5.780179 | 0.854928 | 0.044002 |
| 70 | 1 | 0 | -6.597518 | 0.785226 | 0.563798 |

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**TS-Cat 1o-β-Nitrostyrene**

M062X/6-31G*

E(RM062X) = -513.927272 Hartree

EE+Thermal Free Energy of Correction = -513.823928 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.637453 | 0.476443 | -0.346895 |
| 2 | 6 | 0 | -1.590604 | -0.469023 | 0.01228 |
| 3 | 7 | 0 | -2.901806 | -0.066367 | 0.061473 |
| 4 | 8 | 0 | -3.768195 | -0.849621 | 0.545833 |
| 5 | 8 | 0 | -3.218421 | 1.055354 | -0.369162 |
| 6 | 1 | 0 | -0.941415 | 1.511489 | -0.225541 |
| 7 | 1 | 0 | -1.414607 | -1.49242 | 0.306434 |
| 8 | 6 | 0 | 0.803908 | 0.202248 | -0.183551 |
| 9 | 6 | 0 | 1.664944 | 1.261894 | 0.130253 |
| 10 | 6 | 0 | 3.028945 | 1.043046 | 0.303039 |
| 11 | 6 | 0 | 3.552413 | -0.23927 | 0.164226 |
| 12 | 6 | 0 | 2.70356 | -1.304066 | -0.140352 |
| 13 | 6 | 0 | 1.34251 | -1.086133 | -0.312832 |
| 14 | 1 | 0 | 1.256381 | 2.259505 | 0.262272 |
| 15 | 1 | 0 | 3.680072 | 1.874712 | 0.550589 |
| 16 | 1 | 0 | 4.615362 | -0.411764 | 0.295929 |
| 17 | 1 | 0 | 3.104582 | -2.306725 | -0.244438 |
| 18 | 1 | 0 | 0.695857 | -1.926917 | -0.54593 |

**TS-Cat 1o-enamine**

M062X/6-31G*

E(RM062X) = -2061.803207 Hartree

EE+Thermal Free Energy of Correction = -2061.286851 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -0.865068 | 3.188273 | 0.127863 |
| 2 | 6 | 0 | -2.188938 | 3.759771 | -0.144594 |
| 3 | 6 | 0 | -3.089028 | 2.530533 | -0.203836 |
| 4 | 6 | 0 | -2.467955 | 1.610979 | 0.853808 |
| 5 | 6 | 0 | -0.959375 | 1.815469 | 0.667607 |
| 6 | 6 | 0 | -0.30761 | 0.857574 | -0.327133 |
| 7 | 1 | 0 | -2.167366 | 4.337567 | -1.068989 |
| 8 | 1 | 0 | -2.472424 | 4.43137 | 0.677576 |
| 9 | 1 | 0 | -3.025983 | 2.073306 | -1.196669 |
| 10 | 1 | 0 | -4.134391 | 2.768678 | -0.003705 |
| 11 | 1 | 0 | -2.759002 | 0.563893 | 0.736294 |
| 12 | 1 | 0 | -2.764866 | 1.936926 | 1.854757 |
| 13 | 1 | 0 | -0.417884 | 1.769974 | 1.618134 |
| 14 | 1 | 0 | -0.849824 | 0.871103 | -1.277404 |
| 15 | 1 | 0 | 0.708317 | 1.196088 | -0.542004 |
| 16 | 6 | 0 | 0.23892 | 3.9297 | 0.239732 |
| 17 | 6 | 0 | 0.300567 | 5.272084 | -0.095181 |
| 18 | 6 | 0 | 1.541946 | 6.060723 | 0.218337 |
| 19 | 1 | 0 | -0.636406 | 5.820693 | -0.136792 |
| 20 | 1 | 0 | 1.523961 | 6.455211 | 1.239406 |
| 21 | 1 | 0 | 1.642553 | 6.91839 | -0.453445 |
| 22 | 1 | 0 | 2.434043 | 5.436219 | 0.110964 |
| 23 | 1 | 0 | 1.131005 | 3.383409 | 0.546489 |
| 24 | 7 | 0 | -0.282623 | -0.525933 | 0.176815 |
| 25 | 6 | 0 | 0.059457 | -0.783955 | 1.542373 |
| 26 | 6 | 0 | 1.357886 | -0.509273 | 1.983829 |
| 27 | 6 | 0 | 1.686845 | -0.698215 | 3.326466 |
| 28 | 6 | 0 | 0.742657 | -1.192713 | 4.220329 |
| 29 | 6 | 0 | -0.54925 | -1.469017 | 3.778613 |
| 30 | 6 | 0 | -0.893843 | -1.24705 | 2.449825 |
| 31 | 6 | 0 | 2.390674 | 0.106478 | 1.073485 |
| 32 | 1 | 0 | 2.692295 | -0.464716 | 3.66267 |
| 33 | 1 | 0 | 1.011487 | -1.351882 | 5.25879 |
| 34 | 1 | 0 | -1.296478 | -1.840344 | 4.471393 |
| 35 | 1 | 0 | -1.908339 | -1.424904 | 2.109457 |
| 36 | 16 | 0 | -0.850046 | -1.747413 | -0.798805 |
| 37 | 8 | 0 | -0.517785 | -2.996146 | -0.124961 |
| 38 | 8 | 0 | -0.378228 | -1.477557 | -2.149641 |
| 39 | 6 | 0 | -2.618249 | -1.587247 | -0.845089 |
| 40 | 6 | 0 | -3.397362 | -2.277636 | 0.080839 |
| 41 | 6 | 0 | -4.770954 | -2.065718 | 0.094702 |
| 42 | 6 | 0 | -5.374117 | -1.178791 | -0.804657 |
| 43 | 6 | 0 | -4.569714 | -0.519521 | -1.740024 |
| 44 | 6 | 0 | -3.194196 | -0.721809 | -1.773083 |

| | | | | | |
|---|---|---|---|---|---|
| 45 | 6 | 0 | -6.864964 | -0.971686 | -0.7938 |
| 46 | 1 | 0 | -2.93248 | -2.977278 | 0.767981 |
| 47 | 1 | 0 | -5.386505 | -2.599672 | 0.812383 |
| 48 | 1 | 0 | -5.026232 | 0.159201 | -2.454516 |
| 49 | 1 | 0 | -2.575318 | -0.226492 | -2.514947 |
| 50 | 1 | 0 | -7.276445 | -1.12112 | 0.206356 |
| 51 | 1 | 0 | -7.352703 | -1.686546 | -1.464073 |
| 52 | 1 | 0 | -7.125905 | 0.032494 | -1.134017 |
| 53 | 8 | 0 | 2.581484 | 1.32046 | 1.10972 |
| 54 | 7 | 0 | 3.120089 | -0.730415 | 0.292314 |
| 55 | 6 | 0 | 4.053169 | -0.125262 | -0.646931 |
| 56 | 6 | 0 | 5.21022 | -1.080276 | -0.931204 |
| 57 | 8 | 0 | 4.734923 | -2.349328 | -1.330229 |
| 58 | 6 | 0 | 3.969292 | -2.936993 | -0.291473 |
| 59 | 6 | 0 | 2.725641 | -2.10877 | -0.008925 |
| 60 | 1 | 0 | 4.445078 | 0.78849 | -0.193466 |
| 61 | 1 | 0 | 5.811199 | -0.678974 | -1.748668 |
| 62 | 1 | 0 | 5.832163 | -1.173996 | -0.029816 |
| 63 | 1 | 0 | 3.683886 | -3.935579 | -0.626816 |
| 64 | 1 | 0 | 4.580993 | -3.024112 | 0.61874 |
| 65 | 1 | 0 | 2.073892 | -2.107796 | -0.890734 |
| 66 | 1 | 0 | 2.173484 | -2.524848 | 0.834899 |
| 67 | 6 | 0 | 3.377596 | 0.319559 | -1.948568 |
| 68 | 8 | 0 | 4.005874 | 0.858467 | -2.833323 |
| 69 | 8 | 0 | 2.086852 | 0.055067 | -1.971744 |
| 70 | 1 | 0 | 1.597314 | 0.60907 | -2.639553 |

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**TS-Cat 1o**

M062X/6-31G*

E(RM062X) = -2575.777237 Hartree

EE+Thermal Free Energy of Correction = -2575.132327 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 1.722545 | 0.612317 | 1.338128 |
| 2 | 6 | 0 | 2.521499 | 1.840668 | 1.258743 |
| 3 | 6 | 0 | 1.506738 | 2.882413 | 0.800786 |
| 4 | 6 | 0 | 0.223308 | 2.431054 | 1.50719 |
| 5 | 6 | 0 | 0.274544 | 0.901638 | 1.404426 |
| 6 | 6 | 0 | -0.392274 | 0.327231 | 0.156516 |
| 7 | 1 | 0 | 3.356423 | 1.703774 | 0.571005 |
| 8 | 1 | 0 | 2.92609 | 2.077371 | 2.252549 |
| 9 | 1 | 0 | 1.387101 | 2.829517 | -0.286245 |
| 10 | 1 | 0 | 1.804816 | 3.898484 | 1.062123 |
| 11 | 1 | 0 | -0.682745 | 2.843796 | 1.055948 |
| 12 | 1 | 0 | 0.248225 | 2.73241 | 2.558313 |
| 13 | 1 | 0 | -0.144101 | 0.415684 | 2.291764 |
| 14 | 1 | 0 | -0.003602 | 0.817878 | -0.740921 |
| 15 | 1 | 0 | -0.140768 | -0.731875 | 0.067586 |
| 16 | 6 | 0 | 2.235799 | -0.568531 | 1.689106 |
| 17 | 6 | 0 | 3.594062 | -0.81199 | 1.806633 |
| 18 | 6 | 0 | 4.068858 | -2.1253 | 2.364354 |
| 19 | 1 | 0 | 4.246349 | 0.046681 | 1.940153 |
| 20 | 1 | 0 | 4.114627 | -2.107946 | 3.458031 |
| 21 | 1 | 0 | 5.075019 | -2.363249 | 2.006546 |
| 22 | 1 | 0 | 3.398996 | -2.937149 | 2.065096 |
| 23 | 1 | 0 | 1.50681 | -1.370418 | 1.807012 |
| 24 | 7 | 0 | -1.854691 | 0.497943 | 0.186058 |
| 25 | 6 | 0 | -2.579035 | 0.255682 | 1.396421 |
| 26 | 6 | 0 | -2.634884 | -1.044367 | 1.90926 |
| 27 | 6 | 0 | -3.28535 | -1.283277 | 3.120211 |
| 28 | 6 | 0 | -3.909944 | -0.243715 | 3.801536 |
| 29 | 6 | 0 | -3.856399 | 1.050059 | 3.287957 |
| 30 | 6 | 0 | -3.177309 | 1.301026 | 2.100716 |
| 31 | 6 | 0 | -1.903026 | -2.187564 | 1.251983 |
| 32 | 1 | 0 | -3.307283 | -2.292829 | 3.518721 |
| 33 | 1 | 0 | -4.427181 | -0.441153 | 4.734 |
| 34 | 1 | 0 | -4.327244 | 1.86959 | 3.819795 |
| 35 | 1 | 0 | -3.100643 | 2.312445 | 1.716218 |
| 36 | 16 | 0 | -2.613124 | 1.165524 | -1.134901 |
| 37 | 8 | 0 | -4.044239 | 1.02303 | -0.899523 |
| 38 | 8 | 0 | -1.990382 | 0.600324 | -2.32357 |
| 39 | 6 | 0 | -2.213446 | 2.896013 | -1.135448 |
| 40 | 6 | 0 | -3.053967 | 3.797776 | -0.486336 |

| | | | | | |
|---|---|---|---|---|---|
| 41 | 6 | 0 | -2.677344 | 5.133584 | -0.411324 |
| 42 | 6 | 0 | -1.477541 | 5.578748 | -0.978417 |
| 43 | 6 | 0 | -0.666548 | 4.65533 | -1.646401 |
| 44 | 6 | 0 | -1.028251 | 3.315508 | -1.736454 |
| 45 | 6 | 0 | -1.088913 | 7.031228 | -0.908373 |
| 46 | 1 | 0 | -3.991832 | 3.456375 | -0.060153 |
| 47 | 1 | 0 | -3.326188 | 5.843953 | 0.092117 |
| 48 | 1 | 0 | 0.259333 | 4.989738 | -2.10519 |
| 49 | 1 | 0 | -0.408356 | 2.605486 | -2.275258 |
| 50 | 1 | 0 | -1.494494 | 7.505052 | -0.012296 |
| 51 | 1 | 0 | -1.480354 | 7.571493 | -1.776167 |
| 52 | 1 | 0 | -0.003418 | 7.149189 | -0.906803 |
| 53 | 8 | 0 | -0.801103 | -2.525508 | 1.679806 |
| 54 | 7 | 0 | -2.534966 | -2.843804 | 0.245671 |
| 55 | 6 | 0 | -1.790573 | -3.888233 | -0.442863 |
| 56 | 6 | 0 | -2.749045 | -4.930098 | -1.015121 |
| 57 | 8 | 0 | -3.748808 | -4.32057 | -1.805418 |
| 58 | 6 | 0 | -4.530852 | -3.439555 | -1.016257 |
| 59 | 6 | 0 | -3.67928 | -2.296215 | -0.487055 |
| 60 | 1 | 0 | -1.13047 | -4.368468 | 0.283637 |
| 61 | 1 | 0 | -2.190782 | -5.614308 | -1.655953 |
| 62 | 1 | 0 | -3.207883 | -5.492143 | -0.189488 |
| 63 | 1 | 0 | -5.322462 | -3.048755 | -1.657905 |
| 64 | 1 | 0 | -4.984962 | -3.991848 | -0.180187 |
| 65 | 1 | 0 | -3.309756 | -1.692198 | -1.324301 |
| 66 | 1 | 0 | -4.266316 | -1.657311 | 0.174177 |
| 67 | 6 | 0 | -0.867194 | -3.335563 | -1.533941 |
| 68 | 8 | 0 | -0.161936 | -4.067087 | -2.193812 |
| 69 | 8 | 0 | -0.936633 | -2.024547 | -1.647651 |
| 70 | 1 | 0 | -0.138305 | -1.639731 | -2.102761 |
| 71 | 6 | 0 | 4.176928 | -0.991534 | -0.339599 |
| 72 | 6 | 0 | 3.244781 | -0.419538 | -1.197114 |
| 73 | 7 | 0 | 2.059377 | -1.084942 | -1.386478 |
| 74 | 8 | 0 | 1.264848 | -0.683102 | -2.284236 |
| 75 | 8 | 0 | 1.783768 | -2.066819 | -0.676614 |
| 76 | 1 | 0 | 4.052681 | -2.055152 | -0.161499 |
| 77 | 1 | 0 | 3.361701 | 0.482049 | -1.77876 |
| 78 | 6 | 0 | 5.560811 | -0.481865 | -0.27258 |
| 79 | 6 | 0 | 6.603099 | -1.380776 | -0.011236 |
| 80 | 6 | 0 | 7.922871 | -0.941724 | 0.049451 |
| 81 | 6 | 0 | 8.220018 | 0.403452 | -0.150118 |
| 82 | 6 | 0 | 7.191202 | 1.306961 | -0.419041 |
| 83 | 6 | 0 | 5.874211 | 0.86929 | -0.479685 |
| 84 | 1 | 0 | 6.377215 | -2.434753 | 0.121769 |
| 85 | 1 | 0 | 8.717741 | -1.652803 | 0.248106 |
| 86 | 1 | 0 | 9.247448 | 0.748295 | -0.100798 |
| 87 | 1 | 0 | 7.416859 | 2.355695 | -0.580943 |
| 88 | 1 | 0 | 5.086377 | 1.585474 | -0.693717 |

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**1e-enamine**

M062X/6-31G*

E(RM062X) = -1662.010234 Hartree

EE+Thermal Free Energy of Correction = -1661.617099 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 3.420793 | 0.444591 | 0.662314 |
| 2 | 6 | 0 | 4.331314 | -0.313708 | 1.505768 |
| 3 | 6 | 0 | 3.496317 | -1.527132 | 1.910835 |
| 4 | 6 | 0 | 2.665234 | -1.794589 | 0.650173 |
| 5 | 6 | 0 | 2.343426 | -0.388139 | 0.123243 |
| 6 | 6 | 0 | 0.994656 | 0.141389 | 0.622061 |
| 7 | 1 | 0 | 4.662283 | 0.286711 | 2.360332 |
| 8 | 1 | 0 | 5.230482 | -0.612869 | 0.941264 |
| 9 | 1 | 0 | 2.846547 | -1.266121 | 2.752656 |
| 10 | 1 | 0 | 4.110043 | -2.379072 | 2.208179 |
| 11 | 1 | 0 | 1.762346 | -2.382831 | 0.833416 |
| 12 | 1 | 0 | 3.267182 | -2.33253 | -0.088122 |
| 13 | 1 | 0 | 2.325476 | -0.363546 | -0.972004 |
| 14 | 1 | 0 | 0.888391 | -0.047033 | 1.694659 |
| 15 | 1 | 0 | 0.945802 | 1.22602 | 0.477476 |
| 16 | 6 | 0 | 3.868542 | 1.542348 | -0.047842 |
| 17 | 6 | 0 | 5.047297 | 2.165175 | 0.10159 |
| 18 | 6 | 0 | 5.431972 | 3.381982 | -0.689308 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 1 | 0 | 5.763533 | 1.794817 | 0.831384 |
| 20 | 1 | 0 | 6.351098 | 3.220004 | -1.263676 |
| 21 | 1 | 0 | 5.61365 | 4.249068 | -0.043711 |
| 22 | 7 | 0 | -0.120668 | -0.508994 | -0.080644 |
| 23 | 6 | 0 | -0.917478 | -1.500539 | 0.561348 |
| 24 | 6 | 0 | -1.145812 | -2.750527 | -0.036948 |
| 25 | 6 | 0 | -1.97883 | -3.670304 | 0.604077 |
| 26 | 6 | 0 | -2.547506 | -3.381192 | 1.838549 |
| 27 | 6 | 0 | -2.307357 | -2.146037 | 2.435698 |
| 28 | 6 | 0 | -1.51105 | -1.205795 | 1.790808 |
| 29 | 6 | 0 | -0.569517 | -3.19183 | -1.346509 |
| 30 | 1 | 0 | -2.160599 | -4.622121 | 0.117442 |
| 31 | 1 | 0 | -3.178165 | -4.113768 | 2.32964 |
| 32 | 1 | 0 | -2.755268 | -1.904062 | 3.393433 |
| 33 | 1 | 0 | -1.352411 | -0.224877 | 2.228655 |
| 34 | 16 | 0 | -0.76244 | 0.295167 | -1.38387 |
| 35 | 8 | 0 | -1.609648 | -0.652915 | -2.096849 |
| 36 | 8 | 0 | 0.353337 | 0.951745 | -2.054669 |
| 37 | 6 | 0 | -1.805747 | 1.550535 | -0.69416 |
| 38 | 8 | 0 | -1.100453 | -4.024905 | -2.046231 |
| 39 | 8 | 0 | 0.616264 | -2.651671 | -1.648489 |
| 40 | 1 | 0 | 0.888346 | -3.02467 | -2.502787 |
| 41 | 6 | 0 | -3.081768 | 1.196407 | -0.252429 |
| 42 | 6 | 0 | -3.871364 | 2.164742 | 0.351689 |
| 43 | 6 | 0 | -3.405271 | 3.475329 | 0.522427 |
| 44 | 6 | 0 | -2.125651 | 3.799949 | 0.065553 |
| 45 | 6 | 0 | -1.316093 | 2.843856 | -0.541416 |
| 46 | 6 | 0 | -4.273466 | 4.504857 | 1.195414 |
| 47 | 1 | 0 | -3.449071 | 0.185585 | -0.398172 |
| 48 | 1 | 0 | -4.869459 | 1.905171 | 0.692171 |
| 49 | 1 | 0 | -1.758203 | 4.815005 | 0.180758 |
| 50 | 1 | 0 | -0.327635 | 3.09713 | -0.909951 |
| 51 | 1 | 0 | -5.287316 | 4.486945 | 0.787824 |
| 52 | 1 | 0 | -3.866419 | 5.509685 | 1.070826 |
| 53 | 1 | 0 | -4.348678 | 4.299772 | 2.267709 |
| 54 | 1 | 0 | 3.146709 | 1.912636 | -0.777161 |
| 55 | 1 | 0 | 4.64242 | 3.654405 | -1.395837 |

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**TS-Cat 1e-β-Nitrostyrene**

M062X/6-31G*

E(RM062X) = -513.928426 Hartree

EE+Thermal Free Energy of Correction = -513.825099 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.634577 | 0.473308 | -0.416008 |
| 2 | 6 | 0 | 0.805097 | 0.206795 | -0.223071 |
| 3 | 6 | 0 | 1.653753 | 1.26444 | 0.125964 |
| 4 | 6 | 0 | 3.011722 | 1.042811 | 0.341774 |
| 5 | 6 | 0 | 3.539107 | -0.237944 | 0.205901 |
| 6 | 6 | 0 | 2.702173 | -1.299137 | -0.142981 |
| 7 | 6 | 0 | 1.347563 | -1.079217 | -0.356124 |
| 8 | 1 | 0 | 1.240739 | 2.261701 | 0.247875 |
| 9 | 1 | 0 | 3.654951 | 1.871742 | 0.617482 |
| 10 | 1 | 0 | 4.597349 | -0.41187 | 0.369724 |
| 11 | 1 | 0 | 3.108551 | -2.299068 | -0.252248 |
| 12 | 1 | 0 | 0.708091 | -1.912381 | -0.634078 |
| 13 | 6 | 0 | -1.578671 | -0.452045 | 0.005595 |
| 14 | 7 | 0 | -2.895542 | -0.069267 | 0.0764 |
| 15 | 8 | 0 | -3.723749 | -0.869074 | 0.587631 |
| 16 | 8 | 0 | -3.250235 | 1.044912 | -0.349413 |
| 17 | 1 | 0 | -0.941625 | 1.51405 | -0.374046 |
| 18 | 1 | 0 | -1.384387 | -1.460072 | 0.338446 |

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**TS-Cat 1e-enamine**

M062X/6-31G*

E(RM062X) = -1661.992319 Hartree

EE+Thermal Free Energy of Correction = -1661.595543 Hartree

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | 3.50568 | -0.100132 | 0.303374 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 6 | 0 | 3.784438 | 1.176743 | 0.030991 |
| 3 | 6 | 0 | 4.878205 | 1.866504 | 0.520436 |
| 4 | 6 | 0 | 5.203864 | 3.231784 | -0.020137 |
| 5 | 1 | 0 | 5.704513 | 1.279172 | 0.912114 |
| 6 | 1 | 0 | 5.719348 | 3.841108 | 0.728416 |
| 7 | 1 | 0 | 5.862721 | 3.170921 | -0.89222 |
| 8 | 6 | 0 | 4.433746 | -1.011325 | 0.981115 |
| 9 | 6 | 0 | 3.629186 | -2.305511 | 1.070389 |
| 10 | 6 | 0 | 2.845992 | -2.303122 | -0.24856 |
| 11 | 6 | 0 | 2.450005 | -0.833118 | -0.430944 |
| 12 | 1 | 0 | 4.723598 | -0.607234 | 1.952027 |
| 13 | 1 | 0 | 5.33864 | -1.136736 | 0.370434 |
| 14 | 1 | 0 | 2.948592 | -2.254913 | 1.926627 |
| 15 | 1 | 0 | 4.266344 | -3.182259 | 1.189517 |
| 16 | 1 | 0 | 1.967882 | -2.954042 | -0.236961 |
| 17 | 1 | 0 | 3.495958 | -2.621089 | -1.068374 |
| 18 | 1 | 0 | 2.458338 | -0.526967 | -1.478565 |
| 19 | 6 | 0 | 1.090738 | -0.49139 | 0.177252 |
| 20 | 1 | 0 | 0.969559 | -1.046106 | 1.111179 |
| 21 | 1 | 0 | 1.04466 | 0.571546 | 0.427442 |
| 22 | 7 | 0 | -0.009196 | -0.851102 | -0.733118 |
| 23 | 6 | 0 | -1.019112 | -1.799251 | -0.362564 |
| 24 | 6 | 0 | -1.389613 | -2.74375 | -1.325188 |
| 25 | 6 | 0 | -2.346248 | -3.711561 | -1.04386 |
| 26 | 6 | 0 | -2.918026 | -3.781536 | 0.224534 |
| 27 | 6 | 0 | -2.527776 | -2.871847 | 1.197622 |
| 28 | 6 | 0 | -1.608505 | -1.857829 | 0.914777 |
| 29 | 1 | 0 | -0.907169 | -2.703729 | -2.293996 |
| 30 | 1 | 0 | -2.623724 | -4.427482 | -1.810105 |
| 31 | 1 | 0 | -3.649812 | -4.547239 | 0.45699 |
| 32 | 1 | 0 | -2.938844 | -2.920568 | 2.200379 |
| 33 | 6 | 0 | -1.256575 | -0.952581 | 2.057734 |
| 34 | 16 | 0 | -0.441895 | 0.351812 | -1.826029 |
| 35 | 8 | 0 | -1.217251 | -0.282094 | -2.883632 |
| 36 | 8 | 0 | 0.801256 | 1.048336 | -2.146271 |
| 37 | 6 | 0 | -1.497683 | 1.47075 | -0.96264 |
| 38 | 8 | 0 | -1.152473 | -1.366546 | 3.193411 |
| 39 | 8 | 0 | -1.075585 | 0.315333 | 1.711149 |
| 40 | 1 | 0 | -0.461722 | 0.72988 | 2.372594 |
| 41 | 6 | 0 | -2.851163 | 1.159914 | -0.844016 |
| 42 | 6 | 0 | -3.657286 | 1.98536 | -0.072626 |
| 43 | 6 | 0 | -3.126175 | 3.102281 | 0.584949 |
| 44 | 6 | 0 | -1.76519 | 3.386548 | 0.442161 |
| 45 | 6 | 0 | -0.939559 | 2.574192 | -0.326791 |
| 46 | 6 | 0 | -4.009496 | 3.967153 | 1.444692 |
| 47 | 1 | 0 | -3.260548 | 0.295577 | -1.357102 |
| 48 | 1 | 0 | -4.716319 | 1.763707 | 0.022342 |
| 49 | 1 | 0 | -1.344377 | 4.253841 | 0.942139 |
| 50 | 1 | 0 | 0.119594 | 2.785699 | -0.425626 |
| 51 | 1 | 0 | -4.982279 | 4.126784 | 0.973526 |
| 52 | 1 | 0 | -3.549939 | 4.938992 | 1.633743 |
| 53 | 1 | 0 | -4.188464 | 3.486213 | 2.411547 |
| 54 | 1 | 0 | 4.293295 | 3.758564 | -0.321183 |
| 55 | 1 | 0 | 3.034913 | 1.685335 | -0.575438 |

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**TS-Cat 1e**

M062X/6-31G*

E(RM062X) = -2175.965255 Hartree

EE+Thermal Free Energy of Correction = -2175.439920 Hartree

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.626871 | -1.552387 | 0.963205 |
| 2 | 6 | 0 | -2.156412 | -0.528817 | 1.637147 |
| 3 | 6 | 0 | -3.504312 | -0.223284 | 1.675451 |
| 4 | 6 | 0 | -4.00687 | 0.821557 | 2.633578 |
| 5 | 1 | 0 | -4.201788 | -1.004199 | 1.384156 |
| 6 | 1 | 0 | -4.909447 | 1.307754 | 2.251089 |
| 7 | 1 | 0 | -4.265116 | 0.384853 | 3.60359 |
| 8 | 6 | 0 | -2.419747 | -2.622254 | 0.348677 |
| 9 | 6 | 0 | -1.35384 | -3.496611 | -0.306721 |
| 10 | 6 | 0 | -0.193445 | -3.413926 | 0.693114 |
| 11 | 6 | 0 | -0.213394 | -1.950273 | 1.149518 |
| 12 | 1 | 0 | -3.139901 | -2.205626 | -0.356853 |

| | | | | | |
|---|---|---|---|---|---|
| 13 | 1 | 0 | -2.969553 | -3.167541 | 1.128336 |
| 14 | 1 | 0 | -1.067664 | -3.063793 | -1.270922 |
| 15 | 1 | 0 | -1.701363 | -4.515891 | -0.477442 |
| 16 | 1 | 0 | 0.774492 | -3.684258 | 0.263083 |
| 17 | 1 | 0 | -0.386066 | -4.074567 | 1.542881 |
| 18 | 1 | 0 | 0.05878 | -1.838545 | 2.200587 |
| 19 | 6 | 0 | 0.676301 | -1.039599 | 0.304887 |
| 20 | 1 | 0 | 0.618118 | -1.35532 | -0.739885 |
| 21 | 1 | 0 | 0.31366 | -0.009511 | 0.349169 |
| 22 | 6 | 0 | -3.73978 | 0.819946 | -0.283323 |
| 23 | 6 | 0 | -5.182156 | 0.571771 | -0.480488 |
| 24 | 6 | 0 | -6.102415 | 1.553071 | -0.092123 |
| 25 | 6 | 0 | -7.468007 | 1.36249 | -0.288619 |
| 26 | 6 | 0 | -7.930903 | 0.186149 | -0.870752 |
| 27 | 6 | 0 | -7.022171 | -0.799103 | -1.260356 |
| 28 | 6 | 0 | -5.660172 | -0.608736 | -1.066751 |
| 29 | 1 | 0 | -5.741563 | 2.478382 | 0.347829 |
| 30 | 1 | 0 | -8.167784 | 2.134923 | 0.012289 |
| 31 | 1 | 0 | -8.994523 | 0.034173 | -1.021023 |
| 32 | 1 | 0 | -7.377861 | -1.718799 | -1.712671 |
| 33 | 1 | 0 | -4.963709 | -1.386269 | -1.36796 |
| 34 | 6 | 0 | -2.82163 | 0.392496 | -1.231811 |
| 35 | 7 | 0 | -1.536676 | 0.873294 | -1.173438 |
| 36 | 8 | 0 | -0.748564 | 0.588151 | -2.113942 |
| 37 | 8 | 0 | -1.172154 | 1.578554 | -0.215184 |
| 38 | 1 | 0 | -3.475996 | 1.725334 | 0.255077 |
| 39 | 1 | 0 | -3.019522 | -0.262989 | -2.065977 |
| 40 | 7 | 0 | 2.080628 | -1.107103 | 0.7423 |
| 41 | 6 | 0 | 3.126729 | -1.544291 | -0.135634 |
| 42 | 6 | 0 | 4.0757 | -2.424808 | 0.393647 |
| 43 | 6 | 0 | 5.111897 | -2.913768 | -0.392589 |
| 44 | 6 | 0 | 5.191578 | -2.566383 | -1.739298 |
| 45 | 6 | 0 | 4.231705 | -1.723381 | -2.282181 |
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| 51 | 6 | 0 | 2.230894 | -0.298628 | -2.203697 |
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| 72 | 1 | 0 | -3.248723 | 1.592431 | 2.80159 |
| 73 | 1 | 0 | -1.427808 | 0.117703 | 2.126388 |

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## 7. References.

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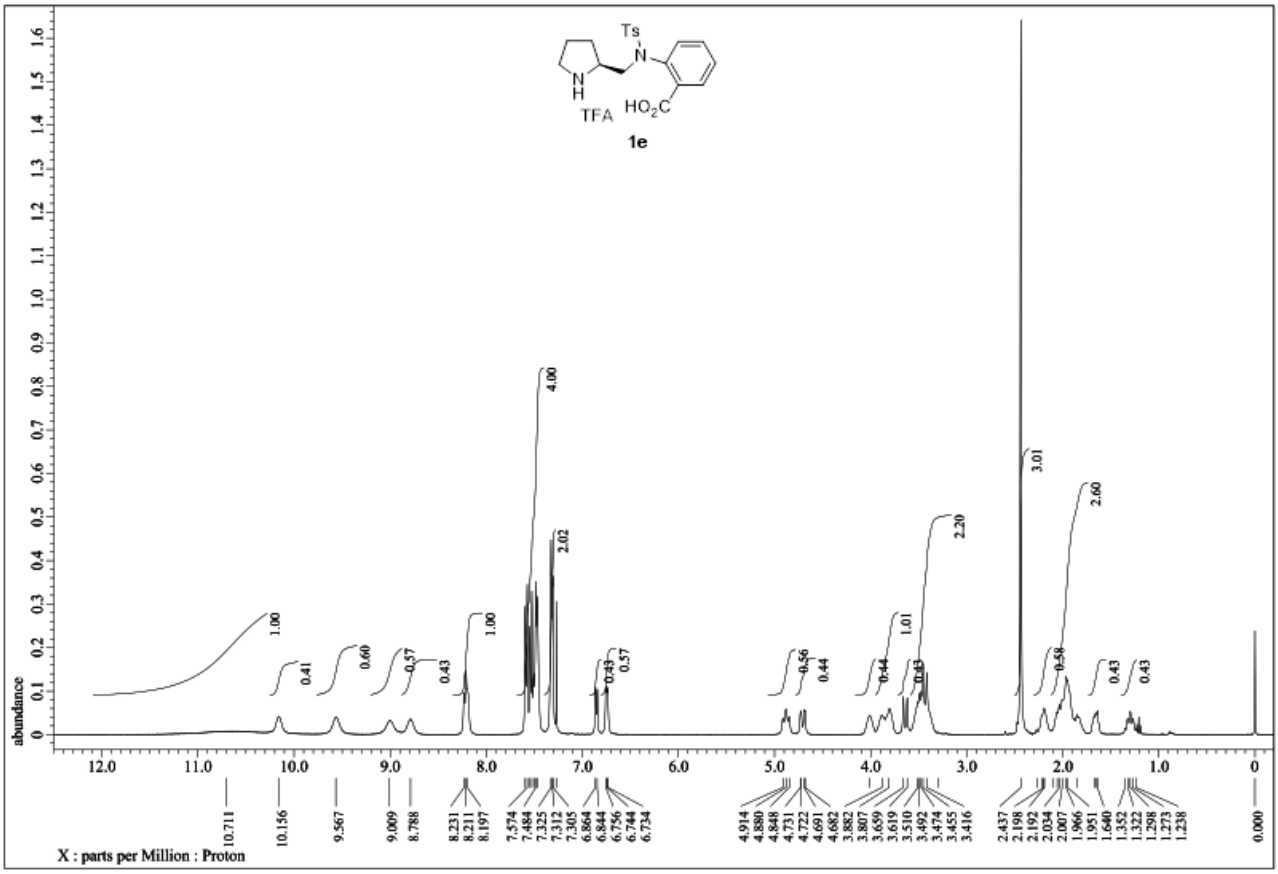
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H
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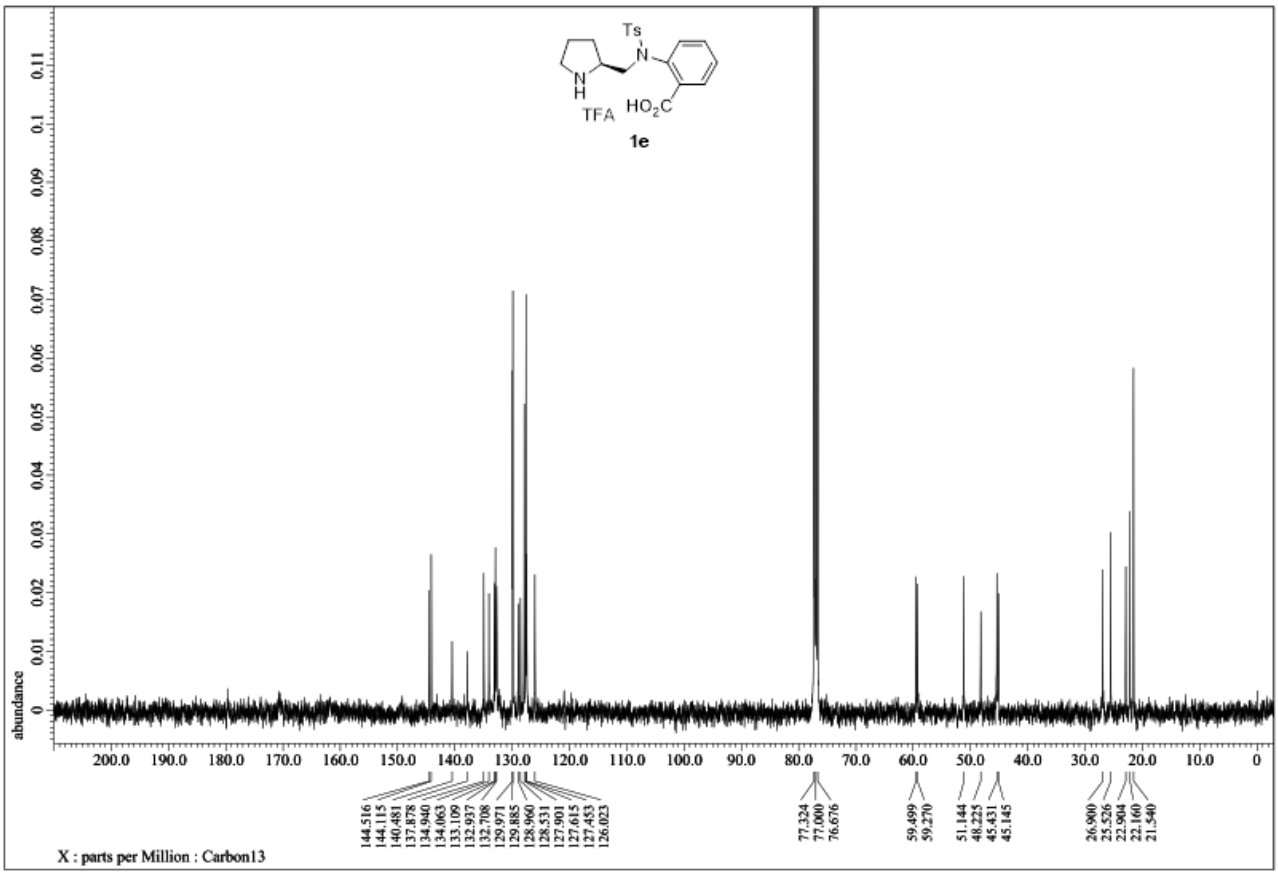
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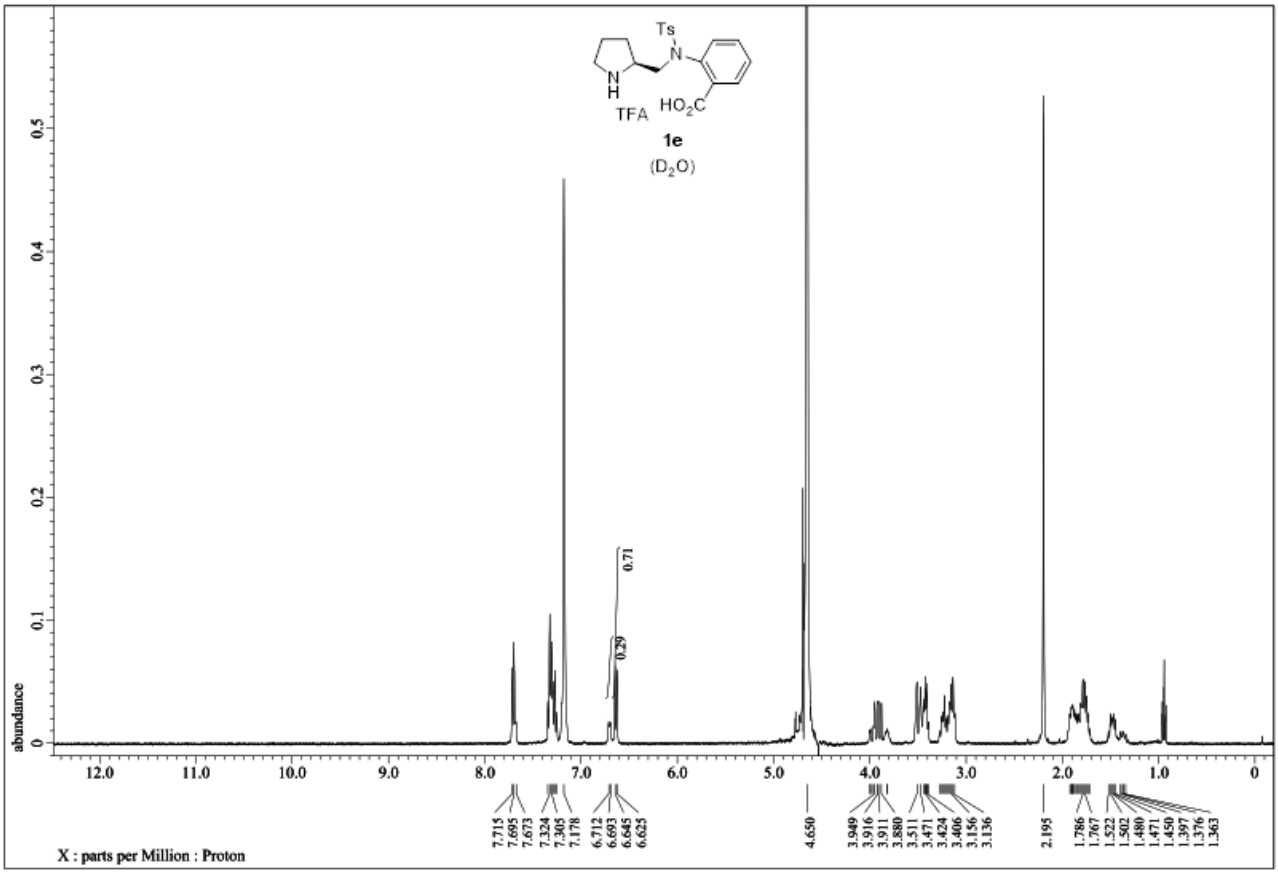
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H
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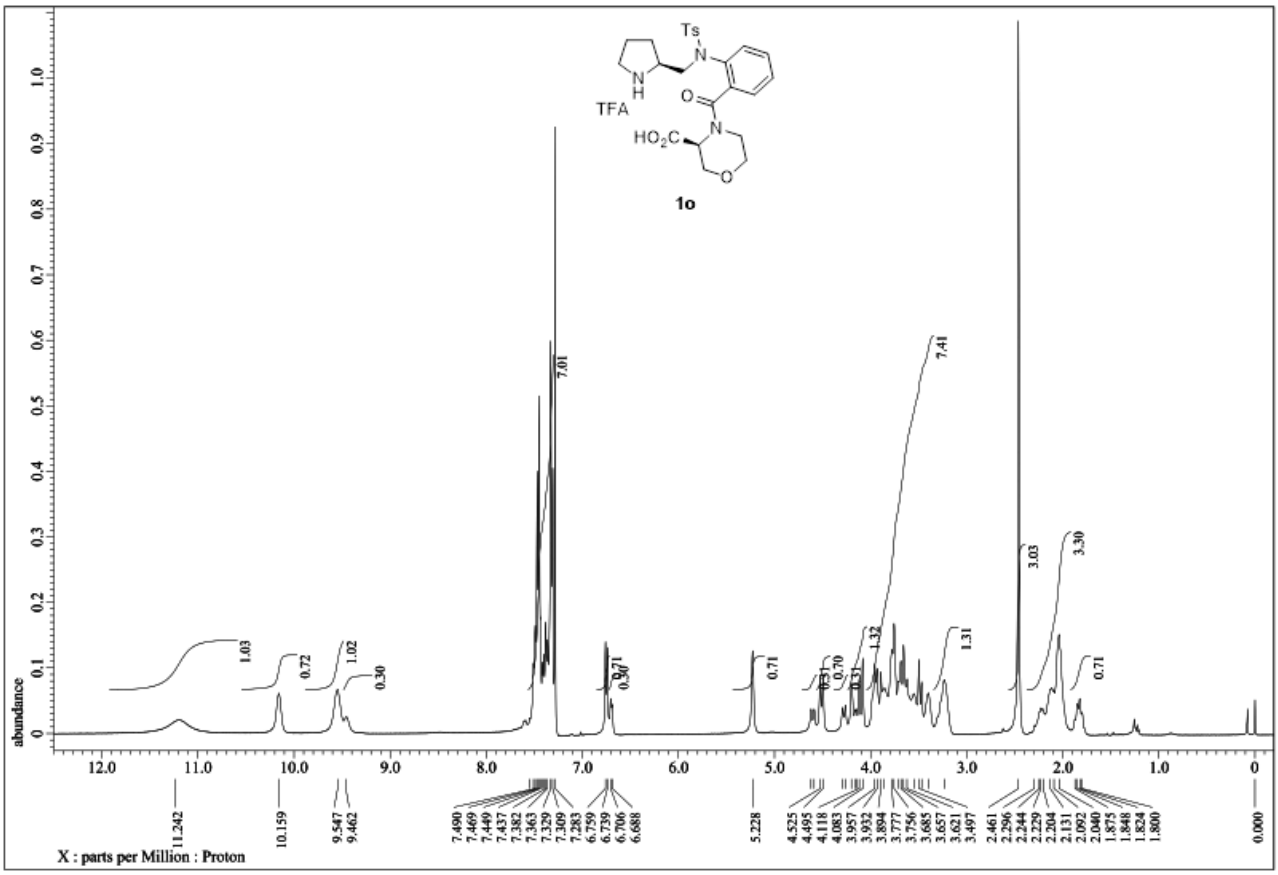
abundance
X : parts per Million : Proton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N
H
TFA
O
N
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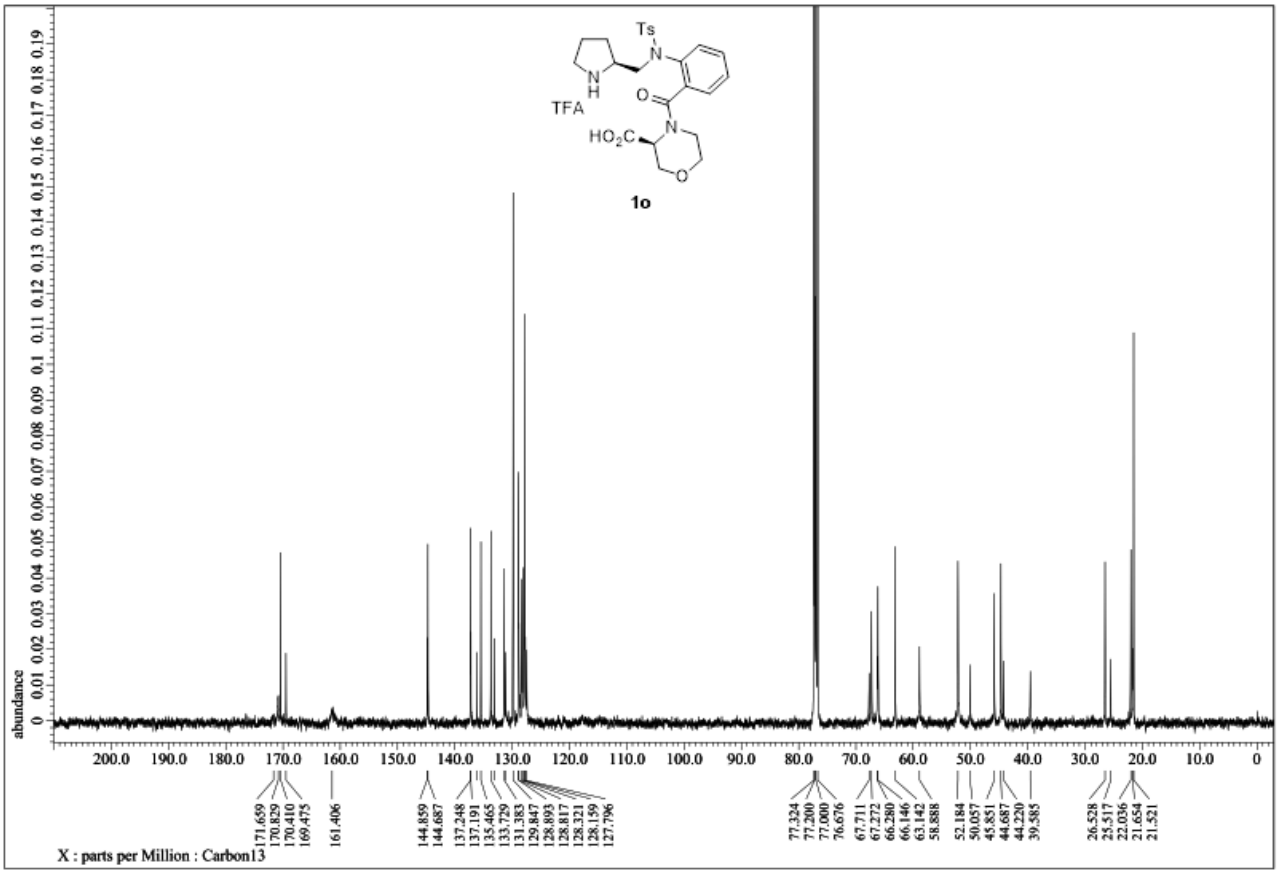
O
1o
abundance
X : parts per Million : Proton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H
TFA
O
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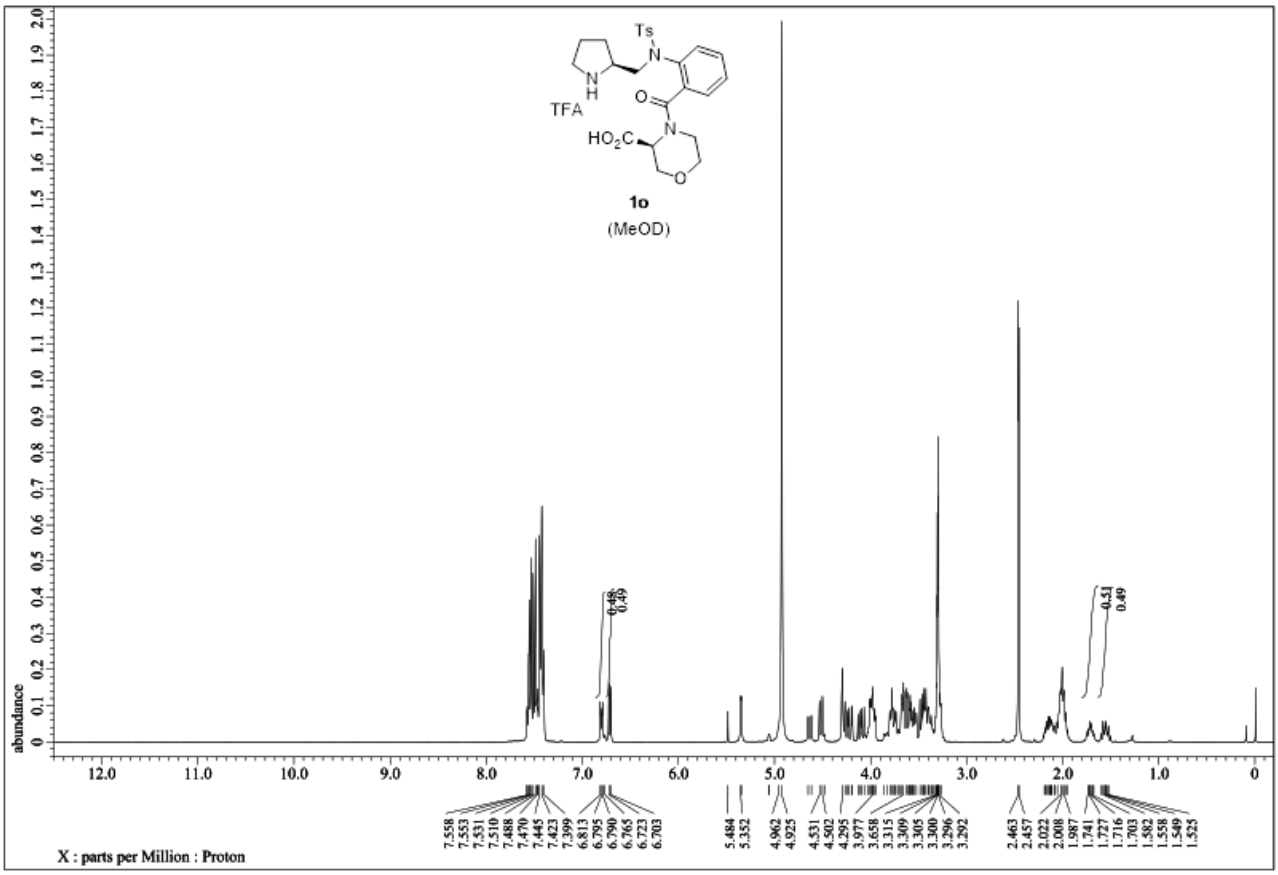
HO2C
O
1o
abundance
X : parts per Million : Carbon13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O
1o
(MeOD)
abundance
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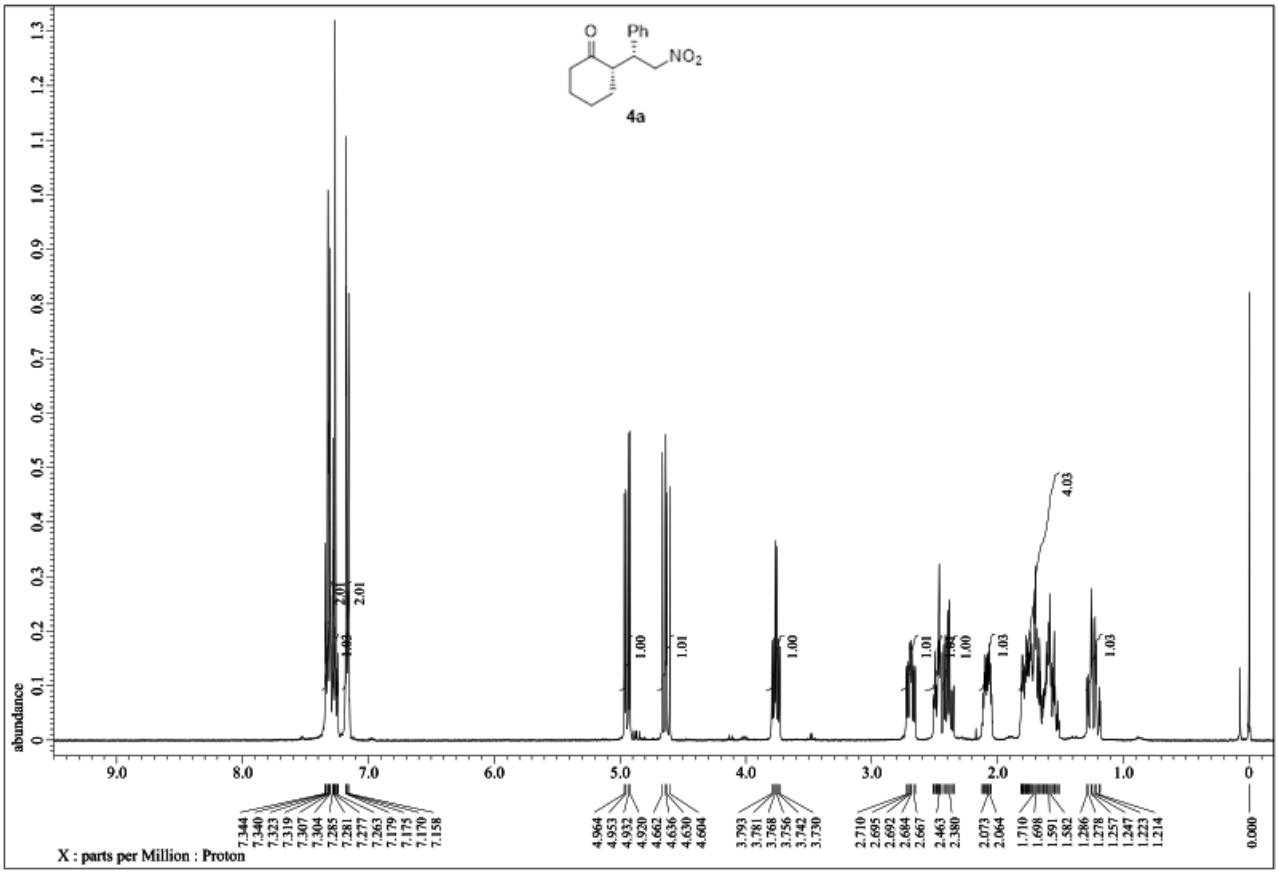
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NO2
4a
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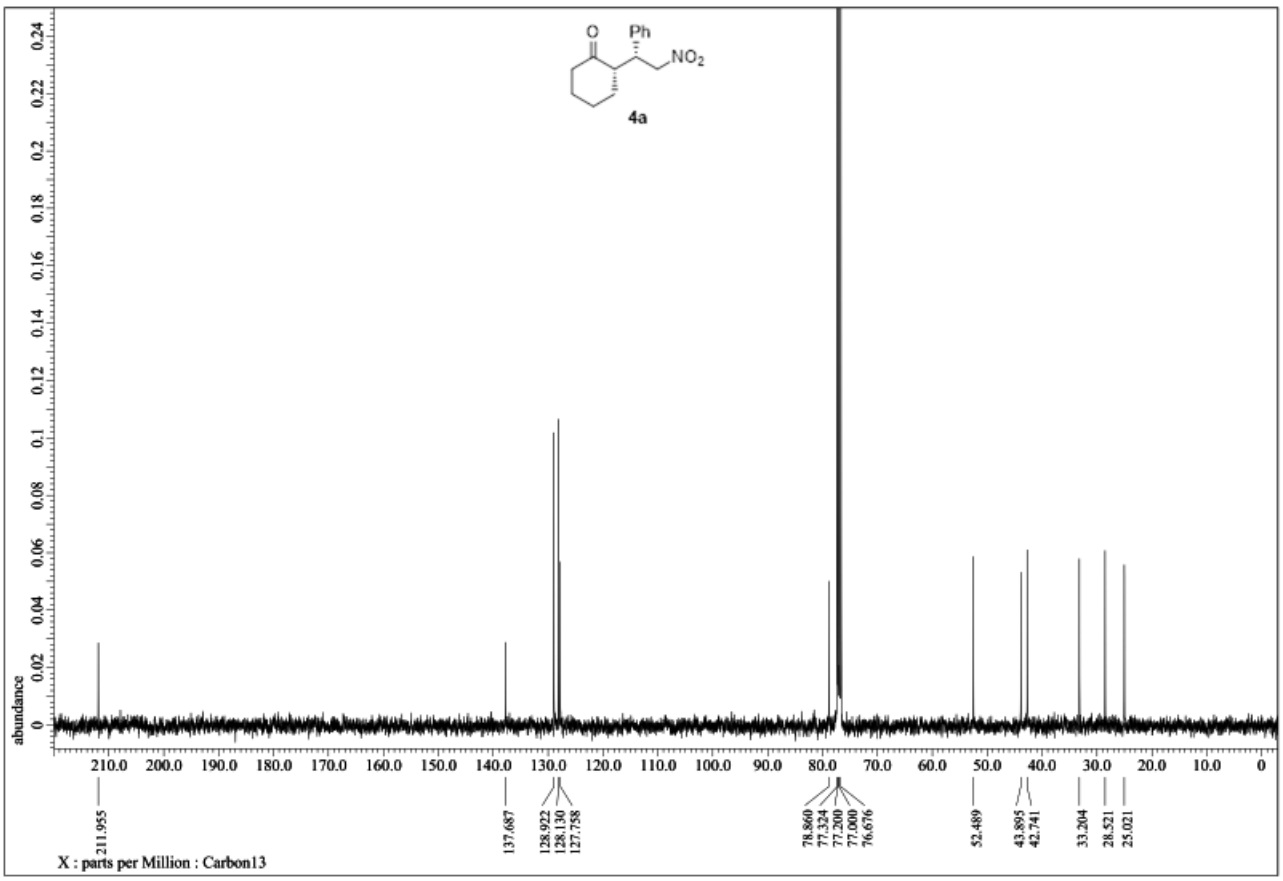
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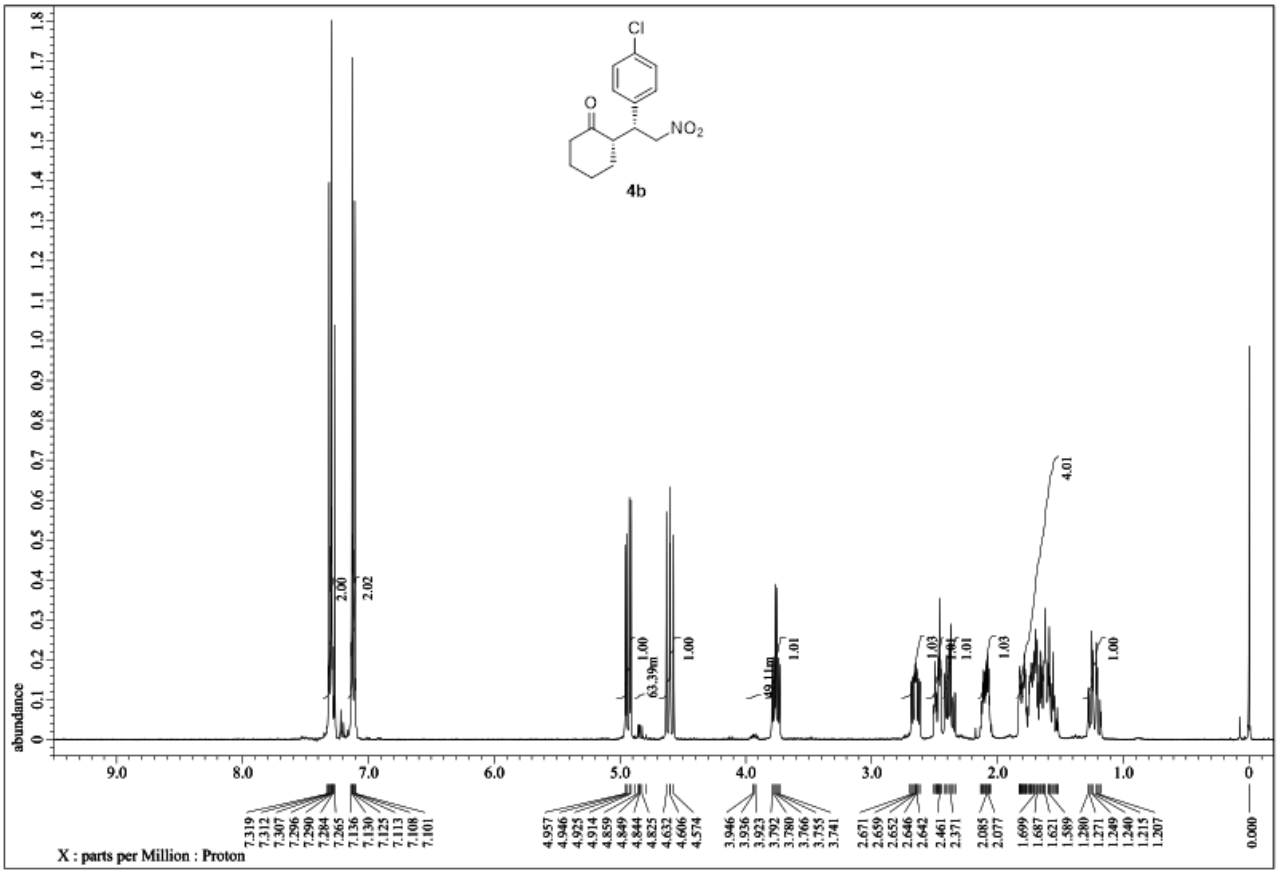
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4b
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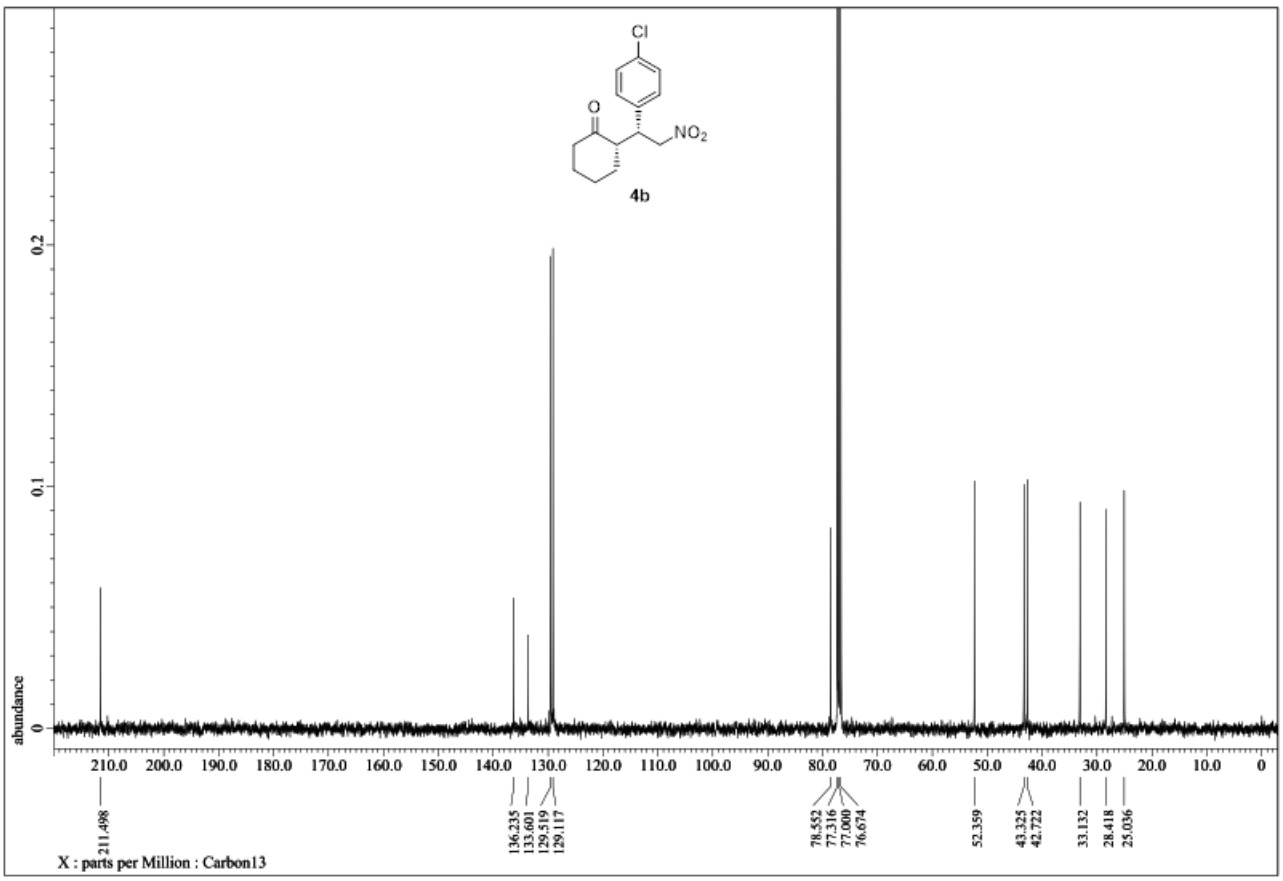
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O
NO2
4b
abundance
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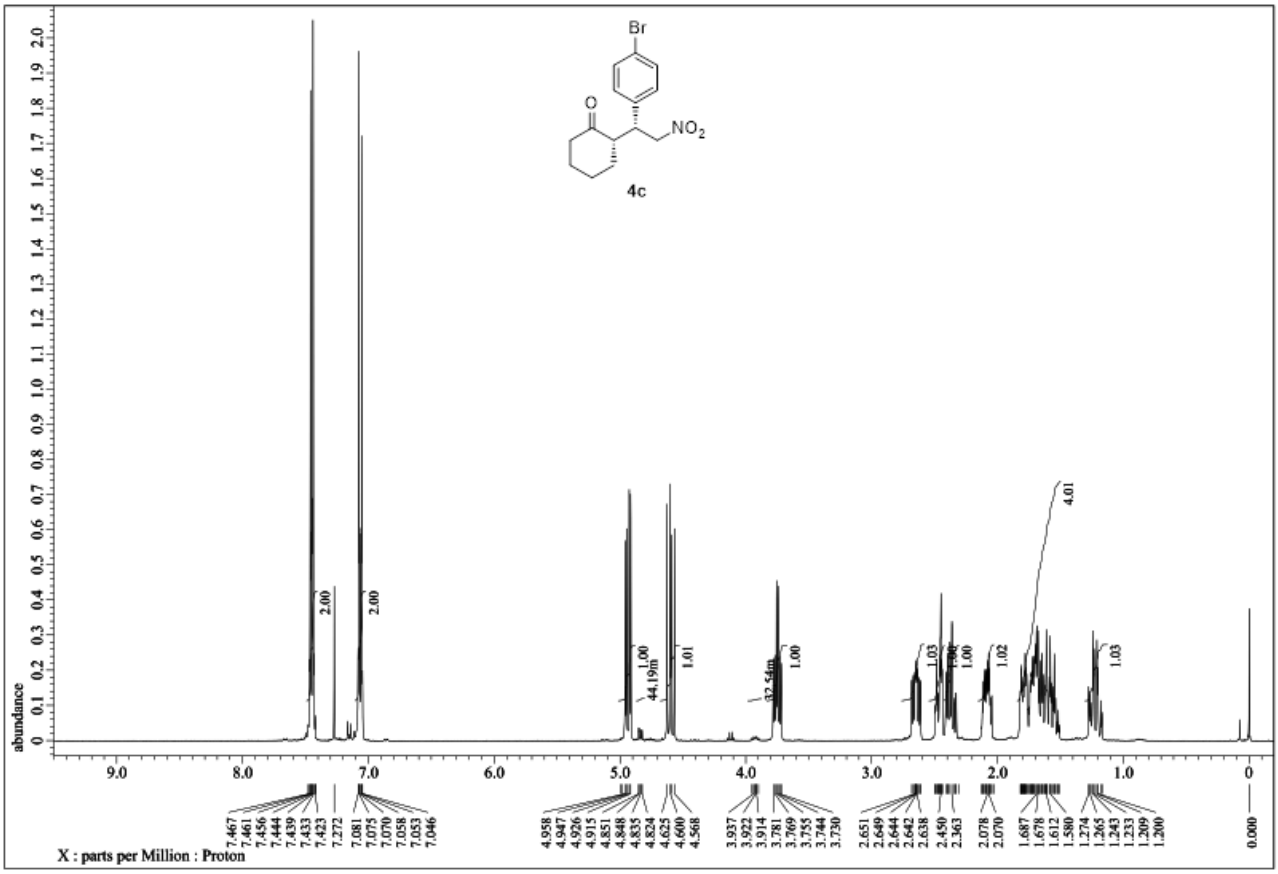
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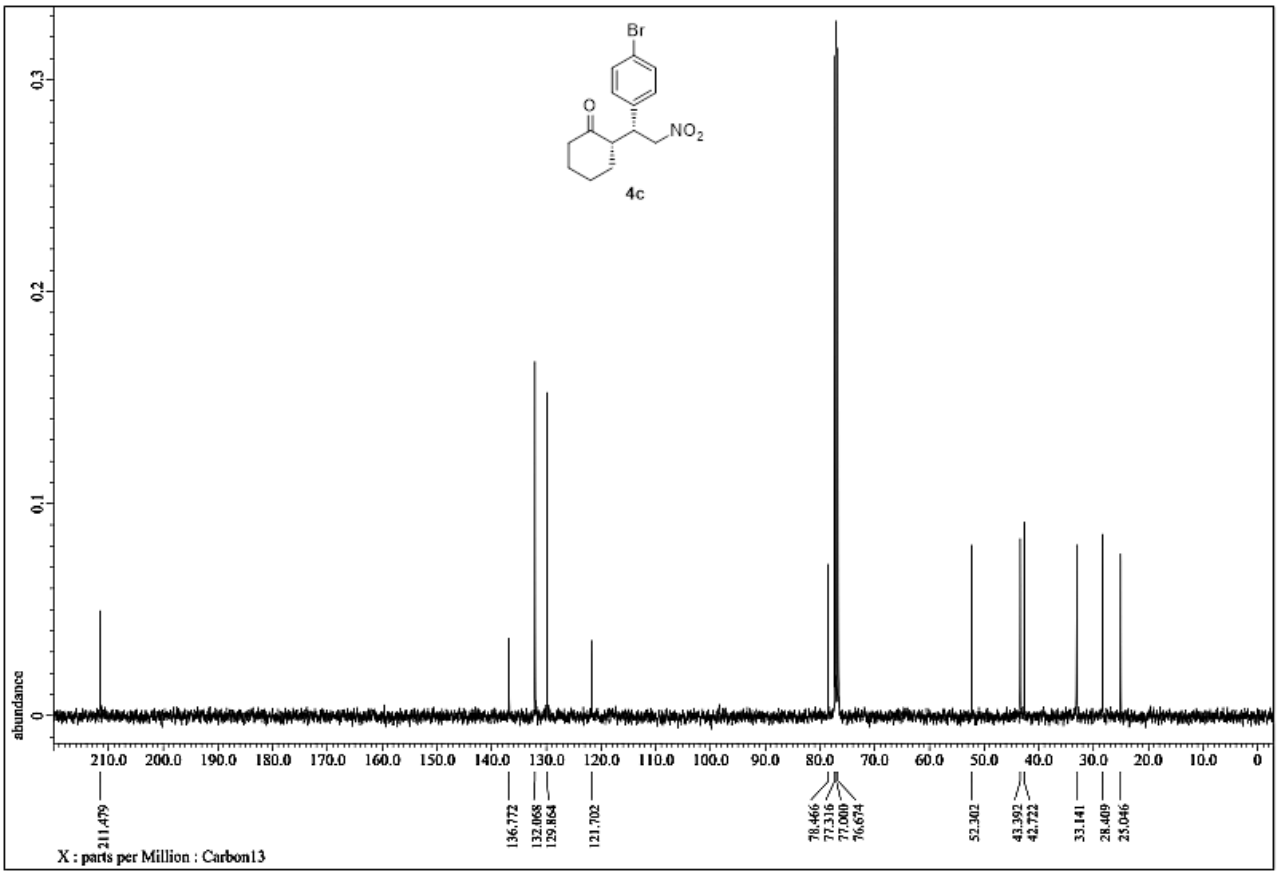
O
NO2
4c
abundance
X : parts per Million : Proton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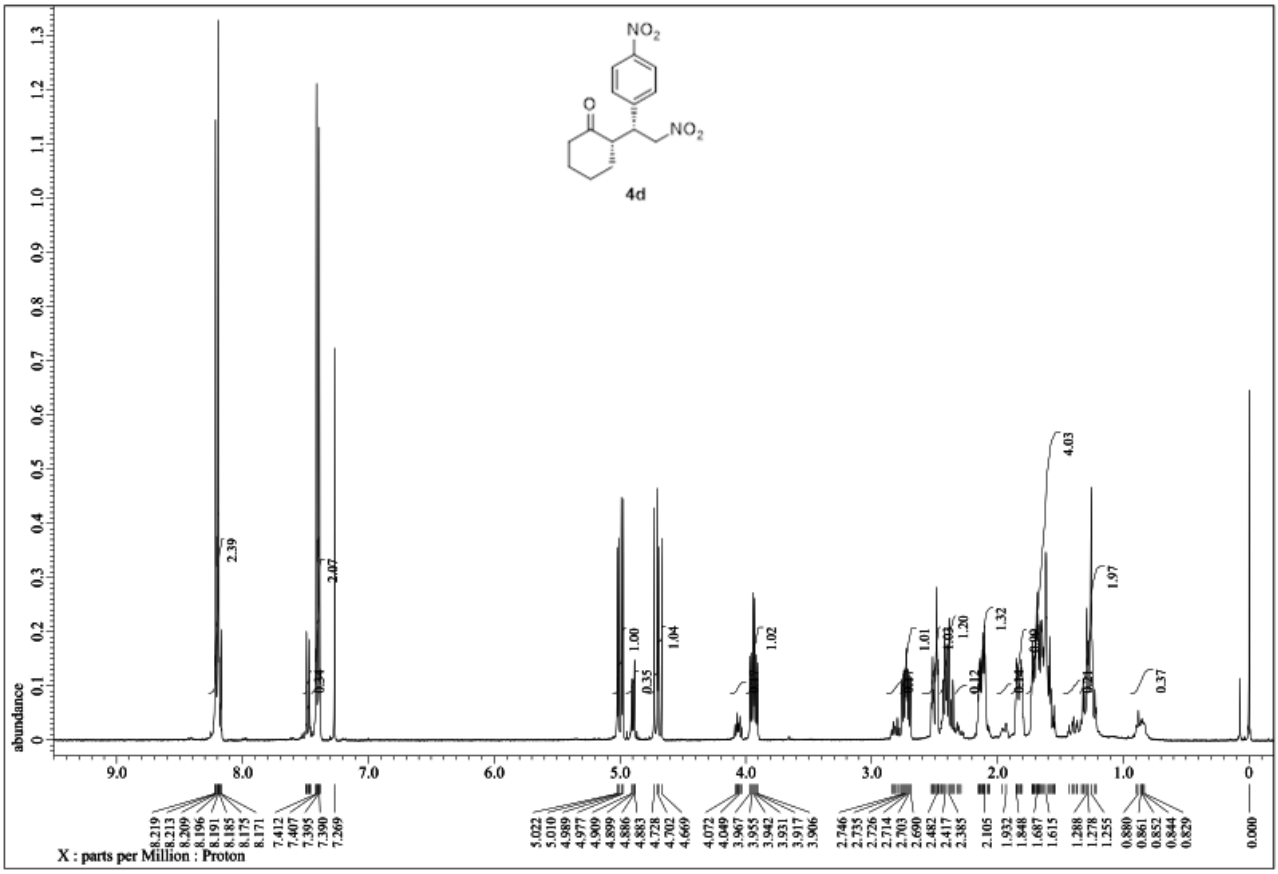
O
NO2
4c
abundance
X : parts per Million : Carbon13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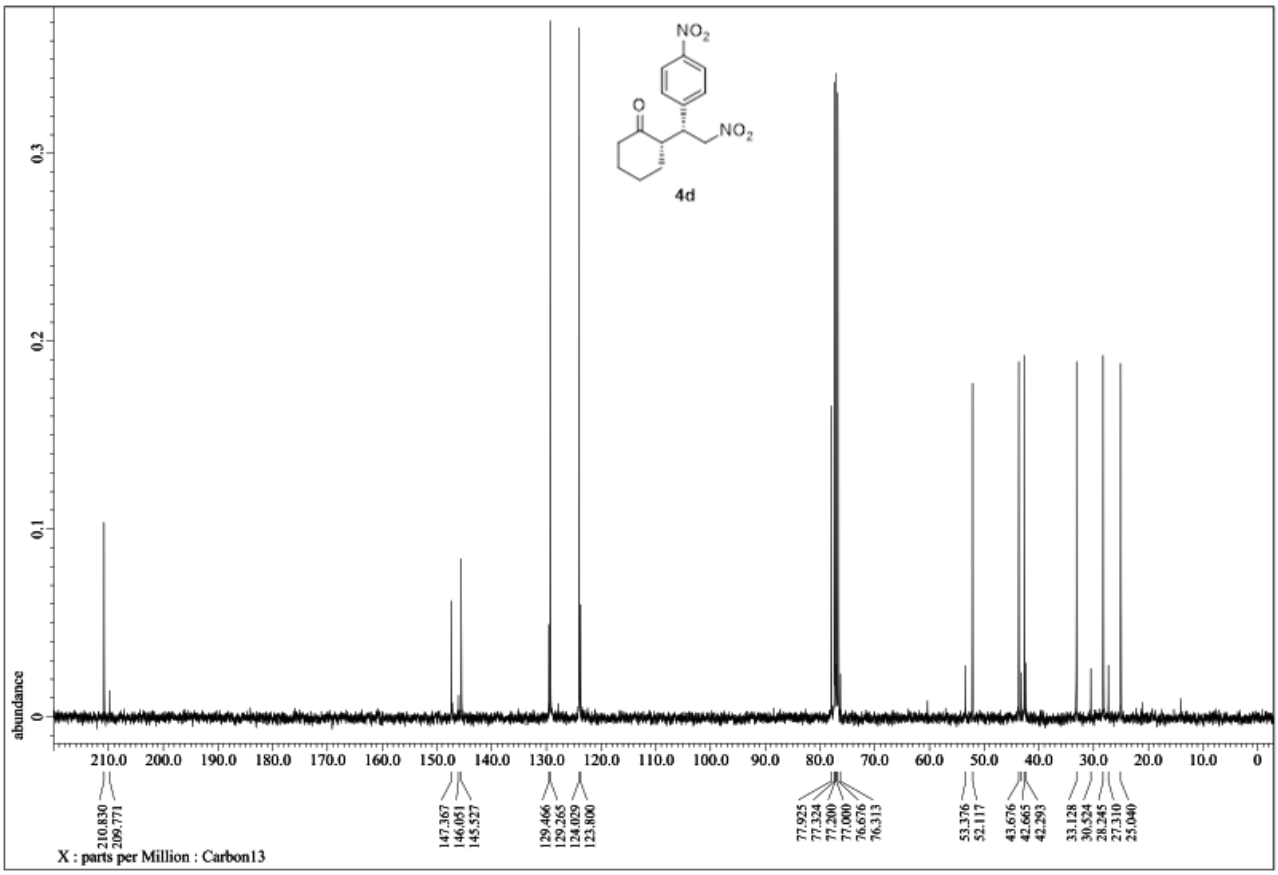
O
NO2
4d
abundance
X : parts per Million : Proton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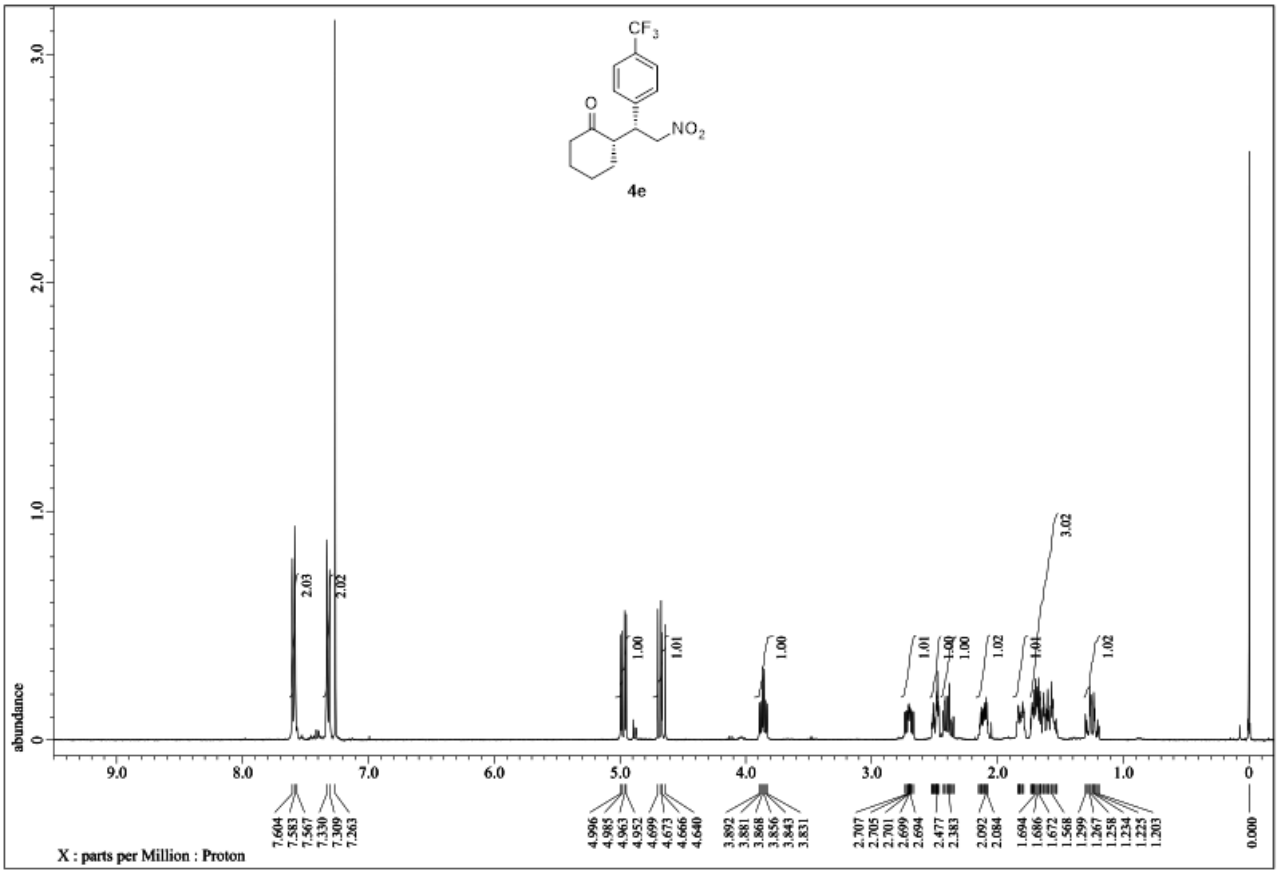
O
NO2
4d
abundance
X : parts per Million : Carbon13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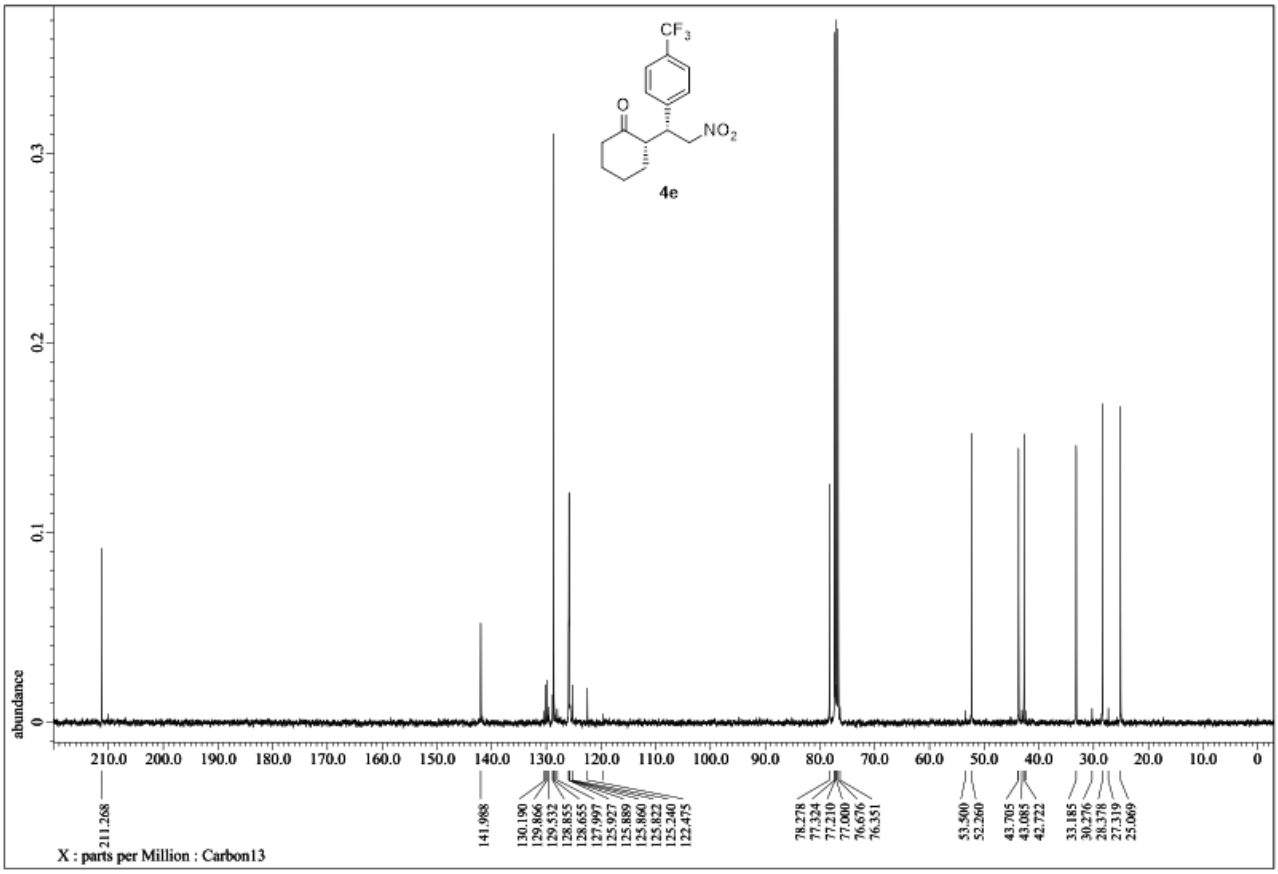
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O
NO2
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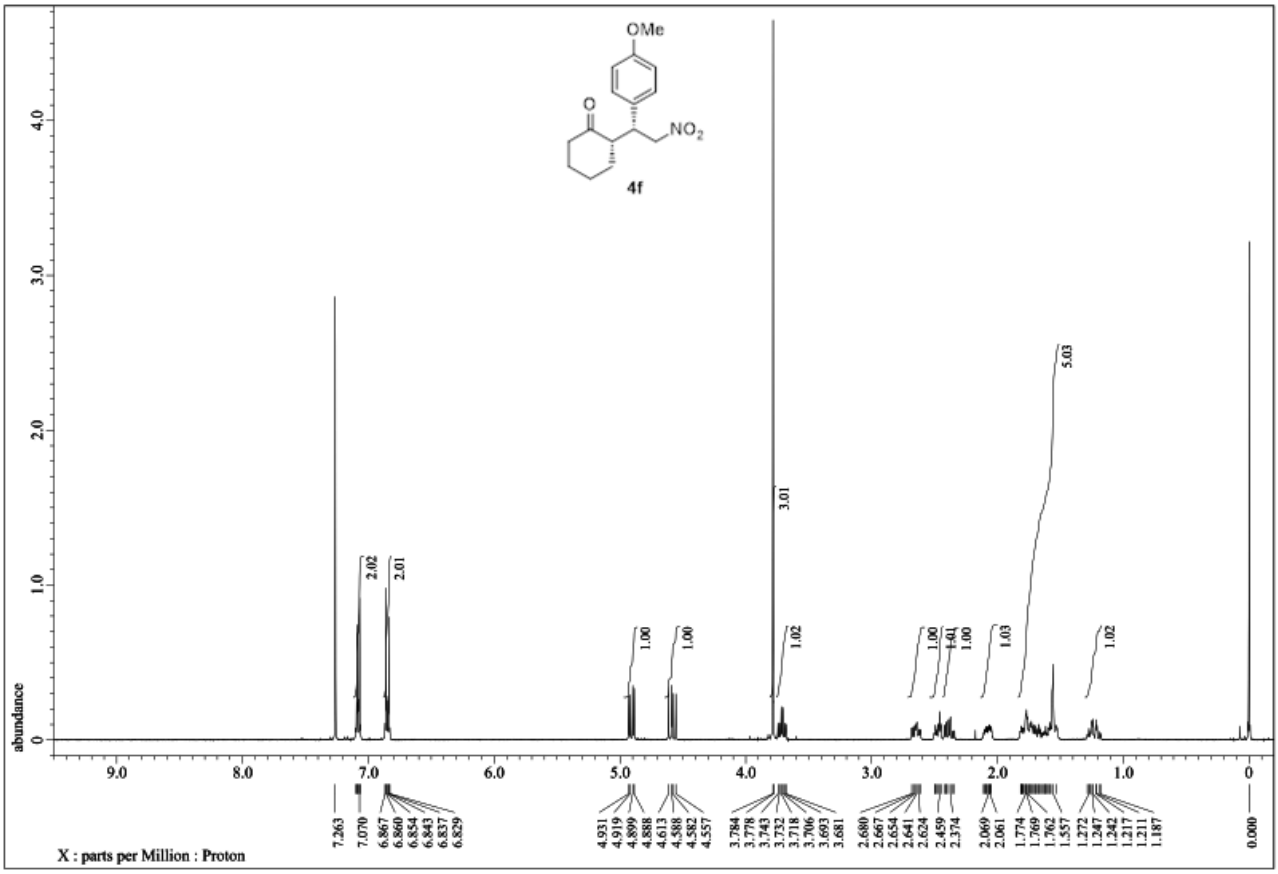
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O
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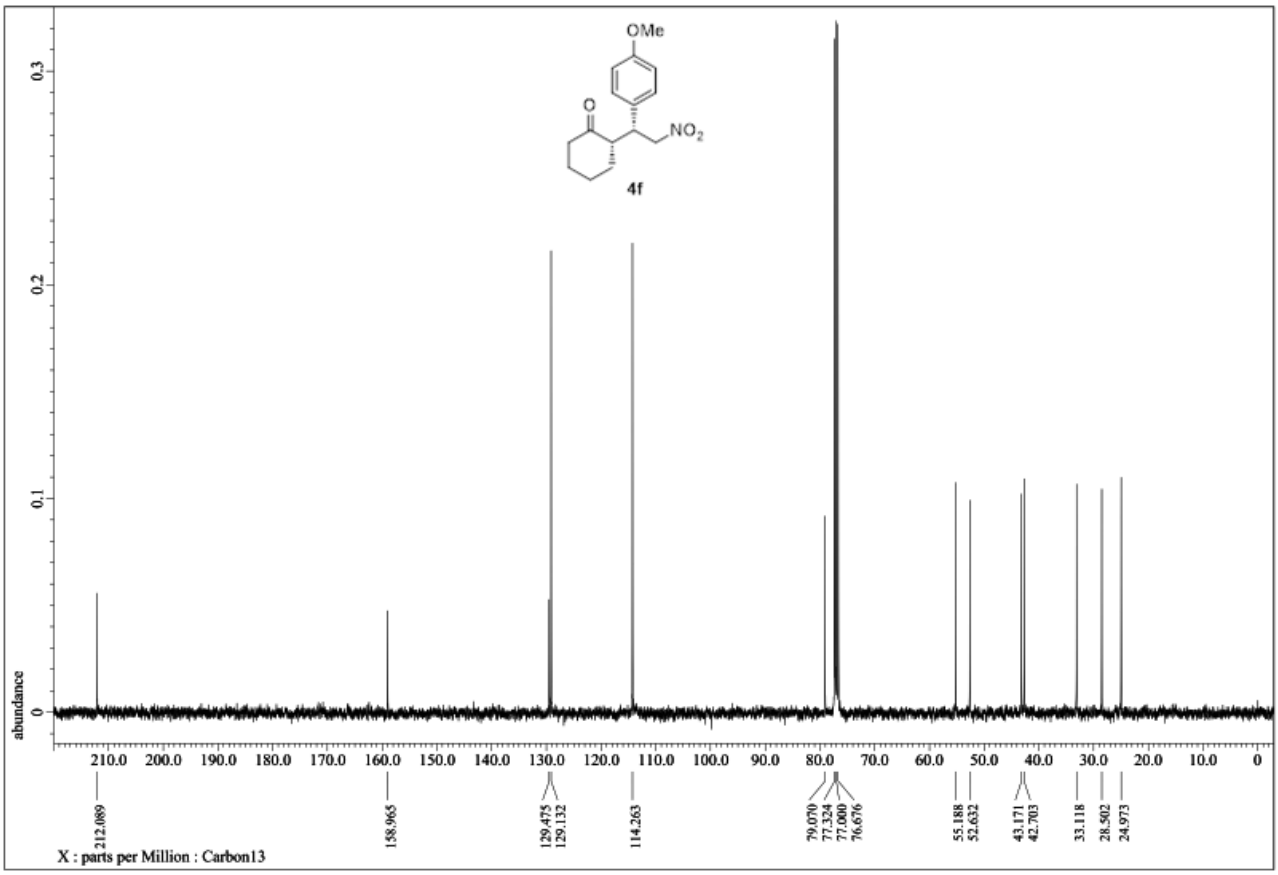
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O
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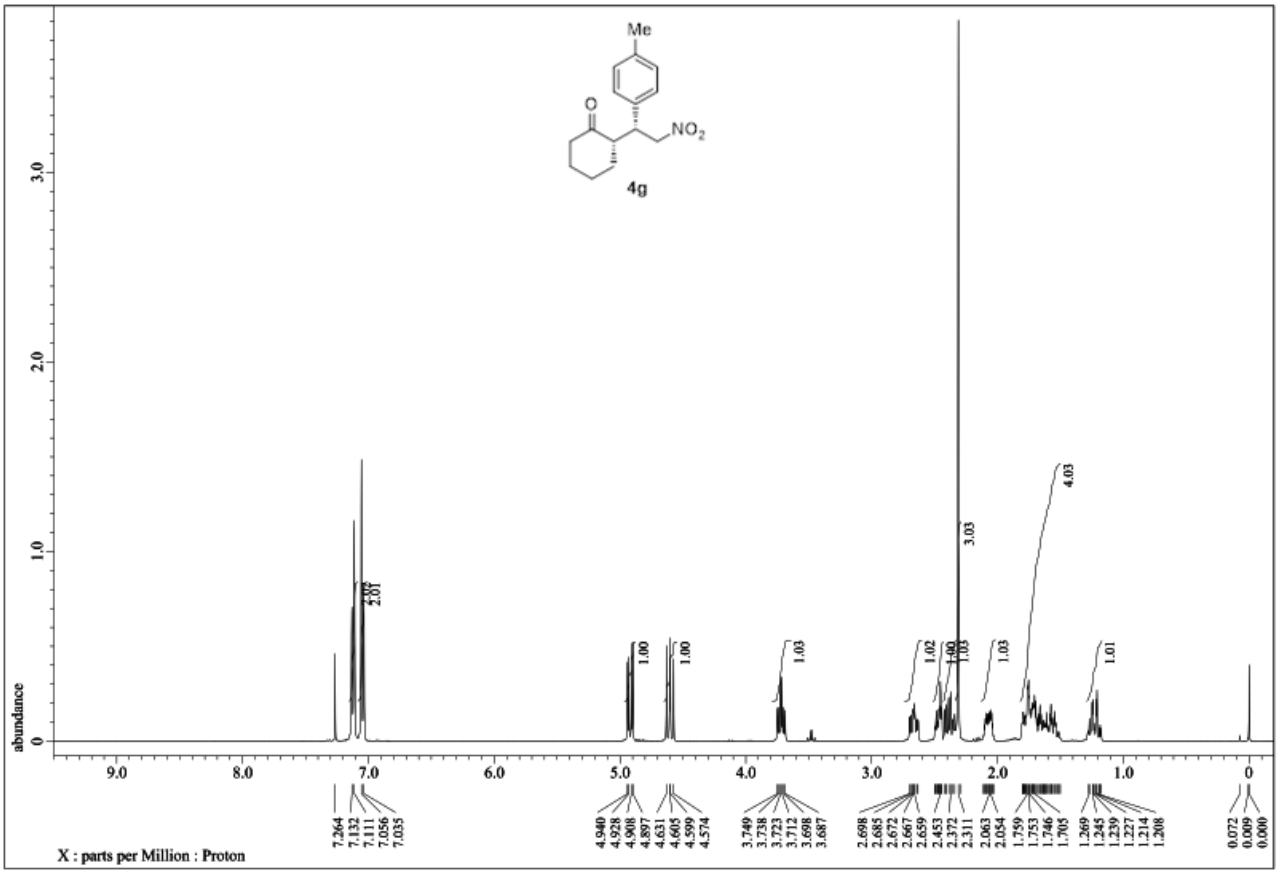
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O
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4g
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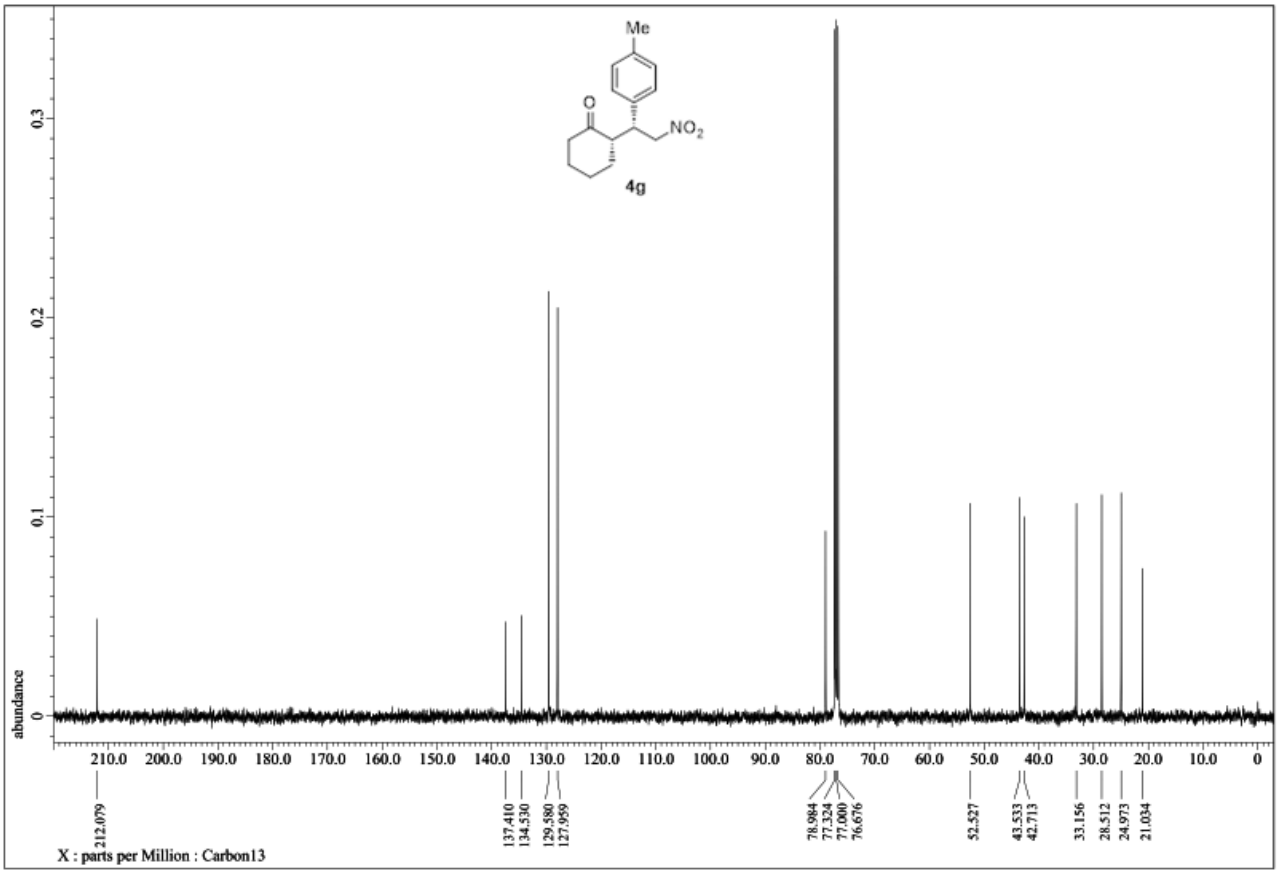
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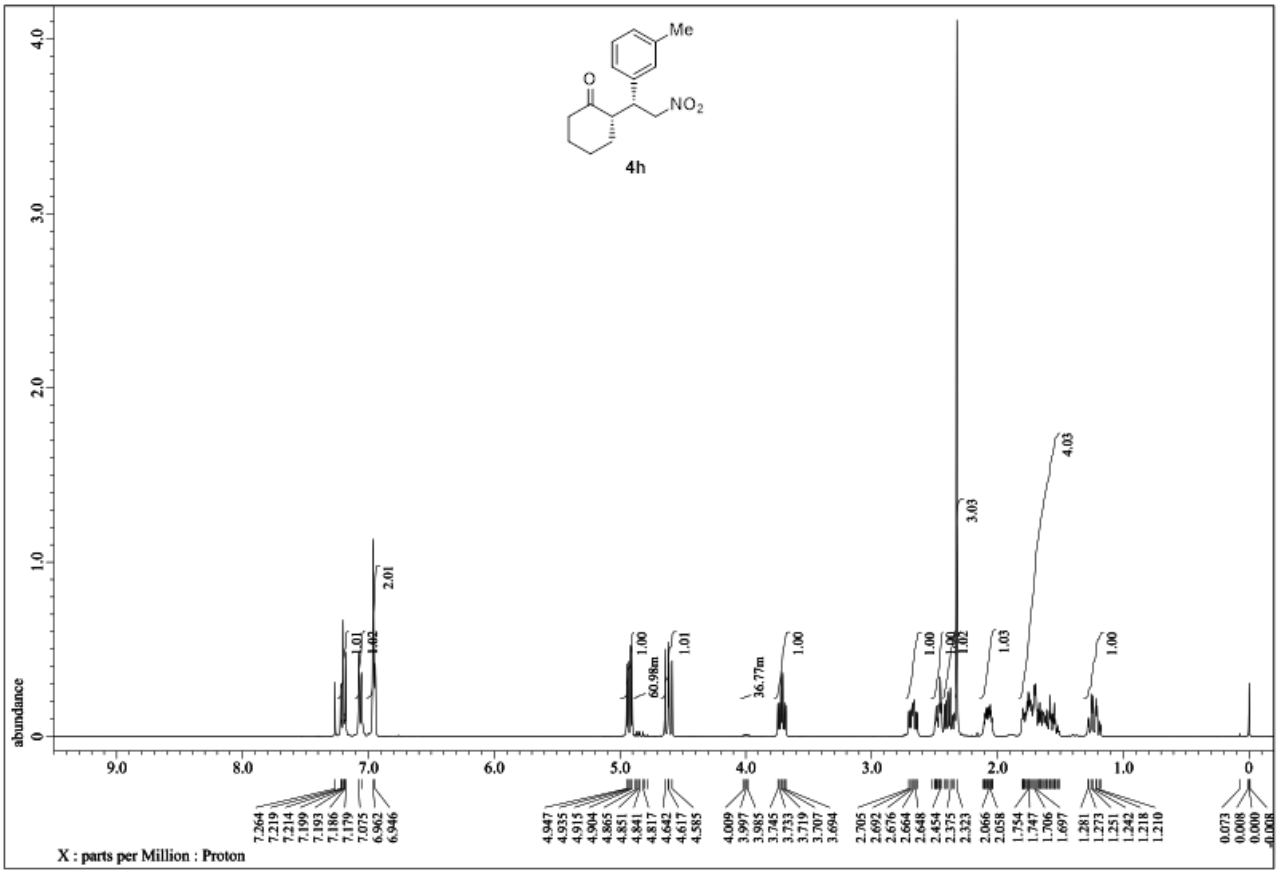
NO2
4g
abundance
X : parts per Million : Carbon13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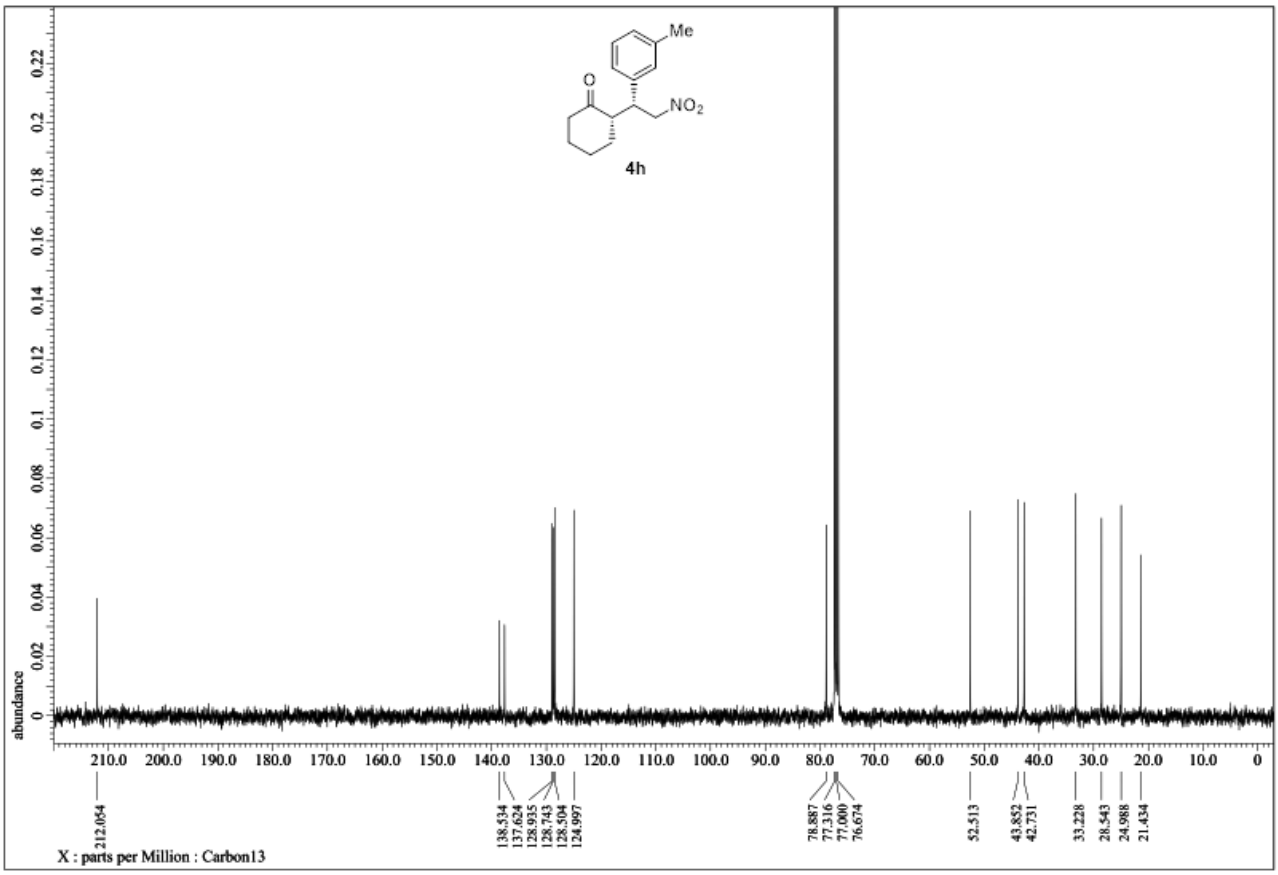
O
NO2
4h
abundance
X : parts per Million : Proton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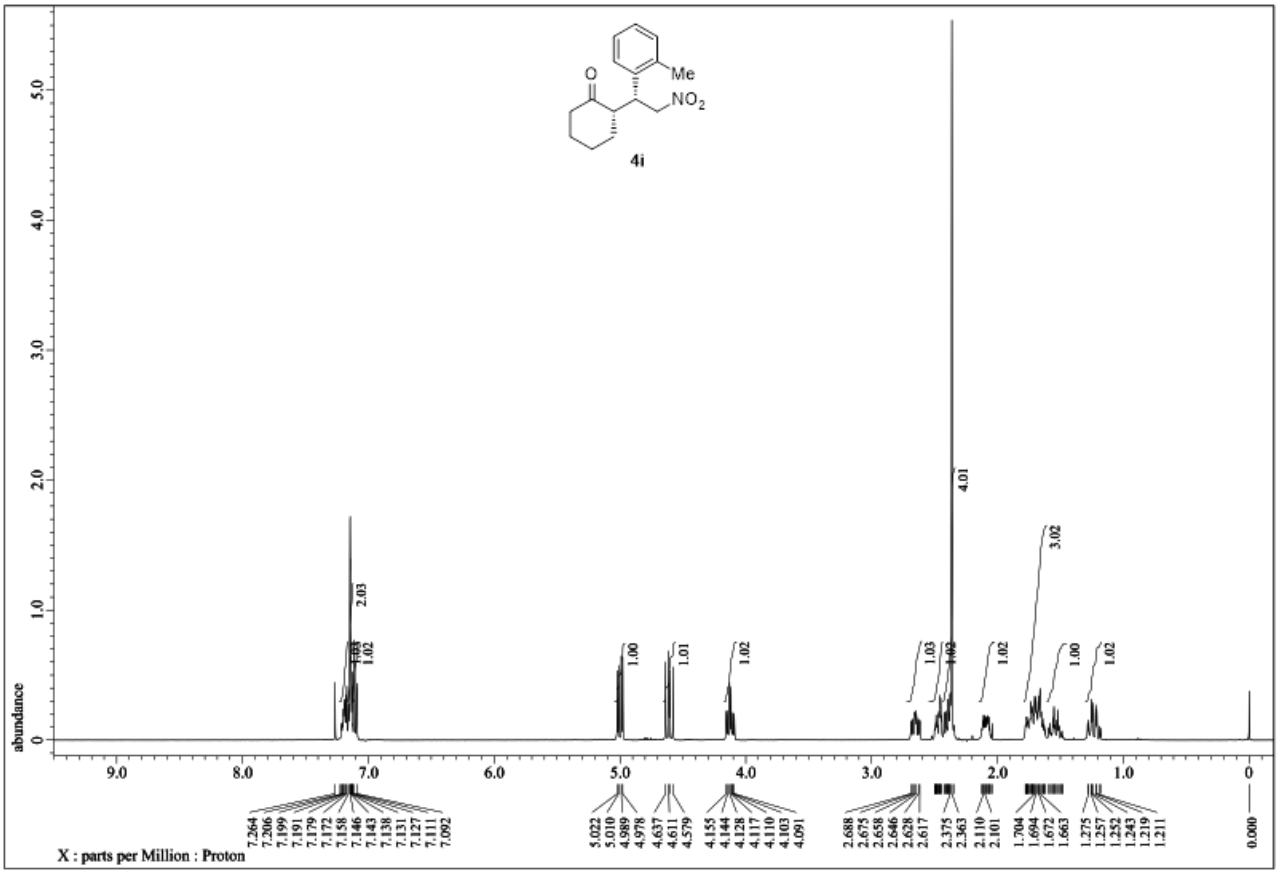
O
NO2
4h
abundance
X : parts per Million : Carbon13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NO2
4i
abundance
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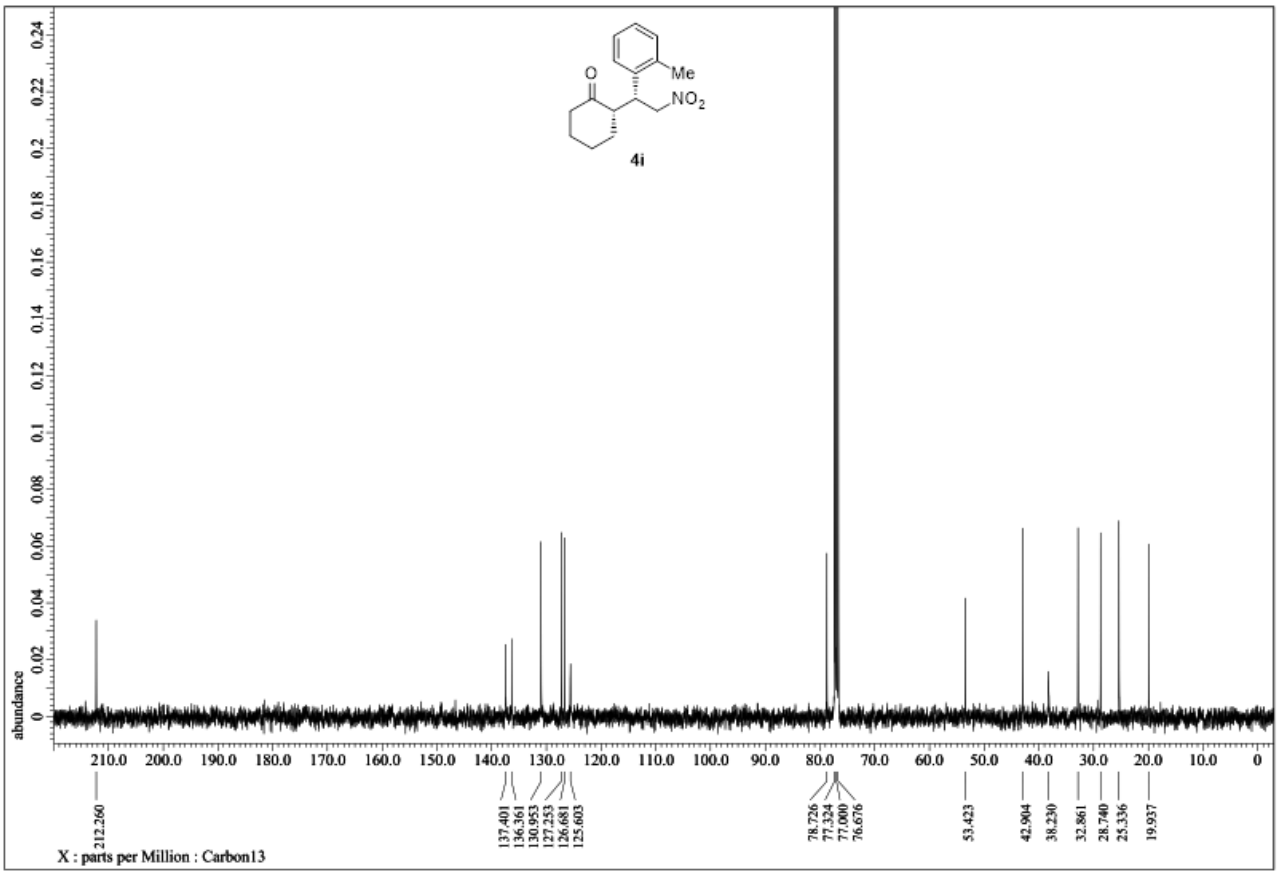
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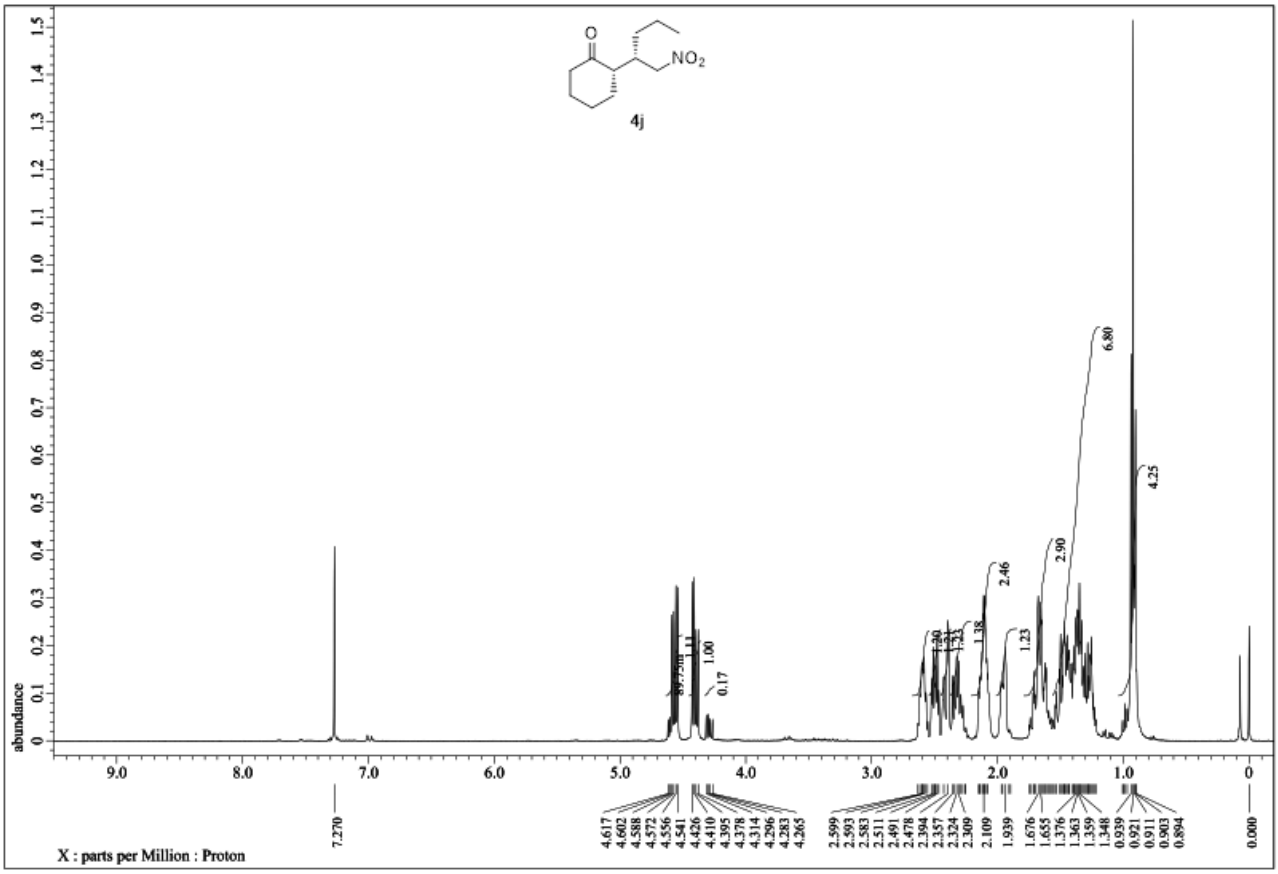
Me
NO2
4i
abundance
X : parts per Million : Carbon13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NO2
4j
abundance
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1.38
1.23
1.00
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4.617
4.602
4.588
4.572
4.556
4.541
4.426
4.410
4.395
4.378
4.314
4.296
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1.655
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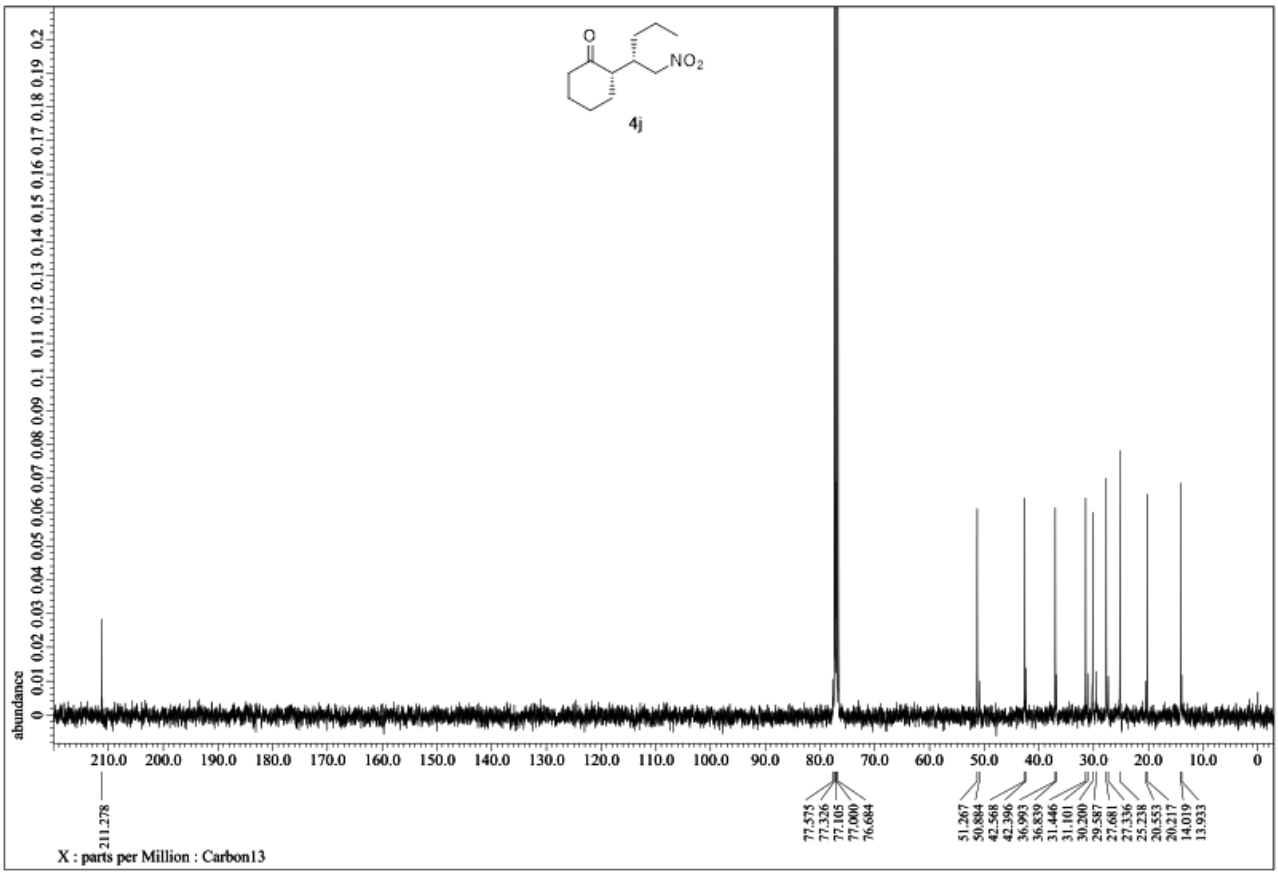
X : parts per Million : Proton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NO2
4j
abundance
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36.839
31.446
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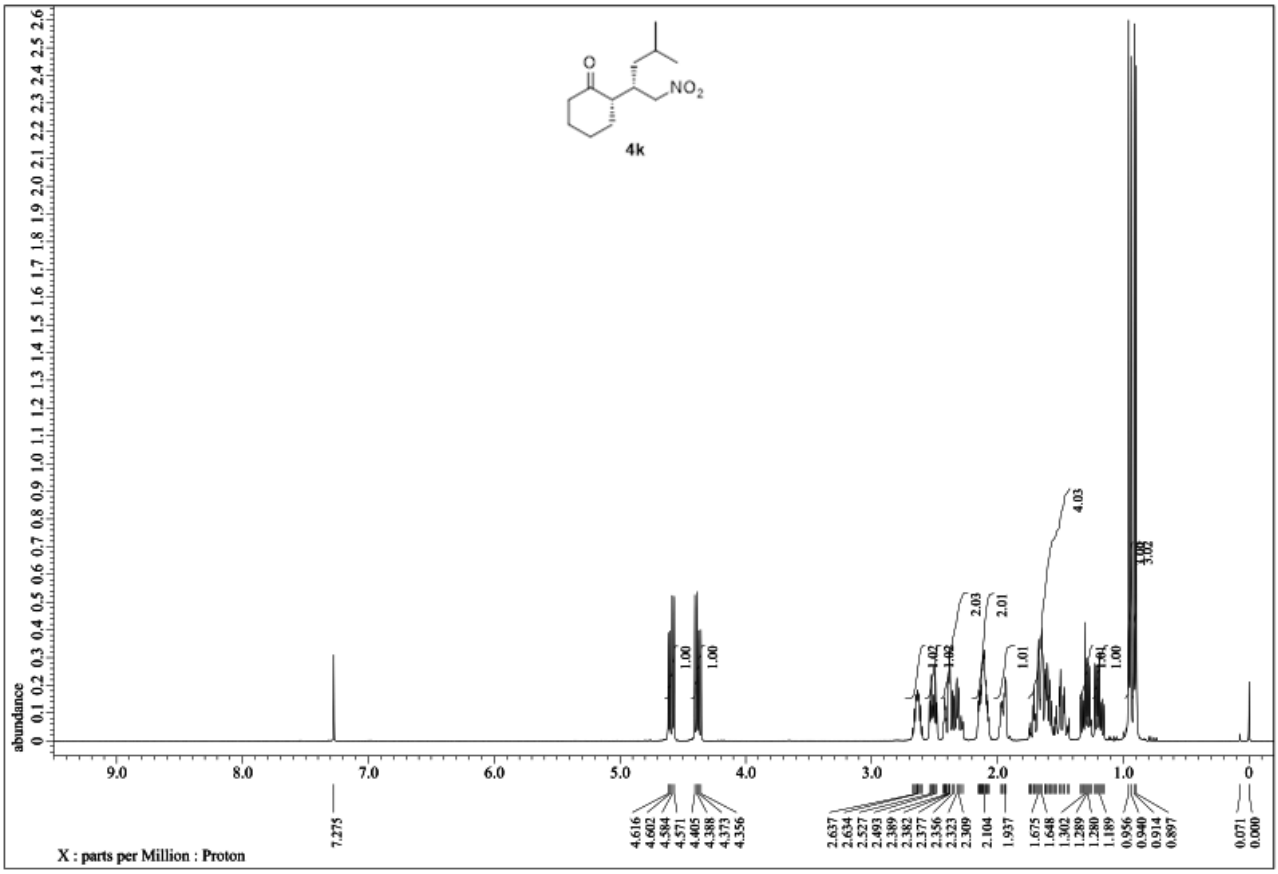
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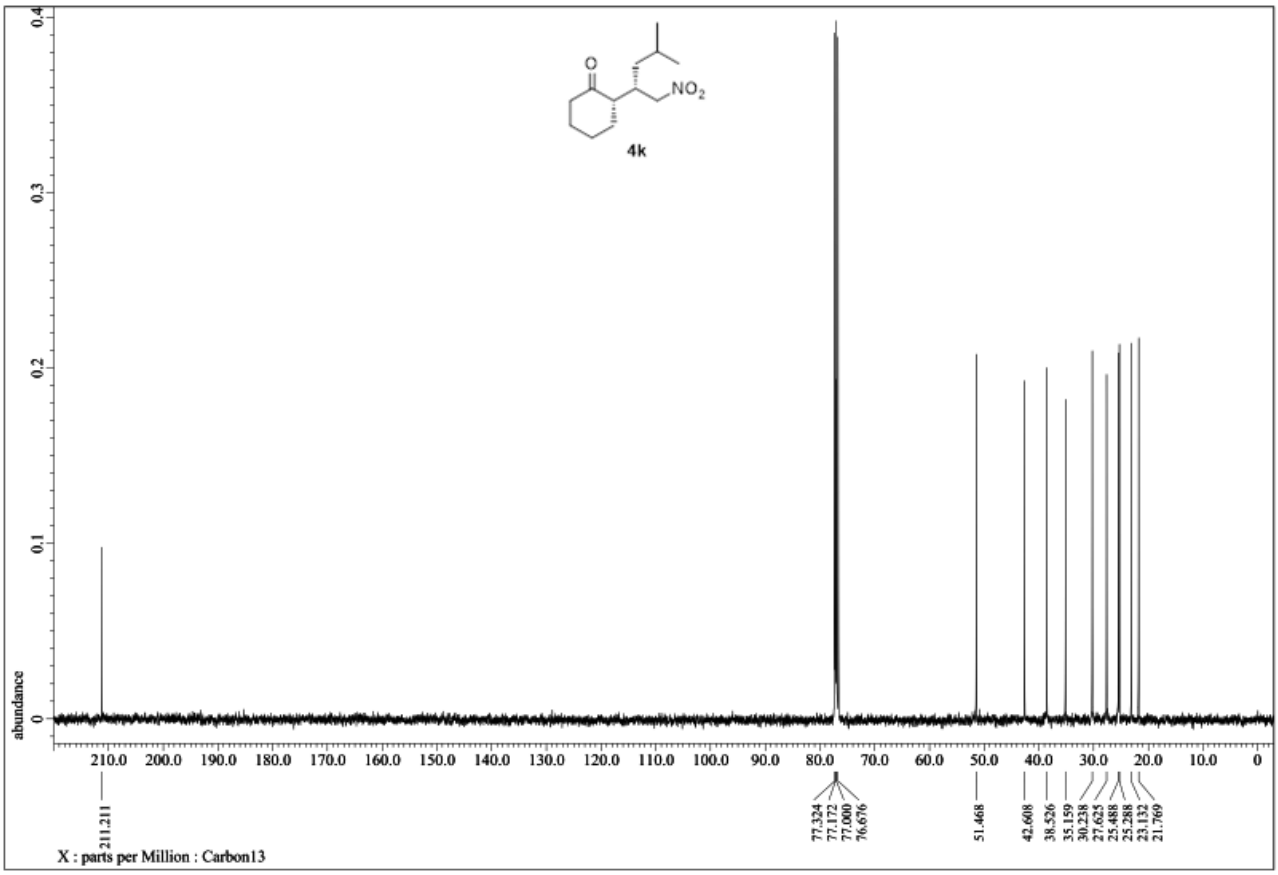
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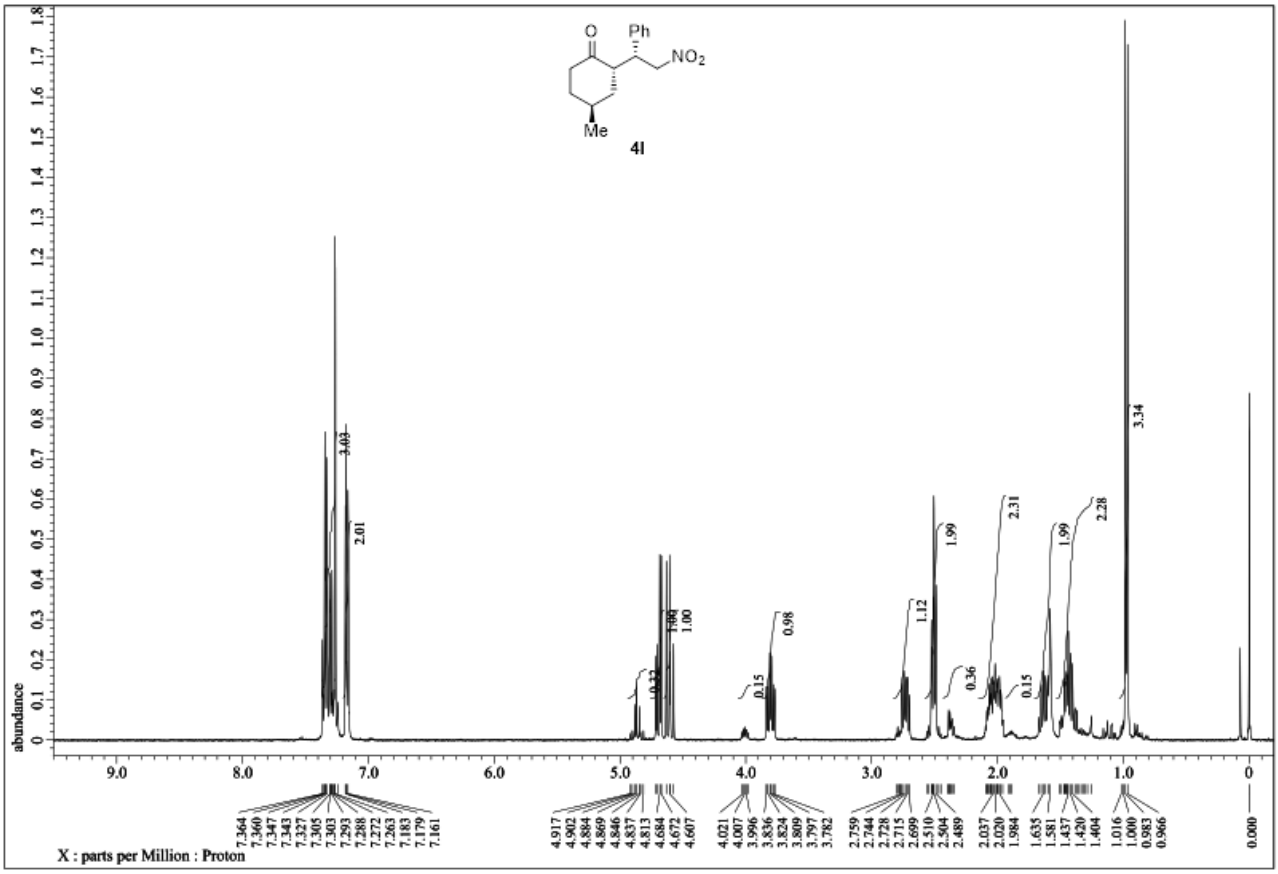
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Me
4l
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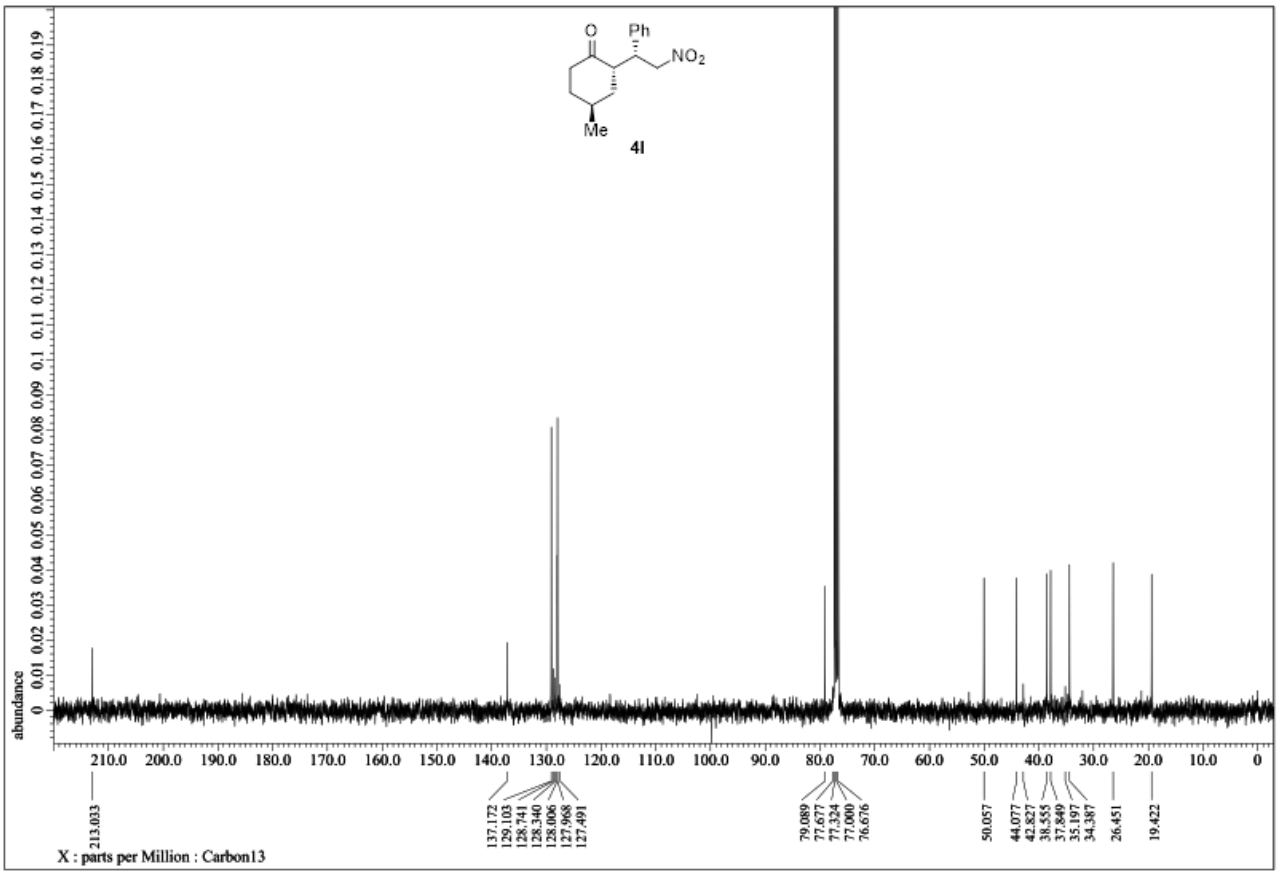
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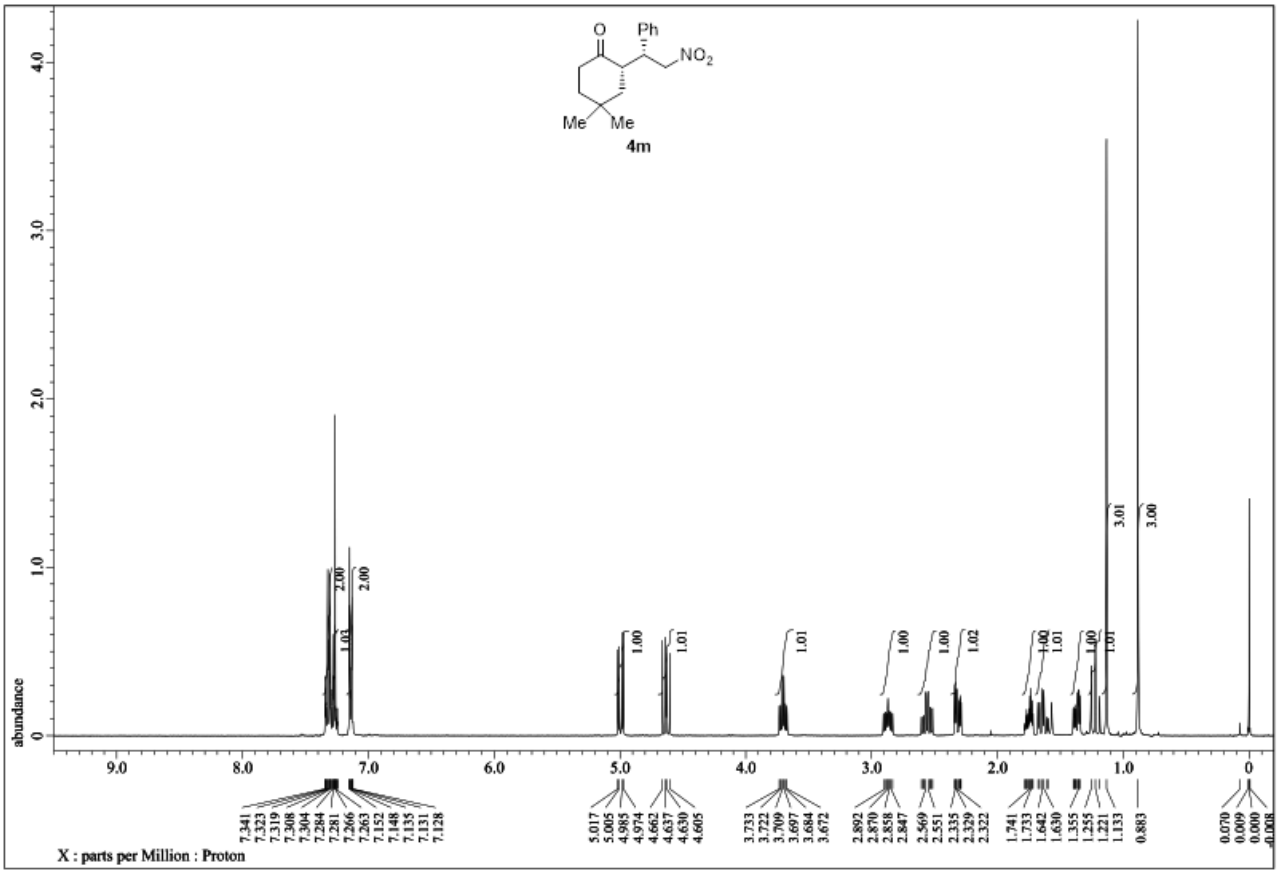
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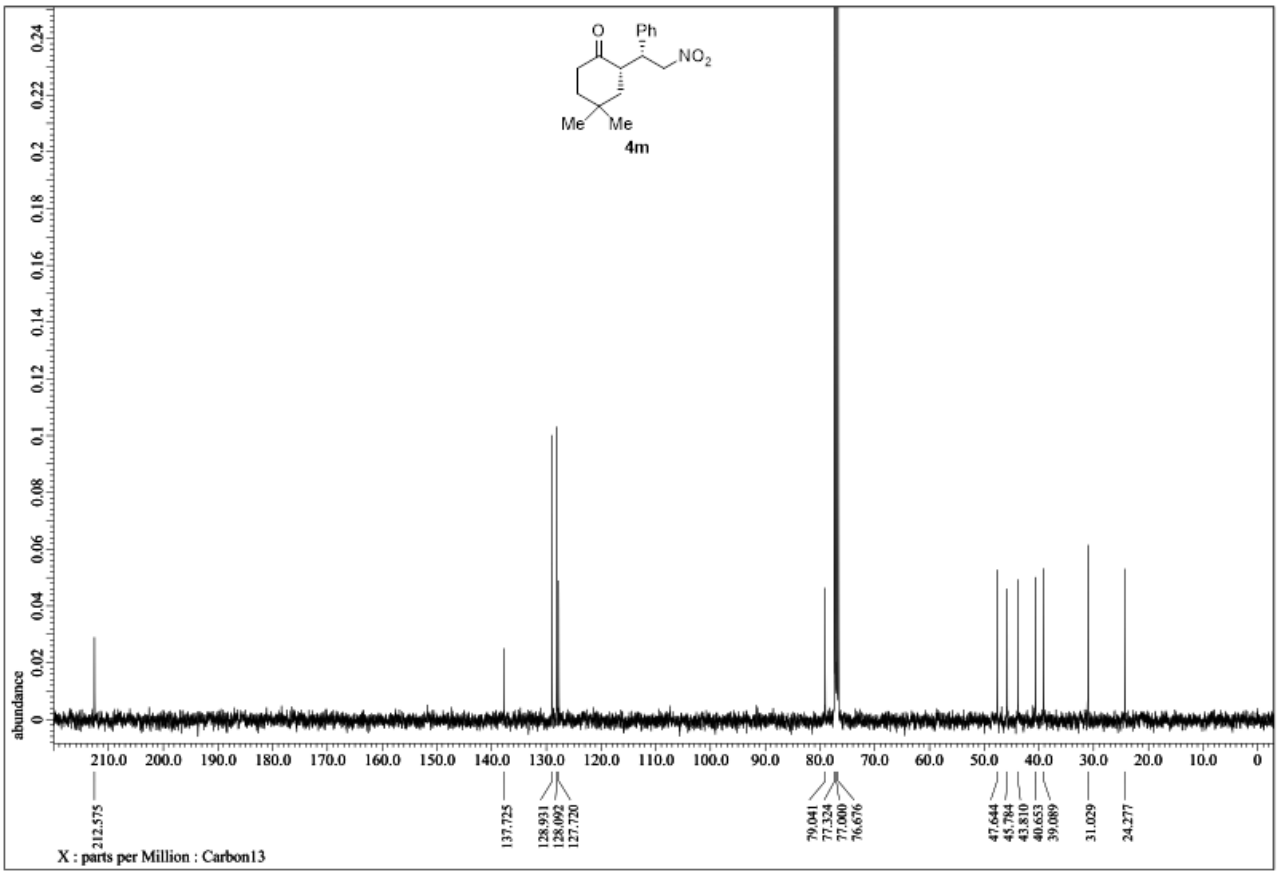
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abundance
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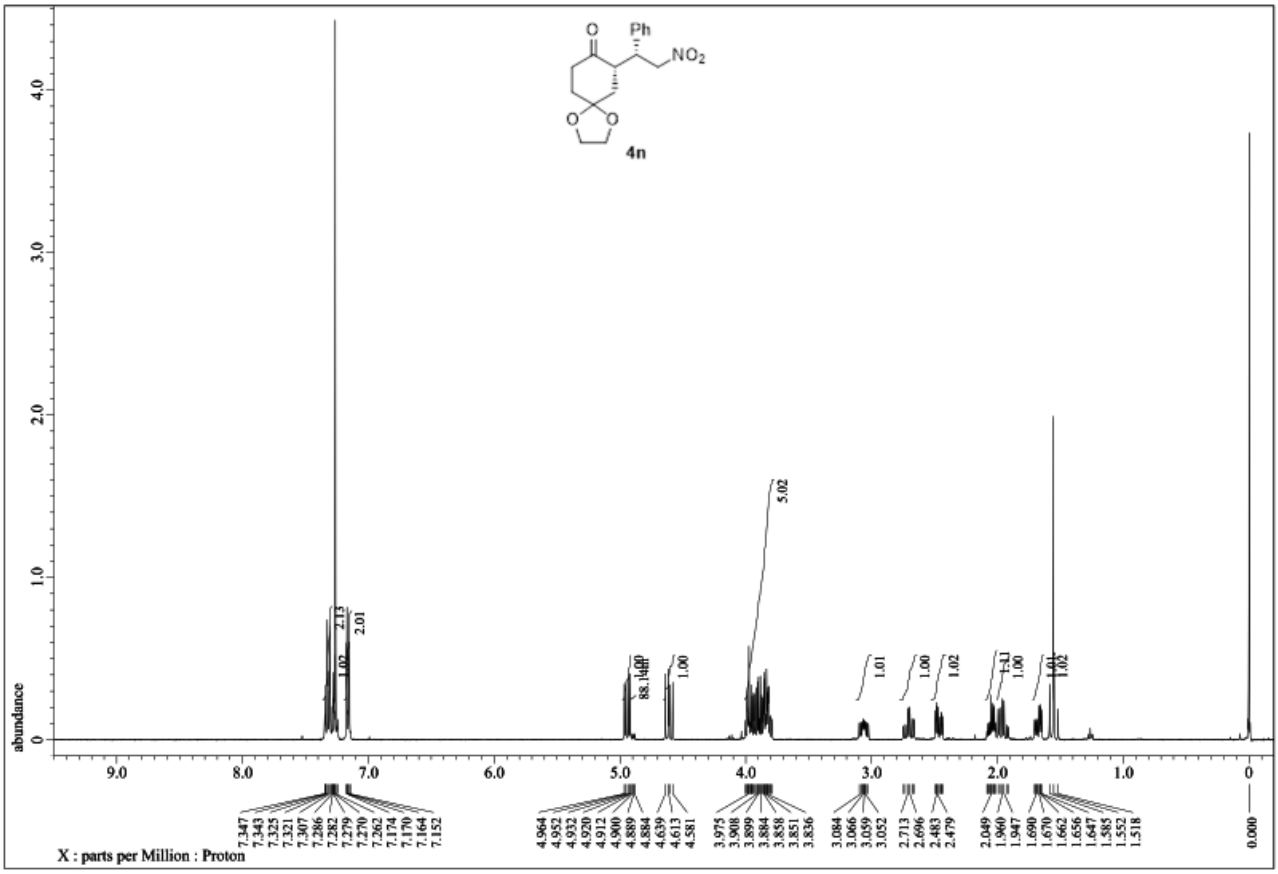
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.02
2.13
2.01
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1.00
1.01
1.00
1.02
1.00
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1.585
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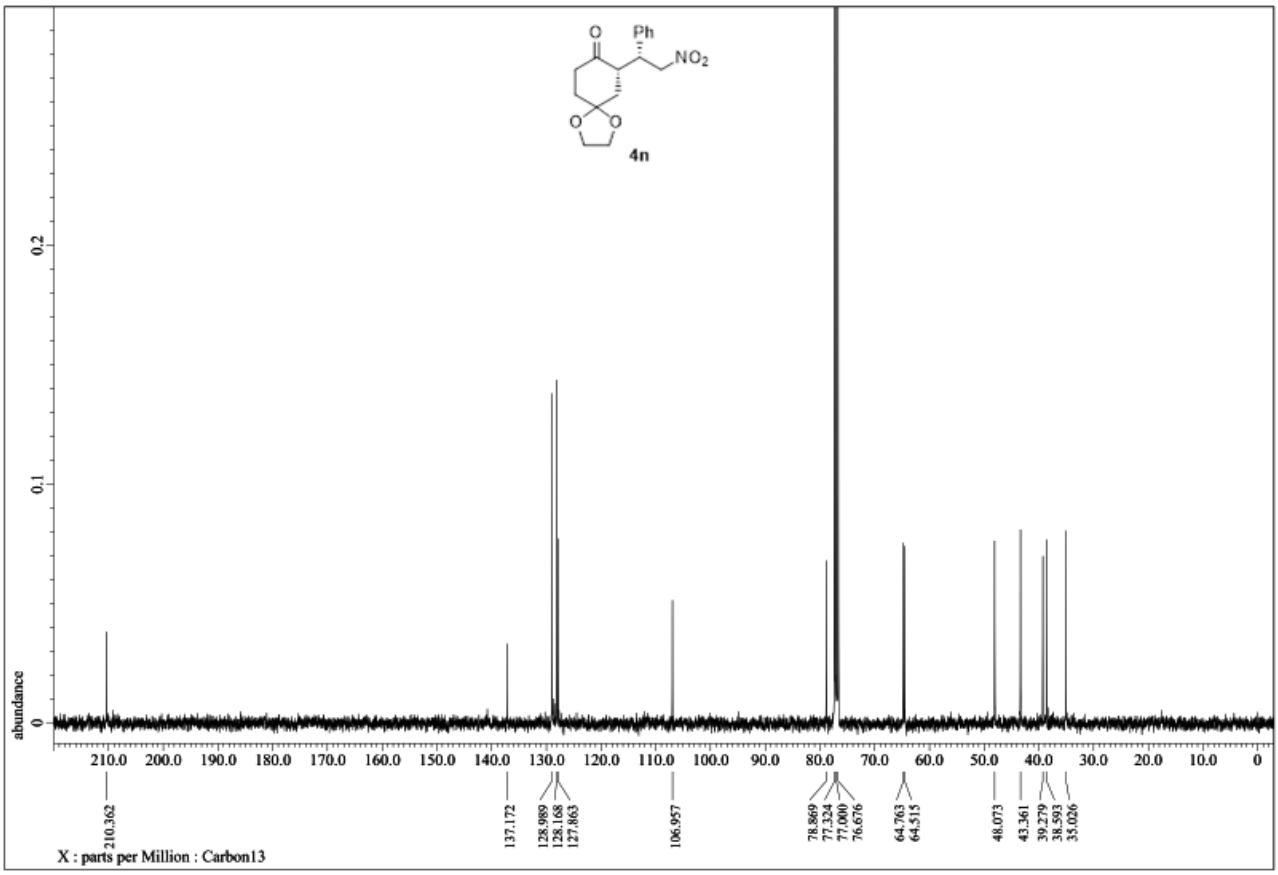
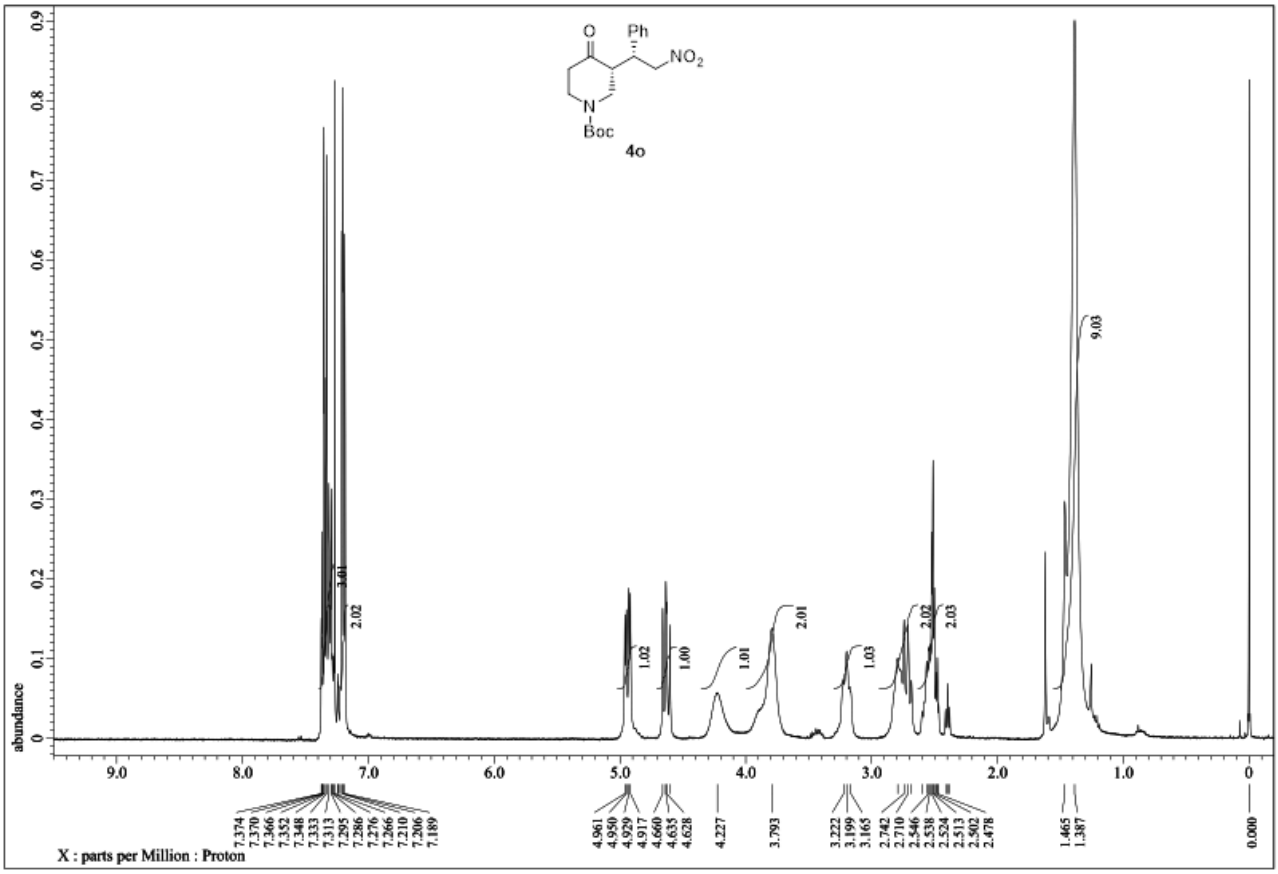
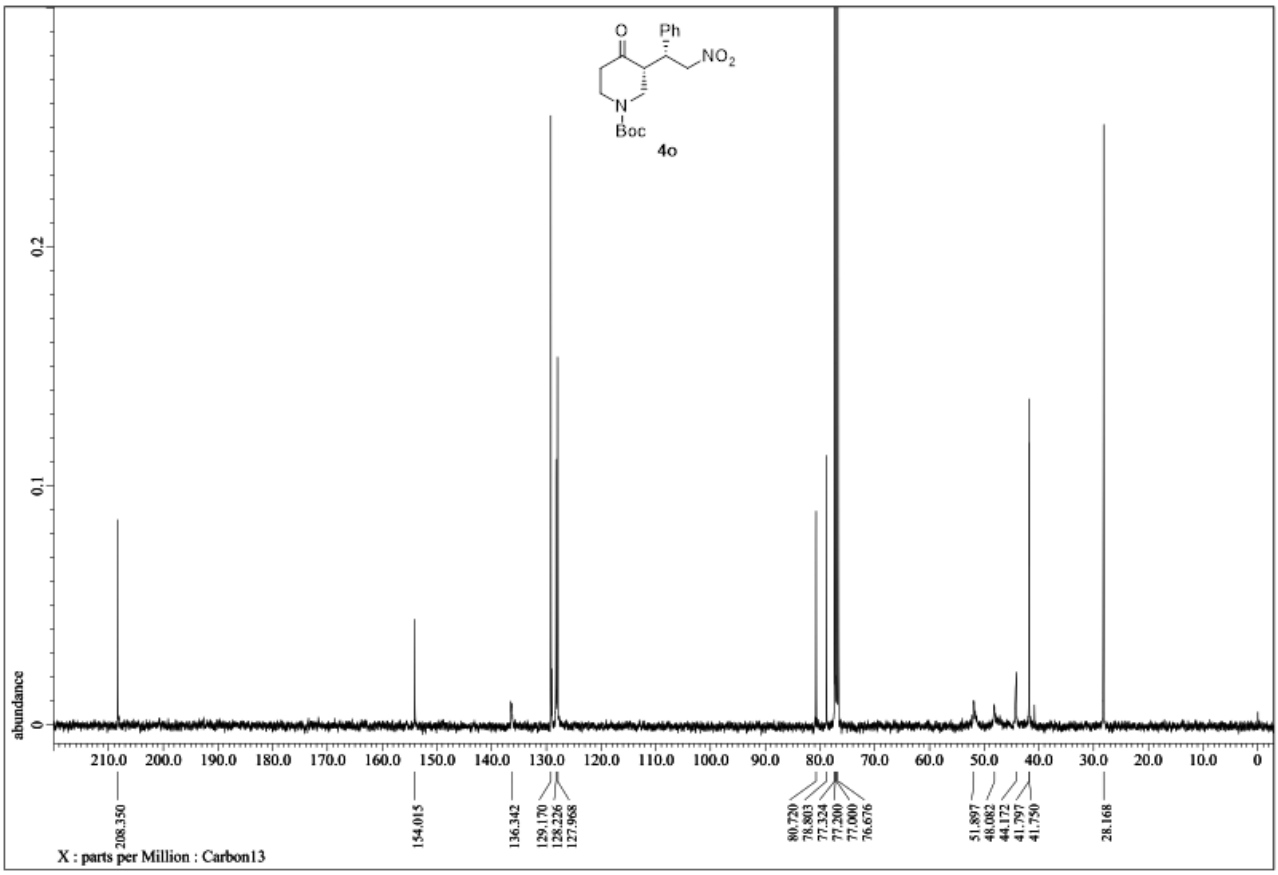
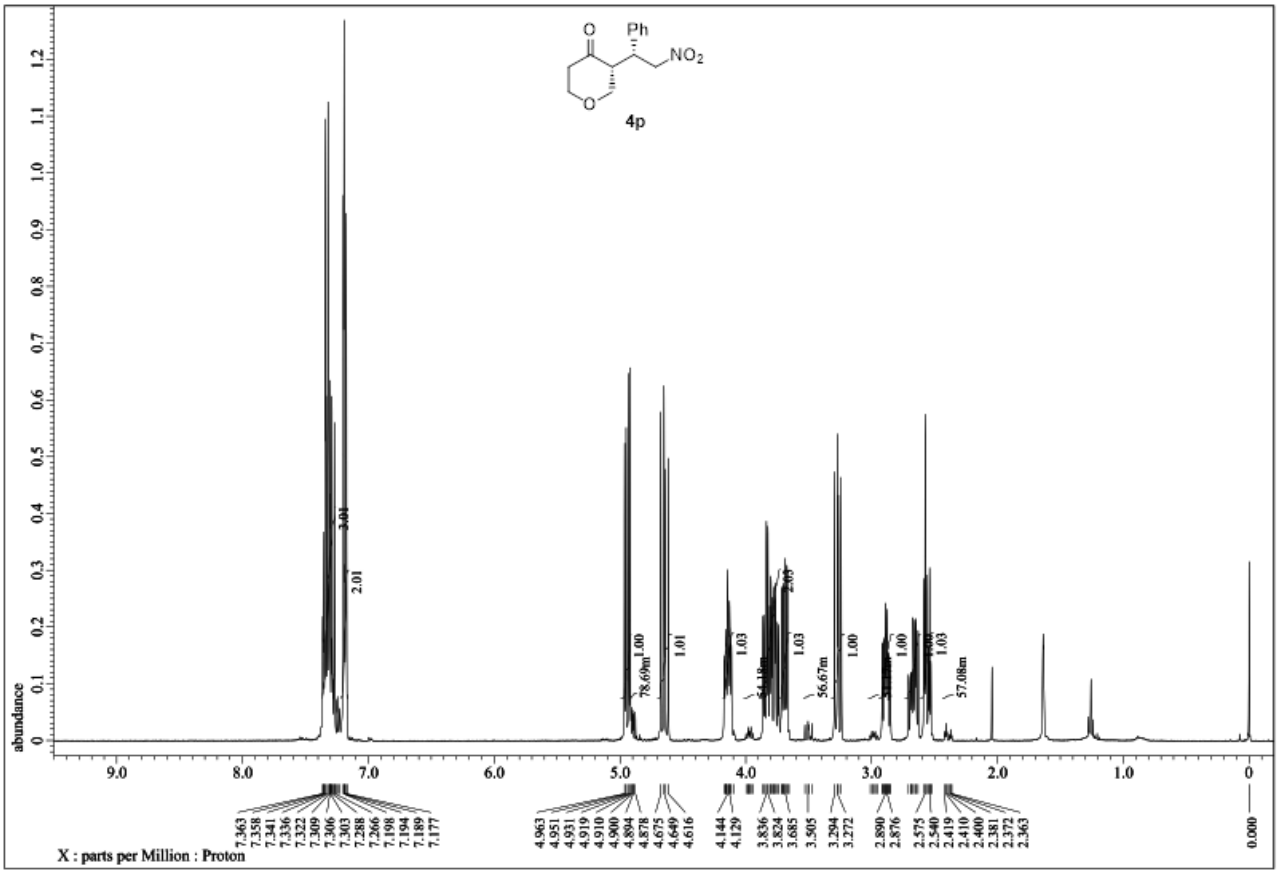
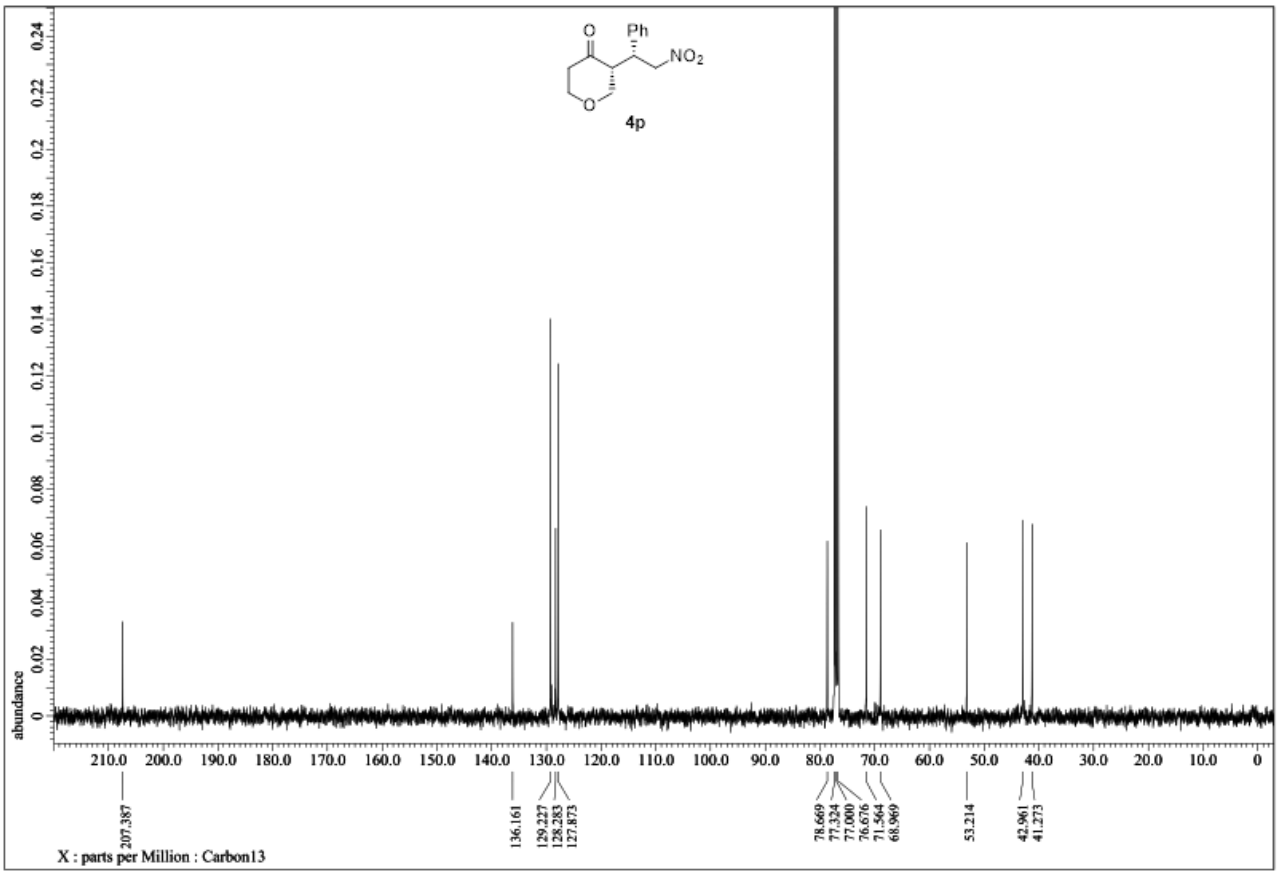
0.000
X : parts per Million : Proton

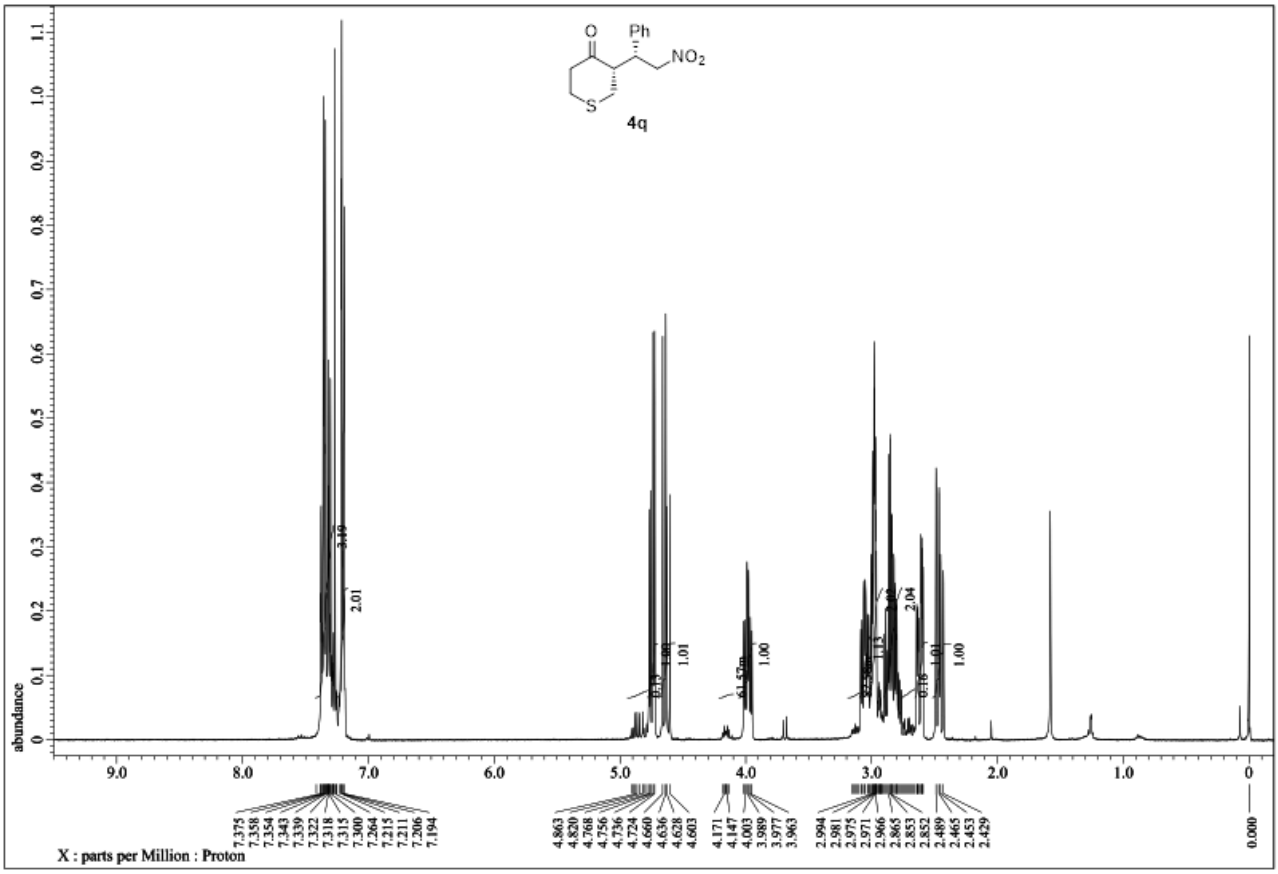

O
Ph
NO2
O
O
4n
abundance
0.2
0.1
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
210.362
137.172
128.989
128.168
127.863
106.957
78.869
77.324
77.000
76.676
64.763
64.515
48.073
43.361
39.279
38.593
35.026
X : parts per Million : Carbon13

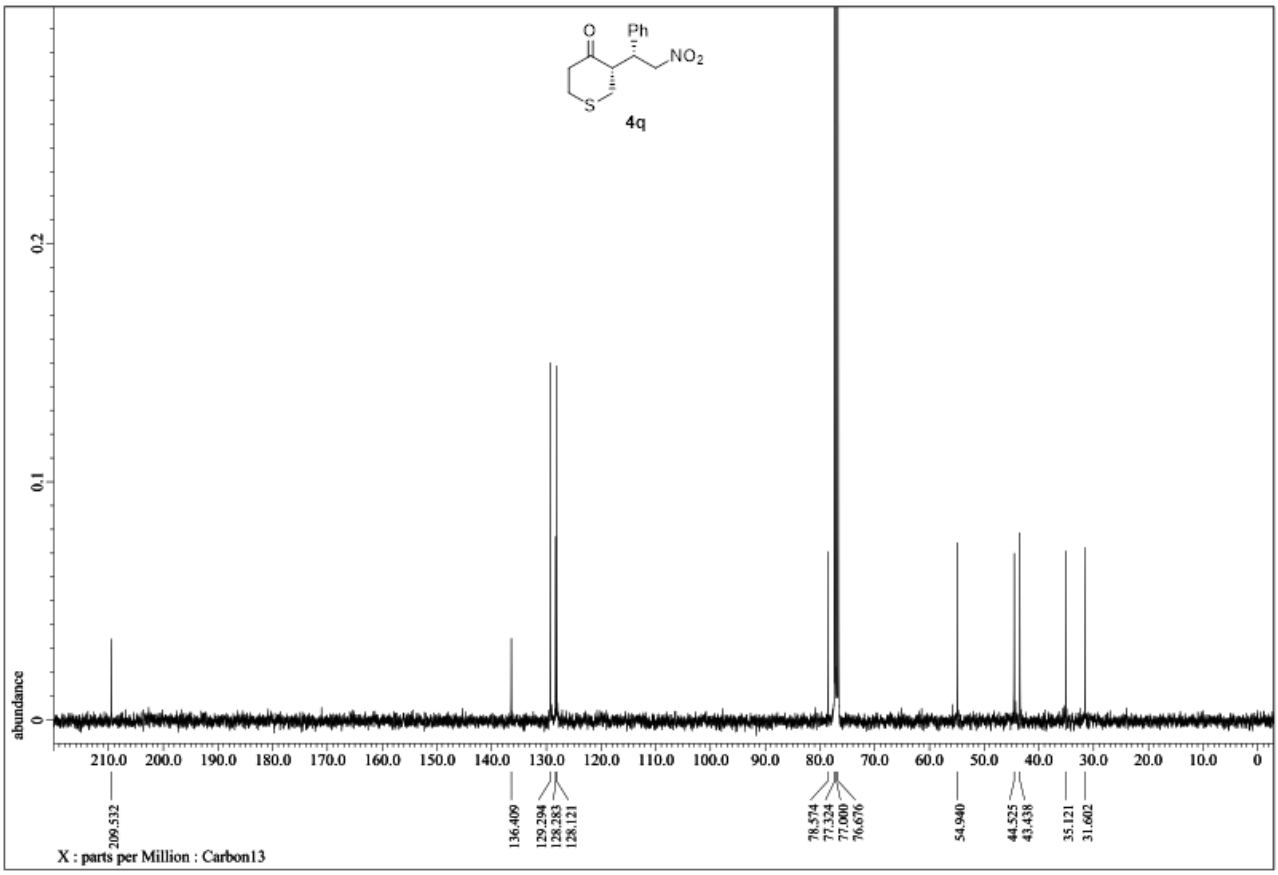

O
Ph
NO2
N
Boc
4o
abundance
X : parts per Million : Proton

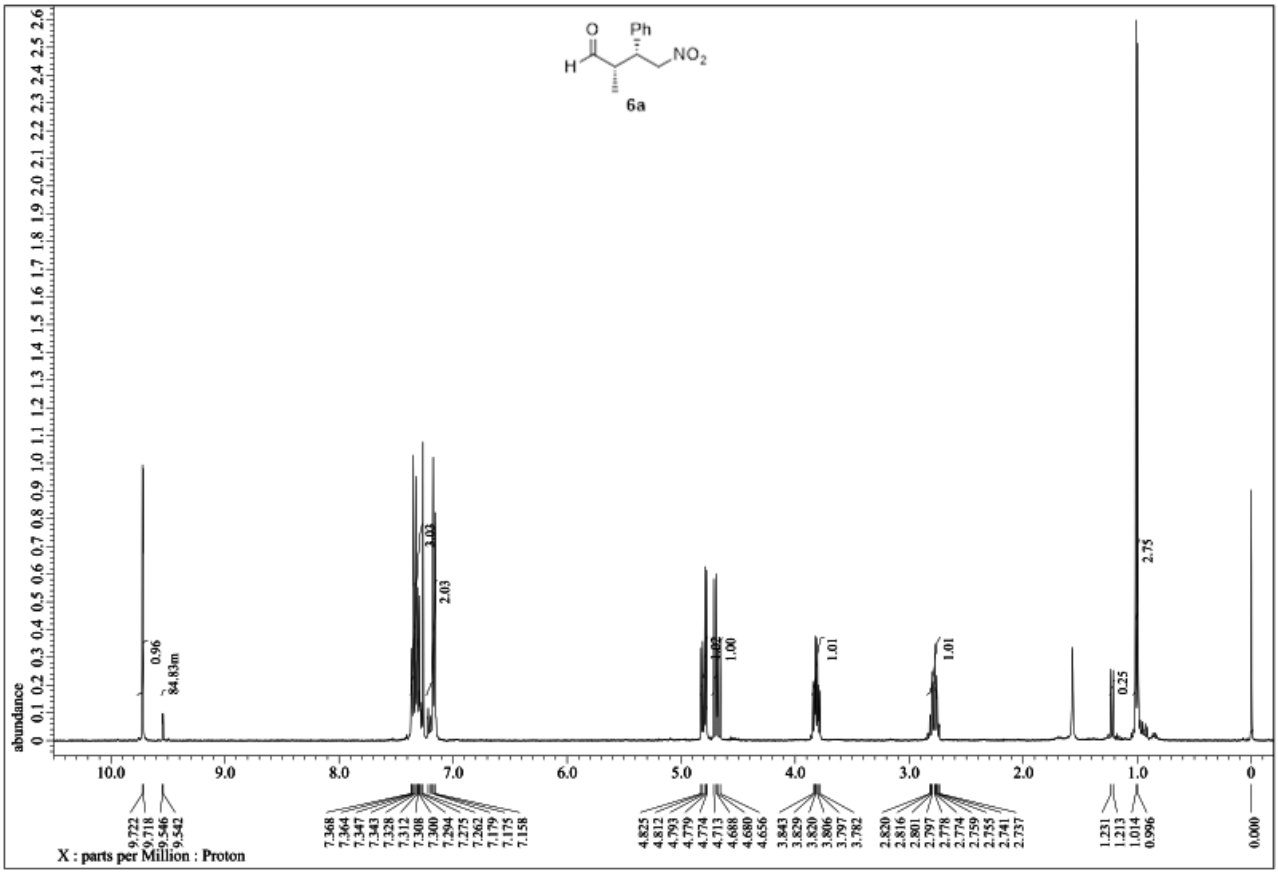

O
Ph
NO2
N
Boc
4o
abundance
X : parts per Million : Carbon13

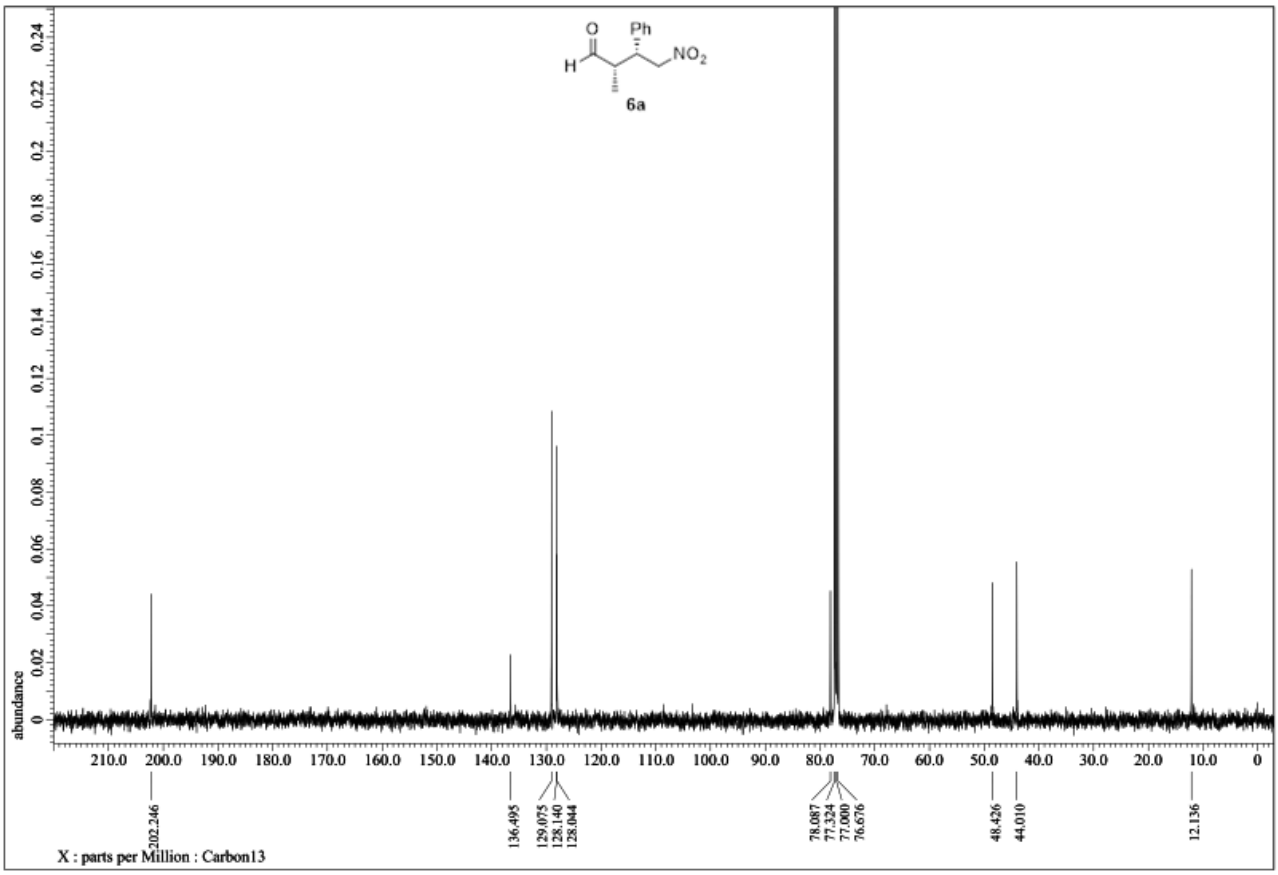

O
Ph
NO2
4p
abundance
X : parts per Million : Proton

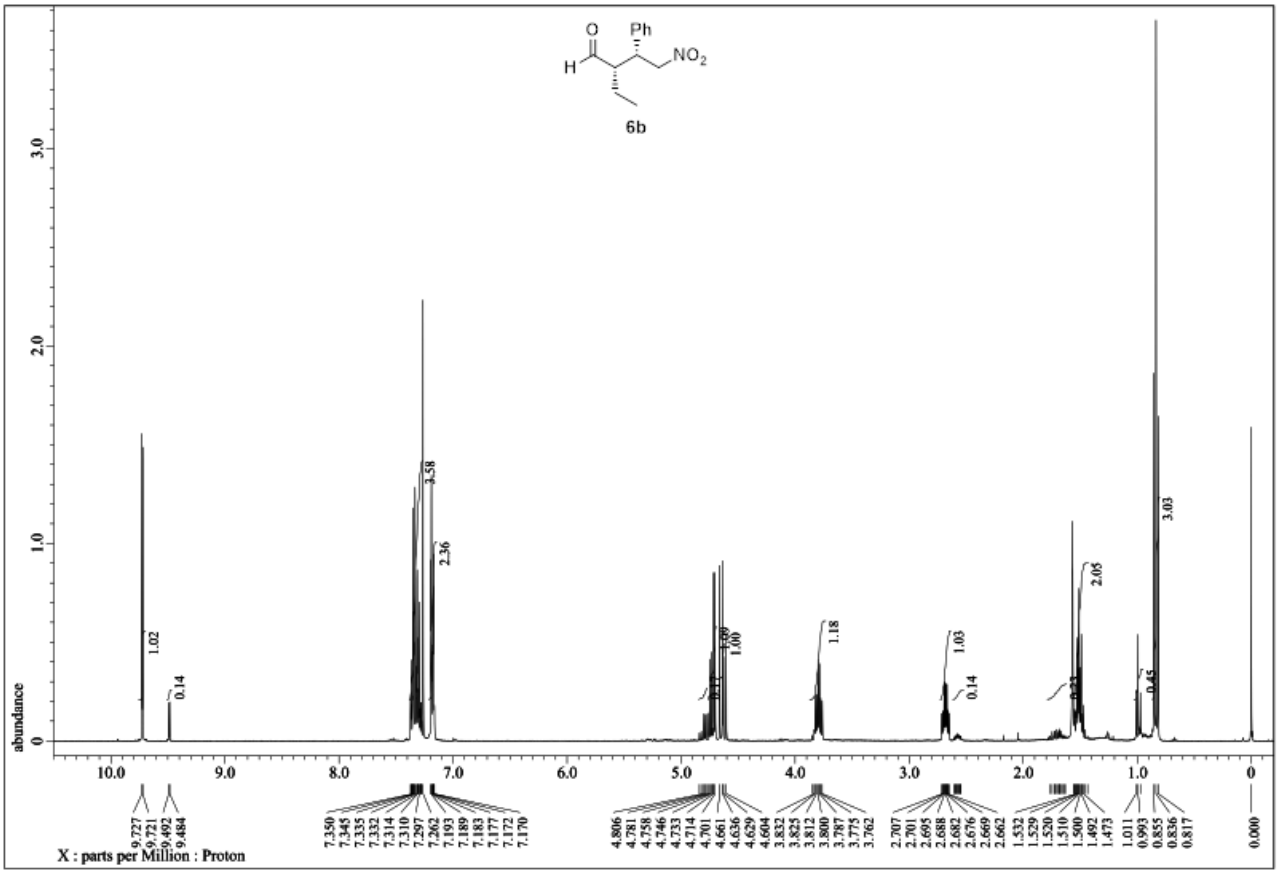

O
Ph
NO2
4p
abundance
X : parts per Million : Carbon13

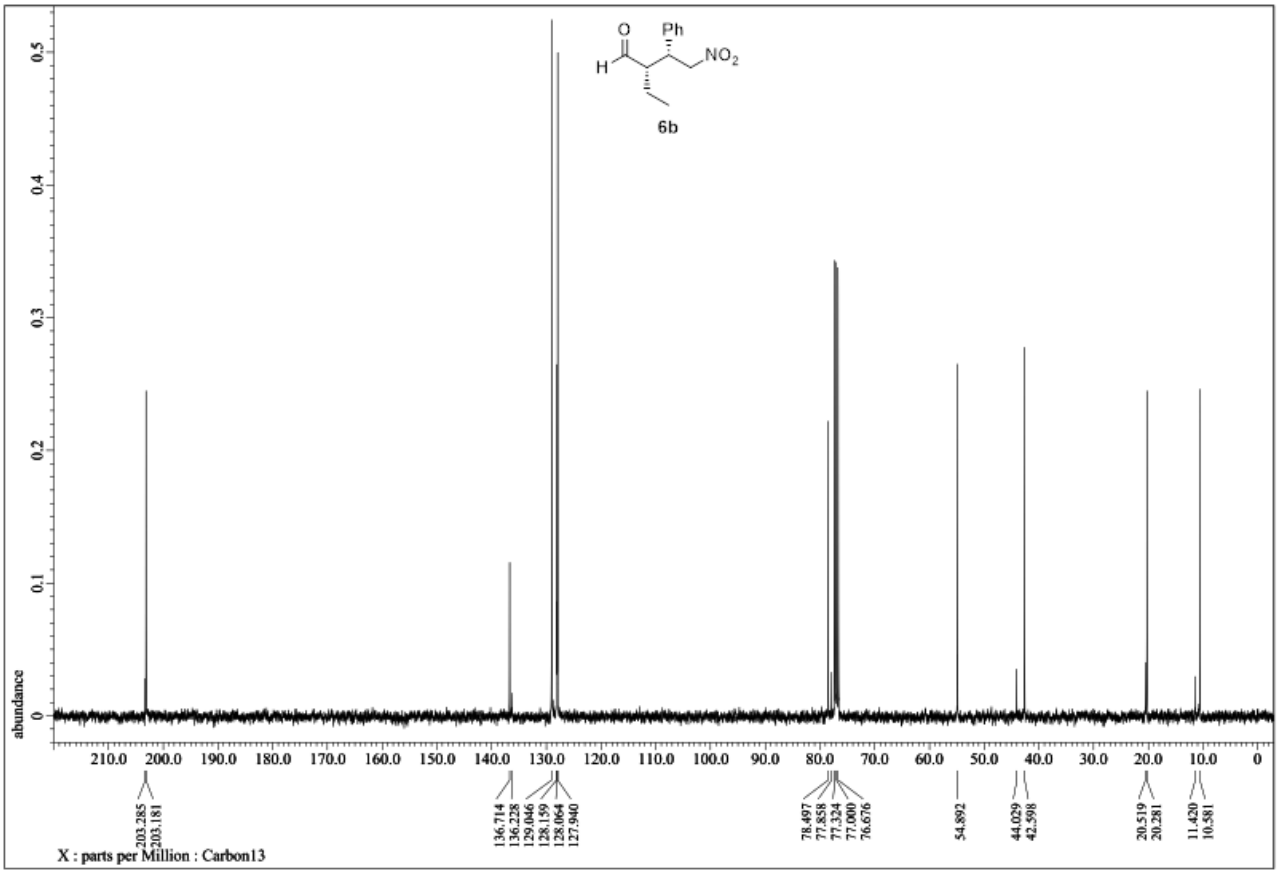

O
Ph
NO2
S
4q
abundance
X : parts per Million : Proton

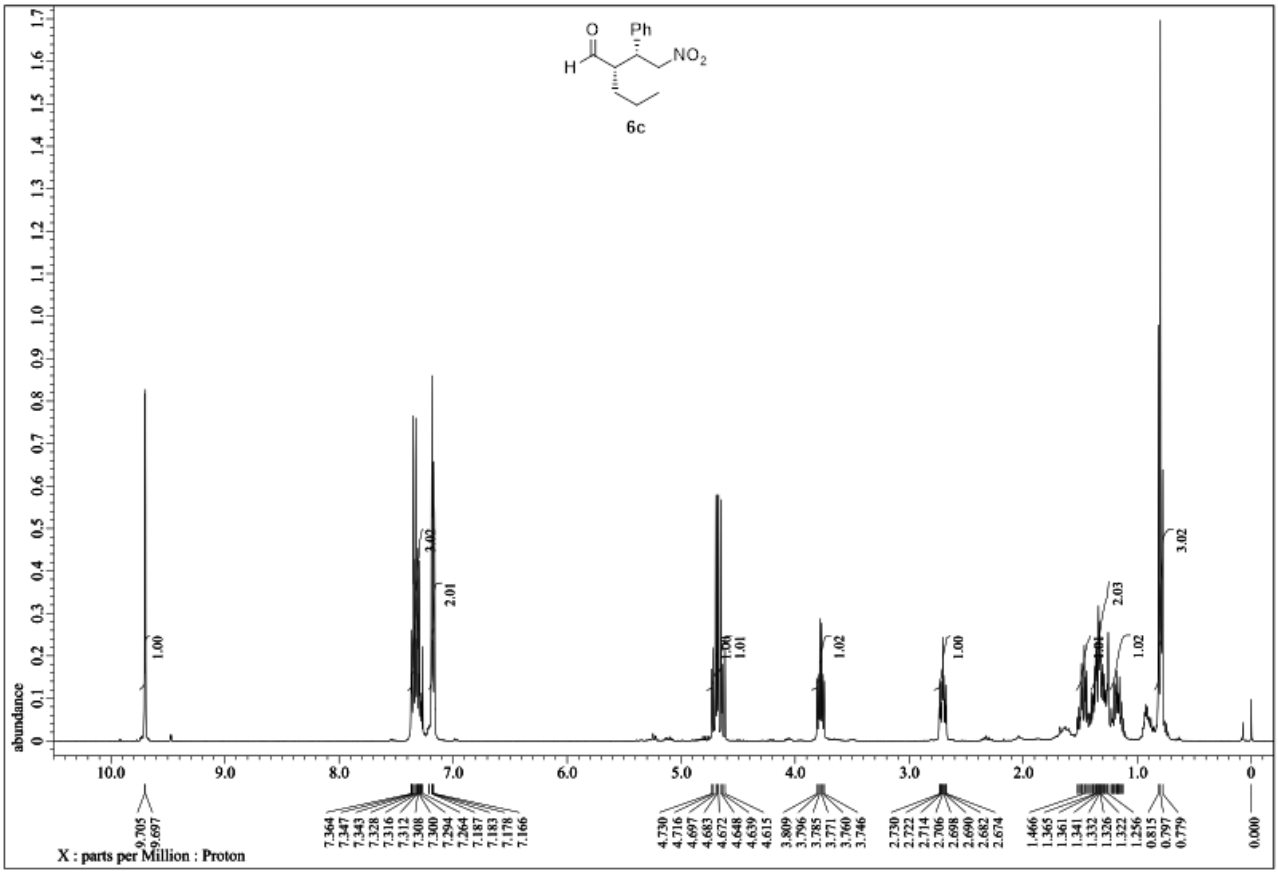

O
Ph
NO2
S
4q
abundance
X : parts per Million : Carbon13

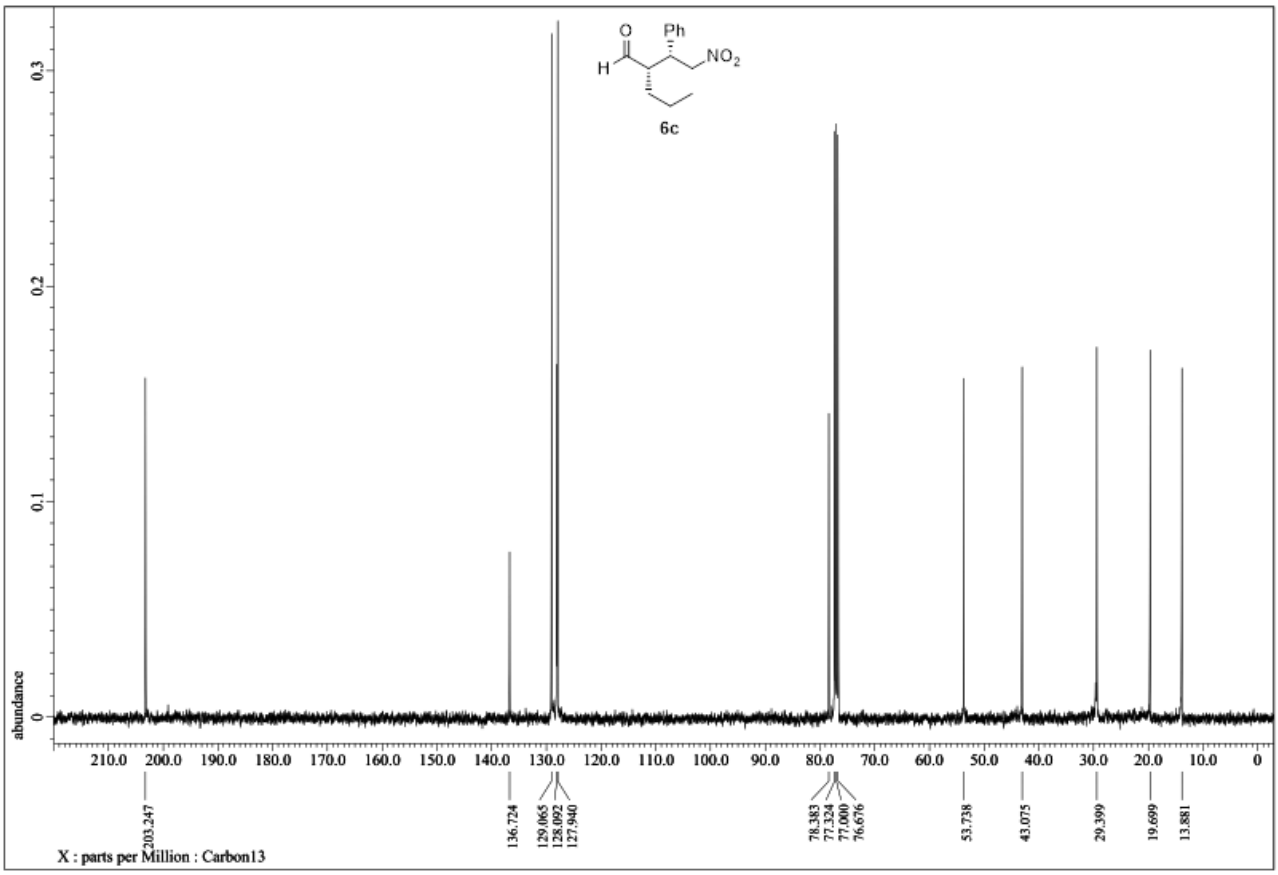

O
Ph
H
NO2
6a
abundance
X : parts per Million : Proton

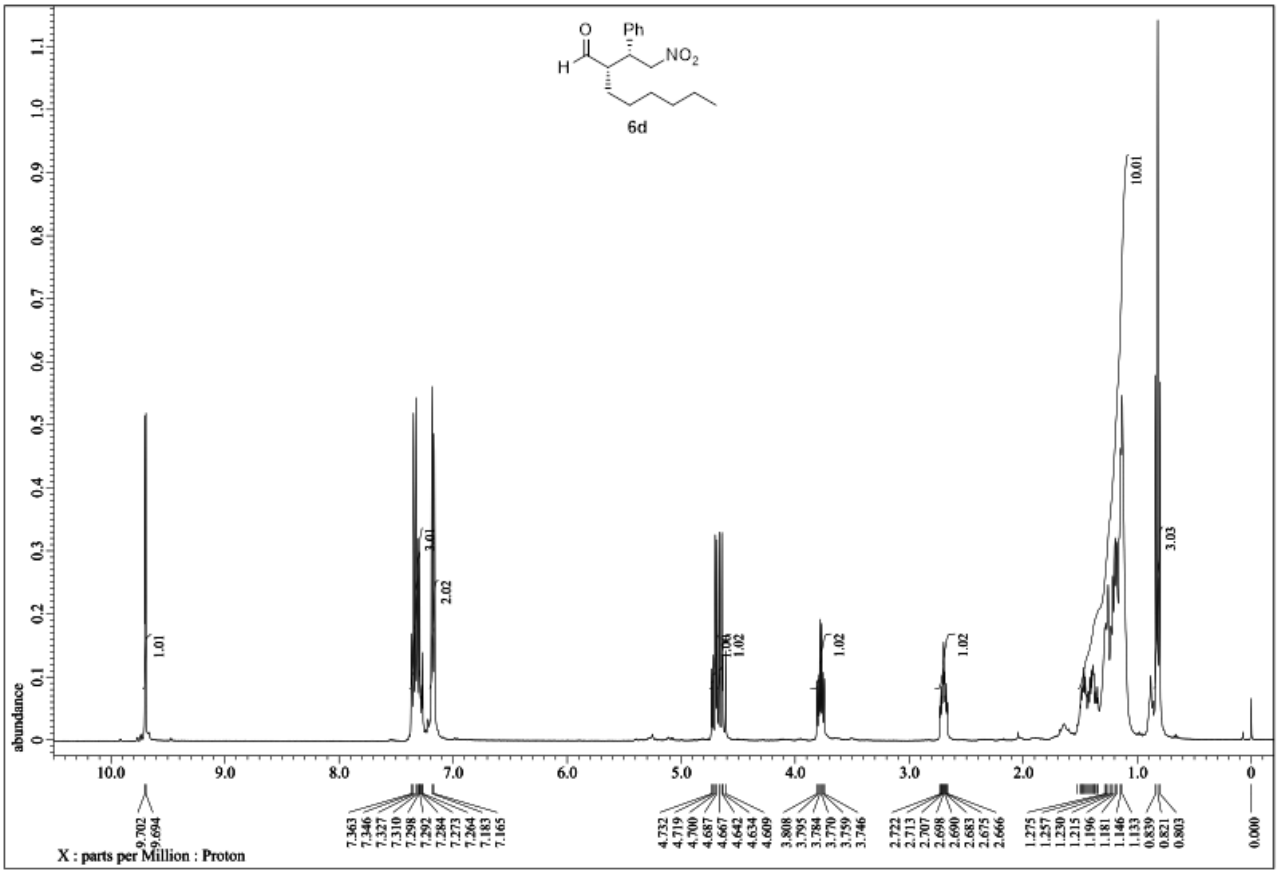

O
Ph
H
NO2
6a
abundance
X : parts per Million : Carbon13

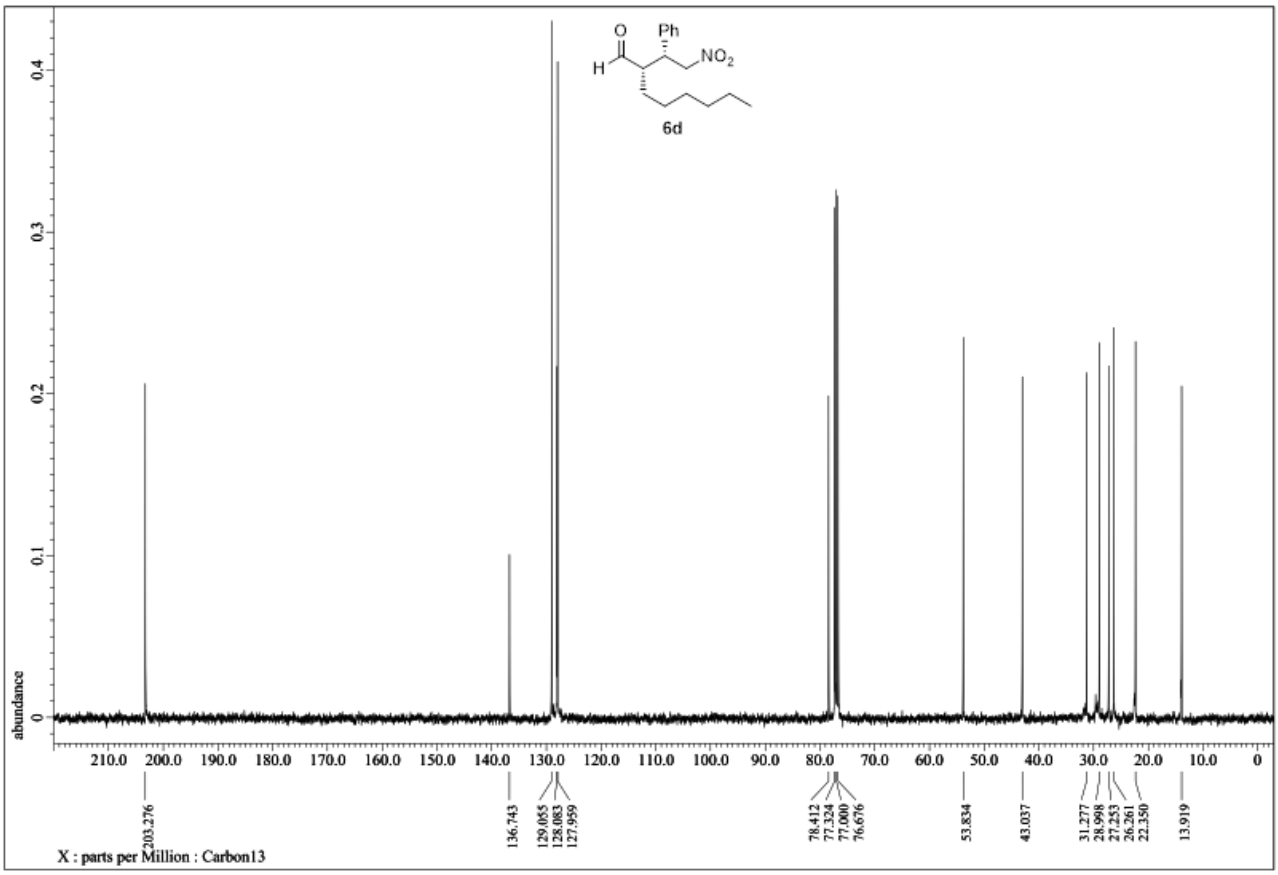

O
Ph
H
NO2
6b
abundance
X : parts per Million : Proton

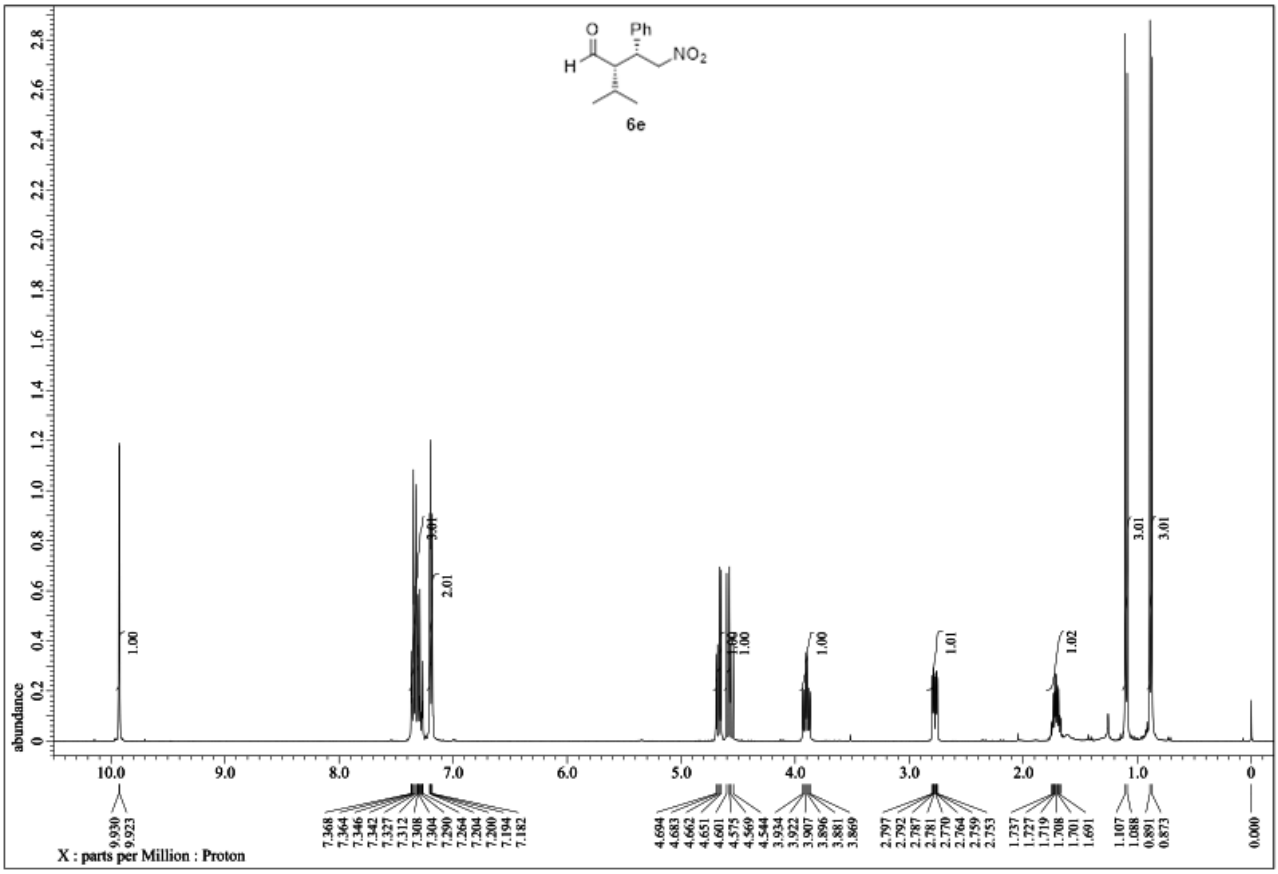

O
Ph
H
NO2
6b
abundance
X : parts per Million : Carbon13

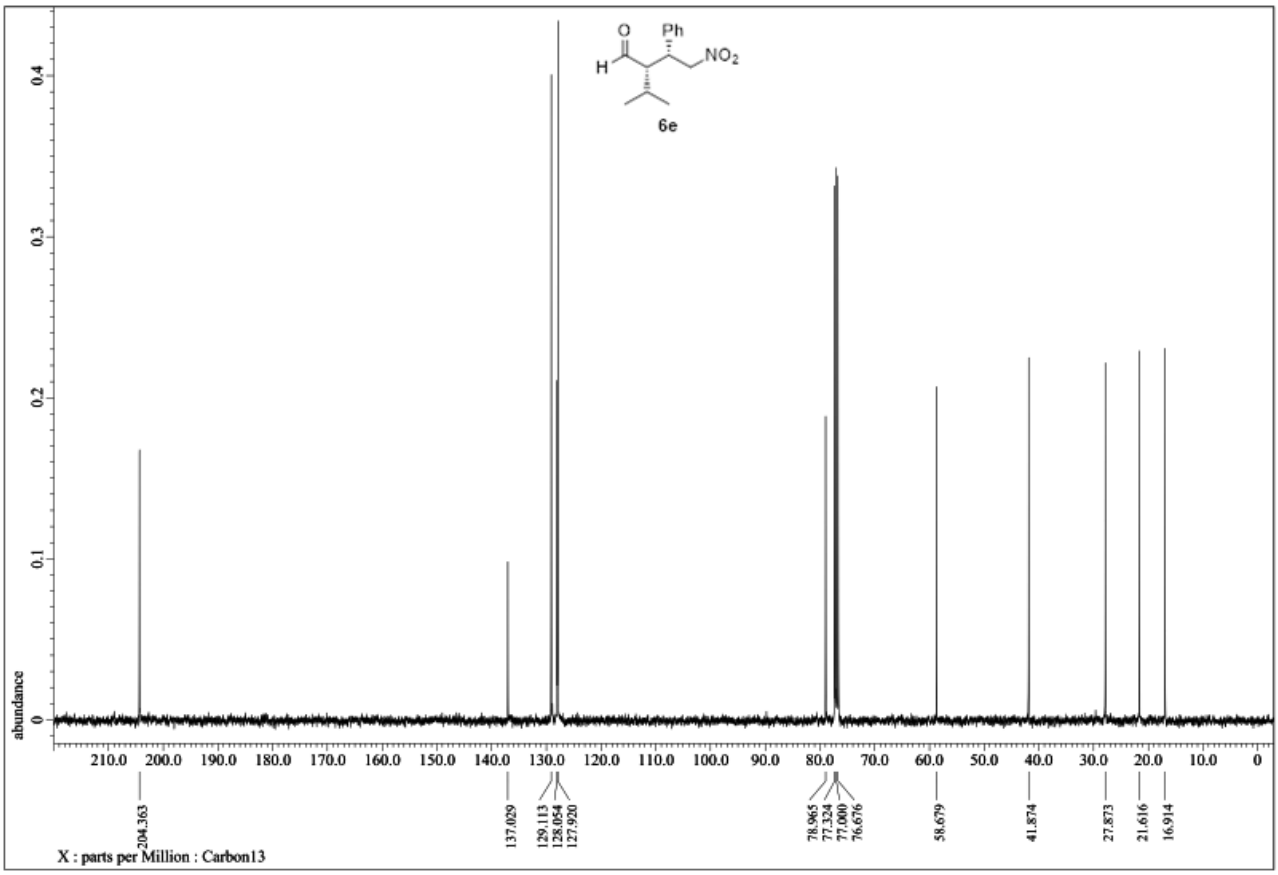

O
H
Ph
NO2
6c
abundance
X : parts per Million : Proton

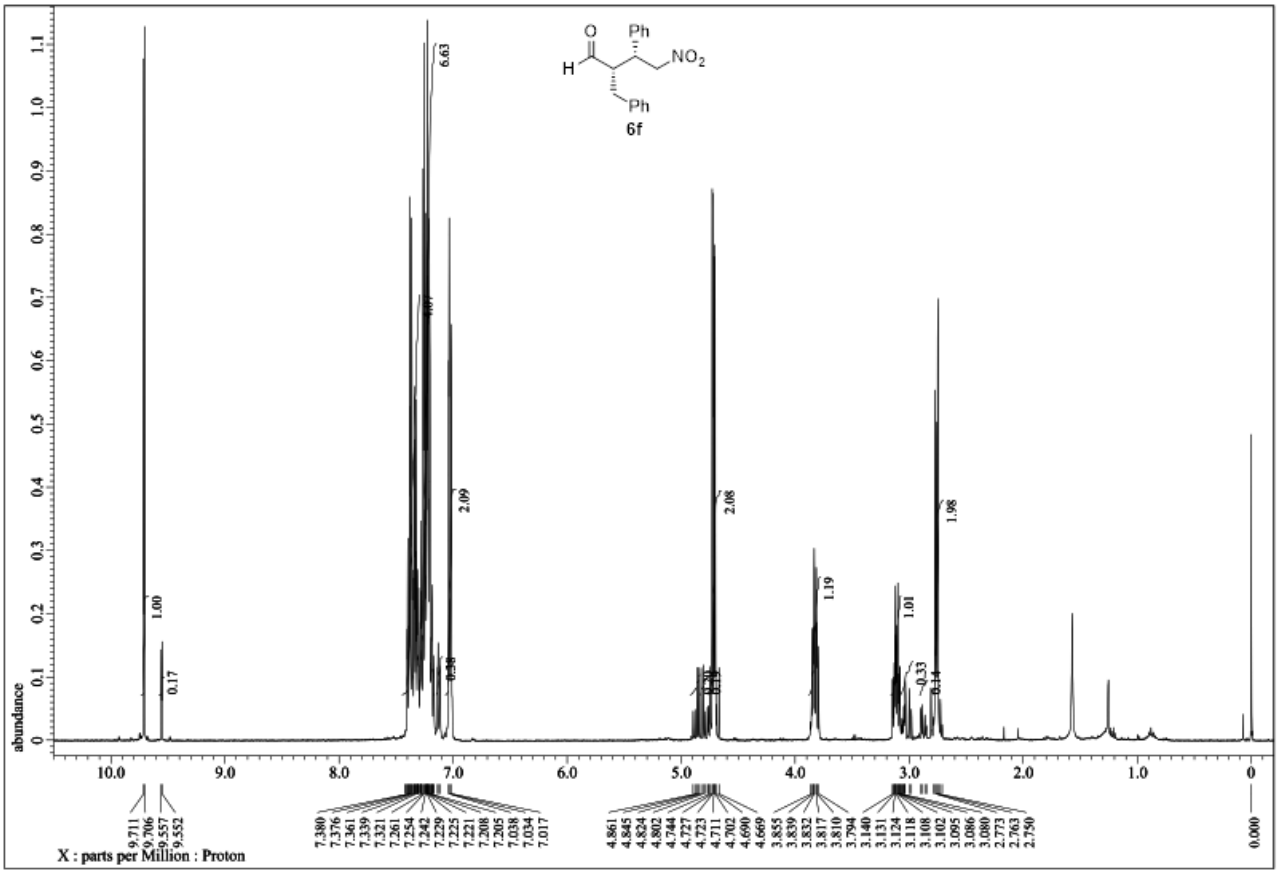

O
H
Ph
NO2
6c
abundance
X : parts per Million : Carbon13

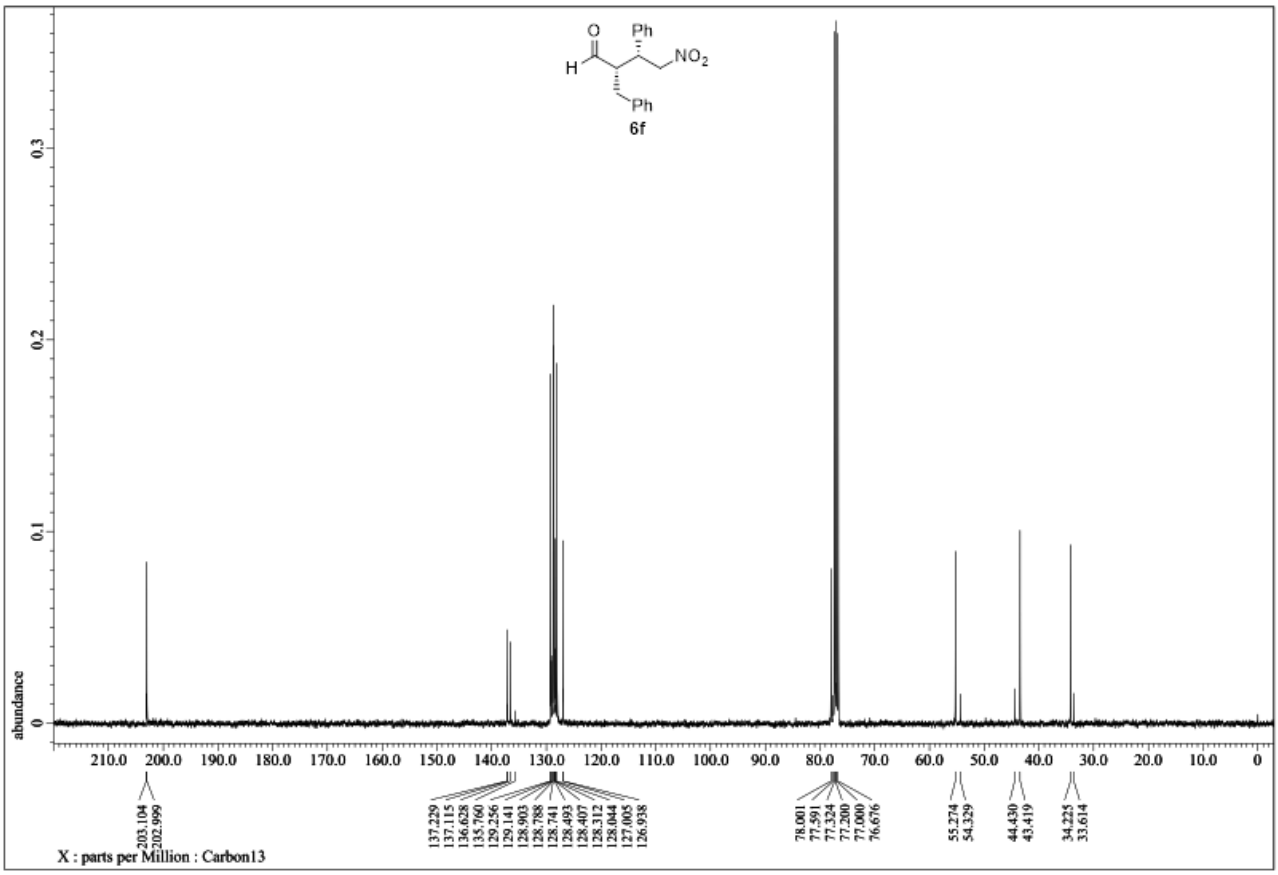

O
Ph
H
NO2
6d
abundance
X : parts per Million : Proton

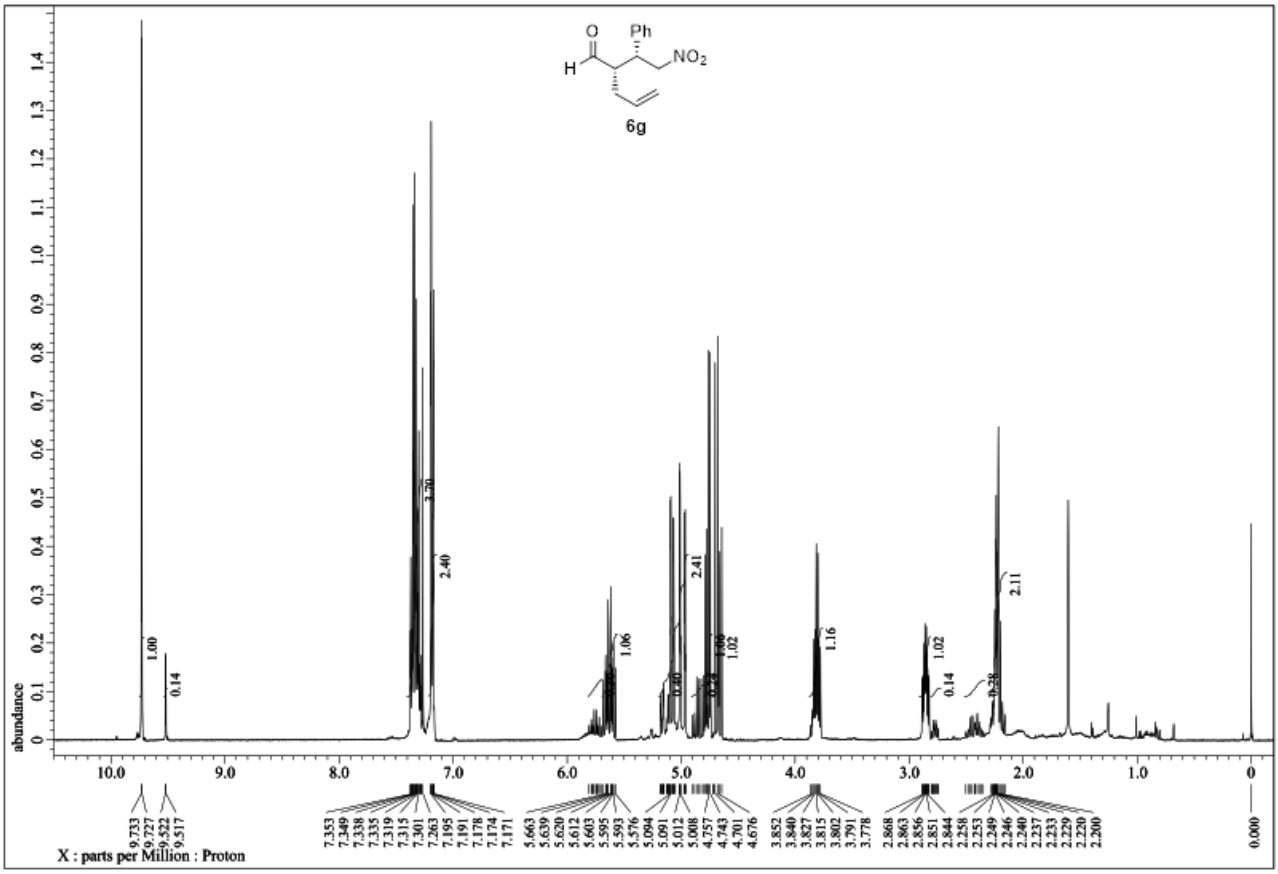

O
Ph
H
NO2
6d
abundance
X : parts per Million : Carbon13

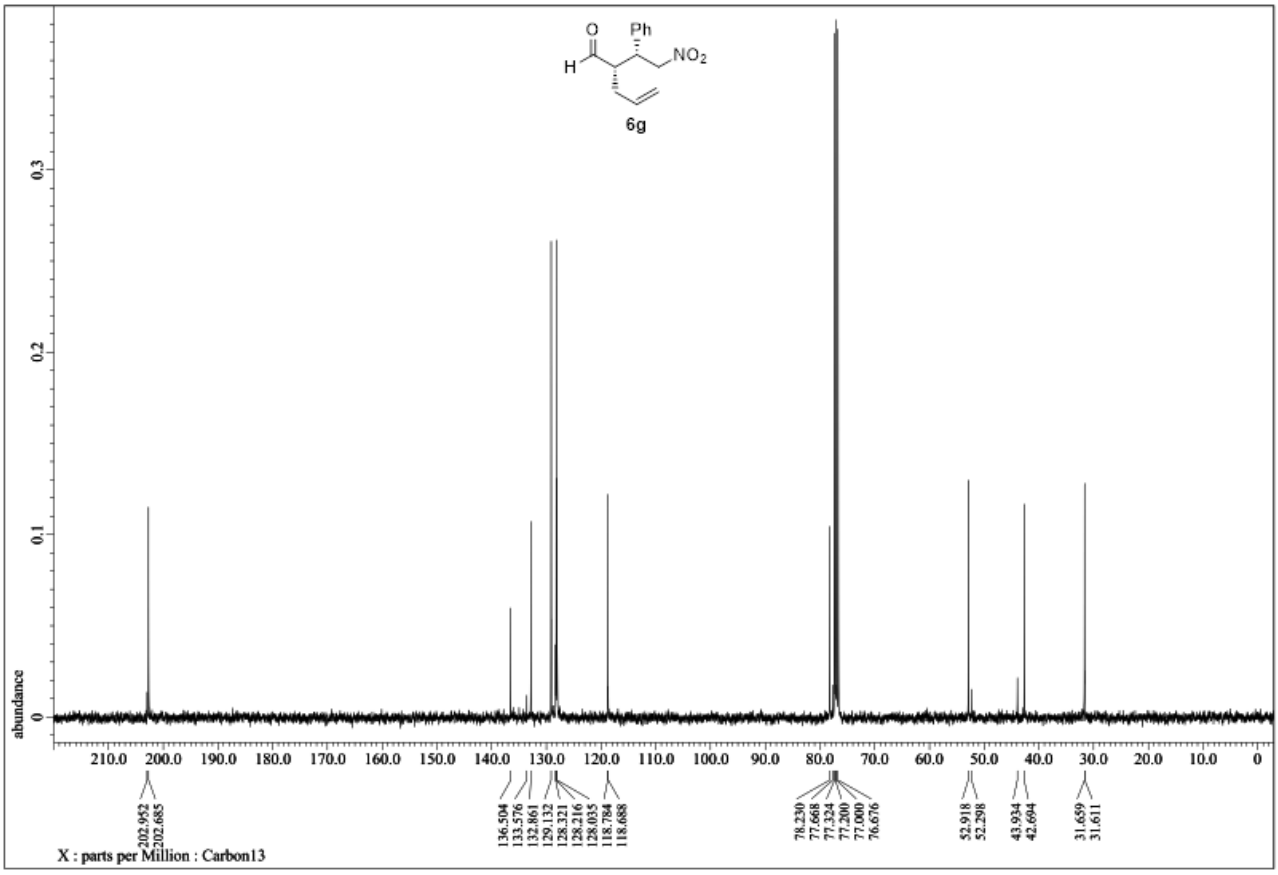

O
Ph
H
NO2
6e
abundance
X : parts per Million : Proton

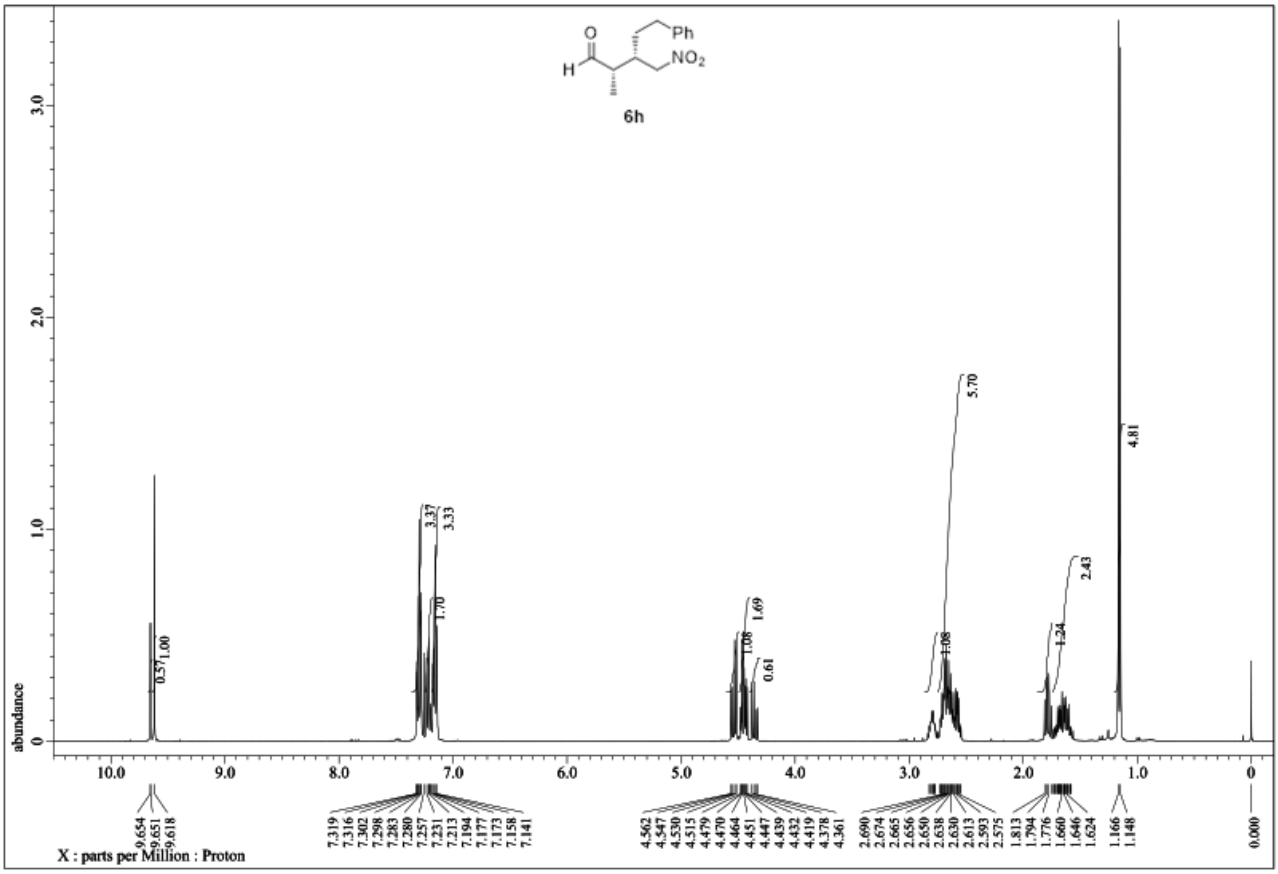

O
Ph
H
NO2
6e
abundance
X : parts per Million : Carbon13

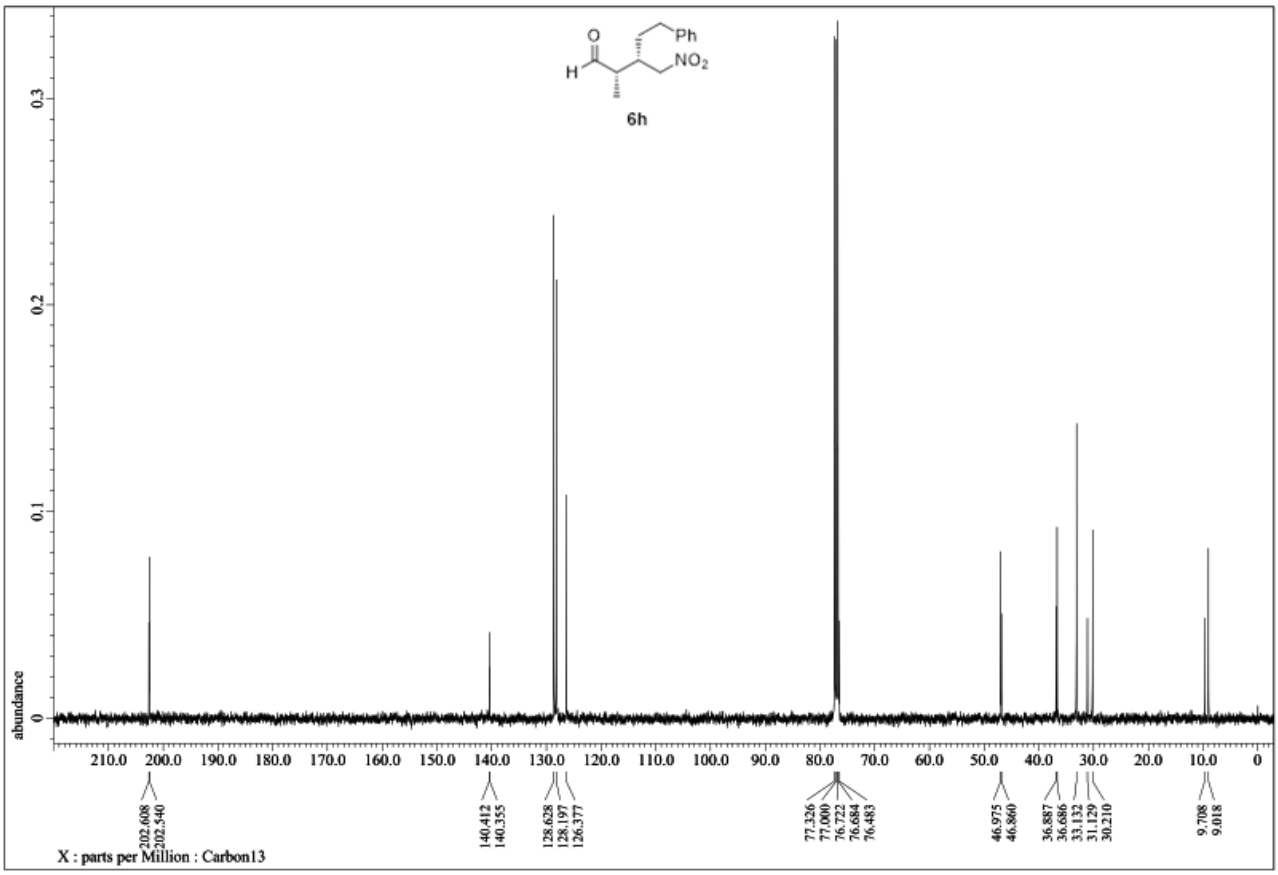

O
Ph
H
NO2
Ph
6f
abundance
X : parts per Million : Proton

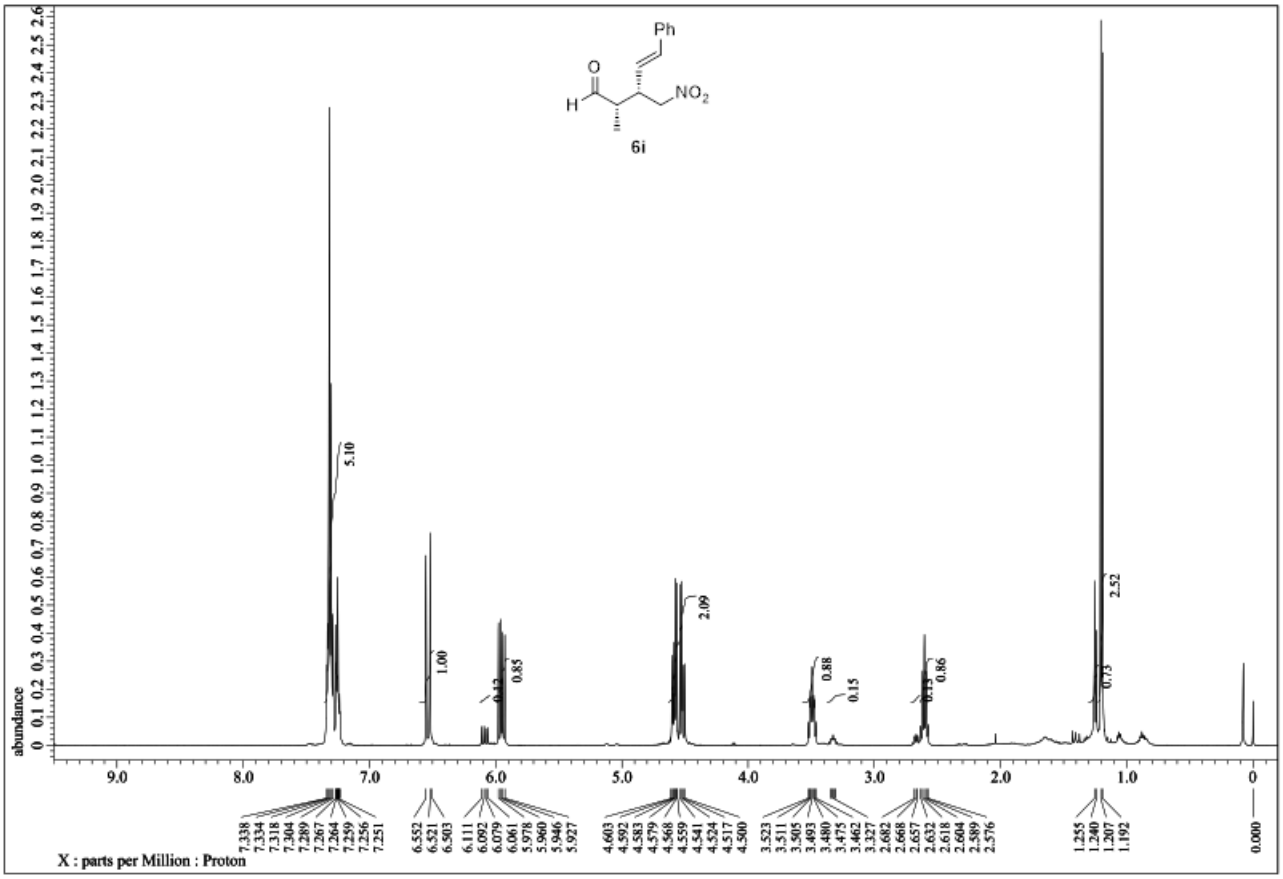

O
Ph
H
NO2
Ph
6f
abundance
X : parts per Million : Carbon13

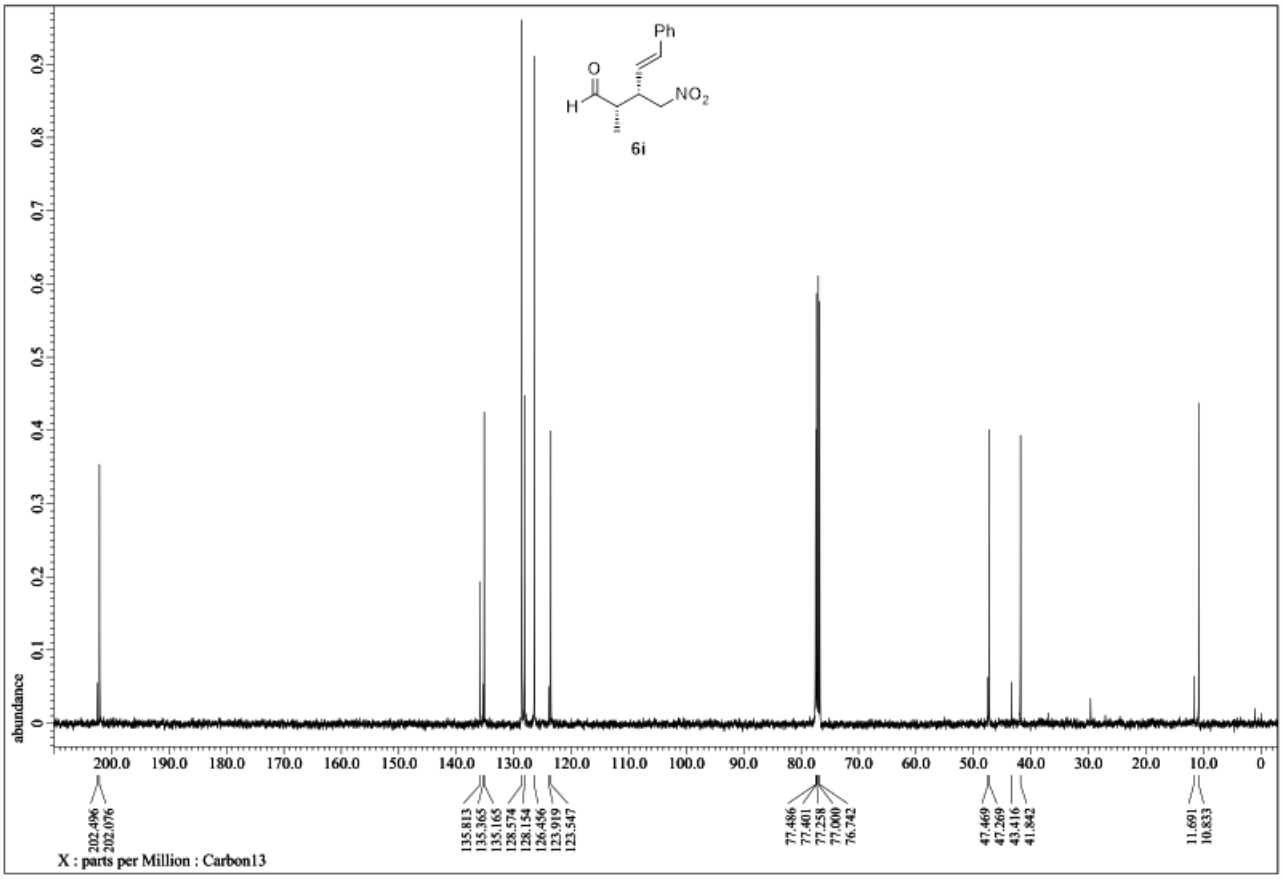

O
Ph
H
NO2
6g
abundance
X : parts per Million : Proton

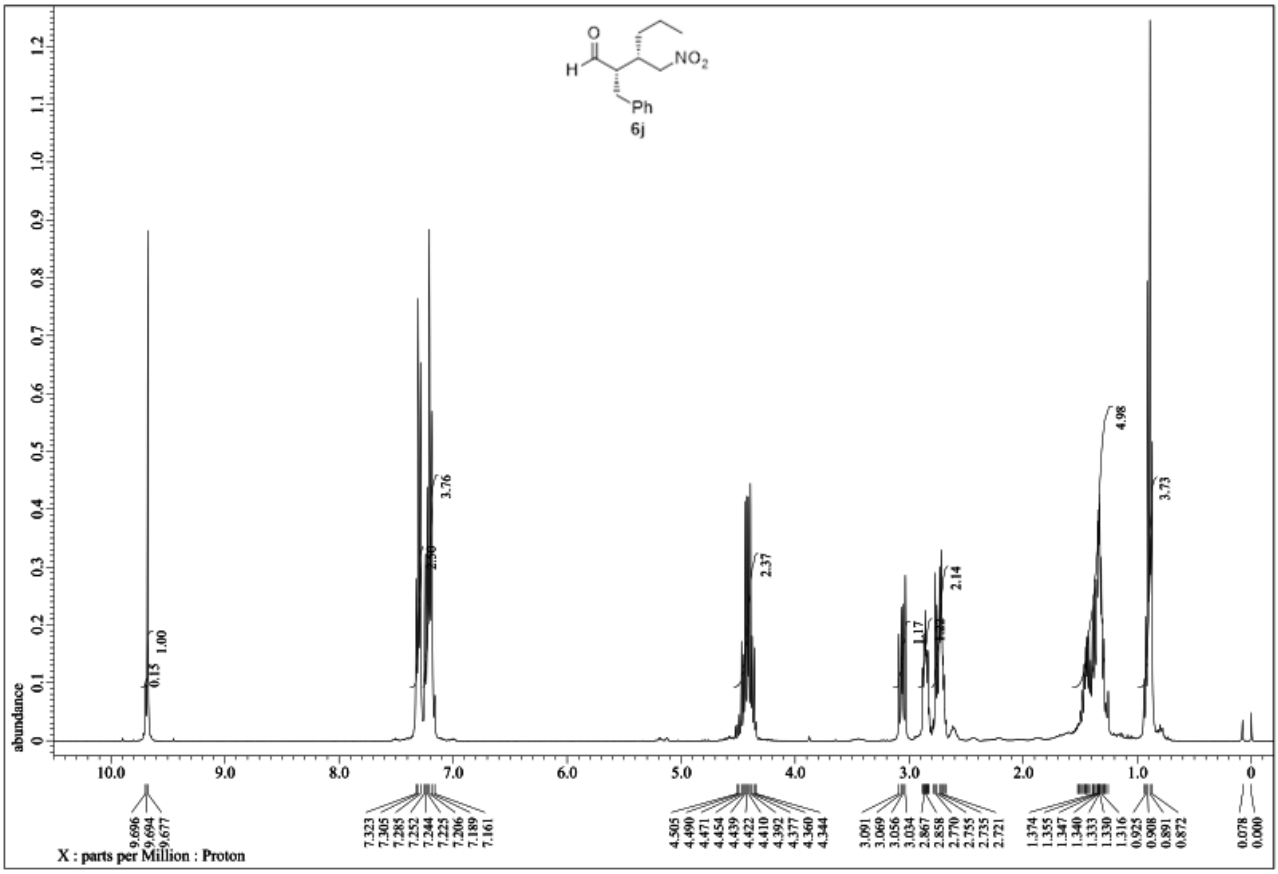

O
Ph
H
NO2
6g
abundance
X : parts per Million : Carbon13

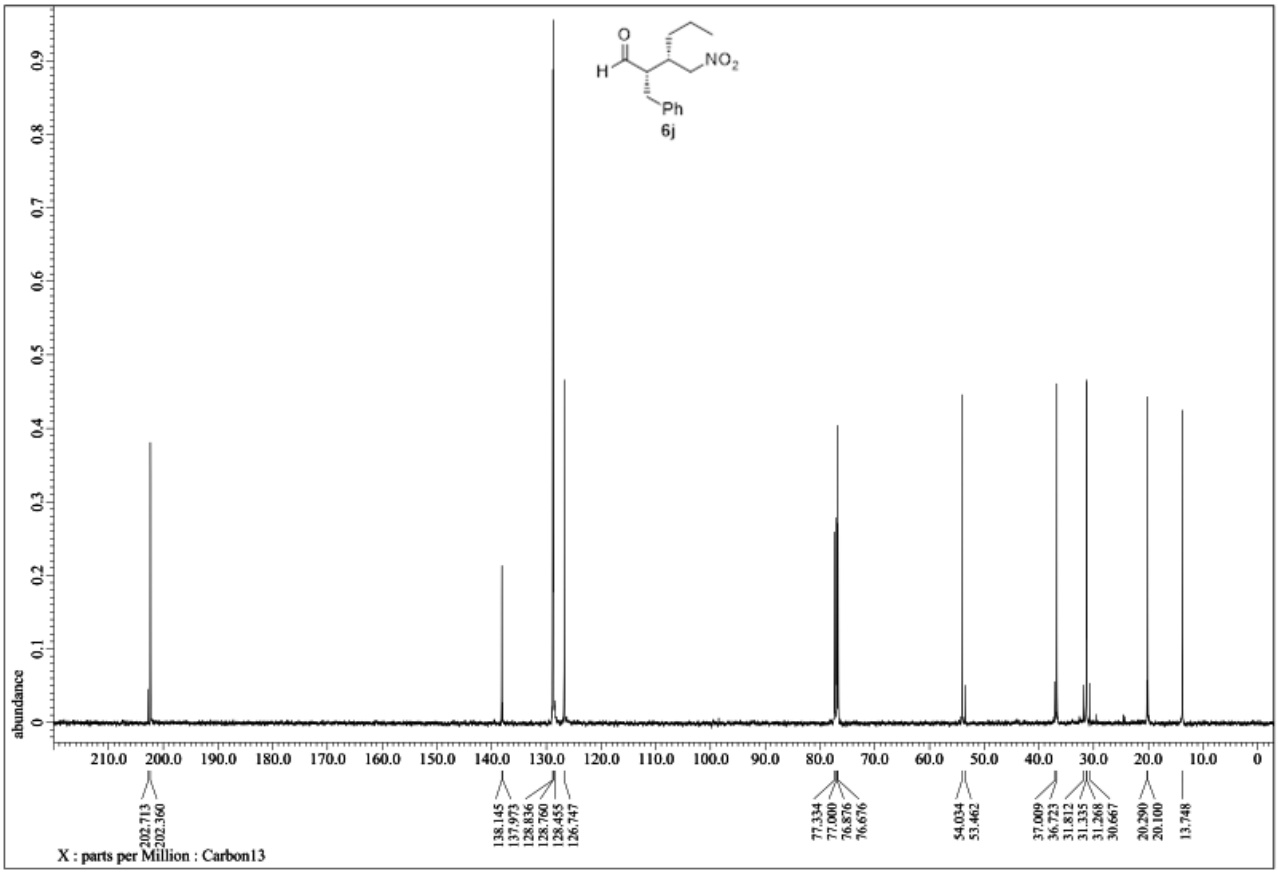

6h
abundance
X : parts per Million : Proton

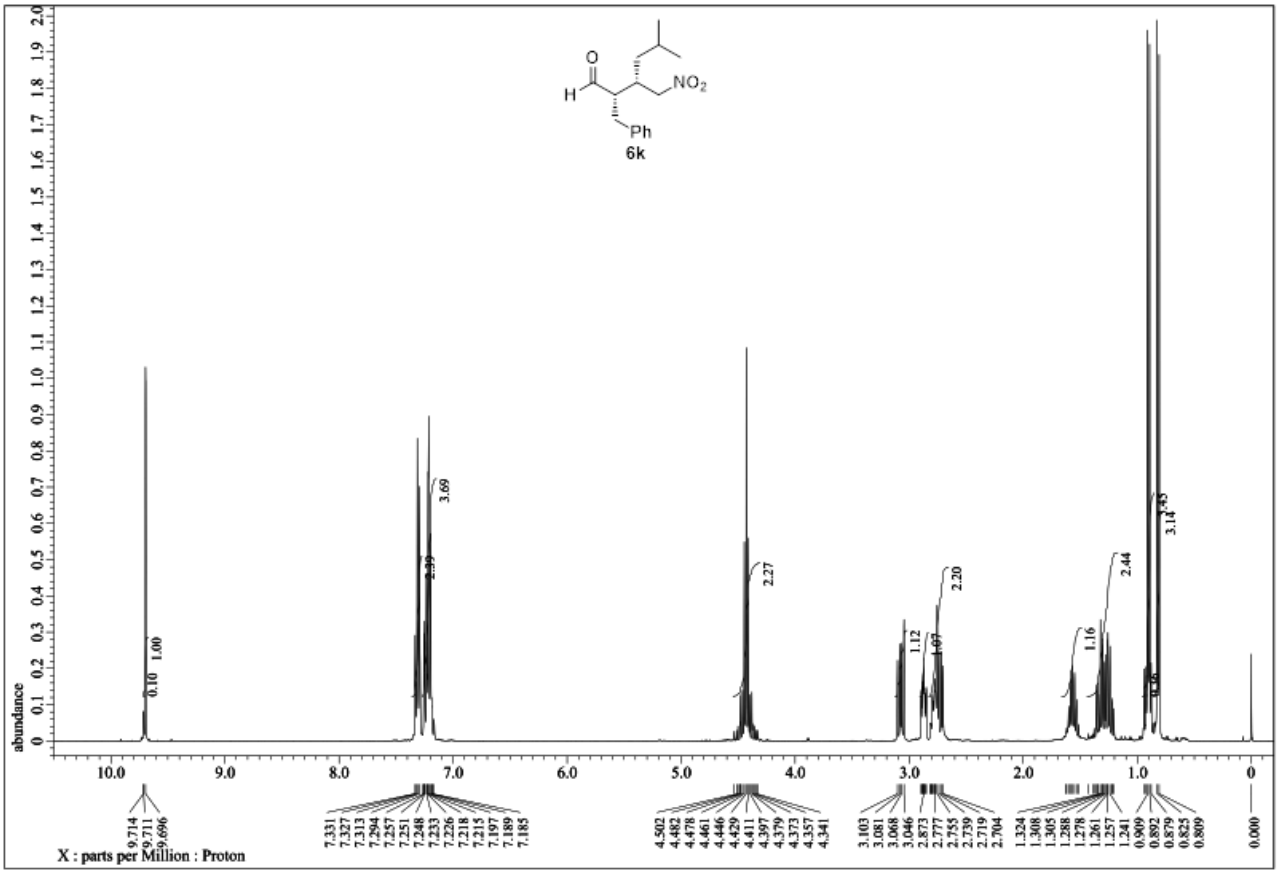

6h
abundance
X : parts per Million : Carbon13

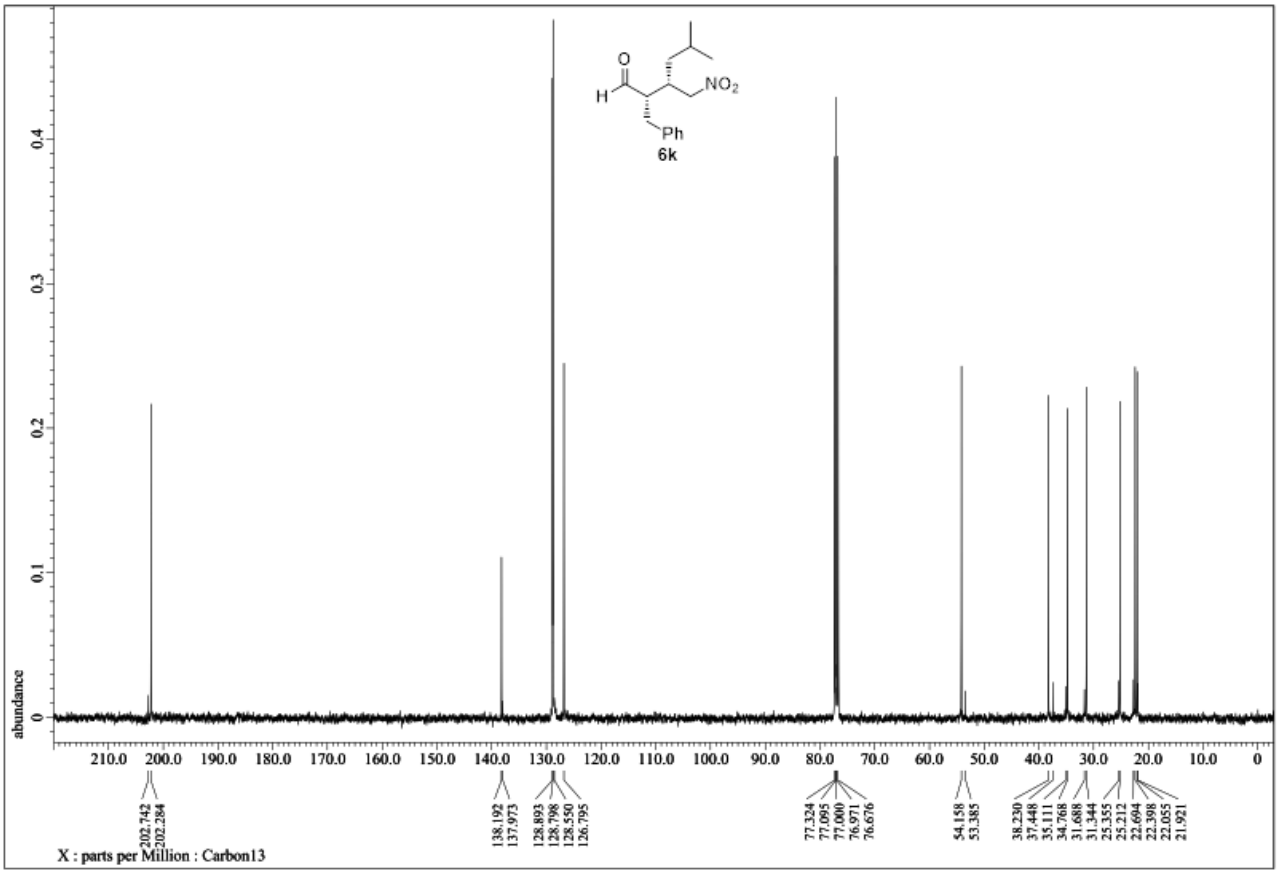

Ph
O
H
NO2
6i
abundance
X : parts per Million : Proton

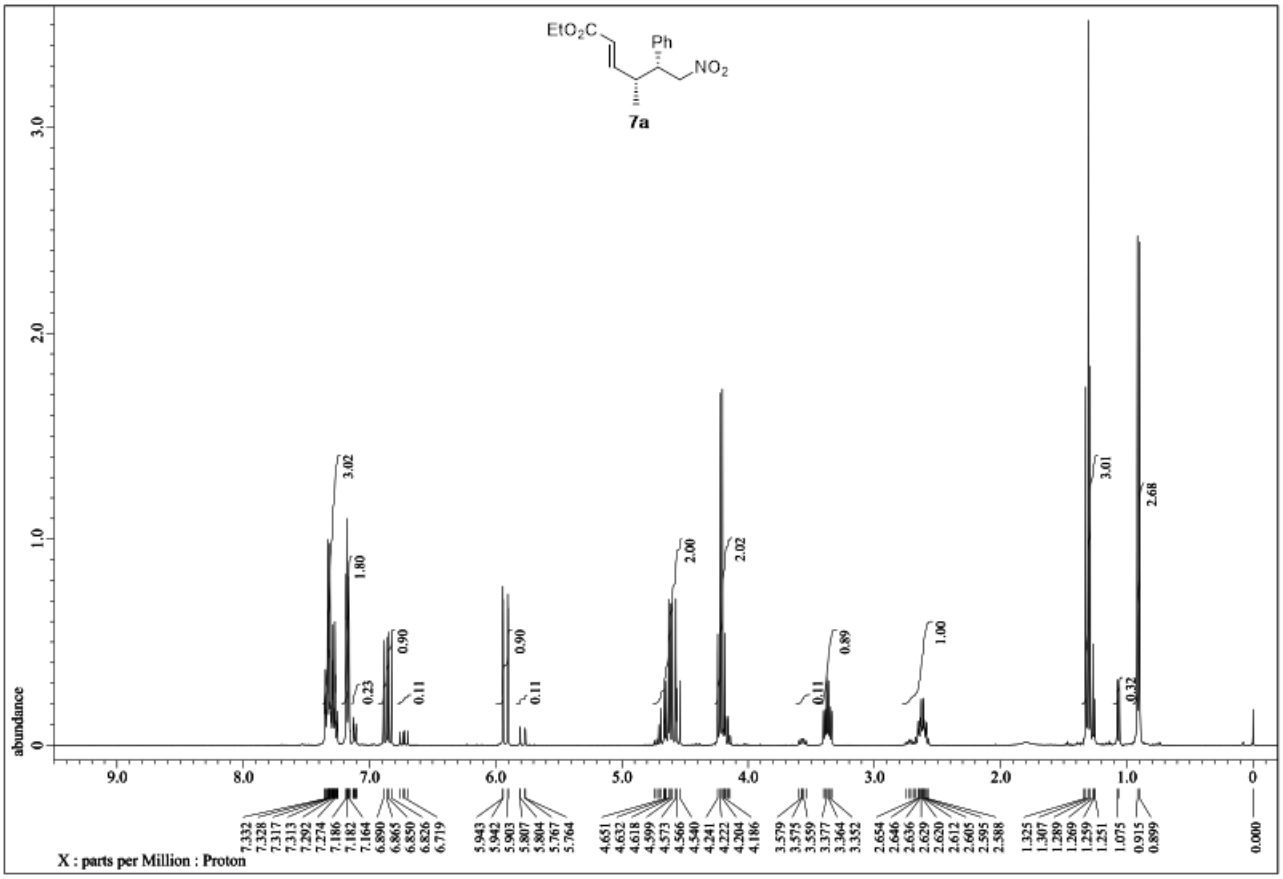

Ph
O
H
NO2
6i
abundance
X : parts per Million : Carbon13

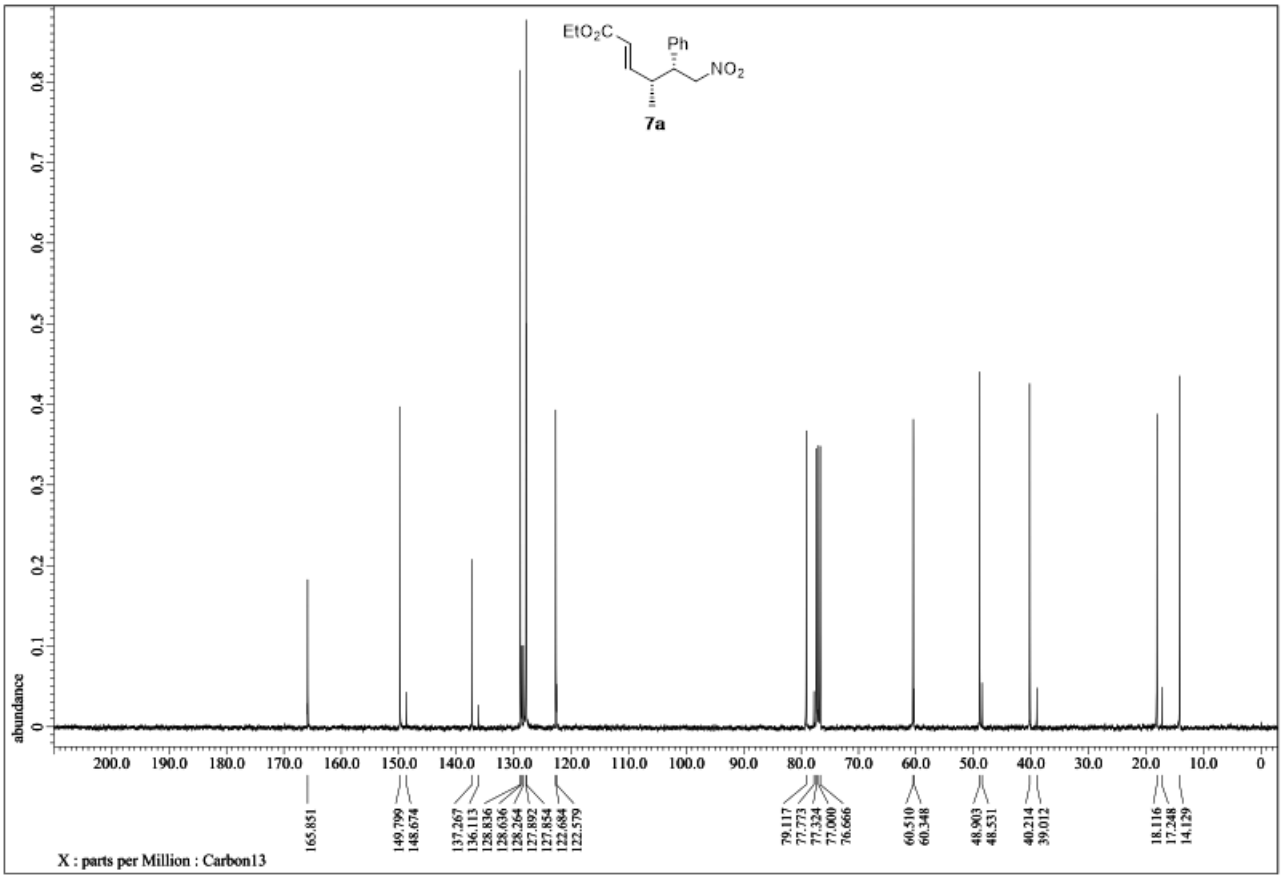

O
H
NO2
Ph
6j
abundance
X : parts per Million : Proton
9.696
9.694
9.677
7.323
7.305
7.285
7.252
7.244
7.225
7.206
7.189
7.161
4.505
4.490
4.471
4.454
4.439
4.422
4.410
4.392
4.377
4.360
4.344
3.091
3.069
3.056
3.034
2.867
2.858
2.770
2.755
2.735
2.721
1.374
1.355
1.347
1.340
1.333
1.330
1.316
0.925
0.908
0.891
0.872
0.078
0.000
0.15
1.00
3.76
2.37
1.17
2.14
4.98
3.73

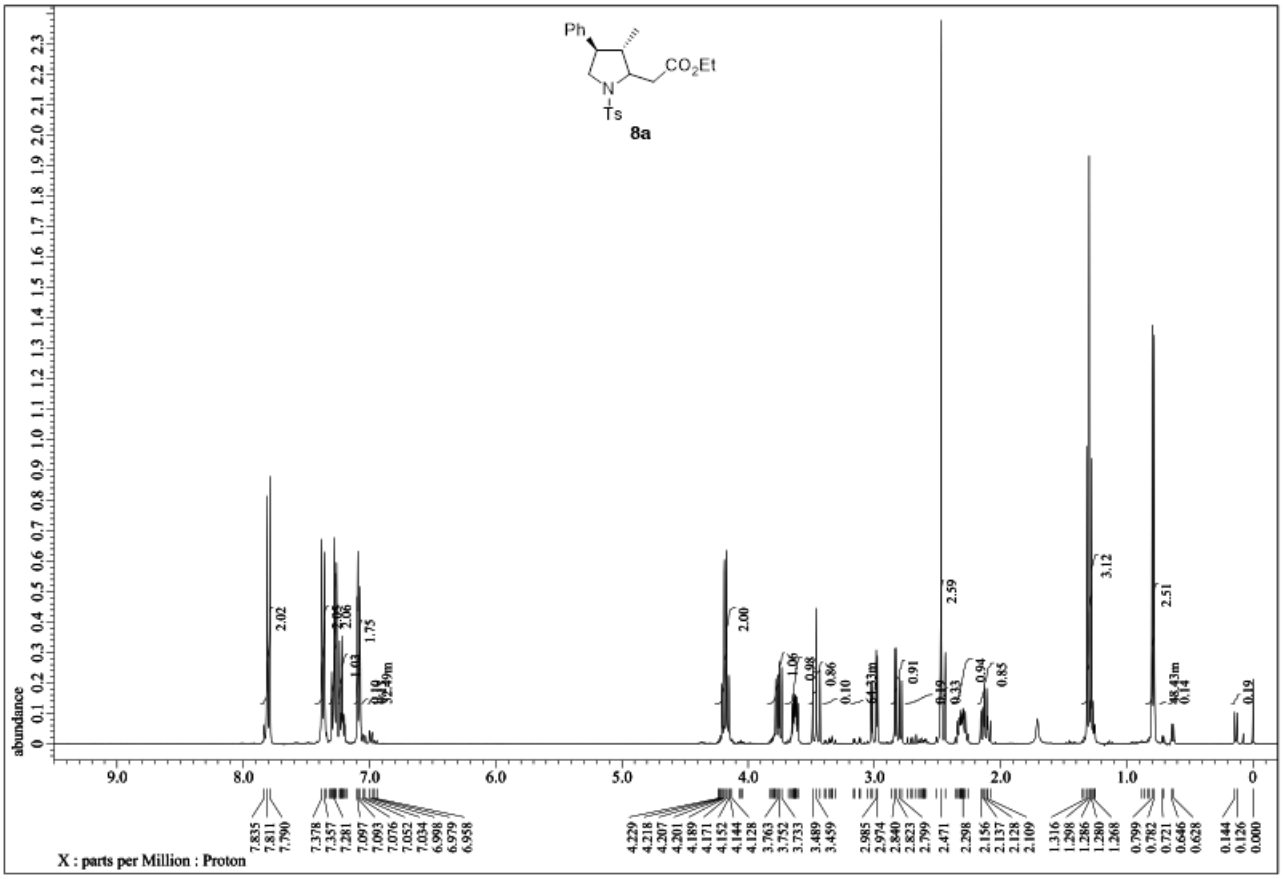

O
H
NO2
Ph
6j
abundance
X : parts per Million : Carbon13
202.713
202.360
138.145
137.973
128.836
128.760
128.455
126.747
77.334
77.000
76.876
76.676
54.034
53.462
37.009
36.723
31.812
31.335
31.268
30.667
20.290
20.100
13.748

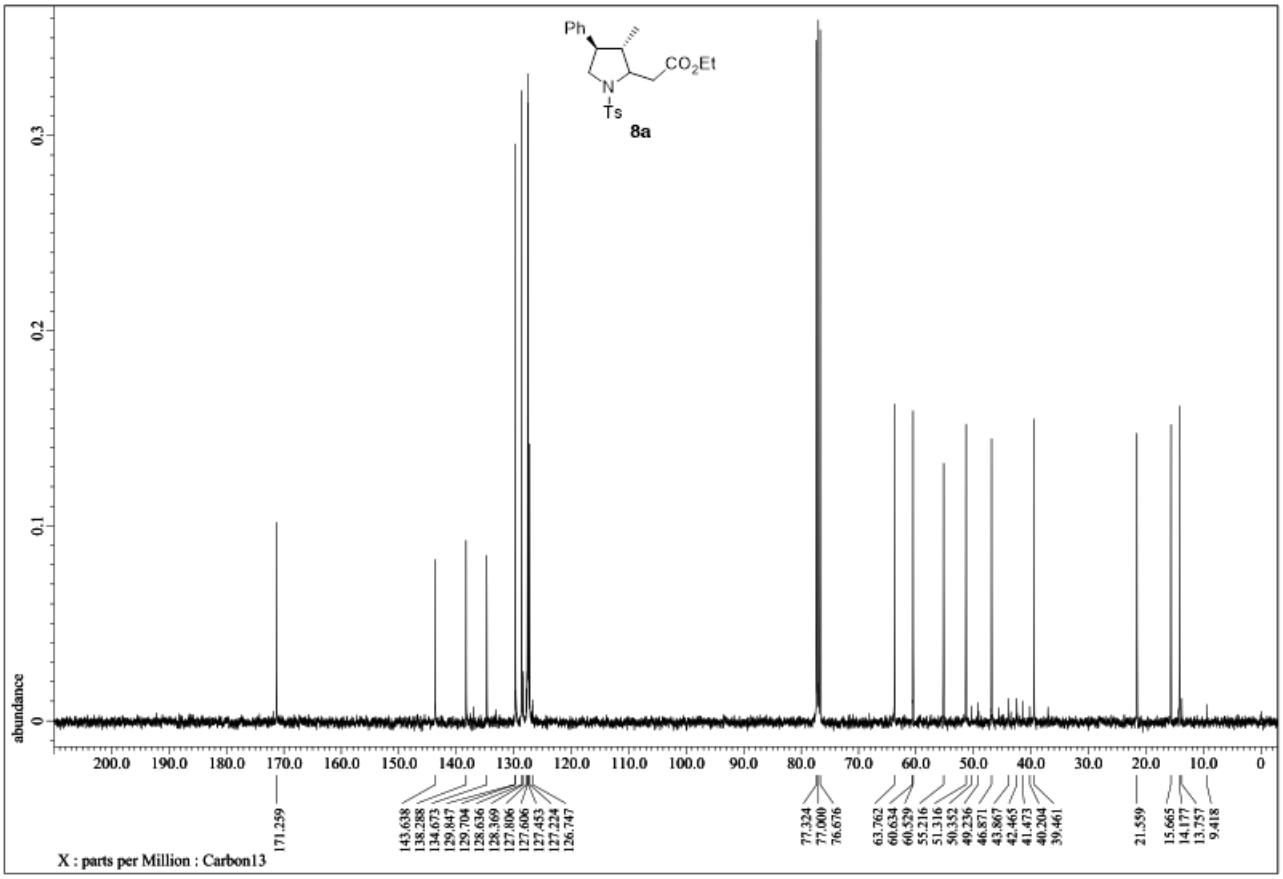

O
H
NO2
Ph
6k
abundance
X : parts per Million : Proton

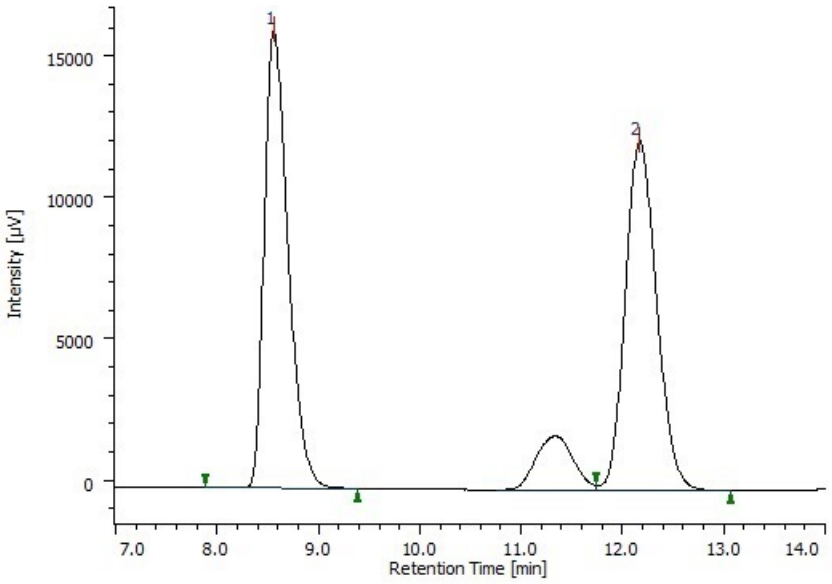

O
H
NO2
Ph
6k
abundance
X : parts per Million : Carbon13

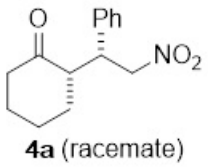

EtO2C
Ph
NO2
7a
abundance
X : parts per Million : Proton


EtO2C
Ph
NO2
7a
abundance
X : parts per Million : Carbon13


Ph
CO2Et
N
Ts
8a
abundance
X : parts per Million : Proton

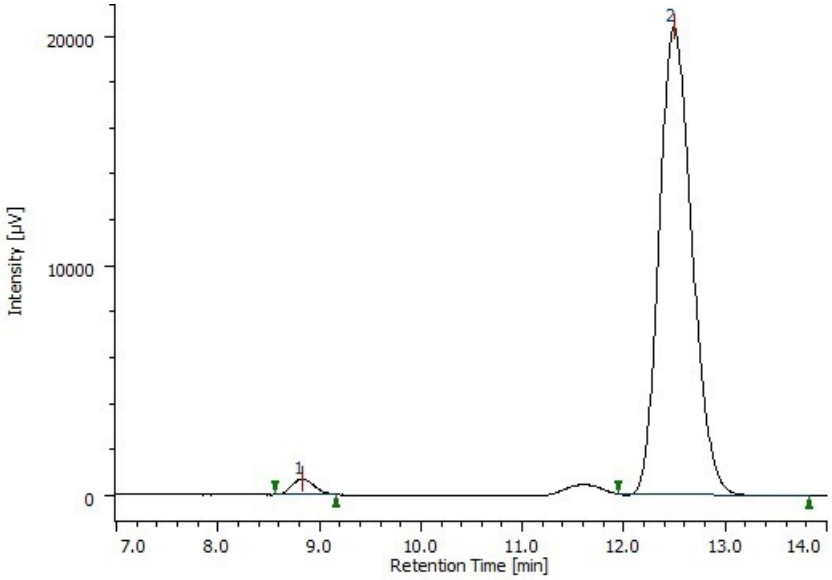

Ph
CO2Et
N
Ts
8a
abundance
X : parts per Million : Carbon13

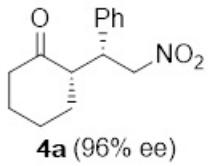



**4a** (racemate)

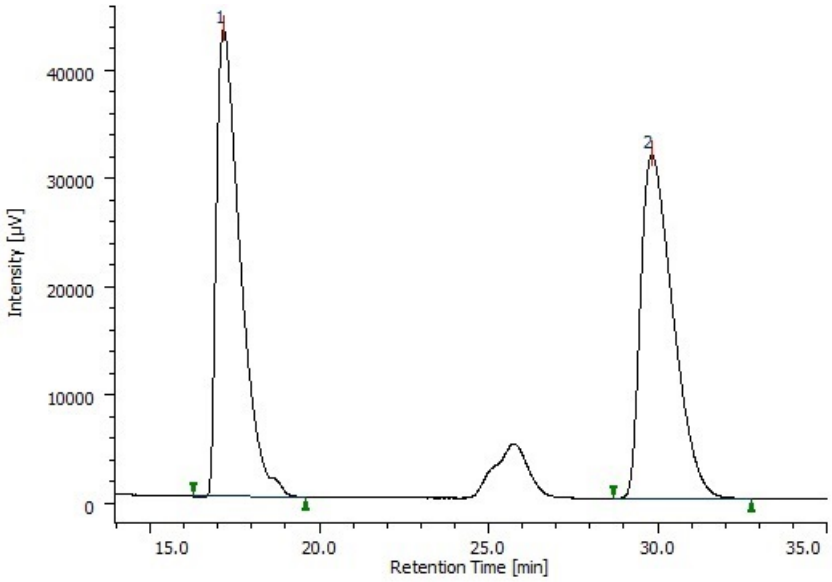
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 8.558 | 262858 | 16171 | 49.9 |
| 2 | 12.158 | 263914 | 12310 | 50.1 |
| Total | | 526772 | 28481 | 100.000 |

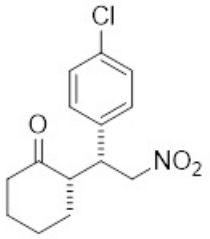



**4a** (96% ee)

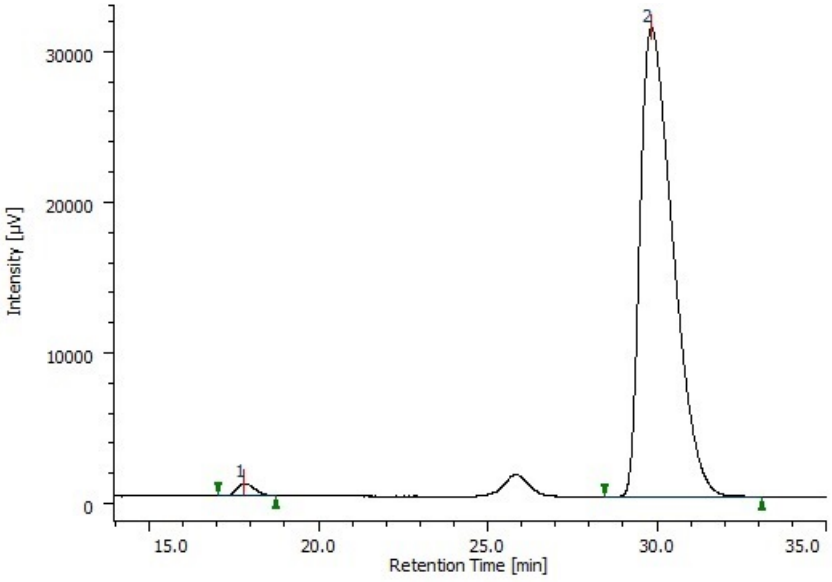
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 8.825 | 10340 | 683 | 2.227 |
| 2 | 12.483 | 454034 | 20304 | 97.773 |
| Total | | 464374 | 20987 | 100.000 |

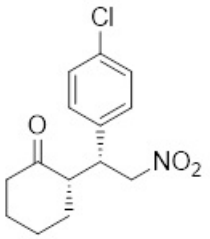



**4b** (racemate)

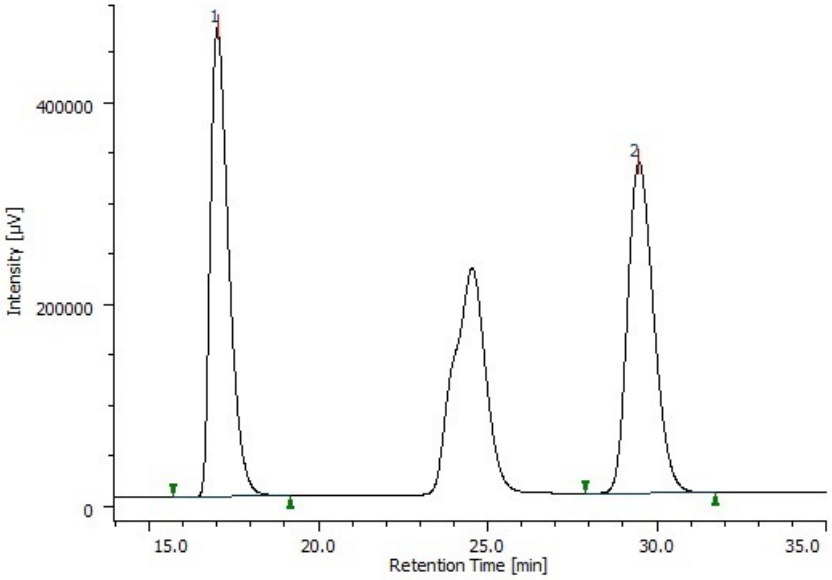
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.167 | 2110973 | 43162 | 50.14 |
| 2 | 29.792 | 2099217 | 31684 | 49.86 |
| Total | | 4210190 | 74846 | 100.000 |

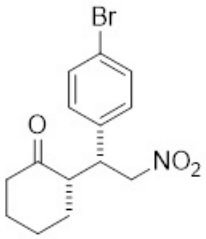



**4b** (97% ee)

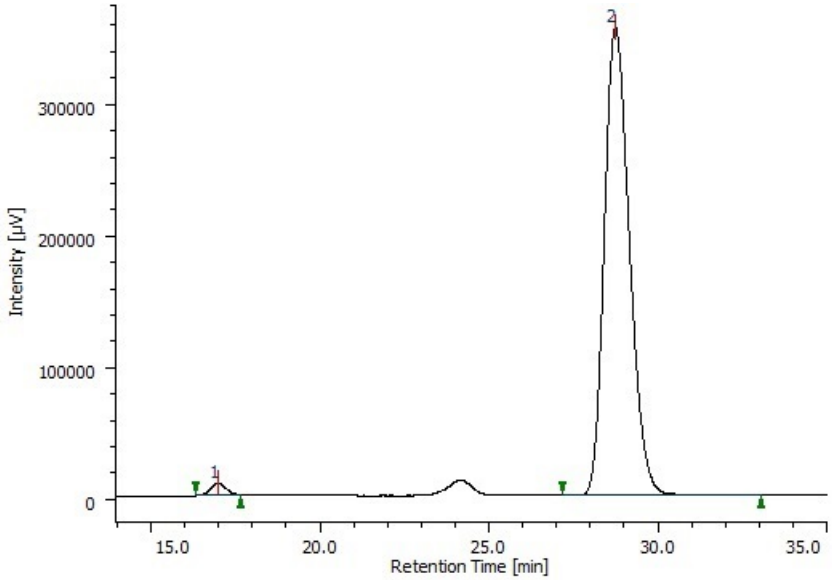
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.800 | 30314 | 821 | 1.431 |
| 2 | 29.808 | 2087889 | 31067 | 98.569 |
| Total | | 2118203 | 31888 | 100.000 |

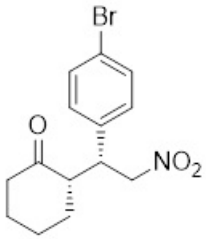



**4c** (racemate)

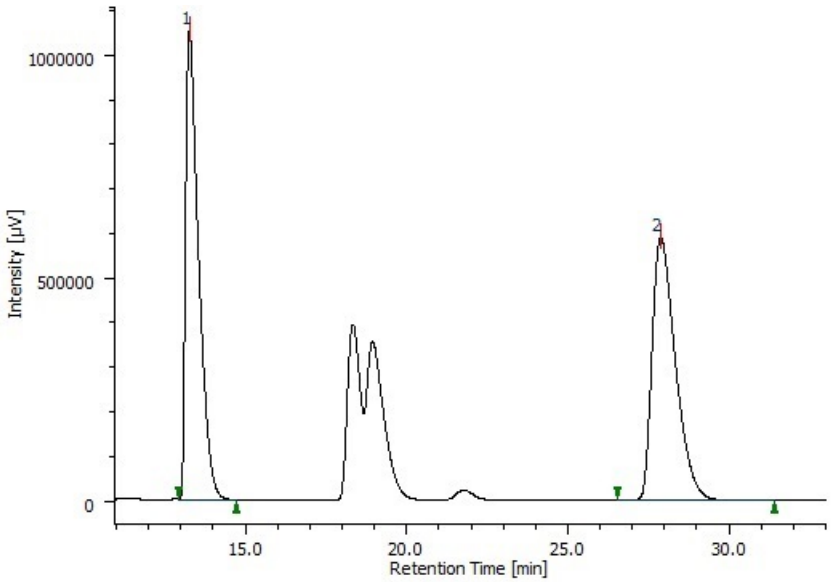
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.008 | 17470360 | 463794 | 50.088 |
| 2 | 29.442 | 17408781 | 326818 | 49.912 |
| Total | | 34879141 | 790612 | 100.000 |

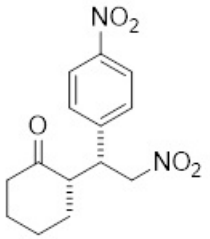



**4c** (97% ee)

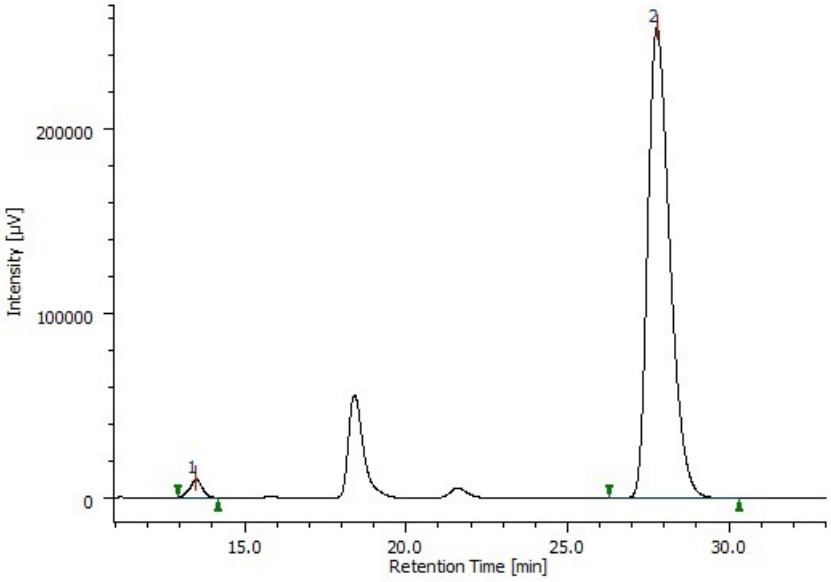
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 16.967 | 290623 | 9128 | 1.562 |
| 2 | 28.708 | 18310933 | 354579 | 98.438 |
| Total | | 18601556 | 363707 | 100.000 |

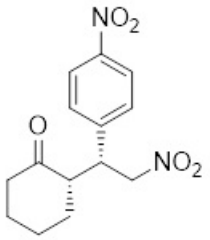



**4d** (racemate)

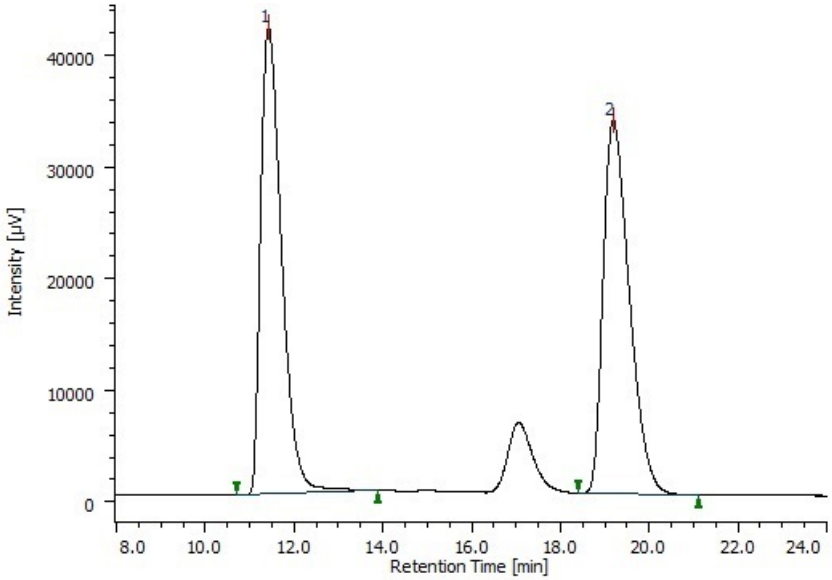
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 13.267 | 29485300 | 1051888 | 49.912 |
| 2 | 27.850 | 29588792 | 588293 | 50.088 |
| Total | | 59074092 | 1640181 | 100.000 |

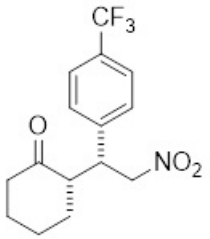



**4d** (96% ee)

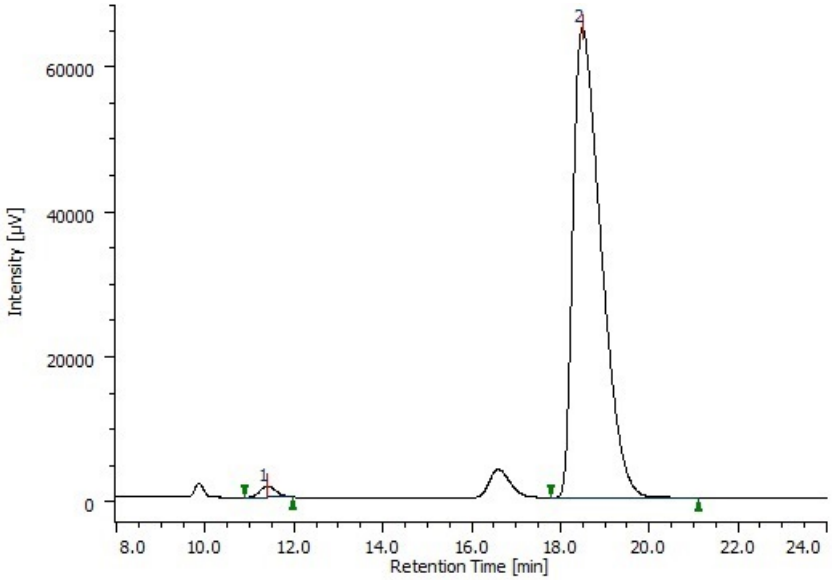
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 13.500 | 264816 | 9850 | 2.155 |
| 2 | 27.733 | 12021987 | 254133 | 97.845 |
| Total | | 12286803 | 263983 | 100.000 |

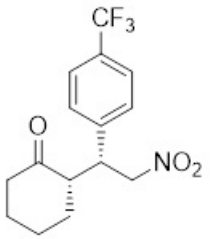



**4e** (racemate)

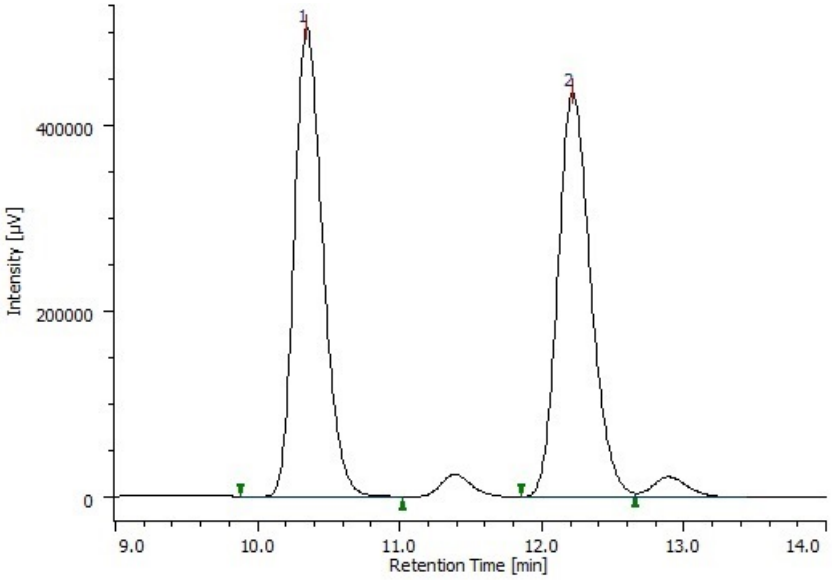
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 11.417 | 1367791 | 41690 | 50.063 |
| 2 | 19.167 | 1364334 | 33352 | 49.937 |
| Total | | 2732125 | 75042 | 100.000 |

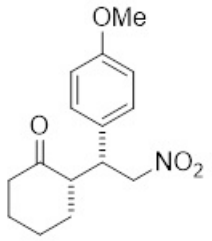



**4e** (97% ee)

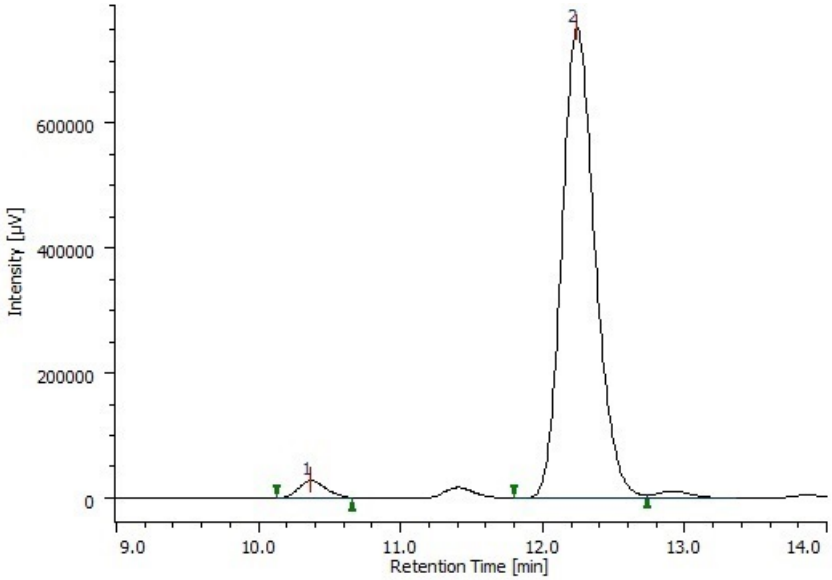
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 11.400 | 38606 | 1530 | 1.346 |
| 2 | 18.475 | 2830572 | 64661 | 98.654 |
| Total | | 2869178 | 66191 | 100.000 |

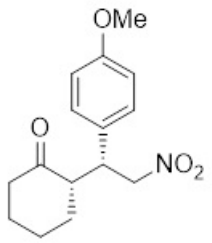



**4f** (racemate)

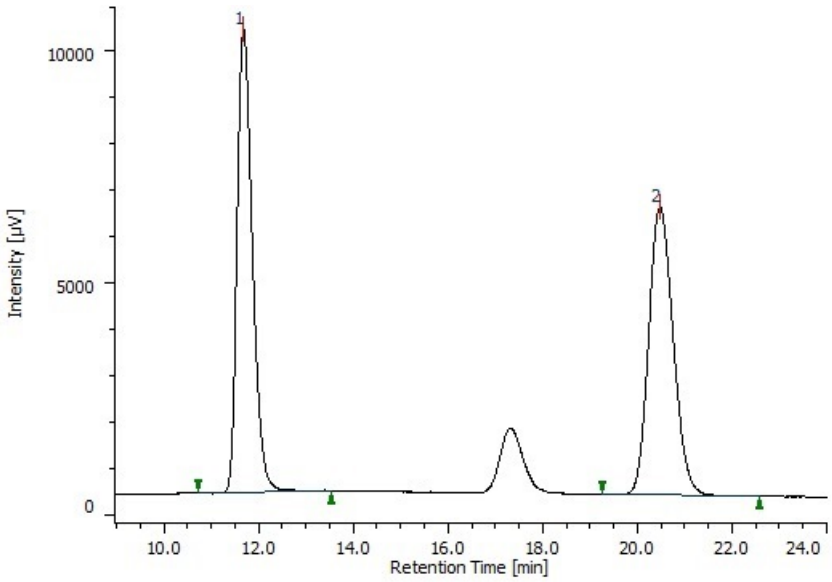
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.342 | 6994803 | 503853 | 50.058 |
| 2 | 12.208 | 6978544 | 434193 | 49.942 |
| Total | | 13973347 | 938046 | 100.000 |

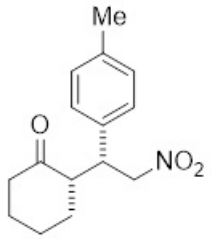



**4f** (94% ee)

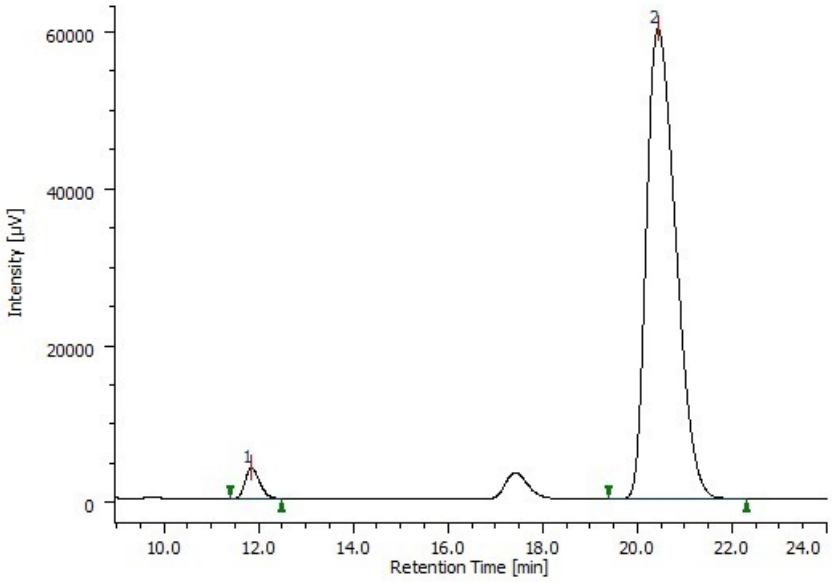
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.367 | 367411 | 27563 | 2.925 |
| 2 | 12.233 | 12193580 | 752017 | 97.075 |
| Total | | 12560991 | 779580 | 100.000 |

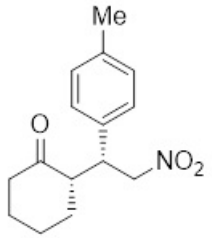



**4g** (racemate)

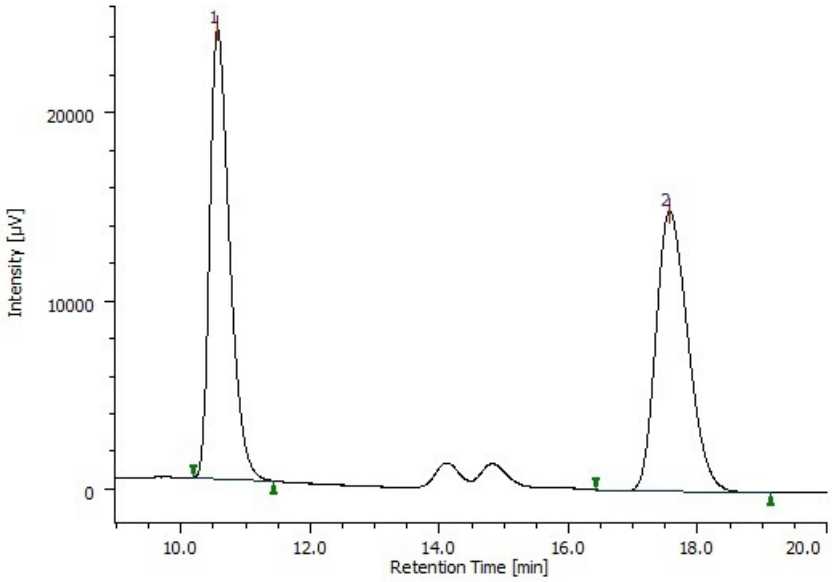
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 11.683 | 221640 | 9925 | 50.158 |
| 2 | 20.458 | 220246 | 6165 | 49.842 |
| Total | | 441886 | 16090 | 100.000 |

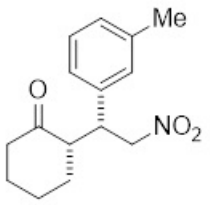



**4g** (94% ee)

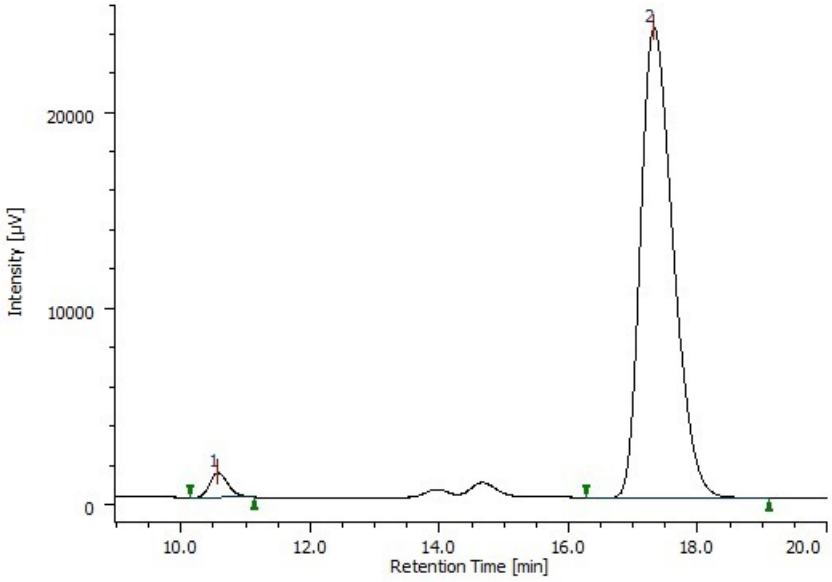
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 11.842 | 82270 | 3886 | 3.111 |
| 2 | 20.417 | 2561967 | 59730 | 96.889 |
| Total | | 2644237 | 63616 | 100.000 |

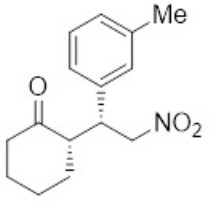



**4h** (racemate)

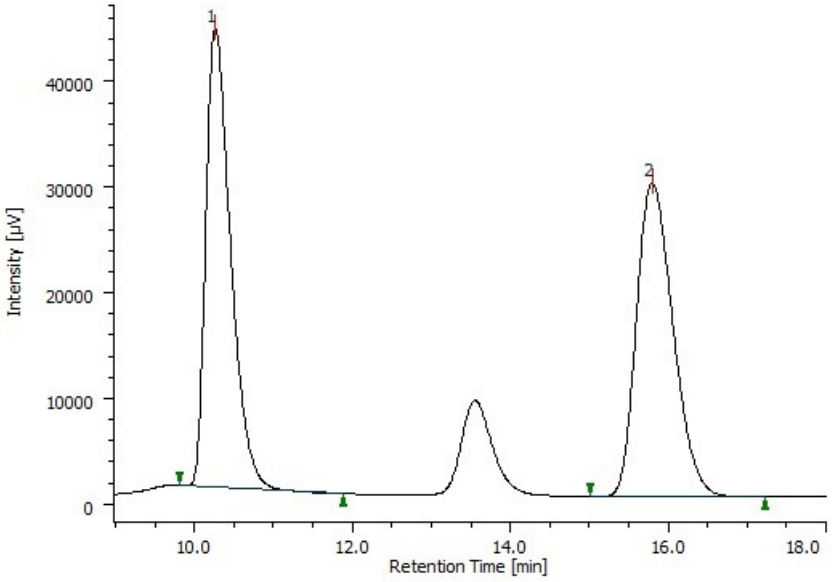
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.567 | 508500 | 23824 | 50.082 |
| 2 | 17.550 | 506830 | 14820 | 49.918 |
| Total | | 1015330 | 38644 | 100.000 |

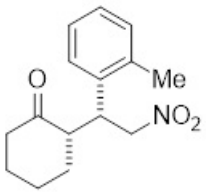



**4h** (94% ee)

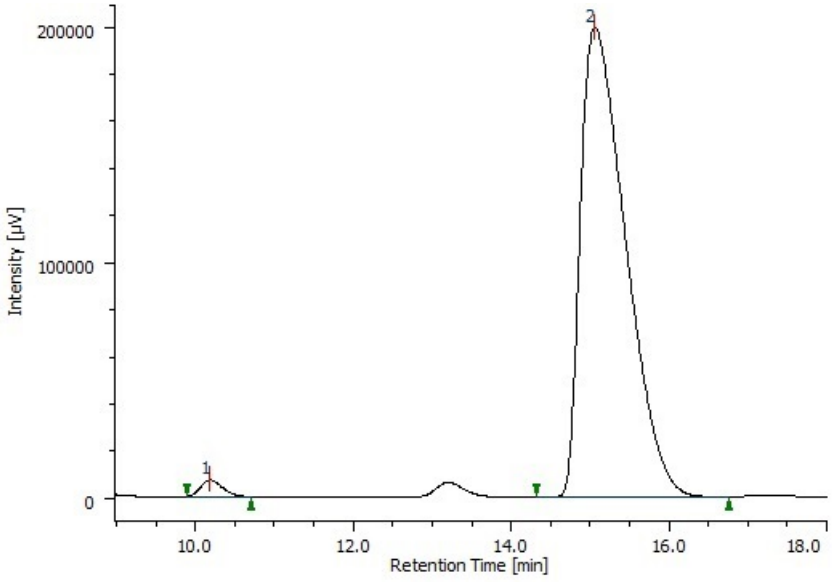
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.567 | 25229 | 1254 | 2.916 |
| 2 | 17.308 | 839965 | 23903 | 97.084 |
| Total | | 865194 | 25157 | 100.000 |

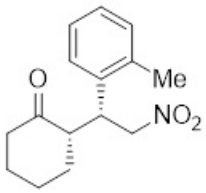



**4i** (racemate)

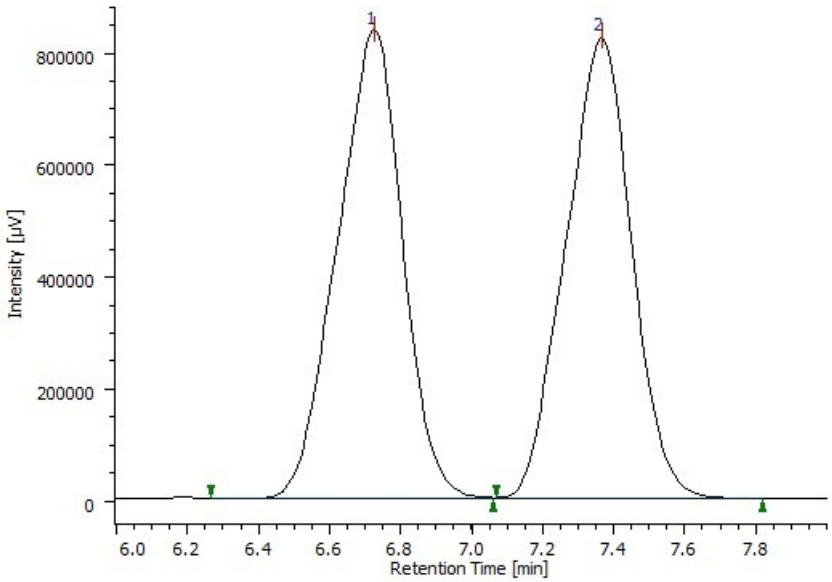
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.267 | 945766 | 43403 | 49.849 |
| 2 | 15.783 | 951496 | 29645 | 50.151 |
| Total | | 1897262 | 73048 | 100.000 |

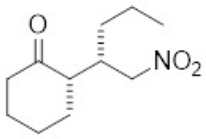



**4i** (97% ee)

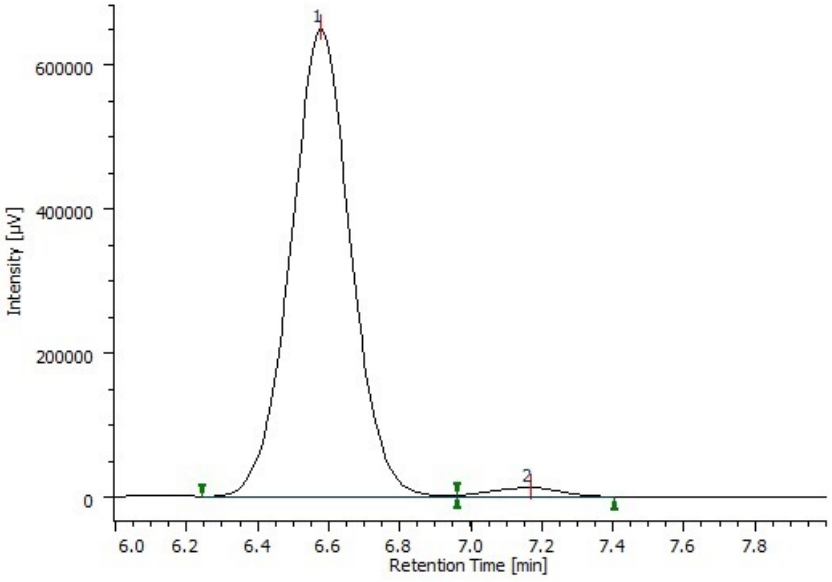
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.183 | 133584 | 6987 | 1.671 |
| 2 | 15.050 | 7860579 | 198655 | 98.329 |
| Total | | 7994163 | 205642 | 100.000 |

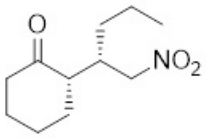



**4j** (racemate)

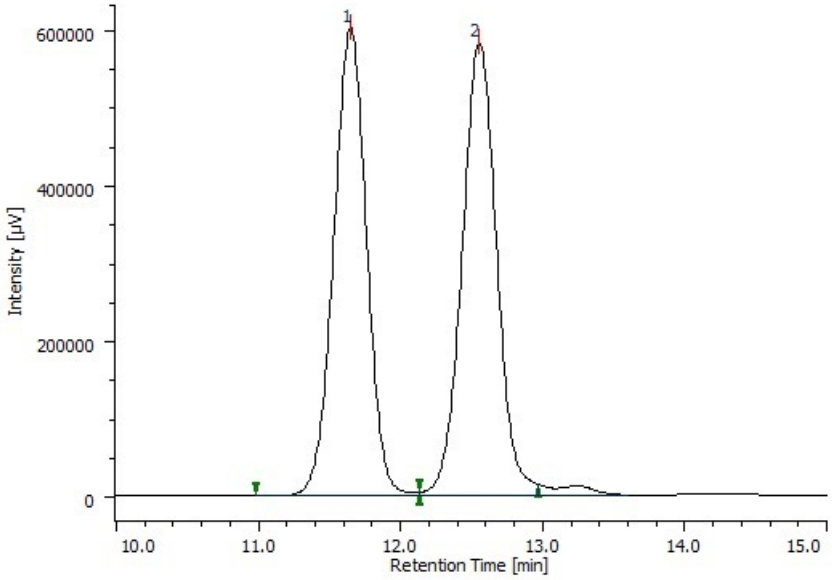
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 6.725 | 10559430 | 834753 | 50.026 |
| 2 | 7.367 | 10548643 | 821374 | 49.974 |
| Total | | 21108073 | 1656127 | 100.000 |

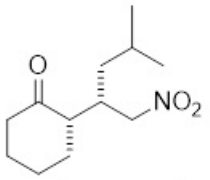



**4j** (96% ee)

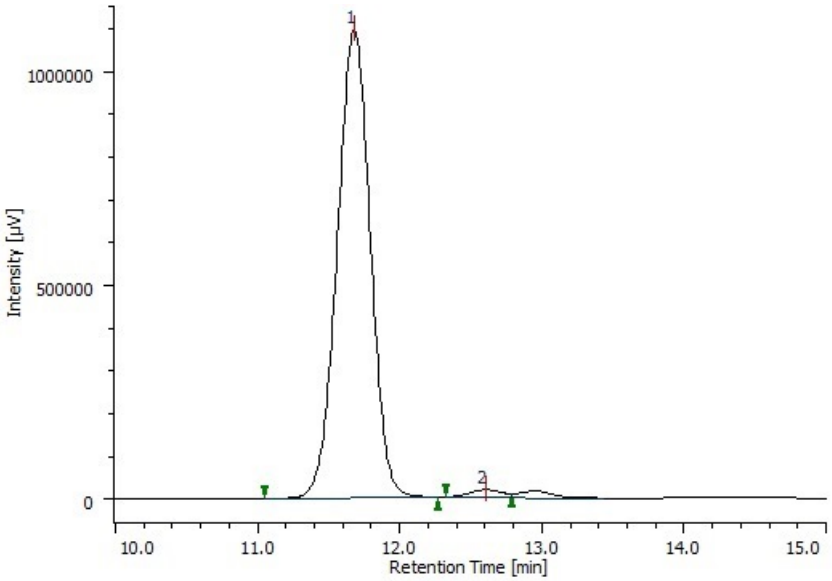
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 6.575 | 7585766 | 649886 | 97.834 |
| 2 | 7.167 | 167953 | 12553 | 2.166 |
| Total | | 7753719 | 662439 | 100.000 |

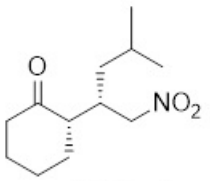



**4k** (racemate)

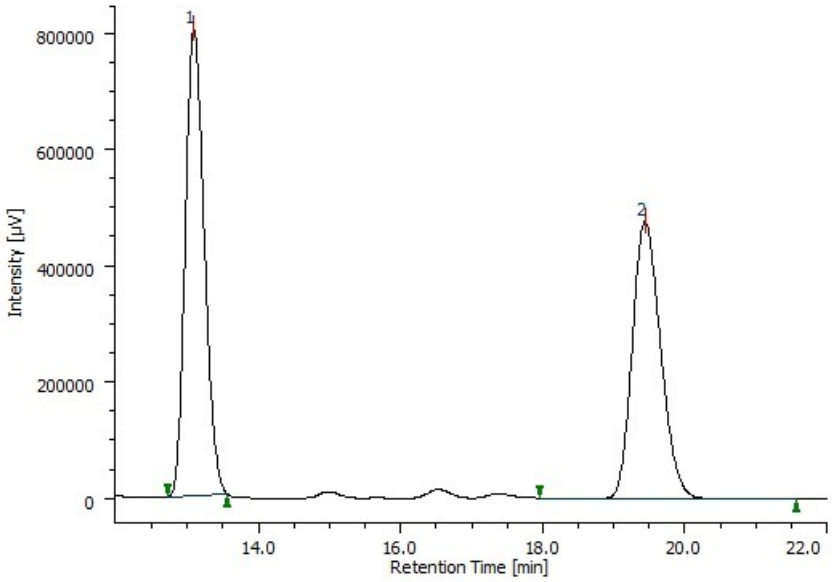
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 11.642 | 9600346 | 599300 | 49.61 |
| 2 | 12.550 | 9751431 | 580322 | 50.39 |
| Total | | 19351777 | 1179622 | 100.000 |

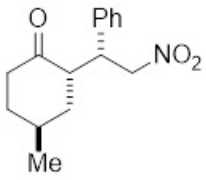



**4k** (97% ee)

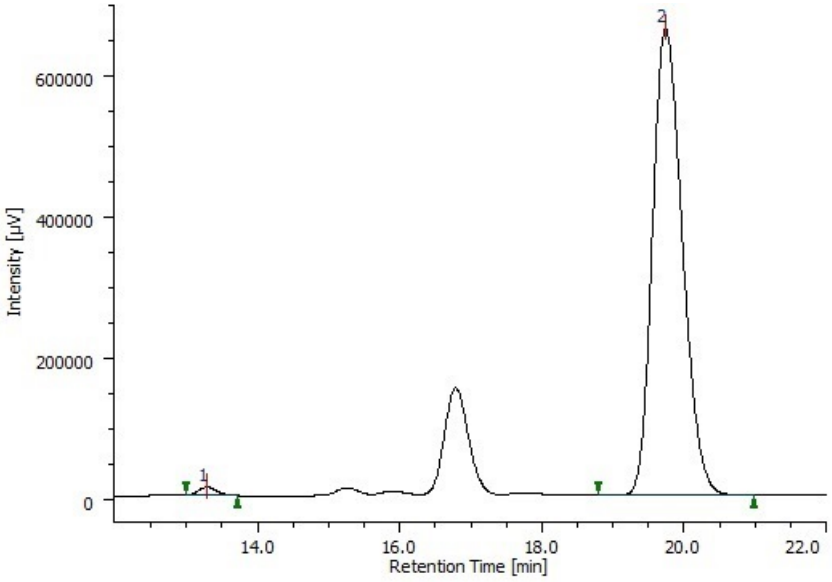
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 11.675 | 17592960 | 1094361 | 98.466 |
| 2 | 12.600 | 274001 | 17388 | 1.534 |
| Total | | 17866961 | 1111749 | 100.000 |

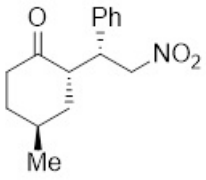



**4l** (racemate)

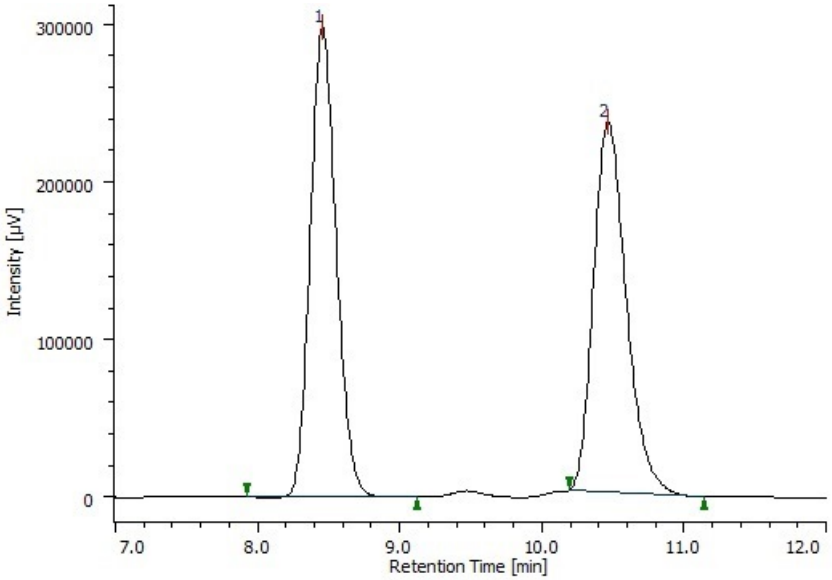
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 13.092 | 14754003 | 800303 | 52.972 |
| 2 | 19.425 | 13098681 | 474274 | 47.028 |
| Total | | 27852684 | 1274577 | 100.000 |

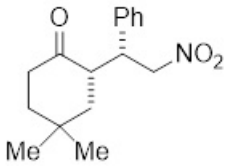



**4l** (98% ee)

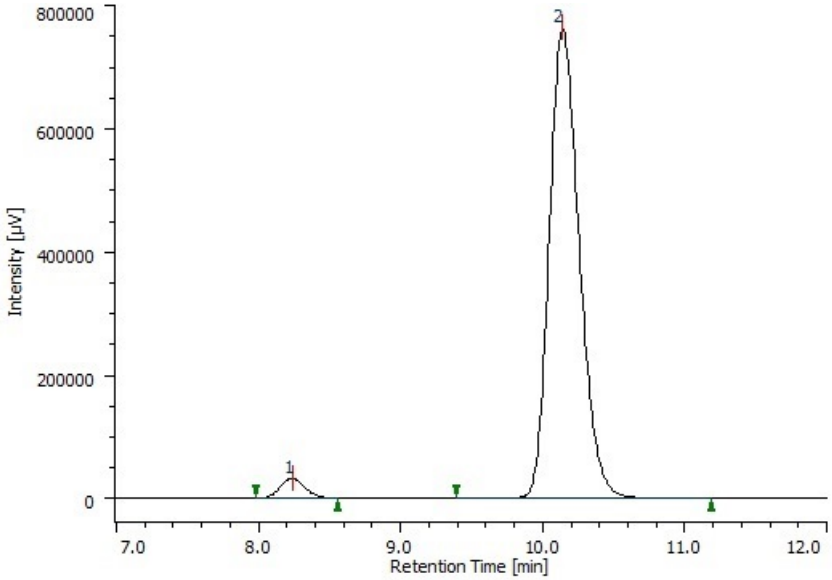
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 13.283 | 209603 | 11526 | 1.077 |
| 2 | 19.725 | 19244439 | 662182 | 98.923 |
| Total | | 19454042 | 673708 | 100.000 |

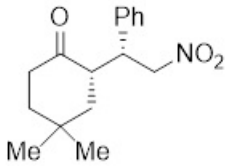



**4m** (racemate)

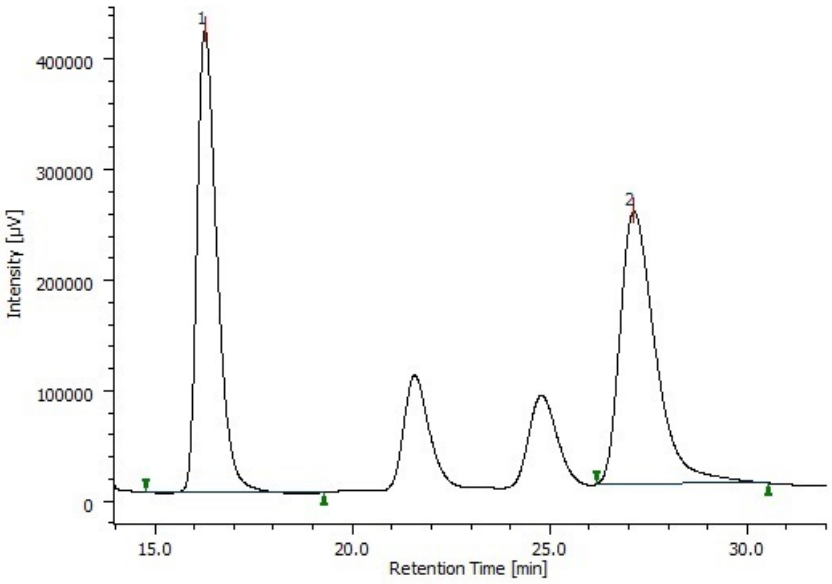
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 8.450 | 3772725 | 297158 | 50.037 |
| 2 | 10.458 | 3767208 | 234497 | 49.963 |
| Total | | 7539933 | 531655 | 100.000 |

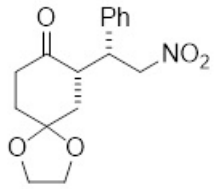



**4m** (93% ee)

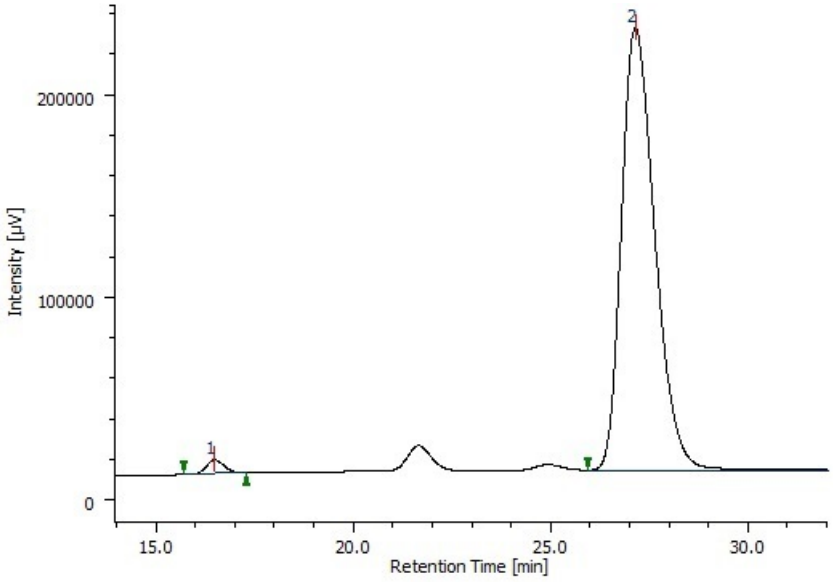
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 8.233 | 388664 | 32316 | 3.371 |
| 2 | 10.133 | 11139833 | 761843 | 96.629 |
| Total | | 11528497 | 794159 | 100.000 |

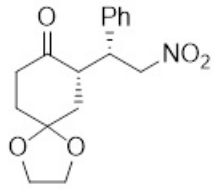



**4n** (racemate)

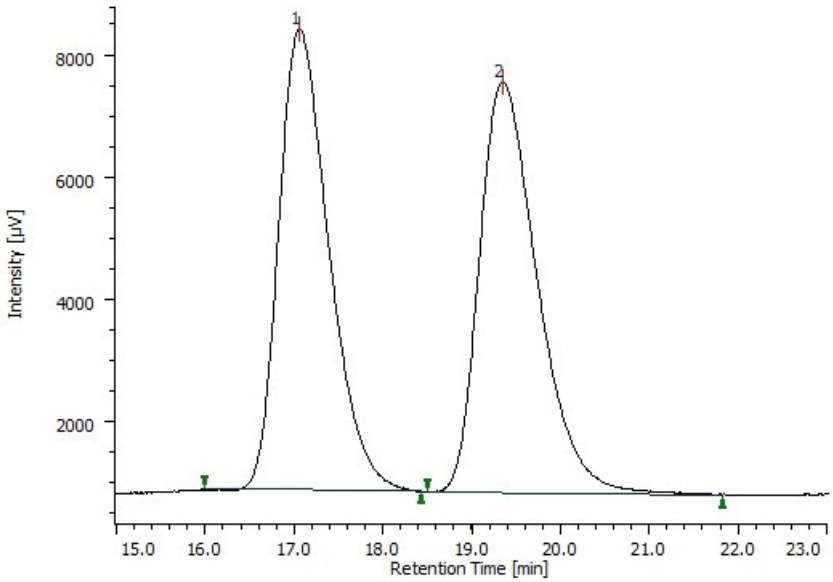
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 16.258 | 14705190 | 418005 | 48.85 |
| 2 | 27.108 | 15397743 | 246330 | 51.15 |
| Total | | 30102933 | 664335 | 100.000 |

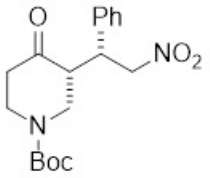



**4n** (97% ee)

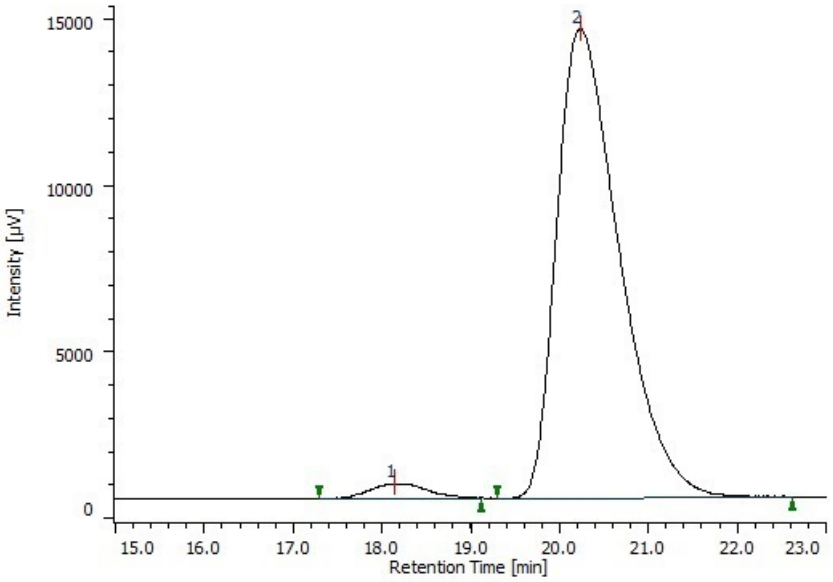
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 16.483 | 217689 | 6821 | 1.64 |
| 2 | 27.125 | 13056865 | 218090 | 98.36 |
| Total | | 13274554 | 224911 | 100.000 |

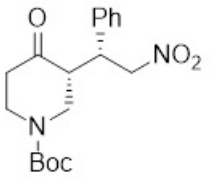



**4o** (racemate)

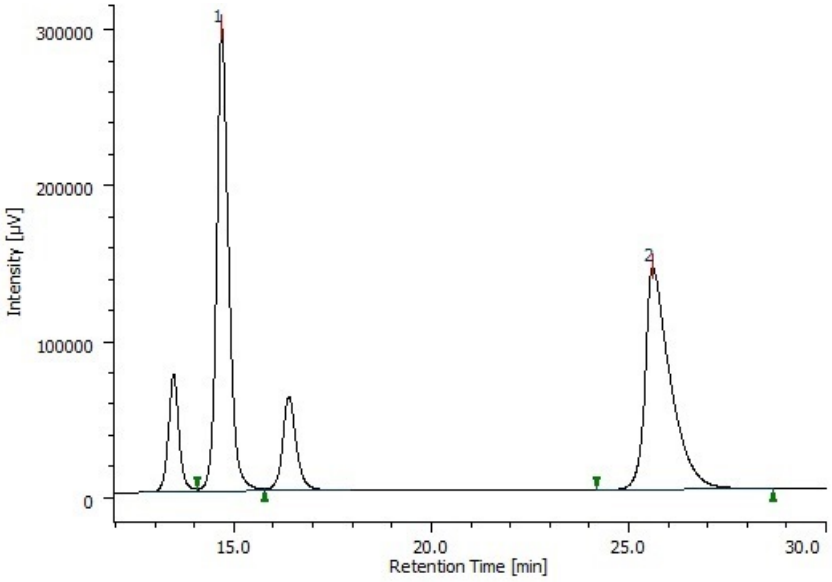
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.058 | 294855 | 7510 | 49.303 |
| 2 | 19.342 | 303196 | 6692 | 50.697 |
| Total | | 598051 | 14202 | 100.000 |

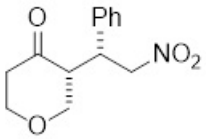



**4o** (95% ee)

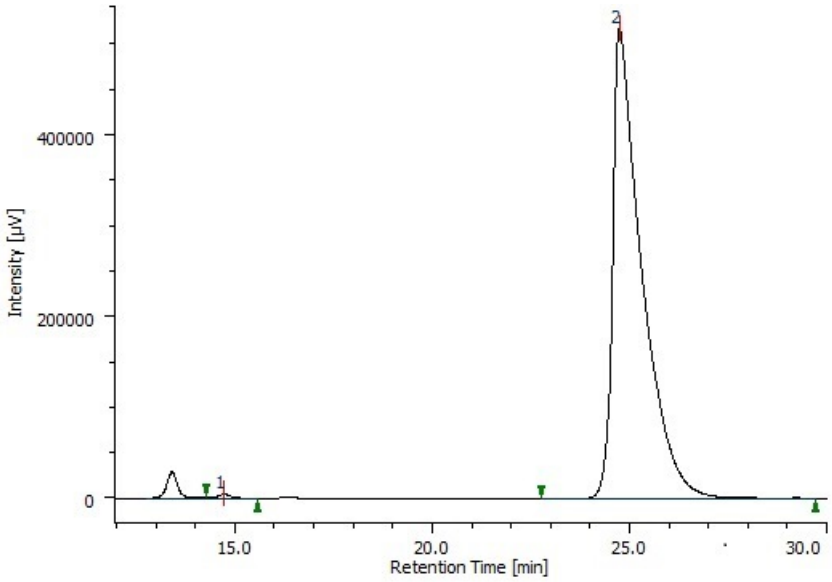
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.700 | 11343 | 264 | 2.555 |
| 2 | 19.683 | 432609 | 9292 | 97.445 |
| Total | | 443952 | 9556 | 100.000 |

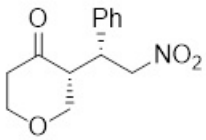



**4p** (racemate)

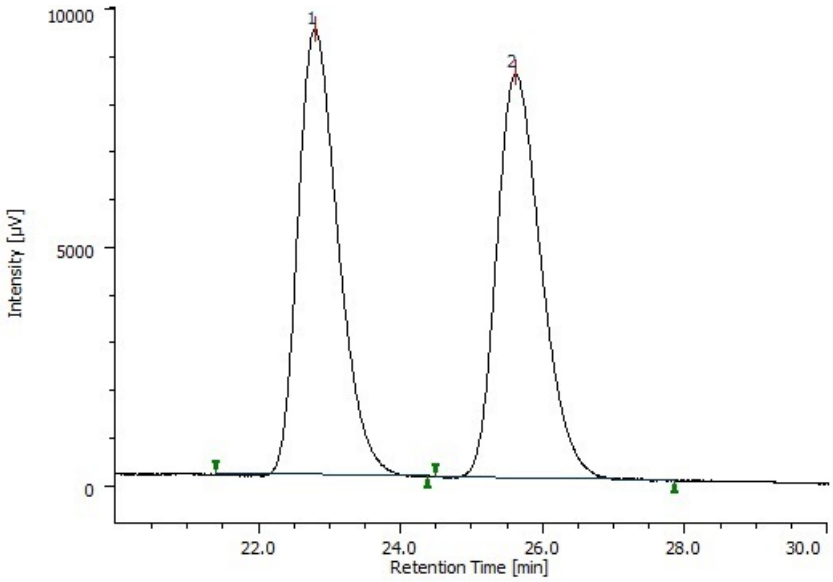
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 14.683 | 6289111 | 296387 | 50.02 |
| 2 | 25.583 | 6284054 | 142222 | 49.98 |
| Total | | 12573165 | 438609 | 100.000 |

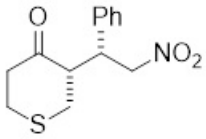



**4p** (99% ee)

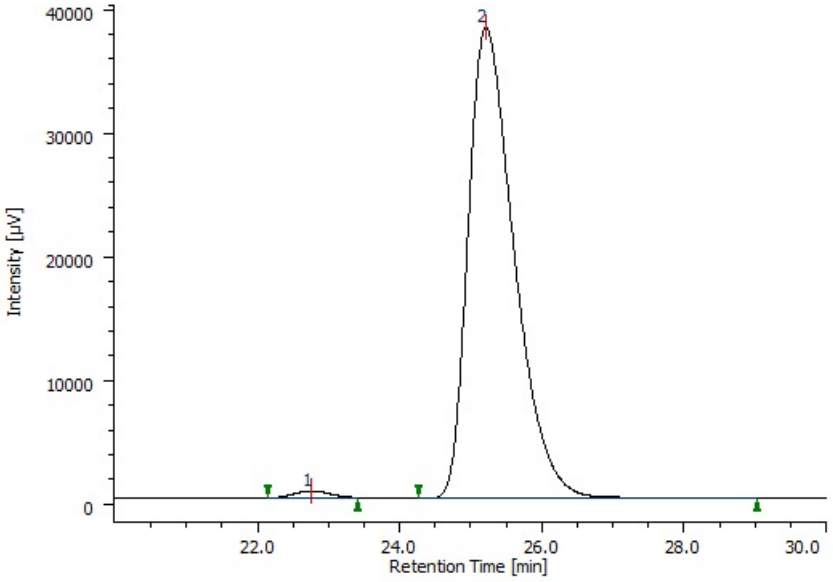
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 14.733 | 94438 | 4429 | 0.356 |
| 2 | 24.717 | 26404752 | 516202 | 99.644 |
| Total | | 26499190 | 520631 | 100.000 |

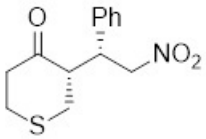



**4q** (racemate)

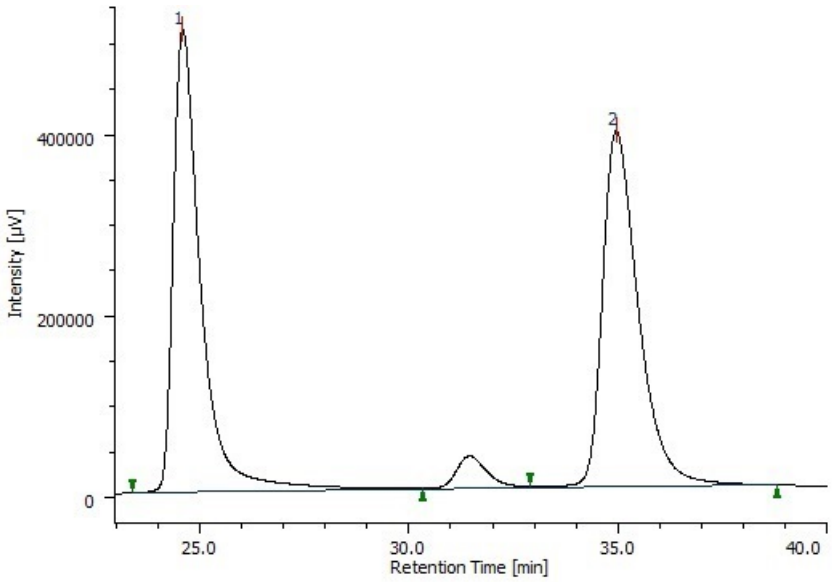
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 22.792 | 364561 | 9310 | 49.89 |
| 2 | 25.608 | 366167 | 8450 | 50.11 |
| Total | | 730728 | 17760 | 100.000 |

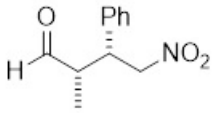



**4q** (98% ee)

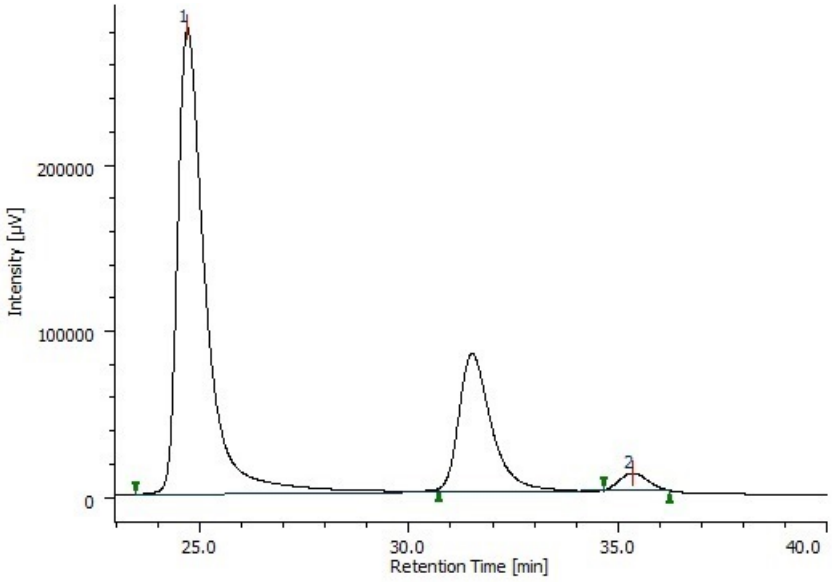
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 22.742 | 19494 | 559 | 1.13 |
| 2 | 25.208 | 1705223 | 37969 | 98.87 |
| Total | | 1724717 | 38528 | 100.000 |

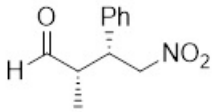



**6a** (racemate)

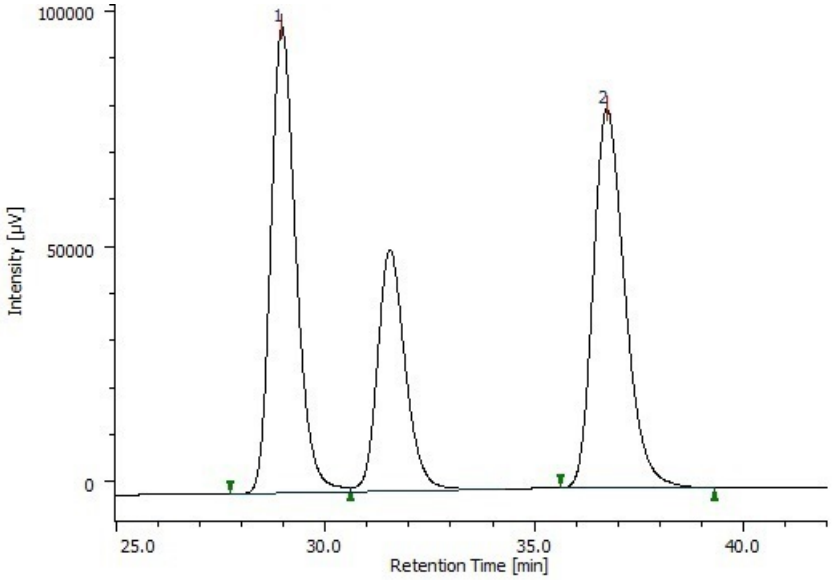
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 24.583 | 24003197 | 509747 | 49.431 |
| 2 | 34.942 | 24555702 | 394002 | 50.569 |
| Total | | 48558899 | 903749 | 100.000 |

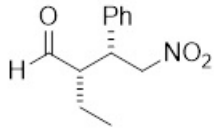



**6a** (93% ee)

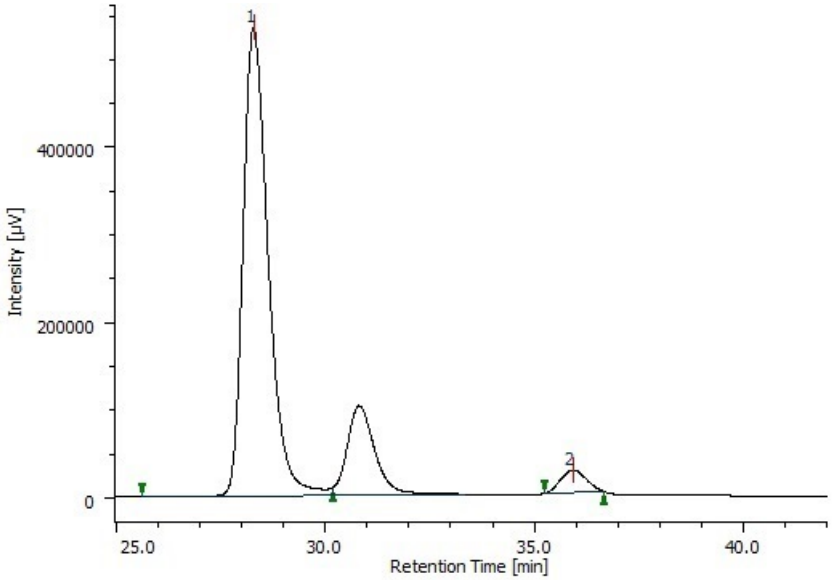
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 24.700 | 13117730 | 280108 | 96.232 |
| 2 | 35.325 | 513576 | 10617 | 3.768 |
| Total | | 13631306 | 290725 | 100.000 |

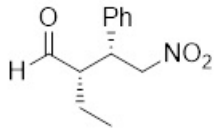



**6b** (racemate)

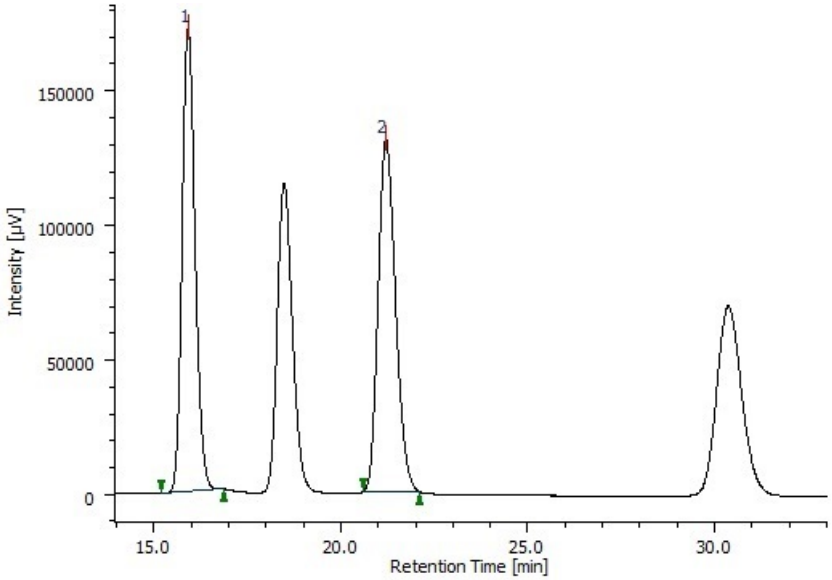
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 28.950 | 4143022 | 98976 | 49.564 |
| 2 | 36.717 | 4215994 | 80389 | 50.436 |
| Total | | 8359016 | 179365 | 100.000 |

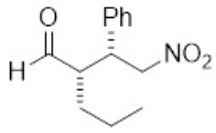



**6b** (91% ee)

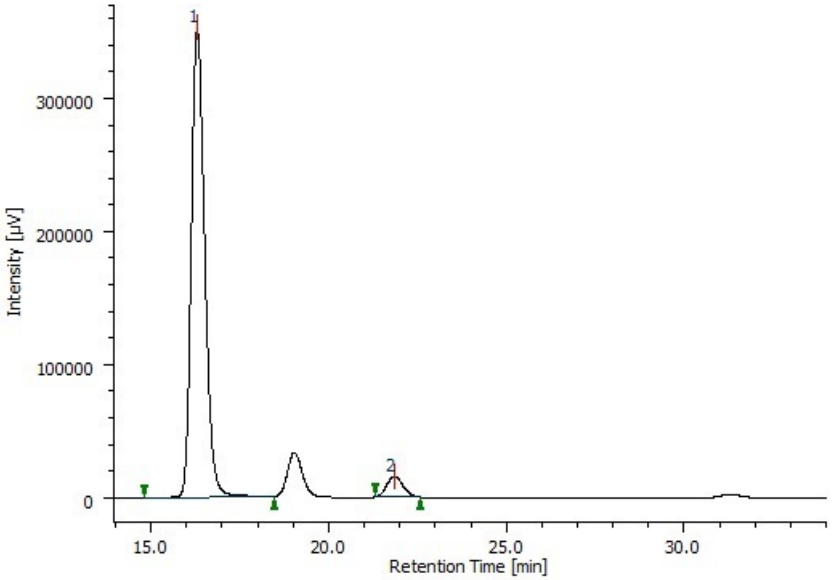
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 28.275 | 22115533 | 532346 | 95.372 |
| 2 | 35.900 | 1073247 | 25200 | 4.628 |
| Total | | 23188780 | 557546 | 100.000 |

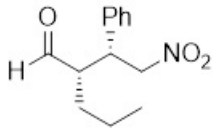



**6c** (racemate)

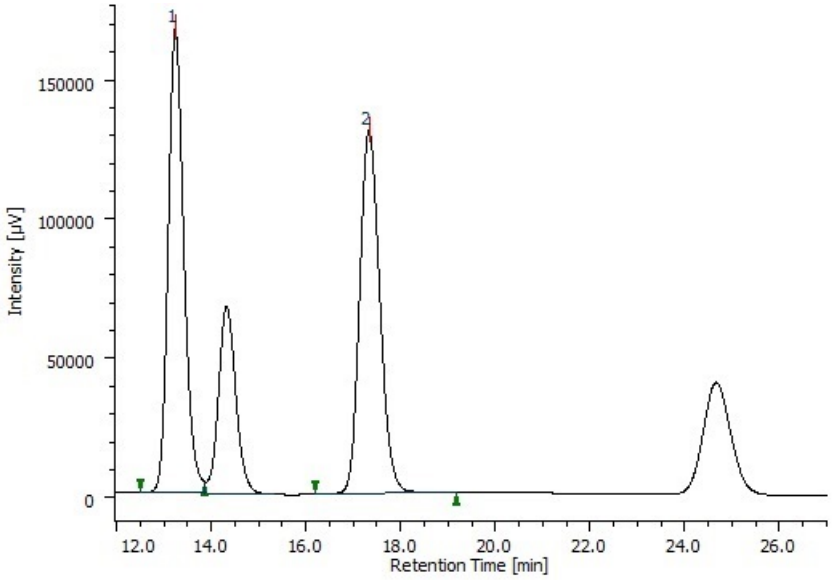
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 15.917 | 4136134 | 171818 | 49.657 |
| 2 | 21.192 | 4193319 | 130416 | 50.343 |
| Total | | 8329453 | 302234 | 100.000 |

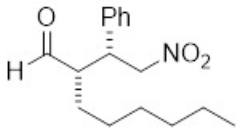



**6c** (90% ee)

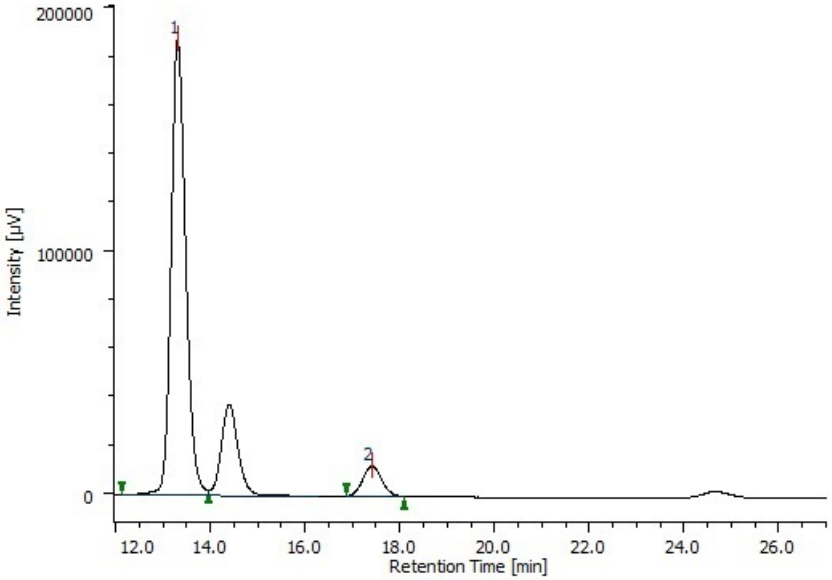
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 16.300 | 9185184 | 351761 | 94.89 |
| 2 | 21.833 | 494611 | 15550 | 5.11 |
| Total | | 9679795 | 367311 | 100.000 |

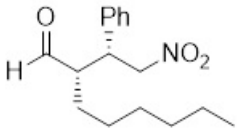



**6d** (racemate)

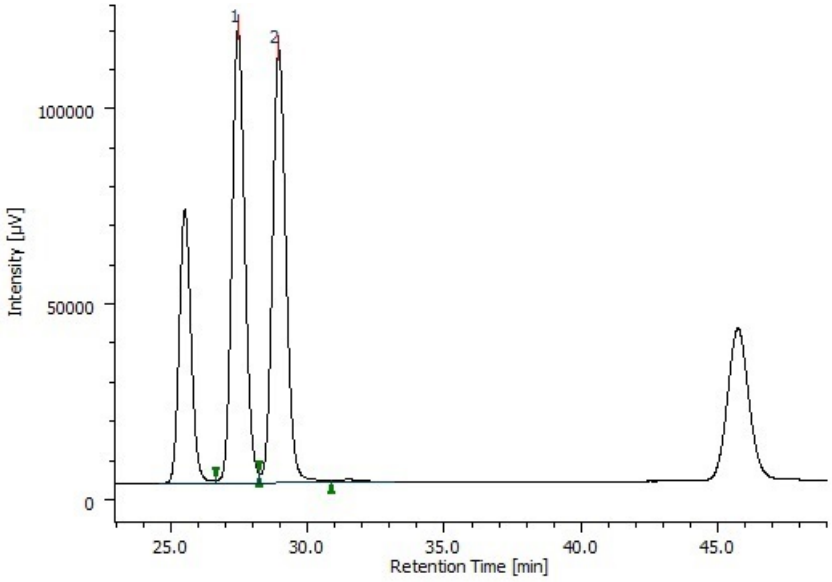
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 13.242 | 3870300 | 166832 | 50.345 |
| 2 | 17.325 | 3817220 | 130098 | 49.655 |
| Total | | 7687520 | 296930 | 100.000 |

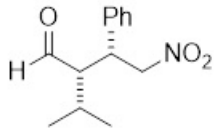



**6d** (84% ee)

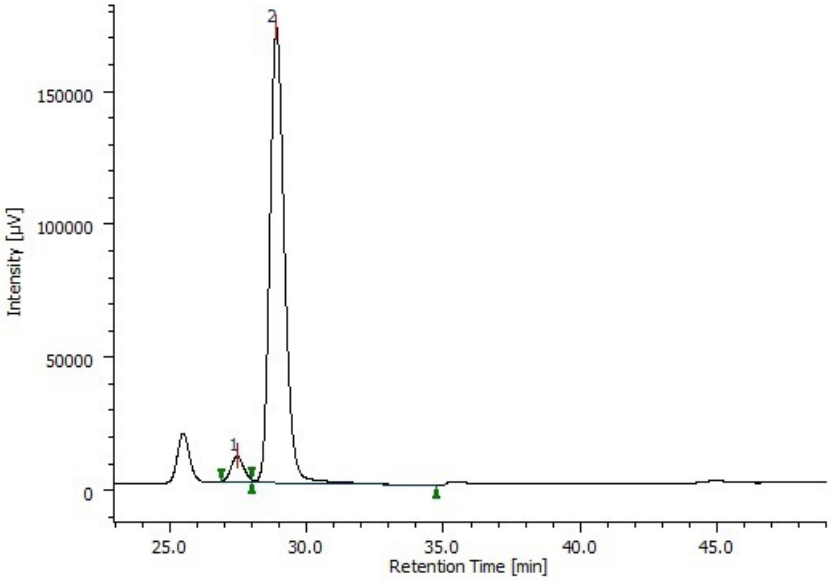
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 13.317 | 4023590 | 186883 | 92.161 |
| 2 | 17.400 | 342232 | 12329 | 7.839 |
| Total | | 4365822 | 199212 | 100.000 |

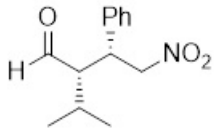



**6e** (racemate)

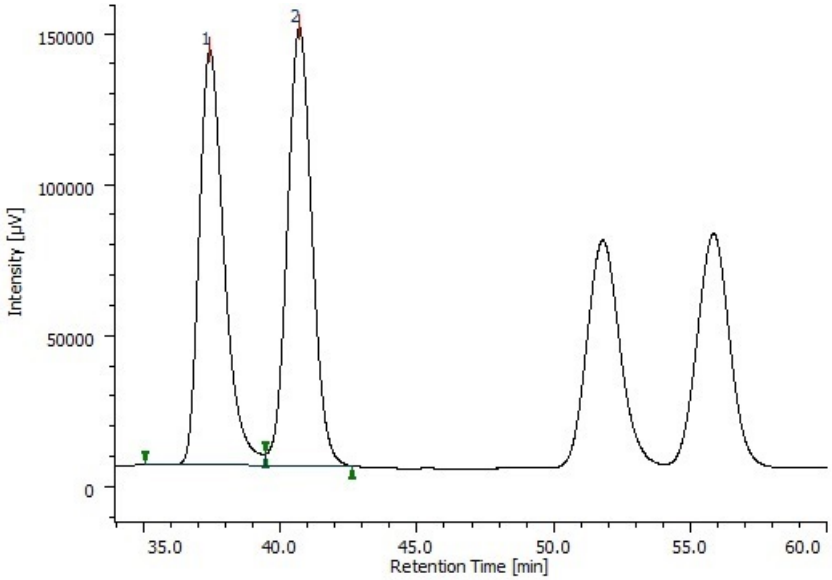
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 27.442 | 3773203 | 116206 | 49.768 |
| 2 | 28.933 | 3808450 | 110727 | 50.232 |
| Total | | 7581653 | 226933 | 100.000 |

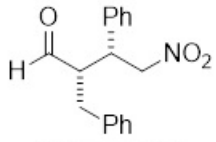



**6e** (91% ee)

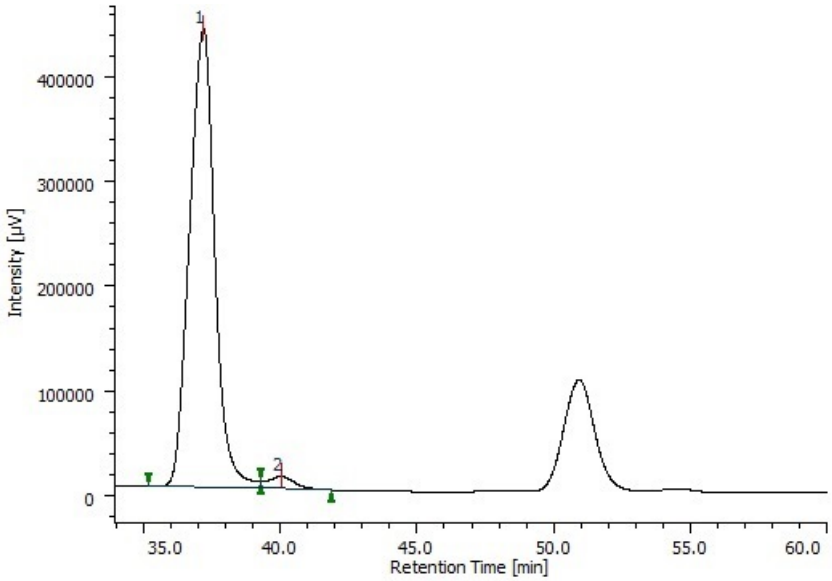
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 27.433 | 313933 | 9668 | 4.685 |
| 2 | 28.883 | 6386675 | 170749 | 95.315 |
| Total | | 6700608 | 180417 | 100.000 |

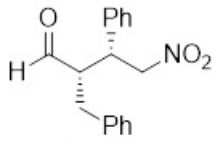



**6f** (racemate)

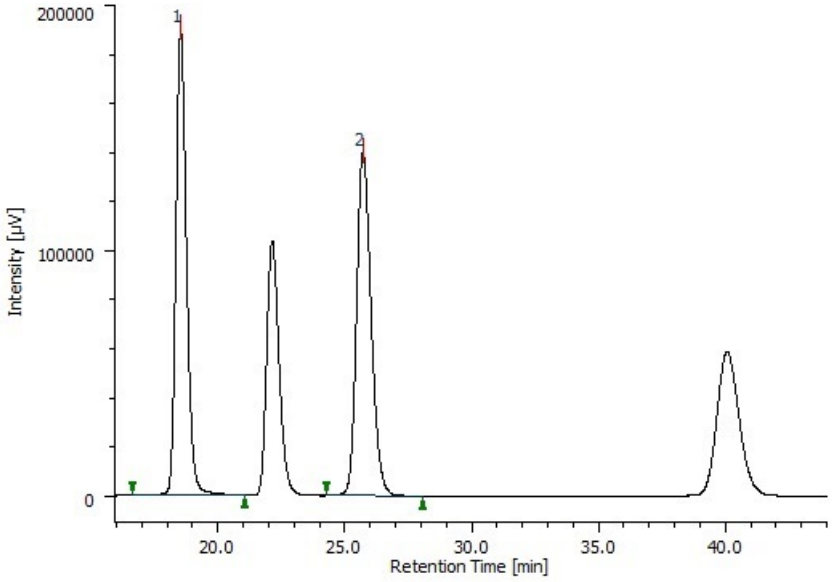
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 37.417 | 8660005 | 136902 | 49.039 |
| 2 | 40.683 | 8999556 | 144583 | 50.961 |
| Total | | 17659561 | 281485 | 100.000 |

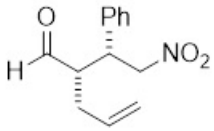



**6f** (94% ee)

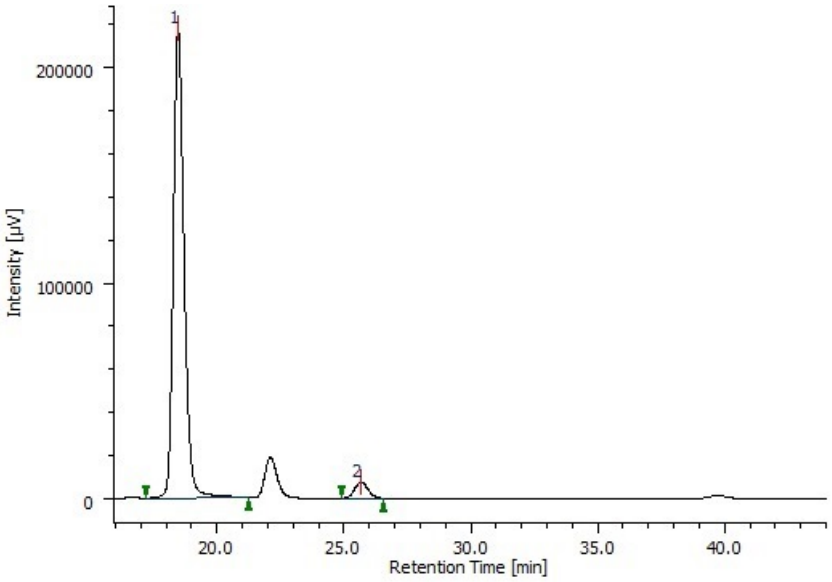
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 37.175 | 28014434 | 436233 | 97.226 |
| 2 | 40.008 | 799424 | 11715 | 2.774 |
| Total | | 28813858 | 447948 | 100.000 |

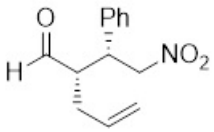



**6g** (racemate)

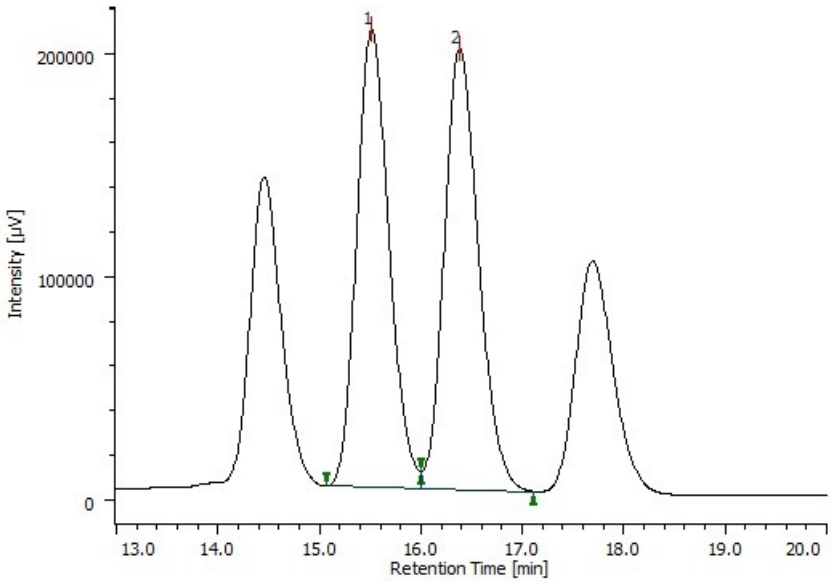
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 18.525 | 5514121 | 190306 | 49.684 |
| 2 | 25.700 | 5584347 | 140059 | 50.316 |
| Total | | 11098468 | 330365 | 100.000 |

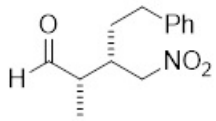



**6g** (92% ee)

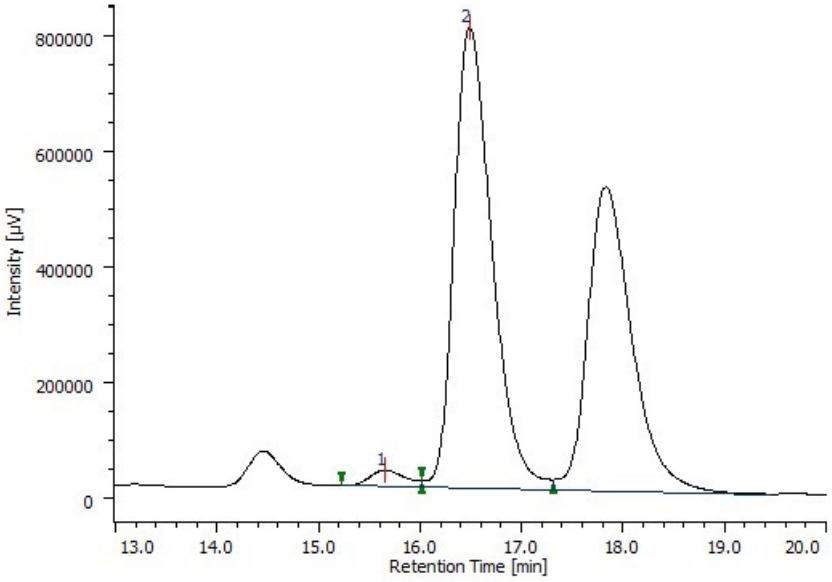
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 18.467 | 6352421 | 216521 | 95.823 |
| 2 | 25.658 | 276898 | 7430 | 4.177 |
| Total | | 6629319 | 223951 | 100.000 |

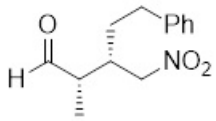



**6h** (racemate)

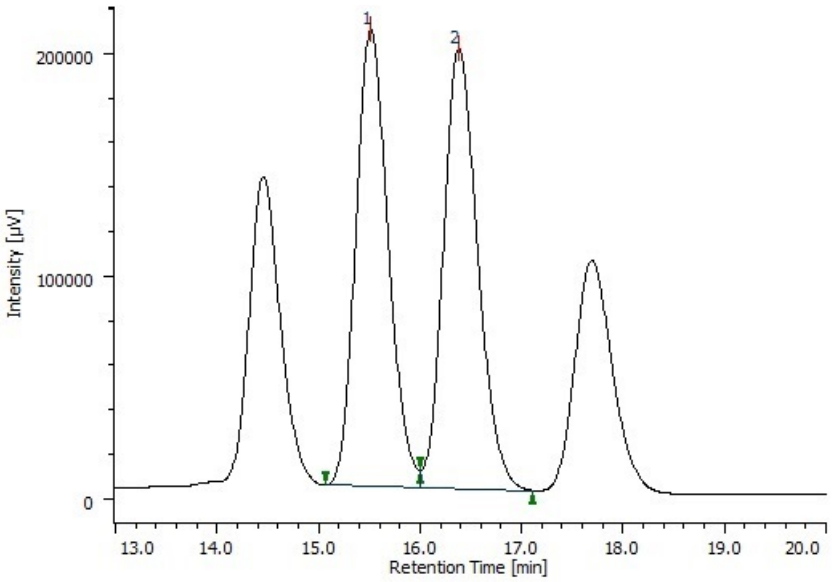
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 15.508 | 4528294 | 204813 | 49.546 |
| 2 | 16.375 | 4611292 | 197166 | 50.454 |
| Total | | 9139586 | 401979 | 100.000 |

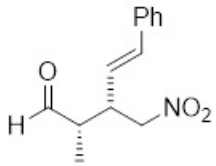



**6h** (94% ee)

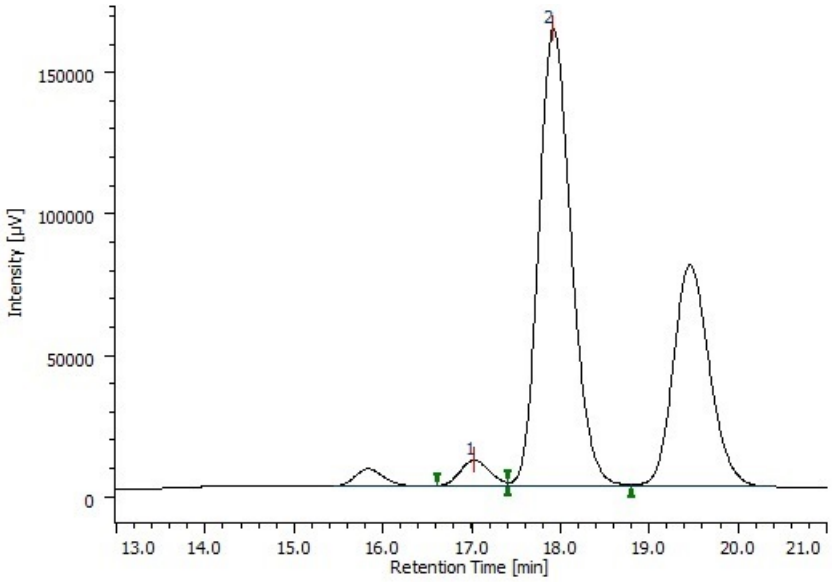
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 15.650 | 683756 | 28067 | 3.219 |
| 2 | 16.483 | 20558734 | 795413 | 96.781 |
| Total | | 21242490 | 823480 | 100.000 |

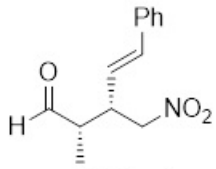



**6i** (racemate)

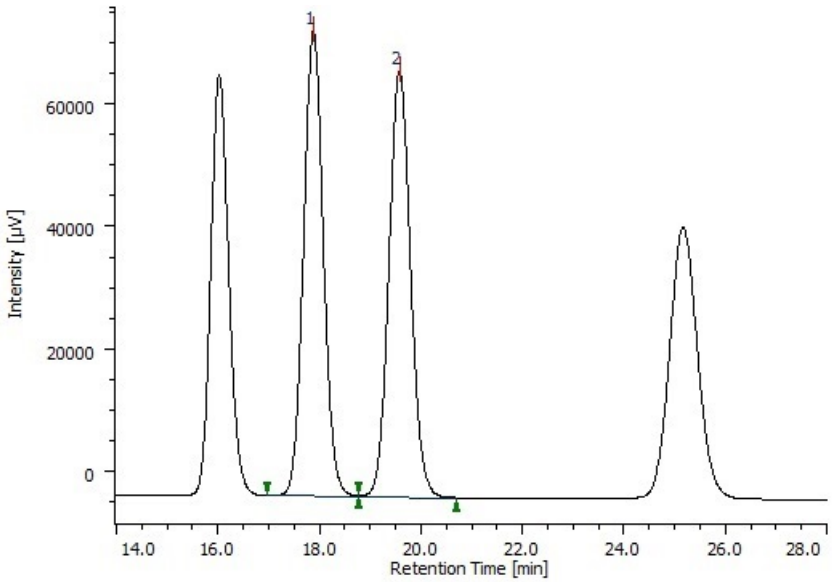
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 15.508 | 4528294 | 204813 | 49.546 |
| 2 | 16.375 | 4611292 | 197166 | 50.454 |
| Total | | 9139586 | 401979 | 100.000 |

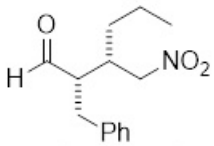



**6i** (90% ee)

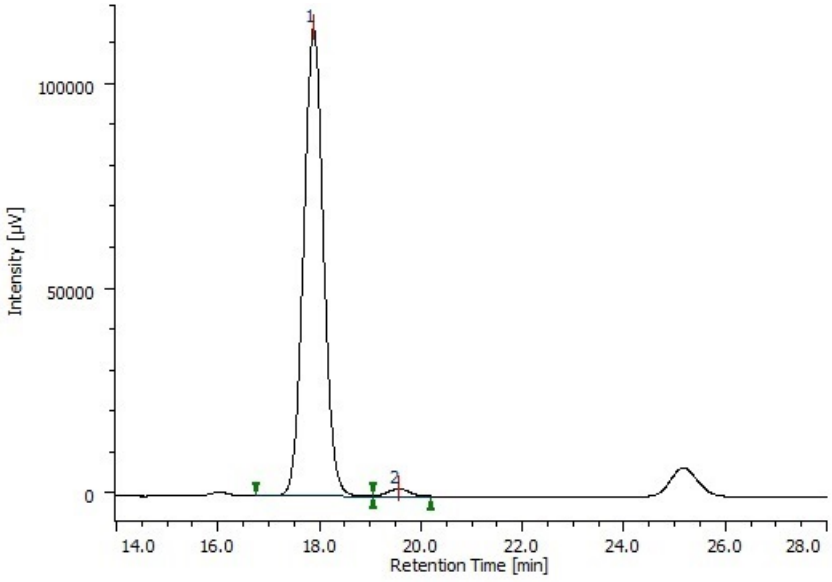
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.025 | 217403 | 9195 | 5.032 |
| 2 | 17.908 | 4103197 | 161442 | 94.968 |
| Total | | 4320600 | 170637 | 100.000 |

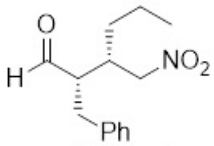



**6j** (racemate)

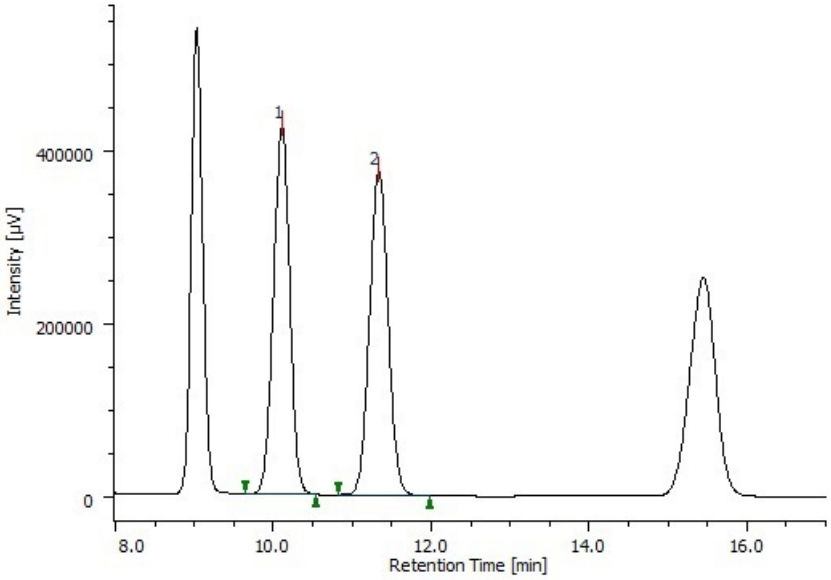
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.875 | 2046686 | 75897 | 49.987 |
| 2 | 19.567 | 2047782 | 69341 | 50.013 |
| Total | | 4094468 | 145238 | 100.000 |

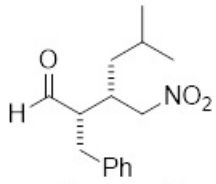



**6j** (97% ee)

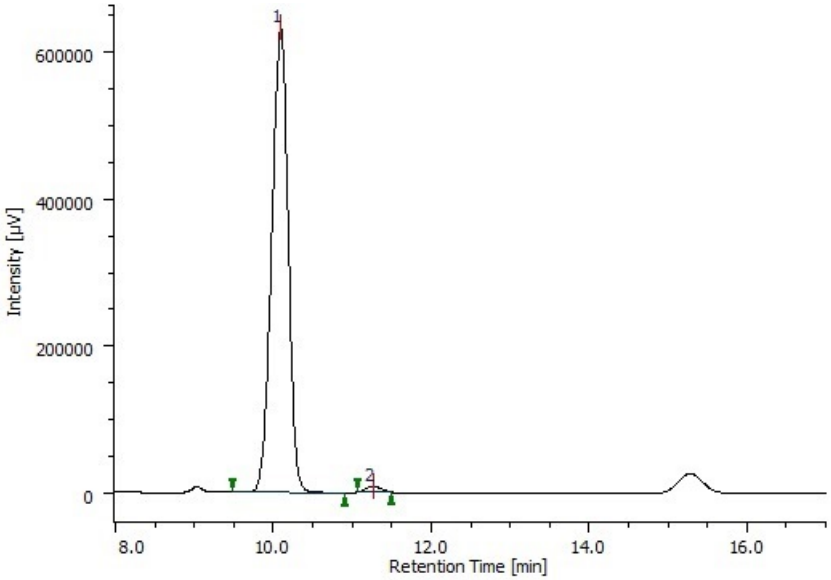
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 17.883 | 3101071 | 114116 | 98.29 |
| 2 | 19.558 | 53945 | 1842 | 1.71 |
| Total | | 3155016 | 115958 | 100.000 |

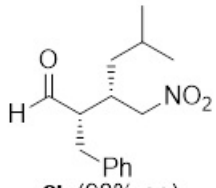



**6k** (racemate)

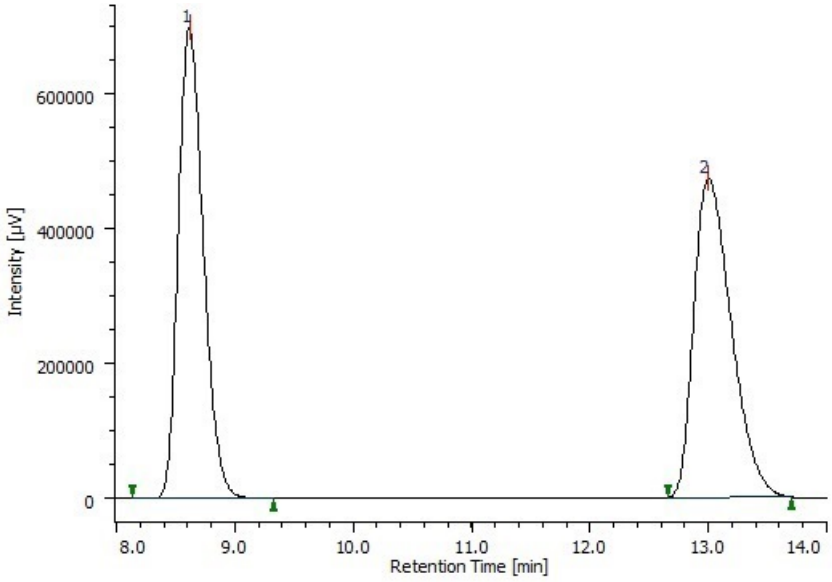
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.108 | 6110462 | 426286 | 49.937 |
| 2 | 11.333 | 6125942 | 374780 | 50.063 |
| Total | | 12236404 | 801066 | 100.000 |

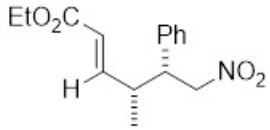



**6k** (98% ee)

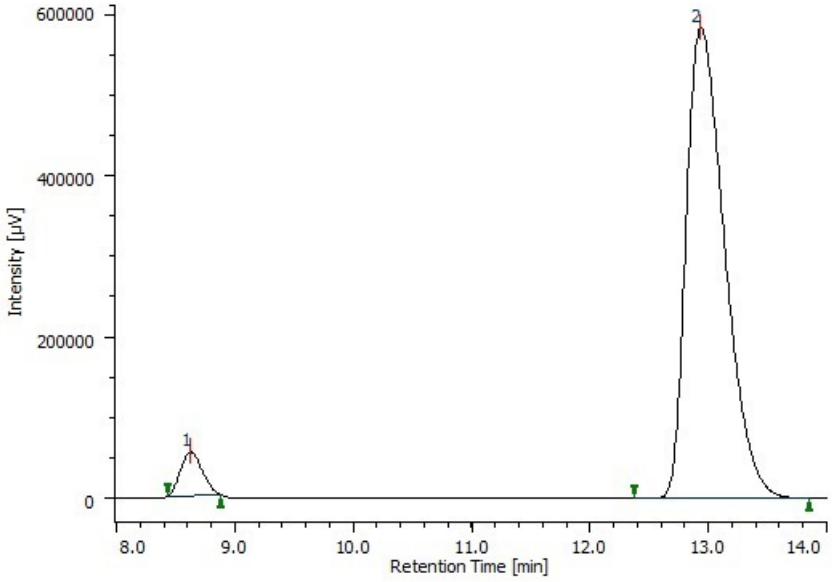
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 10.092 | 9097616 | 630142 | 98.889 |
| 2 | 11.267 | 102190 | 7715 | 1.111 |
| Total | | 9199806 | 637857 | 100.000 |

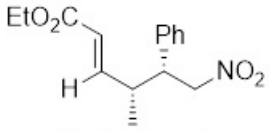



**7a** (racemate)

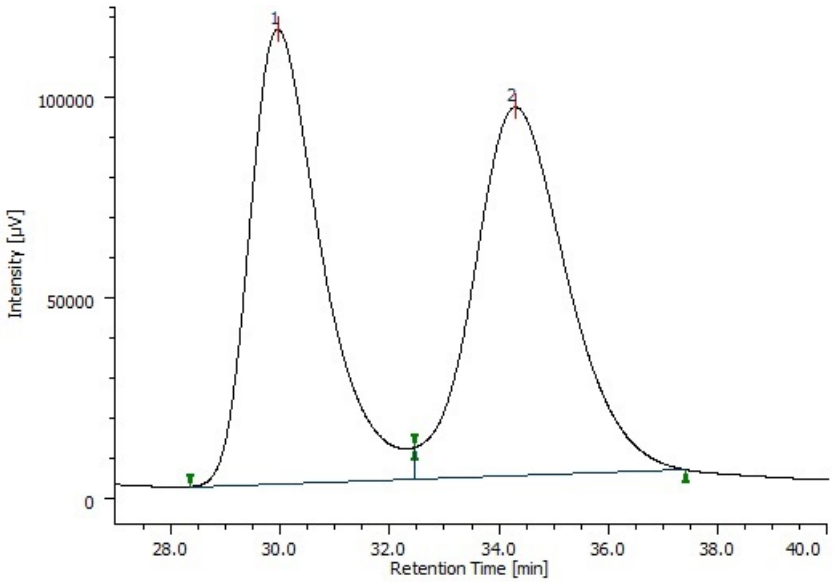
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 8.617 | 10165899 | 695089 | 49.581 |
| 2 | 12.992 | 10337797 | 471295 | 50.419 |
| Total | | 20503696 | 1166384 | 100.000 |

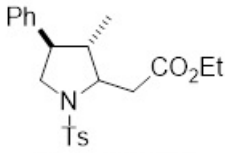



**7a** (90% ee)

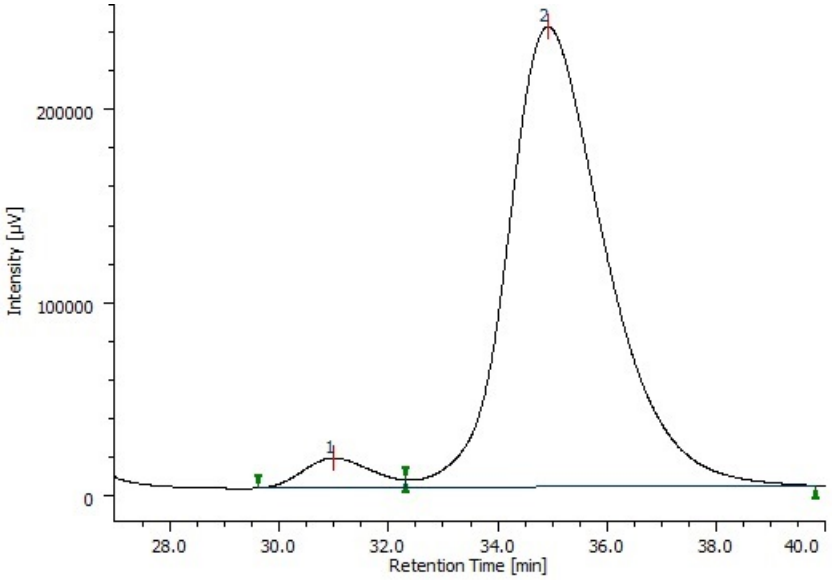
| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 8.625 | 691345 | 54333 | 5.015 |
| 2 | 12.925 | 13095319 | 583066 | 94.985 |
| Total | | 13786664 | 637399 | 100.000 |

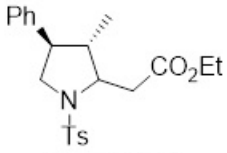



**8a** (racemate)

| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 29.950 | 10378914 | 113126 | 48.726 |
| 2 | 34.283 | 10921558 | 91714 | 51.274 |
| Total | | 21300472 | 204840 | 100.000 |




**8a** (91% ee)

| peak No. | tR (min) | Area | High (μV) | Area (%) |
|---|---|---|---|---|
| 1 | 30.992 | 1325010 | 15207 | 4.283 |
| 2 | 34.908 | 29612181 | 236939 | 95.717 |
| Total | | 30937191 | 252146 | 100.000 |