

Supporting Information

Synthesis and application of chiral *cis*-2,5-disubstituted pyrrolidine organocatalysts

Suraj Singh,[‡] Rohtash Kumar,[‡] Navneet Nandgopal Dubey and Chandrakumar Appayee*

*Department of Chemistry, Indian Institute of Technology Gandhinagar, Gandhinagar,
Gujarat-382055, India*

*E-mail: a.chandra@iitgn.ac.in

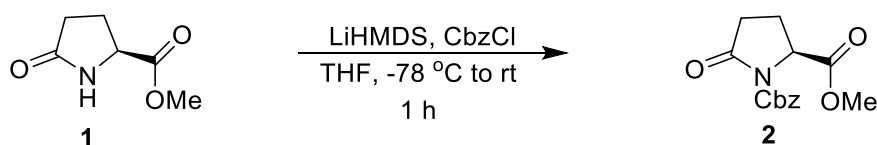
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1. General information

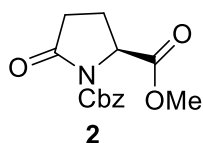
All the reagents and catalysts were purchased from Sigma-Aldrich, TCI, Avra, SRL, BLD pharm and used without further purification unless otherwise mentioned. All the solvents were purchased from Merck or SD Fine and used for the purification of products. Thin-layer chromatography (SiO₂, TLC) was performed on Merck TLC silica gel 60 F₂₅₄ visualized by ultraviolet irradiation, KMnO₄ solution. Column chromatography was performed on Merck silica gel 100-200 using standard flash chromatographic methods. The NMR spectra were recorded on Bruker Advance III (500 MHz) spectrometer and were referenced against the residual solvent peaks [CDCl₃: δ 7.26 ppm (¹H NMR) and 77.16 ppm (¹³C NMR)]. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constant, and integration. Infrared spectra were recorded on Perkin Elmer Spectrum Two FT-IR spectrometer. Selected absorption bands are reported in wave numbers (cm⁻¹). The HRMS data for all the compounds were recorded (in positive ion mode/negative ion mode) with Waters Synapt-G2S ESI-Q-TOF Mass instrument. Chiral HPLC analysis was performed using an Agilent 1200 series, Shimadzu Nexera Semi-Preparative system, and Daicel Chiralpak IC, AS-H, IG, and IA columns (Chiral Technologies Eur., 25 cm \times 4.6 mm I.D.) with isopropanol/hexane as the solvent. Specific rotations were measured with a Rudolph Polarimeter 341 at 589 nm and were reported as $[\alpha]_D^{25}$ (c in g per 100 mL, solvent, *ee*). Racemic products were synthesized by using the *racemic*-diphenylprolinol trimethylsilyl ether. The melting point (M.P.) of solid compounds was recorded on Labindia MR-VIS instrument using glass capillaries. The cinnamaldehyde derivatives were purchased from Sigma-Aldrich, TCI, BLD pharm and used without further purification. The cinnamaldehyde derivatives **9e**,¹ **9j**,¹ **9n**,¹ and **9o**,¹ were prepared according to the reported procedure. The spectral data are consistent with those reported in the literature. Rotational isomers were observed for the compounds **4a**, and **4b**.

2. Experimental procedure for the synthesis of imide **2**²



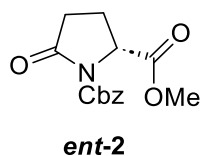
To a stirred solution of lactam **1** (5.0 g, 35.0 mmol, 1 equiv) in anhydrous THF (100 mL) at -78 °C was added LiHMDS (35 mL of 1 M solution in THF, 35.0 mmol, 1 equiv) dropwise, and the solution was stirred at the same temperature for 30 minutes, then benzyl chloroformate (10 mL of 50% solution in toluene, 35.0 mmol, 1 equiv) was also added dropwise at the same temperature. Then, the reaction mixture was stirred at 0 °C for 1 h. After completion of the reaction (monitored by TLC), the reaction mass was quenched with a saturated aqueous solution of NaHCO₃ (30 mL), and extracted with CH₂Cl₂ (3 × 50 mL). The organic phases were combined, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product which was purified using flash column chromatography.

1-benzyl 2-methyl (*S*)-5-oxopyrrolidine-1,2-dicarboxylate (**2**)



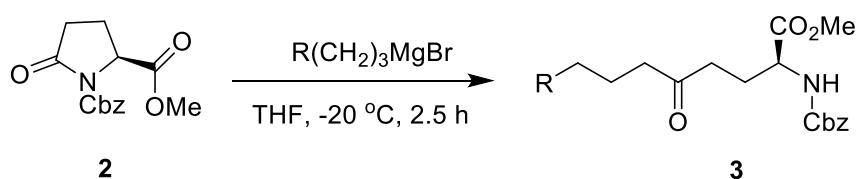
Following experimental procedure, lactam **1** (5.0 g, 35.0 mmol, 1 equiv) was transformed into product **2**, which was purified as a viscous light-yellow oil (7.64 g, 79% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (65:35)]. $R_f = 0.3$ [hexane/EtOAc (50/50)]. $[\alpha]_D^{20} = -43.4$ ($c = 1.0$, EtOH for **2**), lit.³ $[\alpha]_D^{24} = -44.2$ ($c = 0.95$, EtOH for **2**). ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.32 (m, 5H), 5.33 (d, $J = 12.5$ Hz, 1H), 5.21 (d, $J = 12.5$ Hz, 1H), 4.68 (dd, $J = 9.5, 2.5$ Hz, 1H), 3.68 (s, 3H), 2.69-2.61 (m, 1H), 2.54-2.48 (m, 1H), 2.39-2.30 (m, 1H), 2.10-2.05 (m, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 173.0, 171.6, 151.1, 135.1, 128.7, 128.6, 128.3, 68.5, 58.8, 52.8, 31.1, 22.0. IR (neat) ν 2956, 1794, 1744, 1717, 1524, 1456, 1439, 1381, 1300, 1257, 1212, 1181, 1044, 741, 698 cm⁻¹. HRMS (ESI) m/z calcd for C₁₄H₁₅NO₅Na⁺ [M + Na]⁺ 300.0842, found 300.0854.

1-benzyl 2-methyl (*R*)-5-oxopyrrolidine-1,2-dicarboxylate (*ent*-**2**)



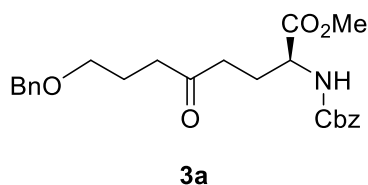
Following experimental procedure, lactam *ent*-**1** (5.0 g, 35.0 mmol, 1 equiv) was transformed into product *ent*-**2** which was purified as a viscous light-yellow oil (7.5 g, 77% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (65:35)]. $R_f = 0.3$ [hexane/EtOAc (50/50)]. $[\alpha]_D^{27} = +32.8$ ($c = 1.0$, CHCl₃ for (+)-**2**).

3. Experimental procedure for the synthesis of compound 3



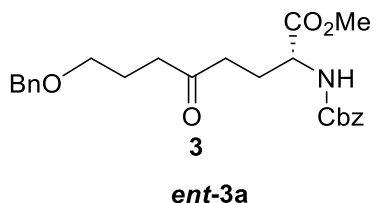
To a stirred solution of imide **2** (1.0 g, 3.61 mmol, 1 equiv) in anhydrous THF (25 mL) at -20 °C was added a solution of R(CH₂)₃MgBr (1 M solution in THF, 10.8 mmol, 3 equiv) [freshly prepared from alkyl bromide (13.16 mmol), magnesium turnings (390 mg, 15.8 mmol), dibromoethane (0.2 mL, 2.63 mmol) in anhydrous THF (14 mL) at reflux], and then the reaction mixture was stirred for 2.5 h at -20 °C. After completion of the reaction (monitored by ¹H NMR), the reaction mass was quenched with a saturated aqueous solution of NH₄Cl (25 mL) and extracted with Et₂O (3 × 30 mL). The organic phases were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product which was purified using flash column chromatography.

Methyl (*S*)-8-(benzyloxy)-2-(((benzyloxy) carbonyl)amino)-5-oxooctanoate (**3a**)



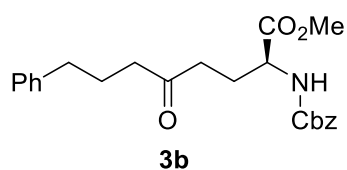
Following experimental procedure, imide **2** (1.0 g, 3.61 mmol, 1 equiv) was transformed into product **3a**, which was purified as a light-yellow oil (772 mg, 50% yield) from the crude reaction mixture using flash column chromatography [Silica gel, (hexane/EtOAc (80:20)]. *R_f* = 0.3 [hexane/EtOAc (70/30)]. [*α*]_D²⁴ = -6.1 (*c* = 1.0, CHCl₃ for **3a**). ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.26 (m, 10H), 5.43 (d, *J* = 7.5 Hz, 1H), 5.09 (d, *J* = 1.5 Hz, 2H), 4.45 (s, 2H), 4.34-4.30 (m, 1H), 3.72 (s, 3H), 3.45 (t, *J* = 6.0 Hz, 2H), 2.56-2.42 (m, 4H), 2.16-2.09 (m, 1H), 1.89-1.84 (m, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 209.4, 172.6, 156.1, 138.4, 136.3, 128.6, 128.5, 128.3, 128.2, 127.74, 127.68, 72.9, 69.3, 67.1, 53.4, 52.6, 39.6, 38.4, 26.4, 23.9. IR (neat) *ν* 3353, 2954, 2859, 1717, 1526, 1454, 1213, 1099, 740, 699 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₄H₂₉NO₆Na⁺ [*M* + Na]⁺ 450.1887, found 450.1899.

Methyl (*R*)-8-(benzyloxy)-2-(((benzyloxy) carbonyl)amino)-5-oxooctanoate (*ent*-**3a**)



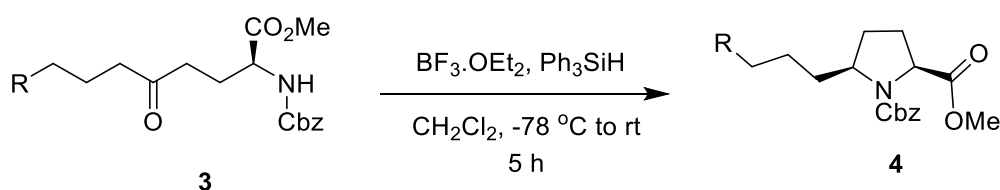
Following experimental procedure, imide *ent*-**2** (5.0 g, 18.03 mmol, 1 equiv) was transformed into product *ent*-**3a** which was purified as a light-yellow oil (3.9 g, 51% yield) from the crude reaction mixture using flash column chromatography [Silica gel, (hexane/EtOAc (80:20)]. *R_f* = 0.3 [hexane/EtOAc (70/30)]. [*α*]_D²⁵ = +4.0 (*c* = 1.0, CHCl₃ for (+)-**3a**).

(S)-2-(((benzyloxy)carbonyl)amino)-5-oxo-8-phenyloctanoate (**3b**)



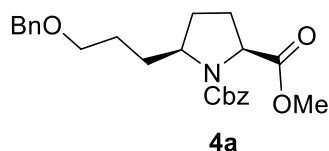
Following experimental procedure, imide **2** (500 mg, 1.81 mmol, 1 equiv) was transformed into product **3b**, which was purified as a light-yellow oil (360 mg, 50% yield) using flash column chromatography [Silica gel, (hexane/EtOAc (80:20)]. $R_f = 0.7$ [hexane/EtOAc (50/50)]. $[\alpha]_D^{26} = +16.4$ ($c = 0.5$, CHCl_3 for **3b**). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35-7.26 (m, 7H), 7.20-7.15 (m, 3H), 5.38 (d, $J = 8.0$ Hz, 1H), 5.09 (s, 2H), 4.36-4.31 (m, 1H), 3.73 (s, 3H), 2.60 (t, $J = 7.5$ Hz, 2H), 2.54-2.37 (m, 4H), 2.17-2.11 (m, 1H), 1.94-1.86 (m, 3H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 209.5, 172.6, 156.1, 141.6, 136.3, 128.7, 128.6, 128.5, 128.4, 128.3, 126.1, 67.2, 53.5, 52.6, 42.1, 38.5, 35.2, 26.5, 25.2. IR (neat) ν 3349, 3029, 2952, 1714, 1525, 1454, 1215, 1053, 748, 700 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_5\text{Na}^+$ $[\text{M} + \text{Na}]^+$ 420.1781, found 420.1786.

4. Experimental procedure for the synthesis of compound 4



$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.7 mL, 5.64 mmol, 4 equiv) was added to a solution of Ph_3SiH (734 mg, 2.82 mmol, 2 equiv) in dry CH_2Cl_2 (3 mL) at rt and stirred for 20 min at the same temperature. Then, the resultant mixture was added dropwise to a stirred solution of ketone **3** (1.41 mmol, 1 equiv) in dry CH_2Cl_2 (7 mL) at -78 °C. The reaction mixture was stirred at the same temperature for 30 min, and then at rt for 5 h. After completion of the reaction (monitored by TLC), the reaction mass was quenched with a saturated aqueous solution of NaHCO_3 (15 mL) at 0 °C and extracted with Et_2O (3×30 mL). The organic phases were combined, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to get the crude product which was purified using flash column chromatography.

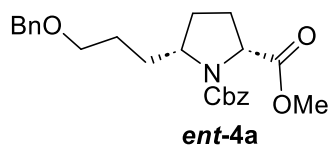
1-Benzyl 2-methyl (2S,5R)-5-(3-(benzyloxy) propyl)pyrrolidine-1,2-dicarboxylate (**4a**)



Following experimental procedure, ketone **3a** (560 mg, 1.41 mmol, 1 equiv) was transformed into product **4a** which was purified as a light-yellow oil (493 mg, 85% yield) from the crude reaction mixture using flash column chromatography [Silica gel, (hexane/EtOAc (80:20)]. $R_f = 0.4$ [hexane/EtOAc (70/30)]. $[\alpha]_D^{23} = -14.4$ ($c = 1.33$, CHCl_3 for **4a**). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34-7.25 (m, 10H), 5.18-5.04 (m, 2H), 4.50 (s, 1.07H), 4.44 (s, 0.86H), 4.40 (t, $J = 7.6$ Hz, 0.47H), 4.34 (t, $J = 7.5$ Hz, 0.54H), 4.00-3.97 (m, 0.54H), 3.96-3.93 (m, 0.44H), 3.74

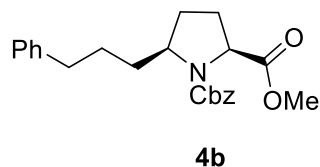
(s, 1.30H), 3.60 (s, 1.54H), 3.55-3.40 (m, 2H), 2.24-2.19 (m, 1H), 2.03-1.95 (m, 2H), 1.90-1.75 (m, 1H), 1.74-1.53 (m, 4H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 173.6, 173.5, 155.2, 154.4, 138.7, 138.6, 136.7, 136.6, 128.54, 128.47, 128.4, 128.1, 128.01, 127.96, 127.74, 127.70, 127.6, 72.9, 70.5, 70.3, 67.3, 67.0, 60.1, 59.8, 59.2, 58.6, 52.3, 52.1, 31.4, 30.7, 30.3, 29.5, 29.2, 28.2, 26.8. IR (neat) ν 2951, 2926, 2855, 1750, 1700, 1408, 1350, 1201, 1173, 1100, 736, 697 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{30}\text{NO}_5^+$ $[\text{M} + \text{H}]^+$ 412.2118, found 412.2125.

1-Benzyl 2-methyl (2*R*,5*S*)-5-(3-(benzyloxy) propyl)pyrrolidine-1,2-dicarboxylate (*ent*-4a)



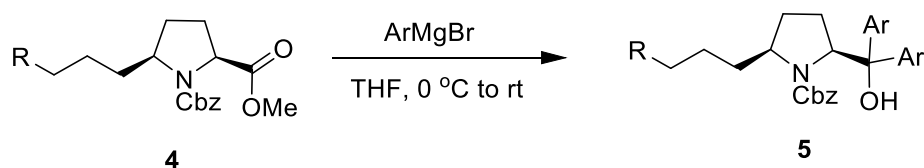
Following experimental procedure, ketone *ent*-3a (3.6 g, 8.56 mmol, 1 equiv) was transformed into product *ent*-4a which was purified as a light-yellow oil (3.1 g, 82% yield) from the crude reaction mixture using flash column chromatography [Silica gel, (hexane/EtOAc (80:20)]. R_f = 0.4 [hexane/EtOAc (70/30)]. $[\alpha]_D^{26} = +15.2$ ($c = 1.0$, CHCl_3 for (+)-4a).

1-Benzyl 2-methyl (2*S*,5*S*)-5-(3-phenylpropyl)pyrrolidine-1,2 dicarboxylate (4b)



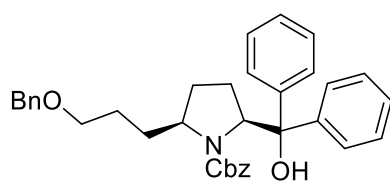
Following experimental procedure, ketone 3b (326 mg, 0.82 mmol, 1 equiv) was transformed into product 4b, which was purified as a light-yellow oil (280 mg, 90% yield) using flash column chromatography [Silica gel, (hexane/EtOAc (85:15)]. $R_f = 0.4$ [hexane/EtOAc (80/20)]. $[\alpha]_D^{24} = -27.4$ ($c = 1.0$, CHCl_3 for 4b). ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.25 (m, 7H), 7.19-7.12 (m, 3H), 5.16-5.05 (m, 2H), 4.39 (t, $J = 7.5$ Hz, 0.45H), 4.34 (t, $J = 7.5$ Hz, 0.55H), 4.05-3.99 (m, 0.56H), 3.95-3.90 (m, 0.48H), 3.73 (s, 1.33H), 3.60 (s, 1.61H), 2.70-2.56 (m, 2H), 2.23-2.18 (m, 1H), 2.07-1.89 (m, 3H), 1.72-1.61 (m, 3H), 1.54-1.48 (m, 1H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 173.7, 173.5, 155.2, 154.4, 142.7, 142.5, 136.8, 136.7, 128.6, 128.5, 128.44, 128.38, 128.1, 128.04, 127.99, 127.8, 125.82, 125.77, 67.3, 67.0, 60.2, 59.8, 59.3, 58.7, 52.3, 52.2, 36.1, 35.9, 34.5, 34.0, 30.3, 29.6, 29.2, 28.6, 28.3. IR (neat) ν 3028, 2949, 1752, 1705, 1497, 1454, 1409, 1352, 1203, 1173, 1113, 750, 699 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_4\text{Na}^+$ $[\text{M} + \text{Na}]^+$ 404.1832, found 404.1840.

5. Experimental procedure for the synthesis of compounds 5a, *ent*-5a, 5b, and 5c



To a solution of ester **4** (1.19 mmol, 1 equiv) in anhydrous THF (5 mL) at 0 °C was added a solution of ArMgBr (1 M solution in THF, 12.0 mmol, 10 equiv) [freshly prepared from aryl bromide (12.0 mmol) magnesium turnings (350 mg, 14.4 mmol) and dibromoethane (0.2 mL, 2.4 mmol) in anhydrous THF (12 mL) at reflux], and the reaction mixture was stirred at 0 °C for 30 min and then 18 h at rt. After completion of the reaction (monitored by TLC), the reaction mass was quenched with a saturated aqueous solution of NH₄Cl (15 mL) and extracted with EtOAc (3 × 30 mL). The organic phases were combined, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product which was purified using flash column chromatography.

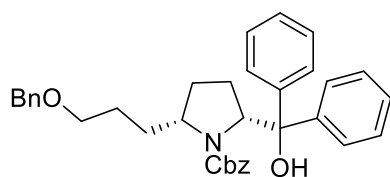
Benzyl (2*R*,5*S*)-2-(3-(benzyloxy)propyl)-5-(hydroxydiphenylmethyl)pyrrolidine-1-carboxylate (5a)



5a

Following experimental procedure, ester **4a** (491 mg, 1.19 mmol, 1 equiv) was transformed into product **5a** which was purified as a light-yellow oil (447 mg, 70% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (90:10)]. $R_f = 0.5$ [hexane/EtOAc (80/20)]. $[\alpha]_D^{22} = -58.6$ ($c = 0.5$, CHCl₃ for **5a**). ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.21 (m, 20H), 5.15 (d, $J = 12.0$ Hz, 1H), 4.98 (dd, $J = 9.0, 4.0$ Hz, 2H), 4.41 (s, 2H), 3.74-3.71 (m, 1H), 3.29-3.23 (m, 2H), 2.12-2.09 (m, 1H), 2.09-1.99 (m, 1H), 1.78-1.74 (m, 2H), 1.31-1.28 (m, 2H), 0.90-0.86 (m, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 159.2, 146.6, 143.6, 138.7, 136.4, 128.7, 128.64, 128.60, 128.5, 128.2, 128.1, 127.9, 127.71, 127.70, 127.64, 127.56, 127.3, 127.2, 127.1, 81.2, 72.9, 70.4, 68.0, 67.8, 60.6, 32.0, 30.2, 28.6, 27.0. IR (neat) ν 3376, 3032, 2925, 2855, 1663, 1448, 1407, 1323, 1103, 1029, 752 cm⁻¹. HRMS (ESI) m/z calcd for C₃₅H₃₇NO₄Na⁺ [M + Na]⁺ 558.2615, found 558.2619.

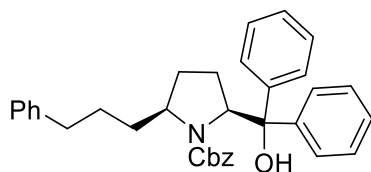
Benzyl (2*S*,5*R*)-2-(3-(benzyloxy)propyl)-5-(hydroxydiphenylmethyl)pyrrolidine-1-carboxylate (*ent*-5a)



***ent*-5a**

Following experimental procedure, ester *ent*-**4a** (2.9 g, 7.04 mmol, 1 equiv) was transformed into product *ent*-**5a** which was purified as a light-yellow oil (2.53 g, 67% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (90:10)]. $R_f = 0.5$ [hexane/EtOAc (80/20)]. $[\alpha]_D^{27} = +52.0$ ($c = 1.0$, CHCl₃ for (+)-**5a**).

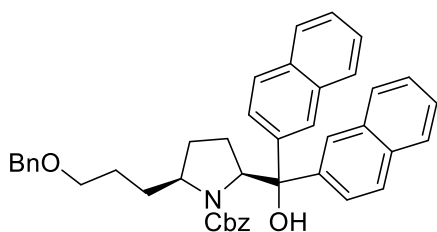
Benzyl (2*S*,5*S*)-2-(hydroxydiphenylmethyl)-5-(3-phenylpropyl)pyrrolidine-1-carboxylate (5b)



5b

Following experimental procedure, ester **4b** (180 mg, 0.47 mmol, 1 equiv) was transformed into product **5b**, which was purified as a light-yellow oil (171 mg, 71% yield) using flash column chromatography [Silica gel, hexane/EtOAc (90:10)]. $R_f = 0.5$ [hexane/EtOAc (80/20)]. $[\alpha]_D^{22} = -55.4$ ($c = 0.5$, CHCl_3 for **5b**). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39-7.36 (m, 4H), 7.33-7.31 (m, 3H), 7.28-7.21 (m, 10H), 7.19-7.16 (m, 1H), 7.06 (d, $J = 7.0$ Hz, 2H), 5.15 (d, $J = 12.5$ Hz, 1H), 4.98-4.95 (m, 2H), 3.72-3.69 (m, 1H), 2.47-2.42 (m, 1H), 2.39-2.35 (m, 1H), 2.13-2.08 (m, 1H), 2.00-1.96 (m, 1H), 1.75-1.70 (m, 1H), 1.61 (bs, 1H), 1.31-1.25 (m, 2H), 0.85-0.75 (m, 2H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 159.3, 146.6, 143.5, 142.5, 136.4, 128.7, 128.6, 128.40, 128.35, 128.2, 128.1, 127.9, 127.7, 127.5, 127.24, 127.17, 126.6, 125.8, 81.2, 68.0, 67.8, 60.6, 35.9, 35.1, 30.1, 28.60, 28.56. IR (neat) ν 3363, 2925, 2855, 1661, 1448, 1406, 1322, 1260, 1098, 1028, 799, 751 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{35}\text{NO}_3\text{Na}^+ [\text{M} + \text{Na}]^+$ 528.2509, found 528.2520.

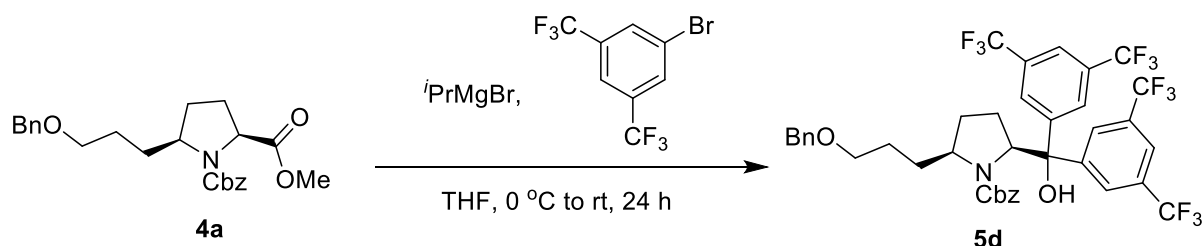
Benzyl (2*R*,5*S*)-2-(3-(benzyloxy)propyl)-5-(hydroxydi(naphthalen-2-yl)methyl)pyrrolidine-1-carboxylate (5c)



5c

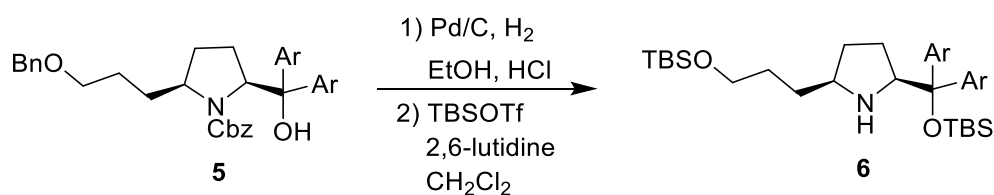
Following experimental procedure, ester **4a** (300 mg, 0.73 mmol, 1 equiv) was transformed into product **5c**, which was purified as a light-yellow oil (325 mg, 70% yield) using flash column chromatography [Silica gel, hexane/Et₂O (80:20)]. $R_f = 0.6$ [hexane/Et₂O (50/50)]. $[\alpha]_D^{20} = -65.4$ ($c = 1.0$, CHCl_3 for **5c**). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.00 (s, 1H), 7.82 (s, 1H), 7.73-7.62 (m, 6H), 7.44-7.35 (m, 6H), 7.27-7.16 (m, 10H), 5.14-5.07 (m, 2H), 4.85 (bs, 1H), 4.20 (s, 2H), 3.69-3.66 (m, 1H), 2.92-2.85 (m, 2H), 2.19-2.07 (m, 2H), 1.70-1.66 (m, 1H), 1.52-1.47 (m, 2H), 1.08 (bs, 2H), 0.74 (bs, 2H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 158.3, 142.7, 139.7, 137.5, 135.2, 131.7, 131.6, 131.51, 131.49, 127.5, 127.43, 127.35, 127.31, 127.29, 127.0, 126.9, 126.70, 126.66, 126.6, 126.5, 126.43, 126.40, 126.1, 125.94, 125.85, 125.7, 125.0, 124.9, 124.1, 80.2, 71.7, 69.0, 67.1, 66.7, 59.4, 30.9, 29.1, 27.5, 25.8. IR (neat) ν 3302, 3058, 2926, 2855, 1661, 1455, 1406, 1321, 1100, 859, 820, 746, 698, 477 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{43}\text{H}_{41}\text{NO}_4\text{Na}^+ [\text{M} + \text{Na}]^+$ 658.2928, found 658.2936.

6. Experimental procedure for the synthesis of benzyl (2*R*,5*S*)-2-(3-(benzyloxy)propyl)-5-(bis(3,5-bis(trifluoromethyl)phenyl)(hydroxy)methyl)pyrrolidine-1-carboxylate (**5d**)



To a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (460 μ L, 2.63 mmol, 4 equiv) in anhydrous THF (3 mL), the isopropylmagnesium(II) bromide (2.6 mL of 1 M solution in THF, 2.63 mmol, 4 equiv) [freshly prepared from 2-bromopropane (760 μ L, 8.13 mmol), magnesium turnings (240 mg, 9.75 mmol) and dibromoethane (140 μ L, 1.62 mmol) in anhydrous THF (8 mL) at reflux] was added dropwise at 0 $^{\circ}$ C under argon atmosphere and then the reaction mixture was stirred at 0 $^{\circ}$ C for 45 min. Then, ester **4a** (270 mg, 0.66 mmol, 1 equiv) in anhydrous THF (1 mL) was added dropwise at the same temperature. The reaction mixture was stirred at rt for 24 h. After completion of the reaction (monitored by TLC), the reaction mass was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted with EtOAc (3 \times 30 mL). The organic phases were combined, washed with brine, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to get the crude product **5d**, which was purified as a light-yellow oil (350 mg, 66% yield) using flash column chromatography [Silica gel, hexane/EtOAc (92:08)]. R_f = 0.6 [hexane/EtOAc (80/20)]. $[\alpha]_D^{22}$ = -32.4 (c = 1.2, CHCl_3 for **5d**). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.90 (s, 2H), 7.85 (s, 1H), 7.83 (s, 3H), 7.34-7.23 (m, 10H), 6.73 (bs, 1H), 5.13 (d, J = 12.5 Hz, 1H), 5.05 (d, J = 12.0 Hz, 1H), 4.93-4.91 (m, 1H), 4.41 (s, 2H), 3.81-3.78 (m, 1H), 3.26 (t, J = 6.5 Hz, 2H), 2.11-2.03 (m, 1H), 1.89-1.81 (m, 2H), 1.70-1.60 (m, 1H), 1.37- 1.31 (m, 2H), 0.88-0.75 (m, 2H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 159.6, 147.6, 145.1, 138.4, 135.7, 131.8 (q, $^2J_{\text{C-F}}$ = 33.3 Hz), 131.5 (q, $^2J_{\text{C-F}}$ = 33.3 Hz), 128.7, 128.6, 128.5, 128.1, 127.82, 127.75, 127.7, 123.3 (q, $^1J_{\text{C-F}}$ = 271.3 Hz), 123.3 (q, $^1J_{\text{C-F}}$ = 271.3 Hz), 122.1, 122.0, 80.2, 73.2, 69.8, 68.6, 68.4, 60.7, 32.3, 29.9, 28.6, 27.0. $^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ -62.7 (s), -62.8 (s). IR (neat) ν 3331, 2927, 2858, 1667, 1370, 1278, 1173, 1133, 901, 698 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{39}\text{H}_{34}\text{F}_{12}\text{NO}_4^+$ [$\text{M} + \text{H}$] $^+$ 808.2291, found 808.2292.

7. Experimental procedure for the synthesis of compounds **6a**, *ent*-**6a**, **6c**, and **6d**

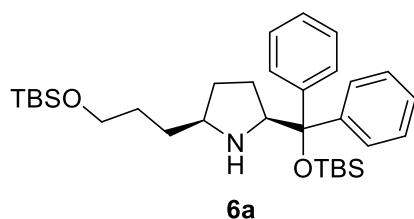


To a solution of **5** (0.75 mmol, 1 equiv) in 6 N aqueous HCl (8 mL) in ethanol (40 mL) was added Pd/C 10% (160 mg, 0.15 mmol, 0.2 equiv), and the reaction mixture was vigorously stirred in the presence of hydrogen at atmospheric pressure for 16 h at rt. After completion of the reaction (monitored by TLC), the reaction mass was filtered through Celite bed and concentrated under reduced pressure to get the crude product as the hydrochloride salt. To this hydrochloride salt triturated in CH_2Cl_2 (20 mL), saturated aqueous solution of NaHCO_3 (20 mL) was added and stirred for 30 min at rt. The CH_2Cl_2 layer was separated, and the aqueous solution was extracted with CH_2Cl_2 (3 \times 20 mL). The organic phases were combined, dried

over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product as a light-yellow oil which was used for the next step without further purification.

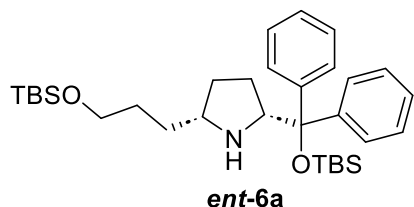
To a stirred solution of crude product in dry CH₂Cl₂ (7.6 mL), 2,6-lutidine (1.10 mL, 9.0 mmol, 12 equiv) was added dropwise at 0 °C, stirred for 15 minutes and then TBSOTf (1.10 mL, 4.50 mmol, 6 equiv) was added slowly at the same temperature. Then, the reaction mixture was stirred for 20 h at rt. After completion of the reaction (monitored by TLC), the reaction was quenched by the careful addition of a saturated aqueous solution of NH₄Cl (20 mL) and extracted with CH₂Cl₂ (3 × 25 mL). The organic phases were combined and washed with a solution of KOH (30 mL of 1 M solution) and brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product which was purified using flash column chromatography.

(2*S*,5*R*)-2-(((tert-butyldimethylsilyl)oxy)diphenylmethyl)-5-(3((tertbutyldimethylsilyl)oxy)propyl)pyrrolidine (6a)



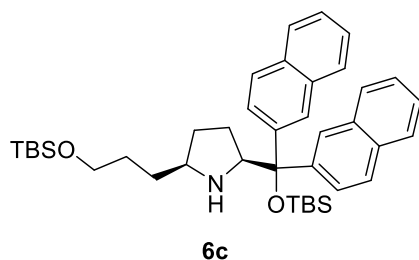
Following experimental procedure, compound **5a** (400 mg, 0.75 mmol, 1 equiv) was transformed into product **6a**, which was purified as a colorless liquid (267 mg, 66% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (97:03) + 0.5% Et₃N]. $R_f = 0.7$ [hexane/EtOAc (80/20)]. $[\alpha]_D^{24} = -20.9$ ($c = 1.0$, CHCl₃ for **6a**). ¹H NMR (500 MHz, CDCl₃) δ 7.56-7.54 (m, 2H), 7.36-7.34 (m, 2H), 7.27-7.22 (m, 6H), 4.05 (t, $J = 6.5$ Hz, 1H), 3.57-3.51 (m, 2H), 3.03-3.00 (m, 1H), 1.68-1.63 (m, 2H), 1.60-1.50 (m, 3H), 1.49-1.41 (m, 2H), 1.35-1.30 (m, 1H), 1.18-1.16 (m, 1H), 0.94 (s, 9H), 0.88 (s, 9H), 0.44 (bs, 1H), 0.02 (s, 6H), -0.25 (s, 3H), -0.45 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 146.5, 145.1, 129.7, 128.8, 127.7, 127.1, 126.9, 126.8, 83.1, 65.1, 63.6, 59.8, 32.5, 31.0, 30.9, 27.6, 26.5, 26.1, 19.2, 18.5, -2.6, -3.1, -5.1. IR (neat) ν 3088, 3060, 3025, 2955, 2929, 2886, 2857, 1472, 1446, 1254, 1098, 1067, 834, 774, 702 cm⁻¹. HRMS (ESI) m/z calcd for C₃₂H₅₄NO₂Si₂⁺ [M + H]⁺ 540.3688 found 540.3699.

(2*R*,5*S*)-2-(((tert-butyldimethylsilyl)oxy)diphenylmethyl)-5-(3((tertbutyldimethylsilyl)oxy)propyl)pyrrolidine (*ent*-6a)



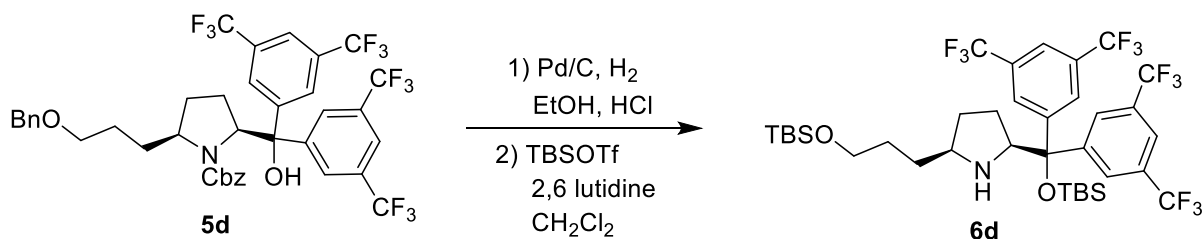
Following experimental procedure, compound ***ent*-5a** (688 mg, 1.28 mmol, 1.0 equiv) was transformed into product ***ent*-6a**, which was purified as a colorless liquid (479 mg, 69% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (97:03) + 0.5% Et₃N]. $R_f = 0.7$ [hexane/EtOAc (80/20)]. $[\alpha]_D^{26} = +16.6$ ($c = 1.0$, CHCl₃ for (+)-**6a**).

(2*S*,5*R*)-2-(((tertbutyldimethylsilyl)oxy)di(naphthalen-2-yl)methyl)-5-(3-((tertbutyldimethylsilyl)oxy)propyl)pyrrolidine (6c)



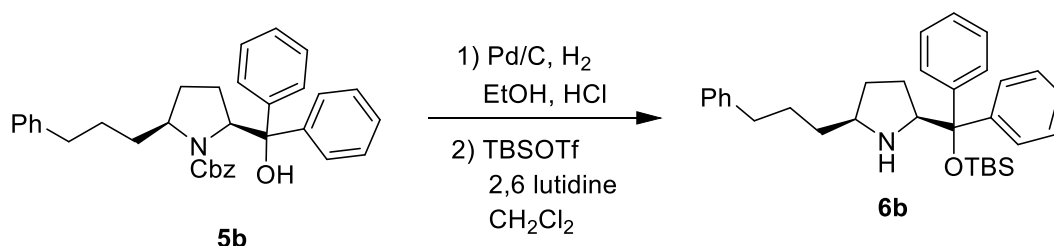
Following experimental procedure, compound **5c** (250 mg, 0.39 mmol, 1 equiv) was transformed into product **6c**, which was purified as a colorless liquid (170 mg, 68% yield) using flash column chromatography [Silica gel, hexane/EtOAc (97:03) + 0.5% Et₃N]. *R_f* = 0.7 [hexane/EtOAc (80/20)]. [*α*]_D²⁵ = -0.4 (*c* = 1.0, CHCl₃ for **6c**). ¹H NMR (500 MHz, CDCl₃) δ 8.22 (s, 1H), 8.04 (s, 1H), 7.85-7.80 (m, 4H), 7.68 (dd, *J* = 8.5, 2.5 Hz, 2H), 7.62 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.50-7.46 (m, 4H), 7.31 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.29 (t, *J* = 6.5 Hz, 1H), 3.55-3.49 (m, 2H), 3.12-3.09 (m, 1H), 1.82-1.78 (m, 1H), 1.78-1.66 (m, 2H), 1.49-1.32 (m, 5H), 1.02 (s, 9H), 0.87 (s, 9H), 0.51-0.45 (m, 1H), 0.01 (d, *J* = 2.0 Hz, 6H), -0.21 (s, 3H), -0.44 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 143.8, 142.6, 132.9, 132.64, 132.61, 128.7, 128.61, 128.56, 128.0, 127.7, 127.60, 127.56, 127.3, 126.9, 126.1, 126.0, 125.9, 125.8, 83.3, 65.2, 63.5, 59.9, 32.5, 31.1, 30.9, 27.7, 26.6, 26.1, 19.3, 18.5, -2.4, -2.8, -5.1. IR (neat) ν 3057, 2954, 2929, 2856, 1506, 1472, 1360, 1252, 1097, 835, 775, 745, 674, 478 cm⁻¹. HRMS (ESI) *m/z* calcd for C₄₀H₅₈NO₂Si₂⁺ [*M* + *H*]⁺ 640.4001 found 640.4005.

(2*S*,5*R*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((tert-butyl dimethylsilyl)oxy)methyl)-5-(3-((tert-butyl dimethylsilyl)oxy)propyl)pyrrolidine (6d)



Following experimental procedure, compound **5d** (260 mg, 0.32 mmol, 1 equiv) was transformed into product **6d**, which was purified as a colorless liquid (130 mg, 50% yield) using flash column chromatography [Silica gel, hexane/EtOAc (99:01) + 0.5% Et₃N]. *R_f* = 0.8 [hexane/EtOAc (90/10)]. [*α*]_D²⁴ = -14.4 (*c* = 1, CHCl₃ for **6d**). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (s, 2H), 7.87 (s, 2H), 7.73 (s, 2H), 4.29 (q, *J* = 4.0 Hz, 1H), 3.56-3.49 (m, 2H), 3.15-3.11 (m, 1H), 1.86-1.82 (m, 2H), 1.62-1.50 (m, 3H), 1.45-1.35 (m, 2H), 1.20-1.14 (m, 2H), 0.93 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H), -0.24 (s, 3H), -0.46 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 147.4, 145.5, 131.8 (q, ²*J*_{C-F} = 32.5 Hz), 130.3 (q, ²*J*_{C-F} = 33.2 Hz), 129.7, 129.2, 126.2, 125.8, 123.6 (q, ¹*J*_{C-F} = 271.3 Hz), 123.3 (q, ¹*J*_{C-F} = 271.3 Hz), 122.0, 122.0, 82.7, 63.4, 63.1, 59.6, 32.5, 30.7, 30.7, 27.4, 26.1, 26.0, 18.9, 18.5, -2.7, -3.3, -5.3. ¹⁹F NMR (470 MHz, CDCl₃) δ -62.8 (s), -63.0 (s). IR (neat) ν 3102, 2957, 2933, 2861, 1473, 1373, 1278, 1175, 1137, 837, 776, 682 cm⁻¹. HRMS (ESI) *m/z* calcd for C₃₆H₅₀F₁₂NO₂Si₂⁺ [*M* + *H*]⁺ 812.3183 found 812.3188.

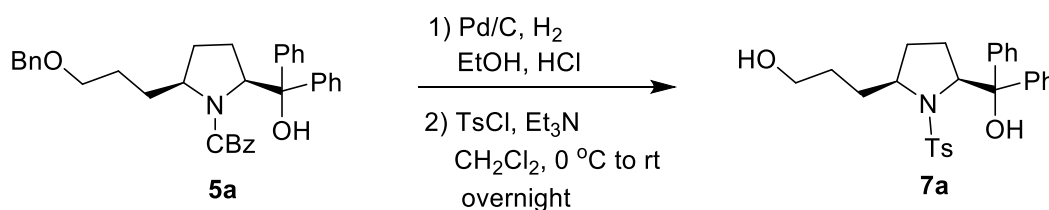
8. Experimental procedure for the synthesis of (2*S*,5*S*)-2-(((tert-butyl dimethylsilyl)oxy)diphenylmethyl)-5-(3-phenylpropyl)pyrrolidine (**6b**)



To a solution of **5a** (147 mg, 0.29 mmol, 1 equiv) in 6 N aqueous HCl (3 mL) in ethanol (15 mL) was added Pd/C 10% (32 mg, 0.03 mmol, 0.1 equiv), and the reaction mixture was vigorously stirred in the presence of hydrogen at atmospheric pressure for 16 h. After completion of the reaction (monitored by TLC), the reaction mass was filtered through Celite bed and concentrated under reduced pressure to get the crude residue as the hydrochloride salt. To this hydrochloride salt triturated in CH₂Cl₂ (15 mL), saturated aqueous solution of NaHCO₃ (15 mL) was added and stirred for 30 min at rt. The CH₂Cl₂ layer was separated, and the aqueous solution was extracted with CH₂Cl₂ (3 × 15 mL). The organic phases were combined, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product as a light-yellow oil which was used for the next step without further purification.

To a stirred solution of crude product in dry CH₂Cl₂ (3 mL), 2,6-lutidine (0.2 mL, 1.74 mmol, 6.0 equiv) was added dropwise at 0 °C, stirred for 15 minutes, and then TBSOTf (0.2 mL, 0.87 mmol, 3.0 equiv) was added slowly at the same temperature. Then, the reaction mixture was stirred for 20 h at rt. After completion of the reaction (monitored by TLC), the reaction was quenched by the careful addition of a saturated aqueous solution of NH₄Cl (15 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The organic phases were combined and washed with a solution of KOH (30 mL of 1 M solution) and brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product **6b**, which was purified as a colorless liquid (80 mg, 57% yield) using flash column chromatography [Silica gel, hexane/EtOAc (97:03) + 0.5% Et₃N]. *R_f* = 0.7 [hexane/EtOAc (80/20)]. [*α*]_D²³ = -31.2 (*c* = 0.5, CHCl₃ for **6b**). ¹H NMR (500 MHz, CDCl₃) δ 7.54-7.52 (m, 2H), 7.35-7.33 (m, 2H), 7.27-7.22 (m, 8H), 7.17-7.12 (m, 3H), 4.05 (t, *J* = 10.0 Hz, 1H), 3.05-3.00 (m, 1H), 2.54 (t, *J* = 10 Hz, 2H), 1.70-1.48 (m, 6H), 1.39-1.30 (m, 1H), 1.21-1.12 (m, 1H), 0.94 (s, 9H), 0.46-0.38 (m, 1H), -0.25 (s, 3H), -0.46 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 146.4, 145.0, 142.8, 129.6, 128.8, 128.5, 128.4, 127.7, 127.1, 126.93, 126.86, 125.7, 83.1, 65.0, 59.8, 36.2, 35.8, 31.0, 29.3, 27.6, 26.5, 19.1, -2.6, -3.1. IR (neat) ν 3060, 3026, 2928, 2855, 1698, 1602, 1446, 1252, 1065, 871, 834, 774, 748, 699 cm⁻¹. HRMS (ESI) *m/z* calcd for C₃₂H₄₄NOSi⁺ [*M* + *H*]⁺ 486.3187, found 486.3192.

9. Experimental procedure for the synthesis of 3-((2*R*,5*S*)-5-(hydroxydiphenylmethyl)-1-tosylpyrrolidin-2-yl)propan-1-ol (**7a**)



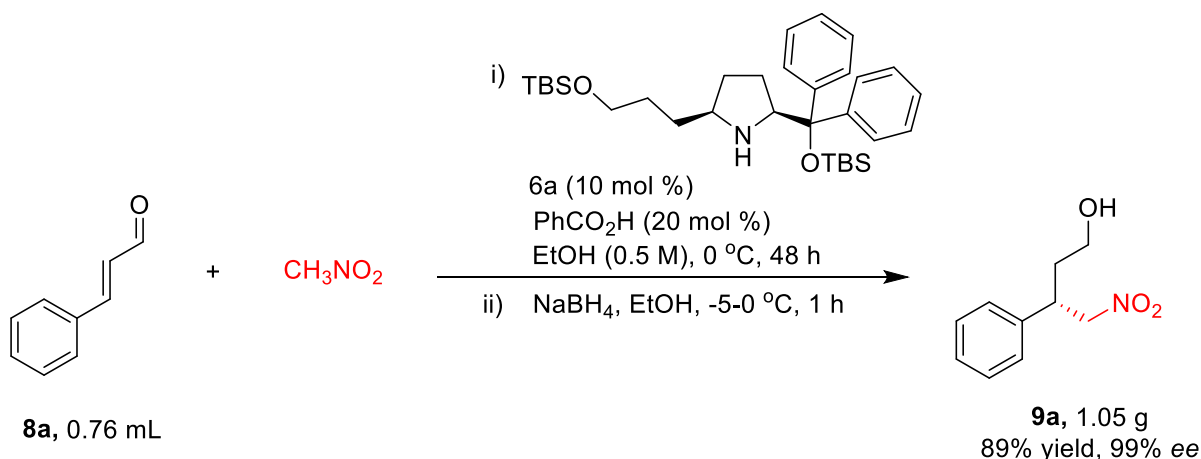
To a solution of *cis*-5-benzyloxypropyl diphenylprolinol **5a** (50 mg, 0.09 mmol, 1 equiv) in 6 N aqueous HCl (1 mL) in ethanol (5 mL) was added Pd/C 10% (20 mg, 0.02 mmol, 0.2 equiv), and the reaction mixture was vigorously stirred in the presence of hydrogen at atmospheric pressure for 16 h at rt. After completion of the reaction (monitored by TLC), the reaction mass was filtered through Celite bed and concentrated under reduced pressure to get the crude product as the hydrochloride salt. To the hydrochloride salt triturated in CH₂Cl₂ (10 mL), saturated aqueous solution of NaHCO₃ (10 mL) was added, and stirred for 30 min at rt. The CH₂Cl₂ layer was separated and the aqueous solution was extracted with CH₂Cl₂ (3 x 10 mL). The organic phases were combined, dried over anhydrous MgSO₄, and concentrated under reduced pressure to get the crude product as a light-yellow oil which was used for the next step without further purification.

To the crude product in dry CH₂Cl₂ (1 mL) was added Et₃N (140 μL, 0.93 mmol, 10 equiv) and TsCl (21 mg, 0.11 mmol, 1.2 equiv) at 0 °C. The reaction mixture was stirred for 12 h at rt. After completion of the reaction (monitored by TLC), the reaction mass was quenched with water and the aqueous phase was extracted with CH₂Cl₂ (3 x 15 mL). The organic phases were combined, and washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to get crude product **7a**, which was purified as white solid (31 mg, 71% yield) using flash column chromatography [Silica gel, hexane/EtOAc (65:35)]. *R_f* = 0.3 [hexane/EtOAc (50:50)]. **M.P.** 75-78 °C. [*α*]_D²¹ = -26.0 (*c* = 1.0, CHCl₃ for **7a**). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 1.5 Hz, 2H), 7.42-7.27 (m, 10H), 4.89 (s, 1H), 4.72 (q, *J* = 3.0 Hz, 1H), 3.56-3.46 (m, 3H), 2.46 (s, 3H), 1.93-1.87 (m, 1H), 1.76-1.60 (m, 3H), 1.42-1.26 (m, 3H), 1.01-0.93 (m, 1H), 0.63-0.57 (m, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 146.4, 144.3, 143.8, 133.9, 130.0, 128.9, 128.2, 128.1, 127.7, 127.6, 127.42, 127.39, 79.3, 68.9, 63.3, 62.7, 32.5, 30.2, 29.7, 29.0, 21.7. **IR** (neat) *ν* 3460, 2926, 1598, 1494, 1448, 1337, 1153, 1090, 1043, 990, 816, 760, 702, 672, 590, 553 cm⁻¹. **HRMS** (ESI) *m/z* calcd for C₂₇H₃₁NO₄SNa⁺ [*M* + Na]⁺ 488.1866 found 488.1889.

10. Reaction optimization for the synthesis of *γ*-nitroalcohol **9a**

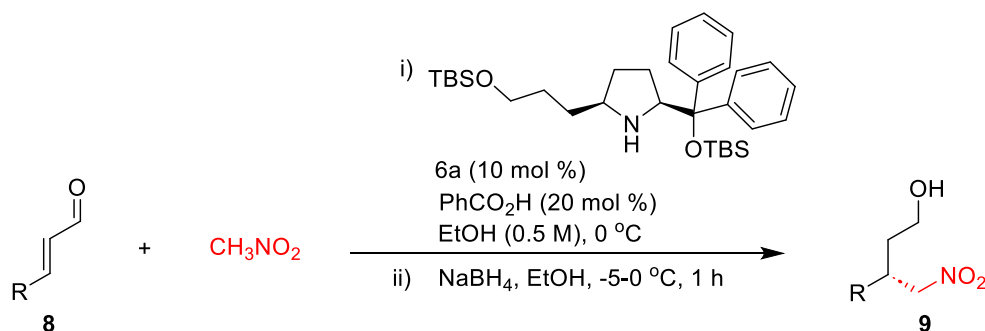
To a solution of organocatalyst **6a-d** (0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv), in EtOH (400 μL, 0.5 M), cinnamaldehyde **8a** (25 μL, 0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) were added at the temperature mentioned in Table 1 (in manuscript) and stirred under argon atmosphere for the given time. After completion of the reaction (monitored by ¹H NMR), to a cooled solution (-5 °C) of NaBH₄ (7 mg, 0.18 mmol, 1 equiv) in EtOH (1.6 mL), a solution of the reaction mixture diluted with EtOH (0.8 mL) was added dropwise. The reaction was stirred for 15 min at -5 °C and 1 h at 0 °C. Then the reaction mass was quenched with pieces of ice, distilled the ethanol over the rota evaporator, washed with a saturated aqueous solution of NaHCO₃ (10 mL), and extracted with EtOAc (3 x 20 mL). The organic phases were combined, washed with brine (15 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to get the crude product **9a**, which was further purified by flash column chromatography.

11. Experimental procedure for gram-scale synthesis of *γ*-nitroalcohol **9a**



To a solution of organocatalyst **6a** (326 mg, 0.6 mmol, 0.1 equiv), and benzoic acid (148 mg, 1.21 mmol, 0.2 equiv), cinnamaldehyde **8a** (0.76 mL, 6.0 mmol, 1 equiv) in EtOH (12 mL, 0.5 M), CH_3NO_2 (6.4 mL, 120.0 mmol, 20 equiv) were added dropwise at 0 °C and stirred under argon atmosphere for 48 h. After completion of the reaction (monitored by ^1H NMR), to a cooled solution (-5 °C) of NaBH_4 (1.15 g, 30.0 mmol, 5 equiv) in EtOH (50 mL), a solution of the reaction mixture diluted with EtOH (10 mL) was added dropwise. The reaction was stirred for 15 min at -5 °C and 1.5 h at 0 °C. Then the reaction mass was quenched with ice, distilled the ethanol over the rota evaporator, washed with a saturated aqueous solution of NaHCO_3 (60 mL), and extracted with EtOAc (4 × 50 mL). The organic phases were combined, washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure to get the crude product, which was purified by flash column chromatography [Silica gel, hexane/EtOAc (75:25)]. $R_f = 0.2$ [hexane /EtOAc (70:30)] to provide product **9a** as a yellow liquid (1.05 g, 89% yield).

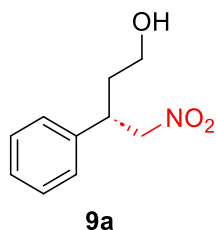
12. Experimental procedure for the synthesis of γ -nitroalcohols **9a-k**



To a solution of organocatalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv), in EtOH (400 μL , 0.5 M), α,β -unsaturated aldehyde **8** (0.2 mmol, 1 equiv) and CH_3NO_2 (214 μL , 4.0 mmol, 20 equiv) were added at 0 °C and stirred under argon atmosphere for the given time mentioned in Scheme 3 (in manuscript). After completion of the reaction (monitored by ^1H NMR), to a cooled solution (-5 °C) of NaBH_4 (7 mg, 0.18 mmol, 1 equiv) in EtOH (1.6 mL), a solution of the reaction mixture diluted with EtOH (0.8 mL) was added dropwise. The reaction was stirred for 15 min at -5 °C and 1 h at 0 °C. Then the reaction mass was quenched with pieces of ice, distilled the ethanol over the rota evaporator, washed with a saturated aqueous solution of NaHCO_3 (10 mL), and extracted with EtOAc (3 × 20 mL). The organic phases were combined, washed with brine (15 mL), dried over Na_2SO_4 , and

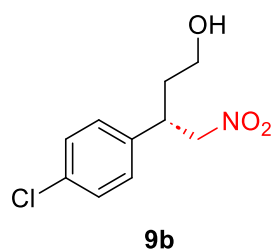
concentrated under reduced pressure to get the crude product **9**, which was further purified by flash column chromatography.

(*S*)-4-Nitro-3-phenylbutan-1-ol (**9a**)



Following the experimental procedure, cinnamaldehyde **8a** (25 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9a** which was purified as a colorless liquid (36 mg, 91% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (75:25)]. $R_f = 0.2$ [hexane/EtOAc (70:30)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm \times 250 mm (hex/IPA = 90:10, 1.0 mL/min, 210 nm), t_R (minor) = 16.5 min, t_R (major) = 19.4 min, >99% *ee*. $[\alpha]_D^{22} = -18.0$ ($c = 1.0$, CH_2Cl_2 for **9a** of >99% *ee*), lit.⁴ $[\alpha]_D^{25} = -13.7$ ($c = 0.5$, CH_2Cl_2 for **9a** of 96% *ee*). ^1H NMR (500 MHz, CDCl_3) δ : 7.35-7.20 (m, 5H), 4.67-4.57 (m, 2H), 3.72-3.65 (m, 1H), 3.61-3.56 (m, 1H), 3.48-3.44 (m, 1H), 1.99-1.86 (m, 2H), 1.75 (bs, 1H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ : 139.0, 129.2, 127.9, 127.7, 80.7, 59.9, 41.2, 35.7. IR (neat) ν 3374, 2922, 1548, 1455, 1380, 1047, 765, 701. NMR data of **9a** match with that reported in the literature.⁵

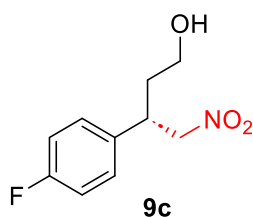
(*S*)-3-(4-chlorophenyl)-4-nitrobutan-1-ol (**9b**)



Following the experimental procedure, *trans*-4-chlorocinnamaldehyde **8b** (33 mg, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9b** which was purified as a colorless liquid (37 mg, 80% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (75:25)]. $R_f = 0.3$ [hexane/EtOAc (70:30)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm \times 250 mm (hex/IPA = 80:20, 1.0 mL/min, 210 nm), t_R (minor) = 8.7 min, t_R (major) = 9.6 min, 99% *ee*. $[\alpha]_D^{26} = -26.2$ ($c = 1.0$, CHCl_3 for **9b** of 99% *ee*), lit.⁶ $[\alpha]_D^{18} = +23.0$ ($c = 1.0$, CHCl_3 for (+)-**9b** of 95% *ee*). ^1H NMR (500 MHz, CDCl_3) δ : 7.31 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.5$ Hz, 2H), 4.67-4.55 (m, 2H), 3.72-3.66 (m, 1H), 3.62-3.58 (m, 1H), 3.47-3.42 (m, 1H), 1.98-1.91 (m, 1H), 1.88-1.81 (m, 1H), 1.71 (bs, 1H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ : 137.5, 133.7, 129.3,

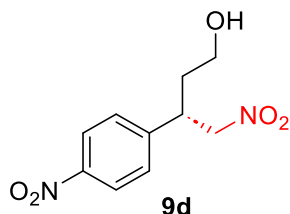
129.1, 80.5, 59.7, 40.5, 35.6. **IR** (neat) ν 3369, 2938, 1550, 1493, 1380, 1094, 1048, 1015, 828. *NMR data of 9b match with that reported in the literature.*⁵

(S)-3-(4-fluorophenyl)-4-nitrobutan-1-ol (9c)



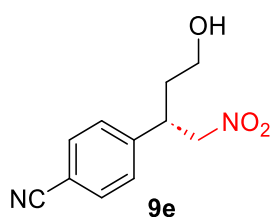
Following the experimental procedure, *trans*-4-fluorocinnamaldehyde **8c** (26 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9c** which was purified as a colorless liquid (32 mg, 75% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (75:25)]. $R_f = 0.4$ [hexane/EtOAc (50:50)]. **HPLC** analysis Daicel Chiralcel IC, 4.6 mm \times 250 mm (hex/IPA = 90:10, 1.0 mL/min, 210 nm), t_R (minor) = 15.6 min, t_R (major) = 18.3 min, 99% *ee*. $[\alpha]_D^{26} = -25.8$ ($c = 0.5$, CH_2Cl_2 for **9c** of 99% *ee*) lit.⁷ $[\alpha]_D^{25} = -10.0$ ($c = 1.0$, CH_2Cl_2 for **9c** of 94% *ee*). **¹H NMR** (500 MHz, CDCl_3) δ : 7.21-7.18 (m, 2H), 7.03 (t, $J = 8.5$ Hz, 2H), 4.67-4.55 (m, 2H), 3.74-3.68 (m, 1H), 3.64-3.59 (m, 1H), 3.49-3.44 (m, 1H), 1.98-1.83- (m, 2H), 1.63 (bs, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl_3) δ : 162.3 (d, $^1J_{\text{C-F}} = 245.0$ Hz), 134.7 (d, $^4J_{\text{C-F}} = 2.5$ Hz), 129.3 (d, $^3J_{\text{C-F}} = 8.8$ Hz), 116.1 (d, $^2J_{\text{C-F}} = 21.3$ Hz), 80.7, 59.8, 40.5, 35.7. **¹⁹F NMR** (470 MHz, CDCl_3) δ : -114.4. **IR** (neat) ν 3370, 2941, 1605, 1549, 1511, 1381, 1225, 1048, 836, 552. *NMR data of 9c match with that reported in the literature.*⁷

(S)-4-nitro-3-(4-nitrophenyl)butan-1-ol (9d)



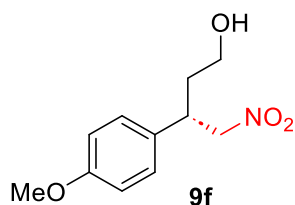
Following the experimental procedure, *trans*-4-nitrocinnamaldehyde **8d** (35 mg, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9d** which was purified as a colorless liquid (39 mg, 82% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (55:45)]. $R_f = 0.3$ [hexane/EtOAc (50:50)]. **HPLC** analysis Daicel Chiralcel IC, 4.6 mm \times 250 mm (hex/IPA = 80:10, 1.0 mL/min, 210 nm), t_R (minor) = 44.7 min, t_R (major) = 48.9 min, 99% *ee*. $[\alpha]_D^{30} = -5.7$ ($c = 1.0$, CHCl_3 for **9d** of 99% *ee*), lit.⁶ $[\alpha]_D^{18} = +7.0$ ($c = 1.0$, CHCl_3 for (+)-**9d** of 95% *ee*). **¹H NMR** (500 MHz, CDCl_3) δ : 8.18 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 4.78-4.64 (m, 2H), 3.91-3.85 (m, 1H), 3.67-3.63 (m, 1H), 3.48-3.44 (m, 1H), 2.05-2.01 (m, 1H), 2.00-1.87 (m, 1H), 1.81 (bs, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl_3) δ : 147.5, 146.9, 128.8, 124.3, 79.8, 59.4, 40.9, 35.4. **IR** (neat) ν 3383, 2926, 1600, 1549, 1518, 1346, 1047, 858, 700. *NMR data of 9d match with that reported in the literature.*⁵

(S)-4-(4-hydroxy-1-nitrobutan-2-yl)benzonitrile (**9e**)



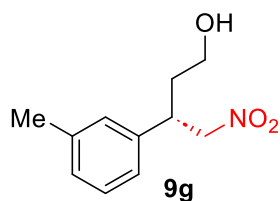
Following the experimental procedure, *trans*-4-cyanocinnamaldehyde **8e** (31 mg, 0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9e** which was purified as a colorless liquid (23 mg, 52% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (65:35)]. $R_f = 0.5$ [hexane /EtOAc (30:70)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm × 250 mm (hex/IPA = 80:20, 1.0 mL/min, 210 nm), t_R (minor) = 20.4 min, t_R (major) = 21.8 min, 99% *ee*. $[\alpha]_D^{24} = -5.5$ ($c = 1.0$, CHCl₃ for **9e** of 99% *ee*). ¹H NMR (500 MHz, CDCl₃) δ: 7.64 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 4.75-4.61 (m, 2H), 3.86-3.80 (m, 1H), 3.67-3.63 (m, 1H), 3.49-3.44 (m, 1H), 2.04-1.97 (m, 1H), 1.92-1.86 (m, 1H), 1.57 (s, 1H). ¹³C {¹H} NMR (126 MHz, CHCl₃) δ: 144.8, 132.9, 128.7, 118.5, 111.9, 79.9, 59.5, 41.1, 35.4. IR (neat) ν 3408, 2950, 2231, 1551, 1436, 1380, 1049, 838, 570. HRMS (ESI) m/z calcd for C₁₁H₁₁N₂O₃⁻ [M - H]⁻ 219.0775, found 219.0774.

(S)- 3-(4-methoxyphenyl)-4-nitrobutan-1-ol (**9f**)



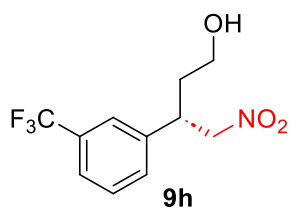
Following the experimental procedure, *trans*-4-methoxycinnamaldehyde **8f** (32 mg, 0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9f** which was purified as a colorless liquid (33 mg, 74% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (73:27)]. $R_f = 0.4$ [hexane /EtOAc (50:50)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm × 250 mm (hex/IPA = 90:20, 1.0 mL/min, 210 nm), t_R (minor) = 15.5 min, t_R (major) = 18.0 min, 99% *ee*. $[\alpha]_D^{22} = -23.3$ ($c = 1.0$, CH₂Cl₂ for **9f** of 99% *ee*), lit.⁵ $[\alpha]_D^{25} = -22.8$ ($c = 0.5$, CH₂Cl₂ for **9f** of 96% *ee*). ¹H NMR (500 MHz, CDCl₃) δ: 7.13 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 4.63-4.52 (m, 2H), 3.78 (s, 3H), 3.66-3.57 (m, 2H), 3.49-3.44 (m, 1H), 1.96-1.82 (m, 2H), 1.73 (bs, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ: 159.1, 130.8, 128.7, 114.5, 81.0, 60.0, 55.4, 40.5, 35.8. IR (neat) ν 3382, 2938, 1612, 1548, 1514, 1381, 1249, 1181, 1031, 832. NMR data of **9f** match with that reported in the literature.⁵

(S)-4-nitro-3-(*m*-tolyl)butan-1-ol (**9g**)



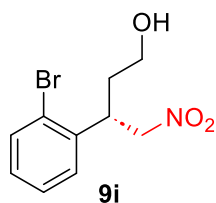
Following the experimental procedure, *trans*-3-methylcinnamaldehyde **8g** (29 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9g** which was purified as a colorless liquid (23 mg, 78% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (77:23)]. $R_f = 0.5$ [hexane /EtOAc (50:50)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm \times 250 mm (hex/IPA = 90:10, 1.0 mL/min, 210 nm), t_R (minor) = 19.8 min, t_R (major) = 23.0 min, 99% *ee*. $[\alpha]_D^{23} = -20.1$ ($c = 1.0$, CHCl_3 for **9g** of 99% *ee*). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.22 (t, $J = 8.0$ Hz, 1H), 7.09-7.07 (m, 1H), 7.02-7.00 (m, 2H), 4.66-4.56 (m, 2H), 3.68-3.57 (m, 2H), 3.50-3.45 (m, 1H), 2.33 (s, 3H), 1.99-1.86 (m, 2H), 1.71 (bs, 1H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 138.9, 138.8, 129.0, 128.7, 128.4, 124.6, 80.8, 60.0, 41.1, 35.7, 21.5. IR (neat) ν 3368, 2924, 1549, 1434, 1380, 1048, 787, 706. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3^-$ [$\text{M} - \text{H}$] 208.0979, found 208.0996.

(S)-4-nitro-3-(3-(trifluoromethyl)phenyl)butan-1-ol (9h)



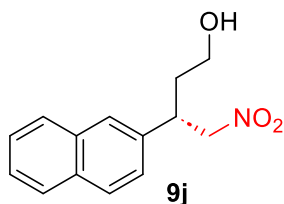
Following the experimental procedure, *trans*-3-trifluoromethylcinnamaldehyde **8h** (32 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9h** which was purified as a colorless liquid (37 mg, 70% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (72:28)]. $R_f = 0.4$ [hexane /EtOAc (50:50)]. HPLC analysis Daicel Chiralcel AS-H, 4.6 mm \times 250 mm (hex/IPA = 80:20, 1.0 mL/min, 210 nm), t_R (major) = 7.5 min, t_R (minor) = 10.4 min, 99% *ee*. $[\alpha]_D^{24} = -12.1$ ($c = 1.0$, CHCl_3 for **9h** of 99% *ee*). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.55 (d, $J = 7.5$ Hz, 1H), 7.49-7.42 (m, 3H), 4.73-4.61 (m, 2H), 3.85-3.79 (m, 1H), 3.66-3.62 (m, 1H), 3.50-3.45 (m, 1H), 2.04-1.95 (m, 1H), 1.94-1.88 (m, 1H), 1.78 (bs, 1H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 140.2, 131.5 (q, $^2J_{\text{C-F}} = 31.3$ Hz), 131.2, 129.7, 124.9 (q, $^3J_{\text{C-F}} = 3.8$ Hz), 124.4 (q, $^3J_{\text{C-F}} = 3.8$ Hz), 124.0 (q, $^1J_{\text{C-F}} = 270.0$ Hz), 80.2, 59.6, 40.9, 35.6. $^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ : -62.6. IR (neat) ν 3370, 2935, 1553, 1380, 1328, 1165, 1124, 1075, 806, 704. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{NO}_3^-$ [$\text{M} - \text{H}$] 262.0697, found 262.0697.

(S)-3-(2-bromophenyl)-4-nitrobutan-1-ol (9i)



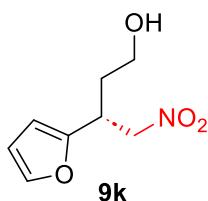
Following the experimental procedure, *trans*-2-bromocinnamaldehyde **8i** (42 mg, 0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9i** which was purified as a colorless liquid (44 mg, 81% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (80:20)]. *R_f* = 0.4 [hexane /EtOAc (70:30)]. **HPLC** analysis Daicel Chiralcel IC, 4.6 mm × 250 mm (hex/IPA = 90:10, 1.0 mL/min, 210 nm), *t_R* (minor) = 17.9 min, *t_R* (major) = 21.3 min, 99% *ee*. [α]_D²⁸ = -4.4 (*c* = 0.5, MeOH for **9i** of 99% *ee*), lit.⁵ [α]_D²⁵ = -3.6 (*c* = 0.92, MeOH for **9i** of 82% *ee*). **¹H NMR** (500 MHz, CDCl₃) δ : 7.61-7.59 (m, 1H), 7.34-7.31 (m, 1H), 7.26-7.23 (m, 1H), 7.17-7.13 (m, 1H), 4.74-4.66 (m, 2H), 4.32-4.26 (m, 1H), 3.66-3.55 (m, 2H), 2.06-1.98 (m, 2H), 1.68 (bs, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃) δ : 138.2, 133.8, 129.3, 128.2, 79.2, 60.0, 39.8, 35.1. **IR** (neat) ν 3368, 2928, 1551, 1473, 1433, 1379, 1024, 757, 659. *NMR data of 9i match with that reported in the literature.*⁵

(*S*)-3-(naphthalen-2-yl)-4-nitrobutan-1-ol (**9j**)



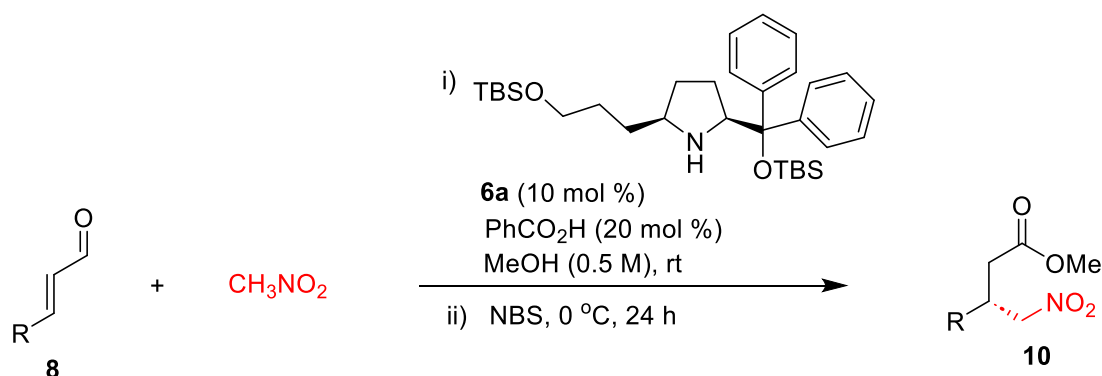
Following the experimental procedure, (*E*)-3-(naphthalen-2-yl)acrylaldehyde **8j** (36 mg, 0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9j** which was purified as a colorless liquid (41 mg, 83% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (70:30)]. *R_f* = 0.4 [hexane /EtOAc (50:50)]. **HPLC** analysis Daicel Chiralcel IC, 4.6 mm × 250 mm (hex/IPA = 90:10, 1.0 mL/min, 210 nm), *t_R* (minor) = 18.2 min, *t_R* (major) = 19.5 min, 99% *ee*. [α]_D²⁷ = -18.7 (*c* = 1.0, CHCl₃ for **9j** of 99% *ee*). **¹H NMR** (500 MHz, CDCl₃) δ : 7.83-7.78 (m, 3H), 7.66 (s, 1H), 7.49-7.46 (m, 2H), 7.33-7.31 (m, 1H), 4.73-4.65 (m, 2H), 3.87-3.84 (m, 1H), 3.61-3.57 (m, 1H), 3.48-3.44 (m, 1H), 2.02-1.97 (m, 2H), 1.59 (bs, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃) δ : 136.3, 133.5, 132.9, 129.1, 127.9, 127.8, 127.1, 126.6, 126.3, 125.0, 80.7, 59.9, 41.3, 35.6. **IR** (neat) ν 3372, 2953, 1549, 1379, 1048, 821, 751, 479. **HRMS** (ESI) *m/z* calcd for C₁₄H₁₅NO₃Na⁺ [*M* + Na]⁺ 268.0944, found 268.0944.

(*R*)-3-(furan-2-yl)-4-nitrobutan-1-ol (**9k**)



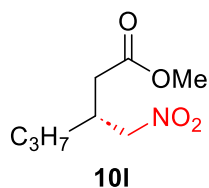
Following the experimental procedure, (*E*)-3-(furan-2-yl)acrylaldehyde **8k** (24 mg, 0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **9k** which was purified as a colorless liquid (28 mg, 75% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (70:30)]. *R_f* = 0.4 [hexane/EtOAc (50:50)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm × 250 mm (hex/IPA = 90:10, 1.0 mL/min, 210 nm), *t_R* (minor) = 15.1 min, *t_R* (major) = 16.9 min, 98% *ee*. [*α*]_D²⁴ = -5.5 (*c* = 1.0, MeOH for **9k** of 98% *ee*), lit.⁵ [*α*]_D²⁵ = -5.7 (*c* = 0.55, MeOH for **9k** of 84% *ee*). ¹H NMR (500 MHz, CDCl₃) δ: 7.35 (q, *J* = 1.0 Hz, 1H), 6.30 (q, *J* = 1.5 Hz, 1H), 6.18 (d, *J* = 3.0 Hz, 1H), 4.69-4.60 (m, 2H), 3.88-3.82 (m, 1H), 3.70-3.66 (m, 1H), 3.59-3.54 (m, 1H), 2.02-1.88 (m, 2H), 1.68 (bs, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ: 152.1, 142.5, 110.5, 107.6, 78.4, 59.9, 35.0, 33.7. IR (neat) ν 3367, 2951, 1552, 1379, 1048, 1012, 740. NMR data of **9k** match with that reported in the literature.⁵

13. Experimental procedure for the synthesis of *γ*-nitroesters 10l-o



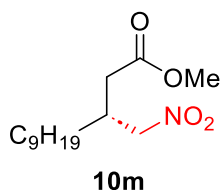
To a solution of organocatalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv), in MeOH (400 μL, 0.5 M), *α,β*-unsaturated aldehyde **8** (0.2 mmol, 1 equiv) and CH₃NO₂ (214 μL, 4.0 mmol, 20 equiv) were added at rt and stirred under argon atmosphere for the given time mentioned in figure 3 (in manuscript). After completion of the reaction (monitored by ¹H NMR), to a cooled (0 °C) solution of the reaction mixture, N-Bromosuccinimide (NBS) (53 mg, 0.3 mmol, 1.5 equiv) was added. The reaction was stirred at 0 °C for 24 h. Then MeOH was evaporated over the rota evaporator and reaction mass was directly purified by flash column chromatography to get the product **10**.

(*R*)-methyl-3-(nitromethyl)hexanoate (10l)



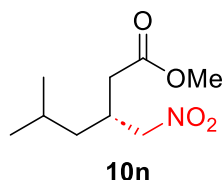
Following the experimental procedure, (*E*)-hex-2-enal **8l** (23 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **10l** which was purified as a colourless liquid (19 mg, 50% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/ Et_2O (90:10)]. $R_f = 0.5$ [hexane/ EtOAc (90:10)]. **HPLC** analysis Daicel Chiralcel AS-H, 4.6 mm \times 250 mm (hex/IPA = 97:03, 1.0 mL/min, RID detector), t_R (minor) = 14.2 min, t_R (major) = 17.5 min, 96% *ee*. $[\alpha]_D^{23} = -1.6$ ($c = 0.5$, CHCl_3 for **10l** of 96% *ee*). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 4.52-4.42 (m, 2H), 3.69 (s, 3H), 2.66-2.61 (m, 1H), 2.45 (d, $J = 6.5$ Hz, 2H), 1.39-1.38 (m, 4H), 0.94-0.91 (m, 3H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 172.1, 78.6, 51.9, 35.7, 34.0, 33.6, 19.7, 13.9. **IR** (cm^{-1}) ν 2958, 2925, 2871, 1736, 1546, 1432, 1378, 1172. **HRMS** (ESI) m/z calcd for $\text{C}_8\text{H}_{16}\text{NO}_4^+$ $[\text{M} + \text{H}]^+$ 190.1074, found 190.1077.

(*R*)-methyl-3-(nitromethyl)dodecanoate (**10m**)



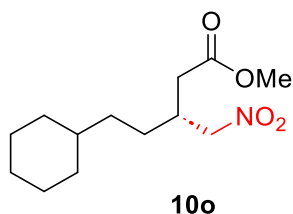
Following the experimental procedure, (*E*)-dodec-2-enal **8m** (43 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **10m** which was purified as a colourless liquid (32 mg, 58% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/ Et_2O (90:10)]. $R_f = 0.4$ [hexane/ EtOAc (90:10)]. **HPLC** analysis Daicel Chiralcel AS-H, 4.6 mm \times 250 mm (hex/IPA = 99:1, 1.0 mL/min, RID detector), t_R (minor) = 9.1 min, t_R (major) = 10.3 min, 95% *ee*. $[\alpha]_D^{28} = -0.6$ ($c = 2.0$, CHCl_3 for **10m** of 95% *ee*). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 4.52-4.42 (m, 2H), 3.69 (s, 3H), 2.64-2.59 (m, 1H), 2.45 (d, $J = 6.5$ Hz, 2H), 1.41-1.38 (m, 2H), 1.29-1.25 (m, 14H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 172.1, 78.6, 51.9, 35.7, 34.3, 31.9, 31.5, 29.6, 29.5, 29.3, 26.5, 22.7, 14.2. **IR** (cm^{-1}) ν 2927, 2857, 1733, 1550, 1433, 1374, 1197, 1168. **HRMS** (ESI) m/z calcd for $\text{C}_{14}\text{H}_{28}\text{NO}_4^+$ $[\text{M} + \text{H}]^+$ 274.2013, found 274.2004.

(*R*)-methyl-5-methyl-3-(nitromethyl)hexanoate (**10n**)



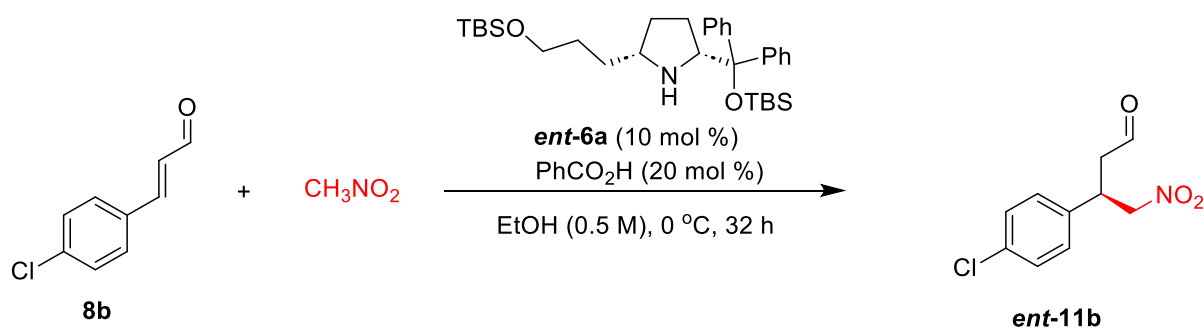
Following the experimental procedure, (*E*)-5-methylhex-2-enal **8n** (27 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **10n** which was purified as a colourless liquid (20 mg, 49% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/Et₂O (90:10)]. R_f = 0.5 [hexane/EtOAc (95:05)]. **HPLC** analysis Daicel Chiralcel IG column, 4.6 mm \times 250 mm (hex/IPA = 99:1, 1.0 mL/min, RID detector), t_R (minor) = 19.8 min, t_R (major) = 16.8 min, 96% *ee*. $[\alpha]_D^{28}$ = -6.6 (c = 1.0, CHCl_3 for **10n** of 96% *ee*), lit.¹⁰ $[\alpha]_D^{25}$ = -7.2 (c = 1.31, CHCl_3 for **10n** of 79% *ee*). **¹H NMR** (500 MHz, CDCl_3) δ : 4.52-4.42 (m, 2H), 3.69 (s, 3H), 2.70-2.65 (m, 1H), 2.44 (d, J = 6.5 Hz, 2H), 1.66-1.62 (m, 1H), 1.27-1.24 (m, 2H), 0.93-0.90 (m, 6H). **¹³C {¹H} NMR** (126 MHz, CDCl_3) δ : 172.1, 78.8, 51.9, 40.6, 35.8, 32.2, 25.1, 22.6, 22.3. **IR** (cm^{-1}) ν 2962, 2923, 2872, 2850, 1737, 1551, 1467, 1383, 1175. *NMR data of 9a match with that reported in the literature.*¹⁰

(*R*)-methyl-4-cyclohexyl-3-(nitromethyl)butanoate (**10o**)



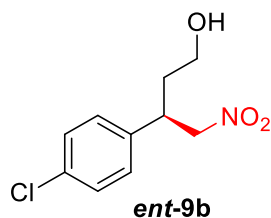
Following the experimental procedure, (*E*)-5-cyclohexylpent-2-enal **8o** (37 μ L, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μ L, 4.0 mmol, 20 equiv) in the presence of the catalyst **6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv) were transformed into the product **10o** which was purified as a colourless liquid (28 mg, 55% yield) from the crude reaction mixture using flash column chromatography [Silica gel, hexane/EtOAc (95:5)]. R_f = 0.4 [hexane/EtOAc (95:05)]. **HPLC** analysis Daicel Chiralcel IA, 4.6 mm \times 250 mm (hex/IPA = 99:01, 1.0 mL/min, RID detector), t_R (major) = 13.3 min, t_R (minor) = 14.5 min, 97% *ee*. $[\alpha]_D^{23}$ = -3.8 (c = 0.5, CHCl_3 for **10o** of 97% *ee*). **¹H NMR** (500 MHz, CDCl_3) δ : 4.51-4.42 (m, 2H), 3.69 (s, 3H), 2.59-2.56 (m, 1H), 2.44 (d, J = 6.5 Hz, 2H), 1.68-1.61 (m, 5H), 1.42-1.40 (m, 2H), 1.23-1.16 (m, 6H), 0.87-0.80 (m, 2H). **¹³C {¹H} NMR** (126 MHz; CDCl_3) δ : 172.1, 78.6, 51.9, 37.6, 35.7, 34.5, 34.1, 33.3, 33.3, 28.8, 26.6, 26.3. **IR** (cm^{-1}) ν 2918, 2851, 1739, 1549, 1438, 1371, 1197, 1169. **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{24}\text{NO}_4^+$ [$\text{M} + \text{H}$]⁺ 258.1700, found 258.1696.

14. Experimental procedure for the synthesis of (*R*)-3-(4-chlorophenyl)-4-nitrobutanal (*ent*-**11b**)



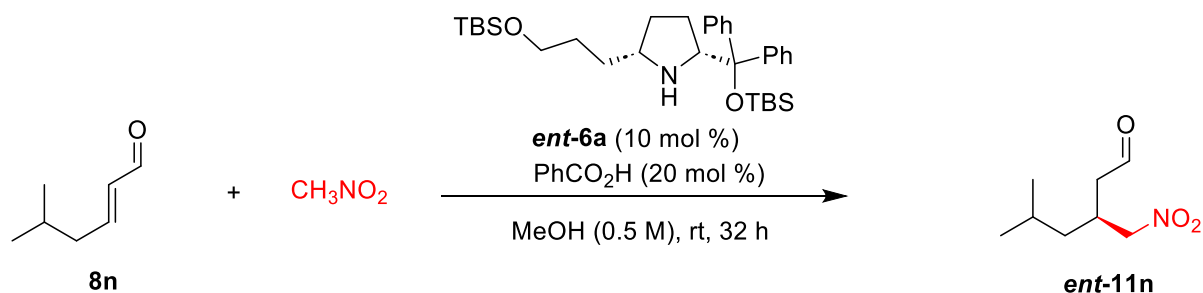
To a solution of organocatalyst **ent-6a** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv), in EtOH (400 μL , 0.5 M), *trans*-4-chlorocinnamaldehyde **8b** (33 mg, 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μL , 4.0 mmol, 20 equiv) were added at 0 °C and stirred under argon atmosphere for 32 h. After completion of the reaction (monitored by ^1H NMR), EtOH was concentrated under reduced pressure, washed with saturated aqueous solution of NaHCO_3 (10 mL), and extracted with EtOAc (3 x 20 mL). The organic phases were combined, washed with brine (15 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to get the crude product **ent-11b**, which was further purified by flash column chromatography using [Silica gel, hexane/EtOAc (80:20)]. $R_f = 0.4$ [hexane/EtOAc (70:30)] as colourless liquid (42 mg, 92% yield). $[\alpha]_D^{19} = +4.6$ ($c = 0.5$, CHCl_3), lit.⁸ $[\alpha]_D^{26} = +20.3$ ($c = 1.0$, CHCl_3 for (+)-**11b** of 90% *ee*). ^1H NMR (500 MHz, CDCl_3) δ : 9.71 (t, $J = 1.0$ Hz, 1H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 4.69-4.57 (m, 2H), 4.09-4.04 (m, 1H), 2.94 (dd, $J = 7.0, 1.0$ Hz, 2H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 198.5, 136.8, 134.1, 129.5, 128.9, 79.2, 46.4, 37.4. IR (neat) ν 2924, 2853, 2739, 1721, 1548, 1494, 1378, 1094, 1014, 829, 535. NMR data of **ent-11b** match with that reported in the literature.⁹

(*R*)-3-(4-chlorophenyl)-4-nitrobutan-1-ol (**ent-9b**)



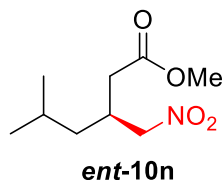
The product **ent-11b** (11 mg, 0.05 mmol, 1 equiv) in EtOH (1 mL) was added dropwise in cooled solution (-5 °C) of NaBH_4 (6 mg, 0.15 mmol, 3 equiv) in EtOH (1 mL). The reaction mixture was stirred for 15 min at -5 °C and 1 h at 0 °C. Then the reaction mass was quenched with pieces of ice, concentrated under reduced pressure, washed with saturated aqueous solution of NaHCO_3 (10 mL), and extracted with EtOAc (3 x 20 mL). The organic phases were combined, washed with brine (15 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to get the crude product **ent-9b**, which was further purified as colourless liquid (10 mg, 88% yield) using flash column chromatography [Silica gel, hexane/EtOAc (75:25)]. $R_f = 0.3$ [hexane/EtOAc (70:30)]. HPLC analysis Daicel Chiralcel IC, 4.6 mm x 250 mm (hex/IPA = 80:20, 1.0 mL/min, 210 nm), t_R (minor) = 9.8 min, t_R (major) = 8.8 min, 99% *ee*. $[\alpha]_D^{20} = +9.6$ ($c = 0.5$, CHCl_3 for (+)-**9b** of 99% *ee*), lit.⁶ $[\alpha]_D^{18} = +23.0$ ($c = 1.0$, CHCl_3 for (+)-**9b** of 95% *ee*).

15. Experimental procedure for the synthesis of (*S*)-5-methyl-3-(nitromethyl)hexanal (*ent*-11n)



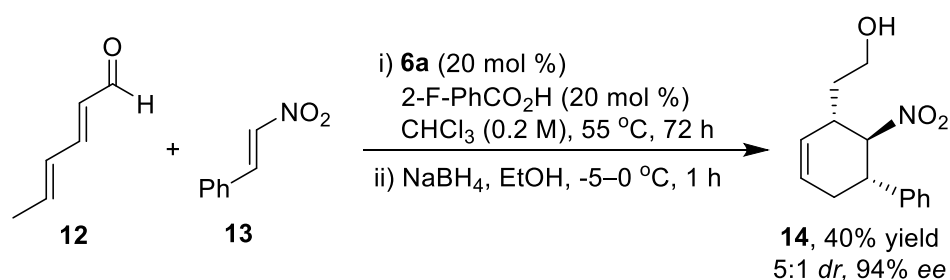
To a solution of organocatalyst **ent-6b** (11 mg, 0.02 mmol, 0.1 equiv), and benzoic acid (5 mg, 0.04 mmol, 0.2 equiv), in MeOH (400 μL , 0.5 M), (*E*)-5-methylhex-2-enal **8n** (27 μL , 0.2 mmol, 1 equiv) and CH_3NO_2 (214 μL , 4 mmol, 20 equiv) were added at rt and stirred under argon atmosphere for 32 h. After completion of the reaction (monitored by ^1H NMR), MeOH was concentrated under reduced pressure to get the crude product **ent-11n**, which was further purified as colourless liquid (18 mg, 51% yield) using flash column chromatography [Silica gel, hexane/ Et_2O (85:15)]. $R_f = 0.2$ [hexane/ EtOAc (95:05)]. $[\alpha]_{\text{D}}^{23} = +3.2$ ($c = 1.0$, CHCl_3 **ent-11n**), lit.⁹ $[\alpha]_{\text{D}}^{28} = -3.7$ ($c = 1.3$, CHCl_3 for (-)-**ent-11n**). ^1H NMR (500 MHz, CDCl_3) δ : 9.78 (s, 1H), 4.48-4.41 (m, 2H), 2.79-2.70 (m, 1H), 2.69-2.55 (m, 2H), 1.66-1.59 (m, 1H), 1.29-1.25 (m, 2H), 0.94-0.90 (m, 6H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 200.0, 78.6, 45.6, 40.7, 30.0, 25.2, 22.5. IR (cm^{-1}) ν 2959, 2876, 1734, 1548, 1434, 1380, 1177. NMR data of **ent-11n** match with that reported in the literature.⁹

(*S*)-methyl-5-methyl-3-(nitromethyl)hexanoate (*ent*-10n)



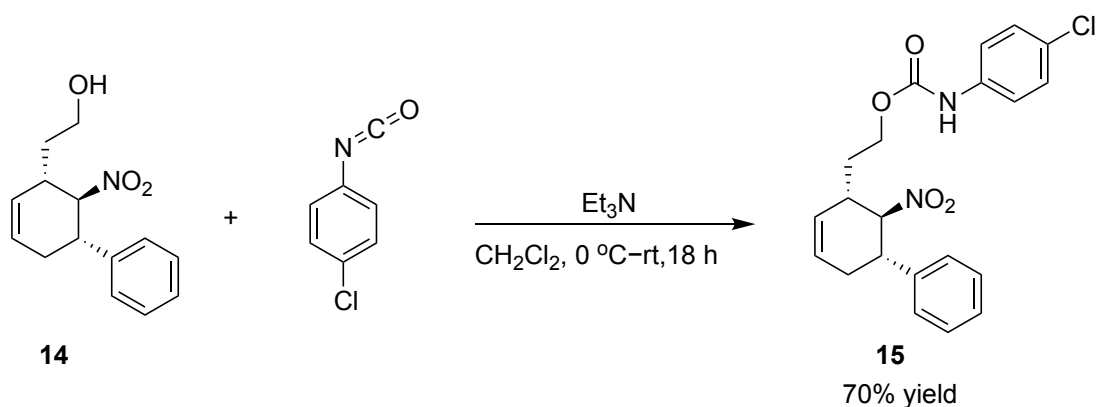
The product **ent-11n** (12 mg, 0.07 mmol, 1 equiv) in MeOH (1 mL) was cooled to 0 $^\circ\text{C}$ and NBS (19 mg, 0.11 mmol, 1.5 equiv) was added. The reaction mixture was stirred at 0 $^\circ\text{C}$ for 24 h. Then MeOH was concentrated under reduced pressure to get the crude product **ent-10n**, which was further purified as colourless liquid (12 mg, 85% yield) using flash column chromatography [Silica gel, hexane/ Et_2O (90:10)]. $R_f = 0.5$ [hexane/ EtOAc (95:05)]. HPLC analysis Daicel Chiralcel IG column, 4.6 mm \times 250 mm (hex/IPA = 99:01, 1.0 mL/min, RID detector), t_{R} (minor) = 17.1 min, t_{R} (major) = 19.3 min, 96% *ee*. $[\alpha]_{\text{D}}^{24} = +7.6$ ($c = 1.0$, CH_2Cl_2 for (+)-**ent-10n** of 96% *ee*), lit¹¹ $[\alpha]_{\text{D}}^{20} = -9.2$ ($c = 0.66$, CH_2Cl_2 for (-)-**ent-10n** of 98% *ee*).

16. Experimental procedure for the synthesis of compound **14**



To a solution of catalyst **6a** (11 mg, 0.02 mmol, 0.2 equiv) and 2-F-PhCO₂H (3 mg, 0.02 mmol, 0.2 equiv) in CHCl₃ (500 μL, 0.2 M) in a 2 mL vial was added 2,4-hexadienal **12** (22 μL, 0.2 mmol, 2 equiv) and stirred at rt for 5 min. Later, nitrostyrene **13** (15 mg, 0.1 mmol, 1 equiv) was added to the reaction mixture and stirred at 55 °C for 72 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to rt and diluted with EtOH (0.5 mL) and added dropwise into a solution of NaBH₄ (6 mg, 0.15 mmol, 1.5 equiv) in EtOH (1.5 mL) at -5 °C. The reaction mixture was stirred for 15 min at -5 °C and 1 h at 0 °C. Then, the reaction mass was quenched with cold water, the solvent was removed under reduced pressure, a saturated aqueous solution of NaHCO₃ (10 mL) was added, and extracted with EtOAc (3 × 20 mL). The organic phases were combined, washed with brine (15 mL), dried over Na₂SO₄, and concentrated under reduced pressure to get the crude product **14** (as an inseparable diastereomeric mixture), which was purified as a light-yellow liquid (10 mg, 40% yield, 5:1 *dr*, determined by ¹H NMR analysis) using flash column chromatography [Silica gel, hexane/EtOAc (80:20)]. *R_f* = 0.4 [hexane /EtOAc (70:30)]. For the characterization of the diastereomeric mixture of **14**, * represents the minor diastereomer, while no mark represents the major diastereomer. **HPLC** analysis Daicel Chiralcel IA, 4.6 mm × 250 mm (hex/IPA = 97:03, 1.0 mL/min, 210 nm), *t_R* (minor) = 39.1 min, *t_R* (major) = 49.7 min, 94% *ee* and *t_R* (minor) = 42.3 min*, *t_R* (major) = 62.6 min*, 45% *ee**. [*α*]_D²² = +31.2 (*c* = 0.5, CHCl₃ for **14** of 5:1 *dr* and 94% *ee*, and 45% *ee**). **¹H NMR** (500 MHz, CDCl₃) δ: 7.33-7.21 (m, 5H), 7.33-7.21* (m, 5H), 5.85-5.81 (m, 1H), 5.85-5.81* (m, 2H), 5.72-5.69 (m, 1H), 5.16* (dd, *J* = 5.5, 11.0 Hz, 1H), 4.82 (dd, *J* = 10.0, 11.5 Hz, 1H), 3.80-3.69 (m, 2H), 3.80-3.69* (m, 2H), 3.52-3.47* (m, 1H), 3.43-3.38 (m, 1H), 3.18-3.12 (m, 1H), 3.09-3.05* (m, 1H), 2.60-2.55* (m, 1H), 2.53-2.46 (m, 1H), 2.42-2.34 (m, 1H), 2.31-2.24* (m, 1H), 1.81-1.76 (m, 1H), 1.74-1.65* (m, 2H), 1.71-1.65 (m, 1H), 1.42* (bs, 1H), 1.42 (bs, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃) δ: 141.5*, 139.7, 128.98*, 128.96, 127.9, 127.6, 127.4*, 127.24*, 127.17, 127.0*, 126.51, 126.48*, 93.2, 89.5*, 60.2*, 59.7, 45.5, 39.3*, 39.2, 35.0*, 34.8, 34.0*, 33.8*, 33.7. **IR** (neat) *ν* 3376, 3032, 2923, 1548, 1372, 1052, 757, 700 cm⁻¹. **HRMS** (ESI) *m/z* calcd for C₁₄H₁₇NO₃Na⁺ [*M* + Na]⁺ 270.1101, found 270.1111.

17. Experimental procedure for the synthesis of carbamate **15**



To a solution of compound **14** (21 mg, 0.08 mmol, 1 equiv) in dry CH_2Cl_2 (500 μL , 0.2 M) was added NEt_3 (11 μL , 0.08 mmol, 1 equiv) and 4-chlorophenyl isocyanate (18 mg, 0.12 mmol, 1.5 equiv) at 0 $^\circ\text{C}$ and the reaction mixture was stirred at rt for 18 h. After the completion of reaction (monitored by TLC), the reaction mass was quenched with water and extracted with EtOAc (3 \times 10 mL). The organic phases were combined, and washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to get crude product **15**, which was purified as white solid (24 mg, 70% yield, 5:1 *dr*, determined by ^1H NMR analysis) using flash column chromatography [Silica gel, hexane/EtOAc (95:05)]. $R_f = 0.7$ [hexane/EtOAc (80:20)]. For the characterization of the diastereomeric mixture of **15**, * represents the minor diastereomer, while no mark represents the major diastereomer. M.P. 143–145 $^\circ\text{C}$. $[\alpha]_D^{21} = +8.8$ ($c = 0.75$, CHCl_3 for **15**). ^1H NMR (500 MHz, CDCl_3) δ : 7.33–7.30 (m, 4H), 7.33–7.30* (m, 4H), 7.27–7.25 (m, 4H), 7.27–7.25* (m, 1H), 7.21–7.19 (m, 1H), 7.21–7.19* (m, 4H), 6.77 (bs, 1H), 6.73* (bs, 1H), 5.86–5.83 (m, 1H), 5.86–5.83* (m, 2H), 5.67 (d, $J = 10.3$ Hz, 1H), 5.16* (dd, $J = 5.6, 10.9$ Hz, 1H), 4.76 (t, $J = 10.7$ Hz, 1H), 4.34–4.21 (m, 2H), 4.34–4.21* (m, 2H), 3.52–3.47* (m, 1H), 3.42–3.37 (m, 1H), 3.16–3.13 (m, 1H), 2.98* (bs, 1H), 2.61–2.55* (m, 2H), 2.52–2.47 (m, 1H), 2.41–2.35 (m, 1H), 2.31–2.25* (m, 1H), 1.97–1.90 (m, 1H), 1.85–1.81* (m, 2H), 1.78–1.70 (m, 1H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 153.3, 141.2*, 139.4, 136.5, 129.21*, 129.16, 129.0, 128.6*, 127.9, 127.53, 127.47*, 127.2*, 127.11*, 127.05, 126.5, 126.3, 120.1, 116.4*, 93.0, 89.3*, 62.6*, 61.9, 45.5, 39.3*, 39.1, 35.1*, 33.63*, 33.57, 31.4, 30.5*. IR (neat) ν 3324, 3001, 2922, 2848, 1711, 1599, 1548, 1494, 1405, 1308, 1221, 1093, 1057, 829, 758, 700, 507 cm^{-1} .

18. References

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19. X-ray single-crystal structure data for the 3-((2*R*,5*S*)-5-(hydroxydiphenylmethyl)-1-tosylpyrrolidin-2-yl)propan-1-ol (**7a**)

Experimental: Colourless crystals of **7a** (C₂₇H₃₁NO₄S) were obtained by crystallization in Ethyl Acetate and Hexane (1:1 v/v) at ambient conditions. Single crystal diffraction data for the **7a** was collected at 273K on a Bruker Kappa APEX-II diffractometer with CCD PHOTON 2.0 detector equipped with I μ S 3.0 Mo K α ($\lambda = 0.71073$ Å) source. X-ray diffraction intensities were collected integrated and scaled with the APEX3 suite. The crystal structure was solved by the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The details of the crystal data collections and data refinement parameters are given in Table S1.

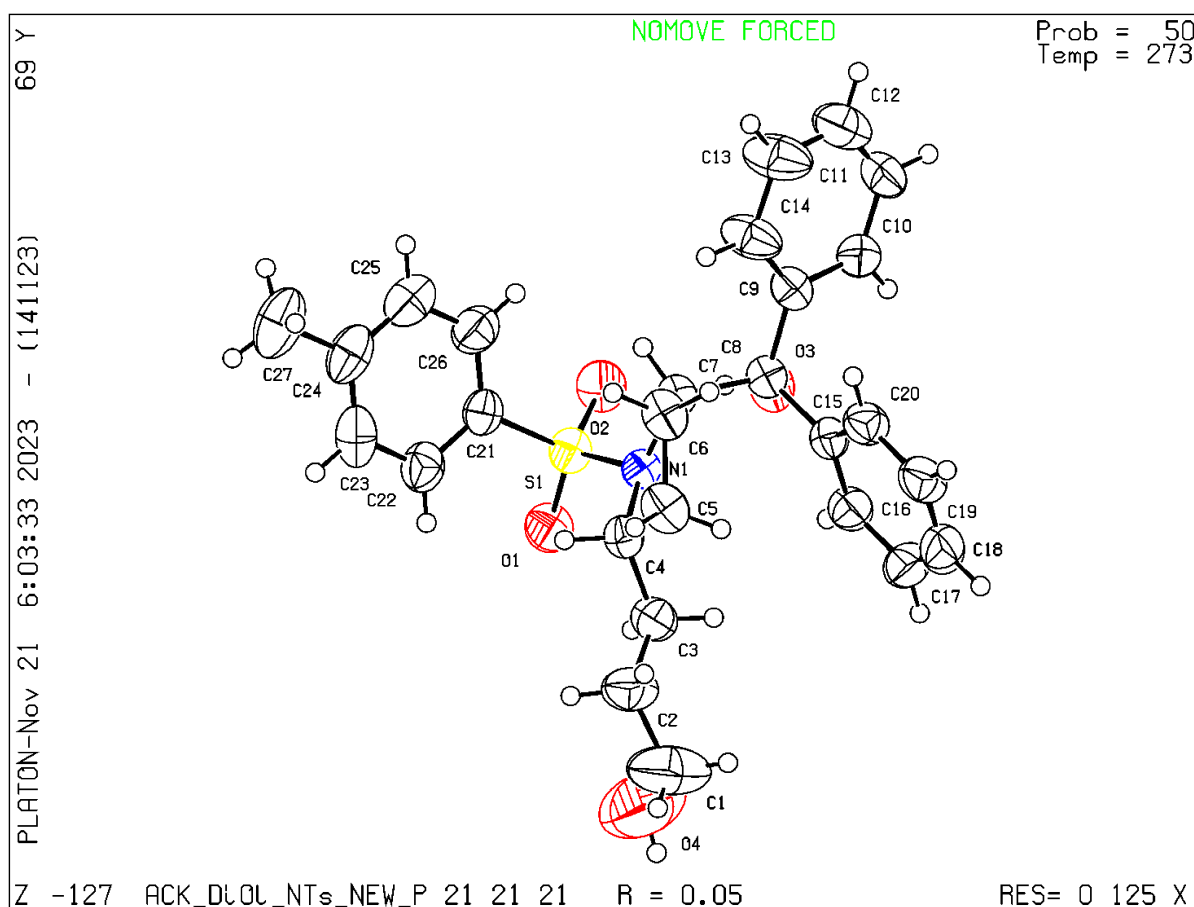


Figure S1. Asymmetric unit of **7a**; thermal ellipsoids are drawn at the 50% probability level.

Table S1 Crystal data and structure refinement for 7a

Identification code	2309956
Empirical formula	C ₂₇ H ₃₁ N O ₄ S
Formula weight	465.59
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 6.2369(3) Å alpha = 90 deg; b = 10.0180(5) Å beta = 90 deg; c = 39.109(2) Å gamma = 90 deg.
Volume	2443.6(2) Å ³
Z	4
Calculated density	1.266 Mg/m ³
Absorption coefficient	0.166 mm ⁻¹
F(000)	992
Crystal size	0.73 x 0.35 x 0.24 mm
Theta range for data collection	2.08 to 22.59 deg.
Index ranges	-6<=h<=6, -10<=k<=10, -42<=l<=42
Reflections collected	54504
Independent reflections	3228 [R(int) = 0.0636]
Reflections observed	I > 2σ(I)
Data Completeness	99.8%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3228 / 0 / 299
Goodness - of - fit on F ²	1.289
Final R indices [I>2σ(I)]	R1 = 0.0462, wR2 = 0.1435
R indices (all data)	R1 = 0.0481, wR2 = 0.1453
Largest diff. peak and hole	0.280 and -0.356 e. Å ⁻³
Flack parameter	0.05(3)

20. X-ray single-crystal structure data for the 2-((1*S*,2*R*,3*S*)-2-nitro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethyl (4-chlorophenyl)carbamate (**15**)

Experimental: Colourless crystals of **15** (C₂₁H₂₁ClN₂O₄) were obtained by crystallization in IPA/EtOAc/hexane (1:2:4 v/v) at ambient conditions. Single crystal diffraction data for the **15** was collected at 294K on a Bruker Kappa APEX-II diffractometer with CCD PHOTON 2.0 detector equipped with I μ S 3.0 Mo K α ($\lambda = 0.71073$ Å) source. X-ray diffraction intensities were collected integrated and scaled with the APEX3 suite. The crystal structure was solved by the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The details of the crystal data collections and data refinement parameters are given in Table S2.

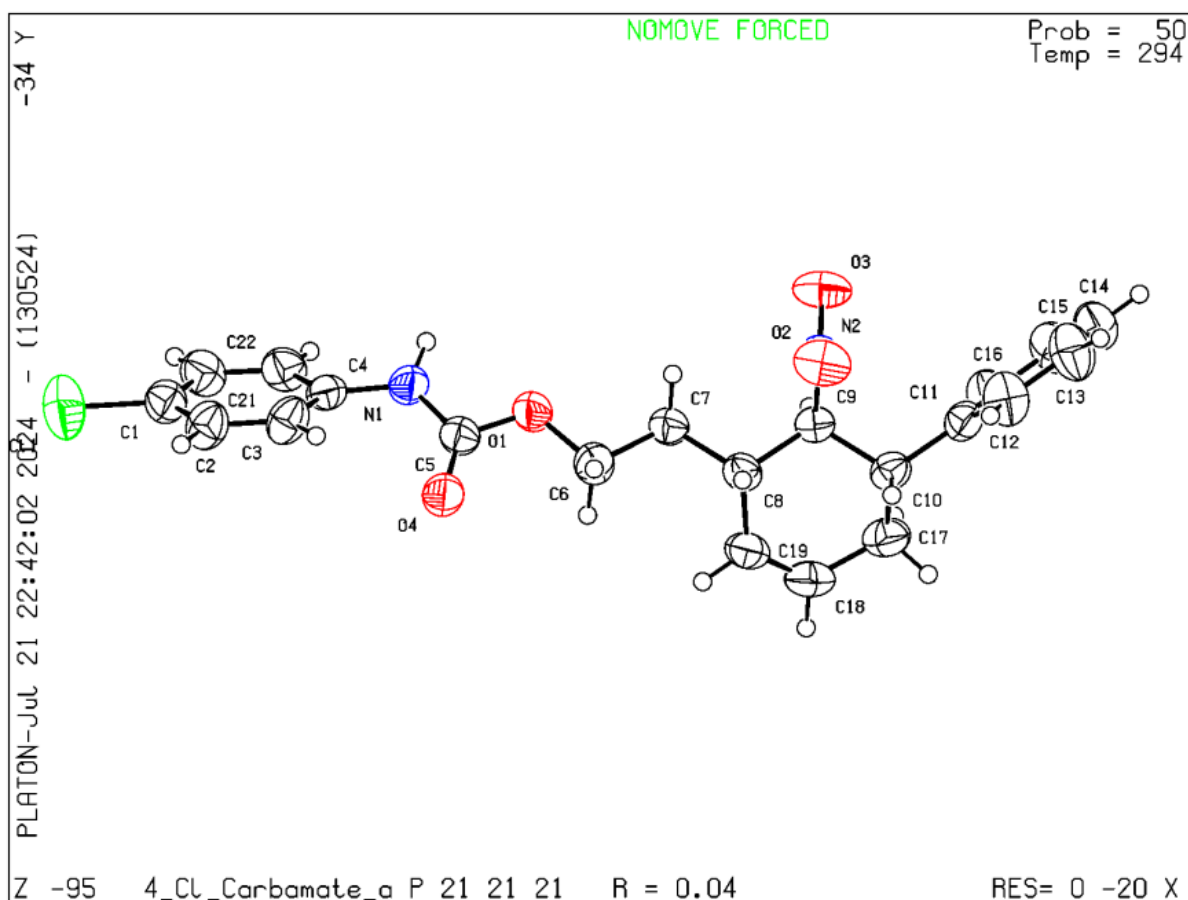


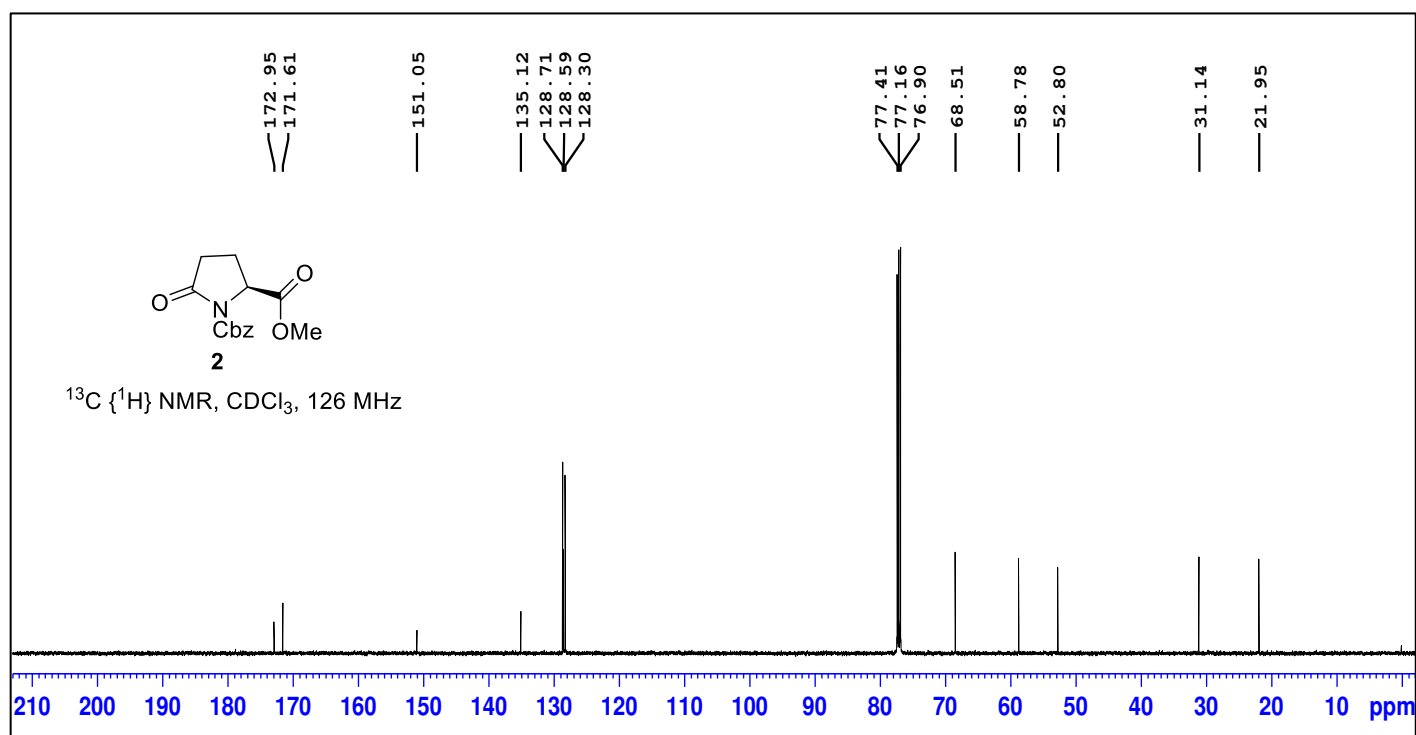
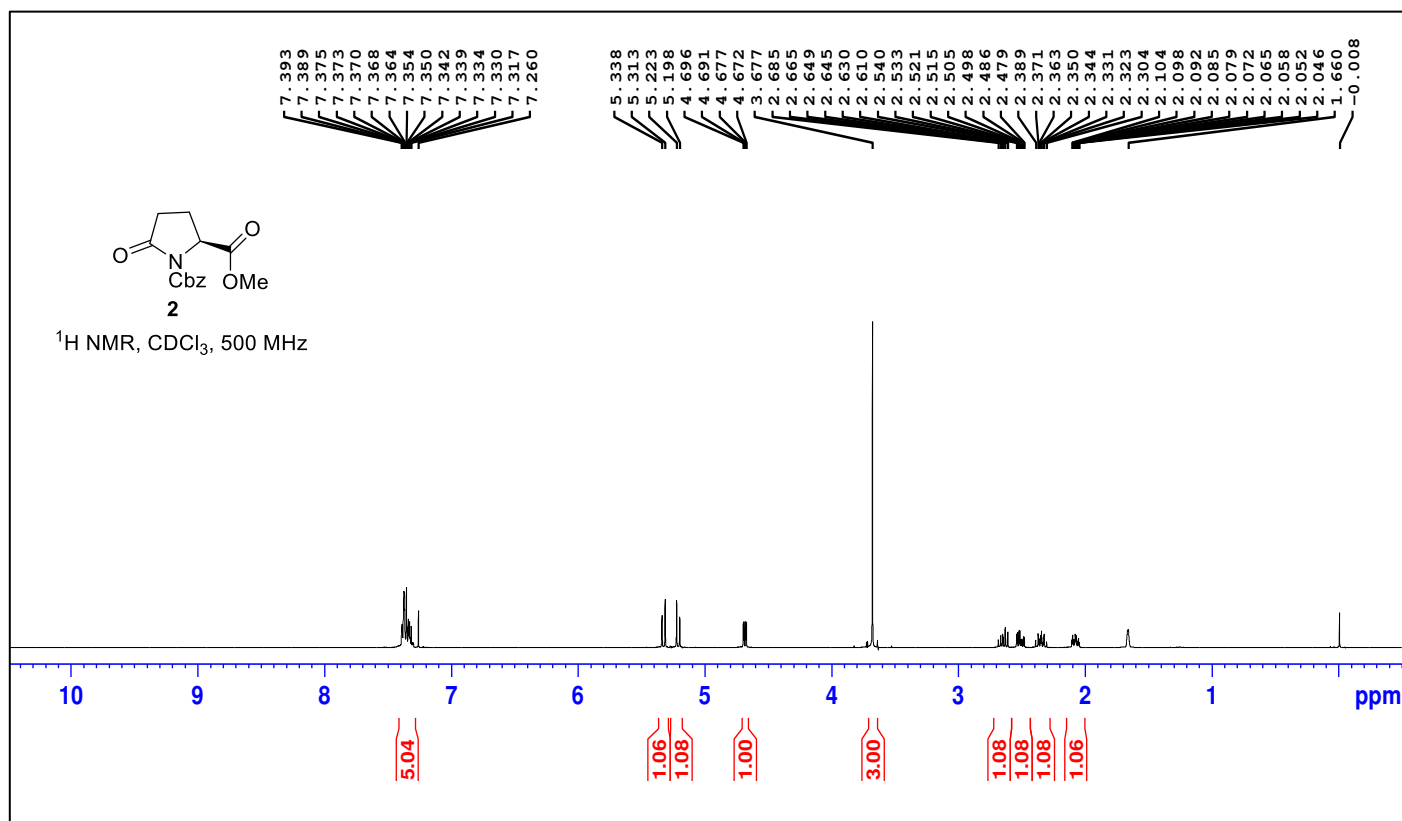
Figure S2. Asymmetric unit of **15**; thermal ellipsoids are drawn at the 50% probability level.

Table S2 Crystal data and structure refinement for 15

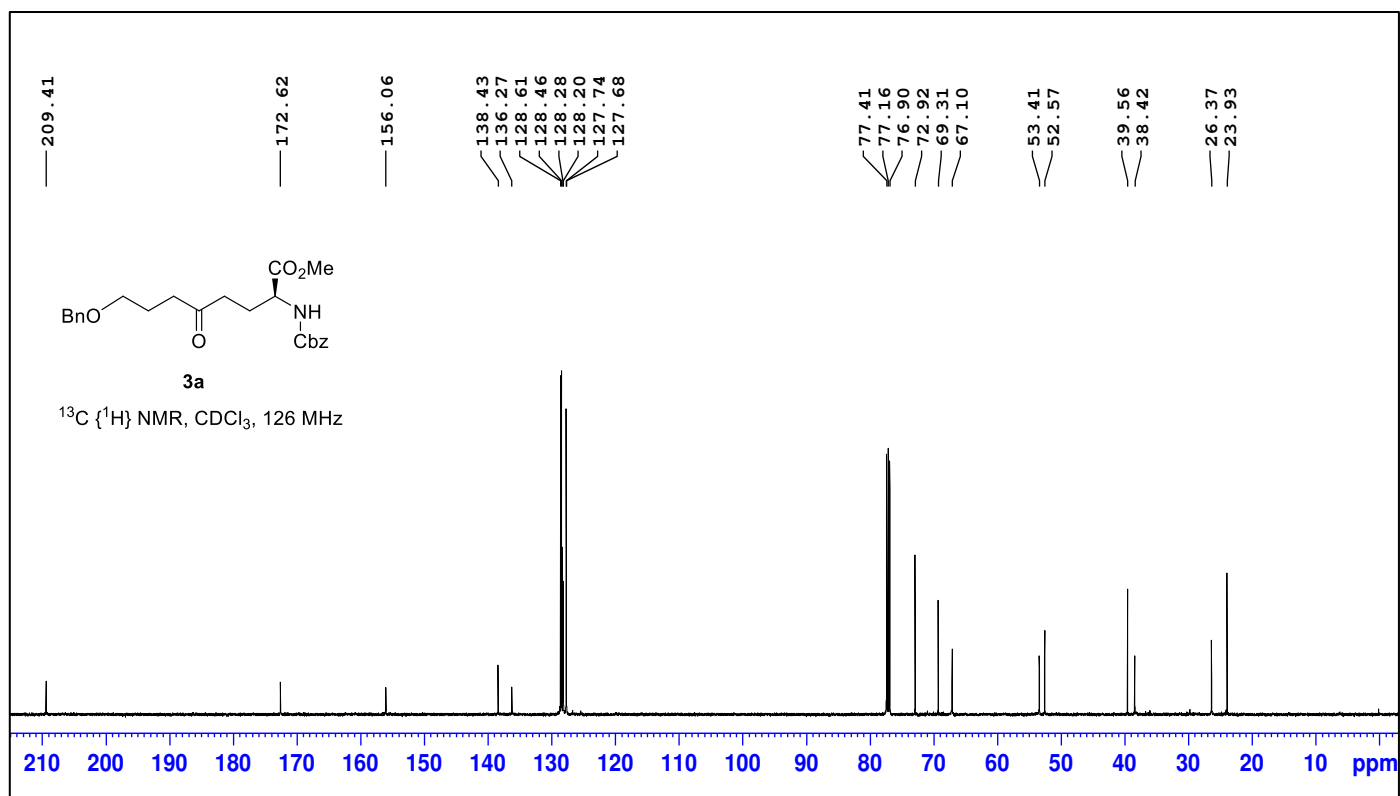
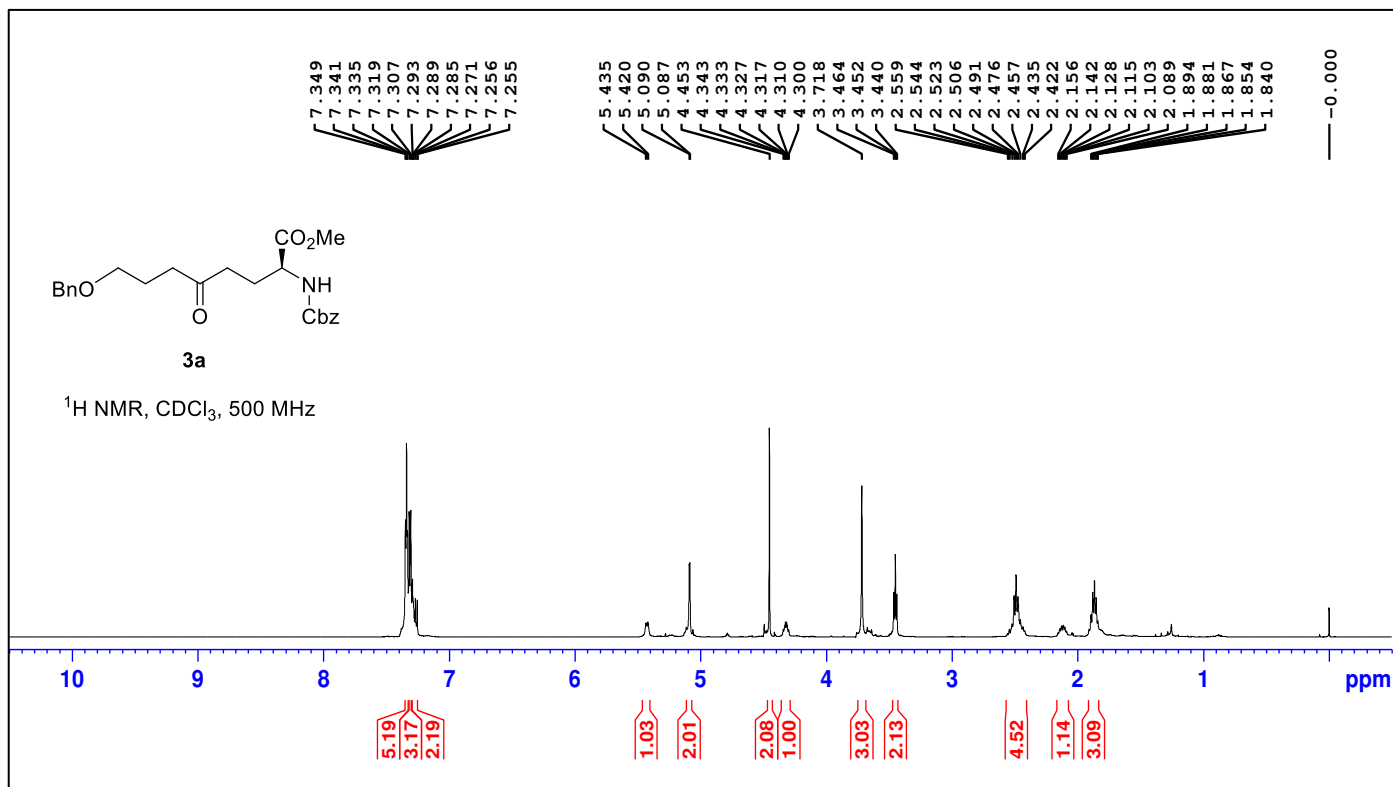
Identification code	2372580
Empirical formula	C ₂₁ H ₂₁ Cl N ₂ O ₄
Formula weight	400.85 g/mol
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 5.1998(8) Å alpha = 90 deg; b = 15.781(3) Å beta = 90 deg; c = 24.305(5) Å gamma = 90 deg.
Volume	1994.4(6) Å ³
Z	4
Calculated density	1.325 Mg/m ³
Absorption coefficient	0.219 mm ⁻¹
F(000)	832
Crystal size	0.094 x 0.151 x 0.184 mm
Theta range for data collection	2.12 to 28.34 deg.
Index ranges	-6<=h<=6, -21<=k<=21, -32<=l<=32
Reflections collected	56769
Independent reflections	4957 [R(int) = 0.0721]
Reflections observed	I > 2σ(I)
Data Completeness	99.9 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4957 / 0 / 256
Goodness - of - fit on F ²	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1270
R indices (all data)	R1 = 0.0627, wR2 = 0.1444
Largest diff. peak and hole	0.163 and -0.268 eÅ ⁻³
Flack parameter	-0.01(3)

21. NMR and HPLC data

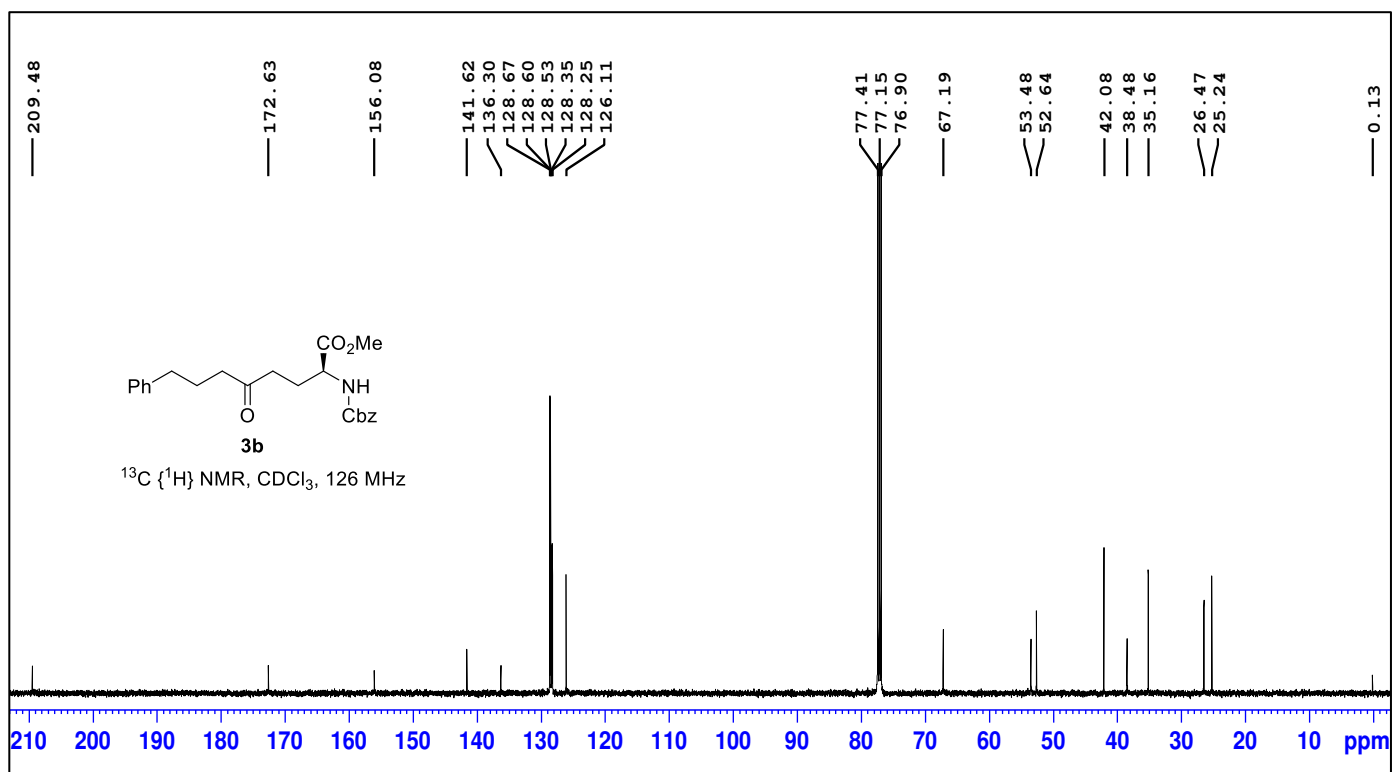
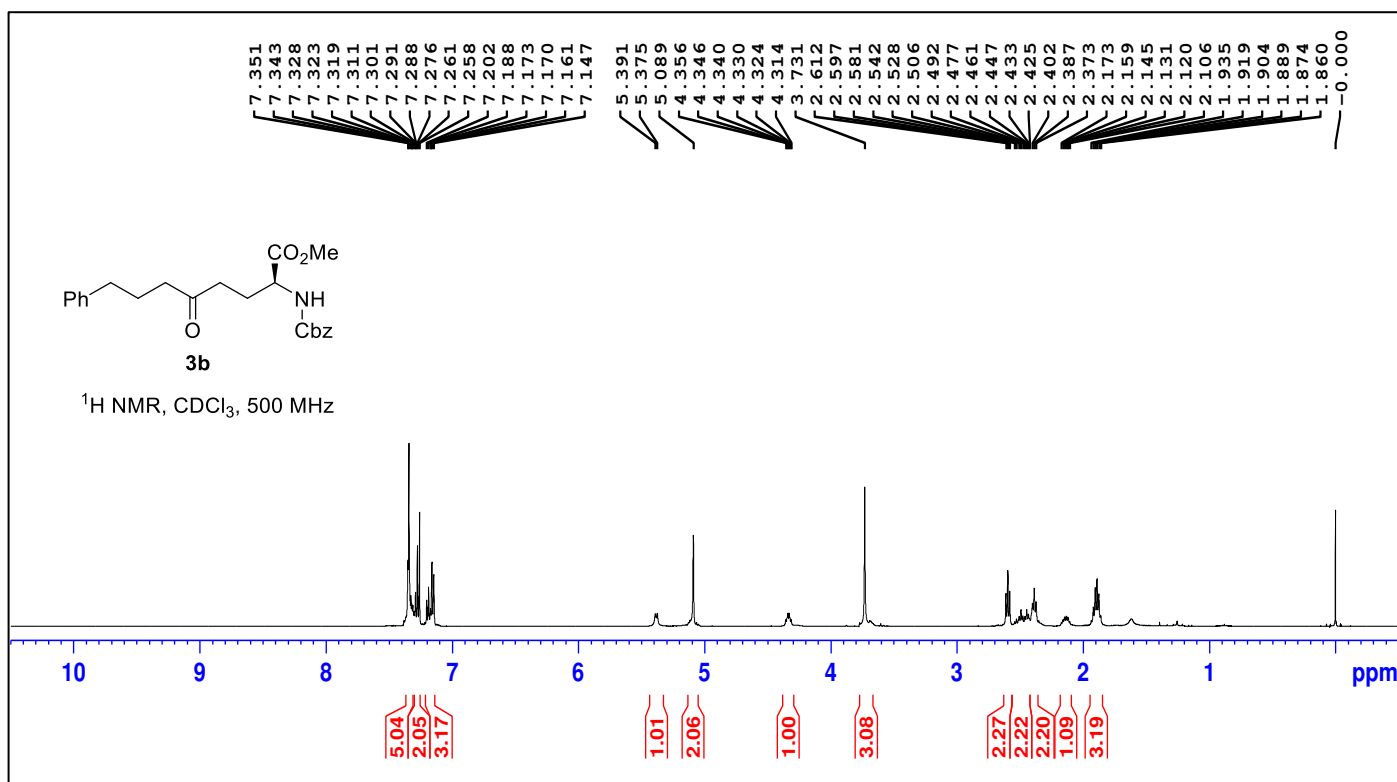
1-benzyl 2-methyl (*S*)-5-oxopyrrolidine-1,2-dicarboxylate (2)



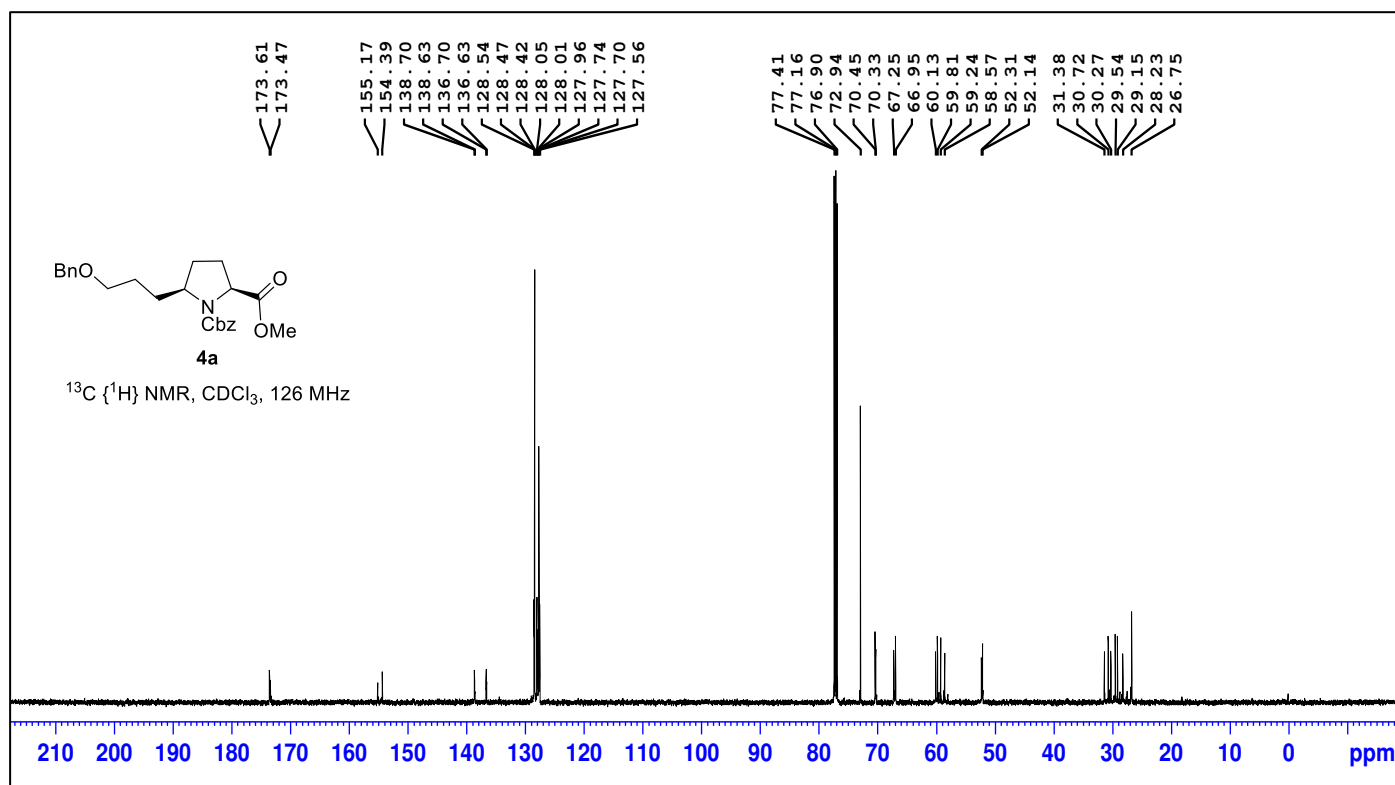
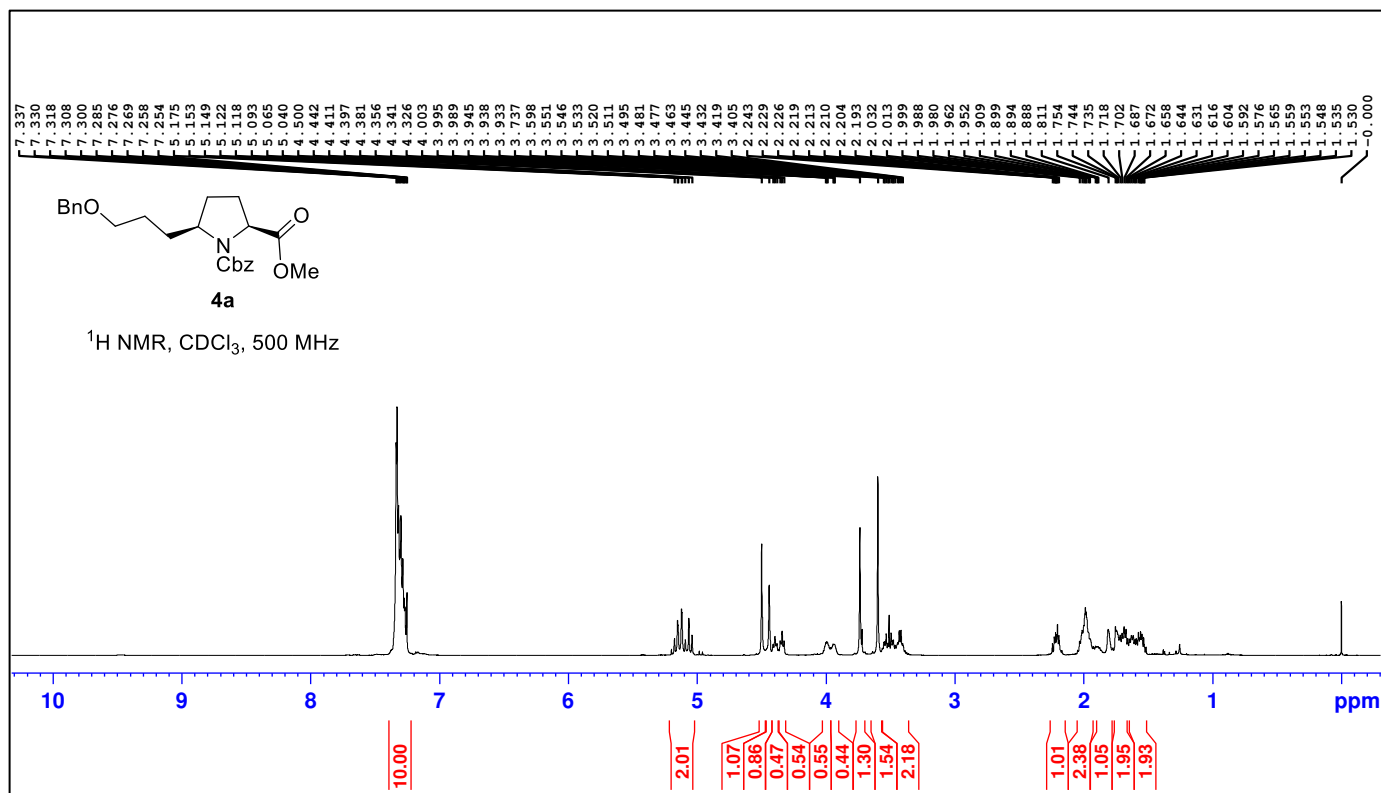
Methyl (*S*)-8-(benzyloxy)-2-(((benzyloxy) carbonyl)amino)-5-oxooctanoate (3a)



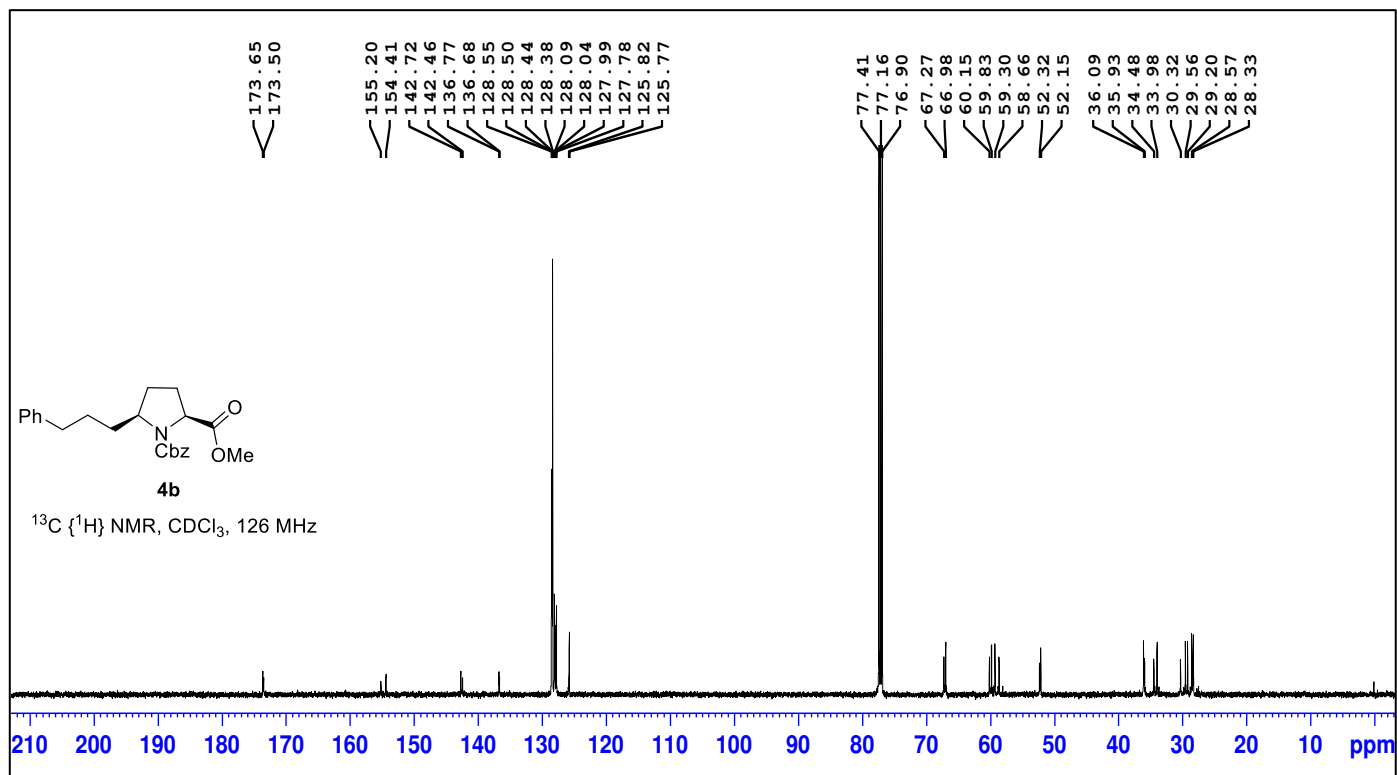
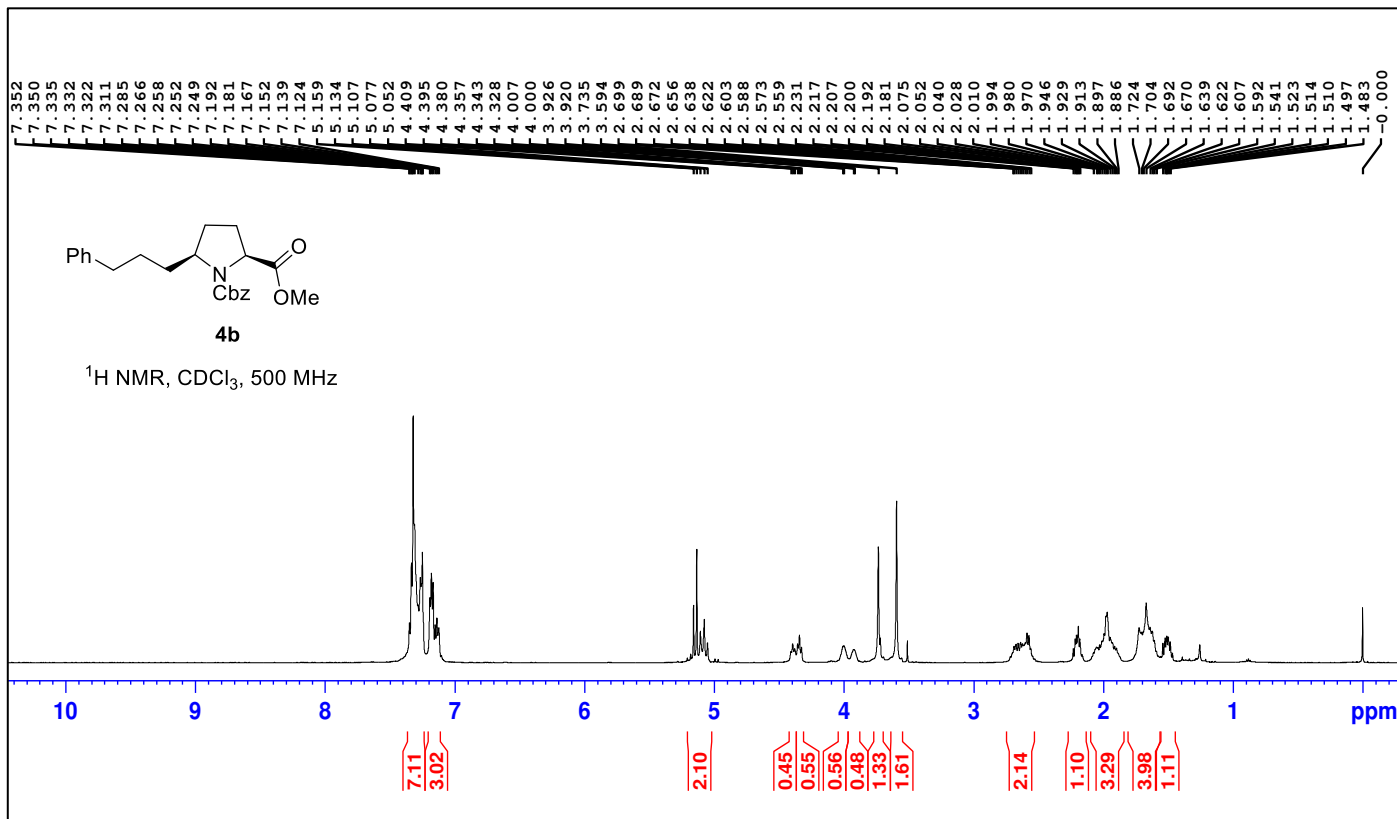
Methyl (*S*)-2-(((benzyloxy)carbonyl)amino)-5-oxo-8-phenyloctanoate (**3b**)



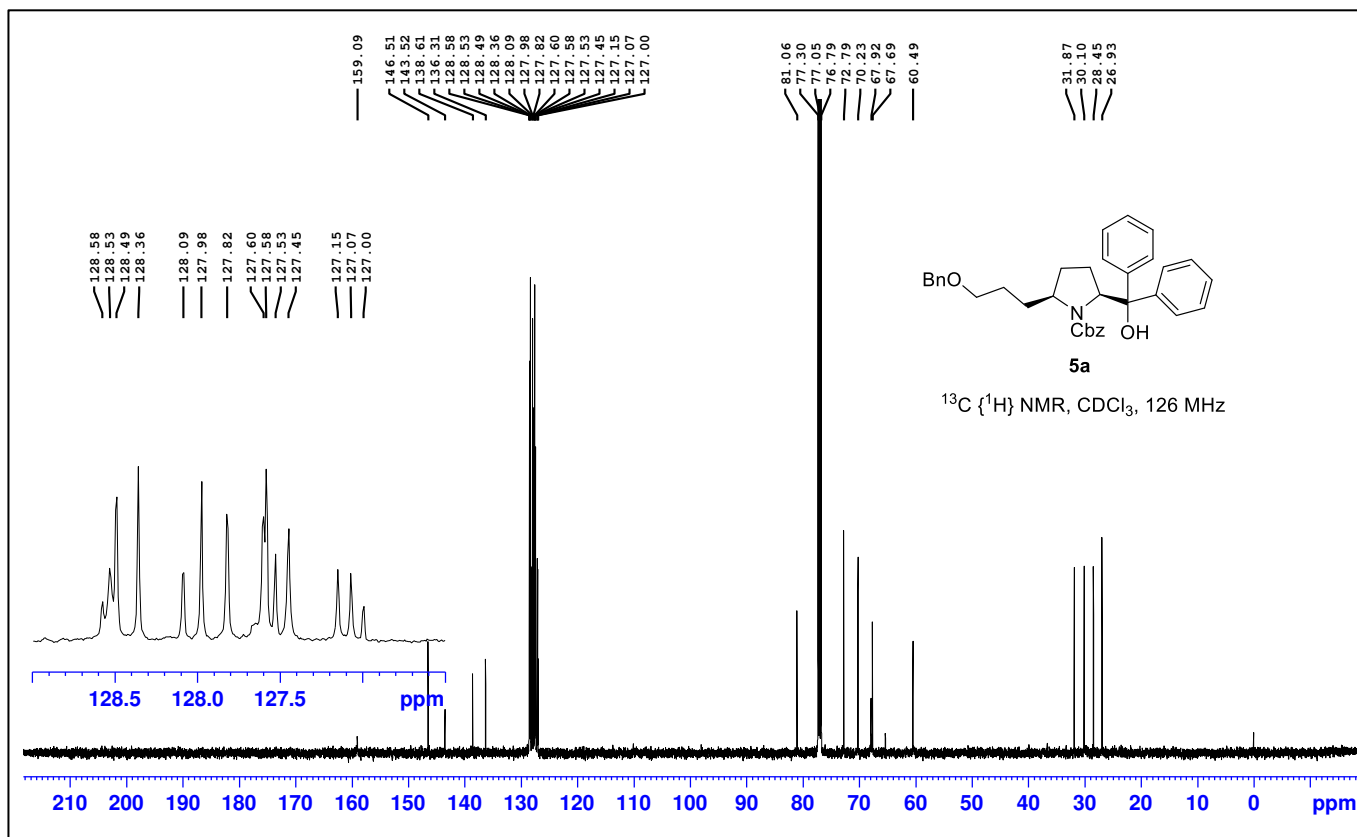
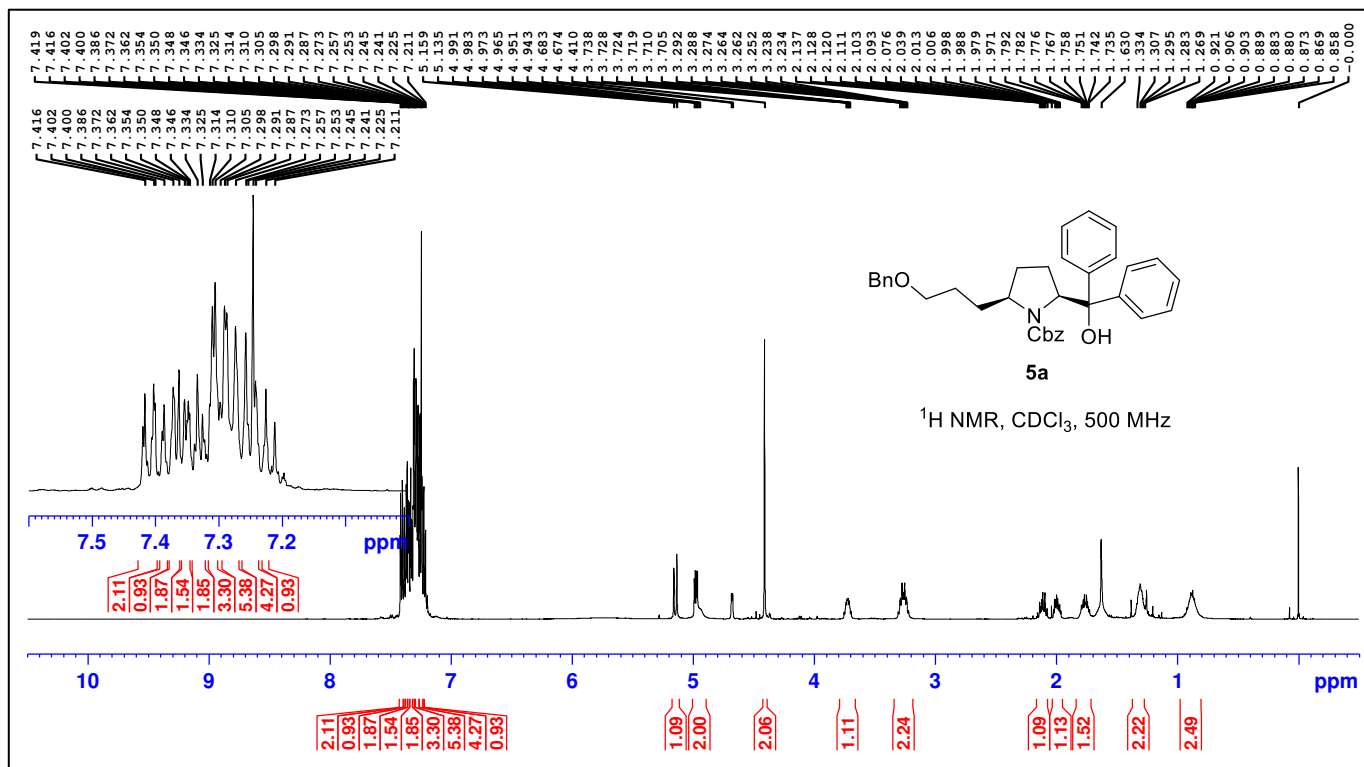
1-benzyl 2-methyl (2*S*,5*R*)-5-(3-(benzyloxy) propyl)pyrrolidine-1,2-dicarboxylate (4a)



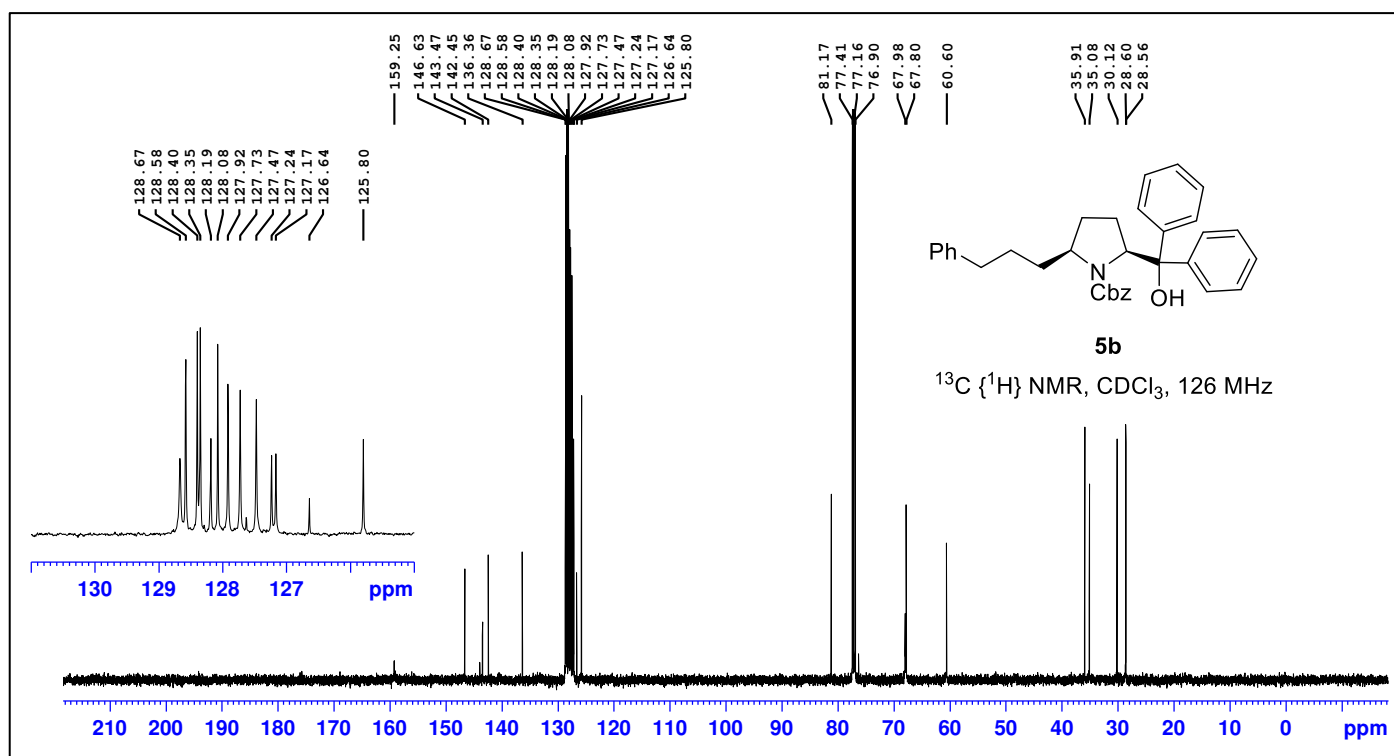
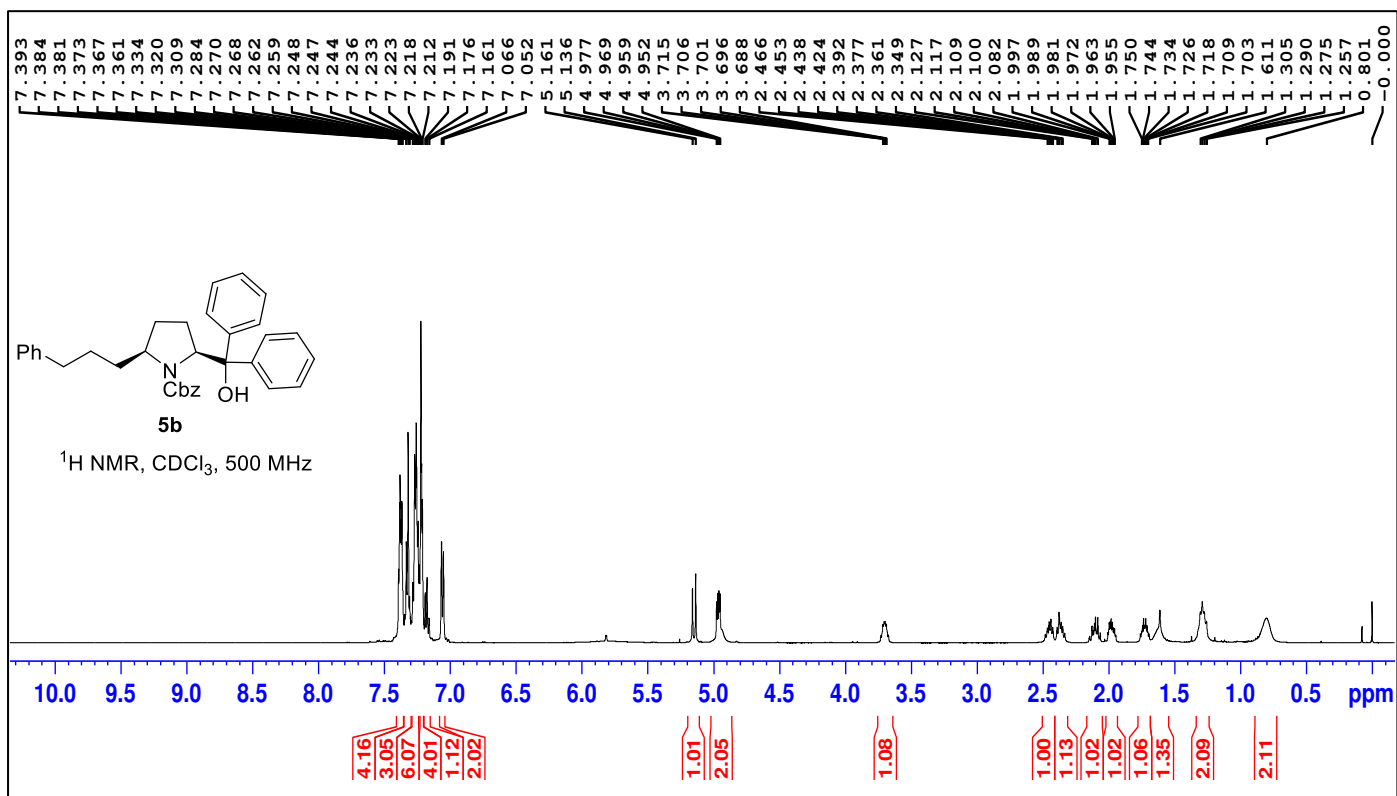
1-benzyl 2-methyl (2*S*,5*S*)-5-(3-phenylpropyl)pyrrolidine-1,2 dicarboxylate (**4b**)



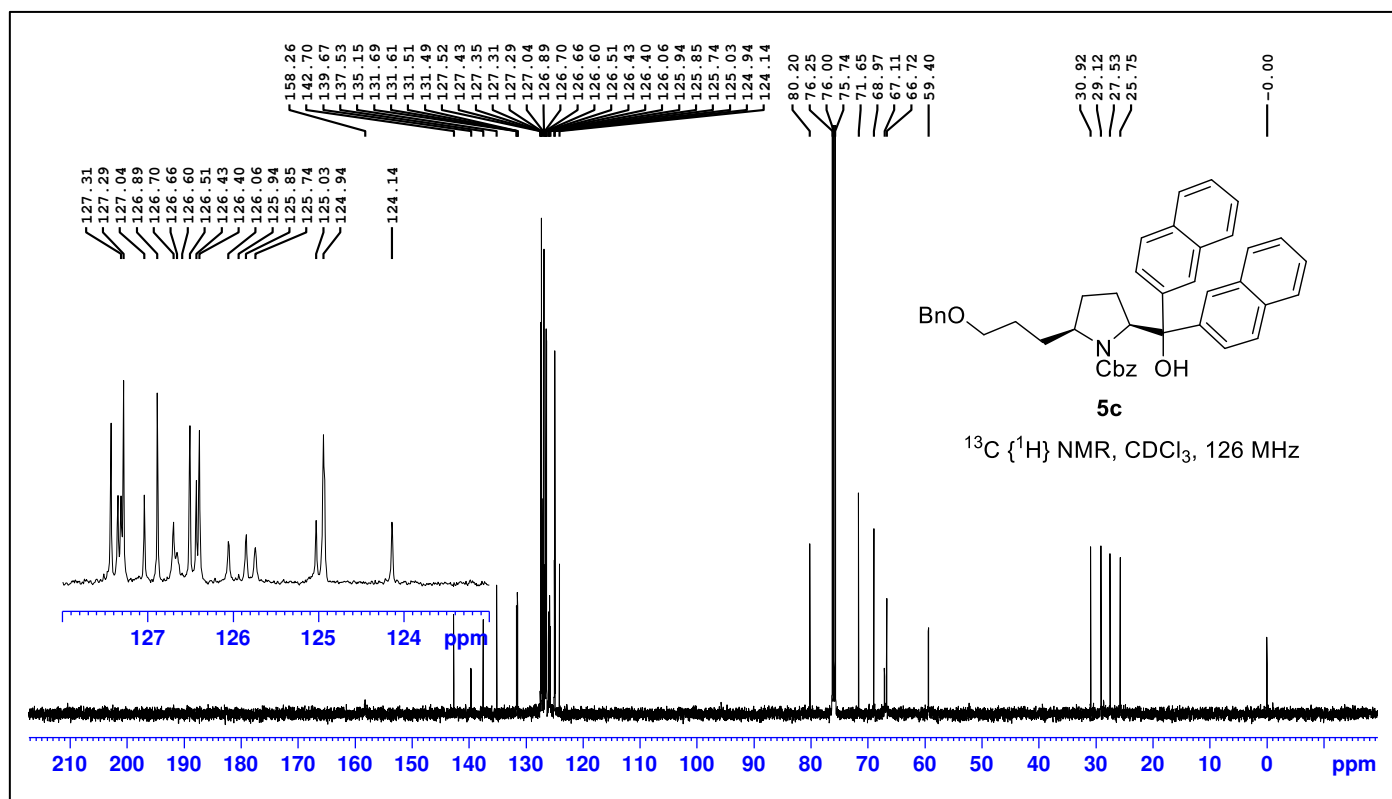
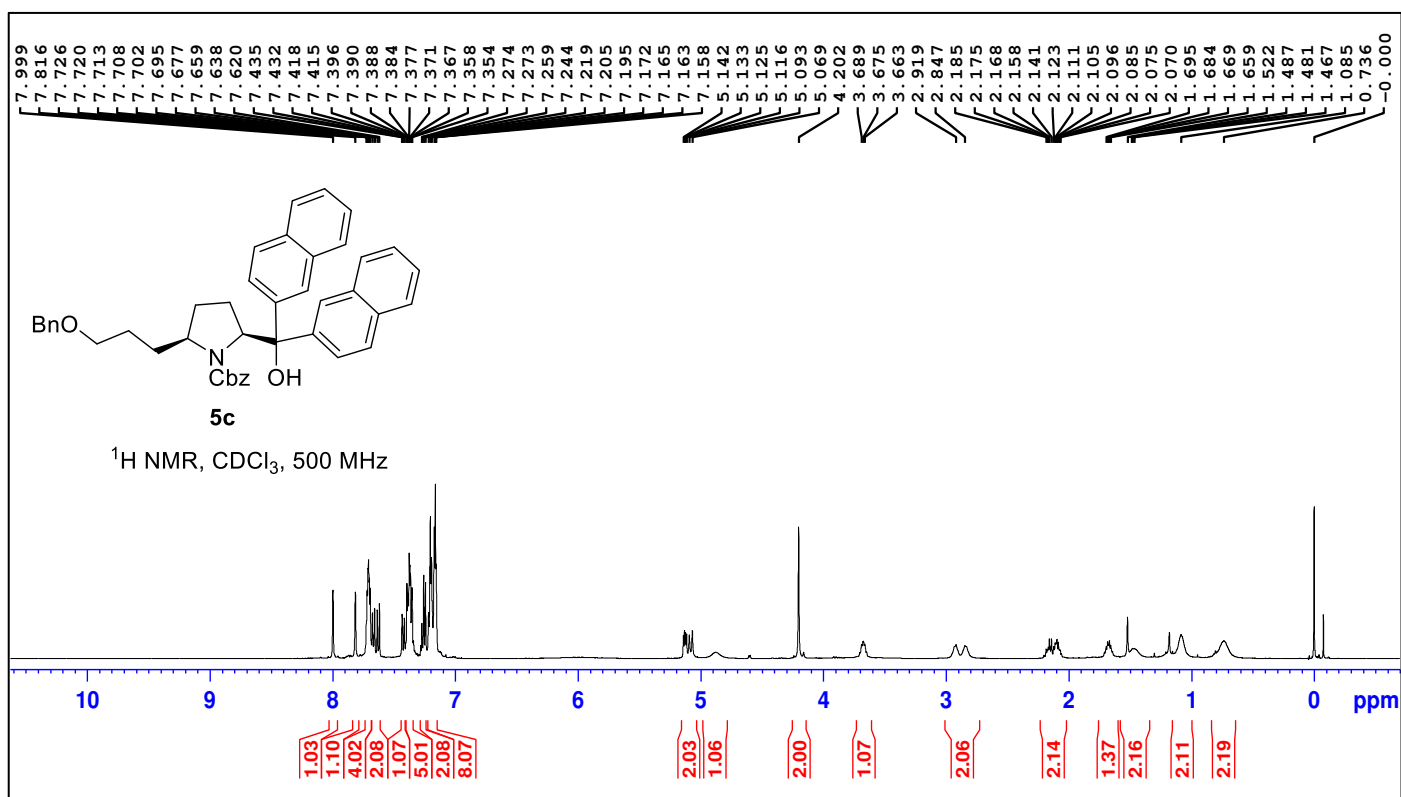
Benzyl (2*R*,5*S*)-2-(3-(benzyloxy)propyl)-5-(hydroxydiphenylmethyl)pyrrolidine-1-carboxylate (5a)



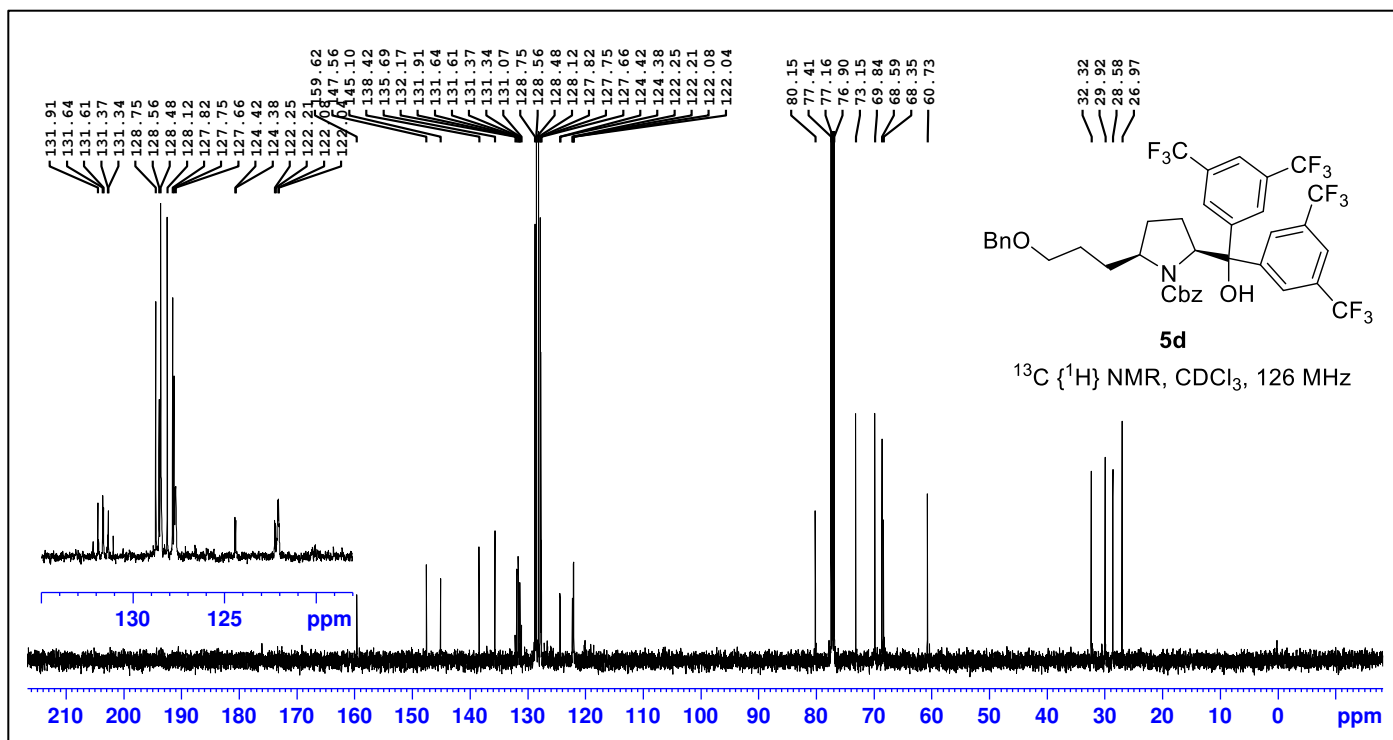
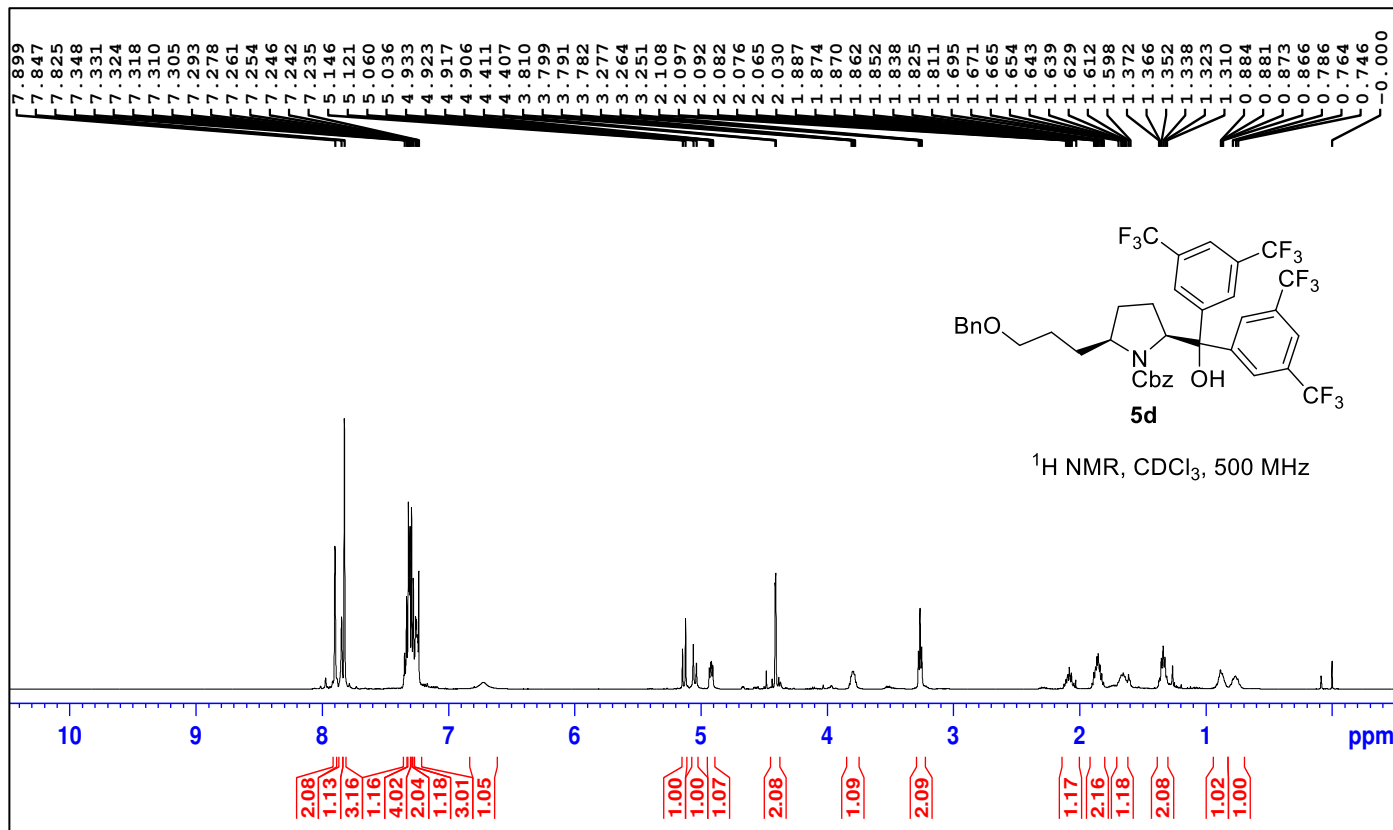
Benzyl (2*S*,5*S*)-2-(hydroxydiphenylmethyl)-5-(3-phenylpropyl)pyrrolidine-1-carboxylate (5b)

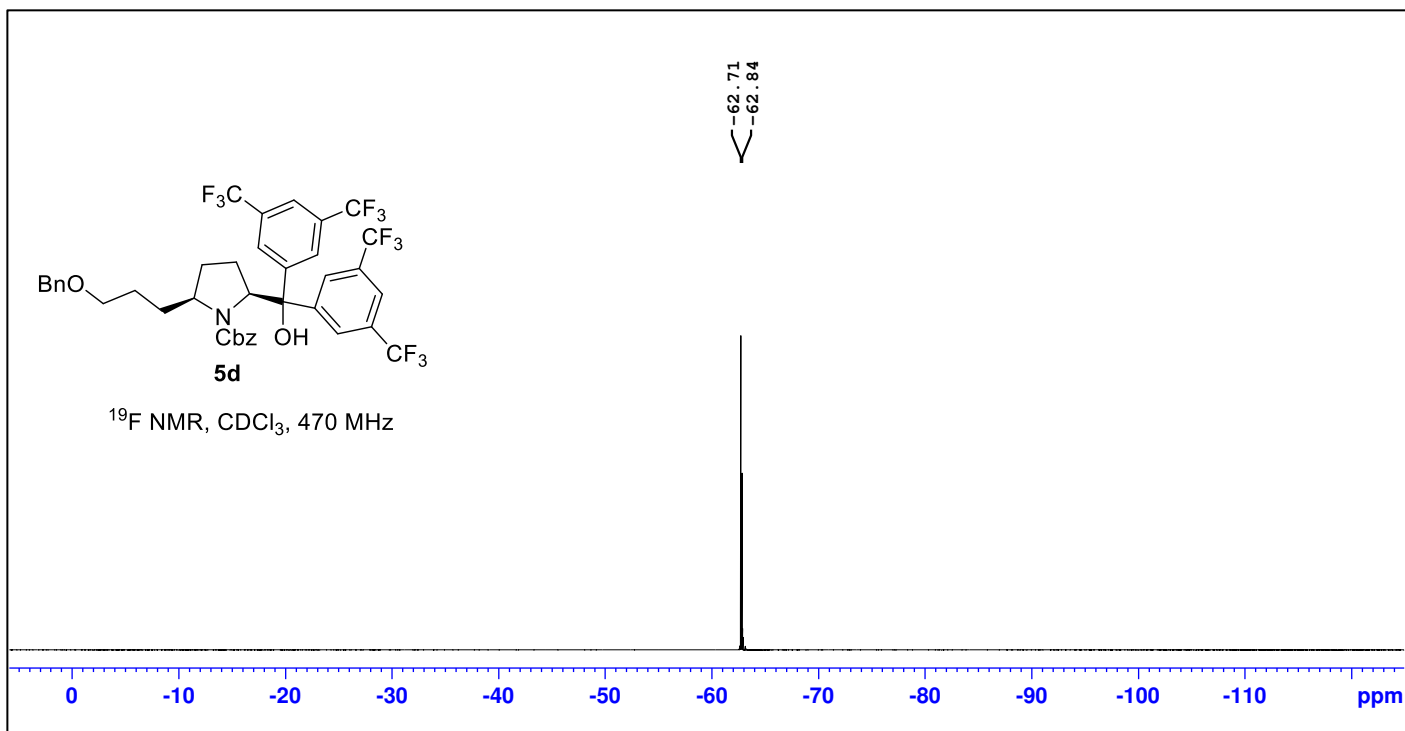


Benzyl (2*R*,5*S*)-2-(3-(benzyloxy)propyl)-5-(hydroxydi(naphthalen-2-yl)methyl)pyrrolidine-1-carboxylate (5c)

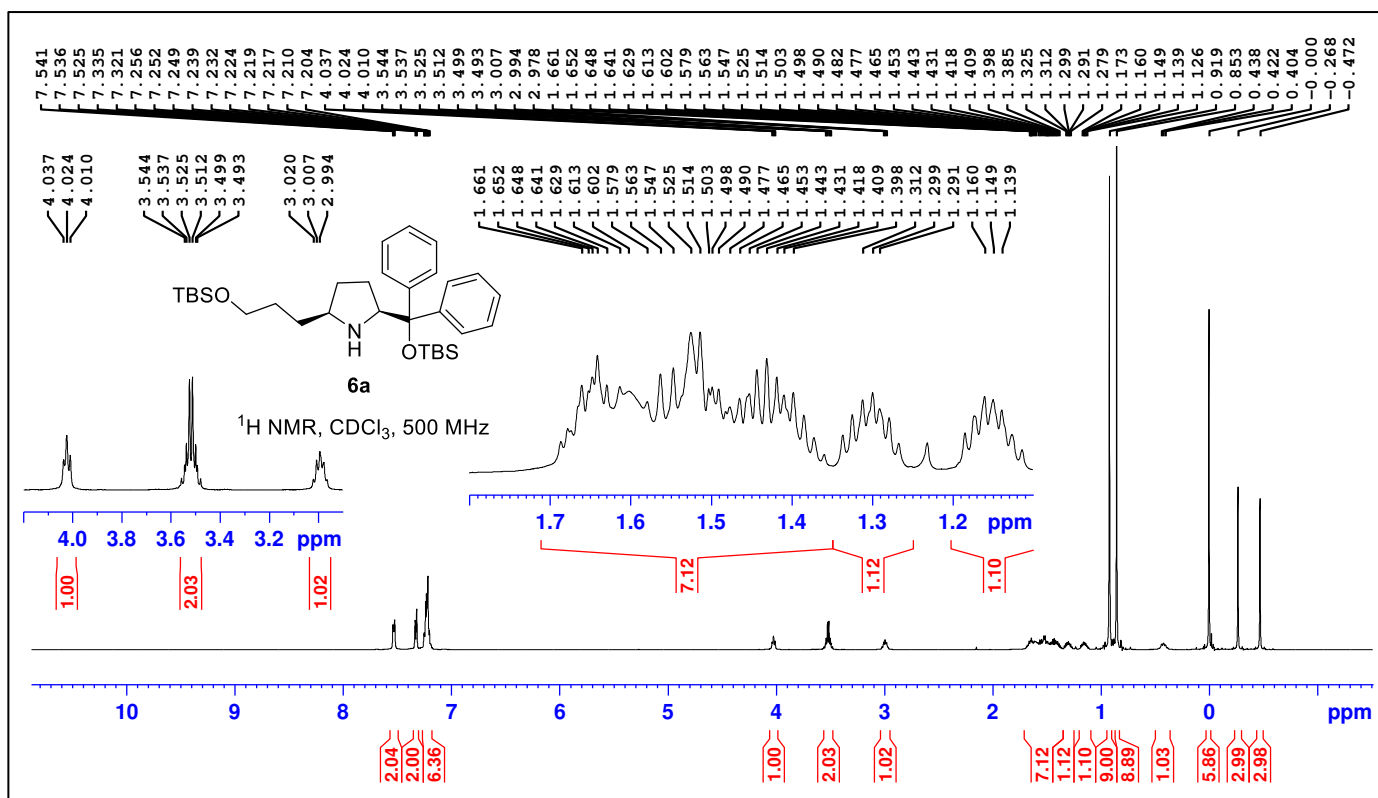


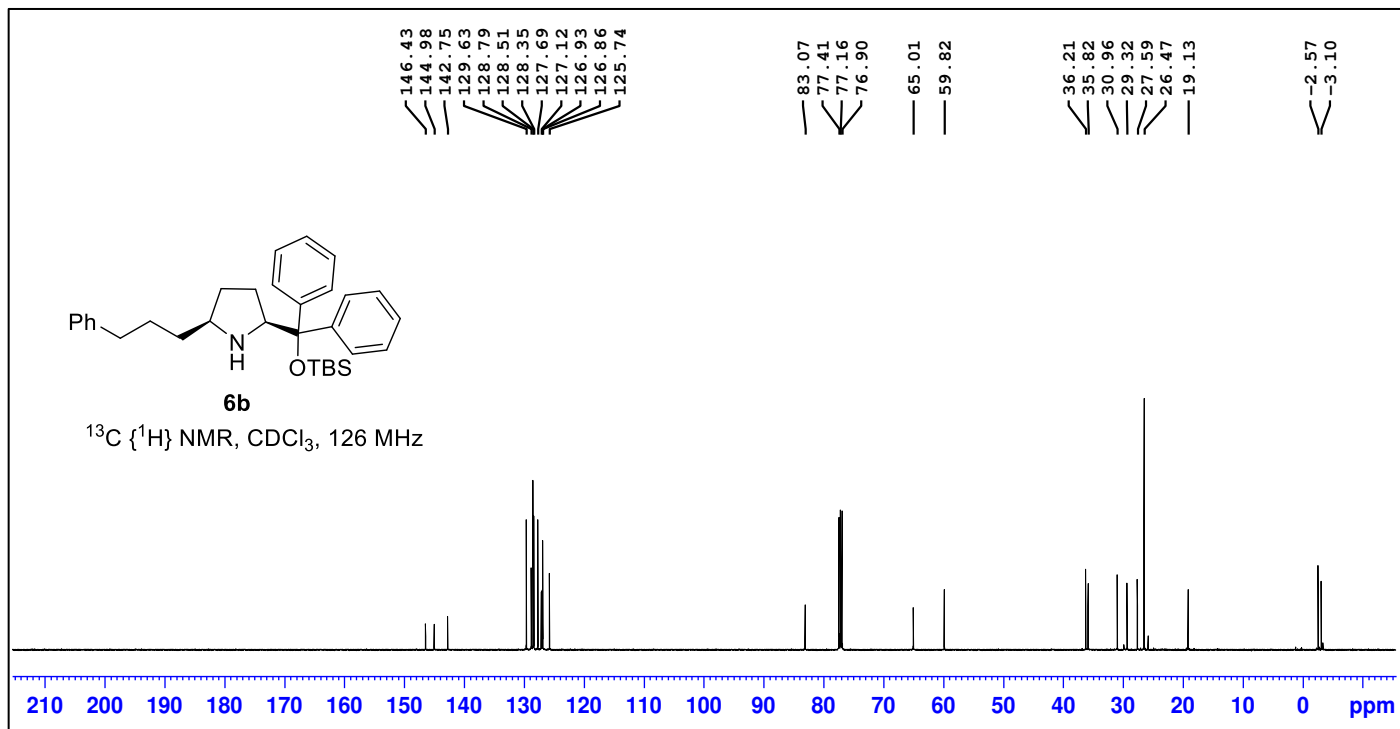
(2*R*,5*S*)-2-(3-(benzyloxy)propyl)-5-(bis(3,5 bis(trifluoromethyl)phenyl)(hydroxy)methyl)pyrrolidine-1-carboxylate (5d)



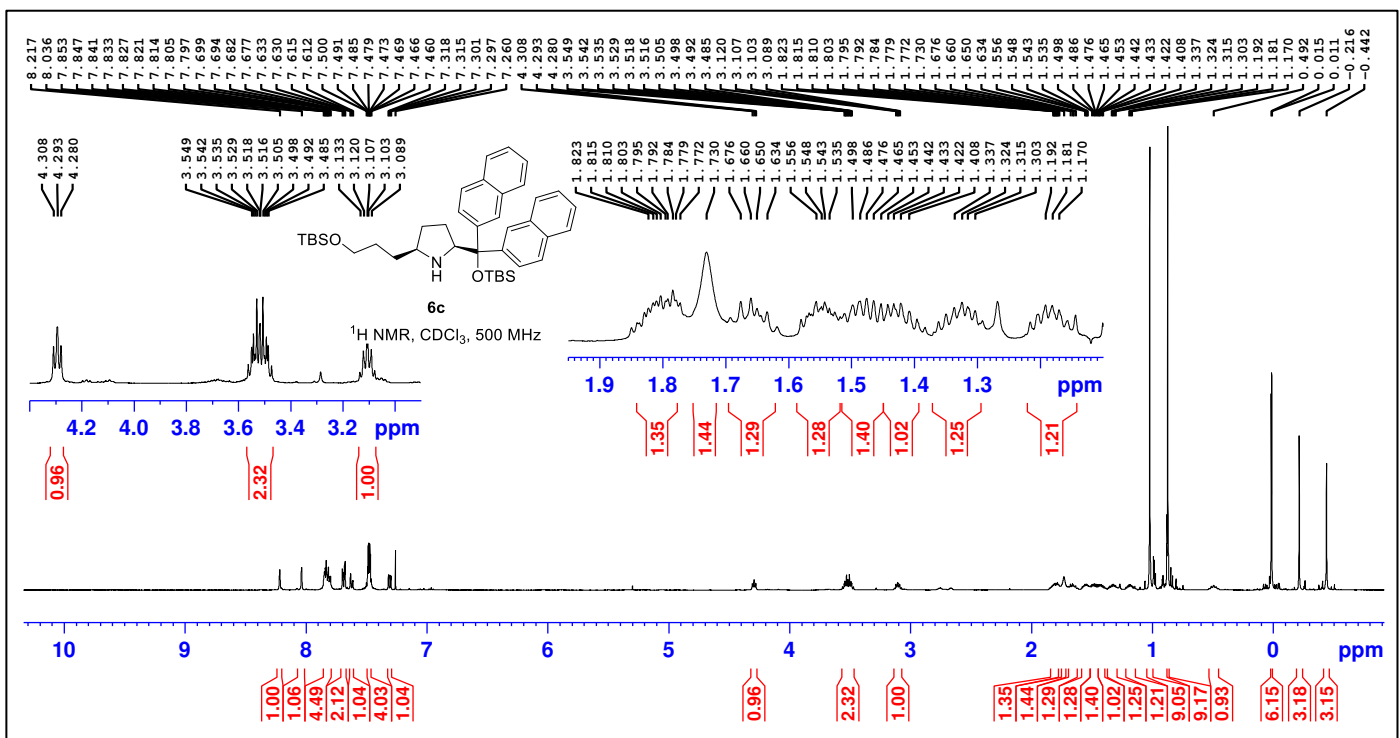


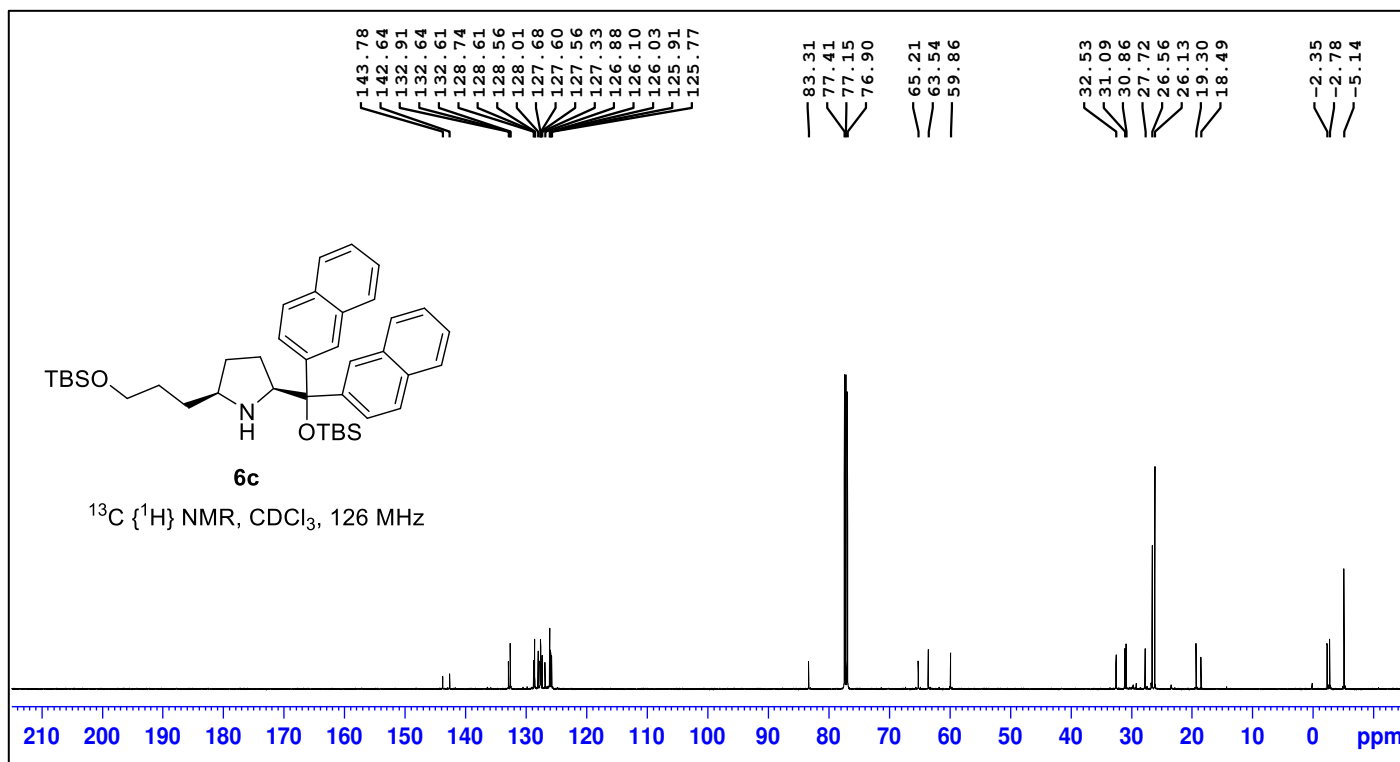
(2*S*,5*R*)-2-(((tert-butyldimethylsilyl)oxy)diphenylmethyl)-5-(3((tertbutyldimethylsilyl)oxy)propyl)pyrrolidine (6a)



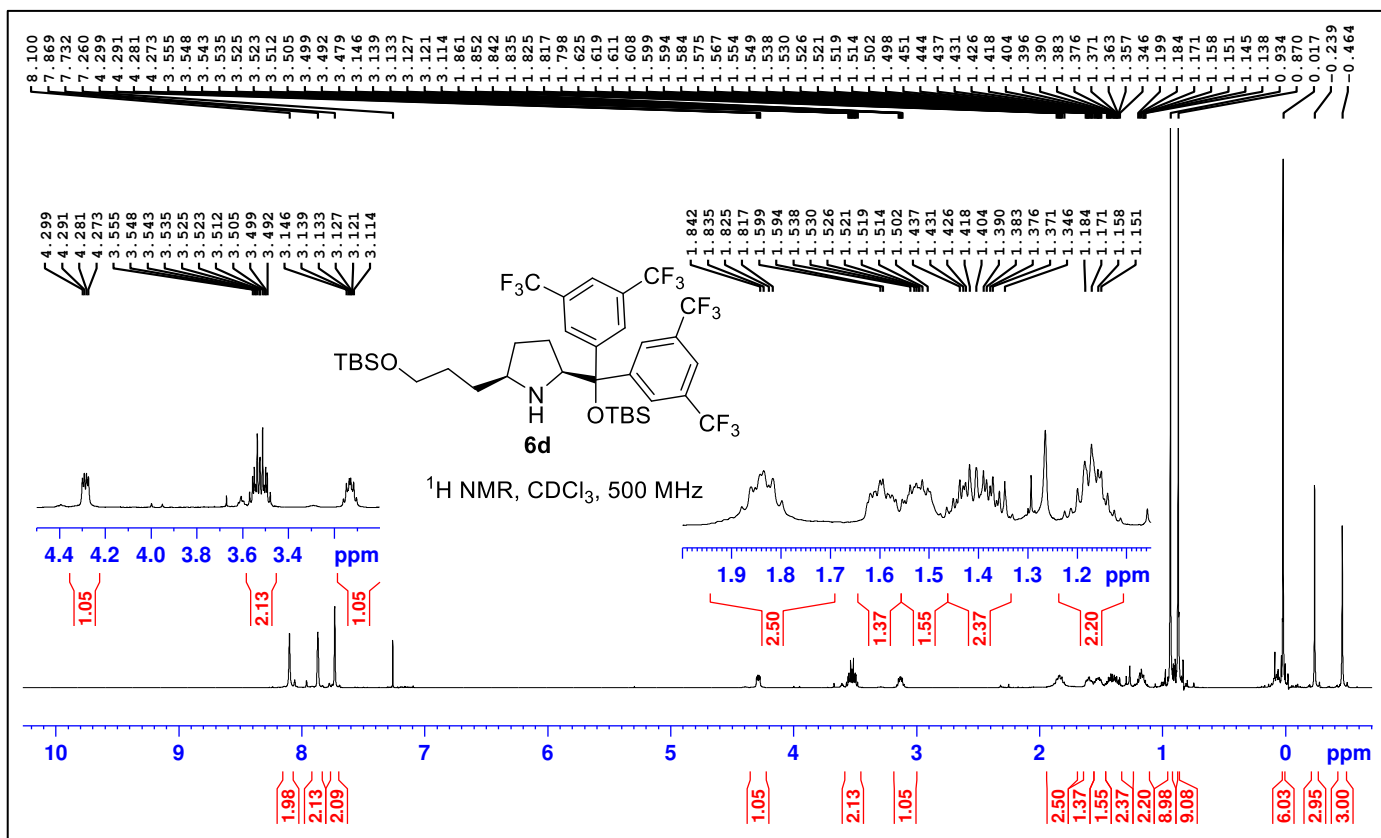


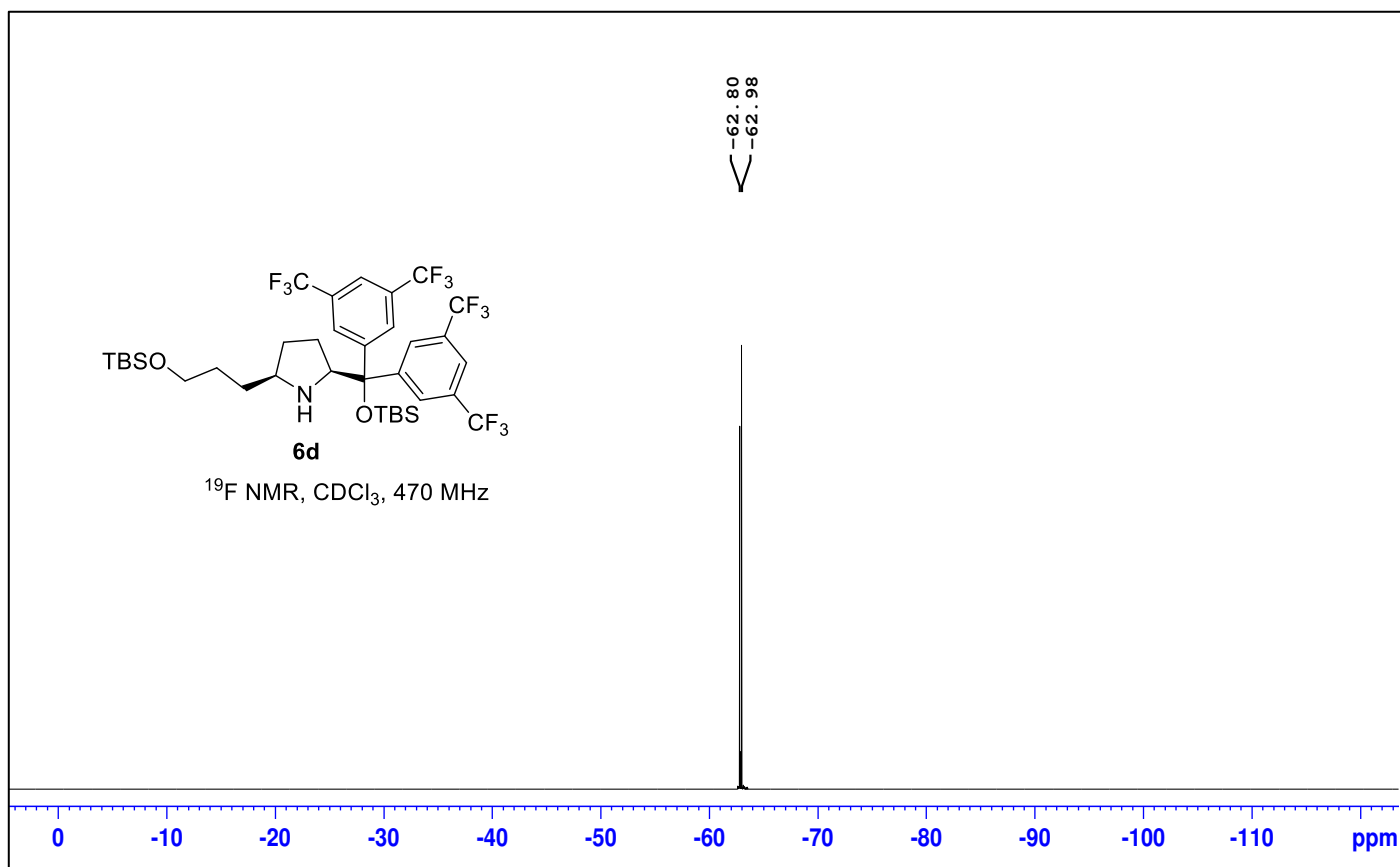
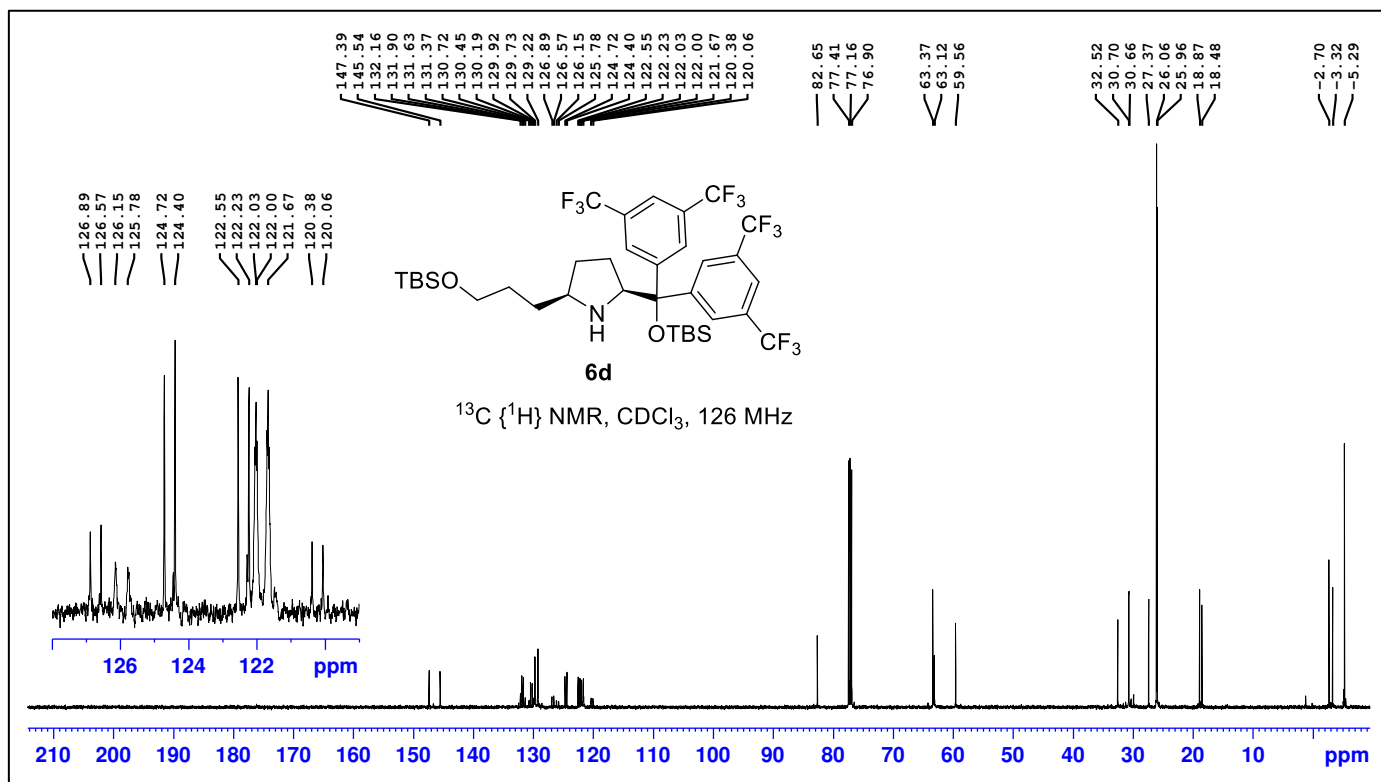
(2*S*,5*R*)-2-(((tertbutyldimethylsilyl)oxy) di(naphthalen-2-yl)methyl)-5-(3-(((tertbutyl dimethylsilyl)oxy)propyl)pyrrolidine (6c**)**



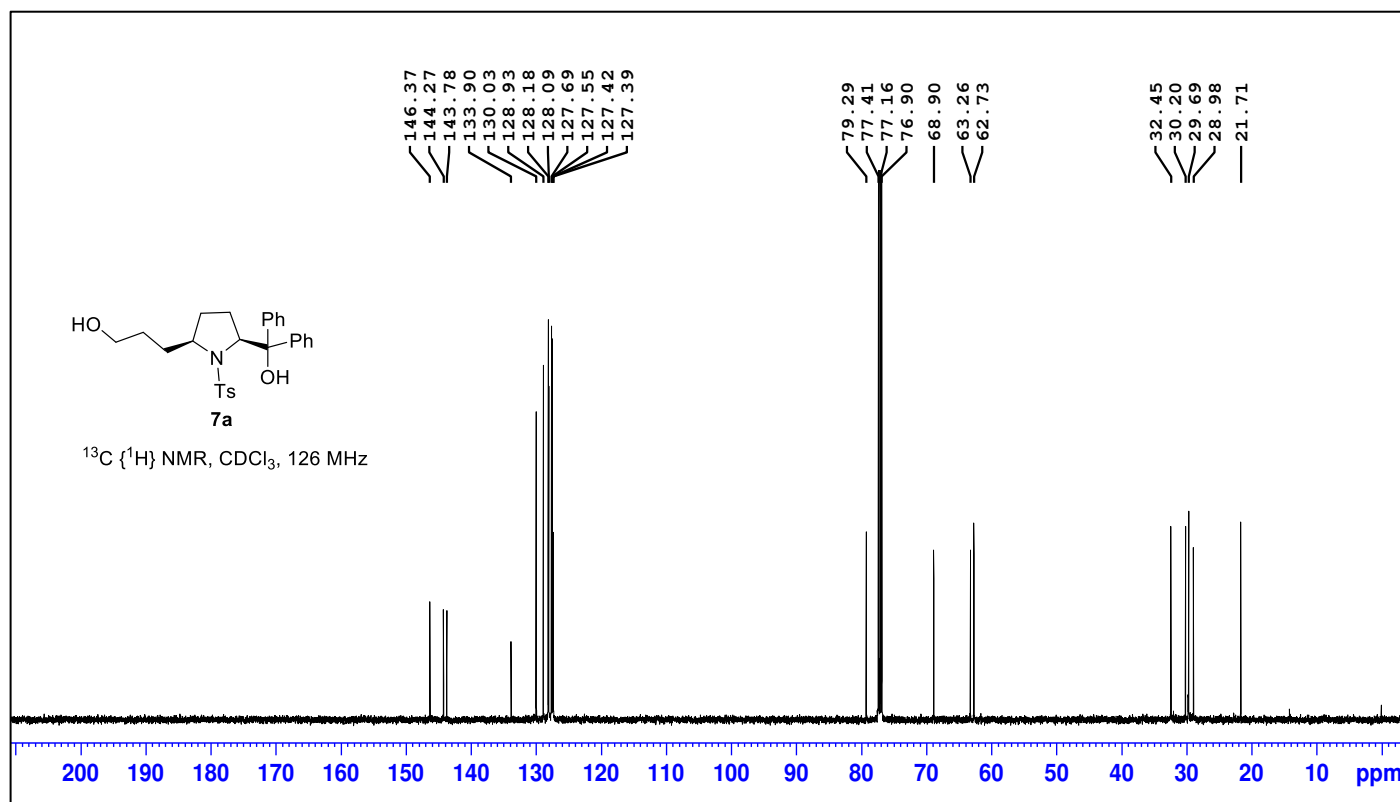
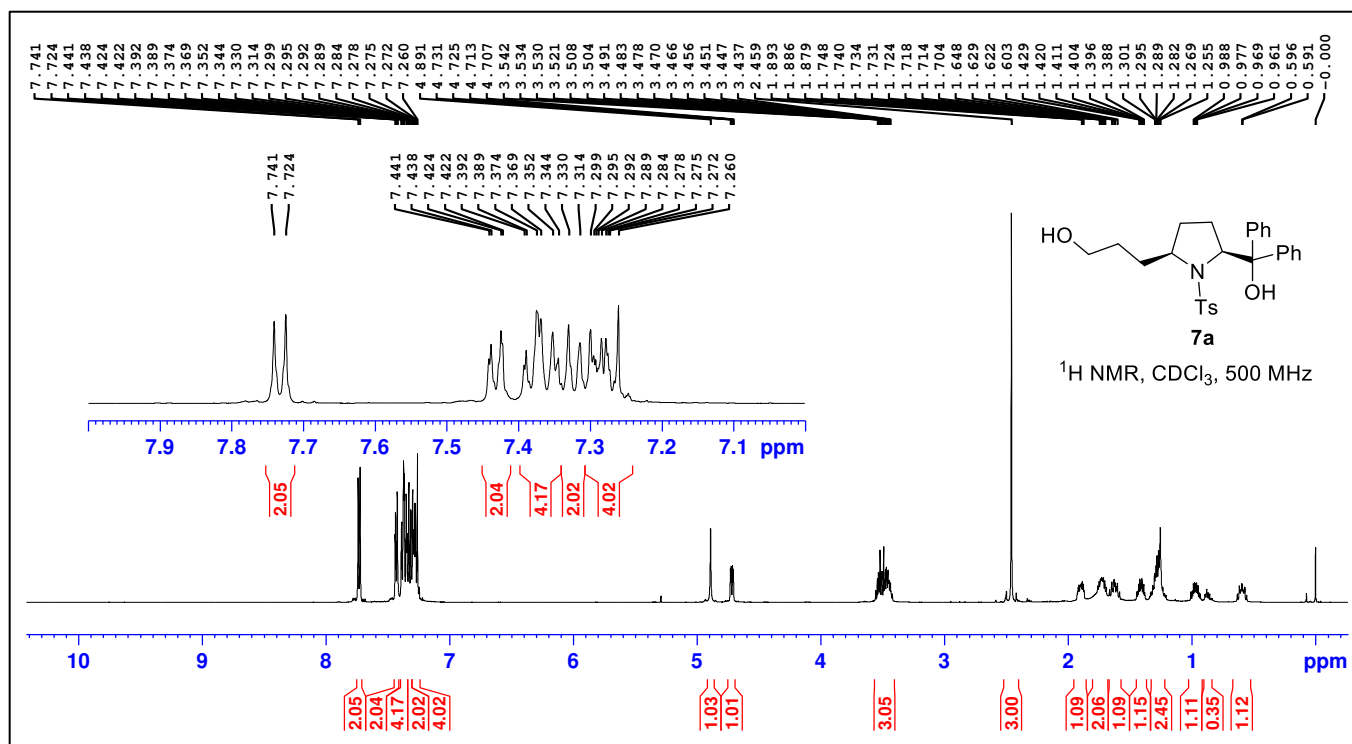


(2*S*,5*R*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((*tert*-butyldimethylsilyl)oxy)methyl)-5-(3-(*tert*-butyldimethylsilyl)oxy)propyl)pyrrolidine (6d**)**

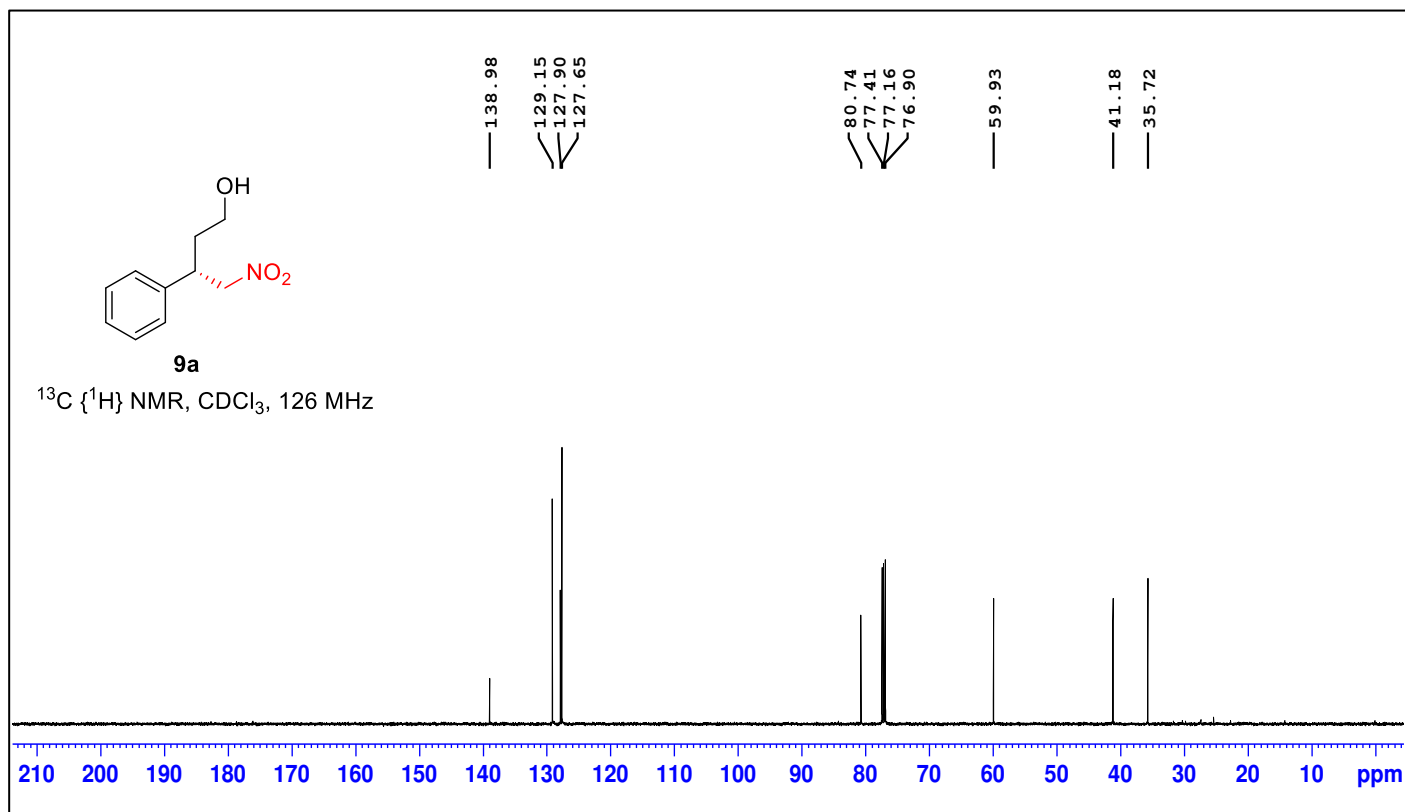
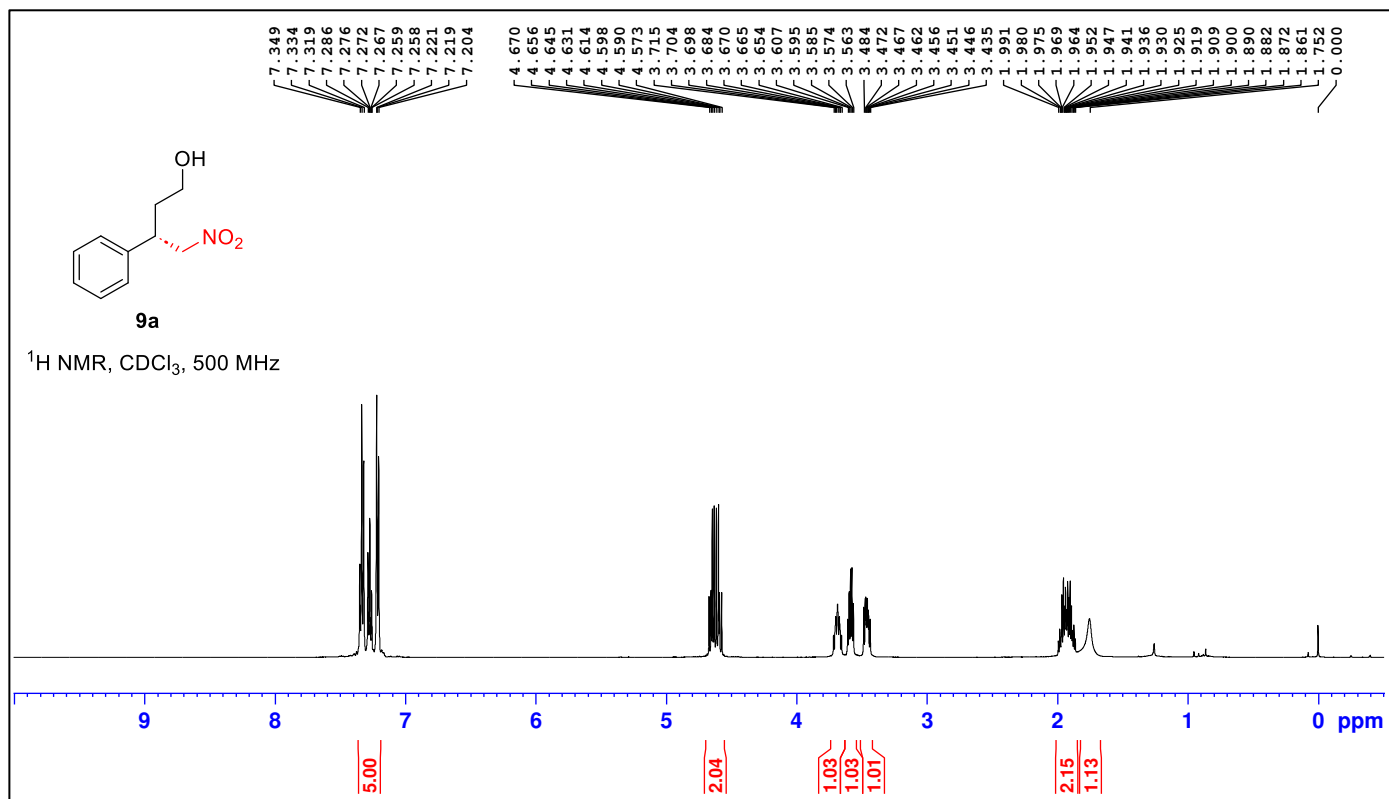




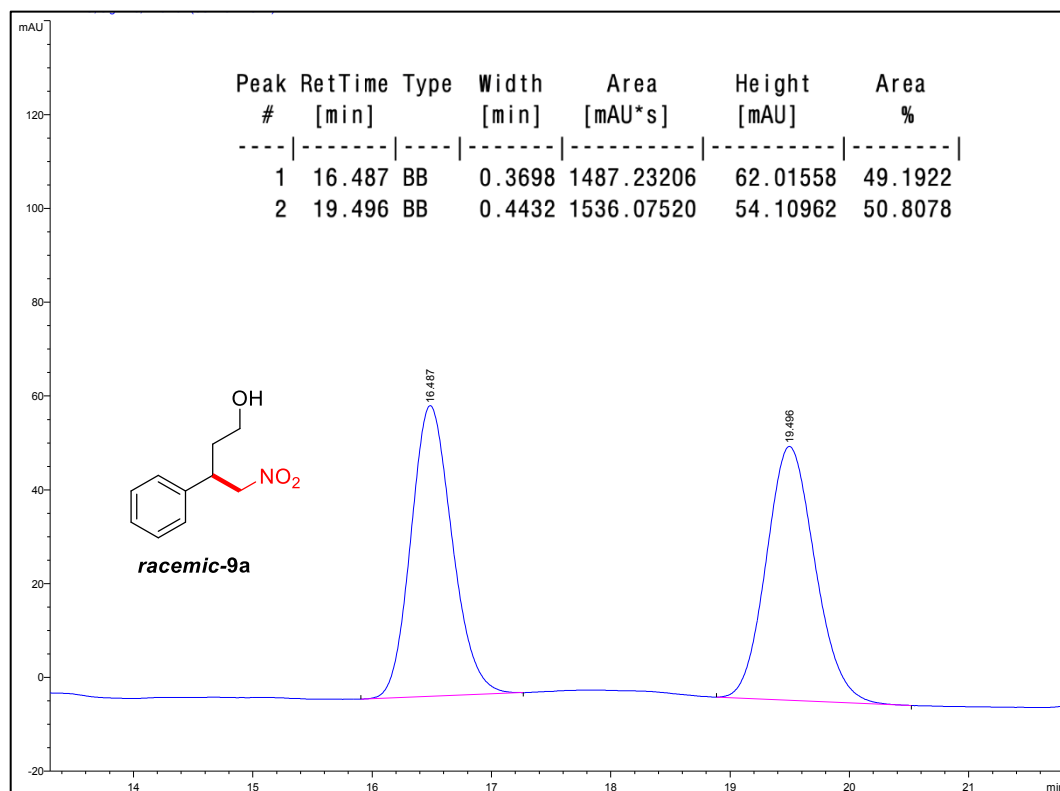
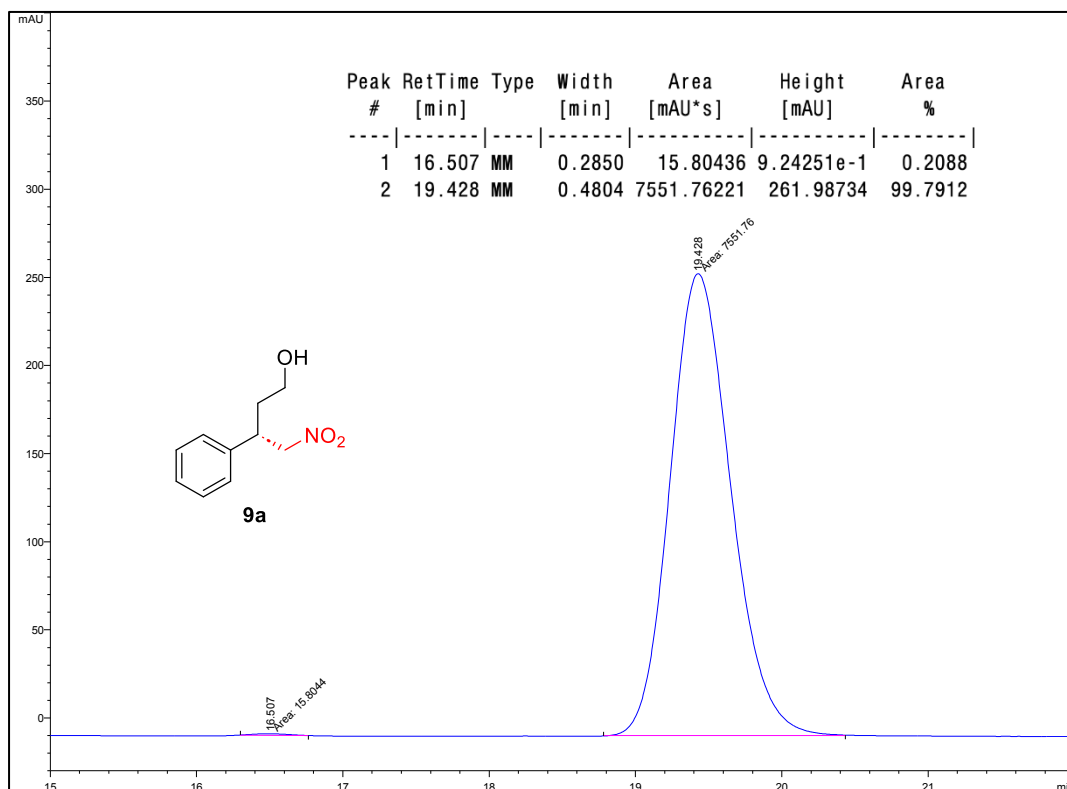
3-((2*R*,5*S*)-5-(hydroxydiphenylmethyl)-1-tosylpyrrolidin-2-yl)propan-1-ol (**7a**)



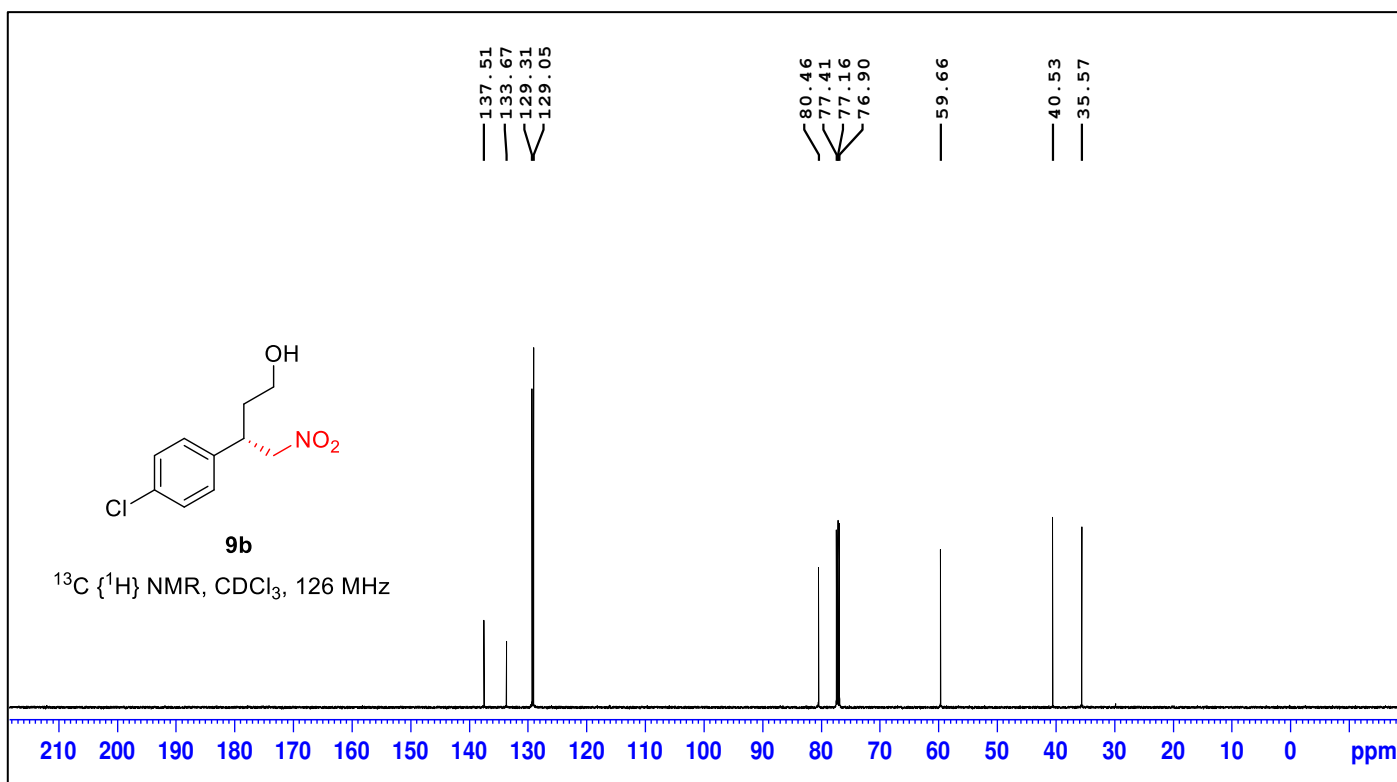
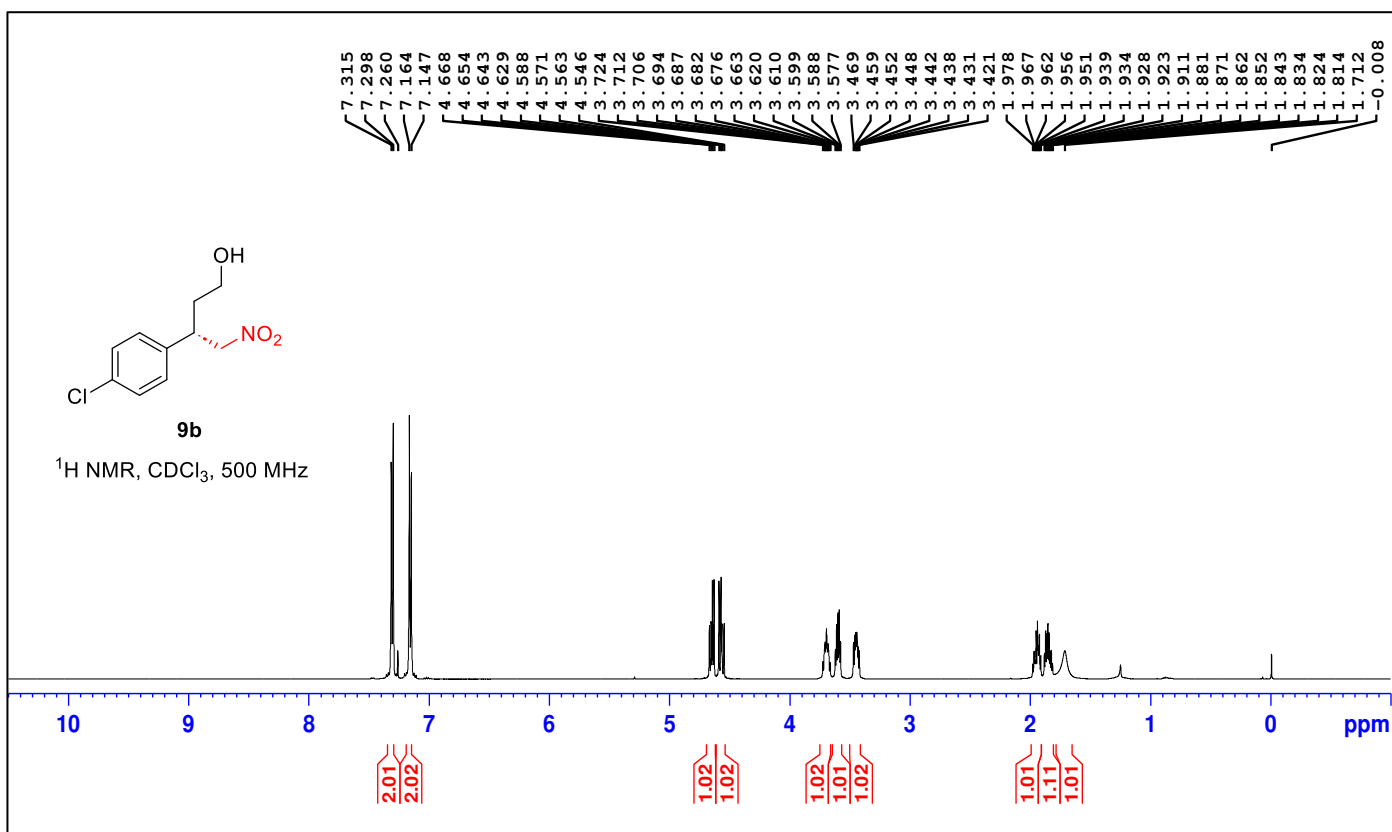
(S)-4-Nitro-3-phenylbutan-1-ol (9a)



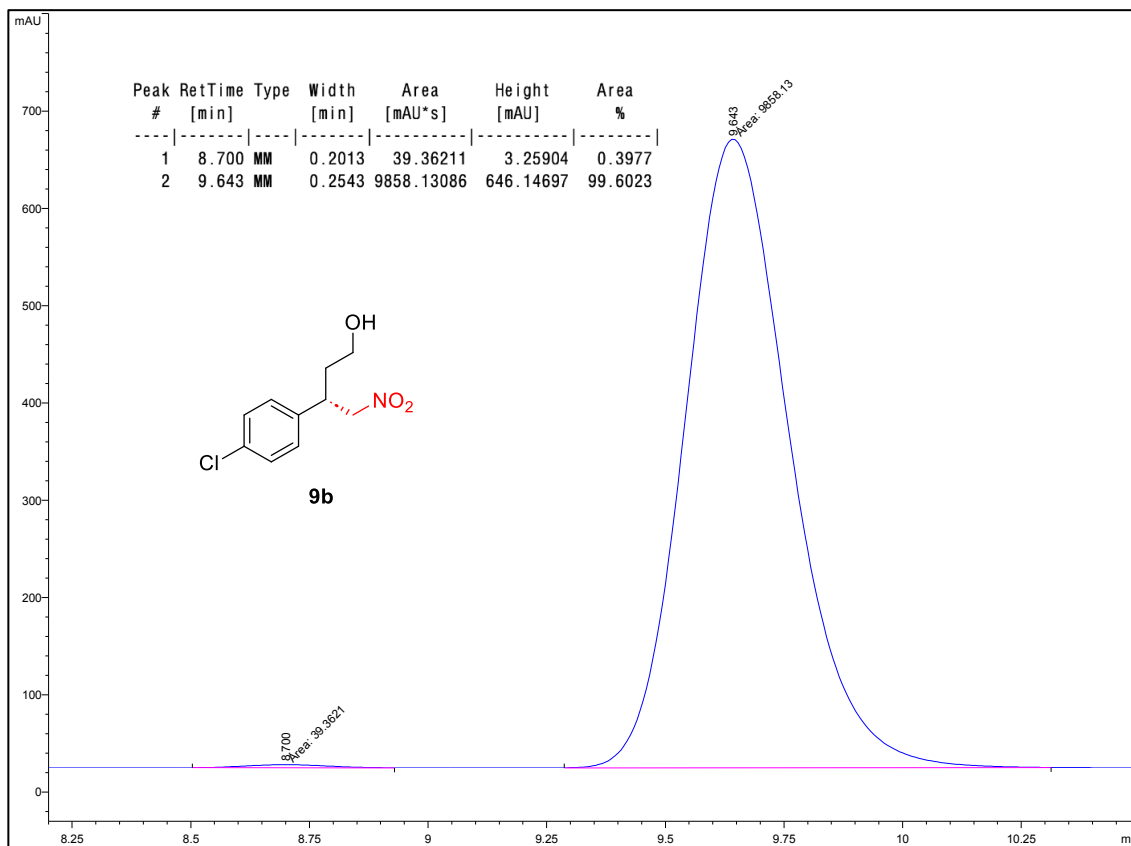
(S)-4-Nitro-3-phenylbutan-1-ol (9a)



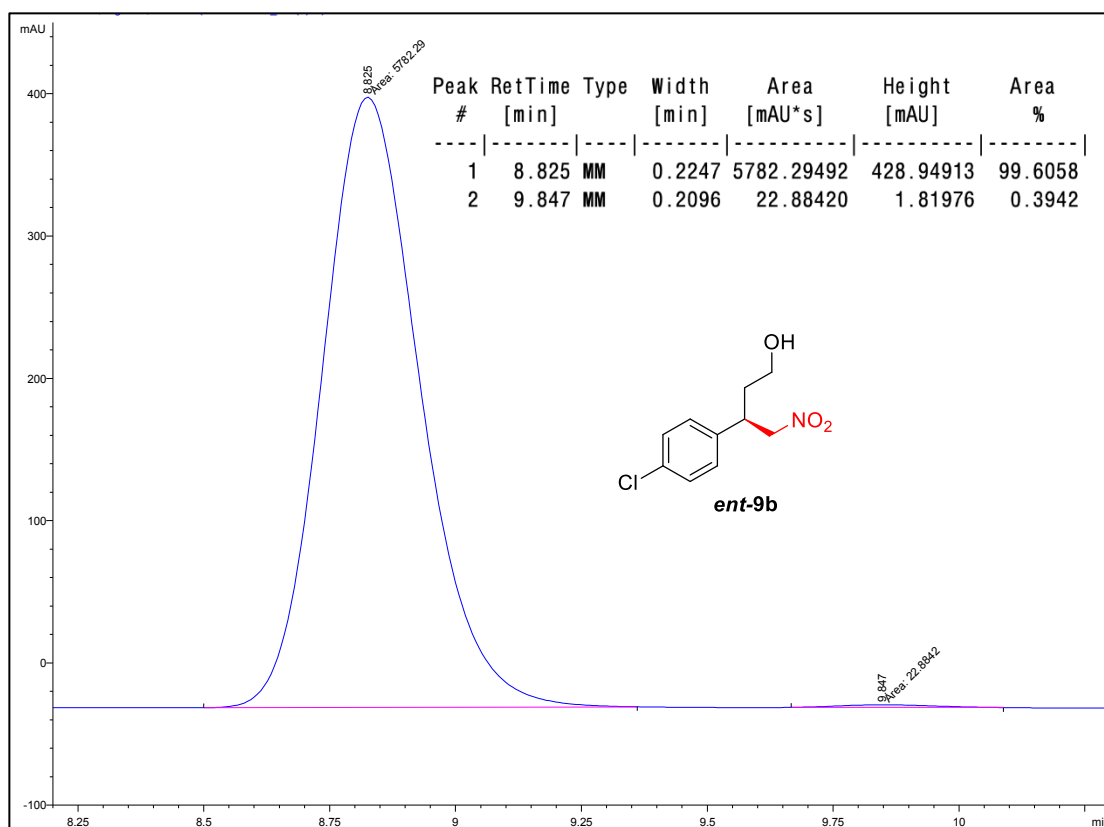
(S)-3-(4-chlorophenyl)-4-nitrobutan-1-ol (9b)

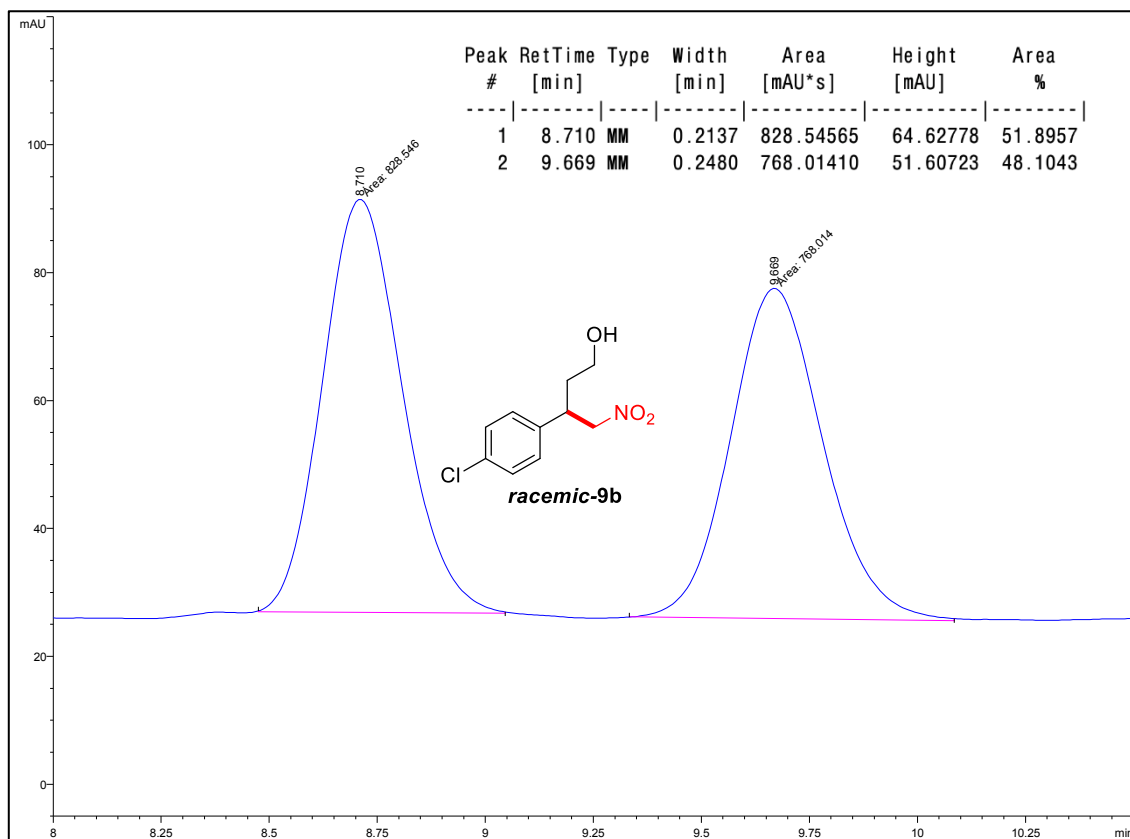


(S)-3-(4-chlorophenyl)-4-nitrobutan-1-ol (9b)

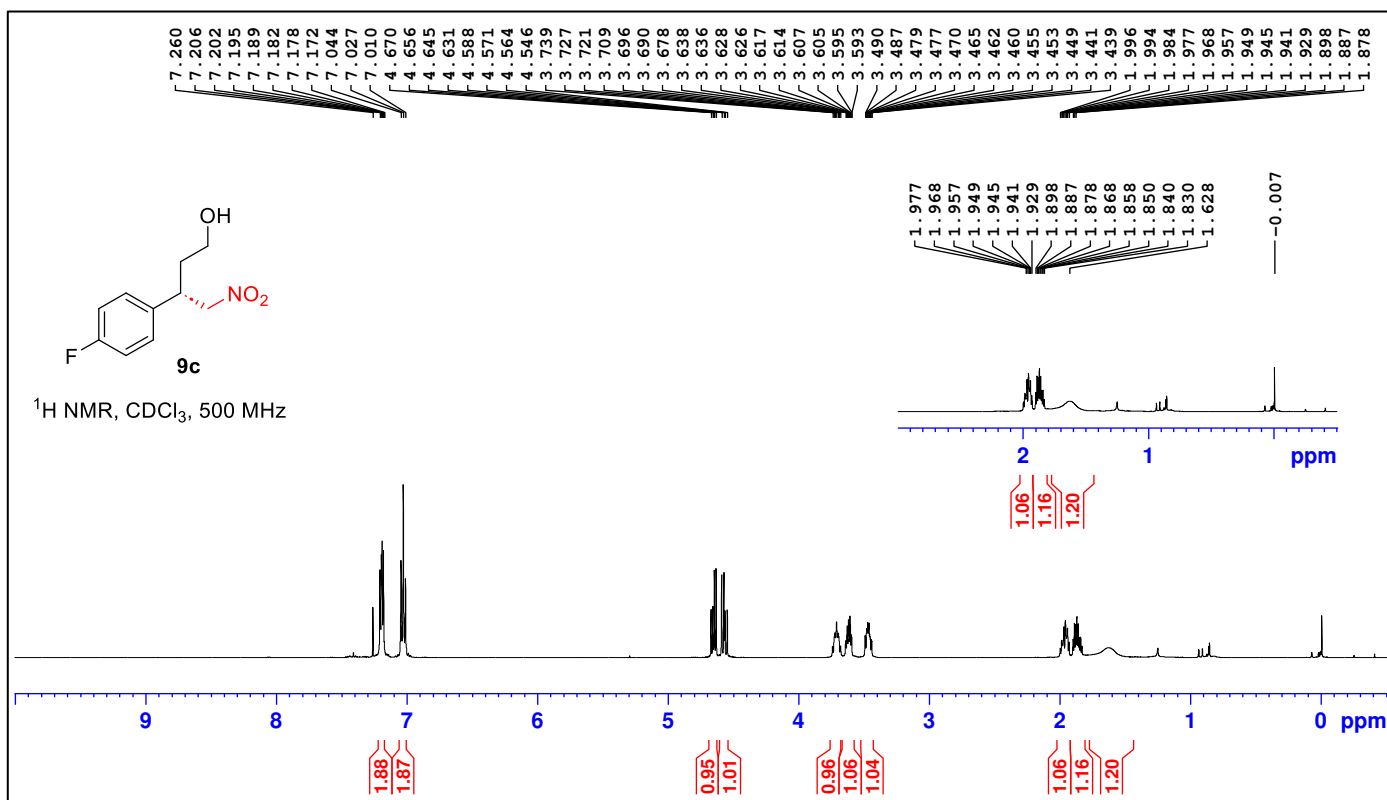


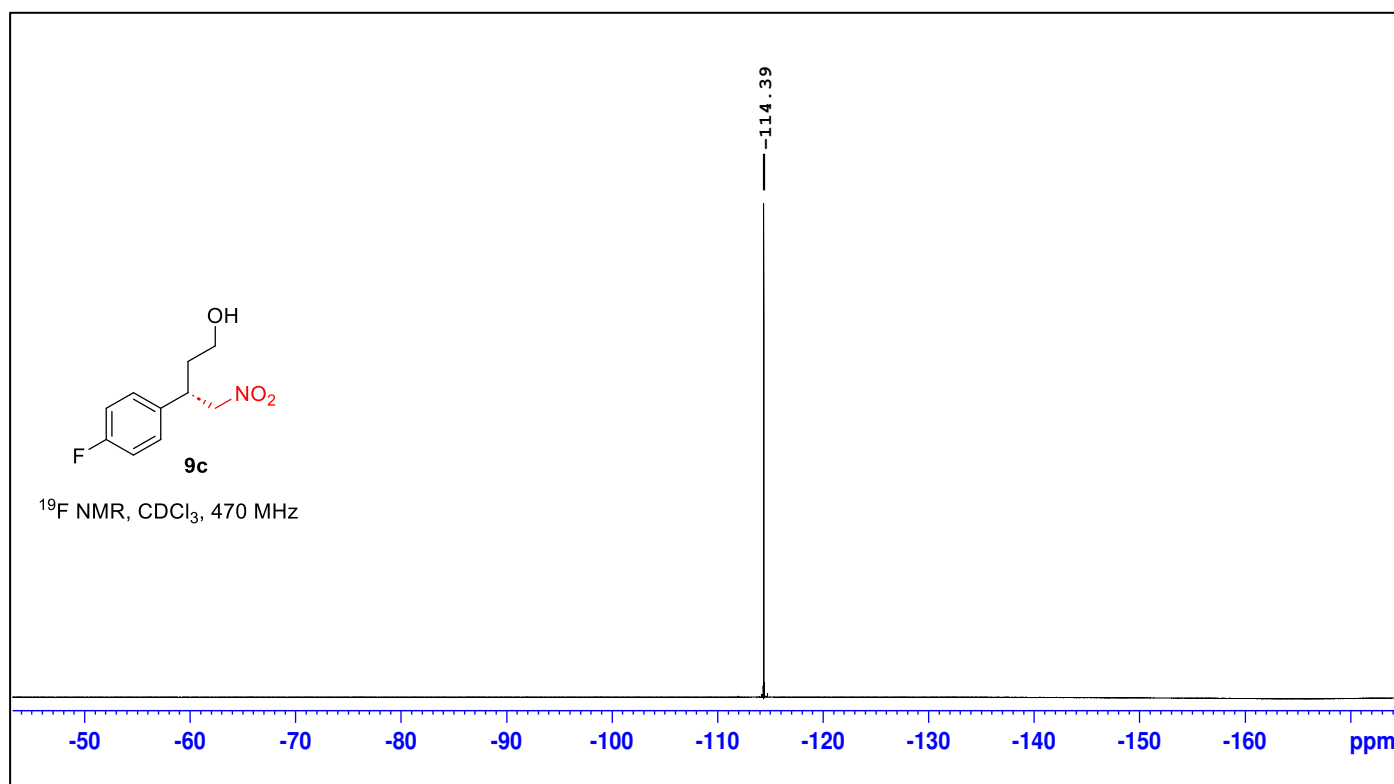
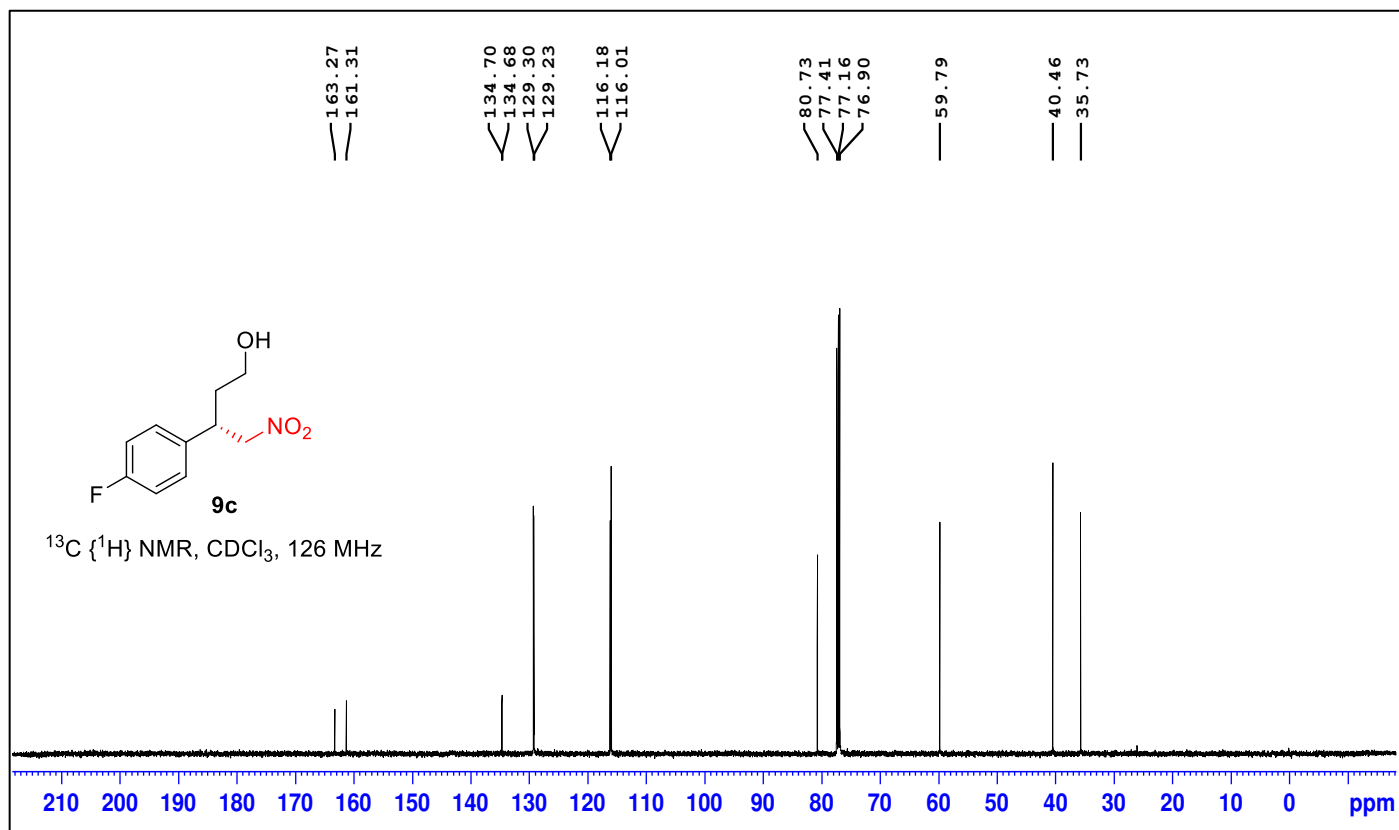
(R)-3-(4-chlorophenyl)-4-nitrobutan-1-ol (ent-9b)



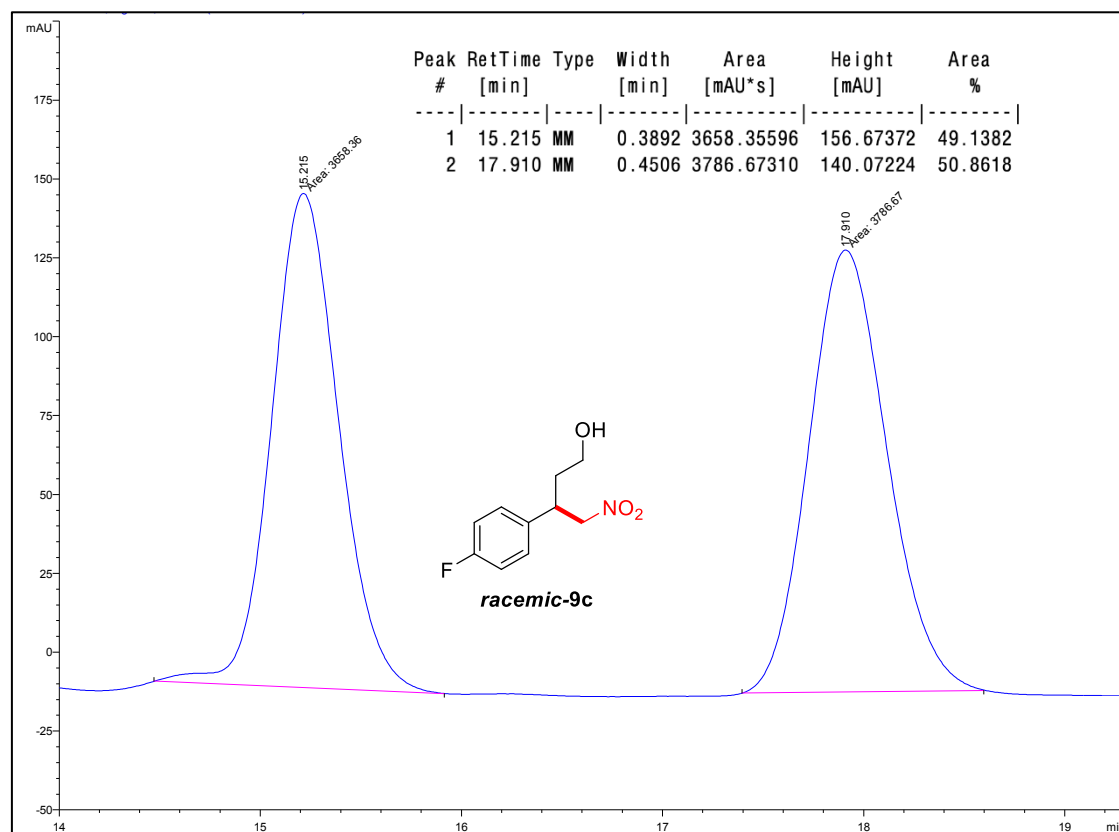
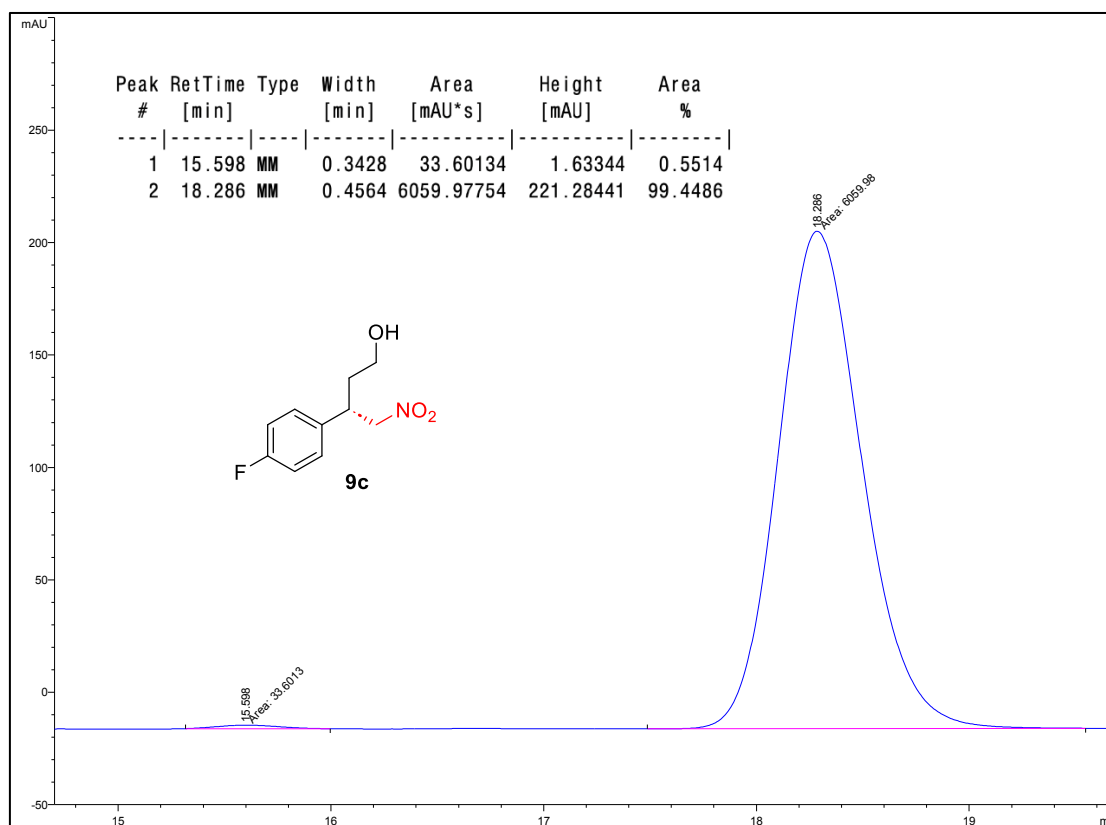


(S)-3-(4-fluorophenyl)-4-nitrobutan-1-ol (9c)

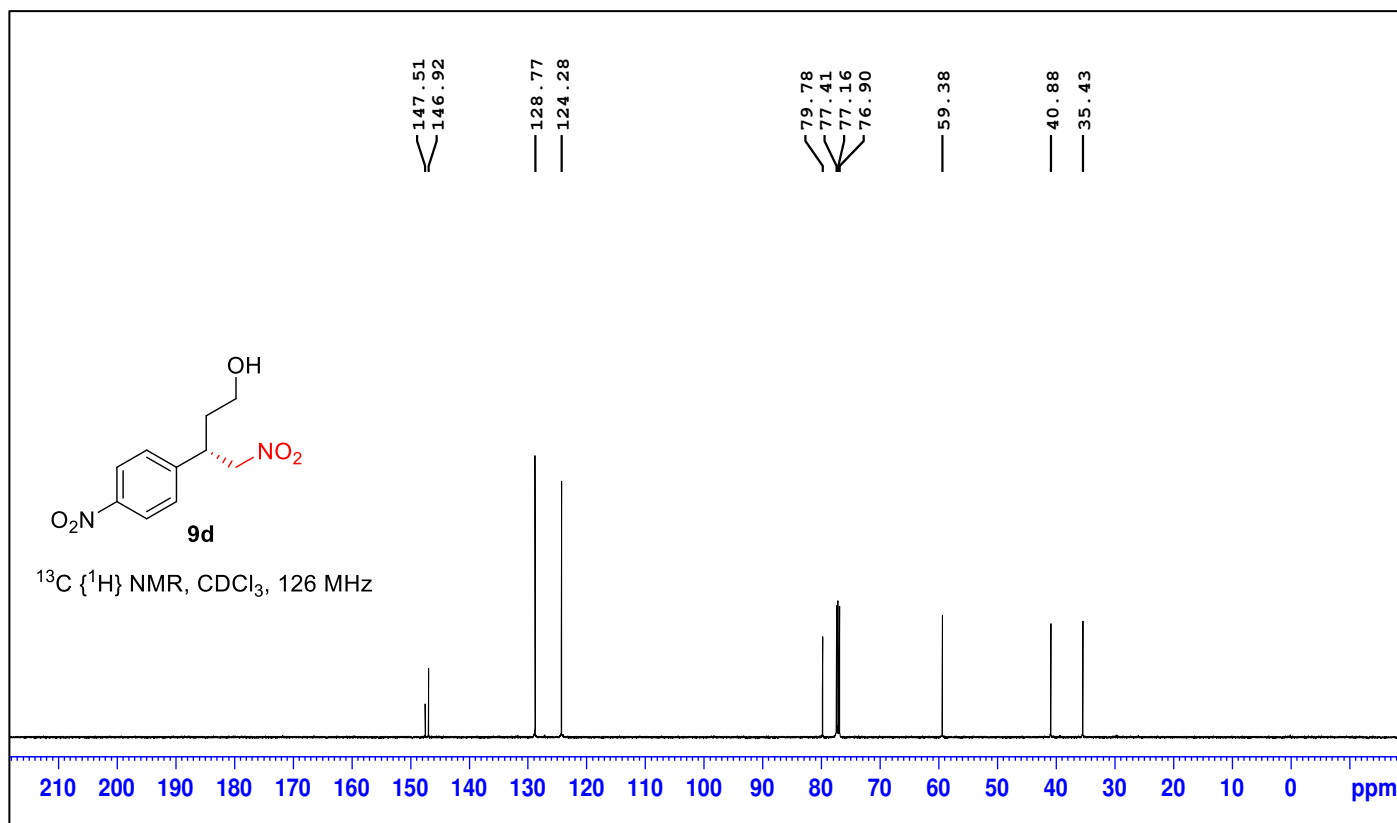
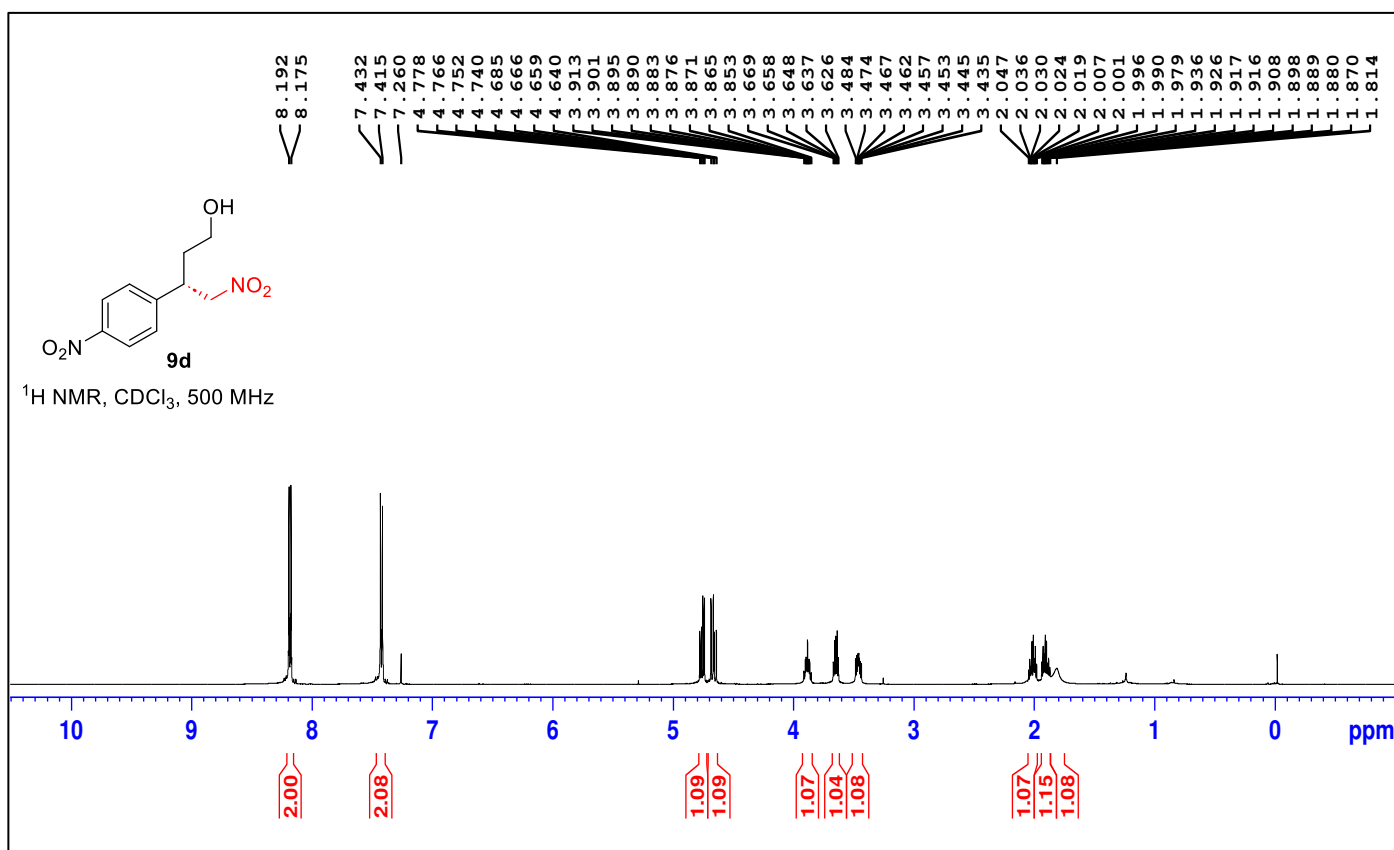




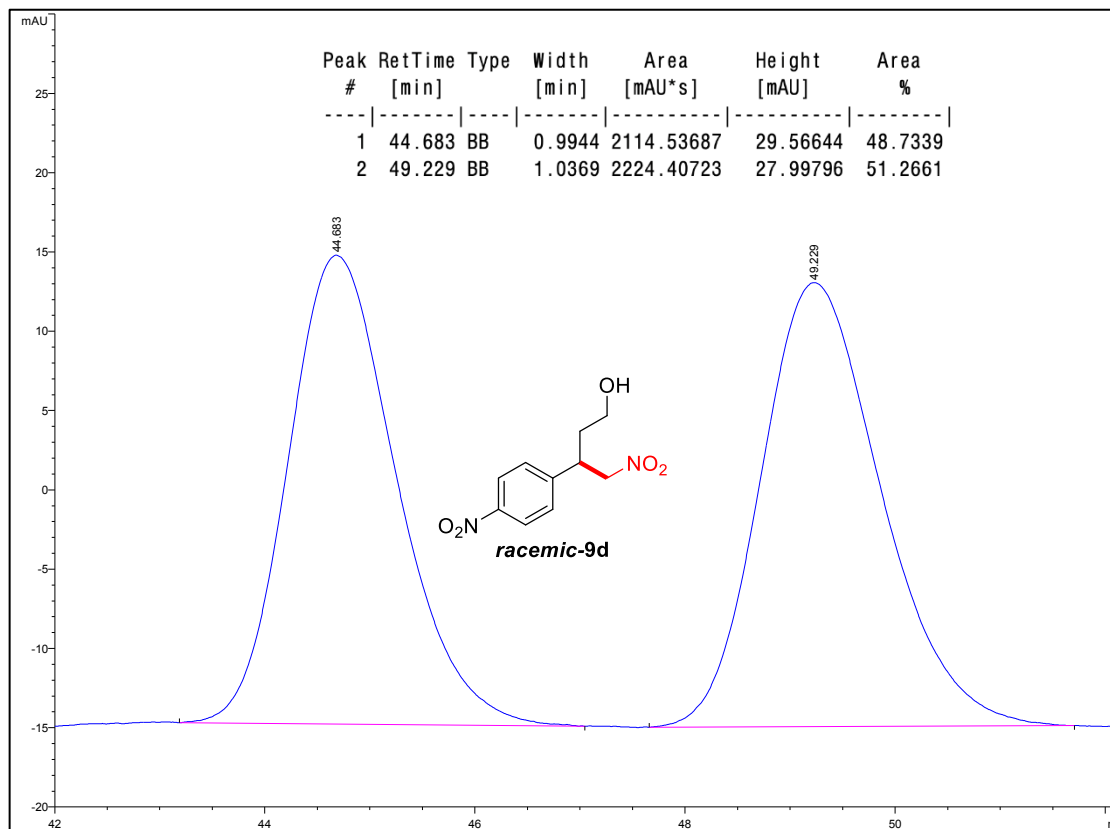
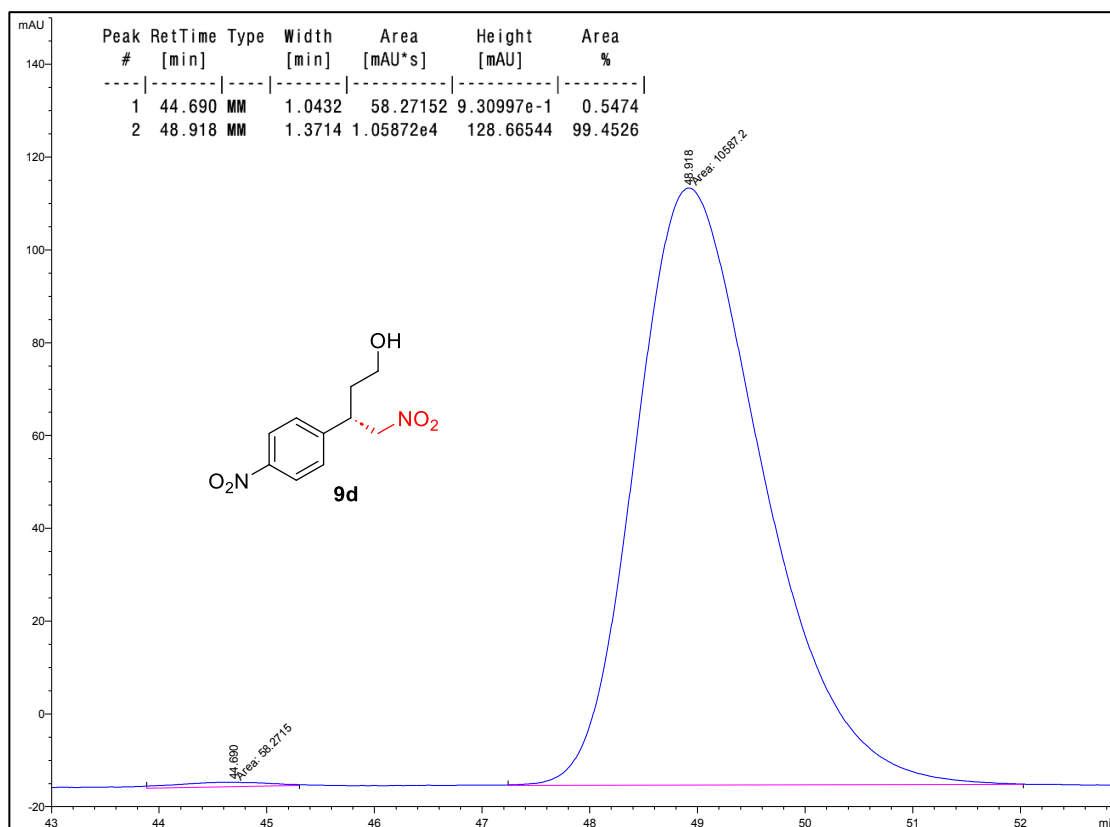
(S)-3-(4-fluorophenyl)-4-nitrobutan-1-ol (9c)



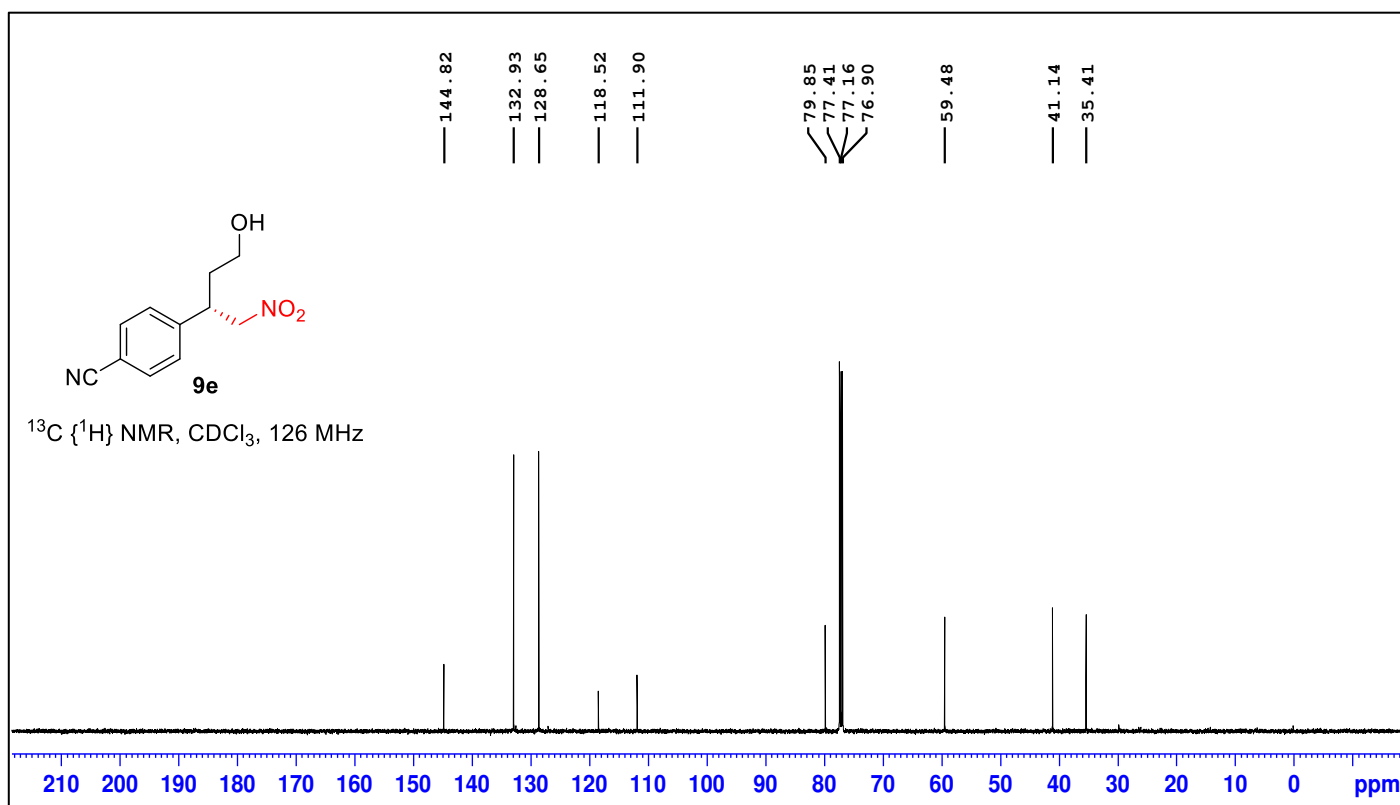
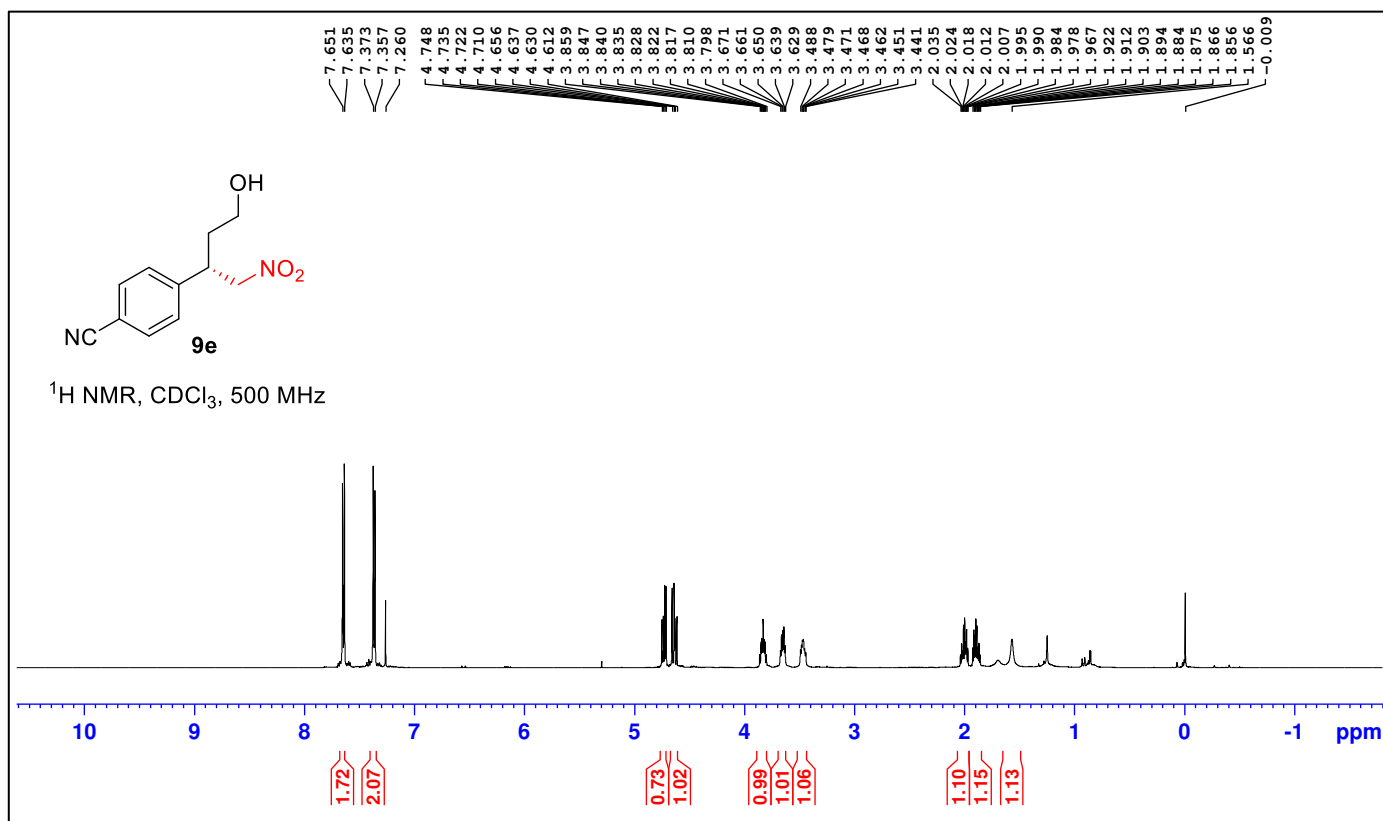
(S)-4-nitro-3-(4-nitrophenyl)butan-1-ol (9d)



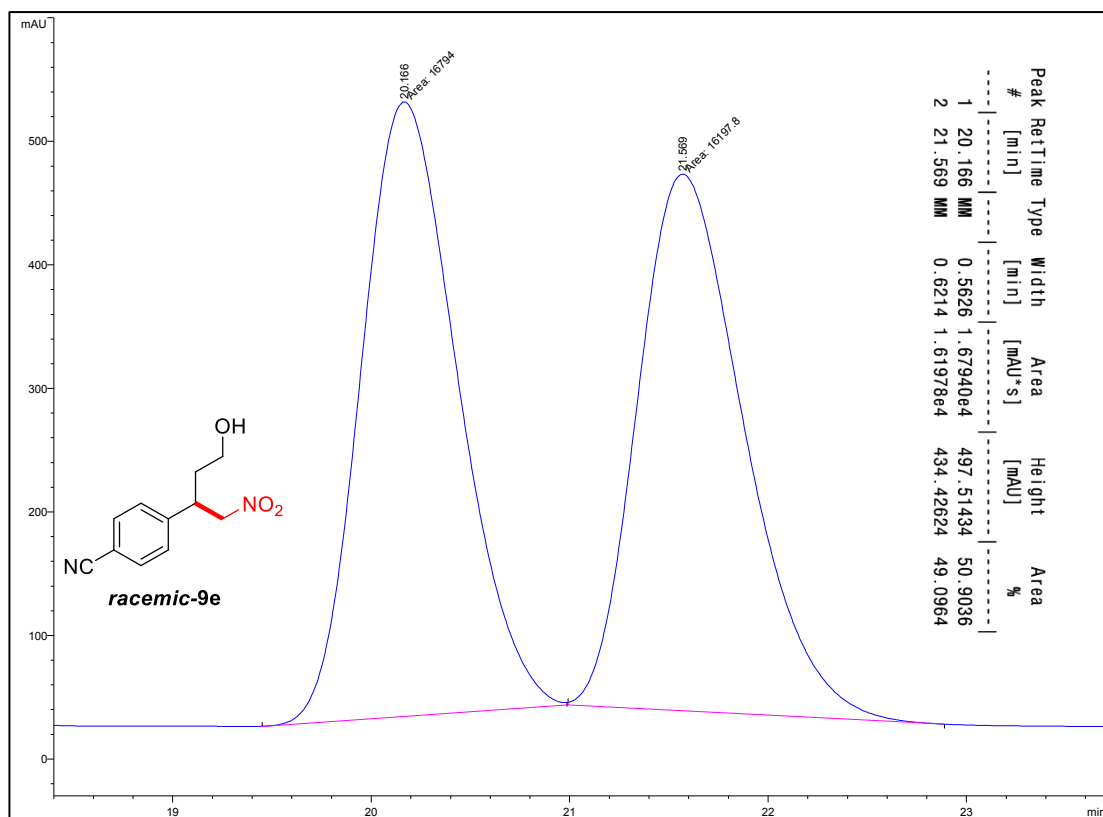
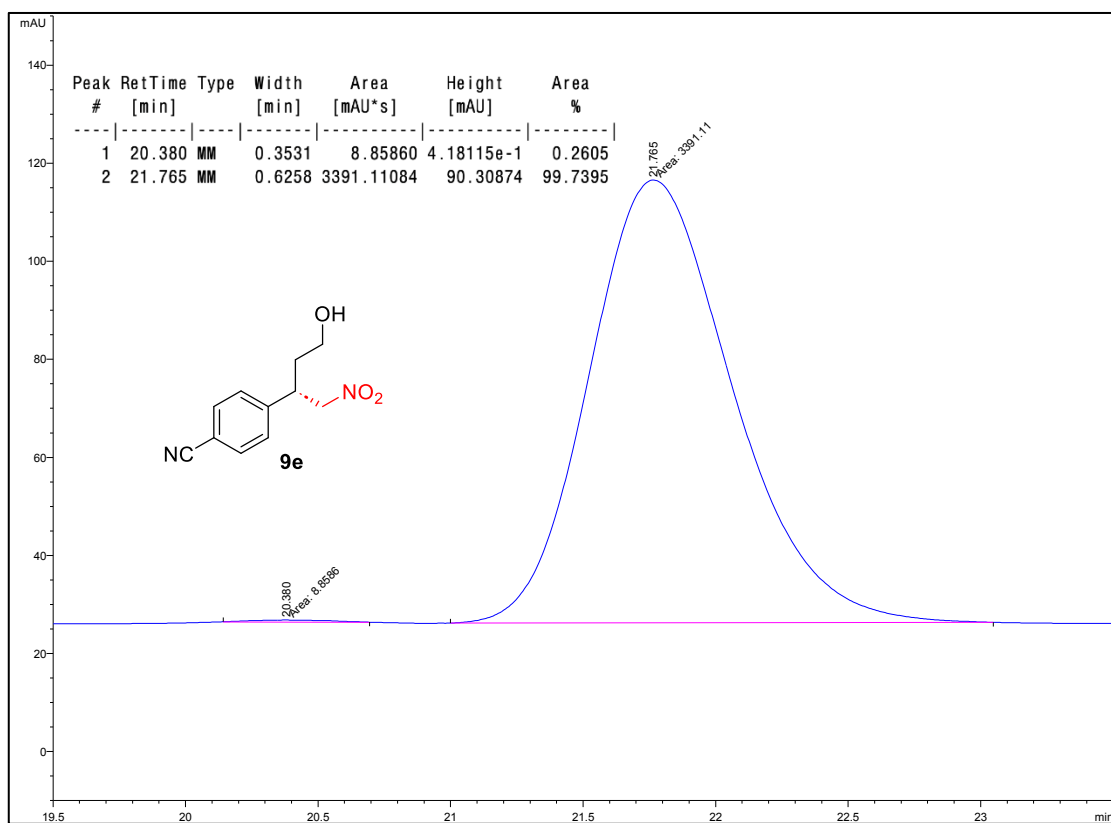
(S)-4-nitro-3-(4-nitrophenyl)butan-1-ol (9d)



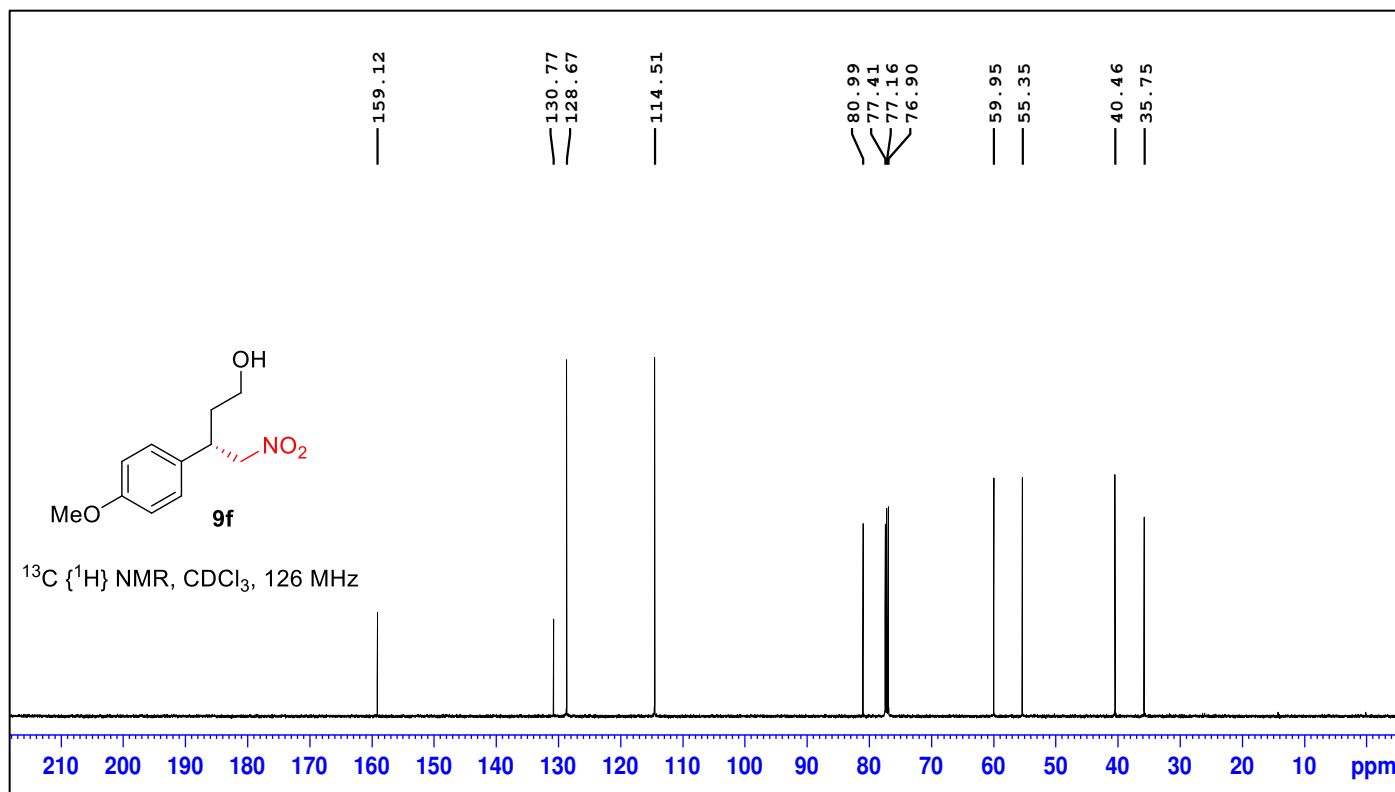
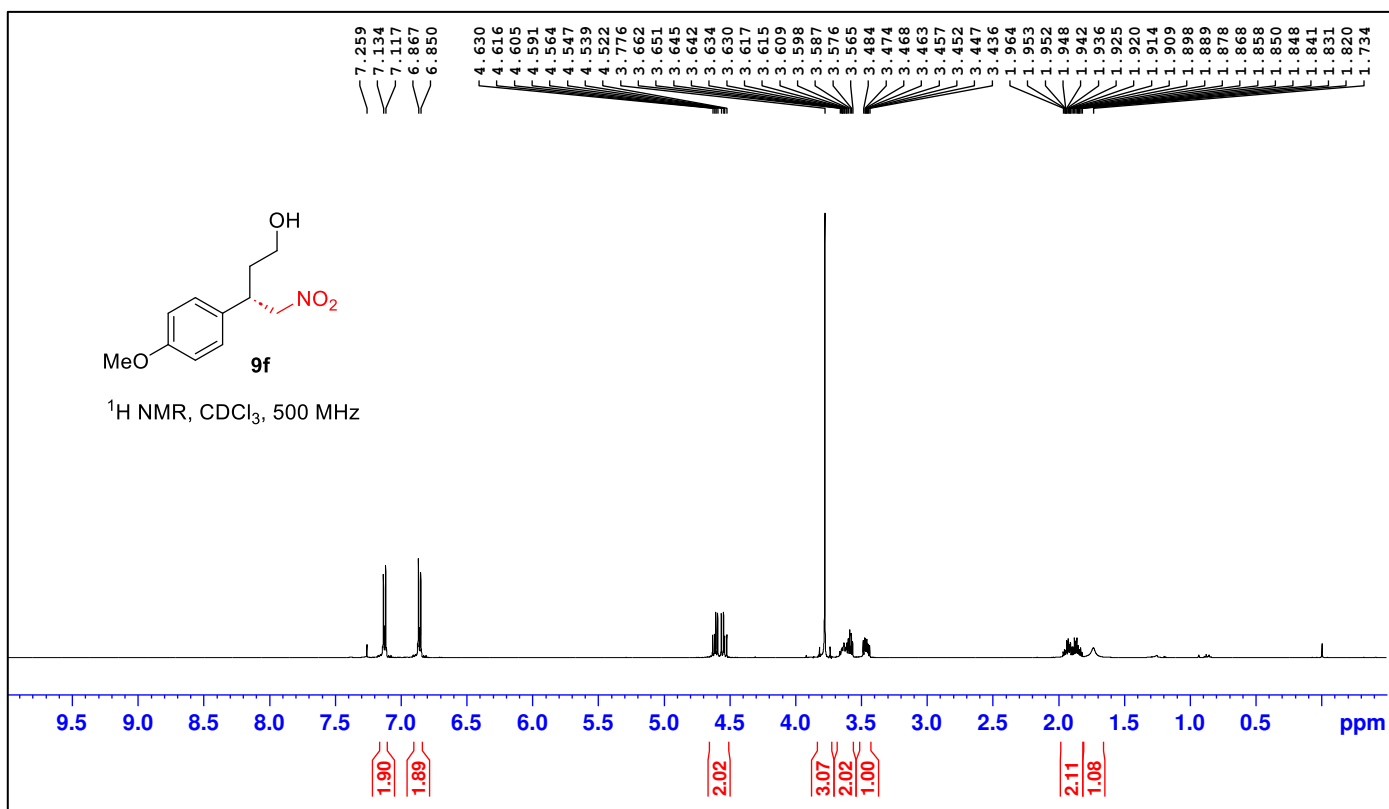
(S)-4-(4-hydroxy-1-nitrobutan-2-yl)benzonitrile (9e)



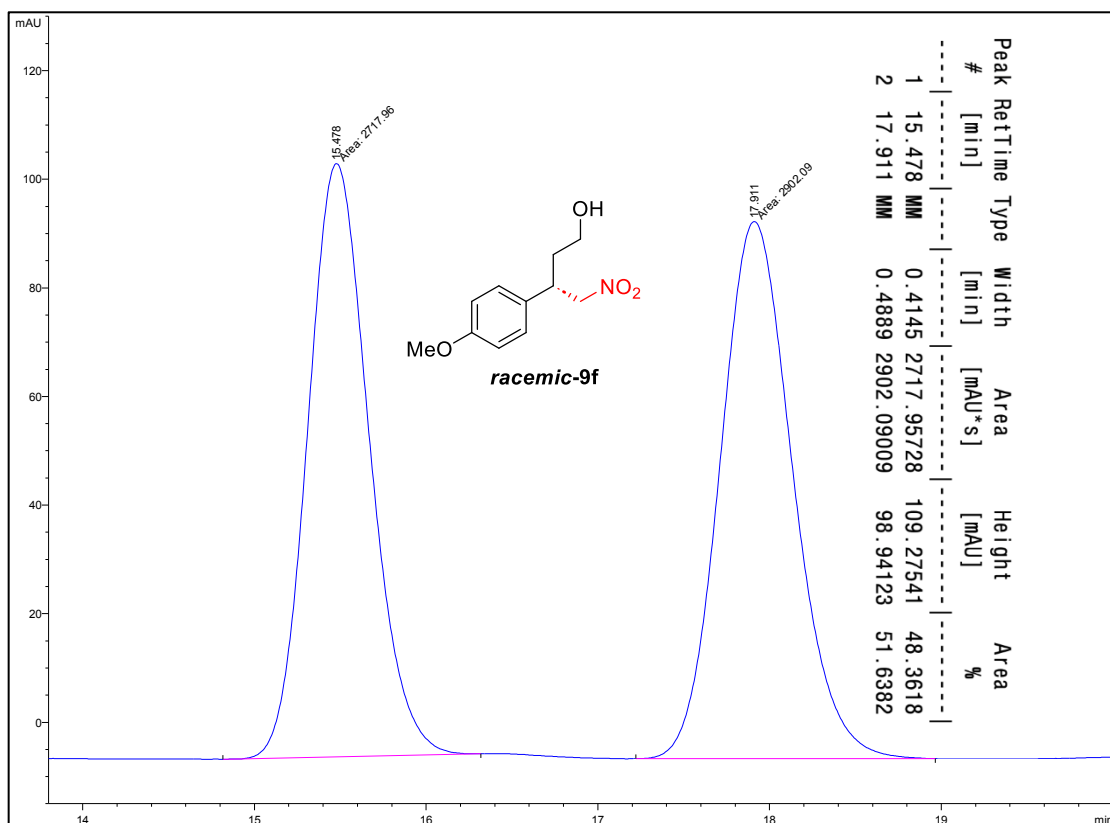
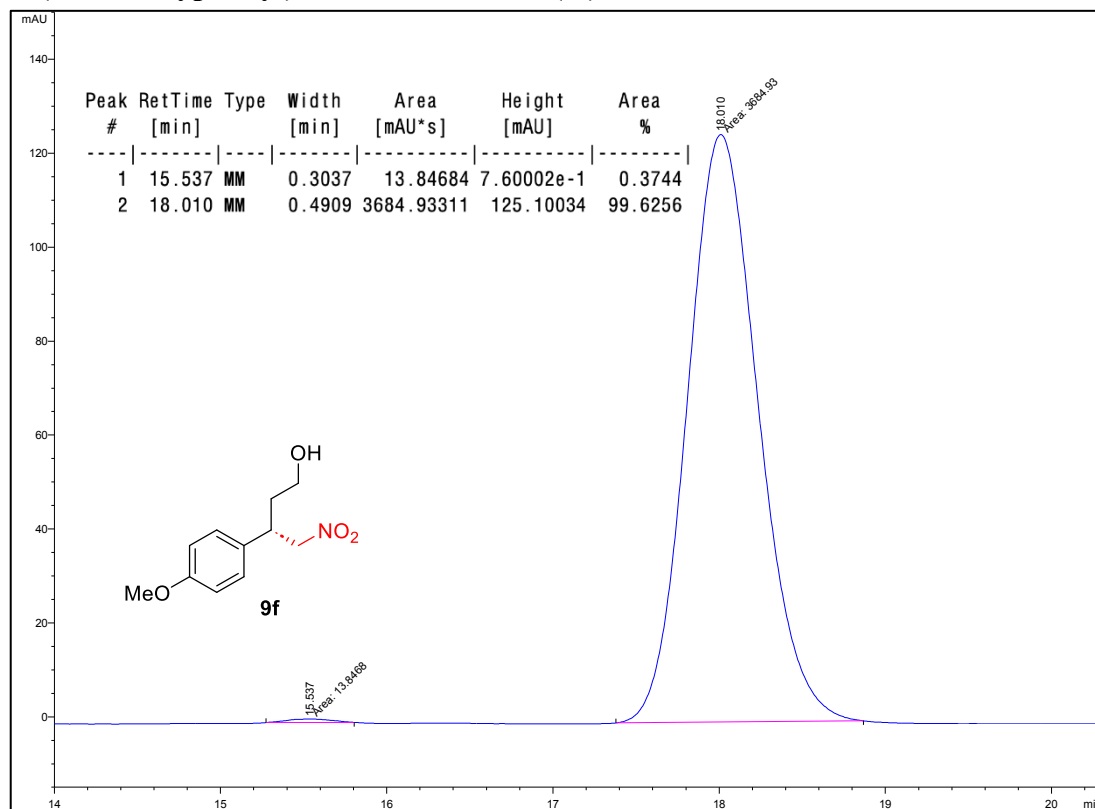
(S)-4-(4-hydroxy-1-nitrobutan-2-yl)benzonitrile (9e)



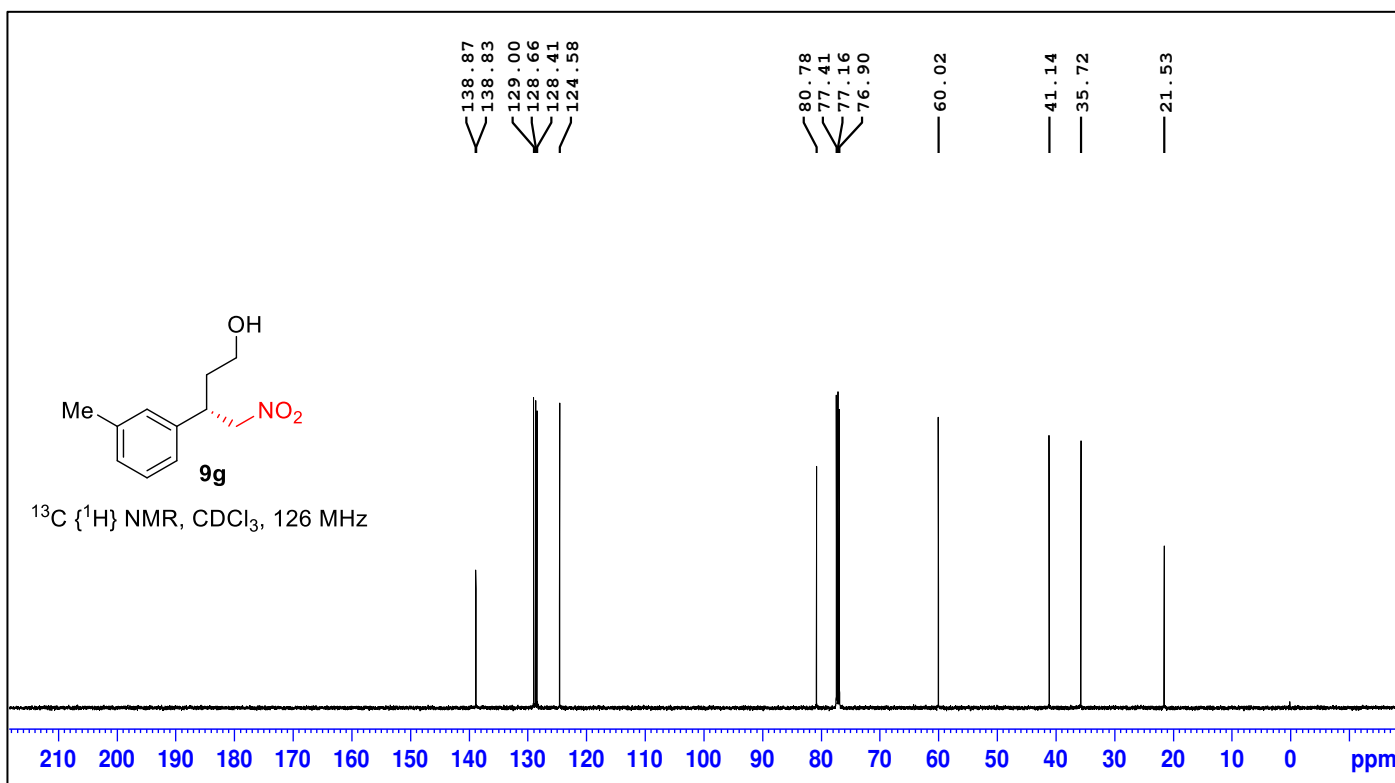
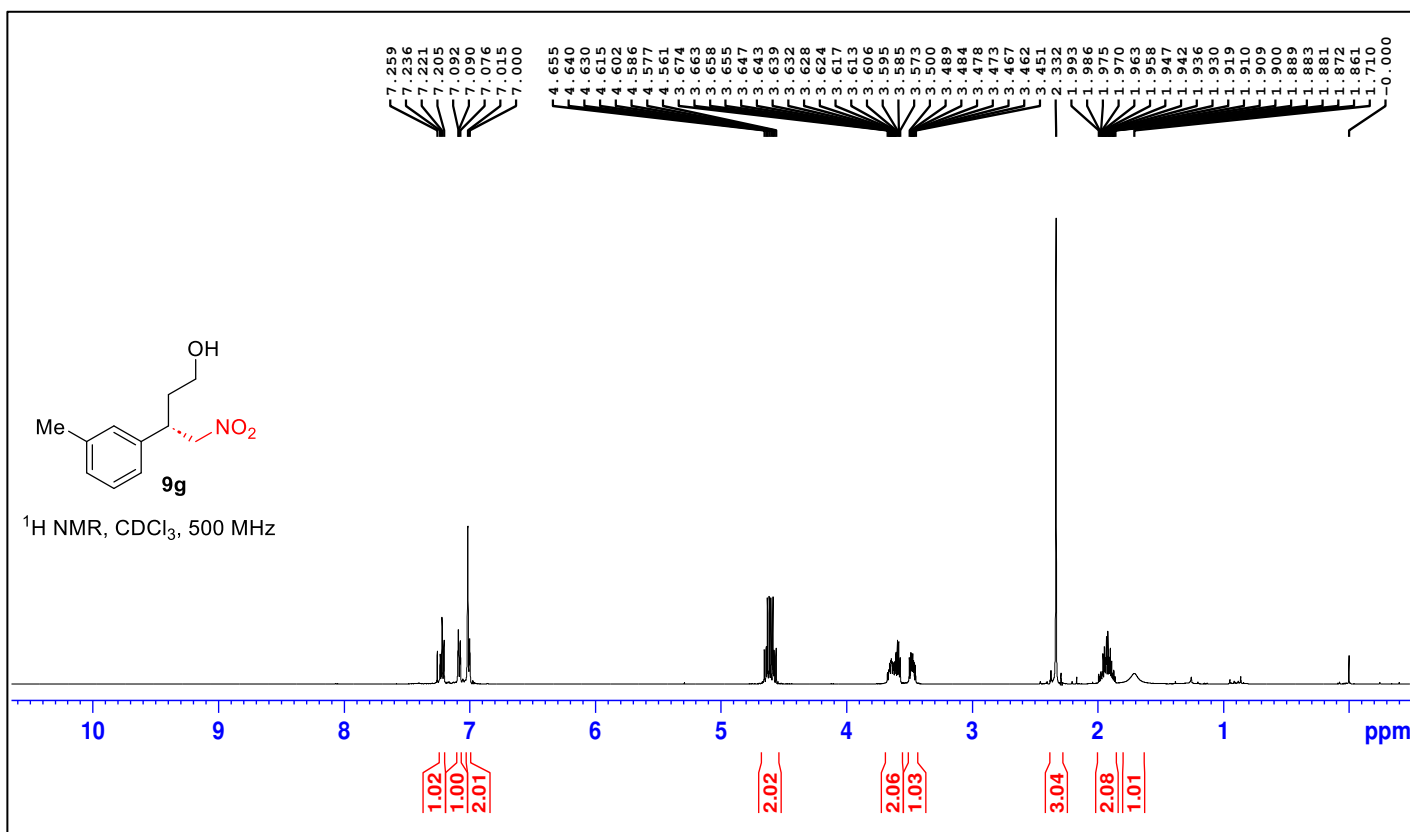
(S)- 3-(4-methoxyphenyl)-4-nitrobutan-1-ol (9f)



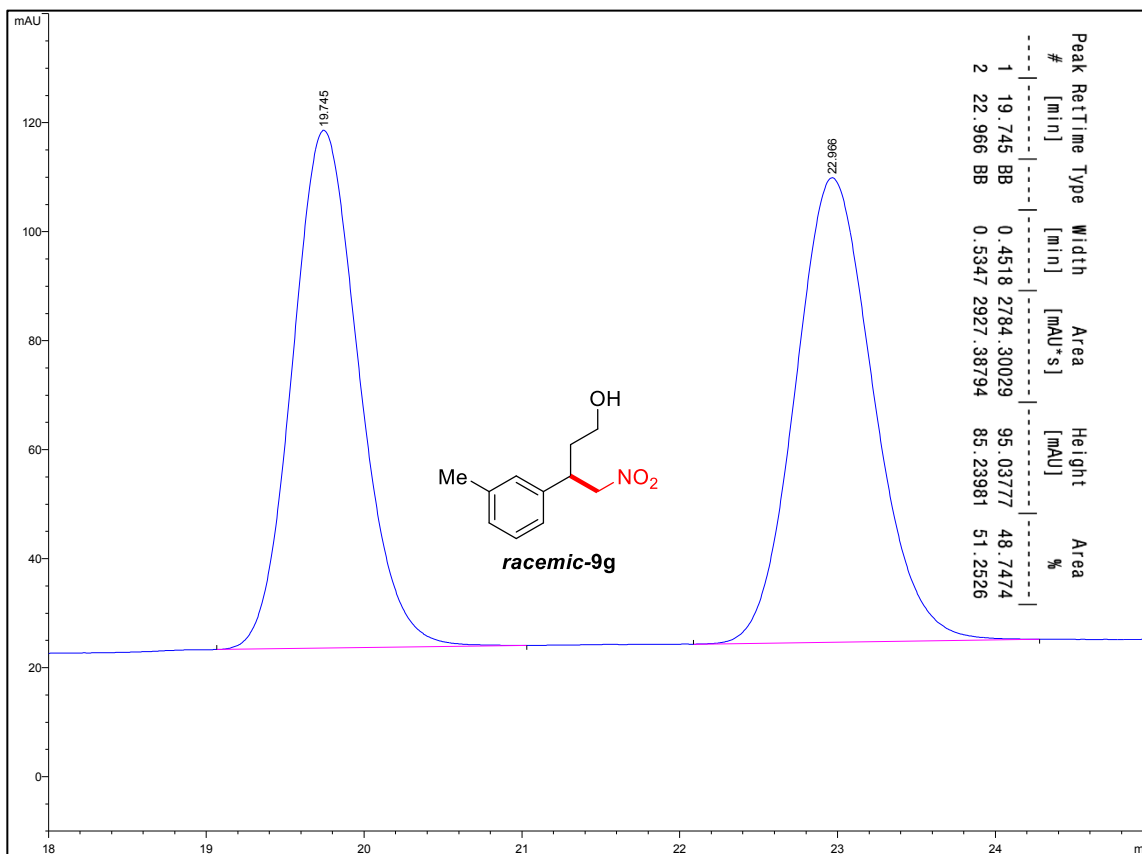
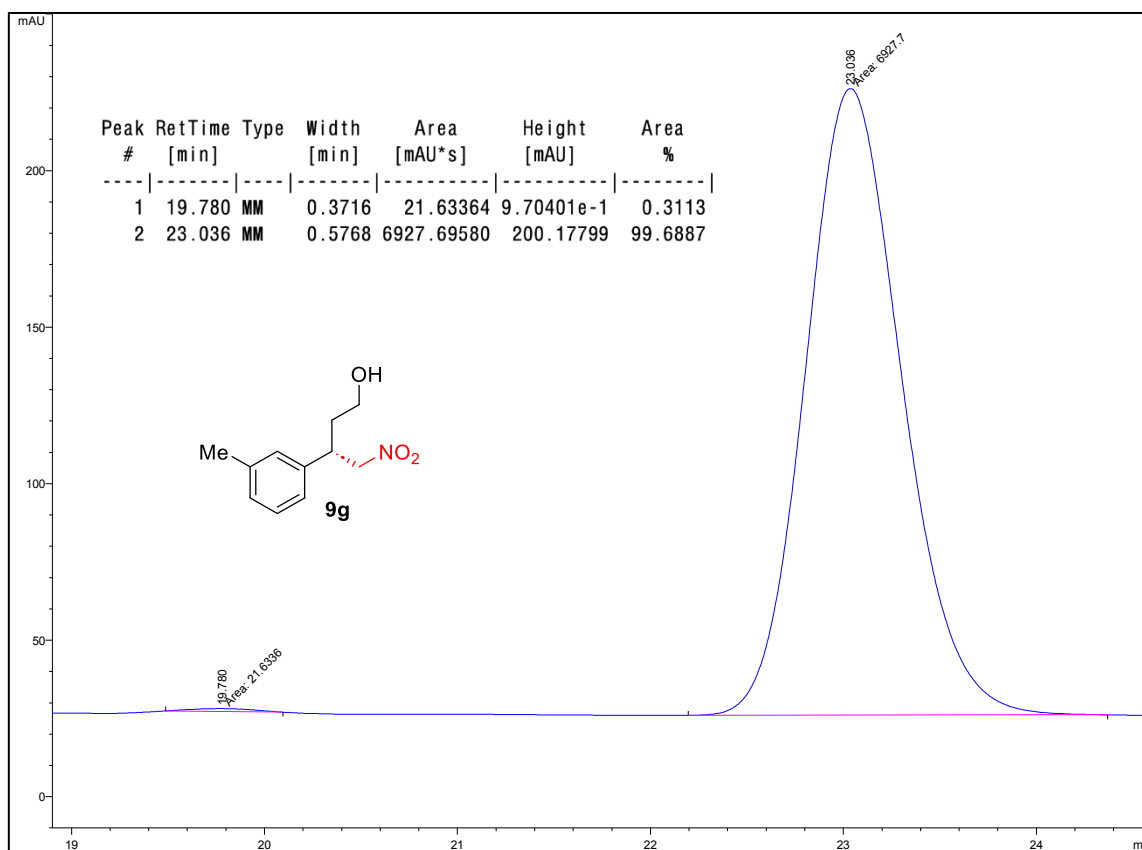
(S)- 3-(4-methoxyphenyl)-4-nitrobutan-1-ol (9f)



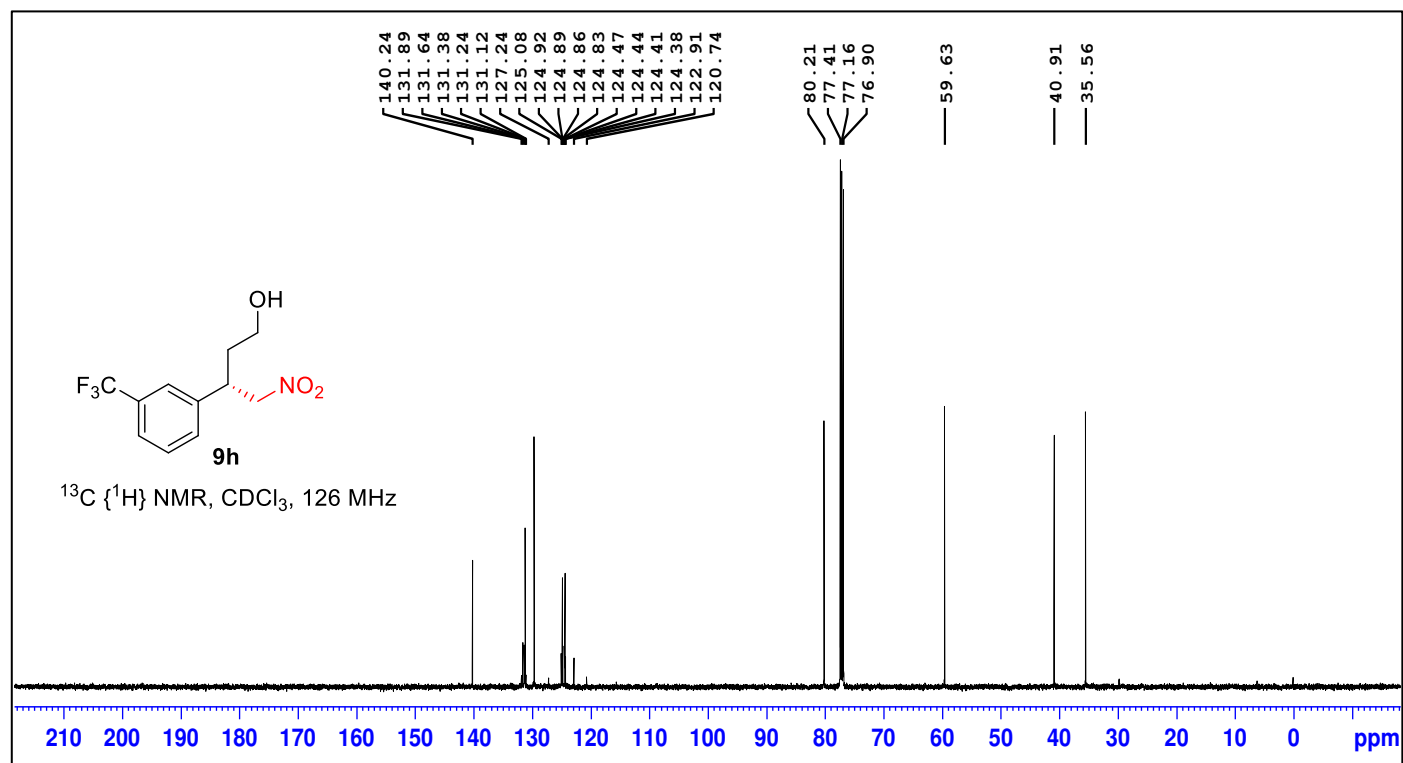
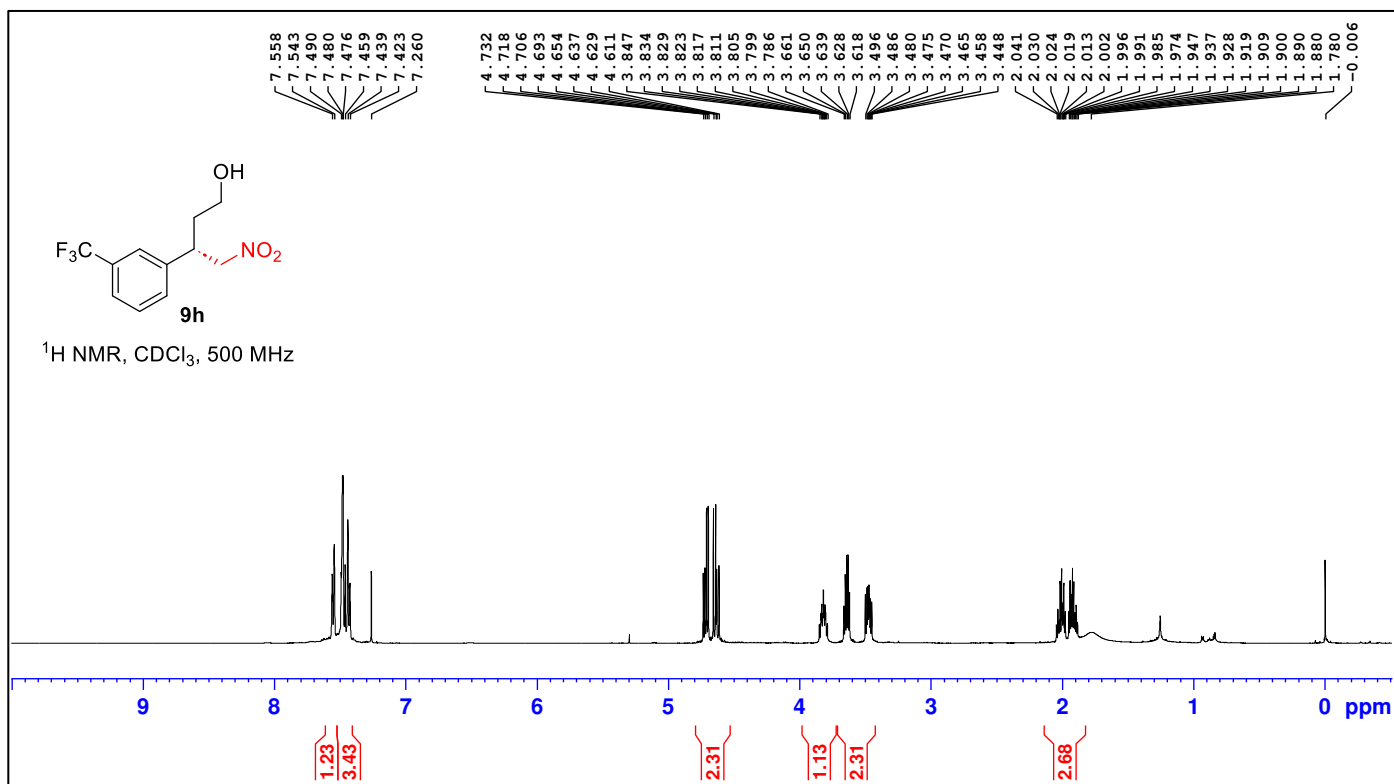
(S)-4-nitro-3-(m-tolyl)butan-1-ol (9g)

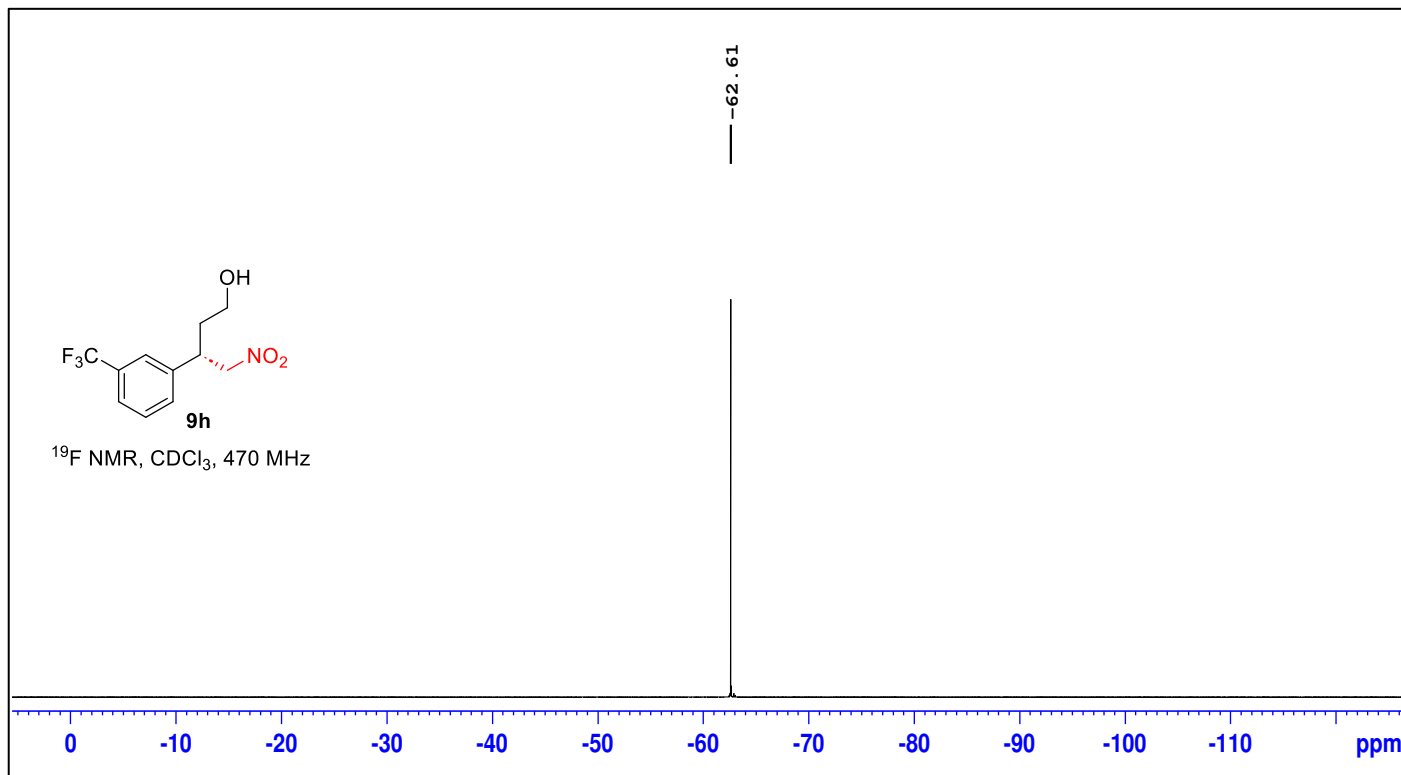


(S)-4-nitro-3-(m-tolyl)butan-1-ol (9g)

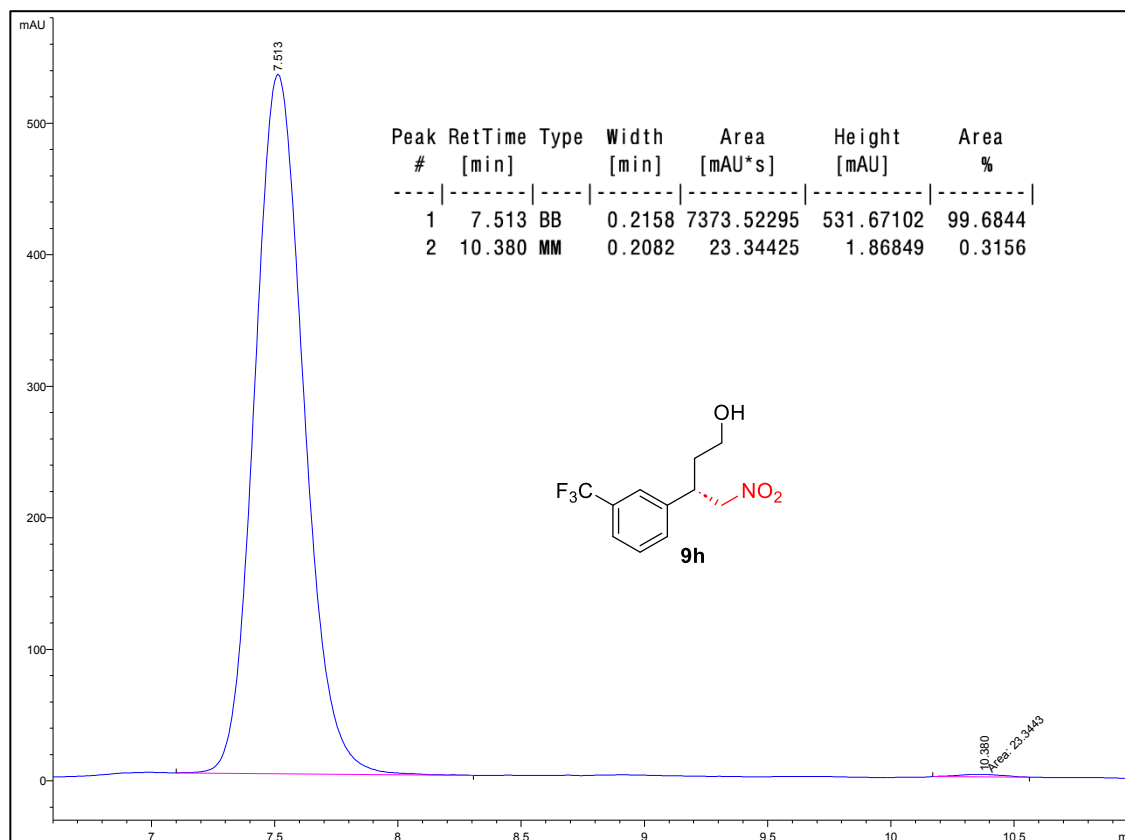


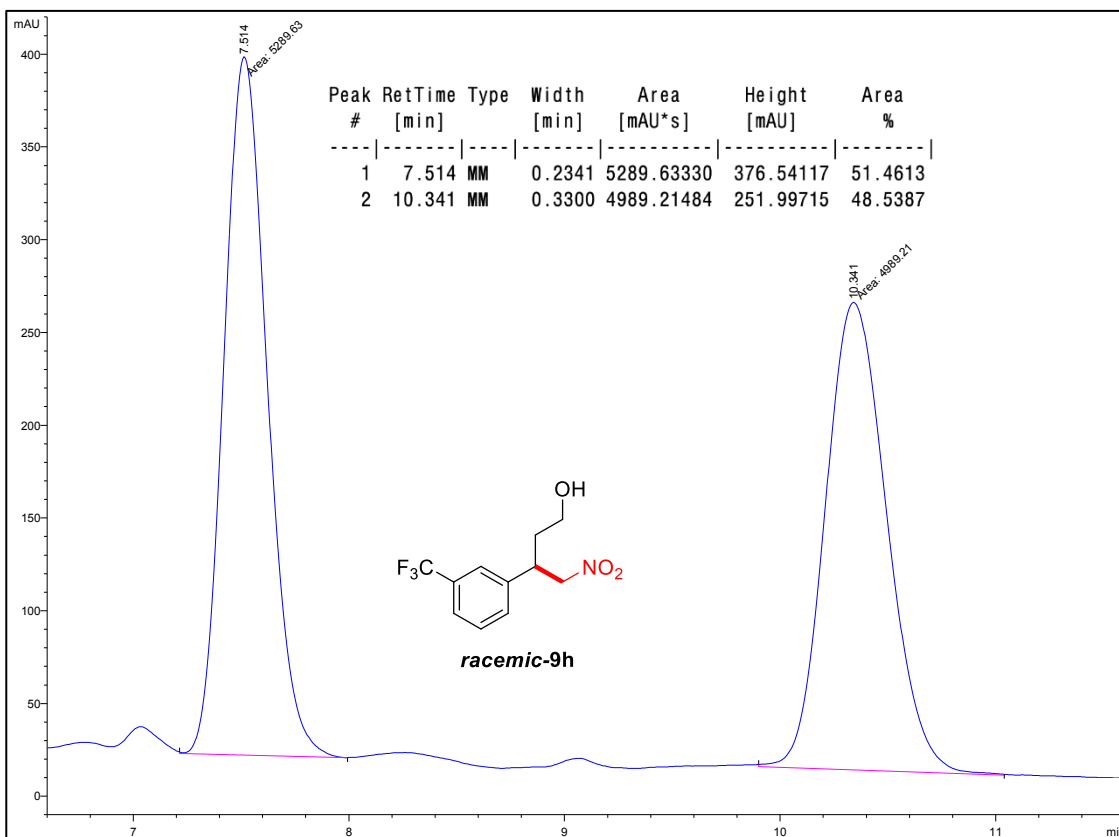
(S)-4-nitro-3-(3-(trifluoromethyl)phenyl)butan-1-ol (9h)



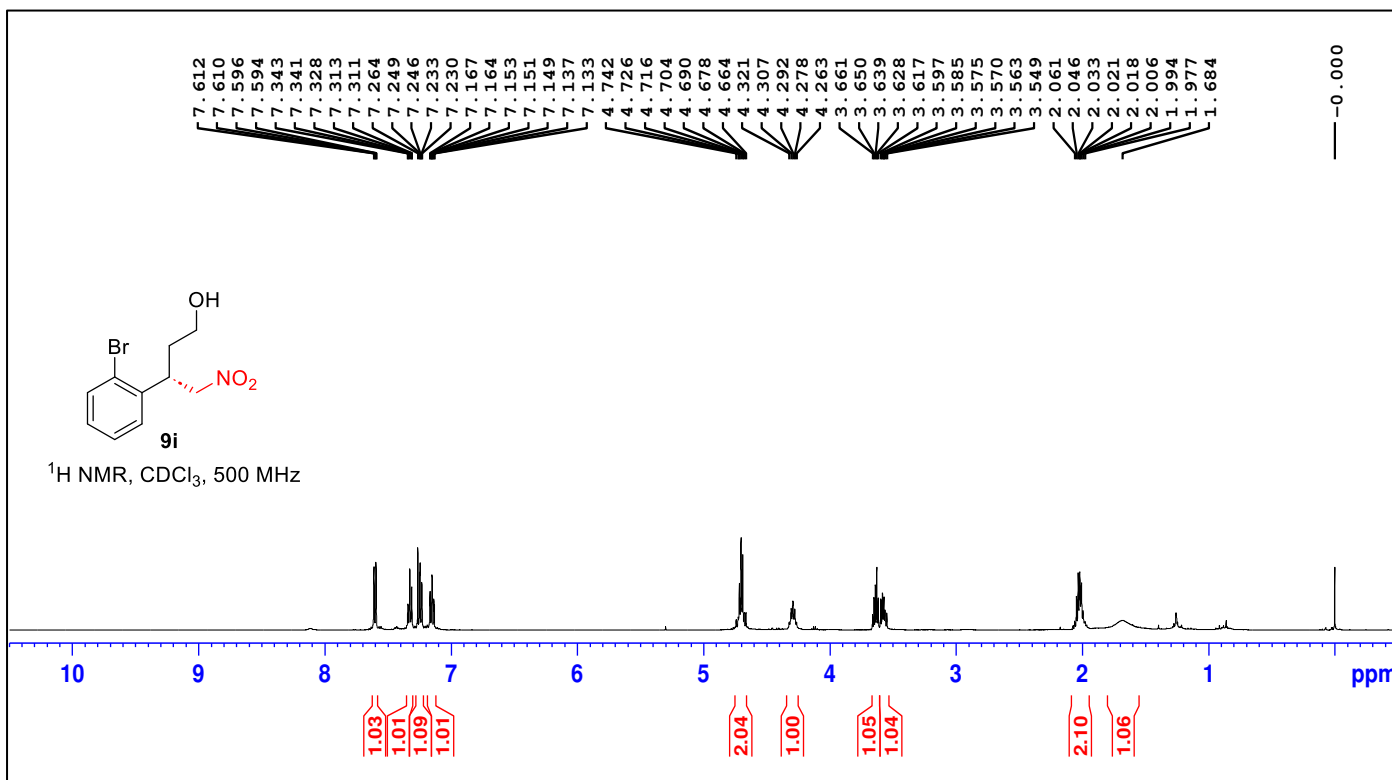


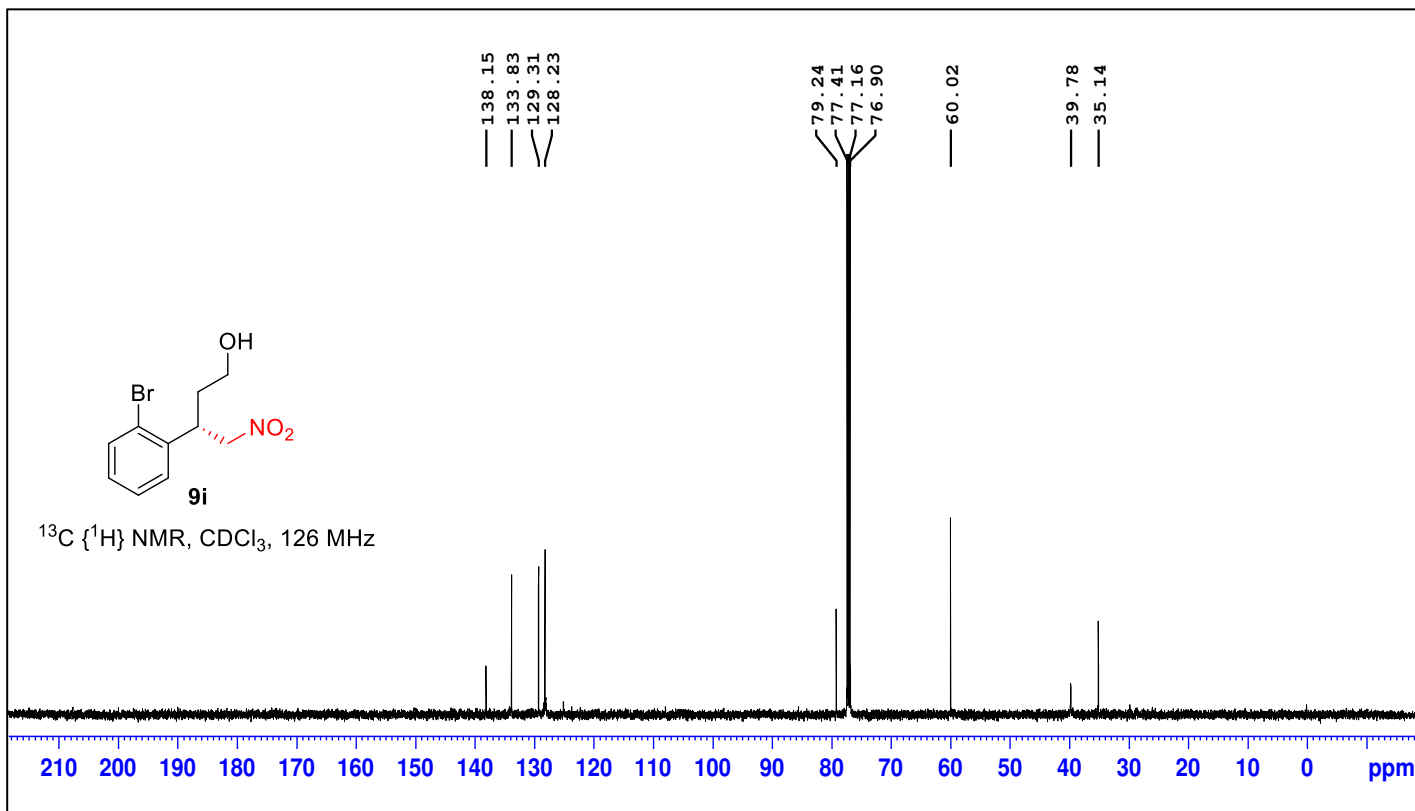
(S)-4-nitro-3-(3-(trifluoromethyl)phenyl)butan-1-ol (9h)



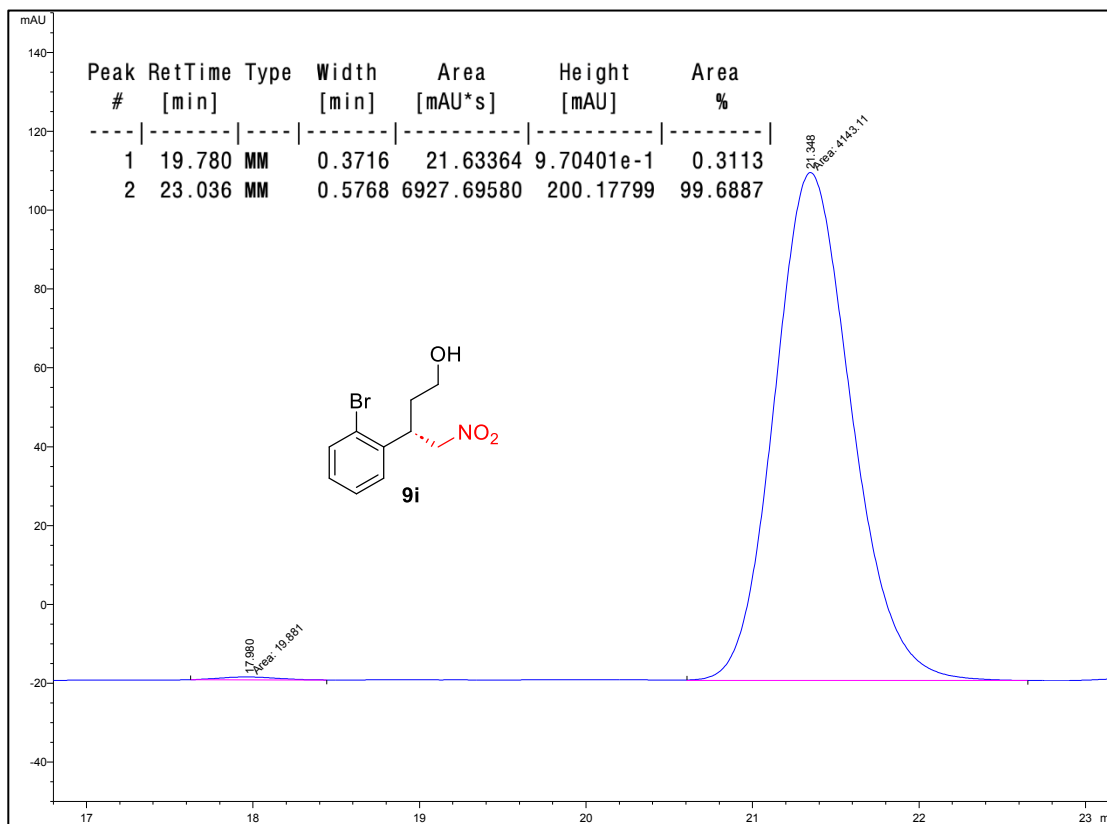


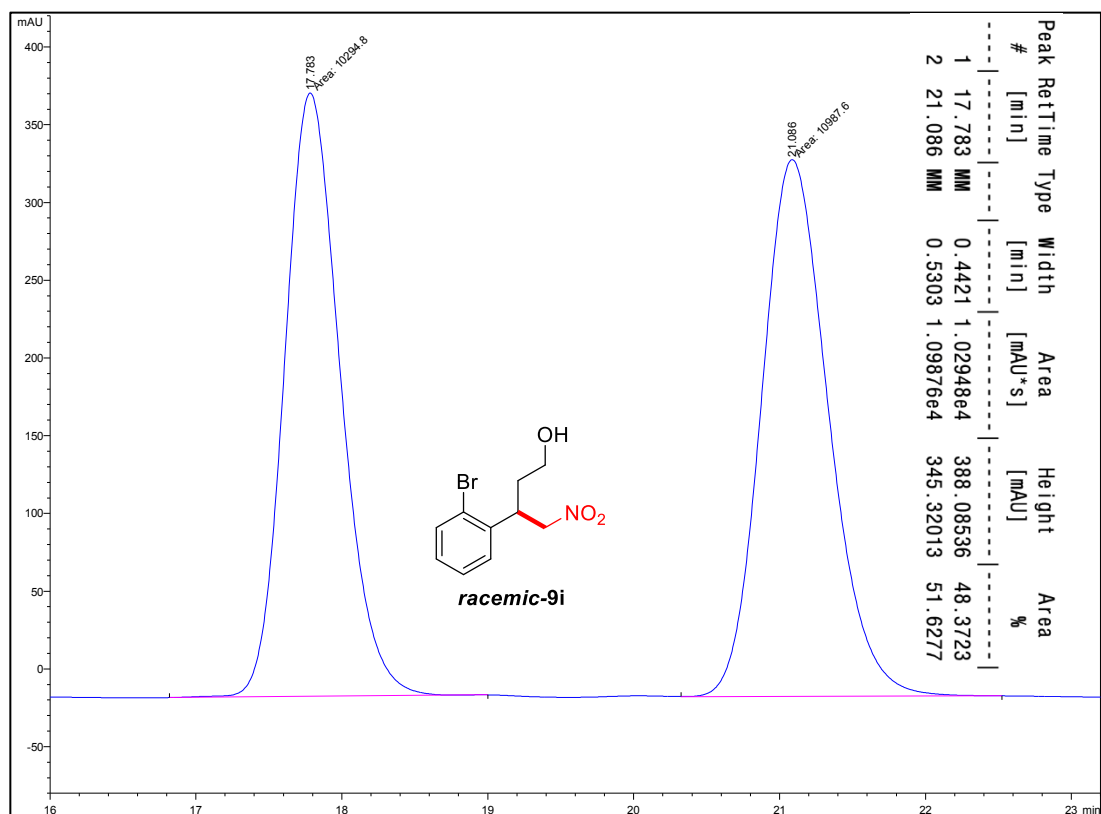
(S)-3-(2-bromophenyl)-4-nitrobutan-1-ol (9i)



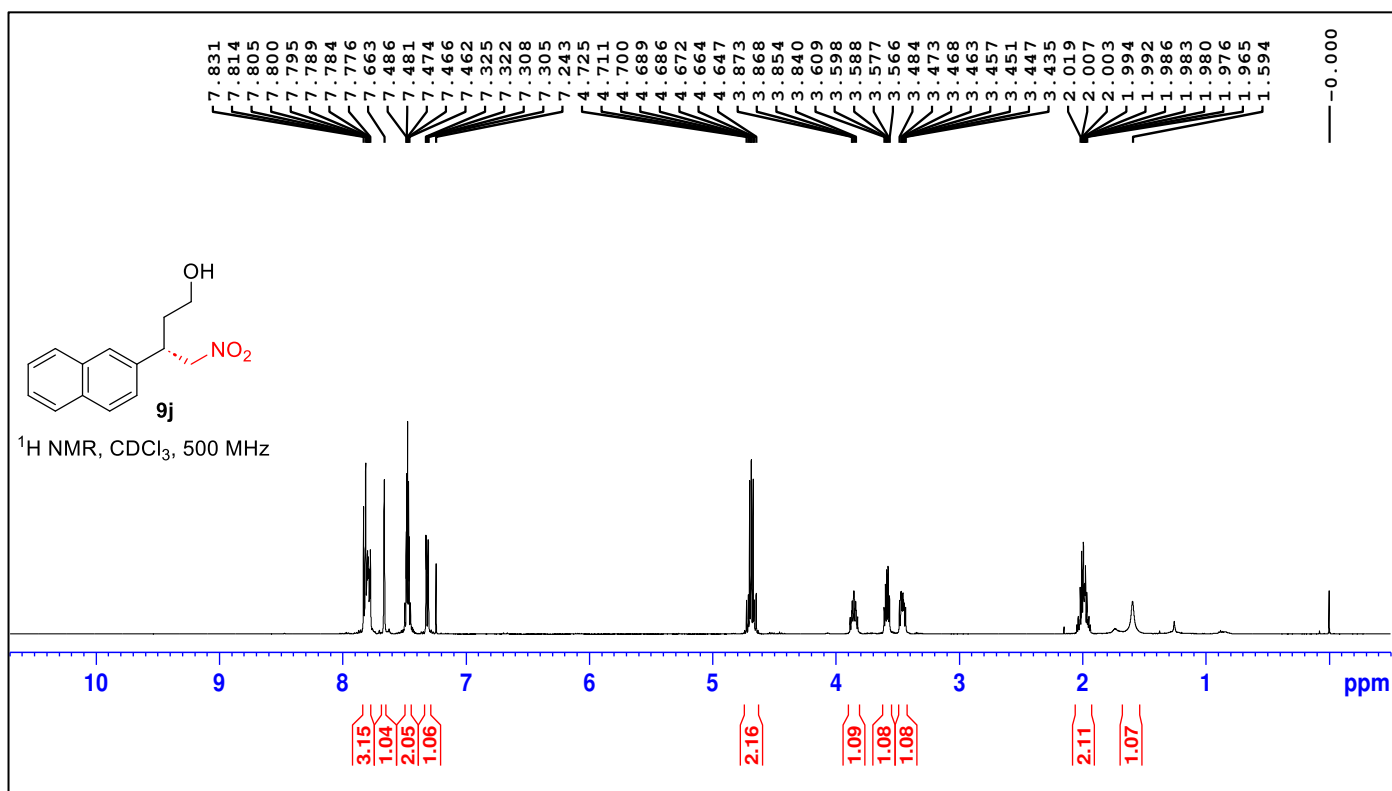


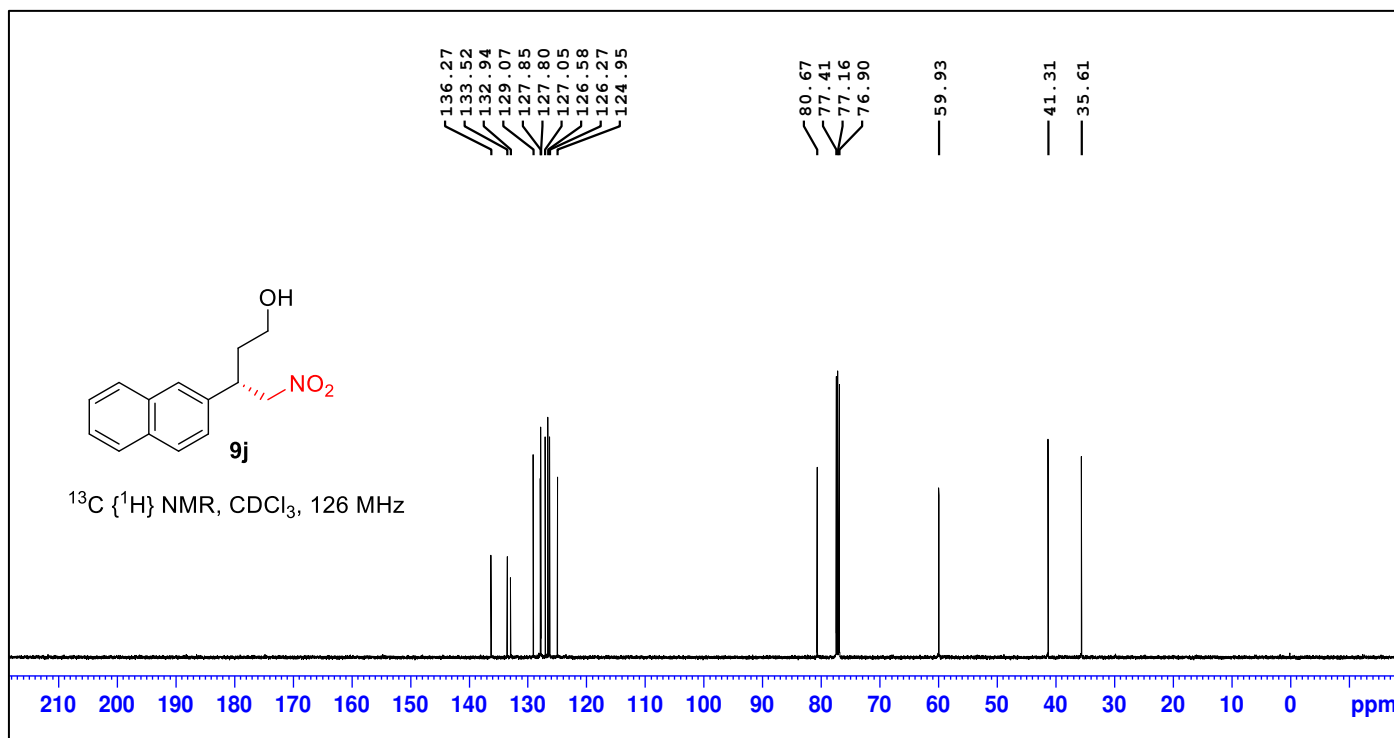
(S)-3-(2-bromophenyl)-4-nitrobutan-1-ol (9i)



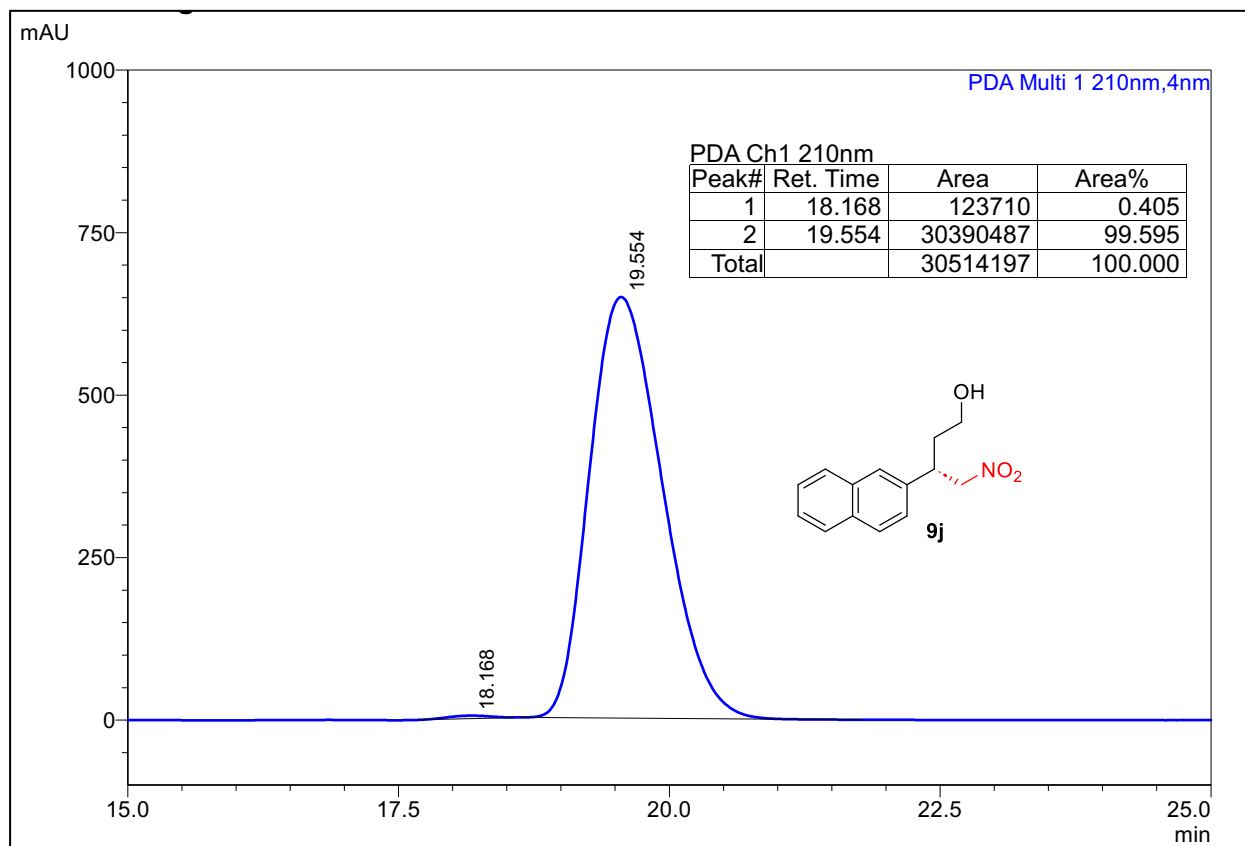


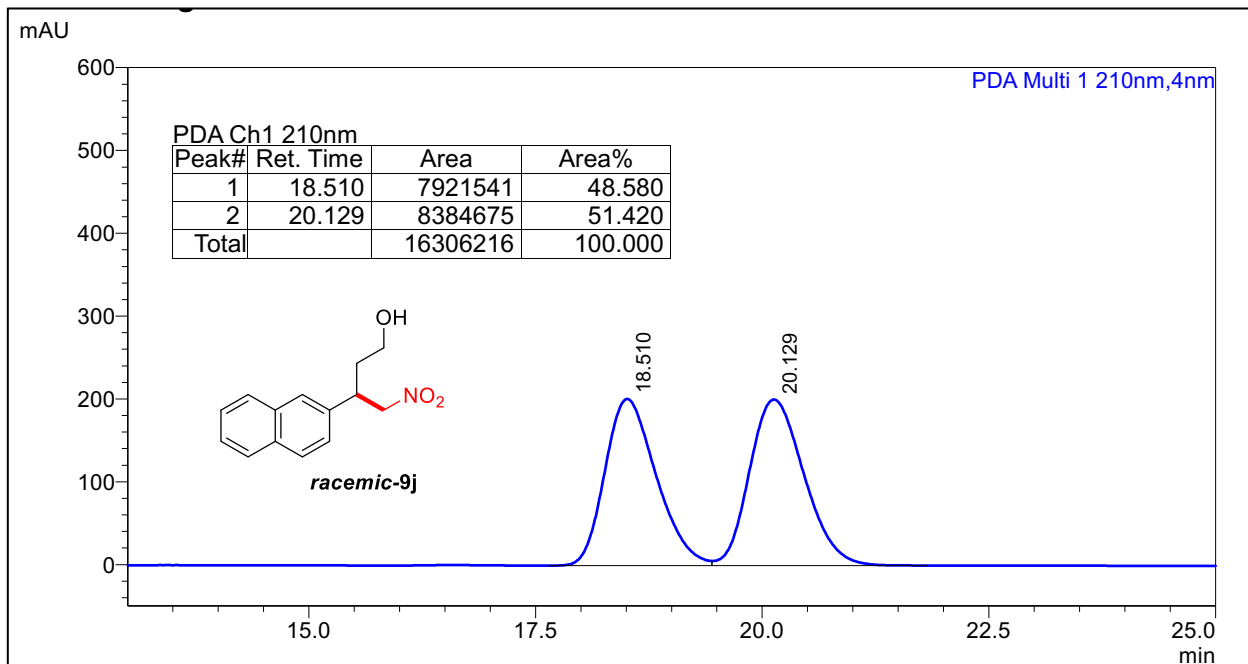
(*S*)-3-(naphthalen-2-yl)-4-nitrobutan-1-ol (9j)



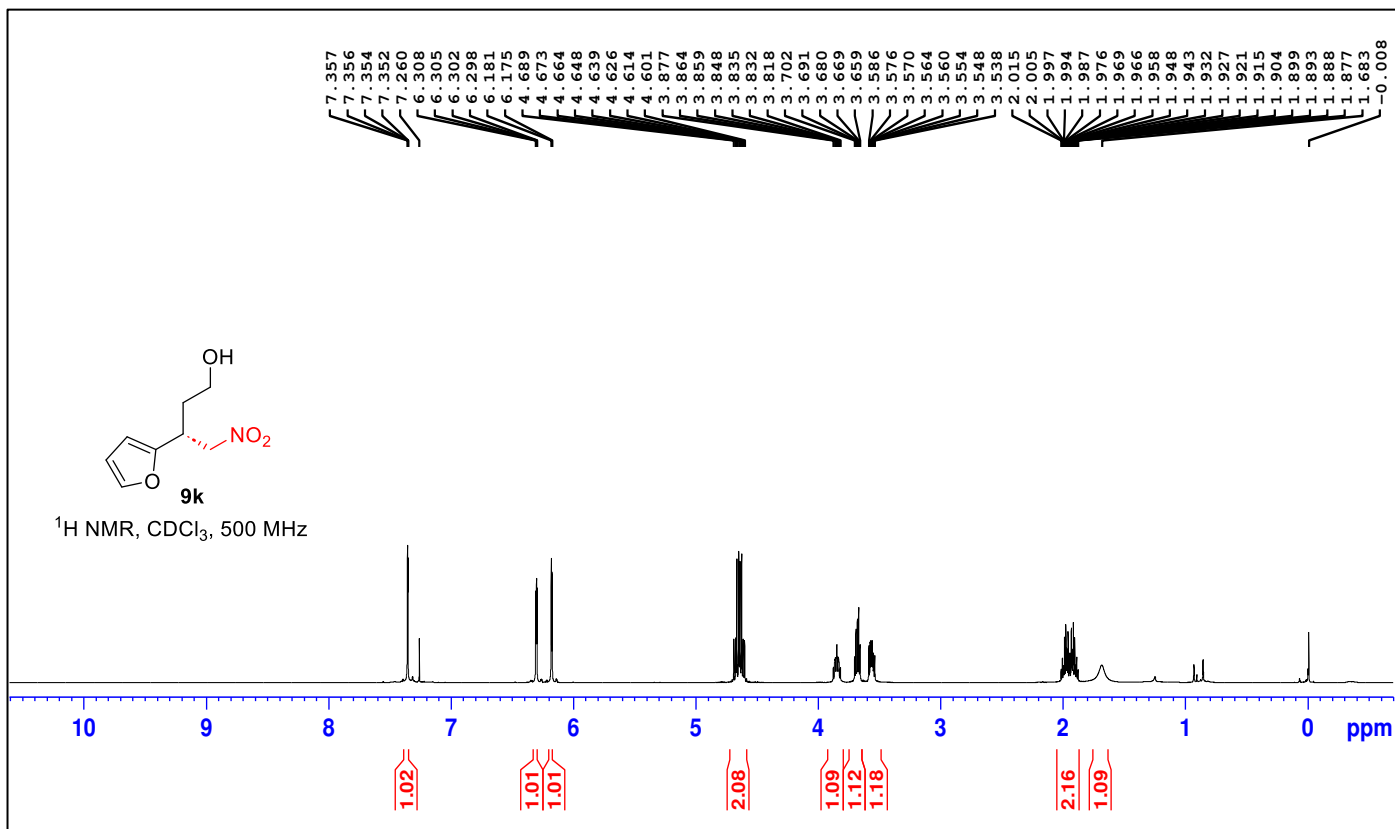


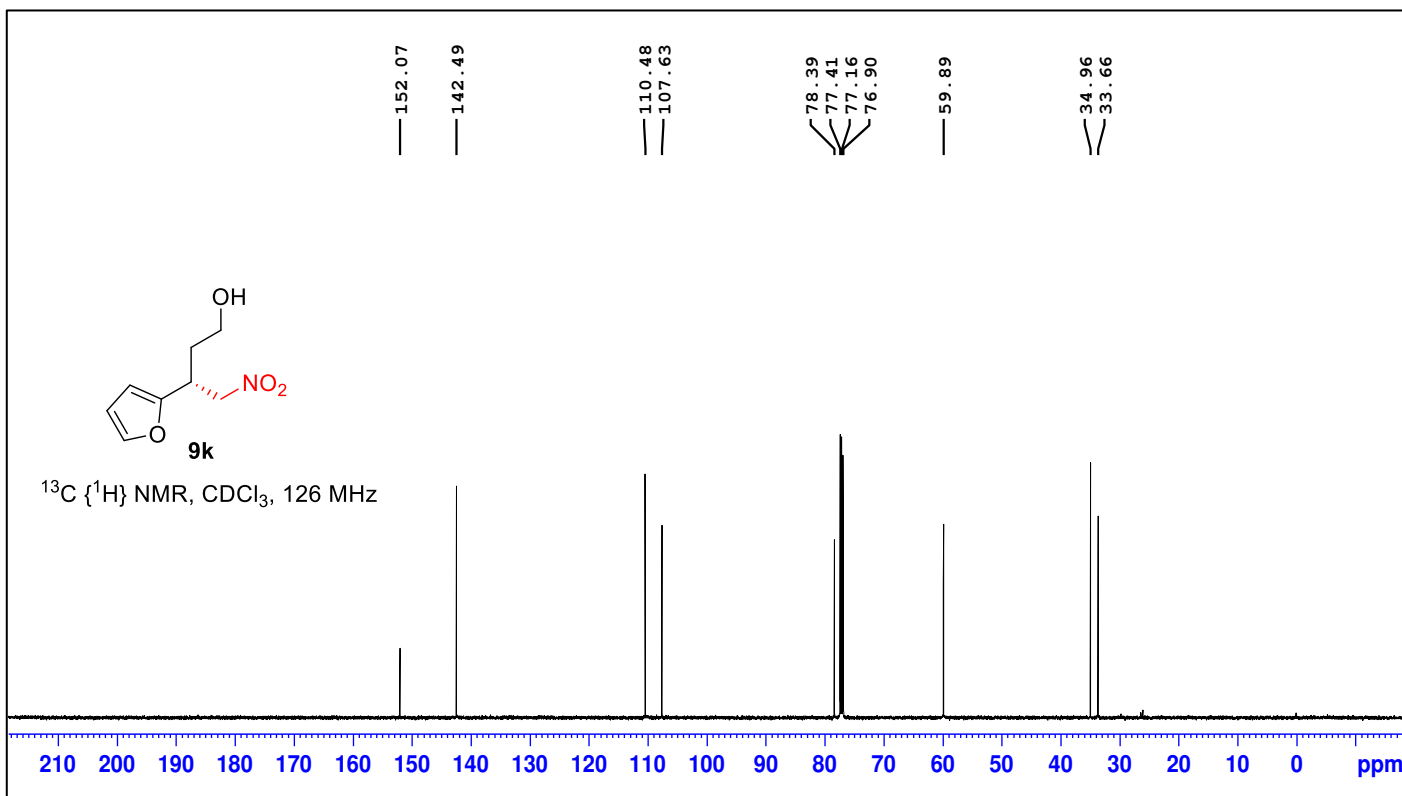
(S)-3-(naphthalen-2-yl)-4-nitrobutan-1-ol (9j)



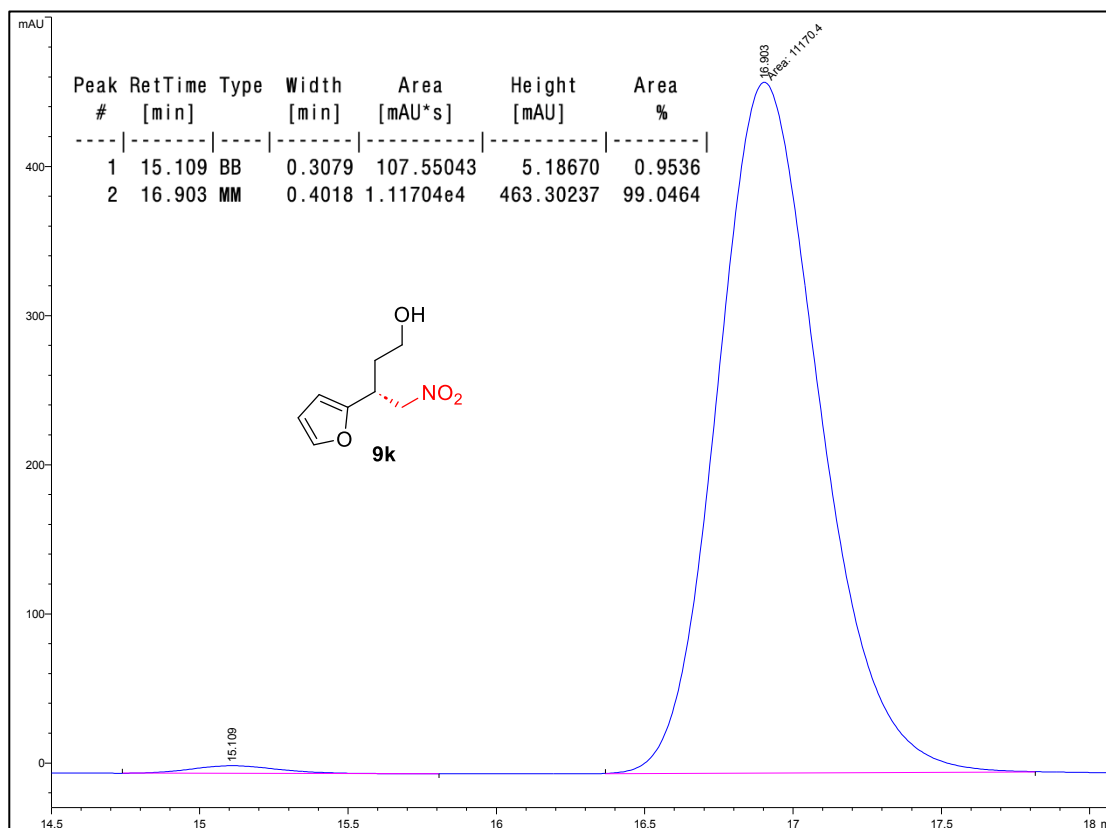


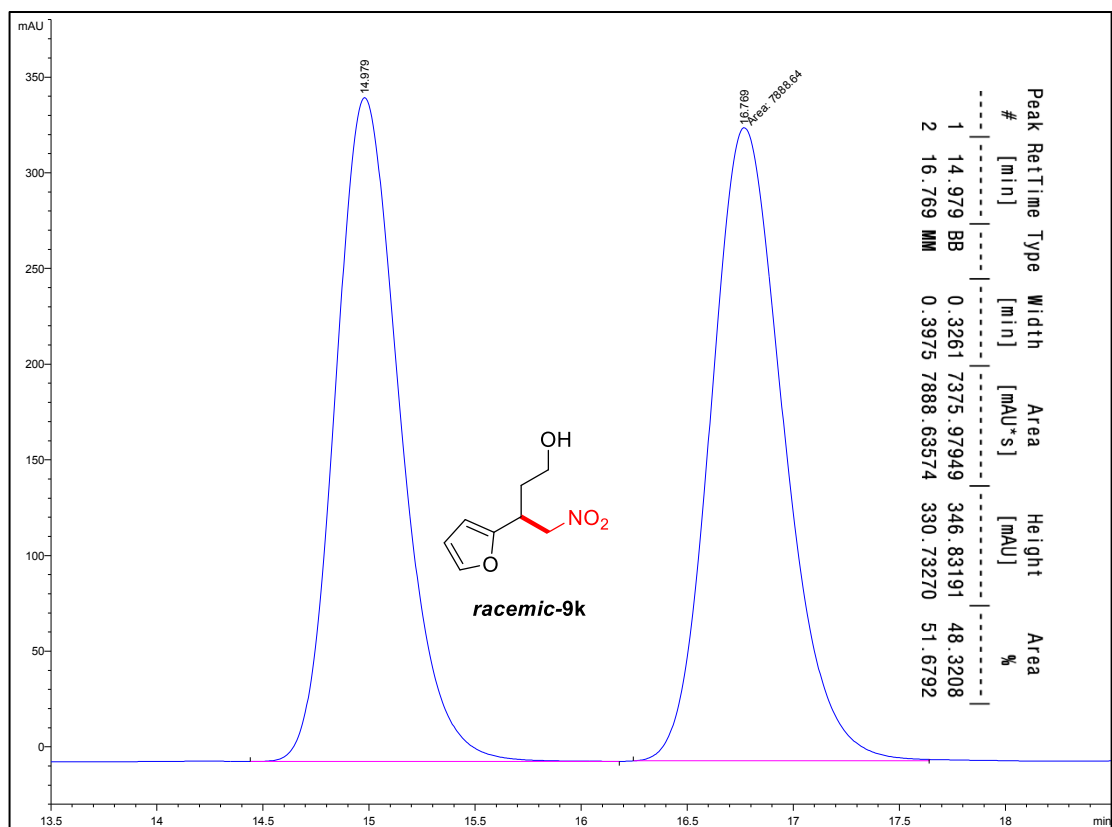
(R)-3-(furan-2-yl)-4-nitrobutan-1-ol (9k)



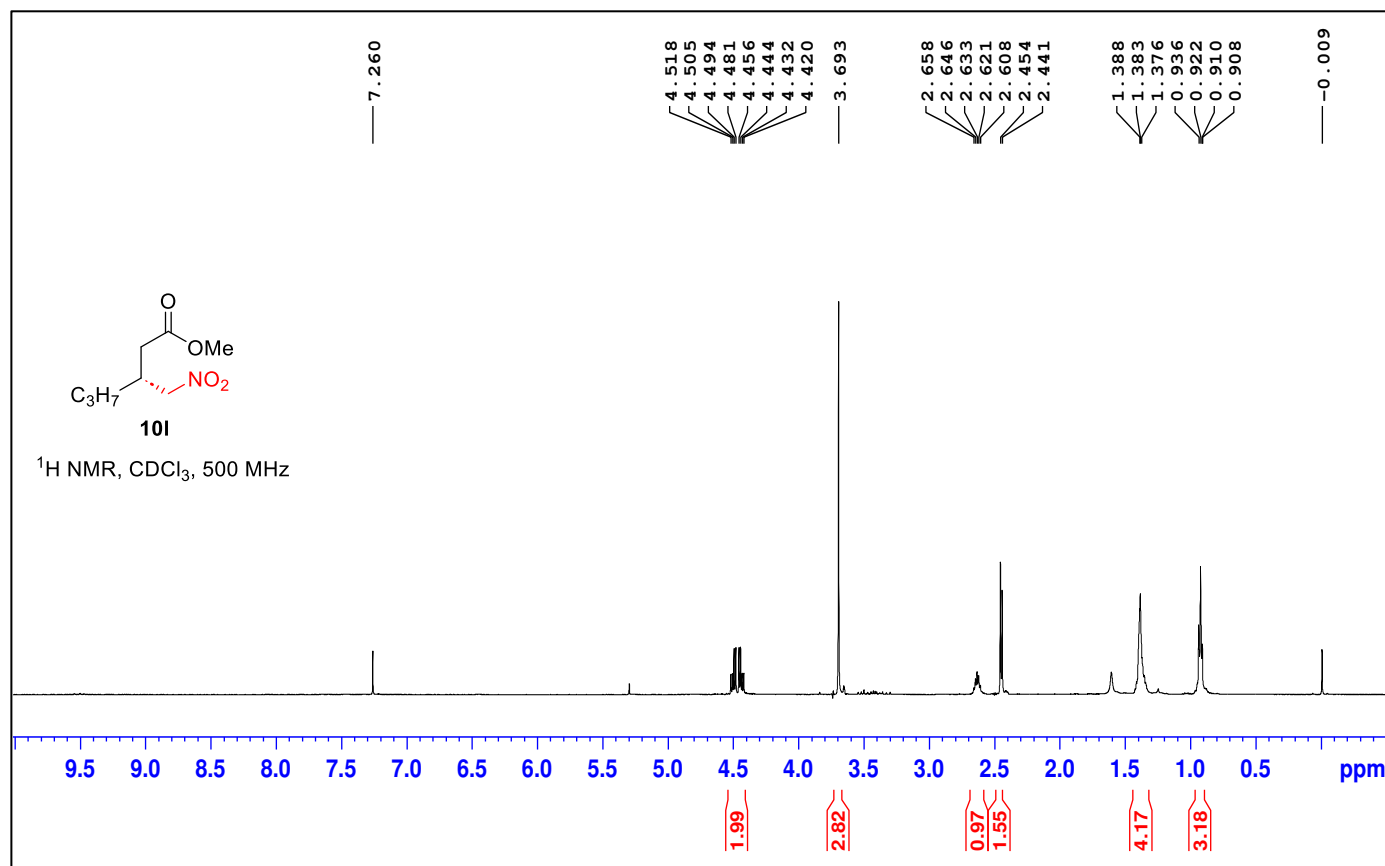


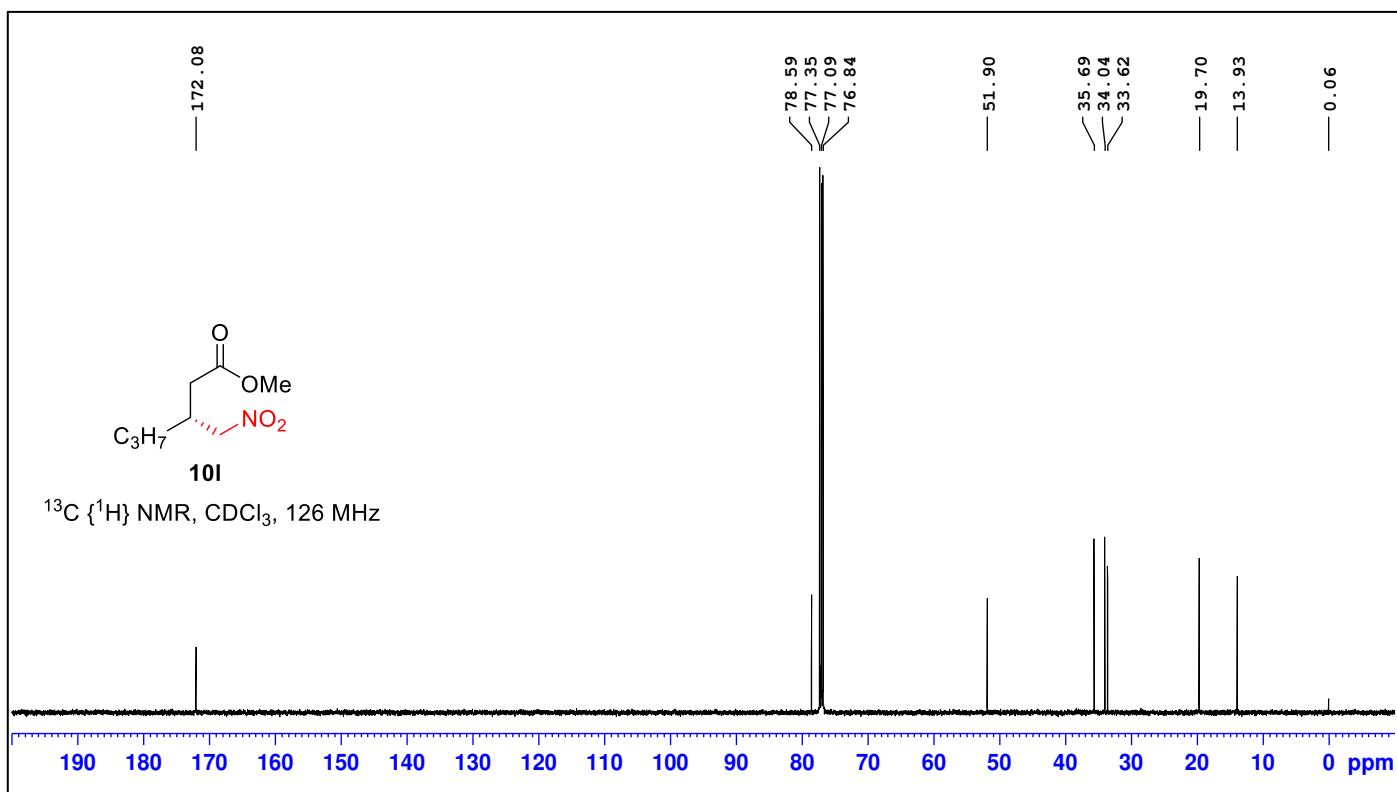
(R)-3-(furan-2-yl)-4-nitrobutan-1-ol (9k)



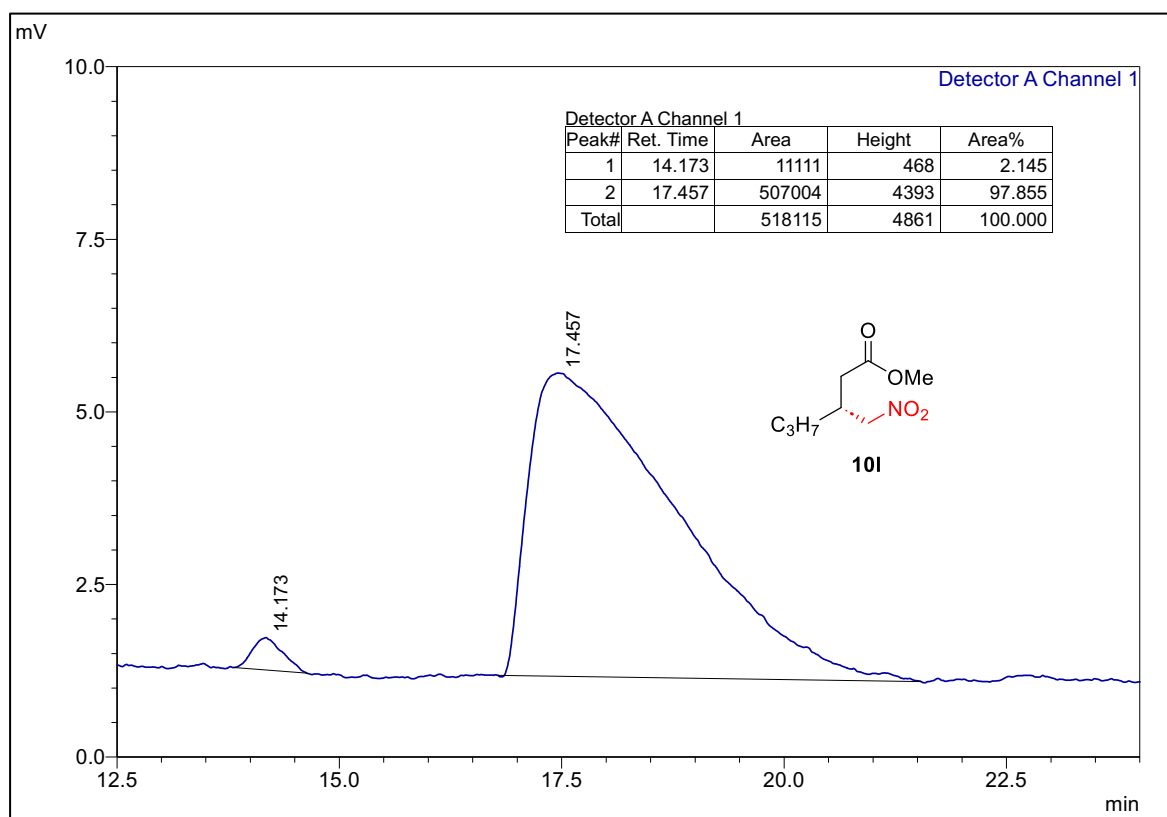


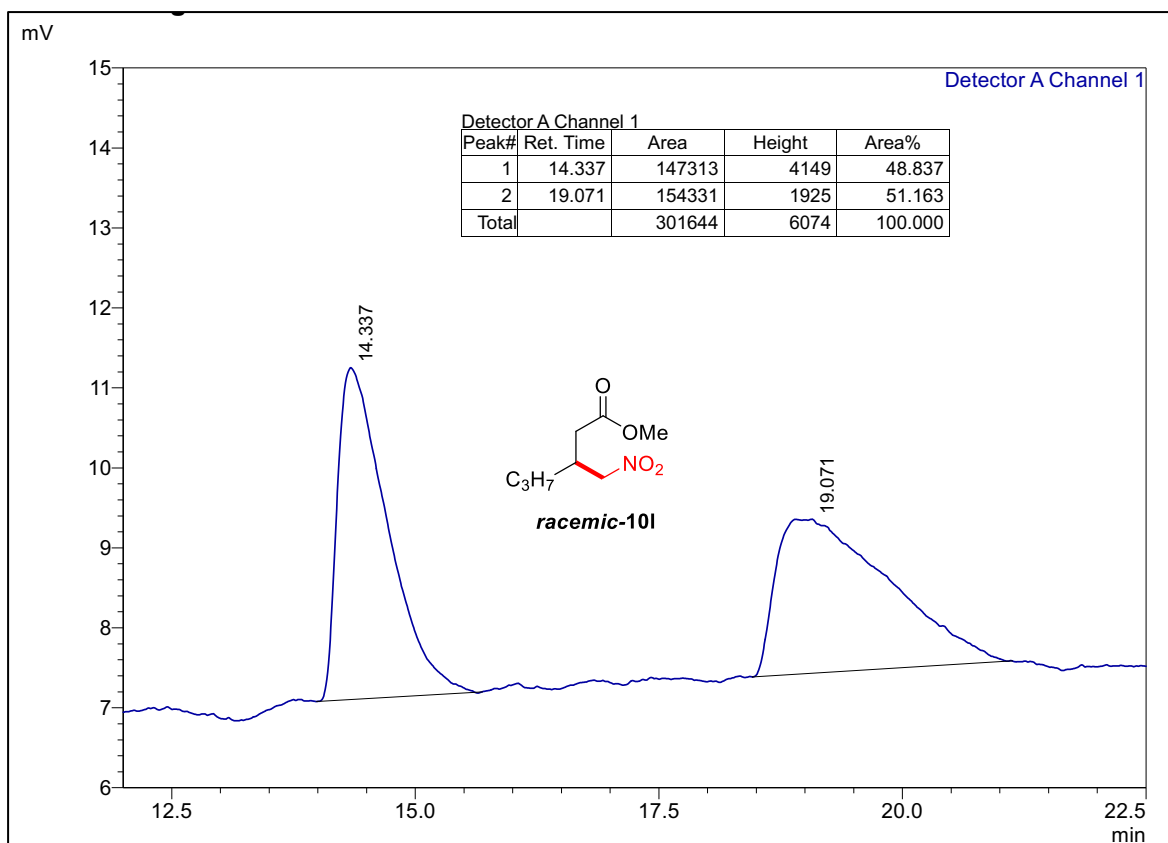
(R)-methyl-3-(nitromethyl)hexanoate (10l)



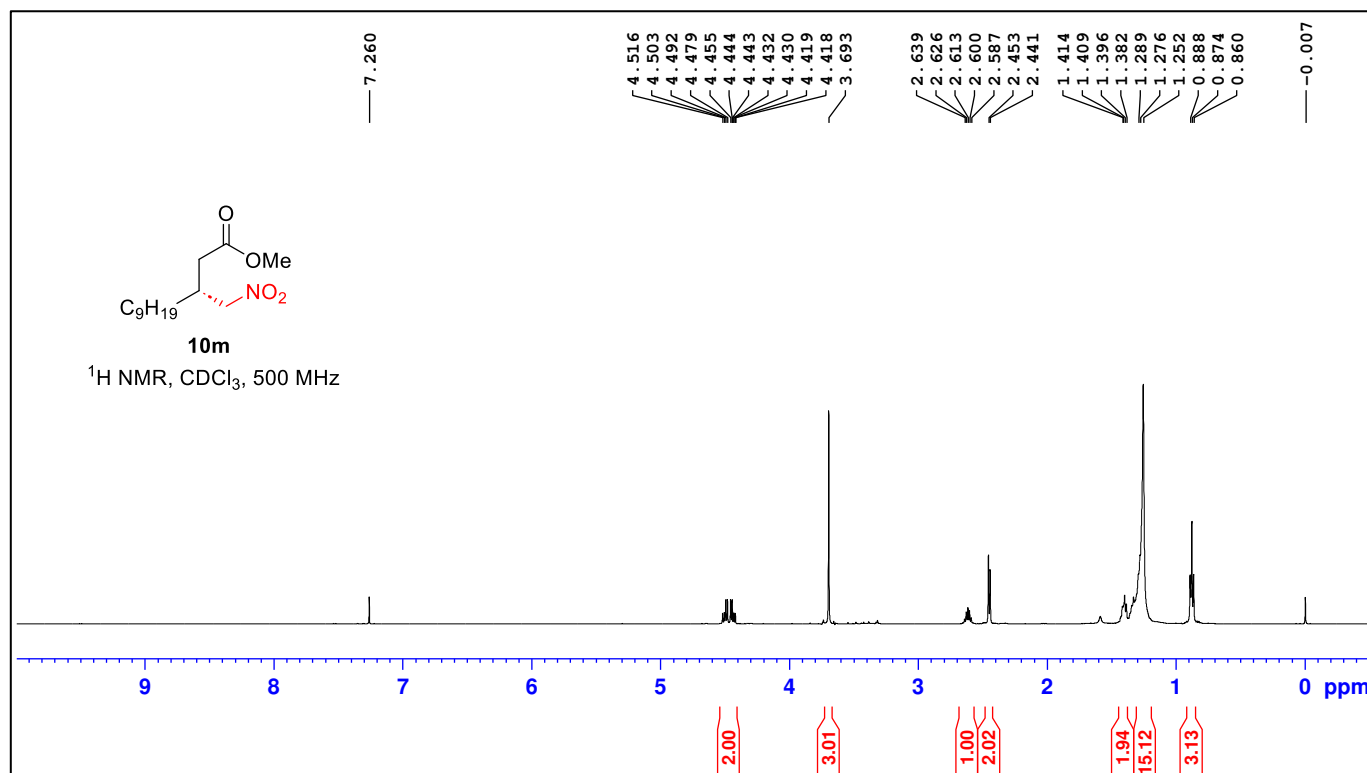


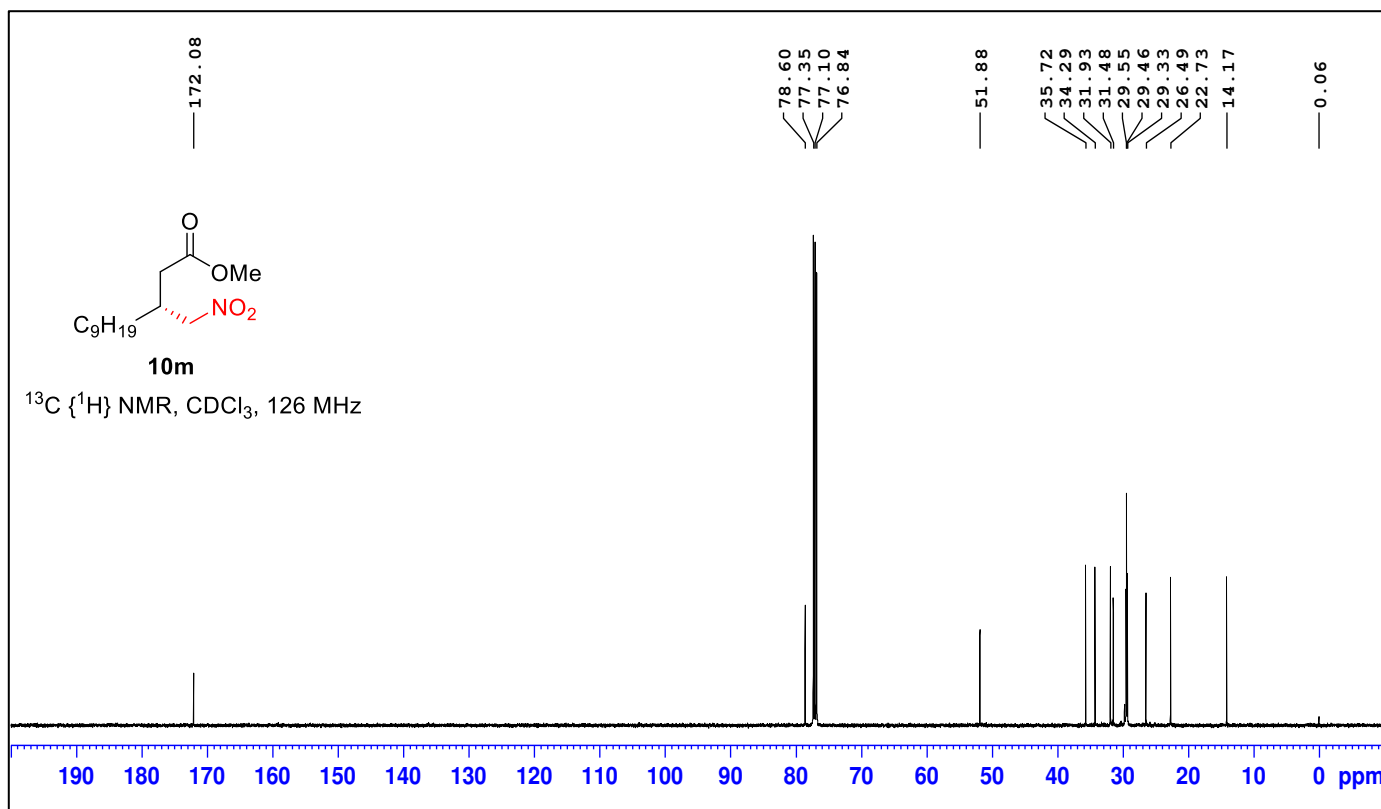
(R)-methyl-3-(nitromethyl)hexanoate (10I)



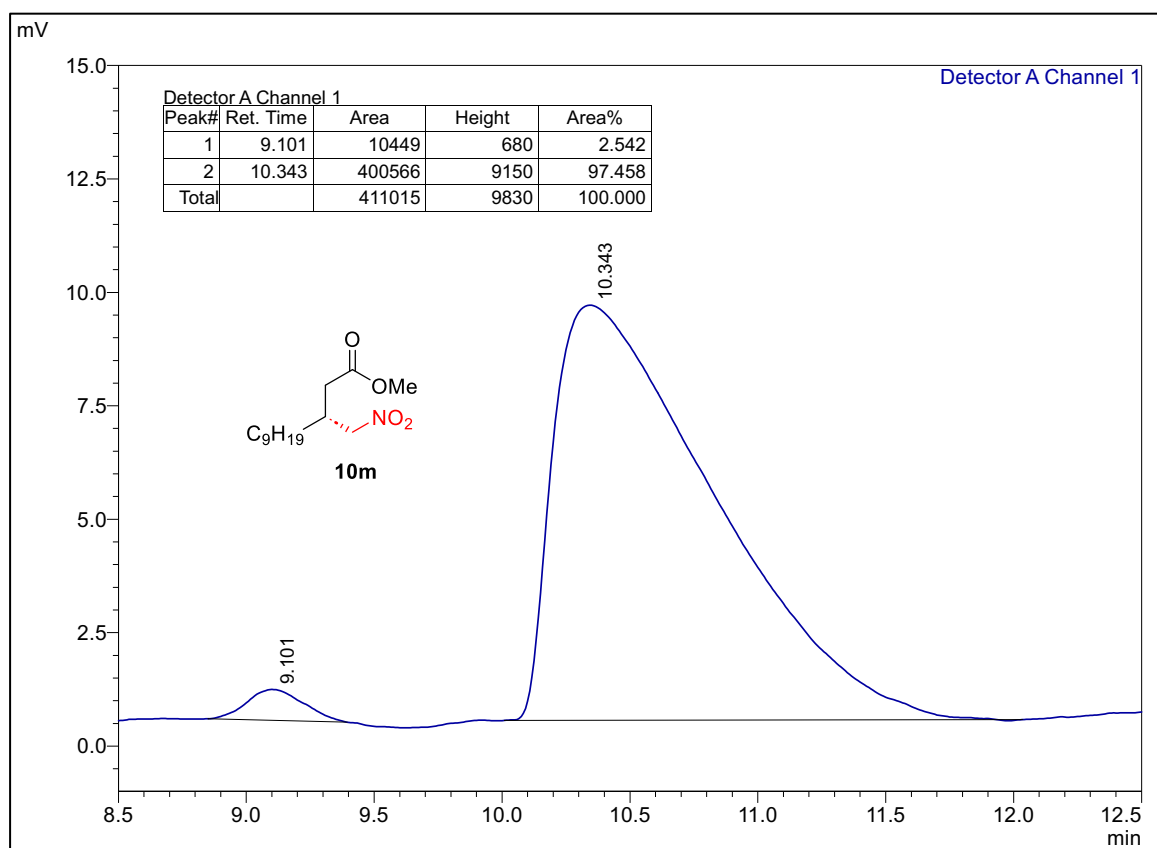


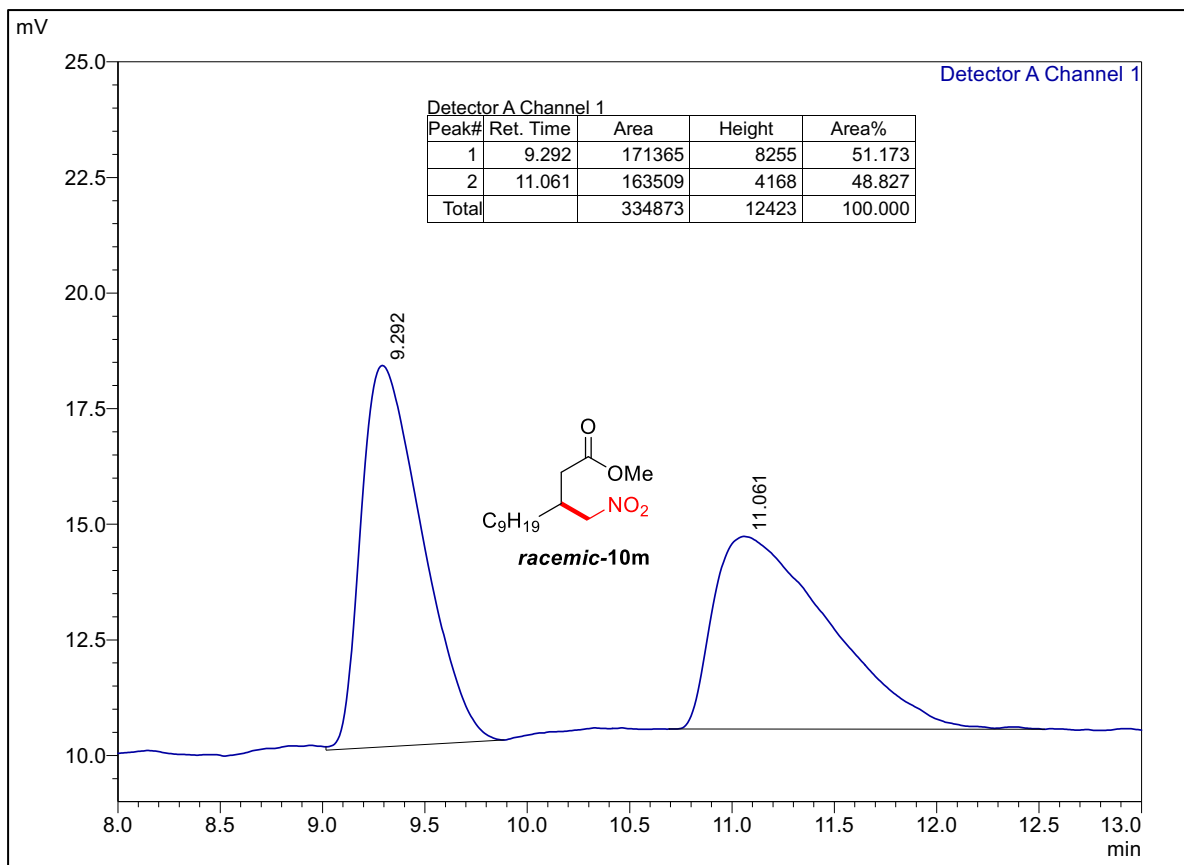
(R)-methyl-3-(nitromethyl)dodecanoate (10m)



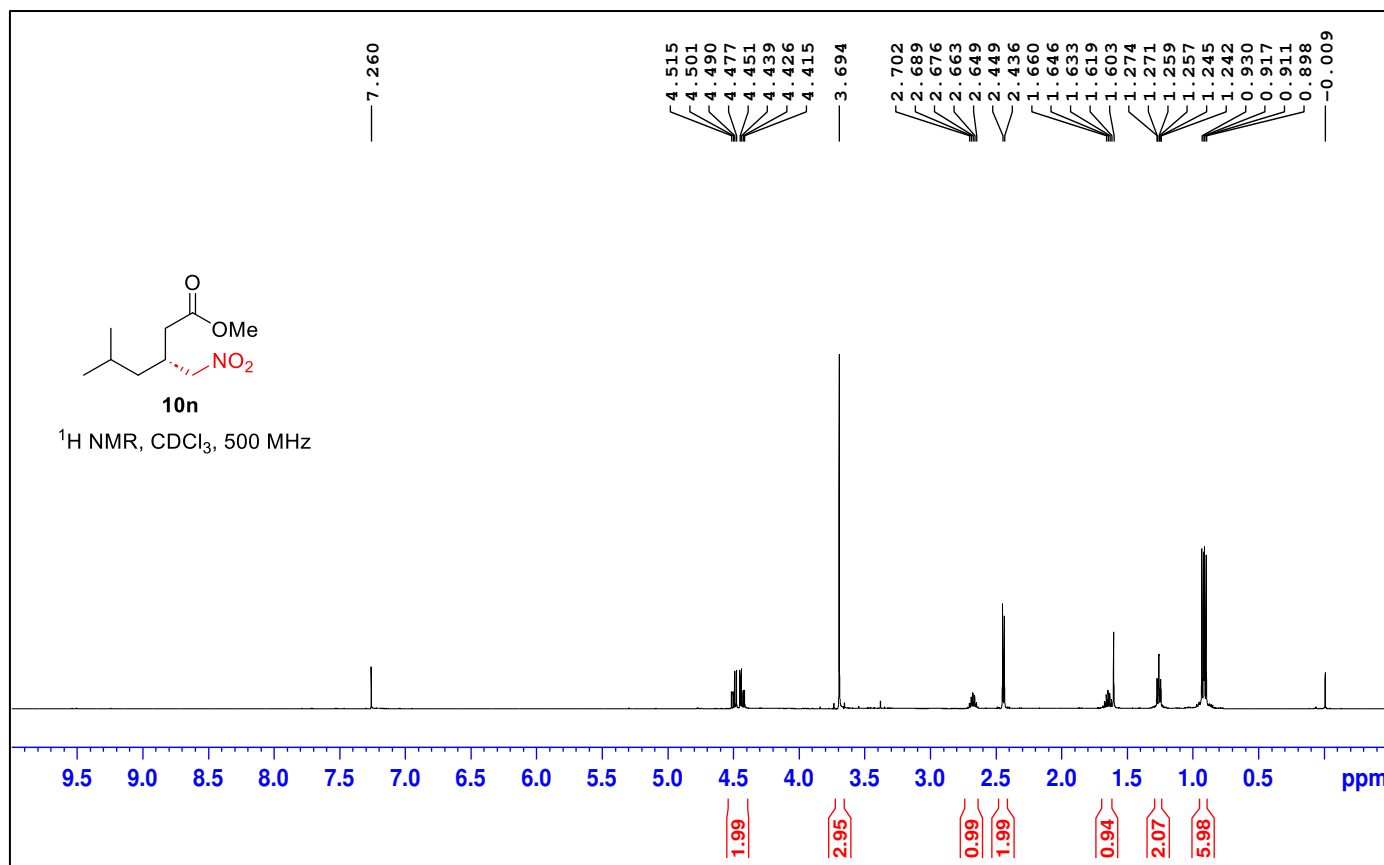


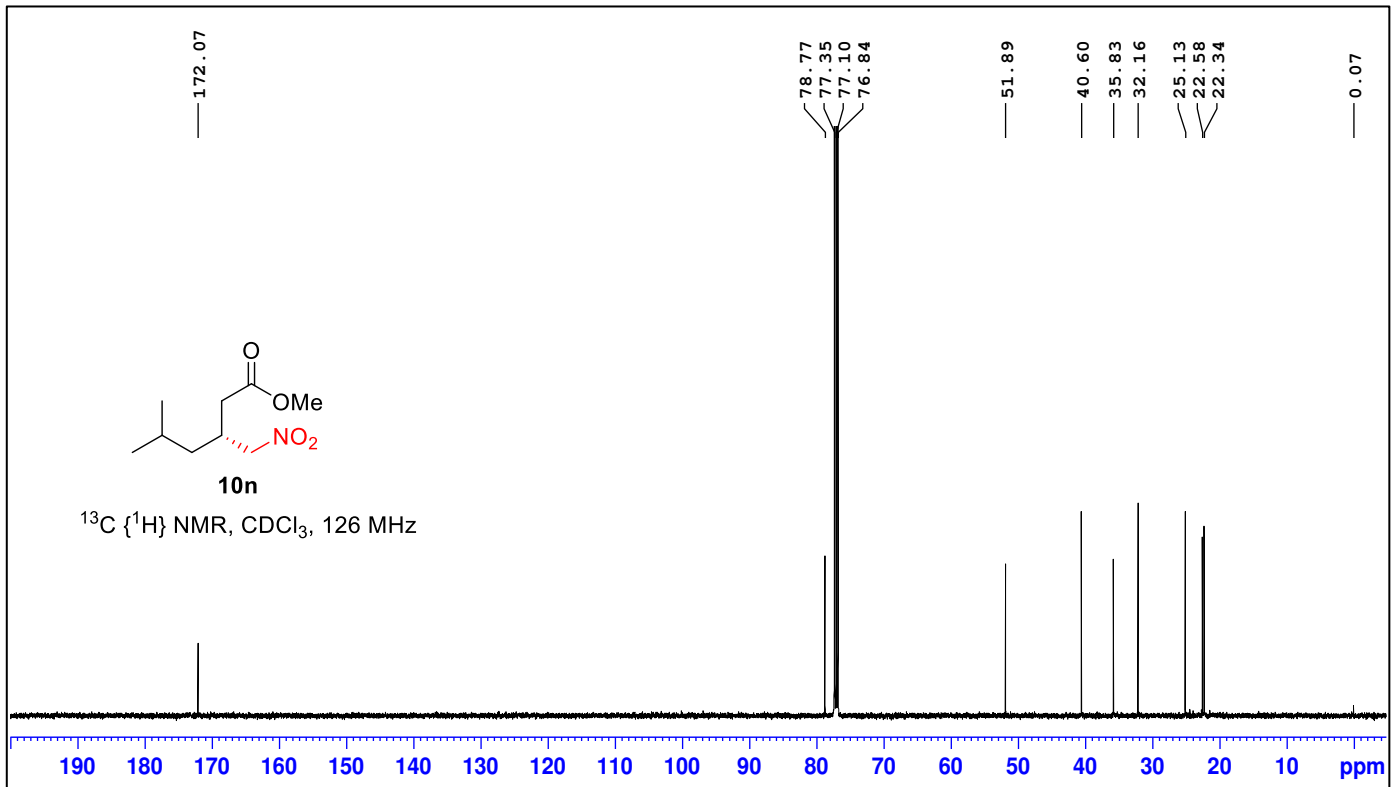
(R)-methyl-3-(nitromethyl)dodecanoate (10m)



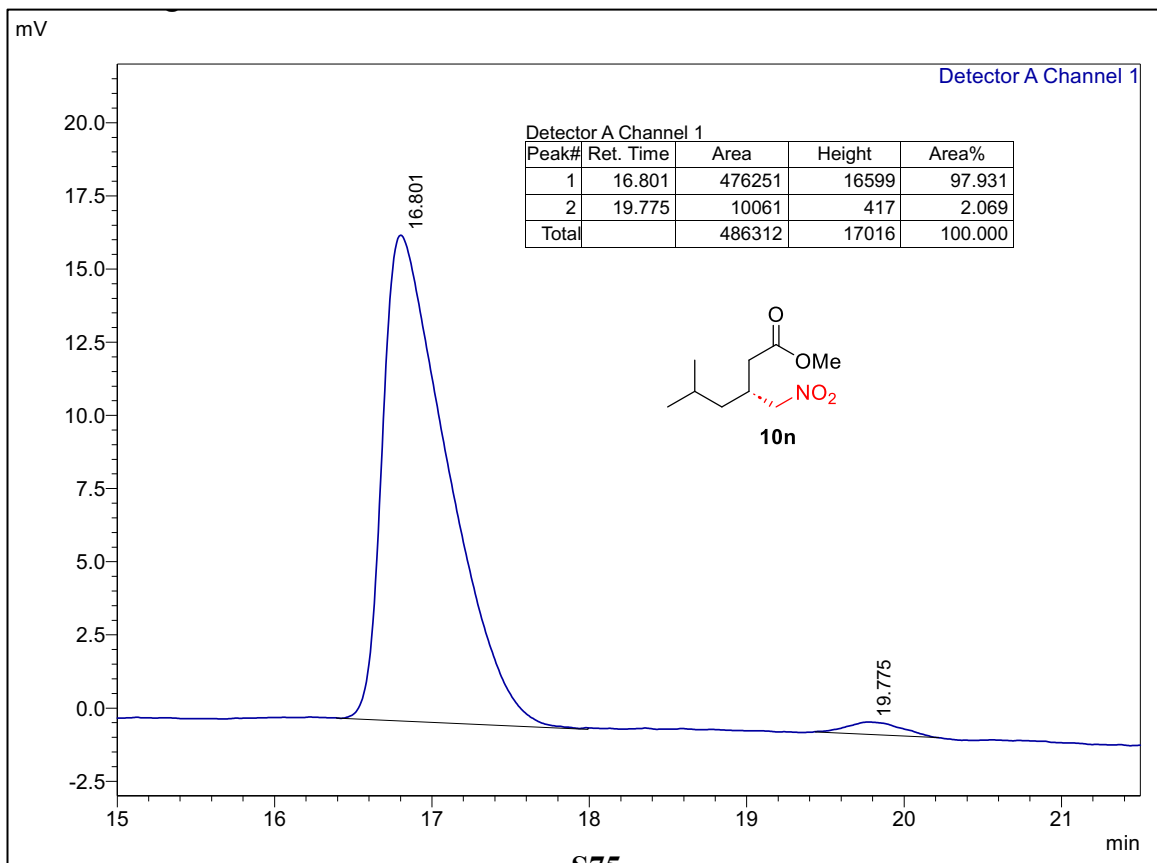


(R)-methyl-5-methyl-3-(nitromethyl)hexanoate (10n)

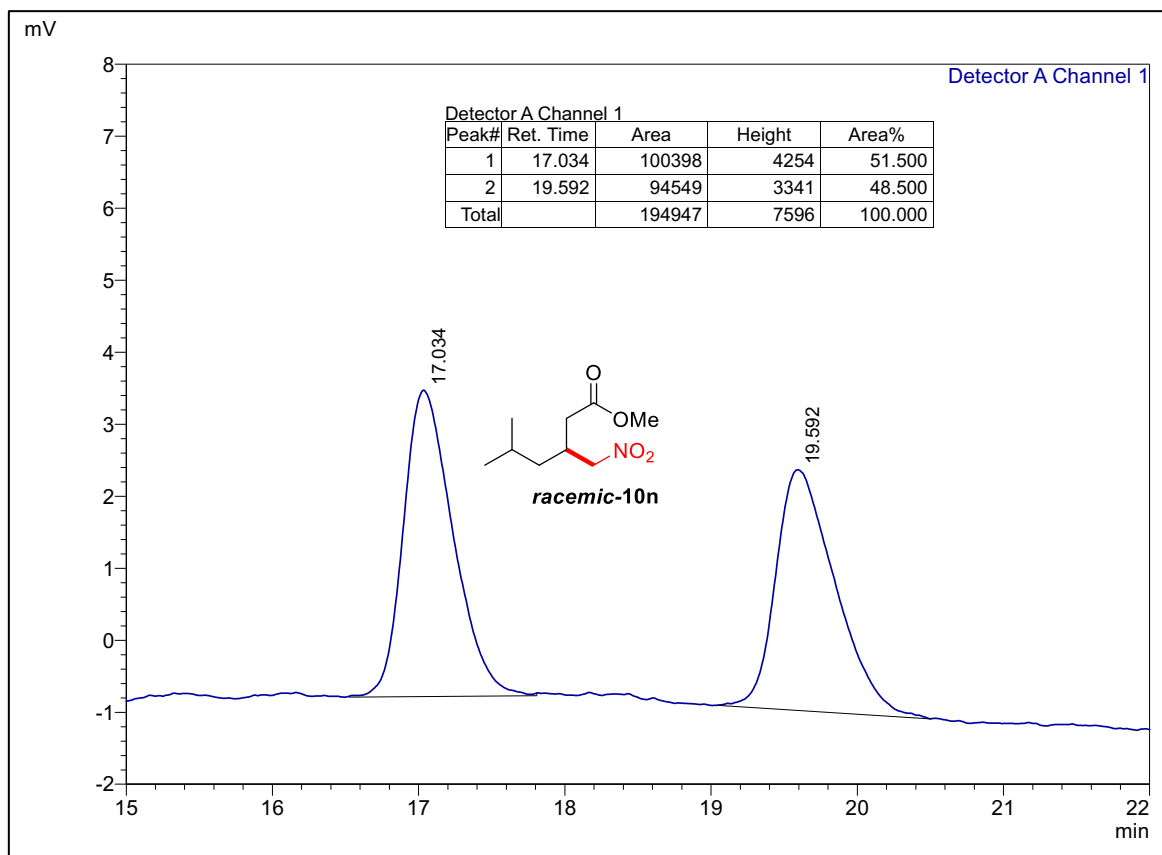
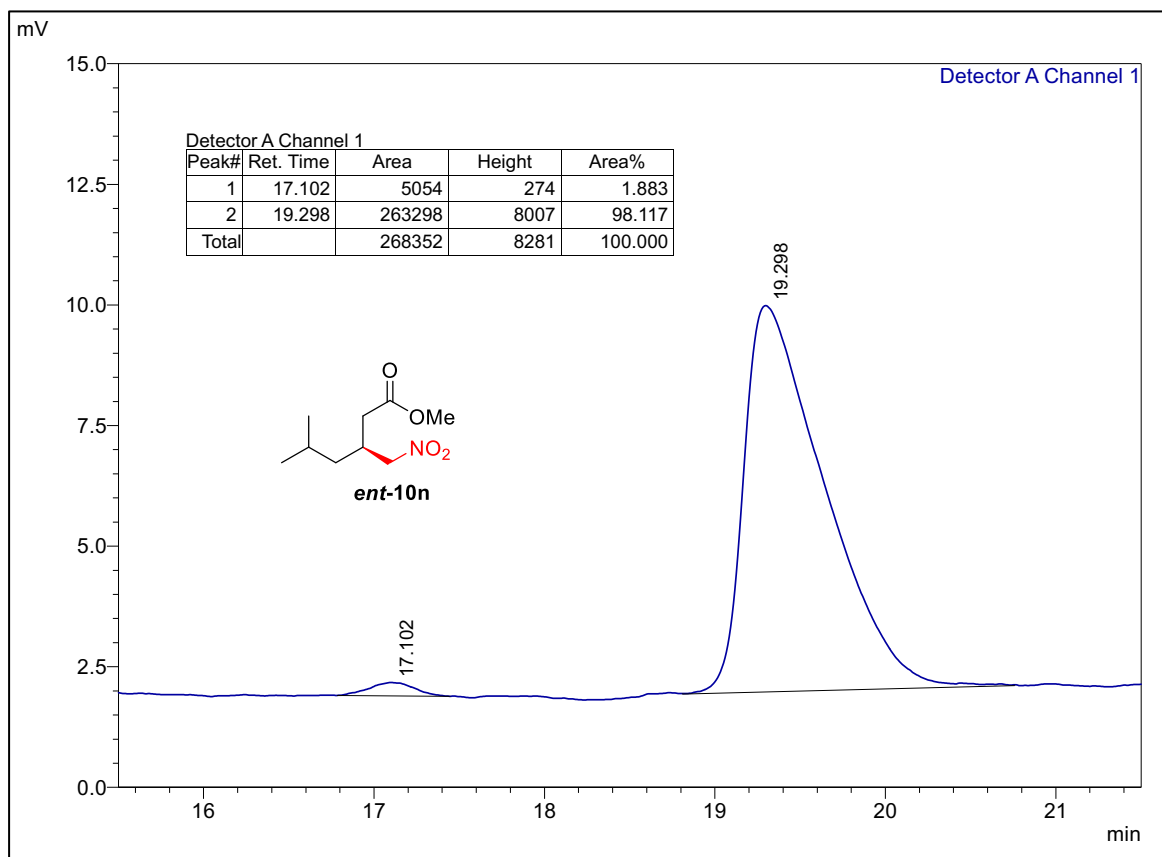




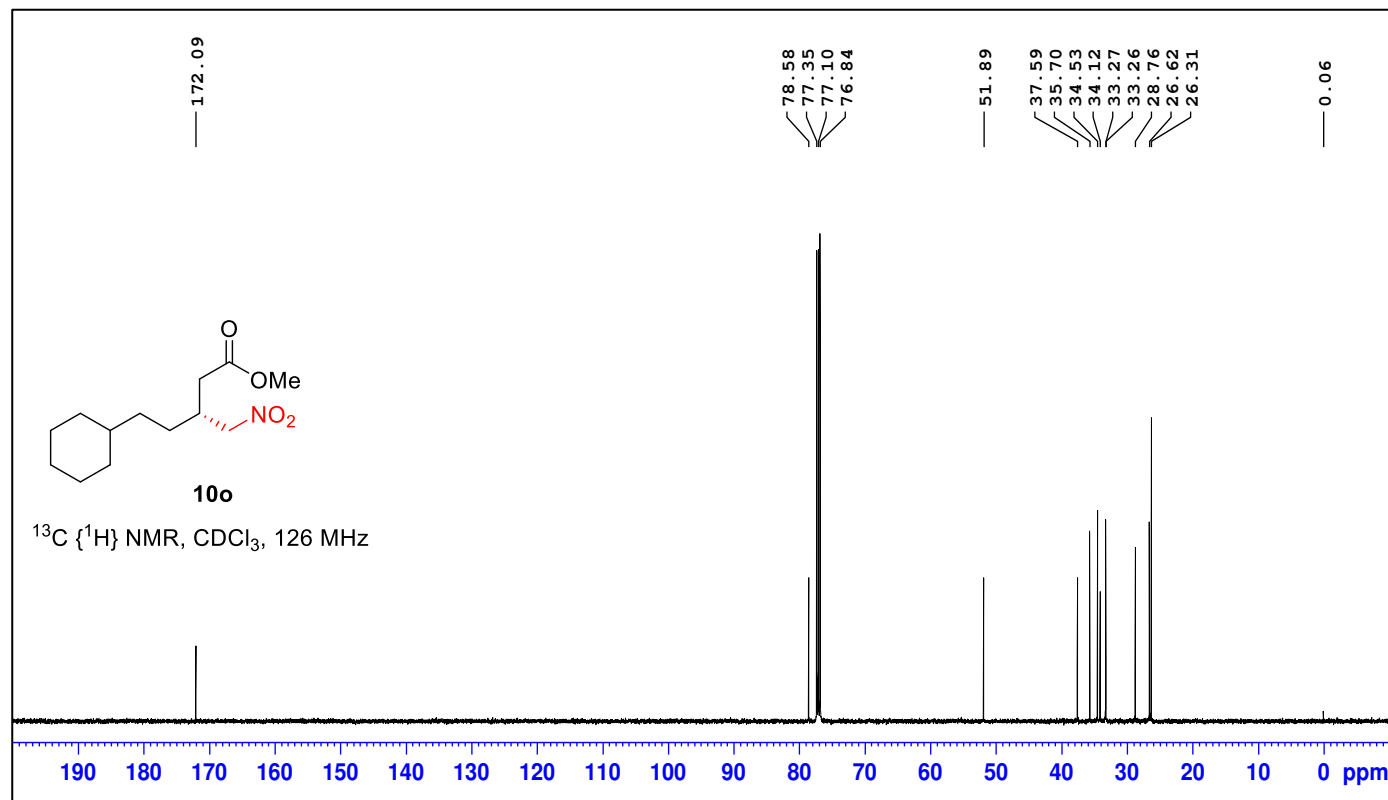
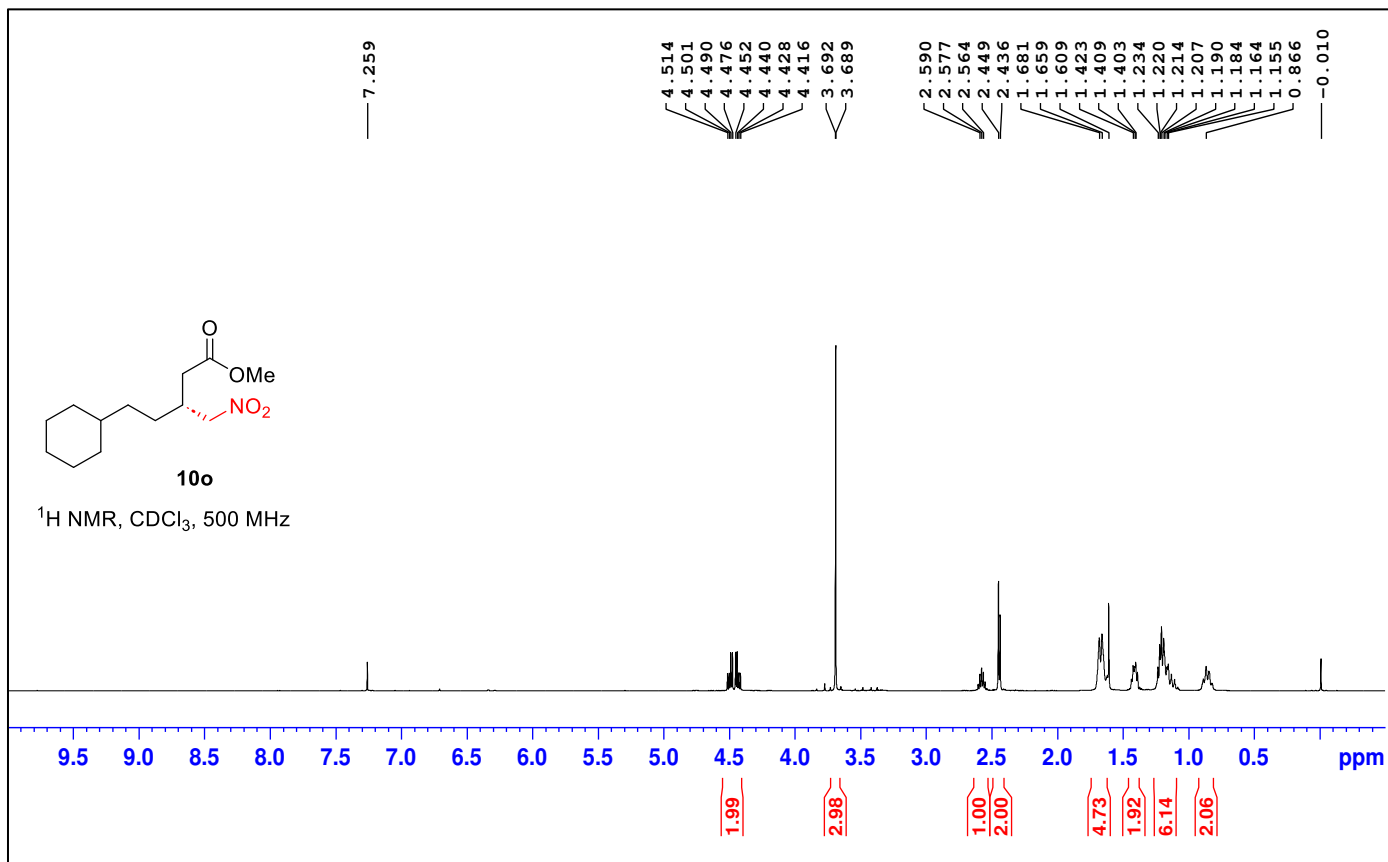
(R)-methyl-5-methyl-3-(nitromethyl)hexanoate (10n)



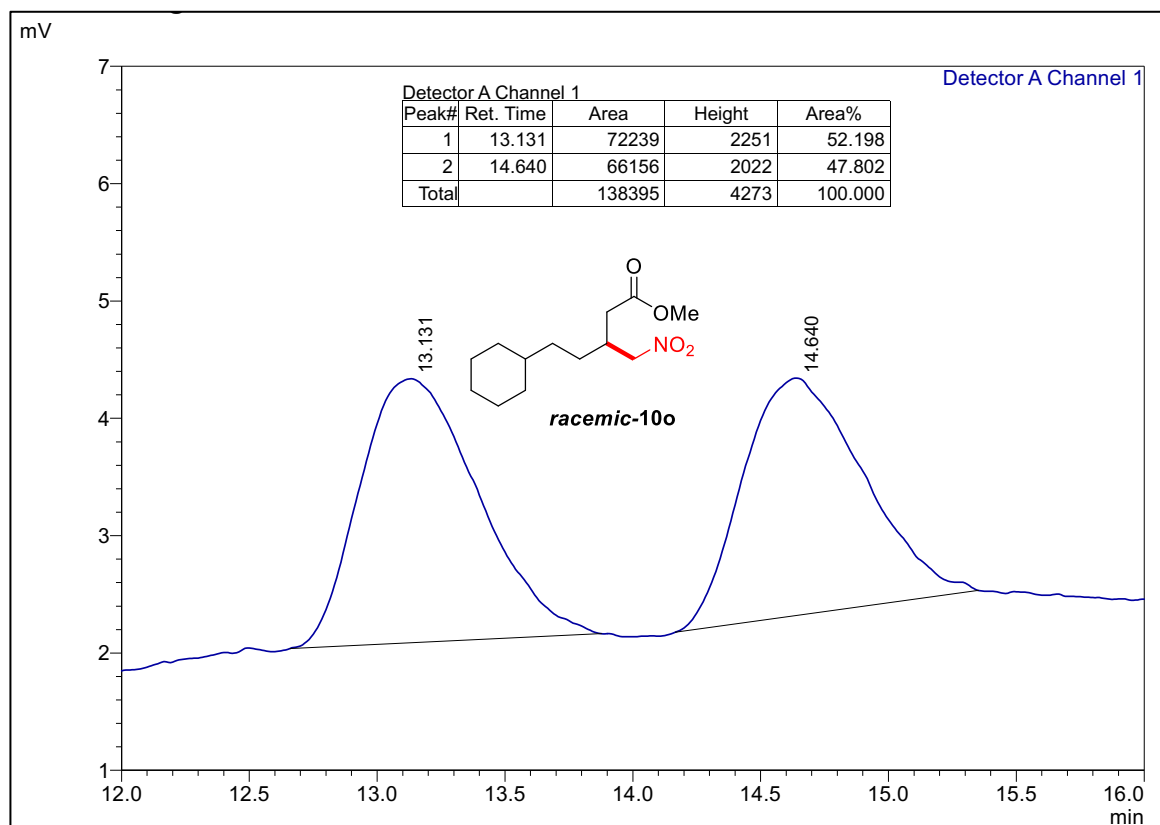
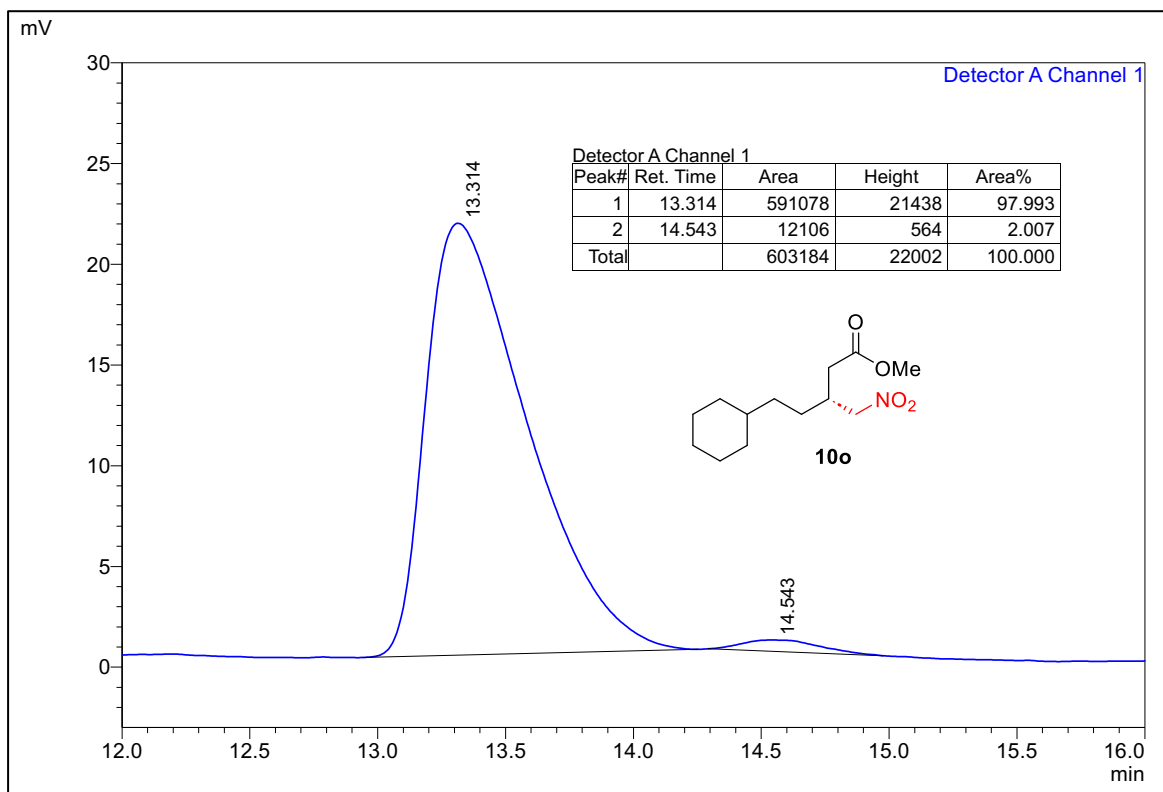
(S)-methyl-5-methyl-3-(nitromethyl)hexanoate (*ent*-10n)



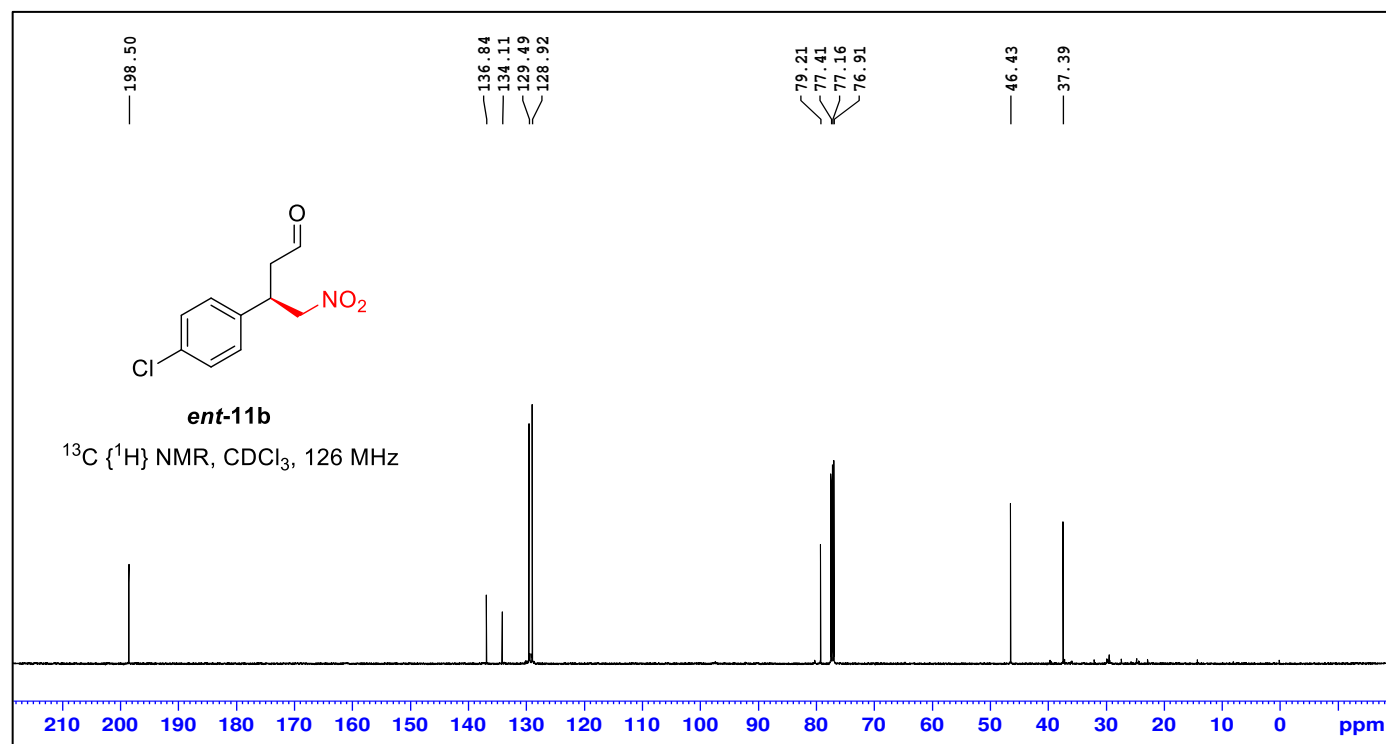
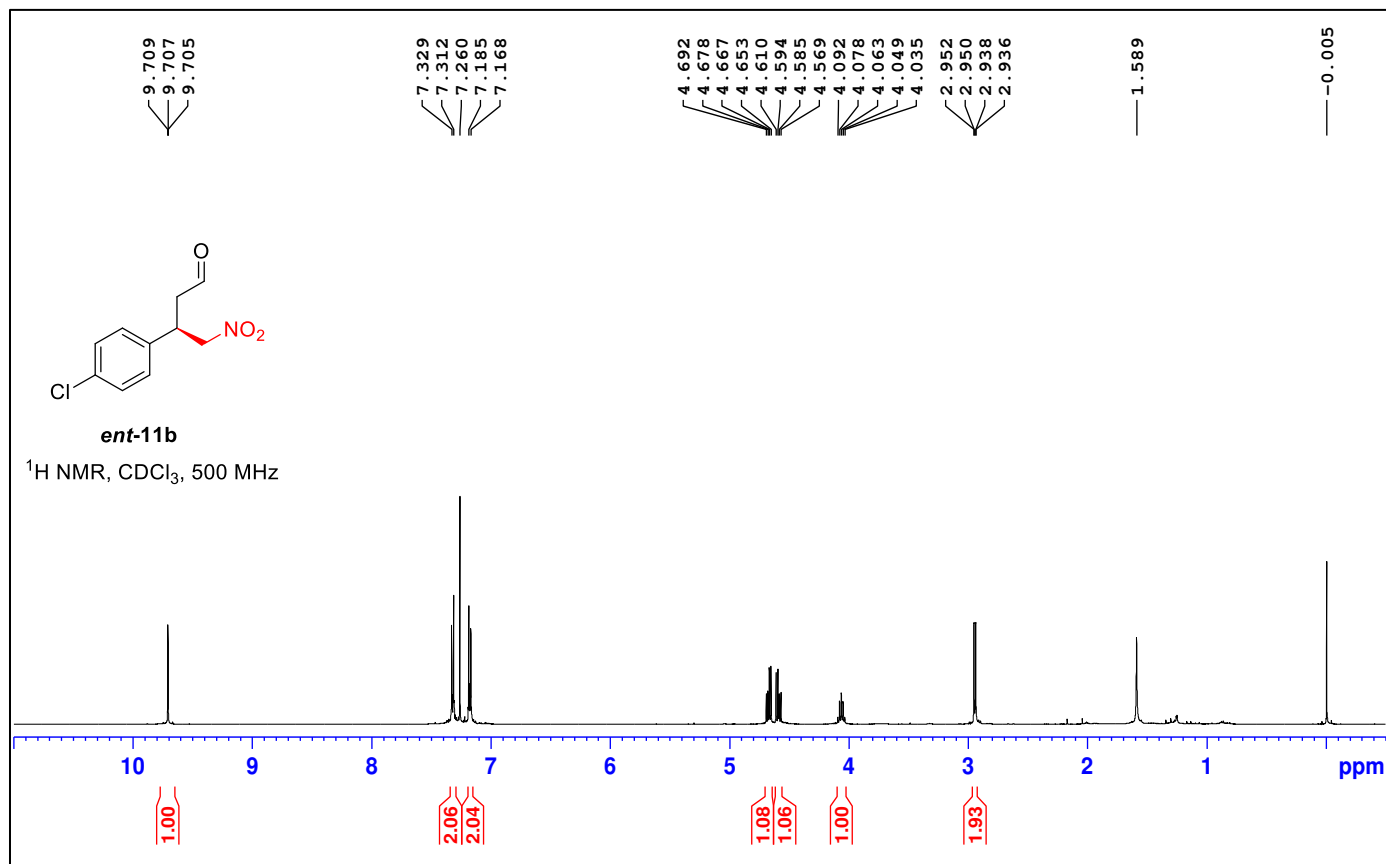
(R)-methyl-4-cyclohexyl-3-(nitromethyl)butanoate (10o)



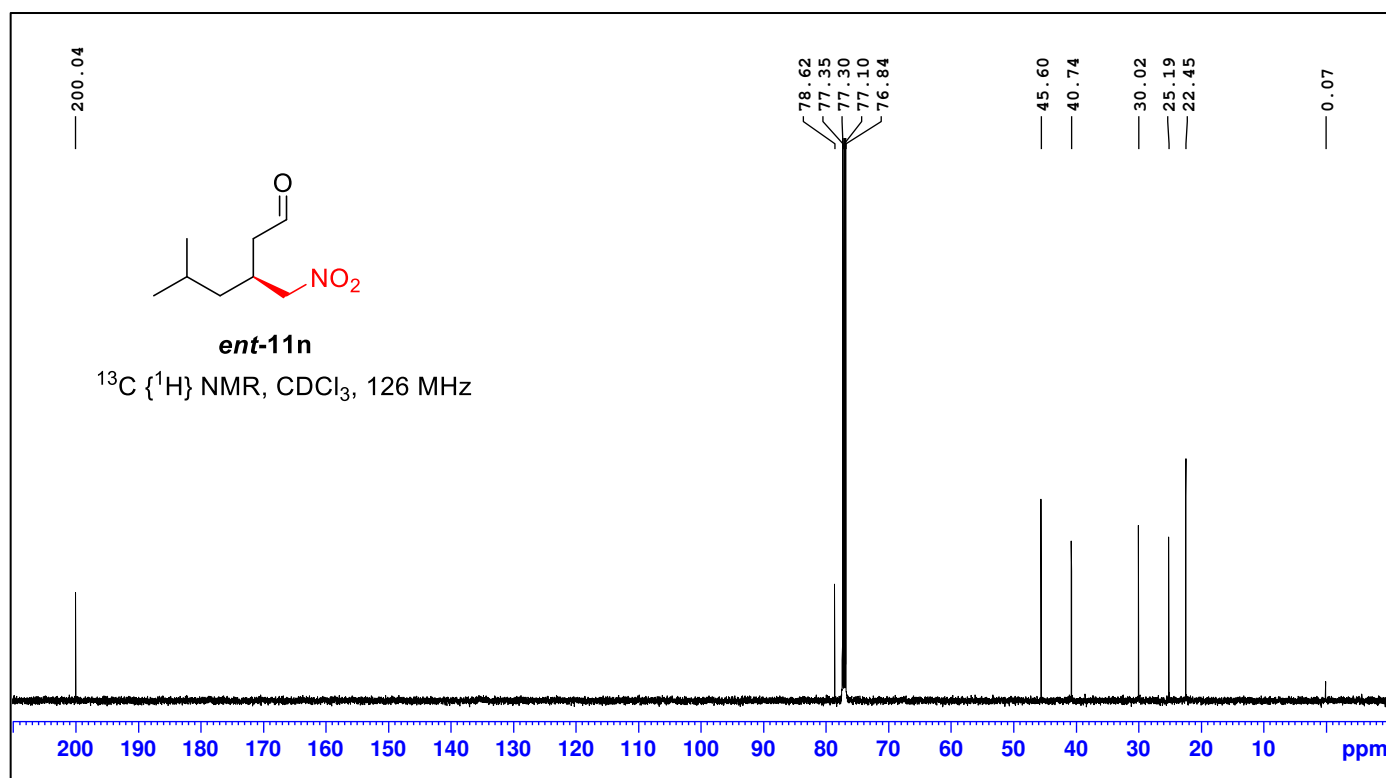
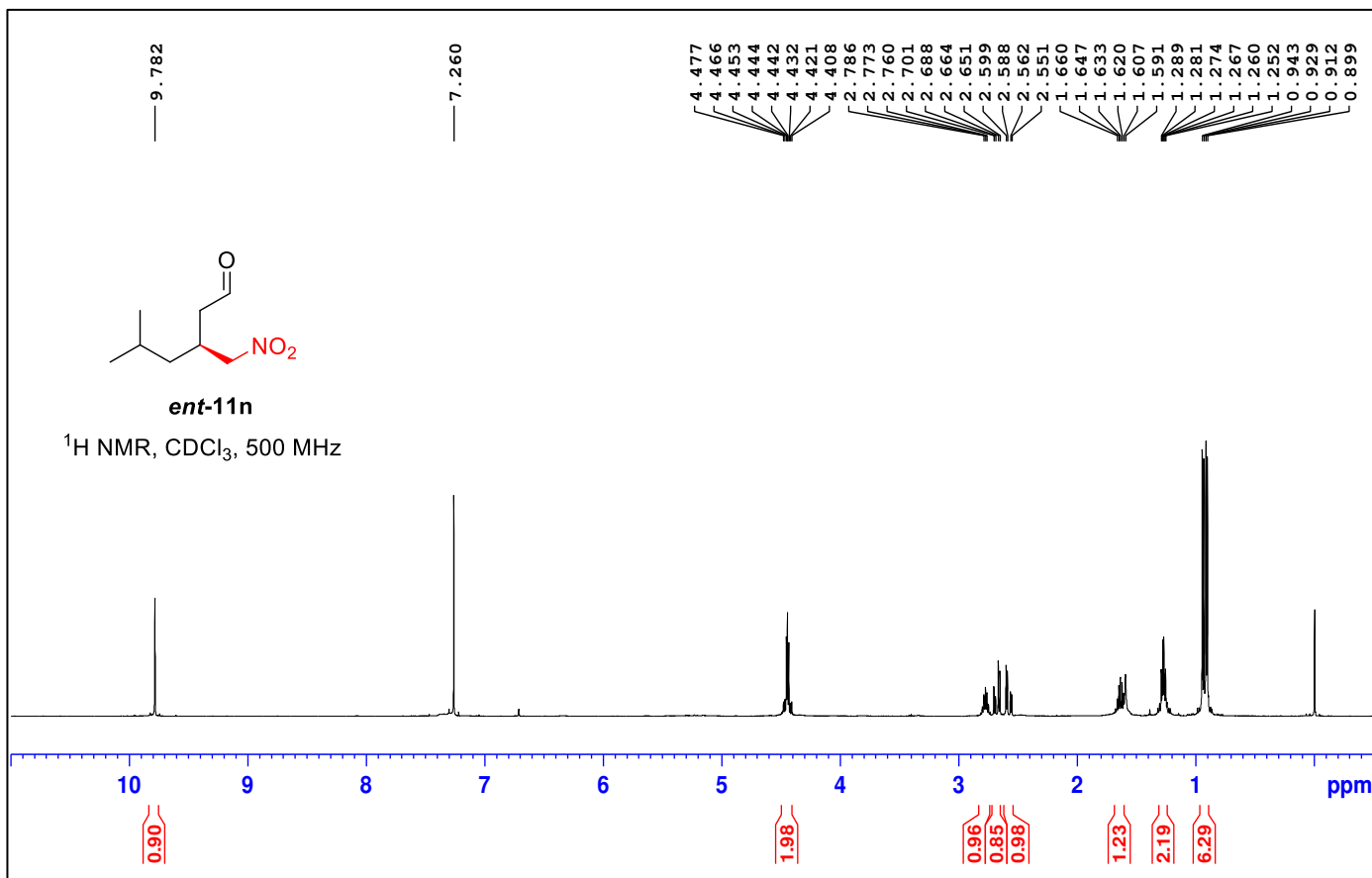
(R)-methyl-4-cyclohexyl-3-(nitromethyl)butanoate (10o)



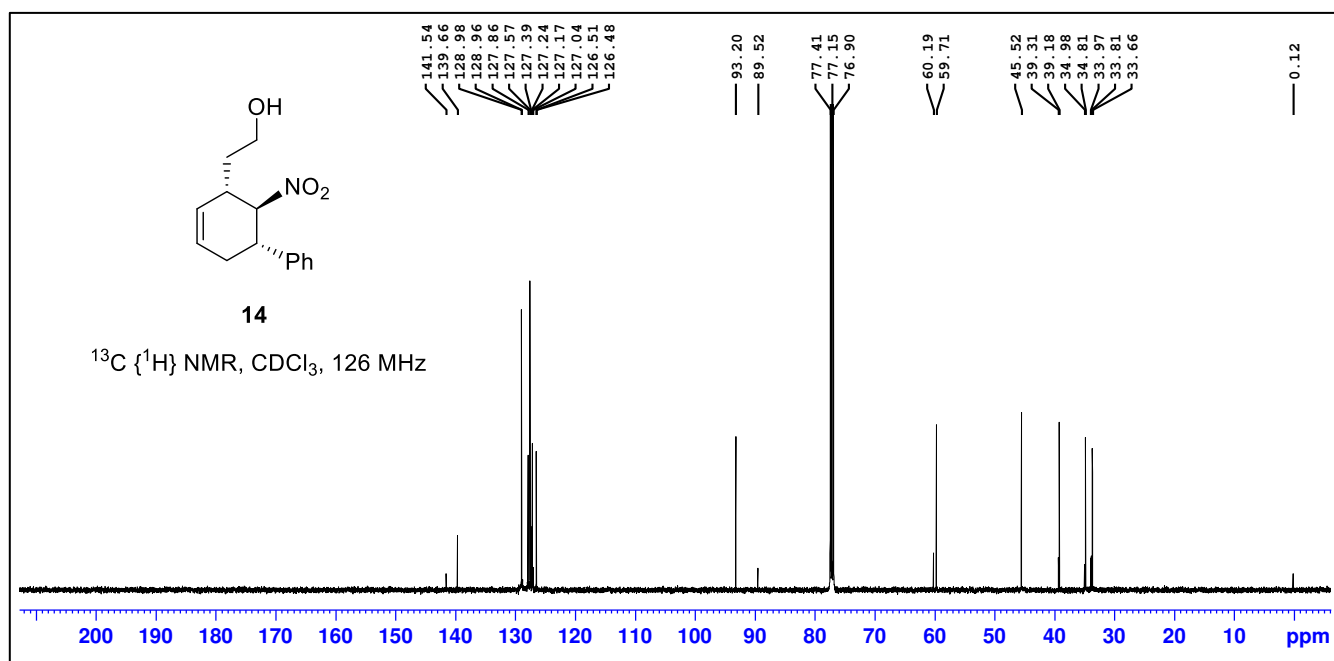
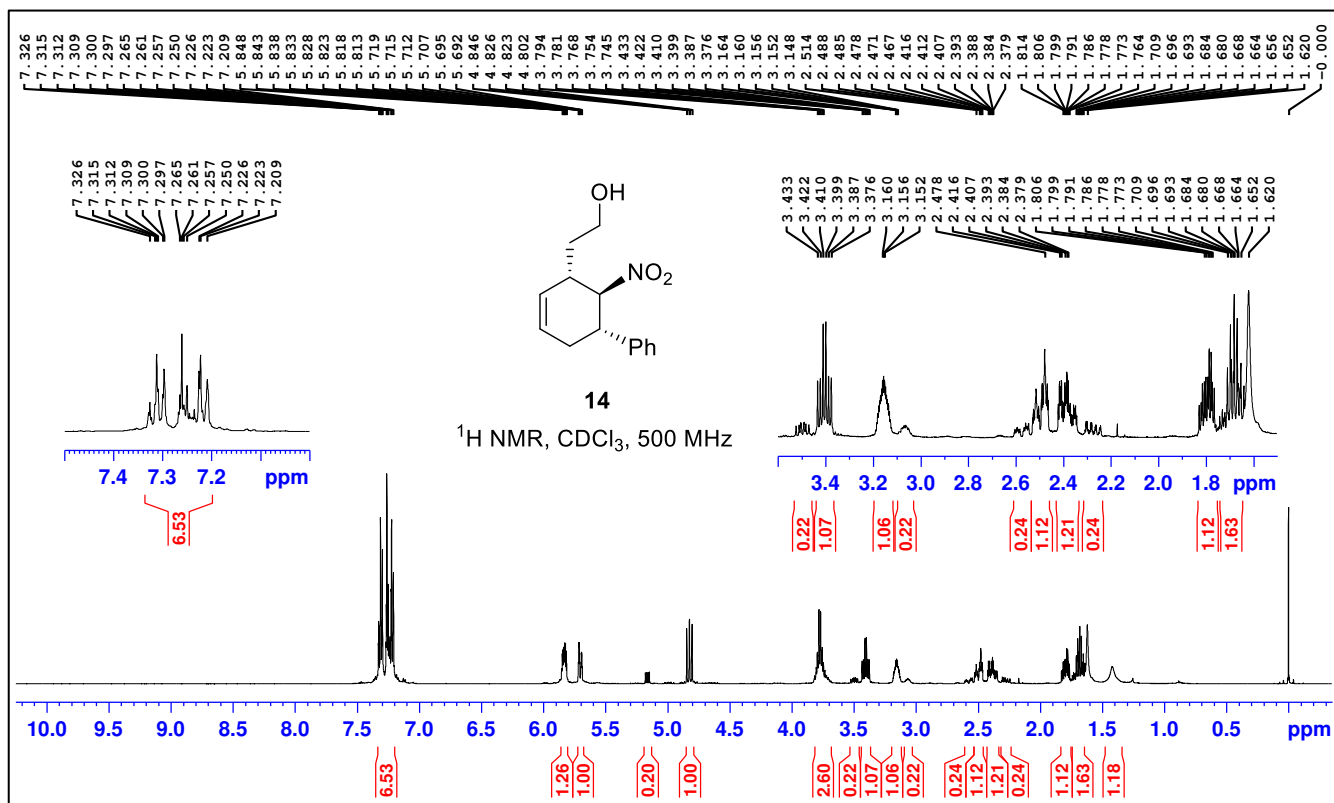
(R)-3-(4-chlorophenyl)-4-nitrobutanal (*ent*-11b)

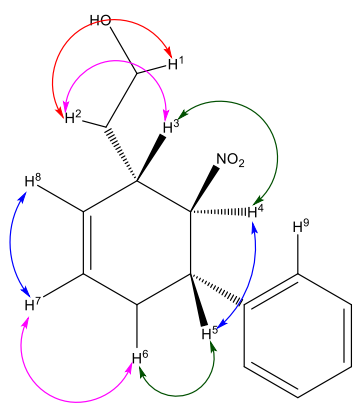


(S)-5-methyl-3-(nitromethyl)hexanal (*ent*-11n)

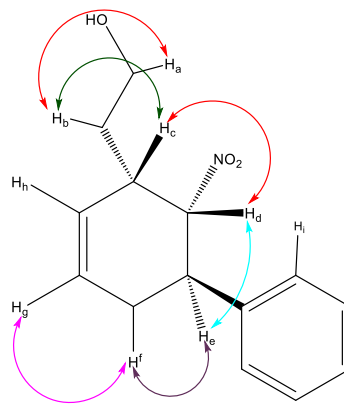


2-((1*S*,2*R*,3*S*)-2-nitro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-ol (14)



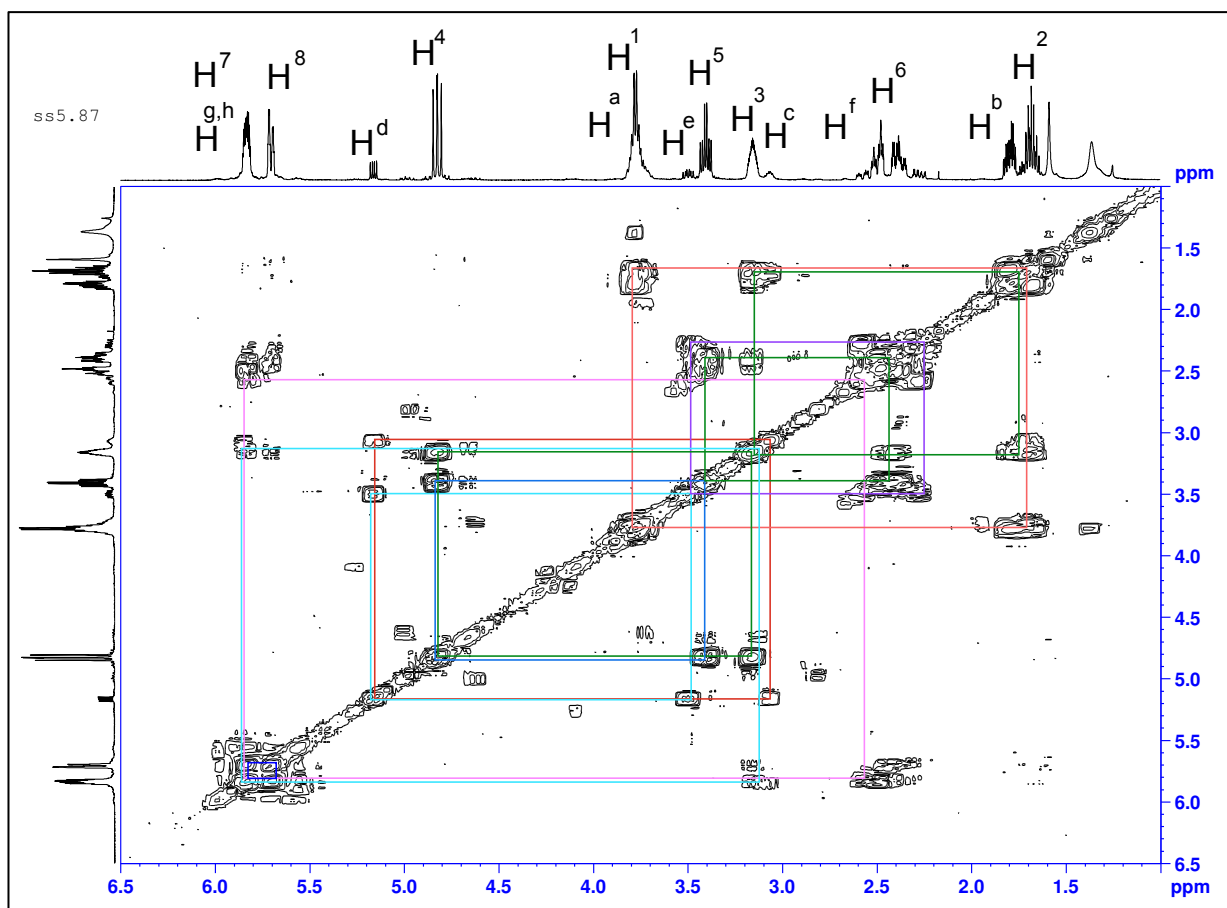


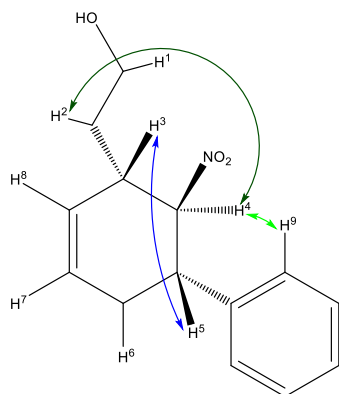
exo-14



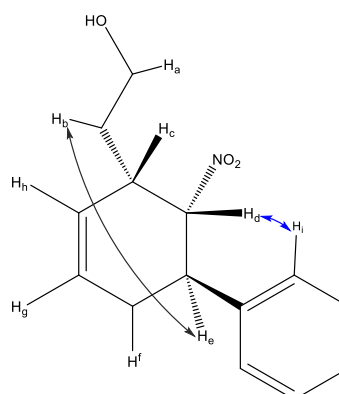
endo-14

COSY spectrum of **14**, CDCl₃, 500 MHz



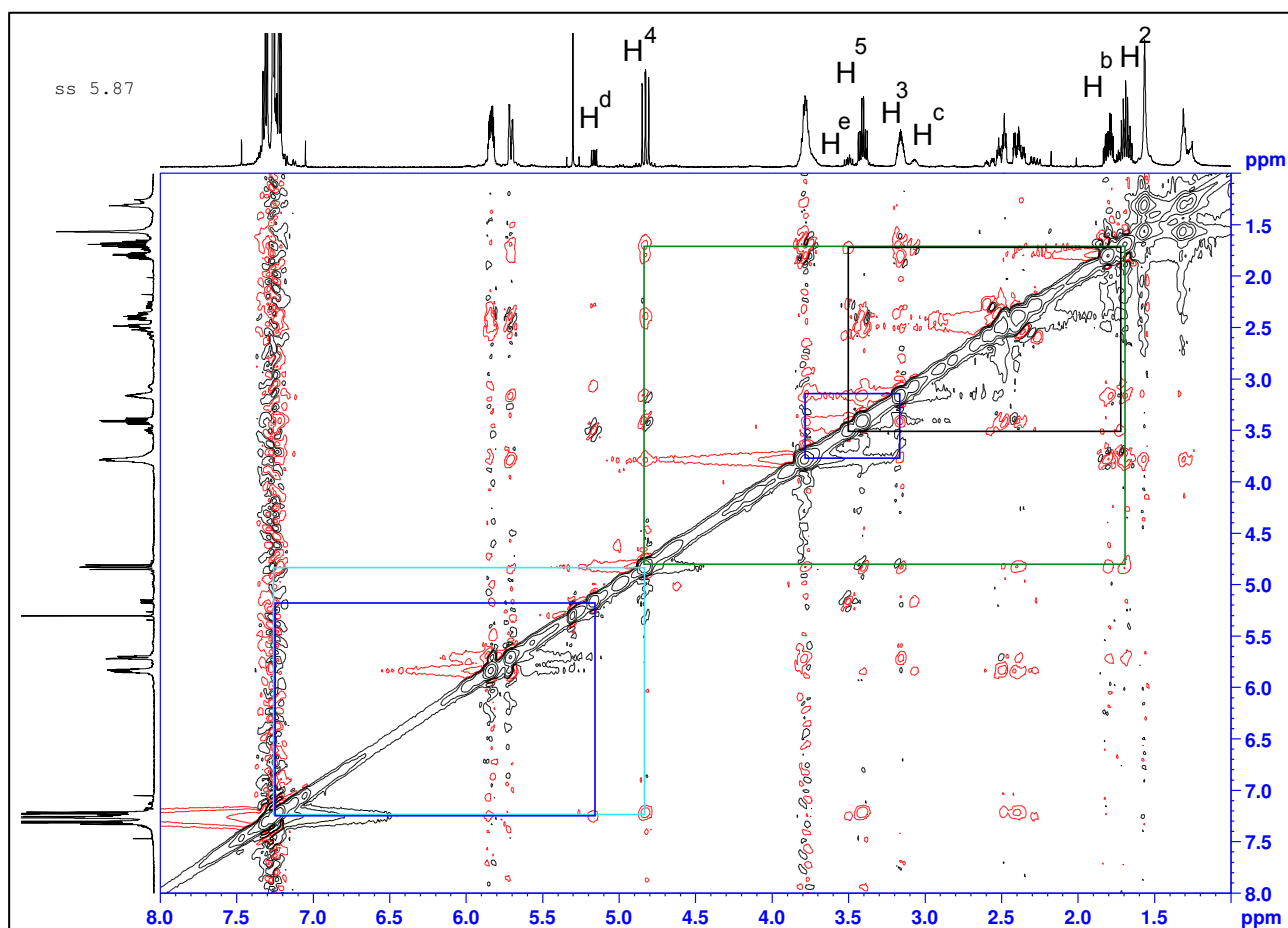


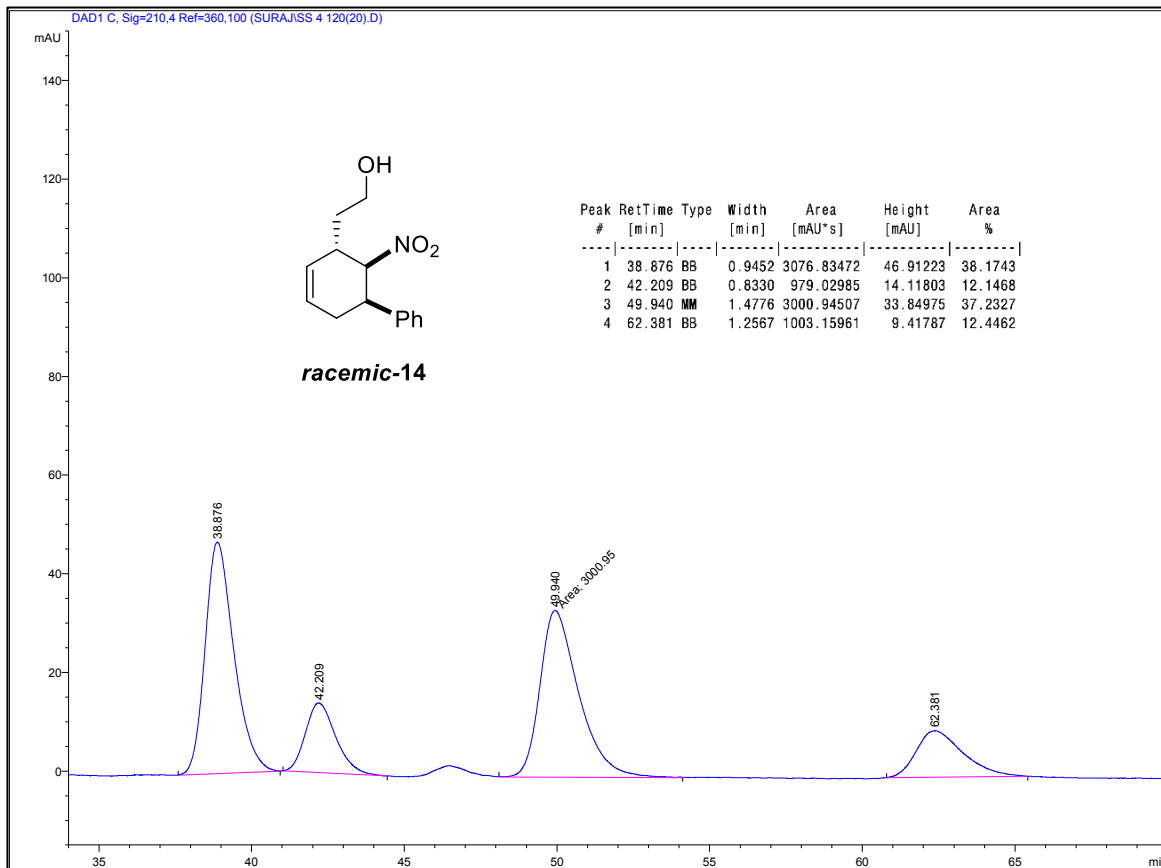
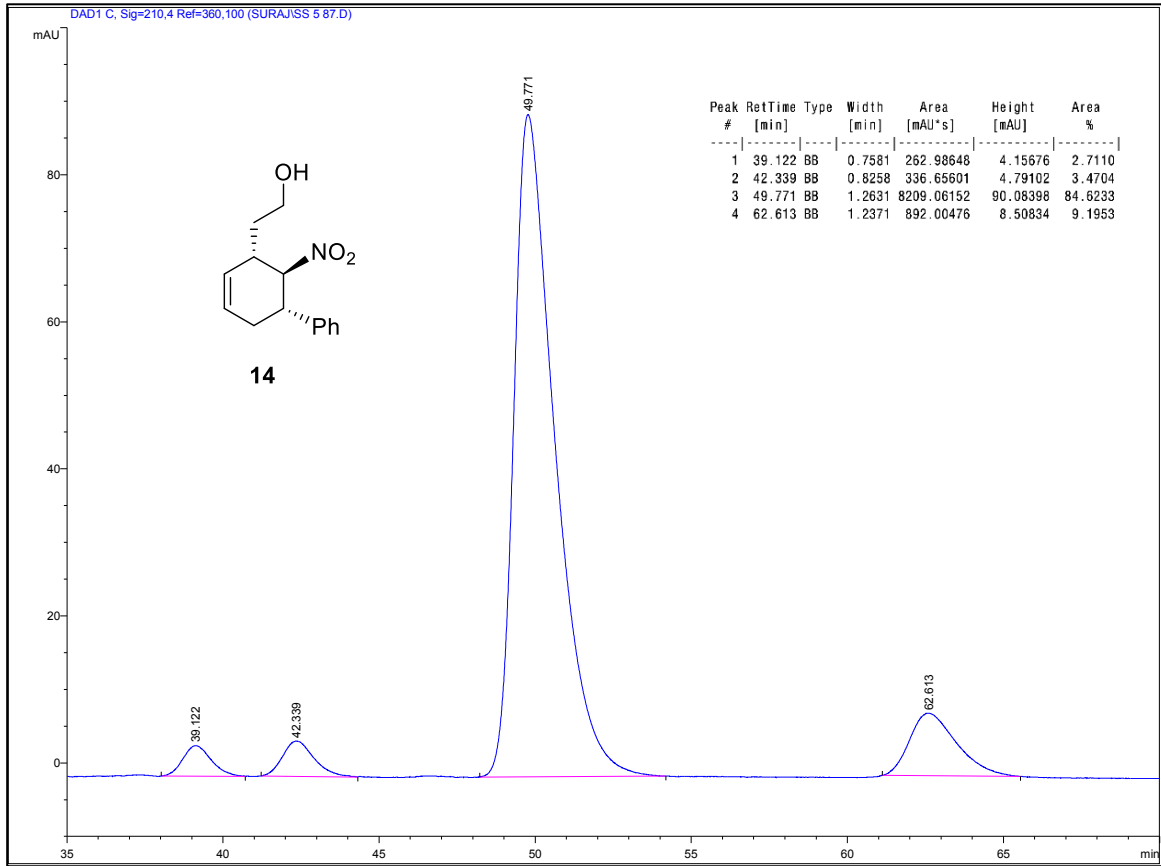
exo-14



endo-14

NOESY spectrum of **14**, CDCl₃, 500 MHz





2-((1*S*,2*R*,3*S*)-2-nitro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethyl (4-chlorophenyl)carbamate (15)

