# Supplementary Information

## Enantioselective Construction of Remote Quaternary Stereocenters

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## General information

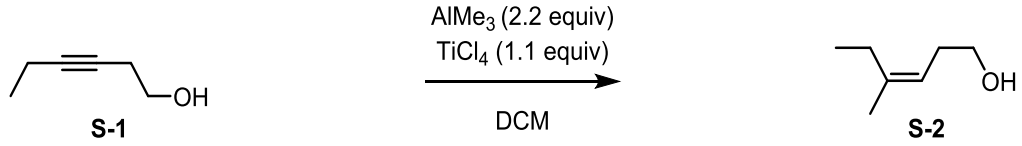
Dry dimethylformamide (DMF) was purchased from Aldrich and stored over activated 3 Å molecular sieves (3 Å MS). Powdered 3 Å MS were activated by flowing $N_2$ through a glass tube of sieves maintained at 200 °C. Alkene substrates were purchased from Aldrich, TCI or Acros, or synthesized according to the procedures outlined below. Alkyne precursors to alkene substrates were purchased from Aldrich. $Pd(CH_3CN)_2(OTs)_2$ was synthesized according to the literature procedure[1]. Ligands were synthesized according to the literature procedure[2]. β-Citronellol, (*S*)-(−)-β-Citronellol, and (*R*)-(+)-β-Citronellol were purchased from Aldrich. $^1$H-NMR spectra were obtained at 500 MHz, chemical shifts are reported in ppm, and referenced to the $CHCl_3$ singlet at 7.26 ppm. $^{13}$C-NMR spectra were obtained at 75 MHz, 100 MHz, or 125 MHz and referenced to the center peak of the $CDCl_3$ triplet at 77.00 ppm. The abbreviations s, d, t, quin, dd, dt, and m stand for the resonance multiplicities singlet, doublet, triplet, quintet, doublet of doublets, doublet of triplets and multiplet, respectively. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid. Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). IR spectra were recorded using a Thermo Nicolet FT-IR. High resolution mass spectrometry (HRMS) data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. Achiral GC (gas chromatography) was performed using a Hewlett Packard HP 6890 series GC system fitted with an Agilent HP-5 column. SFC (supercritical fluid chromatography) analysis was performed at 25–40 ºC, using a Thar instrument fitted with a chiral stationary phase as indicated. Optical rotations were measured (Na D line) on a

Perkin Elmer Model 343 Polarimeter fitted with a micro cell with a 1 dm path length; concentrations are reported in g/100 mL. (*S*)-(+)-**2bb** and (*R*)-(−)-**2bb** are previously reported compounds with a known optical rotation[3,4], and the absolute stereochemistry of products **2a–2n**, **3a–3j** were assigned based on analogy to this compound where possible. The absolute configuration of **2fb** (a derivative of **2f**) was determined by X-ray crystallography to confirm the assignment.

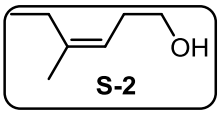
## 2. Experimental section

### 2.1 Synthesis of alkene substrates

**Preparation of (Z)-4-methylhex-3-en-1-ol**[5]




S-1 S-2

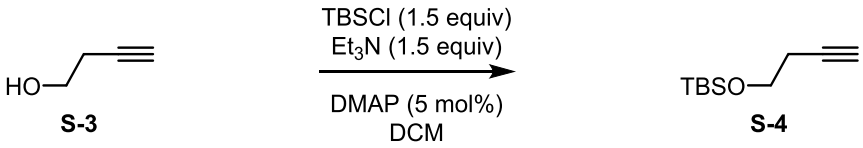


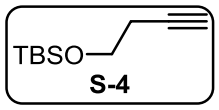

S-2

Neat $(A1Me_3)_2$ (220 mmol, 21.1 mL) was transferred by syringe into 300 mL of $CH_2C1_2$ contained in a 500-mL three-necked round-bottom flask equipped with a gas inlet, rubber septa, and a magnetic stirring bar. The $(AlMe_3)_2$ containing solution was cooled to 0 ºC and alkynol **S-1** (100 mmol, 10.9 mL) was added slowly by syringe through a septum. The liberated methane was vented through the gas inlet and safety bubbler attached to a nitrogen manifold. The above solution was cooled to -78 °C and neat $TiCl_4$ (110 mmol, 12.1 mL) was added dropwise to the reaction. The reaction mixture was stirred at –78 °C for 2 hr, then quenched via syringe addition of 60 mL of methanol precooled to 0 °C. An aqueous 3 N HC1 solution saturated with NaCl (200 mL) was then added. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The combined extracts were washed with $H_2O$ and brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue

was purified by flash chromatography on silica (5–10% EtOAc/hexanes) to give **S-2** (5.4 g, 47%). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 5.08 (t, $J$ = 7.5 Hz 1 H), 3.61–3.58 (m, 2 H), 2.26 (q, $J$ = 7.0 Hz, 1 H), 2.05 (dt, $J_1$ = 7.5 Hz, $J_2$ = 7.0 Hz, 1 H), 1.71 (s, 3 H), 0.97 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 140.9, 119.5, 62.6, 31.2, 24.8, 23.0, 12.8. IR (neat): 3318, 2964, 2933, 2874, 1450, 1376, 1045, 1019, 835 $cm^{-1}$. HRMS $(M+H)^+$ calcd. 115.1123, obsvd. 115.1141.

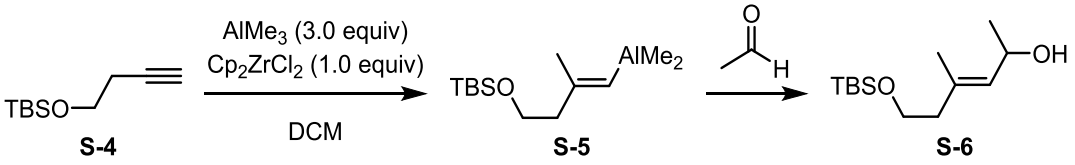
**Preparation of (but-3-yn-1-yloxy)(tert-butyl)dimethylsilane**[6]

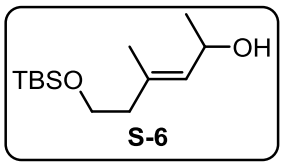



To a stirred solution of **S-3** (200 mmol, 14.0 g) in dry $CH_2Cl_2$ (300 mL), TBSCl (300 mmol, 45.2 g, 1.5 equiv), DMAP (10 mmol, 1.20 g, 0.05 equiv) and $Et_3N$ (300 mmol, 41.8 mL, 1.5 equiv) was added. The reaction solution was stirred at room temperature for 5 h, and then a saturated solution of $NH_4Cl$ was added. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was distilled under vacuum to give **S-4** (31.9 g, 86%). $^{1}$H-NMR (300 MHz, $CDCl_3$) δ = 3.74 (t, $J$ = 4.2 Hz, 2 H), 2.40 (dt, $J_1$ = 2.4 Hz, $J_2$ = 7.2 Hz, 2 H), 1.96 (t, $J$ = 2.4 Hz, 1 H), 2.05 (dt, $J_1$ = 7.5 Hz, $J_2$ = 7.0 Hz, 1 H), 1.71 (s, 3 H), 0.90 (s, 9 H), 0.06 (s, 6 H). $^{13}$C-NMR (75 MHz, $CDCl_3$) δ = 81.5, 69.3, 61.7, 25.9, 22.8, 18.3, –5.3. IR (neat): 3314, 2954, 2929, 2857, 1472, 1254, 1102, 915, 834, 774, 631 $cm^{-1}$.

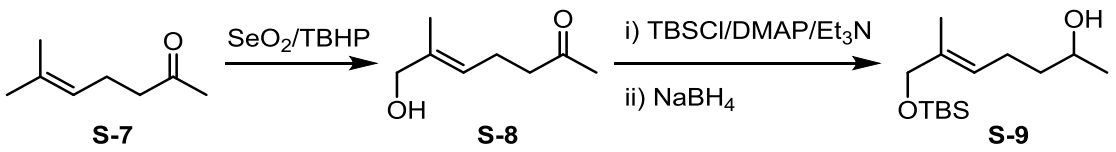
**Preparation of (*E*)-6-((tert-butyldimethylsilyl)oxy)-4-methylhex-3-en-2-ol**[7]

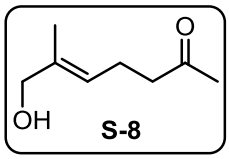



To a stirred solution of $(AlMe_3)_2$ (pyrophoric) (30 mmol, 2.16 g) and $Cl_2ZrCp_2$ (10 mmol, 2.92 g) in dry $CH_2Cl_2$ (100 mL), (but-3-yn-1-yloxy)(tert-butyl)dimethylsilane **S-4** (10 mmol, 1.84g) was added dropwise at 0 °C. The reaction solution was stirred at room temperature for 12 h, and then the reaction mixture was cooled to –30 ºC before acetadehyde (11 mmol, 0.62 mL) was added dropwise. The reaction solution was stirred at –30 ºC for another 3 h, and then a saturated solution of $NH_4Cl$ was added slowly to quench the reaction at 0 ºC. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (5% EtOAc/Hexane) to give **S-6** in 31% yield (765 mg). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.16 (t, *J* = 7.5 Hz, 1 H), 3.67 (t, *J* = 5.5 Hz, 2 H), 3.62 (t, *J* = 6.0 Hz, 2 H), 2.28 (q, *J* = 6.5 Hz, 2 H), 2.24 (t, *J* = 6.5, 2 H), 1.66 (s, 3 H), 1.66 (br, 1 H), 0.88 (S, 9 H), 0.04 (S, 6 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 135.9, 121.9, 62.2, 62.0, 43.1, 31.5, 25.9, 18.3, 16.5, –5.3. IR (neat): 3331, 2955, 2928, 2857, 1472, 1252, 1096, 833, 773, 663 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 267.1756, obsvd. 267.1754.

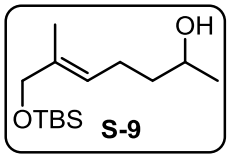
**Preparation of (*E*)-7-((tert-butyldimethylsilyl)oxy)-6-methylhept-5-en-2-ol**





**S-8**

To a solution of 6-methylhept-5-en-2-one (6.31 g, 50.0 mmol) in $CH_2Cl_2$ (100 mL), *t*-BuOOH (10 mL, 5 M in Hexane, 50.0 mmol) was added. The solution was stirred vigorously and then $SeO_2$ (5.55 g, 50.0 mmol) was added. The resulting mixture was stirred for 2 hours and then was diluted with $CH_2Cl_2$, washed with NaOH (10%) and the organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (10% EtOAc/Hexane) to give **S-9** in 45% yield (3.20 g). $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$ = 5.33 (t, *J* = 7.5 Hz, 1 H), 3.96 (s, 2 H), 2.47 (t, *J* = 7.0 Hz, 2 H), 2.28 (q, *J* = 7.0 Hz, 2 H), 2.12 (s, 3 H), 1.77 (br, 1 H), 1.65 (s, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ = 208.5, 135.9, 123.8, 68.5, 43.2, 29.9, 21.9, 13.6. IR (neat): 3400, 2915, 2860, 1706, 1408, 1358, 1228, 1159, 1068, 1009, 862, 574 cm$^{-1}$.

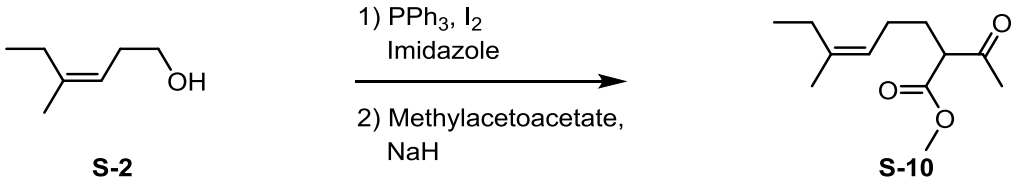


**S-9**

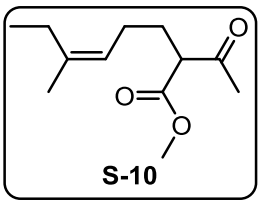
To a stirred solution of **S-8** (10.0 mmol, 1.42 g) in dry $CH_2Cl_2$ (100 mL), TBSCl (15.0 mmol, 2.26 g, 1.5 equiv), DMAP (0.50 mmol, 61.0 g, 0.05 equiv) and $Et_3N$ (15 mmol, 2.09 mL, 1.5 equiv) was added. The reaction solution was stirred at room temperature for 5 h, and then a saturated solution of $NH_4Cl$ was added. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was dissolved in 30 mL THF and treated with $NaBH_4$ (20 mmol, 2 equiv). The reaction solution was stirred at room temperature for 10 h, and then a saturated solution of $NH_4Cl$ was added slowly. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (5% EtOAc/Hexane) to give **S-9** in 70% yield (1.81 g) over two steps. $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$ = 5.41 (t, *J* = 7.5 Hz, 1 H), 4.01 (S, 1 H), 3.84–3.78 (m, 1 H), 2.19–2.06 (m, 2 H), 1.61 (s, 3 H),

1.57–1.46 (m, 2 H), 1.39 (br, 1 H), 1.20 (d, $J$ = 6.0, 3 H), 0.91 (s, 9 H), 0.06 (s, 6 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 135.0, 123.9, 68.5, 67.9, 39.0, 26.0, 23.9, 23.5, 18.4, 13.4, −5.3. IR (neat): 3343, 2956, 2828, 2856, 1462, 1252, 1111, 1063, 833, 773, 666 cm$^{-1}$. HRMS $(M+H)^+$ calcd. 281.1913, obsvd. 281.1912.

**Preparation of (Z)-methyl 2-acetyl-6-methyloct-5-enoate**[8,9]




**S-2** **S-10**

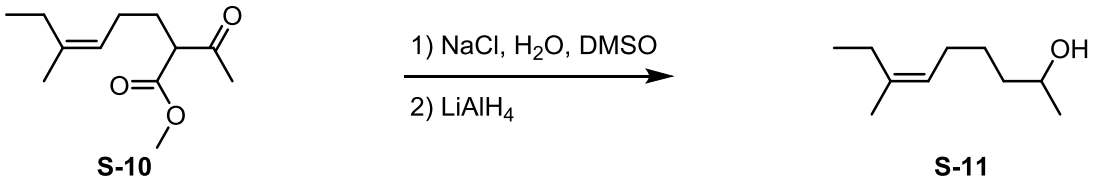



**S-10**

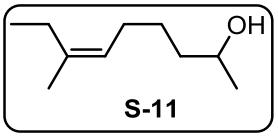
A solution of $PPh_3$ (4.72 g, 18.0 mmol) and 1H-imidazole (1.22 g, 18.0 mmol) in $CH_2Cl_2$ (100 ml) was treated slowly with $I_2$ (6.10 g, 24.0 mmol). To this heterogeneous mixture, (Z)-4-methylhex-3-en-1-ol **S-2** (1.37 g, 12.0 mmol) was added dropwise. After stirring at room temperature for 1 h, the solvent was mostly evaporated and the residue filtered over silica gel (pentane/$Et_2O$ 4 : 1) to give the crude alkyliodide product, which is used in the next step without further purification. To a suspension of NaH (1.02 equiv, 60% in mineral oil) in THF (0.40 M) at 0 ºC was added dropwise methylacetoacetate (2.79 g, 24 mmol, 2.0 equiv) over 15 min. The mixture was allowed to slowly warm to rt over 1 h, and THF solution of above alkyl iodide was then added. The flask was wrapped with aluminum foil, and the mixture was refluxed for 15 h. Saturated $NH_4Cl$ was added, and the mixture was extracted with ether. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica (5–20% EtOAc/hexanes) to give **S-10** (1.22 g, 48%). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.01 (t, $J$ = 7.5 Hz, 1 H), 3.72 (s, 3 H), 3.43 (t, $J$ = 7.5 Hz, 1 H), 2.20 (s, 3 H), 1.99–1.83 (m, 6 H),

1.66 (s, 3 H), 0.93 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 203.2, 170.3, 138.7, 122.3, 59.0, 52.3, 28.8, 28.4, 25.3, 24.7, 22.8, 12.7. IR (neat): 2965, 2875, 1742, 1715, 1435, 1358, 1197, 1144, 989, 840, 734 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 235.1310, obsvd. 235.1310.

**Preparation of (Z)-7-methylnon-6-en-2-ol**




**S-10** **S-11**

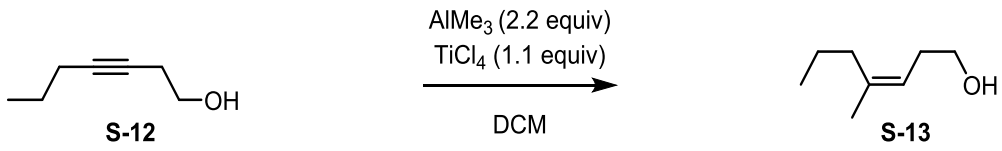



**S-11**

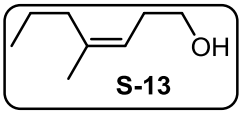
To a flask equipped with a reflux condenser, a solution of ketoester **S-10** (5 mmol, 1.06 g) in DMSO (5 mL), NaCl (5 mmol, 293 mg, 1.0 equiv), $H_2O$ (15 mmol, 270 mg, 3.0 equiv) was added. The reaction solution was stirred at 150 ºC for 8 h, and then cooled to room temperature. The mixture was diluted in 100 mL EtOAc, and washed with $H_2O$ (3x20 mL), and brine (20 mL). The organic layer was dried with $MgSO_4$ and concentrated to give the crude product, which is used in the next step without further purification. To a suspension of $LiAlH_4$ (2.0 equiv) in THF (0.1 M) at 0 ºC was added dropwise the THF solution of the above residue over 5 min. The mixture was allowed to slowly warm to room temperature over 1 hr. Saturated $NH_4Cl$ was added, and the mixture was extracted with ether. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica (5–20% EtOAc/hexanes) to give **S-11** (3.5 mmol, 547 mg, 75% yield). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.08 (t, $J$ = 6.5 Hz, 1H), 3.81–3.77 (m, 1 H), 1.68 (s, 3 H), 1.49–1.33 (m, 5 H), 1.18 (d, $J$ = 3.5 Hz, 3 H), 0.95 (t, $J_1$ = 8.0 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 137.4, 124.0, 68.1, 39.0, 27.5, 26.3, 24.7, 23.5, 22.8,

12.8. IR (neat): 3331, 2964, 2930, 2858, 1455, 1374, 1128, 1085, 1071, 840 $cm^{-1}$. HRMS $(M+H)^+$ calcd. 157.1592, obsvd. 157.1599.

**Preparation of (Z)-4-methylhept-3-en-1-ol**




S-12 S-13

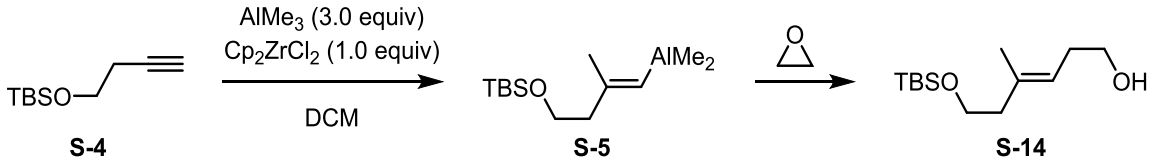


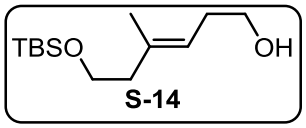

S-13

Neat $(A1Me_3)_2$ (66 mmol, 6.3 mL) was transferred by syringe into 100 mL of $CH_2C1_2$ contained in a 250-mL three-necked round-bottom flask equipped with a gas inlet, rubber septa, and a magnetic stirring bar. The $(A1Me_3)_2$ solution was cooled to 0 ºC and the alkynol (30 mmol, 3.7 mL) was slowly added by syringe through a septum. The liberated methane was vented through a gas inlet and safety bubbler attached to a nitrogen manifold. The resulting solution was cooled to −78 °C and neat $TiCl_4$ (33 mmol, 3.6 mL) was added dropwise to the reaction. The reaction mixture was stirred at −78 °C for 2 hr, and then quenched via syringe addition of 30 mL of methanol precooled to 0 °C. An aqueous 3 N HC1 solution saturated with NaCl (200 mL) was then added. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The combined extracts were washed with $H_2O$ and brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica (5–10% EtOAc/hexanes) to give (*Z*)-4-methylhept-3-en-1-ol, **S-13** (2.0 g, 52%). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.14 (t, *J* = 7.5 Hz, 1 H), 3.62 (t, *J* = 6.5 Hz, 2 H), 2.29 (q, *J* = 6.5 Hz, 2 H), 2.04 (t, *J* = 7.5 Hz, 2 H), 1.72 (s, 3 H), 1.46 (br, 1 H), 1.42 (dt, $J_1$ = 7.5 Hz, $J_2$ = 7.5 Hz, 2 H), 0.90 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 139.2, 120.5, 62.6, 33.9, 31.4, 23.5,

21.2, 14.0. IR (neat): 3327, 2958, 2931, 2871, 1045, 1020 $cm^{-1}$. HRMS $(M+H)^+$ calcd. 129.1279, obsvd. 129.1284.

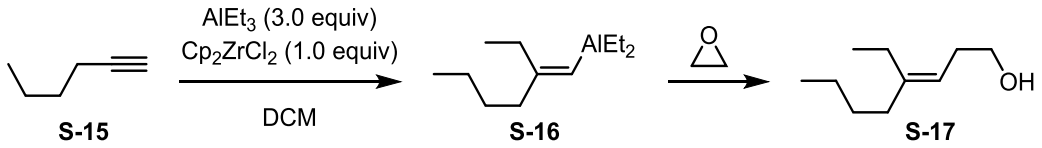
**Preparation of (*E*)-6-((tert-butyldimethylsilyl)oxy)-4-methylhex-3-en-1-ol**

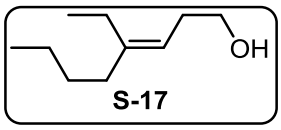



To a stirred solution of $(A1Me_3)_2$ (pyrophoric) (30 mmol, 2.16 g) and $Cl_2ZrCp_2$ (10 mmol, 2.92 g) in dry $CH_2Cl_2$ (100 mL), (but-3-yn-1-yloxy)(tert-butyl)dimethylsilane **S-4** (10 mmol, 1.84g) was added dropwise at 0 °C. The reaction solution was stirred at room temperature for 12 h, and then the reaction mixture was cooled to –30 ºC before ethylene oxide (11 mmol, 4.4 mL, 2.5M in THF) was added dropwise. The reaction solution was stirred at –30 ºC for another 3 h, and then a saturated solution of $NH_4Cl$ was added slowly to quench the reaction at 0 ºC. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (3% EtOAc/Hexane) to give **S-14** in 31% yield (747 mg). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.16 (t, *J* = 7.5 Hz, 1 H), 3.67 (t, *J* = 5.5 Hz, 2 H), 3.62 (t, *J* = 6.0 Hz, 2 H), 2.28 (q, *J* = 6.5 Hz, 2 H), 2.24 (t, *J* = 6.5, 2 H), 1.66 (s, 3 H), 1.66 (br, 1 H), 0.88 (S, 9 H), 0.04 (S, 6 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 135.9, 121.9, 62.2, 62.0, 43.1, 31.5, 25.9, 18.3, 16.5, –5.3. IR (neat): 3346, 2953, 2928, 2856, 1472, 1252, 1092, 1047, 832, 773, 662 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 267.1756, obsvd. 267.1750.

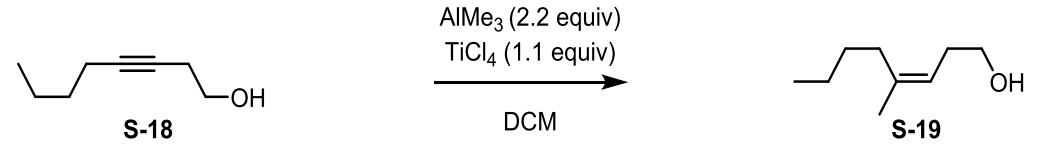
**Preparation of (*E*)-4-ethyloct-3-en-1-ol**

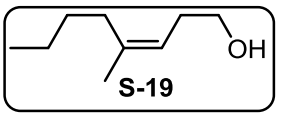



To a stirred solution of $Et_3Al$ (pyrophoric) (15 mmol, 1.71 g) and $Cl_2ZrCp_2$ (5 mmol, 1.46 g) in dry $CH_2Cl_2$ (50 mL), hex-1-yne **S-15** (5 mmol, 0.41 g) was added dropwise at 0 °C. The reaction solution was stirred at room temperature for 12 h, and then the reaction mixture was cooled to –30 ºC before ethylene oxide (5.5 mmol, 2.2 mL, 2.5M in THF) was added dropwise. The reaction solution was stirred at –30 ºC for another 3 hr, and then a saturated solution of $NH_4Cl$ was added slowly to quench the reaction at 0 ºC. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (3% EtOAc/Hexane) to give **S-17** in 46% yield (362 mg). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.05 (t, *J* = 7.5 Hz, 1 H), 3.60 (t, *J* = 5.5 Hz, 2 H), 2.28 (q, *J* = 6.5 Hz, 2 H), 2.06–1.98 (m, 4 H), 1.38–1.24 (m, 5 H), 0.95 (t, *J* = 7.5 Hz, 3 H). 0.88 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 145.2, 118.9, 62.6, 36.3, 31.1, 30.4, 23.1, 22.5, 14.0, 13.3. IR (neat): 3316, 2959, 2927, 2872, 1457, 1377, 1045, 874, 844 cm$^{-1}$. HRMS $(M+H)^+$ calcd. 157.1592, obsvd. 157.1601.

**Preparation of (Z)-4-methyloct-3-en-1-ol**

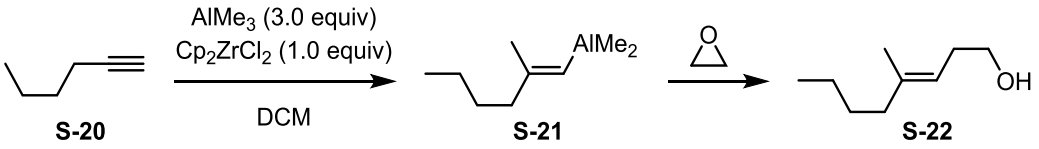


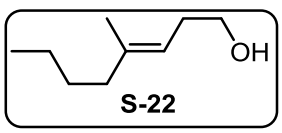




Neat $(A1Me_3)_2$ (66 mmol, 6.3 mL) was transferred by syringe into 100 mL of $CH_2C1_2$ contained in a 250-mL three-necked round-bottom flask equipped with a gas inlet, rubber septa, and a magnetic stirring bar. The

$(A1Me_3)_2$ solution was cooled to 0 ºC and oct-3-yn-1-ol (30 mmol, 3.7 mL) was added slowly by syringe through a septum. The liberated methane was vented through the gas inlet and safety bubbler attached to a nitrogen manifold. The above solution was cooled to -78 °C and neat $TiCl_4$ (33 mmol, 3.6 mL) was added dropwise to the reaction. The reaction mixture was stirred at -45 °C for 0.5 hr, and then quenched via syringe addition of 30 mL of methanol precooled to 0 °C. An aqueous 3 N HC1 solution saturated with NaCl (200 mL) was then added. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The combined extracts were washed with $H_2O$ and brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica (5–10% EtOAc/hexanes) to give **S-17** (2.35 g, 55%). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.11 (t, *J* = 7.5 Hz, 1 H), 3.60 (t, *J* = 6.5 Hz, 2 H), 2.27 (q, *J* = 6.5 Hz, 2 H), 2.04 (t, *J* = 7.5 Hz, 2 H), 1.71 (s, 3 H), 1.55 (br, 1 H), 1.37–1.27 (m, 4 H), 0.90 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 139.4, 120.2, 62.6, 31.6, 31.3, 30.3, 23.5, 22.7, 14.0. IR (neat): 3316, 2956, 2928, 2859, 1455, 1377, 1046, 840 $cm^{-1}$. HRMS $(M+H)^+$ calcd. 143.1436, obsvd. 143.1444.

**Preparation of (*E*)-4-methyloct-3-en-1-ol**



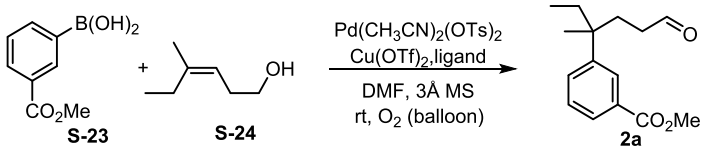




To a stirred solution of $A1Me_3$ (pyrophoric) (30 mmol, 2.16 g) and $Cl_2ZrCp_2$ (10 mmol, 2.92 g) in dry $CH_2Cl_2$ (100 mL), hex-1-yne **S-20** (10 mmol, 0.82 g) was added dropwise at 0 °C. The reaction solution was stirred at room temperature for 12 h, and then the reaction mixture was cooled to –30 ºC before ethylene oxide (11 mmol, 4.4 mL, 2.5M in THF) was added dropwise. The

reaction solution was stirred at –30 ºC for another 3 hr, and then a saturated solution of $NH_4Cl$ was added slowly to quench the reaction at 0 ºC. The mixture was extracted with $CH_2Cl_2$. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (3% EtOAc/Hexane) to give **S-22** in 40% yield (569 mg). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 5.11 (t, *J* = 7.5 Hz, 1 H), 3.61 (t, *J* = 5.5 Hz, 2 H), 2.29 (q, *J* = 6.5 Hz, 2 H), 2.00 (t, *J* = 6.5, 2 H), 1.63 (s, 3 H), 1.52 (br, 1 H), 1.40–1.34 (m, 2 H), 1.31–1.23 (m, 2 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 139.2, 119.4, 62.5, 39.5, 31.5, 30.1, 22.3, 16.1, 14.0. IR (neat): 3319, 2955, 2926, 2859, 1456, 1378, 1045, 875, 842 cm$^{-1}$. HRMS $(M+H)^+$ calcd. 143.1436, obsvd. 143.1434.

## 2.2 Condition optimization

**Table S1** Condition optimization

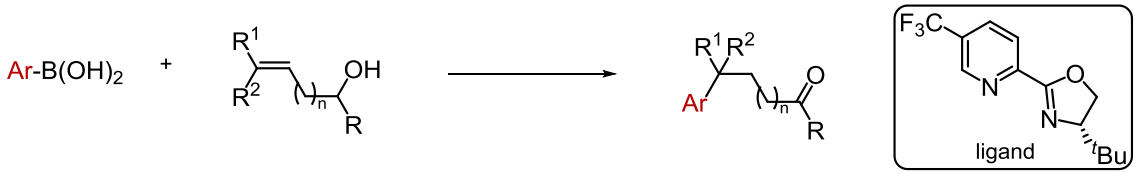



| Entry | Pd/Cu/ligand (mol%) | **S-23** (equiv.) | conv. (%)[a] | yield (%)[a] |
|---|---|---|---|---|
| 1 | 6/6/13 | 3 | 40 | 23 |
| 2[b] | 6/6/13 | 1.5*2 | 68 | 50 |
| 3[b] | 10/4/14 | 1.5*2 | 87 | 76(65)[c]<br>97:3 er[d] |
| 4[b] | 10/0/14 | 1.5*2 | 30 | 22 |
| 5[b] | 0/4/14 | 1.5*2 | 5 | 0 |

[a]Determined by GC analysis using an internal standard. [b]Boronic acid was added in two batches. [c]isolated yield. [d]er value was determined with SFC after reducing the resulting aldehyde to the primary alcohol.

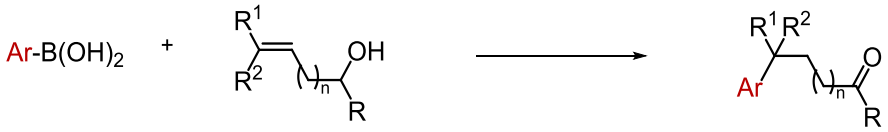
## 2.3 General procedure and characterization data

a) <u>General procedure **A**: enantioselective Heck reaction</u>



To a dry 100 mL Schlenk flask equipped with a stir bar was added $Pd(CH_3CN)_2(OTs)_2$ (26.5 mg, 0.0500 mmol, 10.0 mol%), $Cu(OTf)_2$ (7.24 mg, 0.0200 mmol, 4.00 mol%), ligand (19.1 mg, 0.0700 mmol, 14.0 mol%), 3Å MS (75.0 mg, 150 mg/mmol), and DMF (8 mL). To this flask, a three-way adapter fitted with a balloon of $O_2$ was added, and the flask was evacuated via house vacuum and refilled with $O_2$ three times while stirring. The resulting mixture was stirred for 10 min. To this, a DMF solution (2 mL) of the alkenyl alcohol (0.5 mmol) and corresponding boronic acid (0.75 mmol, 1.5 equiv) was added via syringe. After the resulting mixture was stirred for 12 h at room temperature, a second batch of the corresponding boronic acid (0.75 mmol, 1.5 equiv) as a DMF solution (1 mL) was added via syringe. The resulting mixture was stirred for another 12 h at room temperature. The mixture was diluted with diethyl ether (200 mL) and water (50 mL). The aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic layers were washed with water (3 x 20 mL), brine (1 x 20 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel flash chromatography using 2–10% EtOAc in hexanes containing 0.1% triethylamine to yield an aldehyde product.

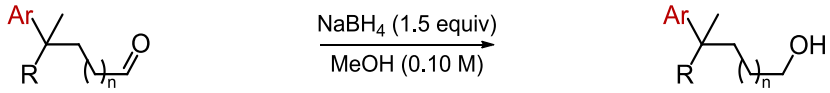
b) <u>General procedure **B**: enantioselective Heck reaction</u>




To a dry 100 mL Schlenk flask equipped with a stir bar was added $Pd(CH_3CN)_2(OTs)_2$ (15.9 mg, 0.0300 mmol, 6.00 mol%), $Cu(OTf)_2$ (5.43 mg, 0.0150

mmol, 3.0 mol%), ligand (12.3 mg, 0.0450 mmol, 9.0 mol%), 3Å MS (75.0 mg, 150 mg/mmol), and DMF (8 mL). To this flask, a three-way adapter fitted with a balloon of $O_2$ was added, and the flask was evacuated via house vacuum and refilled with $O_2$ three times while stirring. The resulting mixture was stirred for 10 min. To this, a DMF solution (2 mL) of the alkenyl alcohol (0.5 mmol) and corresponding boronic acid (1.5 mmol, 3 equiv) was added via syringe. The resulting mixture was stirred for 24 h at room temperature. The mixture was diluted with diethyl ether (200 mL) and water (50 mL). The aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic layers were washed with water (3 x 20 mL), brine (1 x 20 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel flash chromatography using 2–10% EtOAc in hexanes containing 0.1% triethylamine to yield an aldehyde product.

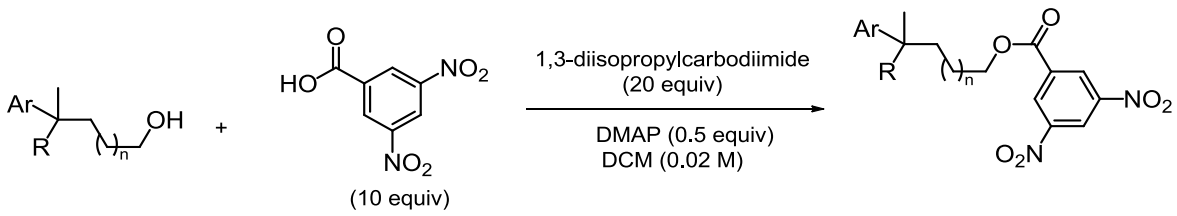
c) General procedure **C**: reduction (used in some cases for chiral separations)



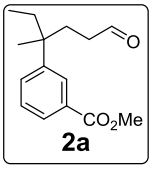

The aldehyde product was dissolved in MeOH (0.1 M) in a 20 mL scintillation vial equipped with a stir bar. The mixture was cooled to 0 $^{o}$C. Sodium borohydride (1.5 equiv) was added, and the resulting mixture was stirred for 30 min. The solvent was removed under reduced pressure, and the resulting residue was transferred to a separatory funnel using diethyl ether (100 mL) and water (20 mL). The aqueous layer was extracted with diethyl ether (2 x 50 mL), and the combined organic layers were washed with water (20 mL), and brine (20 mL). The organic layer was then dried over sodium sulfate, and concentrated under reduced pressure. The resulting mixture was purified using silica gel

flash chromatography with 10–20% EtOAc in hexanes as the eluent to give the alcohol product.

d) General procedure **D**: esterification (used in some cases for chiral separations)



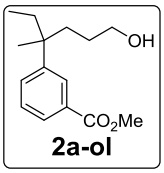

To a mixture of the alcohol (0.100 mmol), DMAP (6.11 mg, 0.0500 mmol), and *p*-nitrobenzoic acid (212 mg, 1.0 mmol) in dichloromethane (5 mL) was added *N*,*N*′-diisopropylcarbodiimide (0.313 mL, 2 mmol) at 0 °C. The resulting mixture was warmed to ambient temperature and stirred for 2 h. The resulting mixture was then filtered through a pad of silica gel with dichloromethane. The filtrate was concentrated, and the residue was stirred with NaOH (aq, 6 M, 10 mL) and dichloromethane (10 mL) at rt overnight and then partitioned between $H_2O$ and dichloromethane. The combined organic extract was then dried over sodium sulfate, and concentrated under reduced pressure. The resulting mixture was purified using silica gel flash chromatography with 5–10% EtOAc in hexanes as the eluent to give the ester product.



**2a**

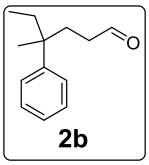
Compound **2a** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D}$ = + 20.2 $^{o}$ (c = 0.32, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.64 (t, *J* = 1.5 Hz, 1 H), 7.94 (s, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 3.91 (s, 3 H), 2.31–2.23 (m, 1 H ), 2.10–2.03 (m, 2 H), 1.90–1.78 (m, 2 H), 1.65–1.58 (m, 1 H), 1.30 (s, 3 H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.1, 167.3, 146.8, 131.0, 130.1, 128.3, 127.6, 127.1, 52.1, 40.7, 39.6,

35.5, 34.5, 22.8, 8.5. IR (neat): 2965, 1722, 1438, 1275, 1194, 1122, 981, 757, 699 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 271.1310, obsvd. 271.1306.



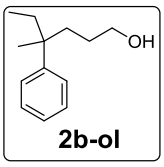
**2a-ol**

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2a-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D = -3^{\circ}$ (c = 0.22, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.64 (s, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 3.90 (s, 3 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 1.81–1.74 (m, 2 H), 1.63–1.57 (m, 2 H), 1.46–1.35 (m, 2 H), 1.31 (s, 3 H), 1.28–1.11 (m, 1 H), 0.66 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 167.5, 147.9, 131.2, 129.9, 128.1, 127.7, 126.8, 63.4, 52.0, 40.9, 38.9, 35.5, 27.7, 23.1, 8.6. IR (neat): 3351, 2942, 2877, 1720, 1438, 1269, 1056, 979, 755, 698 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 273.1467, obsvd. 273.1470.



**2b**

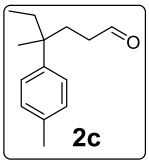
Compound **2b** was prepared according to the general procedure **B**. $[\alpha]^{20}_D = +37^{\circ}$ (c = 0.140, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.62 (t, *J* = 1.5 Hz, 1 H), 7.97 (t, *J* = 8.0 Hz, 2 H), 7.5 (d, *J* = 8.0 Hz, 2 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 2.30–2.23 (m, 1 H), 2.13–2.03 (m, 2 H), 1.85–1.75 (m, 2 H), 1.62–1.55 (m, 1 H), 1.26 (s, 3H), 0.68 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.5, 146.1, 128.2, 126.4, 125.7, 40.5, 39.7, 35.7, 34.6, 22.8, 8.6. IR (neat): 2965, 2932, 2717, 1723, 761, 699, 668 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 213.1255, obsvd. 213.1248.



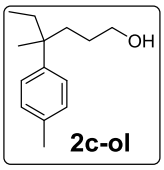
**2b-ol**

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2b-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D = +21^{\circ}$ (c = 0.040, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.32–7.27 (m, 4 H), 7.18–7.15 (m, 1 H), 3.54 (t, *J* = 6.5 Hz, 2 H), 1.80–1.72 (m, 2 H), 1.62–1.54 (m, 2 H), 1.47–1.39 (m, 1 H), 1.32–1.18 (m, 2 H), 1.28 (s, 3H), 0.68

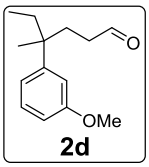
(t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 147.4, 128.0, 126.4, 125.3, 63.6, 40.8, 38.9, 35.6, 27.8, 23.2, 8.6. IR (neat): 3329, 2963, 2926, 2876, 1379, 1057, 761, 699, 668 cm$^{-1}$. HRMS $(M+H)^+$ calcd. 193.1592, obsvd. 193.1602.




Compound **2c** was prepared according to the general procedure **B**. $[\alpha]^{20}_D$ = + 25 $^o$ (c = 0.185, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, $J$ = 1.5 Hz, 1 H), 7.16–7.11 (m, 4 H), 2.32 (s, 3H), 2.30–2.23 (m, 1 H), 2.15–2.01 (m, 2 H), 1.83–1.73 (m, 2 H), 1.61–1.54 (m, 1 H), 1.25 (s, 3H), 0.69 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.6, 143.1, 135.1, 128.9, 126.3, 40.2, 39.8, 35.6, 34.6, 22.9, 20.8, 8.6. IR (neat): 2965, 2921, 2717, 1722, 1513, 1456, 1379, 814, 668, 568 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 227.1412, obsvd. 227.1418.

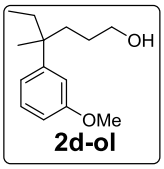



In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2c-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D$ = + 6 $^o$ (c = 0.336, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.18 (d, $J$ = 8.0 Hz, 2 H), 7.10 (d, $J$ = 8.0 Hz, 2 H), 3.53 (t, $J$ = 6.5 Hz, 2 H), 2.32 (s, 3H), 1.78–1.70 (m, 2 H), 1.60–1.53 (m, 2 H), 1.47–1.38 (m, 1 H), 1.30–1.19 (m, 2 H), 1.26 (s, 3H), 0.67 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 144.3, 134.7, 128.7, 126.3, 63.6, 40.4, 38.9, 35.5, 27.8, 23.3, 20.8, 8.6. IR (neat): 3329, 2963, 2938, 2875, 1513, 1456, 1378, 1055, 1019, 814, 723 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 229.1568, obsvd. 229.1567.



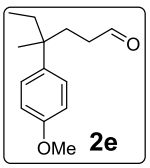

Compound **2d** was prepared according to the general procedure **B**. $[\alpha]^{20}_D$ = + 39.5 $^o$ (c = 0.323, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.38 (t, $J$ = 1.5 Hz, 1 H), 7.23 (t, $J$ = 8.0 Hz, 1 H), 6.86 (dd, $J_1$ = 8.0 Hz, $J_2$ = 2.0 Hz, 1 H), 6.81 (t, $J$ = 2.0 Hz, 1 H), 6.73 (dd, $J_1$ = 8.0 Hz, $J_2$ = 2.0 Hz, 1 H), 3.80 (s, 3H), 2.31–

2.24 (m, 1 H), 2.16–2.01 (m, 2 H), 1.84–1.74 (m, 2 H), 1.62–1.54 (m, 1 H), 1.25 (s, 3H), 0.70 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.5, 159.5, 148.1, 129.1, 118.9, 113.3, 110.1, 55.1, 40.6, 39.7, 35.7, 34.6, 22.8, 8.6. IR (neat): 2964, 2935, 1721, 1599, 1581, 1487, 1463, 1431, 1290, 1251, 1220, 1172, 1046, 874, 776, 701 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 243.1361, obsvd. 243.1363.



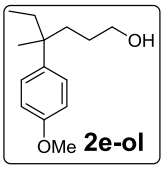
**2d-ol**

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2d-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D$ = + 6 $^o$ (c = 0.291, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.22 (t, $J$ = 8.0 Hz, 2 H), 6.89 (dd, $J_1$ = 8.0, $J_2$ = 2.0 Hz, 1 H), 6.83 (t, $J$ = 2.0 Hz, 1 H), 6.70 (dd, $J_1$ = 8.0, $J_2$ = 2.0 Hz, 1 H), 3.80 (s, 3 H), 3.52 (t, $J$ = 6.5, 2 H), 1.78–1.70 (m, 2 H), 1.60–1.52 (m, 2 H), 1.47–1.36 (m, 2 H), 1.29–1.18 (m, 1 H), 1.26 (s, 3 H), 0.68 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 159.4, 149.3, 128.8, 119.0, 113.3, 109.7, 63.5, 55.1, 40.8, 38.9, 35.6, 27.8, 23.1, 8.6. IR (neat): 3338, 2962, 2938, 2876, 1600, 1581, 1487, 1462, 1430, 1290, 1251, 1047, 774, 701 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 245.1517, obsvd. 245.1517.



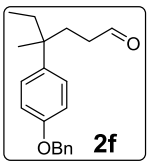
**2e**

Compound **2e** was prepared according to the general procedure **B**. $[\alpha]^{20}_D$ = + 35 $^o$ (c = 0.275, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, $J$ = 1.5 Hz, 1 H), 7.17 (d, $J$ = 8.0 Hz, 2 H), 6.85 (d, $J$ = 8.0 Hz, 2 H), 7.17 (t, $J$ = 8.0 Hz, 1 H), 3.79 (s, 3H), 2.30–2.23 (m, 1 H), 2.14–2.00 (m, 2 H), 1.83–1.72 (m, 2 H), 1.60–1.53 (m, 1 H), 1.24 (s, 3H), 0.69 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.7, 157.5, 138.1, 127.4, 113.5, 55.1, 39.9, 39.7, 35.7, 34.7, 23.0, 8.6. IR (neat): 2963, 1733, 1435, 1345, 1227, 1196, 1145, 1054, 892, 844, 800 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 243.1361, obsvd. 243.1357.



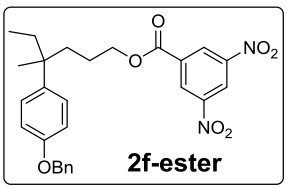
**2e-ol**

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2e-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_{D}$ = + 9.6 $^{o}$ (c = 0.341, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 3.79 (s, 3 H), 3.52 (t, *J* = 6.5 Hz, 2 H), 1.74–1.68 (m, 2 H), 1.59–1.51 (m, 2 H), 1.46–1.37 (m, 1 H), 1.28–1.18 (m, 1 H), 1.25 (s, 3 H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 157.2, 139.4, 127.4, 113.2, 63.6, 55.1, 40.1, 39.0, 35.7, 27.8, 23.3, 8.6. IR (neat): 3329, 2935, 2875, 1610, 1511, 1463, 1247, 1183, 1035, 826 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 245.1517, obsvd. 245.1529.



**2f**

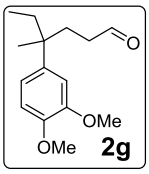
Compound **2f** was prepared according to the general procedure **B**. $[\alpha]^{20}_{D}$ = + 25.2 $^{o}$ (c = 0.66, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.64 (t, *J* = 1.5 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.39 (t, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.94 (d, *J* = 8.0 Hz, 2 H), 5.04 (s, 2 H), 2.31–2.24 (m, 1 H), 2.16–2.00 (m, 2 H), 1.84–1.72 (m, 2 H), 1.61–1.54 (m, 1 H), 1.25 (s, 3 H), 0.70 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.9, 157.1, 138.7, 137.4, 128.8, 128.2, 127.8, 127.7, 114.7, 70.2, 40.2, 40.0, 36.0, 35.0, 23.3, 8.9. IR (neat): 3035, 2964, 2931, 1721, 1608, 1511, 1454, 1244, 1183, 1024, 828, 736, 697 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 319.1678, obsvd. 319.1674.



**2f-ester**

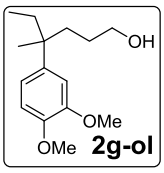
In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_{D}$ = + 17.9 $^{o}$ (c = 0.674, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.21 (t, *J* = 1.5 Hz, 1 H), 9.12 (t, *J* = 1.5 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 8.0 Hz, 2 H), 7.30 (t, *J* = 8.0 Hz, 1 H),

7.22 (d, $J$ = 8.0 Hz, 2 H), 6.94 (d, $J$ = 8.0 Hz, 2 H), 5.04 (s, 2 H), 4.35–4.30 (m, 2 H), 1.85–1.47 (m, 6 H), 1.30 (s, 3 H), 0.71 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 156.7, 148.6, 139.0, 137.1, 134.0, 129.3, 128.5, 127.9, 127.5, 127.3, 122.3, 114.3, 69.9, 67.5, 40.2, 39.1, 35.7, 23.7, 23.2, 8.6. IR (neat): 3101, 2964, 1729, 1544, 1455, 1343, 1279, 1246, 1166, 1075, 730, 699 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 515.1794, obsvd. 515.1805.



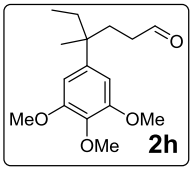
**2g**

Compound **2g** was prepared according to the general procedure **B**. $[\alpha]^{20}_D$ = + 22 $^o$ (c = 0.260, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, $J$ = 1.5 Hz, 1 H), 7.79–6.76 (m, 3 H), 6.85 (d, $J$ = 8.0 Hz, 2 H), 3.86 (s, 3H), 3.85 (s, 3H), 2.31–2.24 (m, 1 H), 2.14–1.99 (m, 2 H), 1.82–1.70 (m, 2 H), 1.60–1.53 (m, 1 H), 1.23 (s, 3H), 0.69 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.5, 148.7, 147.0, 138.8, 118.8, 110.7, 109.9, 55.9, 55.7, 40.3, 39.8, 35.8, 34.7, 22.9, 8.6. IR (neat): 2964, 2934, 1719, 1517, 1463, 1251, 1146, 1026, 912, 807, 728, 647 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 273.1467, obsvd. 273.1467.

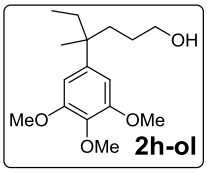


**2g-ol**

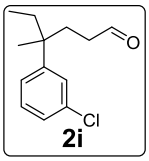
In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2g-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D$ = + 7 $^o$ (c = 0.198, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 6.81–6.79 (m, 3 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.52 (t, $J$ = 6.5 Hz, 2 H), 1.74–1.67 (m, 2 H), 1.59–1.51 (m, 2 H), 1.46–1.35 (m, 2 H), 1.28–1.18 (m, 1 H), 1.24 (s, 3H), 0.68 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 148.4, 146.7, 140.1, 118.7, 110.5, 110.0, 63.5, 55.8, 55.7, 40.5, 39.0, 35.7, 27.7, 23.3, 8.6. IR (neat): 3370, 2936, 2875, 1589, 1512, 1463, 1251, 1146, 1026, 805, 767, 651 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 275.1623, obsvd. 275.1625.



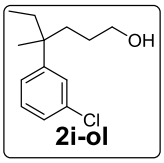

Compound **2h** was prepared according to the general procedure **B**. $[\alpha]^{20}_{D}$ = + 19.4 $^{o}$ (c = 0.520, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.61 (t, *J* = 1.5 Hz, 1 H), 6.41 (s, 2 H), 3.80 (s, 6 H), 3.78 (s, 3 H), 2.29–2.22 (m, 1 H), 2.12–2.06 (m, 1 H), 2.00–1.94 (m, 1 H), 1.78–1.66 (m, 2 H), 1.56–1.49 (m, 1 H), 1.19 (s, 3H), 0.66 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.1, 152.7 142.0, 136.0, 103.9, 60.6, 56.0, 40.7, 39.6, 35.6, 34.5, 22.8, 8.5. IR (neat): 2963, 2933, 1720, 1585, 1512, 1452, 1411, 1339, 1244, 1122, 1008, 830, 771 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 303.1572, obsvd. 303.1571.



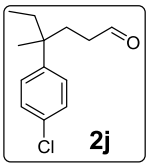

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2h-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_{D}$ = + 7 $^{o}$ (c = 0.220, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 6.45 (s, 2 H), 3.82 (s, 6 H), 3.80 (s, 3 H), 3.52 (t, *J* = 6.5 Hz, 3 H), 1.70–1.64 (m, 2 H), 1.56–1.49 (m, 3 H), 1.42–1.38 (m, 1 H), 1.22 (s, 3 H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 152.6, 143.3, 135.8, 104.0, 63.4, 60.8, 56.1, 41.0, 38.9, 35.7, 27.7, 23.3, 8.6. IR (neat): 3426, 2936, 2875, 1586, 1514, 1452, 1411, 1339, 1244, 1123, 1009, 831 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 305.1729, obsvd. 305.1730.



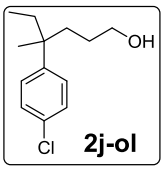

Compound **2i** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D}$ = + 29 $^{o}$ (c = 0.174, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.66 (t, *J* = 1.5 Hz, 1 H), 7.24–7.14 (m, 4 H), 2.31–2.25 (m, 1 H), 2.13–2.00 (m, 2 H), 1.86–1.74 (m, 2 H), 1.62–1.55 (m, 1 H), 1.25 (s, 3H), 0.69 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.2, 148.6, 134.3, 129.5, 126.8, 126.0, 124.6, 39.6, 35.6, 34.5, 22.7, 8.6. IR (neat): 2966, 2926, 2719, 1721, 1594, 1566, 1465, 1412, 1382, 1083, 883, 698 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 247.0866, obsvd. 247.0878.




In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2i-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_{D} = -24^{\circ}$ (c = 0.128, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.26–7.21 (m, 2 H), 7.17–7.14 (m, 2 H), 3.54 (t, *J* = 6.5 Hz, 2 H), 1.77–1.69 (m, 2 H), 1.61–1.54 (m, 2 H), 1.47–1.38 (m, 1 H), 1.26 (s, 3 H), 1.23–1.15 (m. 1 H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 149.8, 134.1, 129.2, 126.8, 125.6, 124.7, 63.4, 41.0, 38.9, 35.6, 27.7, 23.1, 8.6. IR (neat): 3327, 2964, 2938, 2877, 1594, 1567, 1473, 1416, 1380, 1056, 781, 698 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 249.1022, obsvd. 249.1041.

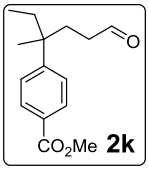



Compound **2j** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D} = +25.6^{\circ}$ (c = 0.315, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.65 (t, *J* = 1.5 Hz, 1 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 2.31–2.23 (m, 1 H), 2.12–1.99 (m, 2 H), 1.85–1.69 (m, 2 H), 1.61–1.54 (m, 1 H), 1.25 (s, 3H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.1, 144.8, 131.6, 128.3, 127.9, 40.4, 39.6, 35.6, 34.5, 22.8, 8.6. IR (neat): 2966, 2927, 2719, 1721, 1491, 1457, 1382, 1109, 1092, 1010, 823 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 247.0866, obsvd. 247.0866.

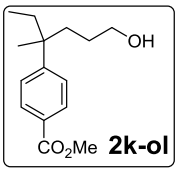



In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2j-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_{D} = +8^{\circ}$ (c = 0.215, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 1.76–1.69 (m, 2 H), 1.61–1.53 (m, 2 H), 1.45–1.34 (m, 1 H), 1.30 (br, 1 H), 1.25 (s, 3H), 1.23–1.15 (m. 1H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 146.0, 131.1, 128.1, 127.9, 63.4, 40.6, 38.9, 35.6, 27.7, 23.1, 8.5. IR

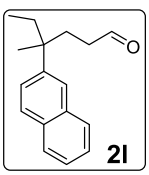
(neat): 3329, 2965, 2939, 2877, 1491, 1264, 1108, 1055, 1011, 823, 736, 668 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 249.1022, obsvd. 249.1030.




Compound **2k** was prepared according to the general procedure **A**. $[\alpha]^{20}_D$ = + 21 $^o$ (c = 0.101, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.65 (t, *J* = 1.5 Hz, 1 H), 7.97 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 3.90 (s, 3H), 2.32–2.23 (m, 1 H), 2.16–2.04 (m, 2 H), 1.88–1.77 (m, 2 H), 1.64–1.58 (m, 1 H), 1.29 (s, 3H), 0.67 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.1, 167.0, 151.9, 129.6, 127.8, 126.5, 52.0, 41.0, 39.6, 35.6, 34.4, 22.7, 8.5. IR (neat): 2965, 2721, 1717, 1609, 1435, 1276, 1190, 1113, 1017, 855, 772, 709 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 271.1310, obsvd. 271.1309.

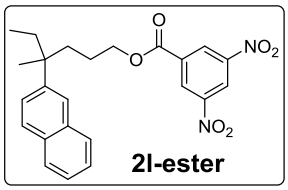



In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2k-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D$ = + 10 $^o$ (c = 0.120, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 3.90 (s, 3 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 1.82–1.75 (m, 2 H), 1.64–1.56 (m, 2 H), 1.46–1.38 (m, 1 H), 1.30 (s, 3H), 1.22–1.13 (m, 1 H), 0.66 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 167.2, 153.2, 129.4, 127.4, 126.5, 63.4, 51.9, 41.3, 38.9, 35.6, 27.7, 23.0, 8.6. IR (neat): 2941, 2877, 1720, 1609, 1435, 1276, 1189, 1116, 1055, 1017, 772, 708 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 273.1467, obsvd. 273.1476.



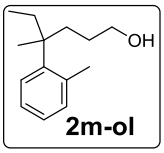

Compound **2l** was prepared according to the general procedure **A**. $[\alpha]^{20}_D$ = + 41.1 $^o$ (c = 0.600, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, *J* = 1.5 Hz, 1 H), 7.82–7.80 (m, 3 H), 7.67 (s, 1H), 7.49–7.44 (m, 3 H), 2.34–2.27 (m, 1 H), 2.20–2.06 (m, 2 H), 1.95–1.88 (m, 2 H), 1.72–1.65 (m, 1 H), 1.39 (s, 3 H),

0.71 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.3, 143.6, 133.2, 131.7, 127.9, 127.8, 127.3, 125.8, 125.4, 125.2, 124.6, 40.7, 39.7, 35.4, 34.3, 22.7, 8.6. IR (neat): 2965, 2929, 1722, 1462, 1382, 856, 819, 748 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 263.1412, obsvd. 263.1417.



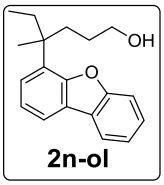
**2l-ester**

In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_D$ = + 35.6 $^o$ (c = 0.880, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.17 (t, $J$ = 1.5 Hz, 1 H), 9.05 (t, $J$ = 1.5 Hz, 2 H), 7.81–7.77 (m, 3 H), 7.68 (s, 1H), 7.49–7.40 (m, 3 H), 4.36–4.31 (m, 2 H), 2.00–1.91 (m, 2 H), 1.78–1.71 (m, 3 H), 1.52–1.47 (m, 1 H), 1.45 (s, 3H), 0.73 (t, $J$ = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 148.6, 144.2, 134.0, 133.3, 131.7, 129.3, 127.9, 127.8, 127.3, 125.9, 125.4, 125.2, 124.7, 122.2, 67.4, 41.1, 39.0, 35.5, 23.8, 22.9, 8.6. IR (neat): 3103, 2965, 1730, 1544, 1462, 1343, 1278, 1166, 1075, 820, 750, 720 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 459.1532, obsvd. 459.1537.

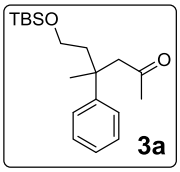


**2m-ol**

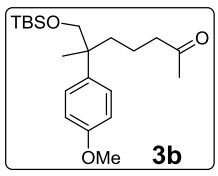
In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2m-ol** was prepared according to general procedure A, followed by general procedure **C**. $[\alpha]^{20}_D$ = – 3 $^o$ (c = 0.25, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.23 (d, $J$ = 8.0 Hz, 1 H), 7.14–7.08 (m, 3 H), 3.54 (t, $J$ = 6.5 Hz, 2 H), 2.48 (s, 3 H), 2.10–2.02 (m, 2 H), 1.59–1.51 (m, 2 H), 1.48–1.40 (m, 2 H), 1.39 (s, 3H), 1.19–1.10 (m, 1 H), 0.67 (t, $J$ = 6.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 143.9, 136.3, 132.6, 128.6, 125.8, 125.5, 63.6, 42.8, 37.0, 33.6, 28.2, 26.1, 23.4, 8.9. IR (neat): 3320, 2963, 2875, 1455, 1379, 1052, 907, 755, 727 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 229.1568, obsvd. 229.1564.




In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2n-ol** was prepared according to general procedure A, followed by general procedure **C**. $[\alpha]^{20}_{D} = -18^{o}$ (c = 0.22, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.0 Hz, 1 H), 7.83 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 3.51 (t, *J* = 6.5 Hz, 2 H), 2.39–2.29 (m, 2 H), 1.81–1.74 (m, 2 H), 1.53–1.44 (m, 1 H), 1.45 (s, 3H), 1.19–1.10 (m, 2 H), 0.68 (t, *J* = 6.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 155.5, 154.3, 131.8, 126.8, 126.3, 124.3, 124.2, 122.5, 122.4, 120.4, 118.5, 111.6, 63.6, 41.3, 36.6, 33.4, 28.2, 23.2, 8.9. IR (neat): 3323, 2963, 2875, 1451, 1409, 1184, 1056, 750 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 305.1517, obsvd. 305.1525.

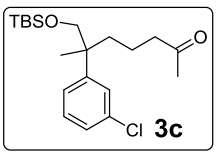



Compound **3a** was prepared according to the general procedure **B**. $[\alpha]^{20}_{D} = +19.3^{o}$ (c = 0.485, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.34–7.29 (m, 4 H), 7.21–7.17 (m, 1 H), 3.55–3.50 (m, 1 H), 3.38–3.33 (m, 1 H), 2.92 (d, 15 Hz, 1H), 2.67 (d, 15 Hz, 1H), 2.11–2.04 (m, 1 H), 1.97–1.91 (m, 1 H), 1.79 (s, 3H), 1.47 (s, 3H), 0.84 (s, 9 H), –0.04 (s, 6 H) $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 207.7, 146.1, 128.3, 126.0, 125.9, 59.9, 56.1, 45.3, 39.4, 31.9, 25.9, 24.3, 18.2, –5.4. IR (neat): 2953, 2928, 2856, 1705, 1471, 1359, 1252, 1085, 833, 698 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 343.2069, obsvd. 343.2072.



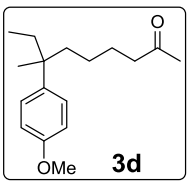

Compound **3b** was prepared according to the general procedure **B**. $[\alpha]^{20}_{D} = -2^{o}$ (c = 0.225, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.0 Hz, 2 H), δ = 6.83 (d, *J* = 8.0 Hz, 2 H), 3.78 (s, 3H), 3.54 (d, *J* = 9.0 Hz, 1H), 3.48 (d, *J* = 9.0 Hz, 1H), 2.34 (t, *J* = 7.5 Hz, 2 H), 2.06 (s, 3 H), 1.71 (dt, *J* = 4.5 Hz, *J* = 13 Hz, 1 H), 1.58 (dt, *J* = 4.5 Hz, *J* = 13 Hz, 1 H), 1.47–1.38 (m,

1 H), 1.34–1.24 (m, 1 H), 1.28 (s, 3H), 0.85 (s, 9H), –0.05 (s, 3H), –0.07 (s, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 209.1, 157.5, 137.7, 127.6, 113.2, 72.1, 55.1, 44.4, 42.4, 37.5, 29.7, 25.8, 22.0, 18.6, 18.2, –5.6, –5.7. IR (neat): 2953, 2929, 2855, 1717, 1513, 1471, 1248, 1184, 1100, 1080, 1035, 830, 774, 668 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 387.2331, obsvd. 387.2338.



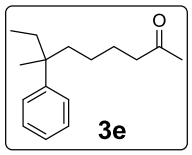
**3c**

Compound **3c** was prepared according to the general procedure **A**. $[\alpha]^{20}_D$ = + 0.6 $^o$ (c = 0.462, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.31 (t, *J* = 1.5 Hz, 2 H), 7.24–7.15 (m, 3 H), 3.52 (s, 2 H), 2.32 (t, *J* = 7.5 Hz, 2 H), 2.08 (s, 3 H), 1.73 (dt, *J* = 4.5 Hz, *J* = 13 Hz, 1 H), 1.55 (dt, *J* = 4.5 Hz, *J* = 13 Hz, 1 H), 1.48–1.39 (m, 1 H), 1.34–1.24 (m, 1 H), 1.28 (s, 3H), 0.83 (s, 9 H), –0.06 (s, 3 H), –0.09 (s, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 208.9, 148.1, 133.9, 129.1, 127.2, 125.9, 124.9, 71.8, 44.2, 43.3, 37.4, 29.8, 25.8, 21.08, 18.4, 18.2, –5.6, –5.7. IR (neat): 2953, 2928, 2855, 1716, 1595, 1568, 1471, 1360, 1252, 1098, 834, 773, 697, 668 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 391.1836, obsvd. 391.1843.

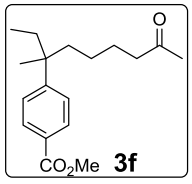


**3d**

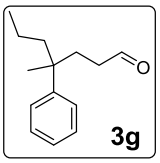
Compound **3d** was prepared according to the general procedure **B**. $[\alpha]^{20}_D$ = + 4 $^o$ (c = 0.226, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 8.0 Hz, 2 H), δ = 6.83 (d, *J* = 8.0 Hz, 2 H), 3.79 (s, 3H), 2.33 (t, *J* = 7.5 Hz, 2 H), 2.08 (s, 3 H), 1.72–1.41 (m, 6 H), 1.21 (s, 3 H), 1.17–1.08 (m, 1 H), 0.98–0.86 (m, 1 H), 0.65 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 209.2, 157.1, 139.7, 127.3, 113.2, 55.1, 43.7, 42.8, 40.3, 35.7, 29.8, 24.5, 23.9, 23.5, 8.6. IR (neat): 2962, 2934, 1714, 1610, 1511, 1463, 1248, 1183, 1035, 827 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 285.1831, obsvd. 285.1833.



Compound **3e** was prepared according to the general procedure **B**. The product **3e** was isolated as a single regioisomer. $[\alpha]^{20}_{D}$ = + 4 $^{o}$ (c = 0.237, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.31–7.25 (m, 4H), 7.18–7.14 (m, 1H), 2.33 (t, *J* = 7.5 Hz, 2 H), 2.07 (s, 3 H), 1.76–1.66 (m, 2 H), 1.58–1.42 (m, 4 H), 1.24 (s, 3H), 1.19–1.09 (m, 1 H), 0.97–0.86 (m, 1 H), 0.66 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 209.2, 147.6, 127.9, 126.4, 125.2, 43.7, 42.8, 40.9, 35.6, 29.8, 24.5, 23.9, 23.3, 8.6. IR (neat): 2963, 2933, 2877, 1714, 1496, 1445, 1361, 1163, 759, 699 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 255.1725, obsvd. 255.1721.

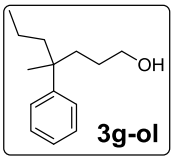


Compound **3f** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D}$ = + 4 $^{o}$ (c = 0.22, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 3.90 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 2 H), 2.07 (s, 3 H), 1.78–1.67 (m, 2 H), 1.60–1.40 (m, 4 H), 1.27 (s, 3H), 1.17–1.08 (m, 1 H), 0.98–0.83 (m, 1 H), 0.64 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 209.0, 167.2, 153.4, 129.3, 127.3, 126.5, 51.9, 43.6, 42.8, 41.5, 35.6, 29.8, 24.4, 23.8, 23.0, 8.5. IR (neat): 2935, 1716, 1435, 1277, 1190, 1116, 1018, 773, 709 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 313.1780, obsvd. 313.1778.

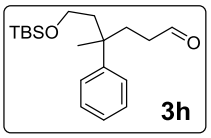


Compound **3g** was prepared according to the general procedure **B**. $[\alpha]^{20}_{D}$ = –21 $^{o}$ (c = 0.113, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, *J* = 1.5 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 3.90 (s, 3H), 2.30–2.23 (m, 1 H), 2.14–2.04 (m, 2 H), 1.86–1.81 (m, 1 H), 1.73–1.68 (m, 1 H), 1.55–1.50 (m, 1 H), 1.29 (s, 3H), 1.26–1.15 (m, 1 H), 1.00–0.87 (m, 1 H), 0.83 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.5, 146.6, 128.2, 126.3, 125.7, 45.8, 40.4, 39.7, 34.9, 23.5, 17.4, 14.7. IR (neat): 2956, 2931, 1704, 1446,

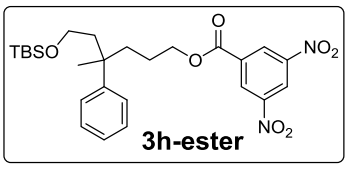
1414, 1303, 1221, 941, 765, 699 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 227.1412, obsvd. 277.1412.




In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **3g-ol** was prepared according to general procedure **C**. $[\alpha]^{20}_D = -15$ ° (c = 0.260, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.32–7.28 (m, 4 H), 7.18–7.15 (m, 1 H), 3.53 (t, *J* = 6.5 Hz, 2 H), 1.77–1.65 (m, 2 H), 1.61–1.49 (m, 2 H), 1.47–1.38 (m, 1 H), 1.30 (s, 3 H), 1.29 (br, 1 H), 1.27–1.13 (m, 2 H), 1.03–0.93 (m, 1 H), 0.82 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 147.8, 128.0, 126.3, 125.3, 63.6, 45.9, 40.6, 39.2, 27.7, 23.8, 17.4, 14.8. IR (neat): 3321, 2954, 2870, 1445, 1379, 1056, 766, 698 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 229.1568, obsvd. 229.1550.

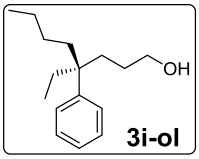



Compound **3h** was prepared according to the general procedure **B**. $[\alpha]^{20}_D = -15$ ° (c = 0.276, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, *J* = 1.5 Hz, 1 H), 7.33–7.26 (m, 4 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 3.55–3.50 (m, 1 H), 3.39–3.34 (m, 1 H), 2.31–2.24 (m, 1 H), 2.14–2.00 (m, 3 H), 1.91–1.83 (m, 2 H), 1.33 (s, 3H), 0.84 (s, 9 H), –0.03 (s, 3 H), –0.04 (s, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.3, 145.9, 128.3, 126.1, 126.0, 59.8, 45.6, 39.4, 39.3, 35.2, 25.9, 23.8, 18.2, –5.3, –5.4. IR (neat): 2928, 2855, 1725, 1471, 1253, 1087, 833, 773, 738, 699 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 343.2069, obsvd. 343.2070.

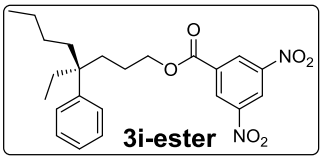



In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_D$ =

–10.4 $^{o}$ (c = 0.408, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 1.5Hz, 1 H), 9.11 (d, *J* = 1.5 Hz, 2 H), 7.34–7.25 (m, 4 H), 7.22–7.17 (m, 1 H), 4.35–4.27 (m, 2 H), 3.56–3.51 (m, 1 H), 3.39–3.34 (m, 1 H), 2.06–2.01 (m, 1 H), 1.90–1.84 (m, 2 H), 1.73–1.67 (m, 2 H), 1.51–1.43 (m, 1 H), 1.38 (s, 3 H), 0.83 (s, 9 H), –0.04 (s, 6 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 148.6, 146.4, 134.0, 129.4, 128.3, 126.1, 125.9, 122.3, 67.3, 59.9, 45.8, 39.8, 39.6, 25.9, 23.9, 23.5, 18.2, –5.3, –5.4. IR (neat): 2928, 2855, 1730, 1544, 1462, 1343, 1276, 1164, 1076, 834, 773, 720, 700 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 539.2190, obsvd. 539.2205.

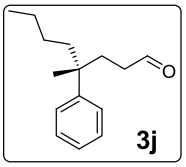



Compound **3i-ol** was prepared according to the general procedure **A**, followed by general procedure **C**.. $[\alpha]^{20}_{D}$ = –2 $^{o}$ (c = 0.237, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.32–7.28 (m, 4 H), 7.18–7.15 (m, 1 H), 3.55 (t, *J* = 6.5 Hz, 2H), 1.72–1.63 (m, 6 H), 1.33–1.25 (m, 5 H), 1.07–0.99 (m, 2 H), 0.86 (t, *J* = 7.5 Hz, 3 H), 0.68 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 147.4, 127.9, 126.6, 125.2, 63.6, 42.9, 36.4, 33.2, 29.5, 27.1, 25.6, 23.4, 14.1, 8.0. IR (neat): 3312, 2930, 2871, 1464, 1378, 1056, 758, 697 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 257.1881, obsvd. 257.1888.

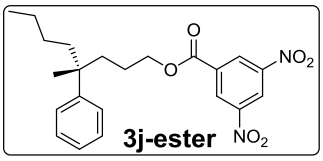



In order to determine the enantiomeric ratio of the product, the corresponding primary ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_{D}$ = –1.6 $^{o}$ (c = 0.318, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 2.0 Hz, 1 H), 9.12 (d, *J* = 2.0 Hz, 2 H), 7.33–7.30 (m, 4 H), 7.20–7.16 (m, 1 H), 4.34 (t, *J* = 6.5 Hz, 2 H), 1.79–1.65 (m, 6 H), 1.58–1.52 (m, 2 H), 1.32–1.22 (m, 2 H), 1.10–0.99 (m, 2 H), 0.86 (t, *J* = 7.5 Hz, 3 H), 0.72 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 148.6,

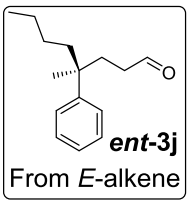
146.8, 134.1, 129.3, 128.1, 126.5, 125.5, 122.3, 67.5, 43.0, 36.1, 33.8, 29.1, 25.6, 23.4, 23.1, 14.0, 8.0. IR (neat): 2958, 2931, 1730, 1544, 1463, 1343, 1276, 1164, 1075, 920, 762, 729, 699 $cm^{-1}$. HRMS $(M^{\bullet})^{+}$ calcd. 428.1947, obsvd. 428.1953.



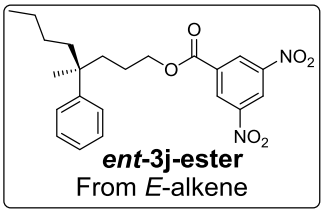

Compound **3j** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D}$ = + 15 $^{o}$ (c = 0.260, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, *J* = 1.5 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 2.30–2.23 (m, 1 H), 2.14–2.03 (m, 2 H), 1.87–1.81 (m, 1 H), 1.76–1.69 (m, 1 H), 1.58–1.52 (m, 1 H), 1.29 (s, 3H), 1.28–1.11 (m, 3 H), 0.97–0.87 (m, 1 H), 0.83 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.6, 146.6, 128.2, 126.3, 125.7, 43.1, 40.2, 39.7, 34.9, 26.4, 23.5, 23.3, 14.0. IR (neat): 2956, 2929, 2860 1723, 1445, 766, 700 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 241.1568, obsvd. 241.1567.




In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_{D}$ = + 11.6 $^{o}$ (c = 0.405, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 1.5 Hz, 1 H), 9.11 (d, *J* = 1.5 Hz, 2 H), 7.34–7.30 (m, 4 H), 7.20–7.17 (m, 1 H), 4.36–4.28 (m, 2 H), 1.89–1.83 (m, 1 H), 1.77–1.43 (m, 5 H), 1.34 (s, 3H), 1.27–1.11 (m, 3 H), 0.99–0.90 (m, 1 H), 0.83 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 148.6, 147.1, 134.1, 129.4, 128.2, 126.2, 125.6, 122.3, 67.4, 43.1, 40.5, 39.4, 26.3, 23.7, 23.6, 23.3, 14.0. IR (neat): 3101, 2957, 2930, 2860, 1729, 1543, 1342, 1276, 1164, 1074, 920, 720, 699 $cm^{-1}$. HRMS $(M^{\bullet})^{+}$ calcd. 414.1791, obsvd. 414.1801.

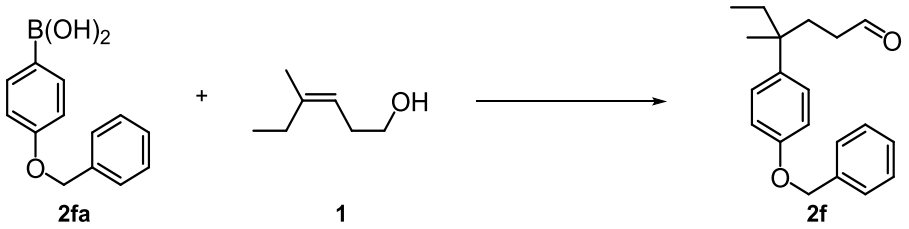



Compound ***ent*-3j** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D} = -13$ ° (c = 0.110, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.63 (t, *J* = 1.5 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 2.30–2.23 (m, 1 H), 2.14–2.03 (m, 2 H), 1.87–1.81 (m, 1 H), 1.76–1.69 (m, 1 H), 1.58–1.52 (m, 1 H), 1.29 (s, 3H), 1.28–1.11 (m, 3 H), 0.97–0.87 (m, 1 H), 0.83 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.7, 146.7, 128.3, 126.4, 125.8, 43.1, 40.2, 39.8, 34.9, 26.4, 23.6, 23.3, 14.1. IR (neat): 2956, 2928, 2859 1723, 1445, 766, 699 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 241.1568, obsvd. 241.1569.




In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_{D}$ = –14.7 ° (c = 0.308, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 1.5 Hz, 1 H), 9.11 (d, *J* = 1.5 Hz, 2 H), 7.34–7.29 (m, 4 H), 7.20–7.17 (m, 1 H), 4.35–4.30 (m, 2 H), 1.89–1.83 (m, 1 H), 1.77–1.43 (m, 5 H), 1.34 (s, 3H), 1.27–1.10 (m, 3 H), 0.97–0.90 (m, 1 H), 0.83 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 148.6, 147.1, 134.1, 129.4, 128.2, 126.2, 125.6, 122.3, 67.4, 43.1, 40.5, 39.4, 26.3, 23.7, 23.6, 23.3, 14.0. IR (neat): 3101, 2957, 2930, 2860, 1729, 1543, 1342, 1276, 1164, 1074, 920, 720, 699 $cm^{-1}$. HRMS $(M^{\bullet})^+$ calcd. 414.1791, obsvd. 414.1803.

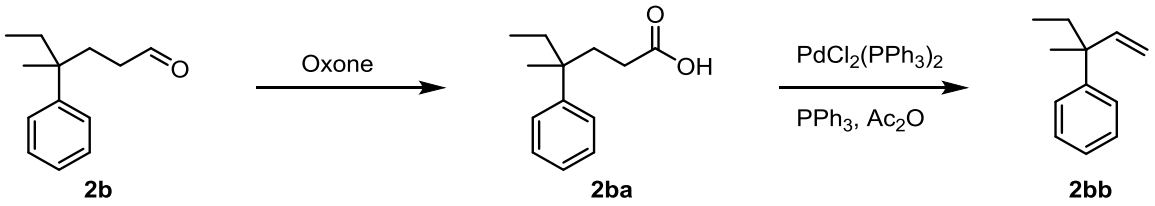
e) <u>Gram-scale synthesis of **2f**</u>

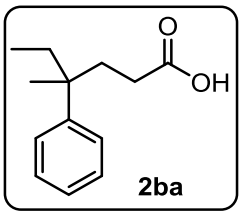


To a dry 250 mL Schlenk flask equipped with a stir bar was added $Pd(CH_3CN)_2(OTs)_2$ (318 mg, 0.60 mmol, 6.0 mol%), $Cu(OTf)_2$ (109 mg, 0.300 mmol, 3.00 mol%), ligand (245 mg, 0.90 mmol, 9.0 mol%), 3Å MS (1.50 g, 150 mg/mmol), and DMF (100 mL). To this flask, a three-way adapter fitted with a balloon of $O_2$ was added, and the flask was evacuated via house vacuum and refilled with $O_2$ three times while stirring. The resulting mixture was stirred for 10 min. To this, a DMF solution (50 mL) of the alkenyl alcohol **1** (1.14 g, 10.0 mmol) and boronic acid **2fa** (6.84 g, 30.0 mmol, 3 equiv) were added via syringe. The resulting mixture was stirred for 24 h at room temperature. The mixture was diluted with diethyl ether (500 mL) and water (100 mL). The aqueous layer was extracted with diethyl ether (2 x 100 mL). The combined organic layers were washed with water (3 x 50 mL), brine (1 x 50 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel flash chromatography using 2–10% EtOAc in hexanes containing 0.1% triethylamine to yield the aldehyde product **2f** (2.28 g, 77% yield).

### 2.4 Determination of absolute configuration

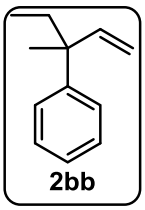
#### 2.4.1 Determination of absolute configuration of product 2b




Aldehyde **2b** (95.2 mg, 0.50 mmol) was dissolved in 5 mL of DMF. Oxone (76.0 mg, 1 equiv) was added and stirred at room temperature for 18 h. A solution of 1N HCl (10 mL) was used to dissolve the salts and EtOAc (50 mL) was added to extract the product. The organic

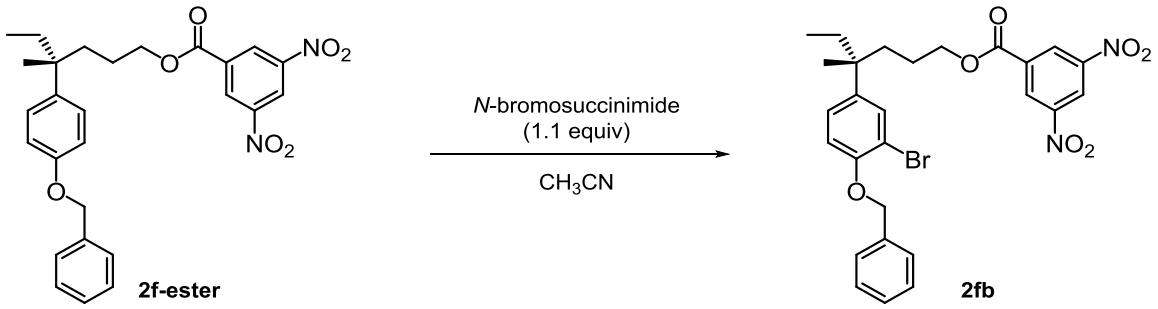
extract was washed with 1N HCl (3x10 mL) and brine, dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to obtain the crude product. The resultant product was purified by silica gel chromatography to give acid **2ba** in 80% yield (82.5 mg). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 7.32 (t, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 2.22–1.98 (m, 3 H), 1.90–1.75 (m, 2 H), 1.63–1.56 (m, 1 H), 1.29 (s, 3 H), 0.70 (d, *J* = 6.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 180.8, 146.1, 128.2, 126.4, 125.7, 40.6, 37.3, 35.6, 29.6, 22.8, 8.5. IR (neat): 2966, 2924, 2878, 1704, 1446, 1414, 1302, 1221, 926, 759, 699 cm$^{-1}$.


2bb

To a 25 mL seal-tube equipped with a teflon stir bar was added acid **2ba** (82.5 mg, 0.40 mmol), $PdCl_2$ (6 mg, 0.030 mmol), $Ph_3P$ (64 mg, 0.20 mmol), and $Ac_2O$ (0.3 mL, 3.2 mmol). The reaction mixture was gradually heated to 240 °C in an oil bath over 45 min. The seal-tube was cooled to room temperature, and the reaction mixture was dissolved in $Et_2O$ (50 mL) and washe with sat. $NaHCO_3$ (2 x 10 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Products were purified by silica gel column to give acid **2bb** in 54% yield (35 mg). $[\alpha]^{20}_D$ = – 10 $^o$ (c = 0. 350, $CHCl_3$). The analysis data is identical with the reported data[3,4]. **Determination of absolute configuration**: literature value ($[\alpha]^{26}_D$ = + 4.55$^o$ (*c* = 1.1, $CHCl_3$)) is assigned to the (*S*)-enantiomer[3]. Therefore, the major enantiomer formed in the relay Heck reaction is (*R*).

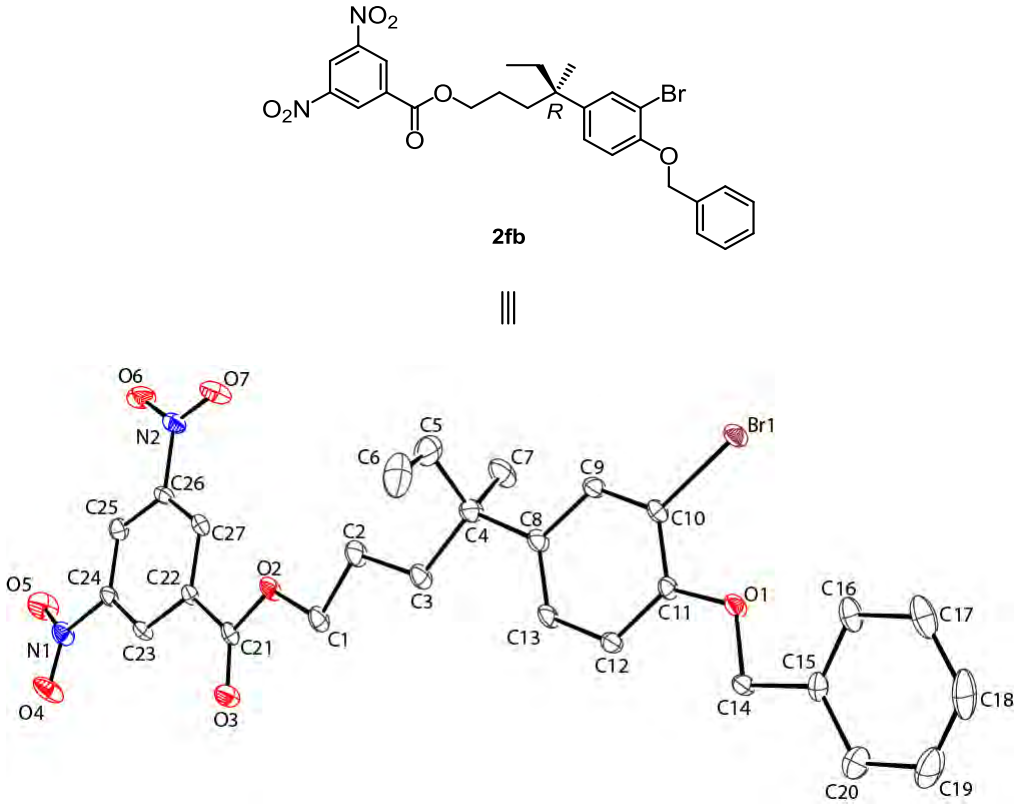
### 2.4.1 Determination of absolute configuration of 2fb by X-ray

#### 2.4.1.1 Preparation of 2fb




To a solution of **2f-ester** (299 mg, 0.610 mmol) in 5 mL of $CH_3CN$ was added *N*-bromosuccinimide (119 mg, 0.670 mmol, 1.1 equiv). After the reaction was complete (4 h), the solvent was evaporated under reduced pressure and the crude product was purified by silica gel chromatography to give **2fb** in 90% yield (313 mg). Single crystals (for X-ray analysis) were obtained by slow evaporation from an acetone solution of **2fb**. $[\alpha]^{20}_D$ = + 14.4 $^o$ (c = 1.01, $CHCl_3$), which corresponds to a >99:1 er (see below for details). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.20 (t, *J* = 1.5 Hz, 1 H), 9.11 (t, *J* = 1.5 Hz, 2 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.46 (s, 1 H), 7.38 (t, *J* = 8.0 Hz, 2 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 5.13 (s, 2 H), 4.38–4.30 (m, 2 H), 1.81–1.46 (m, 6 H), 1.28 (s, 3 H), 0.71 (t, *J* = 7.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.4, 152.9, 148.6, 141.0, 136.6, 134.0, 131.4, 129.3, 128.5, 127.8, 126.9, 126.3, 122.2, 113.4, 112.3, 70.7, 67.2, 40.4, 38.9, 35.5, 23.7, 23.0, 8.5. IR (neat): 3100, 2964, 2878, 1728, 1628, 1542, 1498, 1455, 1342, 1277, 1165, 1075, 921, 729, 720, 695 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 593.0899, obsvd. 593.0901.

### 2.4.1.2 X-ray crystal data of the enantiomerically enriched isomer 2fb




**Crystal data and structure refinement for 2fb.**

**Table S2** Crystal data and structure refinement for mss039.

| | | |
|---|---|---|
| Identification code | mss039 | |
| Empirical formula | $C_{27}$ $H_{27}$ Br $N_2$ $O_7$ | |
| Formula weight | 571.42 | |
| Temperature | 150(1) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | ***P*** 1 | |
| Unit cell dimensions | a = 6.9374(2) Å | □= 95.1307(18)°. |
| | b = 7.6510(3) Å | □= 94.2669(18)°. |
| | c = 12.4360(2) Å | □ = 90.5343(13)°. |
| Volume | 655.53(3) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 1.447 $Mg/m^3$ | |
| Absorption coefficient | 1.616 $mm^{-1}$ | |

| | |
|---|---|
| F(000) | 294 |
| Crystal size | 0.28 x 0.25 x 0.10 $mm^3$ |
| Theta range for data collection | 2.94 to 27.69°. |
| Index ranges | -9<=h<=8, -9<=k<=9, -15<=l<=16 |
| Reflections collected | 4627 |
| Independent reflections | 4627 [R(int) = 0.0000] |
| Completeness to theta = 27.69° | 96.3 % |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.8551 and 0.6604 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4627 / 3 / 335 |
| Goodness-of-fit on $F^2$ | 1.089 |
| Final R indices [I>2sigma(I)] | R1 = 0.0283, wR2 = 0.0644 |
| R indices (all data) | R1 = 0.0294, wR2 = 0.0651 |
| Absolute structure parameter | 0.000(6) |
| Largest diff. peak and hole | 0.398 and -0.367 e.$Å^{-3}$ |

**Table S3** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for mss039. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 4231(1) | 7073(1) | 510(1) | 25(1) |
| O(1) | 369(3) | 5471(3) | 175(1) | 26(1) |
| O(2) | 144(3) | 8767(3) | 8312(1) | 28(1) |
| O(3) | -2720(3) | 8202(3) | 8961(2) | 32(1) |
| O(4) | -3086(4) | 10013(4) | 12884(2) | 45(1) |
| O(5) | -1088(4) | 11973(4) | 13683(2) | 51(1) |
| O(6) | 4849(4) | 13121(4) | 12006(2) | 45(1) |
| O(7) | 5044(4) | 12239(4) | 10319(2) | 45(1) |
| N(1) | -1660(5) | 10944(4) | 12911(2) | 32(1) |
| N(2) | 4188(4) | 12364(3) | 11145(2) | 29(1) |
| C(1) | -502(5) | 7945(4) | 7243(2) | 29(1) |
| C(2) | 1262(5) | 7991(4) | 6590(2) | 31(1) |

| | | | | |
|---|---|---|---|---|
| C(3) | 744(4) | 7436(4) | 5390(2) | 27(1) |
| C(4) | 2398(4) | 7711(4) | 4639(2) | 30(1) |
| C(5) | 4221(5) | 6717(5) | 4957(3) | 46(1) |
| C(6) | 4019(8) | 4756(6) | 4815(3) | 63(1) |
| C(7) | 2942(5) | 9700(5) | 4726(2) | 42(1) |
| C(8) | 1704(4) | 7123(4) | 3458(2) | 24(1) |
| C(9) | 2992(4) | 7338(4) | 2648(2) | 24(1) |
| C(10) | 2467(4) | 6772(4) | 1578(2) | 21(1) |
| C(11) | 697(4) | 5988(3) | 1254(2) | 20(1) |
| C(12) | -618(5) | 5779(5) | 2038(3) | 23(1) |
| C(13) | -77(4) | 6353(4) | 3123(2) | 25(1) |
| C(14) | -1307(4) | 4416(4) | -168(2) | 21(1) |
| C(15) | -1147(5) | 3743(4) | -1339(2) | 24(1) |
| C(16) | 600(7) | 3682(5) | -1798(3) | 32(1) |
| C(17) | 695(6) | 3039(5) | -2873(3) | 43(1) |
| C(18) | -952(7) | 2482(5) | -3493(3) | 52(1) |
| C(19) | -2698(7) | 2532(5) | -3042(3) | 51(1) |
| C(20) | -2818(5) | 3177(5) | -1957(2) | 39(1) |
| C(21) | -1120(6) | 8822(5) | 9069(3) | 23(1) |
| C(22) | -254(4) | 9805(3) | 10094(2) | 20(1) |
| C(23) | -1308(5) | 9889(4) | 11010(2) | 21(1) |
| C(24) | -523(4) | 10813(4) | 11949(2) | 23(1) |
| C(25) | 1255(4) | 11681(4) | 12027(2) | 25(1) |
| C(26) | 2252(4) | 11542(4) | 11101(2) | 23(1) |
| C(27) | 1555(4) | 10636(4) | 10142(2) | 22(1) |

**Table S4** Bond lengths [Å] and angles [°] for mss039.

| | |
|---|---|
| Br(1)-C(10) | 1.899(2) |
| O(1)-C(11) | 1.367(3) |
| O(1)-C(14) | 1.425(3) |
| O(2)-C(21) | 1.332(4) |
| O(2)-C(1) | 1.457(3) |
| O(3)-C(21) | 1.197(5) |
| O(4)-N(1) | 1.210(4) |

| | |
|---|---|
| O(5)-N(1) | 1.225(4) |
| O(6)-N(2) | 1.226(4) |
| O(7)-N(2) | 1.222(3) |
| N(1)-C(24) | 1.478(4) |
| N(2)-C(26) | 1.473(4) |
| C(1)-C(2) | 1.520(4) |
| C(1)-H(1A) | 0.9900 |
| C(1)-H(1B) | 0.9900 |
| C(2)-C(3) | 1.530(4) |
| C(2)-H(2A) | 0.9900 |
| C(2)-H(2B) | 0.9900 |
| C(3)-C(4) | 1.557(4) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(4)-C(5) | 1.527(5) |
| C(4)-C(8) | 1.537(4) |
| C(4)-C(7) | 1.557(5) |
| C(5)-C(6) | 1.499(6) |
| C(5)-H(5A) | 0.9900 |
| C(5)-H(5B) | 0.9900 |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(8)-C(13) | 1.383(4) |
| C(8)-C(9) | 1.414(4) |
| C(9)-C(10) | 1.383(4) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.378(4) |
| C(11)-C(12) | 1.402(4) |
| C(12)-C(13) | 1.403(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.513(4) |

| | |
|---|---|
| C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 |
| C(15)-C(16) | 1.377(6) |
| C(15)-C(20) | 1.386(5) |
| C(16)-C(17) | 1.389(5) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.372(6) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.372(6) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.404(5) |
| C(19)-H(19) | 0.9500 |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.502(4) |
| C(22)-C(23) | 1.396(4) |
| C(22)-C(27) | 1.396(4) |
| C(23)-C(24) | 1.382(4) |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.388(4) |
| C(25)-C(26) | 1.383(4) |
| C(25)-H(25) | 0.9500 |
| C(26)-C(27) | 1.377(4) |
| C(27)-H(27) | 0.9500 |

| | |
|---|---|
| C(11)-O(1)-C(14) | 118.0(2) |
| C(21)-O(2)-C(1) | 117.3(3) |
| O(4)-N(1)-O(5) | 124.5(3) |
| O(4)-N(1)-C(24) | 117.5(3) |
| O(5)-N(1)-C(24) | 117.9(3) |
| O(7)-N(2)-O(6) | 123.9(3) |
| O(7)-N(2)-C(26) | 117.7(3) |
| O(6)-N(2)-C(26) | 118.4(2) |
| O(2)-C(1)-C(2) | 104.9(2) |
| O(2)-C(1)-H(1A) | 110.8 |
| C(2)-C(1)-H(1A) | 110.8 |
| O(2)-C(1)-H(1B) | 110.8 |

| | |
|---|---|
| C(2)-C(1)-H(1B) | 110.8 |
| H(1A)-C(1)-H(1B) | 108.8 |
| C(1)-C(2)-C(3) | 111.4(2) |
| C(1)-C(2)-H(2A) | 109.3 |
| C(3)-C(2)-H(2A) | 109.3 |
| C(1)-C(2)-H(2B) | 109.3 |
| C(3)-C(2)-H(2B) | 109.3 |
| H(2A)-C(2)-H(2B) | 108.0 |
| C(2)-C(3)-C(4) | 114.6(2) |
| C(2)-C(3)-H(3A) | 108.6 |
| C(4)-C(3)-H(3A) | 108.6 |
| C(2)-C(3)-H(3B) | 108.6 |
| C(4)-C(3)-H(3B) | 108.6 |
| H(3A)-C(3)-H(3B) | 107.6 |
| C(5)-C(4)-C(8) | 109.3(2) |
| C(5)-C(4)-C(3) | 112.5(3) |
| C(8)-C(4)-C(3) | 109.8(2) |
| C(5)-C(4)-C(7) | 107.6(3) |
| C(8)-C(4)-C(7) | 108.7(2) |
| C(3)-C(4)-C(7) | 108.7(2) |
| C(6)-C(5)-C(4) | 115.2(3) |
| C(6)-C(5)-H(5A) | 108.5 |
| C(4)-C(5)-H(5A) | 108.5 |
| C(6)-C(5)-H(5B) | 108.5 |
| C(4)-C(5)-H(5B) | 108.5 |
| H(5A)-C(5)-H(5B) | 107.5 |
| C(5)-C(6)-H(6A) | 109.5 |
| C(5)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(5)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(4)-C(7)-H(7A) | 109.5 |
| C(4)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(4)-C(7)-H(7C) | 109.5 |

| | |
|---|---|
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| C(13)-C(8)-C(9) | 116.9(2) |
| C(13)-C(8)-C(4) | 125.0(2) |
| C(9)-C(8)-C(4) | 118.0(2) |
| C(10)-C(9)-C(8) | 120.4(3) |
| C(10)-C(9)-H(9) | 119.8 |
| C(8)-C(9)-H(9) | 119.8 |
| C(11)-C(10)-C(9) | 122.3(2) |
| C(11)-C(10)-Br(1) | 118.36(19) |
| C(9)-C(10)-Br(1) | 119.4(2) |
| O(1)-C(11)-C(10) | 116.4(2) |
| O(1)-C(11)-C(12) | 125.0(3) |
| C(10)-C(11)-C(12) | 118.6(2) |
| C(11)-C(12)-C(13) | 118.9(3) |
| C(11)-C(12)-H(12) | 120.5 |
| C(13)-C(12)-H(12) | 120.5 |
| C(8)-C(13)-C(12) | 122.9(3) |
| C(8)-C(13)-H(13) | 118.5 |
| C(12)-C(13)-H(13) | 118.5 |
| O(1)-C(14)-C(15) | 107.7(2) |
| O(1)-C(14)-H(14A) | 110.2 |
| C(15)-C(14)-H(14A) | 110.2 |
| O(1)-C(14)-H(14B) | 110.2 |
| C(15)-C(14)-H(14B) | 110.2 |
| H(14A)-C(14)-H(14B) | 108.5 |
| C(16)-C(15)-C(20) | 119.7(3) |
| C(16)-C(15)-C(14) | 121.8(3) |
| C(20)-C(15)-C(14) | 118.4(3) |
| C(15)-C(16)-C(17) | 120.3(4) |
| C(15)-C(16)-H(16) | 119.9 |
| C(17)-C(16)-H(16) | 119.9 |
| C(18)-C(17)-C(16) | 120.4(4) |
| C(18)-C(17)-H(17) | 119.8 |
| C(16)-C(17)-H(17) | 119.8 |
| C(19)-C(18)-C(17) | 119.7(3) |

| | |
|---|---|
| C(19)-C(18)-H(18) | 120.1 |
| C(17)-C(18)-H(18) | 120.1 |
| C(18)-C(19)-C(20) | 120.5(3) |
| C(18)-C(19)-H(19) | 119.8 |
| C(20)-C(19)-H(19) | 119.8 |
| C(15)-C(20)-C(19) | 119.3(3) |
| C(15)-C(20)-H(20) | 120.3 |
| C(19)-C(20)-H(20) | 120.3 |
| O(3)-C(21)-O(2) | 125.8(3) |
| O(3)-C(21)-C(22) | 124.2(3) |
| O(2)-C(21)-C(22) | 110.0(3) |
| C(23)-C(22)-C(27) | 120.0(2) |
| C(23)-C(22)-C(21) | 118.5(3) |
| C(27)-C(22)-C(21) | 121.5(2) |
| C(24)-C(23)-C(22) | 118.5(3) |
| C(24)-C(23)-H(23) | 120.7 |
| C(22)-C(23)-H(23) | 120.7 |
| C(23)-C(24)-C(25) | 123.4(3) |
| C(23)-C(24)-N(1) | 118.6(3) |
| C(25)-C(24)-N(1) | 118.0(3) |
| C(26)-C(25)-C(24) | 115.9(3) |
| C(26)-C(25)-H(25) | 122.1 |
| C(24)-C(25)-H(25) | 122.1 |
| C(27)-C(26)-C(25) | 123.6(3) |
| C(27)-C(26)-N(2) | 117.9(2) |
| C(25)-C(26)-N(2) | 118.5(2) |
| C(26)-C(27)-C(22) | 118.7(2) |
| C(26)-C(27)-H(27) | 120.7 |
| C(22)-C(27)-H(27) | 120.7 |

**Table S5** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mss039. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 23(1) | 32(1) | 21(1) | 0(1) | 10(1) | -1(1) |
| O(1) | 28(1) | 34(1) | 16(1) | -2(1) | 6(1) | -11(1) |
| O(2) | 34(1) | 36(1) | 14(1) | -2(1) | 11(1) | -9(1) |
| O(3) | 33(1) | 37(1) | 24(1) | -4(1) | 7(1) | -11(1) |
| O(4) | 50(2) | 51(2) | 36(1) | -6(1) | 25(1) | -18(1) |
| O(5) | 56(2) | 74(2) | 21(1) | -17(1) | 13(1) | -17(1) |
| O(6) | 34(1) | 54(2) | 44(1) | -1(1) | -3(1) | -16(1) |
| O(7) | 35(2) | 48(2) | 54(2) | 0(1) | 16(1) | -13(1) |
| N(1) | 38(2) | 35(2) | 22(1) | -1(1) | 9(1) | -5(1) |
| N(2) | 27(2) | 25(1) | 37(2) | 5(1) | 7(1) | -4(1) |
| C(1) | 39(2) | 31(2) | 15(1) | -2(1) | 6(1) | -9(1) |
| C(2) | 37(2) | 40(2) | 17(1) | -1(1) | 8(1) | -3(1) |
| C(3) | 34(2) | 29(2) | 18(1) | -2(1) | 8(1) | -5(1) |
| C(4) | 27(2) | 43(2) | 20(1) | -3(1) | 5(1) | -4(1) |
| C(5) | 39(2) | 73(3) | 24(2) | -1(2) | 4(1) | 8(2) |
| C(6) | 82(3) | 64(3) | 45(2) | 18(2) | 2(2) | 21(2) |
| C(7) | 51(2) | 49(2) | 25(2) | -7(1) | 12(1) | -20(2) |
| C(8) | 25(1) | 30(2) | 18(1) | 0(1) | 7(1) | -1(1) |
| C(9) | 21(1) | 30(2) | 21(1) | 0(1) | 5(1) | -4(1) |
| C(10) | 23(1) | 22(1) | 18(1) | 0(1) | 9(1) | 1(1) |
| C(11) | 24(1) | 21(1) | 14(1) | -1(1) | 5(1) | -2(1) |
| C(12) | 22(2) | 26(2) | 20(2) | 1(1) | 4(1) | -6(1) |
| C(13) | 27(2) | 32(2) | 17(1) | 1(1) | 11(1) | -2(1) |
| C(14) | 20(2) | 22(1) | 19(1) | 0(1) | 5(1) | -4(1) |
| C(15) | 36(2) | 21(2) | 15(1) | 2(1) | 1(1) | 0(1) |
| C(16) | 47(3) | 31(2) | 19(2) | 0(1) | 11(2) | 2(2) |
| C(17) | 68(3) | 37(2) | 27(2) | 3(1) | 23(2) | 9(2) |
| C(18) | 96(3) | 44(2) | 15(2) | -3(1) | 9(2) | 5(2) |
| C(19) | 71(3) | 51(2) | 26(2) | -4(1) | -15(2) | -8(2) |
| C(20) | 43(2) | 47(2) | 25(2) | -1(1) | -3(1) | -3(2) |
| C(21) | 30(2) | 24(2) | 15(1) | 2(1) | 8(1) | -1(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(22) | 26(1) | 18(1) | 16(1) | 3(1) | 5(1) | -3(1) |
| C(23) | 23(2) | 20(1) | 21(1) | 1(1) | 9(1) | -4(1) |
| C(24) | 26(2) | 28(2) | 14(1) | 1(1) | 7(1) | -4(1) |
| C(25) | 31(2) | 24(1) | 20(1) | 0(1) | 3(1) | -1(1) |
| C(26) | 21(1) | 20(1) | 27(1) | 5(1) | 5(1) | -5(1) |
| C(27) | 26(1) | 20(1) | 20(1) | 4(1) | 8(1) | 1(1) |

**Table S6** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | -1575 | 8606 | 6911 | 34 |
| H(1B) | -944 | 6721 | 7287 | 34 |
| H(2A) | 2251 | 7194 | 6877 | 38 |
| H(2B) | 1823 | 9194 | 6670 | 38 |
| H(3A) | -391 | 8109 | 5143 | 32 |
| H(3B) | 362 | 6179 | 5310 | 32 |
| H(5A) | 5266 | 7075 | 4518 | 55 |
| H(5B) | 4625 | 7077 | 5725 | 55 |
| H(6A) | 5251 | 4232 | 5041 | 76 |
| H(6B) | 3664 | 4376 | 4052 | 76 |
| H(6C) | 3011 | 4379 | 5259 | 76 |
| H(7A) | 3384 | 10092 | 5476 | 50 |
| H(7B) | 1807 | 10370 | 4503 | 50 |
| H(7C) | 3979 | 9891 | 4253 | 50 |
| H(9) | 4225 | 7874 | 2840 | 28 |
| H(12) | -1855 | 5257 | 1838 | 27 |
| H(13) | -974 | 6206 | 3650 | 30 |
| H(14A) | -2487 | 5122 | -97 | 25 |
| H(14B) | -1383 | 3421 | 285 | 25 |
| H(16) | 1745 | 4080 | -1378 | 39 |
| H(17) | 1908 | 2986 | -3181 | 51 |
| H(18) | -883 | 2063 | -4232 | 62 |
| H(19) | -3836 | 2126 | -3468 | 61 |

| | | | | |
|---|---|---|---|---|
| H(20) | -4032 | 3226 | -1650 | 46 |
| H(23) | -2537 | 9324 | 10989 | 25 |
| H(25) | 1756 | 12331 | 12675 | 30 |
| H(27) | 2289 | 10578 | 9525 | 26 |

**Table S7** Torsion angles [°] for mss039.

| | |
|---|---|
| C(21)-O(2)-C(1)-C(2) | -176.9(3) |
| O(2)-C(1)-C(2)-C(3) | -171.0(2) |
| C(1)-C(2)-C(3)-C(4) | 171.4(3) |
| C(2)-C(3)-C(4)-C(5) | 58.4(4) |
| C(2)-C(3)-C(4)-C(8) | -179.5(2) |
| C(2)-C(3)-C(4)-C(7) | -60.7(3) |
| C(8)-C(4)-C(5)-C(6) | -56.3(4) |
| C(3)-C(4)-C(5)-C(6) | 66.0(4) |
| C(7)-C(4)-C(5)-C(6) | -174.2(3) |
| C(5)-C(4)-C(8)-C(13) | 119.8(3) |
| C(3)-C(4)-C(8)-C(13) | -4.1(4) |
| C(7)-C(4)-C(8)-C(13) | -122.9(3) |
| C(5)-C(4)-C(8)-C(9) | -58.4(4) |
| C(3)-C(4)-C(8)-C(9) | 177.6(2) |
| C(7)-C(4)-C(8)-C(9) | 58.8(3) |
| C(13)-C(8)-C(9)-C(10) | -0.8(4) |
| C(4)-C(8)-C(9)-C(10) | 177.6(3) |
| C(8)-C(9)-C(10)-C(11) | 0.1(4) |
| C(8)-C(9)-C(10)-Br(1) | -179.8(2) |
| C(14)-O(1)-C(11)-C(10) | 170.4(2) |
| C(14)-O(1)-C(11)-C(12) | -9.6(4) |
| C(9)-C(10)-C(11)-O(1) | -179.3(2) |
| Br(1)-C(10)-C(11)-O(1) | 0.6(3) |
| C(9)-C(10)-C(11)-C(12) | 0.7(4) |
| Br(1)-C(10)-C(11)-C(12) | -179.4(2) |
| O(1)-C(11)-C(12)-C(13) | 179.2(3) |
| C(10)-C(11)-C(12)-C(13) | -0.8(4) |
| C(9)-C(8)-C(13)-C(12) | 0.7(4) |

| | |
|---|---|
| C(4)-C(8)-C(13)-C(12) | -177.6(3) |
| C(11)-C(12)-C(13)-C(8) | 0.1(5) |
| C(11)-O(1)-C(14)-C(15) | -169.6(2) |
| O(1)-C(14)-C(15)-C(16) | 20.5(4) |
| O(1)-C(14)-C(15)-C(20) | -159.5(3) |
| C(20)-C(15)-C(16)-C(17) | -0.6(5) |
| C(14)-C(15)-C(16)-C(17) | 179.4(3) |
| C(15)-C(16)-C(17)-C(18) | 0.9(6) |
| C(16)-C(17)-C(18)-C(19) | -1.1(6) |
| C(17)-C(18)-C(19)-C(20) | 1.1(6) |
| C(16)-C(15)-C(20)-C(19) | 0.6(5) |
| C(14)-C(15)-C(20)-C(19) | -179.4(3) |
| C(18)-C(19)-C(20)-C(15) | -0.9(6) |
| C(1)-O(2)-C(21)-O(3) | 2.8(5) |
| C(1)-O(2)-C(21)-C(22) | -176.6(2) |
| O(3)-C(21)-C(22)-C(23) | 5.4(5) |
| O(2)-C(21)-C(22)-C(23) | -175.2(3) |
| O(3)-C(21)-C(22)-C(27) | -174.1(3) |
| O(2)-C(21)-C(22)-C(27) | 5.3(4) |
| C(27)-C(22)-C(23)-C(24) | 0.3(4) |
| C(21)-C(22)-C(23)-C(24) | -179.1(3) |
| C(22)-C(23)-C(24)-C(25) | 0.7(5) |
| C(22)-C(23)-C(24)-N(1) | 178.3(3) |
| O(4)-N(1)-C(24)-C(23) | 11.3(5) |
| O(5)-N(1)-C(24)-C(23) | -169.4(3) |
| O(4)-N(1)-C(24)-C(25) | -171.0(3) |
| O(5)-N(1)-C(24)-C(25) | 8.4(5) |
| C(23)-C(24)-C(25)-C(26) | -1.4(4) |
| N(1)-C(24)-C(25)-C(26) | -179.0(3) |
| C(24)-C(25)-C(26)-C(27) | 1.1(4) |
| C(24)-C(25)-C(26)-N(2) | -177.2(3) |
| O(7)-N(2)-C(26)-C(27) | 2.1(4) |
| O(6)-N(2)-C(26)-C(27) | -177.5(3) |
| O(7)-N(2)-C(26)-C(25) | -179.5(3) |
| O(6)-N(2)-C(26)-C(25) | 0.9(4) |
| C(25)-C(26)-C(27)-C(22) | -0.2(4) |

| | |
|---|---|
| N(2)-C(26)-C(27)-C(22) | 178.1(2) |
| C(23)-C(22)-C(27)-C(26) | -0.6(4) |
| C(21)-C(22)-C(27)-C(26) | 178.8(3) |

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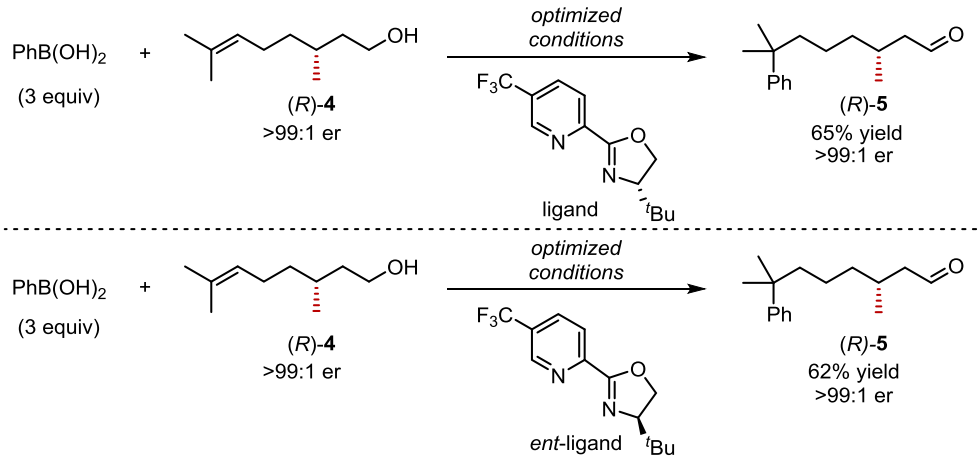
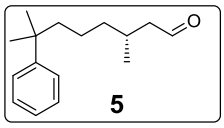
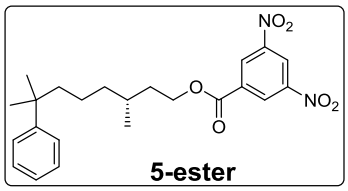
## 2.5 Arylation of citronellol and its derivative

### Arylation of citronellol with *standard ligand* and *ent-ligand*



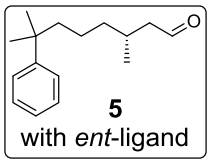




Compound **5** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D} = -14^{\circ}$ (c = 0.206, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.70-9.69 (m, 1H), 7.34–7.28 (m, 4 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 2.32–2.28 (m, 1 H), 2.18–2.12 (m, 1 H), 2.02–1.95 (m, 1 H), 1.65–1.55 (m, 2 H), 1.31 (s, 6H), 1.27–1.05 (m, 4 H), 0.88 (d, *J* = 7.0 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 203.0, 149.4, 128.0, 125.7, 125.3, 51.0, 44.5, 37.6, 37.4, 28.9, 27.9, 22.0, 19.9. IR (neat): 2959, 2932, 2714, 1724, 1461, 1445, 1384, 1366, 764, 698, 570 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 255.1725, obsvd. 255.1721.

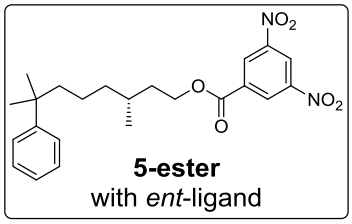



In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general

procedure **C**, followed by general procedure D. $[\alpha]^{20}_D$ = + 4.0 $^o$ (c = 0. 384, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 1.5 Hz, 1 H), 9.13 (d, *J* = 1.5 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, H), 7.29 (t, *J* = 8.0 Hz, 2 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 4.48–4.40 (m, 2 H), 1.81–1.76 (m, 1 H), 1.65–1.54 (m, 4 H),1.30 (s, 6 H), 1.28–1.25 (m, 1 H), 1.19–1.05 (m, 3 H), 0.90 (d, *J* = 6.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.5, 149.5, 148.6, 134.1, 129.3, 128.0, 125.7, 125.3, 122.2, 65.8, 44.6, 37.6, 37.5, 35.3, 29.7, 29.0, 28.9, 21.9, 19.4. IR (neat): 3103, 2932, 1729, 1629, 1599, 1461, 1342, 1274, 1165, 920, 765, 719, 699 $cm^{-1}$. HRMS $(M^{\bullet})^+$ calcd. 428.1947, obsvd. 428.1952.



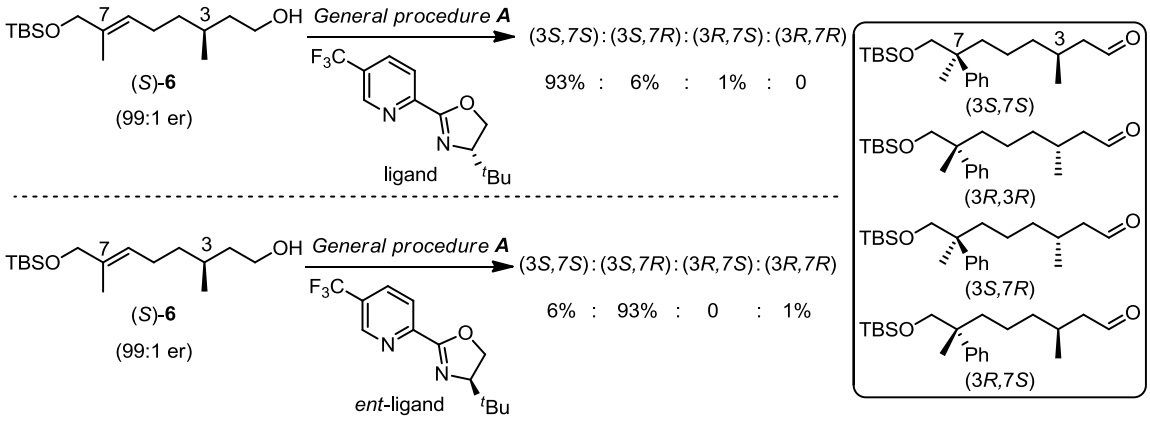

Compound **5** was prepared according to the general procedure **A** with *ent*-ligand. $[\alpha]^{20}_D$ = –10 $^o$ (c = 0.341, $CHCl_3$). ). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.70-9.69 (m, 1H), 7.34–7.28 (m, 4 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 2.32–2.28 (m, 1 H), 2.18–2.12 (m, 1 H), 2.02–1.95 (m, 1 H), 1.65–1.55 (m, 2 H), 1.31 (s, 6 H), 1.27–1.05 (m, 4 H), 0.88 (d, *J* = 7.0 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 203.0, 149.4, 128.0, 125.7, 125.3, 51.0, 44.5, 37.6, 37.4, 28.9, 27.9, 22.0, 19.9. IR (neat): 2959, 2932, 2713, 1723, 1461, 1445, 1384, 1366, 1031, 764, 698, 570 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 255.1725, obsvd. 255.1721.

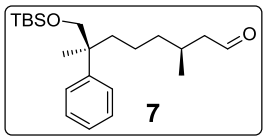



In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_D$ = + 5.0 $^o$ (c = 0.370, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 1.5 Hz, 1 H), 9.13 (d, *J* = 1.5 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 4.48–4.40 (m, 2 H), 1.81–1.76 (m, 1 H), 1.65–1.54 (m, 4 H),1.30 (s, 6 H), 1.28–1.25 (m, 1 H), 1.19–1.05 (m, 3 H), 0.90 (d, *J* = 6.5 Hz, 3 H).

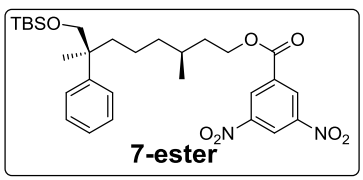
$^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.7, 149.7, 148.9, 134.4, 129.6, 128.2, 126.0, 125.6, 122.5, 65.8, 44.9, 37.9, 37.7, 35.6, 30.0, 29.2, 29.1, 22.2, 19.7. IR (neat): 3102, 2932, 1728, 1628, 1542, 1461, 1342, 1274, 1164, 1074, 920, 765, 719, 699 $cm^{-1}$. HRMS $(M^{\bullet})^+$ calcd. 428.1947, obsvd. 428.1952.

**Arylation of citronellol derivatives**



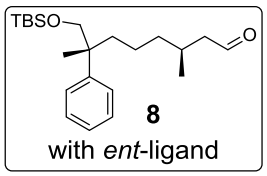




Compound **7** was prepared according to the general procedure **A**. $[\alpha]^{20}_D$ = – 11 $^{o}$ (c = 0.18, $CHCl_3$). $^1$H-NMR (500 MHz, $CDCl_3$) δ = 9.70 (t, *J* = 1.5 Hz, 1H), 7.31–7.28 (m, 4 H), 7.19–7.16 (m, 1 H), 3.57 (d, *J* = 10 Hz, 1 H), 3.52 (d, *J* = 10 Hz, 1 H), 2.31–2.28 (m, 1 H), 2.17–2.11 (m, 1 H), 2.01–1.93 (m, 1 H), 1.77–1.70 (m, 1 H), 1.63–1.57 (m, 1 H), 1.29 (s, 3 H), 1.25–1.02 (m, 2 H), 0.87 (d, *J* = 6.5 Hz, 3 H), 0.84 (s, 9 H), –0.06 (s, 3 H), –0.08 (s, 3H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 203.2, 146.1, 127.9, 126.6, 125.6, 72.0, 51.0, 43.1, 38.0, 37.6, 28.0, 25.8, 22.1, 21.3, 19.9, 18.2, –5.6, –5.7. IR (neat): 2928, 2855, 1707, 1463, 1252, 1091, 835, 774, 698, 668 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 385.2539, obsvd. 385.2544.

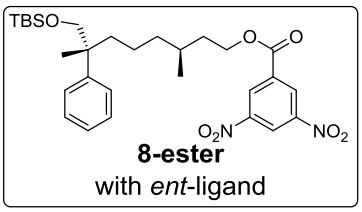



In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general

procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_{D}$ = + 2.1 $^{o}$ (c = 0.341, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 2.0 Hz, 1 H), 9.13 (d, *J* = 2.0 Hz, 2 H), 7.32–7.26 (m, 4 H), 7.18–7.15 (m, 1 H), 4.48–4.40 (m, 2 H), 3.58 (d, *J* = 9.5 Hz, 1 H), 3.53 (d, *J* = 9.5 Hz, 1 H), 1.82–1.72 (m, 2 H), 1.65–1.54 (m, 3 H), 1.36–1.26 (m, 1 H), 1.30 (s, 3 H), 1.21–1.05 (m, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H), 0.84 (s, 9 H), , –0.06 (s, 3 H), –0.08 (s, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.5, 148.6, 146.1, 134.1, 129.4, 127.8, 126.6, 125.6, 122.3, 72.0, 65.6, 43.1, 38.1, 37.7, 35.3, 29.8, 25.8, 22.2, 21.3, 19.5, 18.2, –5.6, –5.7. IR (neat): 2928, 2855, 1730, 1628, 1545, 1462, 1343, 1276, 1256, 1165, 1091, 1075, 1006, 835, 773, 720, 698 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 581.2659, obsvd. 581.2670.




Compound **8** was prepared according to the general procedure **A** with *ent*-ligand. $[\alpha]^{20}_{D}$ = – 18 $^{o}$ (c = 0.128, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.70 (t, *J* = 1.5 Hz, 1H), 7.31–7.29 (m, 4 H), 7.19–7.16 (m, 1 H), 3.57 (d, *J* = 10 Hz, 1 H), 3.52 (d, *J* = 10 Hz, 1 H), 2.31–2.28 (m, 1 H), 2.17–2.12 (m, 1 H), 2.01–1.93 (m, 1 H), 1.78–1.72 (m, 1 H), 1.62–1.57 (m, 1 H), 1.29 (s, 3 H), 1.27–1.14 (m, 3 H), 1.05–0.99 (m, 1 H), 0.87 (d, *J* = 6.5 Hz, 3 H), 0.84 (s, 9 H), –0.06 (s, 3 H), –0.08 (s, 3H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 203.1, 146.1, 127.9, 126.6, 125.7, 72.0, 51.0, 43.1, 38.0, 37.7, 28.0, 25.8, 22.1, 21.4, 19.9, 18.2, –5.6, –5.7. IR (neat): 2928, 2855, 1709, 1470, 1253, 1092, 835, 774, 698 $cm^{-1}$. HRMS $(M+Na)^{+}$ calcd. 385.2539, obsvd. 385.2547.

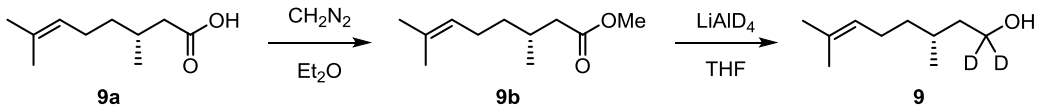



In order to determine the enantiomeric ratio of the product, the corresponding ester was prepared according to general procedure **C**, followed by general procedure **D**. $[\alpha]^{20}_{D}$ = + 0.5 $^{o}$ (c = 0.328, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 9.22 (t, *J* = 2.0 Hz, 1 H), 9.13

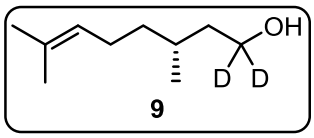
(d, $J$ = 2.0 Hz, 2 H), 7.32–7.26 (m, 4 H), 7.18–7.15 (m, 1 H), 4.47–4.40 (m, 2 H), 3.58 (d, $J$ = 9.5 Hz, 1 H), 3.53 (d, $J$ = 9.5 Hz, 1 H), 1.82–1.74 (m, 2 H), 1.61–1.54 (m, 3 H), 1.36–1.24 (m, 1 H), 1.35–1.14 (m, 3 H), 1.30 (s, 3 H), 1.06–1.00 (m, 1 H), 0.91 (d, $J$ = 6.5 Hz, 3 H), 0.83 (s, 9 H), , –0.06 (s, 3 H), –0.08 (s, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 162.5, 148.6, 146.1, 134.1, 129.4, 127.8, 126.6, 125.6, 122.3, 72.0, 65.6, 43.1, 38.2, 37.7, 35.4, 29.8, 25.8, 22.1, 21.3, 19.5, 18.2, –5.6, –5.7. IR (neat): 2928, 2855, 1731, 1629, 1545, 1462, 1343, 1278, 1256, 1166, 1093, 1006, 836, 774, 729, 721, 699 cm$^{-1}$. HRMS $(M+Na)^+$ calcd. 581.2659, obsvd. 581.2665.

### 2.6 Isotopic labeling experiments

#### 2.6.1 Preparation of 9[10]




9a 9b 9

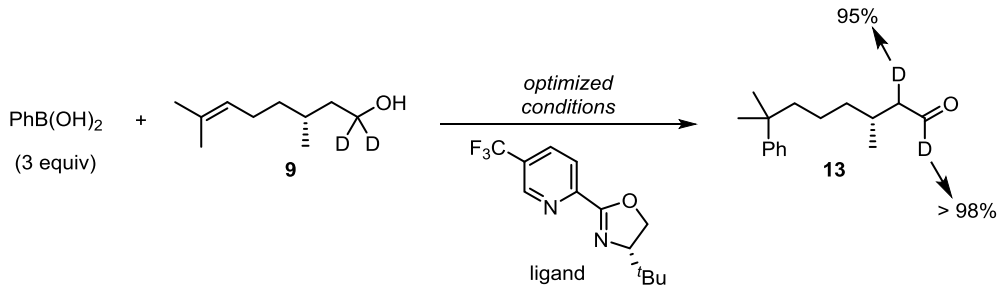



9

Excesses diazomethane was added dropwise to the stirred acid **9a** (10 mmol, 1.70 g) in diethyl ether (30 mL) at 0 °C. After stirring for 30 minutes, the reaction mixture was warmed up to room temperature. The reaction was quenched with acetic acid and the excesses acetic acid was neutralized with aqueous sodium bicarbonate. The mixture was then extracted with diethyl ether (30 mL x 4). The combined organic layer was washed sequentially with water (20 mL) and brine (20 mL), and dried over anhydrous $Na_2SO_4$. After removing the solvent, the residue was diluted with diethyl ether (30 mL) and transferred to a 50 mL round bottom flask equipped with a stir bar and septum. The mixture was cooled to 0 $^{o}$C under nitrogen. Lithium aluminum deuterium (504 mg, 12 mmol, 1.2 equiv) was added, and the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was treated with 1

mL of water, 2 mL KOH (20%), and then 3 mL water. The resulting residue was transferred to a separatory funnel using diethyl ether (50 mL) and water (20 mL). The aqueous layer was extracted with diethyl ether (2 x 30 mL), and the combined organic layers were washed with water (20 mL), and brine (20 mL). The organic layer was then dried over sodium sulfate, and concentrated under reduced pressure. The resulting mixture was purified using silica gel flash chromatography with 10–20% EtOAc in hexanes as the eluent to give the alcohol product **9** (1.14 g, 72% yield over two steps). $[\alpha]^{20}_{D}$ = + 5.1 $^{o}$ (c = 0.394, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 5.08 (t, *J* = 8.0 Hz, 2 H), 2.04–1.90 (m, 2 H), 1.67 (s, 3 H), 1.61–1.52 (m, 2 H), 1.59 (s, 3 H), 1.50 (br, 1 H), 1.20–1.12 (m, 1 H), 0.89 (d, *J* = 6.5 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 131.2, 124.7, 60.2 (t, $J_{C-D}$ = 21 Hz, $CD_2OH$), 39.6, 37.2, 29.1, 25.7, 25.4, 19.6, 17.6. IR (neat): 3325, 2963, 2913, 2855, 2198, 2089, 1452, 1377, 1131, 970, 827 $cm^{-1}$. HRMS $(M+H)^{+}$ calcd. 159.1718, obsvd. 159.1725.

**2.6.1 Heck arylation of 9**




Compound **13** was prepared according to the general procedure **A**. $[\alpha]^{20}_{D}$ = + 6.7 $^{o}$ (c = 0.626, $CHCl_3$). $^{1}$H-NMR (500 MHz, $CDCl_3$) δ = 7.34–7.28 (m, 4 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 2.32–2.28 (m, 0.42 H), 2.18–2.12 (m, 0.62 H), 2.02–1.95 (m, 1 H), 1.65–1.55 (m, 2 H), 1.31 (s, 6H), 1.27–1.05 (m, 4 H), 0.88 (d, *J* = 7.0 Hz, 3 H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ = 202.6 (m), 149.4, 128.0, 125.7, 125.4, 50.8 (m), 44.5, 37.6, 37,4, 28.9, 27.8,

22.0, 19.9. IR (neat): 2959, 2931, 2870, 2066, 1710, 1461, 1445, 1384, 1366, 764, 698, 570 $cm^{-1}$. HRMS $(M+Na)^+$ calcd. 257.1850, obsvd. 257.1854.

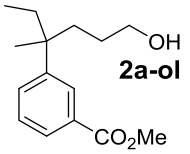
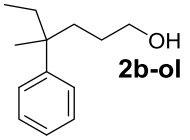
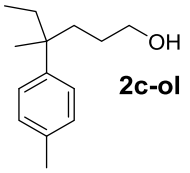
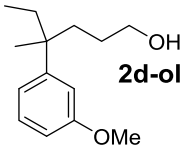
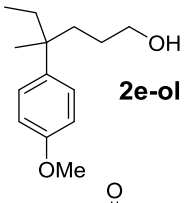
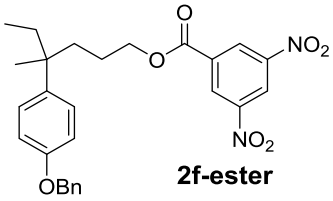
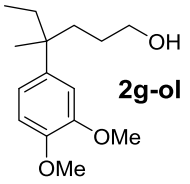
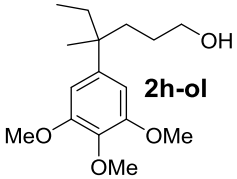
**2.7 Determination of enantiomeric ratio**

**Preparation of racemic products in Figure 2 and 3**

The procedure for the preparation of each corresponding racemic product in Figure 2 and 3 was modified, in which the ligand was omitted from the reaction mixture. The reactions were performed in otherwise identical fashion as the enantiomerically enriched products. The products were purified in the same fashion as described for the enantiomerically enriched products.

## Enantiomeric ratio of products

**Table S8** Products shown in Figure 2a

| entry | compound | conditions | retention time | er |
|---|---|---|---|---|
| 1 |  **2a-ol** | OD-H column, 40.1 °C<br>5% MeOH, 2 mL/min | 14.1 and 14.9 min | 97:3 |
| 2 |  **2b-ol** | AD-H column, 40.2 °C<br>5–15–50% MeOH, 2 mL/min | 5.2 and 5.7 min | 98:2 |
| 3 |  **2c-ol** | AD-H column, 39.9 °C<br>5–15–50% MeOH, 2 mL/min | 4.9 and 5.3 min | 98:2 |
| 4 |  **2d-ol** | AY-H column, 40.2 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 6.5 and 7.2 min | 97:3 |
| 5 |  **2e-ol** | AD-H column, 40.2 °C<br>5–15–50% MeOH, 2 mL/min | 4.8 and 5.4 min | 97:3 |
| 6 |  **2f-ester** | AD-H column, 38.9 °C<br>10% MeOH, 2 mL/min | 26.5 and 28.9 min | 97:3 |
| 7 |  **2g-ol** | AD-H column, 40.0 °C<br>5–15–50% MeOH, 2 mL/min | 9.8 and 13.4 min | 97:3 |
| 8 |  **2h-ol** | AD-H column, 40.0 °C<br>20% MeOH, 2 mL/min | 4.2 and 4.6 min | 97:3 |

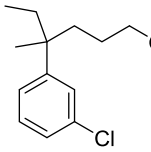
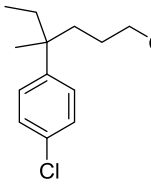
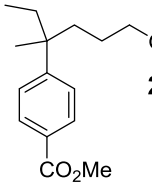
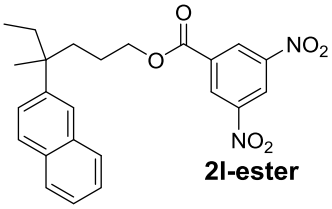
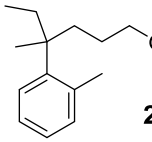
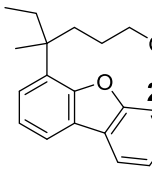
| entry | compound | conditions | retention time | er |
|---|---|---|---|---|
| 9 |  **2i-ol** | AY-H column, 39.9 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 5.4 and 6.2 min | 96:4 |
| 10 |  **2j-ol** | AY-H column, 39.9 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 5.8 and 6.4 min | 99:1 |
| 11 |  **2k-ol** | AY-H column, 26.7 °C<br>5–15–50% MeOH, 2 mL/min | 8.4 and 8.7 min | 99:1 |
| 12 |  **2l-ester** | AD-H column, 39.3 °C<br>20% MeOH, 2 mL/min | 14.4 and 15.8 min | 98:2 |
| 13 |  **2m-ol** | OJ-H column, 40.3 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 6.8 and 7.4 min | 99:1 |
| 14 |  **2n-ol** | AY-H column, 40.0 °C<br>5% MeOH, 2 mL/min | 8.7 and 10.2 min | 97:3 |

**Table S9** Products shown in Figure 2b

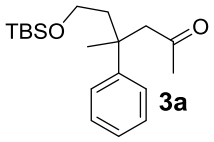
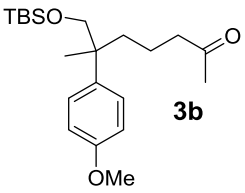
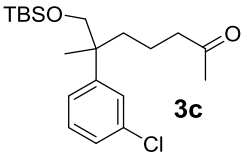
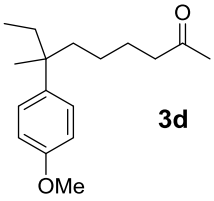
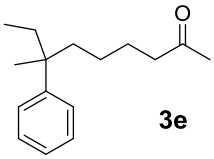
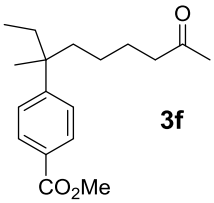
| entry | compound | conditions | retention time | er |
|---|---|---|---|---|
| 1 |  **3a** | OJ-H column, 39.8 °C<br>2% *i*-PrOH, 2 mL/min | 2.9 and 3.9 min | 96:4 |
| 2 |  **3b** | AY-H column, 40.2 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 8.9 and 9.4 min | 93:7 |
| 3 |  **3c** | AY-H column, 40.3 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 7.7 and 8.0 min | 94:6 |
| 4 |  **3d** | AY-H column, 39.8 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 7.0 and 7.7 min | 94.5:5.5 |
| 5 |  **3e** | AD-H column, 26.7 °C<br>5–15–50% MeOH, 2 mL/min | 4.2 and 4.6 min | 97:3 |
| 6 |  **3f** | AY-H column, 39.8 °C<br>5–15–50% *i*-PrOH, 2 mL/min | 3.5 and 4.4 min | 99:1 |

**Table S10** Products shown in Figure 2c and product for X-ray analysis

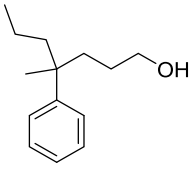
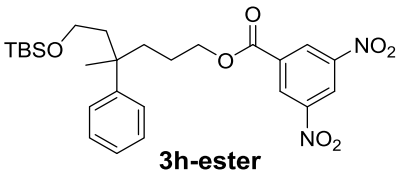
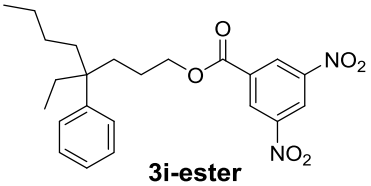
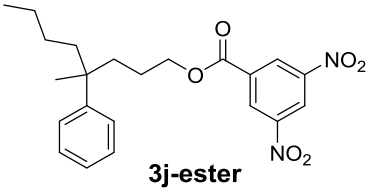
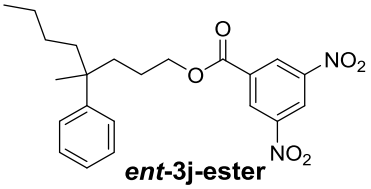
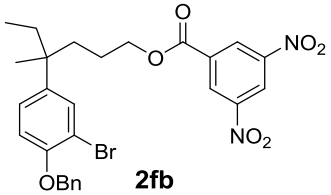
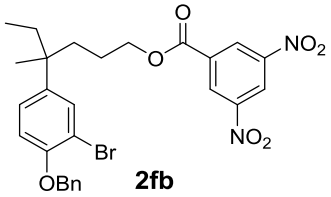
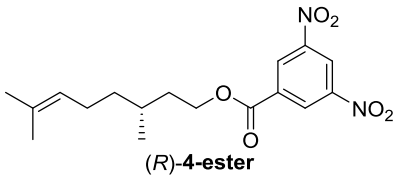
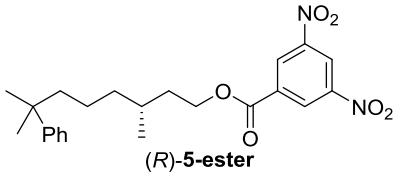
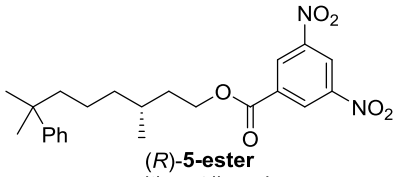
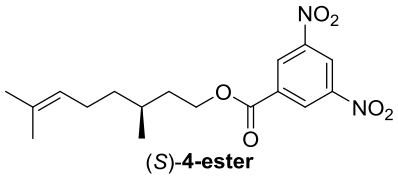
| entry | compound | conditions | retention time | er |
|---|---|---|---|---|
| 1 |  **3g-ol** | AD-H column, 40.2 °C<br>5–15–50% MeOH, 2 mL/min | 4.8 and 5.1 min | 99:1 |
| 2 |  **3h-ester** | AY-H column, 39.8 °C<br>5% MeOH, 2 mL/min | 14.2 and 14.7 min | 99:1 |
| 3 |  **3i-ester** | AD-H column, 40.1 °C<br>5% MeOH, 2 mL/min | 19.4 and 20.6 min | 97:3 |
| 4 |  **3j-ester** | AD-H column, 40.2 °C<br>5% MeOH, 2 mL/min | 18.9 and 21.3 min | 98:2 |
| 5 |  ***ent*-3j-ester** | AD-H column, 40.2 °C<br>5% MeOH, 2 mL/min | 18.9 and 21.3 min | 98:2 |
| 6 |  **2fb** | AY-H column, 39.7 °C<br>5-50% MeOH, 2 mL/min | 9.8 and 10.2 min | 97:3 |
| 7 |  **2fb**<br>(from single crystals) | AY-H column, 39.7 °C<br>5-50% MeOH, 2 mL/min | 9.8 and 10.2 min | >99:1 |

**Table S11** Products shown in Figure 3

| entry | compound | conditions | retention time | er |
|---|---|---|---|---|
| 1 |  (*R*)-**4-ester** | AD-H column, 40.0 °C<br>15% MeOH, 2 mL/min | 8.3 and 9.0 min | >99:1 |
| 2 |  (*R*)-**5-ester** | AY-H column, 40.0 °C<br>5% *i*-PrOH, 2 mL/min | 18.7 and 20.8 min | >99:1 |
| 3 |  (*R*)-**5-ester**<br>with *ent*-ligand | AY-H column, 40.0 °C<br>5% *i*-PrOH, 2 mL/min | 18.7 and 20.8 min | >99:1 |
| 4 |  (*S*)-**4-ester** | AD-H column, 40.0 °C<br>15% MeOH, 2 mL/min | 8.3 and 9.0 min | 99:1 |

## 3. References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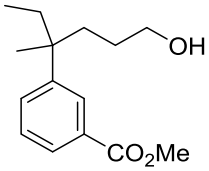
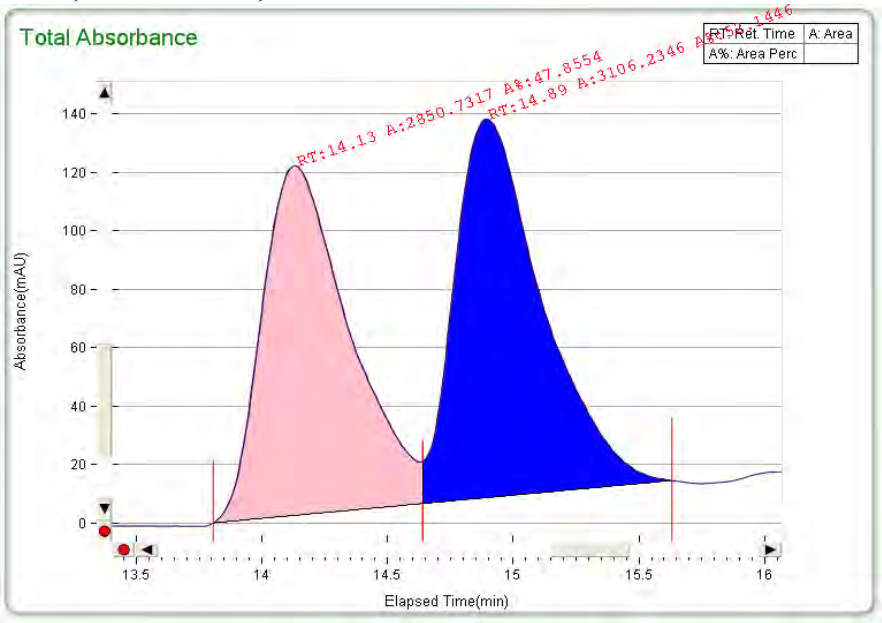
## 4. Chiral separations

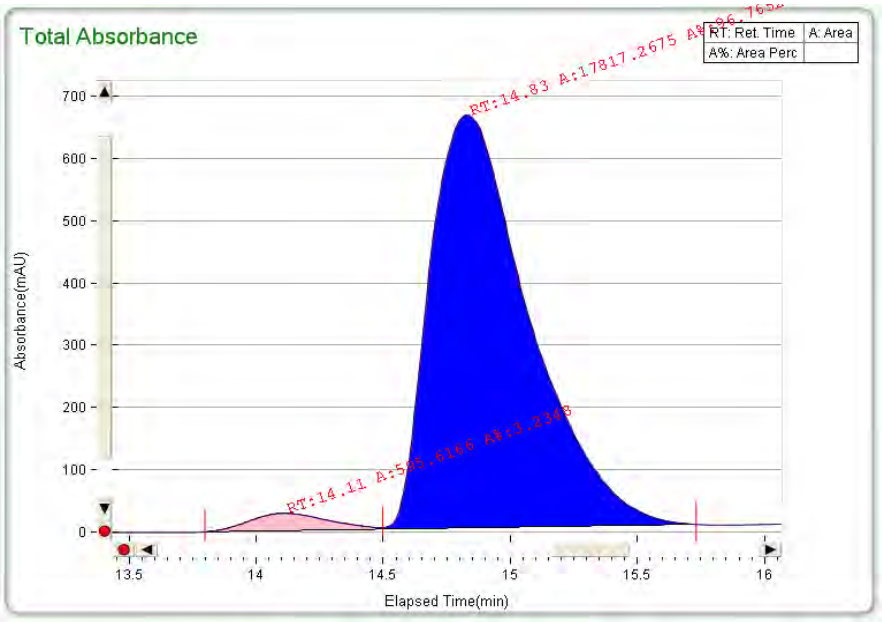



**2a-ol**

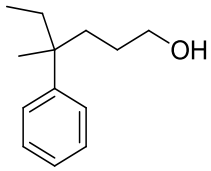
Separation of enantiomers by SFC. Chiralcel® OD-H, 5:95 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.1 °C; $t_1$ = 14.1 min, $t_2$ = 14.9 min.




**(±)-2a-ol**

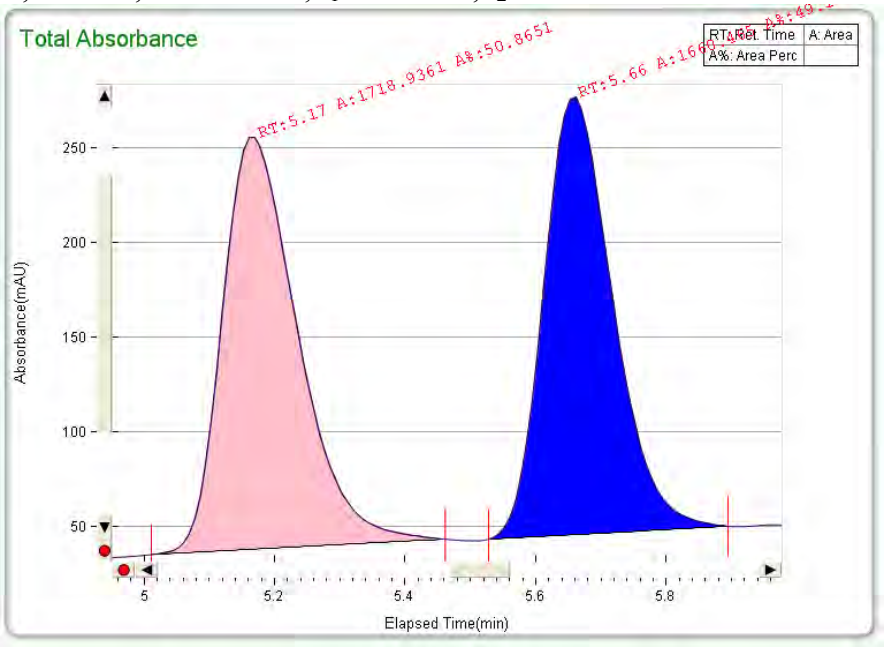



**2a-ol**

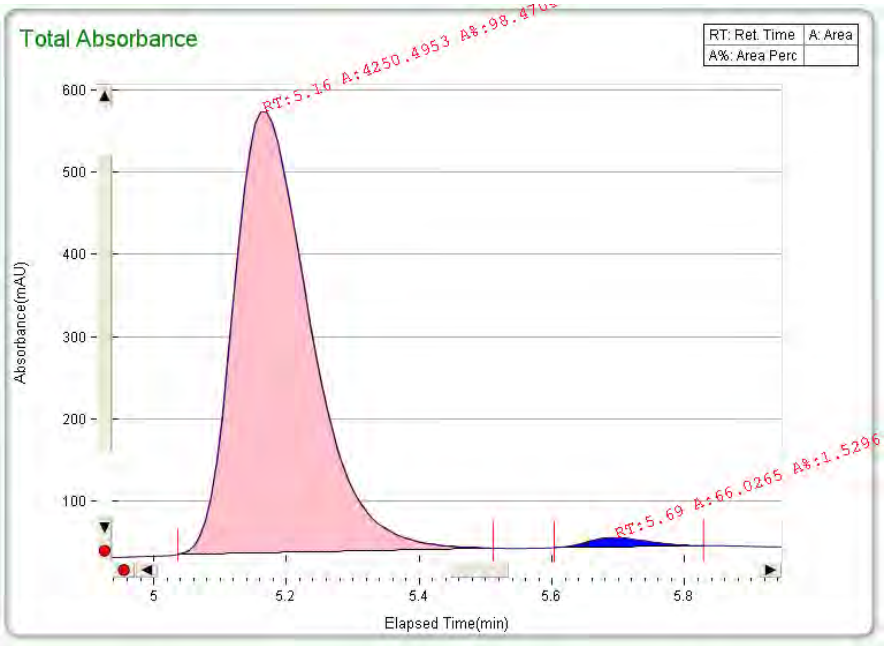



**2b-ol**

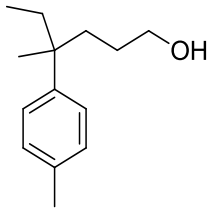
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 5.2 min, $t_2$ = 5.7 min.




**(±)-2b-ol**

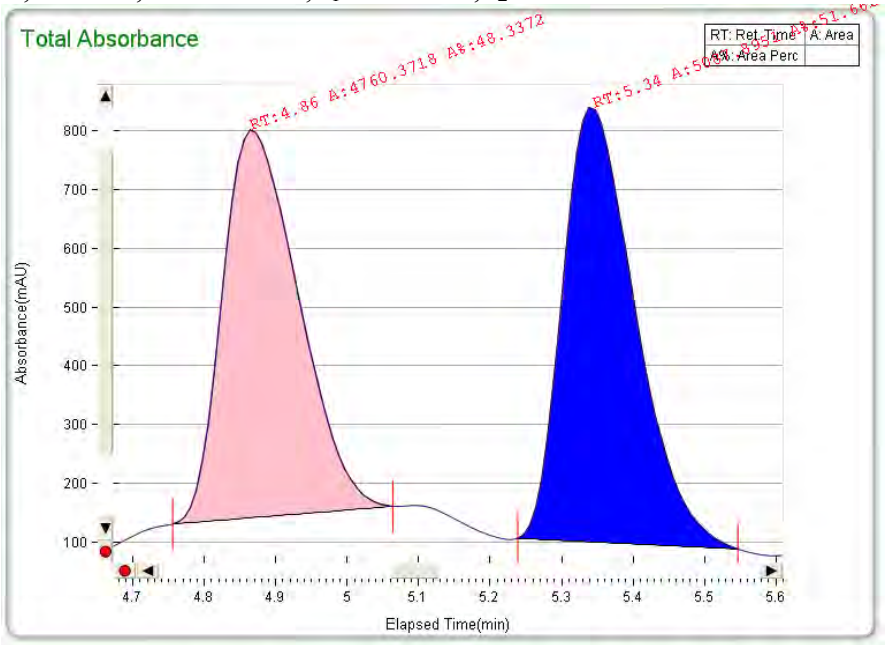



**2b-ol**

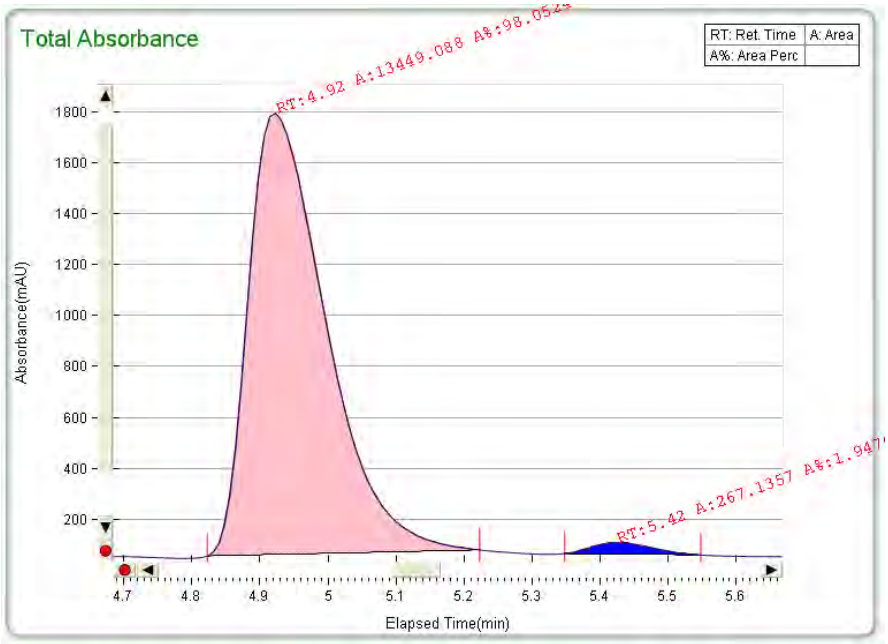



**2c-ol**

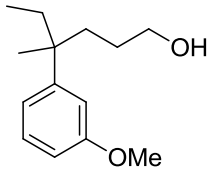
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 39.9 °C; $t_1$ = 4.9 min, $t_2$ = 5.3 min.




**(±)-2c-ol**

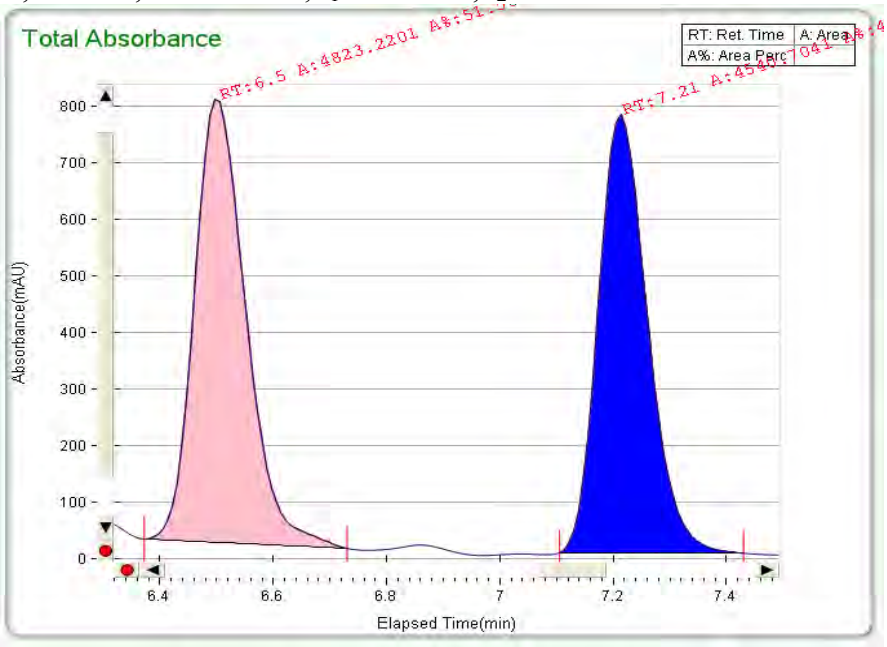



**2c-ol**

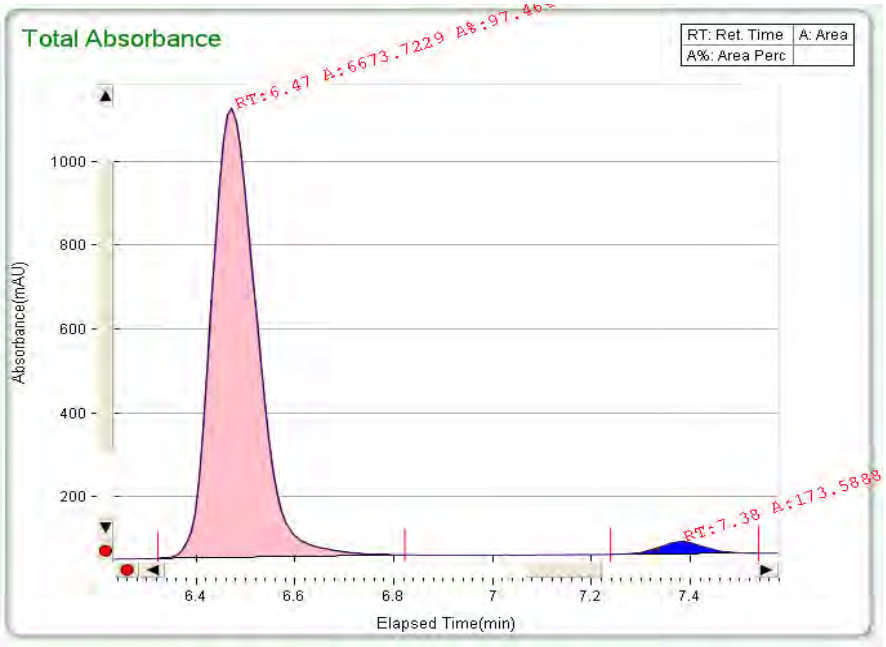



**2d-ol**

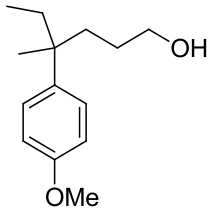
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 6.5 min, $t_2$ = 7.2 min.




(±)-**2d-ol**

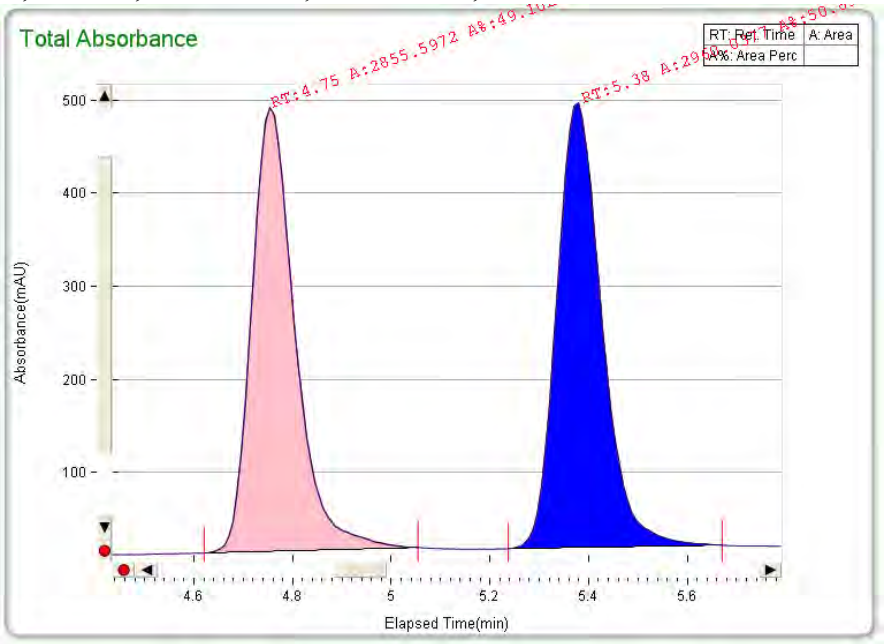



**2d-ol**

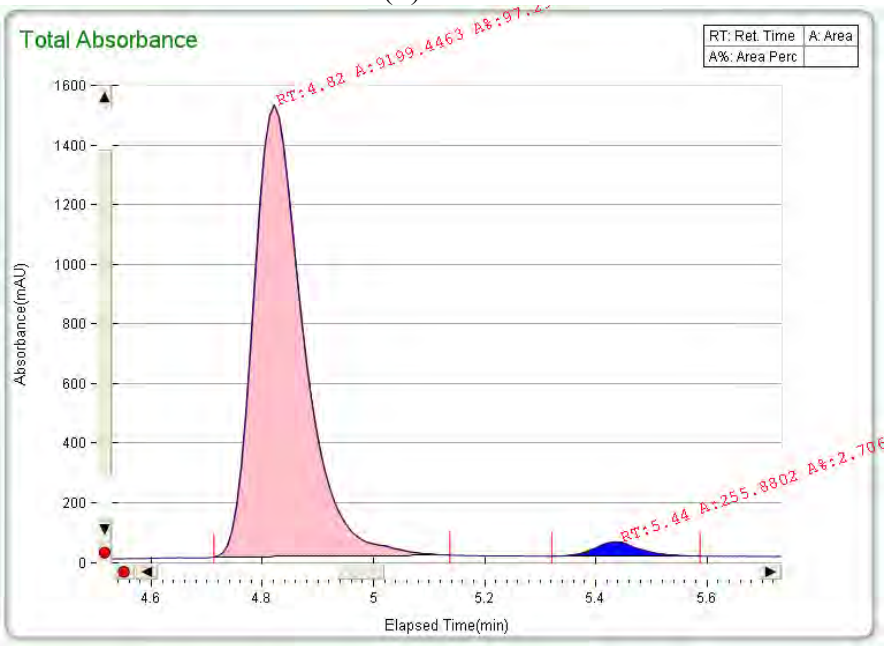



**2e-ol**

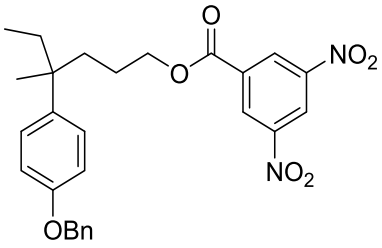
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 4.8 min, $t_2$ = 5.4 min.




(±)-**2e-ol**

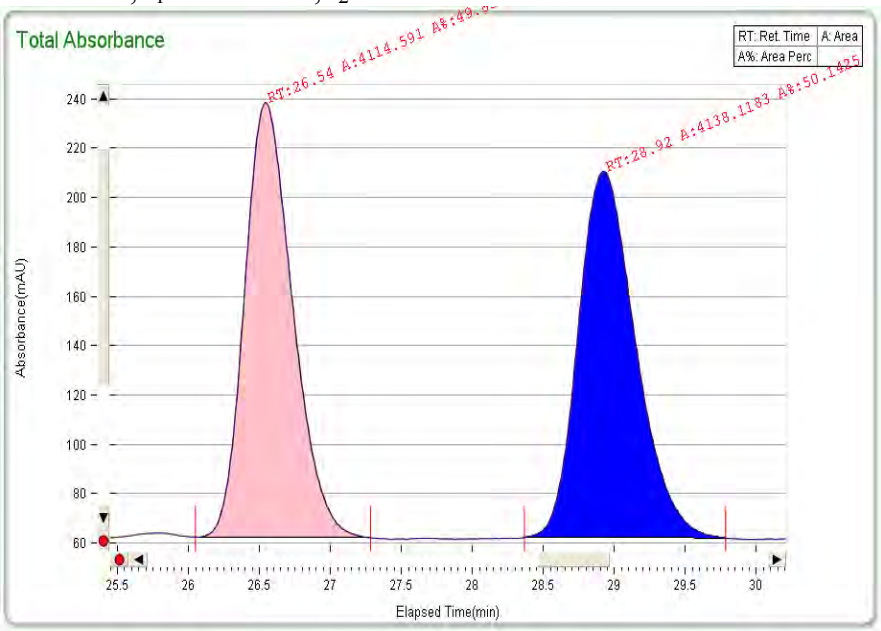



**2e-ol**

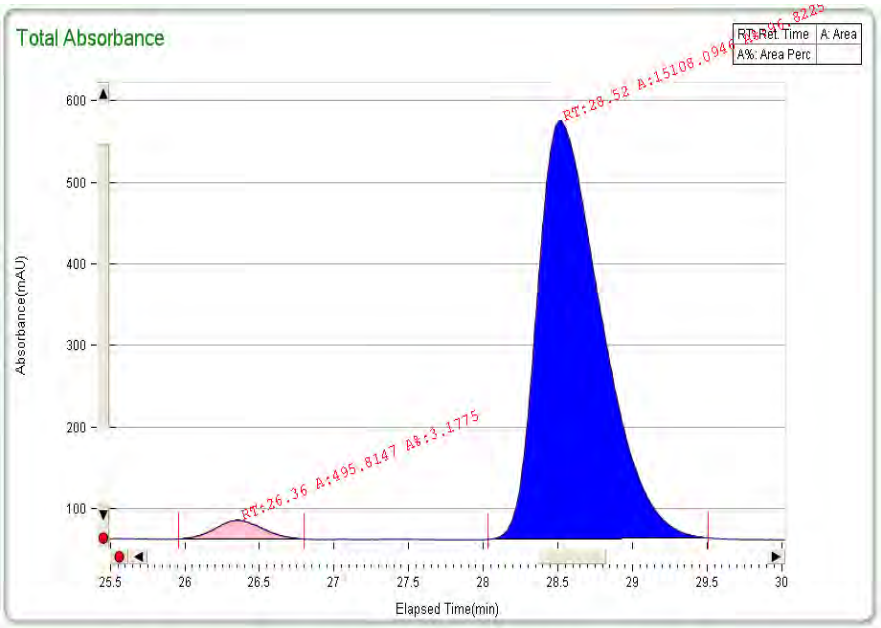



**2f-ester**

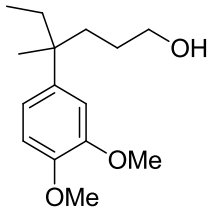
Separation of enantiomers by SFC. Chiralcel® AD-H, 10:90 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 38.9 °C; $t_1$ = 26.5 min, $t_2$ = 28.9 min.




(±)-**2f-ester**

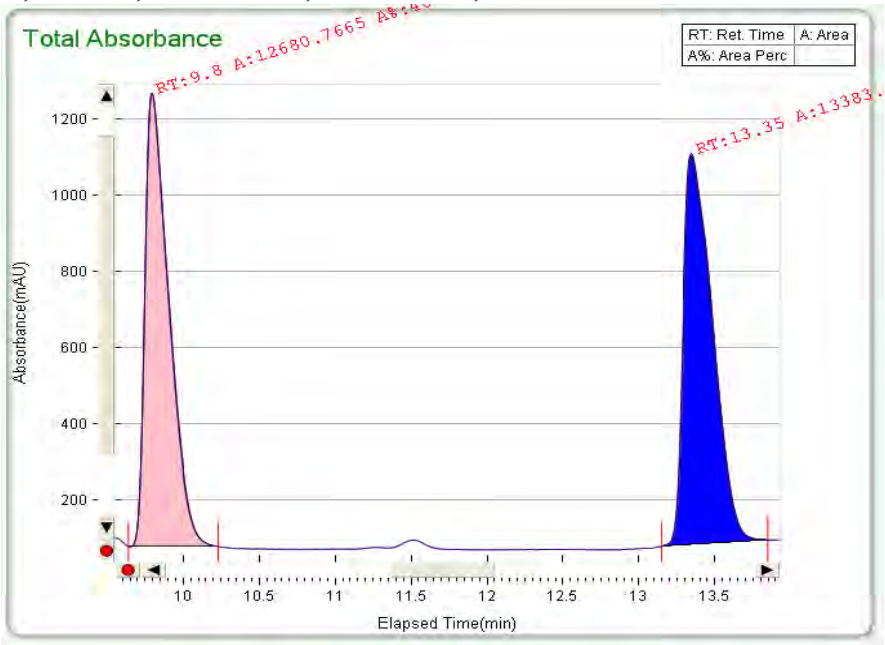



**2f-ester**

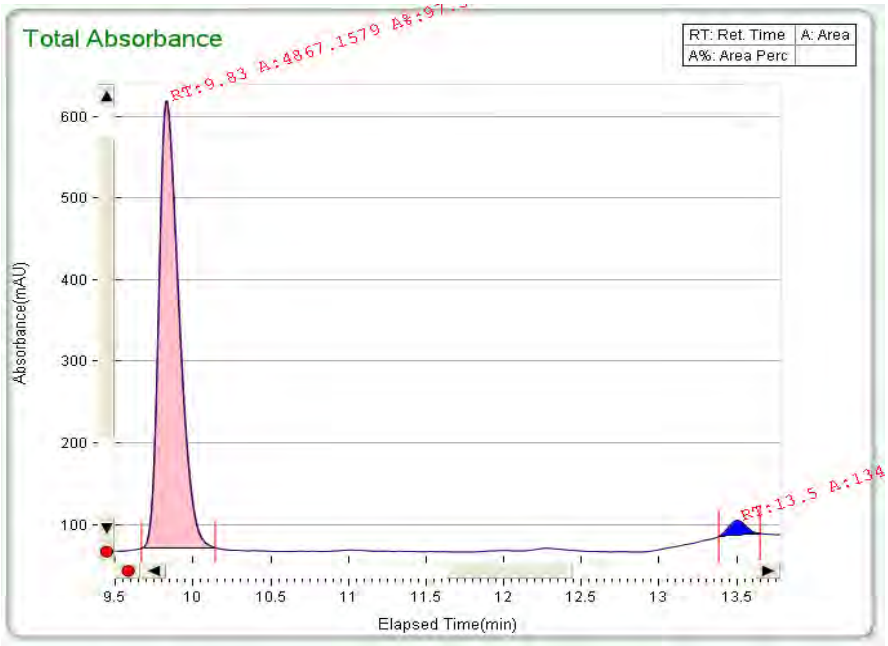



**2g-ol**

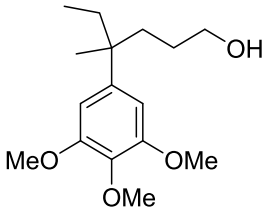
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.0 °C; $t_1$ = 9.8 min, $t_2$ = 13.4 min.




(±)-**2g-ol**

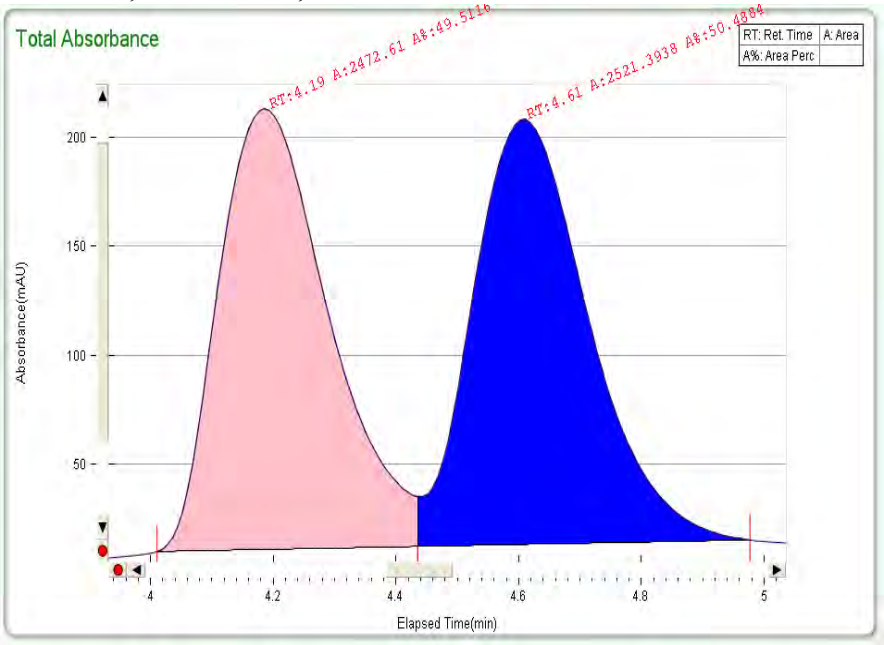



**2g-ol**

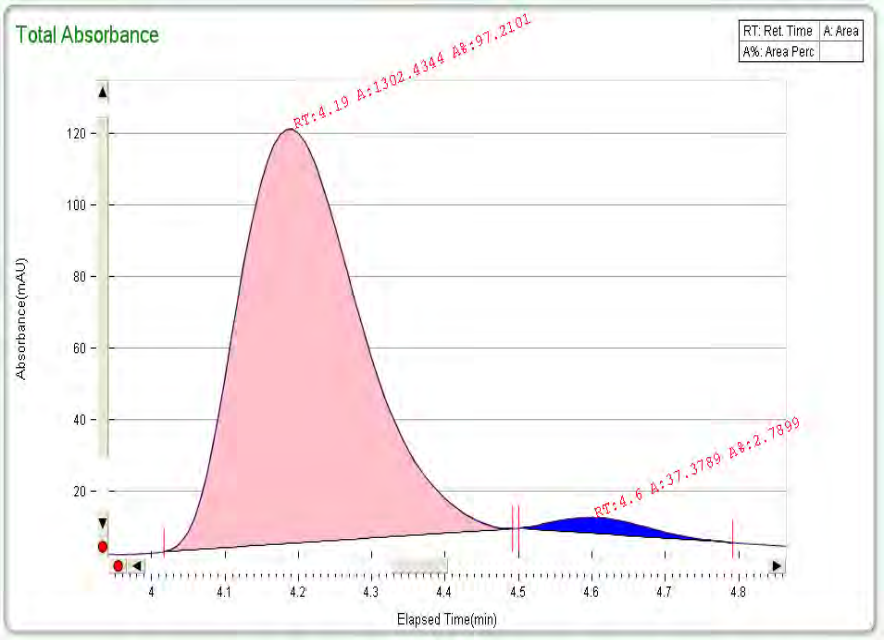



**2h-ol**

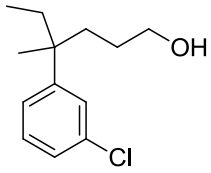
Separation of enantiomers by SFC. Chiralcel® AD-H, 20:80 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.0 °C; $t_1$ = 4.2 min, $t_2$ = 4.6 min.




(±)-**2h-ol**

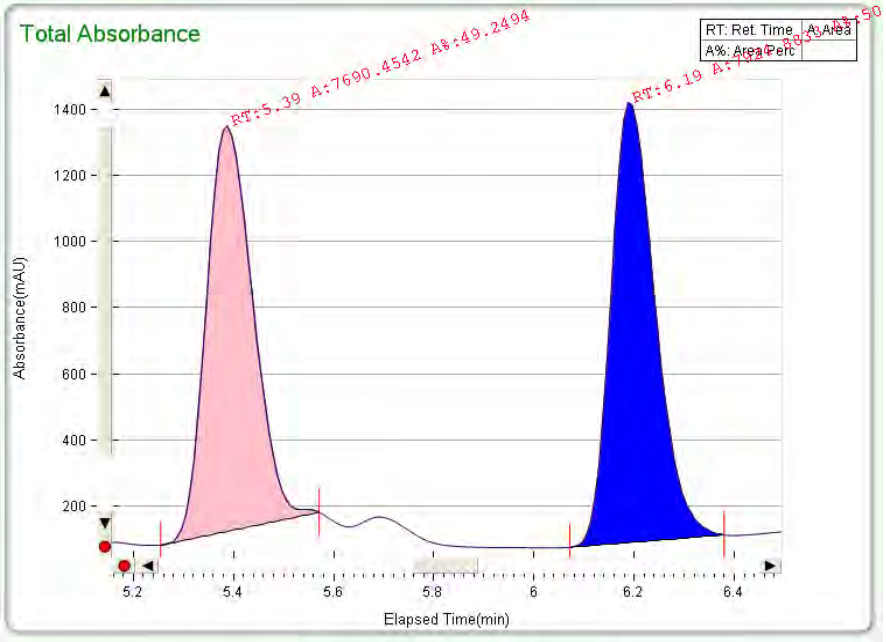



**2h-ol**

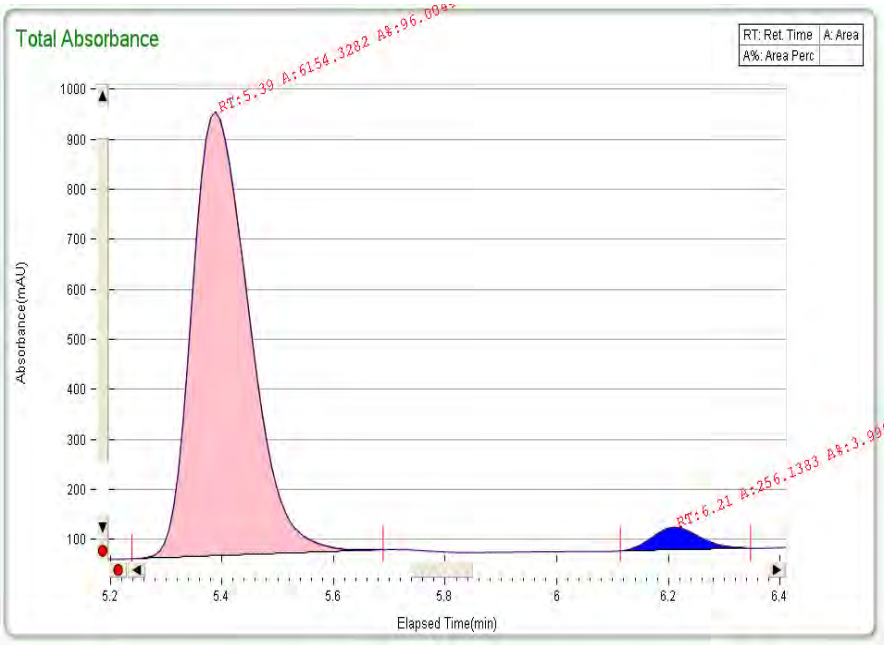



**2i-ol**

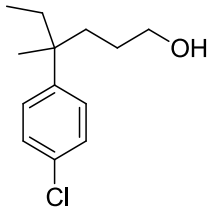
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 39.9 °C; $t_1$ = 5.4 min, $t_2$ = 6.2 min.




(±)-**2i-ol**

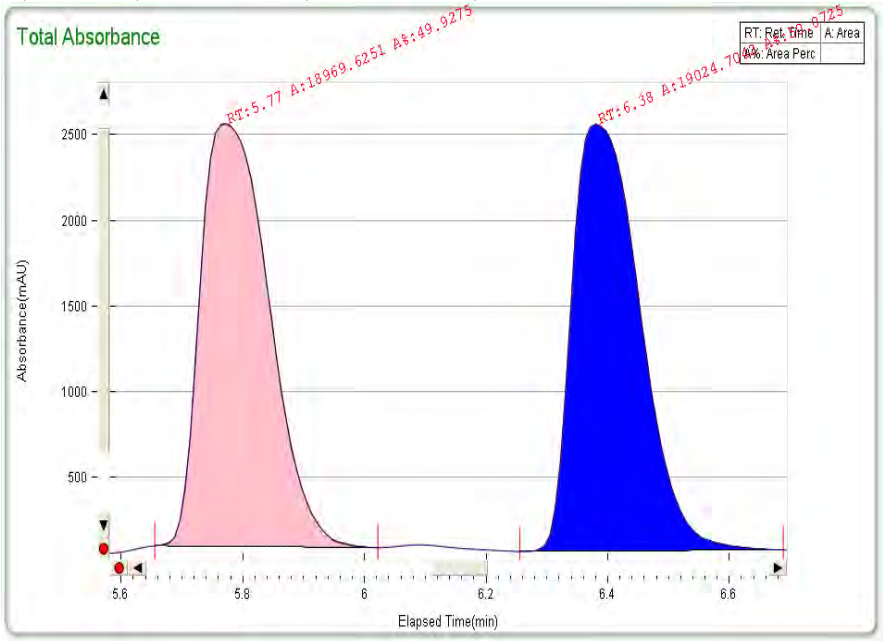



**2i-ol**

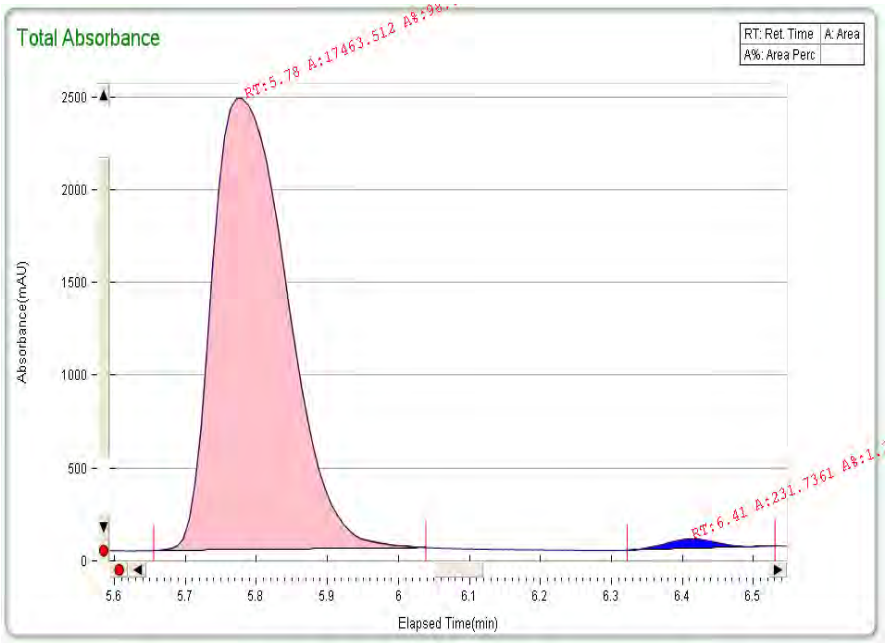



**2j-ol**

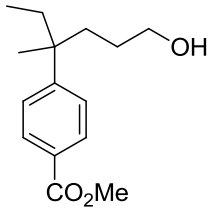
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 39.9 °C; $t_1$ = 5.8 min, $t_2$ = 6.4 min.




(±)-**2j-ol**

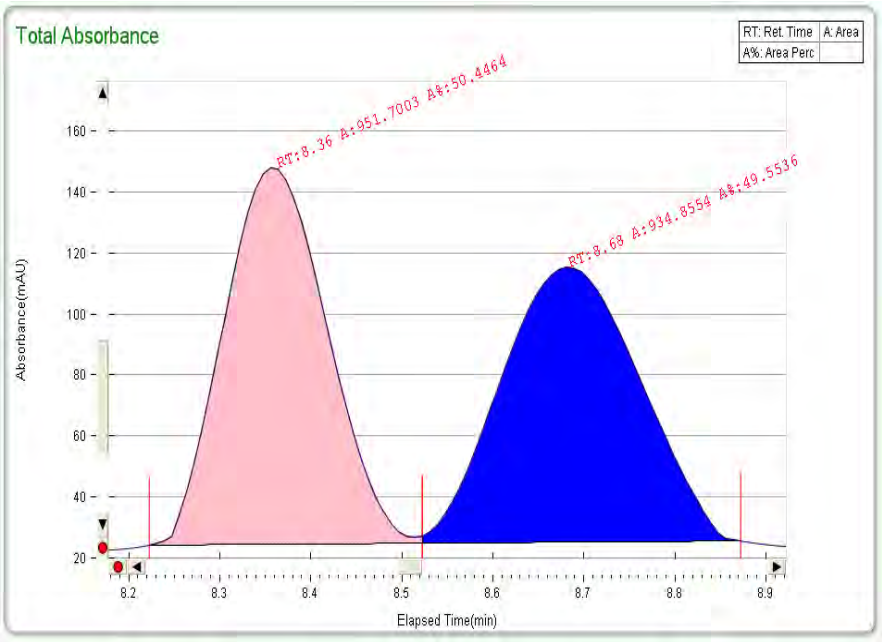



**2j-ol**

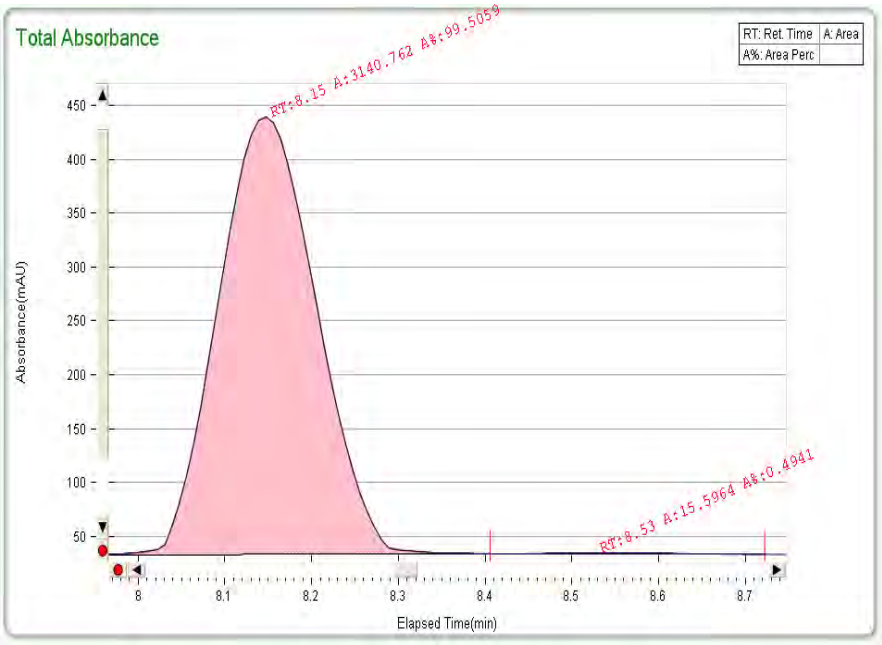



**2k-ol**

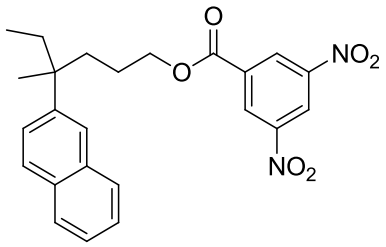
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 26.7 °C; $t_1$ = 8.4 min, $t_2$ = 8.7 min.




(±)-**2k-ol**

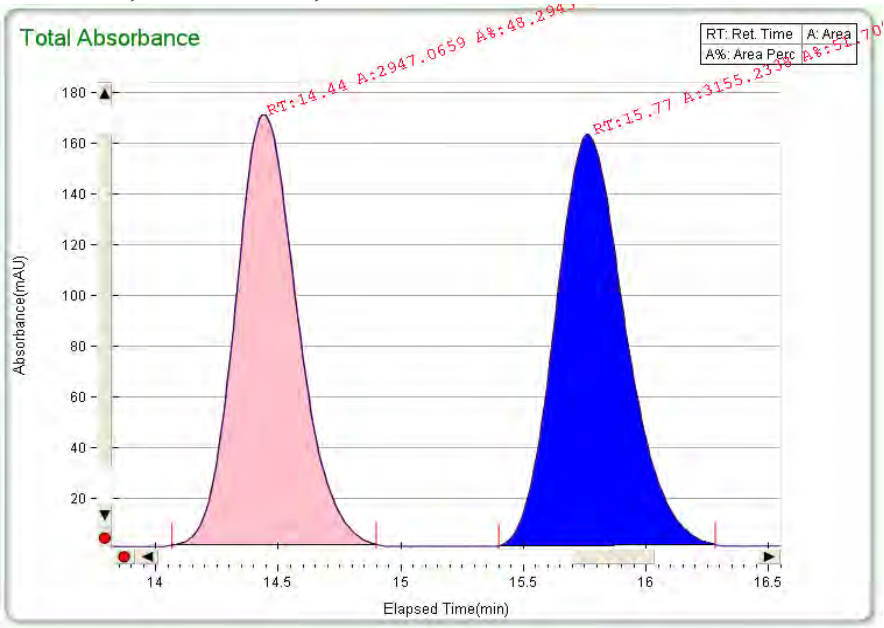



**2k-ol**

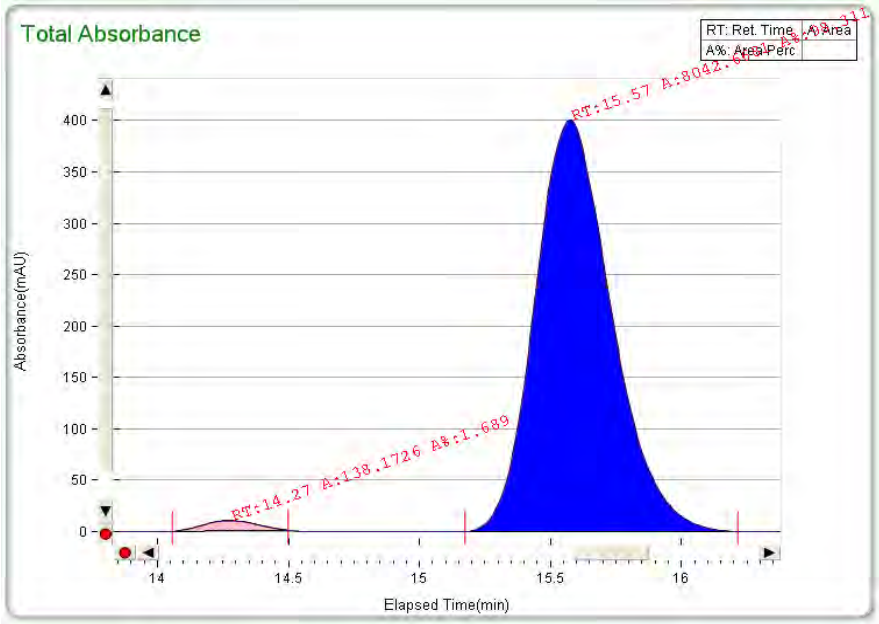



**2l-ester**

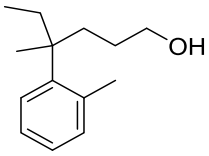
Separation of enantiomers by SFC. Chiralcel® AD-H, 20:80 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 39.3 °C; $t_1$ = 14.4 min, $t_2$ = 15.8 min.




(±)-**2l-ester**

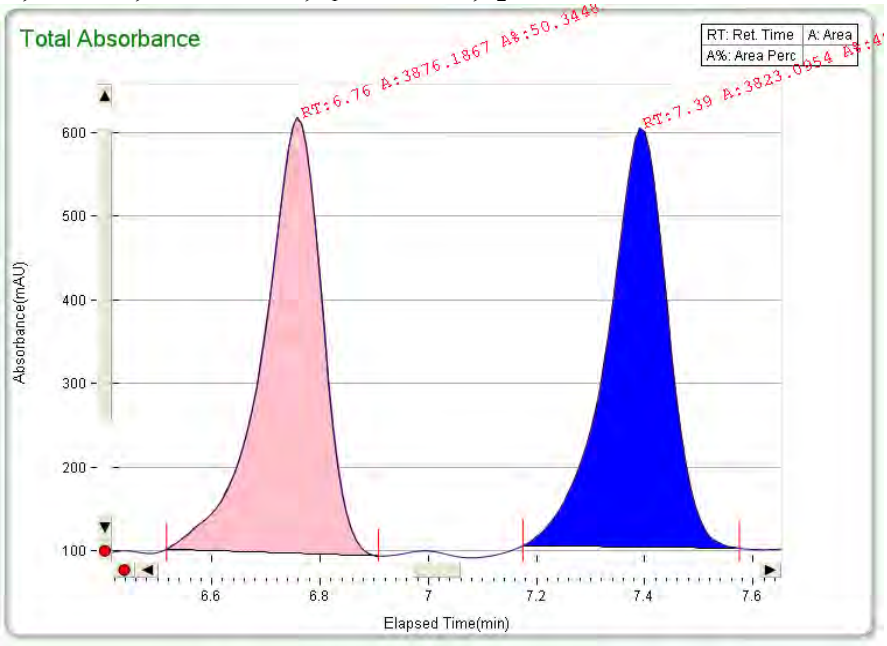



**2l-ester**

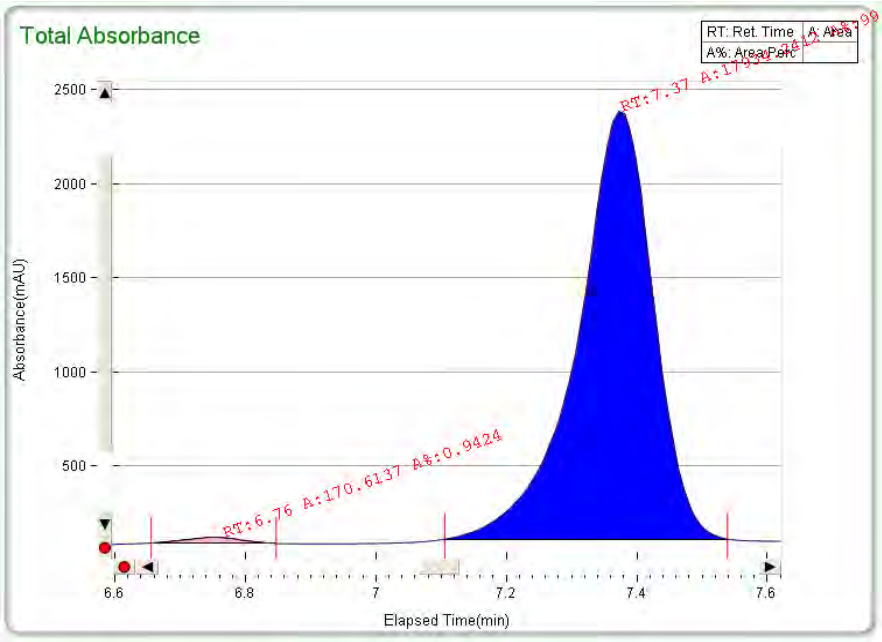



**2m-ol**

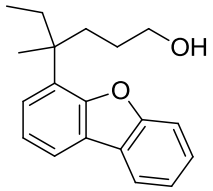
Separation of enantiomers by SFC. Chiralcel® OJ-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 40.3 °C; $t_1$ = 6.8 min, $t_2$ = 7.4 min




(±)-**2m-ol**

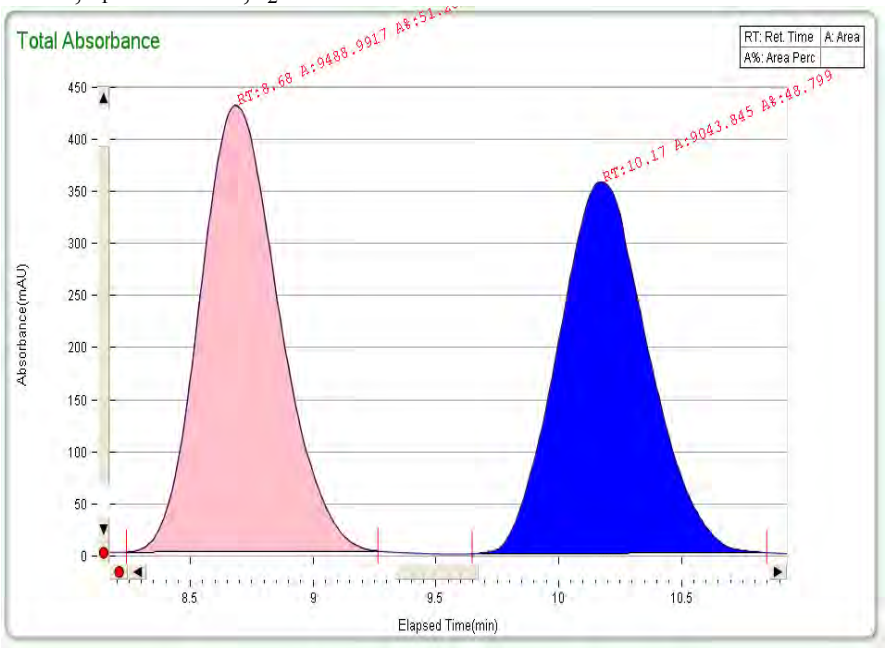



**2m-ol**

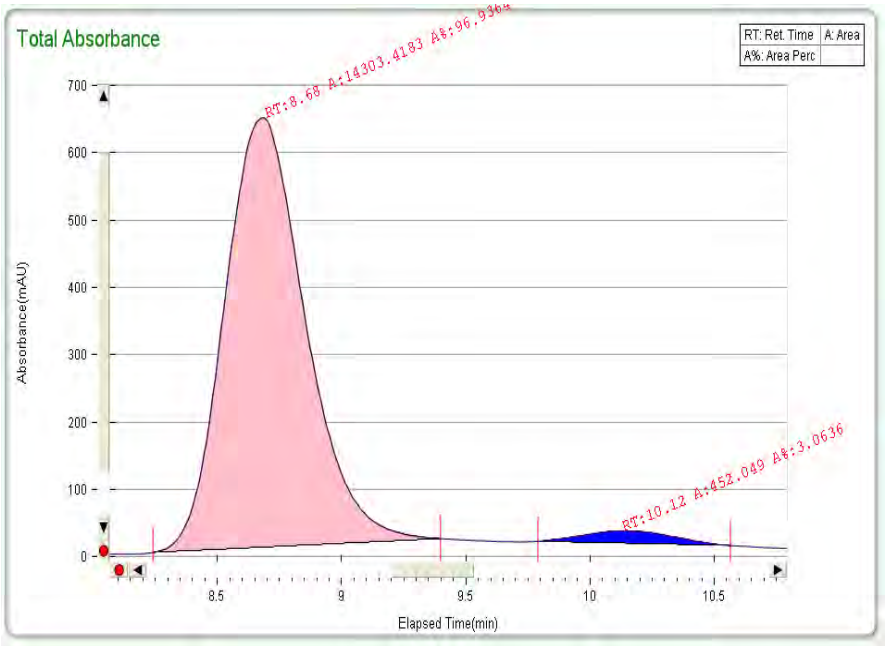



**2n-ol**

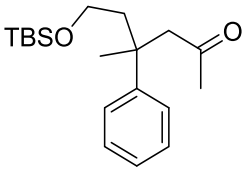
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.0 °C; $t_1$ = 8.7 min, $t_2$ = 10.2 min




(±)-**2n-ol**

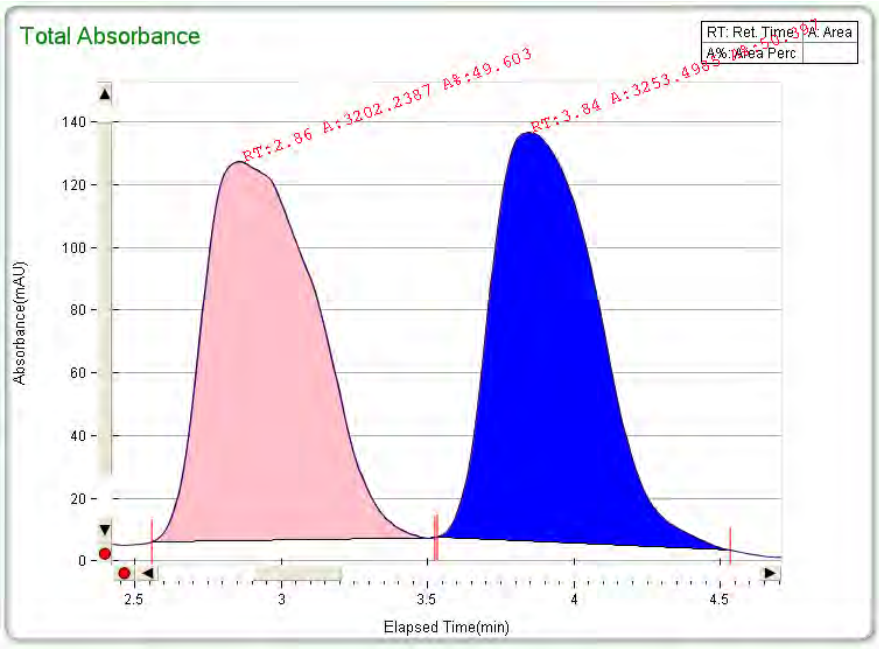



**2n-ol**

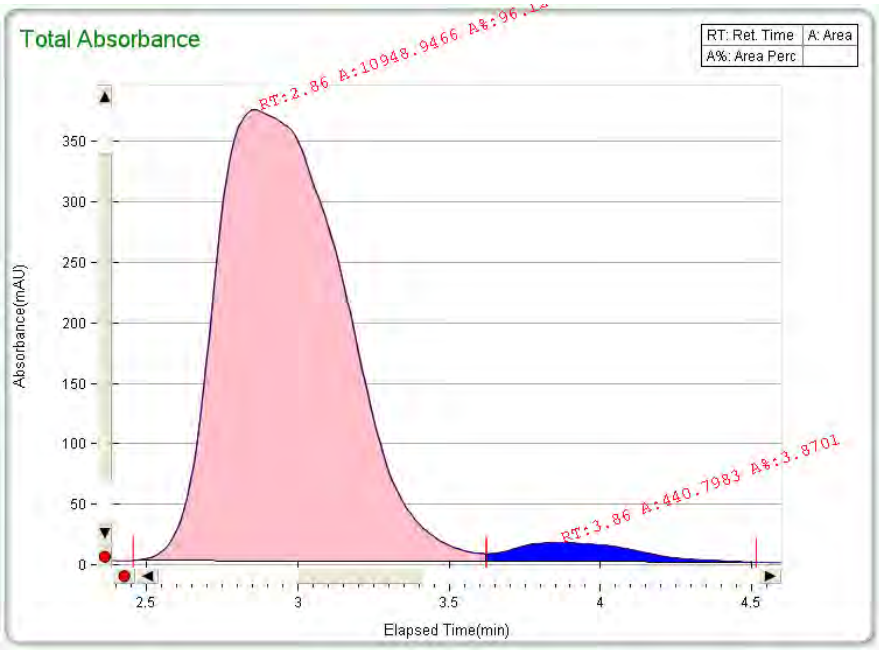



**3a**

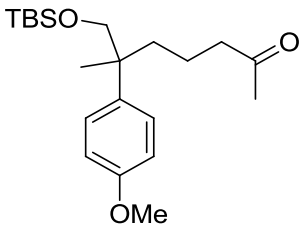
Separation of enantiomers by SFC. Chiralcel® OJ-H, 2:98 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 39.8 °C; $t_1$ = 2.9 min, $t_2$ = 3.8 min.




(±)-**3a**

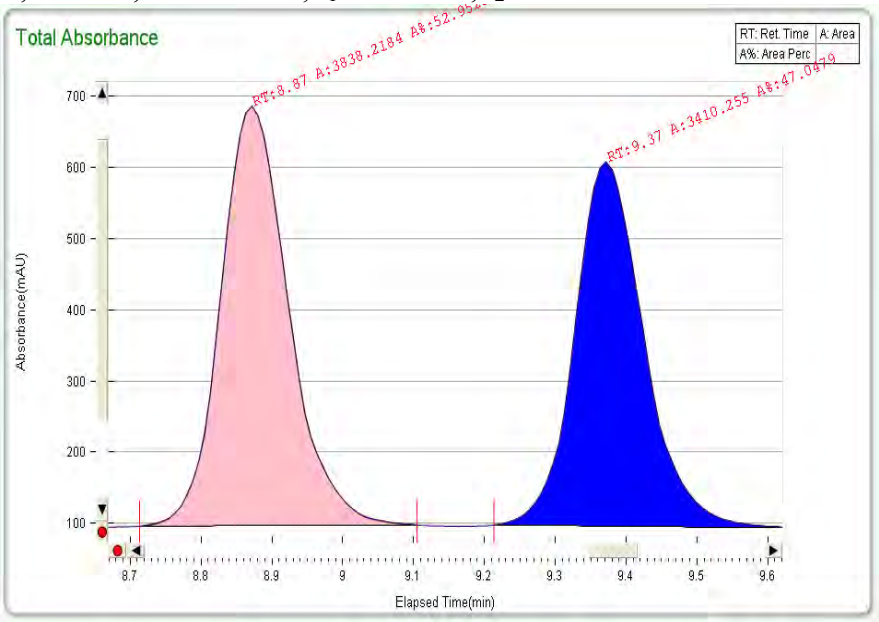



**3a**

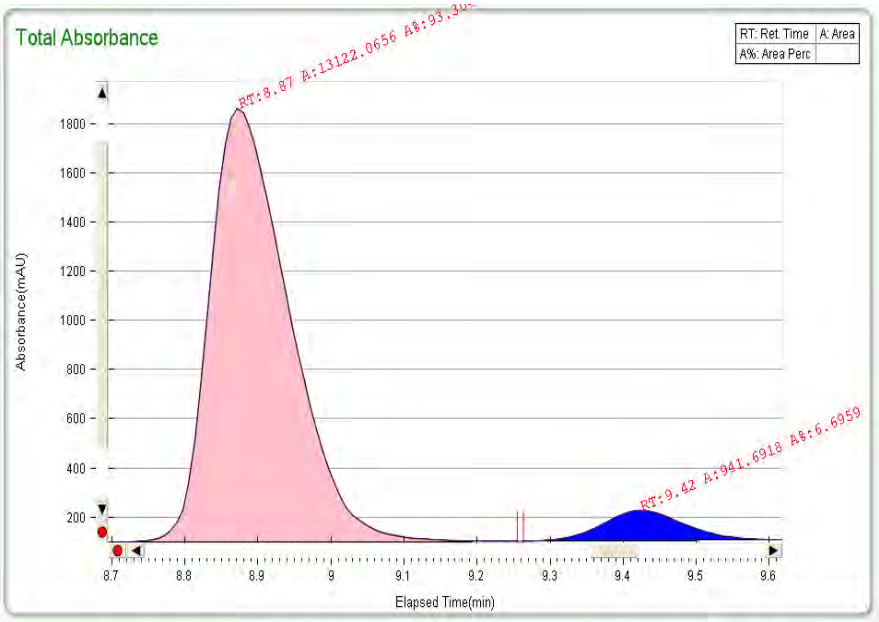



**3b**

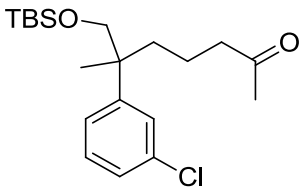
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 8.9 min, $t_2$ = 9.4 min.




(±)-**3b**

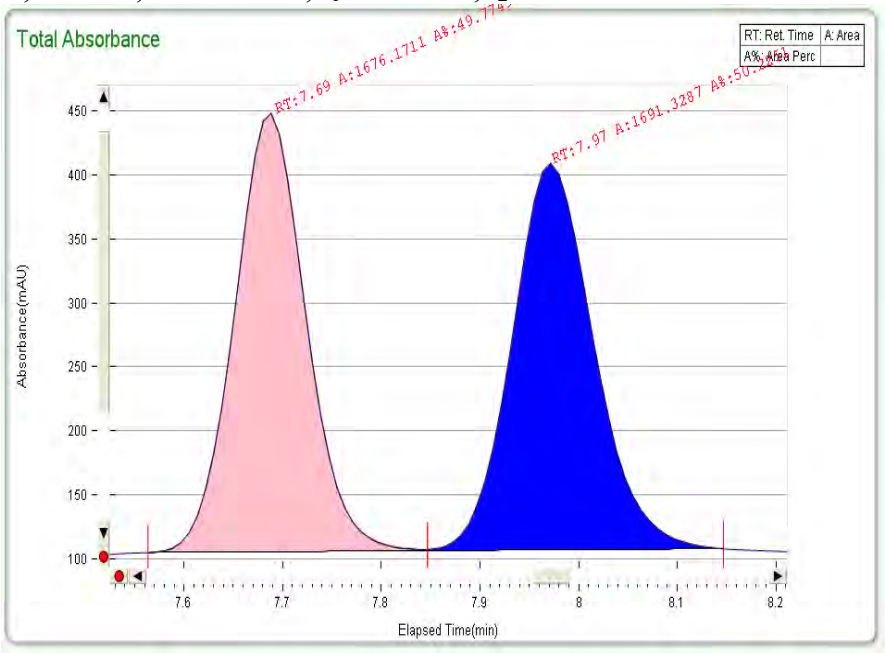



**3b**

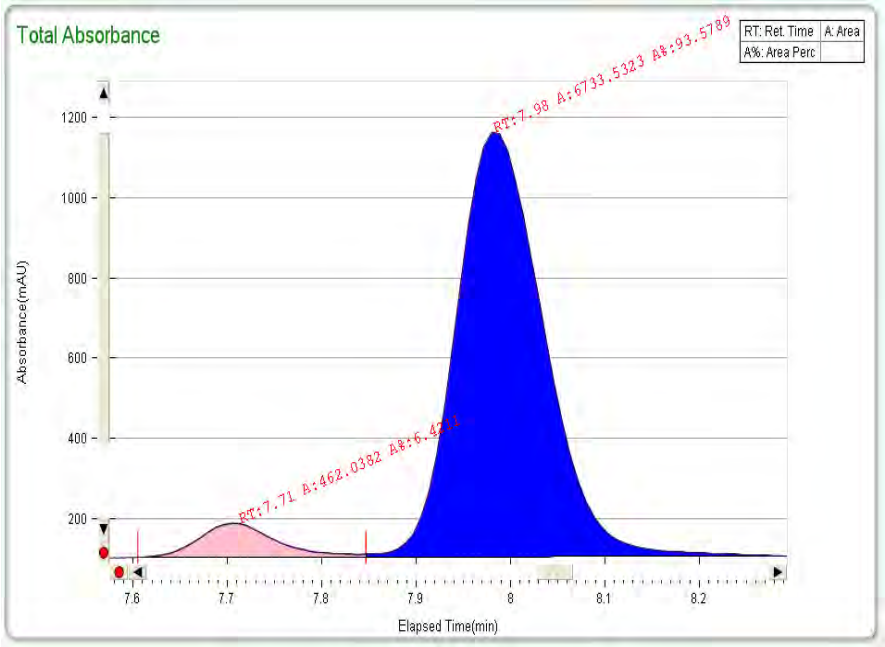



**3c**

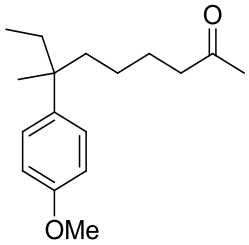
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 40.3 °C; $t_1$ = 7.7 min, $t_2$ = 8.0 min.




(±)-**3c**

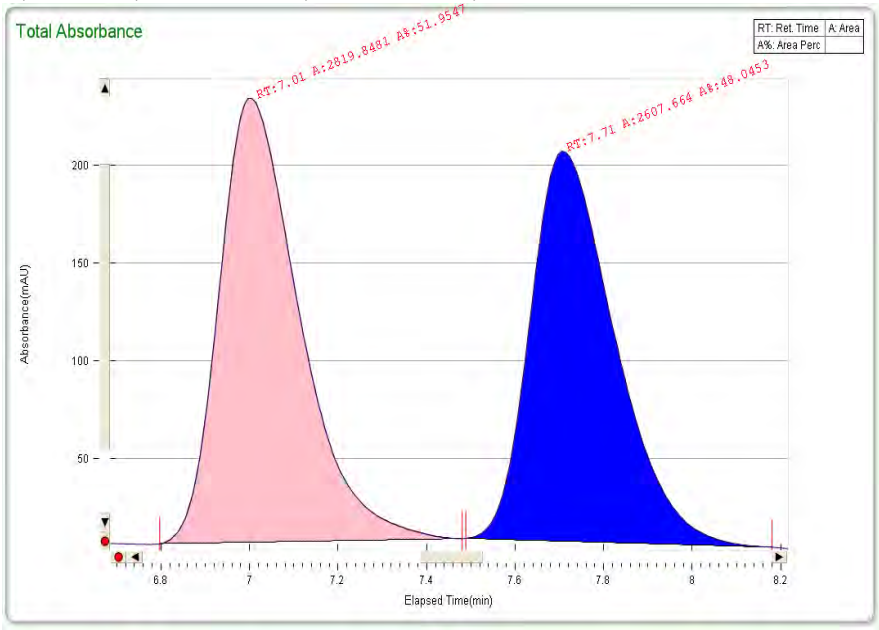



**3c**

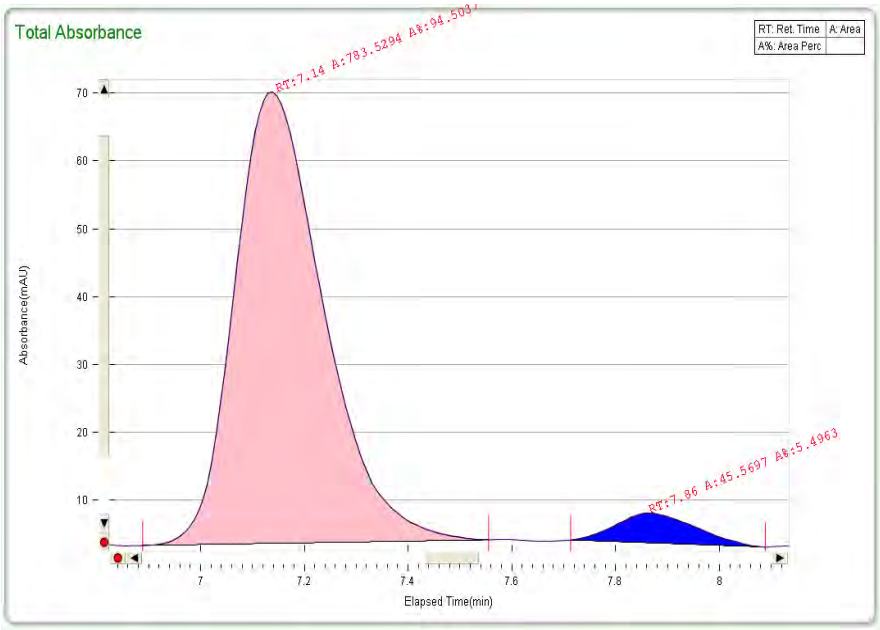



**3d**

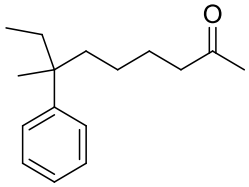
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 39.8 °C; $t_1$ = 7.0 min, $t_2$ = 7.7 min.




(±)-**3d**

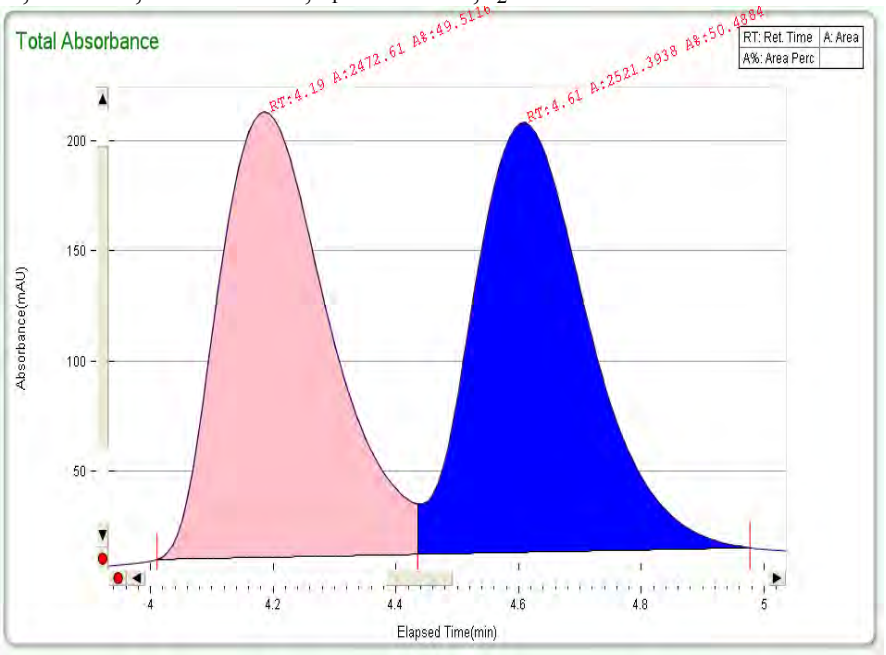



**3d**

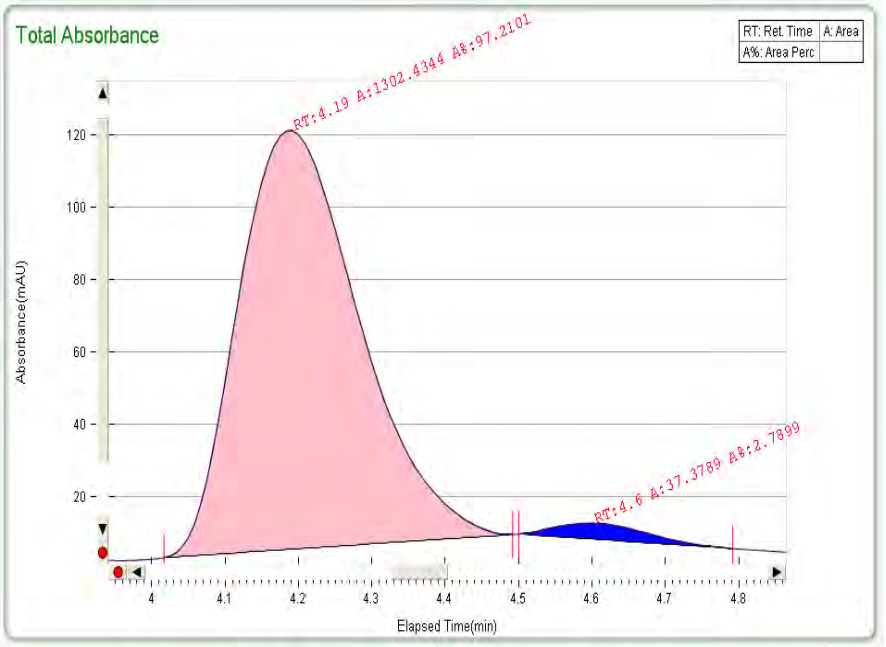


**3e**

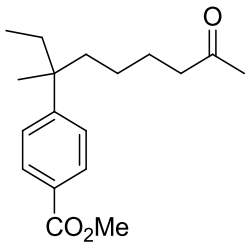
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 26.7 °C; $t_1$ = 4.2 min, $t_2$ = 4.6 min.




(±)-**3e**

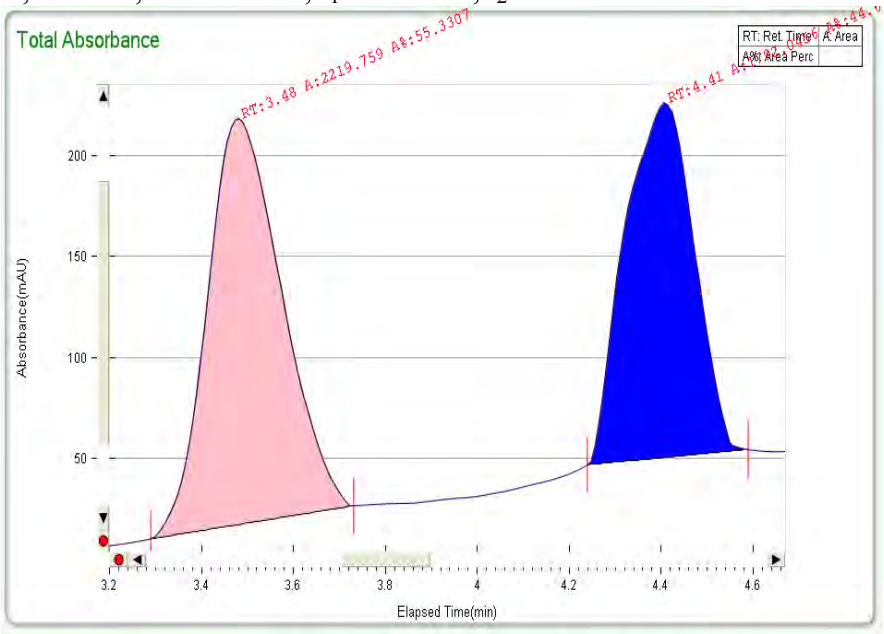



**3e**

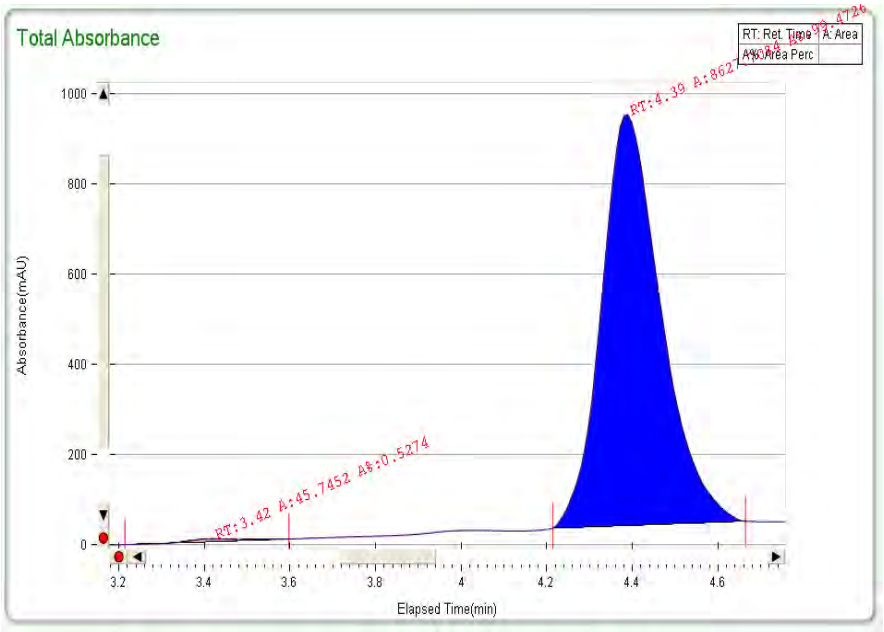



**3f**

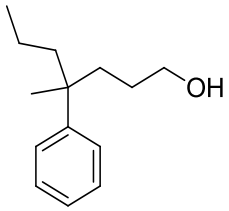
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→15:85→50:50 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 39.8 °C; $t_1$ = 3.5 min, $t_2$ = 4.4 min.




(±)-**3f**

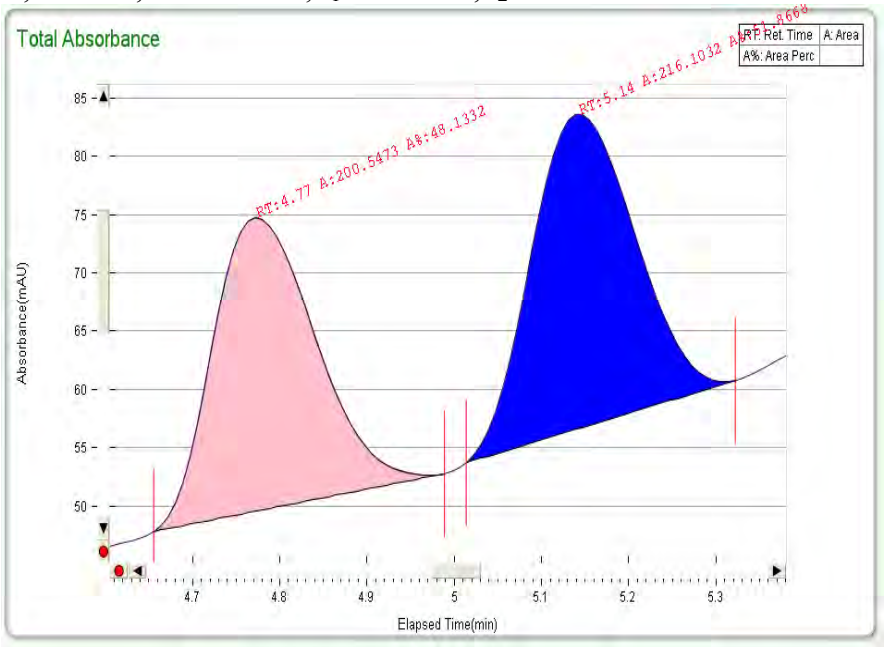



**3f**

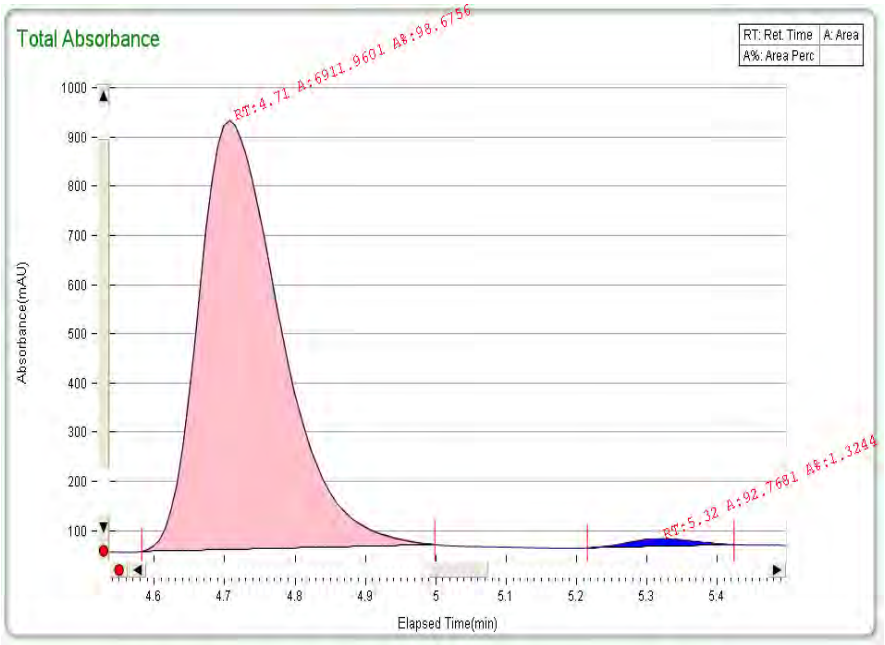



**3g-ol**

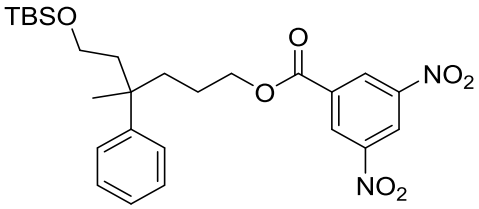
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95→15:85→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 4.8 min, $t_2$ = 5.1 min.




(±)-**3g-ol**

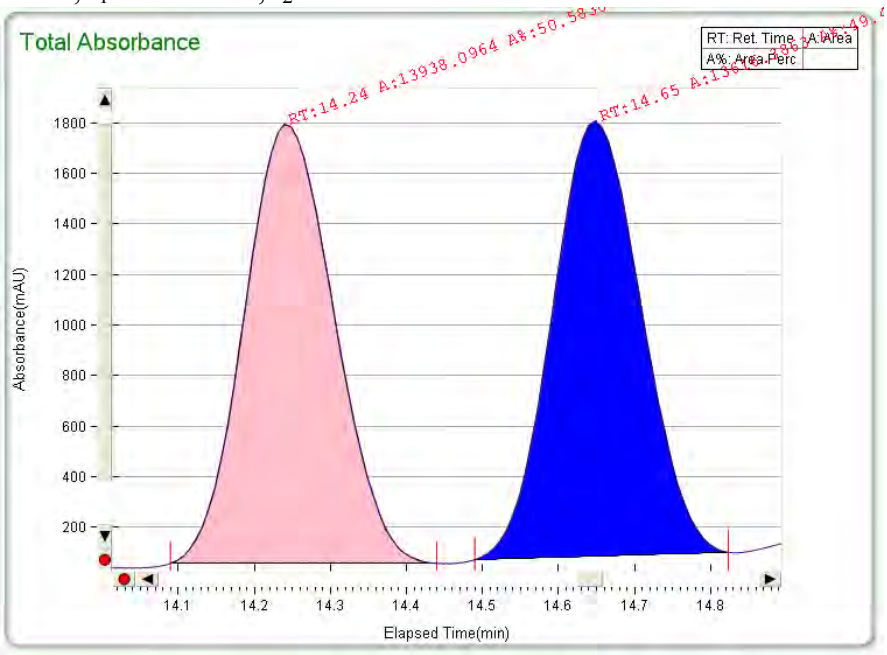



**3g-ol**

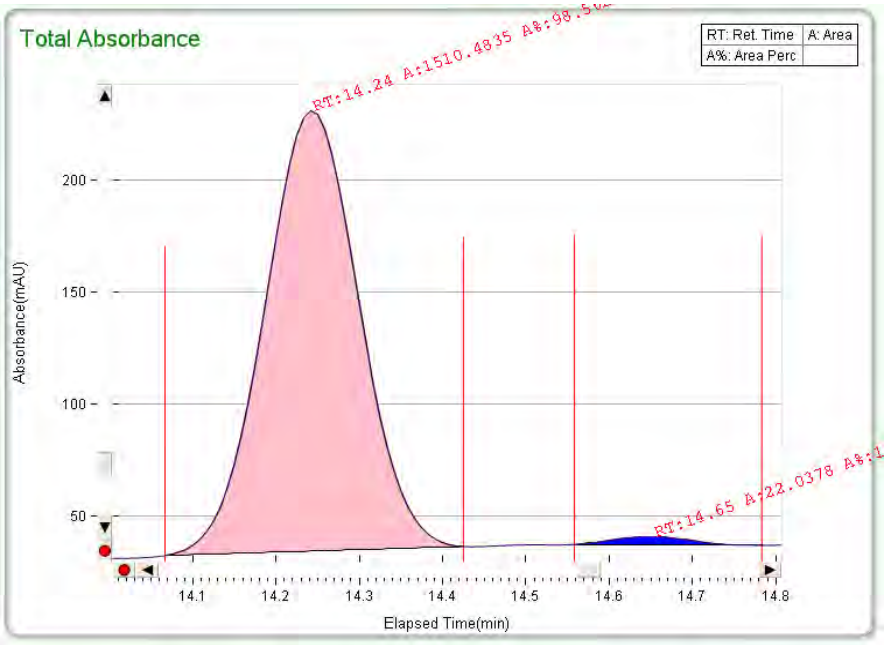



**3h-ester**

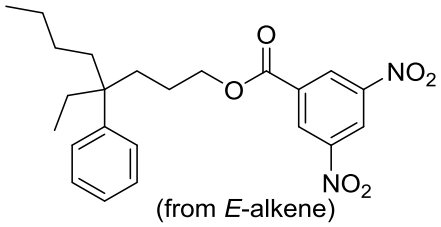
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 39.8 °C; $t_1$ = 14.2 min, $t_2$ = 14.7 min.




(±)-**3h-ester**



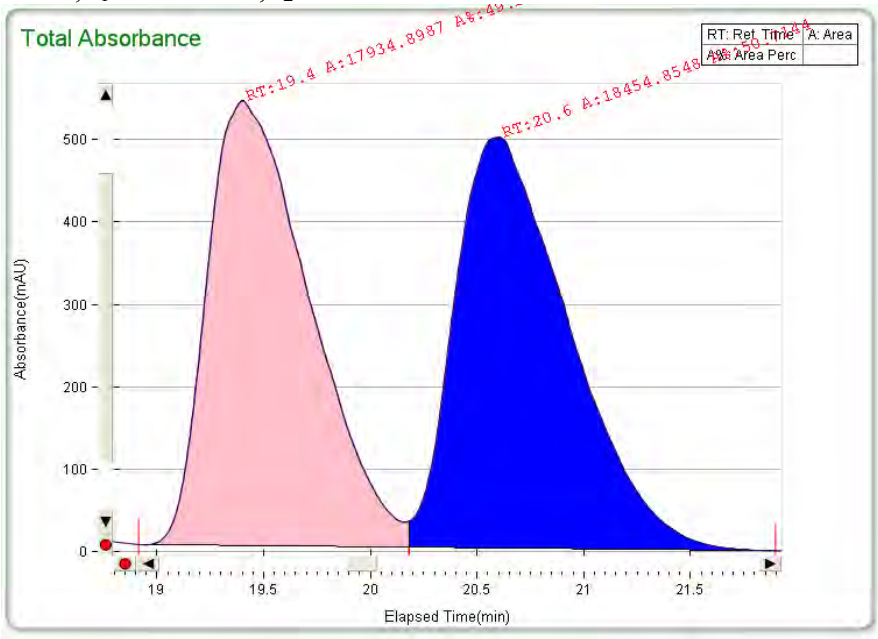

**3h-ester**



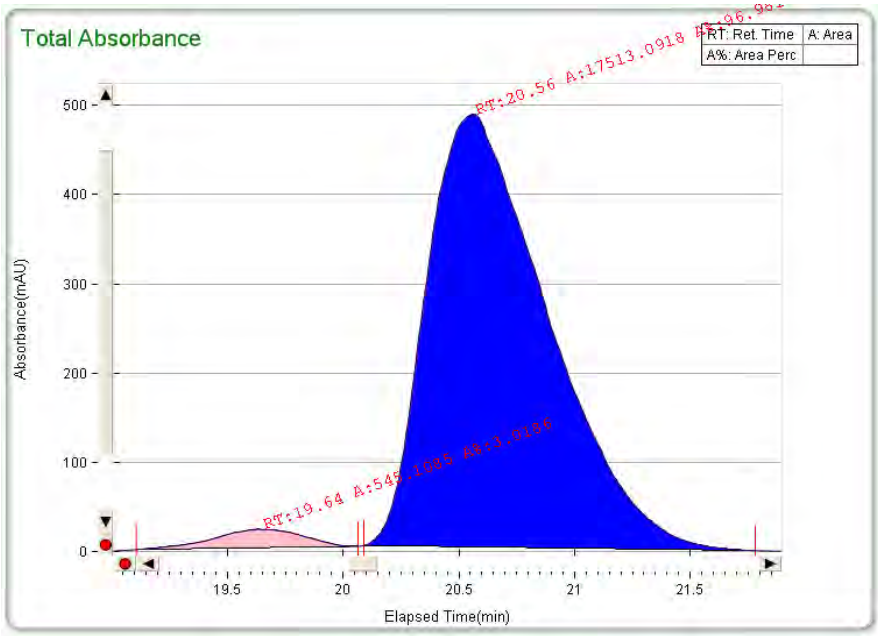

(from *E*-alkene)

**3i-ester**

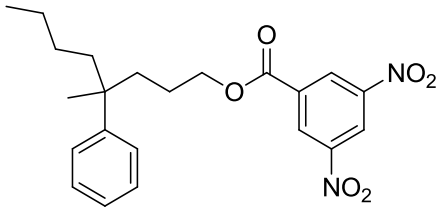
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.1 °C; $t_1$ = 19.4 min, $t_2$ = 20.6 min.




(±)-**3i-ester**

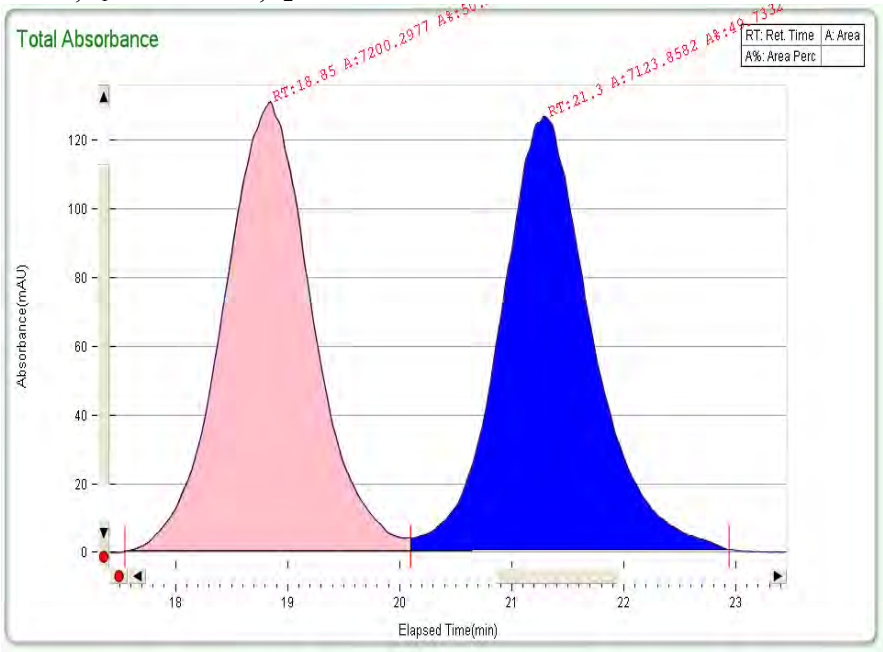



**3i-ester**

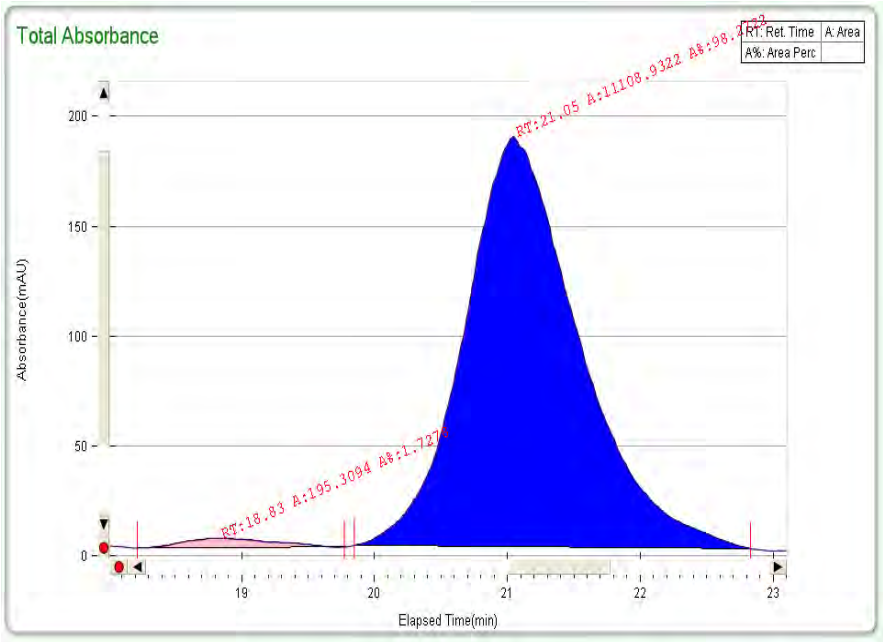



**3j-ester**

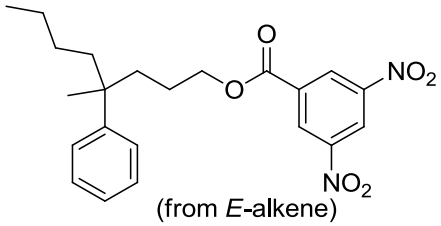
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 18.9 min, $t_2$ = 21.3 min.




(±)-**3j-ester**



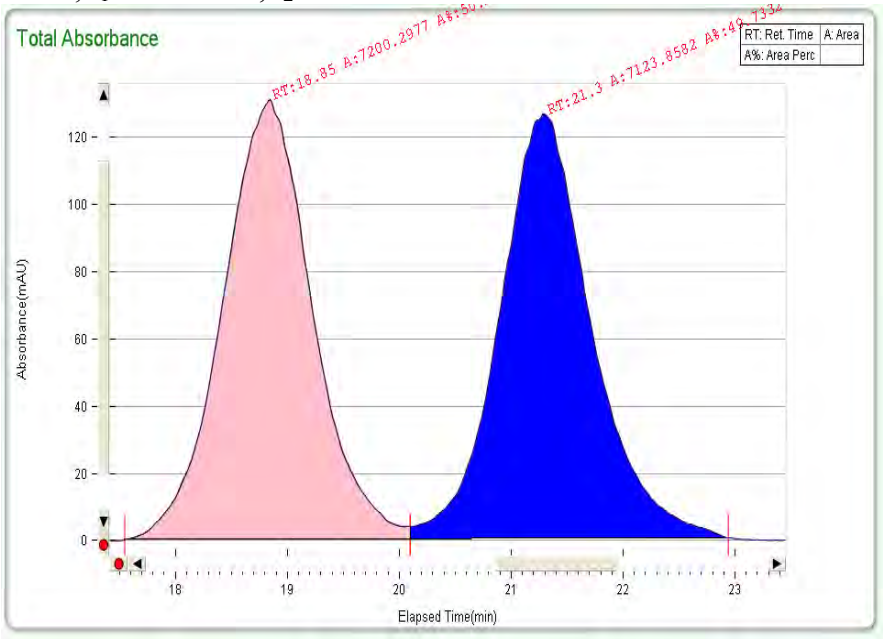

**3j-ester**



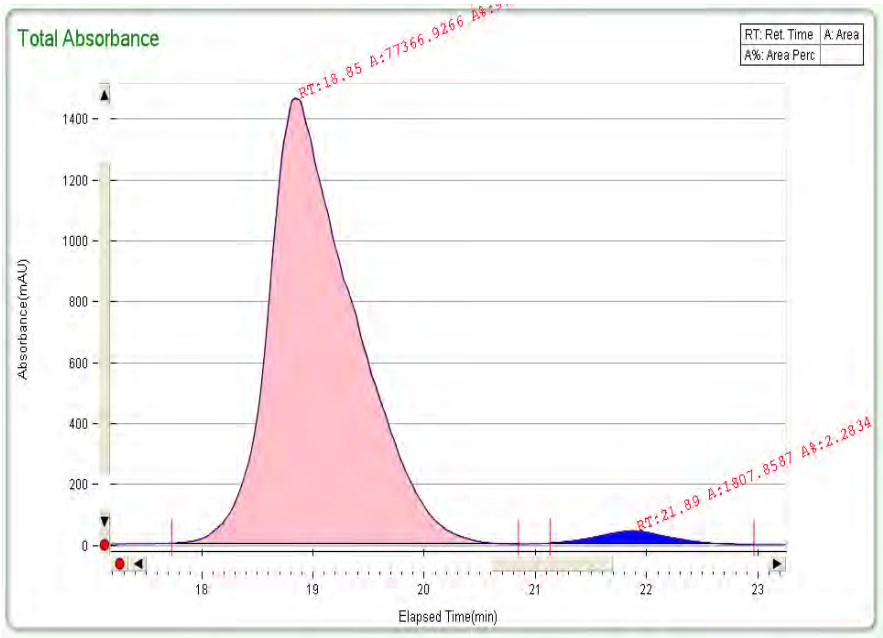

(from *E*-alkene)

**3j-ester**

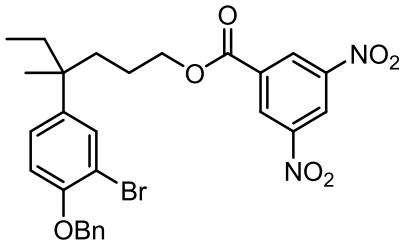
Separation of enantiomers by SFC. Chiralcel® AD-H, 5:95 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.2 °C; $t_1$ = 18.9 min, $t_2$ = 21.3 min.




(±)-**3j**

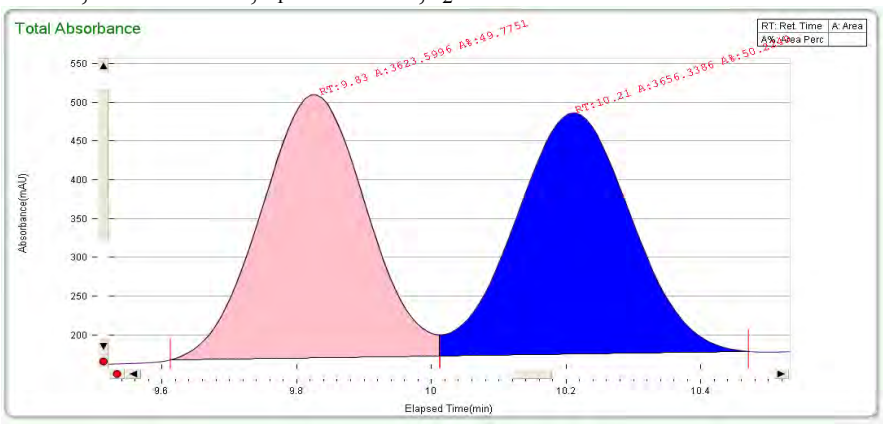



**ent-3j-ester**

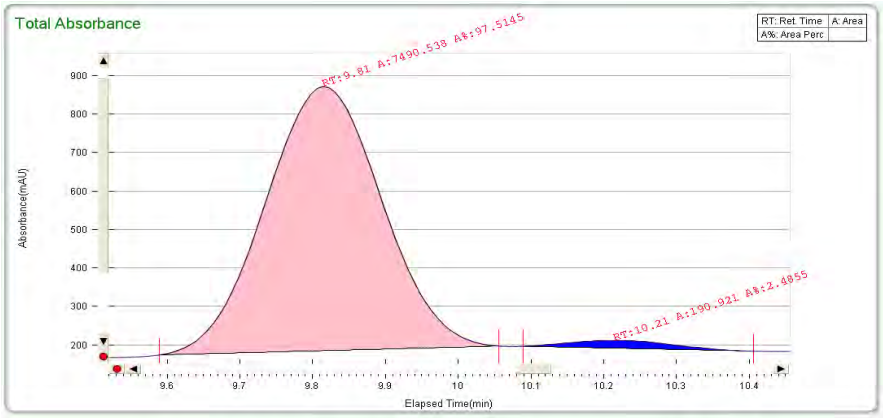



**2fb**

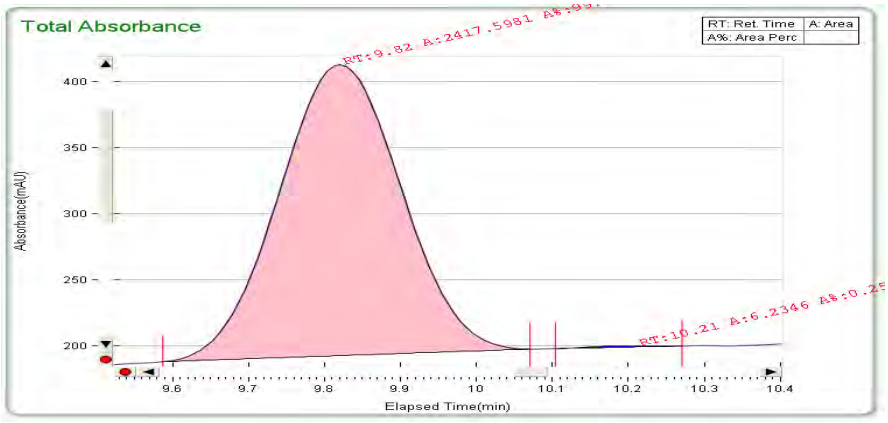
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95→50:50 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 39.7 °C; $t_1$ = 9.8 min, $t_2$ = 10.2 min.



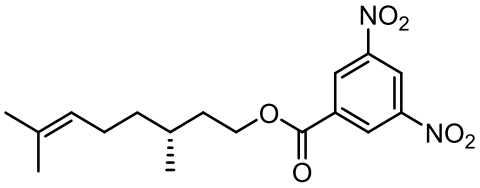

(±)-**2fb**




**2fb**

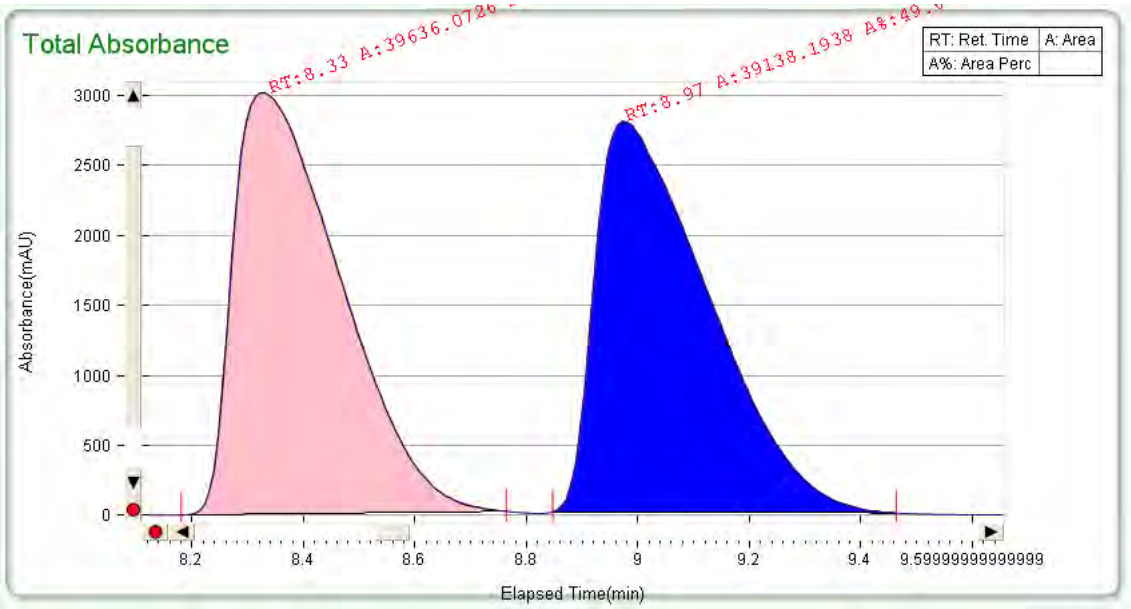



**2fb (**from single crystals**)**

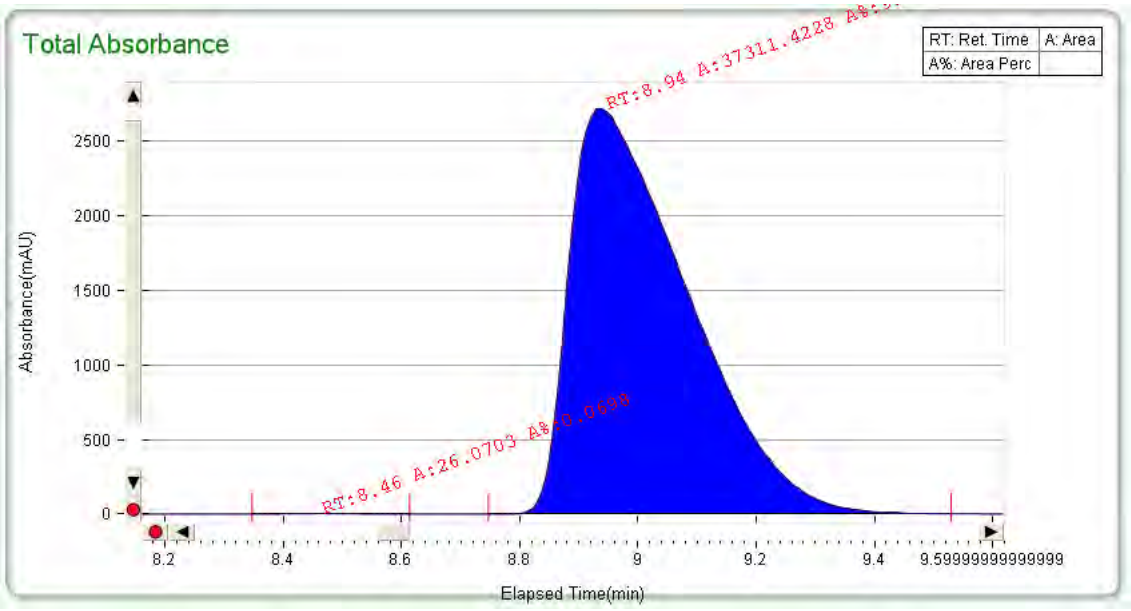



**(*R*)-4-ester**

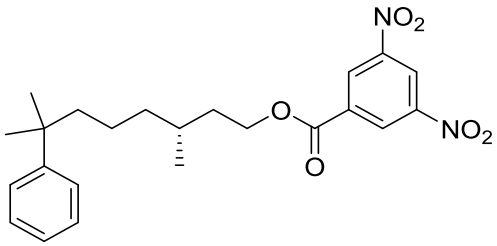
Separation of enantiomers by SFC. Chiralcel® AD-H, 15:85 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.0 °C; $t_1$ = 8.3 min, $t_2$ = 9.0 min.




**(±)-4-ester**

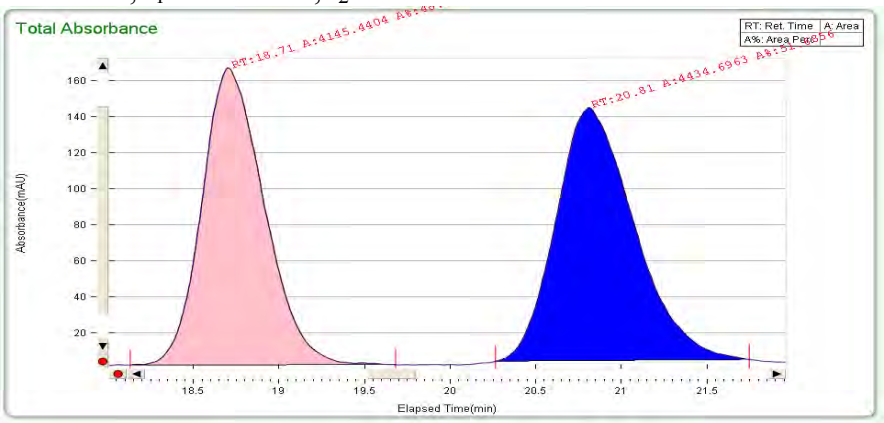



(*R*)-**4-ester**

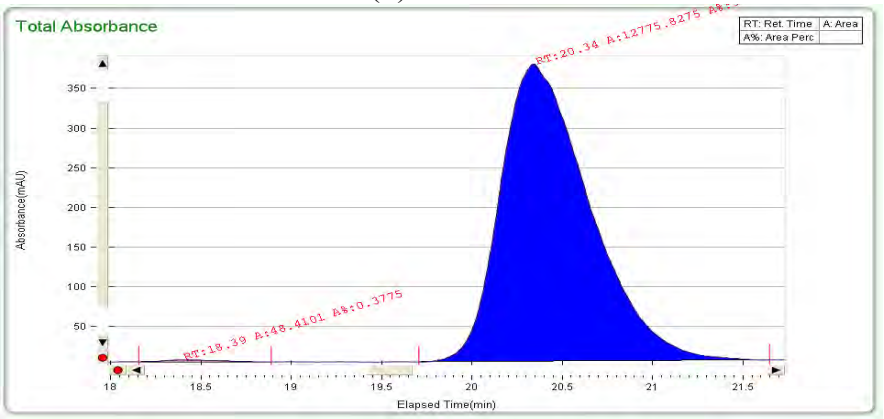



(*R*)-**5-ester**

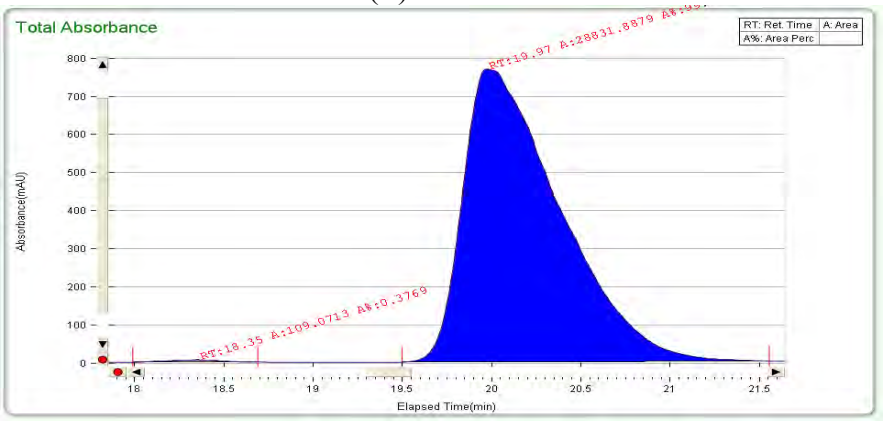
Separation of enantiomers by SFC. Chiralcel® AY-H, 5:95 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 40.0 °C; $t_1$ = 18.7 min, $t_2$ = 20.8 min.



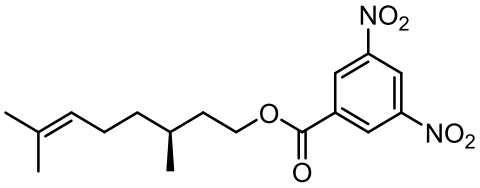

(±)-**5-ester**




(*R*)-**5-ester**

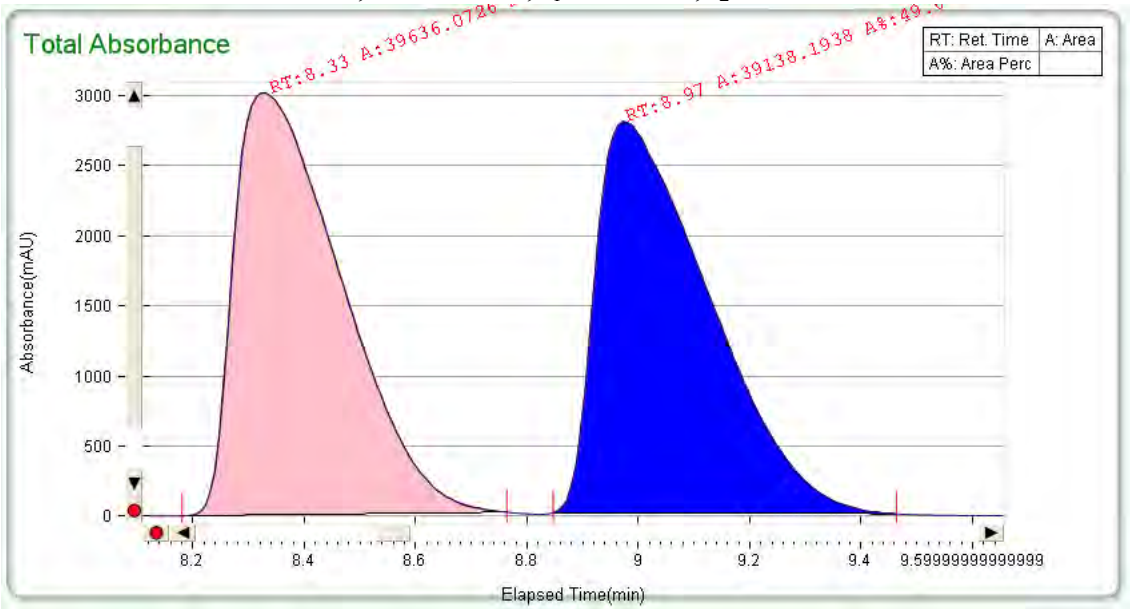



(*R*)-**5-ester** with *ent*-ligand

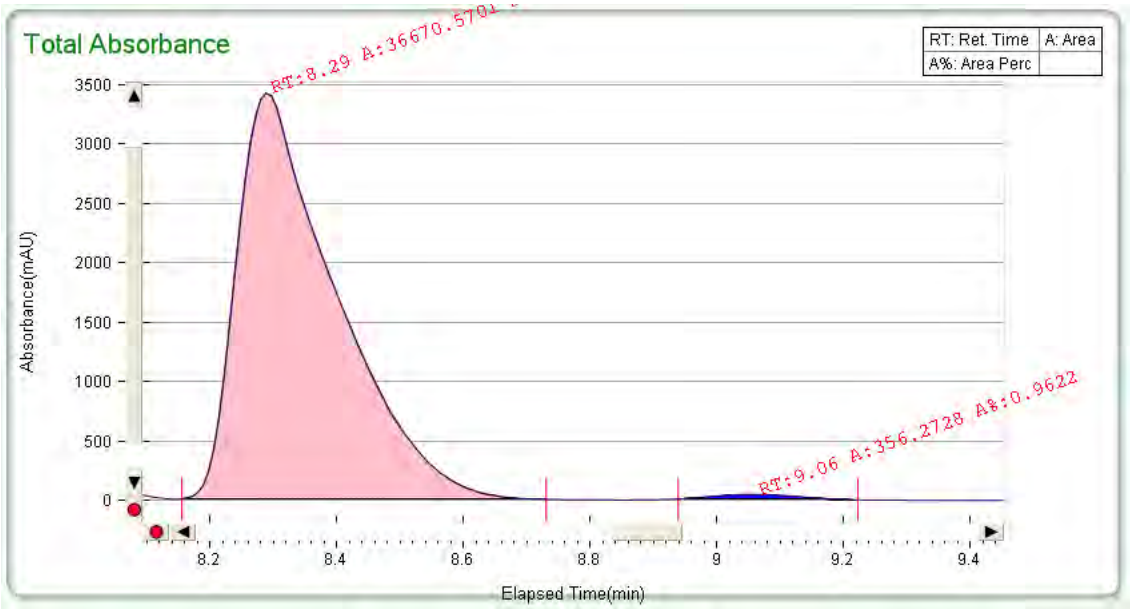



**(*S*)-4-ester**

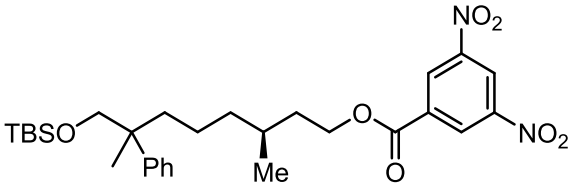
Separation of enantiomers by SFC. Chiralcel® AD-H, 15:85 MeOH/$CO_2$ at 2 mL/min, 160 bar, and 40.0 °C; $t_1$ = 8.3 min, $t_2$ = 9.0 min.




**(±)-4-ester**

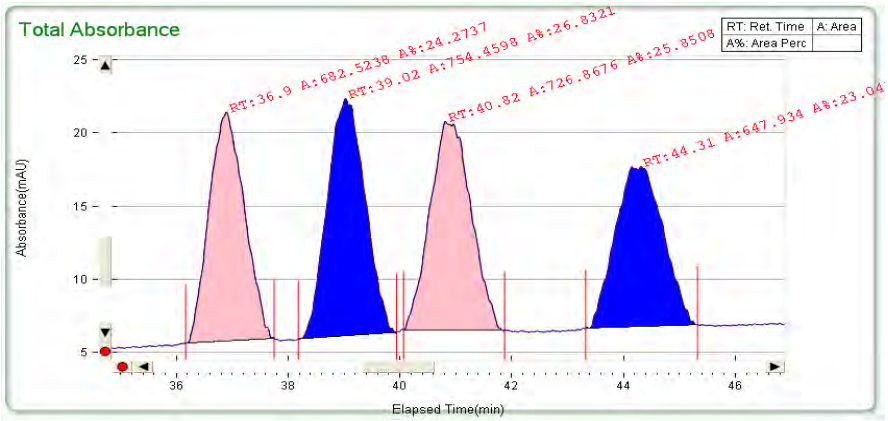



**(*S*)-4-ester**

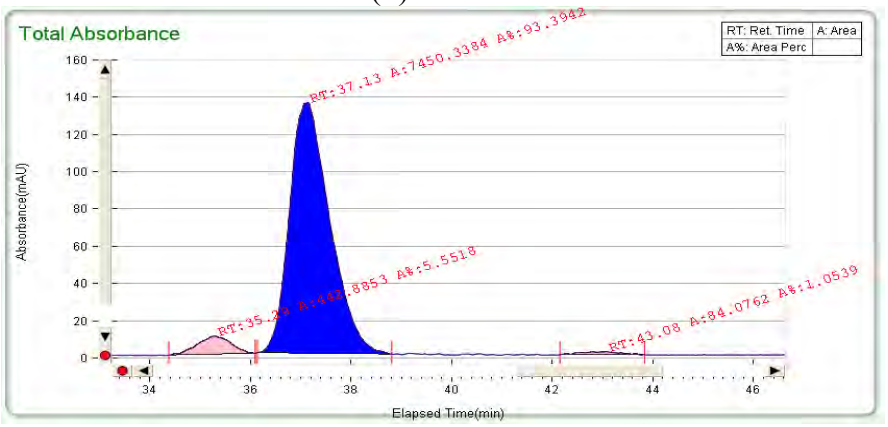



**7-ester**

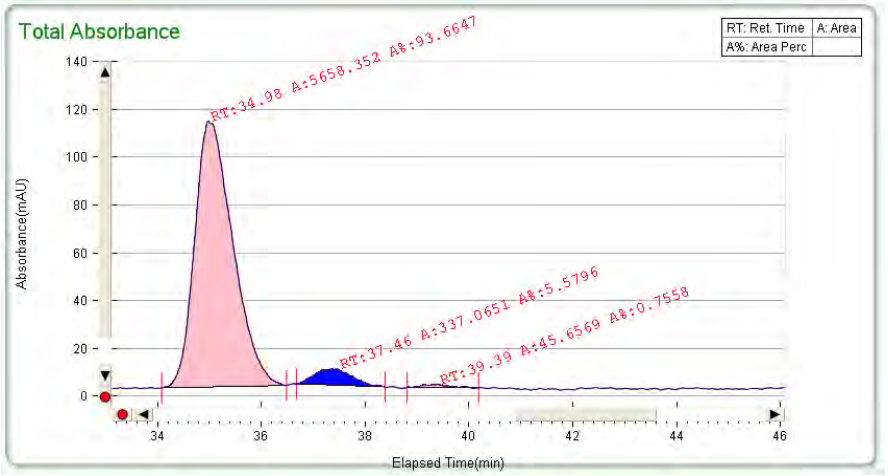
Separation of enantiomers by SFC. Chiralcel® AY-H, 10:90 *i*-PrOH/$CO_2$ at 2 mL/min, 160 bar, and 40.1 °C




(±)-**7-ester**



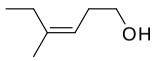

**7-ester**




**8-ester**

mei-03-162-H-500M

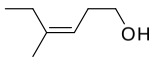
Pulse Sequence: s2pul



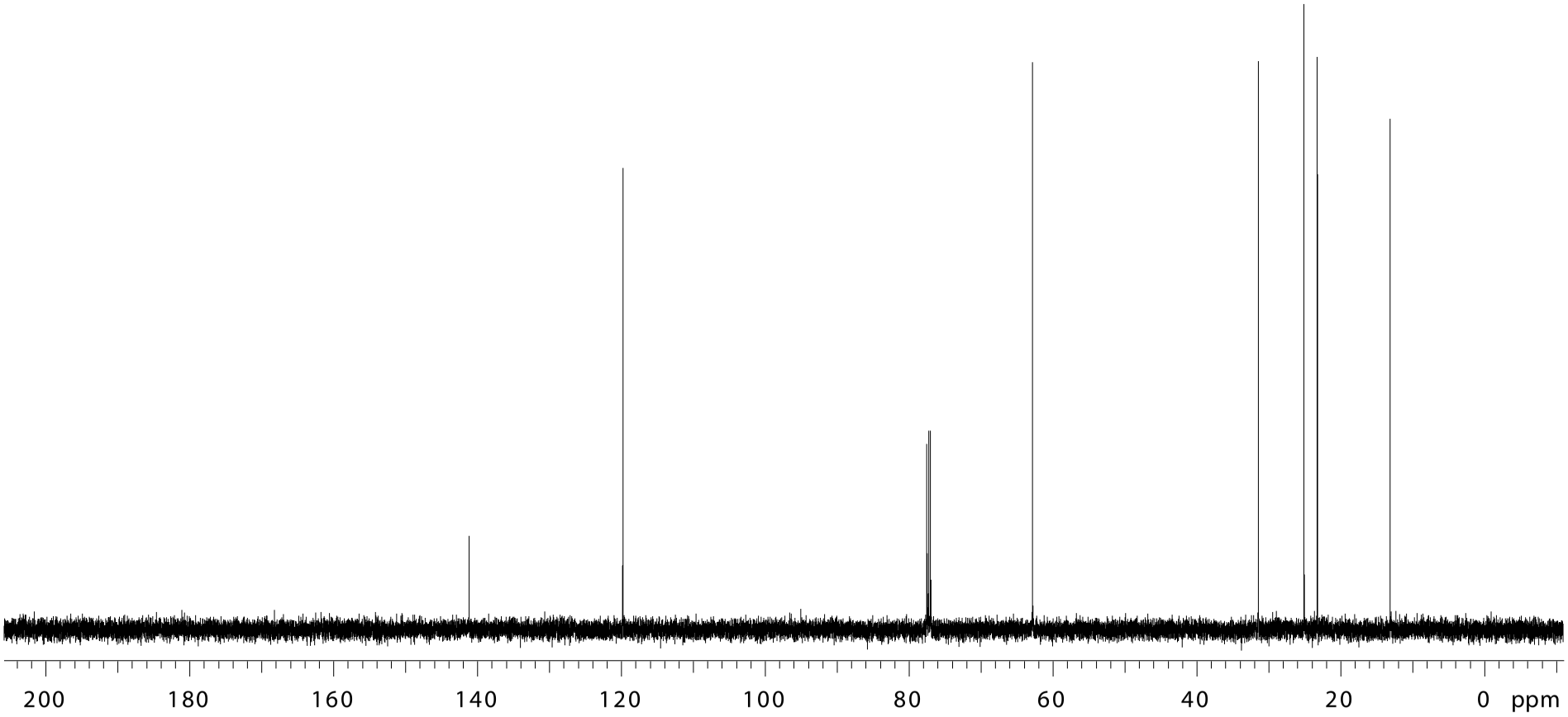

S-2

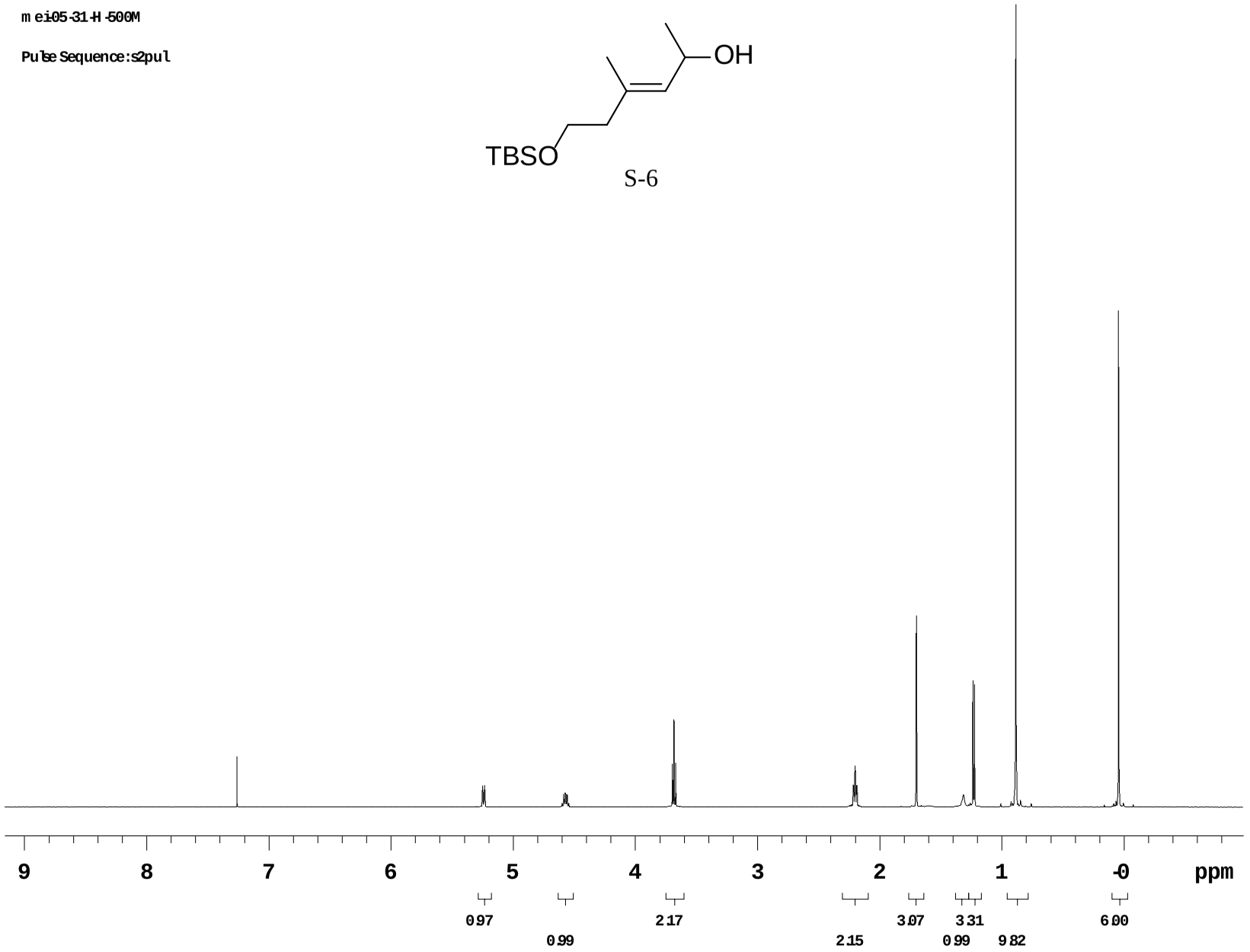
mei-03-162-C-500M

Pulse Sequence: s2pul



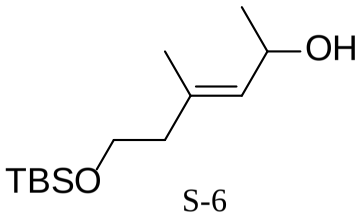

S-2




mei-05-31-H-500M
Pulse Sequence: s2pul
OH
TBSO
S-6
9
8
7
6
5
4
3
2
1
-0
ppm
0.97
0.99
2.17
2.15
3.07
0.99
3.31
9.82
6.00

mei-05-31-C-500M

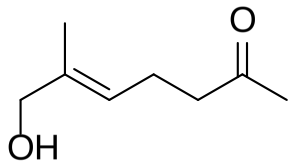
Pulse Sequence: s2pul




S-6

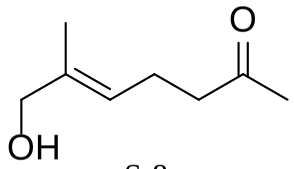
mei-04-141-H-500M

Pulse Sequence: s2pul

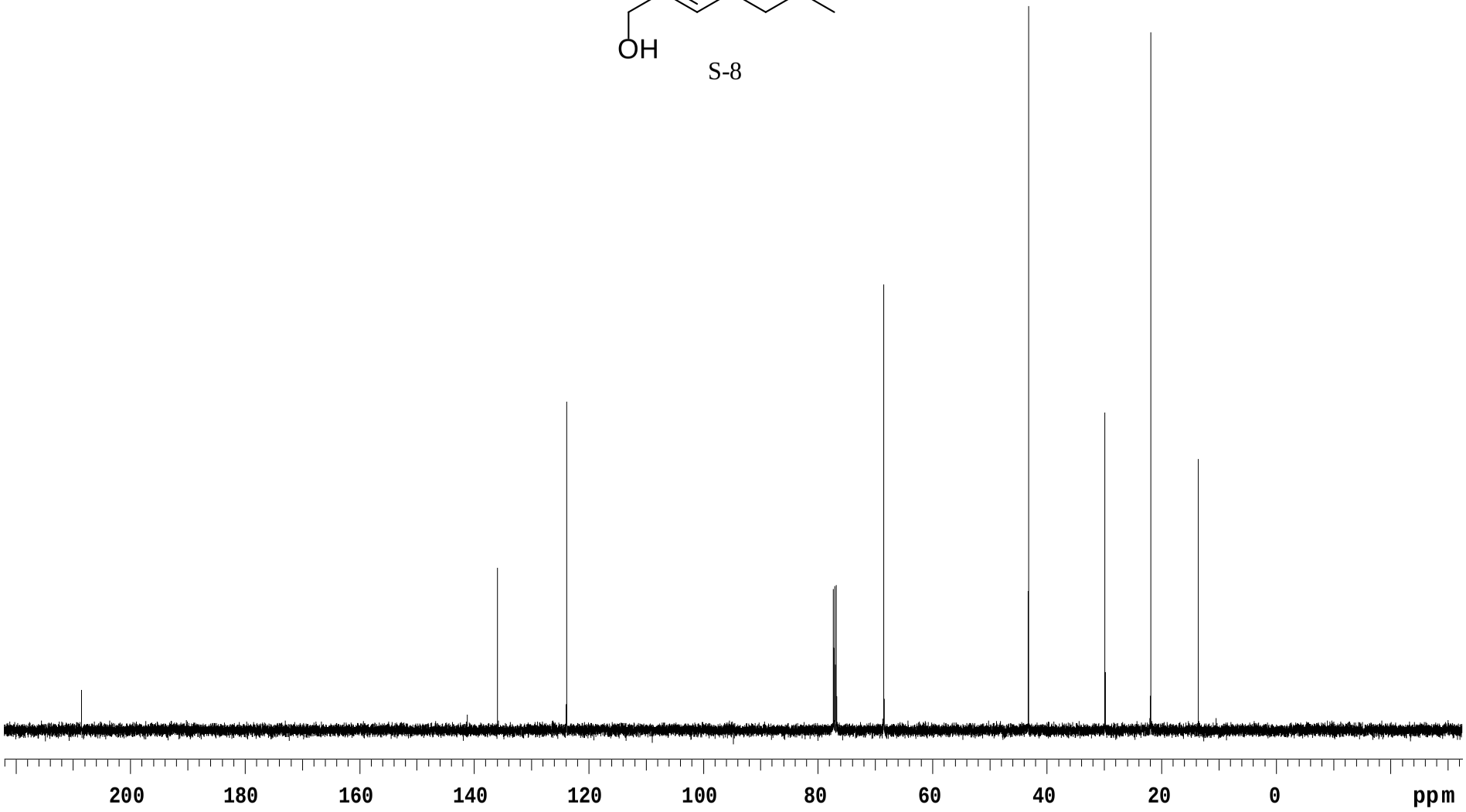


mei-04-141-C-500M

Pulse Sequence: s2pul

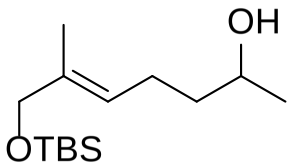




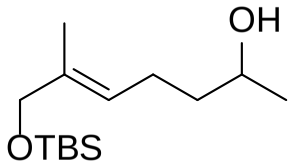
mei-04-143-ol-H-500M

Pulse Sequence: s2pul



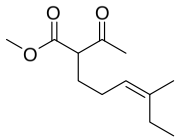
mei-04-143-ol-C-500M

Pulse Sequence: s2pul



mei-04-113-H-500M

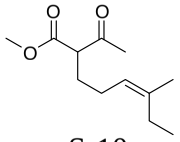
Pulse Sequence: s2pul



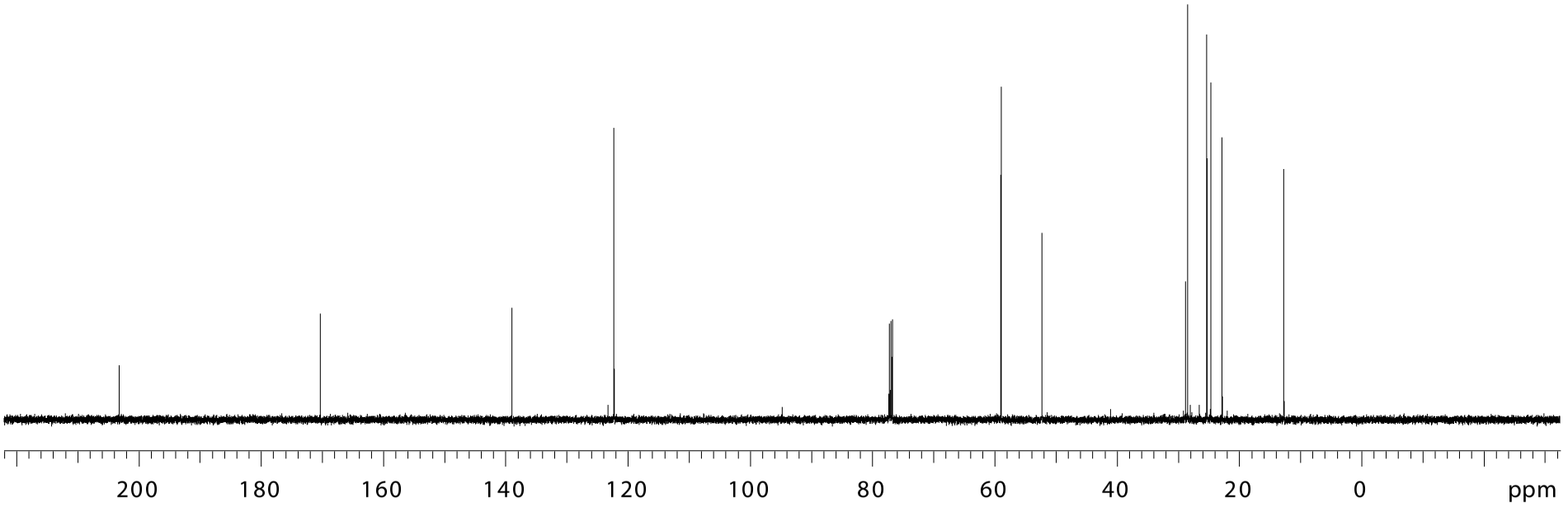
S-10

mei-04-113-C-500M

Pulse Sequence: s2pul

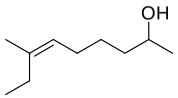


S-10

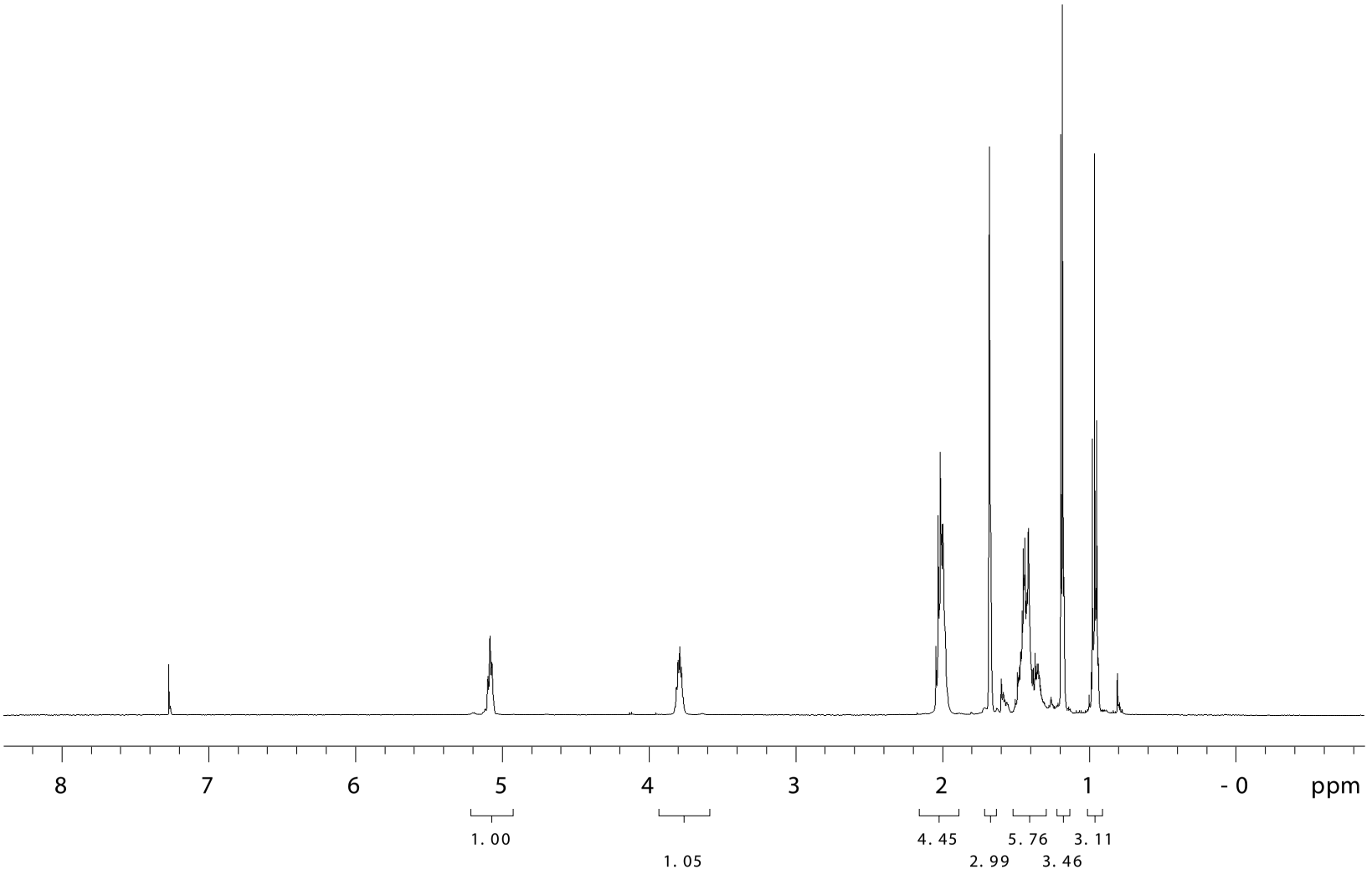


mei-04-98-ol-H-500M

Pulse Sequence: s2pul

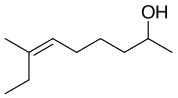



S-11

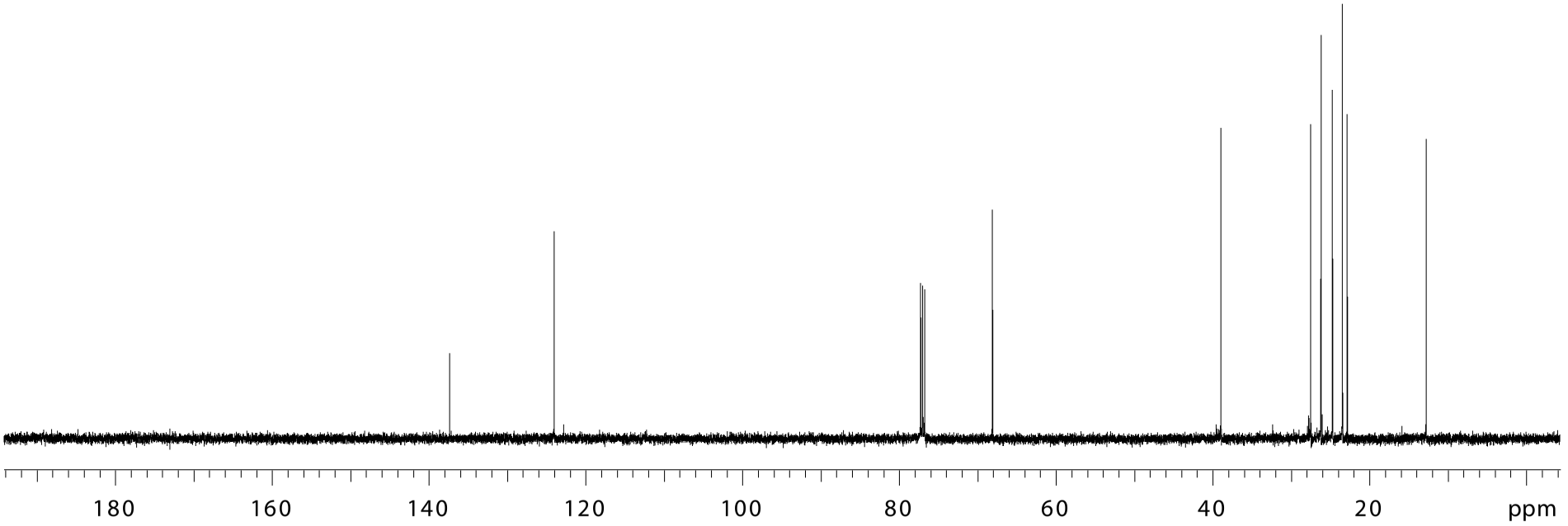


mei-04-98-ol-C-500M

Pulse Sequence: s2pul

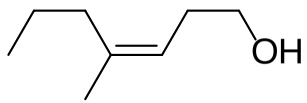




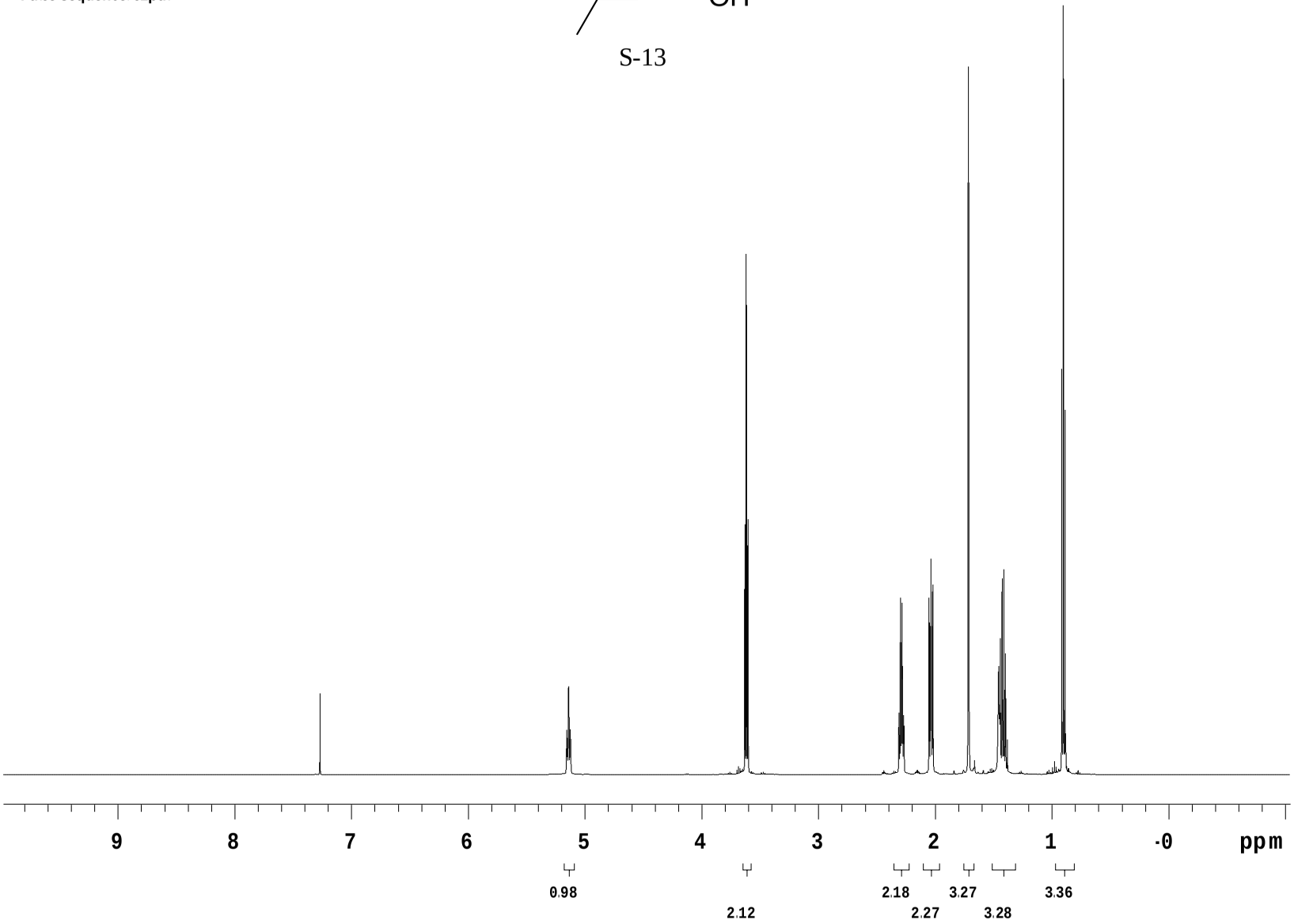



mei-04-127-H-500M

Pulse Sequence: s2pul

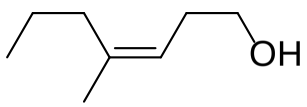




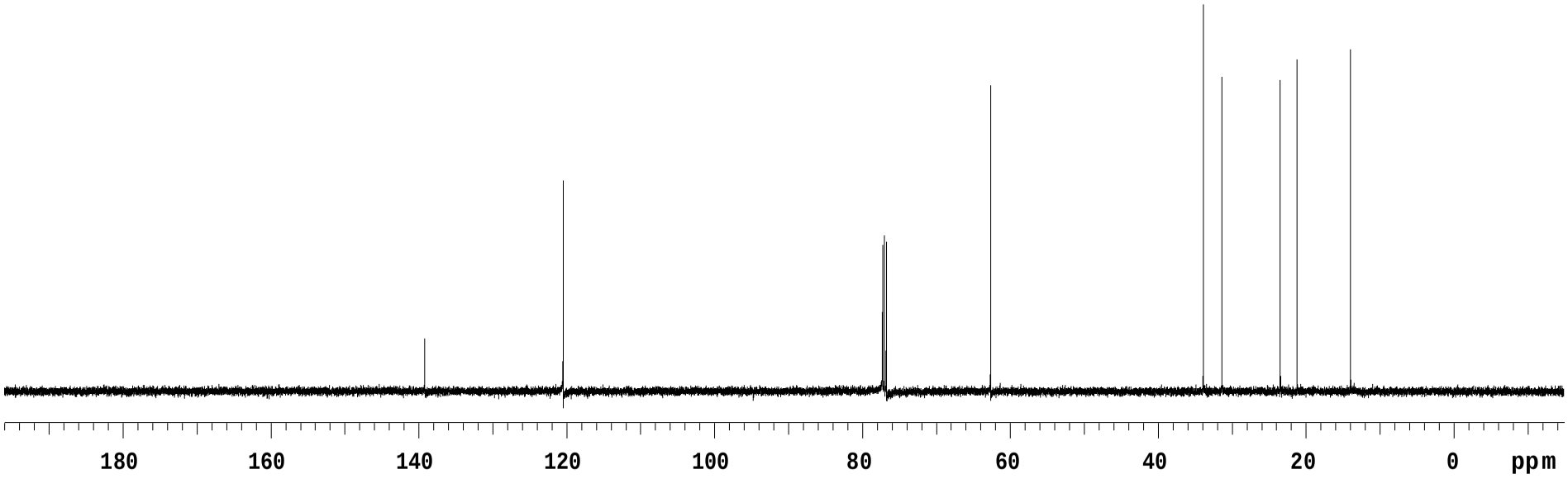



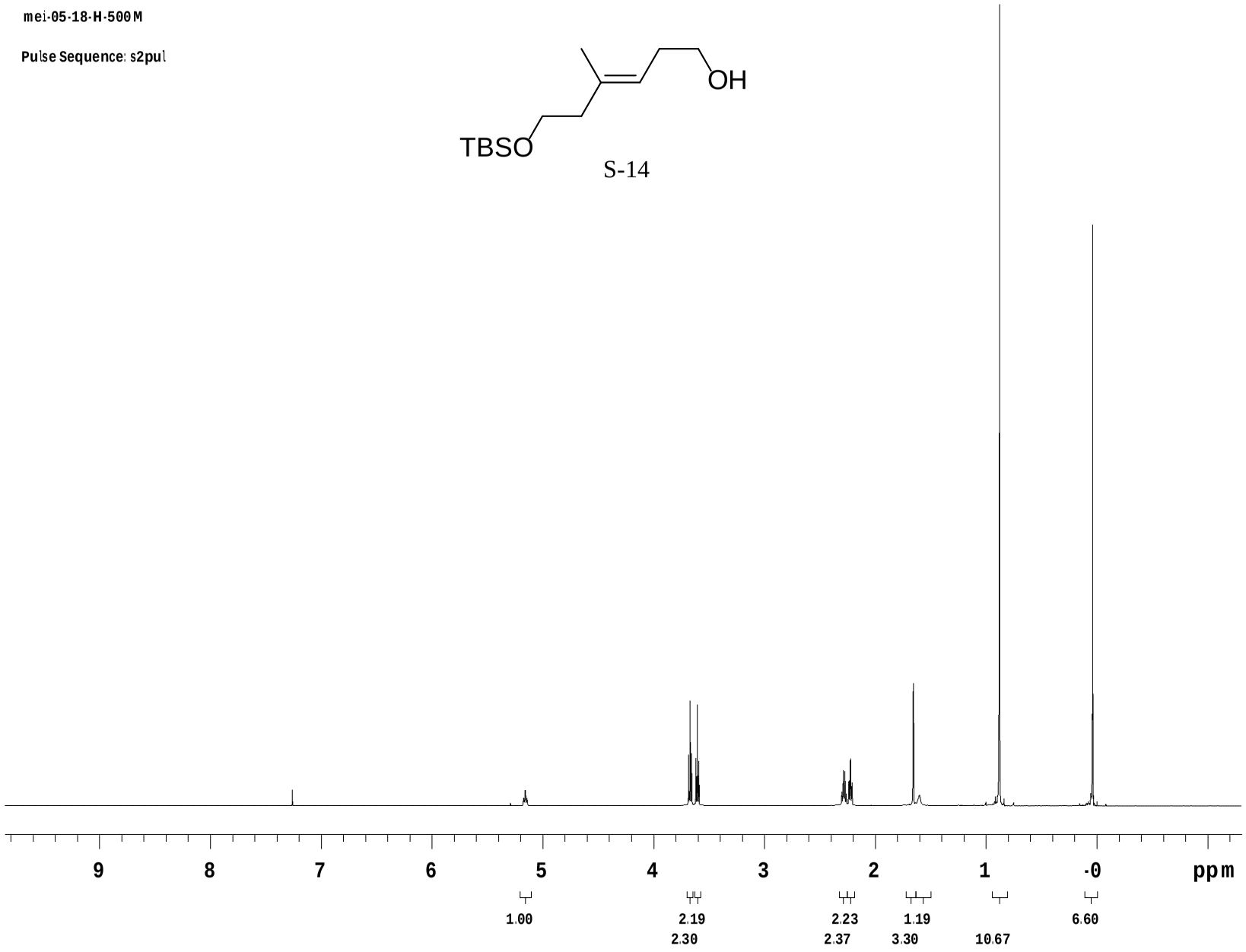
mei-04-127-C-500M

Pulse Sequence: s2pul



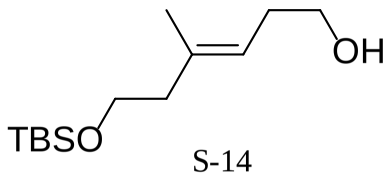



mei-05-18-H-500M
Pulse Sequence: s2pul
OH
TBSO
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.19
2.30
2.23
2.37
1.19
3.30
10.67
6.60

mei-05-18-C-500M

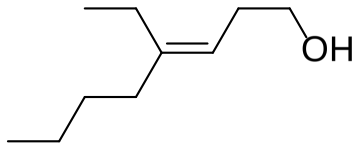
Pulse Sequence: s2pul




S-14

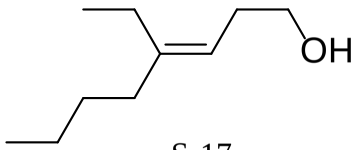
STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul



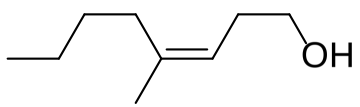
mei-05-72-C-500M

Pulse Sequence: s2pul



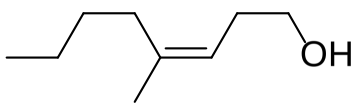
mei-05-48-H-500M

Pulse Sequence: s2pul

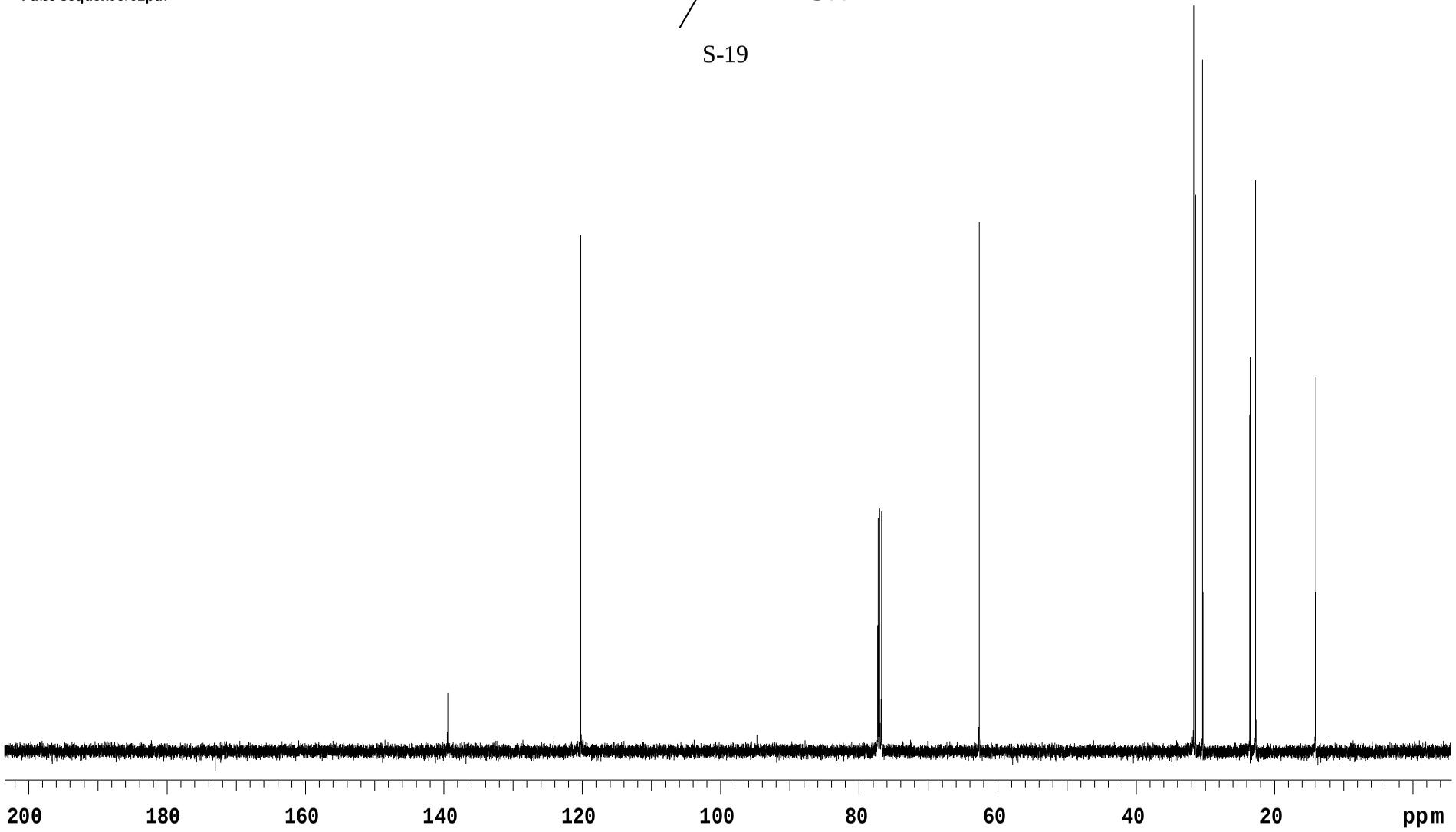


mei-05-48-C-500M

Pulse Sequence: s2pul

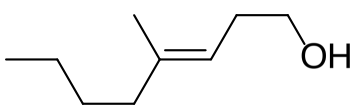




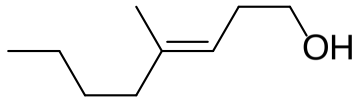
mei-05-42-H-500M

Pulse Sequence: s2pul

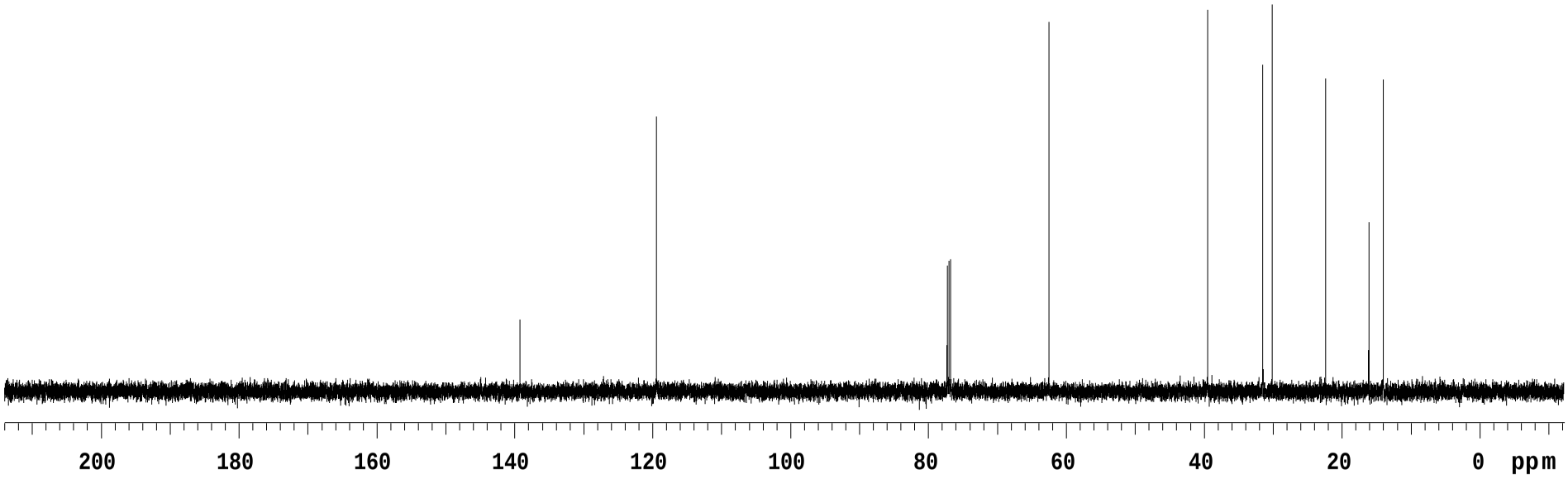


mei-05-42-C-500M

Pulse Sequence: s2pul

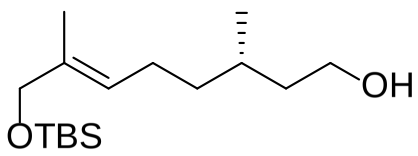




mei-05-81-H-500M

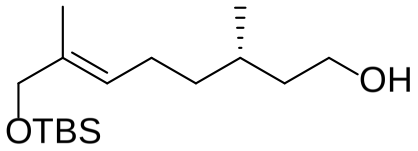
Pulse Sequence: s2pul



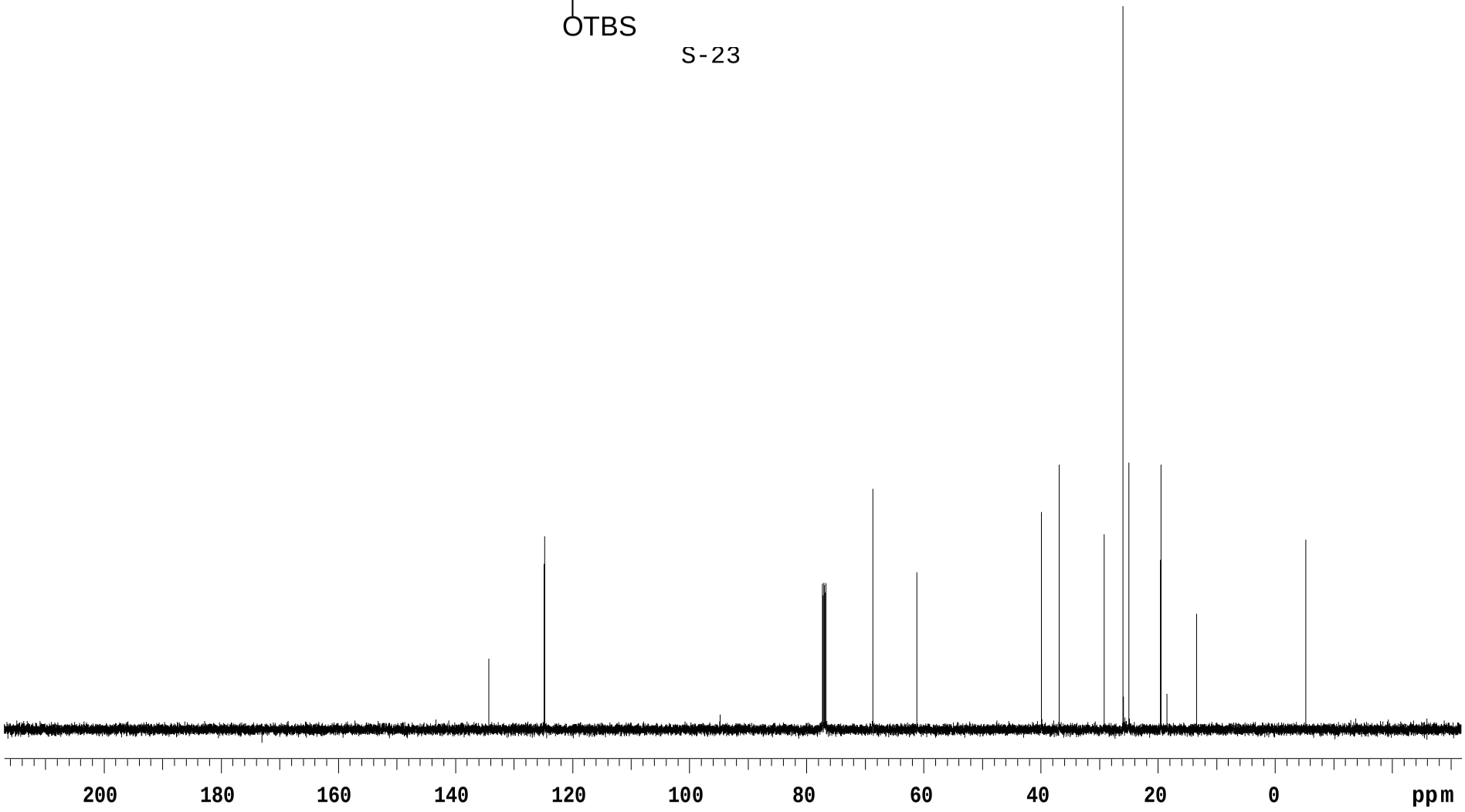

S-23

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

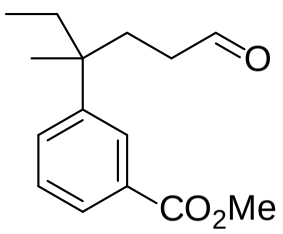



S-23



mei-04-160-7-H-500M

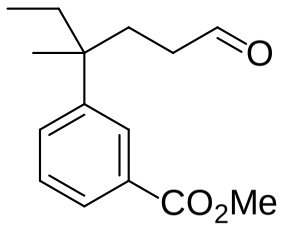
Pulse Sequence: s2pul



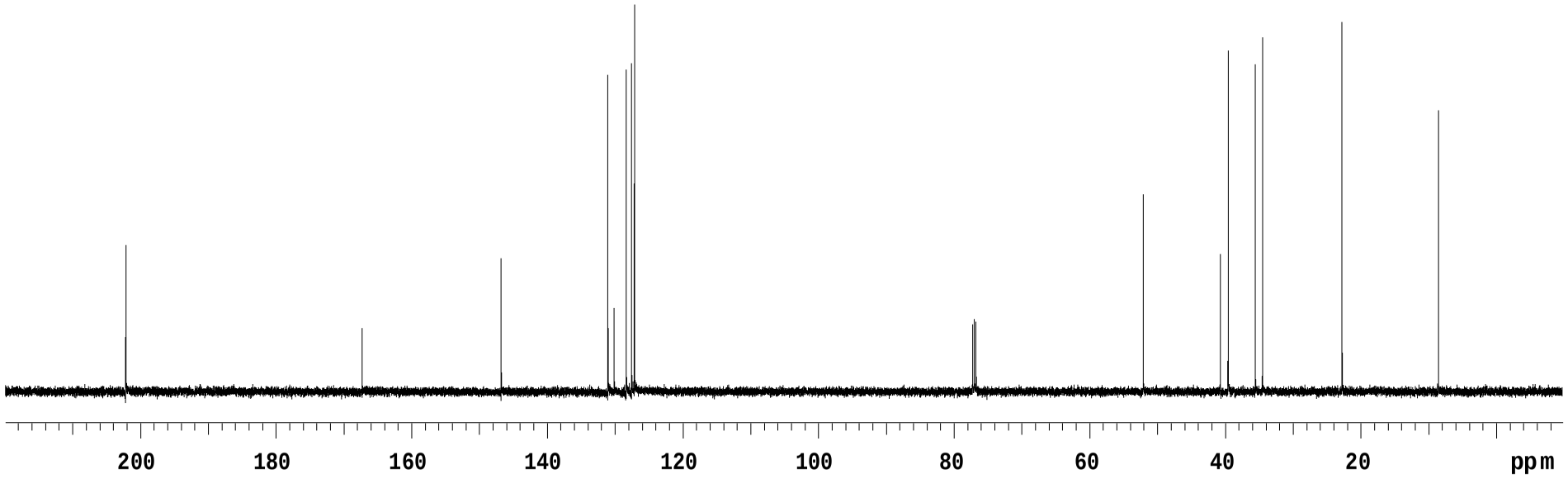

2a

mei-04-160-7-C-500M

Pulse Sequence: s2pul

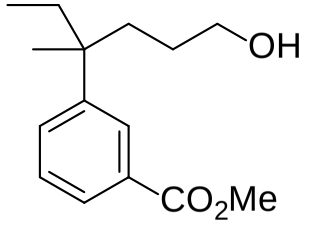



2a

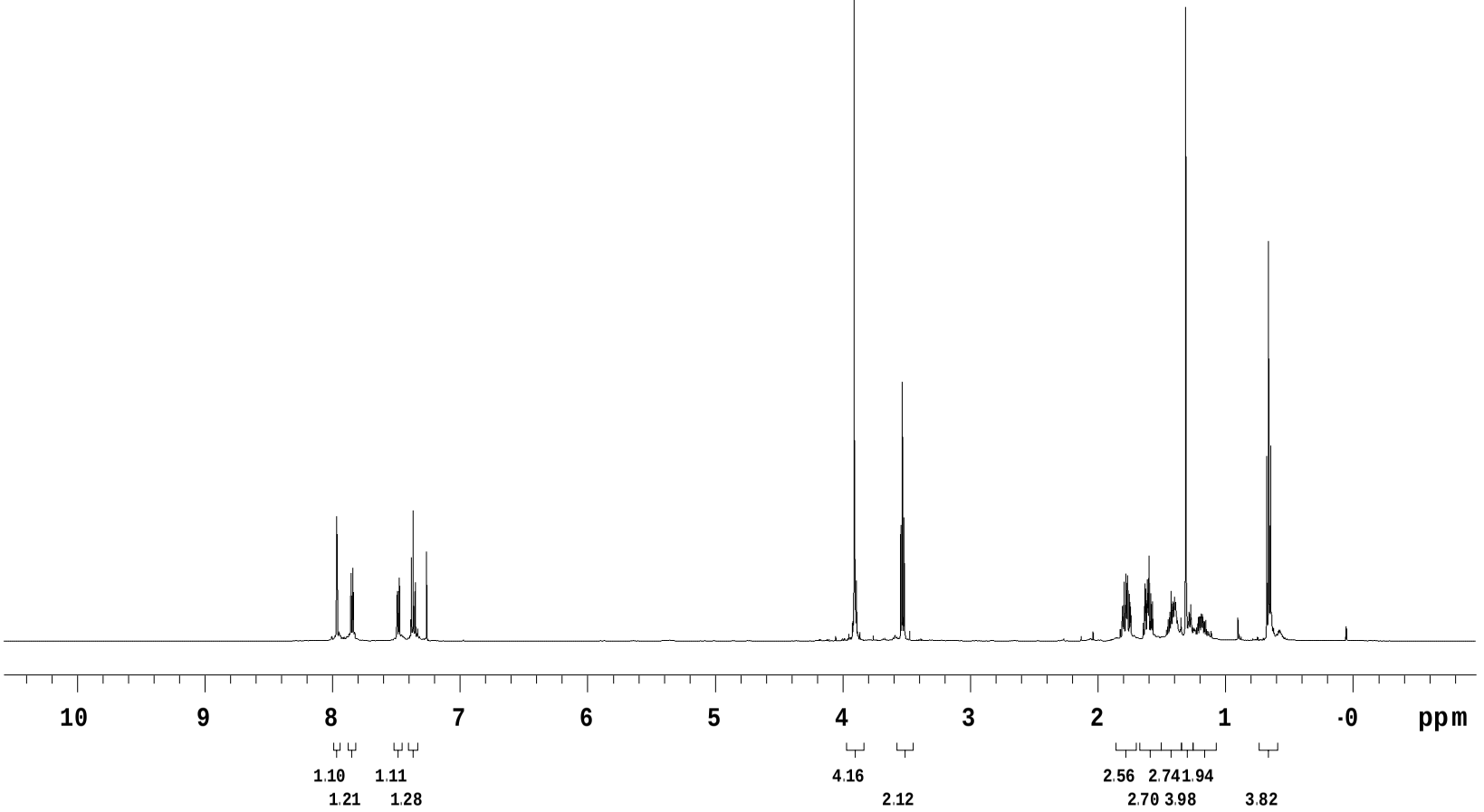


mei-04-160-7-ol-H-500M

Pulse Sequence: s2pul

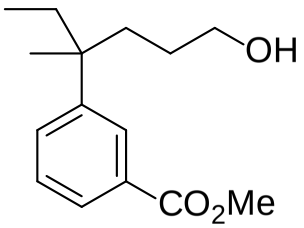



2a-ol

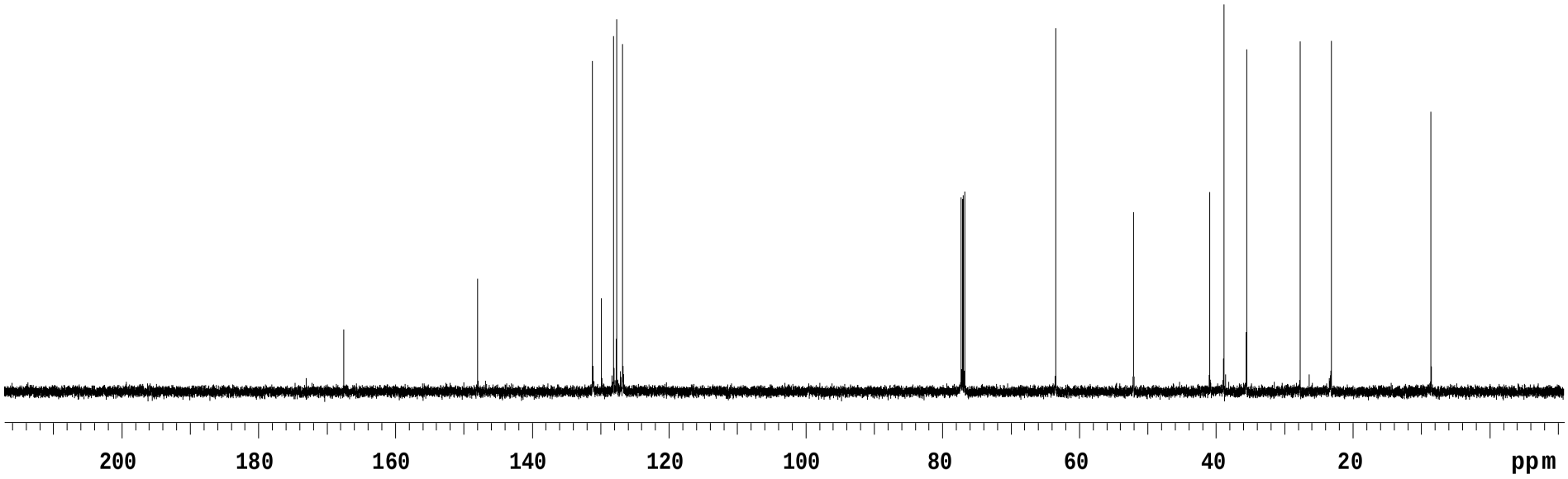


mei-04-160-7-ol-C-500M

Pulse Sequence: s2pul

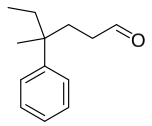



2a-ol

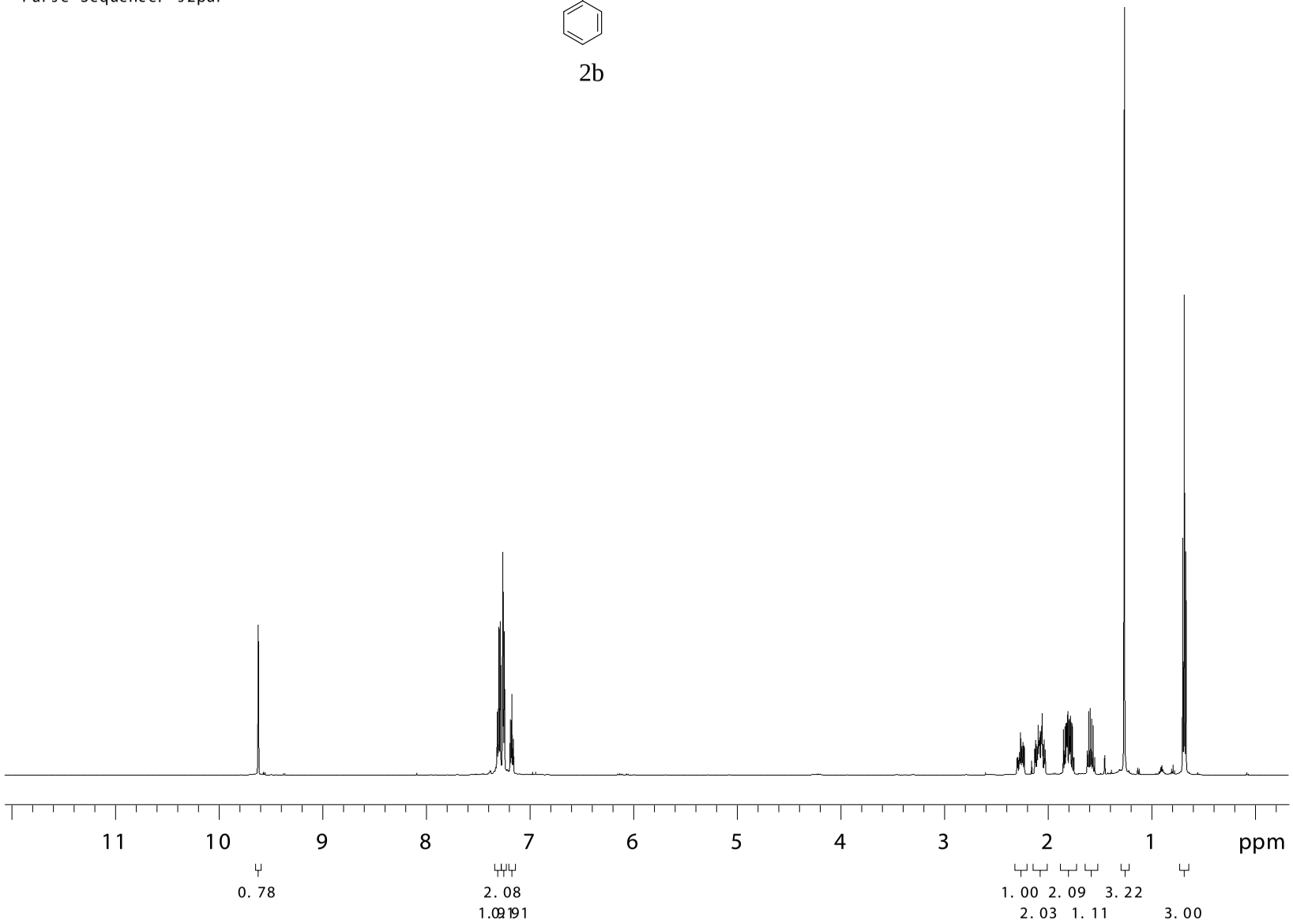


mei-04-32-H-500M

Pulse Sequence: s2pul

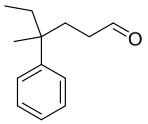



2b

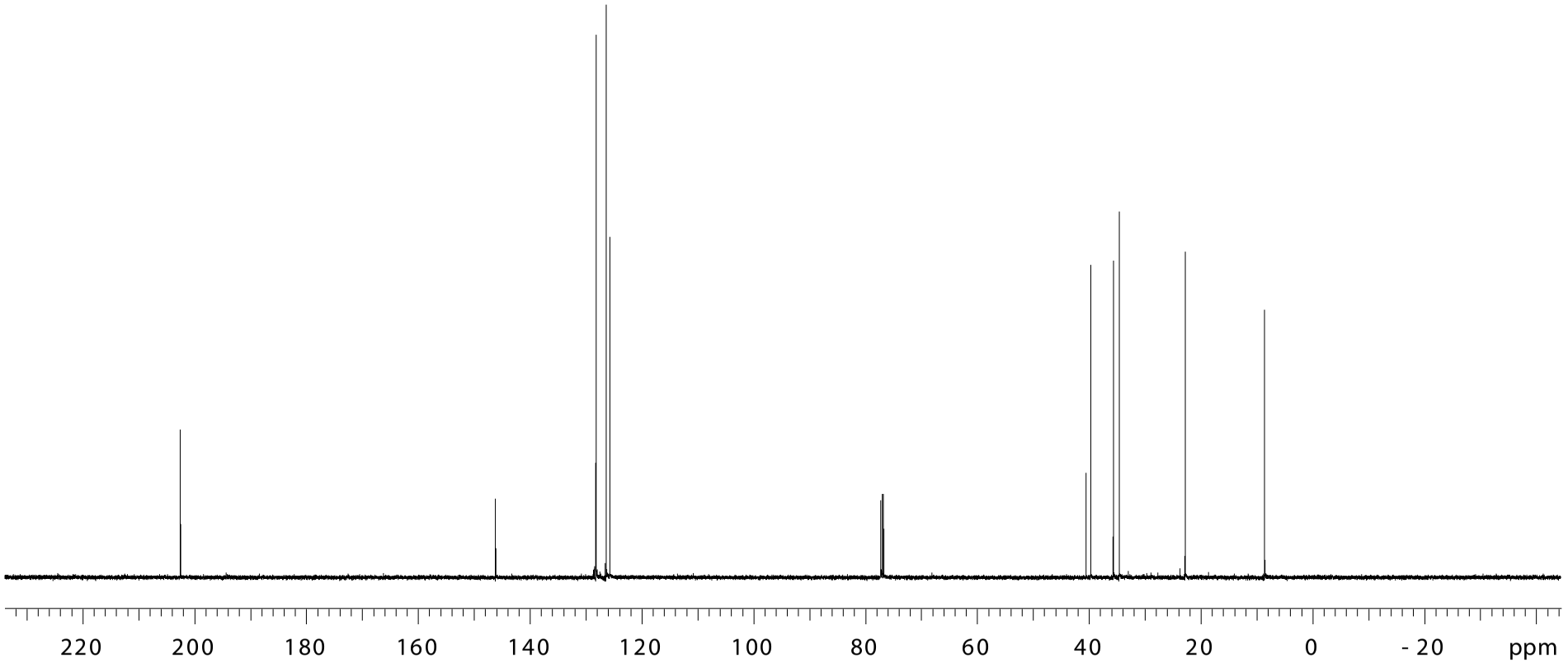


mei-04-32-C-500M

Pulse Sequence: s2pul

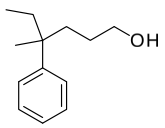



2b



mei-03-163-3-4-ol-H-500M

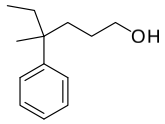
Pulse Sequence: s2pul



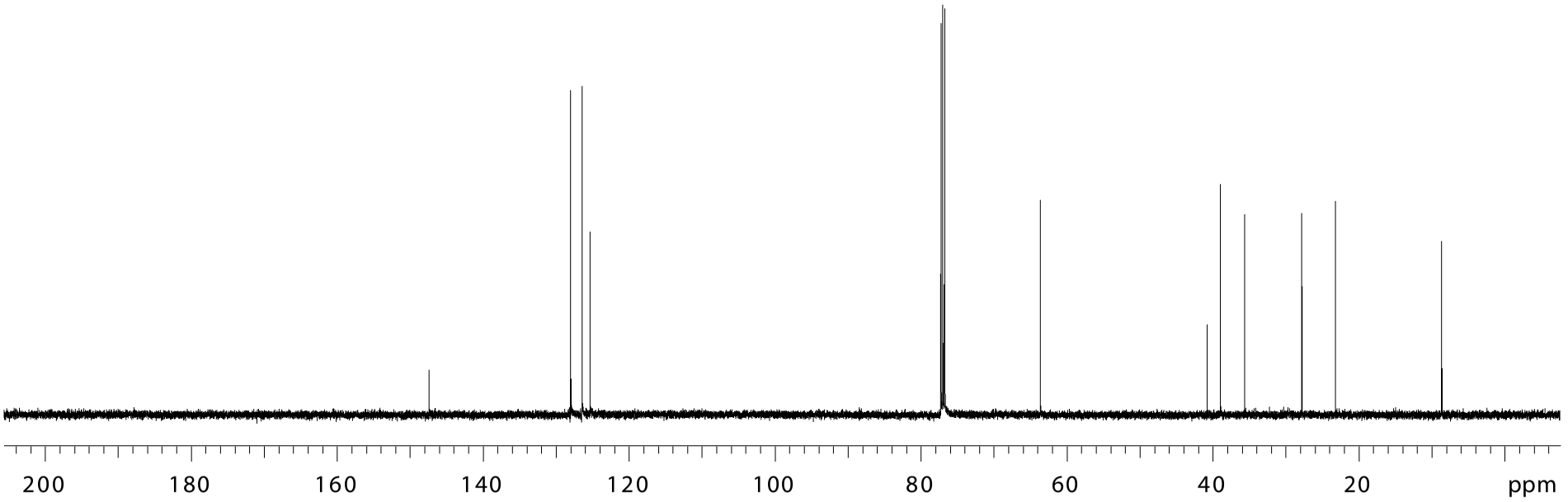

2b-ol

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

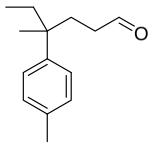



2b-ol



mei-04-120-7-8-H-500M

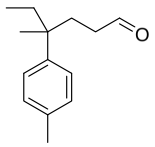
Pulse Sequence: s2pul



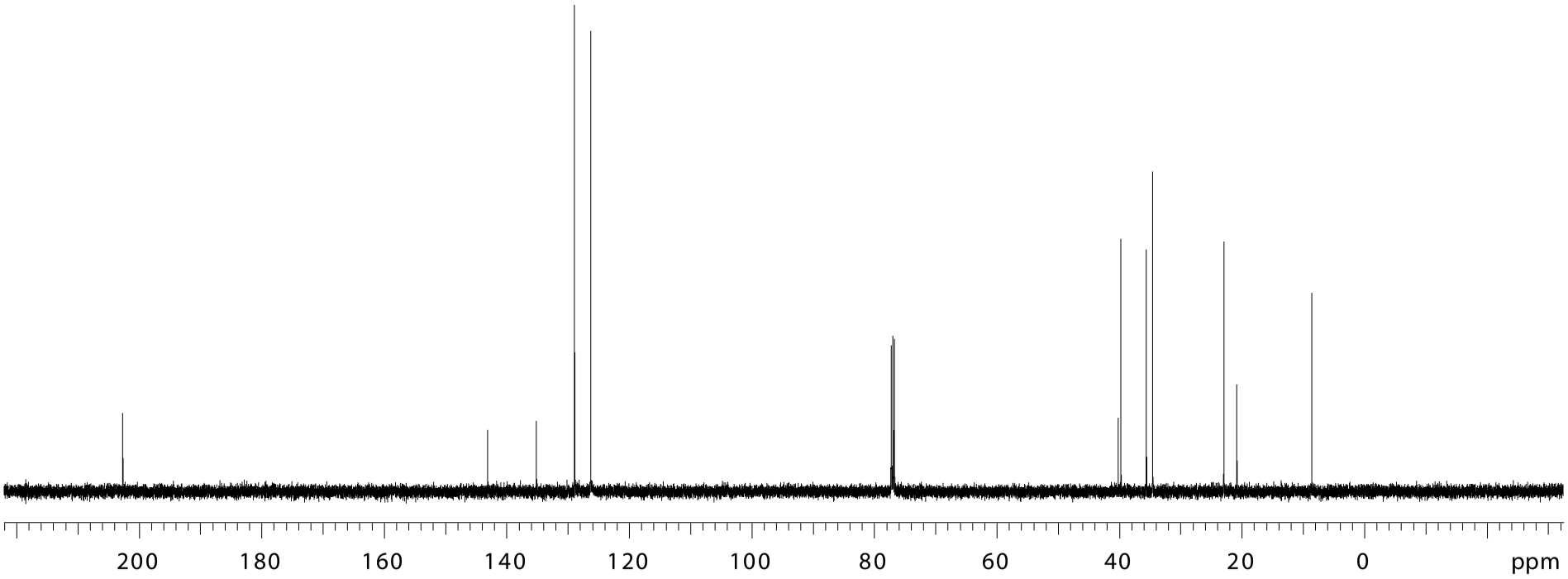

2c

mei-04-120-7-8-C-500M

Pulse Sequence: s2pul

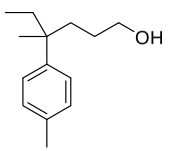



2c



mei-04-120-7-8-ol-H-500M

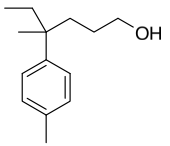
Pulse Sequence: s2pul



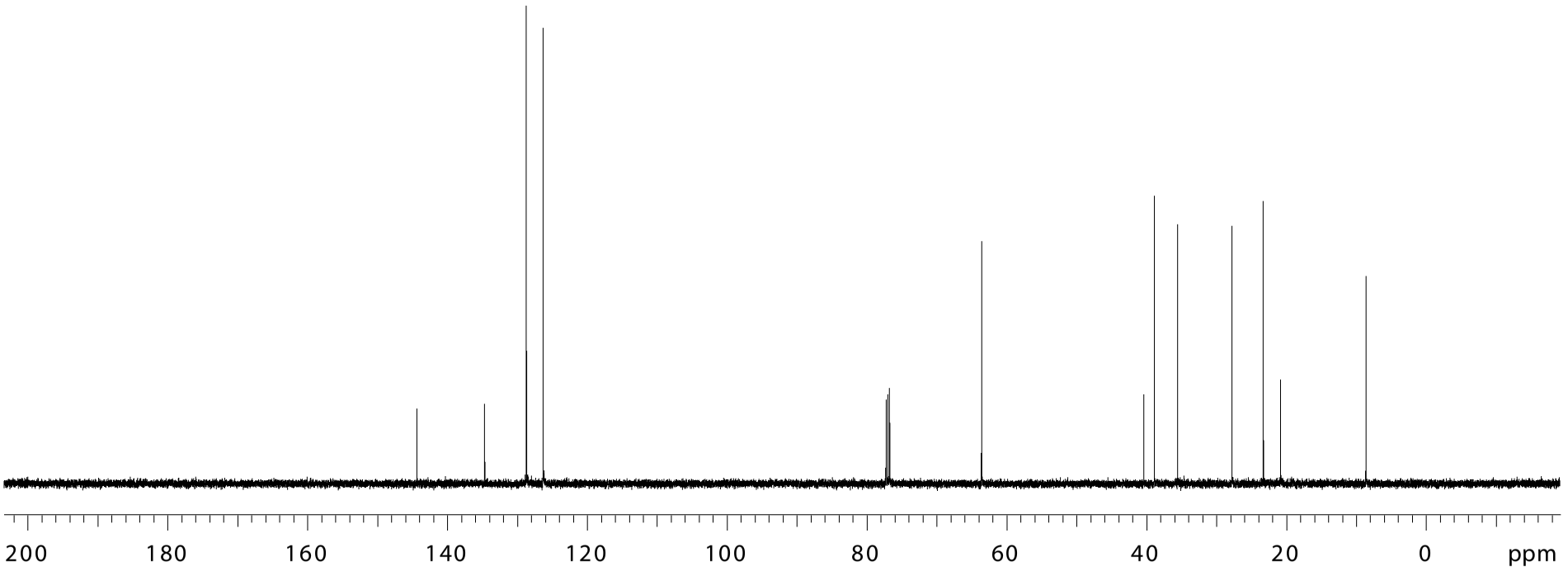

2c-ol

mei-04-120-7-8-ol-C-500M

Pulse Sequence: s2pul

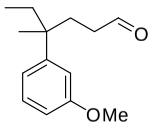



2c-ol

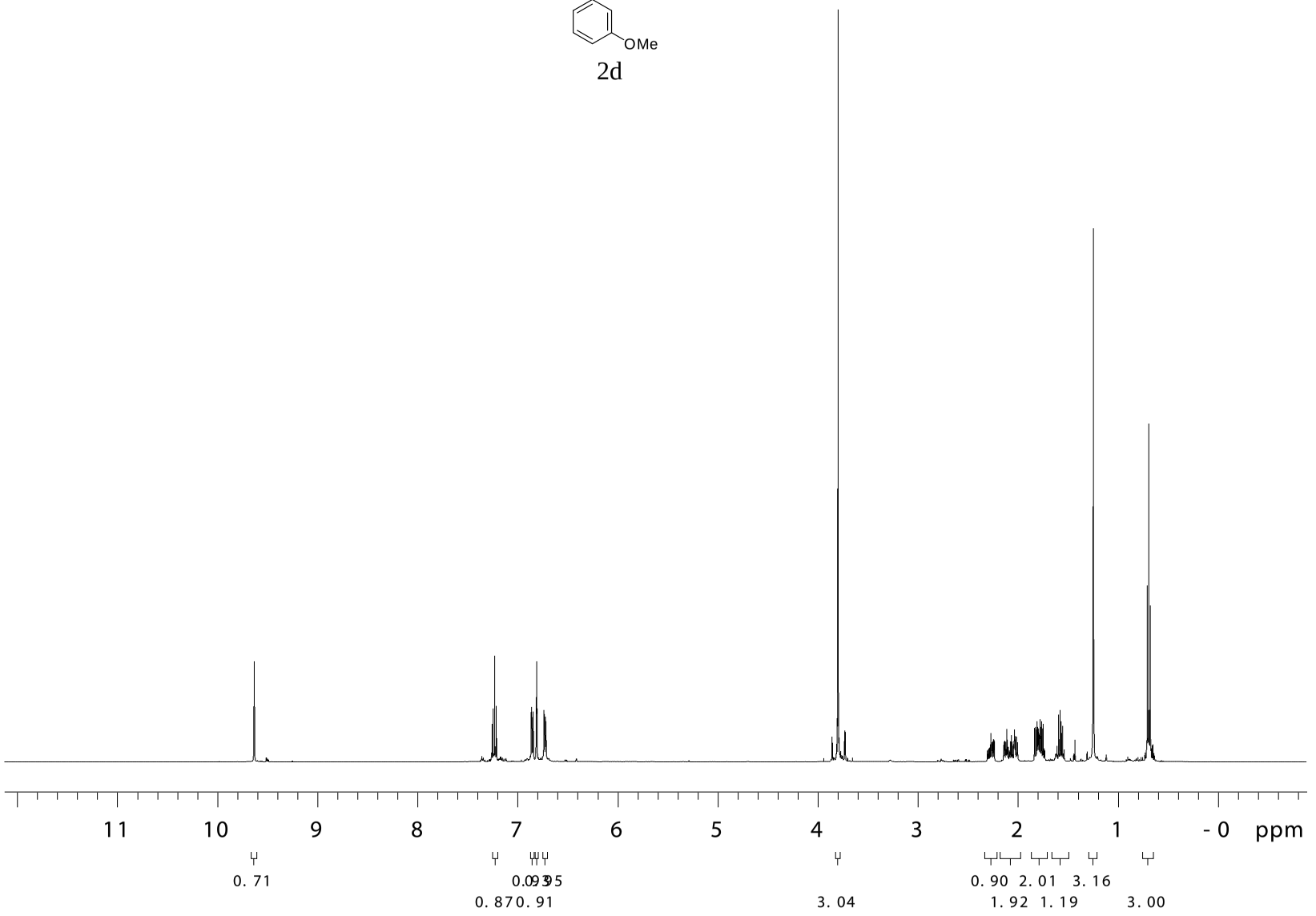


mei-04-120-4-H-500M

Pulse Sequence: s2pul

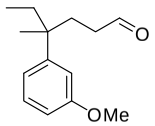



2d

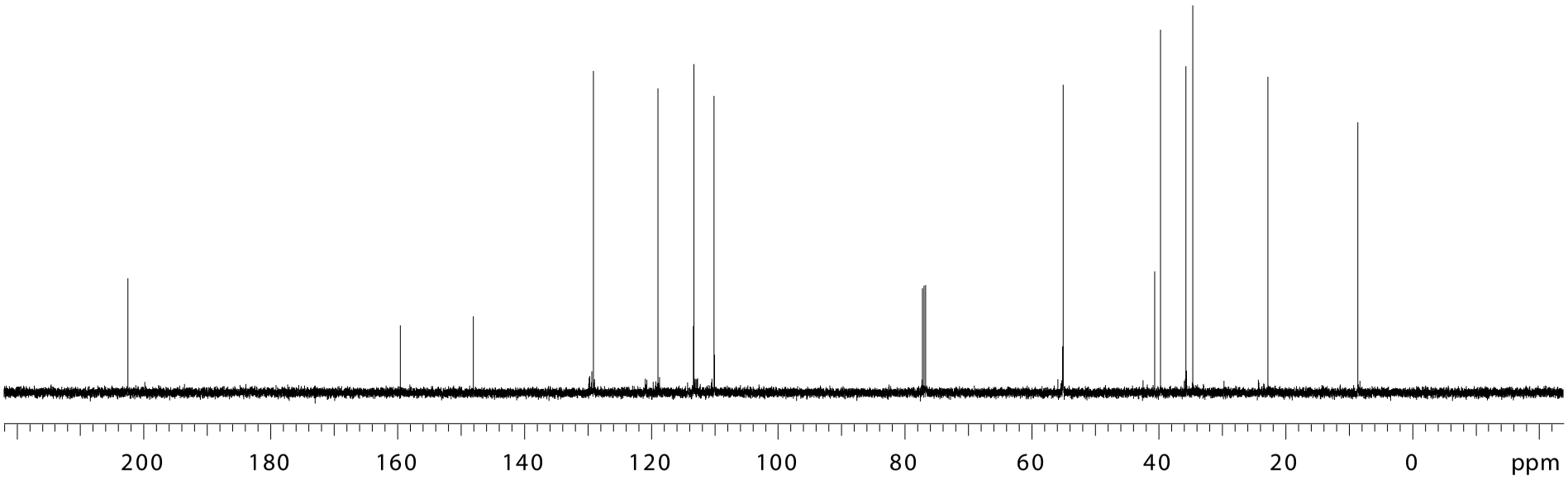


mei-04-120-4-C-500M

Pulse Sequence: s2pul

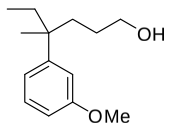



2d



mei-04-120-4-ol-H-500M

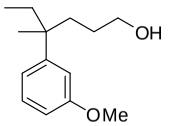
Pulse Sequence: s2pul



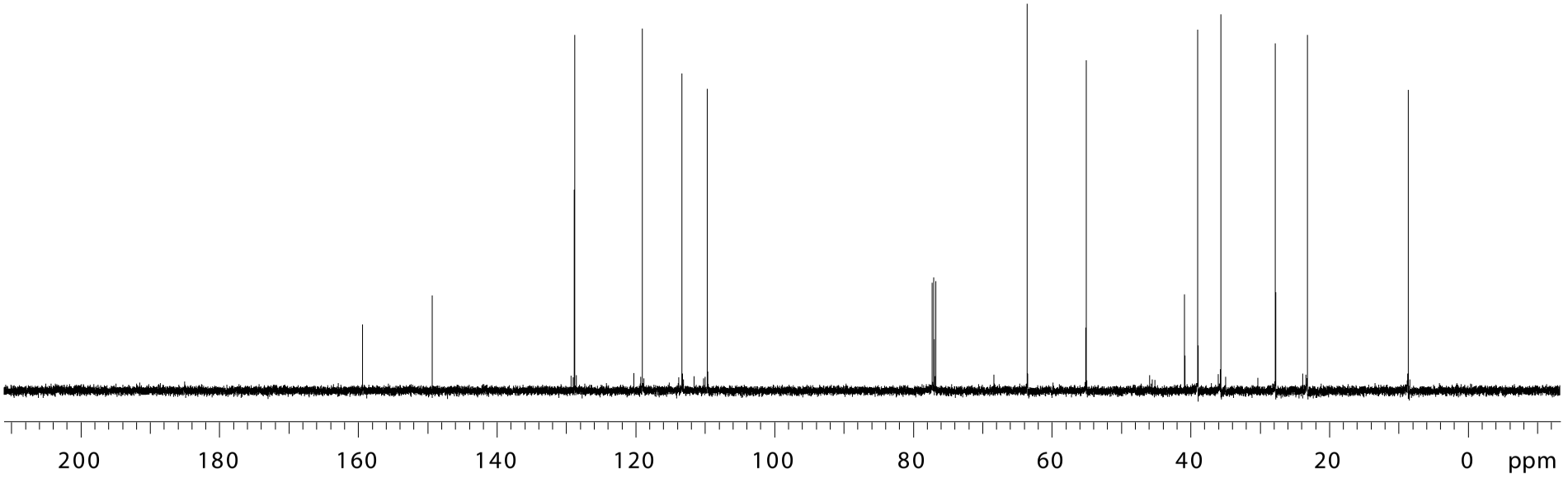

2d-ol

mei-04-120-4-ol-C-500M

Pulse Sequence: s2pul

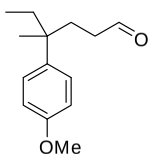



2d-ol



mei-04-120-1-H-500M

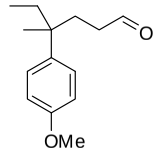
Pulse Sequence: s2pul




2e

STANDARD CARBON PARAMETERS

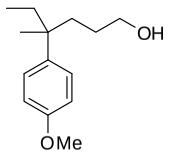
Pulse Sequence: s2pul



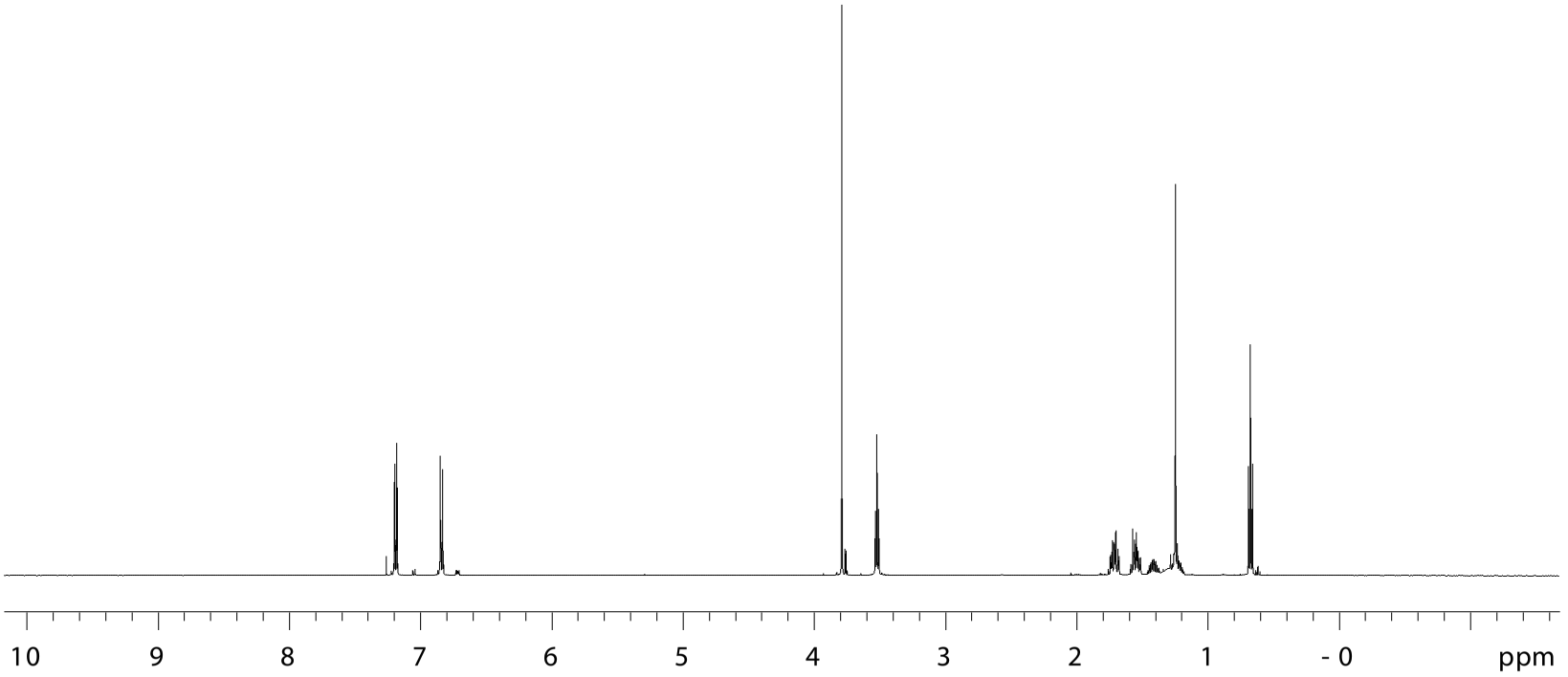

2e

mei-04-120-1-ol-H-500M

Pulse Sequence: s2pul

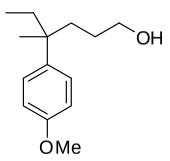



2e-ol

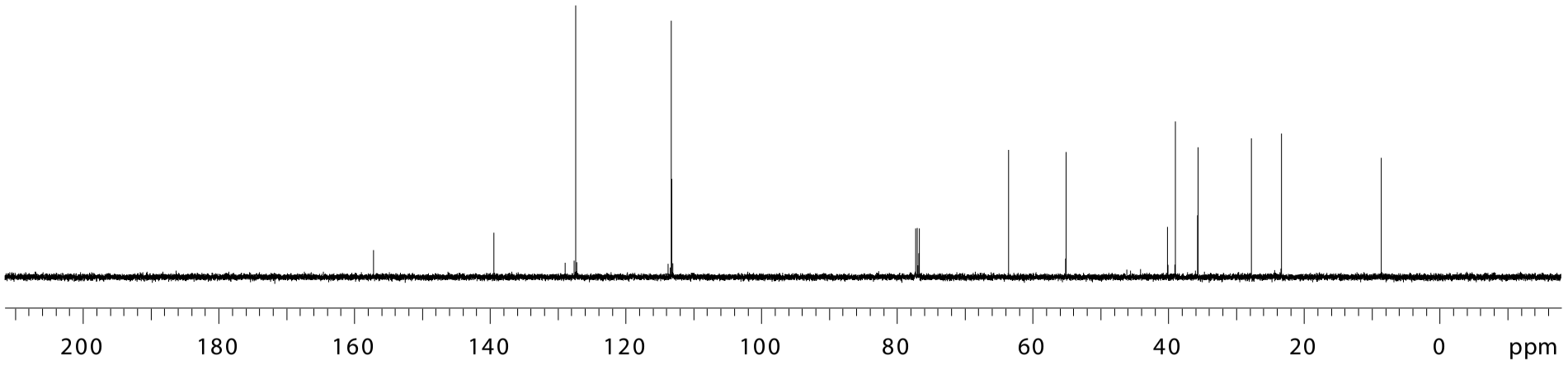


mei-04-120-1-ol-C-500M

Pulse Sequence: s2pul

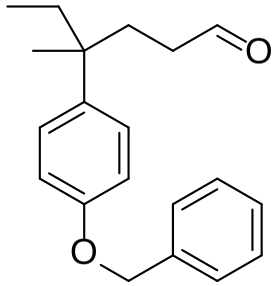



2e-ol



hp2-65-OBn-aldehyde-chiral

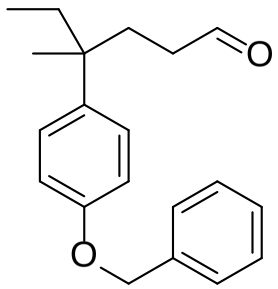
Pulse Sequence: s2pul



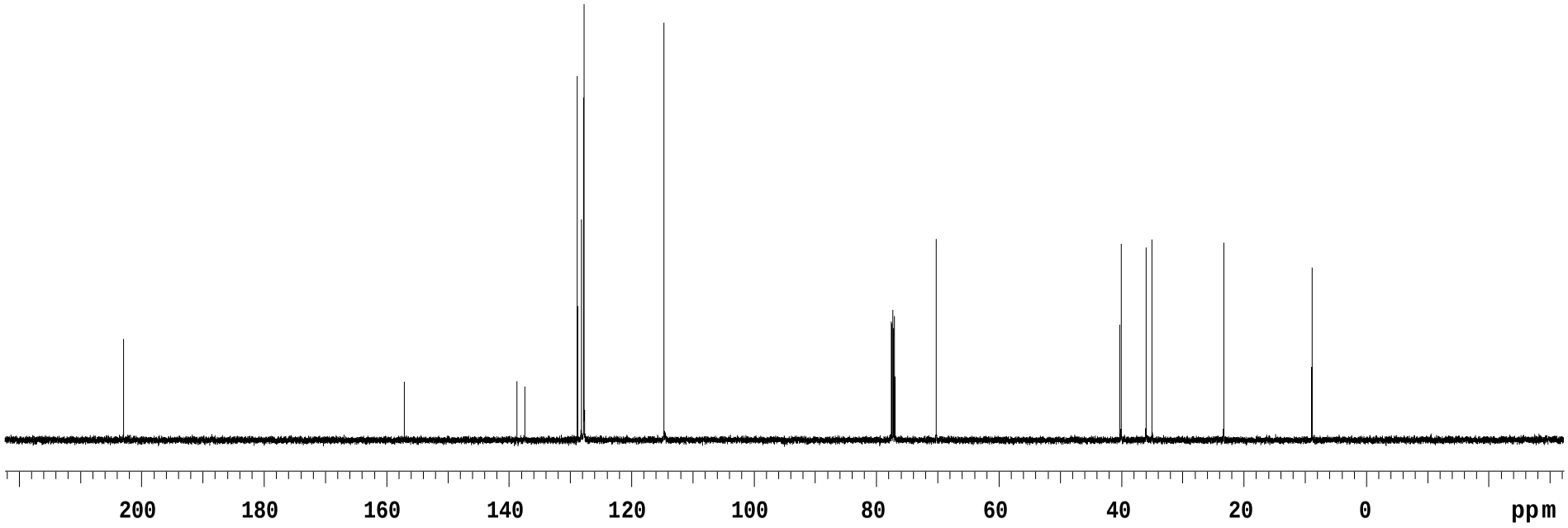

2f

hp2-65-OBn-aldehyde-chiral-C13

Pulse Sequence: s2pul




2f

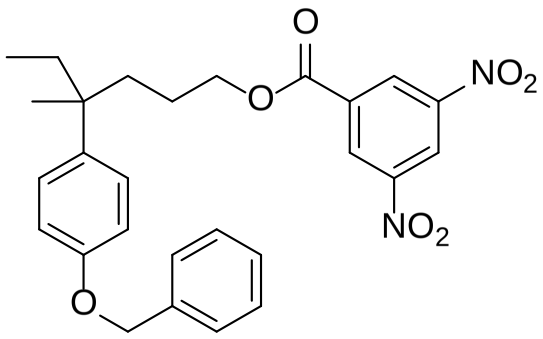


hp2-OBn-ester-chiral

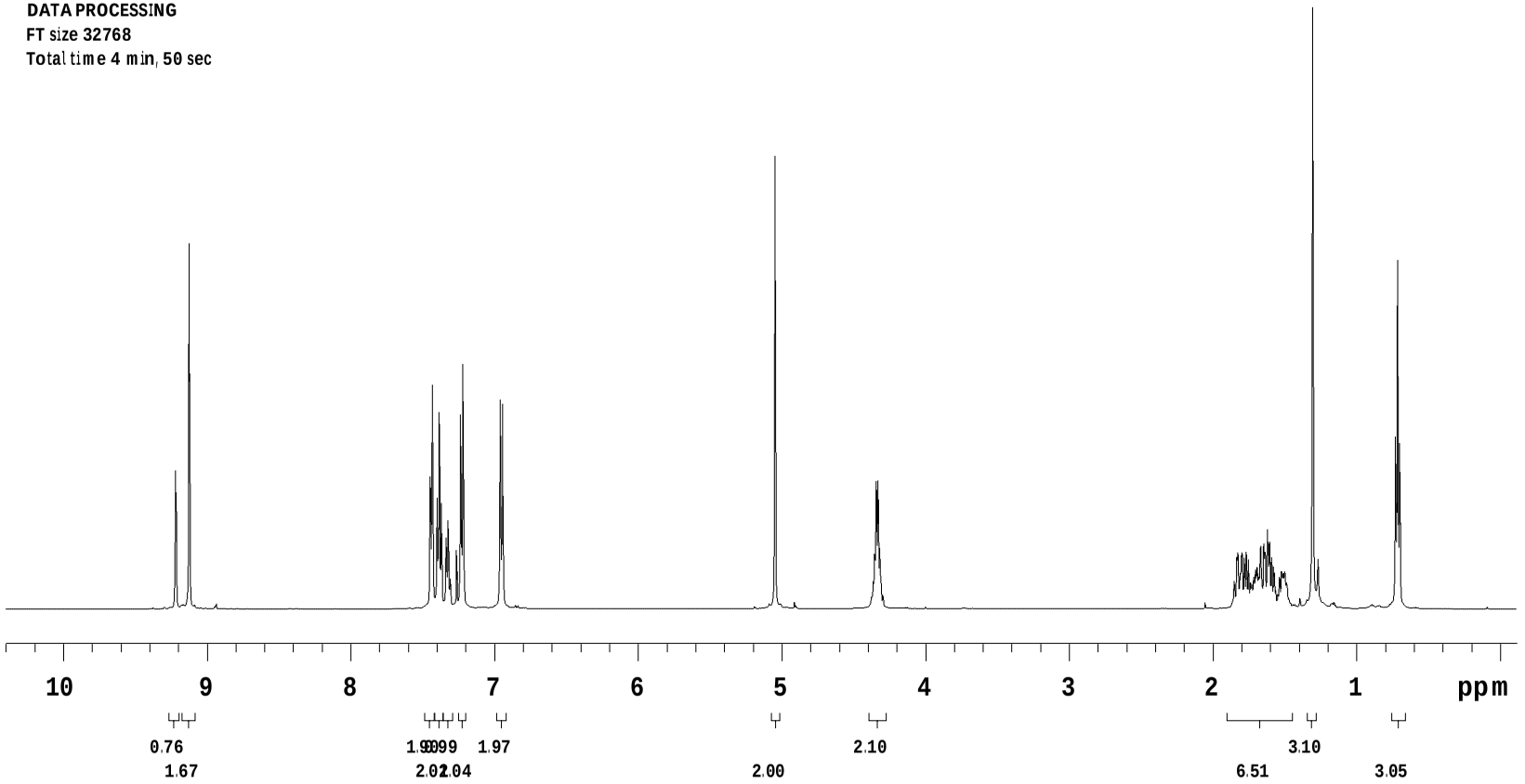
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: hp2-65-OBn-ester-chiral
UNITY-500 "vxr500nmr"

Relax. delay 1.000 sec
Pulse 33.5 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.8137042 MHz
DATA PROCESSING
FT size 32768
Total time 4 min, 50 sec

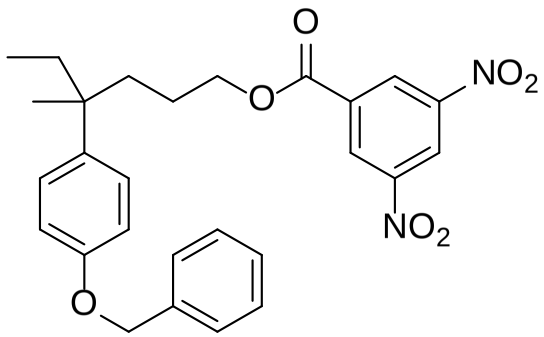



2f-ester

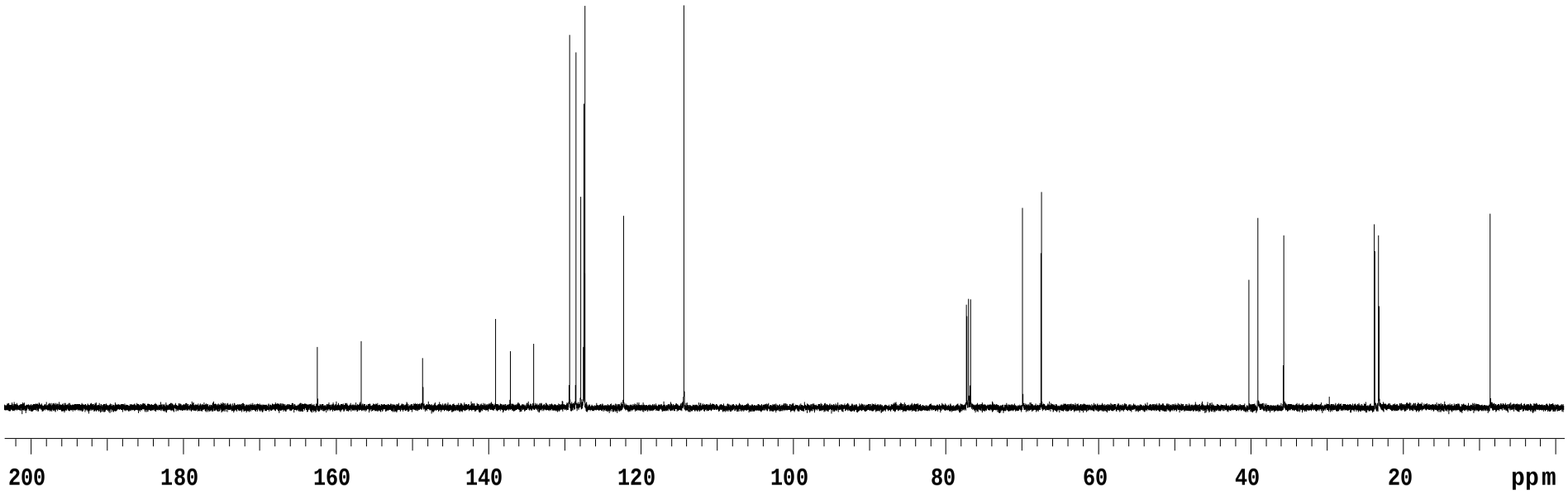


hp2-65-OBn-ester-chiral-C13

Pulse Sequence: s2pul

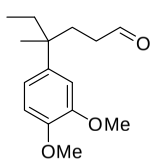



2f-ester



mei-04-120-5-6-H-500M

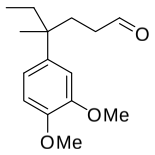
Pulse Sequence: s2pul



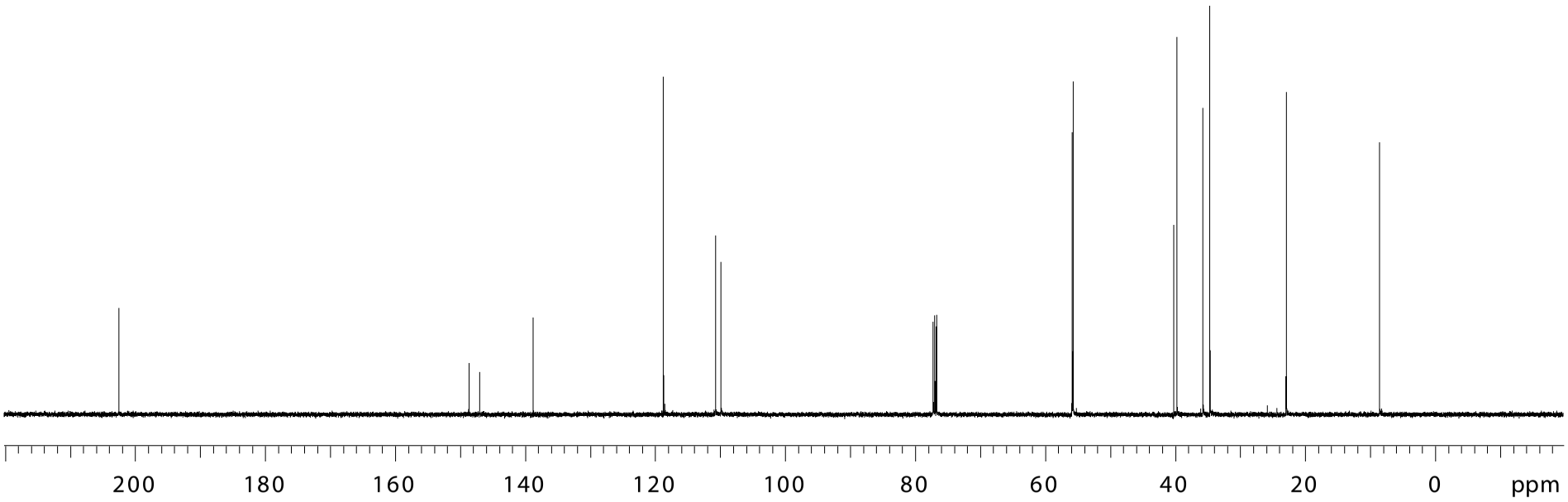

2g

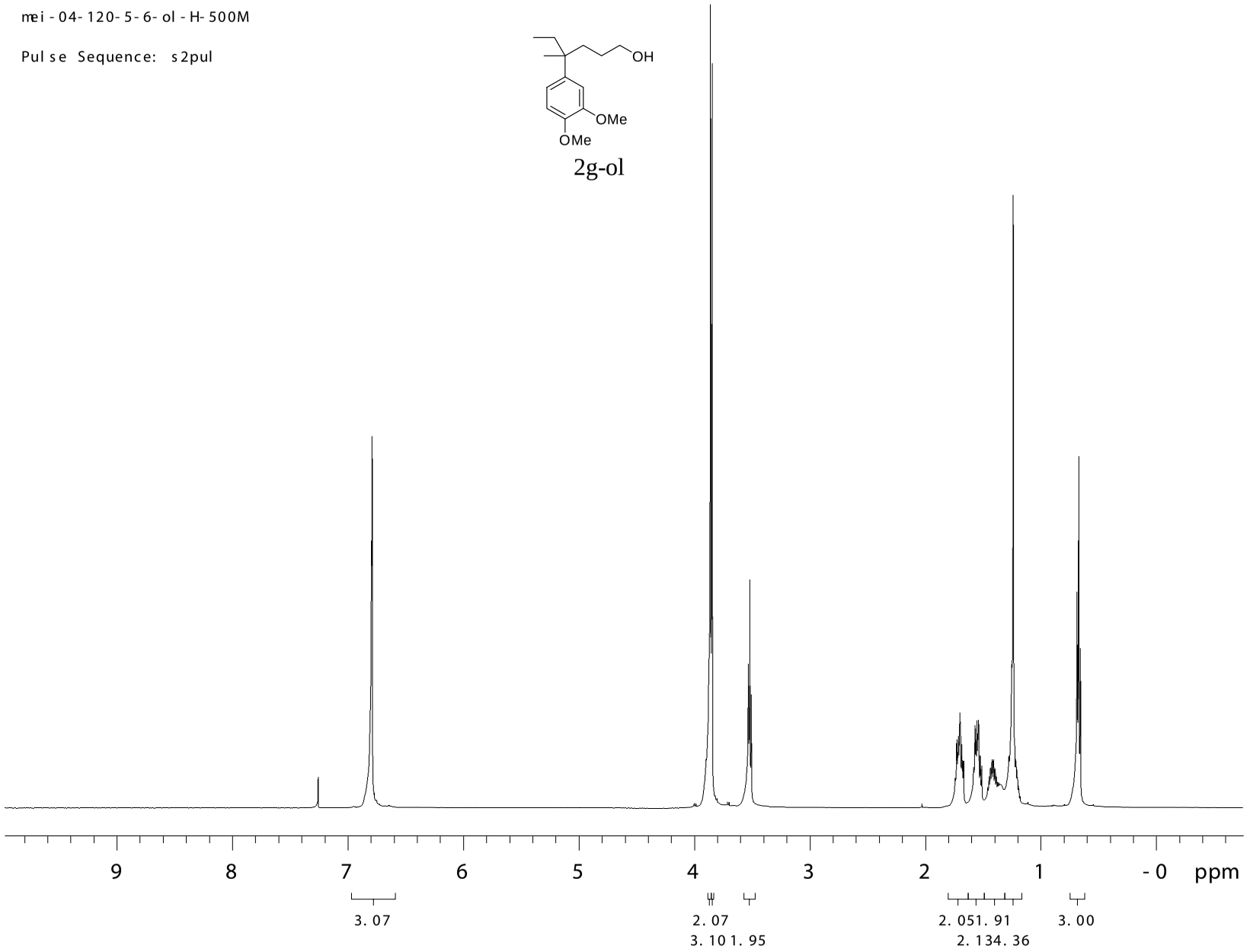
mei-04-120-5-6-C-500M

Pulse Sequence: s2pul



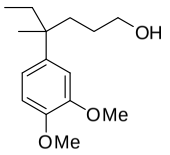

2g



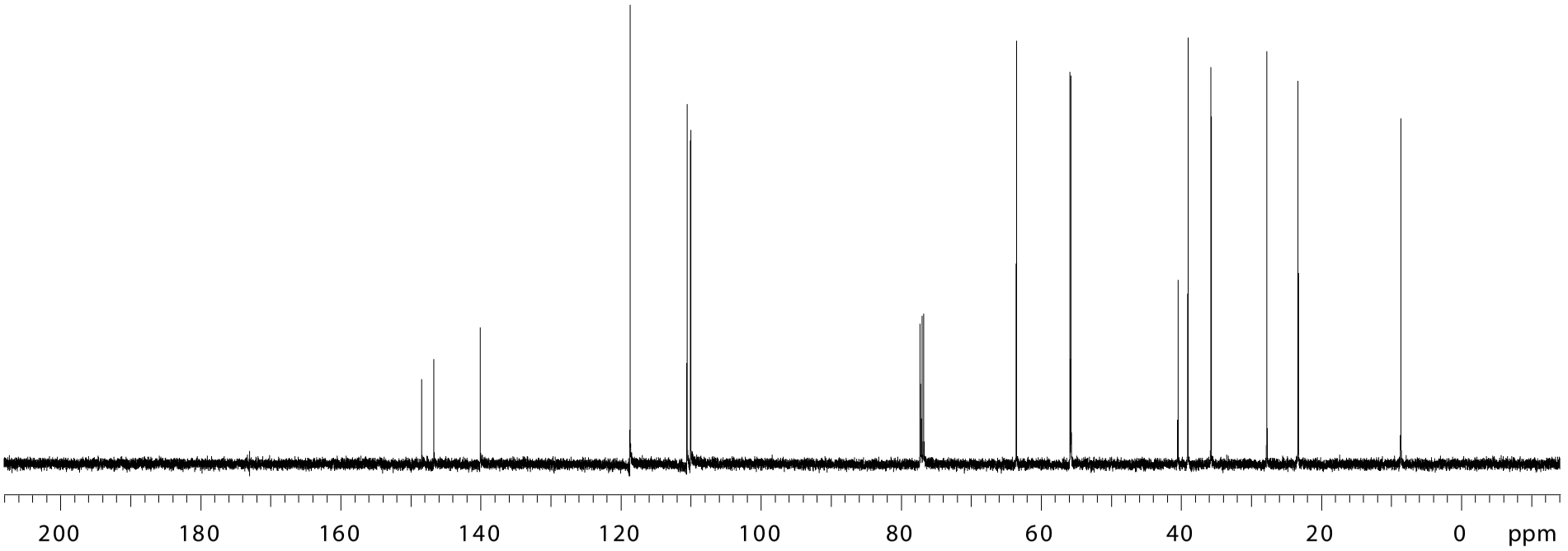

mei-04-120-5-6-ol-H-500M
Pulse Sequence: s2pul
OH
OMe
OMe
2g-ol
9
8
7
6
5
4
3
2
1
-0
ppm
3.07
2.07
3.10
1.95
2.05
1.91
2.13
4.36
3.00

mei-04-120-5-6-C-500M

Pulse Sequence: s2pul

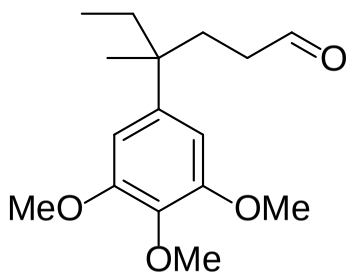



2g-ol

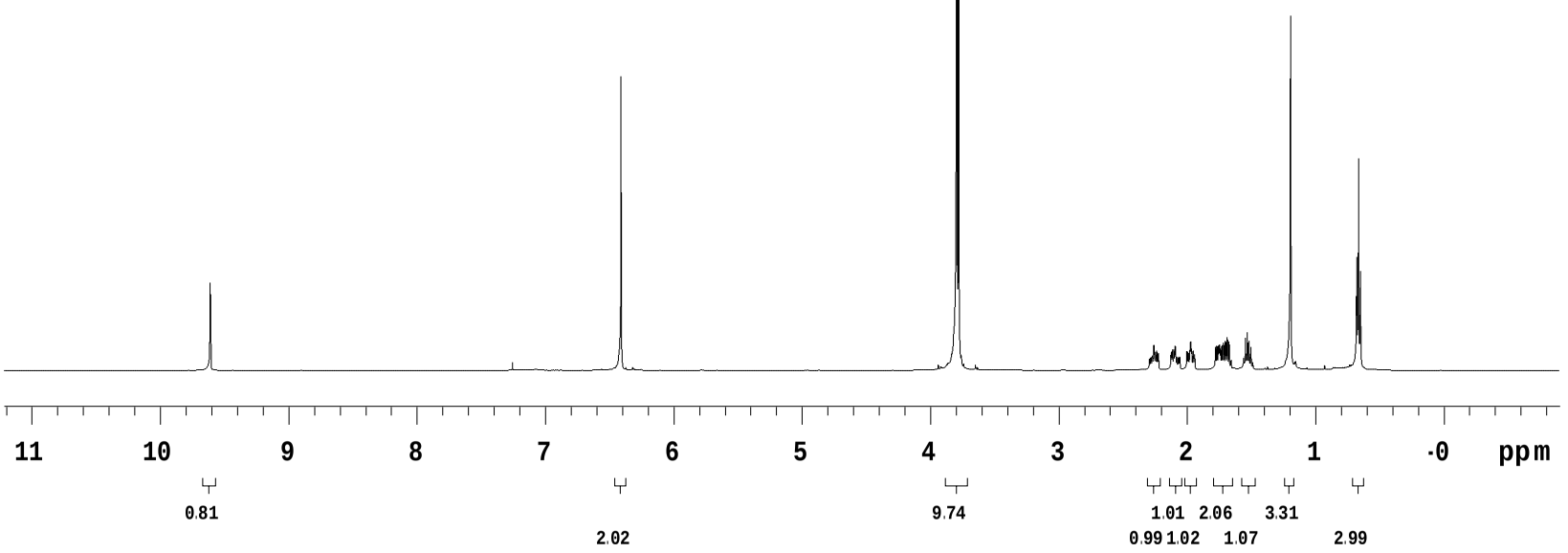


hp-111-pdt-chiral

Pulse Sequence: s2pul

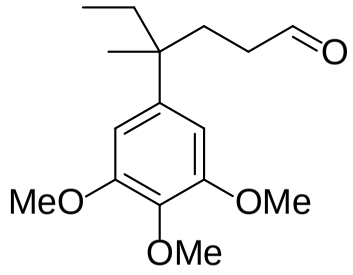



2h



hp-111-pdt-chiral

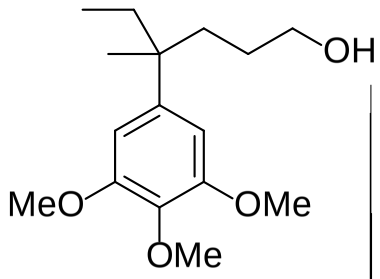
Pulse Sequence: s2pul



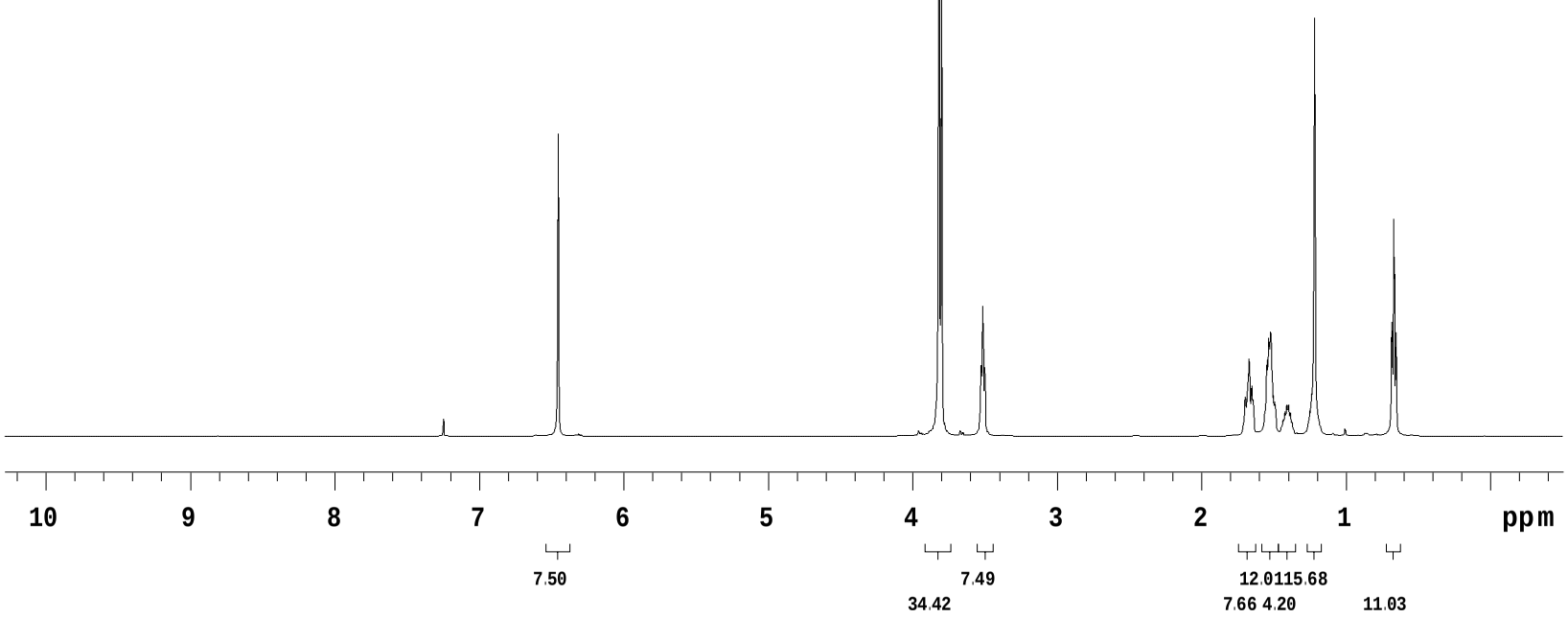

2h

hp2-13-trimethoxy-chiral-alcohol

Pulse Sequence: s2pul

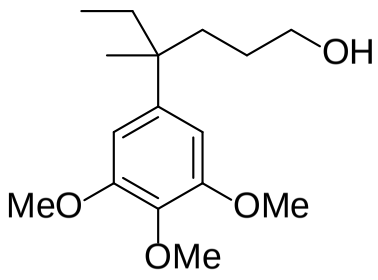



2h-ol



hp2-13-trimethoxy-chiral-alcoholC13

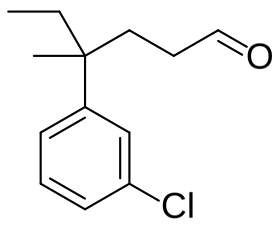
Pulse Sequence: s2pul




2h-ol

mei-04-180-H-500M

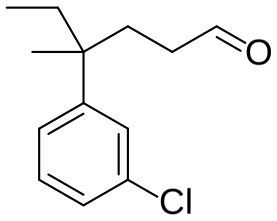
Pulse Sequence: s2pul



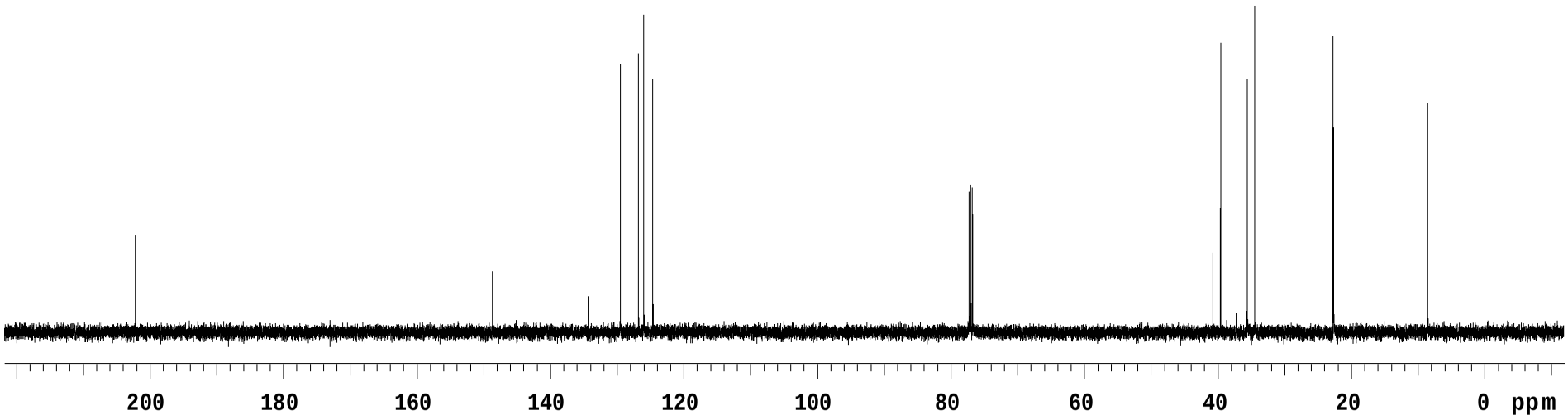

2i

mei-04-180-C-500M

Pulse Sequence: s2pul

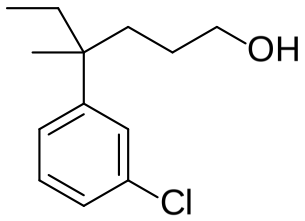



2i



mei-05-180-ol-H-500M

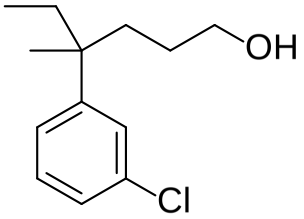
Pulse Sequence: s2pul



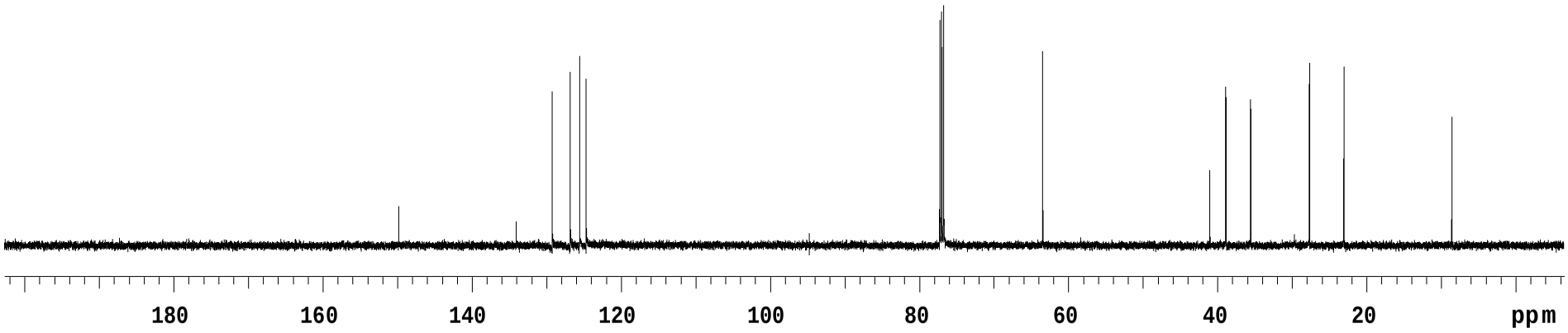

2i-ol

mei-04-180-ol-C-500M

Pulse Sequence: s2pul

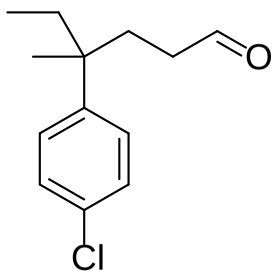



2i-ol



mei-04-154-1-H-500M

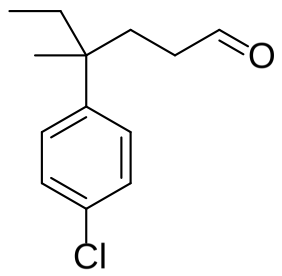
Pulse Sequence: s2pul




2j

mei-04-145-1-C-500M

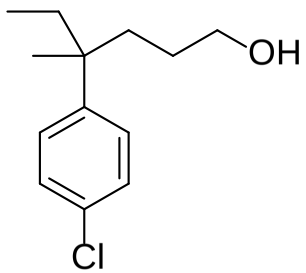
Pulse Sequence: s2pul




2j

mei-04-145-1-2-ol-H-500M

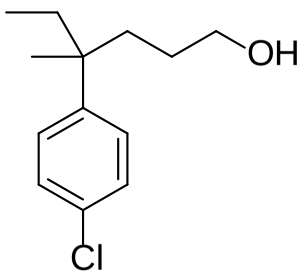
Pulse Sequence: s2pul



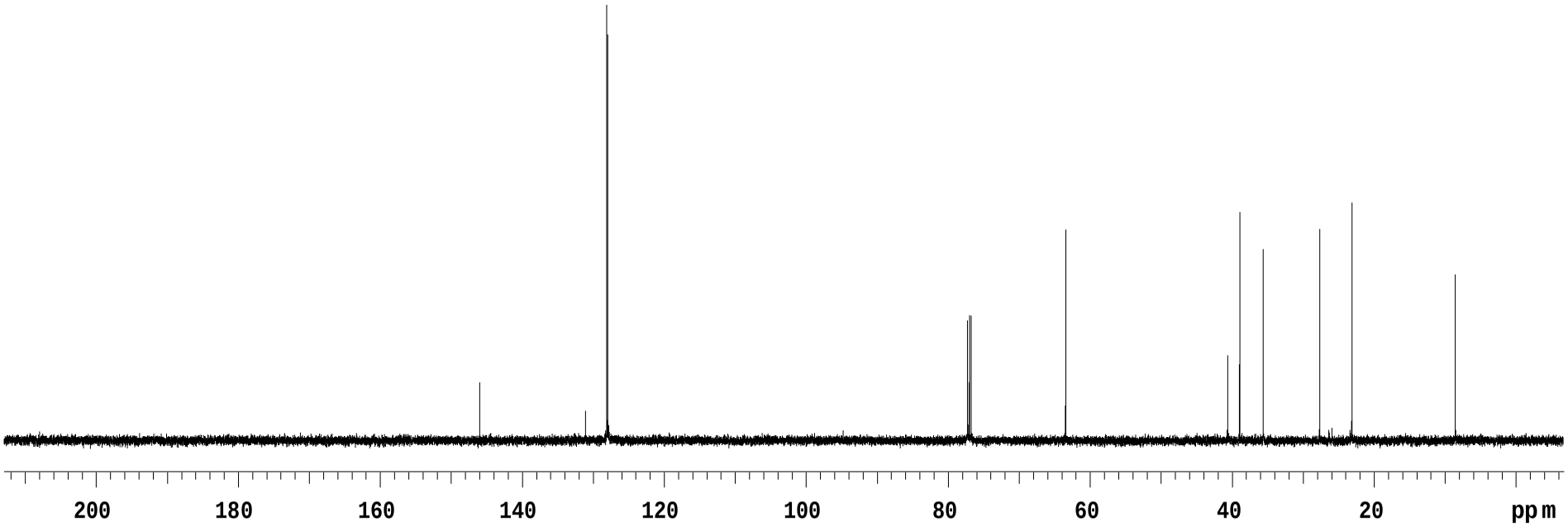

2j-ol

mei-04-145-1-2-ol-C-500M

Pulse Sequence: s2pul

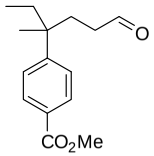



2j-ol



mei-04-94-H-500M

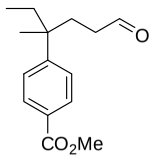
Pulse Sequence: s2pul



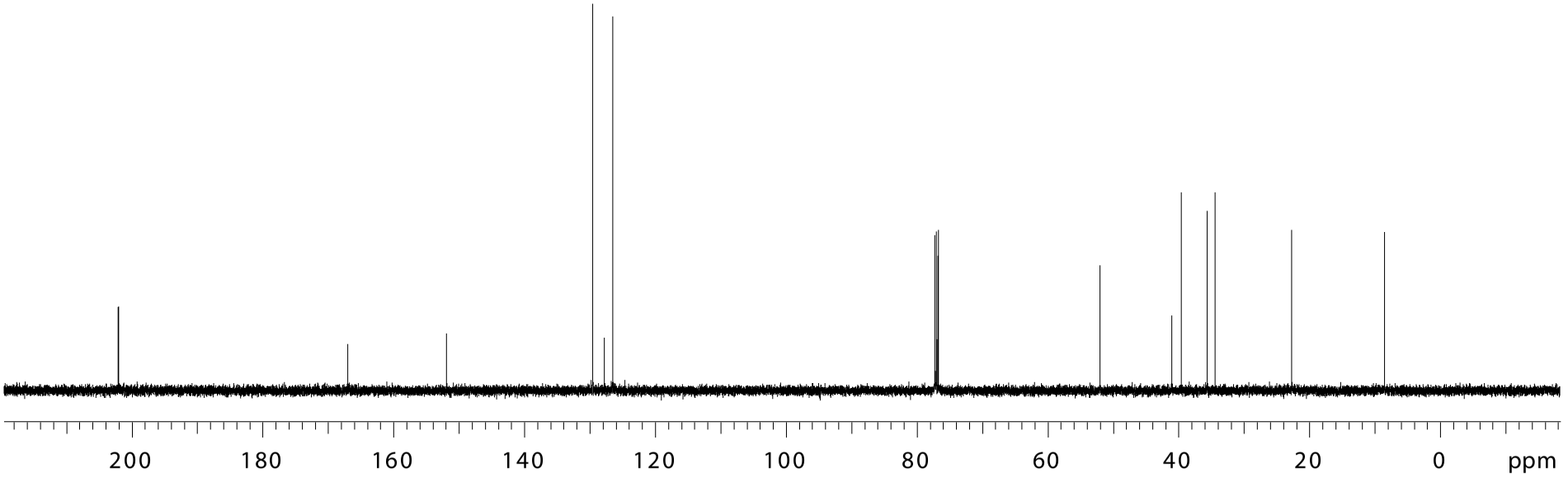

2k

mei-04-94-C-500M

Pulse Sequence: s2pul

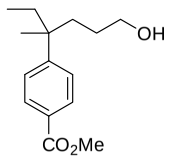



2k



mei-04-94-ol-H-500M

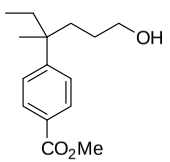
Pulse Sequence: s2pul



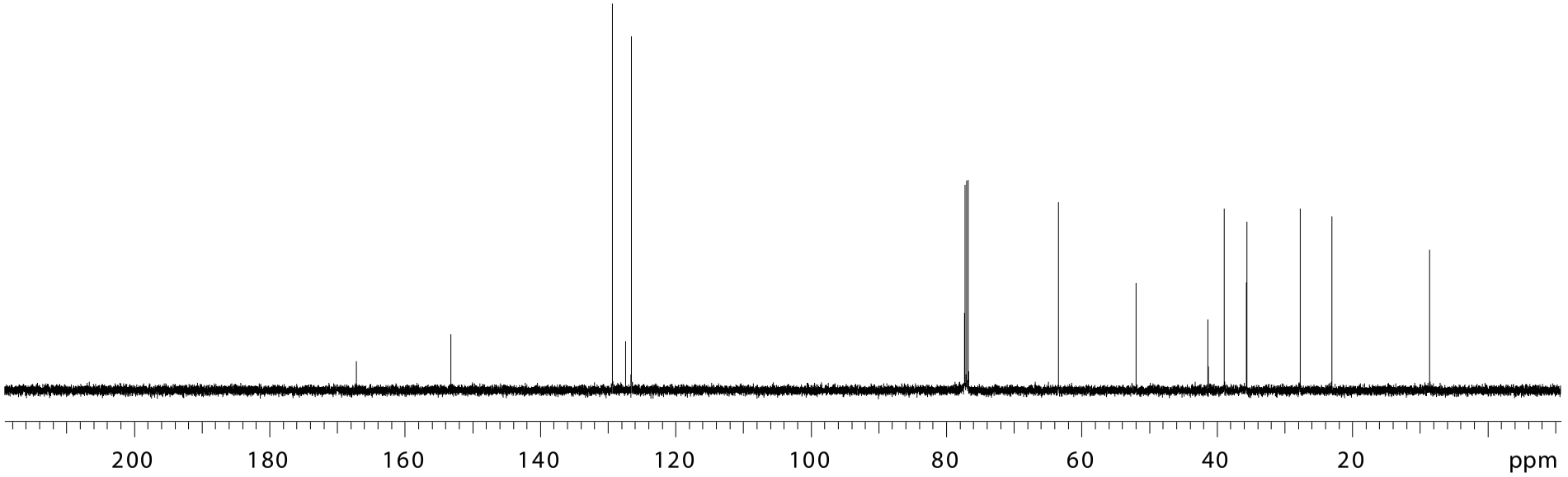

2k-ol

mei-04-94-ol-C-500M

Pulse Sequence: s2pul

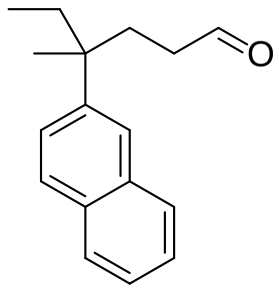



2k-ol



Napthyl-partII-pure-aldehyde-quart

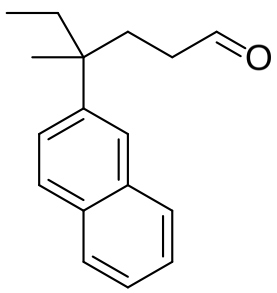
Pulse Sequence: s2pul



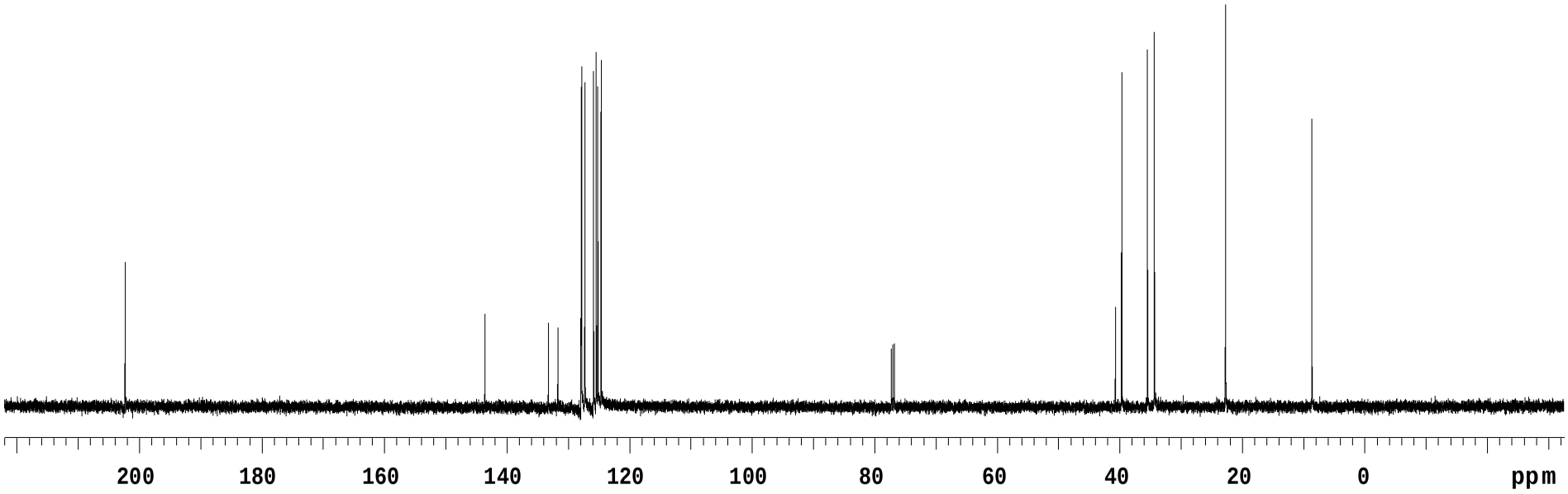

2l

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul

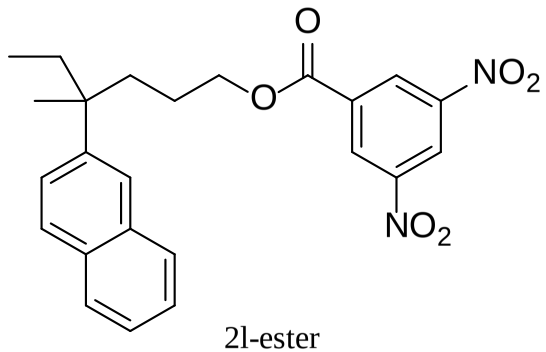



2l



naphthyl-ester-chiral

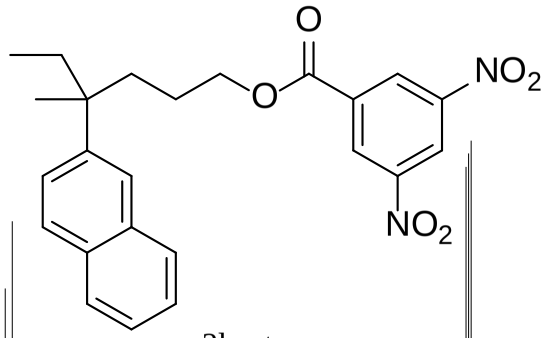
Pulse Sequence: s2pul




2l-ester

hp2-45-napthalene-C13

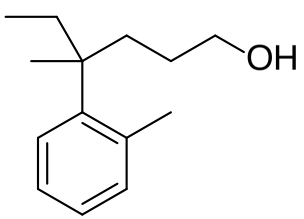
Pulse Sequence: s2pul




2l-ester

mei-05-119-ol-H-500M

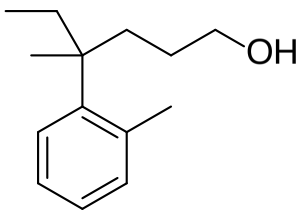
Pulse Sequence: s2pul



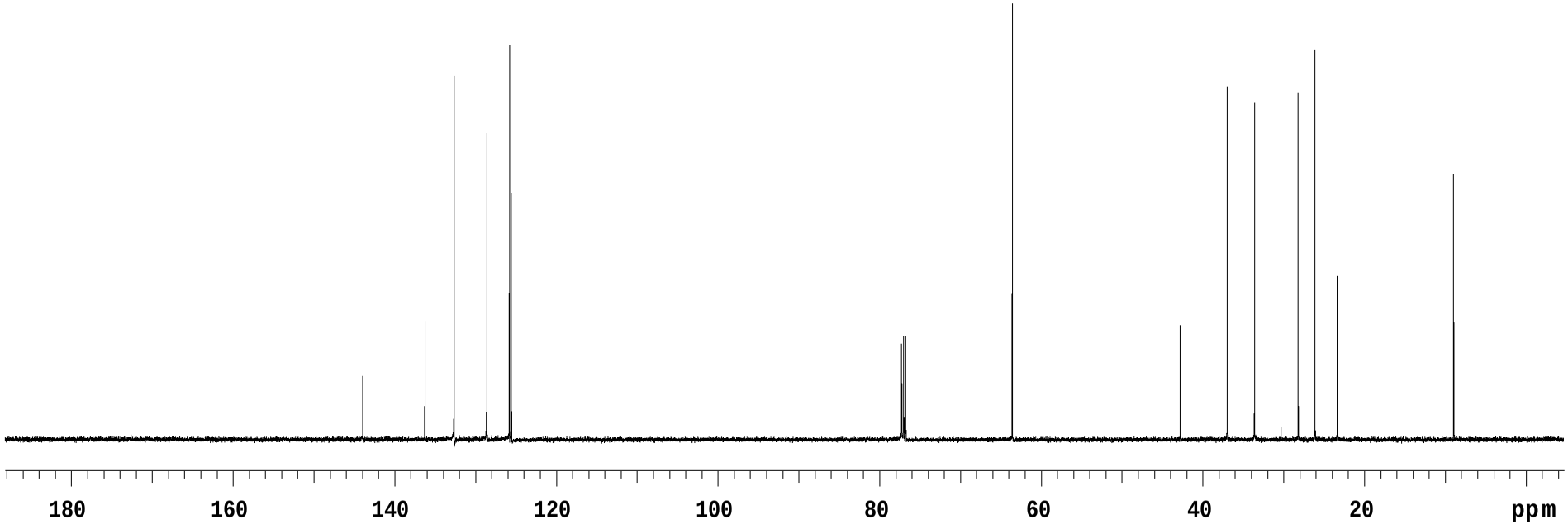

2m-ol

mei-05-119-ol-C-500M

Pulse Sequence: s2pul

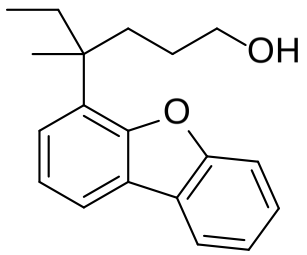



2m-ol



STANDARD PROTON PARAMETERS

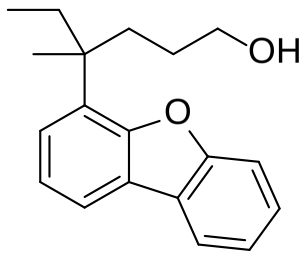
Pulse Sequence: s2pul



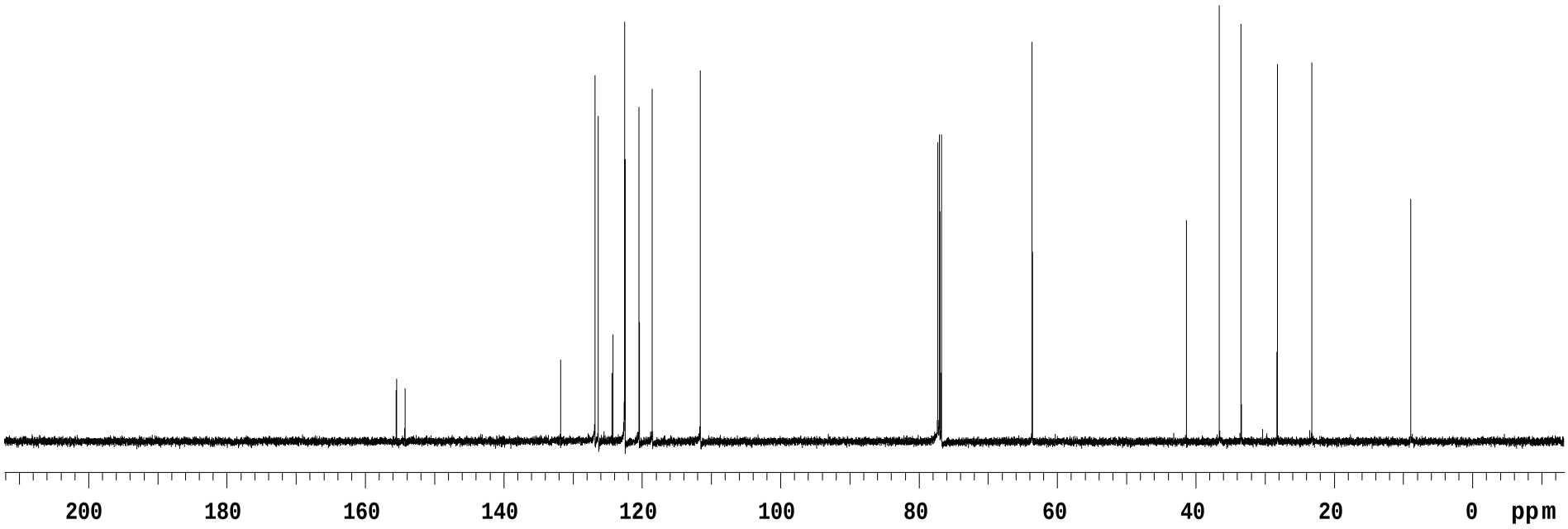

2n-ol

mei-04-170-2-C-500M

Pulse Sequence: s2pul

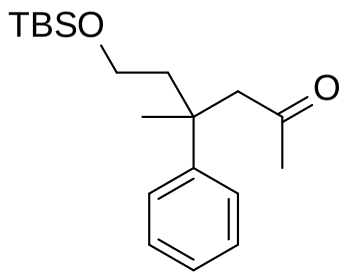



2n-ol



mei-05-45-H-500M

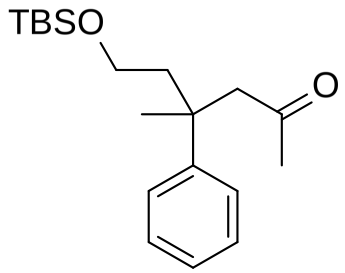
Pulse Sequence: s2pul




3a

mei-05-45-C-500M

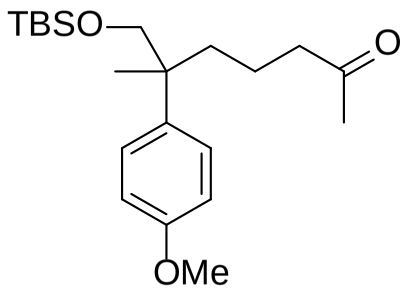
Pulse Sequence: s2pul




3a

mei-04-152-H-500M

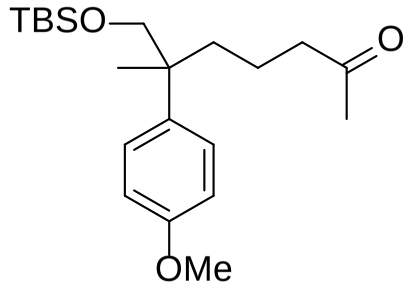
Pulse Sequence: s2pul




3b

mei-04-152-C-500M

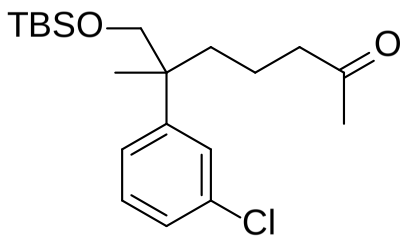
Pulse Sequence: s2pul




3b

mei-04-178-H-500M

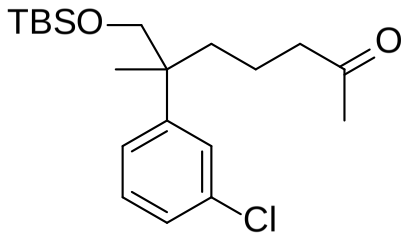
Pulse Sequence: s2pul



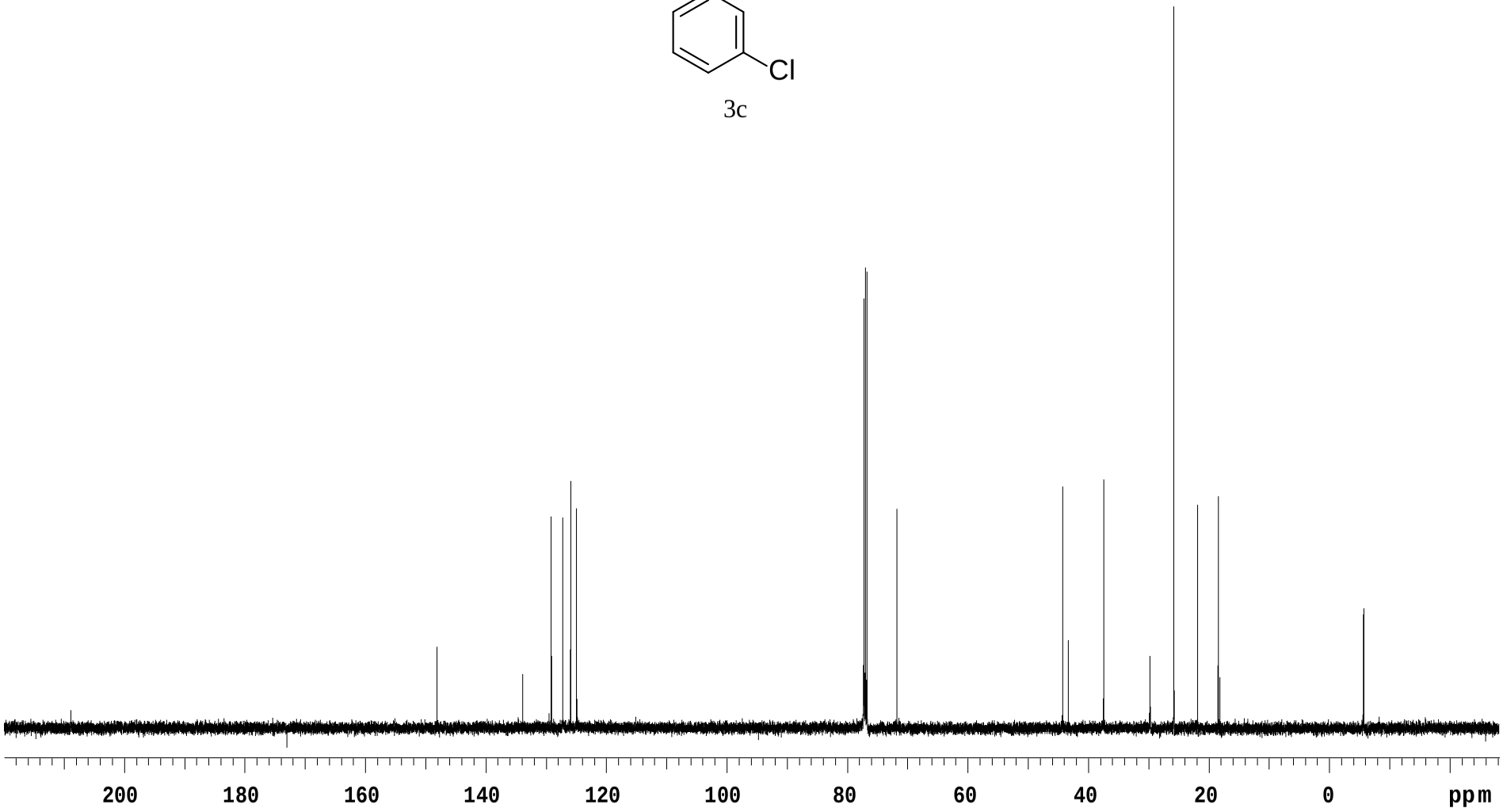

3c

mei-04-178-C-500M

Pulse Sequence: s2pul

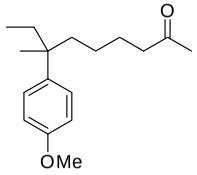



3c



mei-04-124-4-H-500M

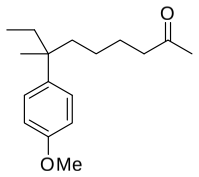
Pulse Sequence: s2pul



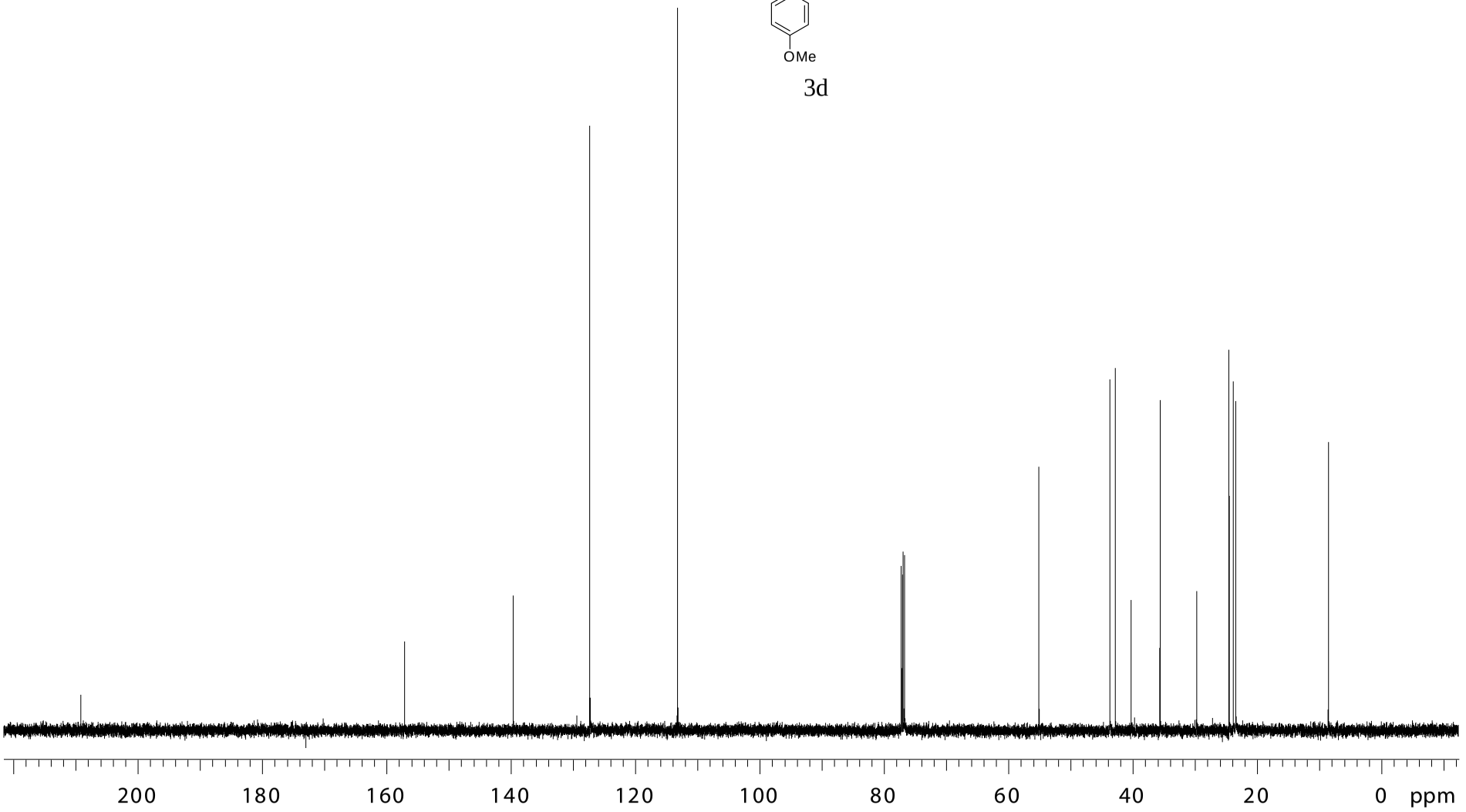

3d

mei-04-124-4-C-500M

Pulse Sequence: s2pul

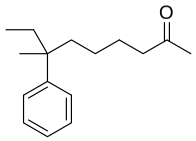



3d



mei-04-107-H-500M

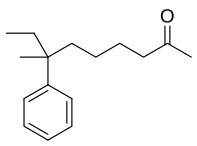
Pulse Sequence: s2pul



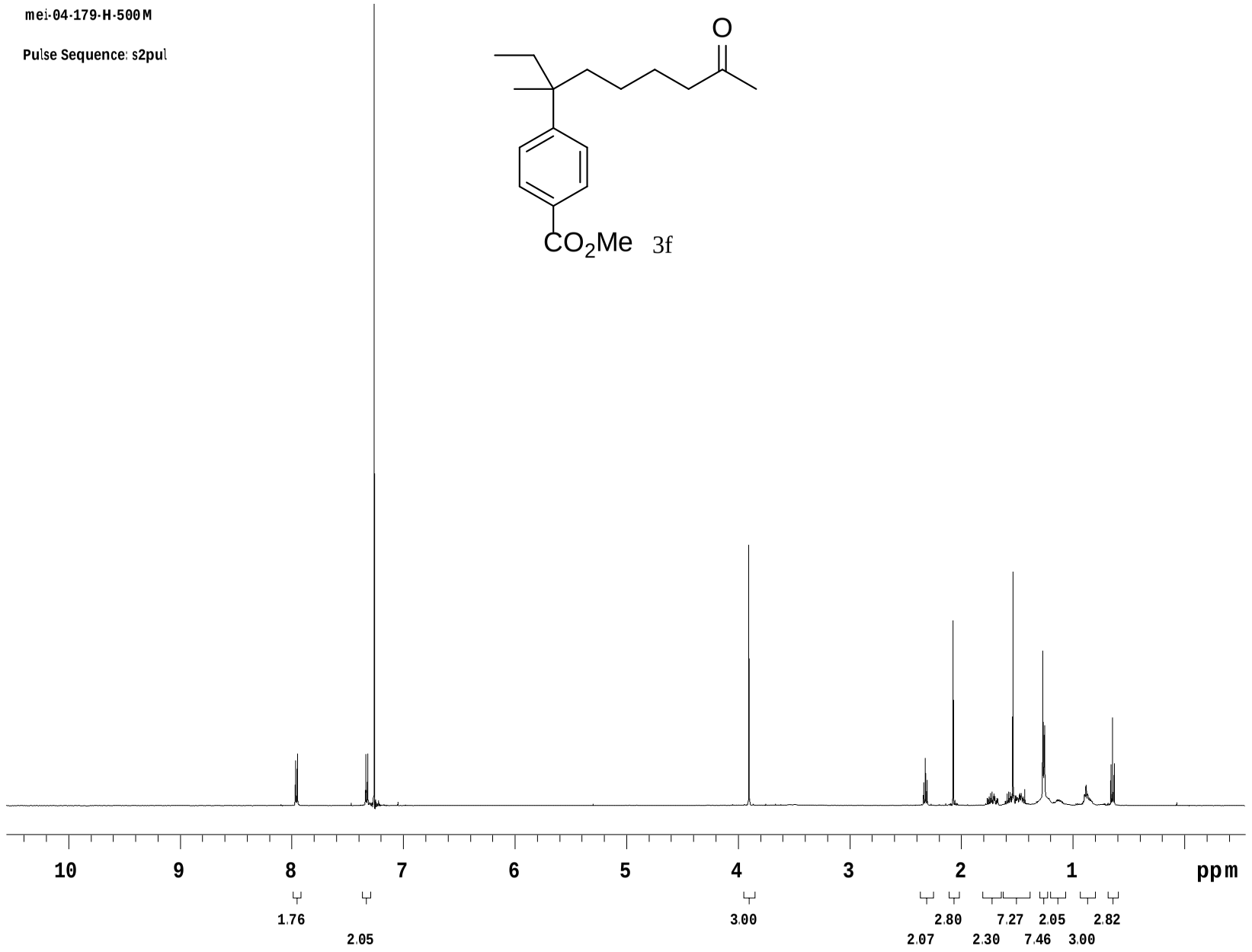
3e

mei-04-107-C-500M

Pulse Sequence: s2pul

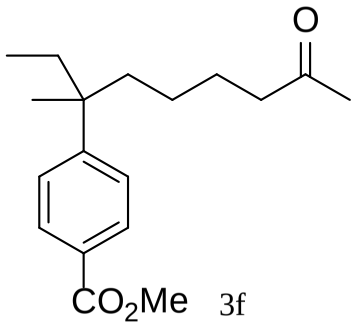



3e

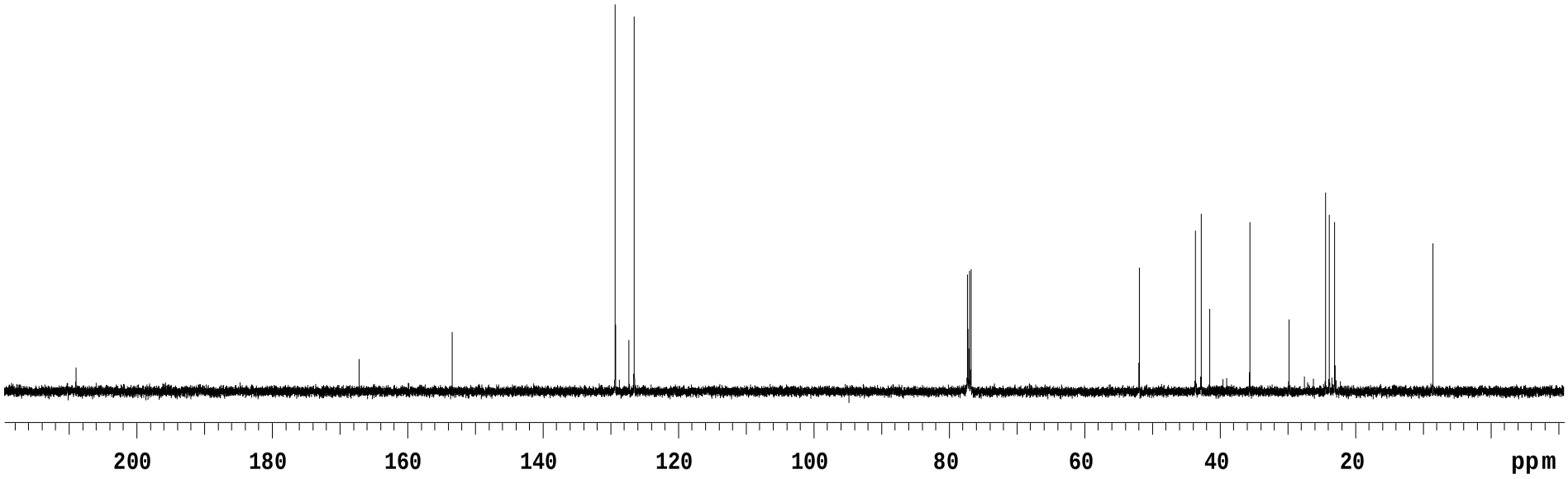

mei-04-179-H-500M
Pulse Sequence: s2pul
O
CO2Me
3f
10
9
8
7
6
5
4
3
2
1
ppm
1.76
2.05
3.00
2.07
2.80
2.30
7.27
7.46
2.05
3.00
2.82

mei-04-179-C-500M

Pulse Sequence: s2pul

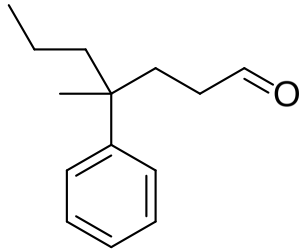



3f

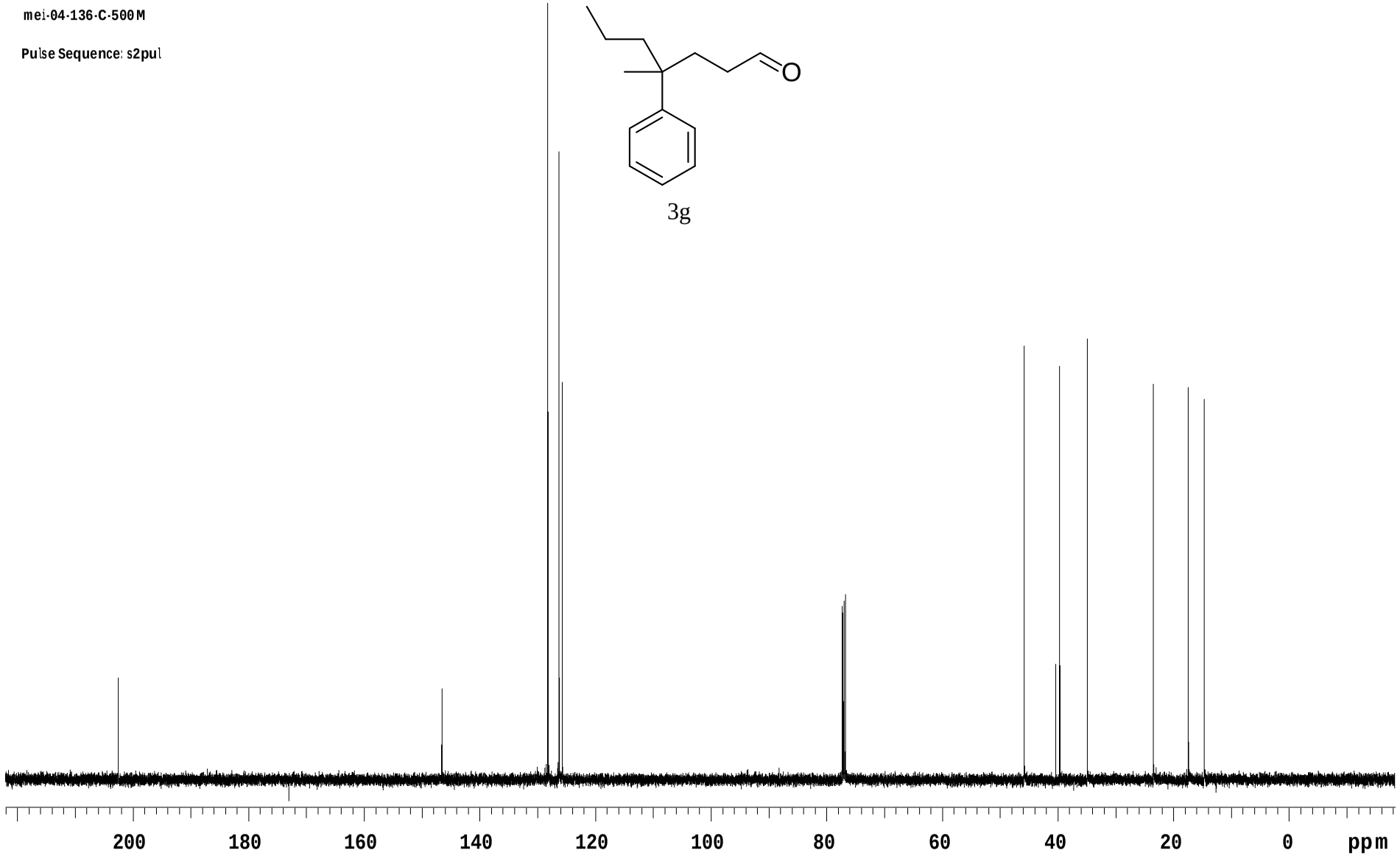


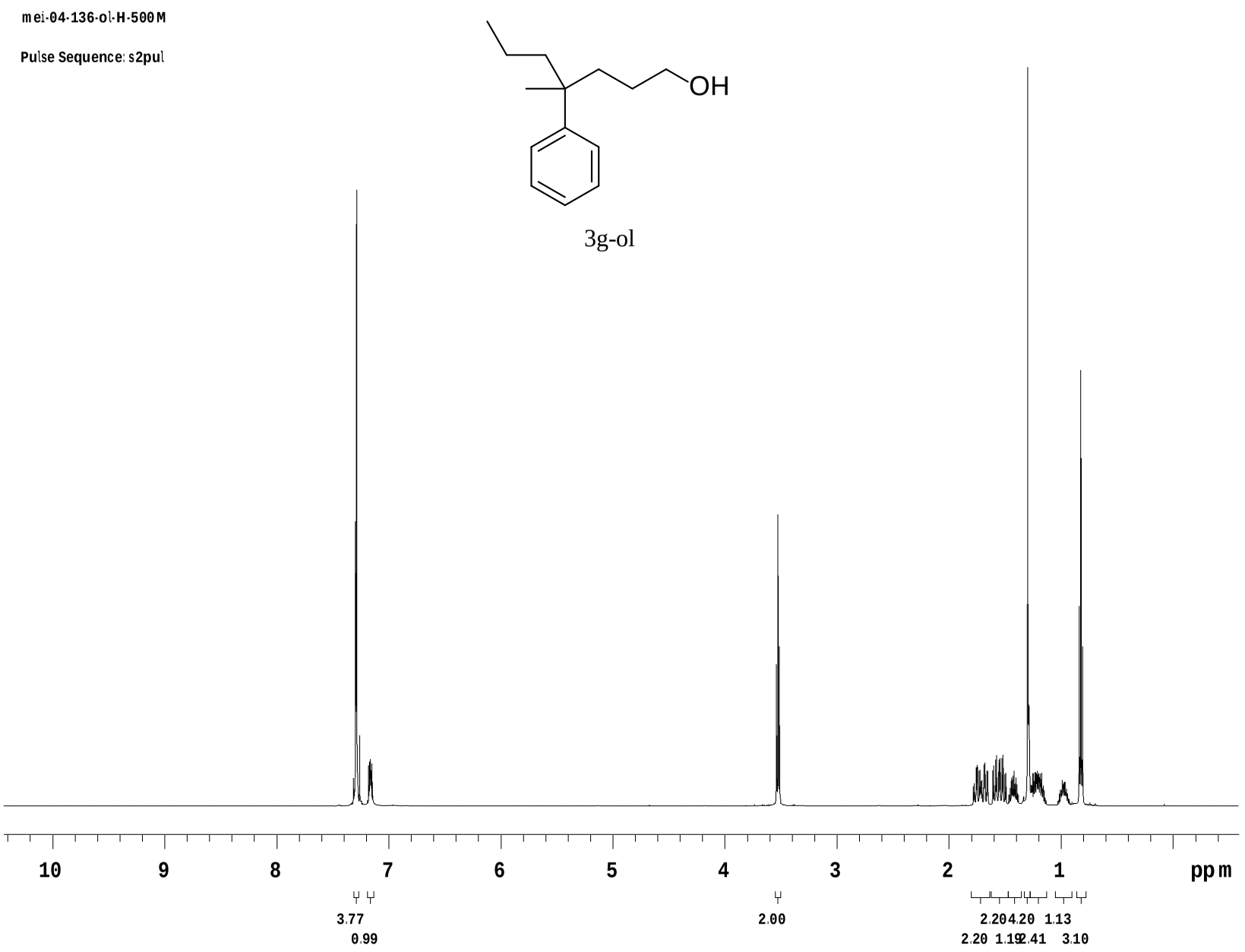
mei-04-136-1-H-500M

Pulse Sequence: s2pul



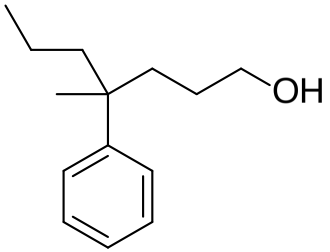

3g


mei-04-136-C-500M
Pulse Sequence: s2pul
O
3g
200
180
160
140
120
100
80
60
40
20
0
ppm

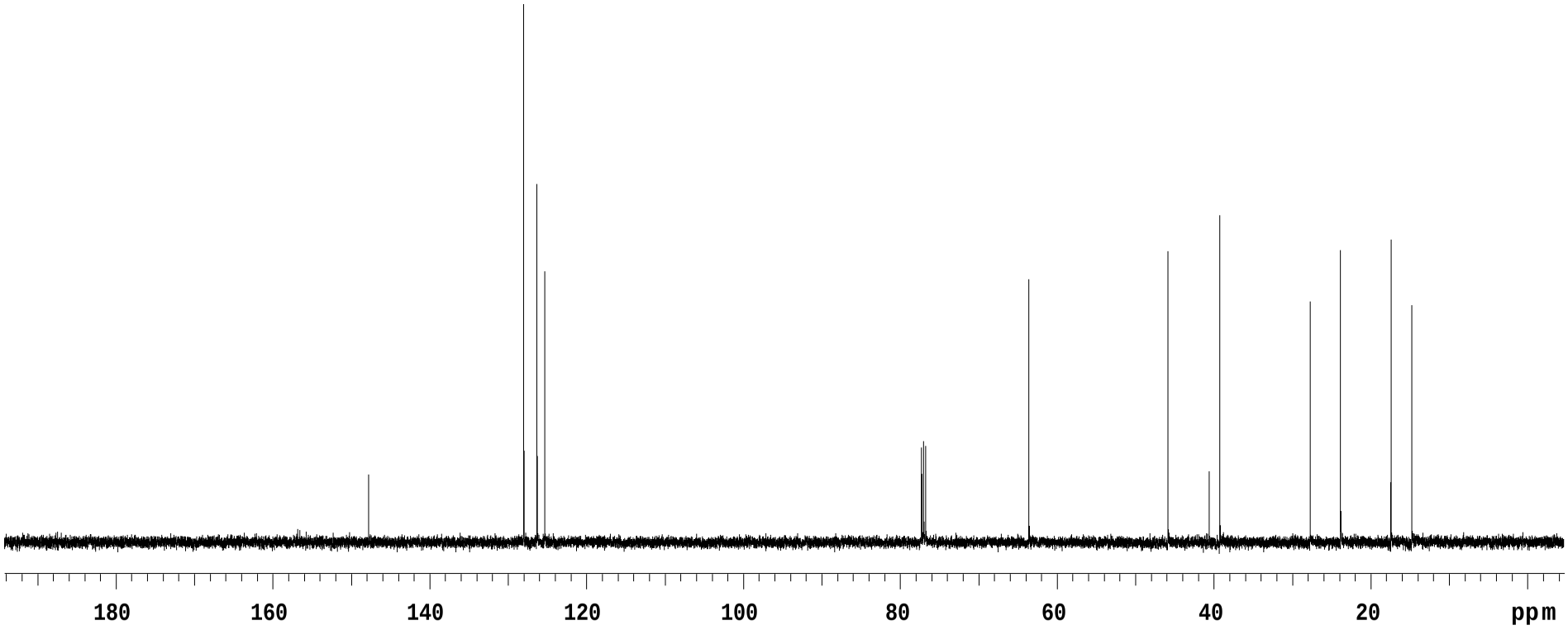

mei-04-136-ol-H-500M
Pulse Sequence: s2pul
OH
3g-ol
10
9
8
7
6
5
4
3
2
1
ppm
3.77
0.99
2.00
2.20
4.20
1.13
2.20
1.19
2.41
3.10

mei-04-136-ol-C-500M

Pulse Sequence: s2pul

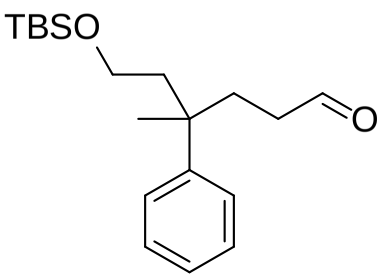



3g-ol



STANDARD PROTON PARAMETERS

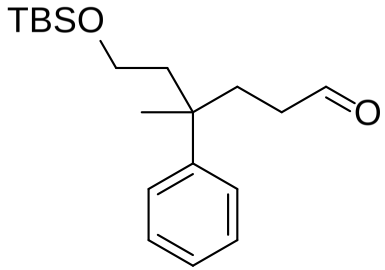
Pulse Sequence: s2pul




3h

mei-05-21-C-500M

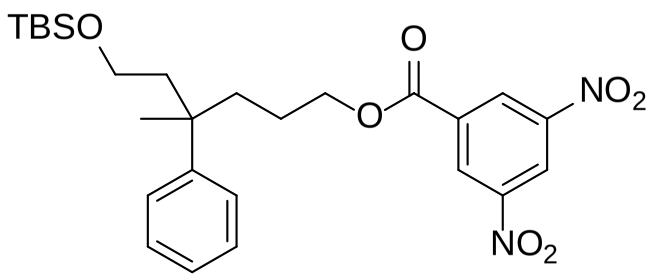
Pulse Sequence: s2pul




3h

mei-05-57-ester-H-500M

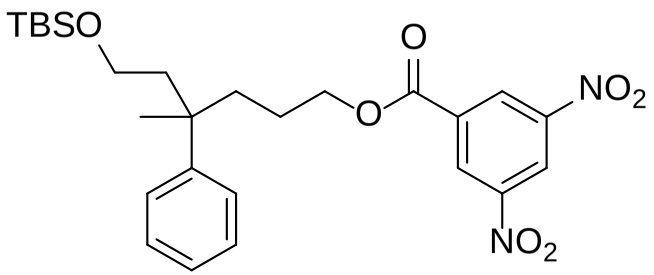
Pulse Sequence: s2pul



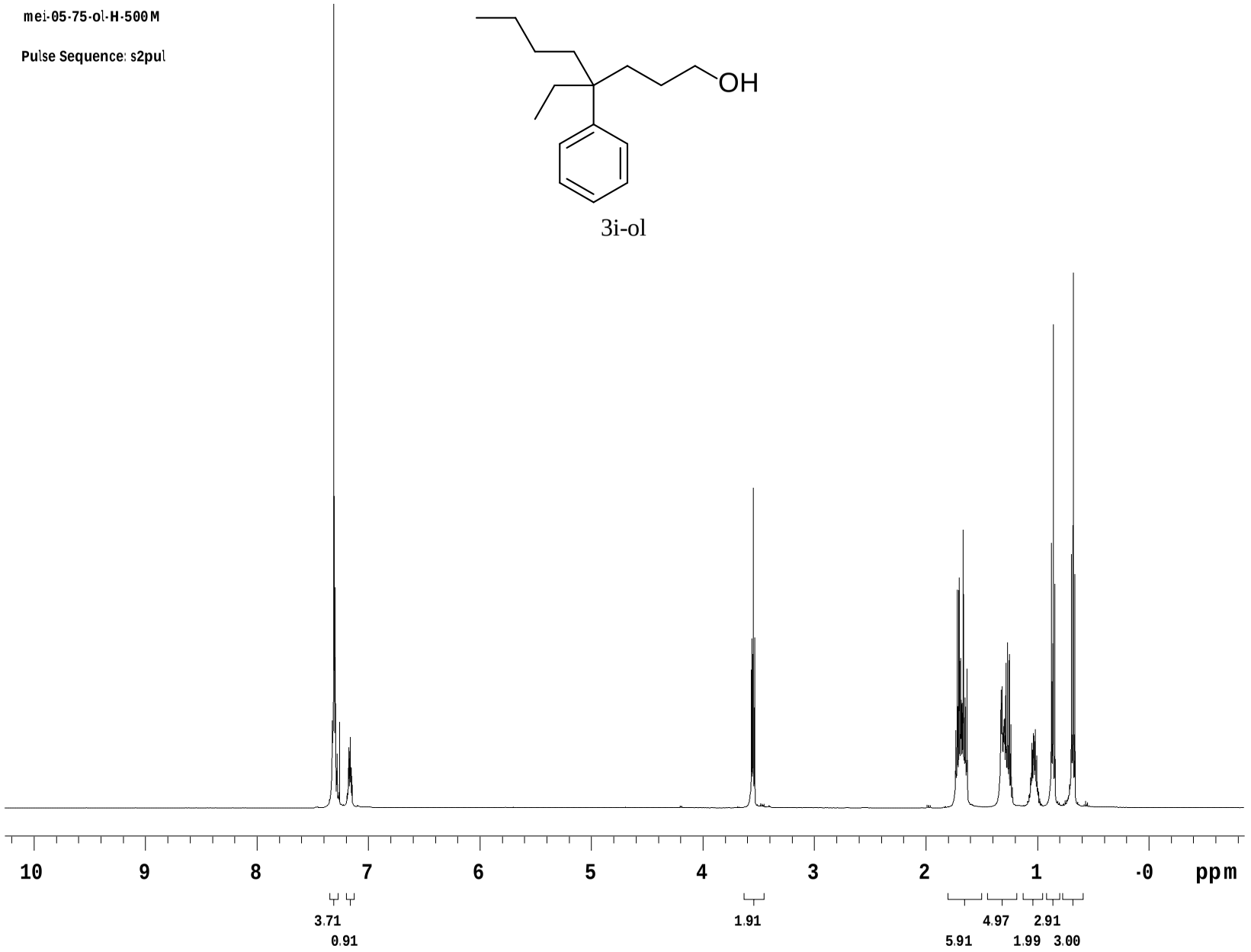

3h-ester

mei-05-57-ester-C-500M

Pulse Sequence: s2pul

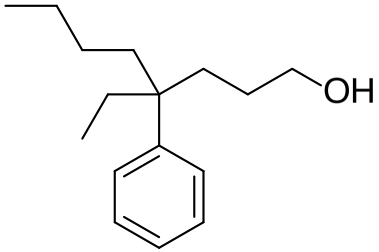



3h-ester

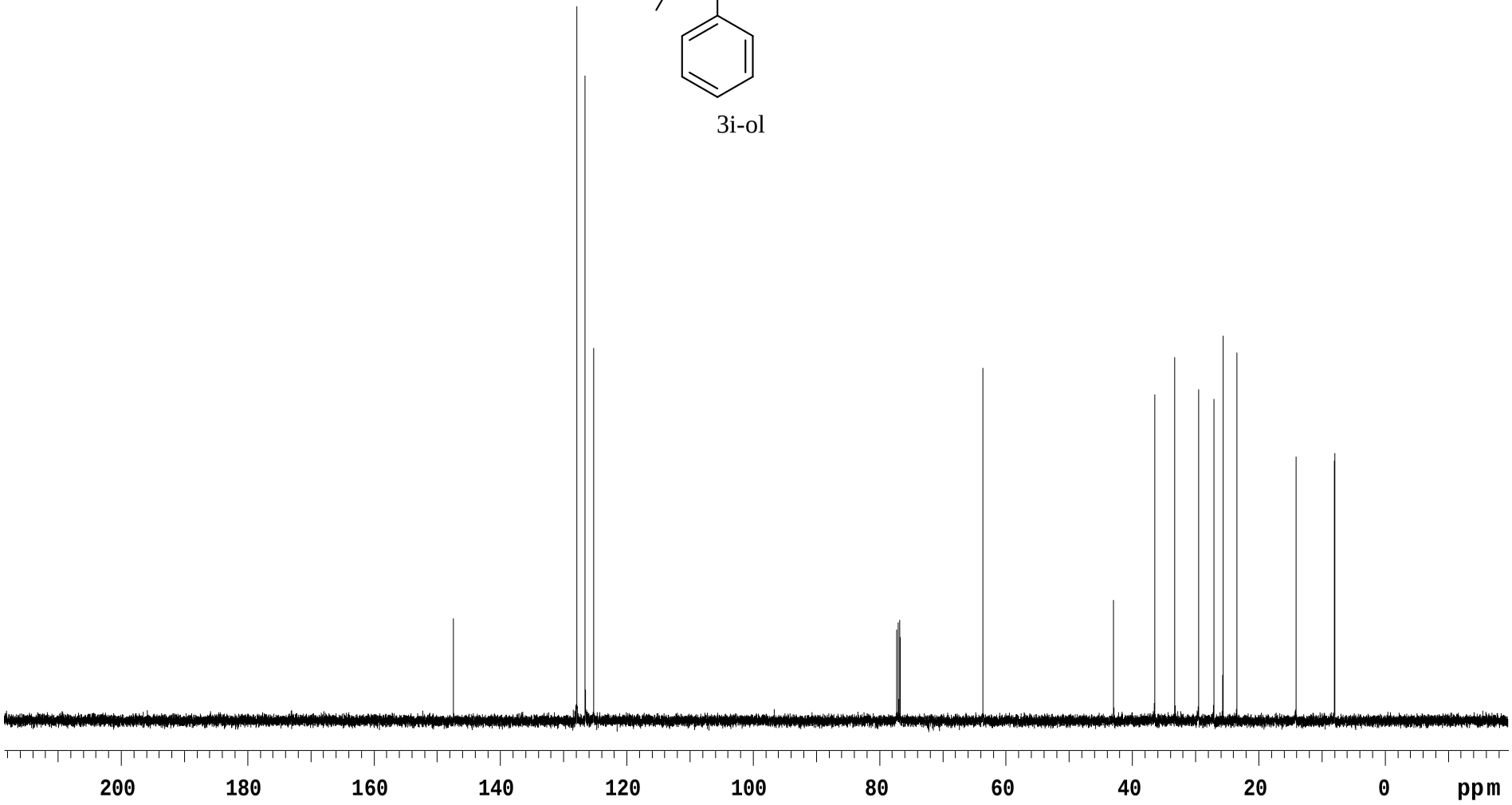

mei-05-75-ol-H-500M
Pulse Sequence: s2pul
OH
3i-ol
10
9
8
7
6
5
4
3
2
1
0
ppm
3.71
0.91
1.91
5.91
4.97
1.99
2.91
3.00

mei-05-75-ol-C-500M

Pulse Sequence: s2pul

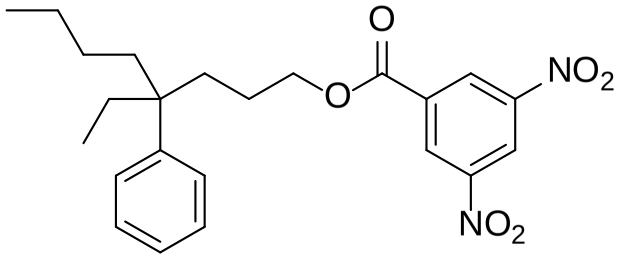



3i-ol

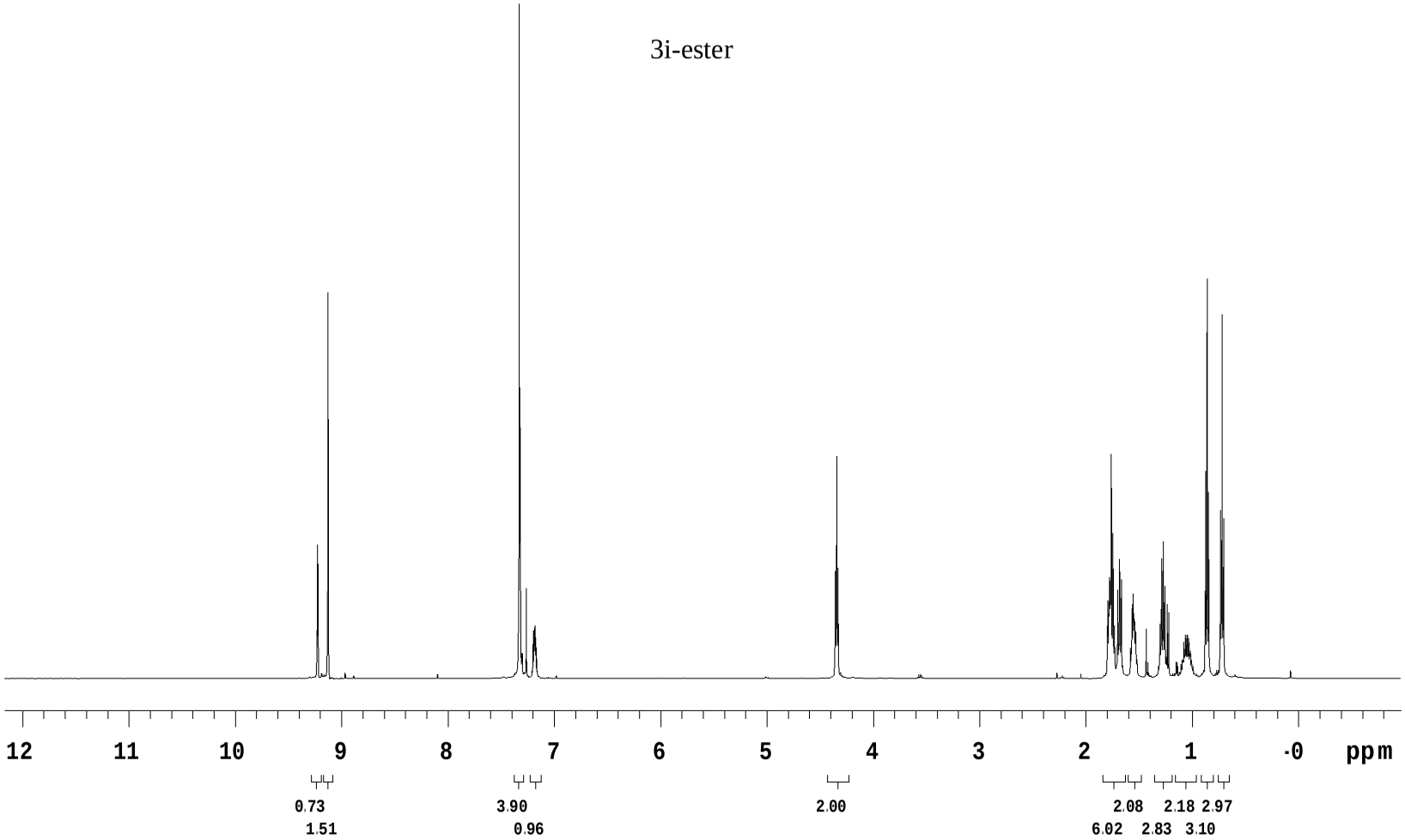


mei-05-75-ester-H-500M

Pulse Sequence: s2pul

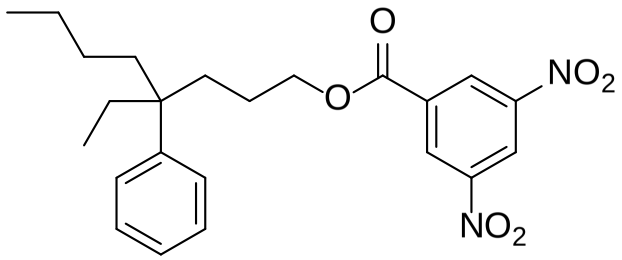



3i-ester

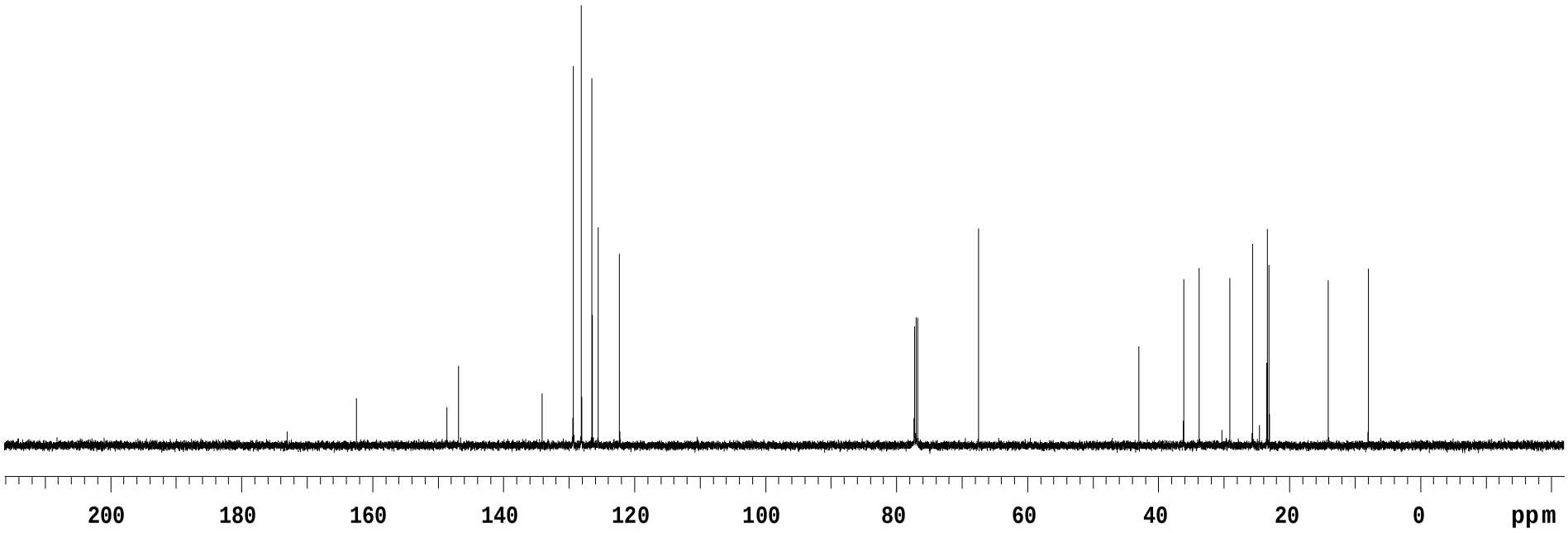


mei-05-75-ester-C-500M

Pulse Sequence: s2pul

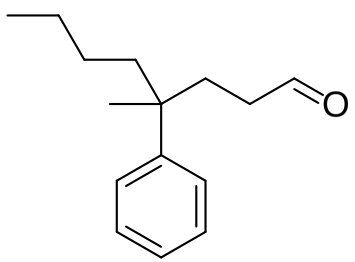



3i-ester



mei-05-50-1-H-500M

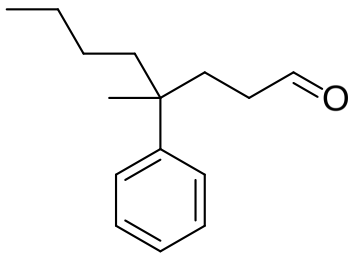
Pulse Sequence: s2pul




3j

mei-05-50-1-C-500M

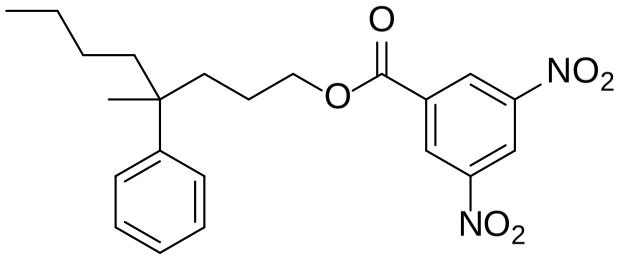
Pulse Sequence: s2pul



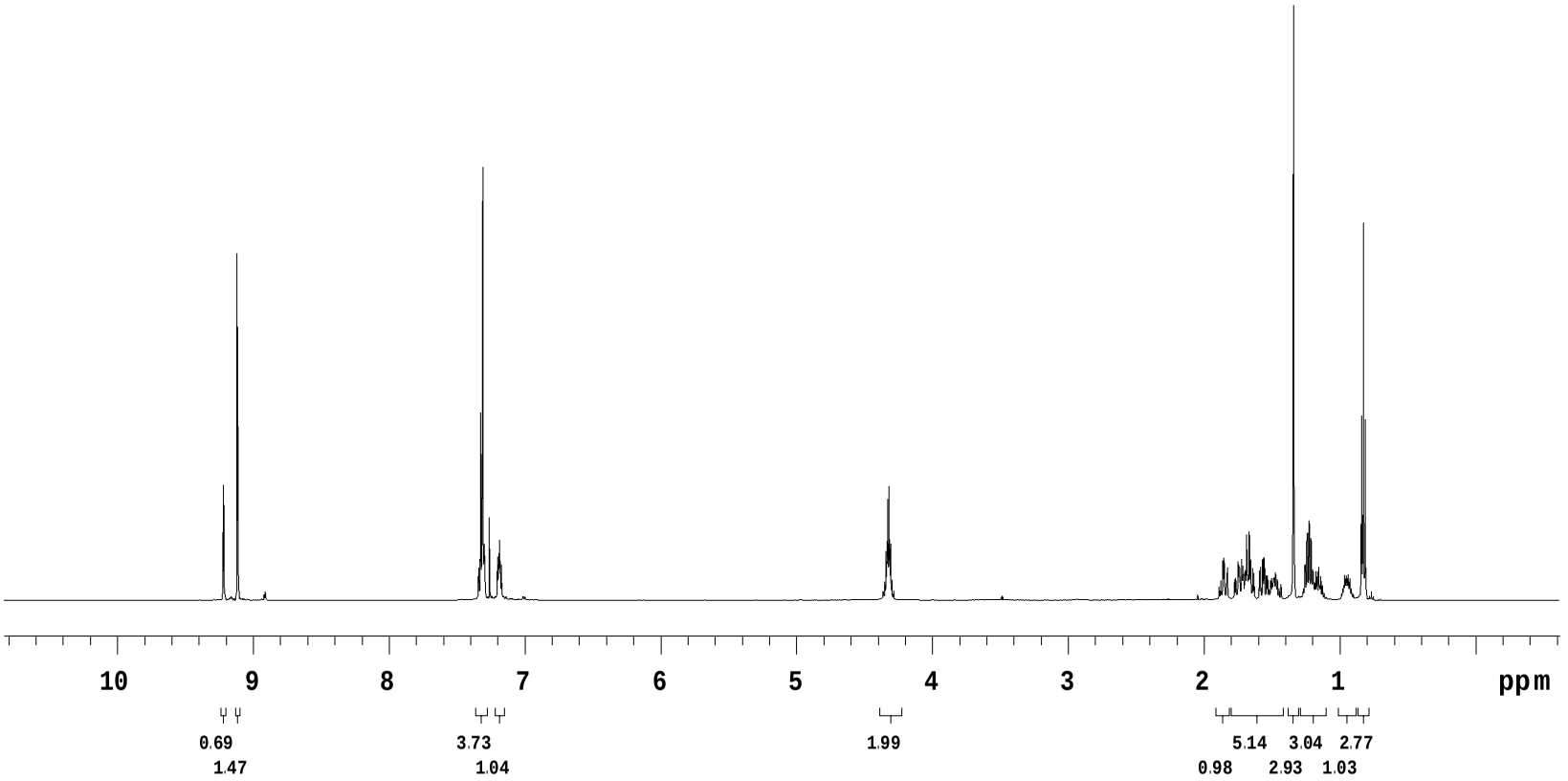

3j

mei-05-50-ester-H-500M

Pulse Sequence: s2pul

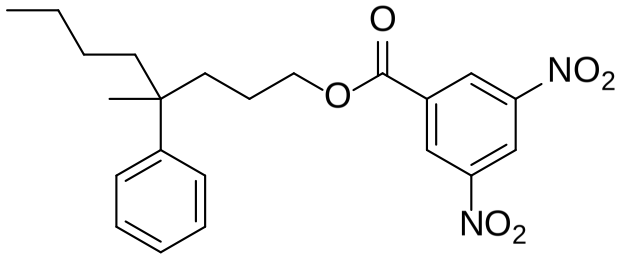



3j-ester

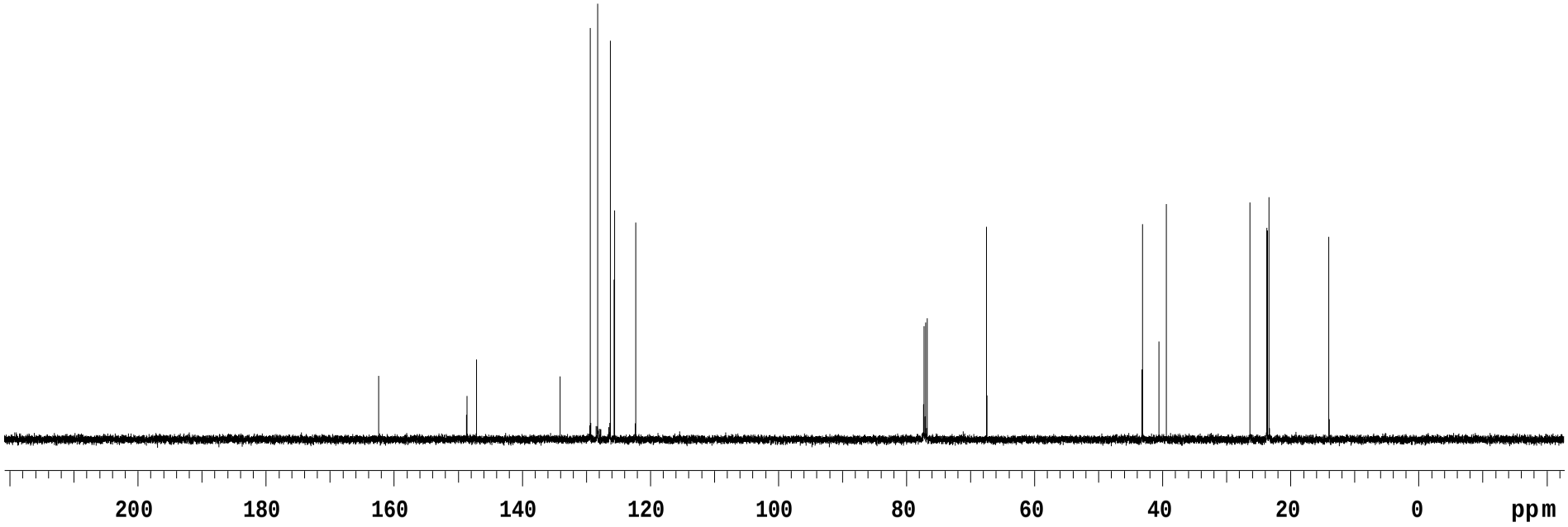


mei-05-50-ester-C-500M

Pulse Sequence: s2pul

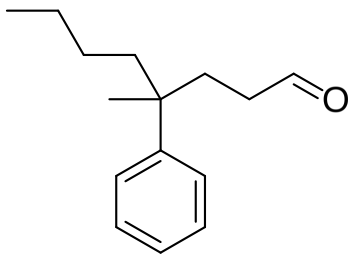



3j-ester



mei-05-51-H-500M

Pulse Sequence: s2pul

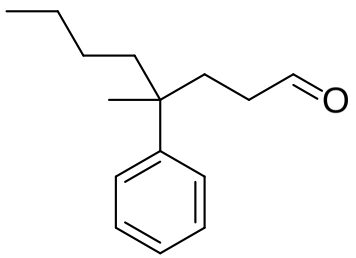



From *E*-alkene

ent-3j

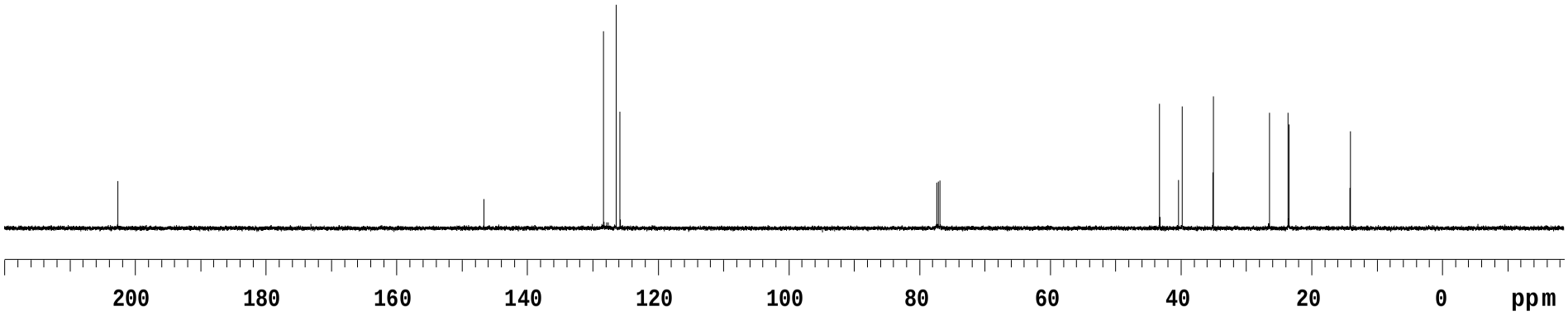
mei-05-51-aldehyde-C-500M

Pulse Sequence: s2pul



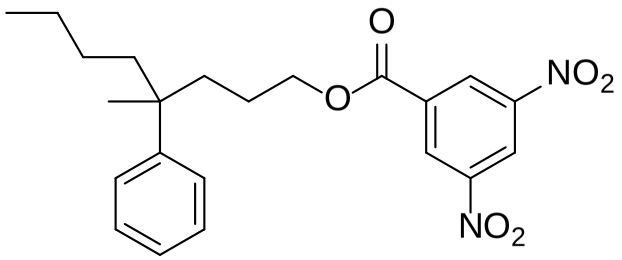

From *E*-alkene

ent-3j



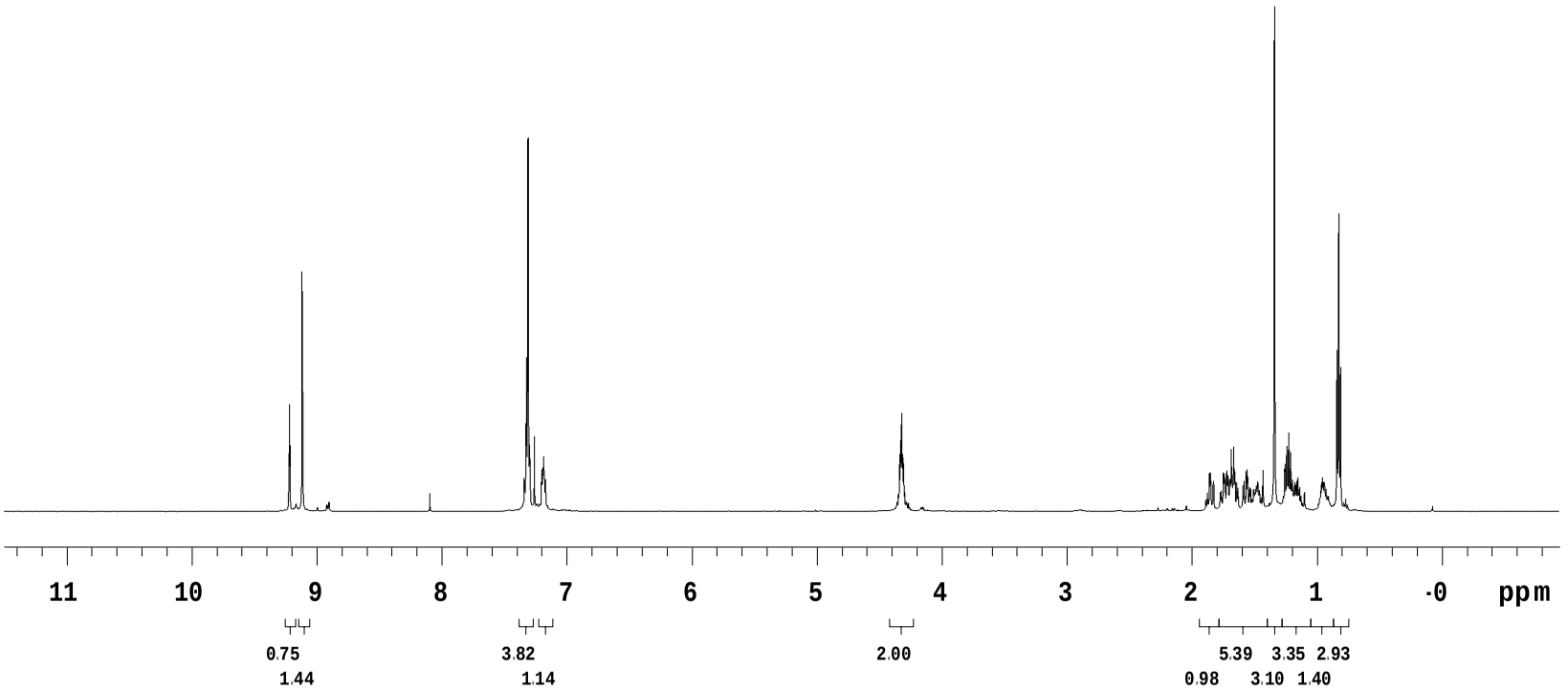
mei-05-51-ester-H-500M

Pulse Sequence: s2pul



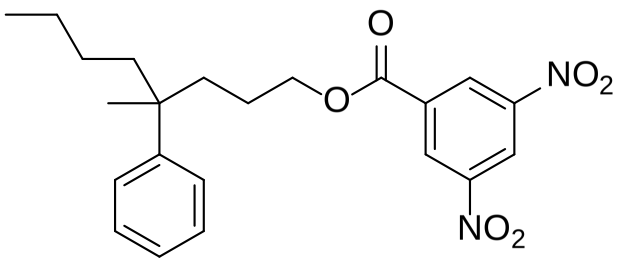

From *E*-alkene

ent-3j-ester



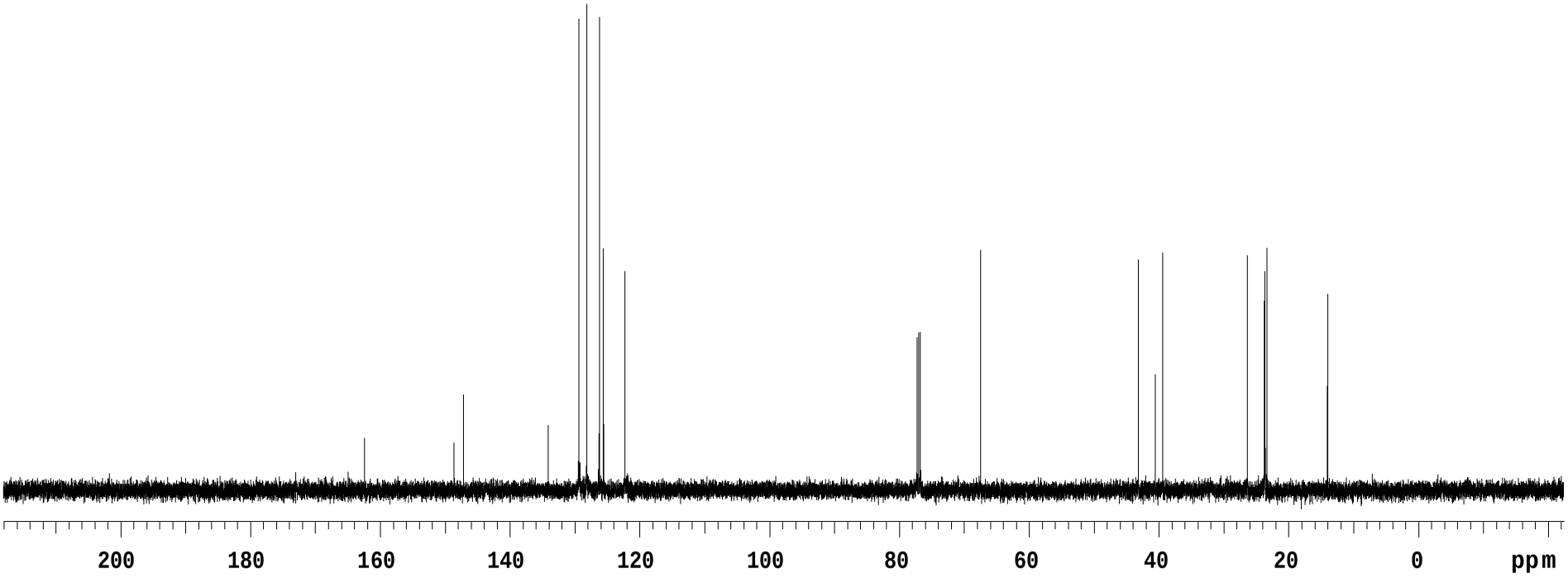
mei-05-51-ester-C-500M

Pulse Sequence: s2pul



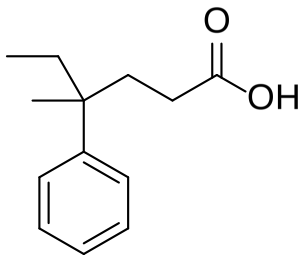

From *E*-alkene

ent-3j-ester



mei-04-185-acid-H-500M

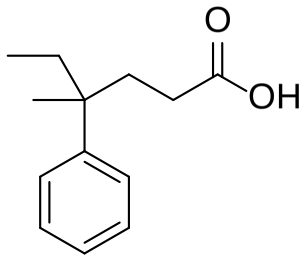
Pulse Sequence: s2pul



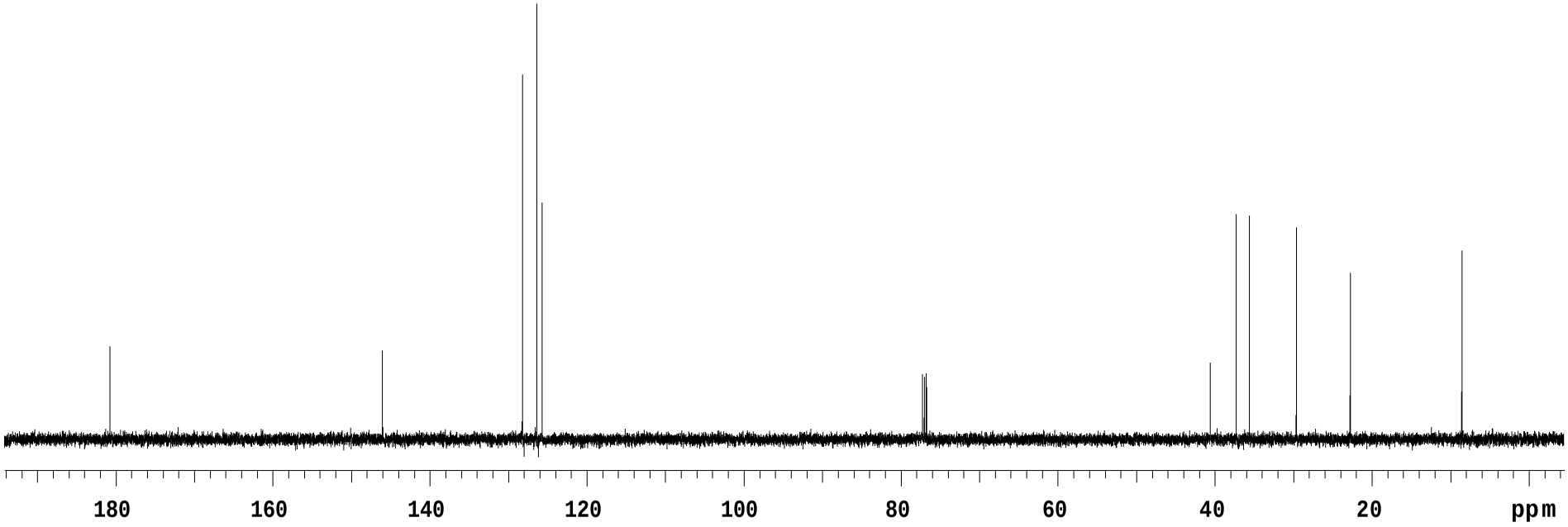

2ba

mei-04-185-acid-C-500M

Pulse Sequence: s2pul

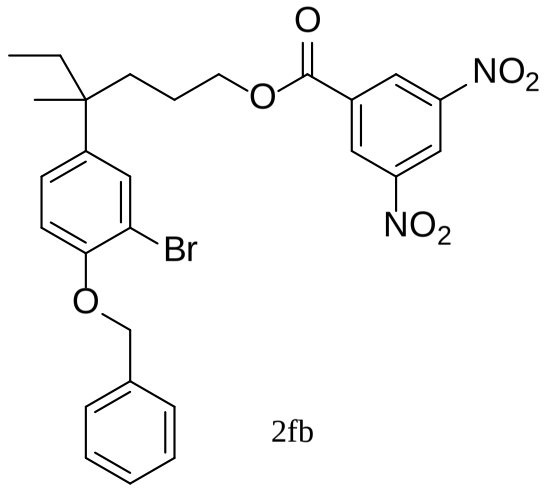



2ba

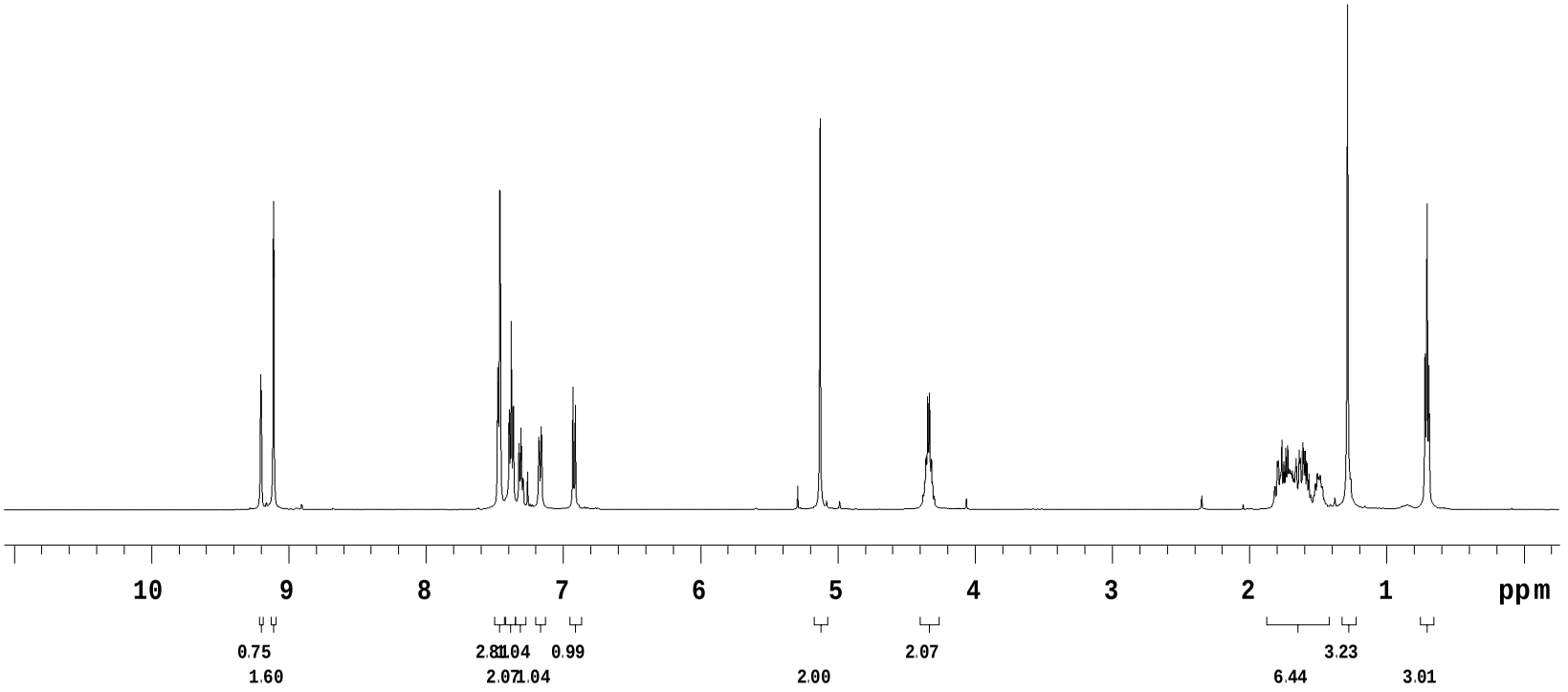


mei-05-141-H-500M

Pulse Sequence: s2pul

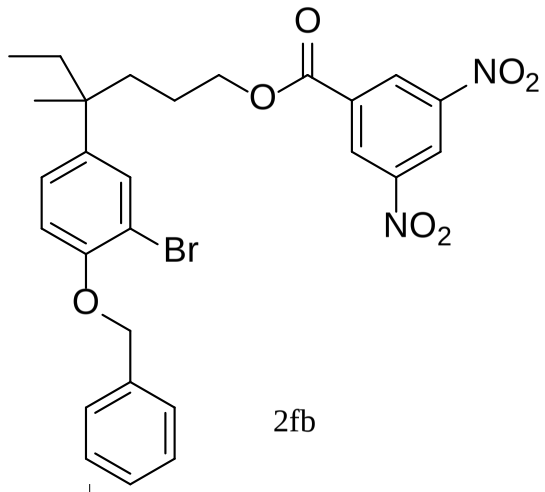



2fb

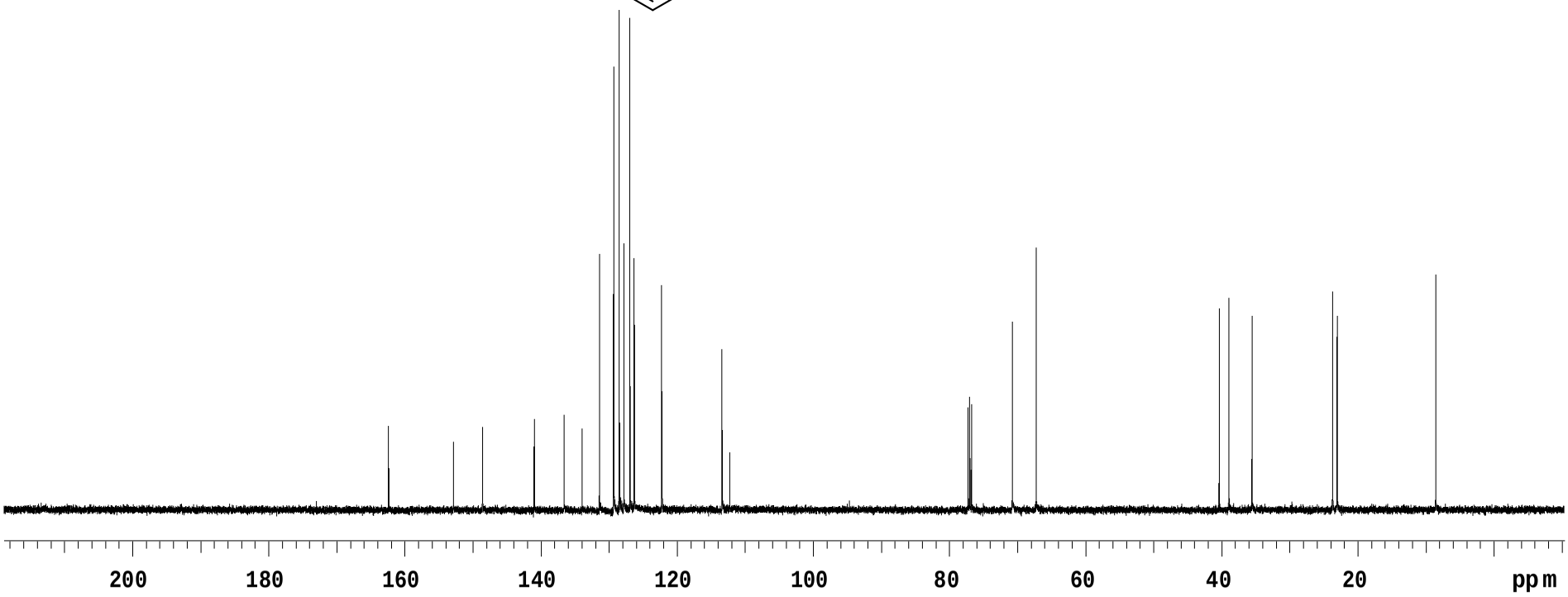


mei-05-141-C-500M

Pulse Sequence: s2pul

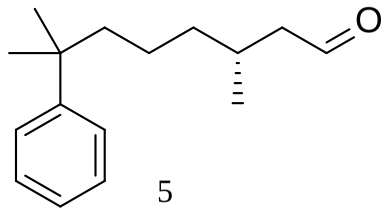



2fb



mei-05-71-2-H-500M

Pulse Sequence: s2pul

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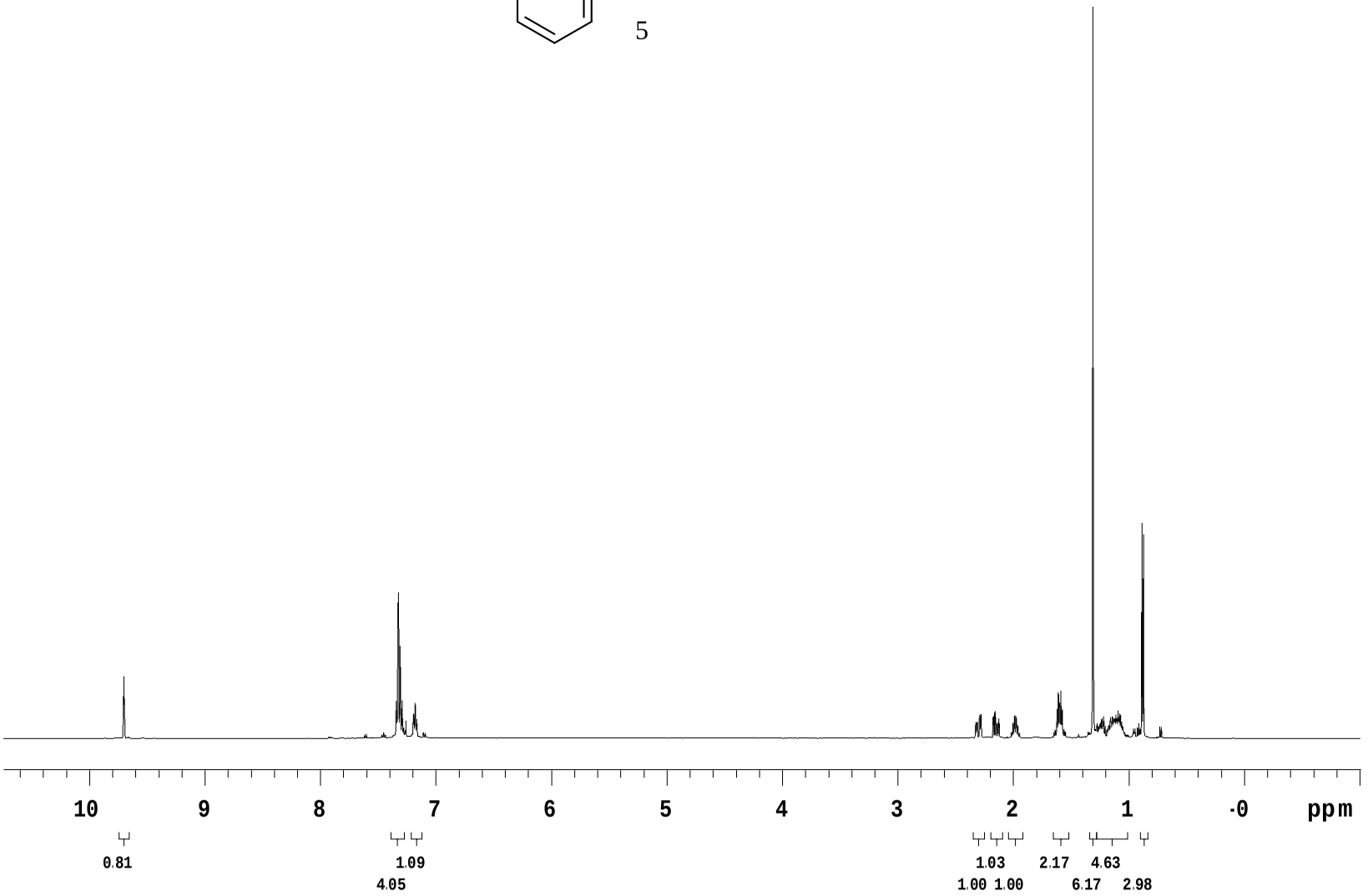
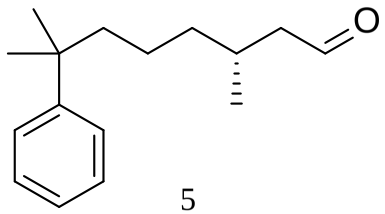


mei-05-71-2-C-500M

Pulse Sequence: s2pul

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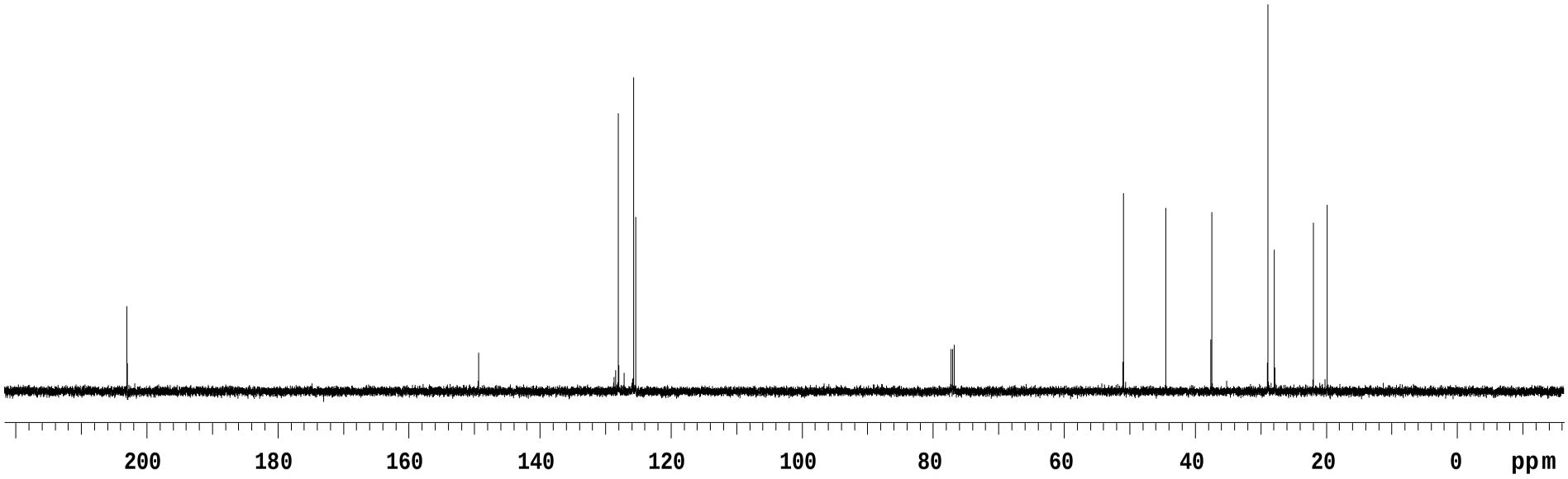
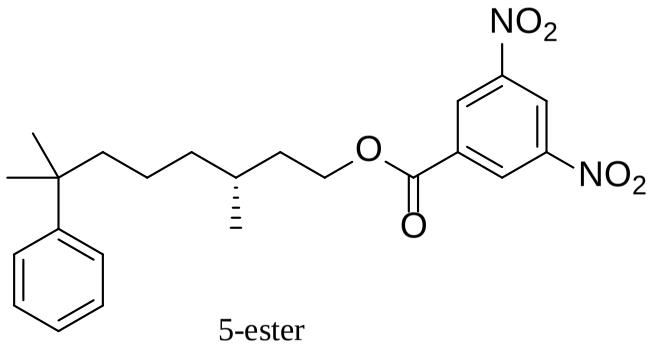
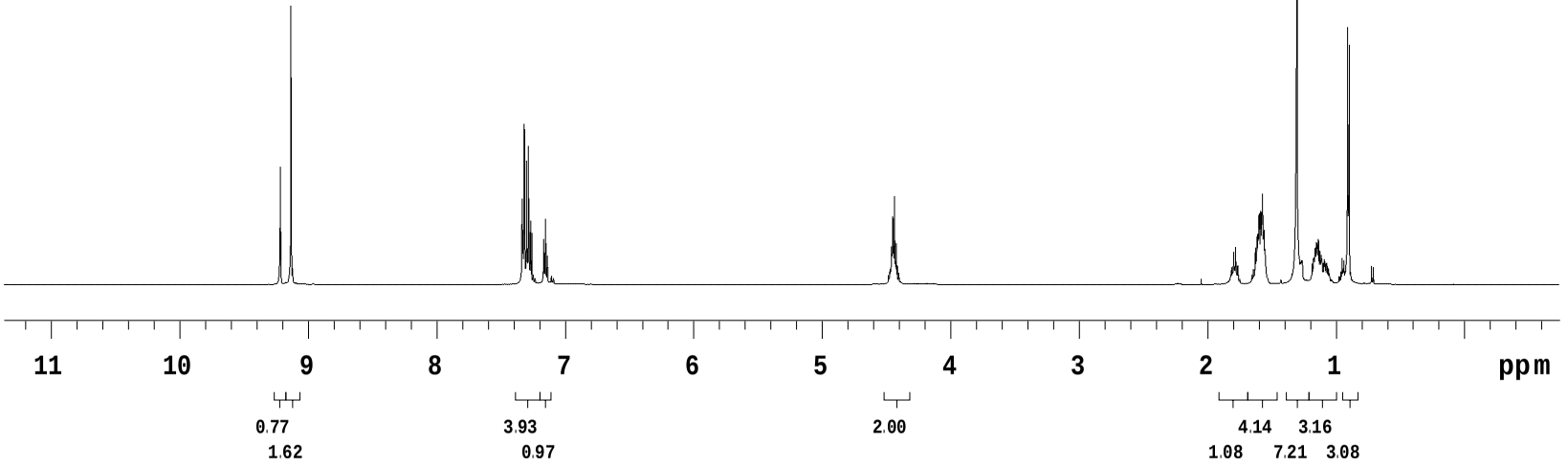


mei-05-71-2-ester-H-500M

Pulse Sequence: s2pul

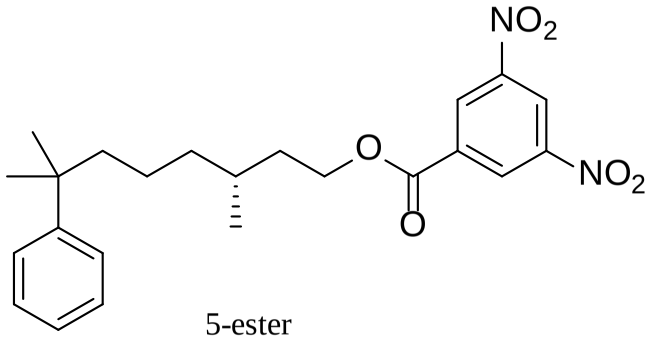



5-ester

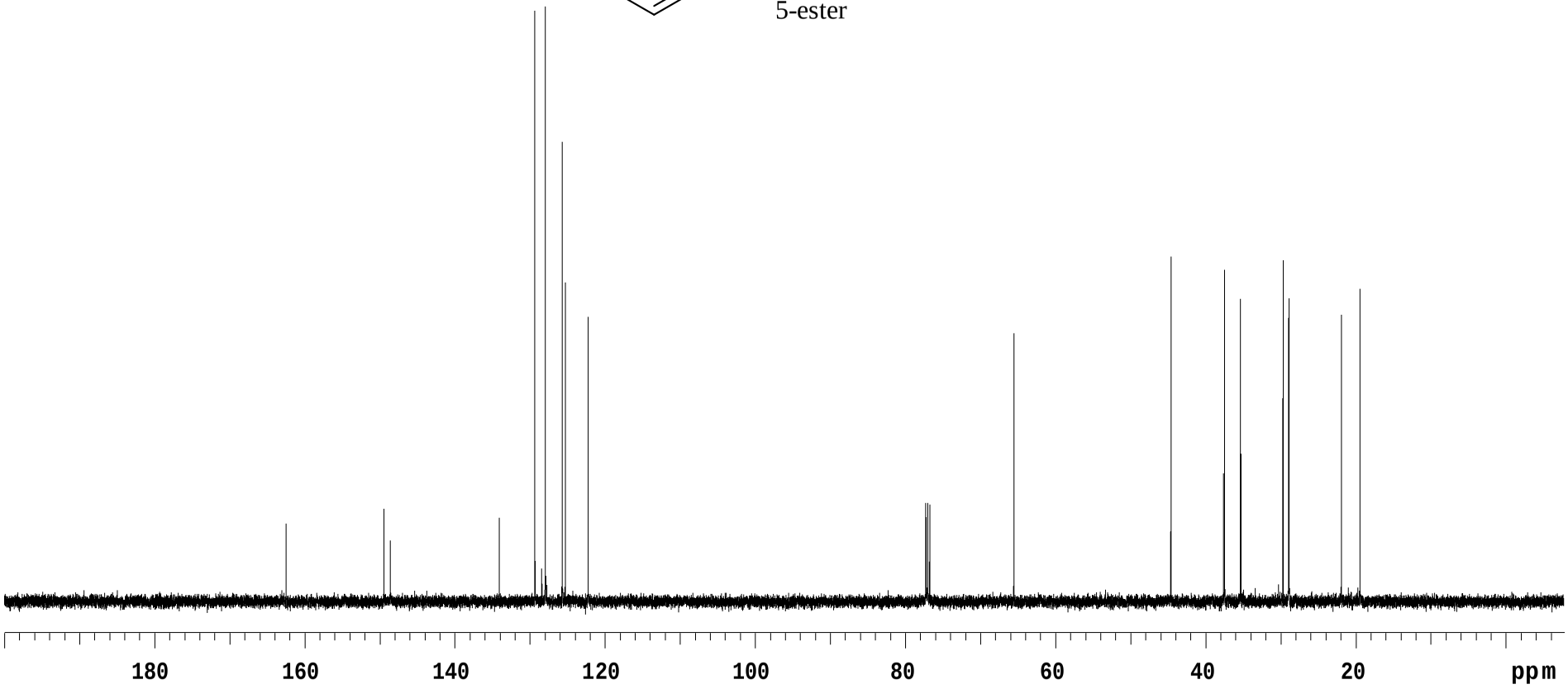


mei-05-71-2-ester-C-500M

Pulse Sequence: s2pul

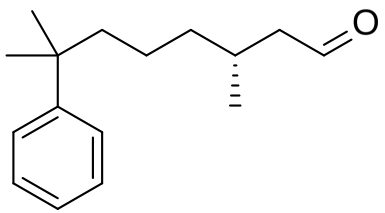



5-ester



mei-05-71-4-H-500M

Pulse Sequence: s2pul

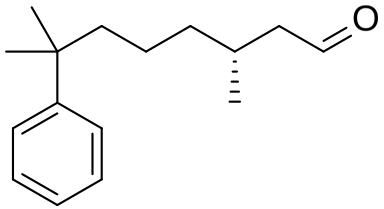



From ent-ligand

5

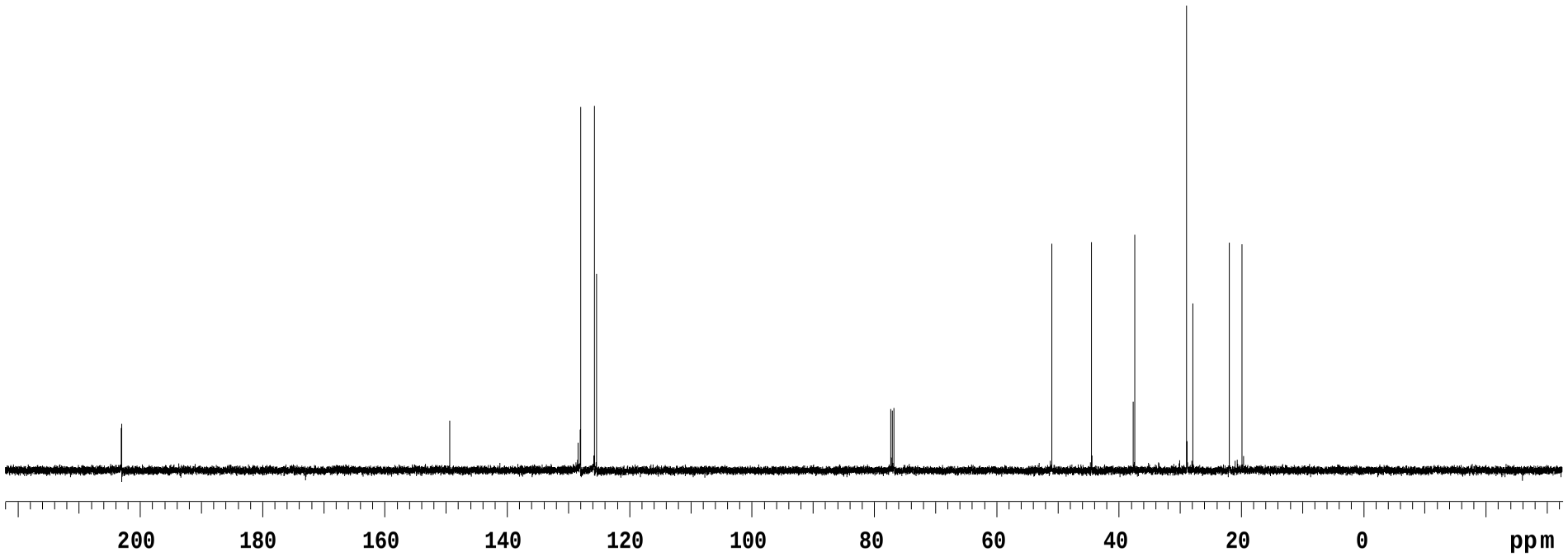
mei-05-71-4-C-500M

Pulse Sequence: s2pul



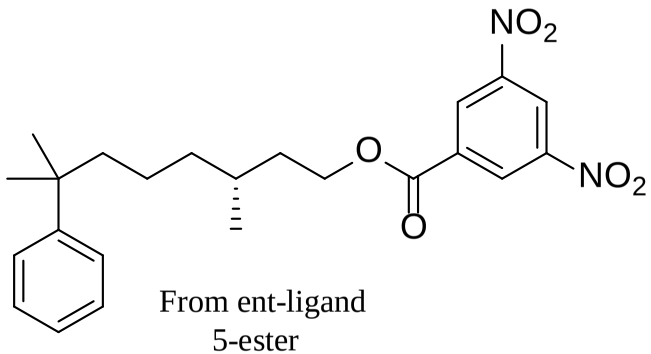

From ent-ligand

5



mei-04-71-4-ester-H-500M

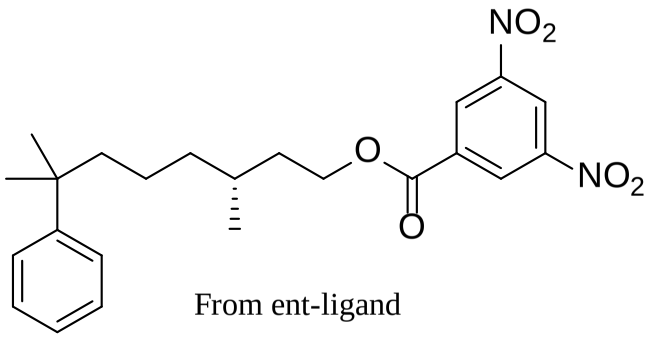
Pulse Sequence: s2pul



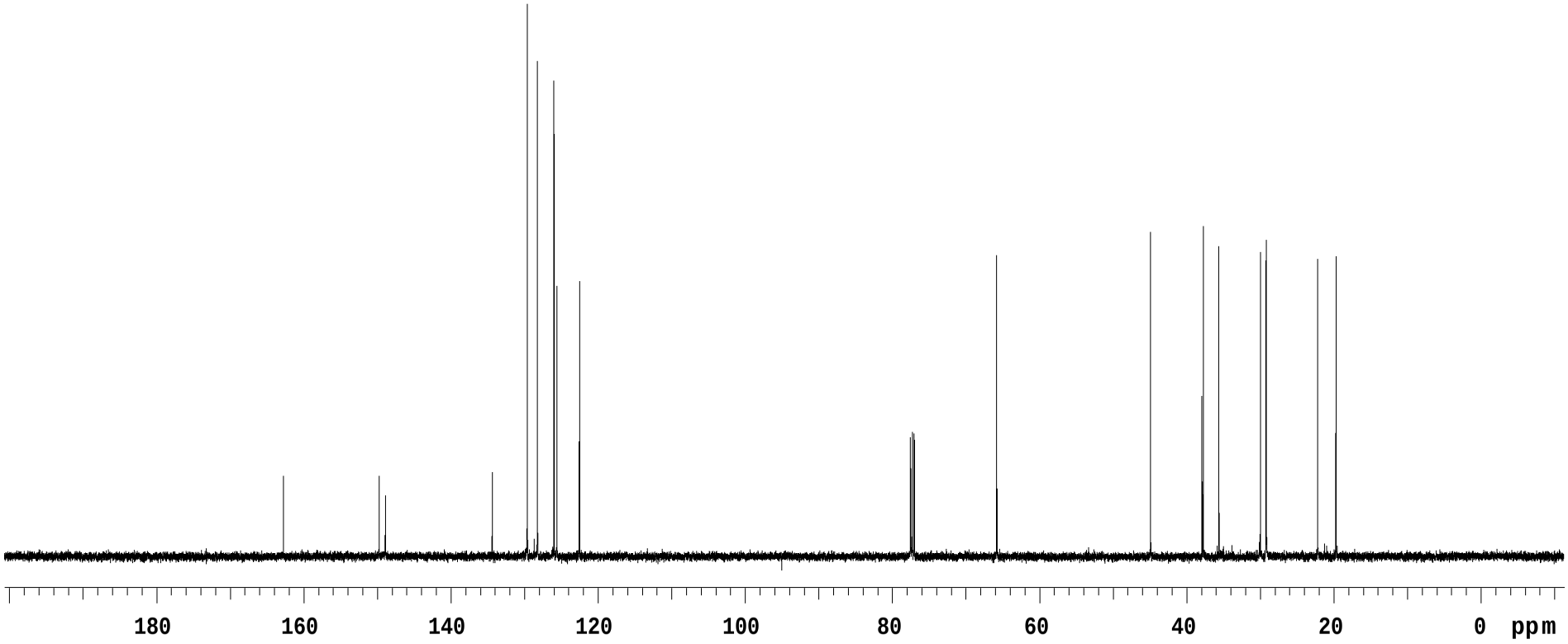

From ent-ligand
5-ester

mei-05-71-4-ester-C-500M

Pulse Sequence: s2pul

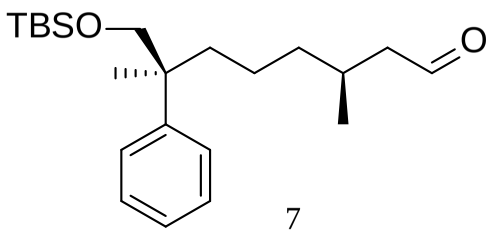



From ent-ligand
5-ester



STANDARD PROTON PARAMETERS

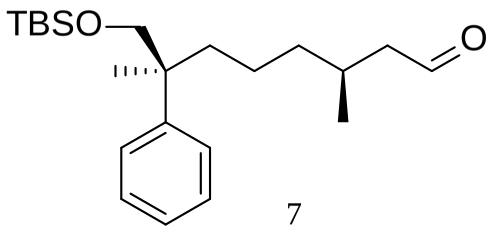
Pulse Sequence: s2pul



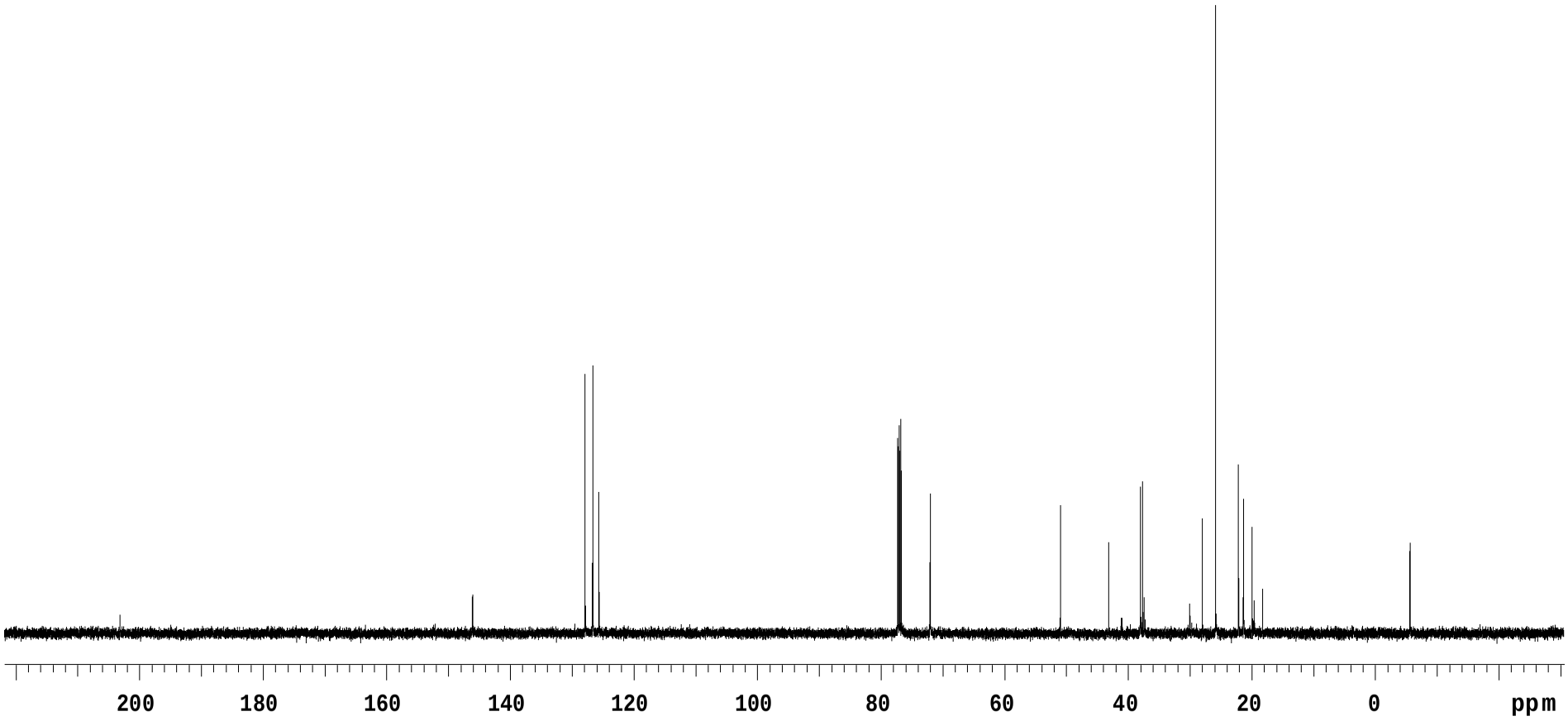

7

mei-05-84-aldehyde-C-500M

Pulse Sequence: s2pul

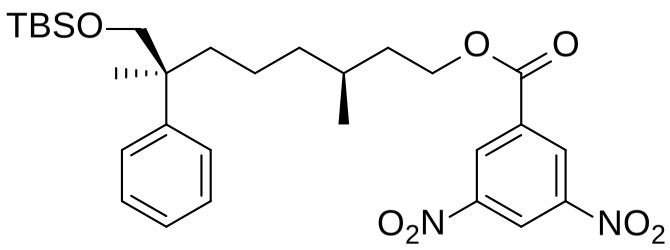



7



mei-05-59-ester-sd-lig-H-500M

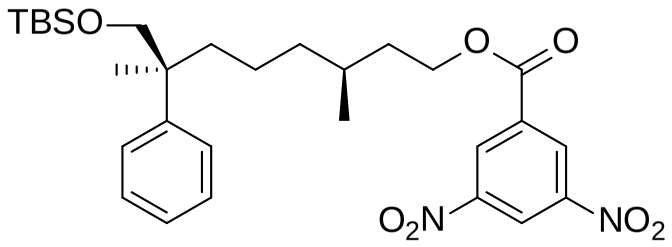
Pulse Sequence: s2pul



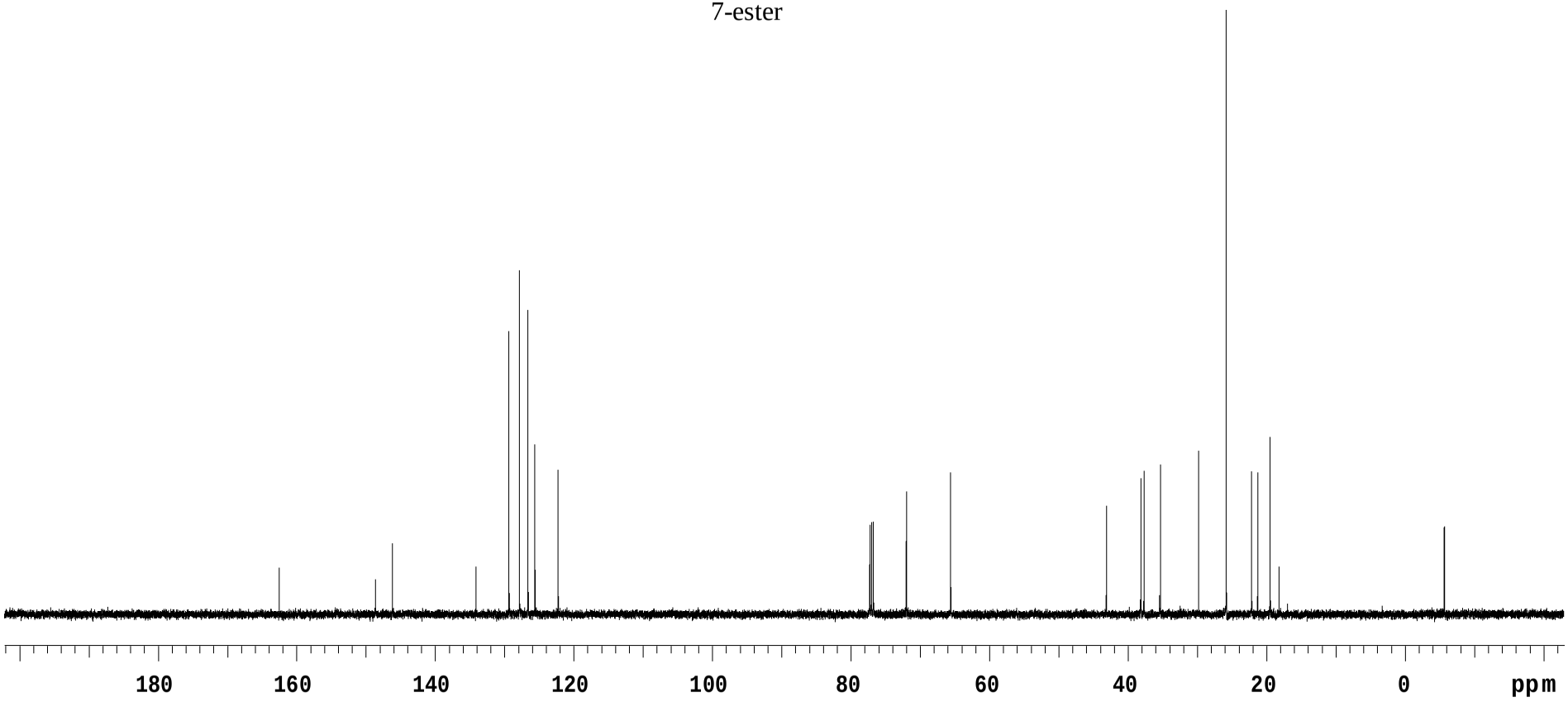

7-ester

mei-05-59-ester-sd-lig-C-500M

Pulse Sequence: s2pul

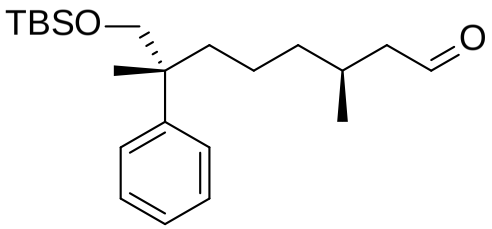



7-ester



mei-05-85-aldehyde-h-500m

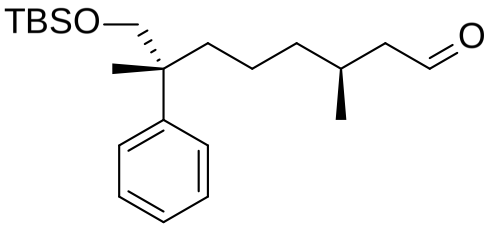
Pulse Sequence: s2pul



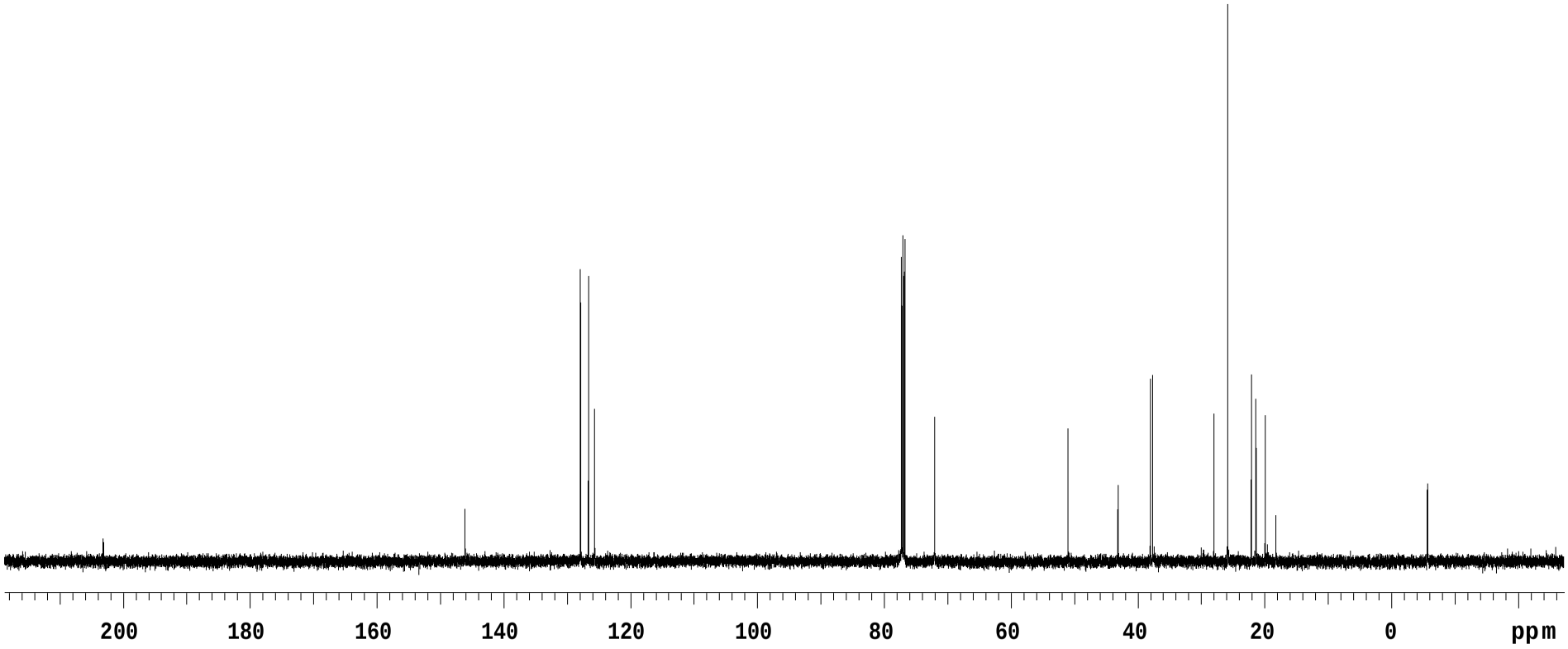

8

mei-05-85-C-aldehyde-500M

Pulse Sequence: s2pul

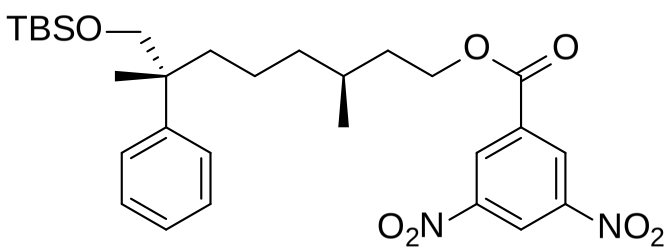



8



mei-05-59-ester-ent-lig-H-500M

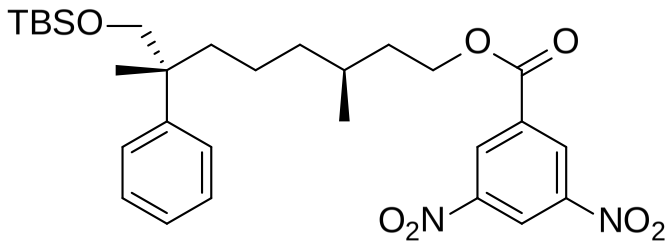
Pulse Sequence: s2pul



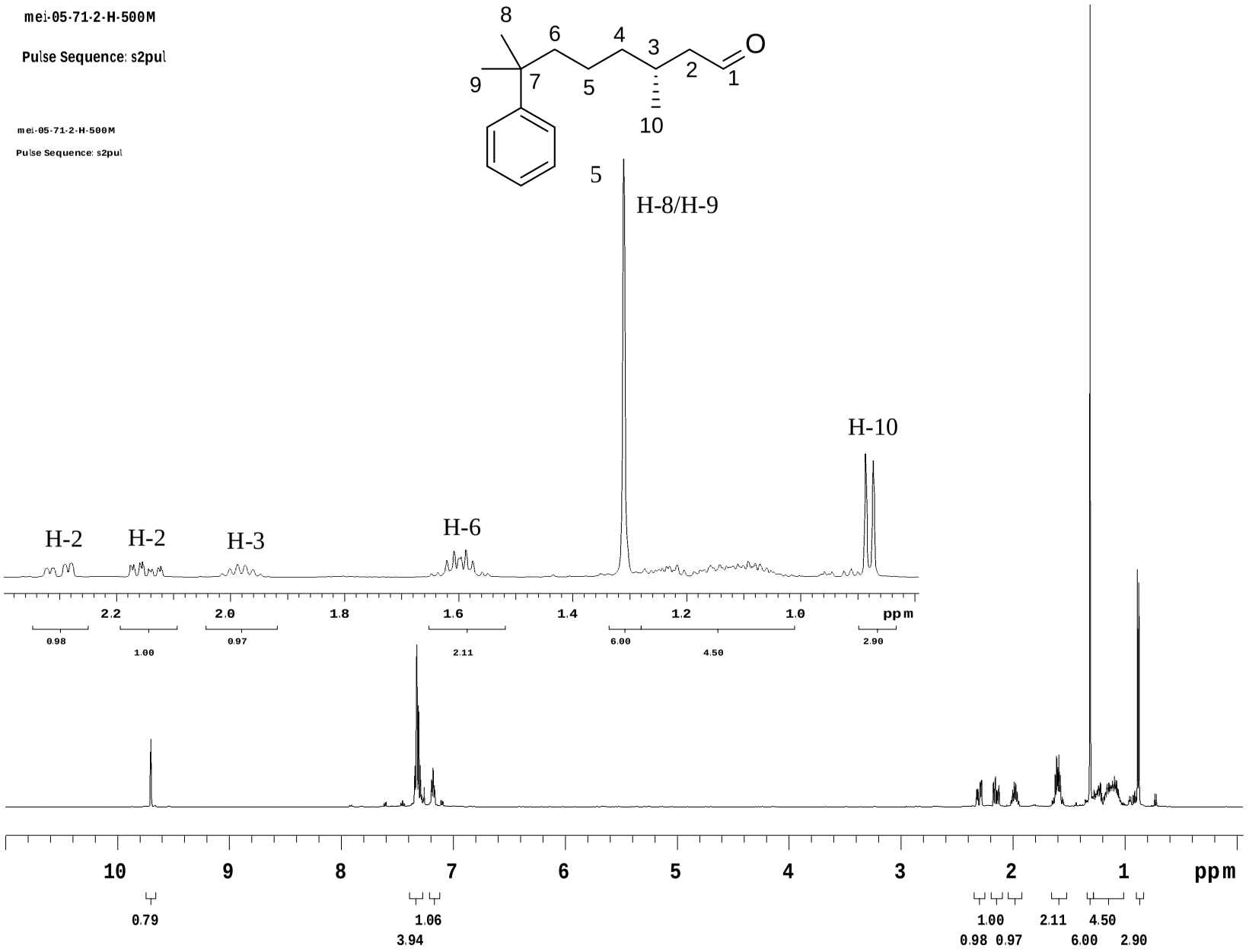

8-ester

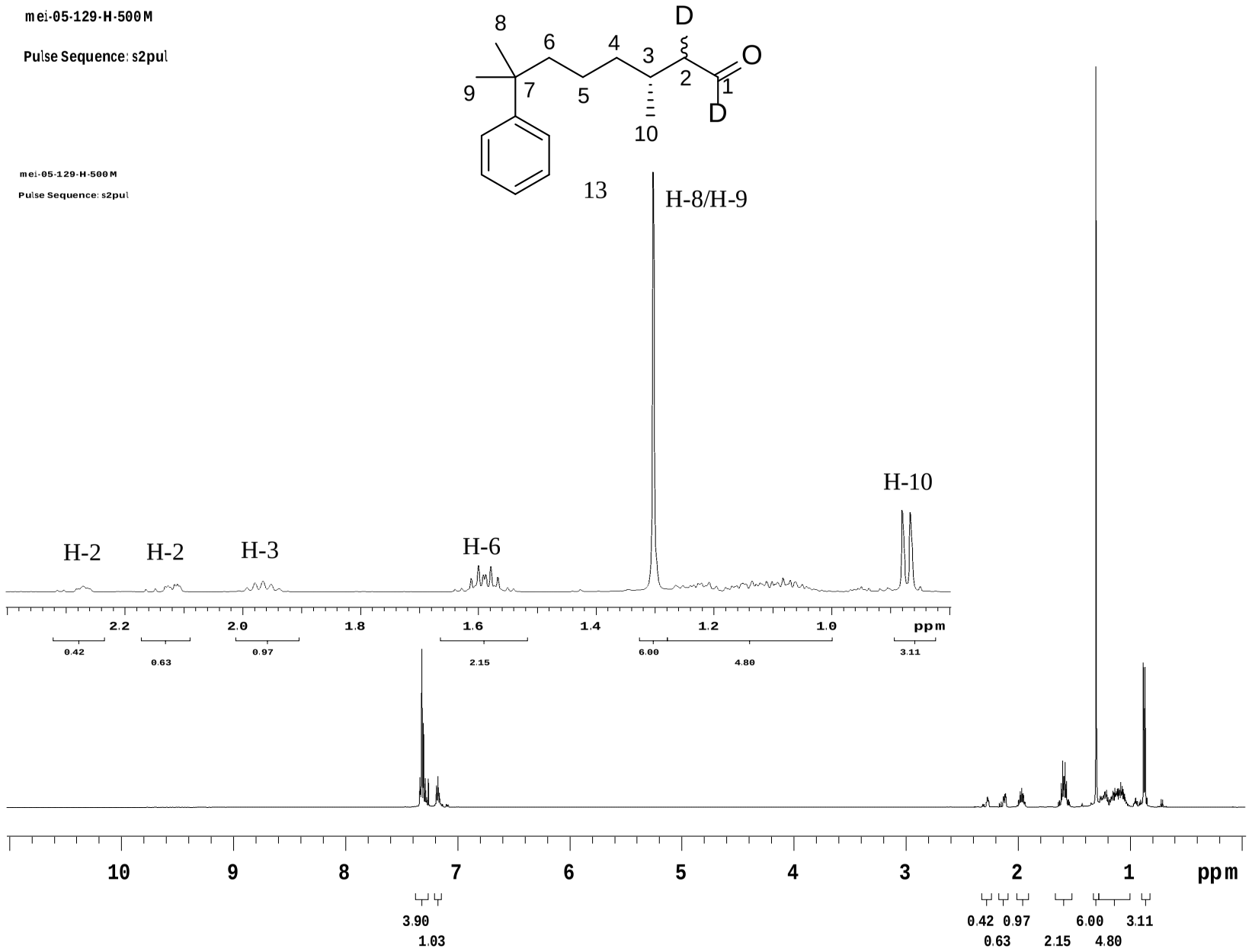
mei-05-59-ester-ent-lig-C-500M

Pulse Sequence: s2pul



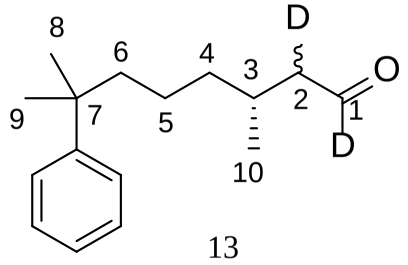

8-ester


mei-05-71-2-H-500M
Pulse Sequence: s2pul
8
6
4
3
2
1
O
9
7
5
10
5
H-8/H-9
H-10
H-2
H-2
H-3
H-6
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm
0.98
1.00
0.97
2.11
6.00
4.50
2.90
10
9
8
7
6
5
4
3
2
1
ppm
0.79
1.06
3.94
1.00
0.98
0.97
2.11
4.50
6.00
2.90


mei-05-129-H-500M
Pulse Sequence: s2pul
D
8
6
4
3
O
2
1
9
7
5
D
10
13
H-8/H-9
H-10
H-2
H-2
H-3
H-6
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm
0.42
0.63
0.97
2.15
6.00
4.80
3.11
10
9
8
7
6
5
4
3
2
1
ppm
3.90
1.03
0.42
0.63
0.97
2.15
6.00
4.80
3.11

mei-05-129-C-500M

Pulse Sequence: s2pul

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