

A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

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1 General Remarks

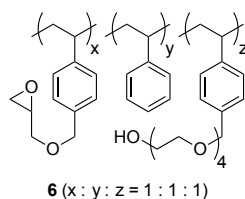
- ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JMN-LA500 or 600 spectrometers operating at 500 MHz or 600 MHz (^1H) respectively. Chemical shifts are reported in parts per million (δ) and are reported relative to internal references of the deuterated solvent (CDCl_3 – 7.24/77.0 ppm; CD_3OD – 3.31/49.0 ppm; $\text{DMSO}-d_6$ – 2.50/39.5 ppm) or tetramethylsilane (0 ppm). Structures of known compounds were confirmed by comparison with commercially available compounds or data obtained from literature. Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad.
- IR spectra were recorded on JASCO FT/IR-6100 spectrometer.
- Direct Analysis in Real Time (DART) mass spectra were recorded on JEOL JMS-T100TD mass spectrometer.
- Inductively coupled plasma (ICP) analysis was performed with Shimadzu ICPS-7510 equipment.
- Melting point was determined on a standard melting point apparatus and is uncorrected.
- Enantiomeric excess was determined by HPLC analysis performed with Shimadzu LC-20AB, SPD-M20A and DGU-20A₃.
- Optical rotation was recorded with a JASCO P-2100 polarimeter at room temperature.
- STEM/EDS images were obtained using a JEOL JEM-2100F instrument operating at 200 kV. All STEM specimens were prepared by placing a drop of the suspension on carbon-coated Cu grids and dried in air (without staining).
- SEM images were obtained using a JEOL JSM-6700F instrument operating at 2.0 kV.
- AuClPPh_3 and $\text{Pd}(\text{OAc})_2$ were purchased from Strem Chemical Inc.
- NaBH_4 was purchased from Wako Pure Chemical Industries, recrystallised with diglyme by heating according to the literature¹ and stored in a glove box. The entire recrystallisation process was carried out under argon atmosphere.
- Ketjenblack (carbon black) EC300J was purchased from Lion Corporation.
- Thin layer chromatography (TLC) was performed on TLC plates (TLC Silica gel 60 F₂₅₄ glass plate) purchased from Merck KGaA and was visualised by UV light or by staining with 5–10% phosphomolybdic acid in ethanol followed by heating.
- Silica gel 60 from Merck KGaA was used for flash column chromatography with technical grade solvents.
- Preparative TLC (PTLC) was performed using Wakogel[®] B-5F from Wako Pure Chemical Industries or Merck KGaA PLC Silica gel 60 F₂₅₄ 0.5 mm.
- EtOH was purchased from Wako Pure Chemical Industries, distilled over Na and dried over MS 3A.
- All other dry solvents were purchased from Wako Pure Chemical Industries and used as is.
- All aldehydes used were either recrystallised or distilled before use.
- Dibenzyl malonate was distilled before use.
- Alcohols **8c**, **8d**, **8e**, **8g** and **8h** were synthesised via the Heck reaction followed by reduction and the procedure is elaborated in this supporting information.
- Alcohols **8b**, and **8j** were synthesised via the HWE reaction followed by reduction and the procedure is elaborated in this supporting information.
- All other reagents were either purchased from Tokyo Chemical Industry (TCI) or Sigma-Aldrich and used as is without further purification.
- Unless otherwise stated, all reactions were carried out under argon atmosphere.

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Note

Unless otherwise stated, stabilisers present in reagents were not removed before use in syntheses of compounds but were removed before use in the fabrication of copolymer **2**. Non-solid monomeric compounds synthesised were stored in DCM or EtOAc as a solution and kept under argon in the refrigerator. A small amount of stabiliser such as 4-*tert*-butylcatechol was added, after purification, to non-solid monomeric compounds before they were stored. Solid monomeric compounds were stored in dark glass bottles at room temperature under argon.

2 Procedure for the preparation of copolymer **2**²

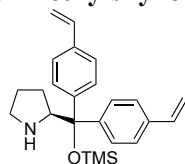


2,2'-Azobis(4-methoxy)-2,4-dimethylvaleronitrile (V-70, 212.5 mg) was added to a stirred solution of styrene (2.4 g, 23.0 mmol), 4-vinylbenzyl glycidyl ether (4.4 g, 23.1 mmol) and 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol (7.0 g, 22.6 mmol) in chloroform (12 mL). The mixture was then degassed by sonication under argon. After stirring for 48 hours at room temperature, the resulting viscous polymer solution was slowly poured into diethyl ether. The solvent layer was then

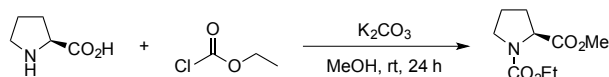
decanted and the remaining precipitated polymer was washed with diethyl ether several times. The polymer was then dissolved in THF and the same precipitation, decantation and washing procedure was repeated two more times before being dried *in vacuo* to afford copolymer **2** as a colourless viscous liquid (7.4 g, 54%). The molar ratio of the components was determined by ¹H NMR analysis in CDCl₃ ($x : y : z = 32 : 34 : 34$). Note: The stabilisers in commercially available styrene were removed by passing it through a short column of basic alumina before use.

3 Preparation of organocatalysts 1, A and B

3.1 (*S*)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether (**1**)³



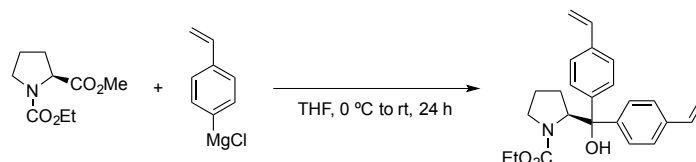
N-Ethoxycarbonyl-L-proline methyl ester



L-Proline (11.51 g, 100 mmol) and K_2CO_3 (17.97 g, 130 mmol) were added to a 300 mL 2-neck round bottom flask attached with a dropping funnel. The flask was flushed with argon and MeOH (200 mL) was added. After stirring the mixture for 5 minutes, ethyl chloroformate (21 mL, 220 mmol) was added dropwise through the dropping funnel. After 24 hours of stirring, the solvent was removed under reduced pressure and water was added to the white sticky residue. The aqueous solution was extracted with DCM three times. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the colourless oil obtained was left to dry under vacuum for 2 days to afford the title compound (14.74 g, 70%).

¹H NMR (500 MHz, $CDCl_3$, rotamers): δ 4.37 (dd, J = 8.6, 3.4 Hz, 0.5H), 4.30 (dd, J = 8.7, 3.5 Hz, 0.5H), 4.18–4.05 (m, 2H), 3.74 (s, 1.5H), 3.72 (s, 1.5H), 3.61–3.43 (m, 2H), 2.27–2.18 (m, 1H), 2.02–1.87 (m, 3H), 1.27 (t, J = 7.1 Hz, 1.5H), 1.20 (t, J = 7.1 Hz, 1.5H); **¹³C NMR (125 MHz, $CDCl_3$, rotamers):** δ 173.4, 173.2, 155.1, 154.5, 61.2, 61.1, 58.9, 58.7, 52.1, 52.0, 46.6, 46.2, 30.8, 29.8, 24.2, 23.4, 14.6, 14.6.

(*S*)-N-Ethoxycarbonyl- α,α -bis(4-vinylphenyl)prolinol

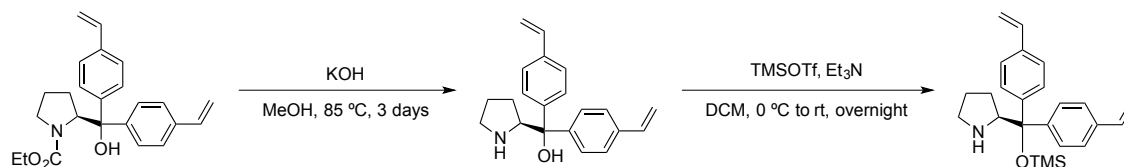


The Grignard reagent was prepared according to standard procedures from Mg (6.50 g, 267.38 mmol) and 4-chlorostyrene (33 mL, 260.38 mmol) in THF (85 mL), with iodine added to initiate the reaction.

N-Ethoxycarbonyl-L-proline methyl ester (13.1 g, 65.10 mmol) was added to a 500 mL 2-neck round-bottom flask attached with a dropping funnel. The flask was flushed with argon and THF (40 mL) was added. The solution was stirred at 0 °C and the Grignard reagent was added dropwise through the dropping funnel. After the complete addition of the Grignard reagent, the reaction mixture was warmed up to room temperature and left to stir for 24 hours before it was cooled to 0 °C again. The reaction was quenched with saturated ammonium chloride solution (200 mL), added dropwise. The slurry was filtered through a pad of Celite and the filtrate was extracted with DCM. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to afford the title compound (14.37 g, 58%) as a yellow liquid.

¹H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 9.6 Hz, 8H), 6.71 (ddd, J = 17.6, 10.9, 1.7 Hz, 2H), 5.74 (dd, J = 17.6, 5.9 Hz, 2H), 5.24 (d, J = 10.9 Hz, 2H), 4.90 (dd, J = 8.9, 3.6 Hz, 1H), 4.18–4.03 (m, 2H), 3.46–3.37 (m, 1H), 2.97 (br, 1H), 2.13–2.04 (m, 1H), 1.95–1.89 (m, 1H), 1.54–1.45 (m, 1H), 1.23 (t, J = 6.4 Hz, 3H), 0.87 (br, 1H); **¹³C NMR (125 MHz, $CDCl_3$):** δ 145.8, 143.2, 136.5, 136.4, 128.3, 127.7, 125.7, 125.3, 113.9, 113.8, 81.4, 65.9, 61.9, 47.7, 29.6, 23.0, 14.6; $[\alpha]_D^{20}$ = –123.7 (c = 0.970, DCM).

(S)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether

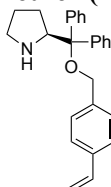


(S)-N-Ethoxycarbonyl- α,α -bis(4-vinylphenyl)prolinol (12.16 g, 32.2 mmol) and *tert*-butyl catechol (12.1 mg as stabiliser) were added to a 300 mL 2-neck round-bottom flask with an attached reflux condenser. The flask was flushed with argon. In a separate 2-neck round bottom flask, KOH (21.88 g, 390 mmol) was dissolved with dry MeOH under argon. The methanolic KOH solution was transferred into the first flask and the reaction mixture was heated to 85 °C. After stirring for 3 days, the solvent was removed under reduced pressure, water was added to the residue and extracted with DCM. The combined organic layers were washed with water twice and brine three times, and dried over Na₂SO₄. The crude oil (8.52 g) obtained after the solvent was removed was used as is for the next step.

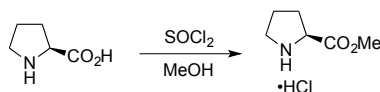
Tert-butyl catechol (2 mg as stabiliser) was added to the 2-neck round-bottom flask containing the crude from the previous step. The flask was flushed with argon and dry DCM was added. The solution was cooled to 0 °C and Et₃N (5.2 mL, 37.3 mmol) was added followed by the dropwise addition of TMSOTf (6.7 mL, 37.1 mmol). The reaction mixture was warmed to room temperature and left to stir overnight. The mixture was quenched with water and extracted with DCM. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude was purified by flash chromatography to afford the title compound (7.56 g, 62% over 2 steps) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 7.40–7.29 (m, 8H), 6.68 (ddd, *J* = 17.6, 10.9, 3.8 Hz, 2H), 5.71 (dd, *J* = 17.6, 5.6 Hz, 2H), 5.20 (dd, *J* = 10.9, 4.1 Hz, 2H), 4.02 (t, *J* = 7.1 Hz, 1H), 2.87–2.83 (m, 1H), 2.79–2.74 (m, 1H), 2.18 (br, 1H), 1.60–1.55 (m, 3H), 1.41–1.34 (m, 1H), –0.09 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ 146.1, 145.1, 136.5, 136.2, 136.1, 128.5, 127.8, 125.5, 125.4, 113.7, 113.6, 82.8, 65.4, 47.1, 27.4, 25.0, 2.2; [α]_D²⁰ = –54.7 (*c* = 0.657, DCM).

3.2 (S)- α,α -Diphenylprolinol 4-vinylbenzyl ether (A)



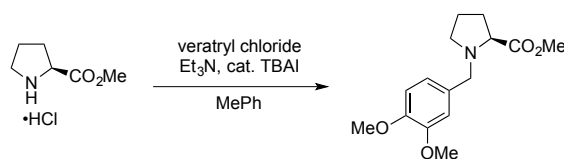
L-proline methyl ester hydrochloride



L-proline (5.87 g, 50.9 mmol) was added to a 100 mL 2-neck round-bottom flask attached with a reflux condenser and dropping funnel. The flask was flushed with argon. Anhydrous MeOH (40 mL) was added via the dropping funnel and the suspension was stirred while cooled in an ice bath. SOCl₂ (5.45 mL, 75 mmol) was added slowly via the dropping funnel and the mixture was allowed to stir for 30 min. It was then removed from the ice bath and warmed to room temperature. The clear colourless solution was then heated to reflux (95 °C) and kept there for 4 hours. After it had cooled to room temperature, excess SOCl₂ and MeOH were removed under reduced pressure to afford the title compound (8.39 g, 99%) as a colourless sticky liquid.

¹H NMR (600 MHz, CD₃OD): δ 4.47 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.86 (s, 3H), 3.45–3.37 (m, 2H), 2.48–2.40 (m, 1H), 2.18–2.05 (m, 3H); ¹³C NMR (150 MHz, CD₃OD): δ 170.4, 60.7, 53.9, 47.1, 29.3, 24.5.

N-(3,4-Dimethoxybenzyl)-L-proline methyl ester



Veratryl chloride was prepared as follows:

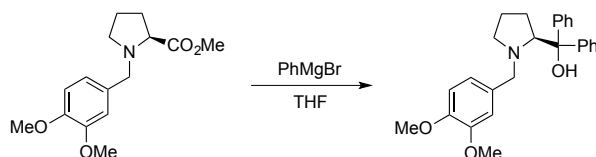
A stirring bar and anhydrous DCM (300 mL) were added to a 500 mL 2-neck round-bottom flask. Veratryl alcohol (10.07 g, 59.9 mmol) was added and the solution was cooled in an ice bath. SOCl_2 (8.8 mL, 121.2 mmol) and pyridine (4.9 mL, 60.7 mmol) were added dropwise consecutively. The solution was allowed to stir for 90 min before water (300 mL) was added. The organics were extracted with DCM and the combined organic layers were dried over MgSO_4 and concentrated *in vacuo* to afford a light yellow oil. The oil was cooled to -78°C upon which it solidified to form veratryl chloride **26** (10.62 g, 95%) as a pale yellow solid that was used as is.

^1H NMR (600 MHz, CDCl_3): δ 6.94–6.92 (m, 2H), 6.83 (d, $J = 8.1$ Hz, 1H), 4.57 (s, 2H), 3.90 (s, 3H), 3.88 (s, 3H); **^{13}C NMR (125 MHz, CDCl_3):** δ 149.2, 149.1, 130.0, 121.1, 111.7, 111.0, 55.9, 55.9, 46.7.

L-proline methyl ester hydrochloride (776.8 mg, 4.69 mmol), *tert*-butylammonium iodide (173.6 mg, 0.47 mmol), and a stirring bar were added to a two-neck round bottom flask (20 mL). The flask was then flushed with argon and MePh (3 mL) and Et_3N (3.3 mL, 23.5 mmol) were added. The mixture was stirred and a white solid was observed. It was then cooled to 0°C and veratryl chloride (963.4 mg, 5.16 mmol) dissolved in MePh (1 mL) was added dropwise. The mixture was then heated to reflux (125 – 130°C) and stirred vigorously. Additional MePh (2 mL) was added to facilitate stirring and the mixture was kept at reflux for 24 h. After the reaction had cooled to room temperature, saturated NaHCO_3 solution was added and the organics were extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO_4 and concentrated *in vacuo*. 2 M HCl solution (20 mL) was added and the aqueous layer was washed with Et_2O . The organic layers were discarded. The aqueous layer was then basified with 2 M NaOH solution and extracted with DCM. The combined organic layers were washed with brine, dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the title compound (1196.8 mg, 91%) as a pale yellow oil.

^1H NMR (500 MHz, CDCl_3): δ 6.89–6.79 (m, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.81 (d, $J = 12.4$ Hz, 1H), 3.65 (s, 3H), 3.54 (d, $J = 12.6$ Hz, 1H), 3.23 (dd, $J = 9.0, 5.9$ Hz, 1H), 3.08–3.05 (m, 1H), 2.40 (q, $J = 8.3$ Hz, 1H), 2.17–2.10 (m, 1H), 1.99–1.89 (m, 2H), 1.83–1.76 (m, 1H); **^{13}C NMR (125 MHz, CDCl_3):** δ 174.6, 148.6, 148.0, 130.8, 121.3, 112.3, 110.6, 65.1, 58.5, 55.8, 53.2, 51.6, 29.3, 22.9; **IR (neat):** 2951, 2834, 1738, 1514, 1460, 1263, 1235, 1158, 1138, 1030 cm^{-1} ; **HRMS (DART):** calculated for $\text{C}_{15}\text{H}_{22}\text{NO}_4^+ [M+\text{H}^+]$ 280.15488, found 280.15512; $[\alpha]_{\text{D}}^{22} = -37.9$ ($c = 0.113$, CHCl_3).

(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol

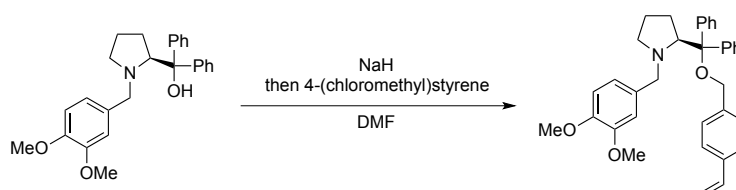


The Grignard reagent was prepared according to standard procedures from Mg (270 mg, 11.1 mmol) and bromobenzene (1.16 mL, 11.0 mmol) in THF (4 mL). The Grignard reagent was cooled in an ice bath before *N*-(3,4-Dimethoxybenzyl)-L-proline methyl ester (1187.1 mg, 4.25 mmol) dissolved in 2 mL of THF was added dropwise. The reaction was then warmed up to room temperature and stirred for 18 hours. It was then cooled again in an ice bath and concentrated HCl (8.5 mL) was added carefully to the solution. After stirring for 2 h, the solution was transferred to a larger flask and concentrated *in vacuo* to form an orange liquid. This liquid was washed with Et_2O and the organic layers were discarded. 1 M NaOH solution was added to the aqueous layer until the pH = 10. The aqueous layer was then shaken with EtOAc in a separatory funnel and the entire mixture was filtered through Celite. The organics were then extracted from the filtrate with EtOAc.

The combined organic layers were washed with brine, dried over MgSO_4 and concentrated *in vacuo* to afford a dark yellow solid. Recrystallisation of the solid with hexane and EtOAc at -78°C afforded the title compound (1199 mg, 70%) as pale yellow crystals.

^1H NMR (500 MHz, CDCl_3): δ 7.74 (d, $J = 7.9$ Hz, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.28 (q, $J = 7.6$ Hz, 4H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.3$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 6.59 (dd, $J = 8.1, 1.9$ Hz, 1H), 6.48 (d, $J = 1.9$ Hz, 1H), 4.90 (br, 1H), 3.98 (dd, $J = 9.5, 4.7$ Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.19 (d, $J = 12.7$ Hz, 1H), 2.99 (d, $J = 12.4$ Hz, 1H), 2.94–2.92 (m, 1H), 2.40–2.35 (m, 1H), 1.99–1.91 (m, 1H), 1.78–1.72 (m, 1H), 1.65–1.61 (m, 2H); **^{13}C NMR (125 MHz, CDCl_3):** δ 148.6, 148.0, 147.8, 146.5, 132.3, 128.0, 128.0, 126.3, 126.2, 125.6, 125.4, 120.5, 111.7, 110.4, 77.9, 70.4, 60.3, 55.7, 55.5, 29.7, 24.2; **IR (KBr):** 3359, 3059, 3007, 2953, 2828, 2806, 1594, 1514, 1455, 1377, 1264, 1237, 1157, 1139, 1028, 867, 814, 753 cm^{-1} ; **HRMS (DART):** calculated for $\text{C}_{26}\text{H}_{30}\text{NO}_3^+ [M+\text{H}^+]$ 404.22257, found 404.22338; $[\alpha]_{\text{D}}^{20} = +120.6$ ($c = 0.113$, CHCl_3); **M.p.** = 121–122 $^\circ\text{C}$.

(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol 4-vinylbenzyl ether

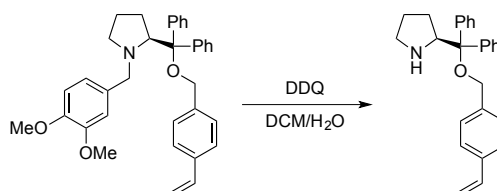


NaH (55%, dispersion in paraffin liquid) (176.8 mg, 4.05 mmol) was added to a 20 mL 2-neck round-bottom flask (20 mL). The flask was flushed with argon and NaH was washed with petroleum ether (5 mL, 3 times). NaH was then dried *in vacuo* with utmost care, ensuring that an argon atmosphere was kept at all times after the vacuum was released. Anhydrous DMF (1.5 mL) was then added and the suspension was cooled in an ice bath.

(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol (190.8 mg, 0.47 mmol) and DMF (1.5 mL) were added to a separate 10 mL 2-neck round-bottom flask (10 mL). This solution was added dropwise to the suspended NaH. Once effervescence of all gas had ceased, the mixture was removed from the ice bath. 4-(chloromethyl)styrene (437 μL , 3.1 mmol) was then added dropwise followed by the addition of *tert*-butylammonium iodide (45.8 mg, 0.124 mmol) dissolved in DMF (0.5 mL) and the reaction mixture was stirred for 18 hours at 50°C . Hexane/EtOAc (2:1) was used to dilute the solution and it was cooled in a ice bath before saturated NH_4Cl was added to quench the reaction. The organics were extracted with hexane/EtOAc (2:1), washed well with brine and dried over MgSO_4 . The residue obtained after concentrating *in vacuo* was purified by flash chromatography (20% EtOAc in hexane) to afford the title compound (458.9 mg, 70%) as yellow sticky flakes.

^1H NMR (500 MHz, CDCl_3): δ 7.69 (dd, $J = 18.7, 7.5$ Hz, 4H), 7.36–7.21 (m, 10H), 6.72–6.64 (m, 4H), 5.69 (d, $J = 17.6$ Hz, 1H), 5.18 (d, $J = 10.9$ Hz, 1H), 4.21 (d, $J = 11.2$ Hz, 1H), 4.12 (d, $J = 12.3$ Hz, 1H), 4.03 (dd, $J = 9.5, 3.1$ Hz, 1H), 3.99 (d, $J = 12.3$ Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.34 (d, $J = 12.7$ Hz, 1H), 2.43–2.40 (m, 1H), 2.12–2.10 (m, 1H), 2.00–1.93 (m, 1H), 1.87–1.82 (m, 1H), 1.28–1.25 (m, 1H), 0.44–0.35 (m, 1H); **^{13}C NMR (125 MHz, CDCl_3):** δ 148.6, 147.5, 140.8, 139.4, 139.0, 136.6, 136.3, 133.9, 130.1, 127.3, 127.2, 127.1, 127.1, 126.8, 126.0, 120.1, 113.3, 111.7, 110.4, 87.6, 70.8, 65.3, 61.7, 55.8, 55.7, 54.7, 28.9, 23.5; **IR (KBr):** 3435, 2952, 1593, 1513, 1446, 1260, 1234, 1154, 1136, 1032, 907, 826, 767 cm^{-1} ; **HRMS (DART):** calculated for $\text{C}_{35}\text{H}_{38}\text{NO}_3^+ [M+\text{H}^+]$ 520.28517, found 520.28522. $[\alpha]_{\text{D}}^{21} = -61.2$ ($c = 0.322$, CHCl_3).

(S)- α,α -Diphenylprolinol 4-vinylbenzyl ether

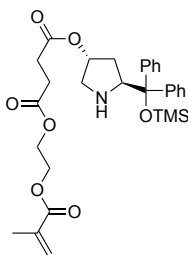


(*S*)-*N*-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol 4-vinylbenzyl ether (408.9 mg, 0.787 mmol), DCM (8 mL) and water (0.4 mL) were added to a 20 mL round-bottom flask. The solution was cooled in an ice bath under open air and DDQ (196.5 mg, 0.866 mmol) was added. The solution turned dark brown/black immediately and became lighter as the reaction progressed. A solid was also observed. After 48 hours, the reaction was quenched with saturated NaHCO₃ solution and the organics were extracted with DCM. The combined organic layers were washed with brine and dried over MgSO₄. A brown liquid was obtained after concentrating *in vacuo*. Purification by preparative TLC (50 % EtOAc in hexane with 1.5% Et₃N using WakoGel) afforded the title compound (226.9 mg, 70%) as a yellow-green liquid.

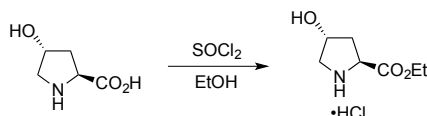
¹H NMR (500 MHz, CDCl₃): δ 7.50–7.45 (m, 4H), 7.36–7.23 (m, 10H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.22 (s, 1H), 5.19 (d, *J* = 11.5 Hz, 1H), 4.33 (d, *J* = 11.4 Hz, 1H), 4.25 (br, 1H), 4.24 (d, *J* = 7.0 Hz, 1H), 2.77–2.72 (m, 1H), 2.59–2.54 (m, 1H), 1.90–1.76 (m, 1H), 1.75–1.69 (m, 1H), 1.55–1.50 (m, 1H), 1.15–1.08 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 143.3, 142.1, 139.0, 136.6, 136.5, 129.1, 128.9, 127.7, 127.5, 127.2, 126.0, 113.4, 85.4, 64.9, 62.6, 47.0, 27.6, 25.4; IR (neat): 2962, 2870, 1492, 1445, 1074, 990, 908, 827, 758 cm⁻¹; HRMS (DART): calculated for C₂₆H₂₈NO⁺ [*M*+H⁺] 370.21709, found 370.21583; [α]_D²¹ = –7.5 (*c* = 0.726, CHCl₃).

The optical purity was determined by first converting the amine into the corresponding amide with acetic anhydride and triethylamine. HPLC analysis with Chiralpak AD-H column, 220 nm. Flow rate = 0.5 mL/min. Hexane:*i*PrOH = 90:10. *t*_R = 44.7 min (*S* isomer), 98.4 min (*R* isomer).

3.3 *O*-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol trimethylsilyl ether (B)⁴



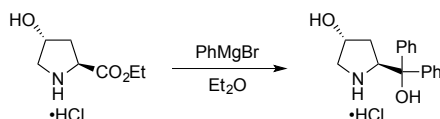
trans-4-Hydroxy-L-proline ethyl ester hydrochloride



trans-4-Hydroxyl L-proline (13.10 g, 99.9 mmol) and a stirring bar were added to a 500 mL 2-neck round-bottom flask attached with a reflux condenser and a dropping funnel. The flask was then flushed with argon and EtOH (120 mL) was added. The reaction mixture was then stirred while cooled in an ice bath. SOCl₂ (11 mL, 151.4 mmol) was added dropwise via the dropping funnel. The flask was then removed from the ice bath and the reaction was heated to reflux (105 °C) for 4 hours. The flask was then cooled in an ice bath and Et₂O (200 mL) was added. The mixture was stirred vigorously and a white solid appeared. The suspension was vacuum-filtered and the white solid washed with 60 mL of Et₂O. The white solid was then dried *in vacuo* at room temperature overnight to afford the title compound (19.10 g, 98%) as a white fibrous solid.

¹H NMR (600 MHz, CD₃OD): δ 4.62–4.59 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.49 (dd, *J* = 12.1, 3.5 Hz, 1H), 3.34–3.31 (m, 1H), 2.45–2.41 (m, 1H), 2.24–2.19 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CD₃OD): δ 170.1, 70.6, 64.0, 59.5, 55.0, 38.6, 14.3.

trans-4-Hydroxy- α,α -diphenyl-L-prolinol hydrochloride

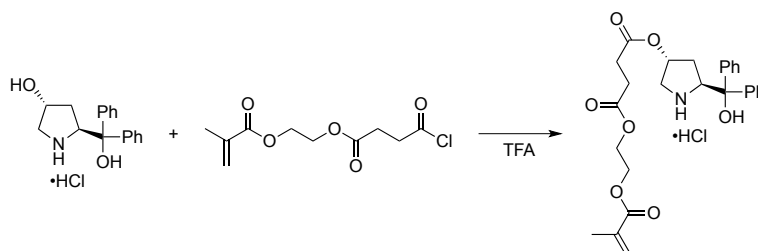


The Grignard reagent was prepared according to standard procedures from Mg (10.41 g, 428.2 mmol) and bromobenzene (45 mL, 428.5 mmol) in Et₂O (150 mL).

trans-4-Hydroxy-L-proline ethyl ester hydrochloride (18.58 g, 95.0 mmol) and a stirring bar were added to a 500 mL 2-neck round-bottom flask attached with a dropping funnel. The flask was flushed with argon and Et₂O (100 mL) was added to form a suspension under stirring. The Grignard reagent was added dropwise via the dropping funnel and the reaction mixture was allowed to stir at room temperature overnight. The dropping funnel was then changed to a reflux condenser and the mixture was refluxed for 4 hours. A sticky brown solid in a clear solution formed at the end of the reflux. The mixture was then cooled in an ice bath and then poured into a 1 L beaker filled with 400 mL of crushed ice. The sticky solid that could not be transferred was cooled in an acetone/dry-ice bath and dilute HCl was added. A white solid in an orange solution was formed. The white solid was obtained by vacuum-filtration and the acidic orange solution was added to the crushed ice mixture. The crushed ice mixture was then shaken with Et₂O and the organic layer was discarded. The aqueous layer was then basified with aqueous NH₃ and the solid formed was obtained via vacuum-filtration. It was washed with water and methyl *tert*-butyl ether (MTBE). All the solids obtained so far were then combined in a flask and dissolved in MeOH and trifluoroacetic acid (TFA). An ice-cold methanolic HCl solution (prepared by dropping 10 mL of acetyl chloride in 50 mL of MeOH under cooling in an ice-bath) was added, followed by the addition of Et₂O. The mixture was stirred quickly for 10 minutes and a precipitate was formed. The precipitate was obtained via vacuum-filtration and washed with Et₂O. A second portion of the precipitate was obtained from the filtrate after it was left to stand. The precipitates were dried *in vacuo* overnight to afford the title compound (14.78 g, 51%) as a white solid.

¹H NMR (600 MHz, CD₃OD): δ 7.70–7.62 (m, 2H), 7.54–7.47 (m, 2H), 7.45–7.22 (m, 6H), 5.05 (dd, *J* = 10.8, 6.7 Hz, 1H), 4.53 (t, *J* = 3.7 Hz, 1H), 3.32 (d, *J* = 3.4 Hz, 1H), 3.21 (d, *J* = 12.1 Hz, 1H), 2.17 (ddd, *J* = 13.8, 10.9, 4.2 Hz, 1H), 1.96 (dd, *J* = 13.8, 6.7 Hz, 1H); **¹³C NMR (150 MHz, CD₃OD):** δ 145.4, 145.4, 129.9, 129.6, 128.8, 128.7, 126.9, 126.7, 78.2, 70.8, 66.7, 55.4, 36.4.

O-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol hydrochloride

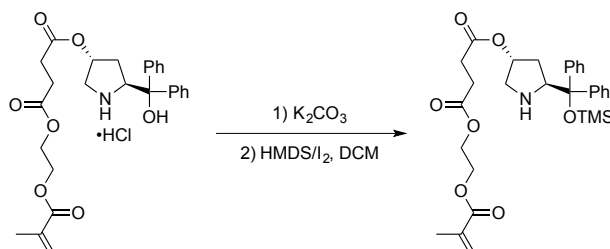


Commercial 2-methacryloyloxyethylsuccinic acid (20.75 g, 90.1 mmol) was added to a 100 mL 2-neck round-bottom flask. A reflux condenser and a dropping funnel were attached and the flask was flushed with argon. SOCl₂ (33 mL, 450 mmol) was added dropwise via the dropping funnel and the mixture was stirred at room temperature for 30 minutes. MEHQ (11 mg) was added and the mixture was heated to 50 °C and kept there for 30 minutes. Excess SOCl₂ was removed *in vacuo* and to give 2-methacryloyloxyethylsuccinoyl chloride as a light yellow oil that was used as is.

trans-4-Hydroxy- α,α -diphenyl-L-prolinol hydrochloride (13.76 g, 45 mmol) was added to a 300 mL round-bottom flask followed by the addition of TFA (50 mL). The mixture was stirred at 0 °C and 2-methacryloyloxyethylsuccinoyl chloride was added slowly with a pipette. The flask was removed from the ice bath and stirring was continued at room temperature for 2 hours. The flask was then cooled in an ice bath again and Et₂O (200 mL) was added under vigorous stirring. A white solid appeared and it was obtained by vacuum-filtration, washed with Et₂O (100 mL) and dried *in vacuo* at room temperature overnight. The solid was dissolved in EtOH (150 mL) with hydroquinone (61 mg) under heating. Hot MTBE (100 mL) was then added and once a bit of solid was observed, heating and stirring were stopped. After 6 hours, the fluffy crystals were obtained by vacuum-filtration and washed with MTBE. The title compound (16.58 g, 71%) was obtained as a white fluffy solid after drying *in vacuo* for 3 days.

¹H NMR (600 MHz, DMSO-*d*₆): δ 10.24 (br, 1H), 8.78 (br, 1H), 7.74–7.66 (m, 2H), 7.53–7.46 (m, 2H), 7.40–7.18 (m, 6H), 6.70 (s, 1H), 6.02 (s, 1H), 5.68 (s, 1H), 5.25 (s, 1H), 5.05–4.98 (m, 1H), 4.28 (s, 4H), 3.48–3.42 (m, 1H), 3.32–3.26 (m, 1H), 2.68–2.60 (m, 4H), 2.32–2.27 (m, 1H), 1.86 (s, 3H), 1.72 (dd, *J* = 14.2, 6.6 Hz, 1H); **¹³C NMR (150 MHz, DMSO-*d*₆):** δ 172.1, 171.5, 166.4, 144.4, 144.2, 135.6, 128.5, 128.3, 127.4, 127.1, 126.2, 126.1, 125.4, 76.9, 72.9, 63.9, 62.4, 62.1, 51.1, 32.4, 28.9, 28.5, 18.0.

O-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol trimethylsilyl ether

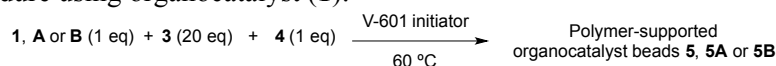


O-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol hydrochloride (1039.8 mg, 2.01 mmol), DCM (8 mL) and saturated K₂CO₃ solution (8 mL) were stirred together vigorously for 5 minutes in a 50 mL round-bottom flask. The organic layer was separated and the aqueous layer was extracted with DCM (4 mL). The combined organic layers were dried over MgSO₄ and the mixture was filtered into another 50 mL round-bottom flask. MgSO₄ was washed with DCM (4 mL). I₂ (9.4 mg, 0.037 mmol) and HMDS (0.63 mL, 3.01 mmol) were added to the DCM solution and it was left to stir for 4 hours at room temperature. Additional I₂ and HMDS (same amount as before) was added because the reaction was incomplete as seen on TLC. The solution was left to stir for an additional 2 hours and MeOH (0.6 mL) was added to quench the reaction. After stirring for 10 minutes, the solvents were evaporated and the oil obtained was dissolved in DCM (8 mL). Sodium sulphate pentahydrate (1025.9 mg, 4.13 mmol) in H₂O (8 mL) was then added and the mixture was stirred for 5 minutes. The organic layer was separated and dried over MgSO₄. MgSO₄ was filtered off and the solvent was evaporated to afford the title compound (1159.3 mg, 90%) as a light yellow oil of good purity that was used as is for polymerisation.

¹H NMR (500 MHz, CDCl₃): δ 7.46–7.25 (m, 10H), 6.12 (s, 1H), 5.58 (m, 1H), 4.99–4.92 (m, 1H), 4.35–4.27 (m, 5H), 2.97–2.90 (m, 2H), 2.68–2.52 (m, 4H), 1.94 (s, 3H), 1.92–1.84 (m, 1H), 1.65 (dd, *J* = 14.3, 6.7 Hz, 1H) –0.10 (s, 9H); **¹³C NMR (125 MHz, CDCl₃):** δ 172.0, 171.9, 167.0, 146.1, 144.9, 135.8, 128.4, 127.7, 127.6, 127.4, 127.1, 127.0, 126.1, 82.7, 75.6, 63.9, 62.3, 62.3, 53.0, 34.6, 29.2, 28.9, 18.2, 2.1.

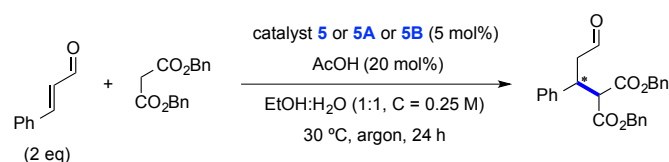
4 Preparation and screening of polymer-supported organocatalysts

Representative procedure using organocatalyst (**1**):



KI (11.9 mg, 0.07 mmol), K₂CO₃ (37.0 mg, 0.27 mmol) and a stirring bar were added to a 100 mL two-neck round bottom flask flushed with argon. Degassed 0.5 wt% poly(vinyl alcohol) solution (32 mL) was added and the solution was stirred gently at a constant rate. In a separate flask, *N*-*tert*-butylacrylamide (**3**) (4069.5 mg, 32 mmol), *N,N'*-methylenebismethacrylamide (**4**) (291.9 mg, 1.6 mmol), (*S*)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether (**1**) (689.5 mg, 1.82 mmol) and dimethyl 2,2'-azobis(2-methylpropionate) (V-601 initiator) (84.8 mg, 0.36 mmol) were dissolved in 9 mL of chloroform and the solution was degassed. The solution of monomers and initiator was then added dropwise to the stirring PVA solution. The suspension was heated to 60 °C. After 24 h, heating and stirring was stopped and the mixture was filtered by suction. The polymer beads were washed with THF/water, THF and then DCM on the funnel. 4658.3 mg (92%) of polymer beads were obtained after drying the beads *in vacuo* for a day at 40 °C.

Examining the activity of various polymer-supported Jørgensen-Hayashi-type organocatalysts.



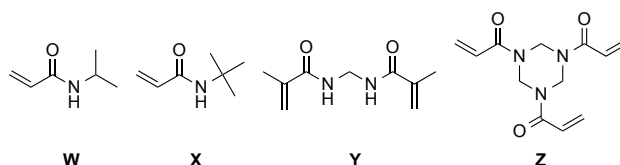
Entry	Catalyst	Immobilized organocatalyst	Yield [%] ^[a]	ee [%] ^[b]
1	5	1	quant.	91
2	5A	A	99	88
3	5B	B	91	86

[a] Yield based on ¹H NMR spectroscopy with 1,1,2,2-tetrachloroethane as the internal standard. [b] Determined by chiral HPLC analysis after oxidation to the corresponding methyl ester.

The reaction proceeded smoothly in all cases at 30 °C, with ethanol and water as the solvent, and 20 mol% of acetic acid as an additive. These conditions were adopted because water is known to accelerate this particular reaction and the addition of acetic acid makes the reaction more efficient.⁵

5 Screening of acrylamide co-monomers

The following acrylamides shown were screened because they were commercially available and seemed like ideal candidates as co-monomers for the suspension copolymerisation.



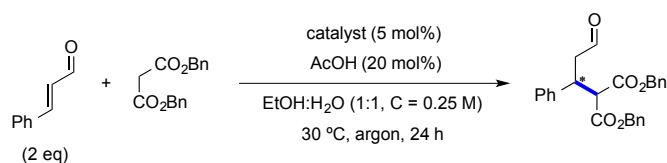
When these acrylamides were screened with organocatalyst (*S*)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether (**1**), the polymer beads formed from **1**, **X** and **Y** were the easiest to handle. The resulting beads were not sticky or did not swell too much in the reaction solvent (EtOH and H₂O) to the point where filtration was difficult. When the beads were too sticky or swelled too much, some loss occurred and the yield of the polymerisation was affected.

Examining various acrylamides to support the Jørgensen-Hayashi-type organocatalyst.

filler monomer (20 eq) + organocatalyst 1 (1 eq) + cross-linking monomer (1 eq) $\xrightarrow[60\text{ }^{\circ}\text{C}]{\text{V-601 initiator}}$ Immobilised organocatalyst				
Entry	Catalyst name	Filler monomer	Cross-linking monomer	Yield [%]
1	WY	W	Y	82
2	WZ	W	Z	76
3	XY	X	Y	86
4	XZ	X	Z	83

Furthermore, the yield and ee of the asymmetric Michael reaction differed, depending on the type of acrylamide used. The results are summarised in the following table:

Difference in catalytic activity depending on acrylamide used.



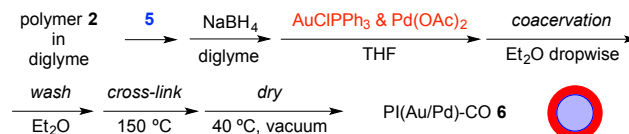
Entry	Catalyst	Yield [%] ^[a]	ee [%] ^[b]
1	WY	quant.	91
2	WZ	90	91
3	XY	quant.	91
4	XZ	98	90

[a] Yield based on ¹H NMR spectroscopy with 1,1,2,2-tetrachloroethane as the internal standard. [b] Determined by chiral HPLC analysis after oxidation to the corresponding methyl ester.

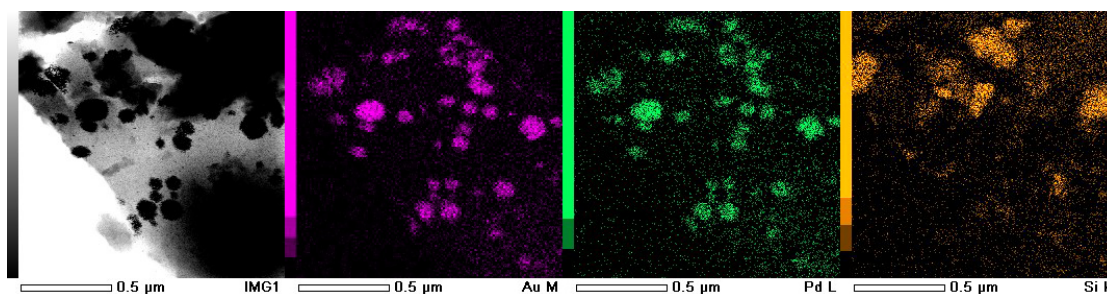
While catalyst WY and XY gave similar results, we decided on catalyst XY (polymer beads **5** in manuscript) for our investigations because beads with this combination of acrylamides exhibited adequate swelling without being too difficult to handle during filtration and work-up.

6 Preparation of coated catalysts

6.1 PI(Au/Pd)-CO (6)



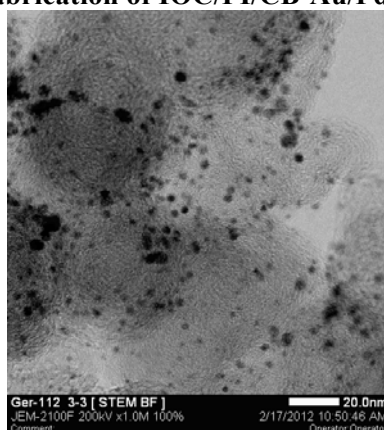
Polymer **2** (1.11 g), diglyme (50 mL) and **5** (1.00 g) were added to a 300 mL round-bottom flask. NaBH₄ (30.5 mg, 0.8 mmol) dissolved in 12.5 mL of diglyme was then added and the mixture was stirred and cooled in an ice bath. AuClPPh₃ (39.7 mg, 0.08 mmol), Pd(OAc)₂ (18.0 mg, 0.08 mmol) were dissolved together in 12.5 mL of diglyme and added to the stirring mixture via a dropping funnel. The flask was removed from the ice bath and allowed to stir at room temperature overnight. Diethyl ether (200 mL) was added via a dropping funnel over 4 h and the liquid was decanted off. The residue was washed with diethyl ether three times and dried *in vacuo* before being heated at 150 °C for 5 h in a vacuum oven. The residue was ground with a mortar and pestle and then washed in THF/water (1:1, 500 mL) overnight. After vacuum filtration, the powder was washed with water, THF and DCM in that order on the funnel and dried at 50 °C for 14 h in a vacuum oven. 1915.8 mg (91%) of a brown/grey powder was obtained and the loading of Au and Pd were determined by ICP analysis. **Au loading: 0.0324 mmol/g, Pd loading: 0.0401 mmol/g.**



Procedure for the preparation of the sample for ICP analysis:

Catalyst **6** (28.19 mg) was placed in a clean test tube and heated with H₂SO₄ (1 mL) to 200 °C. After 30 minutes, a few drops of concentrated HNO₃ were added carefully and the test tube was shaken occasionally. HNO₃ was repeatedly added until a clear orange-red solution was obtained. The excess HNO₃ was then allowed to evaporate under heating. After the solution was cooled to room temperature, 1 mL of aqua regia was added carefully. Effervescence of a gas was observed and the solution turned even clearer. The solution was then transferred to a volumetric flask and made up to 50 mL with water. Concentration of Au: 3.40 ppm, concentration of Pd: 2.40 ppm.

6.2 PI/CB-Au/Pd (used in the fabrication of IOC/PI/CB-Au/Pd 7)

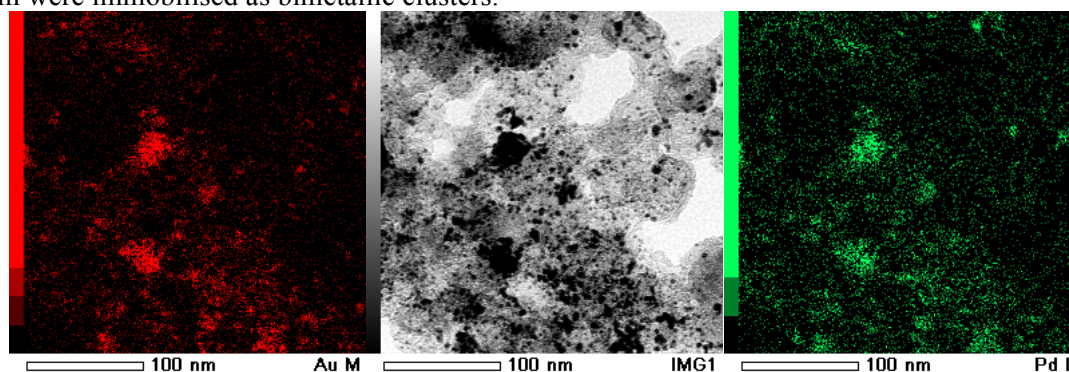


Diglyme (30 mL), Ketjenblack EC300J (500.0 mg) and NaBH₄ (107.0 mg, 2.82 mmol) were added to a 200 mL round bottom flask charged with co-polymer **2** (500.0 mg) and a stirring bar. The suspension was cooled in an ice-bath and stirred under open-air until the Ketjenblack was evenly dispersed. To this suspension was slowly added a THF solution (6 mL) of AuClPPh₃ (138.4 mg, 0.28 mmol) and Pd(OAc)₂ (63.0 mg, 0.28 mmol) mixed together. The ice-bath was removed and the mixture was allowed to stir overnight. Diethyl ether (200 mL) was then added dropwise over one hour and the resulting mixture was vacuum-filtered. The black solid cake obtained at the top of the funnel was rinsed carefully with diethyl ether. The solid was crushed lightly with a mortar and pestle before being transferred to a 100 mL round bottom flask. The flask was flushed with argon and then placed in an oil bath (pre-heated to 170 °C) for 4 h. After allowing the flask to cool to room temperature, THF and water (100 mL respectively) were added and the suspension was stirred vigorously overnight to remove boron. The suspension was then vacuum-filtered and the residue on top of the filter funnel was rinsed with water, THF and DCM in that order two times. The residue was then ground with a mortar and pestle before being dried *in vacuo* overnight to afford PI/CB-Au/Pd (1.01 g). **Au loading: 0.238 mmol/g, Pd loading: 0.239 mmol/g.**

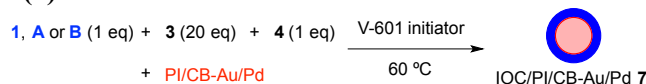
Procedure for the preparation of the sample for ICP analysis:

12.7 mg of PI/CB-Au/Pd was heated to 200 °C in H₂SO₄ (1 mL) and HNO₃ was added dropwise until all solid had dissolved and no more brown fumes were observed. The mixture was cooled to room temperature and aqua regia (1 mL) was added slowly. The resulting mixture was made up to 50 mL with water in a volumetric flask and used in ICP analysis. Concentration of Au: 11.90 ppm, concentration of Pd: 6.46 ppm.

STEM analysis showed good cluster size distribution and EDS mapping analysis showed that gold and palladium were immobilised as bimetallic clusters.



6.3 IOC/PI/CB-Au/Pd (7)

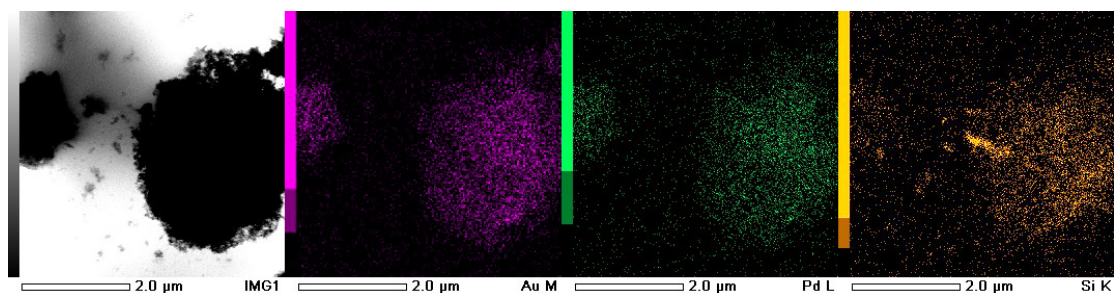


Representative procedure using organocatalyst **1**:

KI (11.9 mg, 0.07 mmol), K₂CO₃ (37.0 mg, 0.27 mmol) and a stirring bar were added to a 100 mL two-neck round-bottom flask flushed with argon. Degassed 0.5 wt% poly(vinyl alcohol) solution (3 mL) was added and the solution was stirred gently at a constant rate. In a separate flask, *N*-*tert*-butylacrylamide (**3**) (258.5 mg, 2.03 mmol), *N,N'*-methylenebismethacrylamide (**4**) (18.3 mg, 0.10 mmol), (*S*)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether (**1**) (44.0 mg, 0.12 mmol) and dimethyl 2,2'-azobis(2-methylpropionate) (V-601 initiator) (6.4 mg, 0.028 mmol) were dissolved in 1.5 mL of chloroform. PI/CB-Au/Pd (83.4 mg) was suspended in that solution and the solution was degassed. The suspension of monomers, initiator and PI/CB-Au/Pd was then added dropwise to the stirring PVA solution. The suspension was heated to 60 °C. After 24 h, heating and stirring was stopped and the mixture was filtered by suction. The polymerised product was washed with THF/water, THF and then DCM on the funnel. 338.2 mg (84%)

A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

of a black powder were obtained after drying *in vacuo* for a day at 40 °C and crushing with mortar and pestle. **Au loading: 0.038 mmol/g, Pd: 0.040 mmol/g.**



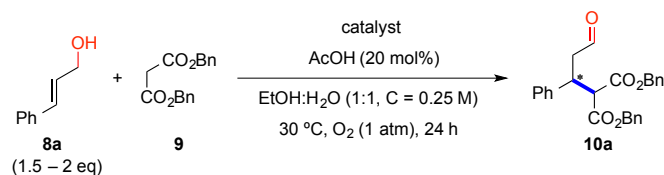
Procedure for the preparation of the sample for ICP analysis:

Catalyst **7** (22.0 mg) was placed in a clean test tube and heated with H₂SO₄ (1 mL) to 200 °C. After 30 minutes, a few drops of concentrated HNO₃ were added carefully and the test tube was shaken occasionally. HNO₃ was repeatedly added until no more brown fumes were observed. The excess HNO₃ was then allowed to evaporate under heating. After the solution was cooled to room temperature, 1 mL of aqua regia was added carefully. Effervescence of a gas was observed and the solution turned even clearer. The solution was then transferred to a volumetric flask and made up to 50 mL with water. Concentration of Au: 3.31 ppm, concentration of Pd: 1.89 ppm.

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7 Optimisation of conditions for the asymmetric TOP

Optimization of conditions for the asymmetric TOP.



Entry	Catalyst	8a eq	Conv [%] ^[a]	Yield [%] ^[b]	ee [%] ^[c]
1	6 (Au = 1, Pd = 1, OC = 5)	2	76	nd	91
2	7 (Au = 1, Pd = 1, OC = 5)	2	nr	–	–
3	PI/CB-Au/Pd (Au = 1, Pd = 1) & 1 (5)	2	39	nd	85
4	6 (Au = 1, Pd = 1, OC = 5)	1.5	70	57	89
5 ^[d]	6 (Au = 1, Pd = 1, OC = 5)	1.5	78	64	90
6	6 (Au = 1, Pd = 1, OC = 5)	1.5	90	63	89
7	6 (Au = 2, Pd = 2, OC = 10)	2	97	75	90

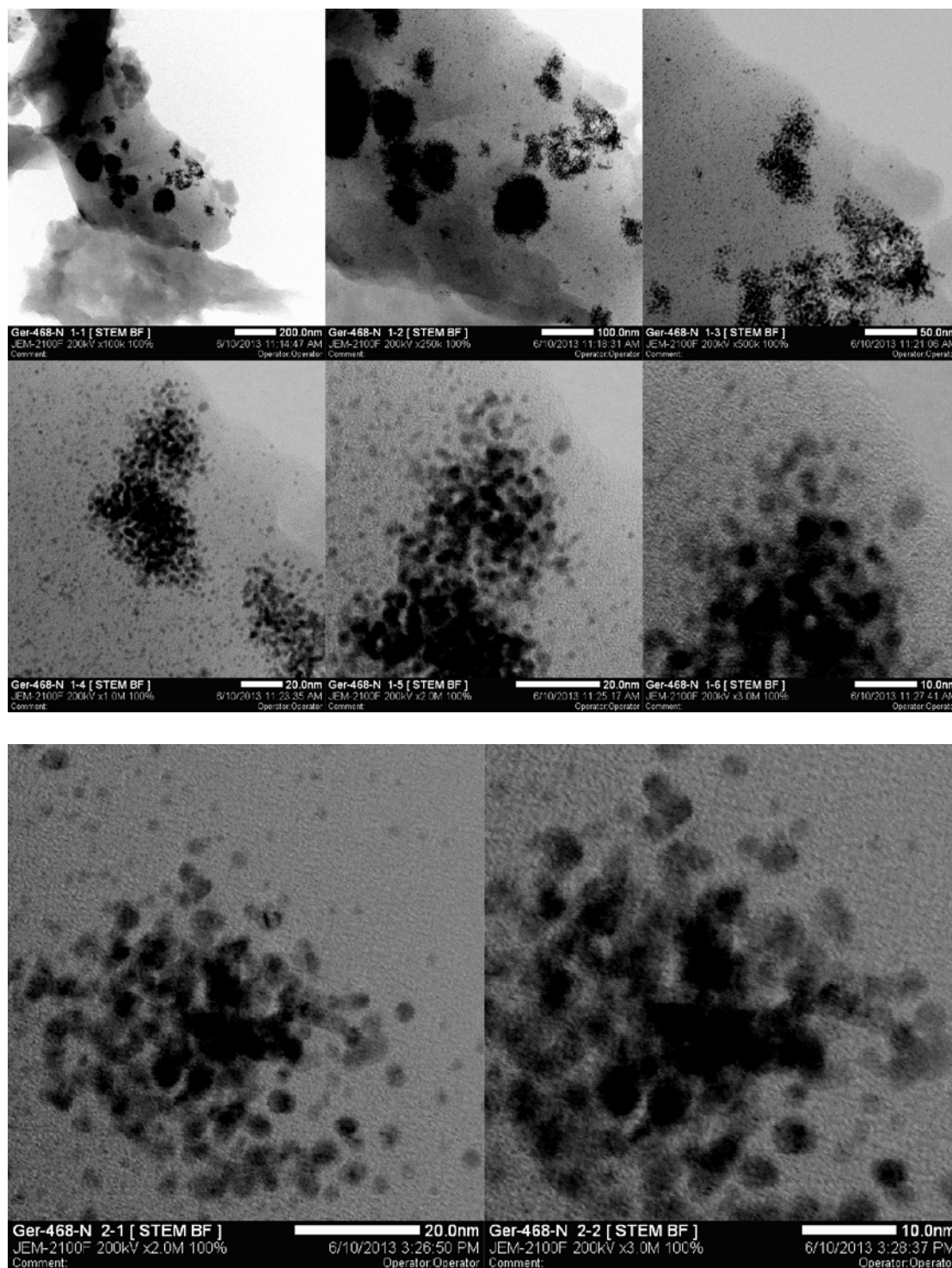
[a] Conversion of **9** based on ¹H NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard (nr = no reaction). [b] Isolated yield (nd = not determined). [c] Determined by chiral HPLC analysis after oxidation to the corresponding methyl ester. [d] 48 h reaction time.

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8 Characterisation of catalysts via STEM, EDS, SEM and TEM analyses

8.1 PI(Au/Pd)-CO (6)

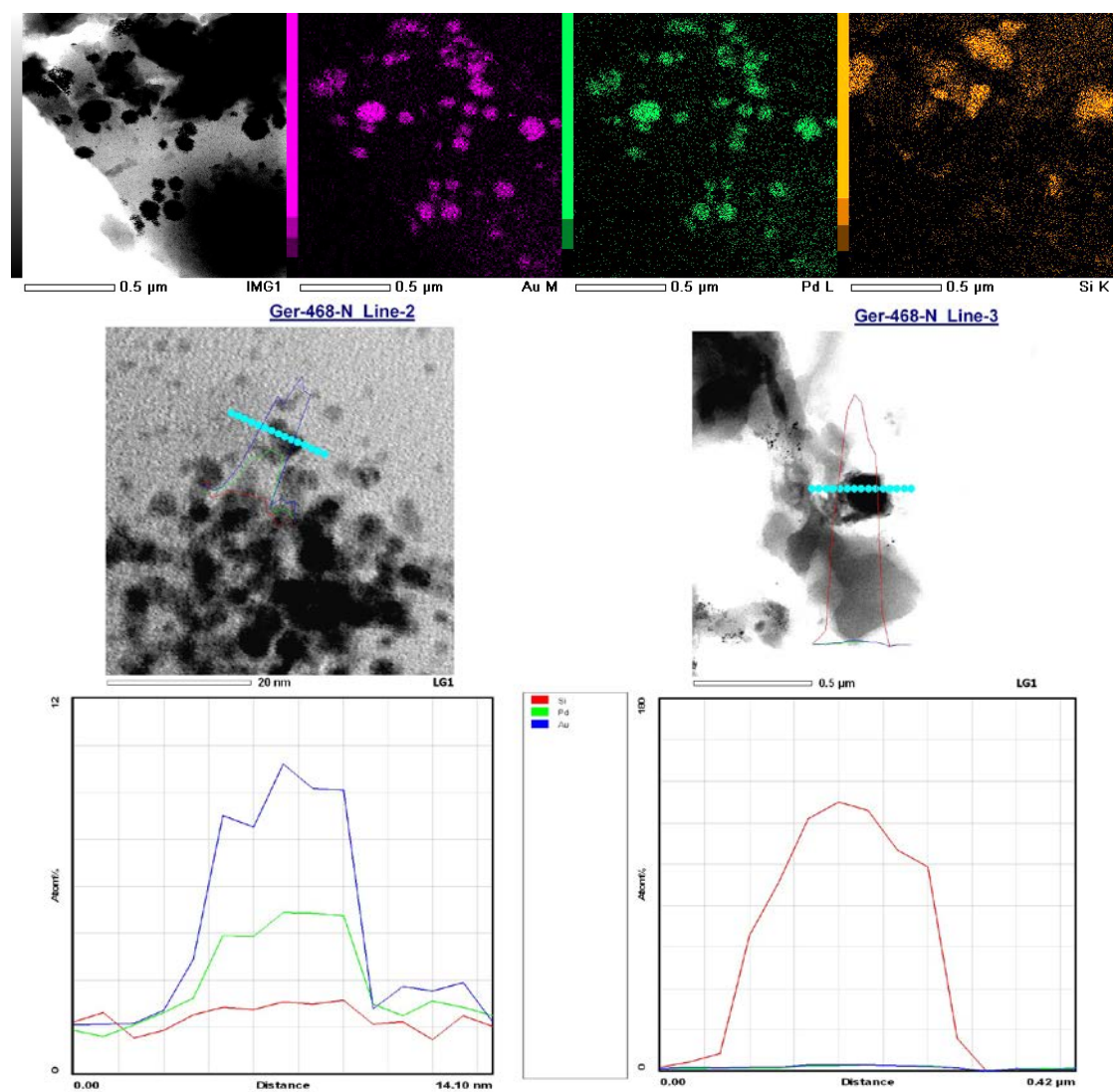
STEM Images:



The formation of nanoclusters ranging from 1–4 nm were confirmed. However, these small nanoclusters formed “colonies” that can be as large as 50–100 nm.

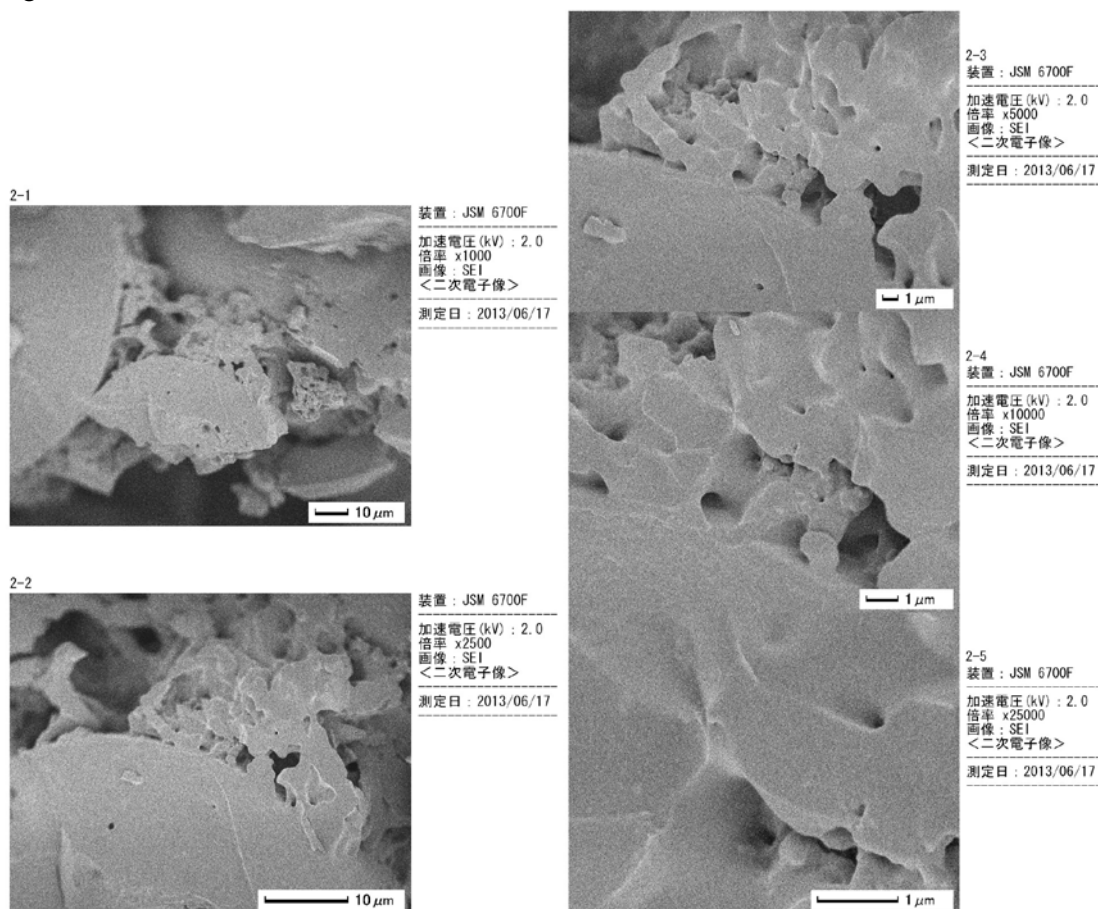
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EDS Mapping and EDS Line Analyses:

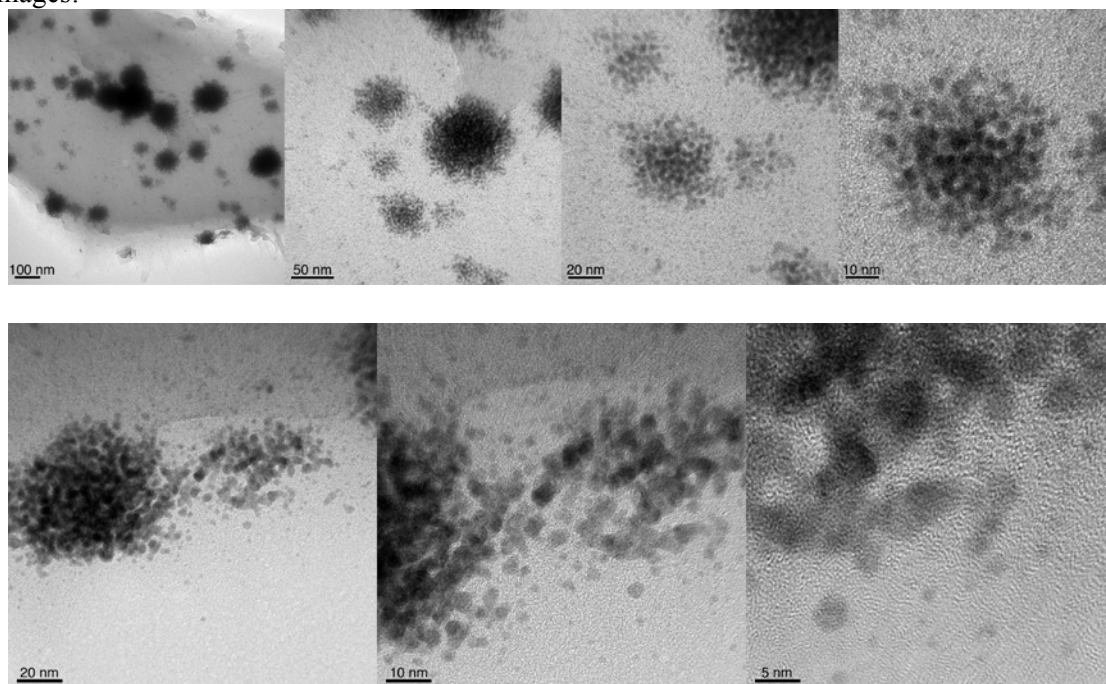


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SEM images:



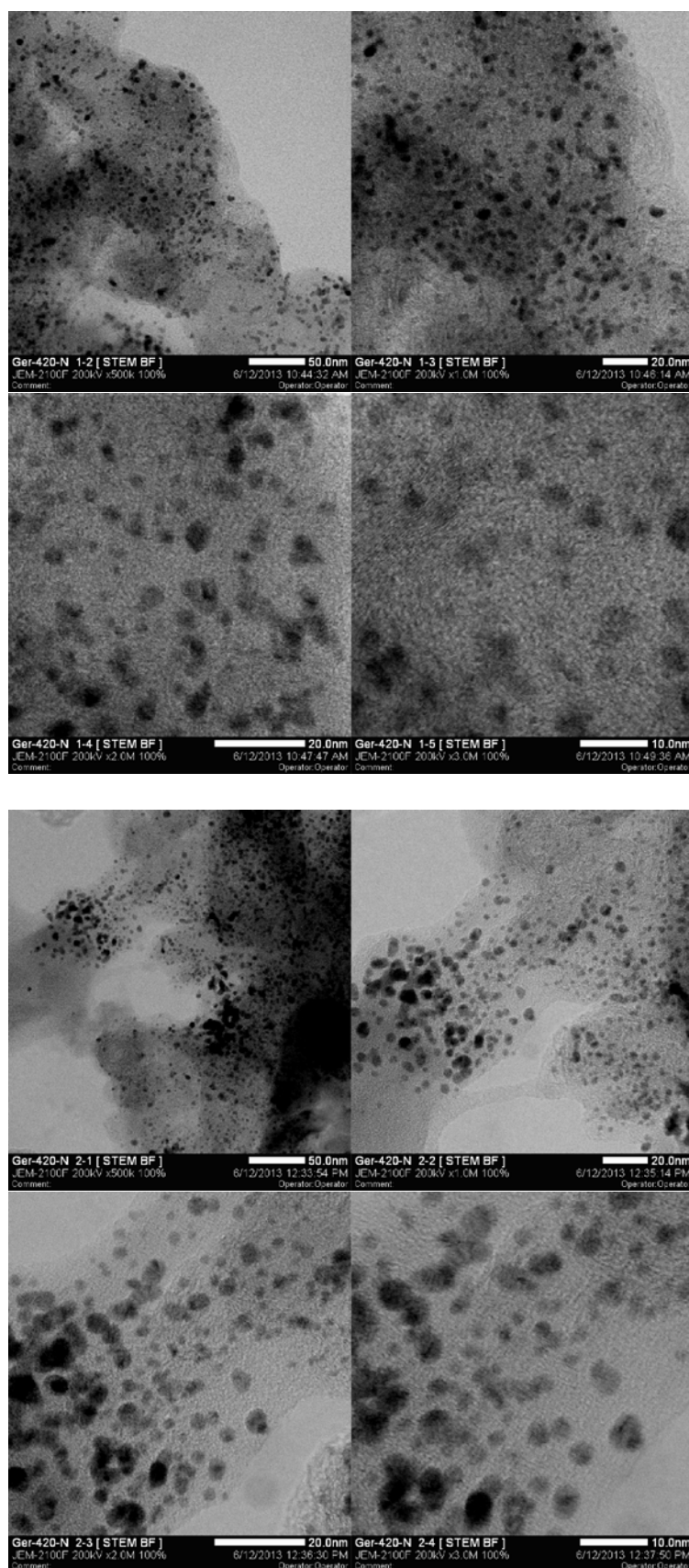
TEM images:



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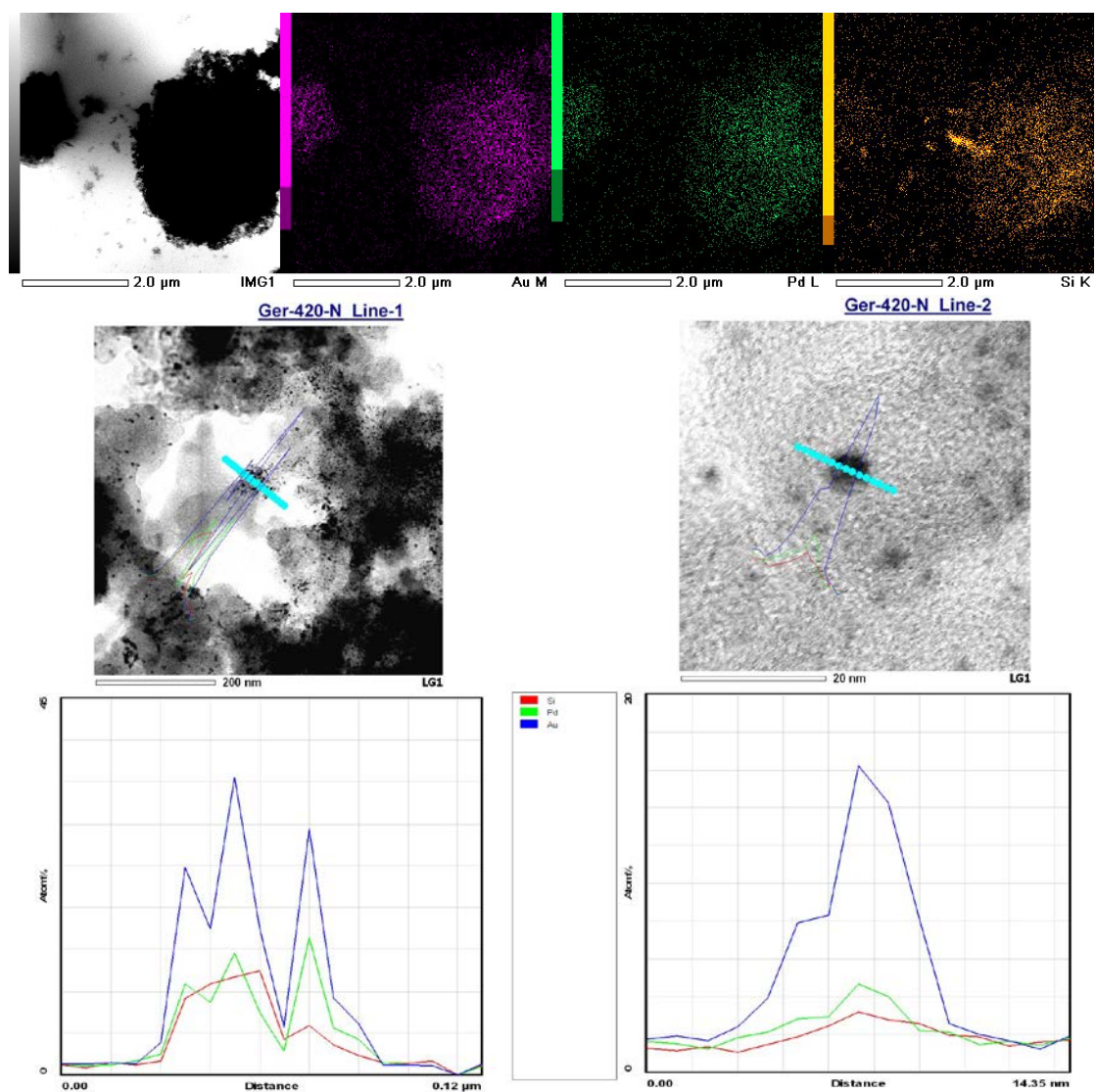
8.2 IOC/PI/CB-Au/Pd (7)

STEM Images:

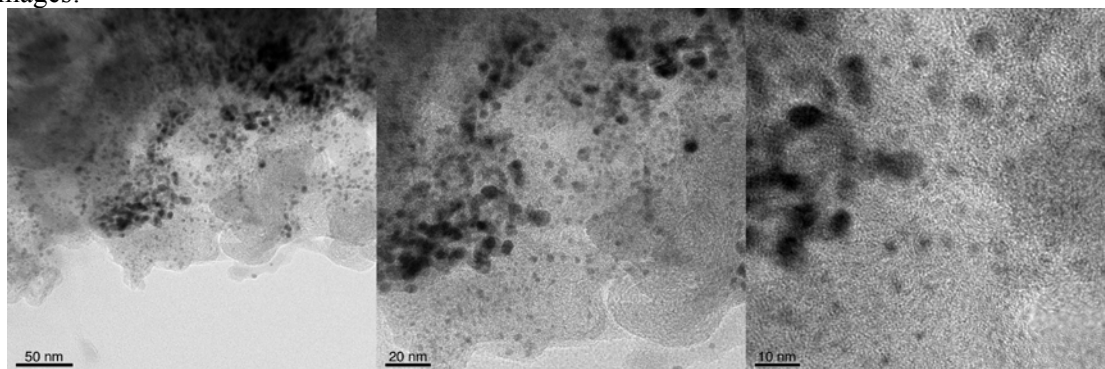


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EDS Mapping and EDS Line Analyses:



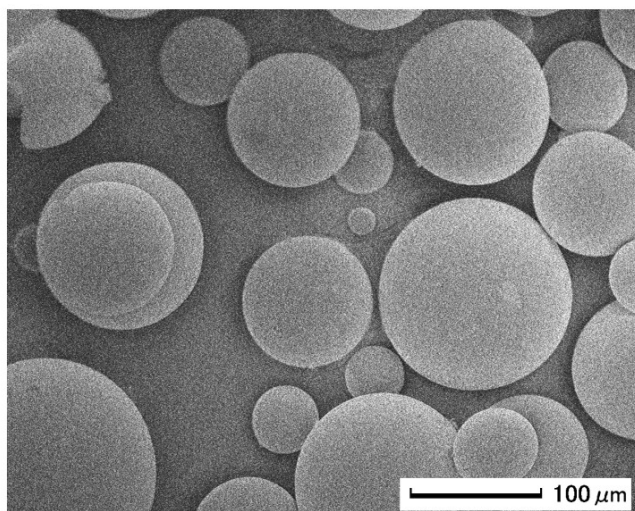
TEM images:



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8.3 Polymer-supported organocatalyst (5)

SEM images:



装置 : JSM 6700F

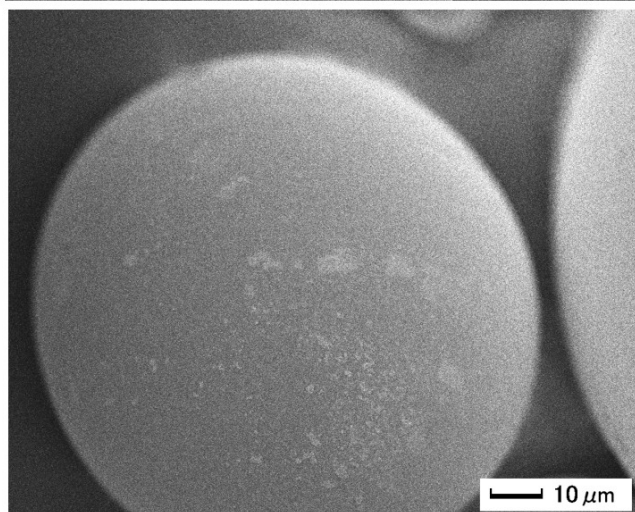
加速電圧 (kV) : 2.0

倍率 x250

画像 : SEI

<二次電子像>

測定日 : 2013/06/17



装置 : JSM 6700F

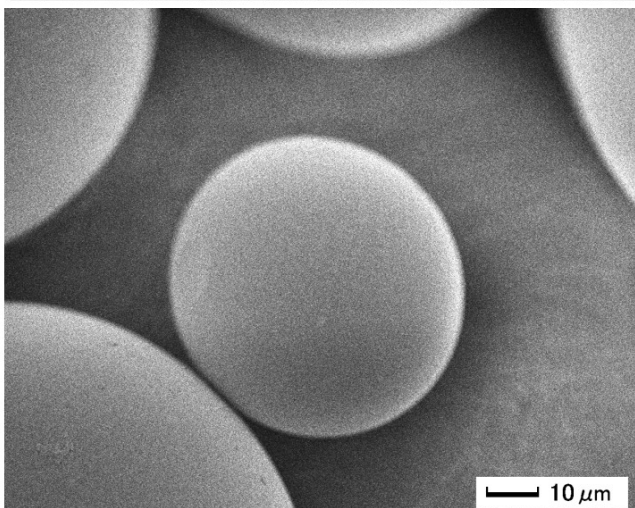
加速電圧 (kV) : 2.0

倍率 x1000

画像 : SEI

<二次電子像>

測定日 : 2013/06/17



装置 : JSM 6700F

加速電圧 (kV) : 2.0

倍率 x1000

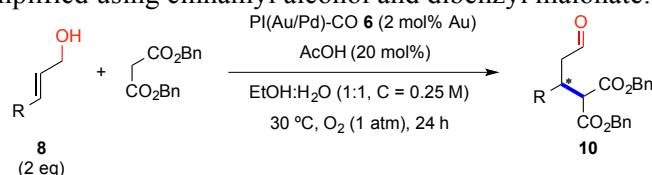
画像 : SEI

<二次電子像>

測定日 : 2013/06/17

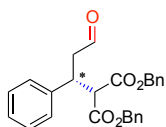
9 Asymmetric tandem oxidation process and characterisation of products

General procedure as exemplified using cinnamyl alcohol and dibenzyl malonate:



Catalyst **6** (144.5 mg, 0.005 mmol Au), cinnamyl alcohol (**8a**) (67.5, 0.50 mmol) and EtOH/H₂O (1:1, 0.5 mL) were added to a round-bottom flask with a stirring bar. The mixture was stirred gently for 30 seconds. Then, dibenzyl malonate (71.5 mg, 0.25 mmol) and acetic acid (3 μ L, 0.05 mmol) were added, followed by the addition of EtOH/H₂O (1:1, 0.5 mL). The flask was flushed with oxygen gas and the mixture was stirred at 30 °C for 24 hours. The catalyst was removed by vacuum-filtration and the catalyst was washed with EtOH (15 mL) and THF (15 mL) while it was on the funnel. The solvents were then removed under reduced pressure and the crude oil was subjected to PTLC (Merck) with EtOAc (20~30% in hexane) to yield the desired product **10a** (78.3 mg, 75%) as a pale yellow solid.

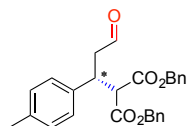
(R)-2-(3-Oxo-1-phenylpropyl)malonic acid dibenzyl ester (**10a**)⁶



Pale yellow solid. Yield: 78.3 mg, 75%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.52 (t, J = 1.5 Hz, 1H), 7.33–7.03 (m, 14H), 5.14 (s, 1H), 5.14 (s, 1H), 4.89 (s, 1H), 4.88 (s, 1H), 4.04 (ddd, J = 9.8, 8.3, 5.8 Hz, 1H), 3.83 (d, J = 9.9 Hz, 1H), 2.88–2.82 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 199.8, 167.7, 167.1, 139.6, 135.0, 134.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.5, 67.4, 67.2, 57.4, 47.2, 39.5.

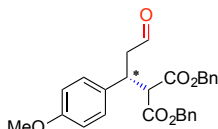
(R)-2-(3-Oxo-1-(4-methylphenyl)propyl)malonic acid dibenzyl ester (**10b**)⁶



Light yellow solid. Yield: 85.6 mg, 79%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.52 (t, J = 1.5 Hz, 1H), 7.39–7.20 (m, 8H), 7.16–7.02 (m, 6H), 5.14 (d, J = 2.5 Hz, 2H), 4.89 (s, 2H), 4.00 (ddd, J = 9.9, 8.6, 5.7 Hz, 1H), 3.80 (d, J = 9.9 Hz, 1H), 2.84–2.82 (m, 2H), 2.28 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 200.0, 167.7, 167.2, 137.1, 136.4, 135.0, 134.9, 129.4, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.8, 67.4, 67.1, 57.5, 47.2, 39.1, 21.0.

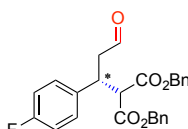
(R)-2-(3-Oxo-1-(4-methoxyphenyl)propyl)malonic acid dibenzyl ester (**10c**)⁶



Pale yellow solid. Yield: 73.9 mg, 66%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.52 (t, J = 1.6 Hz, 1H), 7.38–7.24 (m, 8H), 7.10 (d, J = 8.6 Hz, 2H), 7.06 (dd, J = 7.7, 1.8 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 5.15 (d, J = 1.6 Hz, 2H), 4.91 (s, 2H), 4.00 (ddd, J = 9.8, 9.3, 5.4 Hz, 1H), 3.78 (d, J = 9.9 Hz, 1H), 3.76 (s, 3H), 2.85–2.79 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 200.1, 167.7, 167.2, 158.8, 135.0, 134.9, 131.3, 129.1, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 114.1, 67.4, 67.2, 57.6, 55.1, 47.3, 38.8.

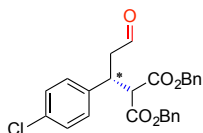
(R)-2-(3-Oxo-1-(4-fluorophenyl)propyl)malonic acid dibenzyl ester (**10d**)⁶



Off-white solid. Yield: 86.9 mg, 80%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.52 (t, *J* = 1.4 Hz, 1H), 7.38–7.24 (m, 8H), 7.14 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.06 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.88 (t, *J* = 8.6 Hz, 2H), 5.15 (d, *J* = 0.7 Hz, 2H), 4.91 (s, 2H), 4.02 (ddd, *J* = 9.6, 4.8, 9.4 Hz, 1H), 3.78 (d, *J* = 9.9 Hz, 1H), 2.90–2.79 (m, 2H); **¹³C NMR (150 MHz, CDCl₃):** δ 199.5, 167.5, 167.0, 161.9 (d, *J* = 243.5 Hz), 135.2 (d, *J* = 3.4 Hz), 134.9, 134.8, 129.7 (d, *J* = 8.5 Hz), 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 115.6 (d, *J* = 21.7 Hz), 67.5, 67.2, 57.3, 47.3, 38.6; **¹⁹F NMR (600 MHz, CDCl₃):** –114.6.

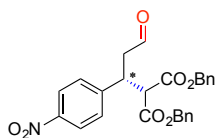
(*R*)-2-(3-Oxo-1-(4-chlorophenyl)propyl)malonic acid dibenzyl ester (**10e**)⁶



Off-white solid. Yield: 94.5 mg, 83%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.52 (s, 1H), 7.38–7.02 (m, 14H), 5.14 (s, 2H), 4.92 (d, *J* = 1.4 Hz, 2H), 4.01 (td, *J* = 9.5, 4.8 Hz, 1H), 3.78 (d, *J* = 9.9 Hz, 1H), 2.90–2.80 (m, 2H); **¹³C NMR (150 MHz, CDCl₃):** δ 199.3, 167.4, 167.0, 138.1, 134.9, 134.7, 133.3, 129.4, 128.8, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 67.5, 67.3, 57.1, 47.1, 38.7.

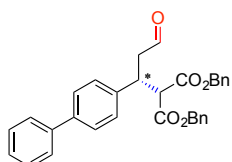
(*R*)-2-(3-Oxo-1-(4-nitrophenyl)propyl)malonic acid dibenzyl ester (**10f**)⁷



Yellow solid. Yield: 41.3 mg, 35%. Absolute configuration was not determined but inferred to be the same as other products because the catalyst was obtained from L-proline.

¹H NMR (600 MHz, CDCl₃): δ 9.54 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.40–7.21 (m, 10H), 7.06 (d, *J* = 8.2 Hz, 2H), 5.15 (s, 2H), 4.93 (d, *J* = 4.6 Hz, 2H), 4.12 (ddd, *J* = 9.7, 9.1, 4.5 Hz, 1H), 3.84 (d, *J* = 9.8 Hz, 1H), 2.99–2.82 (m, 2H); **¹³C NMR (150 MHz, CDCl₃):** δ 198.4, 167.1, 166.7, 147.1, 147.0, 134.7, 134.5, 129.1, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 123.7, 67.7, 67.4, 56.4, 47.0, 38.8.

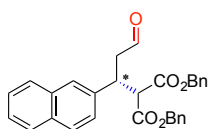
(*R*)-2-(1-(Biphenyl-4-yl)-3-oxopropyl)malonic acid dibenzyl ester (**10g**)⁶



White solid. Yield: 68.2 mg, 56%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.56 (t, *J* = 1.6 Hz, 1H), 7.57–7.01 (m, 19H), 5.16 (s, 2H), 4.91 (s, 2H), 4.09 (ddd, *J* = 9.8, 7.4, 6.7 Hz, 1H), 3.87 (d, *J* = 9.9 Hz, 1H), 2.90 (dd, *J* = 7.1, 1.7 Hz, 2H); **¹³C NMR (150 MHz, CDCl₃):** δ 199.8, 167.6, 167.2, 140.4, 140.2, 138.6, 135.0, 134.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.3, 126.9, 67.5, 67.3, 57.3, 47.1, 39.1.

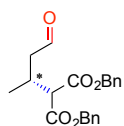
(*R*)-2-(1-(naphthalen-2-yl)-3-oxopropyl)malonic acid dibenzyl ester (**10h**)⁶



Yellow solid. Yield: 72.0 mg, 61%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

¹H NMR (600 MHz, CDCl₃): δ 9.55 (t, *J* = 1.6 Hz, 1H), 7.79–7.63 (m, 4H), 7.45 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.36–7.25 (m, 6H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 2H), 5.16 (d, *J* = 1.7 Hz, 2H), 4.83 (s, 2H), 4.22 (ddd, *J* = 9.9, 8.5, 5.7 Hz, 1H), 3.95 (d, *J* = 10.0 Hz, 1H), 3.00–2.89 (m, 2H); **¹³C NMR (150 MHz, CDCl₃):** δ 199.7, 167.6, 167.1, 137.0, 134.9, 134.7, 133.2, 132.7, 128.6, 128.6, 128.5, 128.3, 128.2, 128.2, 128.0, 127.9, 127.6, 127.1, 126.2, 126.0, 125.7, 67.5, 67.2, 57.4, 47.2, 39.6.

(*R*)-2-(1-Methyl-3-oxopropyl)malonic acid dibenzyl ester (**10i**)⁷

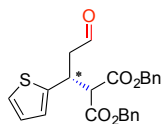


Colourless oil. Yield: 30.4 mg, 34%. Absolute configuration was not determined but inferred to be the same as other products because the catalyst was obtained from L-proline.

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¹H NMR (600 MHz, CDCl₃): δ 9.67 (s, 1H), 7.34–7.28 (m, 10H), 5.14 (s, 4H), 3.48 (d, *J* = 7.0 Hz, 1H), 2.91–2.84 (m, 1H), 2.63 (dd, *J* = 17.6, 4.5 Hz, 1H), 2.39 (ddd, *J* = 17.6, 8.5, 2.0 Hz, 1H), 1.03 (d, *J* = 6.9 Hz, 3H); **¹³C NMR (150 MHz, CDCl₃):** δ 200.7, 168.0, 168.0, 135.1, 128.6, 128.4, 128.3, 67.2, 56.3, 47.9, 27.9, 17.9; **HPLC:** Daicel Chiralpak AD-H, hexane/2-propanol (97/3), flow rate = 0.5 mL/min (τ₁ = 52.8 min (91.30%); τ₂ = 55.4 min (8.70%), 83% *ee*).

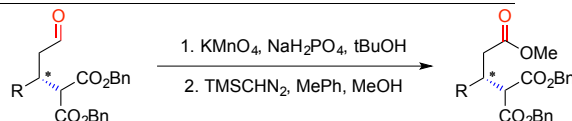
(*R*)-2-(3-Oxo-1-thiophen-2-ylpropyl)malonic acid dibenzyl ester (**10j**)⁶



Yellow solid. Yield: 45.0 mg, 42%. Absolute configuration was determined by comparison of the methyl ester derivative HPLC chart with the data available from literature.⁶

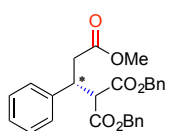
¹H NMR (600 MHz, CDCl₃): δ 9.59 (t, *J* = 1.5 Hz, 1H), 7.34–7.23 (m, 8H), 7.18–7.12 (m, 3H), 6.86–6.82 (m, 2H), 5.14 (d, *J* = 4.1 Hz, 2H), 5.00 (s, 2H), 4.37 (ddd, *J* = 8.8, 7.4, 6.5 Hz, 1H), 3.86 (d, *J* = 8.8 Hz, 1H), 2.92 (d, *J* = 7.1 Hz, 2H); **¹³C NMR (150 MHz, CDCl₃):** δ 199.4, 167.3, 167.0, 142.5, 134.9, 128.6, 128.5, 128.4, 128.3, 128.2, 126.8, 126.0, 124.7, 67.5, 67.4, 57.8, 47.7, 34.7.

10 Obtaining methyl ester derivatives and their characterisation



Representative procedure: **10a** (49.5 mg, 0.12 mmol) was diluted with *t*BuOH (3.6 mL) and 1 M aqueous NaH₂PO₄ (3.6 mL). 1 M aqueous KMnO₄ (3.6 mL) was added successively. After 1 hour of vigorous stirring at 30 °C, saturated NaHSO₃ (6.0 mL) was added and the pH was adjusted to approximately 3 with 1 M HCl. The resulting mixture was extracted 3 times with EtOAc, the combined organic layers were washed with water and brine, and dried over MgSO₄. The organic layer was concentrated in vacuum and the acid obtained was dissolved in toluene (2.4 mL) and MeOH (6.0 mL). TMSCHN₂ (0.6 M in hexane) was added dropwise until the yellow colour persisted. The solution was stirred for an additional 10 minutes and quenched with a drop of concentrated AcOH. The solvents were evaporated under vacuum. The crude product was subjected to PTLC (Wako-Gel) with 20% EtOAc in hexane to give the desired ester (31.8 mg, 59%) as a colourless liquid.

(R)-2-Benzyloxycarbonyl-3-phenylpentanedioic acid 1-benzyl ester 5-methyl ester⁶

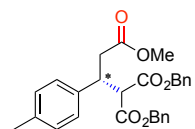


¹H NMR (600 MHz, CDCl₃): δ 7.34–7.17 (m, 13H), 7.04 (dd, *J* = 6.9, 1.5 Hz, 2H), 5.15 (d, *J* = 3.3 Hz, 2H), 4.87 (d, *J* = 5.5 Hz, 2H), 3.95 (ddd, *J* = 10.1, 9.6, 4.6 Hz, 1H), 3.88 (d, *J* = 10.1 Hz, 1H), 3.50 (s, 3H), 2.83 (dd, *J* = 15.7, 4.6 Hz, 1H), 2.73 (dd, *J* = 15.8, 9.7 Hz, 1H);

¹³C NMR (150 MHz, CDCl₃): δ 171.5, 167.7, 167.2, 139.7, 135.2, 135.0, 128.6, 128.6,

128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 127.4, 67.3, 67.1, 57.2, 51.5, 41.5, 38.4; **HPLC:** Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ₁ = 16.2 min (95.14%); τ₂ = 21.8 min (4.86%), 90% *ee*).

(R)-2-Benzyloxycarbonyl-3-(4-methylphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester⁶

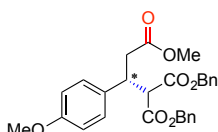


¹H NMR (600 MHz, CDCl₃): δ 7.34–7.22 (m, 8H), 7.08–7.01 (m, 6H), 5.15 (d, *J* = 2.6 Hz, 2H), 4.88 (s, 2H), 3.92 (ddd, *J* = 10.2, 9.5, 4.5 Hz, 1H), 3.85 (d, *J* = 10.3 Hz, 1H), 3.50 (s, 3H), 2.80 (dd, *J* = 15.6, 4.5 Hz, 1H), 2.71 (dd, *J* = 15.7, 9.8 Hz, 1H); **¹³C NMR (150**

MHz, CDCl₃): δ 171.6, 167.7, 167.3, 136.8, 136.5, 135.1, 135.0, 129.2, 128.5, 128.4,

128.2, 128.1, 128.1, 127.8, 67.3, 67.1, 57.3, 41.0, 38.4, 21.1; **HPLC:** Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ₁ = 15.1 min (95.50%); τ₂ = 22.8 min (4.50%), 91% *ee*).

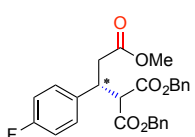
(R)-2-Benzyloxycarbonyl-3-(4-methoxyphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester⁶



¹H NMR (600 MHz, CDCl₃): δ 7.34–7.23 (m, 8H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.04 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.15 (d, *J* = 2.2 Hz, 2H), 4.88 (s, 2H), 3.91 (td, *J* = 10.1, 4.3 Hz, 1H), 3.83 (d, *J* = 10.2 Hz, 1H), 3.75 (s, 3H), 3.50 (s, 3H), 2.80 (dd, *J* = 15.6, 4.6 Hz, 1H), 2.69 (dd, *J* = 15.6, 9.9 Hz, 1H); **¹³C NMR (150 MHz, CDCl₃):** δ

171.6, 167.7, 167.3, 158.6, 135.1, 135.0, 131.5, 129.1, 128.5, 128.4, 128.2, 128.1, 113.8, 67.3, 67.1, 57.4, 55.1, 51.6, 40.7, 38.5; **HPLC:** Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ₁ = 24.5 min (93.71%); τ₂ = 43.8 min (6.29%), 87% *ee*).

(R)-2-Benzyloxycarbonyl-3-(4-fluorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester⁶

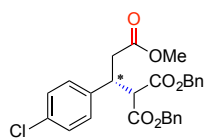


¹H NMR (600 MHz, CDCl₃): δ 7.35–7.24 (m, 8H), 7.14 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.05 (dd, *J* = 7.3, 1.6 Hz, 2H), 6.88 (t, *J* = 8.5 Hz, 2H), 5.15 (s, 2H), 4.89 (s, 2H), 3.93 (ddd, *J* = 10.2, 9.9, 4.4 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.51 (s, 3H), 2.81 (dd, *J* = 15.8, 4.5 Hz, 1H), 2.68 (dd, *J* = 15.8, 10.1 Hz, 1H); **¹³C NMR (150 MHz, CDCl₃):** δ 171.3, 167.5,

167.1, 161.9 (d, *J* = 244.3 Hz), 135.2 (d, *J* = 2.3 Hz), 135.0, 134.8, 129.6 (d, *J* = 7.8 Hz), 128.6, 128.4, 128.4, 128.3, 128.2, 115.3 (d, *J* = 21.4 Hz), 67.4, 67.2, 57.1, 51.6, 40.7, 38.4; **¹⁹F NMR (600 MHz, CDCl₃):** –

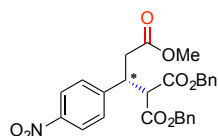
114.8; **HPLC**: Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ_1 = 19.6 min (95.73%); τ_2 = 32.4 min (4.27%), 91% *ee*).

(R)-2-Benzyloxycarbonyl-3-(4-chlorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester⁶



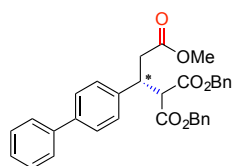
¹H NMR (600 MHz, CDCl₃): δ 7.34–7.03 (m, 14H), 5.16 (s, 2H), 4.90 (s, 2H), 3.92 (td, J = 10.0, 4.4 Hz, 1H), 3.82 (d, J = 10.2 Hz, 1H), 3.50 (s, 3H), 2.80 (dd, J = 15.8, 4.3 Hz, 1H), 2.68 (dd, J = 16.0, 10.1 Hz, 1H); **¹³C NMR (150 MHz, CDCl₃)**: δ 171.2, 167.4, 167.0, 138.0, 135.0, 134.8, 133.1, 129.4, 128.6, 128.6, 128.4, 128.4, 128.3, 128.2, 128.2, 67.4, 67.2, 56.9, 51.6, 40.7, 38.1; **HPLC**: Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ_1 = 20.2 min (95.58%); τ_2 = 32.9 min (4.42%), 91% *ee*).

(R)-2-Benzyloxycarbonyl-3-(4-nitrophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



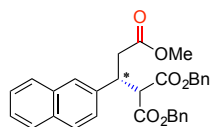
¹H NMR (600 MHz, CDCl₃): δ 7.97 (d, J = 8.3 Hz, 2H), 7.38–7.21 (m, 10H), 7.05 (d, J = 7.4 Hz, 2H), 5.18 (s, 2H), 4.91 (d, J = 3.5 Hz, 2H), 4.03 (ddd, J = 10.4, 9.5, 4.2 Hz, 1H), 3.87 (d, J = 10.0 Hz, 1H), 3.51 (s, 3H), 2.85 (dd, J = 16.0, 4.3 Hz, 1H), 2.72 (dd, J = 16.4, 10.1 Hz, 1H); **¹³C NMR (150 MHz, CDCl₃)**: δ 170.9, 167.1, 166.7, 147.0, 134.8, 134.5, 129.1, 128.6, 128.6, 128.4, 128.3, 123.6, 67.7, 67.4, 56.4, 51.8, 41.0, 37.8; **IR (KBr)**: 1725, 1603, 1516, 1456, 1377, 1351, 1298, 1258, 1157, 1015, 958, 857, 754, 698 cm⁻¹; **HRMS (DART)**: calculated for C₂₇H₂₆NO₈⁺ [M +H]⁺ 492.16584, found 492.16538; **m.p.**: 94–96 °C; [α]_D²³ = –6.30 (c = 0.117, CHCl₃); **HPLC**: Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ_1 = 42.6 min (92.85%); τ_2 = 85.5 min (7.15%), 86% *ee*).

(R)-1,1-dibenzyl 3-methyl 2-(biphenyl-4-yl)propane-1,1,3-tricarboxylate⁶



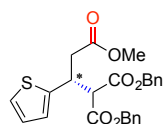
¹H NMR (600 MHz, CDCl₃): δ 7.56–7.03 (m, 19H), 5.17 (s, 2H), 4.90 (d, J = 3.5 Hz, 2H), 4.01 (td, J = 9.9, 4.6 Hz, 1H), 3.91 (d, J = 10.1 Hz, 1H), 3.53 (s, 3H), 2.85 (dd, J = 15.8, 4.6 Hz, 1H), 2.77 (dd, J = 15.9, 9.8 Hz, 1H); **¹³C NMR (150 MHz, CDCl₃)**: δ 171.5, 167.7, 167.3, 140.5, 140.0, 138.7, 135.1, 134.9, 128.7, 128.6, 128.4, 128.4, 128.2, 128.2, 127.3, 127.1, 127.0, 67.4, 67.2, 57.1, 51.6, 41.1, 38.2; **HPLC**: Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ_1 = 24.9 min (95.72%); τ_2 = 51.0 min (4.28%), 91% *ee*).

(R)-1,1-dibenzyl 3-methyl 2-(naphthalen-2-yl)propane-1,1,3-tricarboxylate⁶



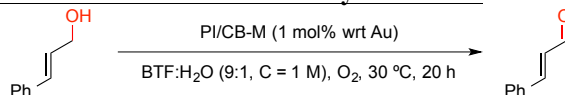
¹H NMR (600 MHz, CDCl₃): δ 7.79–6.87 (m, 17H), 5.17 (s, 2H), 4.81 (s, 2H), 4.14 (td, J = 10.1, 5.1 Hz, 1H), 3.99 (d, J = 10.2 Hz, 1H), 3.47 (s, 3H), 2.91–2.82 (m, 2H); **¹³C NMR (150 MHz, CDCl₃)**: δ 171.4, 167.7, 167.2, 137.1, 135.1, 134.8, 133.3, 132.7, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.6, 127.1, 126.0, 126.0, 125.9, 67.4, 67.2, 57.2, 51.6, 41.5, 38.4; **HPLC**: Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ_1 = 23.9 min (87.09%); τ_2 = 33.8 min (12.91%), 74% *ee*).

(R)-2-Benzyloxycarbonyl-3-thiophen-2-ylpentanedioic acid 1-benzyl ester 5-methyl ester⁶



¹H NMR (600 MHz, CDCl₃): δ 7.33–7.25 (m, 7H), 7.15–7.11 (m, 3H), 6.86–6.83 (m, 2H), 5.15 (d, J = 4.4 Hz, 2H), 4.98 (s, 2H), 4.28 (td, J = 9.2, 4.7 Hz, 1H), 3.92 (d, J = 9.1 Hz, 1H), 3.57 (s, 3H), 2.87 (dd, J = 16.0, 4.7 Hz, 1H), 2.79 (dd, J = 16.0, 9.4 Hz, 1H); **¹³C NMR (150 MHz, CDCl₃)**: δ 171.3, 167.4, 167.1, 142.5, 135.0, 135.0, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 126.7, 125.8, 124.4, 67.4, 67.3, 57.6, 51.7, 39.0, 36.7; **HPLC**: Daicel Chiralpak AD, hexane/2-propanol (80/20), flow rate = 1.0 mL/min (τ_1 = 17.6 min (93.67%); τ_2 = 20.5 min (6.33%), 87% *ee*).

11 Effect of Au/Pd ratio on aerobic oxidation of allylic alcohol



PI/CB-M catalysts with varying ratios of Au to Pd were prepared using the method stated in Section 5.2. These catalysts were then screened to determine the best ratio of Au to Pd for the aerobic oxidation reaction. Representative procedure: The catalyst, cinnamyl alcohol (67.1 mg, 0.50 mmol), BTF (0.45 mL) and H₂O (0.05 mL) were added successively to the reaction flask containing a stirring bar. The flask was flushed with oxygen gas and the mixture was stirred at 30 °C for 20 hours. The catalyst was removed by vacuum-filtration and the catalyst was washed with EtOH (15 mL) and THF (15 mL) while it was on the funnel. The solvents were then removed under reduced pressure and the crude oil was subjected to ¹H NMR analysis with 1,1,2,2-tetrachloroethane added as the internal standard.

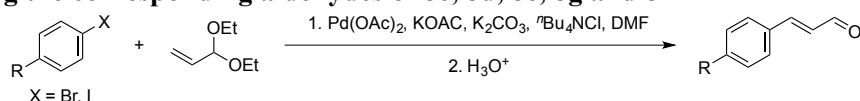
entry	M	NMR yield [%] ^[a]
1	Au	20
2	Au/Pd (1:1)	> 95
3	Au/Pd (2:1)	71
4	Au/Pd (1:2)	92
5	Pd (1 mol% Pd)	27

[a] Determined by ¹H NMR using the peaks at 9.53 ppm and 6.72 ppm.

A bimetallic effect was observed, as evident from the low yields when either only Au or only Pd was used as the catalyst. Although the yield in entry 2 did not differ significantly from that in entry 4, we decided to adopt the 1:1 ratio as the optimal ratio because the catalyst loading for our reaction is based on Au, and a 1:1 ratio of Au to Pd would equate to a lower total metal loading. We assume that having Pd within or near Au nanoclusters improves the catalytic activity of Au via electronic effects.

12 Obtaining alcohols 8c, 8d, 8e, 8g and 8h

12.1 Obtaining the corresponding aldehydes of 8c, 8d, 8e, 8g and 8h

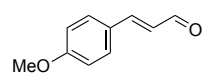


The following procedure is slightly modified procedure from that reported in literature.⁸

Representative procedure:

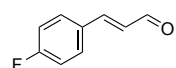
^tBu₄NCl (2226.6 mg, 8 mmol), Pd(OAc)₂ (60.3 mg, 0.27 mmol), KOAc (1577.5 mg, 16 mmol), K₂CO₃ (1660.3 mg, 12 mmol), and 1-chloro-4-iodobenzene (1915.3 mg, 8 mmol) were added to a 100 mL 2-neck round-bottom flask. The flask was attached with a reflux condenser and flushed with argon. Anhydrous DMF (32 mL) was added and the mixture was stirred. Acrolein diethyl acetal (3.7 mL, 24.3 mmol) was added successively and the mixture was heated to 90 °C. After complete consumption of the aryl halide, as confirmed by TLC, the mixture was cooled to room temperature and 2 M HCl (60 mL) was added slowly to quench the reaction. It was then stirred for an additional 10 minutes. It was then diluted with ether and the organic layer was separated. The aqueous layer was further extracted with ether twice and the combined organic layers were washed with water, 2 M HCl and then brine before being dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude was subjected to column chromatography with EtOAc/hexane to afford 4-chlorocinnamaldehyde (896.8 mg, 67%, pure *E* isomer) as a light yellow solid.

p-Methoxy-*trans*-cinnamaldehyde⁸



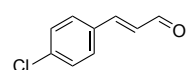
¹H NMR (600 MHz, CDCl₃): δ 9.66 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 15.9 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.61 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 193.7, 162.2, 152.7, 130.3, 126.8, 126.5, 114.5, 55.4.

p-Fluoro-*trans*-cinnamaldehyde⁸



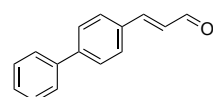
¹H NMR (600 MHz, CDCl₃): δ 9.70 (d, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 8.9, 5.2 Hz, 2H), 7.45 (d, *J* = 15.9 Hz, 1H), 7.13 (t, *J* = 8.5 Hz, 2H), 6.66 (dd, *J* = 15.9, 7.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 193.4, 164.4 (d, *J* = 253.0 Hz), 151.3, 130.5 (d, *J* = 8.7 Hz), 130.3 (d, *J* = 3.0 Hz), 128.4, 116.4 (d, *J* = 22.1 Hz); ¹⁹F NMR (600 MHz, CDCl₃): δ -107.6.

p-Chloro-*trans*-cinnamaldehyde⁸



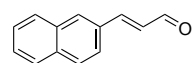
¹H NMR (600 MHz, CDCl₃): δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.52–7.40 (m, 5H), 6.69 (dd, *J* = 16.0, 7.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 193.3, 151.0, 137.2, 132.4, 129.6, 129.4, 128.9.

p-Phenyl-*trans*-cinnamaldehyde⁸



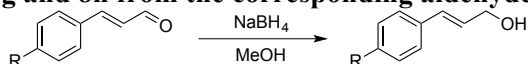
¹H NMR (600 MHz, CDCl₃): δ 9.72 (d, *J* = 7.7 Hz, 1H), 7.68–7.38 (m, 10H), 6.76 (dd, *J* = 16.0, 7.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 193.6, 152.3, 144.0, 139.8, 132.9, 129.0, 128.9, 128.4, 128.1, 127.7, 127.0.

(*E*)-3-Naphthalen-2-yl-propenal⁸



¹H NMR (600 MHz, CDCl₃): δ 9.76 (d, *J* = 7.7 Hz, 1H), 7.98 (s, 1H), 7.89–7.84 (m, 3H), 7.68 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.63 (d, *J* = 15.9 Hz, 1H), 7.55 (quintd, *J* = 7.0, 2.2 Hz, 2H), 6.83 (dd, *J* = 15.9, 7.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 193.6, 152.7, 134.6, 133.2, 131.6, 130.7, 129.0, 128.7, 128.7, 127.9, 127.8, 127.0, 123.5.

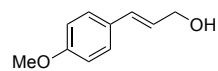
12.2 Obtaining 8c, 8d, 8e, 8g and 8h from the corresponding aldehydes



Representative procedure:

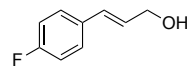
p-Methoxy-*trans*-cinnamaldehyde (302.0 mg, 1.85 mmol) was dissolved in MeOH (10 mL) at room temperature. Sodium borohydride (39.6 mg, 1.05 mmol) was added portion-wise to the stirring solution and the reaction was monitored by TLC. Once all the starting material had been consumed, the reaction was quenched with saturated ammonium chloride solution and extraction was performed with DCM. The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude solid was recrystallised with hexane/toluene to afford the desired alcohol (249.5 mg, 81%) as pale yellow solid flakes.

(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (8c)⁹



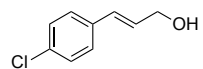
¹H NMR (600 MHz, CDCl₃): δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.30 (br, 2H), 3.81 (s, 3H), 1.48 (br, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 159.3, 131.0, 129.4, 127.6, 126.2, 114.0, 63.9, 55.3.

(*E*)-3-(4-Fluorophenyl)prop-2-en-1-ol (8d)¹⁰



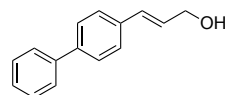
¹H NMR (600 MHz, CDCl₃): δ 7.34 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.31 (d, *J* = 5.7 Hz, 2H), 1.76 (br s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 162.3 (d, *J* = 246.5 Hz), 132.8 (d, *J* = 3.0 Hz), 129.9, 128.2, 127.9 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 21.6 Hz), 63.5; ¹⁹F NMR (600 MHz, CDCl₃): δ −114.2.

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol (8e)¹⁰



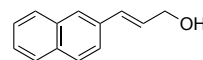
¹H NMR (600 MHz, CDCl₃): δ 7.31–7.25 (m, 4H), 6.56 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.31 (s, 2H), 1.83 (s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 135.1, 133.2, 129.7, 129.1, 128.7, 127.6, 63.4.

(*E*)-3-(4-Biphenyl)prop-2-en-1-ol (8g)¹¹



¹H NMR (600 MHz, CDCl₃): δ 7.62–7.54 (m, 4H), 7.48–7.42 (m, 4H), 7.37–7.32 (m, 1H), 6.66 (d, *J* = 15.9, 1H), 6.42 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.36 (s, 2H), 1.51 (br apparent triplet, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 140.6, 140.5, 135.7, 130.7, 128.8, 128.6, 127.3, 127.3, 126.9, 126.9, 63.8.

(*E*)-3-(Naphthalen-2-yl)prop-2-en-1-ol (8h)⁹



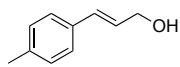
¹H NMR (600 MHz, CDCl₃): δ 7.82–7.75 (m, 3H), 7.71 (br, 1H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.46–7.42 (m, 2H), 6.76 (d, *J* = 16.0, 1H), 6.47 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.36 (d, *J* = 5.7 Hz, 2H), 1.70 (br, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 134.1, 133.5, 133.0, 131.2, 128.8, 128.2, 128.0, 127.6, 126.4, 126.3, 125.9, 123.5, 63.7.

A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

13 Obtaining alcohol 8b

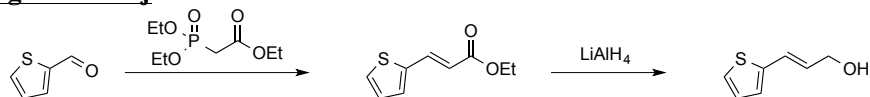
Literature procedure was followed.¹²

(E)-3-(4-Methylphenyl)prop-2-en-1-ol (8b)¹²



¹H NMR (600 MHz, CDCl₃): δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.29 (d, *J* = 5.8 Hz, 2H), 2.33 (s, 3H), 1.66 (br, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 137.5, 133.8, 131.1, 129.3, 127.4, 126.3, 63.8, 21.2.

14 Obtaining alcohol 8j



Representative procedure:

Sodium hydride (55% in mineral oil, 3.96 g, 90 mmol) was added to a 500 mL 2-neck round-bottom flask with a stirring bar. The flask was flushed with argon and dry petroleum ether (20 mL) was added. The suspension was stirred well and sodium hydride was allowed to settle before the petroleum ether added was removed with a syringe. The washing of NaH with petroleum ether was repeated twice to remove the mineral oils. The clean NaH was dried well under vacuum and the flask was flushed with argon again. Dry THF (125 mL) was then added and the suspension was cooled to 0 °C. Triethyl phosphonoacetate (13 mL, 65 mmol) was added dropwise and the mixture was allowed to stir for 30 minutes. Freshly distilled 2-thiophenecarboxaldehyde (4.7 mL, 50 mmol) was then added dropwise. The mixture was stirred for a further 1.5 hours. Once all of the aldehyde had been consumed, the reaction was diluted with diethyl ether (250 mL), followed by the addition of saturated sodium bicarbonate solution (62.5 mL) to quench the reaction. Extraction was performed with diethyl ether and the combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude was passed through a short column of silica gel (~10 cm), eluting with 10% EtOAc in hexane. The solvents were removed under reduced pressure to afford the desired product (8.62 g, 95%) as a light yellow liquid of good purity as confirmed by NMR analysis.

A portion of the intermediate obtained (1101.8 mg, 6.05 mmol) was transferred to a 100 mL 3-neck round-bottom flask. The flask was flushed with argon and diethyl ether (24 mL) was added. After the mixture was cooled to 0 °C, LiAlH₄ was added portion-wise until the reaction was complete, as confirmed by TLC. Water was then added to quench the reaction. Additional Et₂O (12 mL) was added and Na₂SO₄ was added under vigorous stirring to remove water. All solids formed were removed by vacuum-filtration and the filtrate was concentrated under reduced pressure. It was then subjected to column chromatography to afford the desired alcohol (642.1 mg, 76%, *E* isomer) as a light yellow liquid. An analytical sample (colourless liquid) was obtained by bulb-to-bulb distillation of the product.

(*E*)-3-(2-Thienyl)prop-2-en-1-ol (8j)¹³

¹H NMR (600 MHz, CDCl₃): δ 7.16–7.14 (m, 1H), 6.97–6.94 (m, 2H), 6.74 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.7, 5.8 Hz, 1H), 4.27 (d, *J* = 5.8 Hz, 2H), 1.70 (br, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 141.7, 128.1, 127.3, 125.8, 124.4, 124.3, 63.3.

15 Evaluating metal leaching via ICP analysis

Procedure for detecting leaching into solution:

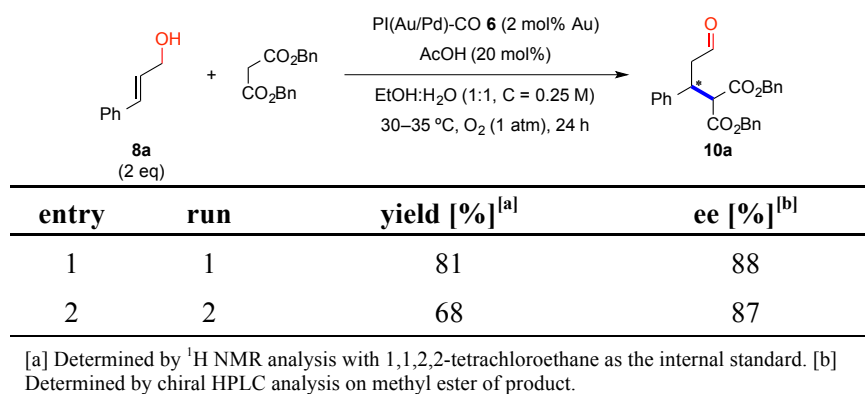
The asymmetric tandem oxidation process was repeated on the same scale with cinnamyl alcohol and dibenzyl malonate. After removing the catalyst from the reaction mixture via vacuum-filtration, the filtrate was concentrated and the crude was analysed via ^1H NMR spectroscopy to determine the yield and conversion, which matched the results obtained earlier for the substrate scope table. The NMR sample was then combined with the remaining crude mixture, transferred to a clean test tube and the solvents were evaporated. The crude was heated to 200 °C in H_2SO_4 (0.5 mL) and HNO_3 was added dropwise until a clear liquid was obtained and no more brown fumes were observed. The mixture was cooled to room temperature and aqua regia (0.5 mL) was added slowly. The resulting mixture was made up to 25 mL with water in a volumetric flask and analysed with ICP. The detection limit was calculated to be 0.07% for Au and 0.02% for Pd. The amount of Au or Pd in the crude mixture was under these detection limits.

Procedure for detecting leached metals that may have stuck onto the reaction flask walls:

A completely new reaction flask was used for the reaction. After the reaction, the catalyst and crude was removed by filtration and the reaction tube was dried well. Aqua regia (0.5 mL) was added to the dried reaction tube to dissolve any metals that might be stuck on the flask walls and the solution was transferred to a 25 mL volumetric flask containing 0.5 mL of H_2SO_4 . The resulting mixture was made up to 25 mL with water and analysed with ICP. The detection limit was calculated to be 0.06% for Au and 0.01% for Pd. The amount of Au or Pd was under these detection limits.

16 Reusing of catalyst

The reaction was carried out following the procedure and scale used for the substrate scope. Then, the catalyst was recovered by filtration and washed in 20 mL of THF and 20 mL of saturated sodium bicarbonate solution for 4 hours. The catalyst was then recovered by filtration and washed well with water and THF on the funnel. Finally, it was washed in 40 mL of THF/H₂O (1:1) overnight and recovered by filtration. It was then transferred to a clean round bottom flask for the next run. The catalyst was then heated at 150 °C for 2 hours under high vacuum to remove solvent and organic impurities that may have stuck onto the catalyst during the first run. After the catalyst had cooled to room temperature, the substrates and solvent were added and the second run was commenced. The amount of substrate and solvent used was adjusted according to the amount of catalyst recovered.



Although the yield decreased slightly, the enantioselectivity was maintained. These results mirror that of other groups who have attempted to reuse the Jørgensen-Hayashi organocatalyst and it appears that this organocatalyst is susceptible to deactivation,^{7,14} although when we first began our investigations, we had expected the immobilised Jørgensen-Hayashi organocatalyst to be recyclable because some groups have reported successful recycling of the catalyst.^{15,16}

Authors' note:

The Jørgensen-Hayashi-type organocatalyst was chosen because it is an effective and general organocatalyst that activates various carbonyl compounds,^{17–19} particularly for the asymmetric Michael addition reaction, giving high yield and enantioselectivity^{5,6} as compared to simple L-proline.^{20,21} In addition, the Jørgensen-Hayashi-type organocatalyst is easily synthesized from readily available L-proline and the introduction of a polymerizable handle is simple.^{4,22,23} Therefore, it was deemed suitable for our investigations.

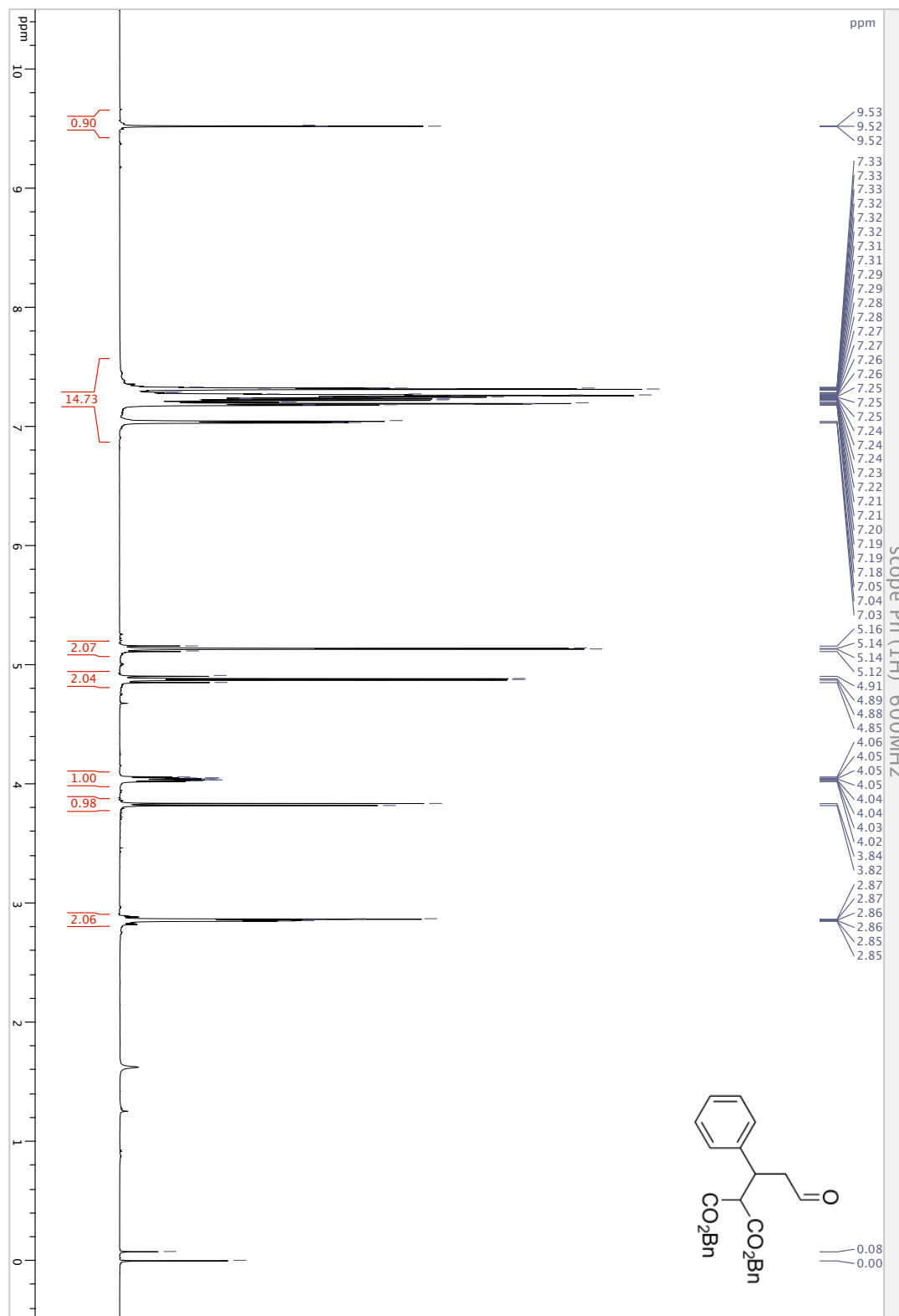
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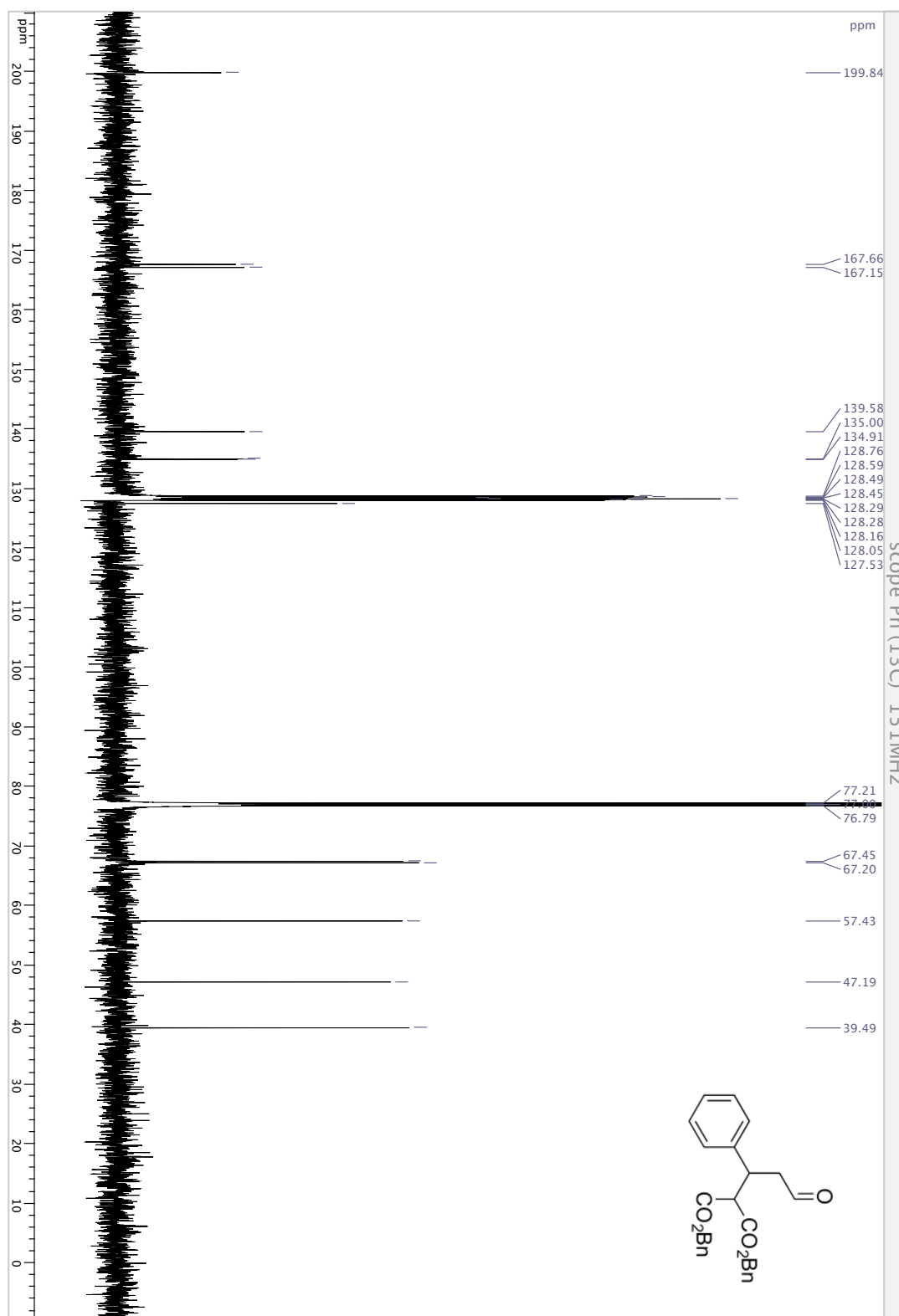
B1 NMR Spectra of Michael Adducts

(R)-2-(3-Oxo-1-phenylpropyl)malonic acid dibenzyl ester (10a)



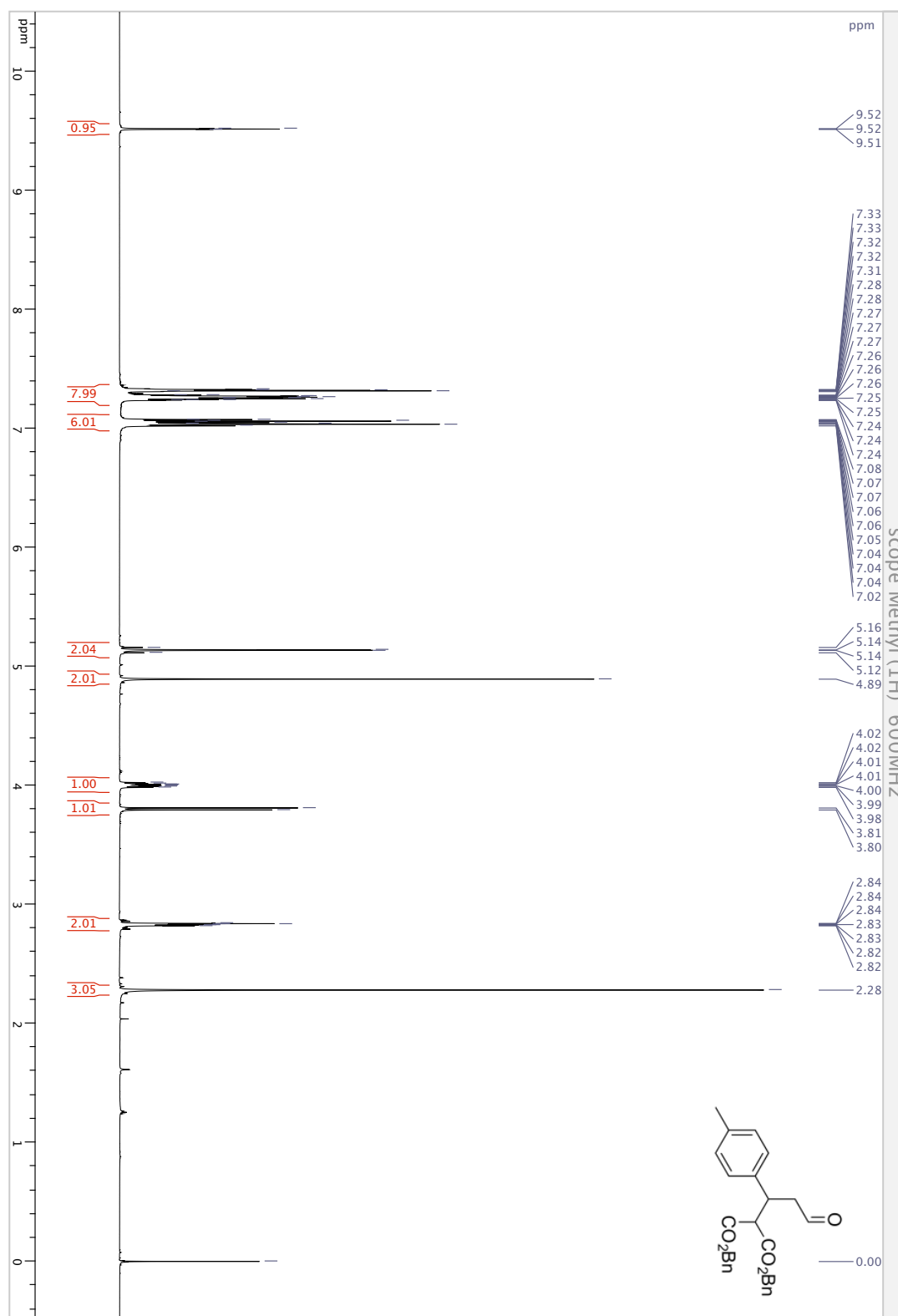
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(R)-2-(3-Oxo-1-phenylpropyl)malonic acid dibenzyl ester (10a)



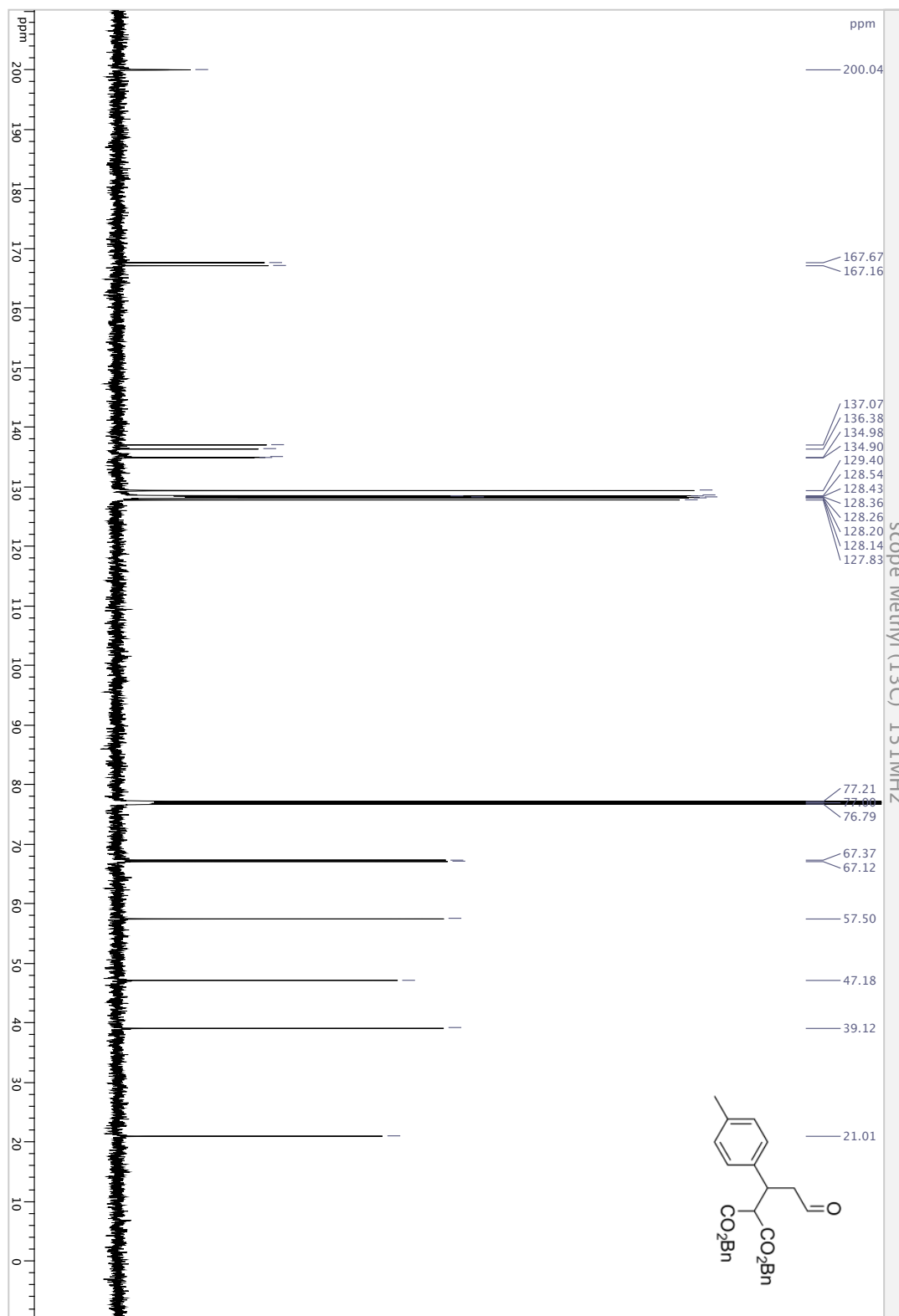
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(R)-2-(3-Oxo-1-(4-methylphenyl)propyl)malonic acid dibenzyl ester (10b)



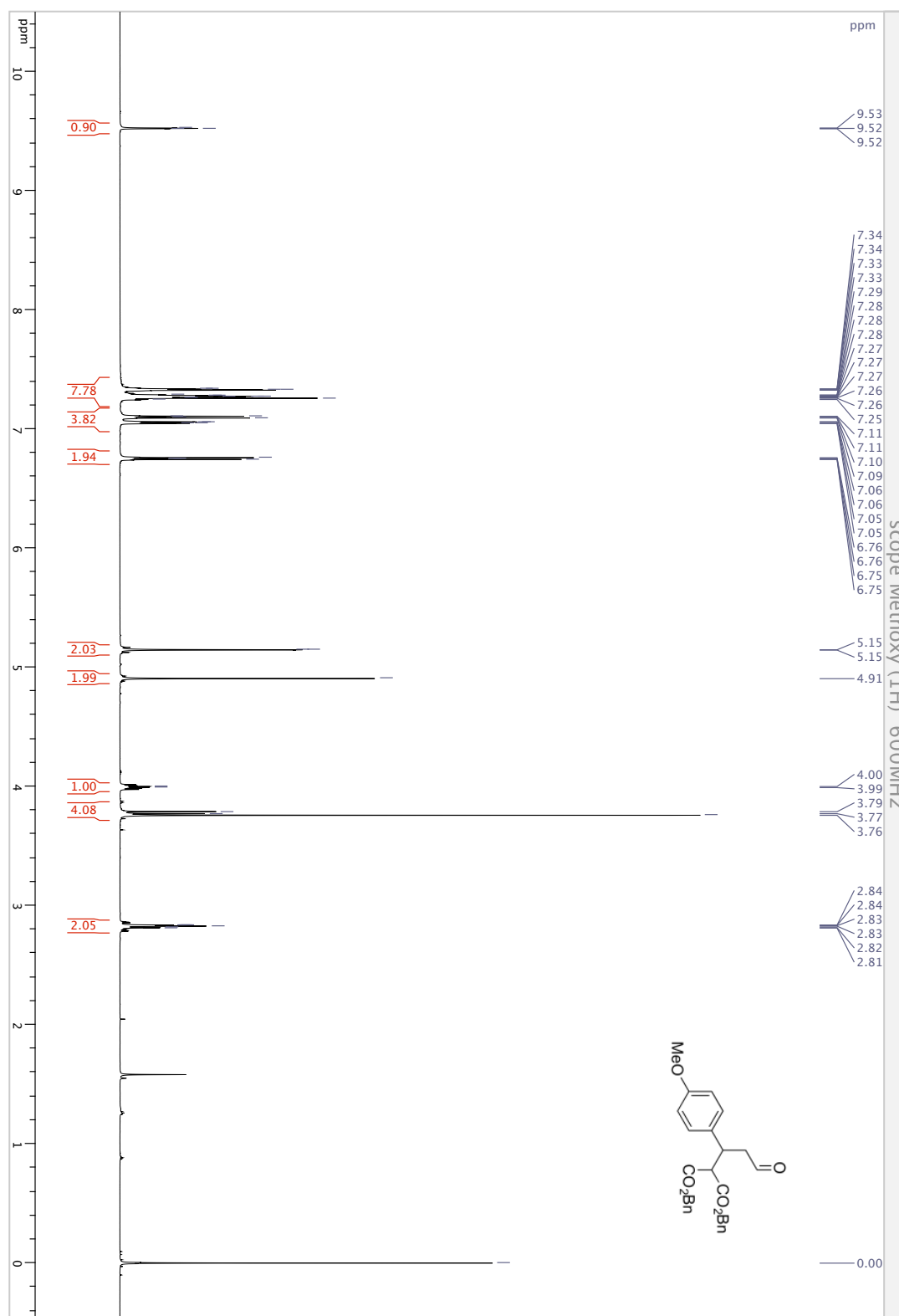
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(R)-2-(3-Oxo-1-(4-methylphenyl)propyl)malonic acid dibenzyl ester (10b)



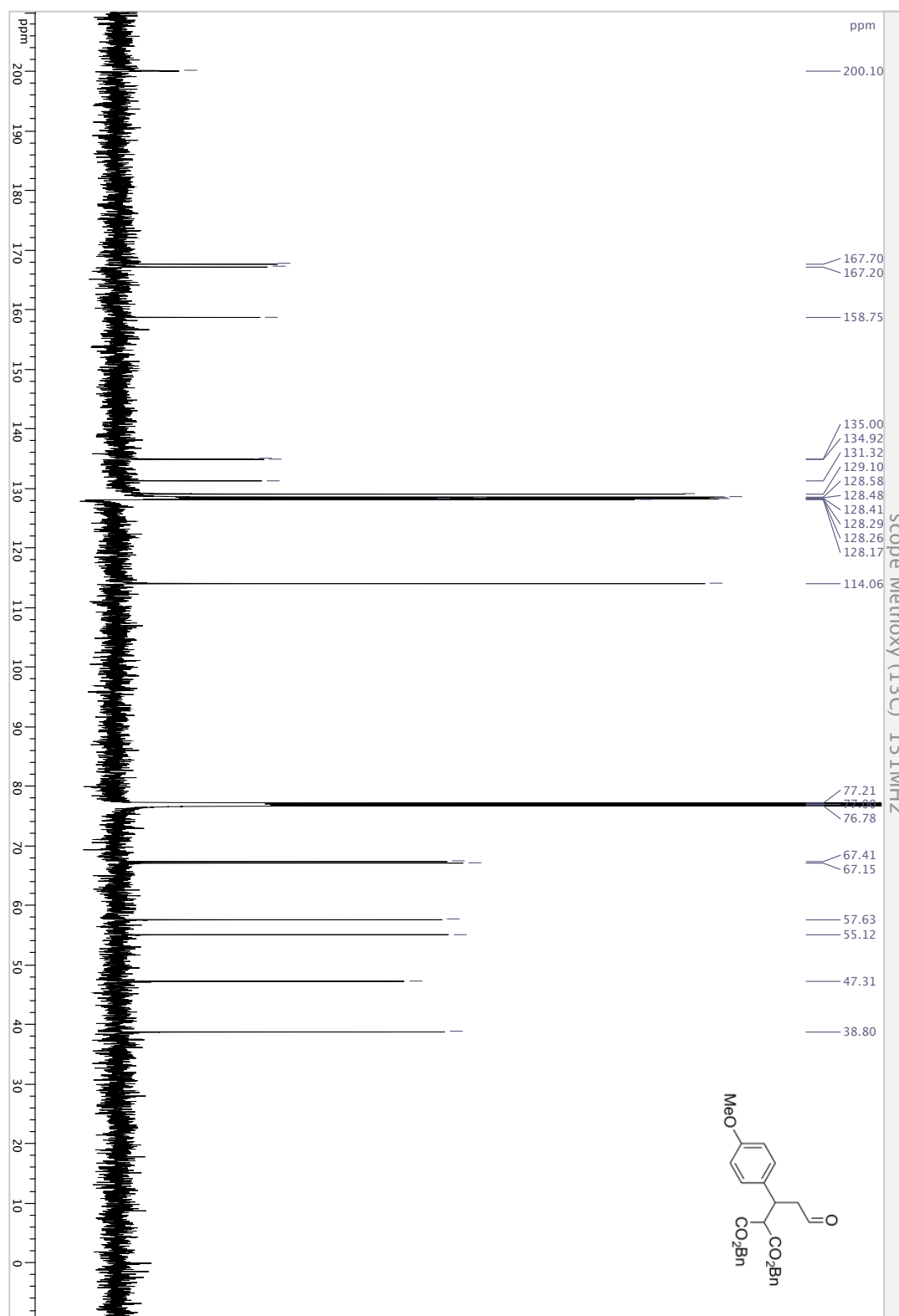
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(R)-2-(3-Oxo-1-(4-methoxyphenyl)propyl)malonic acid dibenzyl ester (10c)



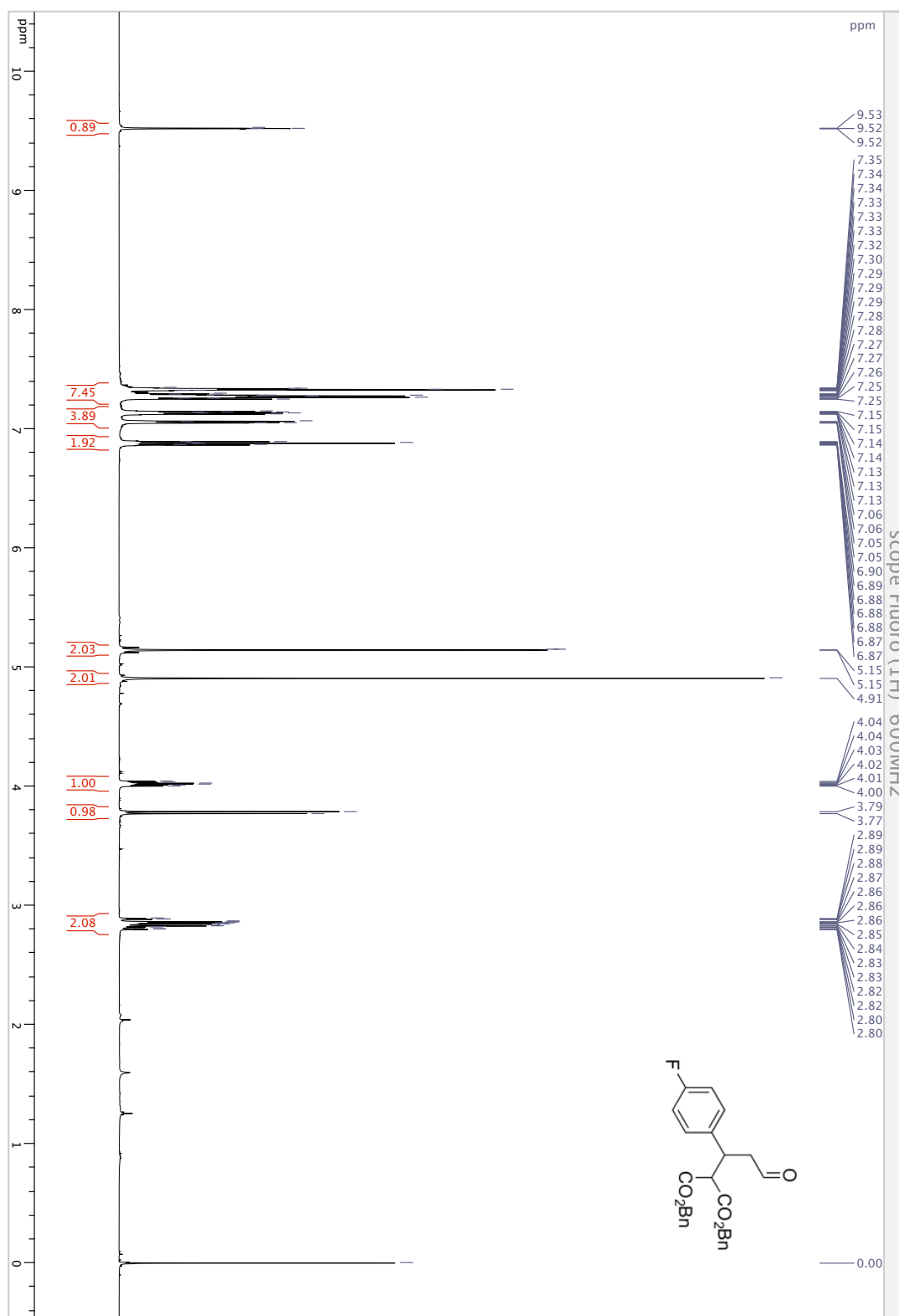
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(R)-2-(3-Oxo-1-(4-methoxyphenyl)propyl)malonic acid dibenzyl ester (10c)



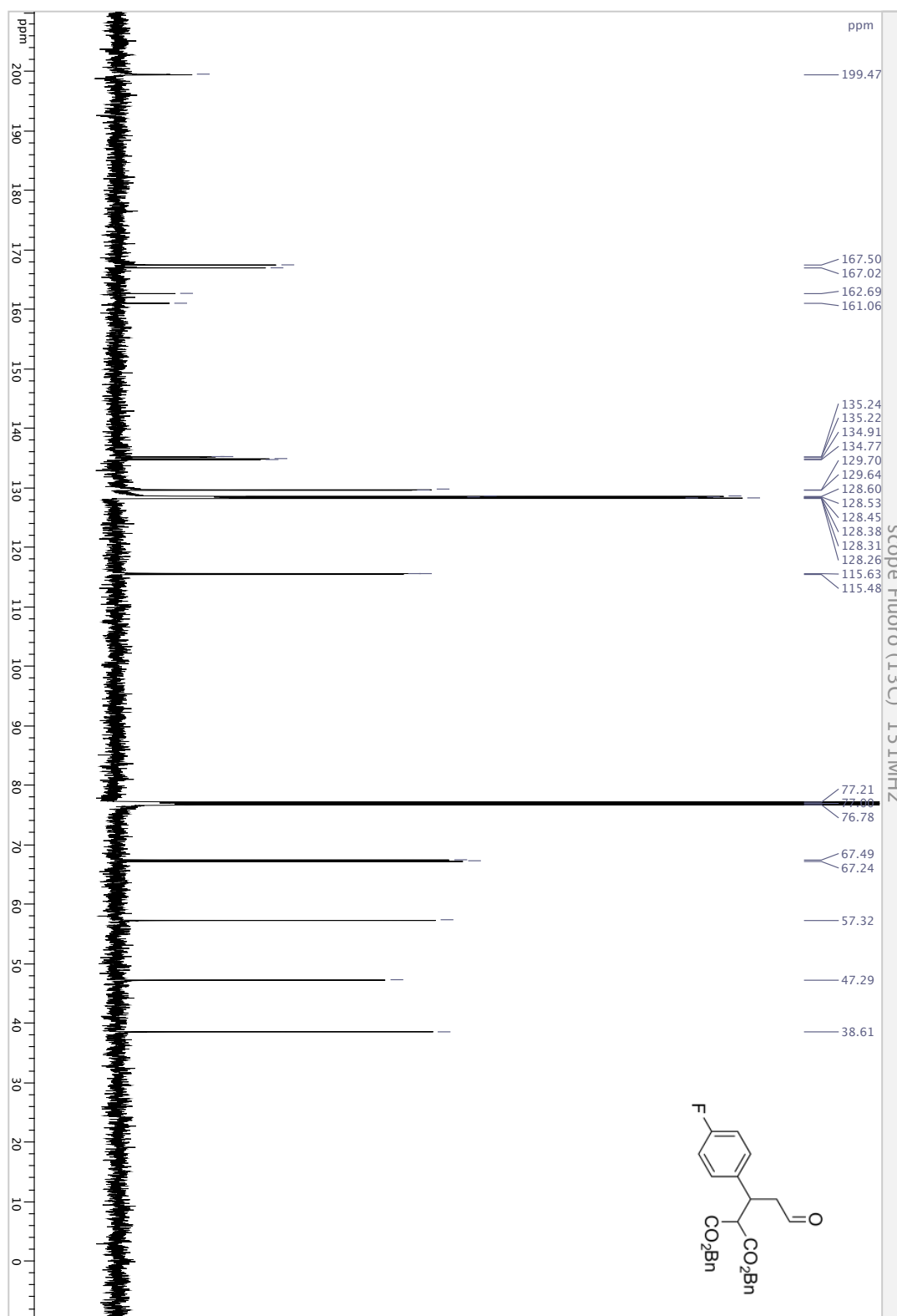
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(R)-2-(3-Oxo-1-(4-fluorophenyl)propyl)malonic acid dibenzyl ester (10d)



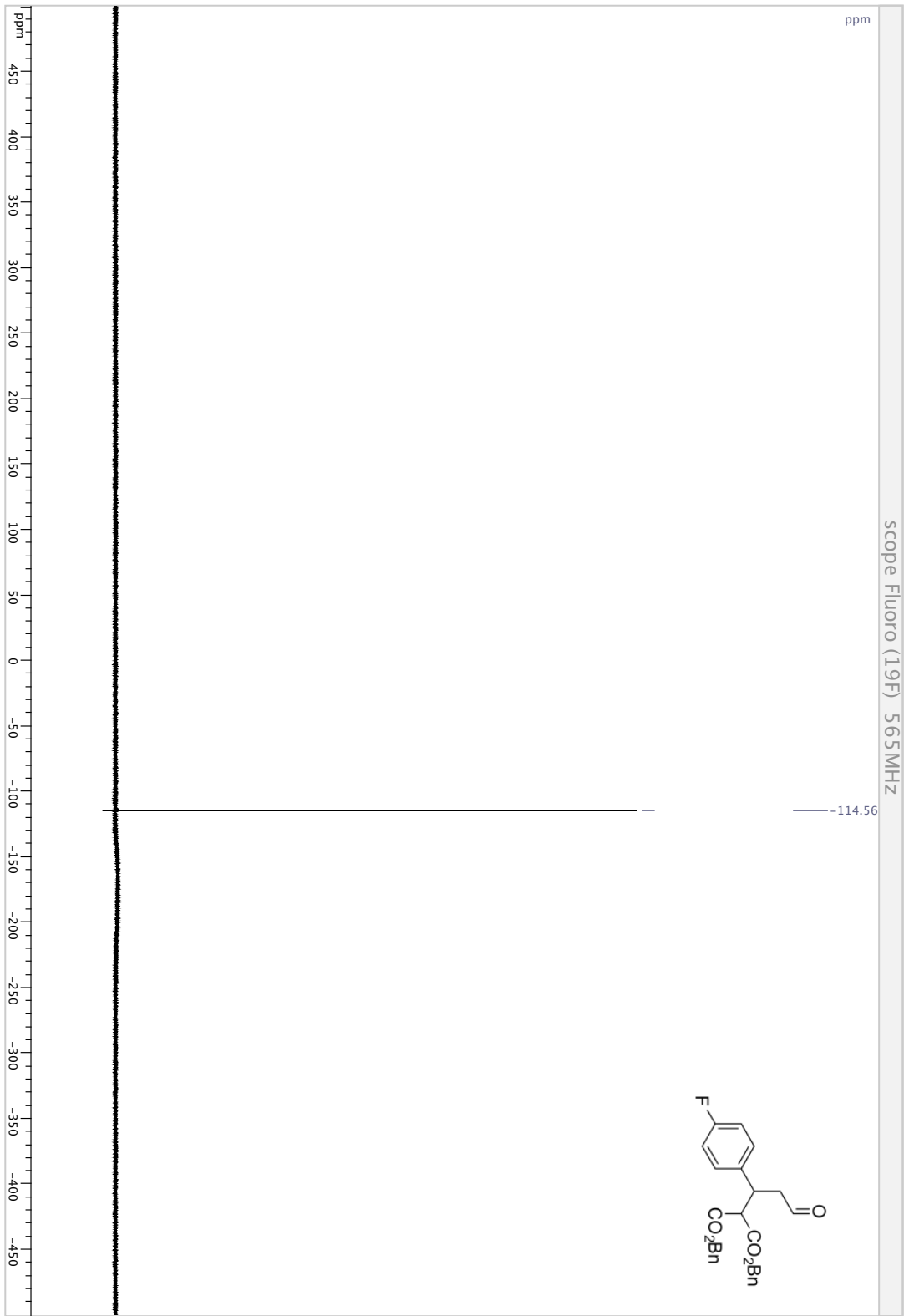
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(R)-2-(3-Oxo-1-(4-fluorophenyl)propyl)malonic acid dibenzyl ester (10d)



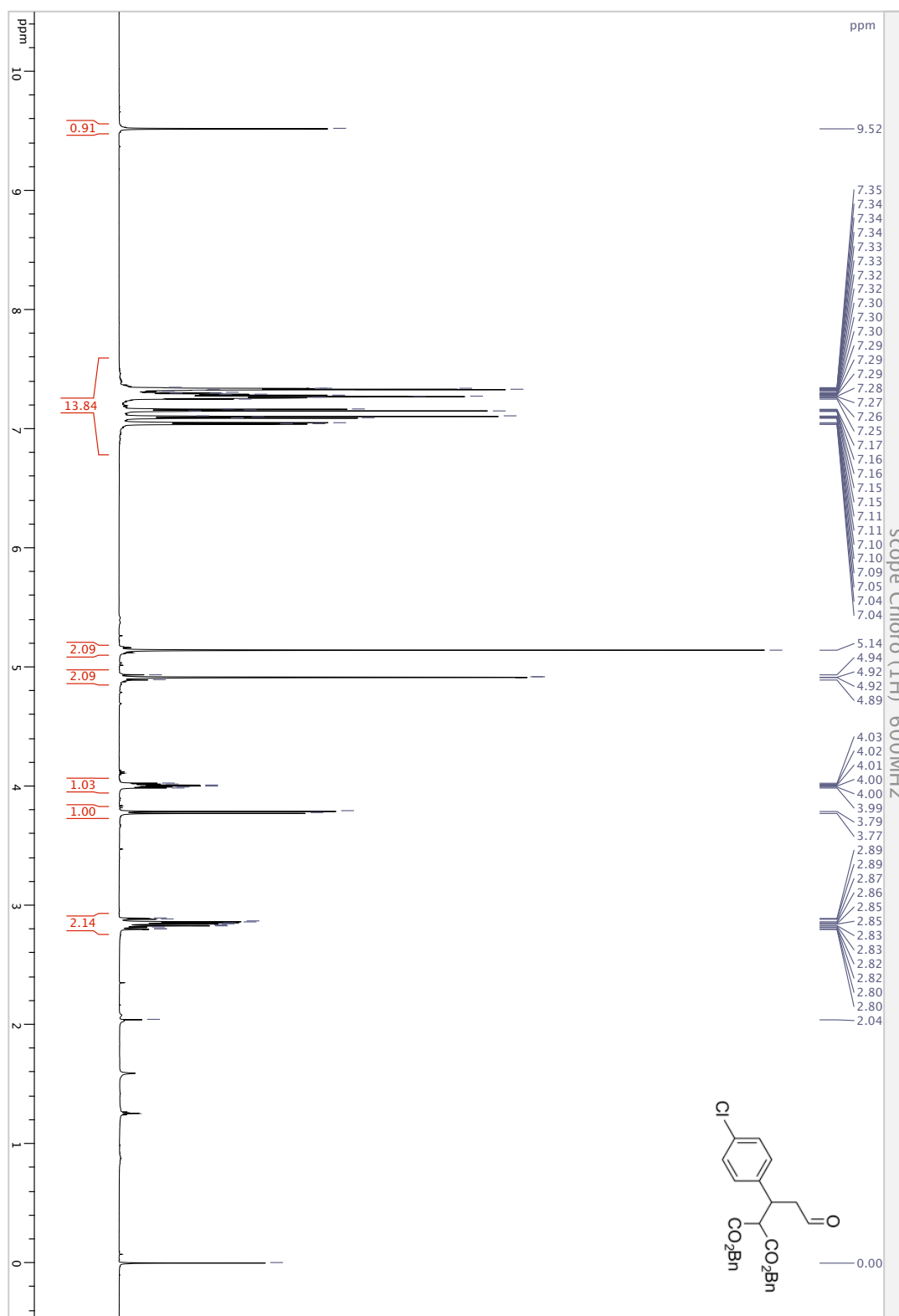
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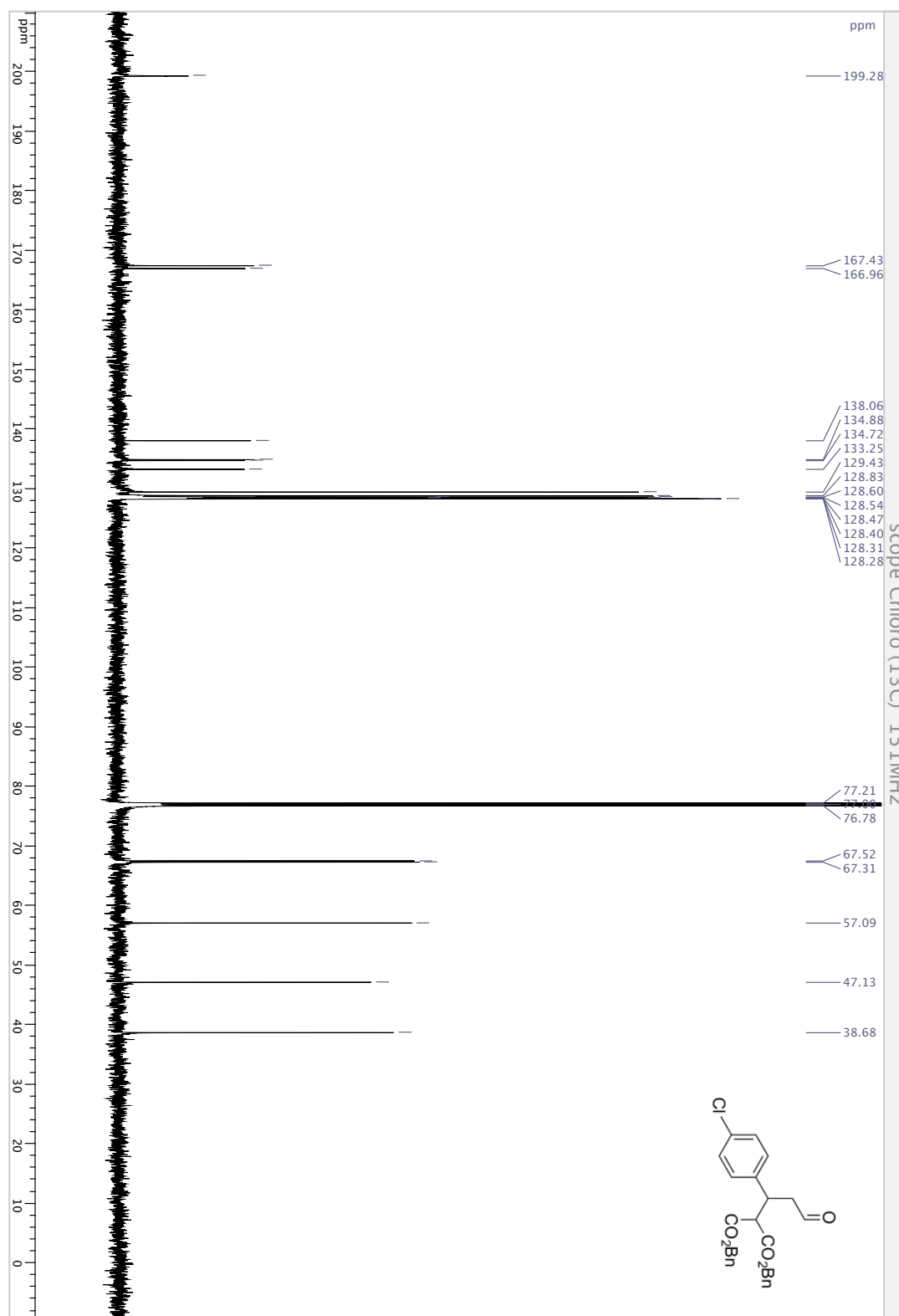
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(R)-2-(3-Oxo-1-(4-chlorophenyl)propyl)malonic acid dibenzyl ester (10e)



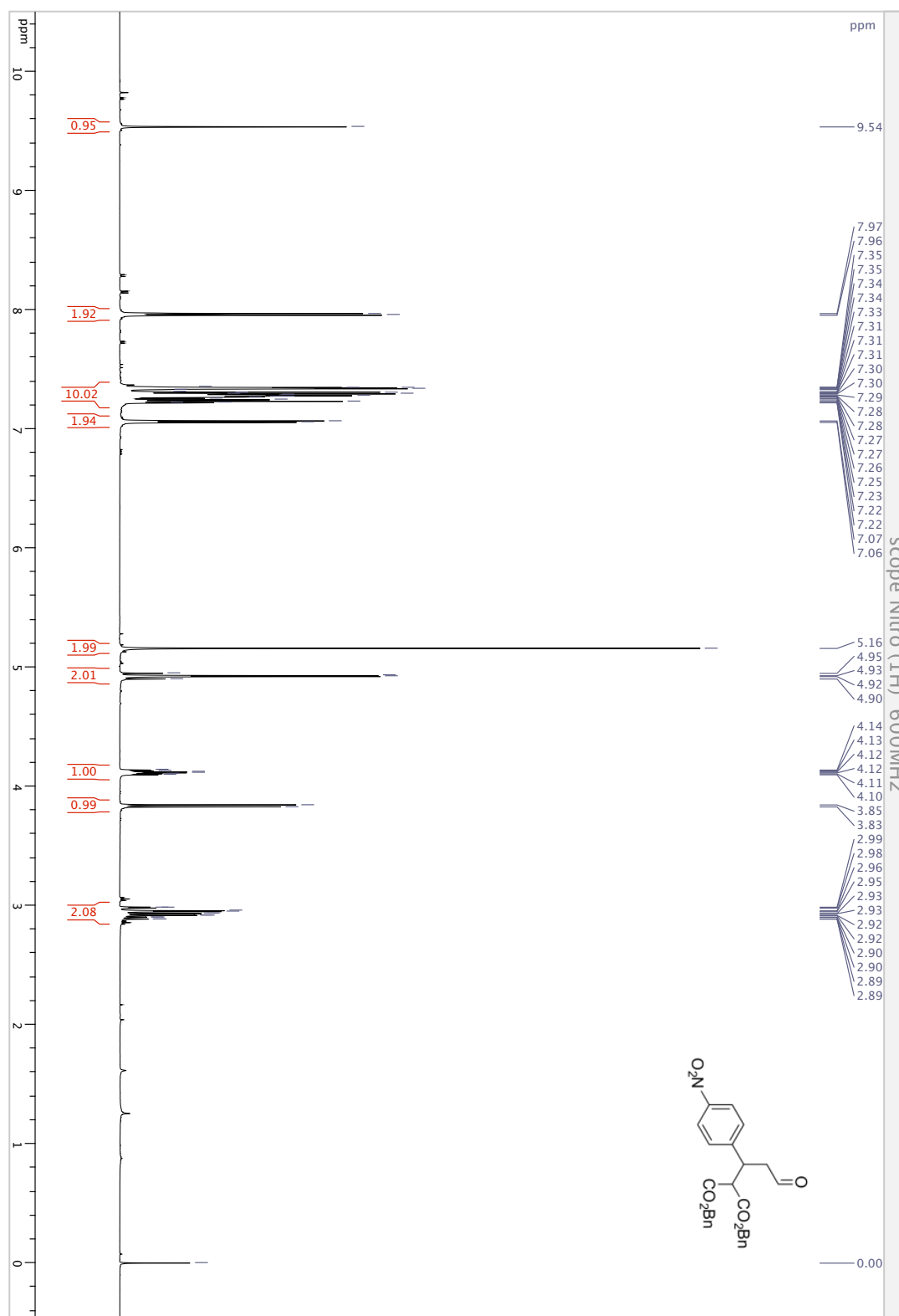
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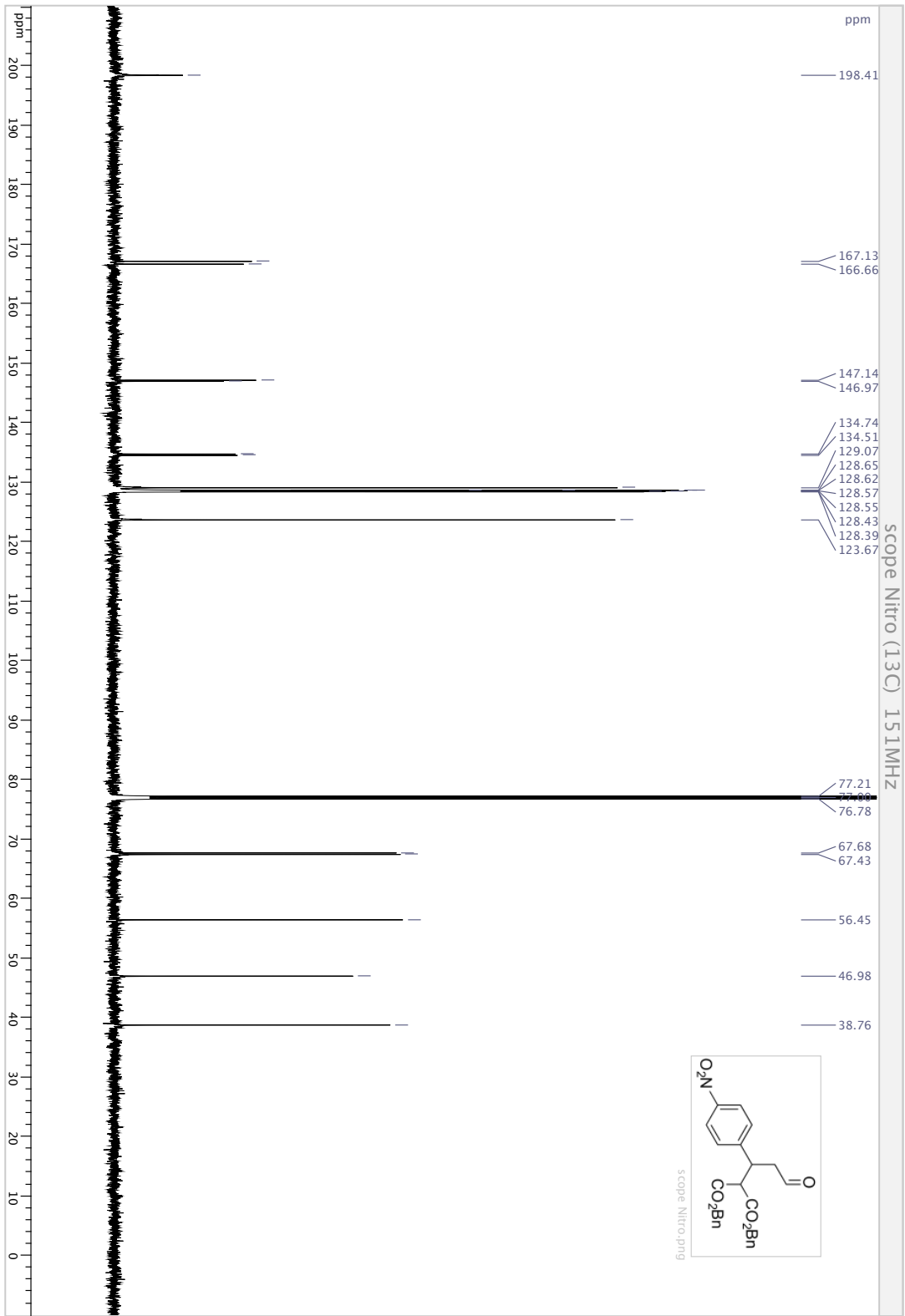
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(R)-2-(3-Oxo-1-(4-nitrophenyl)propyl)malonic acid dibenzyl ester (10f)



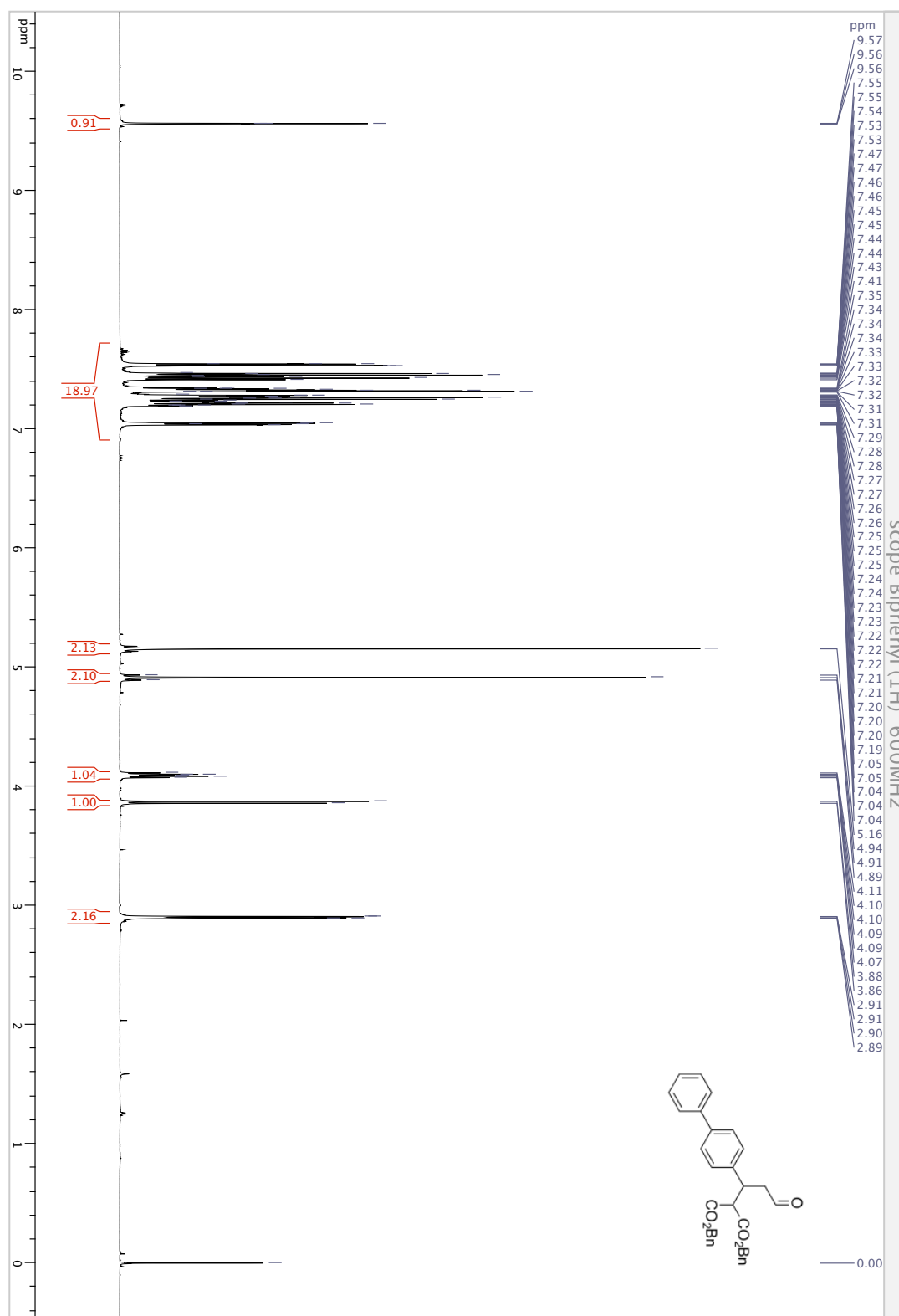
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(R)-2-(3-Oxo-1-(4-nitrophenyl)propyl)malonic acid dibenzyl ester (10f)



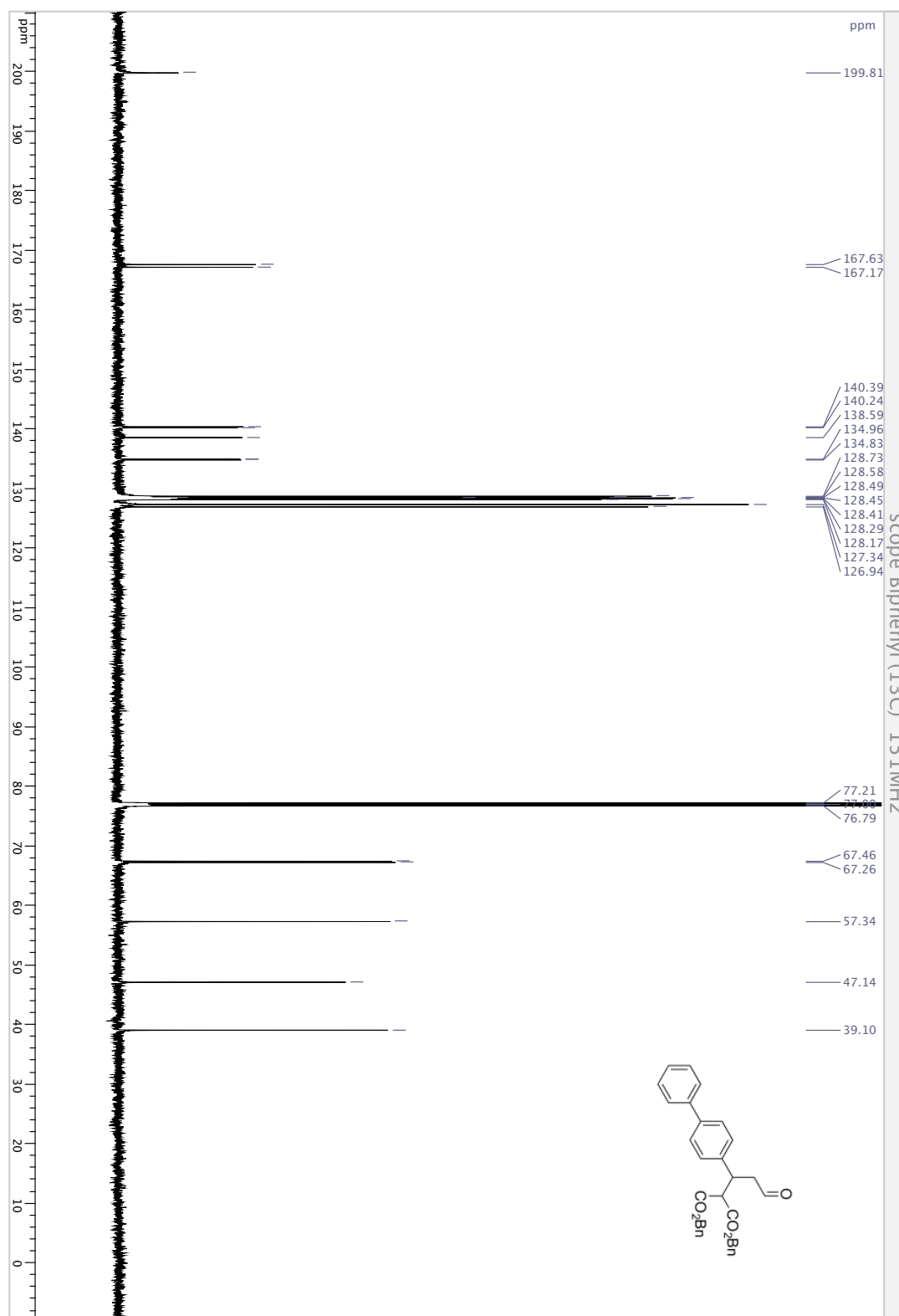
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(R)-2-(1-(Biphenyl-4-yl)-3-oxopropyl)malonic acid dibenzyl ester (10g)



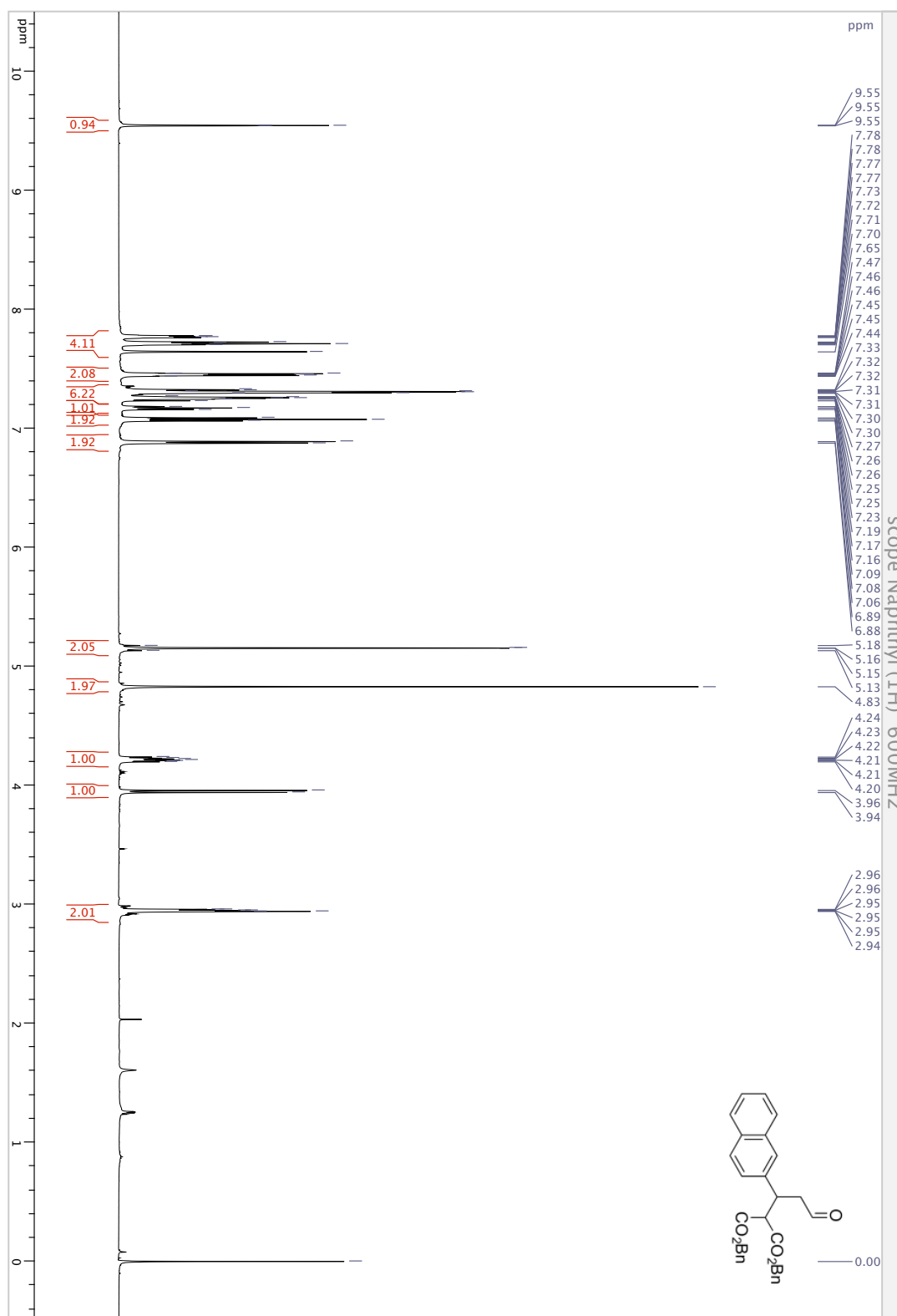
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(R)-2-(1-(Biphenyl-4-yl)-3-oxopropyl)malonic acid dibenzyl ester (10g)



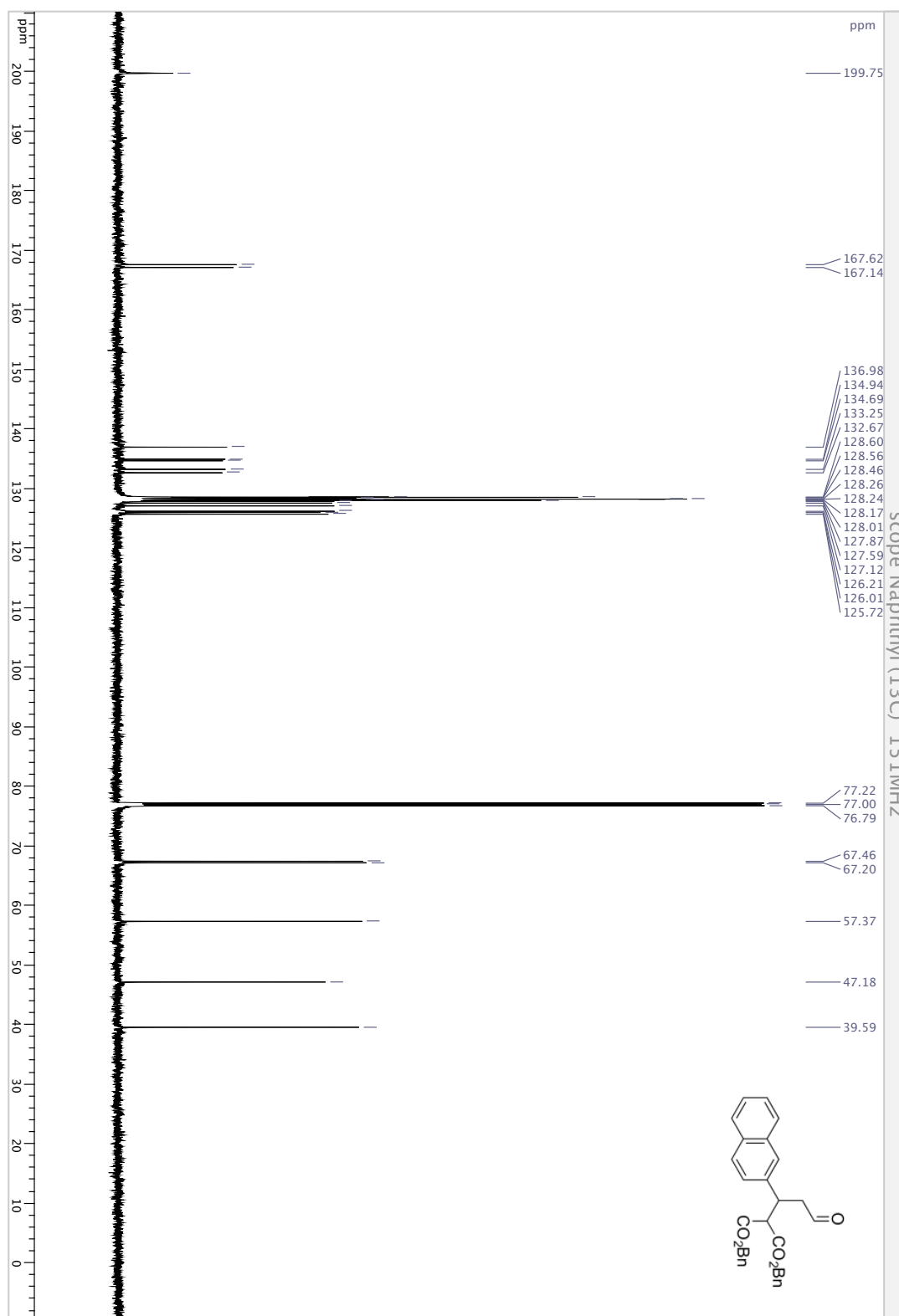
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(R)-2-(1-(naphthalen-2-yl)-3-oxopropyl)malonic acid dibenzyl ester (10h)



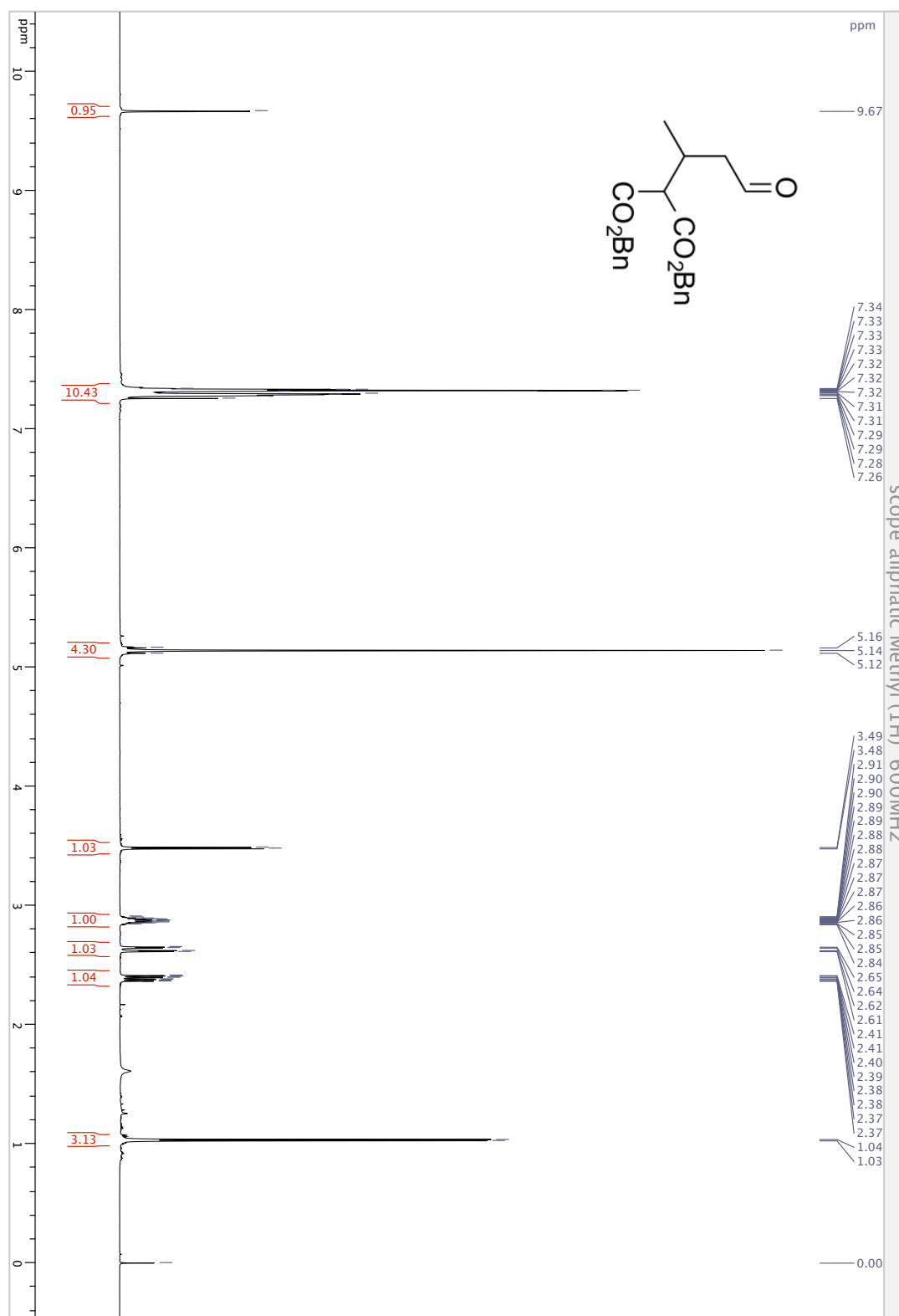
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(R)-2-(1-(naphthalen-2-yl)-3-oxopropyl)malonic acid dibenzyl ester (10h)



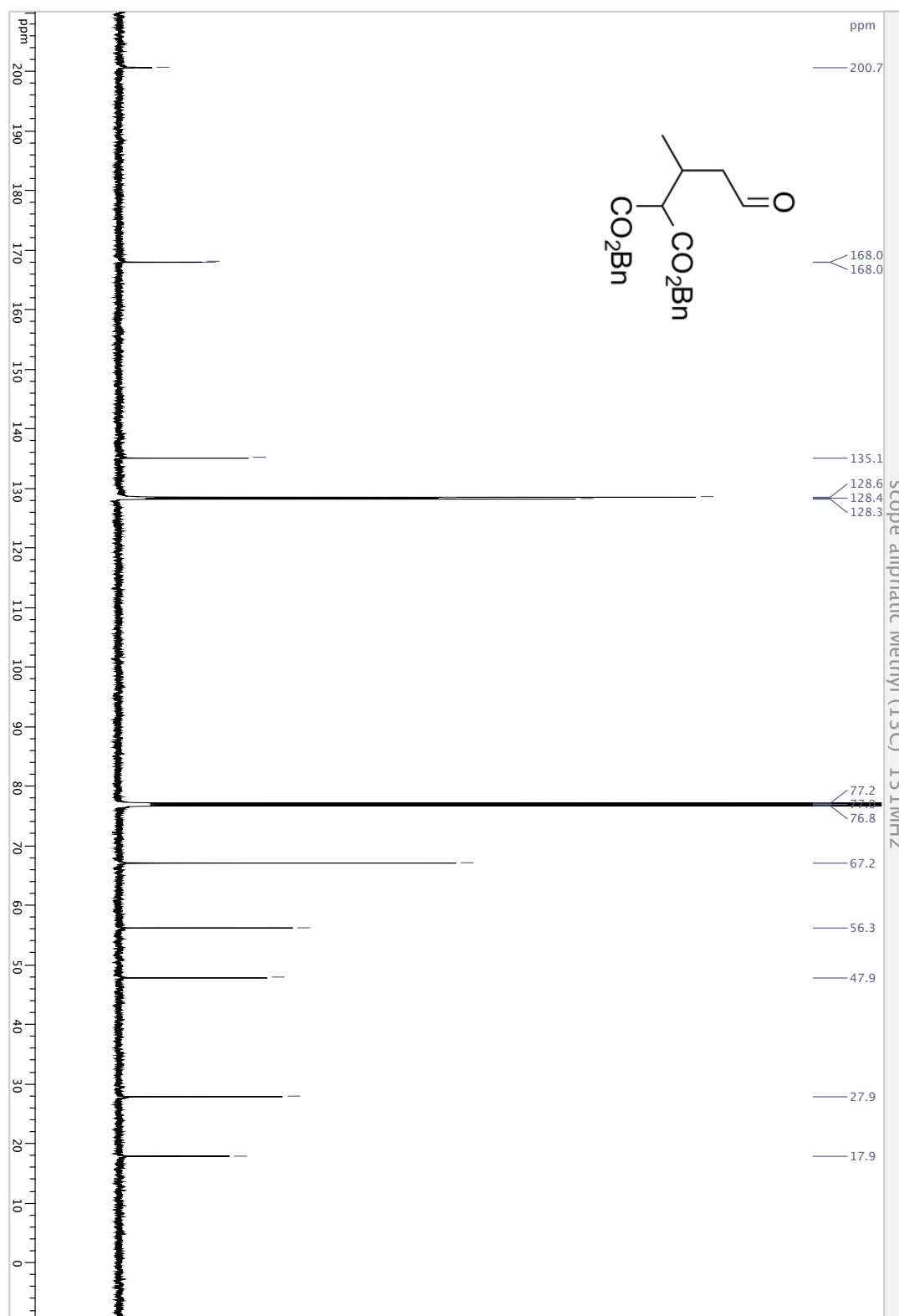
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(R)-2-(1-Methyl-3-oxopropyl)malonic acid dibenzyl ester (10i)



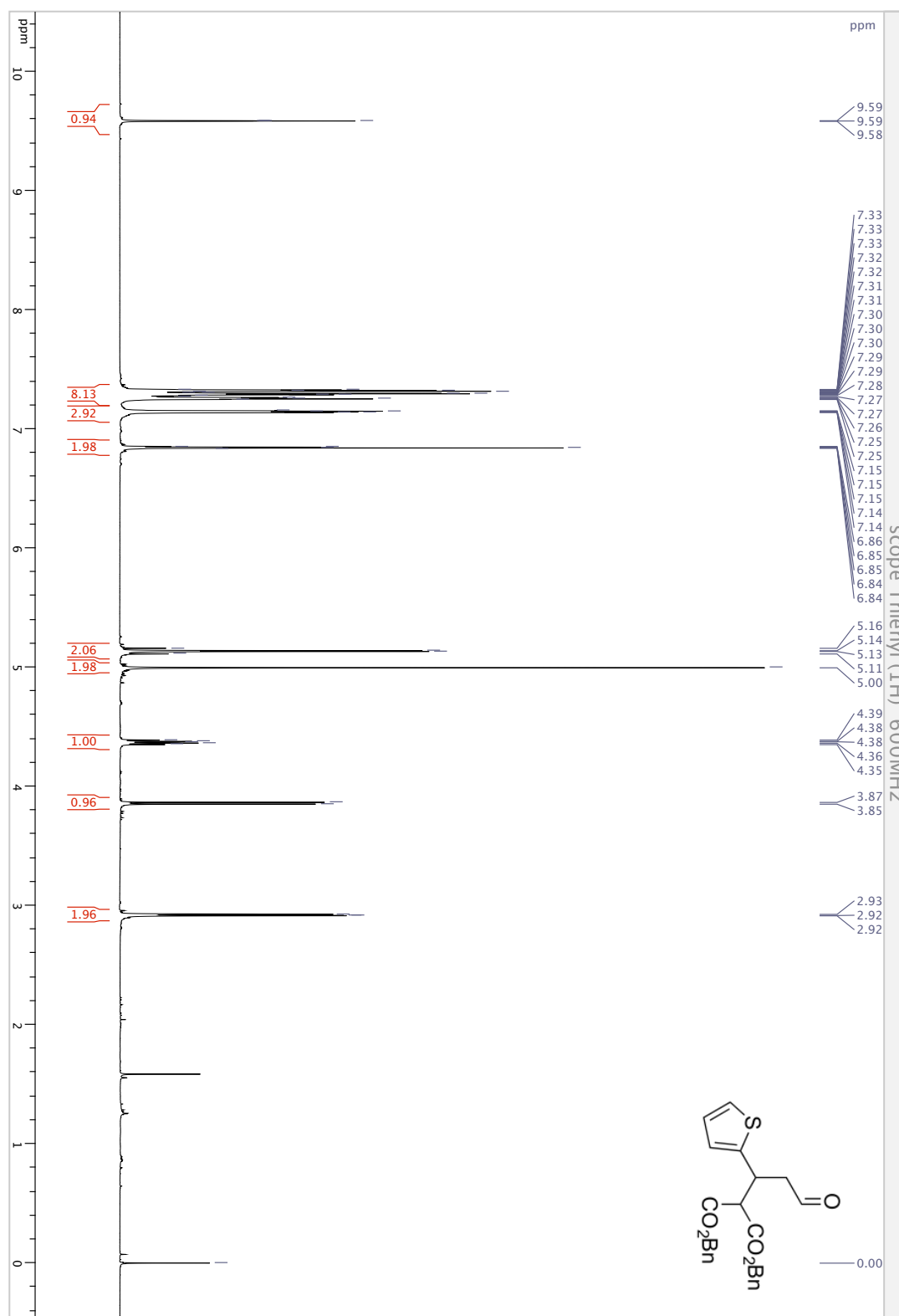
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(R)-2-(1-Methyl-3-oxopropyl)malonic acid dibenzyl ester (10i)



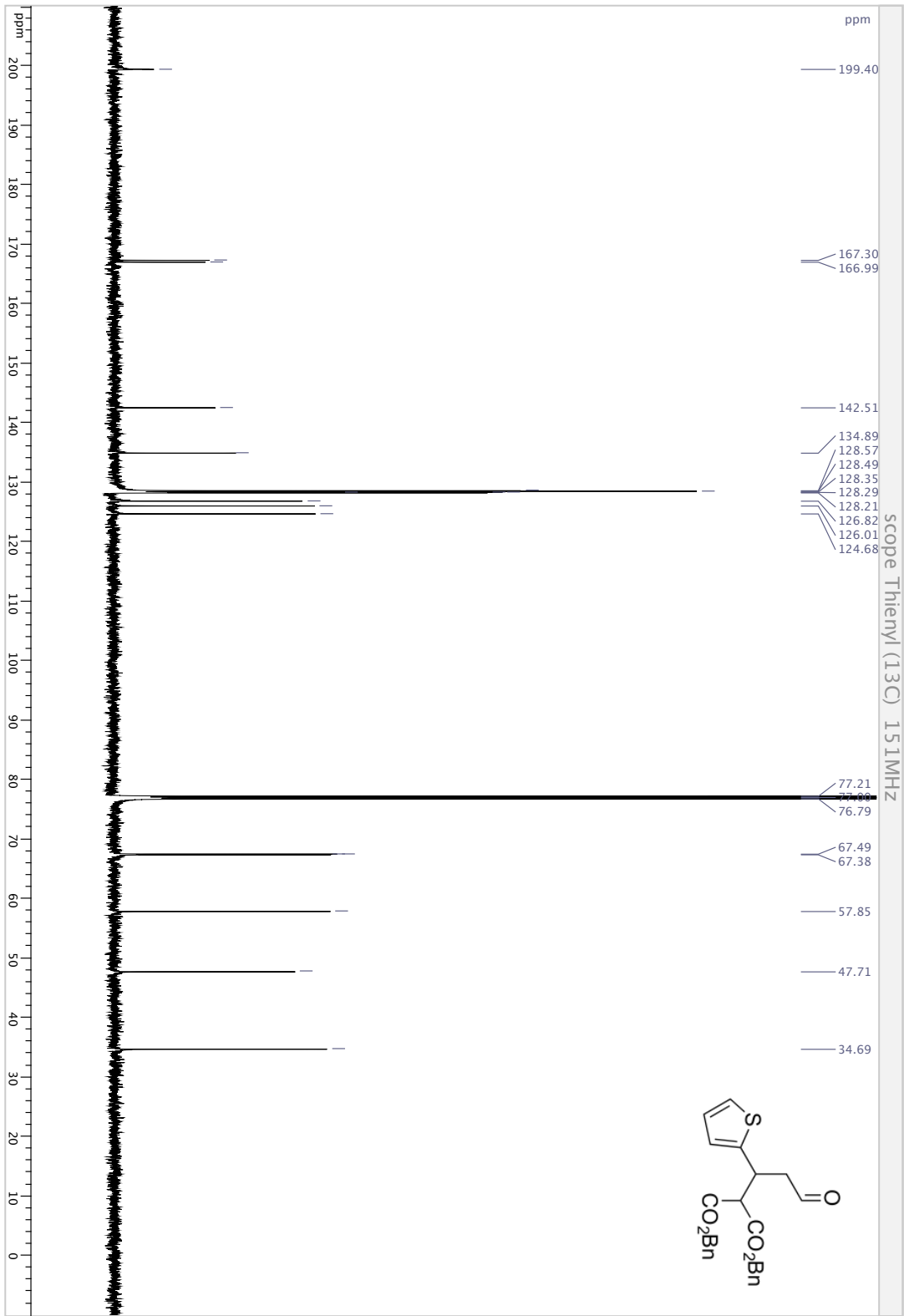
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(R)-2-(3-Oxo-1-thiophen-2-ylpropyl)malonic acid dibenzyl ester (10j)



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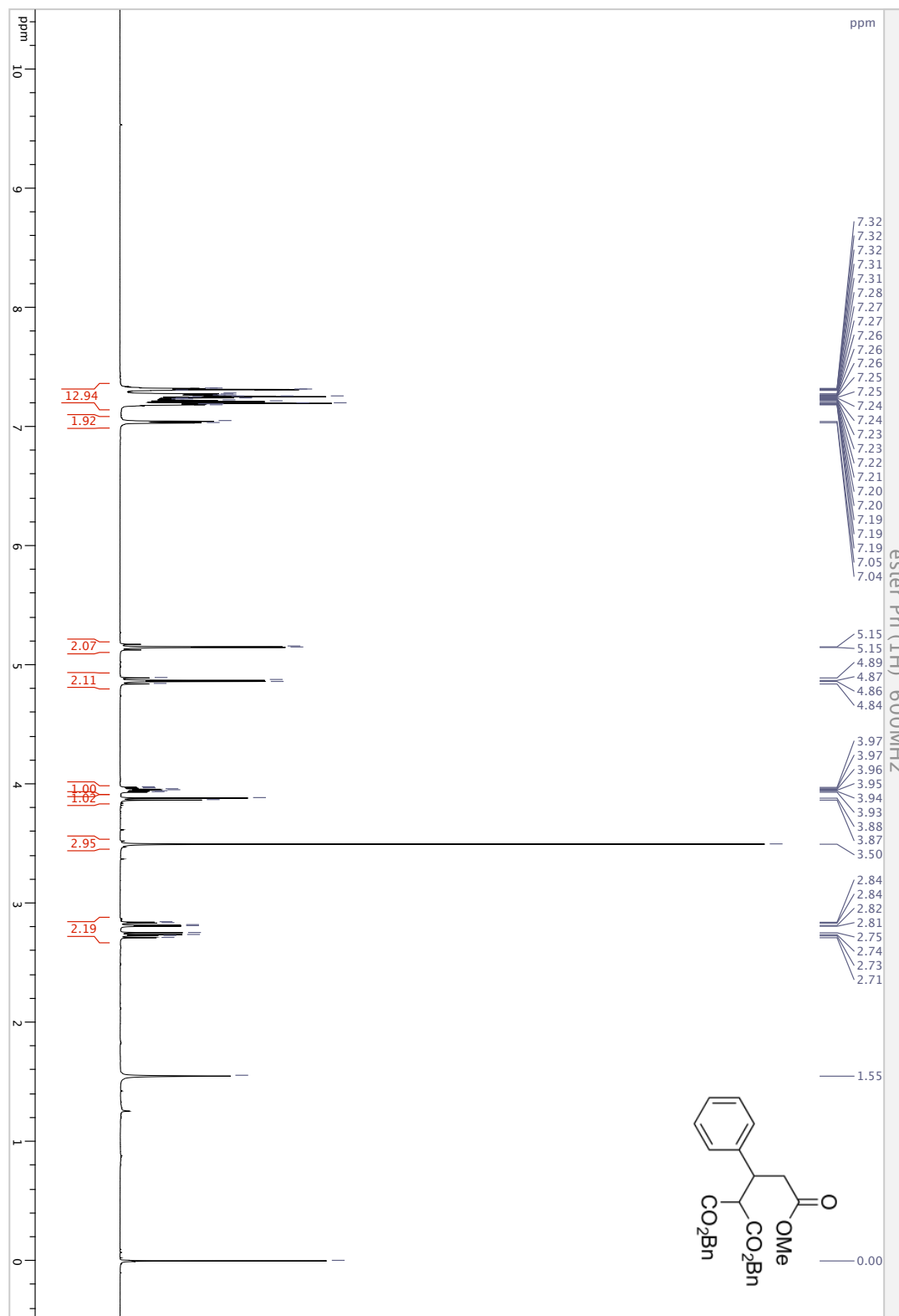
(R)-2-(3-Oxo-1-thiophen-2-ylpropyl)malonic acid dibenzyl ester (10j)



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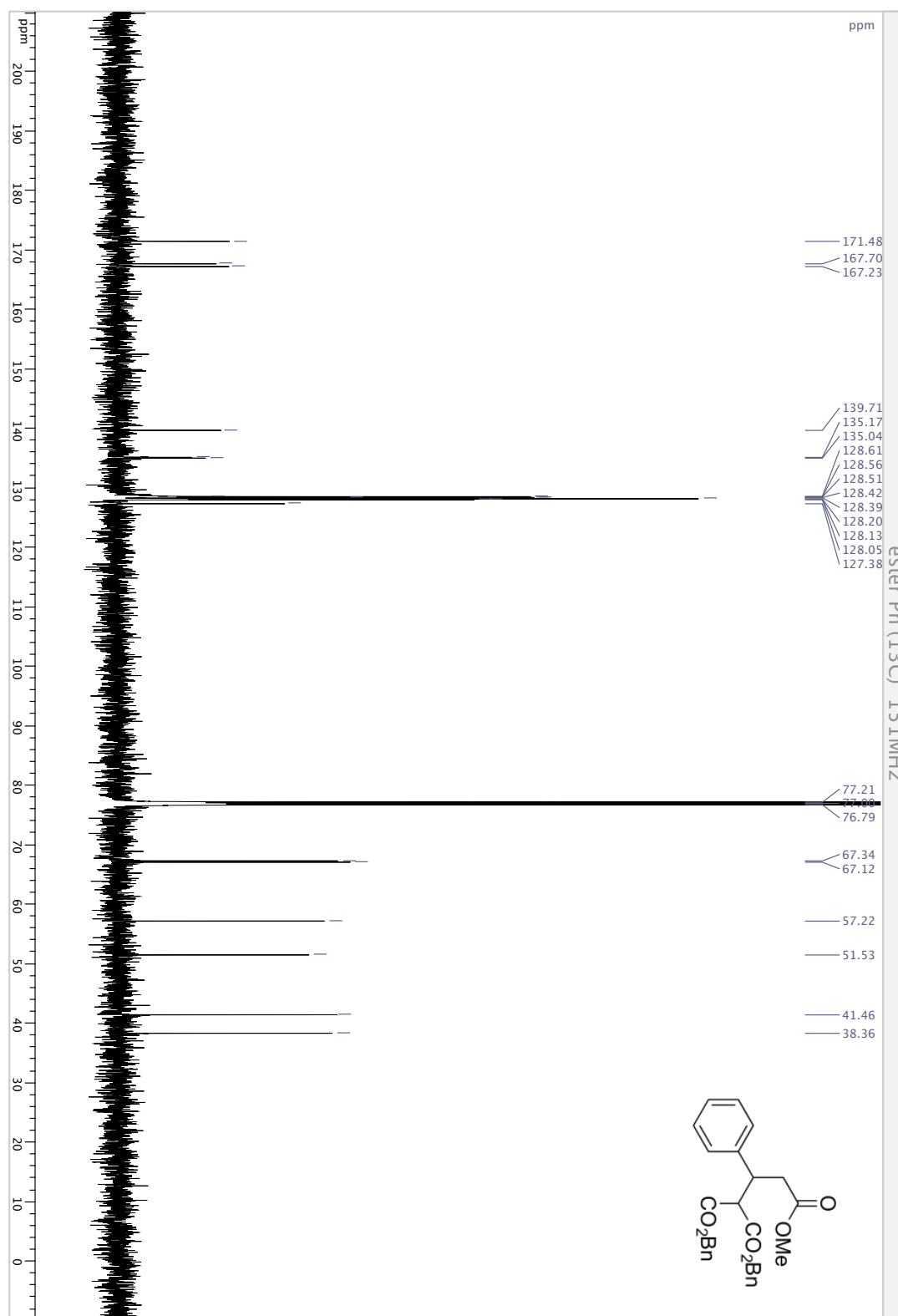
B2 NMR Spectra of Methyl Ester Derivatives of Michael Adducts

(R)-2-Benzyloxycarbonyl-3-phenylpentanedioic acid 1-benzyl ester 5-methyl ester



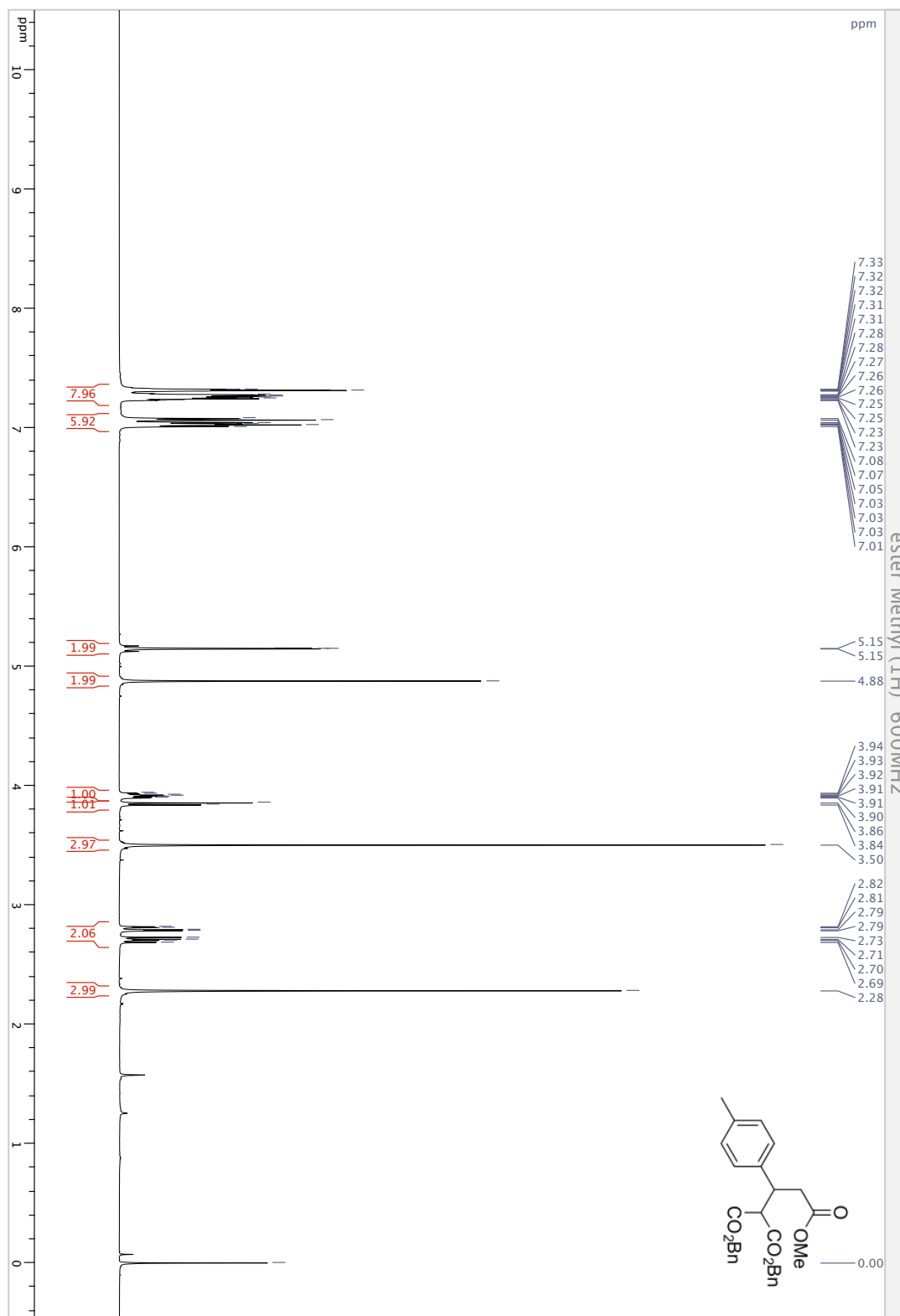
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(R)-2-Benzyloxycarbonyl-3-phenylpentanedioic acid 1-benzyl ester 5-methyl ester



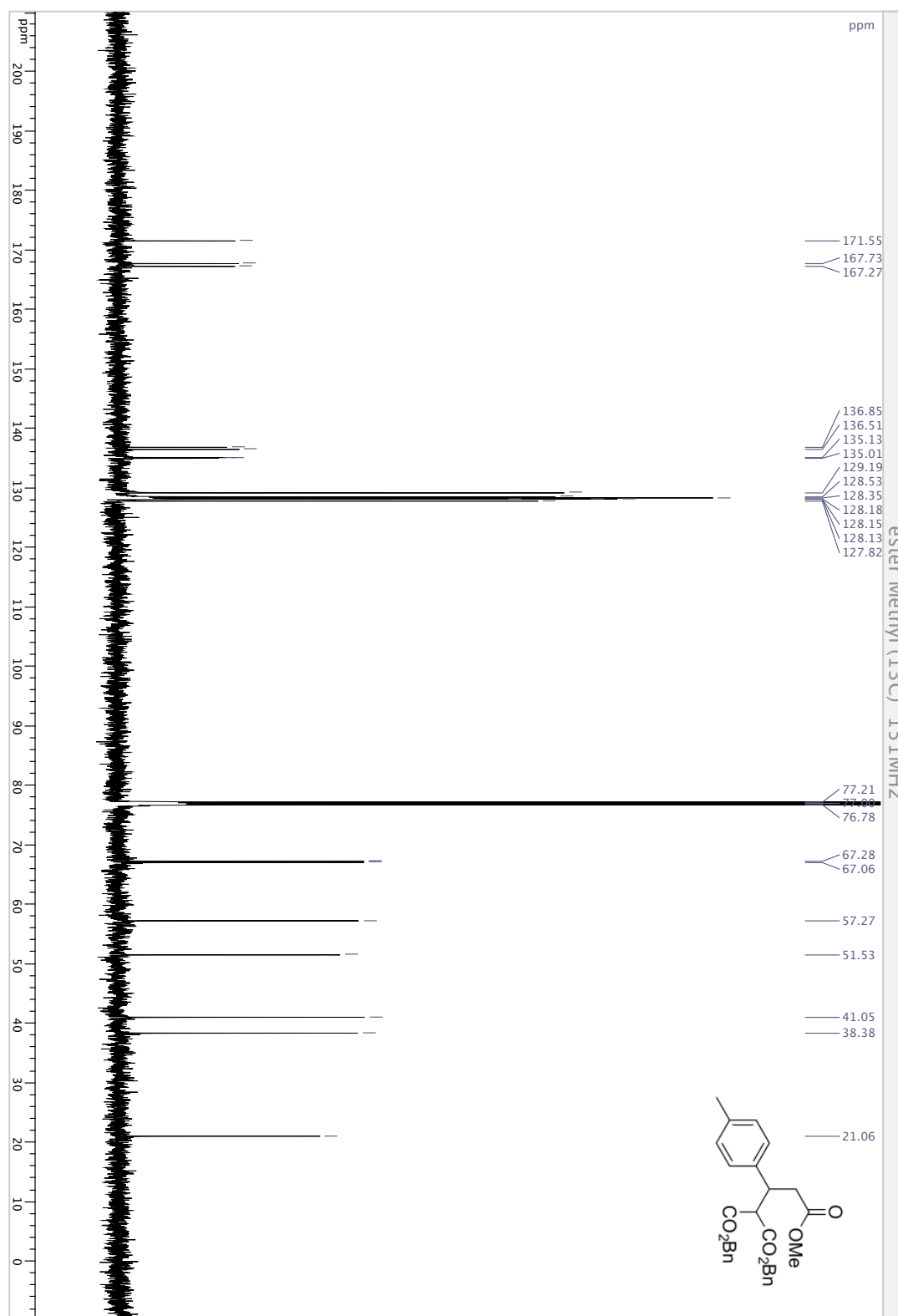
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(R)-2-Benzyloxycarbonyl-3-(4-methylphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



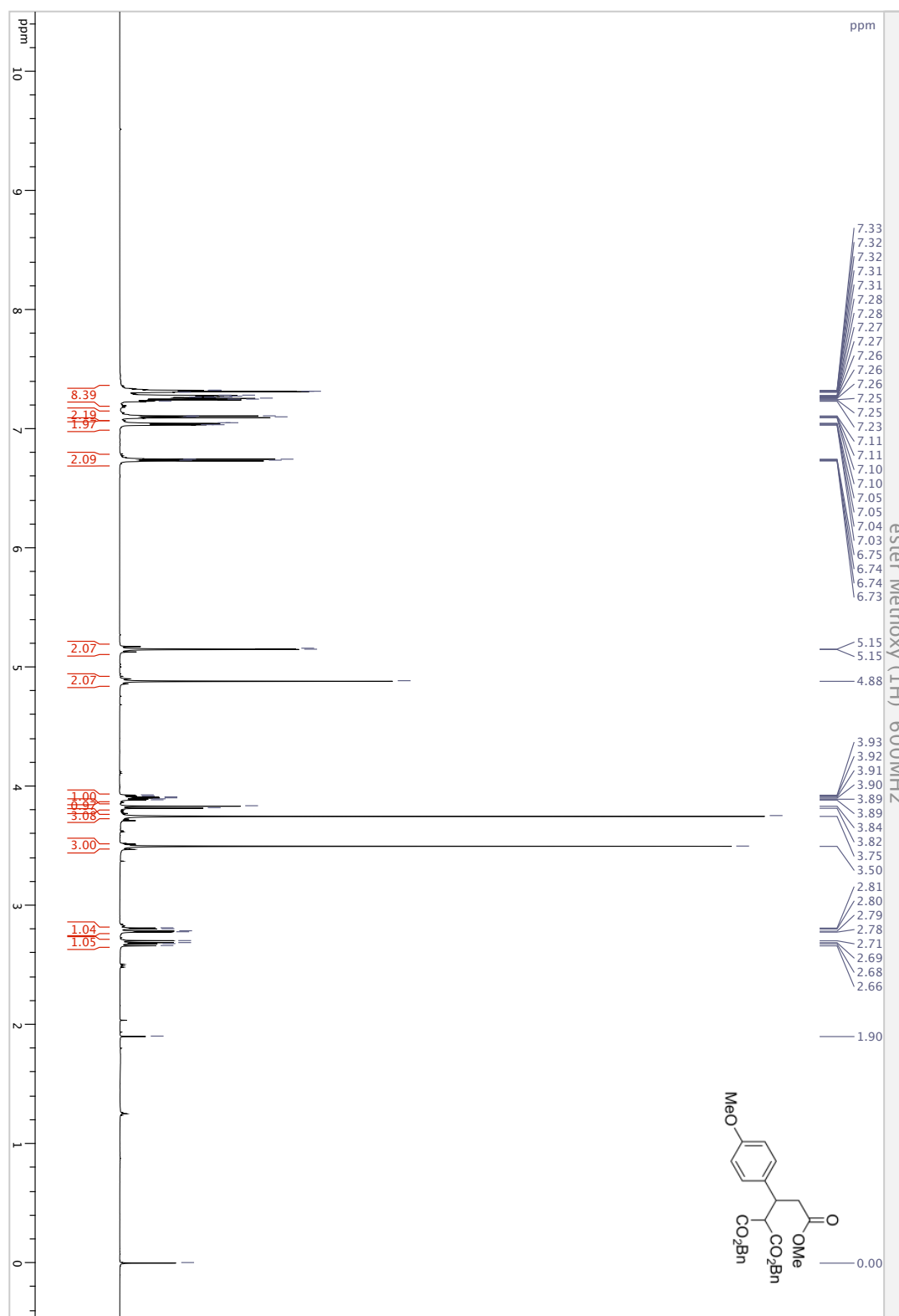
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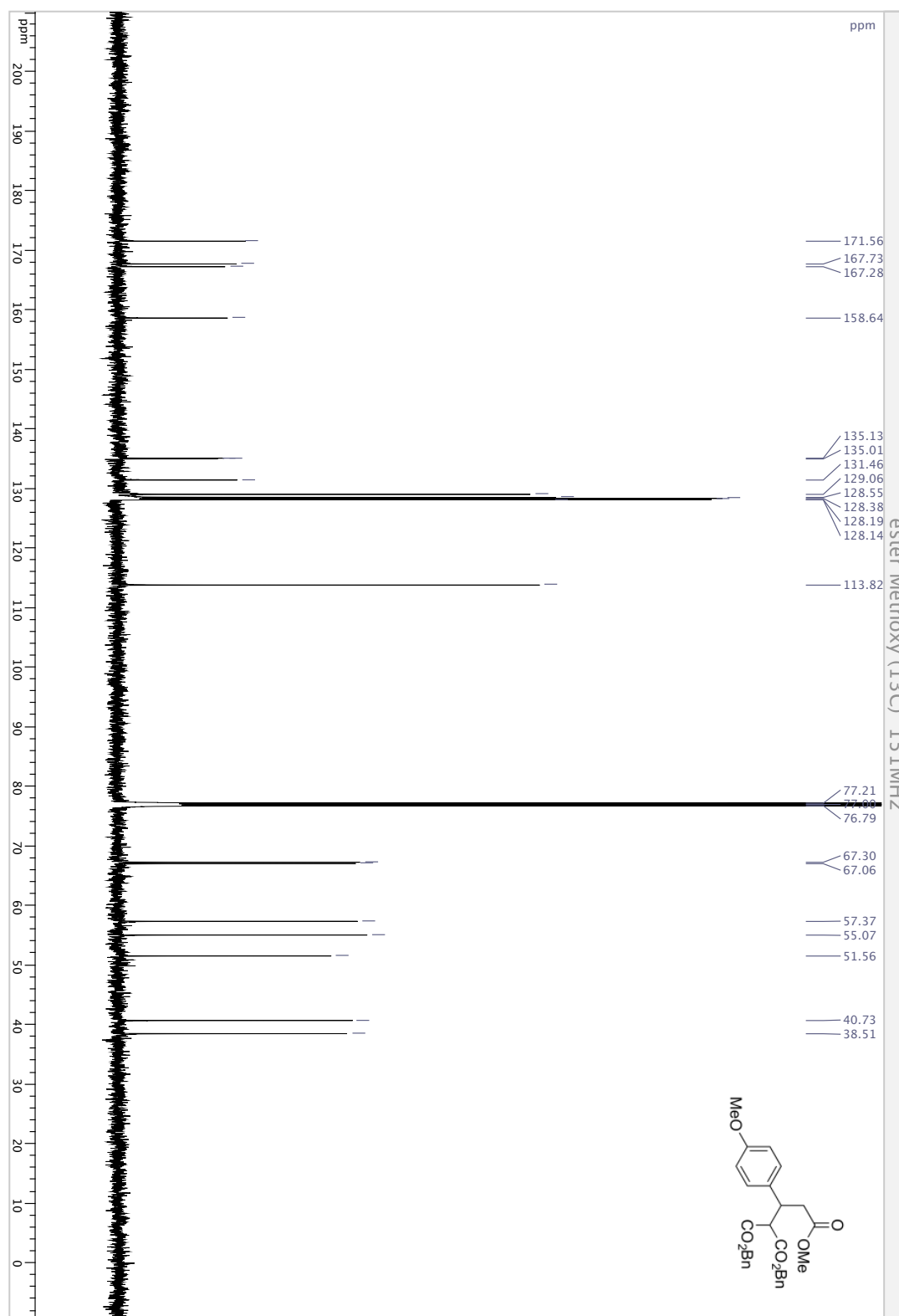
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(R)-2-Benzyloxycarbonyl-3-(4-methoxyphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



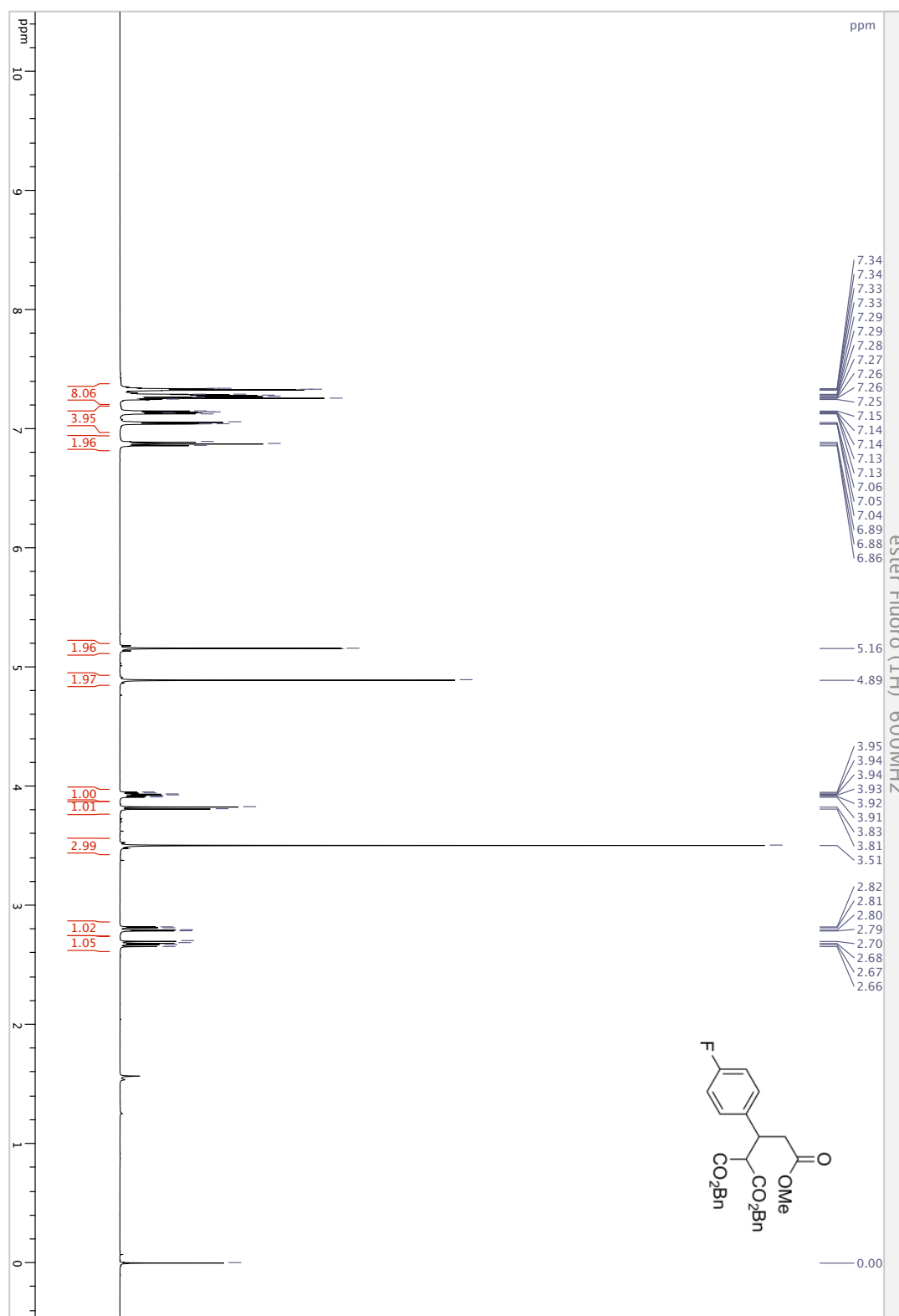
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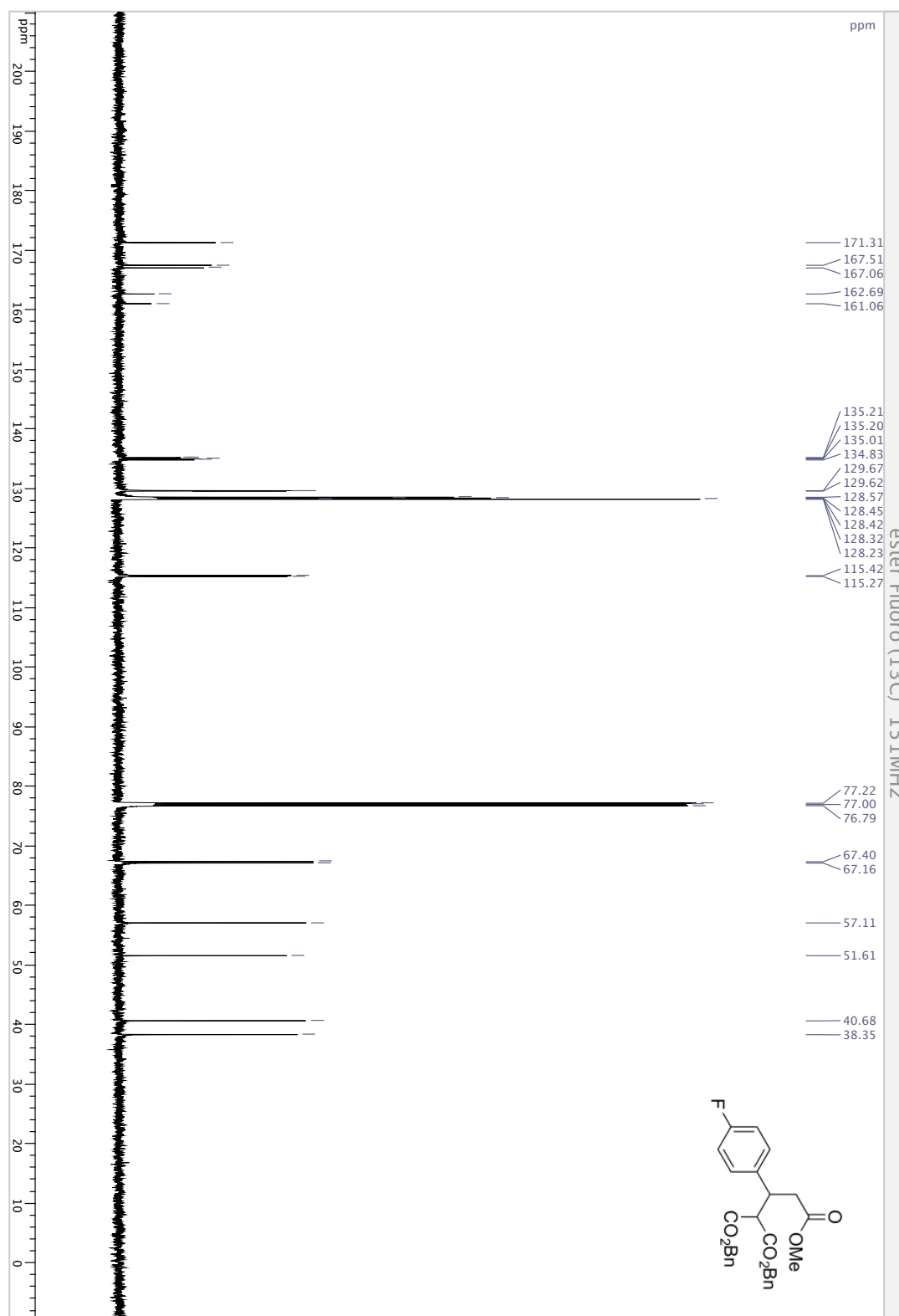
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(R)-2-Benzyloxycarbonyl-3-(4-fluorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



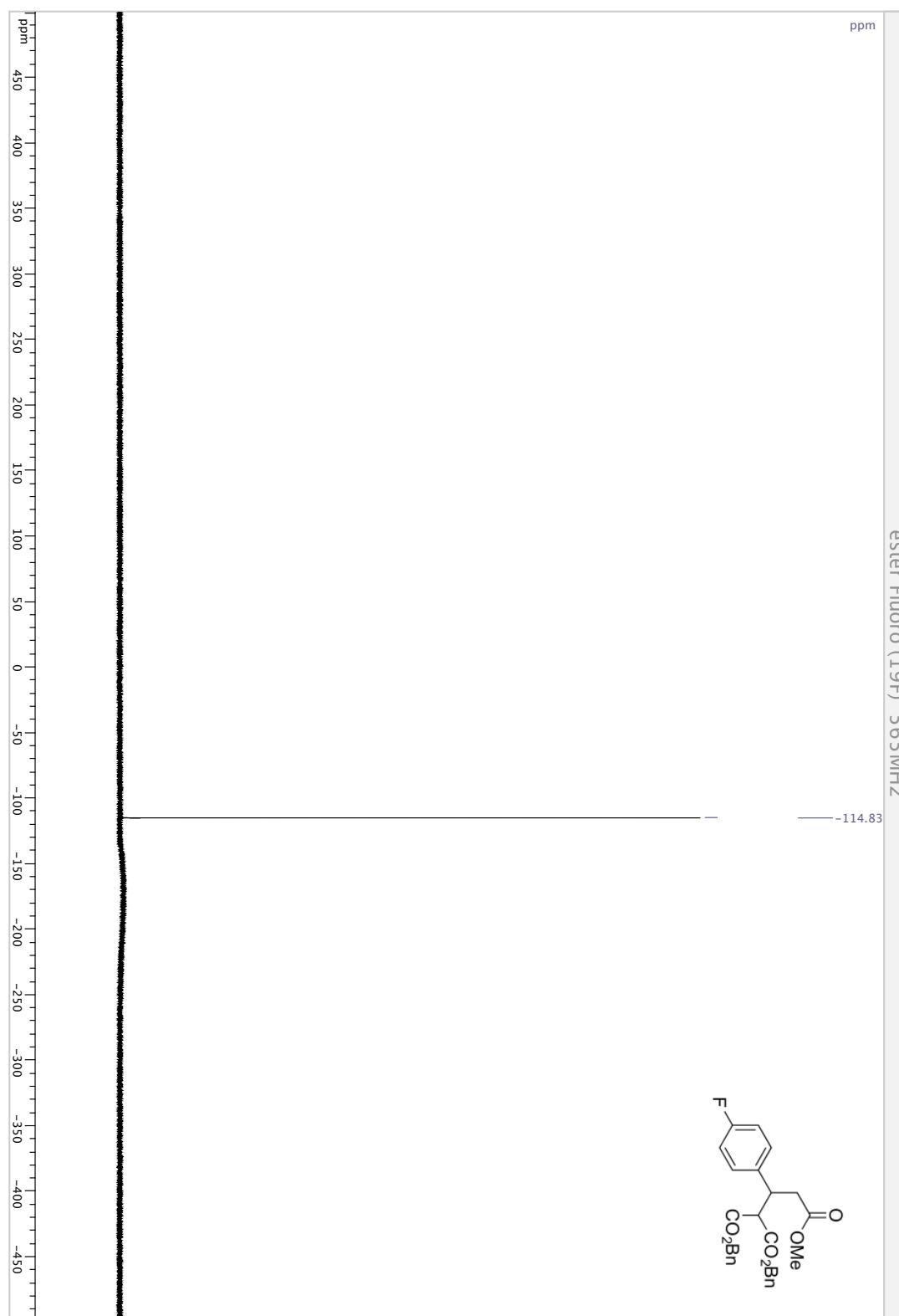
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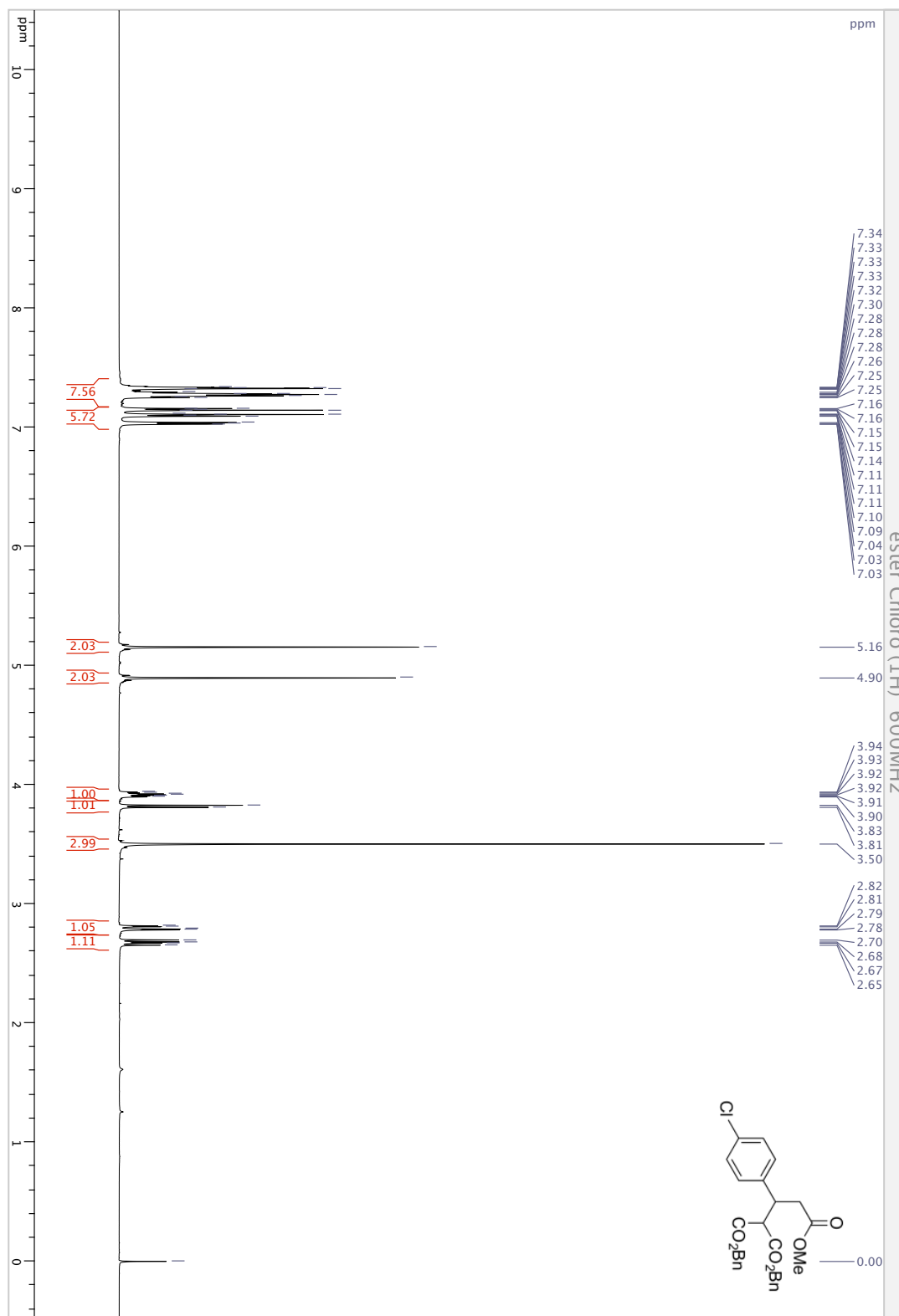
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(R)-2-Benzyloxycarbonyl-3-(4-fluorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



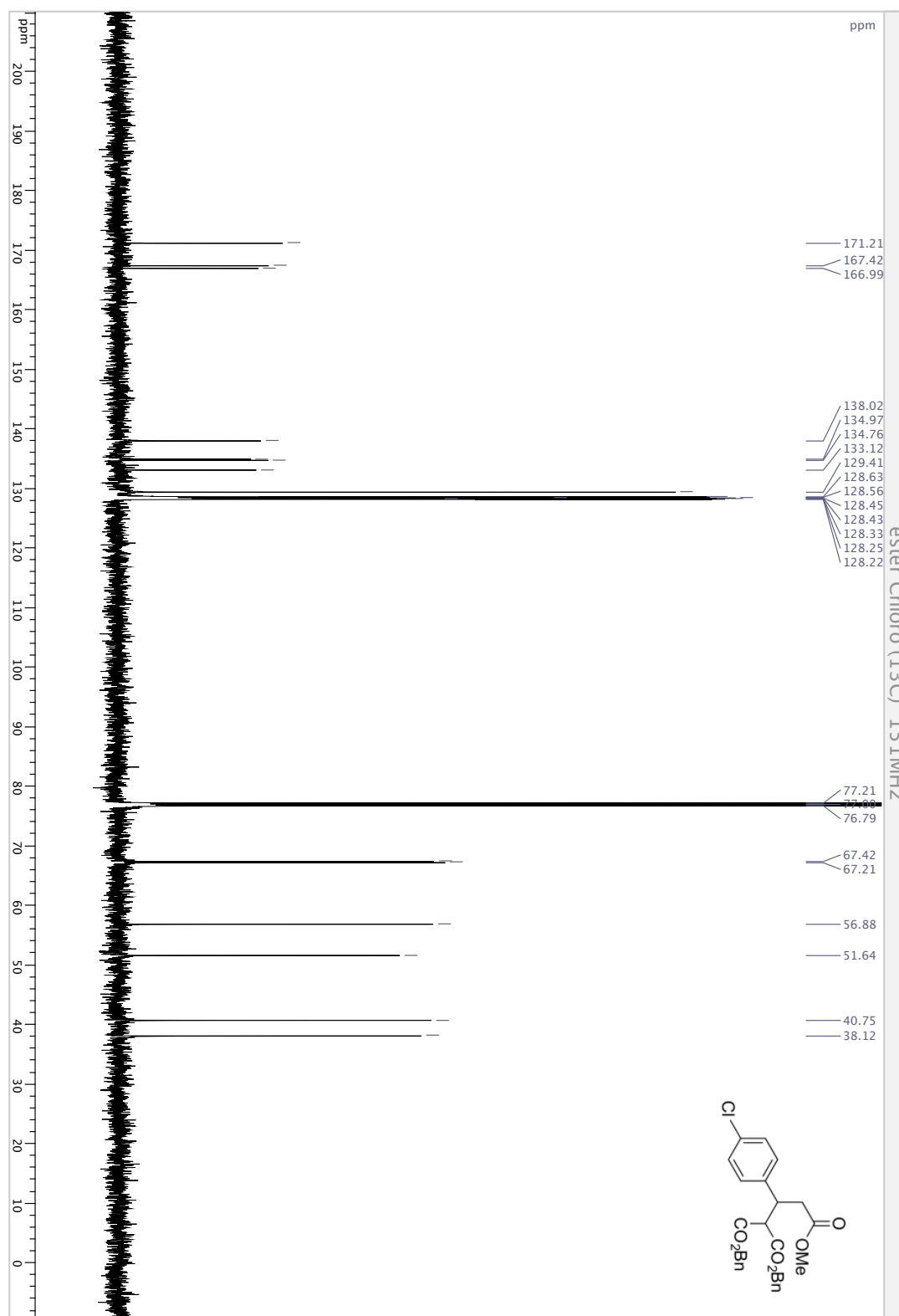
A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(R)-2-Benzyloxycarbonyl-3-(4-chlorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



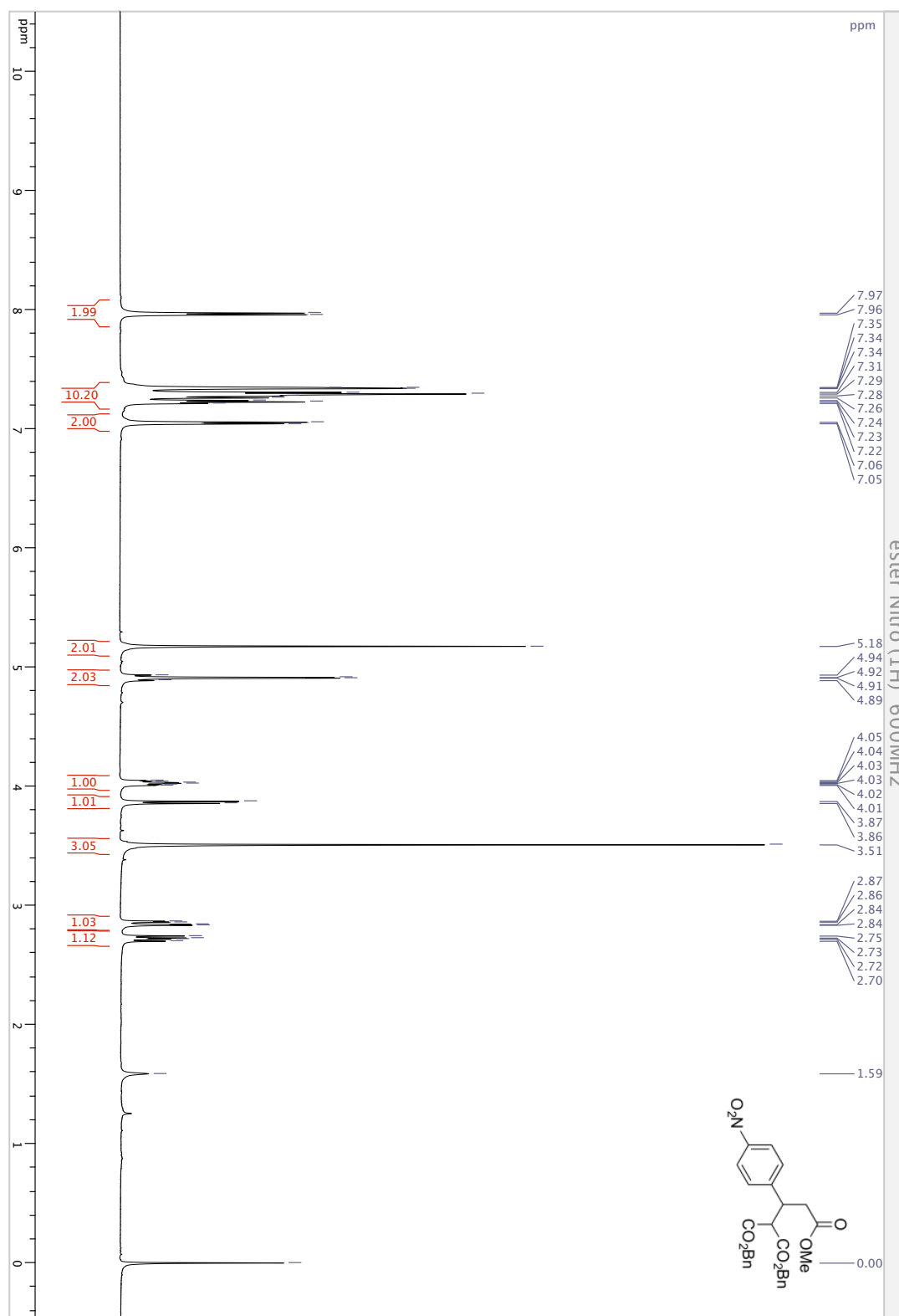
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(R)-2-Benzyloxycarbonyl-3-(4-chlorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



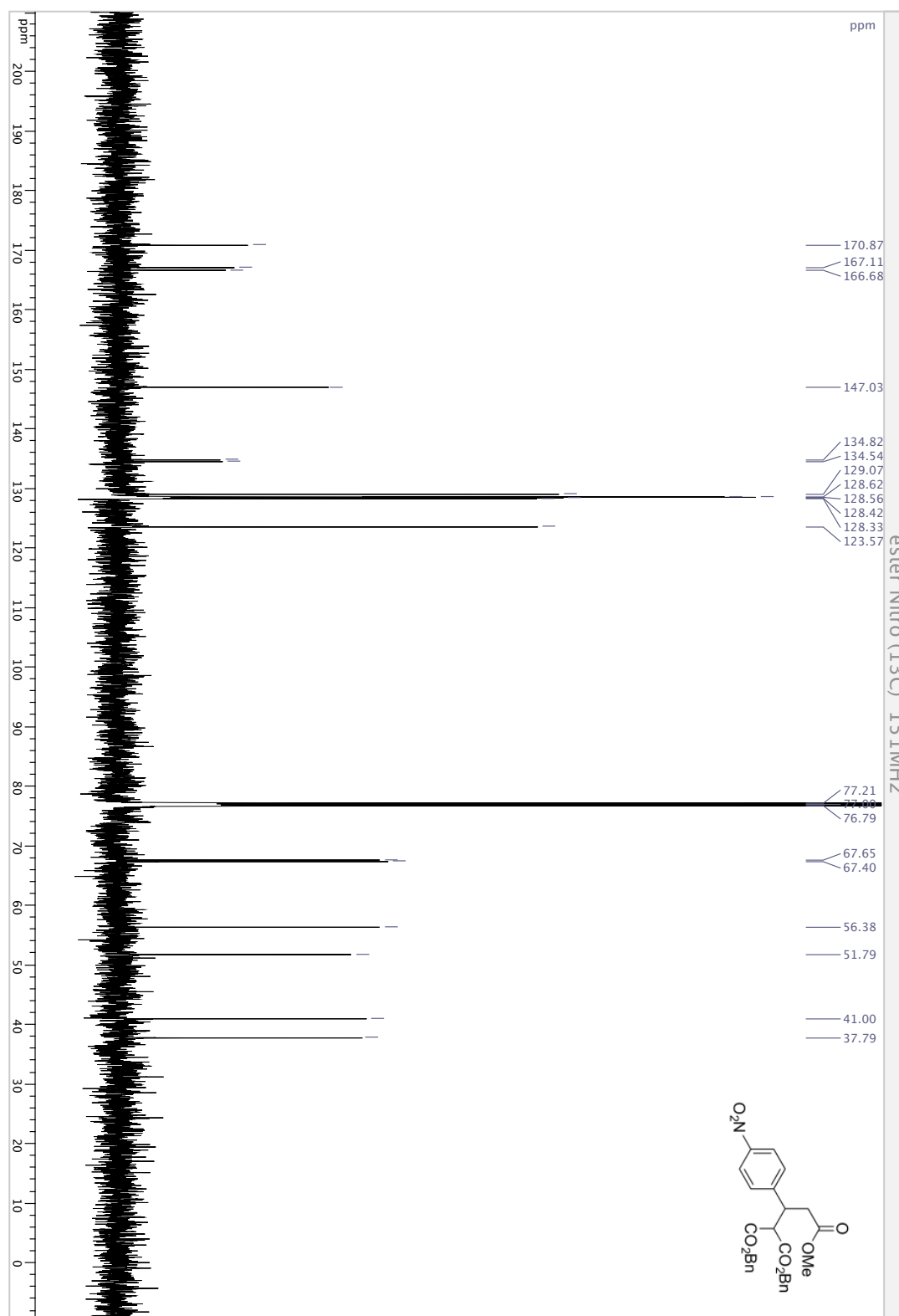
A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(R)-2-Benzyloxycarbonyl-3-(4-nitrophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



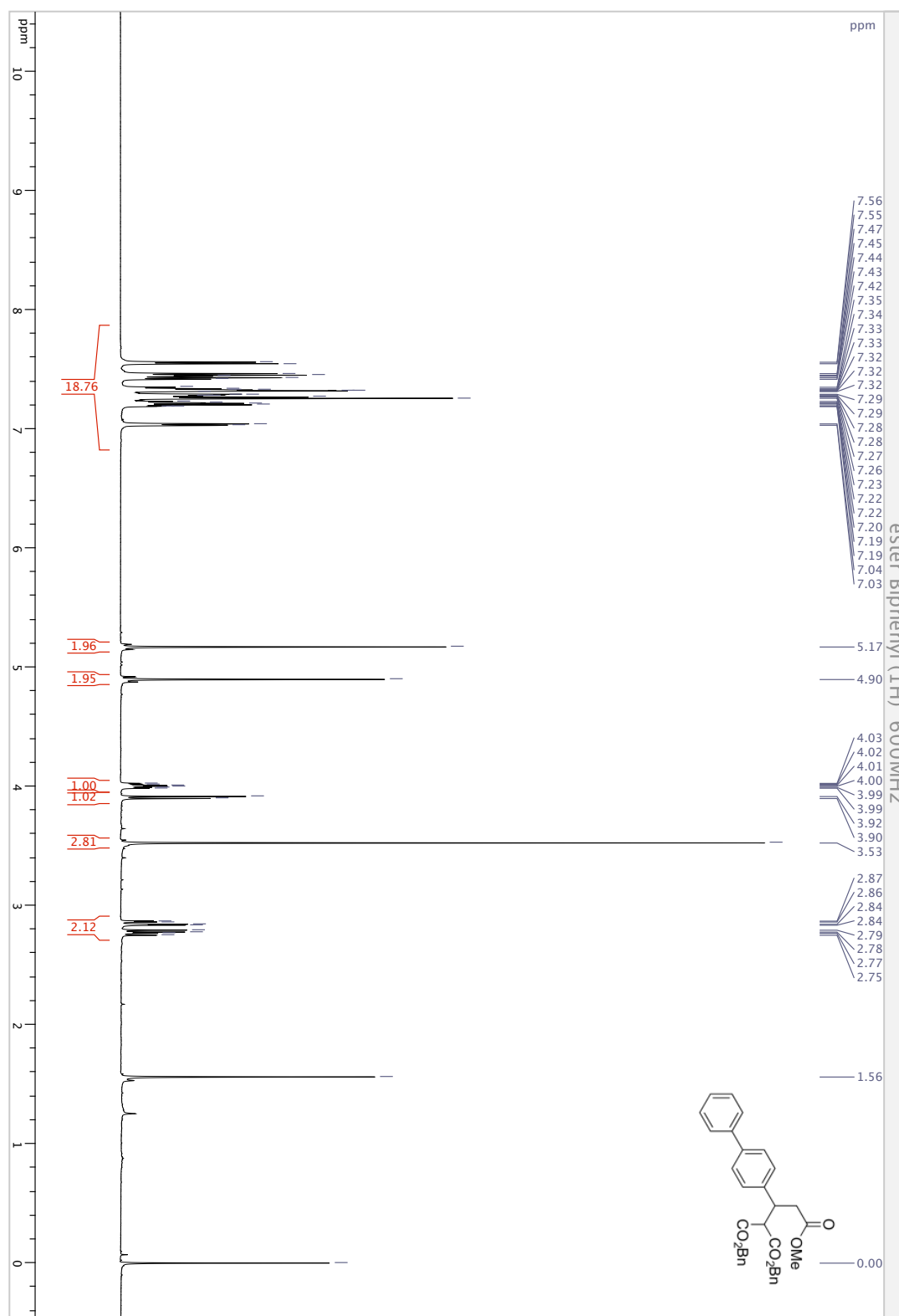
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(R)-2-Benzyloxycarbonyl-3-(4-nitrophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



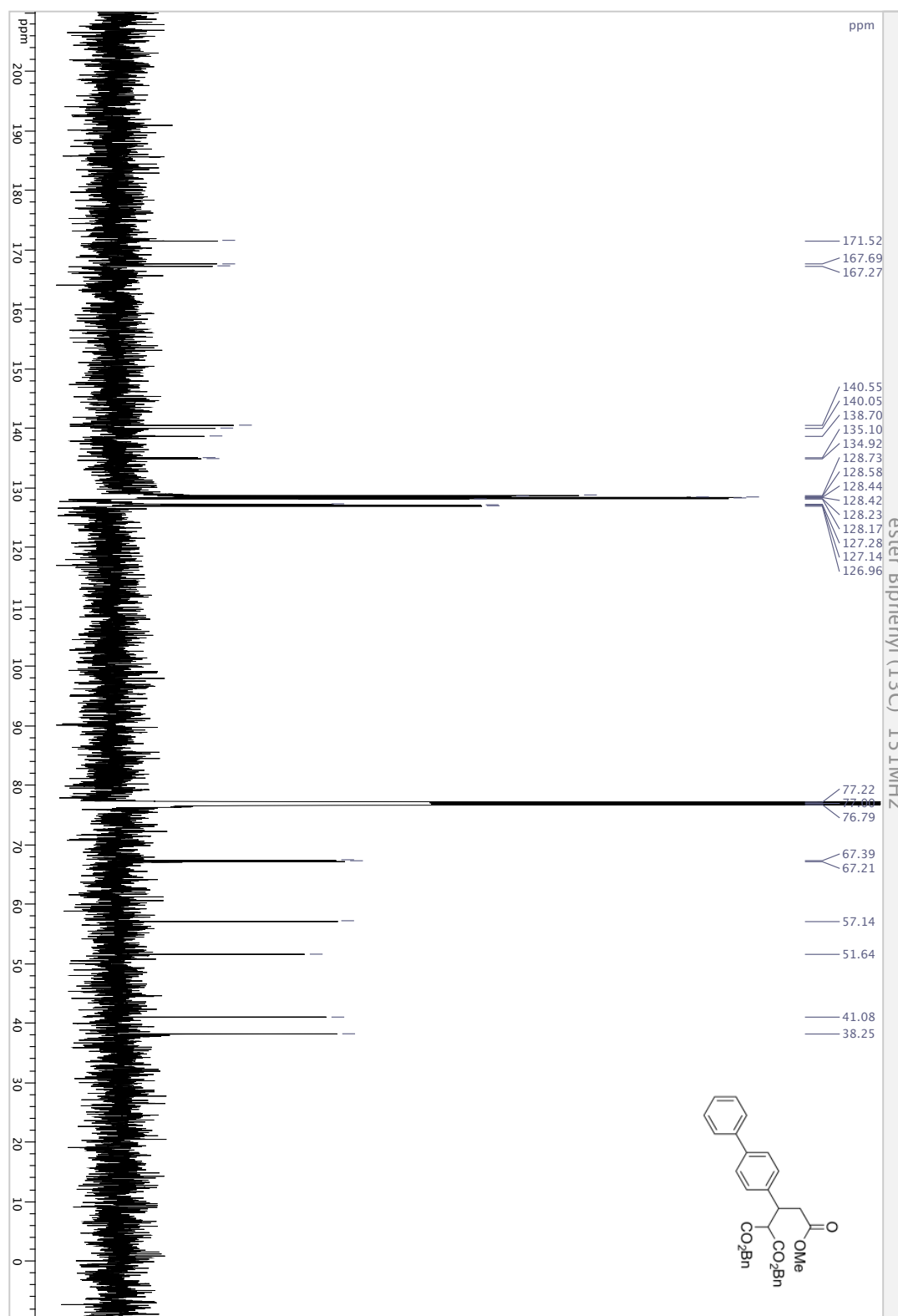
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(R)-1,1-dibenzyl 3-methyl 2-(biphenyl-4-yl)propane-1,1,3-tricarboxylate



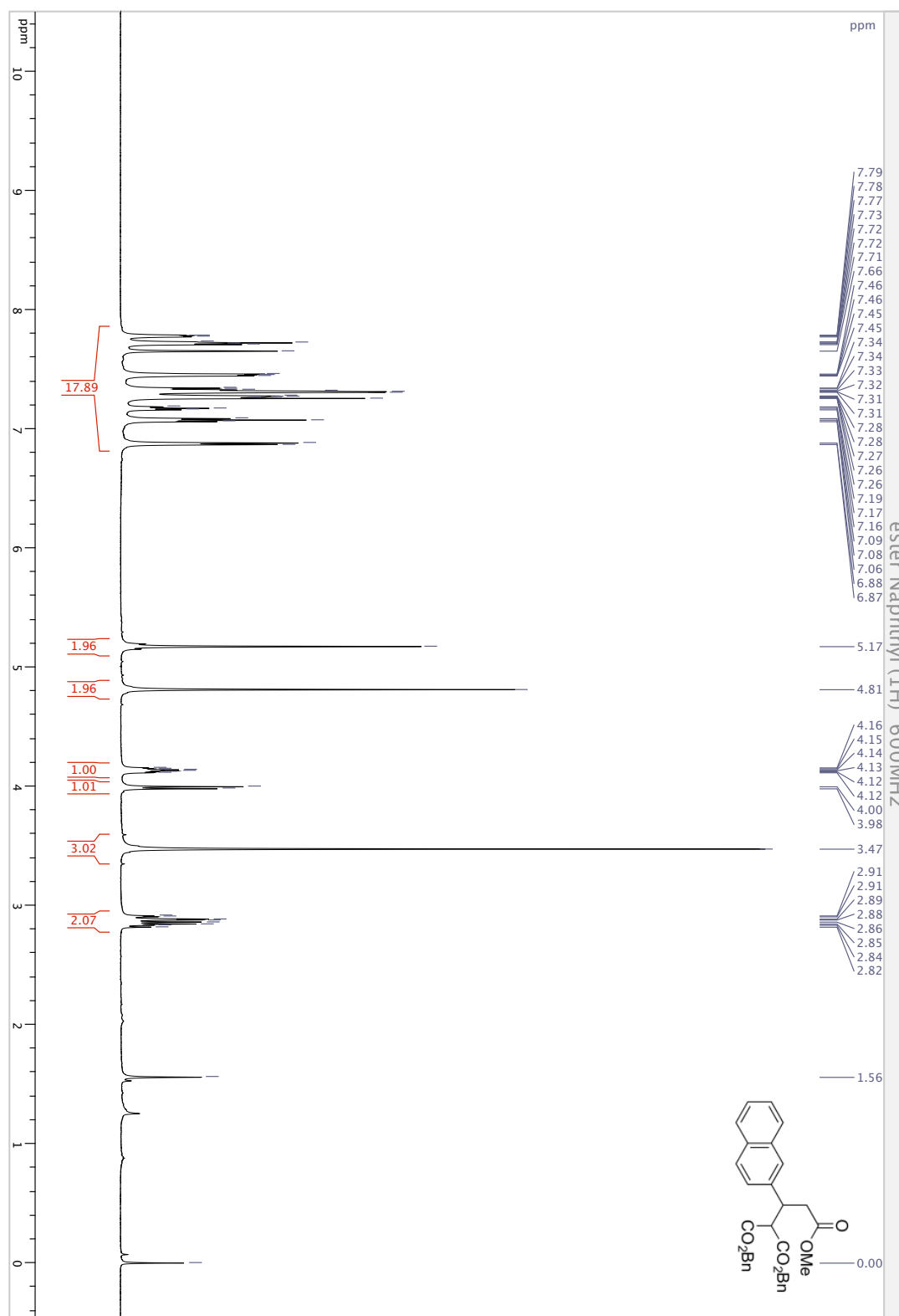
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(R)-1,1-dibenzyl 3-methyl 2-(biphenyl-4-yl)propane-1,1,3-tricarboxylate



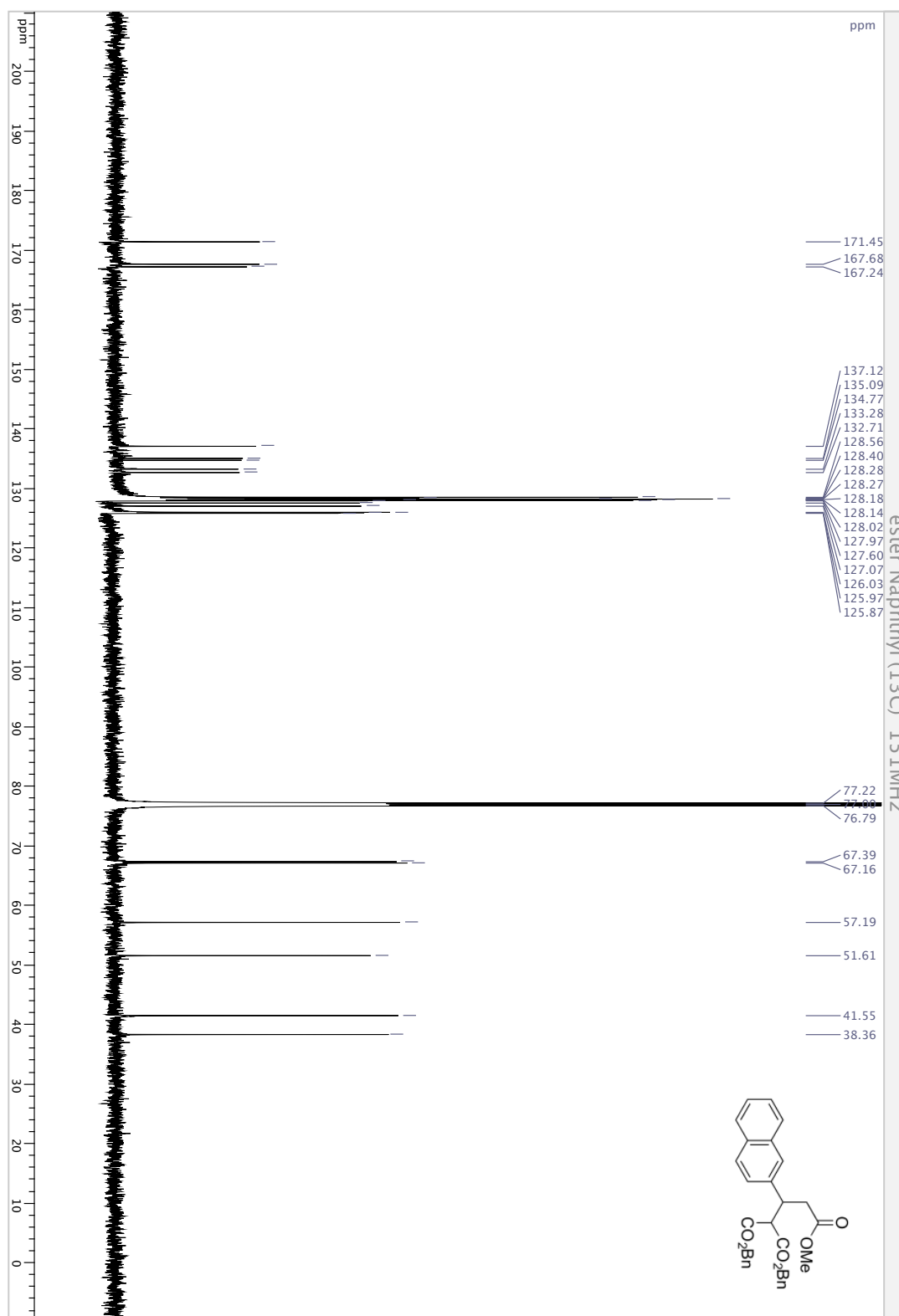
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(R)-1,1-dibenzyl 3-methyl 2-(naphthalen-2-yl)propane-1,1,3-tricarboxylate



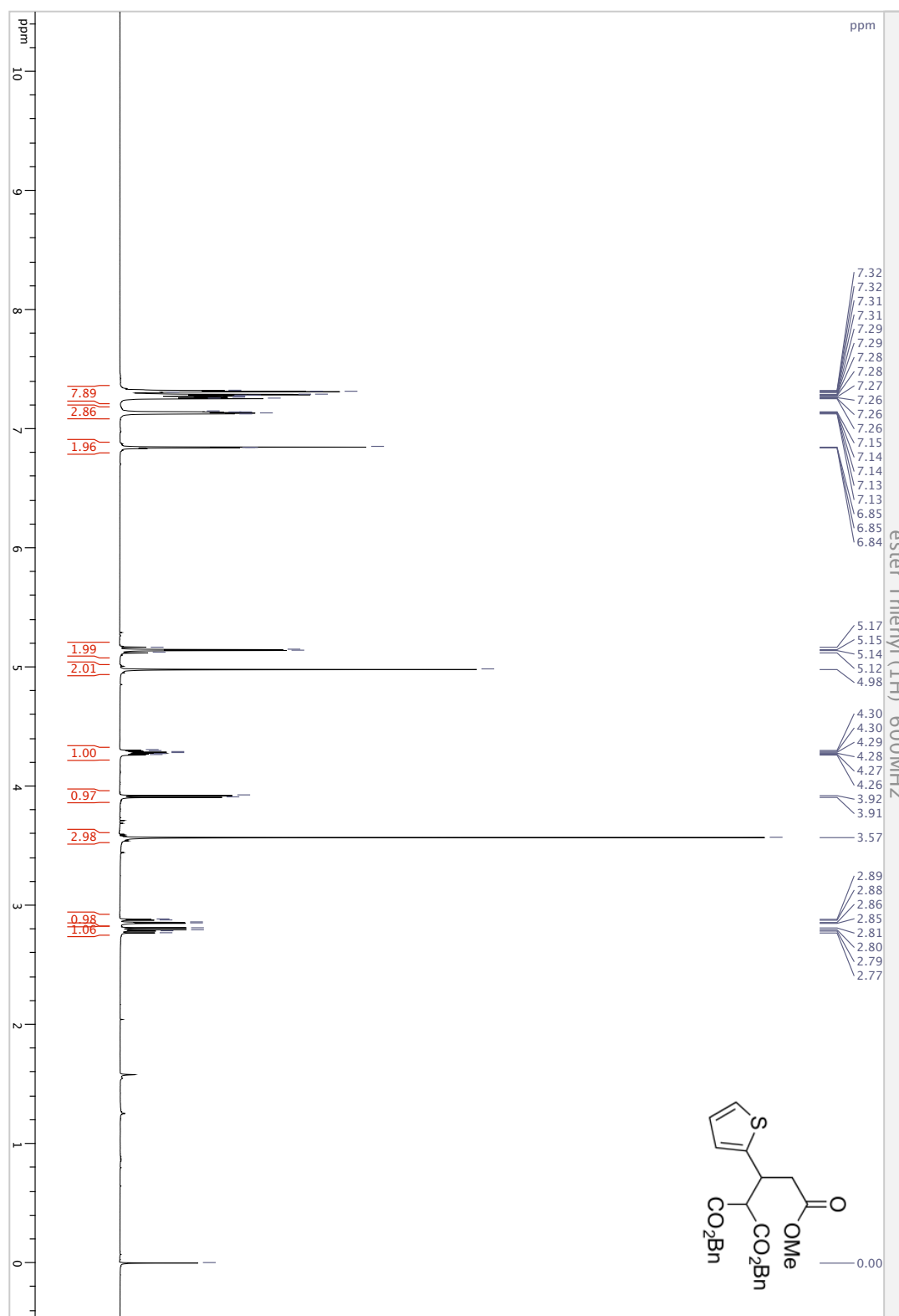
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(R)-1,1-dibenzyl 3-methyl 2-(naphthalen-2-yl)propane-1,1,3-tricarboxylate



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(R)-2-Benzoyloxycarbonyl-3-thiophen-2-ylpentanedioic acid 1-benzyl ester 5-methyl ester



ester Thienyl (13C) 151MHz

Chemical structure: COC(=O)CC(C(=O)OCC1=CC=CC=C1)C(=O)OCC2=CC=CC=C2

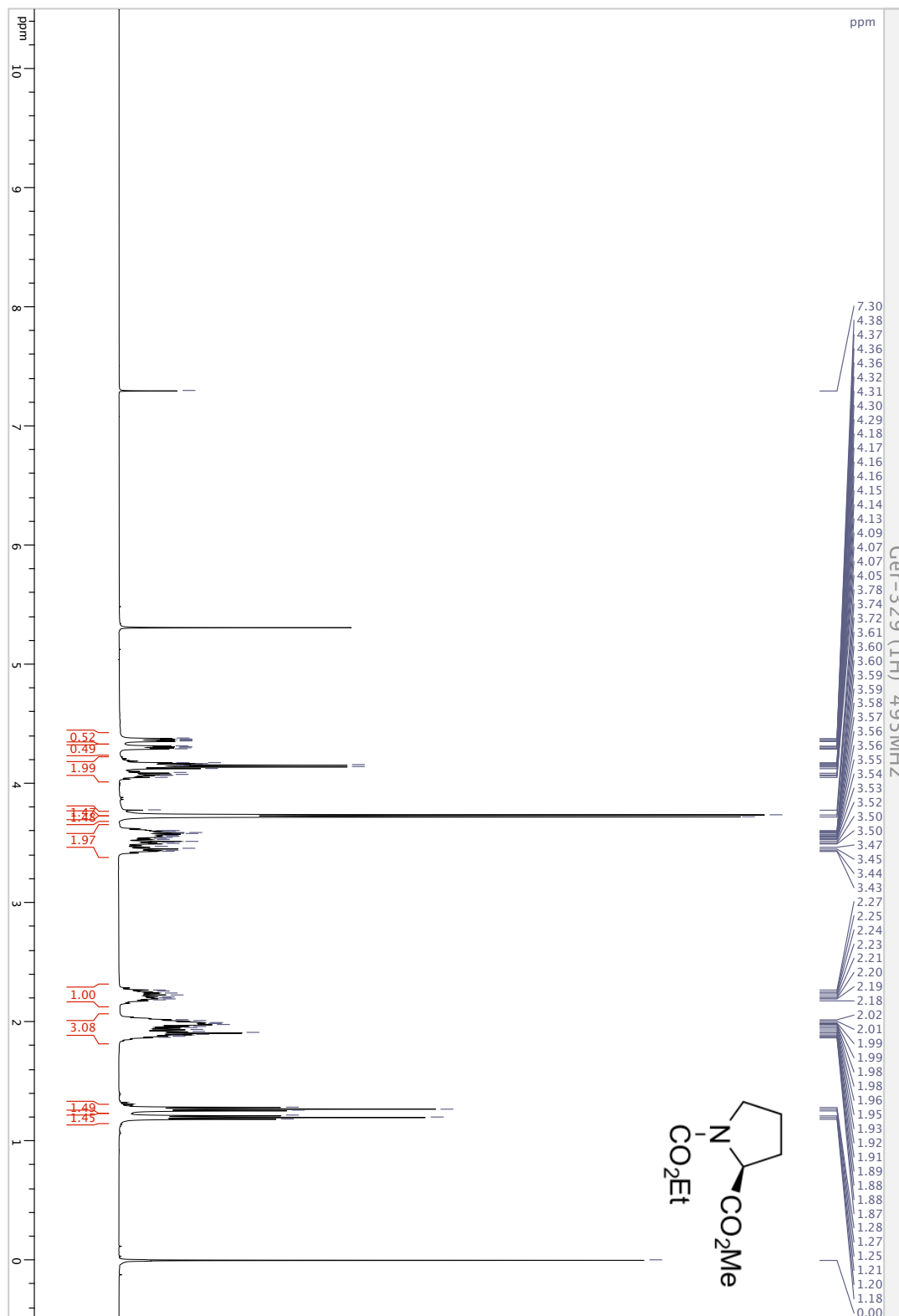
Peak list (ppm):

Peak (ppm)
171.28
167.35
167.05
142.51
135.00
134.96
128.54
128.45
128.40
128.27
128.21
128.17
126.65
125.80
124.42
77.21
77.00
76.79
67.40
67.29
57.58
51.73
39.04
36.74

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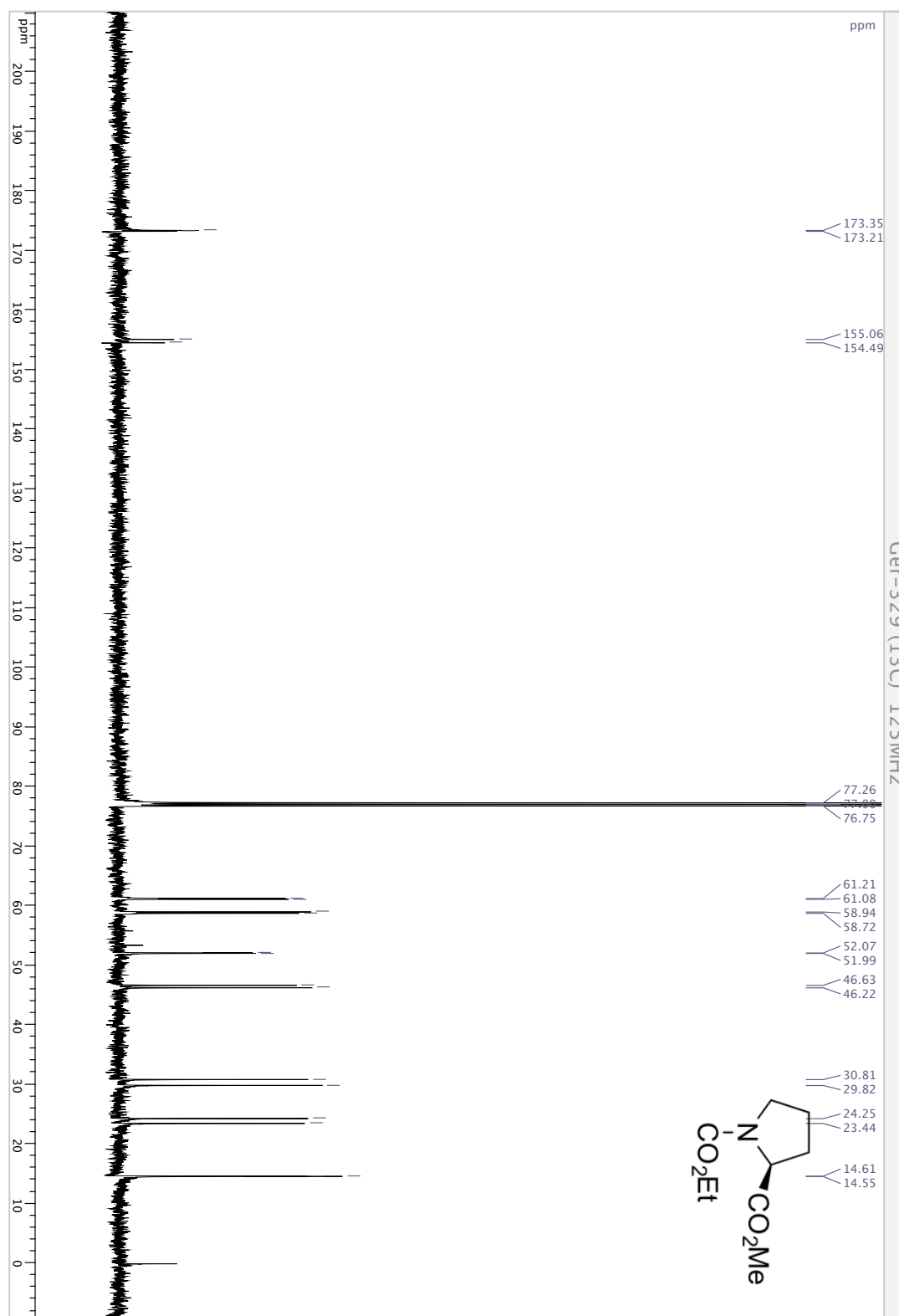
B3 NMR Spectra of Compounds Leading Up to (*S*)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether (1)

***N*-Ethoxycarbonyl-L-proline methyl ester**



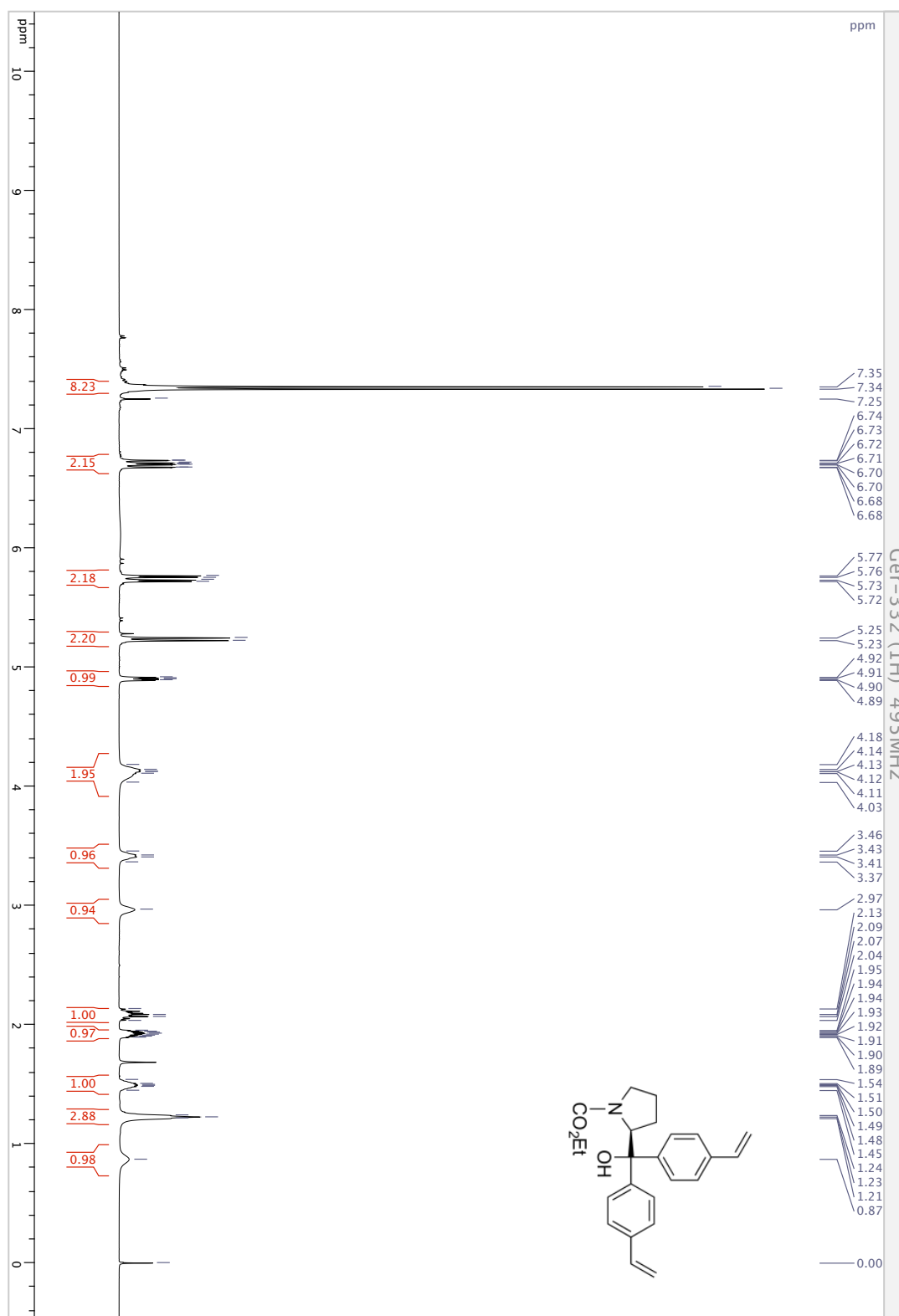
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***N*-Ethoxycarbonyl-L-proline methyl ester**



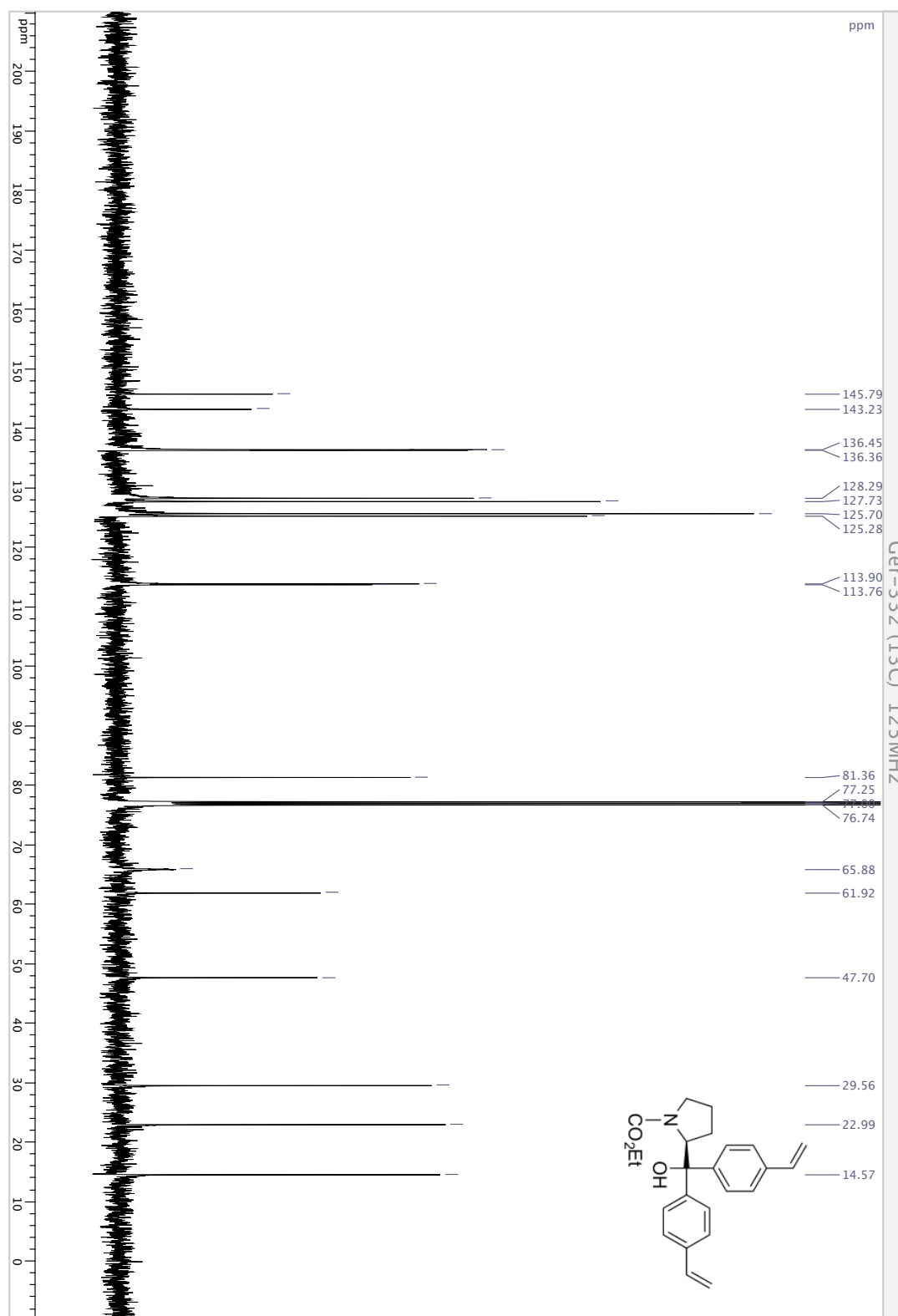
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(S)-N-Ethoxycarbonyl- α,α -bis(4-vinylphenyl)prolinol



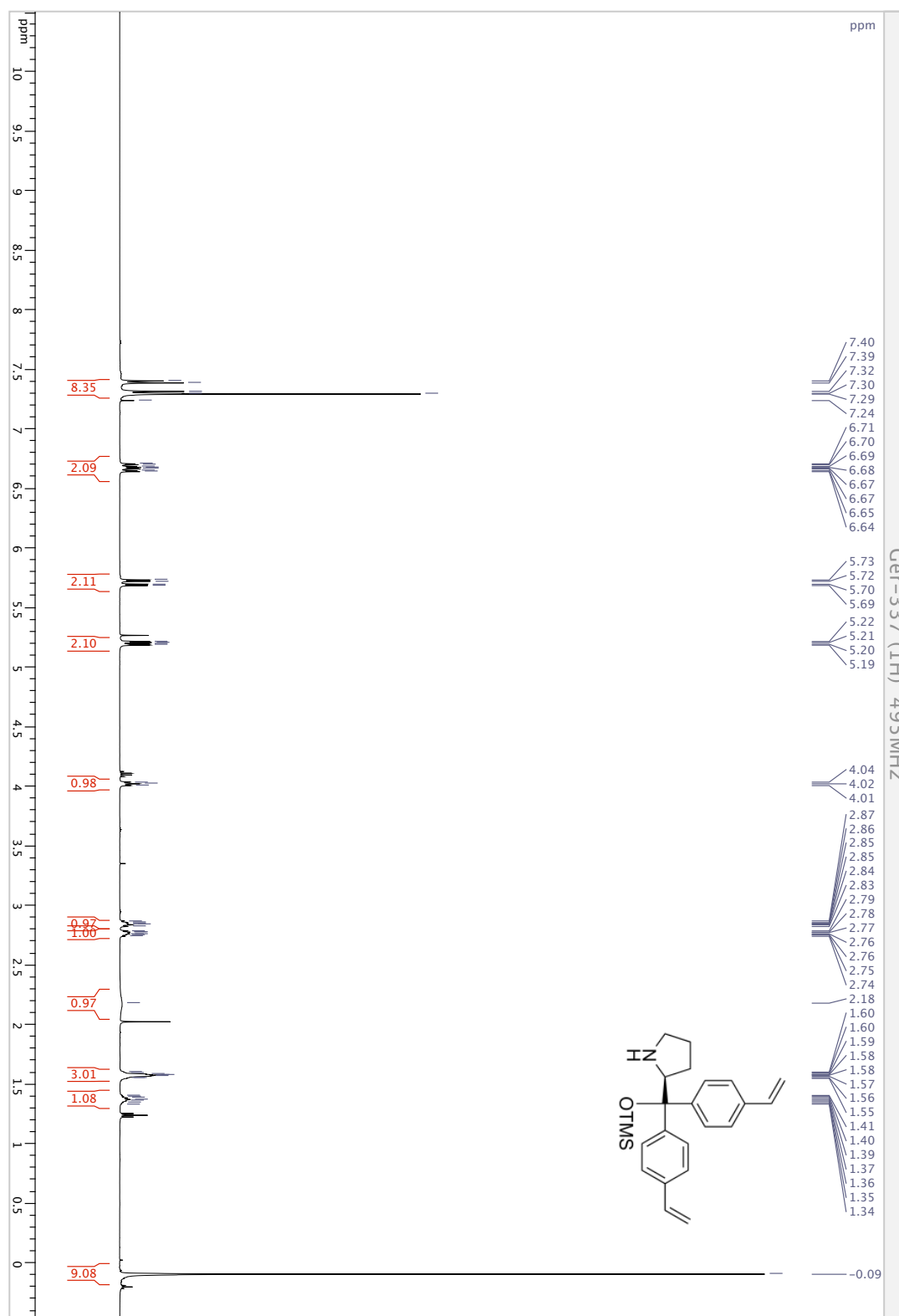
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(S)-N-Ethoxycarbonyl- α,α -bis(4-vinylphenyl)prolinol

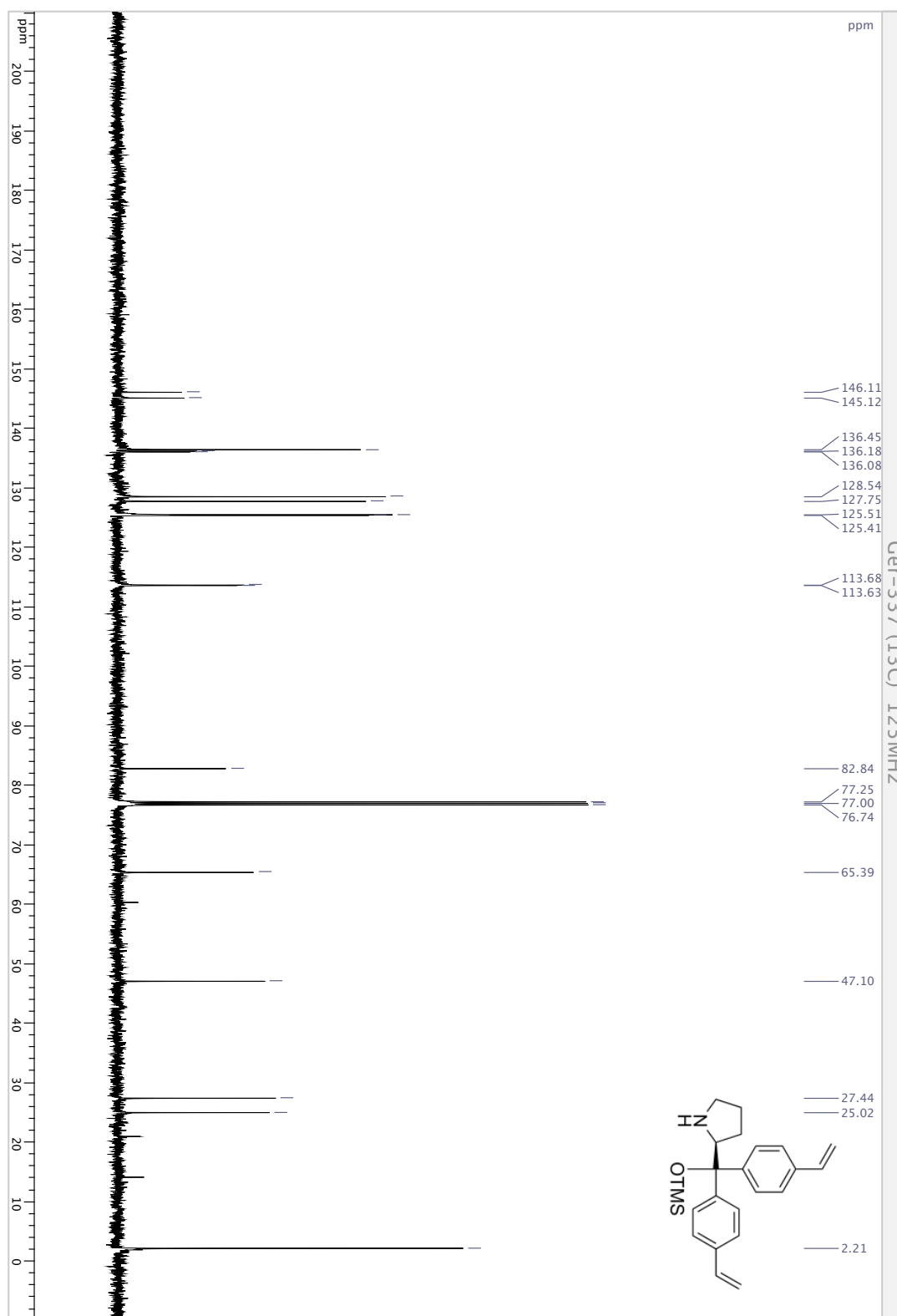


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(S)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether



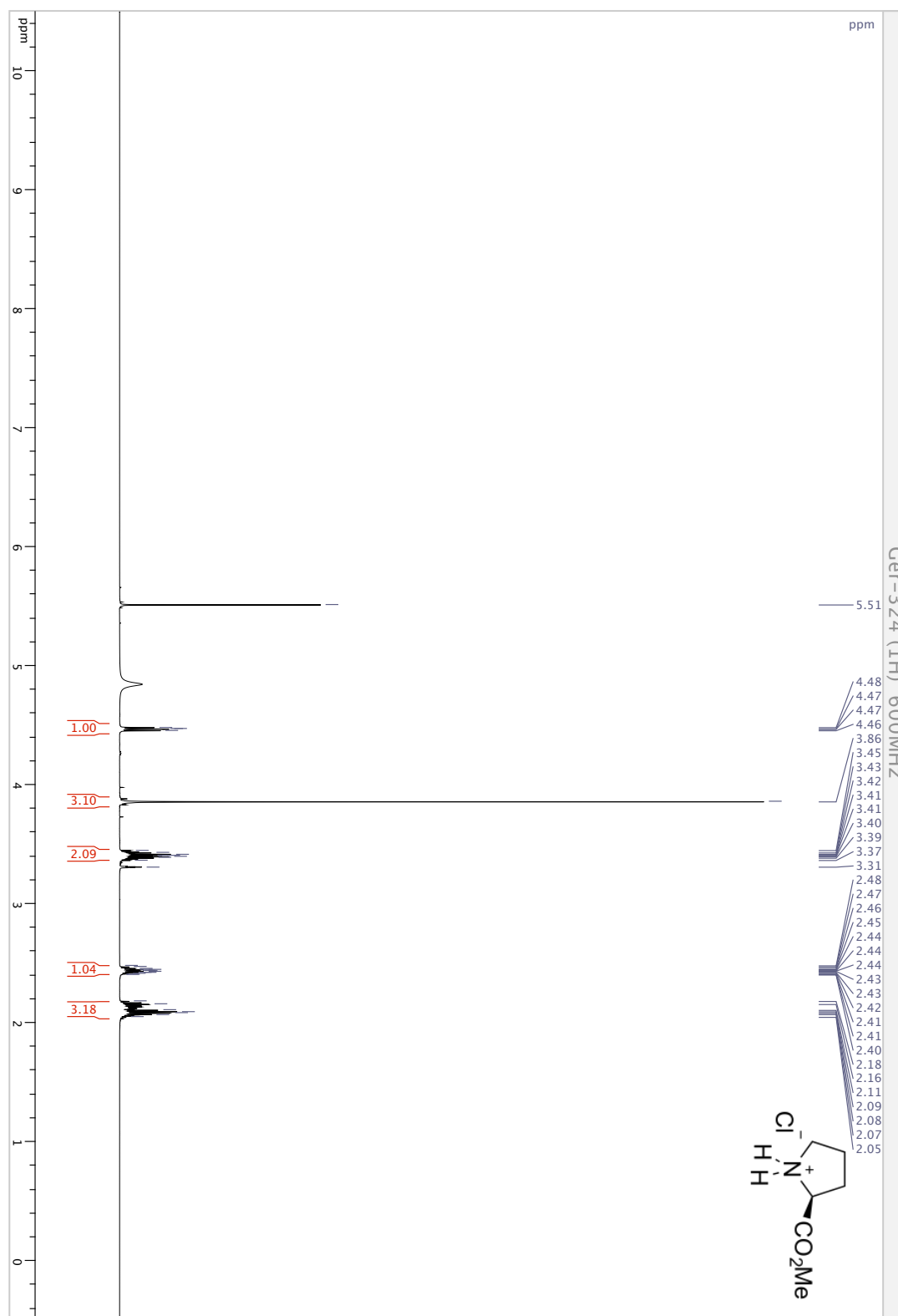
(S)- α,α -Bis(4-vinylphenyl)prolinol trimethylsilyl ether



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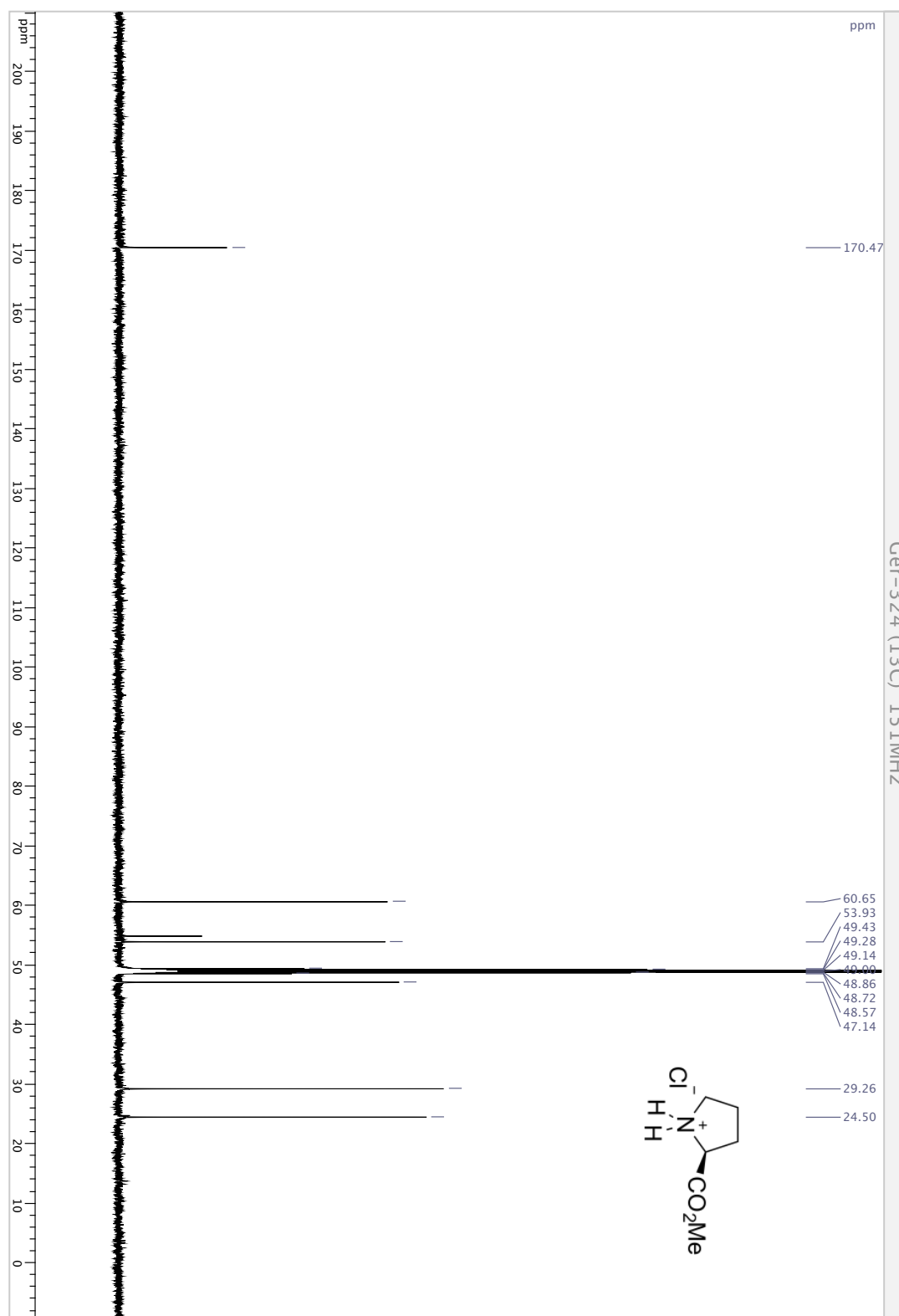
B4 NMR Spectra of Compounds Leading Up to (S)- α,α -Diphenylprolinol 4-vinylbenzyl ether (A)

L-proline methyl ester hydrochloride



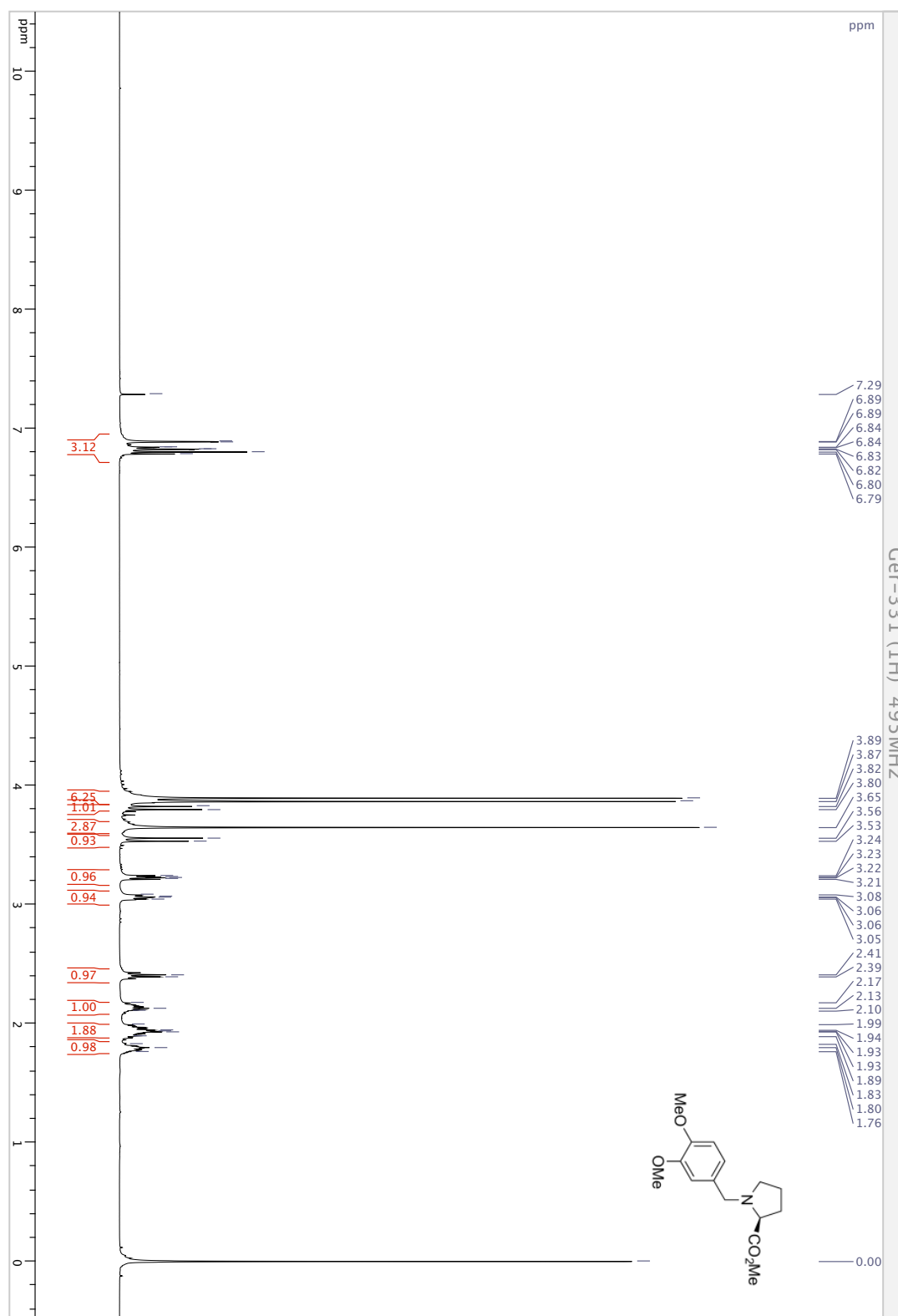
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L-proline methyl ester hydrochloride



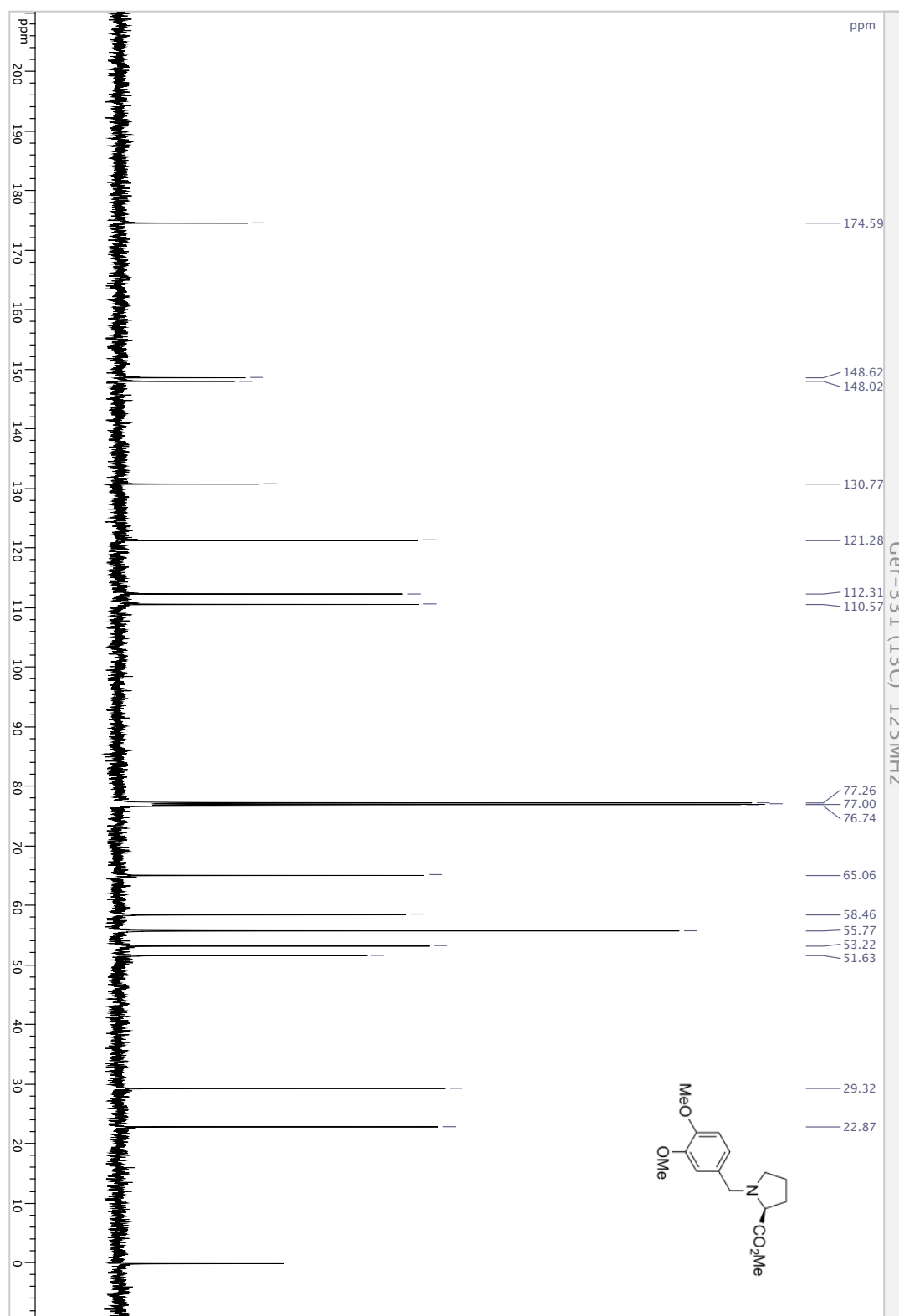
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

***N*-(3,4-Dimethoxybenzyl)-L-proline methyl ester**



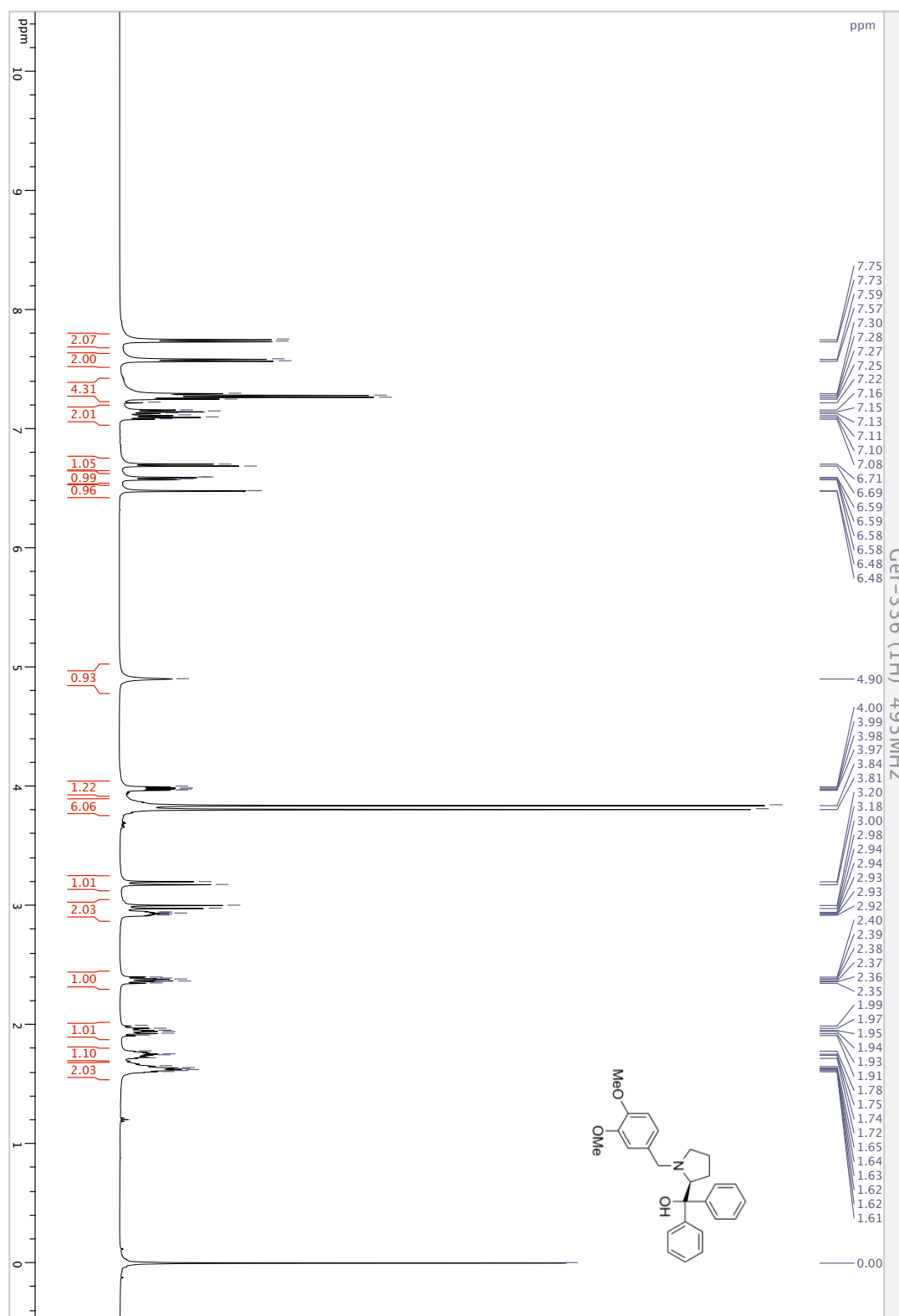
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***N*-(3,4-Dimethoxybenzyl)-L-proline methyl ester**



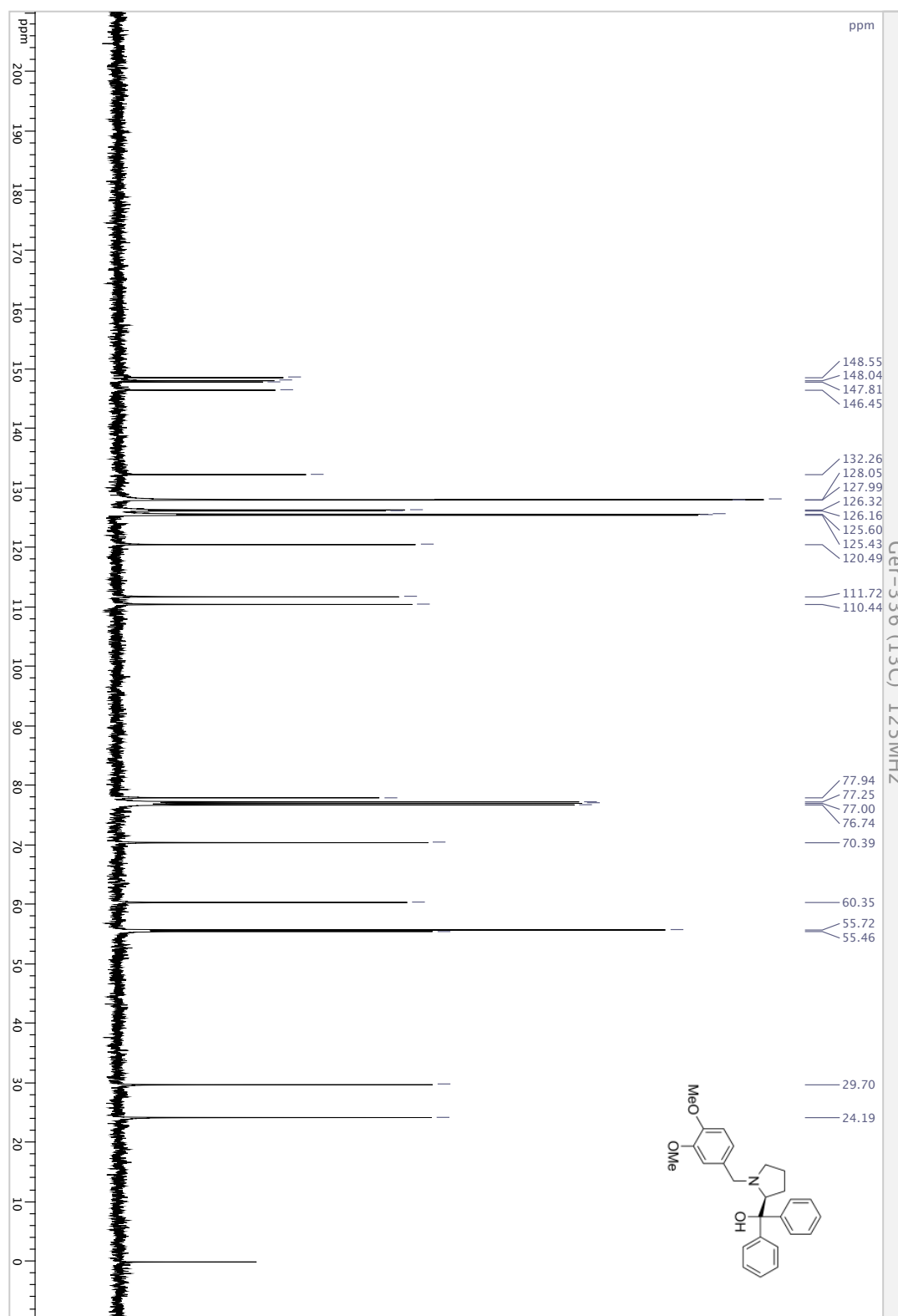
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(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol



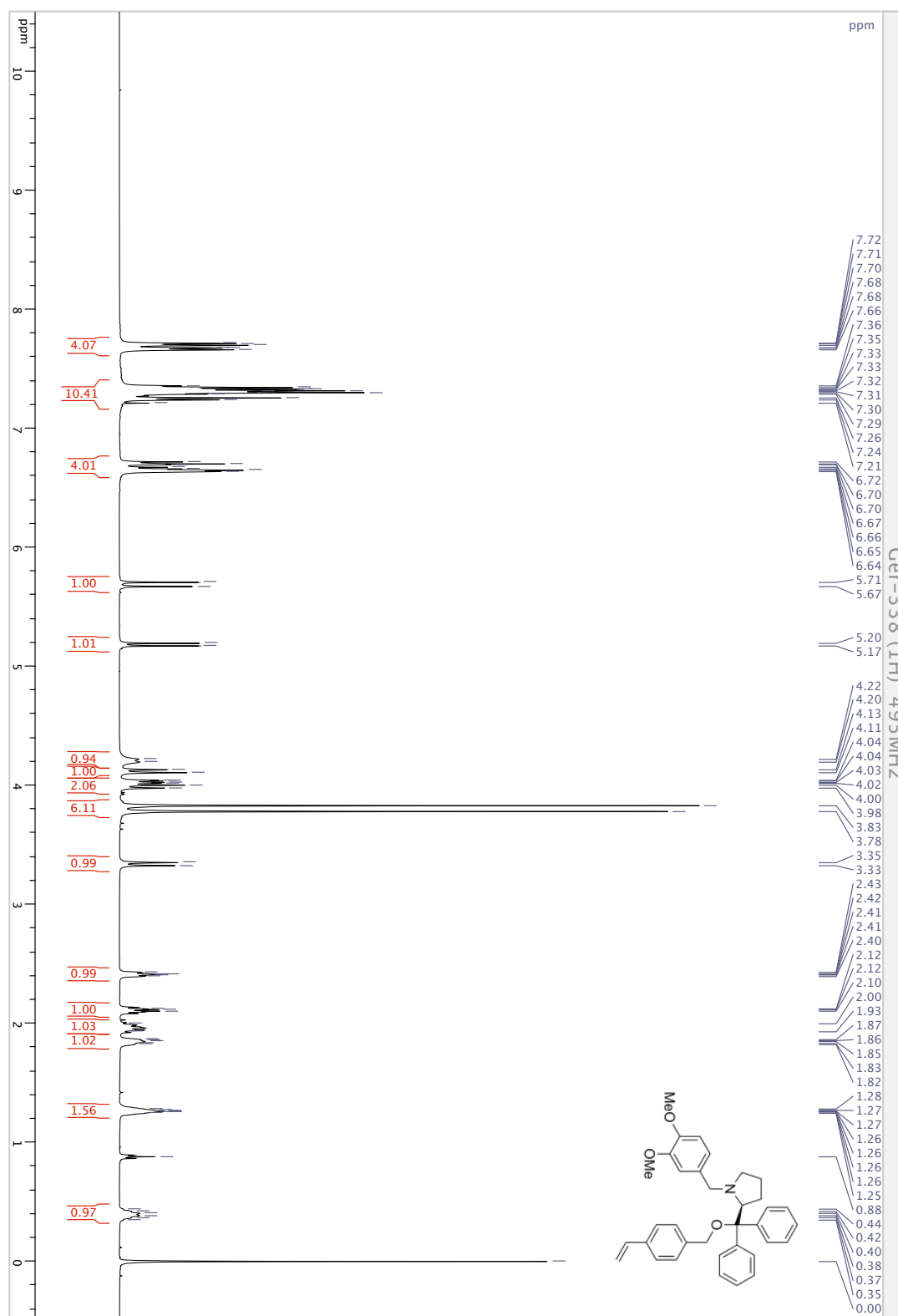
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(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol



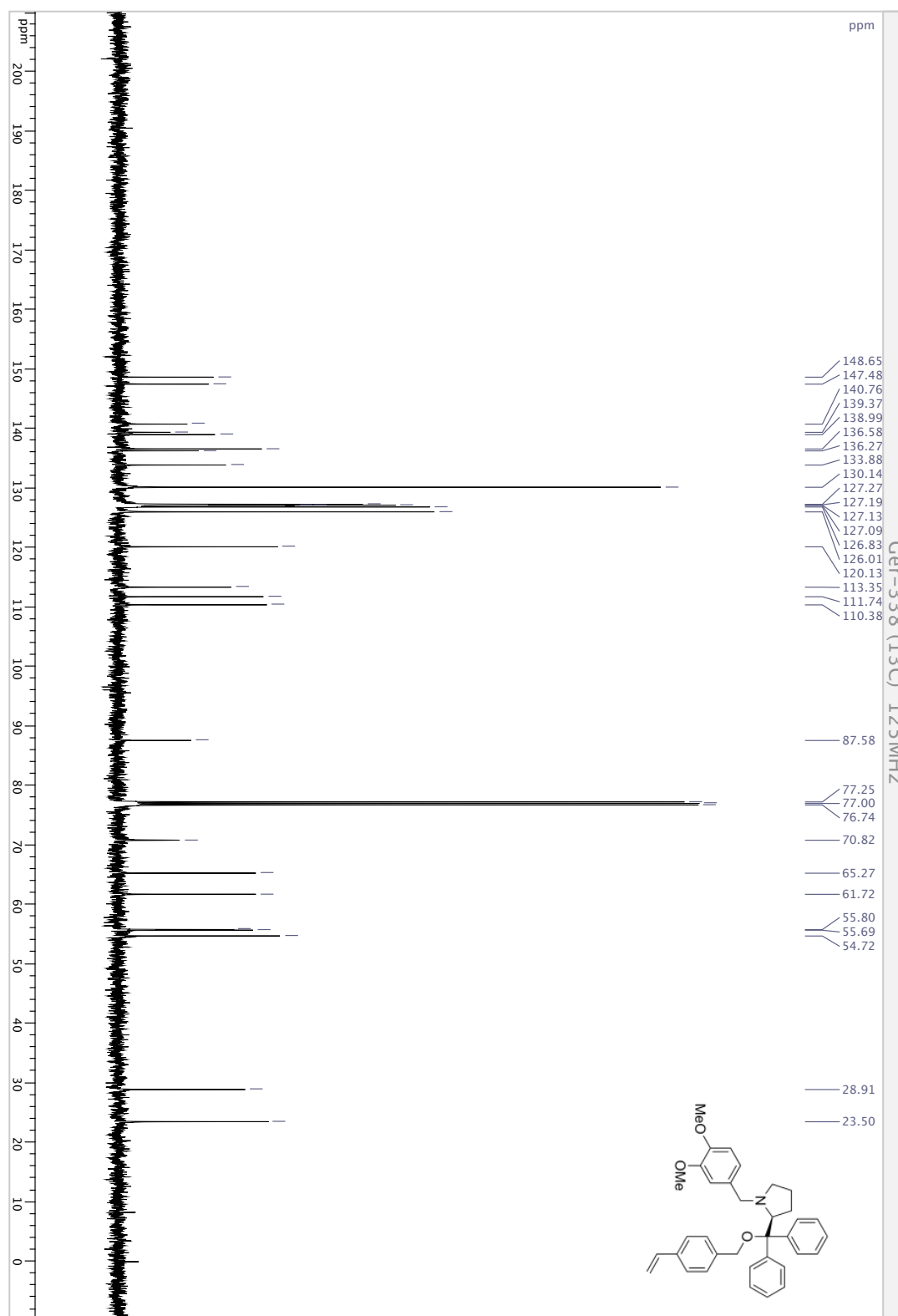
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(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol 4-vinylbenzyl ether

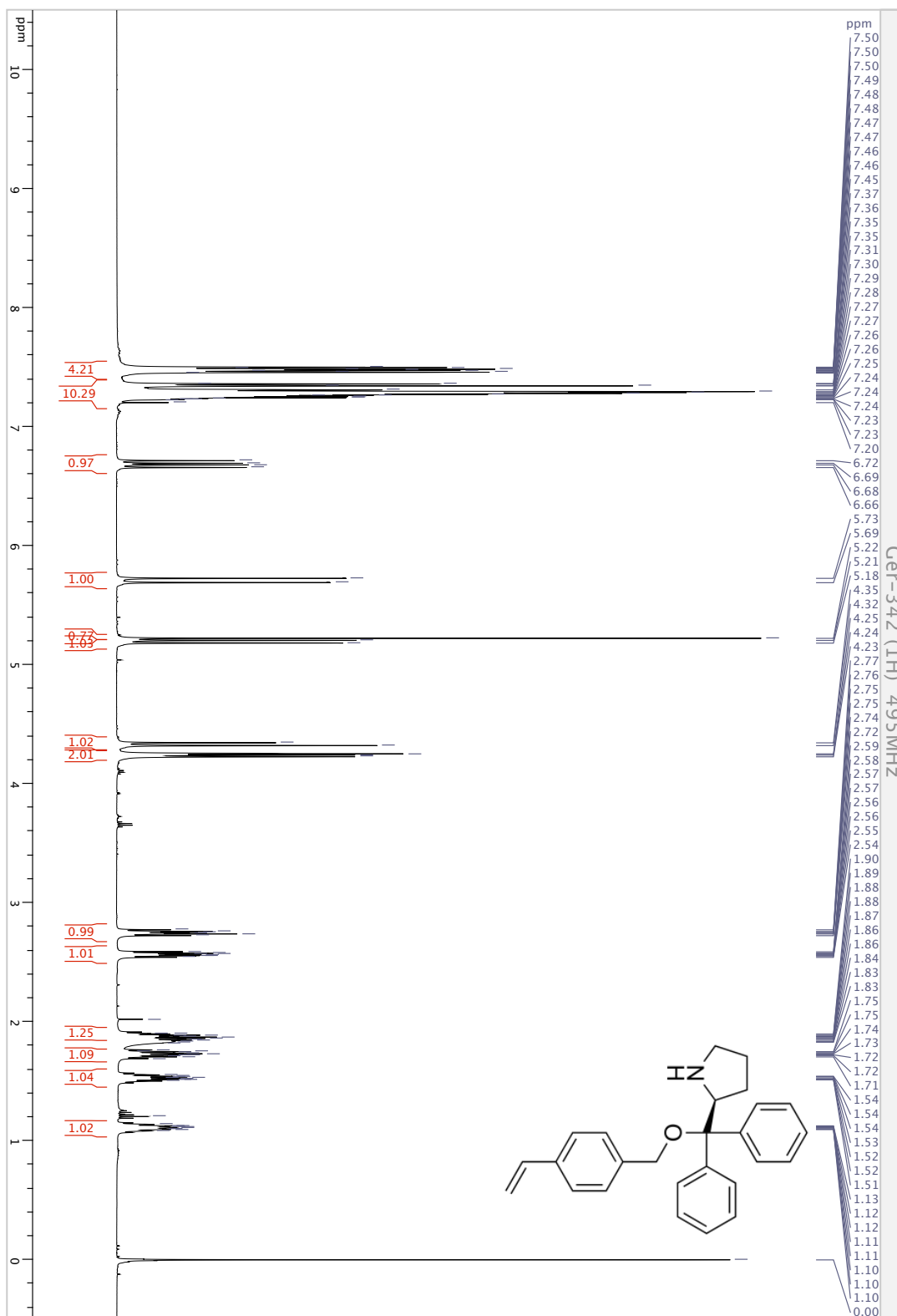


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(S)-N-(3,4-Dimethoxybenzyl)- α,α -diphenylprolinol 4-vinylbenzyl ether

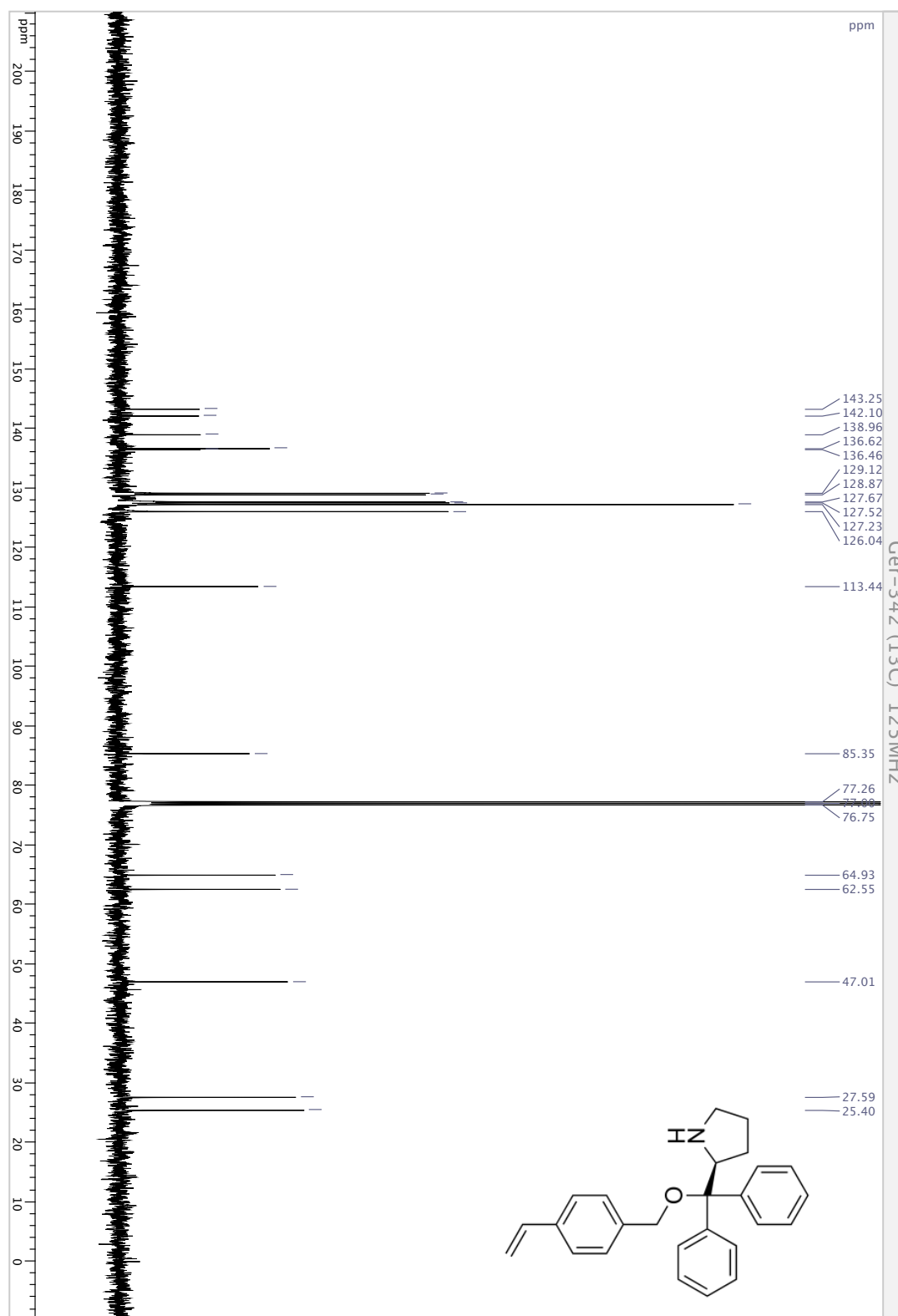


(S)- α,α -Diphenylprolinol 4-vinylbenzyl ether



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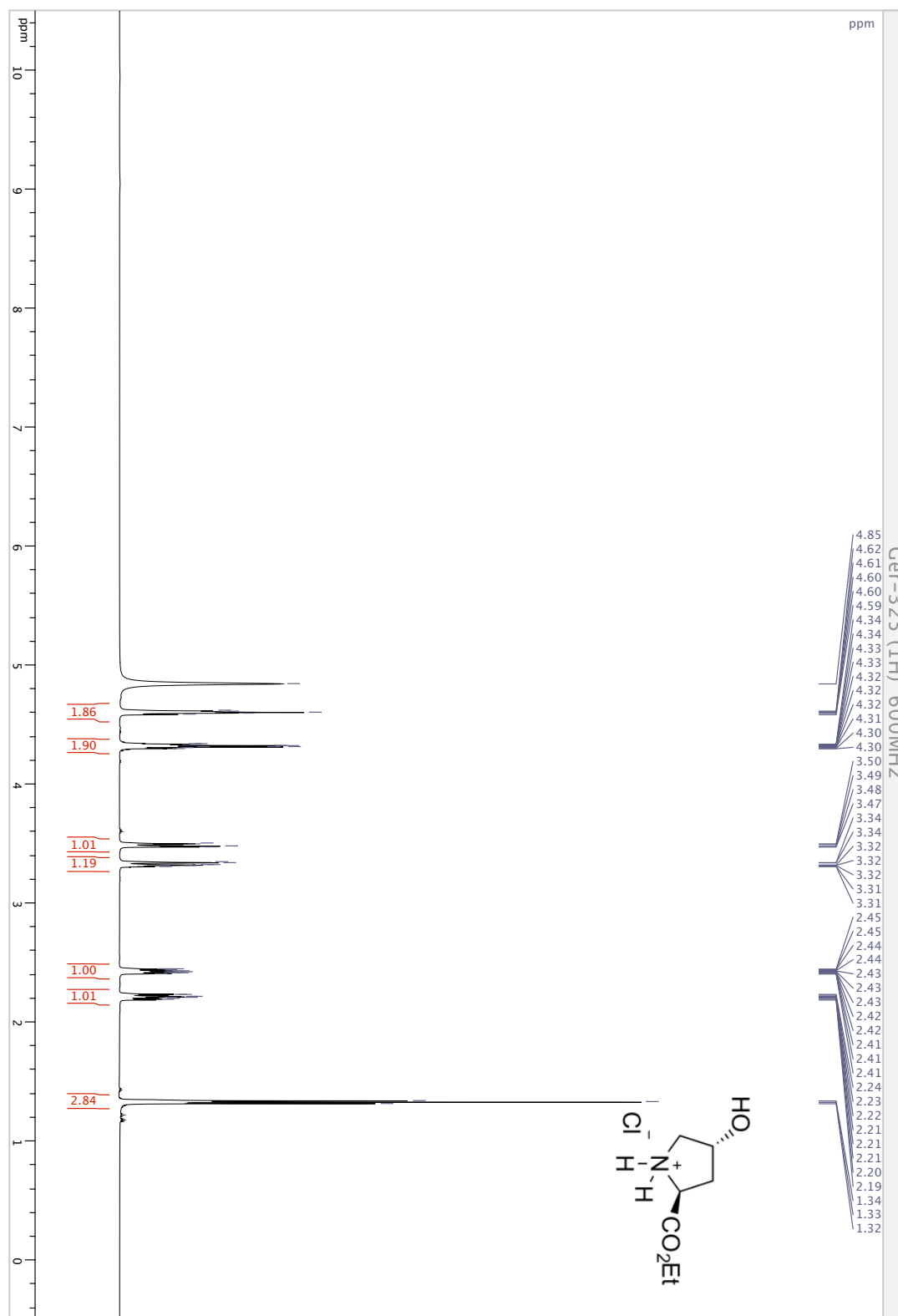
(S)- α,α -Diphenylprolinol 4-vinylbenzyl ether



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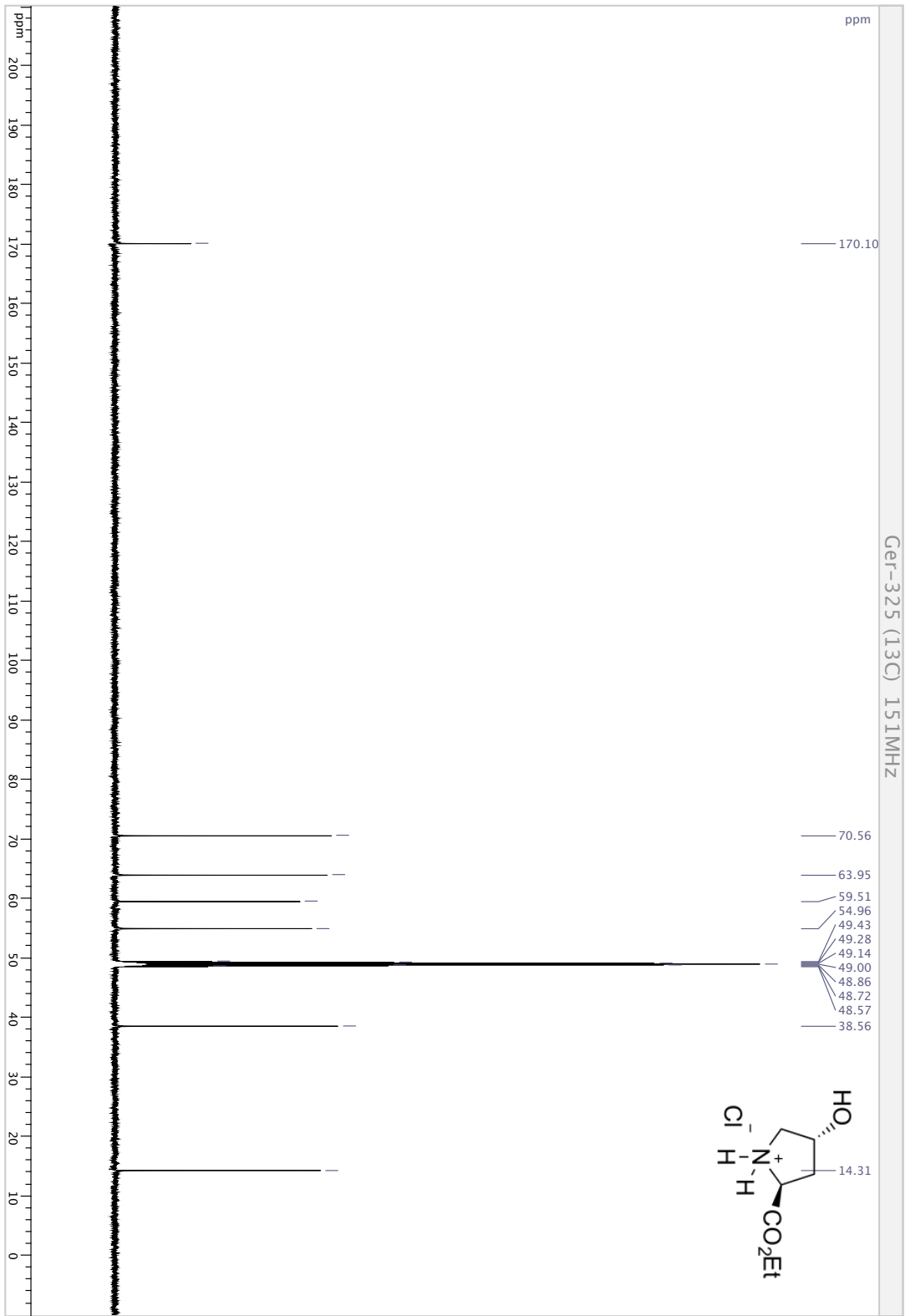
B5 NMR Spectra of Compounds Leading Up to *O*-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol trimethylsilyl ether (B)

***trans*-4-Hydroxy-L-proline ethyl ester hydrochloride**



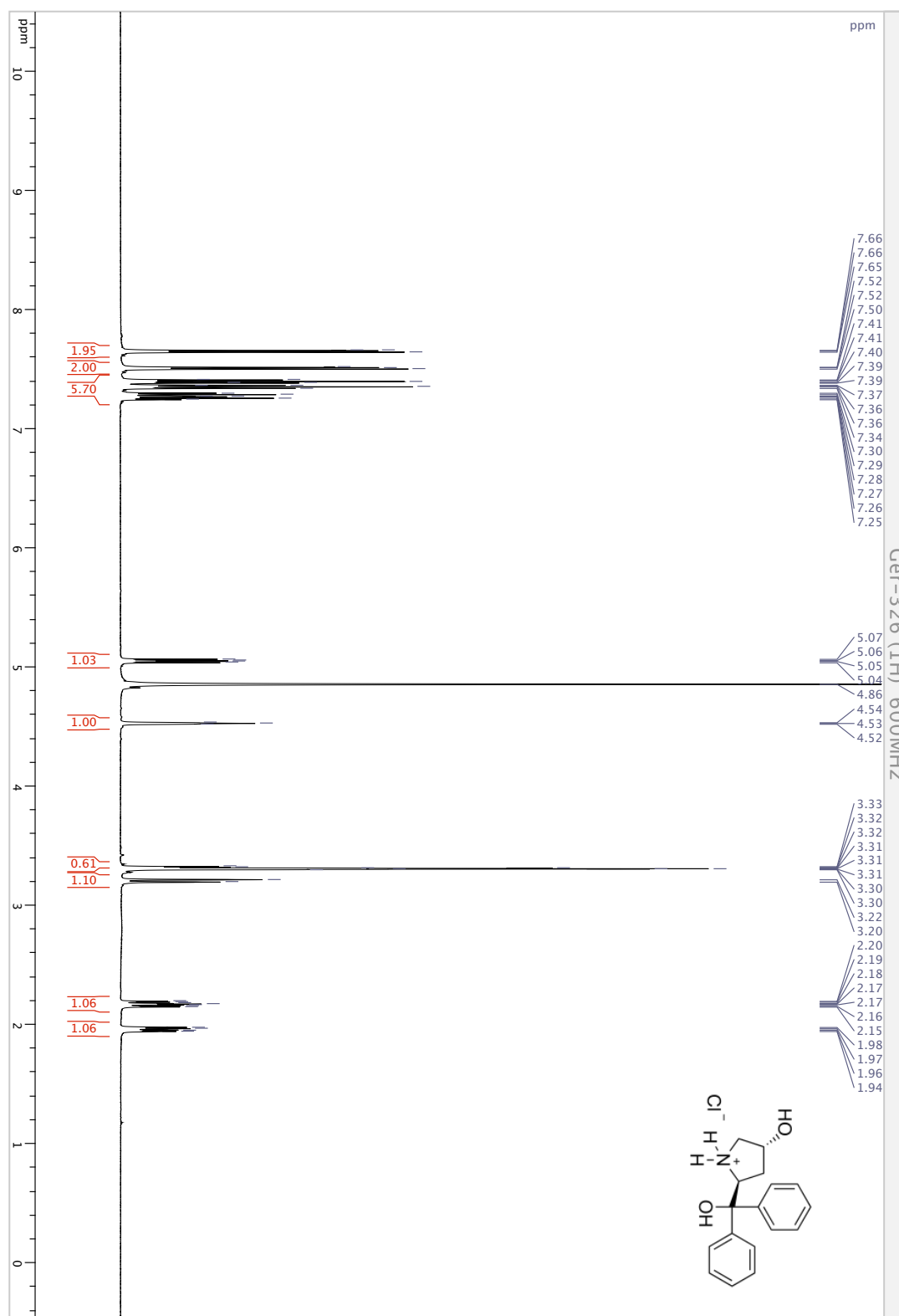
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***trans*-4-Hydroxy-L-proline ethyl ester hydrochloride**



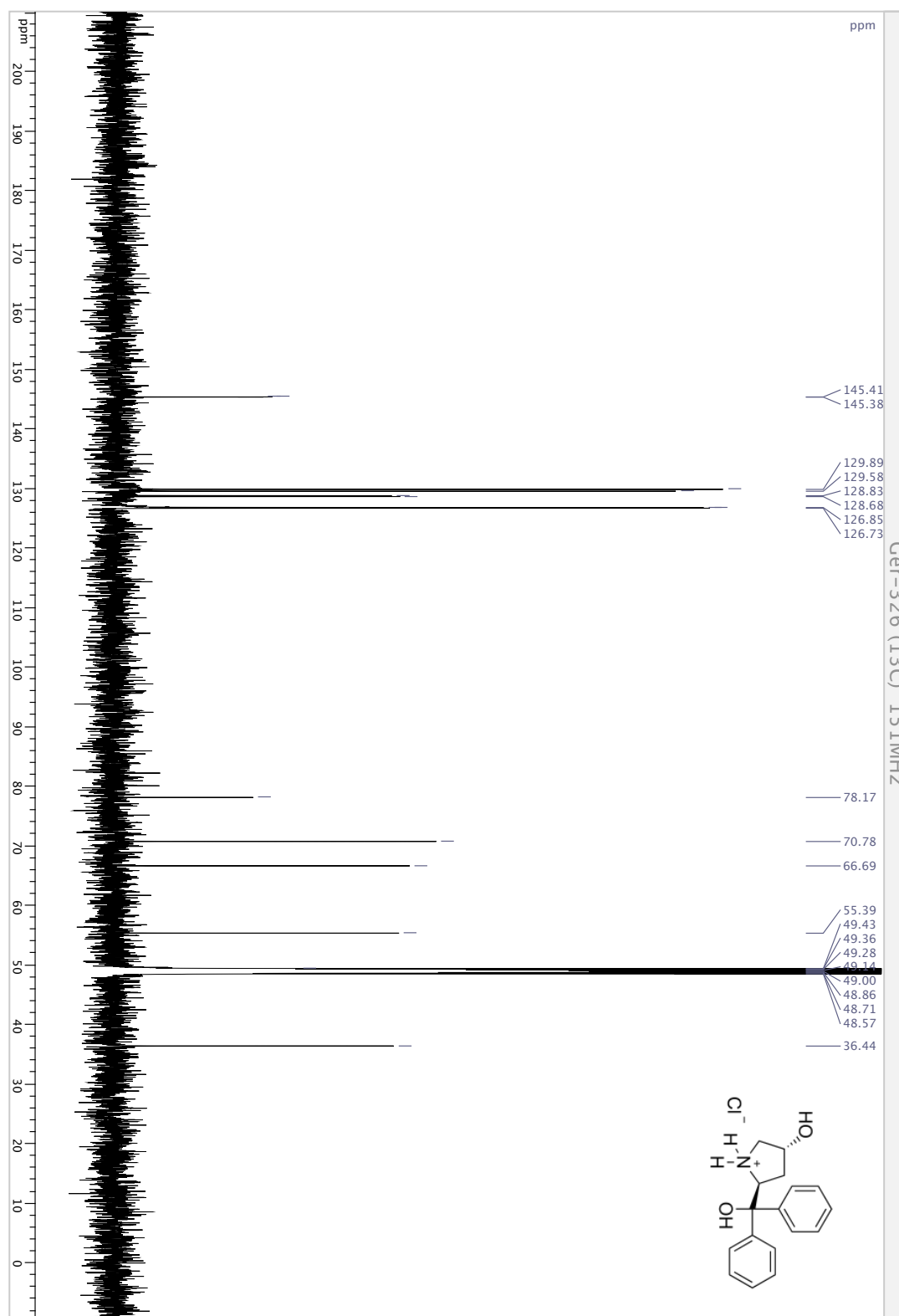
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***trans*-4-Hydroxy- α,α -diphenyl-L-prolinol hydrochloride**



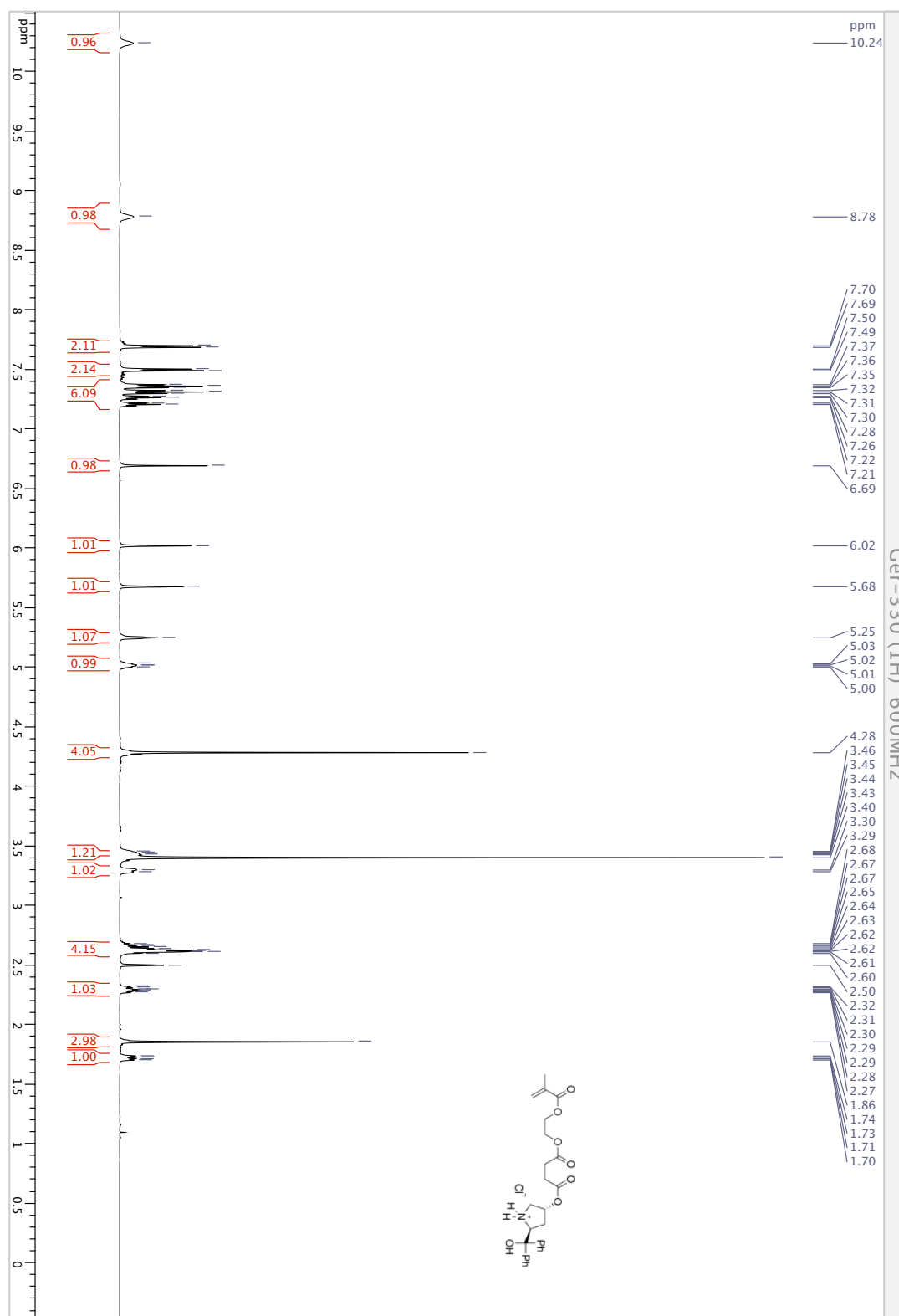
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***trans*-4-Hydroxy- α,α -diphenyl-L-prolinol hydrochloride**



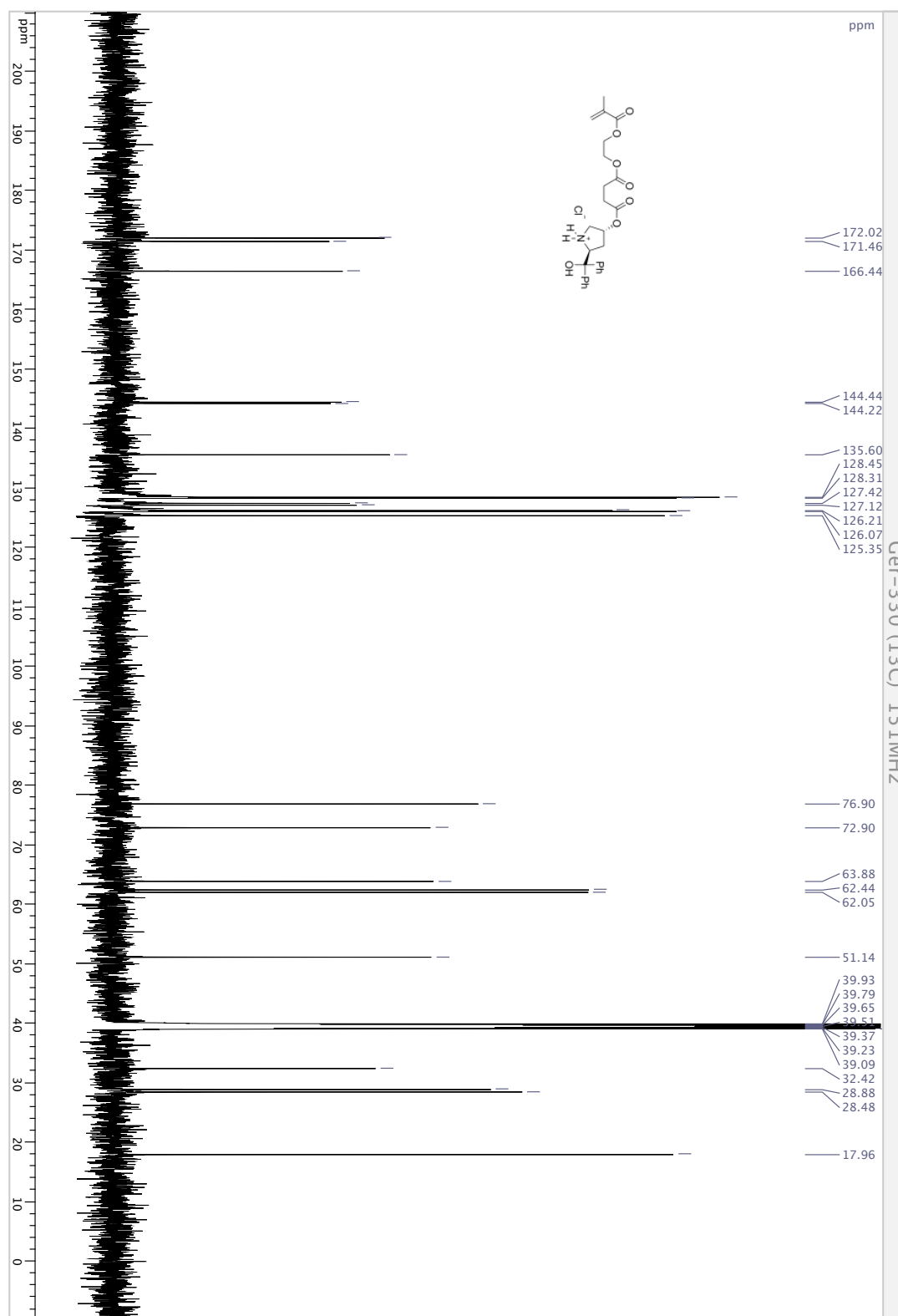
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***O*-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol hydrochloride**



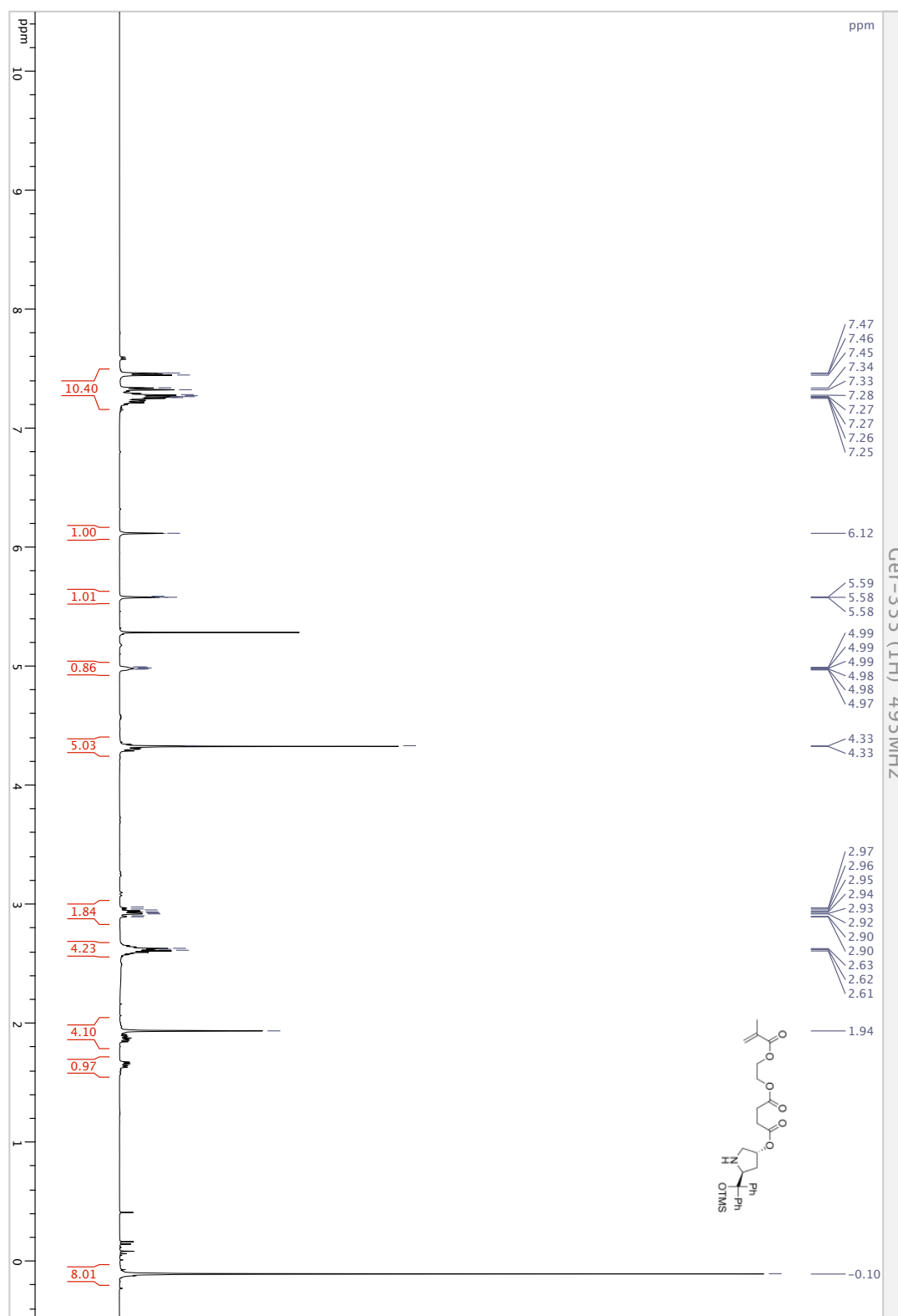
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***O*-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol hydrochloride**



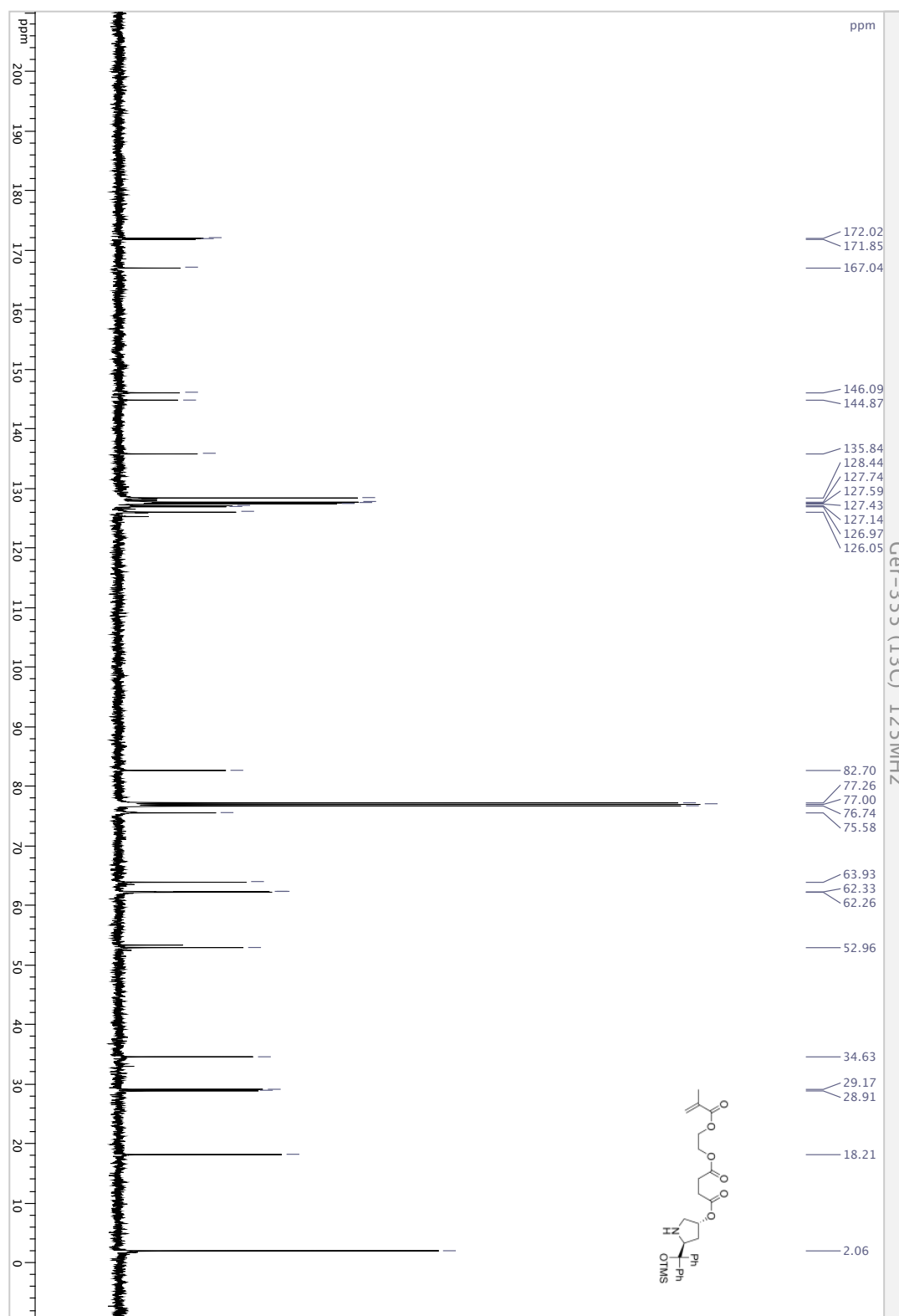
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***O*-(2-Methacryloyloxyethylsuccinoyl)-*trans*-4-hydroxy- α,α -diphenyl-L-prolinol trimethylsilyl ether**



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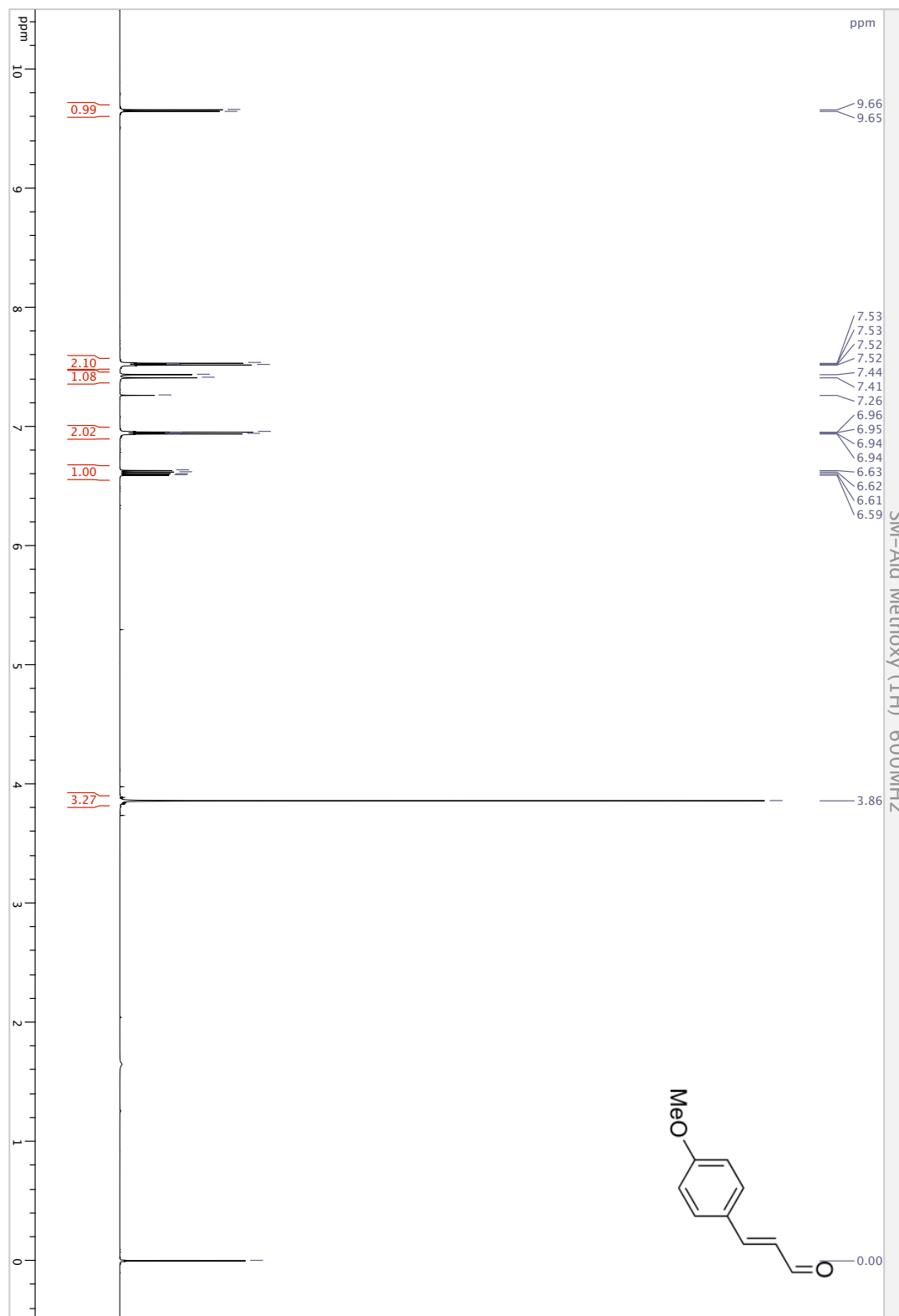
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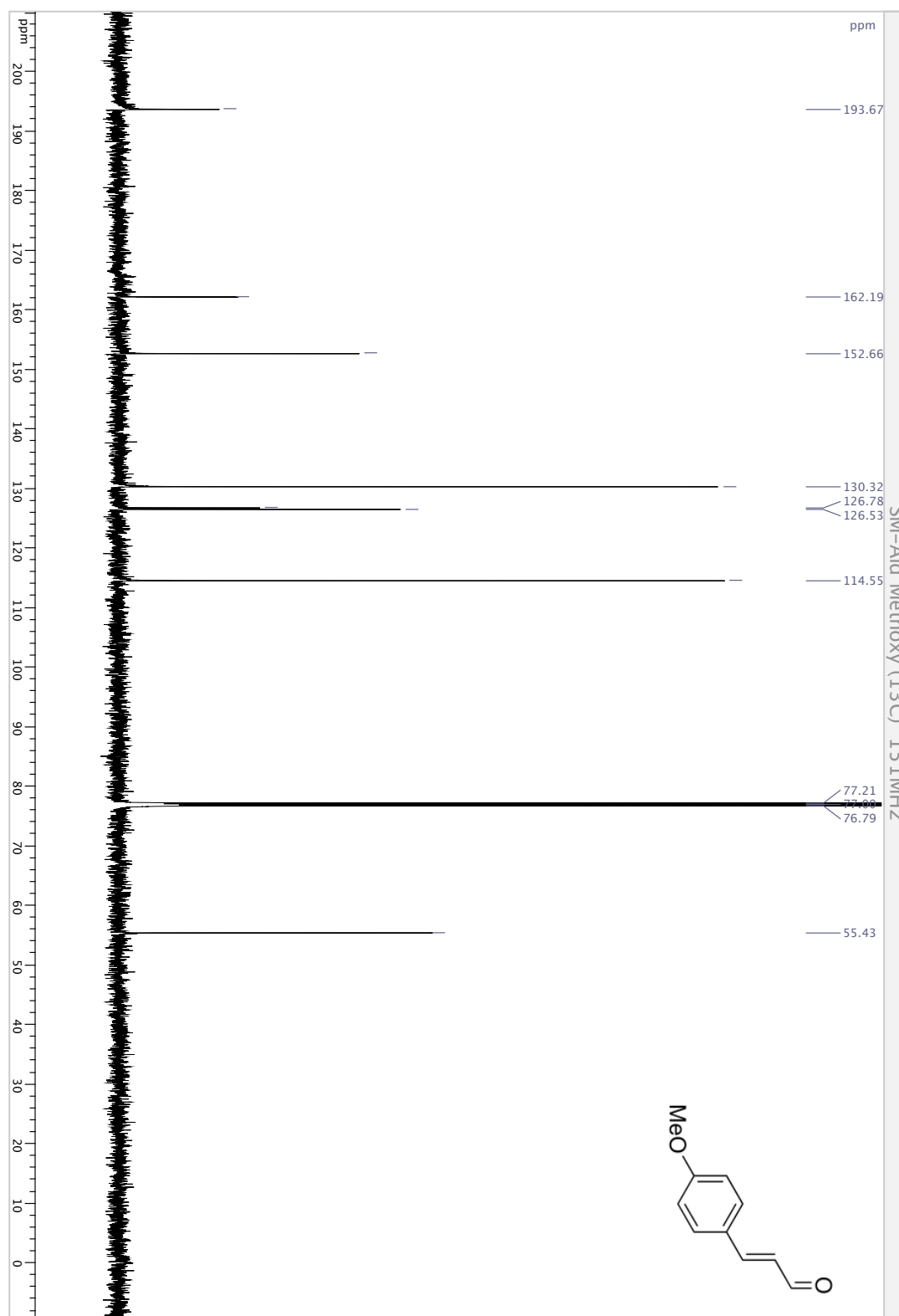
B6 NMR Spectra of *trans*-Cinnamaldehyde Derivatives Synthesised

p-Methoxy-*trans*-cinnamaldehyde



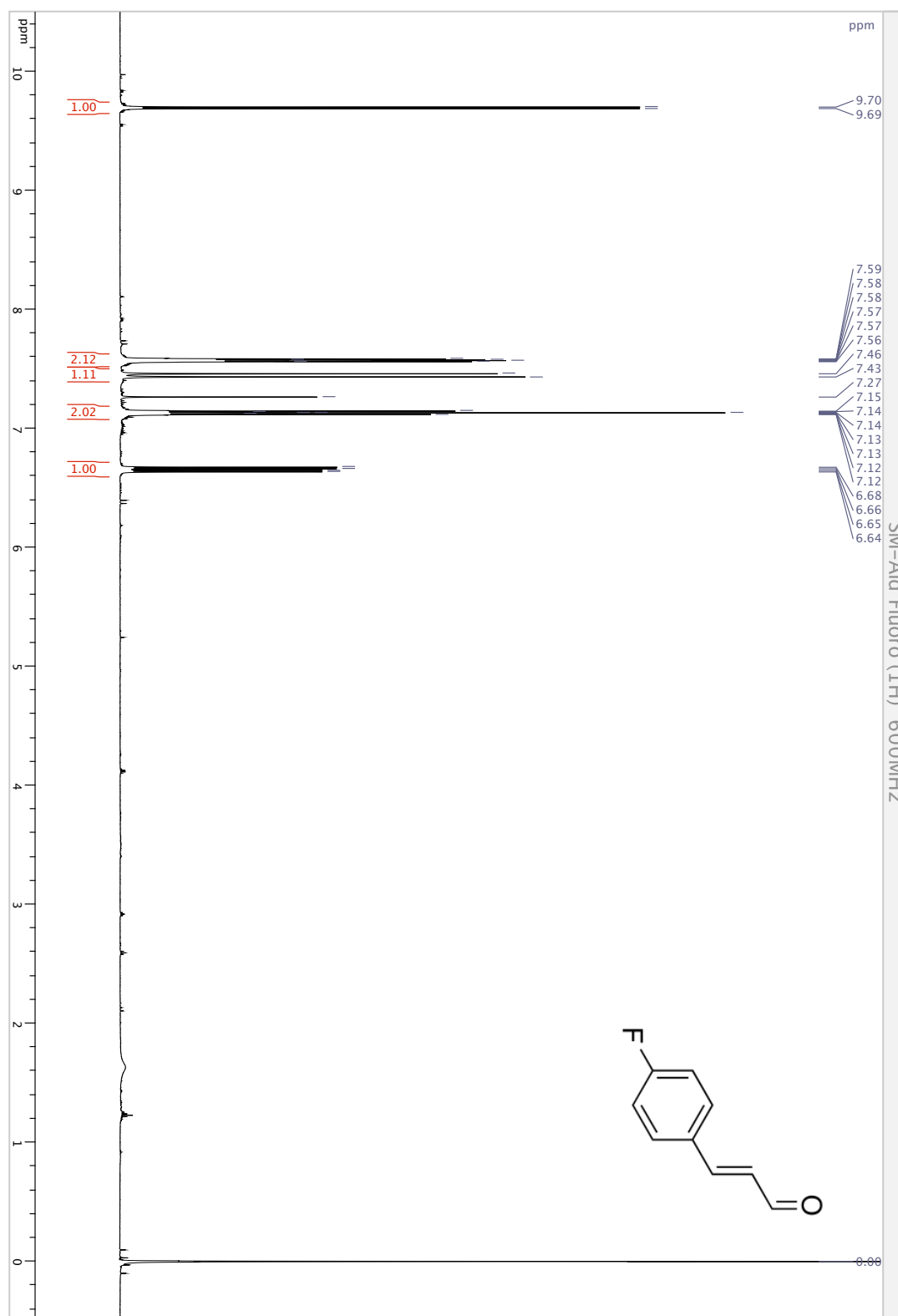
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***p*-Methoxy-*trans*-cinnamaldehyde**



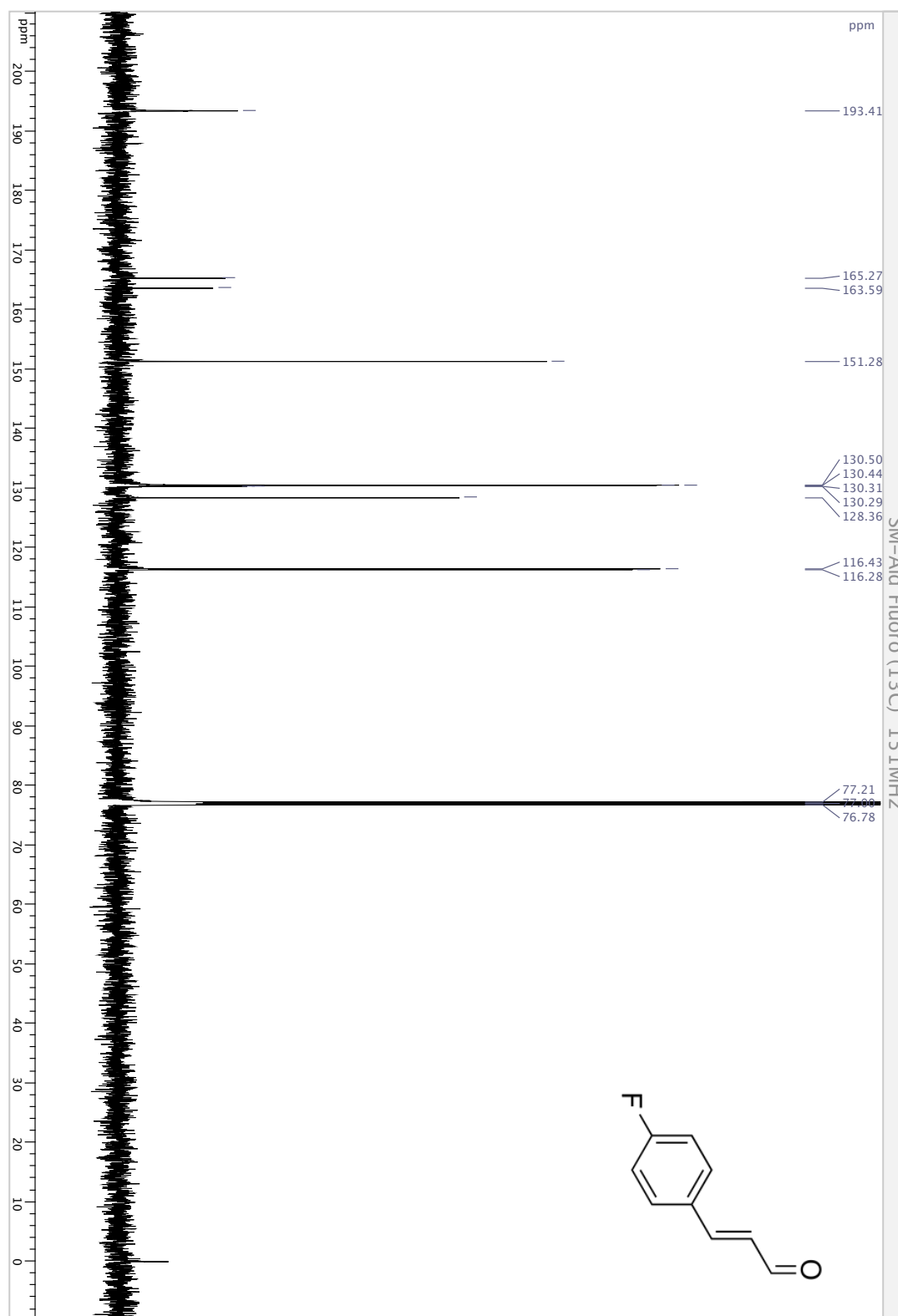
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***p*-Fluoro-*trans*-cinnamaldehyde**



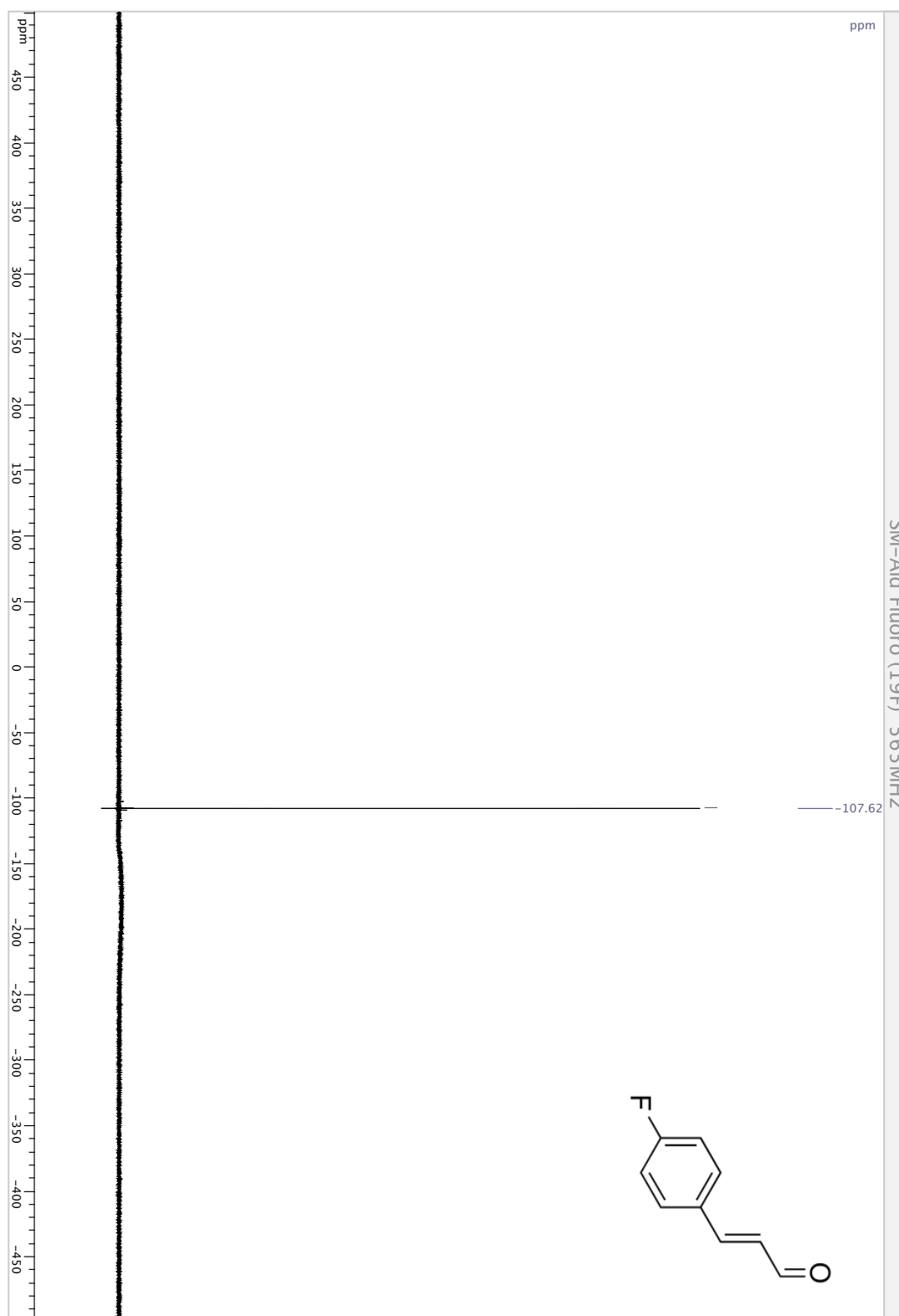
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***p*-Fluoro-*trans*-cinnamaldehyde**



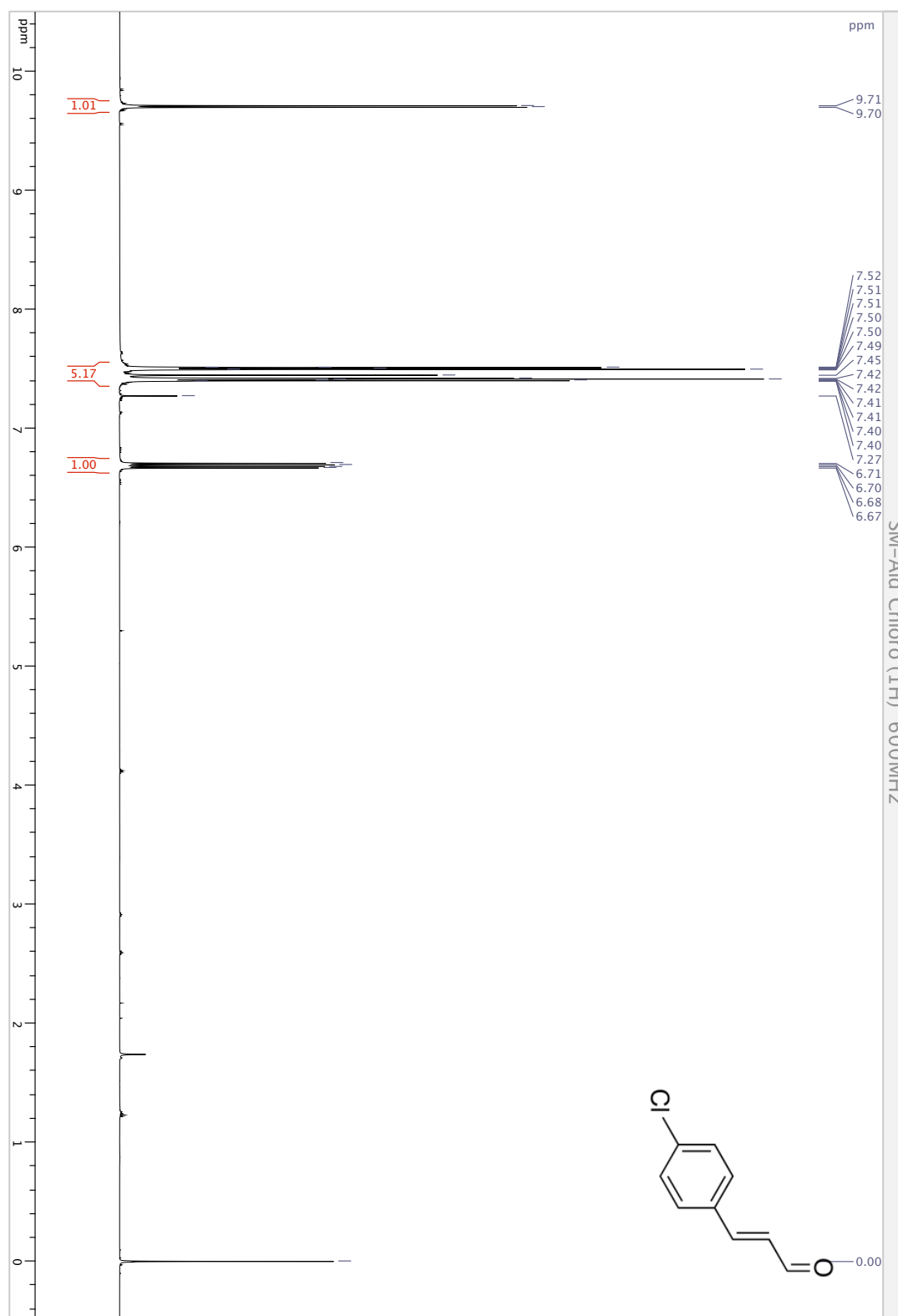
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***p*-Fluoro-*trans*-cinnamaldehyde**



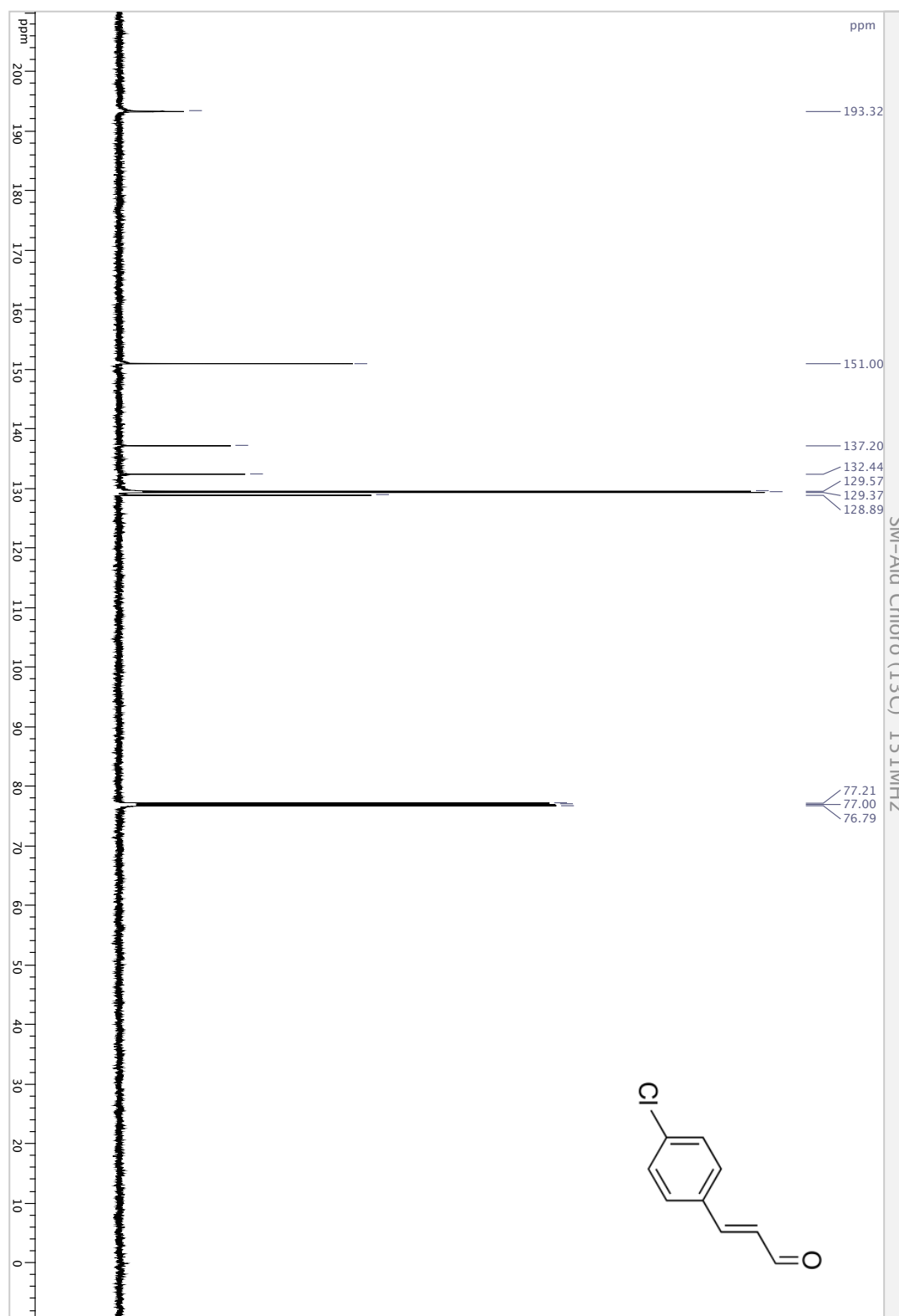
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***p*-Chloro-*trans*-cinnamaldehyde**



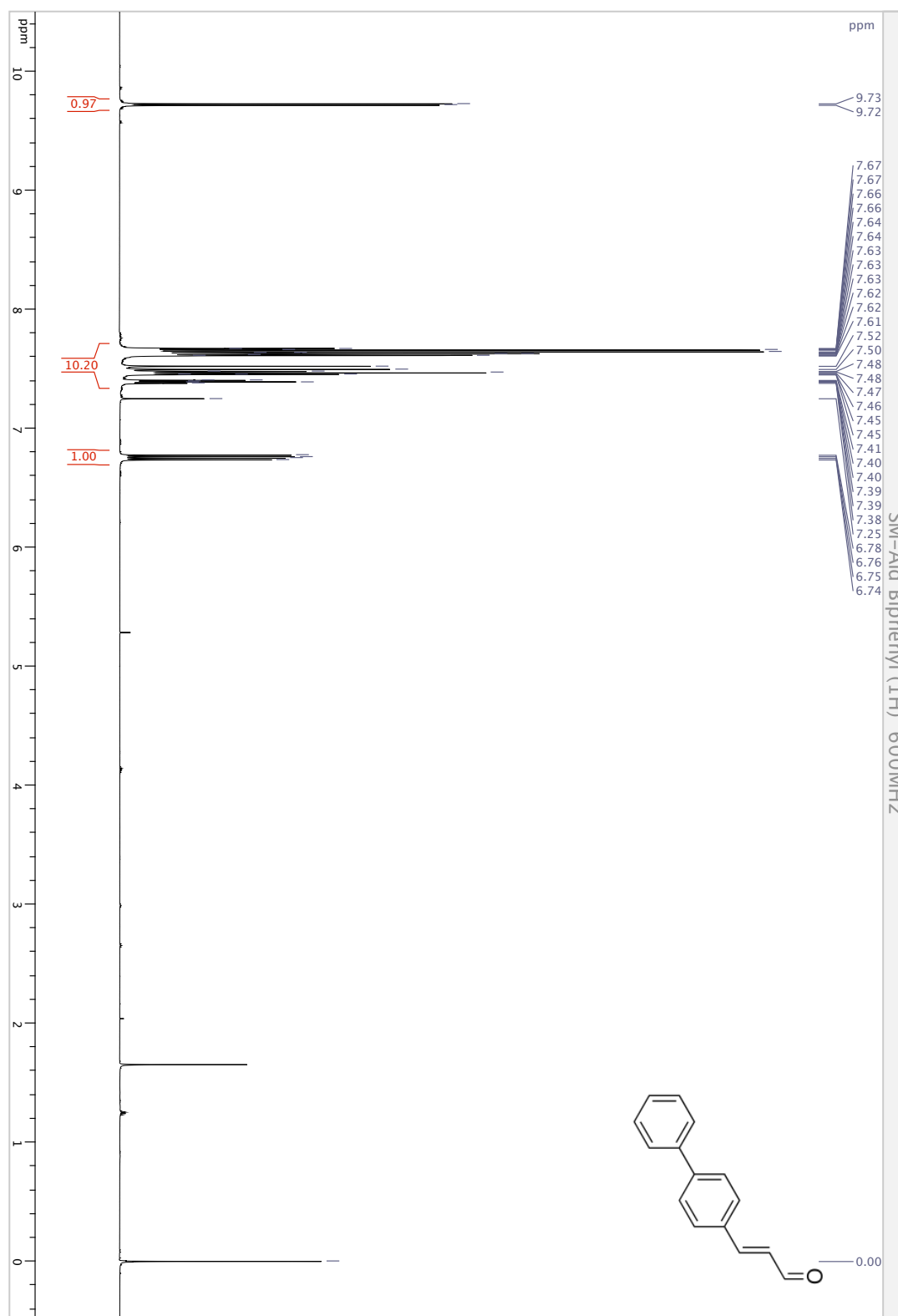
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***p*-Chloro-*trans*-cinnamaldehyde**



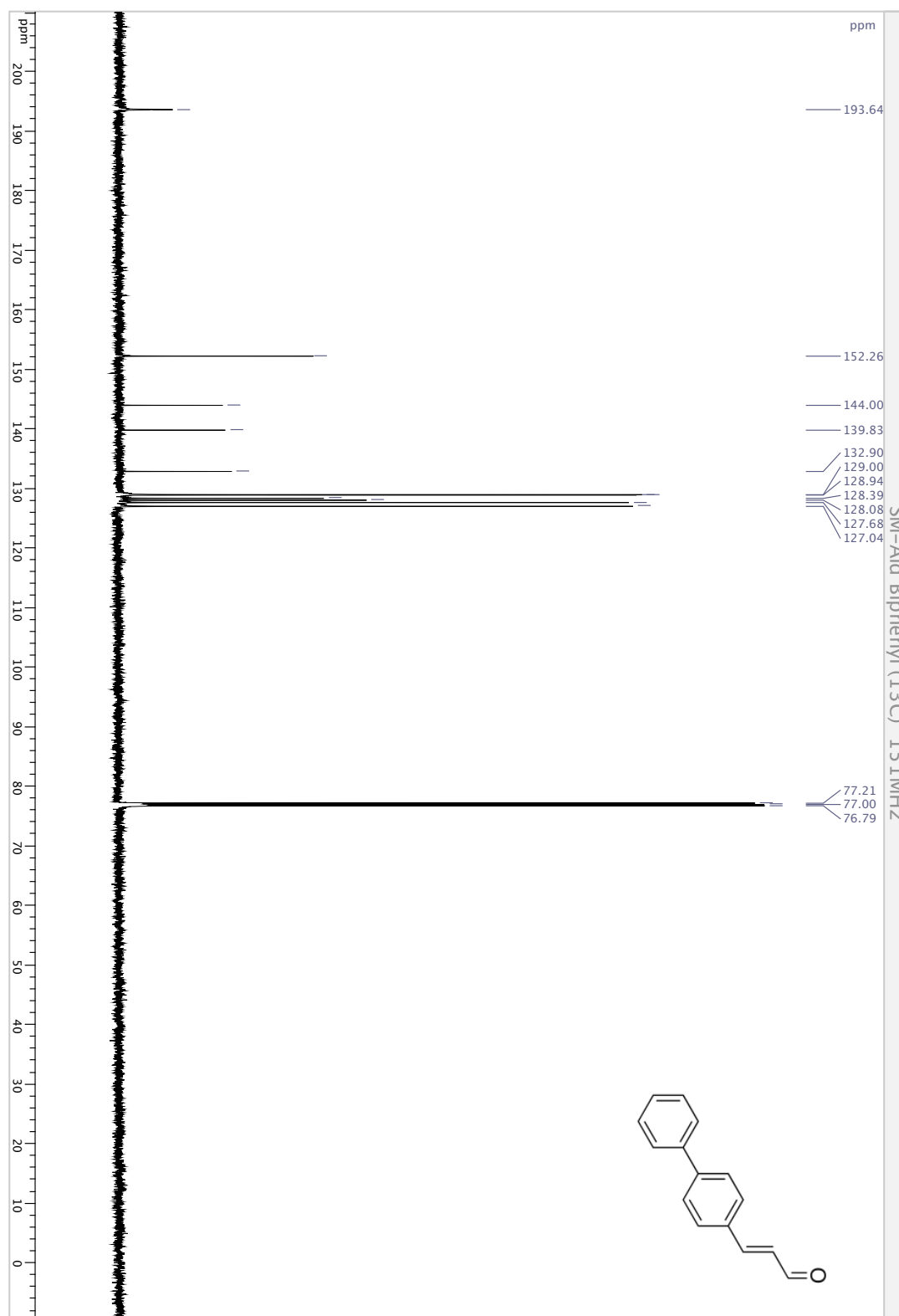
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***p*-Phenyl-*trans*-cinnamaldehyde**



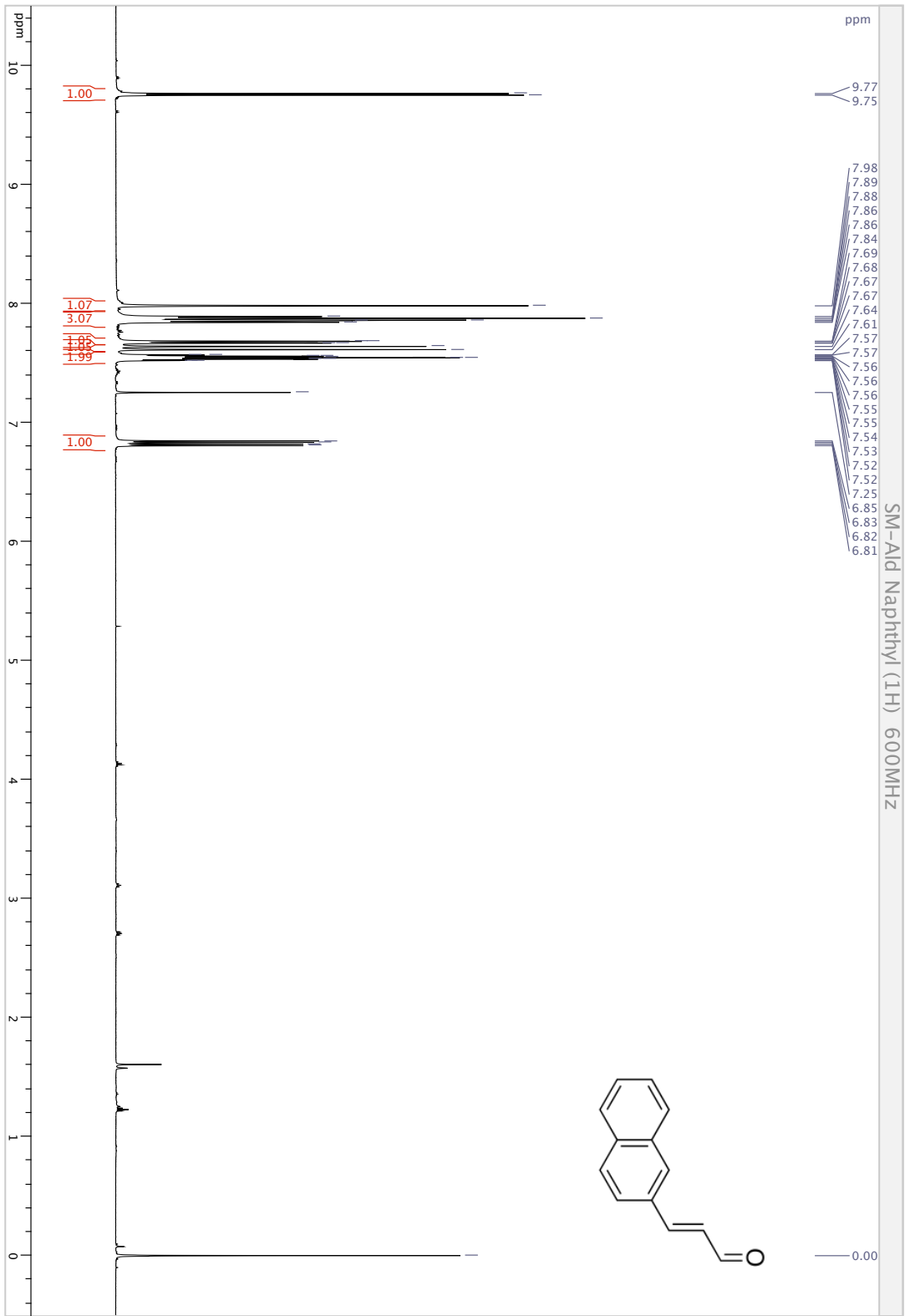
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

***p*-Phenyl-*trans*-cinnamaldehyde**



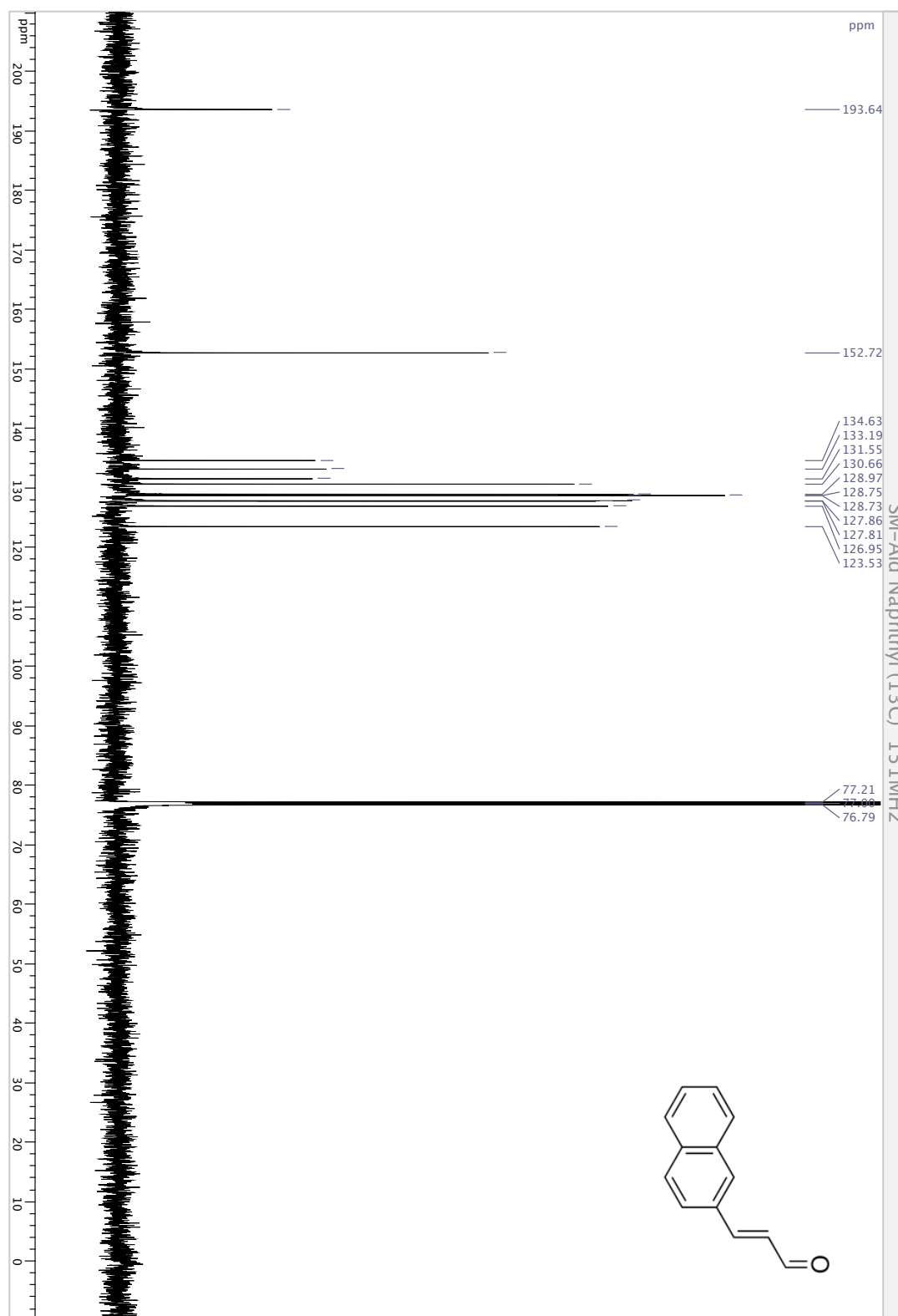
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(E)-3-Naphthalen-2-yl-propenal



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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

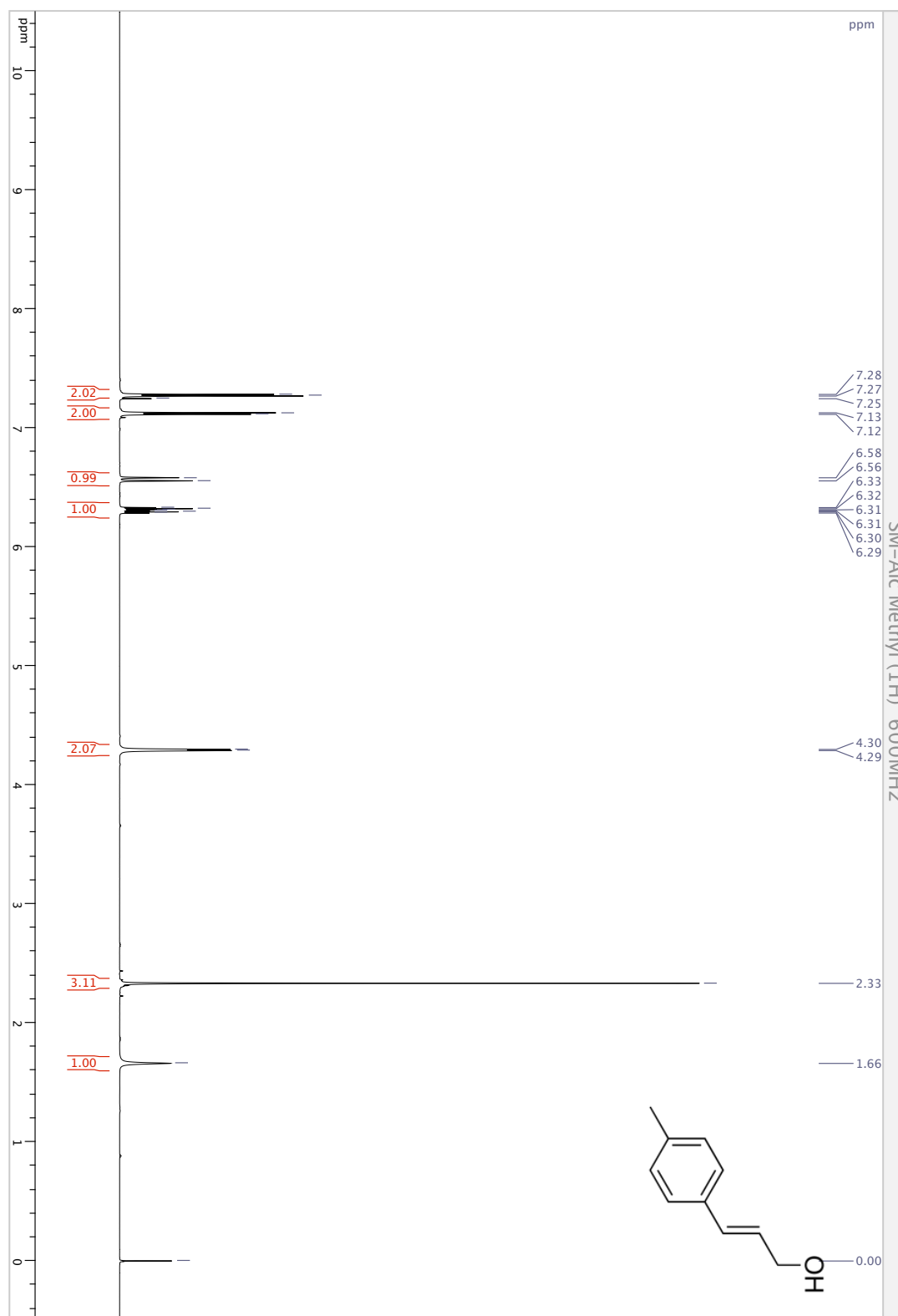
(*E*)-3-Naphthalen-2-yl-propenal



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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

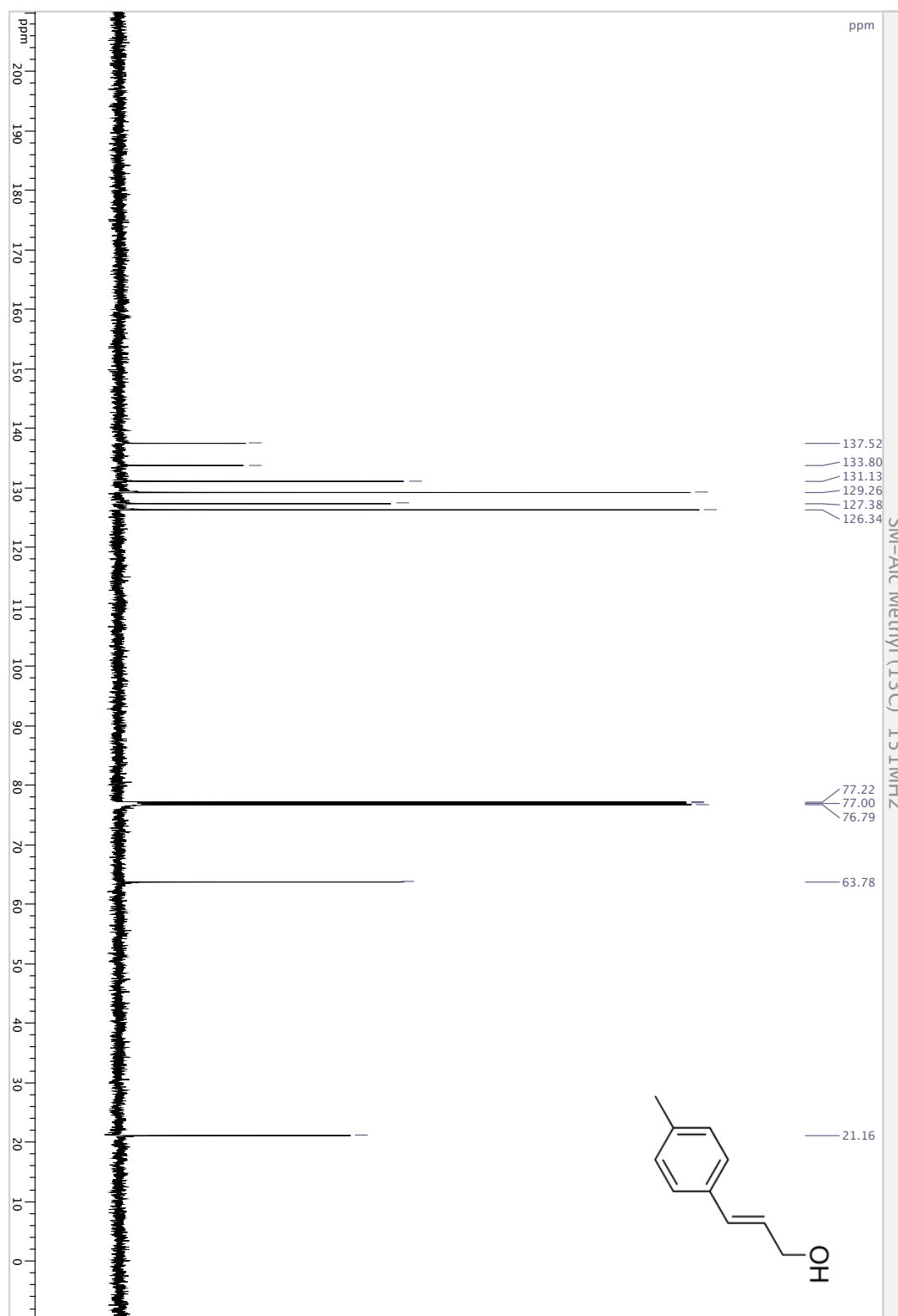
B7 NMR Spectra of Allylic Alcohols Synthesised

(*E*)-3-(4-Methylphenyl)prop-2-en-1-ol (8b)



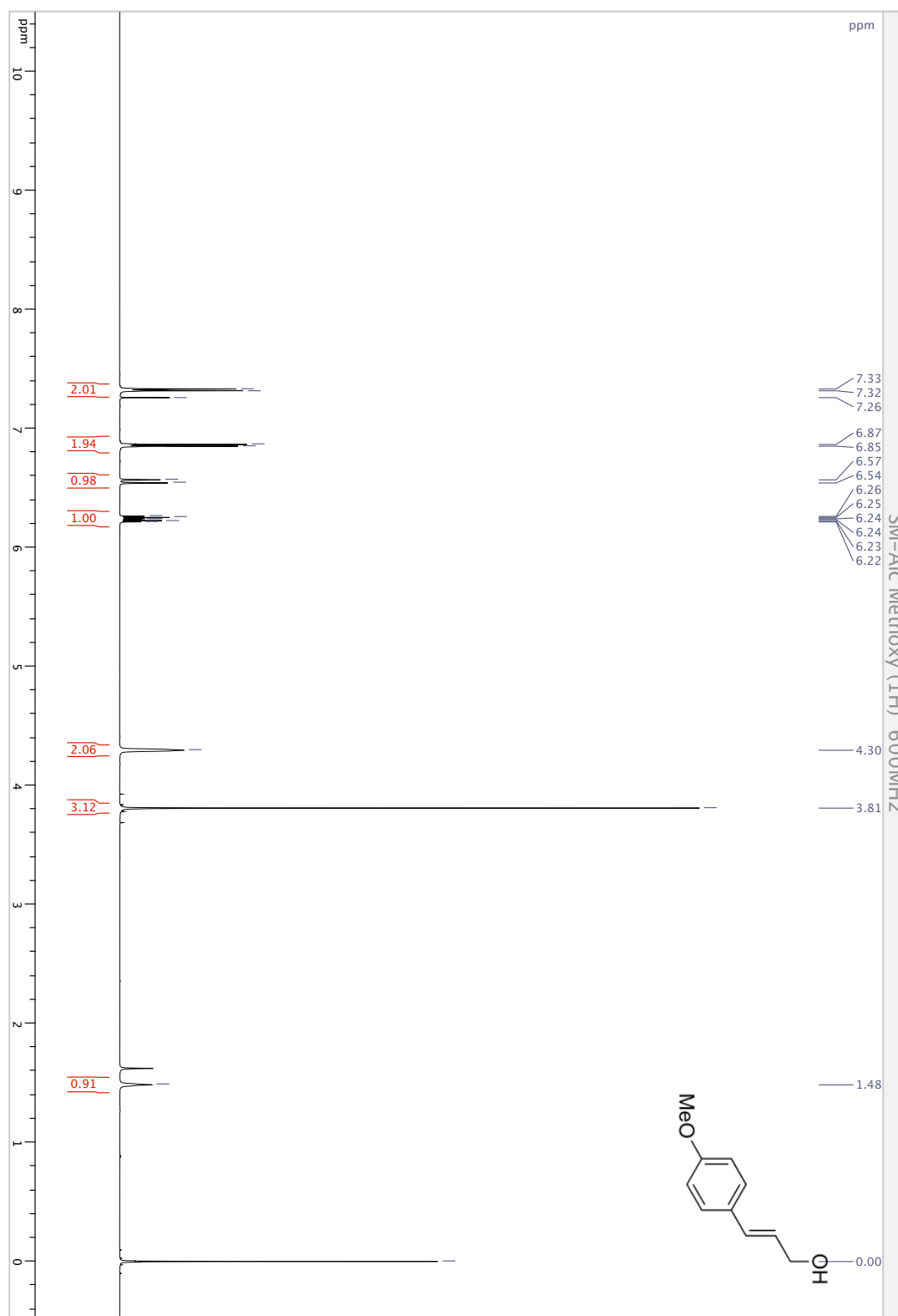
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Methylphenyl)prop-2-en-1-ol (8b)



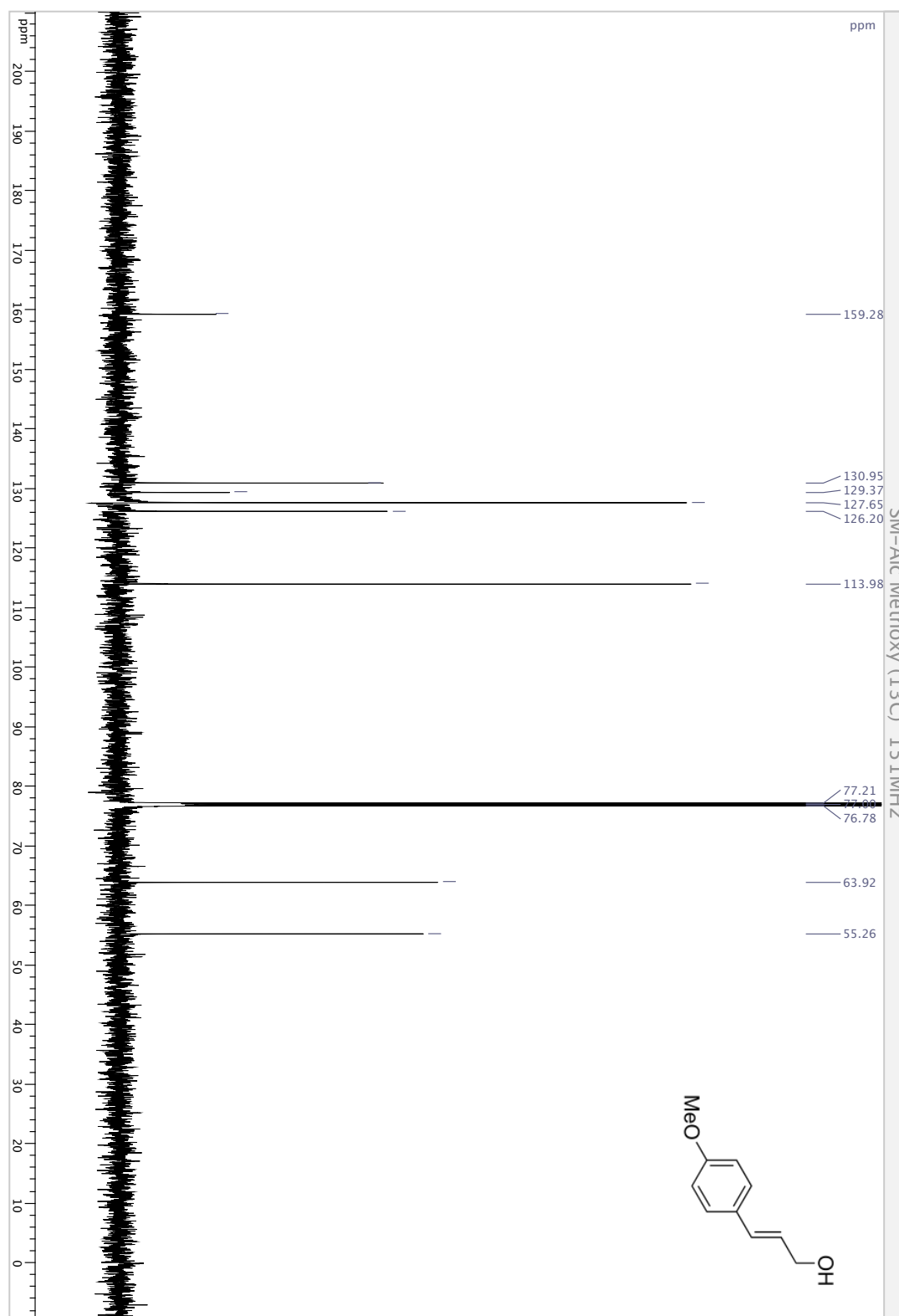
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (8c)



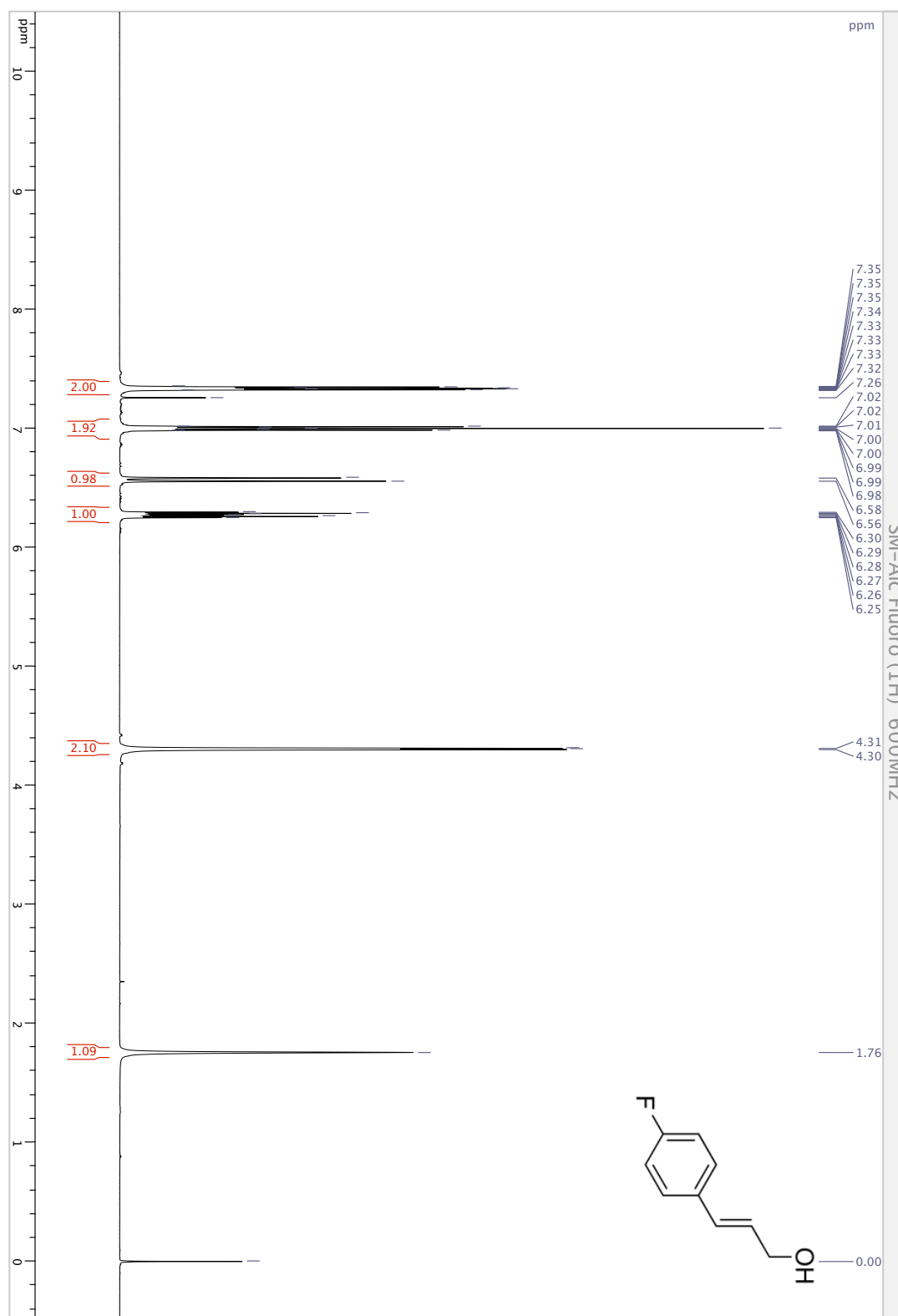
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(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (8c)



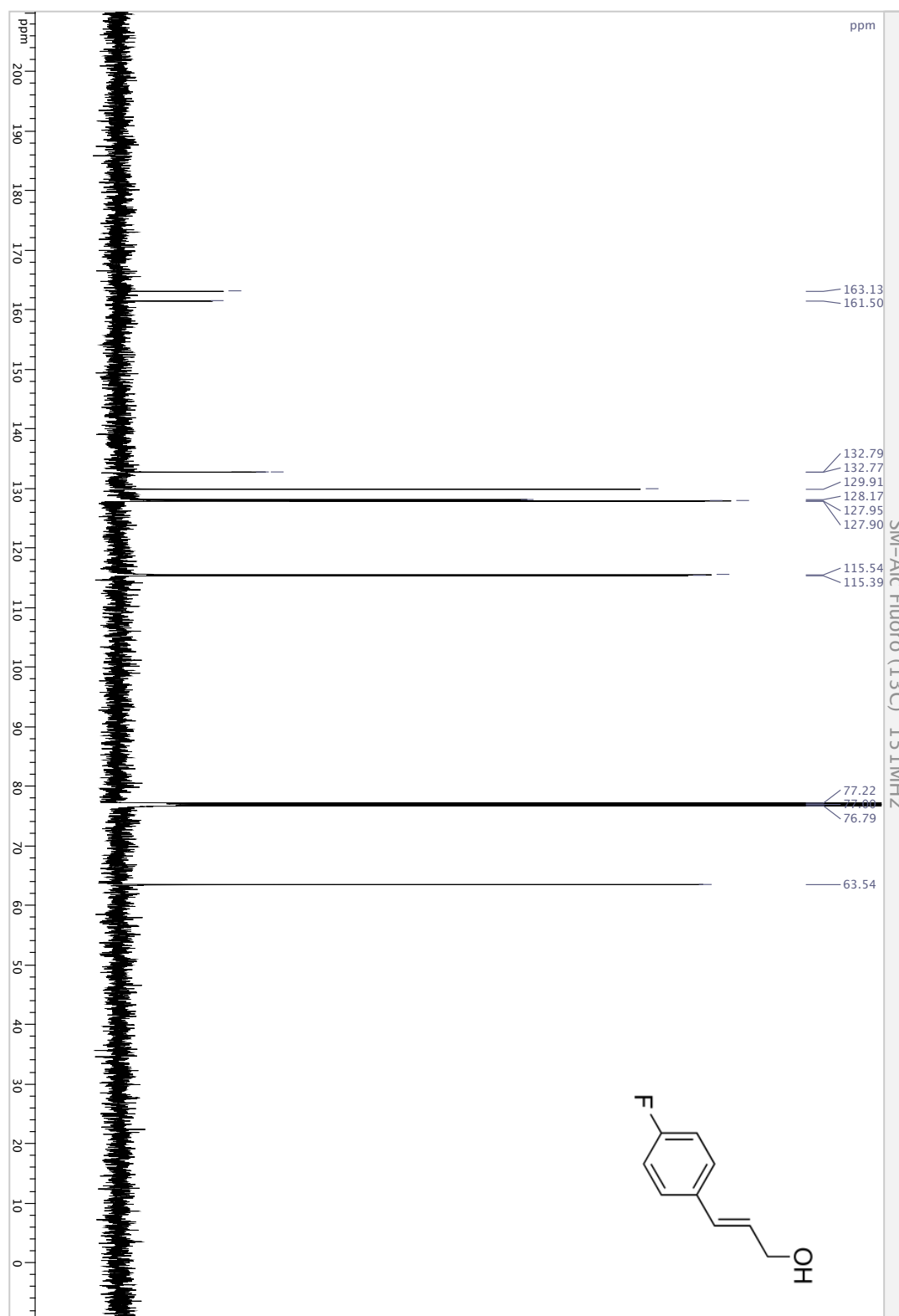
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Fluorophenyl)prop-2-en-1-ol (8d)



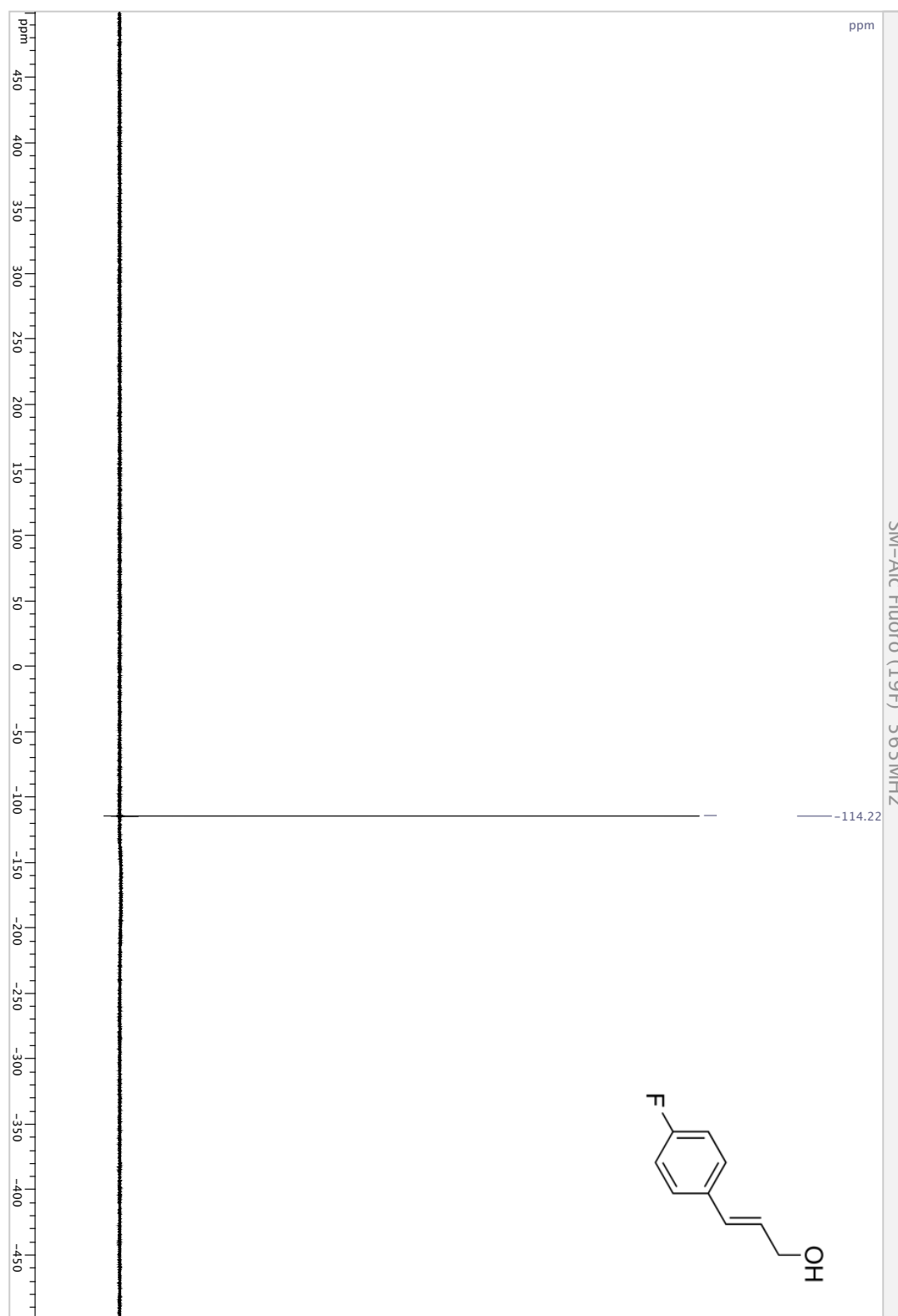
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Fluorophenyl)prop-2-en-1-ol (8d)



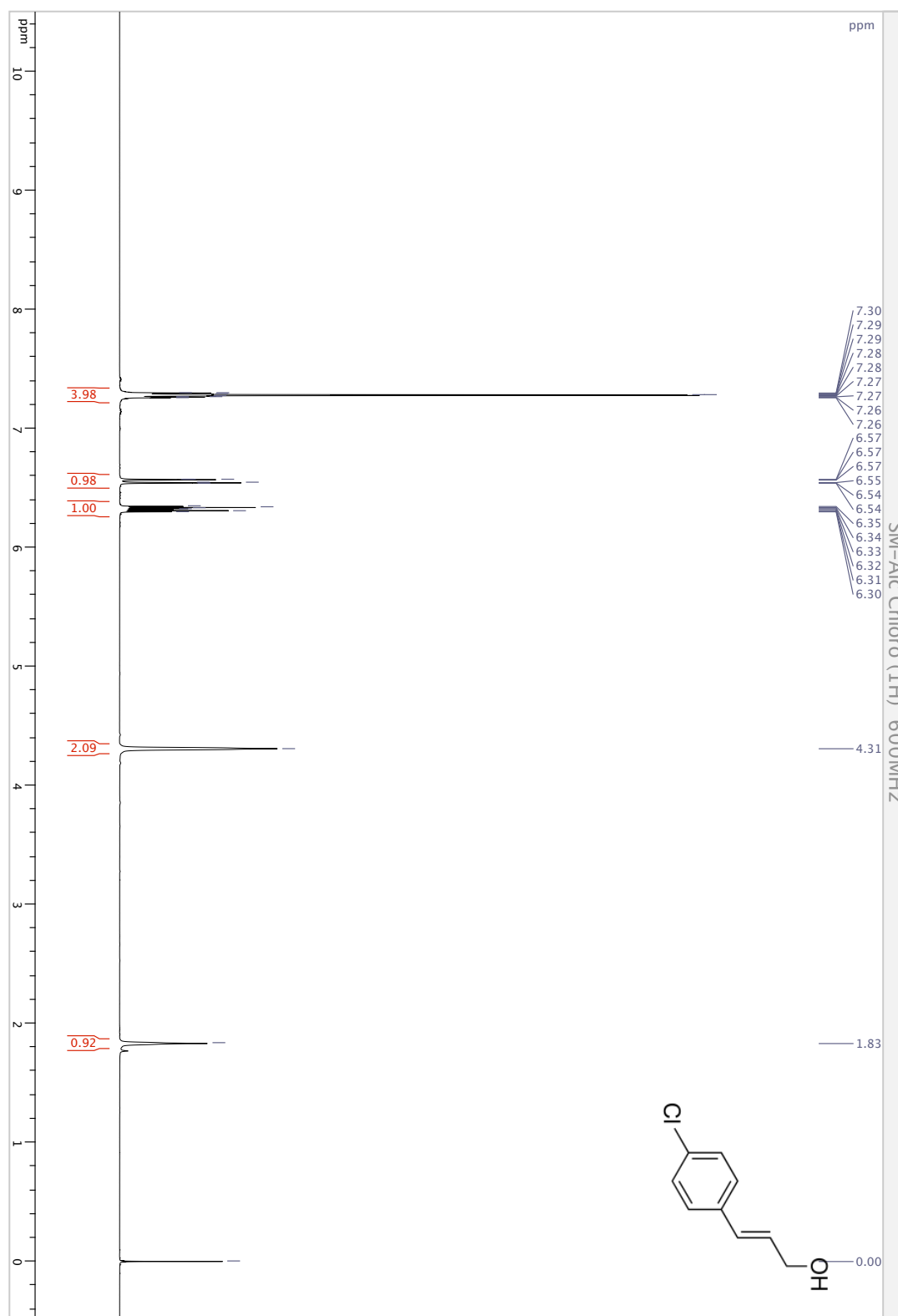
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Fluorophenyl)prop-2-en-1-ol (8d)



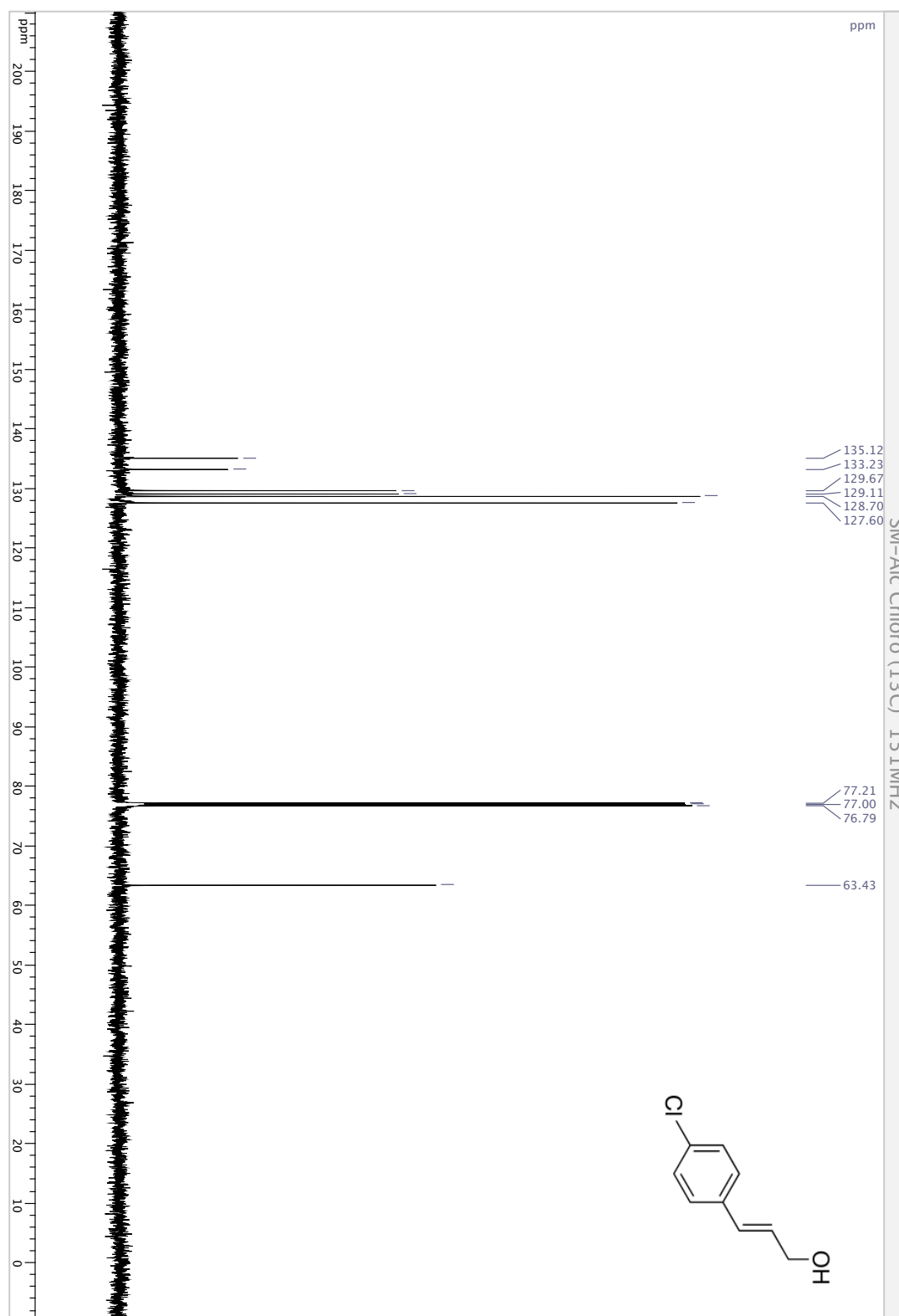
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol (8e)



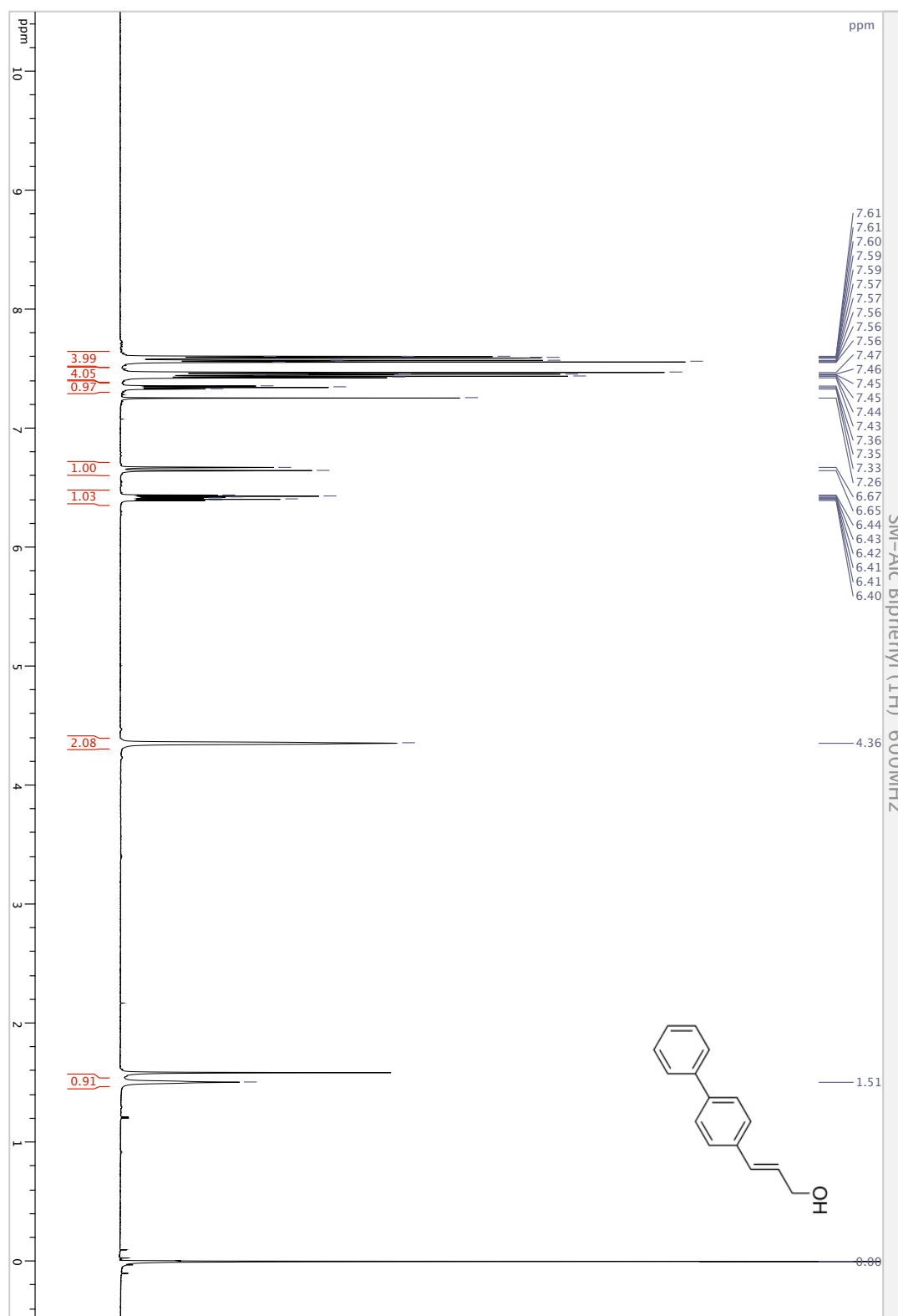
A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol (8e)



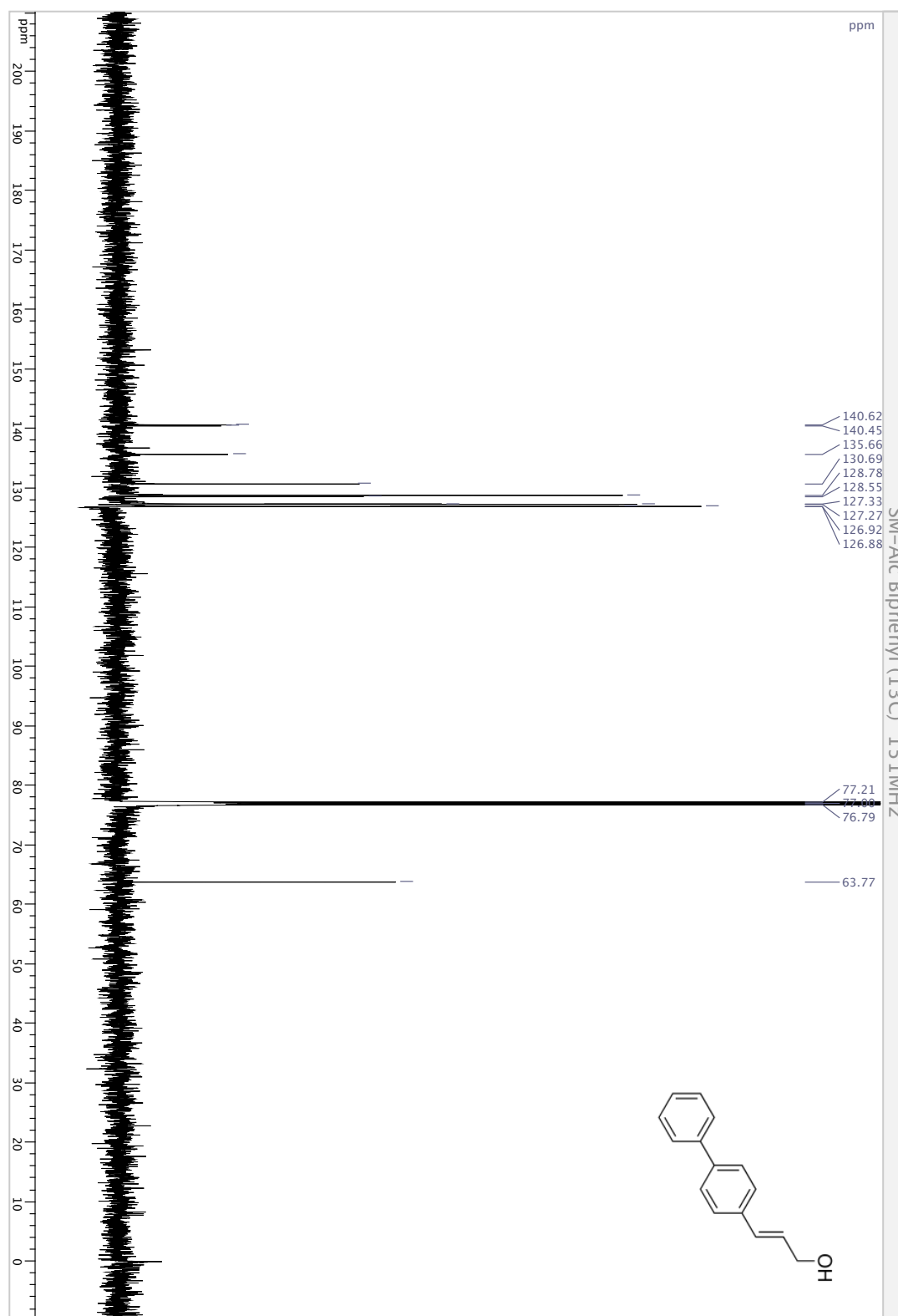
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Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Biphenyl)prop-2-en-1-ol (8g)



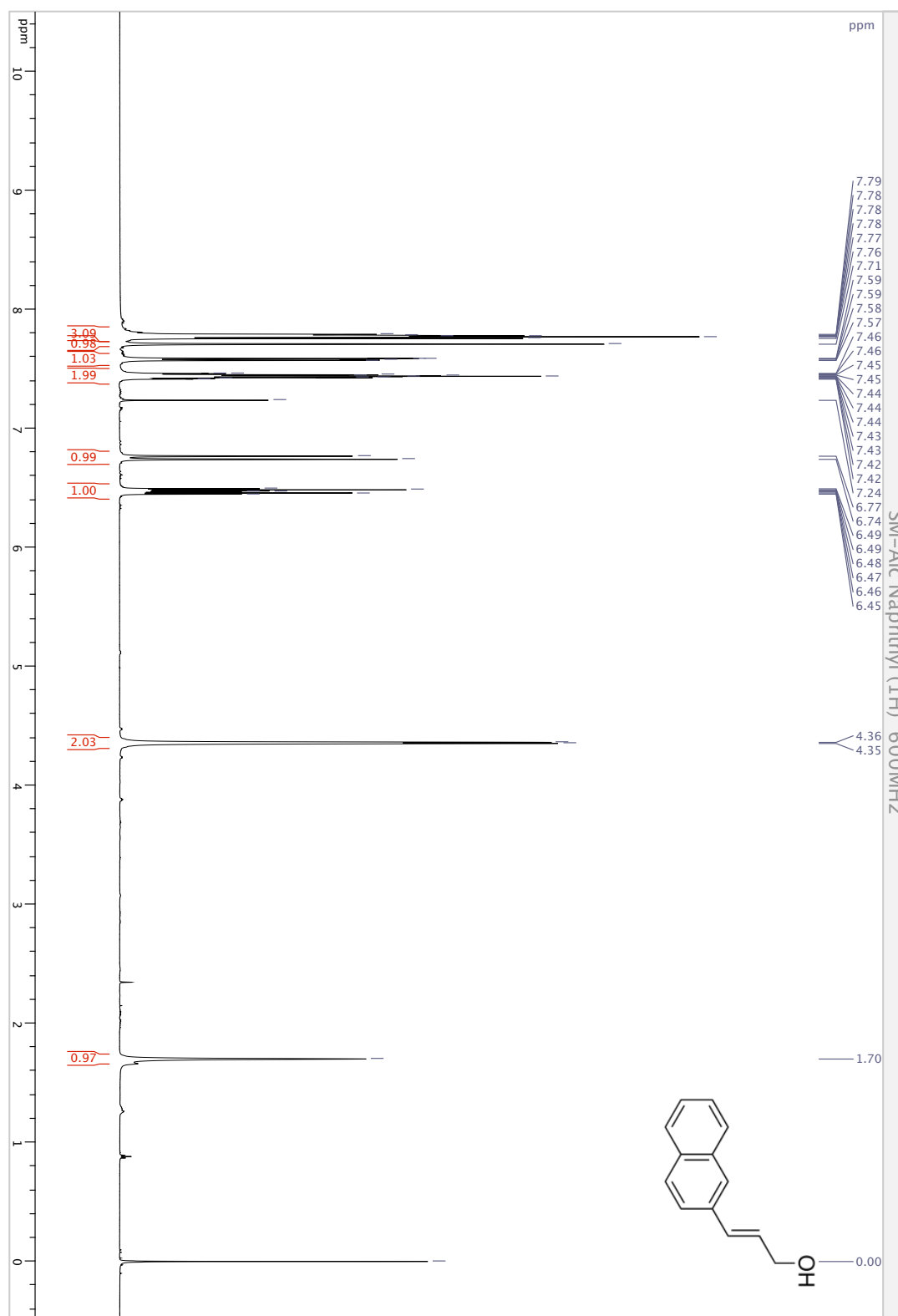
A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(*E*)-3-(4-Biphenyl)prop-2-en-1-ol (8g)



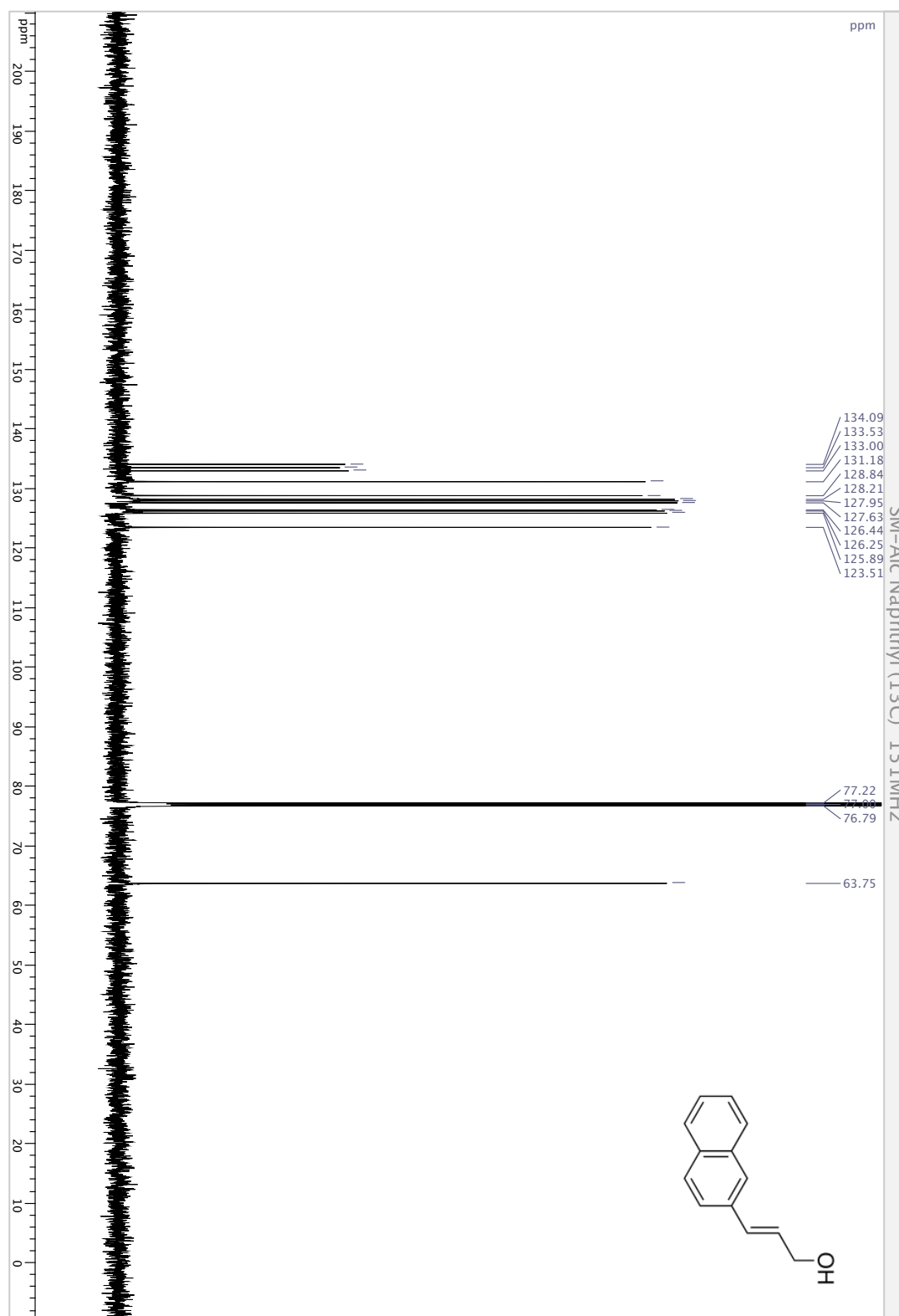
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(E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (8h)



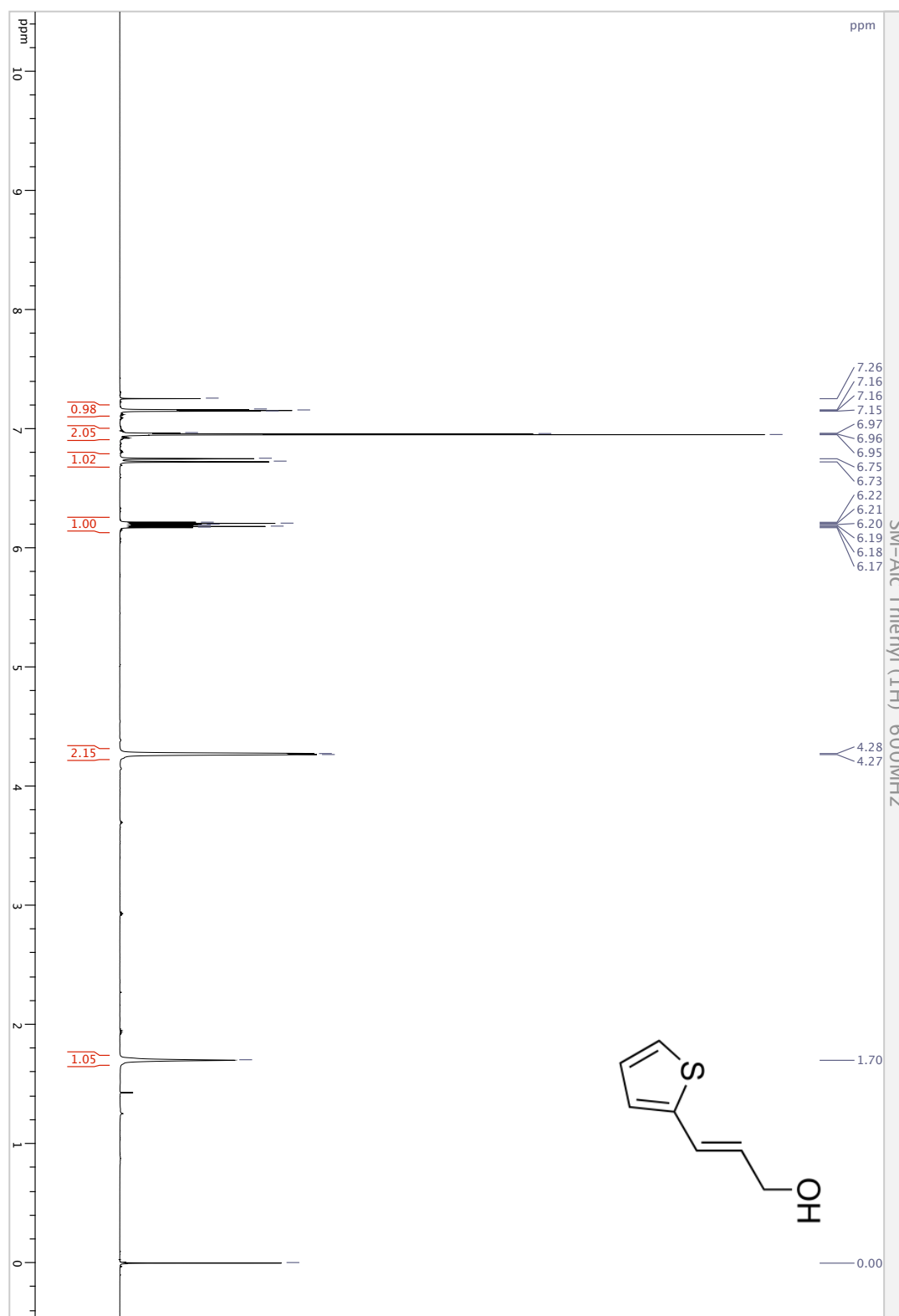
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(E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (8h)



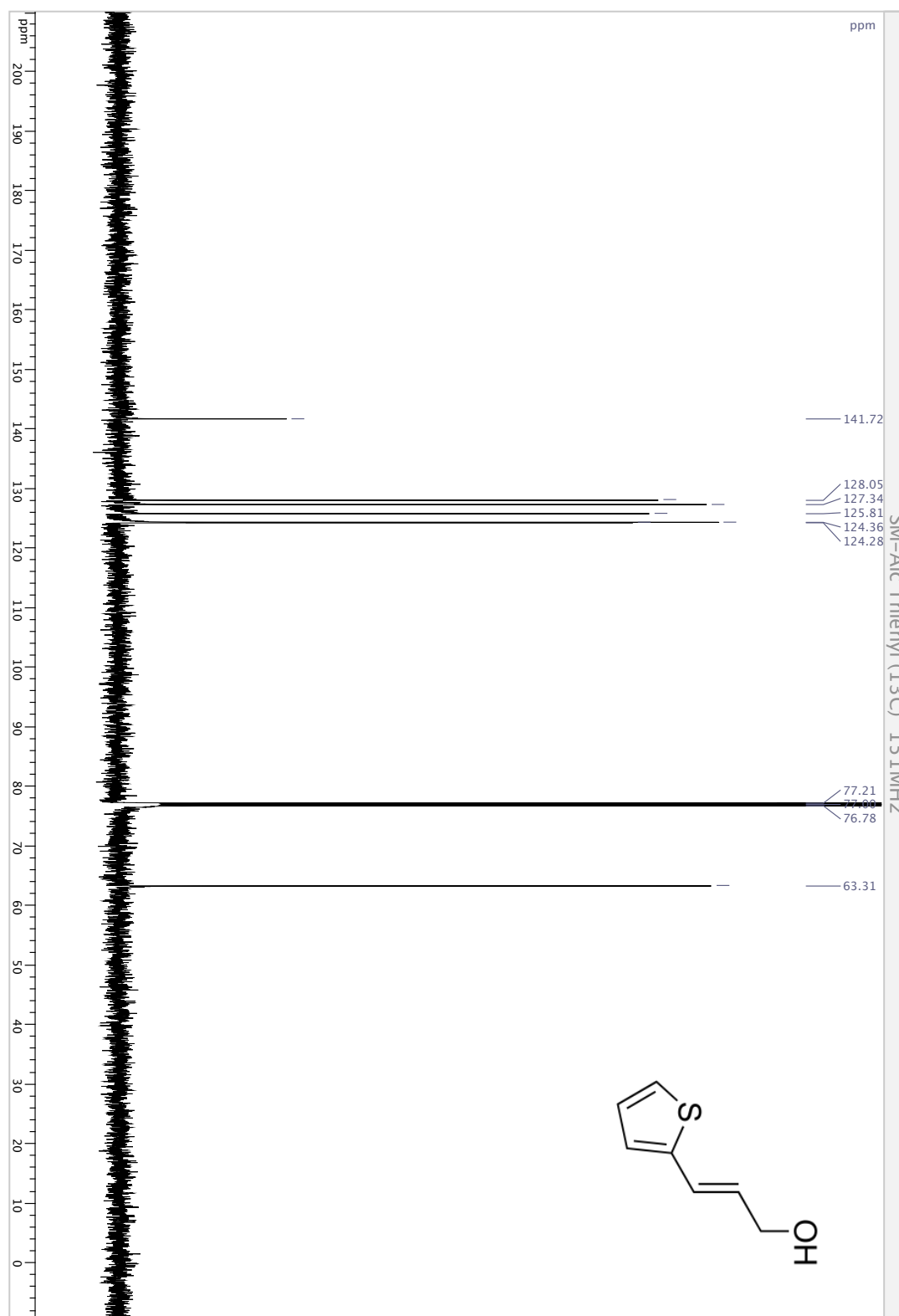
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(E)-3-(2-Thienyl)prop-2-en-1-ol (8j)



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(E)-3-(2-Thienyl)prop-2-en-1-ol (8j)

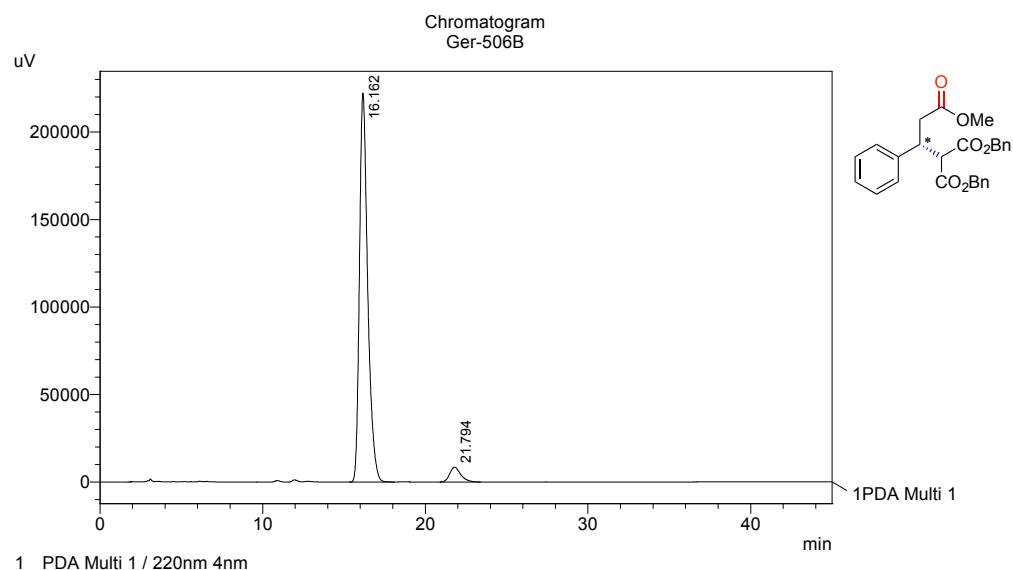


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B8 HPLC Charts

(R)-2-Benzoyloxycarbonyl-3-phenylpentanedioic acid 1-benzyl ester 5-methyl ester

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-506B
Injection Volume : 2 uL
Data Filename : Ger-506B.lcd
Method Filename : Jorgensen 11a.lcm
Date Acquired : 2013/04/18 14:35:45
Data Processed : 2013/04/18 15:31:56

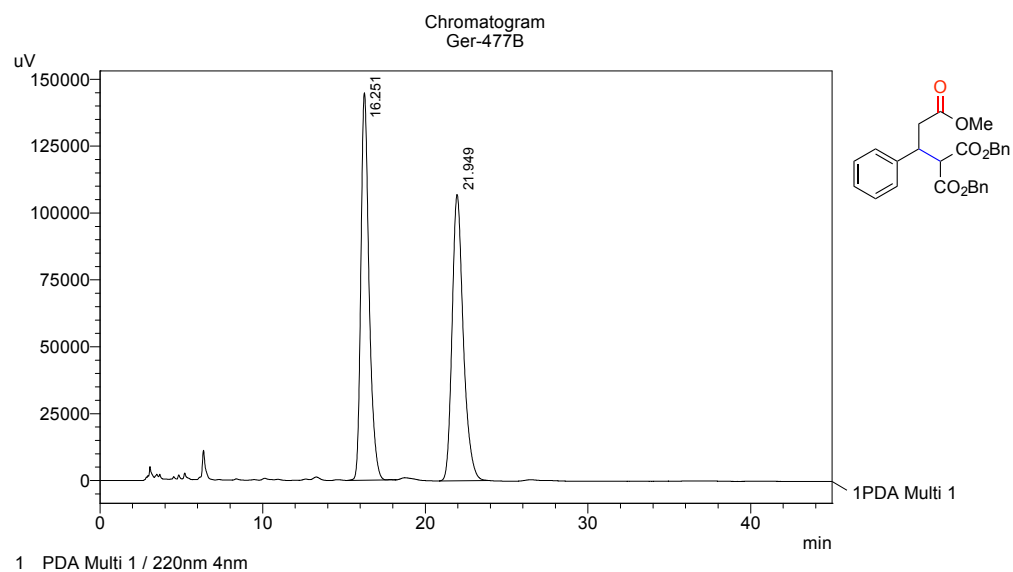


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.162	7855617	222343	95.141	96.333
2	21.794	401222	8464	4.859	3.667
Total		8256839	230807	100.000	100.000

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(rac)-2-Benzyloxycarbonyl-3-phenylpentanedioic acid 1-benzyl ester 5-methyl ester

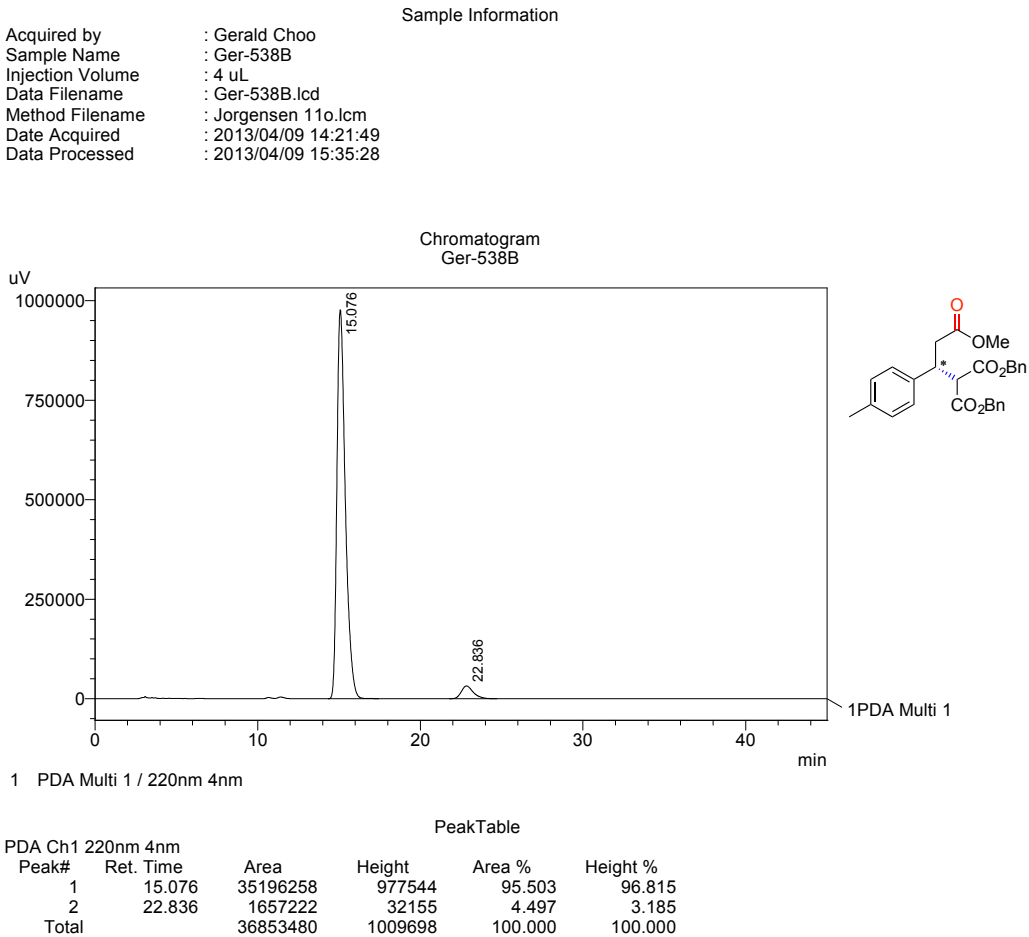
Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-477B
Injection Volume : 3 uL
Data Filename : Ger-477B.lcd
Method Filename : Jorgensen 11a.lcm
Date Acquired : 2013/04/18 13:22:33
Data Processed : 2013/04/18 15:20:59



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.251	5084425	144877	49.813	57.499
2	21.949	5122541	107087	50.187	42.501
Total		10206966	251964	100.000	100.000

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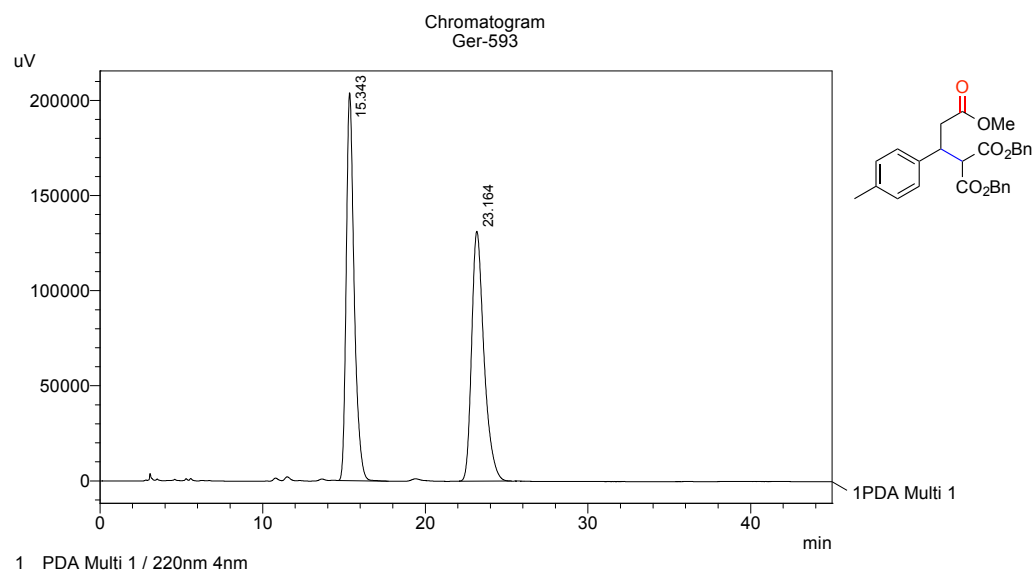
(R)-2-Benzyloxycarbonyl-3-(4-methylphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



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(rac)-2-Benzoyloxycarbonyl-3-(4-methylphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-593
Injection Volume : 4 uL
Data Filename : Ger-593.lcd
Method Filename : Jorgensen 11o.lcm
Date Acquired : 2013/04/09 13:25:58
Data Processed : 2013/04/09 14:17:43



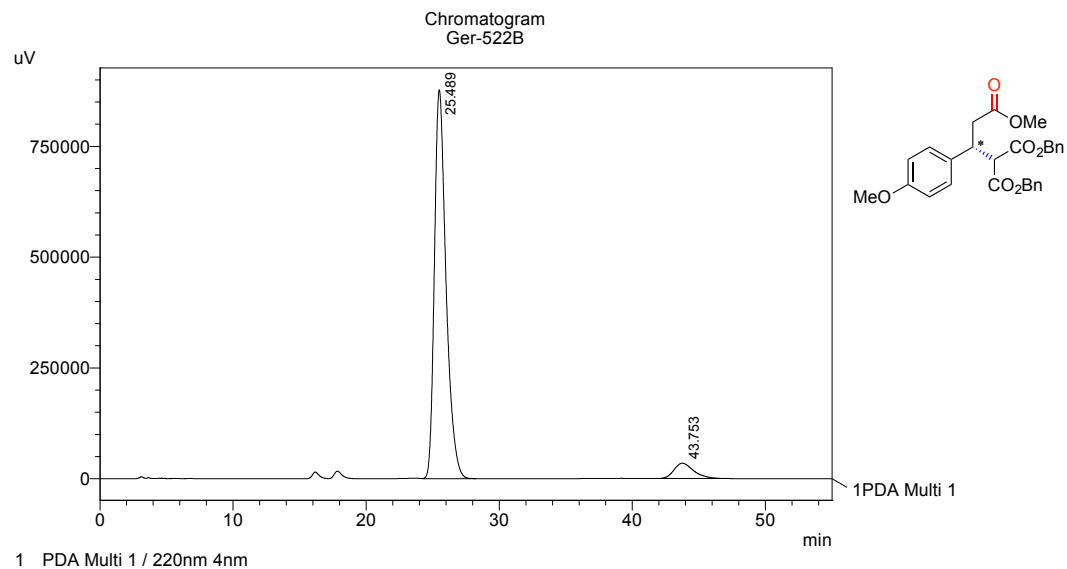
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.343	6919008	203985	49.952	60.823
2	23.164	6932240	131389	50.048	39.177
Total		13851249	335374	100.000	100.000

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(R)-2-Benzoyloxycarbonyl-3-(4-methoxyphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

Acquired by : Gerald Choo
Sample Name : Ger-522B
Injection Volume : 5 uL
Data Filename : Ger-522B.lcd
Method Filename : Jorgensen 11i.lcm
Date Acquired : 2013/03/08 17:48:36
Data Processed : 2013/03/08 19:23:42

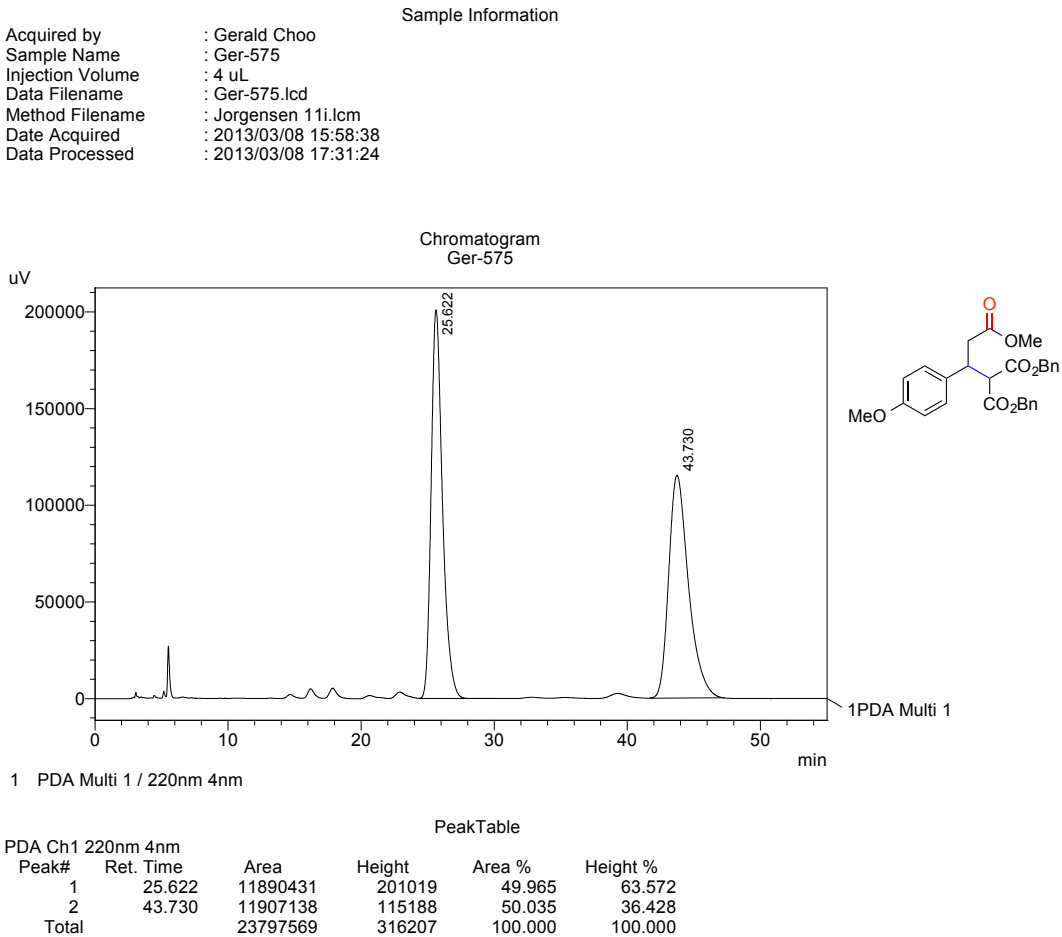
Sample Information



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.489	53206361	877458	93.708	96.209
2	43.753	3572334	34578	6.292	3.791
Total		56778696	912037	100.000	100.000

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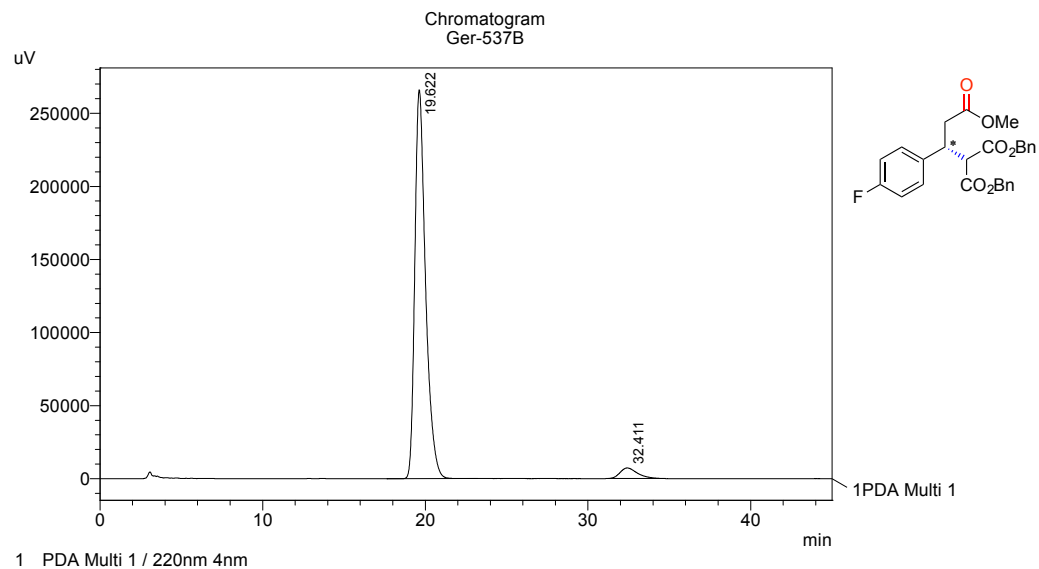
(rac)-2-Benzyloxycarbonyl-3-(4-methoxyphenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



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(R)-2-Benzyloxycarbonyl-3-(4-fluorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-537B
Injection Volume : 4 uL
Data Filename : Ger-537B.lcd
Method Filename : Jorgensen 11m.lcm
Date Acquired : 2013/03/04 14:10:34
Data Processed : 2013/03/04 18:21:03

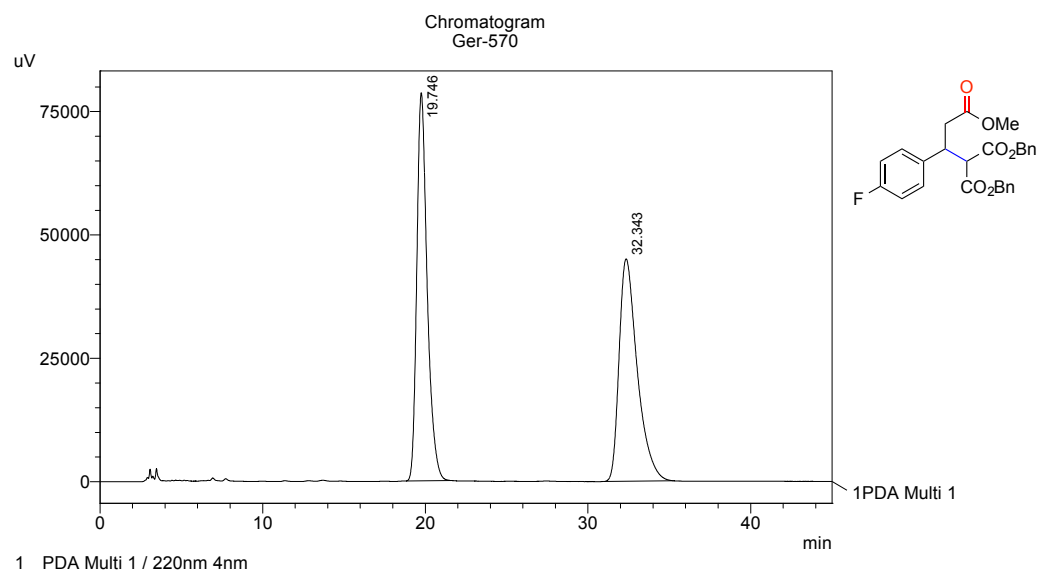


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.622	12210107	266116	95.736	97.348
2	32.411	543885	7249	4.264	2.652
Total		12753992	273365	100.000	100.000

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(rac)-2-Benzyloxycarbonyl-3-(4-fluorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

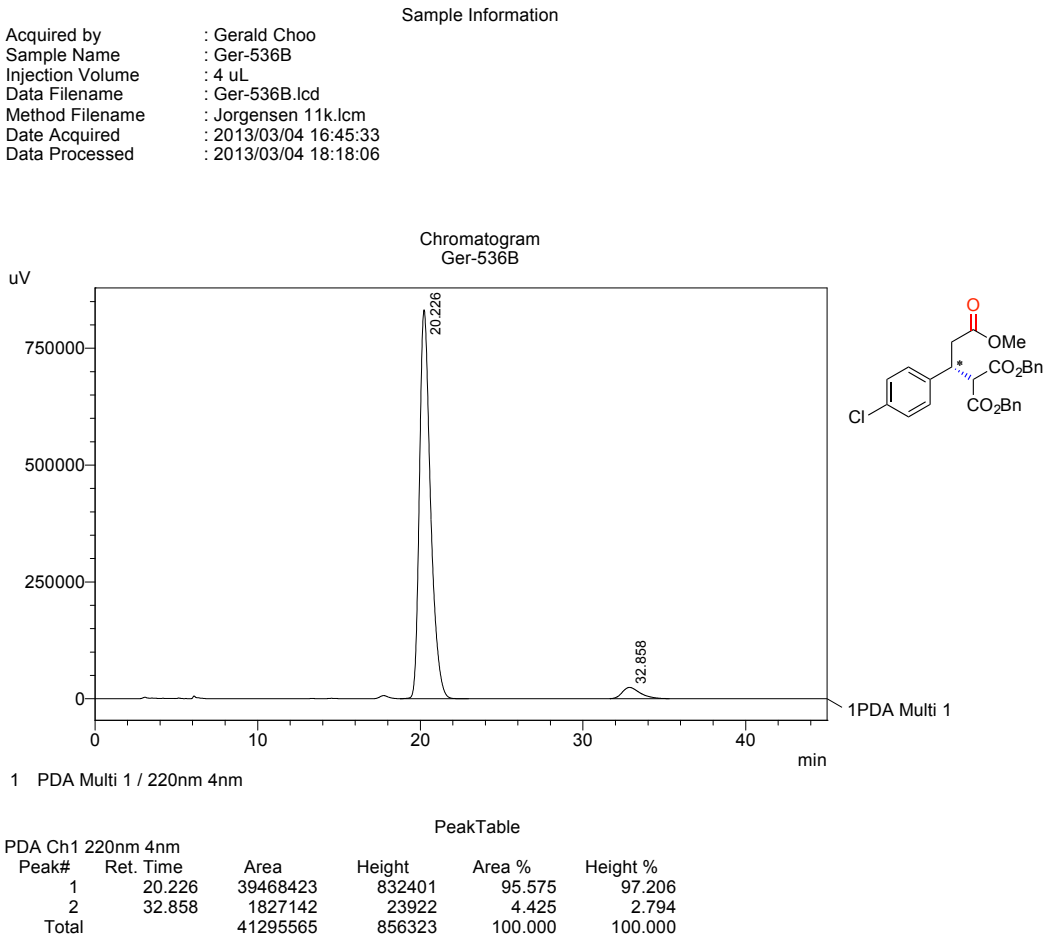
Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-570
Injection Volume : 3 uL
Data Filename : Ger-570.lcd
Method Filename : Jorgensen 11m.lcm
Date Acquired : 2013/03/04 13:17:21
Data Processed : 2013/03/04 14:08:15



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.746	3491132	78668	49.973	63.579
2	32.343	3494926	45065	50.027	36.421
Total		6986058	123733	100.000	100.000

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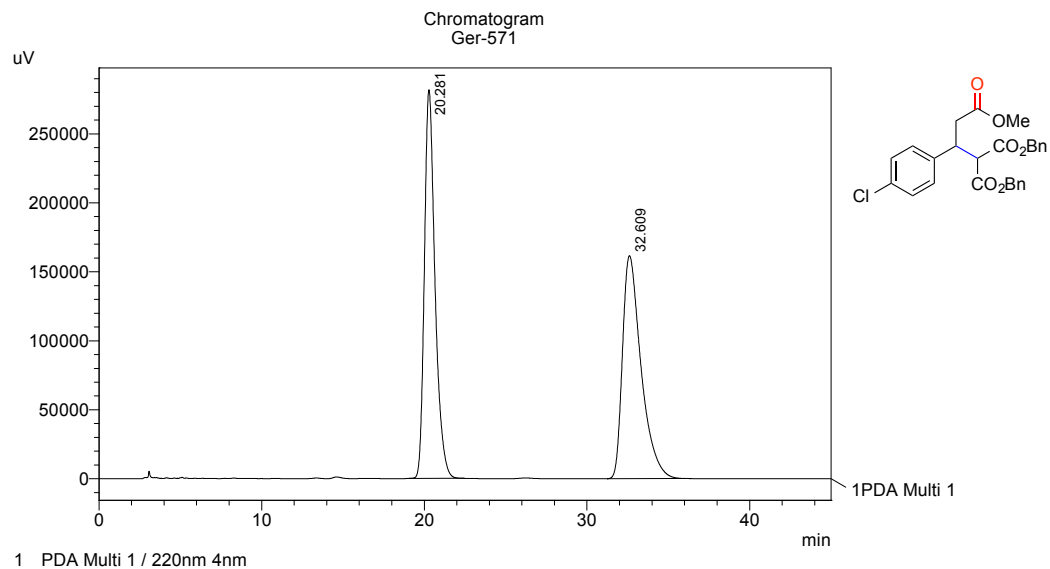
(R)-2-Benzoyloxycarbonyl-3-(4-chlorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester



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(rac)-2-Benzoyloxycarbonyl-3-(4-chlorophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-571
Injection Volume : 5 uL
Data Filename : Ger-571.lcd
Method Filename : Jorgensen 11k.lcm
Date Acquired : 2013/03/04 15:46:03
Data Processed : 2013/03/04 16:41:58

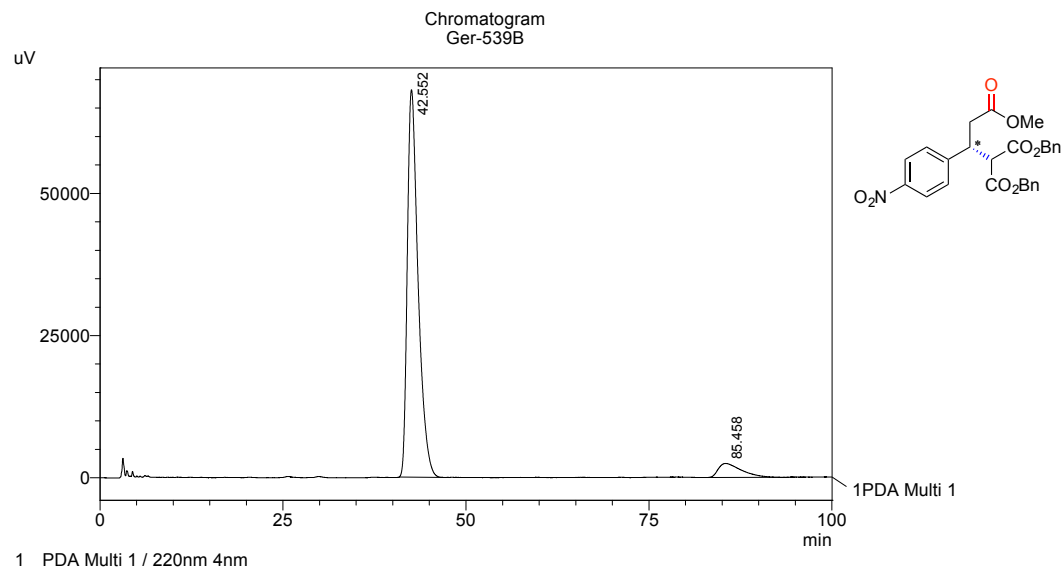


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.281	12794259	281765	49.913	63.544
2	32.609	12838634	161653	50.087	36.456
Total		25632894	443418	100.000	100.000

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(R)-2-Benzyloxycarbonyl-3-(4-nitrophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-539B
Injection Volume : 8 uL
Data Filename : Ger-539B.lcd
Method Filename : paranitro.lcm
Date Acquired : 2013/04/18 15:48:11
Data Processed : 2013/04/18 18:59:16



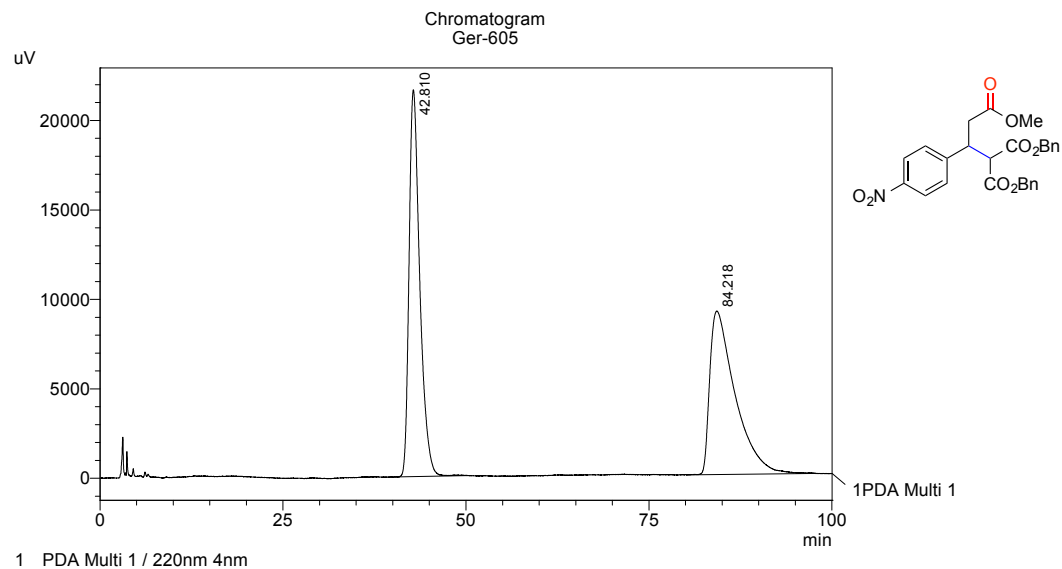
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.552	6983208	68137	92.846	96.517
2	85.458	538081	2459	7.154	3.483
Total		7521289	70596	100.000	100.000

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(rac)-2-Benzyloxycarbonyl-3-(4-nitrophenyl)pentanedioic acid 5-benzyl ester 1-methyl ester

Acquired by : Gerald Choo
Sample Name : Ger-605
Injection Volume : 4 uL
Data Filename : Ger-605.lcd
Method Filename : paranitro.lcm
Date Acquired : 2013/04/18 18:47:47
Data Processed : 2013/04/18 20:48:46

Sample Information

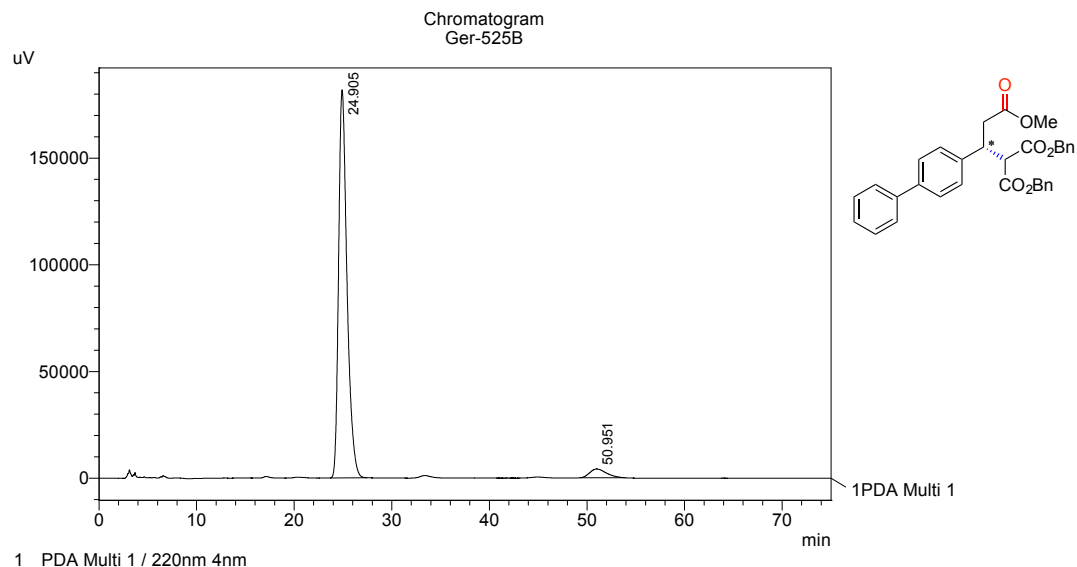


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.810	2203828	21626	50.061	70.293
2	84.218	2198422	9139	49.939	29.707
Total		4402250	30766	100.000	100.000

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(R)-1,1-dibenzyl 3-methyl 2-(biphenyl-4-yl)propane-1,1,3-tricarboxylate

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-525B
Injection Volume : 5 uL
Data Filename : Ger-525B.lcd
Method Filename : Jorgensen 111.lcm
Date Acquired : 2013/03/18 16:25:37
Data Processed : 2013/03/18 18:05:13

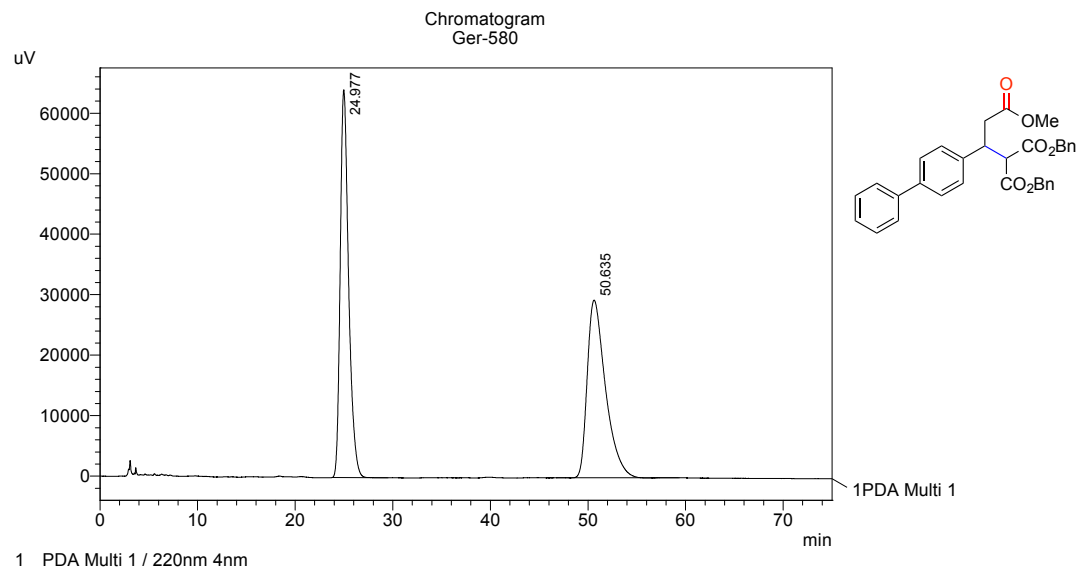


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.905	10878310	181909	95.716	97.789
2	50.951	486850	4114	4.284	2.211
Total		11365160	186023	100.000	100.000

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(rac)-1,1-dibenzyl 3-methyl 2-(biphenyl-4-yl)propane-1,1,3-tricarboxylate

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-580
Injection Volume : 4 uL
Data Filename : Ger-580.lcd
Method Filename : Jorgensen 111.lcm
Date Acquired : 2013/03/18 14:52:30
Data Processed : 2013/03/18 16:09:51

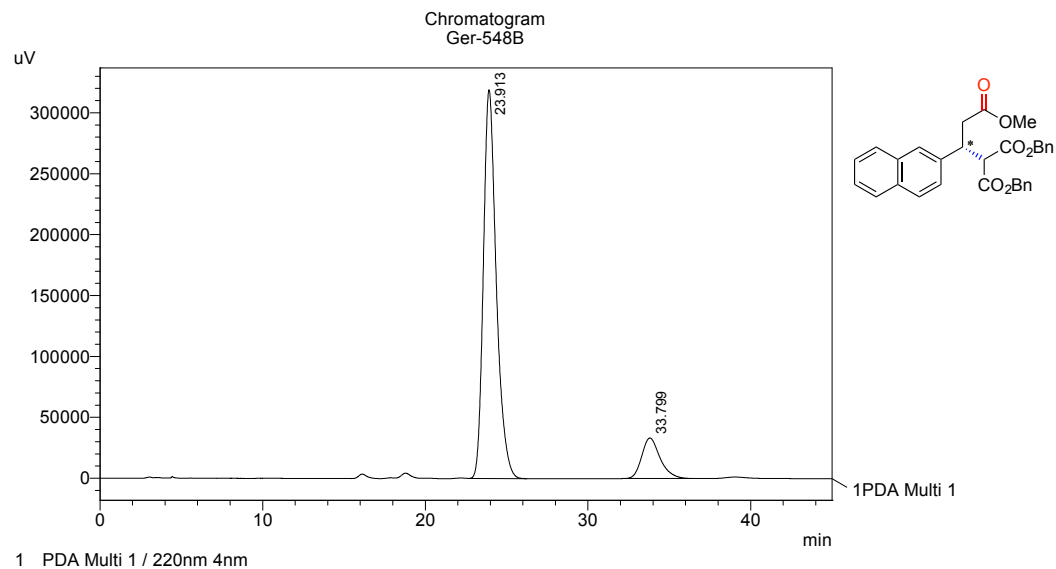


PeakTable						
Peak#	Ret. Time	Area	Height	Area %	Height %	
1	24.977	3840932	64139	50.137	68.592	
2	50.635	3820002	29368	49.863	31.408	
Total		7660933	93507	100.000	100.000	

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(R)-1,1-dibenzyl 3-methyl 2-(naphthalen-2-yl)propane-1,1,3-tricarboxylate

Sample Information
 Acquired by : Gerald Choo
 Sample Name : Ger-548B
 Injection Volume : 0.5 uL
 Data Filename : Ger-548B.lcd
 Method Filename : Jorgensen 11p.lcm
 Date Acquired : 2013/03/18 19:32:12
 Data Processed : 2013/03/18 20:43:58

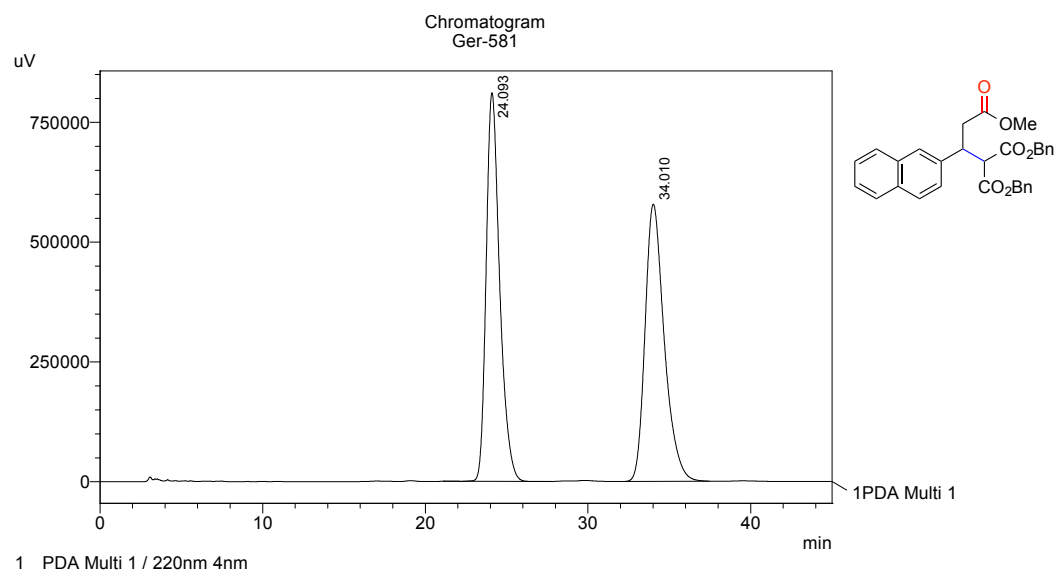


PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.913	17595032	319173	87.090	90.558
2	33.799	2608130	33278	12.910	9.442
Total		20203162	352451	100.000	100.000

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(rac)-1,1-dibenzyl 3-methyl 2-(naphthalen-2-yl)propane-1,1,3-tricarboxylate

Sample Information
Acquired by : Gerald Choo
Sample Name : Ger-581
Injection Volume : 4 uL
Data Filename : Ger-581.lcd
Method Filename : Jorgensen 11p.lcm
Date Acquired : 2013/03/18 18:16:33
Data Processed : 2013/03/18 19:29:01



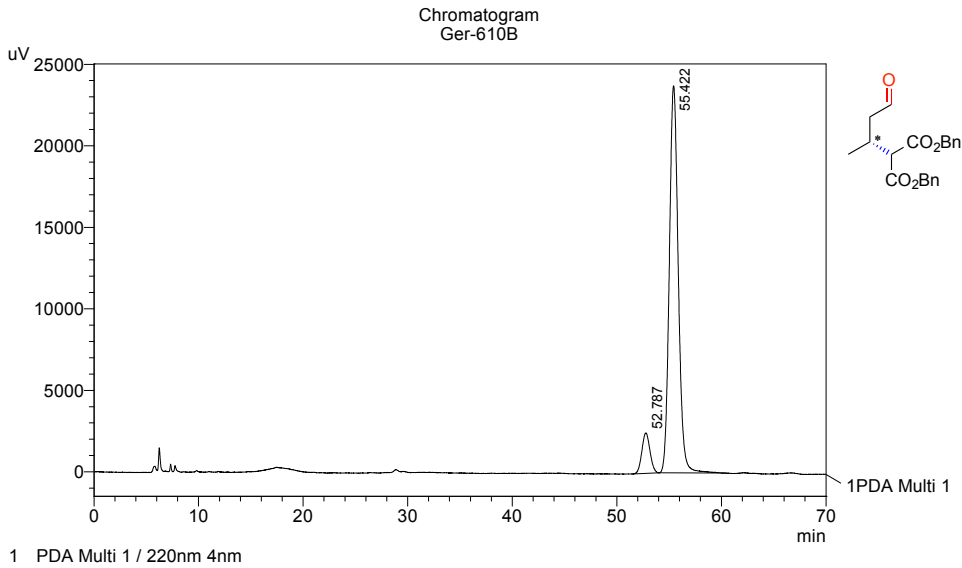
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.093	46852494	811073	49.672	58.378
2	34.010	47470483	578264	50.328	41.622
Total		94322977	1389337	100.000	100.000

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(R)-2-(1-Methyl-3-oxopropyl)malonic acid dibenzyl ester

Acquired by : Gerald Choo
Sample Name : Ger-610B
Injection Volume : 2 uL
Data Filename : Ger-610B.lcd
Method Filename : aliphatic2.lcm
Date Acquired : 2013/04/25 13:20:59
Data Processed : 2013/04/25 14:52:13

Sample Information



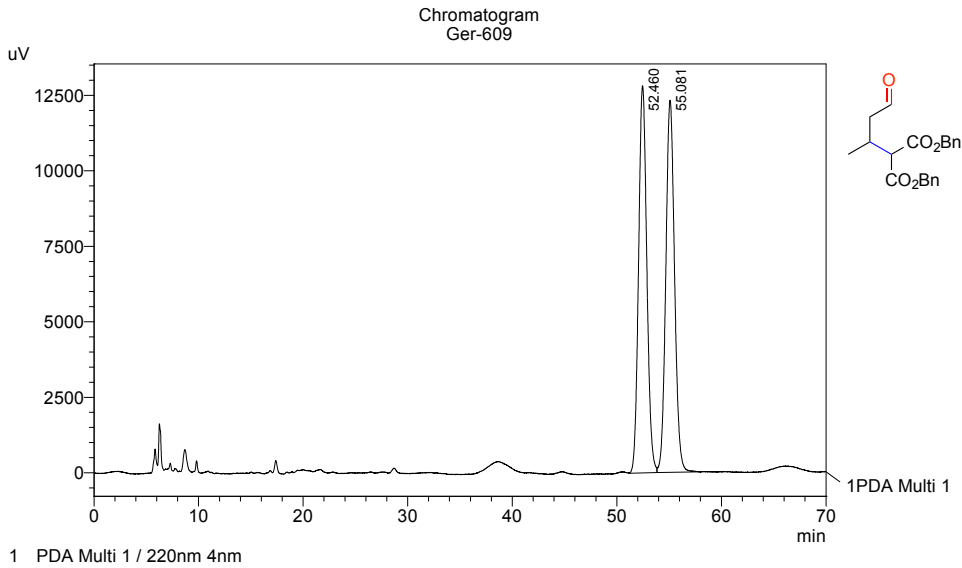
PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.787	134581	2482	8.700	9.461
2	55.422	1412356	23753	91.300	90.539
Total		1546937	26235	100.000	100.000

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(rac)-2-(1-Methyl-3-oxopropyl)malonic acid dibenzyl ester

Acquired by : Gerald Choo
Sample Name : Ger-609
Injection Volume : 2 uL
Data Filename : Ger-609.lcd
Method Filename : aliphatic2.lcm
Date Acquired : 2013/04/25 15:01:35
Data Processed : 2013/04/25 17:07:13

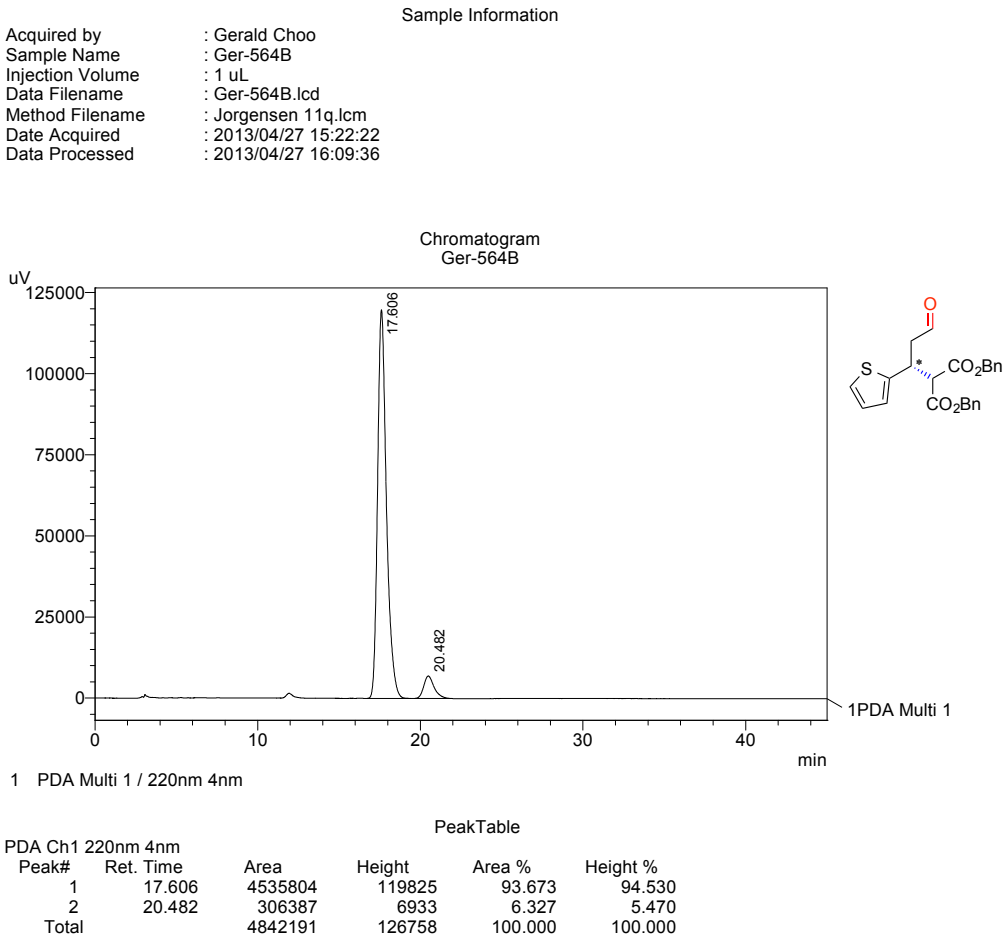
Sample Information



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.460	701764	12824	49.488	50.993
2	55.081	716292	12325	50.512	49.007
Total		1418055	25149	100.000	100.000

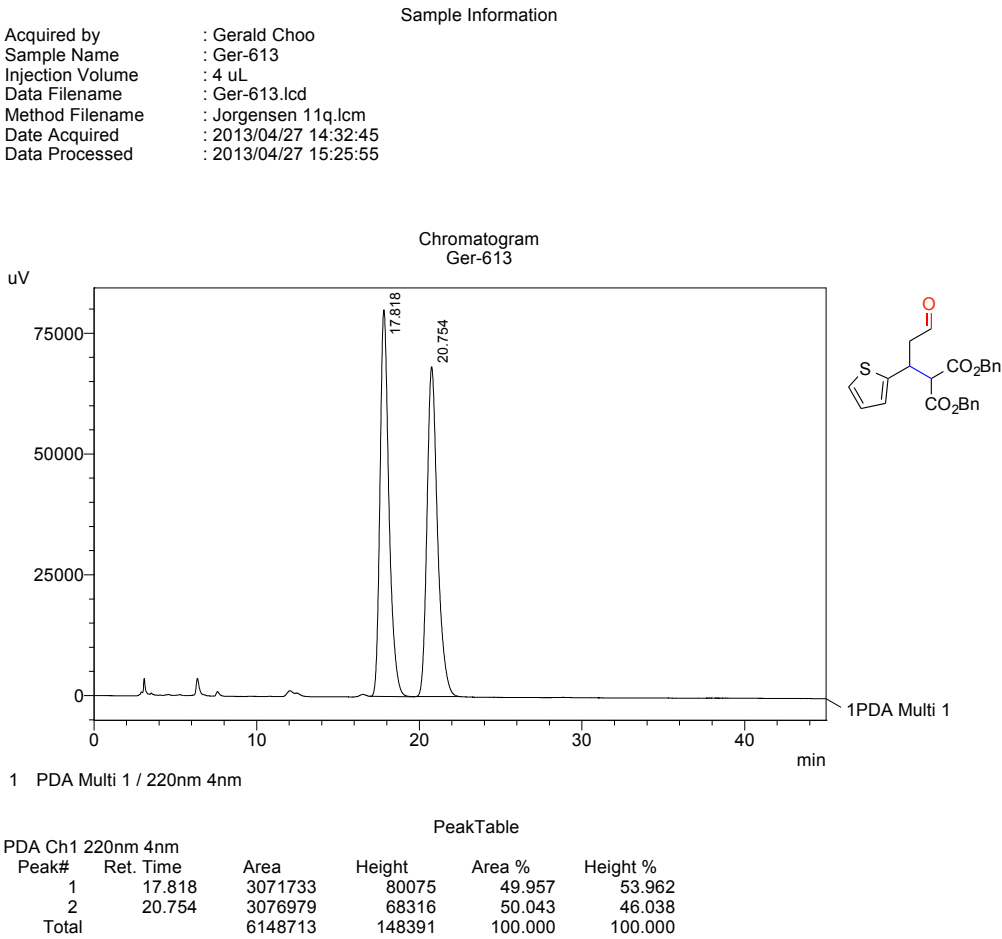
A Heterogeneous Layered Bifunctional Catalyst for the Integration of Aerobic Oxidation and Asymmetric C–C Bond Formation
Hiroyuki Miyamura, Gerald C. Y. Choo, Tomohiro Yasukawa, Woo-Jin Yoo, Shū Kobayashi*

(R)-2-Benzyloxycarbonyl-3-thiophen-2-ylpentanedioic acid 1-benzyl ester 5-methyl ester



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(rac)-2-Benzoyloxycarbonyl-3-thiophen-2-ylpentanedioic acid 1-benzyl ester 5-methyl ester

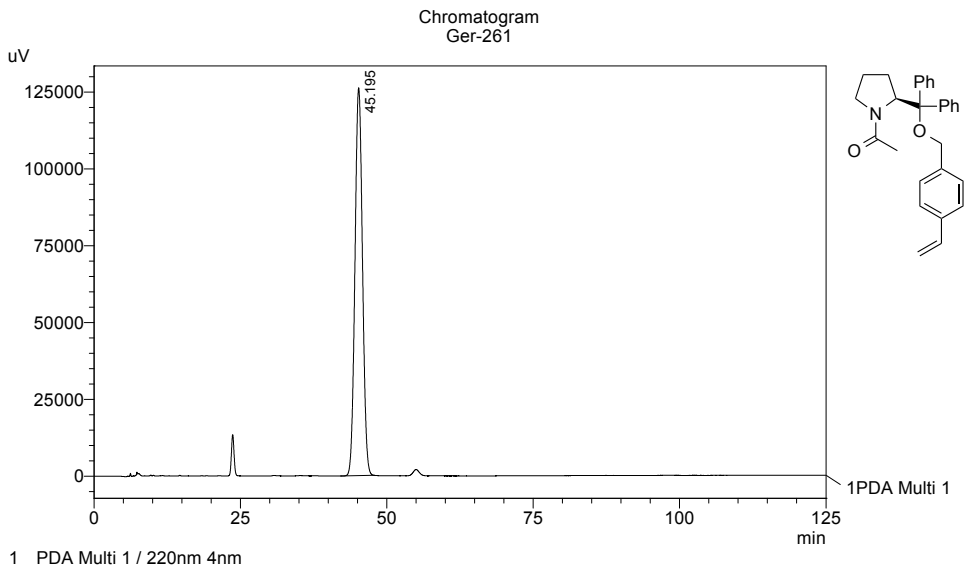


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(S)-N-Acetyl- α,α -diphenylprolinol 4-vinylbenzyl ether

Sample Information

Acquired by : Gerald Choo
Sample Name : Ger-261
Injection Volume : 1 μ L
Data Filename : Ger-261.lcd
Method Filename : Conditions Screening.lcm
Date Acquired : 2012/01/19 19:17:13
Data Processed : 2012/01/20 15:39:41



PeakTable

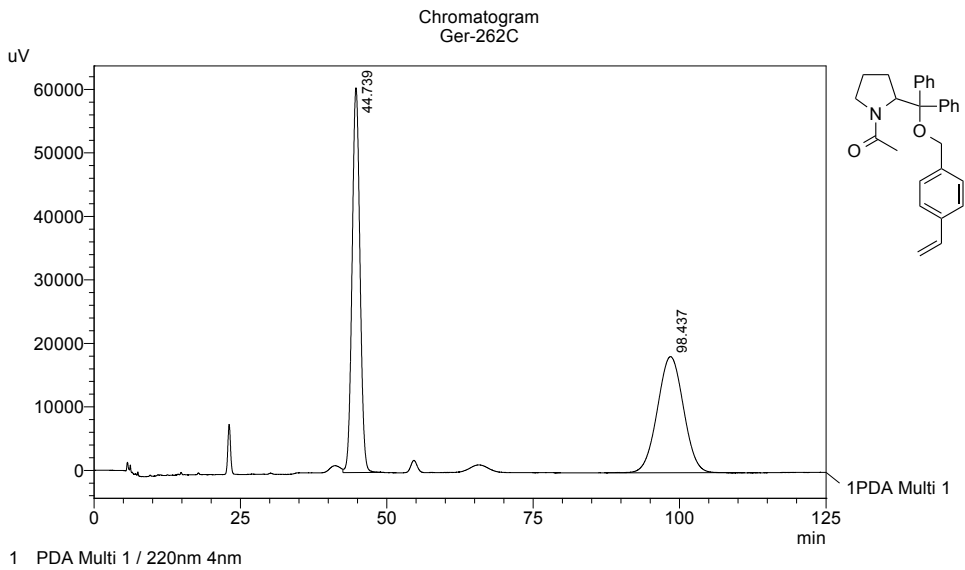
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.195	11258303	126245	100.000	100.000
Total		11258303	126245	100.000	100.000

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(rac)-N-Acetyl- α,α -diphenylprolinol 4-vinylbenzyl ether

Sample Information

Acquired by : Gerald Choo
Sample Name : Ger-262C
Injection Volume : 1 μ L
Data Filename : Ger-262C.lcd
Method Filename : Conditions Screening.lcm
Date Acquired : 2012/01/18 17:49:12
Data Processed : 2012/01/20 15:37:51



PeakTable					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.739	5668355	60629	50.010	76.820
2	98.437	5666158	18294	49.990	23.180
Total		11334513	78923	100.000	100.000