Electronic Supplementary Information for

Enantioselective Protonation of α-Hetero Carboxylic Acid-Derived Ketene Disilyl Acetals under Chiral Ionic Brønsted Acid Catalysis

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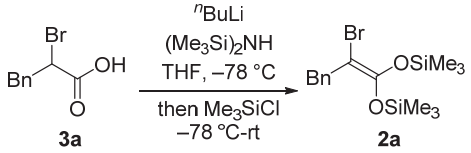
General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz). Chemical shifts are reported in ppm from the solvent resonance (C_6D_6; 7.16 ppm) or tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (C_6D_6; 128.06 ppm, $CDCl_3$; 77.16 ppm). Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) and Chromatorex® TLC plates SO_3H (0.2 mm; Fuji Silysia Chemical ltd.). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.), Silica gel 60 (Merck 1.09385.9929, 230-400 mesh), and Chromatorex® SO_3H MB100-40/75 (spherical, 40-75 μm; Fuji Silysia Chemical ltd.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AD-3 (AD3), CHIRALPAK OJ-H (OJH), CHIRALPAK AD-H (ADH), and CHIRALCEL OD-H (ODH)] with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent.

Toluene, dichloromethane (CH_2Cl_2), diethylether (Et_2O), and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Chiral phosphonium barfates **1**·HBArF (BArF = [3,5-$(CF_3)_2C_6H_3]_4$B) were prepared by following the literature procedure.[1] *p*-Methoxybenzyl (PMB) 2,2,2-trichloroacetimidate was prepared by following literature procedure.[2] Pelleted molecular sieves 4A (MS 4A) was supplied from Merck. Other simple chemicals were purchased and used as such.

Experimental Section:

Preparation and Characterization of Ketene Disilyl Acetals 2

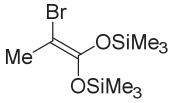
Representative Procedure for Syntheses of 2-Halo Ketene Disilyl Acetals 2[1]:



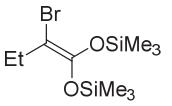
To a solution of $(Me_3Si)_2NH$ (0.58 mL, 2.8 mmol) in THF (2.8 mL) was added a solution of ^{n}BuLi in ^{n}hexane (1.62 M, 1.7 mL, 2.8 mmol) dropwise at 0 °C. After being stirred for 30 min, the mixture was cooled to –78 °C and a solution of **3a** (229.1 mg, 1.0 mmol) in THF (5.0 mL) was slowly introduced. Stirring was continued for 1 h at –78 °C and Me_3SiCl (0.36 mL, 2.8 mmol) was added dropwise to the reaction solution. The reaction mixture was allowed to warm to room temperature over 1 h. All volatiles were removed in vacuo and then, the residue was filtered

[1] D. Uraguchi, N. Kinoshita, T. Ooi, *J. Am. Chem. Soc.* 2010, **132**, 12240.
[2] J. E. Audia, L. Boisvert, A. D. Patten, A. Villalobos, S. J. Danishefsky, *J. Org. Chem.* 1989, **54**, 3738.

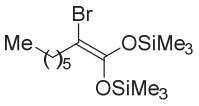
by suction through a pad of Celite with Et_2O. The filtrate was concentrated and the crude residue was purified by standard flash column chromatography on silica gel (H/ethyl acetate (EA) = 30:1) to afford 2-bromo ketene disilyl acetal **2a** (165.8 mg, 0.44 mmol). **2a:** Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (2H, d, J = 7.5 Hz), 7.21 (2H, t, J = 7.5 Hz), 7.08 (1H, t, J = 7.5 Hz), 3.81 (2H, s), 0.27 (9H, s), 0.10 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 149.2, 140.2, 128.9, 128.6, 126.6, 88.1, 40.2, 0.7, 0.3; IR (film): 2959, 1663, 1495, 1454, 1238, 1140, 1026, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{26}O_2{}^{79}BrSi_2{}^+$ ([M+H]$^+$) 373.0649. Found 373.0645.



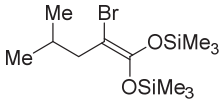
2b: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.13 (3H, s), 0.26 (9H, s), 0.09 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 148.1, 83.3, 21.4, 0.5, 0.2; IR (film): 2961, 2918, 1676, 1439, 1416, 1252, 1233, 1152, 1086, 961, 920, 837 cm^{-1}; HRMS (APCI) Calcd for $C_9H_{22}O_2{}^{79}BrSi_2{}^+$ ([M+H]$^+$) 297.0336. Found 297.0338.



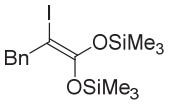
2c: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.47 (2H, q, J = 7.4 Hz), 1.15 (3H, t, J = 7.4 Hz), 0.27 (9H, s), 0.11 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 147.5, 92.1, 27.4, 14.0, 0.6, 0.2; IR (film): 2967, 2936, 1667, 1456, 1418, 1252, 1233, 1148, 1105, 1005, 932, 837 cm^{-1}; HRMS (APCI) Calcd for $C_{10}H_{24}O_2{}^{79}BrSi_2{}^+$ ([M+H]$^+$) 311.0493. Found 311.0492.



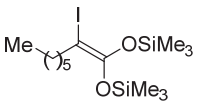
2d: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.50 (2H, t, J = 7.3 Hz), 1.67 (2H, quin, J = 7.3 Hz), 1.40−1.22 (6H, m), 0.89 (3H, t, J = 6.6 Hz), 0.29 (9H, s), 0.14 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 148.1, 90.4, 33.8, 32.0, 29.0, 28.7, 23.1, 14.4, 0.6, 0.3; IR (film): 2957, 2926, 2859, 1667, 1456, 1418, 1252, 1233, 1146, 1123, 1018, 839 cm^{-1}; HRMS (APCI) Calcd for $C_{14}H_{32}O_2{}^{79}BrSi_2{}^+$ ([M+H]$^+$) 367.1119. Found 367.1121.



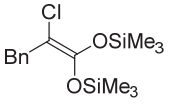
2e: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.36 (2H, d, J = 7.0 Hz), 2.13 (1H, nonet, J = 7.0 Hz), 0.98 (6H, d, J = 7.0 Hz), 0.29 (9H, s), 0.13 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 148.8, 89.2, 43.0, 27.9, 22.2, 0.7, 0.4; IR (film): 2957, 2899, 1667, 1464, 1418, 1252, 1233, 1146, 1126, 1009, 837 cm^{-1}; HRMS (APCI) Calcd for $C_{12}H_{28}O_2{}^{79}BrSi_2{}^+$ ([M+H]$^+$) 339.0806. Found 339.0807.



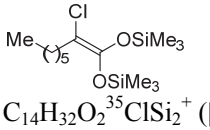
2f: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 (2H, d, J = 7.6 Hz), 7.15 (2H, t, J = 7.6 Hz), 7.03 (1H, t, J = 7.6 Hz), 3.75 (2H, s), 0.22 (9H, s), 0.03 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 150.9, 141.0, 129.0, 128.7, 126.6, 61.9, 42.8, 0.8, 0.3; IR (film): 2959, 1711, 1645, 1495, 1356, 1252, 1225, 1167, 1128, 1020, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{26}O_2ISi_2{}^+$ ([M+H]$^+$) 421.0511. Found 421.0511.



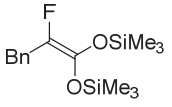
2g: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.43 (2H, t, J = 7.4 Hz), 1.64 (2H, quin, J = 7.4 Hz), 1.40−1.21 (6H, m), 0.89 (3H, t, J = 7.1 Hz), 0.30 (8H, s), 0.13 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 149.8, 64.7, 36.2, 32.0, 30.5, 28.6, 23.1, 14.4, 0.7, 0.3; IR (film): 2957, 2926, 2857, 1649, 1456, 1416, 1252, 1225, 1136, 1119, 995, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{32}O_2ISi_2{}^+$ ([M+H]$^+$) 415.0980. Found 415.0980.



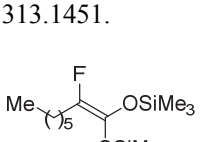
2h: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (2H, d, J = 7.6 Hz), 7.20 (2H, t, J = 7.6 Hz), 7.08 (1H, t, J = 7.6 Hz), 3.72 (2H, s), 0.25 (9H, s), 0.12 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 148.6, 139.9, 128.9, 128.6, 126.6, 96.9, 38.8, 0.7, 0.3; IR (film): 2961, 1672, 1495, 1454, 1417, 1244, 1148, 1044, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{26}O_2{}^{35}ClSi_2{}^+$ ([M+H]$^+$) 329.1154. Found 329.1154.



2i: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.44 (2H, t, J = 7.4 Hz), 1.67 (2H, quin, J = 7.4 Hz), 1.40−1.22 (6H, m), 0.89 (3H, t, J = 6.9 Hz), 0.29 (9H, s), 0.16 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 147.5, 98.6, 32.4, 32.0, 28.9, 28.1, 23.1, 14.3, 0.7, 0.3; IR (film): 2959, 2926, 2859, 1676, 1456, 1416, 1240, 1194, 1152, 1126, 1038, 995, 839 cm^{-1}; HRMS (APCI) Calcd for $C_{14}H_{32}O_2{}^{35}ClSi_2{}^+$ ([M+H]$^+$) 323.1624. Found 323.1626.



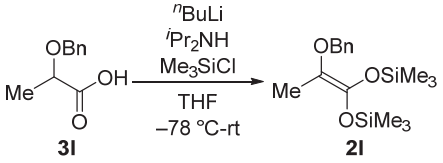
2j: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.32 (2H, d, J = 7.3 Hz), 7.17 (2H, t, J = 7.3 Hz), 7.06 (1H, t, J = 7.3 Hz), 3.66 (2H, d, J_{F-H} = 22.9 Hz), 0.23 (9H, d, J_{F-H} = 1.6 Hz), 0.16 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 141.7 (d, J_{F-C} = 37.7 Hz), 139.1 (d, J_{F-C} = 2.9 Hz), 133.3 (d, J_{F-C} = 224.5 Hz), 128.7, 126.6, 34.0 (d, J_{F-C} = 26.1 Hz), 0.4$_4$ (d, J_{F-C} = 2.9 Hz), 0.3$_5$; IR (film): 2961, 1734, 1495, 1454, 1252, 1229, 1192, 1098, 839 cm^{-1}; HRMS (APCI) Calcd for $C_{15}H_{26}O_2FSi_2{}^+$ ([M+H]$^+$) 313.1450. Found 313.1451.



2k: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 2.41 (2H, td, J_{H-H} = 7.4 Hz, J_{F-H} = 22.6 Hz), 1.60 (2H, quin, J = 7.4 Hz), 1.35 (2H, quin, J = 7.4 Hz), 1.31–1.19 (4H, m), 0.87 (3H, t, J = 7.1 Hz), 0.28 (9H, d, J_{F-H} = 1.4 Hz), 0.20 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 140.9 (d, J_{F-C} = 38.7 Hz), 134.6 (d, J_{F-C} = 224.5 Hz), 32.0, 29.0, 27.4 (d, J_{F-C} = 24.2 Hz), 27.2, 23.0, 14.3, 0.5 (d, J_{F-C} = 2.9 Hz), 0.4; IR (film): 2959, 2928, 2860, 1736, 1458, 1418, 1250, 1215, 1136, 1067, 839 cm^{-1}; HRMS (APCI) Calcd for

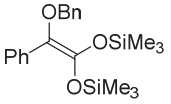
$C_{14}H_{32}O_2FSi_2^+$ ([M+H]$^+$) 307.1919. Found 307.1920.

Representative Procedure for Syntheses of 2-Alkoxy Ketene Disilyl Acetals 2[1]:

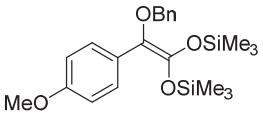


3l **2l**

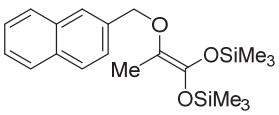
To a solution of ^{i}Pr$_2$NH (0.14 mL, 1.0 mmol) in THF (1.0 mL) was added a solution of ^{n}BuLi in ^{n}hexane (1.63 M, 0.61 mL, 1.0 mmol) dropwise at 0 °C. After being stirred for 30 min at 0 °C, the mixture was cooled to −78 °C and Me$_3$SiCl (0.15 mL, 1.2 mmol) was slowly introduced. Subsequently, a solution of α-alkoxycarboxylic acid **3l** (90.9 mg, 0.5 mmol) in THF (0.30 + 0.20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. All volatiles were removed in vacuo and then, the residue was filtered by suction through a pad of Celite with Et$_2$O. The filtrate was concentrated and the crude residue was purified by standard flash column chromatography on silica gel (H/EA = 20:1). The combined fractions were concentrated and the residue was filtered again by suction through a pad of florisil with Et$_2$O. The filtrate was concentrated to afford 2-alkoxy ketene disilyl acetal **2l** (173.0 mg, 0.5 mmol). **2l:** Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.38 (2H, d, J = 7.3 Hz), 7.19 (2H, t, J = 7.3 Hz), 7.10 (1H, t, J = 7.3 Hz), 4.64 (2H, s), 1.84 (3H, s), 0.27 (9H, s), 0.18 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 143.6, 139.4, 128.4, 128.0, 127.6, 119.1, 71.4, 13.4, 0.7, 0.4; IR (film): 2934, 2903, 1713, 1250, 1211, 1138, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{29}O_3Si_2^+$ ([M+H]$^+$) 325.1650. Found 325.1651.



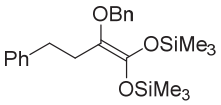
2m: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.91 (2H, d, J = 7.8 Hz), 7.40 (2H, d, J = 7.8 Hz), 7.27 (2H, t, J = 7.8 Hz), 7.19 (2H, t, J = 7.8 Hz), 7.09 (1H, t, J = 7.8 Hz), 7.05 (1H, t, J = 7.8 Hz), 4.72 (2H, s), 0.25 (9H, s), 0.20 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 146.7, 139.1, 135.9, 128.5, 128.4, 127.6, 127.4, 126.5, 125.6, 123.0, 72.5, 0.9, 0.5; IR (film): 3055, 2959, 2901, 1645, 1248, 1140, 1042, 1018, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{31}O_3Si_2^+$ ([M+H]$^+$) 387.1806. Found 387.1806.



2n: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (2H, d, J = 9.2 Hz), 7.43 (2H, d, J = 7.6 Hz), 7.21 (2H, t, J = 7.6 Hz), 7.10 (1H, t, J = 7.6 Hz), 6.89 (2H, t, J = 9.2 Hz), 4.76 (2H, s), 3.33 (3H, s), 0.28 (9H, s), 0.21 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 158.2, 145.6, 139.2, 128.6, 127.6, 127.5, 123.0, 113.9, 72.3, 54.8, 0.9, 0.5, two carbon atoms were not found probably due to overlapping; IR (film): 2957, 2901, 1653, 1508, 1244, 1138, 1024, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{33}O_4Si_2^+$ ([M+H]$^+$) 417.1912. Found 417.1908.

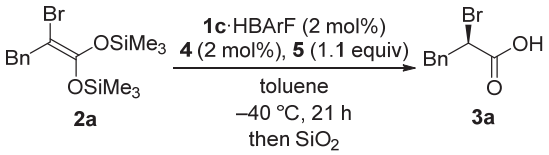


2o: After filtration through a pad of Celite and concentration, the residual material was used for the asymmetric protonation without further purification due to the instability of the title compound. Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (1H, s), 7.70 (1H, dd, J = 1.8, 7.2 Hz), 7.66 (1H, d, J = 8.7 Hz), 7.64 (1H, dd, J = 1.8, 7.2 Hz), 7.52 (1H, dd, J = 1.8, 8.7 Hz), 7.27 (1H, dt, J = 1.8, 7.2 Hz), 7.25 (1H, dt, J = 1.8, 7.2 Hz), 4.79 (2H, s), 1.87 (3H, s), 0.29 (9H, s), 0.17 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 143.6, 136.9, 133.9, 133.5, 128.2, 127.9, 126.7, 126.3, 126.0, 119.2, 71.6, 13.5, 0.7, 0.4, two carbon atoms were not found probably due to overlapping; IR (film): 3055, 2940, 2901, 1728, 1715, 1252, 1211, 1140, 1065, 1020, 841 cm^{-1}; HRMS (APCI) Calcd for $C_{20}H_{31}O_3Si_2^+$ ([M+H]$^+$) 375.1806. Found 375.1807.



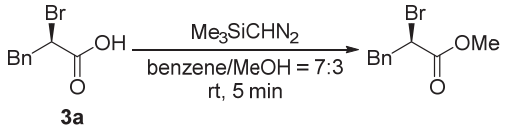
2p: Colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.39 (2H, d, J = 7.3 Hz), 7.23−7.05 (8H, m), 4.66 (2H, s), 2.91 (2H, t, J = 7.9 Hz), 2.57 (2H, t, J = 7.9 Hz), 0.23 (9H, s), 0.17 (9H, s); ^{13}C NMR (101 MHz, C_6D_6) δ 44.3, 142.7, 139.4, 128.9, 128.6, 128.5, 128.0, 127.7, 126.0, 122.5, 71.8, 34.1, 29.6, 0.6, 0.4; IR (film): 3028, 2930, 2901, 1701, 1250, 1211, 1099, 1007, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{35}O_3Si_2^+$ ([M+H]$^+$) 415.2119. Found 415.2121.

Representative Procedure for Chiral Arylaminophosphonium Barfate 1·HBArF-Catalyzed Asymmetric Protonation:

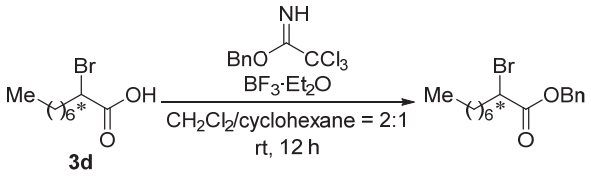


To a solution of 2,6-dimethylphenol **5** (13.5 mg, 0.11 mmol), **1c**·HBArF (3.1 mg, 2.0 μmol), and 2,6-di-*tert*-butylpyridine **4** (0.10 M in toluene, 20 μL, 2.0 μmol) in toluene (0.70 mL) was slowly added a solution of **2a** (37.5 mg, 0.10 mmol) in toluene (0.20 + 0.10 mL) at –40 °C under argon atmosphere. Consumption of **2a** was confirmed by TLC and the reaction mixture was directly subjected to the purification by standard flash column chromatography on silica gel (H/EA = 15:1-0:100 as eluent) to give α-hetero carboxylic acid **3a** in 99% yield (23.1 mg, 0.10 mmol). The enantiomeric excess of **3a** was determined after esterification.

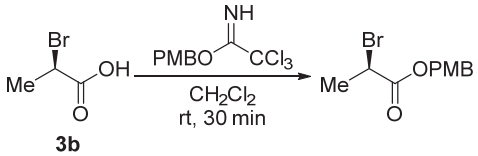
Procedures for Esterification of Chiral α-Hetero Carboxylic Acids:



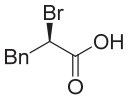
Method A: To a solution of **3a** (22.9 mg, 0.10 mmol) in benzene/MeOH (v/v = 7:3, 1.0 mL) was added a solution of trimethylsilyldiazomethane in Et_2O (2.0 M, 0.1 mL, 0.2 mmol) with stirring at room temperature. The reaction mixture was concentrated and the crude residue was purified by standard flash column chromatography on silica gel to give the corresponding methyl ester. The enantiomeric excess of the methyl ester of **3a** thus obtained was determined by chiral stationary phase HPLC analysis.



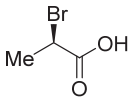
Method B: To a solution of **3d** (23.3 mg, 0.10 mmol) and benzyl 2,2,2-trichloroacetimidate (38 μL, 2.0 equiv) in CH_2Cl_2/cyclohexane (v/v = 2:1, 0.31 mL, cyclohexane was dried by activated MS 4A in advance) was added $BF_3·Et_2O$ (2.1 μL, 16.0 mol%) with stirring at room temperature. After being stirred for 12 h, the reaction mixture was filtered through a pad of Celite with the aid of cyclohexane. The filtrate was concentrated and the residue was purified by standard flash column chromatography on silica gel to afford the corresponding benzyl ester (11.3 mg, 0.035 mmol). The enantiomeric excess of the benzyl ester thus obtained was determined by chiral stationary phase HPLC analysis.



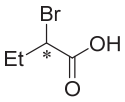
Method C: To a solution of **3b** (13.6 mg, 0.087 mmol) in CH_2Cl_2 (0.18 mL) was added *p*-methoxybenzyl 2,2,2-trichloroacetimidate (30.5 mg, 0.11 mmol) dropwise with stirring at room temperature. Stirring was continued for 30 min and the reaction mixture was filtered through a pad of Celite with the aid of ^{n}hexane. The filtrate was concentrated and the residue was purified by standard flash column chromatography on silica gel to afford the *p*-methoxybenzyl ester (19.8 mg, 0.072 mmol). The enantiomeric excess of the *p*-methoxybenzyl ester thus obtained was determined by chiral stationary phase HPLC analysis.



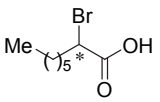
3a[3,4]**:** Analytical and spectral data were in agreement with the literature data. Colorless oil in 99% yield. $[\alpha]^{19}_D$ +16.2 (c = 2.21, CH_2Cl_2) for 93% ee [lit.[3] $[\alpha]^{20}_D$ −13.3 (c = 4.50, CH_2Cl_2) for (*S*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.26 (3H, m), 7.23 (2H, d, J = 8.2 Hz), 4.43 (1H, dd, J = 7.3, 8.2 Hz), 3.47 (1H, dd, J = 8.2, 14.2 Hz), 3.25 (1H, dd, J = 7.3, 14.2 Hz), O-H proton was not found due to broadening. **Methyl ester of 3a**[5,6]**:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. Analytical and spectral data were in agreement with the literature data. HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 9.4 min (*R*), 13.0 min (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.24 (3H, m), 7.21 (2H, d, J = 8.7 Hz), 4.41 (1H, dd, J = 7.1, 8.4 Hz), 3.47 (1H, dd, J = 8.4, 14.3 Hz), 3.24 (1H, dd, J = 7.1, 14.3 Hz).



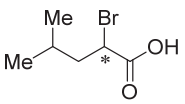
3b[3,7]**:** Analytical and spectral data were in agreement with the literature data. Colorless oil in 87% yield. $[\alpha]^{22}_D$ +28.7 (c = 1.37, $CHCl_3$) for 89% ee [lit.[7] $[\alpha]^{21\text{-}25}_D$ +29.1 (c = 2.00, $CHCl_3$) for (*R*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (1H, q, J = 7.1 Hz), 1.86 (3H, d, J = 7.1 Hz), O-H proton was not found due to broadening. **PMB ester of 3b:** The synthesis was performed according to the Method C and the title compound was obtained as colorless oil. HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 14.1 min (*S*), 15.9 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.7 Hz), 5.13 (2H, s), 4.38 (1H, q, J = 7.0 Hz), 3.80 (3H, s), 1.81 (3H, d, J = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 159.9, 130.3, 127.3, 114.1, 67.6, 55.4, 40.3, 21.7; IR (film): 2959, 2936, 2837, 1732, 1613, 1514, 1445, 1333, 1246, 1150, 1032, 820 cm^{-1}; HRMS(ESI) Calcd for $C_{11}H_{13}O_3{}^{79}BrNa^+$ ([M+Na]$^+$) 294.9940. Found 294.9941.



3c: Colorless oil in 92% yield. $[\alpha]^{22}_D$ +33.5 (c = 1.64, $CHCl_3$) for 92% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (1H, t, J = 7.3 Hz), 2.14 (1H, quin-d, J = 7.3, 14.5 Hz), 2.04 (1H, quin-d, J = 7.3, 14.5 Hz), 1.07 (3H, t, J = 7.3 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 47.2, 28.2, 12.0; IR (film): 2974, 2938, 1709, 1420, 1279, 1223, 1173, 924, 887 cm^{-1}; HRMS (ESI) Calcd for $C_4H_6O_2{}^{79}Br^-$ ([M−H]$^-$) 164.9546. Found 164.9548. **PMB ester of 3c:** The synthesis was performed according to the Method C and the title compound was obtained as colorless oil. HPLC OJH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 22.9 min (minor isomer), 24.7 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.7 Hz), 5.13 (2H, s), 4.17 (1H, t, J = 7.3 Hz), 3.80 (3H, s), 2.10 (1H, quin-d, J = 7.3, 14.6 Hz), 2.00 (1H, quin-d, J = 7.3, 14.6 Hz), 0.99 (3H, t, J = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 159.8, 130.2, 127.4, 114.0, 67.5, 55.3, 47.9, 28.4, 11.9; IR (film): 2970, 2938, 1734, 1613, 1514, 1456, 1246, 1146, 1032, 820 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{15}O_3{}^{79}BrNa^+$ ([M+Na]$^+$) 309.0097. Found 309.0096.



3d: Colorless oil in 93% yield. $[\alpha]^{21}_D$ +31.1 (c = 2.03, $CHCl_3$) for 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (1H, t, J = 7.3 Hz), 2.15−1.94 (2H, m), 1.54−1.22 (8H, m), 0.89 (3H, t, J = 6.9 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 45.5, 34.7, 31.6, 28.6, 27.3, 22.6, 14.2; IR (film): 3013, 2955, 2926, 2857, 1713, 1456, 1422, 1281, 1186, 918 cm^{-1}; HRMS (ESI) Calcd for $C_8H_{14}O_2{}^{79}Br^-$ ([M−H]$^-$) 221.0172. Found 221.0178. **Bn ester of 3d:** The synthesis was performed according to the Method B and the title compound was obtained as colorless oil. HPLC OJH, H/EtOH = 19:1, flow rate = 0.5 mL/min, λ = 210 nm, 10.8 min (minor isomer), 11.4 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.31 (5H, m), 5.20 (2H, s), 4.25 (1H, t, J = 7.5 Hz), 2.13−1.93 (2H, m), 1.50–1.38 (1H, m), 1.38−1.19 (7H, m), 0.87 (3H, t, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 135.3, 128.8, 128.6, 128.4, 67.6, 46.1, 35.0, 31.6, 28.6, 27.3, 22.6, 14.2; IR (film): 2955, 2926, 2857, 1738, 1456, 1263, 1144, 966 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{21}O_2{}^{79}BrNa^+$ ([M+Na]$^+$) 335.0617. Found 335.0617.



3e: Colorless oil in 90% yield. $[\alpha]^{20}_D$ +42.3 (c = 1.73, $CHCl_3$) for 85% ee; ^{1}H NMR (400 MHz, C_6D_6) δ 4.10 (1H, dd, J = 7.2, 8.3 Hz), 1.71 (1H, ddd, J = 6.8, 8.3, 14.5 Hz), 1.69 (1H, ddd, J = 6.8, 7.2, 14.5 Hz), 1.57 (1H, nonet, J = 6.8 Hz), 0.62 (3H, d, J = 6.8 Hz), 0.57 (3H, d, J = 6.8 Hz) , O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 44.1, 43.3, 26.4, 22.4, 21.7; IR (film): 3019, 2959, 2911, 2872, 1713, 1470, 1420, 1285, 1258, 1171, 920, 880 cm^{-1}; HRMS (ESI) Calcd for $C_6H_{10}O_2{}^{79}Br^-$ ([M−H]$^-$) 192.9859. Found 192.9863. **Bn ester of 3e:** The synthesis was performed according to the Method B and the title compound was obtained as colorless oil. HPLC OJH, H/EtOH = 97:3, flow rate = 0.5 mL/min, λ = 210 nm, 12.2 min (minor isomer), 12.9 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.31 (5H, m), 5.22 (1H, d, J = 12.6 Hz), 5.18 (1H, d, J = 12.6 Hz), 4.32 (1H, dd, J = 7.4, 8.2 Hz), 1.98–1.86 (2H, m), 1.75 (1H, nonet, J = 6.7 Hz), 0.94 (3H, d, J = 7.0 Hz), 0.89 (3H, d, J = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 135.3, 128.7, 128.6, 128.3, 67.6, 44.7, 43.5, 26.4, 22.5, 21.7; IR (film): 2959, 2934, 1738, 1456, 1277, 1238, 1148, 1121, 966 cm^{-1}; HRMS

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[5] N. Yoshikawa, Y. M. A. Yamada, J. Das, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc*. 1999, **121**, 4168.
[6] P.-Y. Géant, J. Martínez, X. J. Salom-Roig, *Eur. J. Org. Chem*. 2011, 1300.
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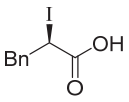
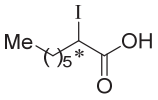
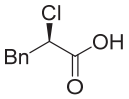
(ESI) Calcd for $C_{13}H_{17}O_2{}^{79}BrNa^+$ ([M+Na]$^+$) 307.0304. Found 307.0304.



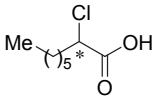
3f: White solid in 92% yield. $[\alpha]^{23}_D$ +38.5 (c = 2.59, $CHCl_3$) for 93% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.28 (3H, m), 7.21 (2H, d, J = 7.8 Hz), 4.54 (1H, dd, J = 7.0, 9.0 Hz), 3.45 (1H, dd, J = 9.0, 14.7 Hz), 3.26 (1H, dd, J = 7.0, 14.7 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 138.2, 129.0, 128.9, 127.5, 42.1, 19.4; IR (film): 3061, 3028, 1701, 1416, 1284, 1240, 1169, 912 cm^{-1}; HRMS (ESI) Calcd for $C_9H_8O_2I^-$ ([M−H]$^-$) 274.9563. Found 274.9576. **Methyl ester of 3f**[8]**:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. Analytical and spectral data were in agreement with the literature data. HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 9.6 min (*R*), 12.3 min (*S*); $[\alpha]^{23}_D$ +53.0 (c = 2.45, $CHCl_3$) for 93% ee [lit.[8] $[\alpha]^{30}_D$ +24.8 (c = 1.0, $CHCl_3$) for (*R*)-isomer 92% ee]; ^{1}H NMR (400 MHz, $CHCl_3$) δ 7.35−7.25 (3H, m), 7.20 (2H, d, J = 7.8 Hz), 4.52 (1H, dd, J = 6.9, 9.3 Hz), 3.70 (3H, s), 3.47 (1H, dd, J = 9.3, 14.3 Hz), 3.26 (1H, dd, J = 6.9, 14.3 Hz).



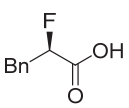
3g: Colorless oil in 99% yield. $[\alpha]^{19}_D$ +48.6 (c = 2.64, $CHCl_3$) for 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (1H, t, J = 7.6 Hz), 2.03–1.94 (2H, m), 1.50–1.37 (1H, m), 1.37−1.29 (7H, m), 0.89 (3H, t, J = 6.9 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 35.9, 31.6, 29.4, 28.5, 22.6, 20.1, 14.2; IR (film): 2955, 2924, 2855, 1703, 1456, 1418, 1277, 1236, 1176, 1098, 909 cm^{-1}; HRMS (ESI) Calcd for $C_8H_{14}O_2I^-$ ([M−H]$^-$) 269.0033. Found 269.0044. **PMB ester of 3g:** The synthesis was performed according to the Method C and the title compound was obtained as colorless oil. HPLC ODH, H/IPA = 19:1, flow rate = 0.5 mL/min, λ = 210 nm, 9.9 min (minor isomer), 10.7 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, d, J = 8.7 Hz), 6.90 (2H, d, J = 8.7 Hz), 5.13 (1H, d, J = 12.6 Hz), 5.10 (1H, d, J = 12.6 Hz), 4.30 (1H, t, J = 7.8 Hz), 3.82 (3H, s), 2.01−1.93 (2H, m), 1.43−1.18 (8H, m), 0.87 (3H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 159.9, 130.3, 127.5, 114.0, 67.4, 55.4, 36.2, 31.6, 29.4, 28.5, 22.6, 21.5, 14.2; IR (film): 2953, 2926, 2855, 1728, 1612, 1514, 1462, 1246, 1171, 1128, 1034, 955, 820 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{23}O_3INa^+$ ([M+Na]$^+$) 413.0584. Found 413.0583.



3h[3]**:** Analytical and spectral data were in agreement with the literature data. Colorless oil in 86% yield. $[\alpha]^{21}_D$ +2.4 (c = 1.60, CH_2Cl_2) for 87% ee [lit.[3] $[\alpha]^{20}_D$ −4.7 (c = 5.0, CH_2Cl_2) for (*S*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.26 (3H, m), 7.25 (2H, d, J = 8.2 Hz), 4.50 (1H, dd, J = 6.8, 7.8 Hz), 3.40 (1H, dd, J = 6.8, 14.3 Hz), 3.20 (1H, dd, J = 7.8, 14.3 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 135.6, 129.5, 128.8, 127.6, 57.4, 40.9; IR (film): 3065, 3030, 1717, 1497, 1454, 1435, 1287, 1194, 916, 831 cm^{-1}; HRMS (ESI) Calcd for $C_9H_8O_2{}^{35}Cl^-$([M−H]$^-$) 183.0207. Found 183.0211. **Methyl ester of 3h:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.3 min (*R*), 15.2 min (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.24 (3H, m), 7.22 (2H, d, J = 8.2 Hz), 4.45 (1H, t, J = 7.5 Hz), 3.74 (3H, s), 3.37 (1H, dd, J = 7.5, 14.2 Hz), 3.17 (1H, dd, J = 7.5, 14.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 136.8, 129.3, 128.8, 127.5, 53.1, 45.2, 41.2; IR (film): 3030, 3005, 1738, 1495, 1454, 1435, 1360, 1227, 1148, 980, 845 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{11}O_2{}^{35}ClNa^+$ ([M+Na]$^+$) 221.0340. Found 221.0341.



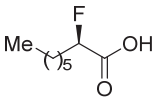
3i: Colorless oil in 92% yield. $[\alpha]^{22}_D$ +18.3 (c = 1.64, $CHCl_3$) for 90% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (1H, dd, J = 5.9, 8.0 Hz), 2.06 (1H, tdd, J = 5.9, 9.8, 13.7 Hz), 1.95 (1H, dddd, J = 5.5, 8.0, 9.9, 13.7 Hz), 1.57–1.39 (2H, m), 1.39–1.24 (6H, m), 0.89 (3H, t, J = 7.1 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 57.2, 34.9, 31.6, 28.6, 26.0, 22.6, 14.1; IR (film): 3017, 2955, 2928, 2859, 1719, 1456, 1422, 1285, 1202, 918 cm^{-1}; HRMS (ESI) Calcd for $C_8H_{14}O_2{}^{35}Cl^-$ ([M−H]$^-$) 177.0677. Found 177.0679. **PMB ester of 3i:** The synthesis was performed according to the Method C and the title compound was obtained as colorless oil. HPLC OJH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 13.4 min (minor isomer), 14.2 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 9.0 Hz), 6.89 (2H, d, J = 9.0 Hz), 5.13 (2H, s), 4.27 (1H, dd, J = 5.9, 7.8 Hz), 3.80 (3H, s), 1.99 (1H, tdd, J = 5.9, 9.6, 14.2 Hz), 1.90 (1H, dddd, J = 5.0, 7.8, 9.4, 14.2 Hz), 1.47−1.18 (8H, m), 0.87 (3H, t, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 159.9, 130.3, 127.3, 114.0, 67.5, 57.5, 55.3, 35.0, 31.6, 28.6, 25.9, 22.5, 14.1; IR (film): 2955, 2928, 2859, 1742, 1612, 1514, 1462, 1246, 1157, 1034, 953, 822 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{23}O_3{}^{35}ClNa^+$ ([M+Na]$^+$) 321.1228. Found 321.1226.



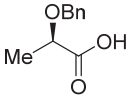
3j[3,9]**:** Analytical and spectral data were in agreement with the literature data. White solid in 93% yield. $[\alpha]^{21}_D$ +38.3 (c = 1.17, CH_2Cl_2) for 88% ee [lit.[3] $[\alpha]^{20}_D$ −7.2 (c = 2.5, CH_2Cl_2) for (*S*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.25 (5H, m), 5.18 (1H, ddd, J_{H-H} = 3.9, 7.8 Hz, J_{F-H} = 49.4 Hz), 3.31 (1H, ddd, J_{H-H} = 3.9, 14.9 Hz, J_{F-H} = 28.9 Hz), 3.20 (1H, ddd, J_{H-H} = 7.8, 14.9 Hz, J_{F-H} = 25.5 Hz), O-H proton was not found due to broadening. **Methyl ester of 3j:** The synthesis was performed according to the Method A

[8] T. Kano, M. Ueda, K. Maruoka, *J. Am. Chem. Soc.* 2008, **130**, 3728.
[9] Y. Takeuchi, K. Nagata, T. Koizumi, *J. Org. Chem*. 1989, **54**, 5453.

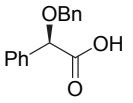
and the title compound was obtained as colorless oil. HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 16.8 min (*R*), 18.1 min (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.21 (5H, m), 5.11 (1H, ddd, J_{H-H} = 4.2, 8.3 Hz, J_{F-H} = 49.0 Hz), 3.24 (1H, ddd, J_{H-H} = 4.2, 14.6 Hz, J_{F-H} = 29.4 Hz), 3.15 (1H, ddd, J_{H-H} = 8.3, 14.6 Hz, J_{F-H} = 25.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (d, J_{F-C} = 27.0 Hz), 135.2, 129.5, 128.7, 127.4, 89.4 (d, J_{F-C} = 190.6 Hz), 52.5, 38.8 (d, J_{F-C} = 21.3 Hz); IR (film): 3032, 2955, 1759, 1740, 1439, 1366, 1285, 1221, 1082, 1022 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{12}O_2F^+$ ($[M+H]^+$) 183.0816. Found 183.0817.



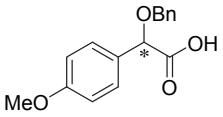
3k[10]**:** Analytical and spectral data were in agreement with the literature data. Colorless oil in 90% yield. $[\alpha]^{24}_D$ +8.5 (*c* = 1.47, $CHCl_3$) for 92% ee; [lit.[10] $[\alpha]^{28}_D$ +9.7 (*c* = 1.25, $CHCl_3$) for (*R*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (1H, td, J_{H-H} = 5.7 Hz, J_{F-H} = 49.6 Hz), 2.02−1.85 (2H, m), 1.56−1.43 (2H, m), 1.42−1.24 (6H, m), 0.89 (3H, t, *J* = 6.9 Hz), O-H proton was not found due to broadening. **PMB ester of 3k:** The synthesis was performed according to the Method C and the title compound was obtained as colorless oil. HPLC OJH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 14.9 min (*S*), 16.0 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, d, *J* = 8.7 Hz), 6.90 (2H, d, *J* = 8.7 Hz), 5.16 (2H, s), 4.91 (1H, ddd, J_{H-H} = 5.6, 6.3 Hz, J_{F-H} = 49.5 Hz), 3.82 (3H, s), 1.94−1.79 (2H, m), 1.50−1.19 (8H, m), 0.88 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2 (d, J_{F-C} = 24.2 Hz), 160.0, 130.5, 127.4, 114.1, 89.1 (d, J_{F-C} = 186.7 Hz), 67.0, 55.4, 32.5 (d, J_{F-C} = 21.3 Hz), 31.6, 28.8, 24.3, 22.6, 14.2; IR (film): 2955, 2928, 2859, 1757, 1738, 1614, 1514, 1414, 1246, 1173, 1134, 1034, 914, 822 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{23}O_3FNa^+$ ($[M+Na]^+$) 305.1523. Found 305.1522.



3l[11]**:** Analytical and spectral data were in agreement with the literature data. White solid in 86% yield. $[\alpha]^{19}_D$ +91.0 (*c* = 1.61, EtOH) for 95% ee [lit.[11] $[\alpha]_D$ +82.7 (*c* = 2.25, EtOH) for (*R*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.30 (5H, m), 4.70 (1H, d, *J* = 11.9 Hz), 4.56 (1H, d, *J* = 11.9 Hz), 4.12 (1H, q, *J* = 7.0 Hz), 1.50 (3H, d, *J* = 7.0 Hz), O-H proton was not found due to broadening. **Methyl ester of 3l**[12]**:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. Analytical and spectral data were in agreement with the literature data. HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.9 min (*R*), 15.2 min (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.27 (5H, m), 4.70 (1H, d, *J* = 11.9 Hz), 4.46 (1H, d, *J* = 11.9 Hz), 4.08 (1H, q, *J* = 6.9 Hz), 1.44 (3H, d, *J* = 6.9 Hz).

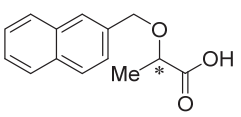


3m: Analytical and spectral data were in agreement with the literature data. White solid in 99 % yield. $[\alpha]^{21}_D$ −98.3 (*c* = 2.44, $CHCl_3$) for 89% ee [lit.[13] $[\alpha]^{25}_D$ −108 (*c* = 2.40, $CHCl_3$) for (*R*)-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.31 (10H, m), 4.96 (1H, s), 4.65 (1H, d, *J* = 11.9 Hz), 4.53 (1H, d, *J* = 11.9 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 136.6, 135.5, 129.2, 129.0, 128.7, 128.4, 128.3, 127.6, 79.2, 71.3; IR (film): 3065, 2891, 1755, 1724, 1456, 1393, 1167, 1086, 1065 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{13}O_3^-$ ($[M-H]^-$) 241.0859. Found 241.0865. **Methyl ester of 3m:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. HPLC AD3, H/IPA = 19:1, flow rate = 0.5 mL/min, λ = 210 nm, 14.1 min (*S*), 14.9 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.44 (2H, m), 7.41−7.28 (8H, m), 4.94 (1H, s), 4.61 (1H, d, *J* = 12.2 Hz), 4.57 (1H, d, *J* = 12.2 Hz), 3.71 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 137.2, 136.3, 128.9, 128.8, 128.6, 128.2, 128.1, 127.5, 79.6, 71.2, 52.4; IR (film): 3030, 3007, 2926, 1748, 1454, 1250, 1207, 1171, 1098, 1026 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}O_3Na^+$ ($[M+Na]^+$) 279.0992. Found 279.0996.

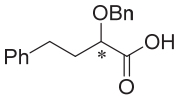


3n: White solid in 93% yield. $[\alpha]^{22}_D$ −116.2 (*c* = 2.53, $CHCl_3$) for 89% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.28 (7H, m), 6.92 (2H, d, *J* = 8.7 Hz), 4.89 (1H, s), 4.60 (1H, d, *J* = 11.9 Hz), 4.51 (1H, d, *J* = 11.9 Hz), 3.81 (3H, s), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 160.3, 136.7, 129.0, 128.7, 128.3, 127.5, 114.4, 78.7, 71.0, 55.5, one carbon was not found probably due to overlapping; IR (film): 3036, 3011, 2880, 2839, 1709, 1609, 1512, 1246, 1096, 1017, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}O_4^-$ ($[M-H]^-$) 271.0965. Found 271.0971. **Methyl ester of 3n:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. HPLC ODH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 8.7 min (minor isomer), 10.0 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, d, *J* = 8.7 Hz), 7.36−7.27 (5H, m), 6.90 (2H, d, *J* = 8.7 Hz), 4.88 (1H, s), 4.58 (1H, d, *J* = 12.4 Hz), 4.53 (1H, d, *J* = 12.4 Hz), 3.80 (3H, s), 3.70 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 160.1, 137.3, 129.0, 128.6, 128.4, 128.2, 128.1, 114.2, 79.1, 71.0, 55.4, 52.4; IR (film): 2951, 2905, 1748, 1611, 1510, 1246, 1207, 1171, 1094, 1028 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}O_4Na^+$ ($[M+Na]^+$) 309.1097. Found 309.1097.

[10] Y.-M. Zhao, M. S. Cheung, Z. Lin, J. Sun, *Angew. Chem., Int. Ed.* 2012, **51**, 10359.
[11] H. Lubin, A. Tessier, G. Chaume, J. Pytkowicz, T. Brigaud, *Org. Lett.* 2010, **12**, 1496.
[12] C. Dubost, B. Leroy, I. E. Markó, B. Tinant, J.-P. Declercq, J. Bryans, *Tetrahedron* 2004, **60**, 7693.
[13] W. A. Bonner, *J. Org. Chem.* 1967, **32**, 2496.

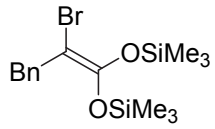


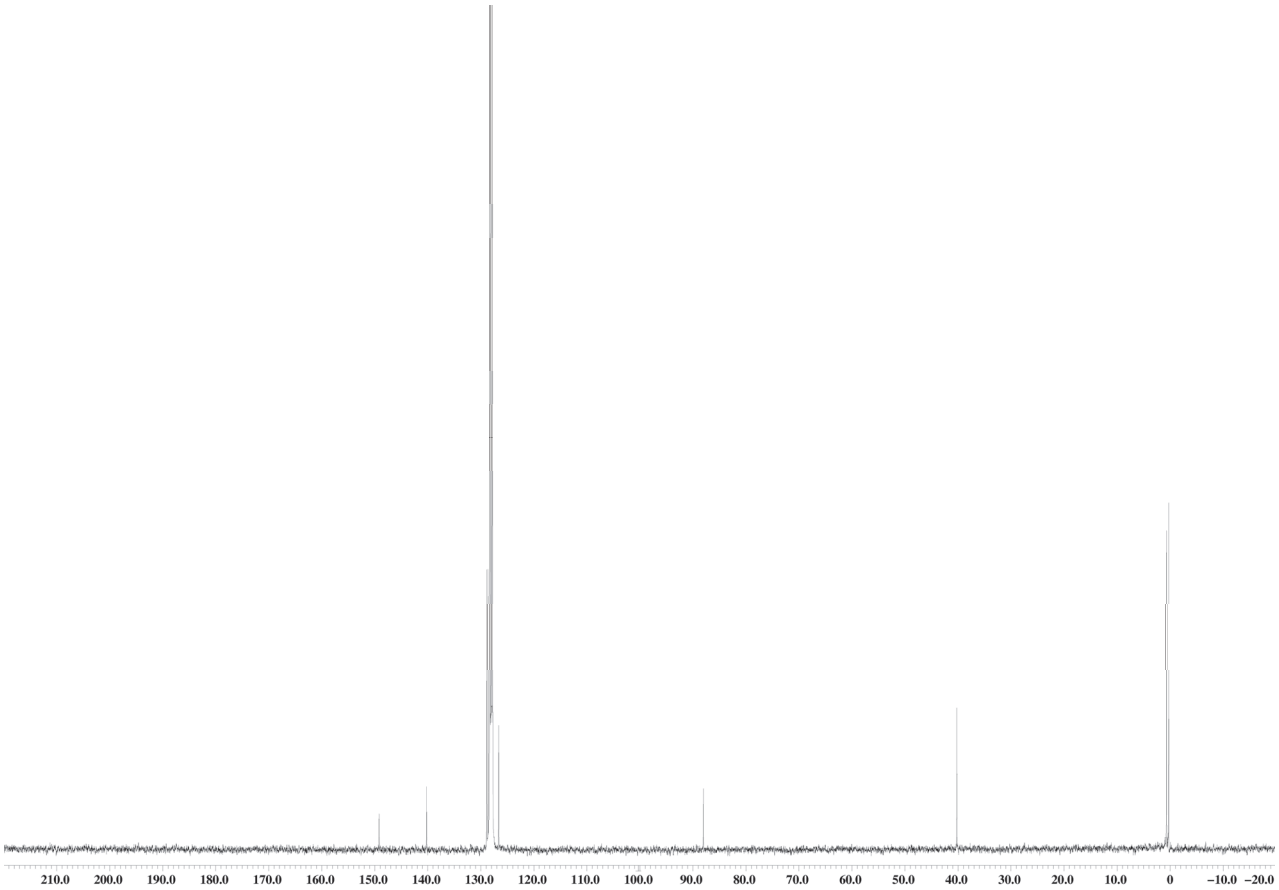
3o: White solid in 92% yield. $[\alpha]^{19}_{D}$ +36.2 (*c* = 2.09, CH_2Cl_2) for 91% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.82 (3H, m), 7.80 (1H, s), 7.53−7.46 (3H, m), 4.85 (1H, d, *J* = 11.9 Hz), 4.75 (1H, d, *J* = 11.9 Hz), 4.18 (1H, q, *J* = 7.0 Hz), 1.53 (3H, t, *J* = 7.0 Hz), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 134.5, 133.3$_2$, 133.2$_9$, 128.6, 128.1, 127.9, 127.2, 126.4, 126.3, 125.9, 73.6, 72.4, 18.5; IR (film): 3050, 2986, 2938, 2897, 1705, 1456, 1262, 1136, 1117, 910, 818 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{13}O_3^-$ ([M−H]$^-$) 229.0859. Found 229.0861. **Methyl ester of 3o:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. HPLC ADH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 10.5 min (minor isomer), 11.5 min (major isomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.81 (3H, m), 7.80 (1H, s), 7.53−7.45 (3H, m), 4.86 (1H, d, *J* = 11.9 Hz), 4.62 (1H, d, *J* = 11.9 Hz), 4.13 (1H, q, *J* = 6.9 Hz), 3.77 (3H, s), 1.47 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 135.1, 133.4, 133.2, 128.4, 128.1, 127.8, 126.9, 126.3, 126.1, 126.0, 74.1, 72.3, 52.1, 18.9; IR (film): 3055, 2951, 2872, 1748, 1435, 1271, 1204, 1140, 1113, 1026, 816 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{16}O_3Na^+$ ([M+Na]$^+$) 267.0992. Found 267.0990.

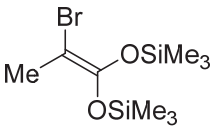


3p: White solid in 99% yield. $[\alpha]^{21}_{D}$ +46.8 (*c* = 2.97, $CHCl_3$) for 90% ee; ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 (2H, d, *J* = 7.2 Hz), 7.17−7.05 (5H, m), 7.04 (1H, t, *J* = 7.2 Hz), 6.96 (2H, d, *J* = 7.2 Hz), 4.52 (1H, d, *J* = 11.4 Hz), 4.10 (1H, d, *J* = 11.4 Hz), 3.80 (1H, dd, *J* = 4.6, 7.8 Hz), 2.71 (1H, ddd, *J* = 5.5, 9.0, 14.1 Hz), 2.62 (1H, td, *J* = 8.1, 14.1 Hz), 2.13−1.96 (2H, m), O-H proton was not found due to broadening; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 140.9, 137.1, 128.7, 128.6$_4$, 128.6$_1$, 128.3, 126.3, 72.8, 34.3, 31.3, two carbon atoms were not found probably due to overlapping; IR (film): 3086, 3030, 2965, 1748, 1456, 1196, 1169, 1088, 1005, 851 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}O_3^-$ ([M−H]$^-$) 269.1172. Found 269.1178. **Methyl ester of 3p:** The synthesis was performed according to the Method A and the title compound was obtained as colorless oil. HPLC ODH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 6.2 min (minor isomer), 8.1 min (major isomer); ^{1}H NMR (400 MHz, C_6D_6) δ 7.34 (2H, d, *J* = 7.3 Hz), 7.23−7.07 (5H, m), 7.04 (1H, t, *J* = 7.3 Hz), 7.00 (2H, d, *J* = 7.3 Hz), 4.67 (1H, d, *J* = 11.4 Hz), 4.20 (1H, d, *J* = 11.4 Hz), 3.86 (1H, dd, *J* = 4.4, 8.7 Hz), 3.30 (3H, s), 2.74 (1H, ddd, *J* = 5.5, 9.2, 14.0 Hz), 2.66 (1H, ddd, *J* = 7.5, 8.7, 14.0 Hz), 2.12 (1H, dtd, *J* = 5.5, 8.7, 14.0 Hz), 2.04 (1H, dddd, *J* = 4.4, 7.5, 9.2, 14.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 141.2, 137.6, 128.6, 128.4$_9$, 128.4$_5$, 128.2, 128.0, 126.2, 77.2, 72.5, 52.0, 34.6, 31.4; IR (film): 3028, 2951, 2926, 1748, 1454, 1204, 1171, 1115, 1028 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{20}O_3Li^+$ ([M+Li]$^+$) 291.1567. Found 291.1572.

Copies of ^{1}H and ^{13}C NMR spectra:



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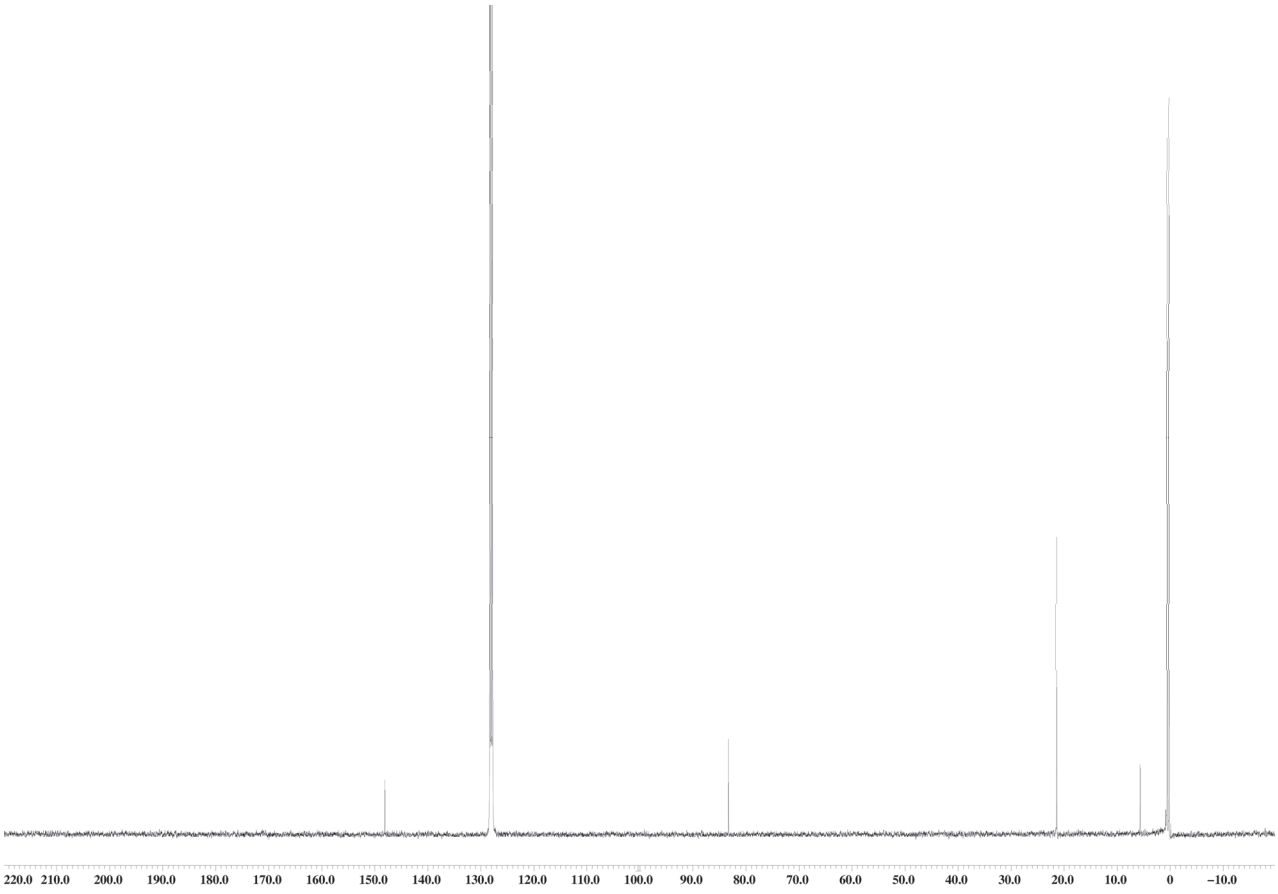
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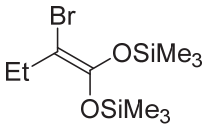
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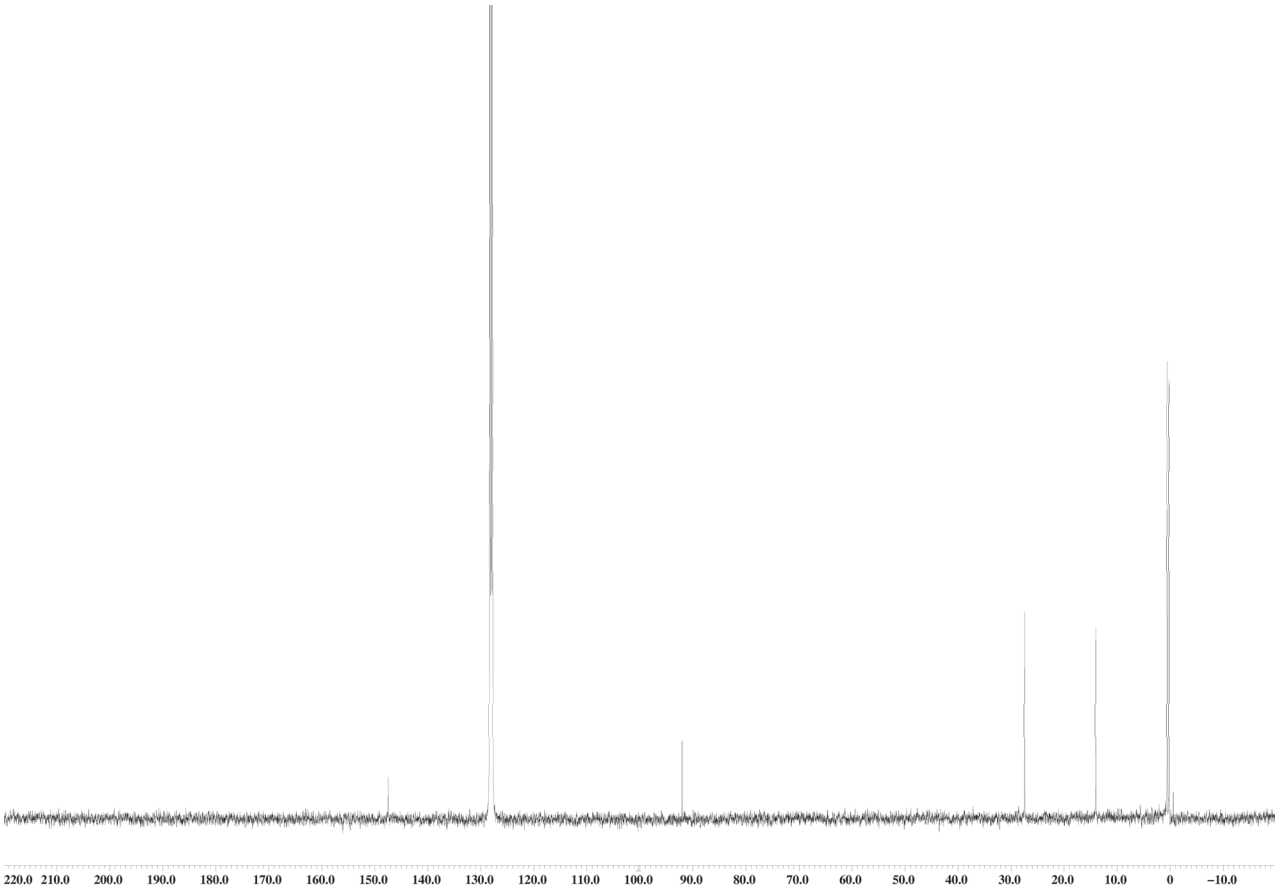
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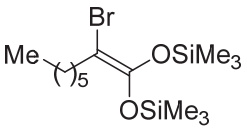
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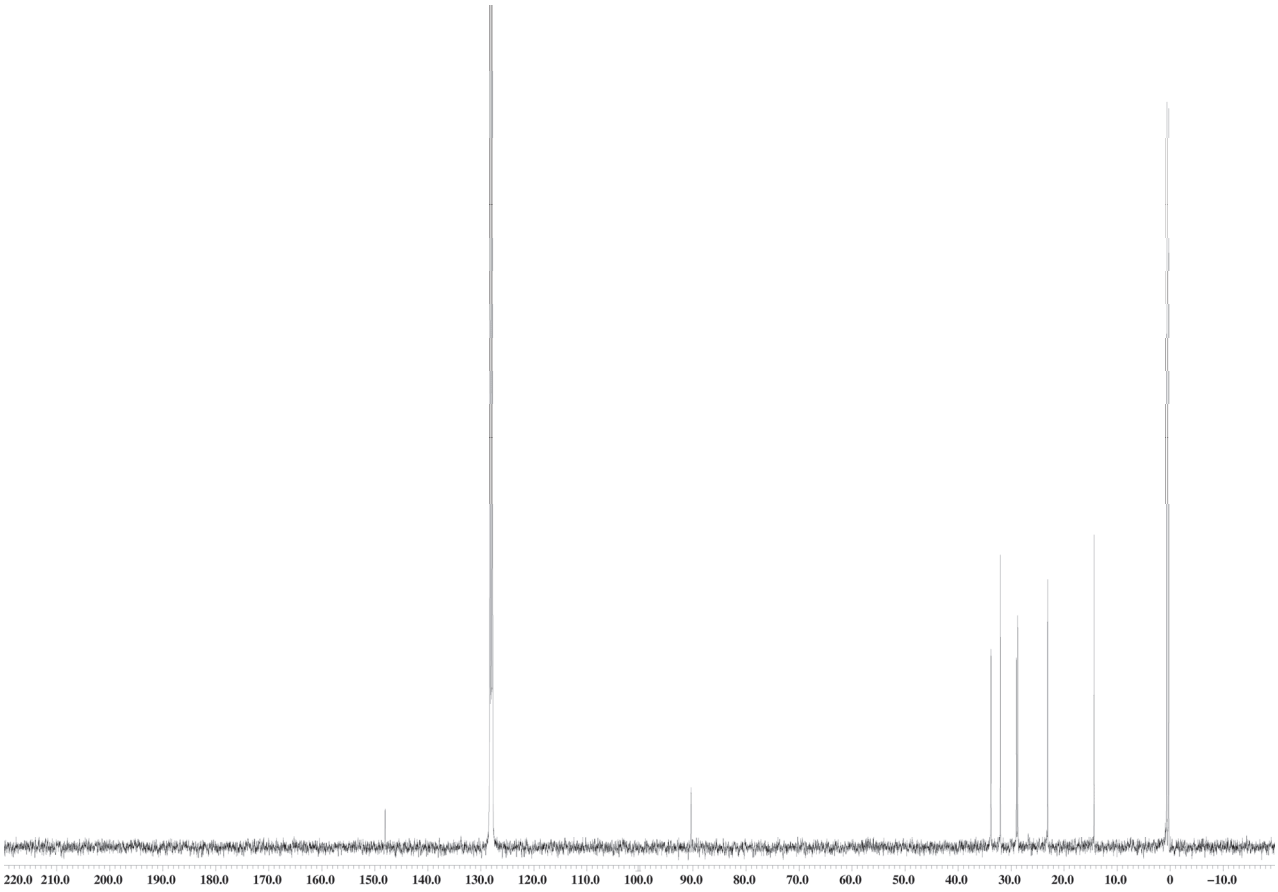
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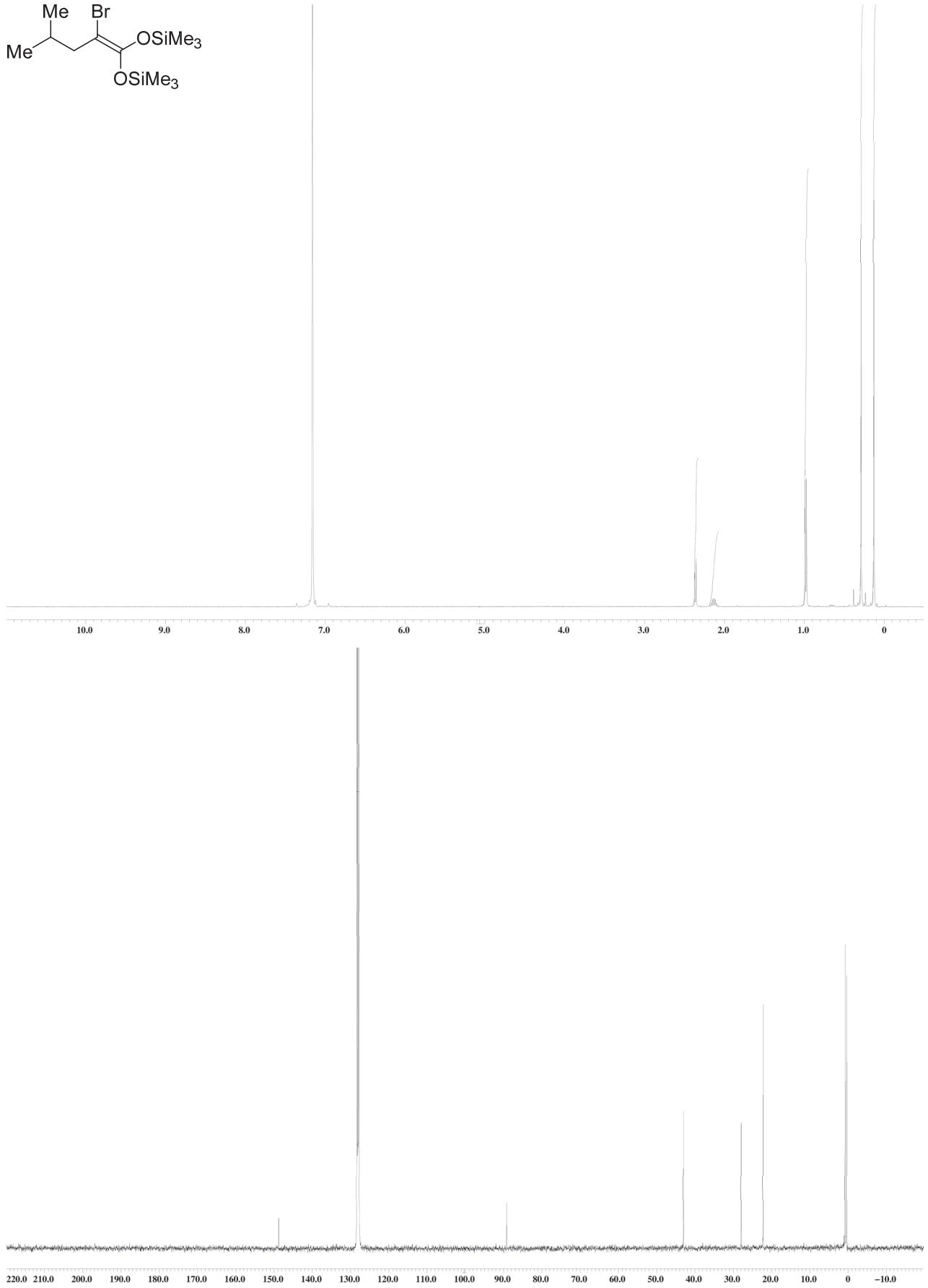
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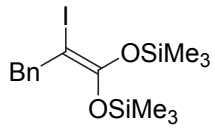
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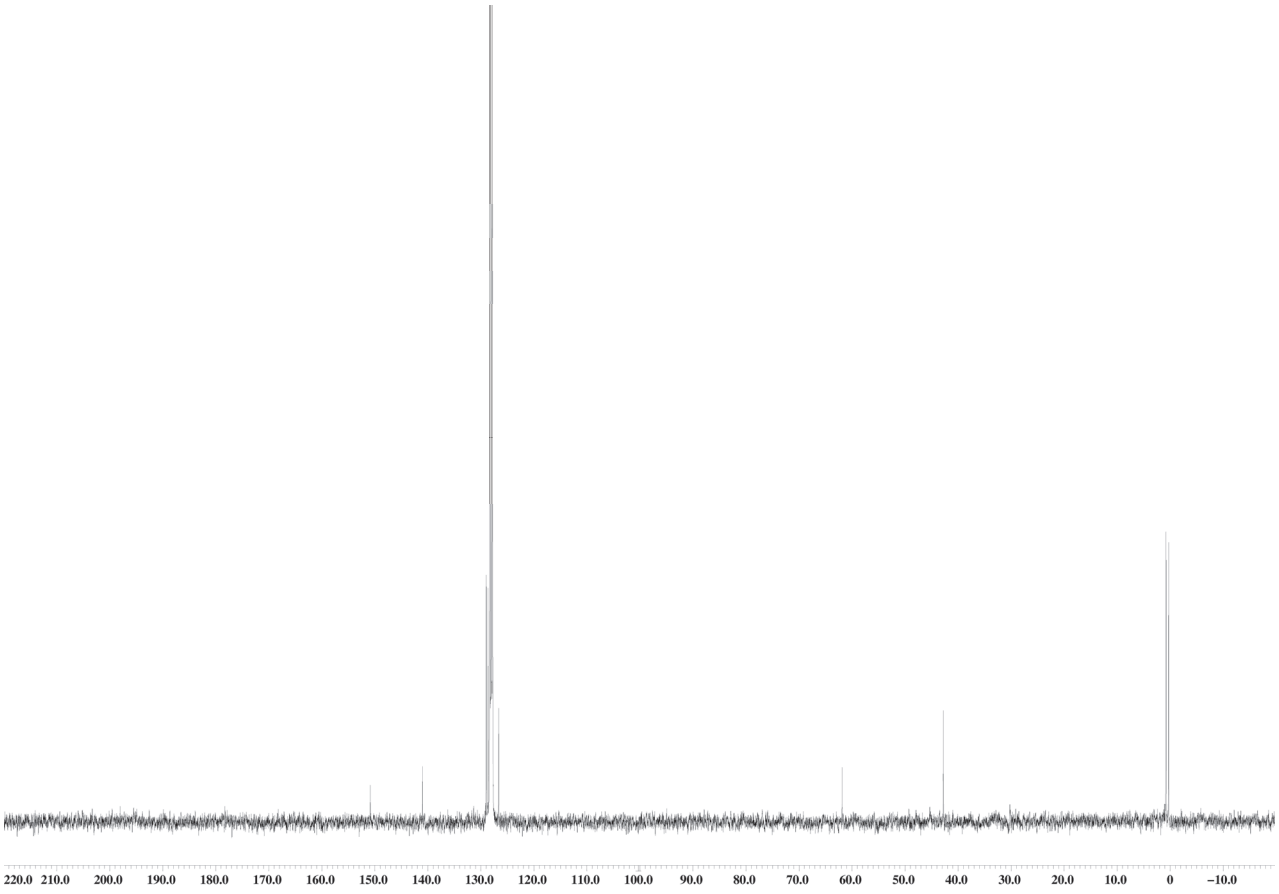
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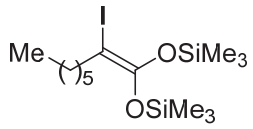
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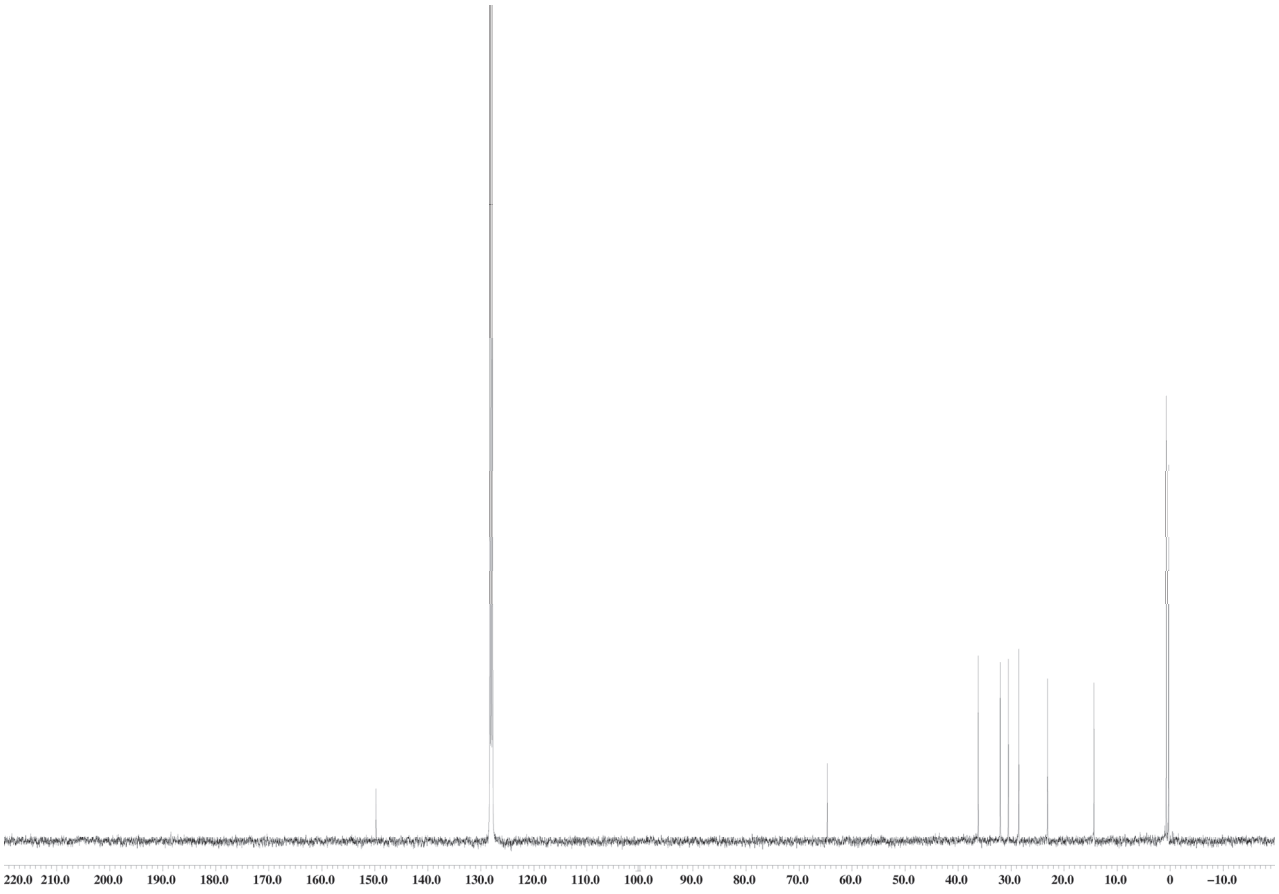
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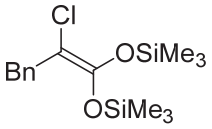
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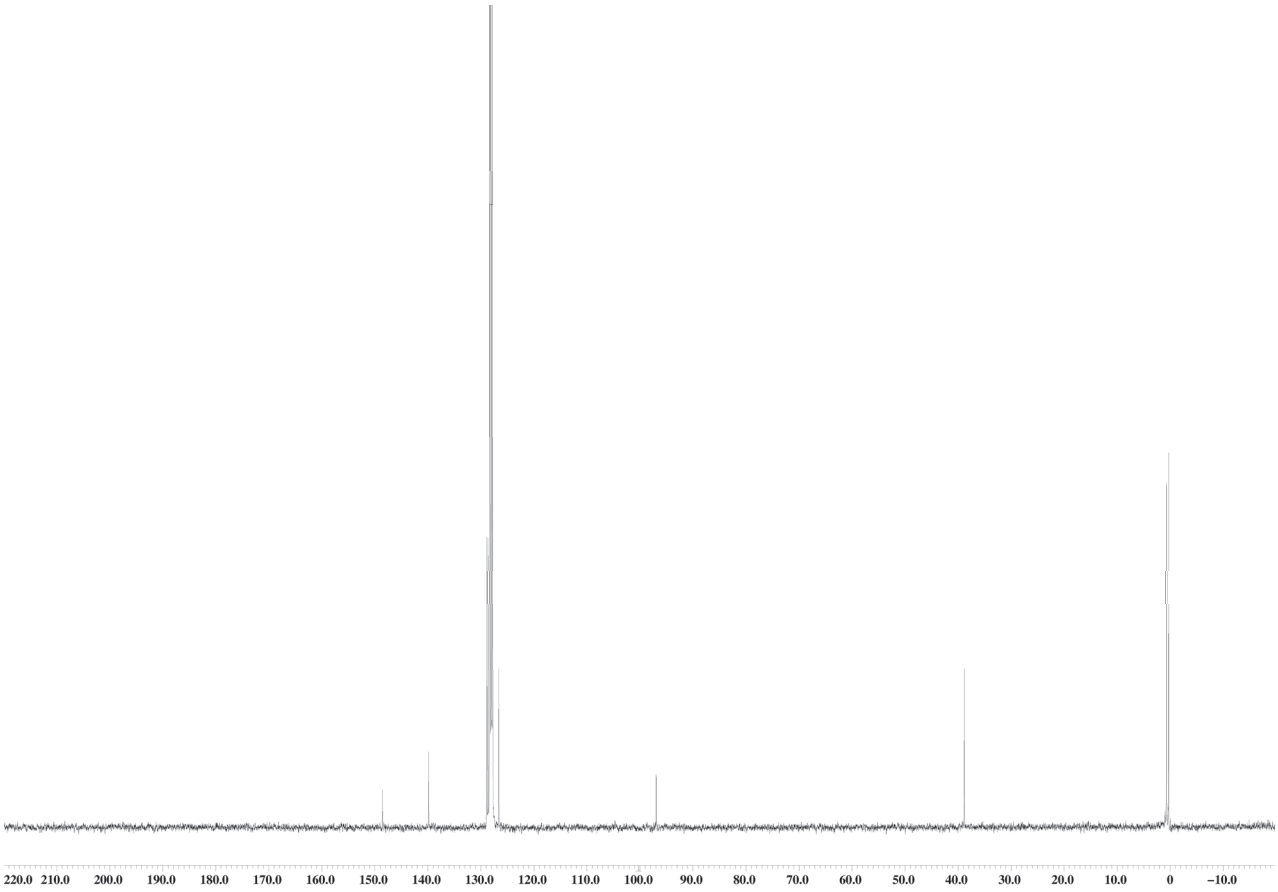
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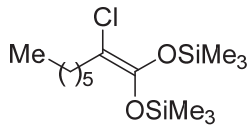
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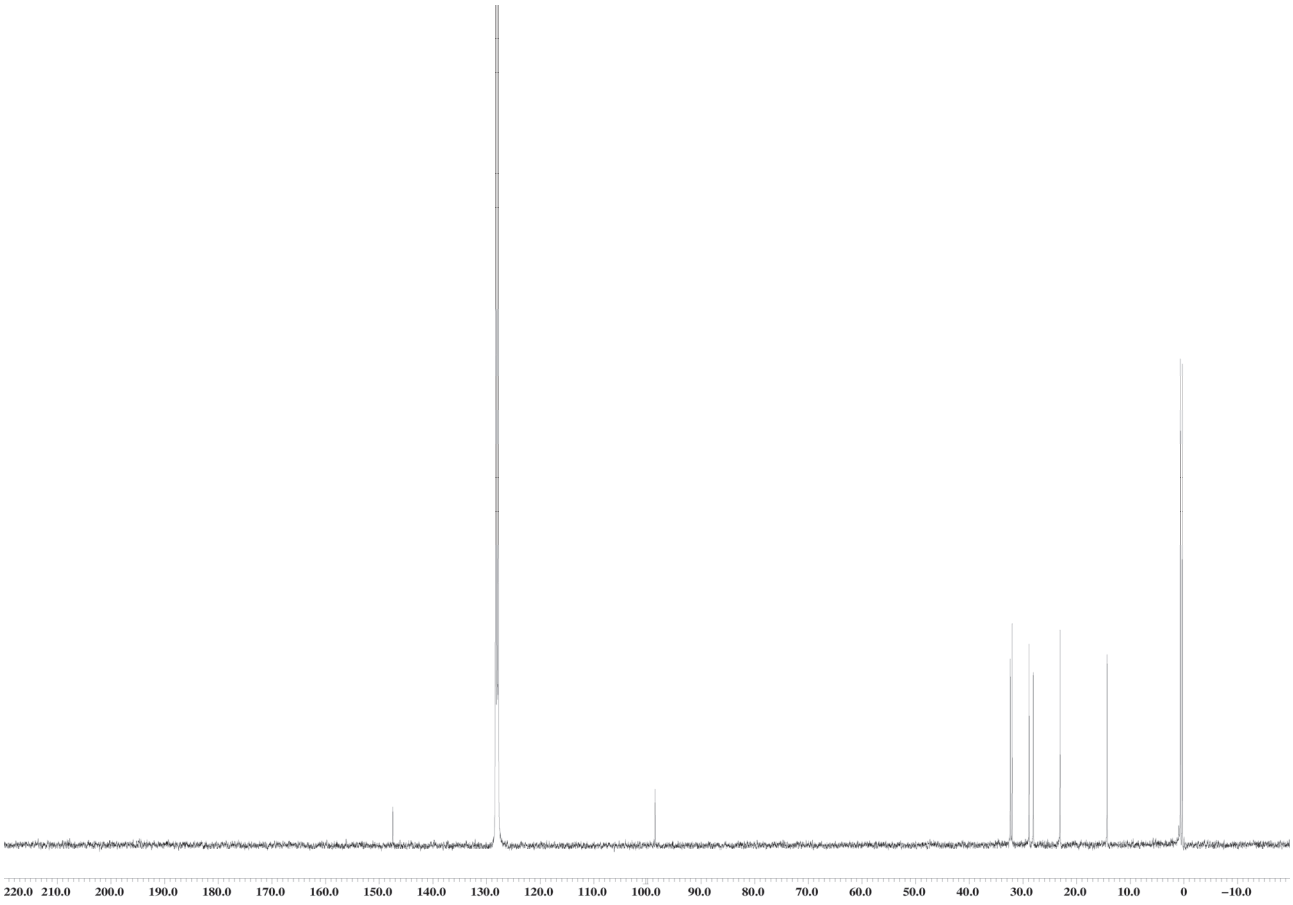
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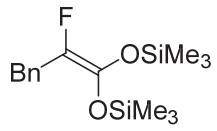
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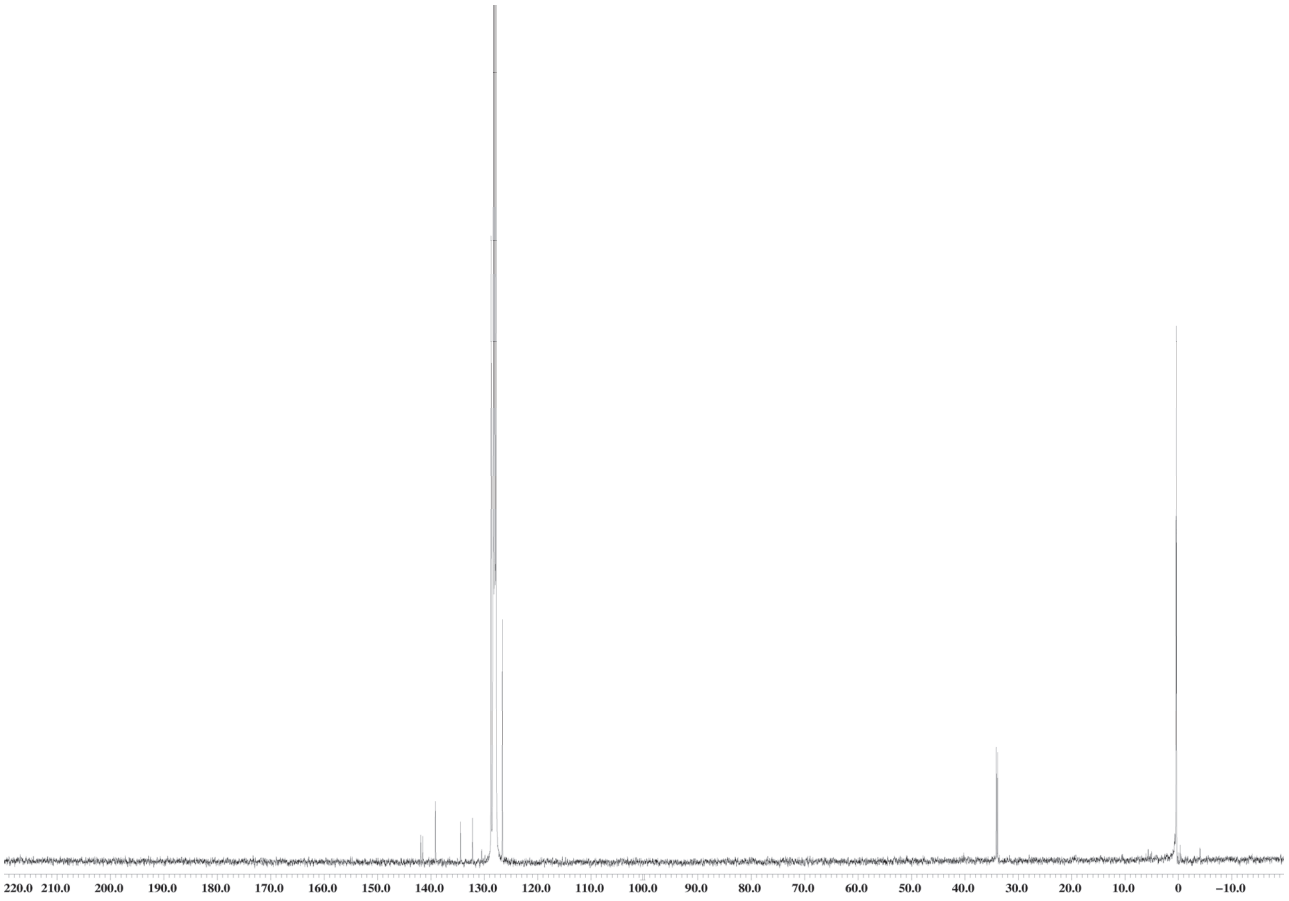
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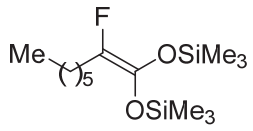
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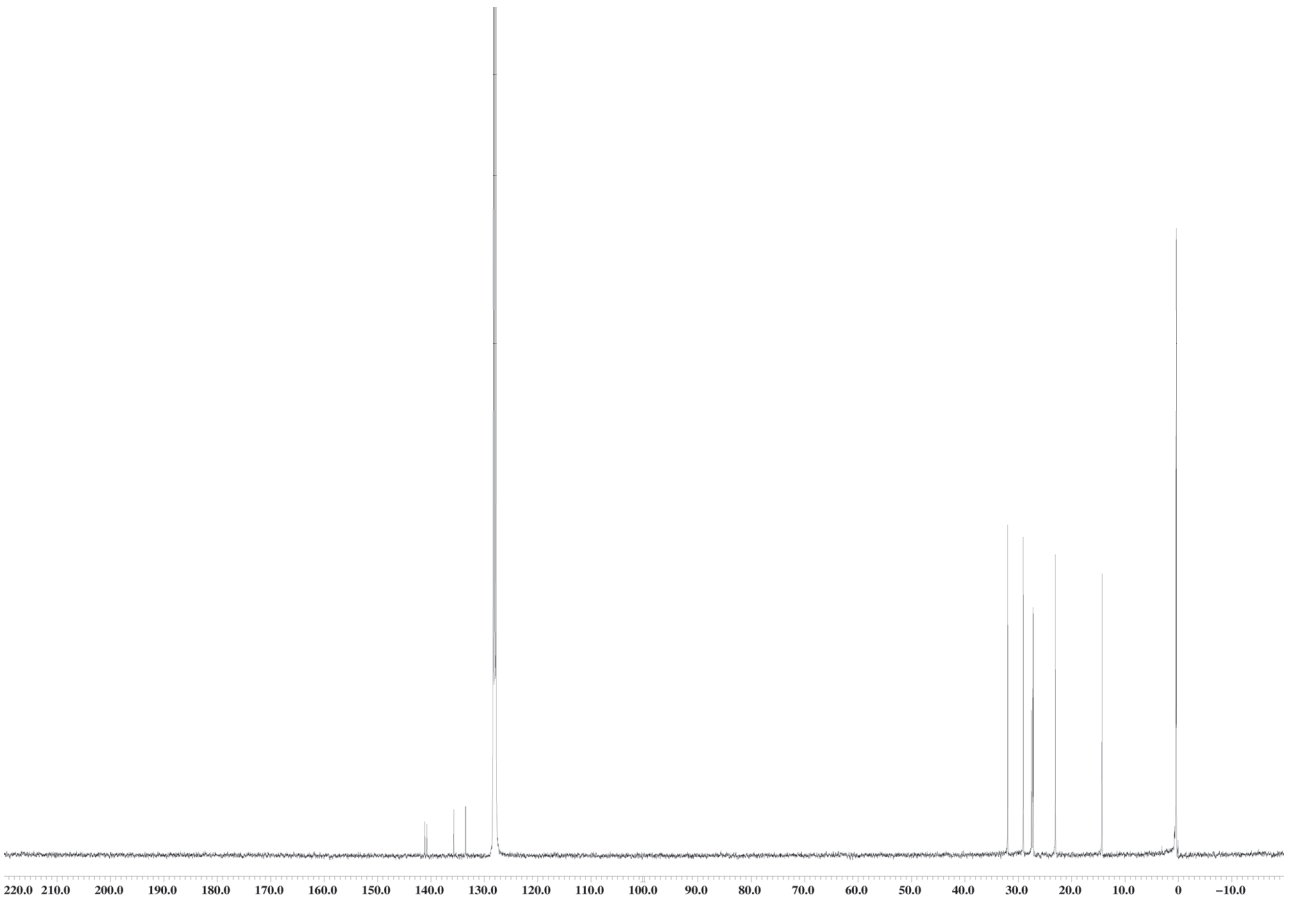
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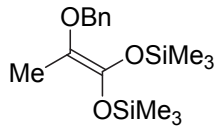
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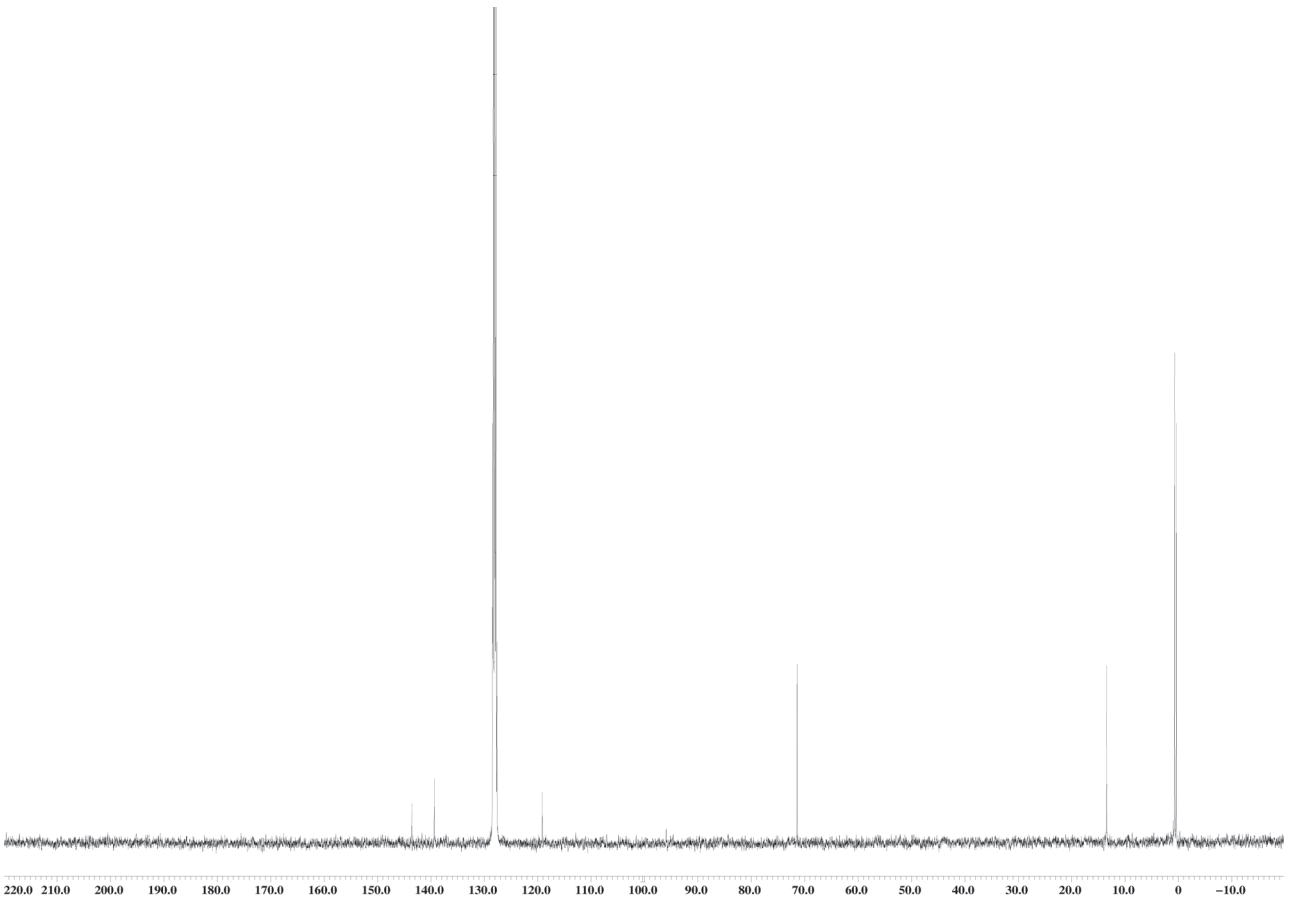
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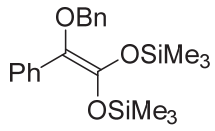
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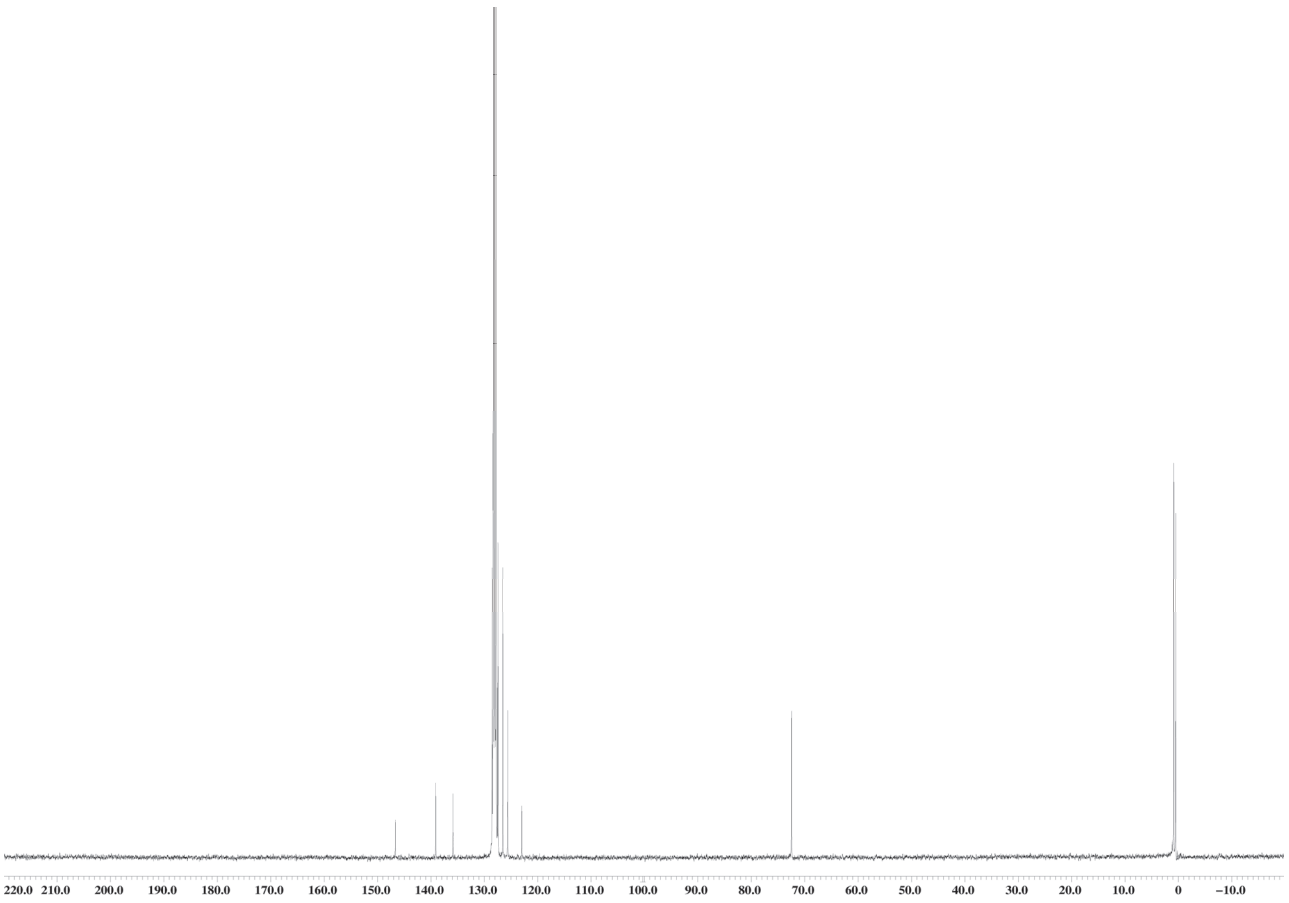
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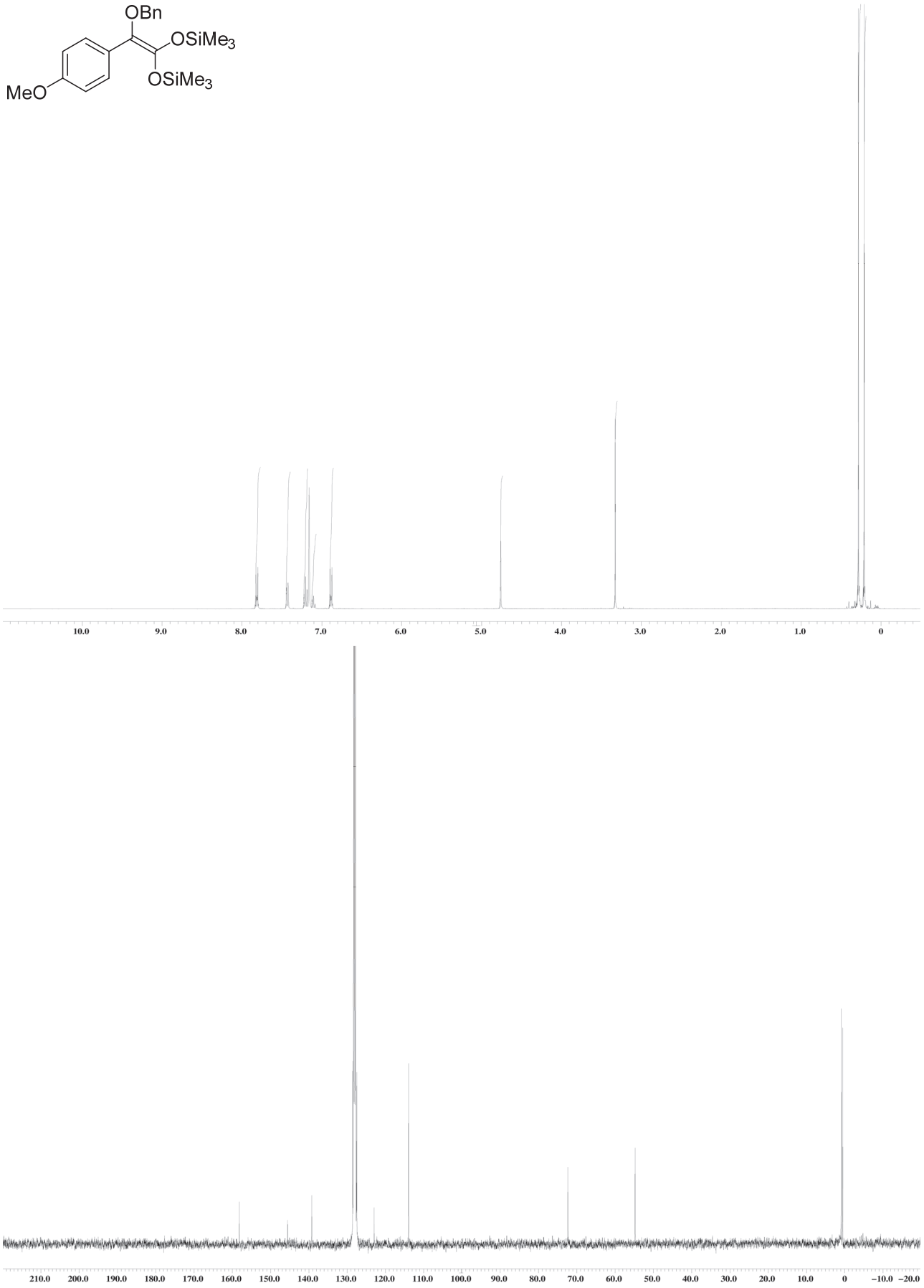
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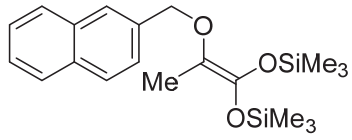
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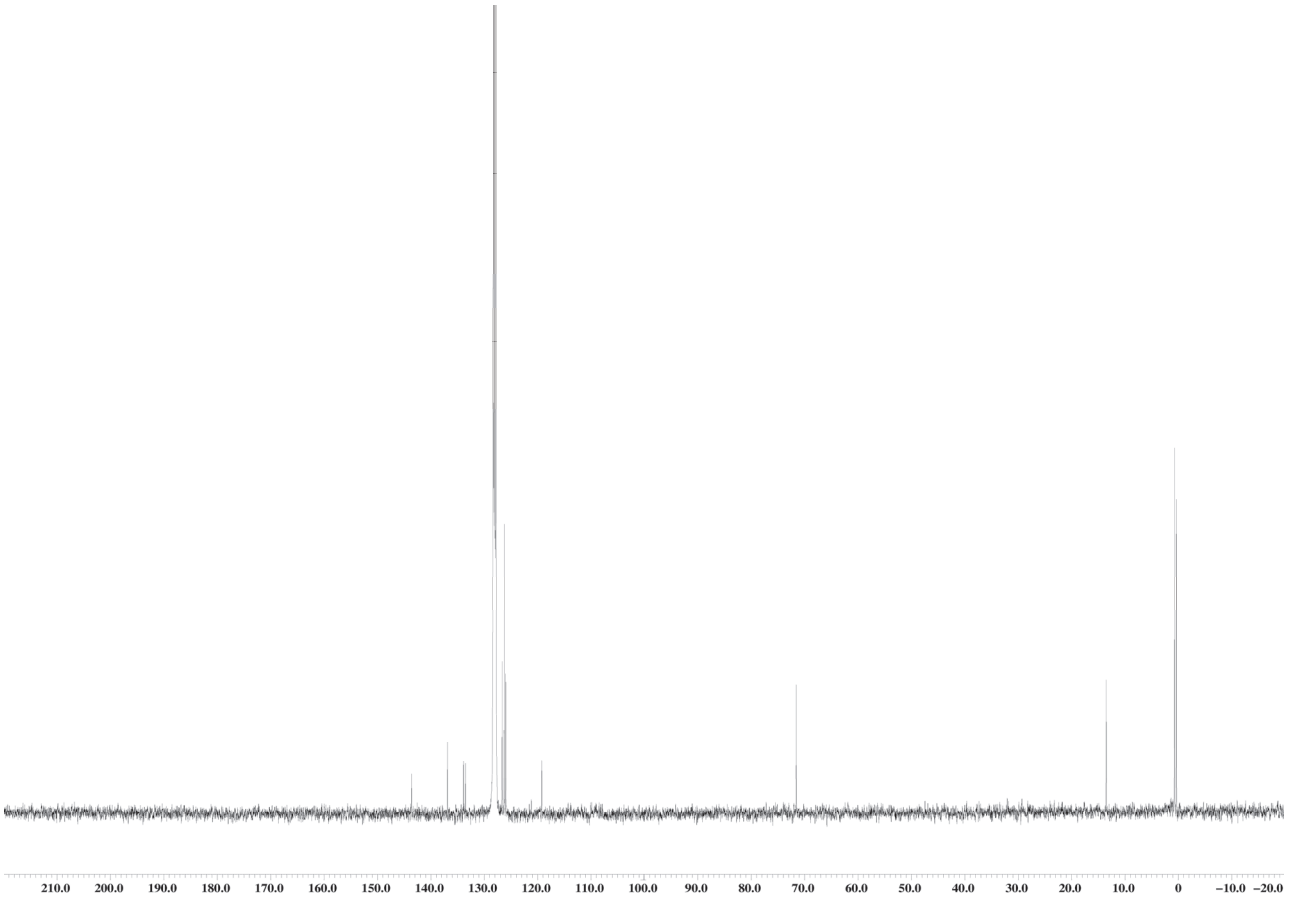
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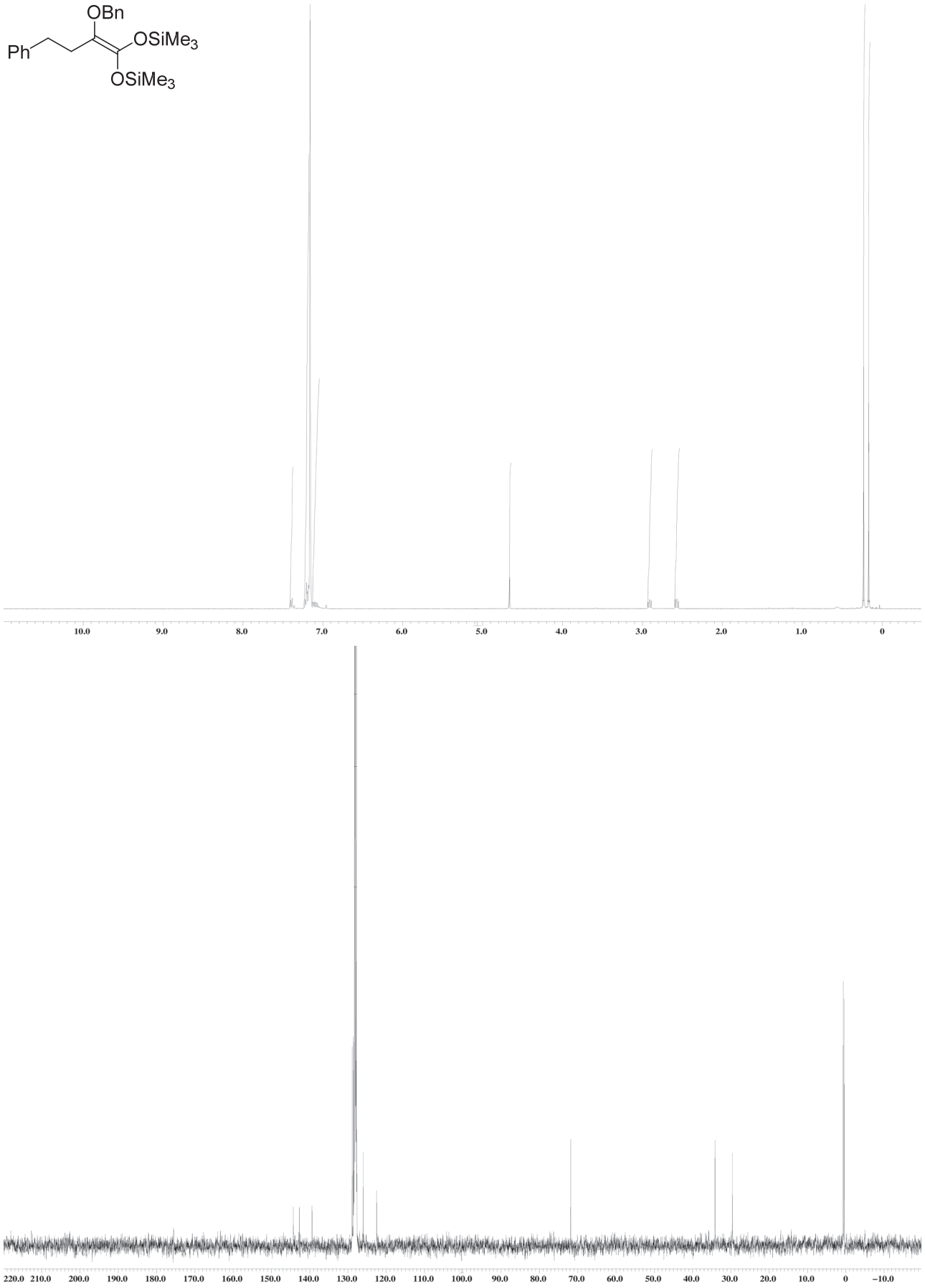
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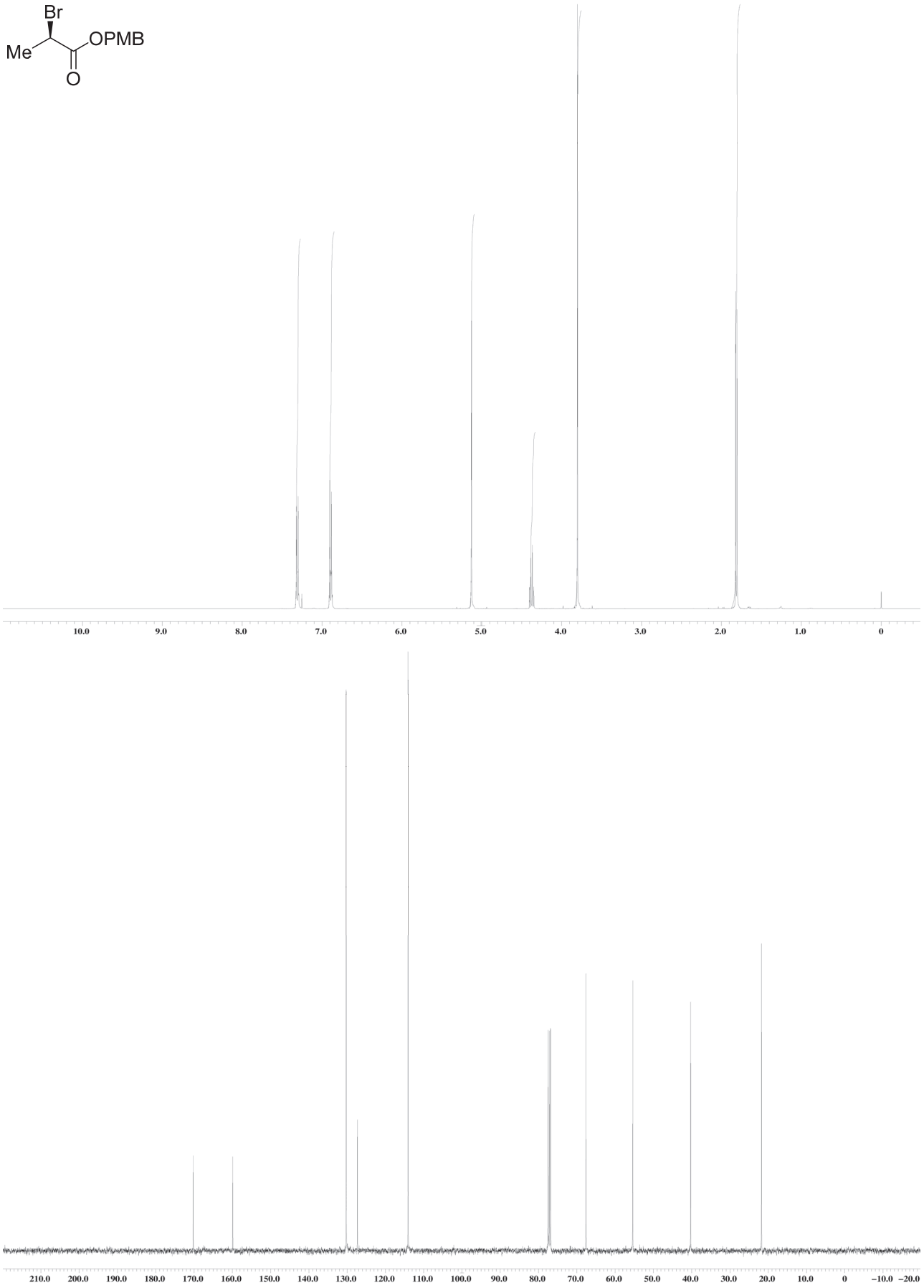
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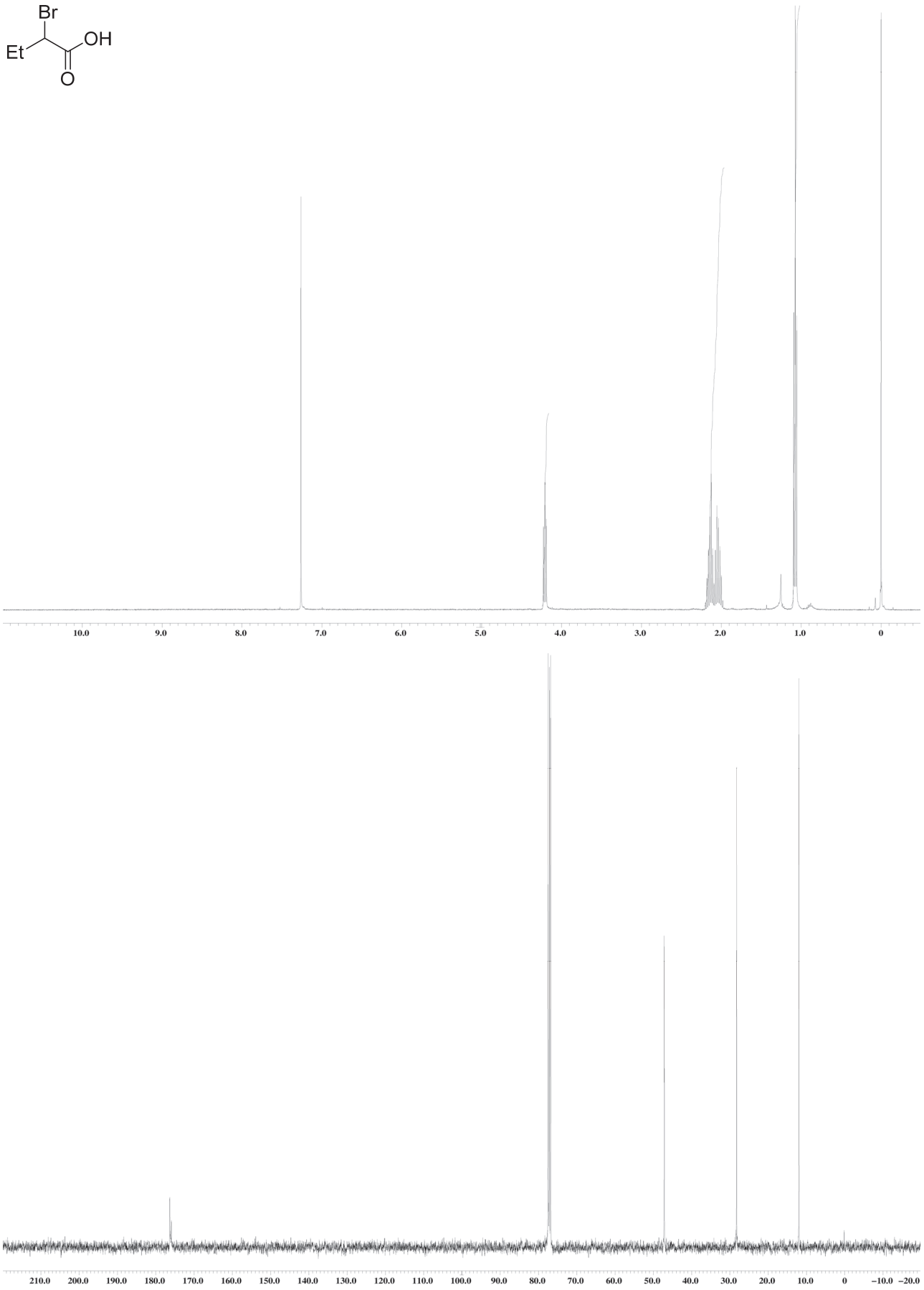
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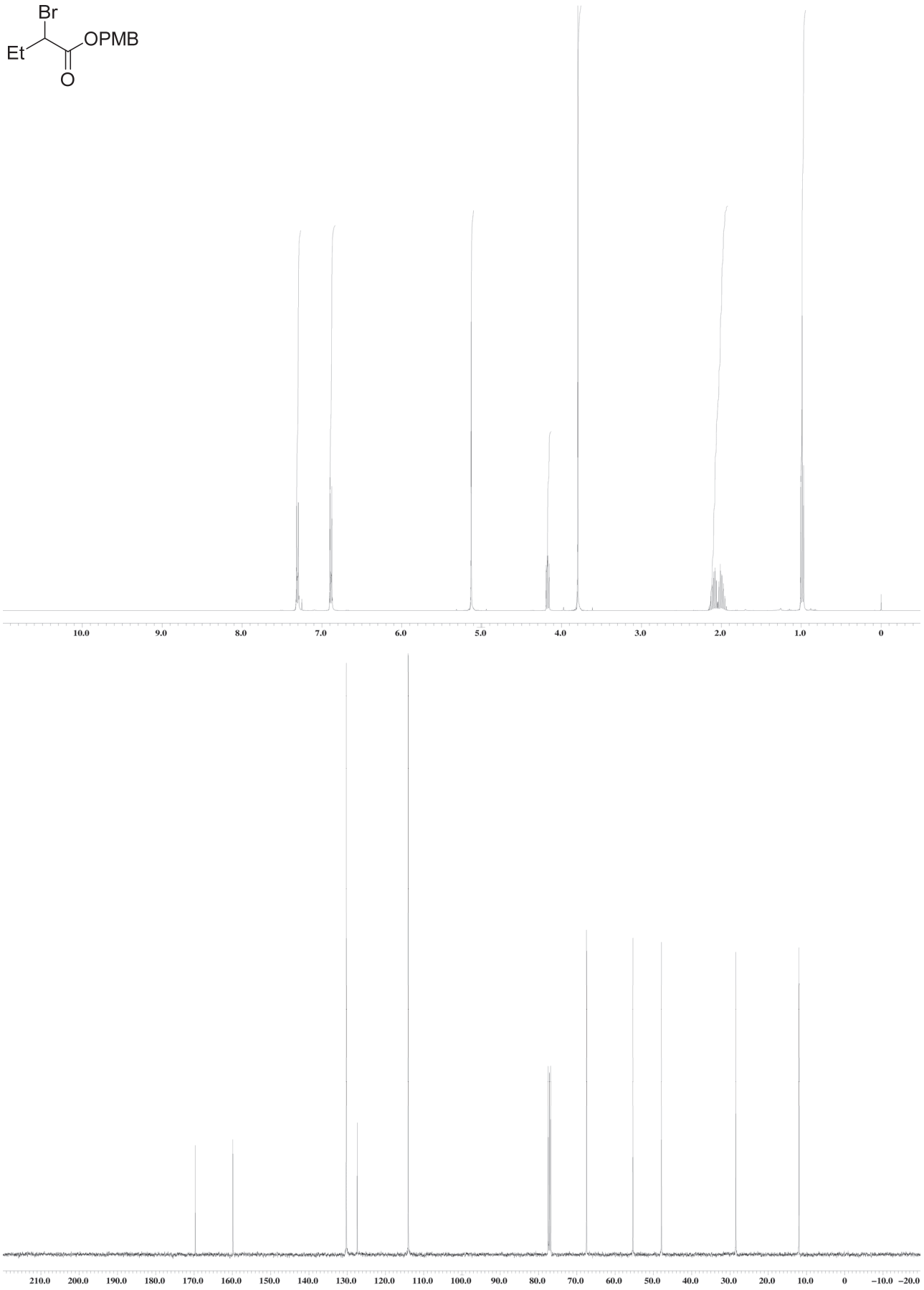
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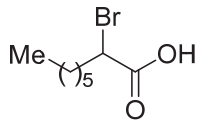
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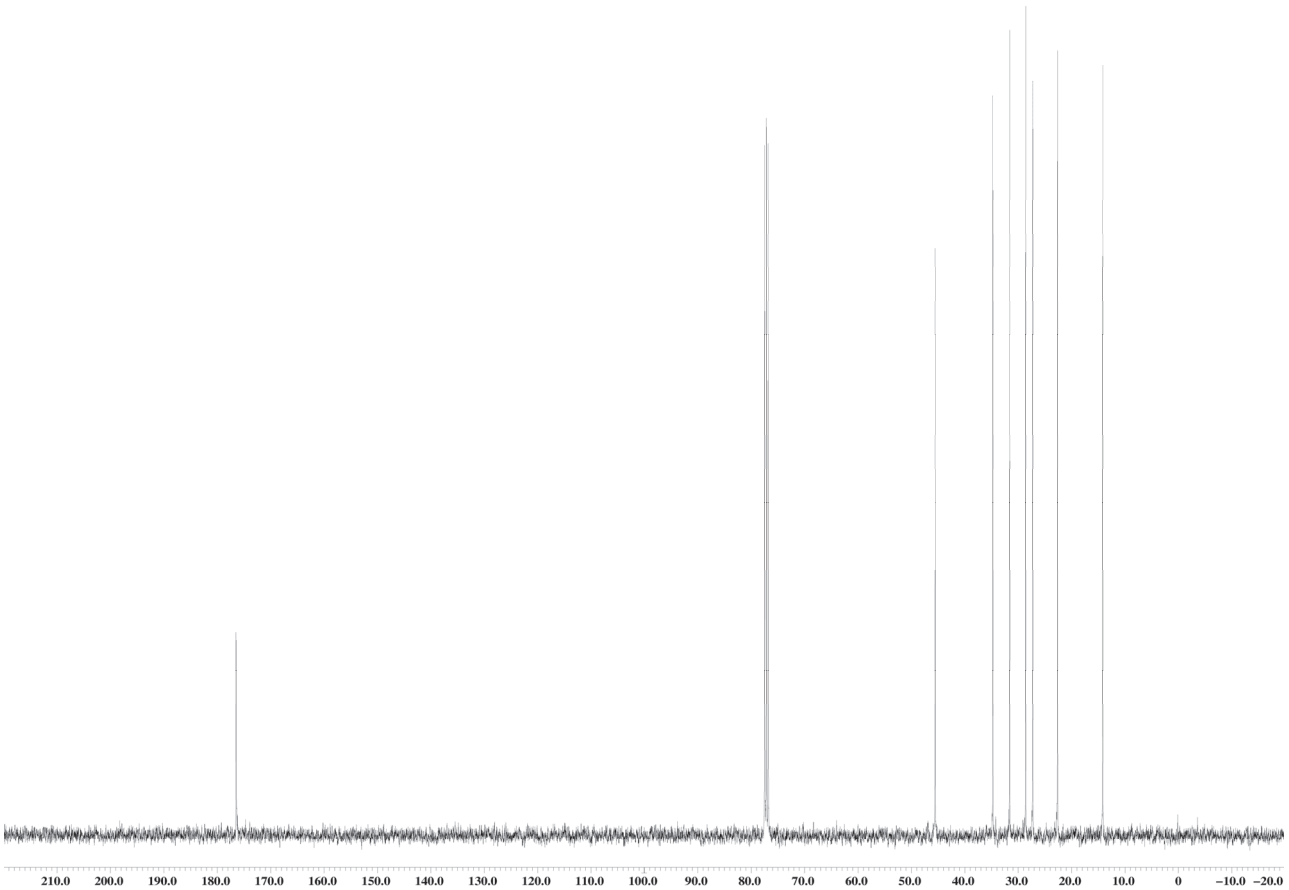
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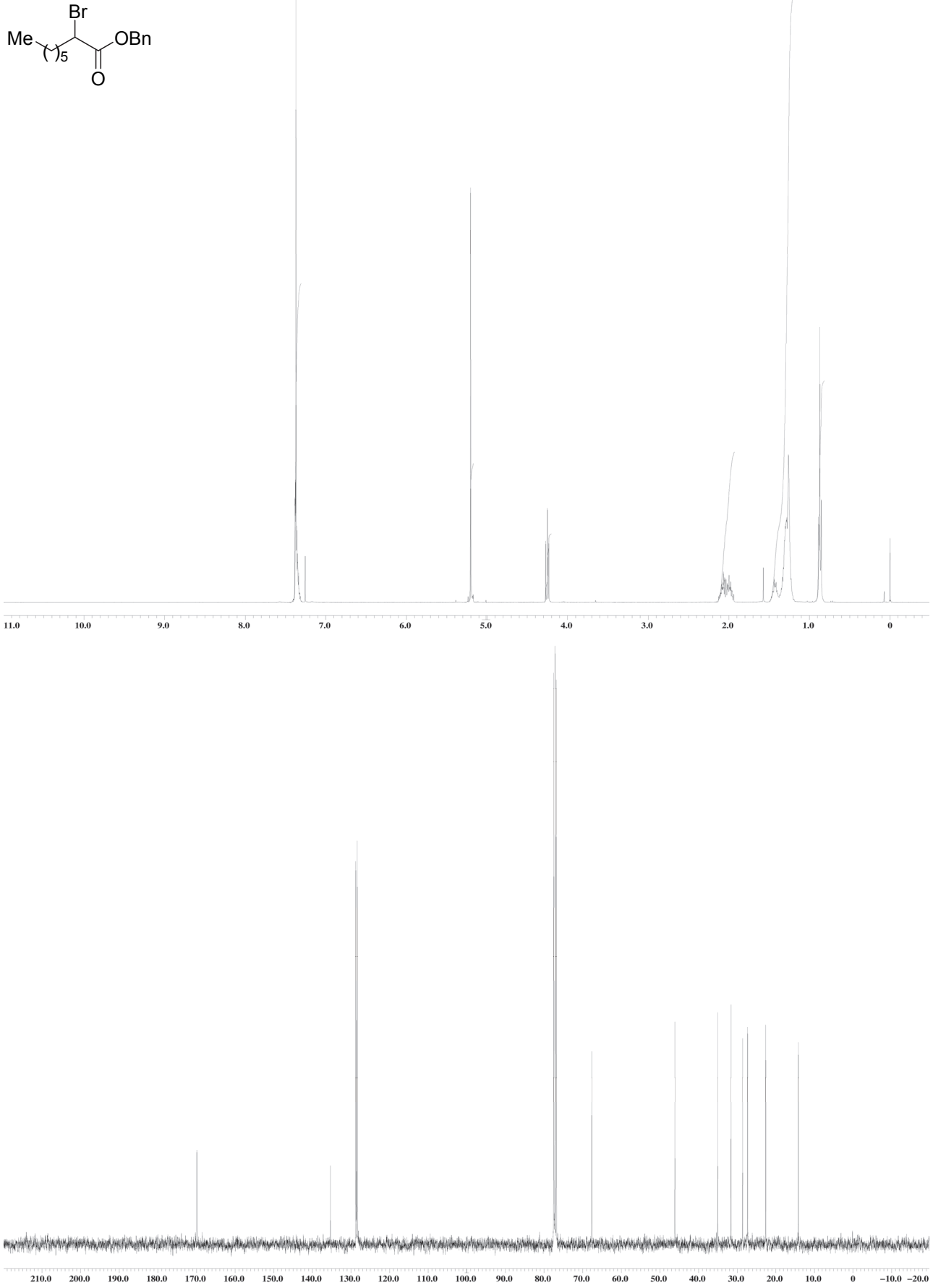
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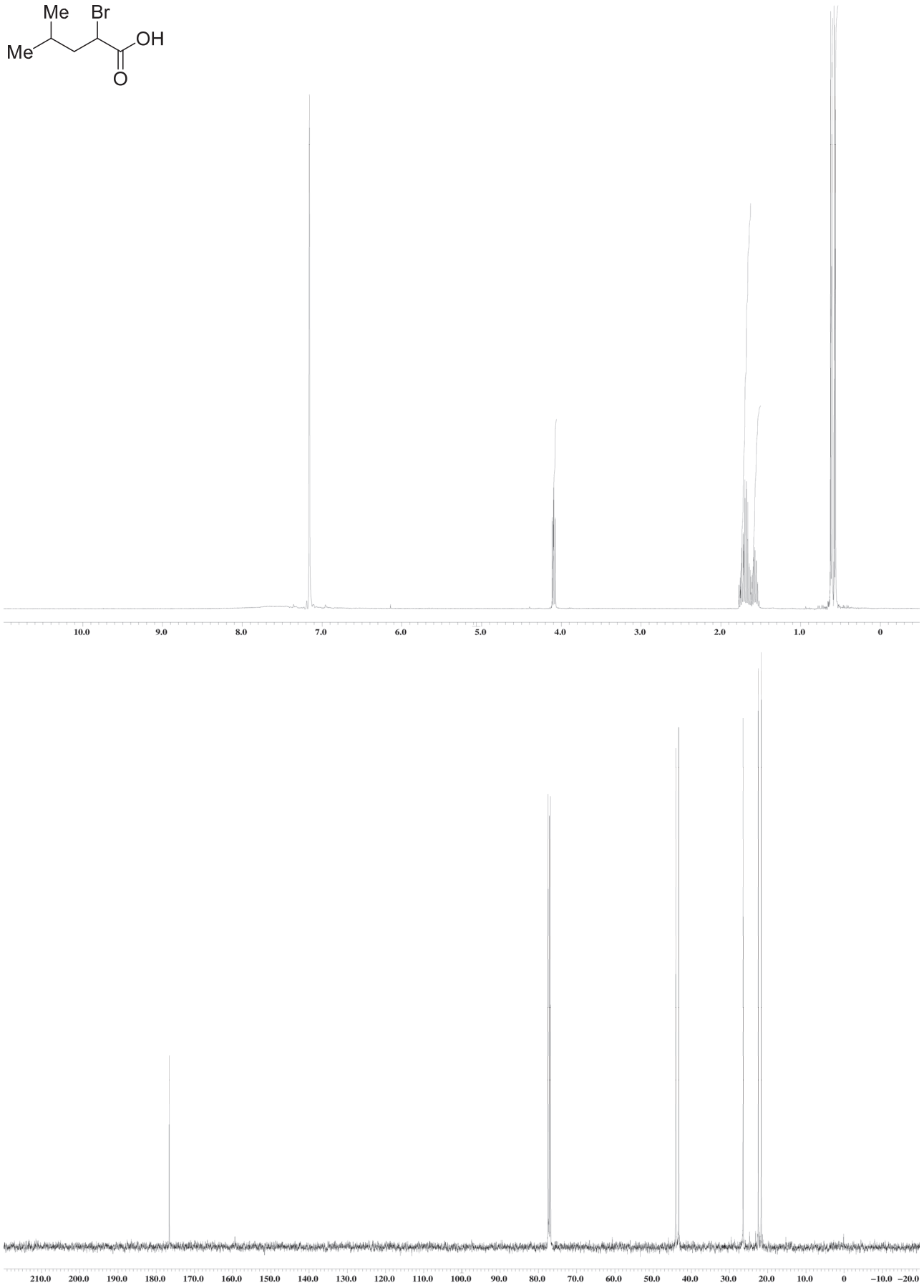
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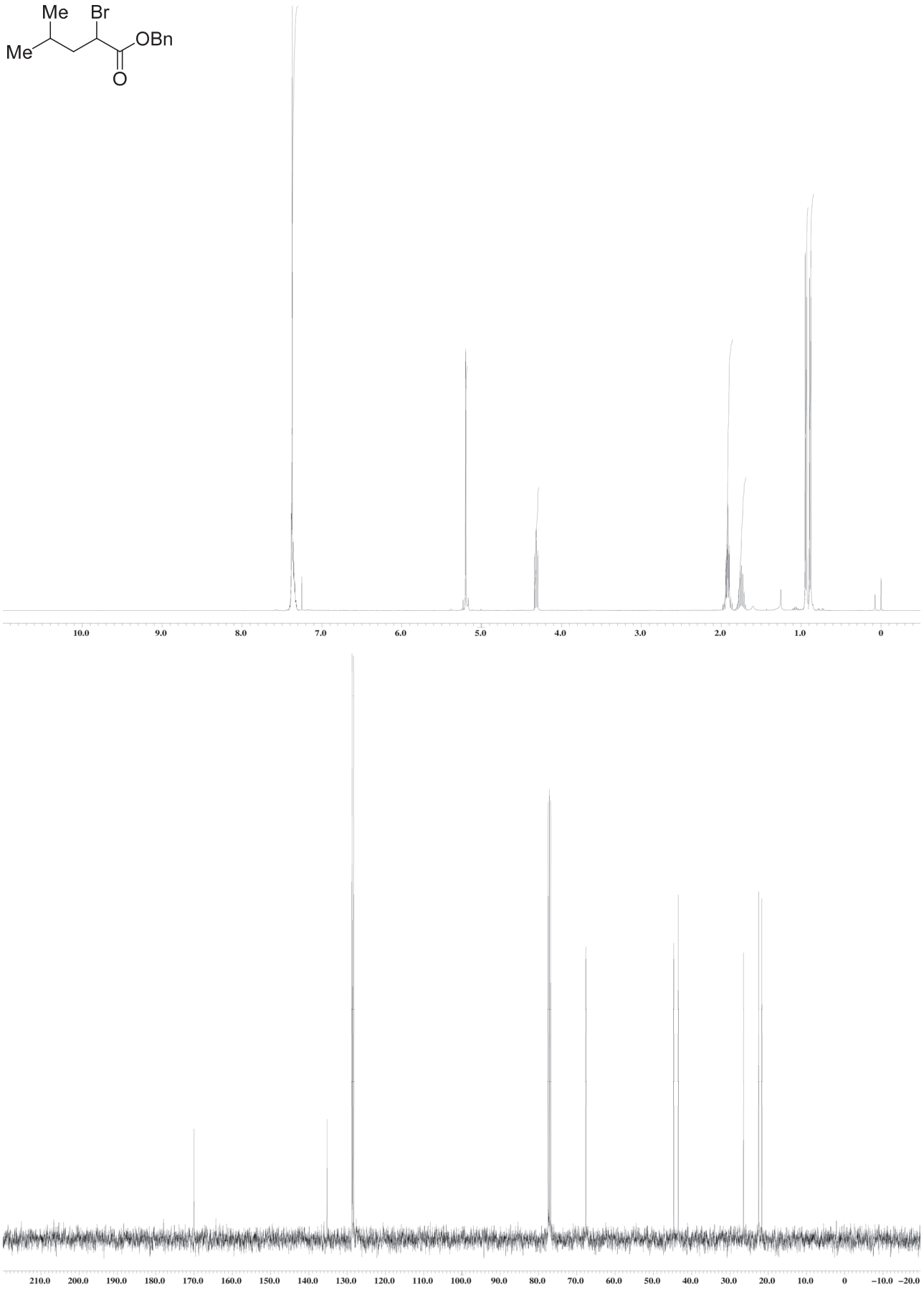
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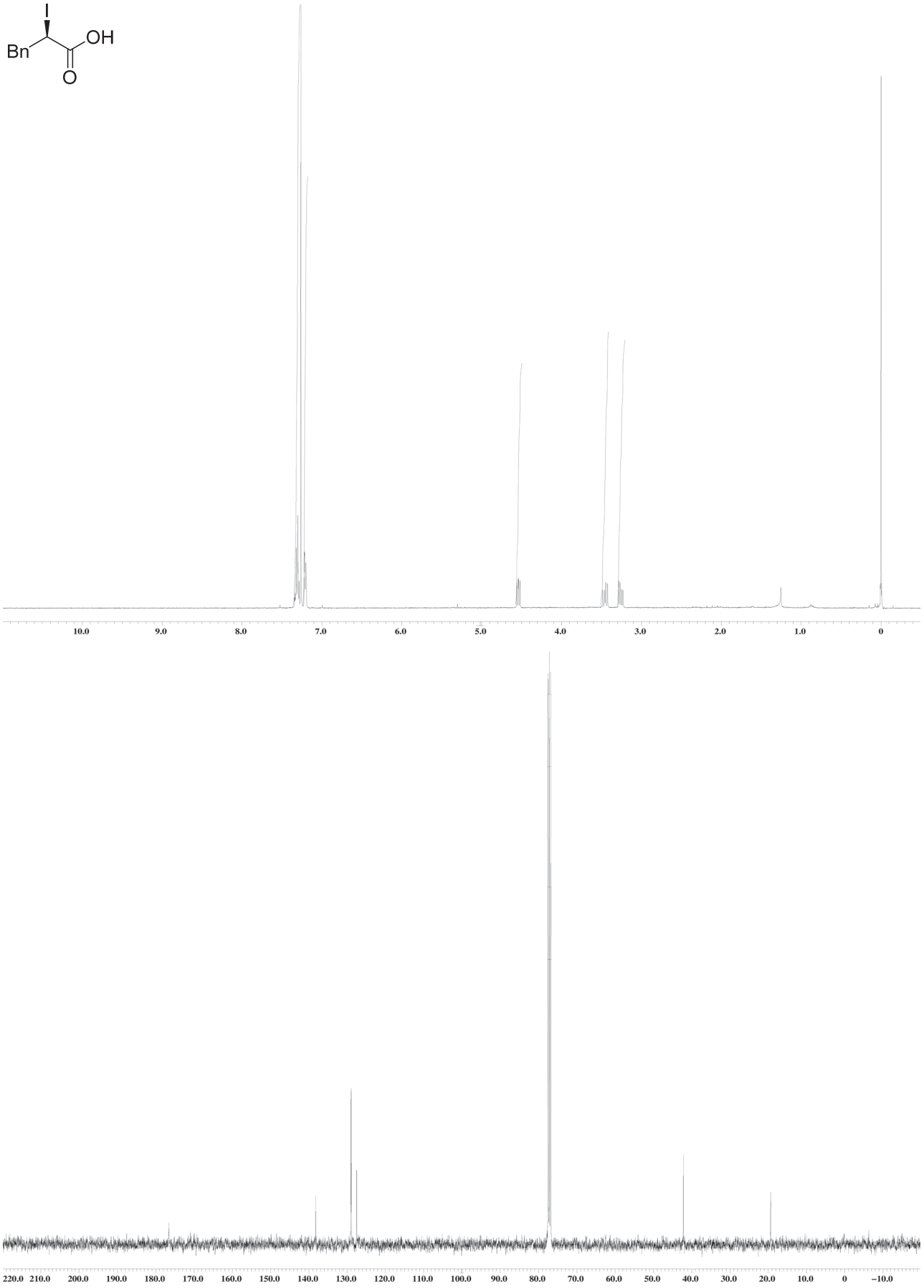
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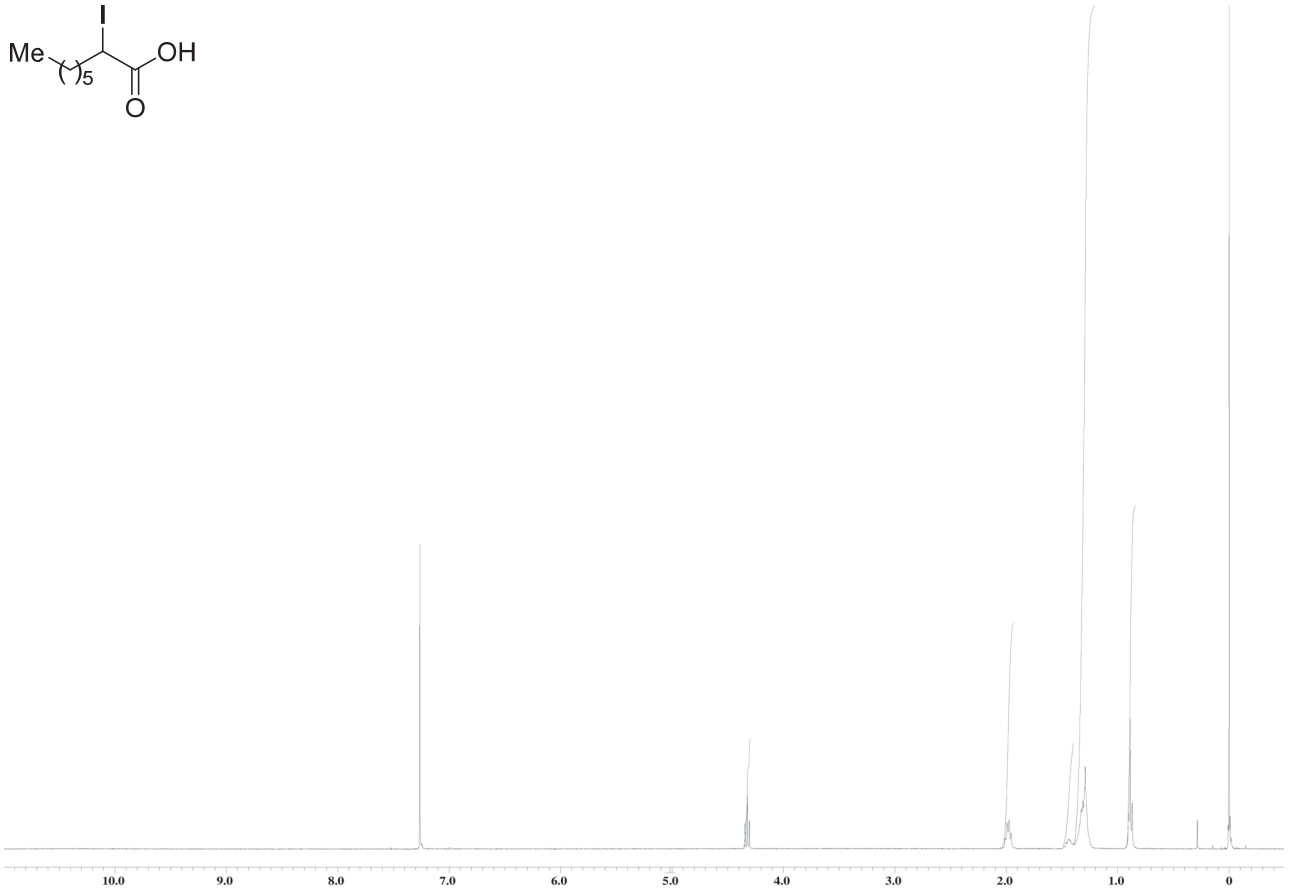
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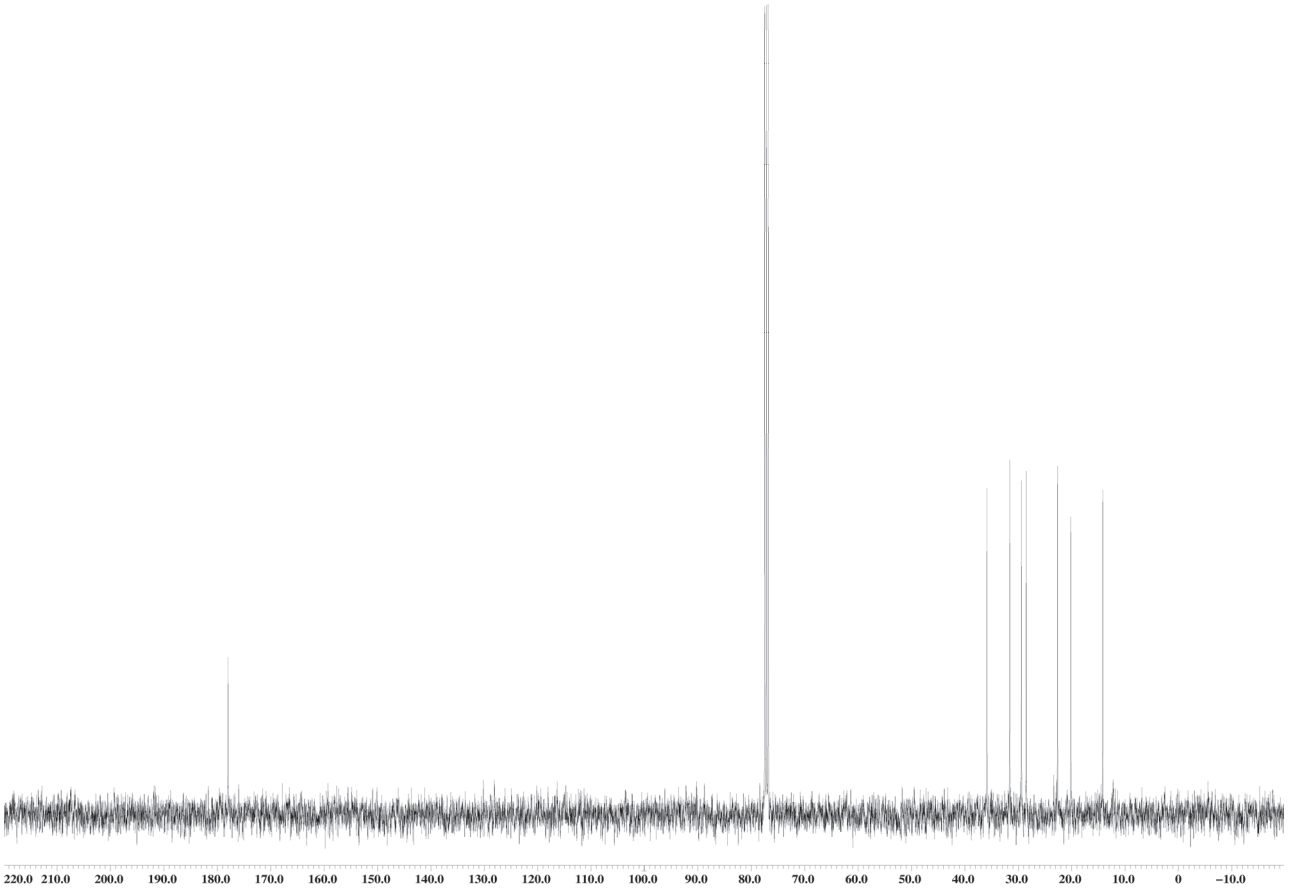
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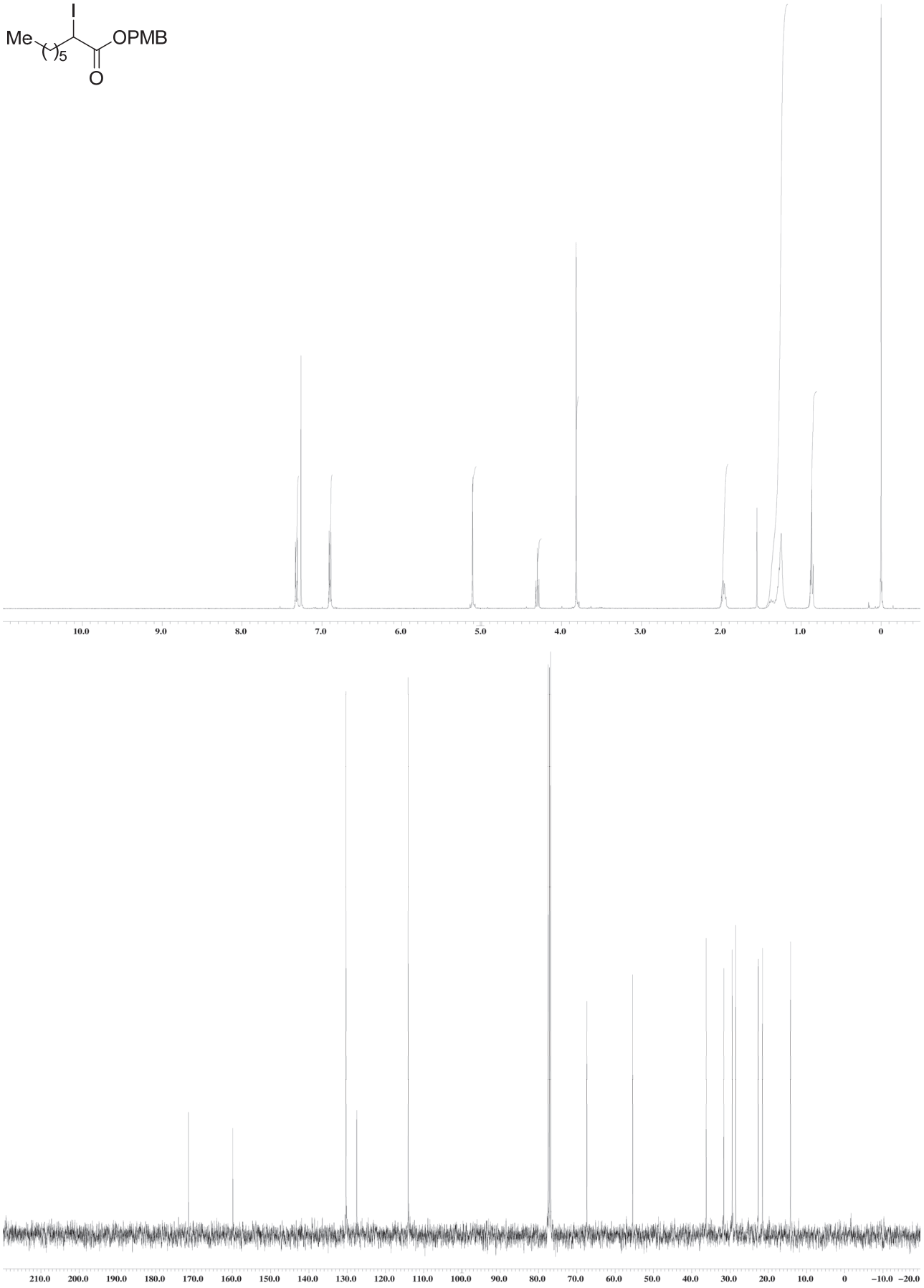
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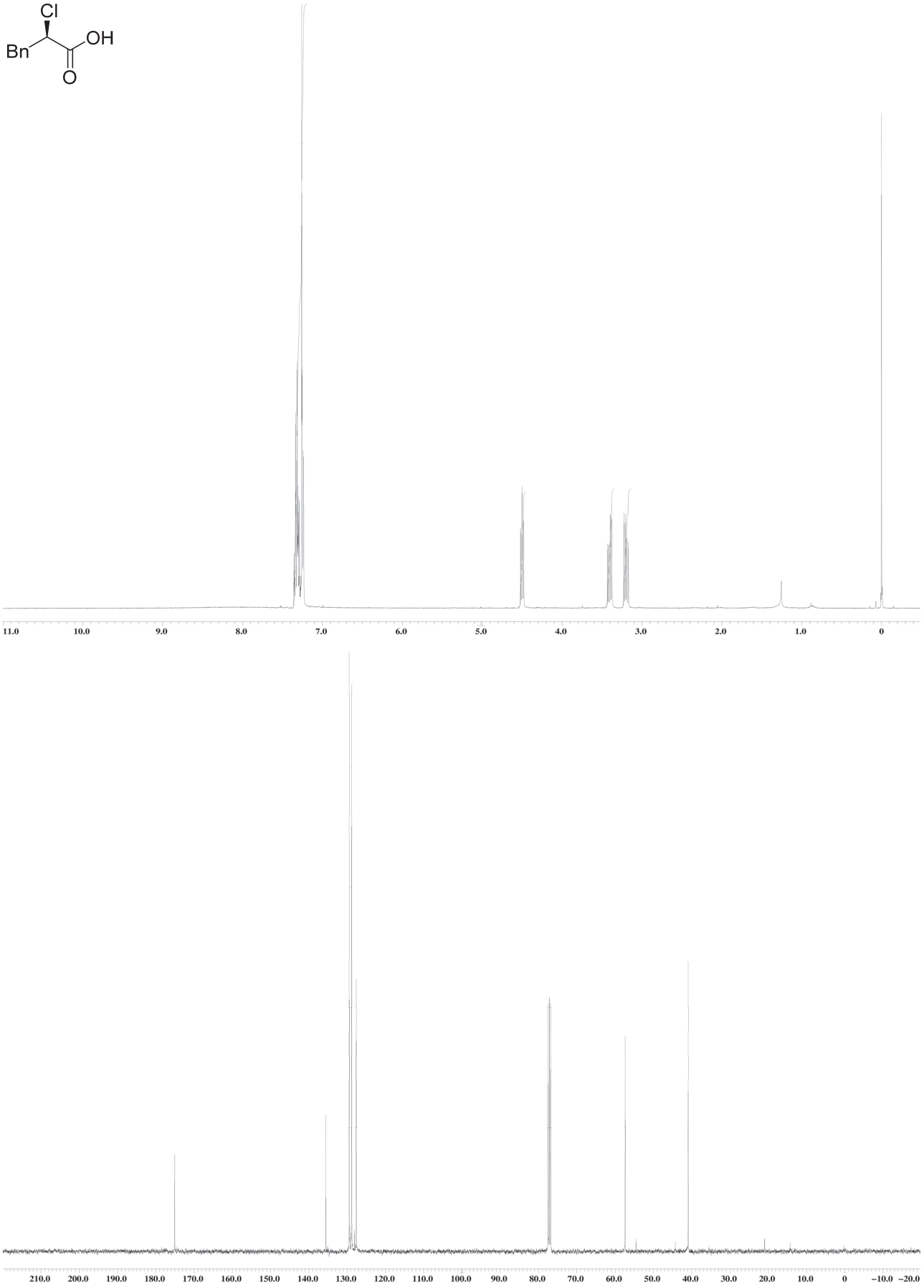
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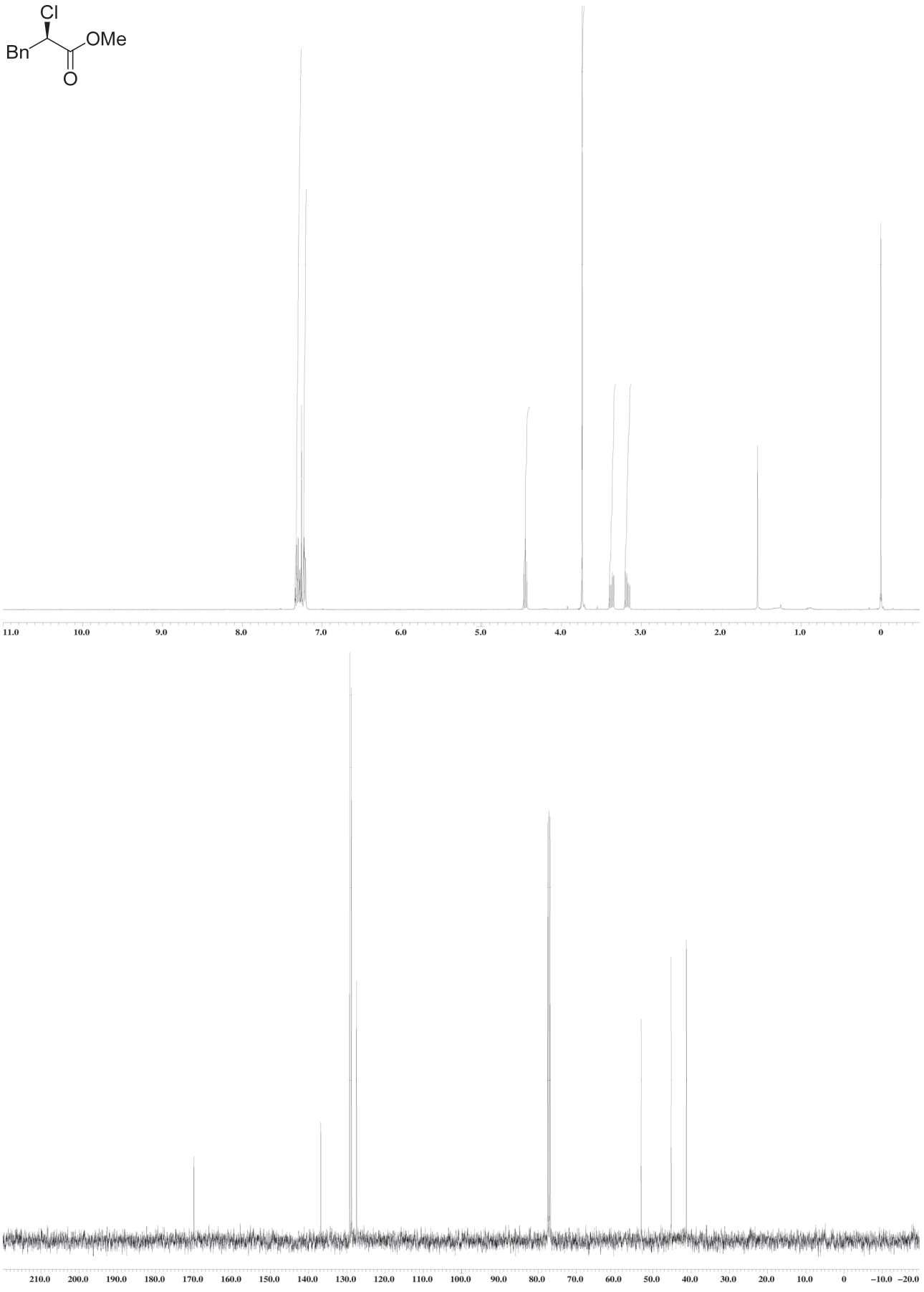
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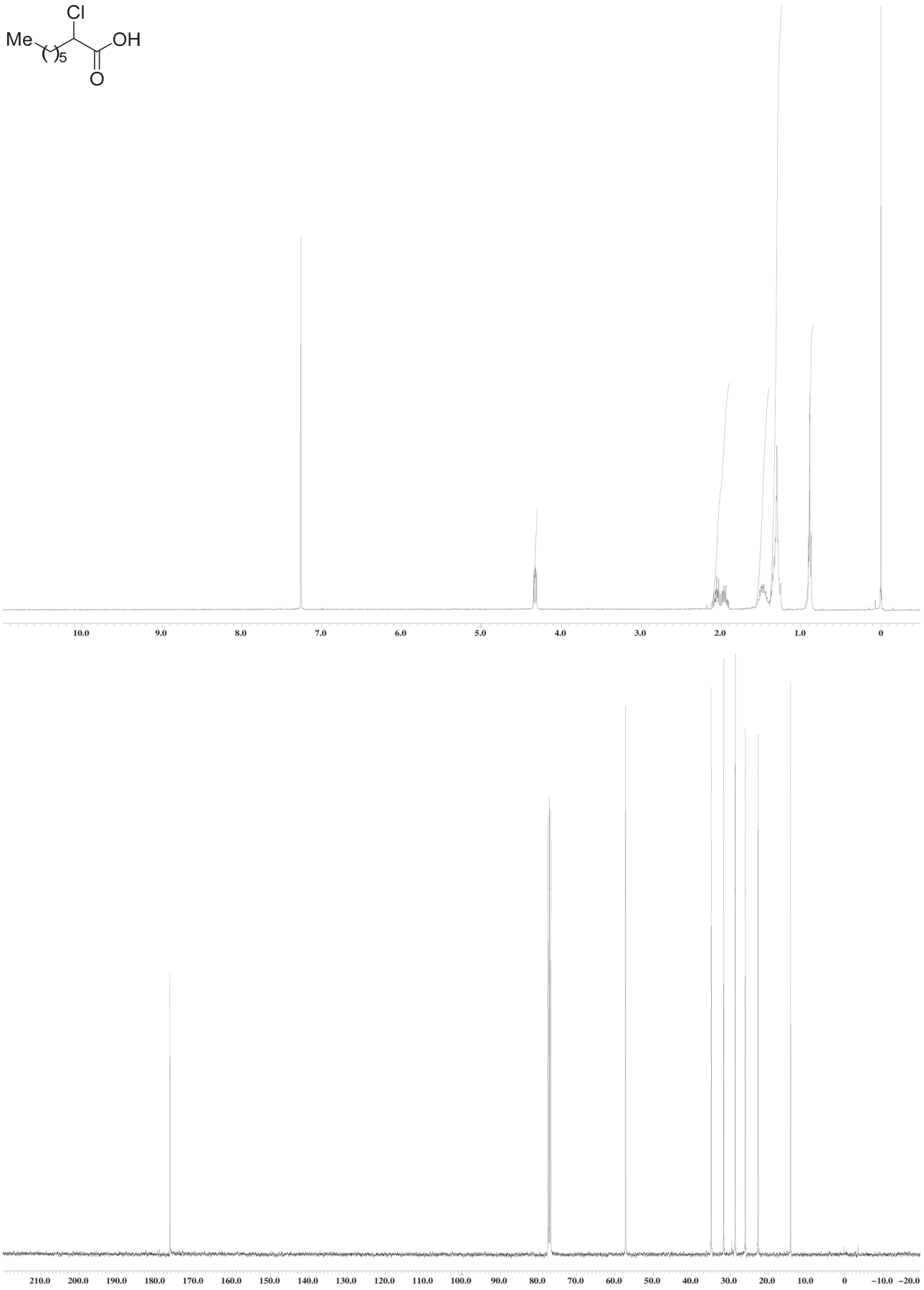
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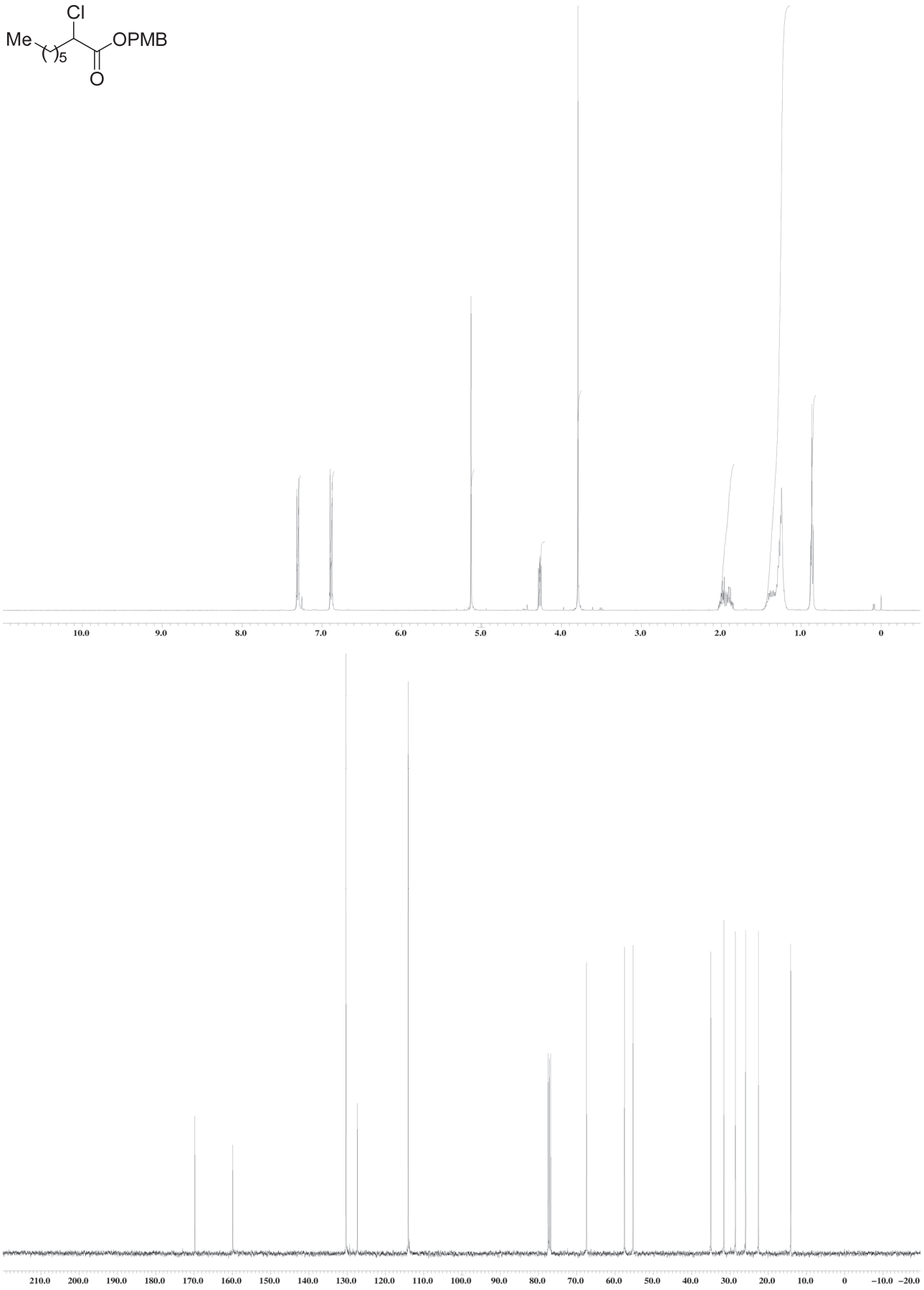
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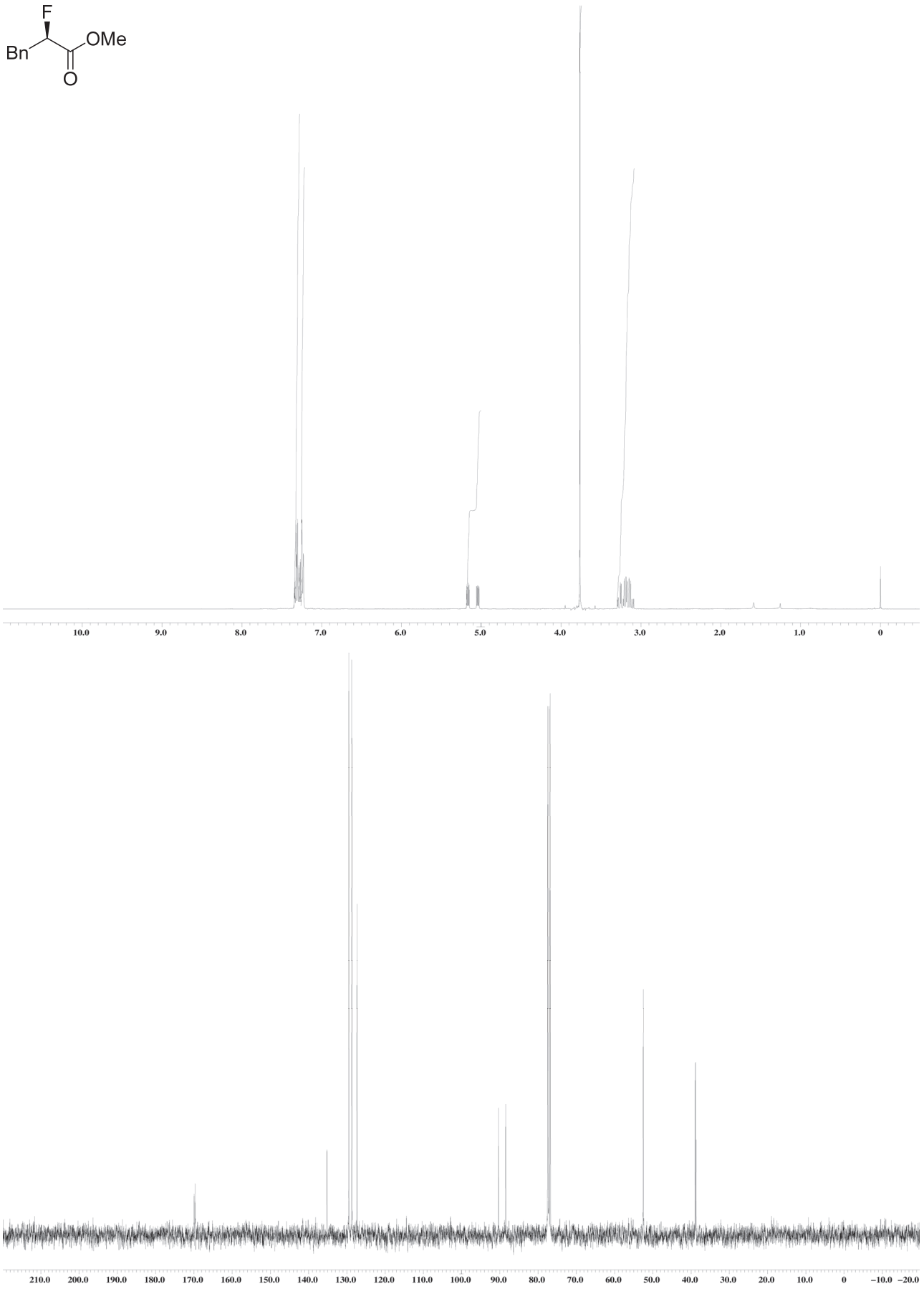
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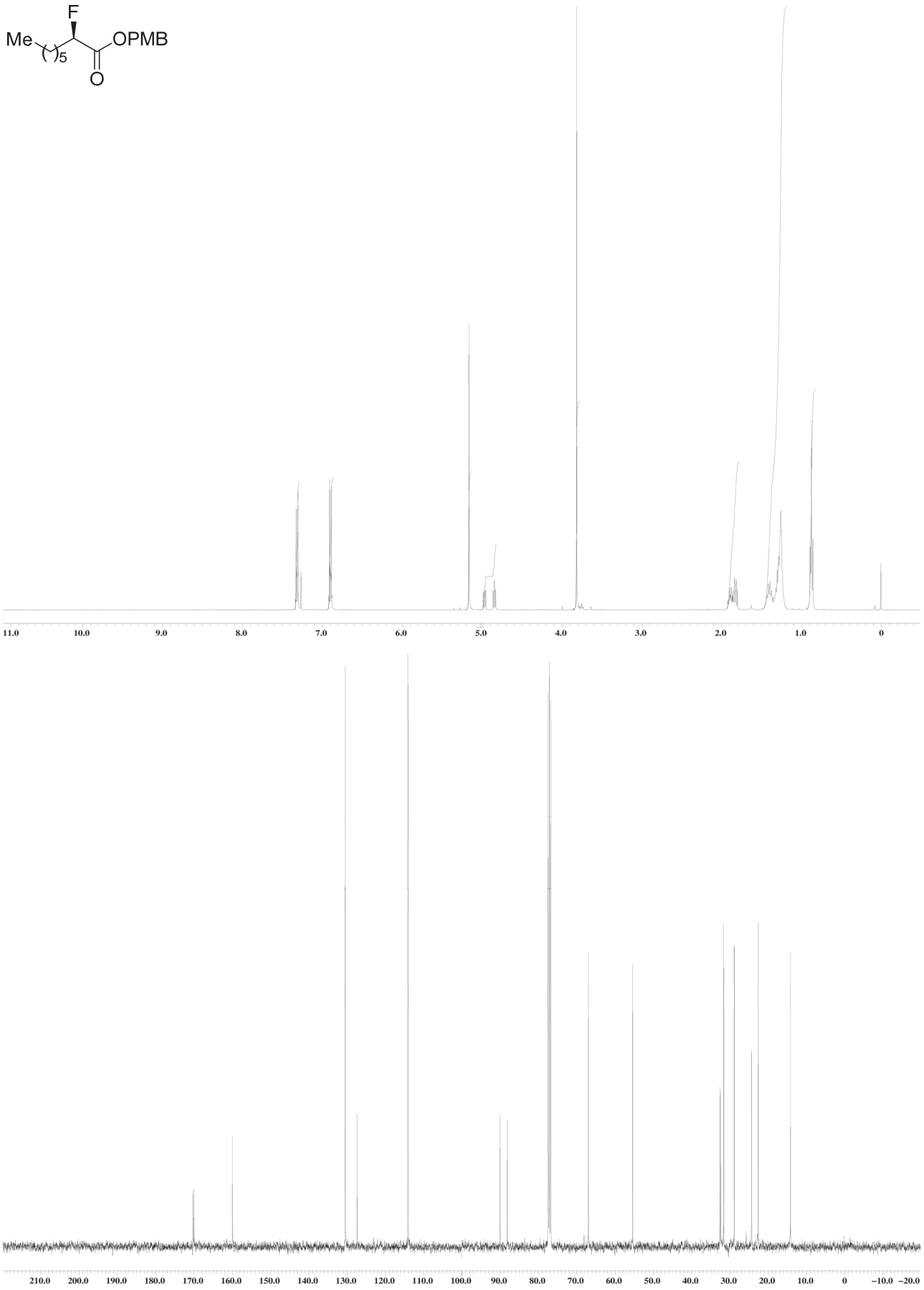
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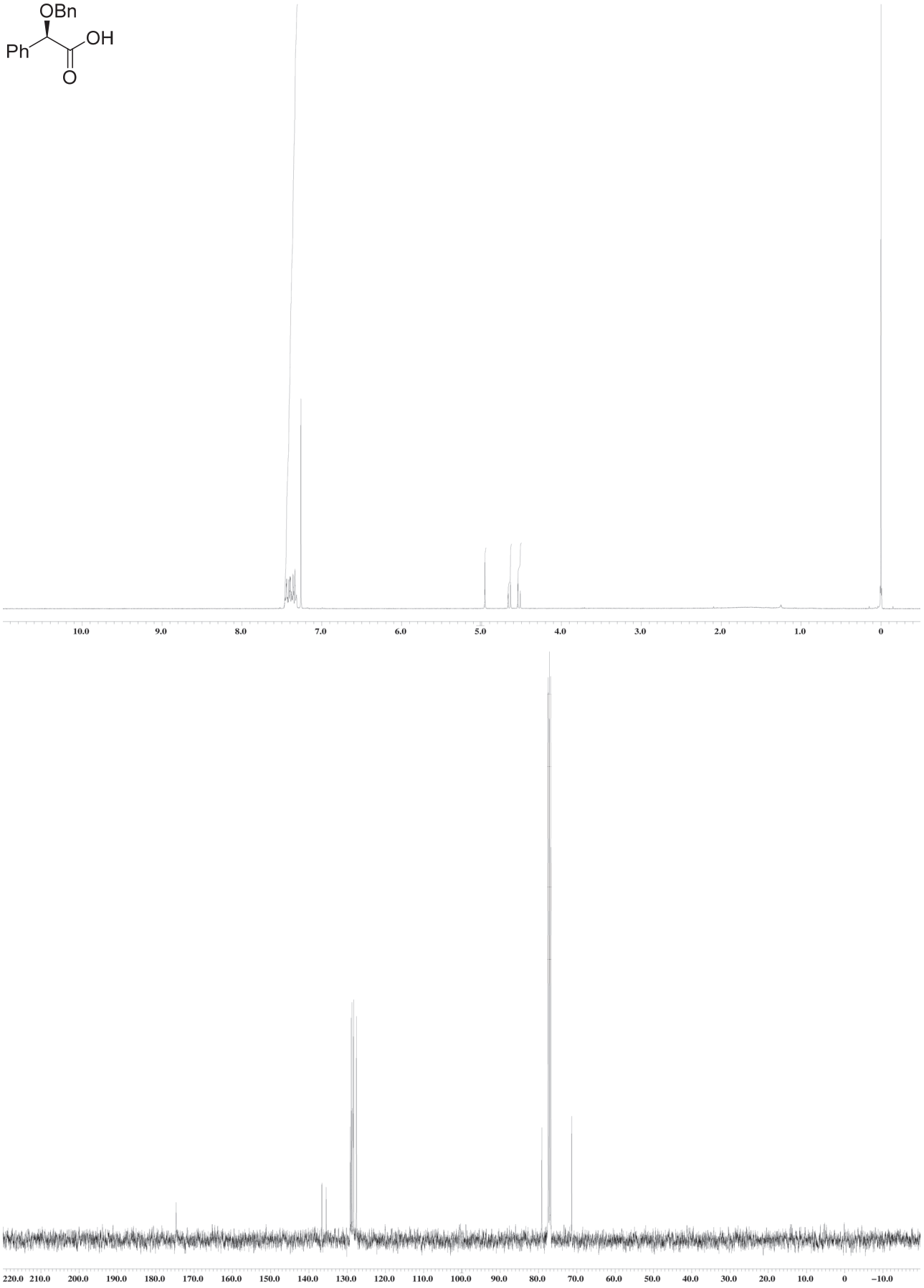
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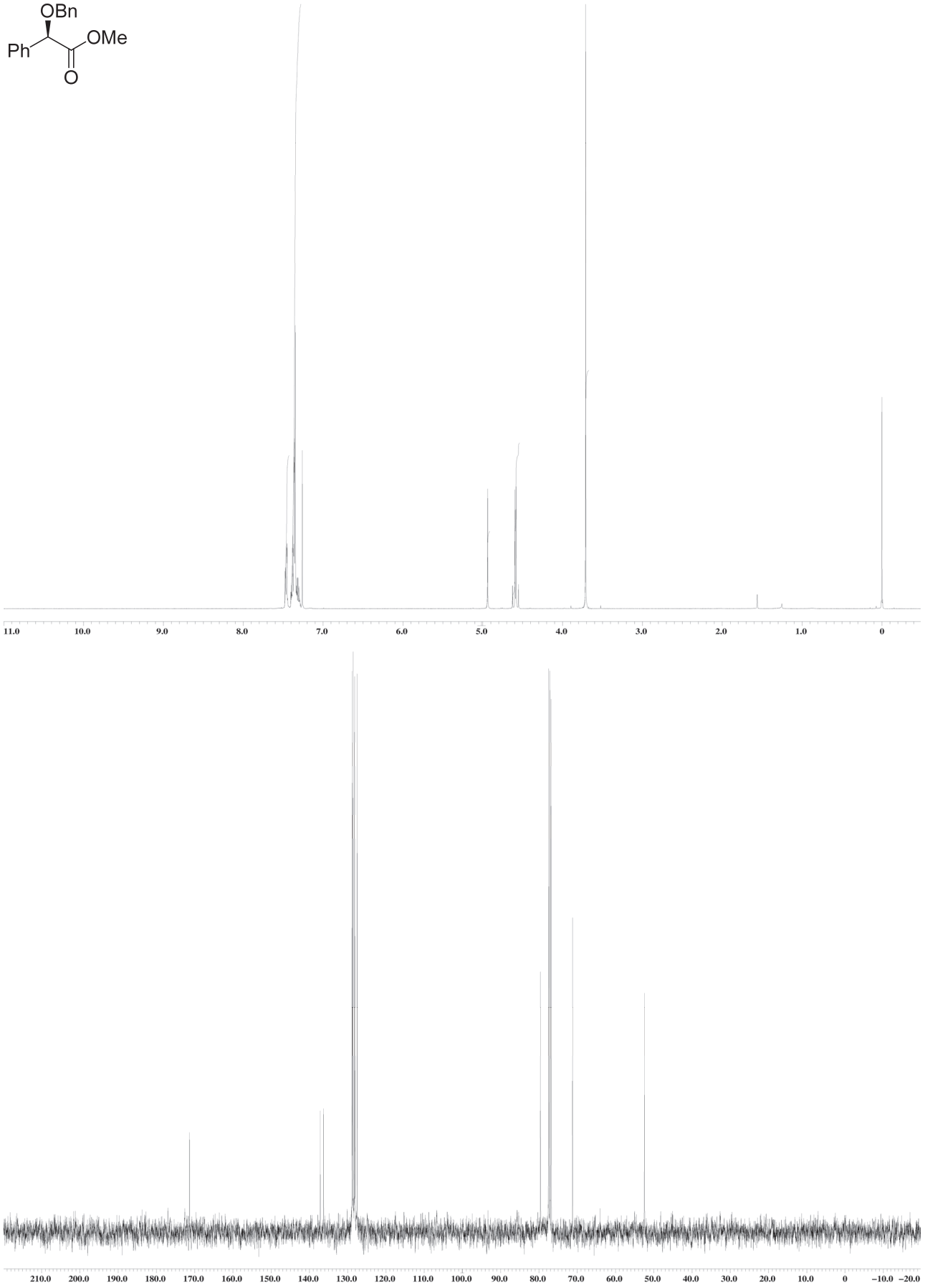
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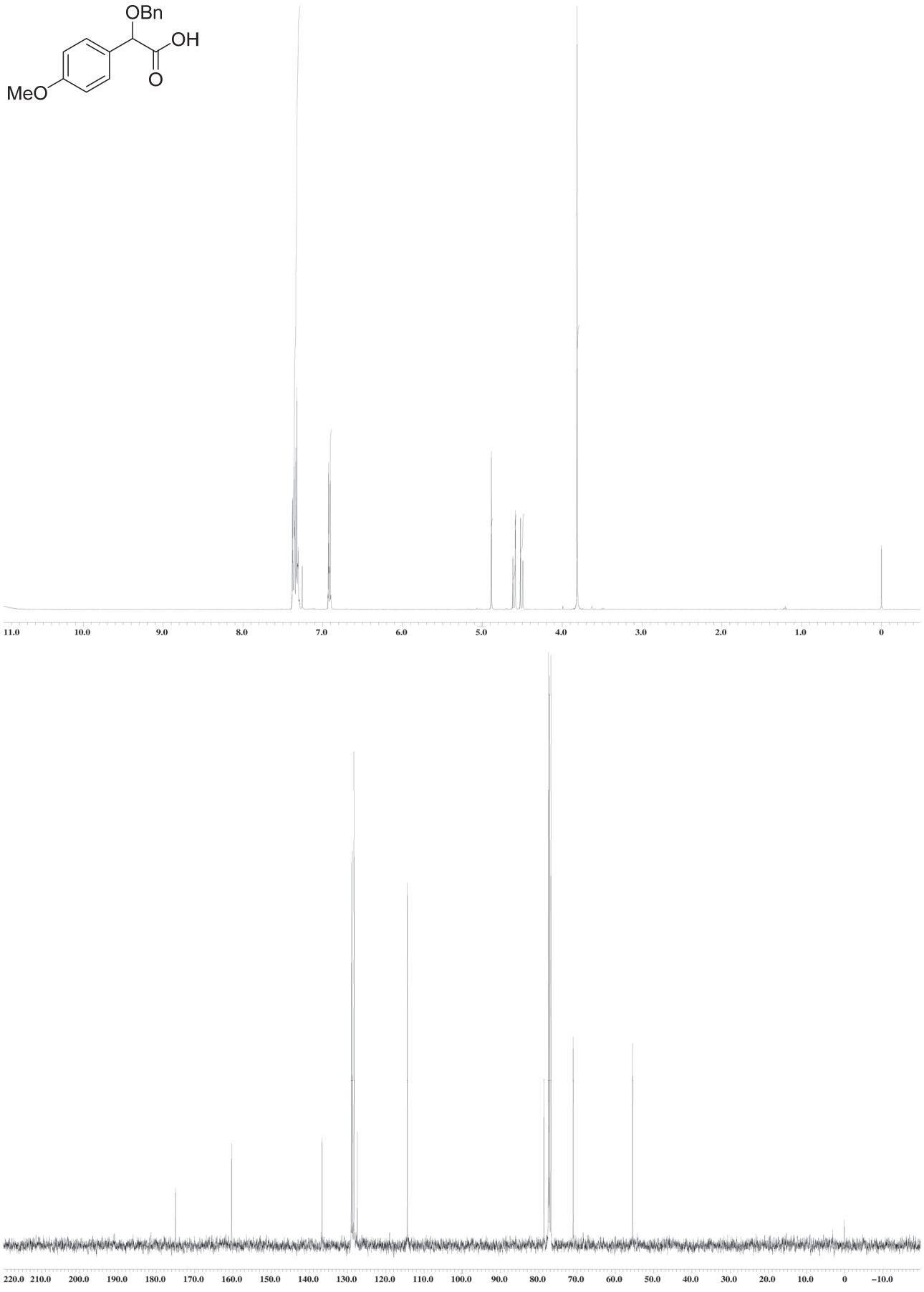
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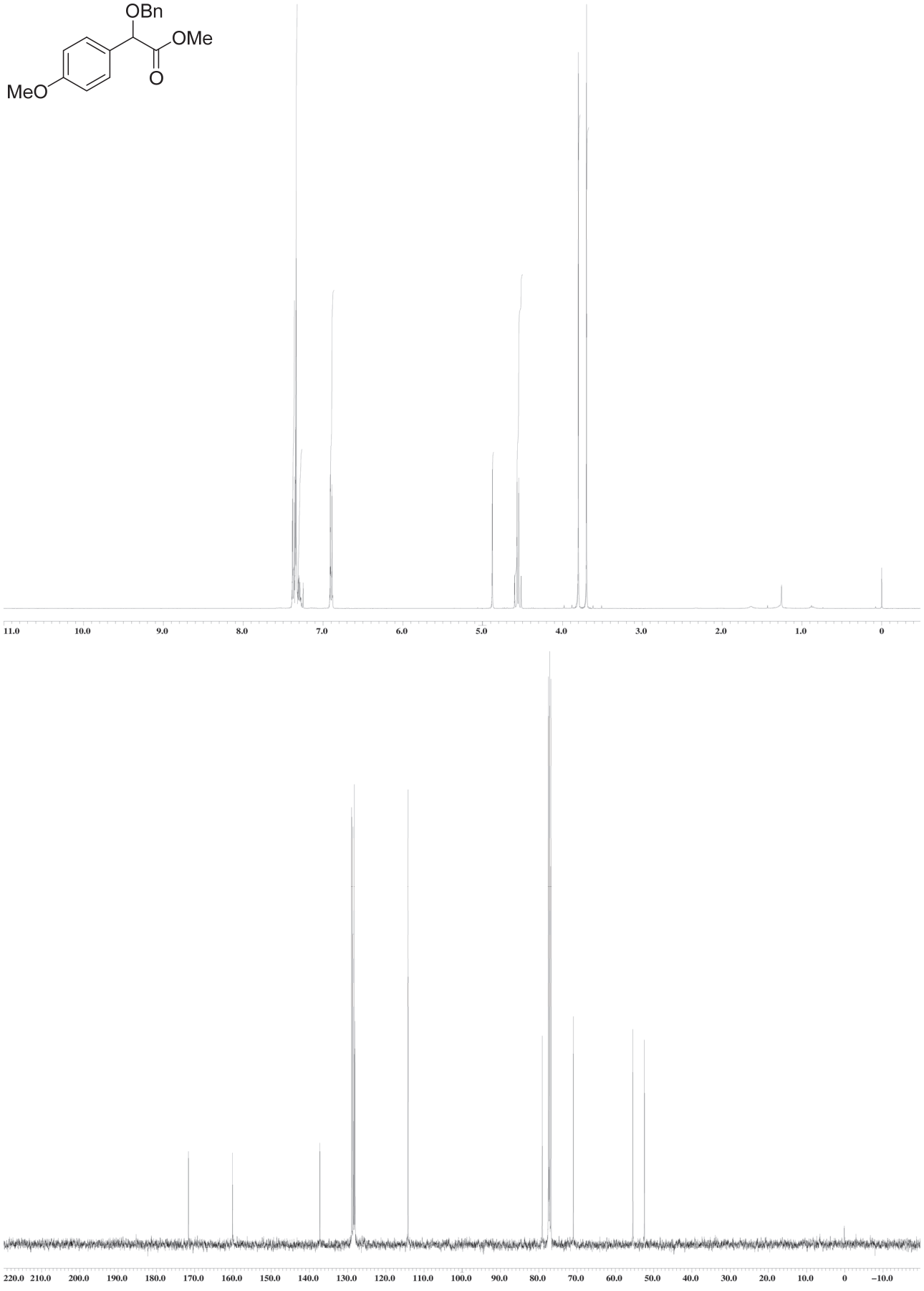
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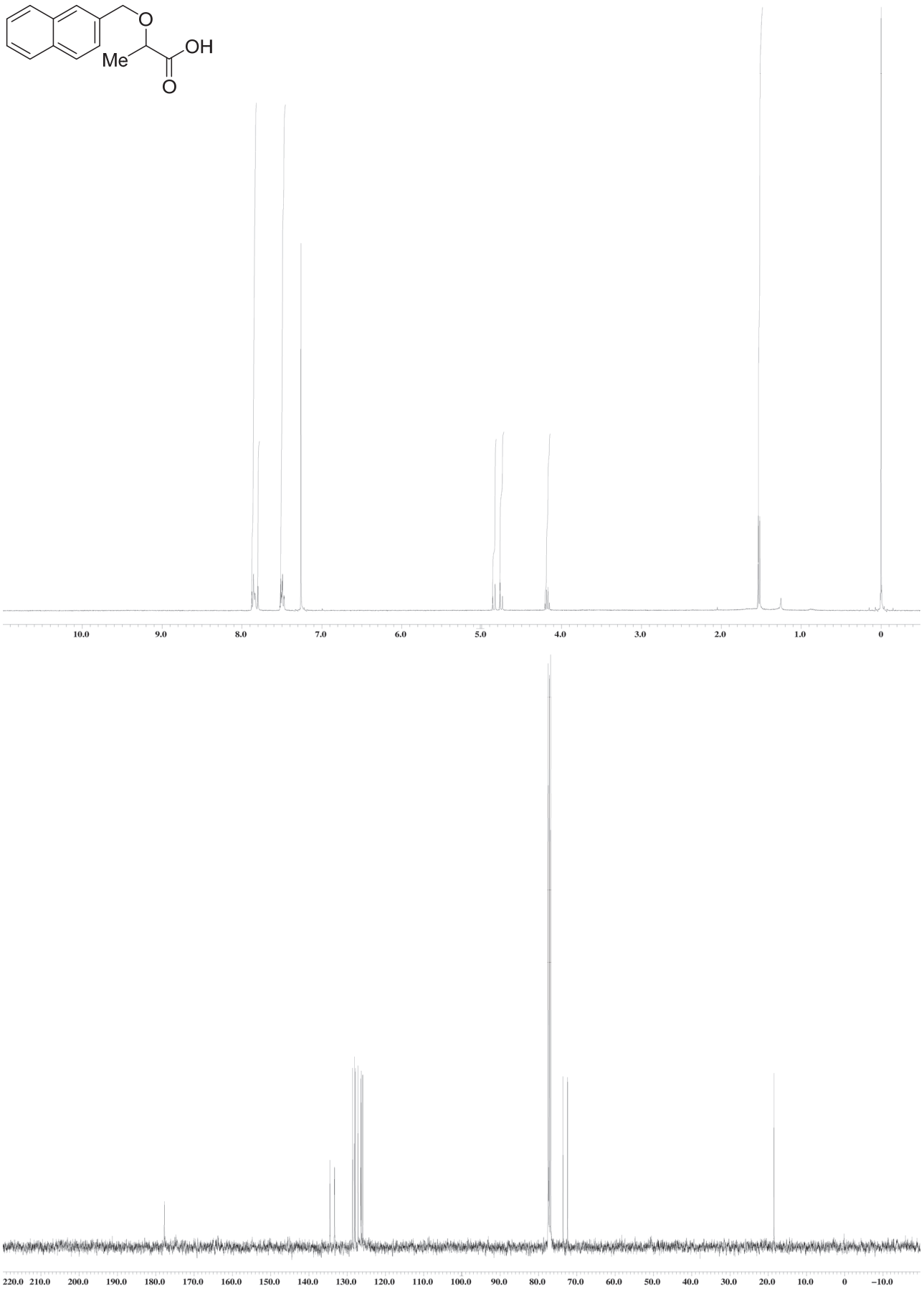
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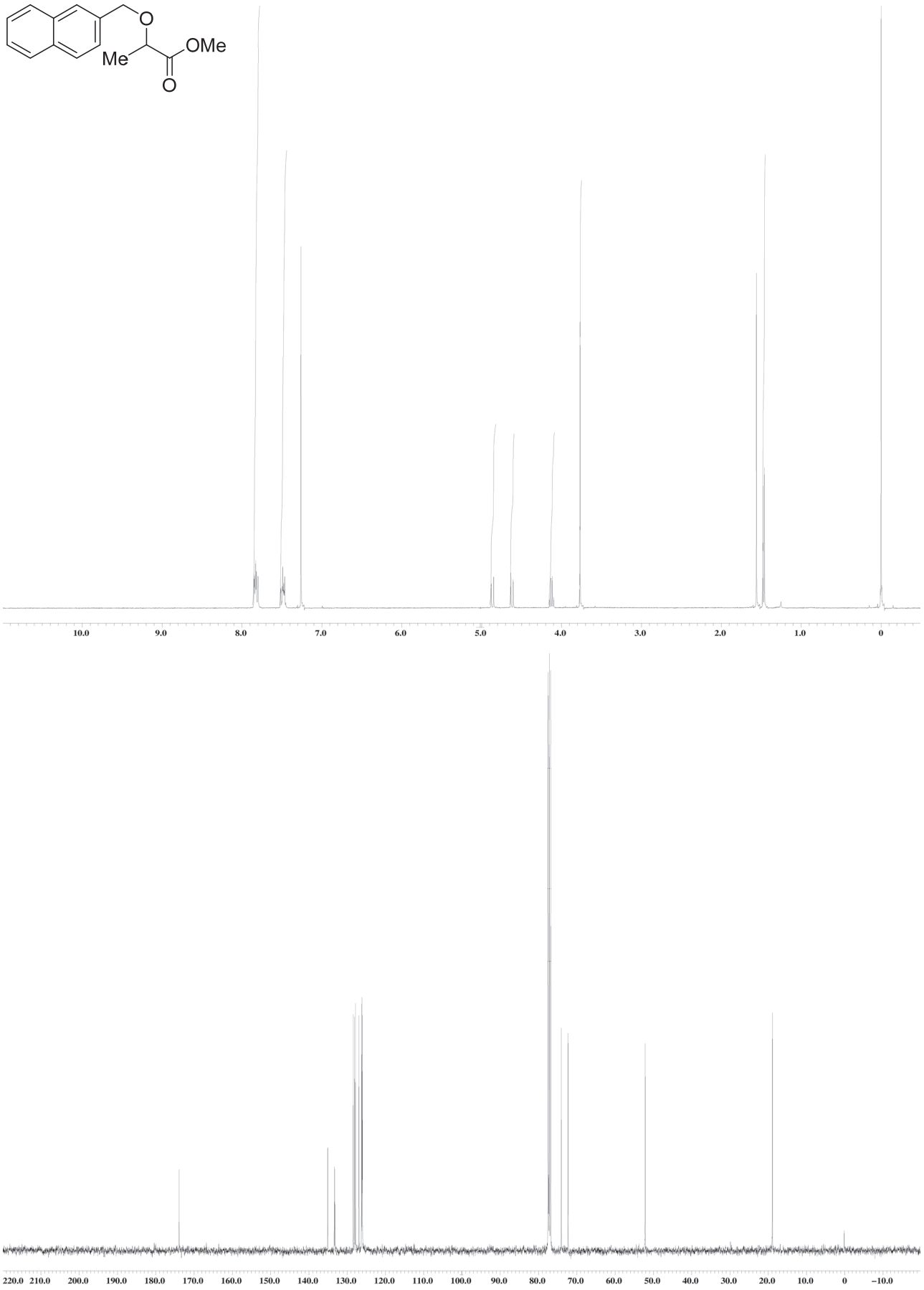
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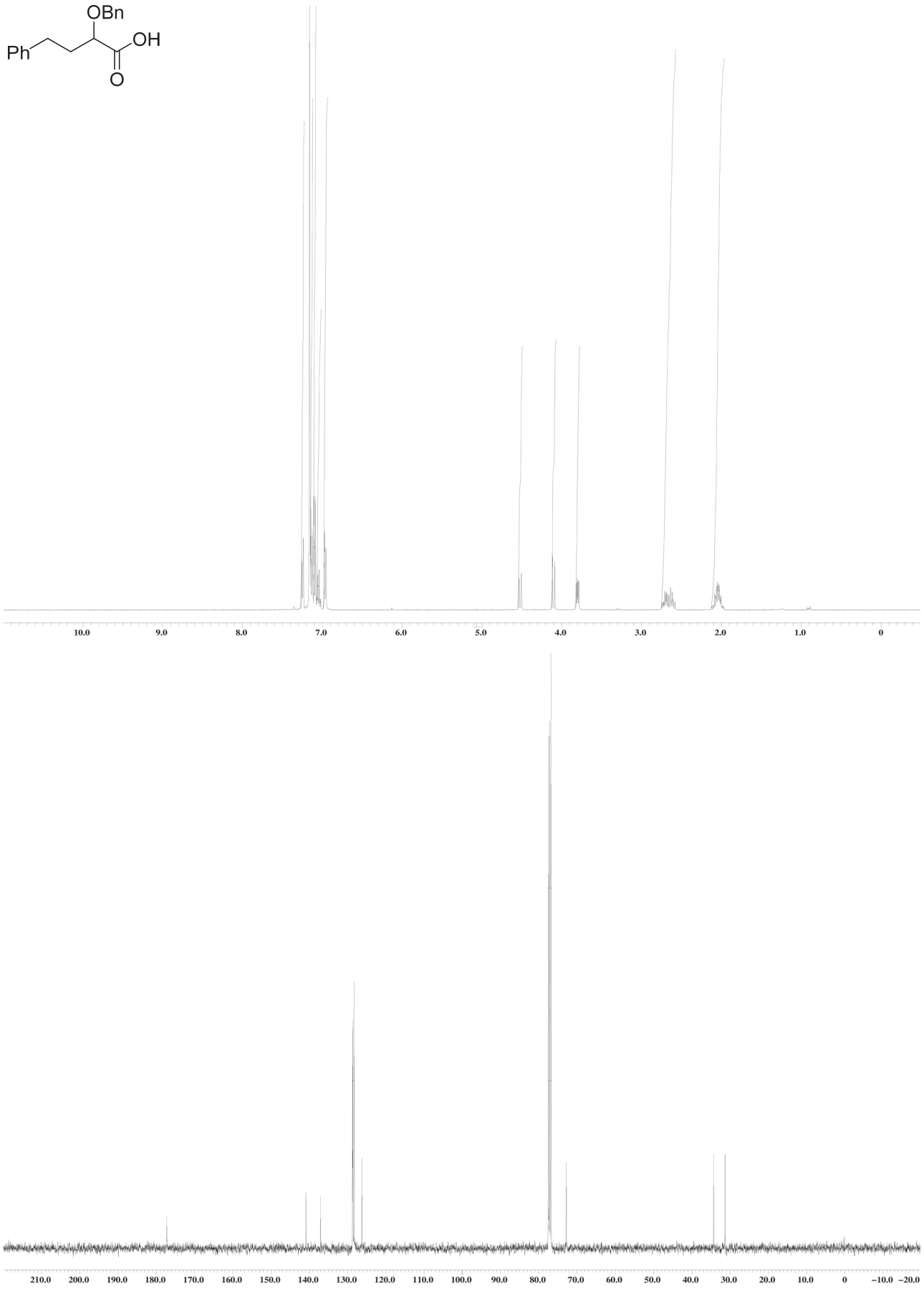
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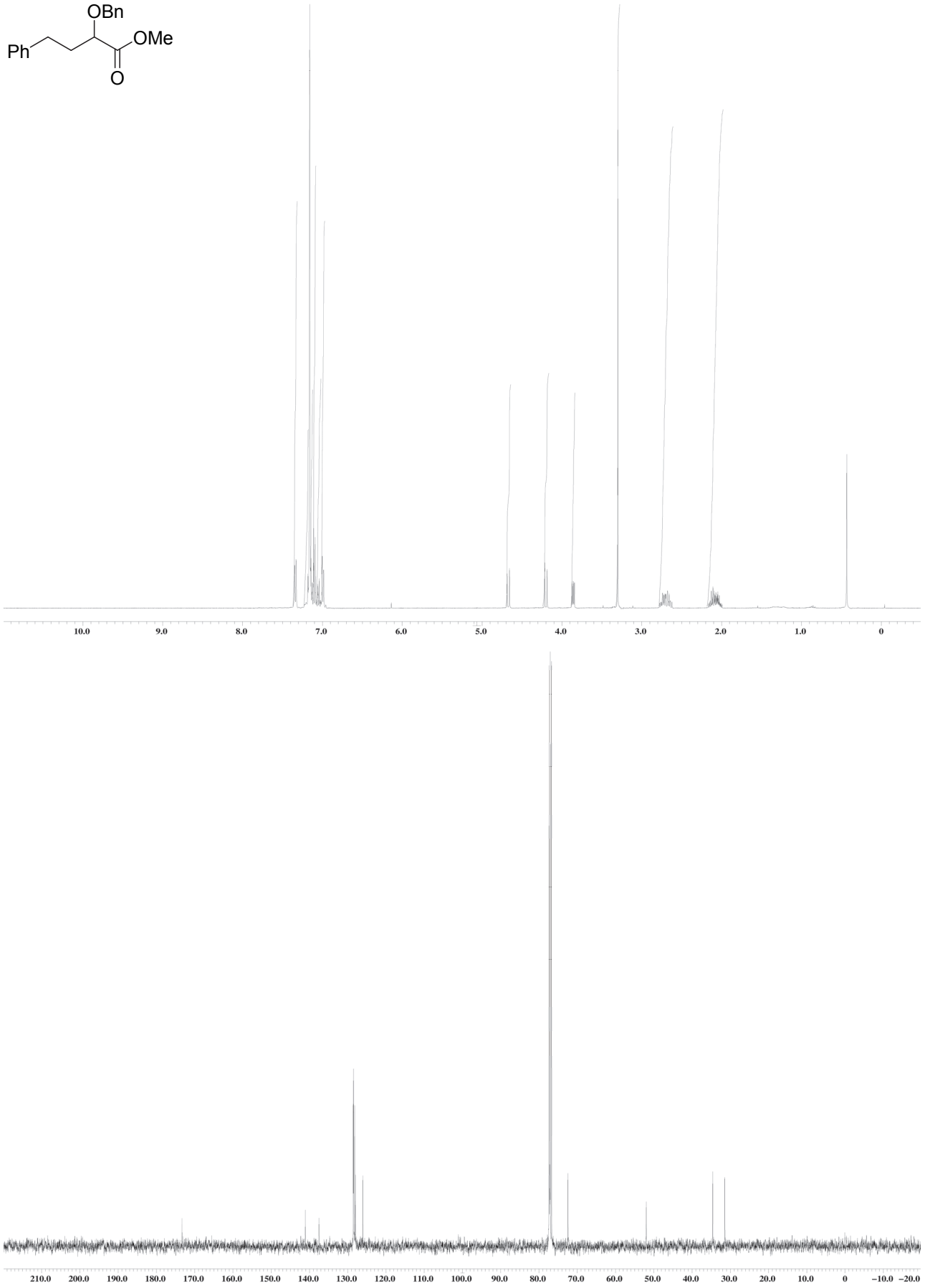
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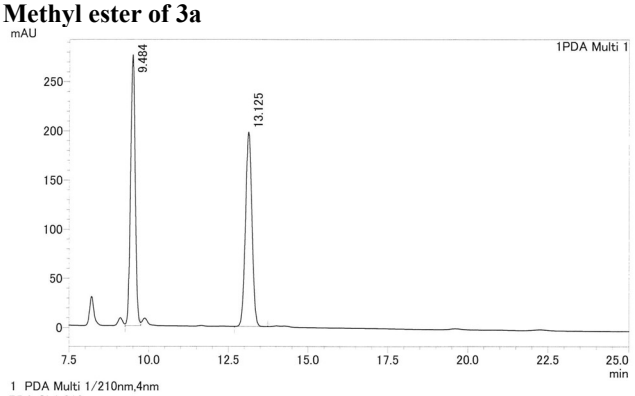
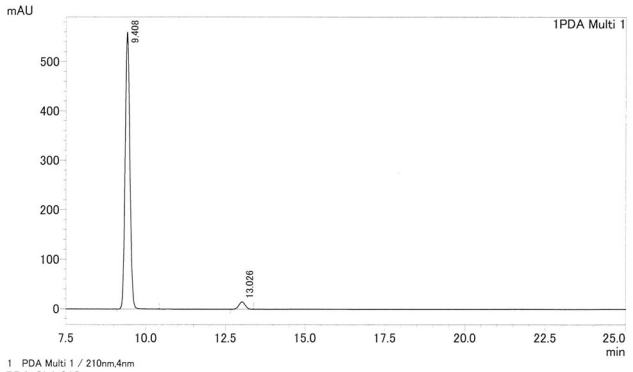
Methyl ester of 3a



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

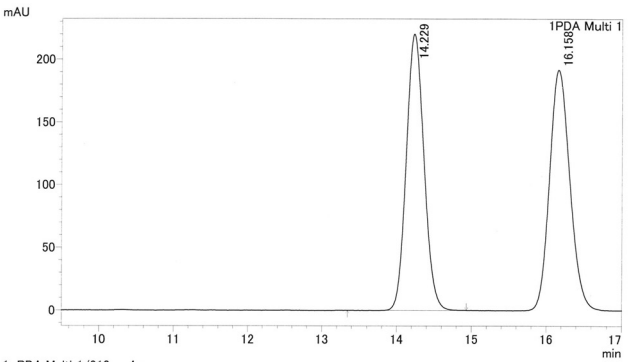
ピーク#	保持時間	面積	面積%
1	9.484	2834868	49.976
2	13.125	2837536	50.024
合計		5672404	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

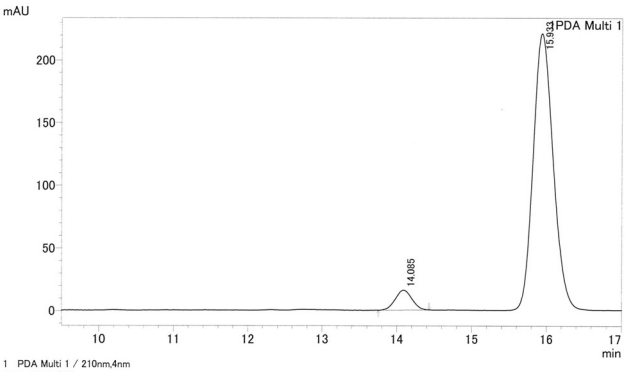
ピーク#	保持時間	面積	面積%
1	9.408	5771330	96.503
2	13.026	209137	3.497
合計		5980467	100.000

PMB ester of 3b



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

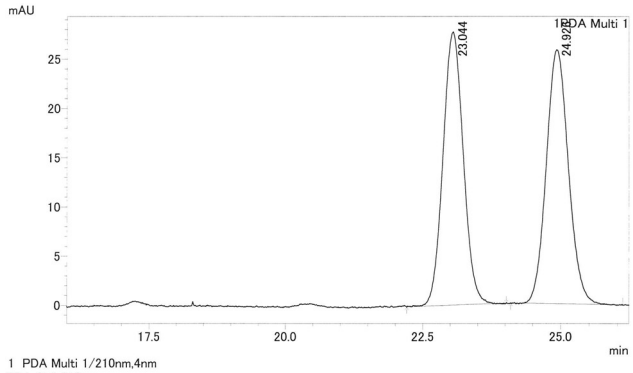
ピーク#	保持時間	面積	面積%
1	14.229	3624141	49.903
2	16.158	3638286	50.097
合計		7262427	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

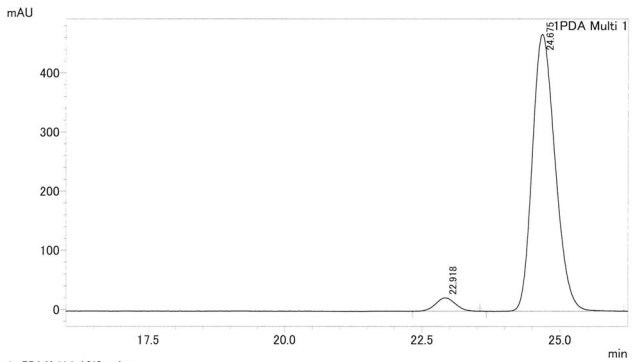
ピーク#	保持時間	面積	面積%
1	14.085	250574	5.740
2	15.933	4115007	94.260
合計		4365582	100.000

PMB ester of 3c



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

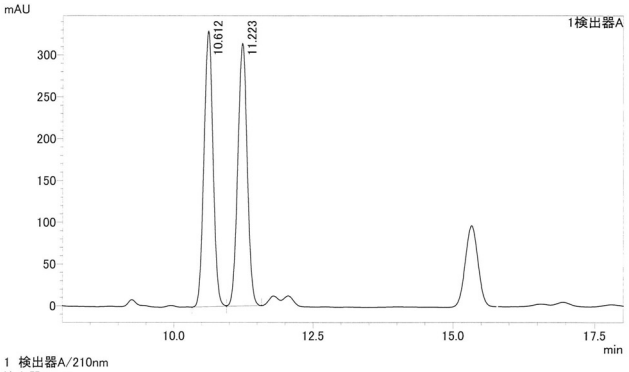
ピーク#	保持時間	面積	面積%
1	23.044	709842	50.001
2	24.926	709806	49.999
合計		1419647	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

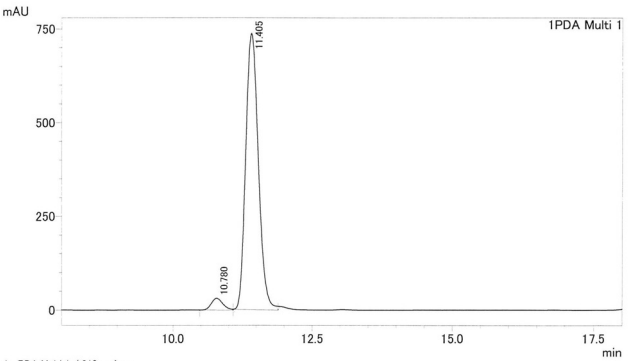
ピーク#	保持時間	面積	面積%
1	22.918	560893	4.036
2	24.675	13337579	95.964
合計		13898472	100.000

Bn ester of 3d



1 検出器A/210nm
検出器A 210nm

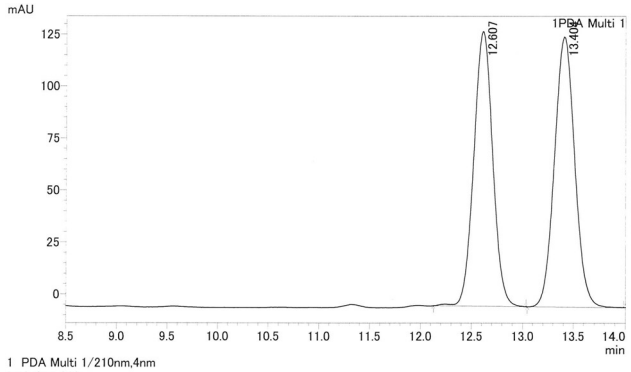
ピーク#	保持時間	面積	面積%
1	10.612	3715166	50.042
2	11.223	3708950	49.958
合計		7424116	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

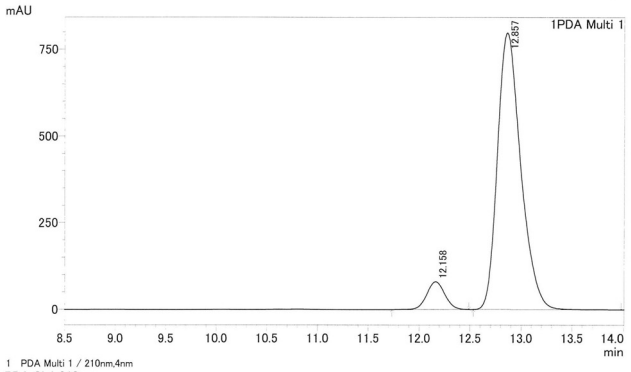
ピーク#	保持時間	面積	面積%
1	10.780	456767	3.747
2	11.405	11734125	96.253
合計		12190891	100.000

Bn ester of 3e



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

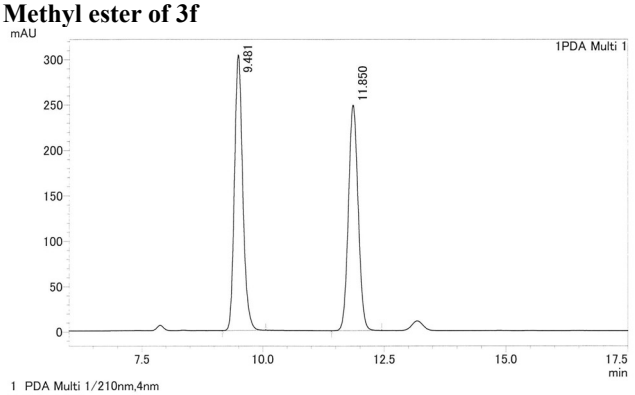
ピーク#	保持時間	面積	面積%
1	12.607	1707456	48.632
2	13.404	1803519	51.368
合計		3510975	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

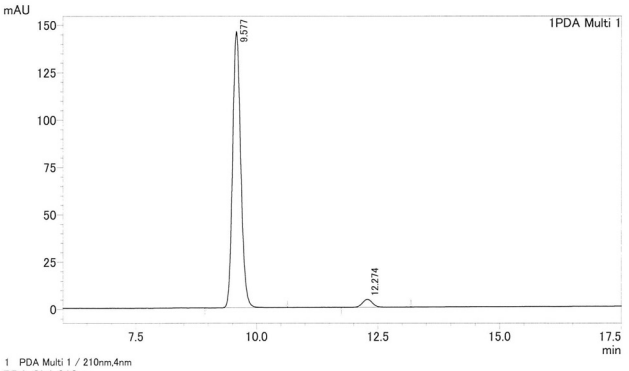
ピーク#	保持時間	面積	面積%
1	12.158	1001159	7.349
2	12.857	12622632	92.651
合計		13623792	100.000

Methyl ester of 3f



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

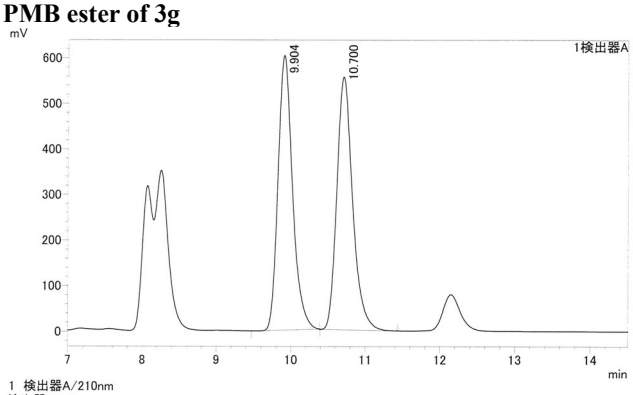
ピーク#	保持時間	面積	面積%
1	9.481	3626752	51.237
2	11.850	3451604	48.763
合計		7078356	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

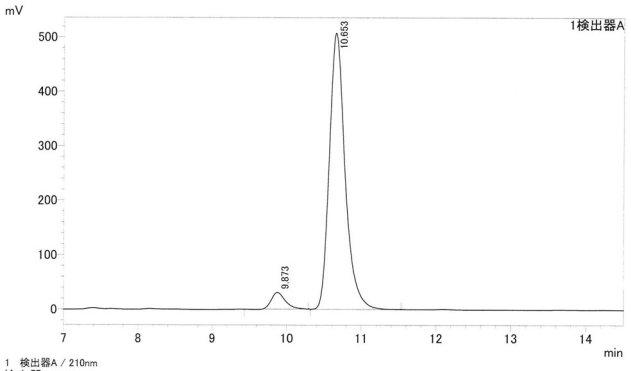
ピーク#	保持時間	面積	面積%
1	9.577	1712332	96.546
2	12.274	61253	3.454
合計		1773586	100.000

PMB ester of 3g



1 検出器A/210nm
検出器A 210nm

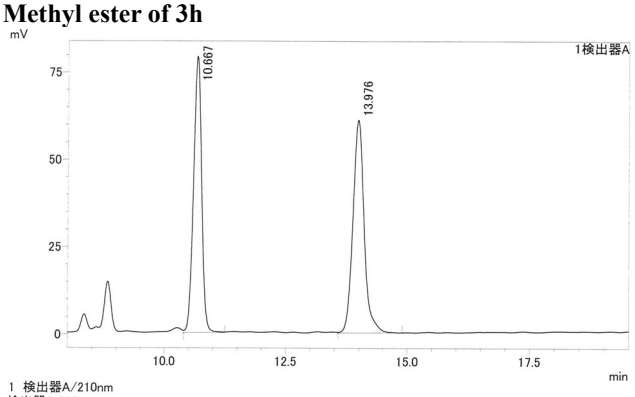
ピーク#	保持時間	面積	面積%
1	9.904	8131872	49.834
2	10.700	8185982	50.166
合計		16317854	100.000



1 検出器A / 210nm
検出器A 210nm

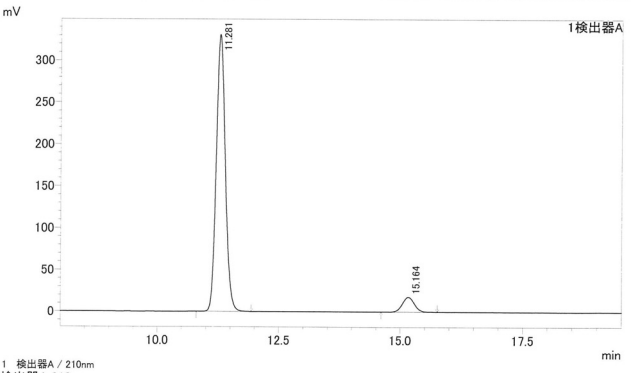
ピーク#	保持時間	面積	面積%
1	9.873	401528	5.088
2	10.653	7489505	94.912
合計		7891033	100.000

Methyl ester of 3h



1 検出器A/210nm
検出器A 210nm

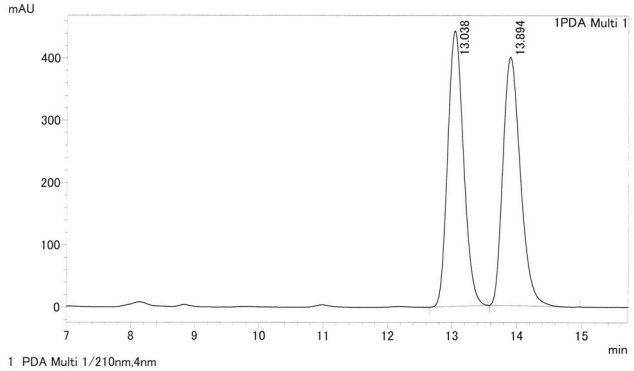
ピーク#	保持時間	面積	面積%
1	10.667	929993	48.499
2	13.976	987546	51.501
合計		1917539	100.000



1 検出器A / 210nm
検出器A 210nm

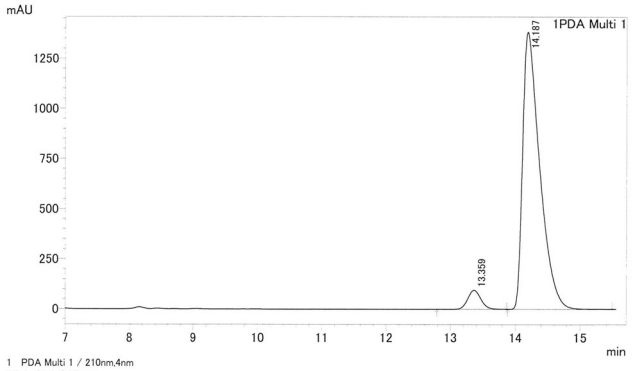
ピーク#	保持時間	面積	面積%
1	11.281	4317389	93.357
2	15.164	307200	6.643
合計		4624589	100.000

PMB ester of 3i



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

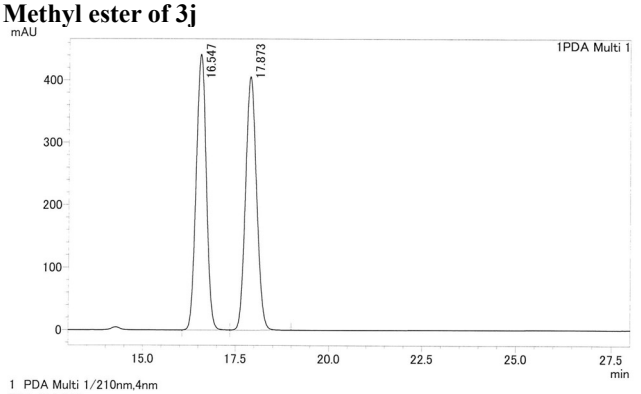
ピーク#	保持時間	面積	面積%
1	13.038	7535229	49.895
2	13.894	7567078	50.105
合計		15102307	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

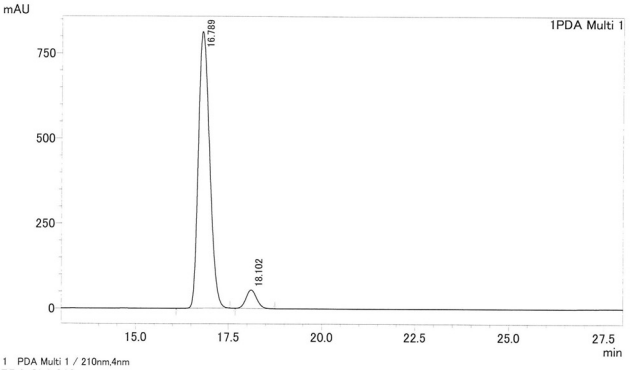
ピーク#	保持時間	面積	面積%
1	13.359	1332623	4.982
2	14.187	25415152	95.018
合計		26747775	100.000

Methyl ester of 3j



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

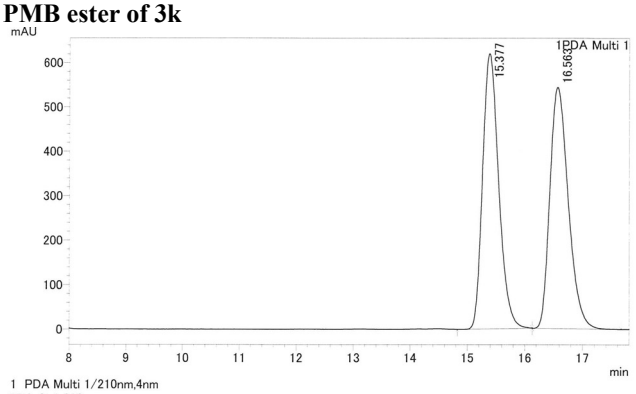
ピーク#	保持時間	面積	面積%
1	16.547	8333725	49.902
2	17.873	8366304	50.098
合計		16700030	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

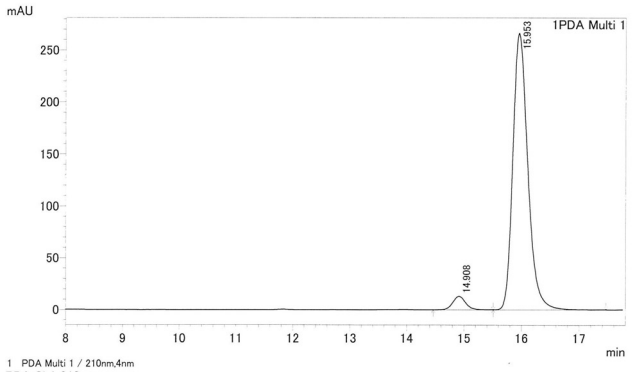
ピーク#	保持時間	面積	面積%
1	16.789	17102325	94.031
2	18.102	1085635	5.969
合計		18187959	100.000

PMB ester of 3k



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

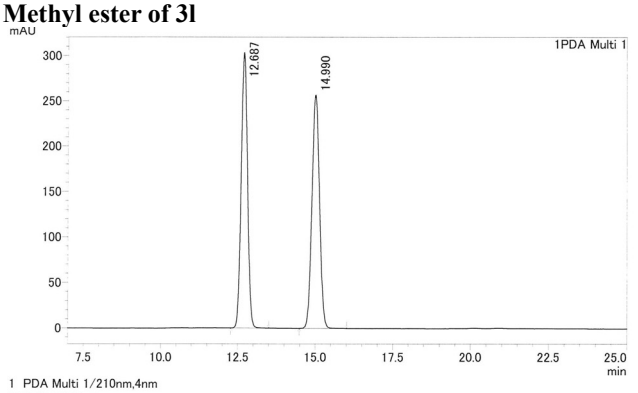
ピーク#	保持時間	面積	面積%
1	15.377	12116360	50.069
2	16.563	12082949	49.931
合計		24199308	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

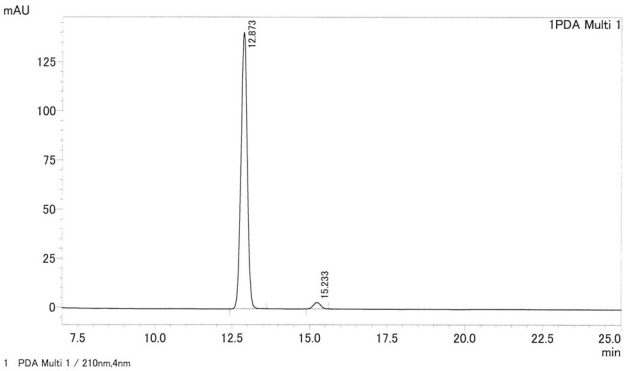
ピーク#	保持時間	面積	面積%
1	14.908	205839	4.096
2	15.953	4819294	95.904
合計		5025133	100.000

Methyl ester of 3l



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

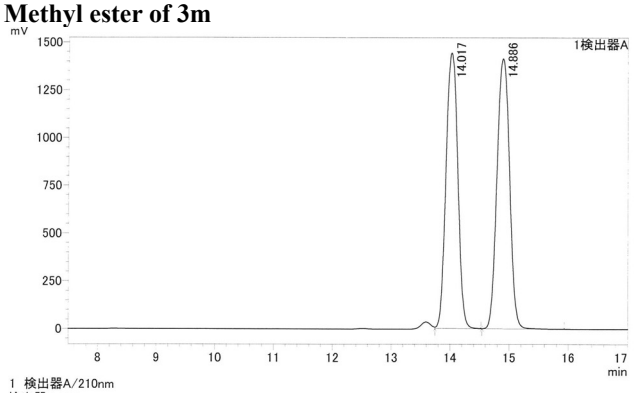
ピーク#	保持時間	面積	面積%
1	12.687	4303090	49.858
2	14.990	4327563	50.142
合計		8630653	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

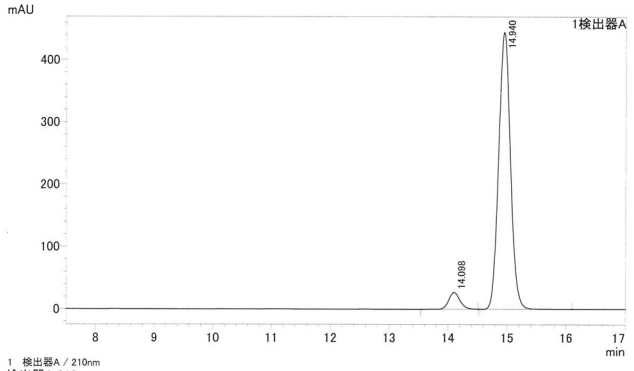
ピーク#	保持時間	面積	面積%
1	12.873	1989506	97.373
2	15.233	53672	2.627
合計		2043177	100.000

Methyl ester of 3m



1 検出器A/210nm
検出器A 210nm

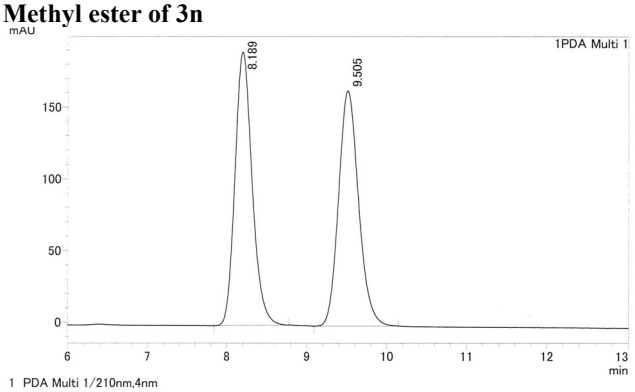
ピーク#	保持時間	面積	面積%
1	14.017	20181272	49.145
2	14.886	20883537	50.855
合計		41064809	100.000



1 検出器A / 210nm
検出器A 210nm

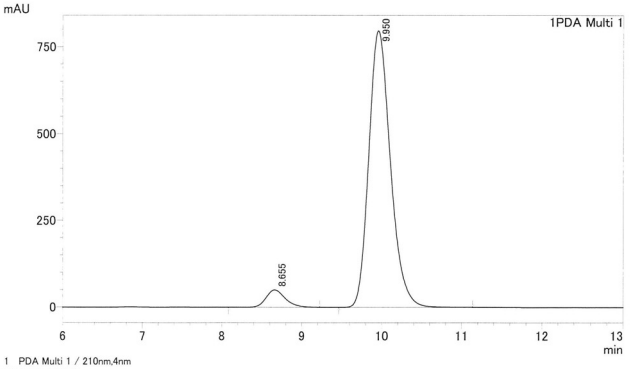
ピーク#	保持時間	面積	面積%
1	14.098	354903	5.454
2	14.940	6151976	94.546
合計		6506879	100.000

Methyl ester of 3n



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

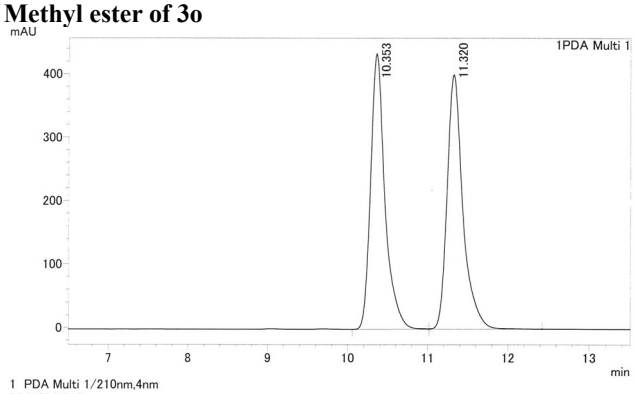
ピーク#	保持時間	面積	面積%
1	8.189	2854111	49.981
2	9.505	2856272	50.019
合計		5710383	100.000



1 PDA Multi 1 / 210nm,4nm
PDA Ch1 210nm

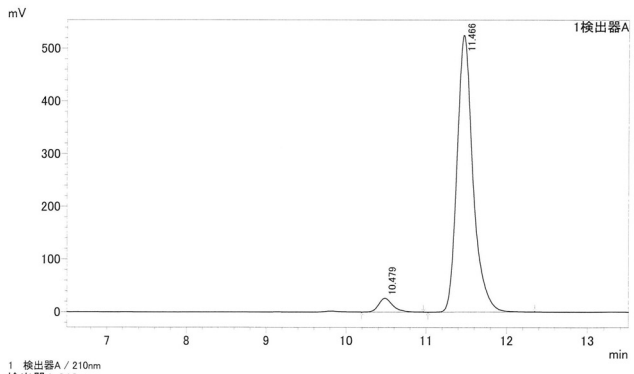
ピーク#	保持時間	面積	面積%
1	8.655	834493	5.283
2	9.950	14960930	94.717
合計		15795423	100.000

Methyl ester of 3o



1 PDA Multi 1/210nm,4nm
PDA Ch1 210nm

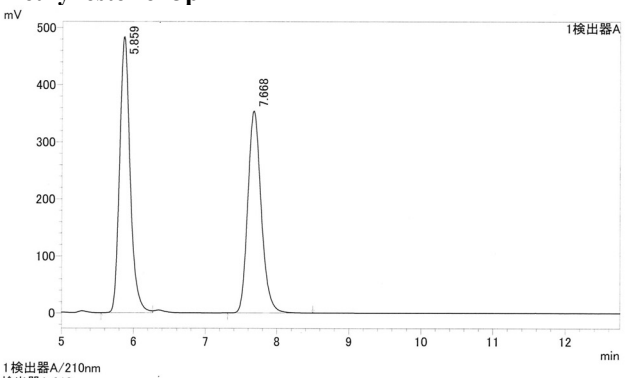
ピーク#	保持時間	面積	面積%
1	10.353	5446585	49.865
2	11.320	5475990	50.135
合計		10922575	100.000



1 検出器A / 210nm
検出器A 210nm

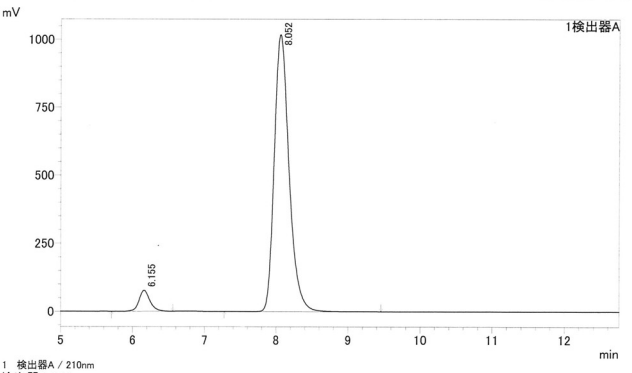
ピーク#	保持時間	面積	面積%
1	10.479	325248	4.295
2	11.466	7248119	95.705
合計		7573367	100.000

Methyl ester of 3p



1検出器A/210nm
検出器A 210nm

ピーク#	保持時間	面積	面積%
1	5.859	4911887	51.644
2	7.668	4599205	48.356
合計		9511092	100.000



1 検出器A / 210nm
検出器A 210nm

ピーク#	保持時間	面積	面積%
1	6.155	807281	5.233
2	8.052	14619794	94.767
合計		15427074	100.000