*Supporting Information for:*

# Nickel-iminophosphine-catalyzed [4+2] cycloaddition of enones with allenes; synthesis of highly substituted dihydropyranes

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## Contents

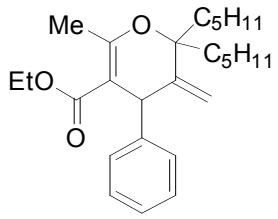
**Instrumentation and Chemicals**

All manipulations of oxygen- and moisture-sensitive materials were conducted in a dry box or with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 ($^{1}$H, 500 MHz; $^{13}$C, 125.7 MHz) spectrometer using tetramethylsilane ($^{1}$H) as an internal standard. $^{1}$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration, and identification. $^{19}$F NMR spectra were measured on a Varian Mercury 200 ($^{19}$F, 188 M Hz) spectrometer with trifluoroacetic acid as an internal standard (! = 0 ppm). $^{31}$P NMR spectra were measured on a Varian Mercury 200 ($^{31}$P, 121 M Hz) spectrometer with phosphoric acid as an internal standard (! = 0 ppm). X-Ray data were taken on a Bruker Smart APEX X-Ray diffracto- meter equipped with a large area CCD detector and Rigaku Mercury CCD apparatus. High-resolution mass spectra were obtained with a Thermo Fisher SCIENTIFIC EXACTIVE spectrometer. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (toluene as an eluent). Infrared spectra (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. TLC analyses were performed by means of Merck Kieselgel 60 $F_{254}$ (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous vanillin solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 μm). Recrystallization was performed with a TECHNO SIGMA Soltra mini. Unless otherwise noted, commercially available reagents were used without purification. 1,4-Dioxane was purchased from Wako Pure Chemical Co. stored over slices of sodium. Bis(1,5-cyclooctadiene)nickel and trimethylphosphine were purchased from Strem Chemicals, Inc. Enones were readily prepared by condensation of keto-ester and aldehyde. All reactions were performed in WHEATON 5.0 mL V-vial with 20–400 screw cap.

**Experimental Procedure for the Nickel-catalyzed Addition and Characterization Data for Products.**

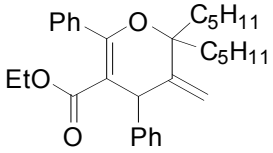
***General procedure.*** The reaction was performed in a 5 mL sealed vessel equipped with a Teflon-coated magnetic stirrer tip. An enone (0.2 mmol) and an allene (0.5 mmol) were added to a solution of Bis(1,5-dicyclooctadiene)nickel (5.5 mg, 0.02 mmol) and (E)-N-(2-(diphenylphosphino)benzylidene)cyclohexanamine (29.7 mg, 0.08 mmol) in 1,4-dioxane (2 mL) in a dry box. The VIAL was taken outside the dry box and heated at 100 °C for the 15 h. The resulting reaction mixture was cooled to ambient temperature and filtered through a silica gel pad, concentrated in vacuo. The residue was purified by flash silica gel column chromatography (30 g, 2x25 cm, hexane/ethyl acetate = 30:1) to give the corresponding dihydro-2H-pyrane derivatives.

**Ethyl 6-methyl-3-methylene-2,2-dipentyl-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3aa).**



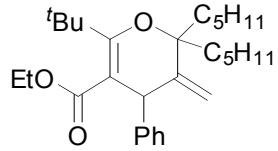

Yield: 98%, colorless oil. TLC: $R_f$ 0.71(hexane/ethyl acetate = 5:1) $^1$H NMR ($CDCl_3$) ! 7.21 (m, 5H; Ph–H), 4.99 (s, 1H; CH-H), 4.91 (d, *J* = 1.5 Hz, 1H; CH-H), 4.45 (s, 1H; CH), 4.01-3.90 (m, 2H; $OCH_2$), 2.34 (s, 3H; $CH_3$), 1.68 (m, 2H; $CH_2$), 1.49 (m, 2H; $CH_2$), 1.33 (m, 8H; $CH_2$), 1.14 (m, 4H; $CH_2$), 0.97 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.89 (t, *J* = 7.5 Hz, 3H; $CH_3$), 0.77 (t, *J* = 7.5 Hz, 3H; $CH_3$). $^{13}$C NMR ($CDCl_3$) ! 167.9, 163.6, 147.0, 143.5, 127.9, 127.9, 125.9, 113.1, 103.2, 84.4, 59.4, 44.4, 35.9, 36.8, 32.1, 31.8, 23.0, 22.5, 22.4, 20.3, 14.0, 14.0, 13.9, 13.9. IR (neat): 2956, 2860, 2363, 1707, 1623, 1457, 1229, 1075, 701 $cm^{-1}$. HRMS ($ESI^+$) found 399.2901, calcd for $[M+H]^+$ 399.2899.

**Ethyl 3-methylene-2,2-dipentyl-4,6-diphenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ba).**




Yield: 18%, yellow oil. TLC: $R_f$ 0.67(hexane/ethyl acetate = 5:1) $^1$H NMR ($CDCl_3$) ! 7.44 (m, 10H; Ph–H), 5.06 (d, *J* = 1.5 Hz, 1H; CH-H), 5.01 (s, 1H; CH-H), 4.59 (s, 1H; CH), 3.81 (q, 2H; $OCH_2$), 1.89 (m, 2H; $CH_2$), 1.63 (m, 2H; $CH_2$), 1.40 (m, 6H; $CH_2$), 1.20 (m, 6H; $CH_2$), 0.90 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.78 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.78 (t, *J* = 7.0 Hz, 3H; $CH_3$). $^{13}$C NMR ($CDCl_3$) ! 167.6, 161.9, 147.2, 143.2, 137.0, 128.9, 128.7, 128.2, 128.1, 127.5, 126.1, 113.6, 105.4, 84.9, 59.6, 44.9, 36.4, 36.4, 32.2, 31.8, 23.1, 23.0, 22.5, 22.4, 14.0, 13.9, 13.5. IR (neat): 2955, 2871, 1694, 1644, 1446, 1329, 1238, 1087, 697 $cm^{-1}$. HRMS ($ESI^+$) found 461.3058, calcd for $[M+H]^+$ 461.3056.

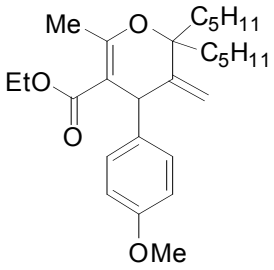
**Ethyl 6-tert-butyl-3-methylene-2,2-dipentyl-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ca).**




Yield: 60%, colorless oil. TLC: $R_f$ 0.76(hexane/ethyl acetate = 5:1) $^1$H NMR ($CDCl_3$) ! 7.24 (m, 5H; Ph–H), 4.88 (d, *J* = 2.0 Hz, 1H; CH-H), 4.78 (d, *J* = 2.0 Hz, 1H; CH-H), 4.29 (t, *J* = 2.0 Hz, 1H; CH), 3.90-3.81 (m, 2H; $OCH_2$), 1.26 (s, 9H; $CH_3$), 1.35-1.84 (m, 16H; $CH_2$), 0.98 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.91 (t, *J* = 6.5 Hz, 3H; $CH_3$), 0.83 (t,

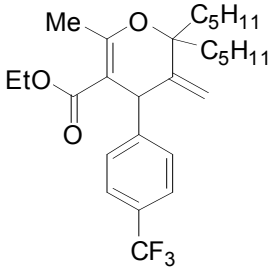
*J* = 7.0 Hz, 3H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 169.4, 164.2, 148.2, 142.7, 128.8, 128.0, 127.9, 126.2, 112.1, 104.6, 82.5, 59.8, 46.6, 37.8, 36.2, 36.1, 32.2, 32.0, 28.7, 28.5, 23.2, 22.9, 22.6, 22.4, 14.0, 13.9, 13.7. IR (neat): 2956, 2859, 1714, 1457, 1087, 699 $cm^{-1}$. HRMS ($ESI^+$) found 441.3374, calcd for $[M+H]^+$ 441.3369.

**Ethyl 4-(4-methoxyphenyl)-6-methyl-3-methylene-2,2-dipentyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3da).**



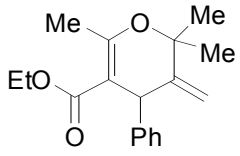

Yield: 98%, colorless oil. TLC: $R_f$ 0.68(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.10 (m, 2H; Ph–H), 6.78 (m, 2H; Ph–H),4.98 (d, *J* = 1.5 Hz, 1H; CH-H), 4.89 (s, 1H; CH-H), 4.40 (s, 1H; CH), 4.02-3.93 (m, 2H; $OCH_2$), 3.76 (s, 3H; $CH_3$), 2.32 (s,3H; $CH_3$), 1.67 (m, 2H; $CH_2$), 1.46 (m, 2H; $CH_2$), 1.31 (m, 8H; $CH_2$), 1.11 (m, 4H; $CH_2$), 1.03 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.89 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.77 (t, *J* = 7.0 Hz, 3H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 168.0, 163.3, 157.9, 147.3, 135.6, 128.8, 113.4, 112.7, 103.5, 84.4, 59.4, 44.2, 43.6, 37.0, 36.8, 32.1, 31.8, 23.0, 22.9, 22.5, 22.4, 20.3, 14.0, 14.0, 13.9. IR (neat): 2955, 2871, 1705, 1615, 1510, 1464, 1377, 1249, 1073,820 $cm^{-1}$. HRMS ($ESI^+$) found 451.2804, calcd for $[M+Na]^+$ 451.2824.

**Ethyl 6-methyl-3-methylene-2,2-dipentyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-5-carboxy late (3ea).**




Yield: 60%, yellow oil. TLC: $R_f$ 0.73(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.50 (d, *J* = 8.0 Hz, 2H; Ph–H), 7.33 (d, *J* = 8.0 Hz, 2H;CH–H), 5.00 (d, *J* = 1.5 Hz, 1H; CH-H), 4.96 (d, *J* = 1.5 Hz, 1H; CH-H), 4.51 (s, 1H; CH), 4.02-3.93 (m, 2H; $OCH_2$), 2.35 (s,3H; $CH_3$), 1.69 (m, 2H; $CH_2$), 1.50 (m, 2H; $CH_2$), 1.32 (m, 8H; $CH_2$), 1.08 (m, 4H; $CH_2$), 1.14 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.91 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.77 (t, *J* = 7.0 Hz, 3H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 167.5, 164.5, 147.9, 146.3, 128.5 (q, *J* = 32.5 Hz ), 128.2, 127.5, (q, *J* = 270.1 Hz), 124.9 (q, *J* = 3.75 Hz), 113.8, 102.4, 84.5, 59.6, 44.3, 36.8, 36.8, 32.1, 31.7, 23.0, 22.9, 22.5, 22.3, 20.5, 14.0, 13.9, 13.8. $^{19}F$ NMR ($CDCl_3$) ! -62.867. IR (neat): 2957, 2861, 1707, 1617, 1326, 1165, 1127, 1068, 734 $cm^{-1}$. HRMS ($ESI^+$) found 467.2776, calcd for $[M+H]^+$ 467.2773.

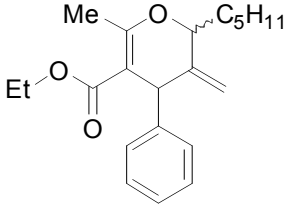
**Ethyl 2,2,6-trimethyl-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ab).**




Yield: 40%, colorless oil. TLC: $R_f$ 0.76(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.24 (m, 2H; Ph–H), 7.18 (m, 3H; Ph–H), 5.05 (d, *J* = 2.0 Hz, 1H; CH-H), 4.61 (d, *J* = 2.0 Hz, 1H; CH-H), 4.48 (s, 1H; CH), 3.97-3.85 (m, 2H; $OCH_2$), 2.30 (s, 3H; $CH_3$), 1.45 (s, 3H; $CH_3$), 1.34 (s, 3H; $CH_3$), 0.93 (t, *J* = 7.0 Hz, 3H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 167.8, 162.7, 150.2, 143.5, 128.3, 128.0, 126.0, 111.1, 104.4, 78.7, 59.4, 44.4, 27.1, 26.7, 20.3, 13.8. IR (neat):

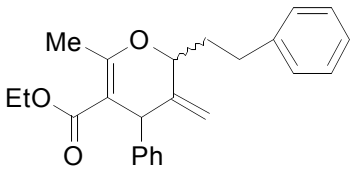
2982, 1706, 1647, 1457, 1377, 1299, 1224, 1123, 1071, 701 $cm^{-1}$. HRMS ($ESI^+$) found 309.1462, calcd for $[M+Na]^+$ 309.1467.

**Ethyl 6-methyl-3-methylene-2-pentyl-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ac/3ac').**



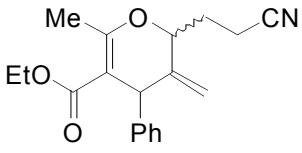

Yield: 91%, colorless oil. TLC: $R_f$ 0.71(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.21 (m, 5H; Ph–H), 5.20 (d, *J* = 1.0 Hz, 0.5H; CH-H), 5.03 (t, *J* = 1.0 Hz, 0.5H; CH-H), 4.96 (s, 0.5H; CH-H), 4.96 (s, 0.5H; CH-H), 4.53 (s, 0.5H; CH), 4.49 (s, 0.5H; CH), 4.39 (t, *J* = 7.0 Hz, 0.5H; CH), 4.23 (dd, *J* = 5.0, 8.0 Hz, 0.5H; CH), 4.03-3.91 (m, 2H; $OCH_2$), 2.35 (s, 1.5H; $CH_3$), 2.34 (s, 1.5H; $CH_3$), 1.70-0.85 (m, 8H; $CH_2$), 0.98 (t, *J* = 7.0 Hz, 1.5H; $CH_3$), 0.96 (t, *J* = 7.0 Hz, 1.5H; $CH_3$), 0.87 (t, *J* = 7.0 Hz, 1.5H; $CH_3$) , 0.79 (t, *J* = 7.0 Hz, 1.5H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 167.9, 167.7, 165.0, 164.8, 145.3, 144.8, 144.3, 142.9, 128.1, 128.0, 128.0, 127.7, 127.4, 127.1, 126.2, 126.0, 112.5, 110.0, 103.5, 103.0, 80.2, 74.7, 59.5, 46.6, 44.9, 32.8, 31.7, 31.3, 30.8, 25.1, 25.1, 22.5, 22.3, 20.1, 20.1, 13.9, 13.9, 13.9. IR (neat): 2956, 2363, 1707, 1623, 1215, 1078, 700 $cm^{-1}$. HRMS ($ESI^+$) found 329.2119, calcd for $[M+H]^+$ 329.2117.

**Ethyl 6-methyl-3-methylene-2-phenethyl-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ad/3ad').**




Yield: 80%, colorless oil. TLC: $R_f$ 0.62(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.24 (m, 10H; Ph–H), 5.24 (d, *J* = 0.5 Hz, 0.5H; CH-H), 5.06 (dd, *J* = 1.0, 2.0 Hz, 0.5H; CH-H), 5.00 (t, *J* = 1.0 Hz, 0.5H; CH-H), 4.98 (s, 0.5H; CH-H), 4.55 (s, 0.5H; CH), 4.52 (s, 0.5H; CH), 4.05-3.90 (m, 2H; $OCH_2$), 2.87-1.76 (m, 4H; $CH_2$), 2.37 (s, 1.5H; $CH_3$), 2.36 (s, 1.5H; $CH_3$), 0.99 (t, *J* = 7.0 Hz, 1.5H; $CH_3$), 0.97 (t, *J* = 7.0 Hz, 1.5H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 167.8, 167.5, 164.9, 164.6, 144.9, 144.4, 144.1, 142.9, 141.4, 141.2, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.8, 127.4, 126.2, 126.1, 125.9, 125.8, 125.6, 112.9, 110.1, 103.5, 103.2, 79.1, 73.6, 59.5, 46.7, 44.8, 34.5, 32.6, 31.7, 31.6, 20.0, 20.0, 13.9, 13.9. IR (neat): 2955, 2346, 1705, 1617, 1453, 1216, 1076, 700 $cm^{-1}$. HRMS ($ESI^+$) found 363.1960, calcd for $[M+H]^+$ 363.1960.

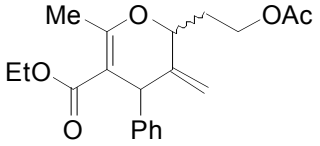
**Ethyl 2-(2-cyanoethyl)-6-methyl-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ae/3ae').**




Yield: 95%, yellow oil. TLC: $R_f$ 0.37(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.22 (m, 5H; Ph–H), 5.31 (s, 0.5H; CH-H), 5.11 (s, 0.5H; CH-H), 5.07 (t, *J* = 1.0 Hz, 0.5H; CH-H), 4.93 (d, *J* = 1.5 Hz, 0.5H; CH-H), 4.57 (s, 0.5H; CH), 4.55 (dd, *J* = 6.5, 9.5 Hz, 0.5H; CH), 4.52 (s, 0.5H; CH), 4.32 (dd, *J* = 4.0, 9.0 Hz, 0.5H; CH), 4.04-3.91 (m, 2H; $OCH_2$), 2.81-1.72 (m, 4H; $CH_2$), 2.35 (s, 1.5H; $CH_3$), 2.34 (s, 1.5H; $CH_3$), 0.99 (t, *J* = 7.0 Hz, 1.5H; $CH_3$), 0.98 (t, *J* = 7.0 Hz, 1.5H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 167.4, 167.2, 163.9, 163.8,

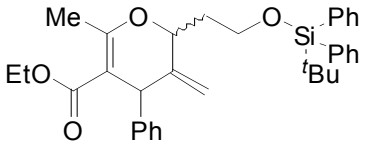
143.7, 143.5, 143.3, 142.2, 128.3, 127.8, 127.5, 127.2, 126.5, 126.5, 118.9, 118.7, 113.7, 110.4, 104.1, 103.6, 77.5, 72.0, 59.7, 59.7, 46.3, 44.4, 28.8, 26.9, 19.8, 19.7, 13.9, 13.8, 13.5, 13.4. IR (neat): 2979, 2248, 1716, 1629, 1373, 1216, 1074, 701 $cm^{-1}$. HRMS ($ESI^+$) found 312.1599, calcd for $[M+H]^+$ 312.1600.

**Ethyl 2-(2-acetoxyethyl)-6-methyl-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3af/3af').**



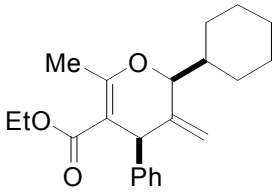

Yield: 78%, yellow oil. TLC: $R_f$ 0.48(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.15 (m, 5H; Ph–H), 5.26 (s, 0.4H; CH-H), 5.06 (s, 0.6H; CH-H), 4.97 (d, $J$ = 1.0 Hz, 0.4H; CH-H), 4.93 (t, $J$ = 0.5 Hz, 0.6H; CH-H), 4.56 (t, $J$ = 7.0 Hz, 0.6H; CH), 4.55 (s, 0.6H; CH), 4.51 (s, 0.4H; CH), 4.36 (dd, $J$ = 4.0, 8.5 Hz, 0.4H; CH), 4.27-4.20 (m, 0.8H; $OCH_2$), 4.04-3.91 (m, 3.2H; $OCH_2$), 2.34 (s, 1.8H; $CH_3$), 2.33 (s, 1.2H; $CH_3$), 2.02 (s, 1.8H; $CH_3$), 1.99 (s, 1.2H; $CH_3$), 1.90 (m, 1H; $CH_2$), 1.76 (m, 1H; $CH_2$), 0.98 (t, $J$ = 7.0 Hz, 1.2H; $CH_3$), 0.96 (t, $J$ = 7.0 Hz, 1.8H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 170.9, 170.8, 167.6, 167.4, 164.4, 164.2, 144.7, 143.9, 143.8, 142.5, 128.1, 128.1, 128.0, 127.7, 127.2, 126.2, 126.2, 112.8, 110.2, 104.1, 103.2, 76.2, 71.1, 60.8, 60.7, 59.6, 46.4, 44.8, 31.9, 29.9, 20.7, 20.7, 19.9, 19.8, 13.8, 13.8. IR (neat): 2979, 2361, 1729, 1615, 1367, 1246, 1074, 702 $cm^{-1}$. HRMS ($ESI^+$) found 367.1518, calcd for $[M+Na]^+$ 367.1521.

**Ethyl 2-(2-(tert-butyldiphenylsilyloxy)ethyl)-6-methyl-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ag/3ag').**




Yield: 94%, yellow oil. TLC: $R_f$ 0.71(hexane/ethyl acetate = 5:1) $^1H$ NMR ($CDCl_3$) ! 7.63 (m, 15H; Ph–H), 5.23 (s, 0.3H; CH-H), 5.06 (s, 0.7H; CH-H), 4.93 (s, 1.0H; CH-H), 4.80 (dd, $J$ = 5.0, 9.0 Hz, 0.7H; CH), 4.67 (dd, $J$ = 3.5, 9.5 Hz, 0.3H; CH), 4.55 (s, 0.7H; CH), 4.52 (s, 0.3H; CH), 4.04-3.92 (m, 2H; $OCH_2$), 3.91-3.87 (m, 0.3H; $CH_2$), 3.81 (m, 0.3H; $CH_2$), 3.70 (m, 0.7H; $CH_2$), 3.54 (m, 0.7H; $CH_2$), 2.32 (s, 2.1H; $CH_3$), 2.31 (s, 0.9H; $CH_3$), 1.97 (m, 0.3H; $CH_2$), 1.92 (m, 0.3H; $CH_2$), 1.78 (m, 0.7H; $CH_2$), 1.68 (m, 0.7H; $CH_2$), 0.98 (t, $J$ = 7.5 Hz, 0.9H; $CH_3$), 0.97 (t, $J$ = 7.5 Hz, 2.1H; $CH_3$). $^{13}C$ NMR ($CDCl_3$) ! 167.9, 167.6, 164.9, 164.7, 145.3, 144.6, 144.2, 142.9, 135.5, 135.5, 135.4, 134.0, 133.7, 133.7, 133.7, 133.6, 129.8, 129.5, 129.5, 129.4, 128.9, 128.8, 128.7, 128.1, 128.0, 127.9, 127.7, 127.6, 127.6, 127.5, 127.3, 126.2, 126.1, 112.5, 109.8, 103.7, 103.1, 76.3, 70.7, 63.7, 59.7, 59.6, 59.5, 46.8, 44.9, 36.0, 33.6, 31.5, 26.8, 26.7, 20.1, 20.0, 19.4, 19.2, 19.1, 14.1, 13.9, 13.9. IR (neat): 2958, 2344, 1705, 1616, 1428, 1239, 1112, 614 $cm^{-1}$. HRMS ($ESI^+$) found 563.2558, calcd for $[M+Na]^+$ 563.2594.

**Ethyl 2-cyclohexyl-6-methyl-3-methylene-4-phenyl-3,4-dihydro-2*H*-pyran-5-carboxylate (3ah/3ah').**




Yield: 94%, colorless crystal. TLC: $R_f$ 0.70(hexane/ethyl acetate = 5:1) $^1$H NMR ($CDCl_3$) ! 7.27 (m, 5H; Ph–H), 5.34 (dd, *J* = 1.0, 1.5 Hz, 1H; CH-H), 4.98 (d, *J* = 1.0, 1.5 Hz, 1H; CH-H), 4.56 (s, 1H; CH), 4.08-3.94 (m, 2H; $OCH_2$), 4.03 (d, *J* = 9.5 Hz, 1H; CH), 2.37 (s, 3H; $CH_3$), 1.98 (m, 1H; CH), 1.63 (m, 1H; $CH_2$), 1.45 (m, 1H; $CH_2$), 1.30 (m, 2H; $CH_2$), 1.00 (t, *J* = 7.0 Hz, 3H; $CH_3$), 0.98 (m, 2H; $CH_2$), 0.80 (m, 2H; $CH_2$), 1.50 (m, 2H; $CH_2$). $^{13}$C NMR ($CDCl_3$) ! 168.1, 164.4, 142.9, 142.3, 127.8, 127.3, 126.0, 114.1, 102.0, 86.2, 59.6, 43.9, 39.2, 30.1, 28.8, 26.2, 25.6, 25.2, 20.2, 14.0. IR (KBr): 2929, 1707, 1604, 1447, 1287, 1208, 1071, 704 $cm^{-1}$. HRMS ($ESI^+$) found 341.2120, calcd for $[M+H]^+$ 341.2117. X-ray single crystal structure analysis (see CIF file).

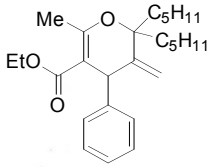
***Oxa*-Nickelacycle (8).**

***Experimental procedure.*** A solution of (*E*)-N-(2-(diphenylphosphino)benzylidene)cyclohexanamine **7** (371 mg, 1.00 mmol) in toluene (2 mL) was added dropwise to a solution of $Ni(cod)_2$ (275 mg, 1.00 mmol) in toluene (3mL). The resulting dark brown solution was stirred at room temperature for 5 min. To this solution was added dropwise a solution of **1a** (218 mg, 1.00 mmol) in 3mL toluene, and the resulting dark red solution was stirred at room temperature for 2 h. Toluene was evaporated. The precipitate was further crystallized in toluene at -30 °C. The dark red crystalline solid was washed with hexane and dried in vacuo to yield **8** (640 mg, 99%). This complex crystallized in benzene at room temperature for X-ray crystal structure analysis. $^1$H NMR (toluene-$d_8$) ! 7.27–6.65 (m, 19H; Ph–H), 4.25 (t, *J* = 10.5 Hz, 1H; CH) 4.05 (m, 2H; $OCH_2$), 3.66 (d, *J* = 12.0 Hz, 1H; CH) 3.00 (d, *J* = 11.0 Hz, 1H; CH), 2.77 (s, 3H; $CH_3$), 1.68–0.66 (m, 10H; $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$) 0.90 (t, *J* = 7.5 Hz,3H; $CH_3$). $^{31}$P NMR (toluene-$d_8$) ! 32.8. $^1$H NMR (THF-$d_8$) ! 7.97–6.65 (m, 19H; Ph–H), 4.26 (t, *J* = 9.5 Hz 1H, CH) 3.76 (m, 2H; $OCH_2$), 3.25 (d, *J* = 12.0 Hz 1H, CH) 2.67 (d, *J* = 12.0 Hz 1H; CH), 2.13 (s, 3H; $CH_3$), 1.81–0.78 (m, 10H; $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$) 0.85 (t, *J* = 7.0 Hz 3H; $CH_3$). $^{13}$C NMR (THF-$d_8$) ! 186.0, 166.6, 162.3, 149.7, 138.7 (d, *J* = 12.0 Hz), 136.1 (d, *J* = 10.1 Hz), 135.8 (d, *J* = 7.2 Hz), 135.6 (d, *J* = 12.4 Hz), 133.4 (d, *J* = 11.9 Hz), 133.2, 132.8 (d, *J* = 8.9 Hz), 132.0, 131.7, 129.8 (d, *J* = 10.0 Hz), 129.3 (d, *J* = 9.5 Hz), 129.1, 128.3, 124.0, 109.1, 57.6, 48.2 (d, *J* = 12.9 Hz), 37.0, 35.6, 33.2, 27.5, 27.2, 26.8, 23.1, 15.6. $^{31}$P NMR (THF-$d_8$) ! 35.3. X-ray single crystal structure analysis (see CIF file).

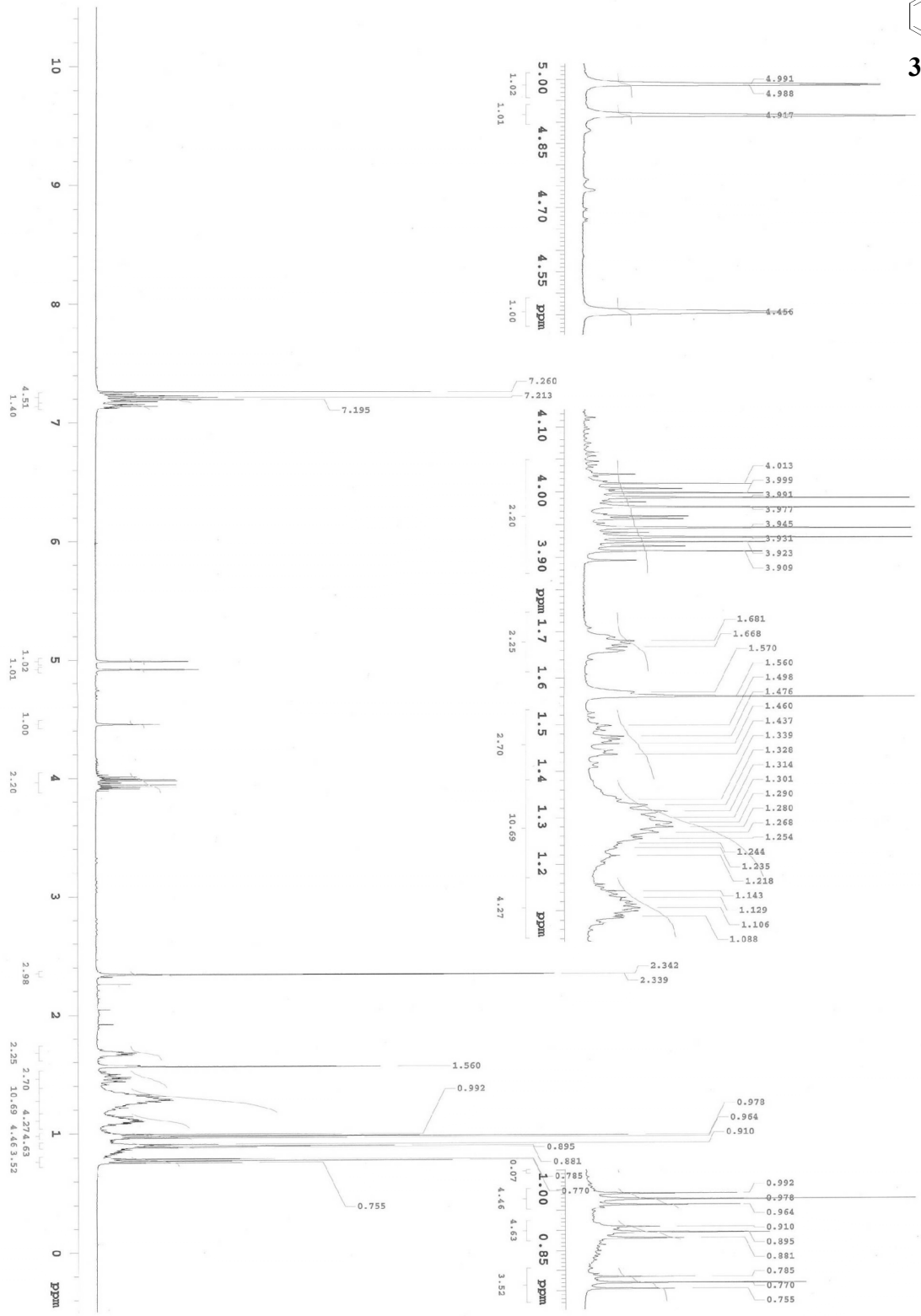
**Reaction of an *oxa*-nickelacycle with an allene.**

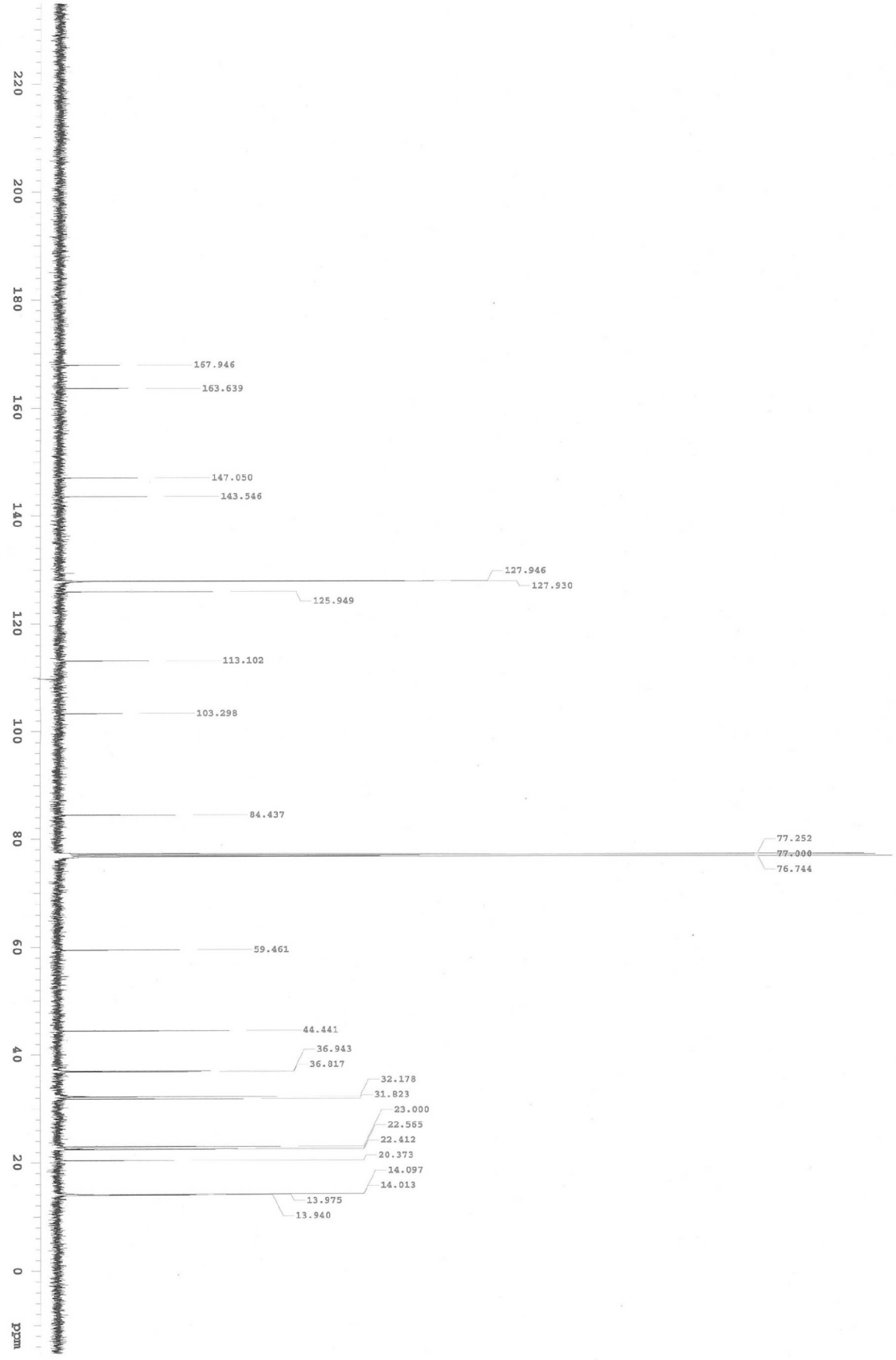
To a solution of *oxa*-nickelacycle **8** (8.6 mg, 0.01 mmol) in 0.3 mL of toluene-$d_8$ was added a solution of cyclopropyl allene **2h** (3.1 mg, 0.025 mmol) in 0.3ml of toluene-$d_8$ at room temperature. The reaction mixture was heated 100 °C for15 h. The solution changed from deep red to yellow. The reaction was followed by $_1$H, $_{31}$P NMR. **3ah** and **3ah'** generated in 77% and 8% respectively.

## $^{1}$H NMR and $^{13}$C NMR Spectra of Products




**3aa**

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77.000
76.744
59.461
44.441
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23.000
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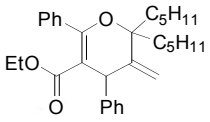
13.940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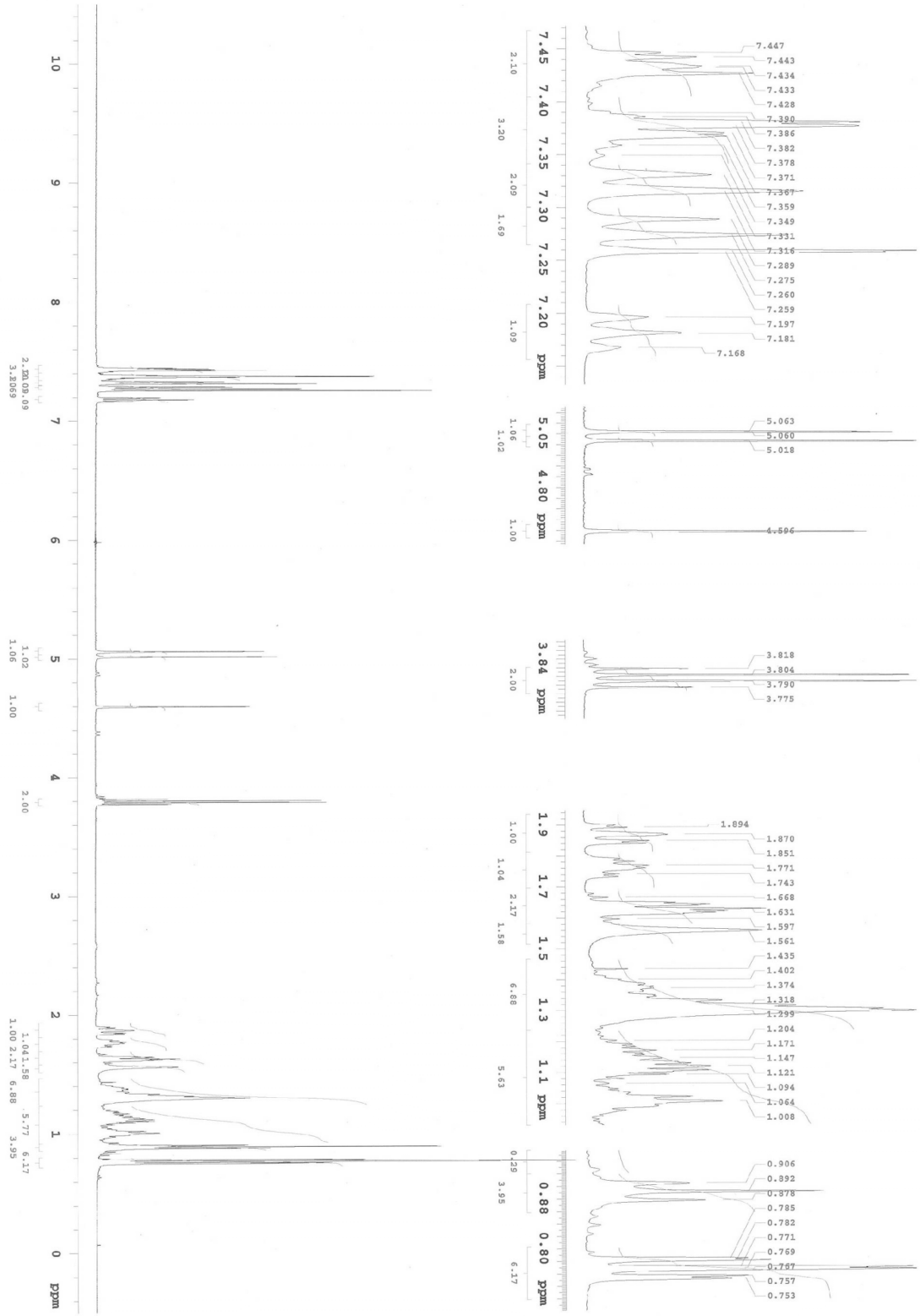
$C_5H_{11}$
EtO
O
Ph

**3ba**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7.168
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5.018
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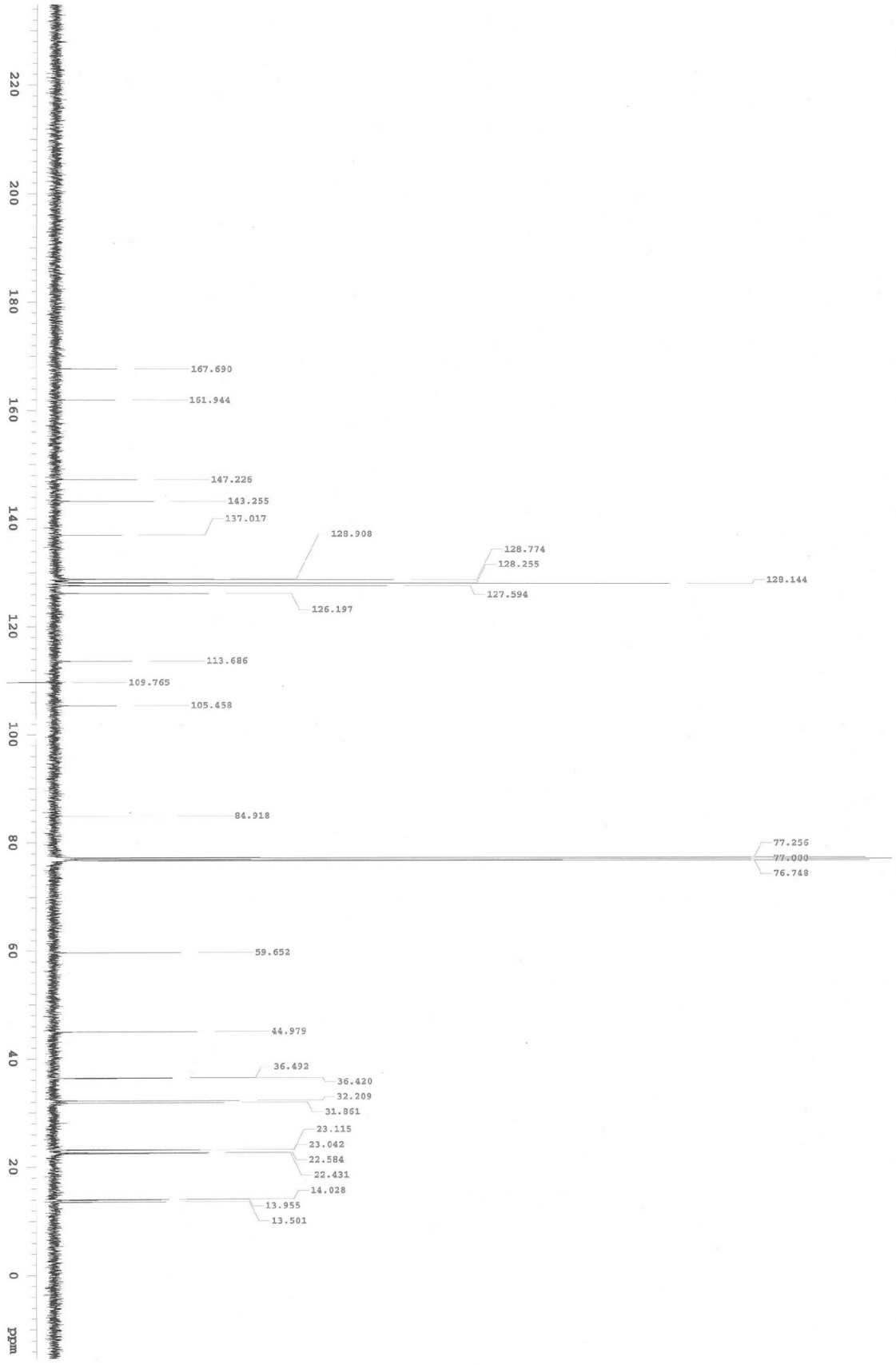
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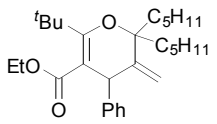
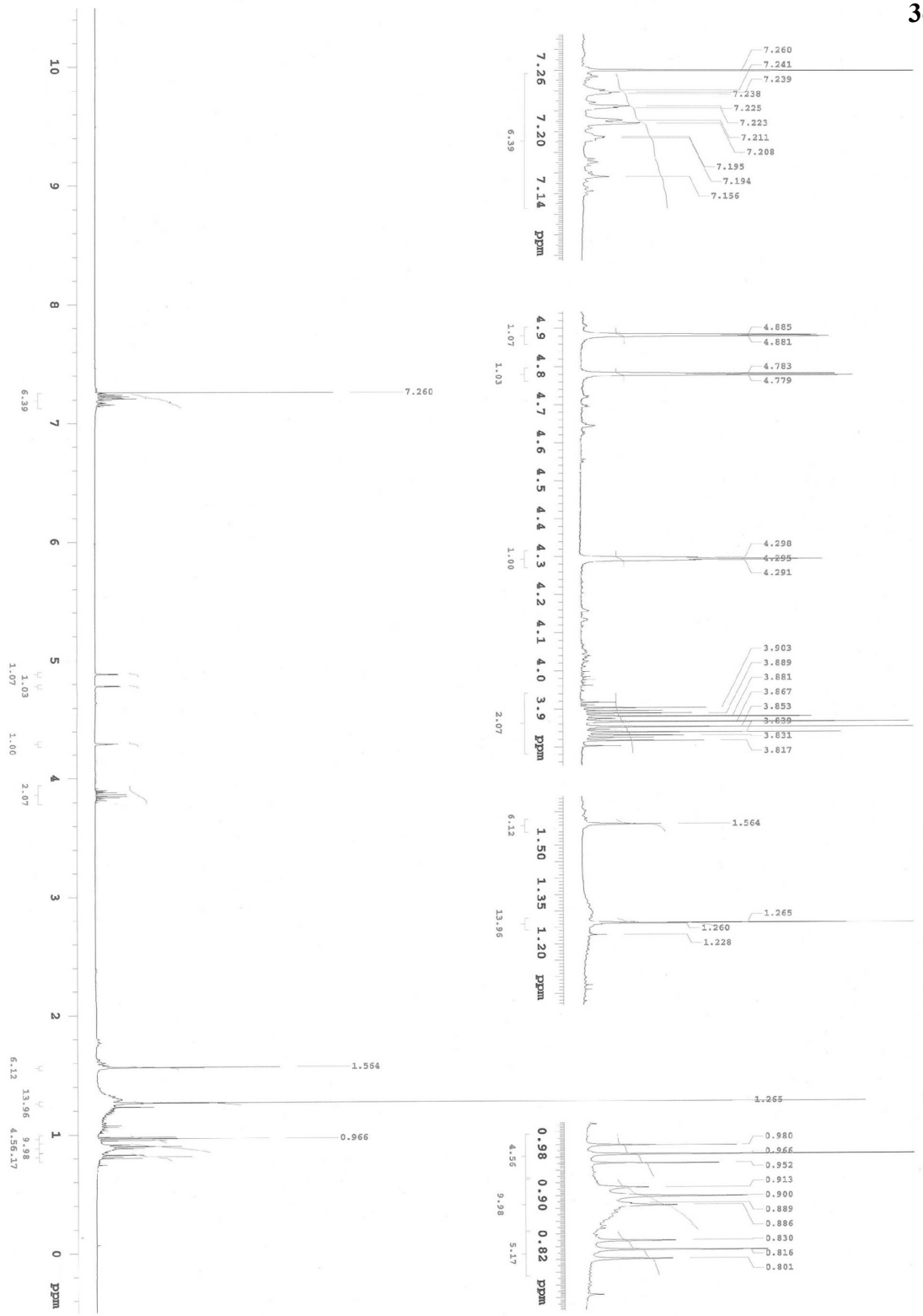
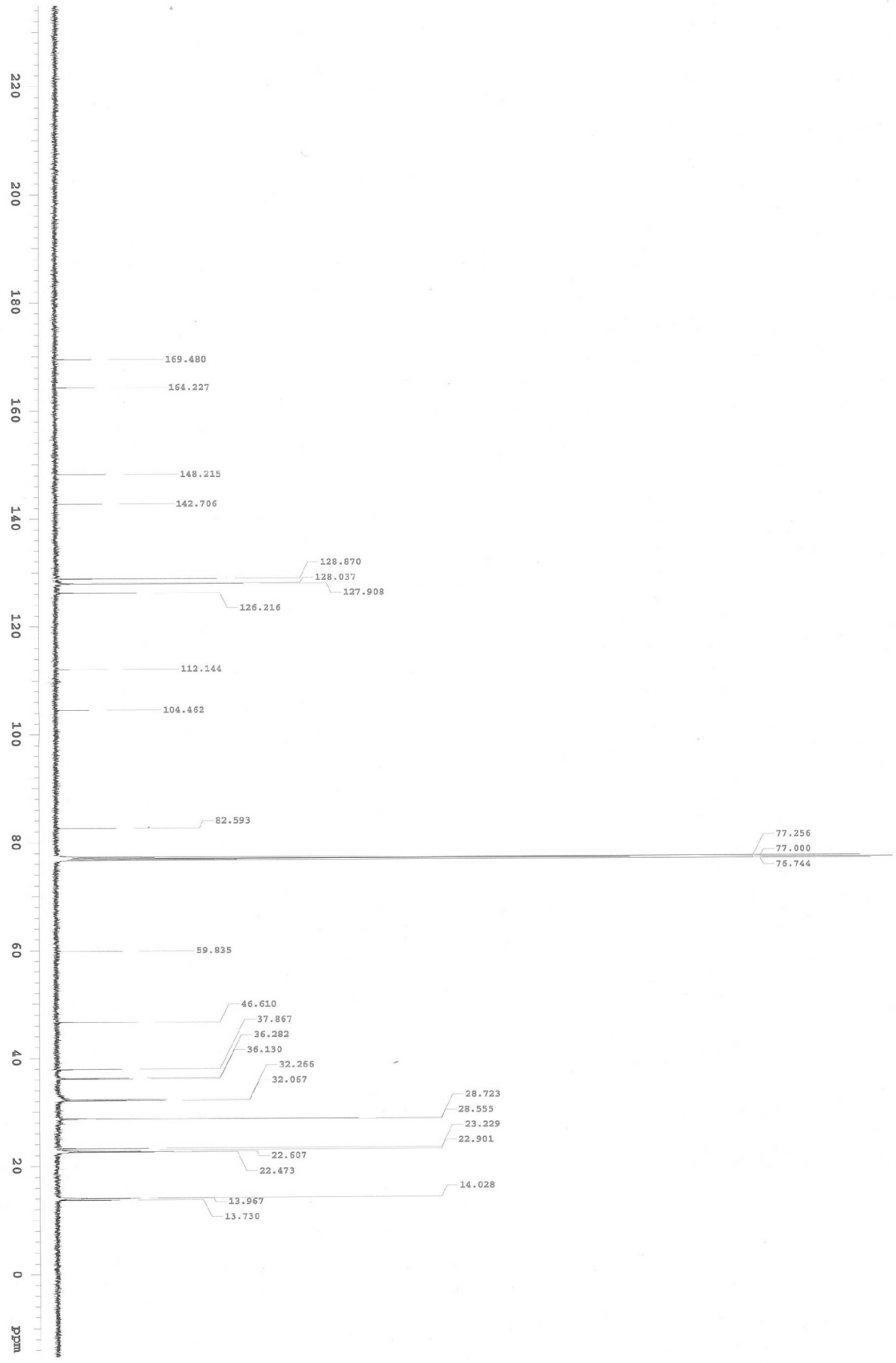
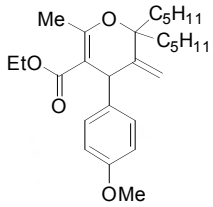



**3ca**



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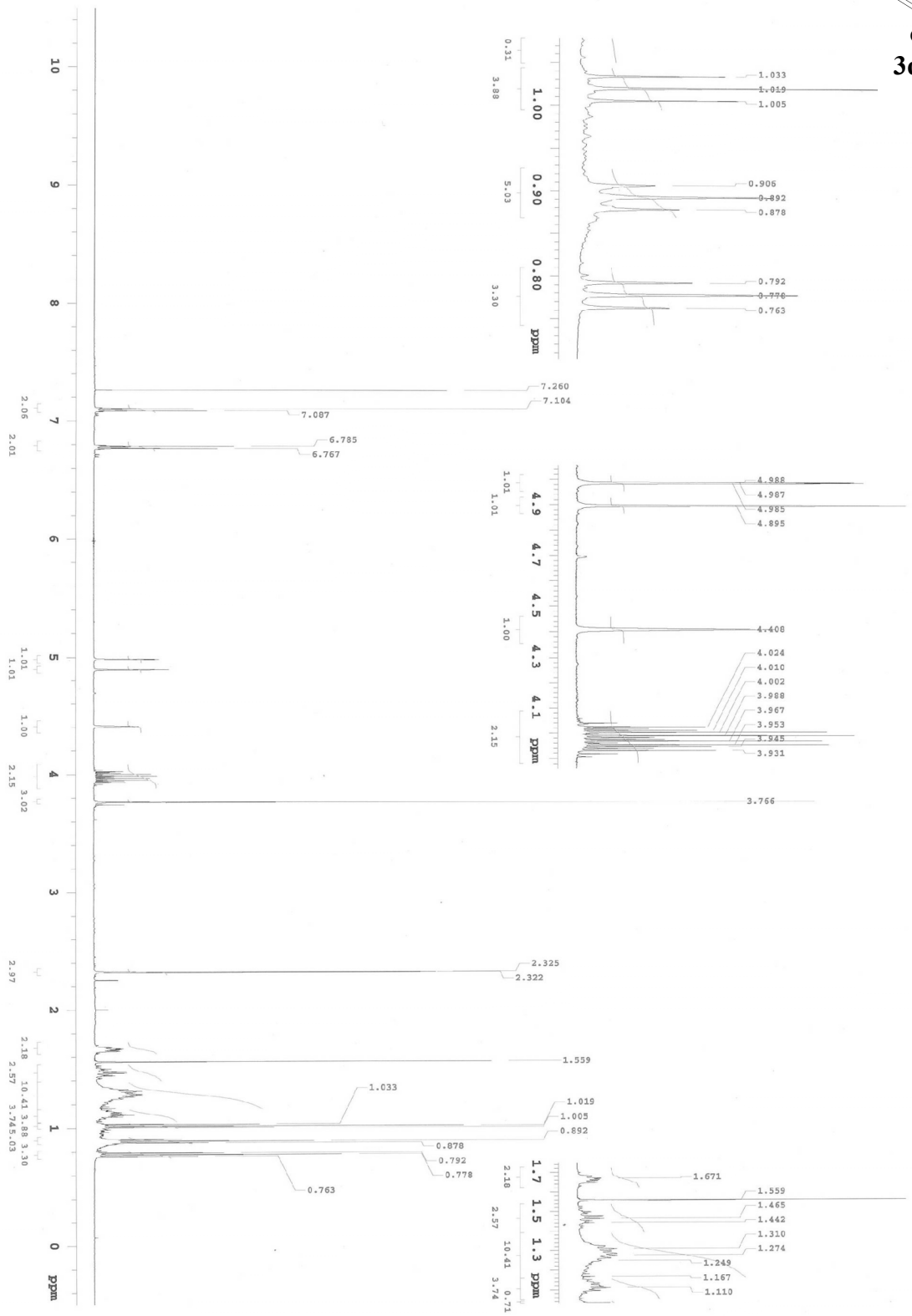
$C_5H_{11}$
EtO
O
OMe

**3da**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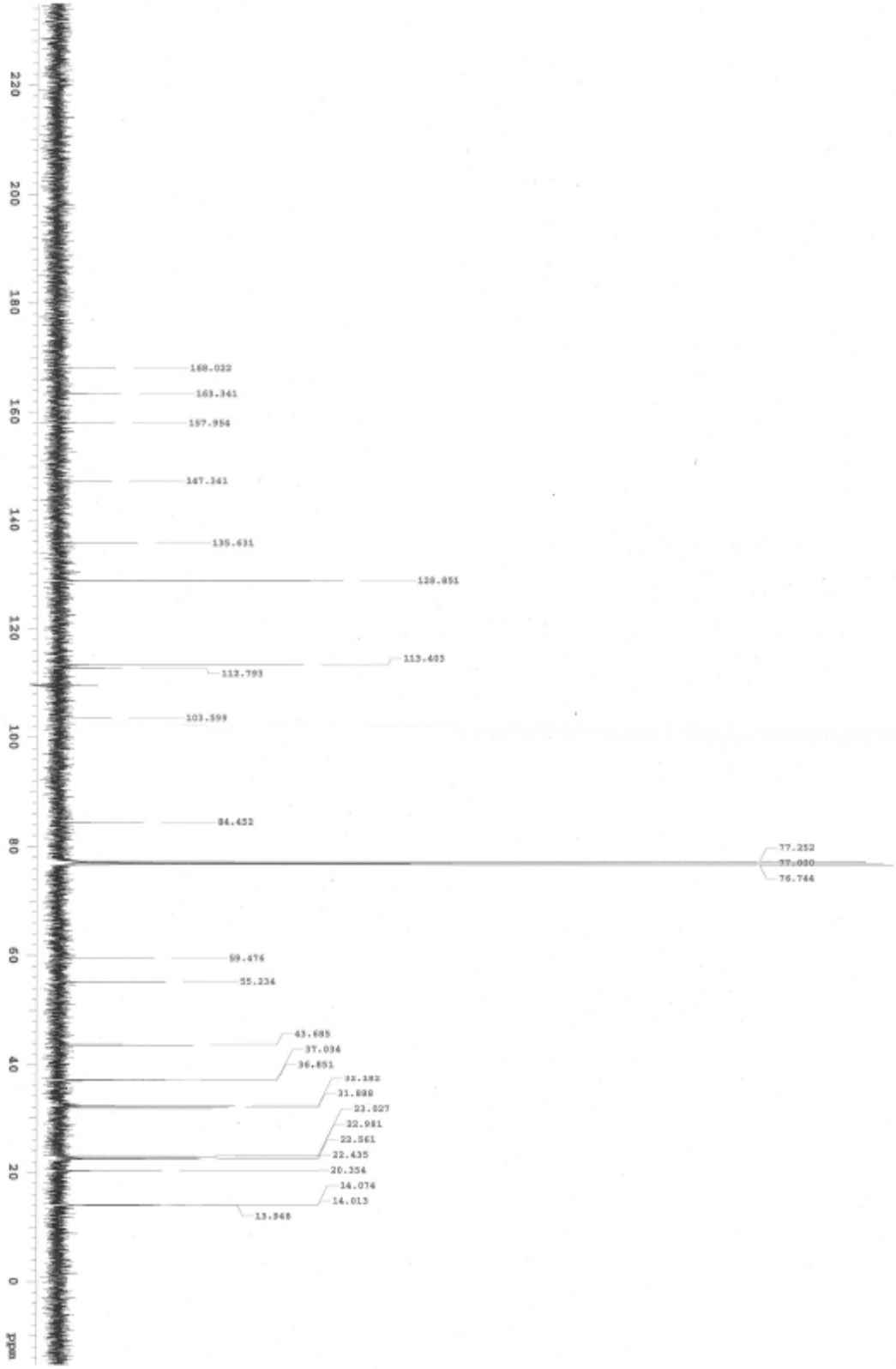
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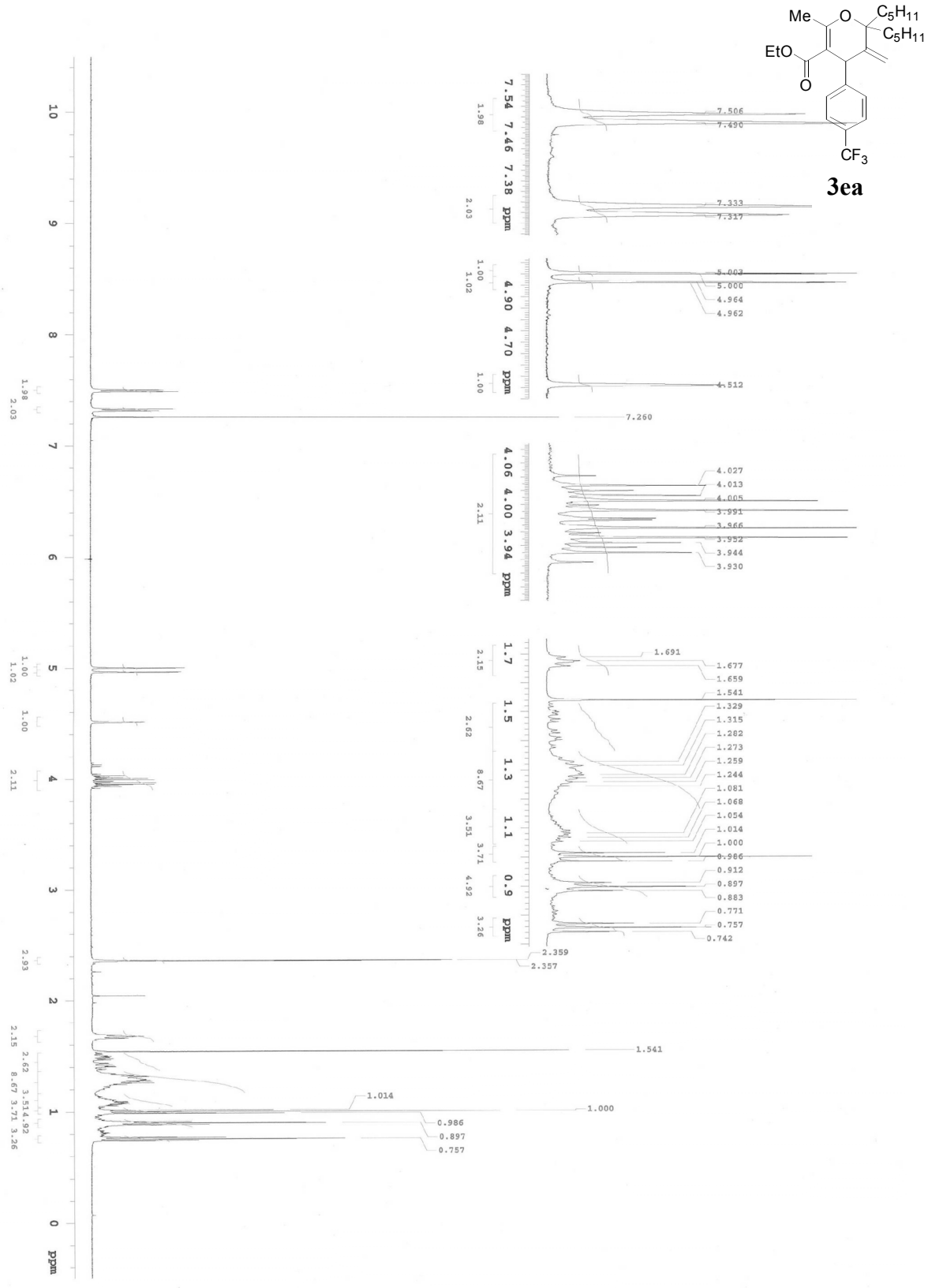
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$C_5H_{11}$
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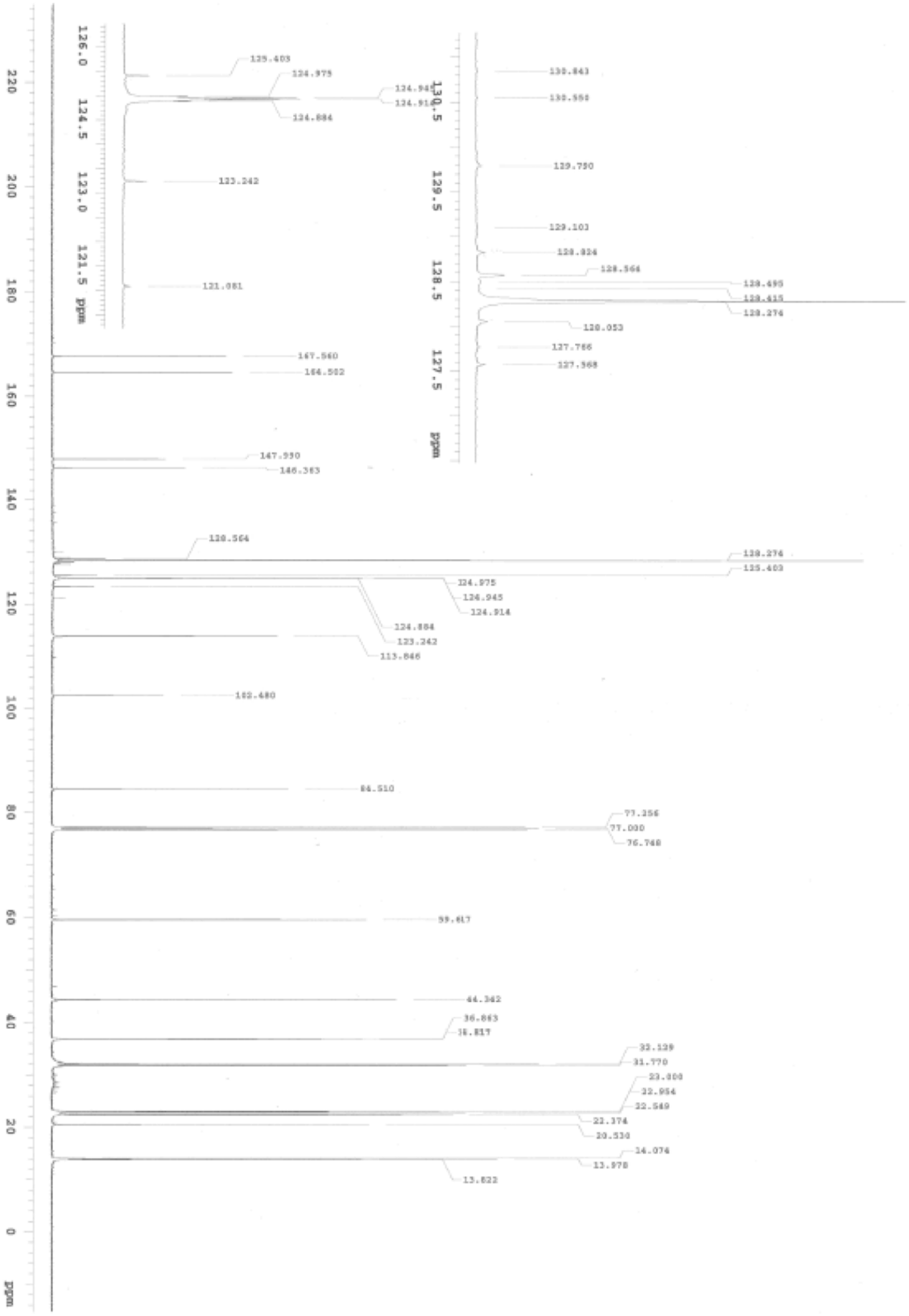
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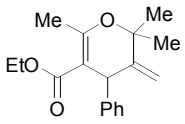
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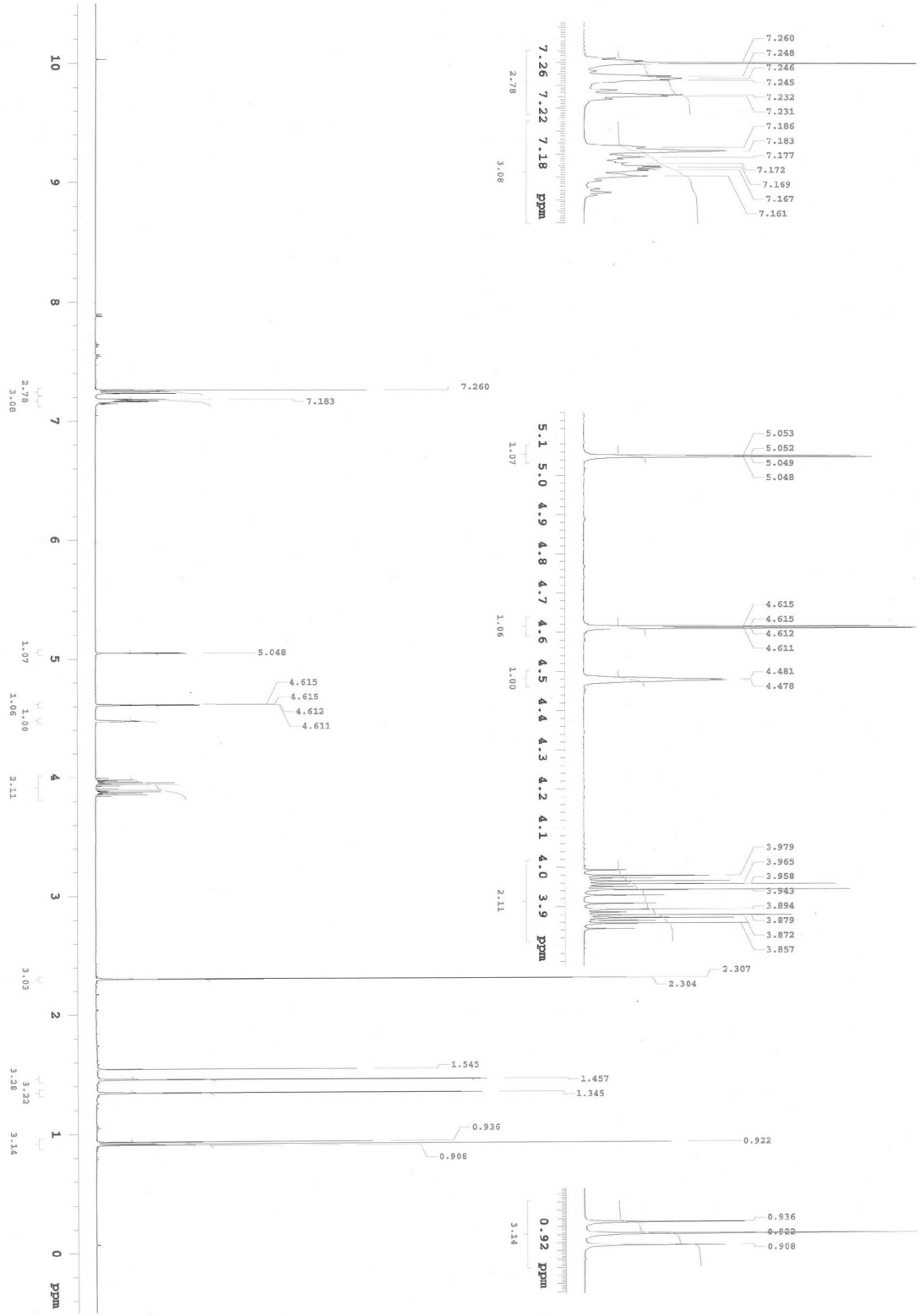
Ph

**3ab**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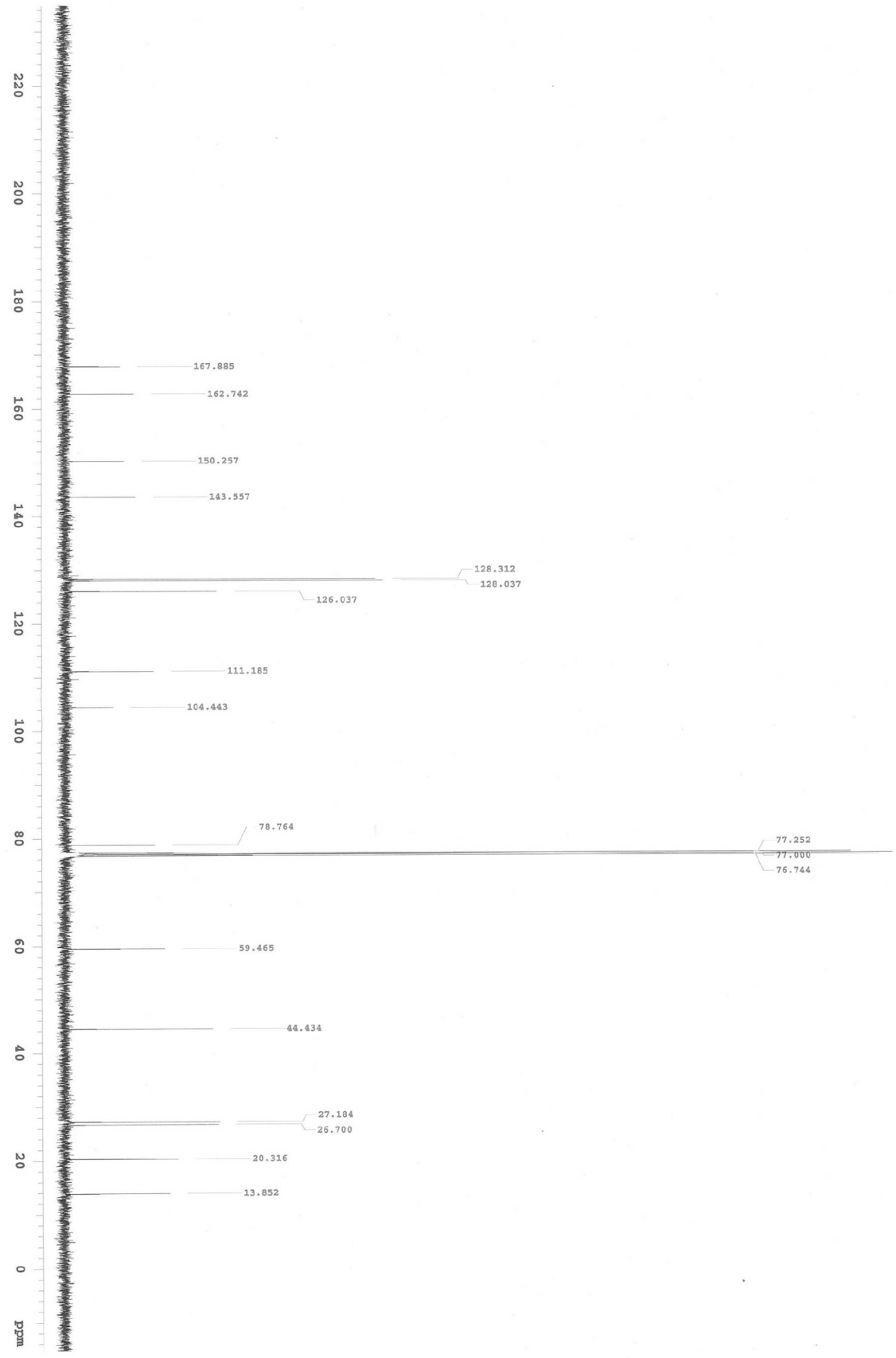
ppm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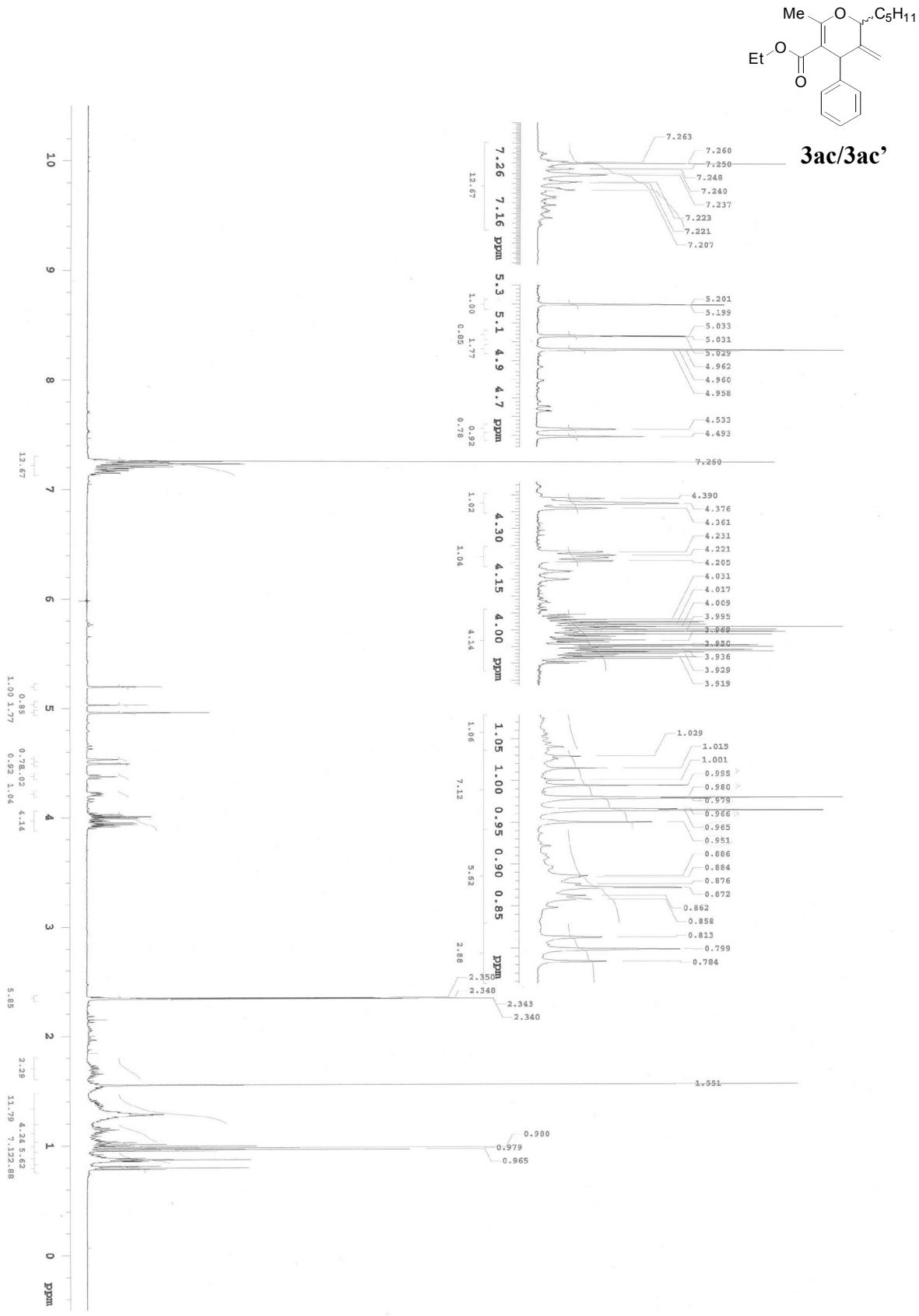
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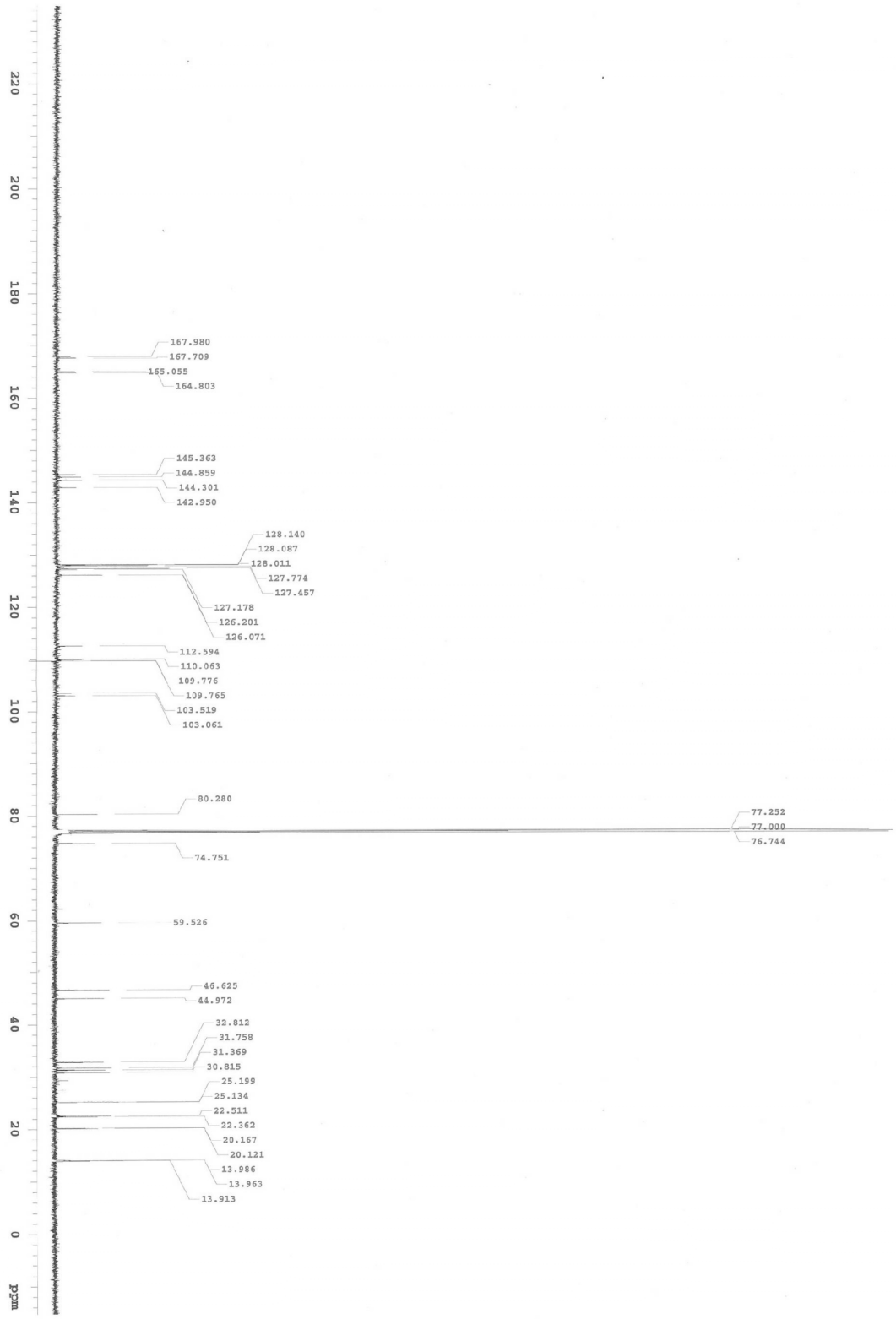
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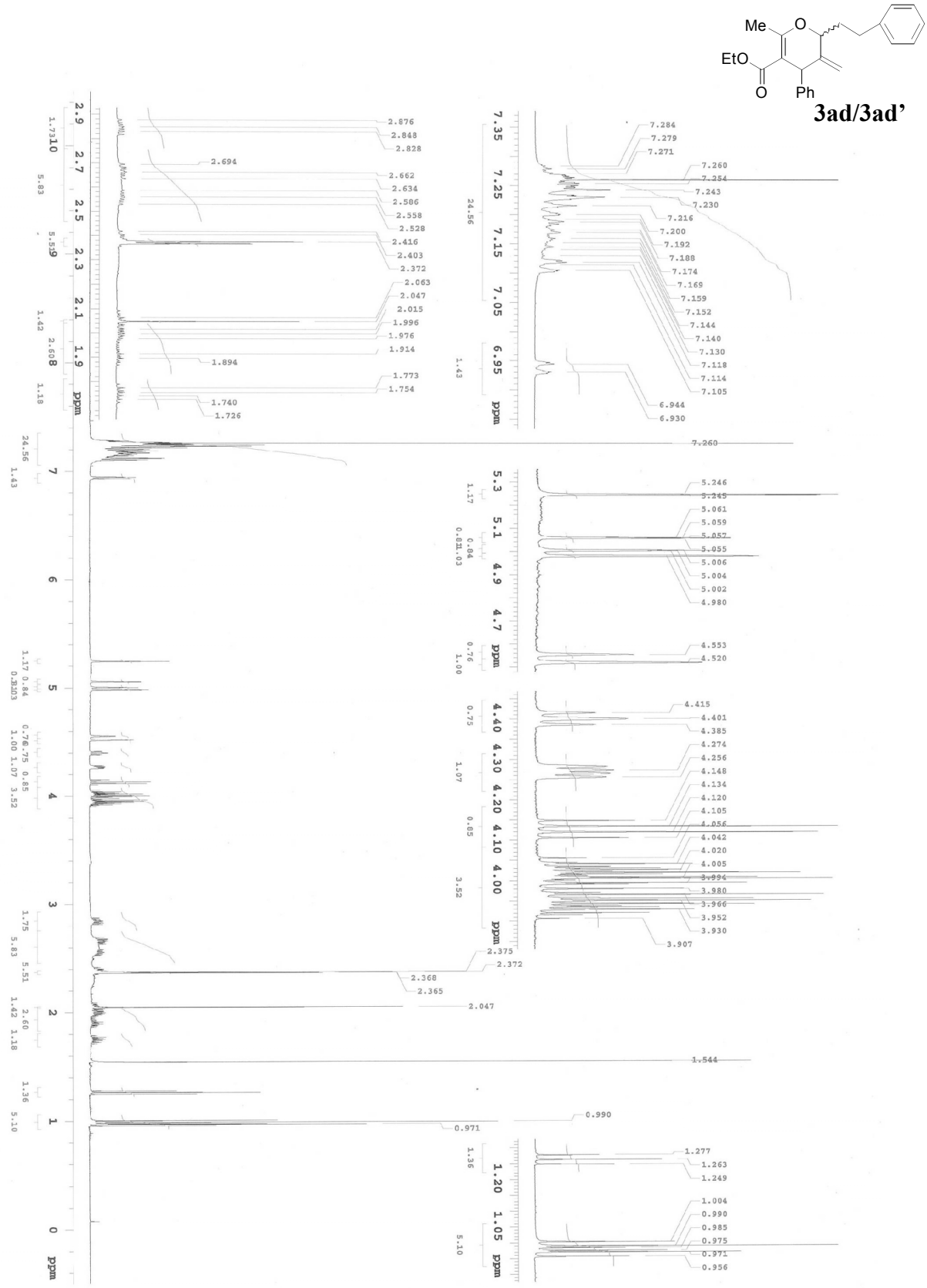
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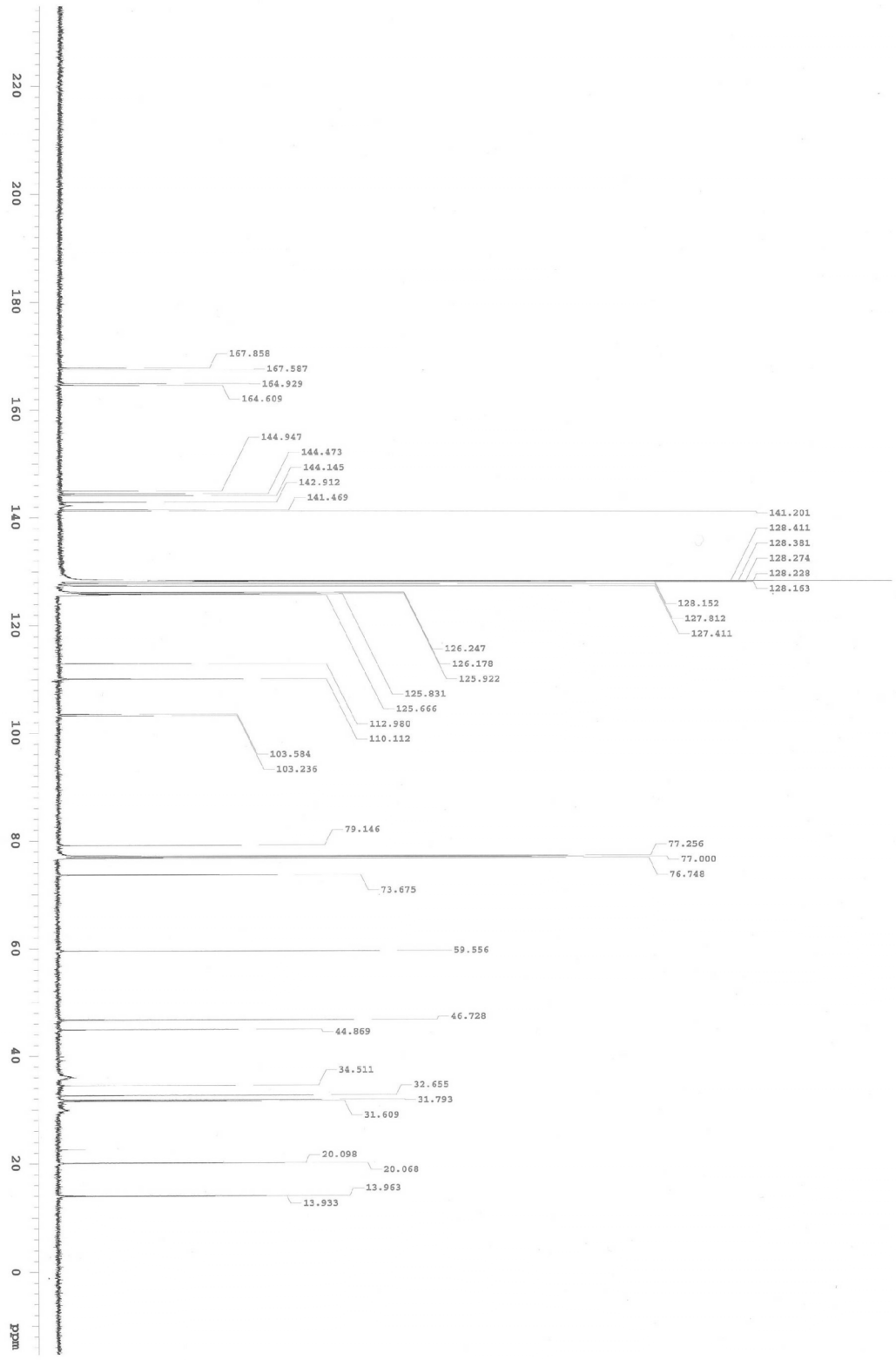
Ph
3ad/3ad'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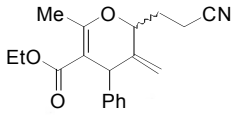
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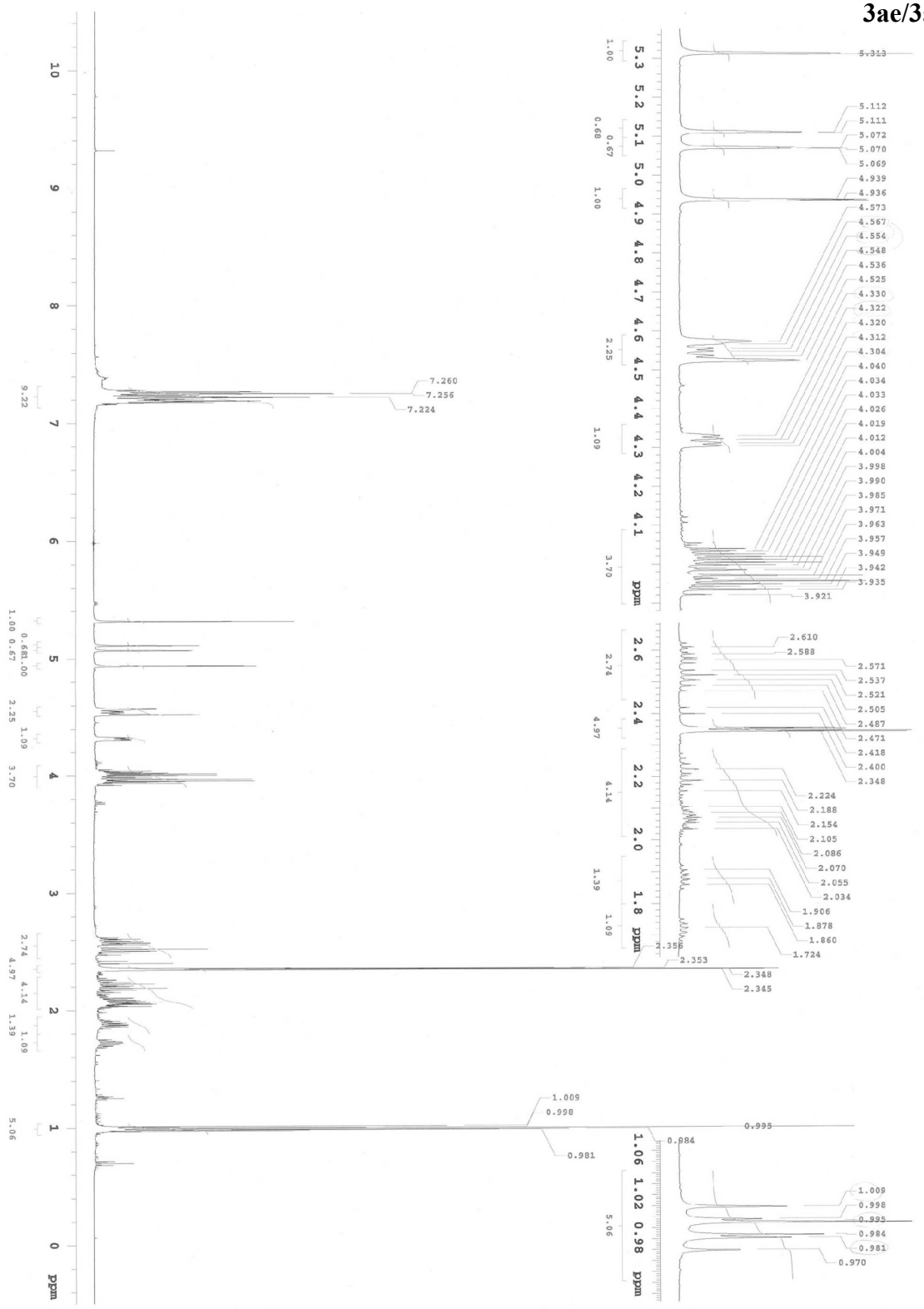
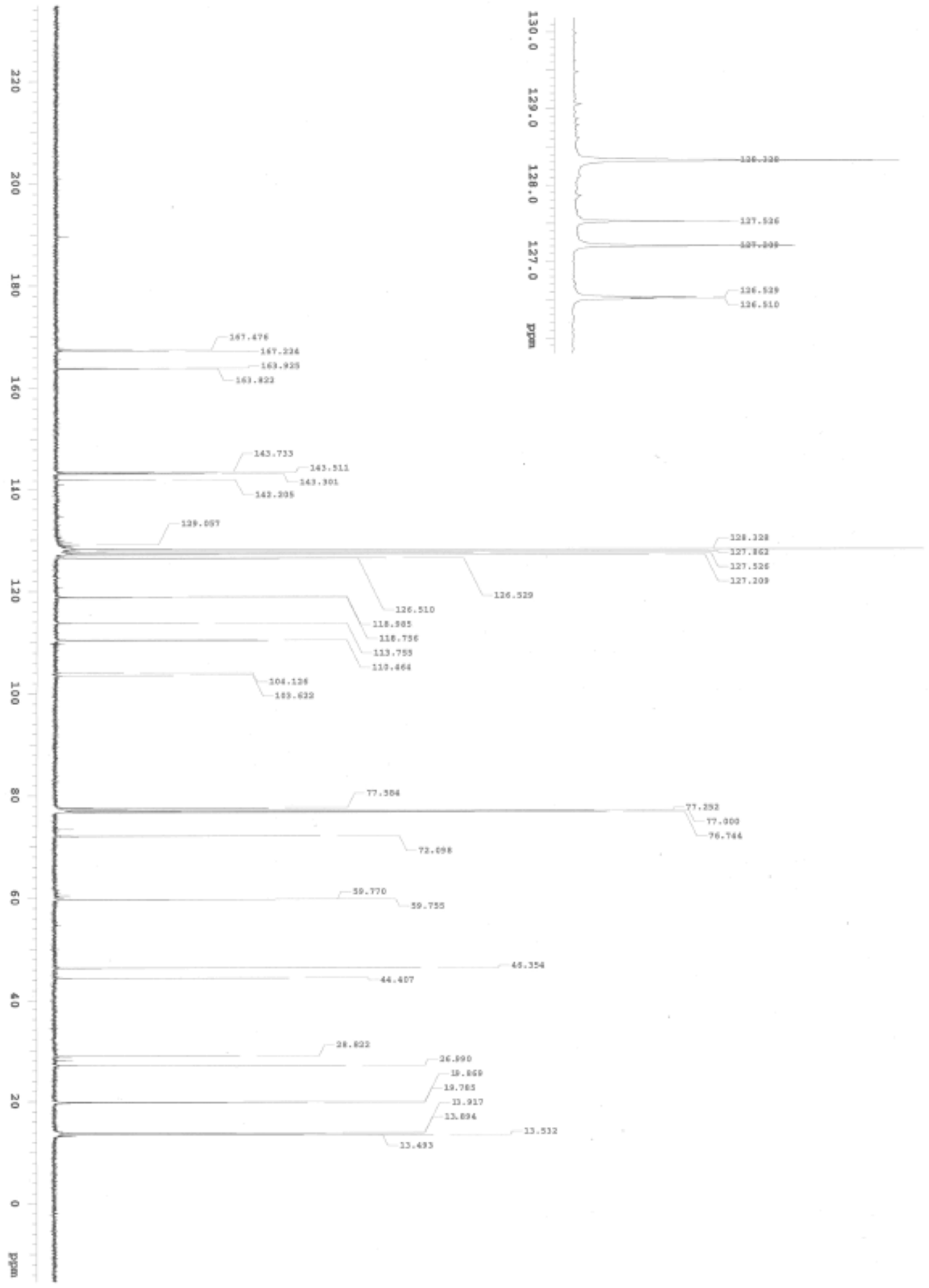
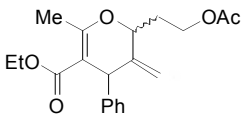
EtO
O
Ph

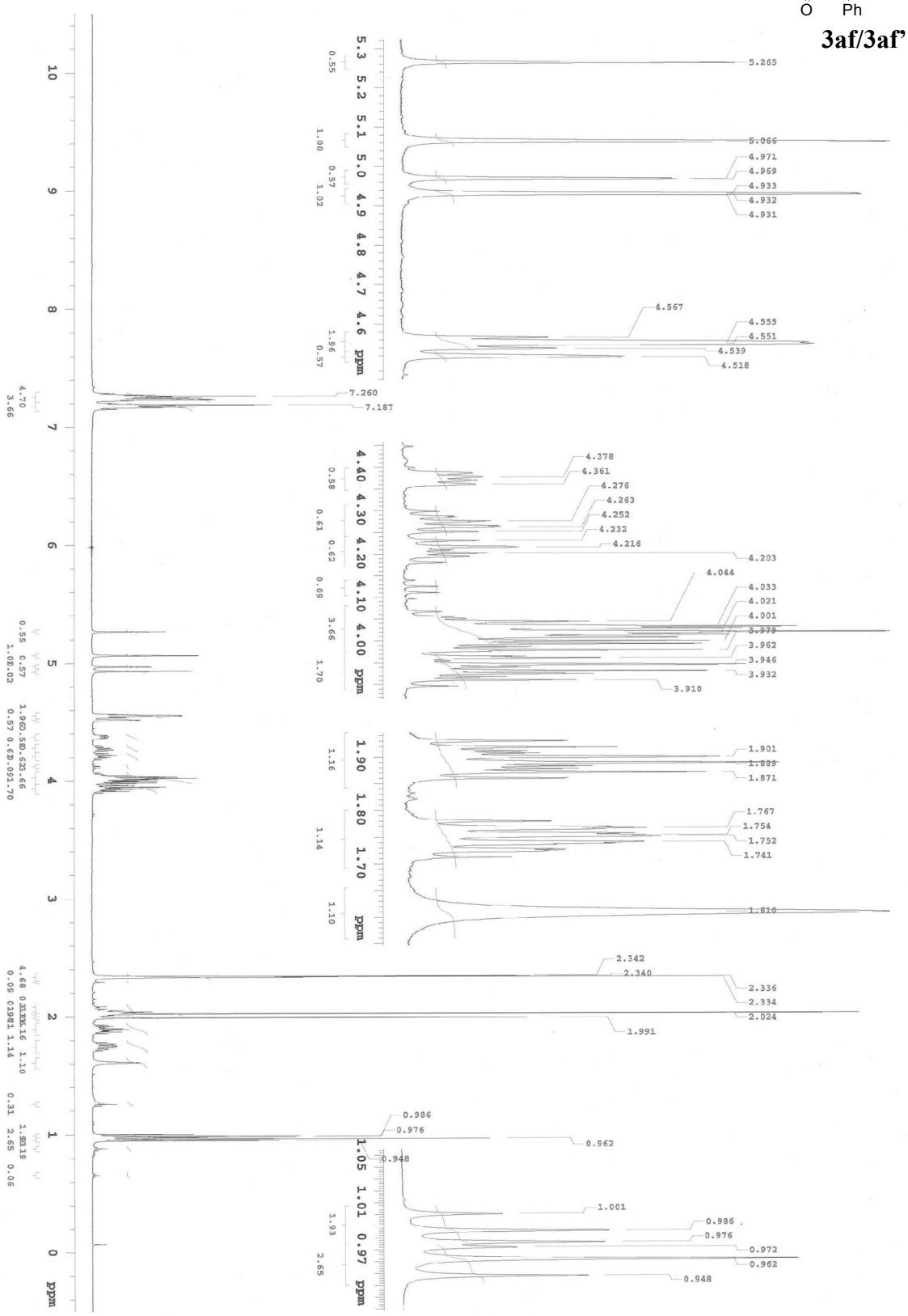
**3ae/3ae'**

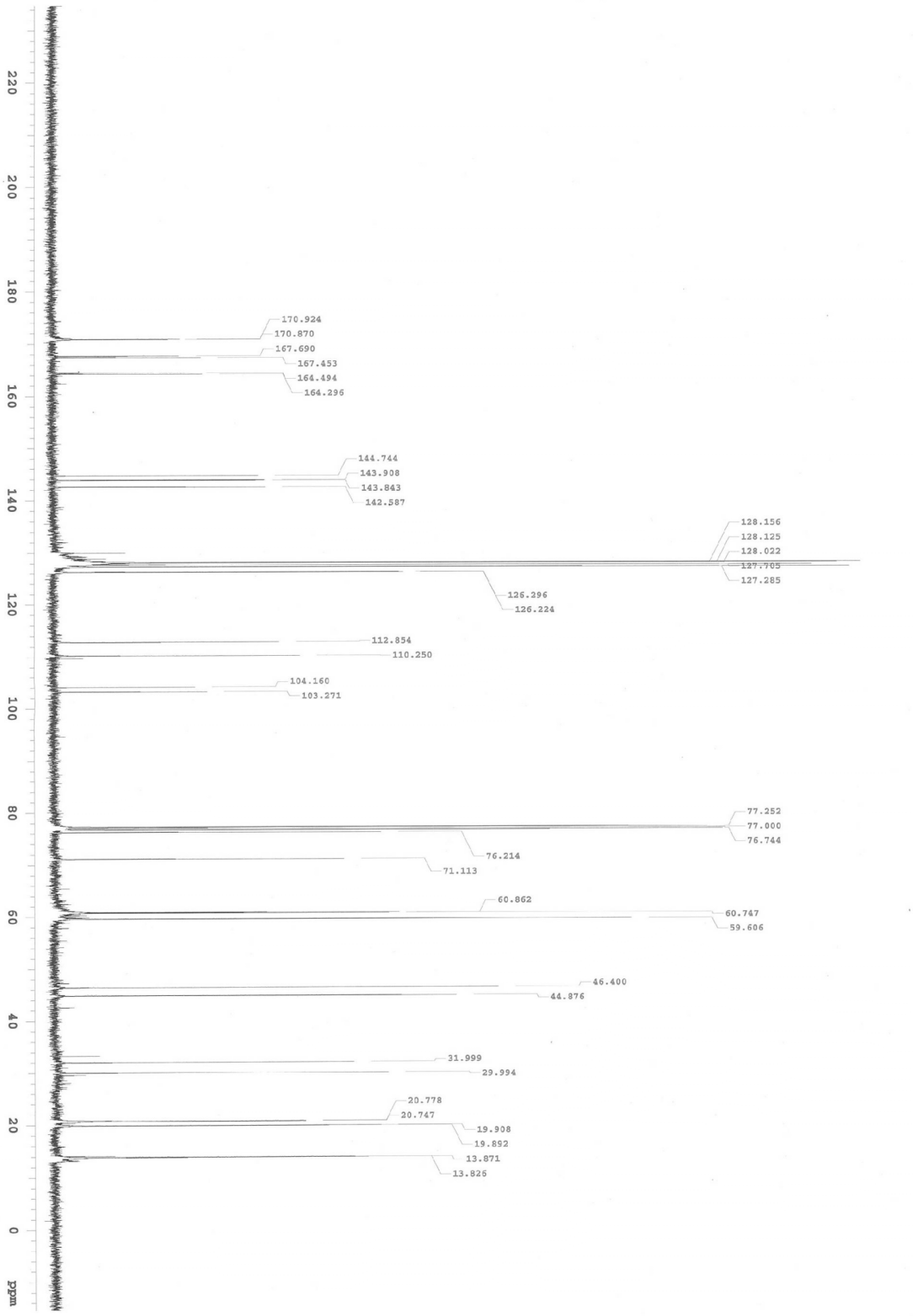

7.260
7.256
7.224
5.313
5.112
5.111
5.072
5.070
5.069
4.939
4.936
4.573
4.567
4.554
4.548
4.536
4.525
4.330
4.322
4.320
4.312
4.304
4.040
4.034
4.033
4.026
4.019
4.012
4.004
3.998
3.990
3.985
3.971
3.963
3.957
3.949
3.942
3.935
3.921
2.610
2.588
2.571
2.537
2.521
2.505
2.487
2.471
2.418
2.400
2.348
2.224
2.188
2.154
2.105
2.086
2.070
2.055
2.034
1.906
1.878
1.860
1.724
2.356
2.353
2.348
2.345
1.009
0.998
0.995
0.984
0.981
0.970
ppm

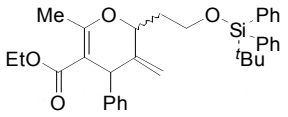

220
200
180
160
140
120
100
80
60
40
20
0
ppm
130.0
129.0
128.0
127.0
ppm
126.529
126.510
167.476
167.234
163.925
163.822
143.733
143.511
143.301
143.205
139.057
128.328
127.862
127.526
127.209
126.529
126.510
118.985
118.736
113.755
113.464
104.126
103.632
77.384
77.292
77.000
76.744
72.698
59.770
59.755
45.354
44.407
28.822
26.890
18.869
18.785
13.917
13.894
13.532
13.493


Me
O
OAc
EtO
O
Ph

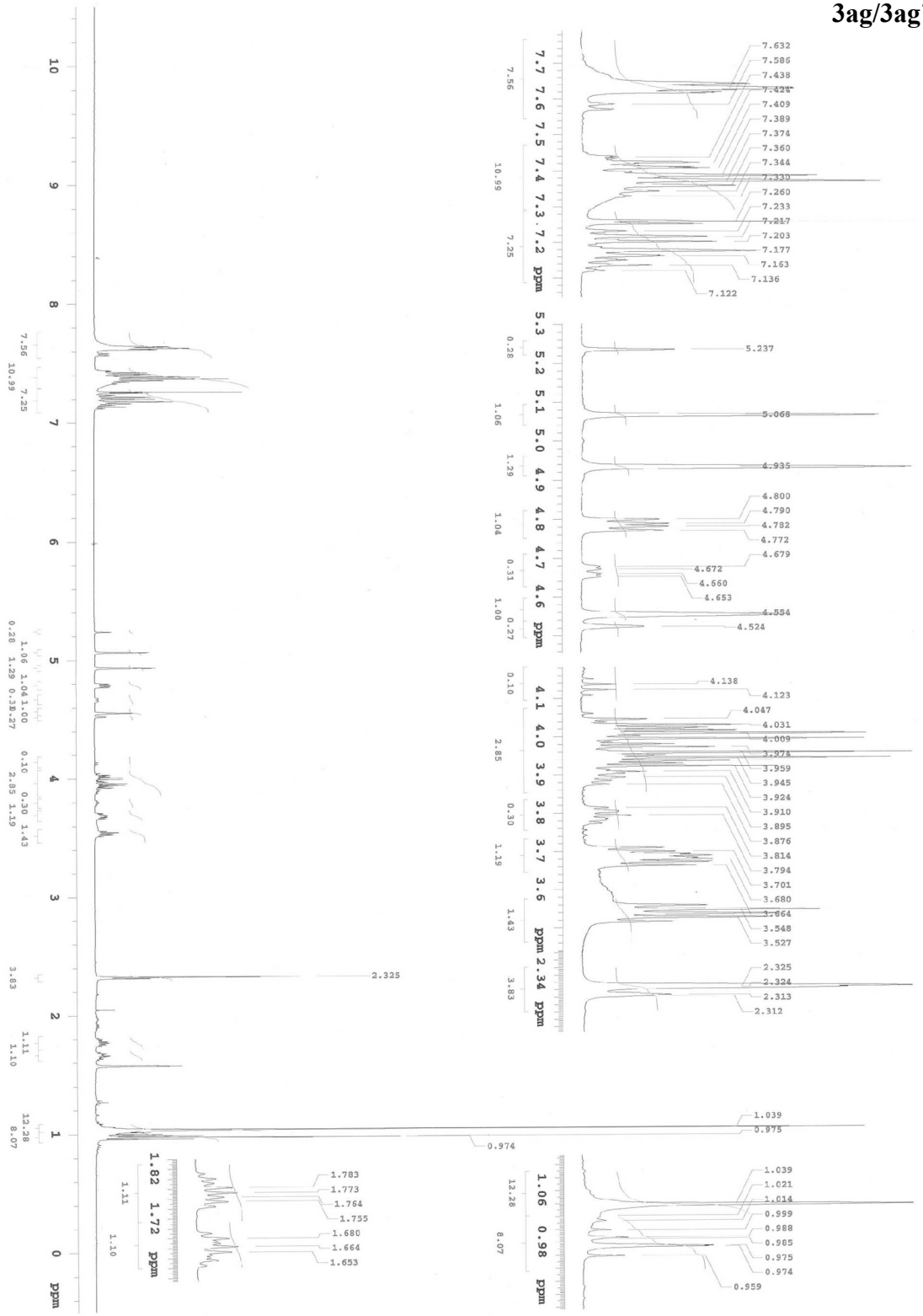
**3af/3af'**

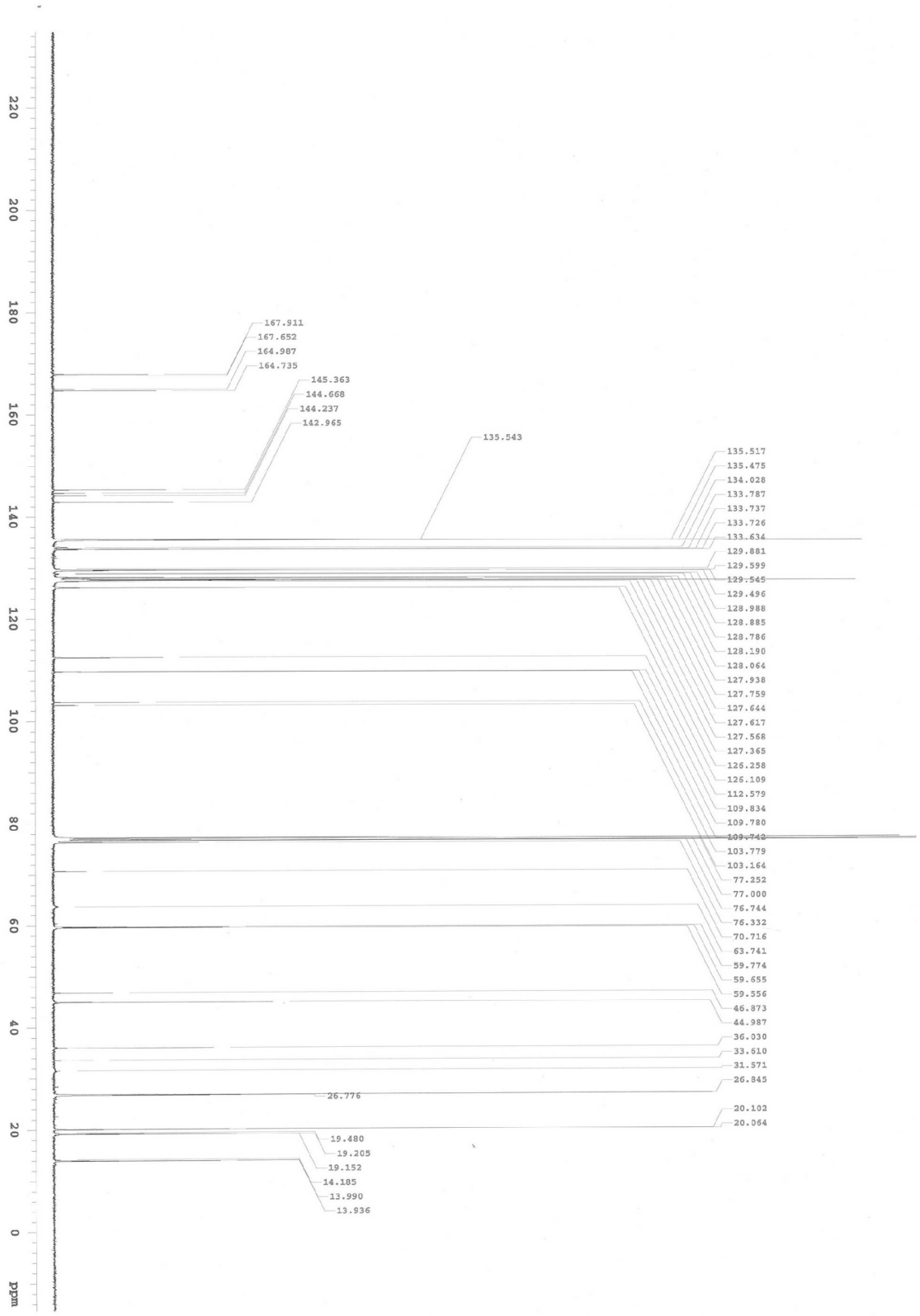

5.265
5.066
4.971
4.969
4.933
4.932
4.931
4.567
4.555
4.551
4.539
4.518
7.260
7.187
4.378
4.361
4.276
4.263
4.252
4.232
4.216
4.203
4.044
4.033
4.021
4.001
3.979
3.962
3.946
3.932
3.910
1.901
1.889
1.871
1.767
1.754
1.752
1.741
1.610
2.342
2.340
2.336
2.334
2.024
1.991
0.986
0.976
0.962
0.948
1.001
0.986
0.976
0.972
0.962
0.948
ppm

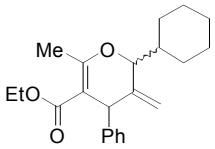

220
200
180
160
140
120
100
80
60
40
20
0
ppm
170.924
170.870
167.690
167.453
164.494
164.296
144.744
143.908
143.843
142.587
128.156
128.125
128.022
127.705
127.285
126.296
126.224
112.854
110.250
104.160
103.271
77.252
77.000
76.744
76.214
71.113
60.862
60.747
59.606
46.400
44.876
31.999
29.994
20.778
20.747
19.908
19.892
13.871
13.825


Me
O
O
Si
Ph
Ph
tBu
EtO
O
Ph

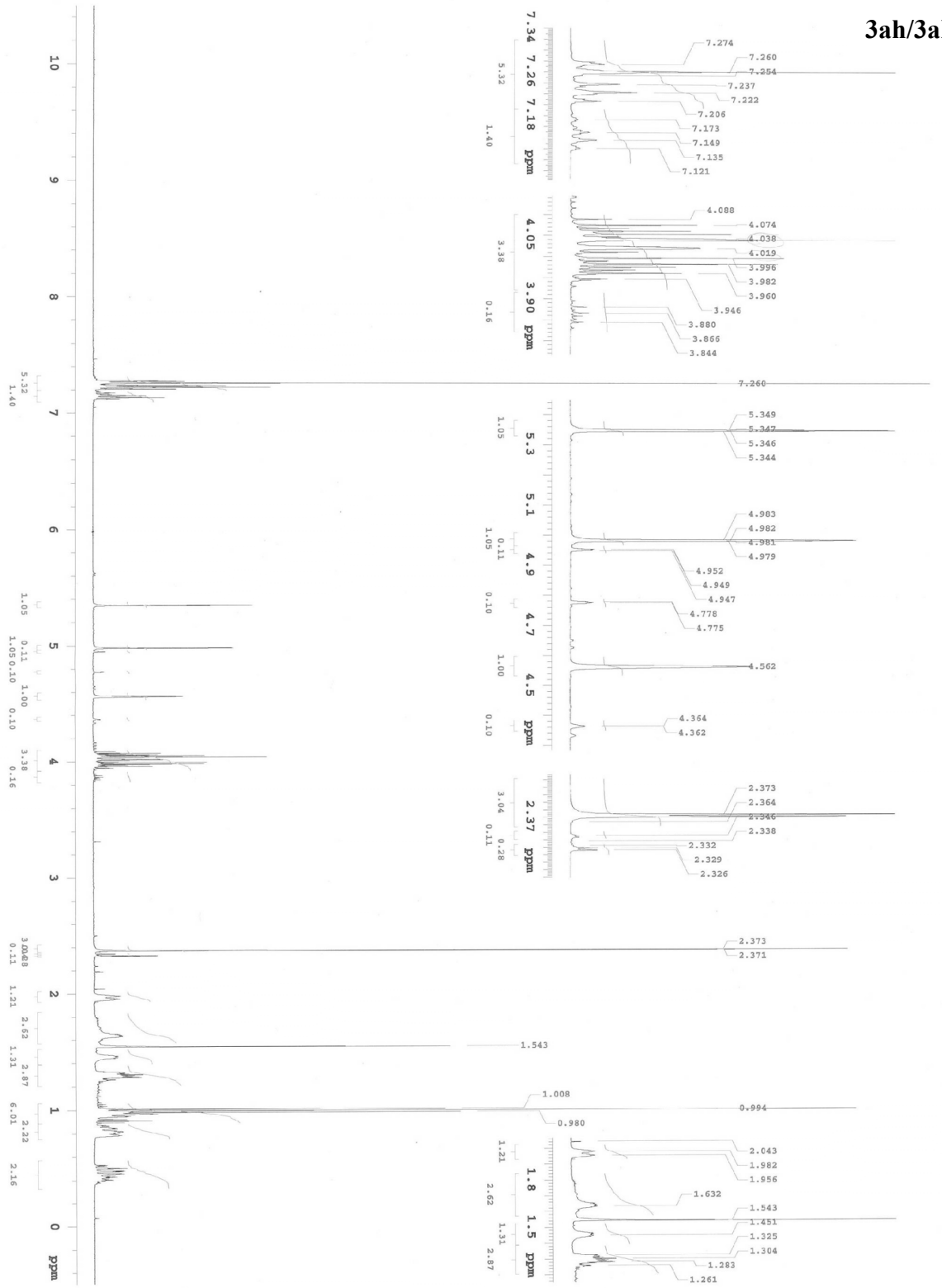
**3ag/3ag'**

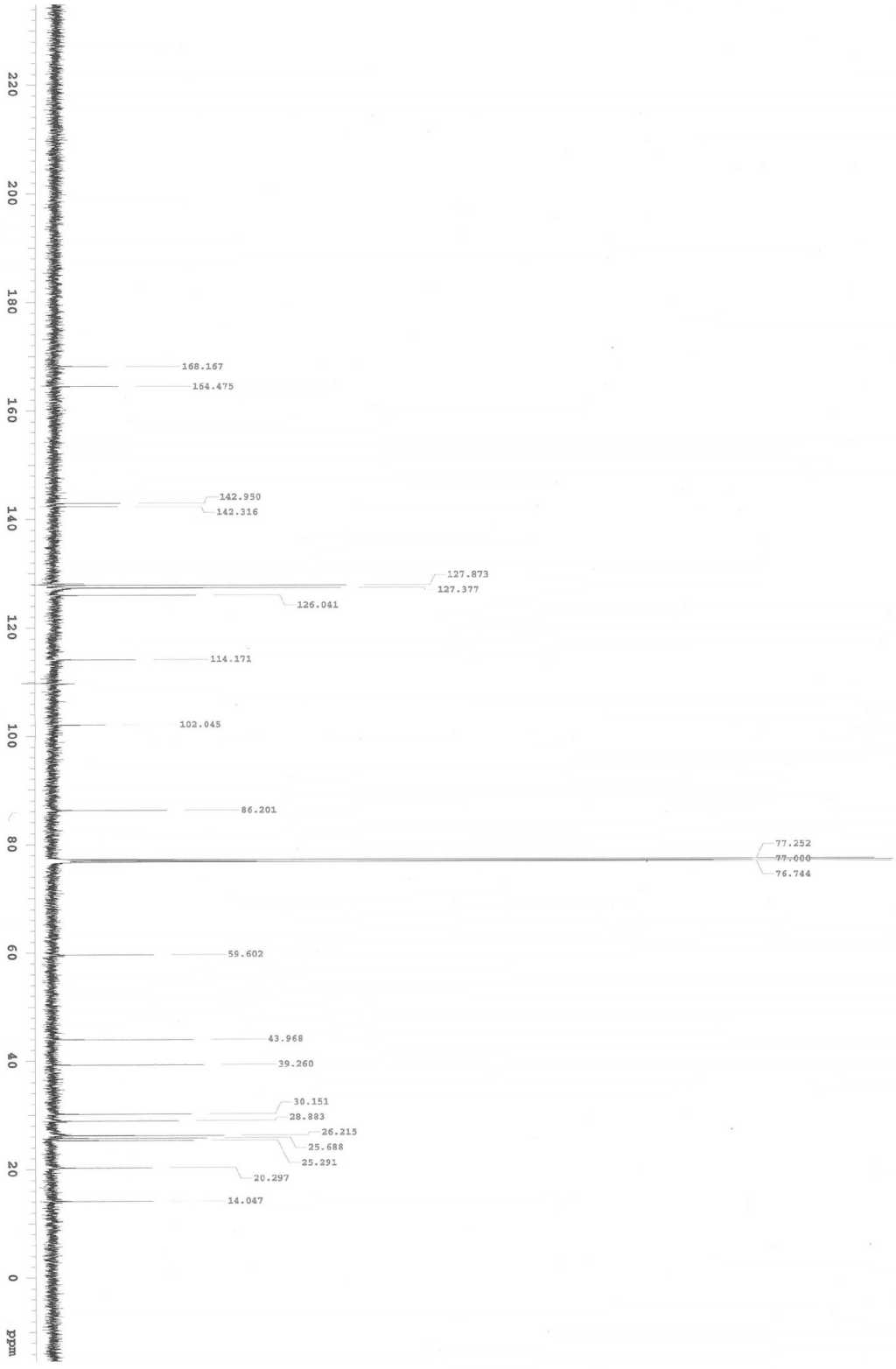

7.632
7.586
7.438
7.428
7.409
7.389
7.374
7.360
7.344
7.339
7.260
7.233
7.217
7.203
7.177
7.163
7.136
7.122
5.237
5.068
4.935
4.800
4.790
4.782
4.772
4.679
4.672
4.560
4.653
4.554
4.524
4.138
4.123
4.047
4.031
4.009
3.974
3.959
3.945
3.924
3.910
3.895
3.876
3.814
3.794
3.701
3.680
3.664
3.548
3.527
2.325
2.324
2.313
2.312
1.039
0.975
0.974
1.783
1.773
1.764
1.755
1.680
1.664
1.653
1.039
1.021
1.014
0.999
0.988
0.985
0.975
0.974
0.959
ppm

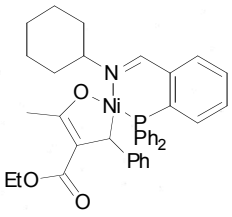

220
200
180
160
140
120
100
80
60
40
20
0
ppm
167.911
167.652
164.987
164.735
145.363
144.668
144.237
142.965
135.543
135.517
135.475
134.028
133.787
133.737
133.726
133.634
129.881
129.599
129.545
129.496
128.988
128.885
128.786
128.190
128.064
127.938
127.759
127.644
127.617
127.568
127.365
126.258
126.109
112.579
109.834
109.780
109.742
103.779
103.164
77.252
77.000
76.744
76.332
70.716
63.741
59.774
59.655
59.556
46.873
44.987
36.030
33.610
31.571
26.845
26.776
20.102
20.064
19.480
19.205
19.152
14.185
13.990
13.936


Me
O
EtO
O
Ph

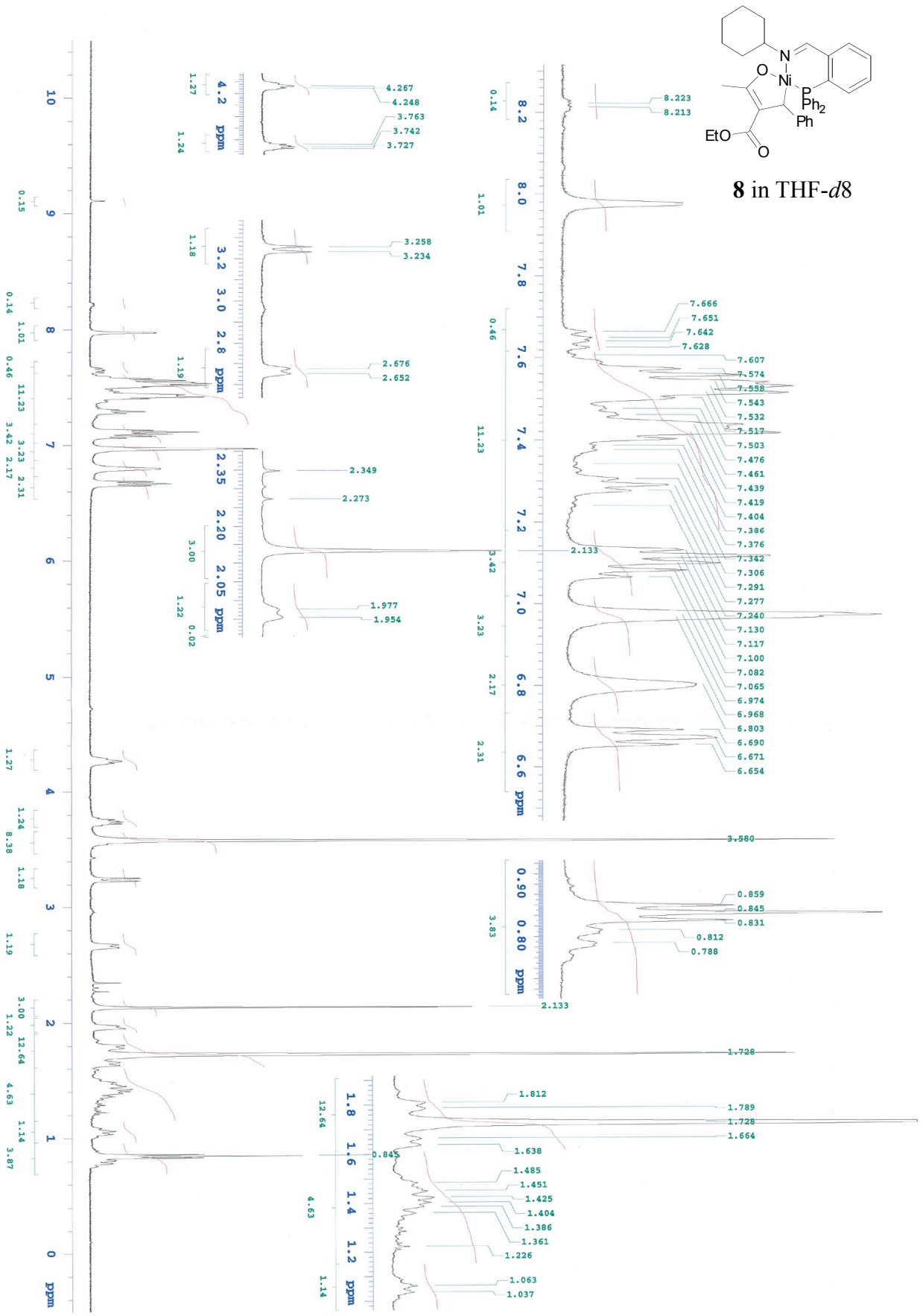
**3ah/3ah'**


7.34 7.26 7.18 ppm
7.274
7.260
7.254
7.237
7.222
7.206
7.173
7.149
7.135
7.121
4.05 3.90 ppm
4.088
4.074
4.038
4.019
3.996
3.982
3.960
3.946
3.880
3.866
3.844
7.260
5.3 5.1 4.9 4.7 4.5 ppm
5.349
5.347
5.346
5.344
4.983
4.982
4.981
4.979
4.952
4.949
4.947
4.778
4.775
4.562
4.364
4.362
2.37 ppm
2.373
2.364
2.346
2.338
2.332
2.329
2.326
2.373
2.371
1.543
1.008
0.994
0.980
1.8 1.5 ppm
2.043
1.982
1.956
1.632
1.543
1.451
1.325
1.304
1.283
1.261
10 9 8 7 6 5 4 3 2 1 0 ppm

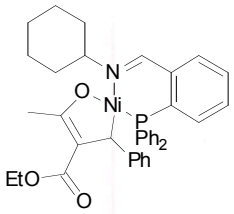

220
200
180
160
140
120
100
80
60
40
20
0
ppm
168.167
164.475
142.950
142.316
127.873
127.377
126.041
114.171
102.045
86.201
77.252
77.000
76.744
59.602
43.968
39.260
30.151
28.883
26.215
25.688
25.291
20.297
14.047




**8** in toluene-*d*8



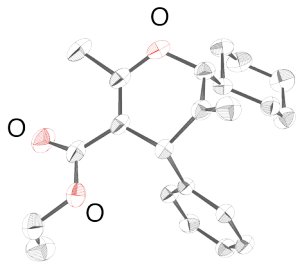

**8** in THF-*d*8


N
O
Ni
P
Ph2
Ph
EtO
O

**8** in THF-*d*8

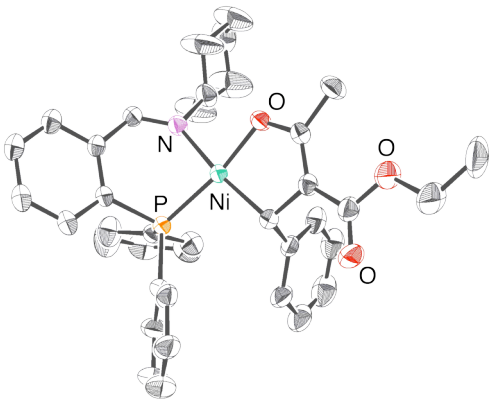

220
200
180
160
140
120
100
80
60
40
20
0
ppm
186.065
166.671
162.334
149.743
138.759
138.663
136.186
136.105
135.834
135.643
135.544
133.475
133.280
132.799
132.055
131.707
130.749
130.341
129.840
129.760
129.382
129.306
129.153
128.378
124.003
109.106
68.557
68.381
68.206
68.030
67.854
67.679
57.699
48.219
48.116
37.068
35.659
33.273
27.573
27.244
26.893
26.443
26.275
26.114
25.954
25.794
25.633
23.136
15.680

## ORTEP Drawing of 3ah




| | | |
|---|---|---|
| Identification code | **3ah** | |
| Empirical formula | C22 H28 O3 | |
| Formula weight | 340.44 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 7.859(2) Å | $\alpha$ = 90°. |
| | b = 13.549(4) Å | $\beta$ = 95.816(5)°. |
| | c = 18.247(6) Å | $\gamma$ = 90°. |
| Volume | 1933.0(10) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.170 Mg/m$^3$ | |
| Absorption coefficient | 0.076 mm$^{-1}$ | |
| F(000) | 736 | |
| Crystal size | ? x ? x ? mm$^3$ | |
| Theta range for data collection | 1.88 to 27.23°. | |
| Index ranges | -9<=h<=9, -16<=k<=17, -23<=l<=18 | |
| Reflections collected | 11596 | |
| Independent reflections | 4202 [R(int) = 0.0256] | |
| Completeness to theta = 27.23° | 97.2 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4202 / 0 / 228 | |
| Goodness-of-fit on F$^2$ | 0.962 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0625, wR2 = 0.2110 | |
| R indices (all data) | R1 = 0.0753, wR2 = 0.2367 | |
| Largest diff. peak and hole | 0.379 and -0.262 e.Å$^{-3}$ | |

## ORTEP Drawing of 8




| | | |
|---|---|---|
| Identification code | **8** | |
| Empirical formula | C38 H40 N Ni O3 P | |
| Formula weight | 648.39 | |
| Temperature | 273(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 10.1100(8) Å | $\alpha$ = 90°. |
| | b = 16.9525(14) Å | $\beta$ = 90.796(2)°. |
| | c = 20.0005(16) Å | $\gamma$ = 90°. |
| Volume | 3427.6(5) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.256 Mg/m$^3$ | |
| Absorption coefficient | 0.649 mm$^{-1}$ | |
| F(000) | 1368 | |
| Crystal size | 1 x 1 x 1 mm$^3$ | |
| Theta range for data collection | 1.57 to 27.06°. | |
| Index ranges | -5<=h<=12, -21<=k<=21, -23<=l<=25 | |
| Reflections collected | 20721 | |
| Independent reflections | 7469 [R(int) = 0.0265] | |
| Completeness to theta = 27.06° | 99.2 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 7469 / 0 / 399 | |
| Goodness-of-fit on F$^2$ | 1.034 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0553, wR2 = 0.1474 | |
| R indices (all data) | R1 = 0.0736, wR2 = 0.1610 | |
| Largest diff. peak and hole | 0.559 and -0.413 e.Å$^{-3}$ | |