Supporting Information for:

Experimental Evidence for Large Ring Metallacycle Intermediates in Polyethylene Chain Growth using Homogeneous Chromium Catalysts.

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Contents

General Experimental.

Air-sensitive reactions were performed using standard Schlenk and vacuum line techniques. Pentane, heptane and toluene were dried by passing through a cylinder filled with commercially available Q-5 catalyst (13 % Cu(II) oxide on Al_2O_3. 1-Nonene was distilled under nitrogen and stored over a potassium mirror. NMR spectra were recorded on a Bruker spectrometer at 250 MHz (^{1}H) and 62.9 MHz (^{13}C) at 293 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. Mass spectra were obtained using either fast atom bombardment (FAB), electron impact (EI), or chemical ionization (CI). GC analyses of oligomers were carried out on a HP-5890 Gas Chromatograph. $CrCl_3(thf)_3$ was prepared according to an established procedure[1]. MAO (10% solution in toluene) was purchased from Witco Corp., 1,2-phenylenediamine and 2,6-pyridinedicarboxylic acid were purchased from Aldrich Chemical Co. All other commercial chemicals were used as received.

Preparation of Complex 2.

N-8-quinolyl tryptycenyl-salicylaldimine: To a slurry of tryptycenyl-salicylaldehyde (0.50 g, 1.33 mmole) suspended in ethanol (10 mL) was added 8-aminoquinoline (0.30 g, excess) and a drop of formic acid. The slurry was stirred at reflux overnight and then cooled to RT. The orange-red product was collected by filtration, washed with ethanol and dried in a vacuum oven at 60°C. Yield 0.55 g 84.7%. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 5.415(s, 1H, H_5), 6.91-7.02(m, 6H, H_2 & H_3), 7.267(t, 1H J = 7.7 Hz, H_c), 7.34-7.50(m, 9H), 7.548(t, 1H J = 7.6 Hz), 8.556(dd, 1H J = 7.9 & 1.6 Hz), 8.178(dd, 1H J = 8.3 & 1.7

Hz), 8.556(dd, 2H *H* = 7.9 & 1.4 Hz, H_d), 8.915(dd, 1H *J* = 4.2 & 1.8 Hz), 9.305(s, 1H, H_a), 14.335(s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 16.86, 162.01, 150.25, 146.27, 145.67, 144.85, 141.90, 136.07, 136.01, 132.94, 129.30, 126.54, 126.01, 125.21, 124.78, 124.38, 123.35, 121.54, 121.44, 120.61, 118.14, 59.33, 55.34. MS(CI+ve) (m/z) 500.60 (M^+ 20%), 129 (Quinoline+ 60%). $C_{36}H_{24}N_2O$ (500.60): Calc. C 86.38, H 4.83, N 5.60; Found C 86.40, H 4.88, N 5.51.

(N-8-quinolyl tryptycenyl-salicylaldiminato)chromium(III) dichloride (**2**): N-8-quinolyl tryptycenyl-salicylaldimine (0.53g, 1.23 mmol) and *p*-tolyl$CrCl_2(thf)_3$ (0.60 g, 1.31 mmol) were reacted by dissolving in thf (20 mL). A brown solid precipitated almost immediately. The slurry was stirred for 1 hour then heated to 50°C for 4 hours. The mixture was allowed to cool to room temperature, the solids recovered by filtration and washed with thf (2 x 10 mL). Yield 0.61 g (84.6%). FAB-MS (m/z) 1137($L_2Cr_2Cl_3^+$, 15%), 550(M-Cl^+, 100%), 513(LCr^+, 80%) $C_{33}H_{23}N_2OCrCl_2$ (586.47): Calc. C 67.59, H 3.95, N 4.78; Found C 67.51, H 3.97, N 4.71.

Ethylene oligomerization Procedure.

A Fisher-Porter bottle, dried and flushed with N_2, was charged with toluene (220 mL), 2,2,4,4,6,8,8-heptamethylnonane standard (~0.5g) and MAO (1.6 M in toluene, 4.4 ml, 7.5 mmol). In the case of co-oligomerization experiments, the co-oligomer (1-nonene, 12 mL) was added prior to MAO. This was followed by injection of an aliquot (**1** - 1 μmol Cr , **2** -5 μmol Cr) of the preactivated catalysts [prepared *in situ* by reacting 10 - 50 μmol of the corresponding pre-catalyst with MAO (2.50 mL 1.6 M), followed by addition of

toluene (50 – 250 mL)]. The reactor was then connected to an ethylene line and charged to the desired pressure. The polymerization reactions were carried out under mechanical stirring, at the required temperature for 70 minutes. Each reaction was terminated by disconnecting the reactor from the ethylene line. After withdrawing a small sample for GC analysis the reaction mixture was hydrolyzed by addition of water (10 mL).

Co-oligomerization of a 50:50 C_2H_4/C_2D_4 mixture using 1 or 2 activated by MAO.

Complexes **1** or **2** (~5 μmol) were placed in a 100 mL, thick-walled Schlenk tube and suspended in toluene (30 mL). After addition of MAO (2.5 mL, 1.6M), the reaction mixture was degassed and then frozen at -196 ^{o}C. The vessel was connected, via a T-connector, to a 400 mL thick-walled glass ampoule charged with a 50:50 mixture of C_2H_4 and C_2D_4 at ~4 bar absolute pressure. After evacuation of the connecting line and the reaction vessel, the reaction mixture was allowed to warm to room temperature and the 50:50 C_2H_4/C_2D_4 mixture was then introduced. After stirring at room temperature for 1 hour, an aliquot was withdrawn, passed through a layer of neutral silica to remove the components of the catalyst mixture, and analysed by GC and GC-MS.

The co-oligomerization experiments have also been conducted by condensing the 50:50 C_2H_4/C_2D_4 mixture directly onto a degassed and frozen (-196 ^{o}C) catalyst/MAO/toluene mixture in a thick-walled glass ampoule, followed by warming to room temperature. Similar product distributions were obtained by the two methods.

Fig. S1. GC-MS trace for the C_{10}, C_{12} and C_{14} fractions obtained from C_2H_4/C_2D_4 (50:50) co-oligomerization using **1**/MAO.

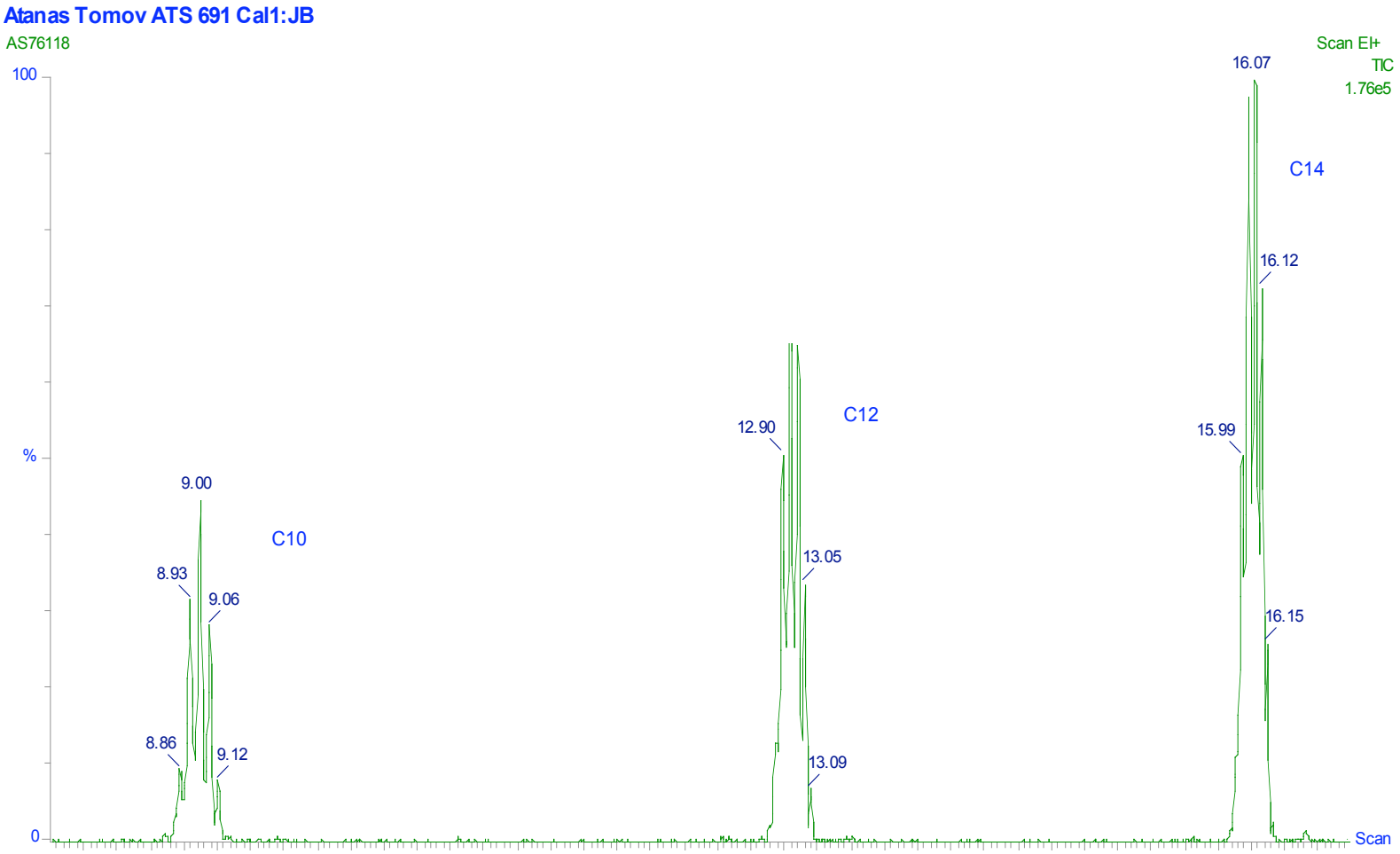


Fig. S2. Mass spectra of isotopomers observed within the C_{10} fraction obtained using **1**/MAO**.**

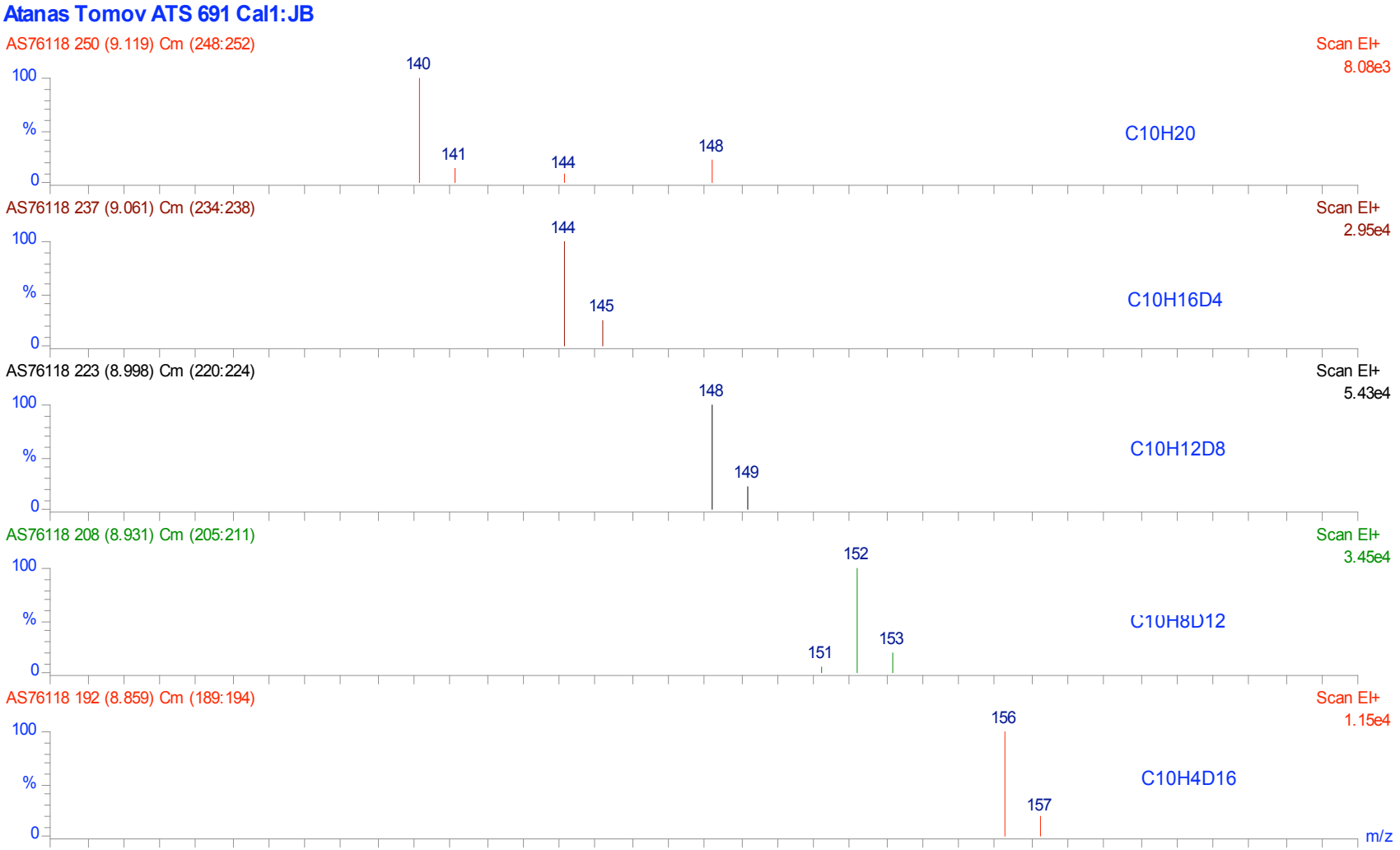


Fig. S3. Selected ion chromatograms showing the individual ion traces for the C_{10} fraction obtained using **1**/MAO**.**

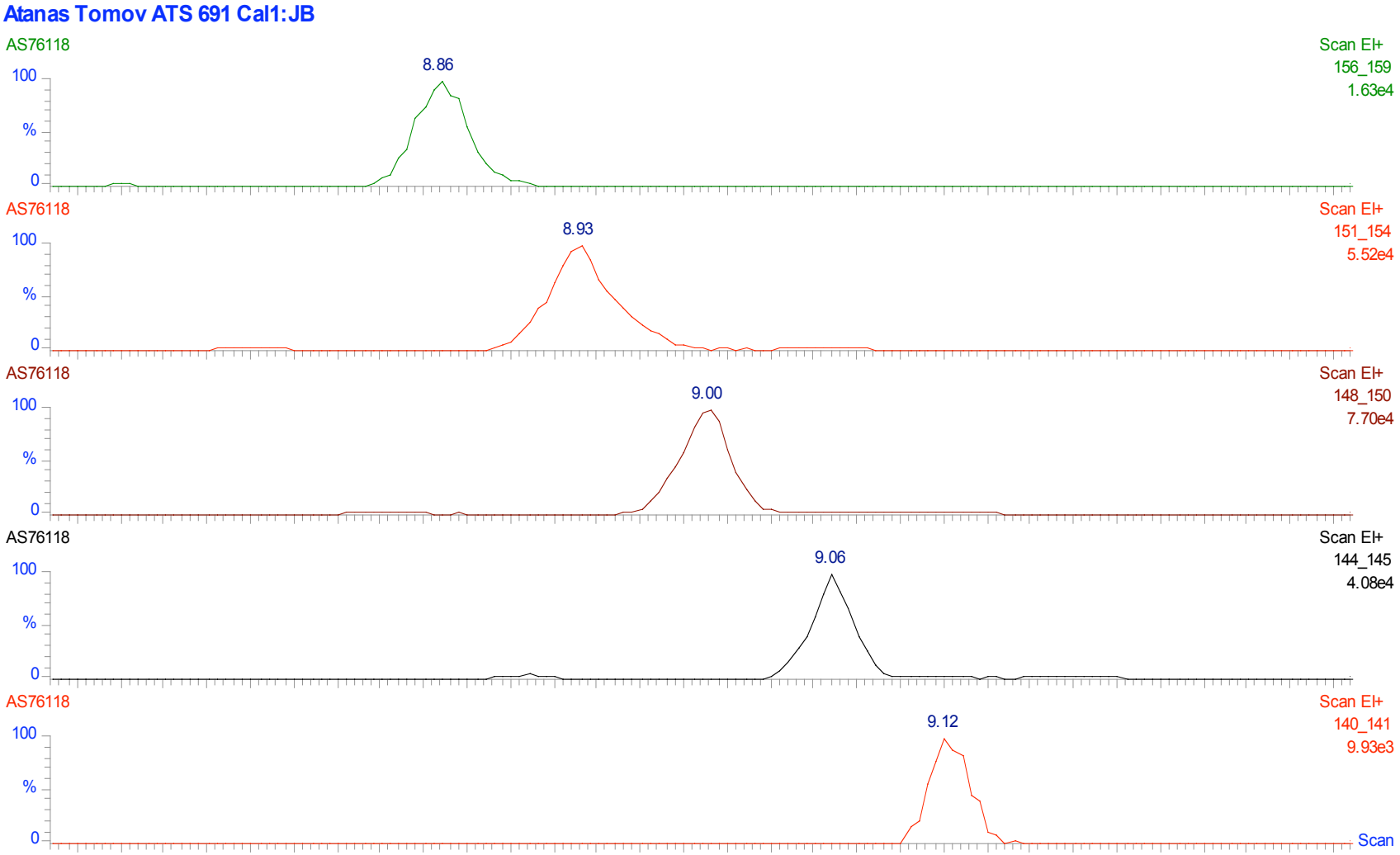


Fig. S4. Mass spectra of isotopomers observed within the C_{12} fraction obtained using **1**/MAO.

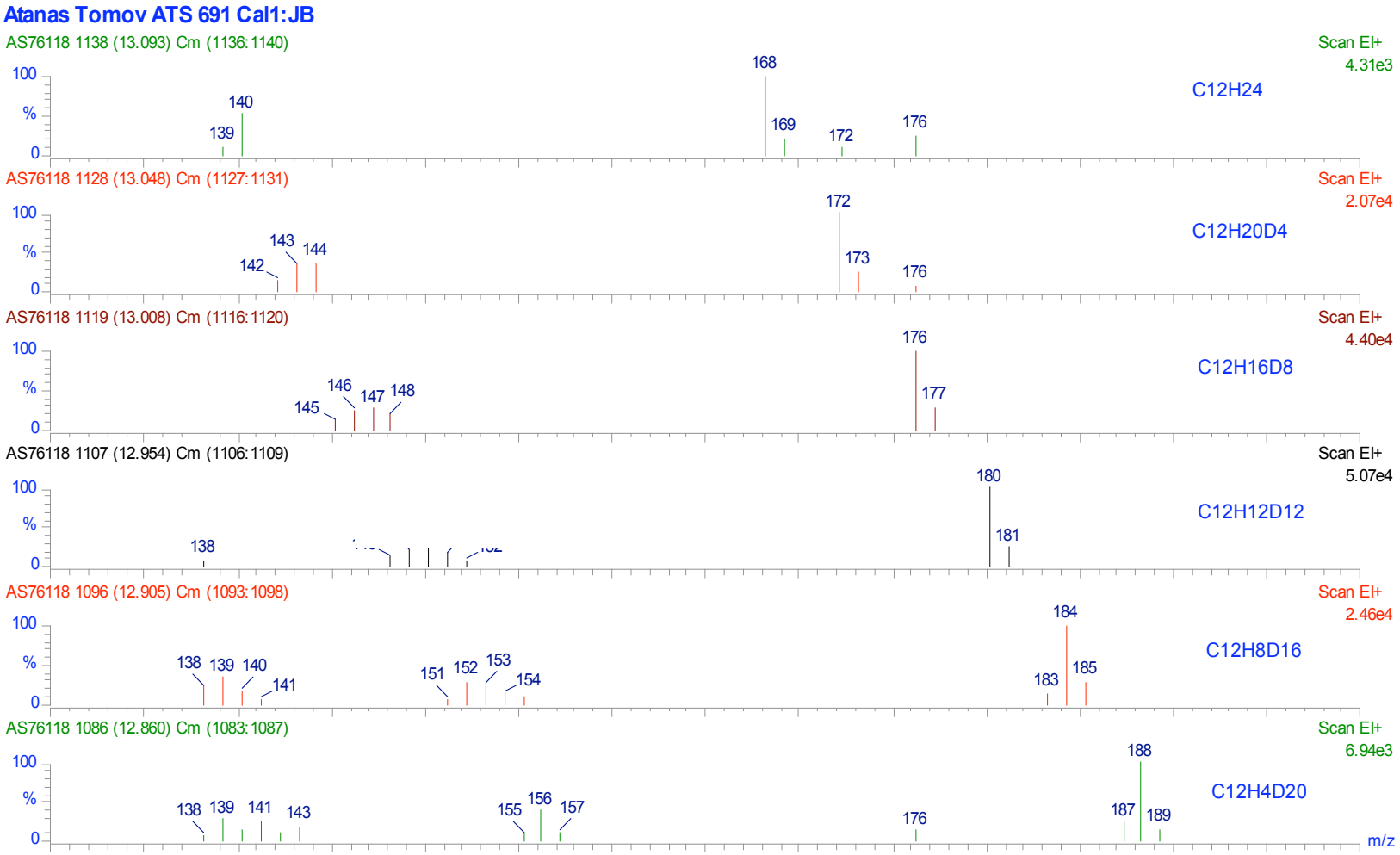


Fig. S5. Selected ion chromatograms showing the individual ion traces for the C_{12} fraction obtained using **1**/MAO**.**

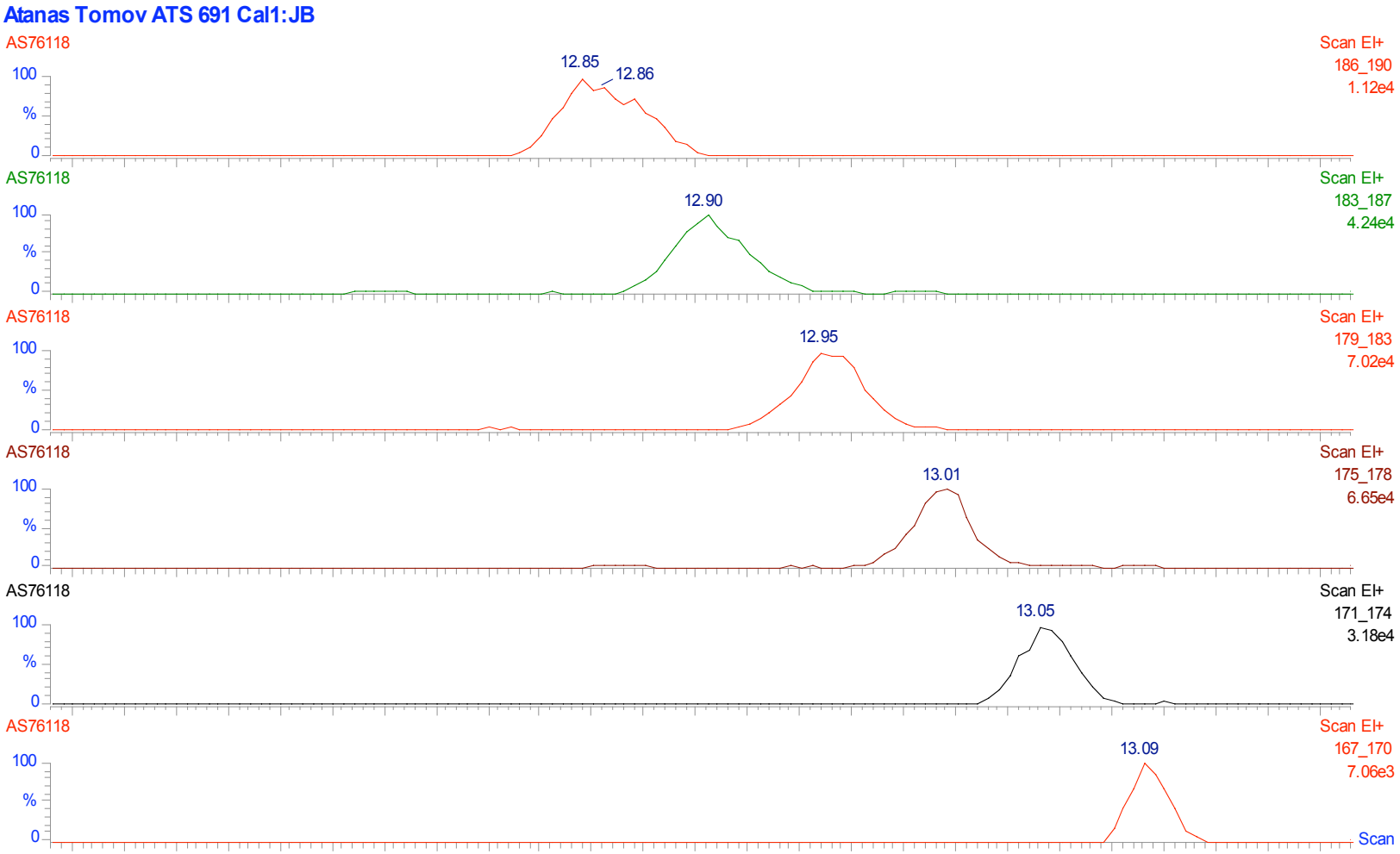


Fig. S6. Mass spectra of isotopomers observed within the C_{14} fraction obtained using **1**/MAO**.**

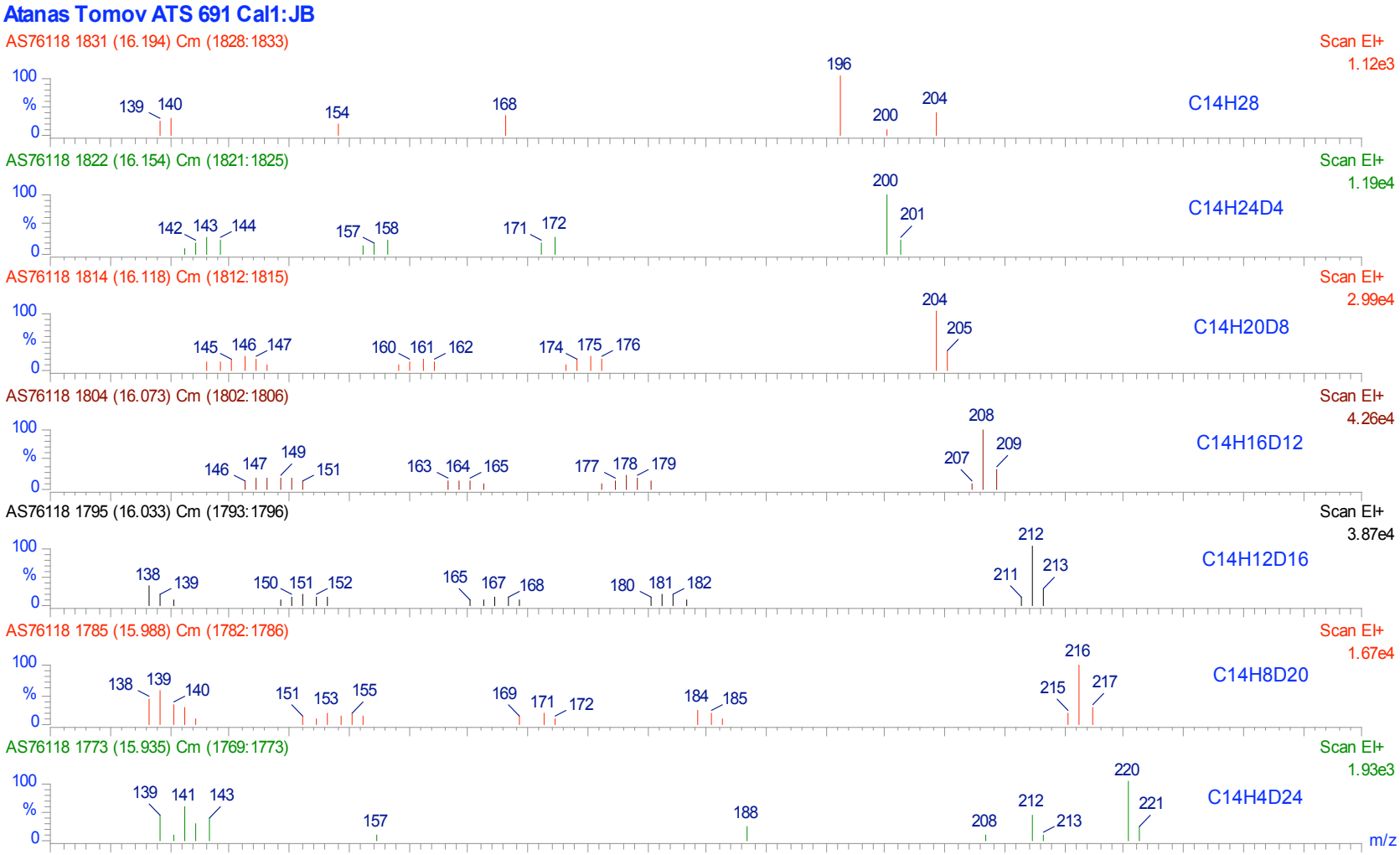


Fig. S7. Selected ion chromatograms showing the individual ion traces for the C_{14} fraction obtained using **1**/MAO.

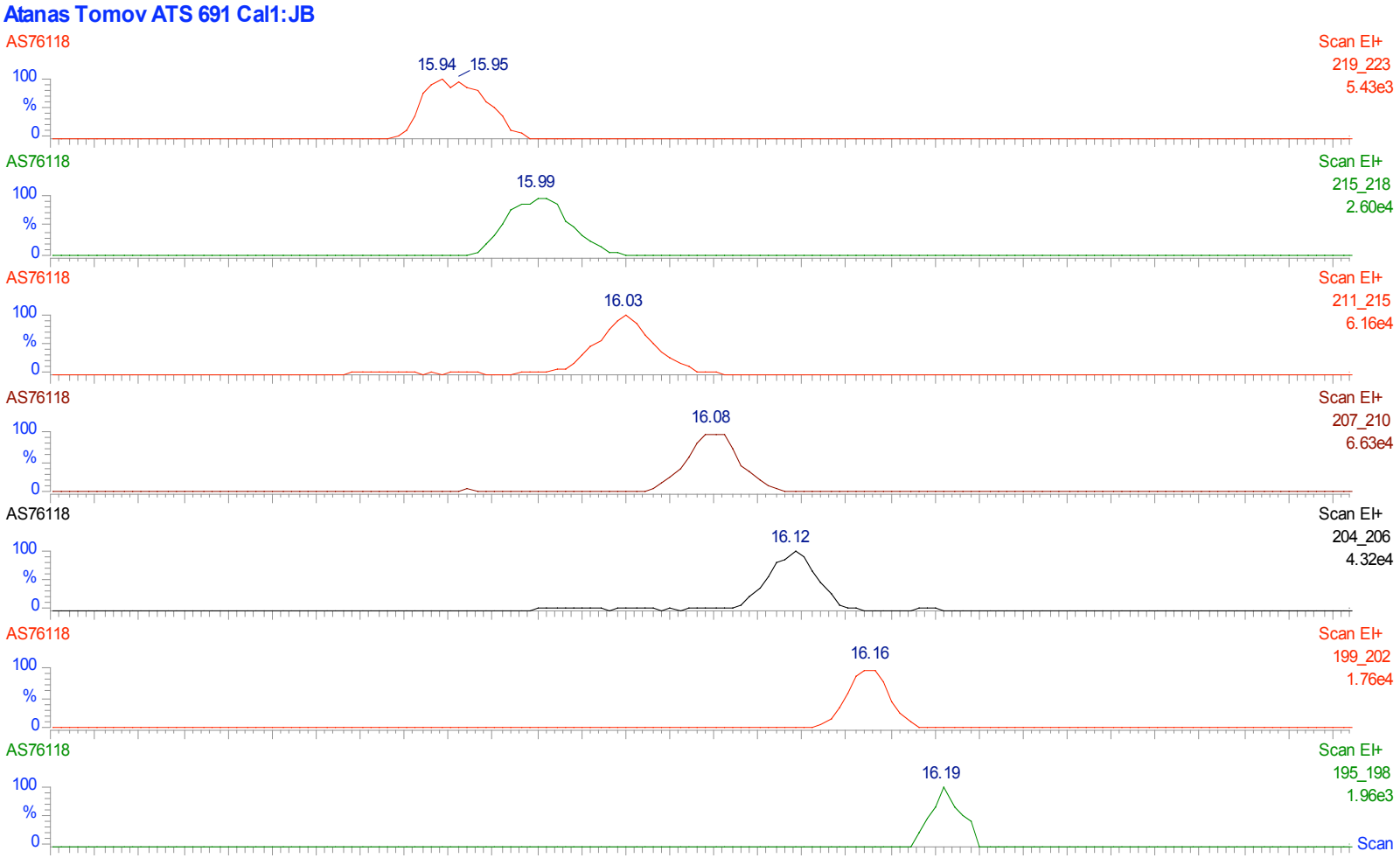


Fig. S8. GC trace of the products obtained from C_2H_4/C_2D_4 (50:50) co-oligomerization using **2**/MAO in the presence of excess Me_3Al.

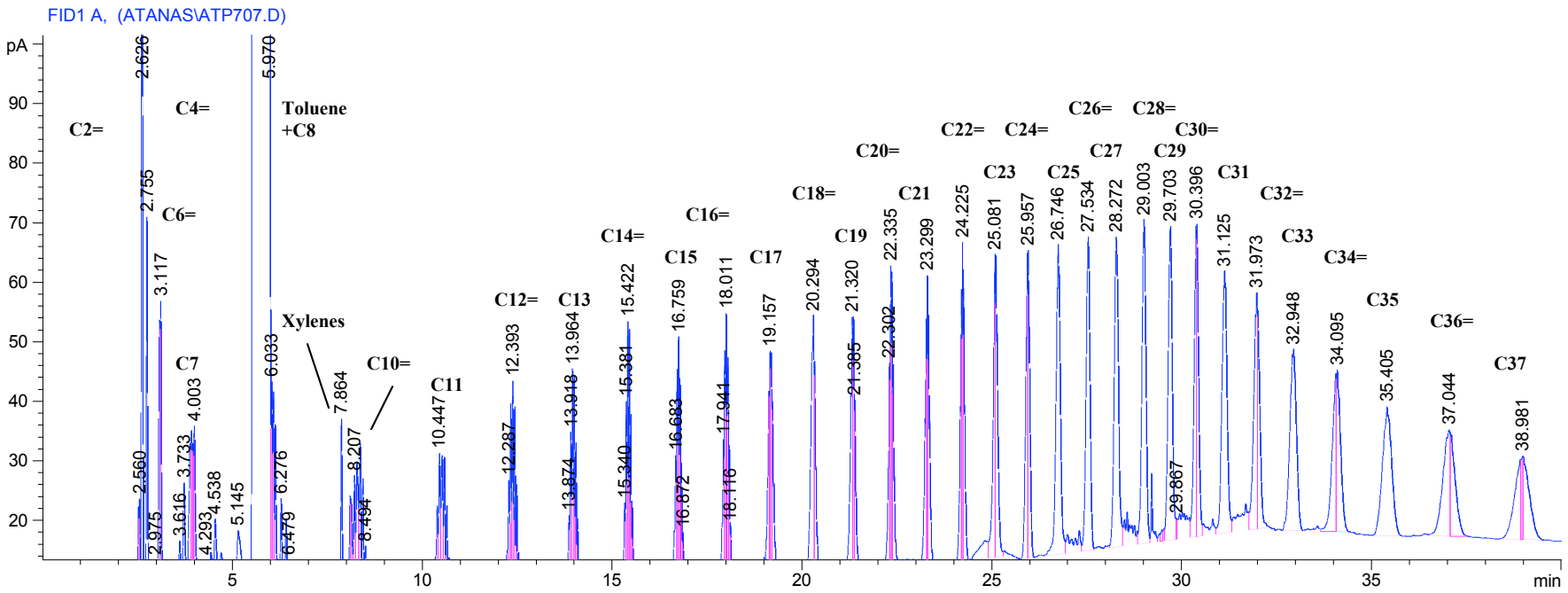
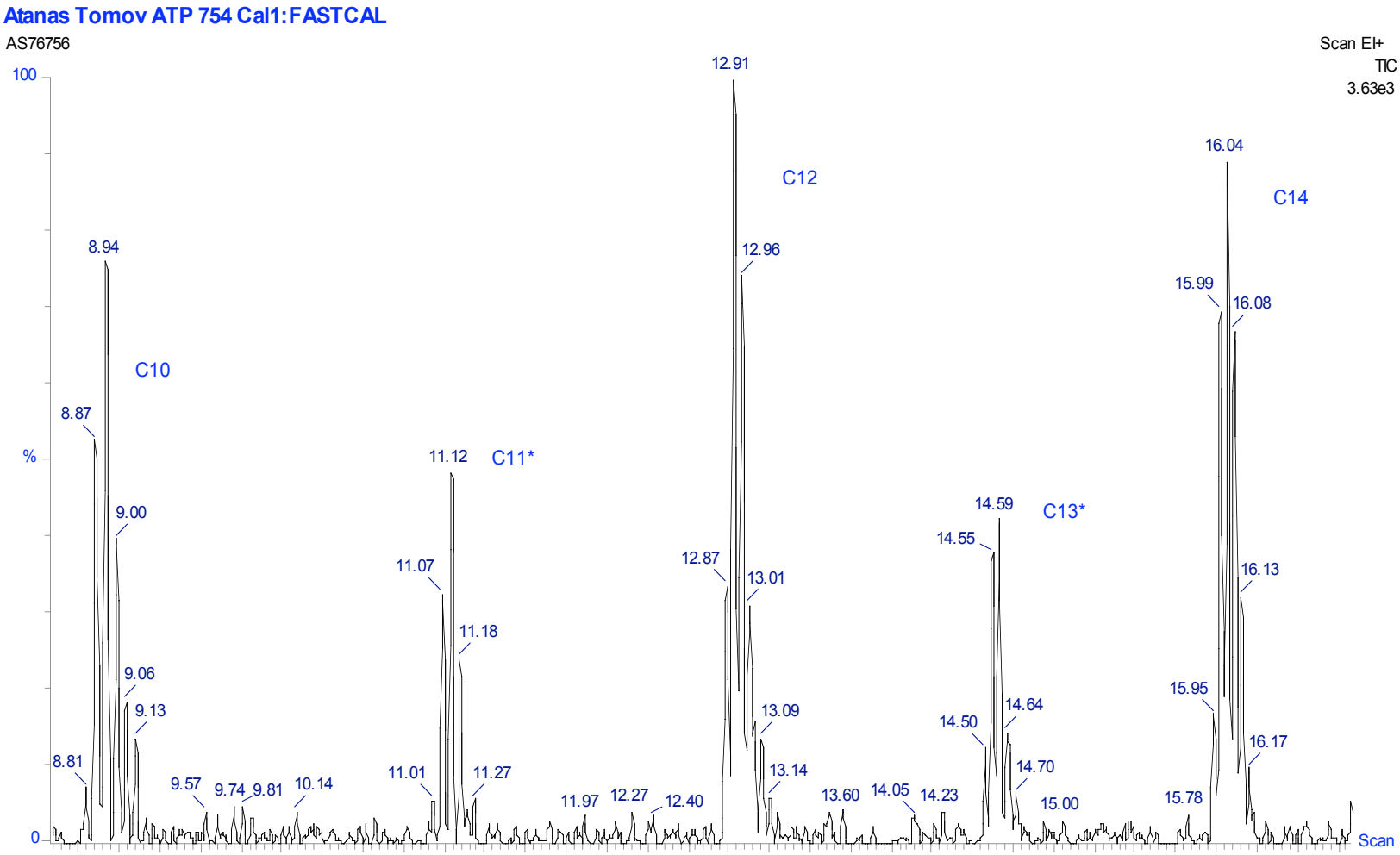


Fig. S9. GC-MS trace for the $C_{10,}$ - C_{14} fraction obtained using **2**/MAO in the presence of excess Me_3Al**.**



* C11 and C13 are products of chain transfer to aluminum

Fig. S10. Mass spectra of isotopomers observed within the C_{10} fraction obtained using **2**/MAO.

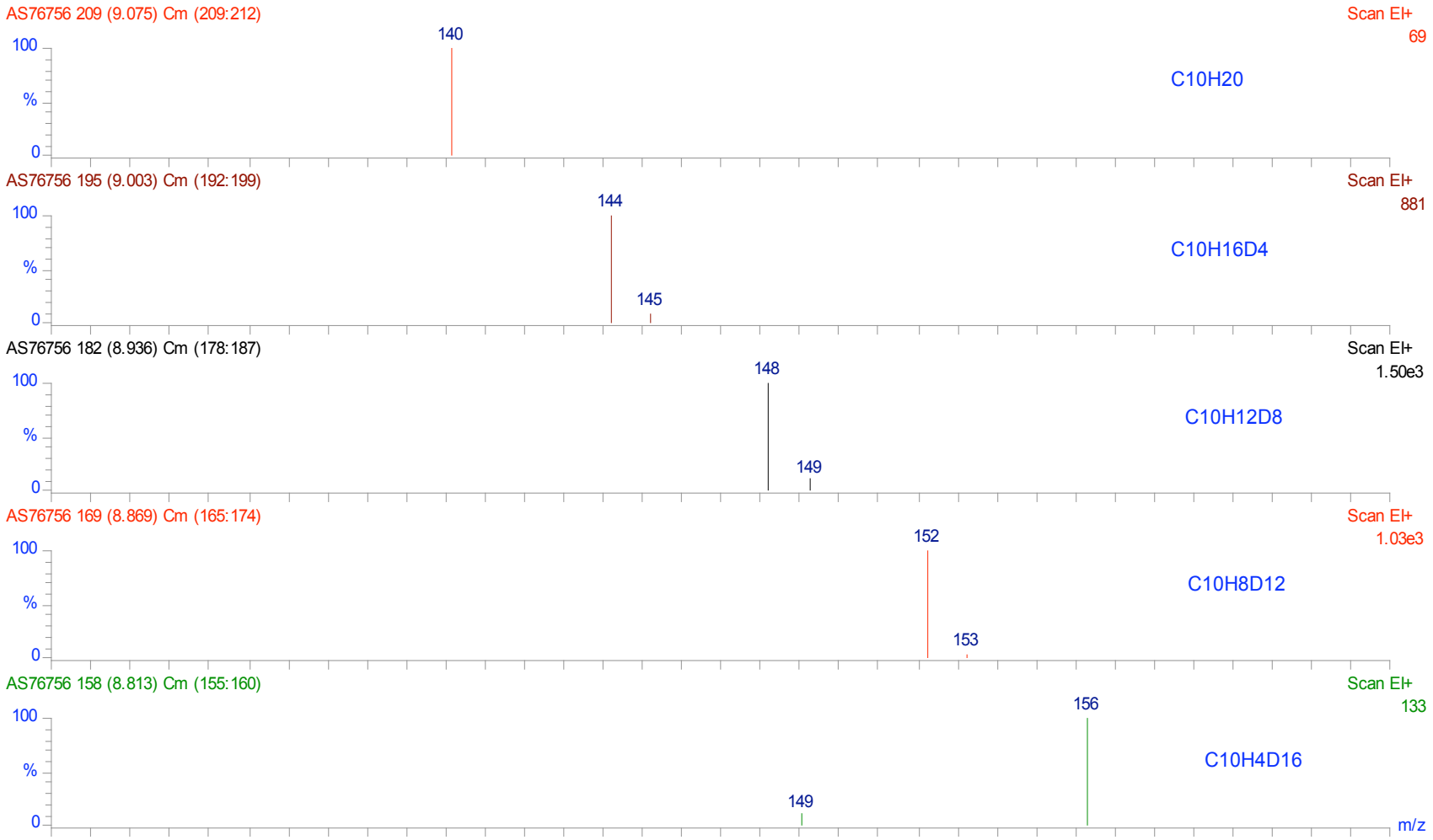


Fig. S11. Selected ion chromatograms showing the individual ion traces for the C_{10} fraction obtained using **2**/MAO**.**

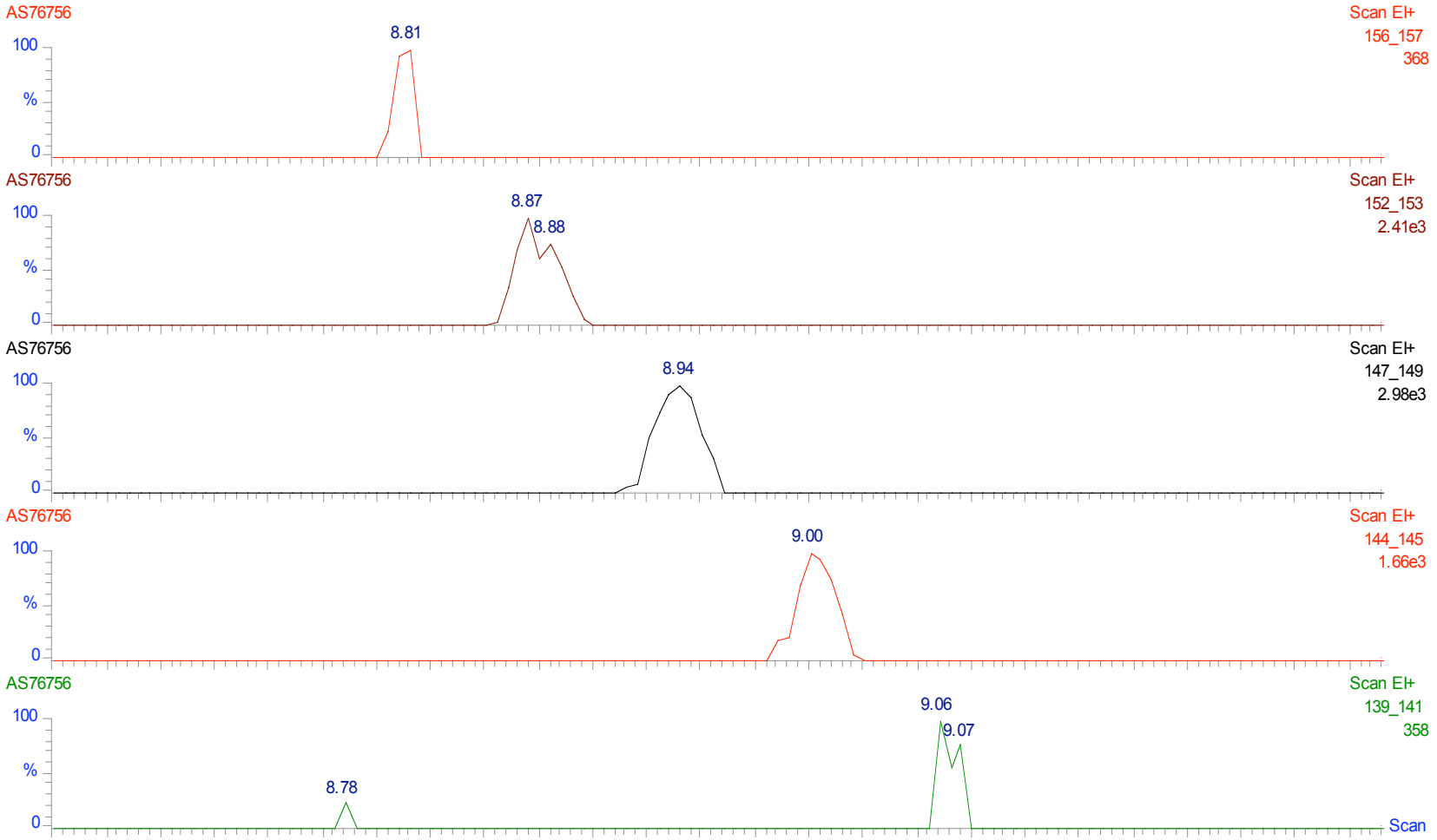
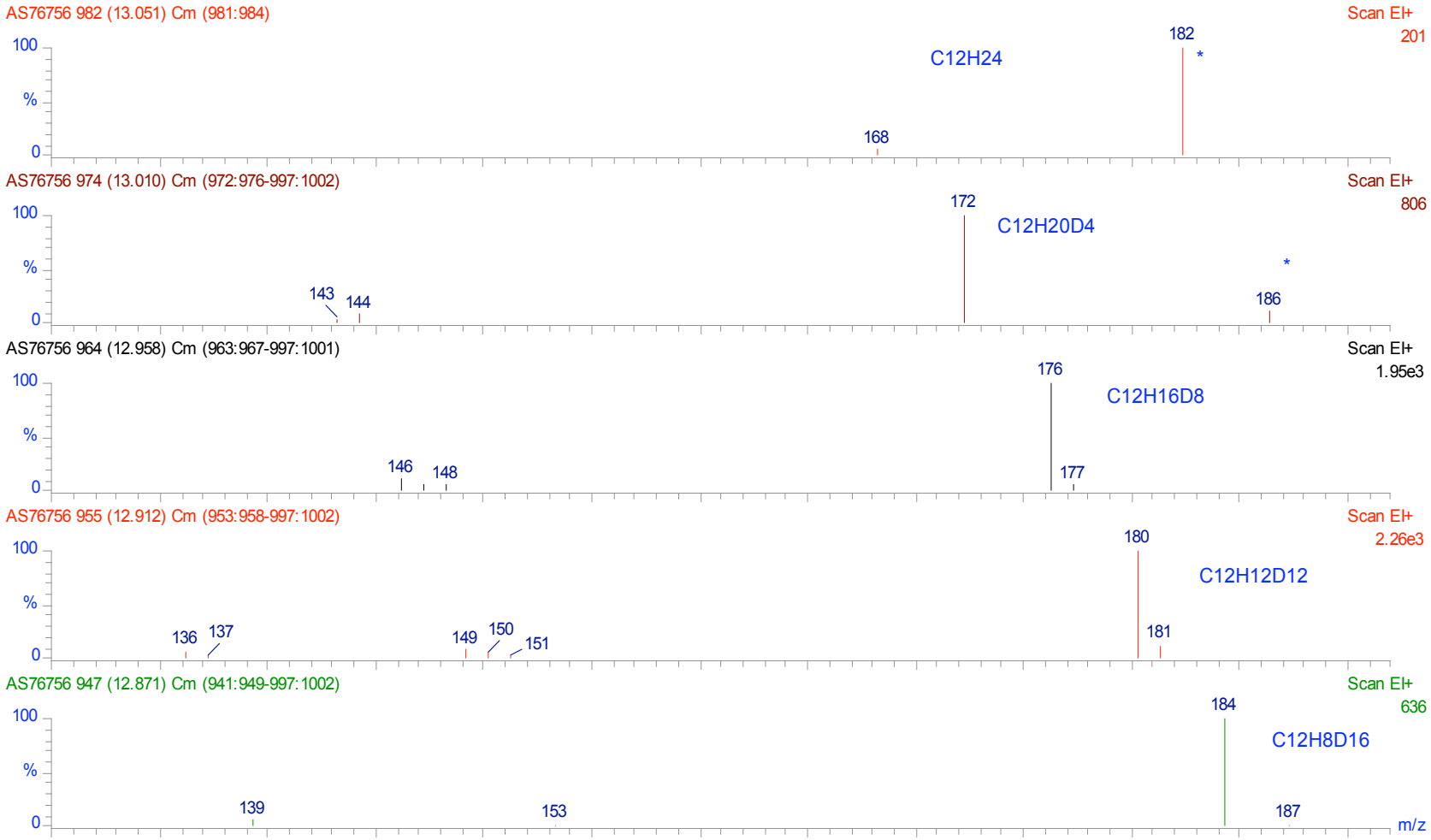


Fig. S12. Mass spectra of isotopomers observed within the C_{12} fraction obtained using **2**/MAO.



* alkanes – $C_{12}H_{14}D_{12}$ and $C_{12}H_{10}D_{16}$

Fig. S13. Selected ion chromatograms showing the individual ion traces for the C_{12} fraction obtained using **2**/MAO

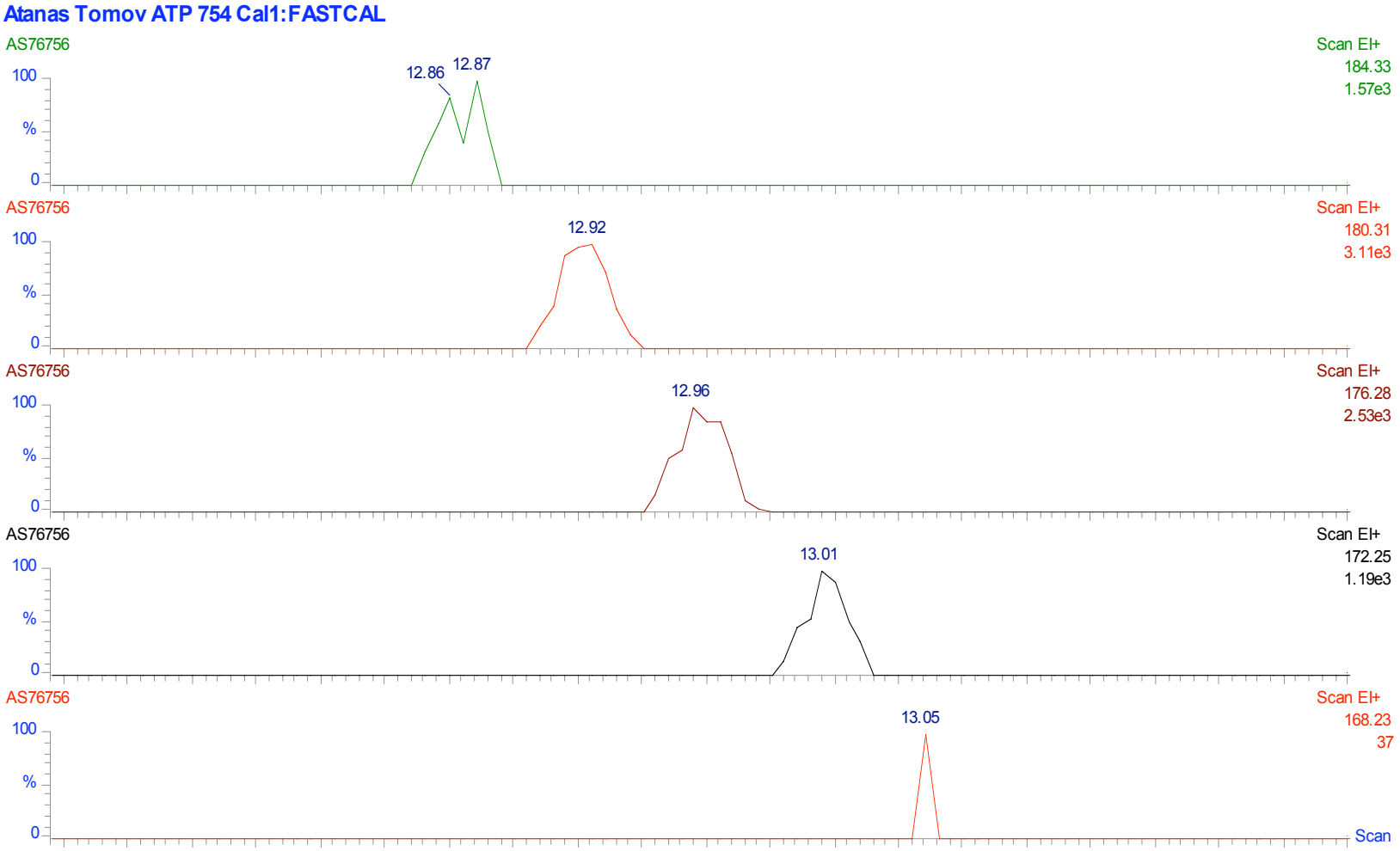
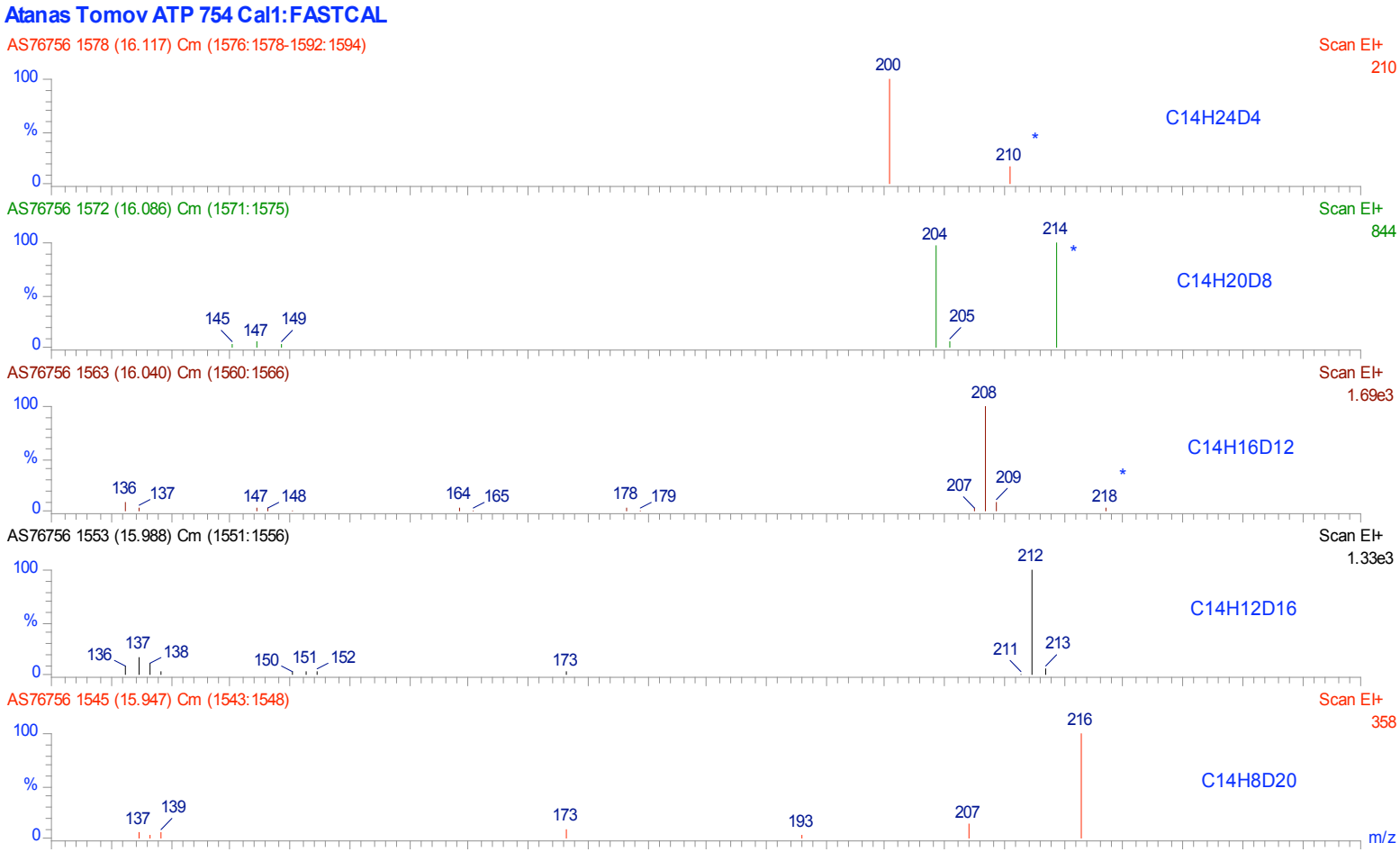


Fig. S14. Mass spectra of isotopomers observed within the C_{14} fraction obtained using **2**/MAO.



* alkanes – $C_{14}H_{18}D_{12}$, $C_{14}H_{14}D_{16}$, $C_{14}H_{10}D_{20}$

Fig. S15. Selected ion chromatograms showing the individual ion traces for the C_{14} fraction obtained using **2**/MAO.

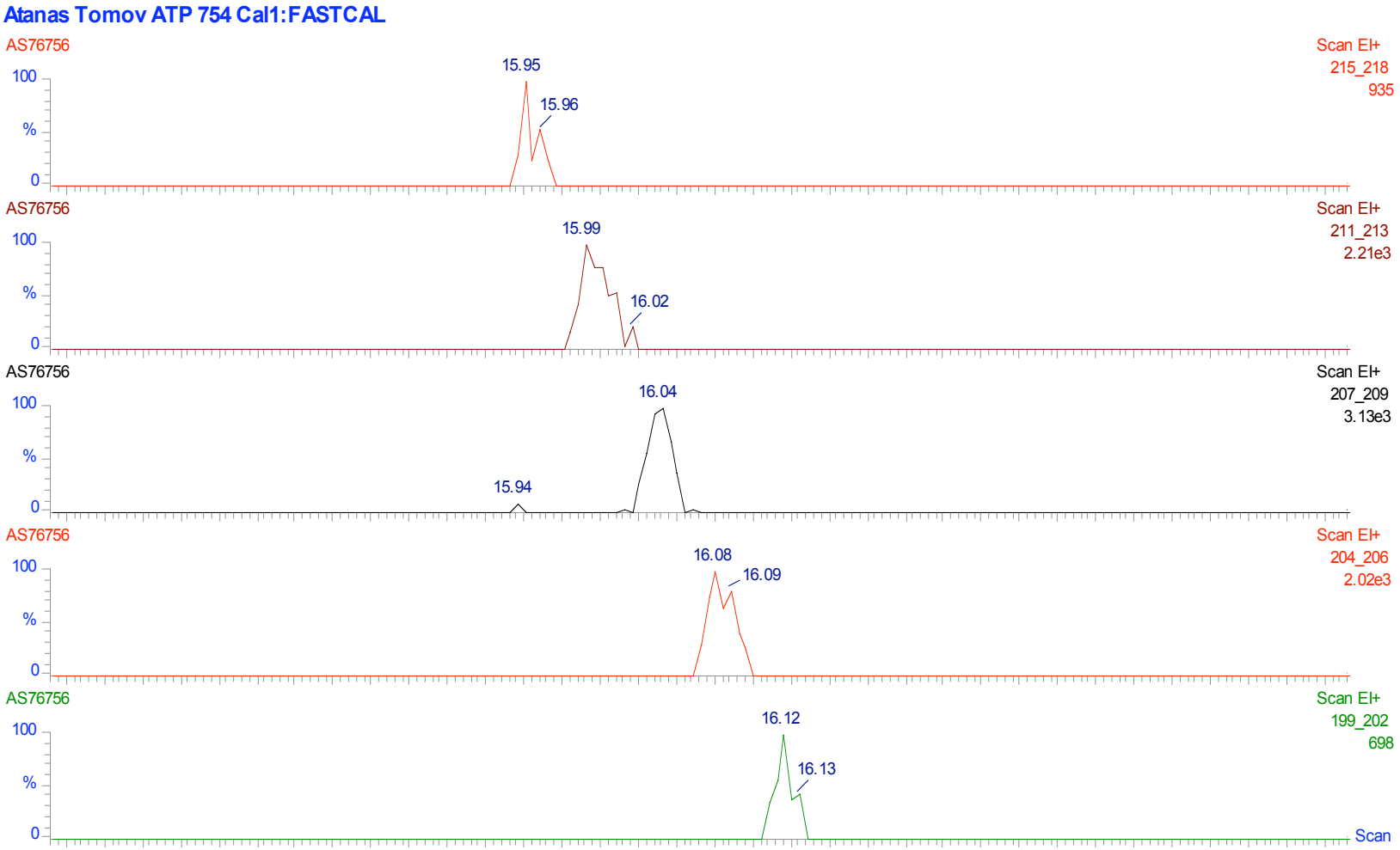


Fig. S16. GC trace of the products arising from ethylene oligomerization using **2**/MAO in the presence of 1-nonene (12 mL); * products of chain transfer to Al.

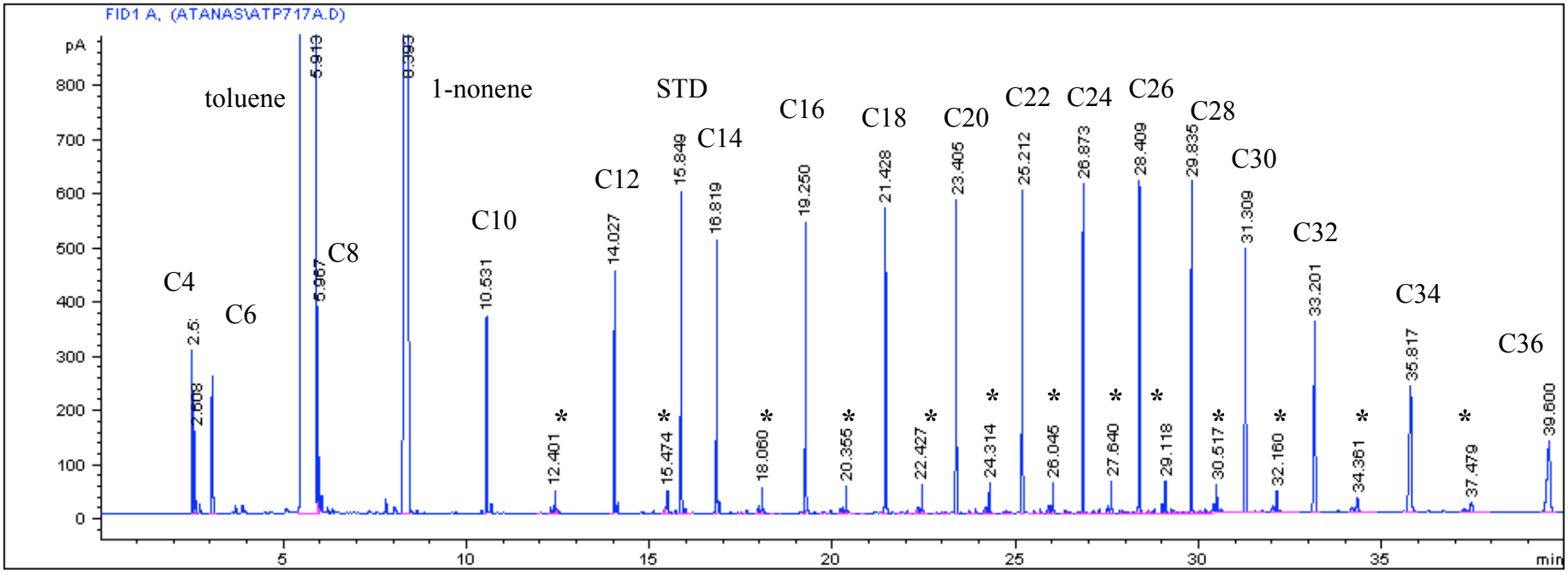
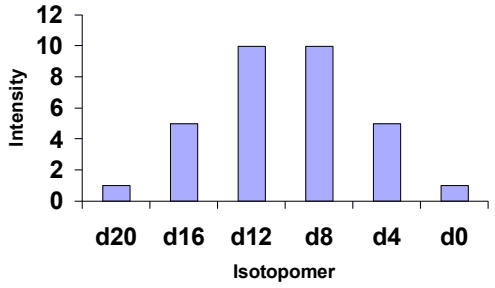


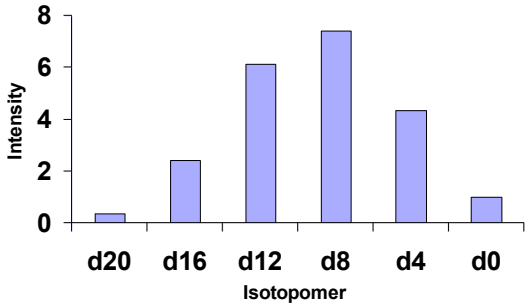
Fig. S17. Calculated and Experimental Isotopomer Distributions for C_2H_4/C_2D_4 (50:50) co-oligomerizations using **1**/MAO.

a) C_{10} fraction

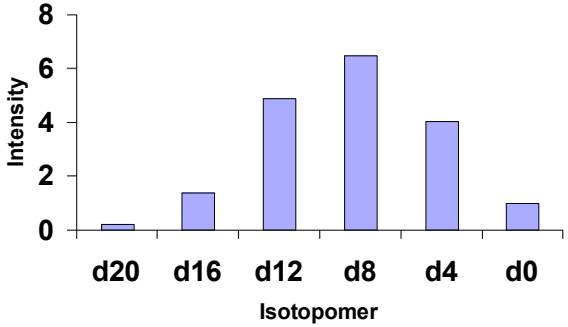
Calculated Isotopomer Distribution for KIE = 1



Calculated Isotopomer Distribution for KIE=1.9

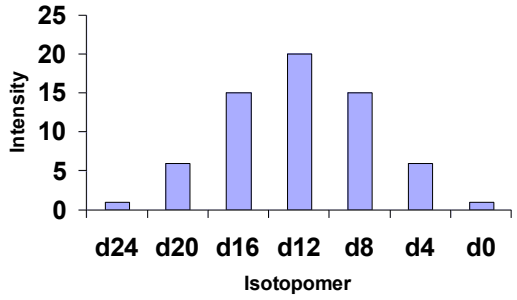


Experimental Isotopomer Distribution

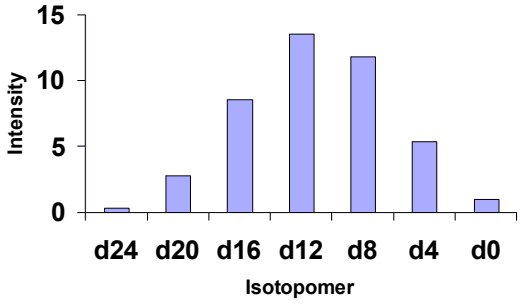


b) **C_{12} fraction**

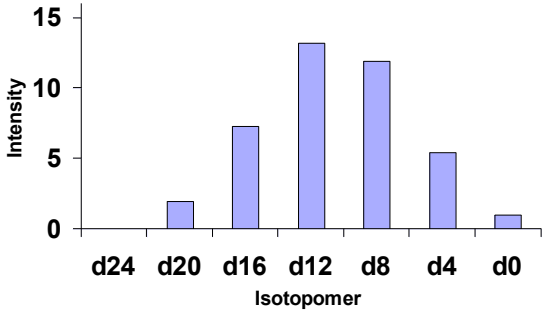
Calculated Isotopomer Distribution for KIE = 1



Calculated Isotopomer Ratio dn/d0 for KIE=1.9

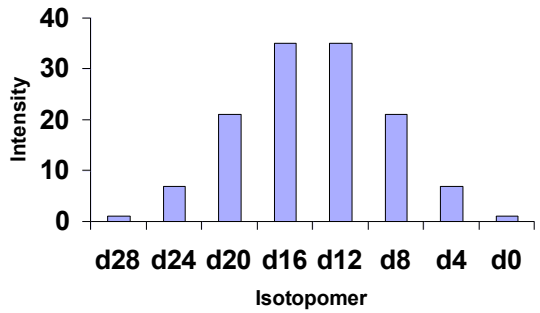


Experimental Isotopomer Distribution

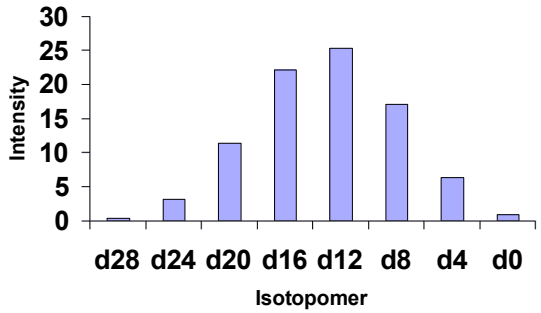


c) C_{14} fraction

Calculated Isotopomer Distribution for KIE=1



Calculated Isotopomer Distribution for KIE=1.9



Experimental Isotopomer Distribution