

Supplementary Material

Use of External Radical Sources in Flash Vacuum Pyrolysis to Facilitate Cyclodehydrogenation Reactions in PAHs

Aaron W. Amick* and Sara E. Martin

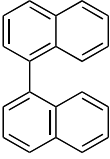
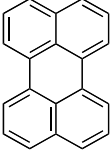
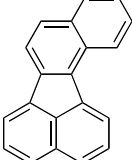
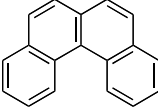
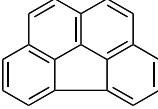
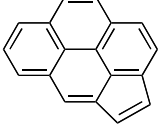
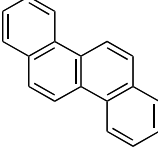
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General Experimental

All solvents and commercial chemicals were used without purification, unless otherwise stated. Proton NMR chemical shifts are reported in ppm downfield from tetramethylsilane with deuteriochloroform ($\delta = 7.26$ ppm) as the reference standard, unless otherwise specified. Carbon NMR shifts are reported in ppm downfield from tetramethylsilane with deuteriochloroform ($\delta = 77.16$ ppm) as the reference standard. Analysis and integration of ^1H -NMR and ^{13}C -NMR was accomplished using MestreC NMR software. Preparative thin layer chromatography was performed on 20 cm \times 20 cm Analtech Uniplate Taper plates, Alumina GF. For column chromatography, silica gel 32 – 63 μm was used. Gas Chromatograph-Mass Spectrometer (GC-MS) analysis was performed on a Thermo Finnigan Trace DSQ with electron impact ionization with a Restek Rtx-PCB (30 m \times 0.25 mm \times 0.25 μm film) column, and GC integrations were accomplished using the Avalon integration program. High-resolution mass spectrometry (HRMS) was performed by the Mass Spectrometry Center, Boston College. All Flash Vacuum Pyrolyses (FVPs) were done according to the procedure developed by Necula and Scott.¹ To ensure an accurate view of the product distributions limited purification was done on each sample. Typically samples were passed through a silica gel plug with dichloromethane as the eluent. Following the plug, samples were concentrated under reduced pressure and dried under high vacuum. These purifications provided better ^1H NMR spectra, however they did not remove higher molecular weight soluble polymers that were created during the pyrolysis and in some cases led to mass recoveries greater than 100%.

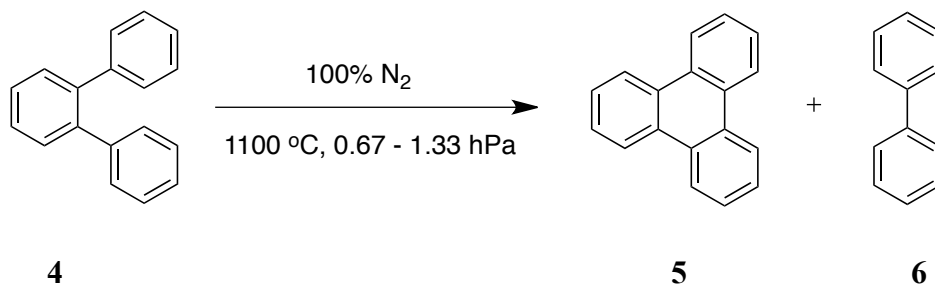
PAH used or Created in this Study	Compound Name and Reference for its ¹ H-NMR Spectrum
	1,1'-binaphthyl Ref. 2
	perylene Ref. 3
	benzo[j]fluoranthene Ref. 4
	benzo[c]phenanthrene Ref. 5
	benzo[ghi]fluoranthene Ref. 6
	cyclopenta[cd]pyrene Ref. 6
	chrysene Ref. 5

External Radical Source Introduction Method

Introduction of external radical was accomplished by splitting the nitrogen carrier gas into two streams that were regulated by flow meters. One flow meter was used for pure nitrogen gas, and the other regulated the flow of nitrogen gas through two reservoirs of the solvent used as the radical generator, connected in series. The pure nitrogen gas stream and the stream carrying the external radical source were combined and used as the carrier gas for FVP. The amount of solvent in the carrier gas (reported in mol%) was determined by capturing the solvent vapors in a liquid nitrogen cooled trap over a period of time. The solvent was removed, and its volume was measured to provide a lower limit for the amount of solvent per unit time. The Scienceware flow meters were calibrated to supply 961 mL/min of gas at a reading of 20 mm. Knowing both the volume of nitrogen gas and the amount of solvent collected per unit time, the mole fractions were calculated, assuming 24.47 L/mol for nitrogen gas.

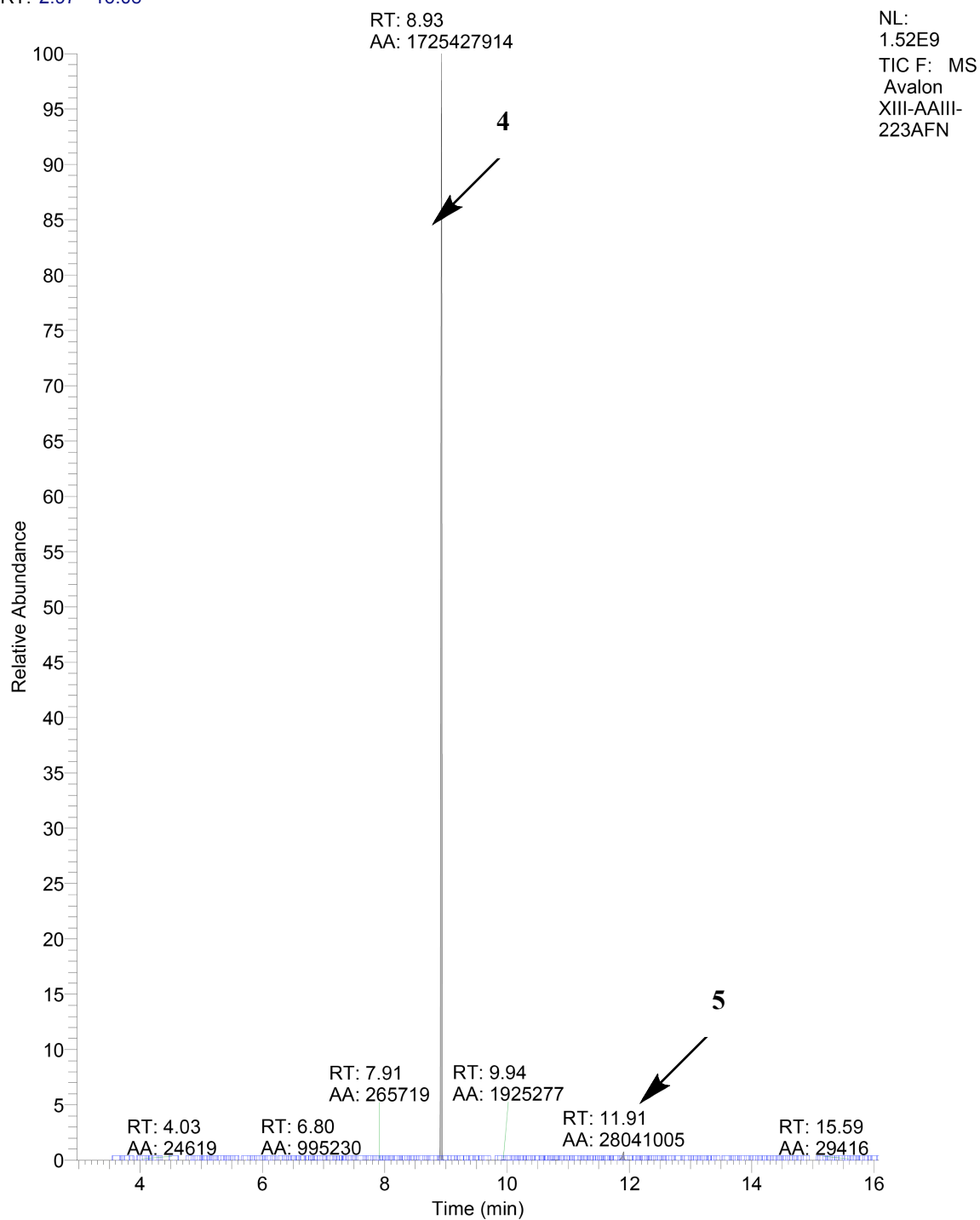
Meter Readings	Gas Diffuser/Sparge Used					
N ₂ /N ₂ Through Solvent	Hex (mL)/min	Hex (mol)/min	N ₂ (mol)/min	Total Moles/min	Mole Fraction Hex	Mole Fraction N ₂
5:15	0.71	0.005427958	0.039231712	0.044659671	12.2%	87.8%
10:10	0.38	0.002905104	0.039231712	0.042136817	6.9%	93.1%
15:05	0.12	0.000917401	0.039231712	0.040149114	2.3%	97.7%

Meter Readings	No Gas Diffuser/Sparge Used					
N ₂ /N ₂ Through Solvent	Hex (mL)/min	Hex (mol)/min	N ₂ (mol)/min	Total Moles/min	Mole Fraction Hex	Mole Fraction N ₂
10:10	0.32	0.002446404	0.039231712	0.041678116	5.9%	94.1%
15:05	0.17	0.001299652	0.039231712	0.040531364	3.2%	96.8%

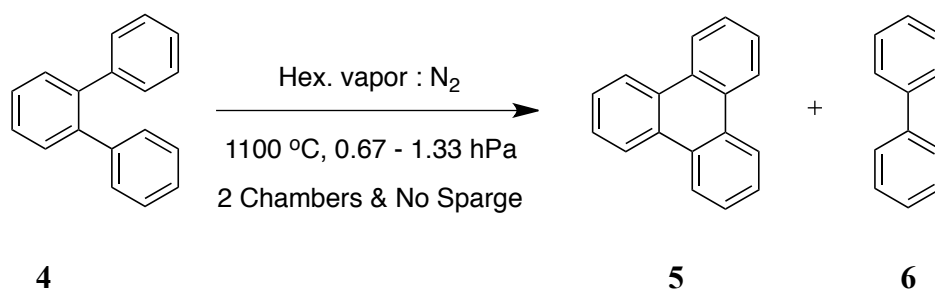


Flash vacuum pyrolysis was performed on 100 mg (0.435 mmol) of *o*-terphenyl (**4**) at 1100 °C with a steady flow of carrier gas with a composition of 100% pure nitrogen gas (final pressure 0.67 - 1.33 hPa) over 4-6 h as previously described.¹ The pyrolysis was accomplished in a quartz tube (length = 105.4 cm and interior diameter = 3.4 cm), in an electric oven (length = 61 cm). The crude pyrolysate was isolated from the cold trap and the quartz tube. GC/MS analysis of the crude pyrolysate was used to determine the product ratios of starting material **4** to triphenylene (**5**) and biphenyl (**6**). This pyrolysis yielded only trace amounts of triphenylene (**5**), with a mass recovery of 87 mg.

RT: 2.97 - 16.08



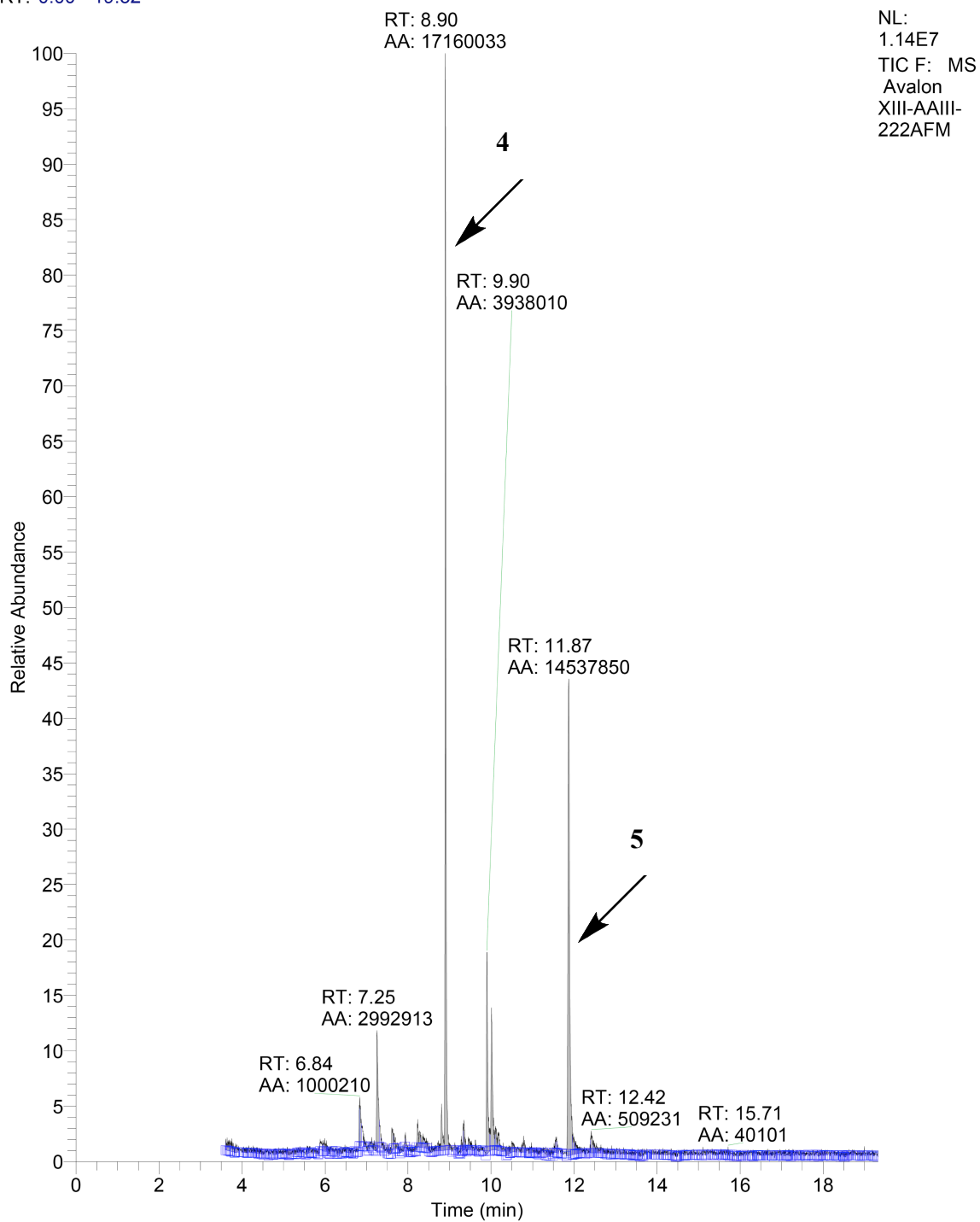
GC analysis of the crude product from the pyrolysis of *o*-terphenyl (**4**) at 1100 °C.



Flash vacuum pyrolysis was performed on 100 mg (0.435 mmol) of *o*-terphenyl (**4**) at 1100 °C with a steady flow of carrier gas with a composition of 3.2 – 5.9 mol% hexane vapor in nitrogen gas (final pressure 0.67 - 1.33 hPa) over 4-6 h utilizing two reservoirs and no sparge, as previously described.¹ The pyrolysis was accomplished in a quartz tube (length = 105.4 cm and interior diameter = 3.4 cm), in an electric oven (length = 61 cm). The crude pyrolysate was isolated from the cold trap and the quartz tube. GC/MS analysis of the crude pyrolysate was used to determine the product ratios of starting material **4** to triphenylene (**5**) and biphenyl (**6**). Mass recoveries for these reactions are shown below.

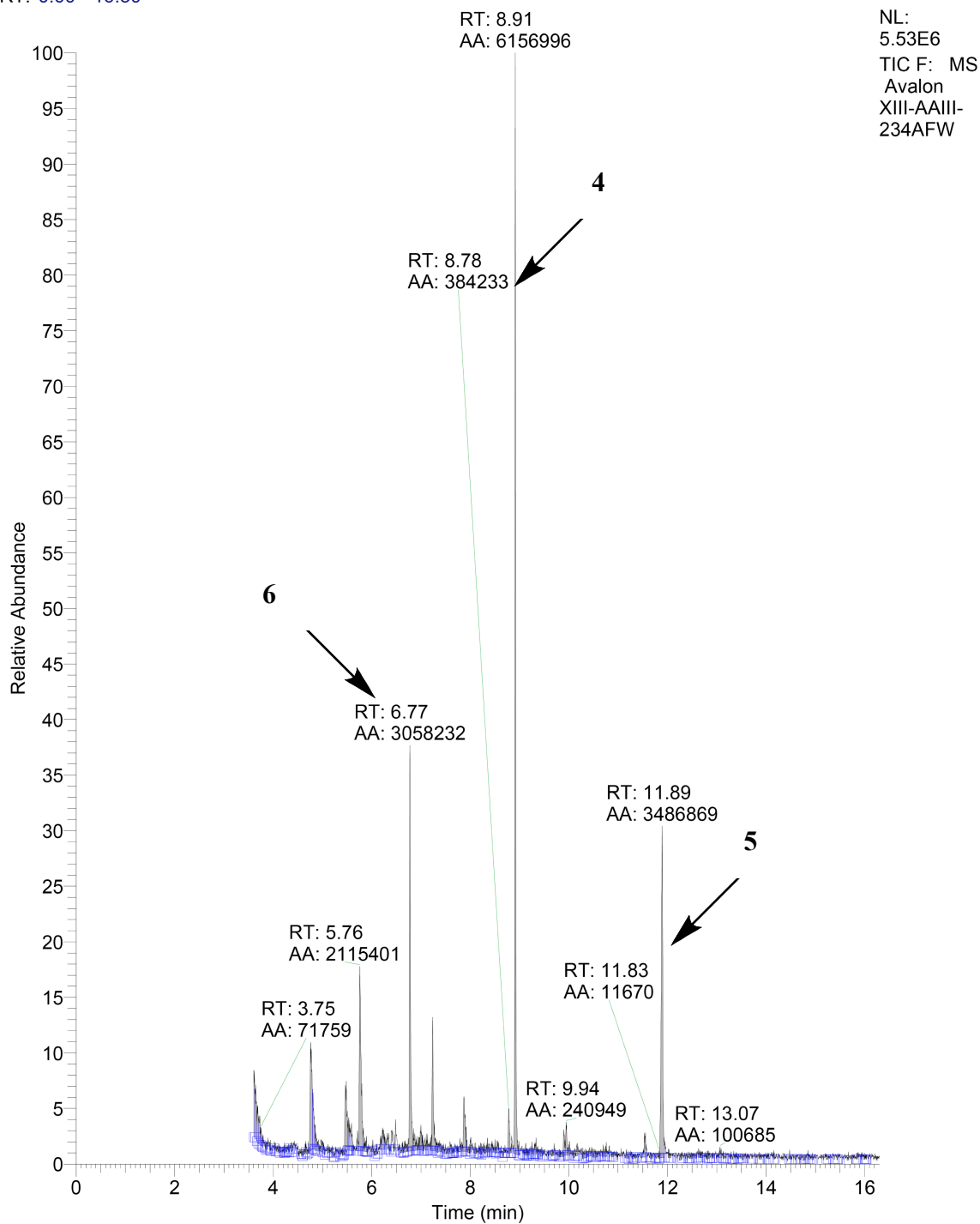
Mole Percent Hexane Vapor	Starting Amount	Mass Recovered
3.2	100 mg	49 mg
5.9	100 mg	95 mg

RT: 0.00 - 19.32

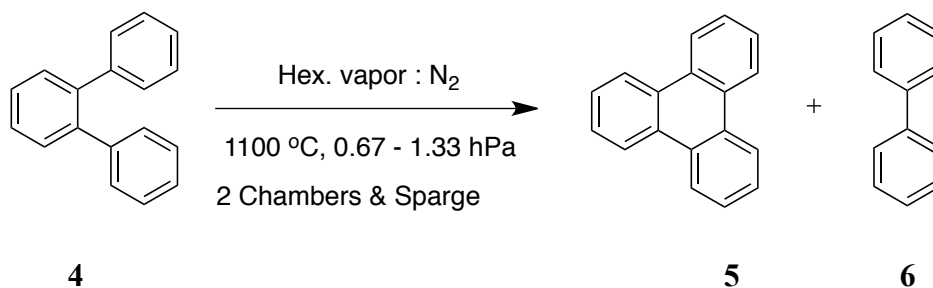


GC analysis of the crude product from the pyrolysis of *o*-terphenyl (**4**) with 3.2 mol% hexanes at 1100 °C.

RT: 0.00 - 16.30



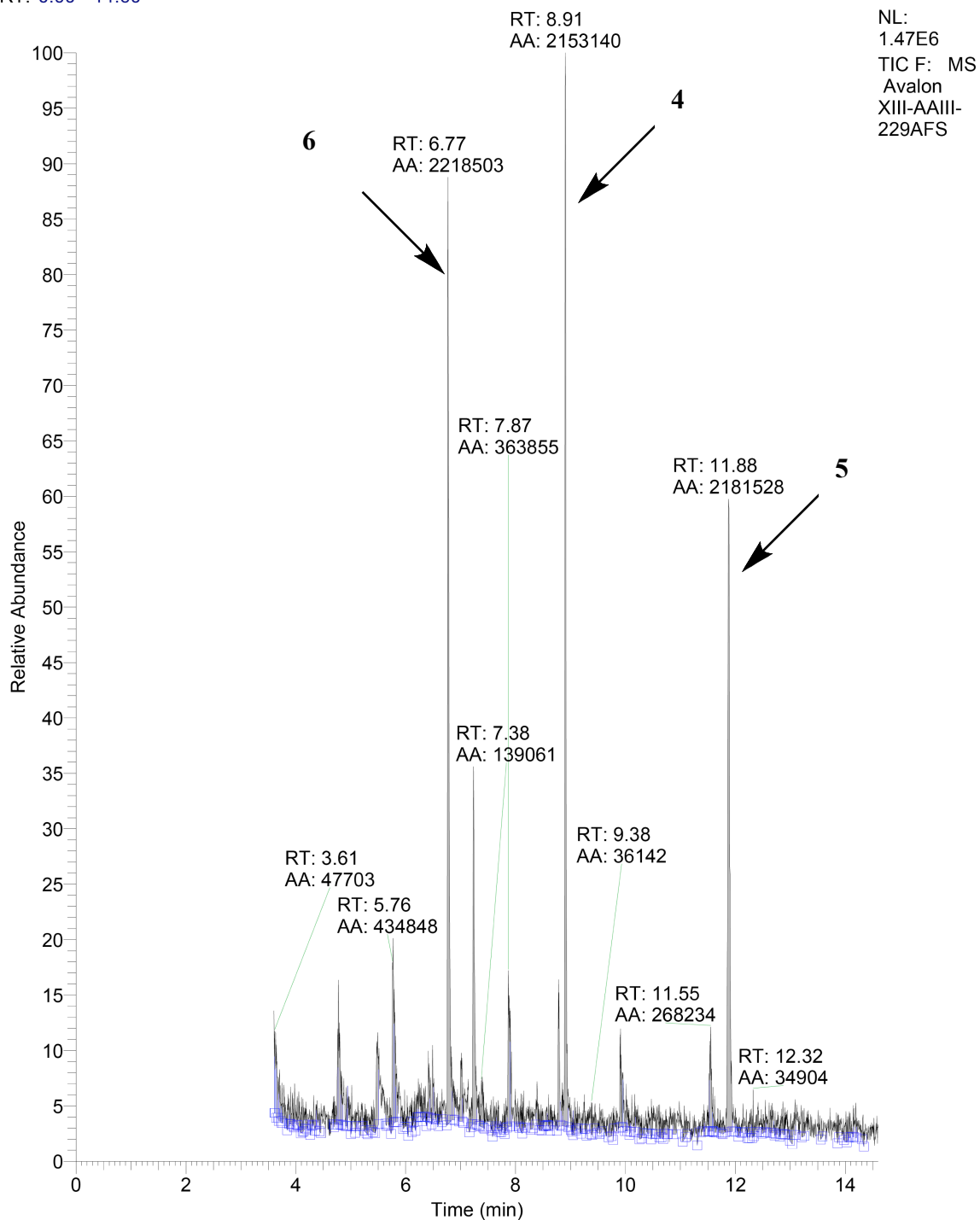
GC analysis of the crude product from the pyrolysis of *o*-terphenyl (**4**) with 5.9 mol% hexanes at 1100 °C.



Flash vacuum pyrolysis was performed on 100 mg (0.435 mmol) of *o*-terphenyl (**4**) at 1100 °C with a steady flow of carrier gas with a composition of 2.3 – 12.2 mol% hexane vapor in nitrogen gas (final pressure 0.67 -1.33 hPa) over 4-6 h utilizing two reservoirs and with a sparge, as previously described.¹ The pyrolysis was accomplished in a quartz tube (length = 105.4 cm and interior diameter = 3.4 cm), in an electric oven (length = 61 cm). The crude pyrolysate was isolated from the cold trap and the quartz tube. GC/MS analysis of the crude pyrolysate was used to determine the product ratios of starting material **4** to triphenylene (**5**) and biphenyl (**6**). Mass recoveries for these reactions are shown below.

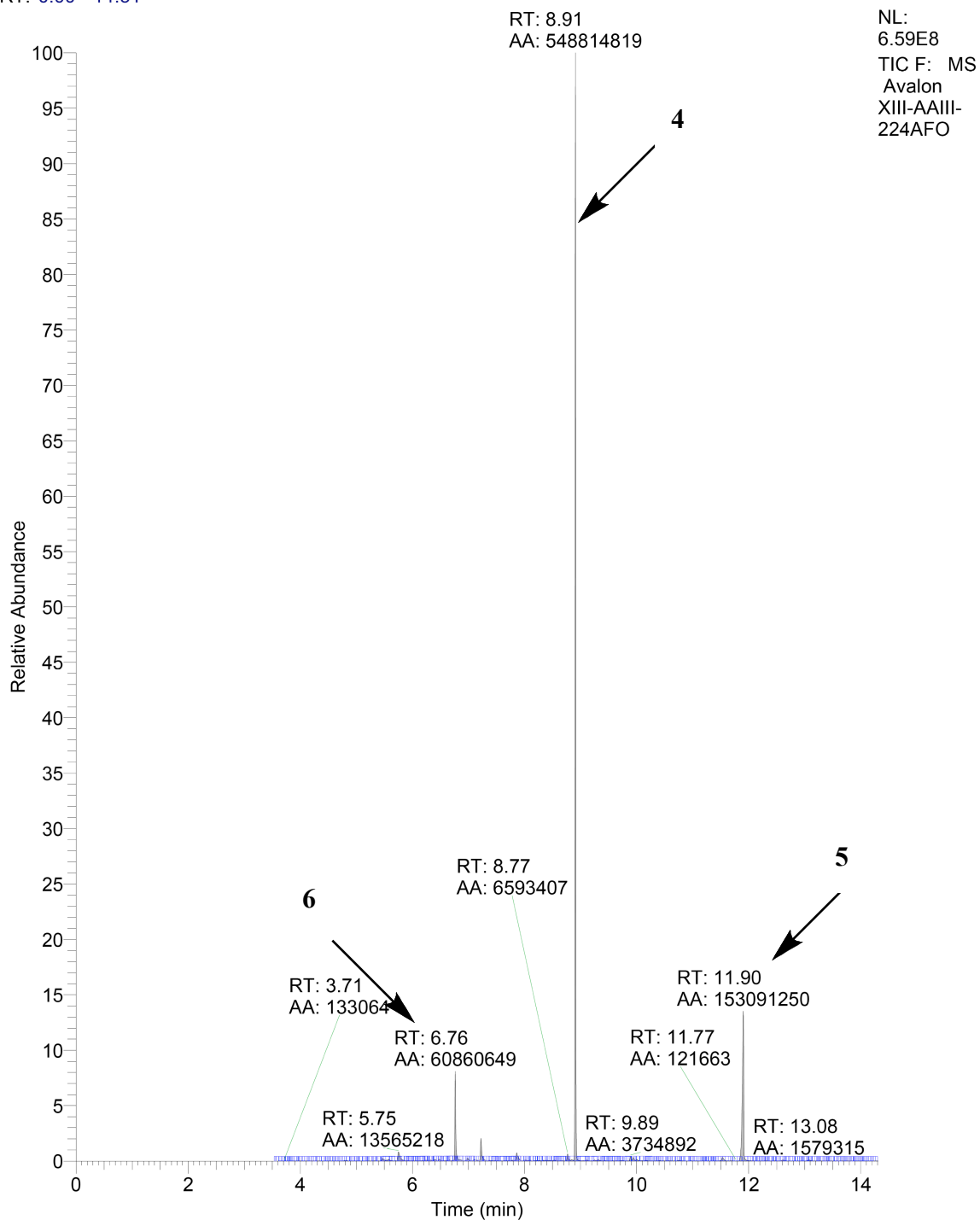
Mole Percent Hexane Vapor	Starting Amount	Mass Recovered
2.3	100 mg	127 mg
6.9	100 mg	99 mg
12.2	100 mg	147 mg

RT: 0.00 - 14.60



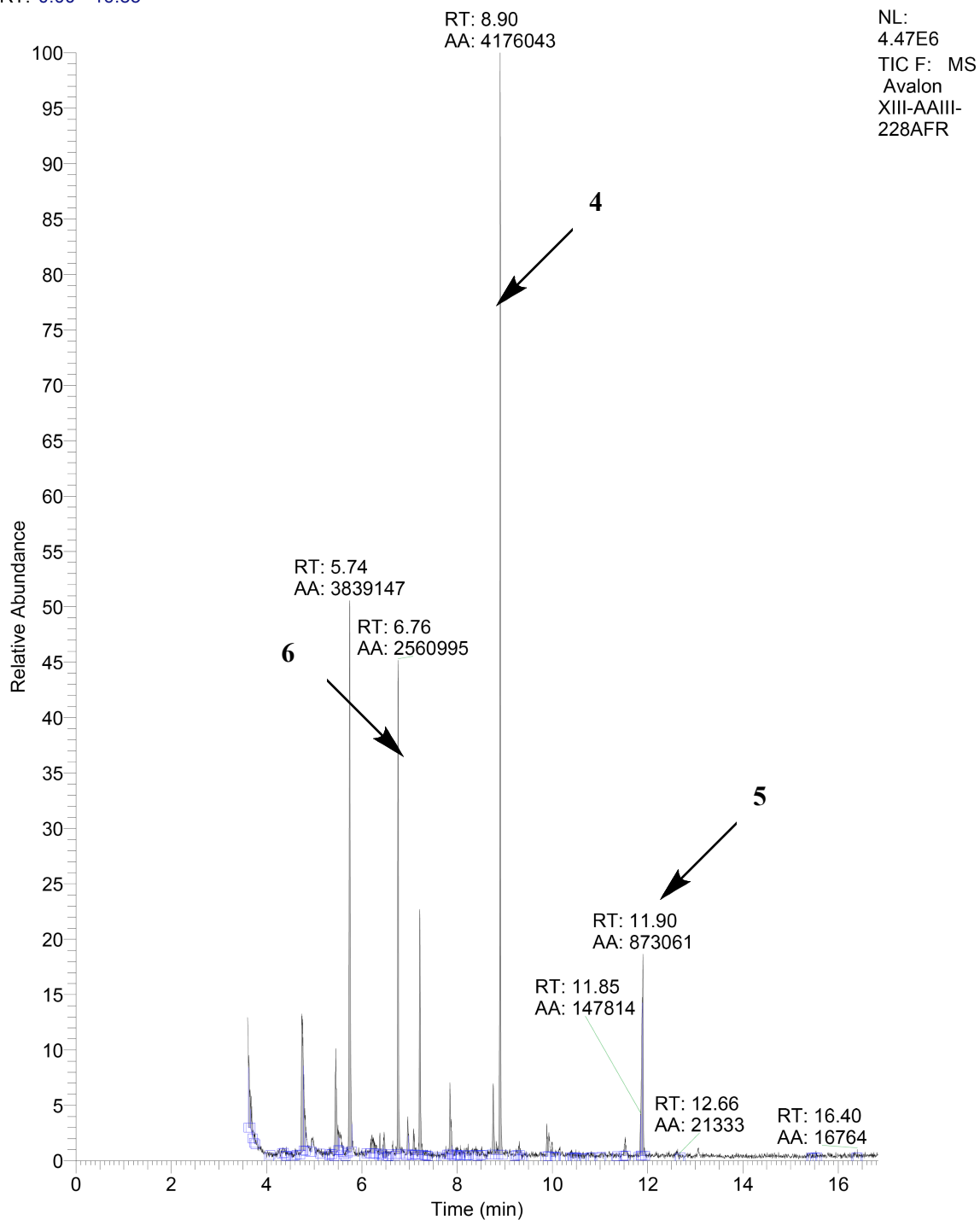
GC analysis of the crude product from the pyrolysis of *o*-terphenyl (4) with 2.3 mol% hexanes at 1100 °C.

RT: 0.00 - 14.31

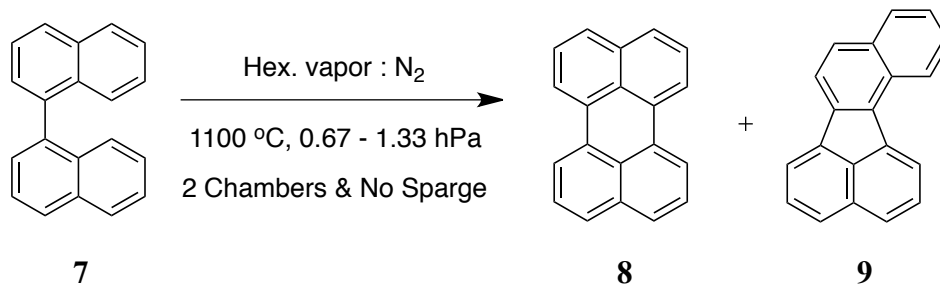


GC analysis of the crude product from the pyrolysis of *o*-terphenyl (**4**) with 6.9 mol% hexanes at 1100 °C.

RT: 0.00 - 16.83

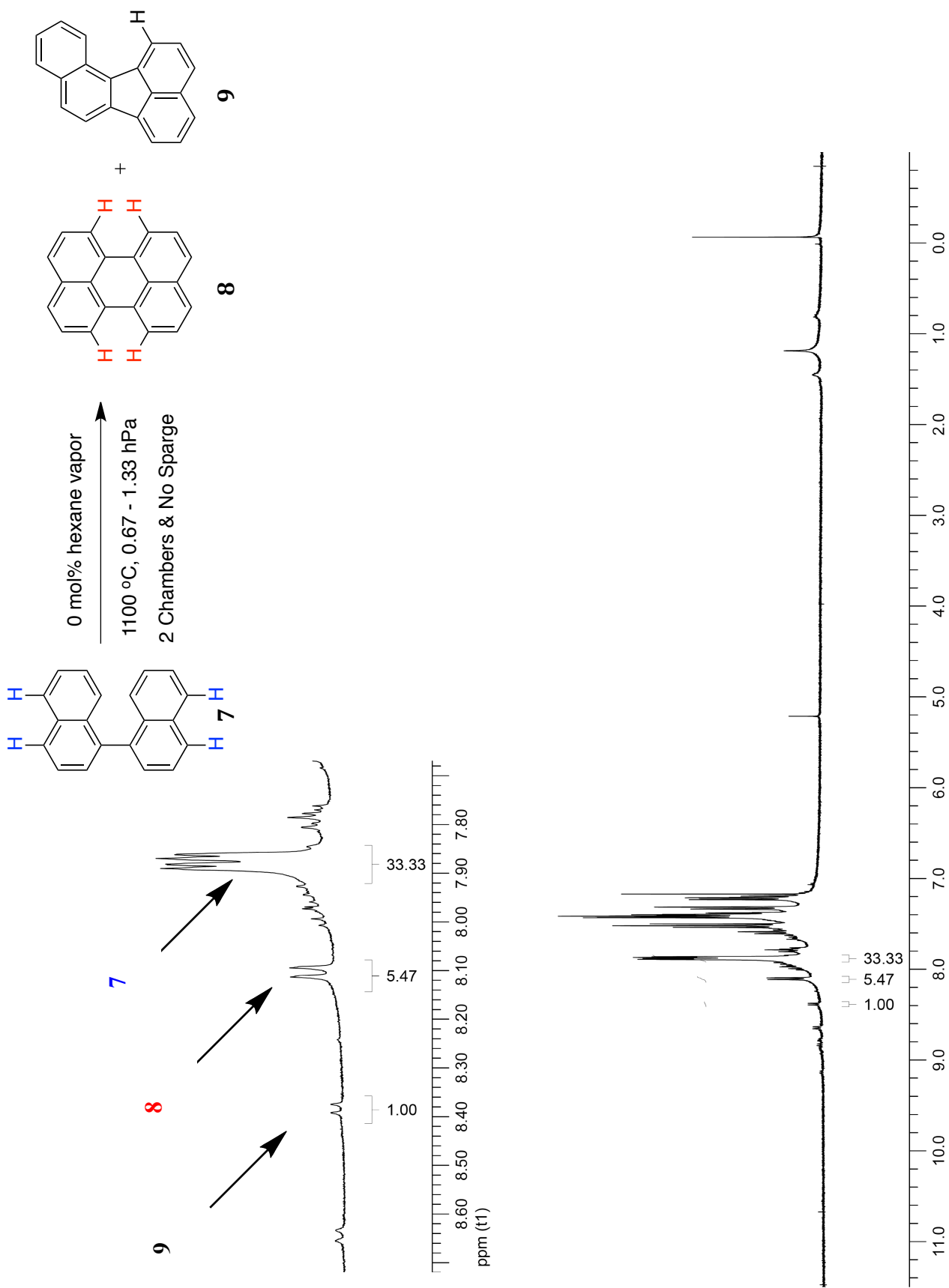


GC analysis of the crude product from the pyrolysis of *o*-terphenyl (**4**) with 12.2 mol% hexanes at 1100 °C.

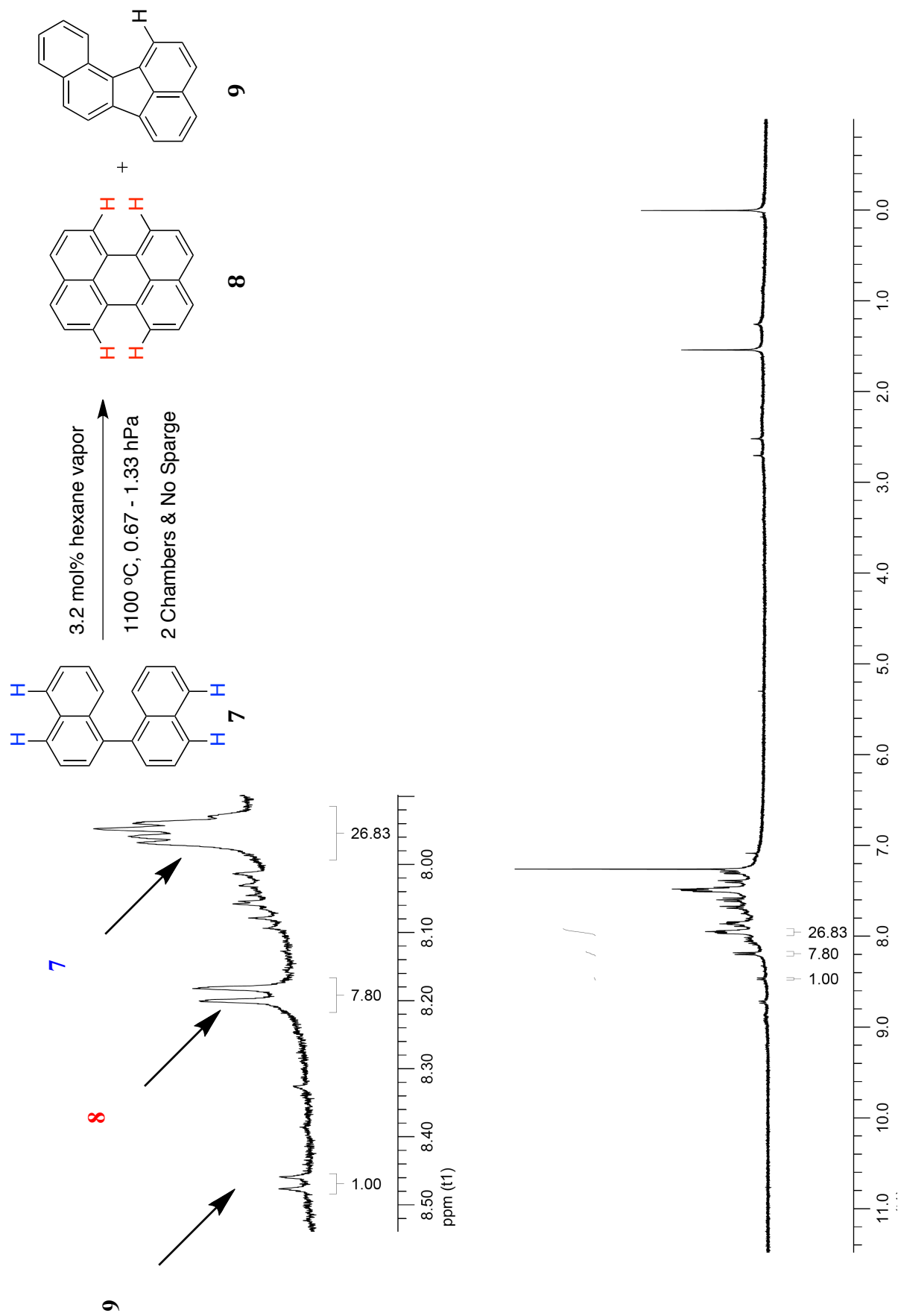


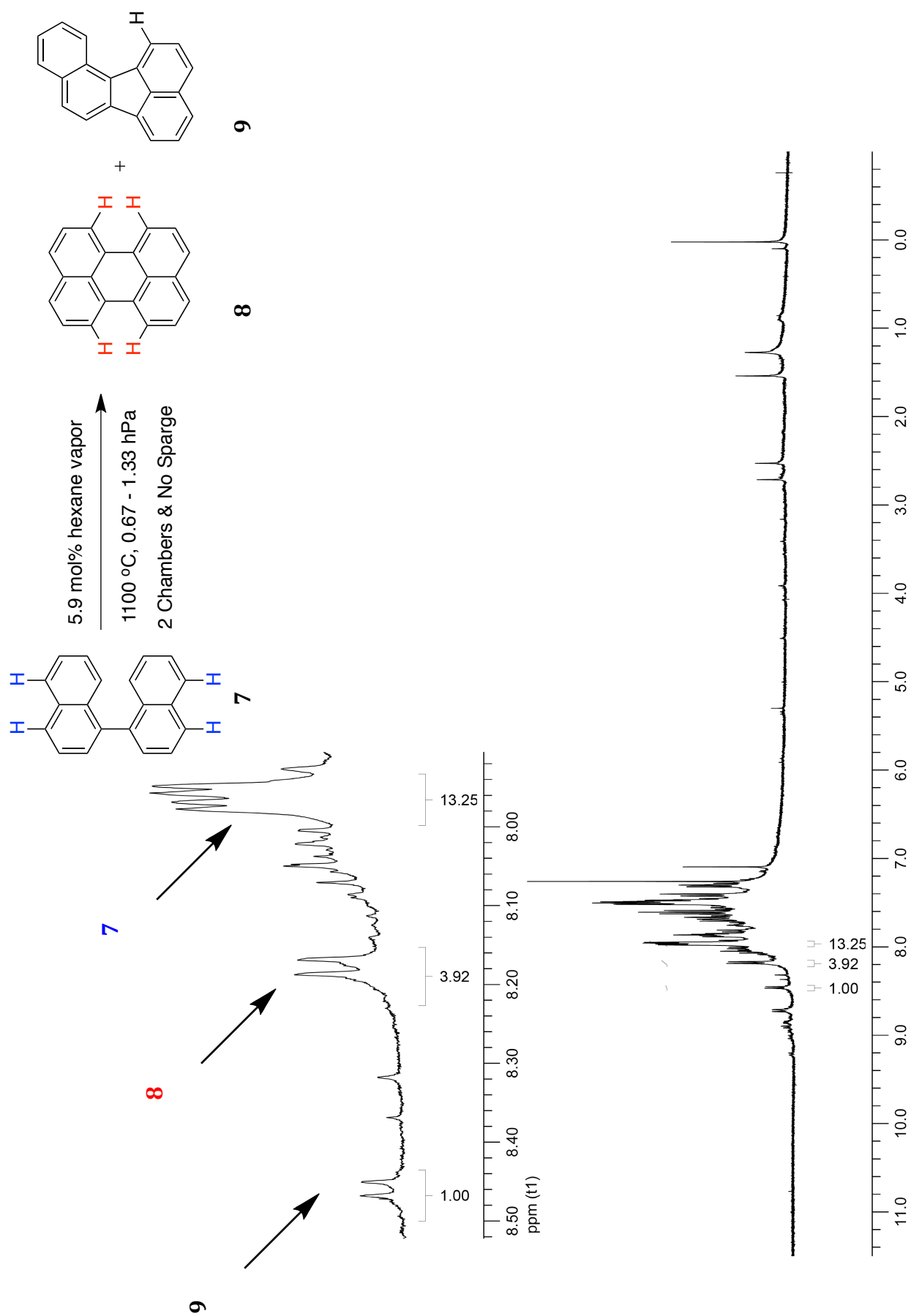
Flash vacuum pyrolysis was performed on 100 mg (0.394 mmol) of 1,1'-binaphthyl (**7**) at 1100 °C with a steady flow of carrier gas with a composition of 0 – 5.9 mol% hexane vapor in nitrogen gas (final pressure 0.67 - 1.33 hPa) over 4-6 h utilizing two reservoirs and with no sparge, as previously described.¹ The pyrolysis was accomplished in a quartz tube (length = 105.4 cm and interior diameter = 3.4 cm), in an electric oven (length = 61 cm). The crude pyrolysate was isolated from the cold trap and the quartz tube, and passed through a silica plug with dichloromethane. ¹H-NMR analysis of the crude pyrolysate was used to determine the product ratio of starting **7** to compounds **8** and **9**. The hydrogen atoms that were integrated to determine the ratios have been highlighted and color-coded on the spectra below. Mass recoveries for these reactions are shown below.

Mole Percent Hexane Vapor	Starting Amount	Mass Recovered
0	100 mg	86 mg
3.2	100 mg	100 mg
5.9	100 mg	92 mg

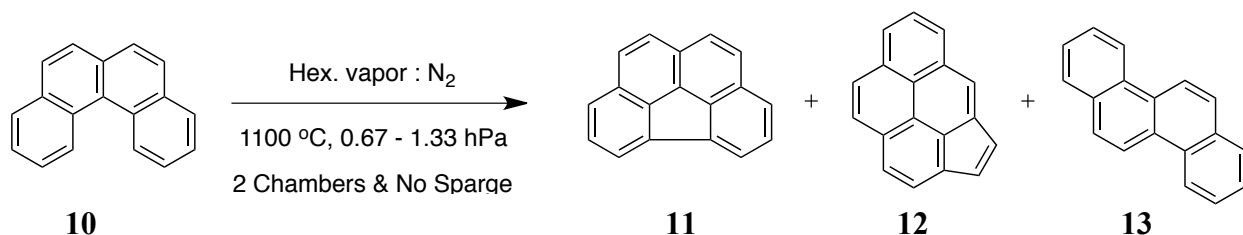


400 MHz $^1\text{H-NMR}$ spectrum of the crude product from the pyrolysis of 1,1'-binaphthyl (**7**) at 1100 °C in CDCl_3 at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.



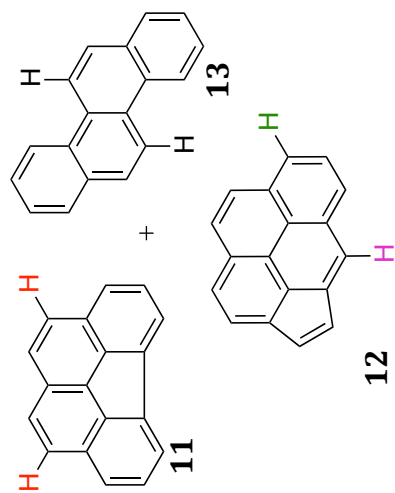


400 MHz $^1\text{H-NMR}$ spectrum of the crude product from the pyrolysis of 1,1'-binaphthyl (7) with 5.9 mol% hexanes vapor at 1100 °C in CDCl_3 at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.



Flash vacuum pyrolysis was performed on 40-80 mg (0.35 mmol) of benzo[*c*]phenanthrene (**10**) at 1100 °C with a steady flow of carrier gas with a composition of 0 – 5.9 mol% hexane vapor in nitrogen gas (final pressure 0.67 - 1.33 hPa) over 4-6 h utilizing two reservoirs and with no sparge, as previously described.¹ The pyrolysis was accomplished in a quartz tube (length = 105.4 cm and interior diameter = 3.4 cm), in an electric oven (length = 61 cm). The crude pyrolysate was isolated from the cold trap and the quartz tube and passed through a silica plug with dichloromethane. ¹H-NMR analysis of the crude pyrolysate was used to determine the ratio of **10** to **11**, **12**, and **13**. The hydrogens that were integrated to determine the product ratios have been highlighted and color-coded on the spectra below. Mass recoveries for these reactions are shown below.

Mole Percent Hexane Vapor	Starting Amount	Mass Recovered
0	40 mg	39 mg
3.2	80 mg	80 mg
5.9	80 mg	109 mg

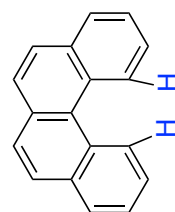


0 mol%
hexane vapor

1100 °C

0.67 - 1.33 hPa

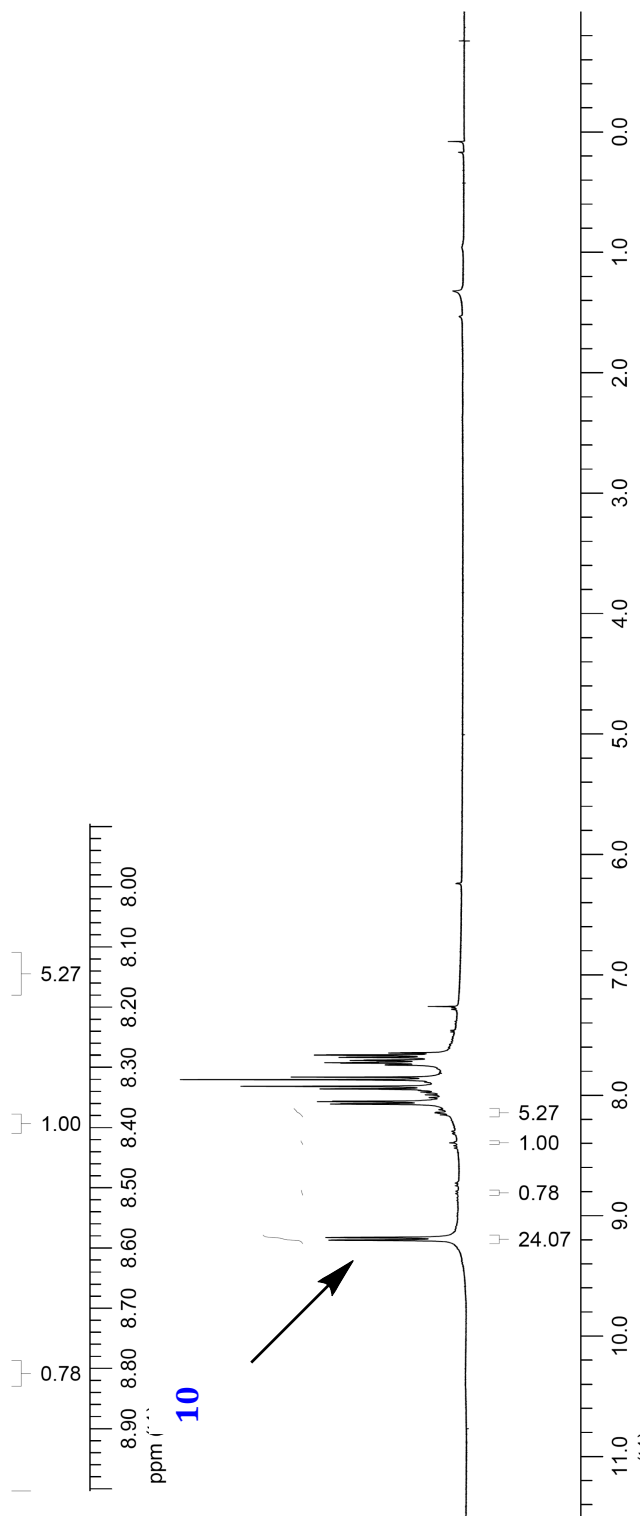
2 Chambers
& No Sparge



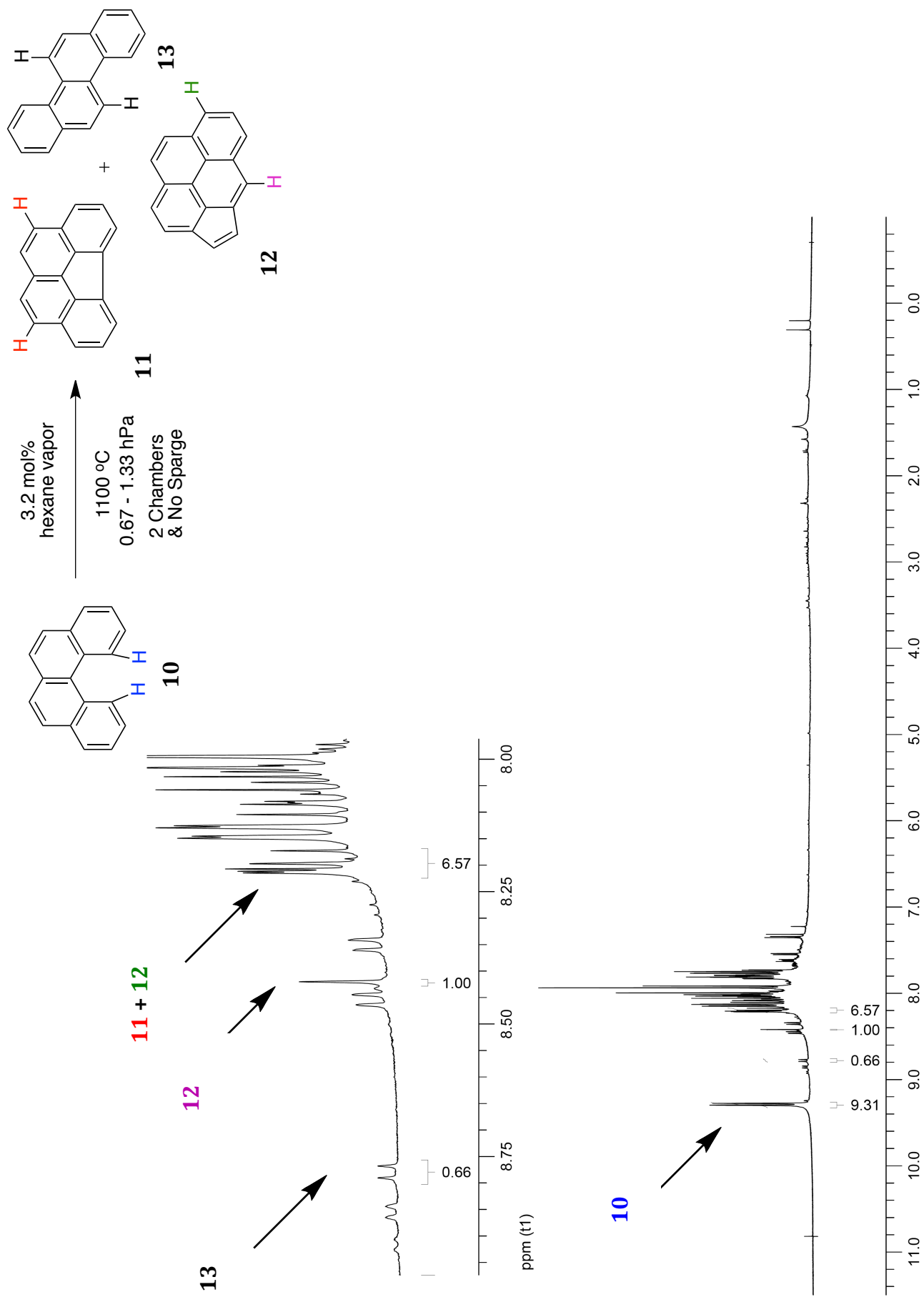
11 + 12

12

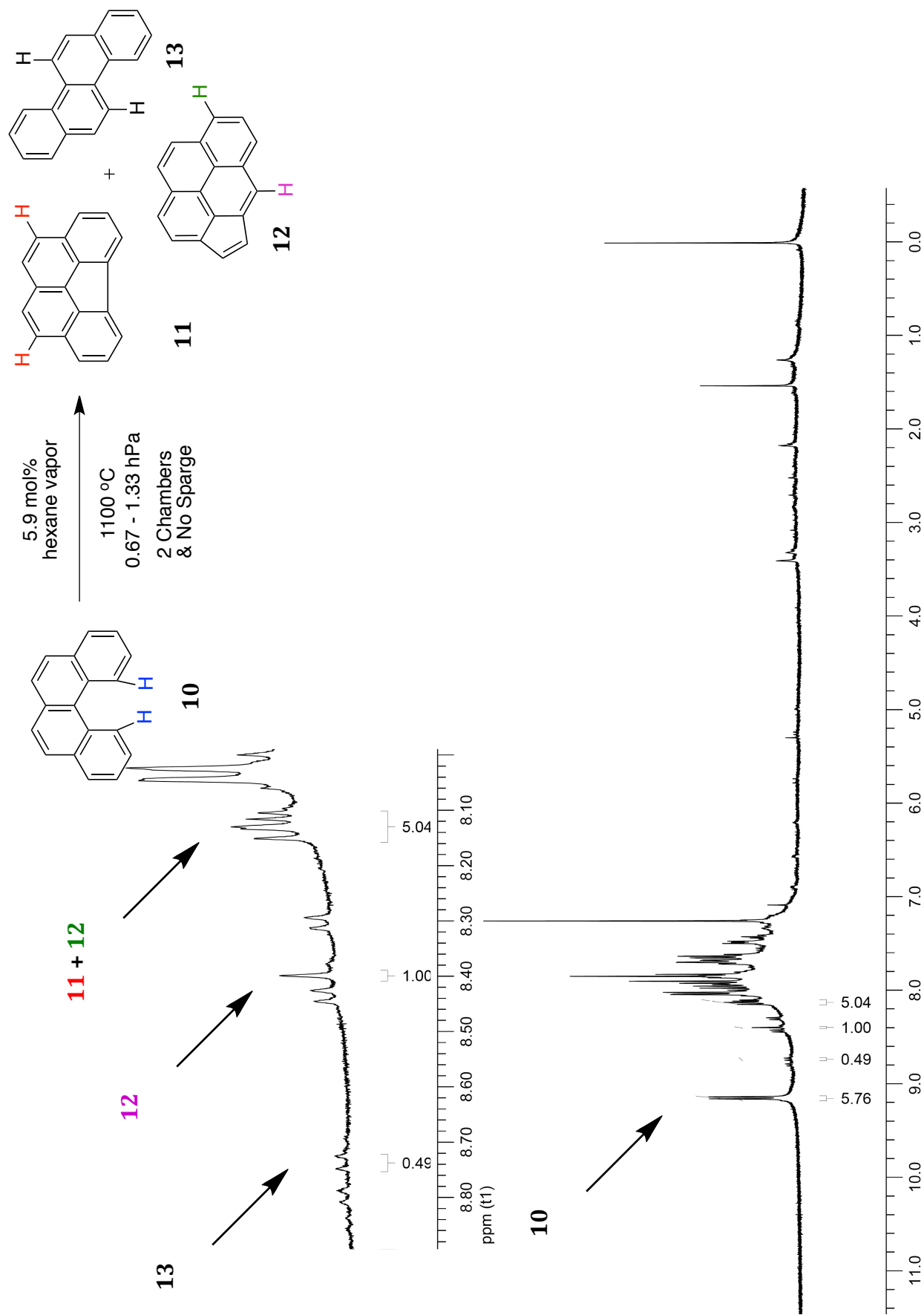
13



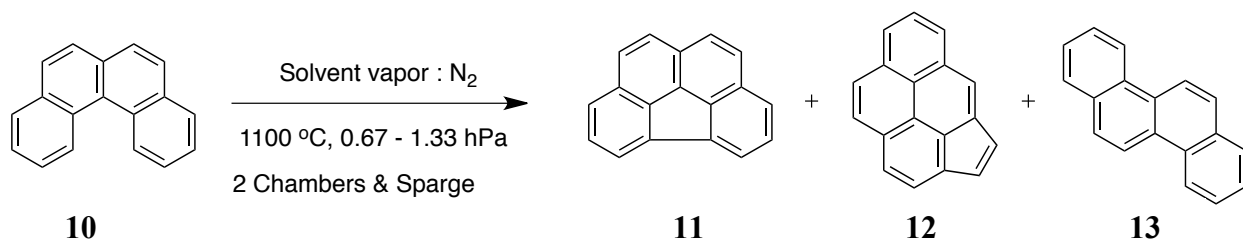
400 MHz ¹H-NMR spectrum of the crude product from the pyrolysis of benzo[*c*]phenanthrene (**10**) at 1100 °C in CDCl₃ at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.



400 MHz ¹H-NMR spectrum of the crude product from the pyrolysis of benzo[c]phenanthrene (**10**) with 3.2 mol% hexanes vapor at 1100 °C in CDCl₃ at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.



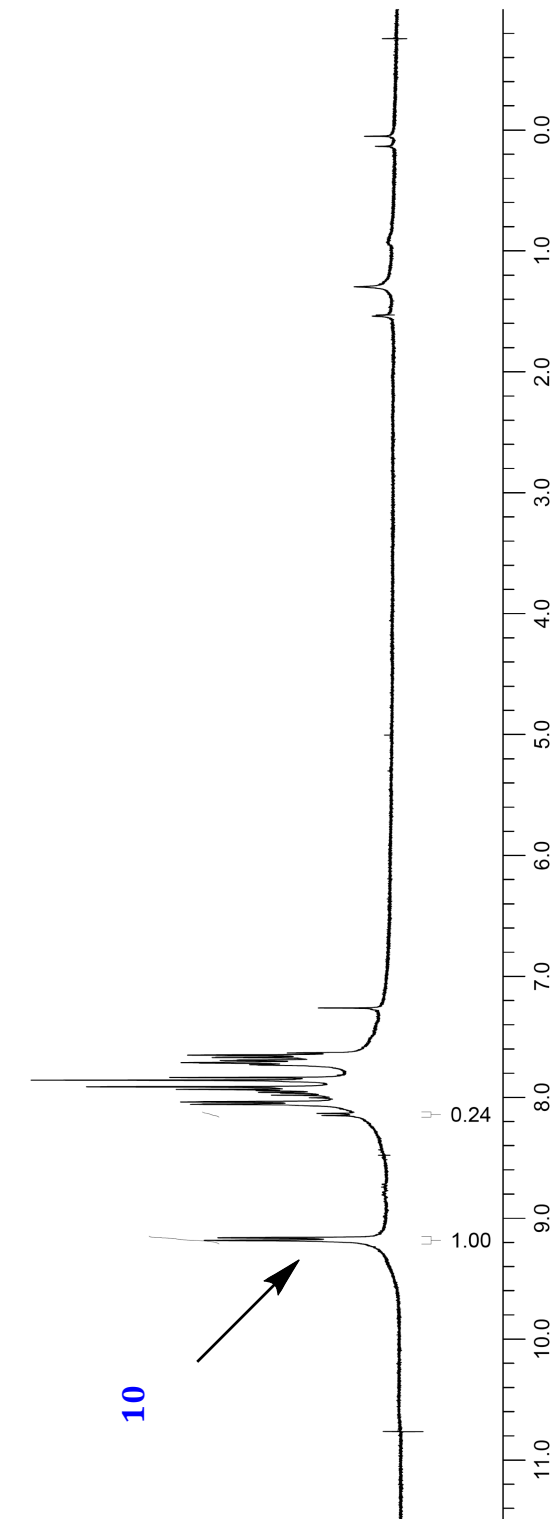
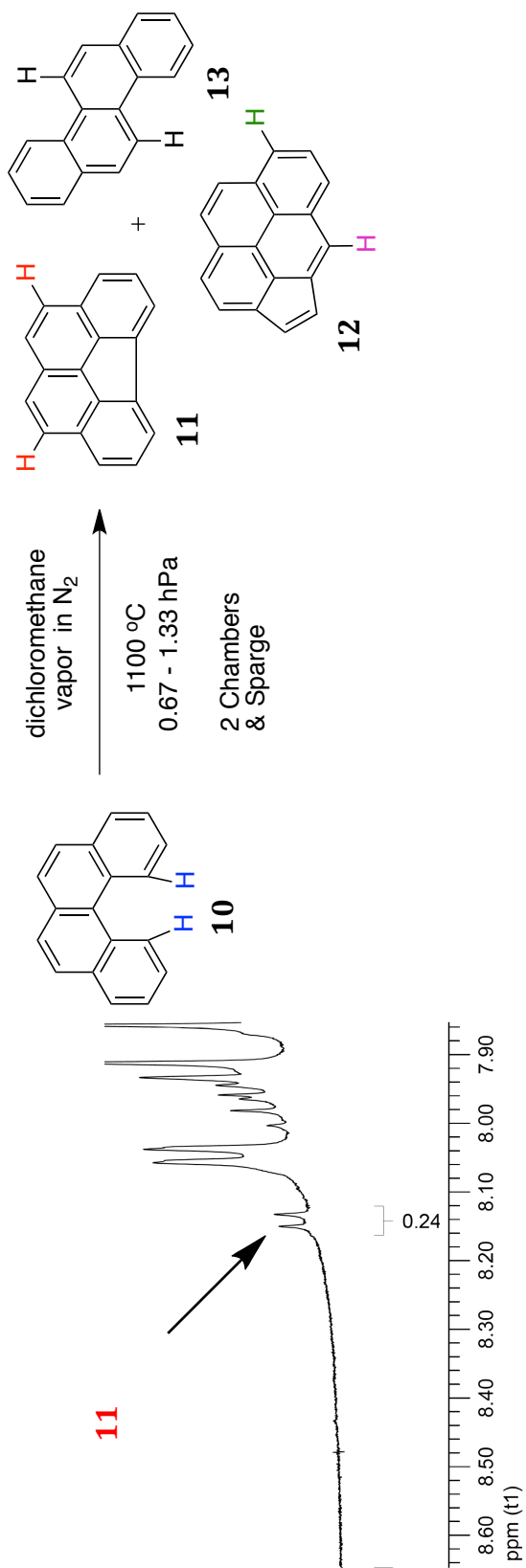
400 MHz $^1\text{H-NMR}$ spectrum of the crude product from the pyrolysis of benzo[*c*]phenanthrene (**10**) with 5.9 mol% hexanes vapor at 1100 °C in CDCl_3 at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.

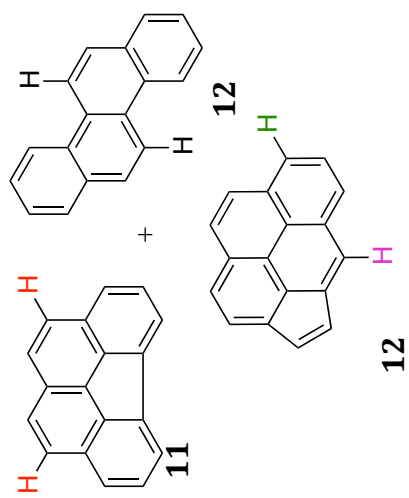


Flash vacuum pyrolysis was performed on 40 mg (0.18 mmol) of benzo[*c*]phenanthrene (**10**) at 1100 °C with a steady flow of nitrogen through the solvent reservoirs (≈ 175 mL/min) and a flow rate of pure nitrogen in the other stream of 786 mL/min (final pressure 0.67 - 1.33 hPa) over 4-6 h utilizing two reservoirs and with sparge, as previously described.¹ The pyrolysis was accomplished in a quartz tube (length = 105.4 cm and interior diameter = 3.4 cm), in an electric oven (length = 61 cm). Four solvents were investigated: dichloromethane, nitromethane, trimethyl orthoformate, and methyl-*tert*-butyl ether. The crude pyrolysate was isolated from the cold trap and the quartz tube and passed through a silica plug with dichloromethane. ¹H-NMR analysis of the crude pyrolysate was used to determine the ratio of **10** to **11**, **12**, and **13**. The hydrogens that were integrated to determine the product ratios have been highlighted and color-coded on the spectra below. The mole percent for each solvent was calculated and listed in the table below as well as the mass recoveries of each reaction.

Solvent Identity	Solvent (mL)/min	Solvent (mol)/min	N ₂ (mol)/min	Total (mol)/min	Mol % Solvent
nitromethane	0.015	0.0003	0.0392	0.0395	0.71%
trimethyl orthoformate	0.65	0.0059	0.0392	0.0452	13.15%
dichloromethane	0.39	0.0061	0.0392	0.0453	13.47%
methyl- <i>tert</i> -butyl ether	0.31	0.0026	0.0392	0.0418	6.23%

Solvent Identity	Starting Amount	Mass Recovered
nitromethane	40 mg	32 mg
trimethyl orthoformate	40 mg	64 mg
dichloromethane	40 mg	32 mg
methyl- <i>tert</i> -butyl ether	40 mg	69 mg

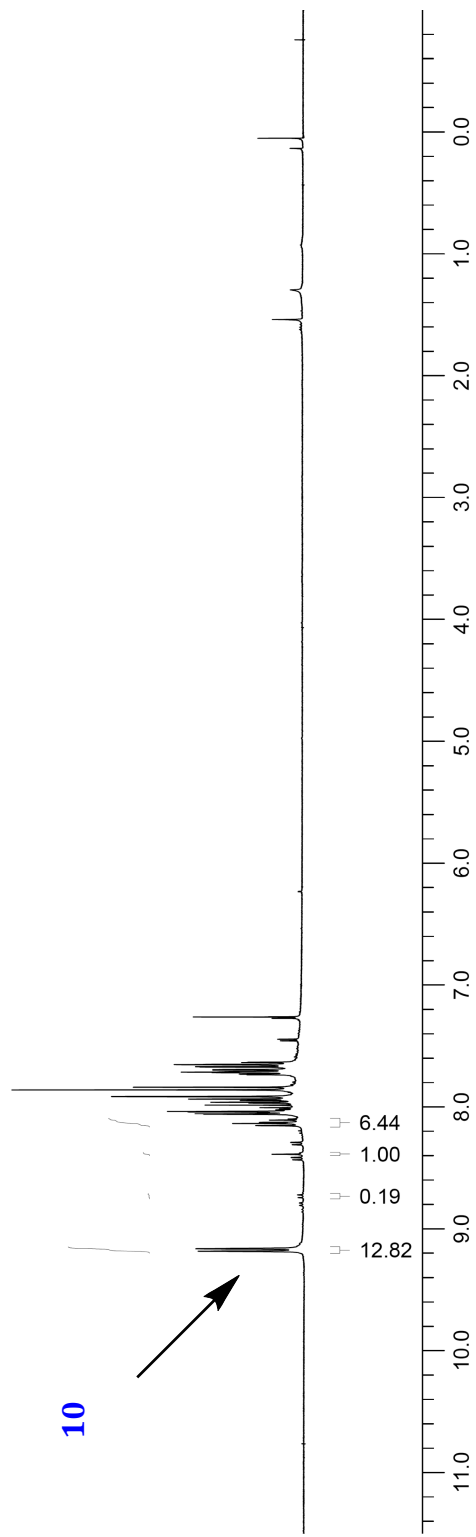
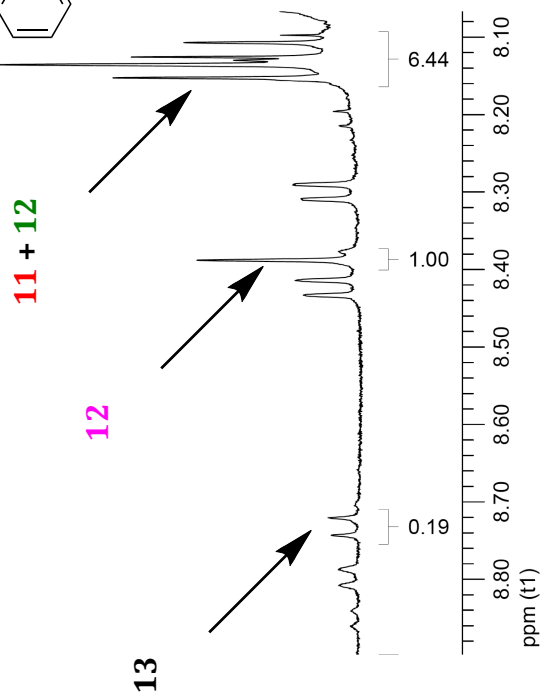
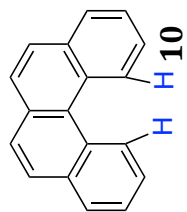




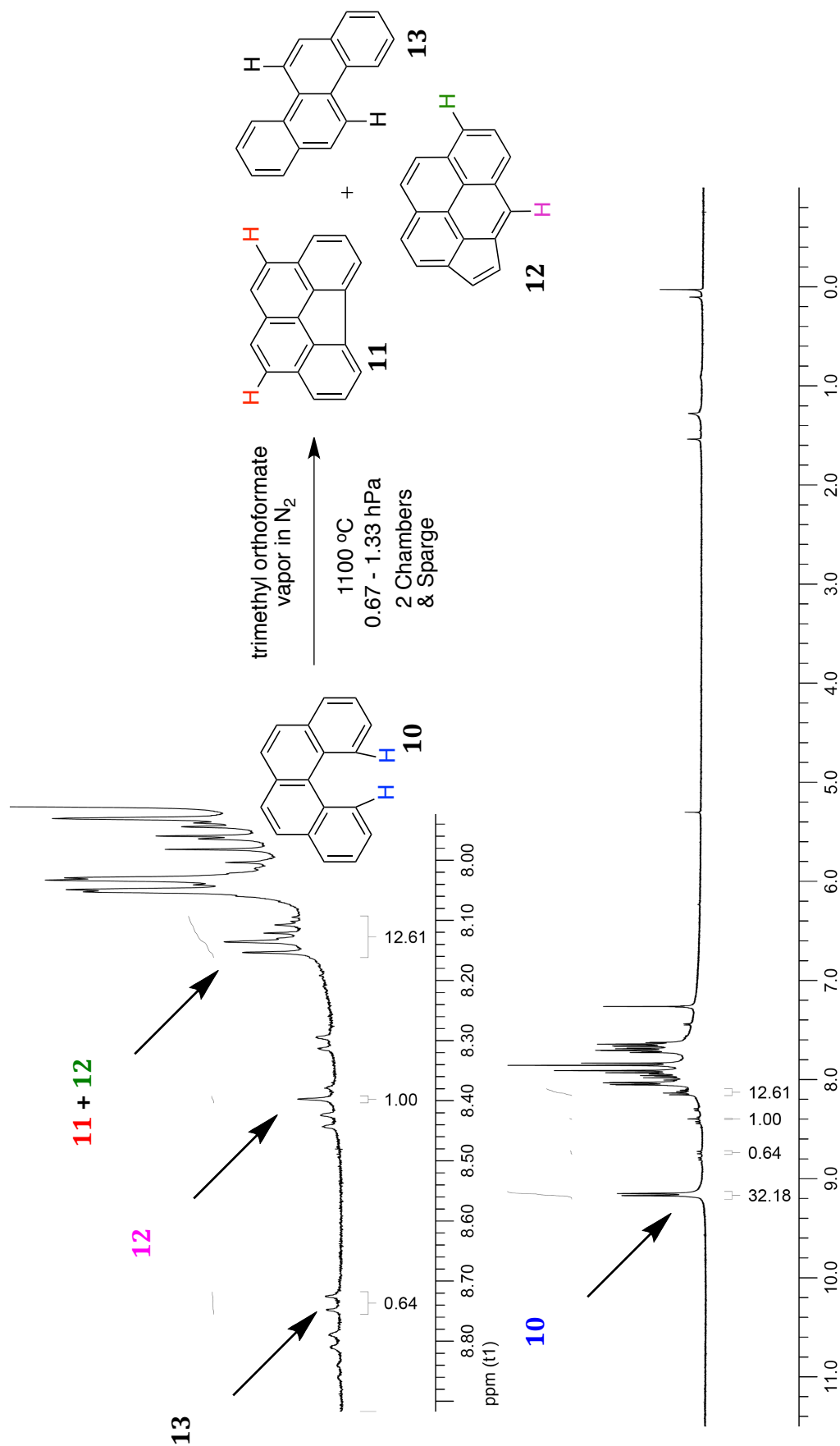
nitromethane
vapor in N₂

1100 °C
0.67 - 1.33 hPa

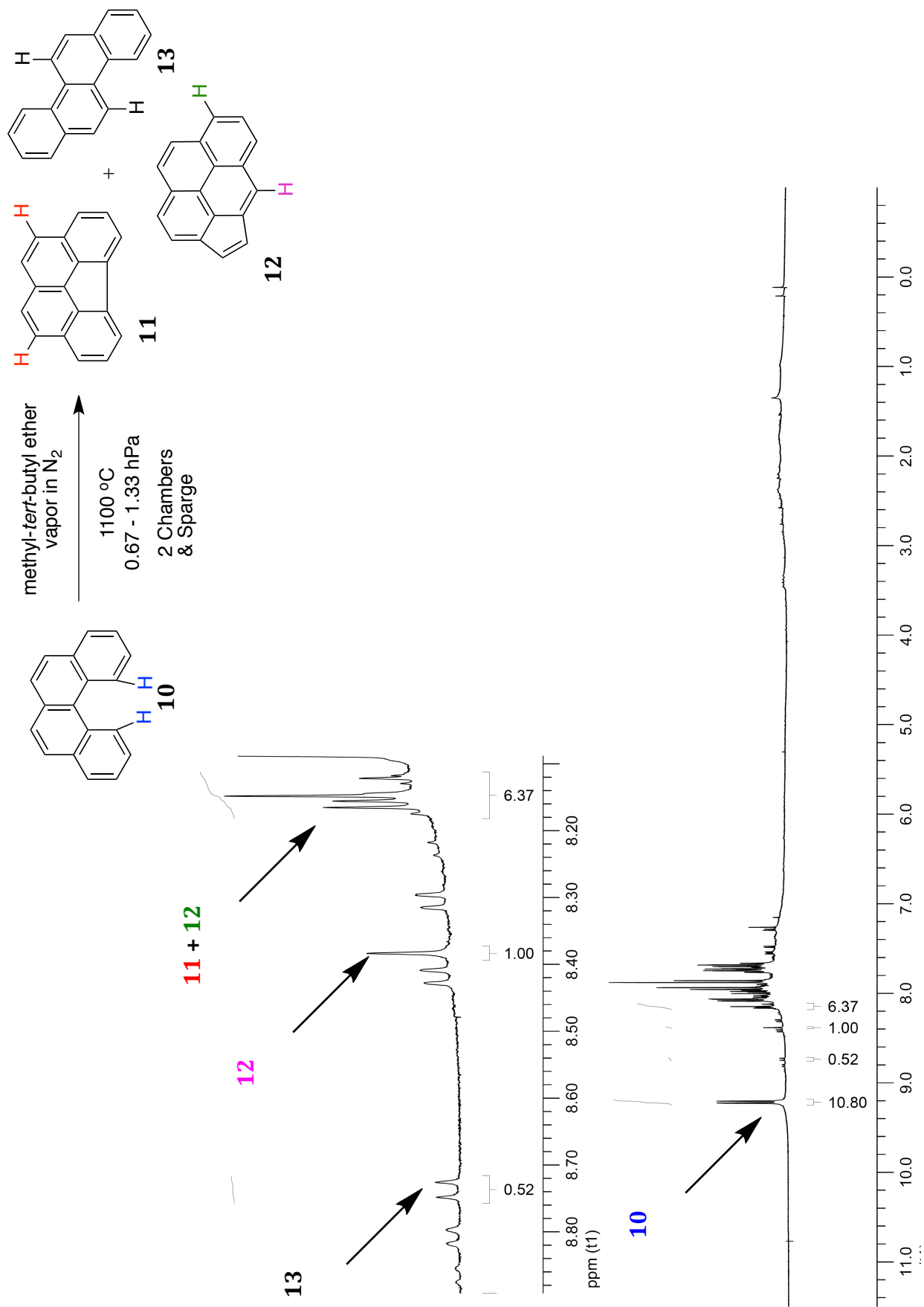
2 Chambers
& Sparge



400 MHz ¹H-NMR spectrum of the crude product from the pyrolysis of benzo[c]phenanthrene (**10**) with N₂-nitromethane vapor at 1100 °C in CDCl₃ at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.



400 MHz ¹H-NMR spectrum of the crude product from the pyrolysis of benzo[*c*]phenanthrene (10) with N₂-trimethyl orthoformate vapor at 1100 °C in CDCl₃ at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.



400 MHz ¹H-NMR spectrum of the crude product from the pyrolysis of benzo[*c*]phenanthrene (**10**) with N₂-methyl-*tert*-butyl ether vapor at 1100 °C in CDCl₃ at 25 °C. The hydrogens that are labeled with an arrow correspond to the colored hydrogens on the structures provided.

References:

- (1) A. Necula, L. T. Scott, *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65.
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- (3) R. A. Begum, N. Chanda, T. V. V. Ramakrishna, P. R. Sharp, *J. Am. Chem. Soc.* **2005**, *127*, 13494.
- (4) J. E. Rice, Z. W. Cai, *J. Org. Chem.* **1993**, *58*, 1415.
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