β-Chlorovinylsilanes as Masked Alkynes in Oligoyne Assembly: Synthesis of the First Aryl-End-Capped Dodecayne

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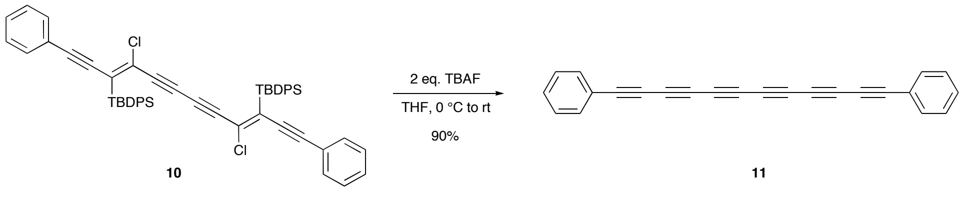
Supporting Information II

β-Chlorovinylsilanes in the Synthesis of Lower Order Oligoynes: Synthesis of Hexaynes

Whilst the dodecayne product **9** exhibited very poor stability, which precluded its isolation, the β-chlorovinylsilane methodology outlined in the paper can be used to generate lower oligoynes, specifically hexaynes, which are much more readily isolated and characterised. We have prepared a range of hexaynes with both aryl and silyl end-caps using this methodology. The syntheses of phenyl-end-capped hexayne **11** and triisopropylsilyl-end-capped hexayne **13** are illustrative:

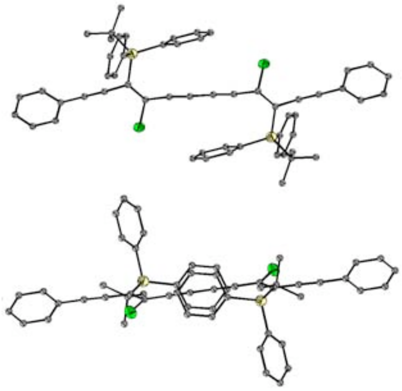
1,12-Diphenyldodeca-1,3,5,7,9,11-hexayne (11)



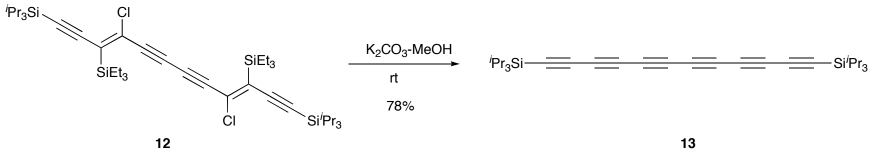
TBAF (0.19 mL of a 1 M solution in THF, 0.186 mmol) was added at 0 °C to a solution of masked hexayne **10** (79 mg, 0.093 mmol) in THF (1.5 mL). After 10 min, the resulting solution was warmed to rt and stirred for 20 min. Concentration of the residue under reduced pressure followed by purification of the residue through a short silica column (eluent: hexane) afforded hexayne **11** as an orange solid (25 mg, 90%); R_f = 0.29 (hexane); UV-Vis (CH_2Cl_2): 301 (210691), 319 (224595), 336 (252436), 353 (144683), 394 (22441), 426 (20247), 464 (10155); ν_{max}(Nujol)/cm^{-1} 2920s, 2853s, 2172m (C≡C), 2157m (C≡C), 1461s, 1377m, 1174w, 997w, 753m, 722w; δ_H(300 MHz; $CDCl_3$) 7.34 (4H, app t, *J* 7.2, Ph*H*), 7.42 (2H, t, *J* 7.4, Ph*H*), 7.54 (4H, dd, *J* 7.0, 1.5, Ph*H*); δ_c(75 MHz; $CDCl_3$) 62.5 (quat. C, *C*≡C), 63.6 (quat. C, *C*≡C), 64.6 (quat. C, *C*≡C), 67.2 (quat. C, *C*≡C), 74.3 (quat. C, *C*≡C), 77.4 (quat. C, *C*≡C), 120.1 (quat. C, *ipso* Ph), 128.6 (CH, Ph), 130.3 (CH, Ph), 133.4 (CH, Ph); *m/z* (EI) 298 (M^+, 100%), 149 (8), 84 (18), 69 (6), 43 (7); HRMS (EI) Found $(M)^+$ 298.0788. $C_{24}H_{10}$ requires $(M)^+$, 298.0782. Data were in agreement with those reported in the literature.[1,2]

The masked hexayne precursor **10** was prepared according to the methodology described in this paper and previously by us.[3] Data for **10**: m. p. 199-201 °C (from hexane); R_f = 0.29 (hexane/Et_2O 10:1); Anal Calcd for $C_{56}H_{48}Cl_2Si_2$: C, 79.31; H, 5.70. Found: C, 79.35; H, 5.49; UV-Vis (CH_2Cl_2) 383 (51752); 401 (48126); 428 (39624); ν_{max}(Nujol)/cm^{-1} 3070m, 2924s, 2187m (C≡C), 1596w, 1503w, 1462s, 1428m, 1377s, 1296w, 1190w, 1110s, 1025w, 998w, 936w, 891w, 848w, 819m, 756m, 741m, 699s, 688s; δ_H(300 MHz; $CDCl_3$) 1.19 (18H, s, SiC(CH_3)$_3$), 7.26-7.39 (18H, stack, Ph*H*), 7.43-7.49 (4H, stack, Ph*H*), 7.58-7.65 (8H, stack, Ph*H*); δ_C(75 MHz; $CDCl_3$) 19.7 (quat. C, Si*C*(CH_3)$_3$), 28.1 (CH_3, SiC(*C*H_3)$_3$), 83.9 (quat. C), 84.2

(quat. C), 91.2 (quat. C), 109.7 (quat. C), 123.3 (quat. C), 127.5 (quat. C), 127.8 (CH, Ph), 128.5 (CH, Ph), 129.1 (CH, Ph), 129.8 (CH, Ph), 130.5 (quat. C), 131.4 (CH, Ph), 132.4 (quat. C), 136.0 (CH, Ph); *m/z* (TOF ES$^+$) 869 [(M+Na)$^+$, 100%]; HRMS (TOF ES$^+$) Found (M)$^+$ 869.2565. $C_{56}H_{48}Cl_2Si_2Na$ requires (M + Na)$^+$, 869.2569. The structure of this compound was confirmed by X-ray crystallography.[4]



1,12-Bis-triisopropylsilyldodeca-1,3,5,7,9,11-hexayne (13)



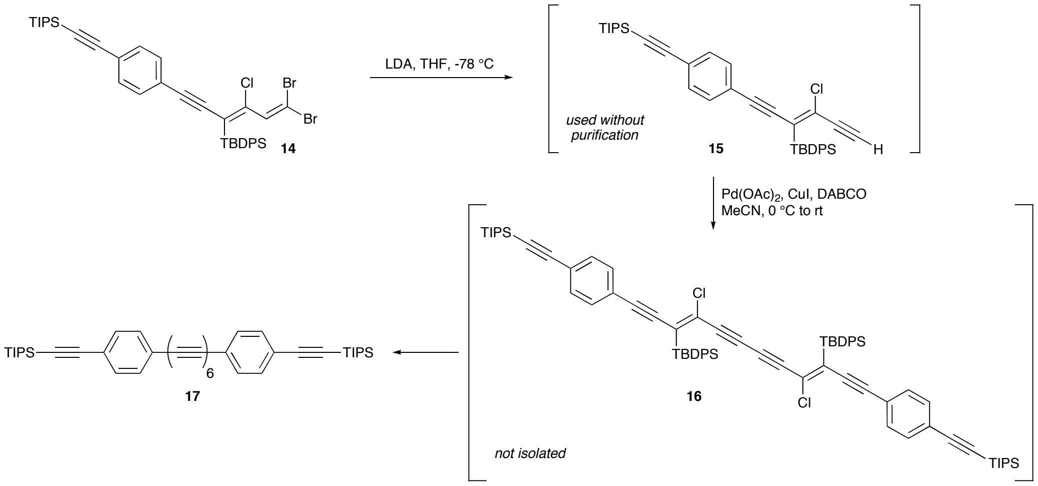
For the formation of silyl-end-capped hexayne **13** we elected to use K_2CO_3 in MeOH to effect dechlorosilylation rather than TBAF, which we more commonly use nowadays, in order to minimise any problems associated with competing deprotection of the silyl end-capping groups. Unmasking the hexayne, once again, proceeded efficiently:

K_2CO_3 (14 mg, 0.092 mmol) was added to a solution of masked hexayne **12** (32 mg, 0.042 mmol) in THF-MeOH (4 mL, 1:1) at rt. After 75 min, the reaction mixture was diluted with hexane (5 mL) and filtered through a short plug of silica. Removal of the solvent under reduced pressure and purification of the residue by silica column chromatography (eluent: hexane) afforded hexayne **13** as a yellow solid (15 mg, 79%); R_f = 0.73 (hexane); UV-Vis (solvent) 261 (53460), 275 (103910), 290 (214480), 308 (274230), 354 (9674), 397 (12860), 409 (9190); δ_H(300 MHz, $CDCl_3$) 1.08 (42H, br s, $Si(CH(CH_3)_2)_3$); δ_C(75 MHz, $CDCl_3$) 11.3 (CH, $Si(CH(CH_3)_2)_3$), 18.5 (CH_3, $Si(CH(CH_3)_2)_3$), 61.3 (quat. C), 62.4 (quat. C), 62.66 (quat. C), 62.72 (quat. C), 87.0 (quat. C), 89.4 (quat. C); *m/z* (EI) 458 [$(M)^+$, 32%], 415 [100, $(M-{}^iPr)^+$], 387 (20), 373 (25), 359 (15), 345 (30), 157 (25). Data were in agreement with those reported in the literature.[5,6]

The masked hexayne precursor **12** was prepared according to the methodology described in this paper and previously by us.[3] Data for **12**: R_f = 0.63 (hexane); UV-Vis (CH_2Cl_2) 398 (39428), 369 (39732), 341 (37537), 320 (34196) 307sh (28062), 292 (23720), 250 (19671); ν_{max}(film)/cm^{-1} 2925s, 2866s, 2111s (C≡C), 1519w, 1636w, 1463s, 883s; δ_H(300MHz; C_6D_6) 0.85 (12H, q, *J* 7.7, $Si(CH_2CH_3)_3$), 0.99 (18H, t, *J* 7.7, $Si(CH_2CH_3)_3$), 1.10 (42H, s, Si^iPr_3); δ_C(75MHz, C_6D_6) 4.0 (CH_2, $SiCH_2CH_3$), 7.5 (CH_3, $SiCH_2CH_3$), 11.7 (CH, $SiCH(CH_3)_2$), 18.8 (CH_3, $SiCH(CH_3)_2$), 80.5 (quat. C), 84.6 (quat. C), 106.3 (quat. C), 113.6 (quat. C), 125.2 (quat. C), 136.1 (quat. C); *m/z* (TOF ES^+) 797.2 [$(M+K)^+$, 19%]; HRMS (TOF ES^+) Found $(M)^+$ 797.3759. $C_{42}H_{72}Cl_2Si_4K$ requires $(M + K)^+$, 797.3725.

Modified approaches to hexayne synthesis:

As discussed in more detail in the paper, the formation of our masked hexayne monomers involves an oxidative coupling (transformation **3** to **4** in the paper). We have investigated a range of methods for carrying out this reaction, and our modified Eglinton-Glaser-Hay copper-mediated coupling reaction is invariably the most effective. On occasions, however, Pd-mediated dimerisations have been effective for carrying out this transformation, *and* an *in-situ* dechlorosilylation, to provide the oligoyne directly in one-pot.[7] This was the case for aryl-end-capped hexayne **17**. Fritsch-Buttenberg-Wiechell reaction on the dibromide precursor **14** proceeded uneventfully to provide the masked triyne **15**, which was used directly in a Pd-mediated oxidative coupling. Rather than generate the masked hexayne **16**, in this case, oxidative dimerisation to **16** was followed by *in situ* two-fold dechlorosilylation, leading directly to hexayne **17**.



1,12-bis(4-(triisopropylsilylethynyl)phenyl)dodecahexa-1,3,5,7,9,11-yne (17)

^{n}BuLi (0.54 mL of a 2.12 M solution in hexane, 1.13 mmol) was added over 5 min to a pre-chilled (0 °C) solution of $^{i}Pr_2NH$ (0.17 mL, 2.26 mmol) in THF (2.5 mL). After

30 min, the resulting LDA solution was cooled to –78 °C and transferred *via* cannula to a cooled (-78 °C) solution of dibromide **14** (147 mg, 0.192 mmol) in THF (2.5 mL). After 15 min, the resulting purple solution was quenched at –78 °C with NH_4Cl solution (8 mL) and allowed to warm to rt. The product was extracted with Et_2O (3 × 5 mL), and the combined extracts were washed with brine (3 × 8 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford the masked triyne **15** as a deep red oil, which was used directly without further purification. Acetonitrile (5 mL), palladium(II) acetate (1 mg, 5 μmol), copper(I) iodide (microspatula tip) and 1,4-diazabicyclo[2.2.2]octane (22 mg, 0.192 mmol) was added to masked triyne **15** at 0 °C. The reaction mixture was stirred for 6 h with warming to rt, at which point the reaction mixture was filtered through a short silica plug, eluting with hexane (20 mL) and 10% Et_2O in hexane (3 × 10 mL). The filtrate was concentrated under reduced pressure and the residue purified by flash column chromatography (10% toluene in hexane) to give hexayne **17** as a dark amber residue (20 mg, 16%); R_f = 0.62 (10% toluene in hexane); UV-Vis (CH_2Cl_2): 267sh (37740), 280 (50780), 295 (68465), 308 (88740), 353 (212240), 375 (147840), 401 (52240), 434 (38660), 473 (18120); ν_{max}(Nujol)/cm^{-1} 2157m (C≡C), 2057w, 1505w, 1494w, 1231w, 1177vw, 1072w, 1016w, 996w, 919vw, 883w, 836m, 784w, 661m; δ_H(300 MHz, $CDCl_3$) 1.12 (42H, s, 6 × Si$CH(CH_3)_2$), 7.42 (4H, A of AB system, $J_{A\text{-}B}$ 8.1, Ar*H*), 7.47 (4H, B of AB system, $J_{B\text{-}A}$ 8.1, Ar*H*); δ_C(75 MHz, $CDCl_3$) 11.3 (CH, 6 × Si$CH(CH_3)_2$), 18.6 (CH_3, 6 × SiCH(CH_3)$_2$), 62.5 (quat. C), 63.8 (quat. C), 65.0 (quat. C), 68.1 (quat. C), 76.0 (quat. C), 95.2 (quat. C), 106.1 (quat. C), 119.7 (quat. C), 125.5 (quat. C), 132.1 (CH, Ph), 133.2 (CH, Ph), 1 resonance (quat. C) not observed (resonance overlap); *m*/*z* (TOF ES$^+$) 799.5 [$(M+Ag+MeOH)^+$, 100%], 767 [45, $(M+Ag)^+$]; the molecular

isotope peak distributions for both $(M+Ag+MeOH)^+$ and $(M+Ag)^+$ match theoretical predictions.

Dibromolefin **14** and masked triyne **15** (not isolated) were prepared according to the methodology described in this paper and previously by us.[3] Data for **14**: Anal Calcd for $C_{39}H_{45}Br_2ClSi_2$: C, 61.21; H, 5.93. Found: C, 61.22; H, 5.78; R_f = 0.61 (10% Et_2O in hexane); ν_{max}(Nujol)/cm^{-1} 3072m, 3050w, 2923s, 2862s, 2154m, 1956w, 1909w, 1662w, 1588w, 1505m, 1490m, 1462s, 1428m, 1404w, 1378m, 1364w, 1232w, 1176w, 1158w, 1107w, 1072w, 1016w, 997m, 936w, 919w, 883m, 836, 818, 768m, 739m, 719, 700s, 677m, 660m, 603s; δ_H(300 MHz; $CDCl_3$) 1.15 (21H, s, 3 × $SiCH(CH_3)_2$), 1.22 (9H, s, $SiC(CH_3)_3$), 6.54 (1H, s, $CH{=}CBr_2$), 7.30-7.50 (10H, stack, Ph*H*), 7.62-7.81 (4H, m, Ph*H*); δ_C(75 MHz; $CDCl_3$) 11.3 (CH, 3 × $SiCH(CH_3)_2$), 18.7 (CH_3, 3 × $SiCH(CH_3)_2$), 19.4 (quat. C, $SiC(CH_3)_3$), 27.9 (CH_3, $SiC(CH_3)_3$), 92.3 (quat. C), 93.2 (quat. C), 98.5 (quat. C), 103.0 (quat. C), 106.7 (quat. C), 122.8 (quat. C), 123.3 (quat. C), 123.7 (quat. C), 128.1 (CH, Ph), 129.9 (CH, Ph), 131.1 (CH, Ph), 132.0 (CH, Ph), 132.3 (quat. C, *ipso*Ph), 135.3 (CH, $CH{=}CBr_2$), 135.9 (CH, Ph), 143.3 (quat. C); *m*/*z* (TOF ES^+) 873.1 [$(M+Ag)^+$, 100%]; HRMS (TOF ES^+) Found $(M+Ag)^+$ 869.0181. $C_{39}H_{45}Si_2ClBr_2{}^{107}Ag$ requires (M+Ag), 869.0166.

Estimating the Effective Conjugation Length for Aryl End-Capped Oligoynes

The dodecayne **9** described in the paper represents the longest aryl-end-capped oligoyne reported to-date. The values for λ_{max} for **9** and the hexaynes **11**, **13** and **17** prepared by us, along with other aryl-end-capped oligoynes prepared by other groups (Figure 1),[2,8,9] are tabulated below (Table 1).

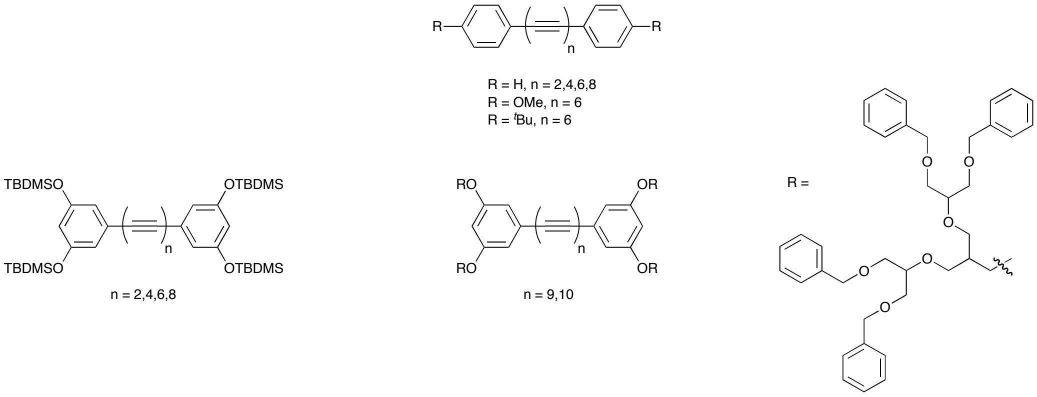
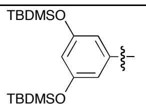
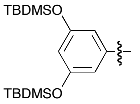
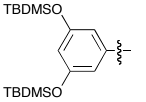
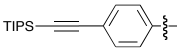
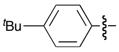
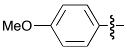
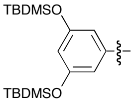
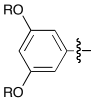
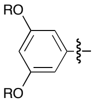
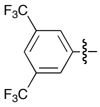


Figure 1. Aryl-end-capped oligoynes prepared by Hirsch[9] and Tykwinski.[2]

Table 1. Values of λ_{max} for a range of oligoynes.

number of conjugated alkynes	end-cap	compound number	λ_{max} / nm	reference
2		-	336	*ref 9*
4		-	403	*ref 9*
4	Ph	-	399	*ref 2*

6		-	467	*ref 9*
6	Ph	**11**	464	this paper
6	Ph	**11**	465	*ref 2*
6		**17**	473	this paper
6		-	469	*ref 2*
6		-	476	*ref 2*
6	TIPS	**13**	409	this paper
8	Ph	-	512	*ref 2*
8		-	514	*ref 9*
9	 see Fig 1	-	532	*ref 9*
10	Ph	-	549	*ref 8*
10	 see Fig 1	-	546	*ref 9*
12		**9**	562	this paper

The empirical Lewis-Calvin equation has been used to investigate how measurable physical parameters in a series of π-conjugated oligomers, such as λ_{max}, vary with conjugation length.

For small values of n:

$$(\lambda_{max})^2 = k\text{n}$$

where n = number of conjugated alkynes and k is a constant.

A plot of $(\lambda_{max})^2$ against n for n = 2-10 for the range of aryl-end-capped oligoynes in Table 1 shows a good linear relationship (Figure 2); however using the value of λ_{max} for dodecayne **9** we see for the first time, a deviation away from this line suggestive that with the dodecayne, we are approaching saturation and the effective conjugation length for this class of aryl-end-capped oligoyne (Figure 2). This can only be confirmed by synthesising even longer-chain oligoynes; the trimer in our series, which will be an octadecamer, will be very insightful.

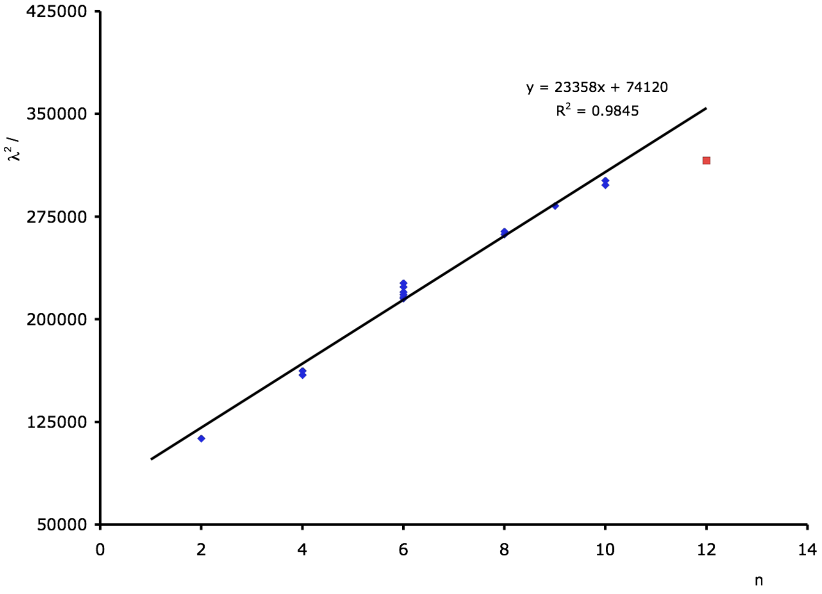


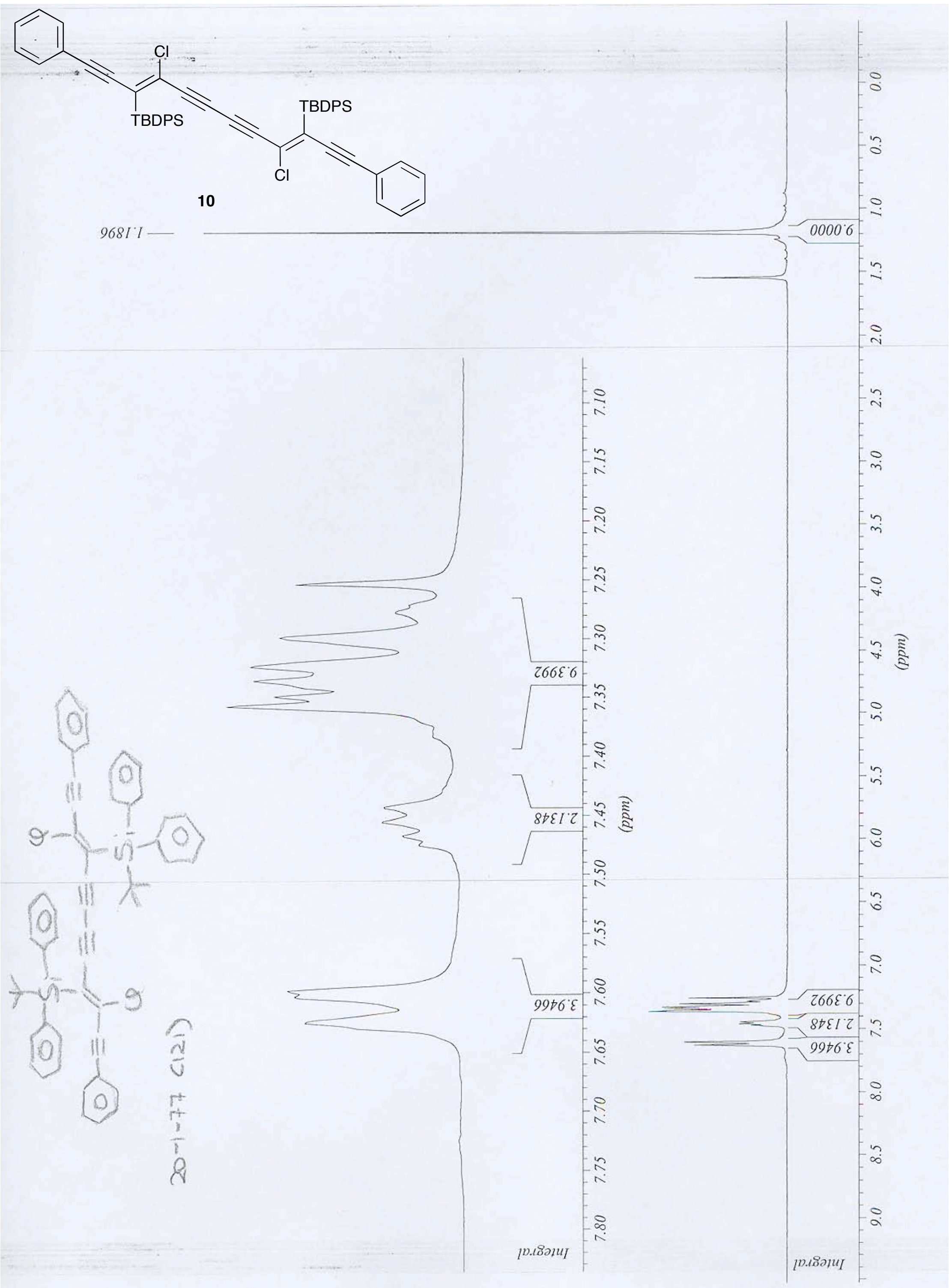
Figure 2. Lewis-Calvin Plot of $(\lambda_{max})^2$ against n.

References

1. J. B. Armitage, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1954, 147.
2. T. Luu, E. Elliott, A. D. Slepkov, S. Eisler, R. McDonald, F. A. Hegmann and R. R. Tykwinski, *Org. Lett.*, 2005, **7**, 51.
3. S. M. E. Simpkins, B. M. Kariuki, C. S. Aricó and Liam R. Cox, *Org. Lett.*, 2003, **5**, 3971.
4. S. M. E. Simpkins, B. M. Kariuki and L. R. Cox, *J. Organomet. Chem.*, 2006, **691**, 5517.
5. S. Eisler, A. D. Slepkov, E. Elliott, T. Luu, R. McDonald, F. A. Hegmann and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2005, **127**, 2666.
6. S. Eisler and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2000, **122**, 10736.
7. J.-H. Li, Y. Liang and Y.-X. Xie, *J. Org. Chem.*, 2005, **70**, 4393.
8. T. R. Johnson and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 5221.
9. T. Gibtner, F. Hampel, J.-P- Gisselbrecht and A. Hirsch, *Chem. Eur. J.*, 2002, **8**, 408.

Scanned Spectra

^{1}H-NMR and ^{13}C-NMR Spectra for compounds **10-14** and **17**. UV spectra for hexaynes **11**, **13** and **17**



10

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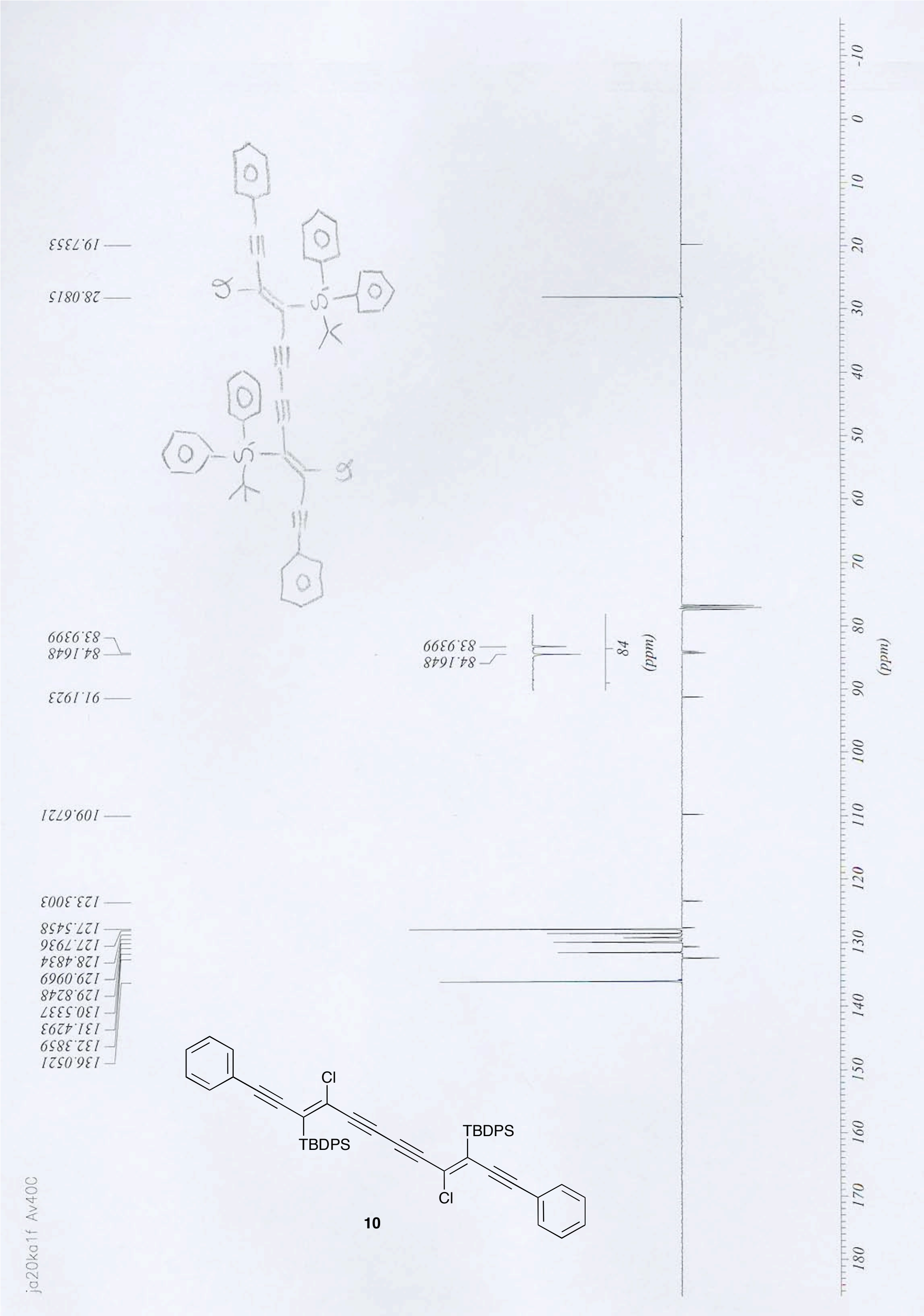
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(ppm)
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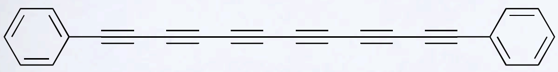
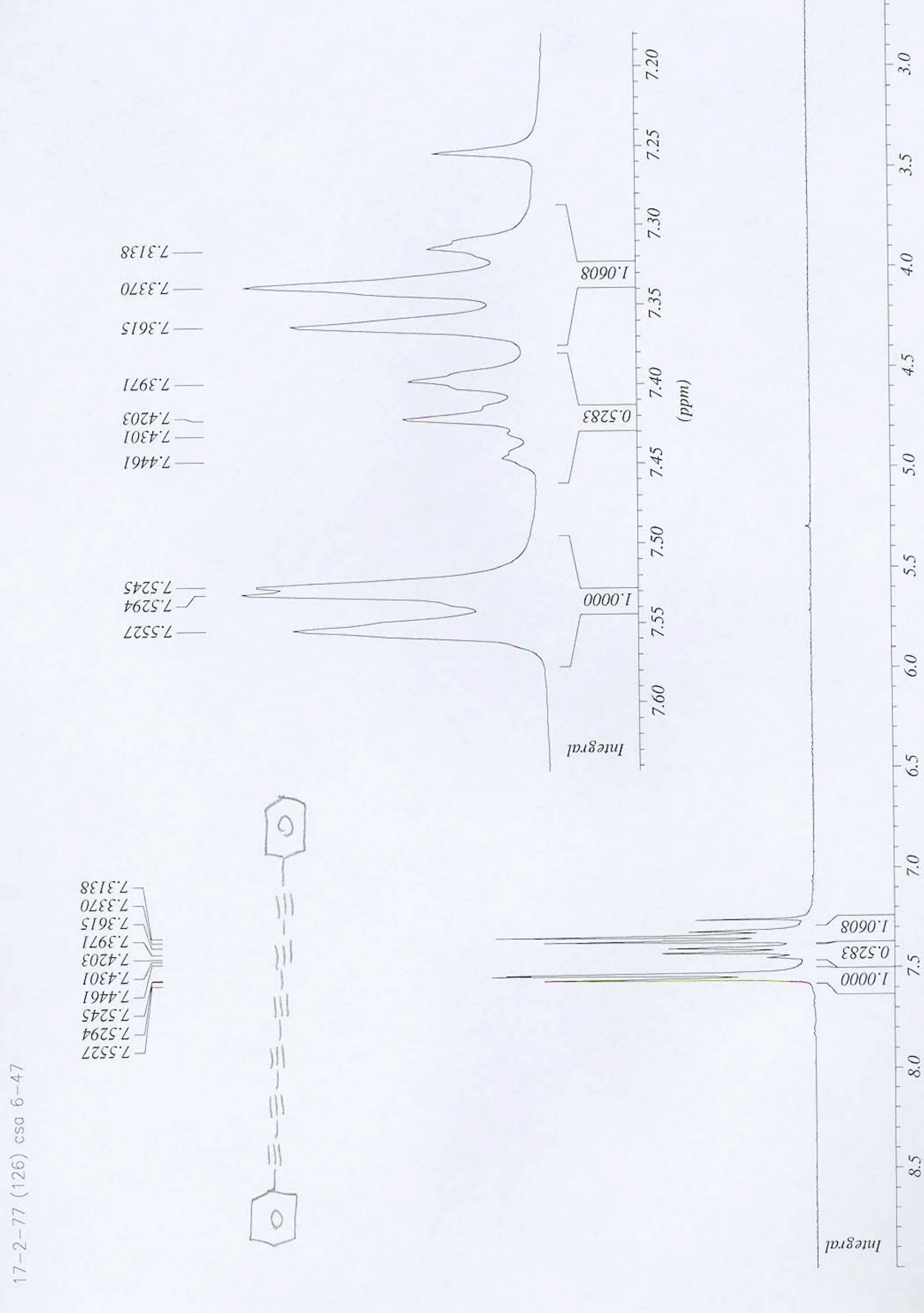


11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Integral
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7.30
7.35
7.40
7.45
7.50
7.55
7.60
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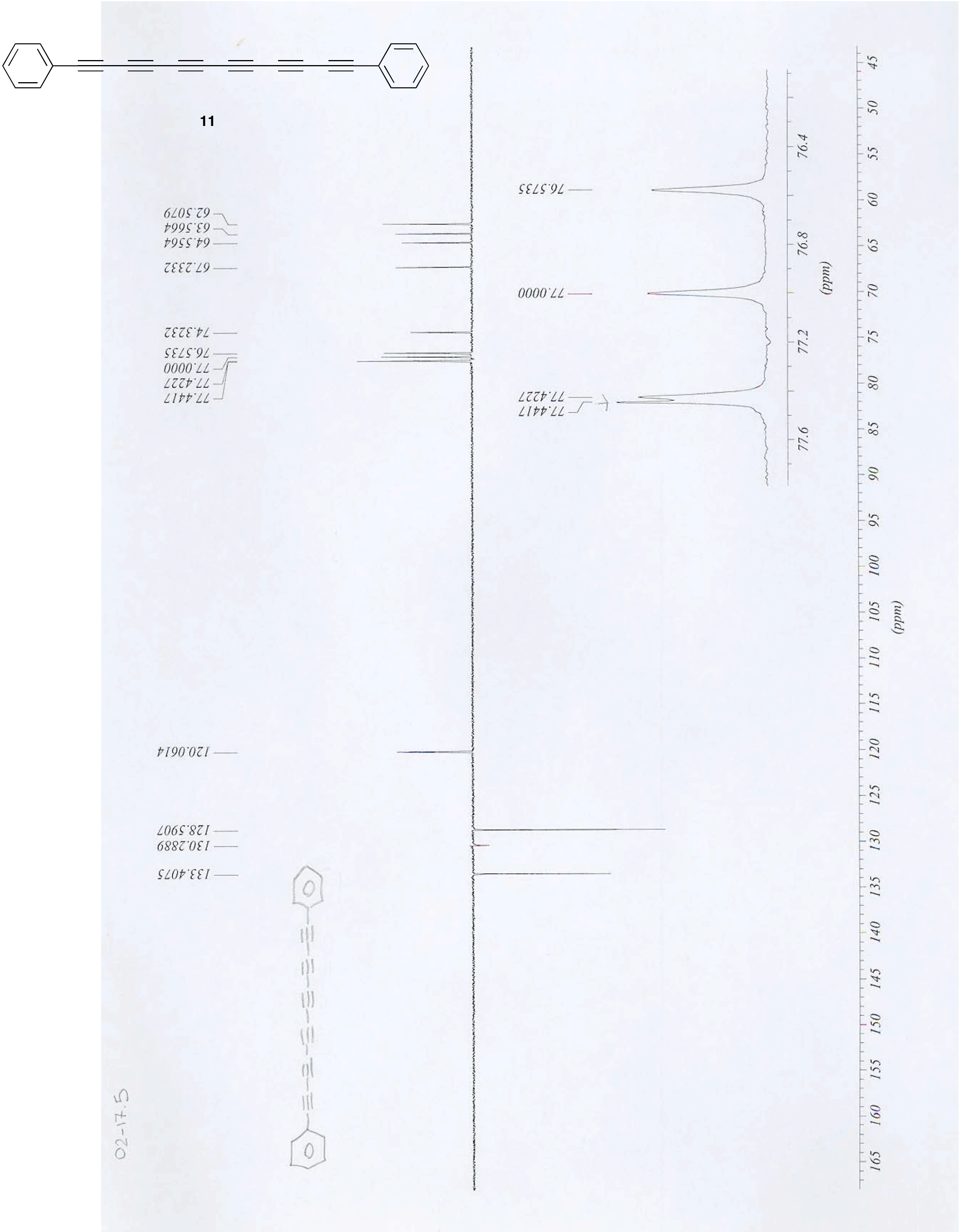
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85
90
95
100
105
110
115
120
125
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135
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155
160
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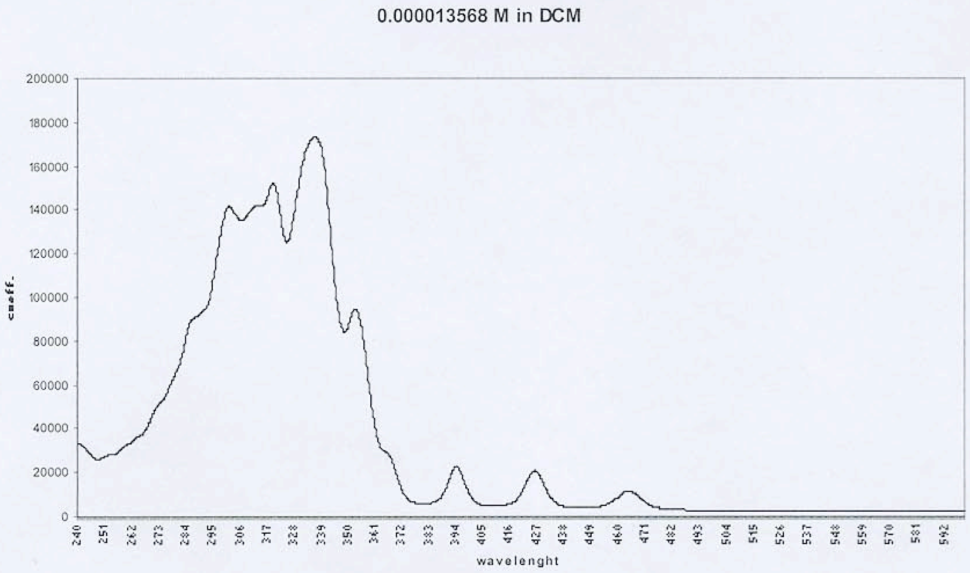
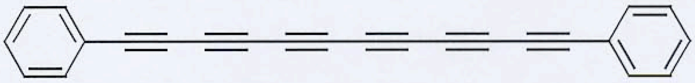
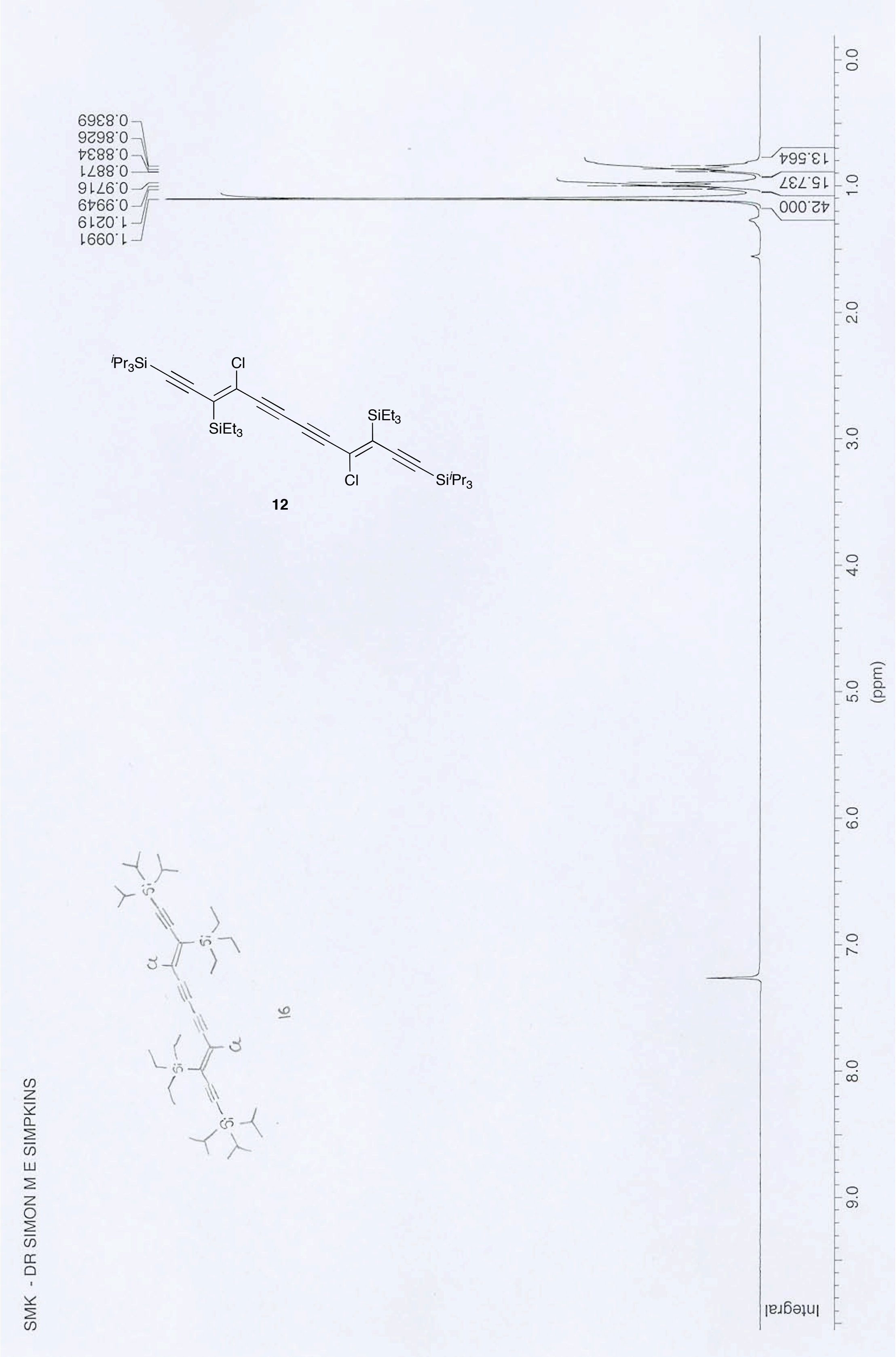
(ppm)
02-17.5

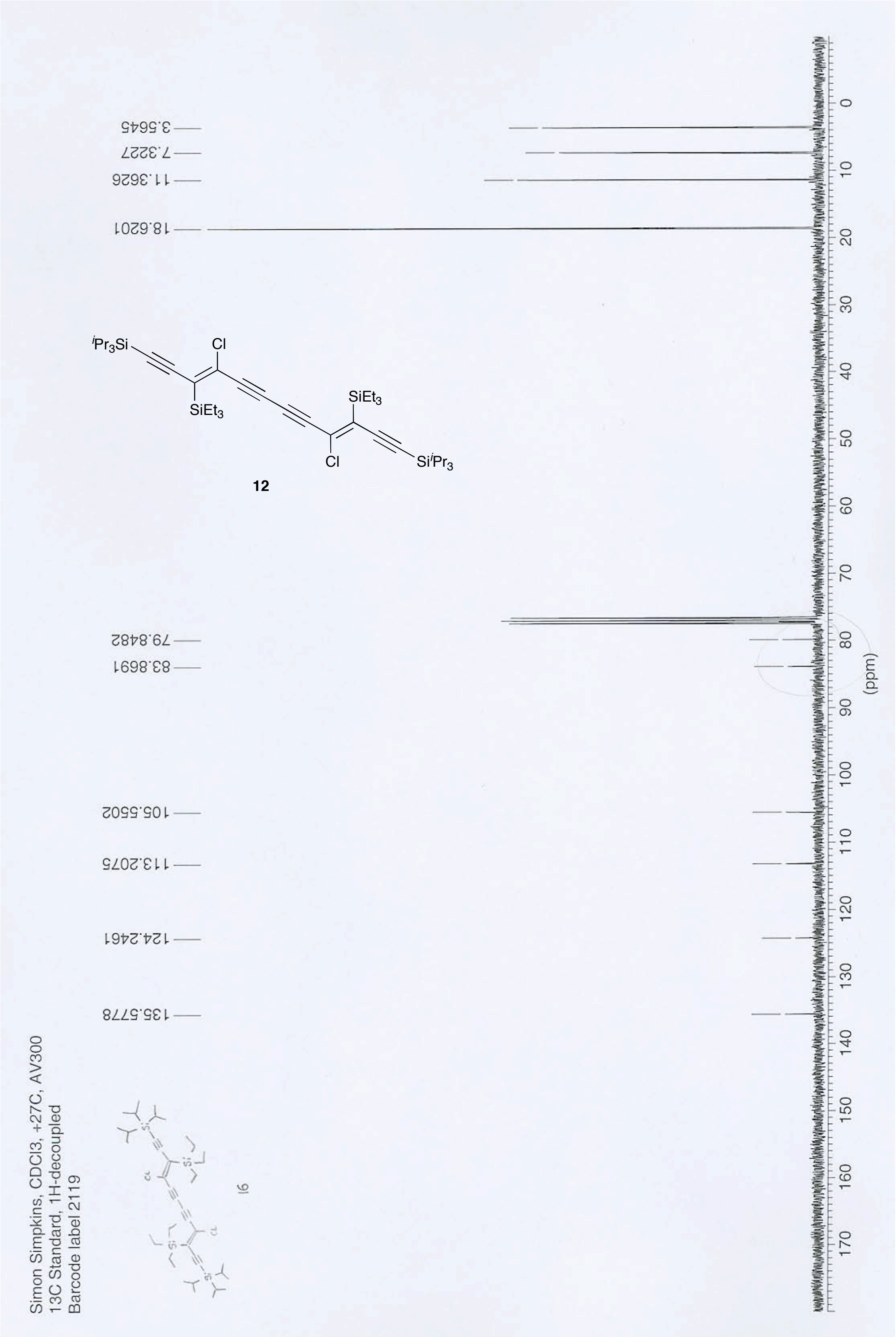


Wavelength (nm)	Extinction Coefficient
301	210 691
319	224 595
336	252 436
353	144 683
394	22 441
426	20 247
464	10 155

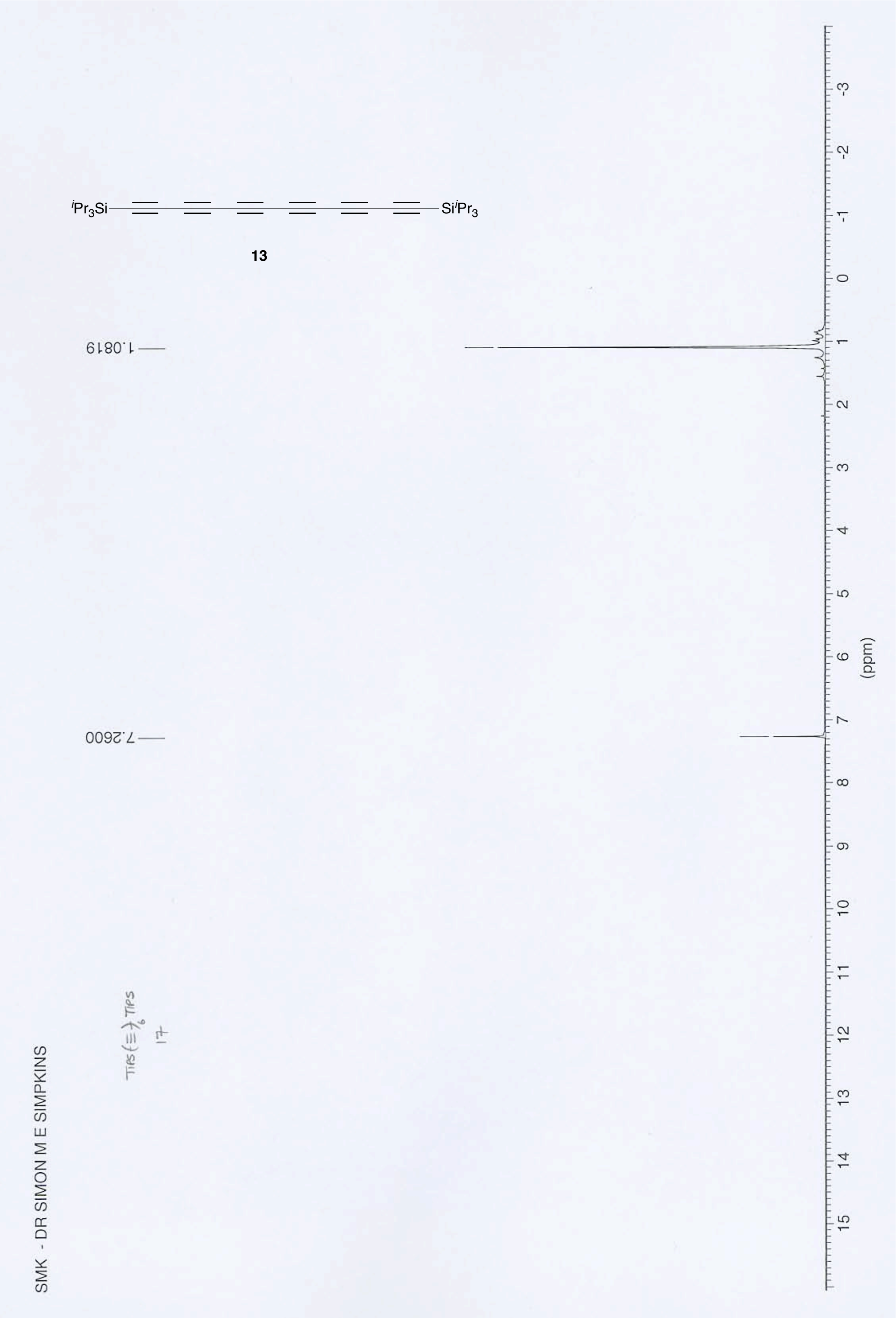


11


0.8369
0.8626
0.8834
0.8871
0.9716
0.9949
1.0219
1.0991
13.564
15.737
42.000
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
(ppm)
Integral
^{i}Pr$_3$Si
Cl
SiEt$_3$
SiEt$_3$
Cl
Si^{i}Pr$_3$
12
Cl
Si
Si
Si
Si
Cl
16
SMK - DR SIMON M E SIMPKINS

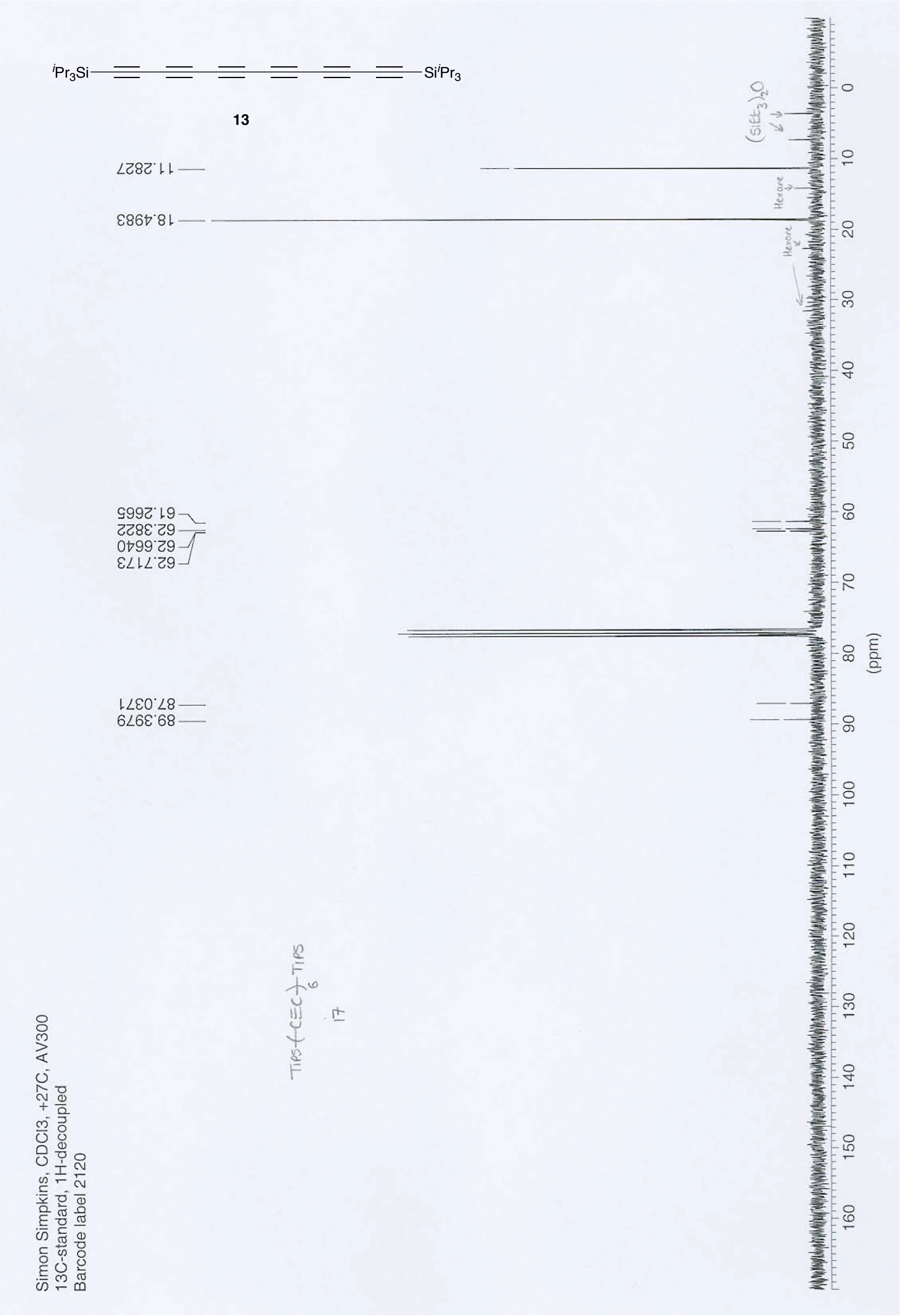

3.5645
7.3227
11.3626
18.6201
79.8482
83.8691
105.5502
113.2075
124.2461
135.5778
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
(ppm)
Simon Simpkins, CDCl3, +27C, AV300
13C Standard, 1H-decoupled
Barcode label 2119
16
iPr3Si
Cl
SiEt3
SiEt3
Cl
SiiPr3

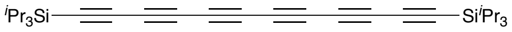
12



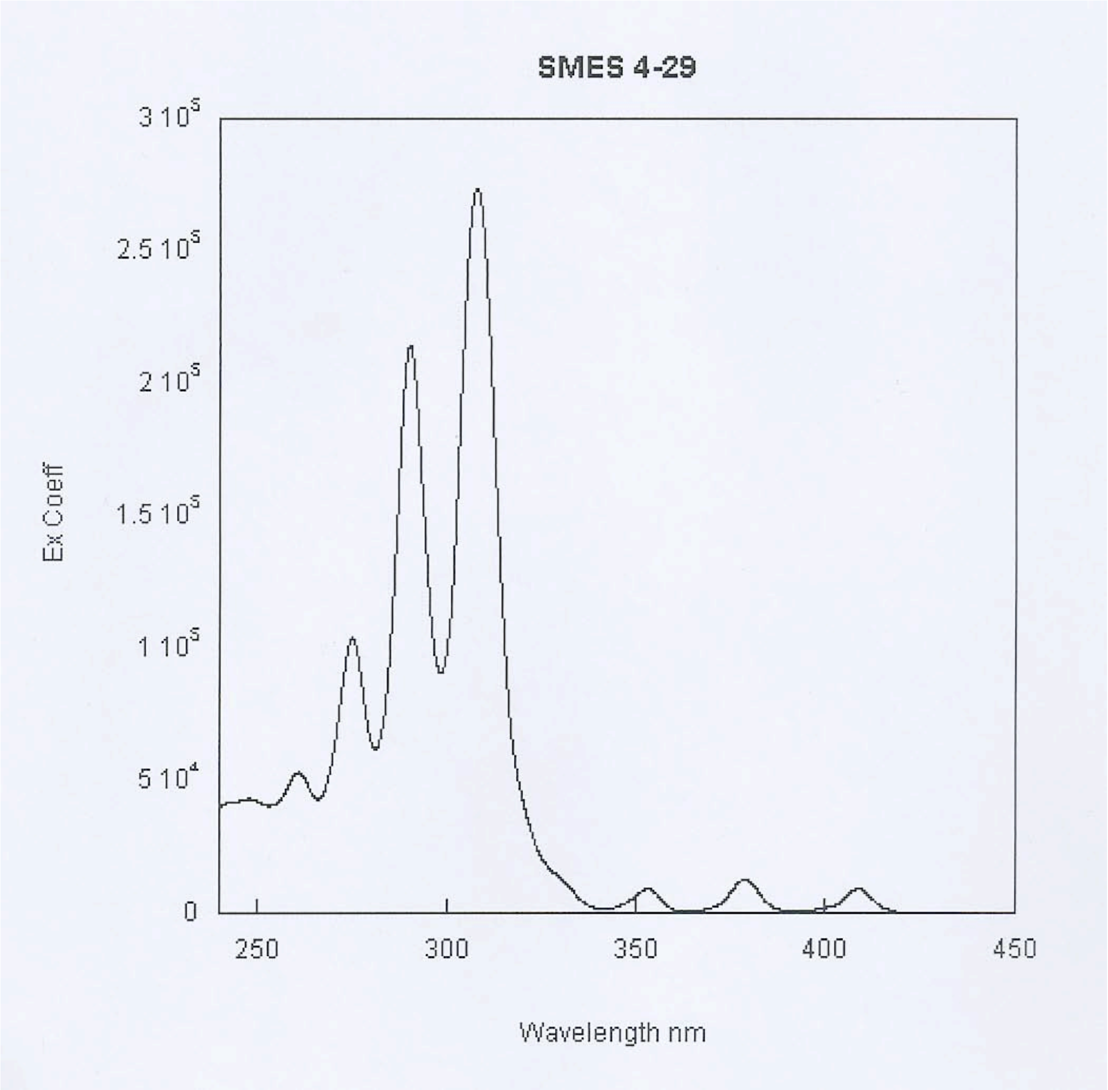
13

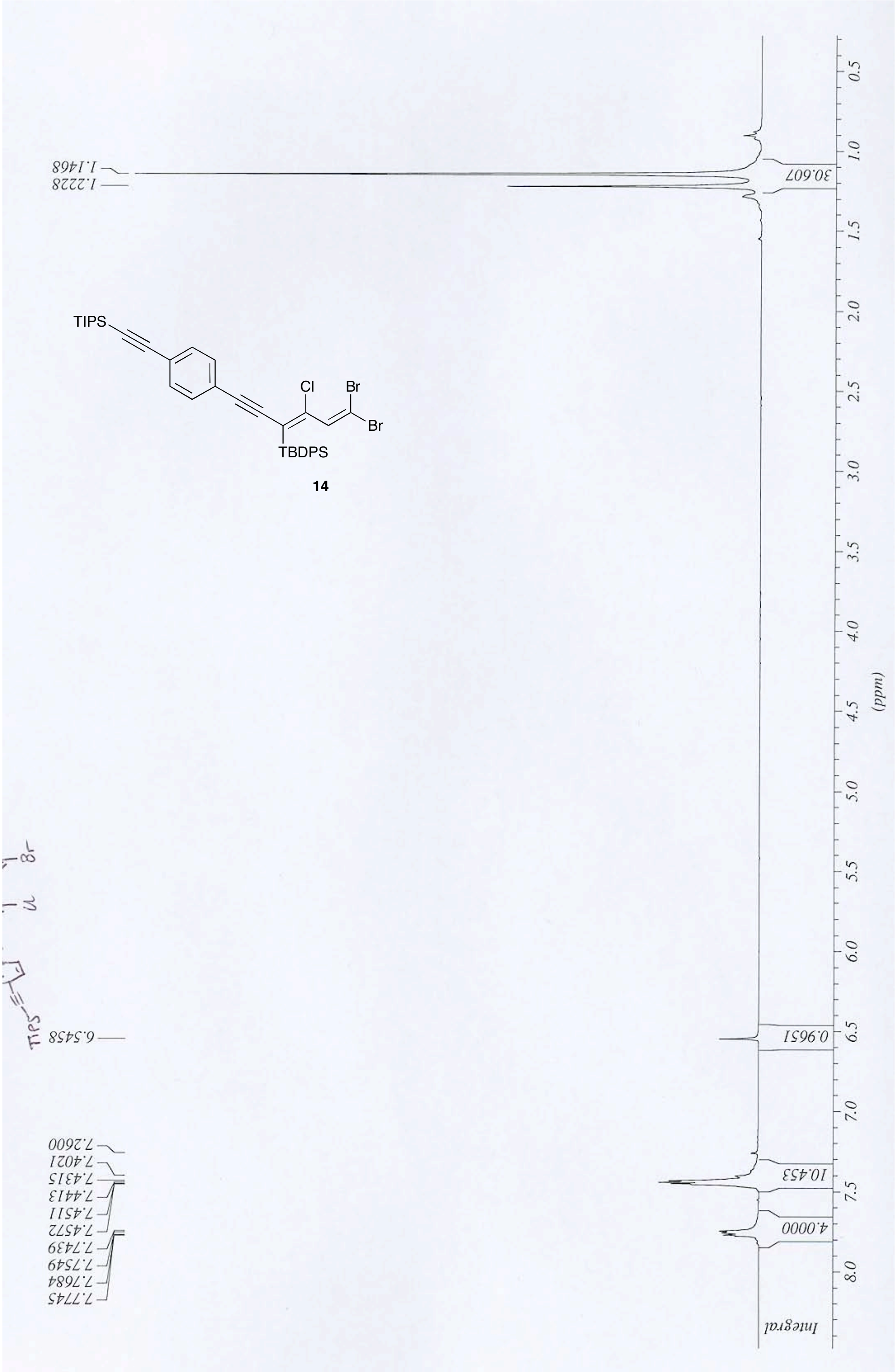
^{i}Pr$_3$Si—≡—≡—≡—≡—≡—≡—Si^{i}Pr$_3$
1.0819
7.2600
-3
-2
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
(ppm)
SMK - DR SIMON M E SIMPKINS
TIPS(≡)$_6$TIPS
17


iPr3Si—≡—≡—≡—≡—≡—≡—SiiPr3
13
11.2827
18.4983
61.2665
62.3822
62.6640
62.7173
87.0371
89.3979
(SiEt3)2O
Hexane
Hexane
TIPS-(C≡C)6-TIPS
17
Simon Simpkins, CDCl3, +27C, AV300
13C-standard, 1H-decoupled
Barcode label 2120
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
(ppm)

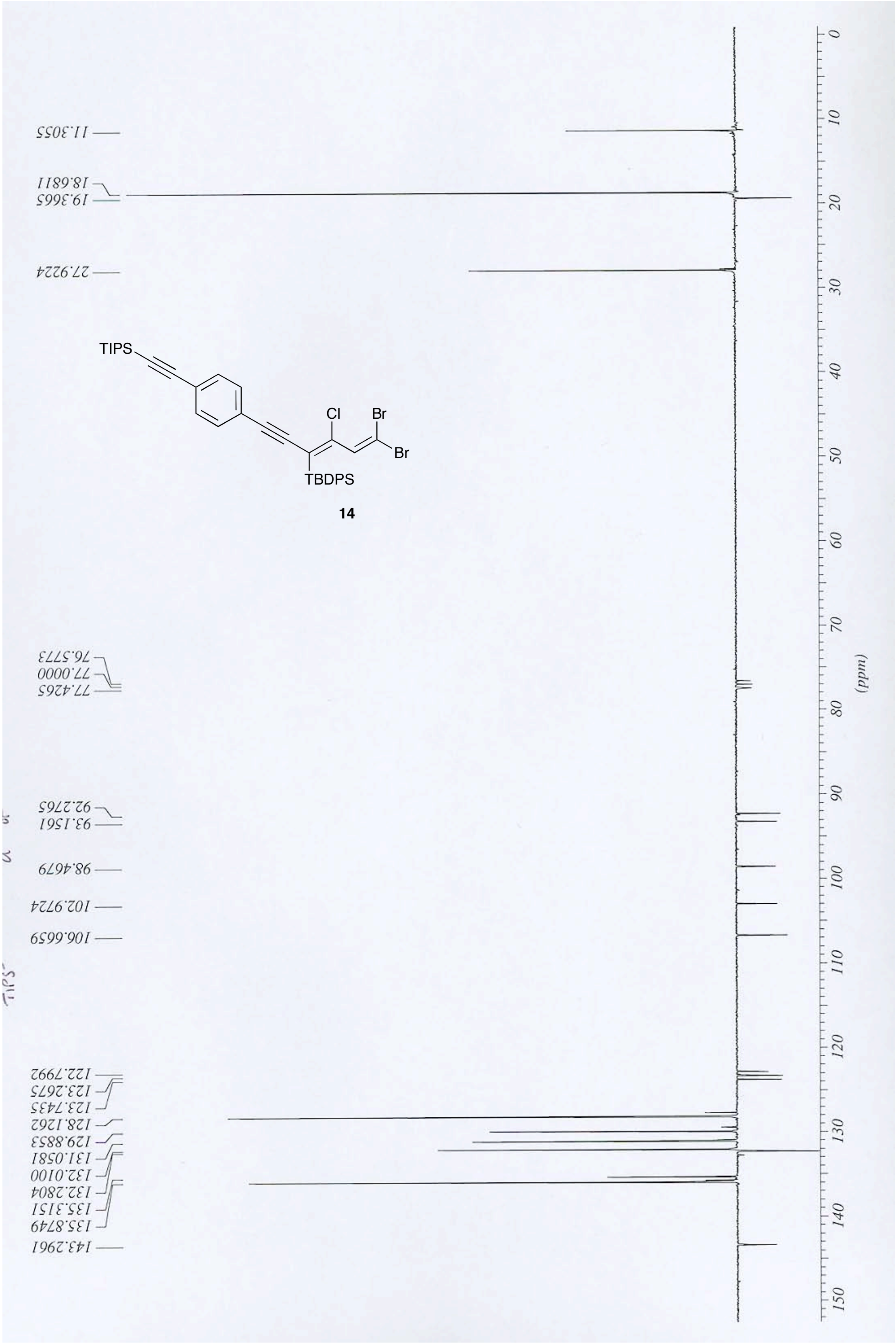

^{i}Pr$_3$Si
Si^{i}Pr$_3$

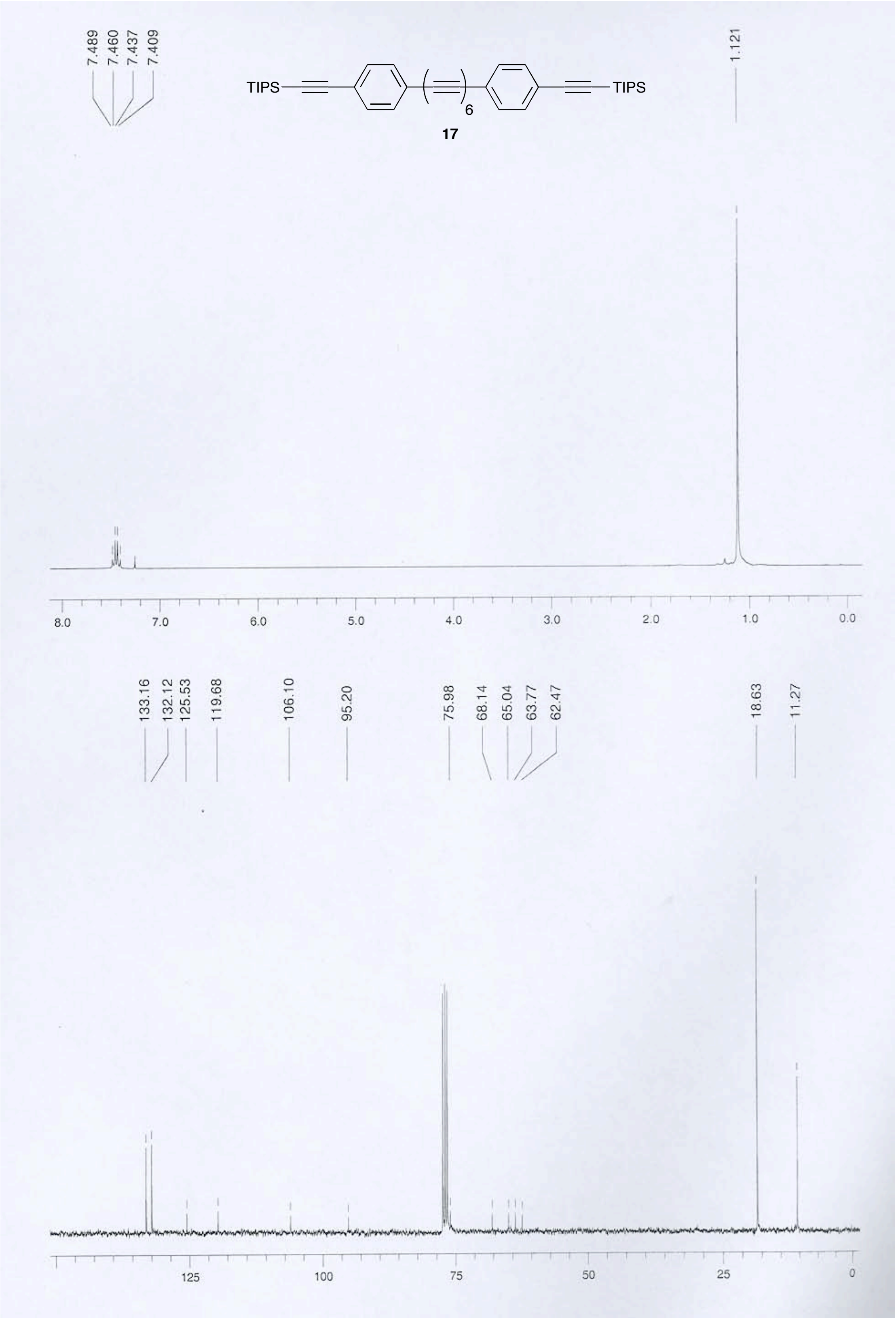
13

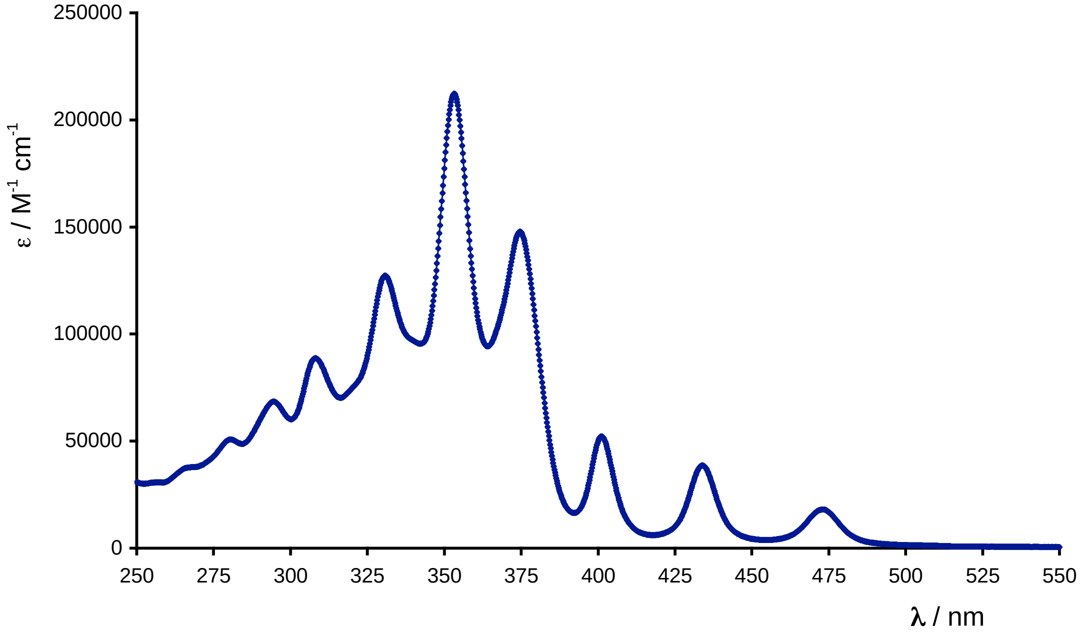

SMES 4-29
Ex Coeff
3 10^5
2.5 10^5
2 10^5
1.5 10^5
1 10^5
5 10^4
0
250
300
350
400
450
Wavelength nm

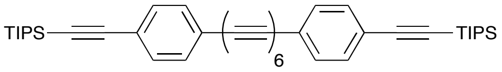

TIPS
Cl
Br
Br
TBDPS
1.1468
1.2228
6.5458
7.2600
7.4021
7.4315
7.4413
7.4511
7.4572
7.4739
7.7549
7.7684
7.7745
30.607
0.9651
10.453
4.0000
Integral
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
(ppm)

14


TIPS
Cl
Br
Br
TBDPS
14
11.3055
18.6811
19.3665
27.9224
76.5773
77.0000
77.4265
92.2765
93.1561
98.4679
102.9724
106.6659
122.7992
123.2675
123.7435
128.1262
129.8853
131.0581
132.0100
132.2804
135.3151
135.8749
143.2961
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
(ppm)


7.489
7.460
7.437
7.409
TIPS
6
TIPS
17
1.121
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
133.16
132.12
125.53
119.68
106.10
95.20
75.98
68.14
65.04
63.77
62.47
18.63
11.27
125
100
75
50
25
0


250000
200000
150000
100000
50000
0
ε / M-1 cm-1
250
275
300
325
350
375
400
425
450
475
500
525
550
λ / nm


TIPS
6
TIPS

17