

# Supplementary Materials

## One-step synthesis of (1-iodovinyl)arenes from trimethylsilyl ethynylarene through the iodotrimethylsilane-mediated hydroiodination

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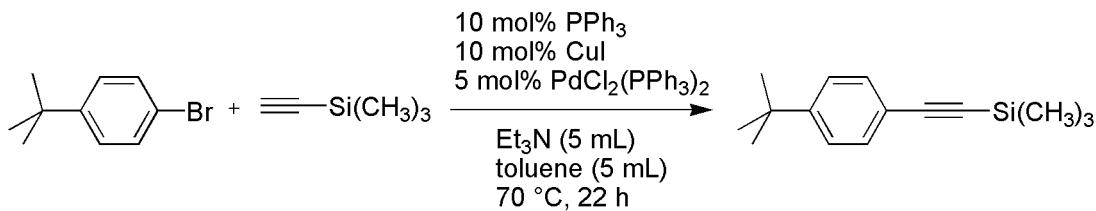
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**a) General:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER-SPECTROSPIN-400 with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shift values, reported in parts per million (ppm), were indirectly referenced to external tetramethylsilane employing resonances due to trace monoprotio-solvent as an internal reference. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Elemental analyses were performed with Yanaco MT-5 CHN-Corder. Mass spectra were reported on a JEOL GC-mate II (for FAB). Column chromatography was carried out with silica gel, Silica Gel 60N (Kanto Chemical Co.). Thin-layer chromatography analyses were performed on Merck silica gel 60 F<sub>254</sub>. Reactions were performed under an argon atmosphere unless otherwise noted.

**b) Materials:** Materials were purchased from Kanto Chemicals, Co., Inc., and Wako Pure Chemicals,

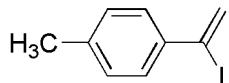
and Tokyo Chemical Industry Co., LTD. All the chemical materials were used without further purification. Compounds of trimethylsilyl ethynylarenes were prepared via Sonogashira cross-coupling. For the cross-coupling reactions, starting materials of trimethylsilyl acetylene, aryl halides, CuI, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and triethylamine were purchased from Tokyo Chemical Industry Co., LTD. and Wako Chemicals, Co., Inc., and used without further purification. In the starting materials for the cross-coupling reactions, arylboronic acid compounds were purchased from Tokyo Chemical Industry Co., LTD. and used without further purification.

**c) Representative procedure for synthesis of trimethylsilyl ethynylarenes via Sonogashira reaction.**

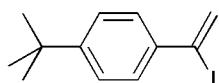


*((4-tert-butylphenyl)ethynyl)trimethylsilane (**2**)*<sup>1</sup>; CuI (95.3 mg, 0.5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (175.0 mg, 0.25 mmol), and PPh<sub>3</sub> (131.1 mg, 0.5 mmol) were added in a Schelenk tube. The whole system was evacuated and backfilled with argon three times, then toluene and Et<sub>3</sub>N (each 5 mL), and 1-bromo-4-*tert*-butylbenzene (0.87 mL, 5 mmol) were added. The reaction mixture was stirred at room temperature for 15 min, and then ethynyltrimethylsilane (2.12 mL, 15 mmol) was added. After heating at 70 °C for 22 h The solution was filtered through a pad of celite and florisil, and the crude product was purified with short-plug column chromatography (Hexane/CHCl<sub>3</sub> = 2/1), and silica gel column chromatography (Hexane only) to yield **2** in 95% (1.09 g) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (dd, *J* = 2.0, 6.6 Hz, 2H), 7.31 (dd, *J* = 2.1, 6.6 Hz, 2H), 1.30 (s, 9H), 0.24 (s, 9H).

**d) Characterization data for compounds in Table 1, entry 1 and Table 2, entry 3**

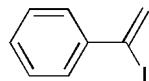


**1-(1-iodovinyl)-4-methylbenzene** (Table 1, entry 1)<sup>2</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.43 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 1.7 Hz, 1H), 6.06 (d, *J* = 1.7 Hz, 1H), 2.38 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 139.2, 129.2, 128.3, 126.8, 108.0, 21.4.

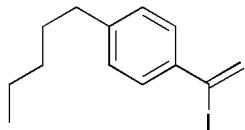


**1-tert-butyl-4-(1-iodovinyl)benzene** (Table 2, entry 3)<sup>3</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 1.7 Hz, 1H), 6.04 (d, *J* = 1.7 Hz, 1H), 1.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 152.3, 139.0, 128.1, 126.8, 125.5, 108.0, 34.9, 31.6.

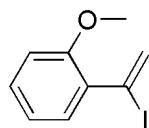
**e) Characterization data for compounds in Table 6**



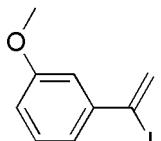
**(1-iodovinyl)benzene** (Table 6, entry 1)<sup>4</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.53-7.50 (m, 2H), 7.36-7.26 (m, 3H), 6.47 (d, *J* = 1.7 Hz, 1H), 6.09 (d, *J* = 1.7 Hz, 1H).



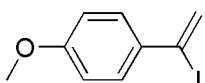
**1-(1-iodovinyl)-4-pentylbenzene** (Table 6, entry 2)<sup>4</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.43 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 1.7 Hz, 1H), 6.04 (d, *J* = 1.7 Hz, 1H), 2.60 (t, *J* = 7.8, 7.8 Hz, 2H), 1.64-1.57 (m, 2H), 1.36-1.28 (m, 4H), 0.89 (t, *J* = 6.9, 6.7 Hz, 3H).



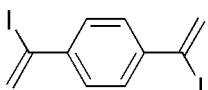
**1-(1-iodovinyl)-2-methoxybenzene** (Table 6, entry 3)<sup>5</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.32-7.24 (m, 2H), 6.91 (td, *J* = 7.5, 7.5, 1.0 Hz 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.28 (d, *J* = 1.1, Hz, 1H), 6.16 (d, *J* = 1.1 Hz, 1H), 3.90 (s, 3H).



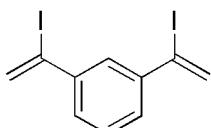
**1-(1-iodovinyl)-3-methoxybenzene**<sup>6</sup> (Table 6, entry 4); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.23 (t, *J* = 8.0, 8.0 Hz, 1H), 7.11-7.09 (m, 1H), 7.05 (t, *J* = 2.2, 2.2 Hz, 1H), 6.84 (ddd, *J* = 7.8, 2.6, 0.9 Hz, 1H), 6.47 (d, *J* = 1.7 Hz, 1H), 6.08 (d, *J* = 1.7 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 159.5, 143.3, 129.4, 127.7, 120.7, 114.6, 114.2, 107.2, 55.6.



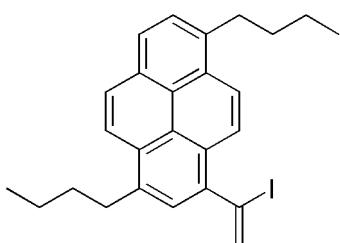
**1-(1-iodovinyl)-4-methoxybenzene** (Table 6, entry 5)<sup>4</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.47 (t, *J* = 9.0 Hz, 2H), 6.84 (t, *J* = 9.0 Hz, 2H), 6.38 (d, *J* = 1.7 Hz, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H).



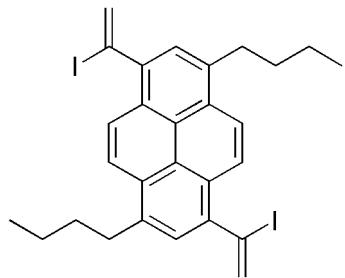
**1,4-bis(1-iodovinyl)benzene** (Table 6, entries 6 and 7)<sup>7</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 (s, 4H), 6.50(d, *J* = 1.8 Hz, 2H), 6.11 (d, *J* = 1.8 Hz, 2H).



**1,3-bis(1-iodovinyl)benzene** (Table 6, entry 8)<sup>8</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 (s, 4H), 7.44 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.26 (t, *J* = 8.0, 8.0 Hz, 2H), 6.50 (d, *J* = 1.8 Hz, 2H), 6.12 (d, *J* = 1.8 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 142.4, 129.1, 128.8, 128.7, 128.2, 106.9.



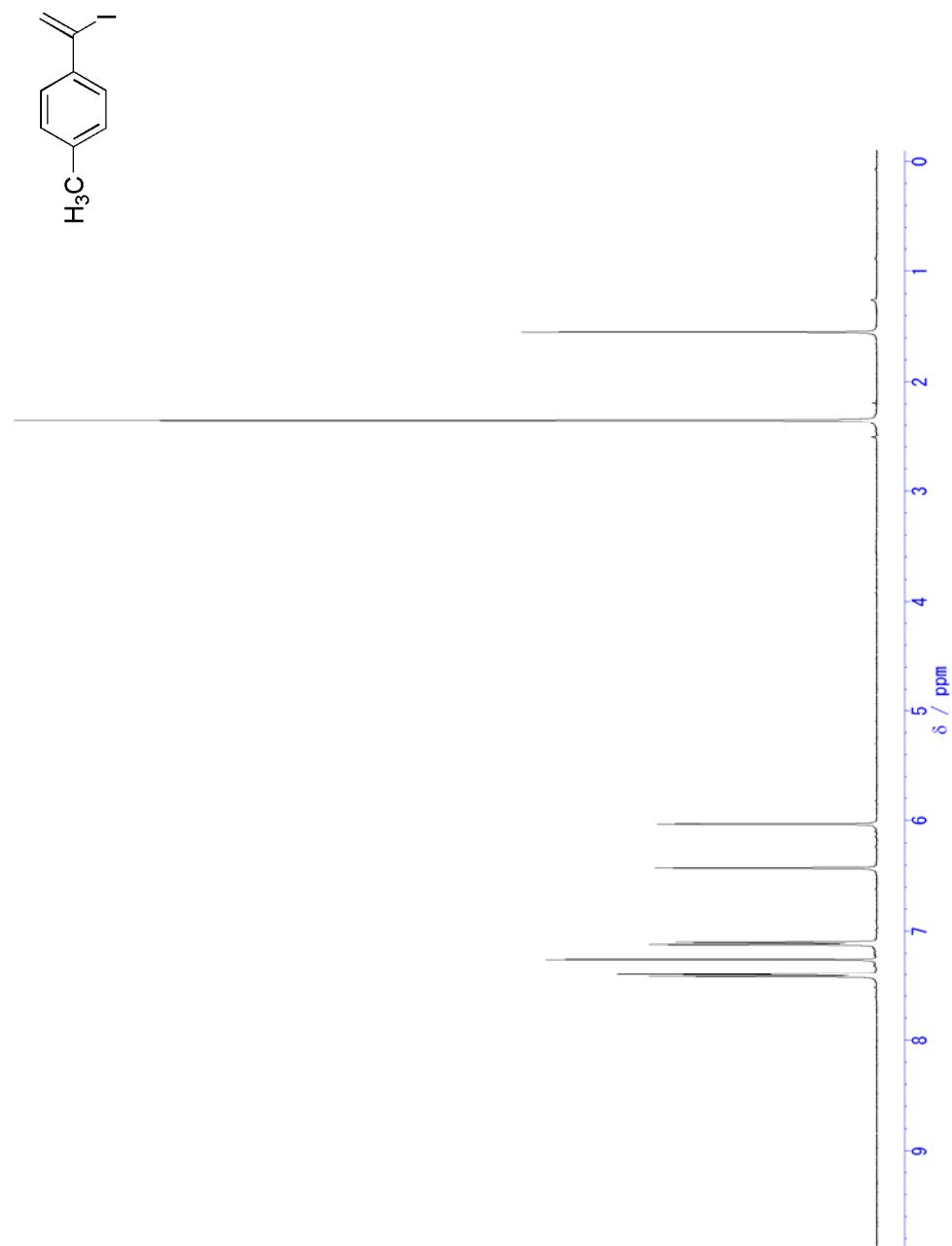
**1,6-dibutyl-3-(1-iodovinyl)pyrene** (Table 6, entry 11); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.41 (d, *J* = 9.5 Hz, 1H), 8.34 (d, *J* = 9.5 Hz, 1H), 8.18 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.82 (s, 1H), 6.49 (s, 1H), 6.41 (s, 1H), 3.34-3.29 (m, 4H), 1.86-1.80 (m, 4H), 1.53-1.47 (m, 4H), 1.02-0.98 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 138.3, 137.8, 136.9, 131.7, 130.0, 129.6, 129.1, 128.1, 128.0, 127.3, 125.9, 125.82, 125.80, 125.2, 124.8, 123.2, 122.8, 104.0, 34.4, 34.2, 33.8, 33.7, 23.3, 23.2, 14.4. FAB-MS *m/z* = 339 [M - I]<sup>+</sup>. Anal. Calcd for C<sub>26</sub>H<sub>27</sub>I: C, 66.96; H, 5.84. Found: C, 67.02; H, 5.84.



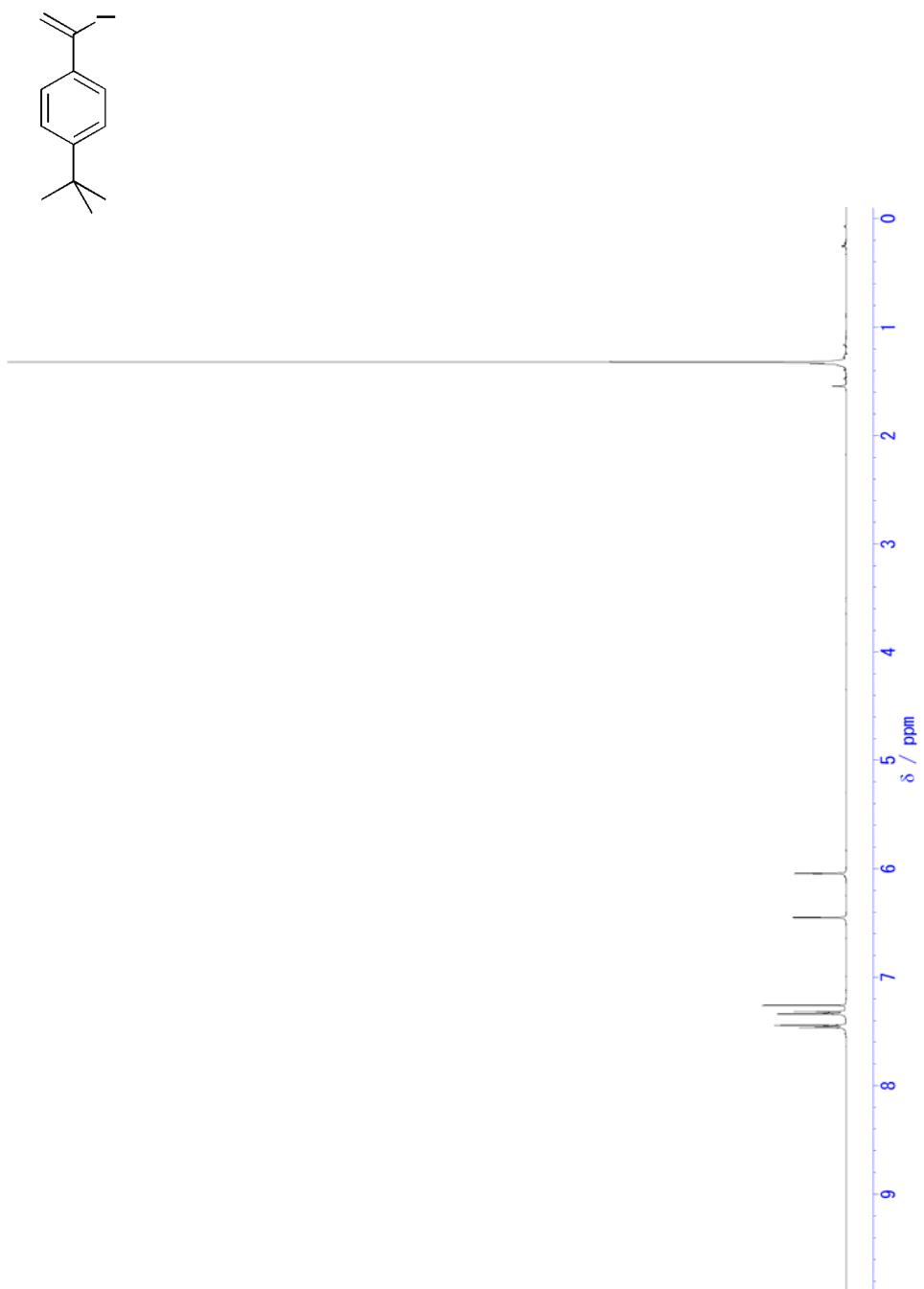
**1,6-dibutyl-3,8-bis(1-iodovinyl)pyrene** (Table 6, entry 12);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.43 (d,  $J = 9.2$  Hz, 2H), 8.29 (d,  $J = 9.2$  Hz, 2H), 7.82 (s, 2H), 6.49 (s, 2H), 6.41 (s, 2H), 3.30 (t,  $J = 7.7$ , 7.7 Hz, 4H), 1.88-1.80 (m, 4H), 1.53-1.48 (m, 4H), 1.01 (t,  $J = 7.4$ , 7.4 Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.7, 137.3, 131.8, 129.4, 127.8, 126.1, 126.0, 125.4, 123.0, 103.0, 34.2, 33.8, 23.3, 14.4. MS (FAB)  $m/z$ : 491 [M - I]<sup>+</sup>. Anal. Calcd for  $\text{C}_{28}\text{H}_{28}\text{I}_2$ : C, 54.39; H, 4.56. Found: C, 54.91; H, 4.54.

f)  $^1\text{H}$  NMR Spectra for a compound in Table 1, entry 1 and Table 2, entry 3

$^1\text{H}$  NMR spectrum (Table 1, entry 1): 1-(1-iodovinyl)-4-methylbenzene

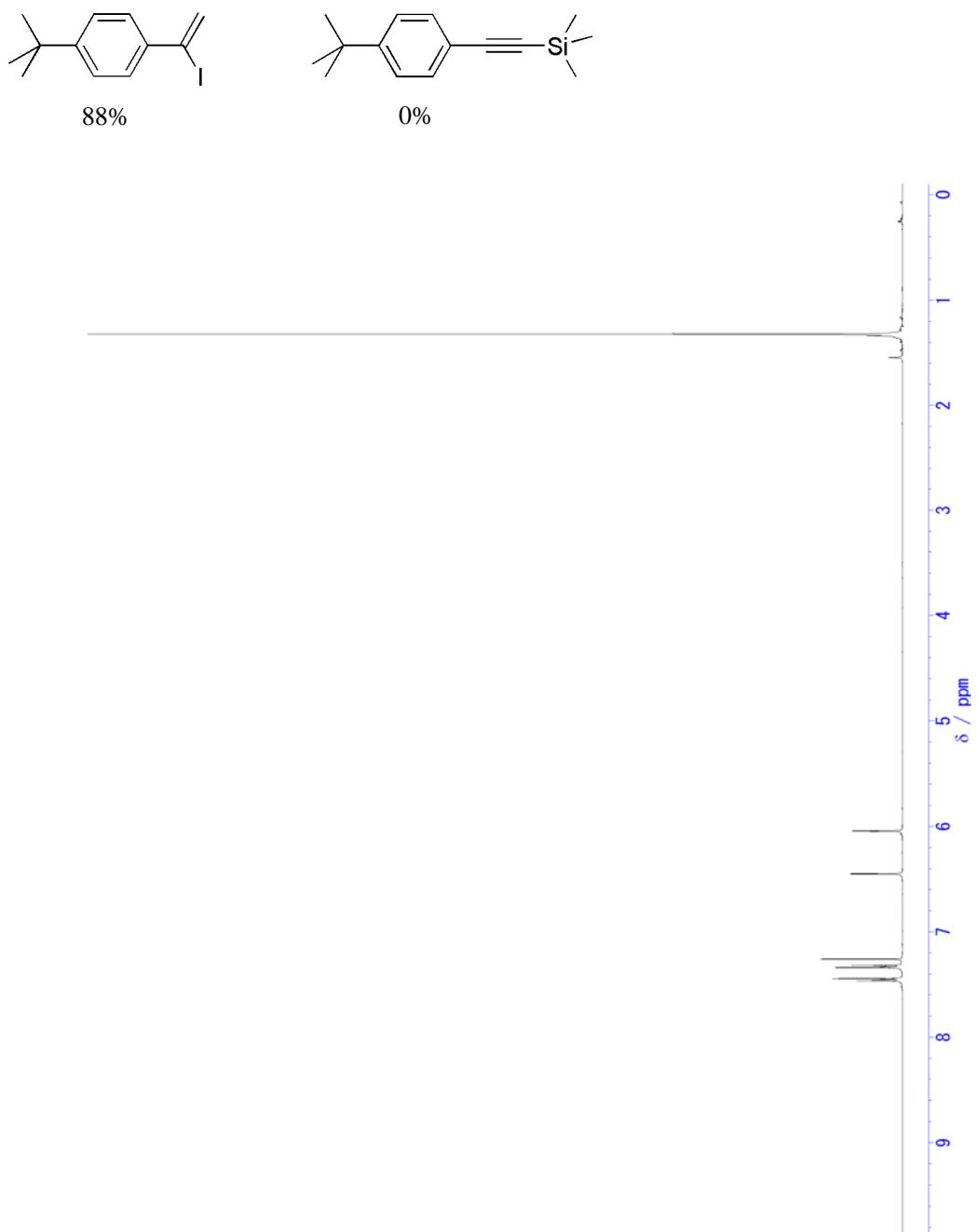


$^1\text{H}$  NMR spectrum (Table 2, entry 3): 1-*tert*-butyl-4-(1-iodovinyl)benzene

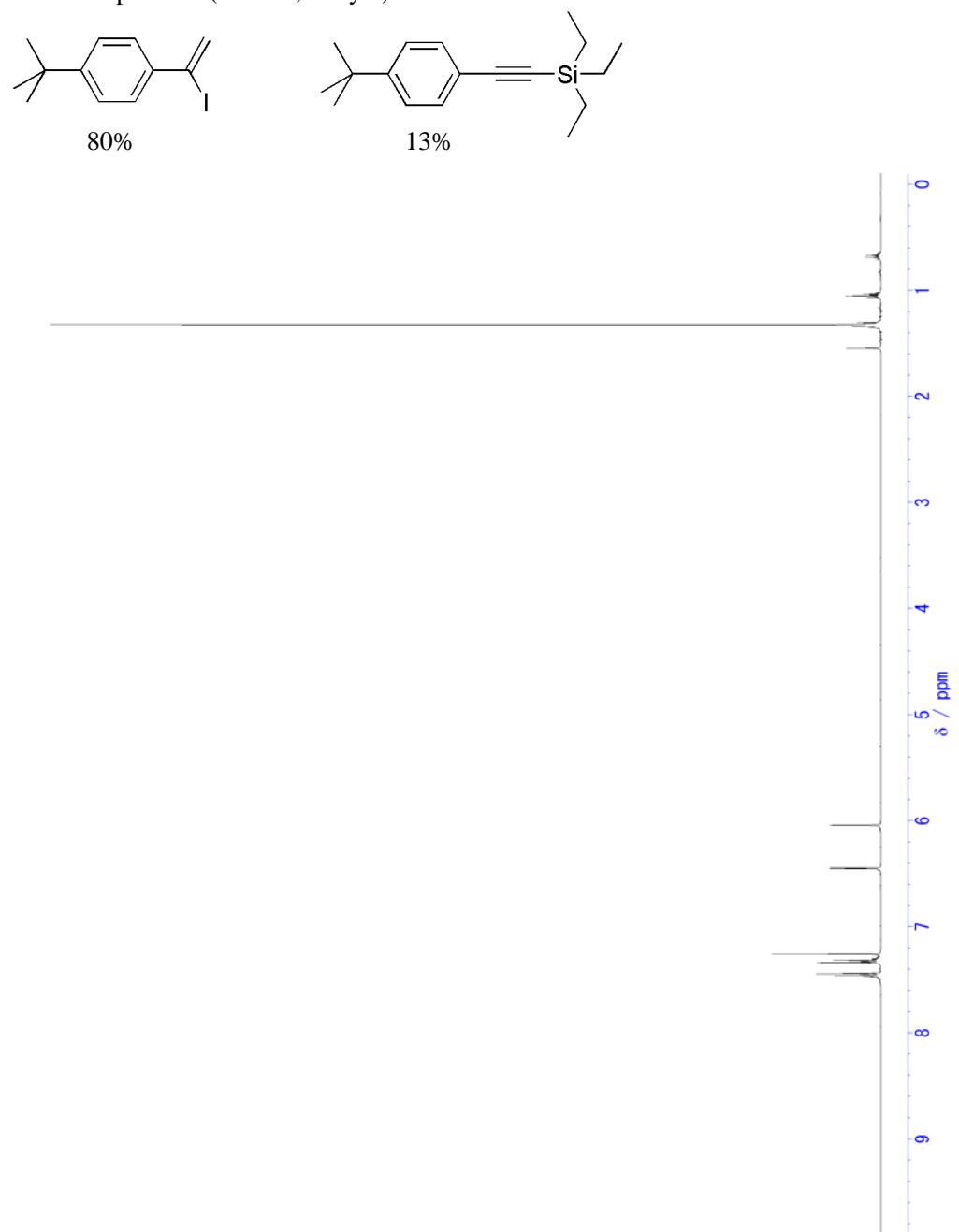


g)  $^1\text{H}$  NMR Spectra in Table 3, 4, and 5

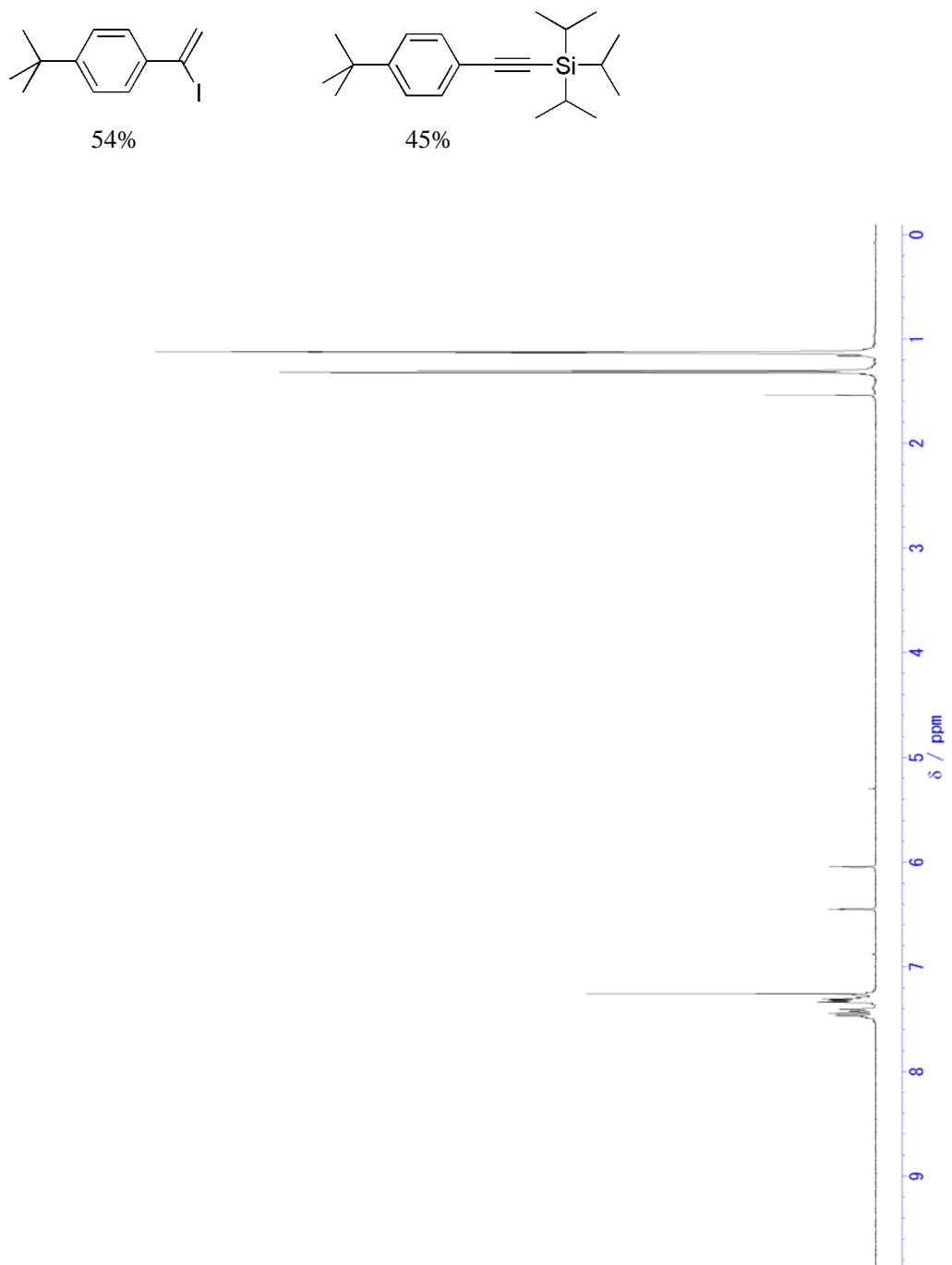
$^1\text{H}$  NMR spectrum (Table 3, entry 1):



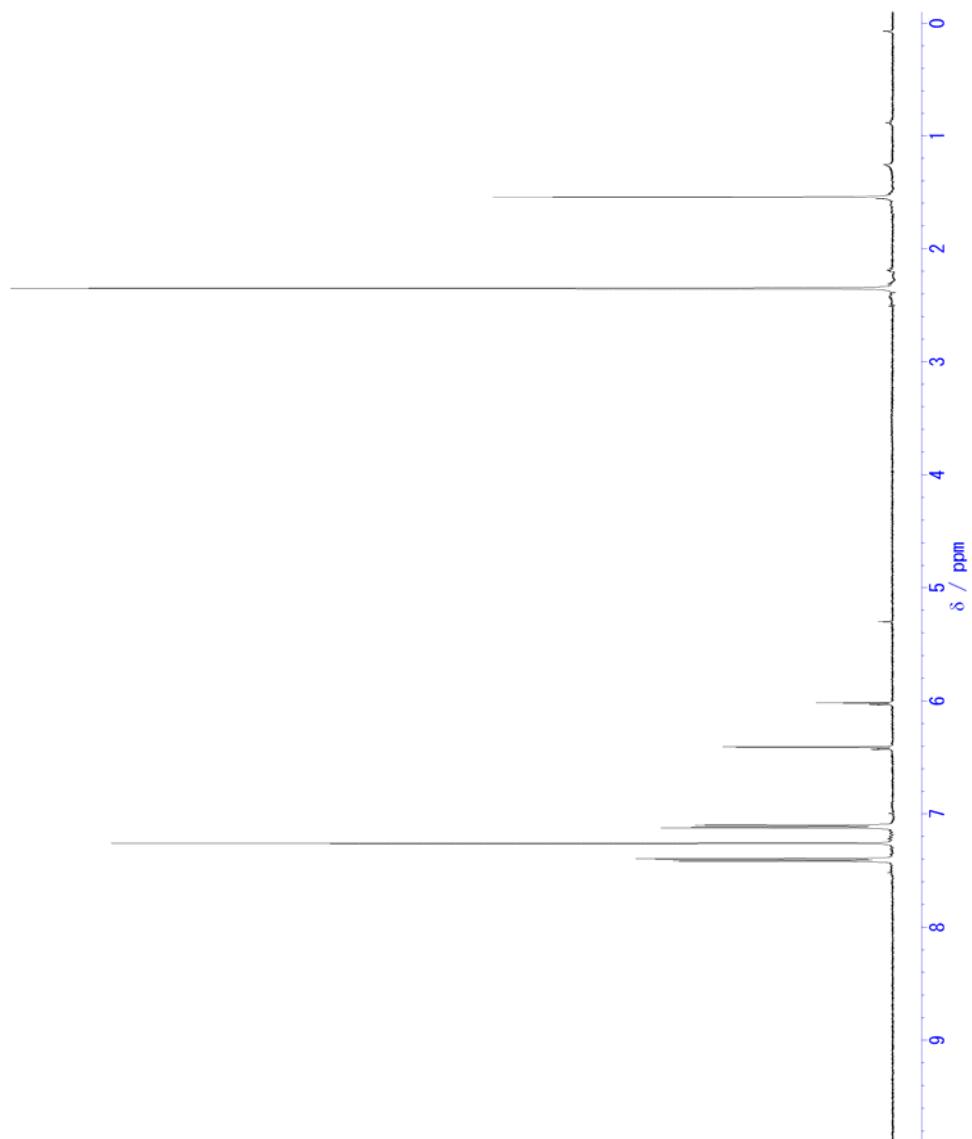
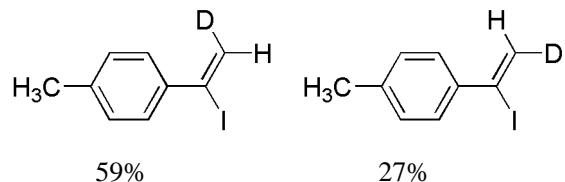
<sup>1</sup>H NMR spectrum (Table 3, entry 1):



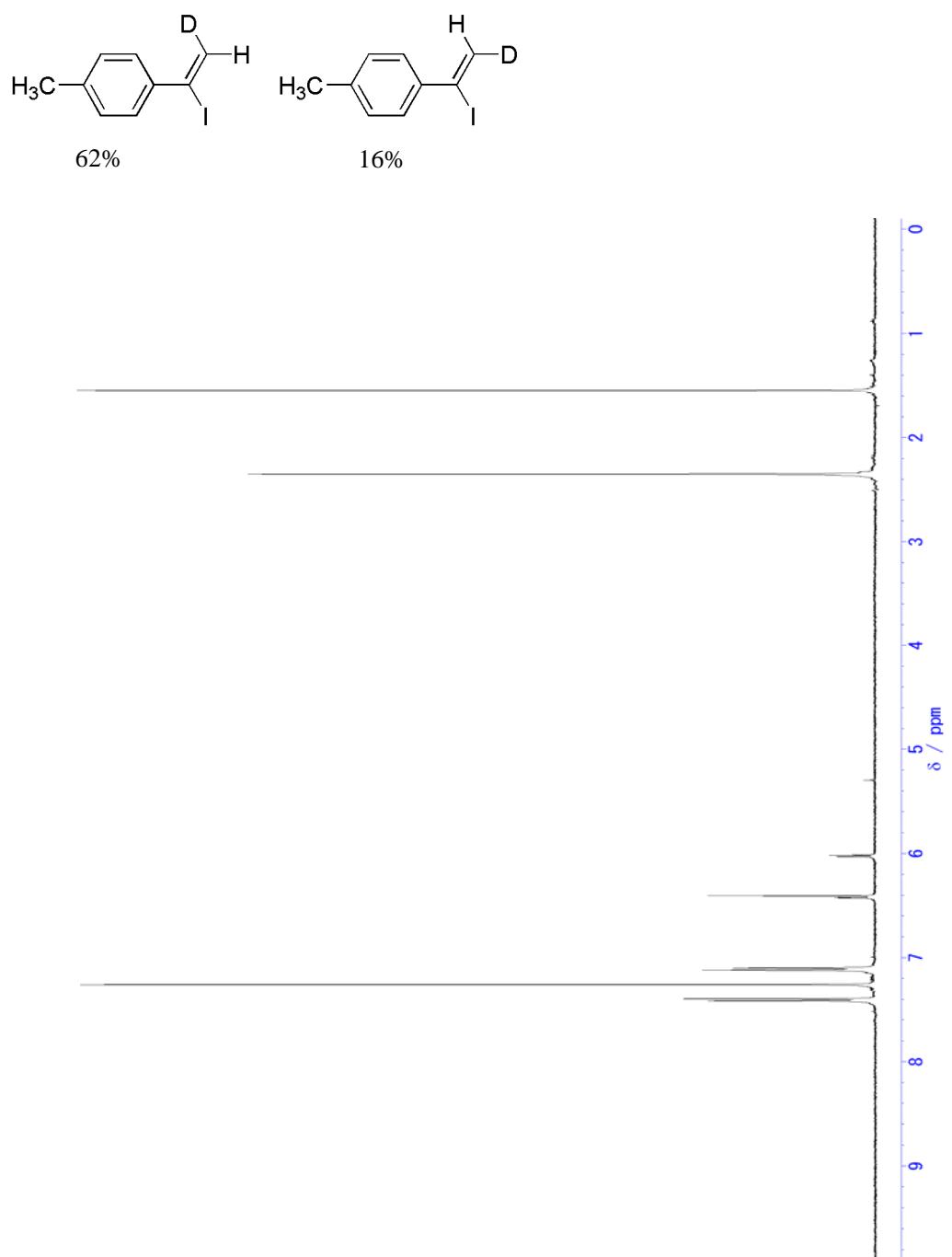
<sup>1</sup>H NMR spectrum (Table 3, entry 1):



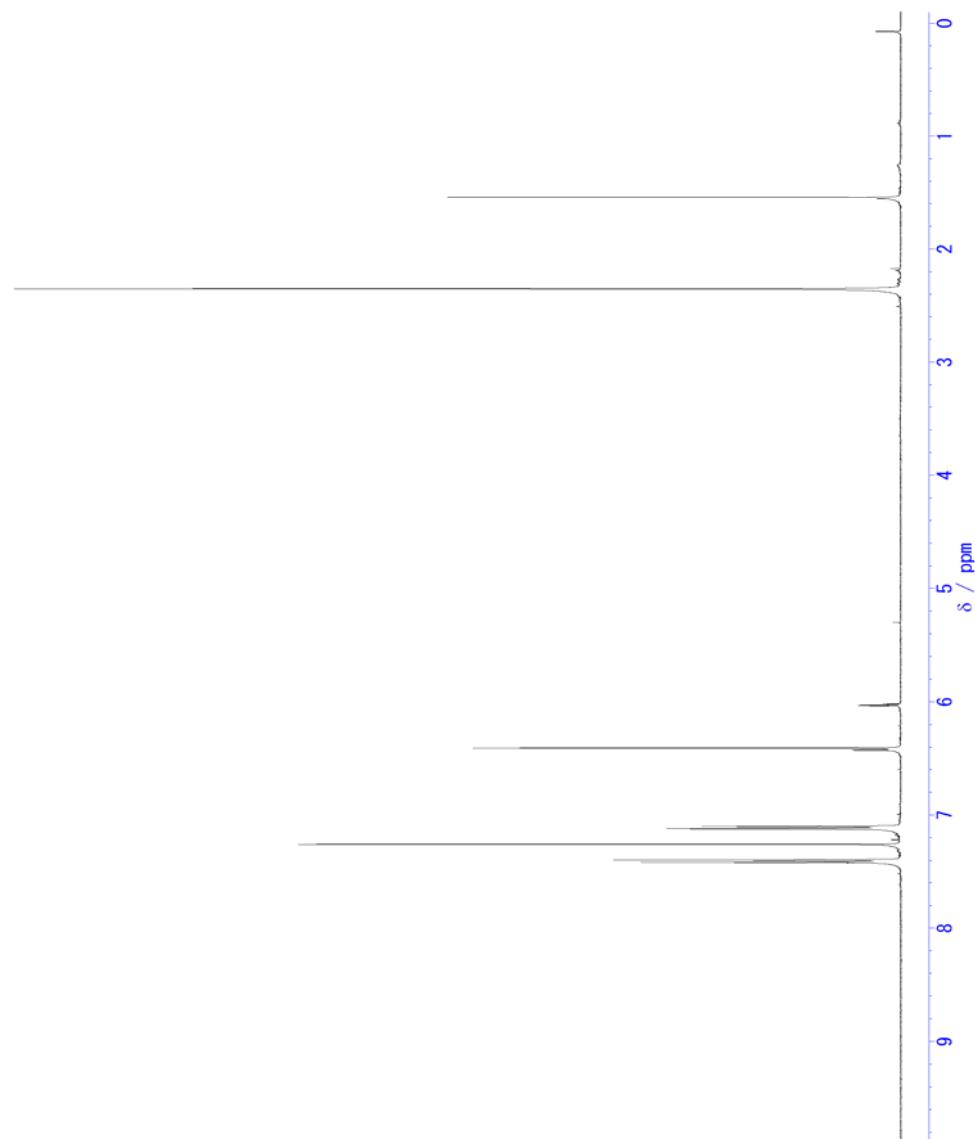
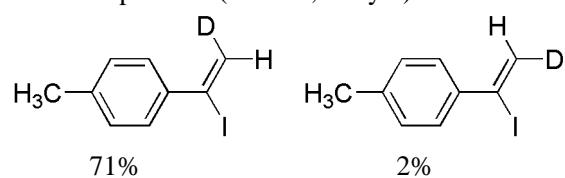
<sup>1</sup>H NMR spectrum (Table 4, entry 1):



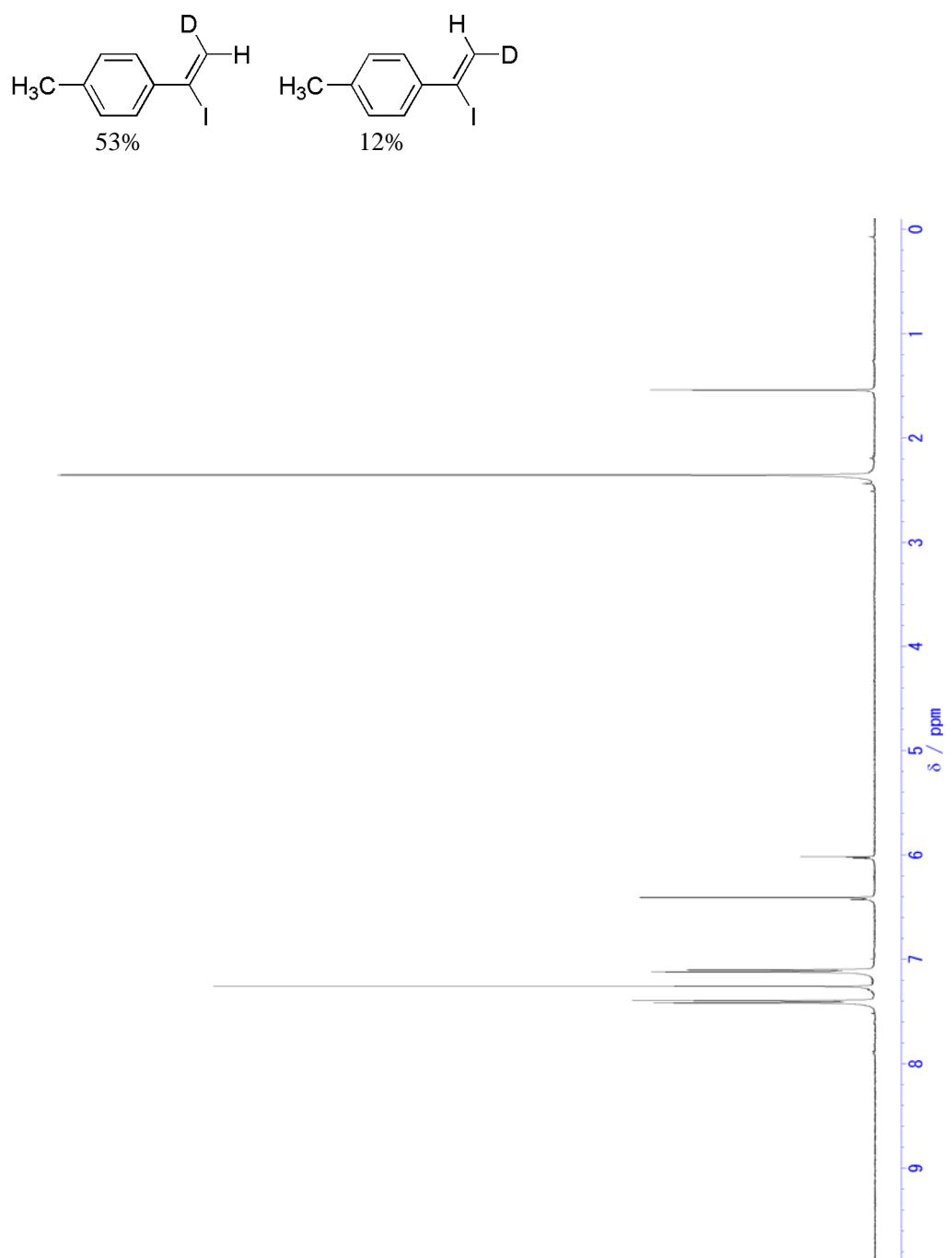
<sup>1</sup>H NMR spectrum (Table 4, entry 2):



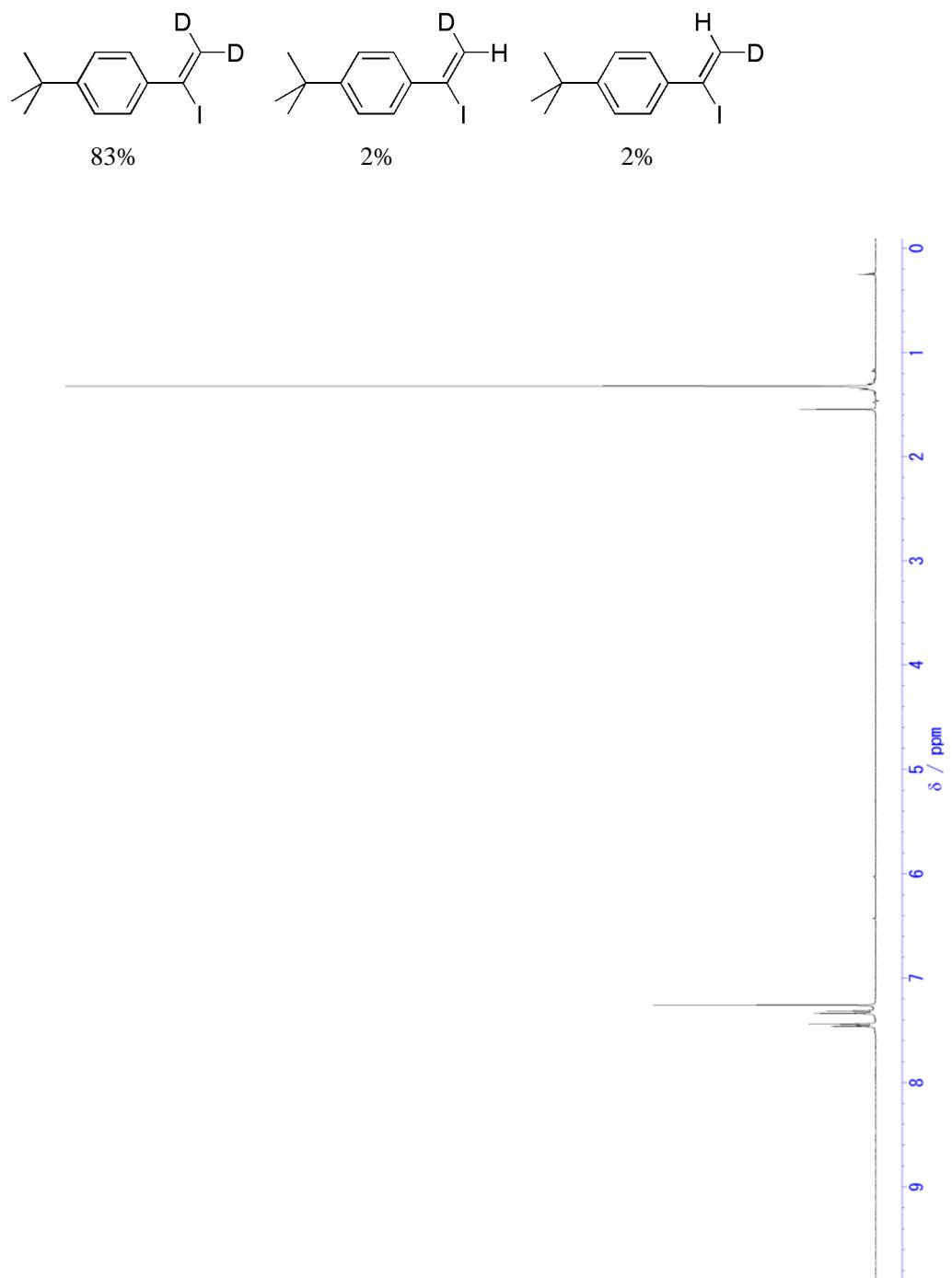
<sup>1</sup>H NMR spectrum (Table 4, entry 3):



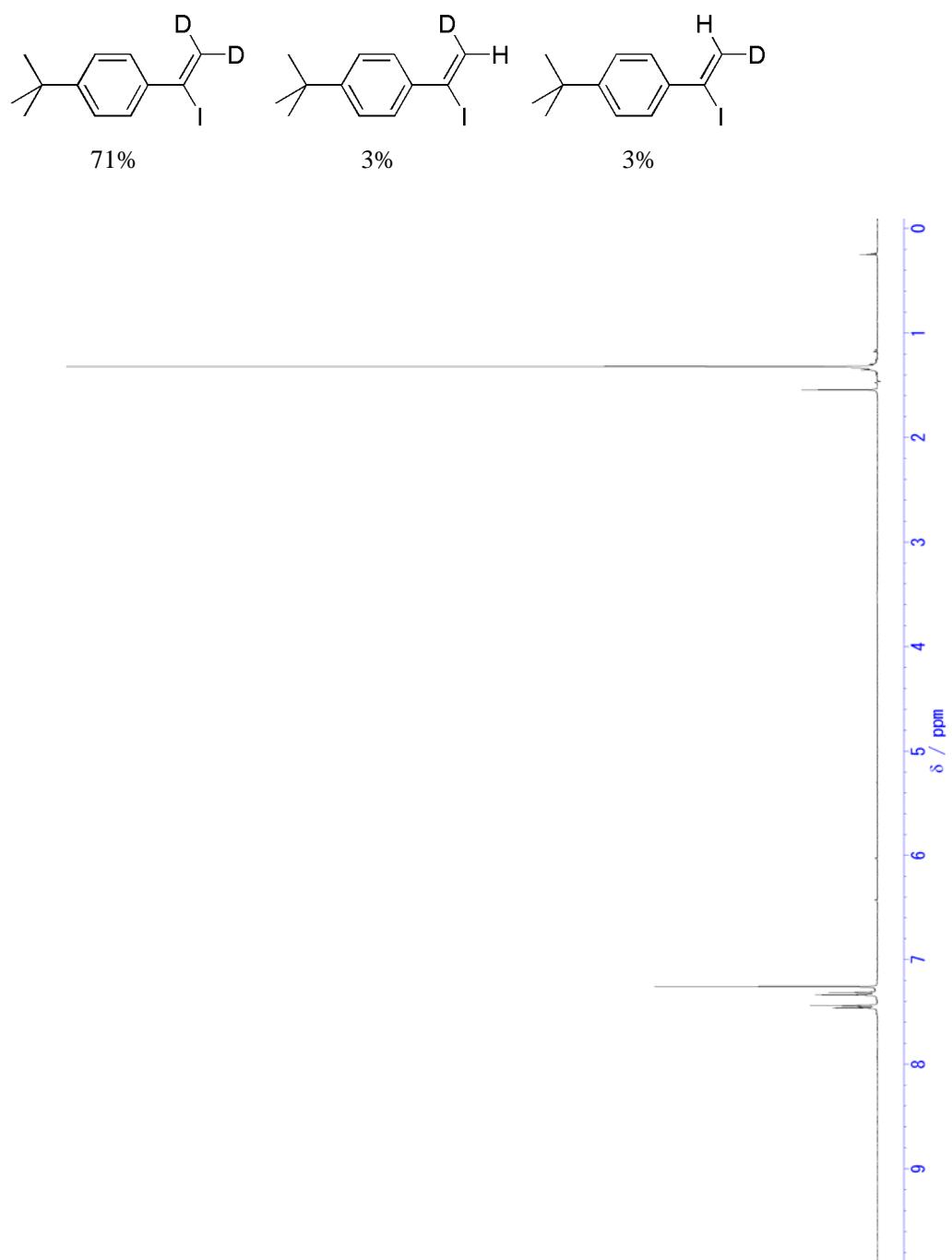
<sup>1</sup>H NMR spectrum (Table 4, entry 4):



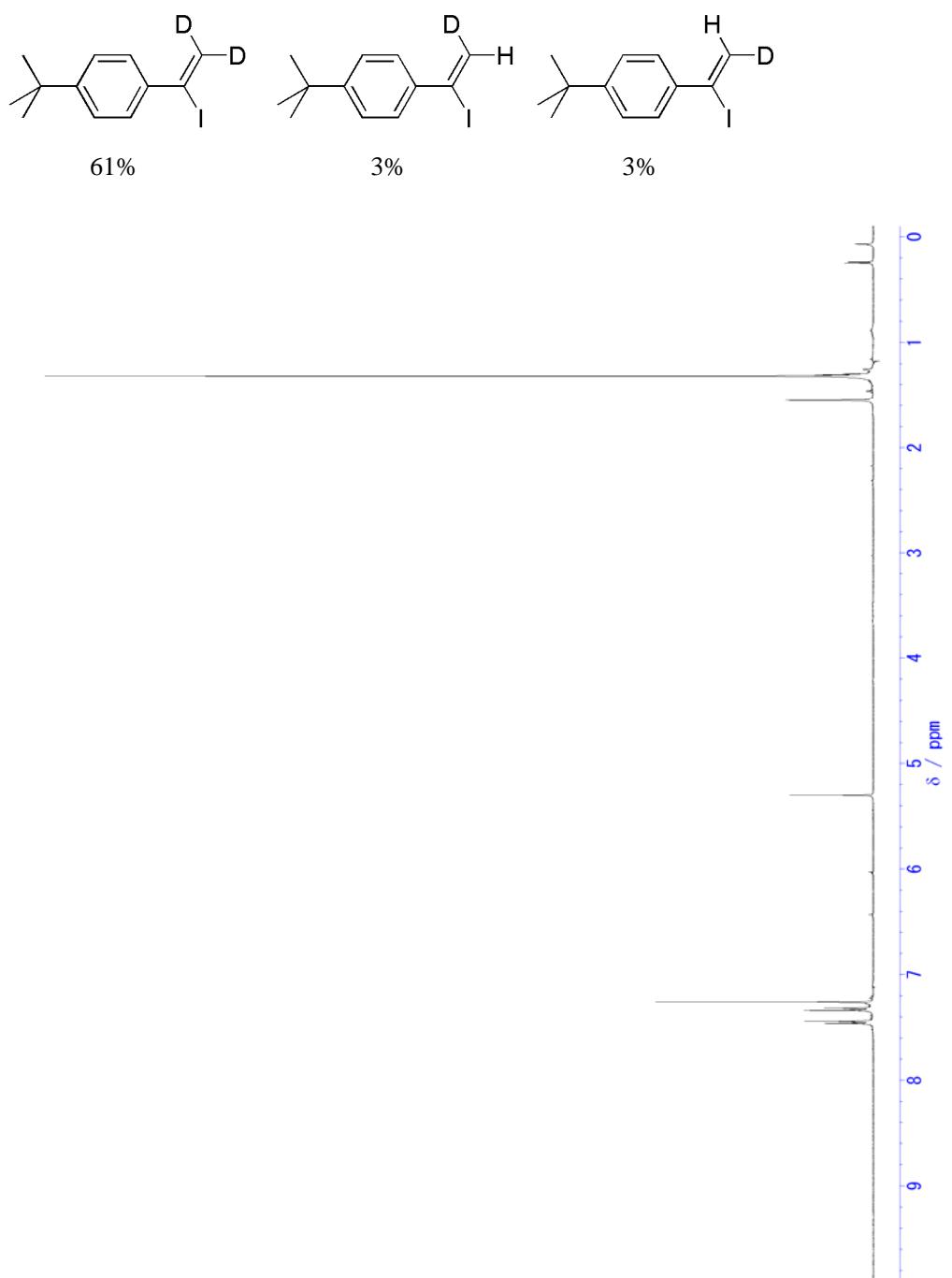
<sup>1</sup>H NMR spectrum (Table 5, entry 1):



<sup>1</sup>H NMR spectrum (Table 5, entry 2):

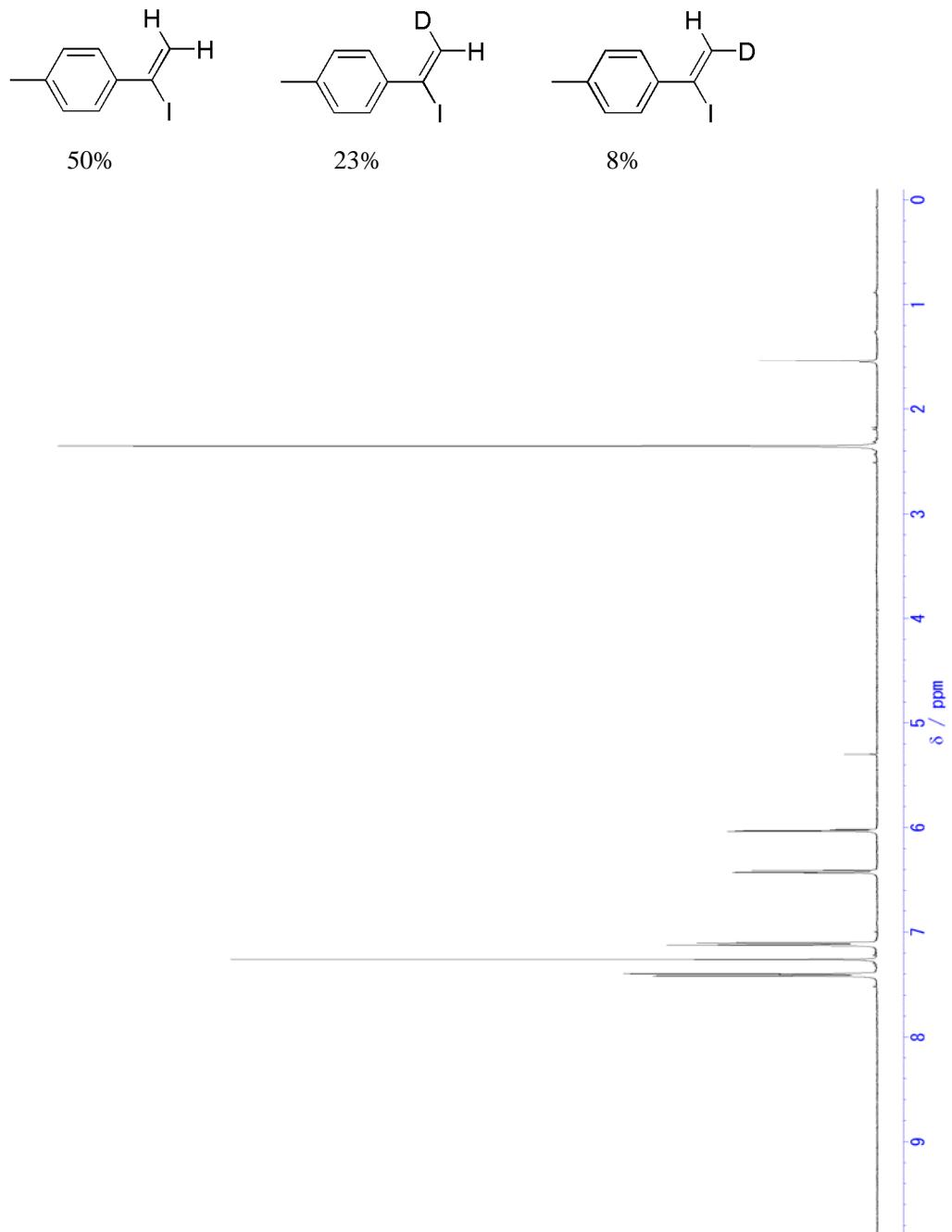


<sup>1</sup>H NMR spectrum (Table 5, entry 3)

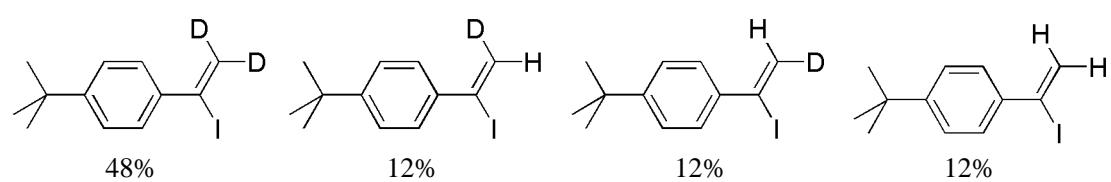


**h)  $^1\text{H}$  NMR Spectra in Scheme 2 and 3**

$^1\text{H}$  NMR spectrum (Scheme 2)

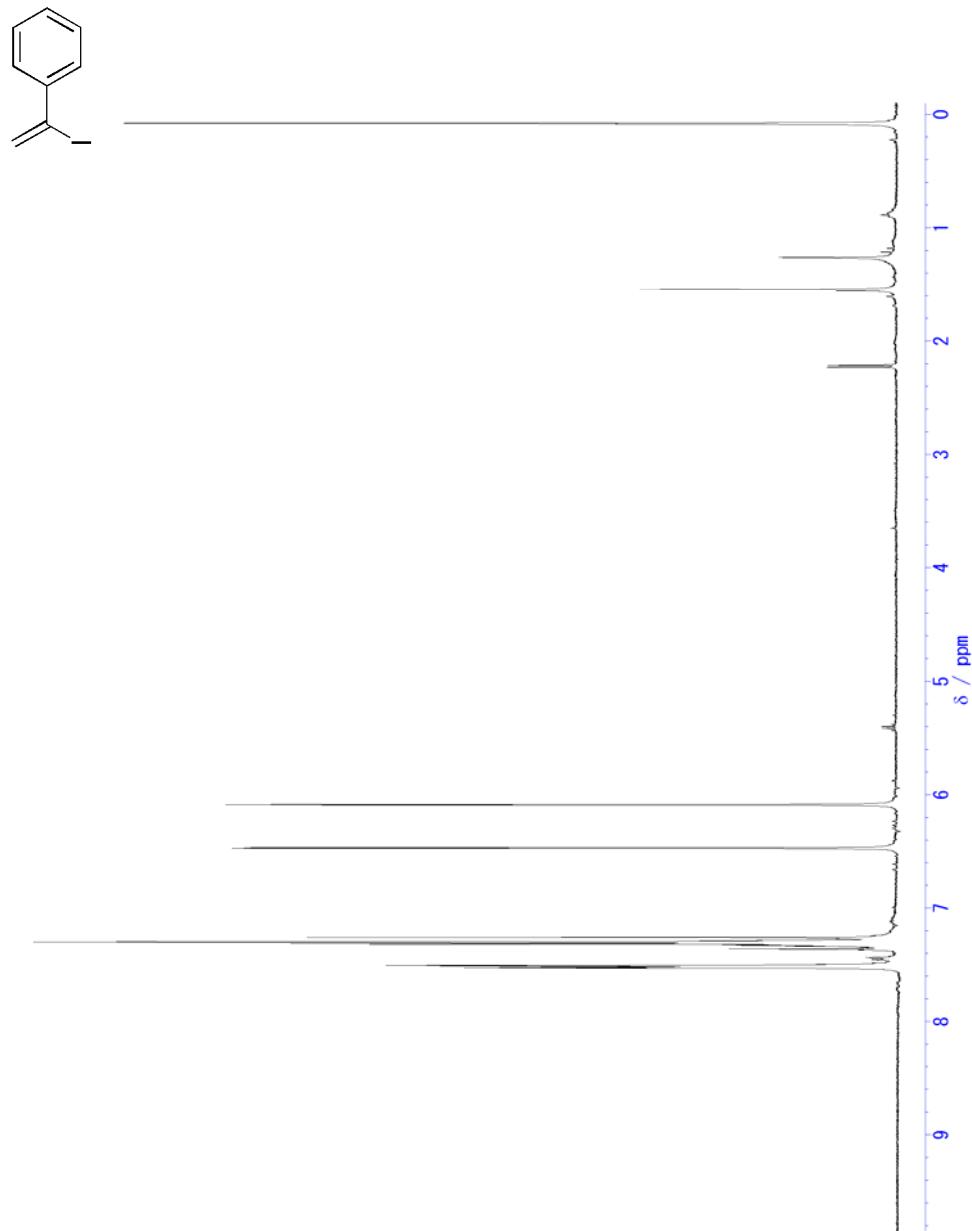


<sup>1</sup>H NMR spectrum (Scheme 3)

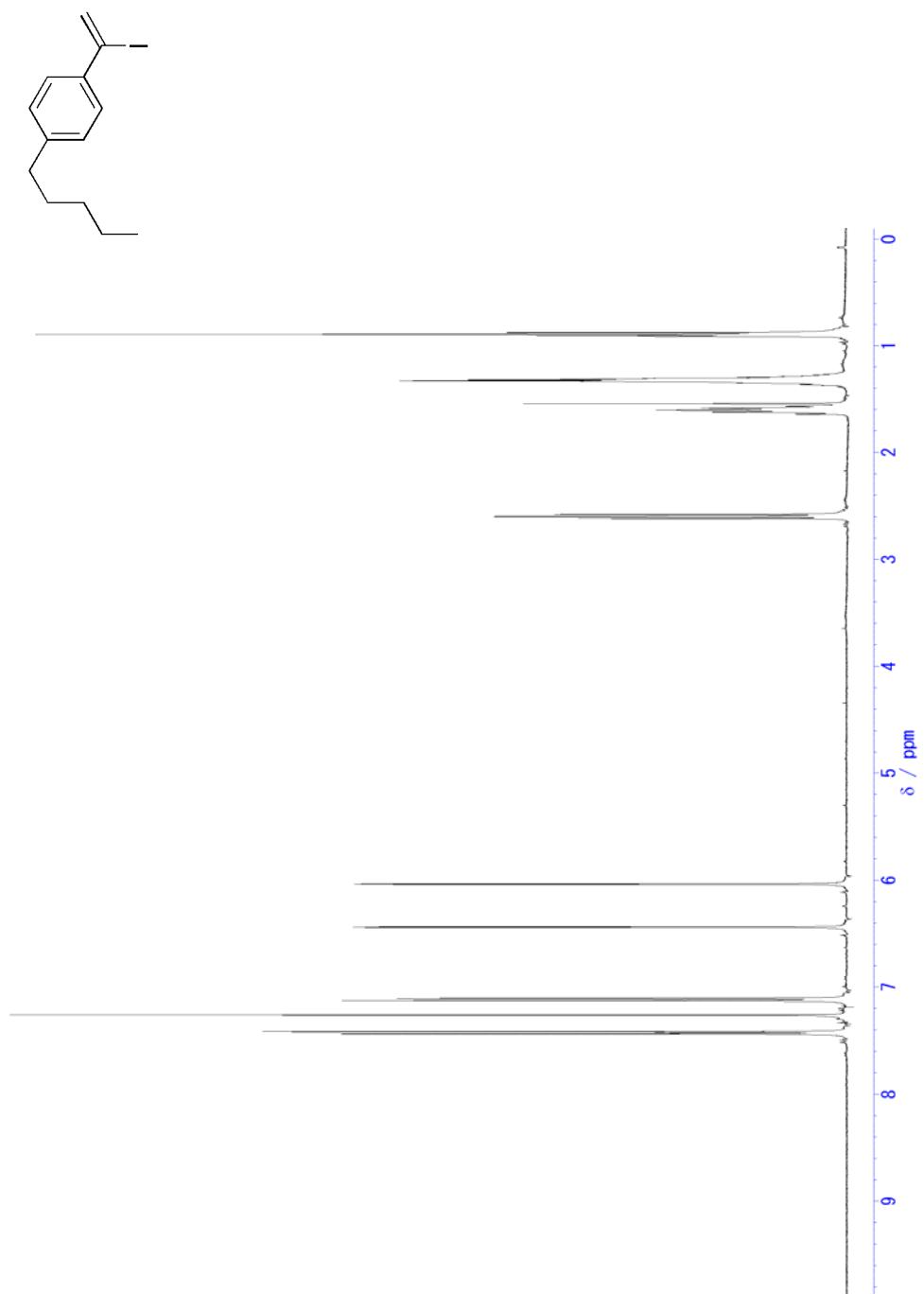


i)  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra in Table 6

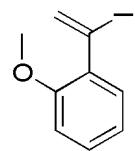
$^1\text{H}$  NMR spectrum (Table 6, entry 1): (1-iodovinyl)benzene



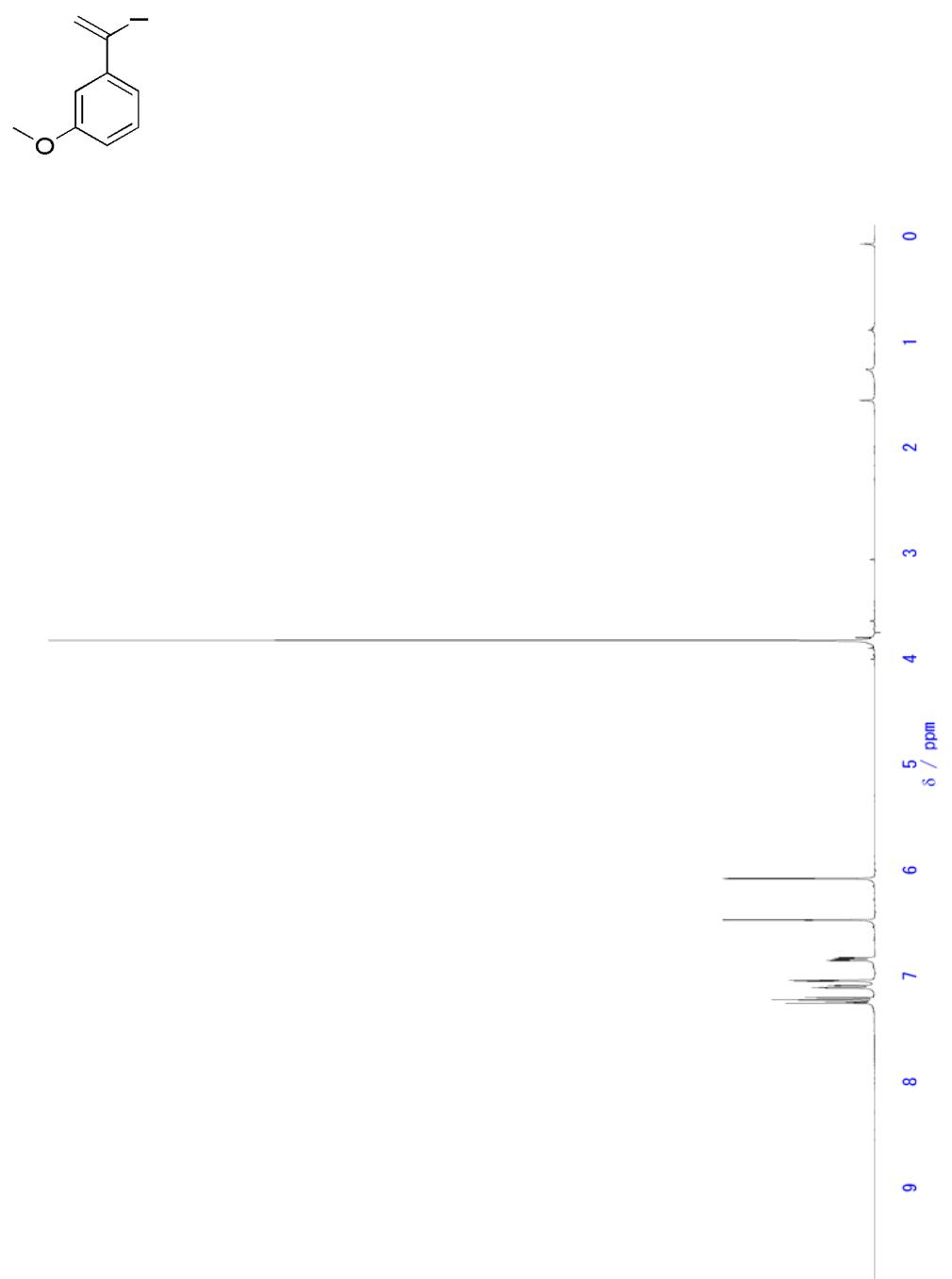
<sup>1</sup>H NMR spectrum (Table 6, entry 2): 1-(1-iodovinyl)-4-pentylbenzene



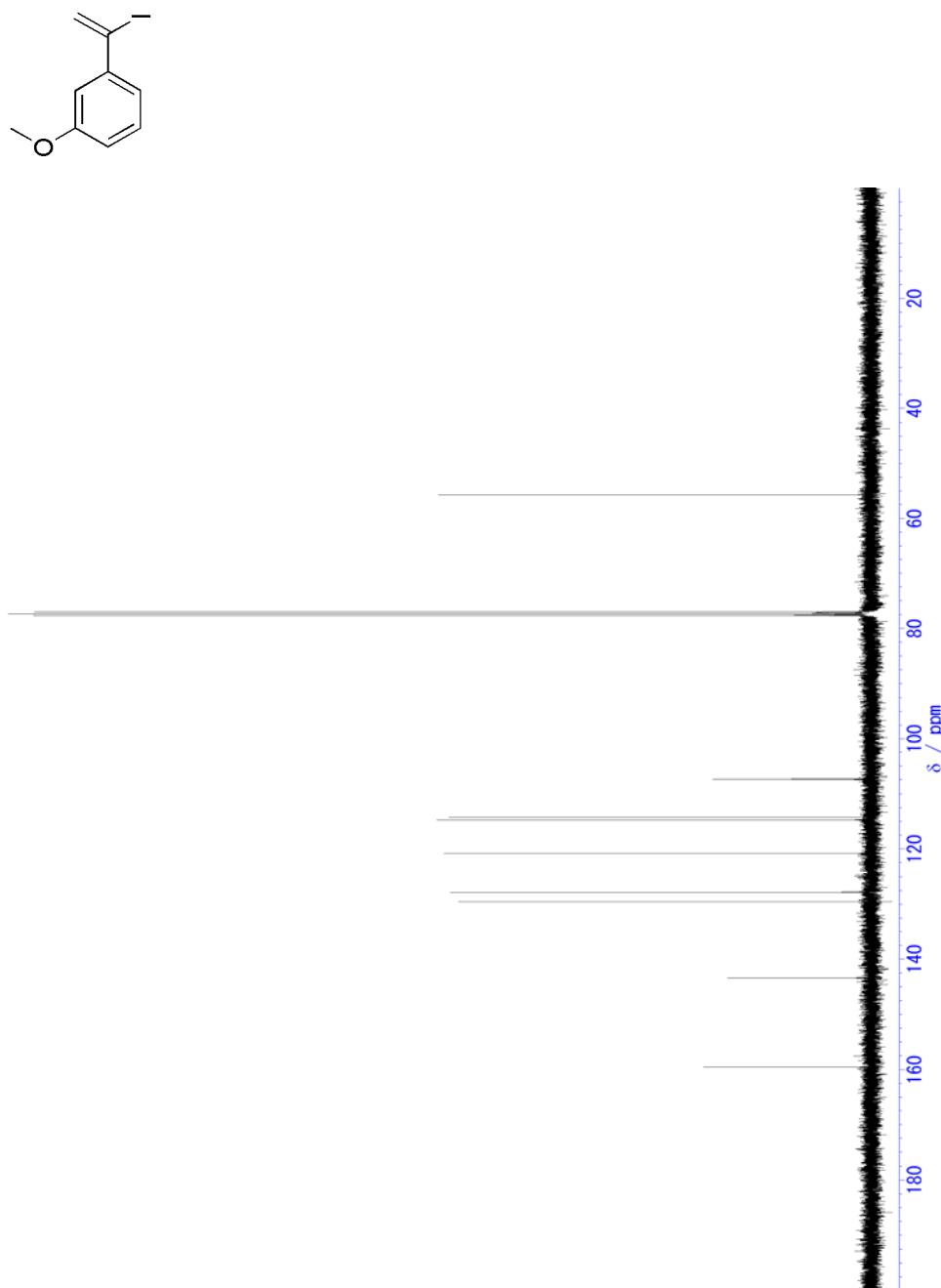
$^1\text{H}$  NMR spectrum (Table 6, entry 3): 1-(1-iodovinyl)-2-methoxylbenzene



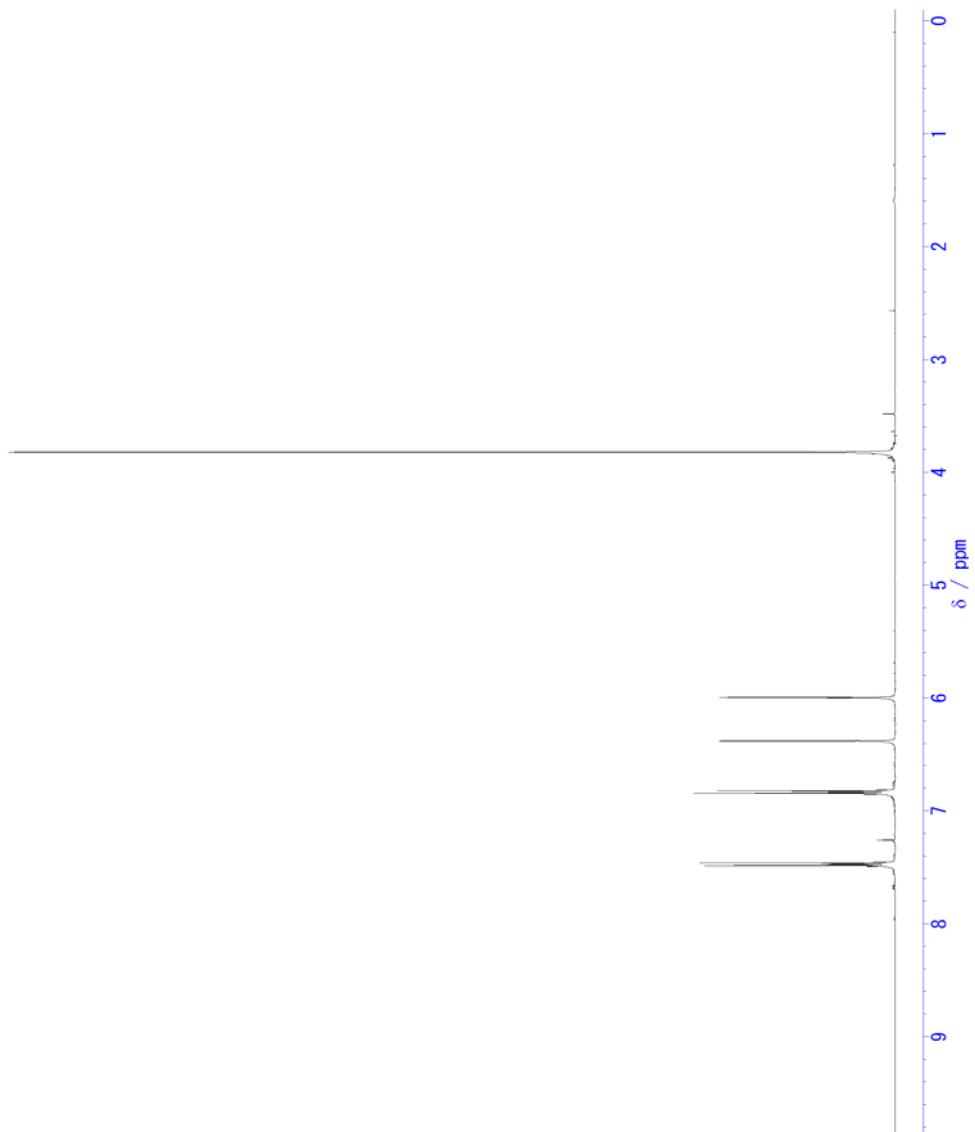
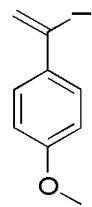
<sup>1</sup>H NMR spectrum (Table 6, entry 4): 1-(1-iodovinyl)-3-methoxylbenzene



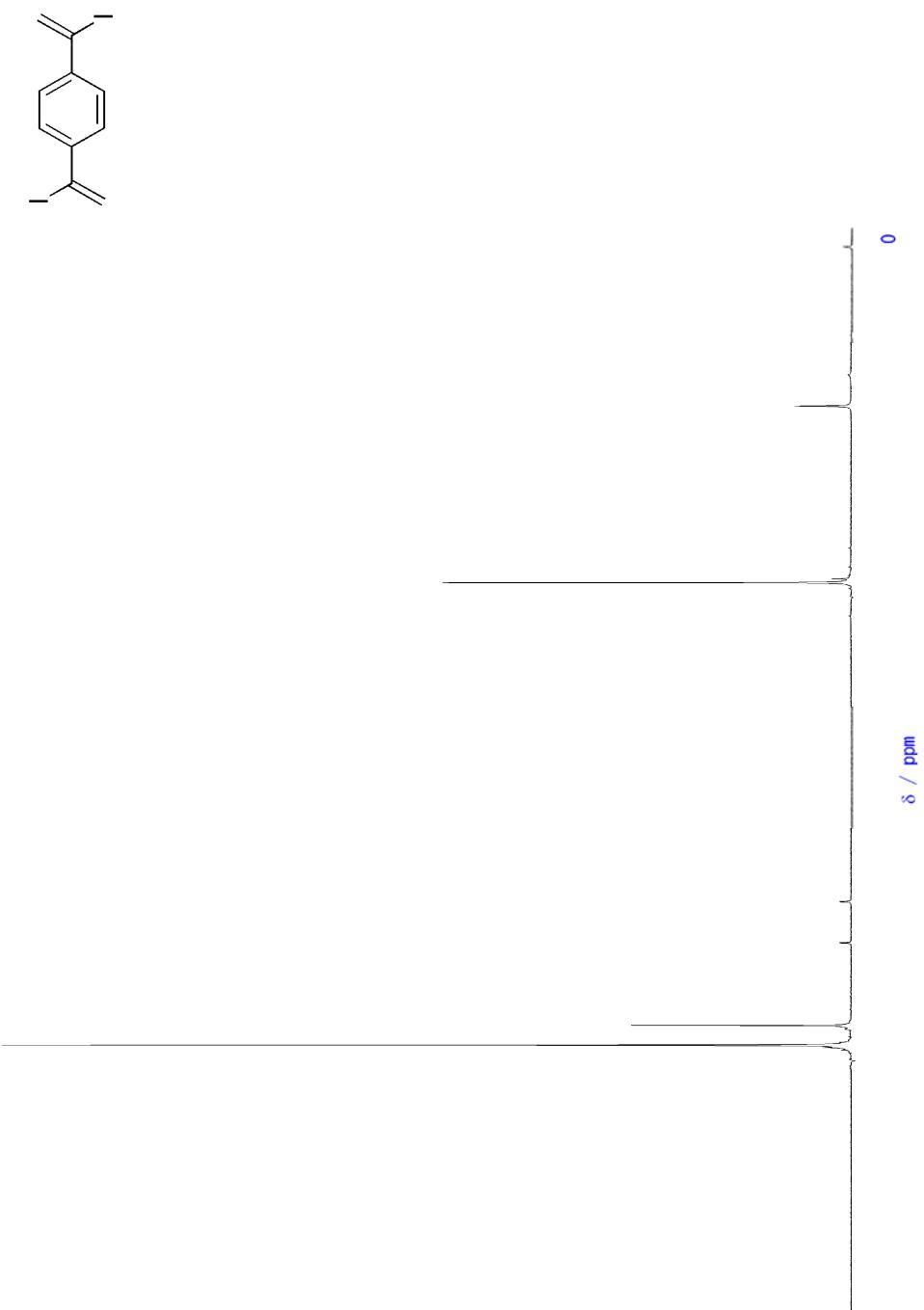
$^{13}\text{C}$  NMR spectrum (Table 6, entry 4): 1-(1-iodovinyl)-3-methoxylbenzene



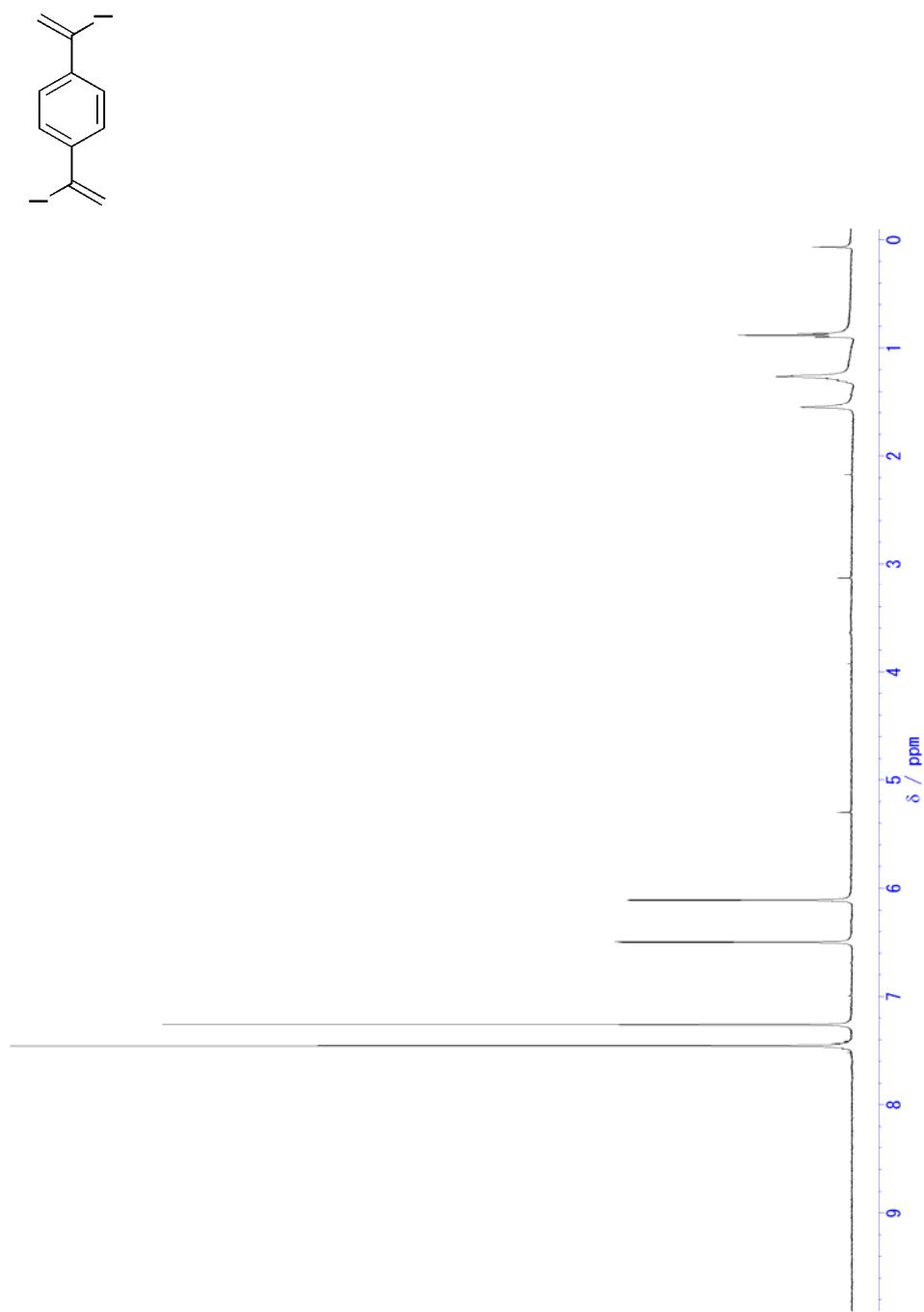
<sup>1</sup>H NMR spectrum (Table 6, entry 5): 1-(1-iodovinyl)-4-methoxylbenzene



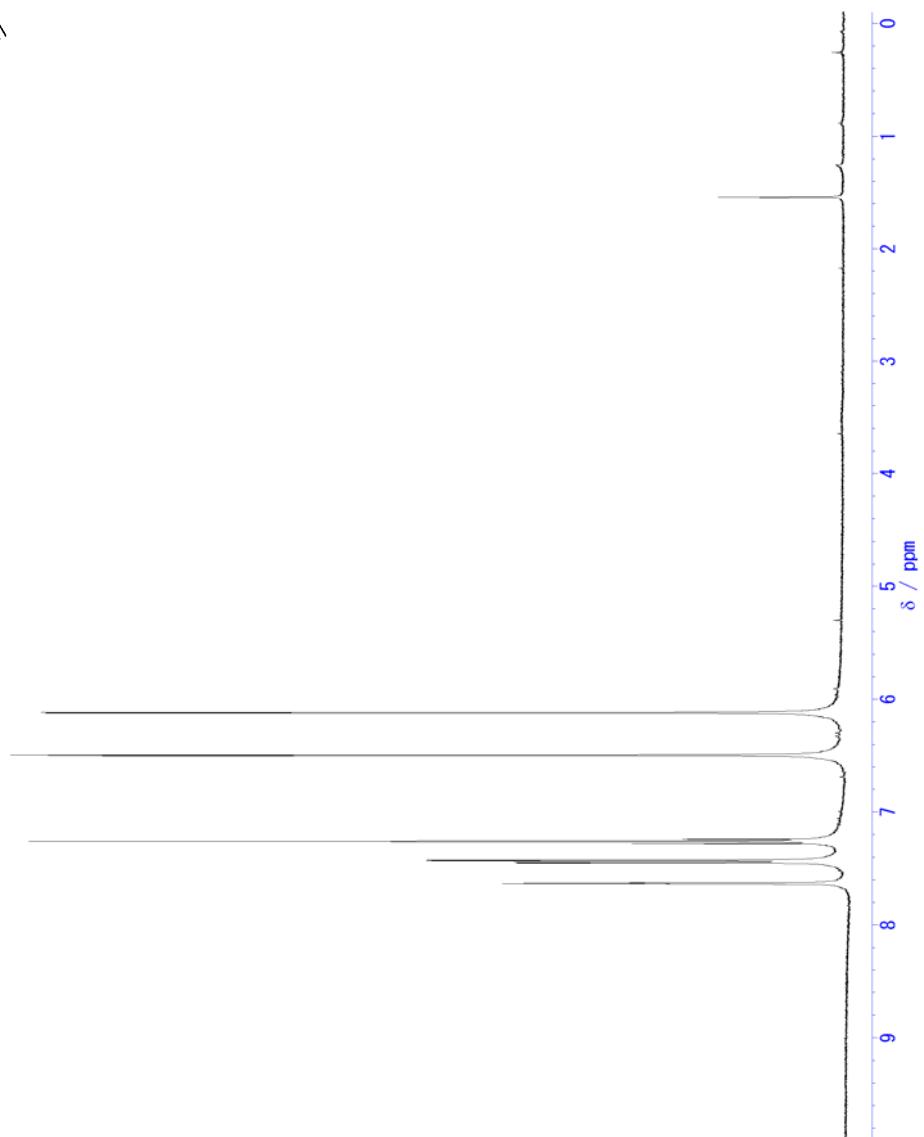
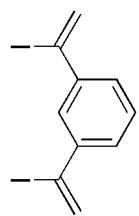
<sup>1</sup>H NMR spectrum (Table 6, entry 6): 1,4-bis(1-iodovinyl)benzene



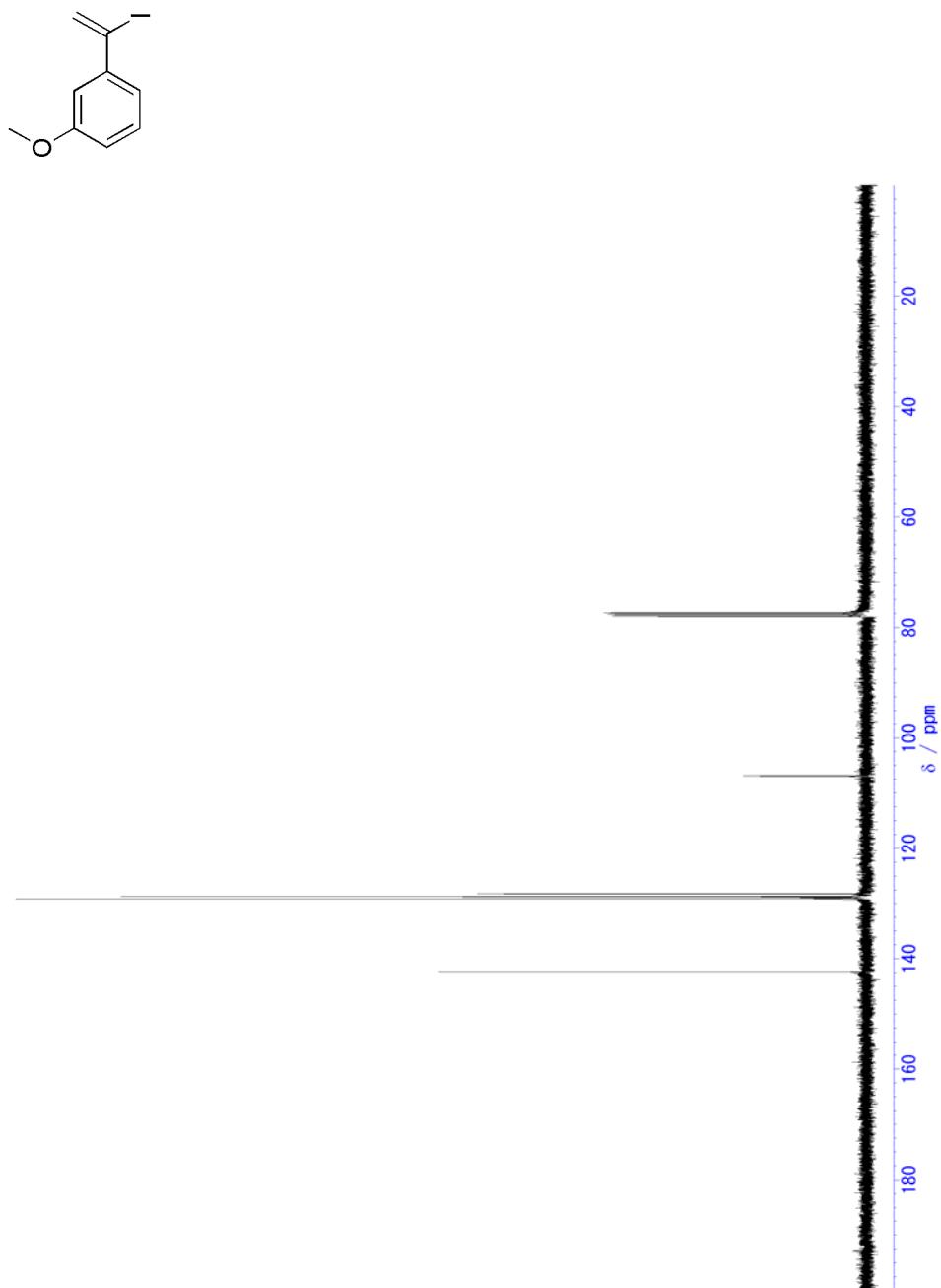
<sup>1</sup>H NMR spectrum (Table 6, entry 7): 1,4-bis(1-iodovinyl)benzene



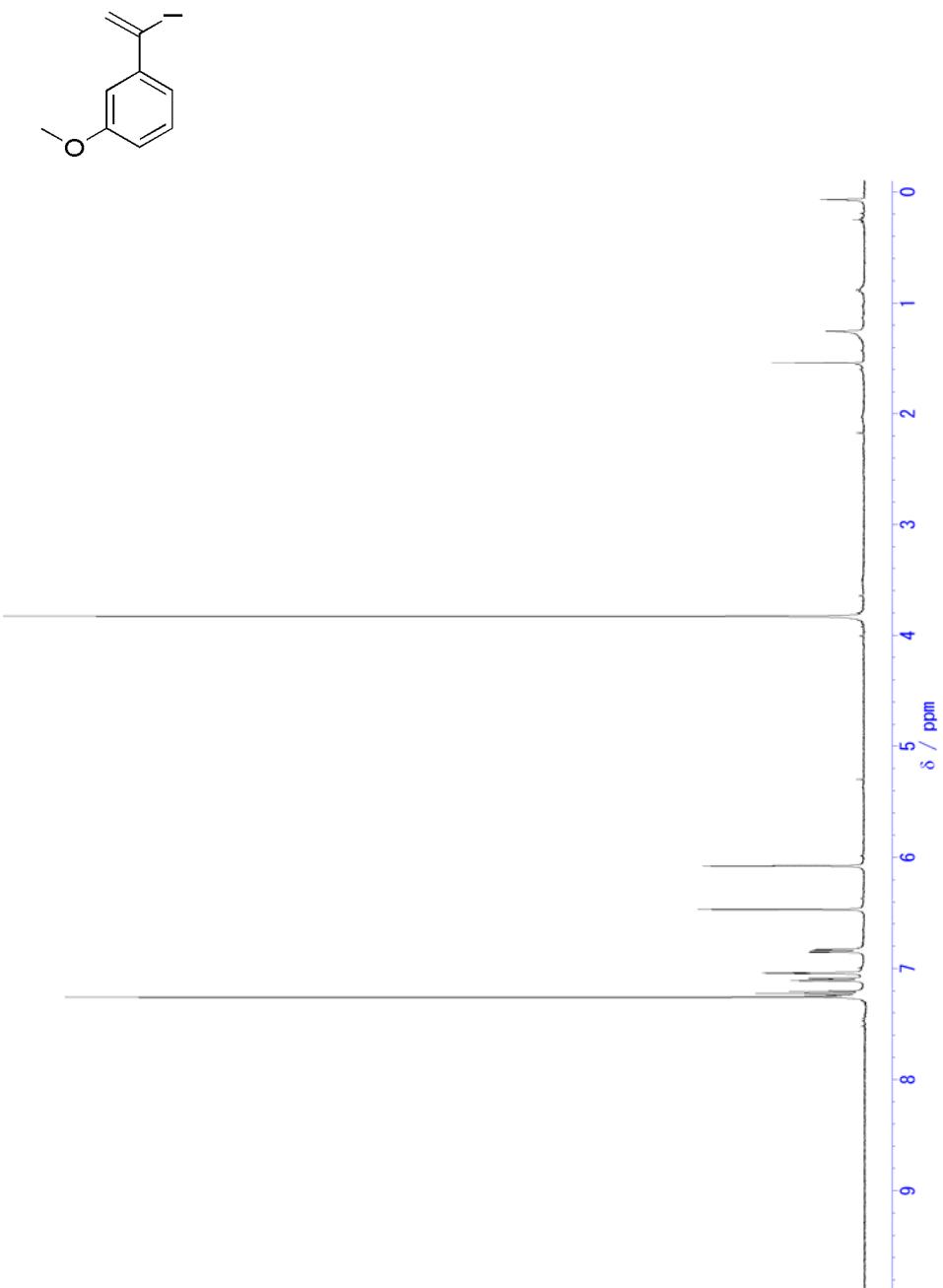
$^1\text{H}$  NMR spectrum (Table 6, entry 8): 1,3-bis(1-iodovinyl)benzene



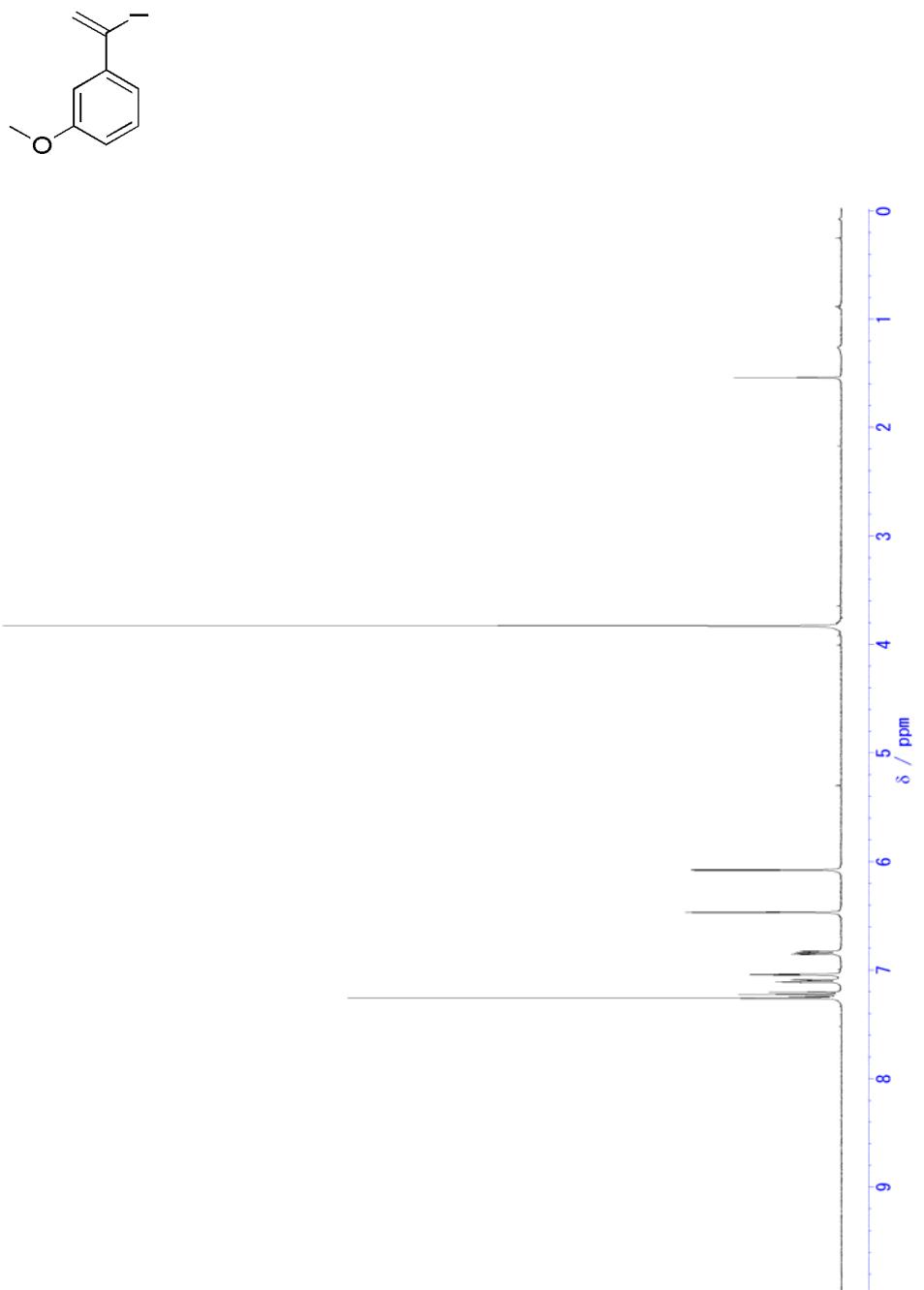
$^{13}\text{C}$  NMR spectrum (Table 6, entry 8): 1,3-bis(1-iodovinyl)benzene



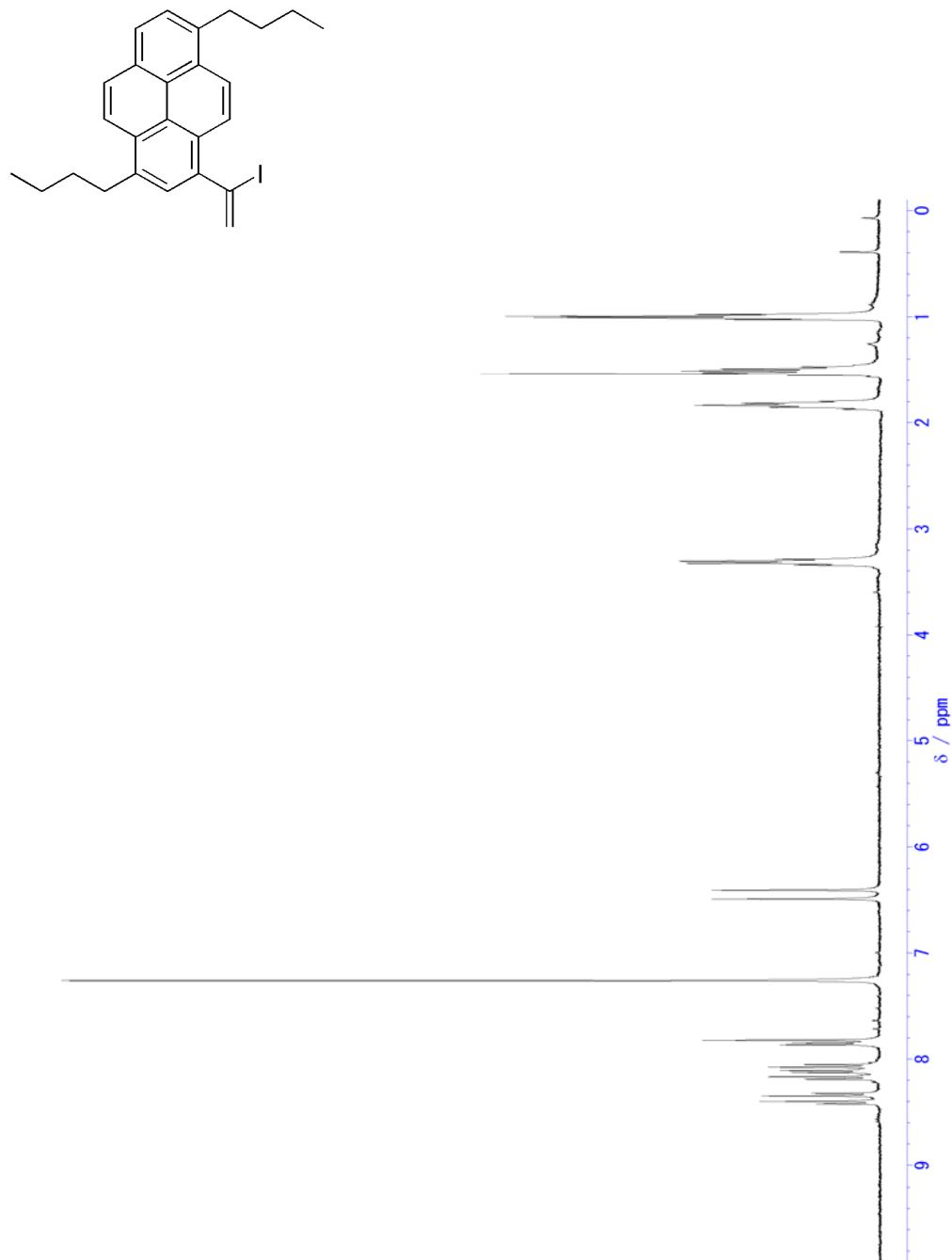
$^1\text{H}$  NMR spectrum (Table 6, entry 9): 1-(1-iodovinyl)-3-methoxybenzene



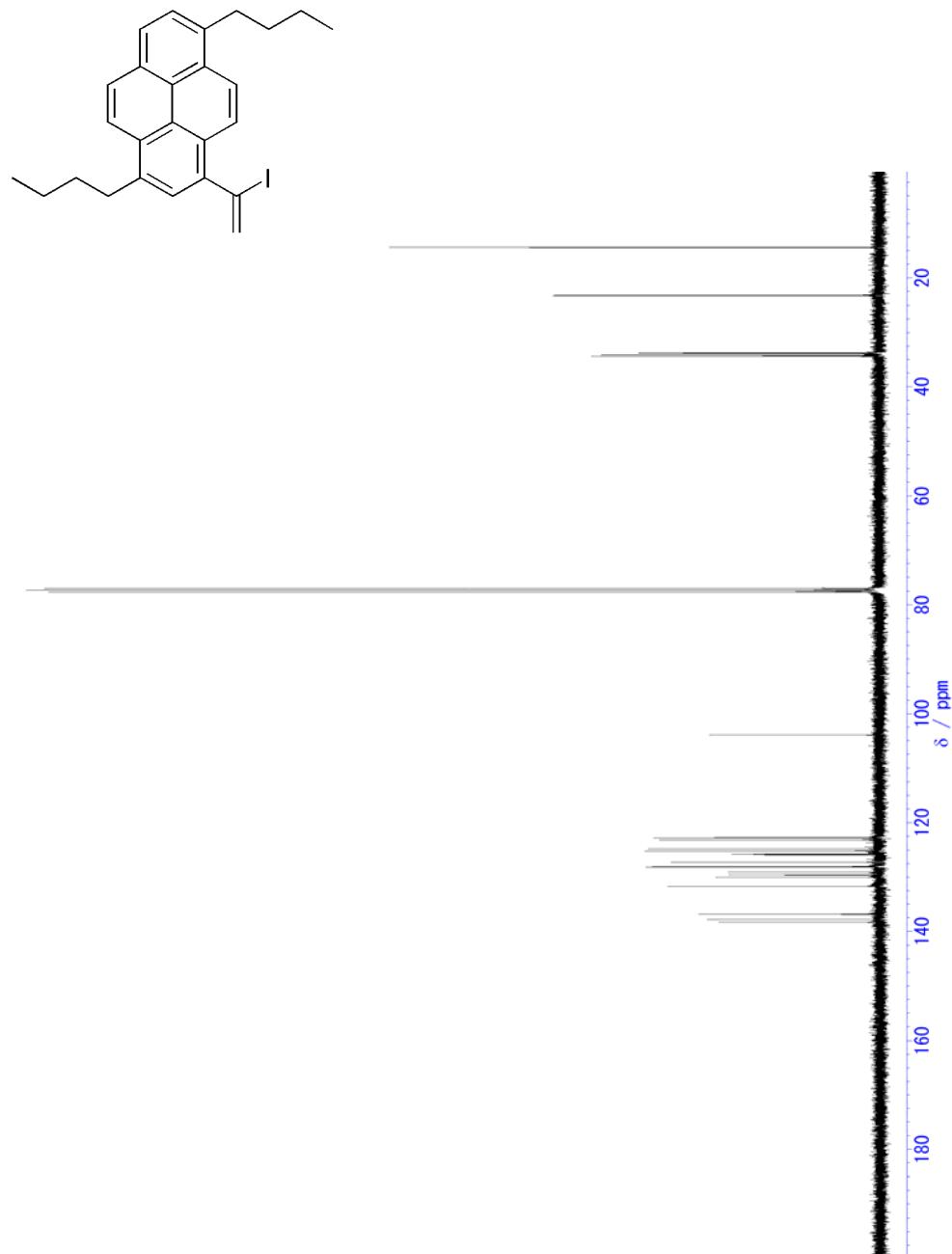
<sup>1</sup>H NMR spectrum (Table 6, entry 10): 1-(1-iodovinyl)-3-methoxybenzene



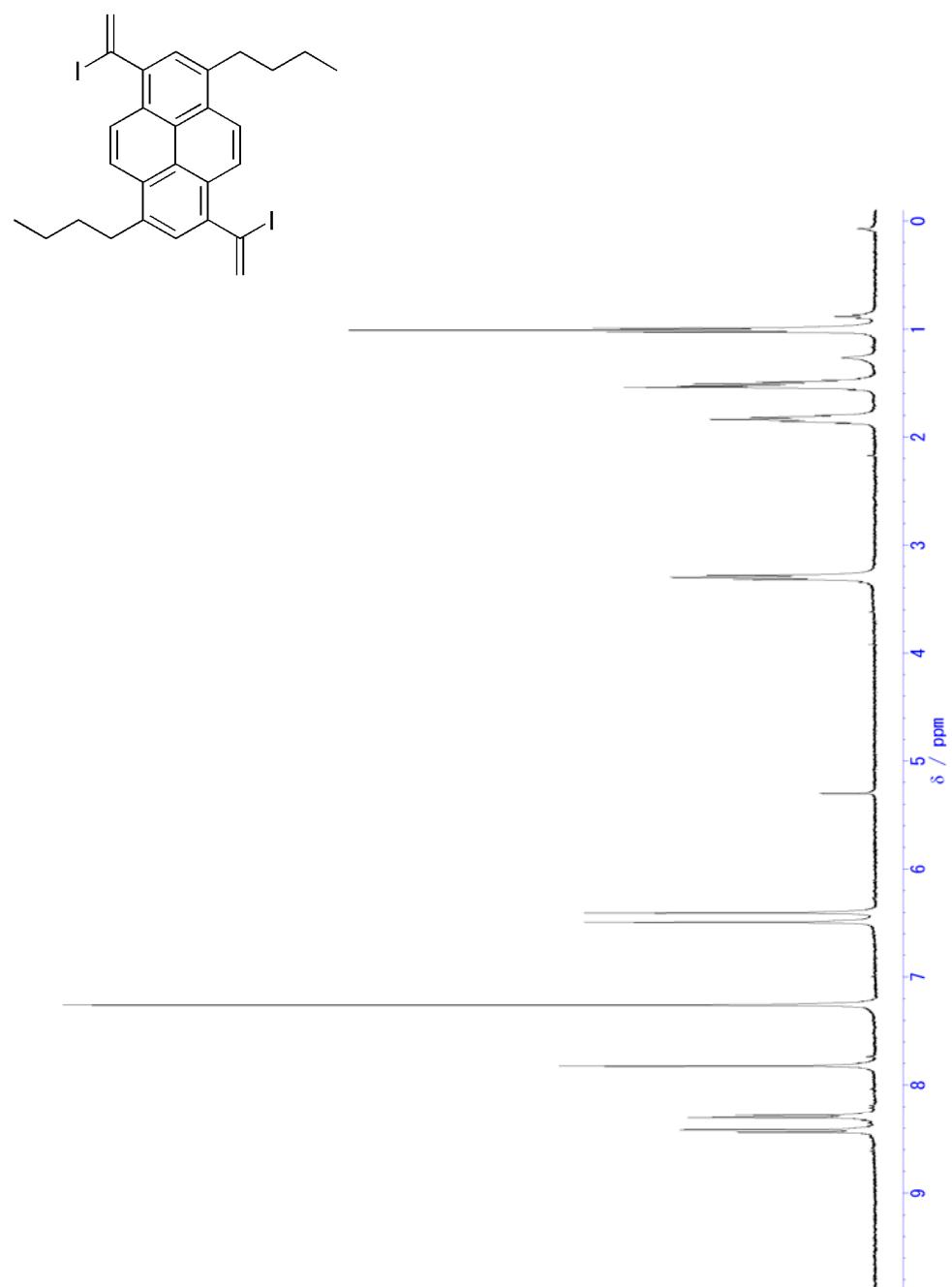
$^1\text{H}$  NMR spectrum (Table 6, entry 11): 1,6-dibutyl-3-(1-iodovinyl)pyrene



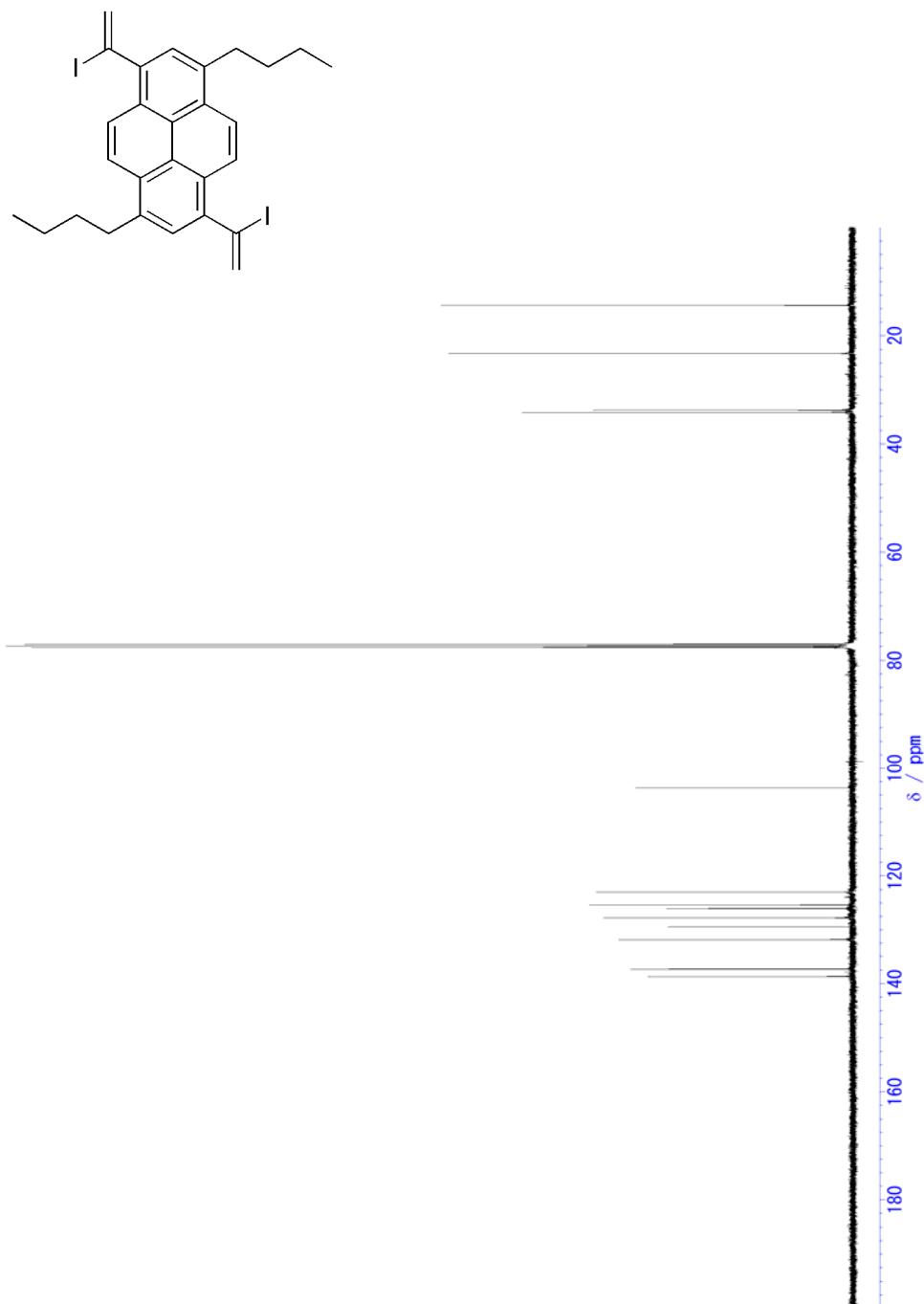
$^{13}\text{C}$  NMR spectrum (Table 6, entry 11): 1,6-dibutyl-3-(1-iodovinyl)pyrene



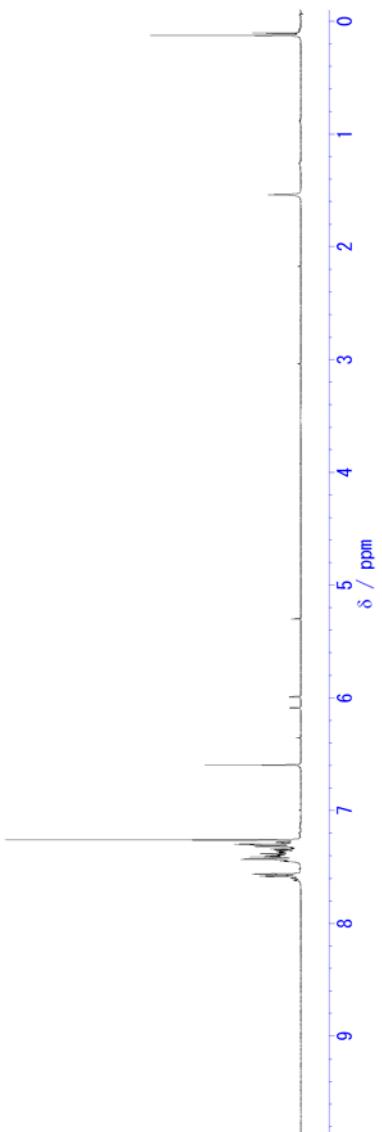
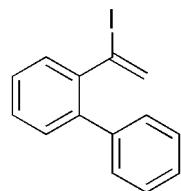
<sup>1</sup>H NMR spectrum (Table 6, entry 12): 1,6-dibutyl-3,8-bis(1-iodovinyl)pyrene



$^{13}\text{C}$  NMR spectrum (Table 6, entry 12): 1,6-dibutyl-3,8-bis(1-iodovinyl)pyrene

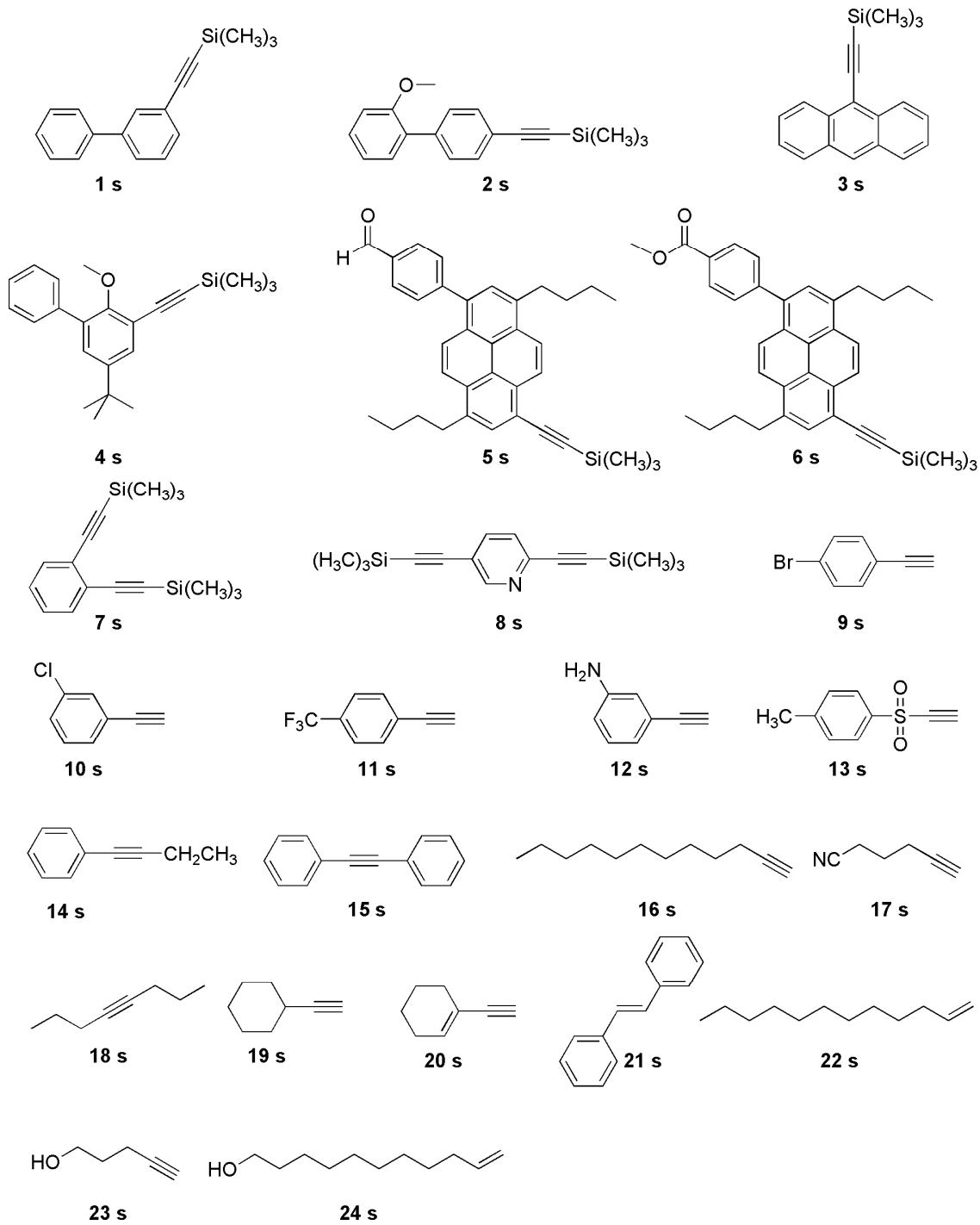


$^1\text{H}$  NMR spectrum (Table 6, entry 13): 2-(1-iodovinyl)biphenyl

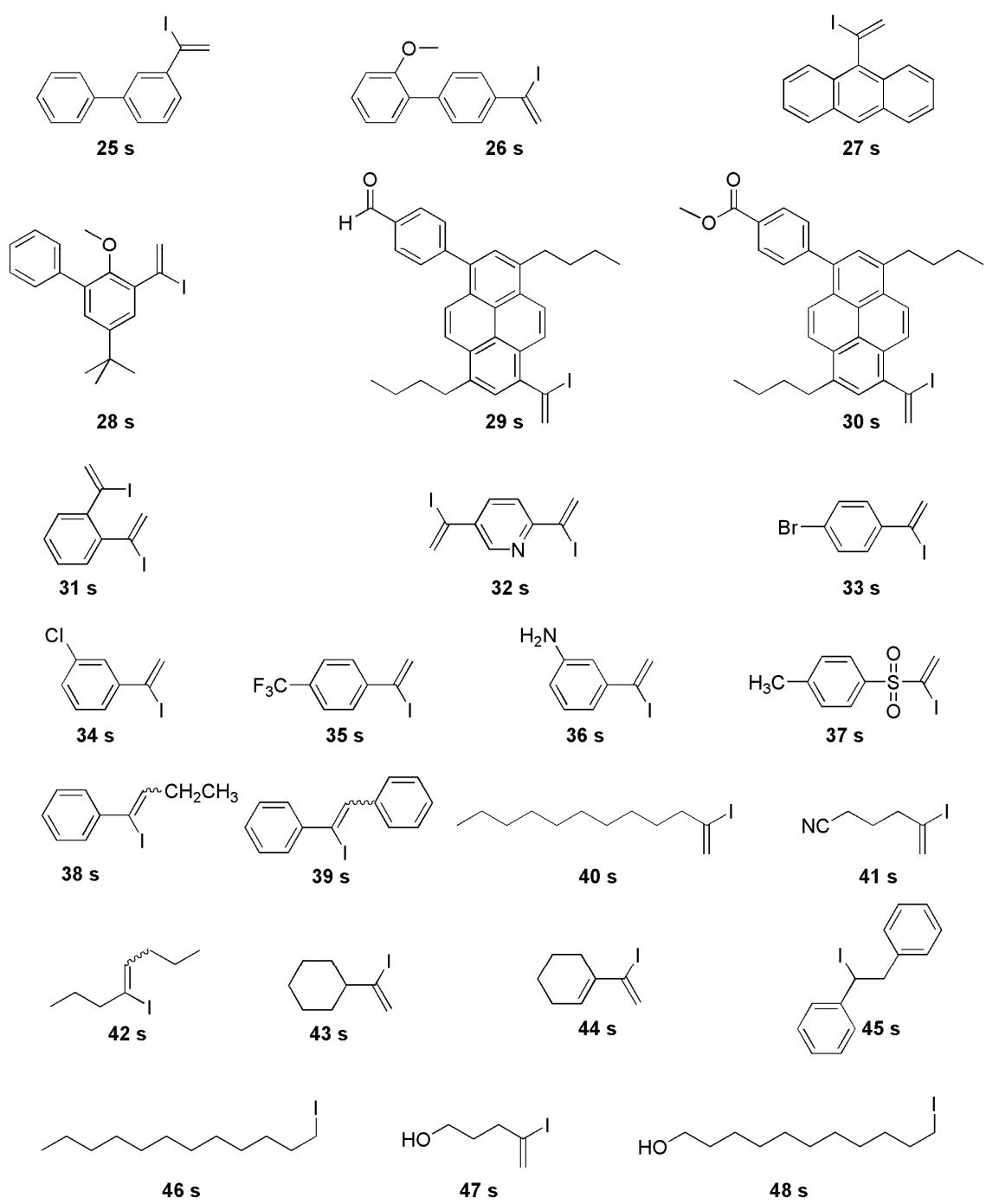


j) **Table 1S. Evaluation of the reactivity of other alkynes and alkenes on this alpha-vinyl iodation.**

Entry	SM	Desired product	Recovered			Remarks
			Yield (%)	SM (%)		
1	1 s	25 s	-	-		TM was decomposed during workup.
2	2 s	26 s	-	-		TM was decomposed during workup.
3	3 s	27 s	0	100		No byproduct was observed on TLC.
4	4 s	28 s	trace	-		4 spots on TLC
5	5 s	29 s	63	37		Determined by $^1\text{H}$ NMR
6	6 s	30 s	44	57		Determined by $^1\text{H}$ NMR
7	7 s	31 s	trace	-		Multi spots on TLC
8	8 s	32 s	0	100		No byproduct was observed on TLC.
9	9 s	33 s	2	74		Determined by $^1\text{H}$ NMR
10	10 s	34 s	0	100		
11	11 s	35 s	0	0		Messy $^1\text{H}$ NMR spectrum of the crude was observed.
12	12 s	36 s	0	100		
13	13 s	37 s	0	100		
14	14 s	38 s	3	92		
15	15 s	39 s	0	83		
16	16 s	40 s	0	~ 99		The crude contained the insoluble materials.
17	17 s	41 s	0	~ 99		Messy $^1\text{H}$ NMR spectrum of the crude was observed.
18	18 s	42 s	0	0		The crude contained the insoluble materials.
19	19 s	43 s	0	0		
20	20 s	44 s	< 77	4		
21	21 s	45 s	0	~ 99		The crude contained the insoluble materials.
22	22 s	46 s	0	69		Messy $^1\text{H}$ NMR spectrum of the crude was observed.
23	23 s	47 s	0	0		
24	24 s	48 s	0	100		



**Figure 1S.** Alkynes and alkenes for Table 1S



**Figure 2S.** Compounds for Table 1S.

## k) References

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