

# **Supporting Information**

## **Cross-conjugated Chromophores: Synthesis of *iso*-Polydiacetylenes with Donor/Acceptor Substitution**

**Catalin Ciulei and Rik R. Tykwinski\***

Department of Chemistry, University of Alberta,  
Edmonton, Alberta, T6G 2G2 Canada  
E-mail: rik.tykwinski@ualberta.ca

1. Experimental and spectroscopic details for compounds **2-4** and **6-13**.
2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for molecules **4**, **9** and **13**

## Experimental

**General.** Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium/benzophenone ketyl. 4-Iodo-*N,N*-dimethylaniline,<sup>1</sup> compound **1**,<sup>2</sup> and compound **5**<sup>3</sup> were made as previously reported. Anhydrous MgSO<sub>4</sub> was used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at H<sub>2</sub>O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of N<sub>2</sub>. A positive pressure of N<sub>2</sub> was essential to the success of all Pd-catalyzed reactions. Degassing of solvents was accomplished by vigorously bubbling N<sub>2</sub> through the solution for at least 45 min. Column chromatography: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada*. Thin Layer Chromatography (TLC): aluminum sheets covered with *silica gel-60 F<sub>254</sub>* from *Macherey-Nagel*; visualization by UV light or KMnO<sub>4</sub> stain. M.p.: *Gallenkamp* apparatus; uncorrected. DSC: *Dupont 900 Differential Thermal Analyzer*. UV/VIS Spectra: *Varian Cary 400* at rt;  $\lambda_{\text{max}}$  in nm ( $\epsilon$  in L M<sup>-1</sup> cm<sup>-1</sup>). IR spectra (cm<sup>-1</sup>): *Nicolet Magna-IR 750* (neat) or *Nic-Plan IR Microscope* (solids). <sup>1</sup>H- and <sup>13</sup>C-NMR: *Varian Gemini-300* and *Bruker AM-300* or *400* instruments, at rt in CDCl<sub>3</sub>; solvent peaks (7.24 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C) as reference. EI MS (*m/z*): *Kratos MS50* instrument. Elemental analyses were effected by Spectral Services at the University of Alberta.

For simplicity, the coupling constants of the aryl protons for the *p*-*N,N*-dimethylaminophenyl and *p*-nitrophenyl moieties have been reported as pseudo first-order, even though they are second-order spin systems.

**Donor-substituted Monomer 2.** A mixture of **1** (325 mg, 0.979 mmol) and K<sub>2</sub>CO<sub>3</sub> (50 mg, 0.36 mmol) in wet THF (5 mL) and MeOH (25 mL) was stirred for 4 h. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl, dried (MgSO<sub>4</sub>) and reduced to 5 mL. Et<sub>3</sub>N (50 mL) was added, and the solution was degassed for 2 h. *p*-Iododimethylaniline (250 mg, 1.01 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (59 mg, 0.08 mmol) and CuI (31 mg, 0.16 mmol) were sequentially added. The mixture was stirred at rt for 20 h. Solvent removal and purification by column chromatography (silica gel-H, hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:1) afforded **2** (229 mg, 63%) as a pale yellow solid. Mp 45-46 °C; UV/VIS (CHCl<sub>3</sub>) 268 (16500), 302 (sh, 15000) 325 (22100) nm; IR (neat) 2942, 2865, 2202, 2150, 1607, 1520, 1365, 809 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 2.95 (s, 6H), 2.063 (s, 3H), 2.059 (s, 3H), 1.09 (s, 21H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 150.0, 132.5, 111.9, 110.7, 104.2, 102.5, 92.3, 92.0, 84.5, 40.3, 22.8, 22.7, 18.8, 11.4; EIMS *m/z* 379 (M<sup>+</sup>, 100); HRMS calcd. for C<sub>25</sub>H<sub>37</sub>NSi 379.2695, found 379.2699. X-Ray.

**Acceptor-substituted Monomer 3.** A mixture of **1** (256 mg, 0.770 mmol) and K<sub>2</sub>CO<sub>3</sub> (58 mg, 0.42 mmol) in wet THF (5 mL) and MeOH (25 mL) was stirred for 4 h. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl, dried (MgSO<sub>4</sub>) and reduced to 5 mL. Et<sub>3</sub>N (50 mL) was added, and the solution was degassed for 1.5 h. *p*-Iodonitrobenzene (187 mg, 0.751 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (21 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) were sequentially added. The mixture was stirred at rt for 19 h. Solvent removal and purification by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:1) afforded **3** (240 mg, 82%) as a bright yellow solid. Mp 70-72 °C; UV/VIS (CHCl<sub>3</sub>) 268 (16200), 351 (15600) nm; IR (CH<sub>2</sub>Cl<sub>2</sub>, cast) 2942, 2865, 2206, 2148, 1592, 1520, 1343, 854 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 2.11 (s, 3H), 2.10 (s, 3H), 1.10 (s, 21H); <sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  157.2, 146.9, 132.0, 130.6, 123.6, 102.8, 101.7, 93.6, 92.1, 89.5, 23.1, 23.0, 18.7, 11.4; EIMS *m/z* 381.2 (M<sup>+</sup>, 27), 338.1573 ([M - *i*-Pr]<sup>+</sup>, 100); HRMS calcd. for C<sub>23</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub>Si

381.2124, found 381.2115. Anal. calcd. for  $C_{23}H_{31}N_2O_2Si$ : C, 72.39; H, 8.19; N, 3.67. Found: C, 72.20; H, 8.20; N, 3.63.

**D–A-substituted Monomer 4.** A solution of **2** (70 mg, 0.18 mmol) and  $Bu_4NF$  (0.7 mL, 1 M in THF) in wet THF (20 mL) was stirred at rt for 1 h.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$ , dried ( $MgSO_4$ ), reduced to 5 mL and added to  $Et_3N$  (20 mL) and THF (20 mL). The solution was degassed for 1.5 h, *p*-iodonitrobenzene (48 mg, 0.19 mmol),  $PdCl_2(PPh_3)_2$  (5 mg, 0.007 mmol) and  $CuI$  (3 mg, 0.02 mmol) were added, and the mixture was stirred at rt for 12 h. Solvent removal and purification by column chromatography (silica gel-H, hexane/ $CH_2Cl_2$  1:1) afforded **4** (44 mg, 70%) as an orange solid. Mp 159–162 °C; UV-VIS ( $CHCl_3$ ) 302 (sh, 26300), 325 (34000) nm; IR ( $CH_2Cl_2$ , cast) 2903, 2198, 1607, 1518, 1341, 854  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.16 (d,  $J$  = 9.0 Hz, 2H), 7.59 (d,  $J$  = 9.0 Hz, 2H), 7.35 (d,  $J$  = 8.9 Hz, 2H), 6.63 (d,  $J$  = 8.9 Hz, 2H), 2.97 (s, 6H), 2.143 (s, 3H), 2.137 (s, 3H);  $^{13}C$  NMR (75.5 MHz,  $CDCl_3$ )  $\delta$  154.9, 150.2, 146.8, 132.6, 132.1, 130.7, 123.6, 111.9, 110.0, 101.5, 93.1, 92.6, 89.2, 83.6, 40.3, 23.03, 23.01; EIMS  $m/z$  344 ( $M^+$ , 100); HRMS calcd. for  $C_{22}H_{20}N_2O_2$  344.1525, found 344.1522.

**Dimer 6.** A mixture of **1** (151 mg, 0.455 mmol) and  $K_2CO_3$  (30 mg, 0.22 mmol) in wet THF (5 mL) and MeOH (15 mL) was stirred for 2 h.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$ , dried ( $MgSO_4$ ), reduced to ca. 5 mL, and added to a degassed solution of **5** (109 mg, 0.365 mmol) in DMF (10 mL).  $Pd(PPh_3)_4$  (21 mg, 0.02 mmol) and  $Et_2NH$  (3 mL) were sequentially added, the solution stirred for 5 min,  $CuI$  (10 mg, 0.05 mmol) was added and the solution stirred at rt for 2 h.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$  and dried ( $MgSO_4$ ). Purification by column chromatography (silica gel, hexane/ $CH_2Cl_2$  1:1) afforded **6** (118 mg, 63%) as a yellow oil. IR ( $CH_2Cl_2$ , cast) 2942, 2149, 1463, 842  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.07 (s, 21H), 0.17 (s, 9H);  $^{13}C$  NMR (50.5 MHz,  $CDCl_3$ )  $\delta$  154.4, 153.7, 103.6, 102.1, 101.8 (2C), 95.7, 92.2, 88.7, 88.2, 22.7 (2C), 22.5 (2C), 18.6, 11.3, -0.05; EIMS  $m/z$  410 ( $M^+$ , 100); HRMS calcd. for  $C_{26}H_{42}Si_2$  410.2825, found 410.2823. Anal. calcd. for  $C_{26}H_{42}Si_2$ : C, 76.02; H, 10.31. Found: C, 76.12; H, 10.58.

**Donor-substituted Dimer 7.** To a solution of **6** (152 mg, 0.370 mmol) in wet THF (3 mL) and MeOH (15 mL) was added  $K_2CO_3$  (27 mg, 0.19 mmol) and the mixture stirred for 5 h.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$ , dried ( $MgSO_4$ ), reduced to ca. 5 mL, and added to a degassed solution of *p*-iodo-*N,N*-dimethylaniline (106 mg, 0.482 mmol) in  $Et_3N$  (40 mL).  $PdCl_2(PPh_3)_2$  (27 mg, 0.04 mmol) and  $CuI$  (14 mg, 0.07 mmol) were added, and the mixture was stirred at rt for 14 h. Solvent removal and purification by column chromatography (silica gel, hexane/ $CH_2Cl_2$  5:2) afforded **7** (96 mg, 56%) as a pale yellow solid. Mp 68–69 °C; UV/VIS ( $CHCl_3$ ) 263 (23800), 295 (sh, 34800), 303 (35700), 325 (sh, 26100); IR (neat) 2942, 2864, 2201, 2142, 1881, 1612, 1523, 1462, 1224, 882, 815  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.30 (d,  $J$  = 9.0 Hz, 2H), 6.61 (d,  $J$  = 9.0 Hz, 2H), 2.95 (s, 6H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 6H), 1.08 (s, 21H);  $^{13}C$  NMR (75.5 MHz,  $CDCl_3$ )  $\delta$  153.6, 151.5, 150.0, 132.5, 111.9, 110.7, 103.9, 102.3, 102.0, 92.1, 92.0, 89.0, 88.2, 84.4, 40.3, 22.8, 22.7 (2C), 22.6, 18.7, 11.4; EIMS  $m/z$  457 ( $M^+$ , 100); HRMS calcd. for  $C_{31}H_{43}NSi$  457.3165, found 457.3164. Anal. calcd. for  $C_{31}H_{43}NSi$ : C, 81.34; H, 9.47; N, 3.06. Found: C, 80.95; H, 9.59; N, 3.03.

**Acceptor-Substituted Dimer 8.** A mixture of **6** (113 mg, 0.276 mmol) and  $K_2CO_3$  (17 mg, 0.12 mmol) in wet THF (1.5 mL) and MeOH (7.5 mL) was stirred at rt for 5 h.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$ , dried

(MgSO<sub>4</sub>), and reduced to 5 mL. The solution was diluted with Et<sub>3</sub>N (50 mL) and degassed for 1.5 h. *p*-Iodonitrobenzene (60 mg, 0.24 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (16 mg, 0.02 mmol), and CuI (7 mg, 0.04 mmol) were added and the mixture was stirred at rt for 14 h. Solvent removal and purification by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:2) afforded **8** (117 mg, 92%) as a bright yellow solid. Mp 58-60 °C; UV-VIS (CHCl<sub>3</sub>) 264 (20000), 293 (24600), 303 (sh, 23100), 358 (12500) nm; IR (CH<sub>2</sub>Cl<sub>2</sub>, cast) 2942, 2209, 2146, 1592, 1520, 1342 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 2.12 (3H), 2.09 (3H), 2.06 (3H), 2.04 (3H), 1.07 (21H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 155.8, 154.3, 146.9, 132.0, 130.6, 123.6, 103.5, 102.0, 101.3, 92.5, 92.1, 89.3, 89.2, 87.7, 23.0, 22.9, 22.8, 22.7, 18.7, 11.4; EIMS *m/z* 459 (M<sup>+</sup>, 52), 416 ([M - *i*-Pr]<sup>+</sup>, 100); HRMS calcd. for C<sub>29</sub>H<sub>37</sub>NO<sub>2</sub>Si 459.2594, found 459.2591. Anal. calcd. for C<sub>29</sub>H<sub>37</sub>NO<sub>2</sub>Si: C, 75.77; H, 8.11; N, 3.05. Found: C, 75.46; H, 8.21; N, 2.97.

**Donor–Acceptor-Substituted Dimer 9.** A solution of **7** (66 mg, 0.15 mmol) and Bu<sub>4</sub>NF (0.3 mL, 1.0 M in THF) in wet THF (25 mL) was stirred at rt for 15 min. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase was separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl, dried (MgSO<sub>4</sub>), reduced to 5 mL and added to a mixture of Et<sub>3</sub>N (20 mL) and THF (20 mL). The solution was degassed for 1.5 h, *p*-iodonitrobenzene (37 mg, 0.15 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mg, 0.007 mmol) and Cu I (4 mg, 0.02 mmol) were added, and the mixture was stirred at rt for 6 h. Solvent removal and purification by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1) afforded **9** (33 mg, 76%) as an orange solid. Mp 154-156 °C; UV-VIS (CHCl<sub>3</sub>) 291 (43500), 325 (sh, 31300) nm; IR (CHCl<sub>3</sub>, cast) 2924, 2202, 1608, 1519, 1342 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 2.95 (s, 6 H), 2.12 (s, 6H), 2.10 (s, 3H), 2.08 (s, 3H); <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>) δ 155.4, 151.9, 150.3, 147.1, 133.0, 132.0, 130.0, 123.4, 112.2, 111.0, 103.0, 102.3, 93.6, 92.2, 90.5, 90.0, 87.9, 85.1, 39.6, 22.8, 22.7 (3C); EIMS *m/z* 422 (M<sup>+</sup>, 100); HRMS calcd. for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> 422.1994, found 422.1987.

**Trimer 10.** A mixture of **6** (274 mg, 0.668 mmol) and K<sub>2</sub>CO<sub>3</sub> (28 mg, 0.20 mmol) in wet THF (10 mL) and MeOH (10 mL) was stirred for 3 h. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl, dried (MgSO<sub>4</sub>), reduced to *ca.* 5 mL, added to a degassed solution of **5** (193 mg, 0.643 mmol) in DMF (30 mL), and degassed for 0.5 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (37 mg, 0.03) d and Et<sub>2</sub>NH (5 mL) were sequentially added, the solution stirred for 5 min, CuI (17 mg, 0.09 mmol) was added, and the solution stirred at rt for 15 h. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl and dried (MgSO<sub>4</sub>). Elution on a silica gel column with hexane afforded **10** (171 mg, 52%) as a yellow solid; Mp 48-50 °C; UV/VIS (CHCl<sub>3</sub>) 255 (25600), 284 (27600) nm; IR (neat) 2946, 2148, 1602, 840 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 2.01 (s, 3H), 1.99 (s, 3H), 1.07 (s, 3H), 1.06 (s, 18H), 0.17 (s, 9H); <sup>13</sup>C NMR (50.5 MHz, CDCl<sub>3</sub>) δ 154.4, 153.8, 152.7, 103.6, 102.1, 101.8, 101.7, 95.7 (2C), 92.1, 88.6, 88.5, 88.3, 87.9, 22.7 (3C), 22.5 (3C), 18.7, 11.3, -0.04; EIMS *m/z* 488 (M<sup>+</sup>, 100); HRMS calcd. for C<sub>32</sub>H<sub>48</sub>Si<sub>2</sub> 488.3295, found 488.3292. Anal. calcd. for C<sub>32</sub>H<sub>48</sub>Si<sub>2</sub>: C, 78.62; H, 9.90. Found: C, 78.27, H, 10.09.

**Donor-substituted Trimer 11.** A mixture of **10** (115 mg, 0.236 mmol) and K<sub>2</sub>CO<sub>3</sub> (25 mg, 0.18 mmol) in wet THF (2 mL) and MeOH (10 mL) was stirred for 4.5 h. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl, dried (MgSO<sub>4</sub>) and reduced to *ca.* 5 mL. Et<sub>3</sub>N (15 mL) was added and the solution was degassed for 1.5 h. *p*-Iodo-*N,N*-dimethylaniline (58 mg, 0.23 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (15 mg, 0.02 mmol) and CuI (7 mg, 0.04 mmol) were sequentially added. The mixture was stirred at rt for 16 h. Solvent removal and purification by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 4:1) afforded **11** (96 mg,

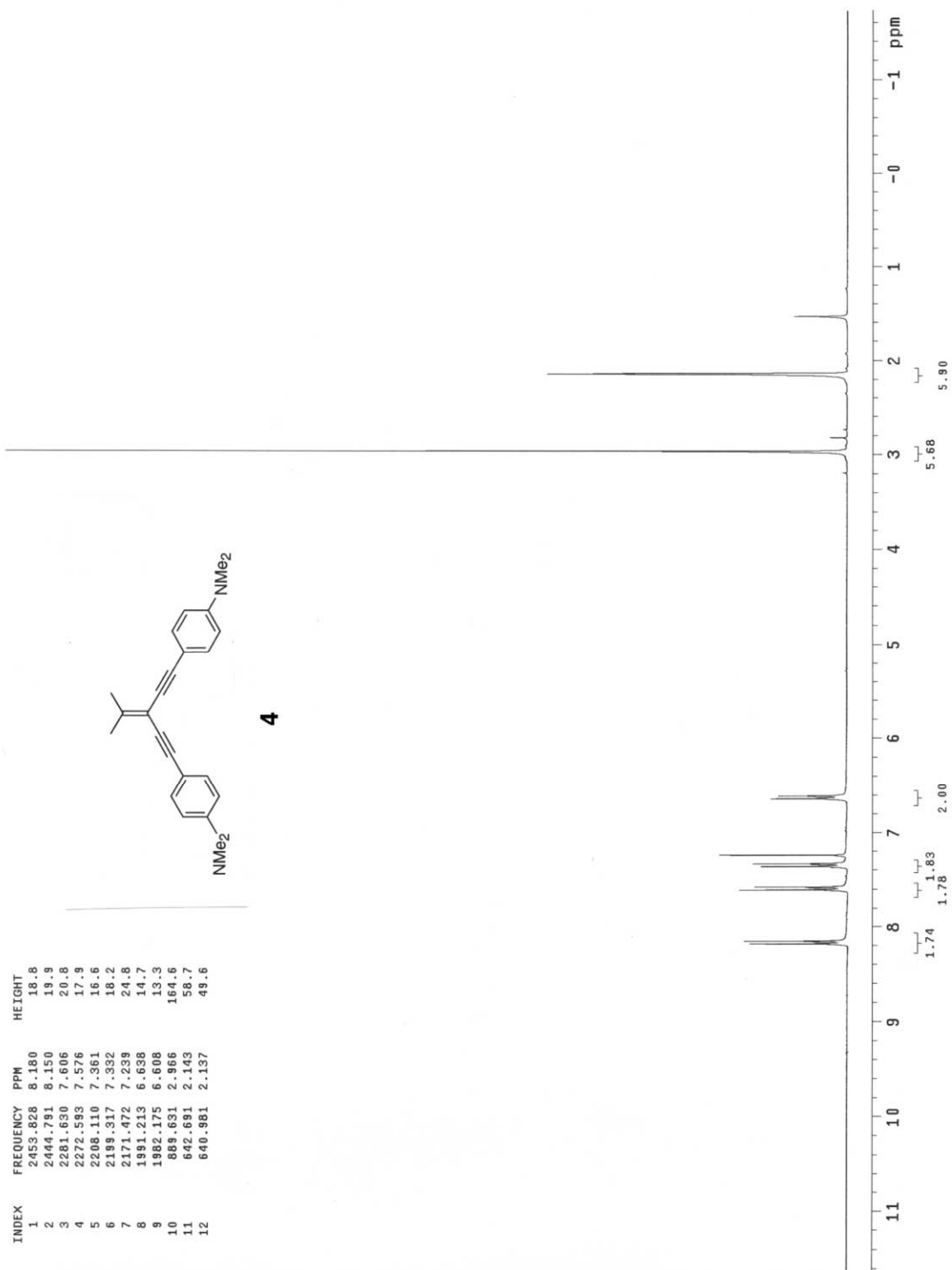
76%) as a pale yellow solid. Mp 111-113 °C; UV/VIS (CHCl<sub>3</sub>) 294 (38600), 325 (sh, 24800) nm; IR (CHCl<sub>3</sub>, cast) 2940, 2196, 2145, 1609, 1520, 1347 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 2.95 (s, 6H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 6H), 2.03 (s, 3H), 2.02 (s, 3H), 1.07 (s, 21H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 153.8, 152.5, 151.5, 150.0, 132.5, 111.9, 110.7, 103.8, 102.2, 102.0, 101.9, 92.2, 92.0, 88.7, 88.7, 88.3, 88.1, 84.5, 40.3, 22.8 (2C), 22.7, 22.65 (2C), 22.60, 18.7, 11.4; EIMS *m/z* 535 (M<sup>+</sup>, 100); HRMS calcd. for C<sub>37</sub>H<sub>49</sub>NSi 535.3634, found 535.3616. Anal. calcd. for C<sub>37</sub>H<sub>49</sub>NSi: C, 82.93; H, 9.22; N, 2.61. Found C, 82.44; H, 9.32; N, 2.54.

**Acceptor-substituted Trimer 12.** A mixture of **10** (14 mg, 0.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (3 mg, 0.02 mmol) in wet THF (0.5 mL) and MeOH (1.5 mL) was stirred at rt for 4 h. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase separated, washed with saturated NH<sub>4</sub>Cl, saturated NaCl, dried (MgSO<sub>4</sub>) and reduced to 5 mL. The solution was diluted with Et<sub>3</sub>N (10 mL) and degassed for 1.5 h. *p*-Iodonitrobenzene (7 mg, 0.03 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mg, 0.002 mmol), and CuI (0.85 mg, 0.004 mmol) were added and the mixture was stirred at rt, under nitrogen, for 15 h. Solvent removal and purification by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:2) afforded **12** (13 mg, 84%) as a bright yellow solid. Mp 77-79 °C; UV-VIS (CHCl<sub>3</sub>) 287 (26600), 307 (sh, 22900), 352 (9770) nm; IR (CH<sub>2</sub>Cl<sub>2</sub>, cast) 2941, 2206, 2145, 1592, 1519, 1342 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.55 (d, *J* = 9.0 Hz, 2H), 2.12 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 6H), 2.02 (s, 3H), 1.06 (s, 21H); <sup>13</sup>C NMR (100.5 MHz, APT, CDCl<sub>3</sub>) δ 155.8, 153.9, 153.2, 146.8, 132.0, 130.6, 123.6, 103.6, 102.1, 101.6, 101.2, 92.3, 92.1, 89.2, 89.1, 88.5, 88.3, 87.3, 23.0, 22.9, 22.8 (2C), 22.6 (2C), 18.6, 11.3; EIMS *m/z* 537 (M<sup>+</sup>, 81), 494 ([M - *i*-Pr]<sup>+</sup>, 100); HRMS calcd. for C<sub>35</sub>H<sub>43</sub>O<sub>2</sub>NSi 537.3063, found 537.3062. Anal. calcd. for C<sub>35</sub>H<sub>43</sub>O<sub>2</sub>NSi: C, 78.16; H, 8.06; N, 2.60. Found: C, 77.48; H, 7.91; N, 1.57.

**D-A-Substituted Trimer 13.** A solution of **11** (22 mg, 0.04 mmol) and Bu<sub>4</sub>NF (0.2 mL, 1 M in THF) in wet THF (10 mL) was stirred at rt, for 45 min. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase was separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. NaCl, dried (MgSO<sub>4</sub>), reduced to 5 mL and added to Et<sub>3</sub>N (10 mL) and THF (10 mL). The solution was degassed for 1.5 h, *p*-iodonitrobenzene (10 mg, 0.04 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (4 mg, 0.005 mmol) and CuI (1 mg, 0.006 mmol) were added, and the mixture was stirred at rt for 19 h. Solvent removal and purification by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1) afforded **12** (17 mg, 83%) as an orange solid. Mp 144-146 °C; UV/VIS (CHCl<sub>3</sub>) 297 (46600), 325 (sh, 35500), 372 (sh, 9560) nm; IR (film) 2906, 2201, 1611, 1521, 1344 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 2.95 (s, 6H), 2.12 (s, 3H), 2.11 (s, 3H), 2.08 (s, 6H), 2.07 (s, 3H), 2.06 (s, 3H); <sup>13</sup>C NMR (75.5, CDCl<sub>3</sub>) δ 155.7, 152.9, 151.6, 150.0, 146.9, 132.5, 132.0, 130.7, 123.6, 111.9, 102.6, 101.8, 101.4, 92.23, 92.18, 89.4 (2C), 89.0, 88.0, 87.9, 87.4, 84.4, 40.2, 23.0 (2C), 22.85 (2C), 22.76, 22.73; EIMS *m/z* 500 (M<sup>+</sup>, 100); HRMS calcd. for C<sub>34</sub>H<sub>32</sub>O<sub>2</sub>N<sub>2</sub> 500.2464, found 500.2458. Anal. calcd. for C<sub>34</sub>H<sub>32</sub>O<sub>2</sub>N<sub>2</sub>: C, 81.36; H, 7.02; N, 5.42. Found: C, 81.39; H, 7.07; N, 5.23.

## References:

- 1) Dawson, D. J.; Frazier, J. D.; Brock, P. J.; Twieg, R. J. in *Polymers for High Technology*; ASC Symp. Ser. Vol. 346; ACS: Washington, D.C., 1987, pp 445-456.
- 2) Zhao, Y.; Tykwinski, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 458-459.
- 3) Stang, P. J.; Fisk, T. E. *Synthesis* **1979**, 438-440





SORIN CIULEI, SC.MDA IN CDCL3, 13C[1H, CPD]

154.927  
150.203  
146.825

132.632  
130.723  
123.604

111.860  
109.985

101.482

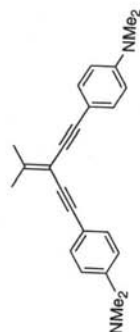
93.072  
92.509  
89.173

83.552

77.461  
77.000  
76.535

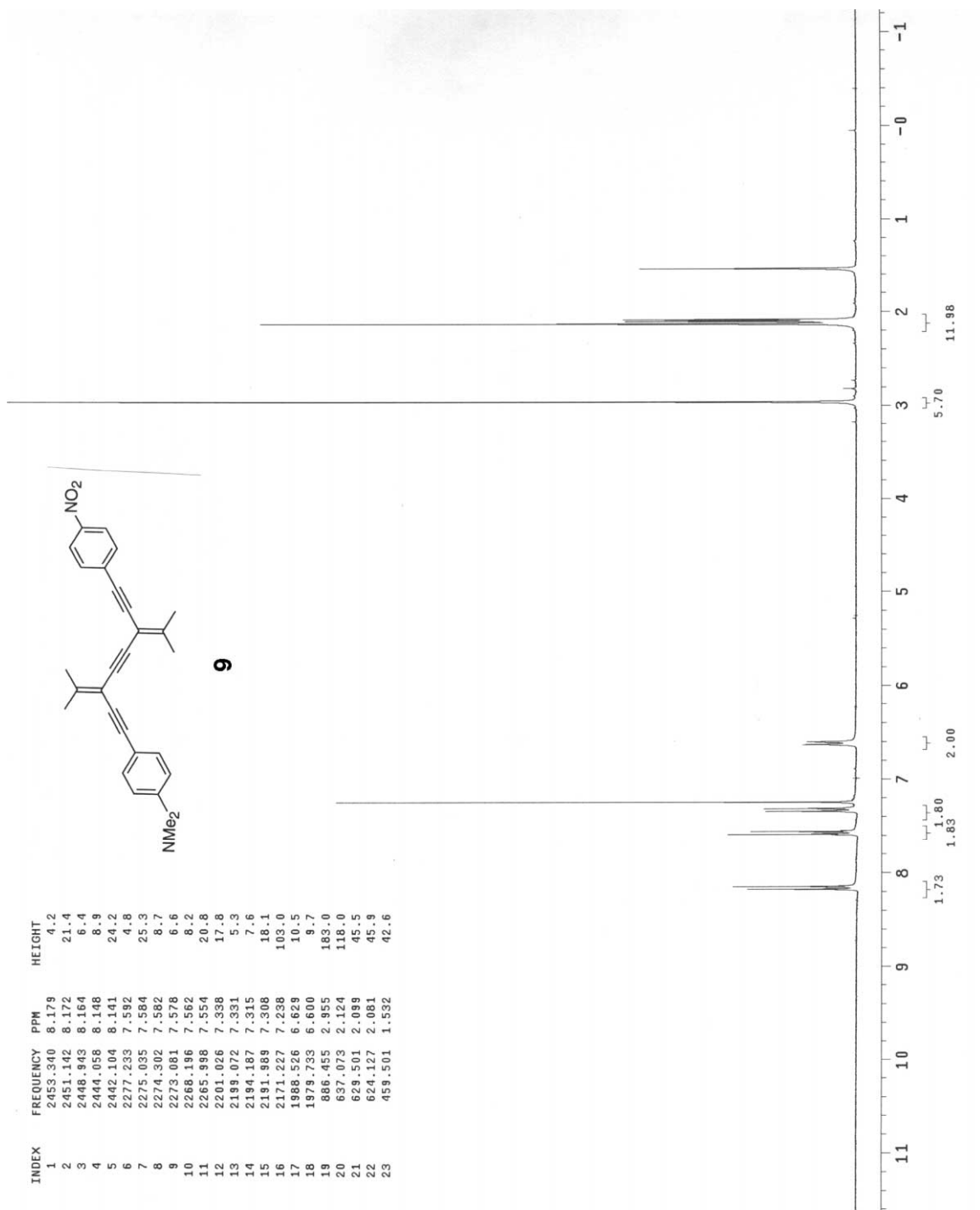
40.267

23.031  
23.007



4

SF 75.459  
SY 112.0  
S1 654.0488  
S1 654.0  
TD 32568  
SW 18518.519  
HZ/PT .565  
PW 0.0  
RD 0.0  
AQ .885  
RG 800  
NS 32000  
TE 297  
FW 23200.000  
O2 4567.000  
DP 18H CPD  
LB 1.200  
GB 0.0  
CX 36.00  
CY 19.00  
F1 209.994P  
F2 -6.002P  
HZ/CM 452.803  
PPM/CM 6.000  
SR -1410.10  
D5 .1000000  
S9 .100.00  
P0 18H 1.90  
RG 0.0  
RD 0.0  
PW 0.0  
DE 33.80  
NS 32000  
DS 2  
D1 .1000000





**BOXER**

JL090F.105  
AU PROG:  
X02.AU  
DATE 10-7-99  
TIME 11:15

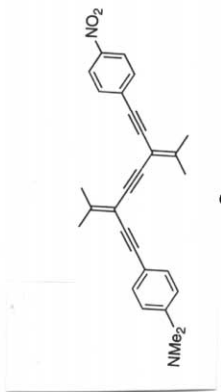
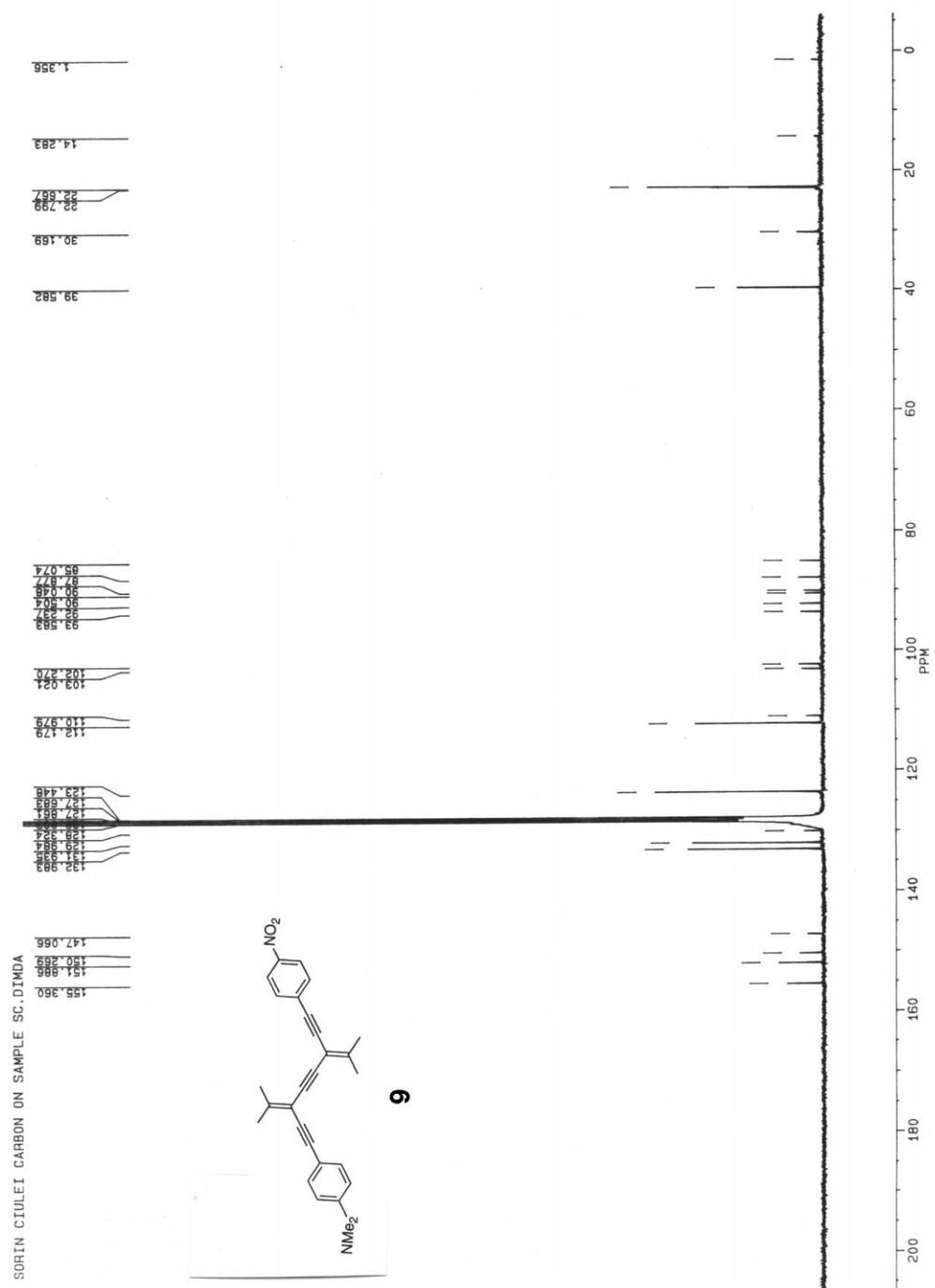
SF 75.469  
SY 112.0  
O1 6140.000  
SI 32768  
TD 32768  
SM 18518.519  
HZ/P1 1.130

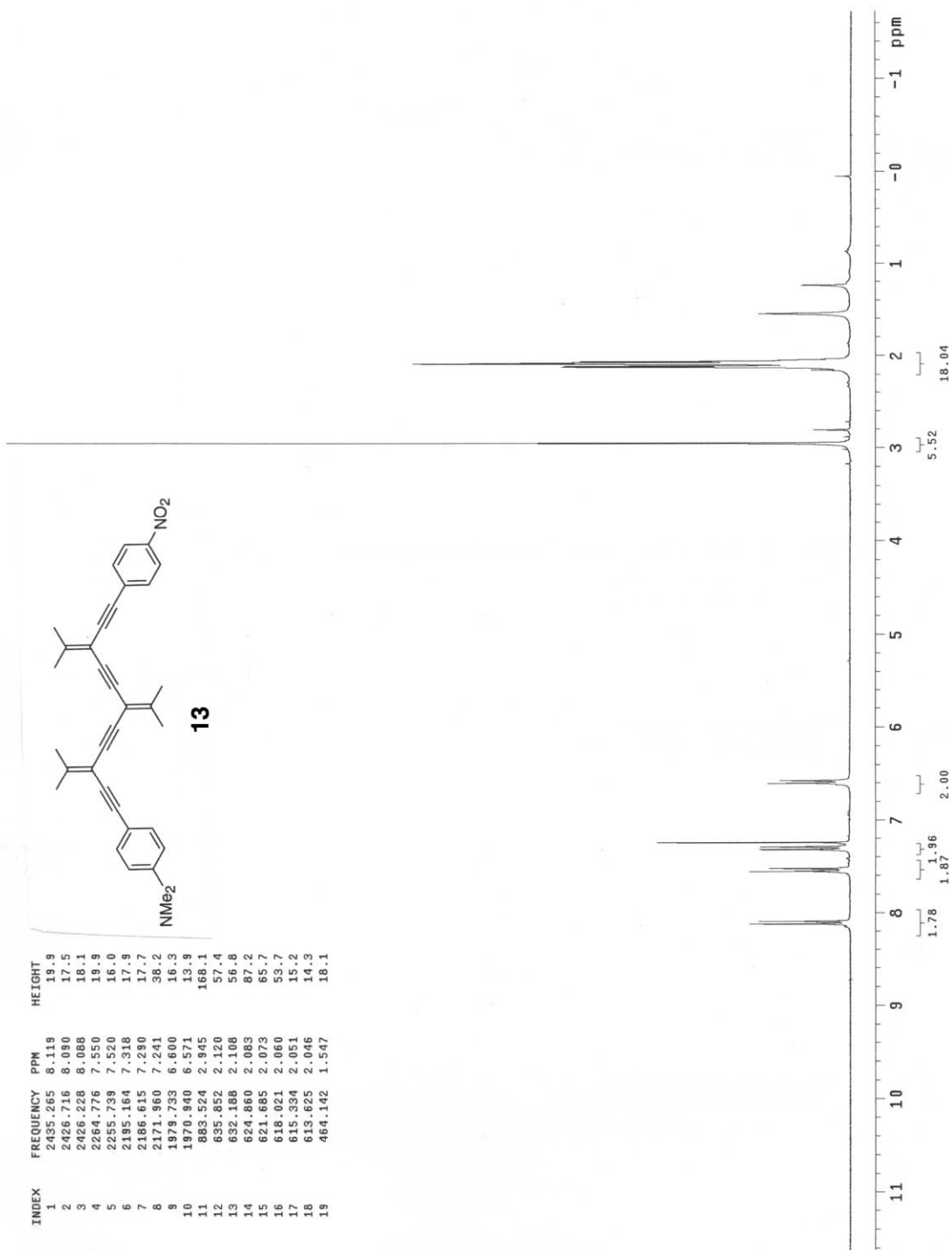
PK 0.0  
RD 0.0  
AG 800.885  
NS 28800  
TE 297

FW 23200  
O2 4425.000  
DP 18H CPD

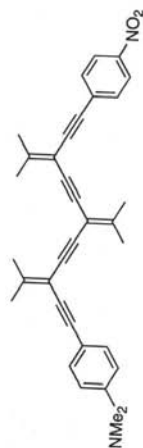
LB 1.200  
GB 0.0  
CX 36.00  
F1 210.013P  
F2 -5.988P  
HZ/CM 452.834  
PPM/CM 6.000  
SR -1424.44

D5 .1000000  
D9 .100.00  
S1 18H 2.00  
P0  
RGA 0.0  
RD 0.0  
DE 33.80  
NS 28800  
DS 2  
D1 .1000000






SORIN CILULEI  
-SC-TRDA IN CDCl<sub>3</sub>, 13C{1H}CPD]



13

  
 AU060F.102  
 AU PRUG:  
 XTE 7-8-99  
 DATE 7-8-99  
 TIME 7:08  
 SF 75.469  
 SY 112.0  
 O1 6140.488  
 S1 65536  
 TD 32768  
 SM 18518.519  
 HZ/PT .565  
 PW 0.0  
 RD 0.0  
 RG 800.885  
 NS 18000  
 TE 297  
 FW 23200  
 O2 4587.000  
 DP 16H CPD  
 LB 1.200  
 GB 0.0  
 CX 36.00  
 CY 0.047P  
 F2 215.979P  
 HZ/CM 452.803  
 PPW/CM 5.000  
 SR -1410.67  
 D5 -.0080000  
 P9 100.00  
 S1 16H  
 P0 1.60  
 RGA  
 RD 0.0  
 PW 0.0  
 DE 33.80  
 NS 18000  
 DS 2  
 D1 1.0000000

