

## **Supporting Information**

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

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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. Anh. 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

( $MgSO_4$ ), and reduced to 5 mL. The solution was diluted with  $Et_3N$  (50 mL) and degassed for 1.5 h. *p*-Iodonitrobenzene (60 mg, 0.24 mmol),  $PdCl_2(PPh_3)_2$  (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/ $CH_2Cl_2$  3:2) afforded **8** (117 mg, 92%) as a bright yellow solid. Mp 58-60 °C; UV-VIS ( $CHCl_3$ ) 264 (20000), 293 (24600), 303 (sh, 23100), 358 (12500) nm; IR ( $CH_2Cl_2$ , cast) 2942, 2209, 2146, 1592, 1520, 1342  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  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);  $^{13}C$  NMR (75.5 MHz,  $CDCl_3$ )  $\delta$  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 ( $M^+$ , 52), 416 ([ $M - i-Pr$ ] $^+$ , 100); HRMS calcd. for  $C_{29}H_{37}NO_2Si$  459.2594, found 459.2591. Anal. calcd. for  $C_{29}H_{37}NO_2Si$ : 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  $Bu_4NF$  (0.3 mL, 1.0 M in THF) in wet THF (25 mL) was stirred at rt for 15 min.  $Et_2O$  and  $H_2O$  were added, the organic phase was separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$ , dried ( $MgSO_4$ ), reduced to 5 mL and added to a mixture of  $Et_3N$  (20 mL) and THF (20 mL). The solution was degassed for 1.5 h, *p*-iodonitrobenzene (37 mg, 0.15 mmol),  $PdCl_2(PPh_3)_2$  (5 mg, 0.007 mmol) and  $CuI$  (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/ $CH_2Cl_2$  1:1) afforded **9** (33 mg, 76%) as an orange solid. Mp 154-156 °C; UV-VIS ( $CHCl_3$ ) 291 (43500), 325 (sh, 31300) nm; IR ( $CHCl_3$ , cast) 2924, 2202, 1608, 1519, 1342  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  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);  $^{13}C$  NMR (75.5 MHz,  $C_6D_6$ )  $\delta$  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 ( $M^+$ , 100); HRMS calcd. for  $C_{28}H_{26}N_2O_2$  422.1994, found 422.1987.

**Trimer 10.** A mixture of **6** (274 mg, 0.668 mmol) and  $K_2CO_3$  (28 mg, 0.20 mmol) in wet THF (10 mL) and MeOH (10 mL) was stirred for 3 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, added to a degassed solution of **5** (193 mg, 0.643 mmol) in DMF (30 mL), and degassed for 0.5 h.  $Pd(PPh_3)_4$  (37 mg, 0.03 d) and  $Et_2NH$  (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.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$  and dried ( $MgSO_4$ ). Elution on a silica gel column with hexane afforded **10** (171 mg, 52%) as a yellow solid; Mp 48-50 °C; UV/VIS ( $CHCl_3$ ) 255 (25600), 284 (27600) nm; IR (neat) 2946, 2148, 1602, 840  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  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);  $^{13}C$  NMR (50.5 MHz,  $CDCl_3$ )  $\delta$  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 ( $M^+$ , 100); HRMS calcd. for  $C_{32}H_{48}Si_2$  488.3295, found 488.3292. Anal. calcd. for  $C_{32}H_{48}Si_2$ : 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  $K_2CO_3$  (25 mg, 0.18 mmol) in wet THF (2 mL) and MeOH (10 mL) was stirred for 4.5 h.  $Et_2O$  and  $H_2O$  were added, the organic phase separated, washed with saturated aq.  $NH_4Cl$ , saturated aq.  $NaCl$ , dried ( $MgSO_4$ ) and reduced to *ca.* 5 mL.  $Et_3N$  (15 mL) was added and the solution was degassed for 1.5 h. *p*-Iodo-*N,N*-dimethylaniline (58 mg, 0.23 mmol),  $PdCl_2(PPh_3)_2$  (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/ $CH_2Cl_2$  4:1) afforded **11** (96 mg,

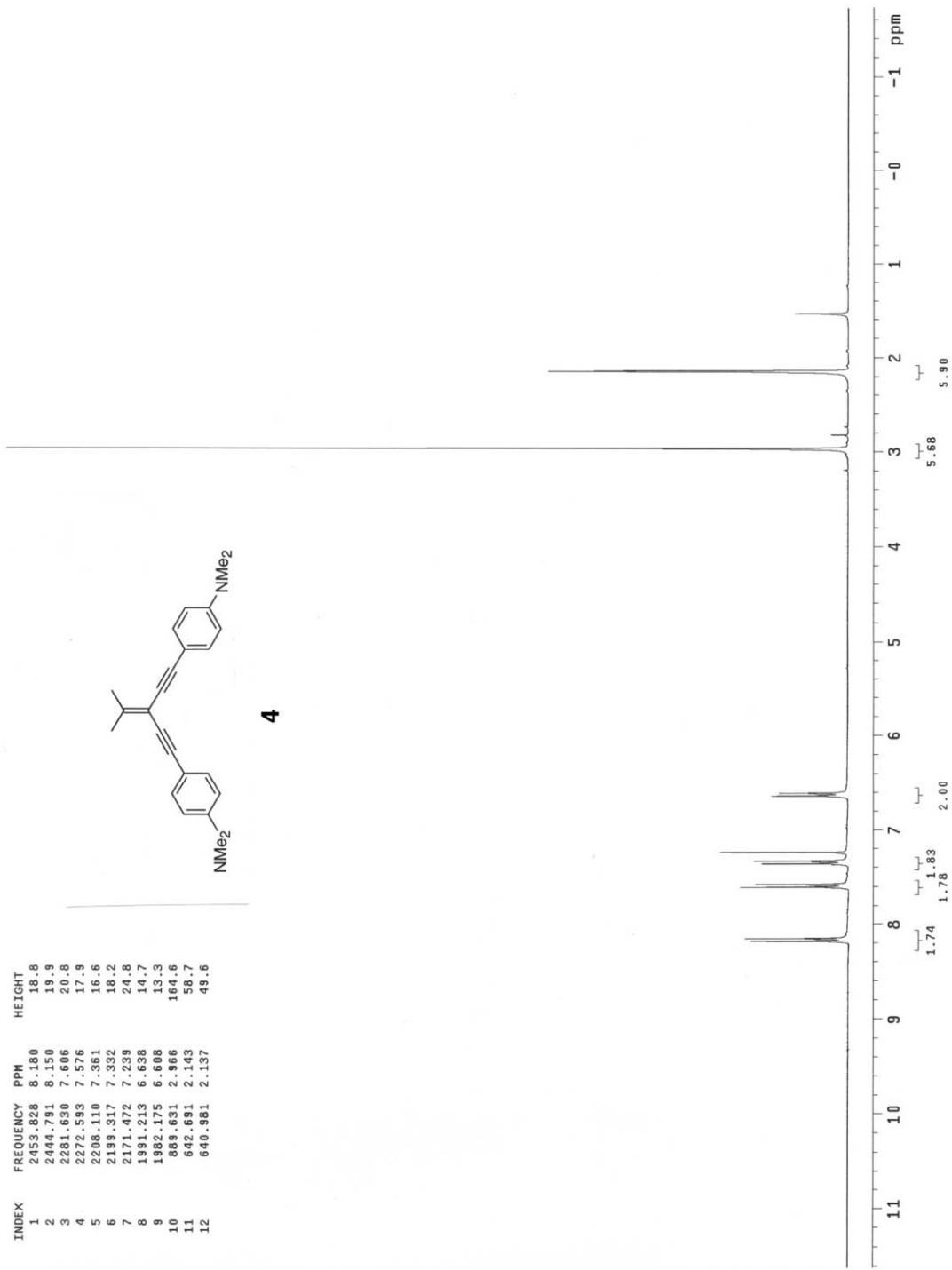
76%) as a pale yellow solid. Mp 111-113 °C; UV/VIS (CHCl<sub>3</sub>) 294 (38600), 325 (sh, 24800) nm; IR (CHCl<sub>3</sub>, cast) 2940, 2196, 2145, 1609, 1520, 1347 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 2.95 (s, 6H), 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.

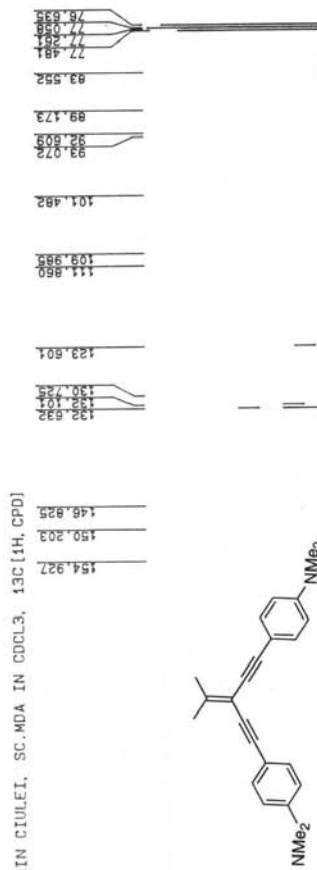
**D-A-Substituted Trimer 13.** A solution of **11** (22 mg, 0.04 mmol) and Bu<sub>4</sub>NF (0.2 mL, 1 M in THF) in wet THF (10 mL) was stirred at rt, for 45 min. Et<sub>2</sub>O and H<sub>2</sub>O were added, the organic phase was separated, washed with saturated aq. NH<sub>4</sub>Cl, saturated aq. 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.; Tykwienski, 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 CDCl<sub>3</sub>, 13C [1H, CPD]



**4**



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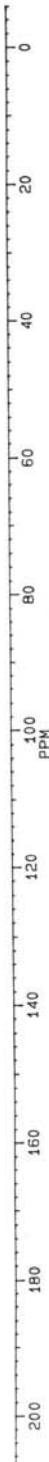
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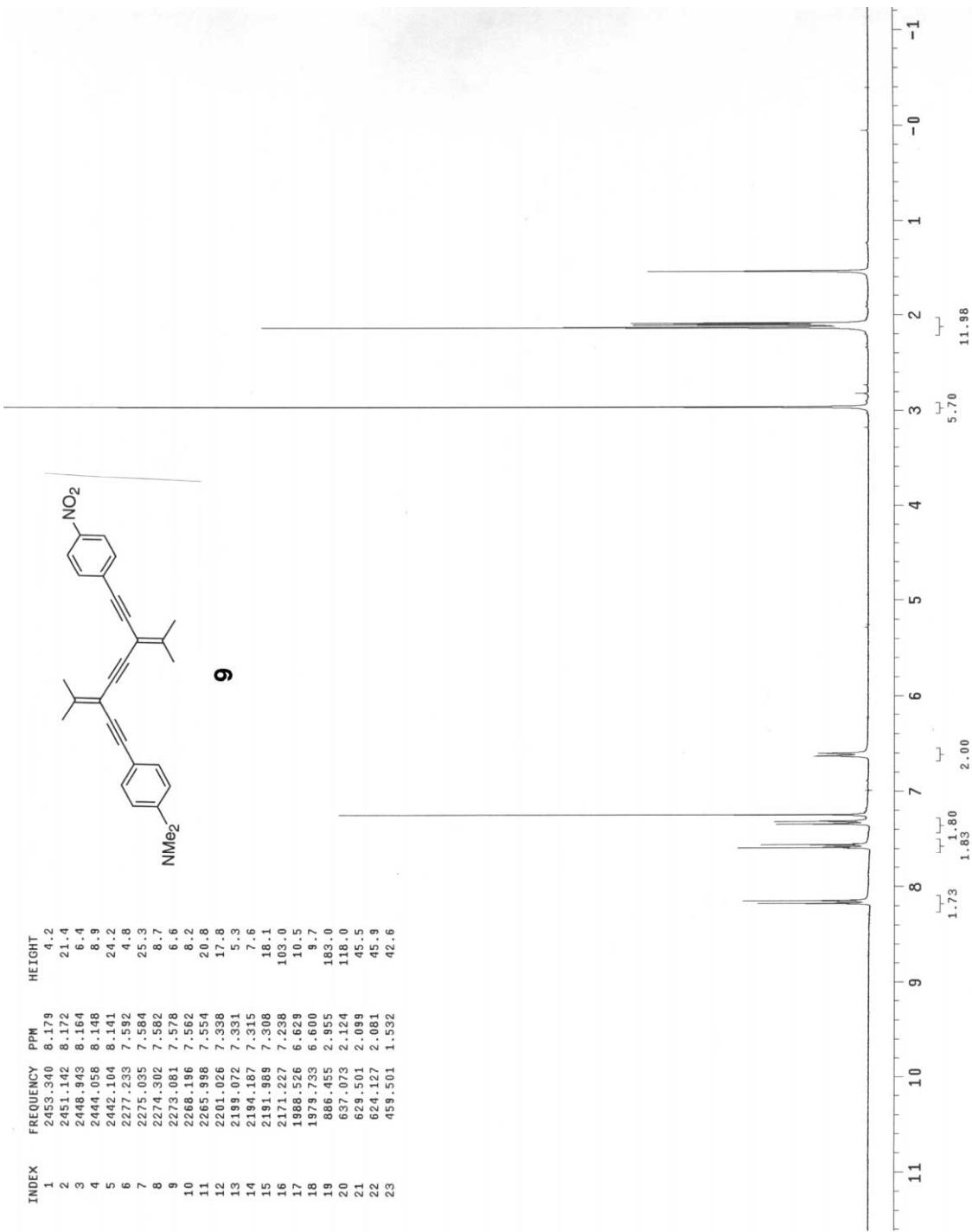
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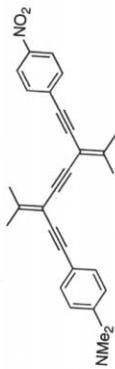
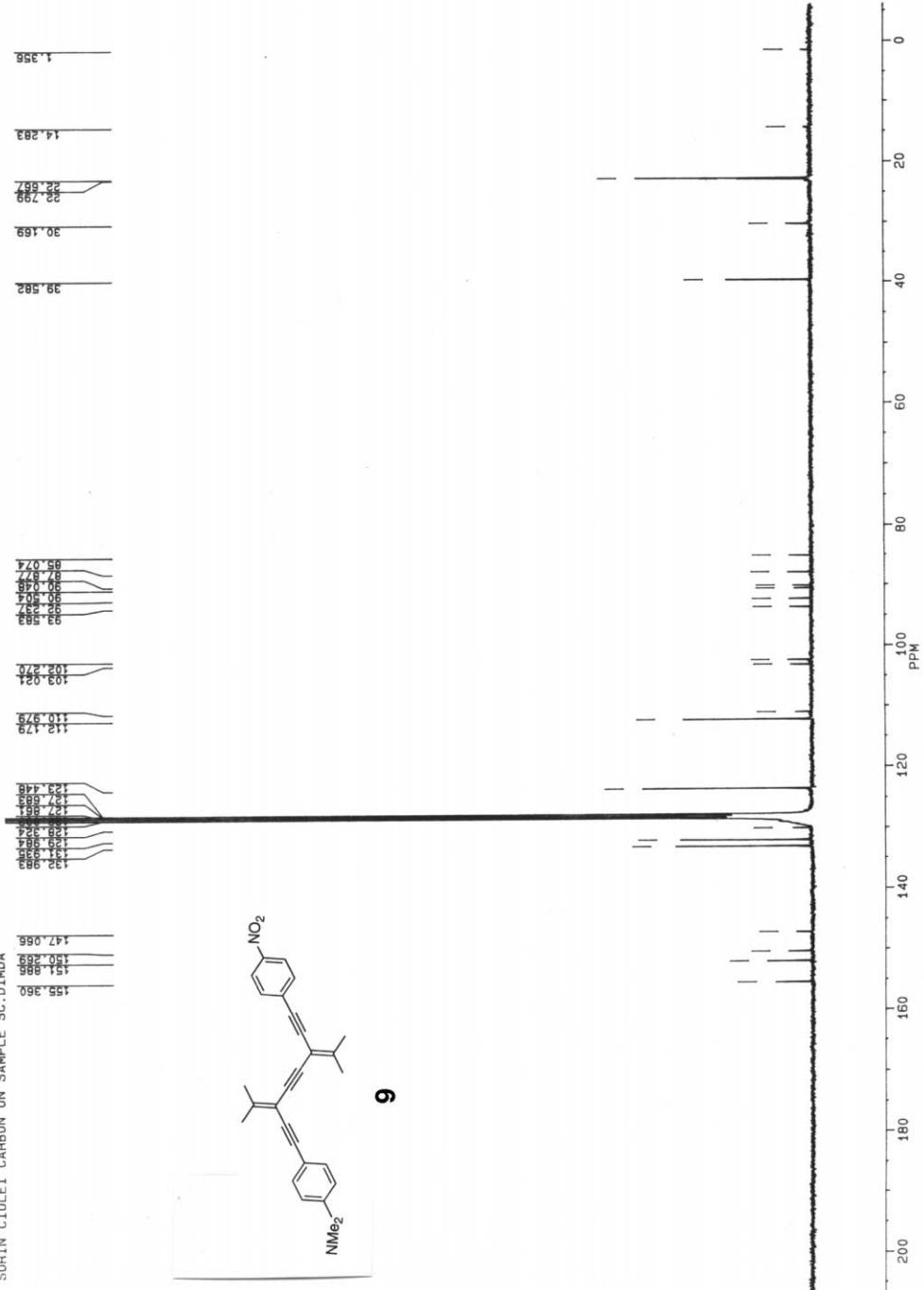
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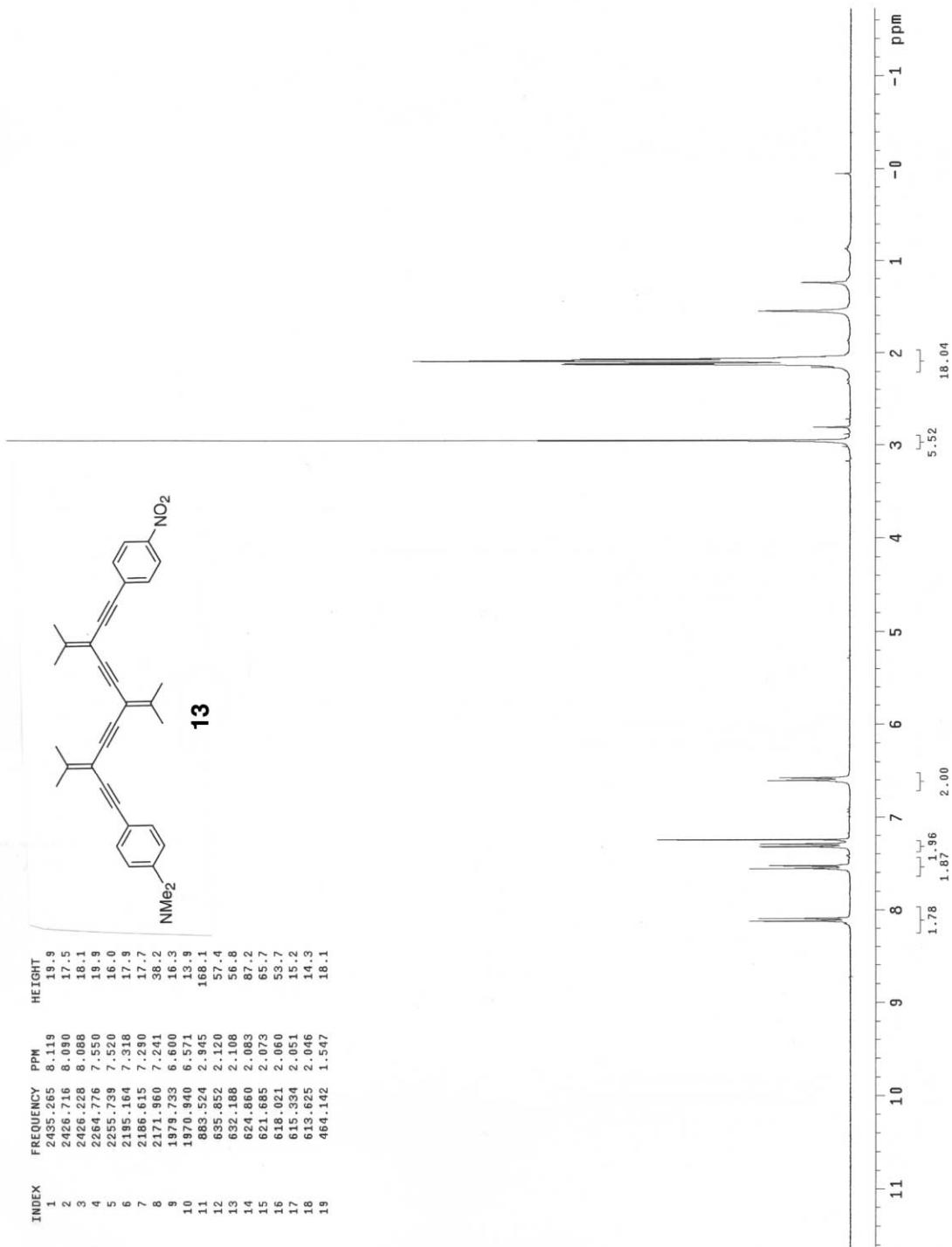
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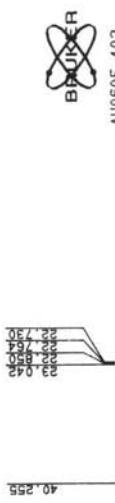




JOHN CUEI  
SC, TRDA IN CDCl<sub>3</sub>, <sup>13</sup>C[<sup>1</sup>H, CPD]



13



40.255

