

The Effect of Molecular Conformation on Single Molecule Conductance: Measurements of π -Conjugated Oligoaryls by STM Break Junction

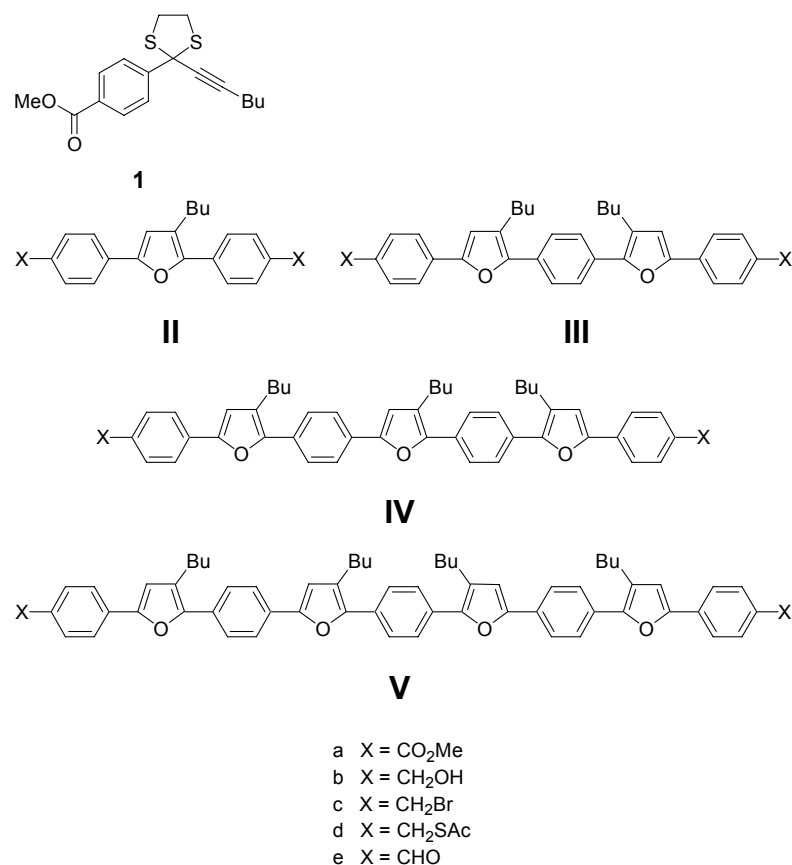
I-Wen Peter Chen,^a Ming-Dung Fu,^a Wei-Hsiang Tseng,^a Chun-hsien Chen,^{*b}
Chih-Ming Chou,^b Tien-Yau Luh^{*b}

^aDepartment of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, 30013

^bDepartment of Chemistry, National Taiwan University, Taipei, Taiwan 10617

E-mail: chhchen@ntu.edu.tw (C.-h.C.); tyluh@ntu.edu.tw (T.-Y.L.)

Chart 1



Experimental Section

Materials. The synthesis of bistiols II and III were reported previously.¹

Dialdehyde (IIe). A solution of IIb1 (403 mg, 1.2 mmol) in CH₂Cl₂ (20 mL) was added slowly to a suspension of activated MnO₂ (2.0 g, 24 mmol) in CH₂Cl₂ (10 mL) at rt. The reaction mixture was stirred for 6 h at rt. After passing through a silica gel bed (5 cm) and washing with EtOAc (30 mL × 5), the combined organic solution was evaporated in vacuo to afford IIe as a yellow solid (358 mg, 90%): IIe: mp 107-108 oC (CH₂Cl₂-hexane); ¹H NMR (400 MHz, CDCl₃) □ 0.99 (t, J = 7.3 Hz, 3 H), 1.46 (sextet, J = 7.3 Hz, 2 H), 1.70 (m, 2 H), 2.78 (t, J = 7.8 Hz, 2 H), 6.89 (s, 1 H), 7.86-7.97 (m, 8 H), 10.01 (s, 1 H), 10.03 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) □ 13.9, 22.6, 26.0, 31.8, 112.7, 124.1, 125.5, 127.9, 130.2, 130.4, 134.6, 135.1, 135.4, 136.6, 148.1, 151.8, 191.4, 191.5; IR (KBr) □ 2954, 2925, 2864, 2828, 2730, 1696, 1599, 1390, 1304, 1213, 1166, 933, 833 cm⁻¹; HRMS (FAB) calcd for C₂₂H₂₁O₃: 333.1491, found: 333.1480;

Diester (IVa). Under Ar atmosphere, n-BuLi (1.76 mL, 2.5 M in hexane, 4.4 mmol) was added in one portion to a solution of 12 (1.28 g, 4 mmol) in THF (100 mL) at -78 oC and the mixture was stirred for 1 h. To this mixture was added slowly a solution of IIe (597 mg, 1.8 mmol) in THF (20 mL) and the mixture was stirred for 30 min at -78 oC, and allowed to warm to rt and stirred for additional 2 h. Then TFA (0.6 mL, 6.6 mmol) was added, the resulting solution was stirred at rt overnight. The mixture was washed with saturated NaHCO₃ (100 mL × 3), dried (MgSO₄) and concentrated in vacuo to give the residue which was chromatographed on silica gel (hexane/ ethyl acetate 10/1) to afford IVa (567 mg, 40%): mp 128-129 oC; ¹H NMR (300 MHz, CDCl₃) □ 0.96-1.02 (m, 9 H), 1.45-1.53 (m, 6 H), 1.68-1.74 (m, 6 H), 2.72-2.79 (m, 6 H), 3.93 (s, 6 H), 6.73 (s, 1 H), 6.81 (s, 1 H), 6.82 (s, 1 H), 7.72-7.82 (m, 12 H), 8.07 (d, J = 8.4 Hz, 4 H); ¹³C NMR (100 MHz, CDCl₃) □ 14.44, 14.47, 14.48, 22.92, 23.04, 23.08, 26.26, 26.35, 32.4, 52.3, 109.6, 111.4, 122.8, 123.5, 124.4, 124.6, 125.1, 125.3, 125.4, 127.8, 128.3, 128.8, 129.2, 129.7, 134.2, 148.3, 150.2, 151.1, 166.2; IR (KBr) □ 2954, 2928, 2869, 1720, 1607, 1434, 1276, 1176, 1107, 933, 838, 770 cm⁻¹; HRMS (FAB) calcd for C₅₂H₅₂O₇: 788.3713, found: 788.3712;

Diol (IVb). Under argon atmosphere, a THF solution (30 mL) of IVa (236 mg, 0.3 mmol) was treated with DIBAL (2.4 mL of 1.0 M solution in hexane, 2.4 mmol) at 0 oC and the mixture was stirred for 30 min at 0 oC, gradually warmed to rt and stirred for additional 5 h. After quenching with 10% NH₄Cl (10 mL) and extracted with ether, the organic layer was dried (MgSO₄), and the solvent was removed in vacuo to give IVb (202 mg, 92%): mp 112-113 oC (CH₂Cl₂-hexane); ¹H NMR (300 MHz, CDCl₃) □ 0.96-1.02 (m, 9 H), 1.46-1.50 (m, 6 H), 1.65-1.70 (m, 8 H), 2.71-2.77 (m,

6 H), 4.72 (s, 4 H), 6.68 (s, 1 H), 6.69 (s, 1 H), 6.70 (s, 1 H), 7.41 (d, $J = 8.1$ Hz, 4 H), 7.73-7.81 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3) \square 14.92, 14.95, 23.5, 26.8, 32.85, 32.89, 65.7, 109.8, 109.9, 123.89, 123.93, 124.6, 124.8, 125.5, 125.6, 127.5, 129.0, 130.0, 130.2, 130.4, 139.7, 147.7, 151.6; IR (KBr) \square 3371, 2954, 2927, 2858, 1658, 1599, 1503, 1047, 1012, 933, 838, 807 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{50}\text{H}_{52}\text{O}_5$: 732.3815, found: 732.3826;

Dibromide (IVc).

Under argon atmosphere, a benzene solution (10 mL) of IVb (146 mg, 0.2 mmol) and PBr_3 (0.04 mL, 140 mg, 0.52 mmol) was stirred for 12 h. The mixture was treated with 10% NaHCO_3 (5 mL), and extracted with CH_2Cl_2 . The organic layer was dried (MgSO_4), and the solvent was removed in vacuo to give IVc (161 mg, 94%): mp 136-137 $^{\circ}\text{C}$ (CH_2Cl_2 -hexane); ^1H NMR (300 MHz, CDCl_3) \square 0.96-1.02 (m, 9 H), 1.43-1.53 (m, 6 H), 1.68-1.73 (m, 6 H), 2.71-2.79 (t, 6 H), 4.54 (s, 4 H), 6.70 (s, 1H), 6.71 (s, 1H), 6.73 (s, 1H), 7.42 (d, $J = 8.2$ Hz, 4 H), 6.69-7.81 (m, embodied a singlet at 7.78, 12 H); ^{13}C NMR (100 MHz, CDCl_3) \square 14.8, 23.4, 26.6, 30.4, 32.1, 32.7, 34.3, 109.9, 110.2, 123.8, 123.9, 124.5, 124.7, 125.4, 125.5, 129.4, 130.1, 130.7, 136.3, 147.8, 151.1; IR (KBr) \square 2956, 2929, 2869, 1603, 1505, 1225, 1201, 1180, 932, 838, 810 cm^{-1} ;

Dibromide (Vc). Under argon atmosphere, a benzene solution (10 mL) of Vb2 (186 mg, 0.2 mmol) and PBr_3 (0.04 mL, 140 mg, 0.52 mmol) was stirred for 12 h. The mixture was treated with 10% NaHCO_3 (5 mL), and extracted with CH_2Cl_2 . The organic layer was dried (MgSO_4), and the solvent was removed in vacuo to give Vc (194 mg, 92%): mp 185-186 $^{\circ}\text{C}$ (CH_2Cl_2 -hexane); ^1H NMR (300 MHz, CDCl_3) \square 0.96-1.03 (m, 12 H), 1.43-1.54 (m, 8 H), 1.68-1.75 (m, 8 H), 2.71-2.80 (m, 8 H), 4.54 (s, 4 H), 6.71 (s, 2 H), 6.73 (s, 2 H), 7.42 (d, $J = 8.2$ Hz, 4 H), 7.69-7.82 (m, embodied a singlet at 7.80, 16 H); ^{13}C NMR (100 MHz, CDCl_3) \square 14.46, 14.50, 23.05, 23.09, 26.29, 26.35, 32.38, 32.43, 34.0, 109.5, 109.9, 123.5, 123.6, 124.2, 124.3, 125.1, 125.2, 128.6, 129.1, 129.5, 129.8, 130.4, 136.0, 147.3, 147.5, 150.7, 151.1; IR (KBr) \square 2955, 2927, 2858, 1611, 1504, 1485, 1465, 1225, 1200, 933, 838, 809 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{64}\text{H}_{64}\text{Br}_2\text{O}_4$: 1054.3171, found: 1054.3185.

Bis-thioacetate (IVd). To a slurry of K_2CO_3 (82 mg, 0.6 mmol) in DMF (10 mL) was slowly added a solution of freshly distilled thioacetic acid (0.04 mL, 0.6 mmol) in DMF (5 mL). After 10 min, this solution was added to a solution of IVc (171 mg, 0.2 mmol) in DMF (10 mL). The reaction flask was wrapped with aluminum foil to protect from ambient light and the mixture was stirred overnight. After removal of solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (40 mL), and washed with water and brine. The organic layer was dried (MgSO_4), the solvent was removed in vacuo, and the residue was chromatographed (silica-gel,

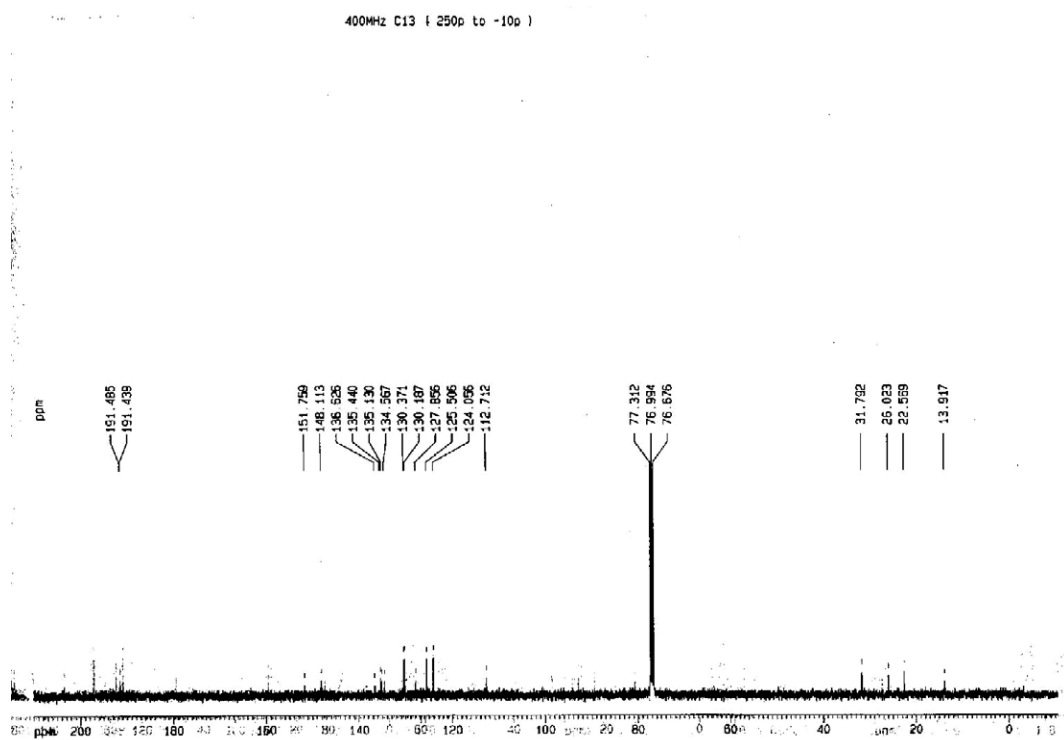
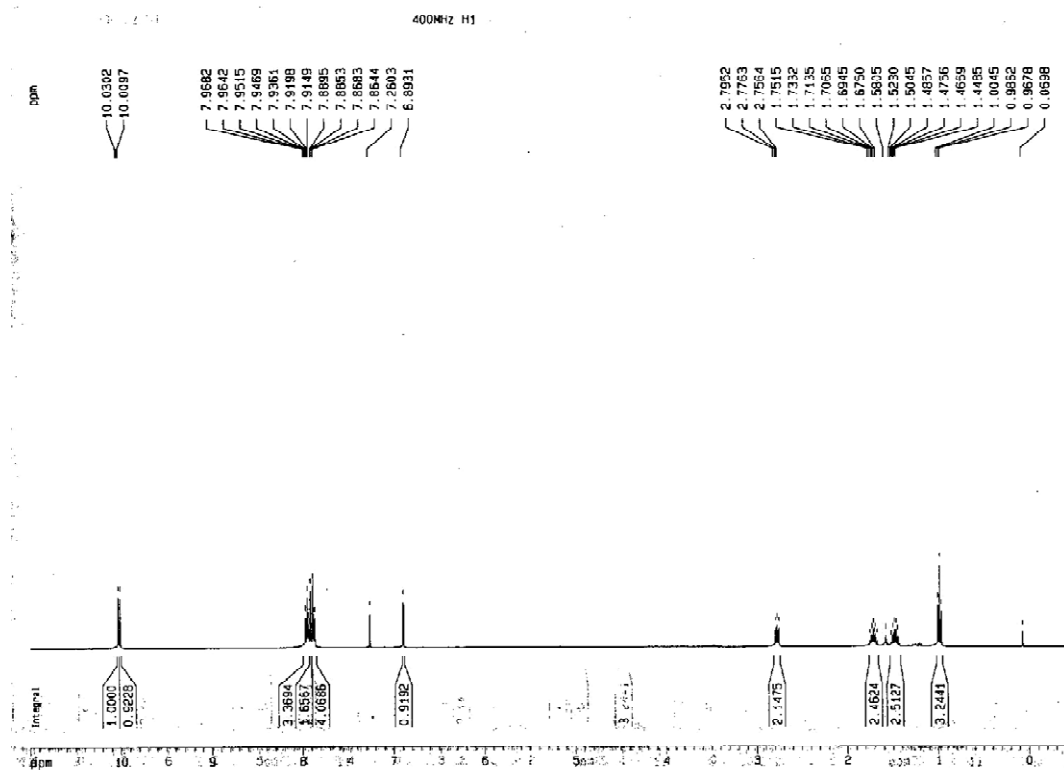
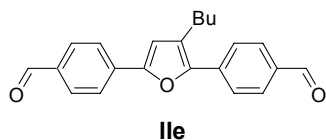
EtOAc/hexane) to give IVd (152 mg, 90%): mp 73-74 oC; ¹H NMR (400 MHz, CDCl₃) □ 0.98-1.03 (m, 9 H), 1.45-1.53 (m, 6 H), 1.69-1.76 (m, 6 H), 2.38 (s, 6 H), 2.74-2.77 (m, 6 H), 4.15 (s, 4 H), 6.66 (s, 1 H), 6.67 (s, 1 H), 6.72 (s, 1 H), 7.32 (d, J = 8.4 Hz, 4 H), 7.66-7.80 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃) □ 14.44, 14.47, 23.0, 26.3, 30.7, 32.34, 32.4, 33.4, 33.6, 109.3, 109.4, 123.4, 123.5, 124.1, 124.3, 125.0, 125.1, 128.5, 128.8, 129.4, 129.9, 136.0, 147.2, 151.0, 194.3; IR (KBr) □ 2956, 2928, 2869, 1690, 1601, 1505, 1132, 1102, 933, 839, 810, 625 cm⁻¹; HRMS (FAB) calcd for C₅₄H₅₆O₅S₂: 848.3569, found: 848.3574.

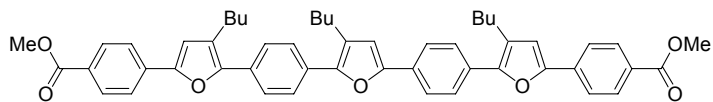
Bis-dithioacetate (Vd). To a suspension of K₂CO₃ (82 mg, 0.6 mmol) in DMF (10 mL) was slowly added a solution of freshly distilled thioacetic acid (0.04 mL, 0.6 mmol) in DMF (5 mL). After 10 min, this solution was added to a solution of Vc (210 mg, 0.2 mmol) in DMF (10 mL). The reaction flask was wrapped with aluminum foil to protect from ambient light and the mixture was stirred overnight. After removal of solvent under reduced pressure, the residue was dissolved in CH₂Cl₂ (40 mL), and washed with water and brine. The organic layer was dried (MgSO₄), the solvent was removed in vacuo, and the residue was chromatographed (silica-gel, EtOAc/hexane) to give Vd (192 mg, 92%): mp 127-128 oC; ¹H NMR (200 MHz, CDCl₃) □ 0.94-1.04 (m, 12 H), 1.41-1.56 (m, 8 H), 1.62-1.77 (m, 8 H), 2.37 (s, 6 H), 2.70-2.81 (m, 8 H), 4.14 (s, 4 H), 6.66 (s, 2 H), 6.73 (s, 2 H), 7.32 (d, J = 8.2 Hz, 4 H), 7.64-7.82 (m, 16 H); ¹³C NMR (100 MHz, CDCl₃) □ 13.98, 14.02, 22.6, 22.7, 25.9, 30.4, 32.0, 32.1, 33.3, 109.6, 123.8, 123.9, 124.1, 124.5, 124.7, 124.9, 125.4, 125.5, 128.9, 129.2, 129.8, 129.9, 130.4, 136.4, 147.7, 151.6, 195.2; IR (KBr) □ 2956, 2928, 2869, 1691, 1602, 1504, 1132, 1102, 933, 839, 810 cm⁻¹; HRMS (FAB) calcd for C₆₈H₇₀O₆S₂: 1046.4614, found: 1046.4603.

Bis-dithiol (IV, or V). Under argon atmosphere, a THF solution (10 mL) of LAH (3 eq.) was treated with a THF solution (10 mL) of IV (85 mg, 0.1 mmol) or V (104 mg, 0.1 mmol) at 0 oC, and stirred for 10 min, then warmed to rt and stirred an additional 30 min. The mixture was cooled to 0 oC and treated with 3 N aqueous HCl under an argon atmosphere until all the solid had dissolved. The biphasic mixture was diluted with EtOAc (20 mL) and water (20 mL). The organic layer was dried (MgSO₄), removed in vacuo to give the desired bis-thiol which was used for the STM studies without further purification.

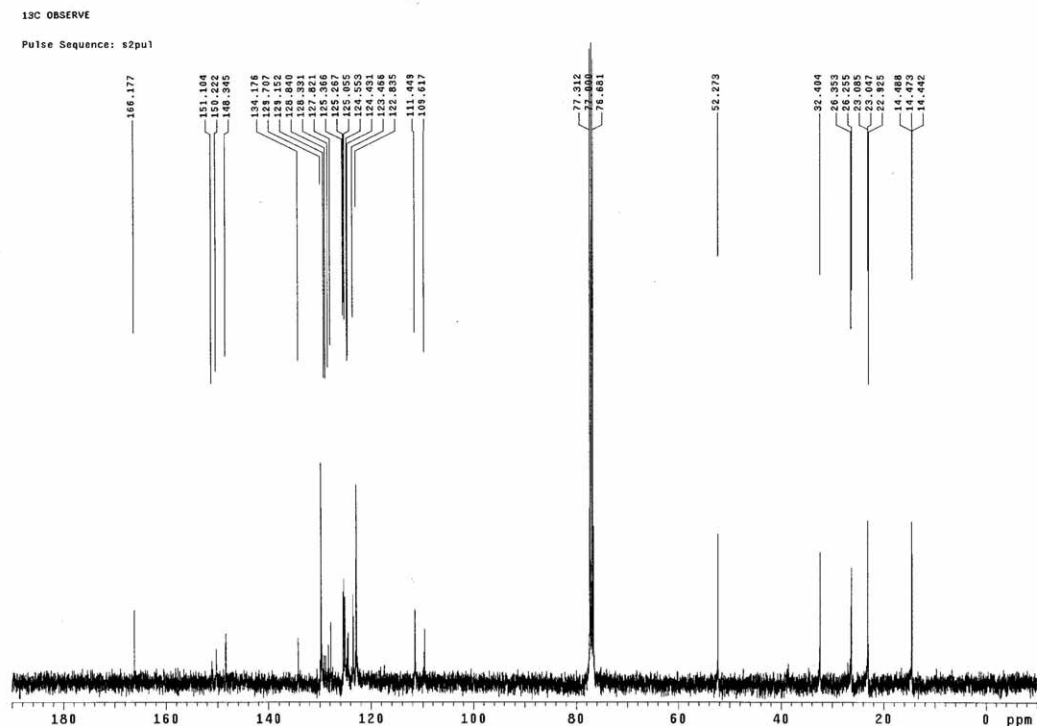
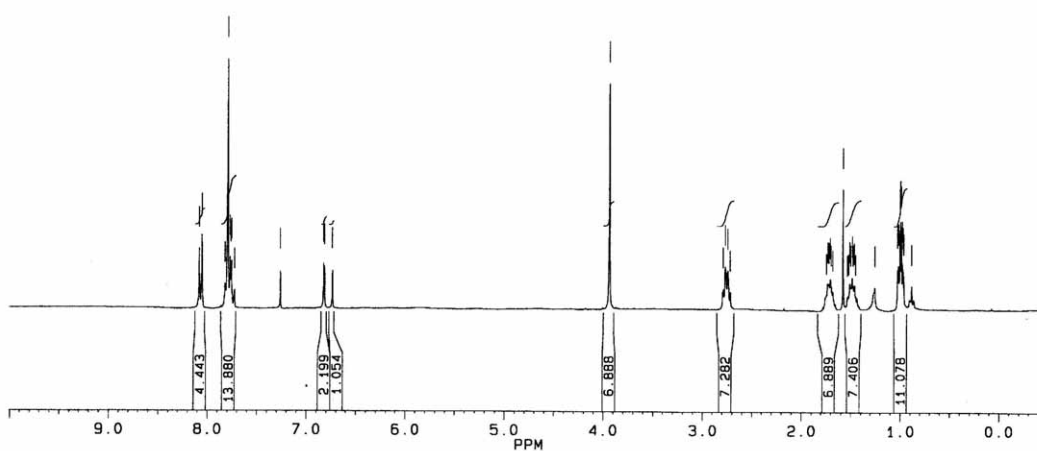
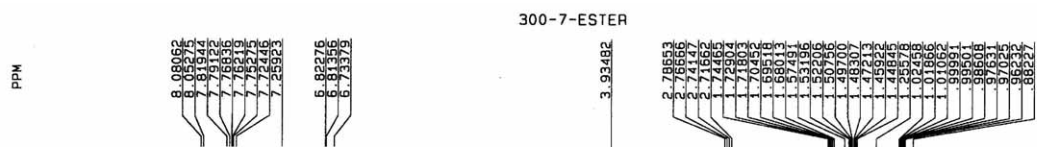
References

- (1) Lin, S.-Y.; Chen, I-W. P.; Chen, C.-h.; Lee, C.-F.; Chou, C.-M.; Luh, T.-Y. *J. Phys. Chem. B* 2005, 109, 7915-7922.
- (2) Lee, C.-F.; Liu, C.-Y.; Song, H.-C.; Luo, S.-J.; Tseng, J.-C.; Tso, H.-H.; Luh, T.-Y. *Chem. Commun.* 2002, 2824-2825.

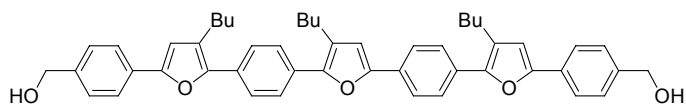




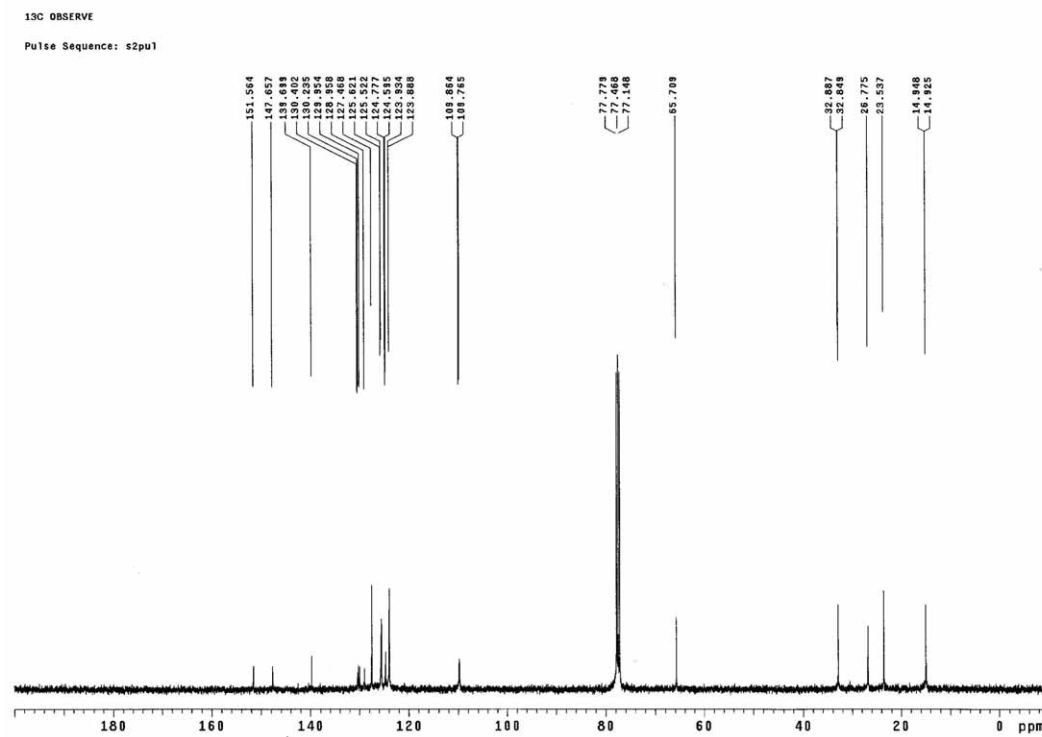
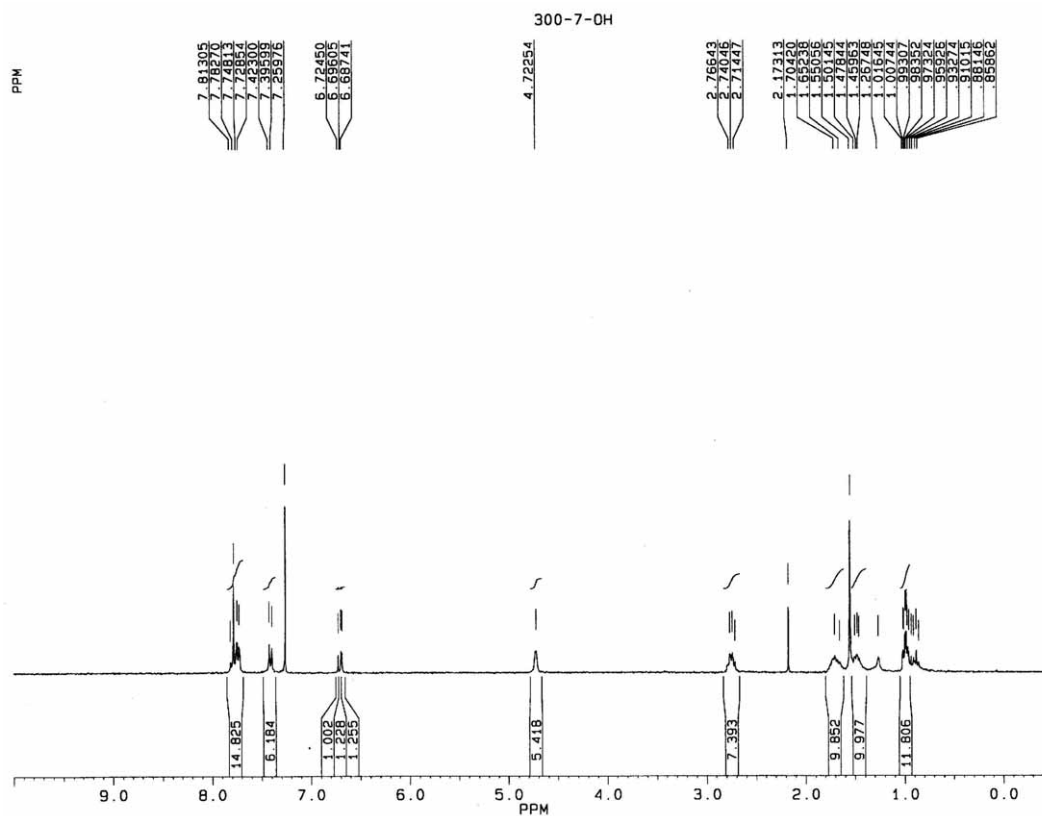
IVa

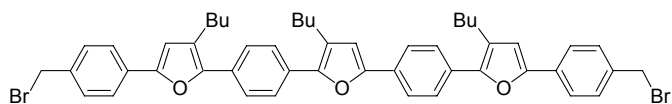


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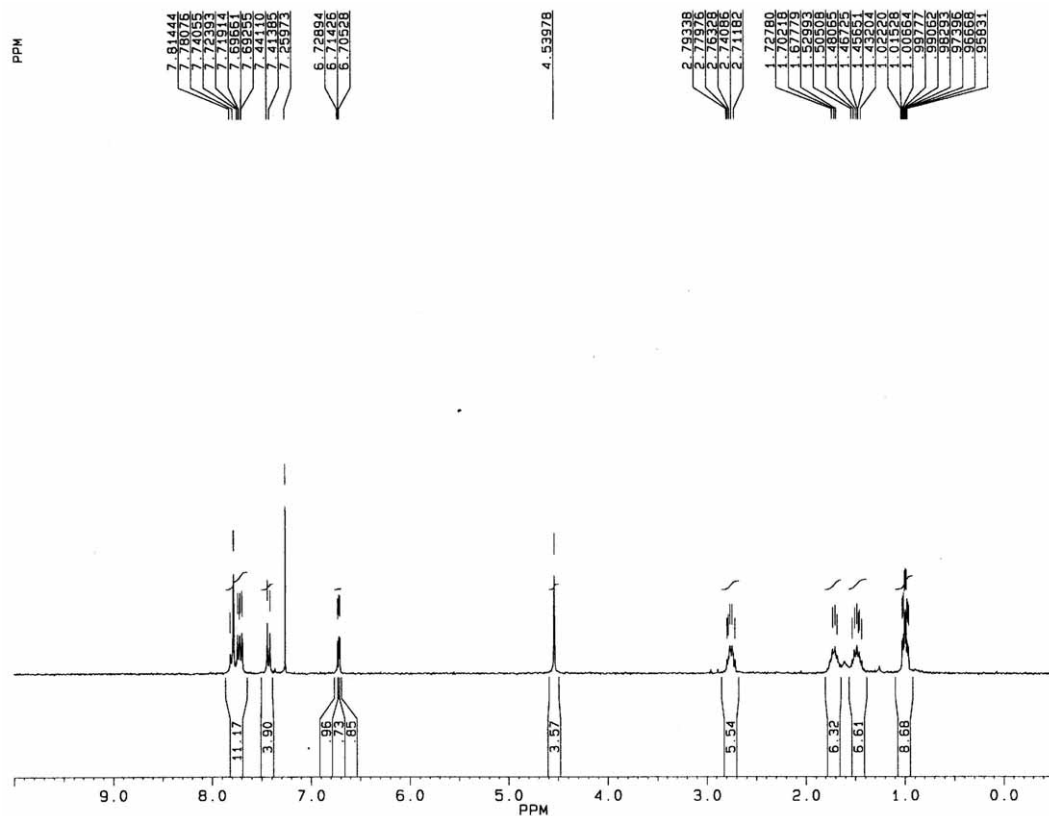


IVb



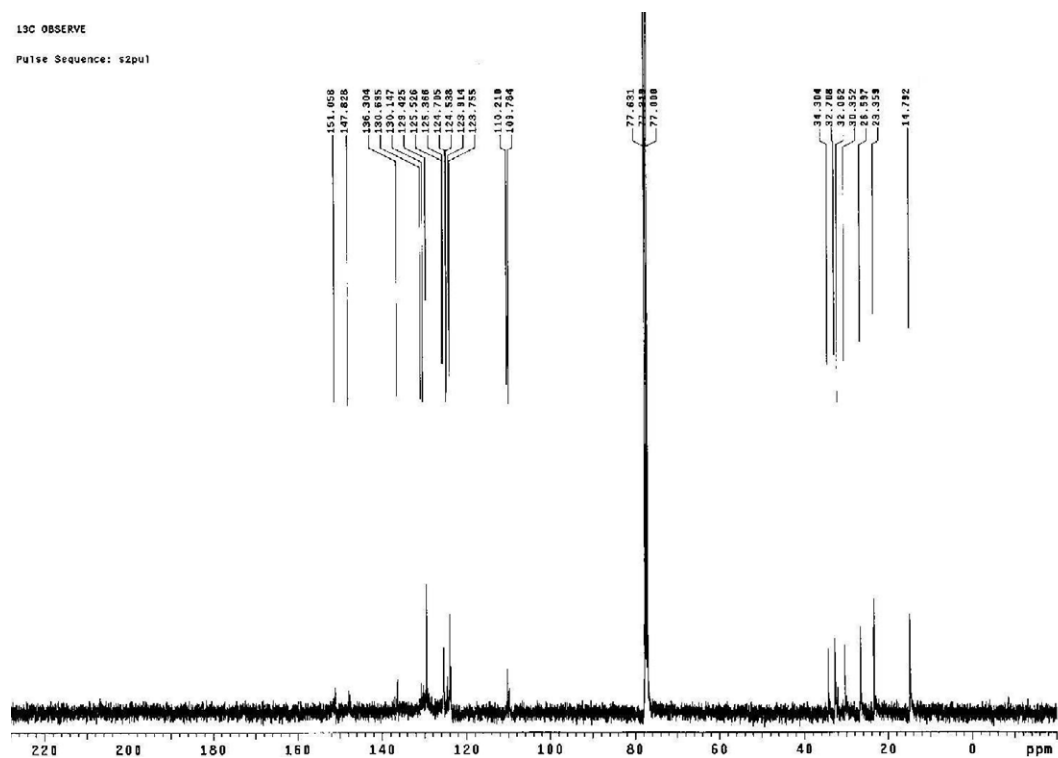


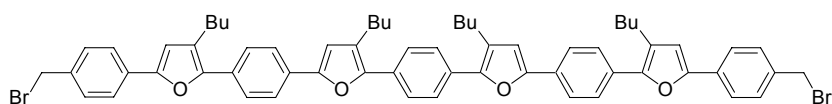
IVc



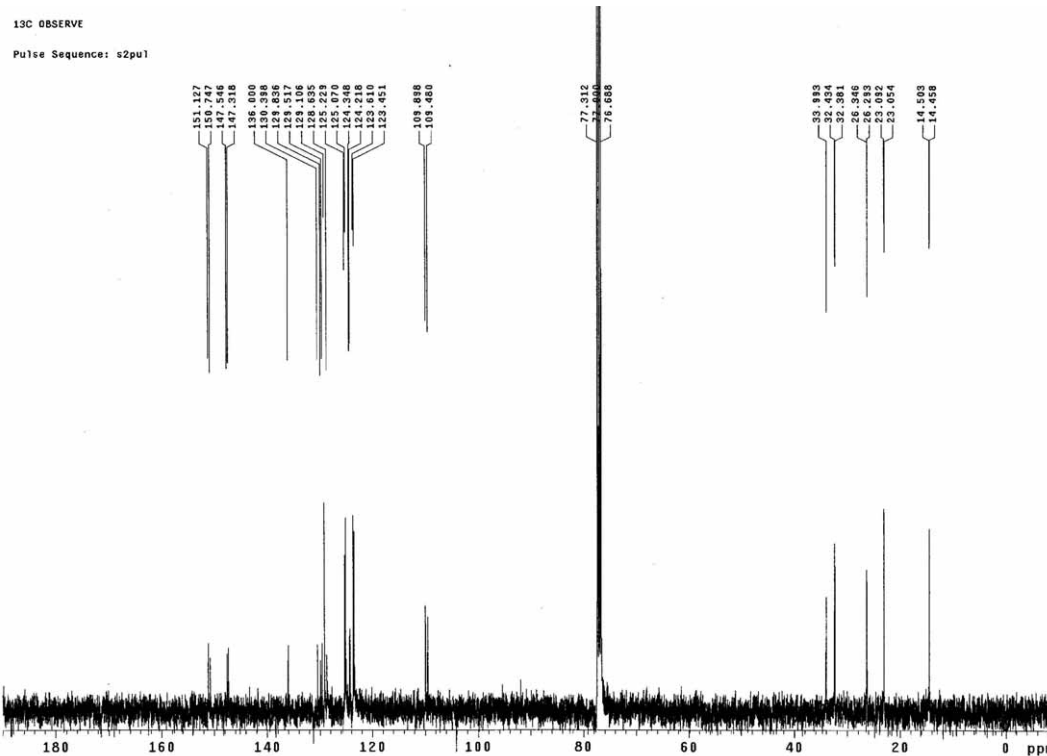
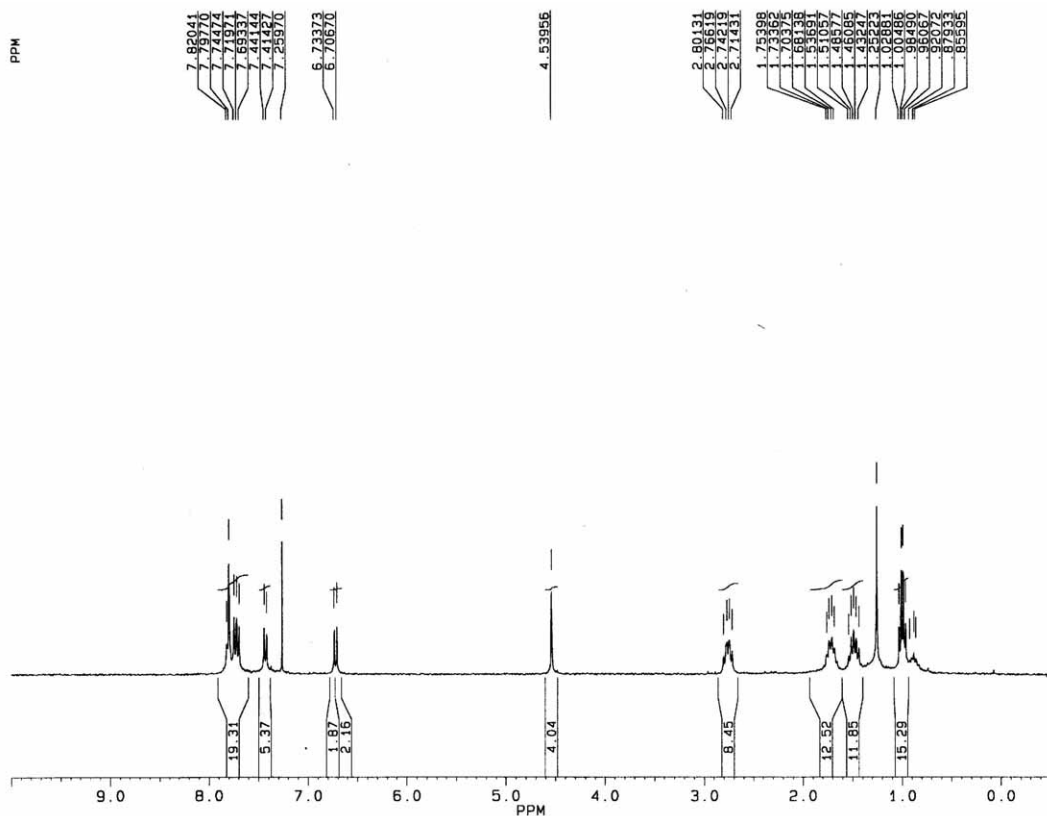
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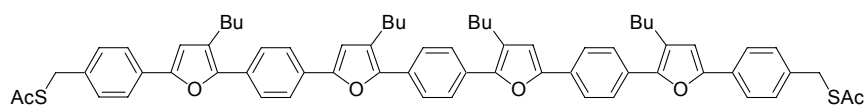




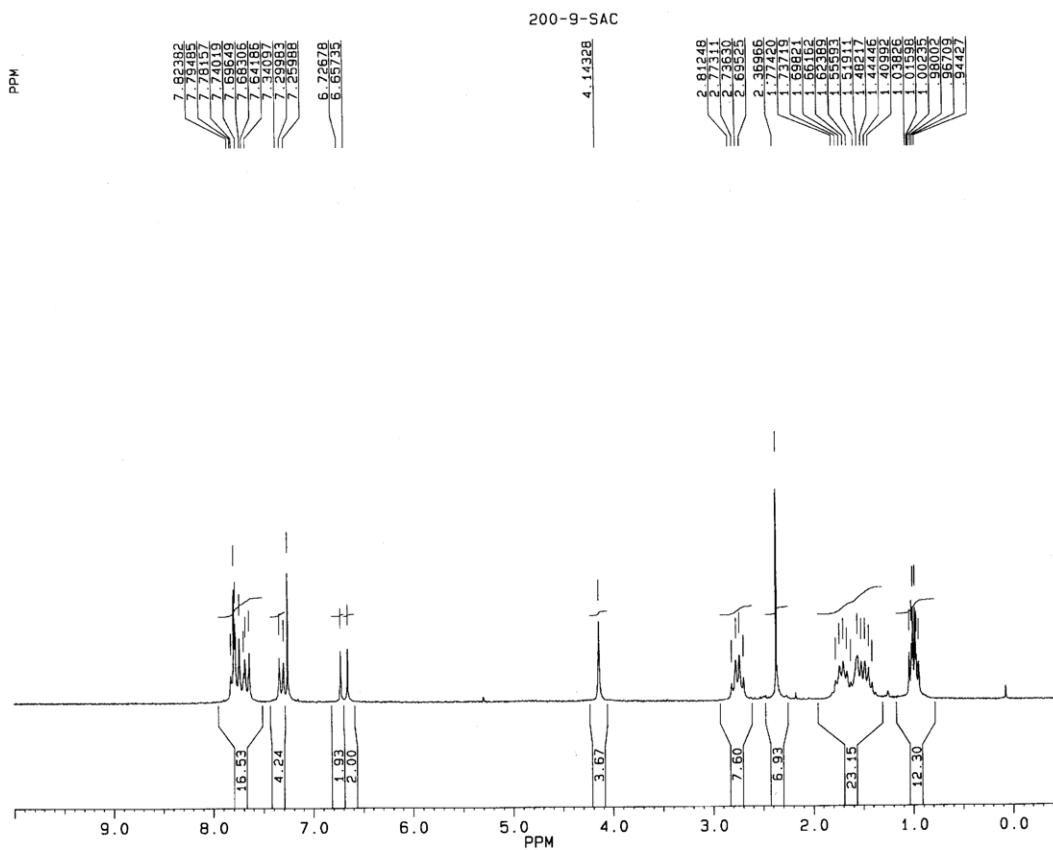
Vc



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Vd



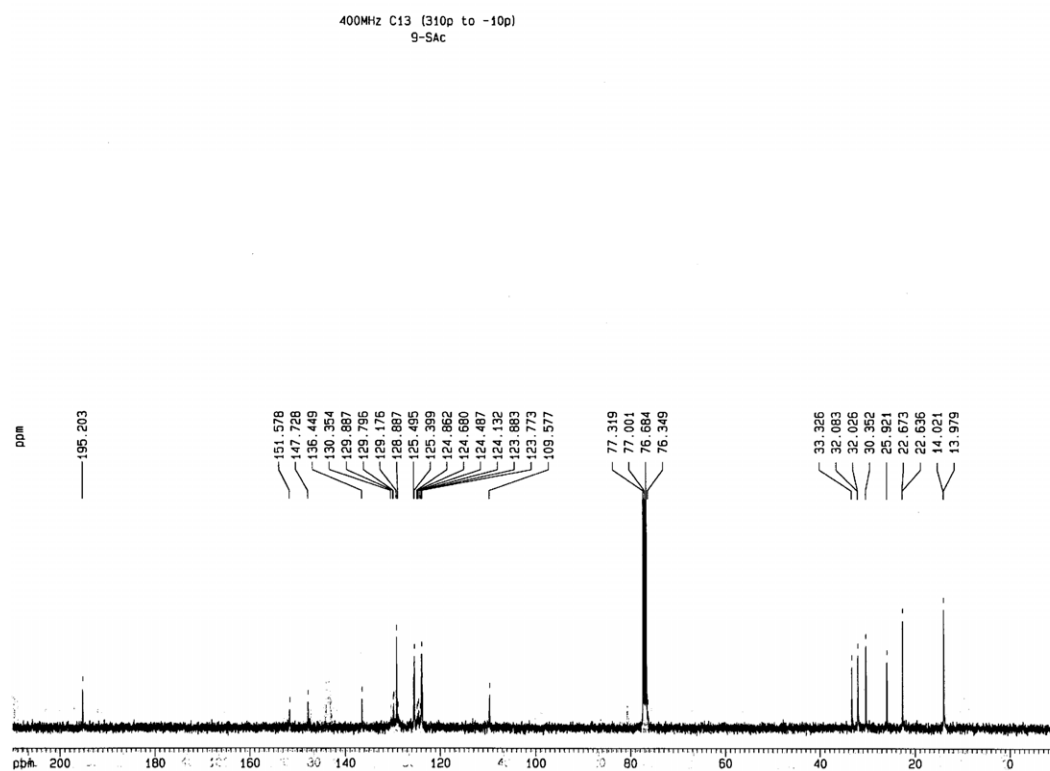


Figure 1S. ORTEP diagram of IIIb. Selected bond distances (\AA) to estimate the electronic coupling constant, \square , are as follows: C(2)-C(11), 73.73; C(11A)-C(11), 17.00.

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