Supplementary Information for:

Charge Transfer Pathway Topology-Optical Band Gap Correlations in Donor/Acceptor-Functionalized Bis(dehydrobenzo[18]annuleno)benzenes†

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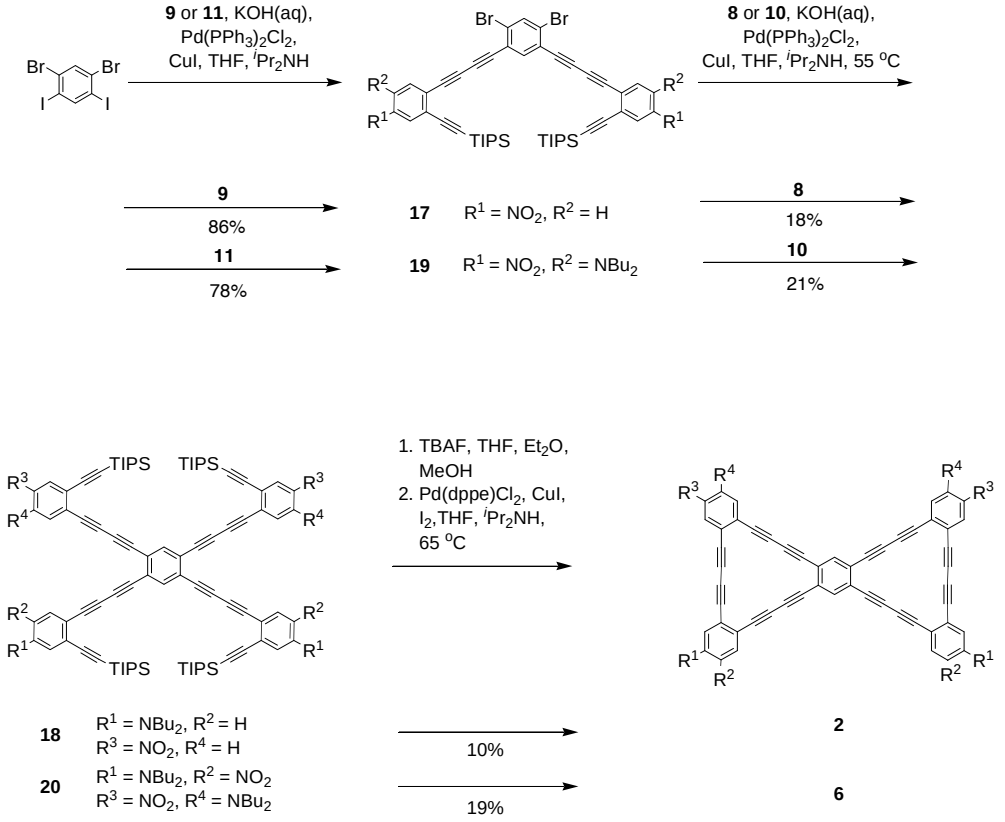
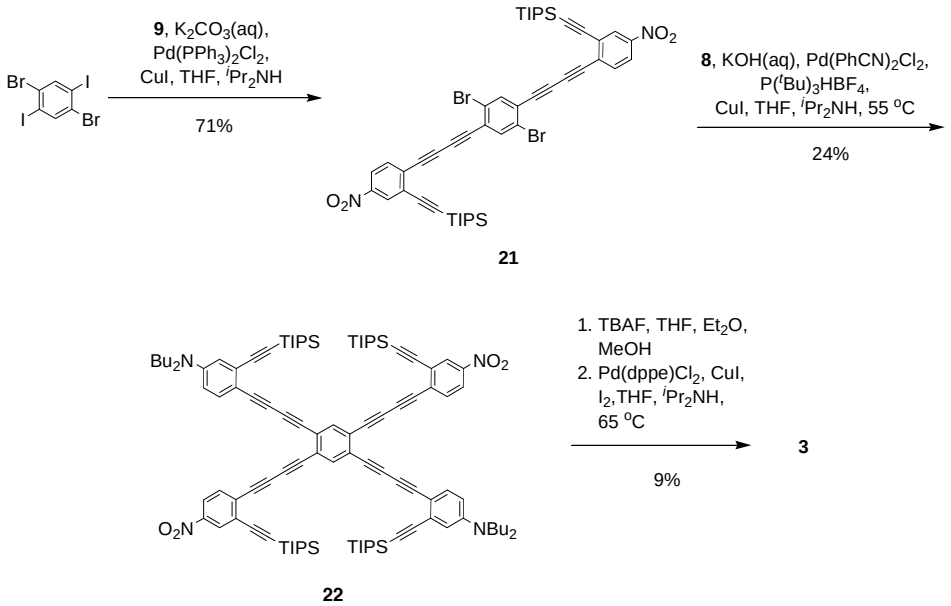
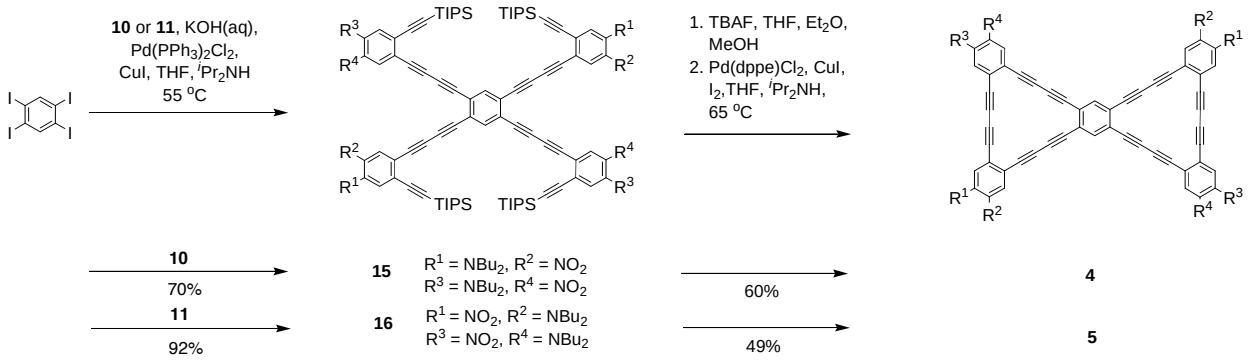


Scheme S1 Synthesis of DBAs **2** and **6**.



Scheme S2 Synthesis of DBA **3**.



Scheme S3 Synthesis of DBAs **4** and **5**.

Acceptor-functionalized arene 17. Segment **9** (500 mg, 1.18 mmol) was cross-coupled to 1,5-dibromo-2,4-diiodobenzene (173 mg, 0.36 mmol) at rt for 24 h using general alkyne coupling procedure B. The crude material was chromatographed on silica gel (4:1 hexanes:CH_2Cl_2) to give **17** (285 mg, 86%) as a yellow powder. Once purified, the product exhibited very poor solubility, thus precluding acquisition of mass spectrometry data. Mp: 170-173 °C. ν_{max}(KBr)/cm^{-1} 2941, 2863, 2150, 1592, 1521, 1455, 1345, 1106, 1062, 884, 853, 814, 745, 723, 680. δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.32 (2 H, d, *J* 2.2), 8.12 (2 H, dd, *J* 9.0, 2.2), 7.91 (1 H, s), 7.67 (1 H, s), 7.66 (2 H, d, *J* 9.0), 1.18 (42 H, s). δ_C(75 MHz; $CDCl_3$; Me_4Si) 147.53, 138.81, 136.69, 133.87, 133.71, 128.89, 127.84, 127.42, 123.71, 122.86, 102.42, 100.49, 81.75, 81.11, 80.96, 79.45, 18.96, 11.46.

DBA precursor 18. Acceptor-functionalized arene **17** (430 mg, 0.860 mmol) was cross-coupled with segment **8** (270 mg, 0.289 mmol) at 55 °C for 72 h using general alkyne coupling procedure C (injection over 12 h). The crude material was chromatographed on silica gel (4:1 hexanes:CH_2Cl_2) to give **18** (85 mg, 18%) as a red oil. λ_{max}(CH_2Cl_2)/nm 342 (log ε/dm^3 mol^{-1} cm^{-1}, 5.05), 363 (5.04), 471 (4.71). ν_{max}(KBr)/cm^{-1} 2955, 2934, 2886, 2861, 2185, 2149, 1655, 1630, 1568, 1557, 1539, 1517, 1499, 1477, 1452, 1346. δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.32 (2 H, t, *J* 2.1), 8.12 (2 H, m), 7.73 (1 H, s), 7.68 (2 H, dd, *J* 9.0, 2.1), 7.59 (1 H, s), 7.33 (2 H, dd, *J* 9.0, 2.7), 6.68 (2 H, d, *J* 2.7), 6.50 (2 H, dd, *J* 9.3, 2.7), 3.28 (8 H, t, *J* 7.8), 1.56 (8 H, quin, *J* 6.4), 1.32 (8 H, sext, *J* 6.8), 1.16 (84 H, s), 0.96 (12 H, t, *J* 7.2). δ_C(75 MHz; $CDCl_3$; Me_4Si) 148.96, 147.35, 140.47, 134.65, 133.98, 130.72, 130.54, 128.99, 127.86, 127.34, 125.12, 122.93, 116.50, 115.03, 113.68, 108.42, 105.78, 104.88, 102.63, 100.64, 100.27, 89.71, 86.07, 84.80, 81.95, 81.24, 81.08,

79.42, 50.85, 29.57, 20.58, 19.04, 14.26, 11.58. *m/z* (APCI) 1639.5 (M^+, 72%), 1640.5 (M^+H^+, 100), 1641 (M^+2H^+, 90).

DBA 2. Precursor **18** (80 mg, 0.049 mmol) was subjected to general Pd-catalyzed cyclization procedure D (36 h). The crude material was purified by filtration through a pad of silica gel followed by concentration in vacuo and trituration with hexanes to afford **3** (4.9 mg, 10%) as a red powder. Once purified, the product exhibited very poor solubility, thus precluding acquisition of ^{13}C-NMR data. Mp: 160-180 °C (dec). $\lambda_{max}(CH_2Cl_2)$/nm 400 (log ε/dm^3 mol^{-1} cm^{-1}, 4.80), 471 (4.82). ν_{max}(KBr)/cm^{-1} 2947, 2924, 2852, 2184, 1719, 1590, 1512, 1461, 1334, 1261, 1214, 1018. δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.40 (2 H, s), 8.05 (1 H, s), 7.98 (2 H, d, *J* 7.8), 7.82 (1 H, s), 7.67 (2 H, d, *J* 9.0), 7.39 (2 H, d, *J* 9.3), 6.65 (2 H, s), 6.59 (2 H, d, *J* 9.0), 3.26 (8 H, t, *J* 8.4), 1.56 (8 H, m), 1.42 (8 H, sext, *J* 8.2), 1.00 (12 H, t, *J* 8.2). *m/z* (APCI) 1010.0 (M^+, 100%), 1011.5 (M^+H^+, 54).

Acceptor-functionalized arene 21. Segment **9** (203 mg, 0.479 mmol) was cross-coupled to 1,4-dibromo-2,5-diiodobenzene (96 mg, 0.197 mmol) at rt for 36 h using general alkyne coupling procedure B. The crude material was chromatographed on silica gel (5:1 hexanes:CH_2Cl_2) to give **21** (131 mg, 71%) as an insoluble yellow powder. Mp: 192.5-195.8 °C (dec). ν_{max}(KBr)/cm^{-1} 2941, 2863, 1653, 1569, 1522, 1458, 1437, 1344, 1067, 995. δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.33 (2 H, d, *J* 2.1), 8.12 (2 H, dd, *J* 8.8, 2.1), 7.74 (2 H, s), 7.68 (2 H, d, *J* 8.8), 1.18 (42 H, s). δ_C(75 MHz; $CDCl_3$; Me_4Si) 147.56, 137.69, 133.88, 130.60, 128.95, 127.41, 126.34, 124.63, 122.86, 102.38, 100.60, 82.01, 81.60,

81.22, 81.21, 18.94, 11.45. *m/z* (APCI) 932.2 ($M^{+}2^{79}Br$, 68%), 934.2 ($M^{+79}Br^{81}Br$, 100), 935.2 ($M^{+13}C^{79}Br^{81}Br$, 81), 936.2 ($M^{+}2^{81}Br$, 58).

DBA precursor 22. Acceptor-functionalized arene **21** (770 mg, 1.52 mmol) was cross-coupled with segment **8** (474 mg, 0.507 mmol) at 55 °C for 72 h using general alkyne coupling procedure C (injection over 6 h). The crude material was chromatographed on silica gel (9:1 hexanes:CH_2Cl_2) to give **22** (193 mg, 24%) as a red oil. $\lambda_{max}(CH_2Cl_2)$/nm 247 (log ε/dm^3 mol^{-1} cm^{-1}, 4.74), 343 (4.63), 386 (4.68), 455(sh) (4.19). ν_{max}(KBr)/cm^{-1} 2954, 2934, 2879, 2180, 1649, 1590, 1562, 1537, 1518, 1488, 1346. δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.32 (2 H, d, *J* 2.2), 8.10 (2 H, dd, *J* 8.6, 2.2), 7.68 (2 H, d, *J* 8.6), 7.57 (2 H, s), 7.34 (2 H, d, *J* 8.8), 6.68 (2 H, d, *J* 2.4), 6.50 (2 H, dd, *J* 8.8, 2.4), 3.28 (8 H, t, *J* 7.8), 1.53 (8 H, quin, *J* 7.2), 1.34 (8 H, sext, *J* 7.4), 1.18 (84 H, s), 0.96 (12 H, t, *J* 7.4). δ_C(75 MHz; $CDCl_3$; Me_4Si) 148.59, 147.40, 137.73, 134.56, 133.93, 131.18, 128.87, 126.24, 125.21, 122.61, 115.04, 111.75, 109.77, 105.80, 102.43, 100.51, 94.66, 86.49, 83.05, 82.75, 82.29, 81.36, 81.28, 80.07, 78.09, 75.83, 75.60, 50.81, 29.50, 20.47, 18.98, 18.93, 14.16, 11.62, 11.49. *m/z* (APCI) 1639.5 (M^{+}, 70%), 1640.5 ($M^{+}H^{+}$, 100), 1641 ($M^{+}2H^{+}$, 81).

DBA 3. Precursor **22** (90 mg, 0.055 mmol) was subjected to general Pd-catalyzed cyclization procedure D (25 h). The crude material was purified by filtration through a pad of silica gel followed by concentration in vacuo and trituration with hexanes to afford **3** (5.0 mg, 9%) as a red powder. Once purified, the product exhibited very poor solubility, thus precluding acquisition of ^{13}C-NMR data. Mp: 160-180 °C (dec). $\lambda_{max}(CH_2Cl_2)$/nm

431 (log ε/dm^3 mol^{-1} cm^{-1}, 4.67), 475 (4.40), 517(sh) (4.10). ν_{max}(KBr)/cm^{-1} 2956, 2924, 2853, 2348, 1734, 1635, 1576, 1522, 1465, 1344, 1214. δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.34 (2 H, d, *J* 2.1), 7.97 (2 H, dd, *J* 7.6, 2.1), 7.69 (2 H, s), 7.58 (2 H, d, *J* 8.7), 7.32 (2 H, d, *J* 8.7), 6.63 (2 H, s), 6.52 (2 H, d, *J* 8.5), 3.21 (8 H, t, *J* 8.4), 1.55 (8 H, m), 1.39 (8 H, sext, *J* 7.0), 0.99 (12 H, t, *J* 7.0). *m/z* (APCI) 1010.0 (M^+, 100%), 1011.5 (M^+H^+, 67).

DBA precursor 15. Segment **10** (71 mg, 0.129 mmol) was cross-coupled to 1,2,4,5-tetraiodobenzene (15 mg, 0.026 mmol) at 55 °C using general alkyne coupling procedure A (12 h). The crude material was chromatographed on silica gel (4:1 hexanes:CH_2Cl_2) to give **15** (113 mg, 70%) as a dark red oil. λ_{max}(CH_2Cl_2)/nm 288 (log ε/dm^3 mol^{-1} cm^{-1}, 5.01), 329 (5.00), 354 (4.99), 384 (4.89), 432 (4.88). ν_{max}(NaCl)/cm^{-1} 2958, 2926, 2861, 2204, 1652, 1596, 1539, 1504, 1475, 1456, 1416. δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.90 (4 H, s), 7.57 (2 H, s), 7.10 (4 H, s), 3.15 (16 H, t, *J* 7.2), 1.53 (16 H, quin, *J* 6.6), 1.28 (16 H, sext, *J* 7.5), 1.24 (84 H, s), 0.89 (24 H, t, *J* 7.5). δ_C(75 MHz; $CDCl_3$; Me_4Si) 145.26, 139.56, 137.89, 131.67, 131.39, 125.62, 124.16, 113.55, 103.58, 99.90, 82.42, 81.32, 79.14, 77.22, 51.76, 29.72, 20.26, 18.93, 14.04, 11.53. *m/z* (APCI) 1984.6 (M^+H^+, 66%), 1986.1 ($M^{+13}C2H^+$, 100).

DBA 4. Precursor **15** (108 mg, 0.054 mmol) was subjected to general Pd-catalyzed cyclization procedure D (40 h). The crude material was filtered through a pad of silica gel followed by concentration in vacuo and trituration with hexanes to afford **4** (44 mg, 60%) as a bright orange powder. Mp: 170-190 °C (dec). λ_{max}(CH_2Cl_2)/nm 387 (log ε/dm^3 mol^{-1} cm^{-1}, 5.14), 451 (5.07). Em. λ_{max}: 459. ν_{max}(NaCl)/cm^{-1} 2952, 2926, 2868, 2191, 1595,

1543, 1502, 1476, 1457, 1431. δ_H(300 MHz; CD_2Cl_2; Me_4Si) 8.00 (4 H, s), 7.83 (2 H, s), 7.31 (4 H, s), 3.18 (16 H, t, *J* 7.5), 1.55 (16 H, quin, *J* 7.5), 1.28 (16 H, sext, *J* 7.5), 0.89 (24 H, t, *J* 7.5). δ_C(75 MHz; CD_2Cl_2; Me_4Si) 144.98, 140.03, 136.40, 131.74, 128.80, 125.19, 124.71, 113.05, 82.38, 81.74, 80.88, 79.80, 79.04, 77.24, 51.94, 29.65, 20.26, 13.79. *m/z* (APCI) 1354.6 (M^+, 100%), 1355.6 (M^+H^+, 88).

DBA precursor 16. Segment **11** (260 mg, 0.472 mmol) was cross-coupled to 1,2,4,5-tetraiodobenzene (46 mg, 0.079 mmol) at 55 °C using general alkyne coupling procedure A (12 h). The crude material was chromatographed on silica gel (4:1 hexanes:CH_2Cl_2) to give **16** (143 mg, 92%) as a dark red oil. λ_{max}(CH_2Cl_2)/nm 318 (log ε/dm^3 mol^{-1} cm^{-1}, 5.16), 360 (4.98), 467 (4.25). ν_{max}(NaCl)/cm^{-1} 2982, 2963, 2882, 2209, 2179, 1717, 1624, 1458, 1436, 1362, 1344, 1318. δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.82 (4 H, s), 7.64 (2 H, s), 7.21 (4 H, s), 3.11 (16 H, t, *J* 6.2), 1.49 (16 H, quin, *J* 6.9), 1.26 (16 H, sext, *J* 6.5), 1.14 (84 H, s), 0.87 (24 H, t, *J* 7.2 Hz). δ_C(75 MHz; $CDCl_3$; Me_4Si) 144.29, 140.94, 138.23, 130.59, 128.60, 125.70, 125.20, 117.01, 102.96, 96.11, 82.64, 81.03, 79.97, 79.40, 51.92, 29.71, 20.26, 18.96, 14.03, 11.53. *m/z* (APCI) 1983.5 (M^+, 70%), 1984.4 (M^+H^+, 72), 1985.6 ($M^{+13}CH^+$, 100).

DBA 5. Precursor **16** (117 mg, 0.059 mmol) was subjected to general Pd-catalyzed cyclization procedure D (40 h). The crude material was filtered through a pad of silica gel followed by concentration in vacuo and trituration with hexanes to afford **5** (38 mg, 49%) as a deep red powder. Mp: 165-180 °C (dec). λ_{max}(CH_2Cl_2)/nm 381 (log ε/dm^3 mol^{-1} cm^{-1}, 5.17), 490 (4.10). ν_{max}(NaCl)/cm^{-1} 2954, 2924, 2868, 2198, 2148, 1638, 1594, 1531,

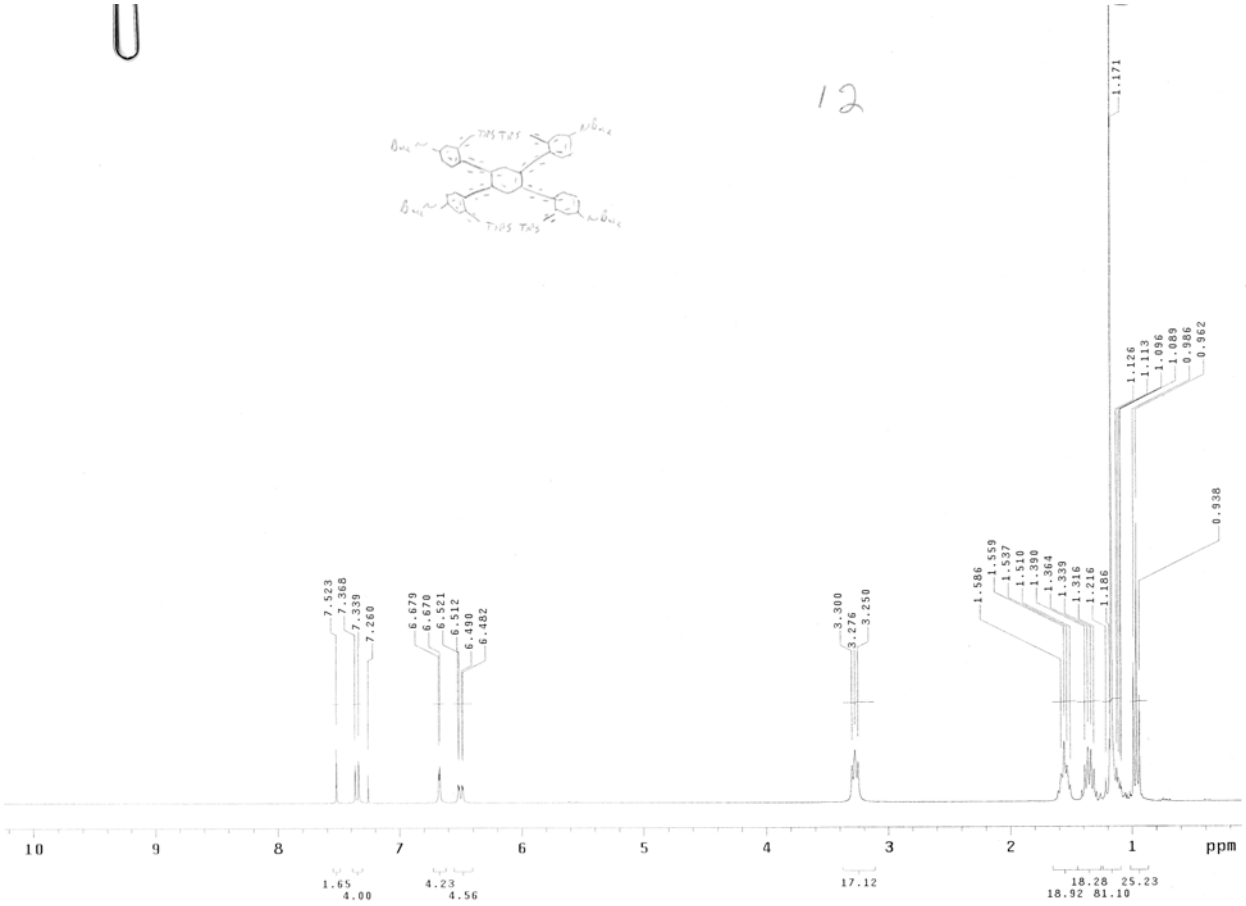
1482, 1435, 1369. δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.96 (4 H, s), 7.82 (2 H, s), 7.29 (4 H, s), 3.18 (16 H, t, *J* 7.5), 1.57 (16 H, quin, *J* 6.9), 1.30 (16 H, sext, *J* 7.2), 0.92 (24 H, t, *J* 7.5). δ_C(75 MHz; $CDCl_3$; Me_4Si) 144.66, 140.26, 137.08, 131.23, 128.73, 125.77, 124.60, 114.15, 100.23, 81.91, 81.22, 80.35, 79.75, 79.65, 51.94, 29.72, 20.33, 14.08. *m/z* (APCI) 1354.6 (M^+, 100%), 1355.3 (M^+H^+, 97).

Acceptor-functionalized arene 19. Segment **11** (260 mg, 0.472 mmol) was cross-coupled to 1,5-dibromo-2,4-diiodobenzene (96 mg, 0.197 mmol) at rt for 16 h using general alkyne coupling procedure B. The crude material was chromatographed on silica gel (9:1 hexanes:CH_2Cl_2) to give **19** (183 mg, 78%) as a red-orange oil. ν_{max}(KBr)/cm^{-1} 2955, 2927, 2860, 2158, 2144, 1652, 1599, 1540, 1508, 1453, 1365, 1340, 1278. δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.89 (1 H, s), 7.82 (2 H, s), 7.61 (1 H, s), 7.21 (2 H, s), 3.12 (8 H, t, *J* 7.2), 1.51 (8 H, quin, *J* 6.9), 1.25 (8 H, sext, *J* 6.9), 1.16 (42 H, s), 0.88 (12 H, t, *J* 7.2). δ_C(75 MHz; $CDCl_3$; Me_4Si) 144.28, 140.91, 138.72, 136.58, 130.60, 128.61, 127.57, 125.25, 123.88, 116.91, 103.01, 96.05, 81.76, 79.87, 79.75, 79.10, 51.96, 29.72, 20.30, 18.98, 14.05, 11.54. *m/z* (APCI) 1188.2 ($MH^{+79}Br^{79}Br$, 40%), 1189.2 ($MH^{+79}Br^{81}Br$, 100), 1190.2 ($MH^{+13}C2^{81}Br$, 87).

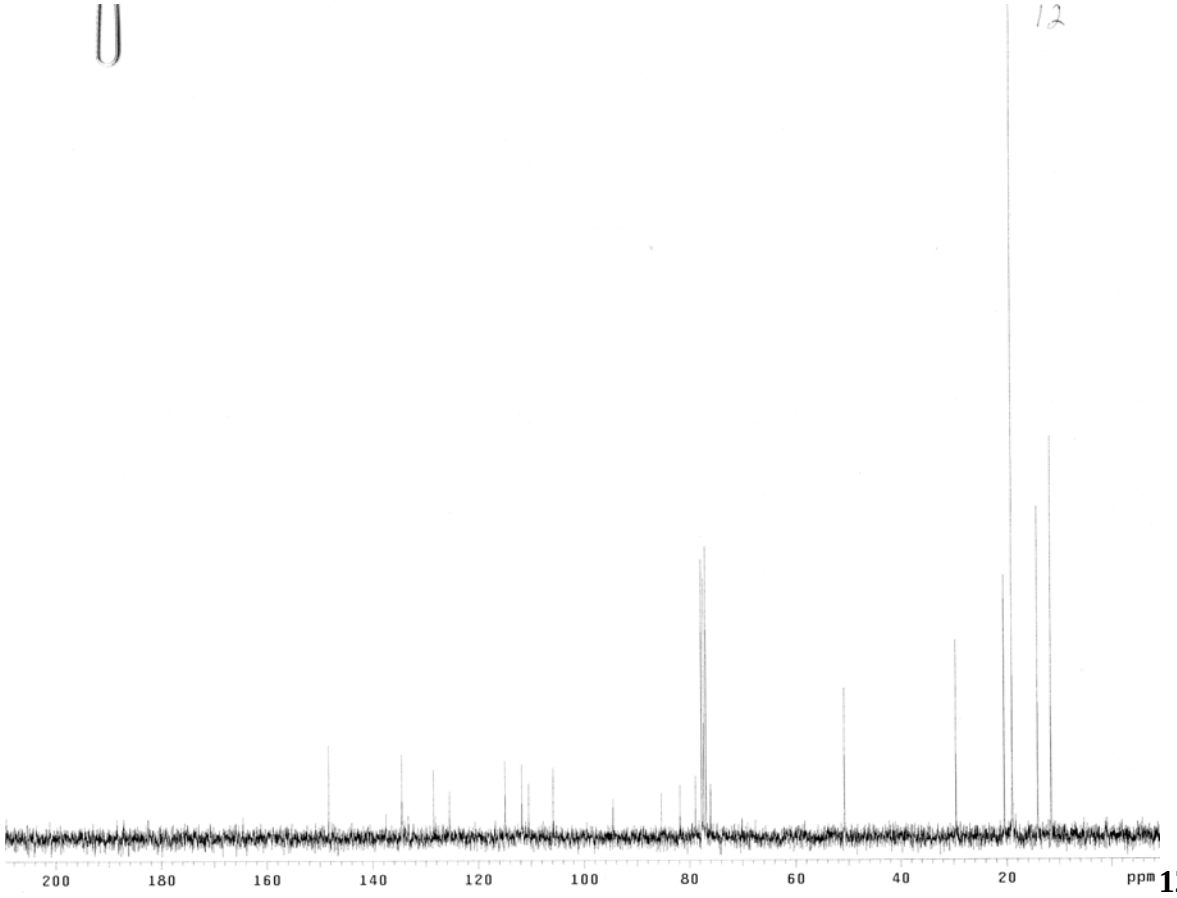
DBA precursor 20. Segment **10** (104 mg, 0.189 mmol) was cross-coupled to acceptor-functionalized arene **19** (90 mg, 0.076 mmol) at 55 °C using general alkyne coupling procedure C (8 h). The crude material was chromatographed on silica gel (5:1 hexanes:CH_2Cl_2) to give **20** (32 mg, 21%) as a dark red oil. λ_{max}(CH_2Cl_2)/nm 320 (log ε/dm^3 mol^{-1} cm^{-1}, 5.01), 354 (4.94), 427 (4.69). ν_{max}(KBr)/cm^{-1} 2954, 2935, 2888, 2859,

2218, 2142, 1653, 1599, 1537, 1504, 1493, 1454, 1367, 1338, 1276. δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.90 (2 H, s), 7.82 (2 H, s), 7.60 (1 H, s), 7.59 (1 H, s), 7.22 (2 H, s), 7.10 (2 H, s), 3.13 (16 H, m), 1.50 (16 H, m), 1.25 (16 H, m), 1.16 (42 H, s), 1.14 (42 H, s), 0.89 (24 H, m). δ_C(75 MHz; $CDCl_3$; Me_4Si) 145.32, 144.31, 140.98, 139.56, 138.09, 138.01, 131.66, 131.39, 130.58, 128.79, 126.16, 125.35, 125.21, 124.13, 117.08, 113.31, 104.36, 103.57, 102.99, 99.89, 96.11, 82.75, 82.42, 81.72, 80.68, 80.30, 79.61, 78.90, 51.98, 51.77, 29.95, 29.72, 20.27, 18.94, 14.01, 11.53.

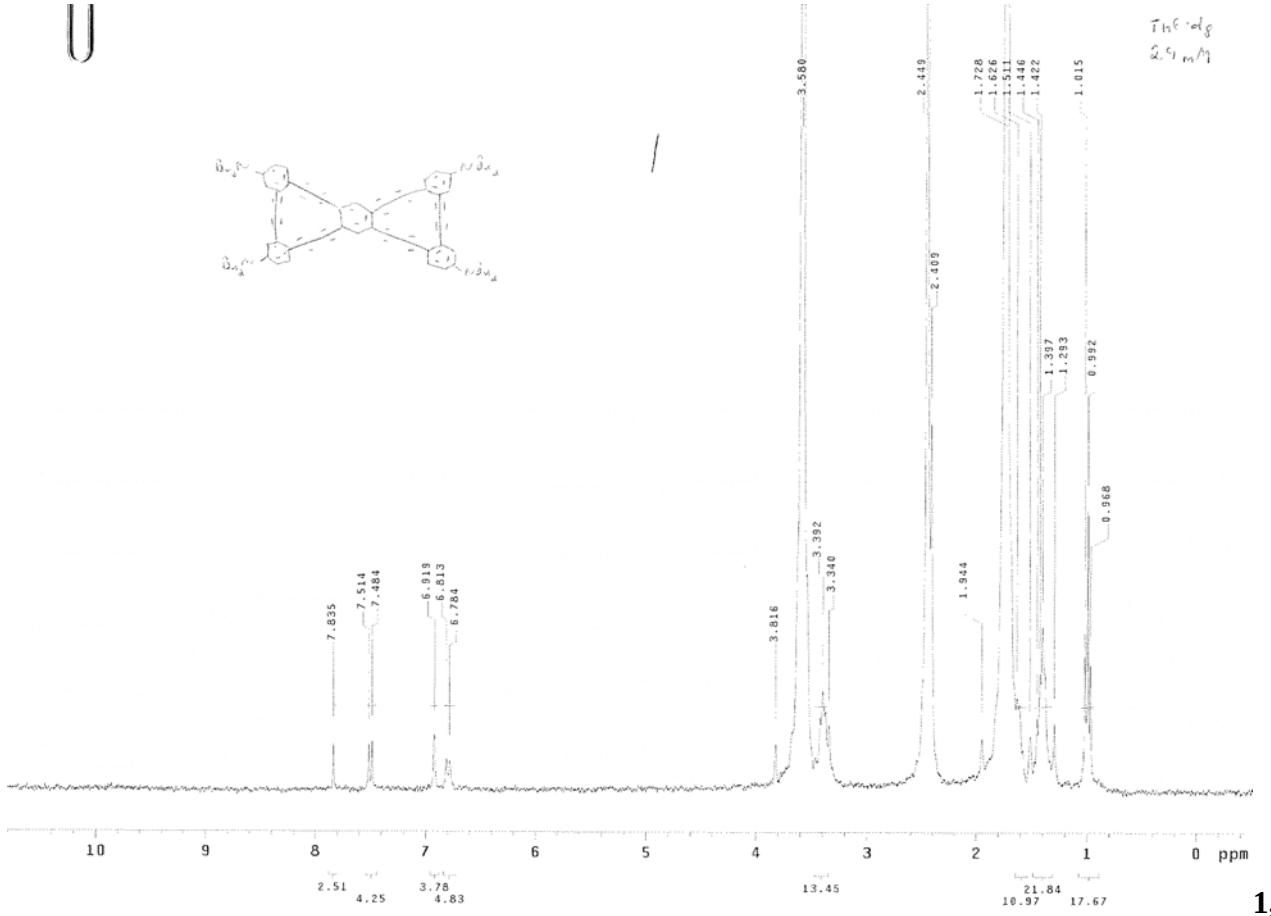
DBA 6. Precursor **20** (32 mg, 0.016 mmol) was subjected to general Pd-catalyzed cyclization procedure D (40 h). The crude material was filtered through a pad of silica gel followed by concentration in vacuo and trituration with hexanes to afford **6** (4 mg, 19%) as a dark orange-red solid. Mp: 150-170 °C (dec). δ_H(300 MHz; CD_2Cl_2; Me_4Si) 8.01 (2 H, s), 7.99 (2 H, s), 7.88 (1 H, s), 7.87 (1 H, s), 7.35 (2 H, s), 7.31 (2 H, s), 3.20 (16 H, m), 1.57 (16 H, m), 1.31 (16 H, m), 0.91 (24 H, m). δ_C(75 MHz; $CDCl_3$; Me_4Si) 145.12, 145.06, 140.00, 139.76, 136.70, 133.56, 131.92, 131.62, 129.73, 129.39, 129.06, 126.59, 124.55, 124.18, 113.41, 113.08, 82.28, 82.20, 81.78, 81.25, 81.22, 81.04, 80.69, 80.42, 80.17, 79.92, 79.40, 77.44, 51.98, 29.96, 29.75, 20.32, 14.03. ν_{max}(NaCl)/cm^{-1} 2958, 2927, 2868, 2851, 2210, 1709, 1594, 1535, 1493, 1457, 1426, 1339. λ_{max}(CH_2Cl_2)/nm 382 (log ε/$dm^3\,mol^{-1}\,cm^{-1}$, 4.84), 404 (4.87), 456 (4.54).



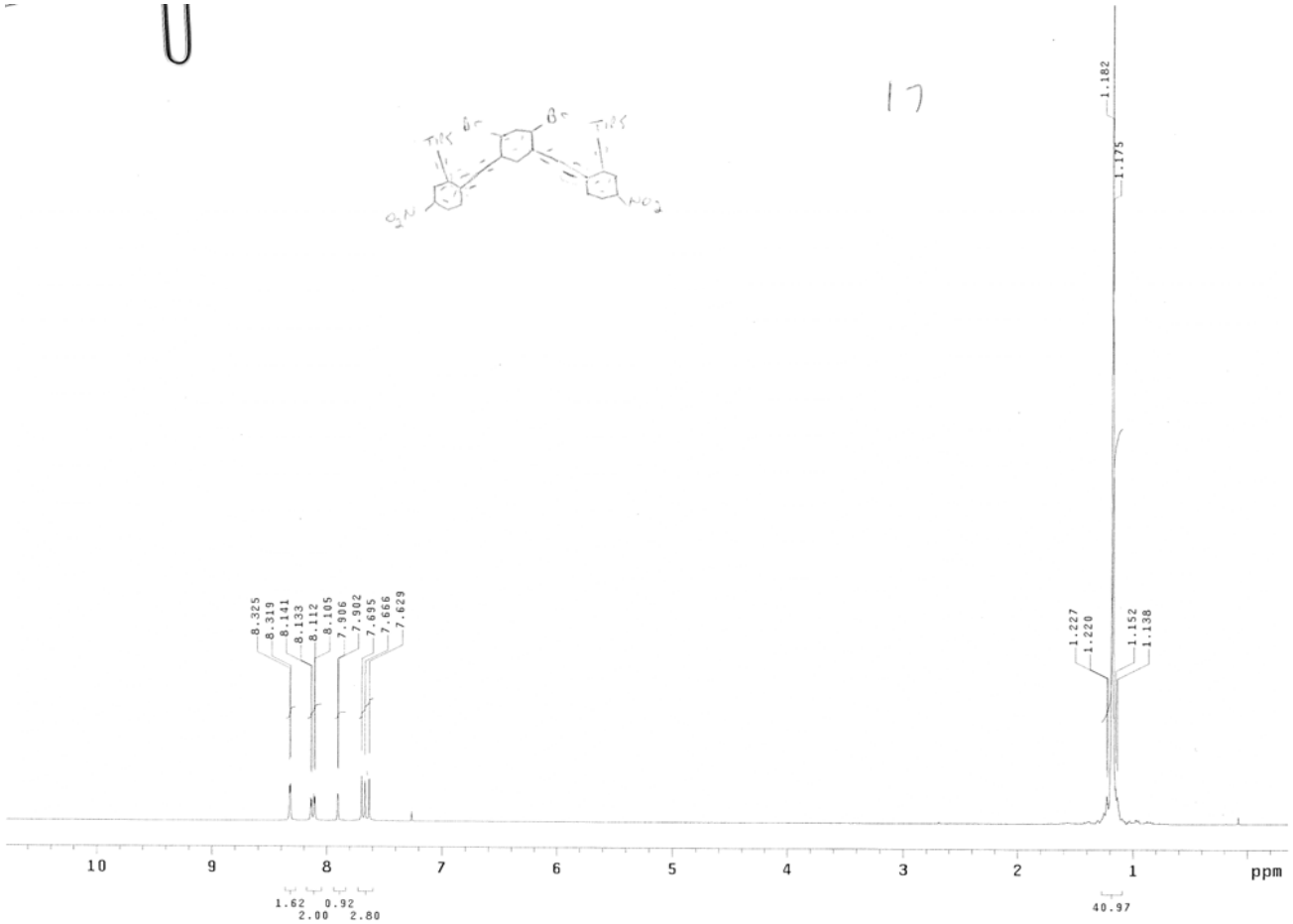
12, 1H-NMR, $CDCl_3$, 300 MHz



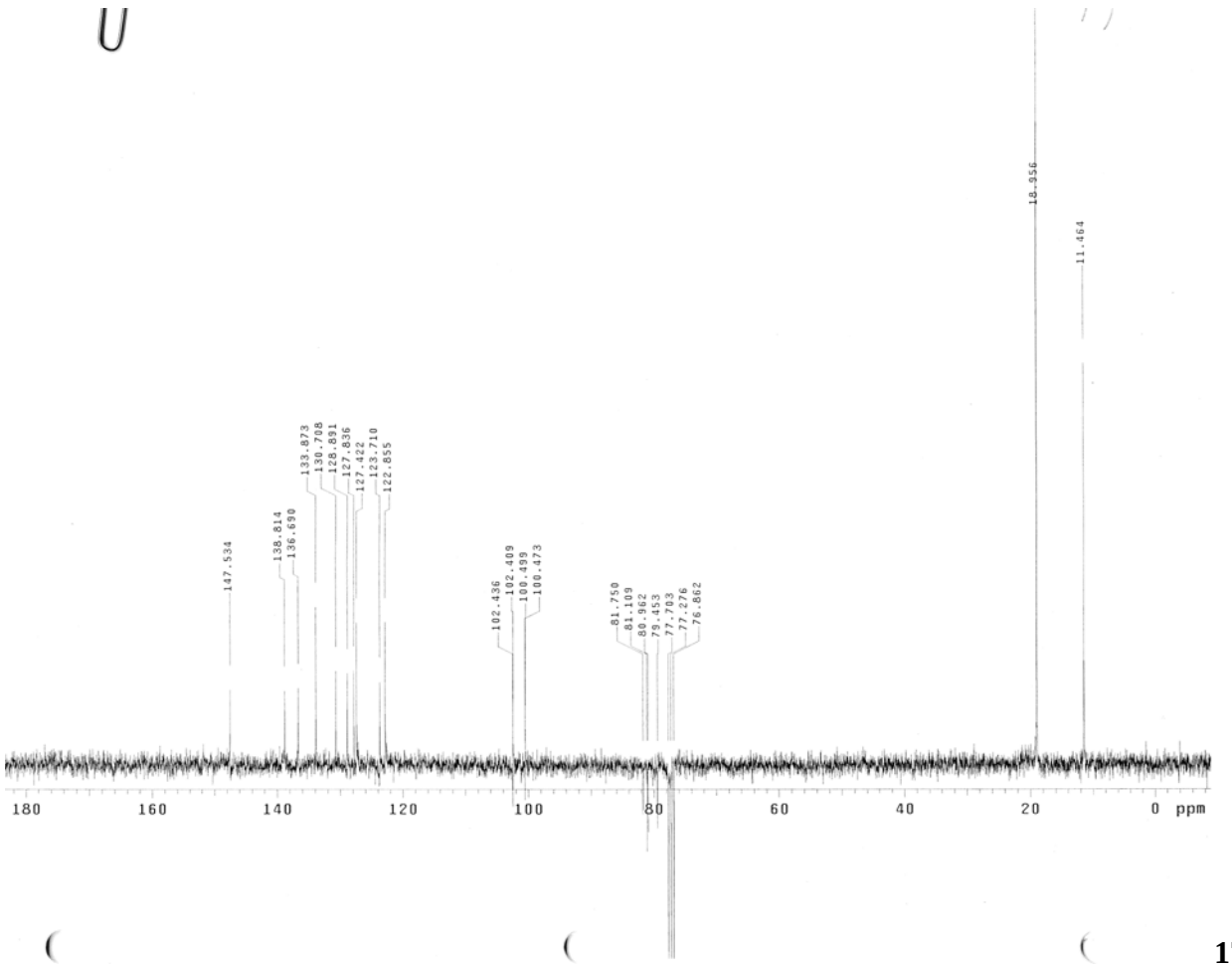
12, 13C-NMR, $CDCl_3$, 75 MHz



1, 1H-NMR, THF-d_8, 300 MHz

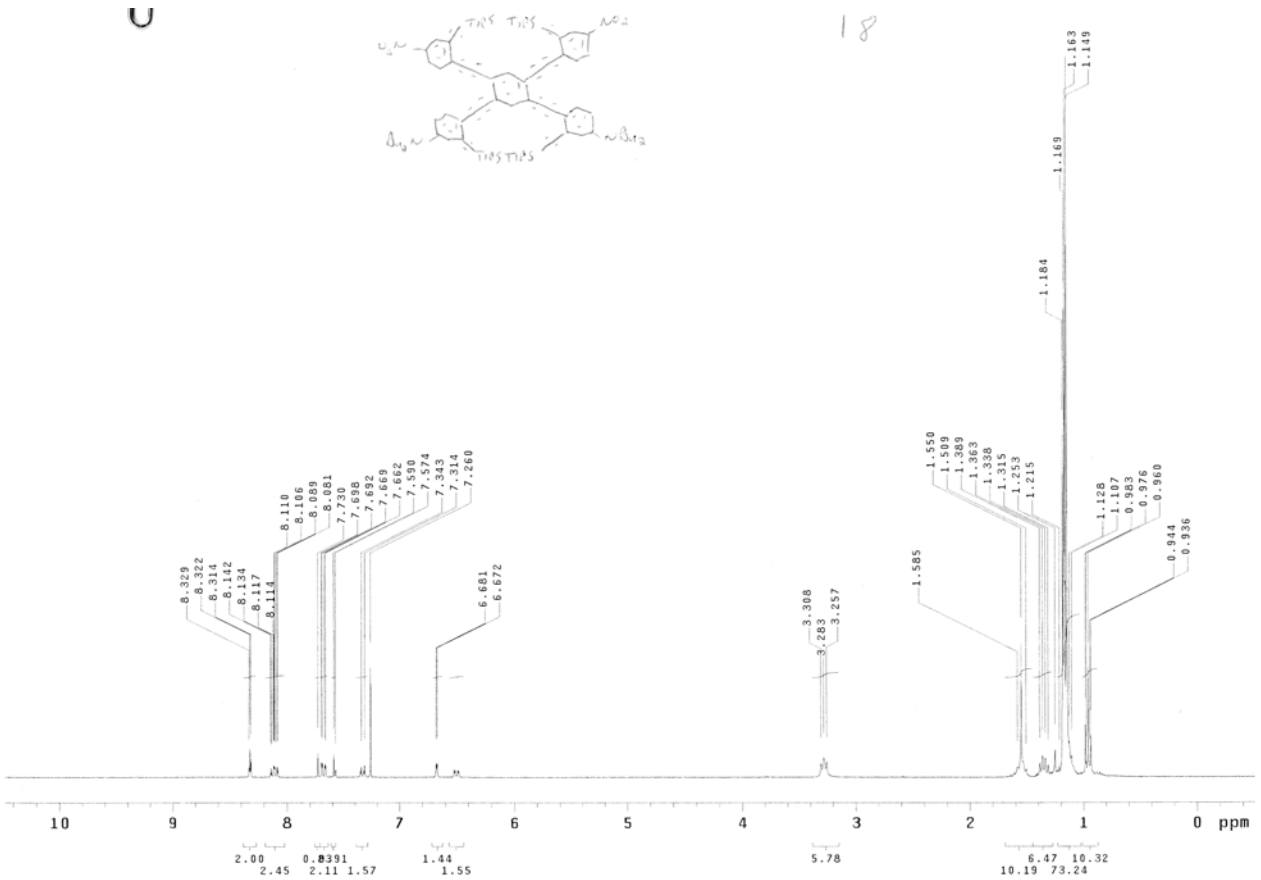


17, 1H-NMR, $CDCl_3$, 300 MHz

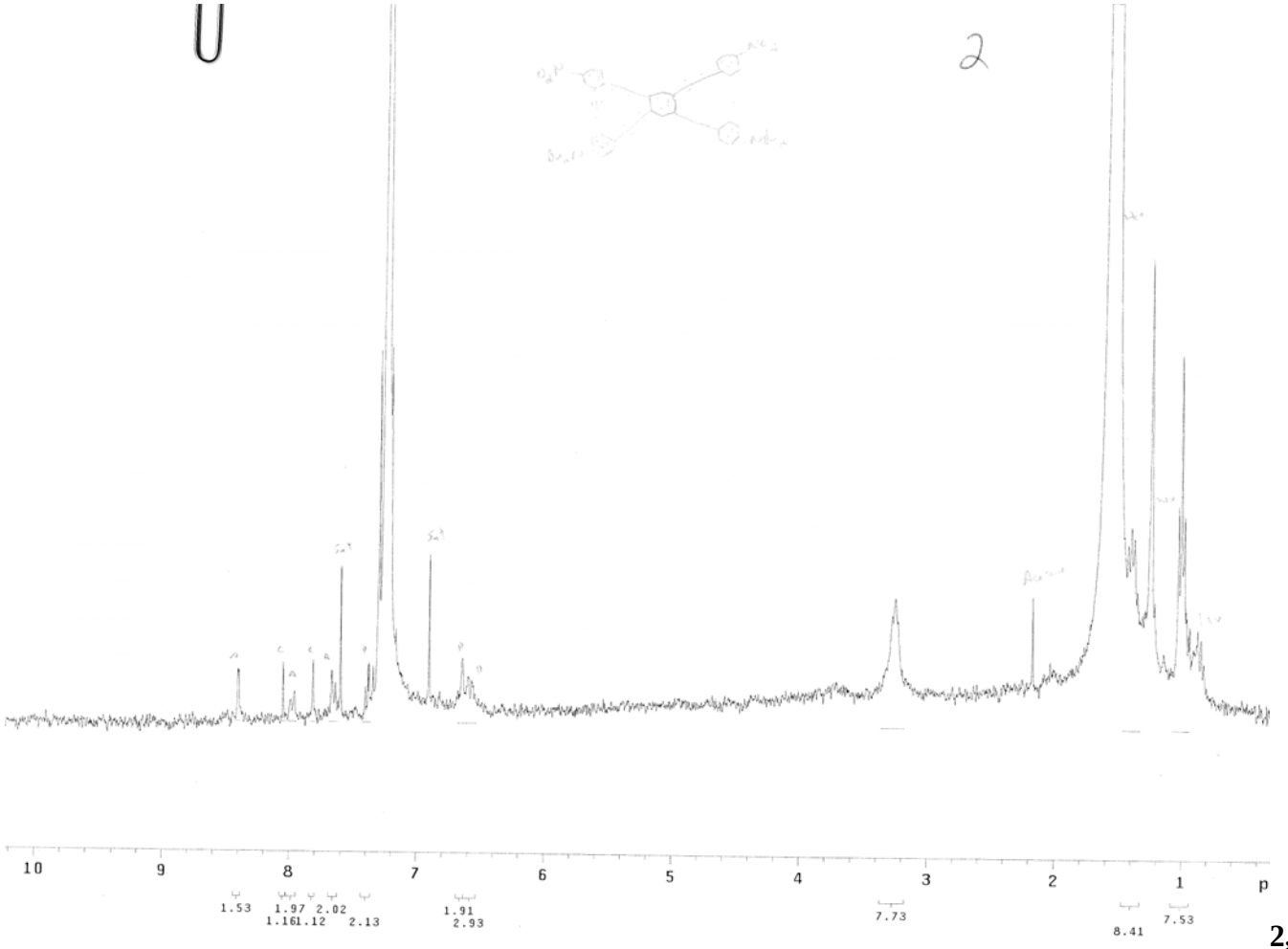


17, 13C-NMR, $CDCl_3$, 75 MHz

(phase inverted around 80 ppm due to instrument error)



18, 1H-NMR, $CDCl_3$, 300 MHz



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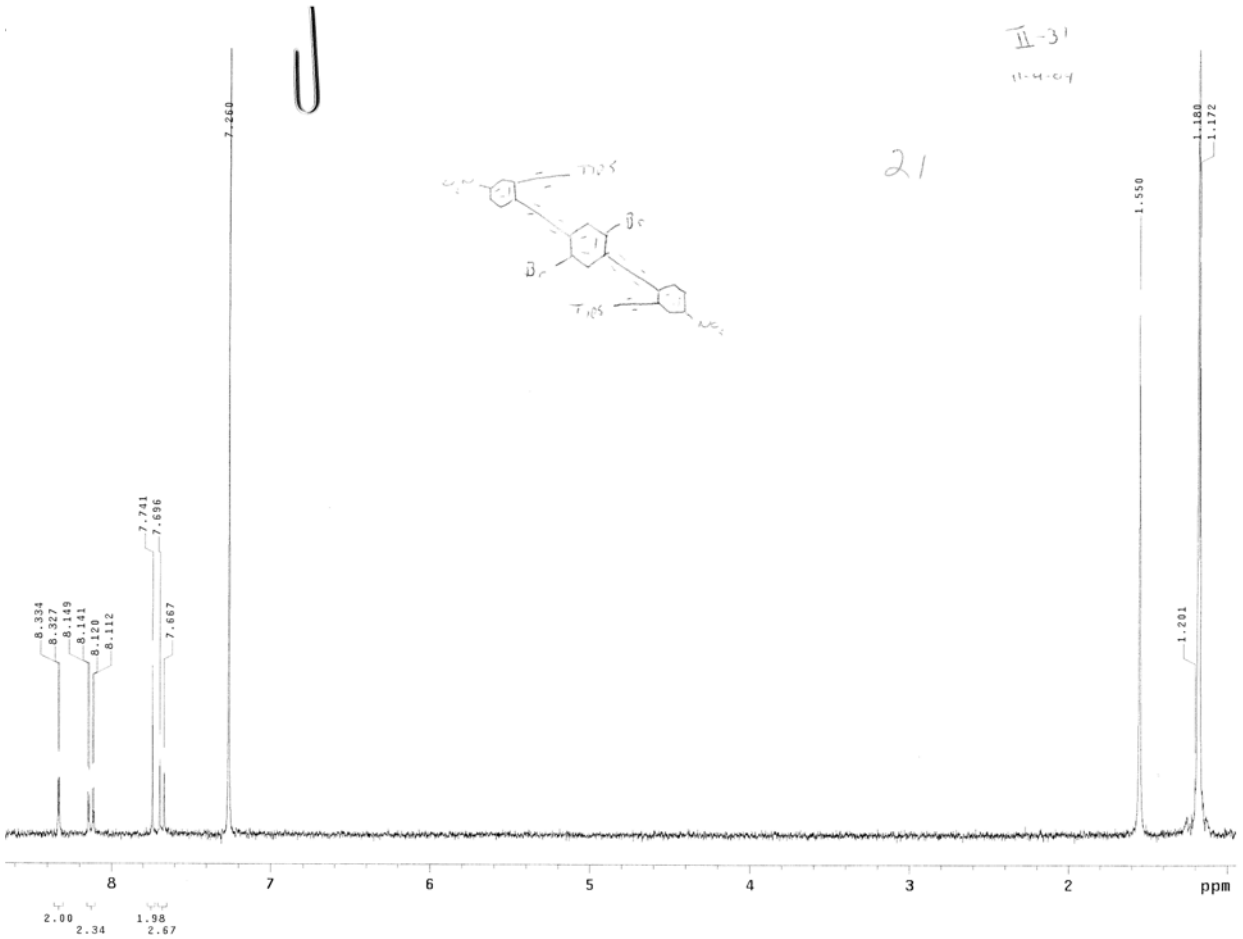
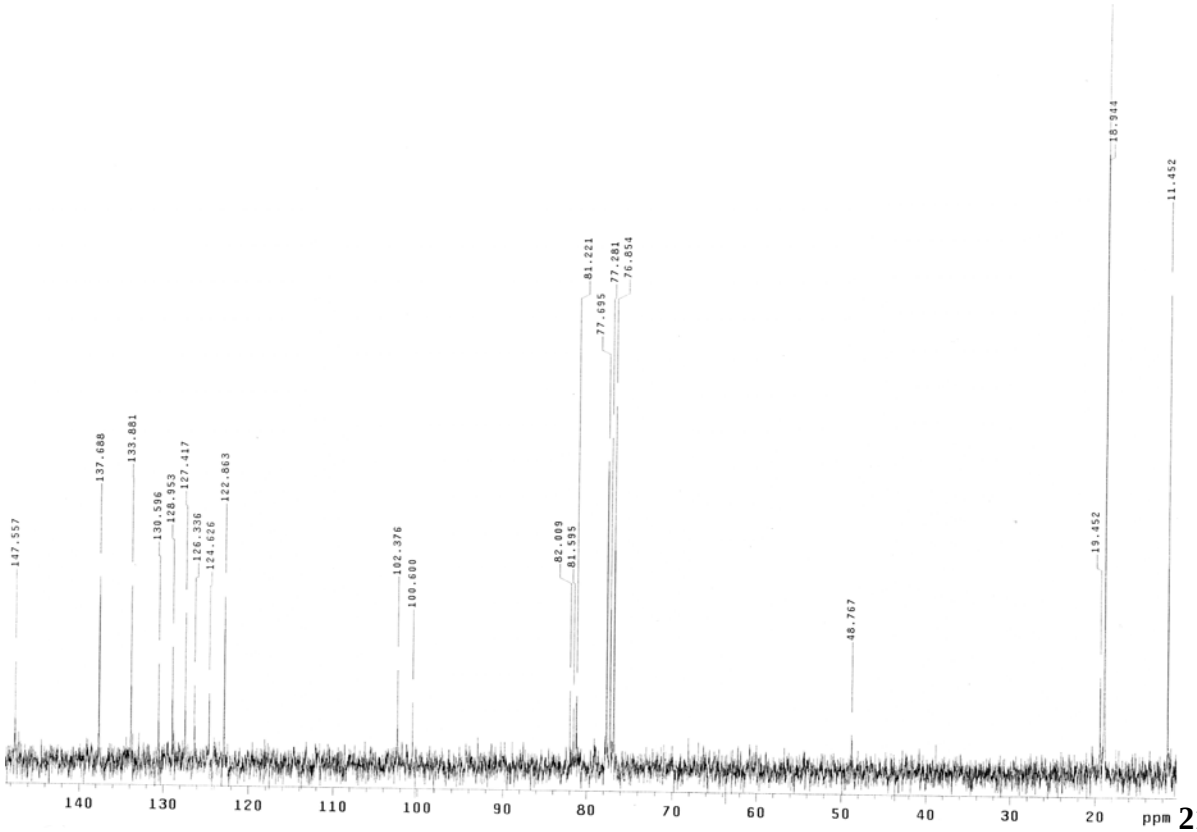
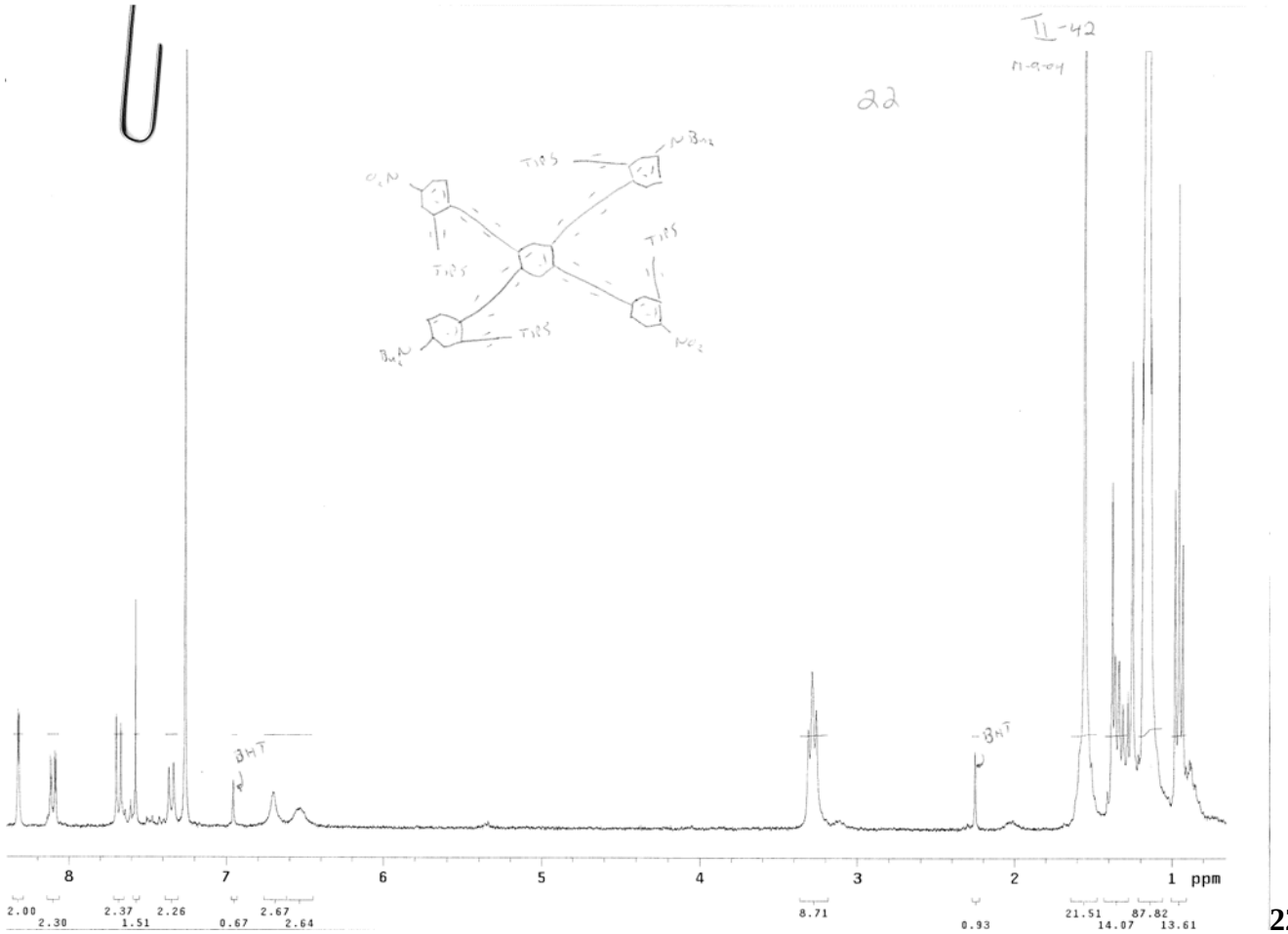


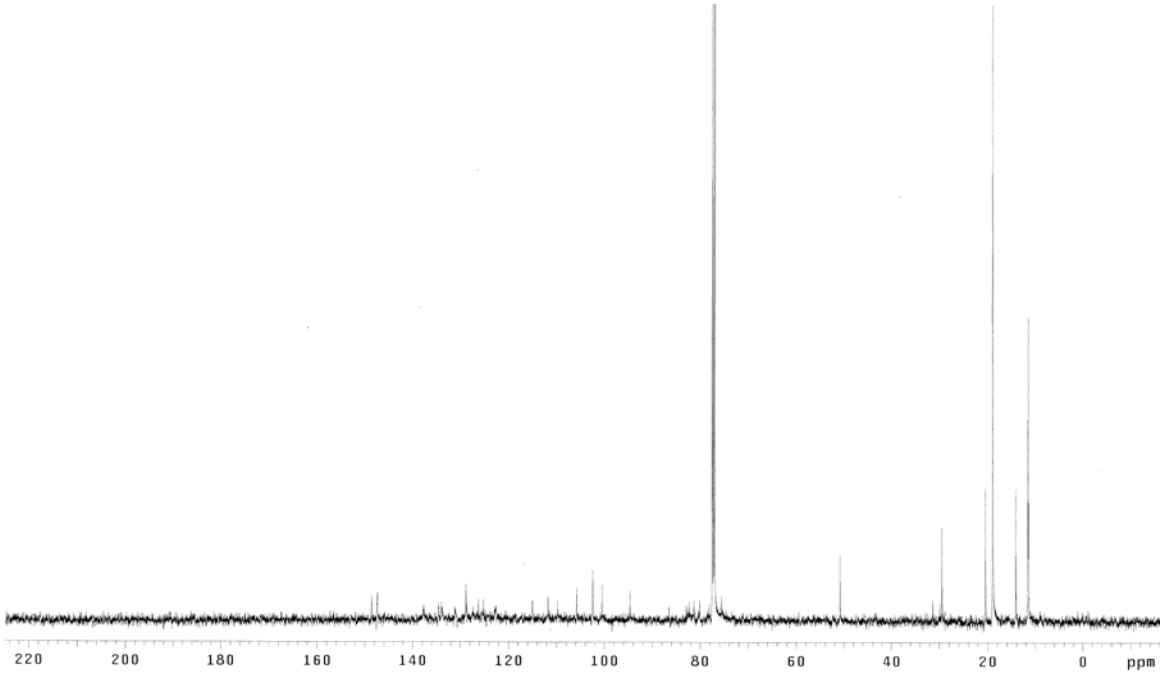
21, 1H-NMR, $CDCl_3$, 300 MHz



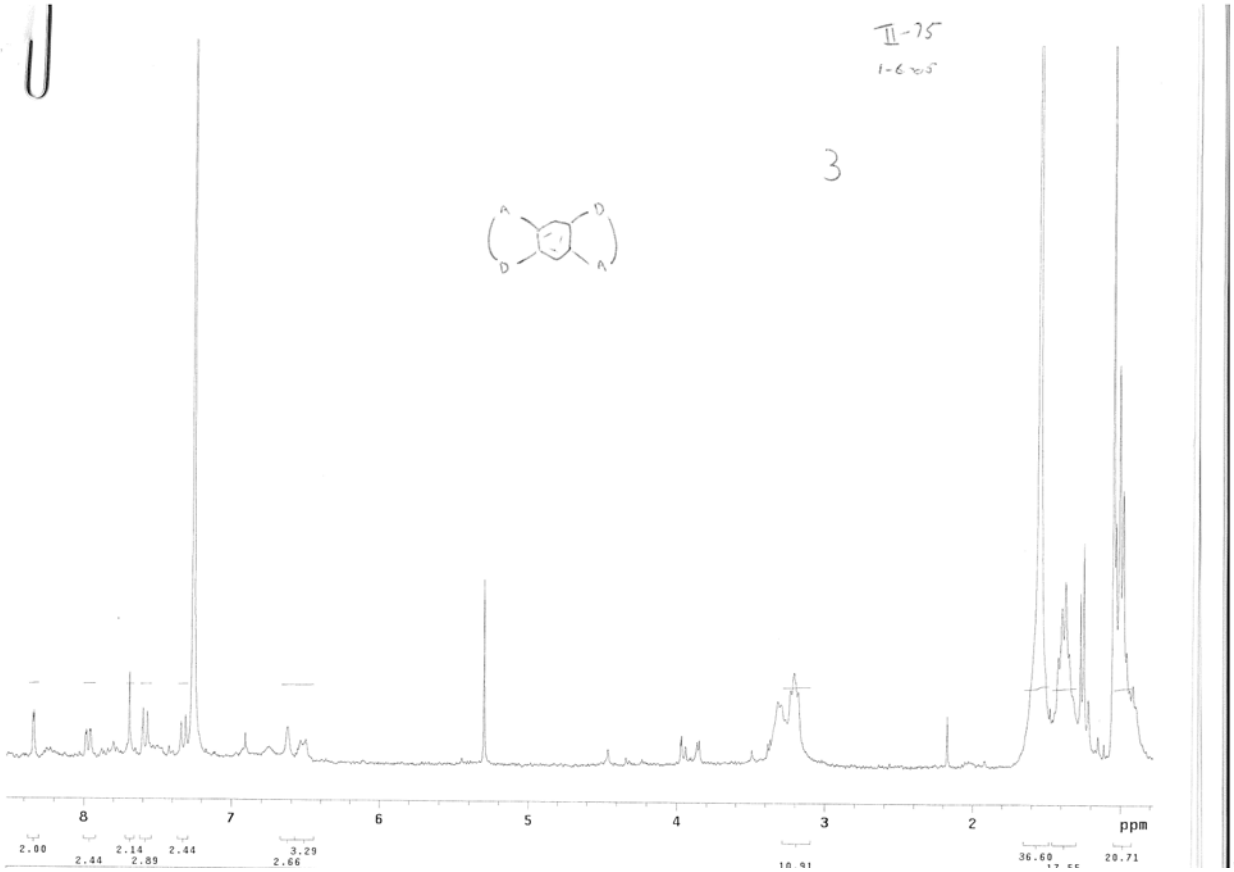
21, 13C-NMR, $CDCl_3$, 75 MHz



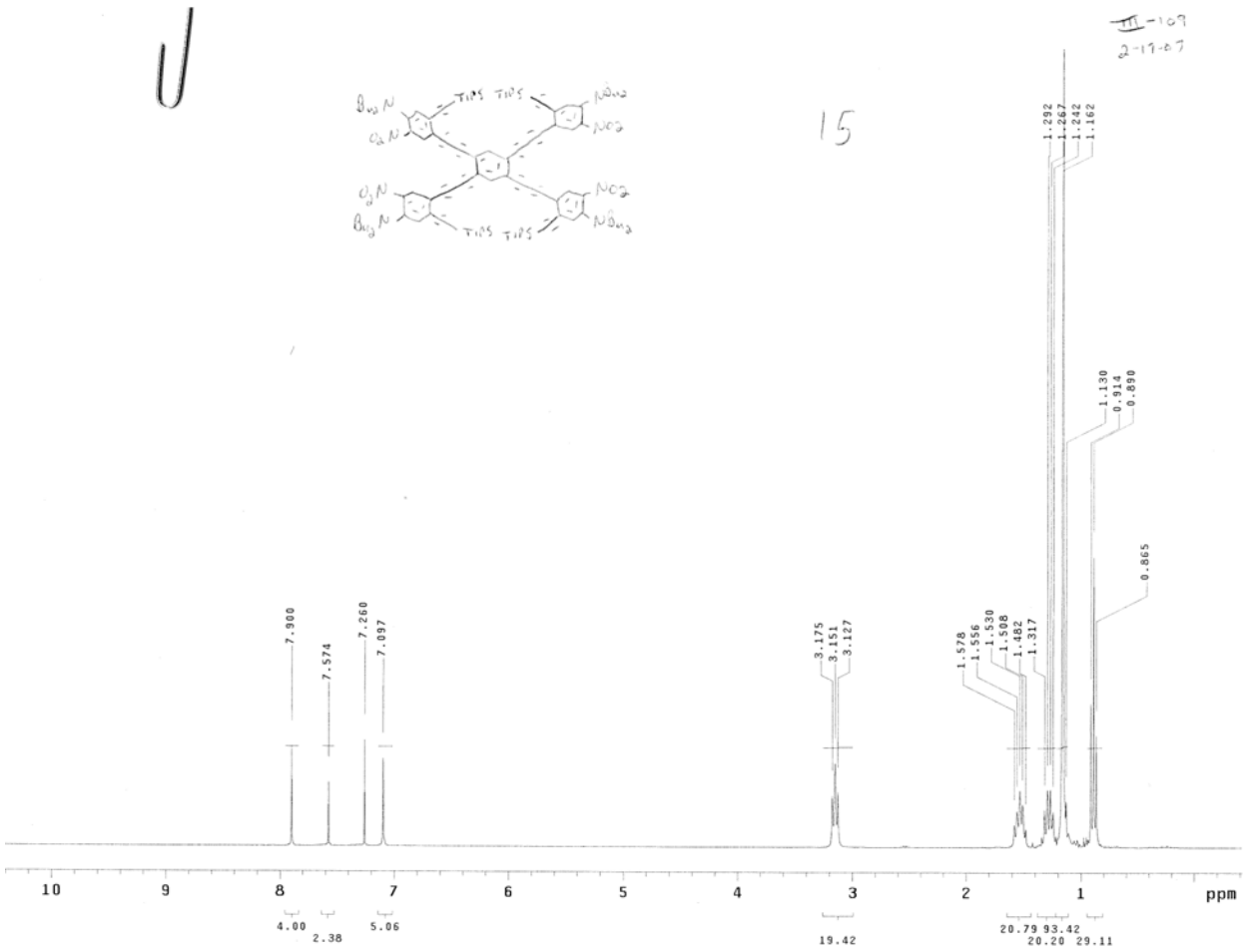
22, 1H-NMR, $CDCl_3$, 300 MHz



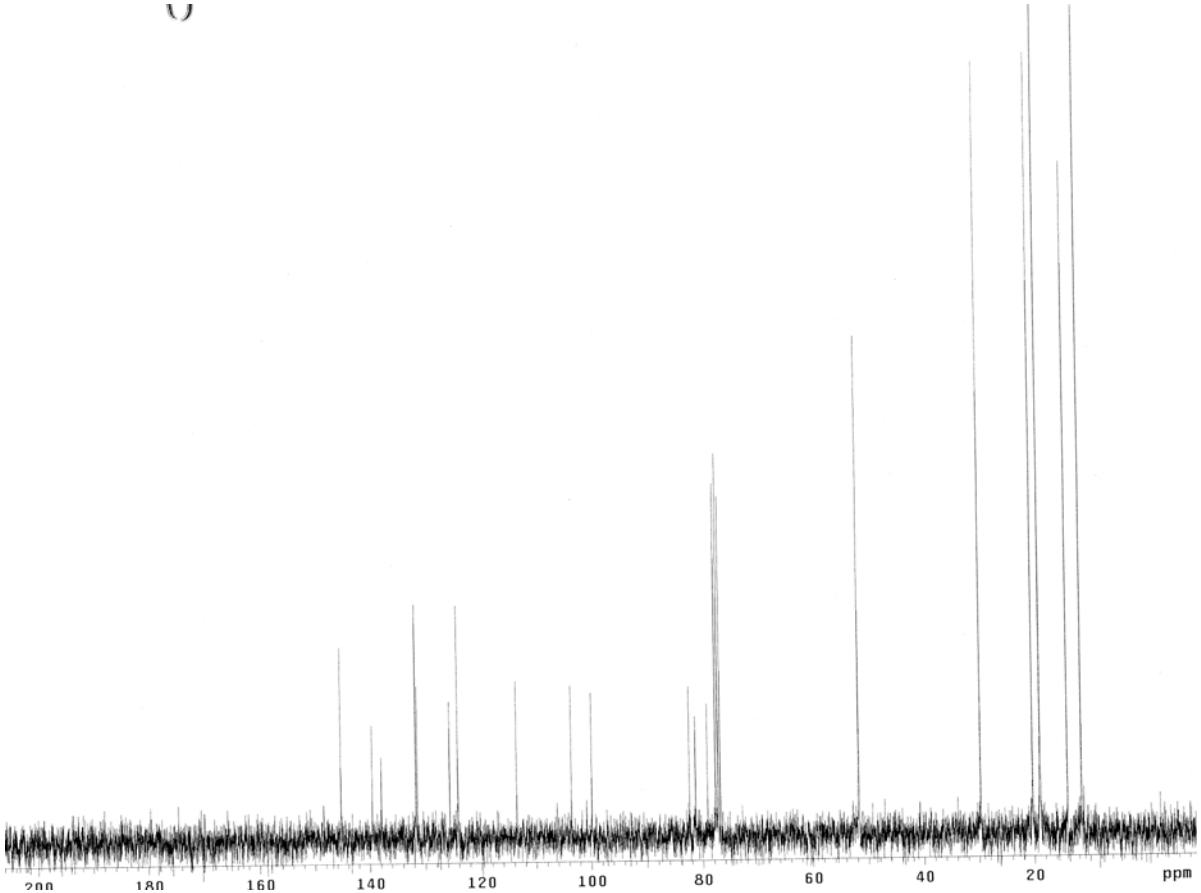
22, 13C-NMR, $CDCl_3$, 75 MHz



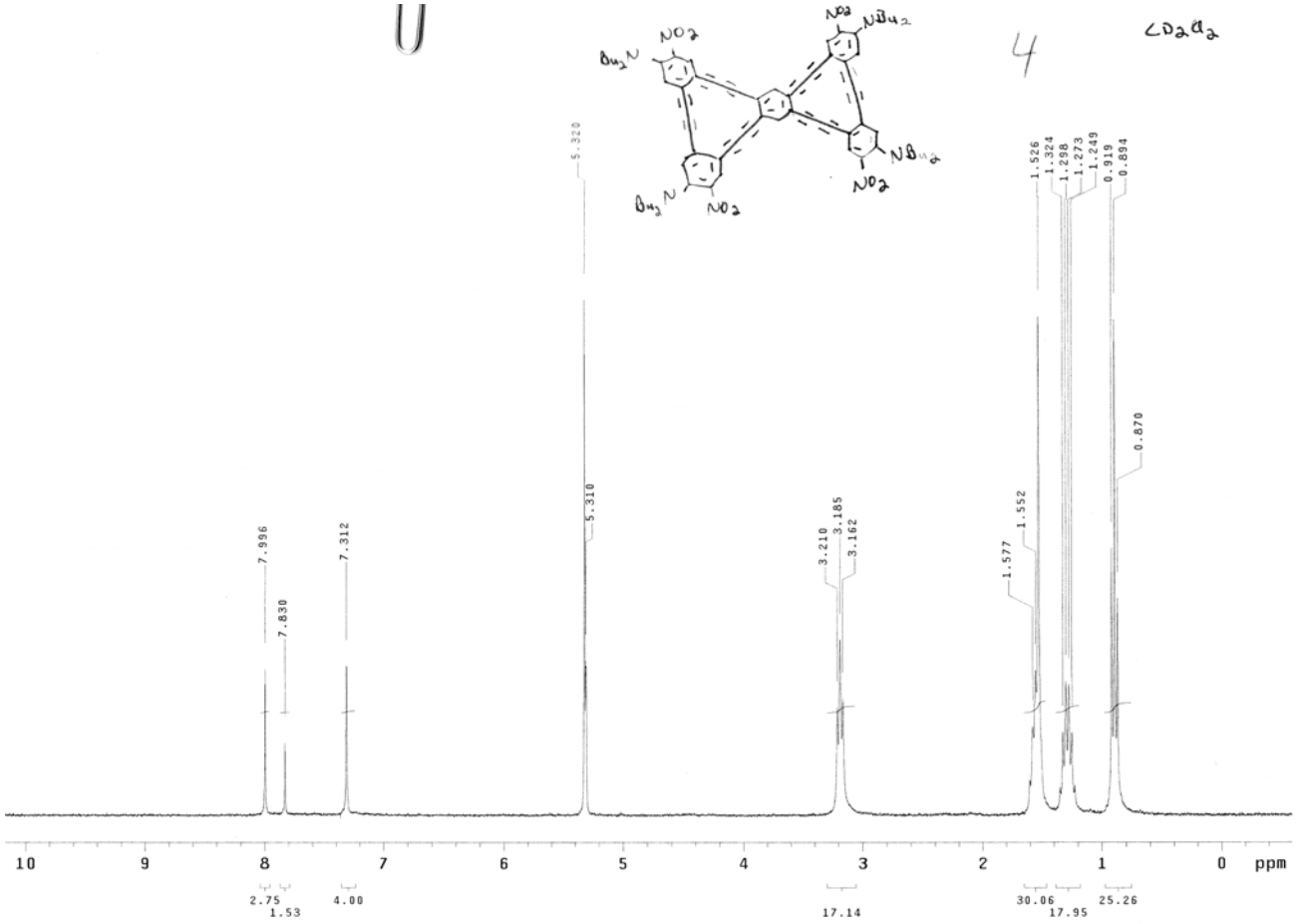
3, 1H-NMR, $CDCl_3$, 300 MHz



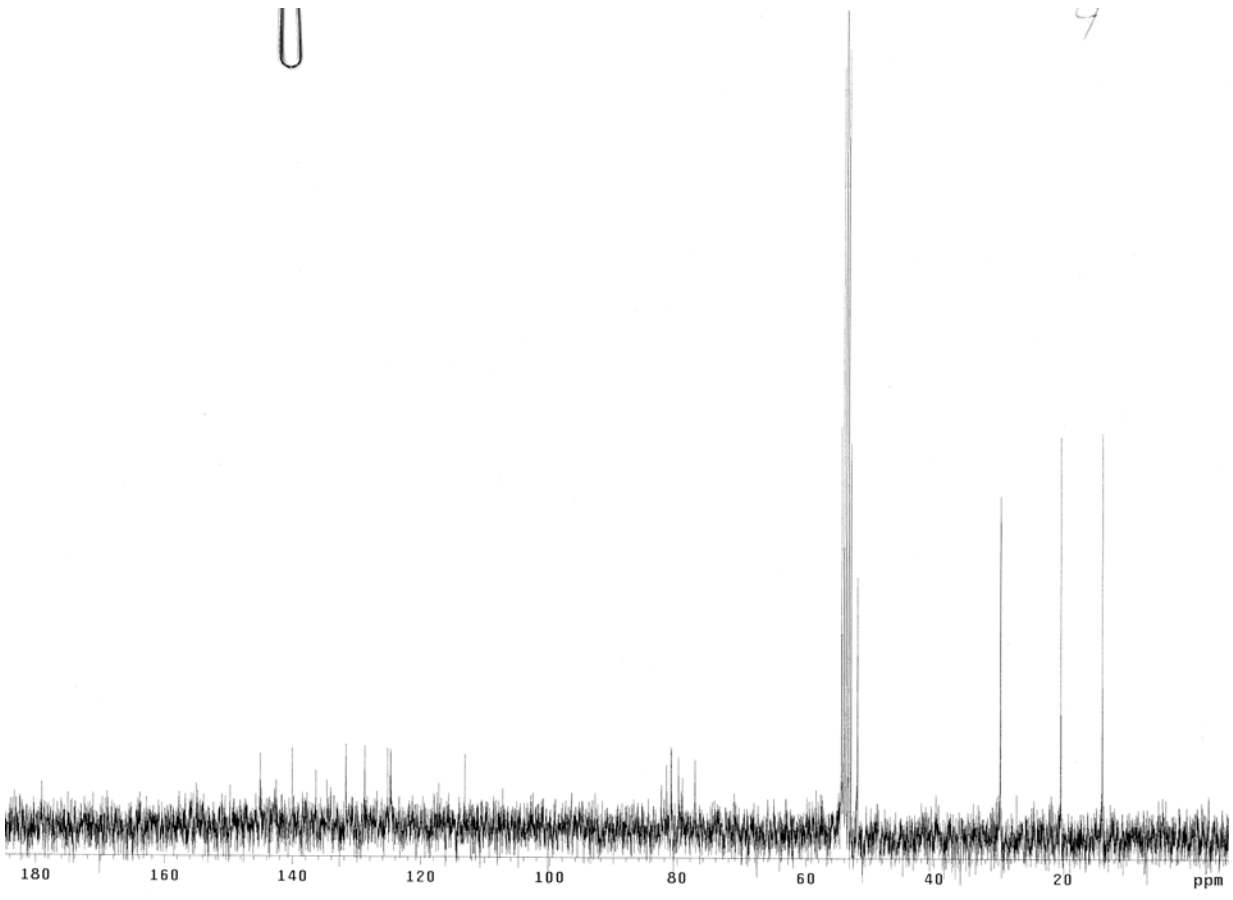
15, 1H-NMR, $CDCl_3$, 300 MHz



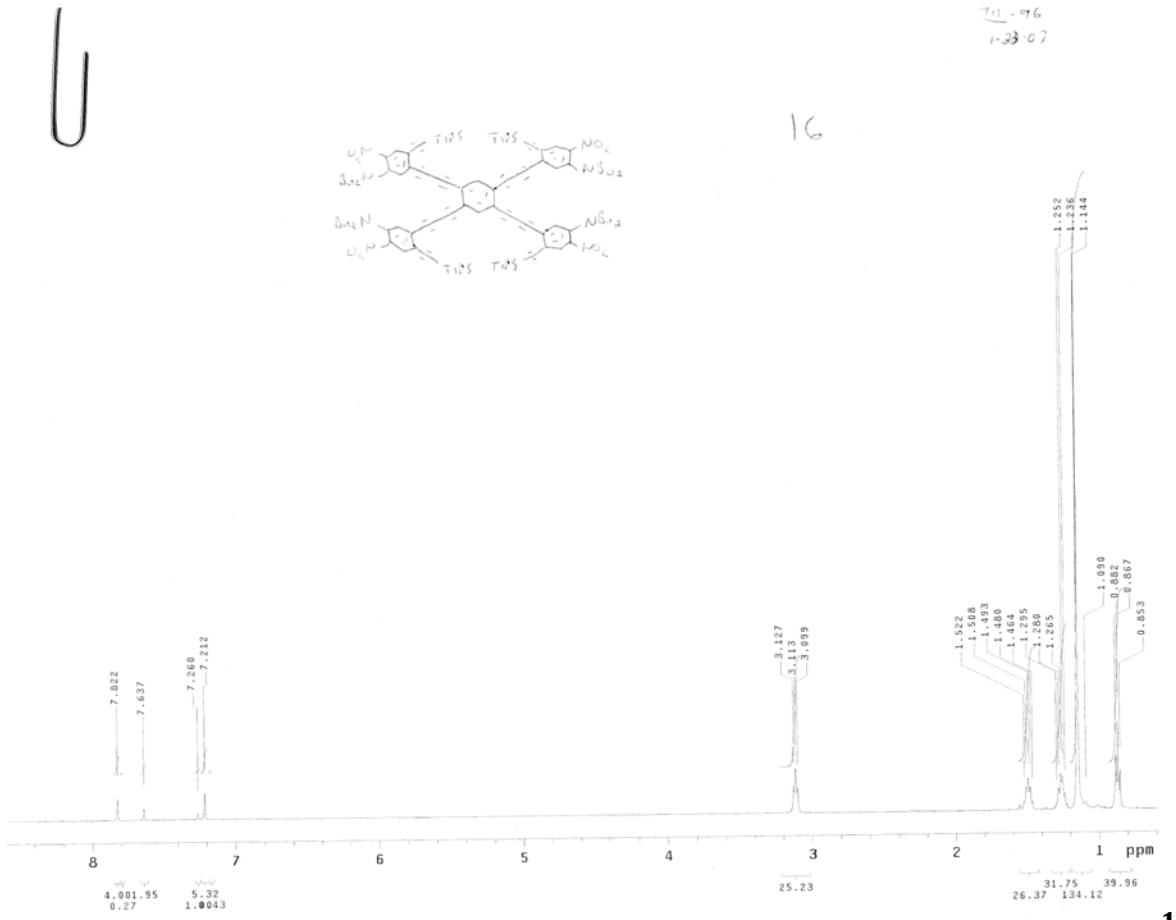
15, 13C-NMR, $CDCl_3$, 75 MHz



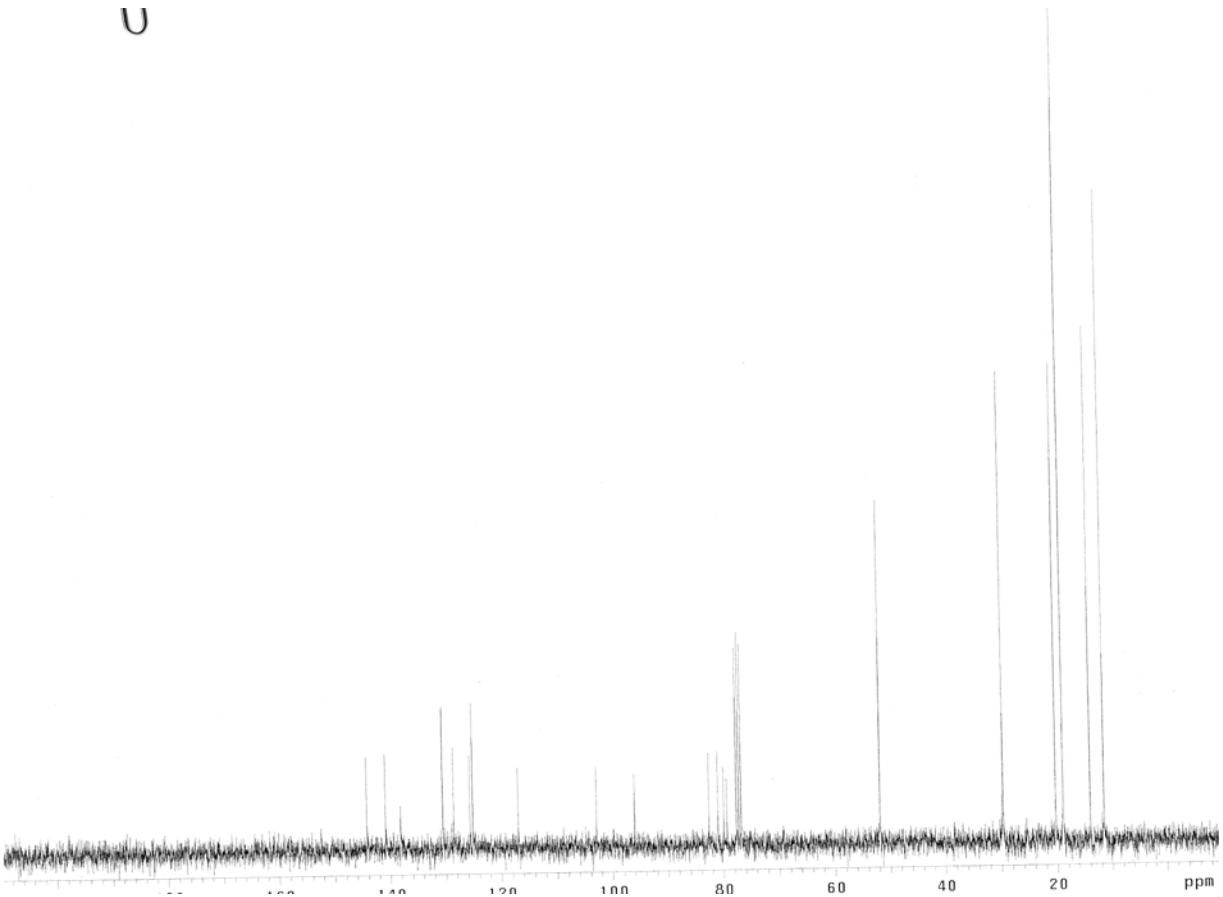
4, 1H-NMR, CD_2Cl_2, 300 MHz



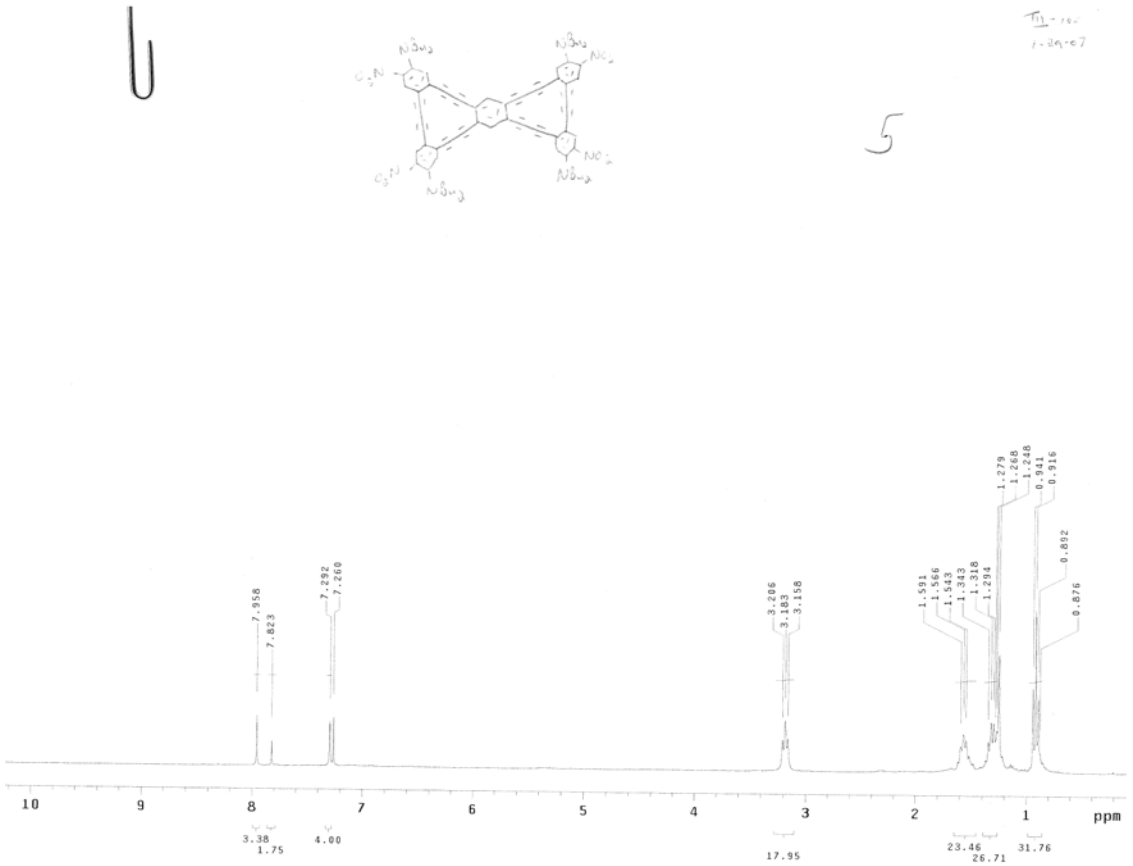
4, 13C-NMR, CD_2Cl_2, 75 MHz



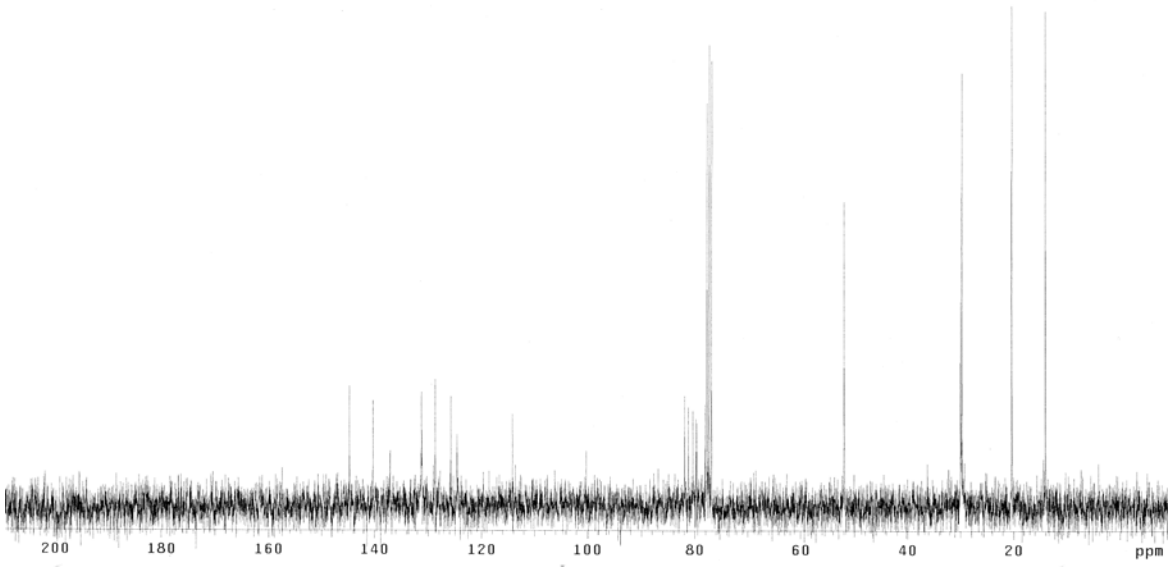
16, 1H-NMR, $CDCl_3$, 300 MHz



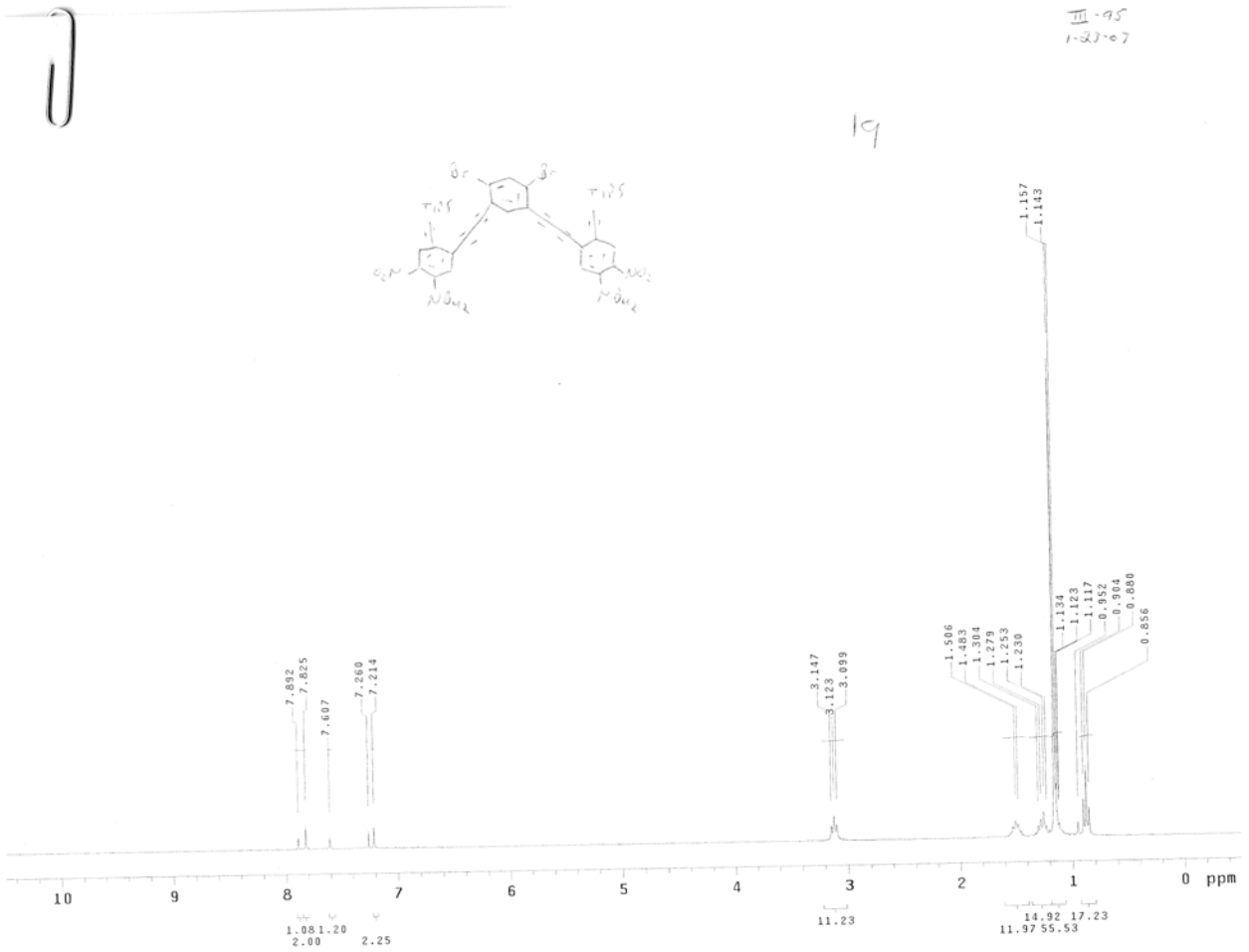
16, 13C-NMR, $CDCl_3$, 75 MHz



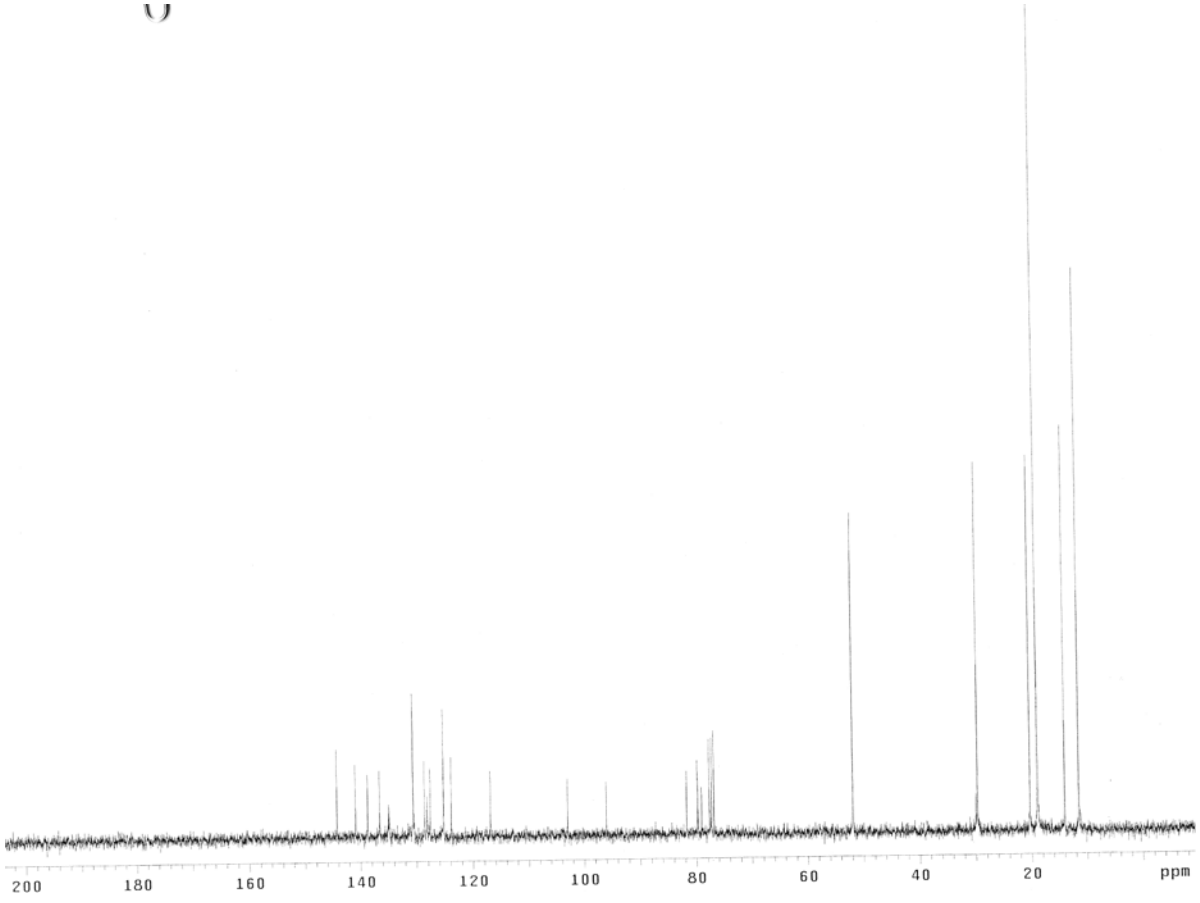
5, 1H-NMR, $CDCl_3$, 300 MHz



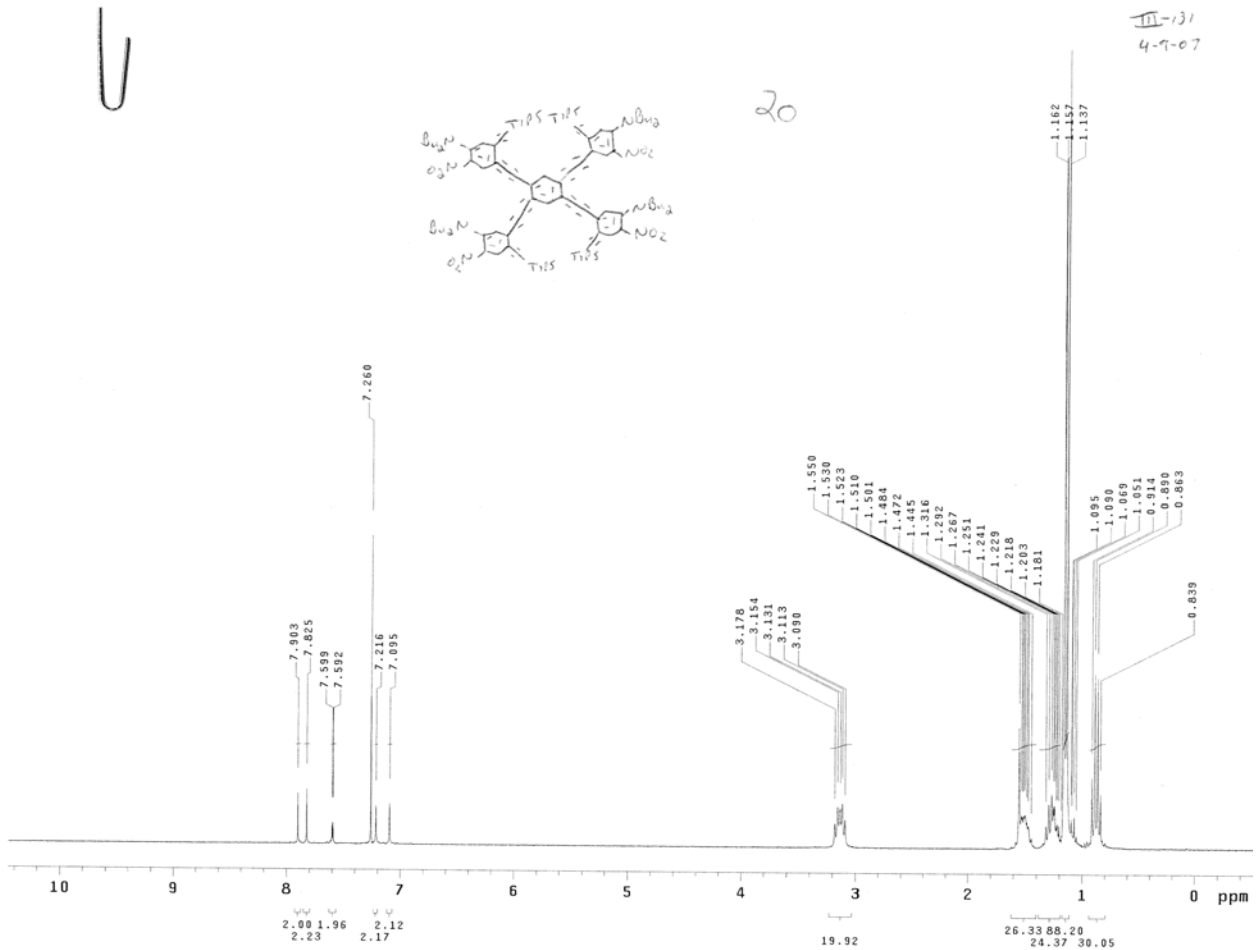
5, 13C-NMR, $CDCl_3$, 75 MHz



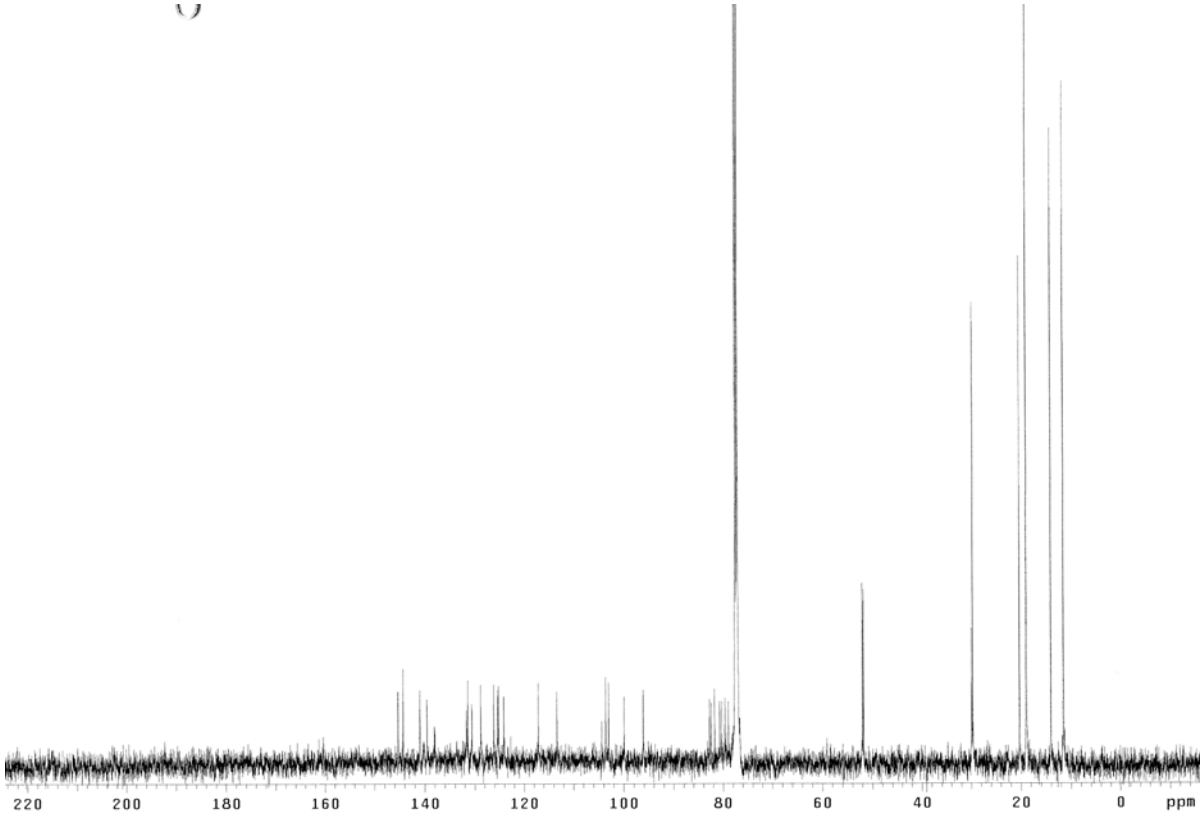
19, 1H-NMR, $CDCl_3$, 300 MHz



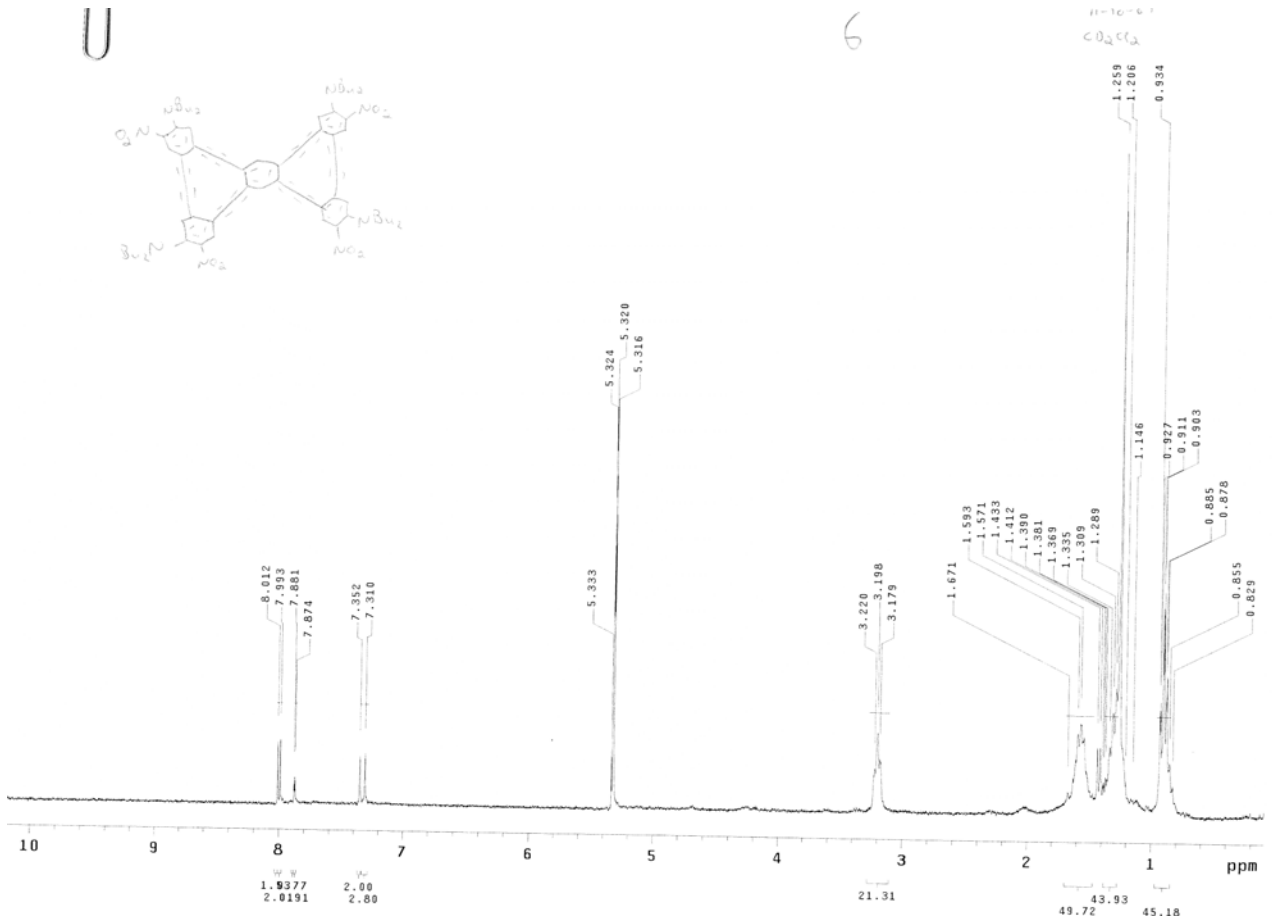
19, 13C-NMR, $CDCl_3$, 75 MHz



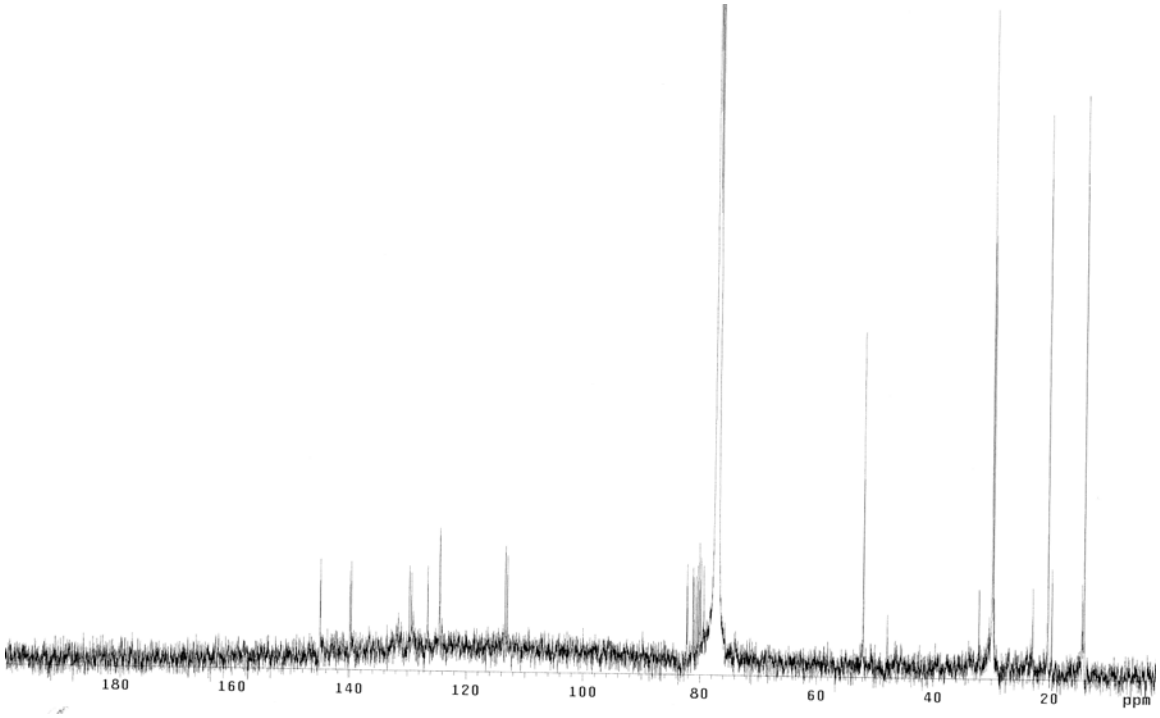
20 1H-NMR, $CDCl_3$, 300 MHz



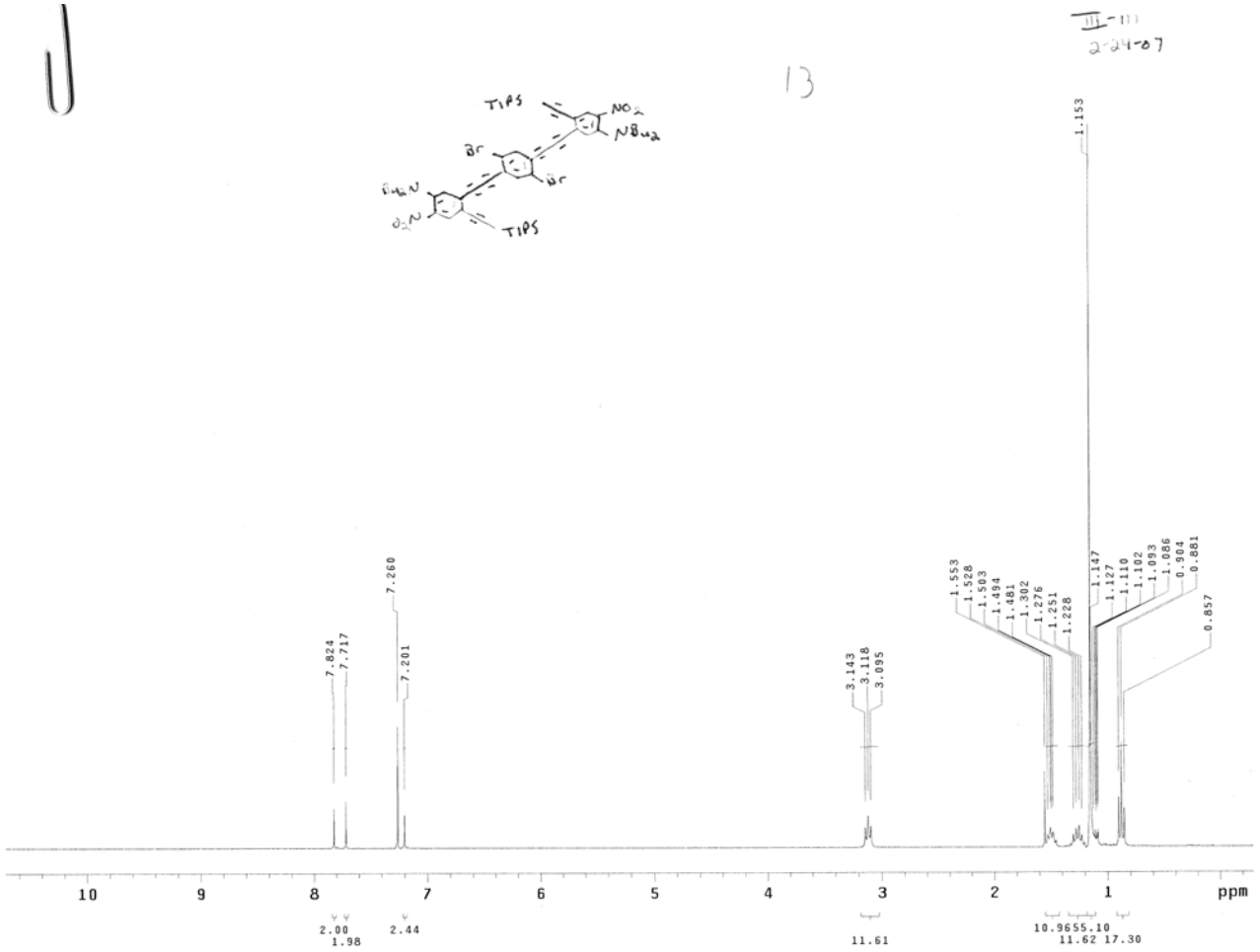
20, 13C-NMR, $CDCl_3$, 75 MHz



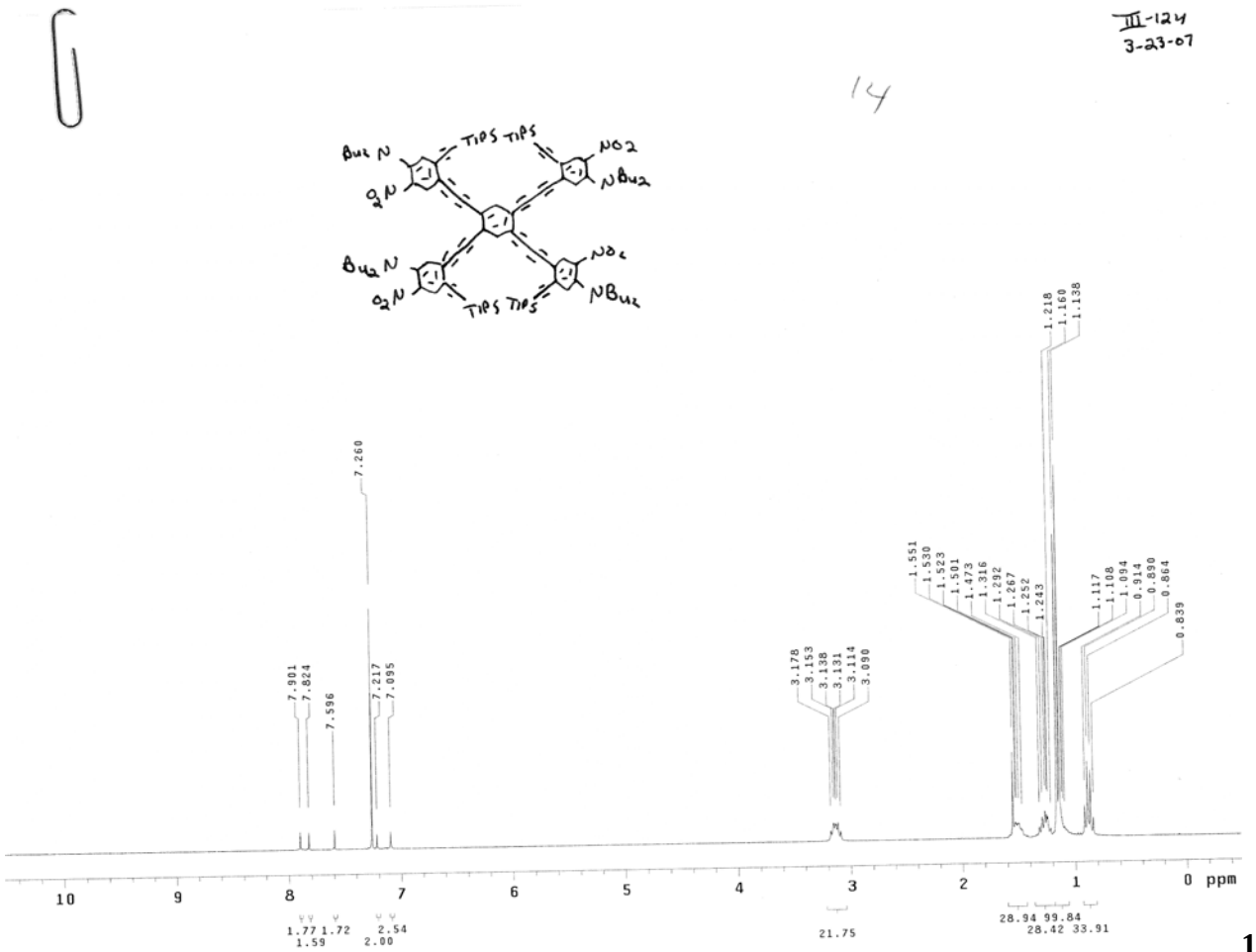
6, 1H-NMR, CD_2Cl_2, 300 MHz



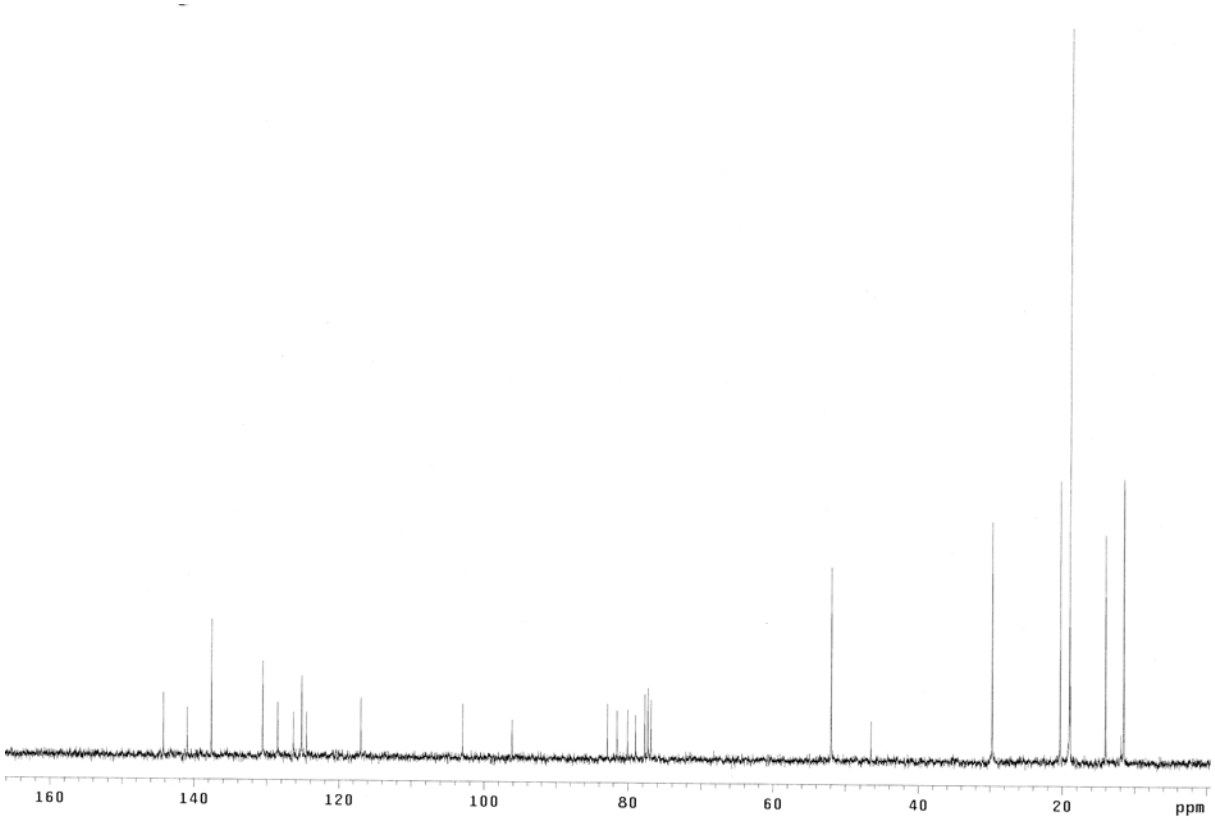
6, 13C-NMR, $CDCl_3$, 75 MHz



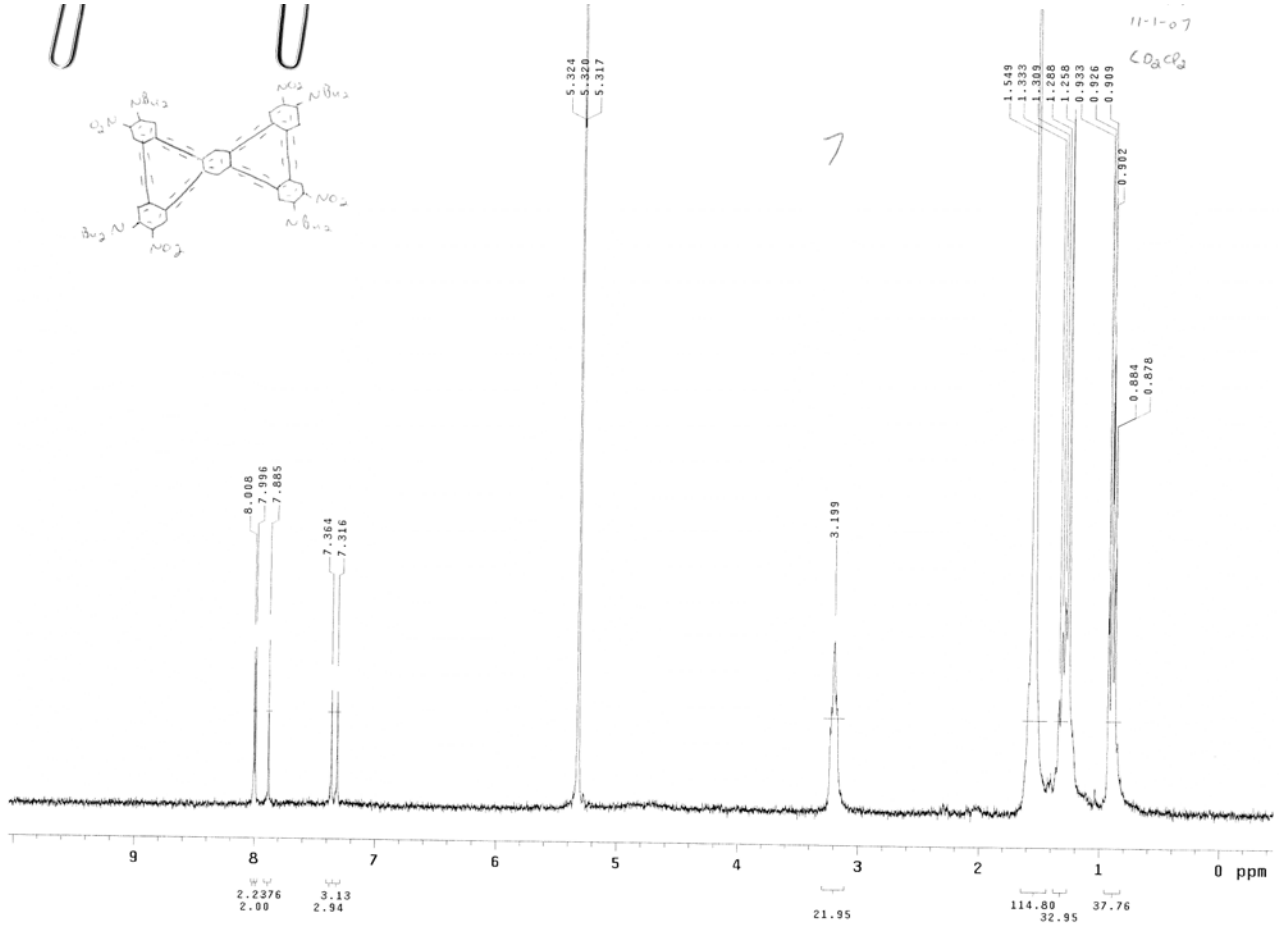
13, 1H-NMR, $CDCl_3$, 300 MHz



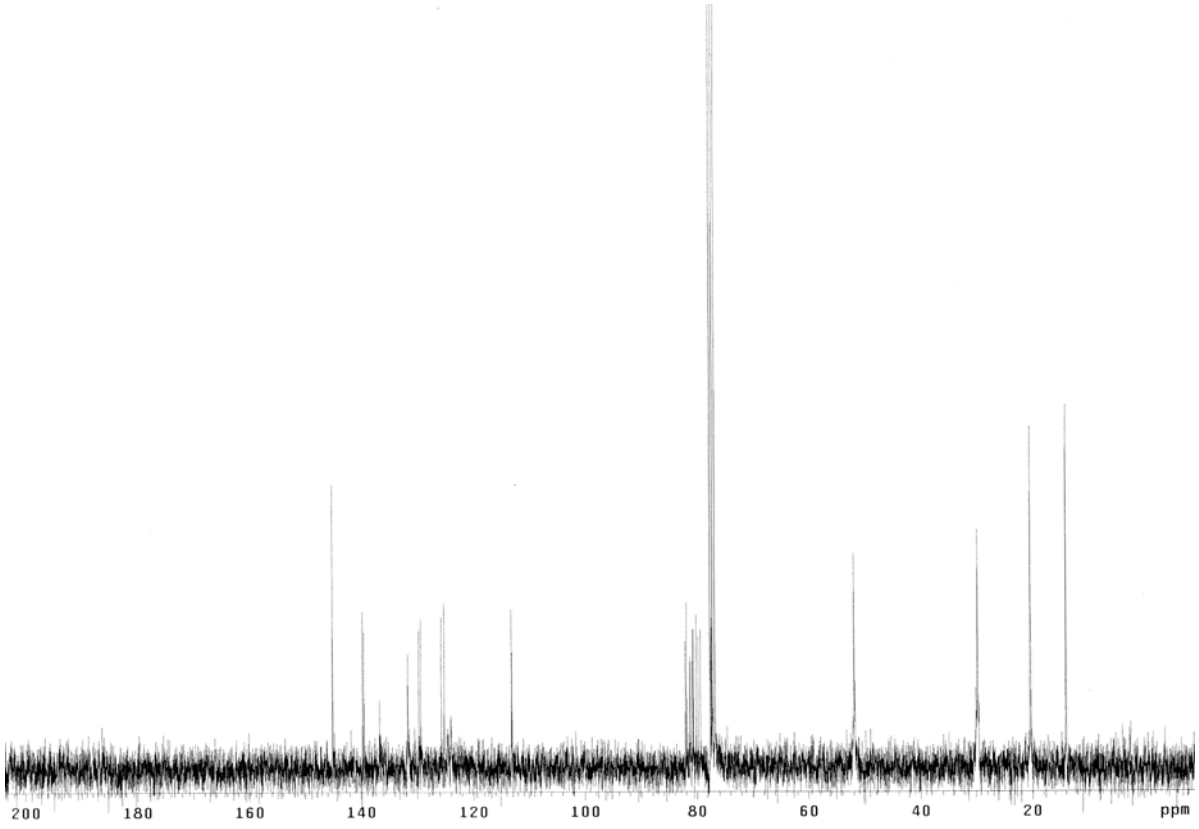
14, 1H-NMR, $CDCl_3$, 300 MHz



14, 1H-NMR, $CDCl_3$, 300 MHz



7, 1H-NMR, CD_2Cl_2, 300 MHz



7, 1H-NMR, $CDCl_3$, 300 MHz