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Buchwald ligand-assisted Suzuki cross-coupling of polychlorobenzenes

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General information. NMR spectra were recorded in $CDCl_3$ on spectrometers Bruker AC-200 (200 MHz for ^1H and 50 MHz for ^{13}C) or Bruker AM-300 (300 MHz for ^1H, 188 MHz for ^{19}F, and 75 MHz for ^{13}C). GC-MS experiments were performed at Agilent Technologies 85973 Network (electron impact, 70 eV) machine connected to Agilent Technologies 6890 gas chromatograph, capillary column HP-5MS 30000×0.25 mm, injector and FID temperatures 280280 °C, temperature program 60→300 °C, 10 deg min^{-1}, then 5 min at 300 °C, helium as the carrier gas, 3 ml min^{-1}. During the analysis, ionic current and FID signal were registered in parallel. The peak areas were corrected, namely, divided by the number of carbon atoms in a molecule (*S*/*n*), and these values were used to calculate molar fractions of the components.

1,2,4,5-Tetrachlorobenzene **1a** (Acros), 1,2,3,4-tetrachlorobenzene **1b**, trichlorobenzenes **4a-c**, dichlorobenzenes **4d-f** (Lancaster) and phenylboronic acid (Aldrich) were used as purchased. Potassium phosphate (Aldrich) was calcined in air and kept in a closed vessel; prior to each experiment the required portion was finely powdered. Ligands **L1-L4** were supplied by DalChem Co.

General procedure for the cross-coupling was performed in general according to the Buchwald protocol [S1]**.** A 10 ml Schlenk tube equipped with a stirring bar was charged with $Pd(OAc)_2$ (7 mg, 0.03 mmol), ligand **L1-L4** (0.06 mmol), PCA (0.5 mmol), $PhB(OH)_2$ (66 mg, 0.55 mmol) and K_3PO_4 (339 mg, 1.6 mmol), and then capped with a rubber septum. Air was removed by repeated evacuation and filling with argon. Toluene (1 ml) was injected. The reaction was processed at 85-90 °C for ca. 7 hours. A heterogeneous aliquot was mixed with more toluene (~ 1:10), filtered through a short pad of silica, and the filtrate was analyzed by GC-MS.

For exhaustive arylation of tri- and tetrachlorobenzenes (0.25 mmol), $Pd(OAc)_2$ (4 mg, 0.018 mmol), ligand **L2** (14 mg, 0.036 mmol), $ArB(OH)_2$ (1.65 mmol) and K_3PO_4 (492 mg, 2.32 mmol) were applied. In attempted full phenylation of C_6Cl_6 (71 mg, 0.25 mmol), amount of $PhB(OH)_2$ was raised to 261 mg (2.15 mmol) and that of K_3PO_4 to 636 mg (3.00 mmol).

When the reaction was not clean, identification of the products was performed by GC-MS. Masses for molecular ions are presented for isotope ^{35}Cl, the isotope clusters were in agreement with the number of chlorine atoms in molecule. Mass values for the observed products are as follows: PhC_6H_4Cl (188); $PhC_6H_3Cl_2$ (222); $PhC_6H_2Cl_3$ (256); PhC_6HCl_4 (290); PhC_6Cl_5 (324); $Ph_2C_6H_4$ (230); $Ph_2C_6H_3Cl$ (264); $Ph_2C_6H_2Cl_2$ (298); $Ph_2C_6HCl_3$ (332); $Ph_2C_6Cl_4$ (366); $Ph_3C_6H_3$ (306); $Ph_3C_6H_2Cl$ (340); $Ph_3C_6HCl_2$ (374); $Ph_3C_6Cl_3$ (408); $Ph_4C_6H_2$ (382); Ph_4C_6HCl (416); $Ph_4C_6Cl_2$ (450); Ph_5C_6H (458); Ph_5C_6Cl (492). When the comparison of retention times with those of authentic samples was not

unambiguous, the mixed probes were also analyzed. Biphenyl and isomeric terphenyls **5d-f** are the common reagents. Triphenylbenzenes **5a-c** and tetraphenylbenzenes **3a,b** were obtained in this work in preparative experiments and were reliably characterized (see below). 2,4,5-Trichlorobiphenyl **2** was obtained and characterized in our previous work [S2].

For preparative isolation of the products (in cases of smooth reactions), the reaction mixture was shaken up with more toluene (~ 5 ml), silica gel (1-2 ml) was added, and this slurry was carefully concentrated on a rotary evaporator equipped with an anti-burst trap. The friable residue was loaded on the top of a chromatography column packed with silica gel. In cases of hydrocarbon products and fluoro derivative **3"a**, elution was performed with light petroleum and then with 10% CH_2Cl_2 in light petroleum; for TLC control (Kieselgel 60 F_{254} plates, Merck), 1:1 CH_2Cl_2–hexane mixture was used, UV visualization. In case of tetramethoxy compound **3'a**, the final eluent was CH_2Cl_2. The proper fractions with the target products were evaporated and, if required, recrystallized from hexane.

2,4,5-Trichlorobiphenyl (2), see Ref. [S2], colourless crystals, mp 73-74 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 7.32-7.50 (m, 6 H), 7.60 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ, ppm): 128.28 (C(2')H and C(4')H), 129.16 (C(3')H), 131.05 (C(5)Cl), 131.16 (C(6)H), 131.33 and 131.95 (C(2)Cl and C(4)Cl), 132.32 (C(3)H), 137.24 (C(1')), 140.38 (C(1)). Mass spectrum, (*m*/*z*): M^+ 256.

1,2,4,5-Tetraphenylbenzene 3a, colourless crystals, mp 258-259 °C (lit. [S3] mp 263-265 °C). ^{13}C NMR ($CDCl_3$, 50 MHz, δ, ppm): 126.6 (4CH), 128.0 (8CH), 129.9 (8CH), 133.0 (2CH), 139.6 (4C), 140.9 (4C). Mass spectrum (*m/z*): M^+ 382. Spectra are close to the literature [S4,S5].

1,2,4,5-Tetrakis(4-methoxyphenyl)benzene 3'a, colourless crystals, mp 244-245 °C (lit. [S5] mp 244-246 °C). Found %: C 81.24, H 6.18; $C_{34}H_{30}O_4$. Calcd. %: C 81.25, H 6.02. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm, *J*/Hz): 3.81 (s, 12H), 6.80 (d, 8H, *J* = 8.8), 7.16 (d, 8H, *J* = 8.8), 7.45 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ, ppm): 55.5 ($4CH_3$), 113.4 (8CH), 130.9 (8CH), 132.8 (2CH), 133.6 (4C), 138.7 (4C), 158.3 (4C). Mass spectrum (*m/z*): M^+ 502. Spectra are close to the literature [S5].

1,2,4,5-Tetrakis(2,4-difluorophenyl)benzene 3"a, colourless crystals, mp 183-184 °C. Found %: C 68.40, H 2.64; $C_{30}H_{14}F_8$. Calcd. %: C 68.45, H 2.68. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm, *J*/Hz): 6.74 (td, 4H, $^3J_{HF}$ = 9.6, $^4J_{HH}$ = 2.2), 6.81 (td, 4H, $^3J_{HH}$ = $^3J_{HF}$ = 8.8, $^4J_{HH}$ = 2.9), 7.18 (q, 4H, $^3J_{HH}$ = $^4J_{HF}$ = 7.8), 7.44 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ, ppm, J_{CF}/Hz): 103.9 (t, 4CH, J_{CF} = 26.2), 111.2 (four lines, 4CH, Δν = 24.7 Hz), 123.9 (four lines, 4C, Δν = 20.3 Hz), 132.3 (t, 4CH, J_{CF} = 7.3), 133.1 (s, 2CH), 134.8 (s, 4C), 159.5 (dd, 4CF, J_{CF} = 250.0, 13.1), 162.5 (dd, 4CF, J_{CF} = 248.5, 11.6). ^{19}F NMR ($CDCl_3$, 188 MHz, δ, ppm): -110.4 (the signals coincide). Mass spectrum (*m/z*): M^+ 526.

1,2,3,4-Tetraphenylbenzene 3b, colourless crystals, mp 194-195 °C (lit. [S6] mp 194-195 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm, *J*/Hz): 6.83 (m, 4H), 6.94 (m, 6H), 7.15 (m, 10H), 7.53 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 125.6 (2CH), 126.1 (2CH), 126.9 (4CH), 127.5 (4CH), 129.3 (2CH), 129.9 (4CH), 131.5 (4CH), 139.9 (2C), 140.3 (2C), 140.9 (2C), 141.8 (2C). Mass spectrum (*m/z*): M^+ 382. Spectra are close to the literature [S7].

1,2,3-Triphenylbenzene 5a, colourless crystals, mp 163-164 °C (lit. [S8] mp 160-161 °C). ^{1}H NMR ($CDCl_3$, 200 MHz, δ, ppm, *J*/Hz): 6.86 (m, 2H), 7.00 (m, 3H), 7.05-7.23 (m, 10H), 7.48 (m, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz, δ, ppm): 125.8 (CH), 126.1 (2CH), 127.2 (2CH), 127.3 (CH), 127.5 (4CH), 129.6 (2CH), 129.9 (4CH), 131.6 (2CH), 139.1 (C), 139.5 (C), 141.9 (2C+2C). Mass spectrum (*m/z*): M^+ 306. Spectra are close to the literature [S5].

1,2,4-Triphenylbenzene 5b, colourless crystals, mp 100-102 °C (lit. [S9] mp 99-100 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm, *J*/Hz): 7.25 (m, 10H), 7.39 (m, 1H), 7.49 (m, 3H), 7.70 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 126.1 (CH), 126.5 (CH), 126.6 (CH), 127.1 (2CH), 127.1 (CH), 127.9 (4CH), 128.8 (2CH), 129.4 (CH), 129.9 (4CH), 131.1 (CH), 139.6 (C), 140.4 (C), 140.6 (C), 141.0 (C), 141.1 (C), 141.5 (C). Mass spectrum (*m/z*): M^+ 306. Spectra are close to the literature [S5].

1,3,5-Triphenylbenzene 5c, colourless crystals, mp 176-178 °C (lit. [S10] mp 176.5 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm, *J*/Hz): 7.42 (m, 3H), 7.50 (m, 6H), 7.73 (m, 6H), 7.82 (c, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz, δ, ppm): 125.2 (3CH), 127.3 (6CH), 127.5 (3CH), 128.8 (6CH), 141.2 (3C), 142.4 (3C). Mass spectrum (*m/z*): M^+ 306. Spectra are close to the literature [S5].

References

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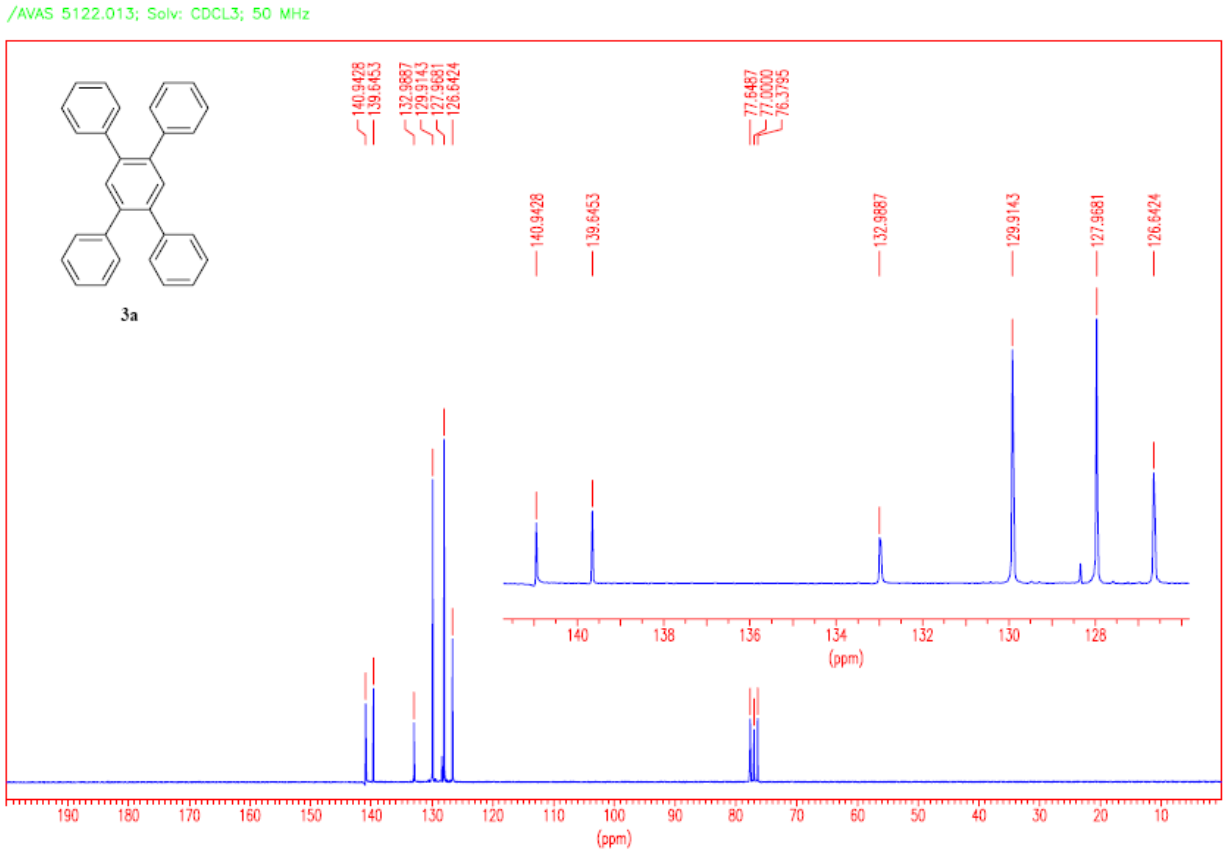
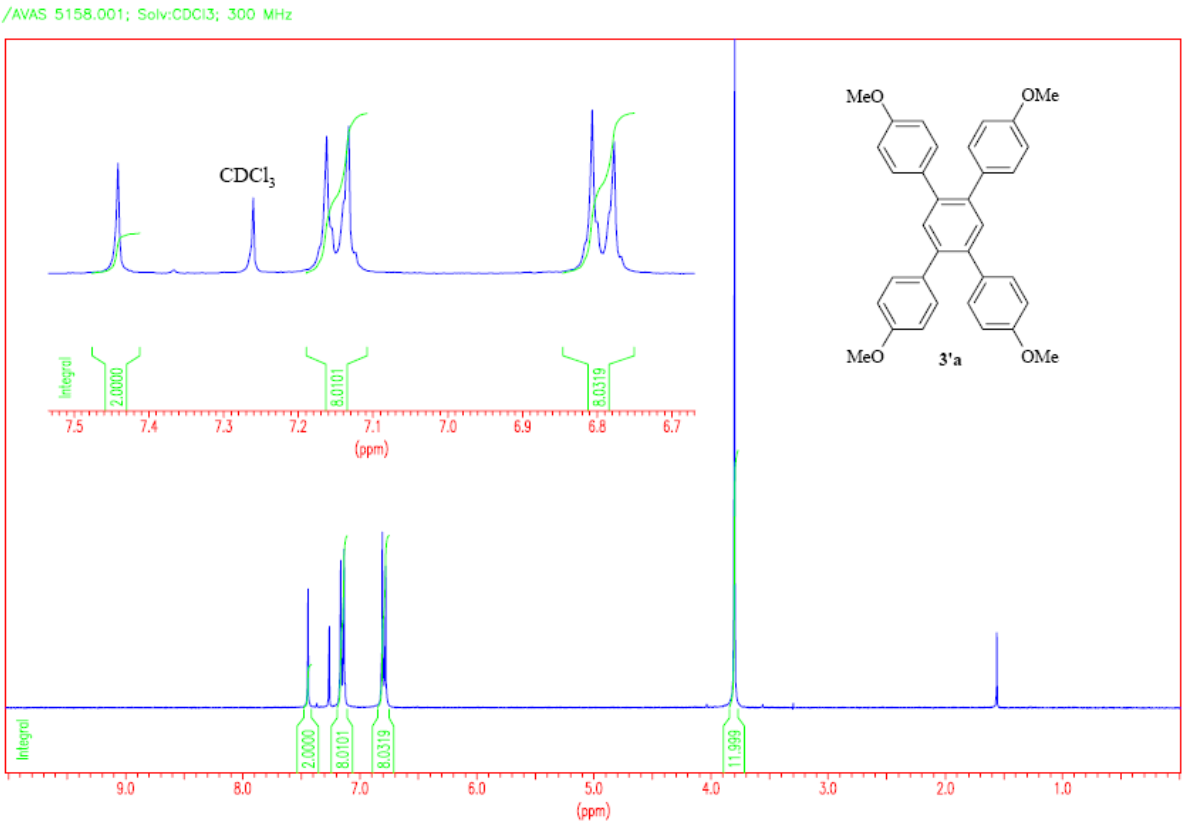
Images of the NMR spectra





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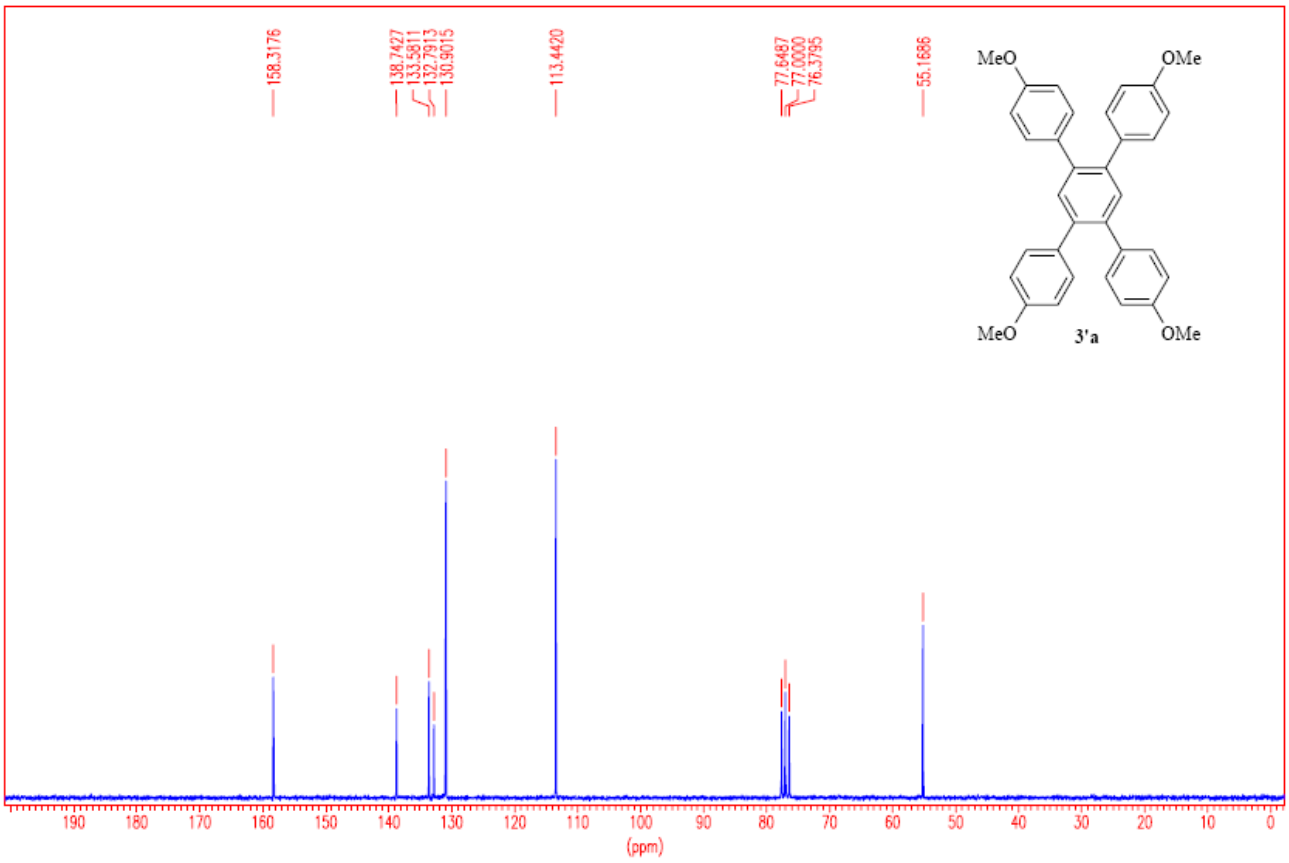

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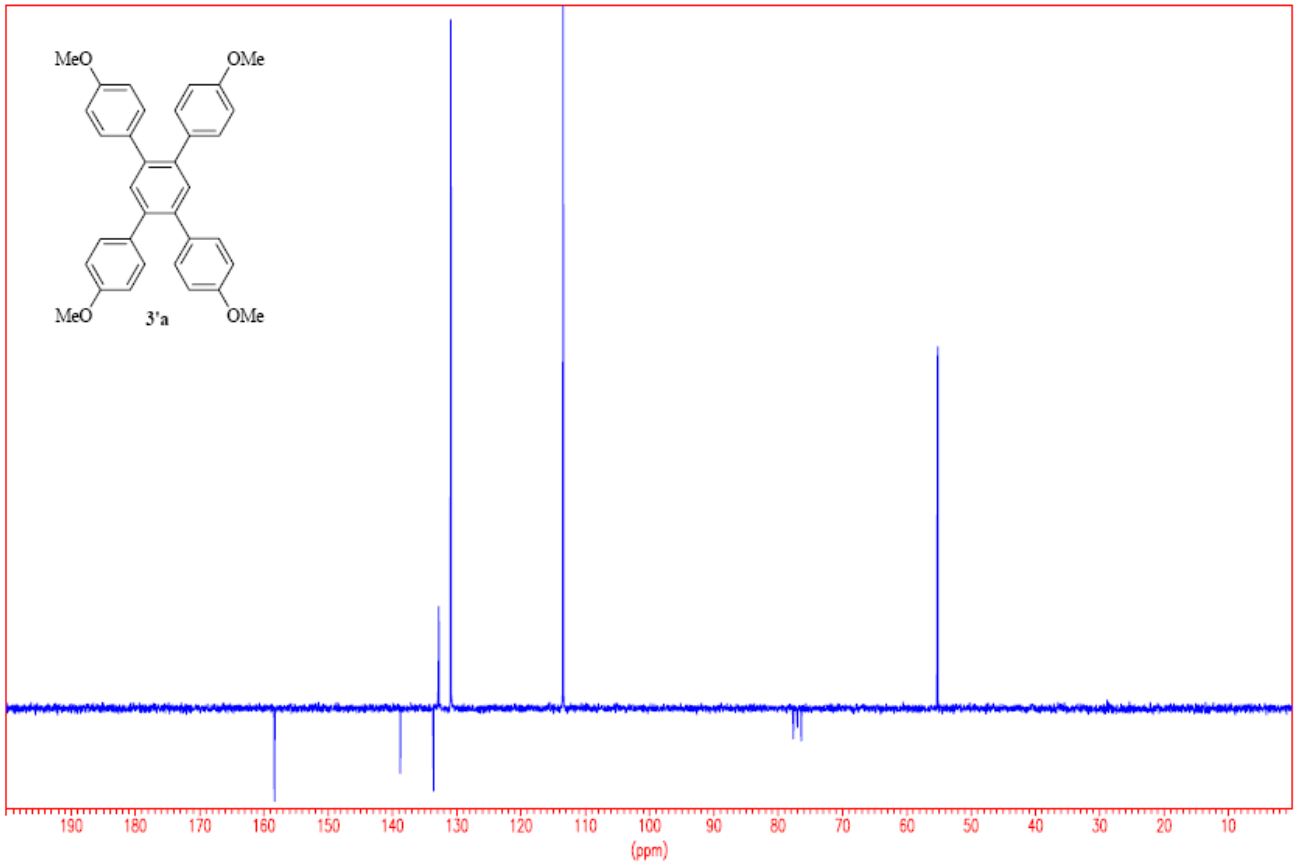

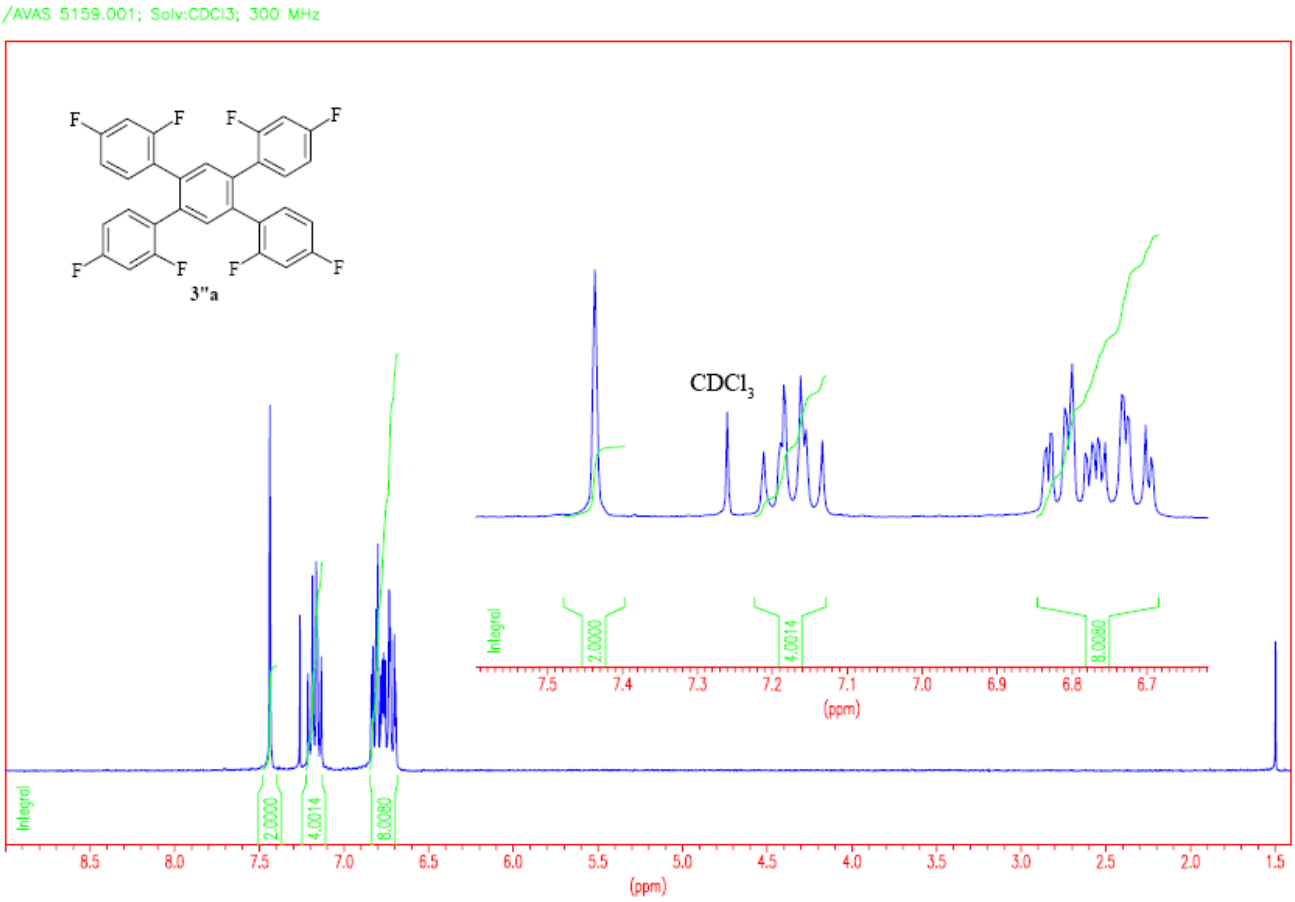
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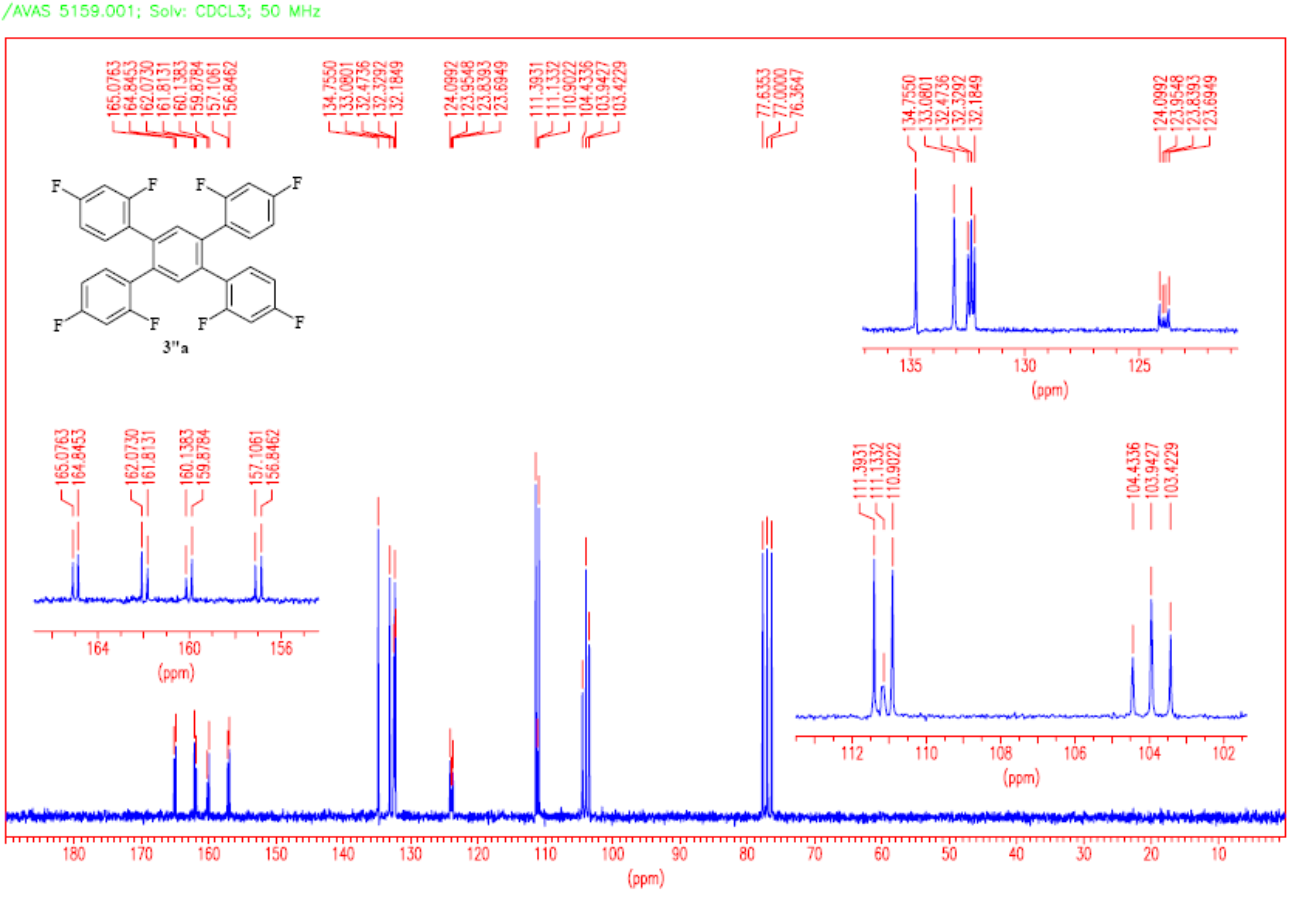
(ppm)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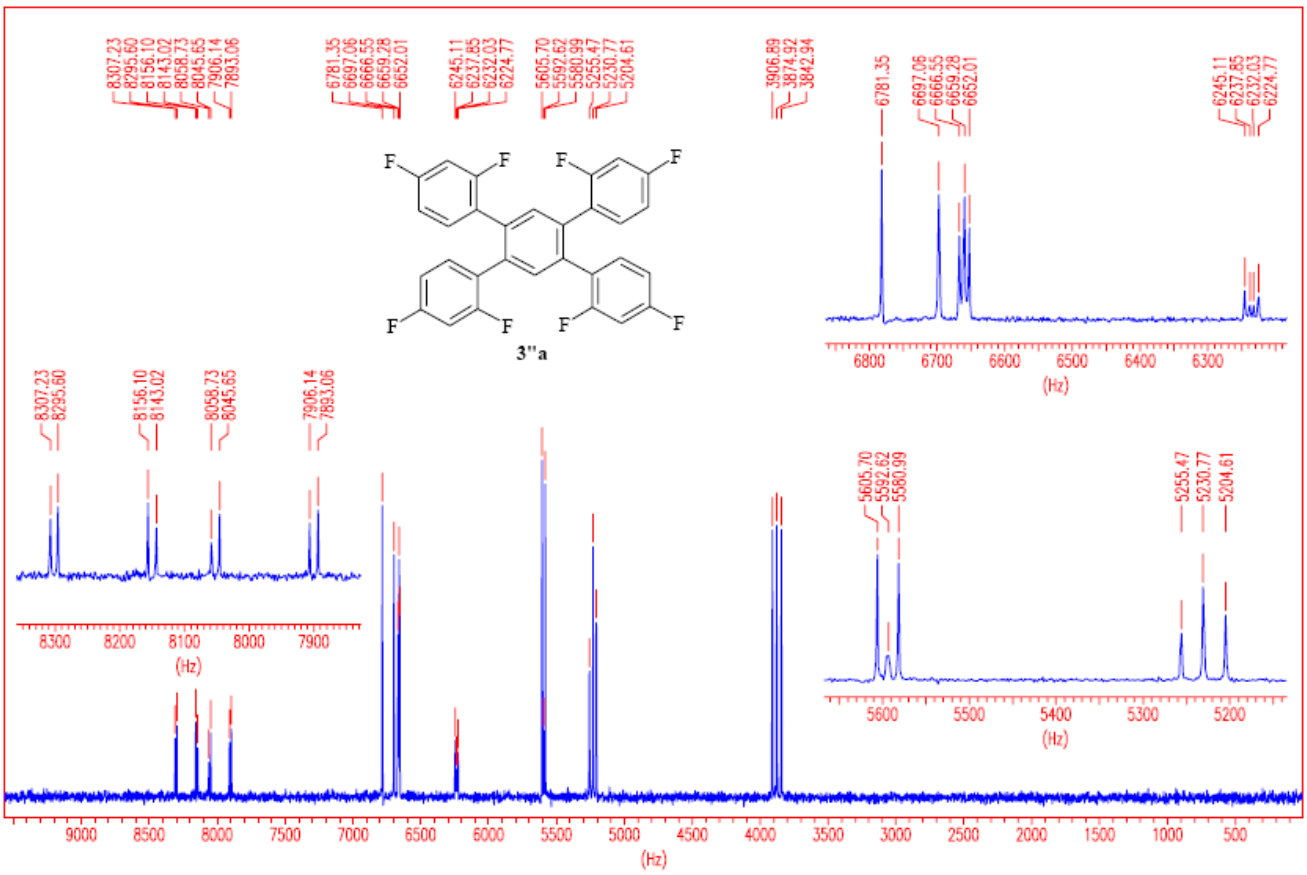

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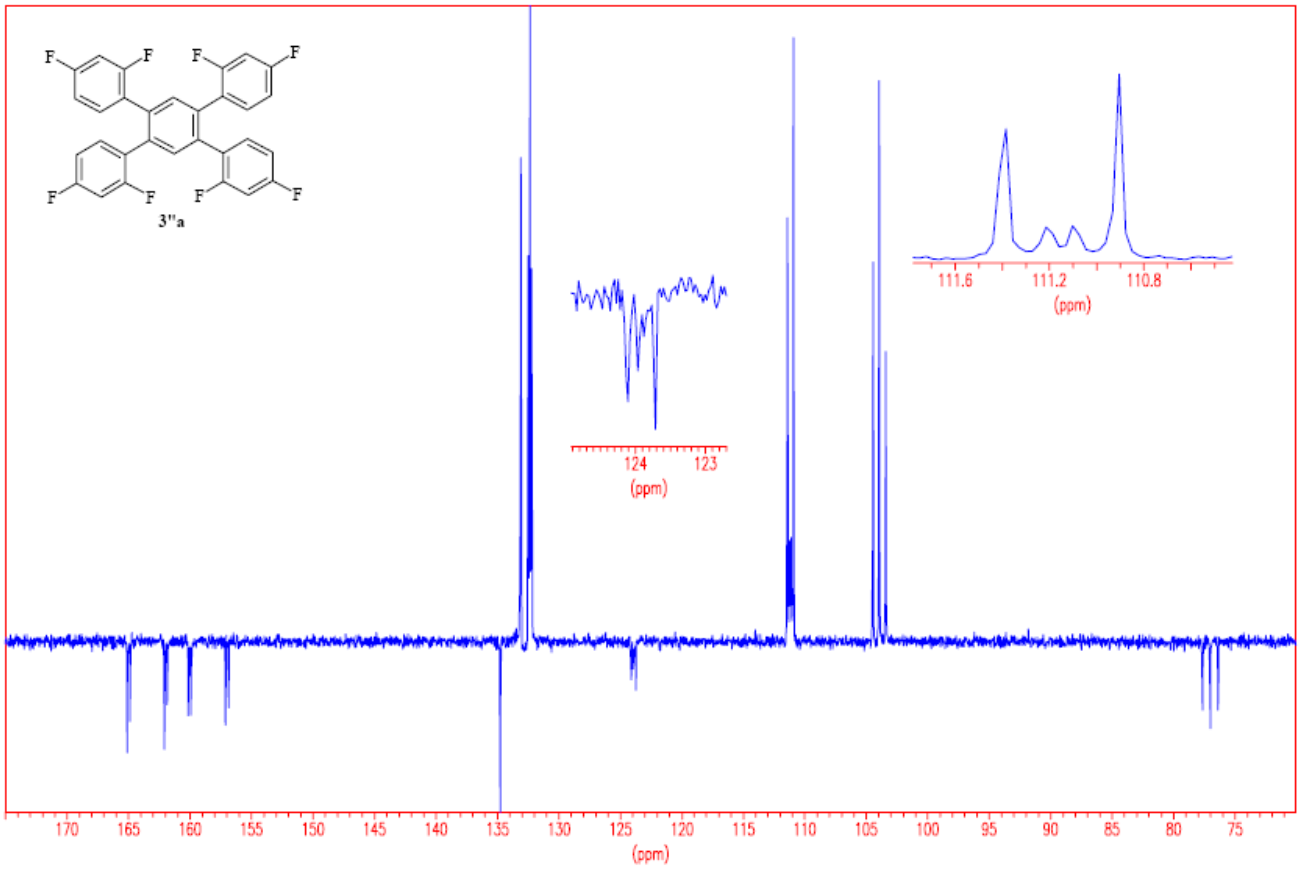

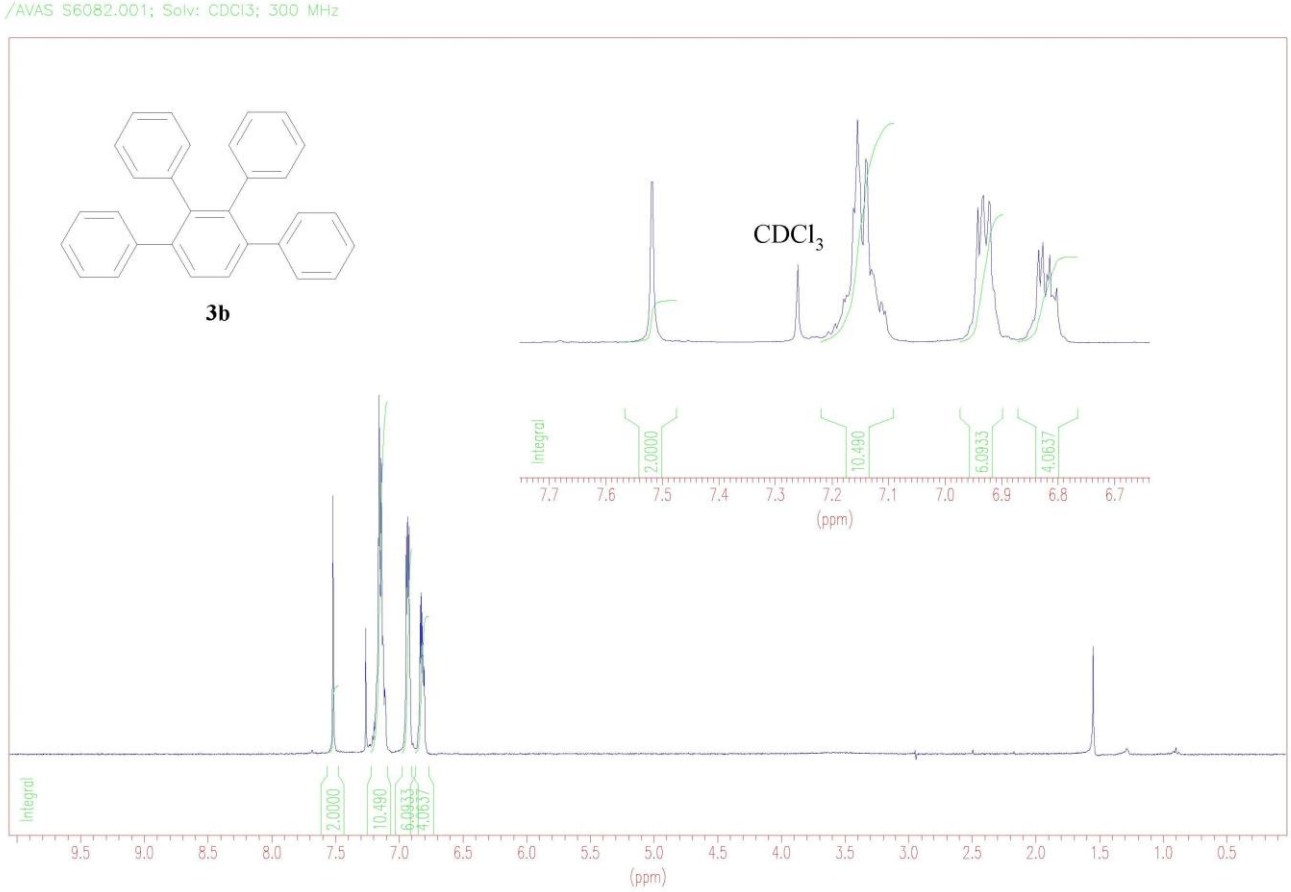
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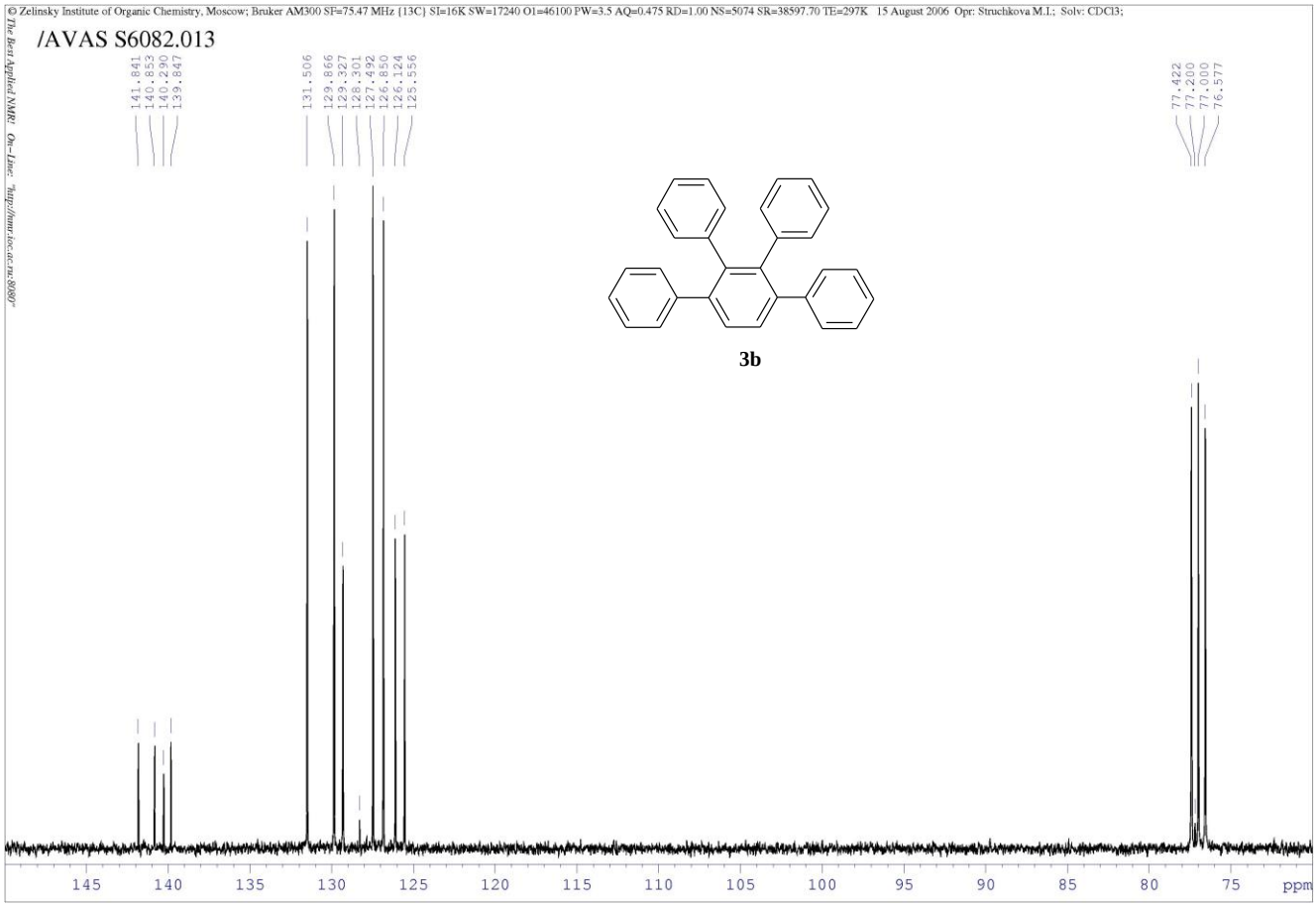
© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=16K SW=17240 O1=46100 PW=3.5 AQ=0.475 RD=1.00 NS=5074 SR=38597.70 TE=297K 15 August 2006 Opr: Struchkova M.I.; Solv: CDCl3;
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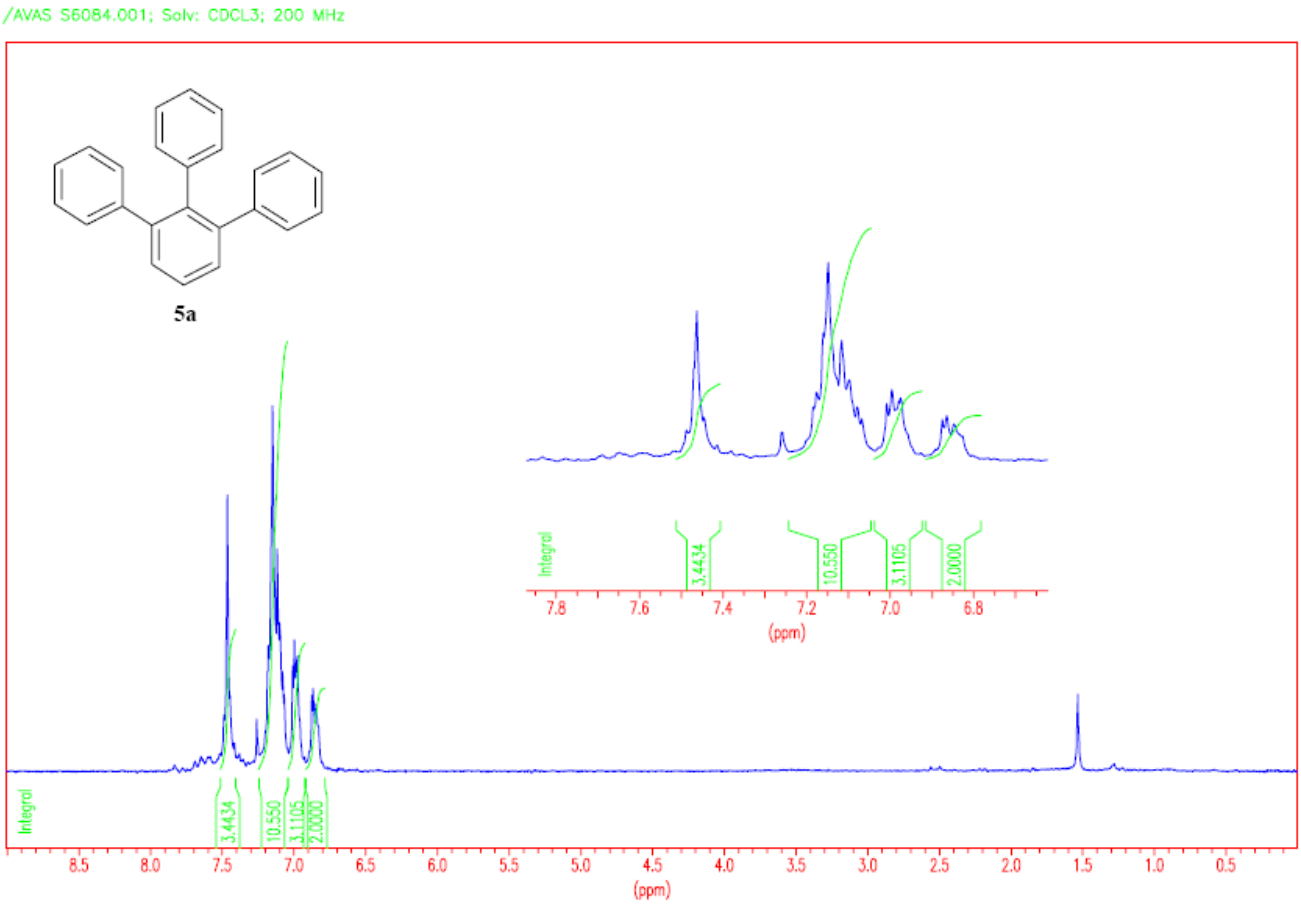
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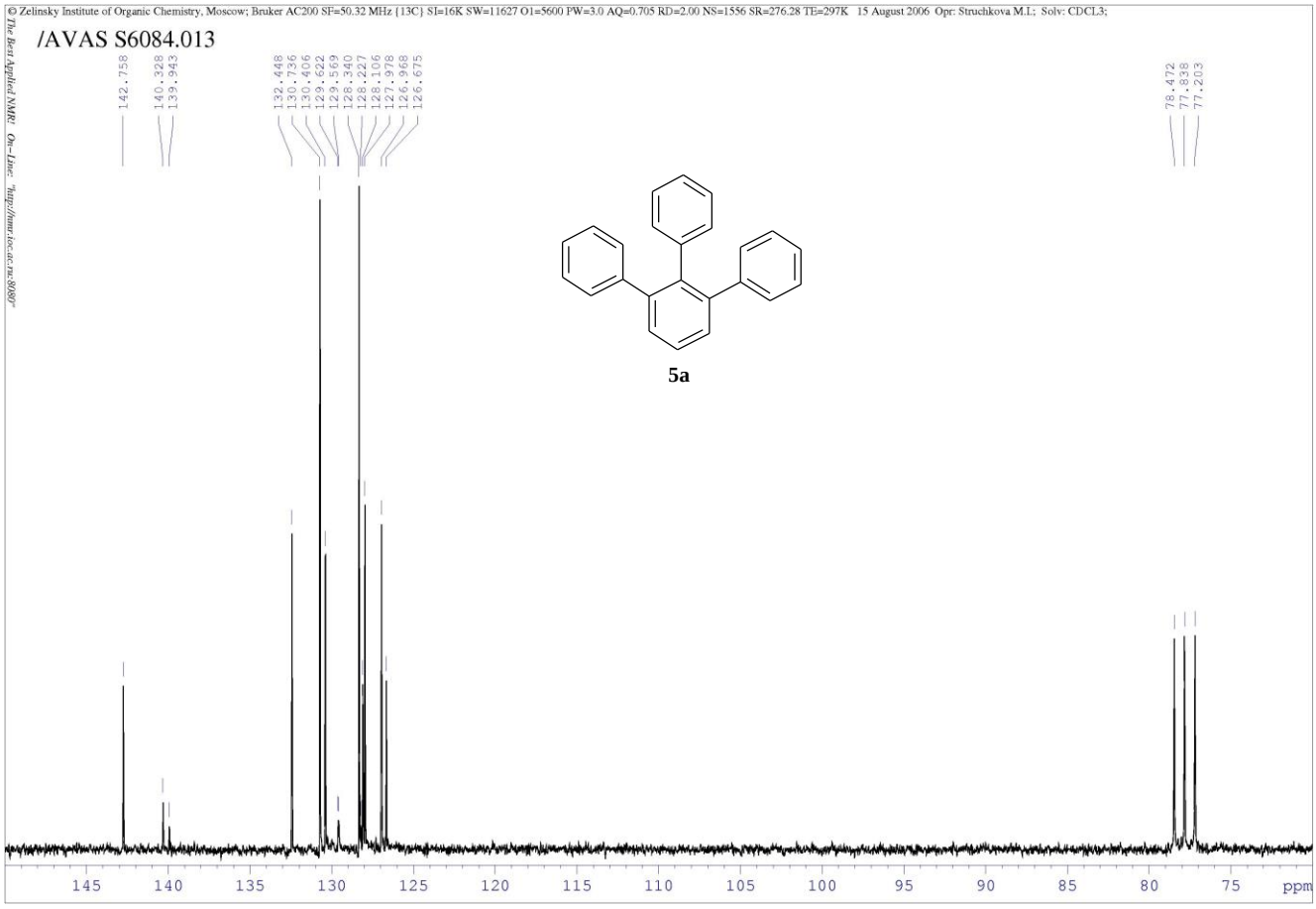
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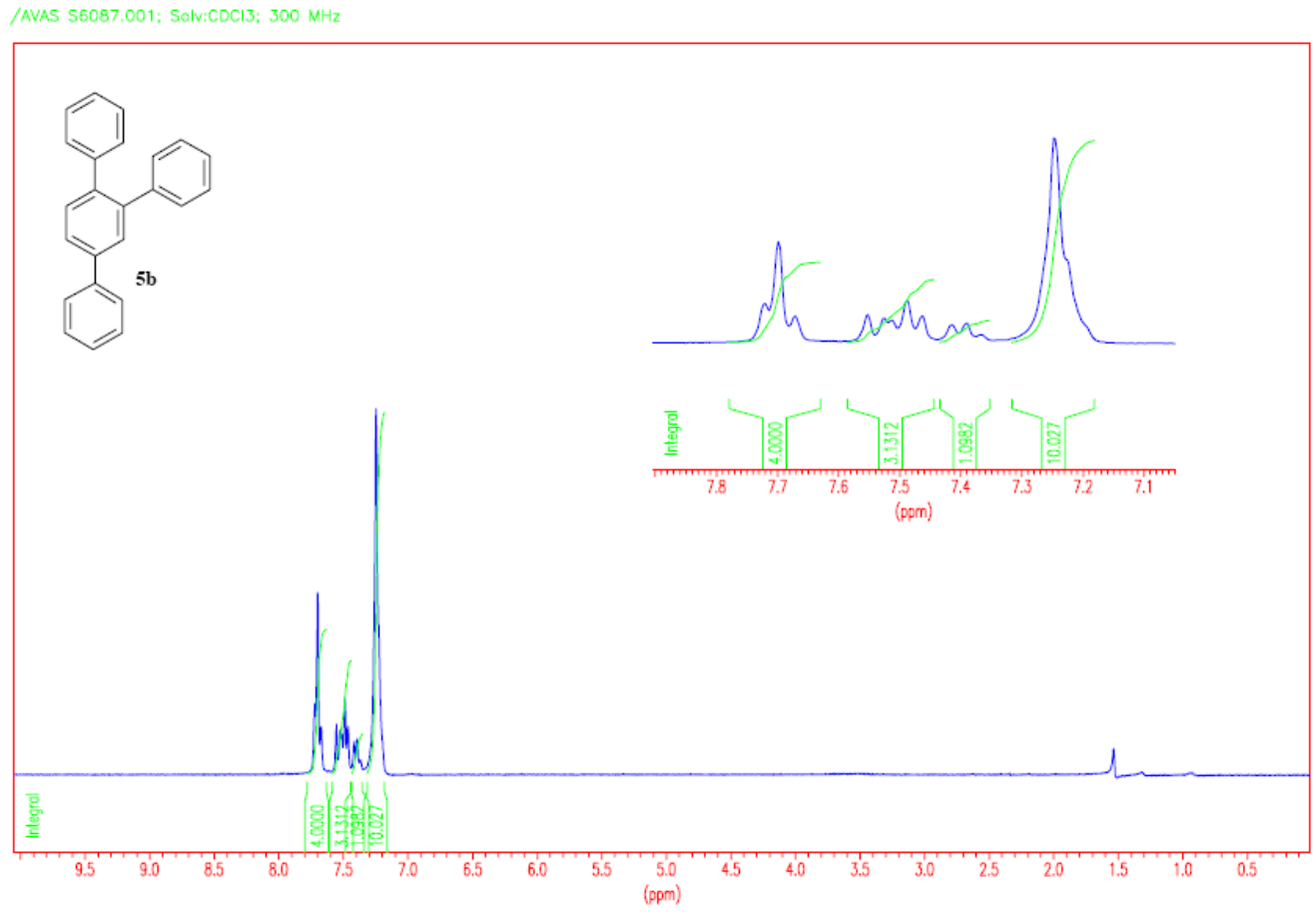
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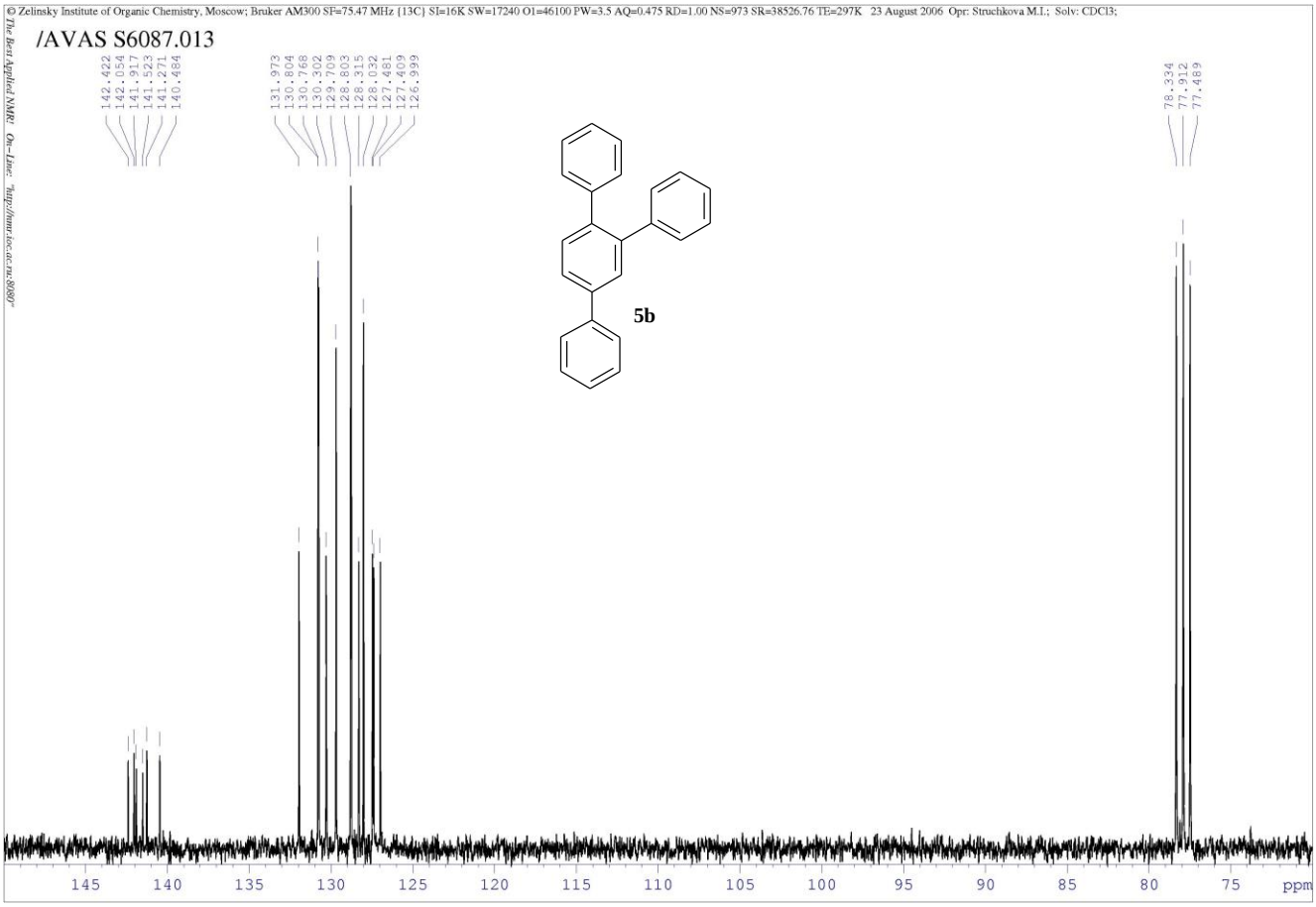
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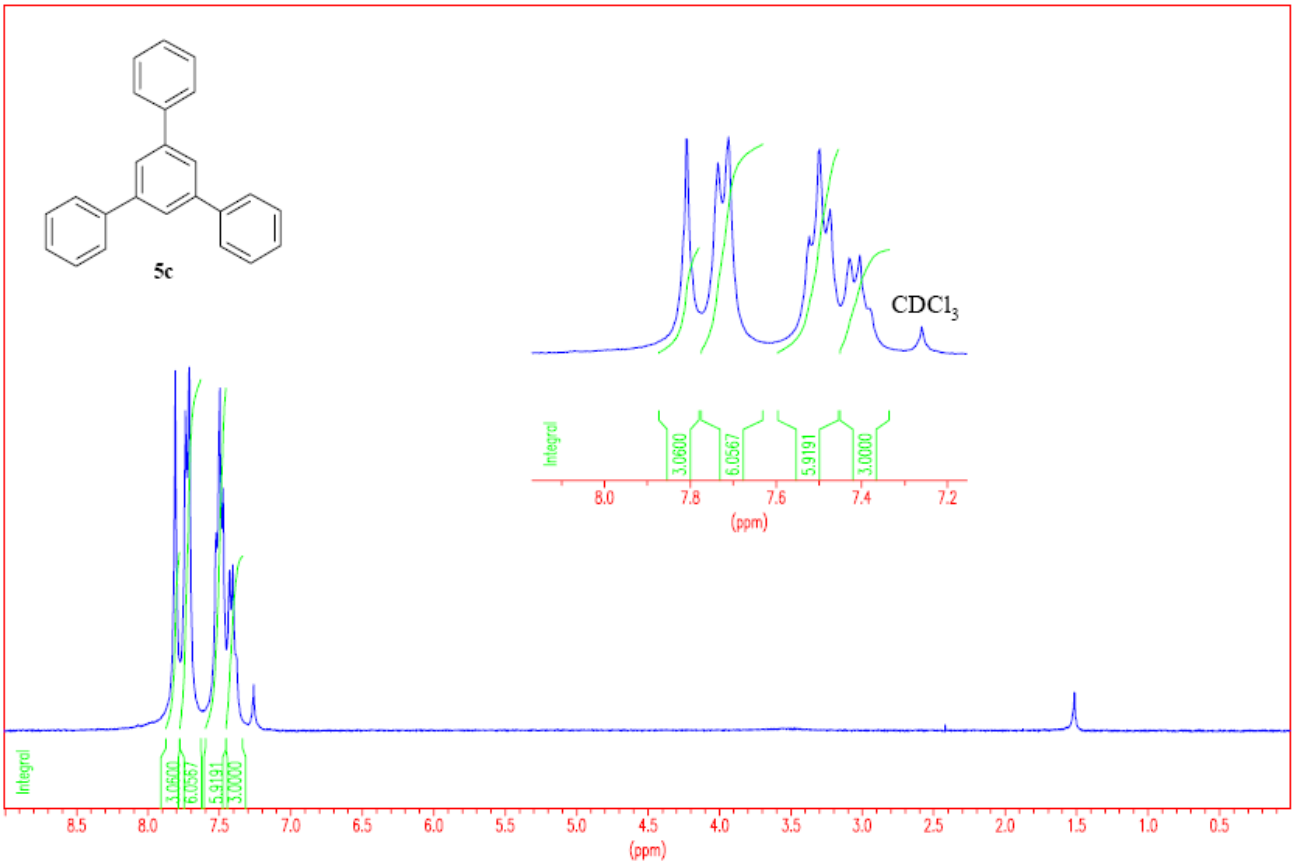

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