

# **An Efficient Catalyst System for Pd-Catalyzed Amination of [2.2]Paracyclophanyl Bromides**

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## **Supporting Information**

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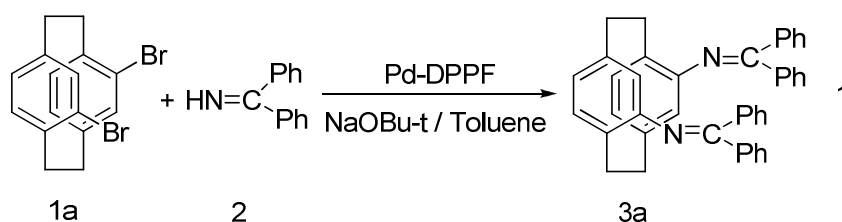
## General Considerations

All reactions were carried out under an atmosphere of argon or nitrogen using Schlenk techniques. All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise. Toluene, THF, DME and 1,4-Dioxane were dried under nitrogen over sodium-benzophenone and handled under nitrogen. *t*-Butanol was dried under nitrogen over sodium and vacuum distilled. Benzhydrylideneamine, sodium *t*-butoxide and [2.2]paracyclophane were prepared according to published procedures. 4,12-dibromo[2.2]paracyclophane **1a**, 4-Bromo[2.2] paracyclophane **1b**, 4,16-dibromo[2.2]paracyclophane **1c**, 4,15- dibromo[2.2]paracyclophane **1d**, and 4,7,12,15- tetrabromo[2.2]paracyclophane **1m** were prepared according to Cram's methods<sup>[1,2]</sup>, *R*<sub>p</sub>-4-bromo-12-methoxy[2.2] paracyclophane **1e** was prepared according to Bolm's method<sup>[5]</sup>; Tetrakis (triphenylphosphine) palladium, Bis(triphenylphosphine)dichloropalladium, 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium dichloromethane, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) and 1,3-bis(2,6- diisopropylphenyl)-4,5-dihydroimidazolium chloride (SIPr·HCl) were purchased from commercial sources. Thin layer chromatography (TLC) was performed on Silica Gel 60 F<sub>254</sub> glass plates and were visualized using UV light (254 nm), iodine or potassium permanganate or phosphomolybdic acid stains. Column chromatography purifications were carried out using silica gel (200-400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 400 and 300 MHz spectrometers at 298K. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent for <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), septet (sept), multiplet (m), and broad (br). Optical rotations were taken on a polarimeter with a wavelength of 589 nm. The concentration "c" has units of g/100mL (or 10 mg/mL) unless otherwise noted. Elemental analyses Found values for carbon, hydrogen, and nitrogen were within 0.4% of the theoretical (Calcd) values for the proposed formula. Mass spectra were measured by electrospray ionization (ESI-MS) in CH<sub>3</sub>OH on a mass spectrometer. Melting points were recorded on a melting point apparatus and are uncorrected. Imidazolium salts, phosphine ligands and Pd precursors for catalyst preparation (Table 1-2) were weighed in a glovebox.

## Synthetic Procedures:

### General procedure A:

#### 4,12-Bis(benzhydrylideneamino)[2.2]paracyclophane **3a**:

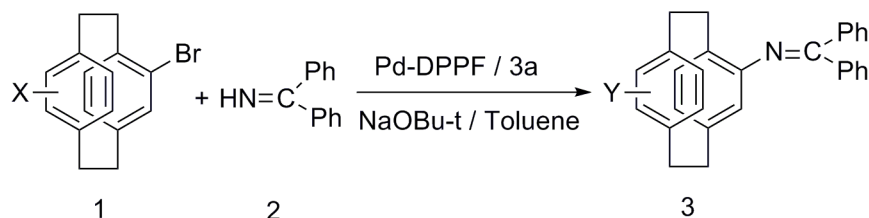


In a glovebox, an oven-dried Schlenk flask were charged with Pd-DPPF (4.1 mg,  $5.0 \times 10^{-3}$  mmol), 4,12-dibromo[2.2]paracyclophane **1a** (366 mg, 1.0 mmol), benzhydrylideneamine (542 mg, 3.0 mmol), sodium *t*-butoxide (288 mg, 3.0 mmol) and toluene (0.60 mL). The mixture was stirred at 110 °C under nitrogen for 8 hours. After the reaction mixture was cooled to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub> (15.0 mL), HOAc was added to the mixture until the stirred solution tested acidic (pH = 6). The acidic solution was washed with water (3 × 10.0 mL), saturated aqueous NaCl solution (3 × 10.0 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a residue, which was purified by recrystallization (ethanol: 50.0mL) to give 4,12-bis(benzhydrylideneamino)[2.2]paracyclophane **3a** as a yellow solid (431 mg, 76%). Mp: 217–219 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT) δ 7.87–7.75 (m, 4H), 7.50–7.37 (m, 6H), 7.25–7.22 (m, 7H), 7.07–7.06 (m, 4H), 6.38–6.36 (m, 2H), 6.24–6.22 (m, 3H), 3.34–3.29 (m, 2H), 3.09–3.02 (m, 2H), 2.86–2.81 (m, 2H), 2.50–2.48 (d, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 164.1, 147.8, 140.6, 140.3, 136.9, 133.7, 132.4, 130.1, 129.1, 128.6, 128.2, 127.9, 127.7, 123.4, 33.4, 32.9. Anal. Calcd. For C<sub>42</sub>H<sub>34</sub>N<sub>2</sub> (566.73): C, 89.01; H, 6.05; N, 4.94. Found: C, 88.80; H, 6.02; N, 4.95.

#### 4-Benzhydrylideneamino-12-bromo[2.2]paracyclophane **3aa**:

Following the general procedure A, starting from 4,12-dibromo[2.2]paracyclophane **1a** and 0.2 mol% Pd-DPPF, a yellow solid was obtained; Yield: 52%, Mp: 206–208 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT) δ 7.87–7.85 (m, 2H), 7.49–7.44 (m, 4H), 7.17–7.15 (m, 3H), 7.04–7.02 (m, 2H), 6.50–6.49 (m, 2H), 6.39–6.37 (d, 1H), 5.23–5.20 (dd, 1H), 5.93 (d, 1H), 3.37–3.25 (m, 3H), 3.03–3.01 (t, 1H), 2.86–2.73 (m, 3H) 2.56–2.50 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 165.1, 148.5, 142.1, 140.1, 140.0, 138.2, 136.7, 134.3, 134.1, 133.5, 132.1, 131.8, 130.3, 129.3, 129.3, 128.3, 128.2, 128.1, 127.6, 126.2, 121.8, 35.5, 33.1, 33.0, 32.7. Anal. Calcd. For C<sub>29</sub>H<sub>24</sub>NBr (466.41): C, 74.68; H, 5.19; N, 3.00. Found: C, 74.79; H, 5.15; N, 3.01.

## General procedure B:



In a glovebox, an oven-dried Schlenk flask were charged with Pd-DPPF (0.5 mol%), 4,12-bis(benzhydrylideneamino)[2,2]paracyclophane (0.5 mol%), bromo[2.2]paracyclophane derivate (0.50 mmol), benzhydrylideneamine (1.5 equiv.), sodium *t*-butoxide (1.5 equiv.) and toluene (2.0 mL). The mixture was stirred at 110 °C under nitrogen for 8 hours. After the reaction mixture was cooled to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub> (15.0 mL), HOAc was added to the mixture until the stirred solution tested acidic (pH 6), washed with water (3 × 10.0 mL), saturated aqueous NaCl solution (3 × 10.0 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a residue, which was purified by silica gel column chromatography using hexanes:ethyl acetate (10:0 – 10:5) as eluent to give the desired product as a yellow solid.

### 4-Benzhydrylideneamino[2.2]paracyclophane 3b:

Following the general procedure B, starting from 4-bromo[2.2]paracyclophane **1b**, a yellow solid was obtained; Yield: 79%, Mp: 208–210 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT) δ 7.89–7.87 (m, 2H), 7.50–7.48 (m, 3H), 7.37–7.35 (m, 1H) 7.17–7.14 (d, 3H), 7.01–7.00 (m, 2H), 6.55–6.46 (m, 3H), 6.27–6.25 (m, 2H), 5.48 (br, 1H), 3.35–3.26 (m, 2H), 3.07–2.89 (m, 4H), 2.79–2.73 (m, 1H), 2.51–2.46 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 165.2, 148.7, 140.0, 139.9, 139.9, 138.9, 136.7, 134.3, 133.2, 132.4, 131.9, 131.4, 130.4, 129.5, 129.3, 129.2, 128.2, 128.2, 128.0, 127.6, 126.7, 35.3, 35.1, 34.0, 33.0. Anal. Calcd. For C<sub>29</sub>H<sub>25</sub>N (387.52): C, 89.88; H, 6.50; N, 3.61. Found: C, 89.92; H, 6.48; N, 3.60.

### 4-Benzhydrylideneamino-15-bromo[2.2]paracyclophane 3d:

Following the general procedure B, starting from 4,15-dibromo[2.2]paracyclophane **1d**, a yellow solid was obtained; Yield: 41%, Mp: 204–206 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 7.86–7.83 (m, 2H), 7.52–7.43 (m, 4H), 7.25–7.11 (m, 4H), 7.10–7.02 (m, 2H), 6.52–6.45 (m, 3H), 5.97 (s, 1H), 3.32–3.21 (m, 3H), 3.17–2.99 (m, 3H), 2.79–2.68 (m, 1H), 2.53–2.44 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 165.9,

148.1, 141.6, 139.8, 139.2, 138.2, 137.4, 136.3, 134.2, 134.1, 133.0, 131.3, 130.8, 130.6, 129.3, 129.2, 128.5, 128.2, 127.8, 126.6, 123.1, 121.7, 35.6, 33.2, 32.8, 32.7, 32.4. Anal. Calcd. For  $C_{29}H_{24}NBr$  (466.41): C, 74.68; H, 5.19; N, 3.00. Found: C, 74.67; H, 5.24; N, 2.82.

#### ***R<sub>p</sub>*-4-Benzhydrylideneamino-12-methoxy[2.2]paracyclophane 3e:**

Following the general procedure B, starting from *R<sub>p</sub>*-4-bromo-12-methoxy[2.2]paracyclophane **1e**, a yellow solid was obtained; Yield: 84%, Mp: 168–170 °C.  $[\alpha]_D^{20} = -436.5$  (c 1.6,  $CH_2Cl_2$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ , RT)  $\delta$  7.86–7.83 (m, 2H), 7.50–7.42 (m, 3H), 7.18–7.15 (m, 3H), 7.03–7.01 (m, 2H), 6.68 (s, 1H), 6.46–6.43 (d, 1H), 6.29–6.22 (m, 2H), 6.11–6.08 (m, 1H), 5.77–5.76 (d, 1H), 3.76 (s, 3H), 3.34–3.22 (m, 3H), 2.98–2.95 (m, 1H), 2.87–2.77 (m, 2H), 2.55–2.46 (m, 2H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , RT)  $\delta$  165.1, 157.3, 148.6, 142.8, 140.6, 139.7, 136.7, 134.6, 134.2, 130.6, 130.4, 129.1, 129.0, 128.6, 128.2, 127.6, 126.9, 124.1, 122.0, 113.3, 54.0, 34.0, 33.5, 32.4, 31.5. Anal. Calcd. For  $C_{30}H_{27}NO \cdot 0.2H_2O$  (421.14): C, 85.56; H, 6.56; N, 3.33. Found: C, 85.77; H, 6.45; N, 3.23.

#### ***S<sub>p</sub>*-4-Benzhydrylideneamino-12-*i*-propoxy[2.2]paracyclophane 3f:**

Following the general procedure B, starting from *S<sub>p</sub>*-4-bromo-12-*i*-propoxy[2.2]paracyclophane **1f**, a yellow solid was obtained; Yield: 62%, Mp: 129–130 °C.  $[\alpha]_D^{20} = -538.7$  (c 0.40,  $CH_2Cl_2$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ , RT)  $\delta$  7.86–7.82 (m, 2H), 7.50–7.43 (m, 3H), 7.19–7.16 (m, 3H), 7.02–6.99 (m, 2H), 6.65 (s, 1H), 6.45–6.42 (d, 1H), 6.33–6.30 (d, 1H), 6.22–6.19 (dd, 1H), 6.12–6.09 (dd, 1H), 5.75–5.74 (d, 1H), 4.55–4.51 (sept, 1H), 3.36–3.32 (m, 2H), 3.23–3.21 (m, 1H), 3.02–2.99 (m, 1H), 2.84–2.75 (m, 2H), 2.52–2.46 (m, 2H), 1.40–1.38 (d, 3H), 1.24–1.22 (d, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , RT)  $\delta$  164.7, 156.1, 148.3, 142.5, 140.6, 139.8, 136.7, 134.7, 134.2, 131.3, 130.3, 130.1, 129.2, 129.0, 128.6, 128.3, 127.7, 127.6, 123.8, 122.4, 115.3, 68.7, 33.9, 33.5, 32.6, 31.7, 23.4, 21.7. Anal. Calcd. For  $C_{32}H_{31}NO$  (445.59): C, 86.25; H, 7.01; N, 3.14. Found: C, 86.34; H, 6.98; N, 3.05.

#### ***S<sub>p</sub>*-4-Benzhydrylideneamino-12-hydroxy[2.2]paracyclophane 3g:**

Following the general procedure B, starting from *S<sub>p</sub>*-4-bromo-12-acetoxy[2.2]paracyclophane **1g**, a yellow solid was obtained; Yield: 75%, Mp: 220–222 °C.  $[\alpha]_D^{20} = -131.6$  (c 1.0,  $CH_2Cl_2$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ , RT)  $\delta$  7.80–7.77 (m, 2H), 7.51–7.43 (m, 3H), 7.20–7.13 (m, 3H), 7.04–7.00 (m, 2H), 6.50–6.49 (d, 1H), 6.45–6.42 (d, 1H), 6.29–6.27 (d, 1H), 6.23–6.12 (m, 3H), 5.54 (br, 1H), 3.33–3.27 (m, 1H), 3.10–3.06 (m, 2H), 2.94–2.86 (m, 3H), 2.59–2.52 (m, 1H), 2.49–2.41 (m, 1H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , RT)  $\delta$  166.8, 154.0, 148.6, 142.5, 140.6, 139.7, 136.8, 135.2, 134.5, 134.4, 130.6, 129.7, 129.5, 129.4, 129.3, 128.6, 128.5, 128.3, 127.6, 125.5, 124.8, 122.0, 118.7, 33.6, 33.4, 32.4, 31.3. HRMS (ESI) Mass calculated for  $C_{29}H_{26}NO$  ( $M^+ + H$ ) 405.2048, found: 405.2058.

#### **4-Benzhydrylideneamino-12-amino[2.2]paracyclophane 3h:**

Following the general procedure B, starting from 4-bromo-12-amino[2.2]paracyclophane **1h**, a yellow solid was obtained; Yield: 55%, Mp: 198–200 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT) δ 7.84–7.82 (m, 2H), 7.50–7.43 (m, 3H), 7.18–7.16 (m, 3H), 7.05–7.03 (m, 2H), 6.37–6.31 (m, 3H), 6.18 (s, 1H), 6.14–6.09 (m, 2H), 3.30 (br, 2H), 3.19–3.16 (t, 1H), 3.09–3.04 (m, 2H), 2.92–2.83 (m, 3H), 2.60–2.56 (m, 1H), 2.50–2.46 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 165.2, 148.5, 144.9, 141.9, 139.9, 139.7, 136.8, 134.9, 134.0, 130.7, 130.3, 129.3, 129.1, 128.3, 128.2, 128.2, 127.6, 124.0, 123.0, 120.5, 118.8, 33.5, 32.7, 32.6, 32.1. Anal. Calcd. For C<sub>29</sub>H<sub>26</sub>N<sub>2</sub> (402.53): C, 86.53; H, 6.51; N, 6.96. Found: C, 86.59; H, 6.60; N, 6.82.

#### **R<sub>p</sub>-4-Benzhydrylideneamino-12-dimethylamino[2.2]paracyclophane 3i:**

Following the general procedure B, starting from R<sub>p</sub>-4-bromo-12-dimethylamino[2.2]paracyclophane **1i**, a yellow solid was obtained; Yield: 96%, Mp: 168–171 °C.  $[\alpha]_D^{20} = -418.6$  (c 2.1, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 7.87–7.84 (m, 2H), 7.49–7.44 (m, 3H), 7.18–7.14 (m, 3H), 7.02–7.68 (m, 2H), 6.57 (d, 1H), 6.44–6.41 (d, 1H), 6.33–6.30 (d, 1H), 6.22–6.15 (m, 2H), 5.69–5.68 (d, 1H), 3.34–3.21 (m, 3H), 3.01–2.94 (m, 1H), 2.85–2.81 (m, 2H), 2.73 (s, 6H), 2.65–2.58 (m, 1H), 2.56–2.49 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 164.6, 151.4, 148.2, 141.5, 140.4, 139.8, 136.7, 135.9, 133.9, 131.0, 130.6, 130.3, 129.1, 129.0, 128.2, 127.6, 125.6, 122.4, 118.4, 43.6, 35.5, 33.6, 33.2, 32.7. Anal. Calcd. For C<sub>31</sub>H<sub>30</sub>N<sub>2</sub> (430.58): C, 86.47; H, 7.02; N, 6.51. Found: C, 86.61; H, 7.03; N, 6.36.

#### **4R<sub>p</sub>, 13S<sub>p</sub>-4-Benzhydrylideneamino-13-methoxy[2.2]paracyclophane 3k:**

Following the general procedure B, starting from 4R<sub>p</sub>,13S<sub>p</sub>-4-bromo-13-methoxy[2.2]paracyclophane **1k**, a yellow solid was obtained; Yield: 98%, Mp: 157–160 °C.  $[\alpha]_D^{20} = +14.0$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 7.88–7.85 (m, 2H), 7.48–7.41 (m, 3H), 7.17–7.11 (m, 3H), 6.94–6.91 (m, 2H), 6.47–6.44 (d, 1H), 6.27–6.24 (dd, 1H), 6.16 (m, 2H), 5.86–5.80 (d, 2H), 3.86 (s, 3H), 3.69–3.60 (m, 1H), 3.45–3.36 (m, 1H), 3.00–2.90 (m, 3H), 2.85–2.77 (m, 1H), 2.69–2.60 (m, 1H), 2.54–2.45 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 165.9, 158.6, 149.0, 141.2, 140.2, 138.5, 137.0, 134.7, 134.5, 130.9, 130.3, 129.3, 128.1, 128.0, 127.6, 127.4, 125.6, 124.7, 115.1, 54.9, 35.3, 35.1, 30.8, 30.5. Anal. Calcd. For C<sub>30</sub>H<sub>27</sub>NO · 0.25H<sub>2</sub>O (422.05): C, 85.38; H, 6.57; N, 3.32. Found: C, 85.65; H, 6.47; N, 3.23.

#### **4R<sub>p</sub>,13S<sub>p</sub>-4-Amino-13-*i*-propoxy[2.2]paracyclophane 3l:**

Following the general procedure B and C, starting from 4R<sub>p</sub>, 13S<sub>p</sub>-4-bromo-13-*i*-propoxy[2.2]paracyclophane **1l**, a white solid was obtained; Yield: 63%; Mp: 79–82 °C;  $[\alpha]_D^{20} = +40.0$  (c 0.10, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT)

$\delta$  6.40–6.37 (d, 1H), 6.33–6.31 (d, 1H), 6.24–6.21 (dd, 1H), 6.11–6.08 (dd, 2H), 5.75–5.74 (d, 1H), 4.22–4.14 (sept, 1H), 3.63–3.53 (m, 1H), 3.34–3.24 (m, 1H), 3.04–2.89 (m, 4H), 2.85–2.74 (m, 2H), 1.30–1.28 (d, 3H), 1.21–1.19 (d, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  157.3, 145.5, 140.8, 140.5, 135.1, 134.9, 129.1, 127.3, 125.3, 124.9, 123.0, 122.2, 72.9, 35.3, 35.1, 31.0, 28.3, 22.7, 22.0. HRMS (ESI) Mass calculated for  $\text{C}_{19}\text{H}_{24}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 283.1891, found: 283.1886.

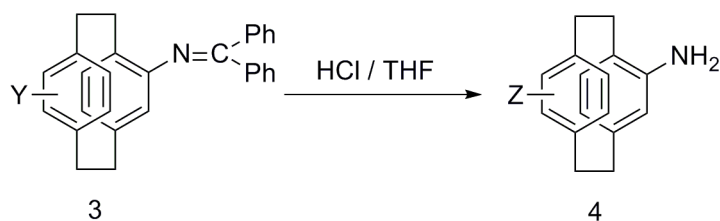
#### 4-Benzhydrylideneamino-7,12,15-tribromo[2.2]paracyclophane **3m**:

Following the general procedure B, starting from 4,7,12,15-tetrabromo[2.2]paracyclophane **1m**, a yellow solid was obtained; Yield: 20%, Mp: 210–211 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  7.83–7.81 (d, 2H), 7.56–7.47 (m, 4H), 7.26–7.20 (m, 5H), 7.15 (s, 1H), 7.06–7.03 (m, 3H), 6.02 (s, 1H), 3.24–3.04 (m, 5H), 2.95–2.89 (m, 1H), 2.86–2.69 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  166.2, 148.6, 141.1, 140.1, 139.7, 138.8, 136.2, 135.3, 134.2, 133.6, 135.5, 130.7, 129.3, 129.2, 128.6, 128.3, 127.9, 125.5, 124.9, 123.5, 121.2, 33.1, 32.7, 32.5, 29.8. Anal. Calcd. For  $\text{C}_{29}\text{H}_{22}\text{NBr}_3$  (624.20): C, 55.80; H, 3.55; N, 2.24. Found: C, 55.84; H, 3.61; N, 2.18.

#### 4,7,12,15-Tetra(benzhydrylideneamino)[2.2]paracyclophane **3ma**:

Following the general procedure B, starting from 4,7,12,15-tetrabromo[2.2]paracyclophane **1m**, a yellow solid was obtained; Yield: 23% Mp: 242–244 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  7.73–7.71 (d, 8H), 7.40–7.18 (m, 24H), 7.03–7.00 (d, 8H), 6.02 (s, 4H), 2.94–2.91 (m, 4H), 2.70–2.67 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  163.8, 146.0, 140.4, 137.1, 132.9, 132.4, 130.1, 129.8, 129.7, 129.1, 128.2, 127.9, 127.9, 127.5, 124.2, 30.7. Anal. Calcd. For  $\text{C}_{68}\text{H}_{52}\text{N}_4$  (925.17): C, 88.28; H, 5.67; N, 6.06. Found: C, 88.14; H, 5.70; N, 5.85.

#### General procedure C:



To a solution of benzhydrylideneamino[2,2]paracyclophane derivate (1.0 mmol) in THF (4.0 mL) was added concentrated HCl (12.0 M, 0.25 mL, 3.0 mmol), and stirred at room temperature for 4h. After the yellow mixture fading, white precipitate formed was filtered, washed with ether (3 × 5.0 mL), and dried in vacuo. The remaining solid (amino[2,2]paracyclophane hydrochloride) in ethanol (4.0 mL) was stirred, saturated NaOH was added dropwise until the stirred mixture tested basic (pH 9). The solvent was removed, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to furnish the desired product as a white solid.

#### **4, 12-Diamino[2.2] paracyclophane 4a:**

Following the general procedure C, starting from 4-amino-12-benzophenone imino[2.2]paracyclophane **3h**, a white solid was obtained, yield: 86%; Starting from 4,12 -bis(benzhydrylideneamino)[2.2]paracyclophane **3a**, **4a** was obtained, yield: 86%; Mp: 216–218 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT) δ 6.39–6.37 (d, 2H), 6.28–6.27 (d, 2H), 6.08–6.06 (dd, 2H), 4.00 (br, 4H), 3.11–3.05 (m, 2H), 2.95–2.92 (m, 4H), 2.68–2.60 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT) δ 140.6, 134.7, 124.1, 123.2, 116.2, 32.3, 31.5. HRMS (ESI) Mass calculated for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub> (M<sup>+</sup> + H) 239.1548, found: 239.1549.

#### **4-Amino-12-bromo[2.2]paracyclophane 4aa (1h):<sup>[7]</sup>**

Following the general procedure C, starting from 4-benzhydrylideneamino-12-bromo [2,2]paracyclophane **3aa**, a white solid was obtained; Yield: 97%, Mp: 201–203 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 6.57–6.55 (d, 1H), 6.42–6.39 (dd, 1H), 6.35–6.33 (d, 1H), 6.14–6.10 (dd, 1H), 6.08–6.07 (d, 1H), 3.50 (br, 2H), 3.39–3.32 (m, 1H), 3.14–2.62 (m, 7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT) δ 144.3, 140.7, 140.6, 137.8, 134.8, 133.9, 131.4, 130.4, 125.4, 123.9, 122.2, 117.1, 35.1, 32.4, 31.8, 31.6. Anal. Calcd. For C<sub>16</sub>H<sub>16</sub>NBr (302.21): C, 63.59; H, 5.34; N, 4.63. Found: C, 63.64; H, 5.48; N, 4.42.

#### **4-Amino[2.2]paracyclophane 4b:<sup>[6]</sup>**

Following the general procedure C, starting from 4-benzhydrylideneamino[2.2]paracyclophane **3b**, a white solid was obtained; Yield: 98%, Mp: 243–245 °C. (lit.6 Mp: 239–241.5 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 7.19–7.15 (dd, 1H), 6.60–6.57 (dd, 1H), 6.40–6.37 (dd, 2H), 6.28–6.25 (d, 1H), 6.14–6.11 (dd, 1H), 5.38–6.37 (d, 1H), 3.49 (br, 2H), 3.18–2.84 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT) δ 144.2, 140.6, 138.5, 138.4, 134.7, 132.9, 131.9, 131.0, 126.3, 124.1, 122.5, 121.8, 34.9, 34.4, 32.5, 31.7. Anal. Calcd. For C<sub>16</sub>H<sub>17</sub>N (223.31): C, 86.05; H, 7.67; N, 6.27. Found: C, 86.28; H, 7.44; N, 6.09.

#### **R<sub>p</sub>-4-Amino-12-methoxy[2.2]paracyclophane 4e:**



Following the general procedure C, starting from *R*<sub>p</sub>-4-benzhydrylideneamino-12-methoxy[2.2]paracyclophane **3e**, a white solid was obtained; Yield: 96%; Mp: 168–170 °C;  $[\alpha]_D^{20} = +80.4$  (c 0.54, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 6.56 (s, 1H), 6.49–6.47 (d, 1H), 6.29–6.26 (d, 1H), 6.18–6.16 (d, 1H), 6.03–6.00 (d, 1H), 5.83 (s, 1H), 3.15 (s, 3H), 3.49 (br, 2H), 3.39–3.31 (m, 1H), 3.11–2.96 (m, 3H), 2.94–2.80 (m, 2H), 2.69–2.49 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 157.4, 144.6, 142.1, 142.0, 135.3, 134.9, 126.9, 124.3, 123.7, 123.3, 117.7, 111.4, 54.3, 33.6, 33.2, 31.9, 31.5. HRMS (ESI) Mass calculated for C<sub>17</sub>H<sub>20</sub>NO (M<sup>+</sup> + H) 254.1545, found: 254.1539.

#### ***S*<sub>p</sub>-4-Amino-12-*i*-propoxy[2.2]paracyclophane 4f:**

Following the general procedure C, starting from *S*<sub>p</sub>-4-benzhydrylideneamino-12-*i*-propoxy[2.2]paracyclophane **3f**, a white solid was obtained; Yield: 91%; Mp: 105–106 °C;  $[\alpha]_D^{20} = -4.1$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 6.54–6.53 (d, 1H), 6.48–6.46 (d, 1H), 6.30–6.27 (d, 1H), 6.15–6.12 (dd, 1H), 6.03–6.00 (dd, 1H), 5.85–5.84 (d, 1H), 4.44–4.35 (sept, 1H), 3.39 (br, 2H), 3.38–3.30 (m, 1H), 3.09–2.97 (m, 3H), 2.92–2.84 (m, 2H), 2.66–2.58 (m, 1H), 2.55–2.45 (m, 1H), 1.45–1.42 (d, 3H), 1.22–1.20 (d, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 156.1, 144.5, 142.0, 141.5, 135.2, 134.9, 128.0, 124.3, 123.7, 123.2, 118.1, 114.5, 69.5, 33.6, 33.0, 32.0, 31.8, 23.4, 21.8. HRMS (ESI) Mass calculated for C<sub>19</sub>H<sub>24</sub>NO (M<sup>+</sup> + H) 282.1858, found: 282.1846.

#### ***R*<sub>p</sub>-4-Amino-12-dimethylamino[2.2]paracyclophane 4i:**

Following the general procedure C, starting from *R*<sub>p</sub>-4-benzhydrylideneamino-12-dimethylamino[2.2]paracyclophane **3i**, a white solid was obtained; Yield: 91%, Mp: 118–120 °C.  $[\alpha]_D^{20} = -27.0$  (c 0.99, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 6.49–6.46 (d, 1H), 6.42 (s, 1H), 6.31–6.29 (d, 1H), 6.15–6.13 (d, 1H), 6.09–6.07 (d, 1H), 5.75 (s, 1H), 3.36–3.32 (m, 3H), 3.12–2.98 (m, 3H), 2.93–2.88 (m, 2H), 2.73 (s, 6H), 2.68–2.61 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 151.4, 144.3, 141.8, 140.6, 136.0, 134.9, 130.6, 125.8, 123.9, 123.1, 117.8, 116.2, 43.8, 35.4, 33.4, 32.9, 31.9. Anal. Calcd. For C<sub>18</sub>H<sub>22</sub>N<sub>2</sub> (266.38): C, 81.16; H, 8.32; N, 10.52. Found: C, 81.24; H, 8.37; N, 10.39.

#### **4*R*<sub>p</sub>,13*S*<sub>p</sub>-4-Amino-13-methoxy[2.2]paracyclophane 4k:**

Following the general procedure C, starting from 4*R*<sub>p</sub>,13*S*<sub>p</sub>-4-benzhydrylideneamino-13-methoxy[2.2]paracyclophane **3k**, a white solid was obtained; Yield: 68%; Mp: 157–160 °C;  $[\alpha]_D^{20} = +28.2$  (c 0.74, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 6.43–6.41 (d, 1H), 6.29–6.26 (d, 1H), 6.24–6.23 (d, 1H), 6.07–6.04 (dd, 1H), 5.97–5.96 (d, 1H), 5.69–5.68 (d, 1H), 3.71 (s, 3H),

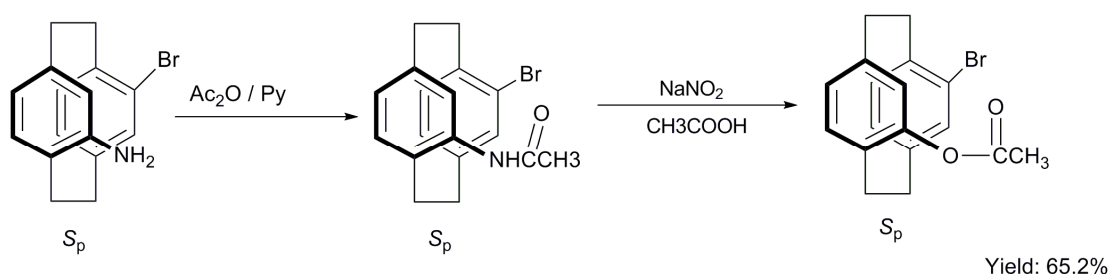
3.62–3.58 (m, 1H), 3.41 (br, 2H), 3.26–3.22 (m, 1H), 3.00–2.87 (m, 4H), 2.82–2.75 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  158.6, 145.2, 141.3, 140.4, 135.2, 134.8, 126.9, 126.0, 124.6, 124.5, 121.7, 115.8, 55.2, 35.5, 35.2, 30.3, 28.6. HRMS (ESI) Mass calculated for  $\text{C}_{17}\text{H}_{20}\text{NO}$  ( $\text{M}^+ + \text{H}$ ) 254.1545, found: 254.1535.

## Substrate preparation:

### $S_p$ -4-Bromo-12-*i*-propoxy[2.2]paracyclophane 1f:

Following a modified version of Bolm's procedure<sup>[5]</sup>, a white solid was obtained; Yield: 95%; Mp: 67–68 °C;  $[\alpha]_{\text{D}}^{20} = +56.4$  (c 0.40,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  6.90–6.89 (d, 1H), 6.50–6.44 (m, 2H), 6.41–6.40 (d, 1H), 6.38 (s, 1H), 6.22–6.19 (dd, 1H), 4.67–4.59 (sept, 1H), 3.44–3.36 (m, 2H), 3.10–2.89 (m, 4H), 2.82–2.72 (m, 1H), 2.58–2.48 (m, 1H), 1.52–1.50 (d, 3H), 1.18–1.16 (d, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  156.0, 142.4, 141.7, 137.9, 135.1, 134.8, 132.7, 131.9, 128.0, 125.9, 123.6, 114.9, 68.8, 35.7, 33.2, 33.1, 32.1, 23.5, 21.4. HRMS (ESI) Mass calculated for  $\text{C}_{19}\text{H}_{22}\text{BrO}$  ( $\text{M}^+ + \text{H}$ ) 345.0854, found: 345.0842.

### $S_p$ -4-Bromo-12-acetoxy[2.2]paracyclophane 1g:<sup>[4]</sup>



An oven-dried flask was charged with  $S_p$ -4-bromo-12-amino[2.2]paracyclophane (400 mg, 1.32 mmol), acetic anhydride (3.30 mL, 31.0 mmol), and one drop of pyridine. The mixture was stirred at room temperature and followed by TLC. After the start material was consumed (24 h), acetic anhydride (1.70 mL, 16.0 mmol) and acetic acid (2.50 mL, 54.0 mmol) were added in one portion. After the reaction mixture was cooled to 0 °C,  $\text{NaNO}_2$  powder (140 mg, 2.00 mmol) was added in equal portions over 2 h, and followed by TLC, stirred at room temperature for 12 h. The white precipitate formed was filtered and washed with water ( $3 \times 2.0$  mL), another crop of white precipitate was obtained by addition of ice-water (20.0 mL) to the filtered solution. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10.0$  mL), the organic layers were combined, washed with brine ( $3 \times 10.0$  mL), dried over anhydrous magnesium sulphate. The solvent was removed to afford red residue, which was

combined with above white precipitate, and purified by chromatography on silica gel (petroleum ether/chloroform = 10:1) to give

*S<sub>p</sub>*-4-bromo-12-acetoxy[2.2]paracyclophane **1g** (296 mg) as a white solid, yield: 65%. Mp: 196–198 °C.  $[\alpha]_D^{20} = +47.0$  (c 1.6, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT) δ 6.97–6.96 (d, 1H), 6.72–6.71 (d, 1H), 6.60–6.57 (m, 1H), 6.53–6.45 (m, 3H), 3.46–3.38 (m, 1H), 3.18–3.01 (m, 3H), 2.94–2.85 (m, 1H), 2.83–2.71 (m, 1H), 2.70–2.66 (m, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 168.9, 148.9, 141.7, 141.5, 138.7, 135.3, 134.9, 133.7, 131.7, 130.7, 130.3, 126.4, 123.5, 35.5, 33.3, 32.6, 31.7, 21.1. Anal. Calcd. For C<sub>18</sub>H<sub>17</sub>BrO<sub>2</sub> (345.23): C, 62.62; H, 4.96. Found: C, 62.81; H, 5.07.

#### ***R<sub>p</sub>*-4-Bromo-12-dimethylamino[2.2]paracyclophane 1i**

To a solution of *R<sub>p</sub>*-4-bromo-12-amino[2.2]paracyclophane (302 mg, 1.0 mmol) in acetone (3.0 mL) was added anhydrous K<sub>2</sub>CO<sub>3</sub> powder (552 mg, 4.0 mmol), and dimethyl sulfate (0.76 mL, 8.0 mmol) was added dropwise over a 30 minute period. The mixture was stirred at room temperature and followed by TLC. After the start material was consumed (36 h), concentrated NH<sub>3</sub> (25%, 1.48 mL, 20.0 mmol) was added dropwise over 10 minutes, and the mixture was stirred at room temperature for 1 h. The mixture was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5.0 mL), and the organic layers were combined. The solvent was removed and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to furnish *R<sub>p</sub>*-4-bromo-12-dimethylamino [2.2]paracyclophane **1i** (313 mg) as a white solid, yield: 95%. Mp: 99–102 °C.  $[\alpha]_D^{20} = -52.0$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, RT) δ 6.78 (s, 1H), 6.52–6.45 (m, 3H), 6.27–6.19 (m, 2H), 3.46–3.41 (m, 2H), 3.02–2.96 (m, 4H), 2.79 (s, 6H), 2.74–2.68 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, RT) δ 140.1, 139.5, 138.4, 135.6, 134.7, 134.4, 131.2, 125.2, 118.3, 43.5, 34.6, 34.3, 34.1, 33.1. Anal. Calcd. For C<sub>18</sub>H<sub>20</sub>NBr (330.26): C, 65.46; H, 6.10; N, 4.24. Found: C, 65.36; H, 6.12; N, 4.16.

#### **4*R<sub>p</sub>*,13*S<sub>p</sub>*-4-Bromo-13-methoxy[2.2]paracyclophane 1k:**

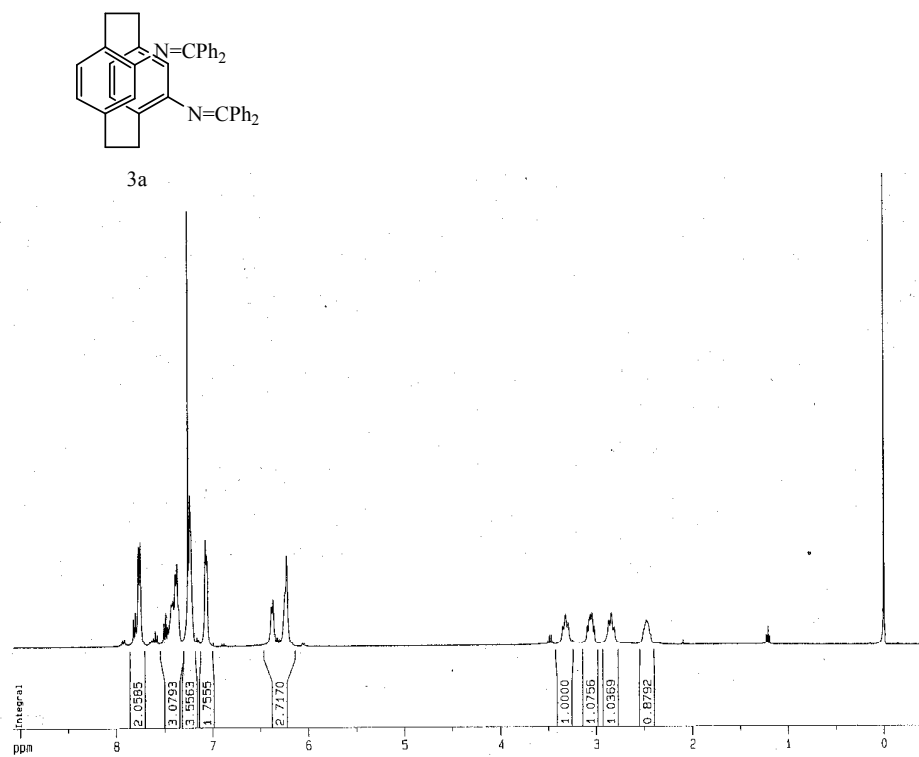
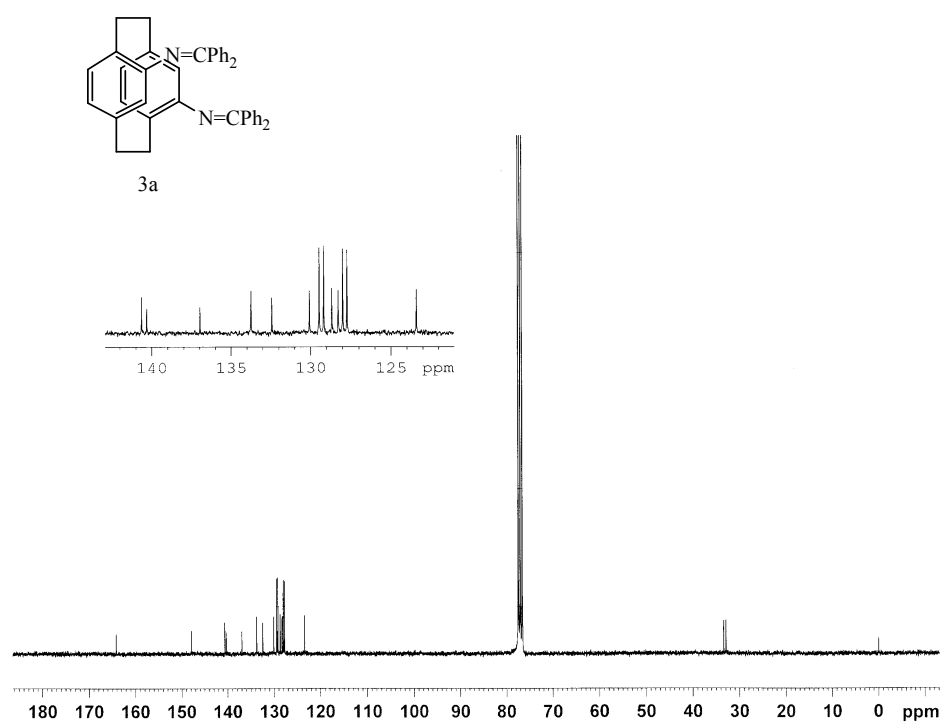
Following a modified version of Bolm's procedure <sup>[5]</sup>, a white solid was obtained; Yield: 92%; Mp: 171–172 °C;  $[\alpha]_D^{20} = -25.4$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (600 MHz, DMSO/CDCl<sub>3</sub>, RT) δ 6.70–6.69 (d, 1H), 6.50–6.49 (d, 1H), 6.48–6.46 (dd, 1H), 6.42–6.41 (d, 1H), 6.30–6.28 (dd, 1H), 5.81–5.80 (d, 1H), 3.74 (s, 3H), 3.62–3.58 (m, 2H), 3.06–3.01 (m, 4H), 2.99–2.95 (m, 1H), 2.75–2.73 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT) δ 158.7, 141.4, 140.5, 138.8, 135.4, 135.3, 134.7, 132.3, 126.7, 124.5, 122.9, 114.8, 54.8, 35.2, 34.7, 34.0, 30.1. HRMS (ESI) Mass calculated for C<sub>17</sub>H<sub>18</sub>BrO (M<sup>+</sup> + H) 317.0541, found: 317.0531.

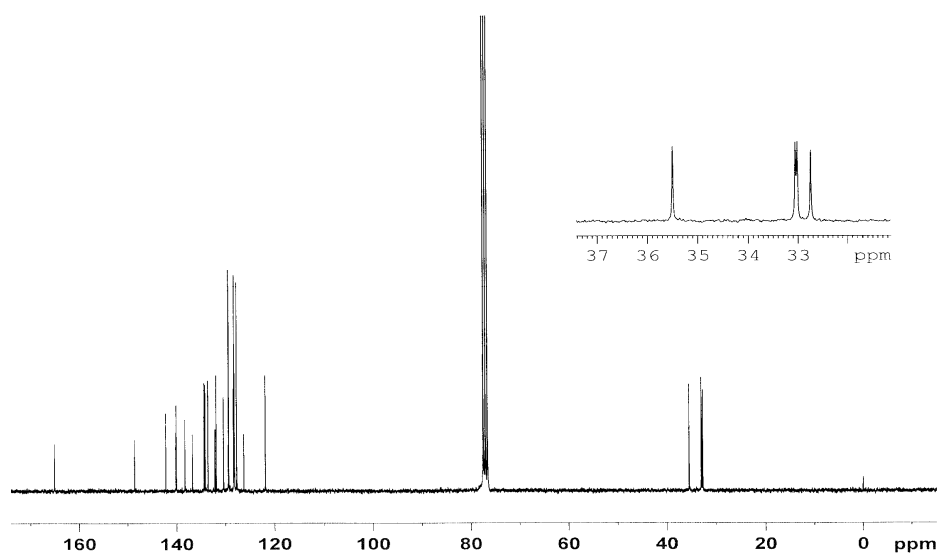
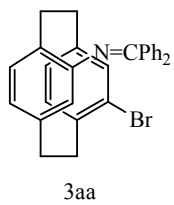
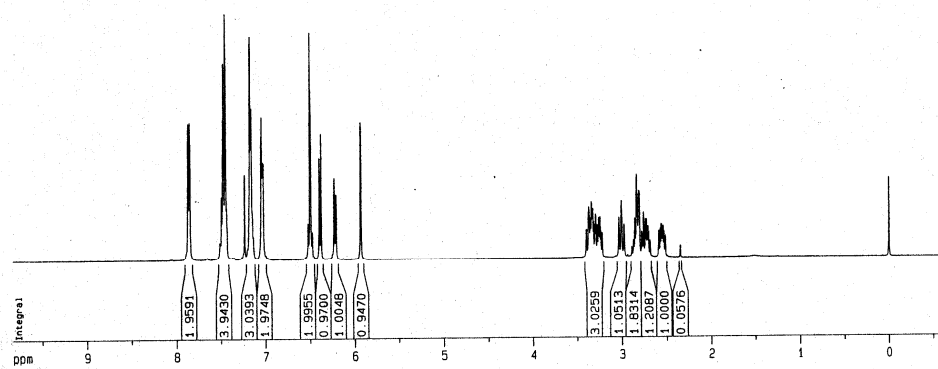
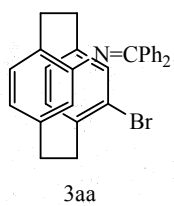
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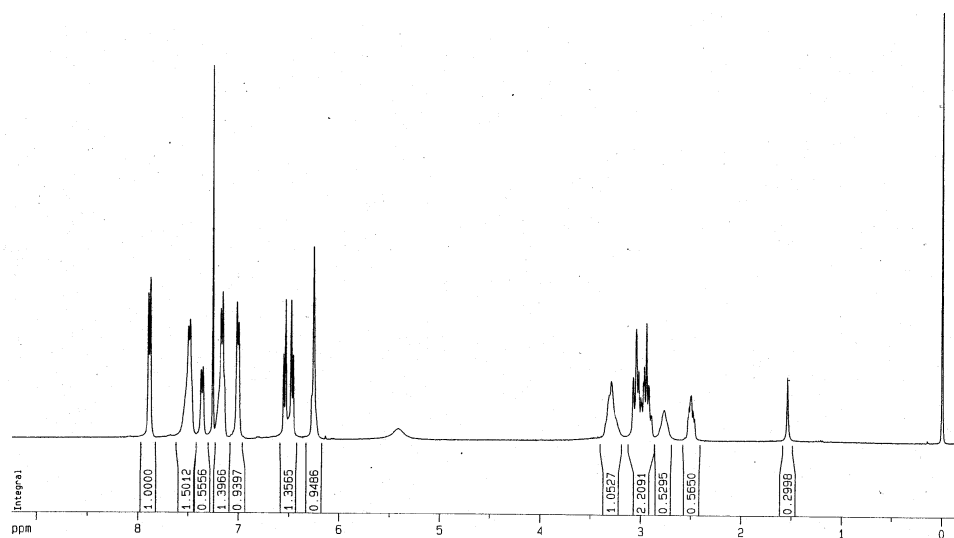
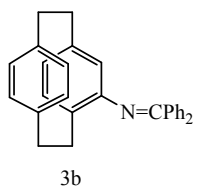
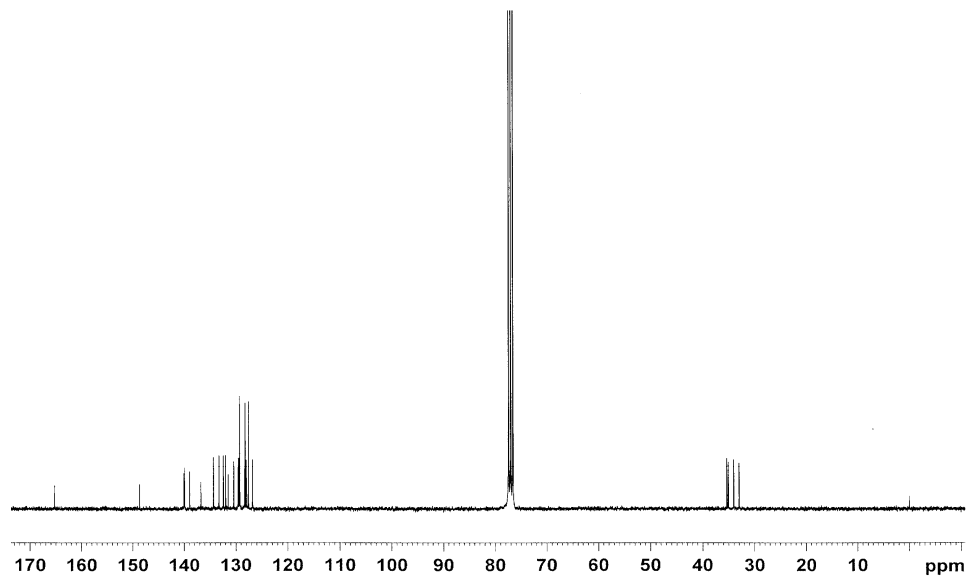
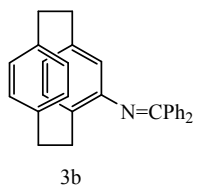
Following a modified version of Bolm's procedure <sup>[5]</sup>, a white solid was obtained; Yield: 82%; Mp: 110–112 °C;  $[\alpha]_D^{20} = -32.9$  (c 0.15, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, RT)  $\delta$  6.70–6.69 (d, 1H), 6.50–6.42 (m, 3H), 6.24–6.21 (dd, 1H), 5.87–5.86 (d, 1H), 4.45–4.37 (sept, 1H), 3.65–3.53 (m, 2H), 3.03–2.87 (m, 5H), 2.74–2.63 (m, 1H), 1.45–1.43 (d, 3H), 1.15–1.13 (d, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, RT)  $\delta$  156.9, 140.7, 140.5, 138.9, 135.5, 135.1, 134.9, 132.2, 127.9, 124.6, 123.3, 118.7, 69.9, 35.2, 34.7, 34.3, 30.2, 22.9, 21.2. HRMS (ESI) Mass calculated for C<sub>19</sub>H<sub>22</sub>BrO (M<sup>+</sup> + H) 345.0854, found: 345.0845.

## References:

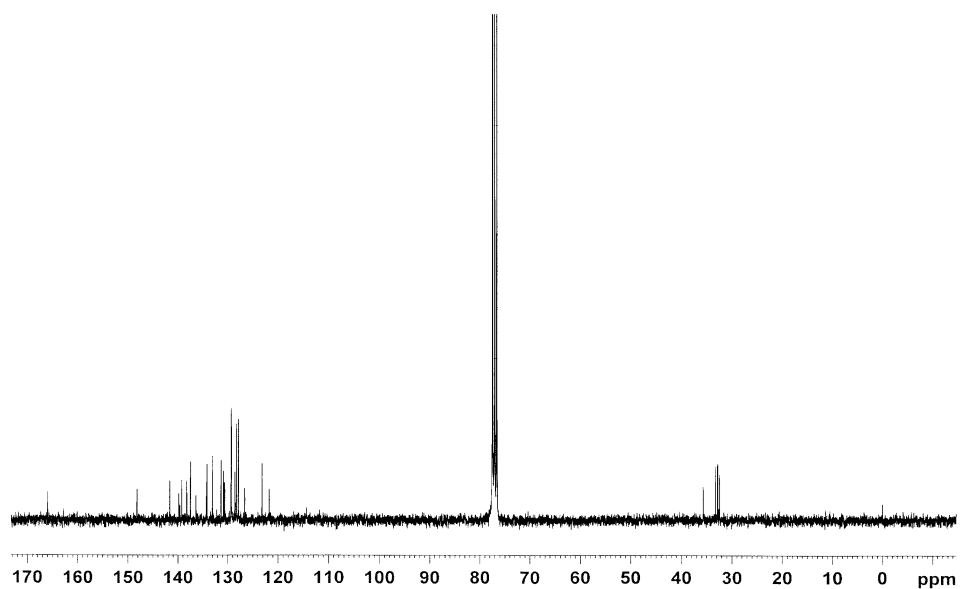
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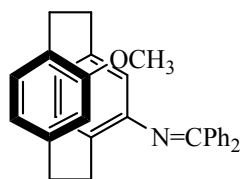




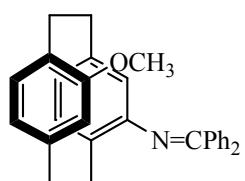
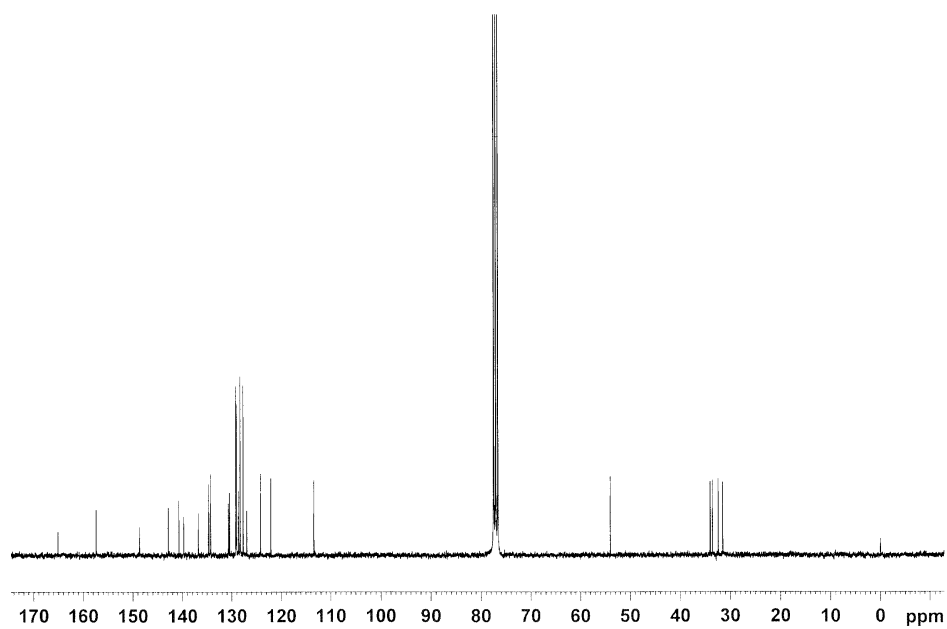




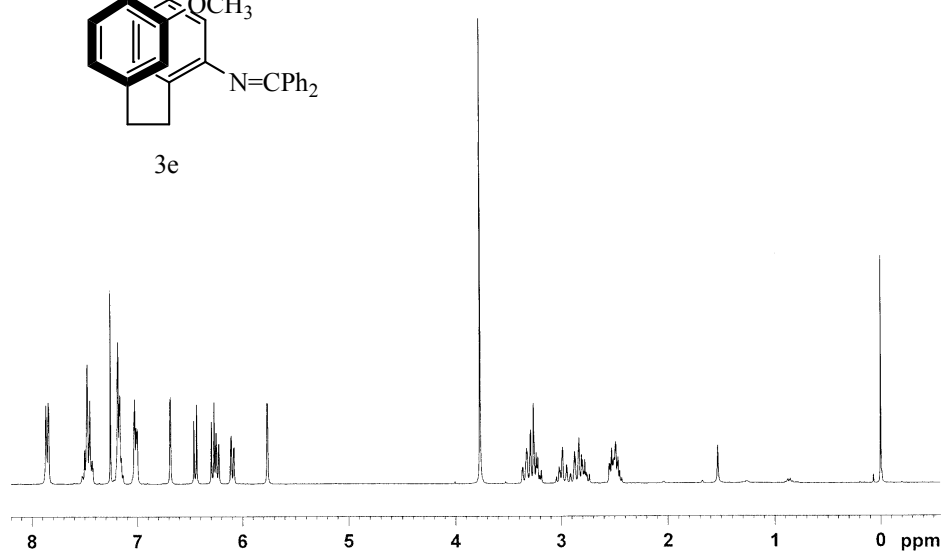


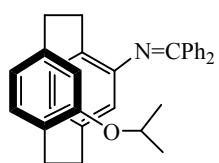


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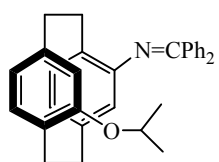
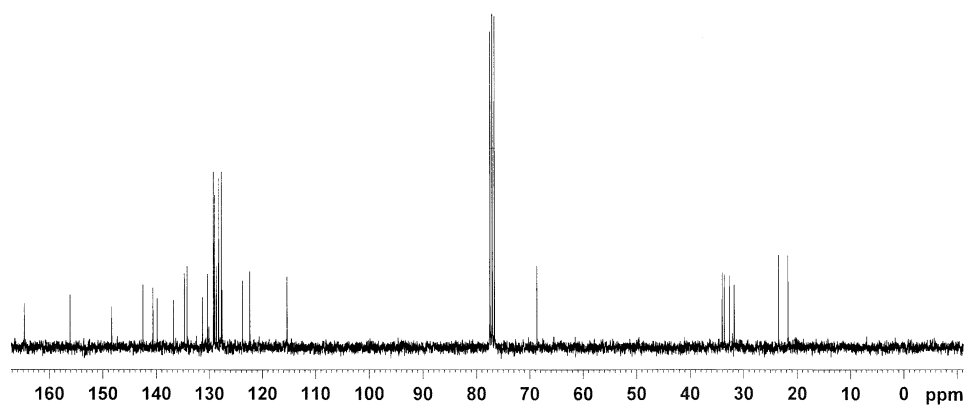


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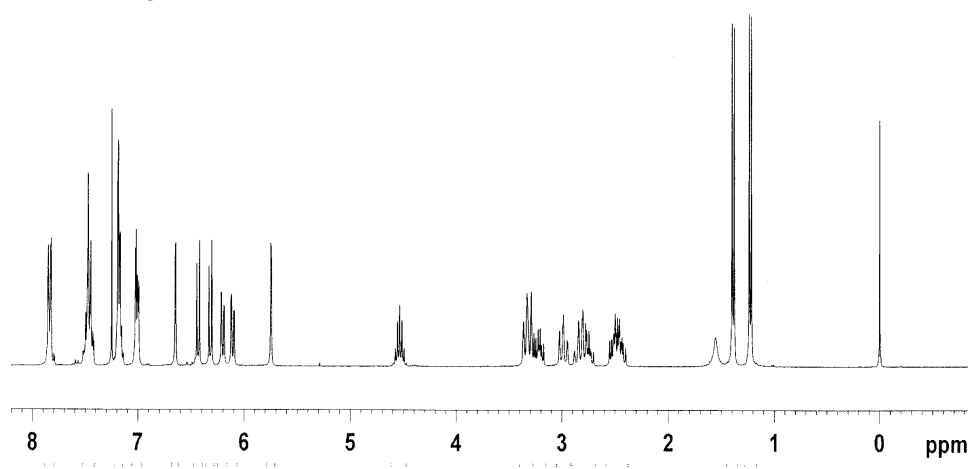


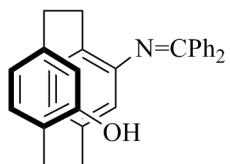


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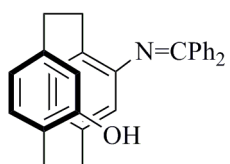
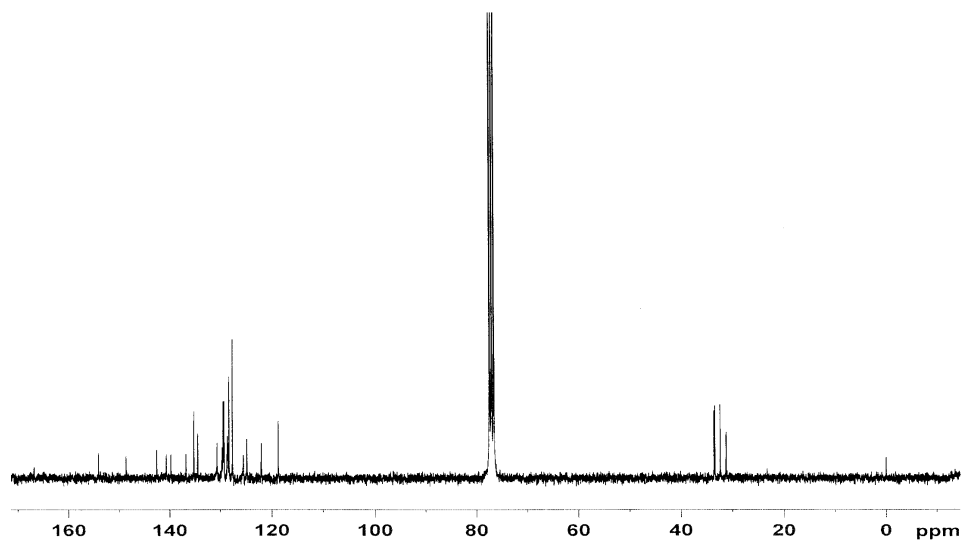


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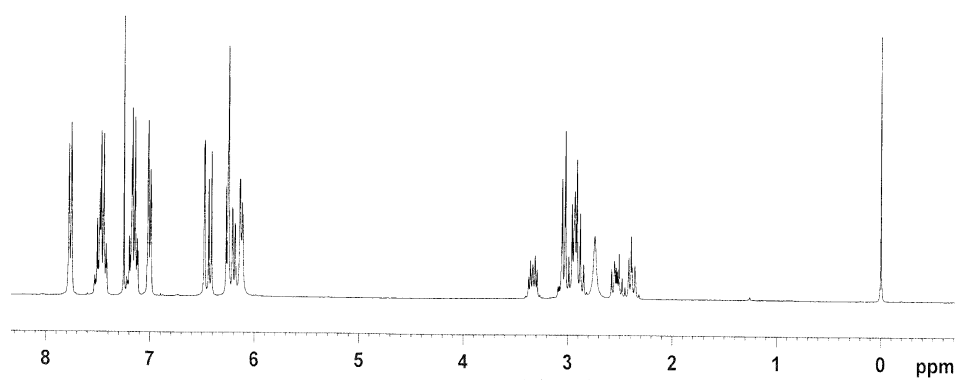


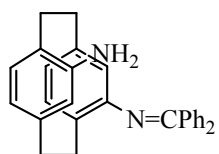


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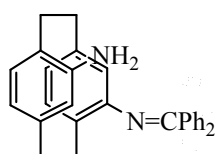
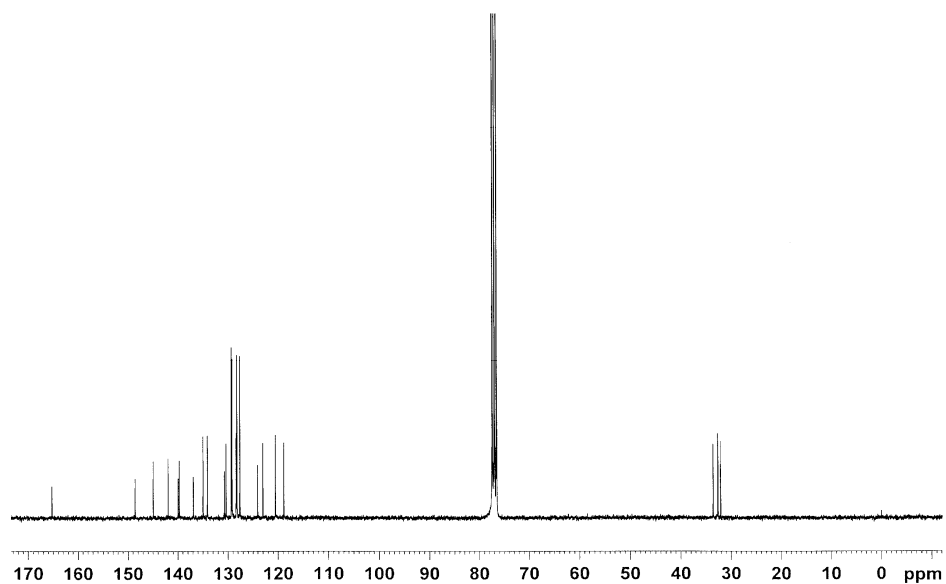


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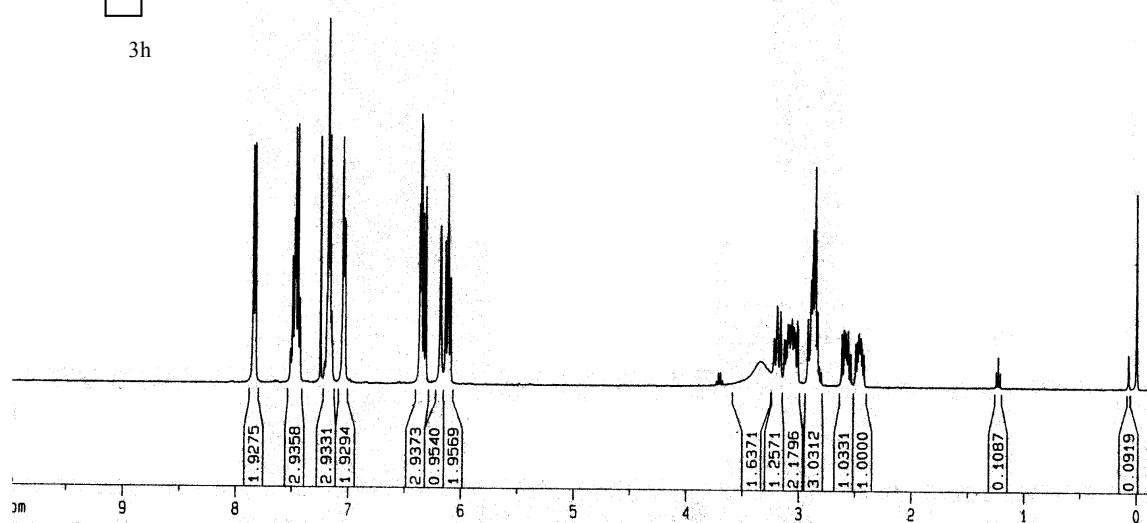


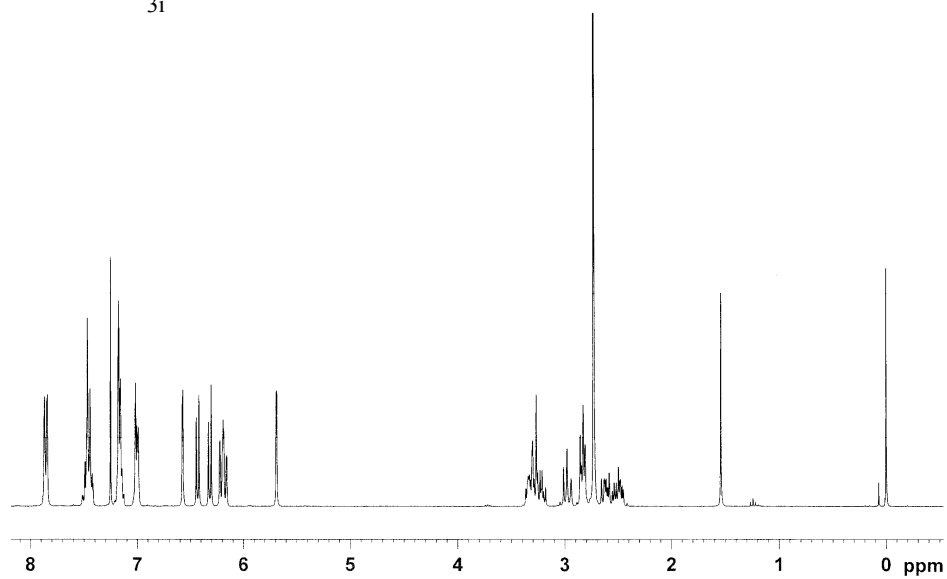
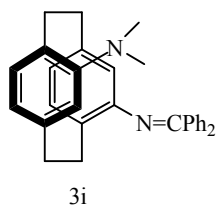
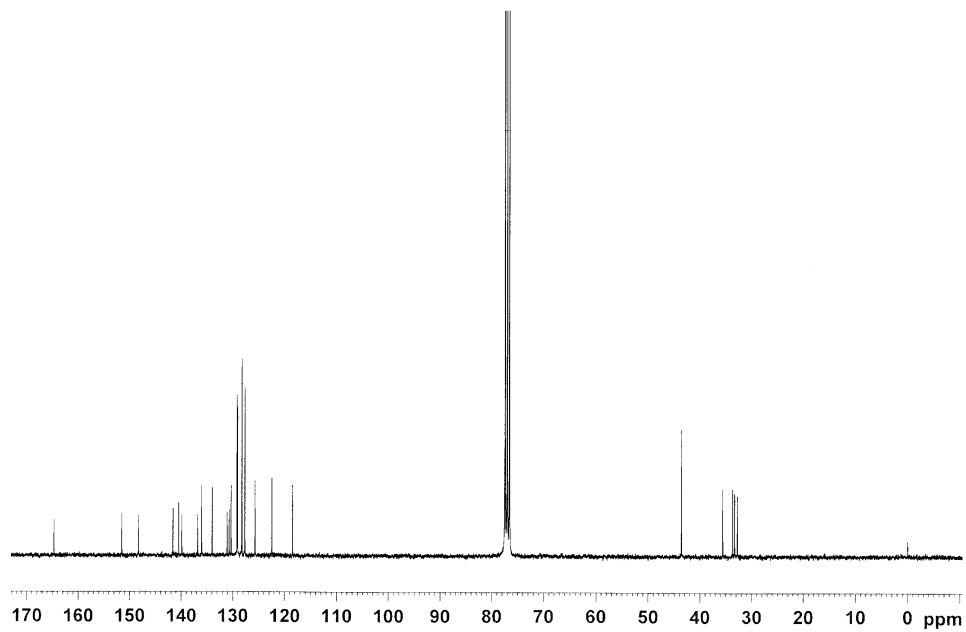
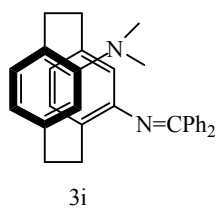


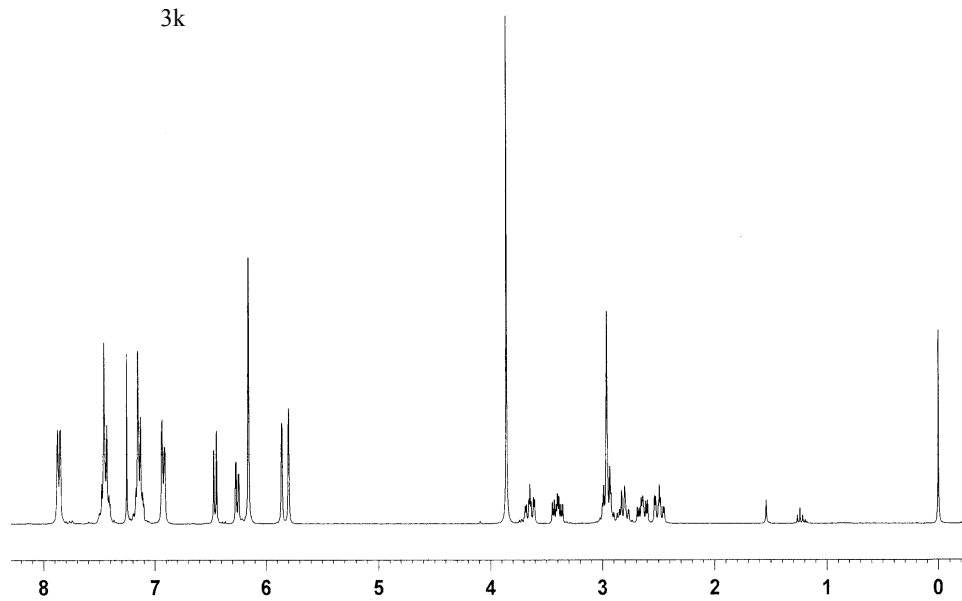
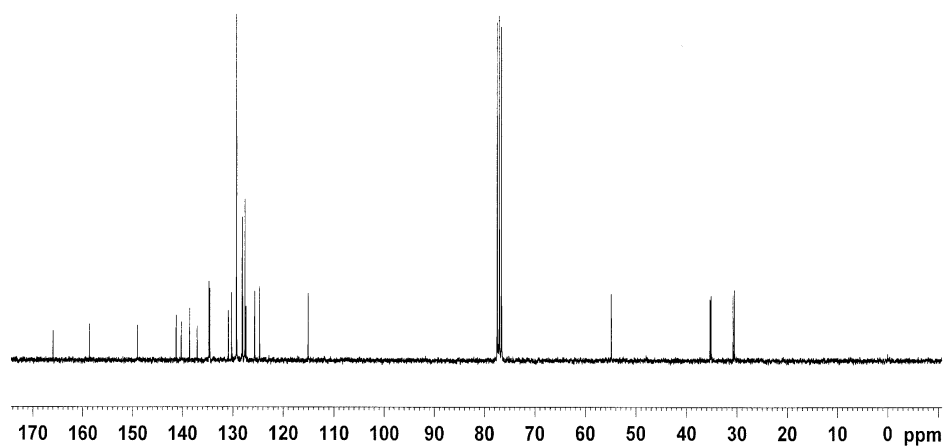
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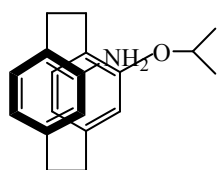


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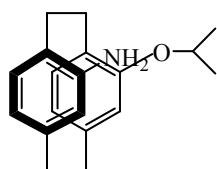
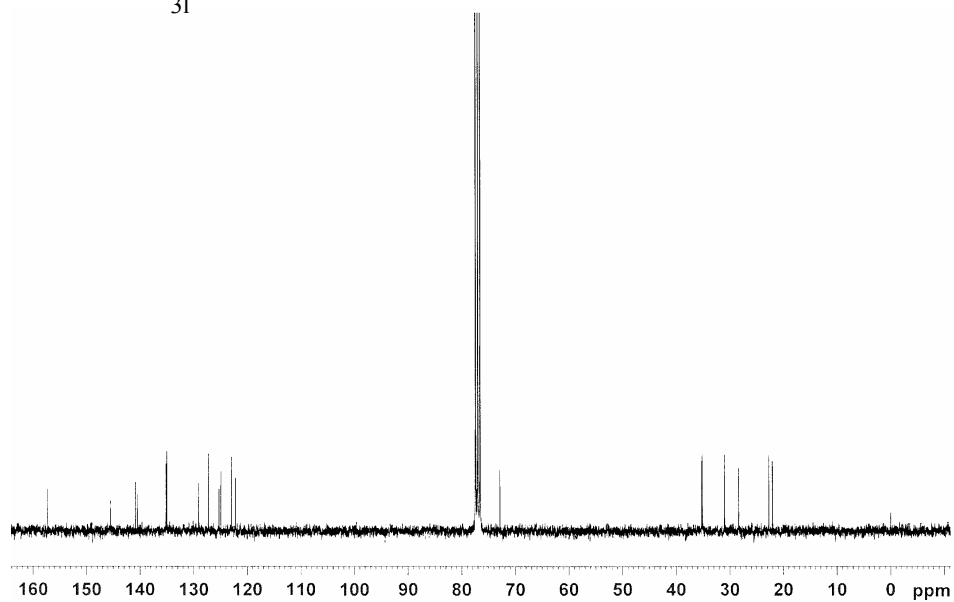




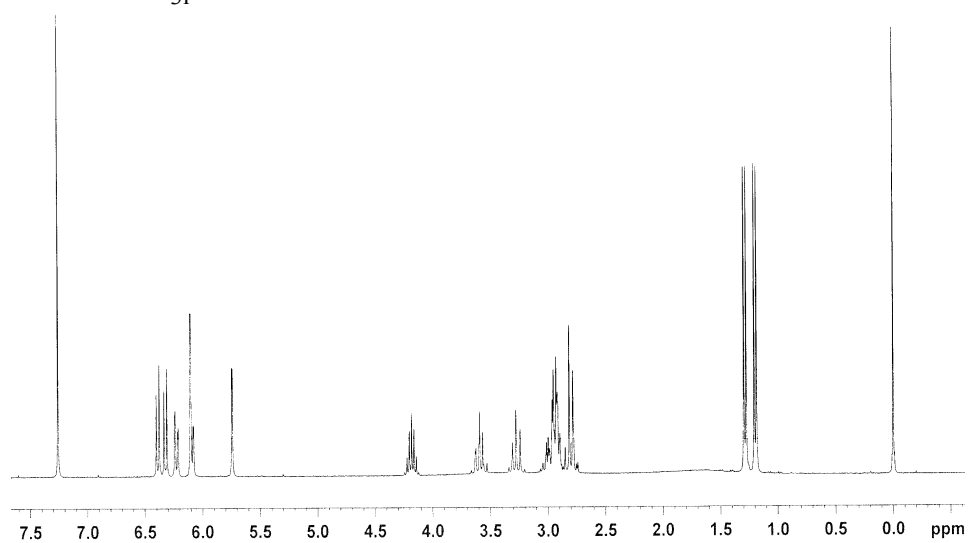




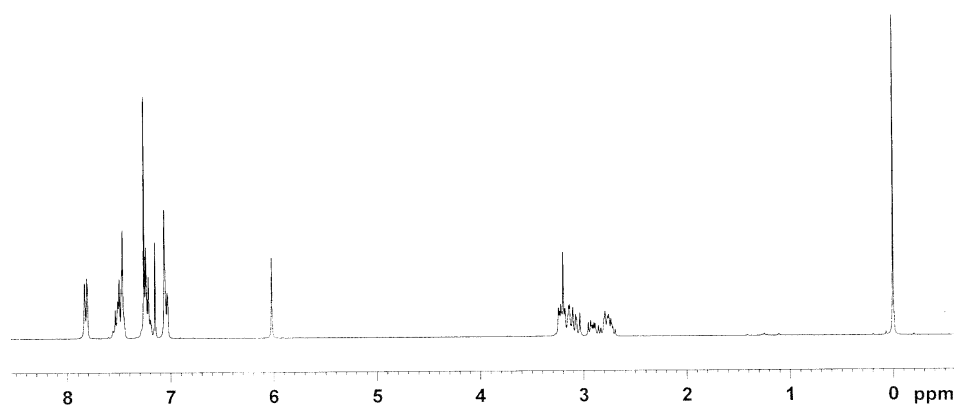
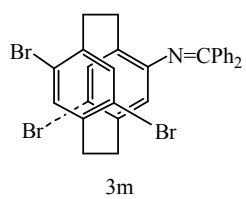
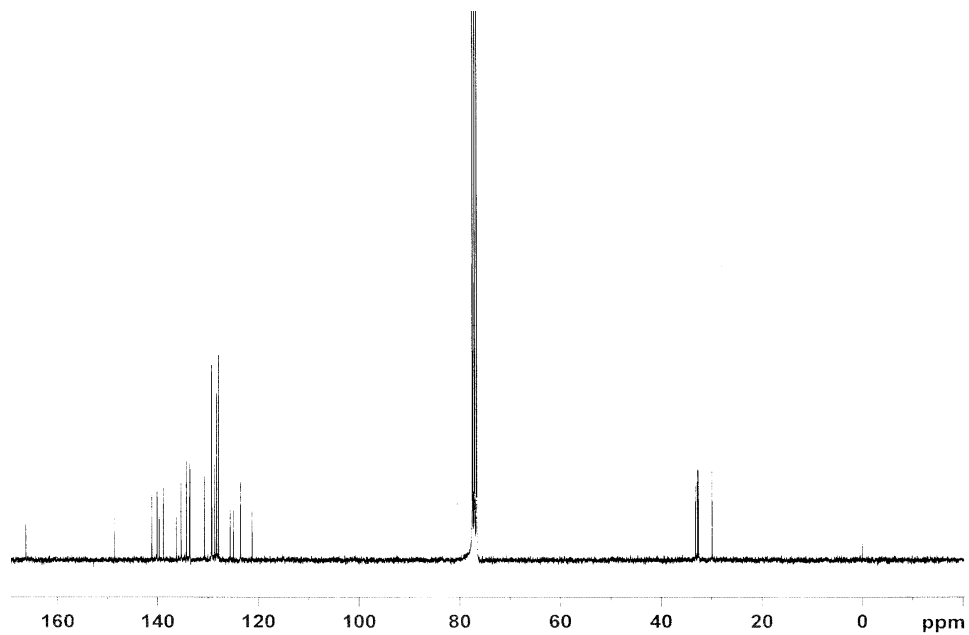
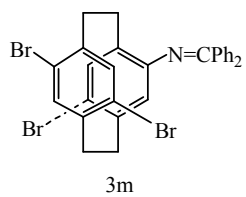
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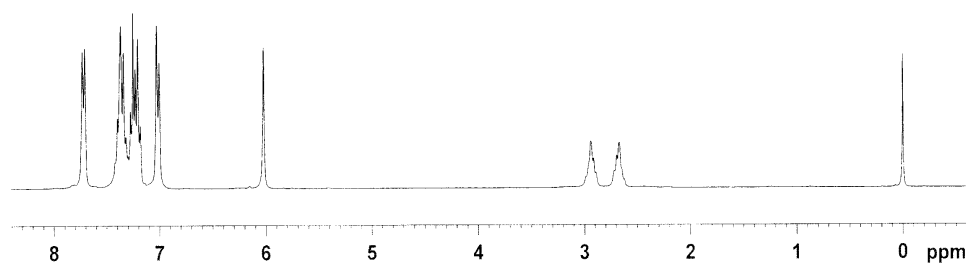
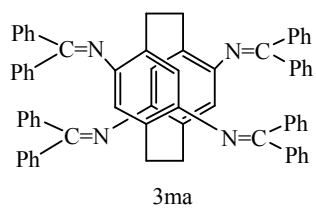
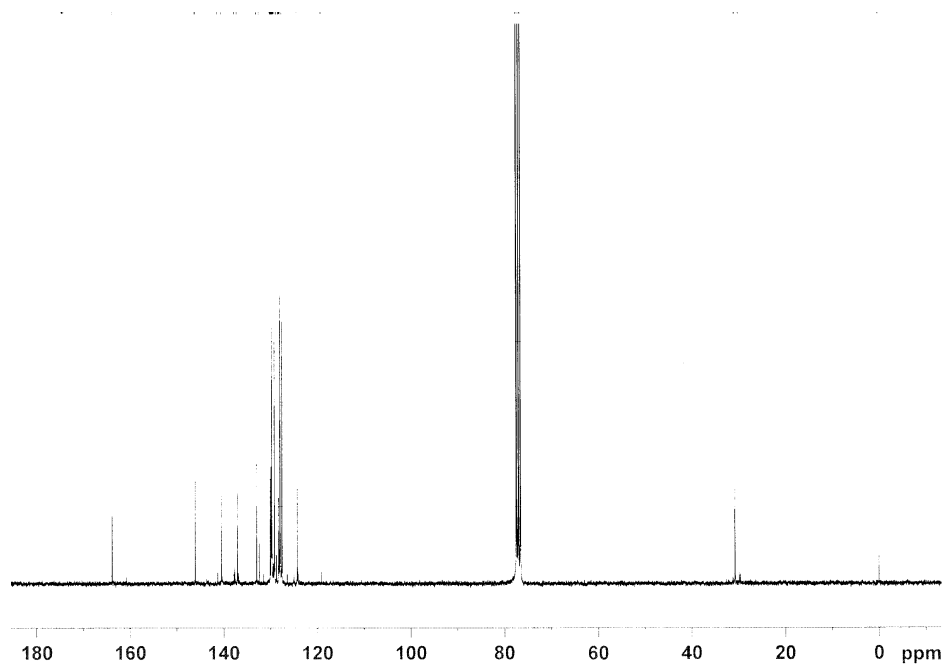
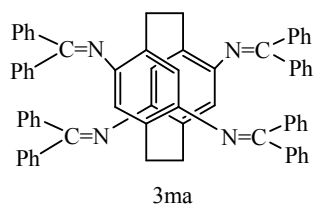


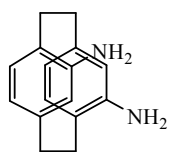
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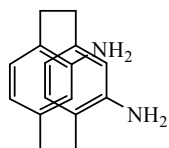
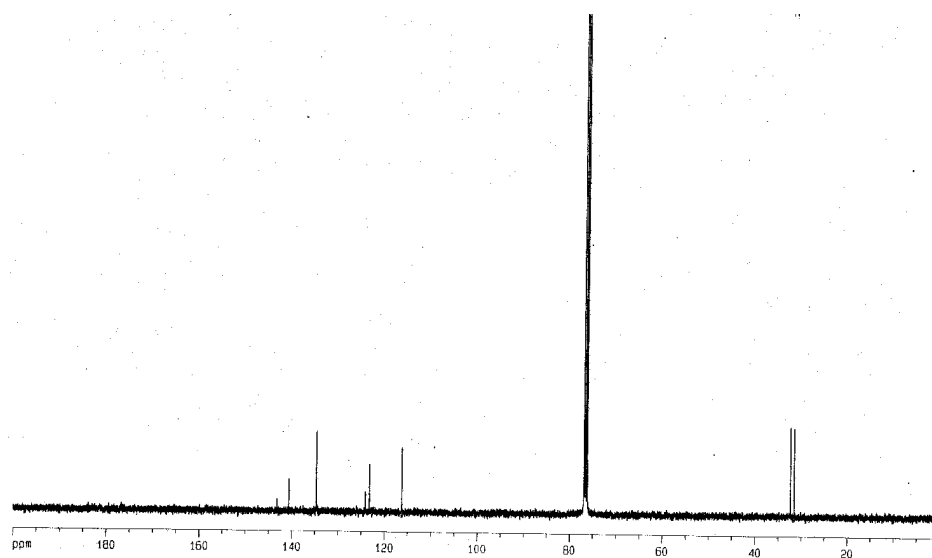




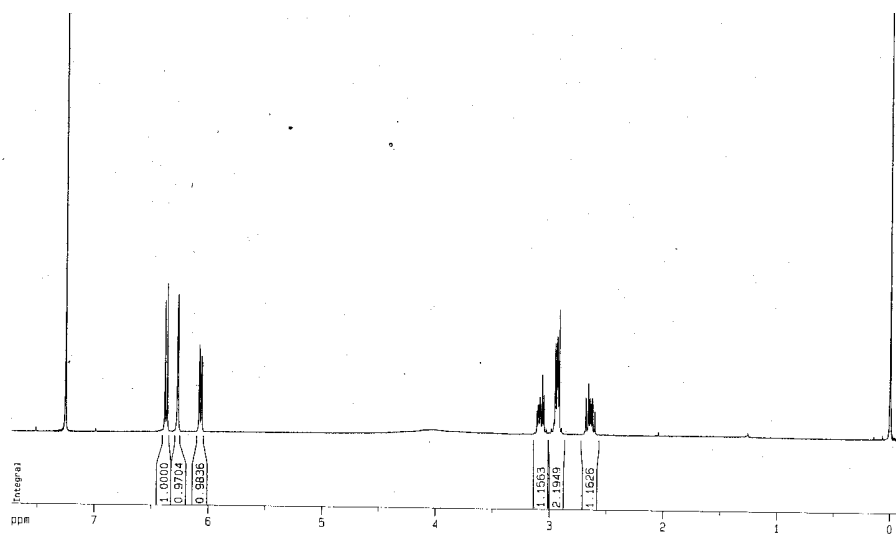


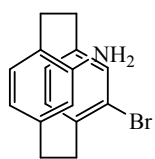


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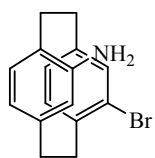
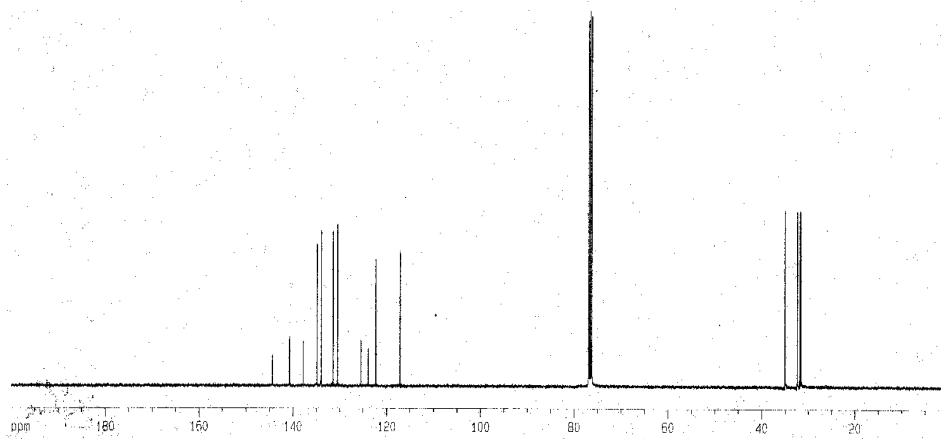


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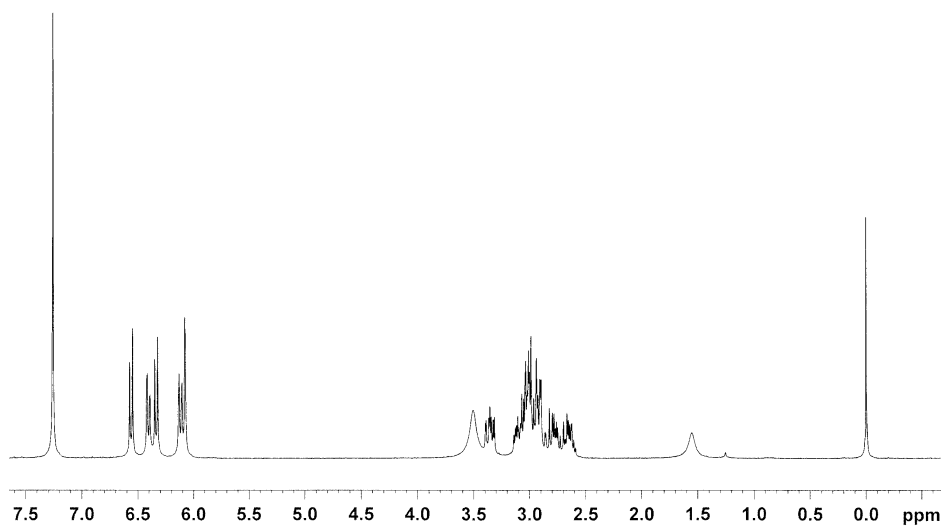


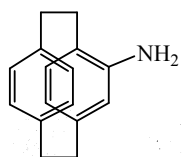


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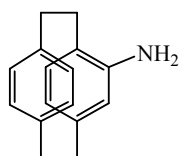
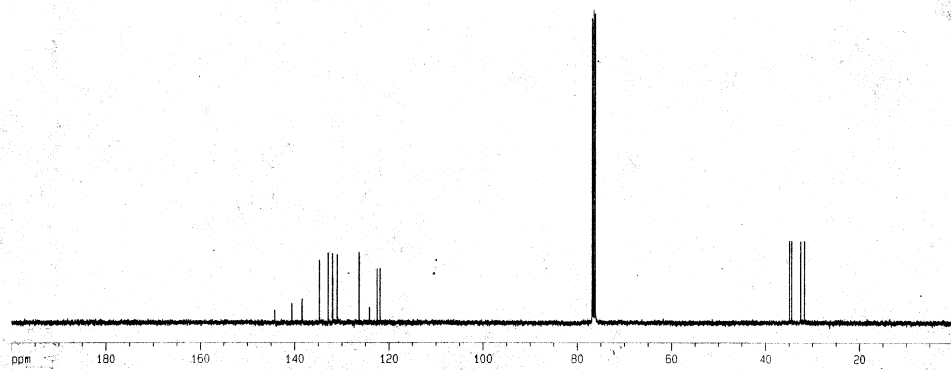


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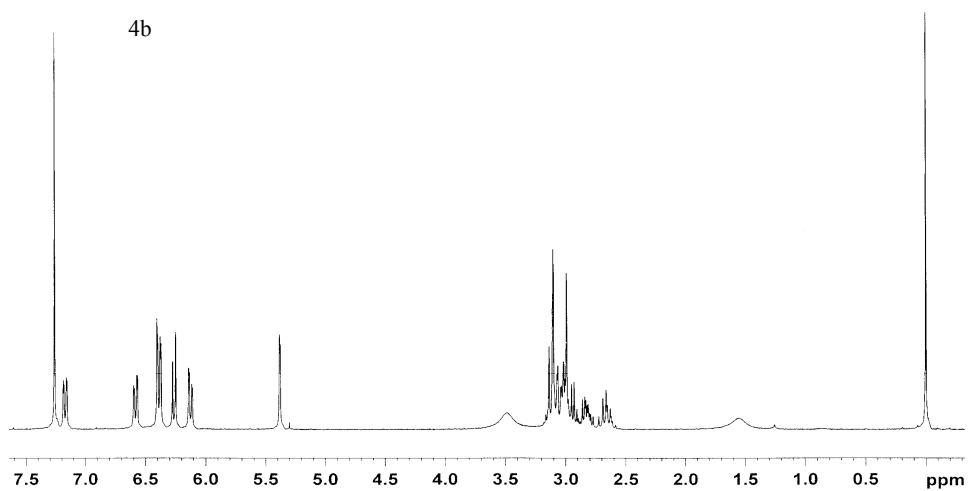


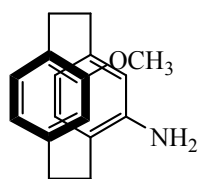


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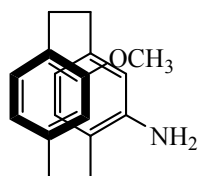
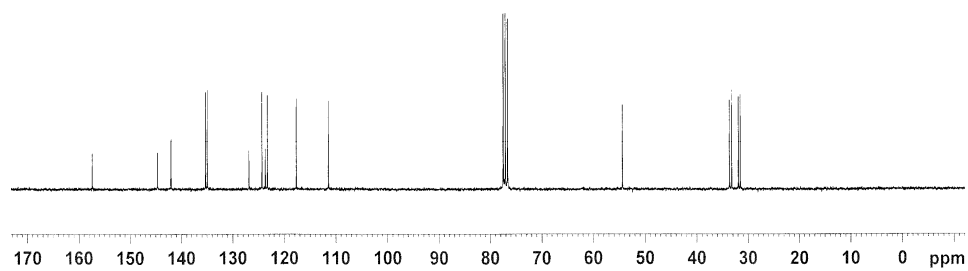


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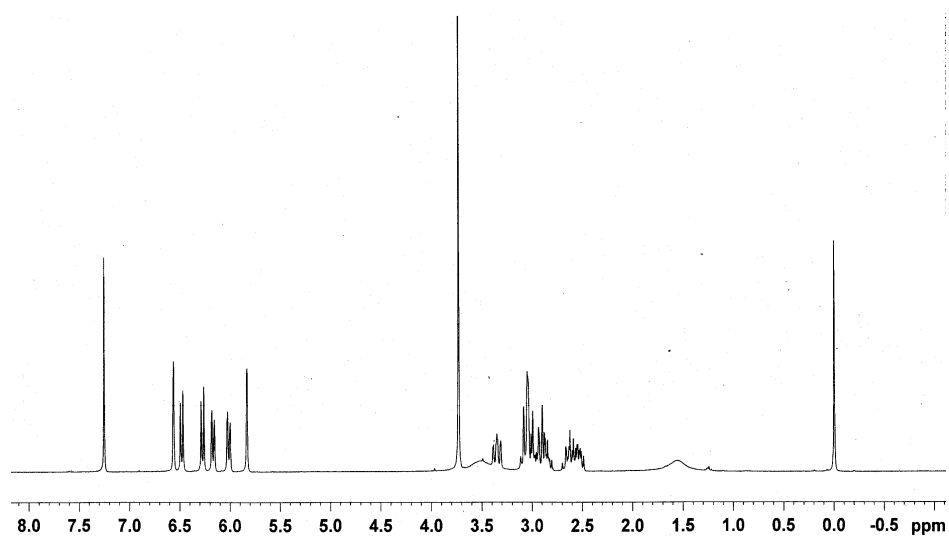


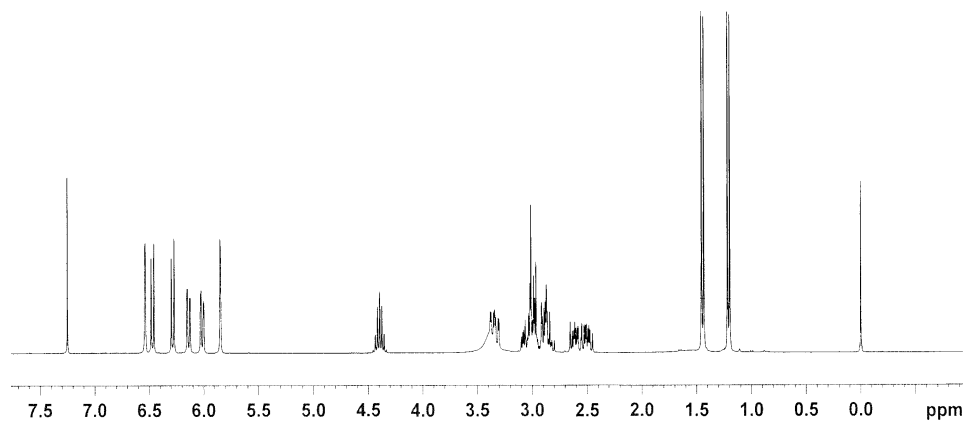
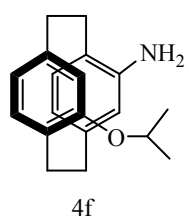
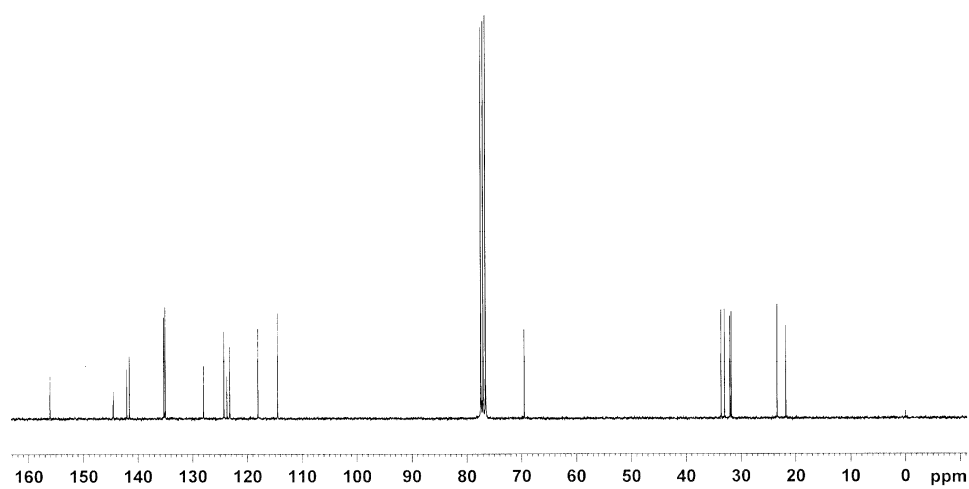
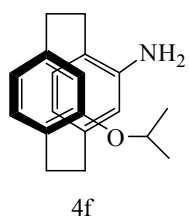


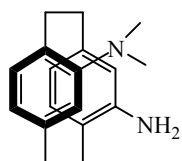
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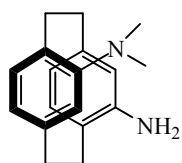
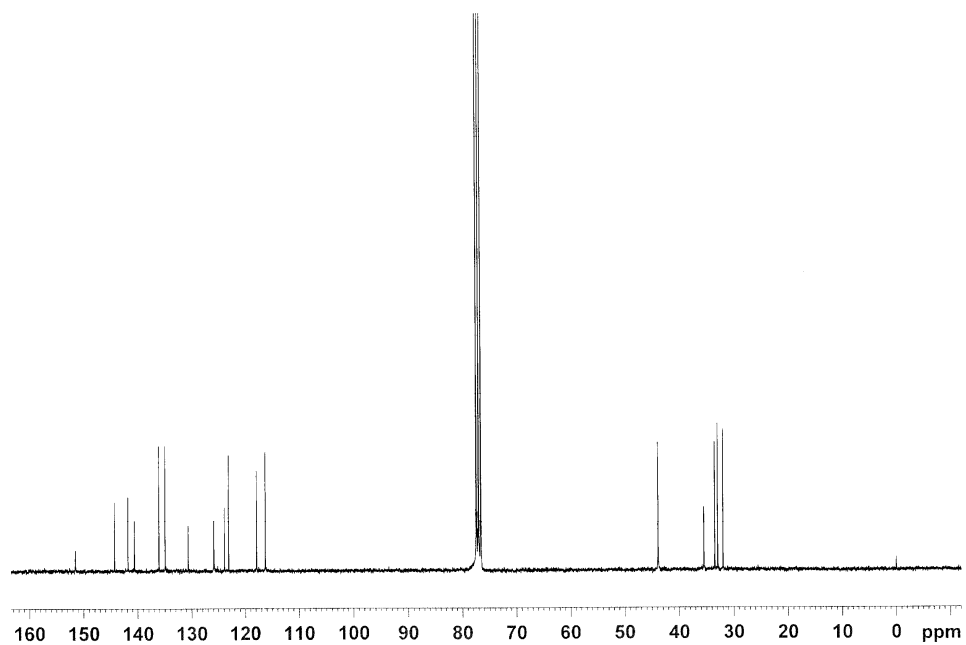
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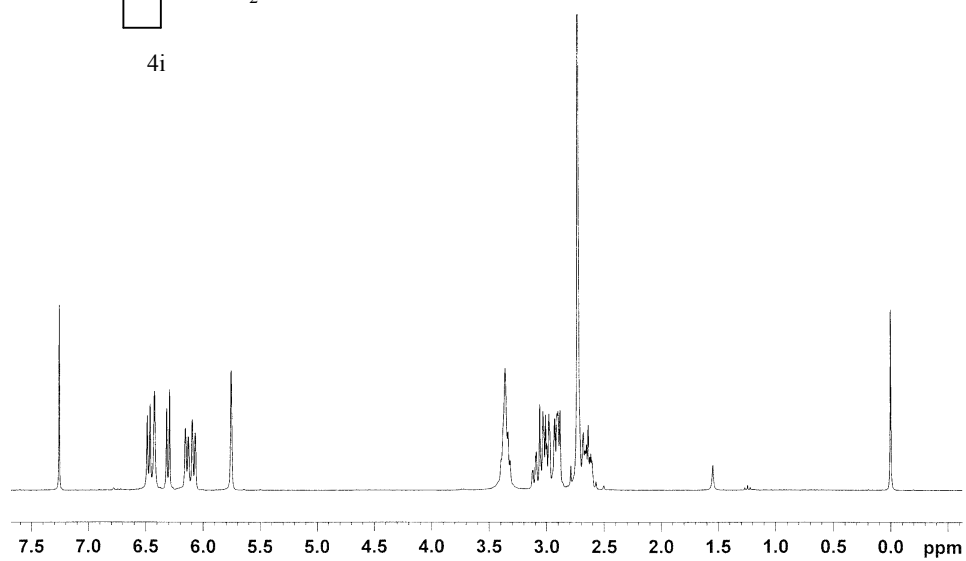




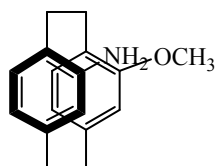
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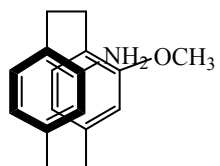
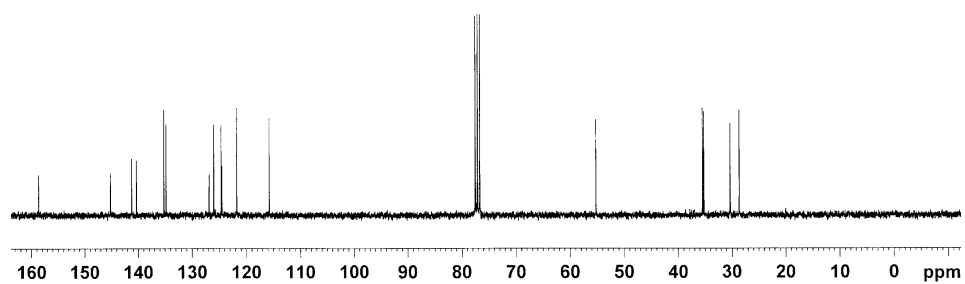
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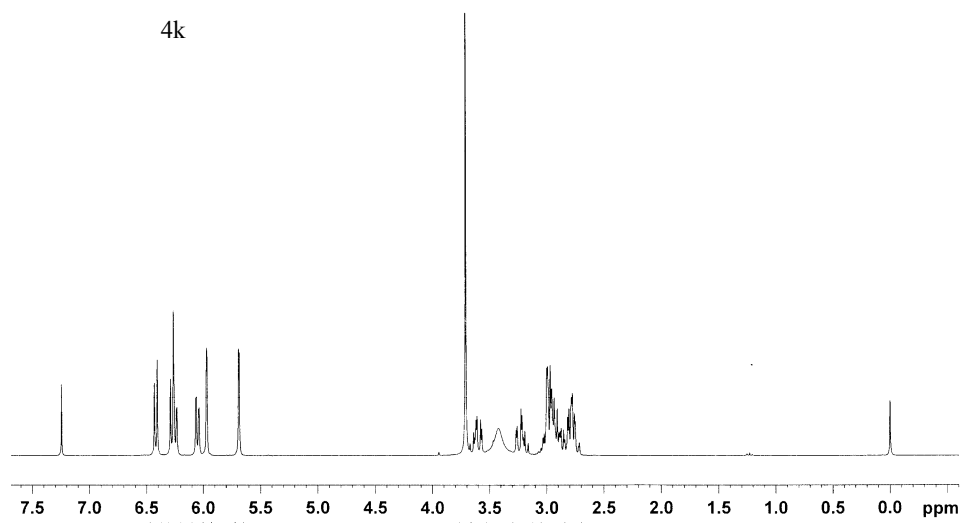


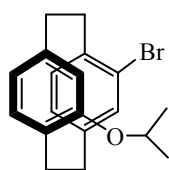


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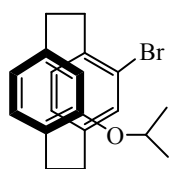
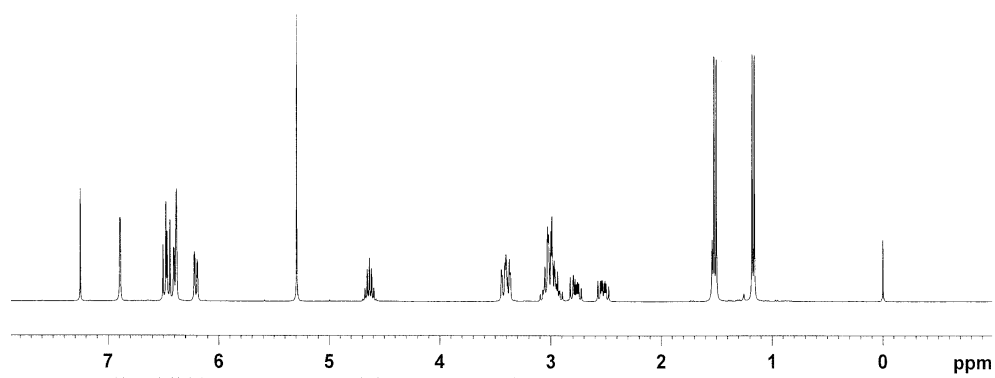


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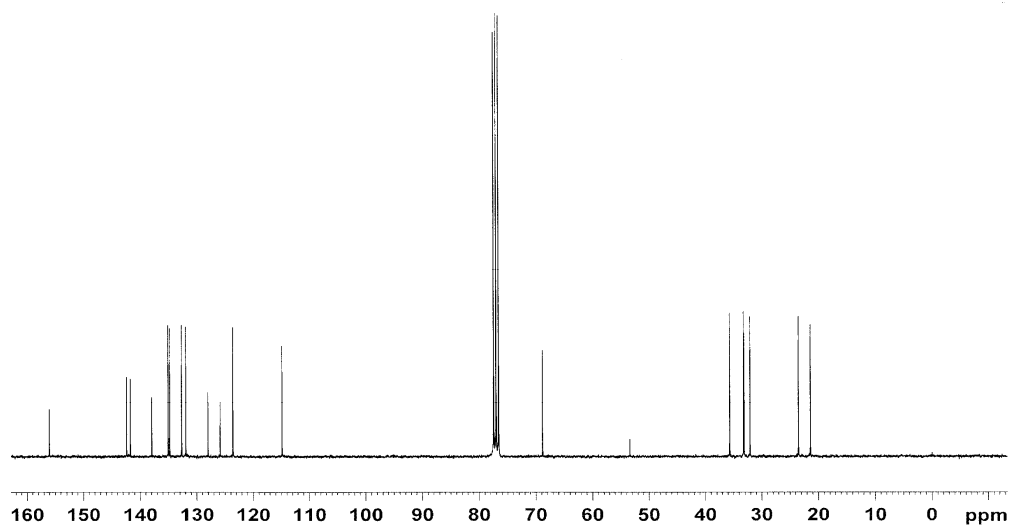


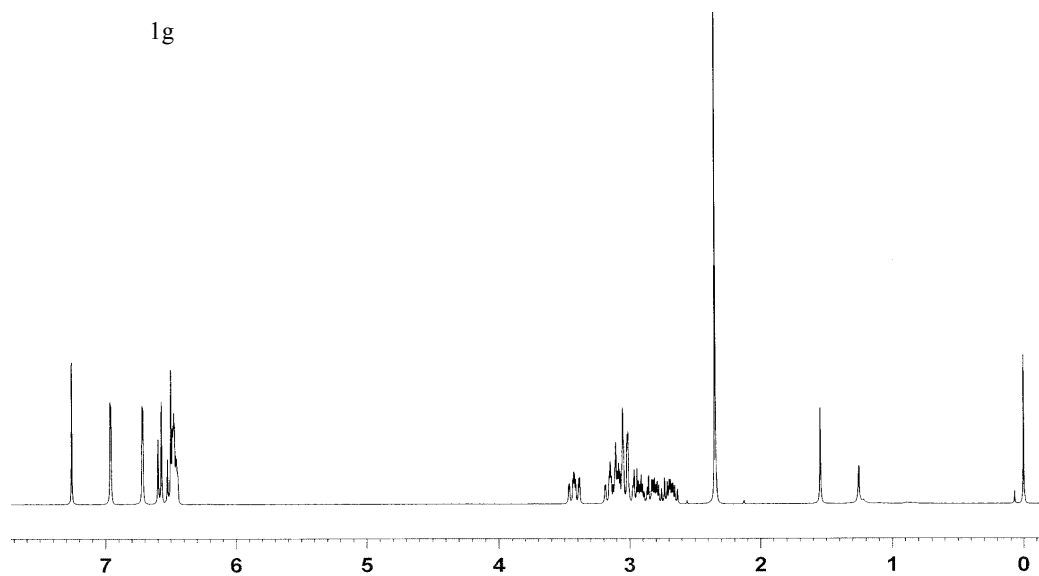
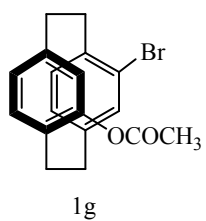
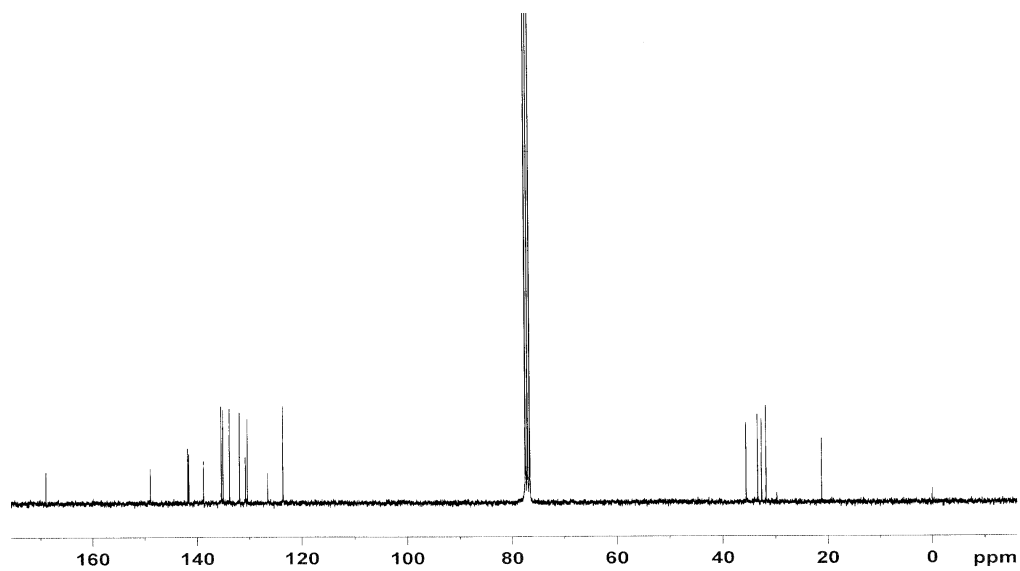
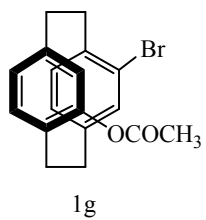


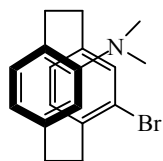
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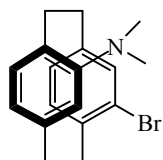
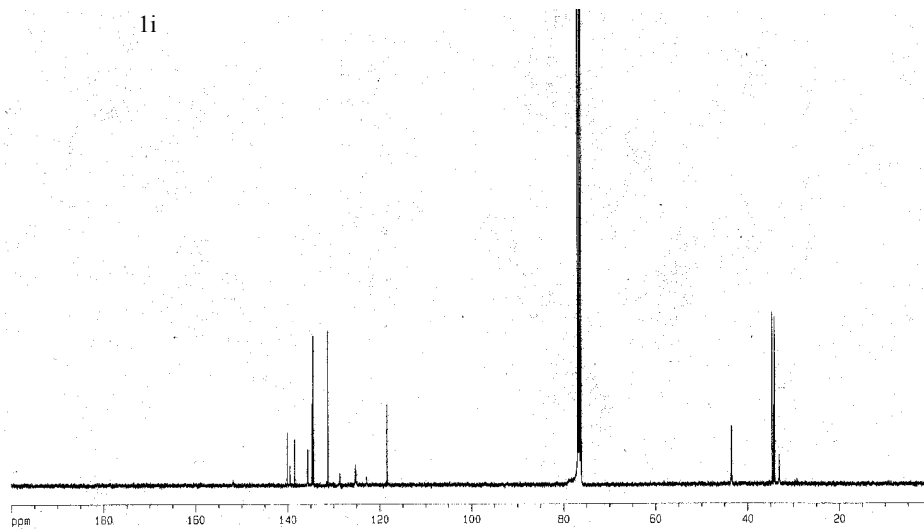
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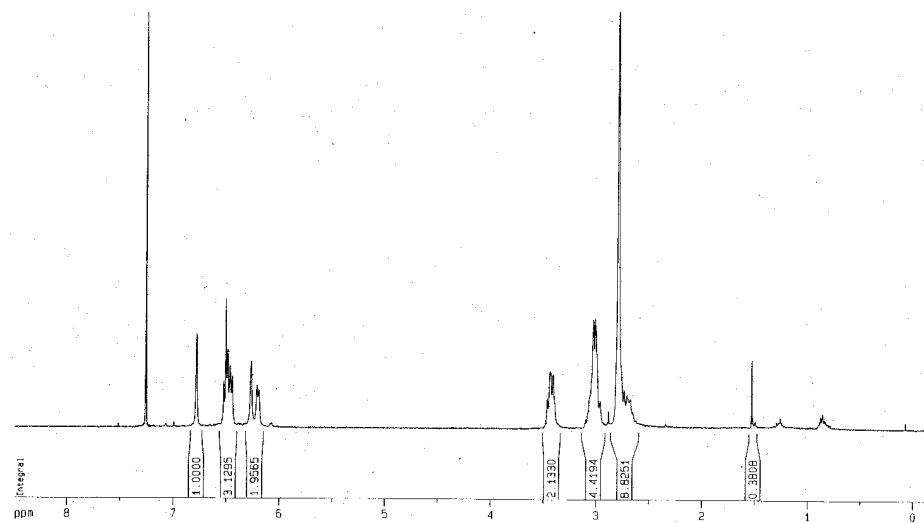


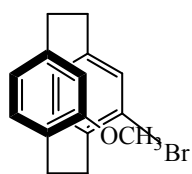


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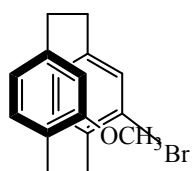
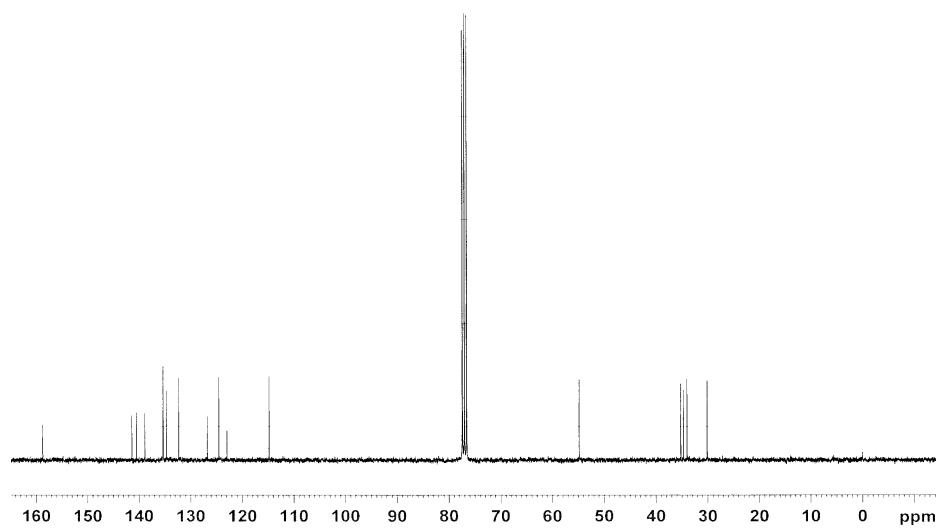


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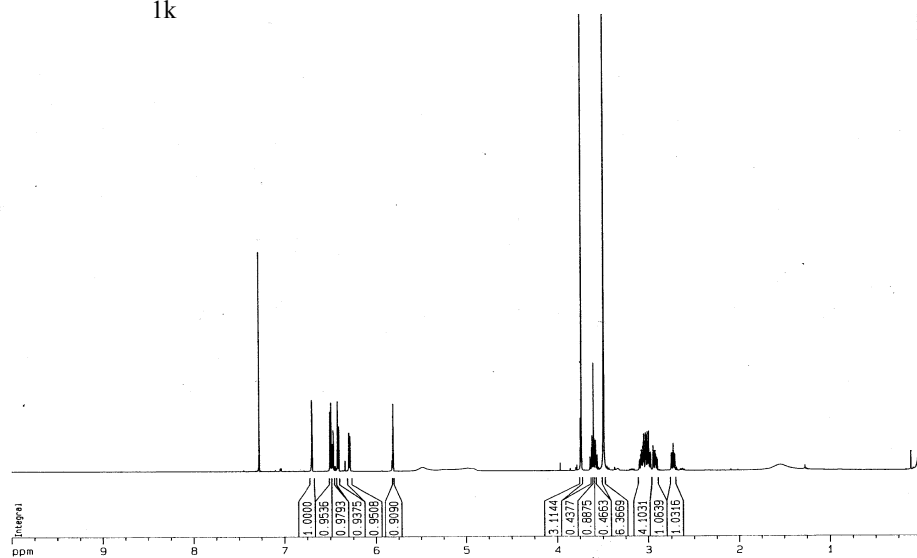


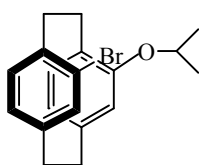


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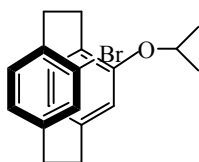
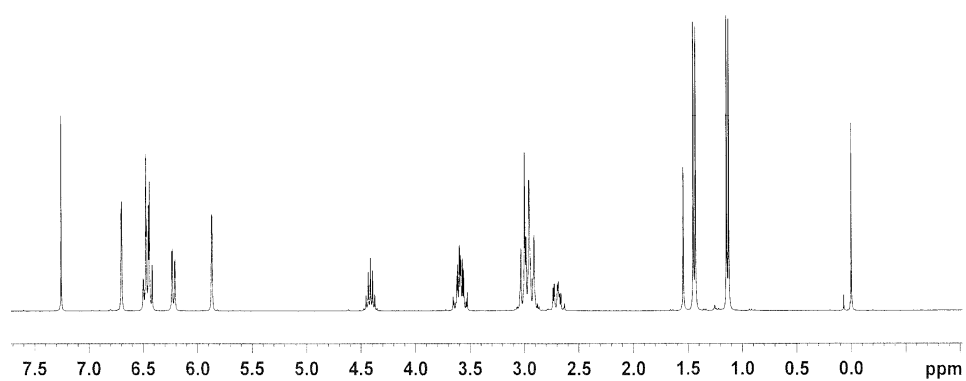


1k





11



11

