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of Reliable Methods
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of Organic Compounds

Working with Hazardous Chemicals

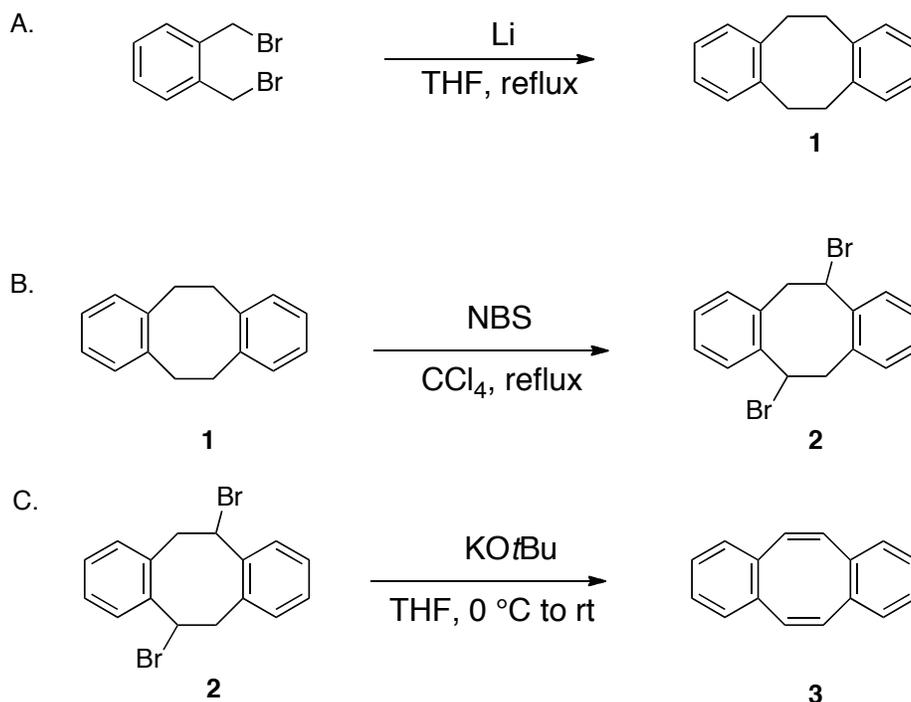
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Dibenzo[*a,e*]cyclooctene: Multi-gram Synthesis of a Bidentate Ligand



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Checked by Tohru Fukuyama and Takuya Nishimura.

Discussion Addendum *Org. Synth.* **2020**, *97*, 66-78

*Caution! Once α,α' -dibromo-*o*-xylene is dissolved in an organic solvent it becomes lachrymatory. The use of granular lithium on a larger scale requires special care due to the exothermic formation of lithium bromide.*

1. Procedure

A. *5,6,11,12-Tetrahydrodibenzo[*a,e*]cyclooctene (1)*. A 1-L, three-necked round-bottomed flask, equipped with a 4-cm egg-shaped magnetic stirring bar, a reflux condenser, an internal thermometer and a 250-mL pressure-equalizing dropping funnel (capped with a rubber septum), is flame-dried and purged with argon. Degassed THF (200 mL) (Note 1) is added and subsequently granular lithium (6.63 g, 956 mmol, 2.5 equiv) (Note 2). The dropping funnel is charged with a solution of freshly sublimed α,α' -dibromo-*o*-xylene (101 g, 382 mmol) in degassed THF (150 mL)

(Note 3). This solution is then added dropwise to the stirred suspension of granular lithium over a period of 1.5 h, which begins to reflux after 20 min. During the period of addition the internal temperature of the mixture is kept between 65 °C and 70 °C (Note 4). After complete addition, the mixture is refluxed for 2 h (oil bath) until TLC-analysis indicates complete consumption of the substrate (Notes 5, 6 and 7).

The reaction mixture is allowed to cool to room temperature and is then, for removal of residual lithium, filtered through a fritted glass funnel (5.0 cm diameter, porosity 0). The funnel is subsequently rinsed with THF (100 mL) (Note 1). The filtrate is concentrated by rotary evaporation at a bath temperature of 40 °C (255-225 mmHg) and then at 50 °C (7.5 mmHg) for 1 h in order to remove THF (Note 8). Dichloromethane (700 mL) is added to the residue. After stirring for 2 min, insoluble material (Note 9) is removed by filtration with a fritted glass funnel (8.0 cm diameter, porosity 4) filled with silica gel (100 g) (Note 10). The residue is washed with dichloromethane (700 mL) and the filtrate dried over Na₂SO₄ (50 g). The latter is removed by filtration and the filtrate concentrated at 40 °C by rotary evaporation (675-525 mmHg and then 15 mmHg) for 1 h. The crude product remains as a pale yellow semifluidic mass (40.5 g), which solidifies under vacuum overnight (25 °C, 0.3 mmHg). Finally, the product is purified by Kugelrohr distillation (air bath temperature 130–175 °C, 0.25 mmHg) (Note 11) to yield pure **1** (19.6 g, 49%) as colorless plates (Note 12).

B. 5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene (2). Under an atmosphere of argon in a flame-dried, 500-mL, three-necked round-bottomed flask, equipped with a reflux condenser and a 4-cm egg-shaped magnetic stirring bar, **1** (19.2 g, 92.3 mmol) is dissolved in carbon tetrachloride (200 mL) (Note 13). NBS (35.3 g, 198.4 mmol, 2.15 equiv) (Notes 14 and 15) is added, and the stirred mixture is then refluxed at 85 °C (oil bath temperature). After 2 h NMR analysis (Note 16) indicates complete consumption of the starting material **1** (Note 17). The hot suspension (65 °C) is filtered through a fritted glass funnel (8.0 cm diameter, porosity 3), and the remaining succinimide is washed with carbon tetrachloride (400 mL) (Note 18). The solvent of the filtrate is evaporated under gradually reduced pressure (40 °C, 225 to 18 mmHg). A pale yellow residue remains, which is scraped off the inner wall of the flask, poured into a fritted glass funnel (7.0 cm diameter, porosity 3), washed with distilled water (300 mL) and dried overnight under vacuum (25 °C, 0.3 mmHg) to give 35.4 g of crude **2** as a pale yellow solid (Note 19).

C. *Dibenzo[a,e]cyclooctene* (**3**). Under an atmosphere of argon in a flame-dried, 250-mL, single-necked round-bottomed flask equipped with a magnetic stirring bar, **2** (34.1 g crude product) is dissolved in THF (150 mL) (Note 1). Under an atmosphere of argon in a second flame-dried, 500-mL, single-necked round-bottomed flask equipped with a magnetic stirring bar, potassium *tert*-butoxide (41.6 g, 371 mmol, 4 equiv, assuming 100% purity of **2**) (Note 20) is dissolved in THF (100 mL) (Note 1). The resulting cloudy solution is then cooled with an ice bath. At 0 °C the solution of **2** is transferred through a teflon tube (1.5 mm internal diameter) over a period of 15 min into the 500-mL flask. During the period of addition the color changes from orange to brown and finally to black. Then the ice bath is removed, the mixture is allowed to warm to room temperature and is stirred for 2 h until TLC-analysis indicates complete consumption of the dibromide **2** (Notes 21 and 22). Distilled water (15 mL) is added and the black mixture is poured onto a pad of silica gel (diameter 10 cm x 4 cm height) that has already been wetted with diethyl ether. The pad is rinsed with 700 mL of diethyl ether, and the eluent is collected directly as a single fraction, dried over Na₂SO₄ (40 g), filtered and concentrated at 40 °C by rotary evaporation (675 to 75 mmHg) and then at 15 mmHg for 1 h. The crude product remains as a brown solid (18.5 g) (Note 23), which is scraped off the inner wall of the flask and dried overnight under vacuum (25 °C, 0.3 mmHg). Purification by Kugelrohr distillation (air bath temperature 130–145 °C, 0.2 mmHg) (Note 24, 25) affords 13.0 g (69%, two steps from **1**) of *dibenzo[a,e]cyclooctene* (**3**) as colorless plates (Note 26).

2. Notes

1. THF 99.9+% was purchased from Kanto Chemicals Co., Inc., and was purified using a Glass Contour Solvent System; The submitters purchased from Sigma-Aldrich, Inc. and processed through a Solvent Purification System (M. Braun SPS-800, filter material: MB-KOL-A, MB-KOL-M; catalyst: MB-KOL-C).

2. Granular lithium, 99.9+%, was purchased from Sigma-Aldrich, Inc. and was used as received.

3. α,α' -Dibromo-*o*-xylene, 96%, was purchased from Aldrich Chemical Co., Inc. and was sublimed in a Kugelrohr distillation apparatus, which was equipped according to Note 11 (air bath temperature 130–150 °C, 0.07 mmHg) yielding white crystals, which were rinsed out of the receiver flask with diethyl ether. The solvent was removed via rotary evaporation and

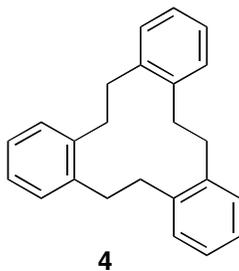
the residual colorless crystals were dried under vacuo for 2 h (25 °C, 0.04 mmHg).

Upon use of α,α' -dibromo-*o*-xylene as purchased, i. e. without purification, the yield of **1** dropped to 44-46%, and the submitters have experienced problems with drying the crude product before purification by Kugelrohr distillation.

4. The addition of α,α' -dibromo-*o*-xylene may cause a rapid rise of temperature. The addition may need to be temporarily suspended upon onset of the exothermic reaction.

5. The TLC analysis was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F₂₅₄ and PE as eluent; detection: UV-light (254 nm) or aqueous KMnO₄ (1% KMnO₄ + 5% Na₂CO₃ in H₂O), $R_f(\alpha,\alpha'$ -dibromo-*o*-xylene) = 0.21, $R_f(\mathbf{1}) = 0.18$, $R_f(\mathbf{4}) = 0.12$ (Note 7).

6. The submitters also monitored the reaction by the GC/MS analysis with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5972 series mass selective detector and a HP-1 column (25 m \times 0.2 μ m; 0.33 mm film thickness, carrier gas: helium). For reaction control the following parameters were used; temperature-program: 50 °C for 3 min; heating rate 20 °C/min; 250 °C for 10 min; injection-temperature 250 °C). GC/MS (EI): $t_R(\alpha,\alpha'$ -dibromo-*o*-xylene) = 8.9 min, $m/z = 264$ [M⁺]; $t_R(\mathbf{1}) = 10.9$ min, $m/z = 208$ [M⁺]; $t_R(\mathbf{4}) = 11.5$ min, $m/z = 312$ [M⁺].



7. The by-product 5,6,11,12,17,18-hexahydro-tribenzo[a,e,i]cyclododecene (**4**) was identified by the following data: mp = 184–185 °C (lit.,² 184.5 °C); ¹H NMR (CDCl₃, 300.13 MHz) δ : 3.04 (s, 12 H, CH₂), 7.20–7.36 (m, 12 H, Aryl); ¹³C NMR (CDCl₃, 75.48 MHz) δ : 37.45 (t, CH₂), 126.87, 130.61 (2 d, C-Ar), 140.22 (s, C_{quart.}-Ar); IR (KBr): 3058, 3011, 2939, 2864, 1913, 1489, 1473, 1450, 1158, 1051, 1040 cm⁻¹; HRMS: Calcd. for C₂₄H₂₄: 312.1878. Found: 312.1888; MS (EI, 70 eV): m/z (%): 312 (40), 207 (100), 193 (30), 178 (30), 115 (40), 105 (35), 91 (25), 78 (25).

8. At ca. 75 mmHg a white solid precipitates.

9. The material is LiBr.

10. Silica gel (0.04-0.100 mm) was purchased from Kanto Chemical.

11. Purification by Kugelrohr distillation was carried out in an apparatus equipped with a straight oven tube (29 mm neck fit and 20 cm length) and a cooled 100-mL single bulb receiver flask. A high vacuum pump was used to reduce the pressure.

The submitters reported that fraction 1 (130–160 °C, 0.08–0.05 mmHg) yielded 17.3 g of **1**, fraction 2 (160–180 °C, 0.05 mmHg) yielded 4.2 g of **1** and the triple-coupled by-product **4** as a mixture and fraction 3 (185–250 °C, 0.06 mmHg) yielded 3.8 g of **4** as a pale brown solid. Fraction 2 was subjected to Kugelrohr distillation again to yield 3.3 g of pure **1**.

On a smaller scale run (6.6 g, 25 mmol, of α,α' -dibromo-*o*-xylene) **1** and **4** were isolated via chromatography on a column (2.5 x 50 cm) of 70 g silica gel with petroleum ether (35-60 °C) as eluent. The product **1** was obtained in fractions 5-15 (100-mL fractions) and **4** in fractions 20-33. After evaporation of the solvent by rotary evaporation (40 °C, 262 mmHg) **1** was obtained as colorless plate shaped crystals (1.09 g, 42%) and the by-product **4** as colorless needles (0.14 g, 6%).

12. Compound **1** has the following physicochemical properties: mp = 108–109 °C (lit.¹⁰ mp 108.5–110 °C); ¹H NMR (CDCl₃, 400 MHz) δ : 3.06 (s, 8 H, CH₂), 6.99 (s, 8 H, Aryl-H); ¹³C NMR (CDCl₃, 100 MHz) δ : 35.12 (t, CH₂), 126.07, 129.64 (d, C-Ar), 140.57 (s, C_{quart.}-Ar); IR (KBr): 3060, 3011, 2939, 2899, 2845, 2359, 1914, 1491, 1476, 1450, 1157, 1079, 1050.cm⁻¹; Anal. Calcd. for C₁₆H₁₆: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.87. HRMS: Calcd. for C₁₆H₁₇: 209.1330. Found: 209.1321; MS (EI, 70 eV): *m/z* (%): 208 (54), 193 (100), 178 (40), 165 (11), 152 (5), 130 (7), 116 (24), 104 (29), 91 (13), 78 (27).

13. Carbon tetrachloride (99%, extra pure) was purchased from Kanto Chemical and was used as received.

14. NBS, 99%, purchased from Aldrich Chemical Co., Inc was used as received.

15. The use of 2.15 equiv of NBS was necessary for the complete consumption of the substrate. With only 2.0 equiv of NBS the product was obtained as a mixture of undesired monobrominated product and desired product **2** in a ratio of 14/86, which was determined via its proton NMR spectrum.

16. Analysis via TLC monitoring was unsuccessful, because the R_f values of the dibrominated product **2** and the monobrominated intermediate

are the same. Therefore, even if the spot of **1** has disappeared and only the spot of the dibrominated product **2** is visible, conversion might still be incomplete.

17. NMR analysis was conducted in the following manner; a portion of reaction mixture (approximately 10-15 μl) was removed by Pasteur pipette or capillary and dissolved in CDCl_3 . Completion of the reaction was confirmed by disappearance of monobrominated intermediate peaks found in the ^1H NMR (400 MHz) spectrum at $\delta = 3.04$ (s), 3.06 (s), 3.48–3.76 (m), 3.96 (dd, $J = 11.0, 14.2$ Hz).

The submitters monitored the reaction by GC/MS, For reaction control the “default”-method was used (see Note 6). GC/MS (EI): t_{R} (succinimide) = 5.9 min, $m/z = 99$ [M^+]; t_{R} (**1**) = 10.9 min, $m/z = 208$ [M^+]; t_{R} (monobrominated intermediate) = 12.5 min, $m/z = 286$ [M^+]; t_{R} (**2**) = 14.8 min, $m/z = 366$ [M^+].

18. The yield of crude product was significantly lower if the solution was filtered after allowing it to cool to room temperature.

19. Compound **2** was used in the next step without further purification. The compound can, however, be purified by recrystallization: The solid (3.0 g) is dissolved in 12 mL of hot carbon tetrachloride at 85 $^{\circ}\text{C}$ (oil bath temperature). The yellow solution is allowed to cool slowly to room temperature by turning off the heating of the oil bath. Then the flask is cooled to 6 $^{\circ}\text{C}$ (refrigerator) overnight, and the resulting crystals are collected by suction filtration through a small Büchner funnel (diameter 2 cm), washed with 4 mL of ice-cold dichloromethane, and then dried under vacuum (0.04 mmHg, 14 h) to provide 1.3 g of **2** as colorless rods with the following physicochemical properties: mp = 188–189 $^{\circ}\text{C}$ (lit.¹⁰ mp 188–189 $^{\circ}\text{C}$); ^1H NMR (CDCl_3 , 400 MHz) δ : 3.65 (dd, $J = 8.2, 14.2$ Hz, 2 H), 4.29 (dd, $J = 11.0, 14.2$ Hz, 2 H), 5.33 (dd, $J = 11.0, 8.2$ Hz, 2 H), 6.95–7.11 (m, 8 H, Ar-H) ^{13}C NMR (CDCl_3 , 100 MHz) δ : 43.65 (d, C-2), 52.98 (s, C-1), 127.88, 129.03, 130.78, 130.92 (4 d, C-Ar), 136.32, 138.33 (2 s, C_{quart}); IR (KBr): 3062, 3018, 2892, 1961, 1600, 1579, 1490, 1449, 1312, 1110, 1084 cm^{-1} ; Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{Br}_2$: C, 52.49; H, 3.85; Br, 43.65. Found: C, 52.37; H, 4.03; Br, 43.72. HRMS: Calcd. for $\text{C}_{16}\text{H}_{14}^{79}\text{Br}^{81}\text{Br}$: 365.9442. Found: 365.9457; MS (EI, 70 eV): 287 (22), 285 (23), 205 (100), 191 (20), 178 (15), 165 (10), 115 (11), 101 (16), 89 (23).

20. Potassium *tert*-butoxide (97%) was purchased from Fluka, stored in a Schlenk flask under argon and was used as received.

21. The TLC analysis was carried out according to Note 5, $R_f(\mathbf{2}) = 0.11$, $R_f(\mathbf{3}) = 0.20$.

22. The submitters also monitored reaction by GC/MS. For GC/MS-control the “default”-method was used (see Note 6). GC/MS (EI): $t_R(\mathbf{3}) = 10.9$ min, $m/z = 204$ [M^+]; $t_R(\mathbf{2}) = 14.8$ min, $m/z = 366$ [M^+].

23. If after rotary evaporation the crude product remains as a semifluid mass and cannot be scraped off the inner walls of the flask, it is dissolved in diethyl ether and the solvent is evaporated once more.

24. Kugelrohr distillation was carried out in an apparatus equipped according to Note 11. The first fraction, up to 85 °C, is *tert*-butanol.

25. From a smaller scale run (0.62 g, 2.98 mmol of **1**) **3** was isolated via chromatography on a column (3.0 x 15 cm) of 25 g silica gel with petroleum ether (35-60 °C) as eluent. The desired product **3** was obtained in fractions 2-3 (50-mL fractions), which were concentrated by rotary evaporation (40 °C, 262 mmHg) to yield **3** as colorless plates (0.44 g, 72% over two steps).

26. Physicochemical properties of dibenzo[a,e]cyclooctene **3**: mp 108–109 °C (lit.¹⁰ 109.5–110 °C); $^1\text{H NMR}$ (CDCl_3 , 300.13 MHz) δ : 6.72 (s, 4 H, CH), 7.02–7.11 (m, 8 H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ : 126.76 (d, CH), 129.03, 133.18 (2 d, C-Ar), 137.00 (s, $\text{C}_{\text{quart.}}$ -Ar); IR (KBr): 3054, 3010, 1922, 1815, 1650, 1490, 1432, 1400, 1153, 1088, 1039 cm^{-1} ; Anal. Calcd. for $\text{C}_{16}\text{H}_{12}$: C, 94.08; H, 5.92. Found C, 94.14; H, 6.14. HRMS: Calcd. for $\text{C}_{16}\text{H}_{13}$: 205.1017. Found: 205.1017. MS (EI, 70 eV): 204 (79), 203 (100), 202 (63), 176 (5); 150 (4), 101 (30), 88 (10), 76 (7).

Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with “Prudent Practices in the Laboratory”; National Academies Press; Washington, DC, 2011.

3. Discussion

Dibenzo[a,e]cyclooctene (dbcot = **3**) is a strongly binding diene ligand for transition metal ions, and its transition metal complexes show interesting properties for the use in catalysis.^{3,4,5,6} However, applications are limited because of poor accessibility of **3**. Commercial sources until now only offer very small amounts of the compound (milligram scale).

The first synthesis of **3** was reported in 1946 by Fieser et al.,⁷ who condensed *o*-phthalaldehyde and *o*-phenylenediacetonitrile in the presence of sodium ethoxide to obtain a dicyano derivative of **3**. Three more steps afforded the title compound in an overall yield of 6%. A Wittig approach described by Griffin et al. starting from *o*-phthalaldehyde led to an overall yield of 15%.⁸ Other routes led either to low yields,⁹ as well, and/or required inconvenient reaction conditions, such as the use of sodium powder,¹⁰ Ni(CO)₄ and mercury amalgam.¹¹ Another approach is the photolytic-induced isomerization of dibenzobarrelene (9,10-dihydro-9,10-ethenoanthracene) to **3**.^{12,13} Dibenzobarrelene can be prepared by Diels-Alder cycloaddition of anthracene and *trans*-1,2-dichloroethylene,¹³ dimethylacetylene carboxylate¹⁴ or phenyl vinyl sulfoxide¹⁵ as dienophile in the key step.

The procedure described herein in detail is a modification of a method published by Wudl et al.¹⁶ Though in principal straightforward and elegant, this synthesis in our hands suffered from poor reproducibility of the first step due to the use of a large excess of hazardous material like powdered lithium sand and difficult purification of the hydrocarbon **1** by chromatography. Our aim was the development of a protocol that could be run reliably on a multigram scale. This aim was reached by lowering the amounts of reagents and solvents needed and the application of Kugelrohr distillation instead of column chromatography for purification.

Concerning the properties of **3** as a ligand for transition metal complexes,³ preorganization of the double bonds leads to very stable transition metal complexes. From 1953 onwards, coordination compounds with **3** as ligand have been prepared (silver,¹⁷ palladium,¹¹ molybdenum, chromium).¹⁸ In 1983, Crabtree et al. demonstrated exceptional stability for several molybdenum, rhodium and iridium complexes.¹⁹ Their work showed that **3** is an excellent ligand, which binds more strongly to these metal centers than cod and resists further transformations such as hydrogenation. Because of its tight binding **3** was employed as a catalyst poison in order to distinguish between homogeneously and heterogeneously-catalyzed reactions.²⁰ More recent publications describe syntheses and organometallic coordination chemistry of a variety of Ir-,²¹ Rh-,²¹ Pd-,^{22,23} and Pt-²³ complexes of **3**.

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2. Baker, W.; Banks, R.; Lyon, D. R.; Mann, F. G. *J. Chem. Soc.* **1945**, 27-30.
3. Defieber, C.; Grützmacher, H.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 4482-4502.
4. Läng, F.; Breher, F.; Stein, D.; Grützmacher, H. *Organometallics* **2005**, *24*, 2997-3007.
5. Spiess, S.; Welter, C.; Franck, G.; Taquet, J.-P.; Helmchen, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 7652-7655.
6. Franck, G.; Brödner, K.; Helmchen, G. *Org. Lett.* **2010**, *12*, 3886-3889.
7. Fieser, L. F.; Pechet, M. *J. Am. Chem. Soc.* **1946**, *68*, 2577-2580.
8. Griffin, C. E.; Peters, J. A. *J. Org. Chem.* **1963**, *28*, 1715-1716.
9. Kagan, J.; Chen, S.; Agdeppa, D.; Watson, W.; Zabel, V. *Tetrahedron Letters* **1977**, *18*, 4469-4470.
10. Cope, A. C.; Fenton, S. W. *J. Am. Chem. Soc.* **1951**, *73*, 1668-1673.
11. Avram, M.; Dinu, D.; Mateescu, G.; Nenitzescu C. D. *Chem. Ber.* **1960**, *93*, 1789-1794.
12. Rabideau, P. W.; Hamilton, J. B.; Freidman, L. *J. Am. Chem. Soc.* **1968**, *90*, 4465-4466.
13. Wang, X.; Hou, X.; Zhou, Z.; Mak, T.; Wong, H. *J. Org. Chem.* **1993**, *58*, 7498-7506.
14. Figeys, H. P.; Dralants, A. *Tetrahedron* **1972**, *28*, 3031-3036.
15. Doecke, C. W.; Klein, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 1597-1599.
16. Chaffins, S.; Brettreich, M.; Wudl, F. *Synthesis* **2002**, 1191-1194.
17. Wittig, G.; Eggers, H.; Duffner, P. *Liebigs Ann. Chem.* **1958**, *619*, 10-27.
18. Müller, J.; Göser, P.; Elian, M. *Angew. Chem. Internat. Et.* **1969**, *8*, 374-375. Brown, M.; Zubkowski, J. D.; Valente, E. J.; Yang, G.; Henry, W. P.; *J. Organomet. Chem.* **2000**, *613*, 111-118.
19. Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 621-627.
20. Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855-859.
21. Singh, A.; Sharp, P. R. *Inorganica Chimica Acta* **361** **2008**, 3159-3164.

22. DeGray, J. A.; Geiger, W. E.; Lane, G. A.; Rieger, P. H. *Inorg. Chem.* **1991**, *30*, 4100-4102.
23. Singh, A.; Sharp, P. R. *Organometallics* **2006**, *25*, 678-683.

Appendix

Chemical Abstracts Nomenclature; (Registry Number)

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene; (1460-59-9)
 α,α' -Dibromo-*o*-xylene, 1,2-Bis(bromomethyl)benzene; (91-13-4)
Tetrahydrofuran; (109-99-9)
Lithium; (7439-93-2)
5,6,11,12,17,18-Hexahydro-tribenzo[a,e,i]cyclododecene; (4730-57-8)
5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene; (94275-22-6)
N-Bromosuccinimide; (128-08-5)
Carbon tetrachloride; (56-23-5)
Dibenzo[a,e]cyclooctene; (262-89-5)
Potassium *tert*-butoxide; (865-47-4)



G. Helmchen (b. 1940) is a Professor Emeritus at the Institute of Organic Chemistry of the Ruprecht-Karls-Universität Heidelberg. He pursued undergraduate studies at the TH Hannover (Dipl.-Chem. 1965) and graduate work under the guidance of Prof. V. Prelog at the ETH Zürich (Dr. sc. techn. 1971). He then carried out a Habilitationsarbeit at the TU Stuttgart (1975-1980). In 1980 he was appointed Professor C3 at the Universität Würzburg. In 1985 he moved to Heidelberg. His interest in catalysis dates back to ca. 1990.



Géraldine Franck, was born in Munich (Germany) in 1979. She studied chemistry in Heidelberg and Bristol and received her diploma degree from the Ruprecht-Karls-Universität Heidelberg in 2006. Under the guidance of Prof. G. Helmchen she completed her Ph.D. in 2010. Her research interests are the application of Ir-catalyzed allylic substitution reactions in syntheses of chiral building blocks and natural products.

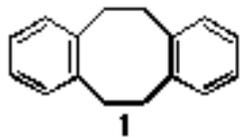


Marcel Brill was born in 1986 in Göttingen, Germany. He started studying chemistry at the Ruprecht-Karls-Universität in Heidelberg in 2005. During a practical course of advanced organic chemistry he worked on the synthesis of dbcot in the group of Prof. G. Helmchen. In 2010 he received his diploma degree in chemistry under the supervision of Prof. P. Hofmann. The same year he started his Ph.D. studies where he is currently working on the development of chiral NHC ligands and their application in enantioselective catalysis.

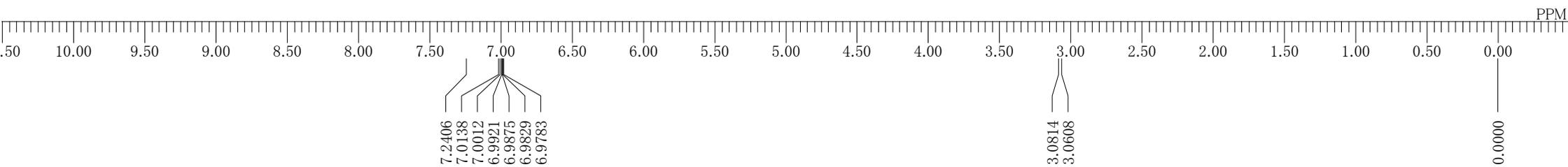


Takuya Nishimura was born in 1983 in Kanagawa, Japan. He received his B.S. in 2007 from the University of Showa Pharmaceutical Science. He is pursuing his Ph.D. at the Graduate School of Pharmaceutical Sciences, The University of Tokyo, under the guidance of Professor Tohru Fukuyama. His research interests are in the area of natural product synthesis.

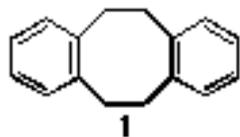
5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (1)



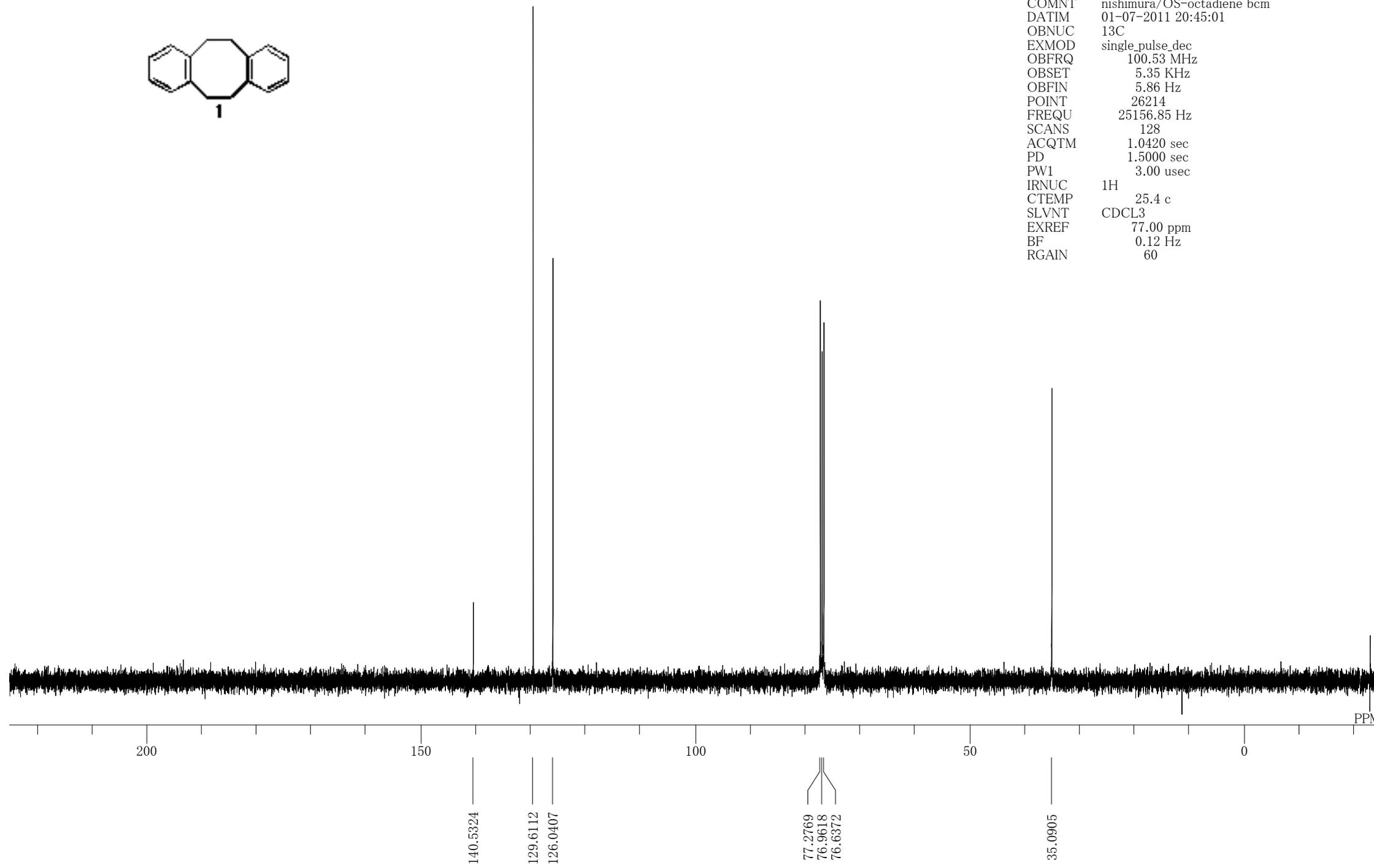
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OBFIN 7.29 Hz
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FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.85 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50



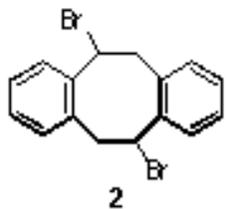
5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (1)



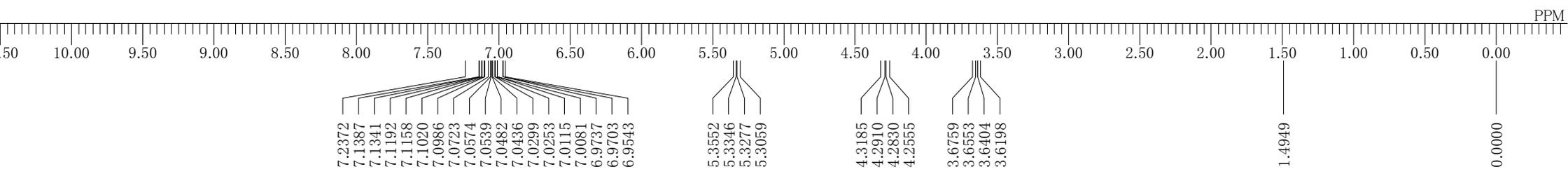
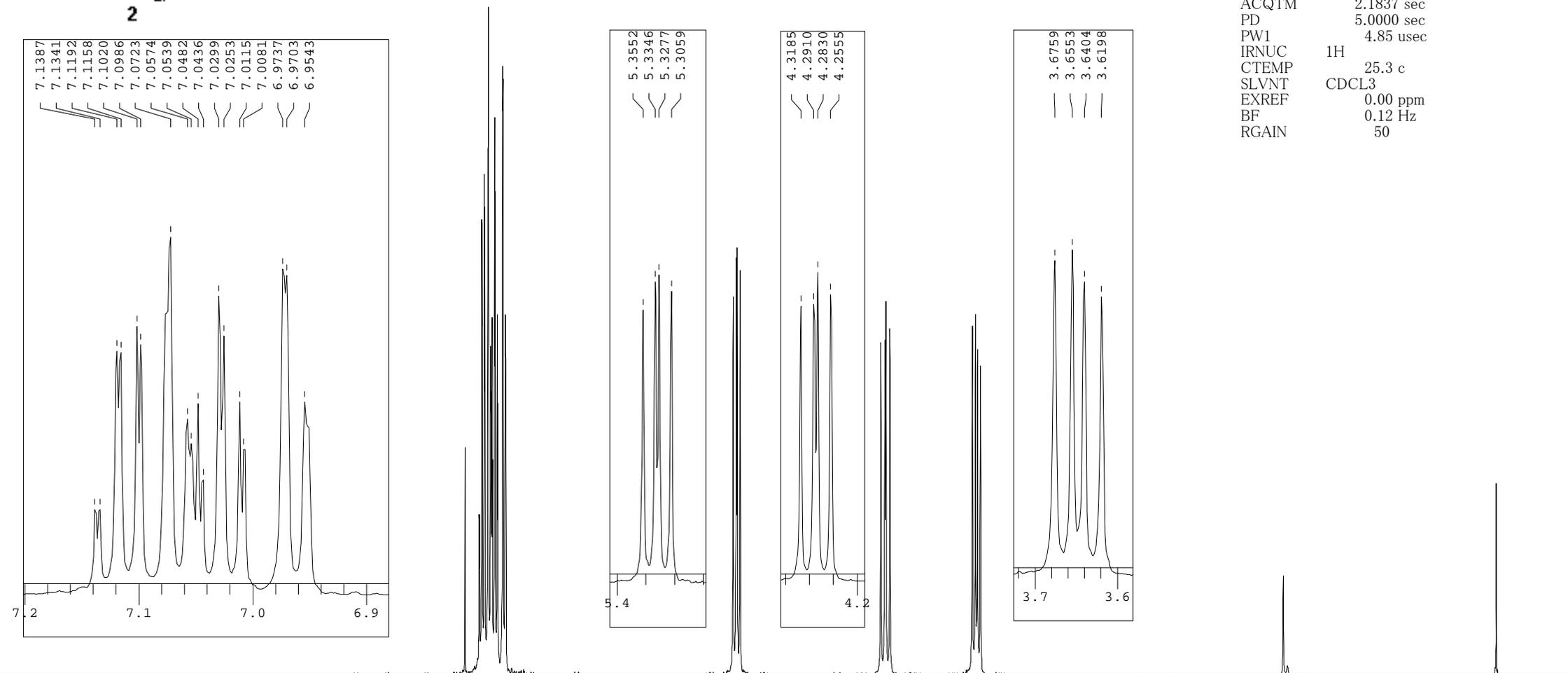
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OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25156.85 Hz
SCANS 128
ACQTM 1.0420 sec
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SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



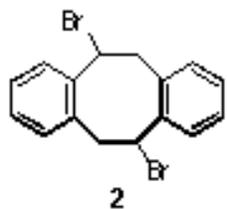
5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (2)



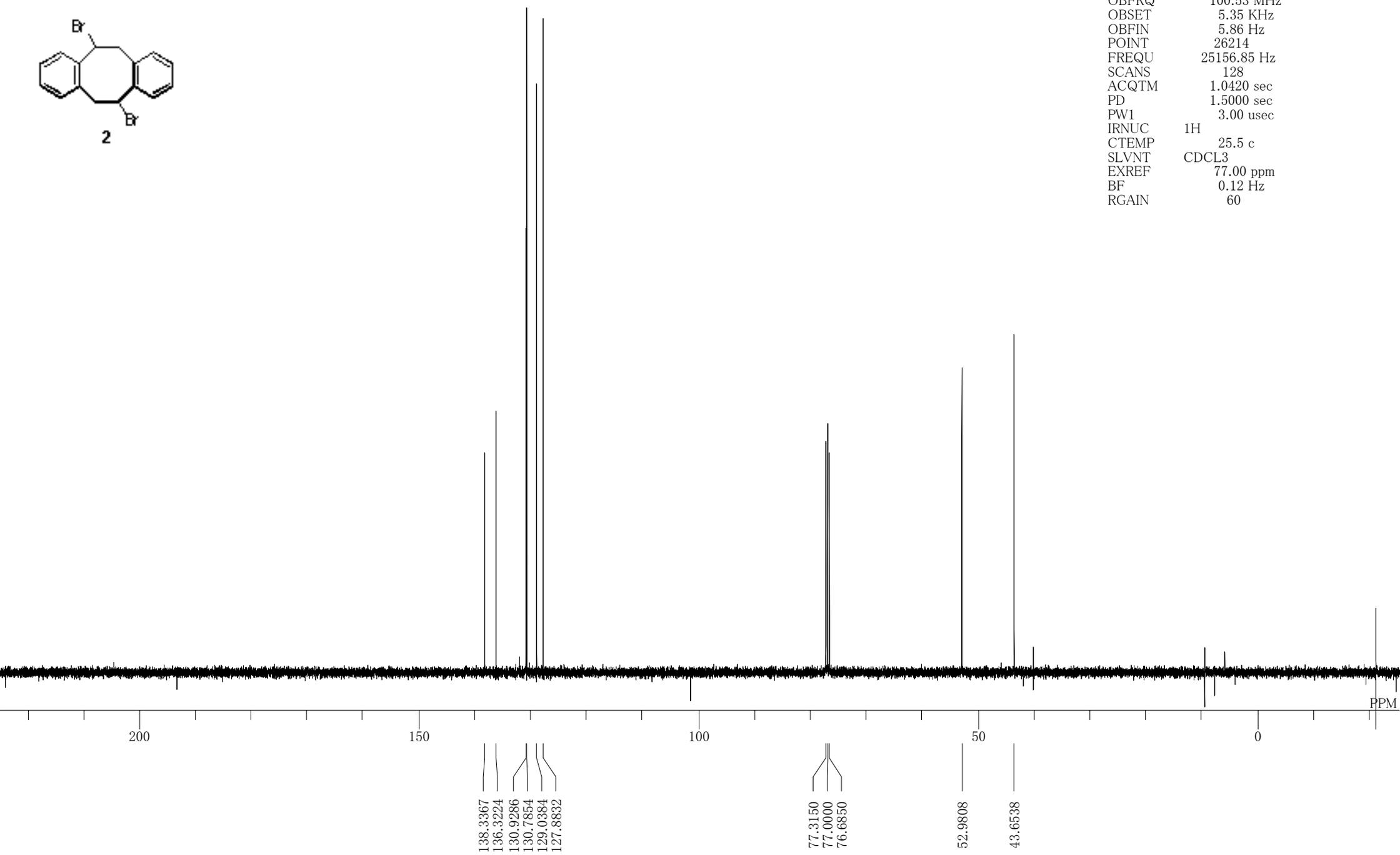
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 EXMOD single_pulse.ex2
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 OBFIN 7.29 Hz
 POINT 13107
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 SCANS 8
 ACQTM 2.1837 sec
 PD 5.0000 sec
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 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 50



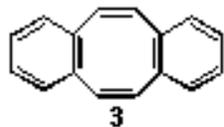
5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (2)



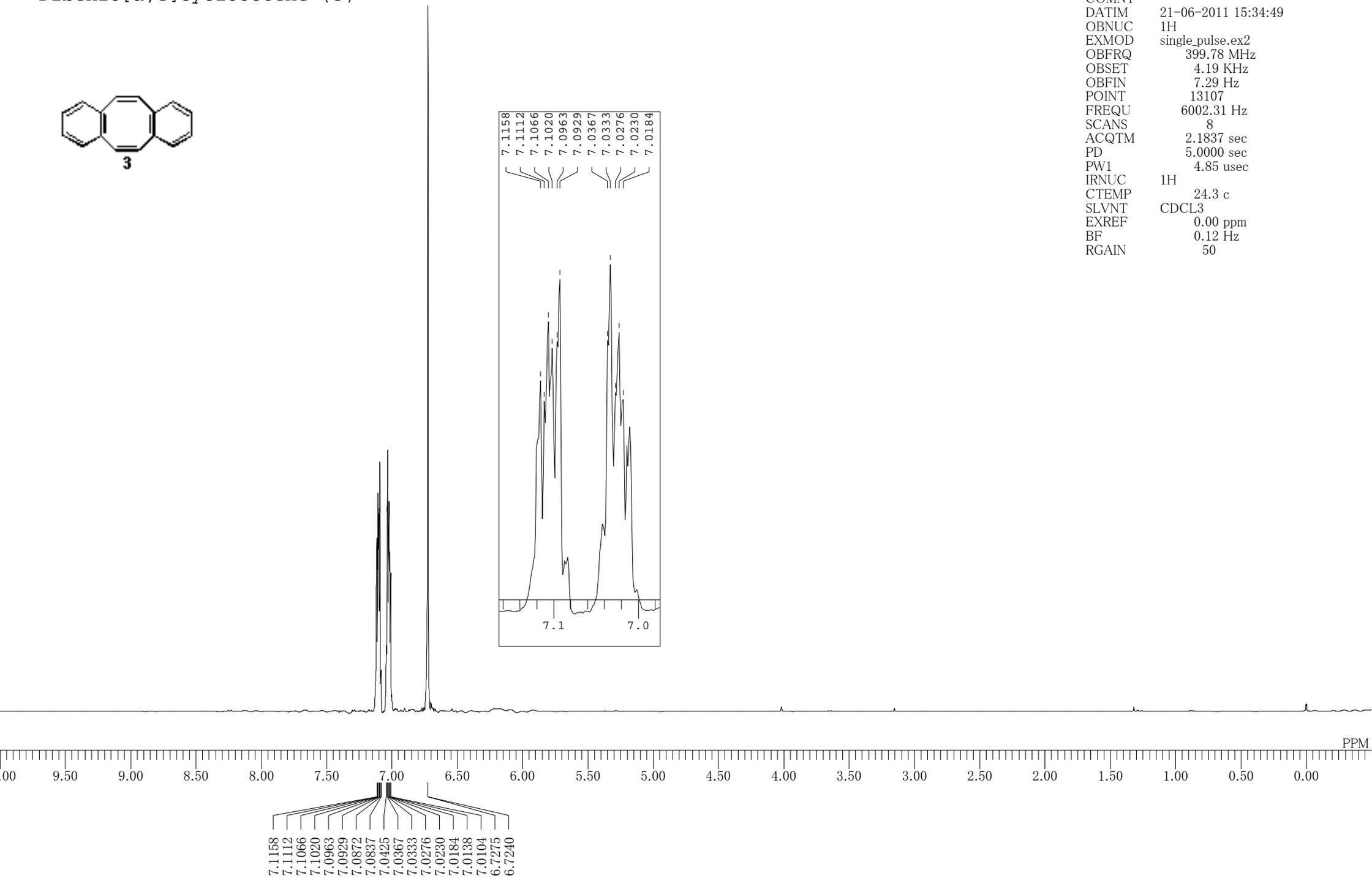
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EXMOD single_pulse_dec
OBFREQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25156.85 Hz
SCANS 128
ACQTM 1.0420 sec
PD 1.5000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



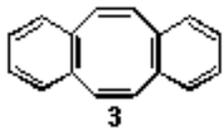
Dibenzo[a,e]cyclooctene (3)



DFILE
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OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 4.85 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50



Dibenzo[a,e]cyclooctene (3)



DFILE
COMNT
DATIM 21-06-2011 15:40:23
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25156.85 Hz
SCANS 66
ACQTM 1.0420 sec
PD 1.5000 sec
PW1 3.00 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

