Electronic Supplementary Information

Synthesis and solid-state structures of a macrocyclic receptor based on the 2,6-bis(2-anilinoethynyl)pyridine scaffold

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General Methods. ^{1}H and ^{13}C NMR spectra were obtained on a Varian 300 MHz spectrometer (^{1}H: 299.95 Hz, ^{13}C: 75.43 Hz), Inova 500 MHz spectrometer (^{1}H: 500.10 MHz, ^{13}C: 125.75 MHz) or Varian 600 MHz spectrometer (^{1}H: 599.98 MHz, ^{13}C: 150.87 MHz). Chemical shifts (δ) are expressed in ppm using non-deuterated solvent present in the bulk deuterated solvent ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm; $(CD_3)_2SO$: ^{1}H 2.5 ppm, ^{13}C 39.52 ppm). Unless specified, solvents were obtained from distillation using published literature procedures directly before use. Mass spectra were acquired Waters LCT Premier ESI-MS in positive mode using acetone as a solvent. UV-Vis spectra were acquired with a Hewlett-Packard 8453 UV-Visible spectrophotometer equipped with a 250 nm cutoff filter. Fluorescence data was acquired with a Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrophotometer. HPLC performed using a JAI Recycling Preparative HPLC (Model LC-9101) with a JAIGEL-1H preparative column.

Bisnitroarene 2. To a solution of 1,7-dibromoheptane (0.99 mL, 5.78 mmol) in dry DMF (10 mL) was added K_2CO_3 (3.19 g, 23.1 mmol) and 4-nitrophenol (2.01 g, 14.4 mmol). The resultant mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the solution was poured into water and extracted three times with CH_2Cl_2. The combined organic layers were washed with water and then brine, dried over $MgSO_4$, and filtered. The solution was concentrated at reduced pressure and the residue purified by chromatography (SiO_2, CH_2Cl_2 as eluent) to furnish **2** (2.06 g, 95%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 9.2 Hz, 4H), 6.91 (d, J = 9.2 Hz, 4H), 4.04 (t, J = 6.4 Hz, 4H), 1.89–1.75 (m, 4H), 1.57–1.39 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.25, 141.28, 125.88, 114.42, 68.82, 29.02, 28.92, 25.87. UV-vis ($CHCl_3$) λ_{max} (ε) 313 nm (45100 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{19}H_{27}N_2O_2^+$ [MH^+] 315.2073, found 315.2063.

Bisaniline 3. Nitroarene **2** (2.06 g, 5.49 mmol) was dissolved in THF (9 mL) and Et_3N (1 mL), and a catalytic amount (spatula tip) of 30% Pd/C was added. The mixture was sealed in a par flask, pressurized to 60 psi H_2 and stirred overnight. The mixture was filtered over a thin pad of Celite and the solid washed with EtOAc. The solution was concentrated at reduced pressure to afford aniline **3** (1.66 g, 96%) as a pale orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, J = 8.8 Hz, 4H), 6.62 (d, J = 8.8 Hz, 4H), 3.90 (t, J = 6.5 Hz, 4H), 3.48 (s, 4H), 1.90–1.68 (m, 4H), 1.60–1.23 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.88, 139.87, 116.15, 115.39, 68.34, 29.17,

29.00, 25.83. UV-vis ($CHCl_3$) λ_{max} (ε) 302 nm (8000 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{19}H_{23}N_2O_6^+$ [MH^+] 375.1556, found 375.1555.

Bisisocyanate 4. Aniline **3** (0.150 g, 0.477 mmol) was added to a flame-dried flask and diluted in anhydrous PhMe (240 mL). Anhydrous HCl was bubbled through the reaction mixture resulting in a suspended salt solution. A 20% solution of phosgene in PhMe (4.77 mmol) was added and the reaction was heated to reflux. The reaction was determined to be complete when the suspended salt solution cleared. The reaction was concentrated under reduced pressure, with an in-line aqueous NaOH trap, to remove any excess HCl and phosgene. Due to stability issues the reaction mixture was carried on crude, but determined to be complete by ^{1}H NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, J = 8.9 Hz, 4H), 6.81 (d, J = 8.9 Hz, 4H), 3.92 (t, J = 6.5 Hz, 4H), 1.83–1.74 (m, 4H), 1.52–1.45 (m, 4H), 1.46–1.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.07, 125.92, 125.71, 124.31, 115.50, 68.40, 29.28, 29.24, 26.10.

Macrocycle 1c. All glassware was flame-dried before use. In a 1 L round bottom flask was added core **5**[1,2] (201 mg, 0.47 mmol) and freshly distilled, dry PhMe (235 mL), and the flask was equipped with an addition funnel. The crude solution of isocyanate **4** was transferred via cannula into the funnel and was added dropwise over the course of 24 h. The crude macrocycle was first purified by preparative TLC (95:5 CH_2Cl_2/EtOAc, R_f = 0.5) and then by preparative HPLC ($CHCl_3$) to afford receptor **1c** (40 mg, 11%) as a light tan solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.34 (s, 2H), 8.20 (s, 2H), 8.02 (d, J = 8.9 Hz, 2H), 7.96 (t, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 2.3 Hz, 2H), 7.45 (dd, J = 8.9, 2.3 Hz, 2H), 7.27 (d, J = 8.9 Hz, 4H), 6.77 (d, J = 8.9 Hz, 4H), 3.92 (t, J = 6.0 Hz, 4H), 1.79–1.68 (m, 4H), 1.53–1.45 (m, 4H), 1.45–1.38 (m, 2H), 1.29 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.99, 152.41, 144.43, 142.92, 138.27, 137.40, 132.31, 129.46, 127.76, 127.49, 120.10, 119.92, 114.68, 110.02, 93.13, 86.35, 66.95, 33.94, 30.98, 27.26, 26.21, 24.70. UV-vis ($CHCl_3$) λ_{max} (ε) 261 nm (59500 $cm^{-1}M^{-1}$), 347 nm (17700 $cm^{-1}M^{-1}$). HRMS (EI+) calcd for $C_{50}H_{54}N_5O_4^+$ [MH^+] 788.4176, found 788.4139.

X-ray Crystallographic Details. Diffraction intensities for **1c•H_2O** and **1c•HCl** were collected at 193(2) and 100(2) K on a Bruker Apex2 CCD diffractometer using MoKα radiation λ= 0.71073 Å and CuKα radiation λ= 1.54178 Å, respectively. Space groups were determined based on systematic absences. Absorption corrections were applied by SADABS.[3] Structures were solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-

squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms in **1c•HCl** and H atoms in the terminal methyl groups in **1c•H_2O** were refined in calculated positions in a rigid group model. Other H atoms in **1c•H_2O** were found from the residual density map and refined with isotropic thermal parameters. Solvent hexane and pentane molecules (in **1c•H_2O** and **1c•HCl**, respectively) are disordered over several positions. These molecules were treated by SQUEEZE.[4] Corrections of the X-ray data by SQUEEZE (223 and 193 electron/cell, respectively for **1c•H_2O** and **1c•HCl**) are close to the required values of 200 and 168 electron/cell for four hexane and pentane molecules in the full unit cells. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.[5]

References

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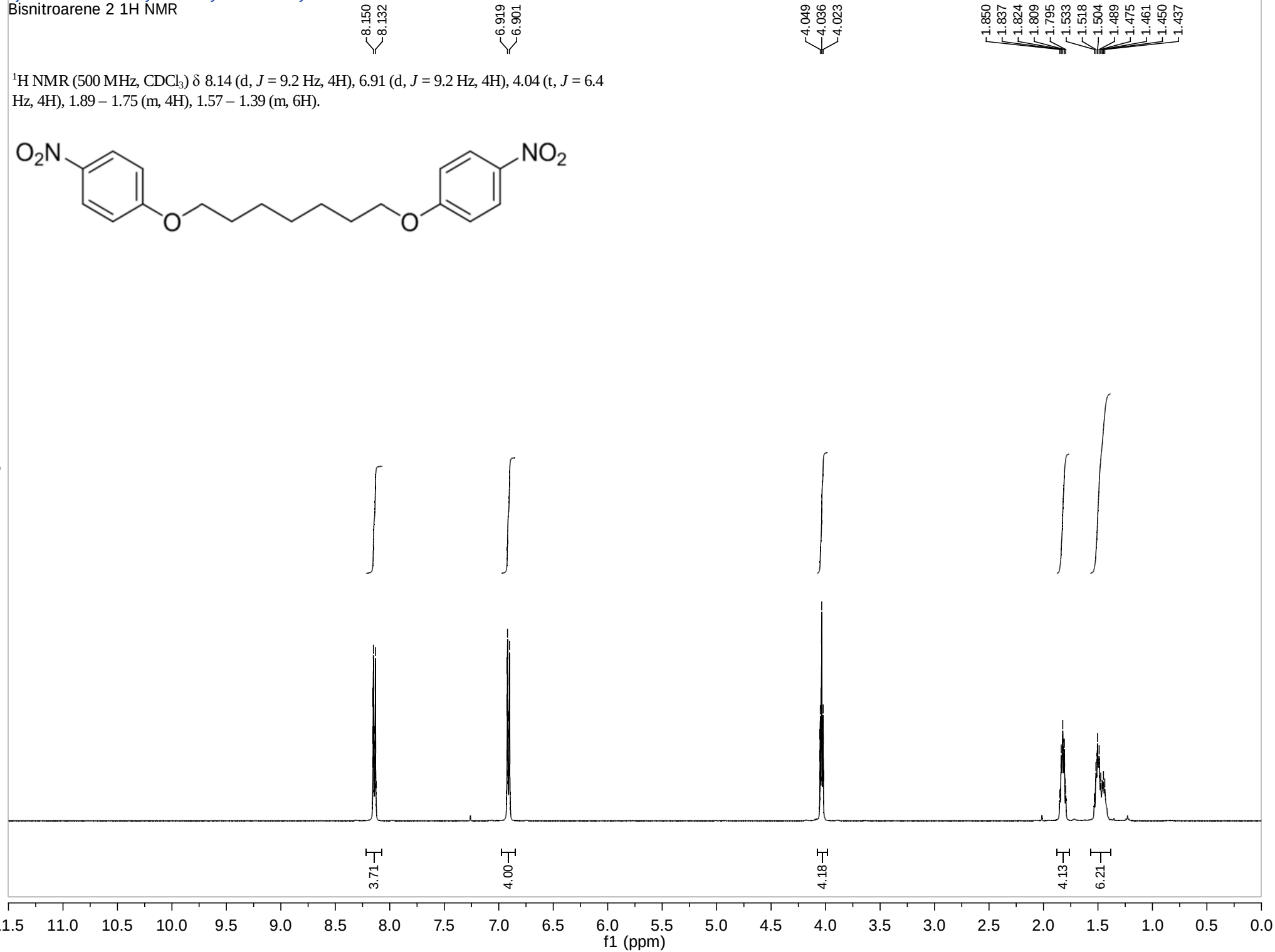
2. J. M. Engle, C. N. Carroll, D. W. Johnson and M. M. Haley, *Chem. Sci.*, 2012, **3**, 1105–1110.

3. G. M. Sheldrick, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, 1998.

4. P. Van der Sluis and A. L. Spek, *Acta Cryst., Sect. A,* 1990, **A46**, 194-201.

5. SHELXTL-6.10 *Program for Structure Solution, Refinement and Presentation*, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

Bisnitroarene 2 1H NMR



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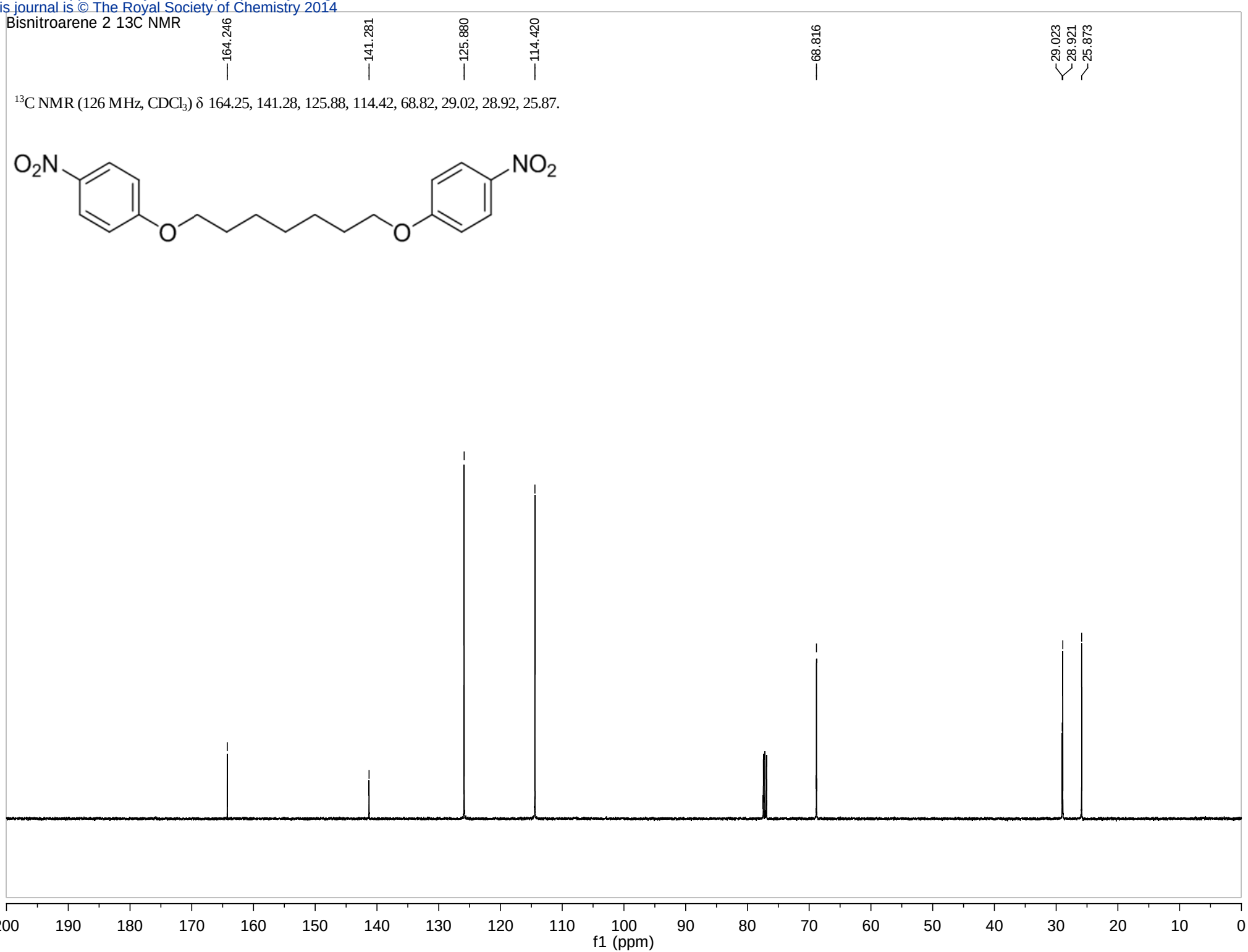

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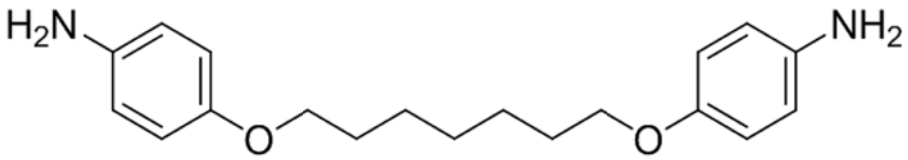
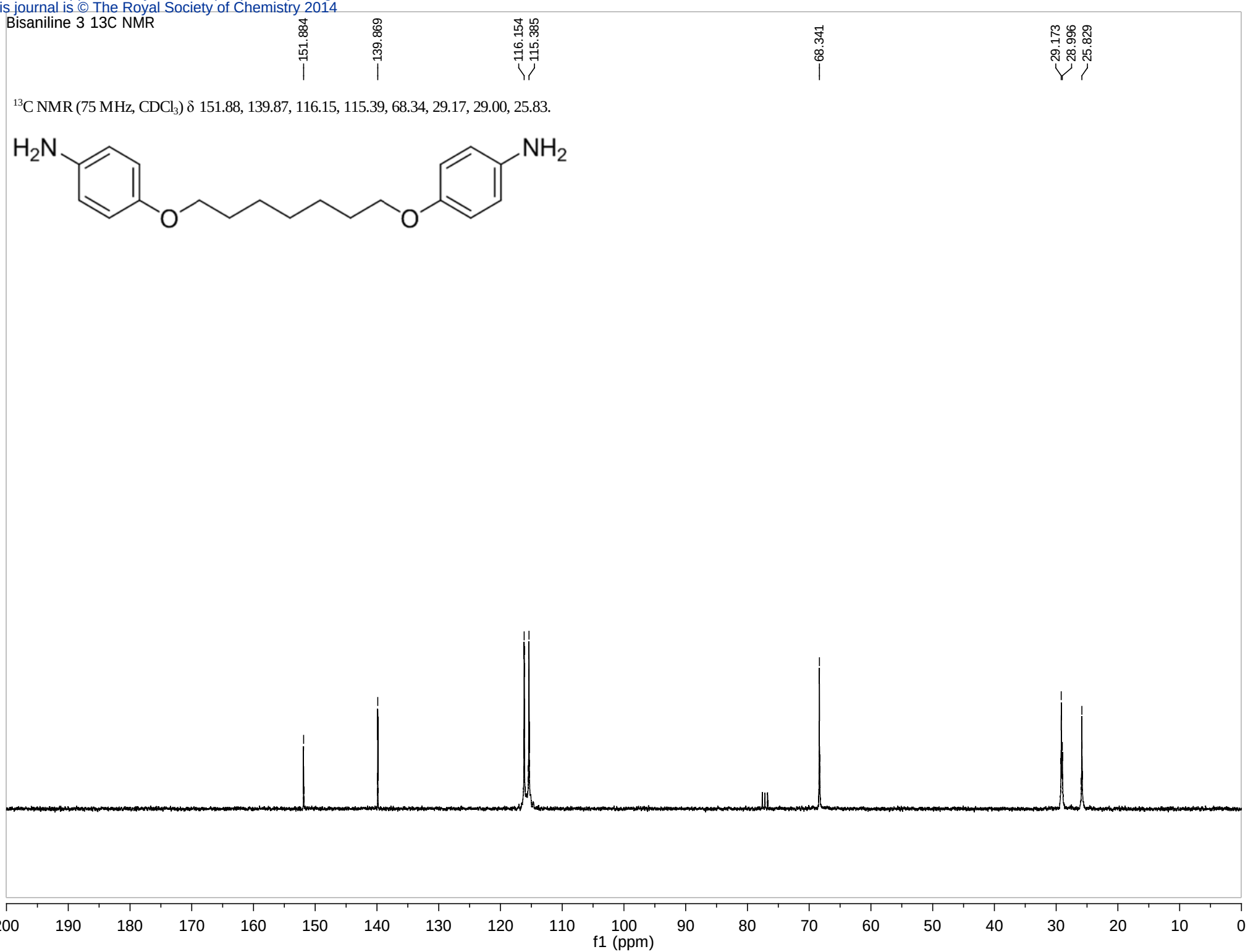
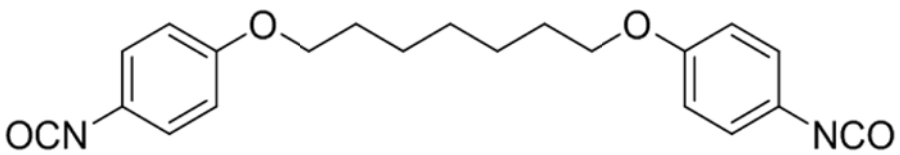


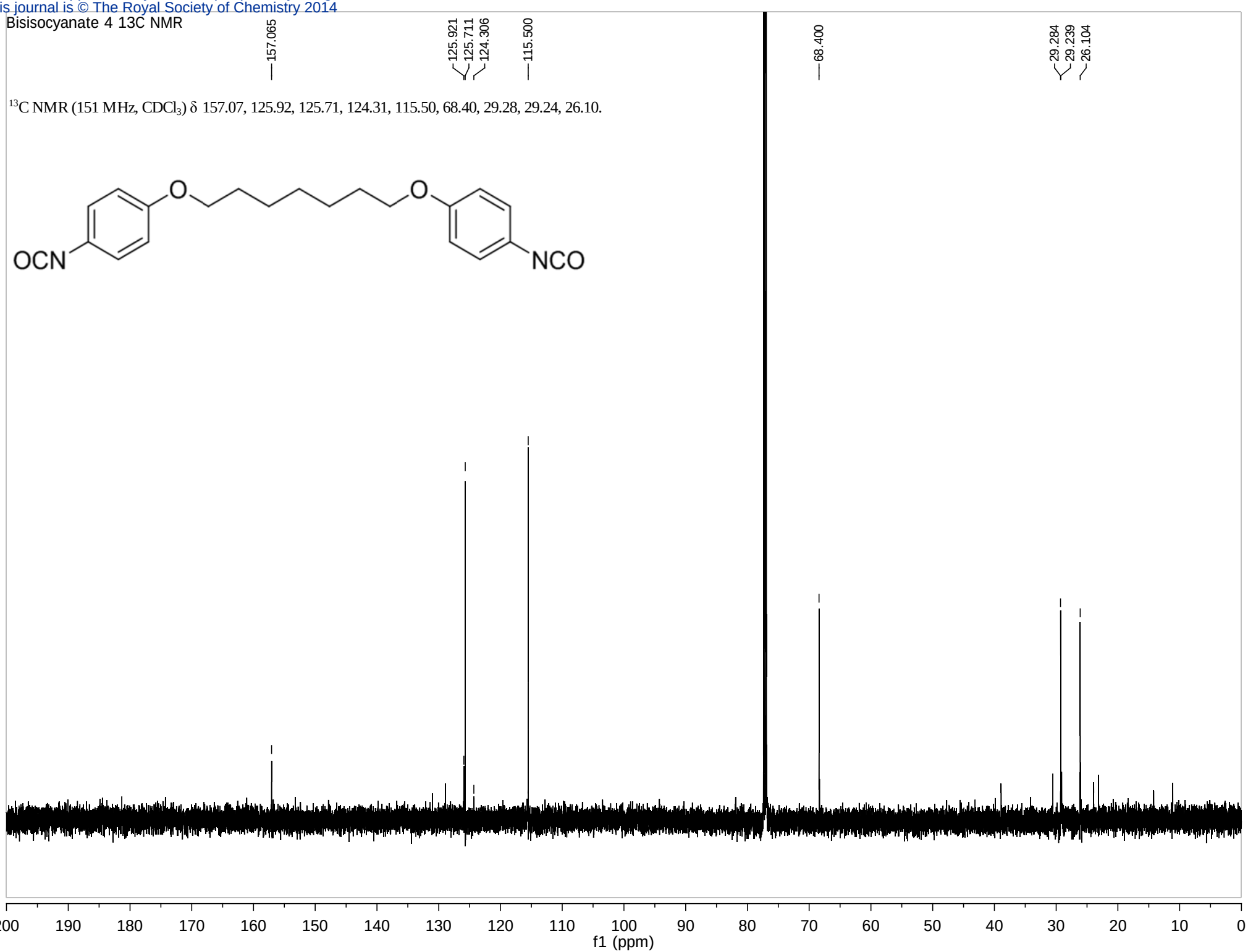


Bisisocyanate 4 1H NMR

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.9 Hz, 4H), 6.81 (d, *J* = 8.9 Hz, 4H), 3.92 (t, *J* = 6.5 Hz, 4H), 1.83 – 1.74 (m, 4H), 1.52 – 1.45 (m, 4H), 1.46 – 1.39 (m, 2H).



Bisisocyanate 4 13C NMR



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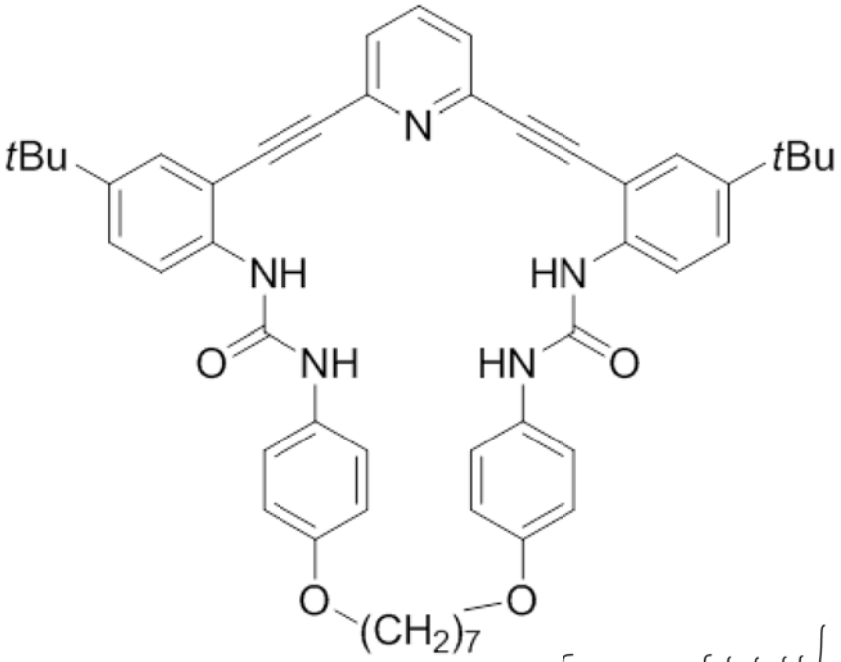
Macrocycle 1c 1H NMR

^{1}H NMR (600 MHz, DMSO-d6) δ 9.34 (s, 2H), 8.20 (s, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.96 (t, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 2.3 Hz, 2H), 7.45 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 4H), 6.77 (d, *J* = 8.9 Hz, 4H), 3.92 (t, *J* = 6.0 Hz, 4H), 1.79 – 1.68 (m, 4H), 1.53 – 1.45 (m, 4H), 1.45 – 1.38 (m, 2H), 1.29 (s, 18H).



Macrocycle 1c 13C NMR

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119.920
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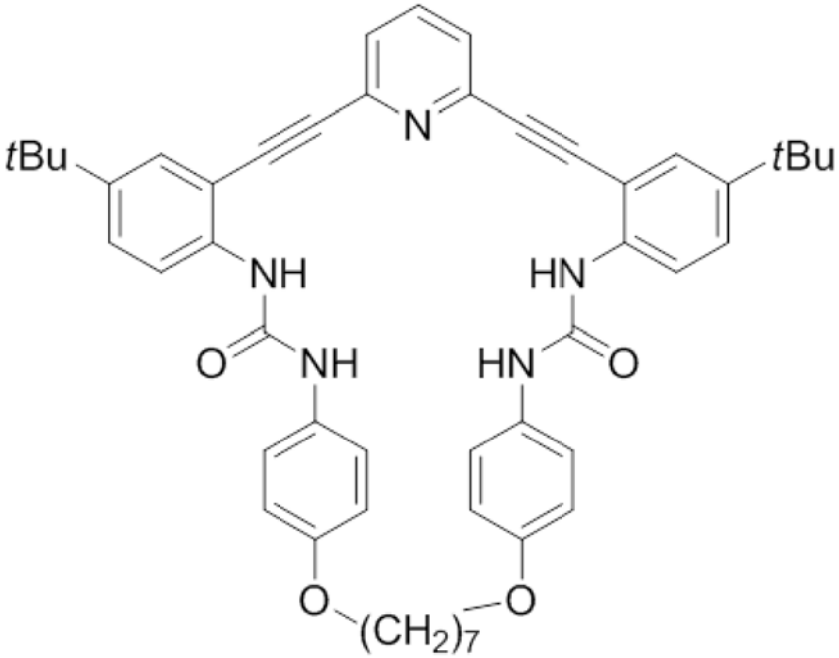
110.017
93.132
86.355
66.950
33.944
30.979
27.259
26.212
24.695

^{13}C NMR (151 MHz, DMSO-d6) δ 153.99, 152.41, 144.43, 142.92, 138.27, 137.40, 132.31, 129.46, 127.76, 127.49, 120.10, 119.92, 114.68, 110.02, 93.13, 86.35, 66.95, 33.94, 30.98, 27.26, 26.21, 24.70.



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