# Supplementary Material

# Preparation of symmetrical C2-C2-linked bis- and tris-6-bromoindoles by Sonogashira couplings and 5-*endo-dig* cyclization induced by $nBu_4NF$

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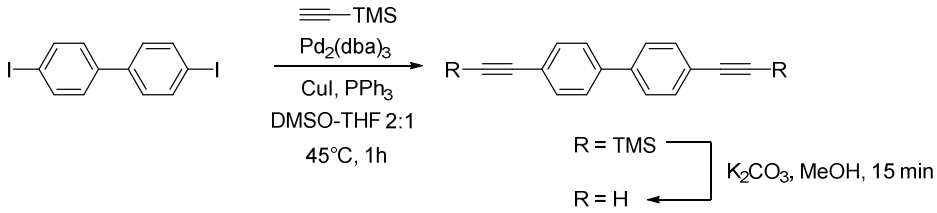
## Preparation of dialkynes 3a-h

**3,6-diethynyl-9-hexyl-9H-carbazole (3a)** was prepared according to the reported procedure: Zhang, W.; Cho, H. M.; Moore, J. S. *Org. Synth*. **2007**, *84*, 177-191. 1-Iodohexane was used instead of the 1-bromotetradecane used in the original report for N-alkylation of carbazole.

**4,4'-diethynyl-1,1'-biphenyl (3b)** was prepared according to the following procedure:

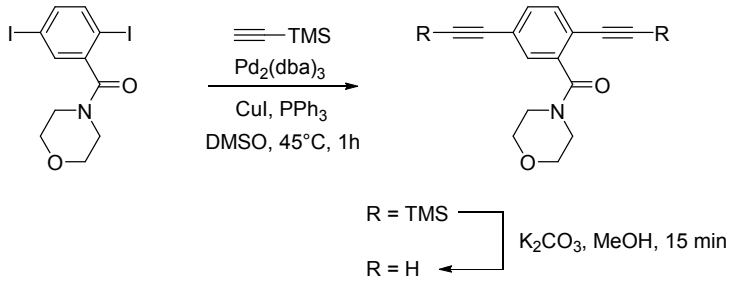



**Sonogashira coupling**. In a dry round bottom flask equipped with a stirring bar and septum under a $N_2$ atmosphere was added 405 mg (1 mmol, 1 equiv.) of 4,4'-diiodo-biphenyl, 23 mg (0.05 mmol, 0.05 equiv) of $Pd_2(dba)_3$, 6 mg (0.03 mmol, 0.03 equiv.) of CuI and 16 mg (0.06 mmol, 0.06 equiv.) of $PPh_3$ 10 mL of DMSO and 5 mL of THF. The flask was purged using vacuum, then a current of $N_2$. Then 240 µL (2.2 mmol, 2.2 equiv.) of trimethylsylilacetilene and 350 µL (2.5 mmol, 2.5 equiv.) of $iPr_2NH$ were added to the flask. The mixture was left stirring at 45 ºC during 1 h. Then the reaction mixture was diluted with 100 mL of ethyl acetate) and washed with water (2X100 mL) then with brine (1x100mL). The organic portion was dried over anh. $Na_2SO_4$, filtered and concentrated under vacuum. Column chromatography eluting with hexane gave 236 mg (76%) of a yellow solid, mp 158-160 ºC; $R_f$ = 0.60 (5% EtOAc/hexanes); IR (KBr) 3040, 2957, 2886, 2158, 1489 $cm^{-1}$; $^1H$ RMN (400 MHz, $CDCl_3$): δ 7.51 (s, 8H), 0.24 (d, J = 0.5 Hz, 18H); $^{13}C$ RMN (100 MHz, $CDCl_3$): δ 140.2, 132.4, 126.7, 122.4, 104.8, 95.2, -0.1.

**Deprotection**. In a round bottom flask containing an stirring bar and under a $N_2$ atmosphere was added 186 mg (0.78 mmol, 1 equiv) the bis protected acetylene from the previous step, 1.078 g (7.8 mmol, 10 equiv) de $K_2CO_3$ and 5 mL of methanol. The mixture was

stirred for 15 min at room temperature and then concentrated under vacuum. The residue was chromatographed using 95:5 hexanes:EtOAc to obtain 99 mg (63%) of **3b** as a yellow solid, mp 160-162 ºC; $R_f$ = 0.43 (5% EtOAc/hexanes); IR (KBr) ν 3275, 3038, 2922, 2852, 2107, 1490 $cm^{-1}$; $^1$H RMN (400 MHz, $CDCl_3$): δ 7.56 (m, 8H), 3.15 (s, 2H); $^{13}$C RMN (100 MHz, $CDCl_3$): δ 140.5, 132.6, 126.9, 121.4, 83.4, 78.1.

**2,5-diethynyl-morpholinebenzamide** (**3c)** was prepared according to the following procedure:




**Sonogashira coupling**. In a round bottom flask equipped with a stirring bar and under a $N_2$ atmosphere was added 221 mg (0.49 mmol, 1 equiv.) of 2,5-diiodo morpholine benzamide,* 13 mg (0.025 mmol, 0.05 equiv.) of $Pd_2(dba)_3$, 3 mg (0.015 mmol, 0.03 equiv) of CuI, and 8 mg (0.03 mmol, 0.06 equiv) of $PPh_3$. Then was added 5 mL de DMSO and the flask was purged with vacuum followed by a current of $N_2$. Then, 150 µL (1.05 mmol, 2.1 equiv.) of trimethylsylilacetilene and 180 µL (1.25 mmol, 2.5 equiv.) of $iPr_2NH$ were added and the mixture was stirred at 45 ºC for 1 h. Then the crude was diluted with 100 mL of ethyl acetate and washed with water (3X60 mL) and brine 1x100 mL. The organic portion was dried over $Na_2SO_4$, filtered and concentrated under vacuum. Column chromatography using hexane:ethyl acetate gradients (95:5, 90:10, 80:20) gave 166.4 mg (86%) the compound **3c** as a yellow solid. mp 155-157 ºC; $R_f$ = 0.83 (20% EtOAct/ 80% hexanes); IR (KBr) 3035, 2922, 2860, 2162, 1646, 1251 $cm^{-1}$; $^1$H RMN (400 MHz, $CDCl_3$): δ 7.41 (m, 3H), 3.75, (m, 8H), 0.24 (m, 18H); $^{13}$C RMN (100 MHz, $CDCl_3$): δ 167.8, 139.0, 132.6, 132.2, 130.2, 124.1, 120.0,

103.7, 101.8, 100.6, 98.0, 67.1, 66.8, 47.4, 42.2, 0.1.

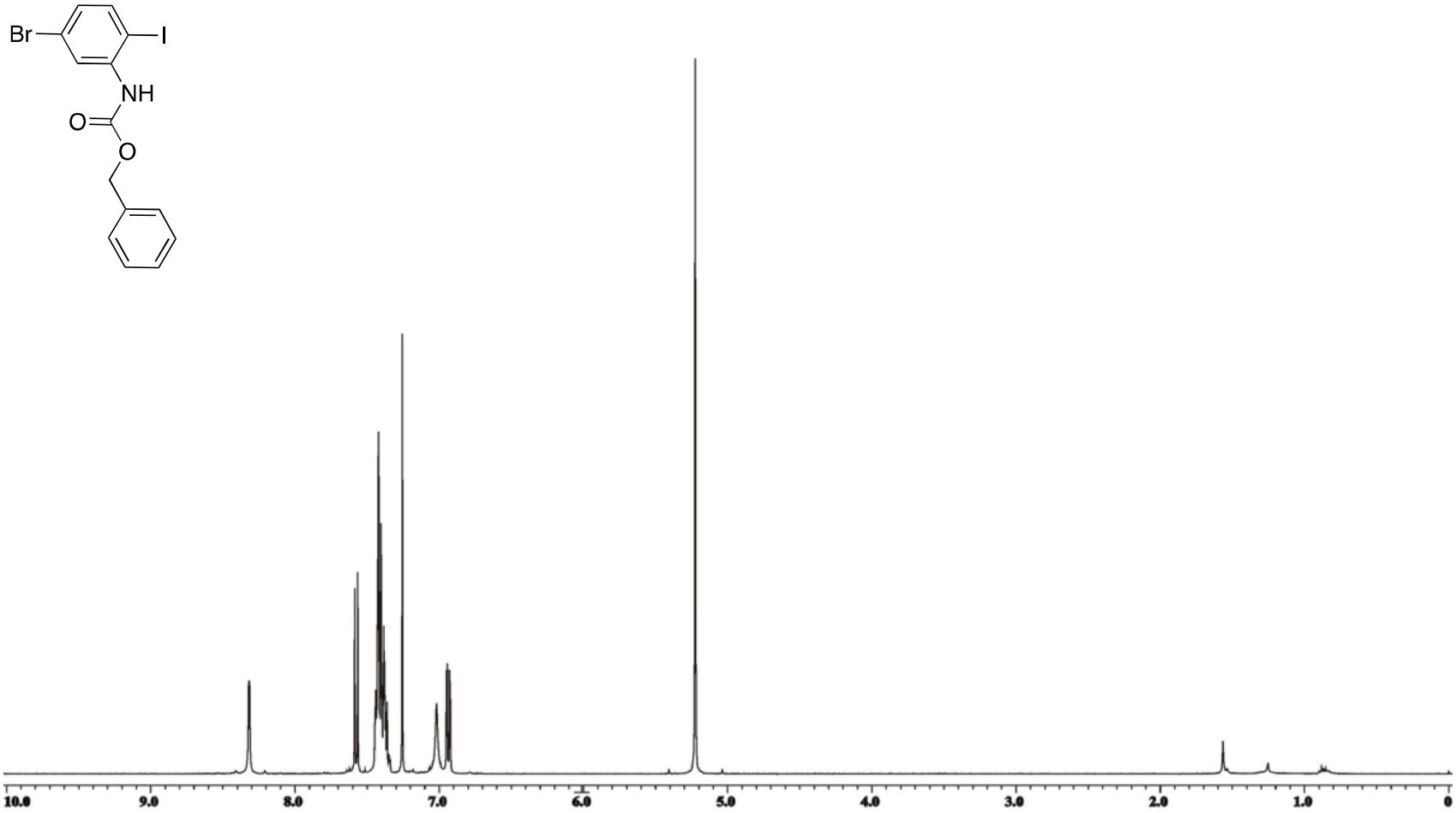
**Deprotection**. In a round bottom flask containing an stirring bar, under a $N_2$ atmosphere was added 133 mg (0.35 mmol, 1 equiv) of the coupling product from the previous step, 434 mg (3.5 mmol, 10 equiv) de $K_2CO_3$ and 5 mL of methanol and the mixture was stirred at room temperature for 15 min. Column chromatography using gradients of hexanes:ethyl acetate gave 70.4 mg (84%) of **3c** as a white solid. mp 129-131 ºC; $R_f$ = 0.33 (40% AcOEt/hexanes); IR (KBr) 3222, 3054, 2924, 2845, 2101, 1627, 1467 $cm^{-1}$; $^1$H RMN (400 MHz, $CDCl_3$): δ 7.49-7.41 (m, 3H), 3.76 (s, 2H), 3.29-3.27 (m, 4H), 3.26-3.23 (m, 4); $^{13}$C RMN (100 MHz, $CDCl_3$): δ 167.44, 139.25, 132.9, 132.4, 129.94, 123.36, 119.28, 82.87, 80.29, 66.82, 66.64, 47.27, 42.11.

*For preparation of 2,5-diiodo-morpholinebenzamide see: Flores-Jarillo, M.; Ayala-Mata, F.; Zepeda-Vallejo, G.; Vázquez García, R. A.; Ramos-Ortiz, G.; Mendez-Rojas, M. A.; Suarez-Castillo, O. R.; Alvarez-Hernandez, A. *J. Mex. Chem. Soc*. **2015**, *59*, 151-160. *In press*.

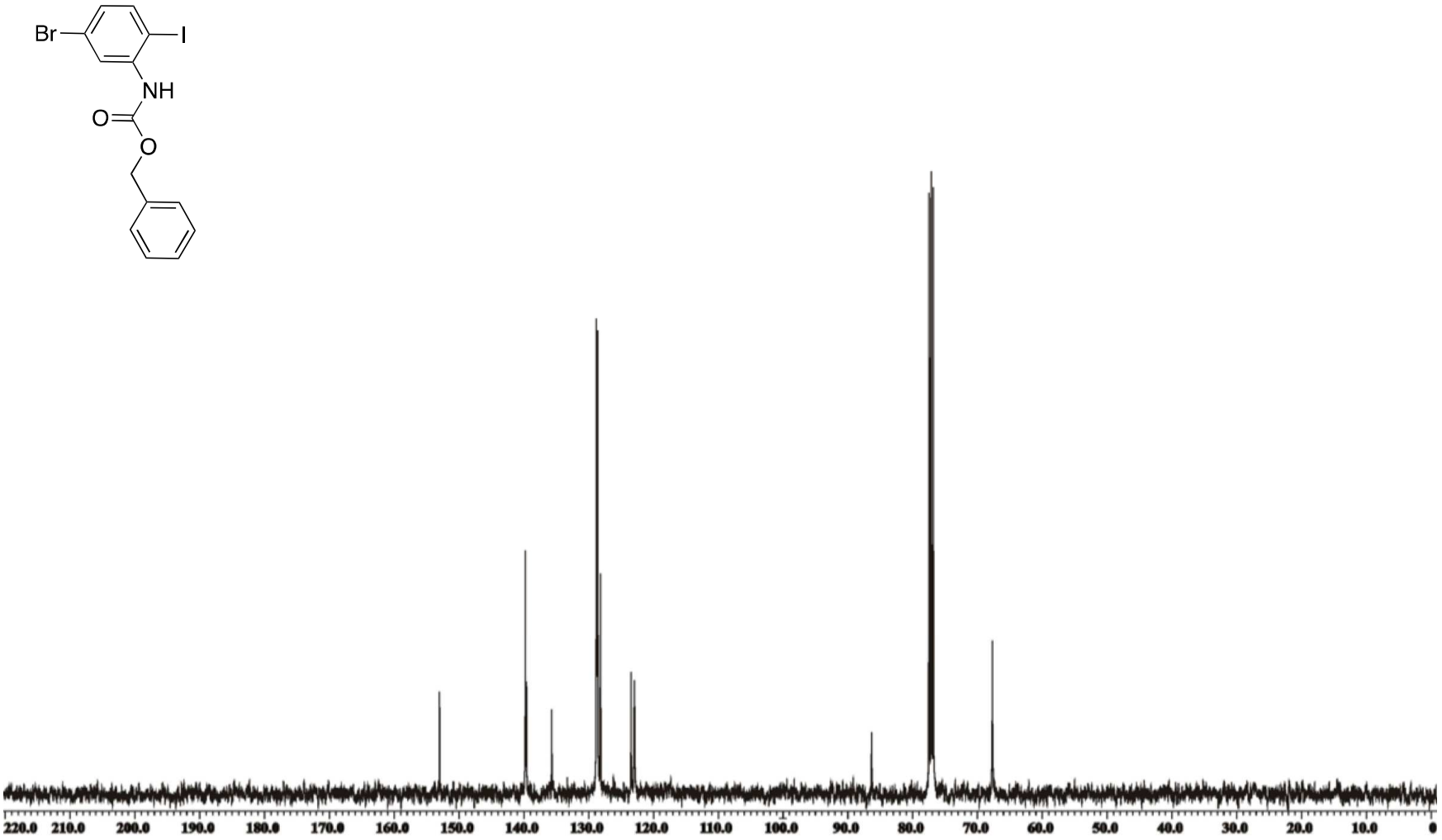
**Alkynes 3d-i.**

These compounds were prepared according to the reported procedure: Wang, Y.; Ji, K.; Lan, S.; Zhang, L. *Angew. Chem. Int. Ed.* **2012**, **51**, 1915-1918. See the supporting material.

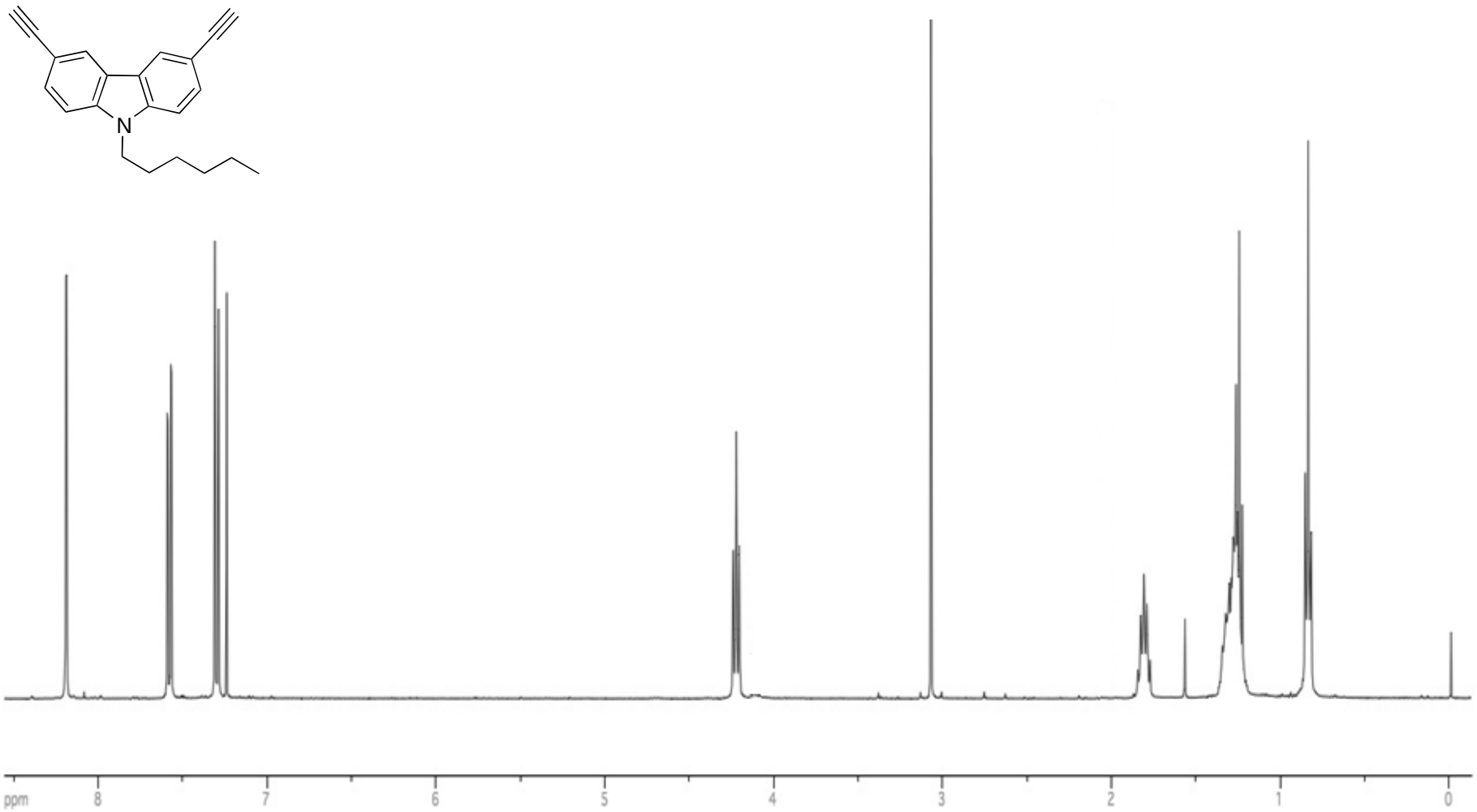
# $^{1}$H and $^{13}$C NMR Spectra



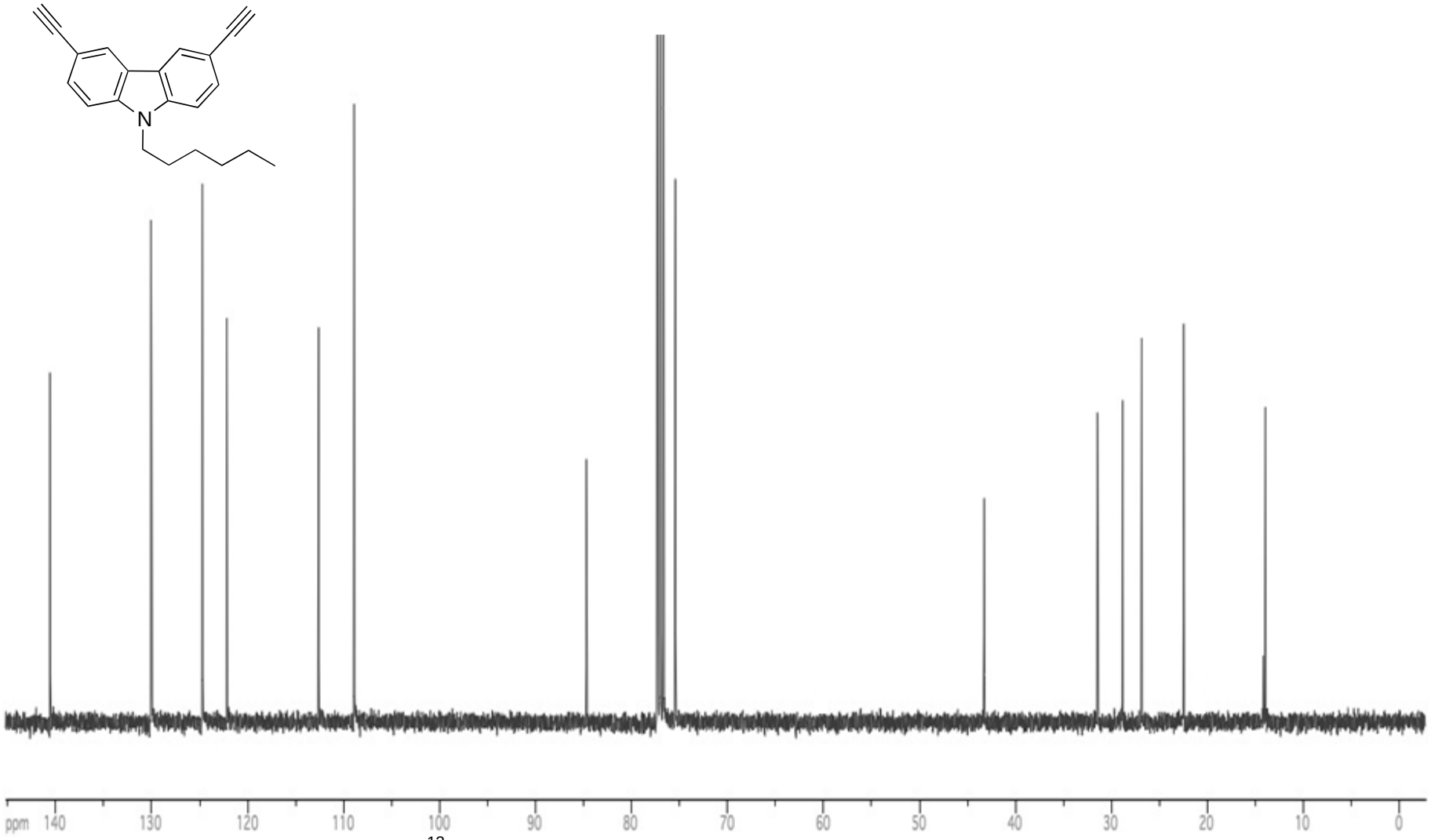

$^{1}$H NMR spectrum of **2** in acetone-*d6* 400 MHz.



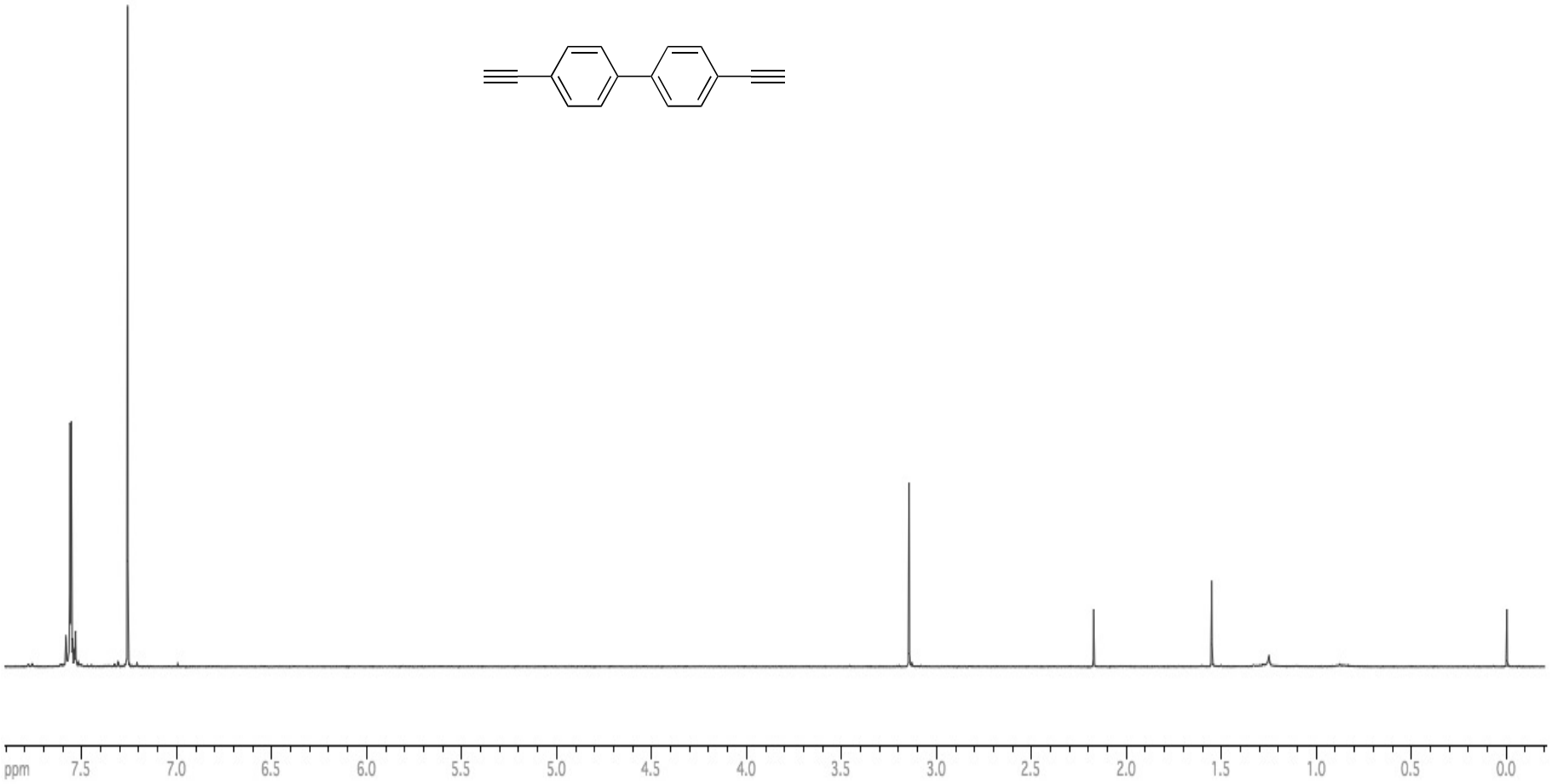

$^{13}$C NMR spectrum of **2** in acetone-*d6* 100 MHz.



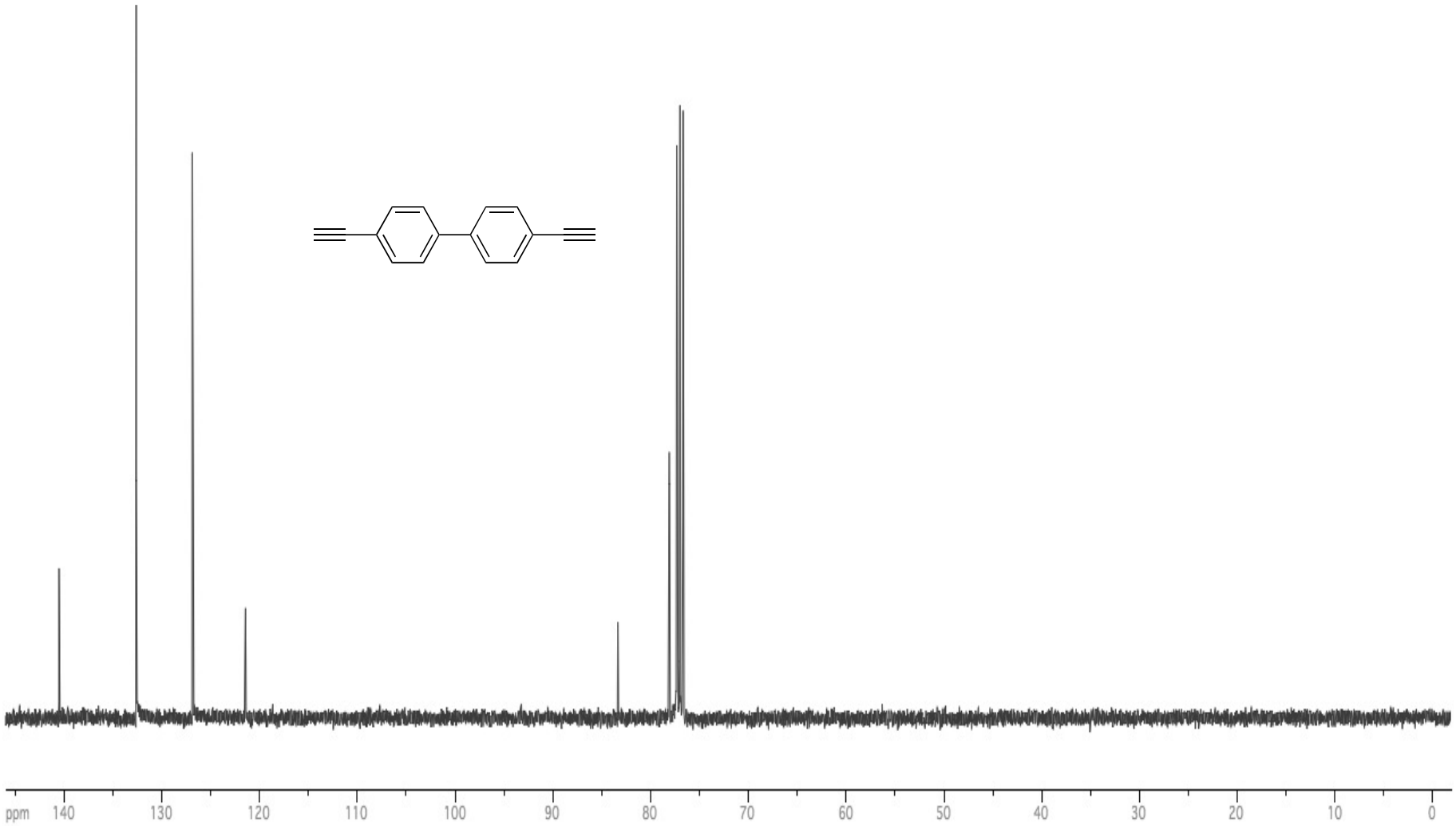

$^{1}$H NMR spectrum of **3a** in $CDCl_3$ 400 MHz



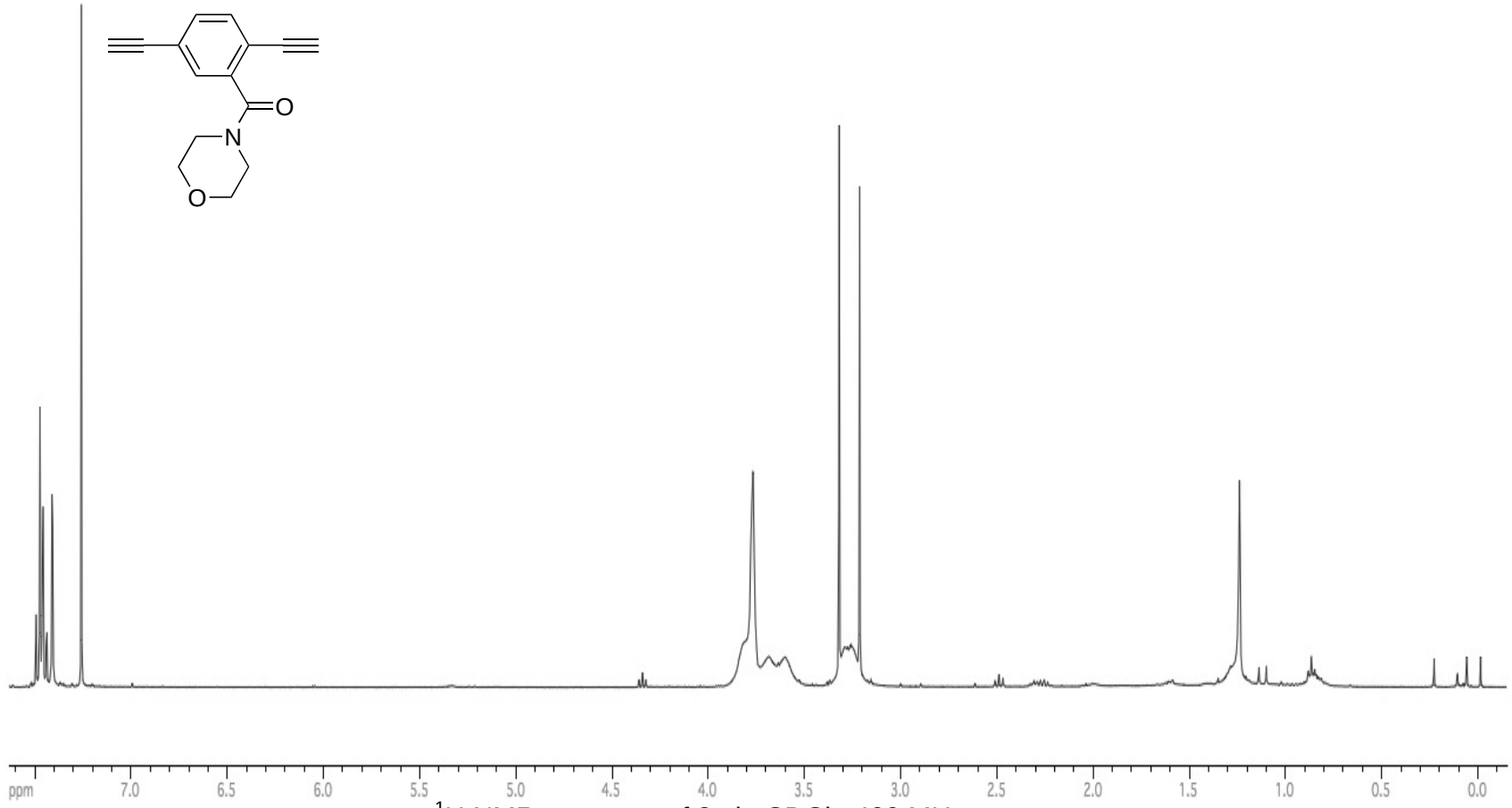

$^{13}$C NMR spectrum of **3a** in $CDCl_3$ 100 MHz



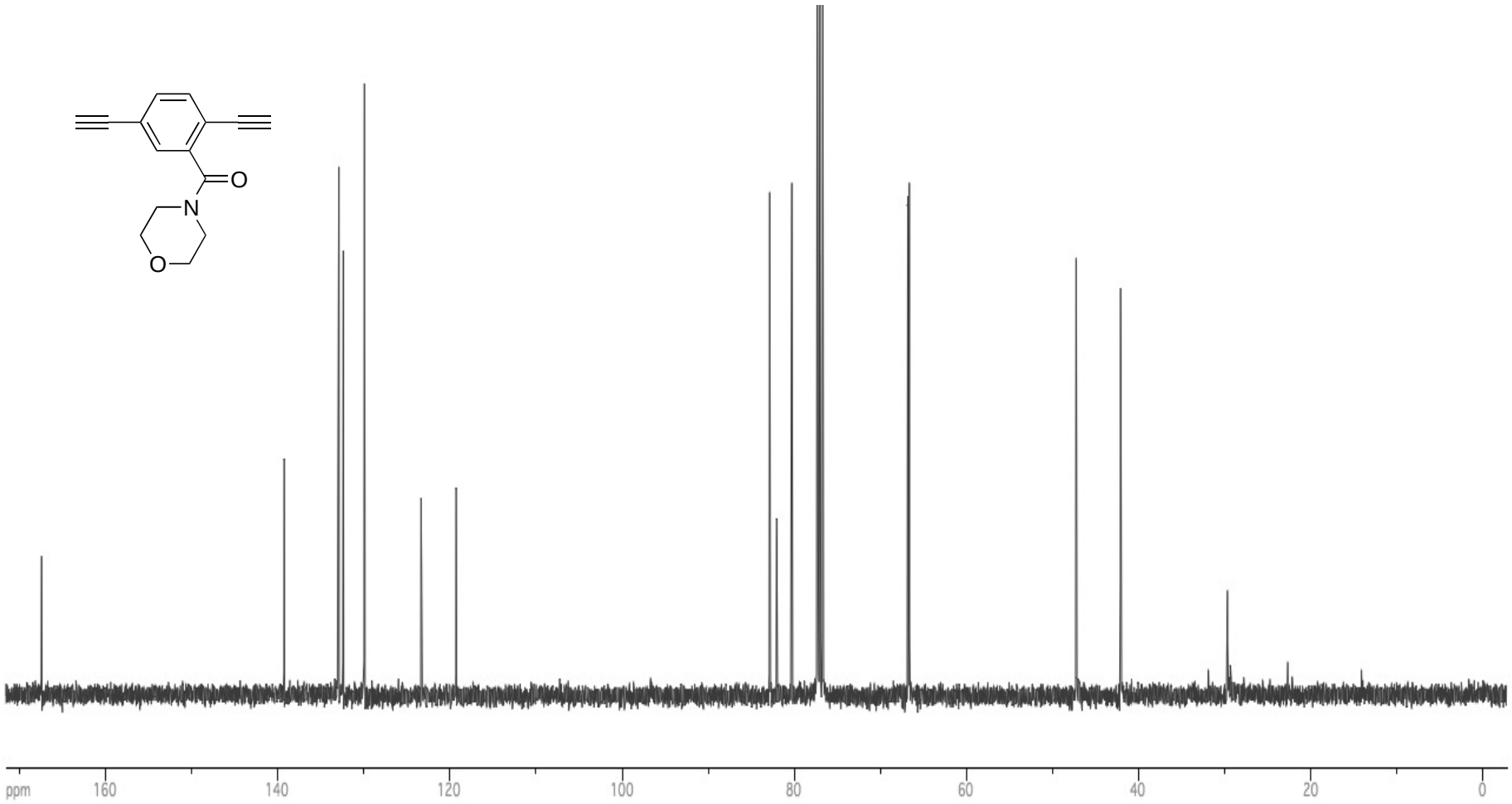

$^{1}$H NMR spectrum of **3b** in $CDCl_3$ 400 MHz



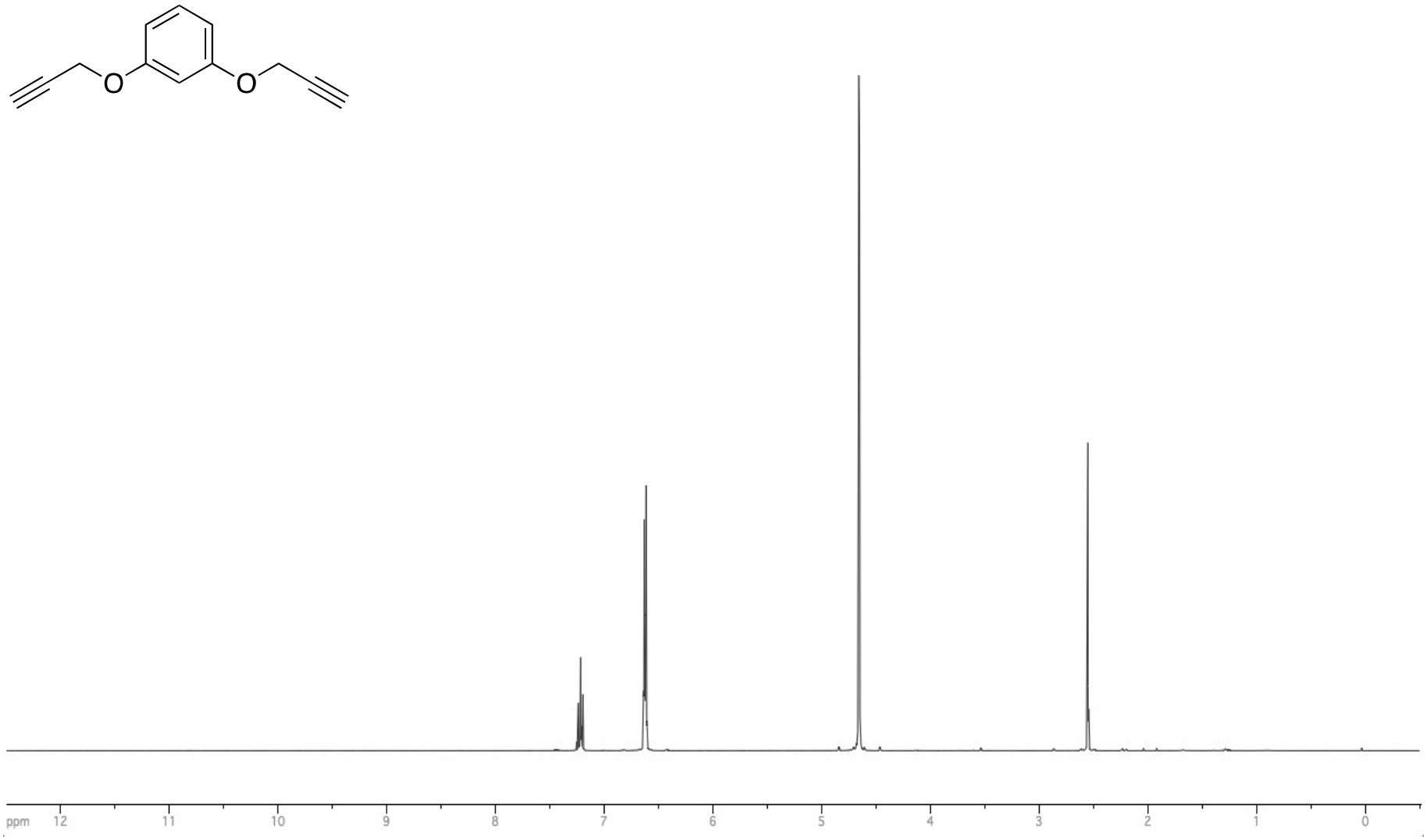

$^{13}$C NMR spectrum of **3b** in $CDCl_3$ 100 MHz



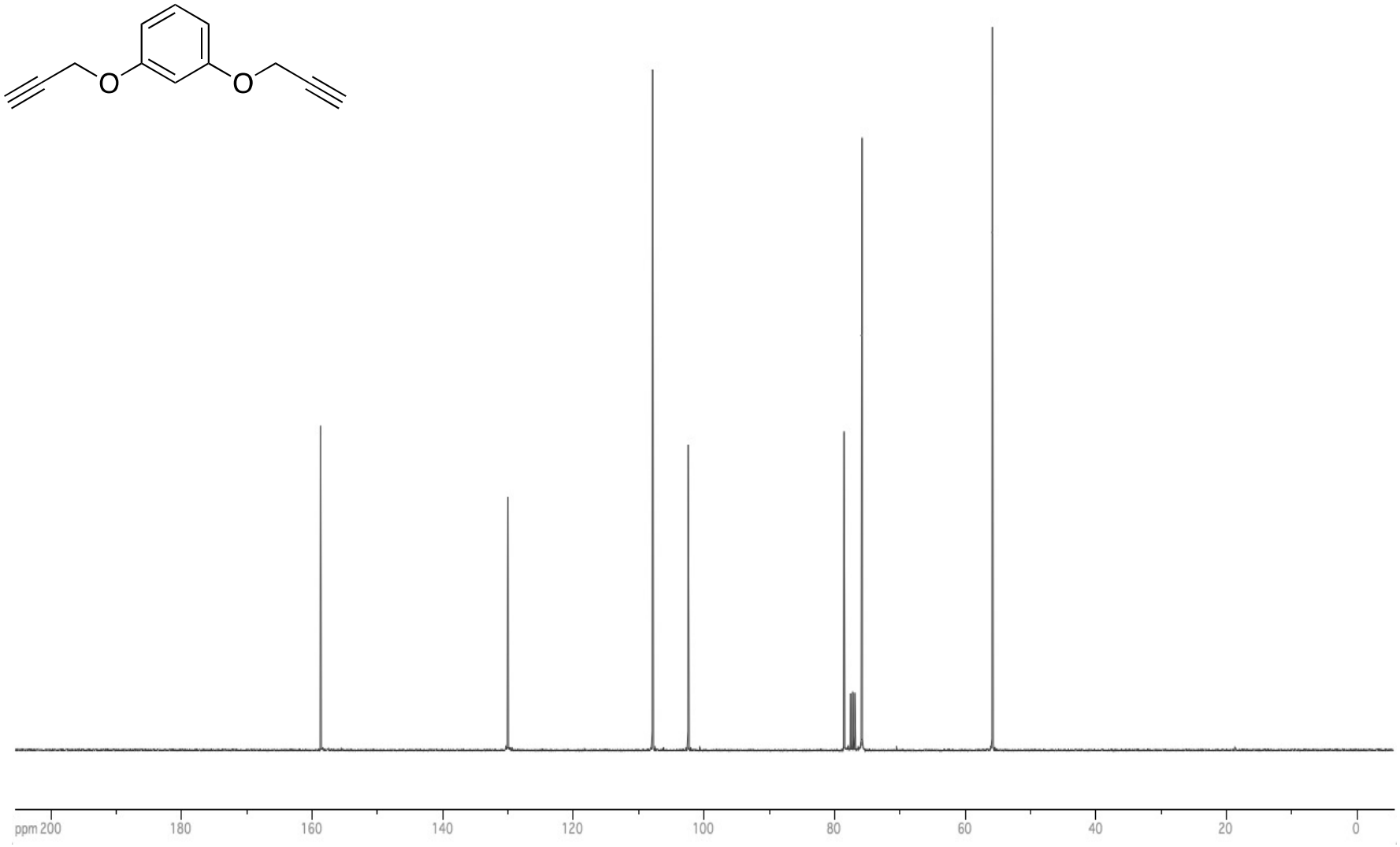

$^1$H NMR spectrum of **3c** in $CDCl_3$ 400 MHz




$^{13}$C NMR spectrum of **3c** in $CDCl_3$ 100 MHz




$^1$H NMR spectrum of compound **3d** in $CDCl_3$ 400 MHz

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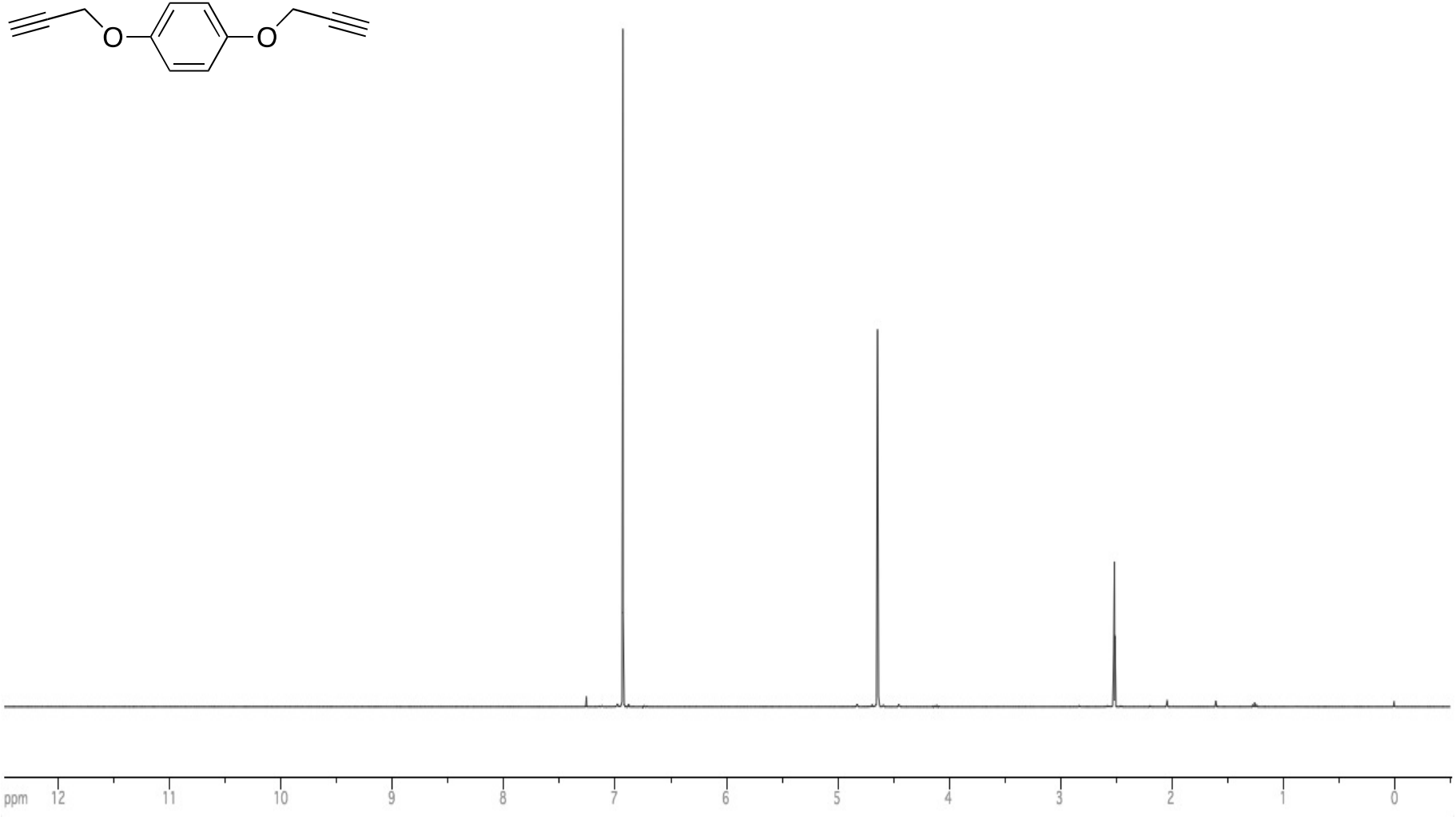


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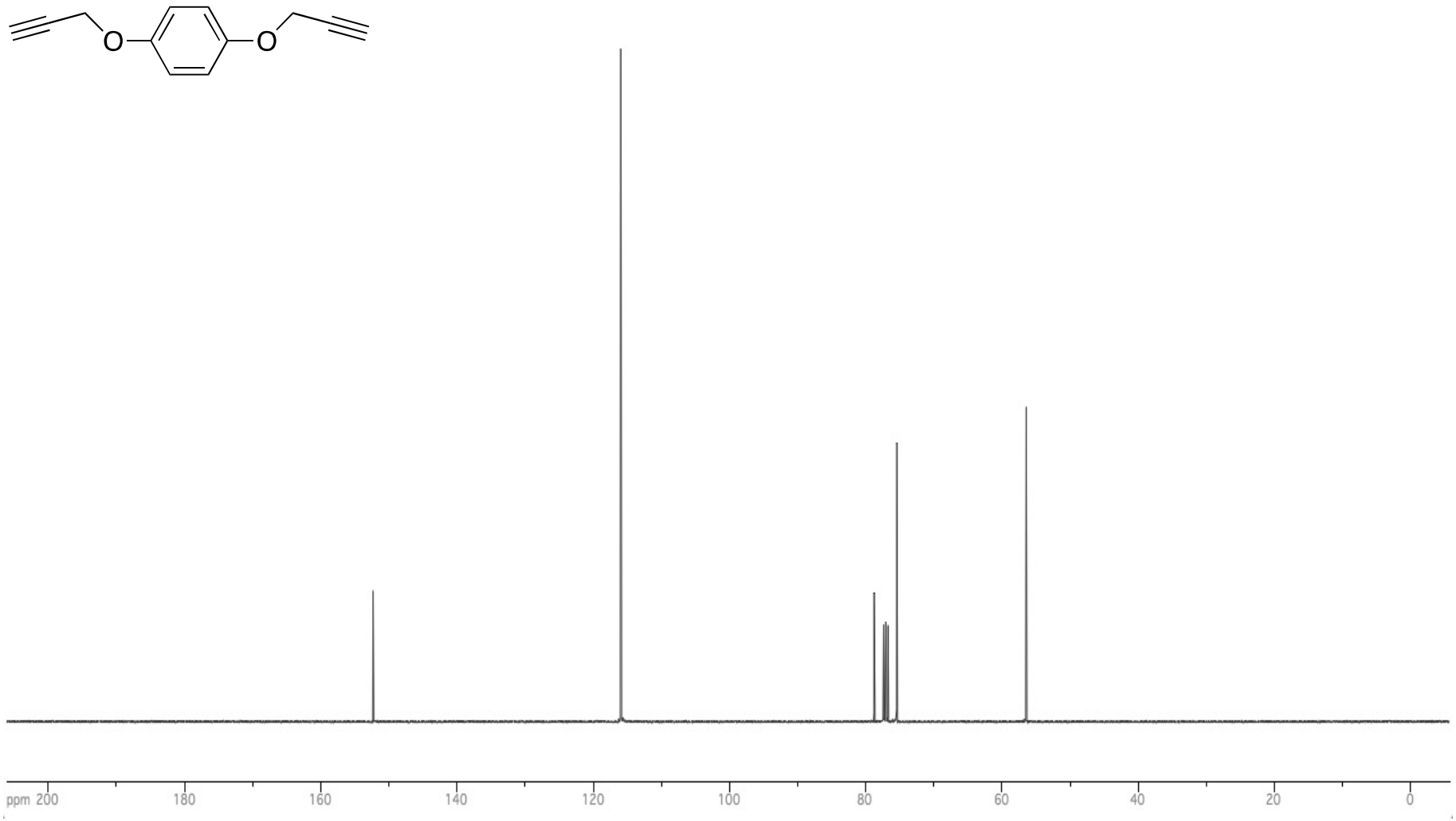
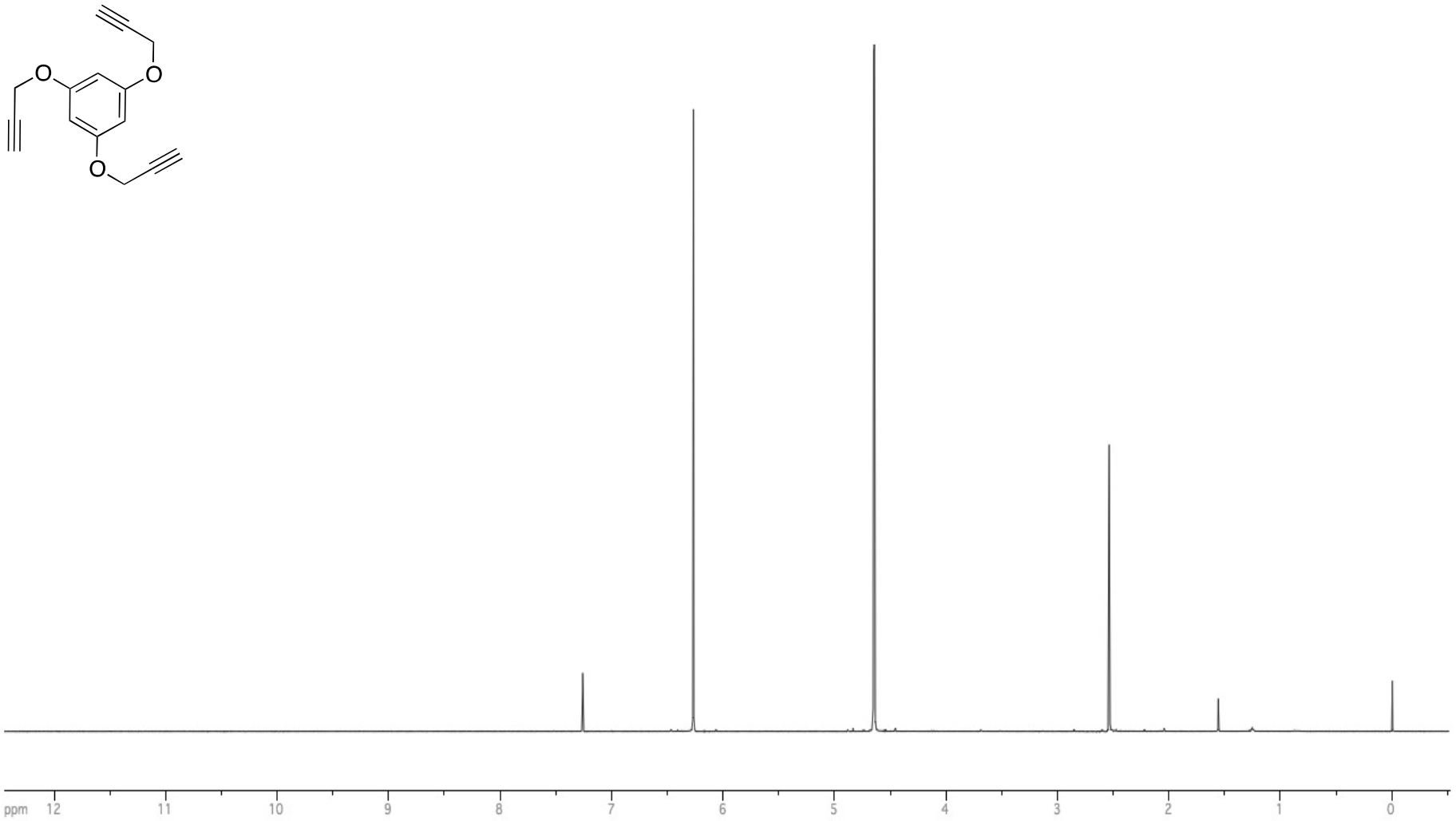
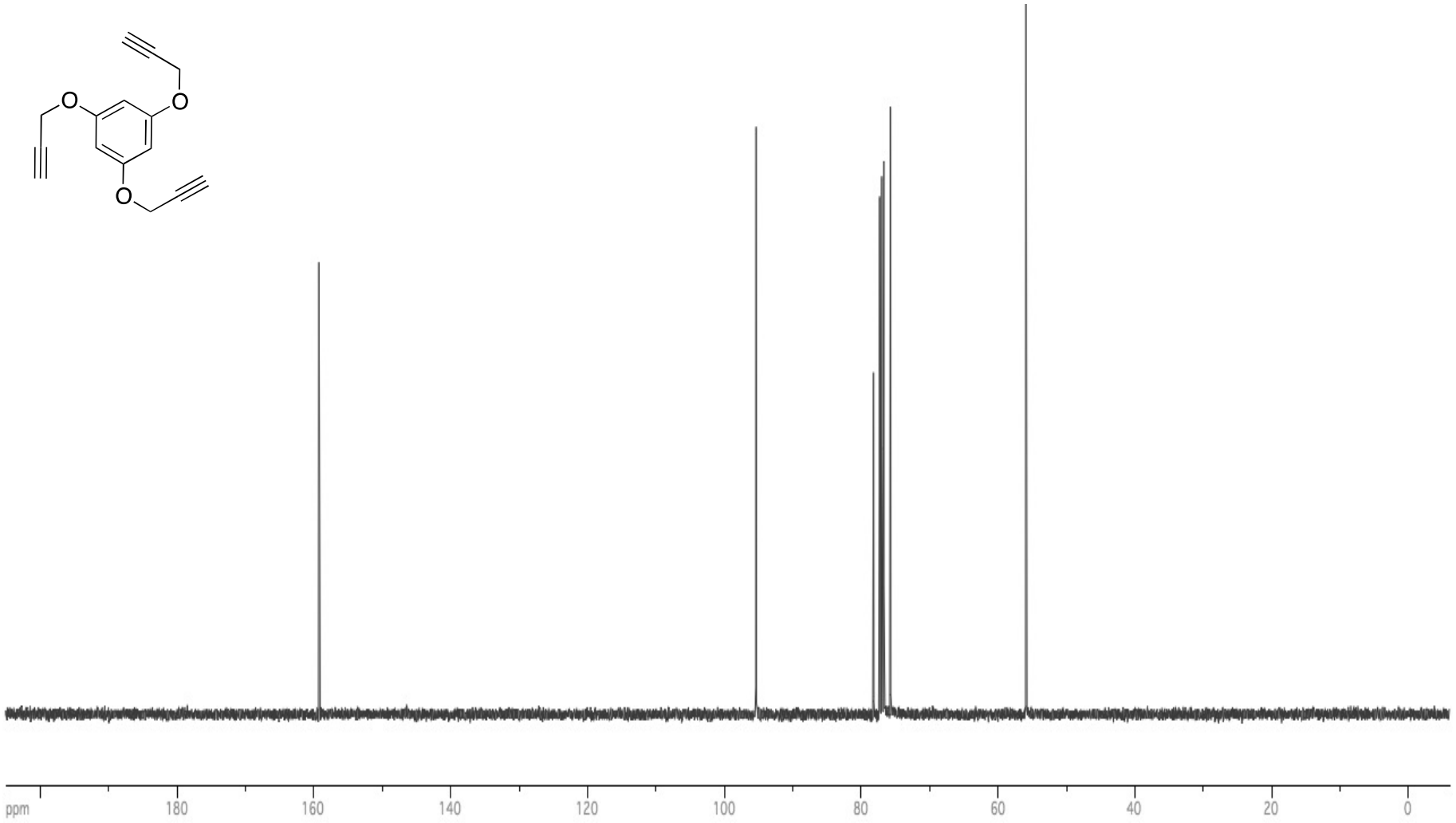


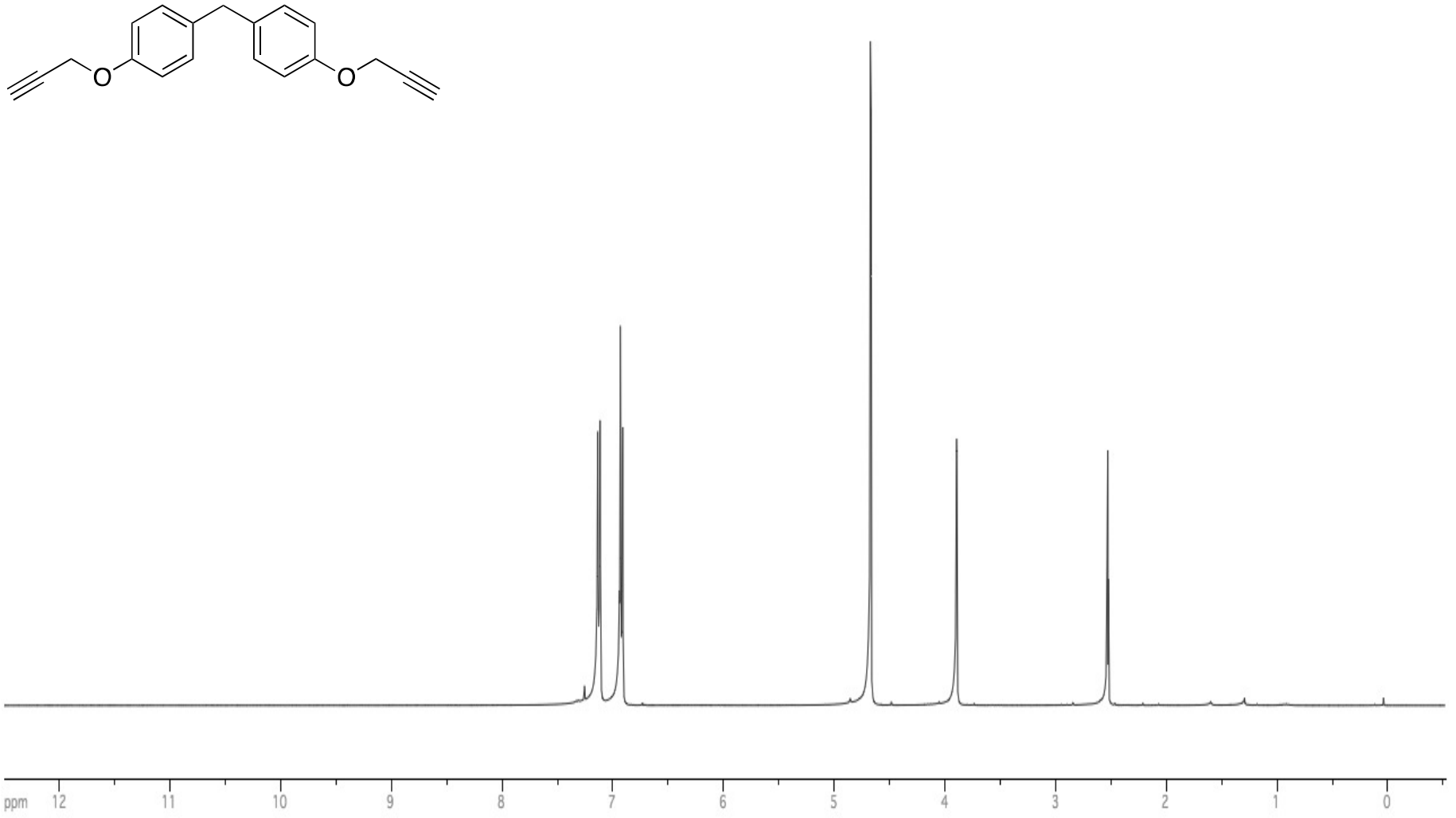

$^{13}$C NMR spectrum of compound **3e** in $CDCl_3$ 100 MHz




$^{1}$H NMR spectrum of compound **3f** in $CDCl_3$ 400 MHz




$^{13}$C NMR spectrum of compound **3f** in $CDCl_3$ 100 MHz

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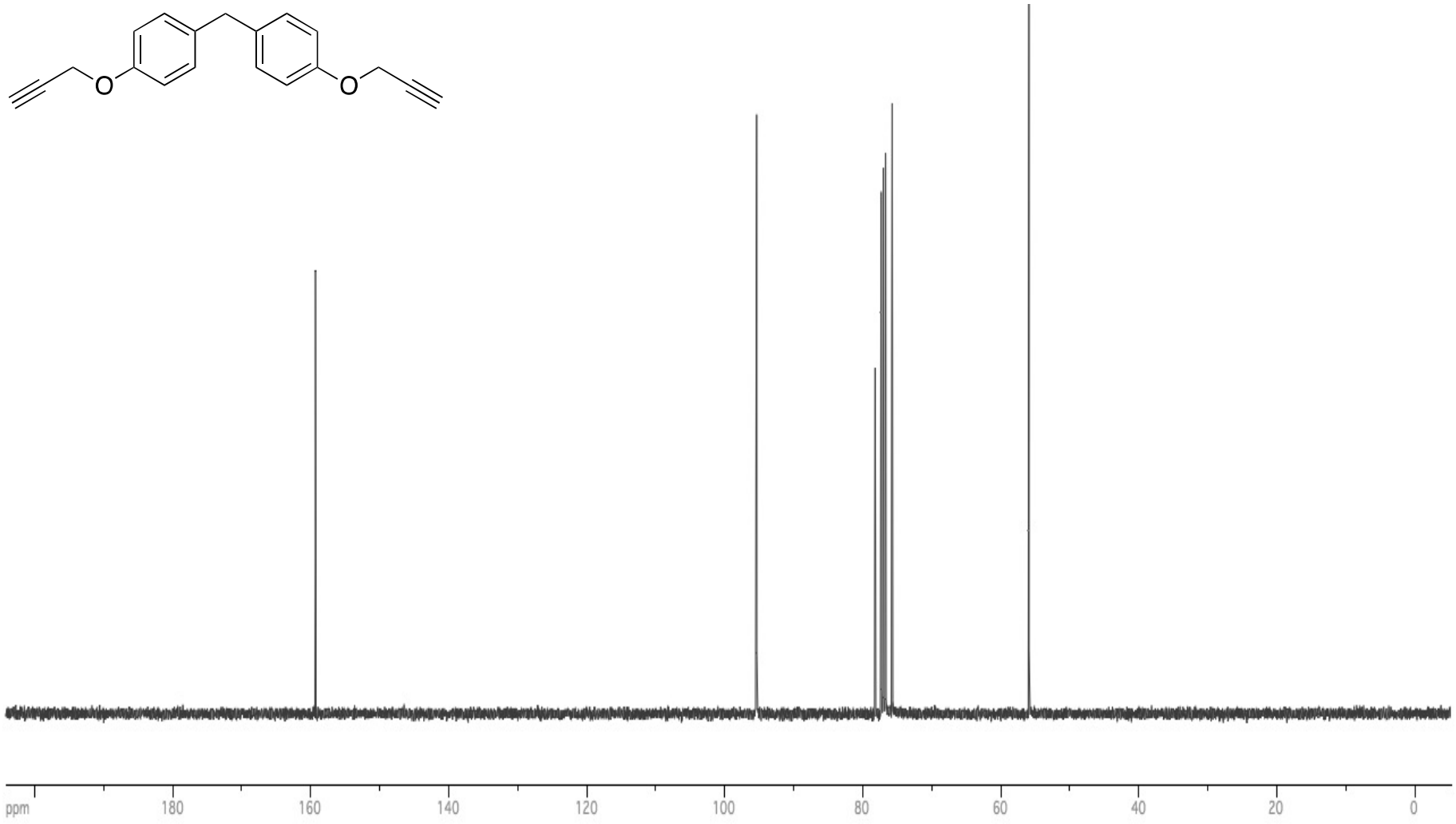
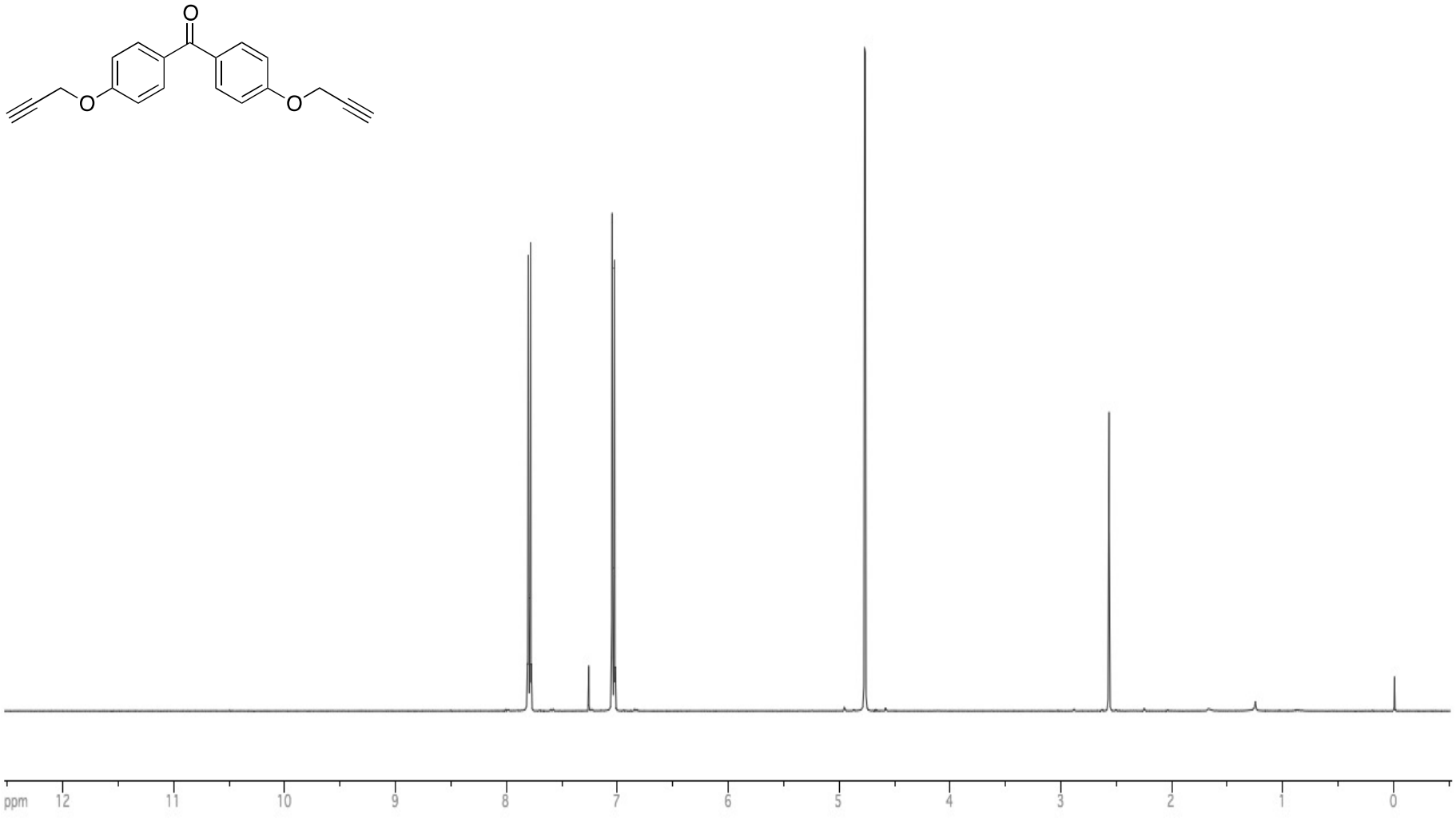
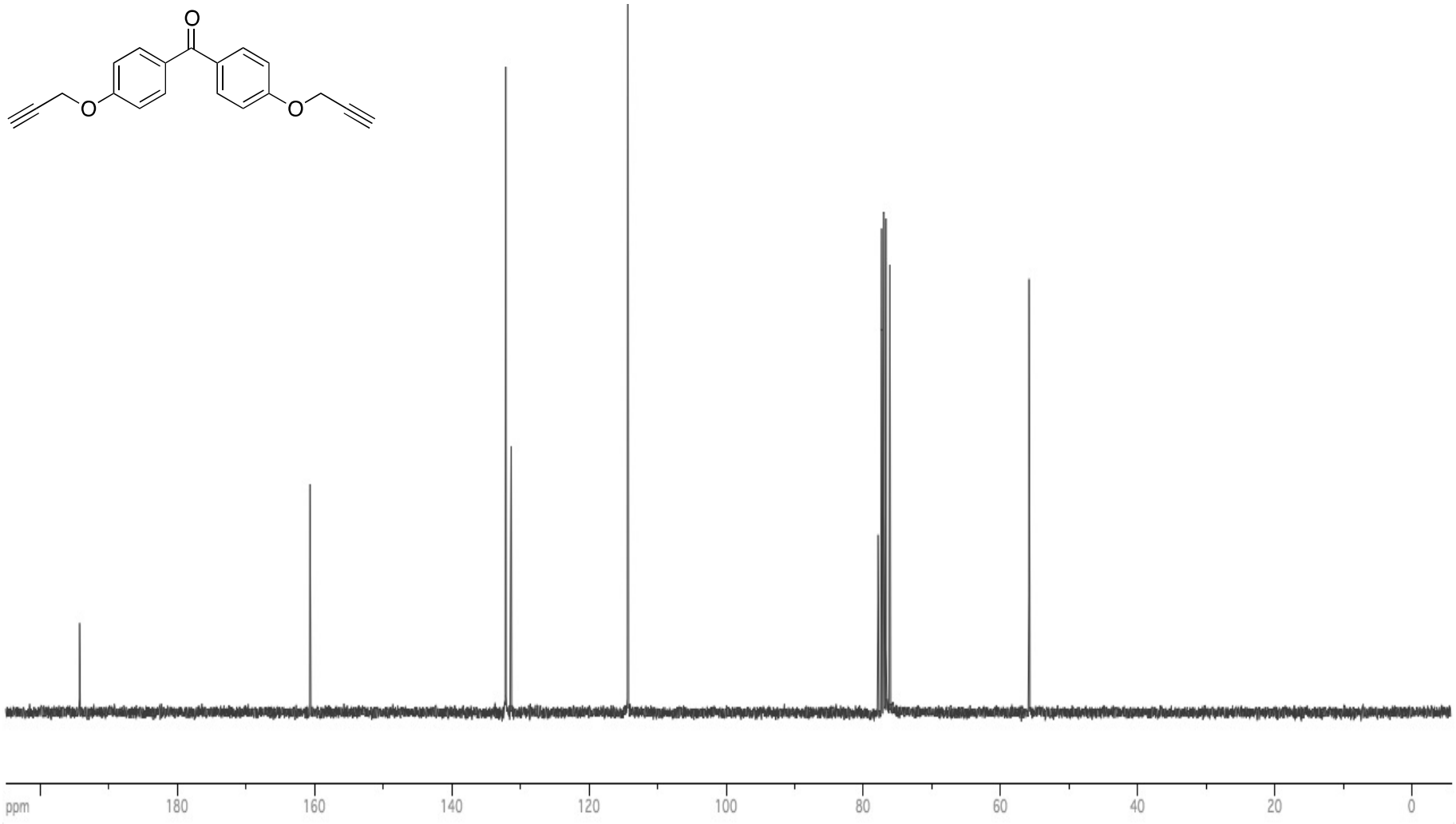


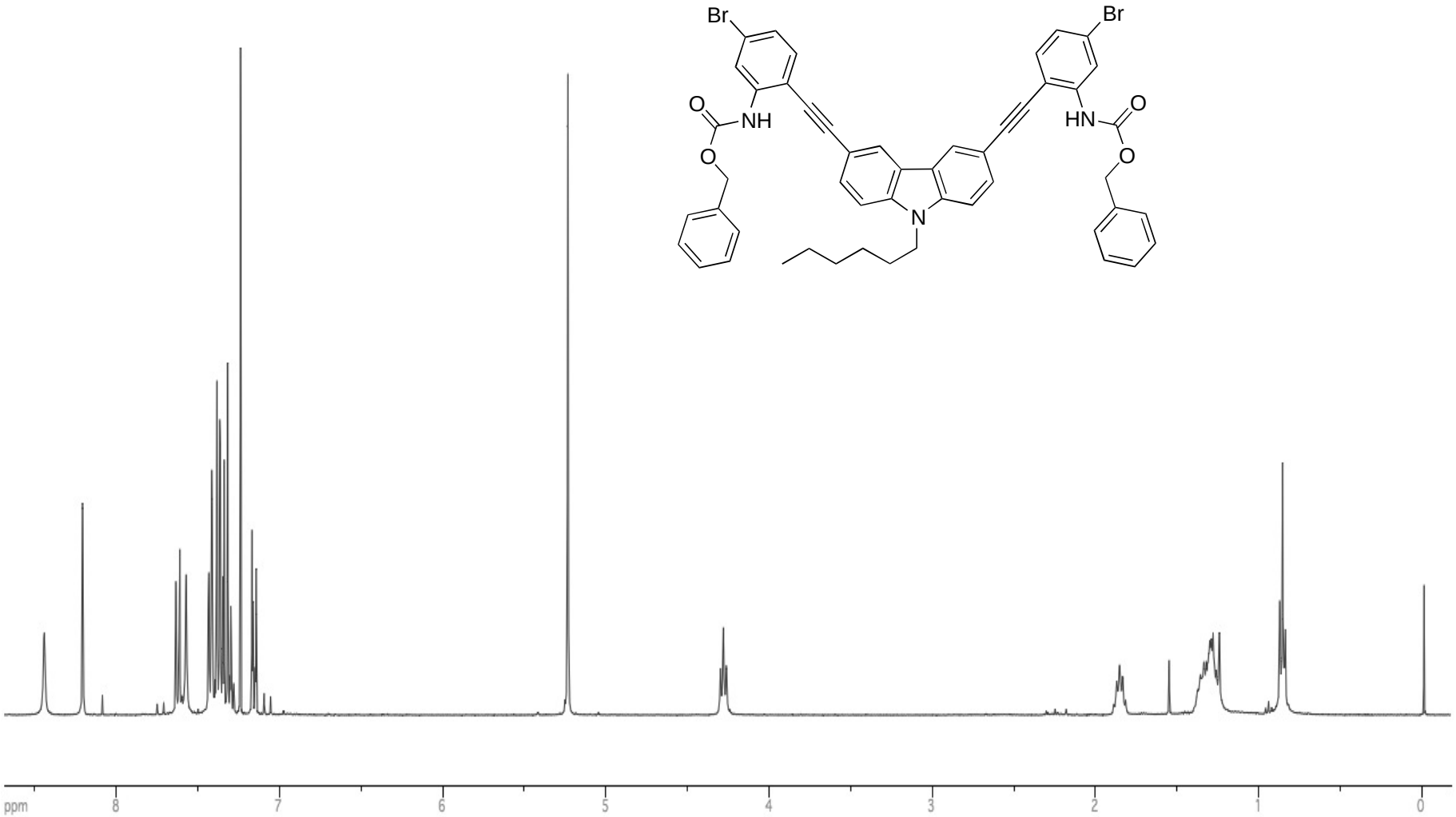

$^{13}$C H NMR spectrum of compound **3g** in $CDCl_3$ 100 MHz



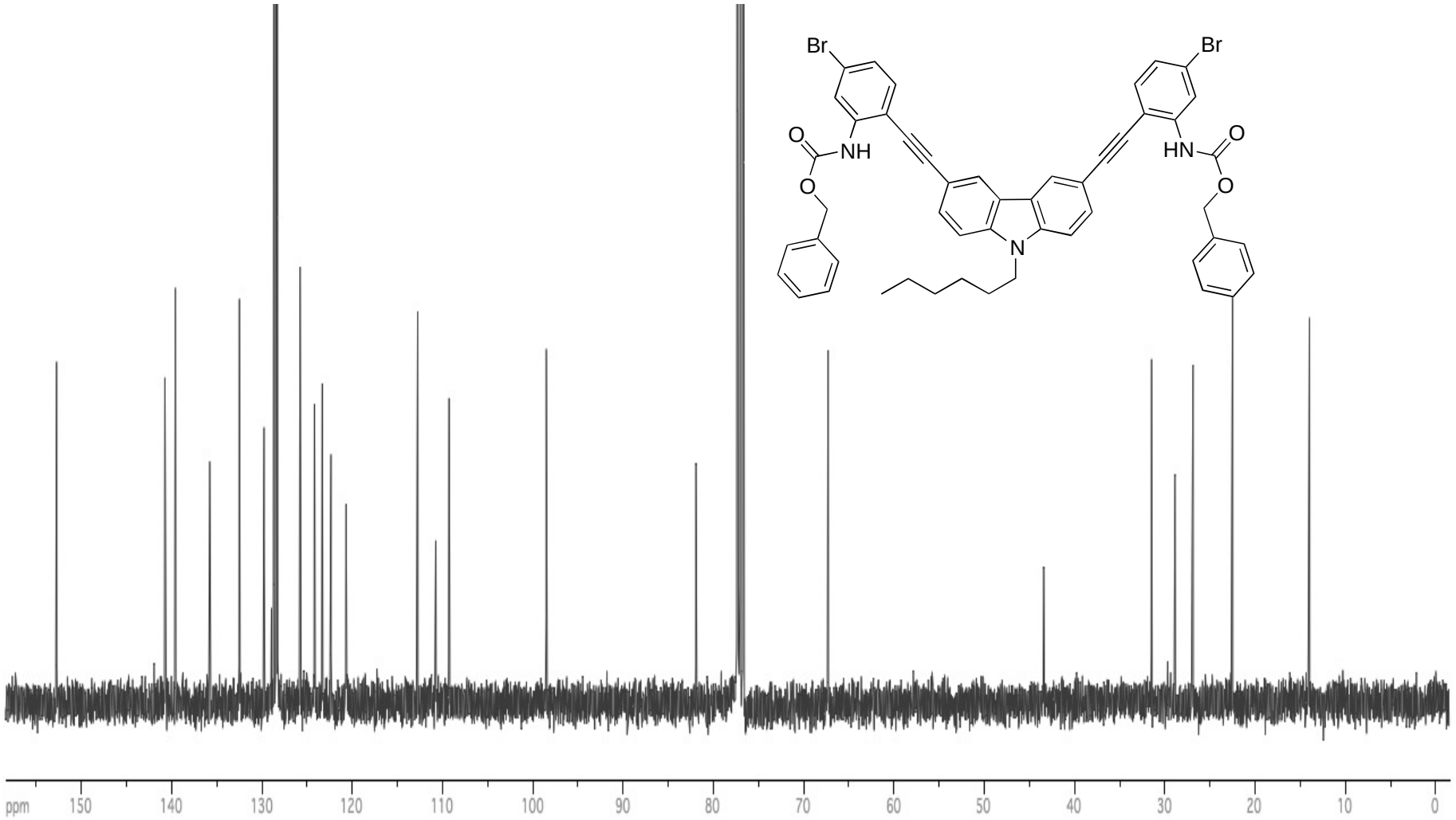

$^{1}$H NMR spectrum of compound **3h** in $CDCl_3$ 400 MHz



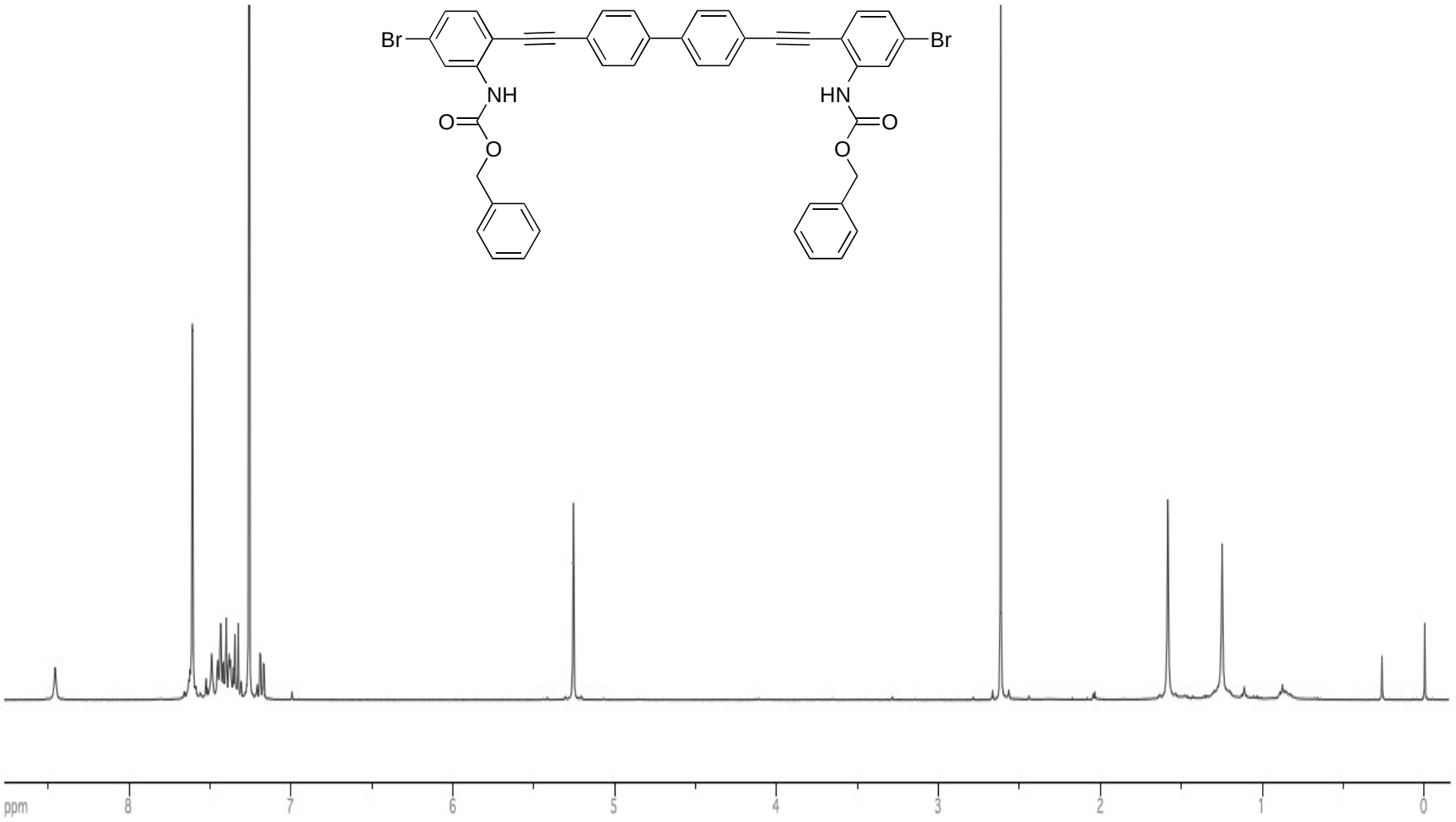

$^{13}$C NMR spectrum of compound **3h** in $CDCl_3$ 100 MHz




$^1$H NMR spectrum of **4a** in $CDCl_3$ 400 MHz




$^{13}C$ NMR spectrum of **4a** in $CDCl_3$ 100 MHz

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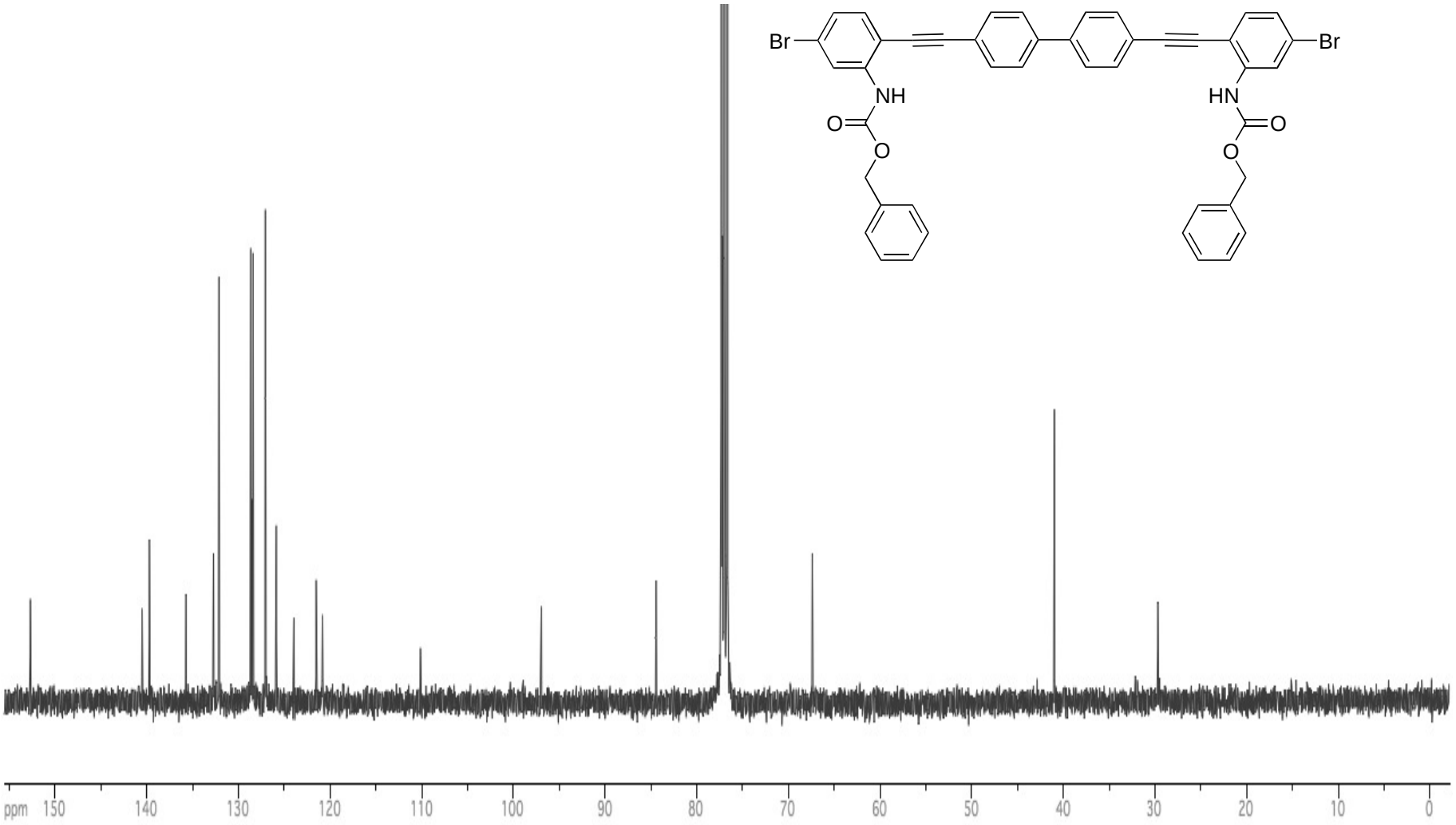


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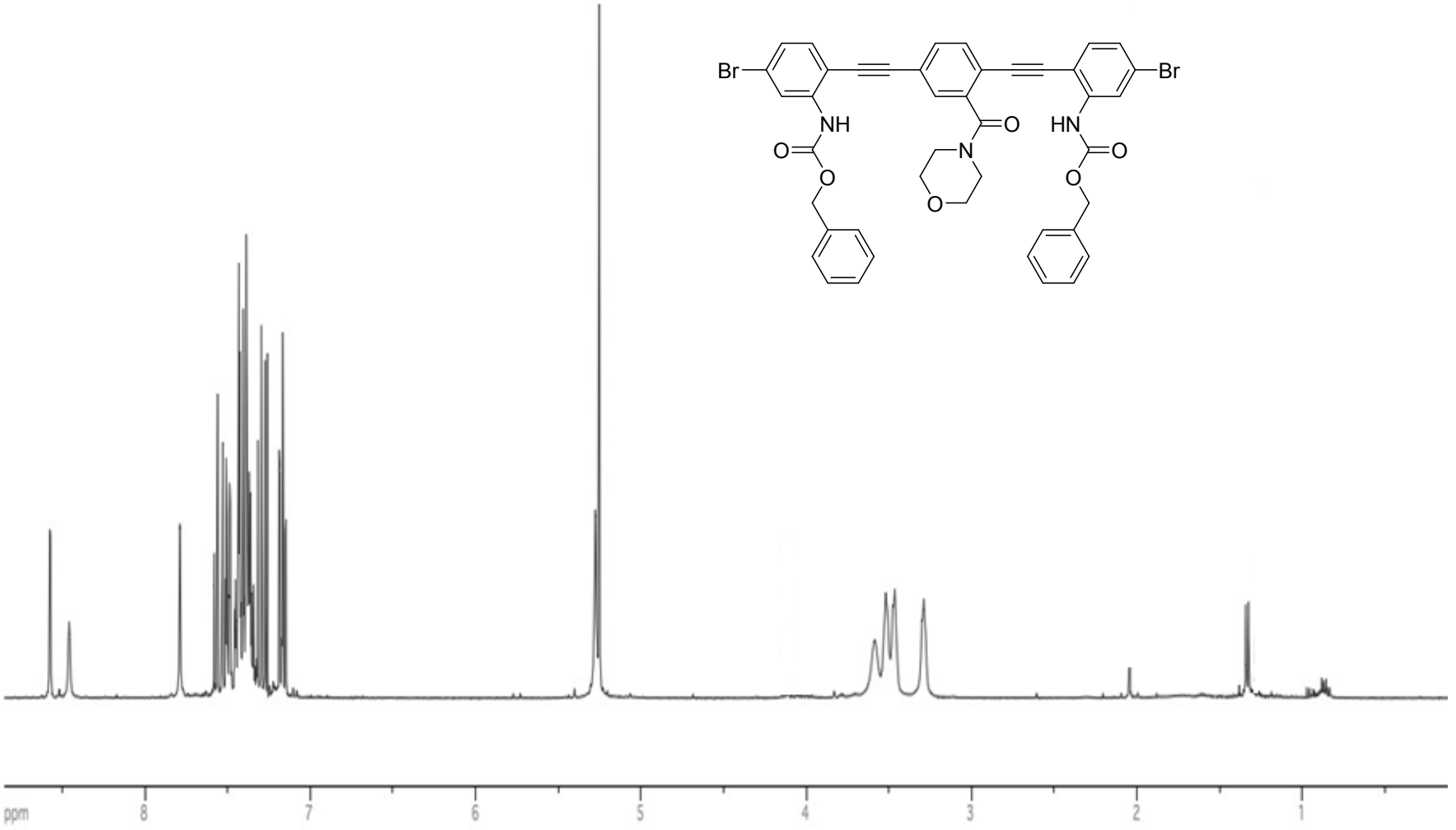


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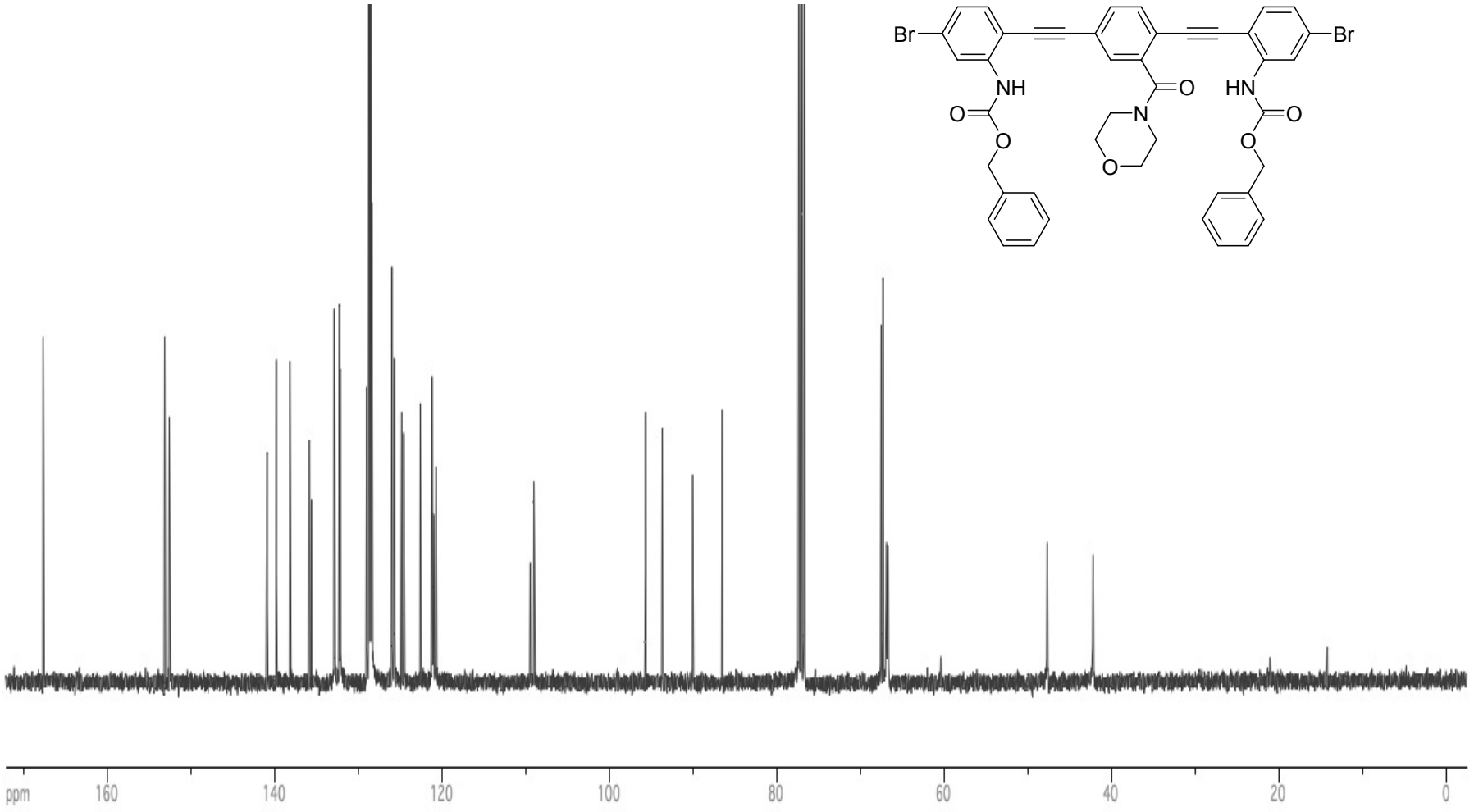


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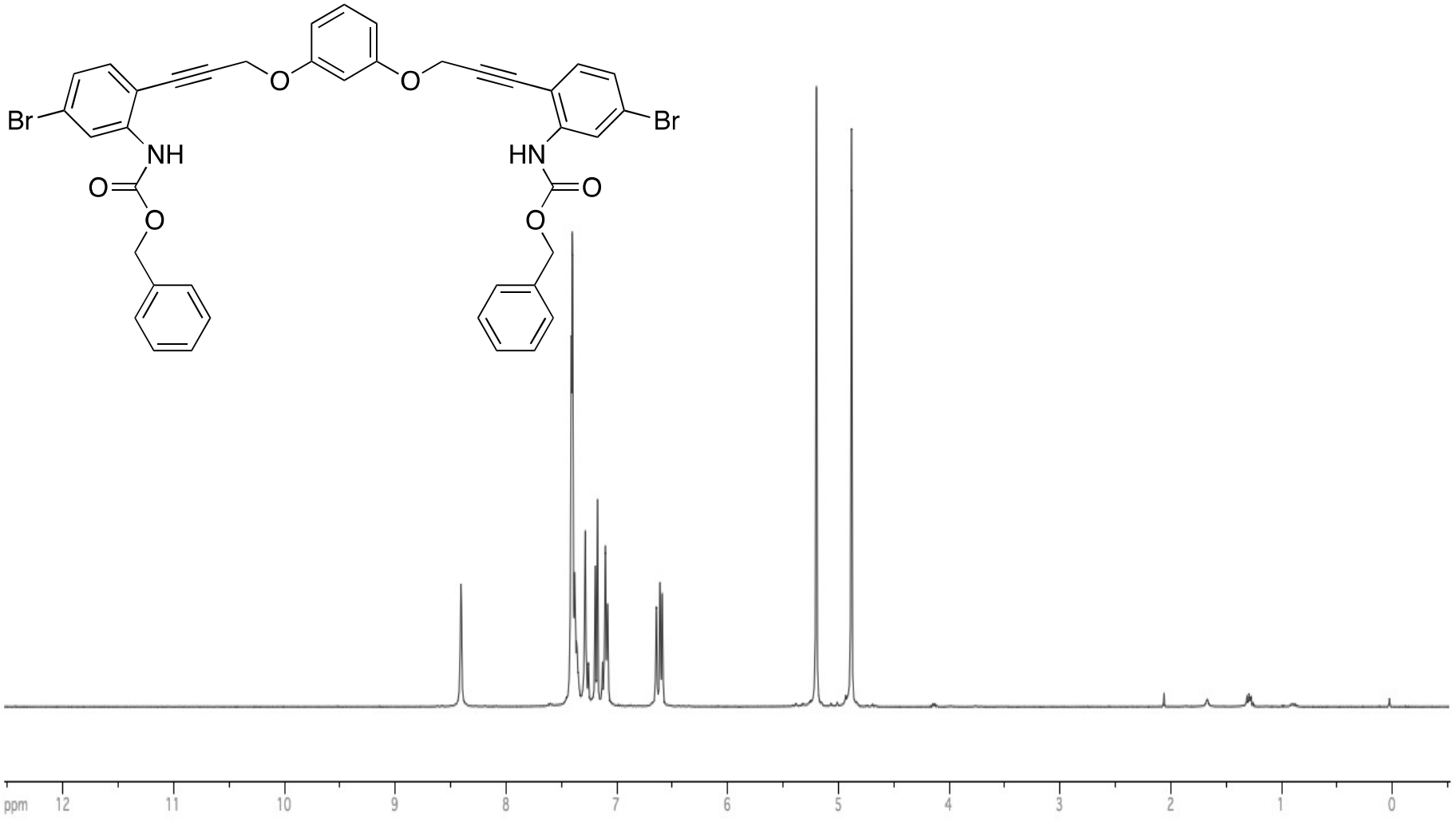


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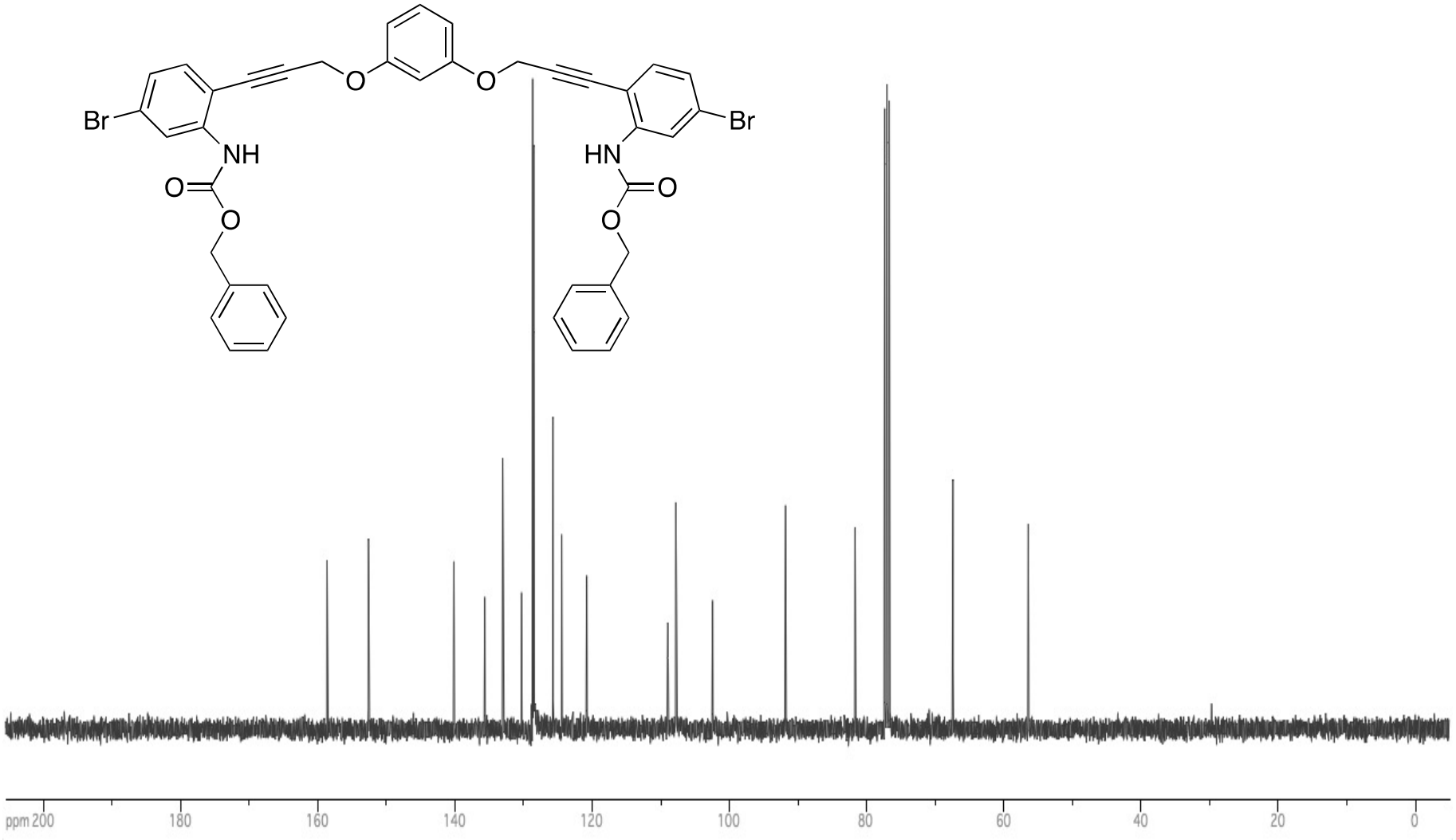


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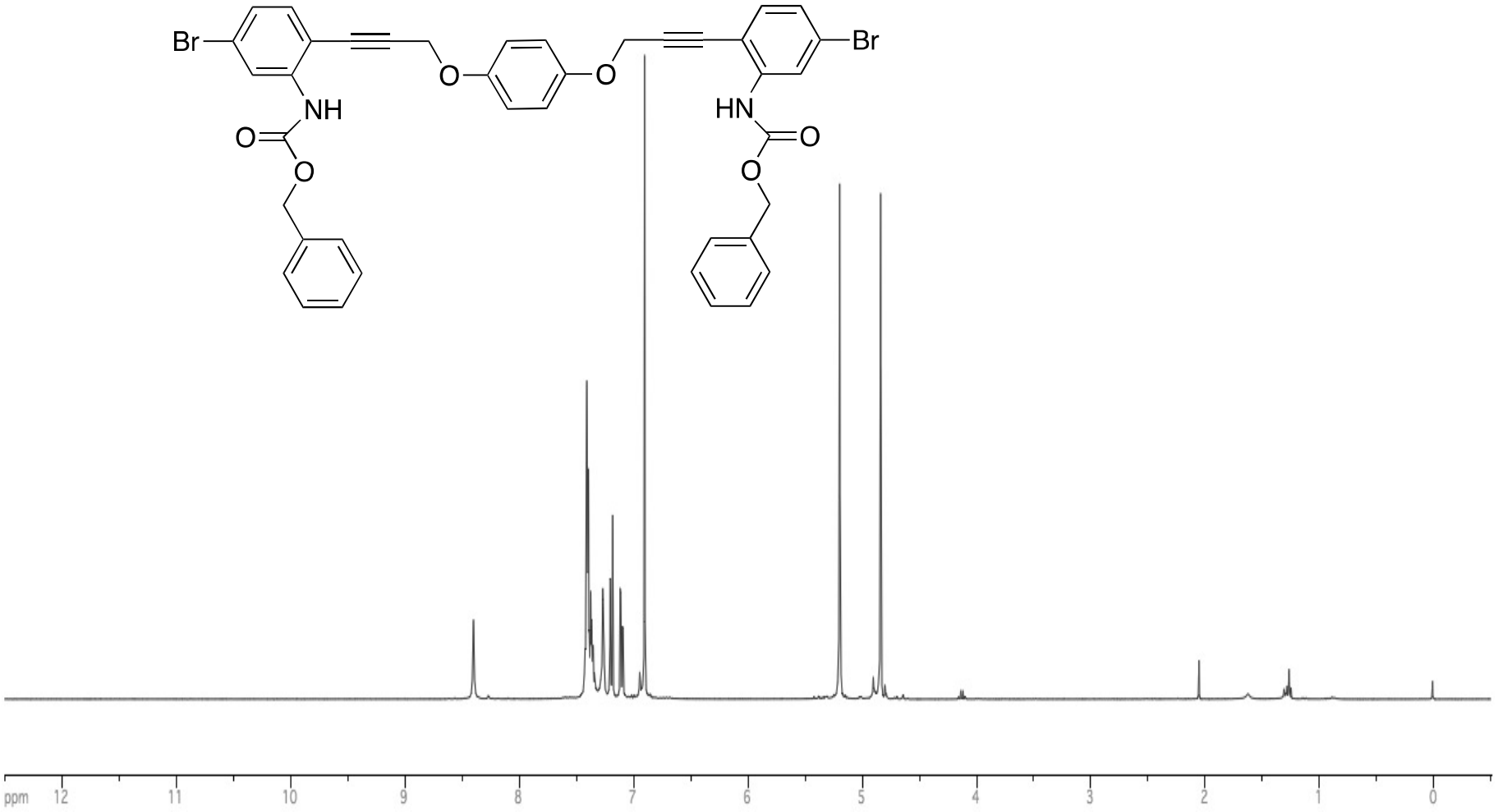


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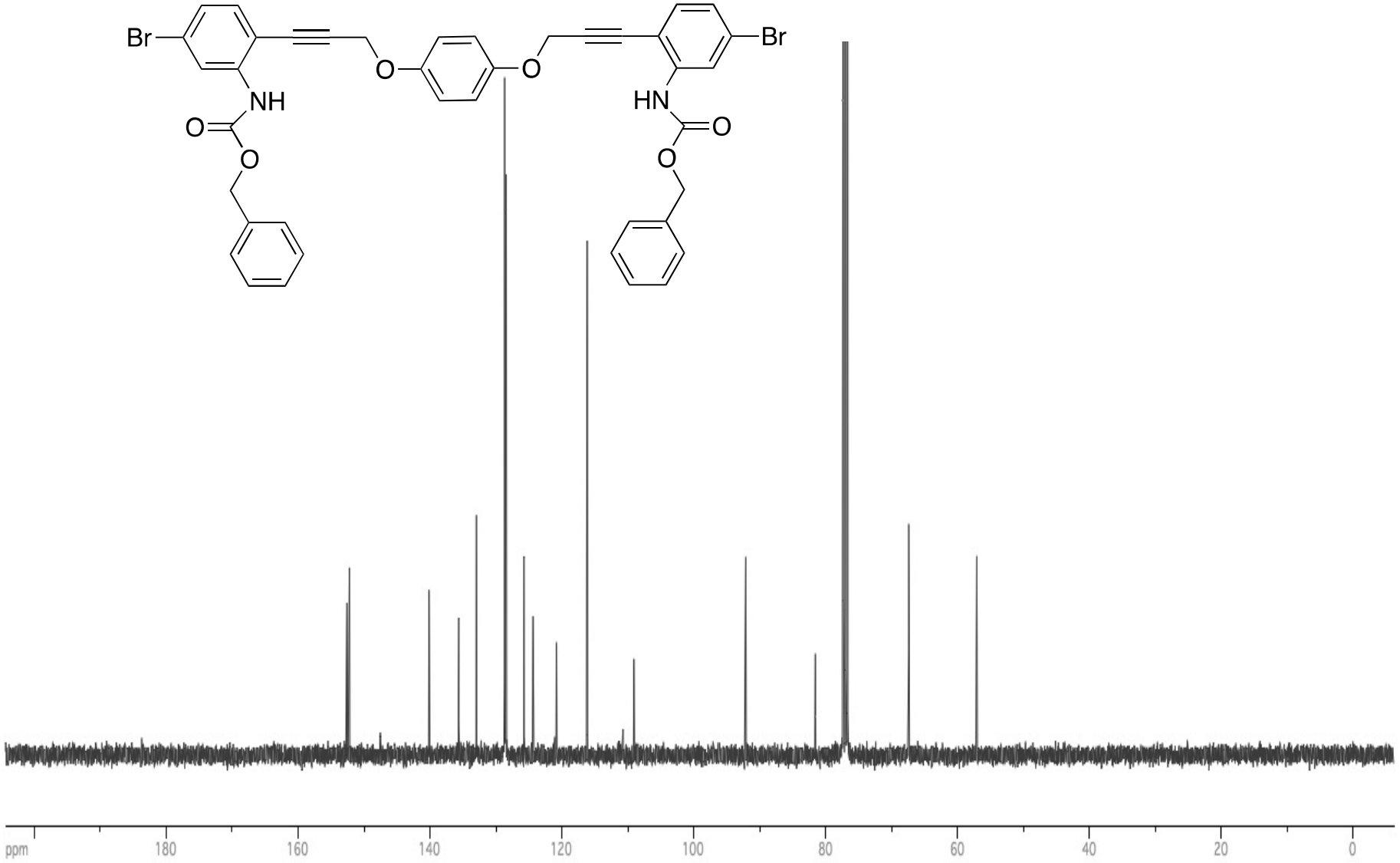


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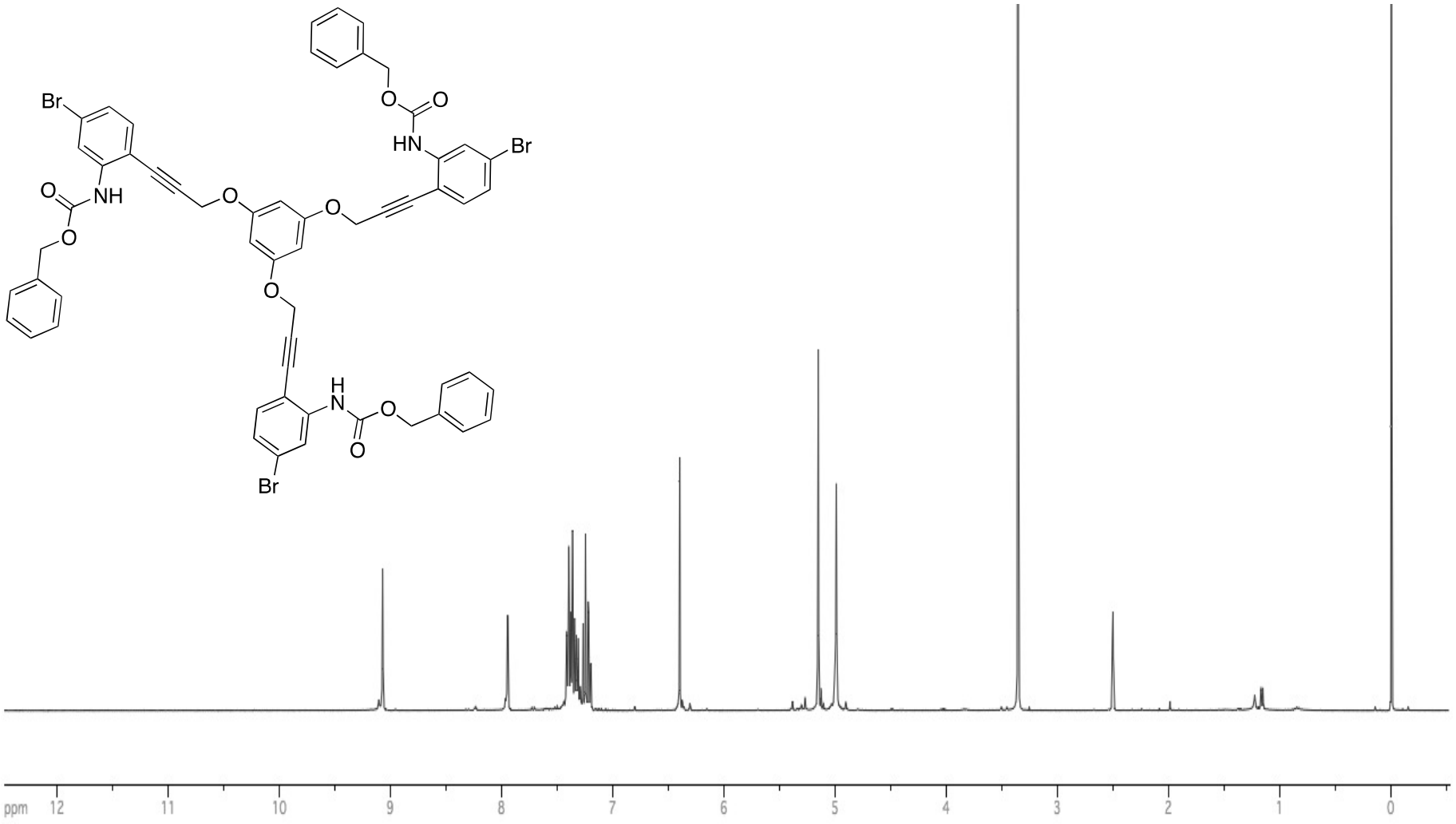


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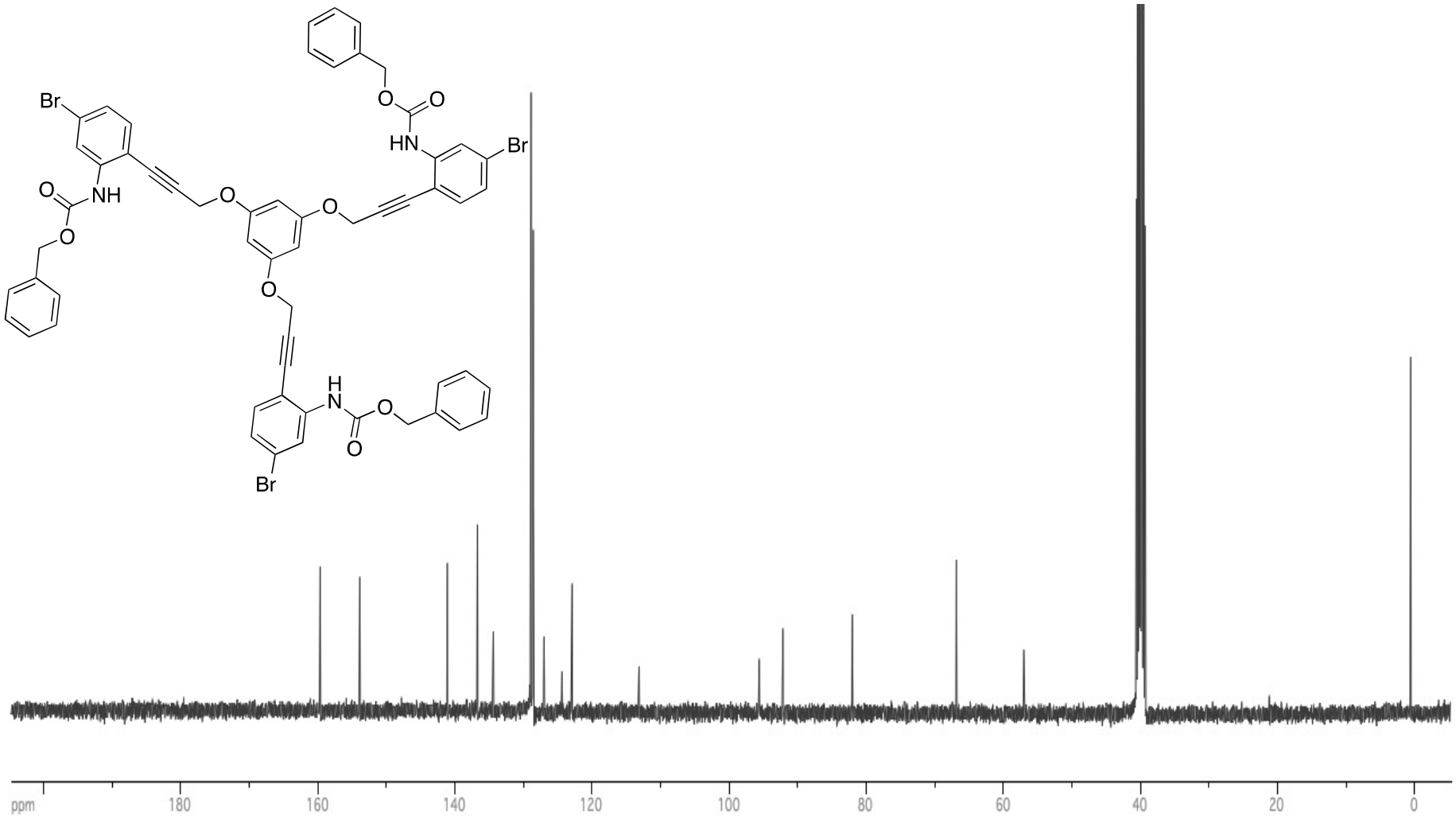


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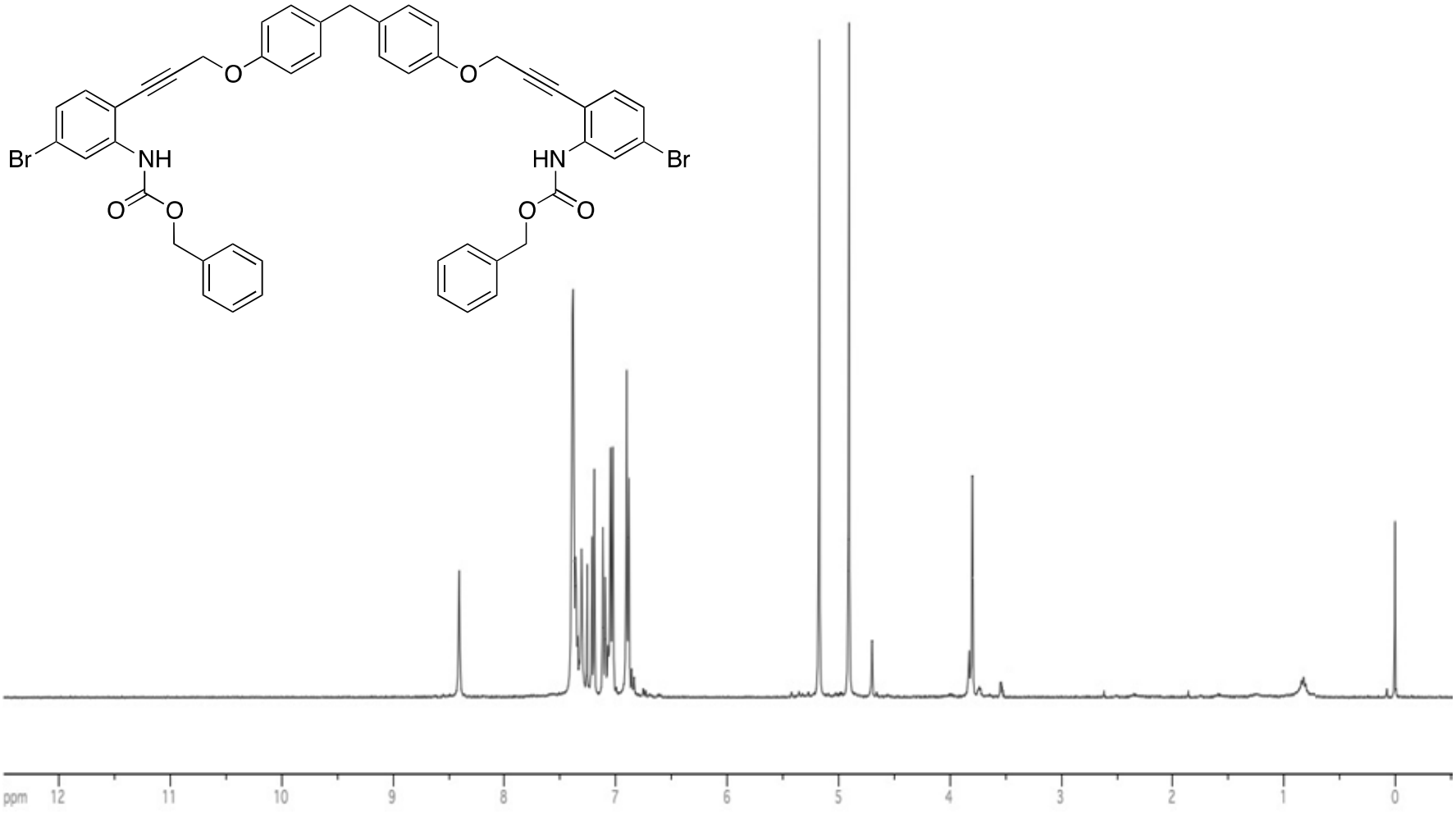


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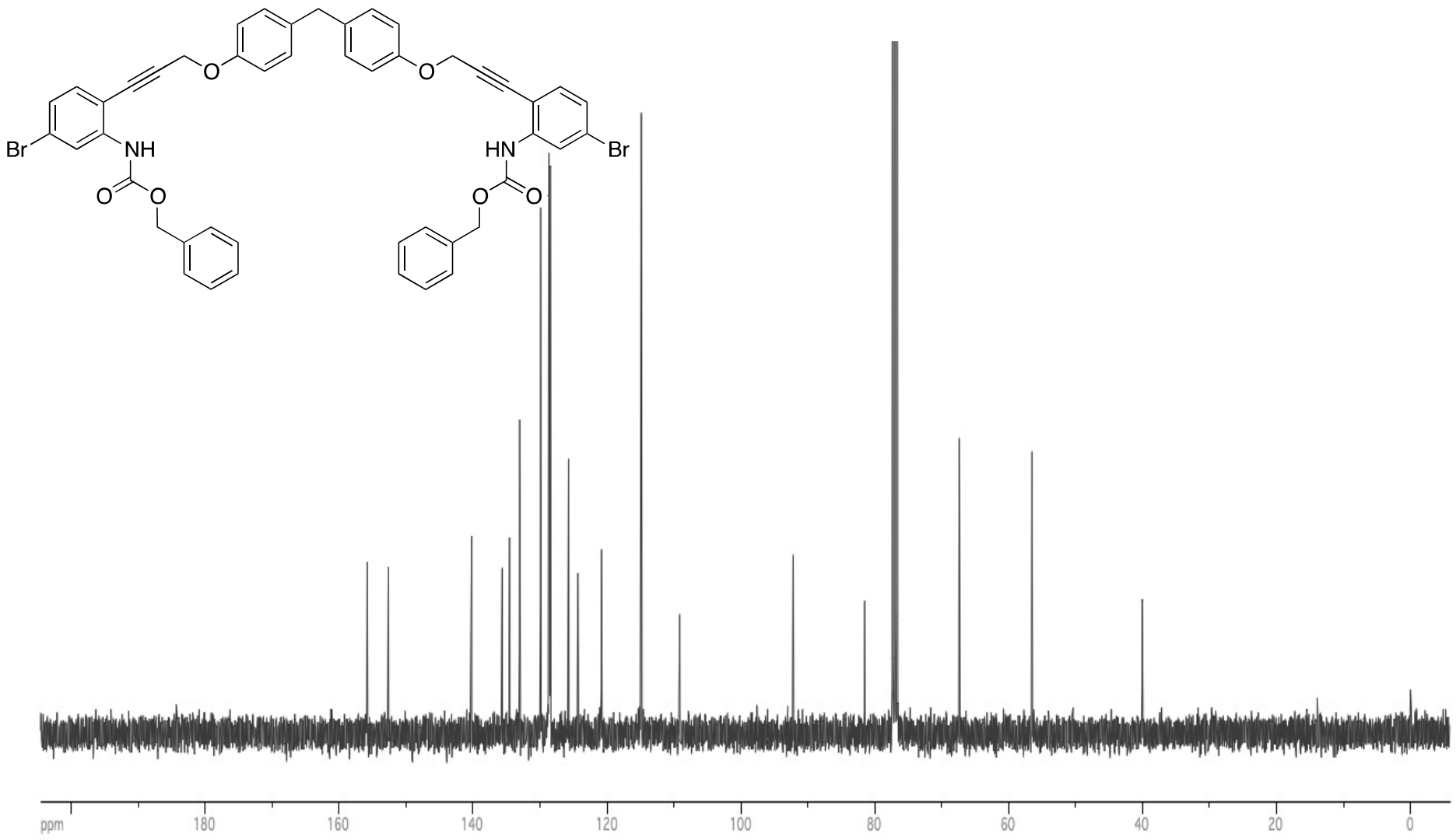


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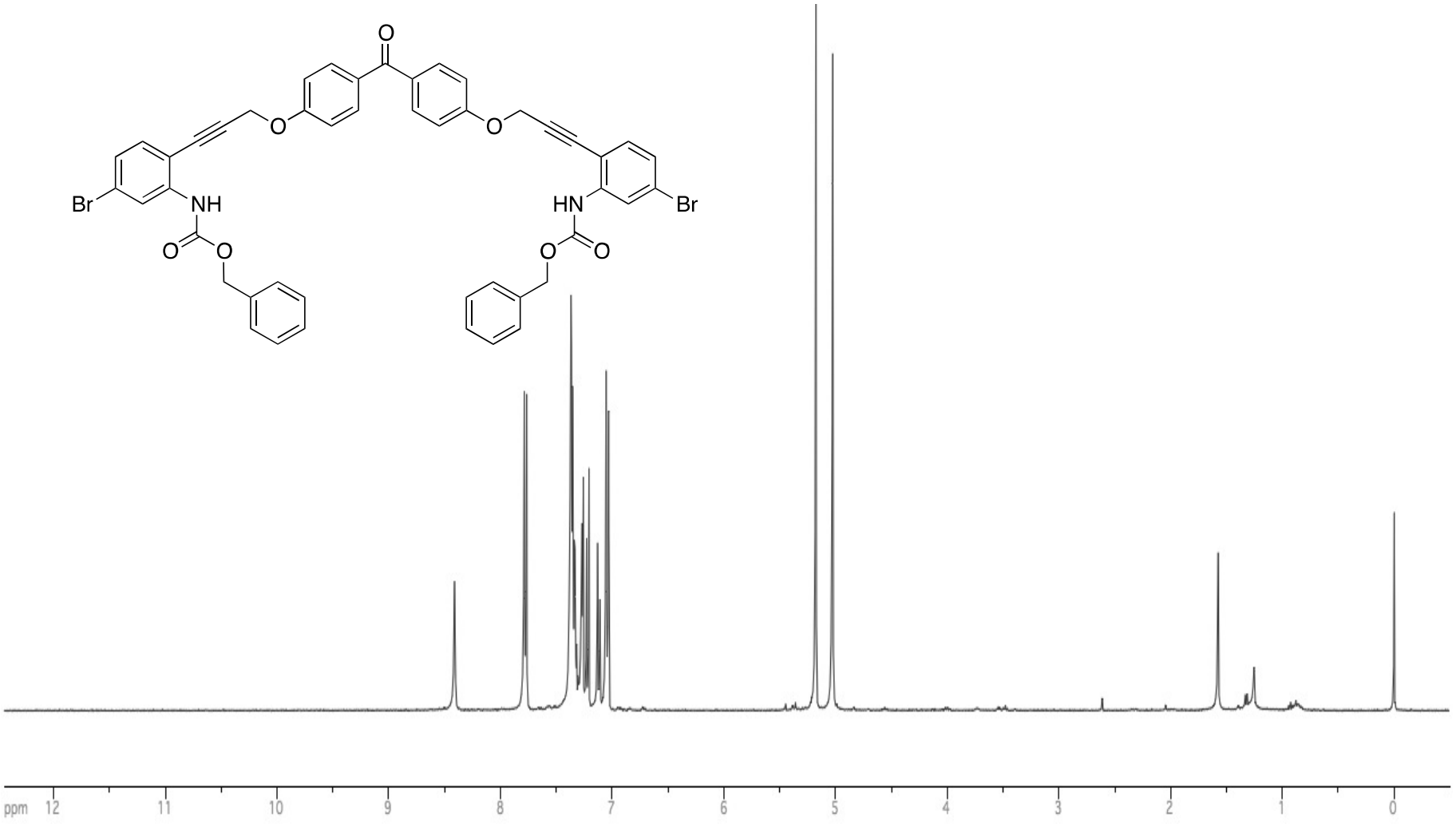


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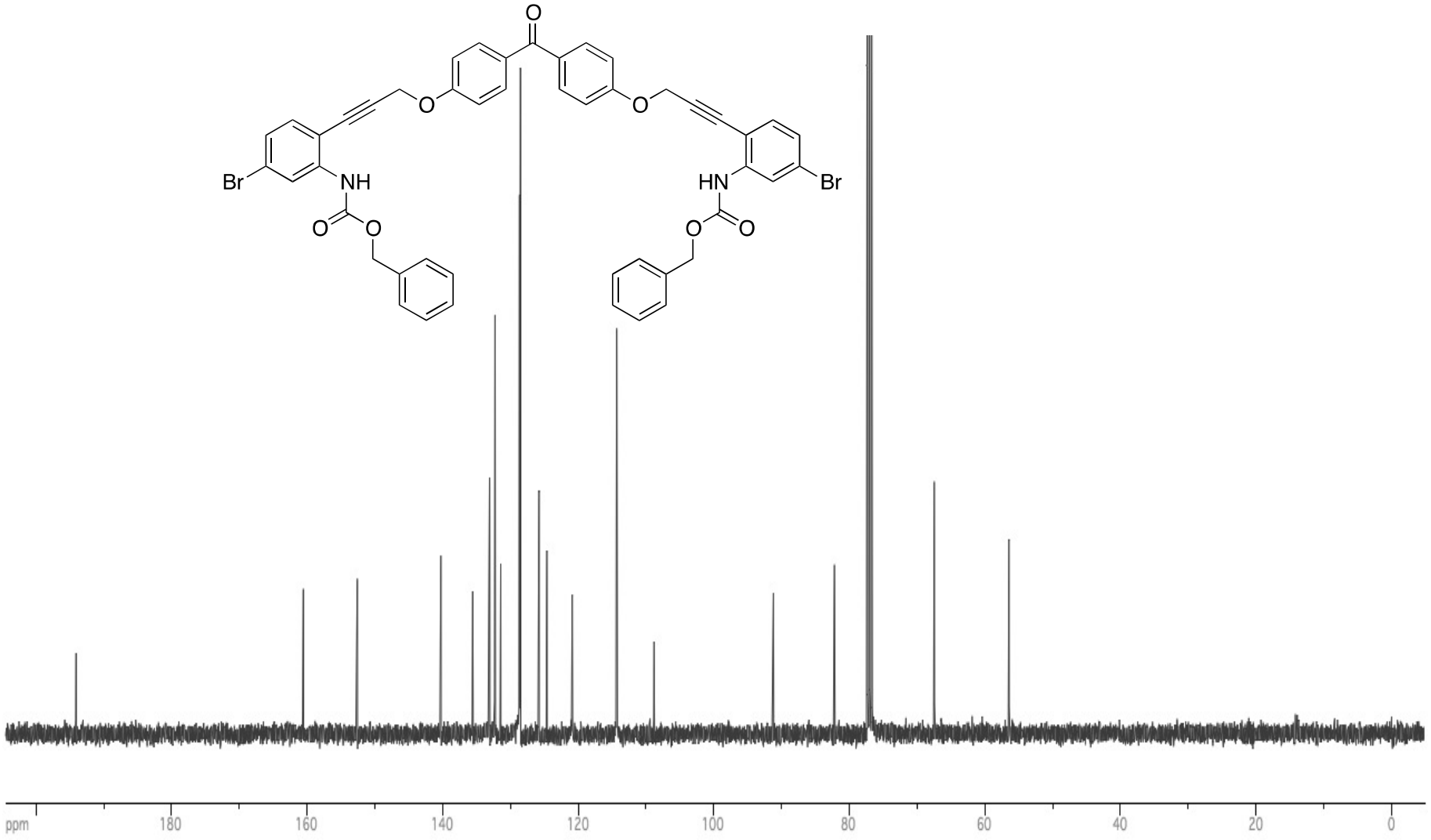


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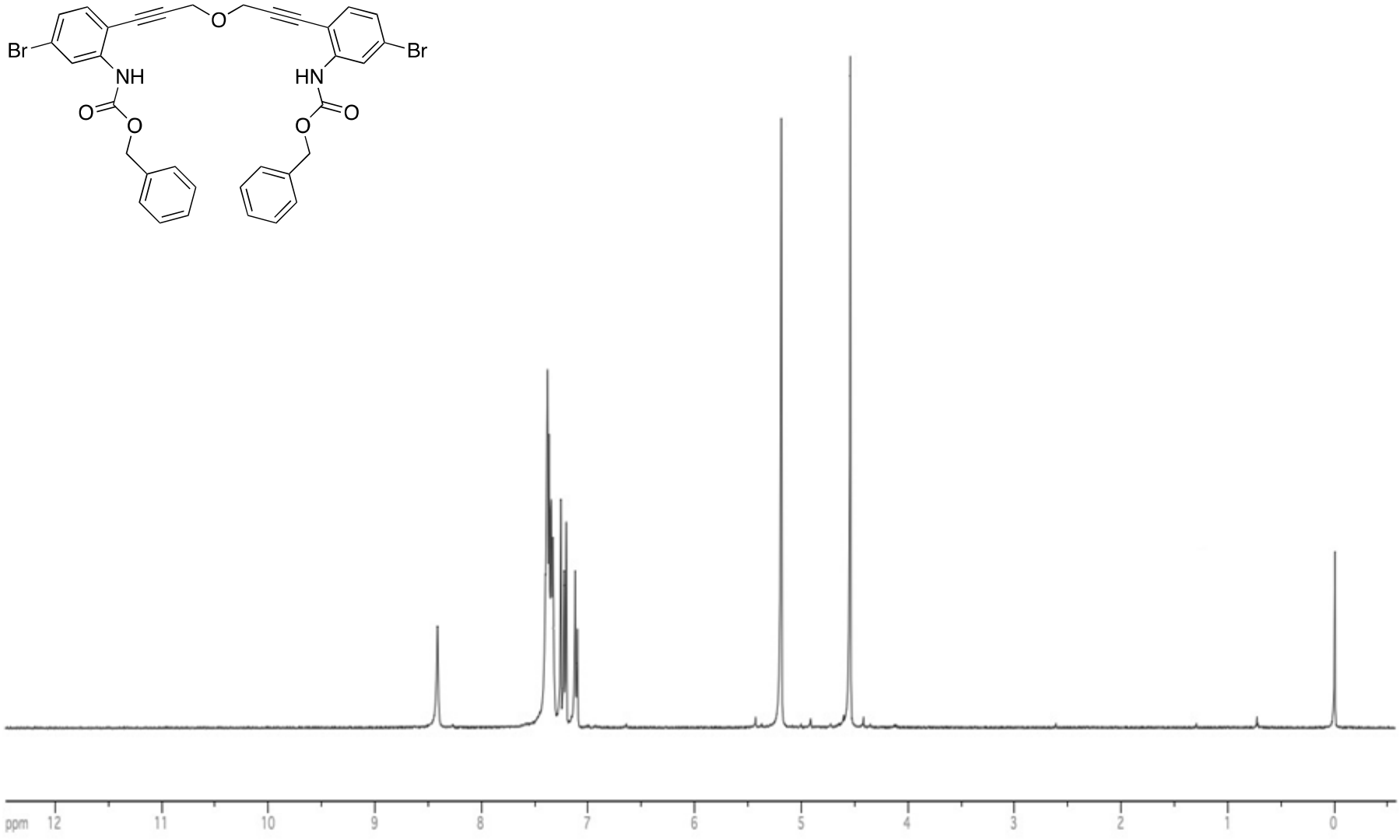


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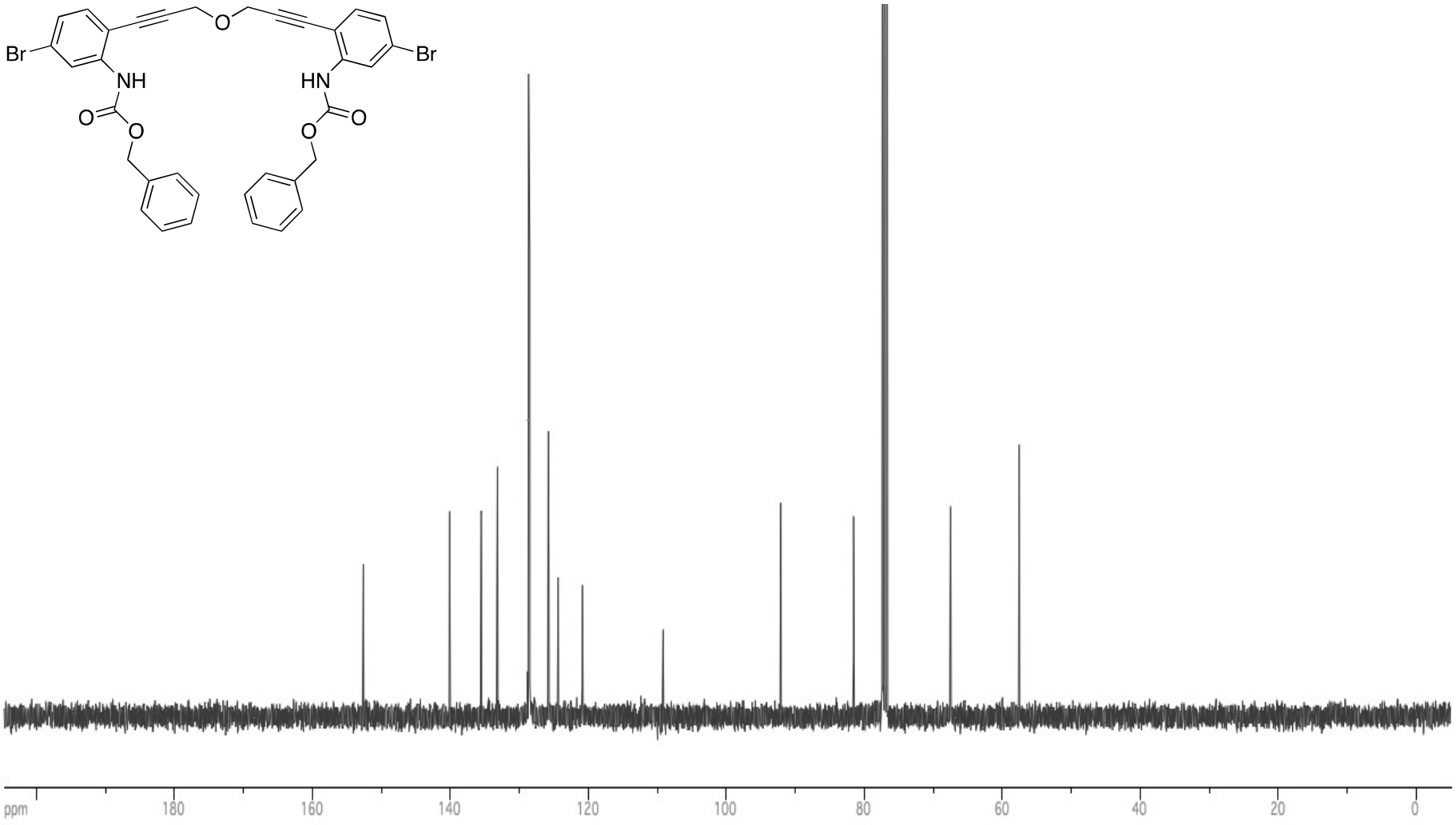
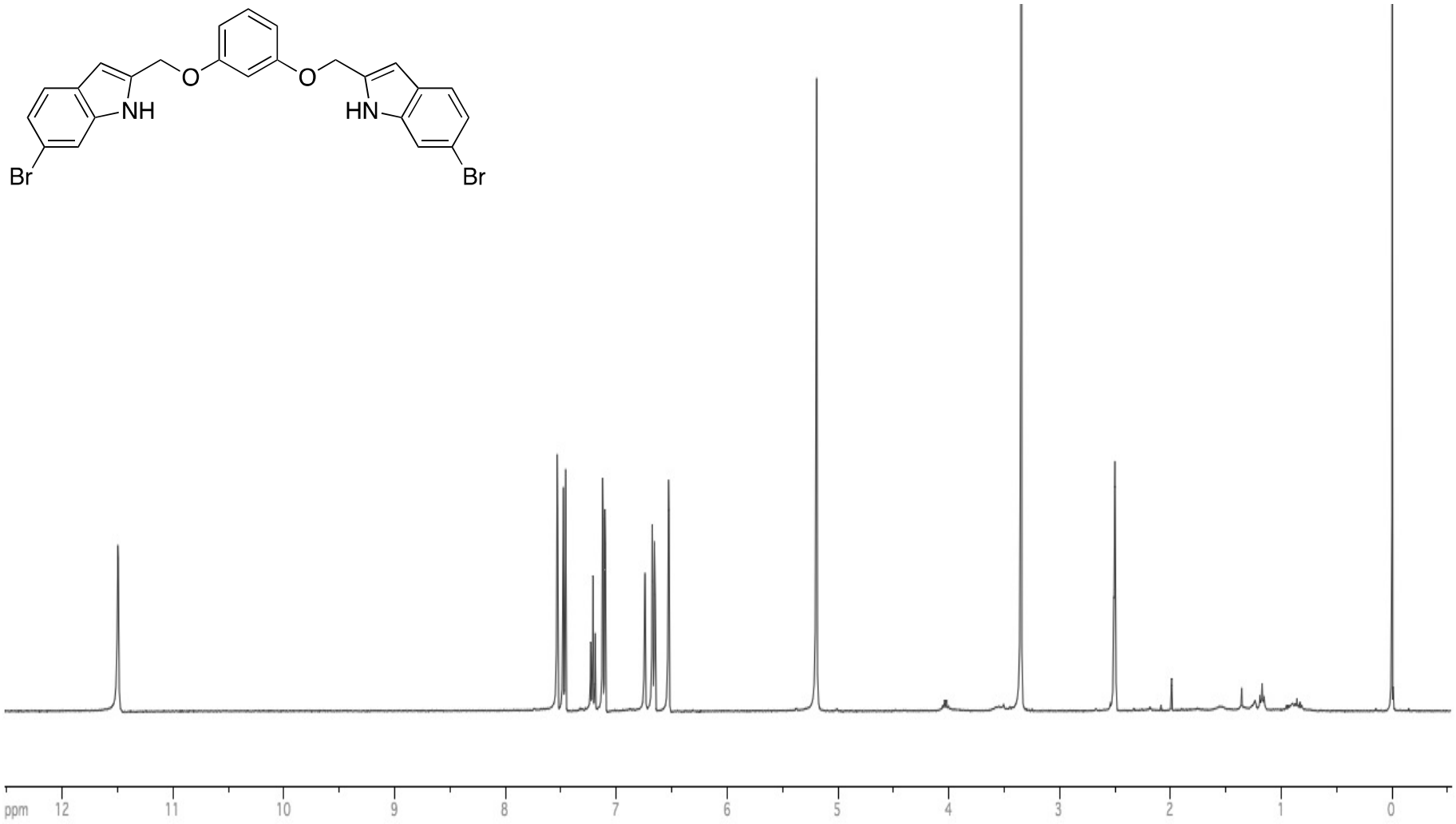
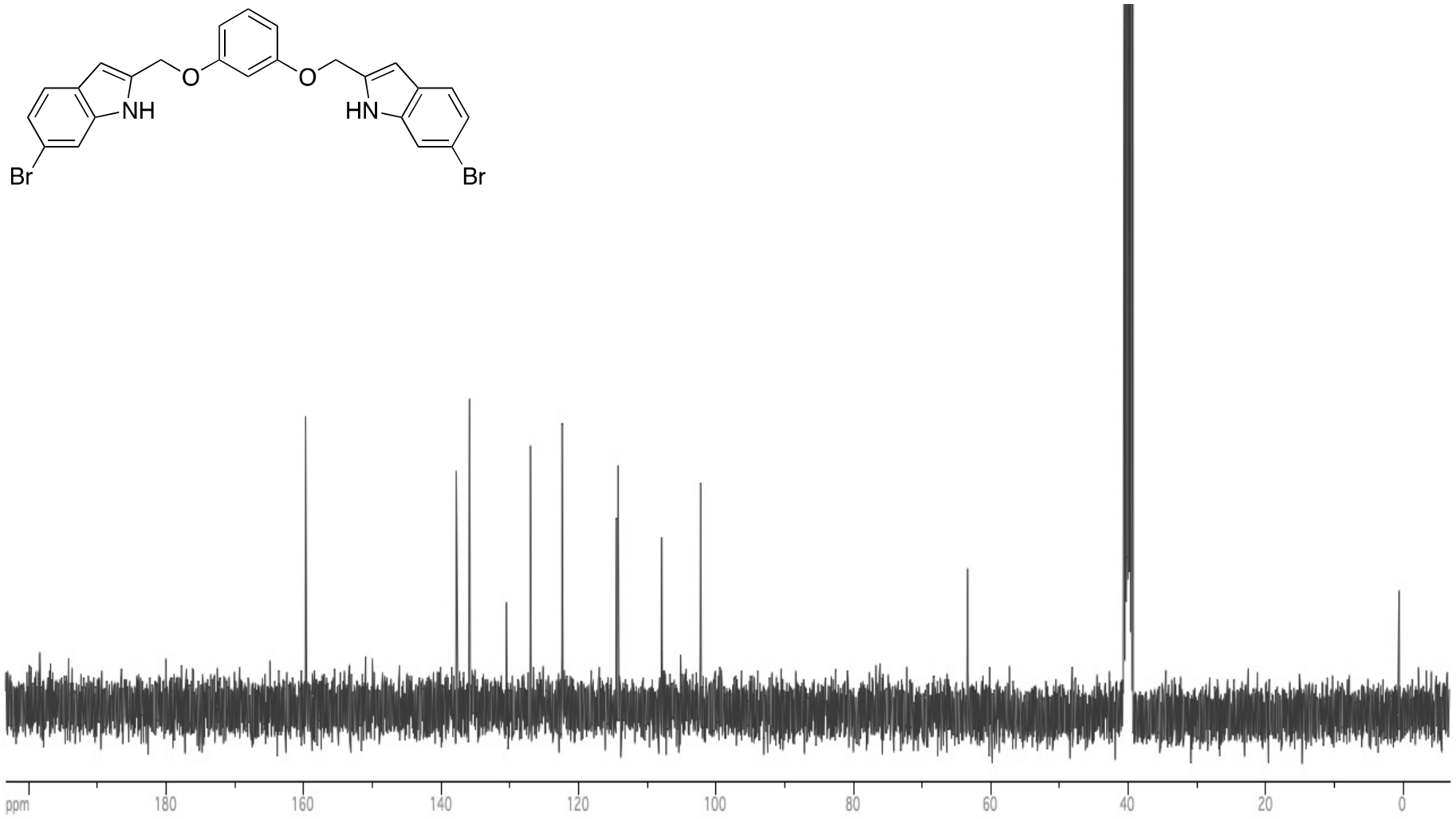


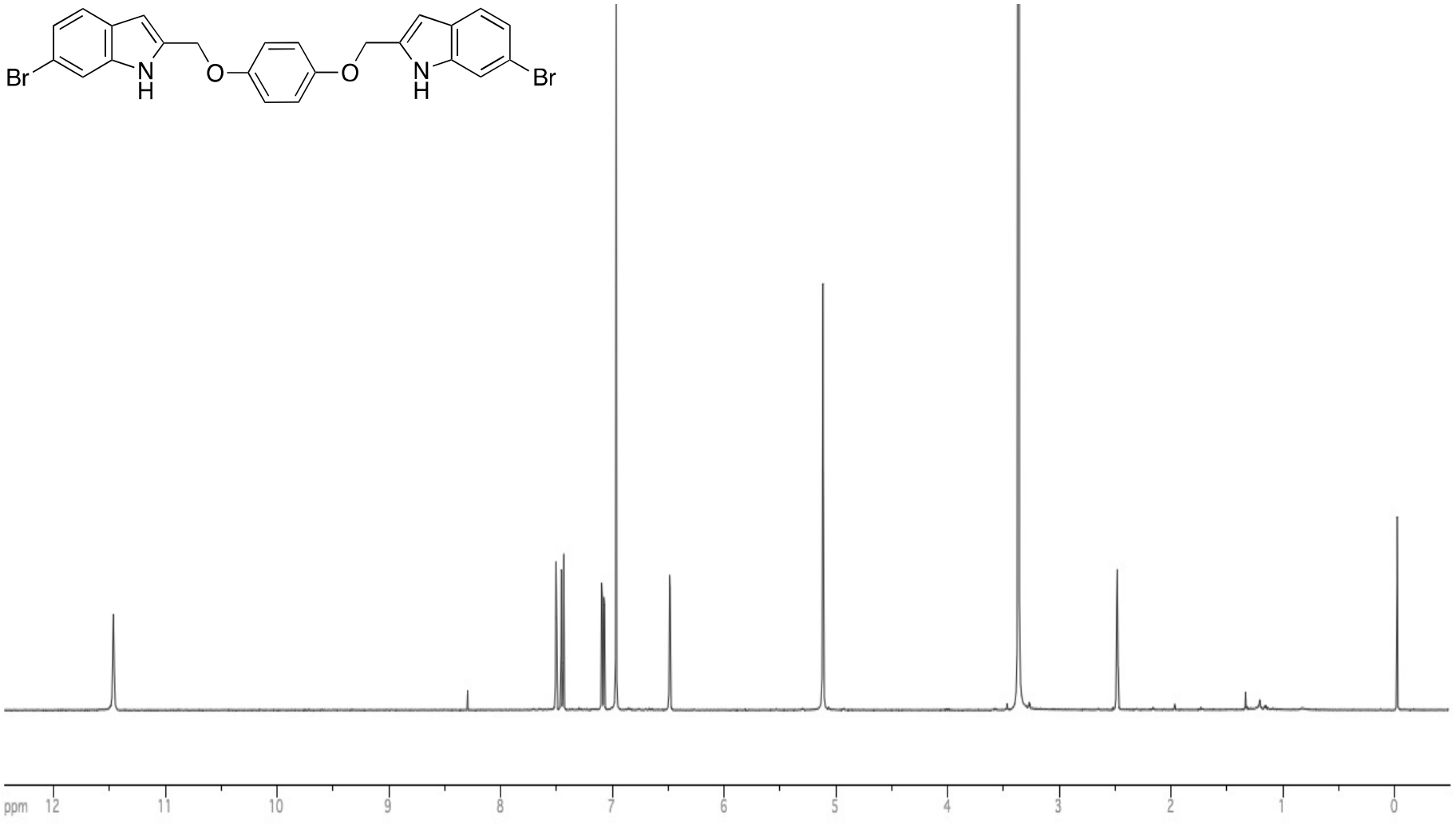

$^{13}$C NMR spectrum of compound **4i** in $CDCl_3$ 100 MHz



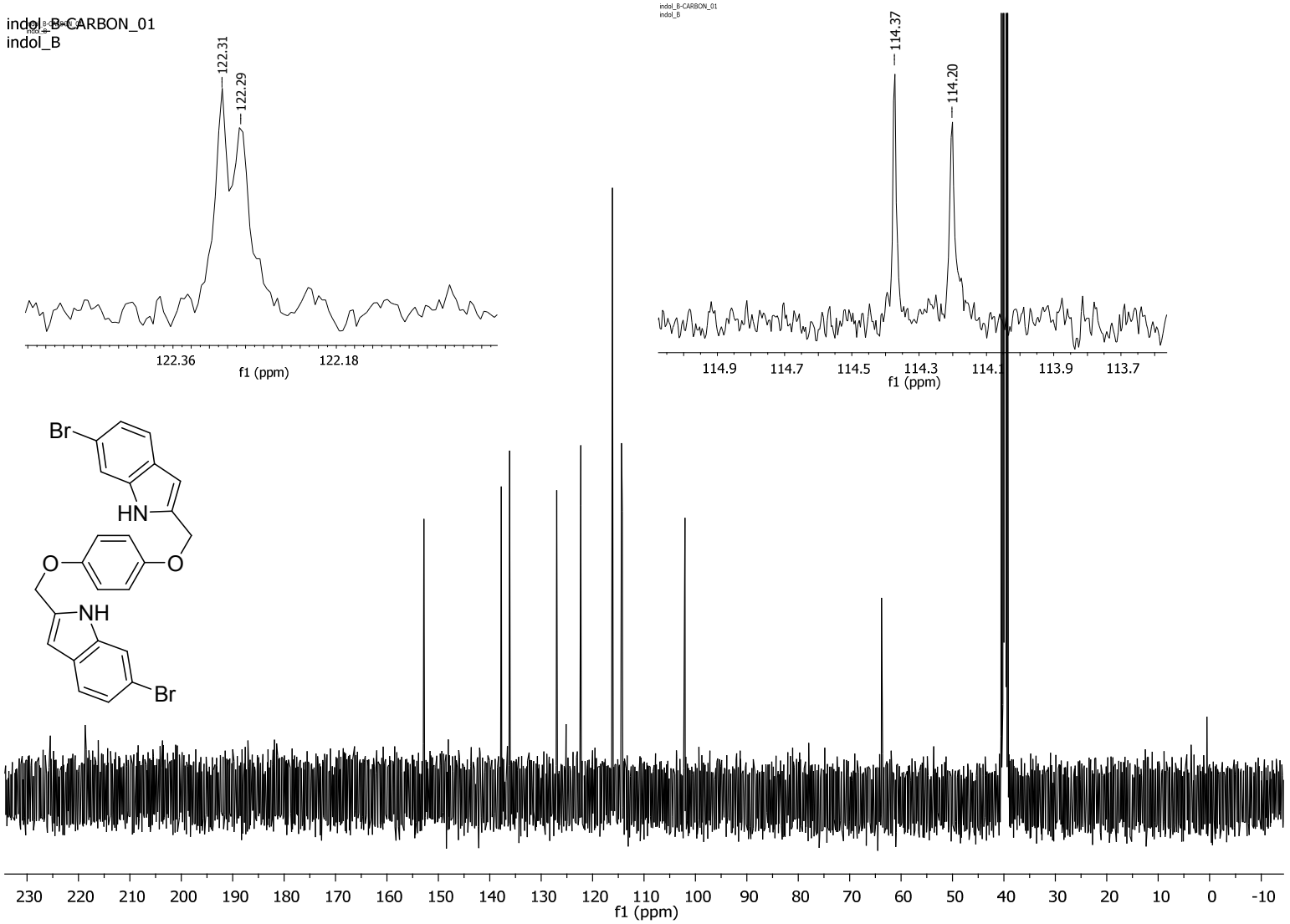

$^{1}$H NMR spectrum of compound **5d** in DMSO-*d6* 400 MHz



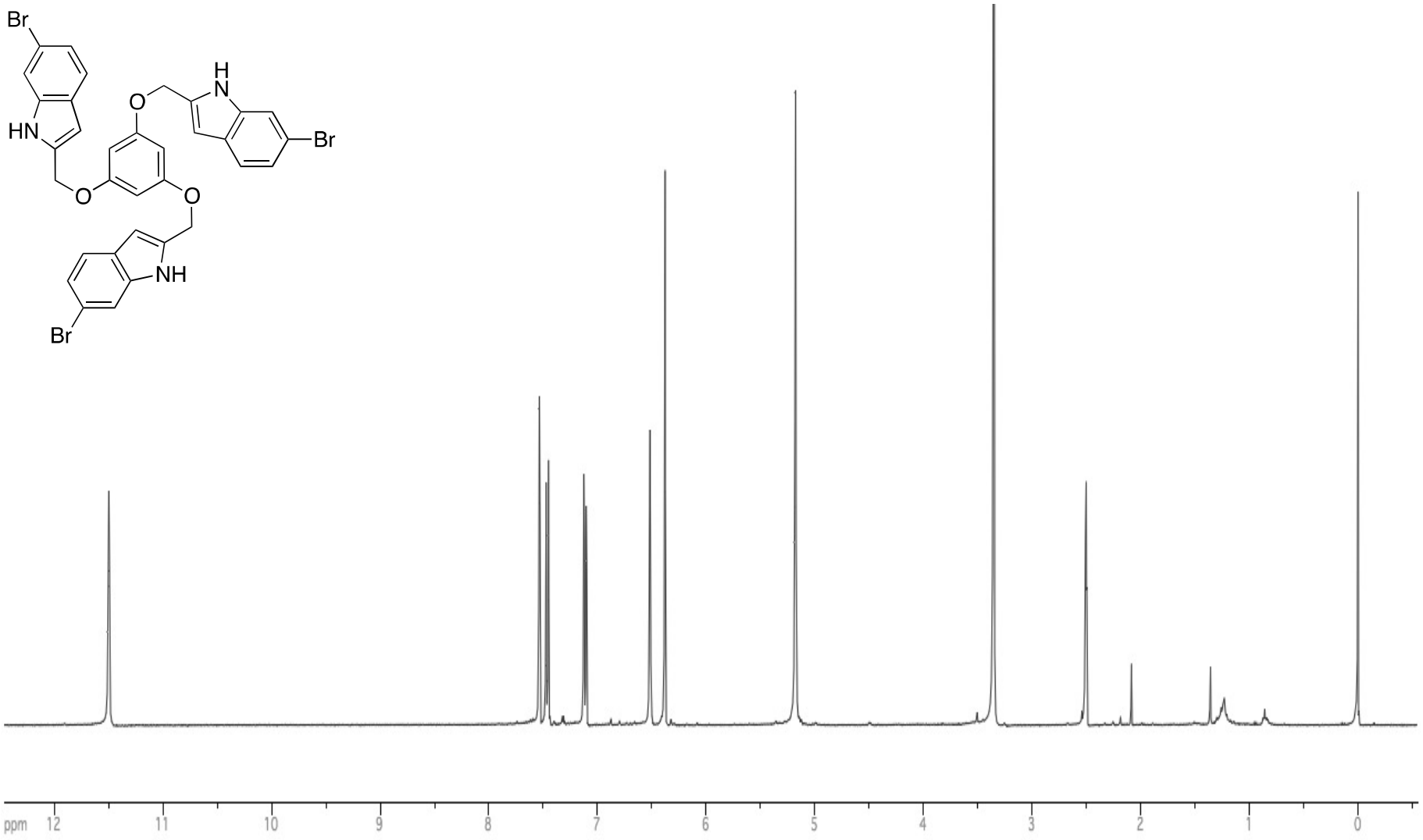

$^{13}$C NMR spectrum of compound **5d** in DMSO-*d6* 100 MHz



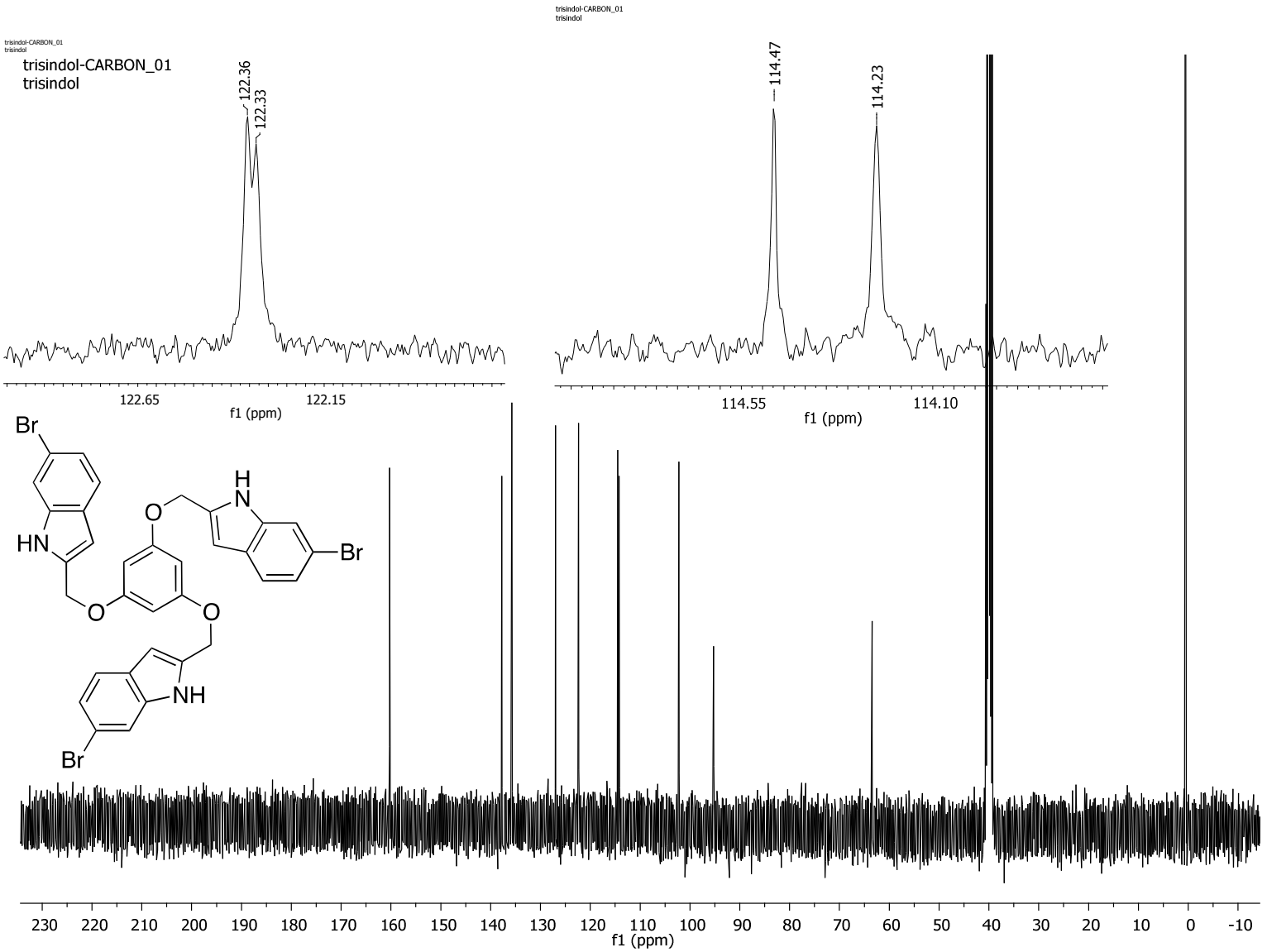

$^{1}$H NMR spectrum of compound **5e** in DMSO-*d6* 400 MHz



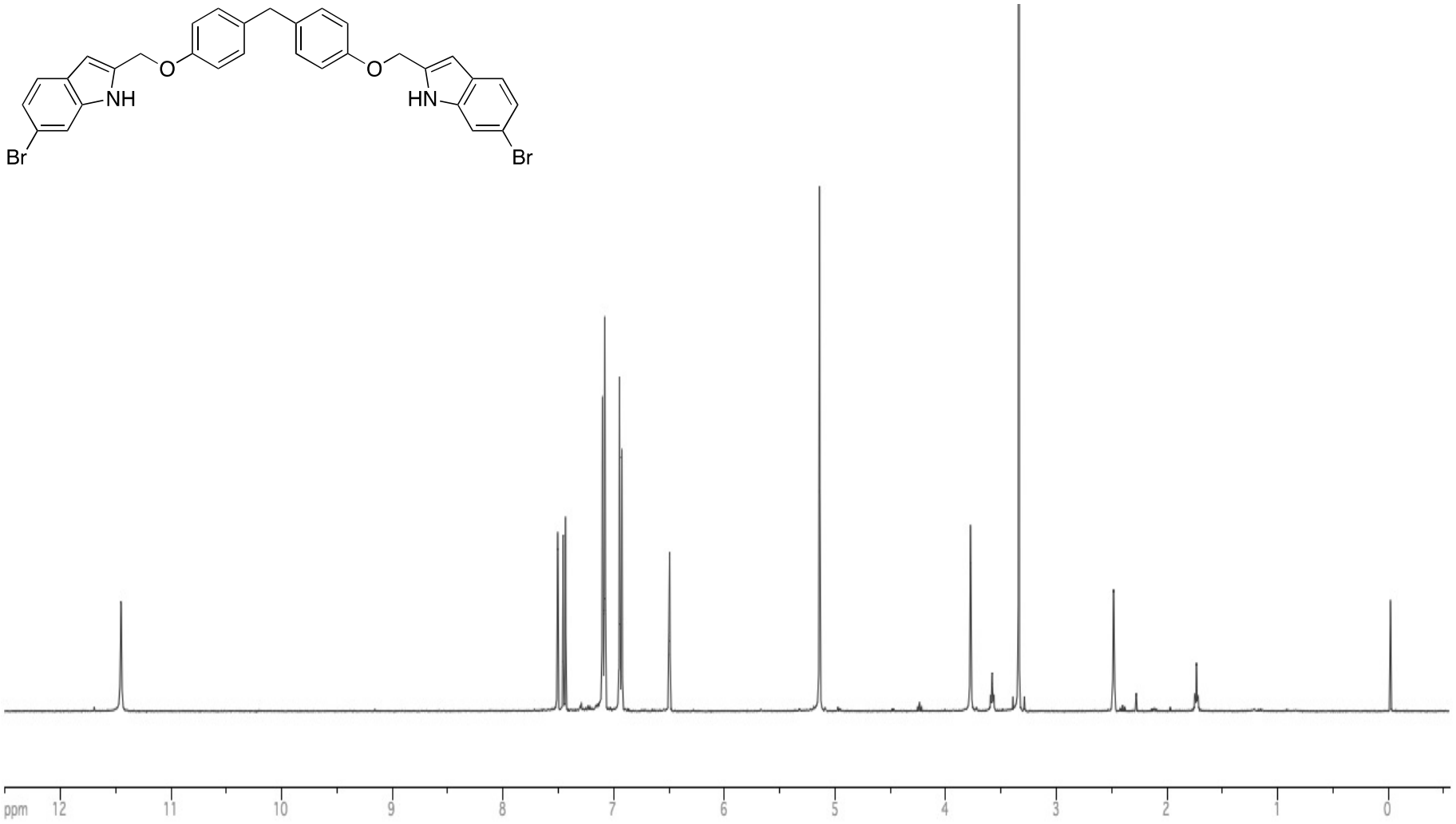

$^{13}$C NMR spectrum of compound **5e** in DMSO-*d6* 100 MHz



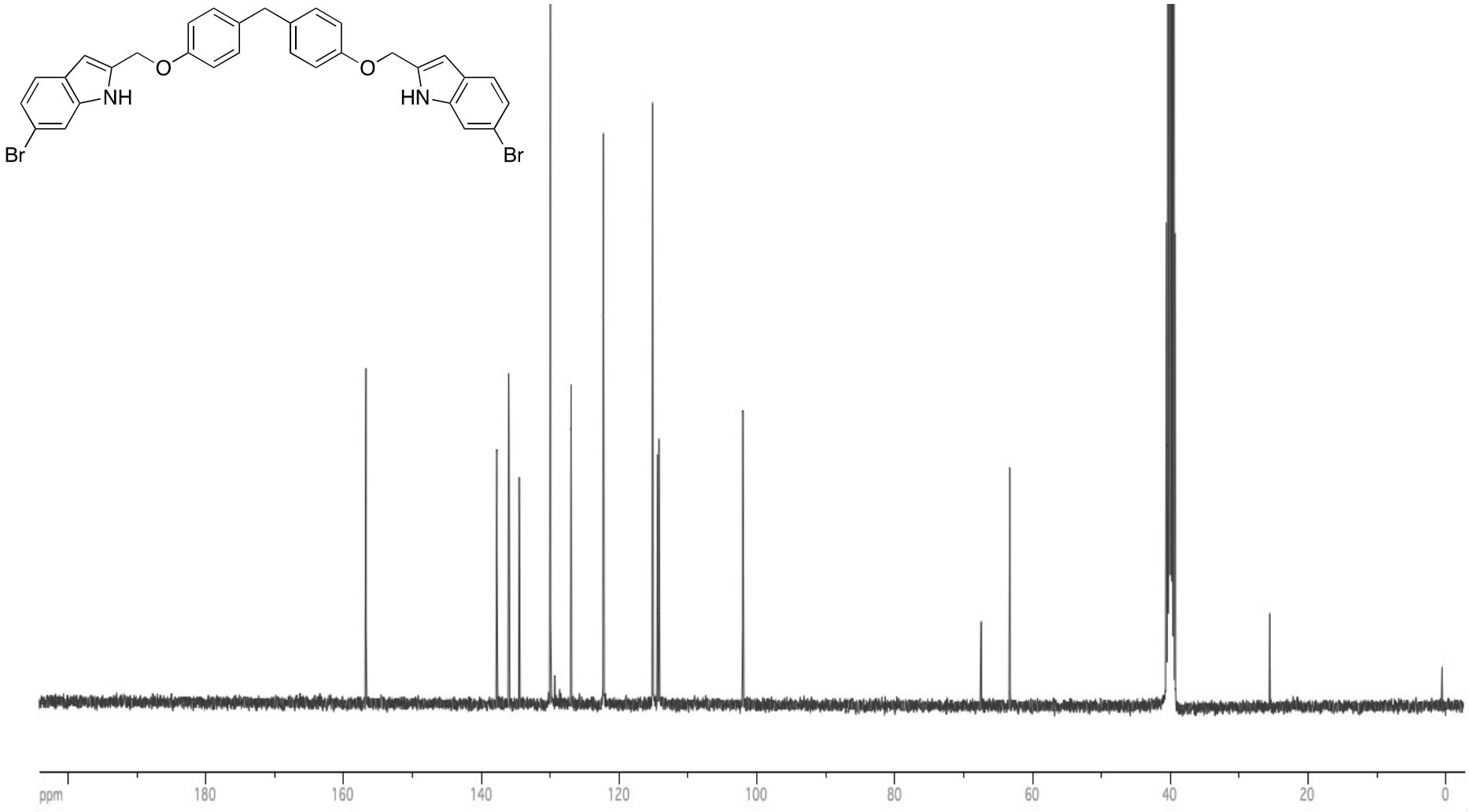

$^{1}$H NMR spectrum of compound **5f** in DMSO-*d6* 400 MHz



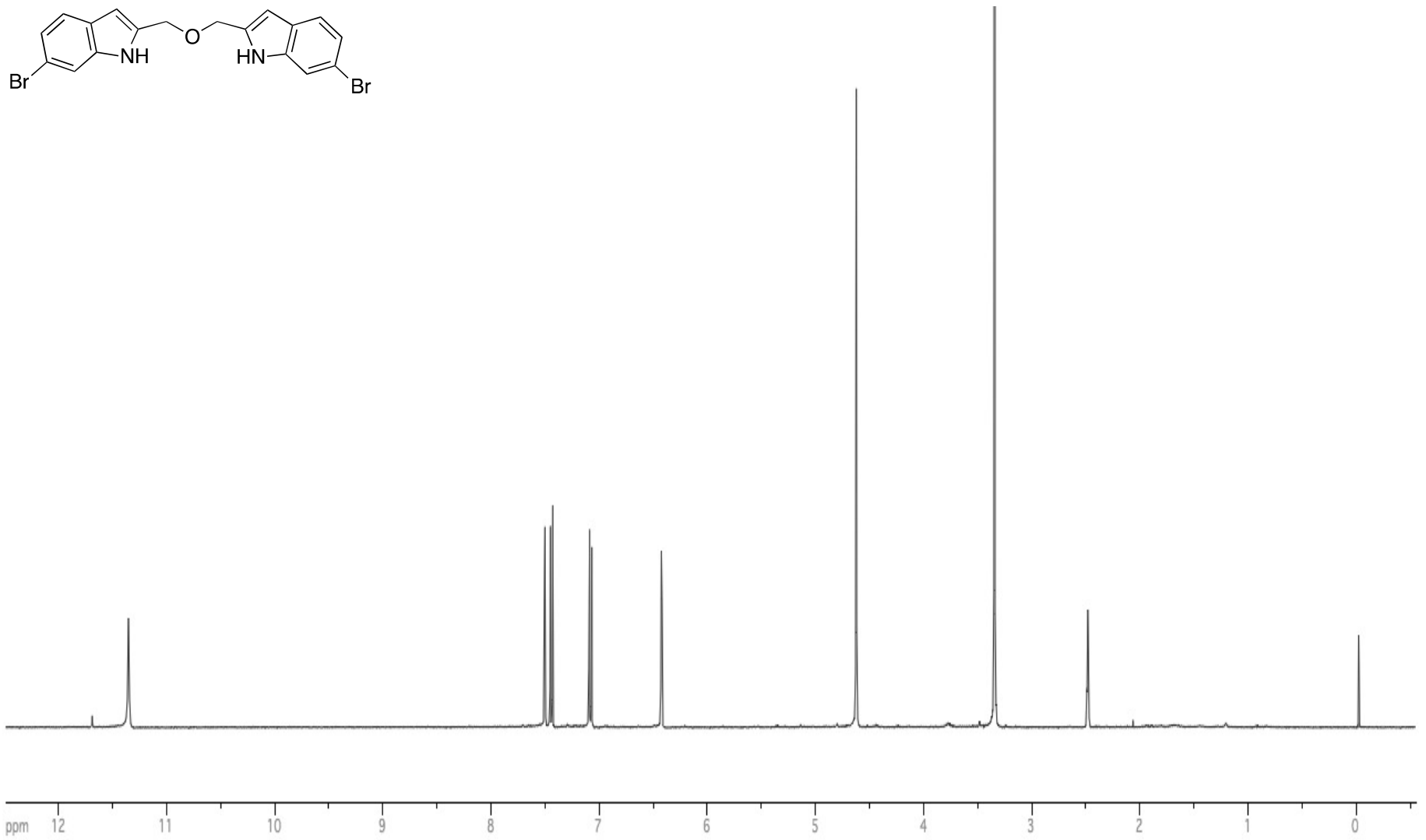

$^{13}$C NMR spectrum of compound **5f** in DMSO-*d6* 100 MHz



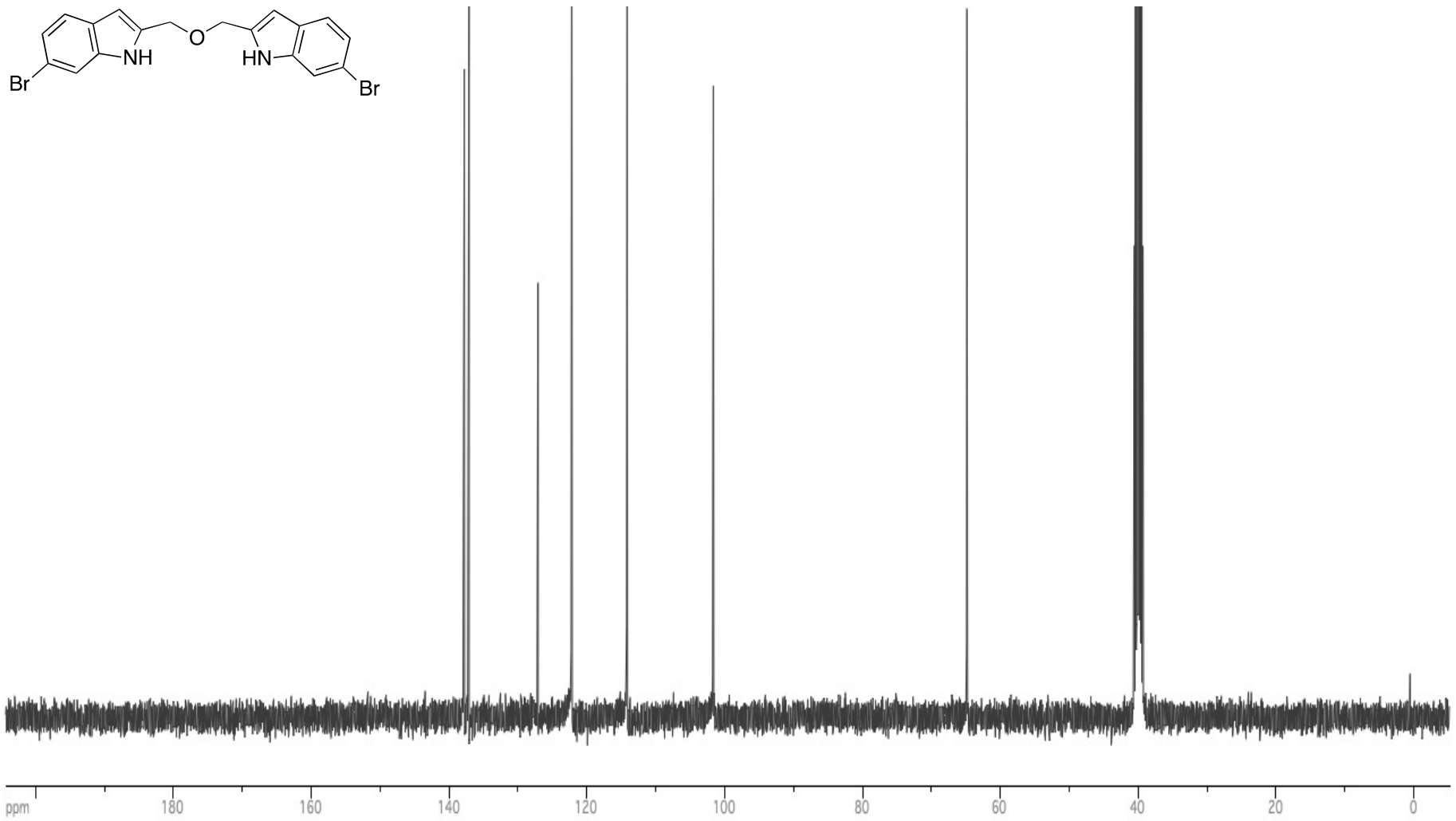

$^{1}$H NMR spectrum of compound **5g** in DMSO-*d6* 400 MHz




$^{13}$C NMR spectrum of compound **5g** in DMSO-*d6* 100 MHz




$^{1}$H NMR spectrum of compound **5i** in DMSO-*d6* 400 MHz




$^{13}$C NMR spectrum of compound **5i** in DMSO-*d6* 100 MHz