Supplementary Material (ESI) for Chemical Communications


# A versatile catalyst system for Suzuki-Miyaura syntheses of sterically hindered biaryls employing a cyclobutene-1,2-bis(imidazolium) salt

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## Supplementary Material

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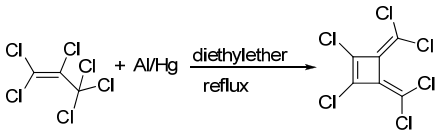
**General considerations**

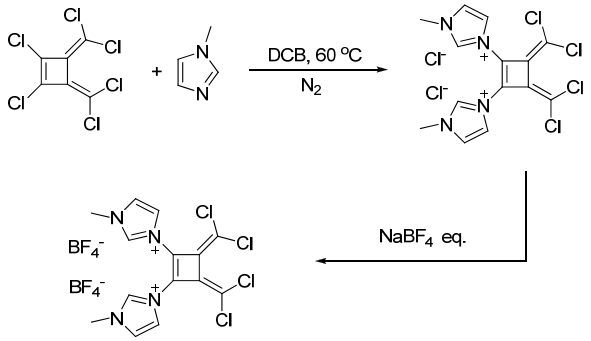
Toluene and diethylether were dried over sodium according standard procedures before usage. All reactions for the ligand synthesis and Suzuki-Miyaura reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. Flash-chromatography was performed with silica gel 60 (0.040-0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 and Bruker Avance III 600 MHz. $^{1}$H NMR spectra were recorded at 400 MHz or 600 MHz. $^{13}$C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Commercially available aryl chlorides, bromides, iodides and boronic acids were purchased and used as received. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet and m = multiplet. FT-IR spectra were obtained on a Bruker Vektor 22 in the range of 400 to 4000 cm$^{-1}$. Solids were measured as pellets (2.5%) in KBr and oils were measured as films in NaCl plates. The mass spectra were measured with a Hewlett Packard HP 5989 and a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). For column chromatography, silica gel was used. Yields are not optimized.

**Preparation of Perchloro-(3,4-dimethylenecyclobutene) 2:**




This compound was prepared according to a literature procedure.[1] After crystallization a colorless solid was obtained, mp. 145 - 146 $^{o}$C (147-148 $^{o}$C)[1]. $^{13}$C NMR (100 MHz, $CDCl_3$ ) δ 136.3, 131.8, 109.8; IR (KBr): 1692, 1608, 1570, 1132, 944, 778 cm$^{-1}$; *m/z* (70 ev) 284 [$M^+$]. Found: C, 25.4%. Calc. for $C_6Cl_6$: C, 25.3%.

**Preparation of Precursor 3:**

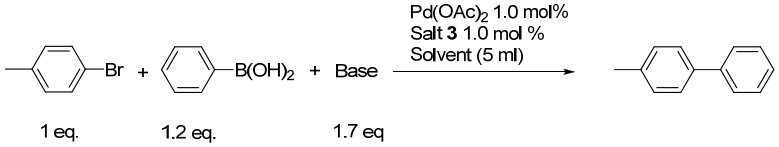



[1] A. Fujino, Y. Nagata, T. Sakan, T. *Bull. Chem. Soc. Jpn*. 1965, **38**, 295.

To a stirring solution of 0.85 g (3 mmol) of perchloro-(3,4-dimethylenecyclobutene) **2** in DCB was added 0.82 g (10 mmol) of 1-methylimidazol. The reaction mixture was stirred at 60 $^{o}$C under nitrogen for 4 hours. The light brown precipitate was filtered under nitrogen and dried. Then, to an aqueous solution of the chloride was added an aqueous solution of excess $NaBF_4$. A precipitate formed immediately. The solid was filtered off, washed with 4 portions of water, and dried under vacuum. A colorless solid was obtained in 73% yield, mp 201-203 $^{o}$C. $^{1}$H NMR (600 MHz, DMSO) δ 9.59 (s, 1H), 7.99 (m, 1H), 7.96 (m, 1H), 3.94 (s, 3H) ppm; $^{13}$C NMR (150 MHz, DMSO) δ 138.7, 133.0, 129.2, 124.7, 123.1, 114.9, 36.6 ppm; IR (KBr): 3425, 3147, 1635, 1545, 1064, 731 cm$^{-1}$; *m/z* (ESI): $[M + BF_4]^+$ = 464.6, $[M^{2+}/2]$ = 188.9. Found: C, 30.3; H, 2.3; N, 10.0%. Calc. for $C_{14}H_{12}B_2Cl_4F_8N_4$: C, 30.5; H, 2.2; N, 10.2%.

**Reaction Optimization:**

For optimizing the reaction conditions we selected 4-bromotoluene and phenylboronic acid as a reference reaction.

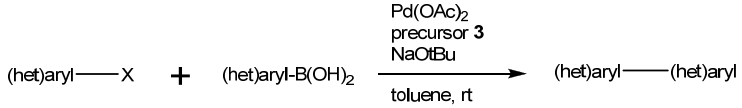



Initially, the effects of solvents were investigated. Polar solvents such as DMF and dioxane were inefficient for this catalytic system. Isopropanol and THF were used, but the yields were only moderate. Subsequently, the effect of the base was tested. After screening many different bases, the best combination as identified to be NaOtBu in toluene. $K_2CO_3$, $Na_2CO_3$ and $Et_3N$ were completely inefficient for this reaction. CsF had only a moderate effect. Then, the ratio of the ligand concentration with respect to the Pd salt (L:Pd ratio) was changed, but no positive effect was observed. The temperature was also varied. The following table summarizes our results.

**Table.** Optimization of the reaction conditions.

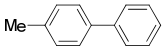
| Entry | Base | Solvent | T ($^{o}$C) | T (h) | Yield(%) |
|---|---|---|---|---|---|
| 1 | $Na_2CO_3$ | DMF | 100 | 4 | 0 |
| 2 | $K_2CO_3$ | Dioxane | 100 | 4 | 0 |
| 3 | $Et_3N$ | THF | Reflux | 4 | 0 |
| 4 | NaOtBu | Iso-propanol | 60 | 1.5 | 43 |
| 5 | NaOtBu | Dioxane | 100 | 3 | 9 |
| 6 | CsF | THF | reflux | 2 | 17 |
| 7 | $Et_3N$ | DMF | 100 | 4 | 0 |
| 8 | CsF | Iso-propanol | 60 | 1.5 | 33 |
| 9 | $K_2CO_3$ | Toluene | 100 | 4 | 5 |
| 10 | $Na_2CO_3$ | Toluene | 100 | 4 | 5 |
| 11 | $Et_3N$ | Toluene | 100 | 3 | 4 |
| 12 | CsF | Toluene | 60 | 1.5 | 36 |
| 13 | NaOtBu | Toluene | 45 | 0.5 | 96 |
| 14 | NaOtBu | Toluene | rt | 0.5 | 96 |

**General Procedure for Suzuki-Miyaura Coupling Reactions of Aryl Halides and Triflates with Aryl Boronic Acids at Room Temperature:**



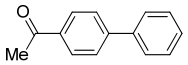

A flame-dried two-necked flask was charged with the salt **3**, arylboronic acid, $Pd(OAc)_2$, and base, capped with a rubber septum, and then evacuated and refilled with nitrogen. The aryl halide or triflate and toluene were added sequentially via a syringe. Aryl halides and triflates which were solids at room temperature were added during the initial charge, prior to the evacuation. The reaction mixture was stirred at room temperature for the indicated period of time. Then, filtration and column chromatography gave the corresponding products.

**4-Methyl-biphenyl (Table 1, entry 1):**




A mixture of phenylboronic acid (146.5 mg, 1.20 mmol), 4-bromotoluene (171 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 1 mol% of $Pd(OAc)_2$ (2.5 mg, 0.01 mmol), and **3** (5.6 mg, 0.01 mmol) in toluene (5 mL) was stirred at room temperature for 30 min. The reaction mixture was diluted with petroleum ether (10 mL), filtered through a thin pad of silica gel and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel (petroleum ether) to provide 161 mg (96%) of a the title compound as colorless solid, mp 48-49 $^oC$ (46-47 $^oC$; ref.[2]). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 4H), 7.51-7.22 (m, 5H), 2.39 (s, 3H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 141.2, 141.2, 138.4, 137.0, 129.5, 128.7, 127.2, 127.0, 21.1 ppm; IR (KBr): 3055, 2986, 1560, 1463 $cm^{-1}$; *m/z* (70 ev) 168 [$M^+$]. Found: C, 92.8; H, 7.0%. Calc. for $C_{13}H_{12}$: C, 92.8; H, 7.2%.

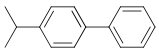
**1-(1,1´-Biphenyl-4-yl)ethan-2-one (Table 1, entry 2):**




A mixture of phenylboronic acid (146.5 mg, 1.20 mmol), 1-(4-chlorophenyl)ethanone (155 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred. A colorless solid was obtained after 1 h stirring at room temperature in 92% yield (181 mg), mp. 117-118 $^oC$ (121-122 $^oC$, ref.[3]). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.63-7.61 (m, 2H), 7.48-7.44 (m, 2H), 7.41-7.37 (m, 1H), 2.63 (s, 3H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 197.7, 145.7, 139.8, 135.8, 129.0, 128.9, 128.2, 127.3, 127.2, 26.6 ppm; IR (KBr): 3073, 2998, 2916, 1680, 1602, 1403, 1358, 1264, 960, 765 $cm^{-1}$; *m/z* (70 ev) 196 [$M^+$]. Found: C, 85.6; H, 6.0%. Calc. for $C_{14}H_{12}O$: C, 85.7; H, 6.2%.

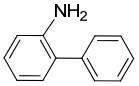
[2] V. Martínez-Barrasa, A. García de Viedma, C. Burgos, J. Alvarez-Builla, J. *Org. Lett.* 2000, **2**, 3933.
[3] W. Han, C. Liu, Z. Jin, *Adv. Synth. Catal.* 2008, **350**, 501.

**4-Isopropylbiphenyl (Table 1, entry 3):**



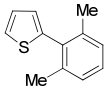
A mixture of phenylboronic acid (146.5 mg, 1.20 mmol), 1-chloro-4-isopropylbenzene (155 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred. After 1 h stirring at room temperature and column chromatography, 184 mg (94%) of the title compound were obtained as colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.41- 7.37 (m, 2H), 7.31 (m, 3H), 2.93 (sept., J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.1, 141.3, 138.9, 128.8, 127.2, 127.1, 127.1, 127.0, 33.9, 24.1 ppm; IR (NaCl): 3028, 2960, 2869, 1946, 1907, 1674, 1601, 1582, 1486, 1519, 1214, 965, 836 $cm^{-1}$; *m/z* (70 ev) 196 [$M^+$]. Found: C, 91.6; H, 8.3%. Calcd for $C_{15}H_{16}$: C, 91.8; H, 8.2%.

**2-Amino-biphenyl (Table 1, entry 4):**



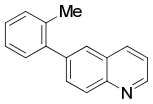

A mixture of phenylboronic acid (146.5 mg, 1.20 mmol), 2-iodoaniline (219 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 1 mol% of $Pd(OAc)_2$ (2.5 mg, 0.01 mmol), and **3** (5.6 mg, 0.01 mmol) in toluene (5 mL) was stirred. A brown solid was obtained in 90% (152 mg) yield, mp 44-45 $^o$C (44-46 $^o$C, ref.[4]) after 3.5 h at room temperature. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.46-7.41 (m, 4H), 7.35-7.33 (m, 1H), 7.16-7.11 (m, 2H), 6.81 (td, J = 7.4, 1.1 Hz, 1H), 6.75 (dd, J = 8.0, 0.9 Hz, 1H), 3.73 (s, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.4, 130.4, 129.0, 128.7, 128.4, 127.5, 127.1, 118.6, 115.5 ppm; IR (KBr): 3480, 3387, 3025, 1615, 1500, 1480, 1435, 1284, 1156, 1007, 752, 703 $cm^{-1}$; *m/z* (70 ev) 169 [$M^+$]. Found: C, 85.3; H, 6.7; N, 8.4%. Calc. for $C_{12}H_{11}N$: C, 85.2; H, 6.6; N, 8.3%.

**2-(2,6-Dimethylphenyl)thiophene (Table 1, entry 5):**




A mixture of 2,6-dimethylphenylboronic acid (180 mg, 1.20 mmol), 2-iodothiophene (210 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 1 mol% of $Pd(OAc)_2$ (2.5 mg, 0.01 mmol), and **3** (5.6 mg, 0.01 mmol) in toluene (5 mL) was stirred. After 3.5 h stirring at room temperature and column chromatography, 171 mg (91%) of title compound were obtained as colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 4.8, 1.0 Hz, 1H), 7.24-7.12 (m, 4H), 6.88 (dd, J = 4.8, 1.0 Hz, 1H), 2.21 (s, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.4, 134.0, 128.0, 127.2, 127.0, 126.2, 125.3, 20.8 ppm; IR (NaCl): 3138, 3057, 2967, 2856, 1584, 1443, 1238, 835 $cm^{-1}$; *m/z* (70 ev) 188 [$M^+$]. Found: C, 76.4; H, 6.5%. Calcd for $C_{12}H_{12}S$: C, 76.6; H, 6.4%.

**6-(2-Methylphenyl)quinoline (Table 1, entry 6):**

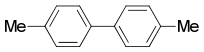



A mixture of 2-methylphenylboronic acid (163.2 mg, 1.20 mmol), 6-quinolinyl trifluoromethanesulfonate (277.3 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was

[4] A. Ohwada, S. Nara, T. Sakamoto, Y. Kikugawa, *J. Chem. Soc., Perkin Trans 1* 2001, **22**, 3064.

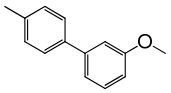
stirred. A light yellow oil was obtained after 3 h stirring at room temperature in 93 % yield (204 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.0, 1.6 Hz, 1H), 8.14 (d, J = 8.2 Hz, 2H), 7.73-7.69 (m, 2H), 7.40 (q, J = 4.0 Hz, 1H), 7.32-7.27 (m, 4H), 2.30 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.4, 141.1, 140.4, 136.1, 135.5, 131.4, 130.5, 130.0, 129.1, 128.2, 127.8, 127.6, 126.0, 121.4, 20.5 ppm; IR (KBr): 3061, 3017, 2924, 1592, 1569, 1487, 1214, 1120, 798 cm$^{-1}$; *m/z* (70 ev) 219 [$M^+$]. Found: C, 87.5; H, 6.0, N, 6.3%. Calc. for $C_{16}H_{13}N$: C, 87.6; H, 6.0; N, 6.4%.

**4, 4´-Dimethylbiphenyl (Table 1, entry 7):**



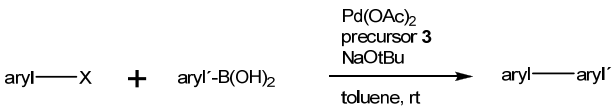

A mixture of p-tolyl boronic acid (163.2 mg, 1.20 mmol), p-tolyl trifluoromethane sulfonate (240.2 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred at room temperature for 75 min. The reaction mixture was diluted with petroleum ether (10 mL), filtered through a thin pad of silica gel and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel (petroleum ether) to provide 170 mg (93%) of a the title compound as colorless solid, mp 118-119 $^o$C (120-122 $^o$C).[5] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J= 7.9 Hz, 4H), 7.15 (d, J = 7.9 Hz, 4H), 2.31 (s, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.3, 136.7, 129.5, 126.8, 21.1 ppm; IR (KBr): 3023, 2922, 2843, 1907, 1512, 806 cm$^{-1}$; *m/z* (70 ev) 182 [$M^+$]. Found: C, 92.3; H, 7.7%. Calc. for $C_{14}H_{14}$: C, 92.3; H, 7.8%.

**3-Methoxy-4'-methylbiphenyl (Table 1, entry 8):**




A mixture of 3-methoxy phenyl boronic acid (182.4 mg, 1.20 mmol), p-tolyl trifluoromethane sulfonate (240.2 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was stirred at room temperature for 120 min. The reaction mixture was diluted with petroleum ether (10 mL), filtered through a thin pad of silica gel and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel (petroleum ether) to provide 175 mg (88%) of a the title compound as light yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 2H), 7.33 (t, J = 7.9 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.9, 1H), 7.12- 7-10 (m, 1H), 6.87 (dd, J = 7.9, 2.0 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.8, 142.6, 138.1, 137.1, 129.6, 129.4, 126.9, 119.4, 112.6, 112.3, 55.2, 21.0 ppm; IR (NaCl): 3031, 2932, 1610, 1475, 1296, 1172, 1030, 810 cm$^{-1}$; *m/z* (70 ev) 198 [$M^+$]. Found: C, 84.7; H, 7.3%. Calc. for $C_{14}H_{14}O$: C, 84.8; H, 7.1%.

**General Procedure for the Suzuki-Miyaura Coupling Reactions of Aryl Bromides and Chlorides with Aryl Boronic Acids to Sterically Hindered Biaryls:**

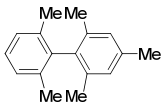



A flame-dried two-necked flask was charged with salt **3**, arylboronic acid, $Pd(OAc)_2$, and base, capped with a rubber septum, and then evacuated and backfilled with nitrogen. To the flask was sequentially added aryl halide and toluene via a syringe (aryl halides which were solids at room temperature were added during the initial charge, prior to evacuation/backfill) and then the

[5] A. Wang, W. Lu, *Org. Lett.* **11**, 2009, 1079.

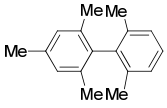
reaction mixture was stirred at the mentioned temperature for the indicated period of time. Then, filtration and column chromatography gave the corresponding product.

**2,4,6,2´,6´-Pentamethylbiphenyl (Table 2, entry 1):**



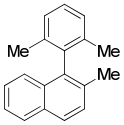

A two necked dry flask equipped with a stirring bar was charged with 2,4,6-trimethylphenylboronic acid (1.2 mmol, 196.8 mg), NaOtBu (2 mmol, 192.2 mg), salt **3** (0.02 mmol, 11.2 mg), and $Pd(OAc)_2$ (0.02 mmol, 5 mg), and was purged with nitrogen three times. 2,6-Dimethylbromobenzene (1 mmol, 185 mg) in toluene (5.0 mL) was then added via syringe and the reaction was stirred at 60 $^oC$ for 3.5 h. After this time, petroleum ether was added (5 mL) and the mixture was filtered through a plug of celite. The solvent was then evaporated and the residue was purified by flash column chromatography. A colorless oil was obtained in 87% yield (195 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.16-7.11(m, 3H), 6.95 (s, 2H), 2.17 (s, 3H), 1.88 (s, 6H), 1.86 (s, 6H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 140.0, 137.0, 136.1, 135.7, 135.2, 128.2, 127.4, 126.7, 21.1, 19.9, 19.7 ppm; IR (NaCl): 3057, 2936, 1618, 1573, 1234, 843, 764 $cm^{-1}$; *m/z* (70 ev) 224 [$M^+$]. Found: C, 91.2; H, 8.8%. Calc. for $C_{17}H_{20}$: C, 91.0; H, 9.0%.

**2,4,6,2´,6´-Pentamethylbiphenyl (Table 2, entry 2):**



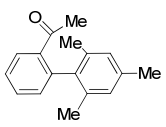

A mixture of 2,6-dimethylphenylboronic acid (180 mg, 1.20 mmol), 2-chloromesitylene (154.6 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. After 4 h stirring at 90 $^oC$ and column chromatography, 177 mg (79%) of title compound was obtained as a colorless oil. All data were identical to those above (entry 1).

**1-(2,6-Dimethylphenyl)-2-methylnaphthalene (Table 2, entry 3):**




A mixture of 2,6-dimethylphenylboronic acid (180 mg, 1.20 mmol), 1-bromo-2-methylnaphthalene (221 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. A colorless oil was obtained after 4.5 h stirring at 70 $^oC$ in 86 % yield (211 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.75-7.66 (m, 3H), 7.34-7.16 (m, 2H), 7.13-7.07 (m, 4H), 2.01 (s, 3H), 1.73 (s, 6H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 138.4, 136.8, 136.4, 132.7, 132.3, 131.9, 128.6, 127.9, 127.3, 127.3, 127.0, 126.1, 125.0, 124.9, 20.0, 19.9 ppm; IR (NaCl): 3057, 2958, 2863, 1634, 1587, 1043, 832, 786 $cm^{-1}$; *m/z* (70 ev) 246 [$M^+$]. Found: C, 92.5; H, 7.2%. Calc. for $C_{19}H_{18}$: C, 92.6; H, 7.4%.

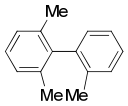
**1-(2´,4´,6´-Trimethylbiphenyl-3-yl)ethanone (Table 2, entry 4):**




A mixture of 2,4,6-trimethylphenylboronic acid (196.8 mg, 1.20 mmol), 1-(2-chlorophenyl) ethanone (154.6 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was

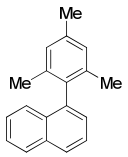
charged in a flask. A colorless oil was obtained after 3 h stirring at 50 °C in 91 % yield (217 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (dt, J = 7.4, 1.0 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.33 (dt, J = 7.4, 1.0 Hz, 1H), 6.95 (s, 2H), 2.62 (s, 3H), 2.36 (s, 3H), 1.98 (s, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 198.2, 145.6, 137.8, 137.3, 137.0, 135.8, 134.1, 129.3, 128.8, 128.2, 126.5, 26.7, 21.0, 20.7 ppm; IR (NaCl): 3126, 3033, 2924, 1674, 1564, 1235, 843 cm$^{-1}$; *m/z* (70 ev) 238 [$M^+$]. Found: C, 85.5; H, 7.7%. Calc. for $C_{17}H_{18}O$: C, 85.7; H, 7.6%.

**2,6,2´-Trimethyl biphenyl (Table 2, entry 5):**



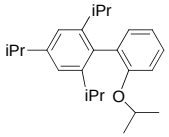

A mixture of 2,6-dimethylphenylboronic acid (180 mg, 1.20 mmol), 2-chlorotoluene (126.6 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. After 3 h stirring at 60 °C and column chromatography, 175 mg (89%) of the title compound were obtained as colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 3H), 7.23-7.16 (m, 3H), 7.11-7.07 (m, 1H), 2.15 (s, 3H), 2.04 (s, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.7, 136.0, 135.8, 130.1, 128.7, 127.2, 127.1, 126.8, 126.0, 20.3, 19.5 ppm; IR (NaCl): 3064, 3012, 2914, 1483, 1387, 1126, 826 cm$^{-1}$; *m/z* (70 ev) 196 [$M^+$]. Found: C, 91.9; H, 8.0%. Calc. for $C_{15}H_{16}$: C, 91.8; H, 8.2%.

**1-(2,4,6-Trimethylphenyl)naphthalene (Table 2, entry 6):**




A mixture of 2,4,6-trimethylphenylboronic acid (197 mg, 1.20 mmol), 1-chloronaphthalene (162.6 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. After 4.5 h stirring at 90 °C and column chromatography, 221 mg (90%) were obtained as colorless solid, mp 65-67 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 2H), 7.61-7.51 (m, 3H), 7.30-7.21 (m, 2H), 7.00 (s, 2H), 2.38 (s, 3H), 1.87 (s, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.5, 136.9, 133.5, 132.9, 128.3, 128.1, 128.1, 127.9, 127.8, 126.6, 126.0, 125.8, 125.7, 125.4, 21.1, 20.3 ppm; IR (KBr): 3021, 2920, 1493, 1445, 1024, 850, 769 cm$^{-1}$; *m/z* (70 ev) 246 [$M^+$]. Found: C, 92.8; H, 7.2%. Calc. for $C_{19}H_{18}$: C, 92.6; H, 7.4%.

**2,4,6-Triisopropyl-2'-isopropoxybiphenyl (Table 2, entry 7):**

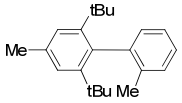



Following the general procedure, a mixture of 2-isopropoxyphenylboronic acid (216 mg, 1.20 mmol), 1-bromo-2,4,6-triisopropylbenzene (283 mg, 1.0 mmol), NaOtBu (163.5 mg, 1.7 mmol), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. After 7 h stirring at 90 °C and column chromatography, 155 mg (46%) of the title compound were obtained as colorless solid, mp 68-70 °C (71-73 °C, ref.[6]); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 1H), 7.07-6.92 (m, 5H), 7.01 (s, 2H), 4.39 (sept, J = 6.2 Hz, 1H), 2.90 (sept, J = 7.2 Hz, 1H), 2.54 (sept, J = 7.0 Hz, 2H), 1.29

[6] T. Hoshi, I. Saitoh, T. Nakazawa, T. Suzuki, J.-i. Sakai, H. Hagiwara, *J. Org. Chem*. 2009, **74**, 4013.

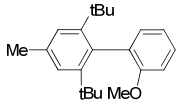
(d, J = 7.0 Hz, 6H), 1.13-1.01 (m, 18H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3, 147.1, 146.5, 133.3, 131.8, 130.4, 127.6, 120.0, 119.6, 112.8, 69.1, 34.2, 30.5, 24.5, 24.1, 21.9 ppm; IR (KBr): 3021, 2967, 2845, 1495, 1461, 1246, 1011, 843 cm$^{-1}$; *m/z* (70 ev) 338 [M$^+$]. Found: C, 85.3; H, 10.0%. Calc. for $C_{24}H_{34}O$: C, 85.2; H, 10.1%.

**2,6-Di-tert-butyl-2',4-dimethylbiphenyl (Table 2, entry 8):**



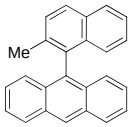

A mixture of 2-methylphenylboronic acid (163.2 mg, 1.20 mmol), 2-bromo-1,3-di-tert-butyl-5-methylbenzene (283.2 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. A colorless solid was obtained after 10 h stirring at 110 °C in 39 % yield (115 mg), mp 43-44 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 4H), 6.98 (s, 2H), 2.31 (s, 3H), 2.27 (s, 3H), 1.43 (s, 18H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.6, 141.9, 141.2, 135.8, 132.6, 132.5, 130.2, 128.3, 125.6, 116.1, 34.3, 30.4, 21.2, 20.5 ppm; IR (KBr): 3075, 3015, 2964, 2843, 1574, 1523, 1422, 1124, 781 cm$^{-1}$; *m/z* (70 ev) 294 [M$^+$]. Found: C, 89.6; H, 10.4%. Calc. for $C_{22}H_{30}$: C, 89.7; H, 10.3%.

**2,6-Di-tert-butyl-4-methyl-2´-methoxy-biphenyl (Table 2, entry 9):**



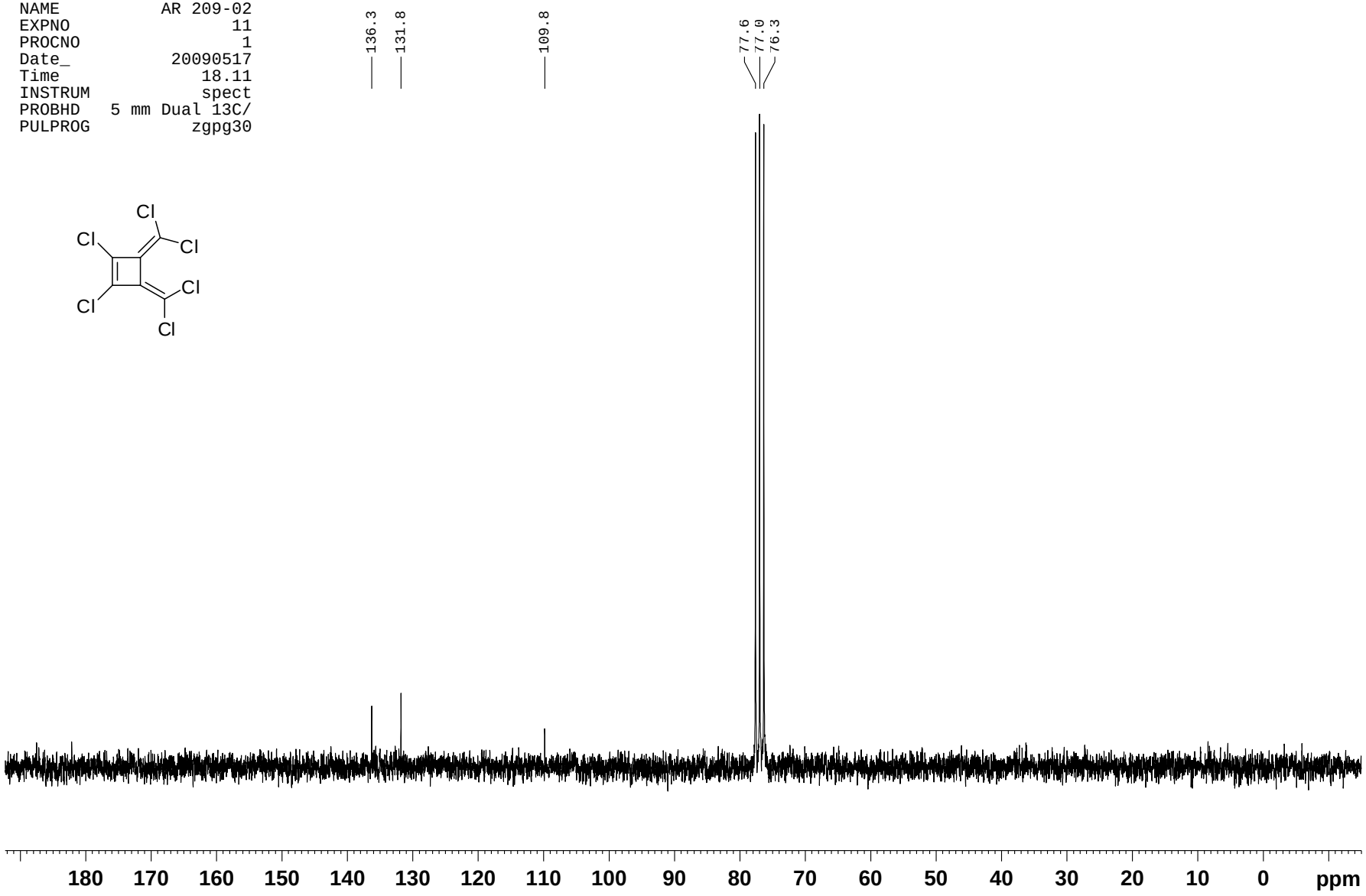

A mixture of 2-methoxyphenylboronic acid (182.4 mg, 1.20 mmol), 2-bromo-1,3-di-tert-butyl-5-methylbenzene (283.2 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol) and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. A pale yellow solid was obtained after 10 h stirring at reflux temperature in 37% yield (115 mg), mp 54-56 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 1H), 7.41-7.35 (m, 1H), 7.07 (s, 2H), 6.97-6.87 (m, 2H), 3.83 (s, 3H), 2.36 (s, 3H), 1.52 (s, 18H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.4, 148.1, 134.1, 132.8, 130.4, 128.9, 127.4, 126.4, 118.3, 112.9, 54.4, 32.5, 28.6, 19.6 ppm; IR (KBr): 3103, 3034, 2974, 2863, 1602, 1572, 1478, 1201, 1115, 786 cm$^{-1}$; *m/z* (70 ev) 310 [M$^+$]. Found: C, 85.3; H, 9.6%. Calc. for $C_{22}H_{30}O$: C, 85.1; H, 9.7%.

**9-(2-Methylnaphthalen-1-yl)anthracene (Table 2, entry 10):**




Following the general coupling procedure, a mixture of 1-(2-methylnaphthyl)boronic acid (223.2 mg, 1.20 mmol), 9-chloroanthracene (212.7 mg, 1.0 mmol), NaOtBu (2 mmol, 192.2 mg), 2 mol% of $Pd(OAc)_2$ (5 mg, 0.02 mmol), and **3** (11.2 mg, 0.02 mmol) in toluene (5 mL) was charged in a flask. 251 mg of the title compound (79%) were isolated by flash chromatography as a white solid, mp. 148 - 150 °C (151-153 °C, ref.[7]); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.14 (d, J = 8.2 Hz, 2H), 8.04-7.97 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.52-7.37 (m, 3H), 7.34-7.25 (m, 4H), 7.14 (m, 1H), 6.89 (d, J = 8.0 Hz, 1H), 2.01 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.1 133.7, 132.1, 131.6, 130.5 (overlapping signals), 128.7, 128.6, 127.9, 127.8, 126.6, 126.3, 126.2, 126.1, 125.7, 125.2, 124.9, 20.2 ppm; IR (KBr): 3064, 2978, 2832, 1637, 1583, 1067, 853, 773 cm$^{-1}$; *m/z* (70 ev) 318 [M$^+$]. Found: C, 94.5; H, 5.6%. Calc. for $C_{25}H_{18}$: C, 94.3; H, 5.7%.

[7] M. G. Organ, S. Galimsiz, M. Sayah, K. H. Hoi, A. J. Lough, *Angew. Chem. Int. Ed*. 2009, **48**, 2283.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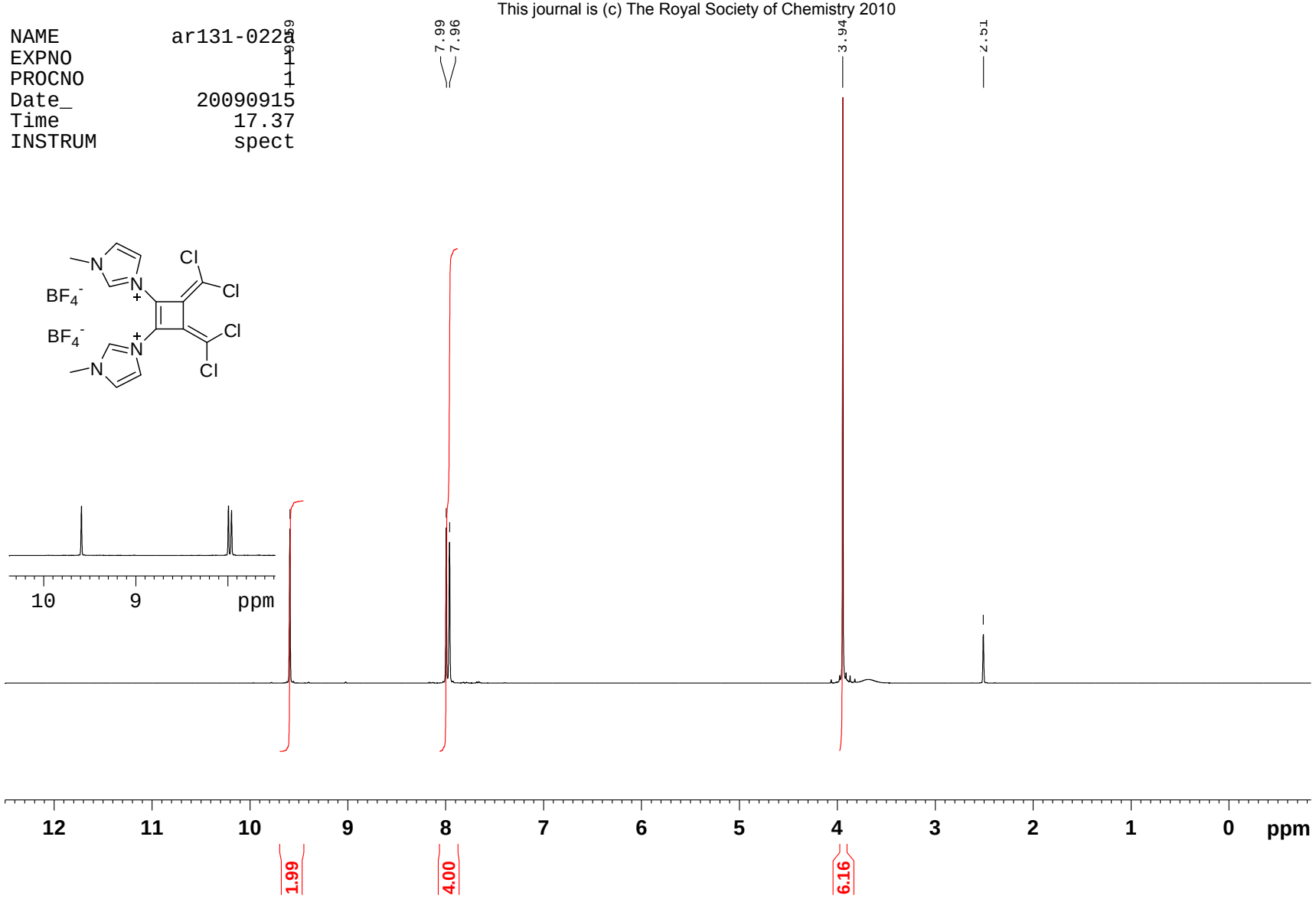
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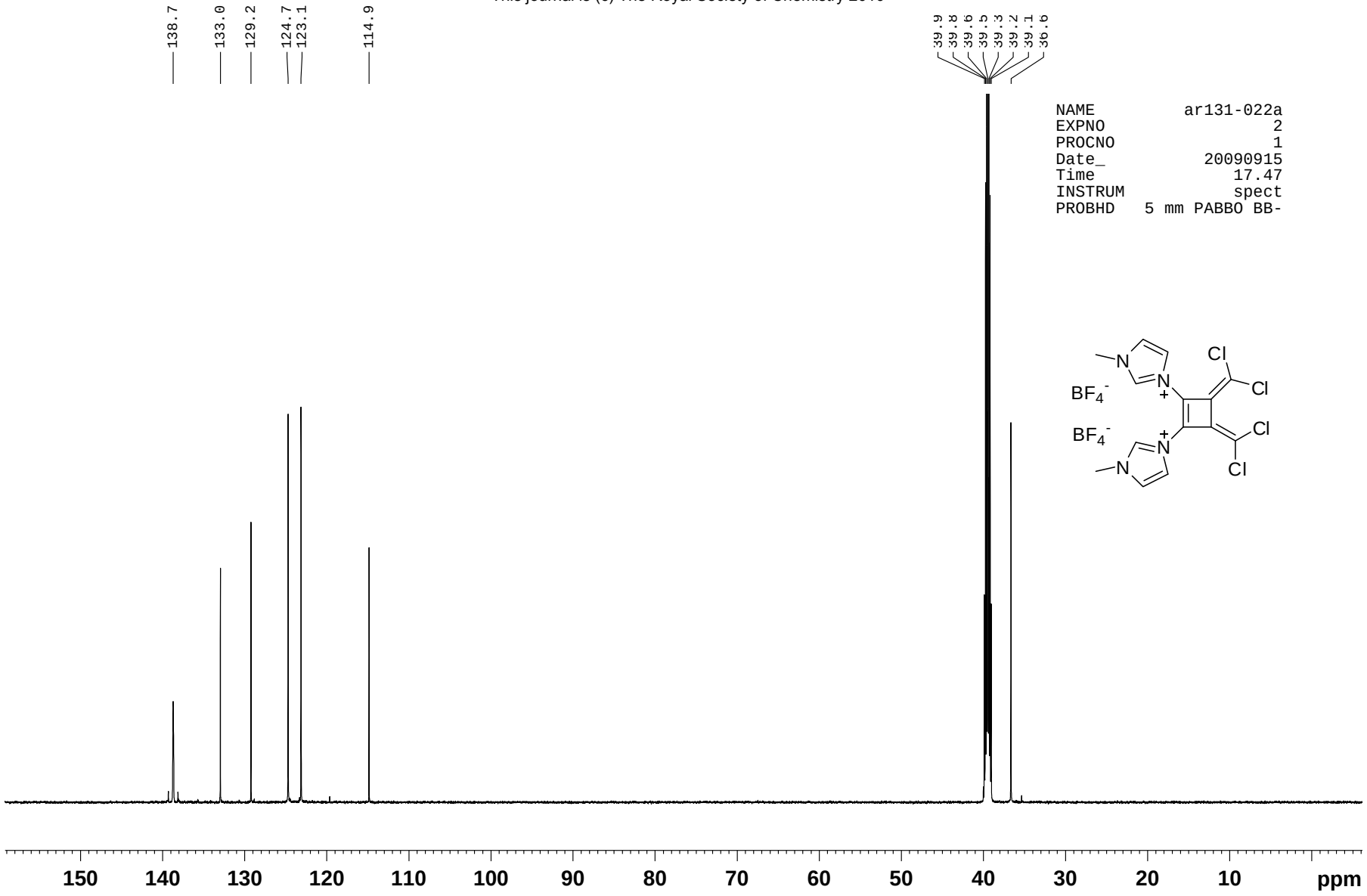
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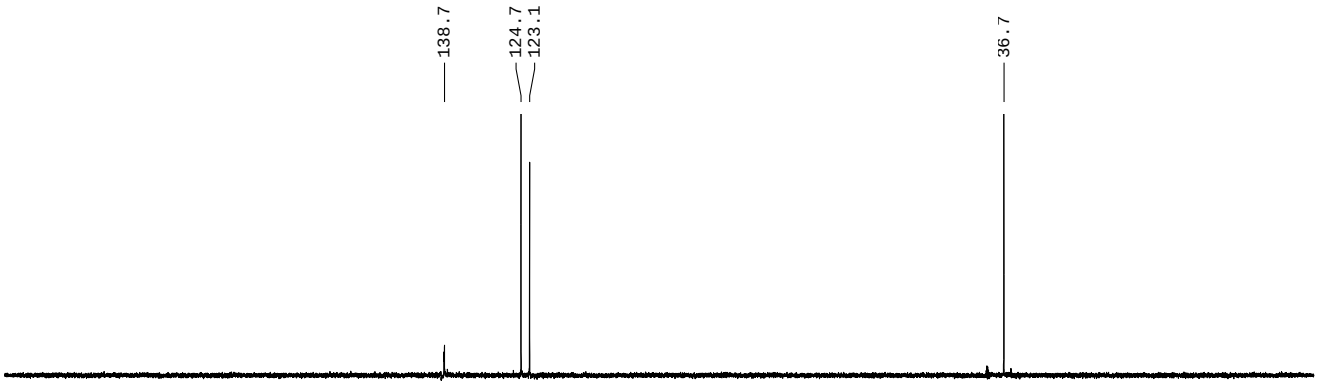


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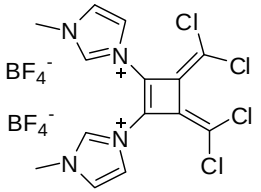


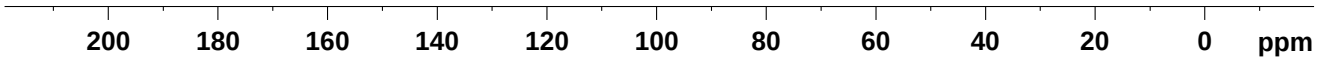

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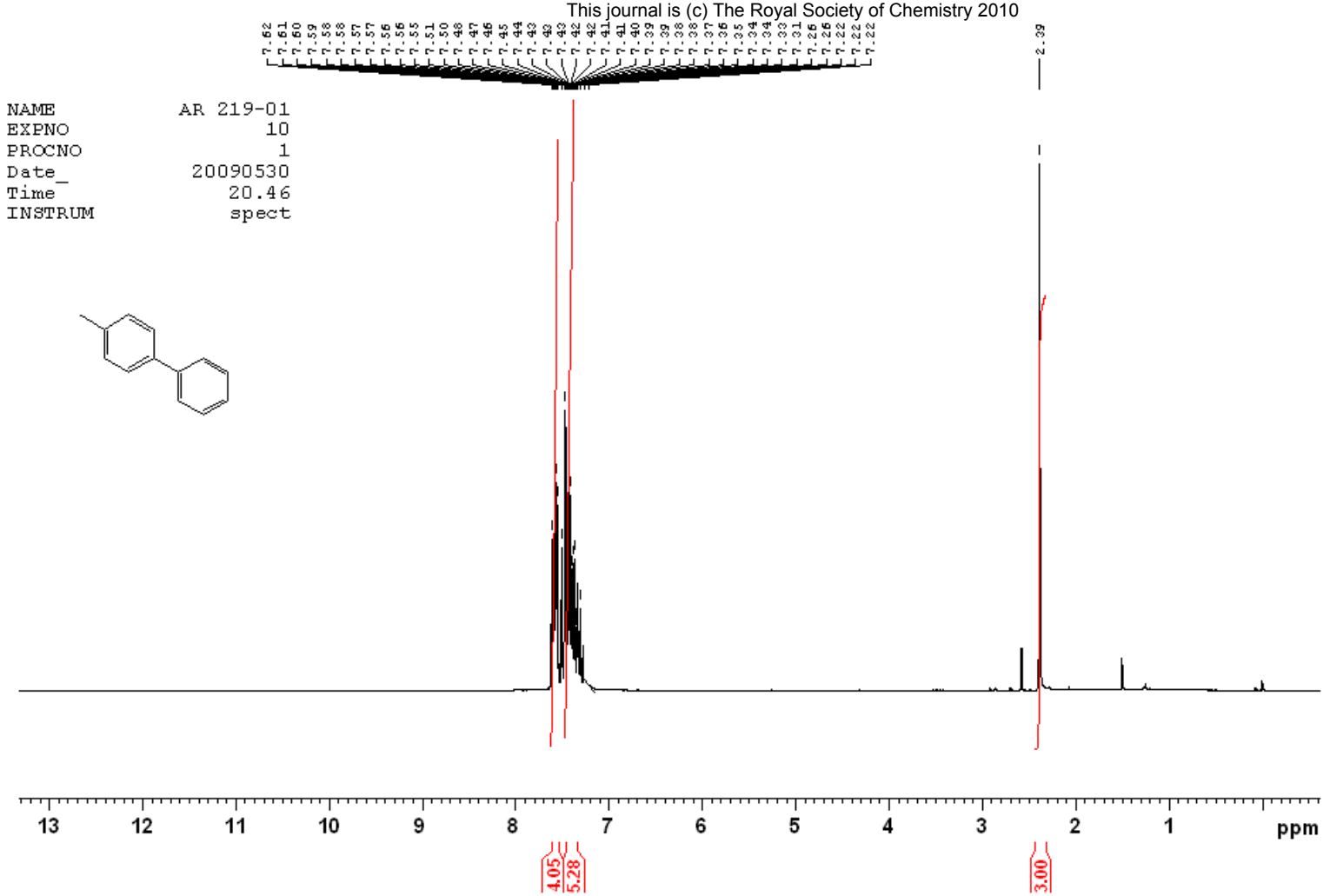

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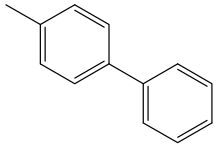

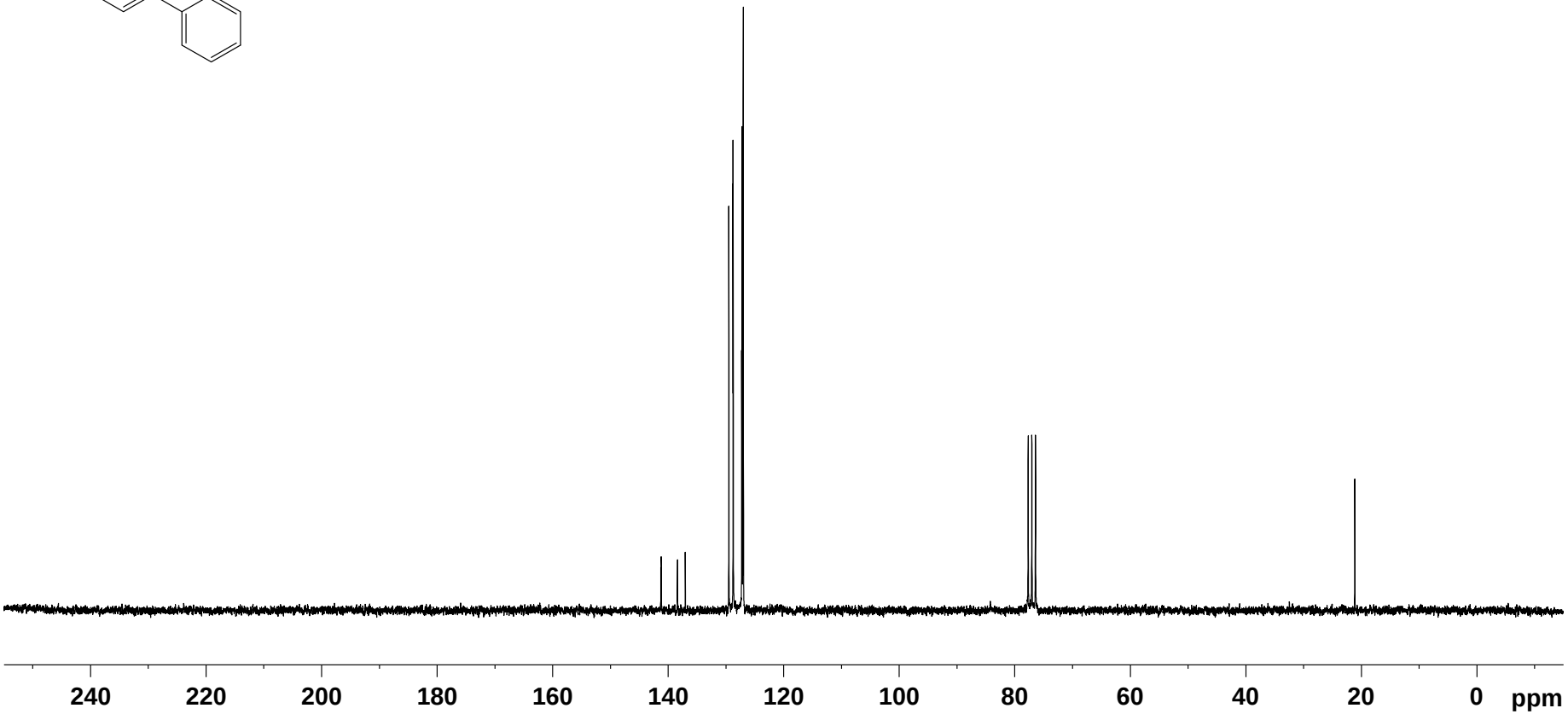

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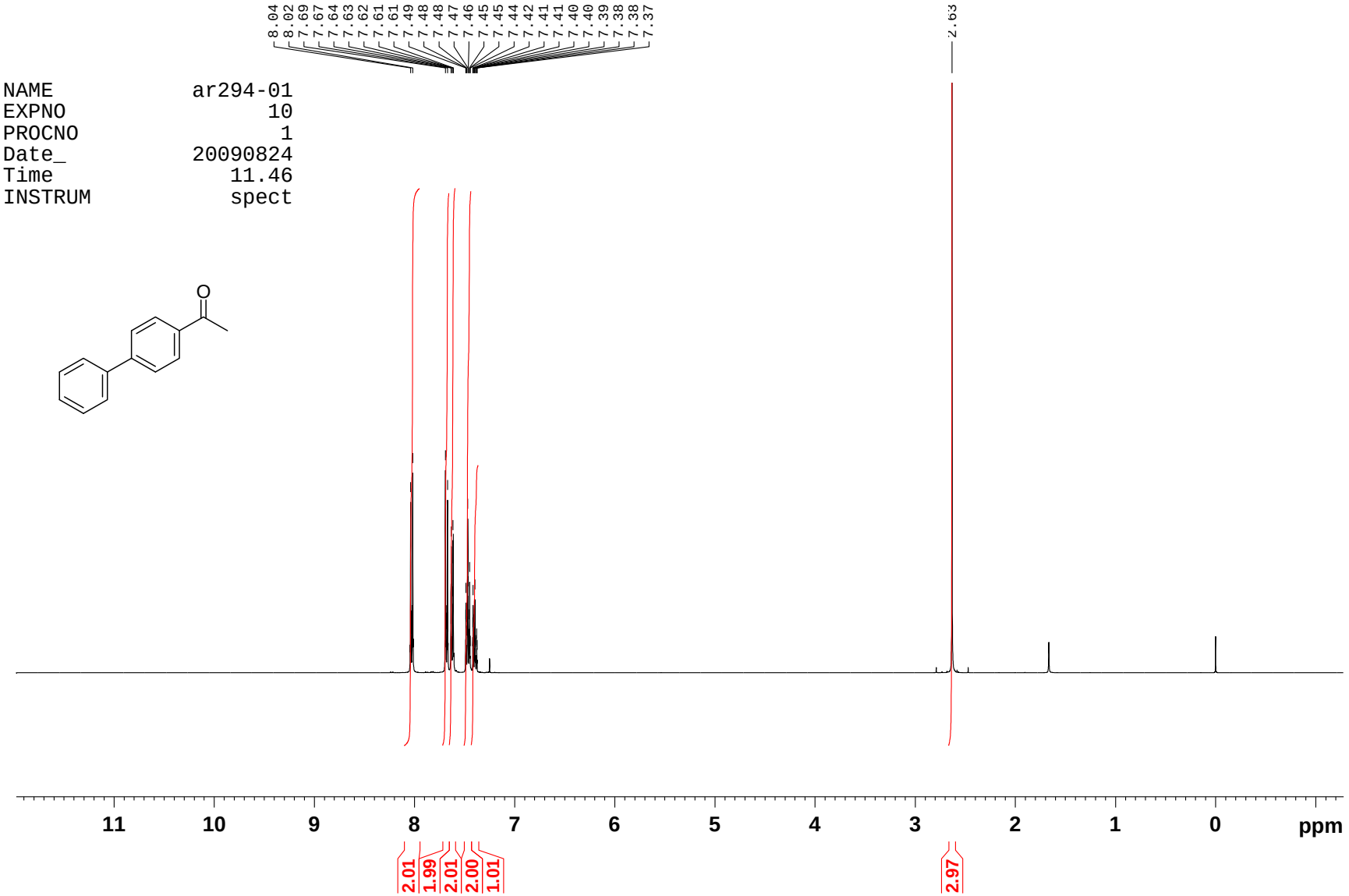

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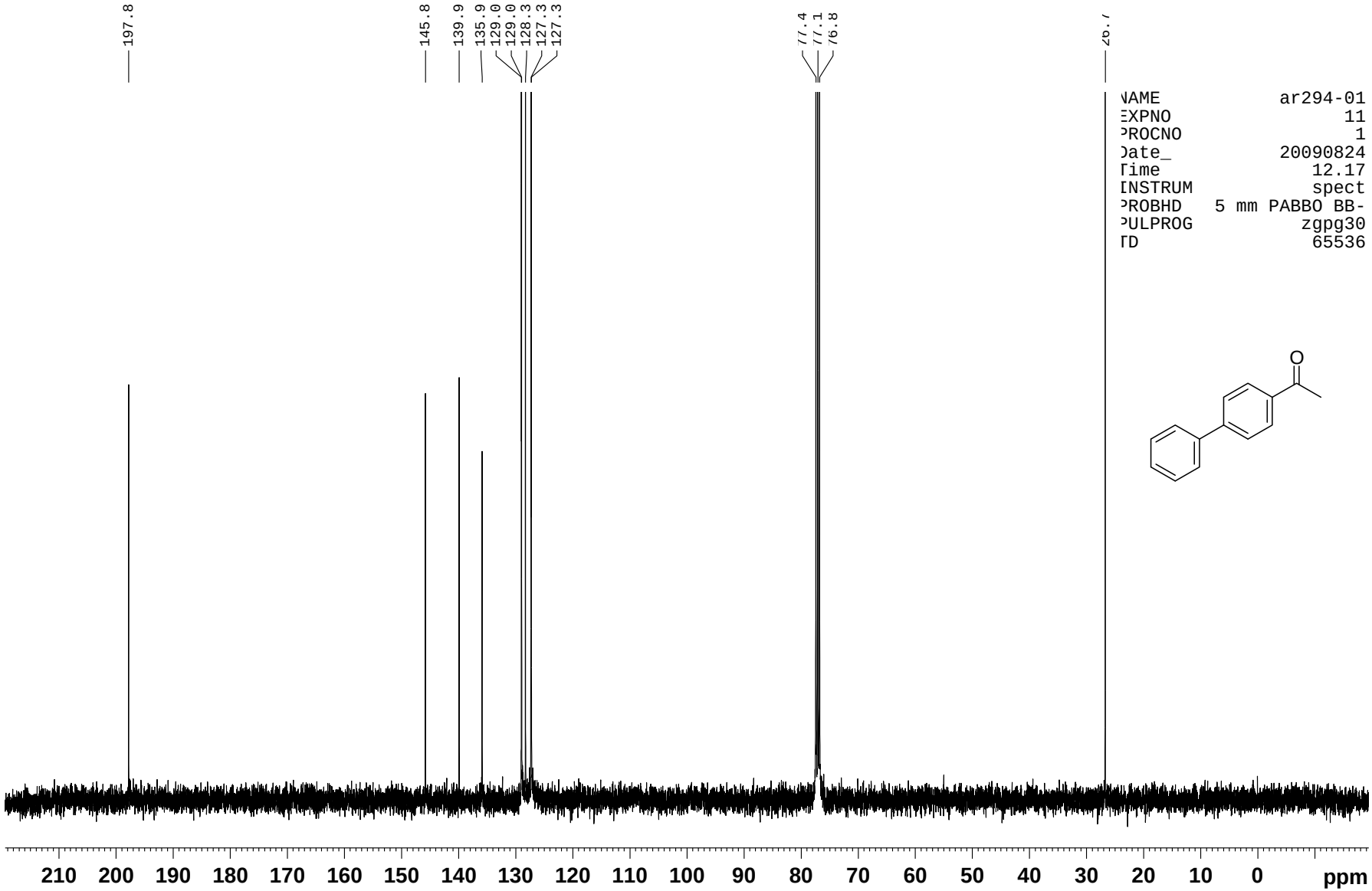

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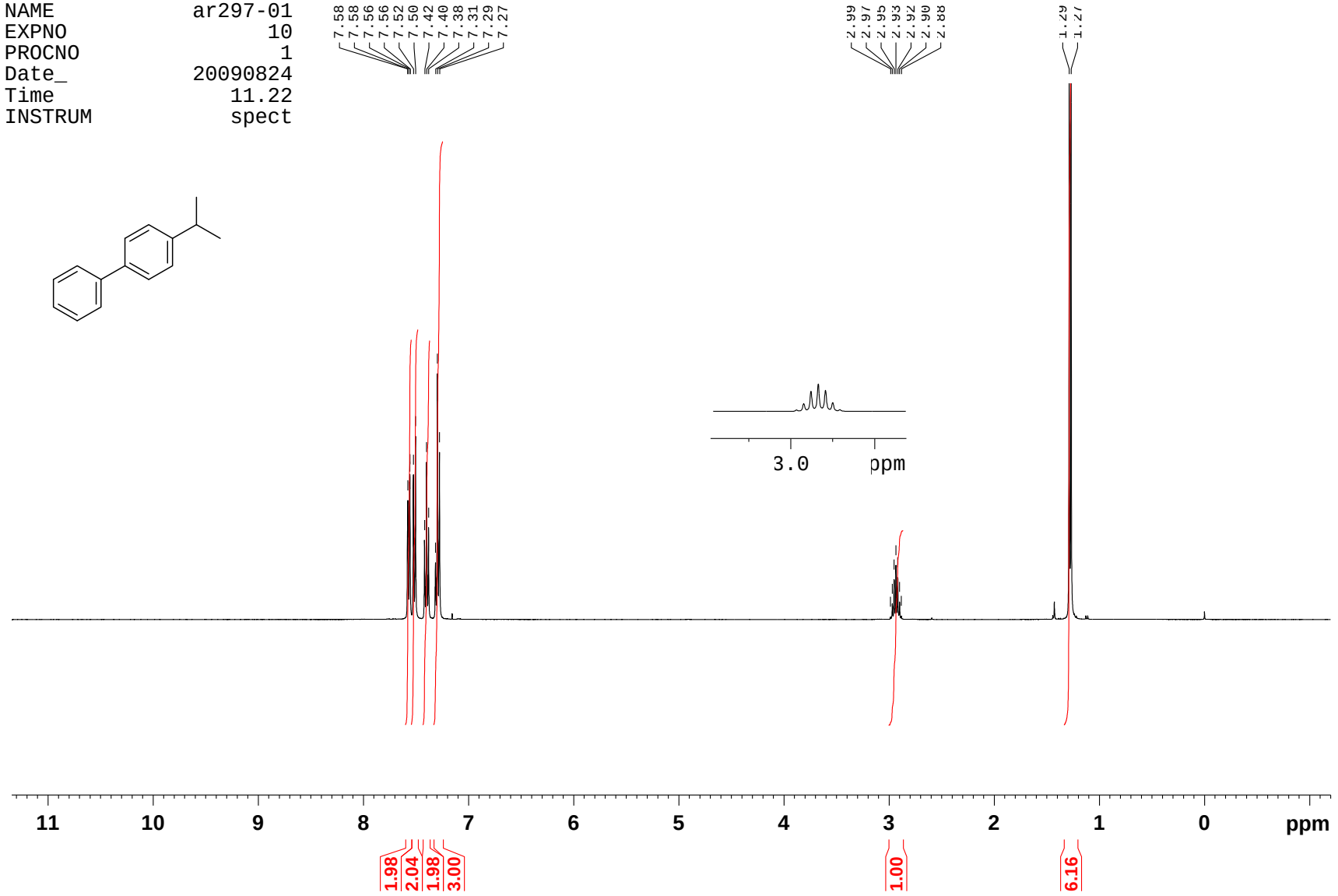

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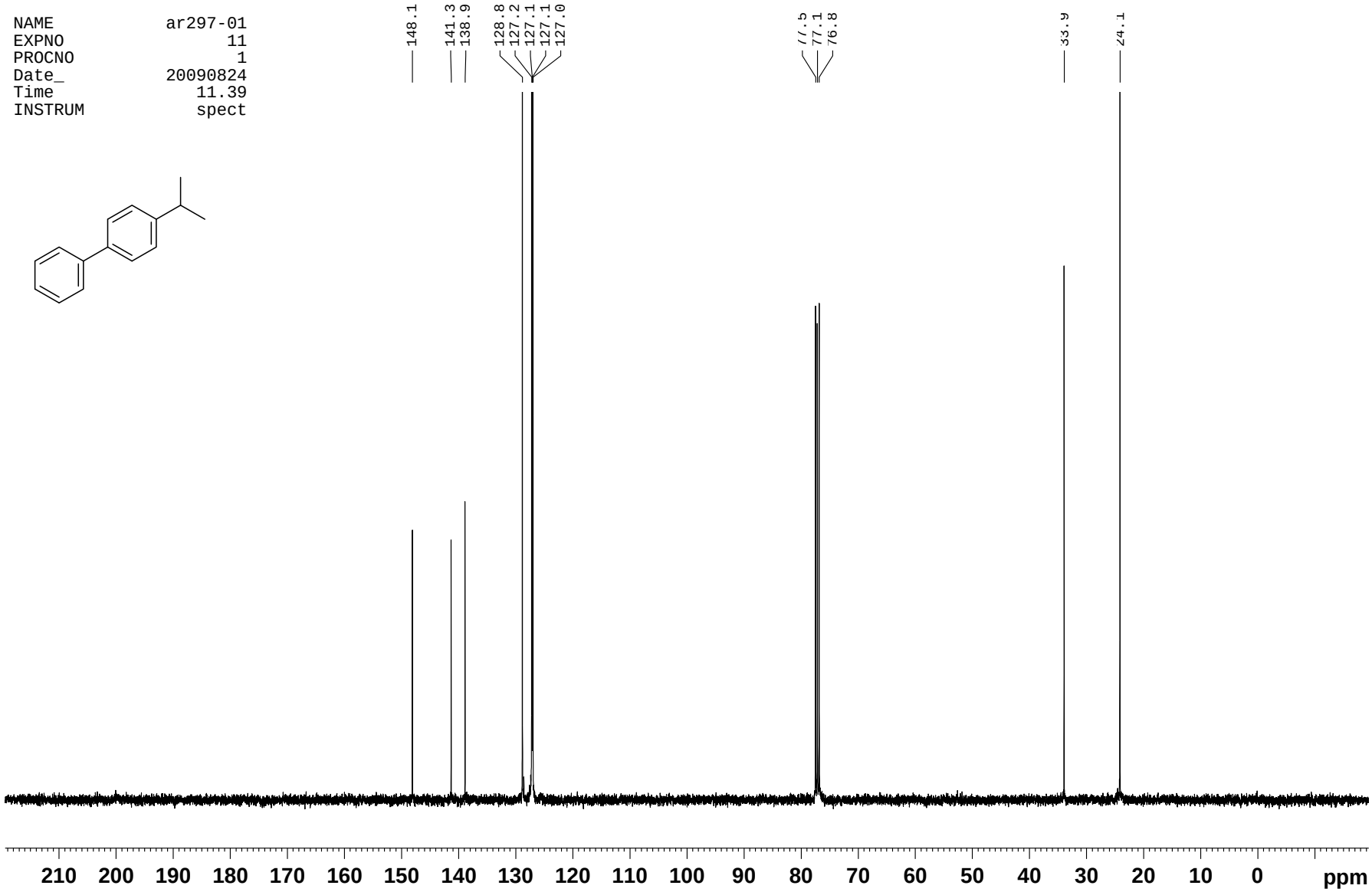

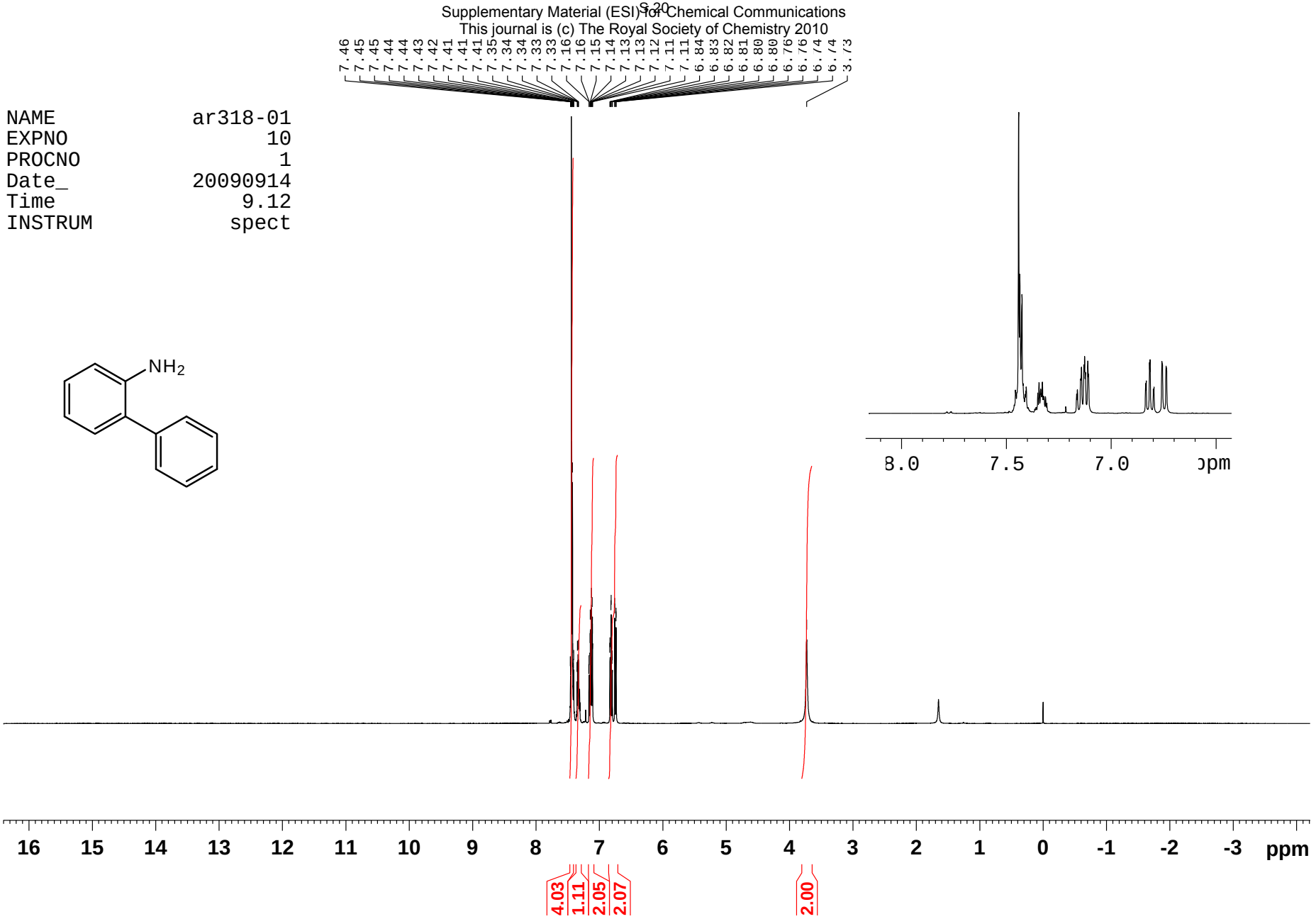
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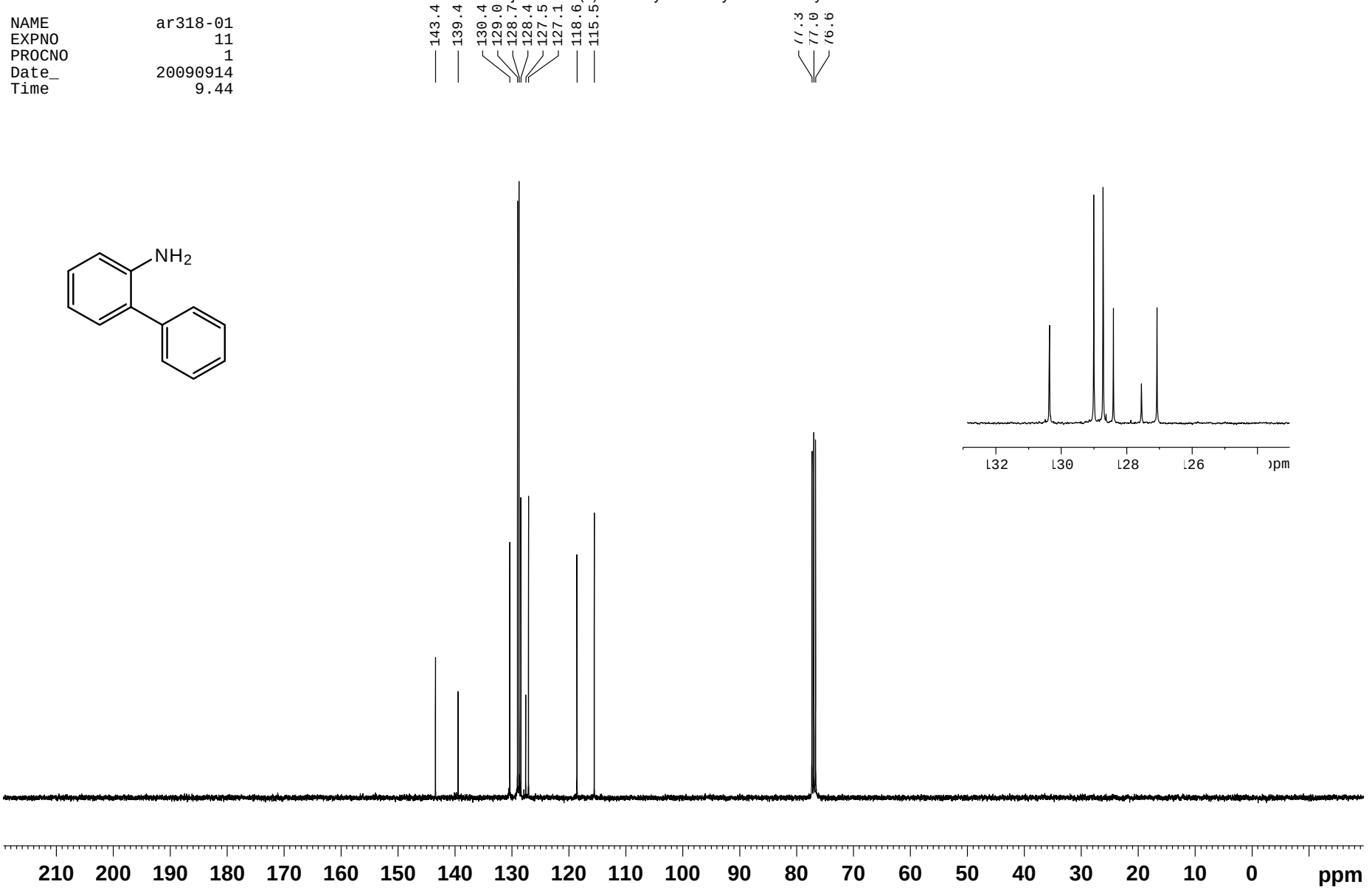

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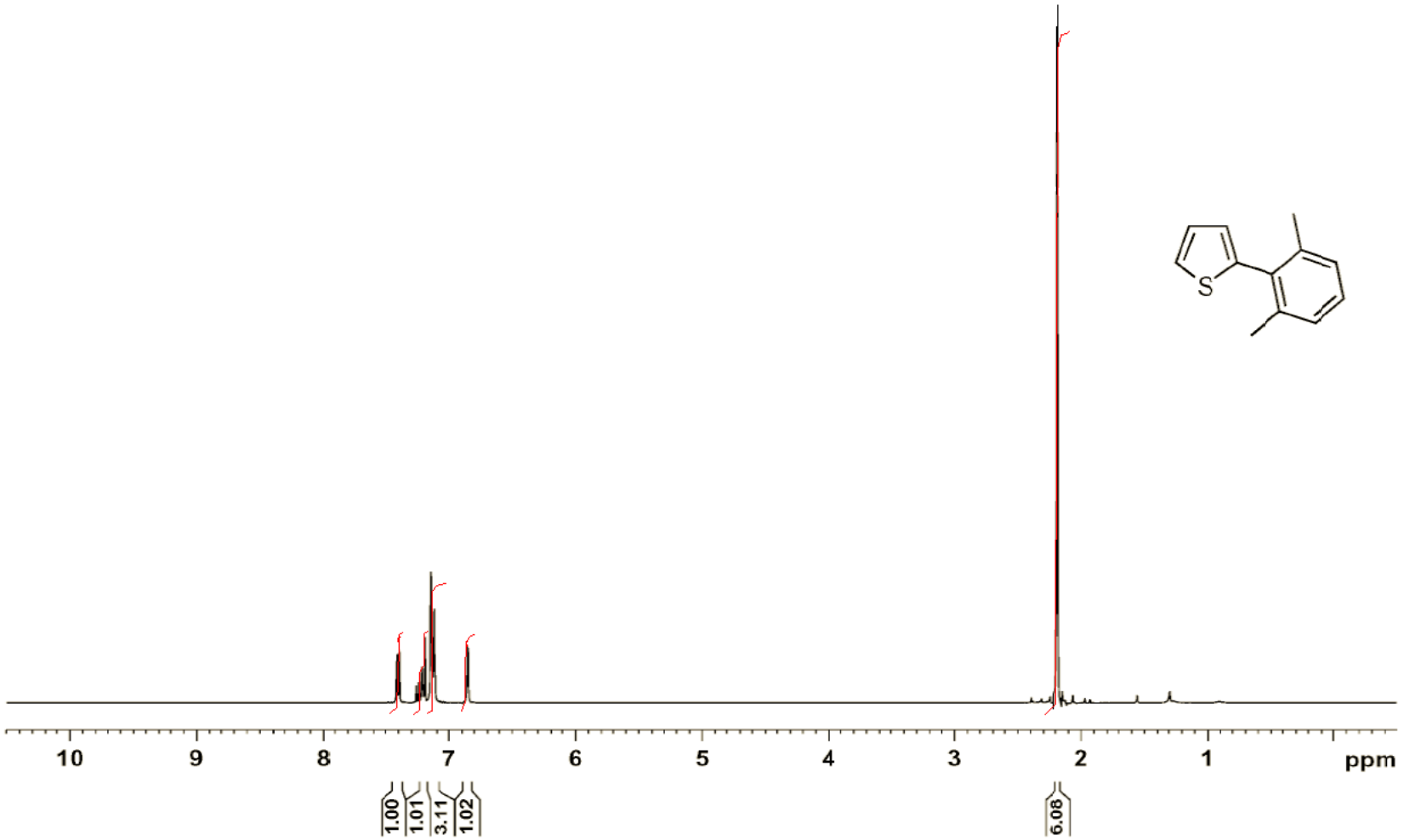

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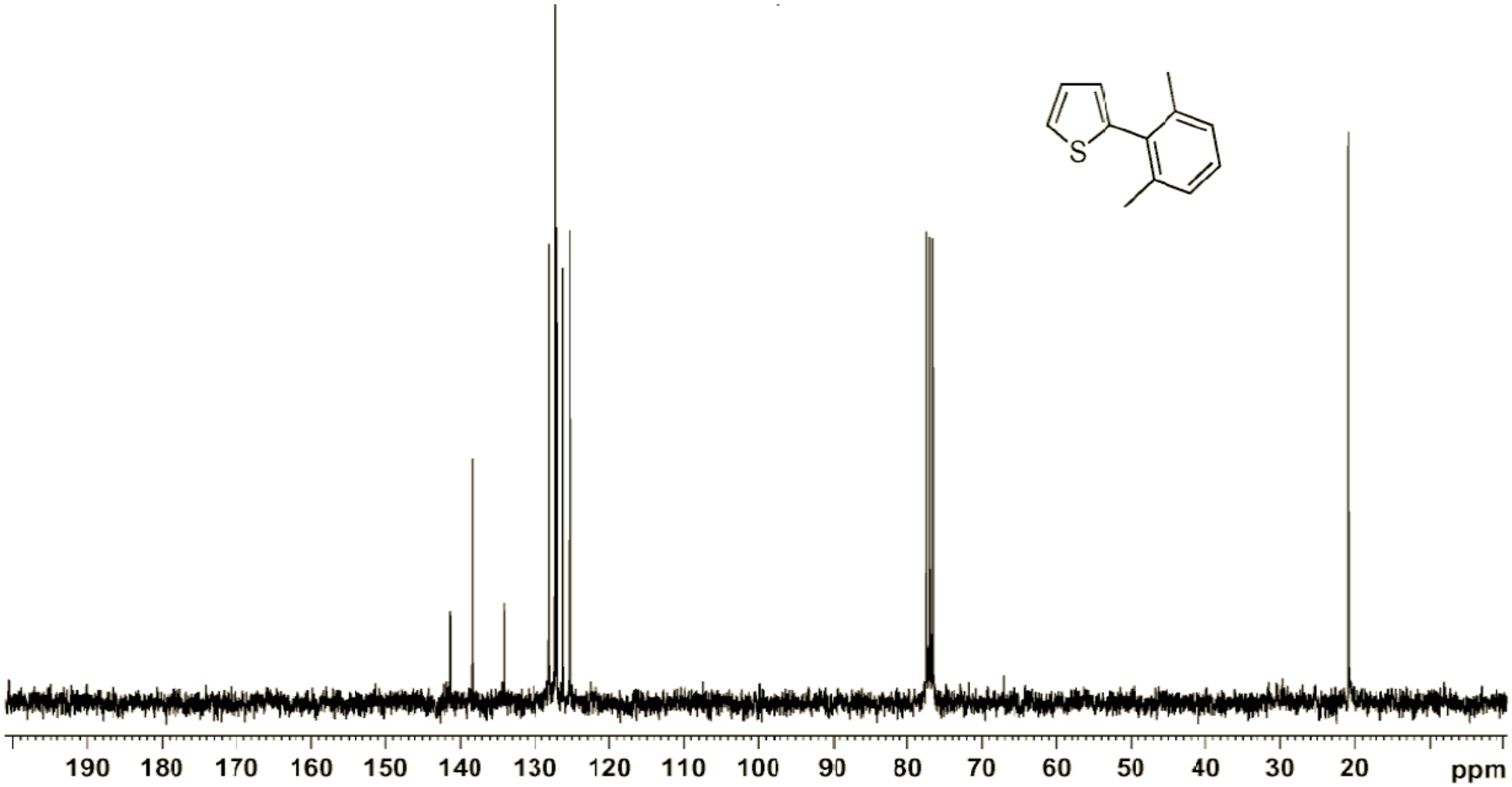

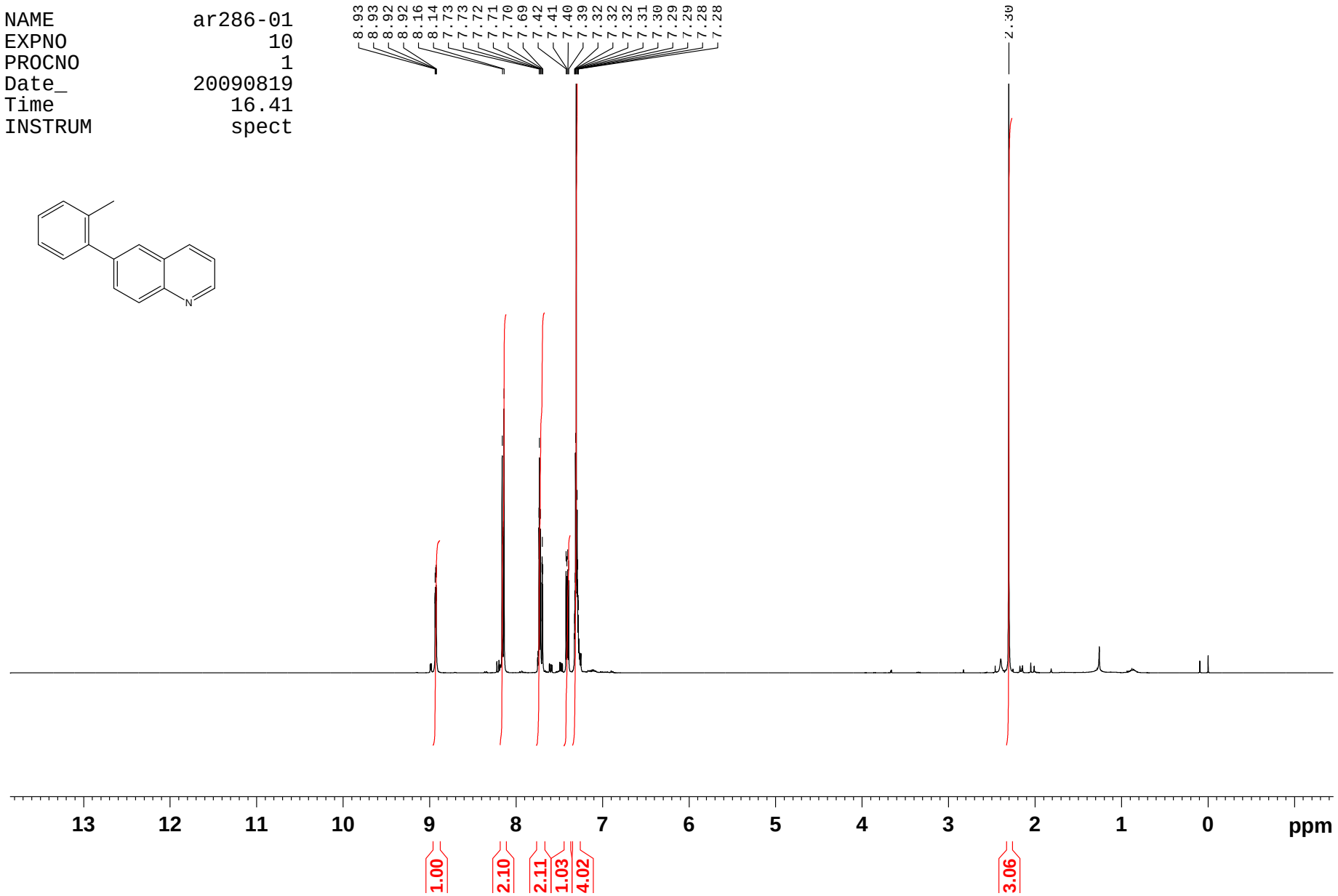
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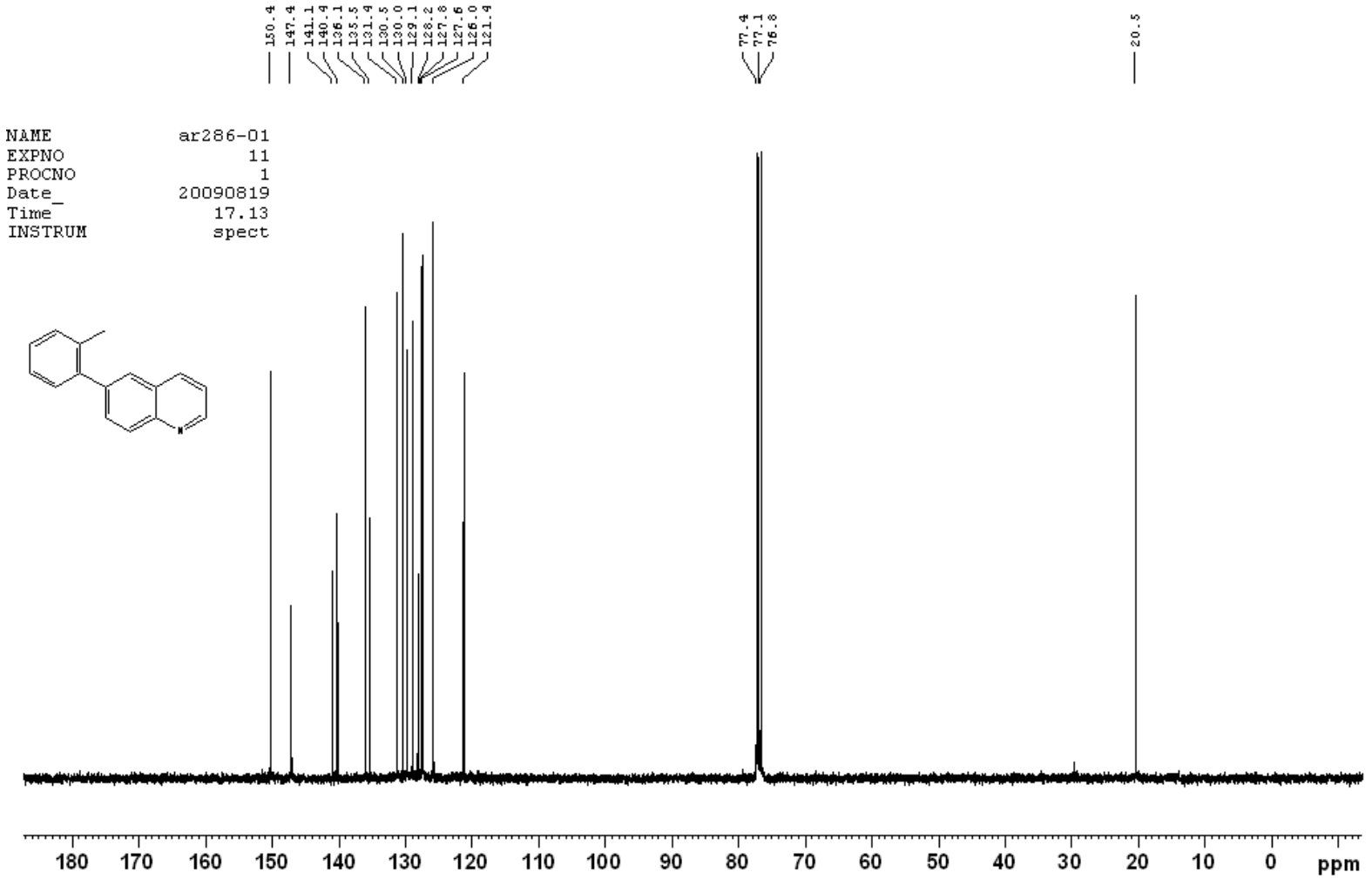

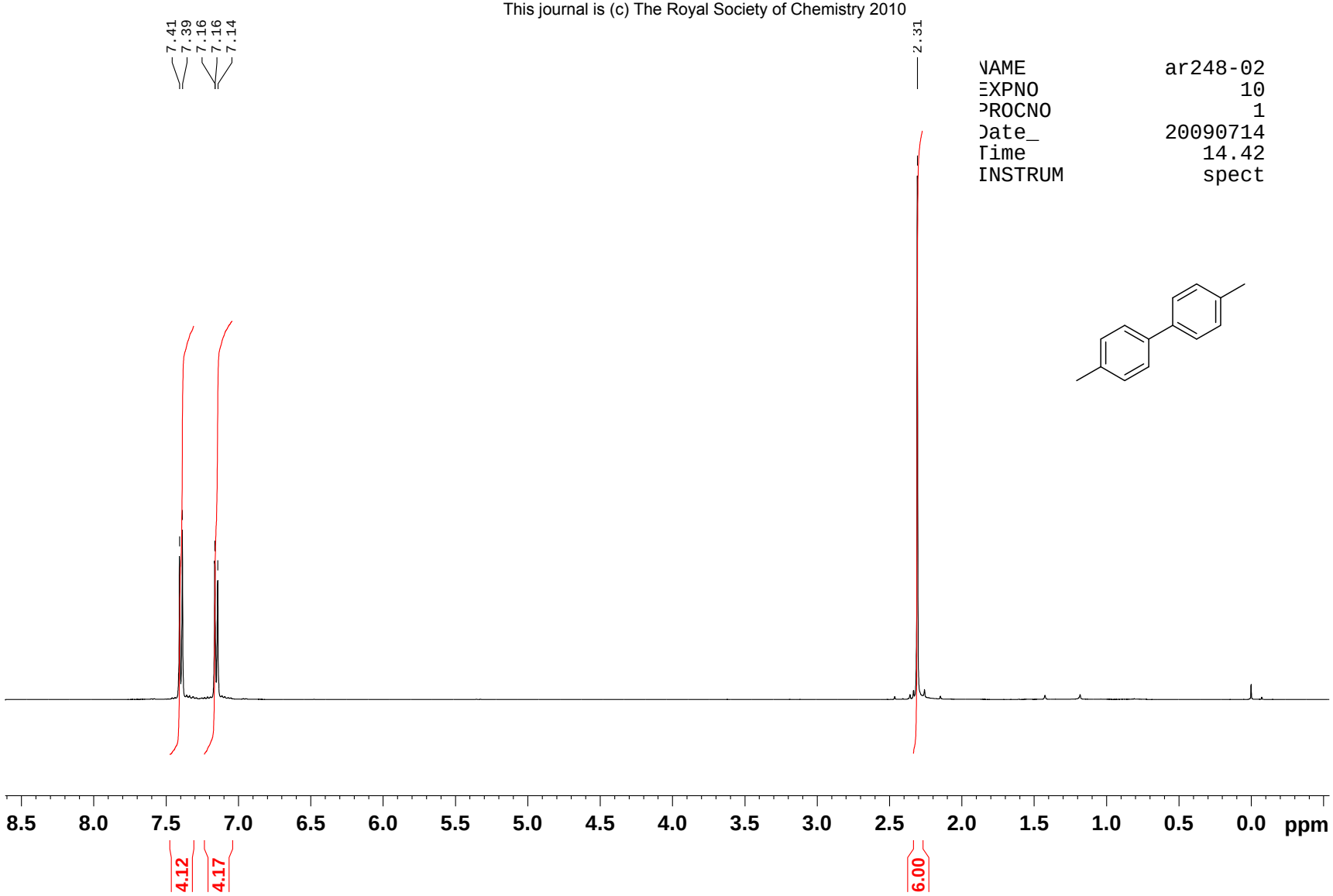

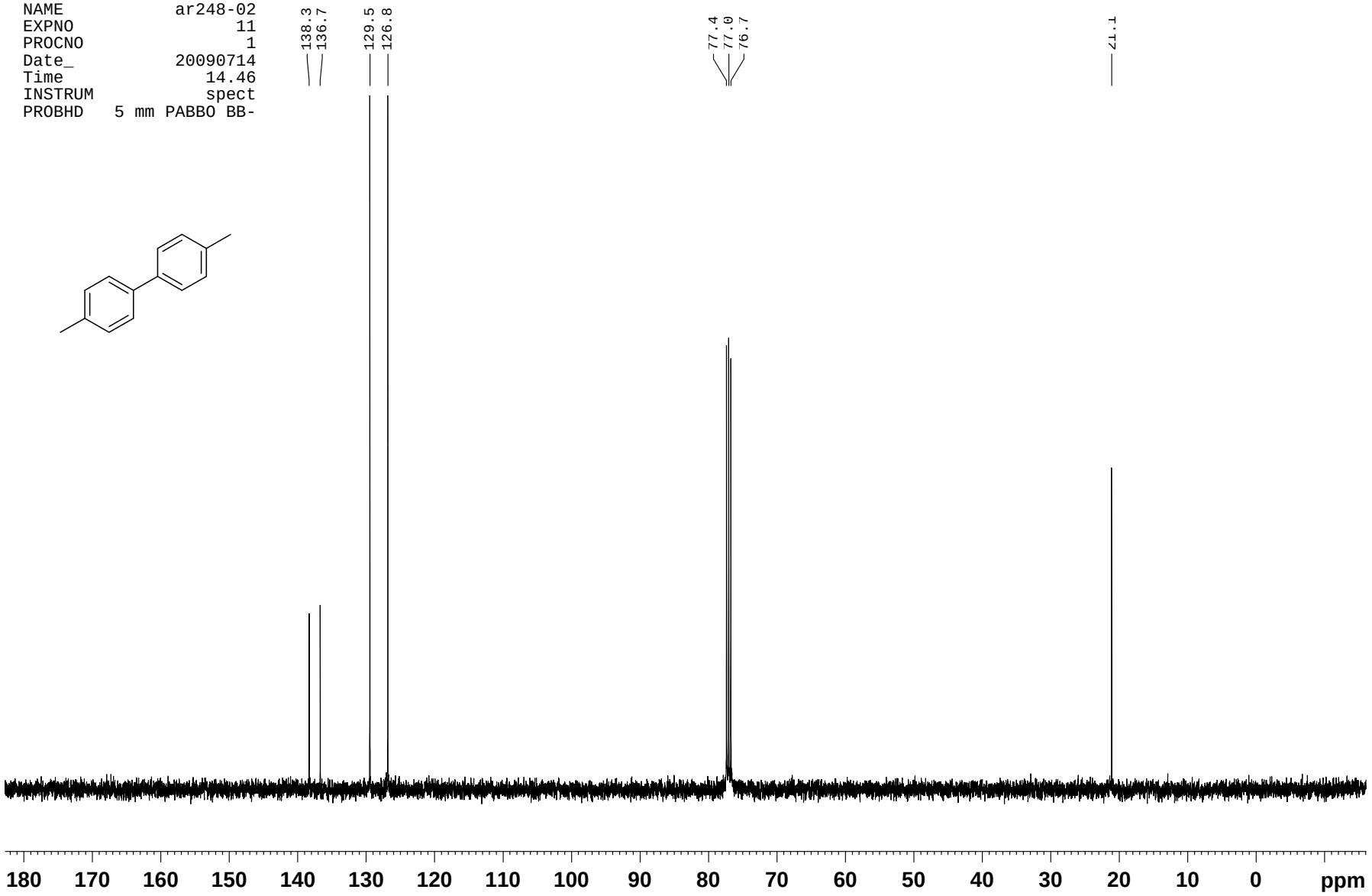

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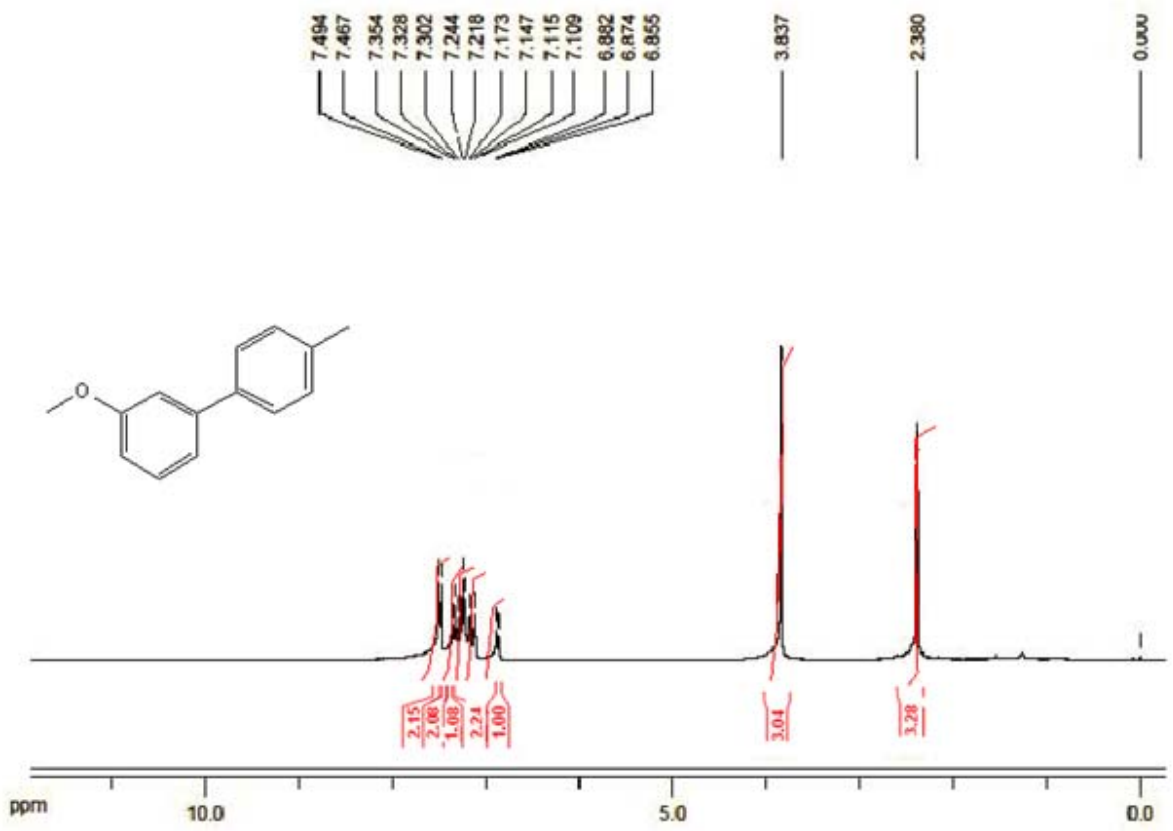

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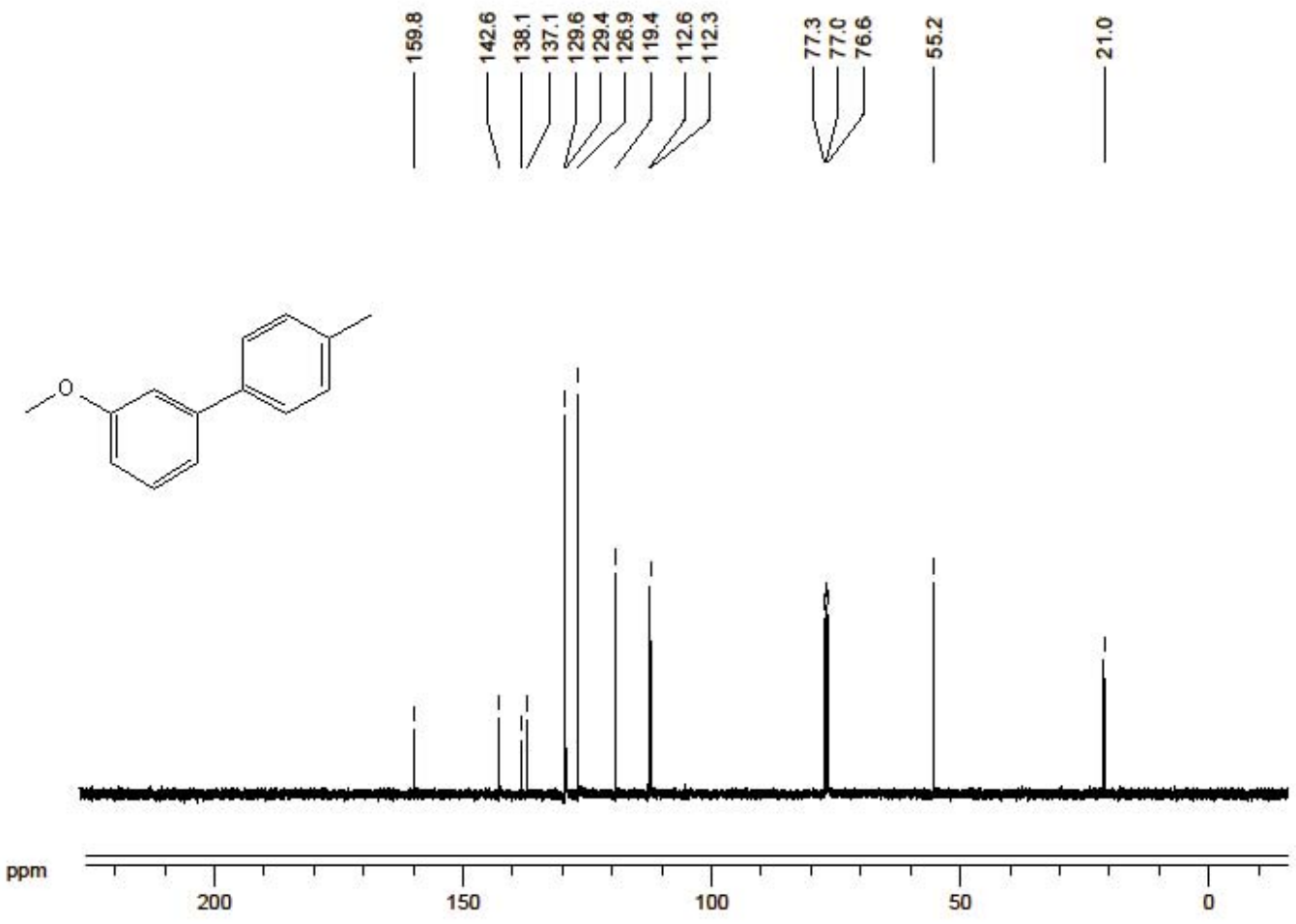

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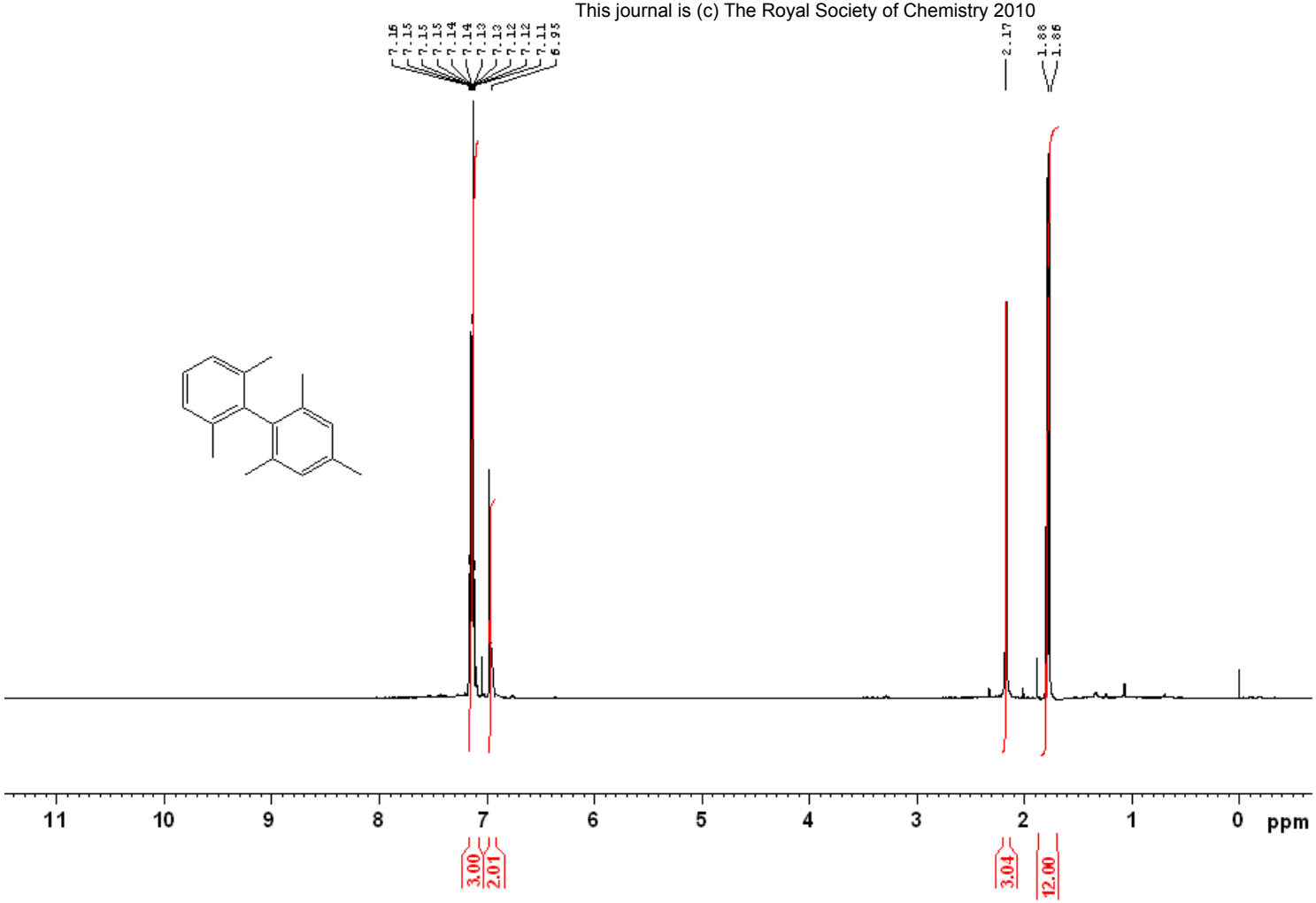

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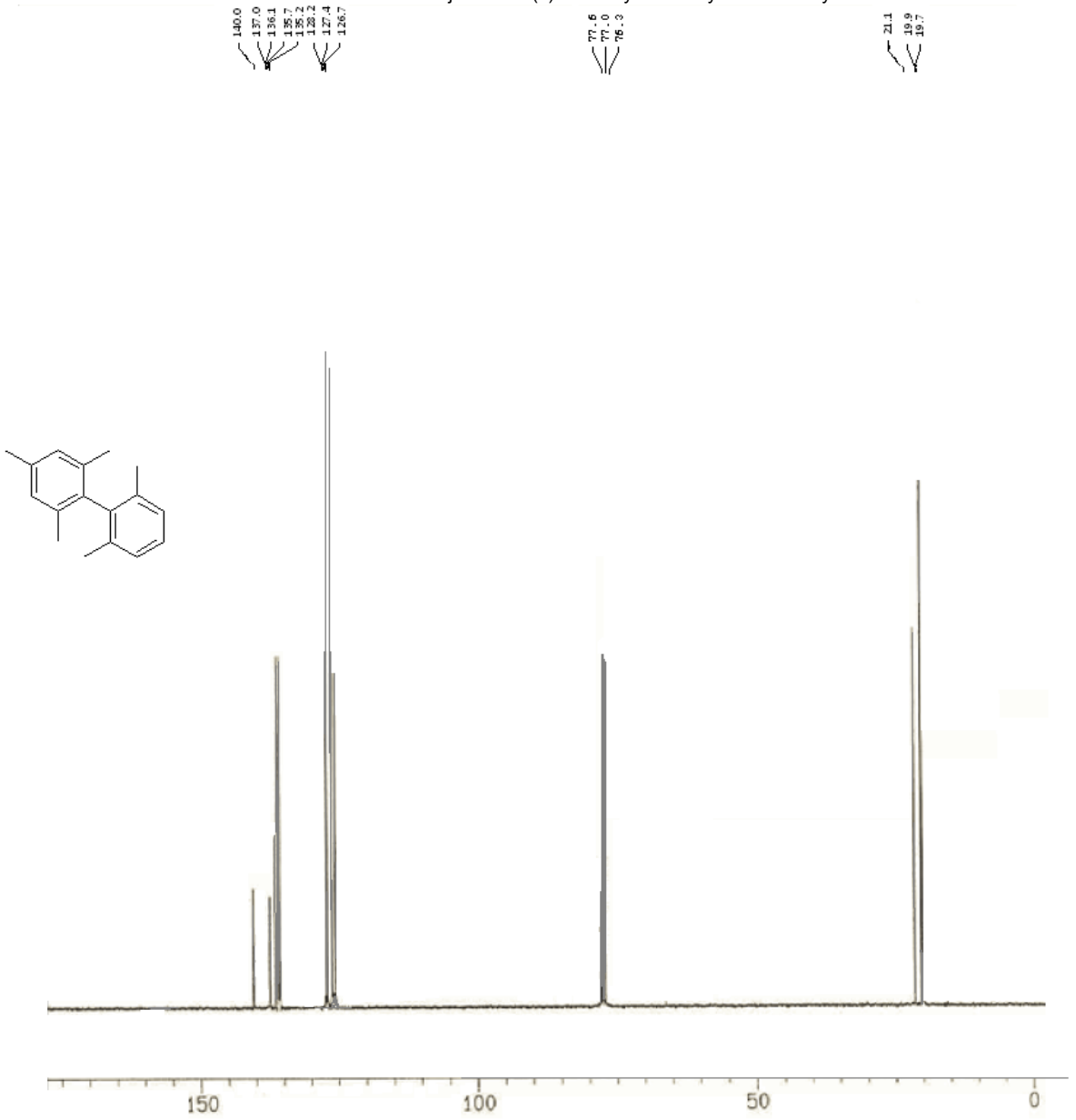

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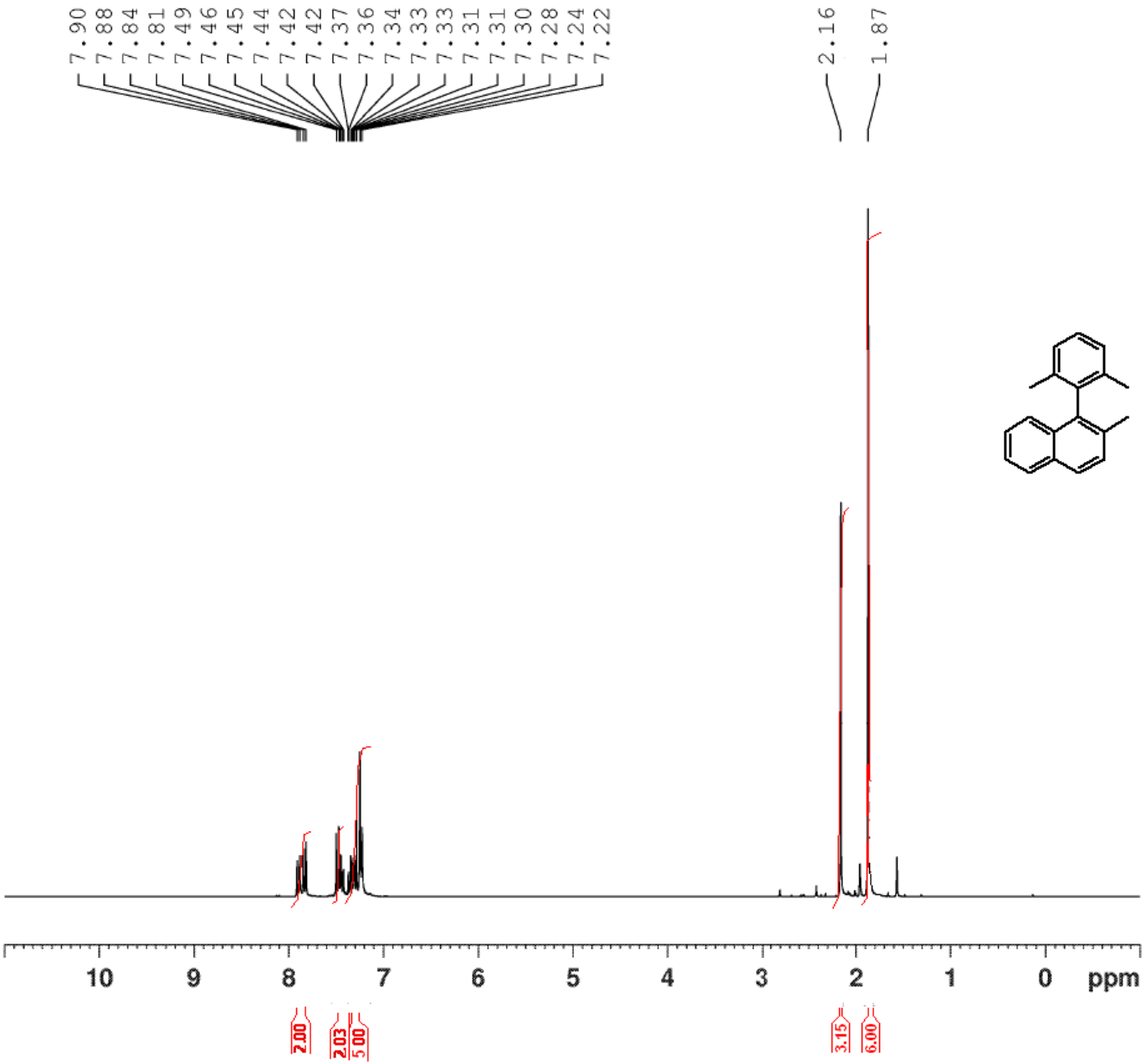

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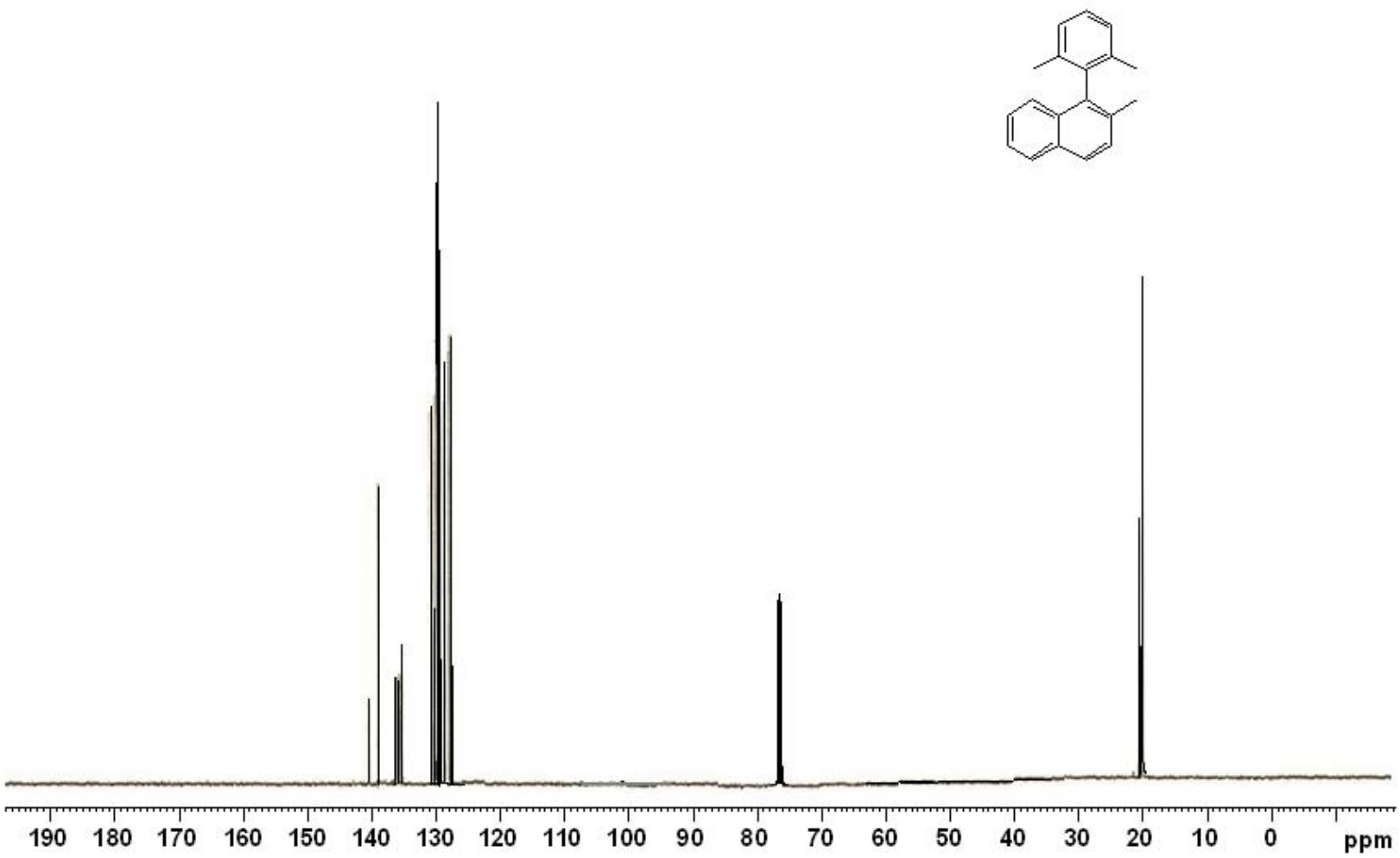

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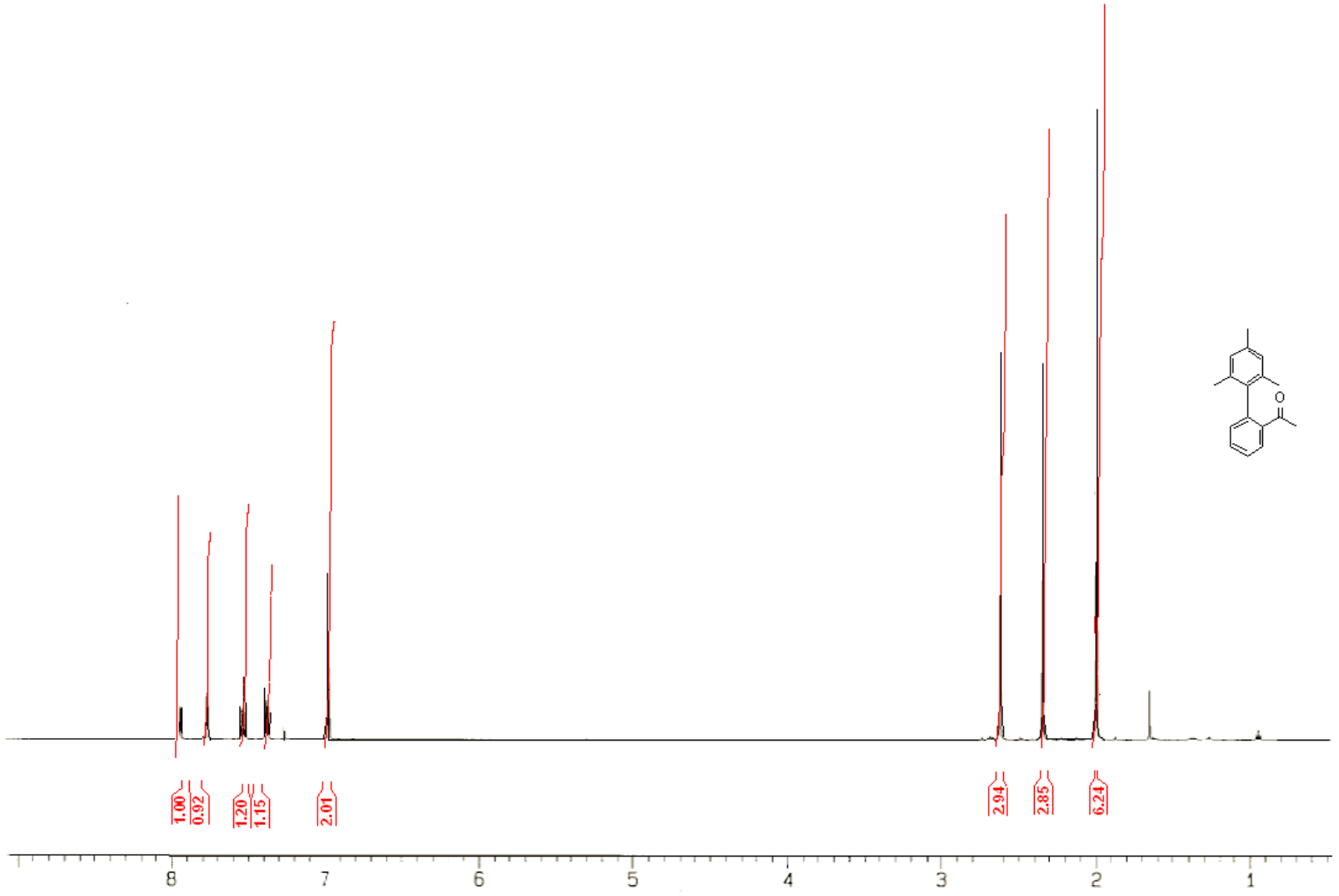

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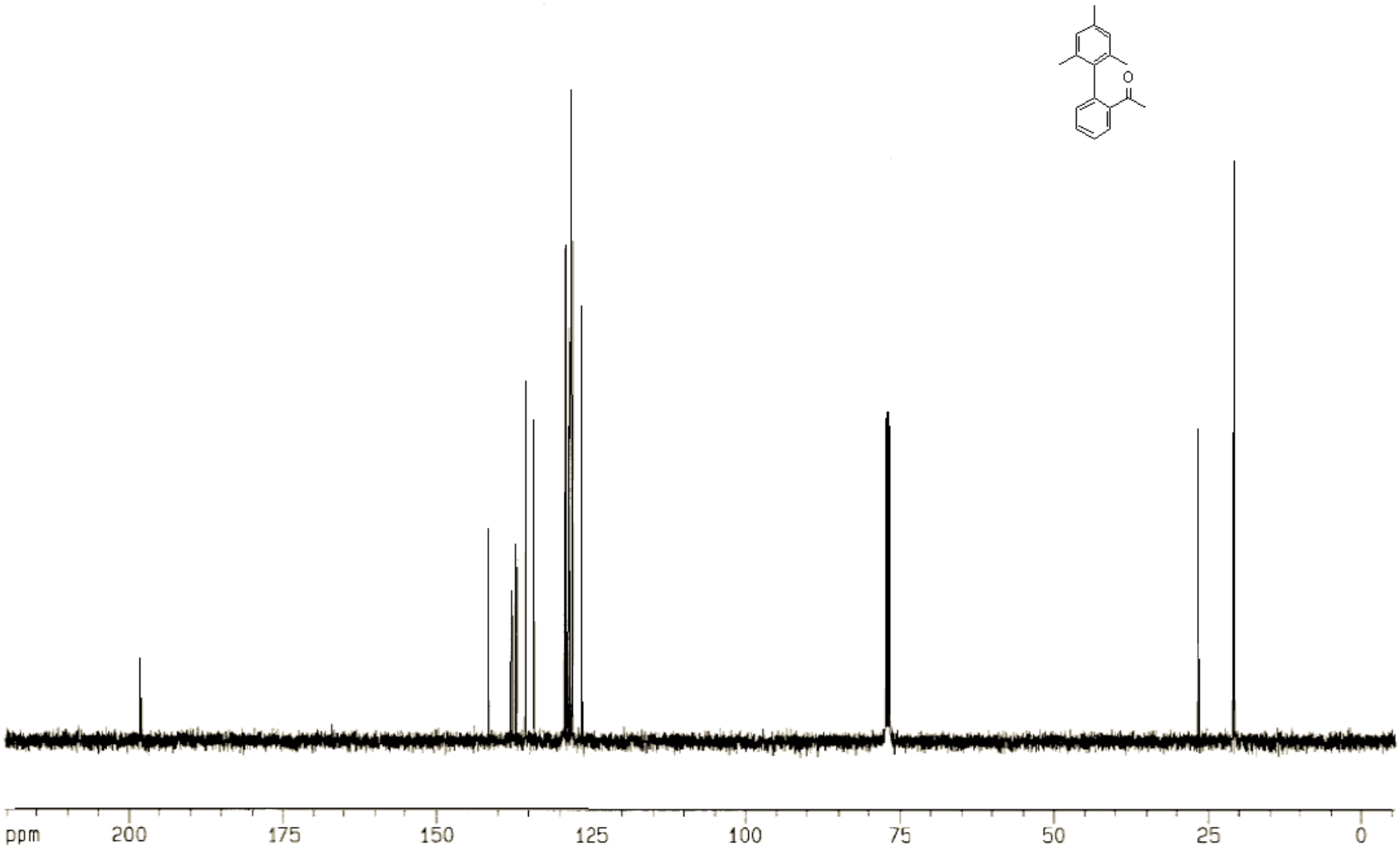

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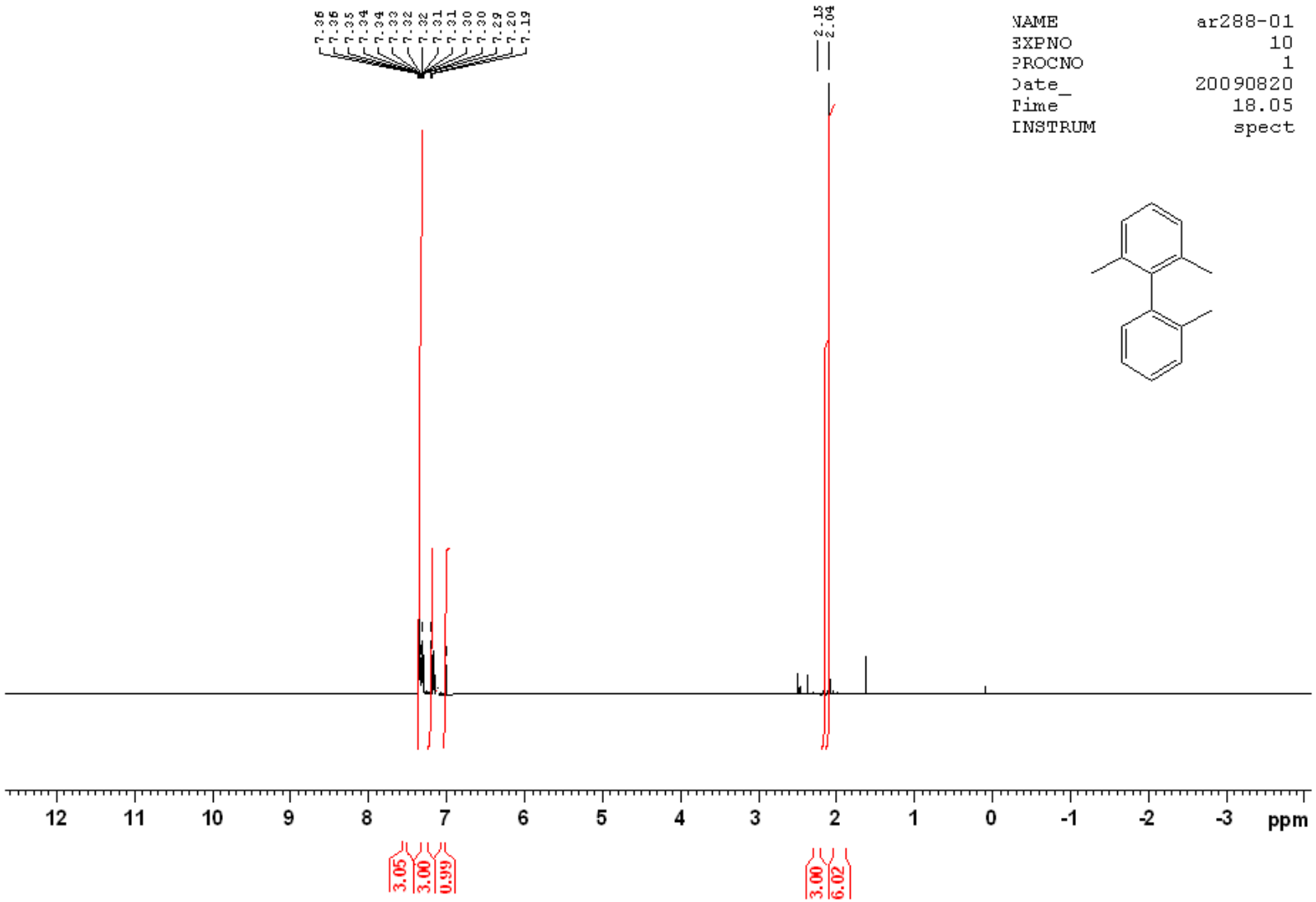

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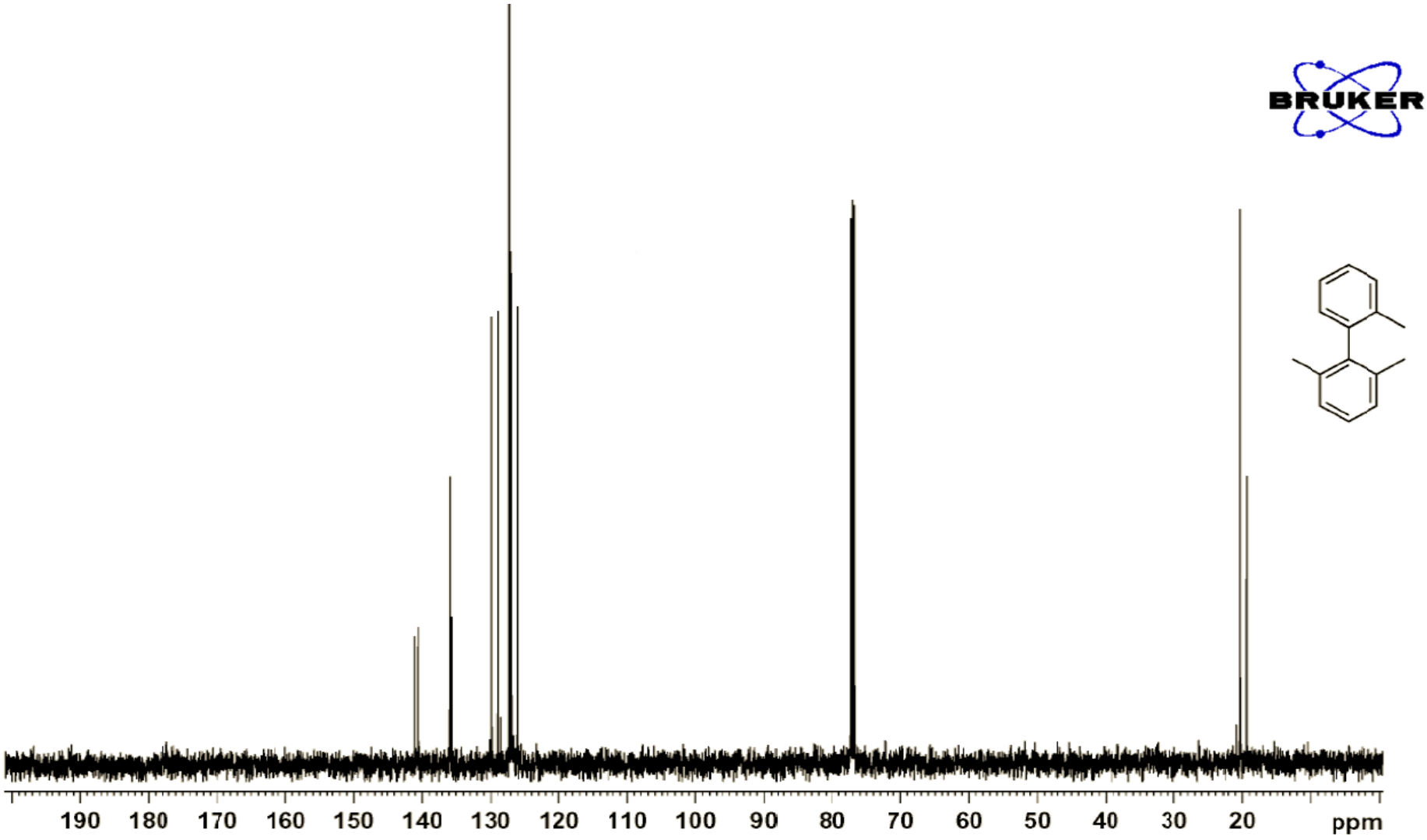

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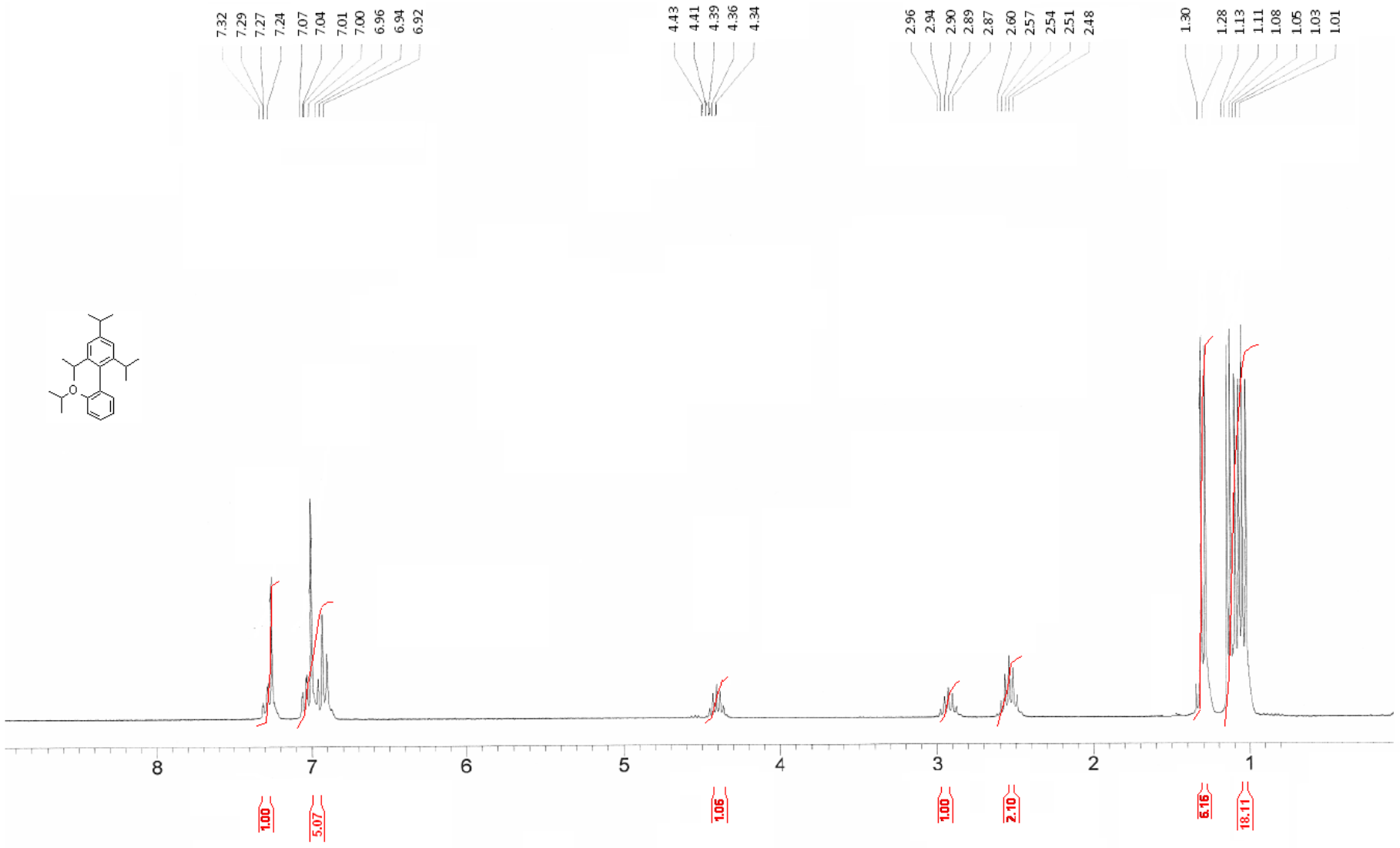

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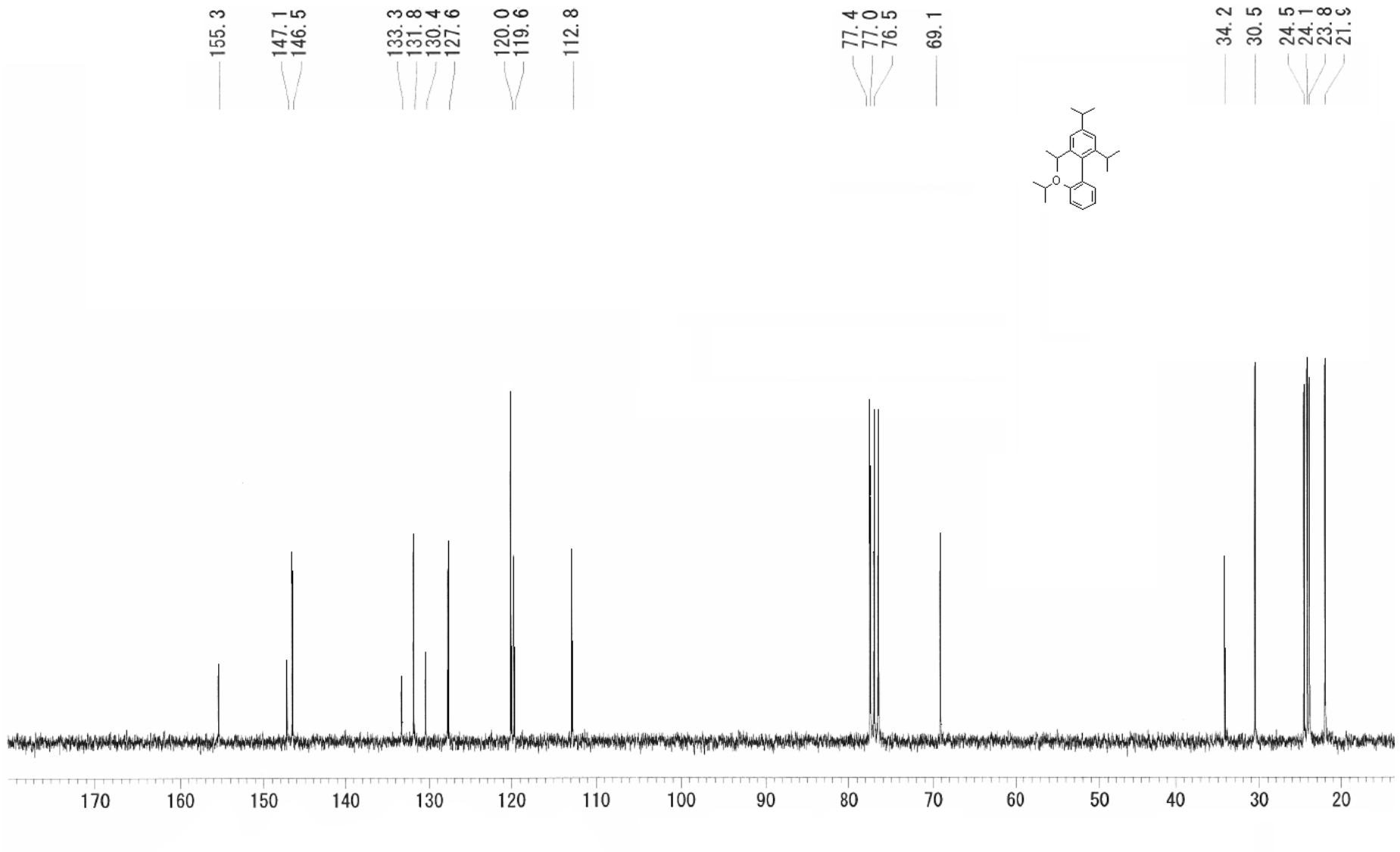

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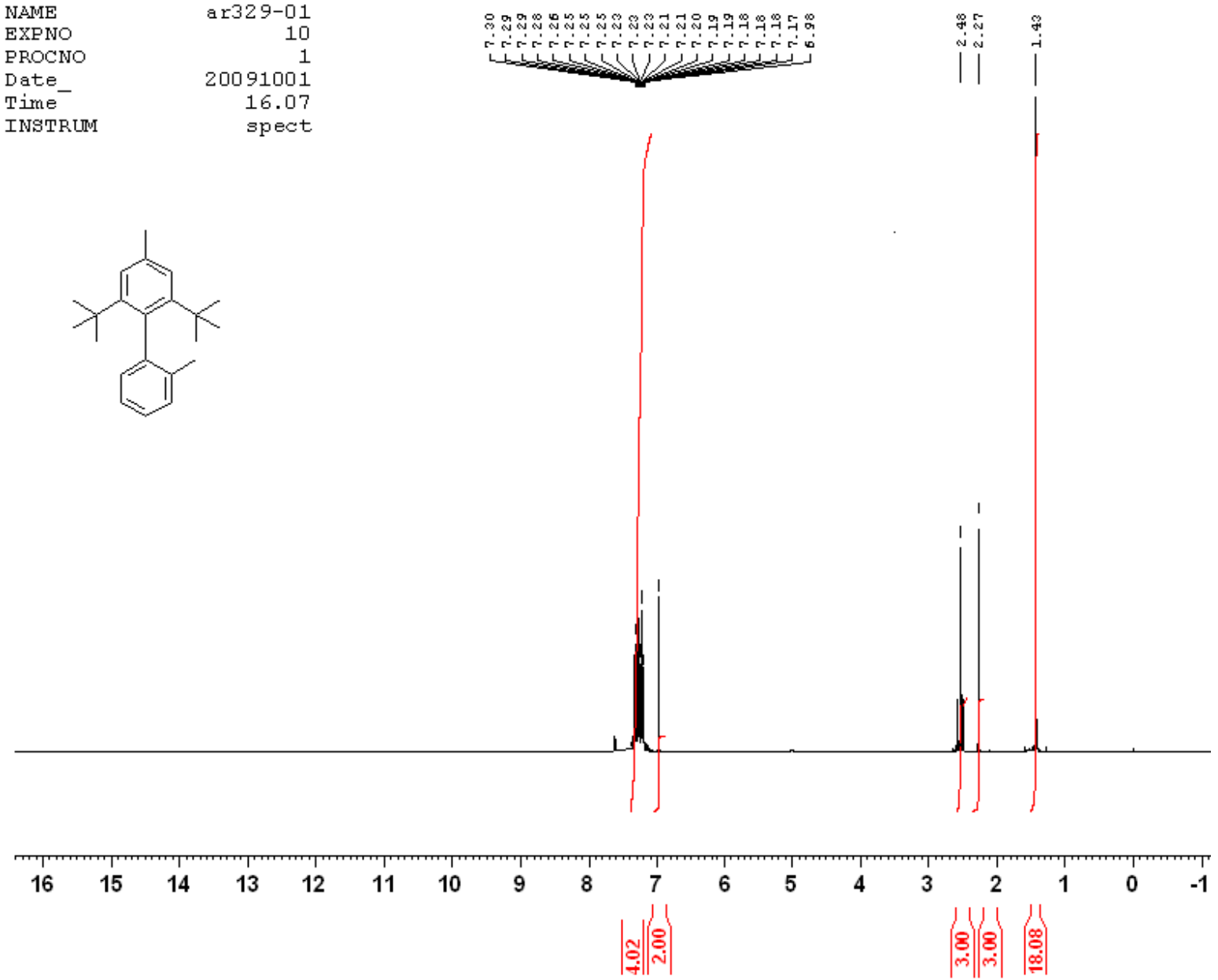

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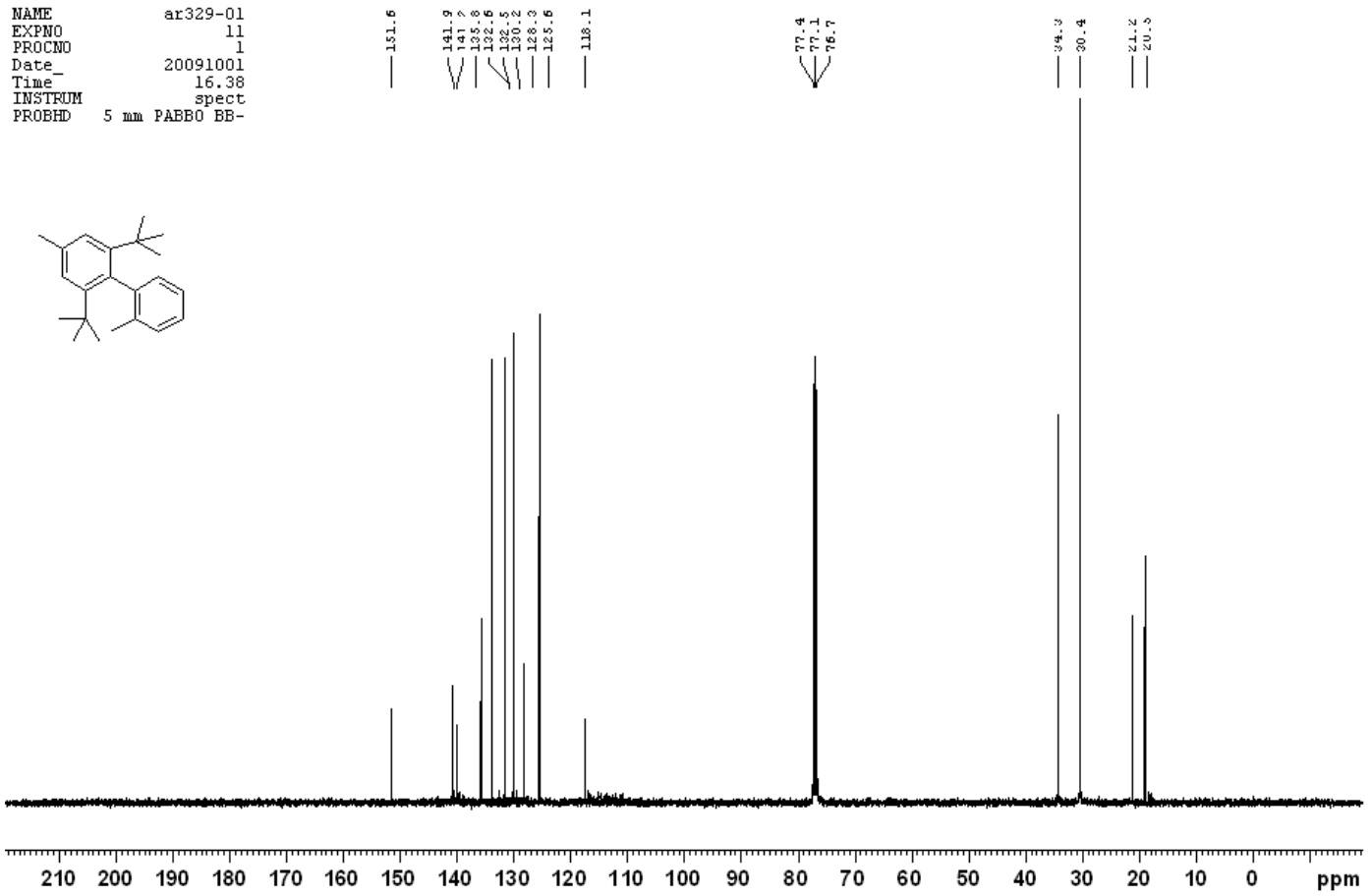

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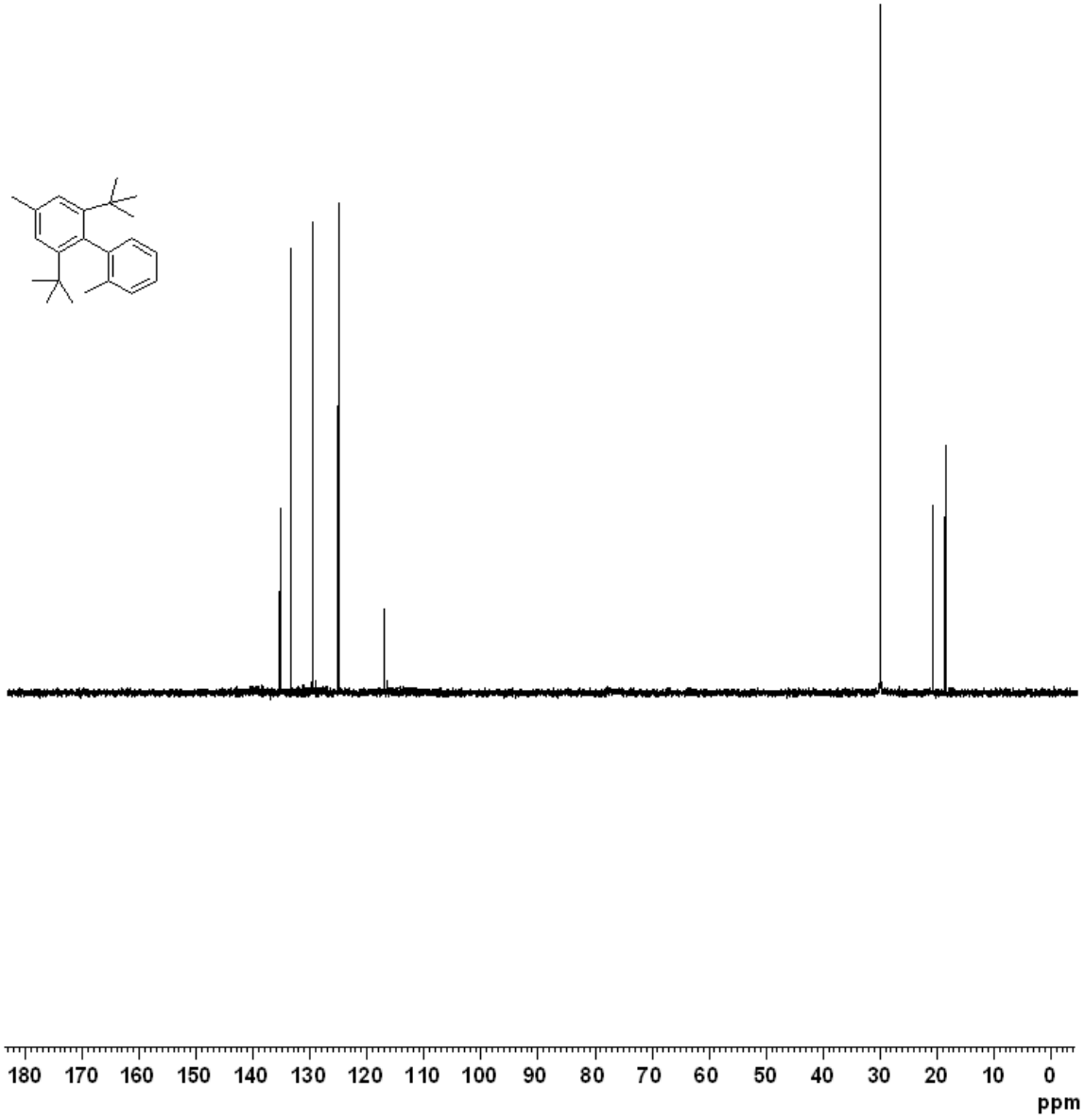

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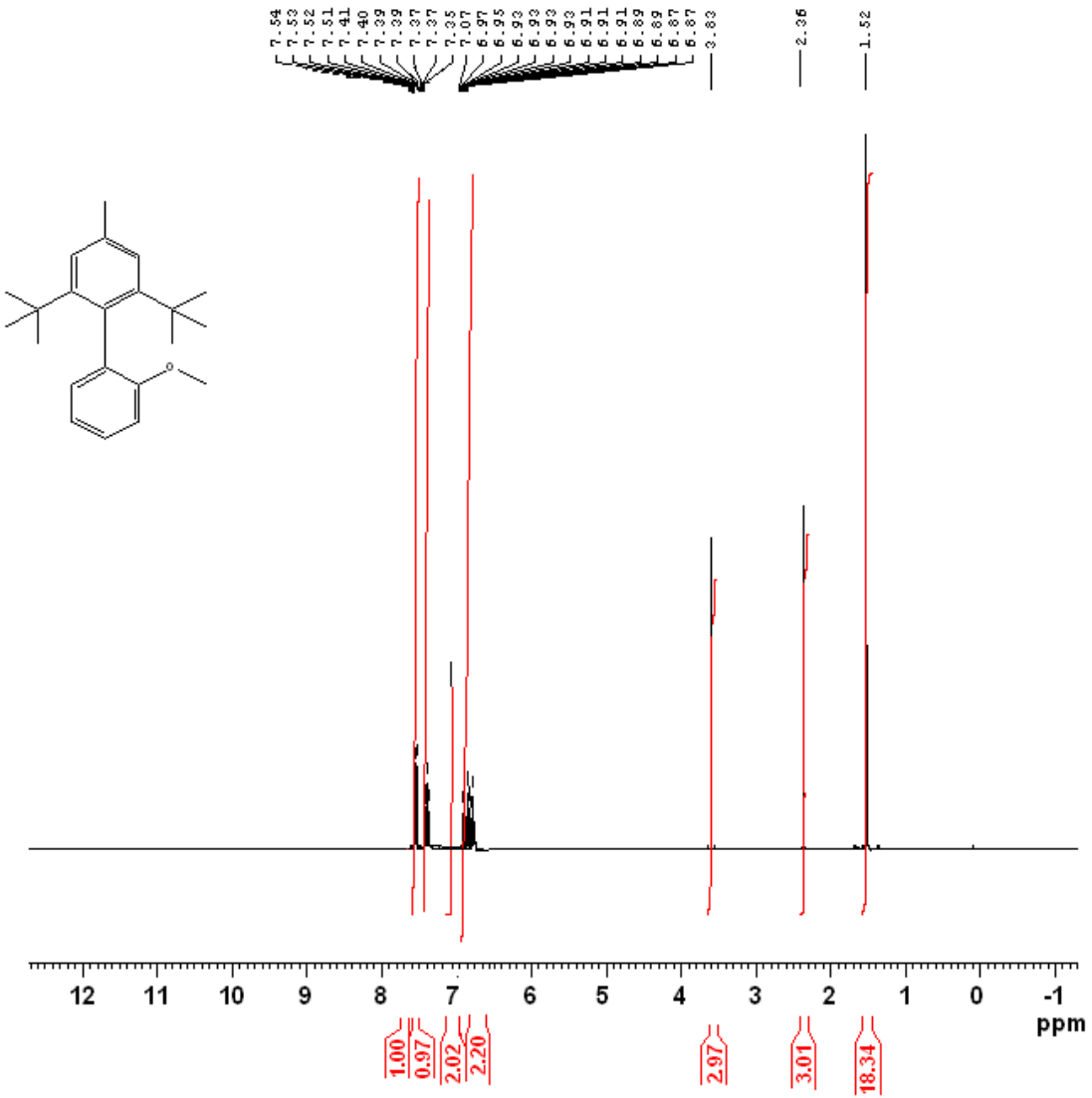

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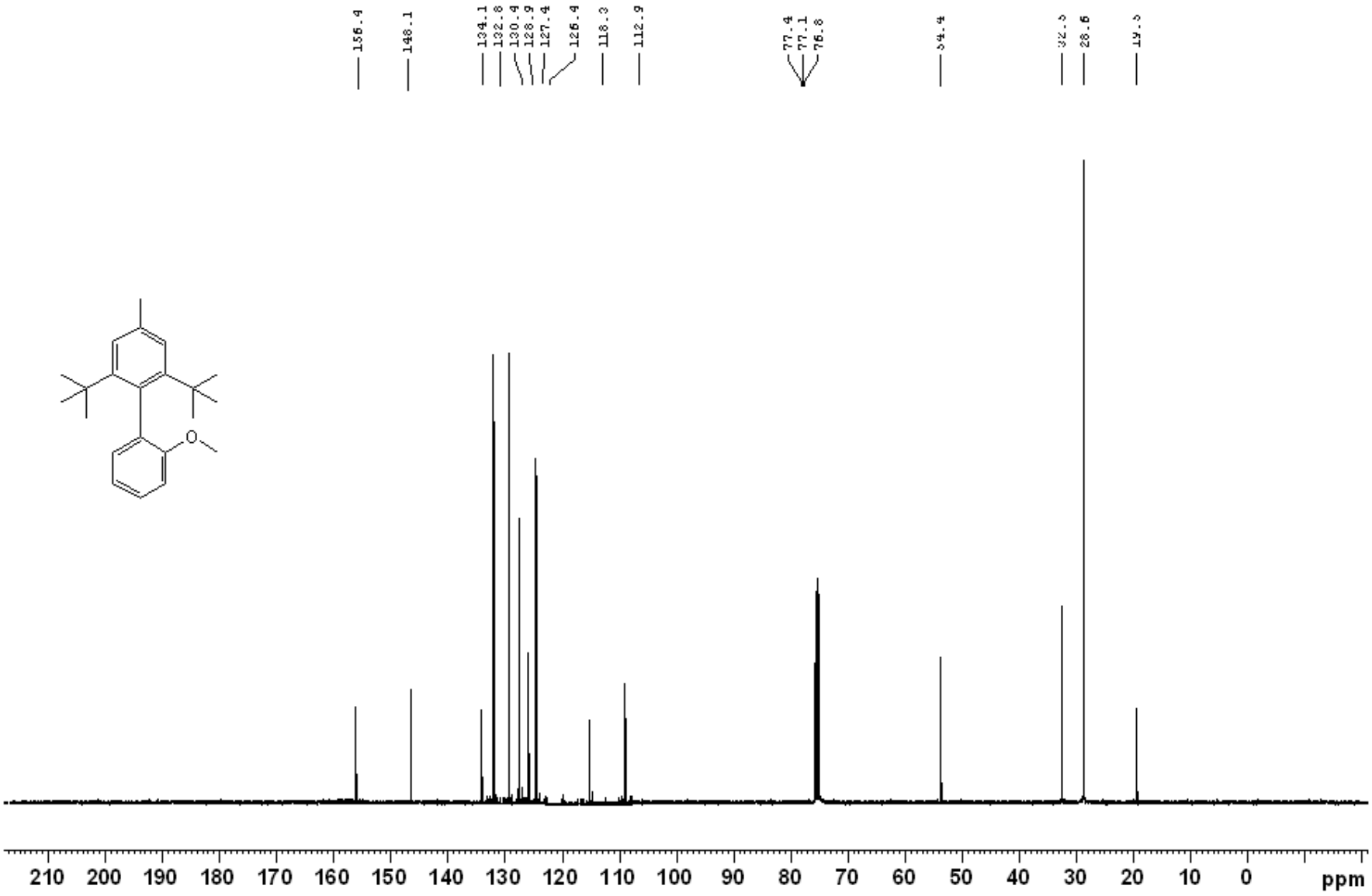

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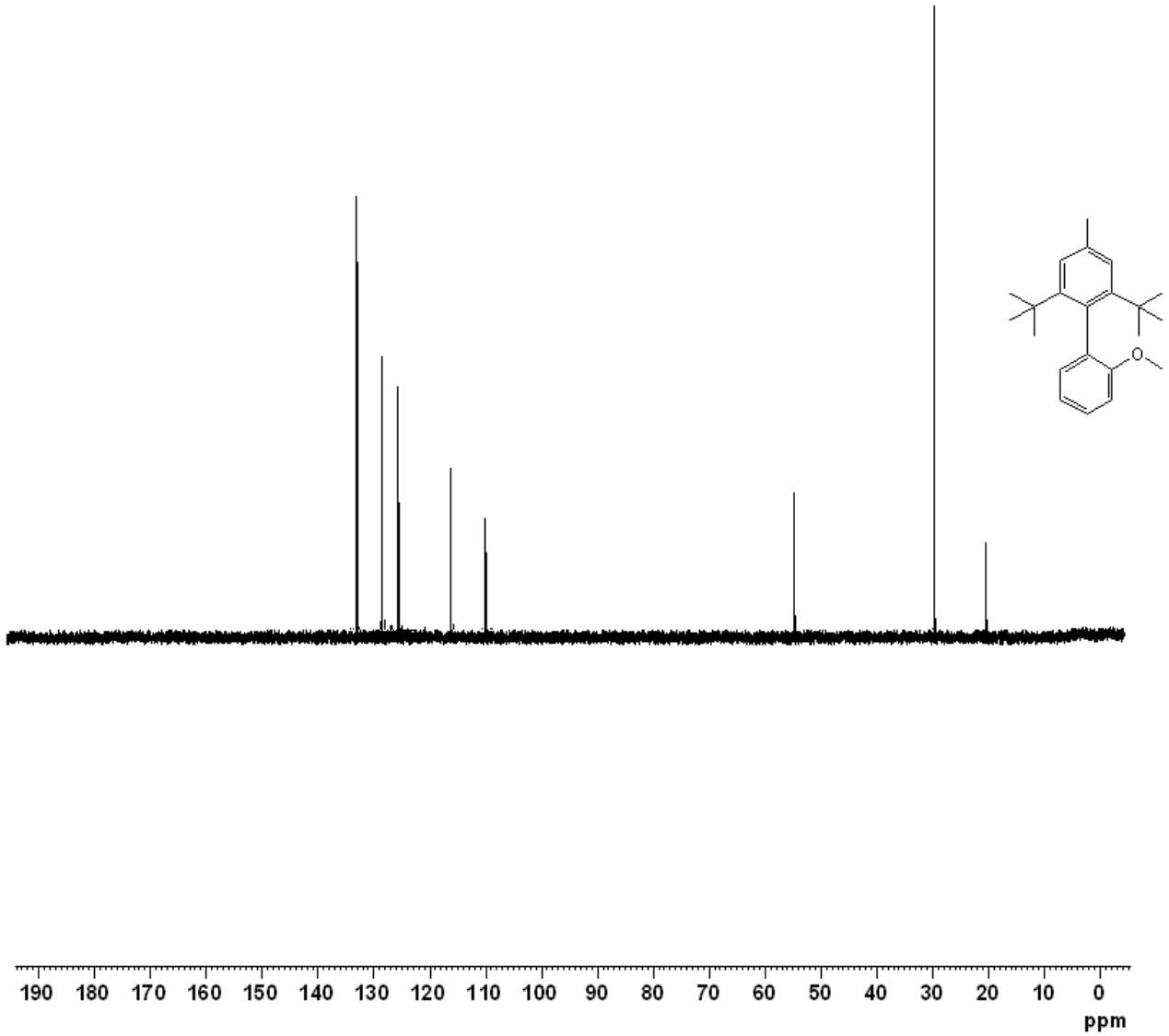

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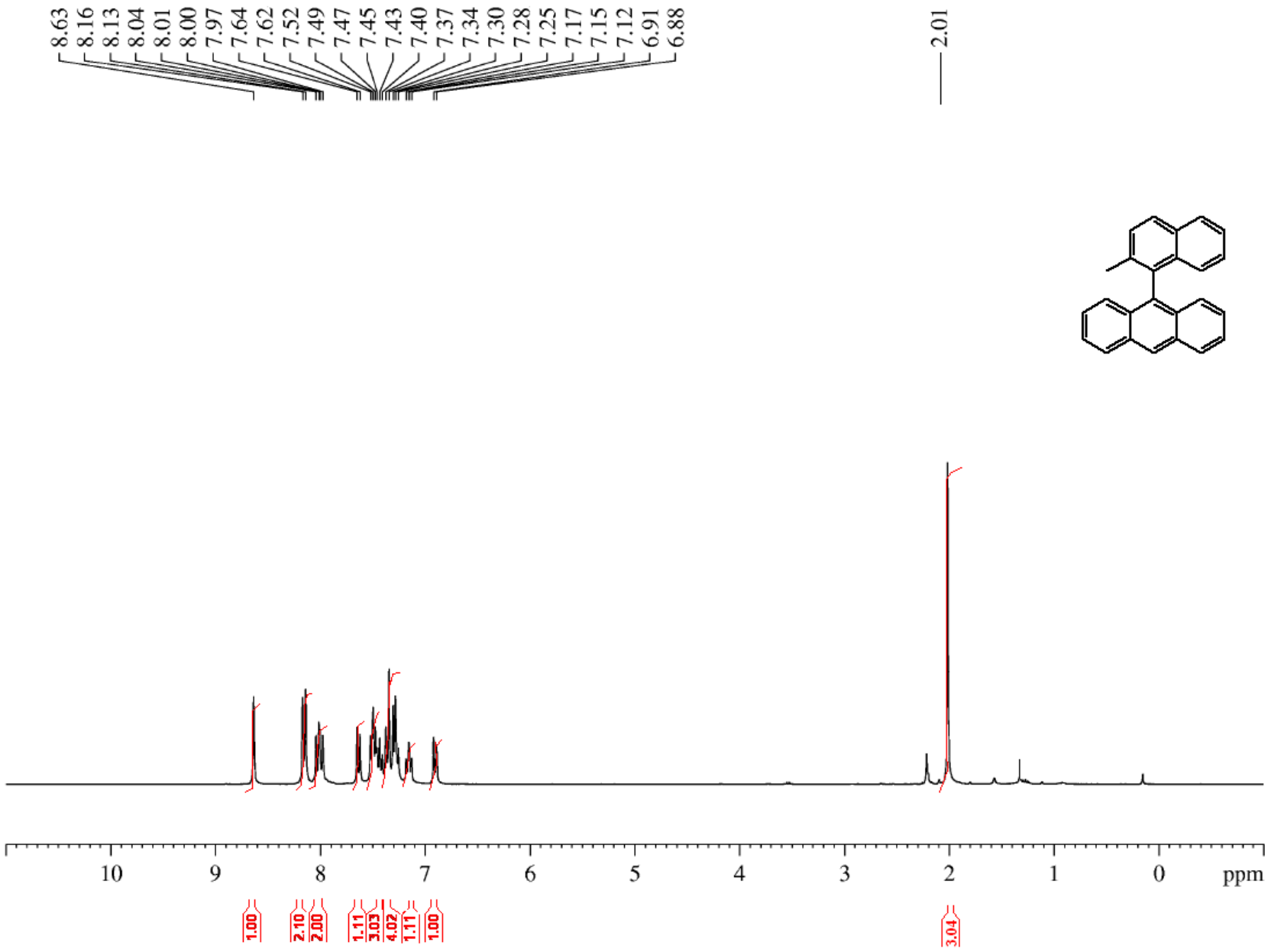

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