

## Zinc Chloride-Promoted Aryl Bromide-Alkyne Cross-Coupling Reactions at Room Temperature

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## General

**Materials.** Unless otherwise stated, all starting materials and reagents were purchased from commercial sources and used without further purification. THF was distilled from sodium benzophenone ketyl. Diisopropylamine was stored under Ar gas. ZnCl<sub>2</sub> (ACS grade, 97%, Strem), ZnBr<sub>2</sub> (98%, Strem), ZnI<sub>2</sub> (98%, Aldrich), and Zn(OTf)<sub>2</sub> (98%, Strem) were used as received and stored in a dessicator. No further drying of the zinc salts was undertaken. CuI (99.999%, PURATREM grade, Strem) was stored under Ar gas.

**General Methods.** All reactions were prepared in an argon-filled glove box and run under an inert atmosphere. The reaction vessels used, unless otherwise specified, were 20 mL vials fitted with PTFE/silicone septa. All glassware was oven-dried before use. All reactions were prepared in an argon-filled dry box. Reactions were monitored by thin layer chromatography (Merck silica gel F254, 0.25 mm) and visualized under UV irradiation at 254 nm. Flash chromatography was performed using silica gel (60 Å, 230-400 mesh). Reaction yields shown in Table 3 of the main text are an average of two runs; the following procedures are representative and the yields may differ from the table. Procedures and yields for the preparation of **1**, 4-bromophenyl triflate, and 3-bromophenyl triflate are based on a single run.

**Physical Characterization.** Melting points were obtained either using an electrothermal melting temperature apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual solvent peaks or TMS (δ = 0 ppm). <sup>19</sup>F NMR was calibrated using CFCl<sub>3</sub> (δ = 0 ppm) as an external standard. Chemical shifts (δ) are expressed in parts per million (ppm). Splitting constants (J) are expressed in Hz. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; td, triplet of doublets; m, multiplet. GC samples (using dodecane as an internal standard) were injected onto a capillary column. The injector temperature was 250 °C and the detector temperature was 280 °C with a H<sub>2</sub> carrier gas flow of 16 mL/min. The column temperature program was as follows: 100 °C

for 3 min, ramp to 300 °C at 40 °C/min, then hold for 3 min for a total run time of 11.00 min.

## Synthetic Procedures

**Preparation and handling of Pd(I) Dimer 1.**<sup>1</sup> A solution of tri-*tert*-butyl phosphine (639 mg, 3.02 mmol) in 20 mL of MeOH was added to a stirred suspension of [(2-methylallyl)PdCl]<sub>2</sub> (560 mg, 1.51 mmol) in 40 mL of MeOH under argon, immediately followed by addition of NaOH (60.5 mg, 1.51 mmol) in 20 mL MeOH. The solution turned yellow and was stirred at room temperature for 1h. **1** was obtained as a yellow precipitate. The precipitate was washed with a small amount of methanol, dissolved in benzene and passed through a PTFE filter (pore size 0.45 μm) to remove residual Pd black. The filtrate was lyophilized to give 1.06 g (91% yield) of pure complex **1** as a yellow powder. The <sup>1</sup>H NMR and <sup>13</sup>C NMR corresponded to the values reported in the literature for this compound. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution.<sup>2</sup> **1** can be handled in ambient atmosphere for short periods of time (up to a week) but should be stored under inert gas when not in use. When appropriately stored, **1** has a shelf life of ~1 year before noticeable decomposition occurs. Over time, the canary yellow solid develops a green tinge. Impure **1** can be purified via trituration of a THF solution of **1** into pentane.

**4-bromophenyl triflate.**<sup>3</sup> An oven-dried 250 mL 2-necked flask under an atmosphere of nitrogen was charged with 4-bromophenol (5.19 g, 30 mmol, 1 equiv), dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and pyridine (7.2 mL, 90 mmol, 3 equiv), and cooled to 5 °C in a water bath. Trifluoromethanesulfonic anhydride (6.05 mL, 36 mmol, 1.2 equiv) was added dropwise to the solution. The resulting red solution was stirred for 4 h at room temperature. The solution was then passed through a plug of SiO<sub>2</sub> (50 g), and eluted with 200 mL of a solution of 1:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>. The solvent was evaporated, and the resulting oil was dissolved in 100 mL Et<sub>2</sub>O, washed with saturated aq. CuSO<sub>4</sub> twice (to remove excess

<sup>1</sup> CAS No. 62586-36-1. Werner, H.; Kühn, A. *J. Organomet. Chem.* **1979**, *179*, 439-445. Procedure adapted from Elliott, E. L.; Ray, C. R.; Kraft, S.; Atkins, J. R.; Moore, J. S. *J. Org. Chem.* **2006**, *71*, 5282-5290.

<sup>2</sup> CCDC 285926 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

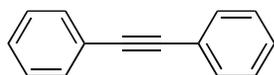
<sup>3</sup> CAS No. 66107-30-0. Kamikawa, T.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 8922-8925.

pyridine) and brine, and then dried over MgSO<sub>4</sub>. The solvent was evaporated, and the crude material was purified further via Kugelrohr distillation to give 4-bromophenyl triflate as a slightly yellow oil (7.33 g, 80% yield). NMR and MS data match that of the literature. The product was stored in a desiccator under nitrogen gas.

**3-bromophenyl triflate.**<sup>4</sup> The same procedure for the preparation of 4-bromophenyl triflate described above was used with 3-bromophenol (5.19 g, 30 mmol) to give 3-bromophenyl triflate as a colorless oil (7.54 g, 82% yield). NMR and MS data match that of the literature. The product was stored in a desiccator under nitrogen gas.

### General Procedure for the Preparation of Substituted Alkynes with Catalytic ZnCl<sub>2</sub>.

The following general procedure was used for the preparation of substrates in Table 3. In a glove box, a 20 mL vial with stirbar and PTFE/silicone septum-lined cap was charged with, in order, the aryl bromide (3 mmol, 1 equiv), ZnCl<sub>2</sub> (41 mg, 0.3 mmol, 0.1 equiv), THF (7 mL), HN(*i*-Pr)<sub>2</sub> (3 mL), and Pd(I) dimer **1** (21 mg, 0.03 mmol, 0.01 equiv). The solution was stirred to dissolve the solids, and then the alkyne (3 mmol, 1 equiv) was added. (*NOTE: the alkyne must be added last to avoid catalyst decomposition and excess alkyne addition byproduct formation*). The vial was capped, removed from the glove box, and stirred at room temperature for the specified amount of time. The solution was diluted with EtOAc, and passed through a plug of silica gel (10 g) and eluted with 100 mL EtOAc to remove H<sub>2</sub>N(*i*-Pr)<sub>2</sub>Br and Zn salt. The solution was evaporated, and the residue was purified by column chromatography on silica gel.



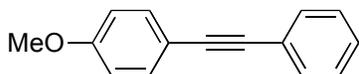
**Table 3, Entry 1. Diphenylacetylene.**<sup>5</sup> 1 hour. Purification by column chromatography (99:1 hexane:EtOAc) gave the product in 93% yield (0.495 g). White solid. mp 59-60 °C (lit. 58-61 °C).

<sup>4</sup> CAS No. 66107-31-1. Espino, G.; Kurbangalieva, A. Brown, J. M. *Chem. Commun.* **2007**, 1742-1744.

<sup>5</sup> CAS No. 501-65-5. Nakagawa, K.; Onoue, H.; Minami, K. *Chem. Commun.* **1966**, 730-731.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.59-7.54 (m, 4H), 7.41-7.33 (m, 6H).

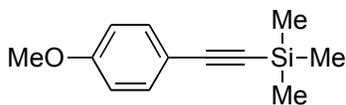
$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  131.7, 128.48, 128.40, 123.4, 89.5.



**Table 3, Entry 2. 4-methoxydiphenylacetylene.**<sup>6</sup> 1 hour. Purification by column chromatography (6:1 hexane: $\text{CH}_2\text{Cl}_2$ ) gave the product in 90% yield (0.562 g). Pale yellow solid. mp 58-59 °C (lit. 58-61 °C).

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.53-7.51 (m, 2H), 7.50-7.47 (m, 2H), 7.36-7.32 (m, 3H), 6.90-6.88 (m, 2H), 3.83 (s, 3H).

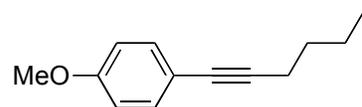
$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  159.7, 133.2, 131.6, 128.4, 128.1, 123.7, 115.5, 114.1, 89.5, 88.2, 55.4.



**Table 3, Entry 3. (2-(4-methoxyphenyl)ethynyl)trimethylsilane.**<sup>7</sup> 2 hours. Purification by column chromatography (10:1 hexane: $\text{CH}_2\text{Cl}_2$  with 3%  $\text{NEt}_3$ ) gave the product in 89% yield (0.551 g). Yellow oil.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J = 8.8$  Hz, 2H), 6.82 (d,  $J = 8.8$  Hz, 2H), 3.80 (s, 3H), 0.24 (s, 9H).

$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  159.8, 133.6, 115.4, 113.9, 105.3, 92.5, 55.4, 0.2.



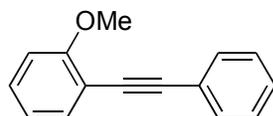
**Table 3, Entry 4. 1-(4-methoxyphenyl)-1-hexyne.**<sup>8</sup> 2 hours. Purification by column chromatography (99:1 hexane:EtOAc) gave the product in 91% yield (0.512 g). Yellow oil.

<sup>6</sup> CAS No. 7380-78-1. Colacino, E.; Daich, L.; Martinez, J.; Lamaty, F. *Synlett* **2007**, 1279-1283.

<sup>7</sup> CAS No. 3989-14-8. Sakai, N.; Annaka, K.; Konakahara, T. *Org. Lett.* **2004**, *6*, 1527-1530.

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.34 (d,  $J = 8.9$  Hz, 2H), 6.81 (d,  $J = 8.9$  Hz, 2H), 3.79 (s, 3H), 2.39 (t,  $J = 7.0$  Hz, 2H), 1.60-1.54 (m, 2H), 1.50-1.44 (m, 2H), 0.94 (t,  $J = 7.3$  Hz, 3H).

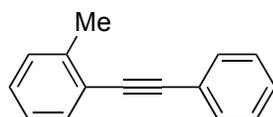
$^{13}\text{C}$  NMR (101 MHz;  $\text{CDCl}_3$ ):  $\delta$  159.1, 133.0, 116.4, 113.9, 88.9, 80.3, 55.4, 31.1, 22.2, 19.3, 13.8.



**Table 3, Entry 5. 2-methoxydiphenylacetylene.**<sup>9</sup> A modification to the General Procedure was used. The alkyne (as a solution in 1 mL THF) was added dropwise over 2 hours, then stirred at room temperature for an additional two hours. Purification by column chromatography (hexane  $\rightarrow$  10:1 hexane: $\text{CH}_2\text{Cl}_2$ ) gave the product in 83% yield (0.521 g). Yellow oil.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.60-7.57 (m, 2H), 7.53 (dd,  $J = 7.6, 1.8$ , Hz, 1H), 7.38-7.30 (m, 4H), 6.96 (td,  $J = 7.5, 1.0$  Hz, 1H), 6.93-6.91 (m, 1H), 3.94 (s, 3H).

$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  160.2, 133.8, 131.9, 130.0, 128.50, 128.37, 123.8, 120.7, 112.7, 110.9, 93.7, 86.0, 56.1.



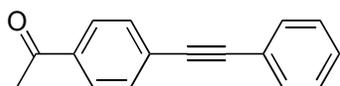
**Table 3, Entry 6. 2-methyldiphenylacetylene.**<sup>3</sup> One hour. Purification by column chromatography (40:1 hexane:  $\text{CH}_2\text{Cl}_2$ ) gave the product in 94% yield (0.519 g). Colorless oil.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.56 (dd,  $J = 7.9$  Hz, 1.8 Hz, 2H), 7.52 (d,  $J = 7.5$  Hz, 1H), 7.36 (m, 3H), 7.25 (m, 2H), 7.19 (m, 1H), 2.54 (s, 3H).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ):  $\delta$  140.3, 132.0, 131.7, 129.6, 128.50, 128.45, 128.32, 125.7, 123.7, 123.2, 93.5, 88.5, 20.9.

<sup>8</sup> Xie, C.; Liu, L.; Zhang, Y.; Xu, P. *Org. Lett.* **2008**, *10*, 2393.

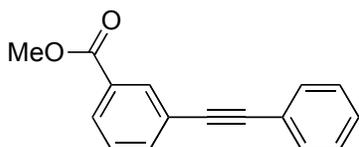
<sup>9</sup> CAS No. 41398-67-8. Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 10292-10296.



**Table 3, Entry 7. 4-acetyldiphenylacetylene.**<sup>10</sup> 20 minutes. Purification by column chromatography (9:1 hexane:EtOAc) gave the product in 95% yield (0.628 g). Pale yellow solid. mp 100-101 °C (lit. 97-103 °C).

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.55 (m, 2H), 7.37 (m, 3H), 2.62 (s, 3H).

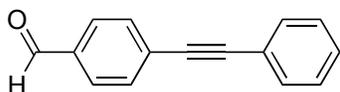
<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 197.5, 136.3, 131.87, 131.83, 128.9, 128.58, 128.40, 128.33, 122.8, 92.8, 88.7, 26.8.



**Table 3, Entry 8. Methyl 3-(phenylethynyl)benzoate.**<sup>11</sup> 30 minutes. Purification by column chromatography (10:1 hexane:EtOAc) gave the product in 99% yield (0.703 g). Yellow solid. mp 76-78 °C (lit. 77-79 °C).

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 8.21 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.56-7.53 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.38-7.36 (m, 3H), 3.94 (s, 3H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 166.6, 135.8, 132.9, 131.8, 130.6, 129.3, 128.70, 128.64, 128.55, 123.9, 123.0, 90.4, 88.4, 52.4.



**Table 3, Entry 9. 4-(phenylethynyl)benzaldehyde.**<sup>12</sup> 20 minutes. Purification by column chromatography (1:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) gave the product in 93% yield (0.574 g). Yellow solid. mp 98-100 °C (lit. 98-100 °C).

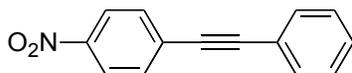
<sup>10</sup> CAS No. 1942-31-0. Komaromi, A.; Tolnai, G. L.; Novak, Z. *Tetrahedron Lett.* **2008**, *49*, 7294-7298.

<sup>11</sup> CAS No. 207845-32-7. Sorensen, U. S.; Pombo-Villar, E. *Tetrahedron* **2005**, *61*, 2697-2703.

<sup>12</sup> CAS No. 57341-98-7. Elangovan, A.; Wang, Y.; Ho, T. *Org. Lett.* **2003**, *5*, 1841-

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  10.02 (s, 1H), 7.88-7.85 (m, 2H), 7.68 (d,  $J = 8.1$  Hz, 2H), 7.57-7.54 (m, 2H), 7.41-7.35 (m, 3H).

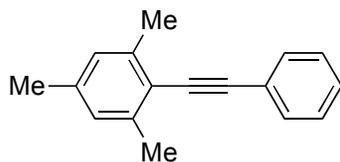
$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  191.5, 135.5, 132.2, 131.9, 129.7, 129.1, 128.6, 122.6, 93.6, 88.6.



**Table 3, Entry 10. 4-nitrodiphenylacetylene.**<sup>13</sup> 20 minutes. Purification by column chromatography (10:1 hexane:EtOAc) gave the product in 99% yield (0.668 g). Yellow solid. mp 119-121 °C (lit. 121-123 °C).

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.24-8.21 (m, 3H), 7.68-7.66 (m, 3H), 7.58-7.55 (m, 3H), 7.41-7.37 (m, 5H).

$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  147.1, 132.4, 132.0, 130.4, 129.4, 128.7, 123.8, 122.2, 94.8, 87.7.



**Table 3, Entry 11. 2,4,6-trimethyldiphenylacetylene.**<sup>14</sup> 16 hours. Purification by column chromatography (hexane  $\rightarrow$  10:1 hexane: $\text{CH}_2\text{Cl}_2$ ) gave the product in 73% yield (0.481 g). White solid. mp 36-38 °C (lit. 36-37 °C).

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.55-7.54 (m, 2H), 7.38-7.31 (m, 3H), 6.91 (s, 2H), 2.49 (s, 6H), 2.31 (s, 3H).

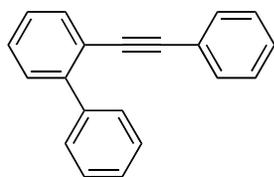
$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  140.1, 137.7, 131.3, 128.3, 127.9, 127.6, 124.0, 119.9, 97.0, 87.3, 21.3, 21.0.

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1844.

<sup>13</sup> CAS No. 1942-30-9. Kakusawa, N.; Yamaguchi, K.; Kurita, J. *J. Organomet. Chem.* **2005**, *690*, 2956-2966.

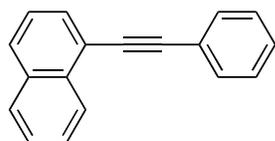
<sup>14</sup> CAS No. 29778-31-2. Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002-11.



**Table 3, Entry 12. 2-(phenylethynyl)biphenyl.**<sup>15</sup> 2 hours. Purification by column chromatography (hexane → 10:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) gave the product in 92% yield (0.699 g). Pale yellow oil.

<sup>1</sup>H NMR (499 MHz; CDCl<sub>3</sub>): δ 7.74-7.70 (m, 3H), 7.53-7.31 (m, 11H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 144.0, 140.6, 132.9, 131.4, 129.57, 129.49, 128.6, 128.34, 128.19, 128.0, 127.6, 127.1, 123.5, 121.7, 92.3, 89.5.



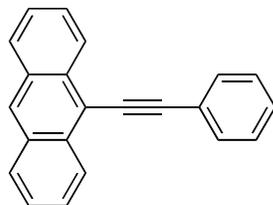
**Table 3, Entry 13. 1-(phenylethynyl)naphthalene.**<sup>16</sup> 1 hour. Purification by column chromatography (99:1 hexane:EtOAc) gave the product in 94% yield (0.609 g). Colorless oil.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 8.49 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 12.6, 8.2 Hz, 2H), 7.80 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.69 (dt, *J* = 8.0, 1.9 Hz, 2H), 7.63 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.45-7.38 (m, 3H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 133.40, 133.35, 131.8, 130.5, 128.9, 128.57, 128.52, 128.44, 126.9, 126.6, 126.4, 125.4, 123.5, 121.0, 94.5, 87.7.

<sup>15</sup> CAS No. 10271-65-5. Moon, J.; Jeong, M.; Nam, H.; Ju, J.; Moon, J. H.; Jung, H. M.; Lee, S. *Org. Lett.* **2008**, *10*, 945-948.

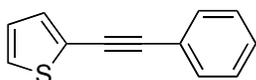
<sup>16</sup> CAS No. 4044-57-9. Elangovan, A.; Wang, Y.; Ho, T. *Org. Lett.* **2003**, *5*, 1841-1844.



**Table 3, Entry 14. 9-(phenylethynyl)anthracene.**<sup>17</sup> 5 hours. Purification by column chromatography (hexane → 10:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) gave the product in 86% yield (0.718 g). Highly fluorescent, yellow solid. mp 110-112 °C.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 8.69 (d, *J* = 8.7 Hz, 2H), 8.44 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.82-7.80 (m, 2H), 7.64-7.61 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.50-7.42 (m, 3H).

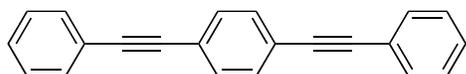
<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 132.6, 131.6, 131.1, 128.65, 128.48, 128.44, 127.7, 126.72, 126.56, 125.6, 123.6, 117.2, 100.7, 86.3.



**Table 3, Entry 15. 2-(phenylethynyl)thiophene.**<sup>18</sup> 1 hour. Purification by column chromatography (99:1 hexane:EtOAc) gave the product in 91% yield (0.516 g). White solid. mp 50-51 °C (lit. 49-51 °C).

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.55-7.52 (m, 2H), 7.39-7.35 (m, 3H), 7.30 (d, *J* = 4.1 Hz, 2H), 7.04-7.02 (m, 1H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 132.0, 131.5, 128.54, 128.50, 127.38, 127.22, 123.4, 123.0, 93.2, 82.7.



**Table 3, Entry 16. 1,4-bis(phenylethynyl)benzene.**<sup>19</sup> The reaction was run with 2 equiv phenylacetylene (0.612 g, 6 mmol). 2 hours. Purification by column chromatography

<sup>17</sup> CAS No. 87337-07-3. Dang, H.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 355-356.

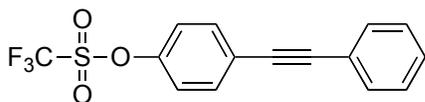
<sup>18</sup> CAS No. 4805-17-8. Katritzky, A. R.; Abdel-Fattah, A. A. A.; Wang, M. *J. Org. Chem.* **2002**, *67*, 7526-7529.

<sup>19</sup> CAS No. 1849-27-0. Lydon, D. P.; Porres, L.; Beeby, A.; Marder, T. B.; Low, P. J. *New J. Chem.* **2005**, *29*, 972-976.

(10:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) gave the product in 88% yield (0.545 g). White to pale yellow solid. mp 181-184 °C (lit. 183 °C).

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.54 (m, 4H), 7.52 (s, 4H), 7.36 (m, 6H).

<sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>): δ 131.6, 131.5, 128.5, 128.4, 123.1, 123.0, 91.2, 89.1.

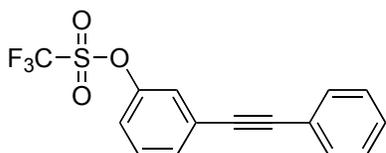


**Table 3, Entry 17. 4-(2-phenylethynyl)phenyl trifluoromethanesulfonate.**<sup>20</sup> This reaction was performed on a 1 mmol scale with 2 mL THF and 1 mL HN(*i*-Pr)<sub>2</sub>. 20 minutes. Purification by column chromatography (10:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) gave the product in 89% yield (0.89 mmol, 0.290 g). Colorless solid. mp 61-62 °C.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 7.59-7.55 (m, 2H), 7.52-7.48 (m, 2H), 7.35-7.32 (m, 3H), 7.25-7.21 (m, 2H).

<sup>13</sup>C NMR (101 MHz; CDCl<sub>3</sub>): δ 149.1, 133.6, 131.9, 129.0, 128.6, 124.2, 122.7, 121.7, 118.3 (q, *J* = 318 Hz), 91.4, 87.5.

<sup>19</sup>F NMR (376 MHz; CDCl<sub>3</sub>): δ -74.0.



**Table 3, Entry 18. 3-(2-phenylethynyl)phenyl trifluoromethanesulfonate.** This reaction was performed on a 1 mmol scale with 2 mL THF and 1 mL HN(*i*-Pr)<sub>2</sub>. 20 minutes. Purification by column chromatography (10:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) gave the product in 89% yield (0.290 g). Yellow oil.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 7.54-7.51 (m, 3H), 7.42-7.34 (m, 5H), 7.23-7.21 (m, 1H).

<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>): δ 149.4, 131.7, 130.3, 129.1, 128.6, 126.0, 124.3, 122.4, 121.3, 118.9 (q, *J* = 321 Hz), 91.7, 87.2.

<sup>19</sup>F NMR (376 MHz; CDCl<sub>3</sub>): δ -73.1.

<sup>20</sup> CAS No. 166663-45-2. Kamikawa, T.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 8922-8925.

IR (film,  $\text{cm}^{-1}$ ): 3081, 2217, 1952, 1882, 1803, 1695, 1607, 1570, 1495, 1424, 1213, 1140, 943, 848, 754.

MS (EI+): 326.0 (98), 262.0 (10), 165.1 (100), 139.0 (10), 115.0 (5), 69.0 (10).

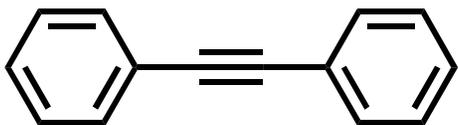
HRMS (EI+): Calc'd for  $\text{C}_{15}\text{H}_9\text{F}_3\text{O}_3\text{S}$ : 326.02246; Found 326.02198.

Anal. Calc'd for  $\text{C}_{15}\text{H}_9\text{F}_3\text{O}_3\text{S}$ : C 55.21, H 2.78; Found: C 55.00, H 2.75.

**Procedure for Cross-Coupling in the Presence of  $\text{ZnCl}_2$  and/or Trace  $\text{CuI}$  (Table 4).**

All manipulations were performed in an argon-filled glove box.  $\text{CuI}$  (1.0 mg, 0.0052 mmol) was added to a 100 mL volumetric flask. Dry, degassed THF (95 mL) and  $\text{HN}(i\text{-Pr})_2$  (5 mL) were added, then the flask was sealed, removed from the glove box, and sonicated for 10 minutes. The flask was returned to the glove box. In a 20 mL vial with septum-lined cap and stirbar was added, in order, 4-bromoanisole (0.187 g, 1 mmol), dodecane (20  $\mu\text{L}$ ), THF (9 mL),  $\text{HN}(i\text{-Pr})_2$  (3 mL),  $\text{ZnCl}_2$  (14 mg, 0.1 mmol) 1.0 mL of the  $\text{CuI}$  solution ( $5.2 \times 10^{-5}$  mmol), **1** (7 mg, 0.01 mmol), and phenylacetylene (120  $\mu\text{L}$ , 1.1 mmol). The solutions were stirred under Ar at room temperature and analyzed by GC.

Table 3 Entry 1



131.74  
128.48  
128.40  
123.39

89.50

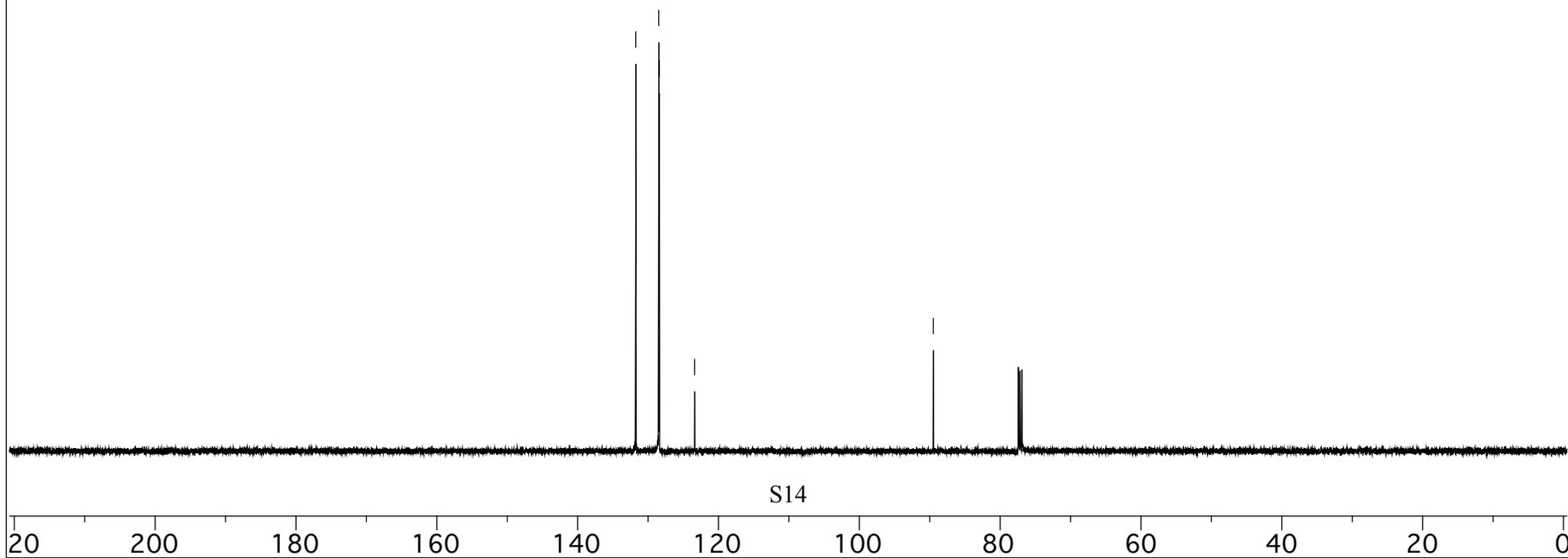


Table 3 Entry 1

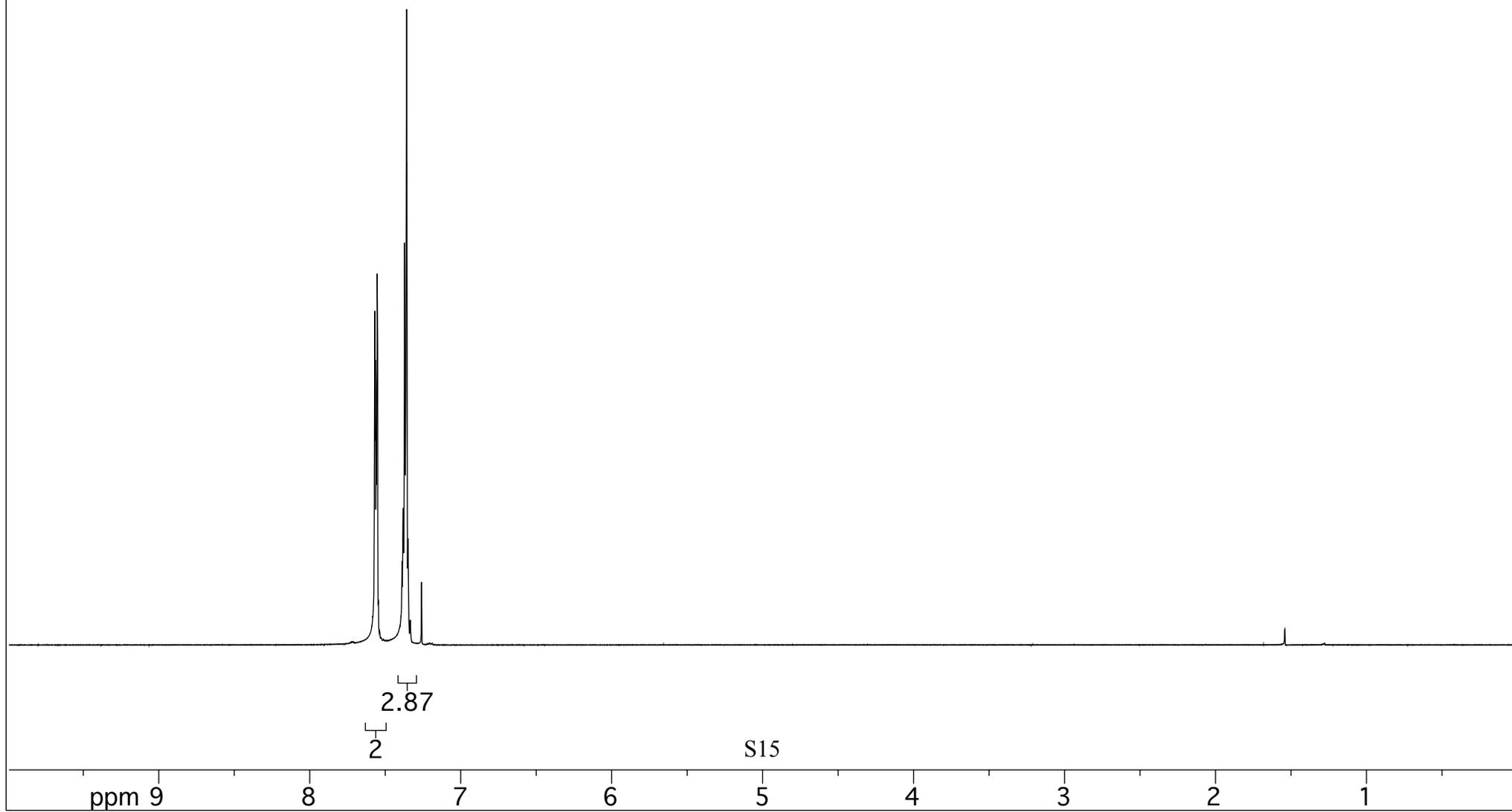
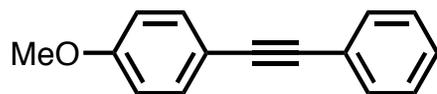


Table 3 Entry 2



159.73

133.18

131.58

128.44

128.07

123.71

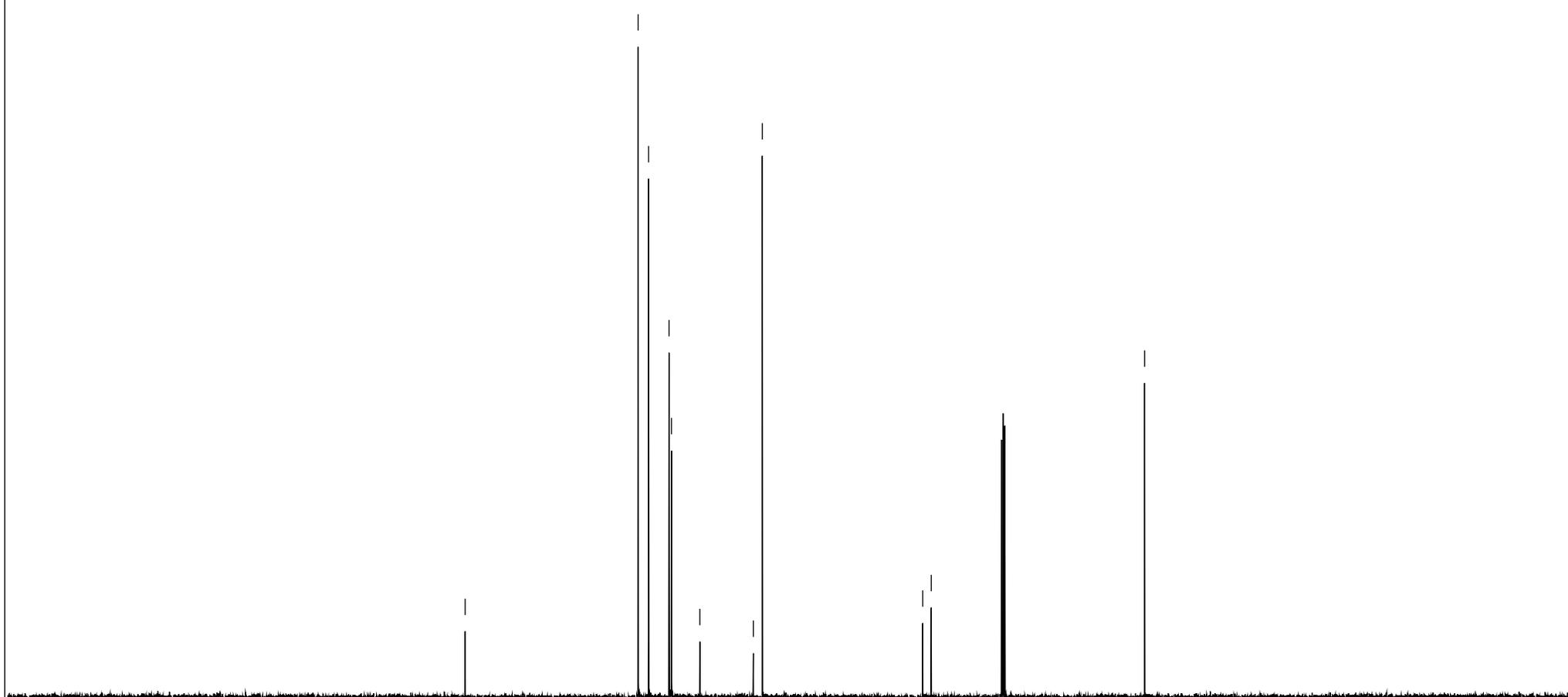
115.49

114.12

89.50

88.19

55.44



S16

220

200

180

160

140

120

100

80

60

40

20

0

Table 3 Entry 2

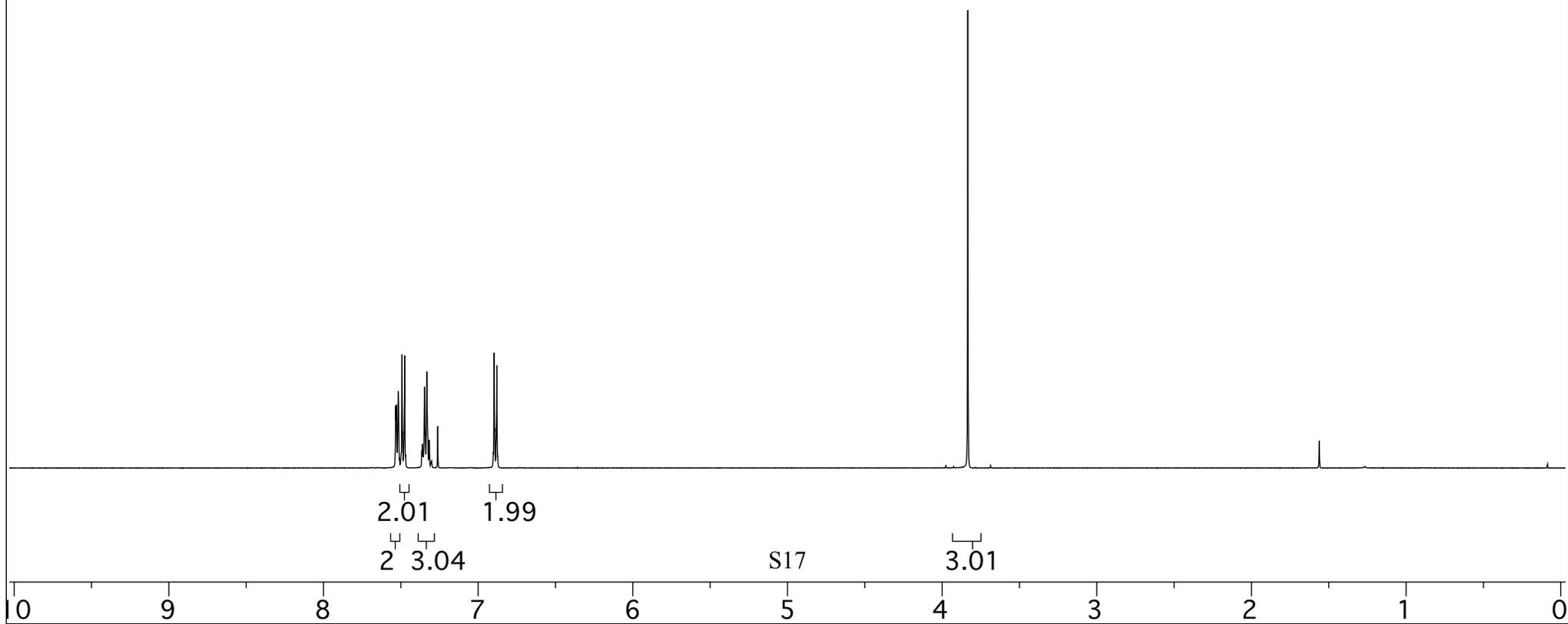
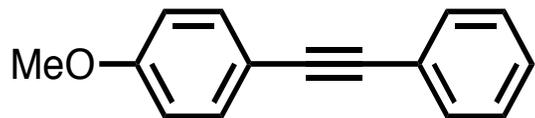
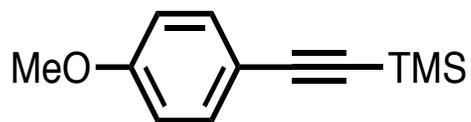


Table 3 Entry 3



159.85

133.59

115.37

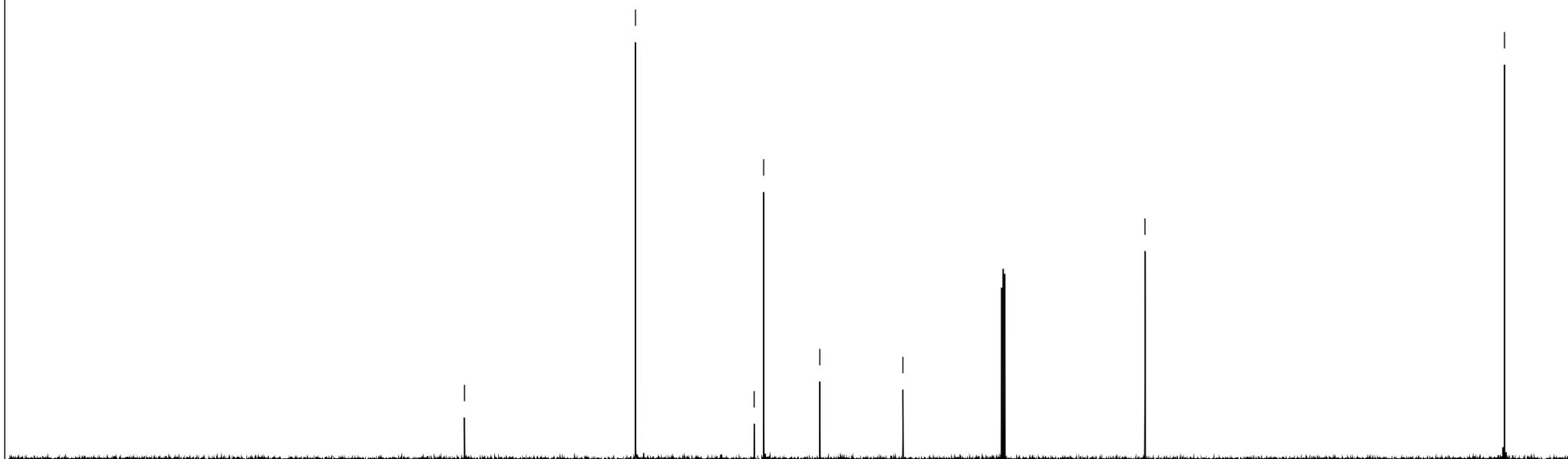
113.92

105.31

92.55

55.39

0.21



S18

220

200

180

160

140

120

100

80

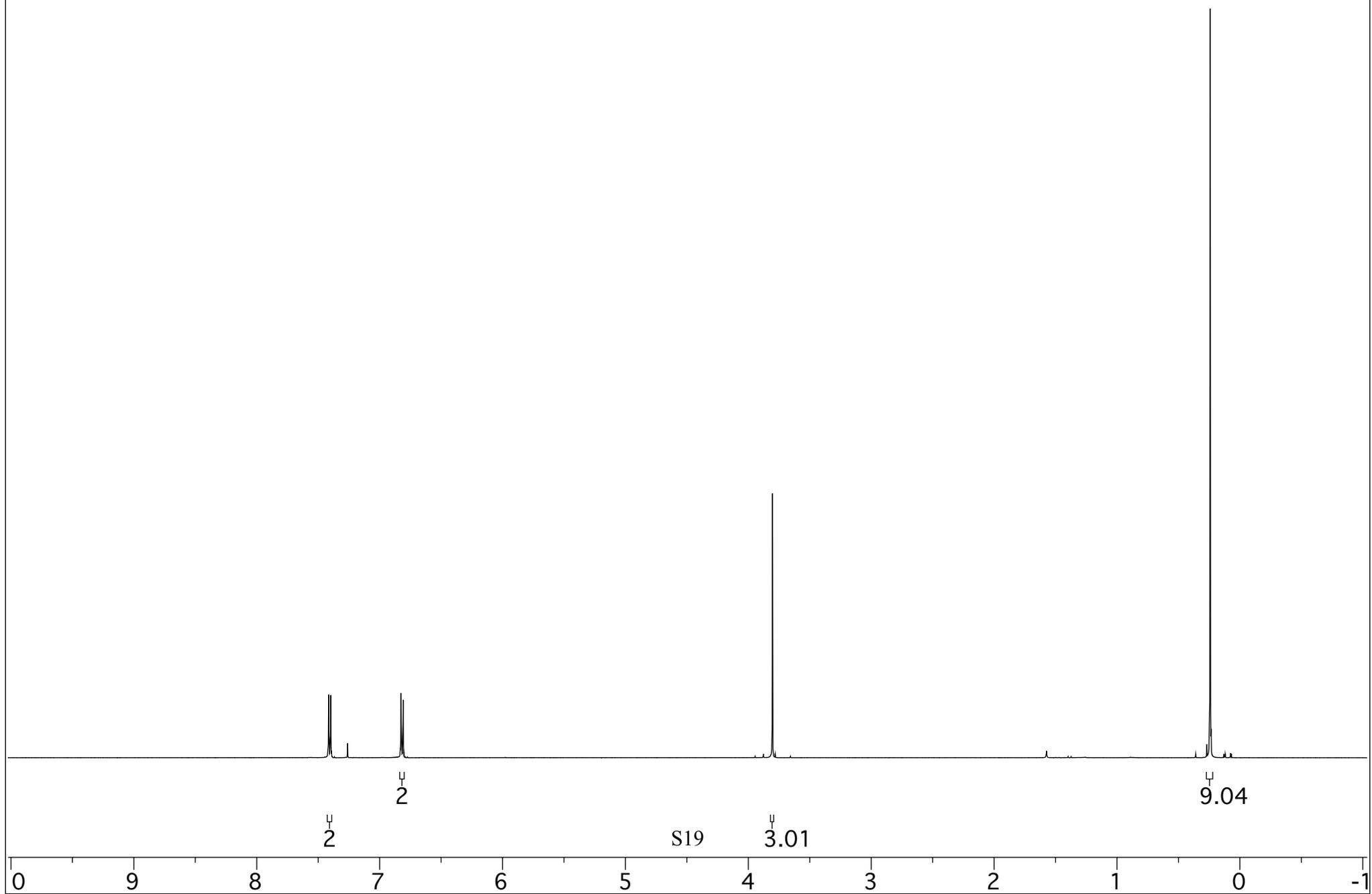
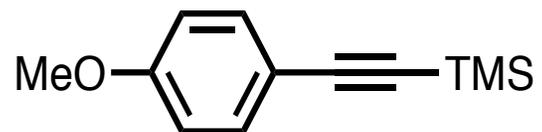
60

40

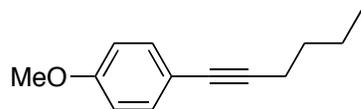
20

0

Table 3 Entry 3



Tabl3 3 Entry 4



159.09

132.99

116.38

113.92

88.91

80.35

55.40

31.12

22.19

19.26

13.84

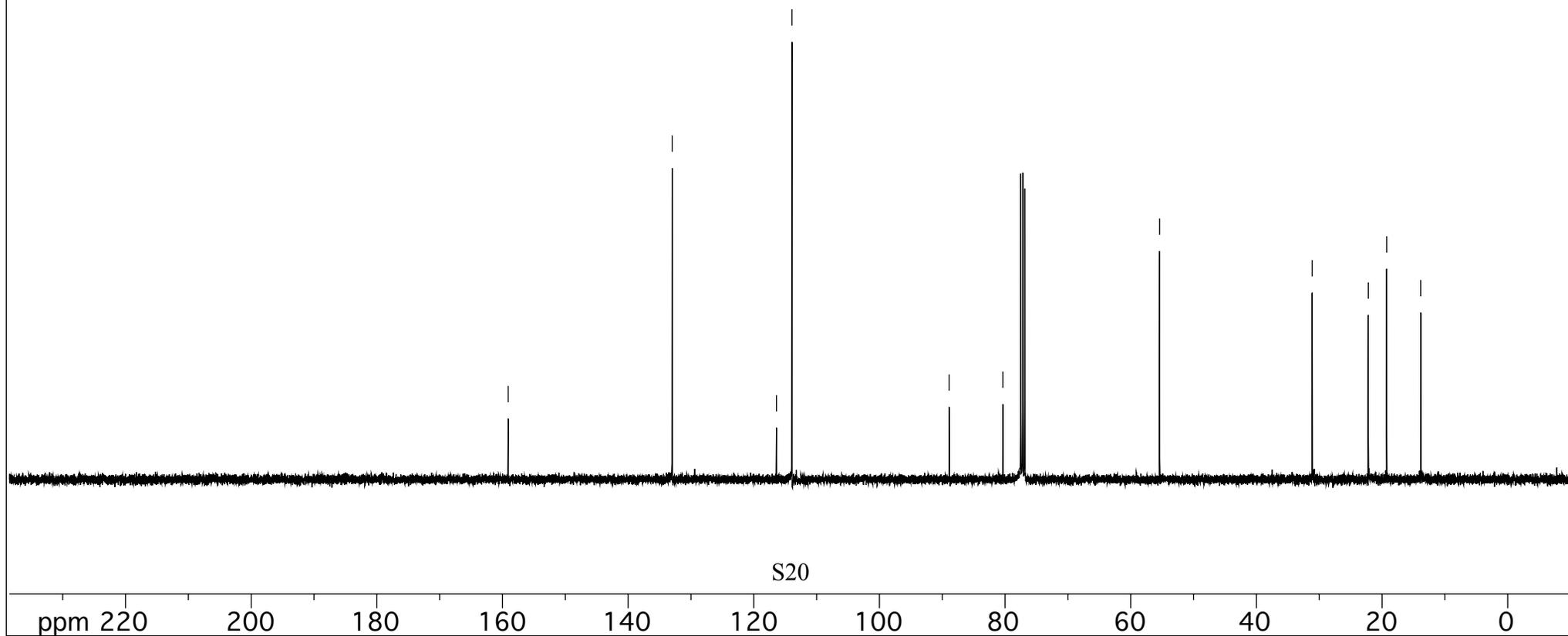


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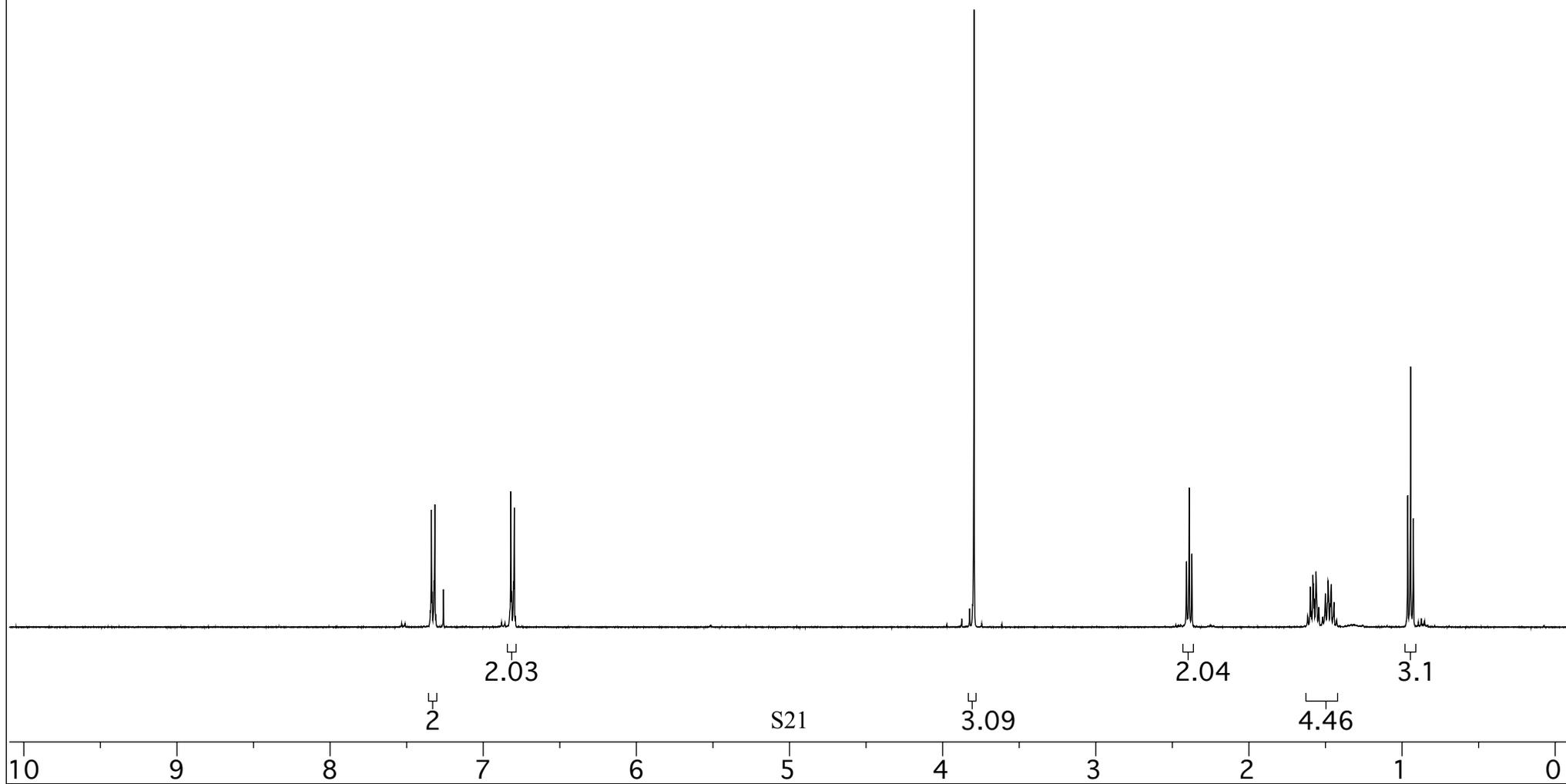
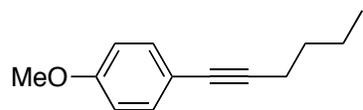
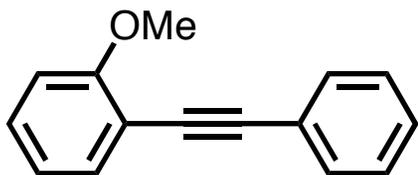


Table 3 Entry 5



160.16

133.83

131.92

130.03

128.50

128.37

123.80

120.74

112.66

110.93

93.68

85.99

56.09

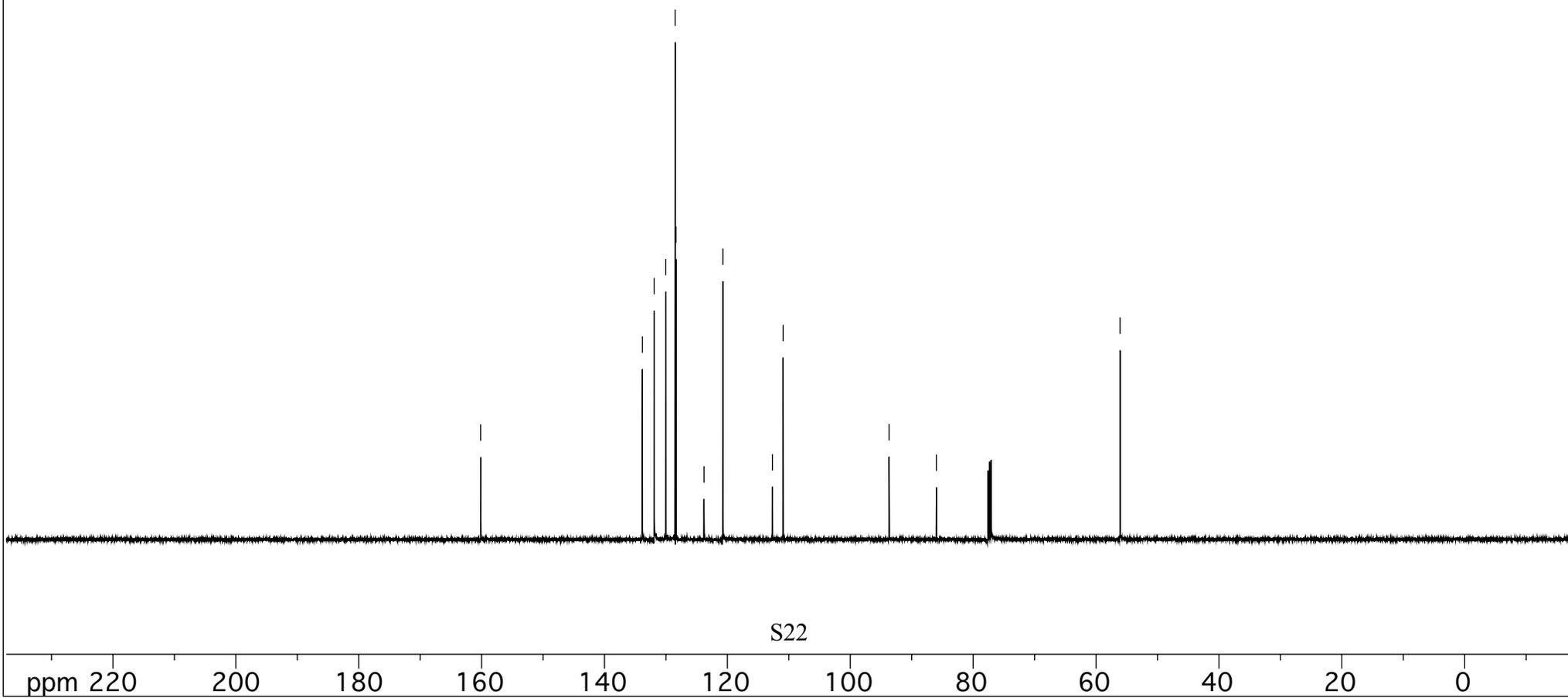


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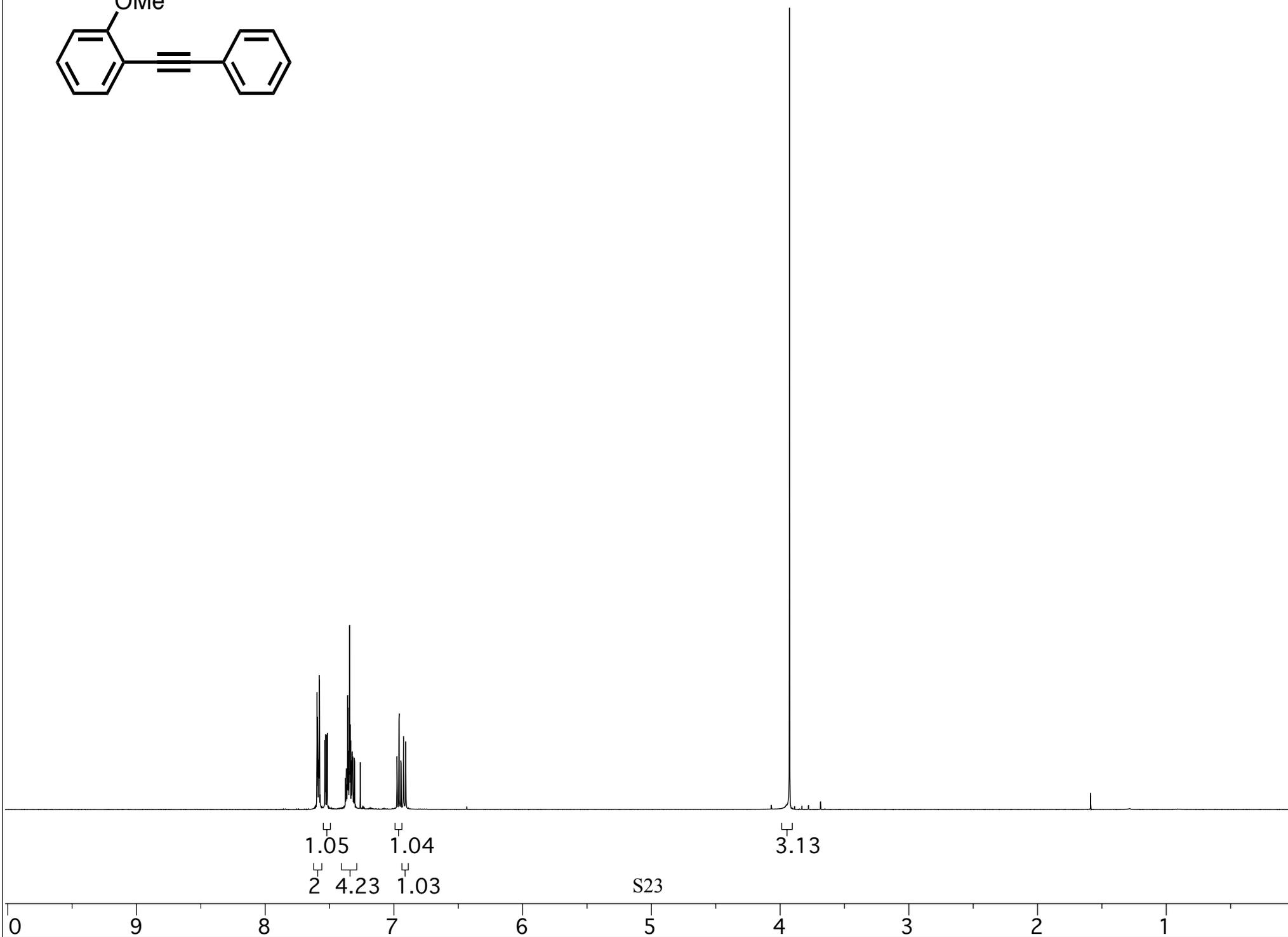
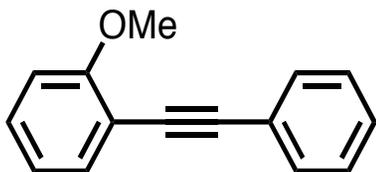
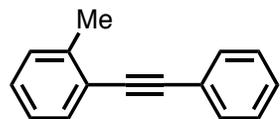


Table 3 Entry 6



140.33  
131.97  
131.65  
129.61  
128.50  
128.45  
128.32  
125.73  
123.69  
123.16

93.48  
88.48

20.91

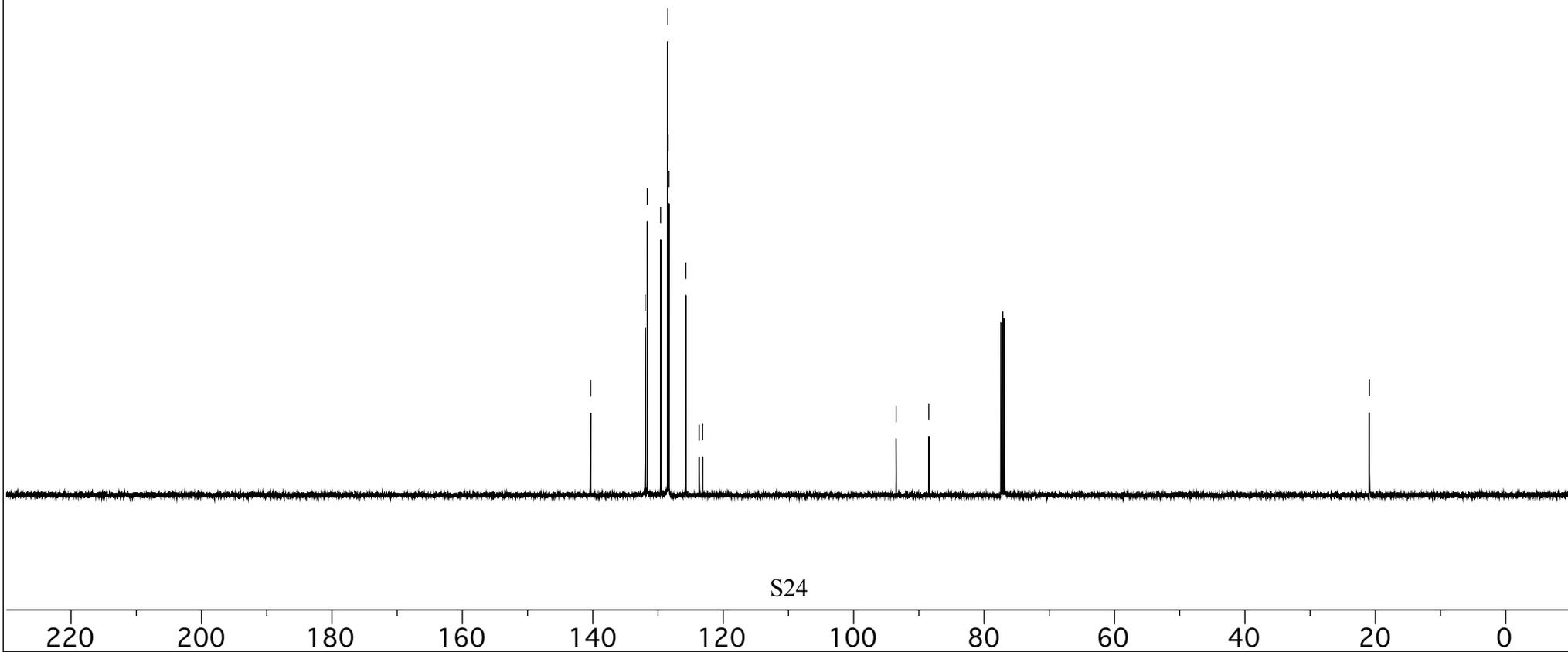
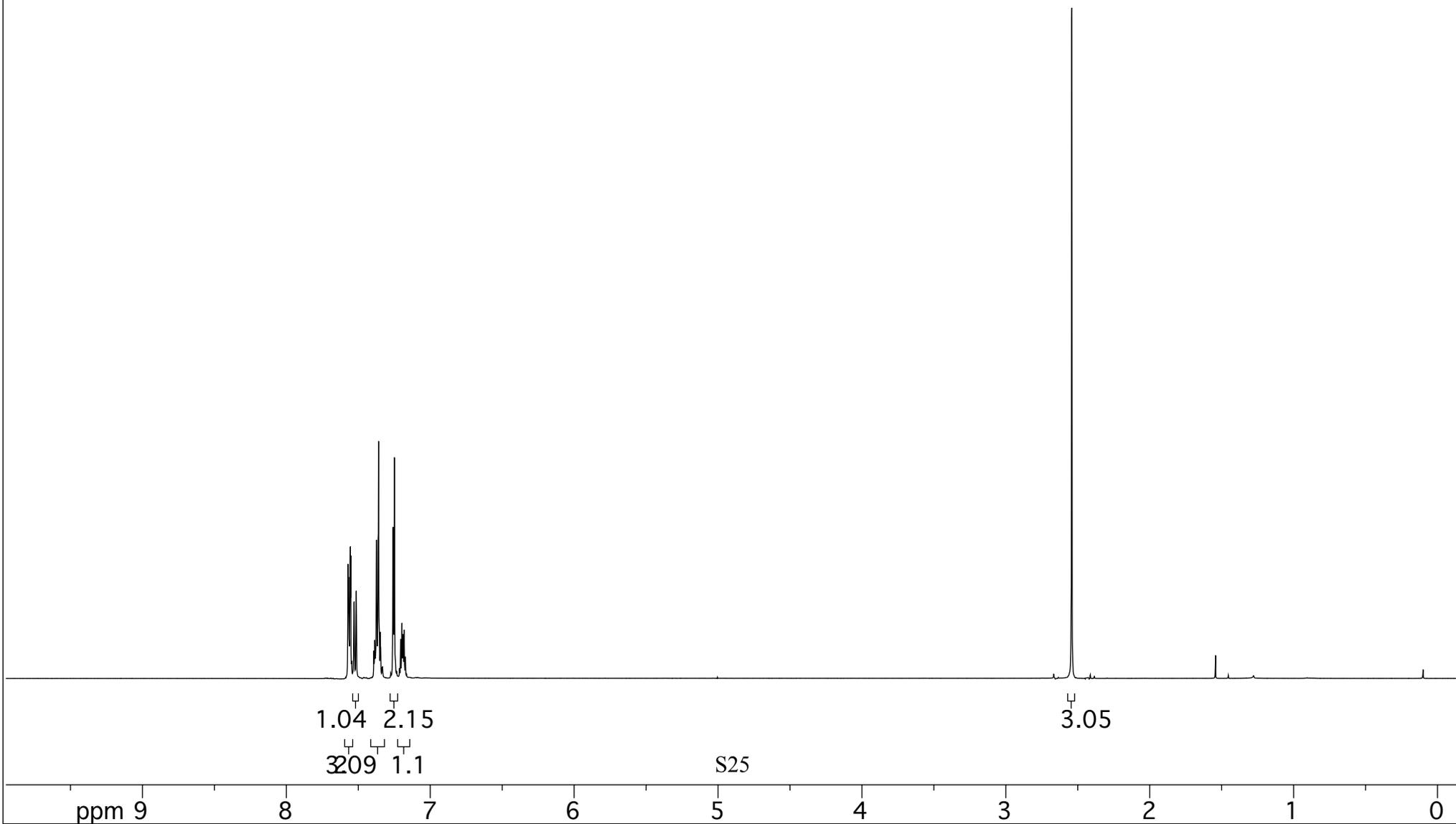
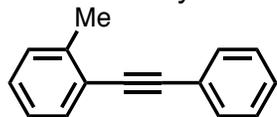
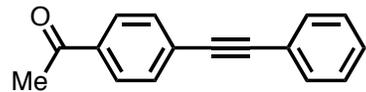


Table 3 Entry 6



S25

Table 3 Entry 7

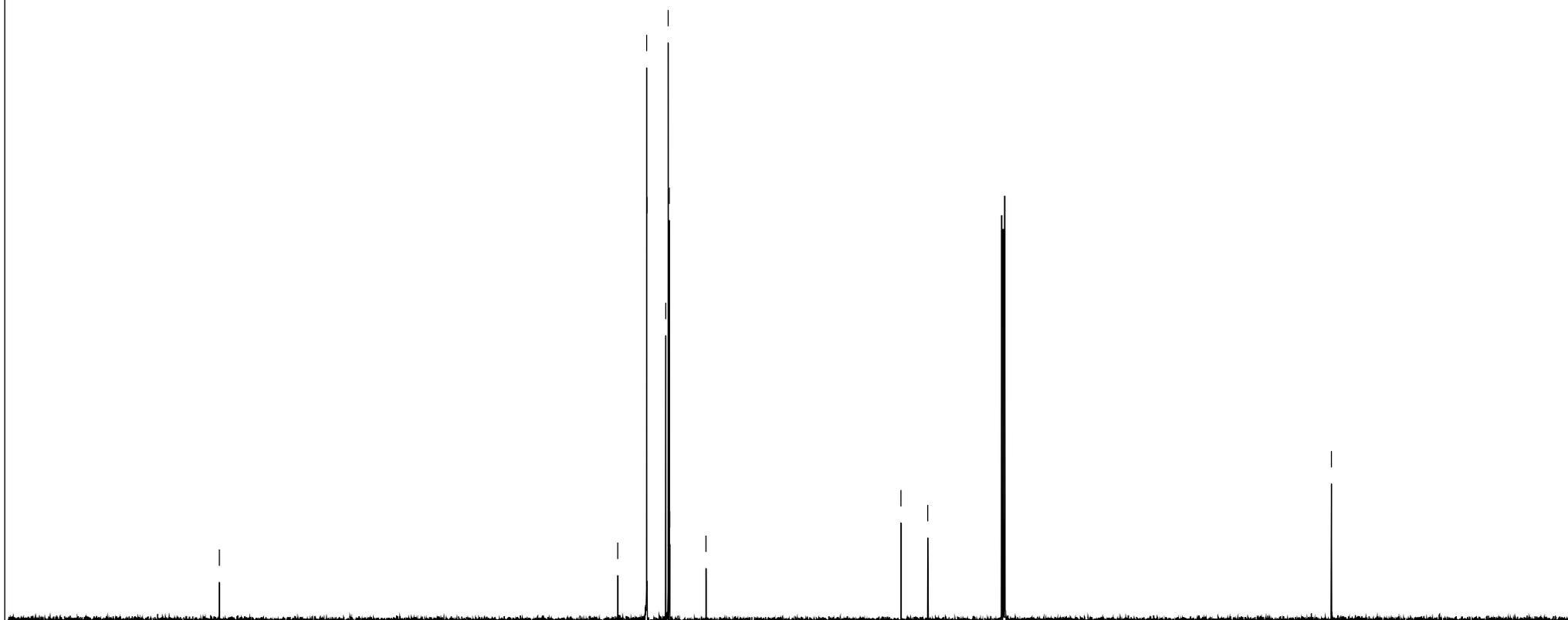


197.29

136.14  
131.71  
131.66  
128.78  
128.41  
128.24  
128.16  
122.60

92.67  
88.56

26.60



S26

220

200

180

160

140

120

100

80

60

40

20

0

Table 3 Entry 7

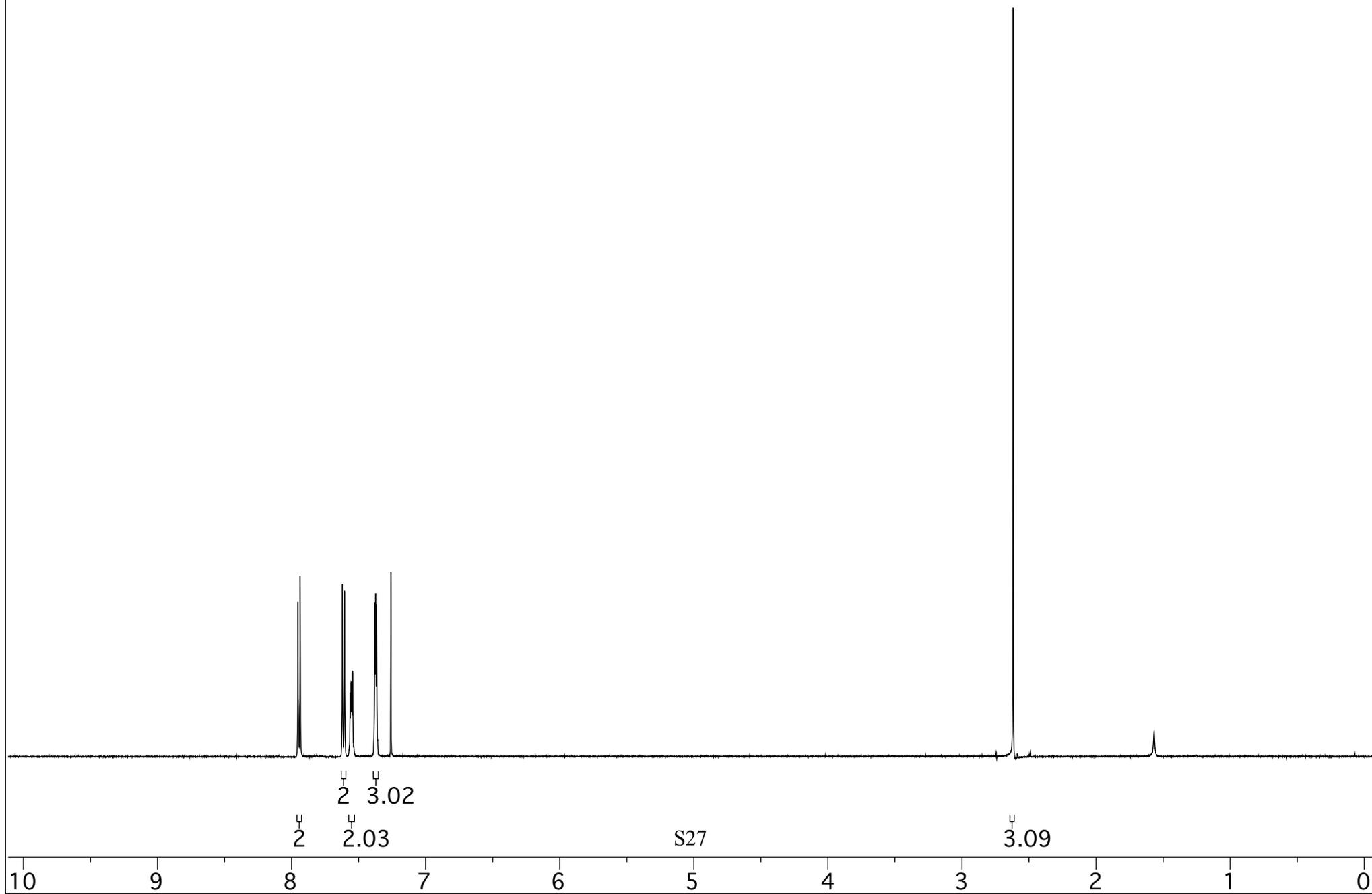
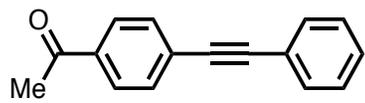
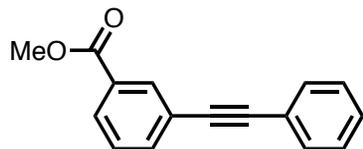


Table 3 Entry 8



166.58

135.83  
132.89  
131.82  
130.59  
129.35  
128.70  
128.64  
128.55  
123.90  
123.00

90.42  
88.45

52.45

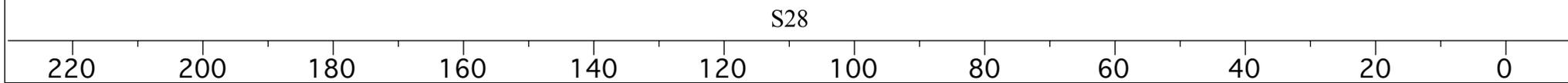


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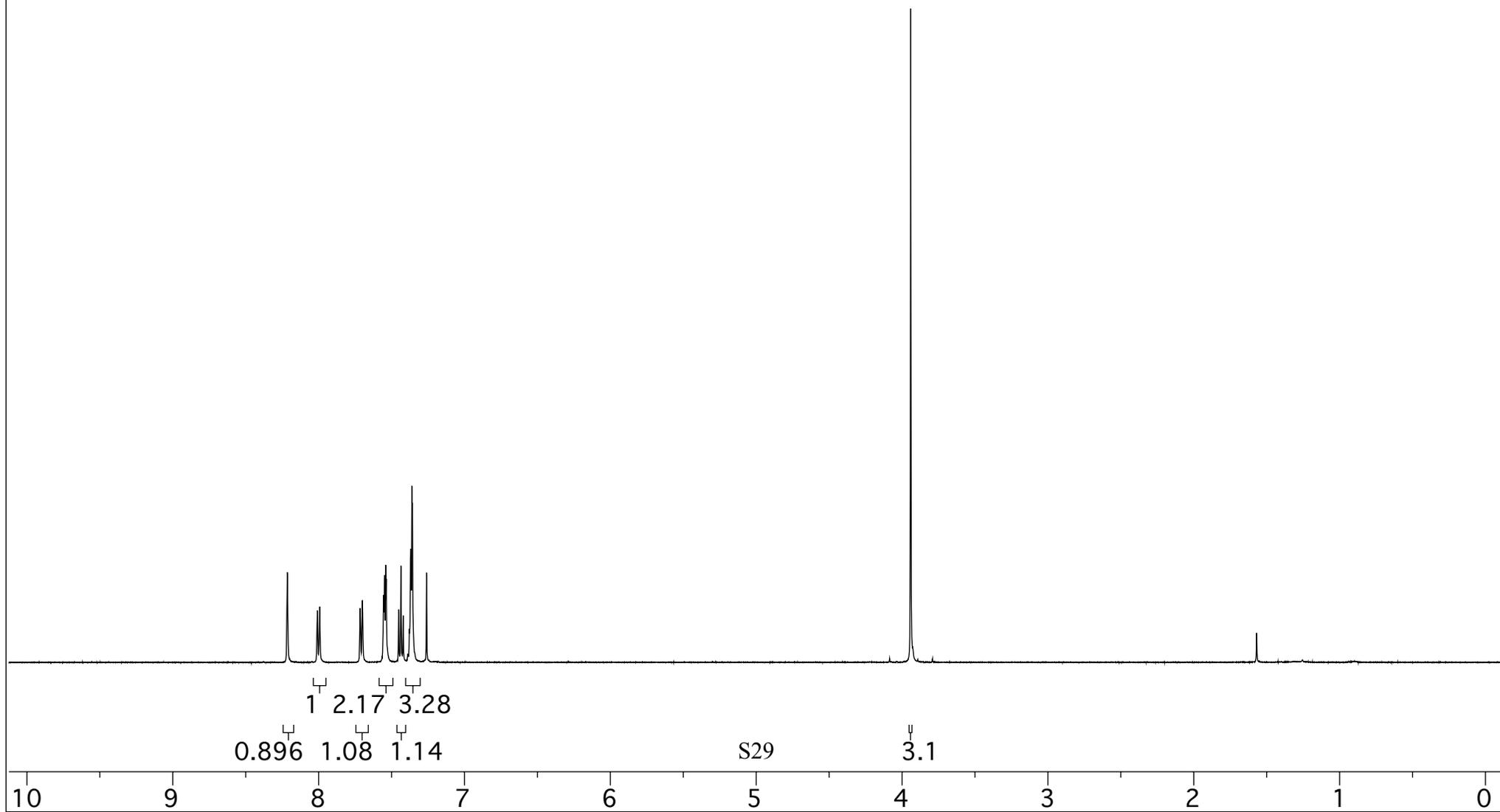
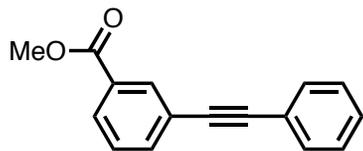
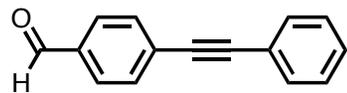


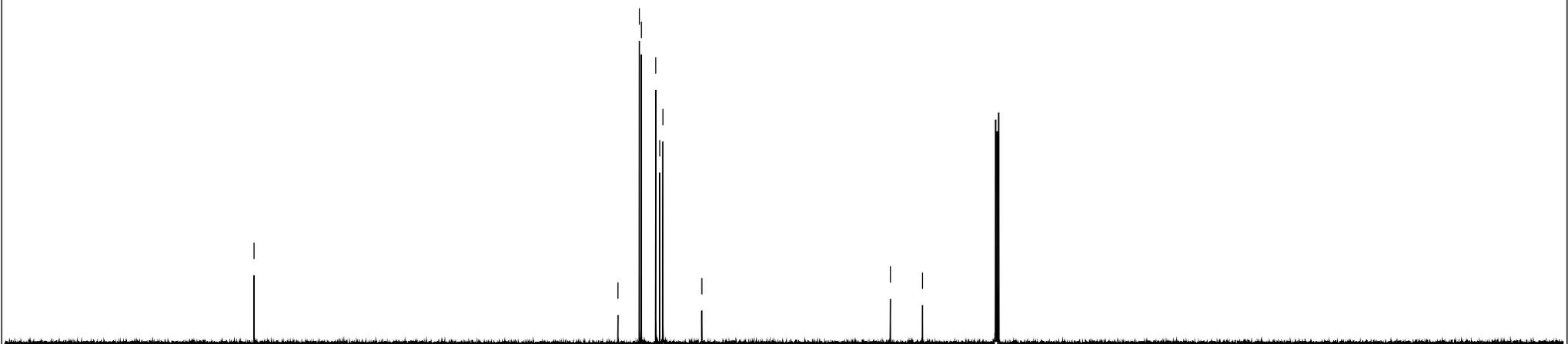
Table 3 Entry 9



191.55

135.52  
132.23  
131.92  
129.71  
129.10  
128.61  
122.61

93.58  
88.64



220 200 180 160 140 120 100 80 60 40 20 0

S30

Table 3 Entry 9

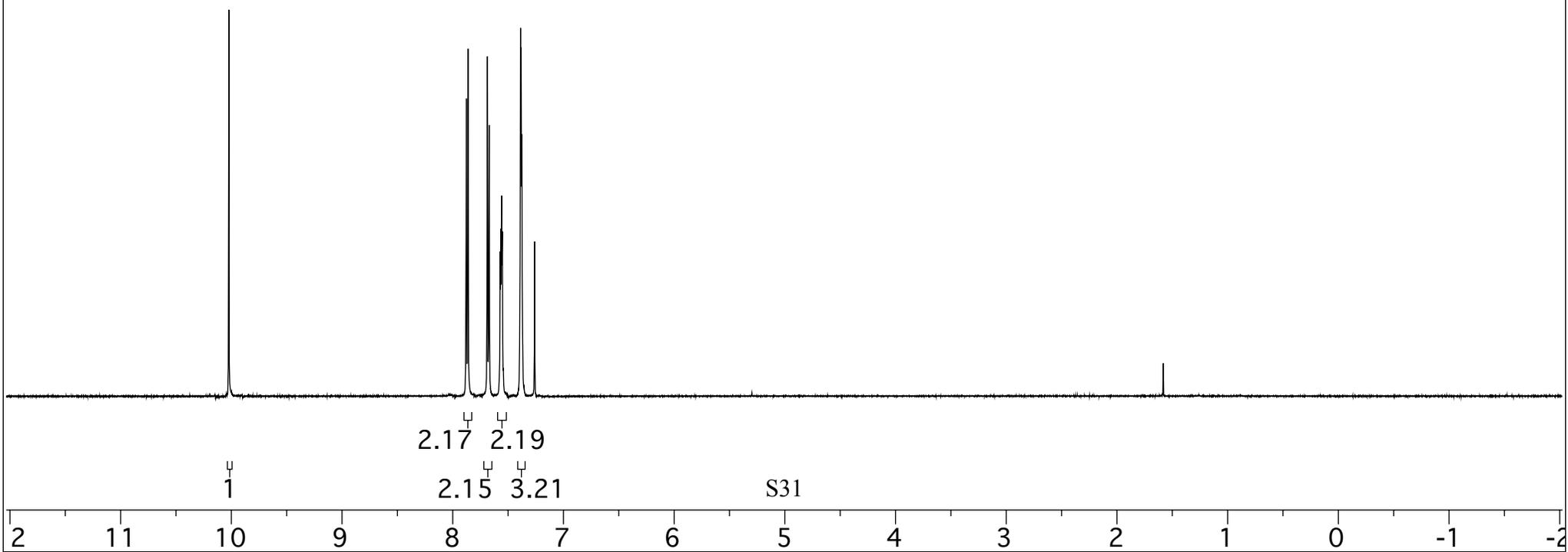
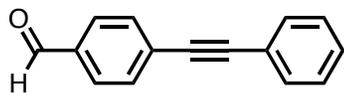
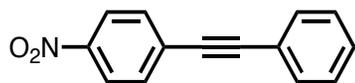


Table 3 Entry 10



147.06  
132.38  
131.96  
130.37  
129.40  
128.66  
123.76

94.83  
87.68

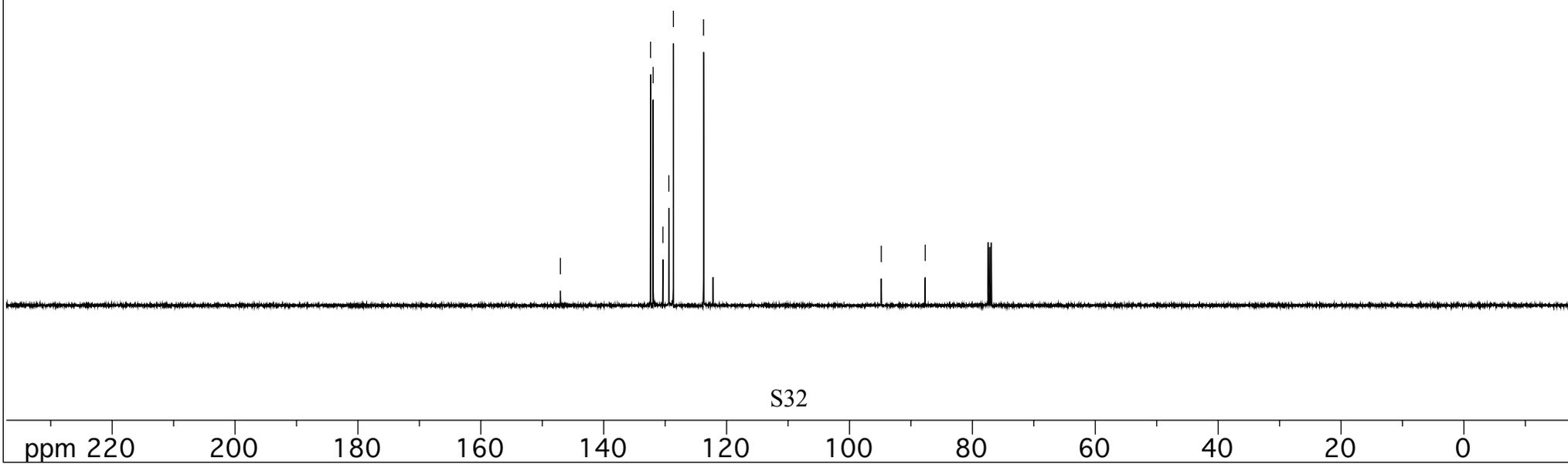


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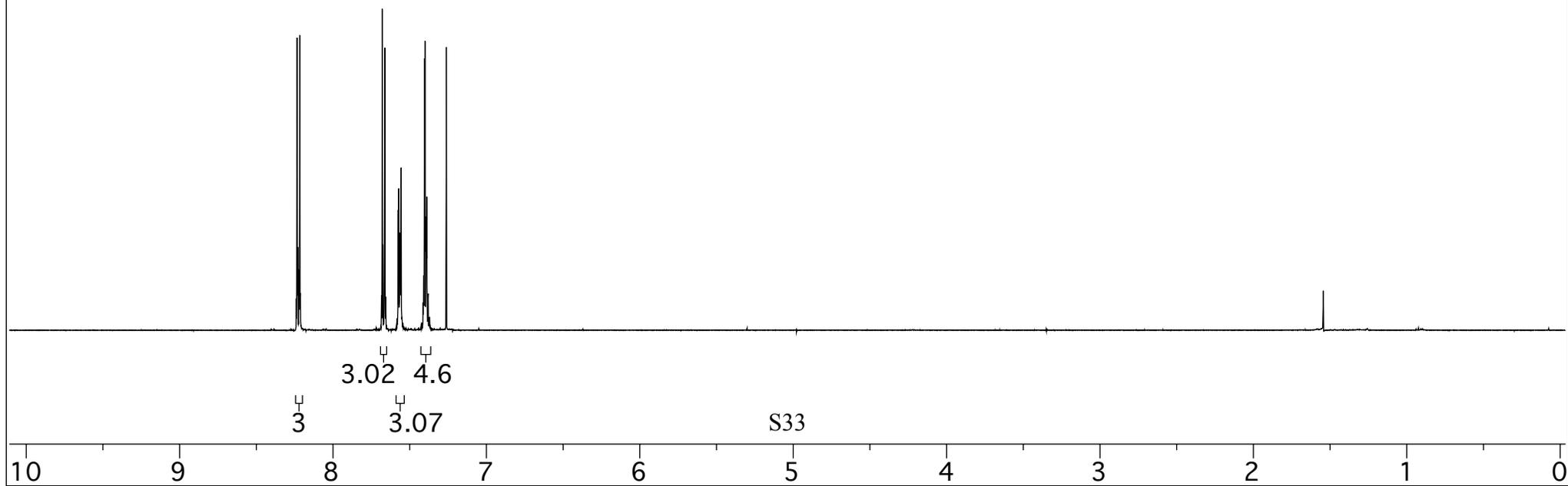
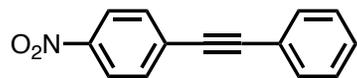
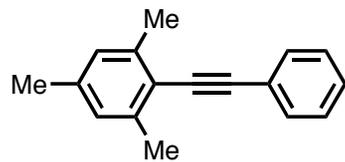


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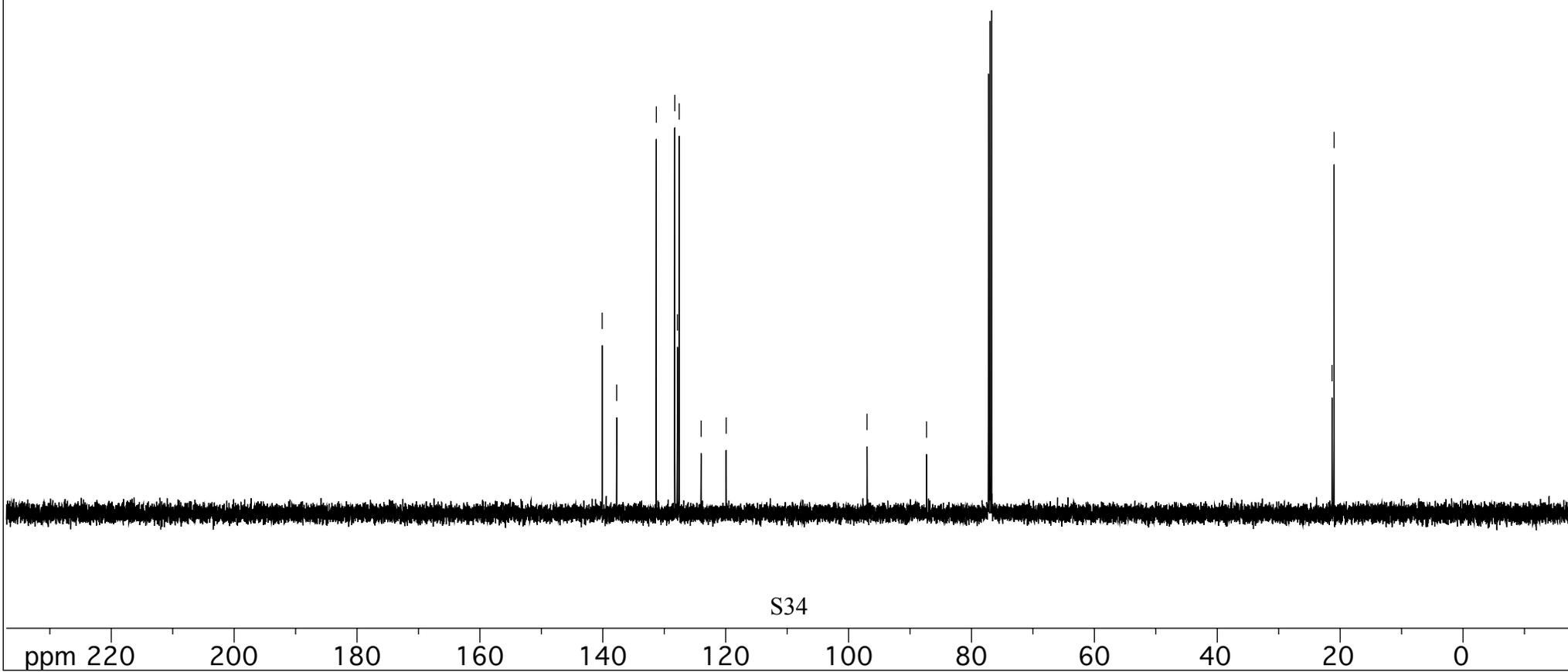


140.10  
137.74  
131.29  
128.29  
127.86  
127.57  
124.00  
119.92

97.00

87.31

21.32  
20.98



S34

Table 3 Entry 11

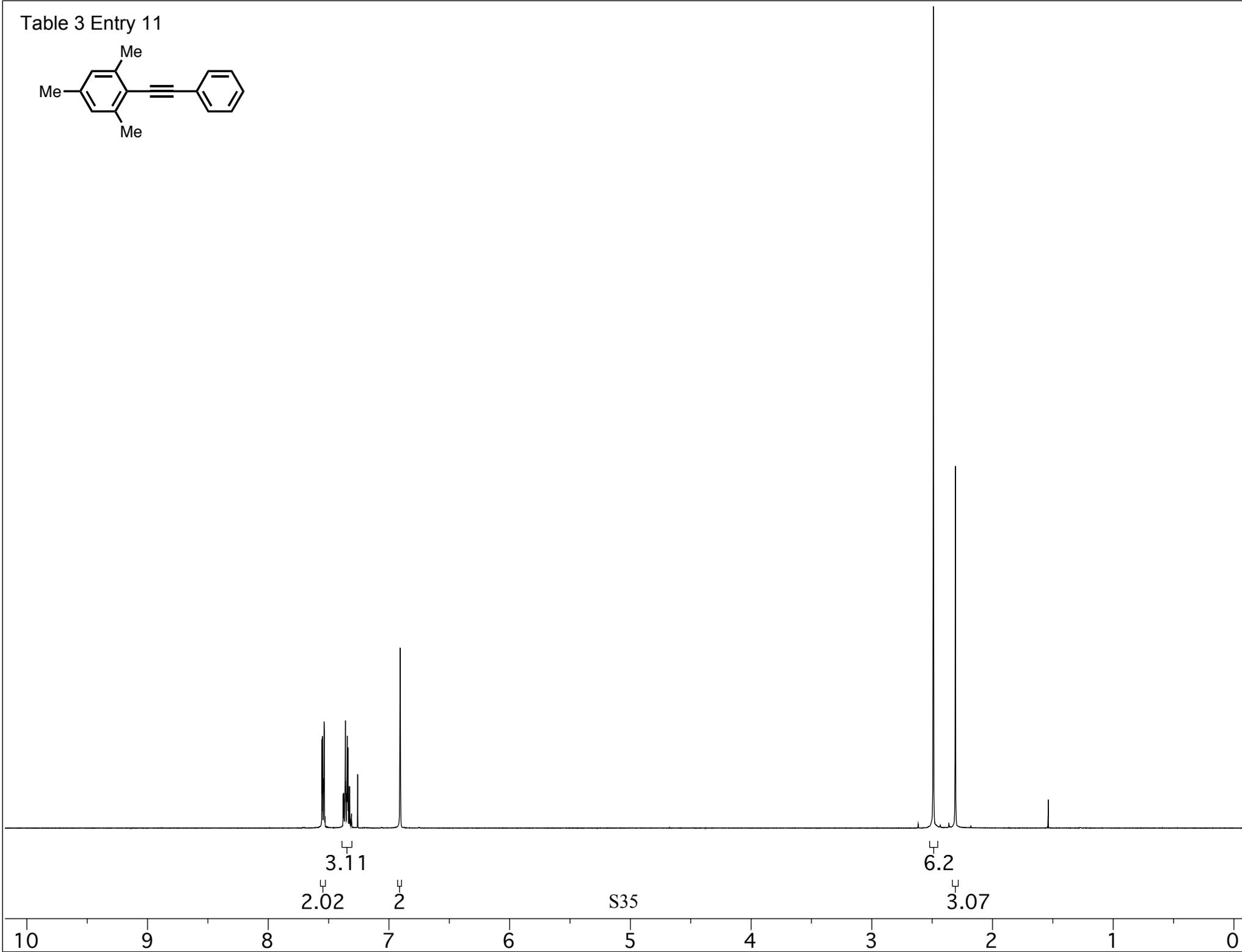
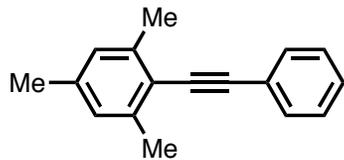
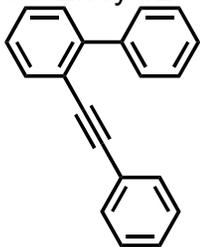


Table 3 Entry 12



143.98  
140.63  
132.93  
131.43  
129.57  
129.49  
128.62  
128.34  
128.19  
127.97  
127.55  
127.14  
123.53  
121.65

92.30  
89.48

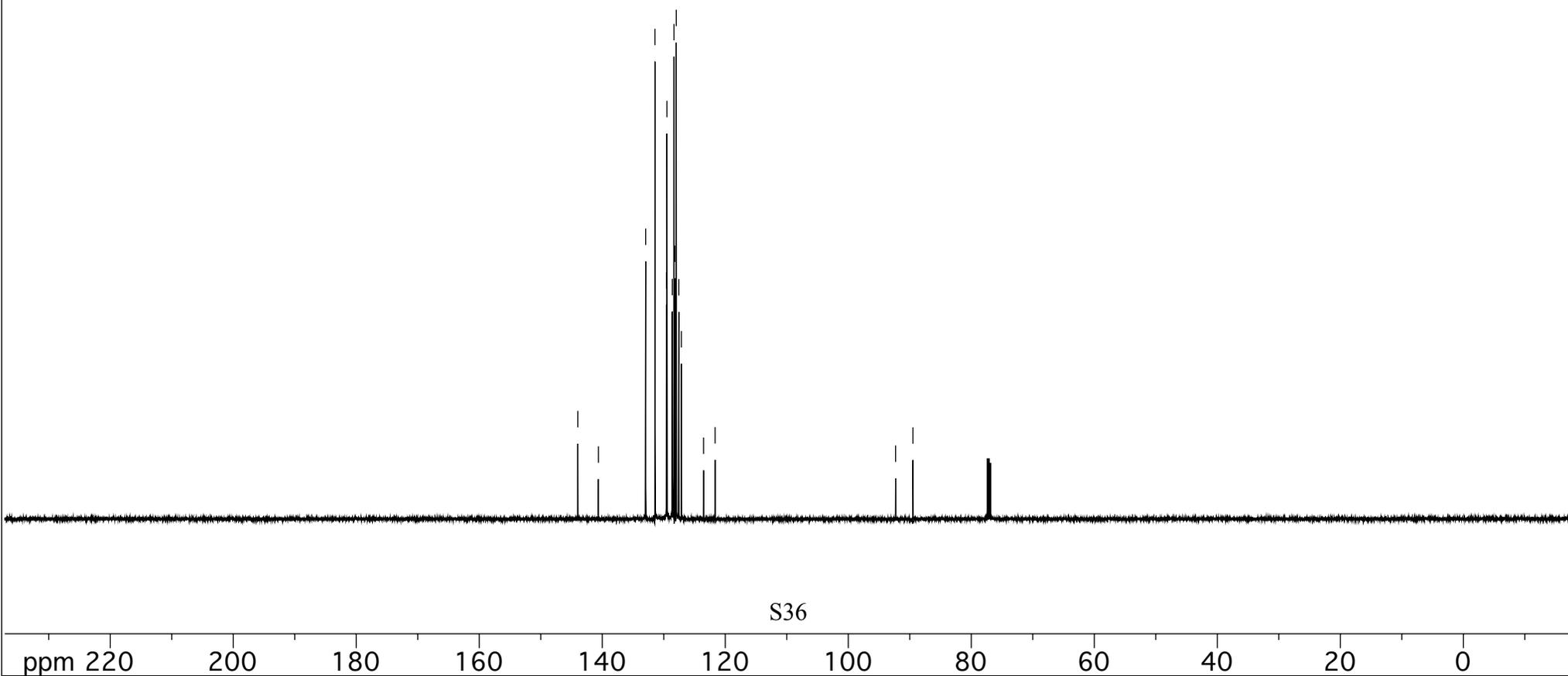


Table 3 Entry 12

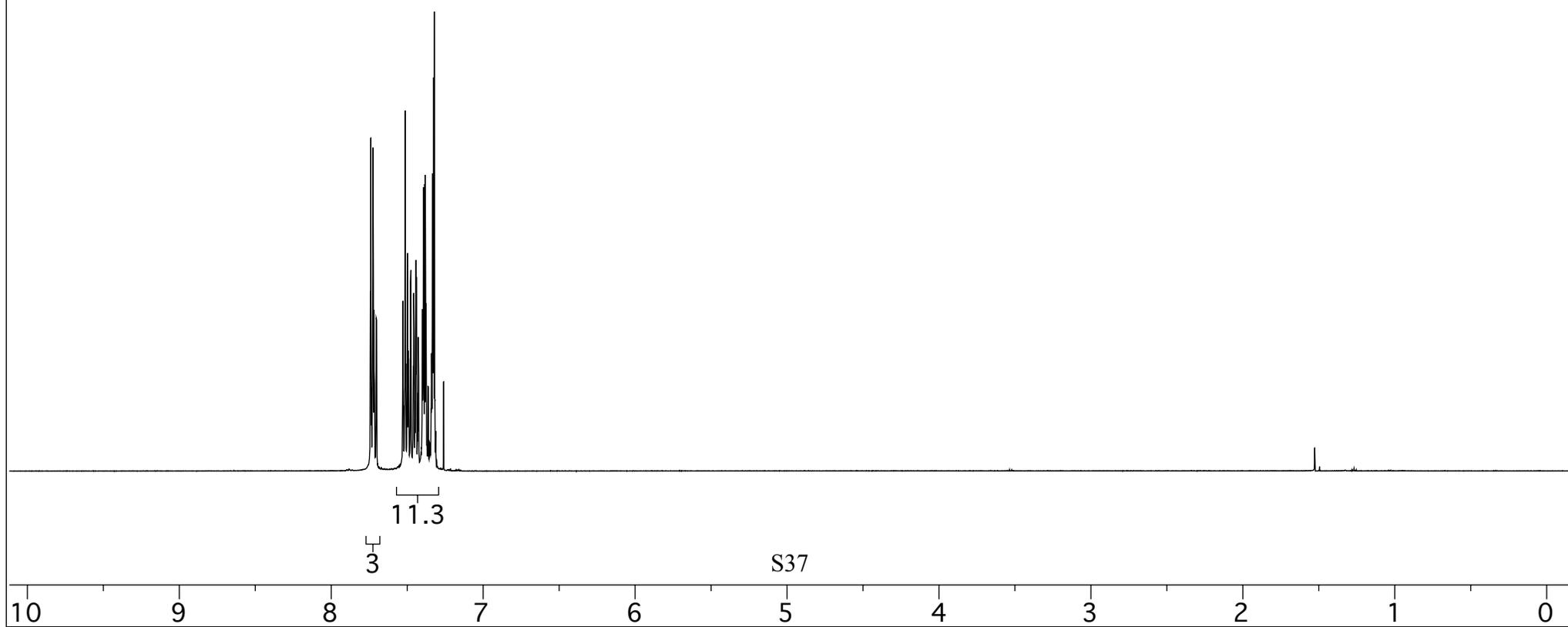
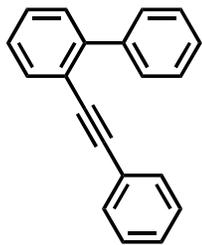
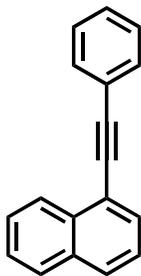


Table 3 Entry 13



133.40  
133.35  
131.80  
130.50  
128.90  
128.57  
128.52  
128.44  
126.91  
126.56  
126.36  
125.41  
123.54  
121.03

94.46

87.67

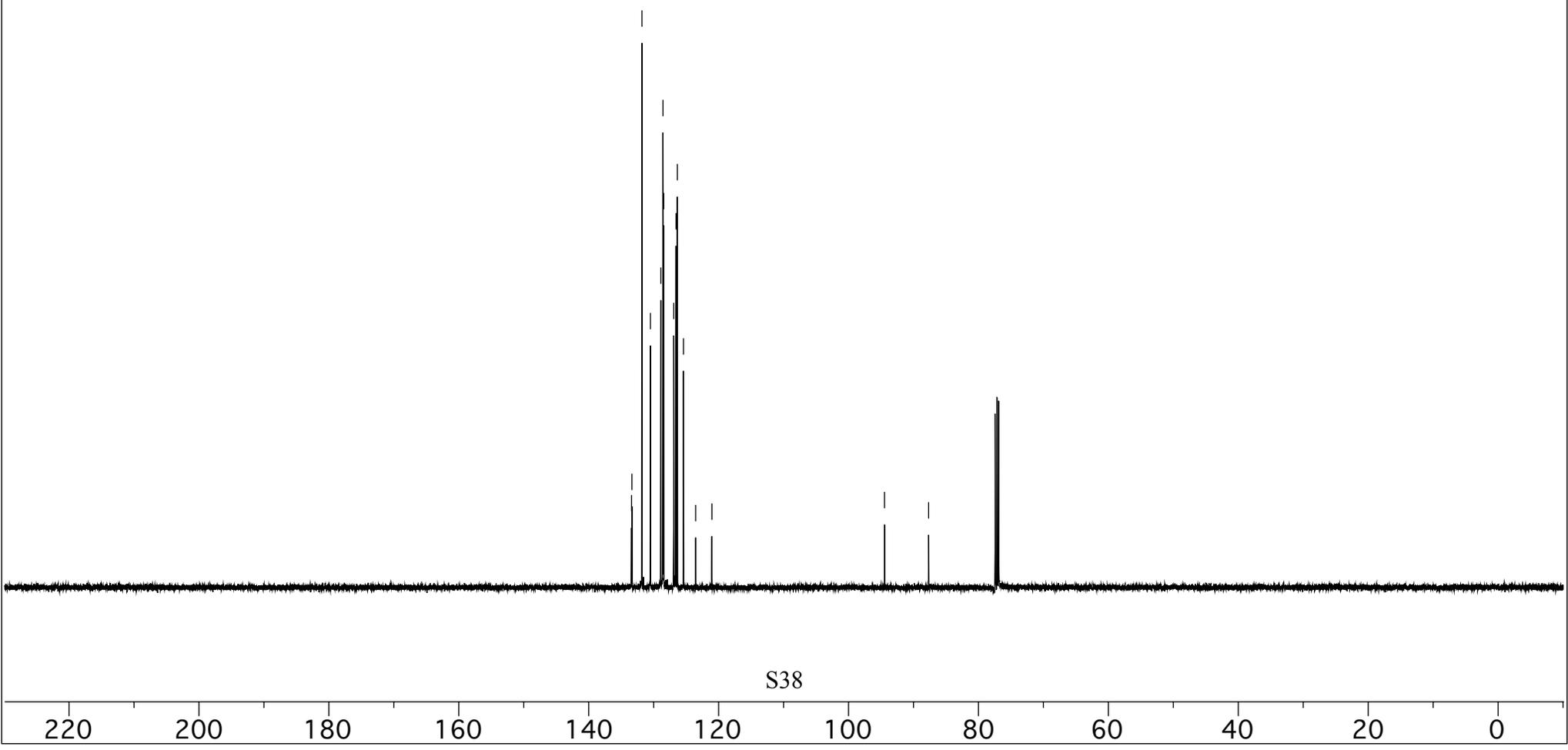


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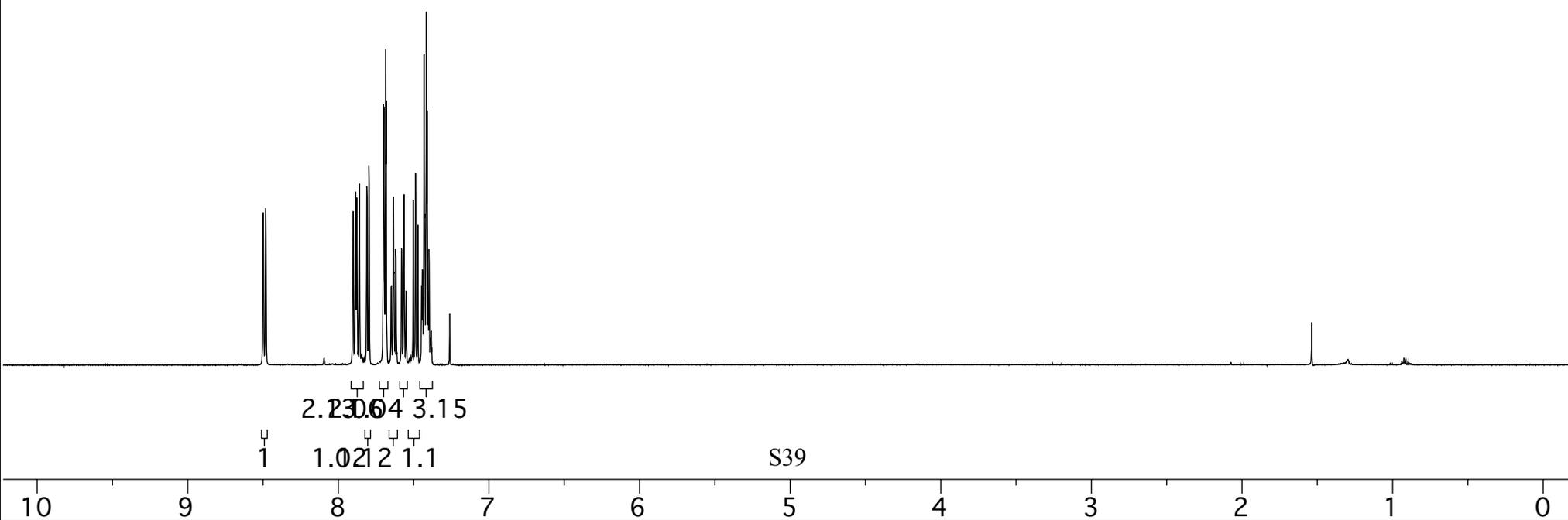
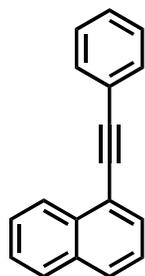
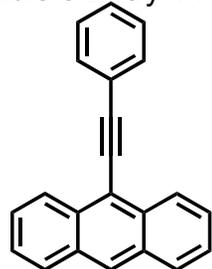


Table 3 Entry 14



132.56  
131.62  
131.14  
128.65  
128.48  
128.44  
127.67  
126.72  
126.56  
125.63  
123.60  
117.23  
100.71  
86.28

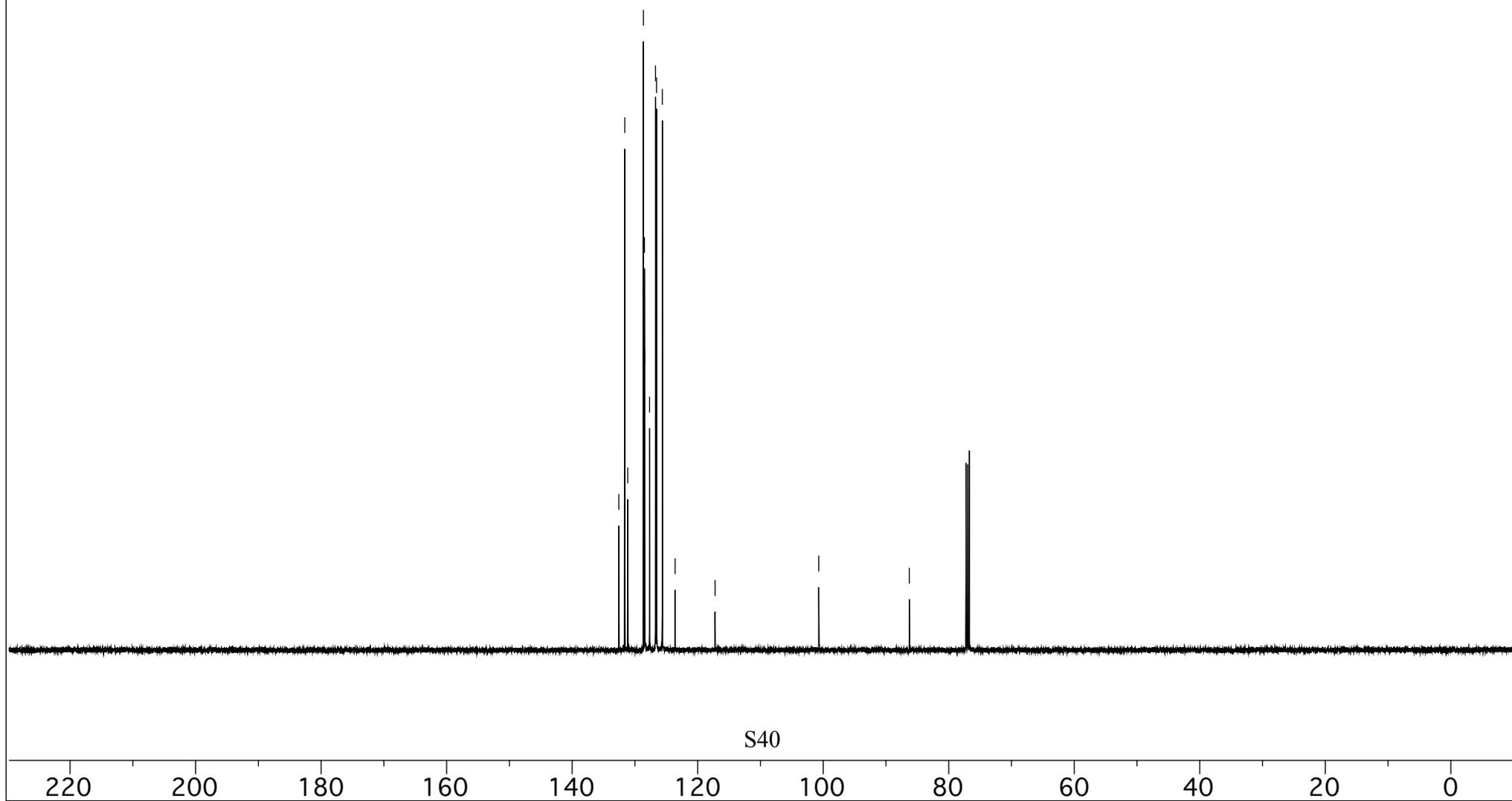


Table 3 Entry 14

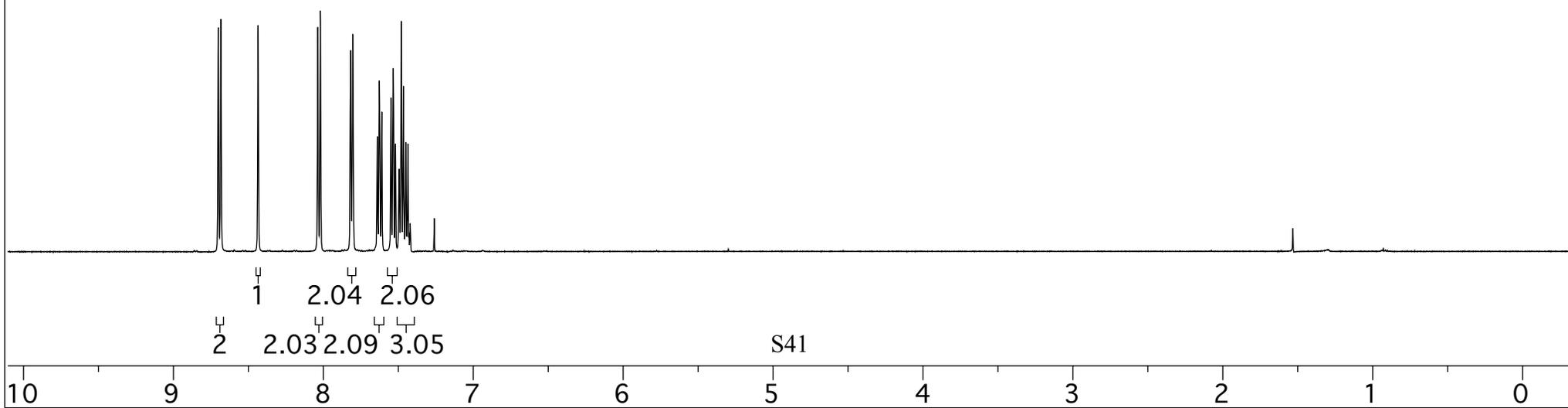
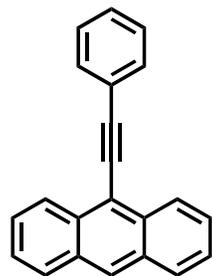
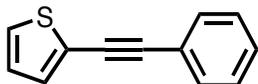


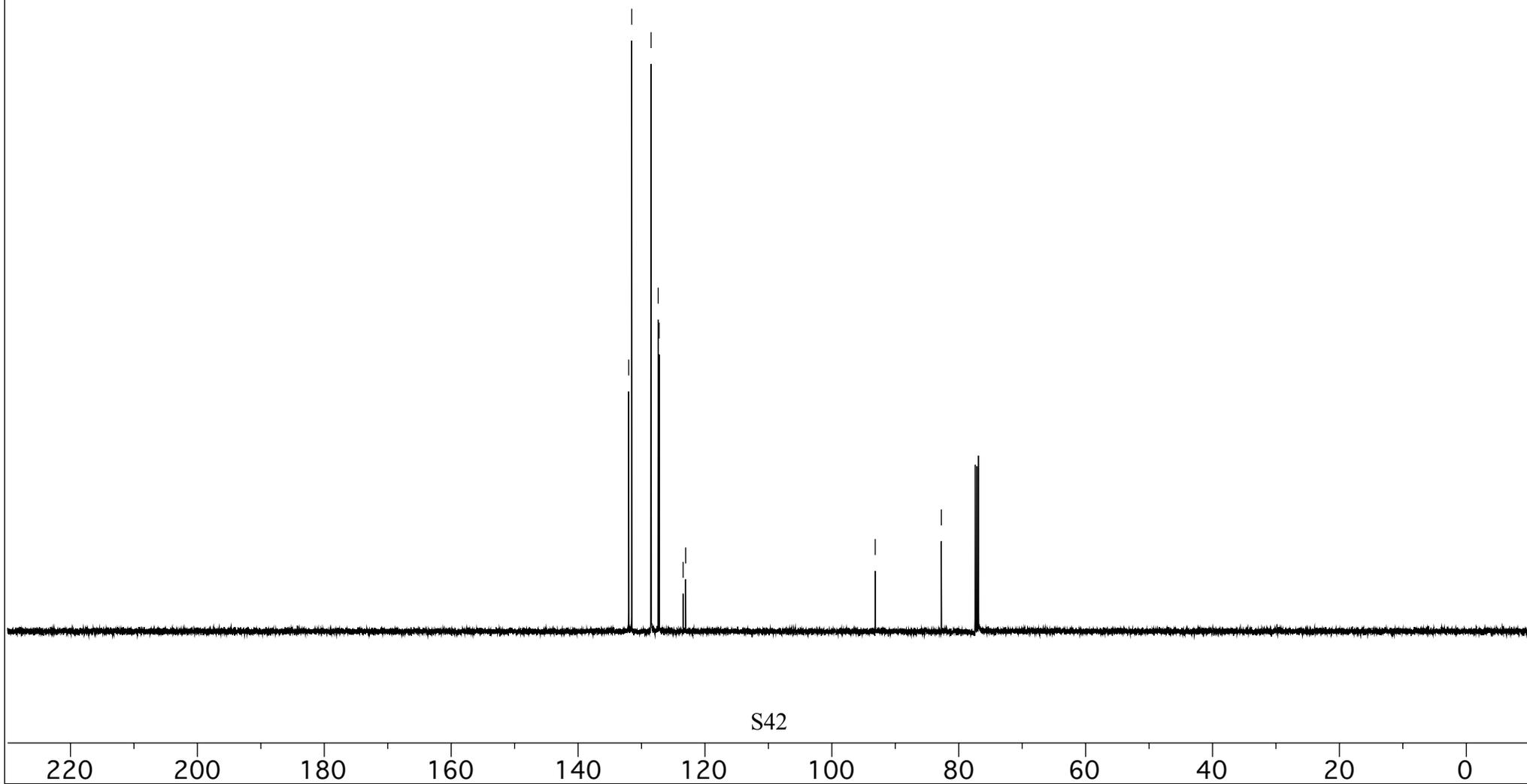
Table 3 Entry 15



132.02  
131.54  
128.54  
128.50  
127.38  
127.22  
123.44  
123.04

93.16

82.75



S42

Table 3 Entry 15

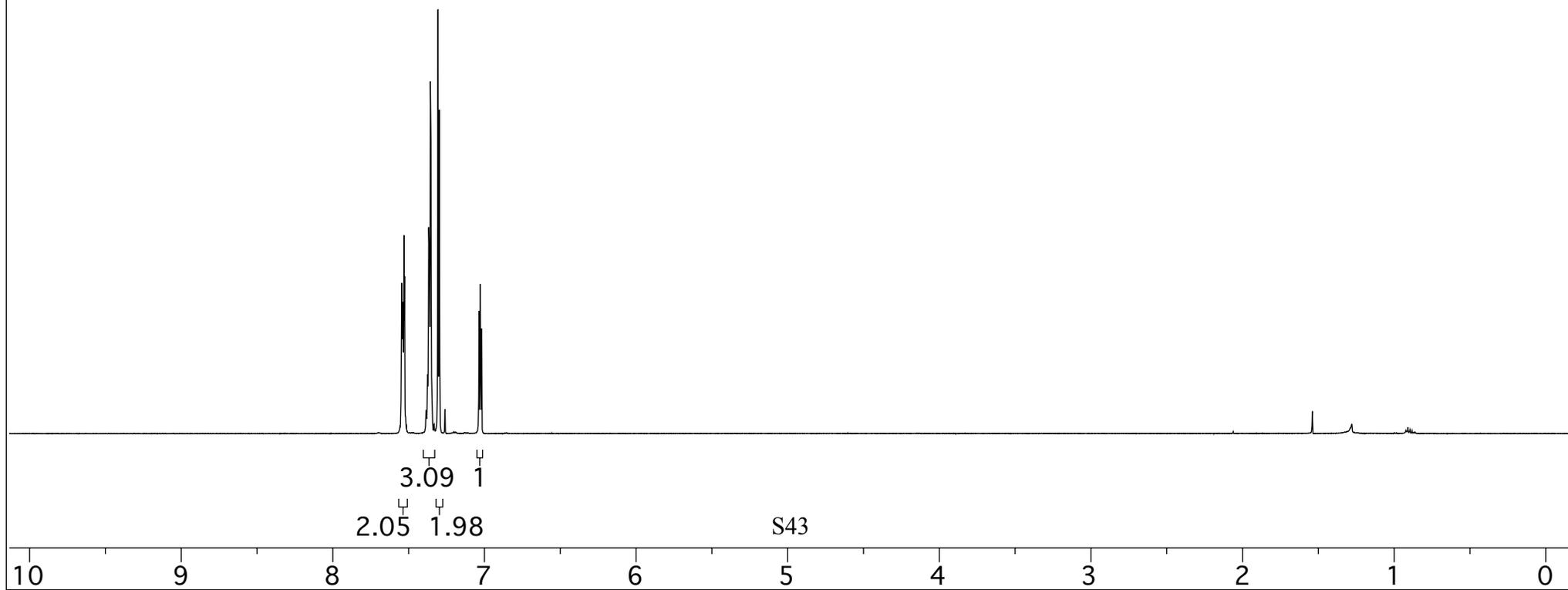
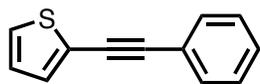
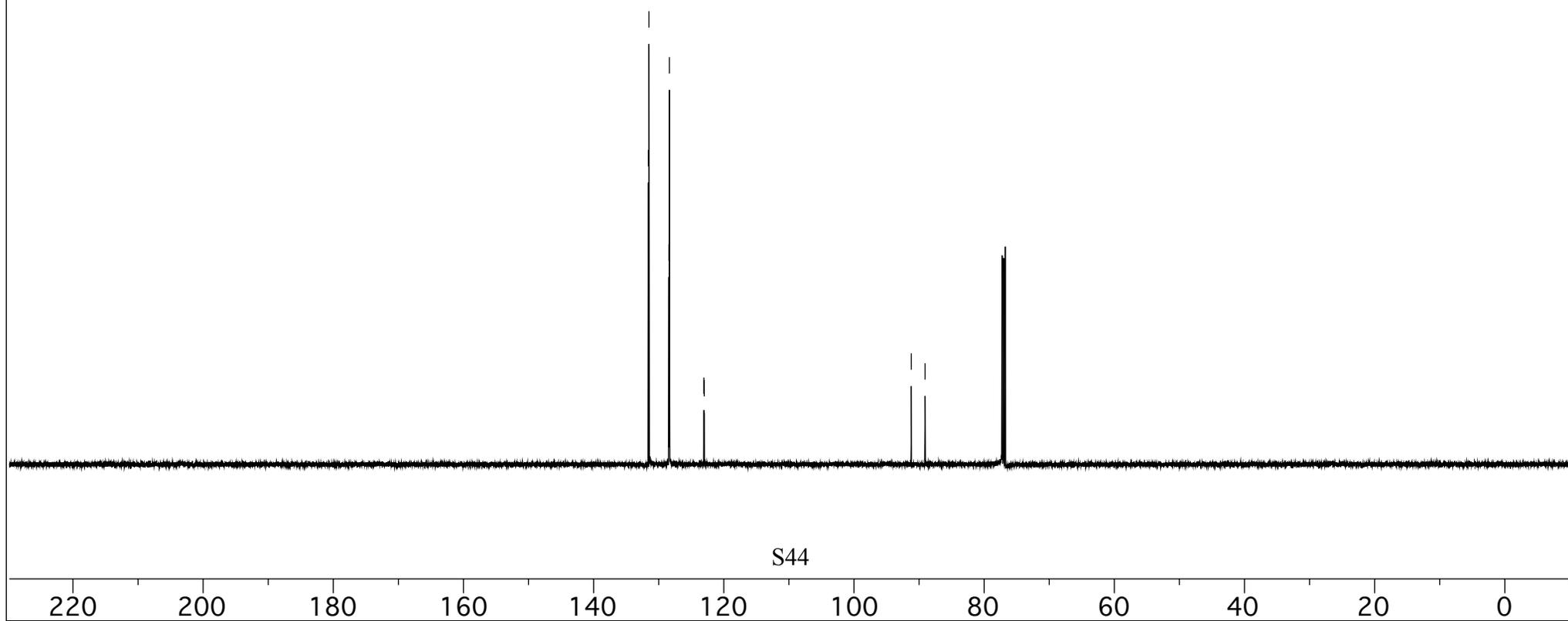


Table 3 Entry 16



131.60  
131.50  
128.44  
128.36  
123.06  
123.00

91.20  
89.08



S44

Table 3 Entry 16

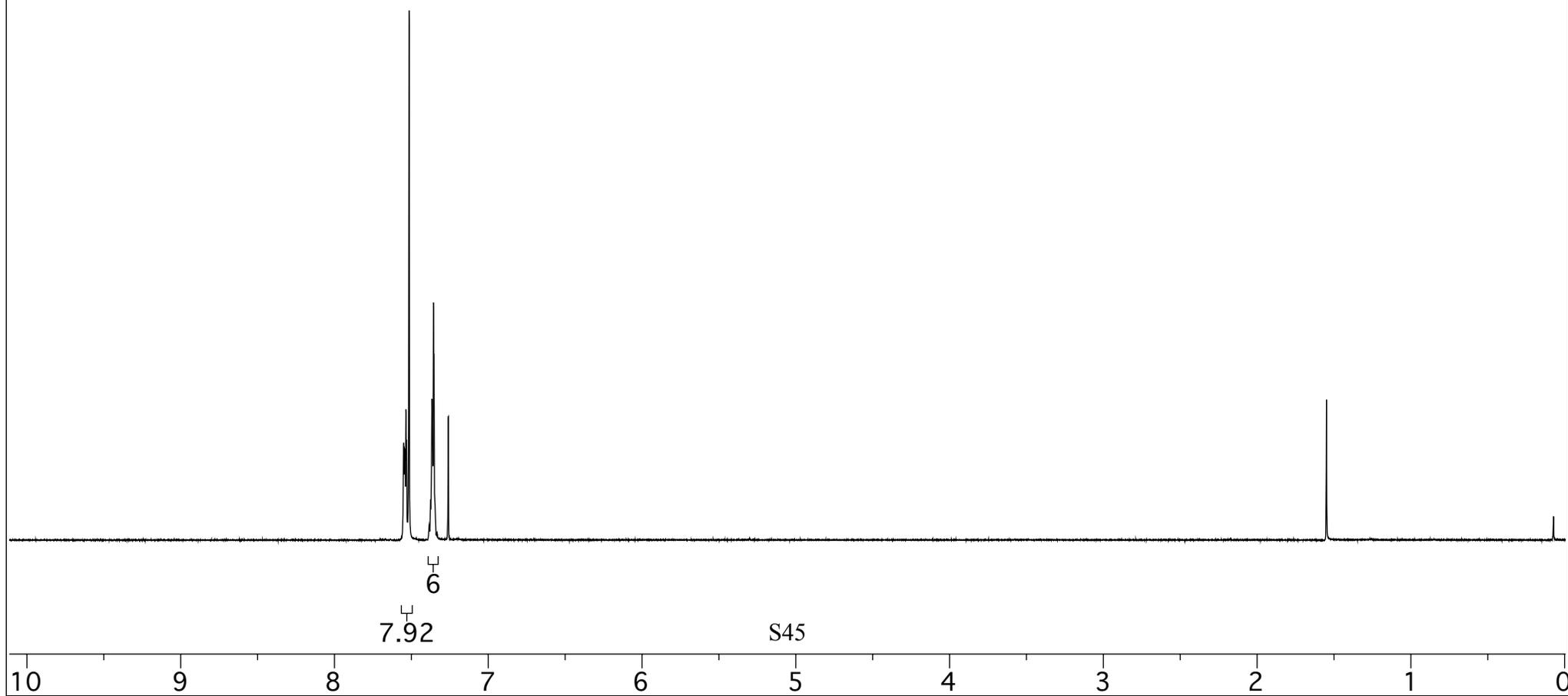
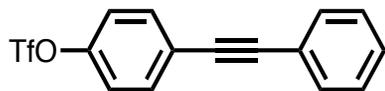
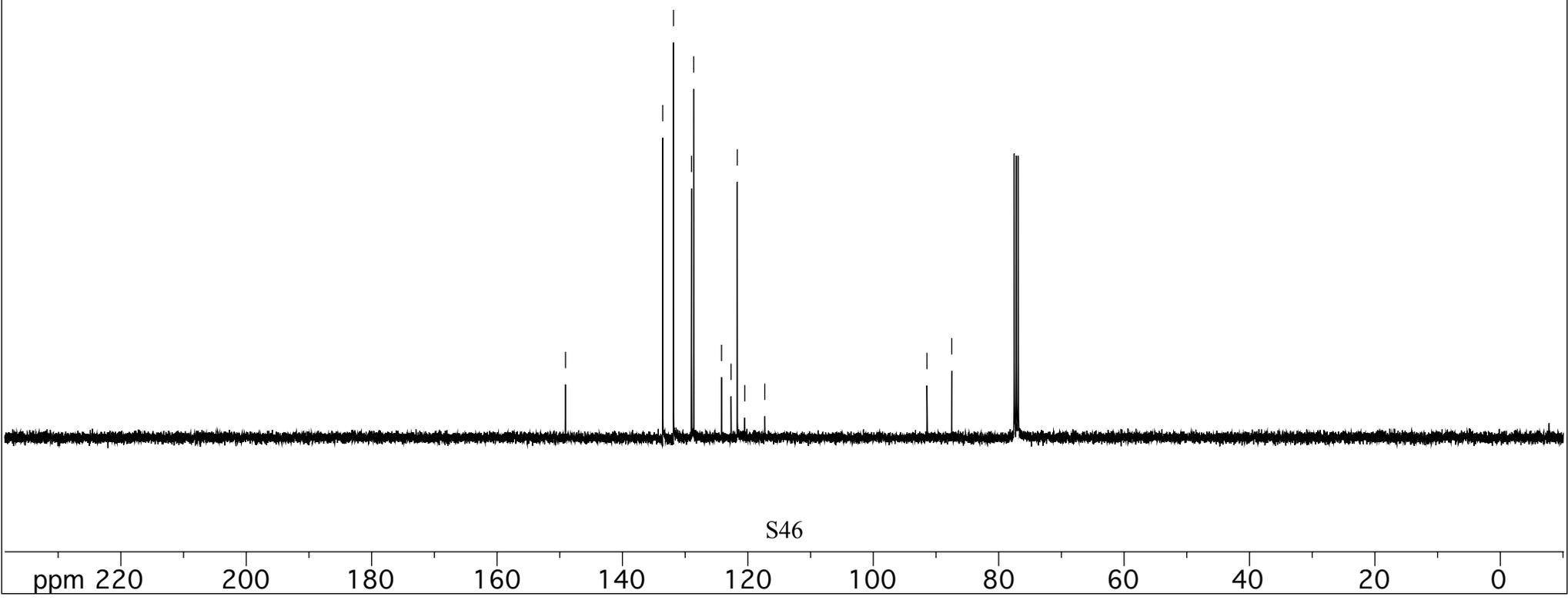


Table 3 Entry 17



149.09  
133.58  
131.87  
128.99  
128.64  
124.20  
122.68  
121.69  
120.49  
117.30

91.44  
87.49



S46

Table 3 Entry 17

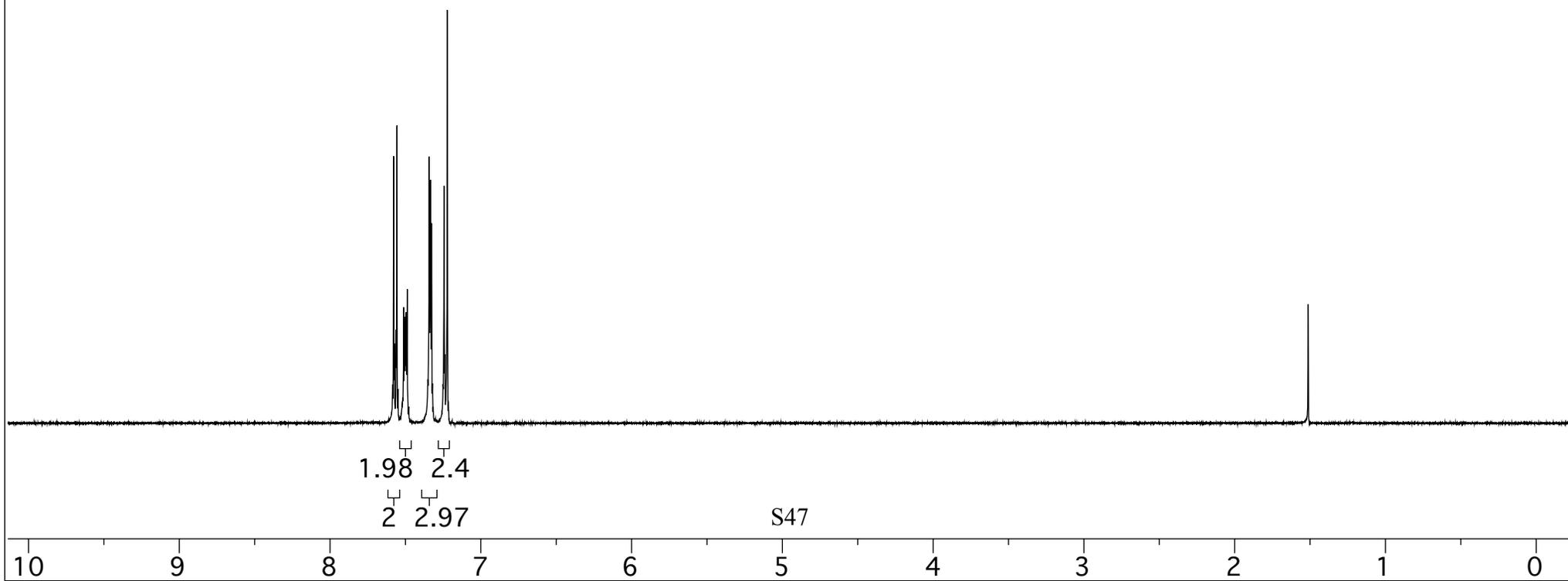
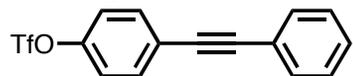
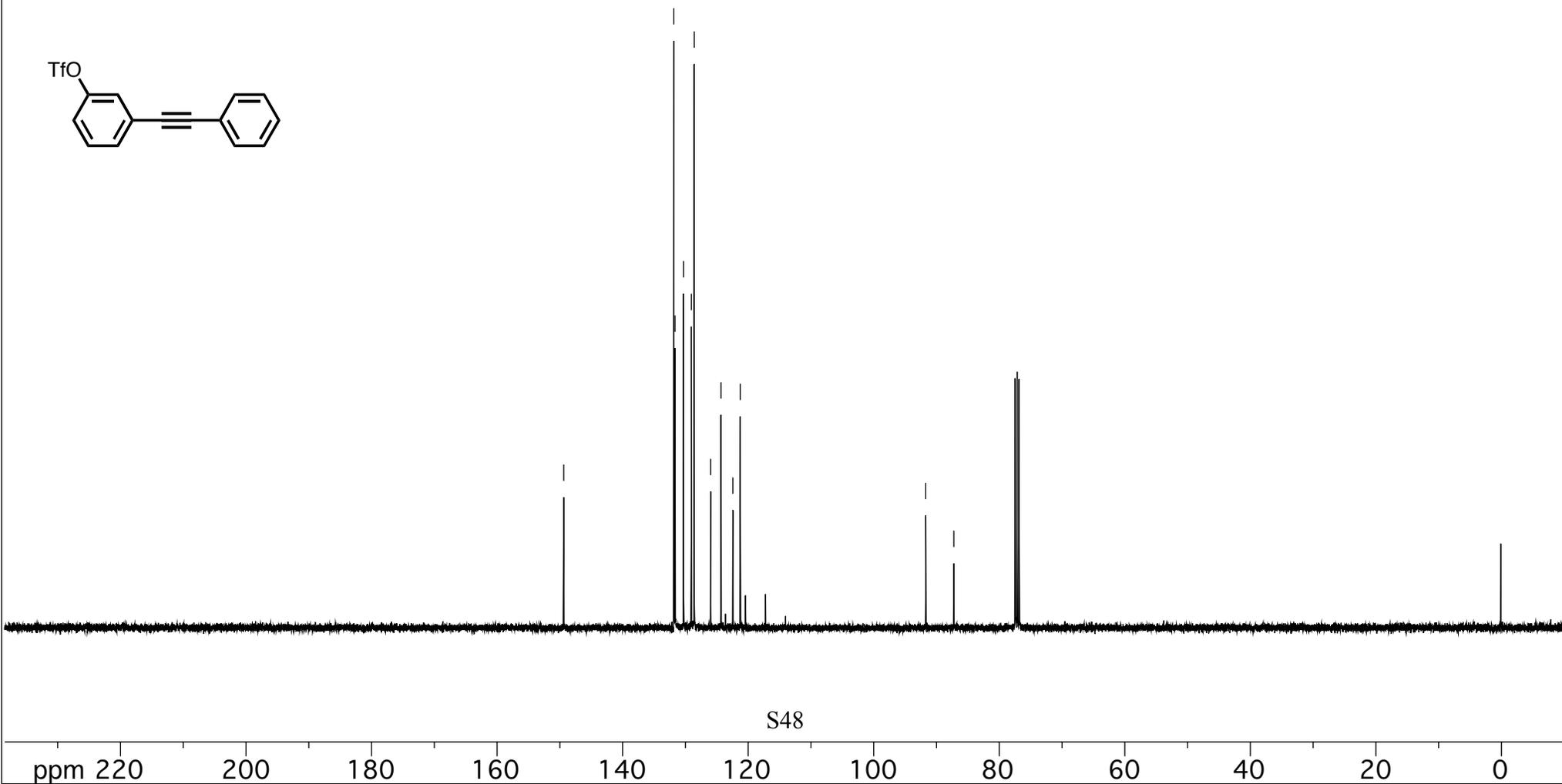
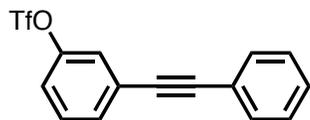


Table 3 Entry 18

149.38  
131.85  
131.66  
130.30  
129.06  
128.60  
125.98  
124.33  
122.43  
121.26

91.71  
87.24



S48

Table 3 Entry 18

