Supporting Information for

Gold-Catalyzed Cyclization of 1,6-Diynyl Dithioacetals via 1,7-Carbene Transfer and Aromatic C-H Functionalization

Wei Xu, Ming Chen, Ning Sun and Yuanhong Liu*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, People's Republic of China

Fax: (+86) 021-64166128, E-mail: yhliu@sioc.ac.cn

Contents:

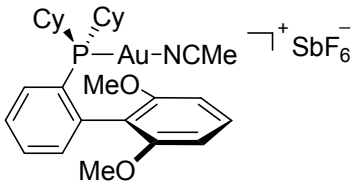
General Methods. All reactions were carried out under argon unless noted. DCM, DCE were

distilled from CaH_2. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). MeCN was purified using Innovative Technology Solvent Purifier. Unless noted, all commercial reagents were used without further purification. (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (catalyst **A**) was purchased from Aldrich Chemical Company. Gold complexes **B**-**D** and **F** were prepared by stirring the [Au(L)Cl][1] complex and $AgSbF_6$ in MeCN at room temperature for 12 h or overnight.[2] The structure of complex **C** was confirmed by X-ray diffraction. Gold complex **E** was prepared by published method.[3] $AgSbF_6$ was purchased from Stream Chemical Company.

^1H and ^{13}C NMR spectra were recorded at room temperature or 60 ^oC in $CDCl_3$ (containing 0.03% TMS), on Varian XL-400 MHz spectrometer, Agilent 400 MHz NMR spectrometer, or Agilent vnmrs 600 MHz spectrometer. ^1H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference in $CDCl_3$; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra was obtained by using Agilent Technologies 5973N. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. IR spectra were obtained by using a Nicolet iS10 spectrometer. Melting points were measured using a SGW-4 microscopic melting point apparatus and were uncorrected. Single crystal X-ray diffraction data were collected at 293(2) K for catalyst **C**, **2f**, **2h**, **2o**, **2o** and **2o'**, **6** and **17**, 273.15 K for **2g** on Bruker SMART diffractometer or Bruker APEX-II diffractometer.

Synthesis and characterization of SPhosAu(MeCN)SbF_6 (catalyst C).[2]

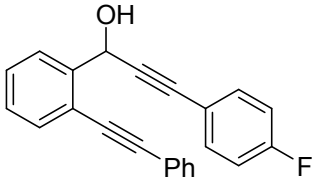
To a flask were added SphosAuCl (1.286 g, 2.0 mmol), $AgSbF_6$ (687.2 mg, 2.0 mmol) and MeCN (20 mL). The reaction mixture was stirred at room temperature overnight. Then the mixture was filtered through a pad of celite twice and the filter cake was washed with MeCN. The solvent was reduced under the reduced pressure, and pentane was added resulting in the immediate precipitation of a white solid. The solid was filtered and dried under the reduced pressure to give SPhosAu(MeCN)SbF_6 (1.5 g, 85%) as a white solid.



catalyst C

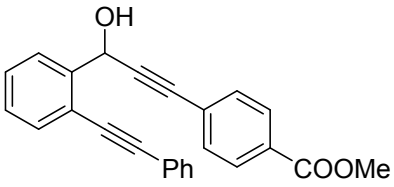
^{1}H NMR($CDCl_3$, 400 MHz) δ = 7.62-7.48 (m, 4H), 7.18(s, 1H), 6.76(d, *J* =8.0 Hz, 2H), 3.70 (s, 6H), 2.46(s, 3H), 2.24-2.21 (m, 2H), 1.97(s, 2H), 1.82-1.69 (m, 8H), 1.39-1.23 (m, 10H), ^{13}C NMR($CDCl_3$, 100 MHz) δ = 157.55, 142.10 (d, $^{2}J_{C\text{-}P}$ = 11.5 Hz), 133.10 (d, $^{2}J_{C\text{-}P}$ = 9.6 Hz), 131.76, 131.74, 131.71, 131.65, 130.15, 127.67 (d, $^{3}J_{C\text{-}P}$ = 8.3 Hz), 124.28 (d, $^{1}J_{C\text{-}P}$ = 30.3 Hz), 118.84, 118.41 (d, $^{3}J_{C\text{-}P}$ = 6.7 Hz), 104.18, 55.48, 35.94 (d, $^{1}J_{C\text{-}P}$ = 35.6 Hz), 30.71 (d, $^{3}J_{C\text{-}P}$ = 2.8 Hz), 29.19, 26.38, 26.37(d, $^{2}J_{C\text{-}P}$ = 27.0 Hz), 25.48, 2.12; ^{31}P NMR ($CDCl_3$) δ = 35.45. Anal. Calcd for $C_{28}H_{38}AuF_6NO_2PSb$: C, 38.03; H, 4.33; N, 1.58. Found: C, 37.75; H, 4.29; N, 1.55.

1,6-Diyne-4-en-3-ols (**s-1**) were synthesized according to the published method,[4] and the characterization of new compounds are shown as follows:



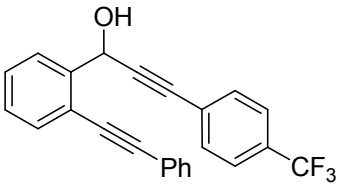
s-1b

3-(4-Fluorophenyl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (s-1b). White solid. M.p. 102.5-103.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.58-7.54 (m, 3H), 7.42-7.30 (m, 7H), 6.97-6.93 (m, 2H), 6.13 (d, *J* = 4.8 Hz, 1H), 2.94 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.53 (d, $^{1}J_{C\text{-}F}$ = 249.6 Hz), 142.11, 133.63 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 132.48, 131.52, 128.90, 128.63, 128.39, 128.35, 128.29, 126.66, 122.70, 121.34, 118.51 (d, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 115.48 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 95.08, 87.99 (d, $^{5}J_{C\text{-}F}$ = 1.5 Hz), 86.53, 85.35, 63.66. IR (film): 3353, 3056, 3029, 2215, 1600, 1506, 1493, 1443, 1380, 1229, 1185, 1155, 1093, 1015, 963, 834, 818, 755, 690 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{15}OF$ $[M]^{+}$: 326.1107, found 326.1114.



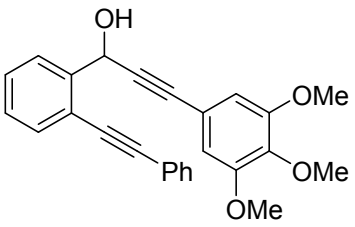
s-1d

Methyl 4-(3-hydroxy-3-(2-(phenylethynyl)phenyl)prop-1-yn-1-yl)benzoate (s-1d). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.76 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.59-7.54 (m, 3H), 7.48-7.46 (m, 2H), 7.42-7.32 (m, 5H), 6.16 (s, 1H), 3.89 (s, 3H), 3.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.47, 141.86, 132.51, 131.62, 131.51, 129.65, 129.36, 128.93, 128.67, 128.41, 128.38, 127.16, 126.67, 122.67, 121.37, 95.17, 91.33, 86.47, 85.49, 63.66, 52.21. IR (film): 3415, 3056, 3026, 2995, 2948, 2213, 1703, 1604, 1492, 1435, 1405, 1363, 1308, 1274, 1176, 1108, 1018, 965, 858, 755, 690 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{18}O_3$ $[M]^+$: 366.1256, found 366.1263.



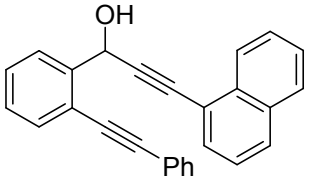
s-1e

1-(2-(Phenylethynyl)phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol (**s-1e**). Yellow solid. M.p. 74.1-75.4 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.57-7.49 (m, 7H), 7.39-7.29 (m, 5H), 6.15 (d, *J* = 4.8 Hz, 1H), 3.12 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.77, 132.52, 131.92, 131.50, 130.10 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 128.93, 128.69, 128.42, 128.39, 126.61, 126.25, 125.10 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 123.79 (q, $^{1}J_{C\text{-}F}$ = 271 Hz), 122.65, 121.35, 95.25, 90.80, 86.47, 84.92, 63.61. IR (film): 3362, 3059, 3026, 2212, 1615, 1563, 1493, 1443, 1404, 1320, 1166, 1123, 1105, 1067, 1016, 964, 841, 813, 754, 712, 689 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{15}OF_3$ $[M]^+$: 376.1075, found 376.1071.



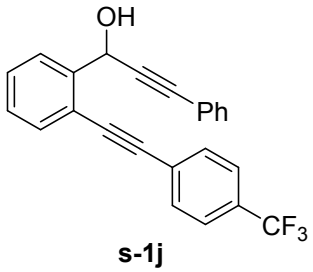
s-1g

1-(2-(Phenylethynyl)phenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-ol (s-1g). Light orange solid. M.p. 94.3-95.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.59-7.57 (m, 3H), 7.41-7.31 (m, 5H), 6.65 (s, 2H), 6.13 (d, *J* = 4.0 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 6H), 2.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.87, 142.26, 138.78, 132.49, 131.51, 128.86, 128.60, 128.39, 128.20, 126.60, 122.78, 121.24, 117.45, 108.82, 95.15, 87.42, 86.68, 86.30, 63.73, 60.85, 55.94. IR (film): 3426, 3056, 2995, 2936, 2836, 1578, 1504, 1449, 1411, 1344, 1237, 1128, 1060, 1033, 1001, 834, 758, 691 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{22}O_4$ $[M]^+$: 398.1518, found 398.1529.



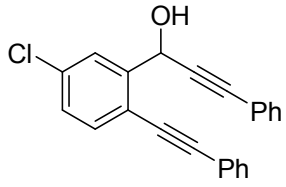
s-1h

3-(Naphthalen-1-yl)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (s-1h). White solid. M.p. 97.2-98.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.86-7.78 (m, 3H), 7.68-7.56 (m, 4H), 7.48-7.32 (m, 8H), 6.31 (s, 1H), 2.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.35, 133.24, 133.02, 132.62, 131.62, 130.66, 128.97, 128.95, 128.63, 128.40, 128.30, 128.15, 126.76, 126.69, 126.35, 126.17, 125.07, 122.76, 121.39, 120.09, 95.21, 93.22, 86.68, 84.61, 64.03. IR (film): 3366, 3057, 2218, 1600, 1586, 1493, 1443, 1396, 1277, 1186, 1100, 1054, 1025, 949, 800, 773, 756, 689, 669 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{18}O$ $[M]^+$: 358.1358, found 358.1352.



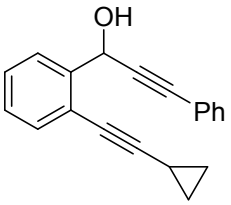
s-1j

3-Phenyl-1-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (s-1j). White solid. M.p. 113.0-114.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 1H), 7.63-7.61 (m, 2H), 7.56-7.54 (m, 3H), 7.43-7.37 (m, 3H), 7.33-7.22 (m, 4H), 6.14 (d, J = 5.6 Hz, 1H), 2.99 (d, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.41, 132.60, 131.74, 131.66, 130.08 (q, $^{2}J_{C\text{-}F}$ = 30.7 Hz), 129.43, 128.56, 128.30, 128.23, 126.73, 126.60 (q, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 125.25 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.83 (q, $^{1}J_{C\text{-}F}$ = 271 Hz), 122.29, 120.72, 93.42, 88.96, 88.22, 86.53, 63.52. IR (film): 3343, 3064, 2218, 1614, 1489, 1404, 1322, 1168, 1125, 1105, 1065, 1016, 998, 964, 841, 755, 691 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{15}OF_3$ $[M]^+$: 376.1075, found 376.1083.



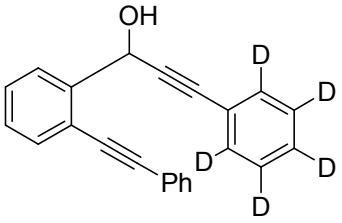
s-1n

1-(5-Chloro-2-(phenylethynyl)phenyl)-3-phenylprop-2-yn-1-ol (s-1n). Light yellow solid. M.p. 125.7-127.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 2.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.49-7.43 (m, 3H), 7.36-7.33 (m, 3H), 7.31-7.24 (m, 4H), 6.11 (s, 1H), 2.86 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.88, 134.78, 133.53, 131.75, 131.56, 128.80, 128.66, 128.44, 128.26, 126.99, 122.50, 122.15, 119.87, 95.92, 87.57, 86.79, 85.61, 63.19. IR (film): 3367, 3081, 3056, 3034, 2212, 1590, 1490, 1472, 1442, 1405, 1262, 1179, 1108, 1087, 1031, 998, 968, 878, 822, 753, 722, 688 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{15}OCl$ $[M]^+$: 342.0811, found 342.0813.



s-1q

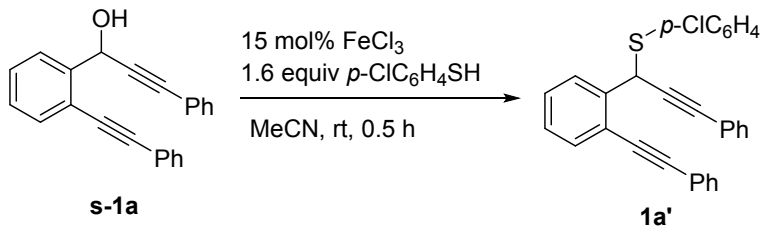
1-(2-(Cyclopropylethynyl)phenyl)-3-phenylprop-2-yn-1-ol (s-1q). Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.47-7.40 (m, 3H), 7.32-7.22 (m, 5H), 6.00 (d, *J* = 6.0 Hz, 1H), 2.92 (d, *J* = 6.0 Hz, 1H), 1.53-1.46 (m, 1H), 0.91-0.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.15, 132.49, 131.68, 128.41, 128.18, 128.11, 128.03, 126.61, 122.51, 122.01, 99.53, 88.26, 86.22, 72.92, 63.76, 8.81, 0.29. IR (film): 3395, 3059, 3009, 2337, 2228, 1702, 1598, 1489, 1443, 1363, 1228, 1185, 1090, 1030, 997, 952, 840, 812, 754, 690 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{16}O$ $[M]^+$: 272.1201, found 272.1205.



s-1a-*d*$_5$

3-(Phenyl-*d*$_5$)-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (s-1a-*d*$_5$). Yellow oil. M.p. 73.3-74.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.54-7.52 (m, 3H), 7.35-7.24 (m, 5H), 6.15 (d, *J* = 5.6 Hz, 1H), 3.10 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.15, 132.32, 131.45, 131.21(t, $J_{C\text{-}D}$ = 25.1 Hz), 128.79, 128.48, 128.28, 128.12, 127.59 (t, $J_{C\text{-}D}$ = 24.3 Hz), 126.60, 122.67, 122.14, 121.26, 94.96, 88.36, 86.57, 86.25, 63.52. IR (film): 3357, 3056, 3028, 2274, 2226, 1600, 1564, 1492, 1443, 1386, 1271, 1182, 1095, 1016, 963, 948, 831, 819, 754, 689 cm^{-1}. HRMS (EI) calcd for $C_{23}OH_{11}D_5$ $[M]^+$: 348.1515, found 348.1501.

Synthesis of (4-chlorophenyl)(3-phenyl-1-(2-(phenylethynyl)phen-yl)prop-2-yn-1-yl)-sulfane (1a').[5]

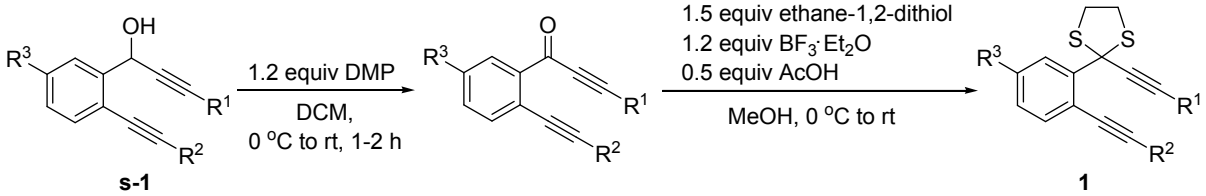


s-1a **1a'**

To a solution of 3-phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (**s-1a**) (616.8 mg, 2 mmol) in MeCN (20 mL) were added 4-chlorobenzenethiol (458.5 mg, 3.2 mmol) and ferric chloride (48.7 mg, 0.30 mmol) at room temperature. After stirring at the same temperature for 0.5 h, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: dichloromethane = 20:1 to 10:1 to 5:1) to afford **1a'** (853.1 mg, 98%) as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.47-7.45 (m, 2H), 7.40-7.37 (m, 4H), 7.31-7.15 (m, 10H), 5.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.41, 136.09, 134.78, 132.12, 131.62, 131.47, 131.43, 128.61, 128.47, 128.34, 128.32, 128.27, 128.20, 127.88, 127.722, 122.716, 122.55, 121.95, 95.44, 87.17, 86.83, 86.68, 42.68. IR (film): 3078, 3058, 3026, 2215, 1598, 1571, 1491, 1474, 1442, 1387, 1272, 1158, 1093, 1070, 1028, 1014, 914, 825, 752, 688, 668 cm^{-1}. HRMS (EI) calcd for $C_{29}H_{19}SCl$ [M]$^+$: 434.0896, found 434.0900.

General procedure for the synthesis of 1,6-diynyl dithioacetals 1.

Typical procedure for the synthesis of 2-(phenylethynyl)-2-(2-(phenylethynyl)phenyl) -1,3-dithiolane (1a).



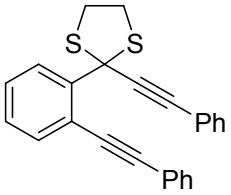
s-1 **1**

For **1a**, $R^1 = R^2$ = Ph, R^3 = H

To a solution of the alcohol **s-1a** (925.1 mg, 3 mmol) in dichloromethane (20 mL) was added Dess-Martin periodinane (1.53 g, 3.6 mmol) at 0 °C. The resulting solution was warmed up to room temperature and stirred for 1 h. After the starting material was consumed, the mixture was filtered through silica gel, quenched with saturated sodium bicarbonate solution, extracted with dichloromethane, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the residue

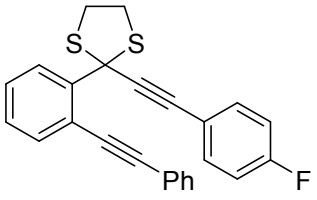
was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the ketone as a yellow oil.

To a solution of above ketone in methanol (20 mL) were added acetic acid (90.1 mg, 1.5 mmol), boron trifluoride diethyl etherate (0.45 mL, 3.6 mmol) and ethane-1,2-dithiol (0.38 mL, 4.5 mmol) at 0 ^{o}C.[6] The resulting solution was warmed up to room temperature and stirred for 10 h. Then the mixture was quenched with 10% sodium hydroxide solution, extracted with dichloromethane, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1) to afford **1a** as a pale yellow oil, which could be solidified upon treating with ethyl acetate. Overall yield: 52% (601.3 mg).



1a

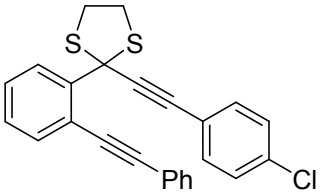
Pale yellow solid. M.p. 106.4-106.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.05 (m, 1H), 7.66-7.59 (m, 3H), 7.34-7.27 (m, 7H), 7.23 -7.15(m, 3H), 3.72-3.64 (m, 2H), 3.52-3.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.89, 134.33, 131.59, 131.35, 128.21, 128.05, 127.93, 127.87, 127.75, 125.58, 123.54, 122.77, 122.75, 98.89, 90.65, 89.03, 84.88, 61.93, 40.87. IR (film): 3076, 3056, 2920, 2329, 1711, 1597, 1570, 1491, 1466, 1441, 1278, 1069, 1030, 916, 882, 754, 719, 690 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{18}S_2$ $[M]^+$: 382.0850, found 382.0852.



1b

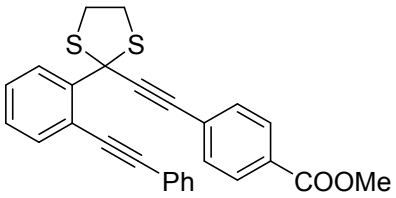
2-((4-Fluorophenyl)ethynyl)-2-(2-(phenylethynyl)phenyl)-1,3-dithiolane (**1b**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 20:1 to 10:1) afforded the title product as a yellow oil in 49% overall yield (3 mmol scale, 587.7

mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 1H), 7.65-7.60 (m, 3H), 7.32-7.23 (m, 7H), 6.87-6.82 (m, 2H), 3.67-3.60 (m, 2H), 3.48-3.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.14 (d, $^1J_{C\text{-}F}$ = 247.7 Hz), 142.91, 134.16, 133.38 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 131.20, 128.23, 128.18, 127.77 (d, $^2J_{C\text{-}F}$ = 14.8 Hz), 125.34, 123.37, 122.58, 118.74 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 115.25, 115.03, 98.78, 90.30, 89.00, 83.56, 61.75, 40.77. IR (film): 3058, 2921, 2341, 2215, 1599, 1506, 1492, 1468, 1441, 1279, 1230, 1155, 1092, 1014, 952, 835, 756, 691 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}FS_2$ [M]$^+$: 400.0756, found 400.0753.



1c

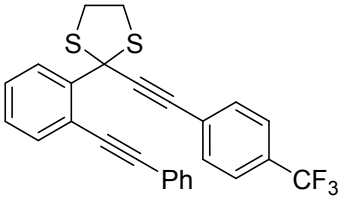
2-((4-Chlorophenyl)ethynyl)-2-(2-(phenylethynyl)phenyl)-1,3-dithiolane (**1c**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 5:1) afforded the title product as a yellow oil in 47% overall yield (3 mmol scale, 587.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 1H), 7.65-7.60 (m, 3H), 7.31-7.27 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.69-3.61 (m, 2H), 3.49-3.42 (m 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.74, 134.09, 133.86, 132.65, 131.14, 128.21, 128.15, 127.82, 127.69, 125.28, 123.29, 122.53, 121.11, 98.78, 91.61, 88.96, 83.37, 61.65, 40.75. IR (film): 3054, 2921, 2212, 1597, 1489, 1466, 1441, 1397, 1277, 1091, 1014, 882, 828, 754, 730, 690 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}S_2Cl$ [M]$^+$: 416.0460, found 416.0455.



1d

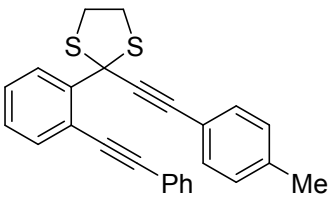
Methyl 4-((2-(2-(phenylethynyl)phenyl)-1,3-dithiolan-2-yl)ethynyl)benzoate (**1d**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 4:1 to 2:1) afforded the title product as a light yellow oil in 53% overall yield (1.7 mmol scale, 400.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 1H), 7.85-7.82 (m, 2H), 7.66-7.59 (m, 3H),

7.37-7.36 (m, 1H), 7.35-7.33 (m, 1H), 7.32-7.27 (m, 5H), 3.85 (s, 3H), 3.68-3.61 (m, 2H), 3.50-3.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.41, 142.55, 134.26, 131.49, 131.27, 129.20, 129.09, 128.35, 128.26, 127.96, 127.88, 127.53, 125.47, 123.37, 122.71, 98.95, 93.77, 88.91, 83.84, 61.67, 52.07, 40.91. IR (film): 3051, 2948, 2923, 2212, 1720, 1603, 1492, 1435, 1404, 1308, 1275, 1191, 1175, 1107, 1019, 858, 768, 756, 691 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{20}O_2S_2$ [M]$^+$: 440.0905, found 440.0899.



1e

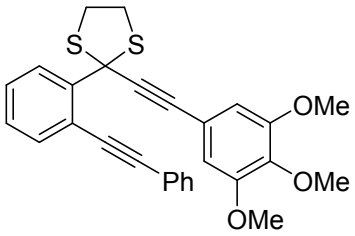
2-(2-(Phenylethynyl)phenyl)-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3-dithiolane (**1e**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 20:1 to 15:1 to 10:1 to 8:1) afforded the title product as an orange oil in 54% overall yield (2 mmol scale, 486.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.10 (m, 1H), 7.73-7.68 (m, 3H), 7.48-7.43 (m, 4H), 7.38-7.34 (m, 5H), 3.71-3.66 (m, 2H), 3.51-3.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.57, 134.16, 131.69, 131.18, 129.50 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 128.33, 128.21, 127.91, 127.84, 126.56 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 126.44 (q, $^1J_{C\text{-}F}$ = 270.6 Hz), 125.37, 124.76 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.34, 122.67, 98.90, 93.35, 88.97, 83.12, 61.57, 40.81. IR (film): 3054, 2918, 2212, 1614, 1594, 1492, 1442, 1405, 1320, 1276, 1166, 1122, 1104, 1067, 1014, 950, 913, 880, 841, 754, 715, 690 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{17}F_3S_2$ [M]$^+$: 450.0724, found 450.0723.



1f

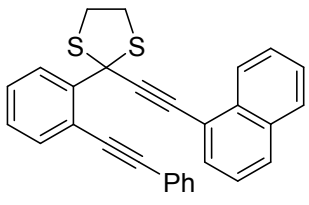
2-(2-(Phenylethynyl)phenyl)-2-(p-tolylethynyl)-1,3-dithiolane (**1f**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1

to 8:1 to 6:1 to 4:1) afforded the title product as a light yellow solid in 41% overall yield (3 mmol scale, 485.1 mg). M.p. 111.1-112.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 1H), 7.65-7.60 (m, 3H), 7.31-7.20 (m, 7H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.69-3.61 (m, 2H), 3.49-3.41 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.05, 138.13, 134.36, 131.52, 131.39, 128.72, 128.22, 127.86, 127.71, 125.63, 123.62, 122.78, 119.73, 98.89, 89.84, 89.07, 85.15, 62.08, 40.88, 21.38. IR (film): 3055, 3026, 2920, 2862, 2216, 1960, 1904, 1597, 1569, 1509, 1492, 1467, 1441, 1416, 1278, 1241, 1178, 1105, 1069, 1024, 950, 916, 881, 816, 754, 737, 690 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}S_2$ $[M]^+$: 396.1006, found 396.1001.



1g

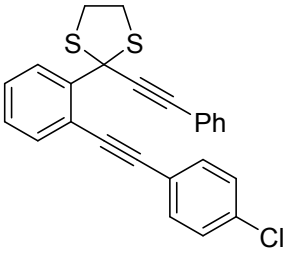
2-(2-(Phenylethynyl)phenyl)-2-((3,4,5-trimethoxyphenyl)ethynyl)-1,3-dithiolane (**1g**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: tetrahydrofuran = 8:1 to 5:1 to 2:1) afforded the title product as a yellow solid in 28% overall yield (3 mmol scale, 392.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 1H), 7.70-7.63 (m, 3H), 7.33-7.28 (m, 5H), 6.51 (s, 2H), 3.76 (s, 3H), 3.70-3.62 (m, 2H), 3.54 (s, 6H), 3.49-3.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.51, 143.22, 138.25, 134.02, 131.24, 128.16, 127.78, 127.54, 125.00, 123.43, 122.44, 117.58, 108.46, 98.49, 89.44, 89.20, 84.33, 61.70, 60.56, 55.50, 40.61. IR (film): 3059, 2998, 2962, 2936, 2837, 2215, 1575, 1502, 1492, 1463, 1431, 1410, 1348, 1235, 1183, 1126, 1069, 1030, 1002, 836, 757, 734, 692 cm^{-1}. HRMS (EI) calcd for $C_{28}H_{24}O_3S_2$ $[M]^+$: 472.1167, found 472.1173.



1h

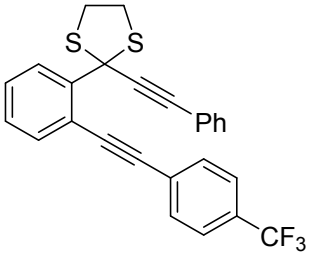
2-(Naphthalen-1-ylethynyl)-2-(2-(phenylethynyl)phenyl)-1,3-dithiolane (**1h**). Column

chromatography on neutral aluminum oxide (eluent: petroleum ether: toluene = 2:1 to 3:2) afforded the title product as an orange oil in 49% overall yield (3 mmol scale, 630.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.10-8.08 (m, 1H), 7.69-7.59 (m, 5H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.28-7.12 (m, 7H), 3.65-3.57 (m, 2H), 3.44-3.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.80, 134.39, 133.24, 132.83, 131.30, 130.40, 128.52, 128.18, 128.13, 127.93, 127.89, 127.77, 126.50, 126.29, 126.11, 125.63, 124.90, 123.46, 122.75, 120.39, 98.92, 95.77, 89.19, 83.12, 62.22, 40.90. IR (film): 3056, 2921, 2215, 1597, 1585, 1505, 1492, 1466, 1441, 1395, 1279, 1264, 1158, 1104, 1017, 972, 947, 911, 875, 800, 774, 754, 735, 690 cm^{-1}.HRMS (EI) calcd for $C_{29}H_{20}S_2$ $[M]^+$: 432.1006, found 432.1009.



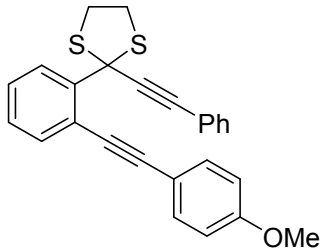
1i

2-(2-((4-Chlorophenyl)ethynyl)phenyl)-2-(phenylethynyl)-1,3-dithiolane (**1i**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1 to 8:1 to 5:1 to 3:1) afforded the title product as a light yellow oil in 40% overall yield (3 mmol scale, 498 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.63-7.61 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.33-7.16 (m, 9H), 3.69-3.61 (m, 2H), 3.48-3.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.08, 134.26, 134.21, 132.57, 131.55, 128.57, 128.17, 128.14, 128.02, 127.80, 125.59, 122.70, 122.42, 122.06, 97.66, 90.61, 89.99, 84.87, 61.93, 40.86. IR (film): 3056, 2921, 2315, 2215, 1597, 1489, 1441, 1397, 1278, 1088, 1031, 1014, 828, 754, 729, 690 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}S_2Cl$ $[M]^+$: 416.0460, found 416.0466.



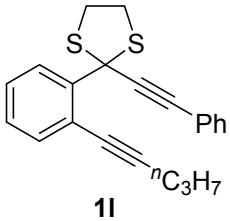
1j

2-(Phenylethynyl)-2-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-1,3-dithiolane (**1j**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 20:1 to 10:1) afforded the title product as a light orange oil in 49% overall yield (2.4 mmol scale, 528.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.64 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.34-7.25 (m, 4H), 7.20-7.12 (m, 3H), 3.66-3.58 (m, 2H), 3.45-3.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.33, 134.39, 131.50, 131.45, 129.68 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 128.50, 128.20, 128.00, 127.81, 127.28, 126.57 (q, $^{1}J_{C\text{-}F}$ = 271.0 Hz), 125.61, 125.08 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 122.58, 121.99, 97.19, 91.37, 90.57, 84.93, 61.85, 40.84. IR (film): 3054, 2920, 2215, 1613, 1489, 1467, 1442, 1403, 1320, 1280, 1167, 1122, 1104, 1064, 1014, 841, 753, 702, 690 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{17}F_3S_2$ $[M]^+$: 450.0724, found 450.0722.



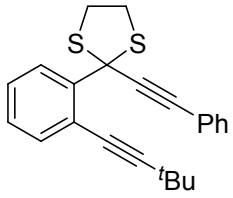
1k

2-(2-((4-Methoxyphenyl)ethynyl)phenyl)-2-(phenylethynyl)-1,3-dithiolane (**1k**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1 to 6:1) afforded the title product as an orange oil in 40% overall yield (3 mmol scale, 495.7 mg) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 1H), 7.64-7.60 (m, 1H), 7.57-7.54 (m, 2H), 7.35-7.27 (m, 4H), 7.24-7.15 (m, 3H), 6.86-6.82 (m, 2H), 3.81 (s, 3H), 3.71-3.63 (m, 2H), 3.51-3.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.60, 142.67, 134.08, 132.88, 131.64, 128.05, 127.97, 127.73, 127.53, 125.51, 123.11, 122.86, 115.78, 113.90, 99.10, 90.71, 87.84, 84.74, 62.01, 55.24, 40.85. . IR (film): 3054, 2921, 2835, 2377, 2349, 2290, 2212, 1738, 1605, 1568, 1511, 1490, 1466, 1441, 1303, 1288, 1249, 1174, 1147, 1106, 1030, 832, 755, 691, 664 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}OS_2$ $[M]^+$: 412.0956, found 412.0970.



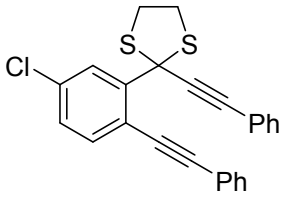
1l

2-(2-(Pent-1-yn-1-yl)phenyl)-2-(phenylethynyl)-1,3-dithiolane (**1l**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: toluene= 3:1) afforded the title product as a light yellow oil in 29% overall yield (3 mmol scale, 301.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 1H), 7.51-7.49 (m, 1H), 7.42-7.40 (m, 2H), 7.25-7.18 (m, 5H), 3.62-3.55 (m, 2H), 3.42-3.34 (m, 2H), 2.45 (t, J = 7.2 Hz, 2H), 1.68-1.58 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.44, 134.51, 131.47, 127.96, 127.91, 127.51, 126.99, 125.30, 123.46, 122.95, 100.45, 90.66, 84.42, 79.84, 61.89, 40.66, 22.03, 21.71, 13.71. IR (film): 3057, 2961, 2927, 2869, 2229, 1597, 1489, 1469, 1441, 1338, 1277, 1070, 1031, 755, 721, 691 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}S_2$ $[M]^+$: 348.1006, found 348.1016.



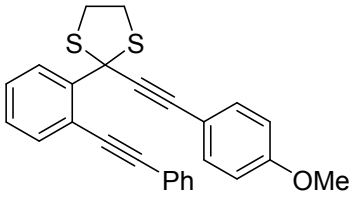
1m

2-(2-(3,3-Dimethylbut-1-yn-1-yl)phenyl)-2-(phenylethynyl)-1,3-dithiolane (**1m**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1 to 8:1) afforded the title product as a light orange oil in 49% overall yield (3 mmol scale, 527.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 1H), 7.50-7.48 (m, 1H), 7.42-7.40 (m, 2H), 7.25-7.18 (m, 5H), 3.61-3.53 (m, 2H), 3.38-3.30 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.94, 134.41, 131.61, 127.97, 127.90, 127.41, 126.97, 125.00, 123.46, 122.99, 107.86, 90.60, 84.06, 78.40, 62.06, 40.48, 30.39, 28.23. IR (film): 3054, 2967, 2922, 2856, 2236, 2204, 1597, 1490, 1467, 1441, 1361, 1295, 1278, 1201, 1069, 1031, 921, 851, 753, 720, 690, 662 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{22}S_2$ $[M]^+$: 362.1163, found 362.1165.



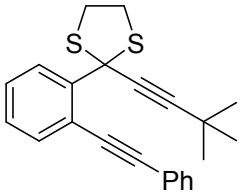
1n

2-(5-Chloro-2-(phenylethynyl)phenyl)-2-(phenylethynyl)-1,3-dithiolane (**1n**). Column chromatography on basic aluminum oxide (eluent: toluene) afforded the title product as a light yellow oil in 30% overall yield (3 mmol scale, 375.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 0.8 Hz, 1H), 7.61-7.55 (m, 3H), 7.32-7.15 (m, 9H), 3.69-3.61 (m, 2H), 3.48-3.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.16, 135.35, 133.76, 131.62, 131.37, 128.46, 128.27, 128.23, 127.99, 127.79, 125.98, 123.24, 122.52, 121.31, 99.81, 89.73, 88.07, 85.19, 61.39, 41.03. IR (film): 3078, 3058, 2921, 2329, 2215, 1596, 1582, 1491, 1458, 1442, 1391, 1278, 1168, 1107, 1069, 908, 825, 755, 727, 689 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}S_2Cl$ $[M]^+$: 416.0460, found 416.0453.



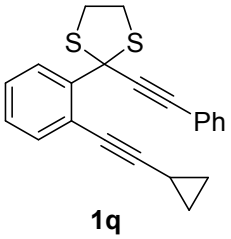
1o

2-((4-Methoxyphenyl)ethynyl)-2-(2-(phenylethynyl)phenyl)-1,3-dithiolane (**1o**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 4:1 to 3:1 to 3:2) afforded the title product as a light yellow oil in 36% overall yield (3 mmol scale, 444 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.65-7.61 (m, 3H), 7.33-7.25 (m, 7H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.70-3.63 (m, 2H), 3.50-3.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ159.26, 143.17, 134.17, 132.92, 131.24, 128.14, 127.78, 127.57, 125.39, 123.46, 122.58, 114.73, 113.48, 98.74, 89.08, 89.05, 84.75, 62.03, 54.97, 40.75. IR (film): 3056, 2959, 2920, 2831, 2210, 1604, 1568, 1508, 1492, 1465, 1441, 1292, 1277, 1248, 1172, 1106, 1033, 832, 756, 691 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}OS_2$ $[M]^+$: 412.0956, found 412.0949.



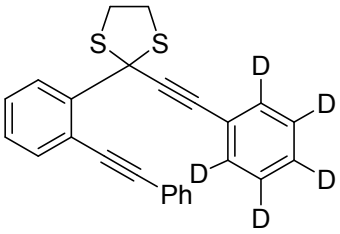
1p

2-(3,3-Dimethylbut-1-yn-1-yl)-2-(2-(phenylethynyl)phenyl)-1,3-dithiolane (**1p**). Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 20:1) afforded the title product as a yellow oil in 78% overall yield (3 mmol scale, 852.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 1H), 7.67-7.60 (m, 3H), 7.39-7.23 (m, 5H), 3.64-3.56 (m, 2H), 3.42-3.34 (m, 2H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.08, 134.28, 131.37, 128.18, 128.13, 127.62, 127.37, 125.46, 123.86, 122.65, 98.66, 93.82, 89.32, 79.67, 61.93, 40.58, 30.58, 27.55. IR (film): 3051, 2967, 2921, 2218, 1598, 1492, 1468, 1441, 1416, 1361, 1264, 1202, 1100, 1069, 1026, 952, 916, 881, 851, 827, 754, 738, 690 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{22}S_2$ $[M]^+$: 362.1163, found 362.1166.



1q

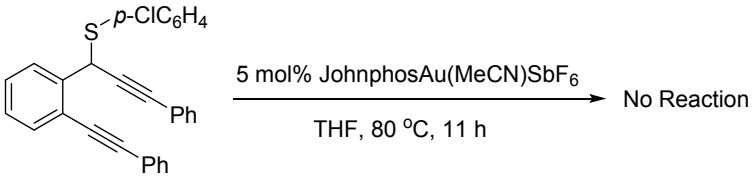
2-(2-(Cyclopropylethynyl)phenyl)-2-(phenylethynyl)-1,3-dithiolane (1q). Column chromatography on basic aluminum oxide (petroleum ether: dichloromethane = 15:1 to 10:1 to 5:1) afforded the title product as a light yellow solid in 26% overall yield (3 mmol scale, 271 mg). M.p. 107.3-108.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 1H), 7.50-7.44 (m, 3H), 7.28-7.19 (m, 5H), 3.66-3.59 (m, 2H), 3.46-3.39 (m, 2H), 1.53-1.49 (m, 1H), 0.94-0.90 (m, 2H), 0.83-0.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.75, 134.28, 131.58, 128.04, 127.97, 127.53, 126.94, 125.17, 123.40, 122.92, 103.28, 90.72, 84.23, 75.01, 61.90, 40.65, 8.07, 0.80. IR (film): 3058, 3009, 2920, 2228, 1597, 1489, 1471, 1441, 1278, 1179, 1070, 1053, 1030, 953, 869, 826, 810, 754, 719, 691 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{18}S_2$ $[M]^+$: 346.0850, found 346.0846.



1a-d_5, D = 98%

Column chromatography on basic aluminum oxide (petroleum ether: dichloromethane = 5:1 to 4:1 to 3:1) afforded the title product as a yellow oil in 33% overall yield (3 mmol scale, 388.1mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 1H), 7.65-7.59 (m, 3H), 7.32-7.25 (m, 5H), 3.67-3.59 (m, 2H), 3.47-3.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.90, 134.32, 131.34, 131.17 (t, $J_{C\text{-}D}$ = 23.6 Hz), 128.22, 128.21, 127.87, 127.75, 127.42 (t, $J_{C\text{-}D}$ = 24.3 Hz), 125.56, 123.52, 122.71, 98.88, 90.62, 89.01, 84.81, 61.91, 40.87. IR (film): 3056, 2956, 2920, 2285, 2269, 2216, 1954, 1597, 1562, 1491, 1467, 1441, 1418, 1384, 1319, 1278, 1264, 1214, 1159, 1069, 1026, 952, 916, 881, 832, 819, 754, 736, 690 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{13}D_5S_2$ $[M]^+$: 387.1164, found 387.1165.

Reaction of 1a' in the presence of gold catalyst.

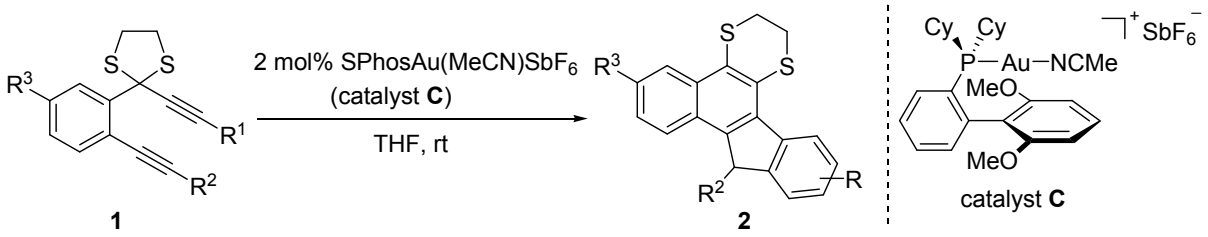


1a'

To a sealable Schlenk tube were added **1a'** (0.2 mmol, 87.0 mg), THF (4 mL) and catalyst **A** (0.01 mmol, 7.7 mg). The tube was sealed and the mixture was stirred at 80 °C for 11 h. No reaction was observed as monitored by thin-layer chromatography. When the reaction was carried out in the presence of 5 mol% of catalyst **C**, no reaction occurred after stirring the reaction mixture at 80 °C for 11 h.

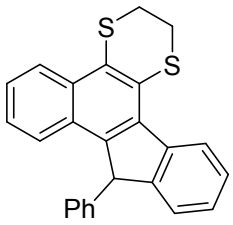
General procedure for the synthesis of benzo[*a*]fluorenes 2.

Typical procedure for the synthesis of 2a.



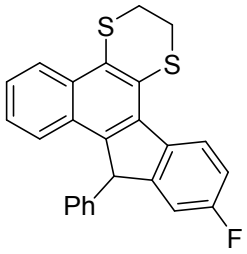
For **2a**, $R^1 = R^2 = Ph$, $R^3 = H$

To a Schlenk tube were added 1,6-diynyl dithioacetal **1a** (0.2 mmol, 76.5 mg), THF (4 mL) and catalyst **C** (0.004 mmol, 3.5 mg). After the reaction mixture was stirred at room temperature for 1 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1) to afford **2a** in 90% yield (68.9 mg) as a light yellow solid.



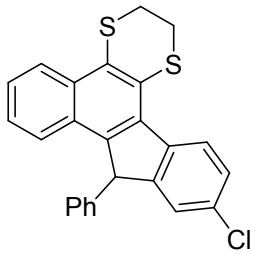
2a

9-Phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2a). M.p. 194.0-195.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 7.6 Hz, 1H), 8.32 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.39-7.33 (m, 2H), 7.28-7.13 (m, 6H), 7.05 (d, J = 6.4 Hz, 2H), 5.22 (s, 1H), 3.48-3.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.20, 141.81, 141.31, 140.66, 137.44, 131.72, 130.25, 128.86, 128.59, 127.93, 127.81, 126.79, 126.71, 126.69, 125.88, 125.74, 125.29, 124.59, 124.56, 123.68, 53.72, 30.97, 29.93. IR (film): 3060, 2917, 2342, 1711, 1597, 1546, 1494, 1461, 1415, 1360, 1342, 1288, 1220, 1174, 1124, 1074, 1030, 780, 754, 732, 701, 668 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{18}S_2$ $[M]^+$: 382.0850, found 382.0856.



2b

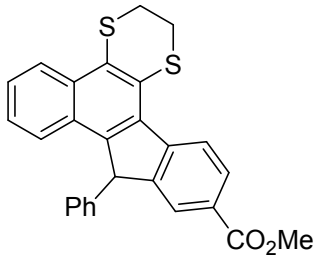
11-Fluoro-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2b). Following the general procedure, **1b** (0.3 mmol, 120.2 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 1.5 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1 to 8:1 to 6:1) afforded the title product in 88% yield (105.8 mg) as a light yellow solid. M.p. 223.2-224.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, J = 8.4, 5.6 Hz, 1H), 8.32 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.25-7.17 (m, 4H), 7.06-7.02 (m, 3H), 6.98-6.95 (m, 1H), 5.18 (s, 1H), 3.52-3.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.04 (d, $^{1}J_{C\text{-}F}$ = 245.2 Hz), 160.81, 151.61 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 141.18, 141.05 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 136.70, 136.64 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 131.54, 130.62, 129.04, 128.11, 127.86, 127.77, 127.02, 125.90, 125.64 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 125.14, 123.73, 113.71 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 112.00 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 53.64, 31.03, 29.98. IR (film): 3056, 3020, 2918, 1591, 1548, 1494, 1473, 1451, 1371, 1345, 1294, 1276, 1269, 1211, 1168, 1120, 950, 877, 855, 826, 817, 748, 739, 726, 698 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}FS_2$ $[M]^+$: 400.0756, found 400.0757.



2c

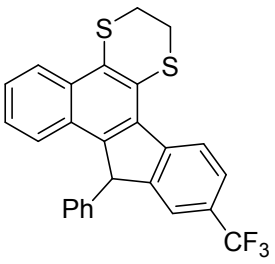
11-Chloro-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2c). Following the general procedure, **1c** (0.3 mmol, 125.1 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 1 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1 to 10:1) afforded the title product in 77% yield (96.5 mg) as a light yellow solid. M.p. 259.1-260.6 ^{o}C. ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.26-7.20 (m, 5H), 7.04 (d, *J* = 6.8 Hz, 2H), 5.19 (s, 1H), 3.53-3.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.92, 141.23, 140.98, 139.24, 136.54, 132.54, 131.86, 130.77, 129.08, 128.30, 127.82, 127.08, 127.06, 126.16, 125.98, 125.49, 125.27, 124.90, 123.78, 53.62, 31.07, 29.98. IR (film): 3056, 3026, 2923, 1599, 1566, 1545, 1494, 1461, 1415, 1340, 1323, 1288, 1263, 1167, 1135, 1098, 1073, 1028, 921, 906, 886, 848, 829, 816, 752, 740, 700, 679 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}S_2Cl$ $[M]^+$: 416.0460, found 416.0458.



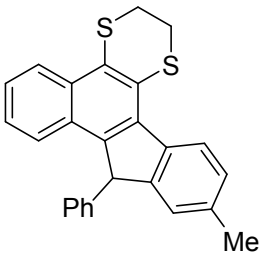
2d

Methyl 9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine-11-carboxylate (2d). Following the general procedure, **1d** (0.3 mmol, 132.2 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 4 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 10:1 to 5:1) afforded the title product in 65% yield (85.7 mg) as a light yellow solid. M.p. 243.2-244.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.89 (s, 1H) 7.61 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.27-7.18 (m, 4H), 7.06 (d, *J* = 6.8 Hz, 2H), 5.24 (s, 1H), 3.87 (s, 3H), 3.50- 3.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.10, 149.11, 145.24, 143.10, 140.90, 136.38, 132.16, 130.81, 129.04, 128.75, 128.68, 127.98, 127.84, 127.75, 127.01, 126.57, 126.02, 125.56, 125.45, 124.22, 123.74, 53.64, 52.00, 31.03, 29.92. IR (film): 2922, 2851, 1713, 1609, 1494, 1440, 1290, 1255, 1235, 1164, 1108, 754, 734, 702 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{20}O_2S_2$ $[M]^+$: 440.0905, found 440.0901.



2e

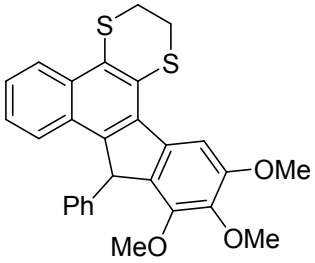
9-Phenyl-11-(trifluoromethyl)-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2e). Following the general procedure, **1e** (0.3 mmol, 135.2 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 2 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1 to 15:1) afforded the title product in 71% yield (96.1 mg) as a light yellowe solid. M.p. 225.0-226.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.46 (s, 1H), 7.40-7.37 (m, 1H), 7.23-7.15 (m, 4H), 7.01-6.99 (m, 2H), 5.09 (s, 1H), 3.46-3.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.44, 144.03 (q, $^{4}J_{C\text{-}F}$ = 1.6 Hz), 142.48, 140.60, 135.97, 132.09, 130.82, 129.10, 128.45, 128.26 (q, $^{2}J_{C\text{-}F}$ = 31.9 Hz), 127.79, 127.64, 127.15, 127.11 (q, $^{1}J_{C\text{-}F}$ = 268.3 Hz), 126.56, 126.03, 125.45, 124.58, 124.13 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.69, 121.15 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 53.66, 30.94, 29.84. IR (film): 3059, 3026, 2922, 2845, 2337, 1713, 1617, 1601, 1545, 1495, 1453, 1440, 1404, 1327, 1291, 1269, 1155, 1137, 1114, 1065, 1028, 926, 901, 853, 827, 758, 702, 679 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{17}F_3S_2$ $[M]^+$: 450.0724, found 450.0730.



2f

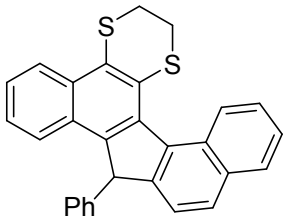
11-Methyl-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2f). Following the general procedure, **1f** (0.3 mmol, 119.0 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 1 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 85%

yield (101.0 mg) as a light yellow solid. M.p. 232.5-233.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.39-7.35 (m, 1H), 7.23-7.15 (m, 5H), 7.08-7.06 (m, 3H), 5.20 (s, 1H), 3.50-3.12 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.48, 142.07, 140.94, 138.06, 137.63, 136.65, 131.57, 130.05, 128.89, 128.38, 128.06, 127.90, 127.67, 126.69, 125.70, 125.67, 125.33, 125.20, 124.34, 123.70, 53.65, 31.00, 29.94, 21.43. IR (film): 3051, 3017, 2918, 2845, 1743, 1712, 1599, 1545, 1493, 1478, 1450, 1413, 1367, 1343, 1322, 1288, 1219, 1173, 1145, 1075, 1027, 813, 794, 750, 740, 724, 702, 668, 655 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}S_2$ $[M]^+$: 396.1006, found 396.1000.



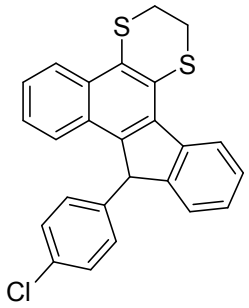
2g

10,11,12-Trimethoxy-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2g). Following the general procedure, **1g** (0.3 mmol, 141.8 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 4 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1 to 15:1) afforded the title product in 82% yield (115.6 mg) as a light yellow solid. M.p. 180.8-181.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.36-7.32 (m, 1H), 7.27-7.08 (m, 6H), 5.35 (s, 1H), 4.00 (s, 3H), 3.87 (s, 3H), 3.48-3.28 (m, 4H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.24, 149.53, 142.71, 141.53, 141.36, 136.90, 136.68, 134.92, 131.54, 130.78, 128.42, 128.35, 128.14, 127.85, 126.35, 125.84, 125.71, 124.86, 123.71, 104.67, 60.73, 59.86, 56.29, 51.78, 31.30, 30.16. IR (film): 3059, 3023, 2992, 2933, 2826, 1712, 1600, 1581, 1492, 1476, 1463, 1412, 1372, 1342, 1289, 1249, 1194, 1114, 1045, 1034, 992, 931, 832, 755, 729, 701 cm^{-1}. HRMS (EI) calcd for $C_{28}H_{24}O_3S_2$ $[M]^+$: 472.1167, found 472.1172.



2h

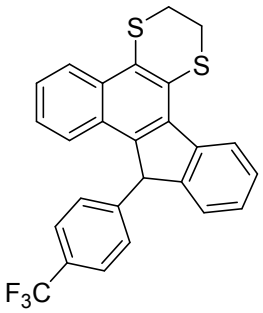
9-Phenyl-2,3-dihydro-9*H*-dibenzo[1,2:5,6]fluoreno[3,4-*b*][1,4]dithiine (2h). Following the general procedure, **1h** (0.3 mmol, 129.8 mg), DCE (6 mL) and catalyst **C** (0.015 mmol, 13.3 mg) were stirred for 4.5 h at room temperature. Column chromatography on neutral aluminum oxide (eluent: petroleum ether: ethyl acetate = 30:1 to 20:1) afforded the title product in 45% yield (58.1 mg) as a light yellow solid. M.p. 242.1-243.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78-7.72 (m, 2H), 7.59-7.42 (m, 4H), 7.32-7.28 (m, 1H), 7.23-7.17 (m, 3H), 7.12-7.10 (m, 2H), 5.39 (s, 1H), 3.60-3.50 (m, 2H), 3.19-3.13 (m, 1H), 3.06-2.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.33, 142.60, 140.90, 140.32, 136.12, 134.54, 133.89, 133.15, 132.86, 129.02, 128.79, 128.36, 128.34, 128.25, 128.08, 128.03, 127.00, 126.25, 126.00, 125.23, 125.11, 124.86, 124.18, 122.35, 54.86, 35.08, 33.52. IR (film): 3058, 3026, 2921, 2850, 1738, 1711, 1600, 1539, 1491, 1452, 1414, 1362, 1301, 1285, 1219, 1030, 955, 854, 809, 773, 753, 713, 700 cm^{-1}. HRMS (EI) calcd for $C_{29}H_{20}S_2$ $[M]^+$: 432.1006, found 432.1008.



2i

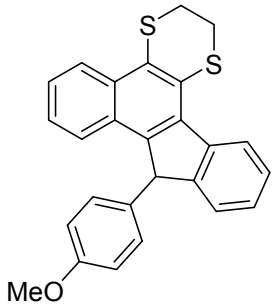
9-(4-Chlorophenyl)-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2i). Following the general procedure, **1i** (0.3 mmol, 125.1 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 1.5 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 79% yield (98.3 mg) as a light yellow solid. M.p. 202.6-204.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d,

J = 7.6 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.41-7.33 (m, 2H), 7.26-7.15 (m, 5H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 1H), 3.49-3.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.69, 140.74, 140.67, 140.45, 137.48, 132.44, 131.75, 130.54, 129.17, 129.08, 128.59, 127.78, 127.03, 126.80, 126.02, 125.90, 125.10, 124.73, 124.48, 123.79, 52.96, 30.96, 29.94. IR (film): 3060, 2919, 2845, 1949, 1893, 1546, 1488, 1461, 1407, 1370, 1340, 1320, 1287, 1263, 1167, 1124, 1090, 1032, 1014, 905, 871, 846, 832, 805, 780, 751, 735 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}S_2Cl$ [M]$^+$: 416.0460, found 416.0463.



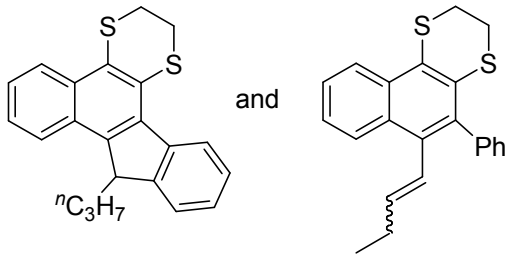
2j

9-(4-(Trifluoromethyl)phenyl)-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2j). Following the general procedure, **1j** (0.3 mmol, 135.2 mg), DCE (6 mL) and catalyst **C** (0.015 mmol, 13.3 mg) were stirred for 3 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 10:1 to 5:1) afforded the title product in 85% yield (115.3 mg) as a light yellow solid. M.p. 107.0-108.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 7.51-7.36 (m, 5H), 7.28-7.22 (m, 3H), 7.20-7.16 (m, 2H), 5.27 (s, 1H), 3.53-3.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.26, 146.15, 140.79, 140.44, 137.64, 131.78, 130.77, 129.03 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 128.62, 128.15, 127.72, 127.22, 126.89, 126.79 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 126.11, 126.05, 125.93 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.99, 124.85, 124.55, 123.87, 53.29, 30.98, 29.97. IR (film): 3065, 2918, 1712, 1616, 1546, 1500, 1463, 1418, 1361, 1322, 1288, 1221, 1163, 1120, 1107, 1066, 1032, 1018, 905, 854, 813, 773, 752, 729, 660 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{17}F_3S_2$ [M]$^+$: 450.0724, found 450.0727.



2k

9-(4-Methoxyphenyl)-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2k). Following the general procedure, **1k** (0.3 mmol, 123.8 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 2 h at room temperature. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30:1 to 20:1) afforded the title product in 82% yield (101.5 mg) as a light yellow solid. M.p. 204.5-205.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.38-7.31 (m, 2H), 7.26-7.17 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.14 (s, 1H), 3.66 (s, 3H), 3.42-3.28 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.25, 149.53, 141.46, 140.53, 137.25, 133.71, 131.71, 130.09, 128.76, 128.56, 127.95, 126.69, 126.66, 125.84, 125.67, 125.32, 124.54, 124.47, 123.64, 114.21, 55.03, 52.93, 30.93, 29.89. IR (film): 3056, 2998, 2956, 2912, 2829, 2335, 1712, 1609, 1545, 1508, 1460, 1439, 1413, 1340, 1320, 1299, 1288, 1250, 1174, 1107, 1033, 846, 811, 789, 777, 751, 722 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}OS_2$ $[M]^+$: 412.0956, found 412.0953.



2l **3l** (*E*/*Z* = 1.8:1)

9-Propyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2l) and (*E* or *Z*)-6-(but-1-enyl)-5-phenyl-2,3-dihydronaphtho[2,1-*b*][1,4]dithiine (3l). Following the general procedure, **1l** (0.3 mmol, 104.6 mg), THF (6 mL) and catalyst **C** (0.015 mmol, 13.3 mg) were stirred for 13 h at room temperature. Then the solution was filtered through celite, the solvent

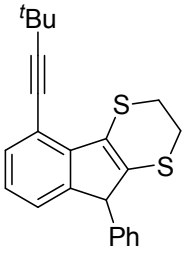
was evaporated under the reduced pressure and the residue was purified by recycling preparative HPLC to afford **3l** in 25% yield (26.1 mg) as a mixture of *E*/*Z* isomers and **2l** in 19% yield (19.5 mg) as a colorless oil.

For the characterization data of 2l:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.6 Hz, 1H), 8.41-8.37 (m, 1H), 8.06-8.02 (m, 1H), 7.58 (dd, *J* = 7.2, 0.4Hz, 1H), 7.53-7.48 (m, 2H), 7.42-7.31 (m, 2H), 4.40-4.37 (m, 1H), 3.50-3.31 (m, 4H), 2.31-2.22 (m, 1H), 2.14-2.04 (m, 1H), 0.92-0.82 (m, 2H), 0.71 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.76, 142.01, 141.70, 136.64, 131.57, 129.44, 129.02, 127.99, 126.56, 126.11, 125.82, 125.70, 124.70, 124.53, 124.08, 123.60, 46.59, 36.33, 31.19, 30.08, 17.65, 14.23. IR (film): 3062, 2954, 2923, 2868, 1712, 1544, 1498, 1462, 1415, 1360, 1338, 1287, 1219, 1172, 1156, 1125, 1032, 751, 659 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}S_2$ $[M]^+$: 348.1006, found 348.1002.

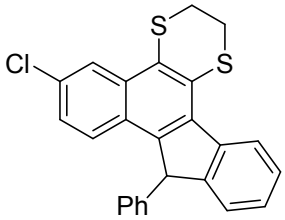
For the characterization data of 3l:

Light yellow oil. *E*/*Z* = 1.8:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz), 8.15 (d, *J* = 8.4 Hz), 7.97 (d, *J* = 8.4 Hz), 7.53-7.49 (m), 7.45-7.34 (m), 7.19 (d, *J* = 6.8 Hz), 6.17 (d, *J* = 16.4 Hz), 6.14 (d, *J* = 11.2 Hz), 5.62-5.55 (m), 3.34-3.30 (m), 3.23-3.20 (m), 2.06-1.99 (m), 1.71 (br), 0.84-0.77 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.85, 139.39, 139.34, 137.93, 137.56, 136.14, 132.42, 131.54, 131.50, 131.24, 130.63, 130.02, 129.83, 129.80, 129.52, 127.94, 127.91, 127.43, 127.26, 126.96, 126.69, 126.20, 126.14, 126.05, 125.76, 125.38, 125.26, 125.13, 125.04, 122.56, 30.60, 30.49, 28.67, 28.62, 26.32, 22.62, 13.42, 13.20. HRMS (EI) calcd for $C_{22}H_{20}S_2$ $[M]^+$: 348.1006, found 348.1001.



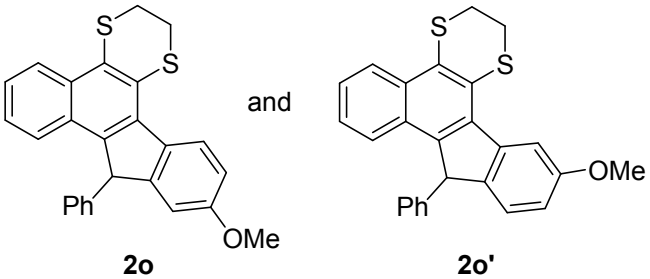
4m

5-(3,3-Dimethylbut-1-yn-1-yl)-9-phenyl-2,3-dihydro-9*H*-indeno[1,2-*b*][1,4]dithiine (4m). Following the general procedure, **1m** (0.3 mmol, 108.8 mg), DCE (6 mL) and catalyst **C** (0.015 mmol, 13.3 mg) were stirred for 2 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ketone = 100:1) afforded the title product in 87% yield (94.3 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 4H), 7.08-7.06 (m, 2H), 6.98-6.93 (m, 2H), 4.46 (s, 1H), 3.33-3.21 (m, 4H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.63, 143.09, 138.92, 133.55, 131.88, 128.69, 128.29, 127.31, 124.77, 124.33, 122.42, 113.99, 102.35, 77.63, 58.95, 30.54, 28.26, 26.87, 26.81. IR (film): 3060, 3026, 2967, 2923, 2865, 2221, 1713, 1600, 1577, 1521, 1493, 1462, 1452, 1417, 1361, 1294, 1211, 1074, 1030, 880, 804, 790, 771, 747, 701, 667 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{22}S_2$ [M]$^+$: 362.1163, found 362.1158.



2n

6-Chloro-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2n). Following the general procedure, **1n** (0.3 mmol, 125.1 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 1.5 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product in 73% yield (91.6 mg) as a light yellow solid. M.p. 199.5-201.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.30 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.28-7.14 (m, 6H), 7.01 (d, *J* = 6.8 Hz, 2H), 5.15 (s, 1H), 3.51-3.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.07, 141.51, 141.25, 140.35, 137.72, 132.51, 132.17, 130.22, 129.33, 128.99, 127.81, 126.94, 126.93, 126.78, 126.54, 126.22, 124.67, 124.61, 122.99, 53.71, 31.16, 29.90. IR (film): 3062, 3023, 2921, 2845, 1601, 1543, 1489, 1461, 1454, 1413, 1318, 1288, 1263, 1155, 1128, 1086, 1028, 983, 922, 874, 838, 802, 775, 752, 731, 700 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}S_2Cl$ [M]$^+$: 416.0460, found 416.0453.



2o **2o'**

11-Methoxy-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2o) and 12-Methoxy-9-phenyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2o').

Following the general procedure, **1o** (0.3 mmol, 123.8 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg) were stirred for 5 h at room temperature. Column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1 to 15:1) afforded the title product in an overall yield of 87% (107.1 mg, the ratio of **2o** and **2o'** was 1.8:1 determinted by ^{1}H NMR) as a light yellow solid.

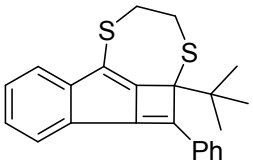
Following the general procedure, **1o** (0.5 mmol, 206.3 mg), THF (10 mL) and catalyst **A** (0.025 mmol, 19.3 mg) were stirred for 6 h at room temperature. Column chromatography on basic aluminum oxide (petroleum ether: ethyl acetate 10:1) afforded the title product in an overall yield of 82% (168.4 mg, the ration of **2o** and **2o'** was 1:1.4 determinted by ^{1}H NMR) as a light yellow solid.

For the characterization data of 2o:

M.p. 173.1-174.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.40-7.36 (m, 1H), 7.26-7.18 (m, 4H), 7.10-7.08 (m, 2H), 6.92-6.85 (m, 2H), 5.25 (s, 1H), 3.78 (s, 3H), 3.52-3.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.97, 151.38, 141.94, 140.43, 137.59, 133.70, 131.32, 130.25, 128.96, 128.11, 128.06, 127.89, 126.80, 125.77, 125.48, 125.40, 125.04, 123.76, 112.15, 110.80, 55.40, 53.81, 31.11, 30.06. IR (film): 3062, 3020, 2995, 2917, 2831, 1711, 1602, 1579, 1544, 1493, 1478, 1452, 1419, 1369, 1343, 1322, 1284, 1252, 1223, 1171, 1132, 1085, 1073, 1044, 1033, 1022, 937, 853, 821, 749, 725, 702 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}OS_2$ $[M]^+$: 412.0956, found 412.0960.

For the characterization data of 2o':

^{1}H NMR (400 MHz, CDCl3) δ 8.31 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 0.8 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.38-7.31 (m, 1H), 7.23-7.11 (m, 5H), 7.05-7.01 (m, 2H), 6.75 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.13 (s, 1H), 3.85 (s, 3H), 3.44-3.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.77, 142.49, 142.18, 141.92, 141.63, 137.23, 131.78, 130.62, 128.84, 128.69, 127.87, 127.71, 126.61, 125.93, 125.76, 125.28, 124.86, 123.72, 112.38, 110.46, 55.50, 52.99, 31.17, 30.10.

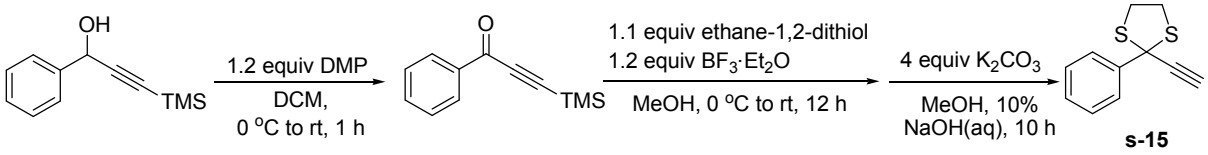


6

1a-(*tert*-Butyl)-1-phenyl-3,4-dihydro-1a*H*-2,5-dithiabenzo[*a*]cyclobuta[*cd*]azulene (6). Following the general procedure, **1p** (0.3 mmol, 109 mg), DCE (6 mL) and catalyst **C** (0.015 mmol, 13.3 mg) were stirred for 5 h at 50 °C. Column chromatography on basic aluminum oxide (eluent: petroleum ether: dichloromethane = 50:1 to 20:1) afforded the title product in 35% yield (38.1 mg) as a orange solid. M.p. 104.6-105.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.38-7.32 (m, 3H), 7.22 (dt, *J* = 7.2, 0.8 Hz, 1H), 3.50 (bs, 1H), 3.18 (bs, 1H), 3.01 (bs, 1H), 2.72 (bs, 1H), 1.27 (s, 9H). ^{13}C NMR (150.8 MHz, $CDCl_3$, 60 °C) δ 151.56, 148.48, 147.11, 146.15, 133.52, 130.05, 129.54, 128.99, 128.74, 128.55, 124.45, 123.62, 121.47, 113.18, 72.66, 38.70, 33.92, 32.71, 28.41. IR (film): 2957, 2922, 2864, 2853, 1536, 1488, 1478, 1459, 1443, 1423, 1390, 1360, 1301, 1274, 1194, 1107, 1061, 979, 915, 894, 753, 730, 689 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{22}S_2$ $[M]^+$: 362.1163, found 362.1157.

Synthesis of substrate 15.

1) Synthesis of 2-ethynyl-2-phenyl-1,3-dithiolane (s-15).



s-15

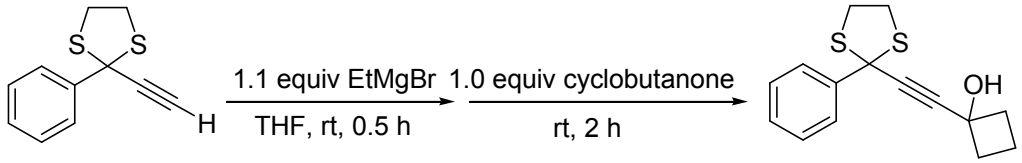
To a solution of the 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ol (3.065 g, 15 mmol) in dichloromethane (50 mL) was added Dess-Martin periodinane (7.63 g, 18 mmol) at 0 °C. The resulting solution was warmed up to room temperature and stirred for 1 h. After the starting

material was consumed, the mixture was filtered through silica gel, quenched with saturated sodium bicarbonate solution, extracted with dichloromethane, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the ketone 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-one (2.738 g, 90%) as a light yellow oil.

To a solution of above ketone (2.023 g, 10 mmol) in methanol (20 mL) were added boron trifluoride diethyl etherate (1.51 mL, 12 mmol) and ethane-1,2-dithiol (0.92 mL, 11 mmol) at 0 ^oC. The resulting solution was warmed up to room temperature and stirred for 12 h. Then the mixture was quenched with 10% sodium hydroxide solution, extracted with dichloromethane, washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure to afford an orange oil.

To a solution of the above crude product in methanol (20 mL) were added potassium carbonate (5.53 g, 40 mmol) and 5 mL 10% sodium hydroxide solution. The reaction mixture was stirred at room temperature for 10 h. After the reaction was complete, the mixture was quenched with hydrochloric acid (1 M), extracted with dichloromethane, washed with brine solution and dried over anhydrous Na_2SO_4. Then solvent was evaporated under the reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) to afford **s-15** (1.733 g, 84%) as a green oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.34-7.23 (m, 3H), 3.65-3.54 (m, 4H), 3.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.57, 128.15, 127.92, 127.17, 85.42, 60.89, 40.92. IR (film): 3283, 3056, 3026, 2925, 2107, 1594, 1493, 1446, 1418, 1314, 1276, 1177, 1033, 1010, 873, 694, 653 cm^{-1}. HRMS (EI) calcd for $C_{11}H_{10}S_2$ $[M]^+$: 206.0224, found 206.0219.

2) Synthesis of 15.

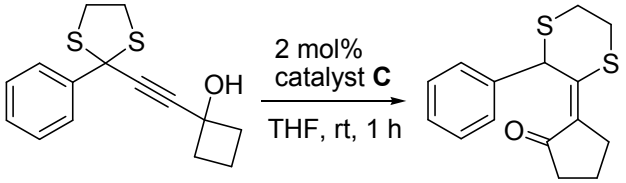


s-15, 1.2 equiv **15**

To a solution of **s-15** (495.2 mg, 2.4 mmol) in THF (20 mL) was added EtMgBr (0.73

mL, 2.2 mmol, 3 M) at room temperature. After the reaction mixture was stirred at the same temperature for 0.5 h, cyclobutanone (140.2 mg, 2 mmol) was added. The resulting solution was stirred for 2 h. Then the mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 4:1, with 1% triethylamine) to afford **15** (490.3 mg, 89%) as a yellow solid. M.p. 86.2-87.9 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.38-7.28 (m, 3H), 3.73-3.67 (m, 4H), 2.57-2.47 (m, 3H), 2.36-2.29 (m, 2H), 1.90-1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.49, 128.30, 128.17, 127.47, 90.25, 85.27, 67.92, 61.59, 41.21, 38.45, 13.01. IR (film): 3382, 2990, 2935, 1492, 1446, 1420, 1316, 1266, 1244, 1169, 1122, 1054, 1029, 957, 721, 695 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{16}OS_2$ $[M]^+$: 276.0643, found 276.0652.

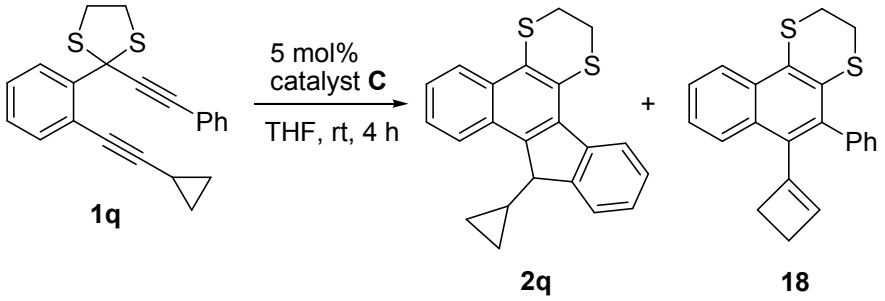
Synthesis of (*E*)-2-(3-Phenyl-1,4-dithian-2-ylidene)cyclopentan-1-one (17).



15 **17**

To a sealable Schlenk tube were added **15** (0.3 mmol, 82.9 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg). Then the tube was sealed and the reaction mixture was stirred at room temperature for 1 h. The solvent was filtered through celite, then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 40:1 to 20:1 to 5:1, with 1% triethylamine) to afford **17** in 74% yield (61.2 mg) as a light yellow solid. M.p. 113.1-115.0 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.25-7.21 (m, 1H), 6.84 (s, 1H), 3.18-3.10 (m, 1H), 2.89-2.75 (m, 4H), 2.69- 2.63 (m, 1H), 2.47-2.32 (m, 2H), 2.01-1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.82, 149.89, 139.71, 128.68, 128.37, 127.01, 126.66, 40.65, 39.21, 30.19, 26.81, 24.85, 19.03. IR (film): 3053, 3026, 2959, 2913, 2831, 1683, 1564, 1490, 1445, 1409, 1294, 1229, 1212, 1182, 1067, 1006, 815, 762, 697, 663 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{16}OS_2$ $[M]^+$: 276.0643, found 276.0642.

Transformation of 1q in the presence of gold catalyst C.



To a Schlenk tube were added **1q** (0.3 mmol, 104.0 mg), THF (6 mL) and catalyst **C** (0.015 mmol, 13.3 mg). After the reaction mixture was stirred at room temperature for 4 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on basic aluminum oxide (eluent: petroleum ether: ethyl acetate = 20:1) to afford product **2q** in 29% yield (29.8 mg) as a light yellow solid and **18** in 40% yield (42.0 mg) as a light yellow solid.

9-Cyclopropyl-2,3-dihydro-9*H*-benzo[1,2]fluoreno[3,4-*b*][1,4]dithiine (2q).

M.p. 131.1-133.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.0 Hz, 1H), 8.40-8.37 (m, 1H), 8.25-8.22 (m, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.51-7.48 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 4.01 (d, *J* = 8.0 Hz, 1H), 3.44-3.33 (m, 4H), 1.13-1.05 (m, 1H), 0.69-0.64 (m, 2H), 0.48-0.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.76, 142.66, 141.40, 136.33, 131.69, 129.90, 129.08, 128.45, 126.85, 126.00, 125.96, 125.83, 125.52, 124.56, 124.48, 123.91, 48.88, 31.21, 30.19, 16.12, 5.83, 3.18. IR (film): 3063, 3004, 2954, 2921, 2852, 2342, 1713, 1544, 1500, 1463, 1415, 1339, 1323, 1286, 1171, 1126, 1031, 751, 731, 700, 668 cm^{-1}.HRMS (EI) calcd for $C_{22}H_{18}S_2$ $[M]^+$: 346.0850, found 346.0840.

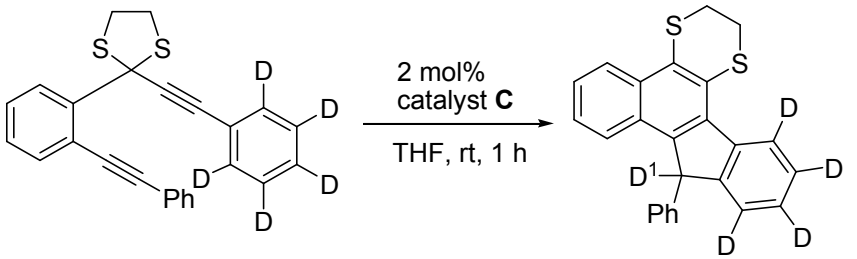
6-(Cyclobut-1-en-1-yl)-5-phenyl-2,3-dihydronaphtho[1,2-*b*][1,4]dithiine (18).

M.p. 179.4-181.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.26 (m, 2H), 7.54-7.40 (m, 5H), 7.27-7.24 (m, 2H), 5.96 (s, 1H), 3.34-3.31 (m, 2H), 3.23-3.21 (m, 2H), 2.32 (d, *J* = 2.8 Hz, 2H), 2.21-2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.98, 139.24, 137.44, 135.74, 131.33, 130.71, 130.49, 129.86, 129.19, 127.75, 127.53, 126.76, 126.51, 126.22, 125.55,

122.55, 34.48, 30.43, 28.68, 27.77. IR (film): 3053, 2958, 2921, 2853, 1698, 1533, 1488, 1440, 1417, 1358, 1321, 1290, 1262, 1243, 1178, 1099, 1070, 1028, 917, 865, 801, 757, 699, 684, 668 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{18}S_2$ $[M]^+$: 346.0850, found 346.0847.

Deuterium-labeling experiments.

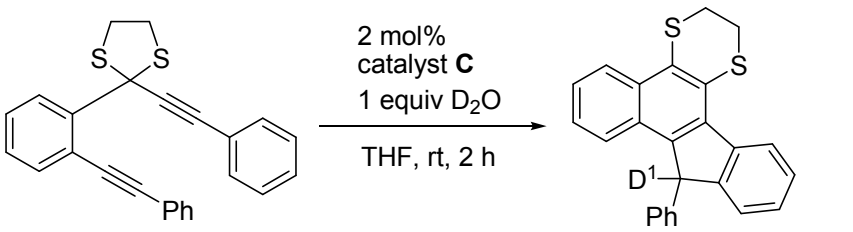
Reaction of 1a-d_5 in the presence of gold catalyst C.



1a-d_5, D = 98% **2a**-d_5, 71%, D^1 = 85%

To a Schlenk tube were added **1a-d_5** (0.3 mmol, 116.3 mg), THF (6 mL) and catalyst **C** (0.006 mmol, 5.3 mg). After the reaction mixture was stirred at room temperature for 1 h, the solvent was filtered through celite and evaporated under the reduced pressure. The ^{1}H NMR of the crude reaction mixture indicated that the deuterium incorporation of D^1 in **2a-d_5** was 85%. Then the crude product was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) to afford **2a-d_5** in 71% yield (82.6 mg) as a light yellow solid. The deuterium incorporation of D^1 in isolated **2a-d_5** was 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.26-7.17 (m, 4H), 7.07 (d, J = 6.8 Hz, 2H), 5.27 (s, 0.15H), 3.51-3.37 (m, 4H). ^{13}C NMR (150.8 MHz, $CDCl_3$) δ 149.14, 141.86, 141.38, 140.68, 137.61, 131.83, 130.42, 128.92, 128.71, 128.07, 127.86, 126.77, 126.41 (t, $J_{C\text{-}D}$ = 18.5 Hz), 126.21 (t, $J_{C\text{-}D}$ = 18.5 Hz), 125.94, 125.82, 125.35, 124.23 (t, $J_{C\text{-}D}$ = 22.3 Hz), 123.77, 53.82, 53.43 (t, $J_{C\text{-}D}$ = 19.0 Hz), 31.10, 30.08. IR (film): 3059, 3020, 2919, 2848, 1600, 1543, 1493, 1447, 1416, 1365, 1327, 1289, 1263, 1172, 1080, 1029, 893, 835, 818, 750, 737, 700 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{13}D_5S_2$ $[M]^+$: 387.1164, found 387.1158.

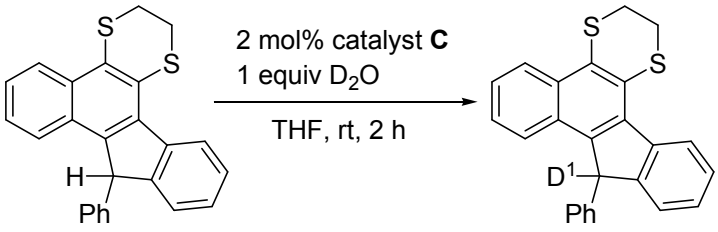
Reaction of 1a in the presence of 1.0 equiv of D_2O.



1a **2a**-d_1, 64%, D^1 = 20%

To a Schlenk tube were added **1a** (0.3 mmol, 114.8 mg), THF (6 mL), D_2O (0.3 mmol, 6.0 mg) and catalyst **C** (0.006 mmol, 5.3 mg). After the reaction mixture was stirred at room temperature for 2 h, the solvent was filtered through celite and evaporated under the reduced pressure. The ^1H NMR of the crude reaction mixture indicated that the deuterium incorporation of D^1 in **2a**-d_1 was 20%. Then the crude product was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) to afford **2a**-d_1 in 64% yield (73.1 mg) as a light yellow solid. The deuterium incorporation of D^1 in isolated **2a**-d_1 was 20%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.39-7.33 (m, 2H), 7.28-7.15 (m, 6H), 7.05 (d, J = 7.2 Hz, 2H), 5.21 (s, 0.8H), 3.44-3.32 (m, 4H). HRMS (EI) calcd for $C_{25}H_{17}DS_2$ $[M]^+$: 383.0913, found 383.0921.

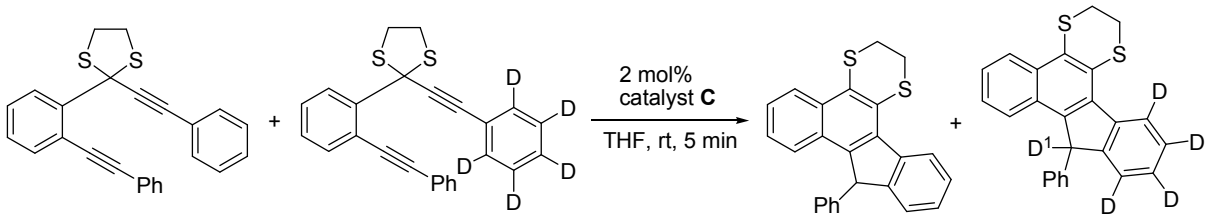
Reaction of 2a in the presence of 1.0 equiv of D_2O.



2a 90%, D^1 = 0%

To a Schlenk tube were added **2a** (0.3 mmol, 114.8 mg), THF (6 mL), D_2O (0.3 mmol, 6.0 mg) and catalyst **C** (0.006 mmol, 5.3 mg). After the reaction mixture was stirred at room temperature for 2 h, the solvent was filtered through celite and evaporated under the reduced pressure. The ^1H NMR of the crude reaction mixture indicated that no deuterium incorporation was found in **2a**. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) to afford **2a** in 90% yield (103.5 mg, 0% deuterium incorporation) as a light yellow solid.

Determination of Intermolecular Kinetic Isotope Effect (KIE).



1a **1a**-d_5 **2a**, 25% **2a**-d_5, 23%

To a Schlenk tube were added **1a** (0.15 mmol, 57.4 mg), **1a**-d_5 (0.15 mmol, 58.1 mg), THF (3 mL) and catalyst **C** (0.003 mmol, 2.7 mg). After the reaction mixture was stirred at room temperature for 5 minutes, the mixture was filtered through silica gel quickly and washed with ethyl acetate. Then the solvent was evaporated under the reduced pressure, and mesitylene (0.15 mmol, 20.8 μL) was added as the internal standard. The ^{1}H NMR of the crude reaction mixture indicated that the yield of **2a** was 25% and the yield of **2a**-d_5 was 23%. Then k_H/k_D = 1.1.

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2 a) C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2005, **44**, 6146; b) Y. Matsuda, S. Naoe, S. Oishi, N. Fujii and H. Ohno, *Chem.-Eur. J.*, 2015, **21**, 1463.

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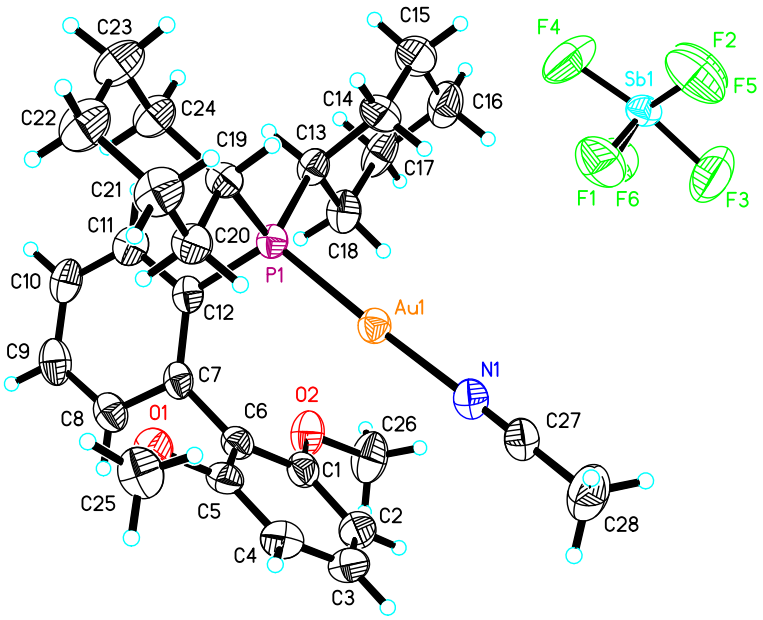

Figure S1. X-ray crystal structure of **catalyst C**

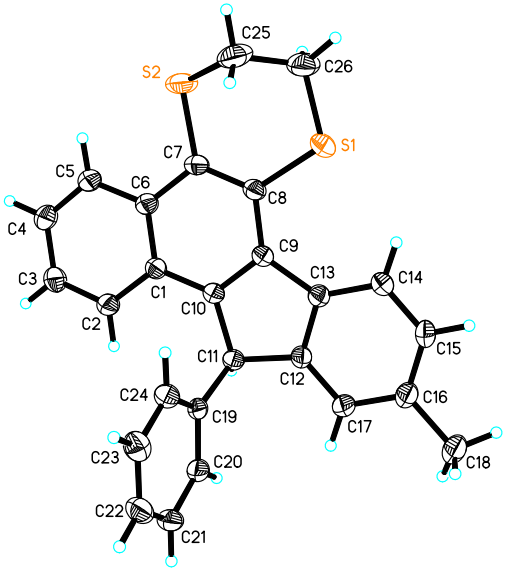

Figure S2. X-ray crystal structure of compound **2f**

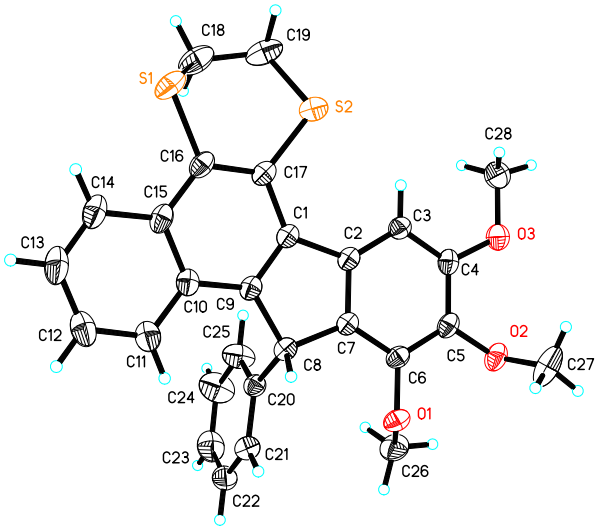

Figure S3. X-ray crystal structure of compound **2g**

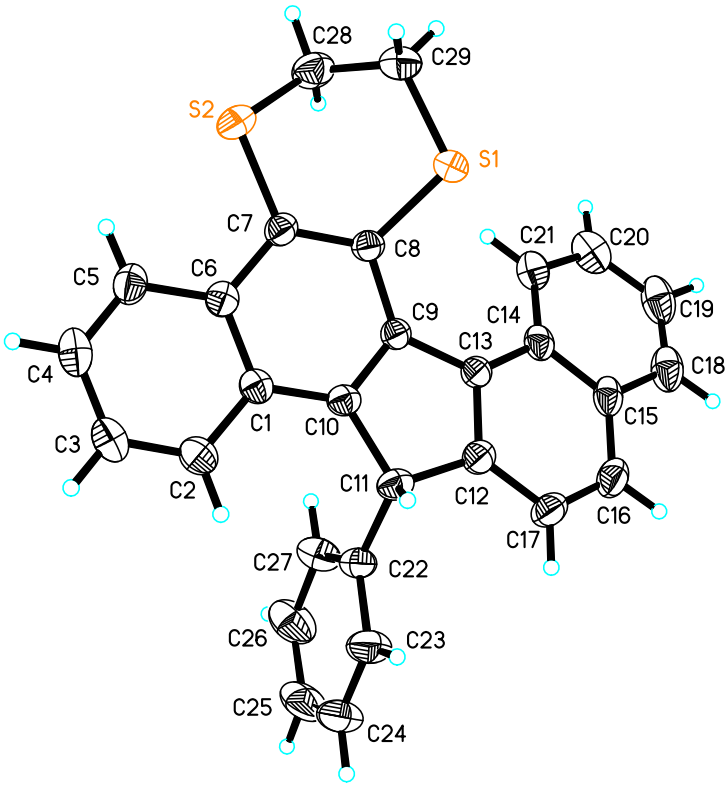

Figure S4. X-ray crystal structure of compound **2h**

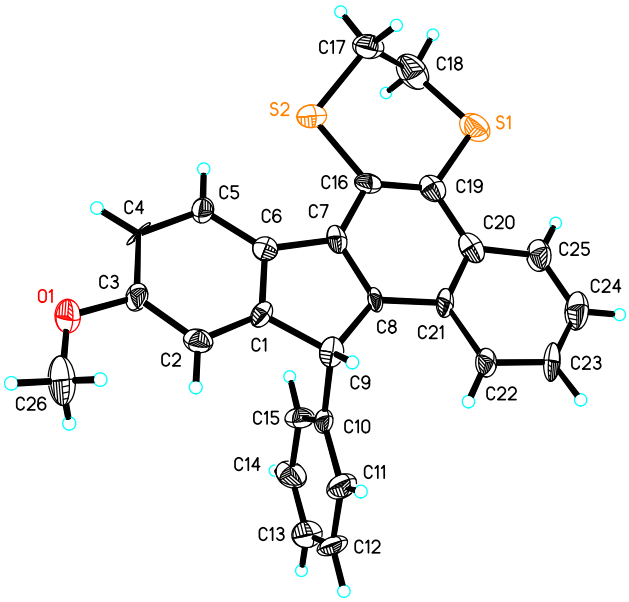

Figure S5. X-ray crystal structure of compound **2o**

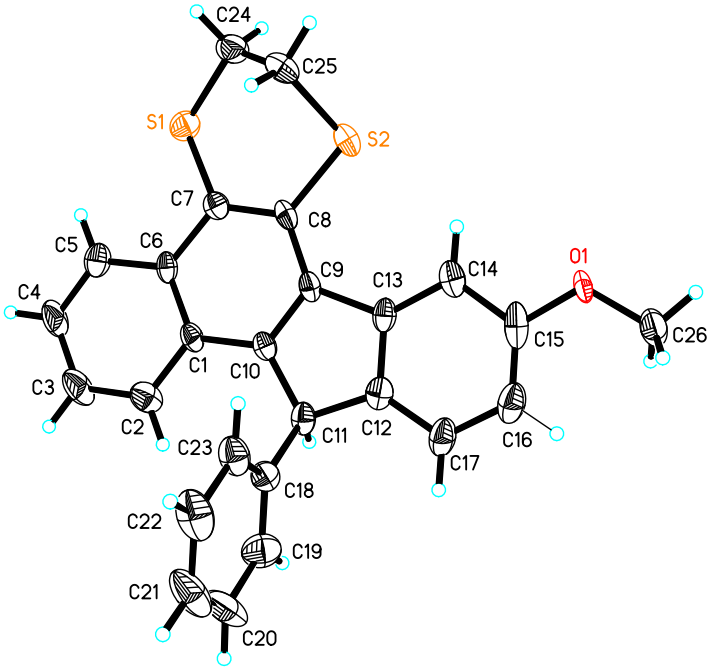

Figure S6. X-ray crystal structure of compound **2o'**
(The X-ray crystallographic analysis indicated a statistically disordered isomer superposition of 80% **2o'** and 20% **2o**.

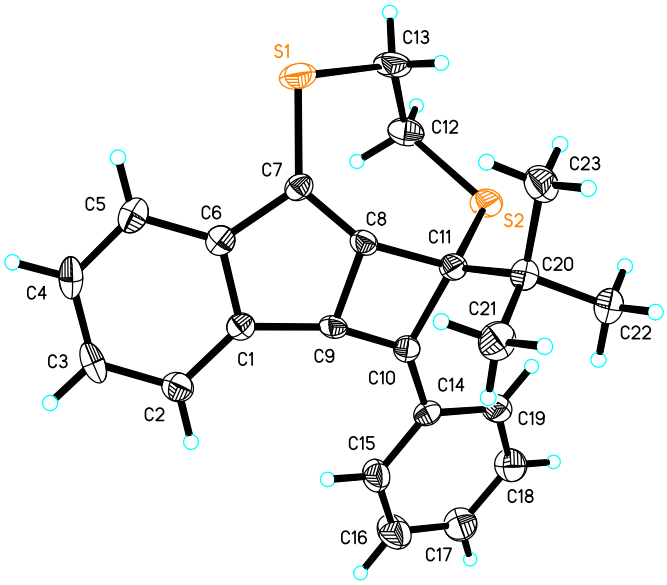

Figure S7. X-ray crystal structure of compound **6**

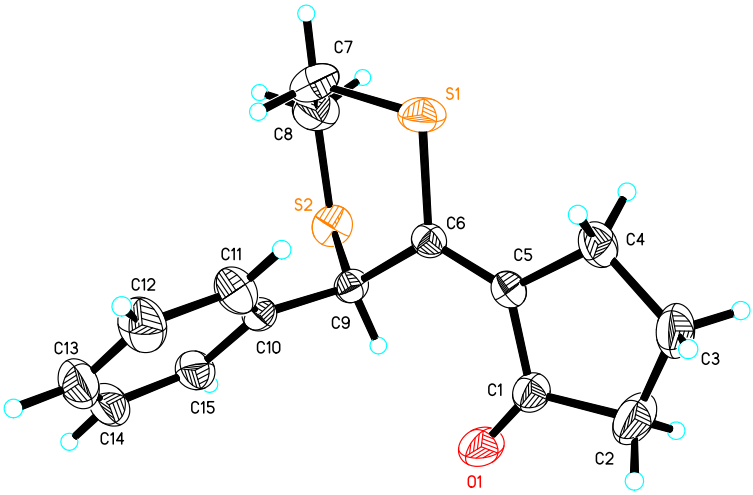

Figure 8. X-ray crystal structure of compound **17**


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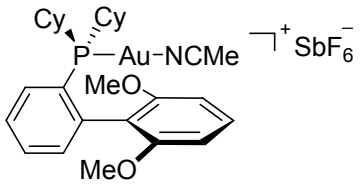
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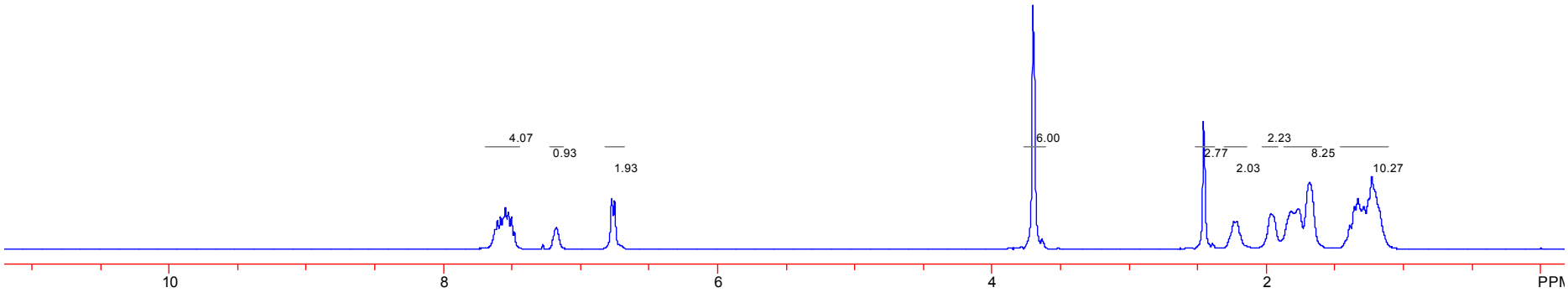
−

catalyst C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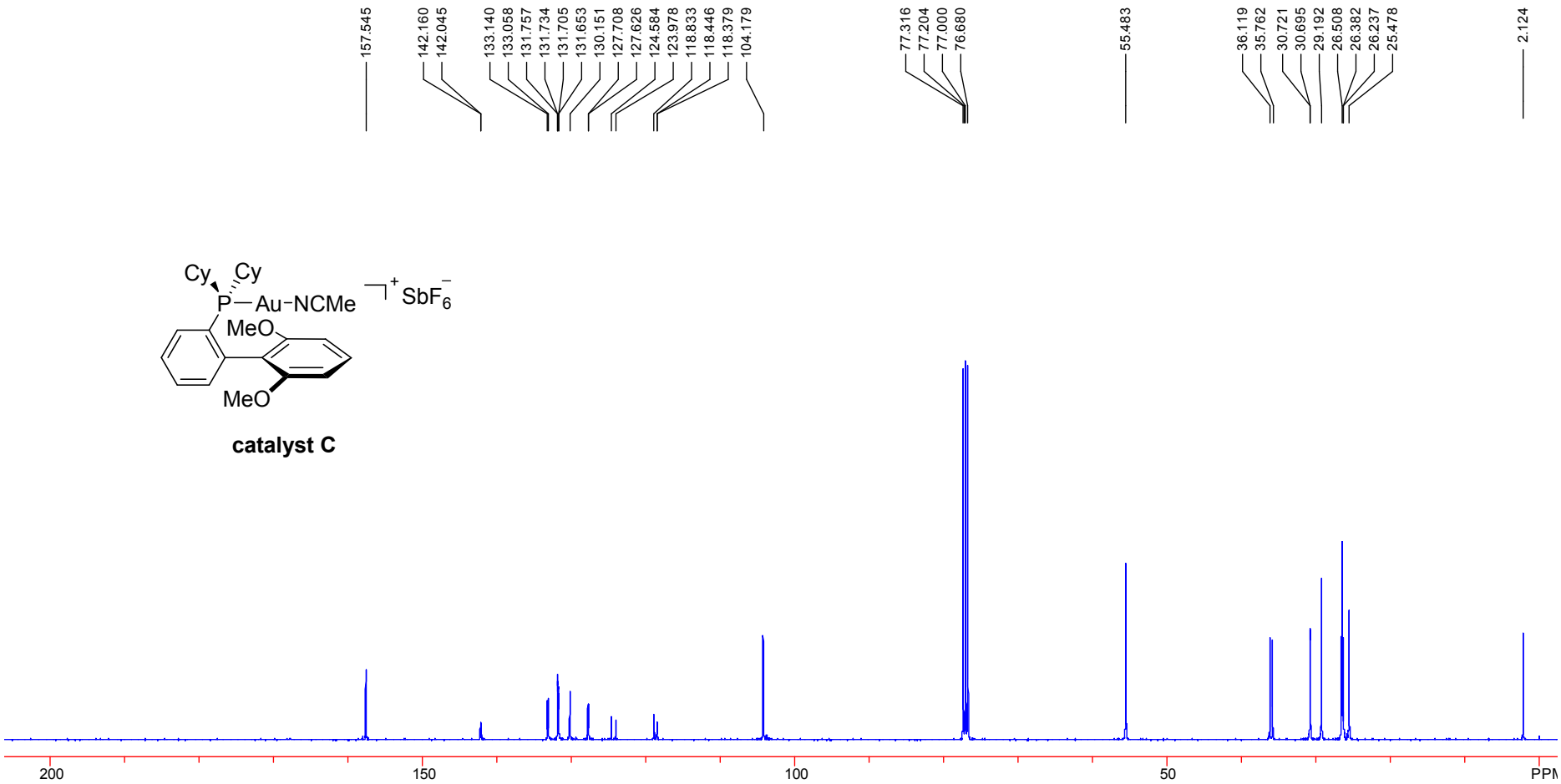
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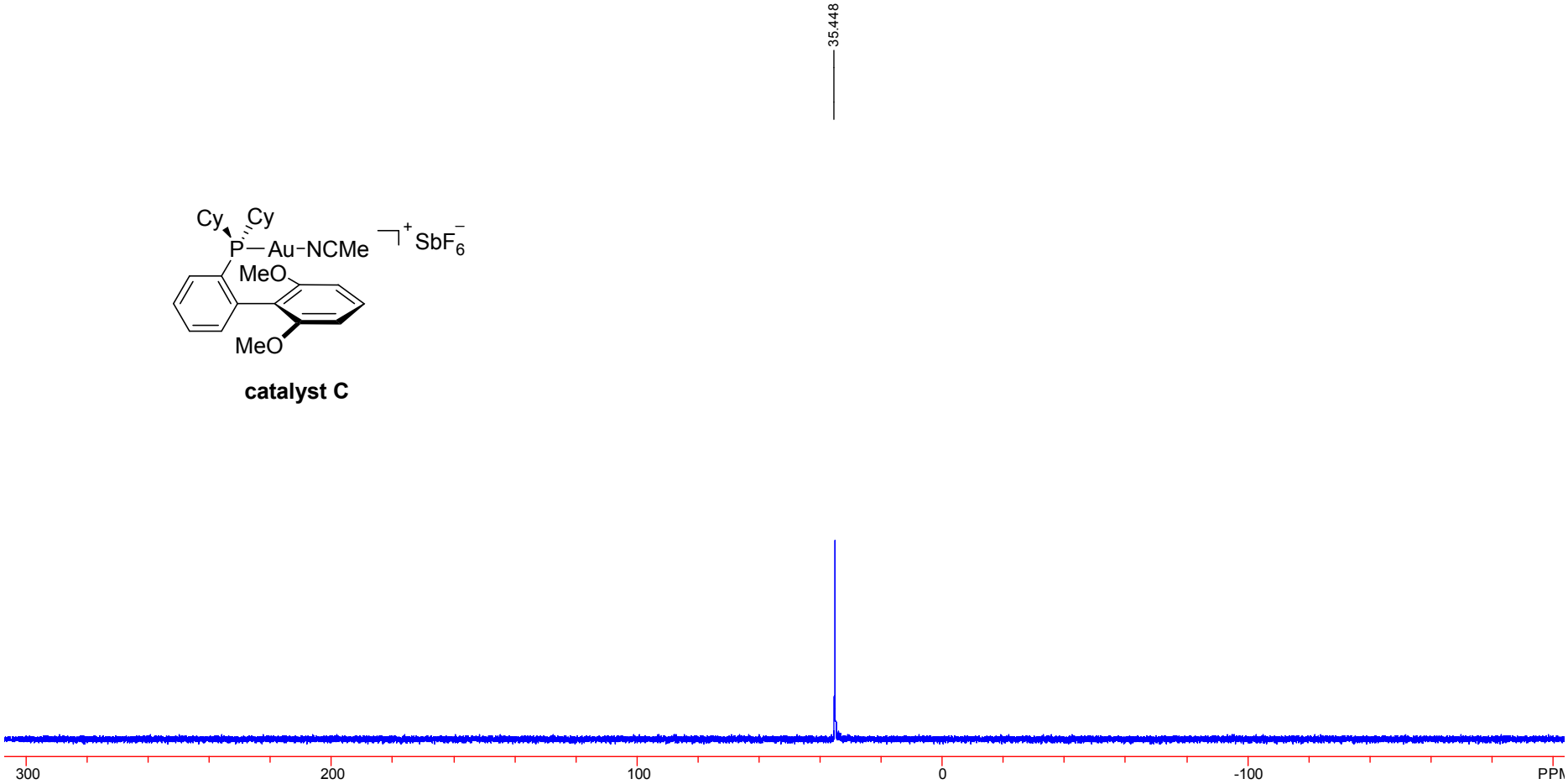
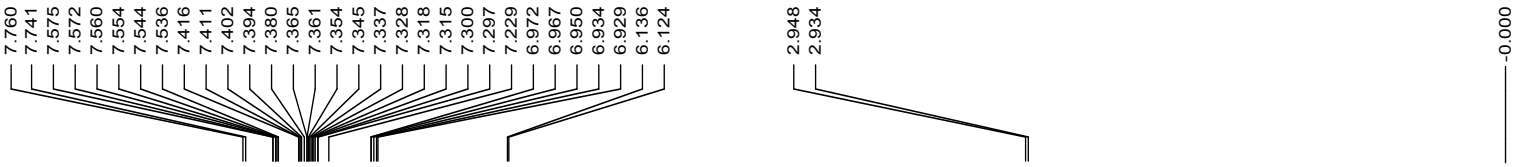
catalyst C

catalyst C

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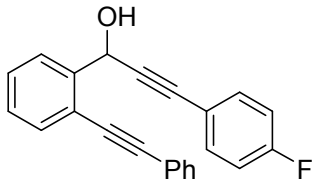
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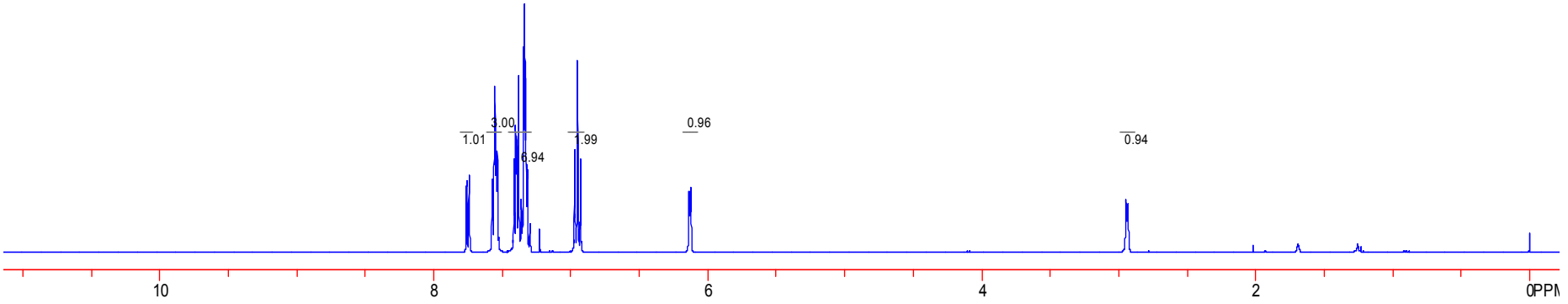
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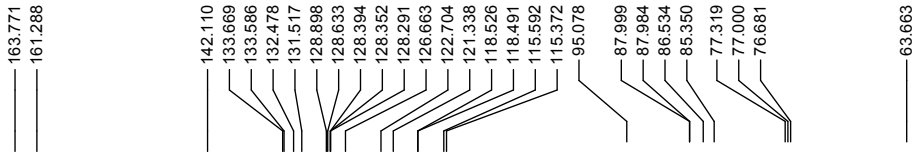
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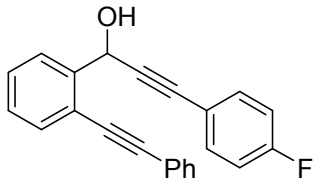
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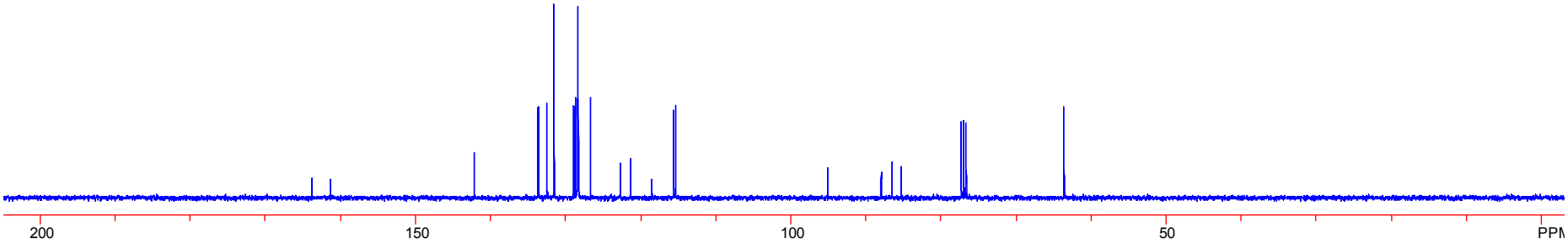
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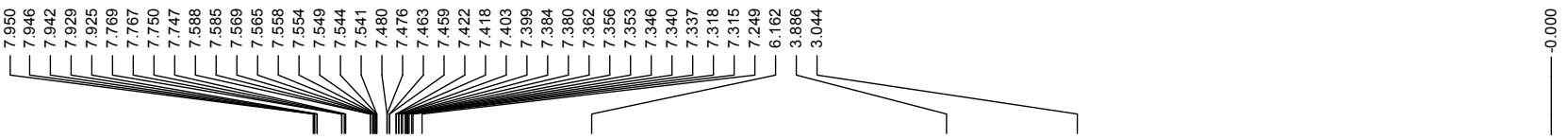
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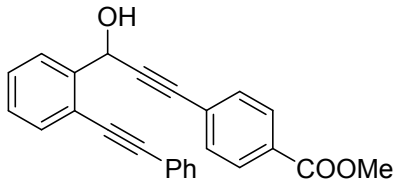
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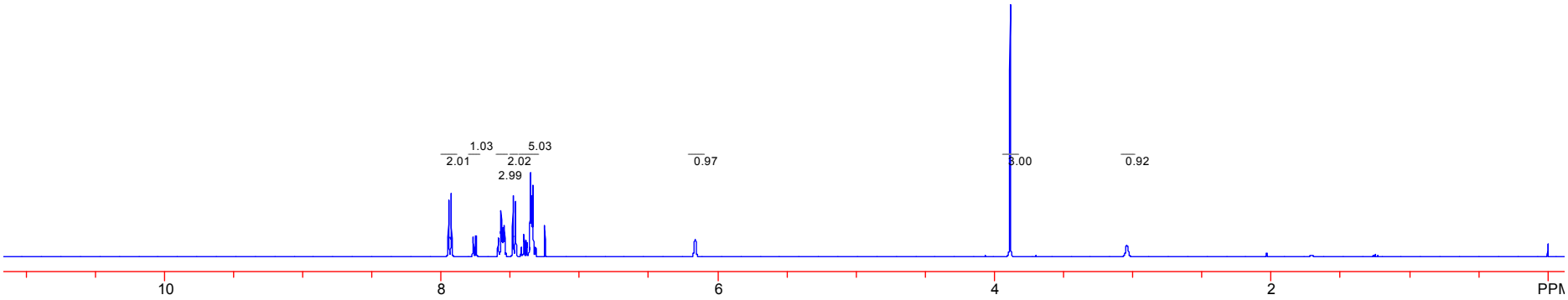
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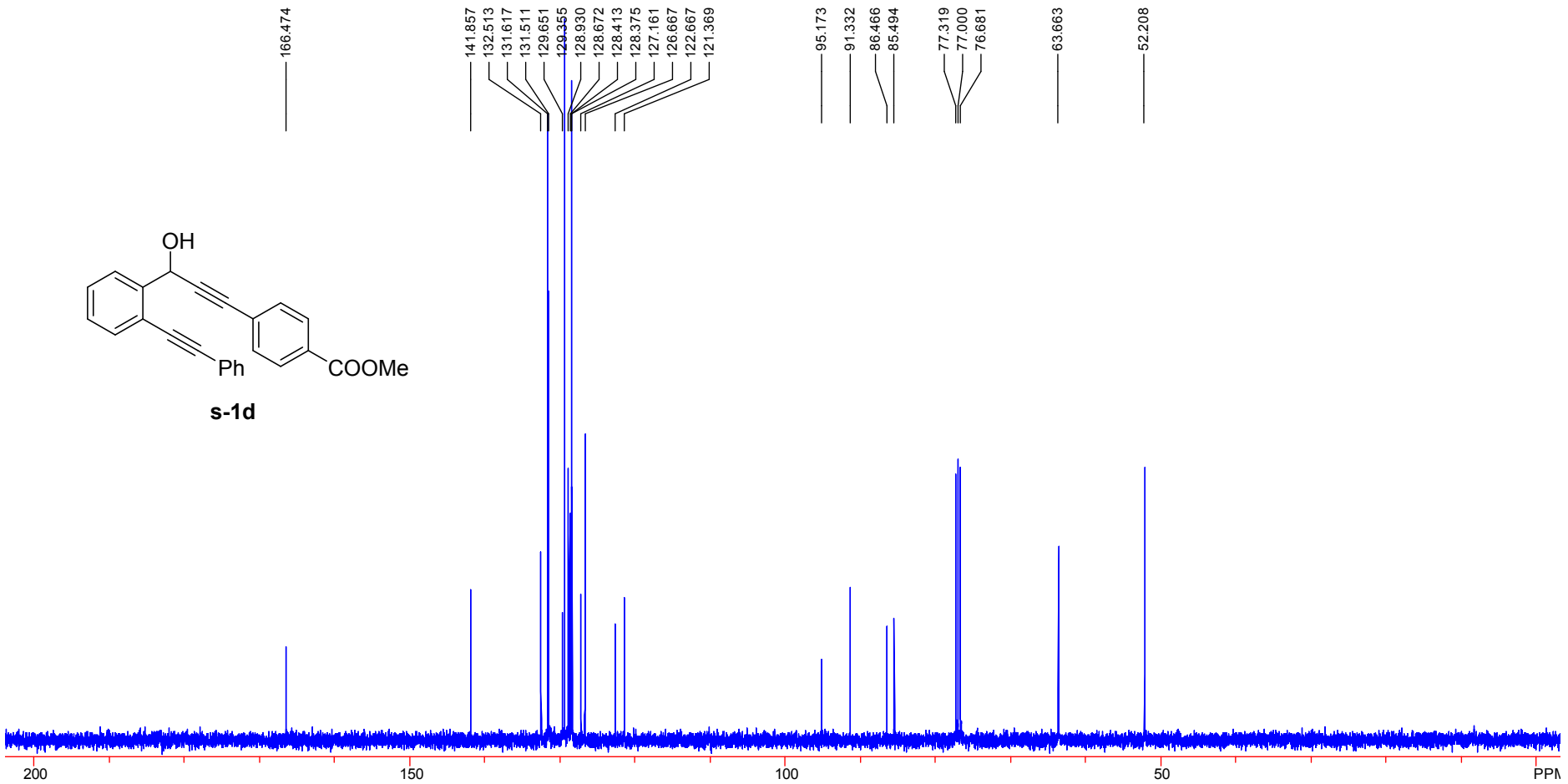
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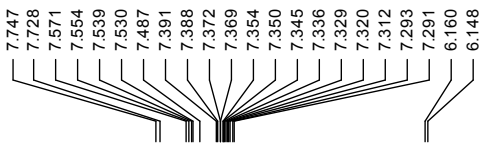
PPM

s-1d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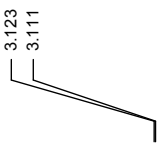
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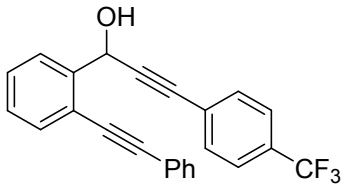
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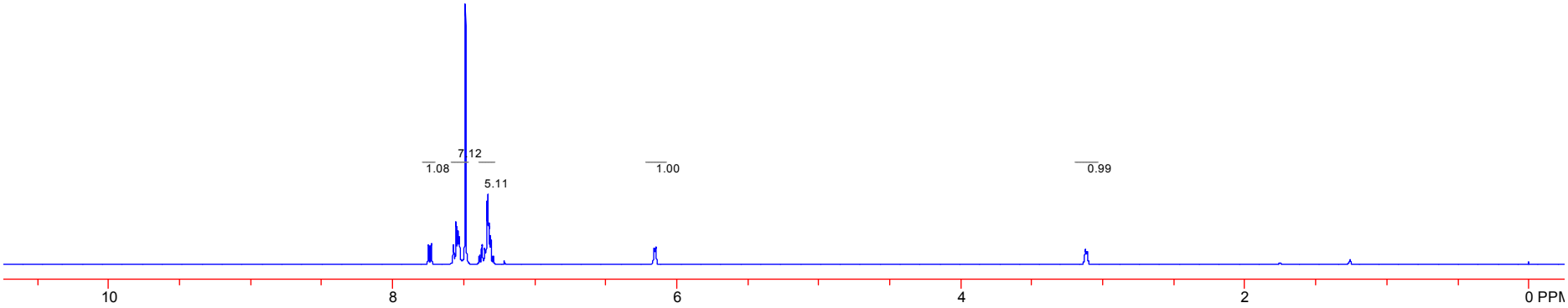
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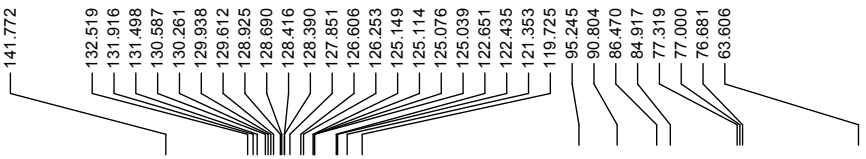
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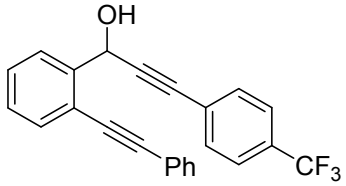
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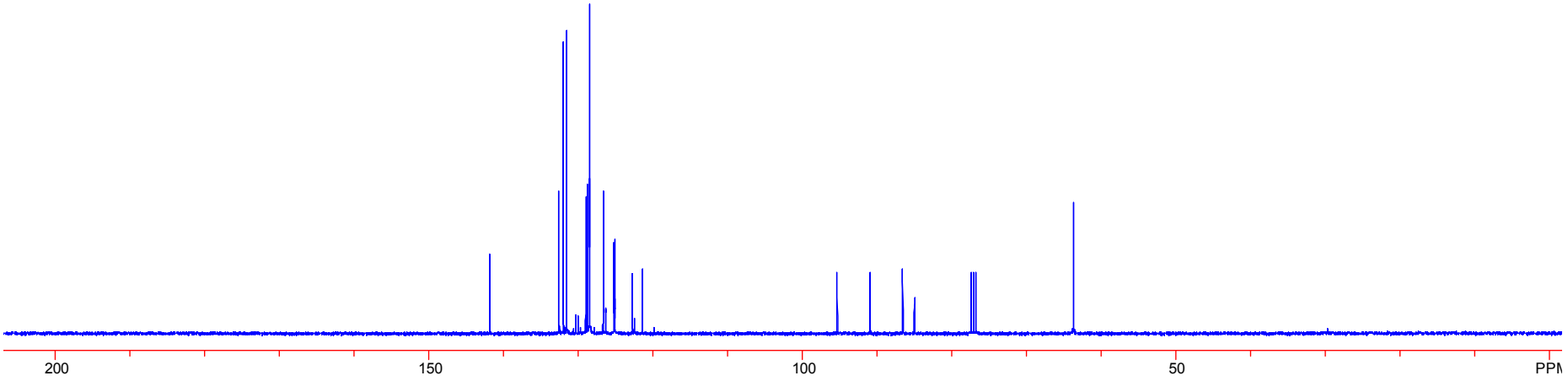
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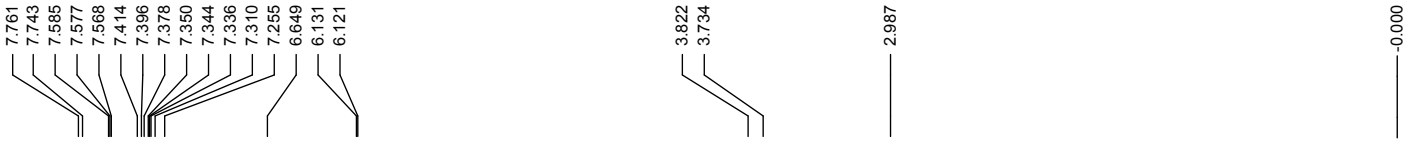
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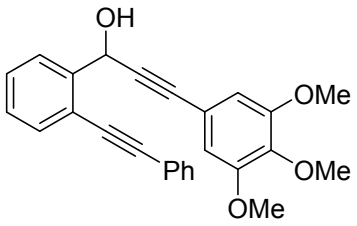
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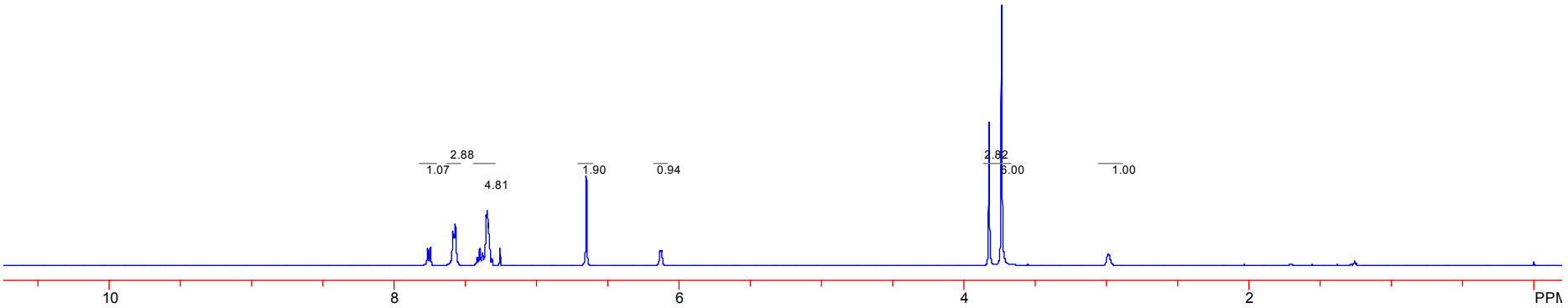
OMe
OMe
Ph

s-1g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4
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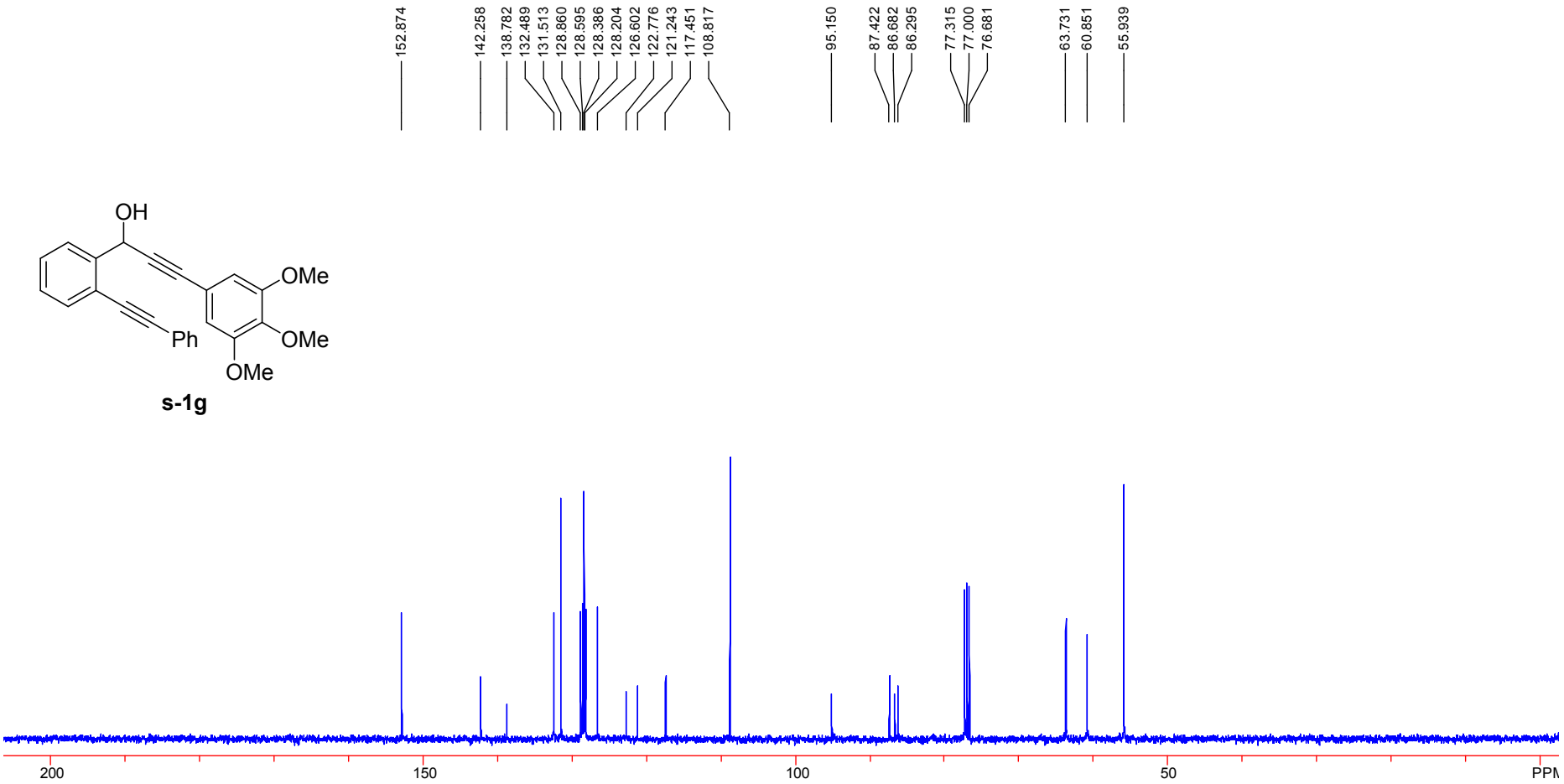
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OMe
OMe
OMe
Ph
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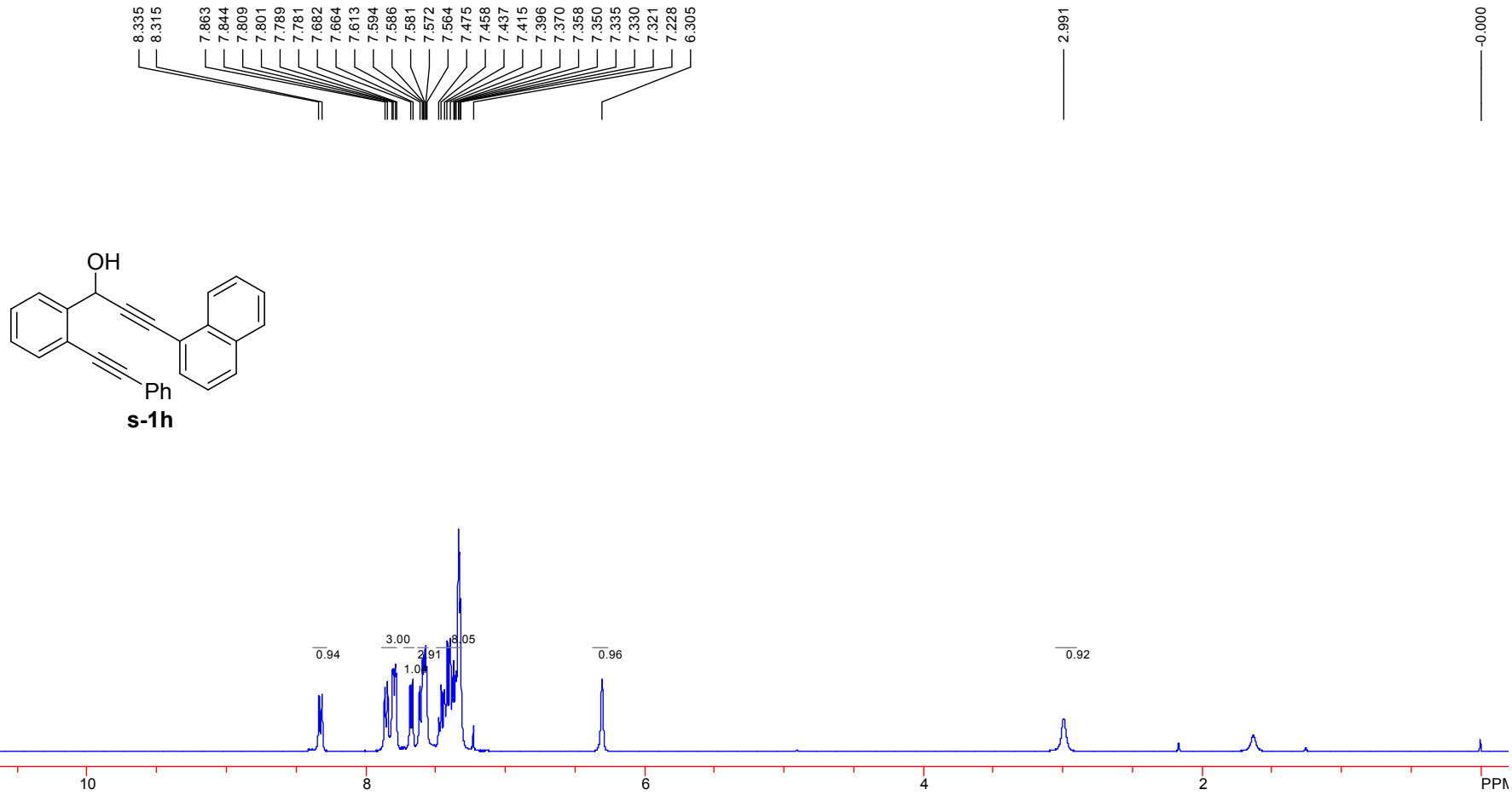
100
50
PPM

s-1g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OH
Ph
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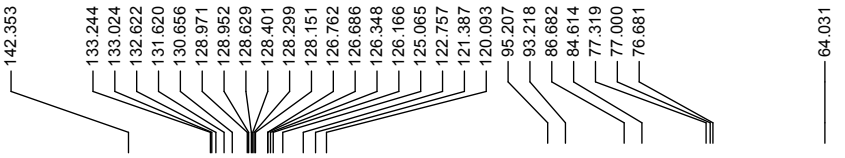
PPM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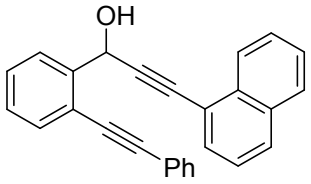
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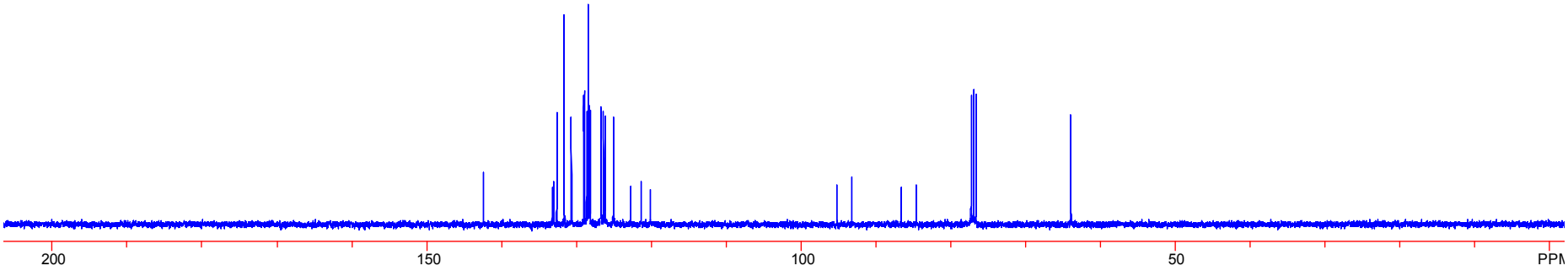
Ph

s-1h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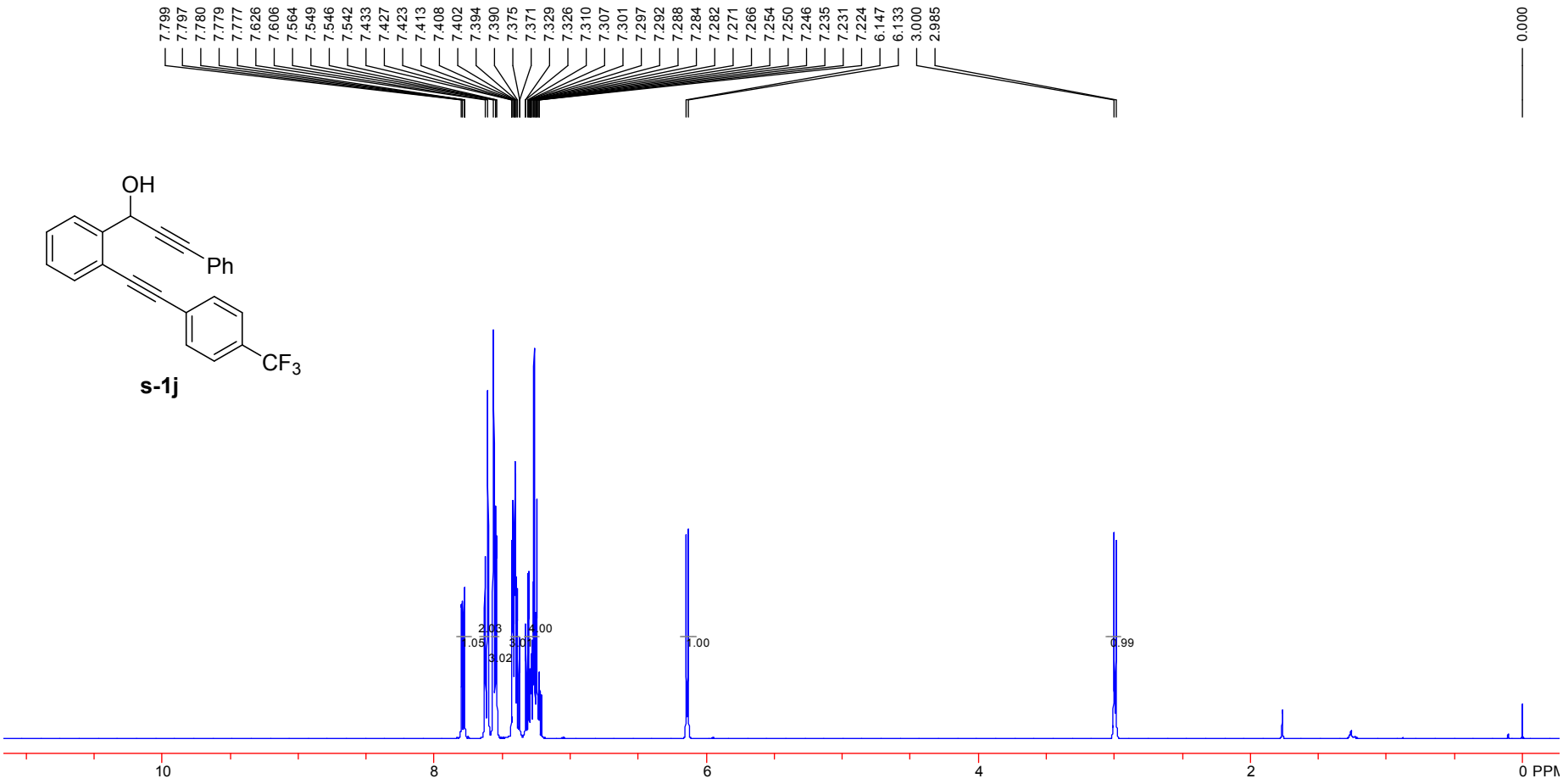
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7.310
7.307
7.301
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7.292
7.288
7.284
7.282
7.271
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7.235
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Ph
CF3
s-1j
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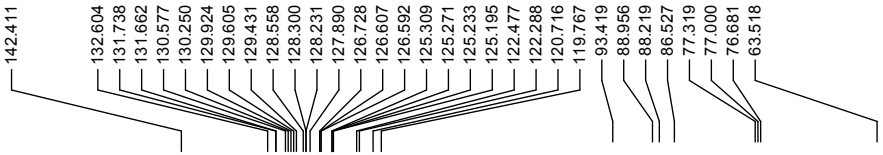
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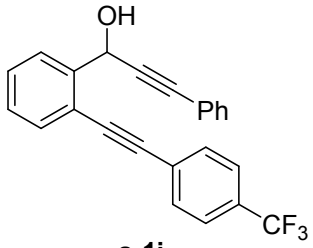
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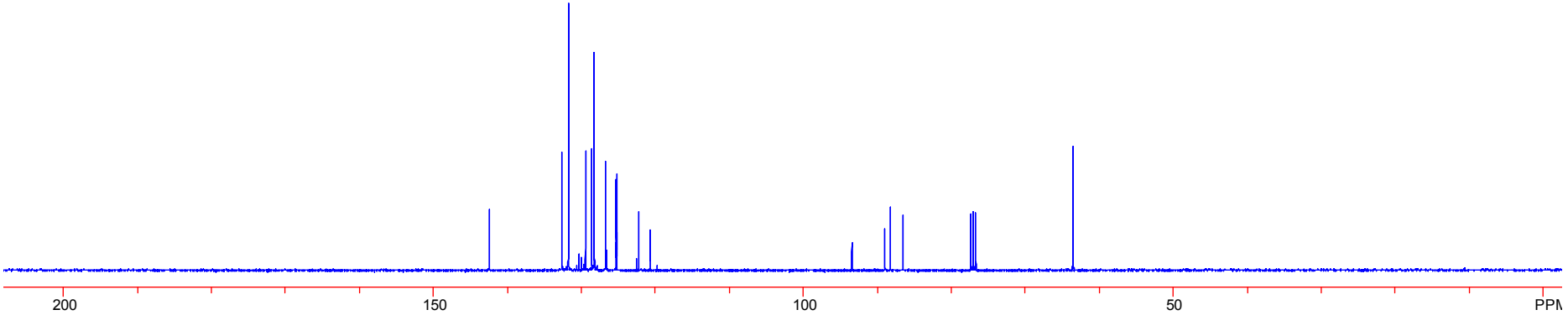
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100
50
PPM


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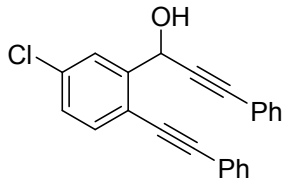
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Ph
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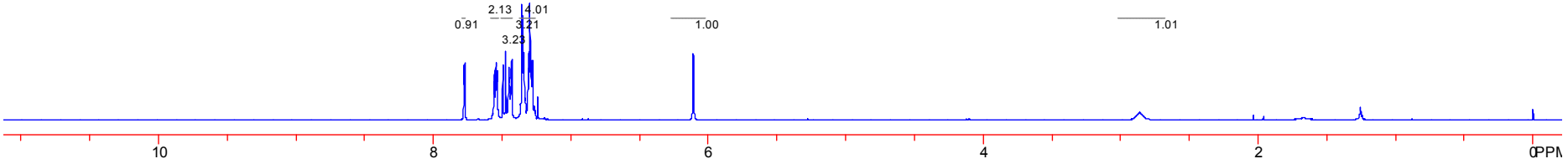
s-1n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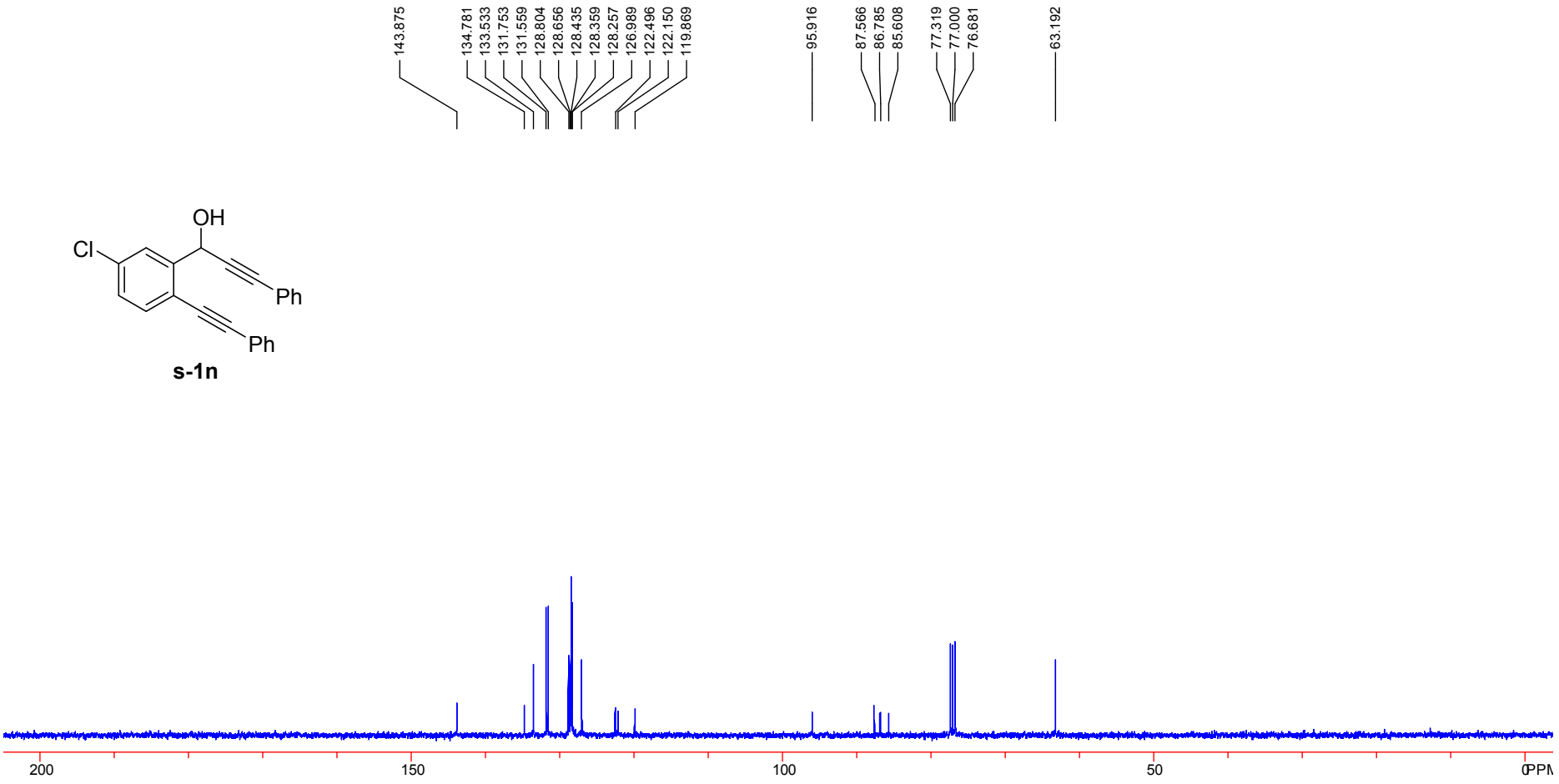
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Ph
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s-1n
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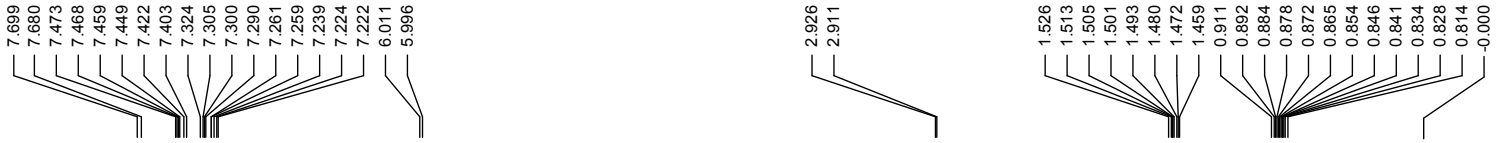
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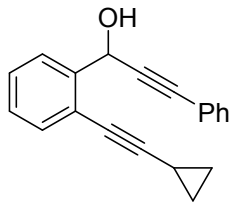
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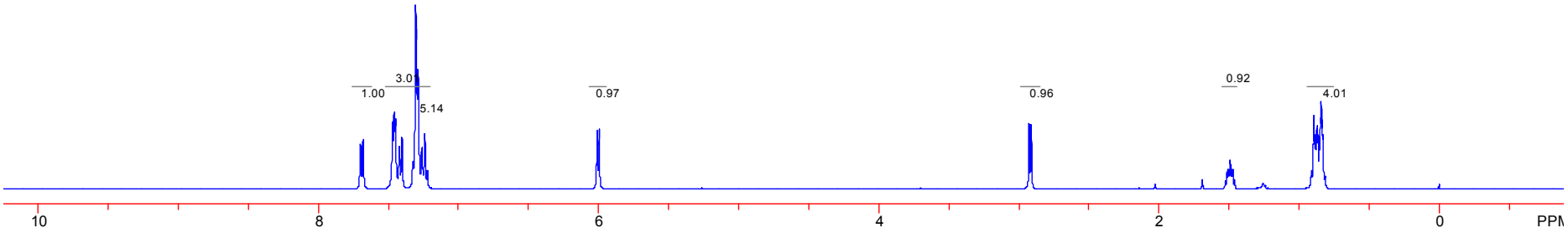
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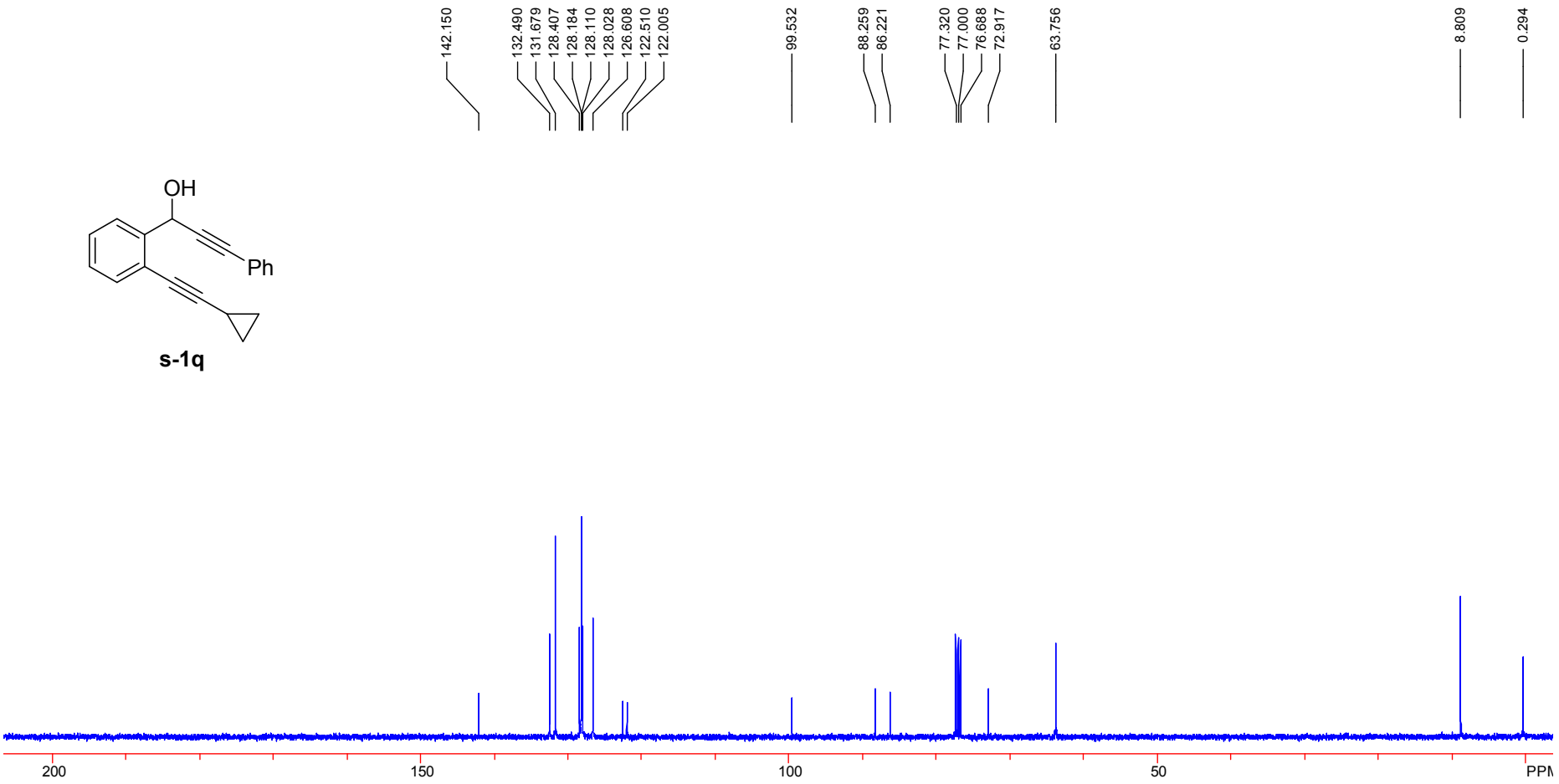
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Ph
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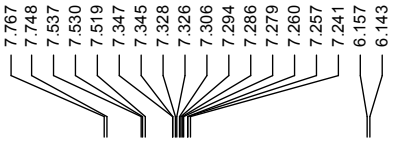
50
PPM

s-1q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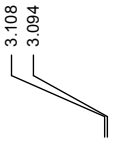
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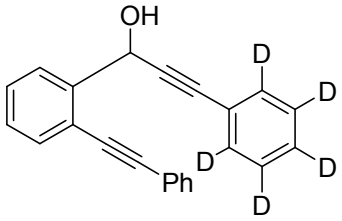
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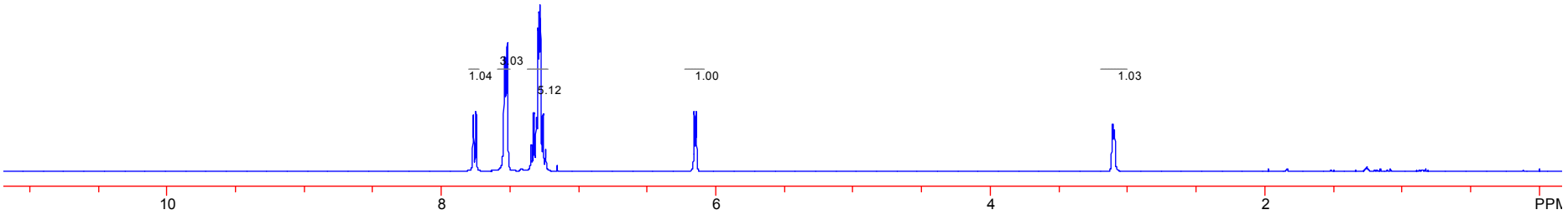
s-1a-d_5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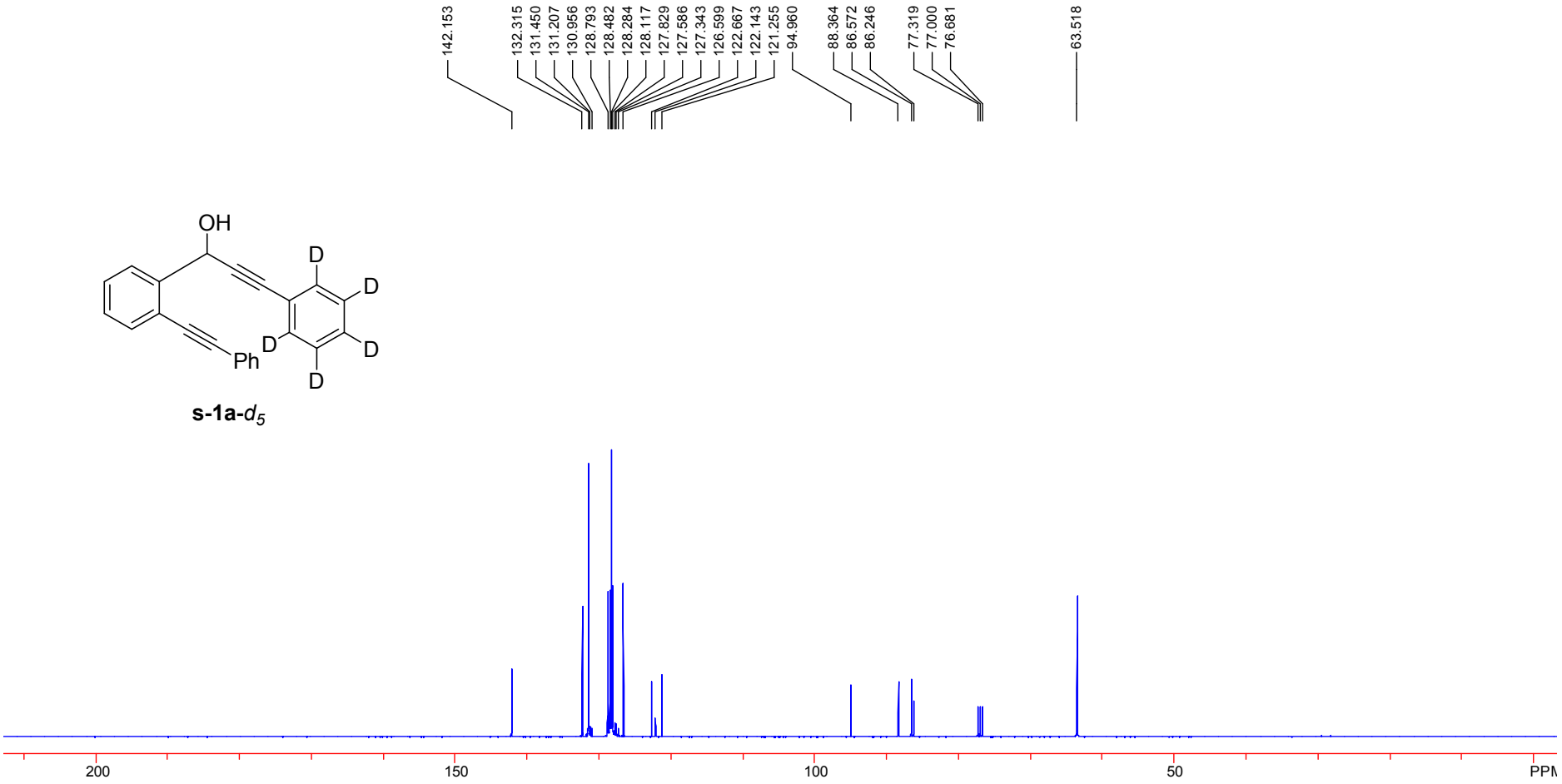
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94.960
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86.572
86.246
77.319
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D
D
D
D
D
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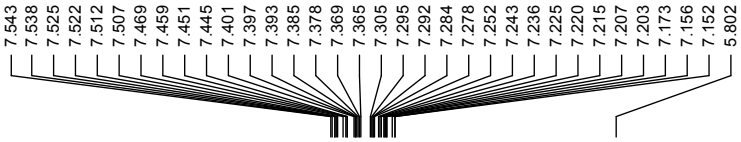
150
100
50
PPM

s-1a-d_5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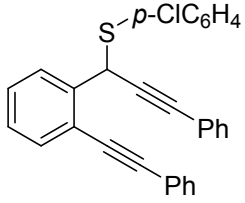
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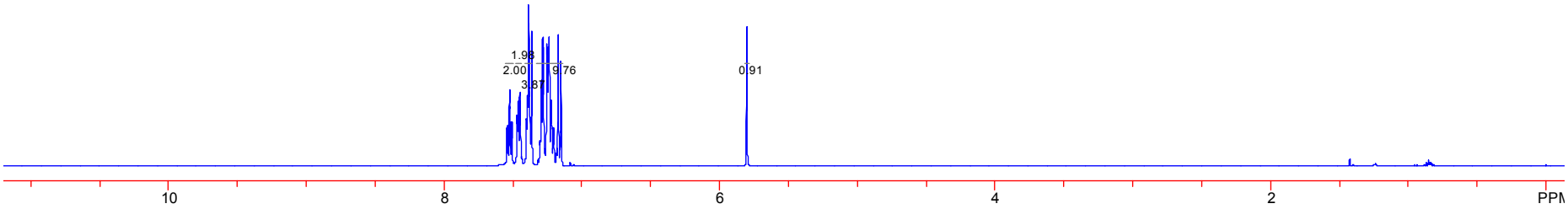
Ph
Ph

1a'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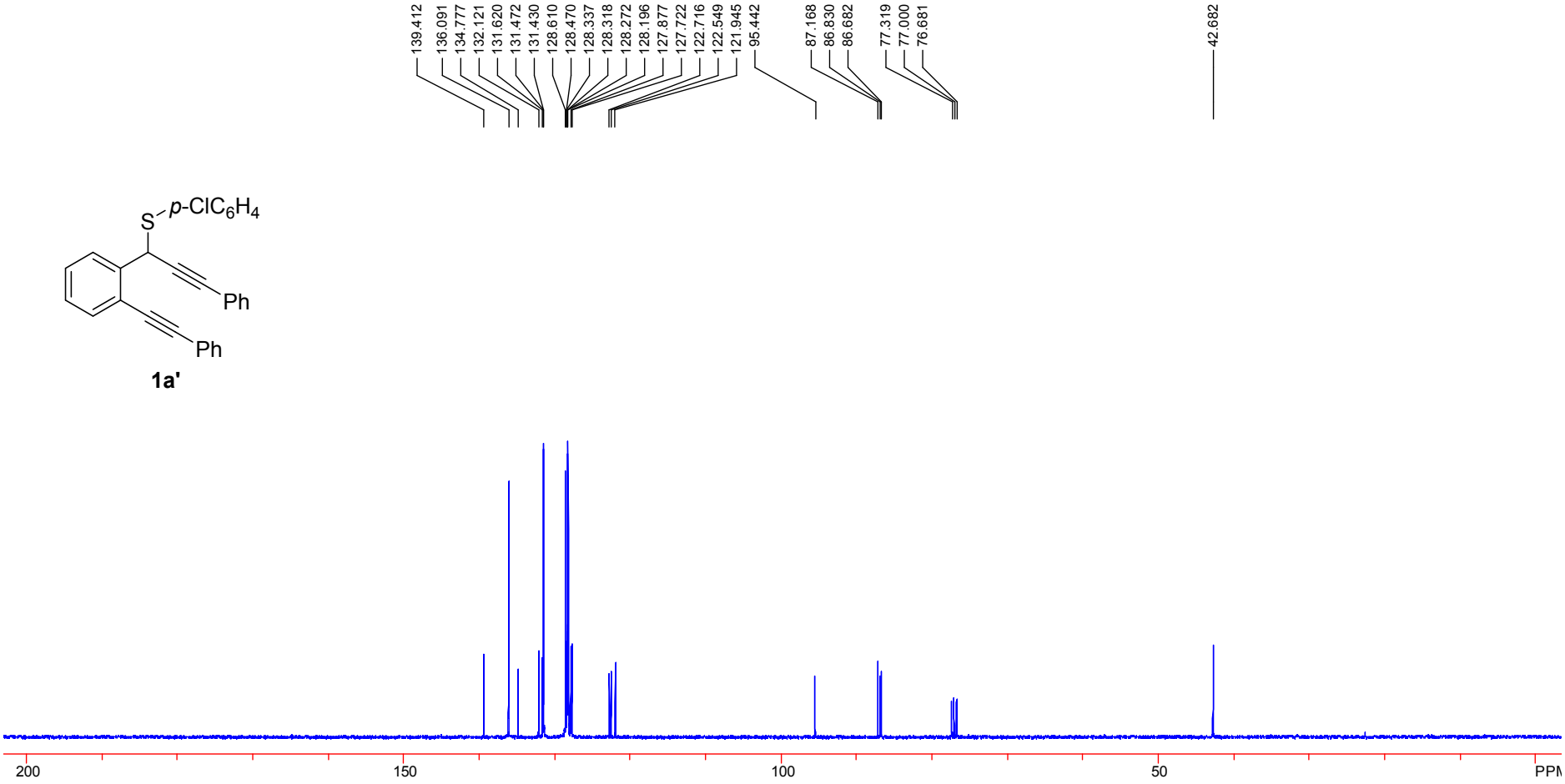
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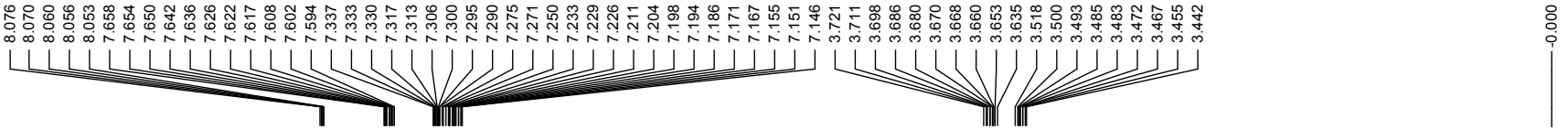
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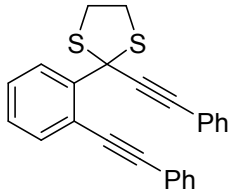
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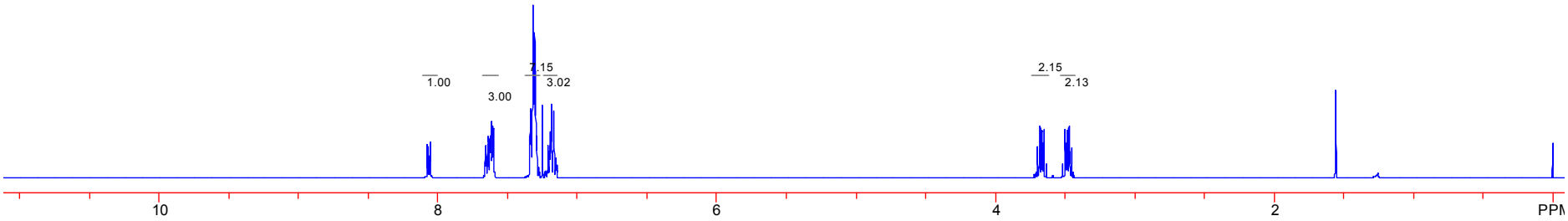
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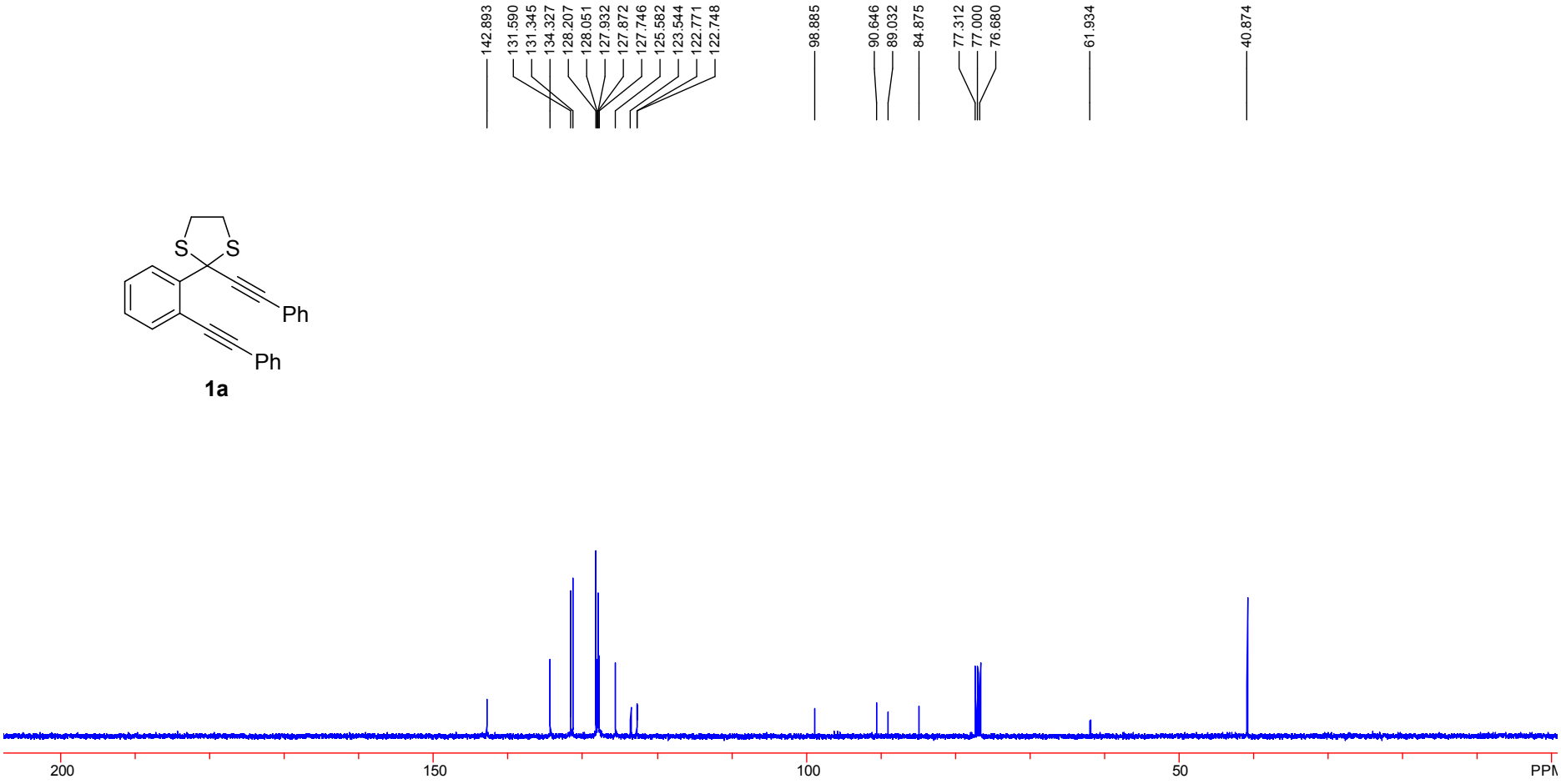
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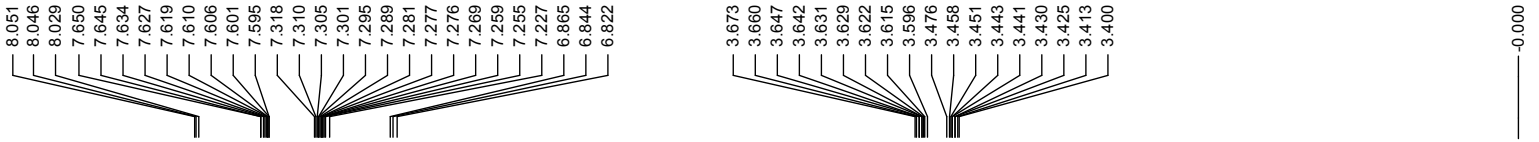
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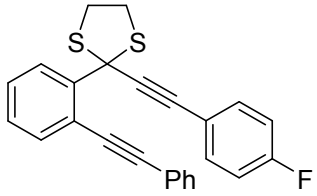
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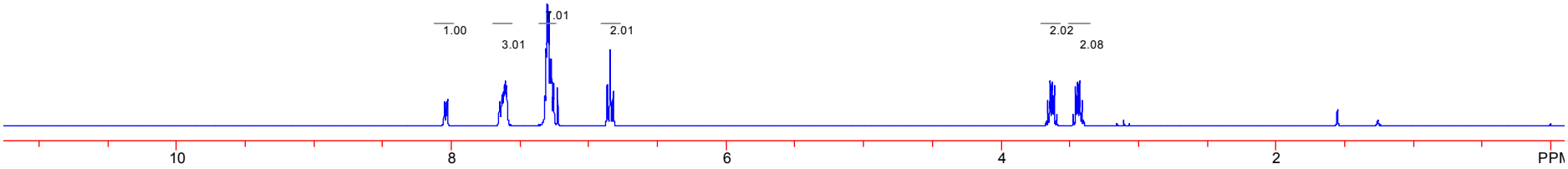
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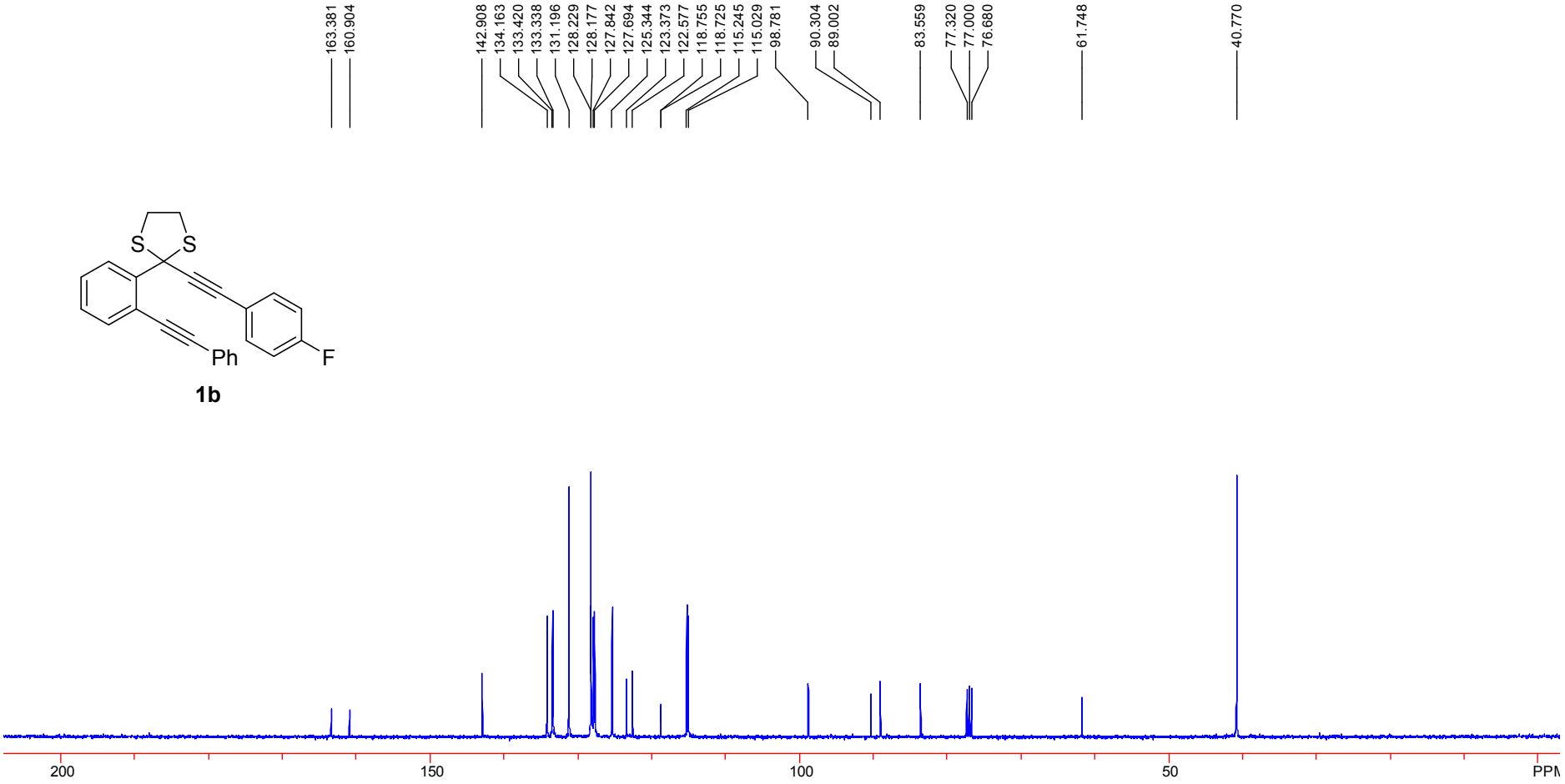
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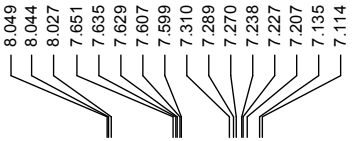
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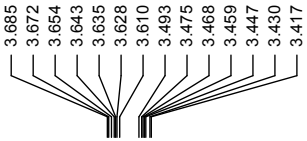
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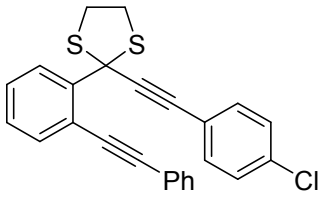
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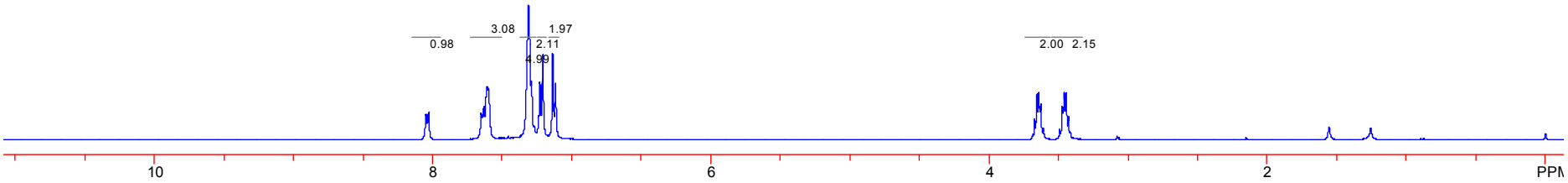
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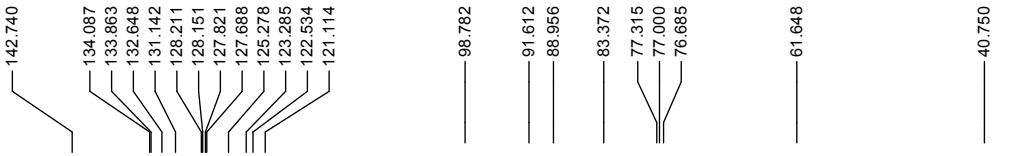
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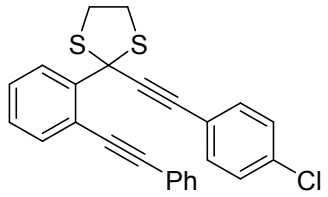
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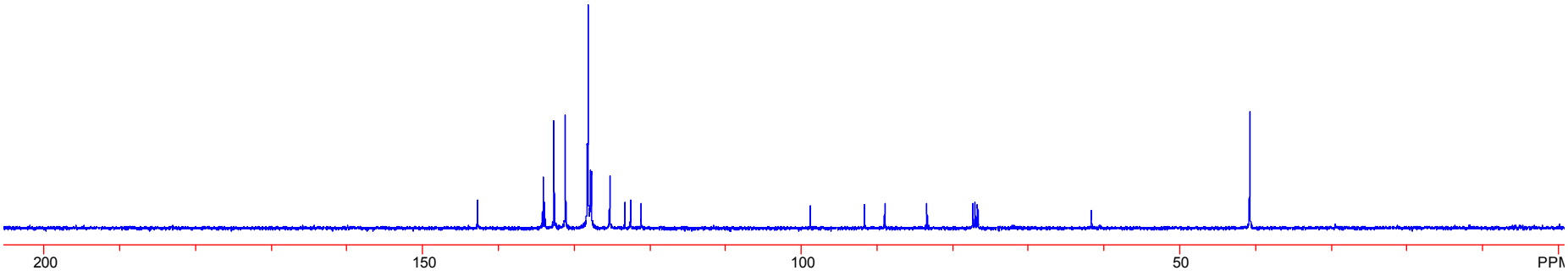
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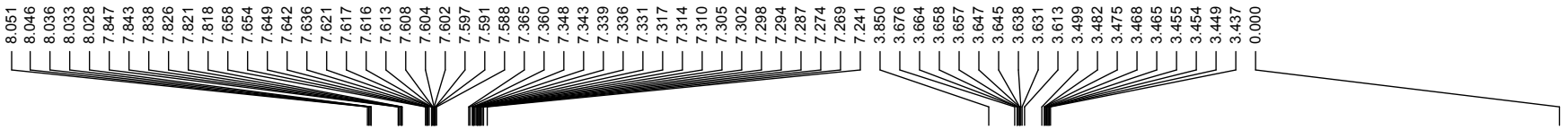
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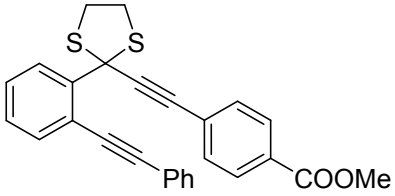
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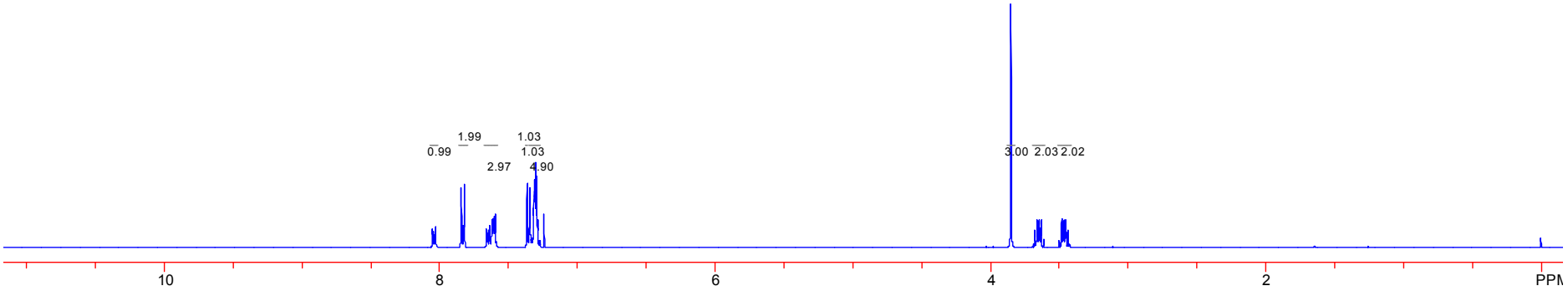
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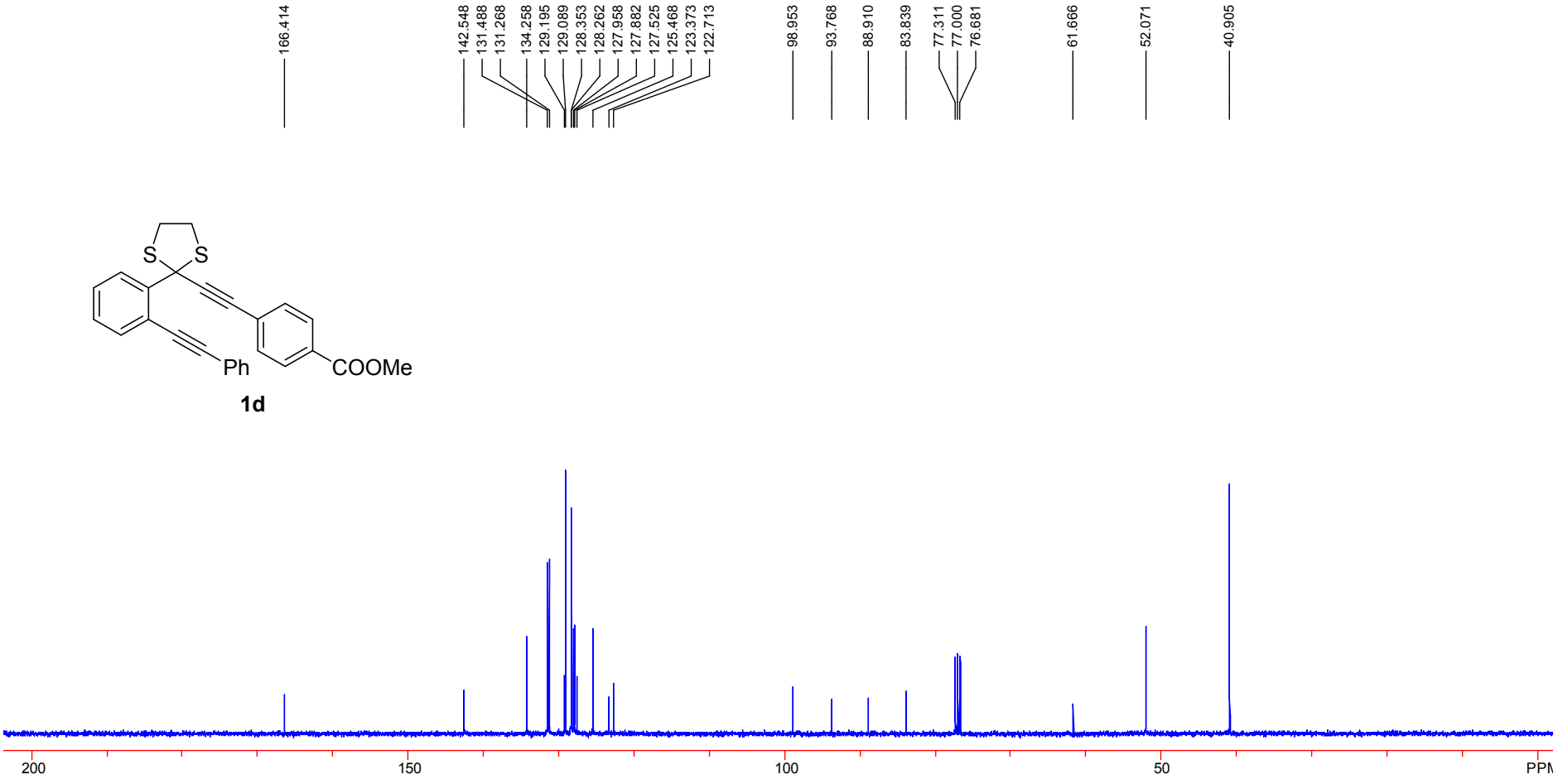
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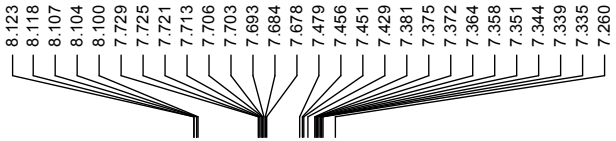
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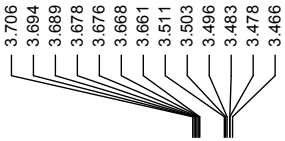
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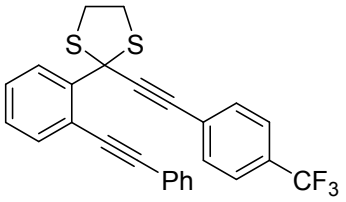
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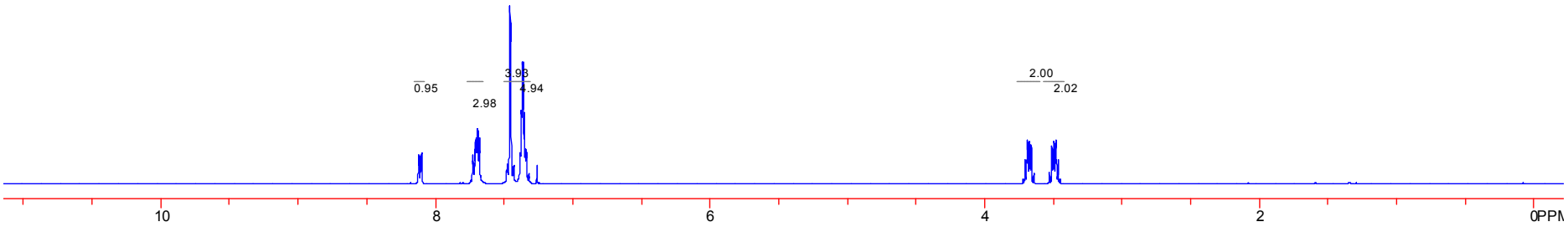
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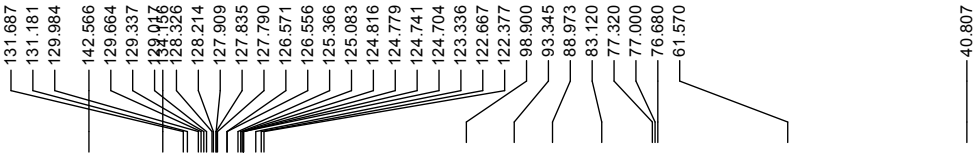
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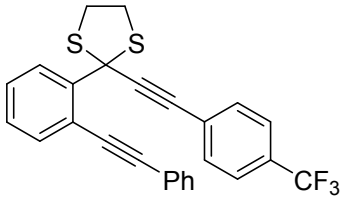
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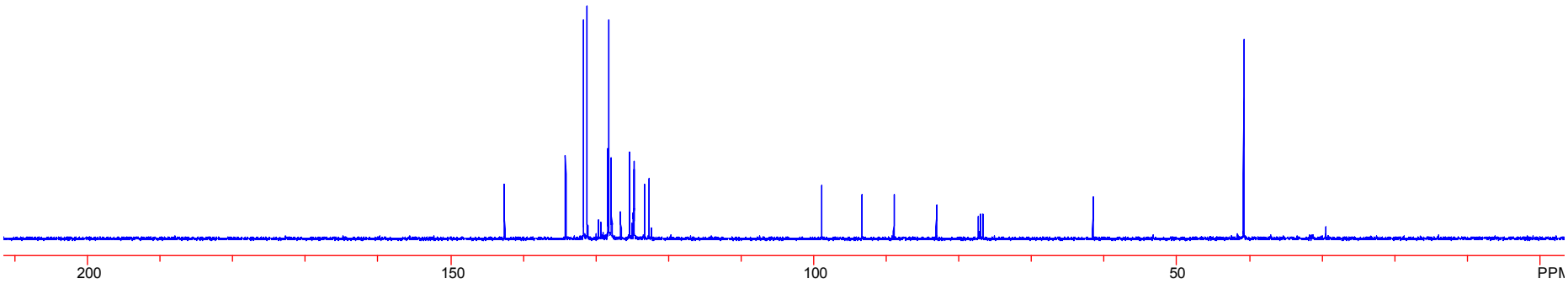
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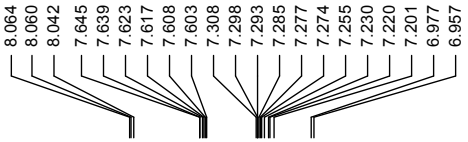
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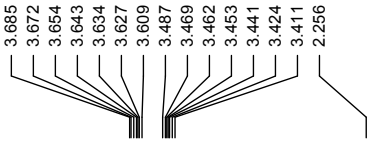
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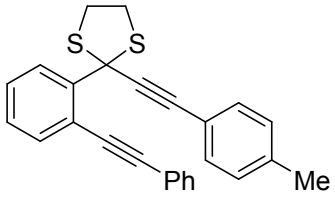
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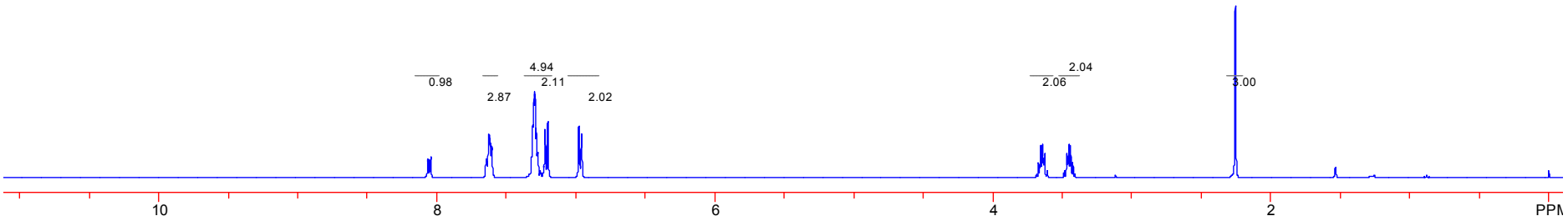
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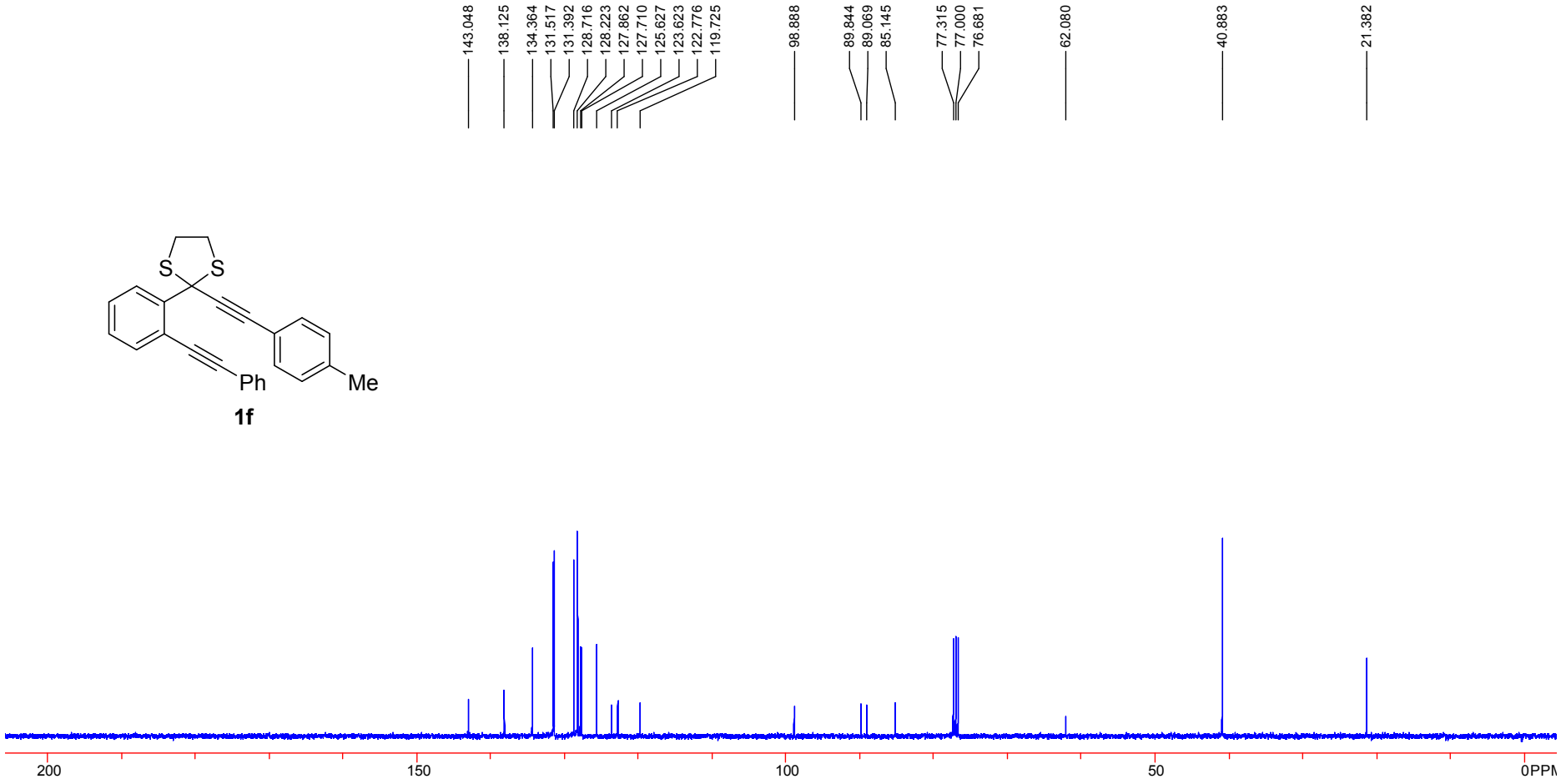
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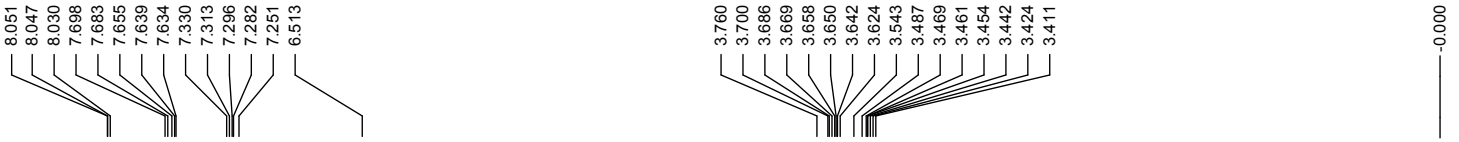
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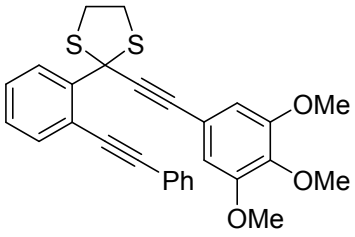
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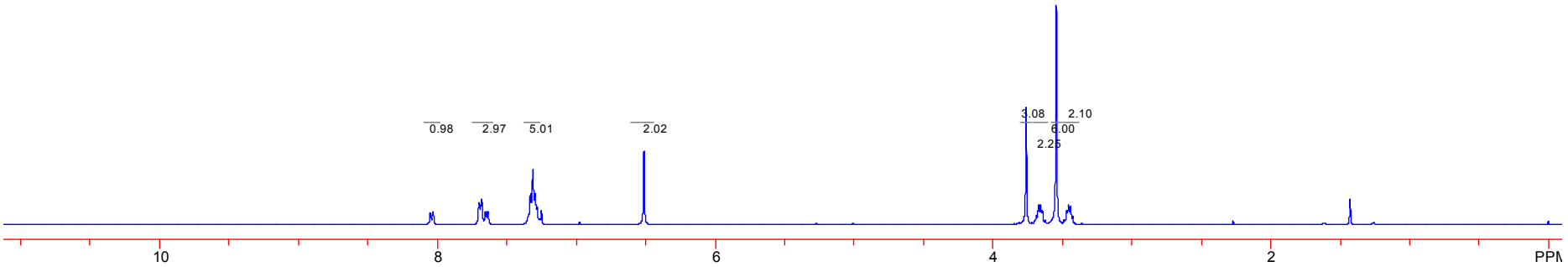
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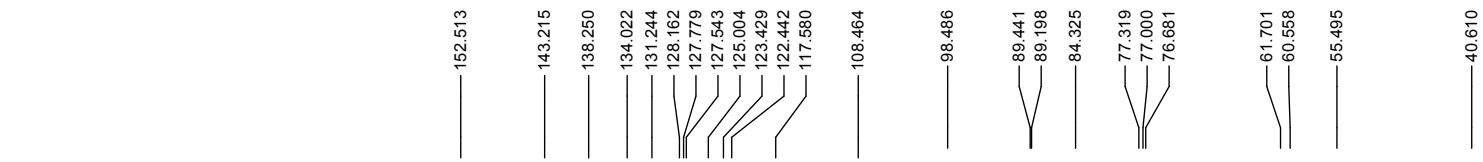
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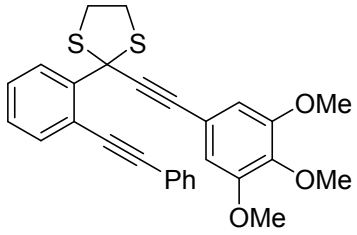
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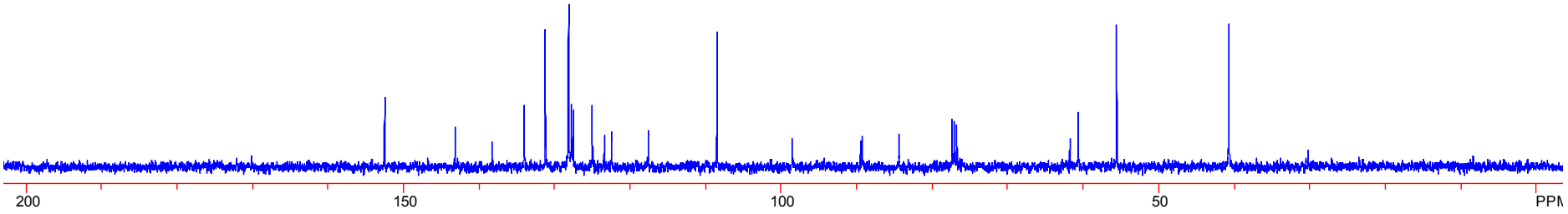
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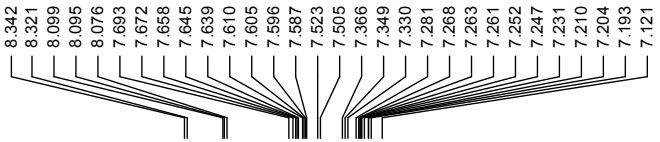
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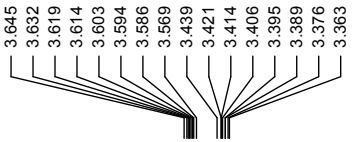
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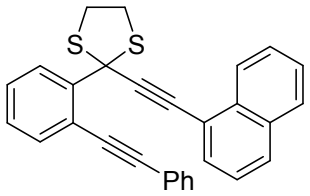
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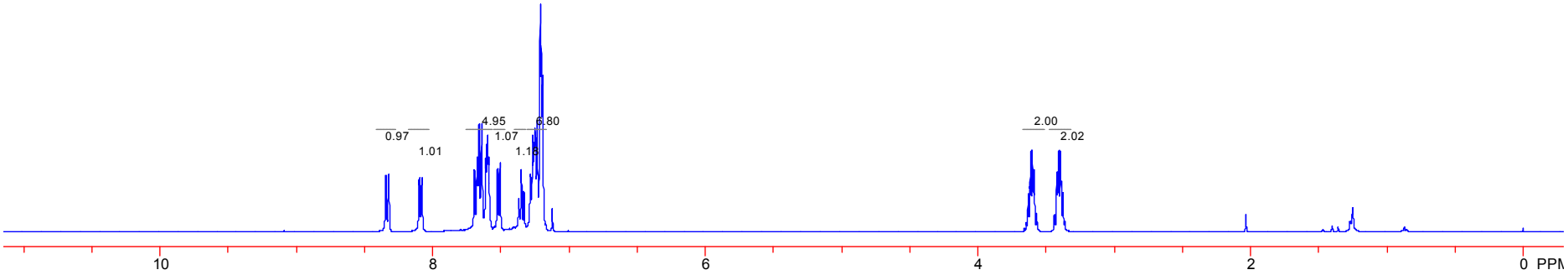
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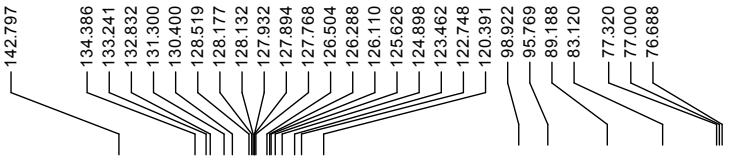
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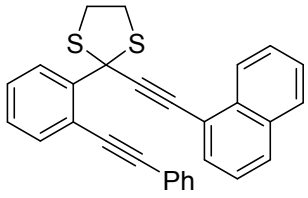
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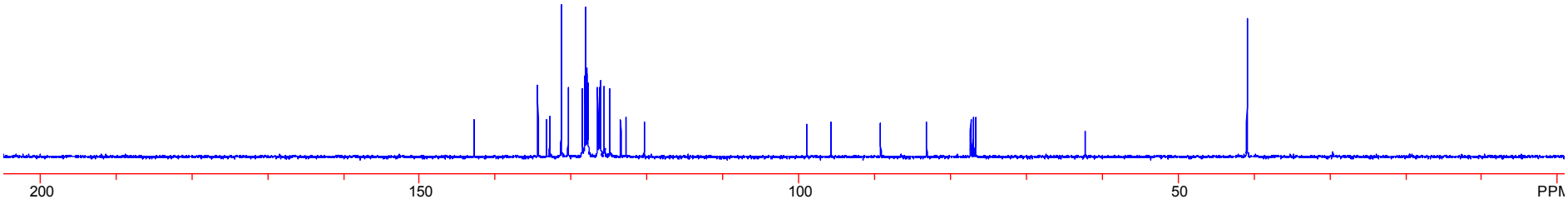
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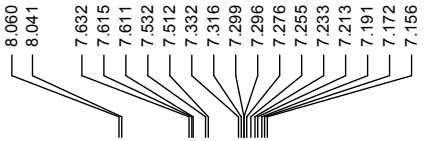
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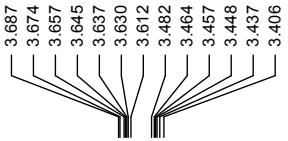
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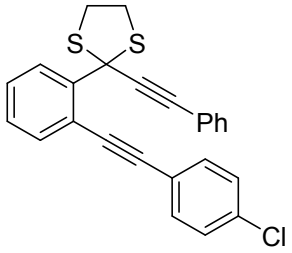
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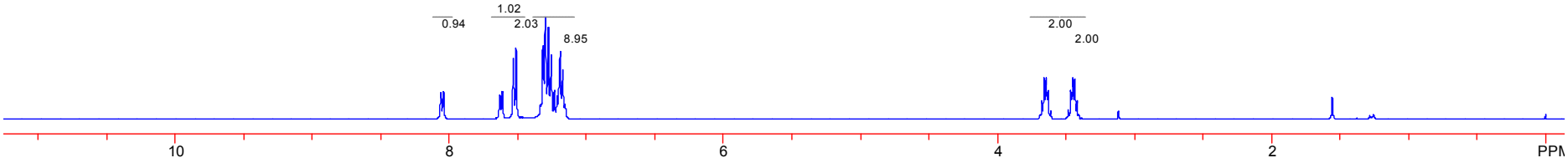
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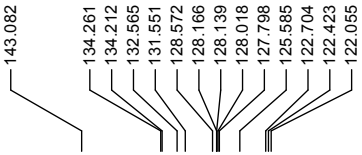
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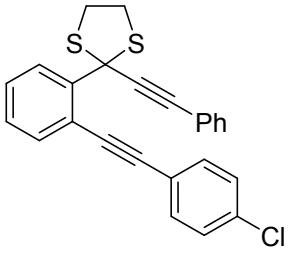
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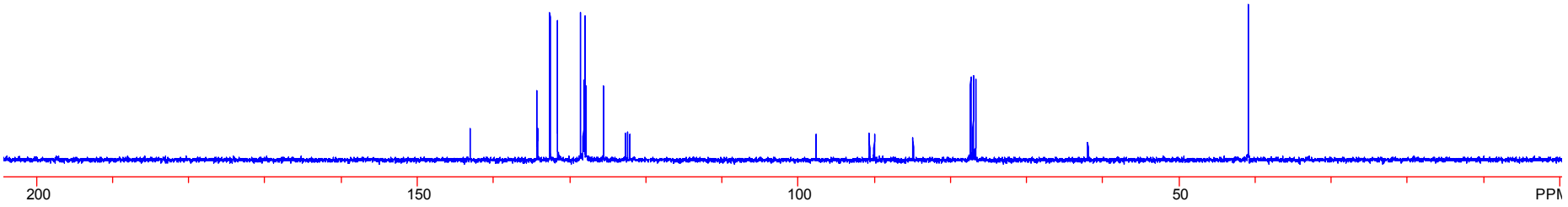
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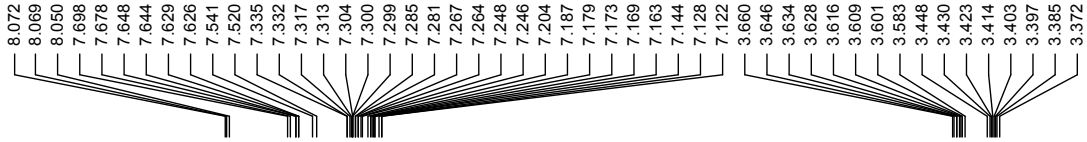
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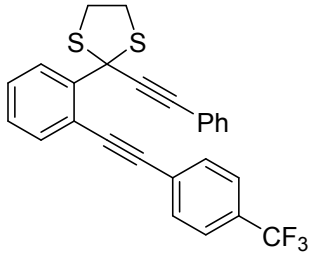
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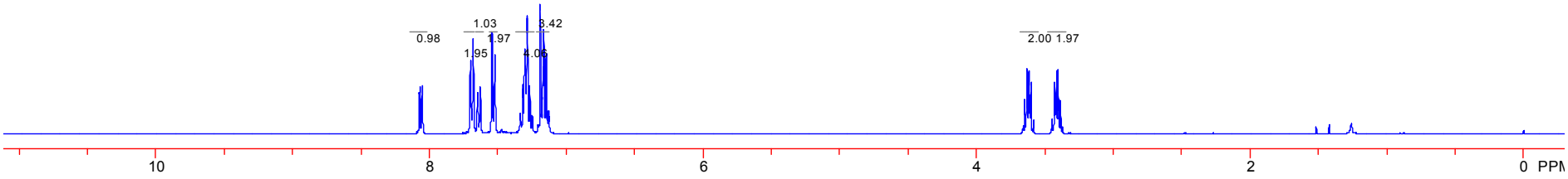
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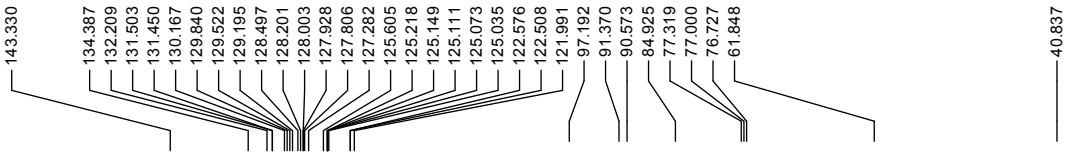
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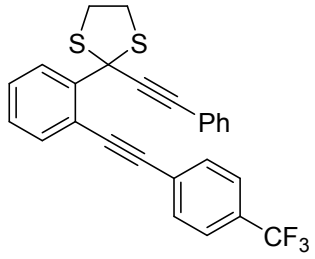
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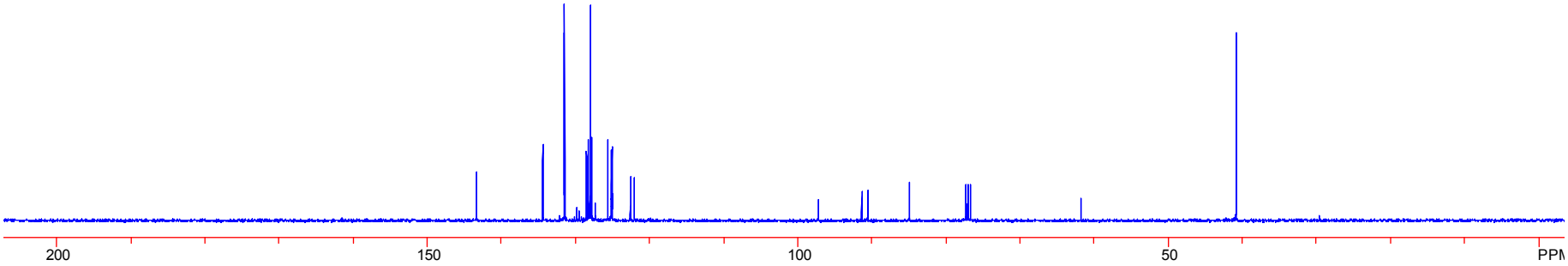
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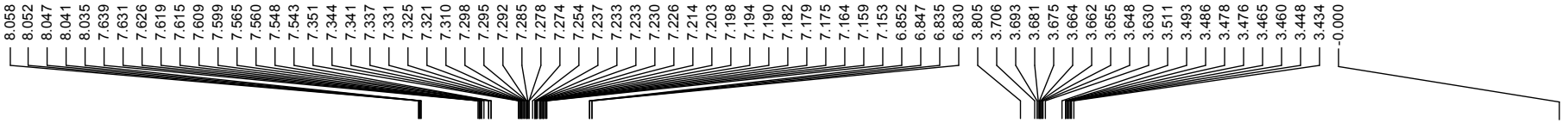
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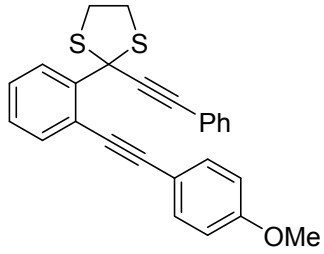
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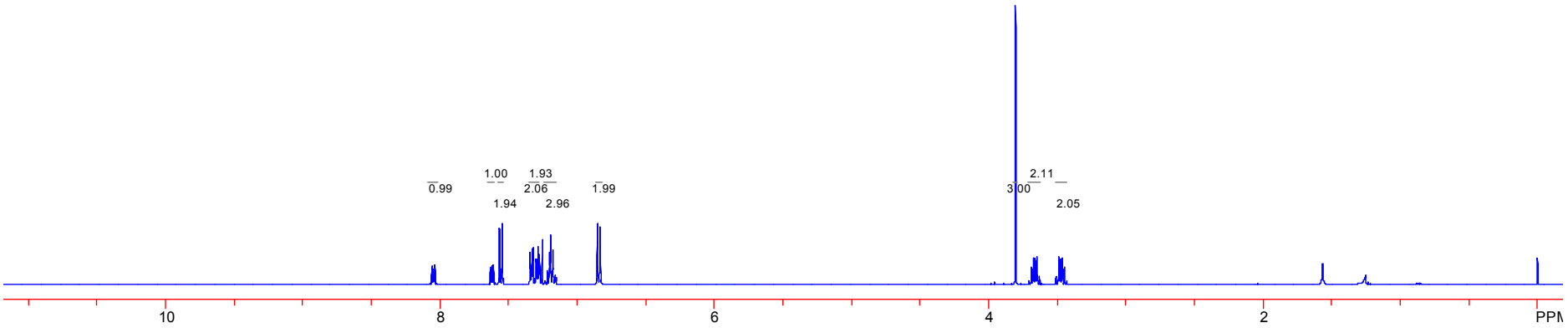
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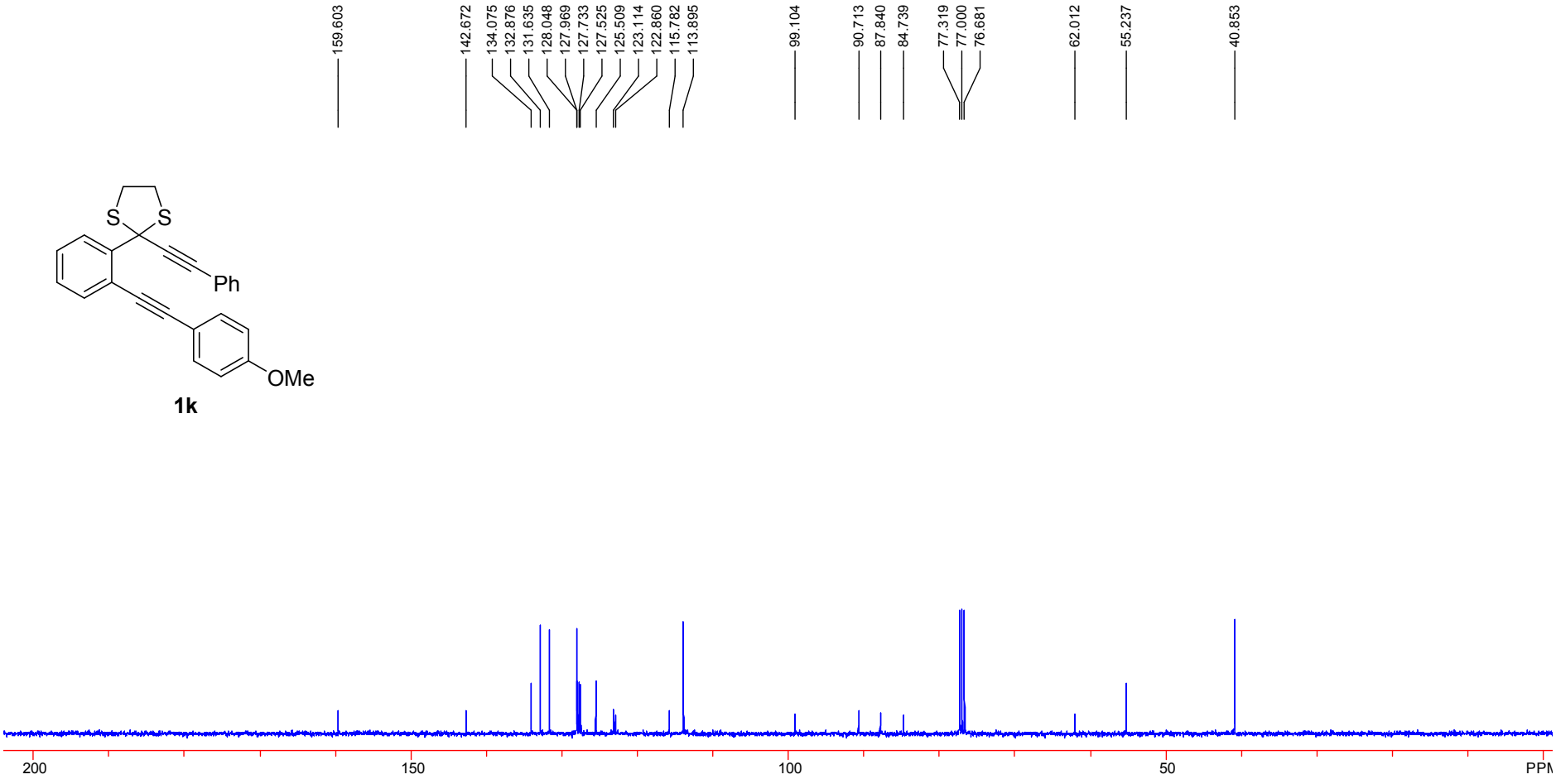
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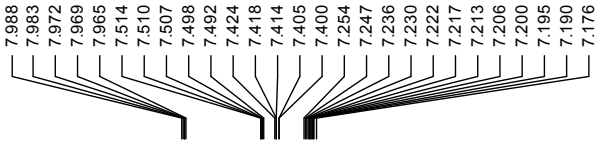
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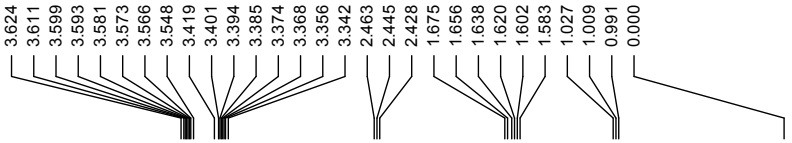
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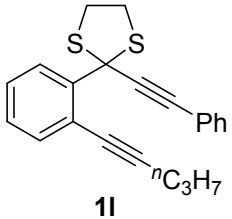
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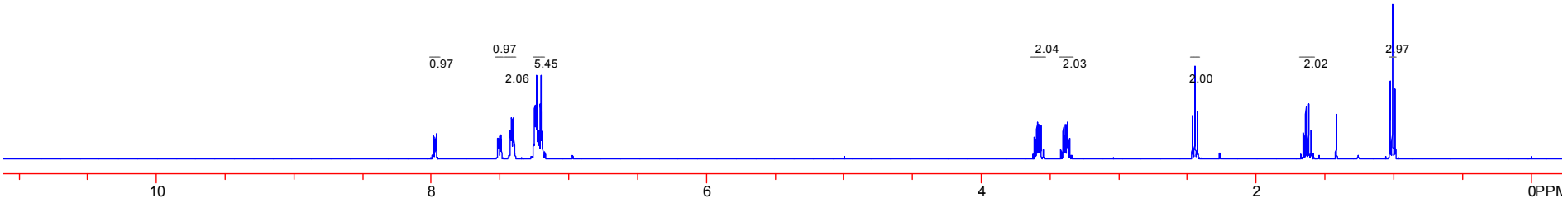
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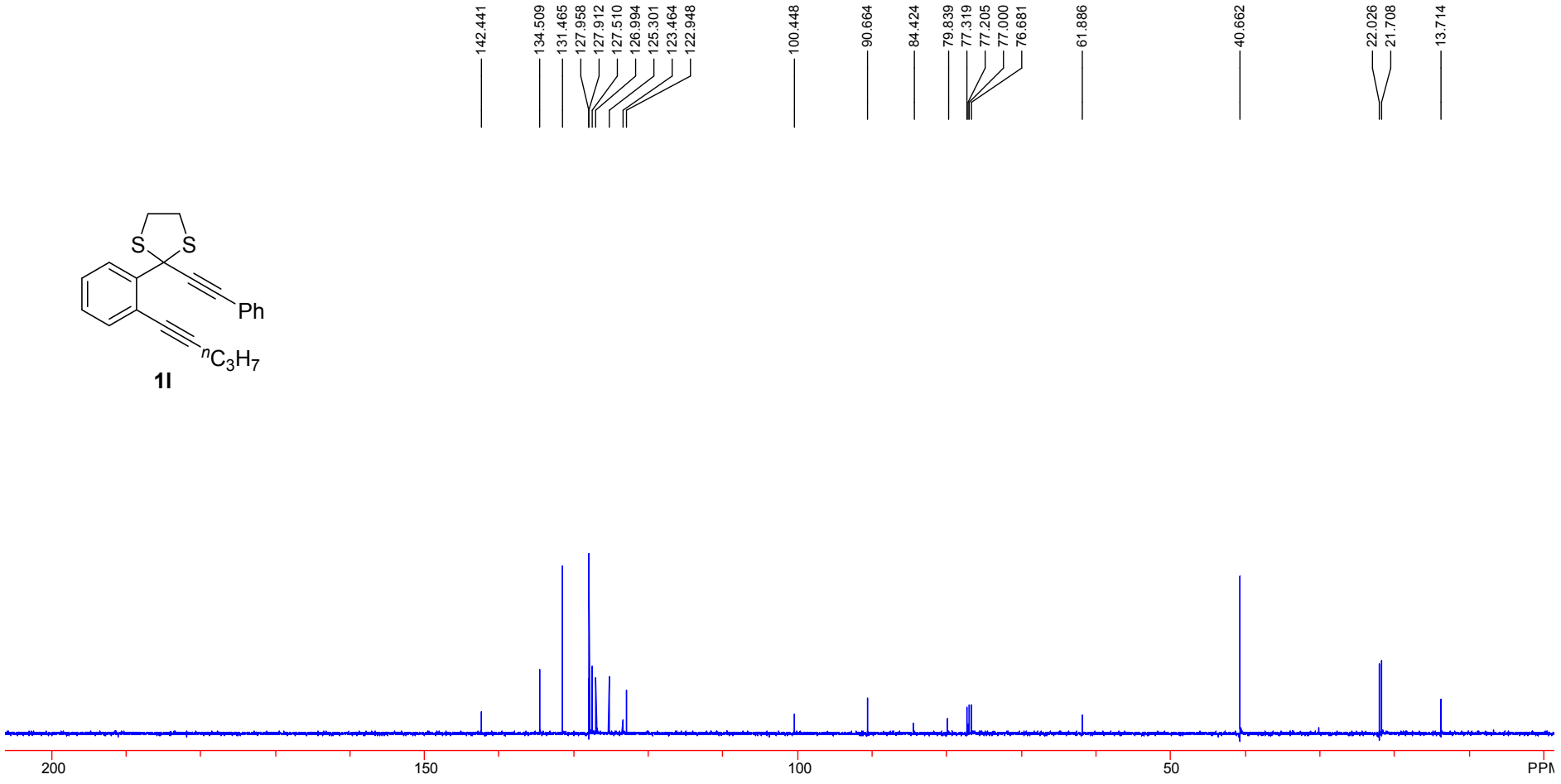
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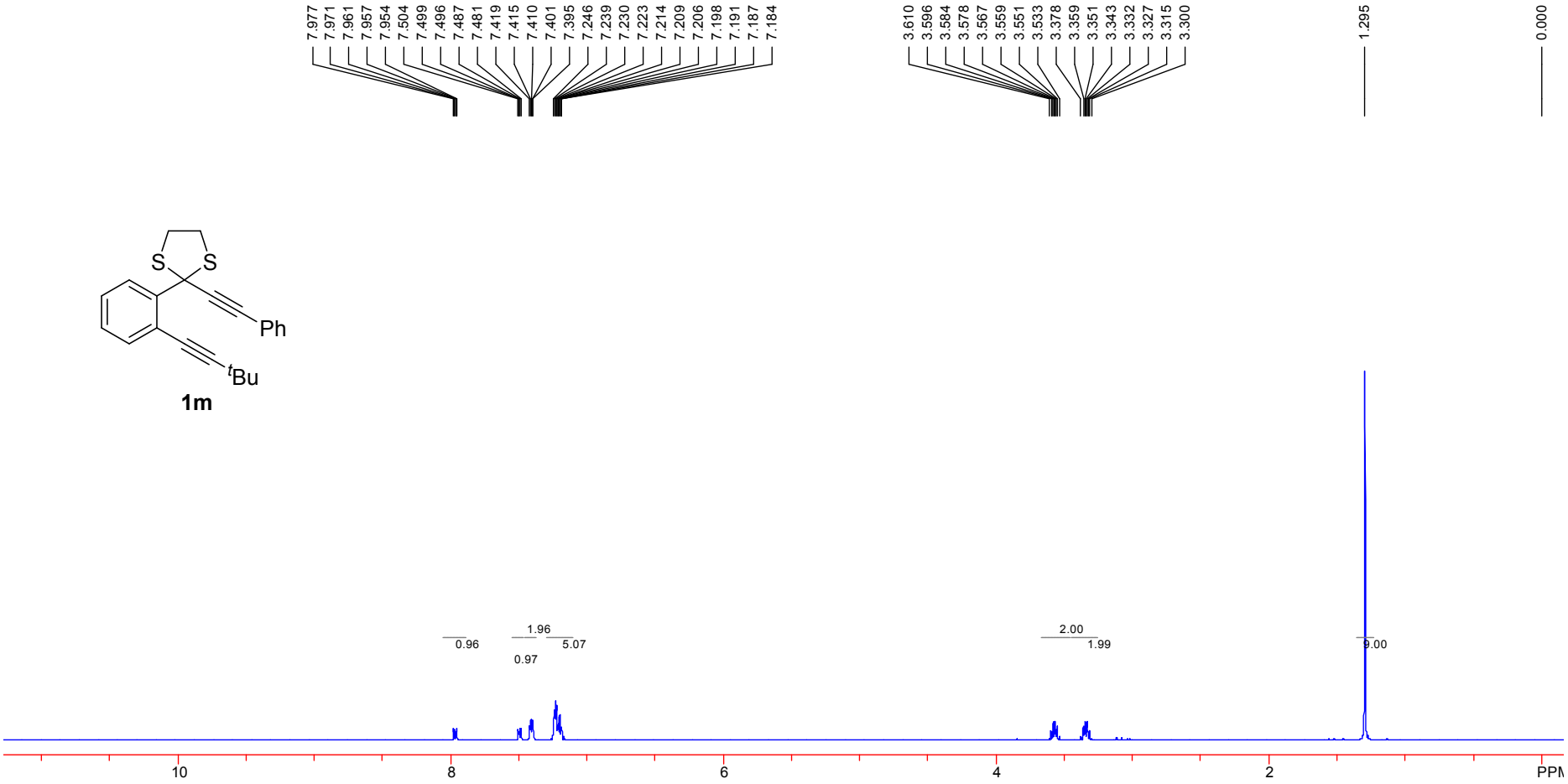
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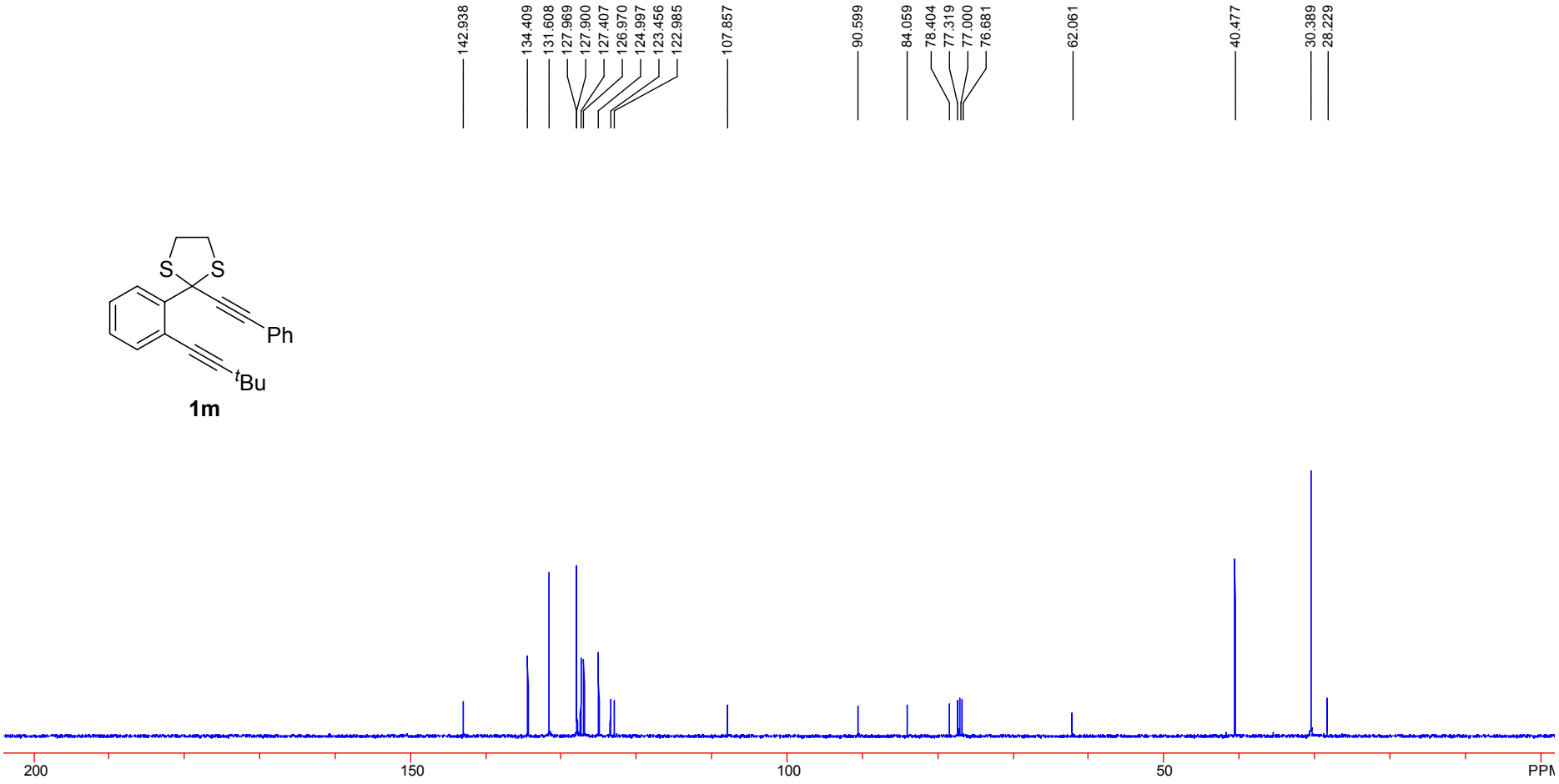
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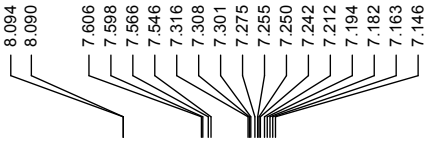
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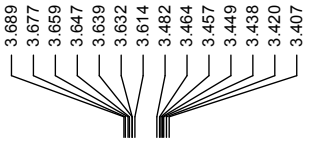
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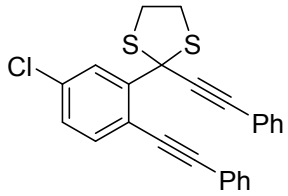
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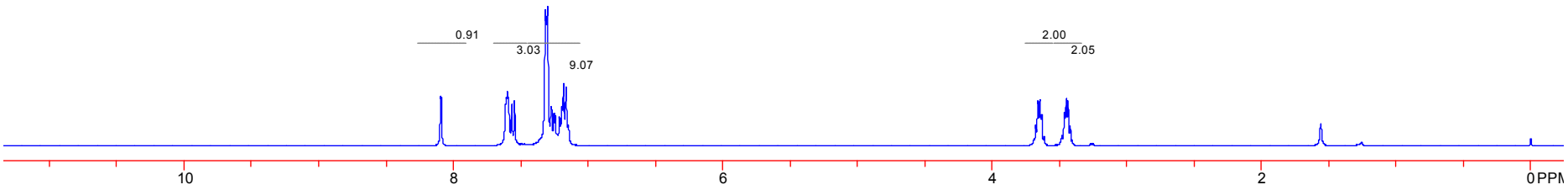
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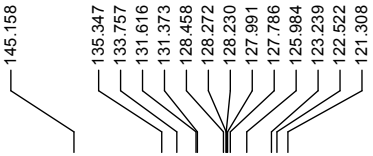
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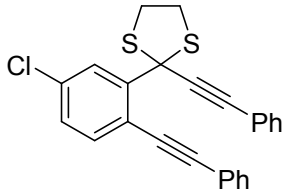
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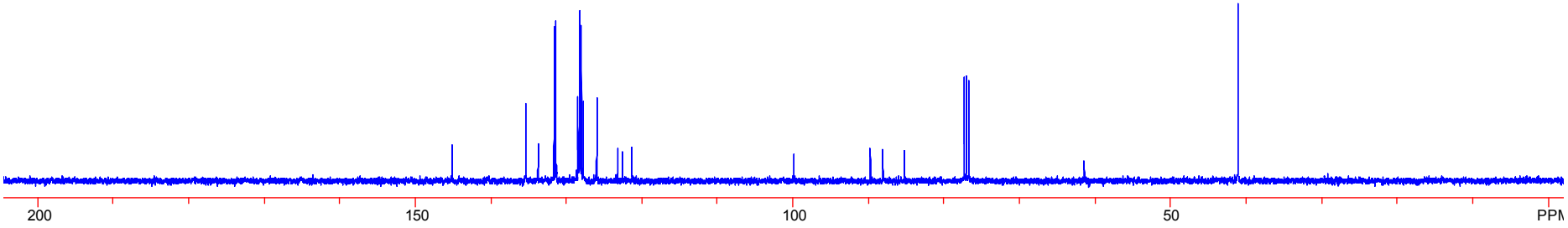
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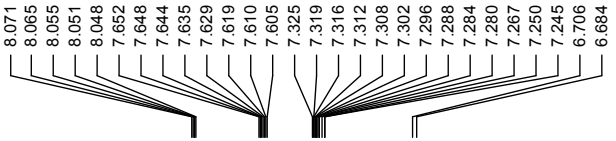
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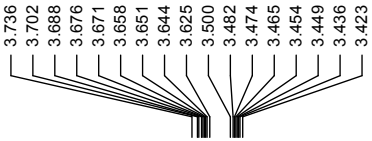
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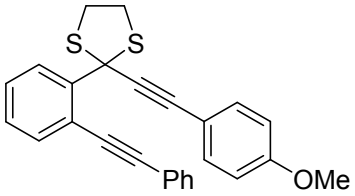
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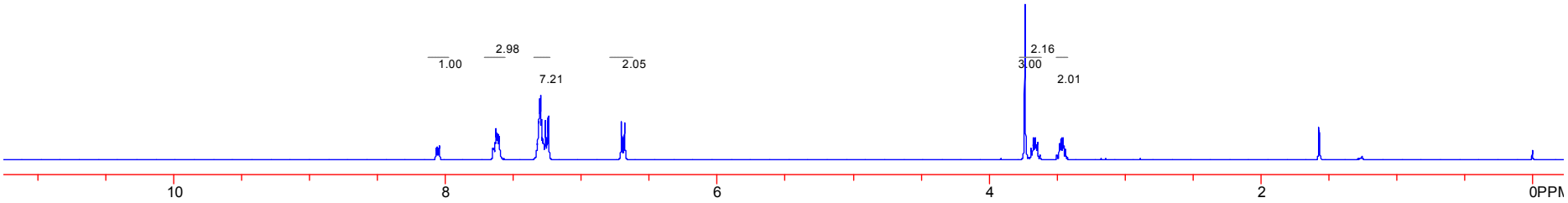
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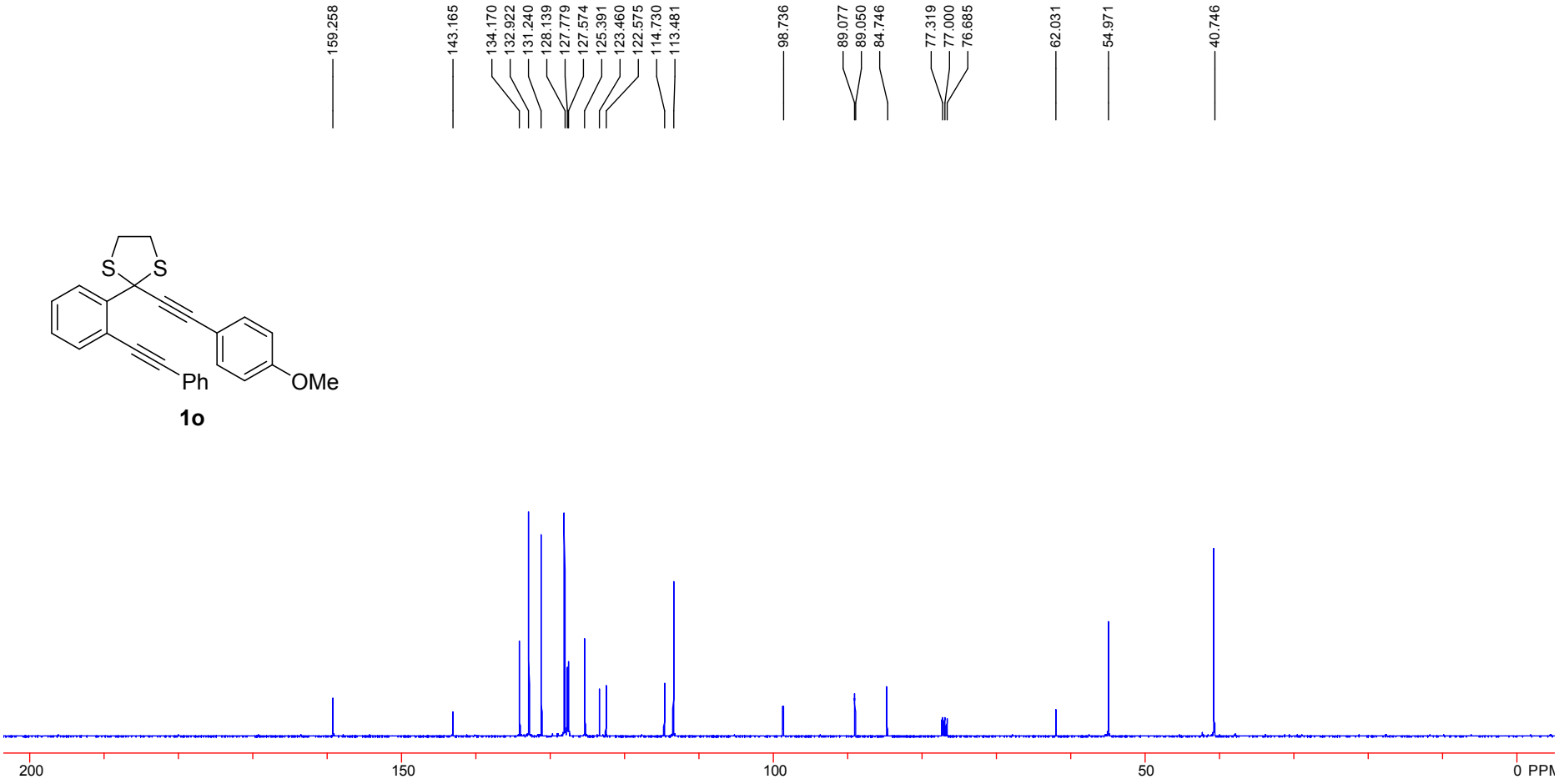
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OMe
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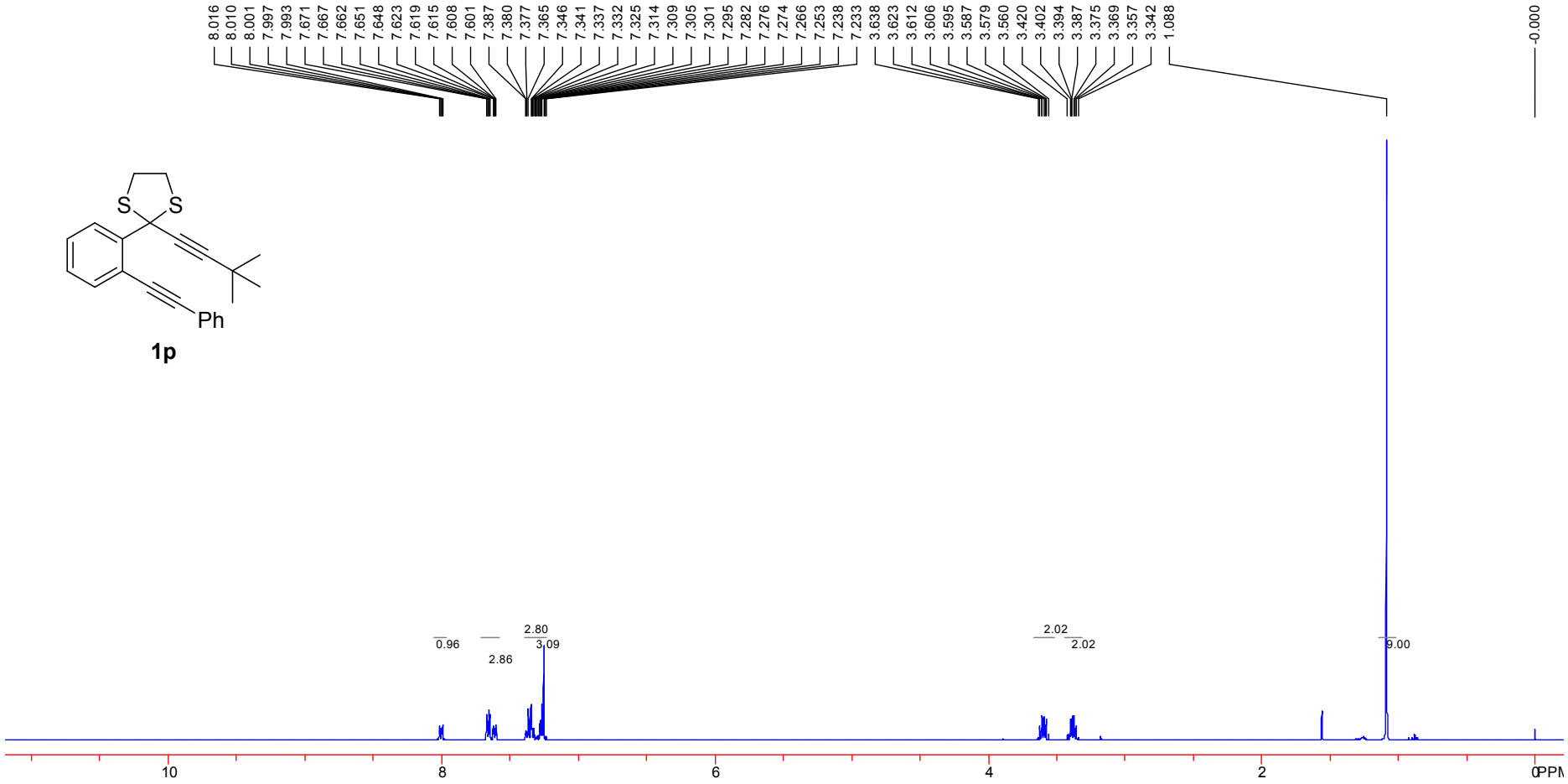
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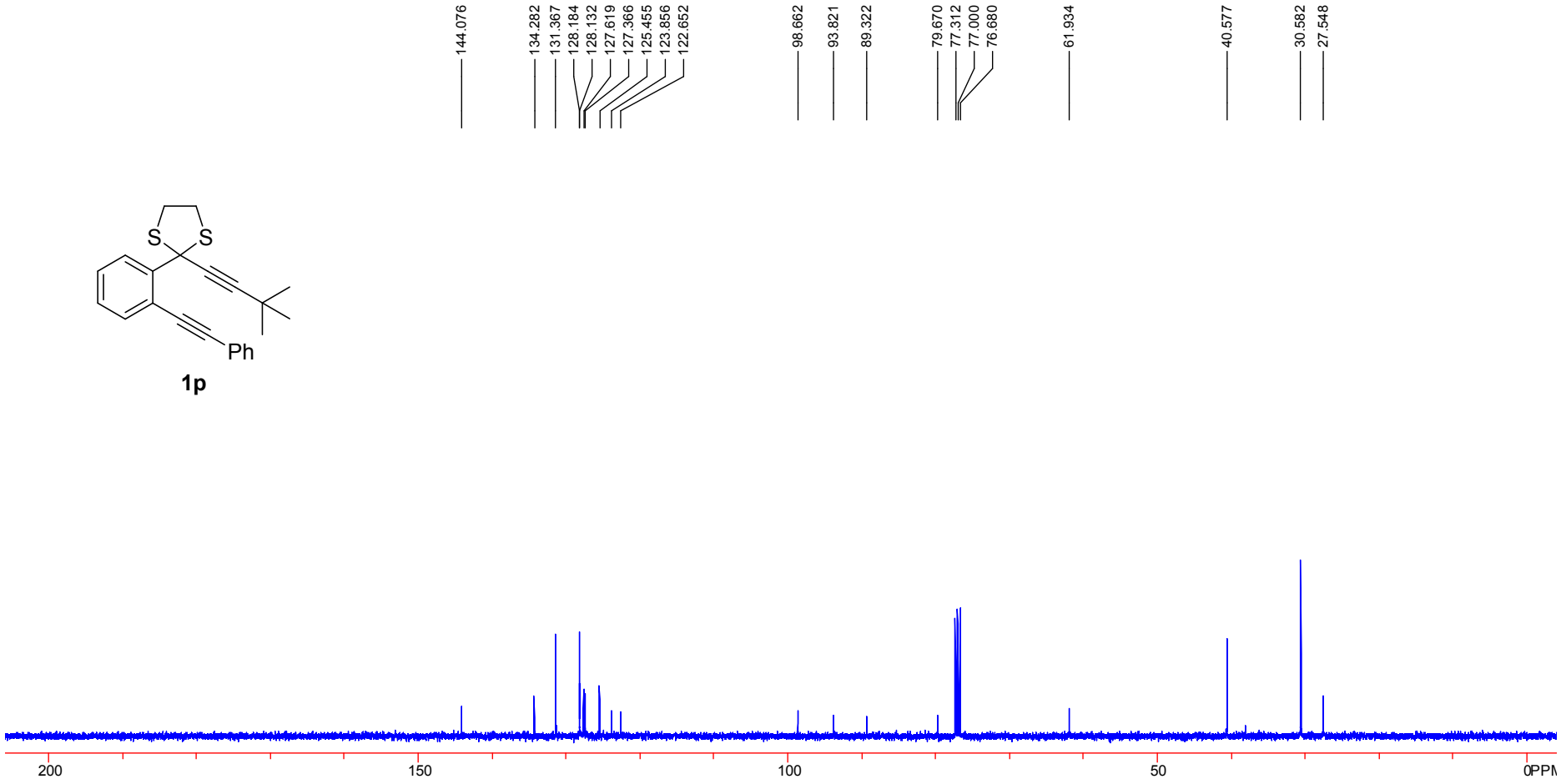
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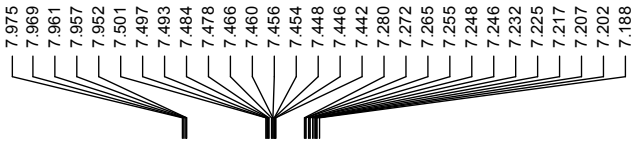
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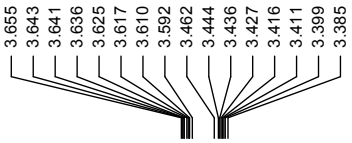
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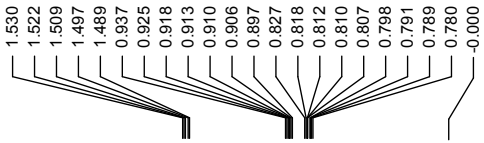
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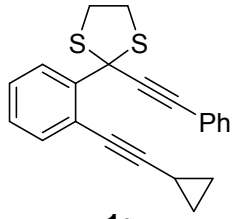
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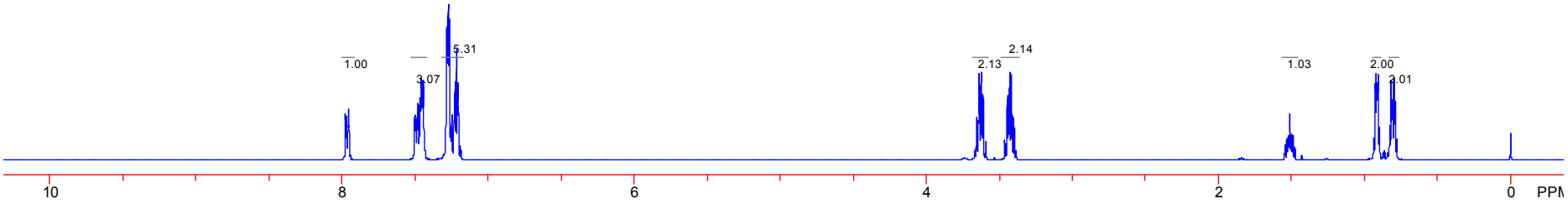
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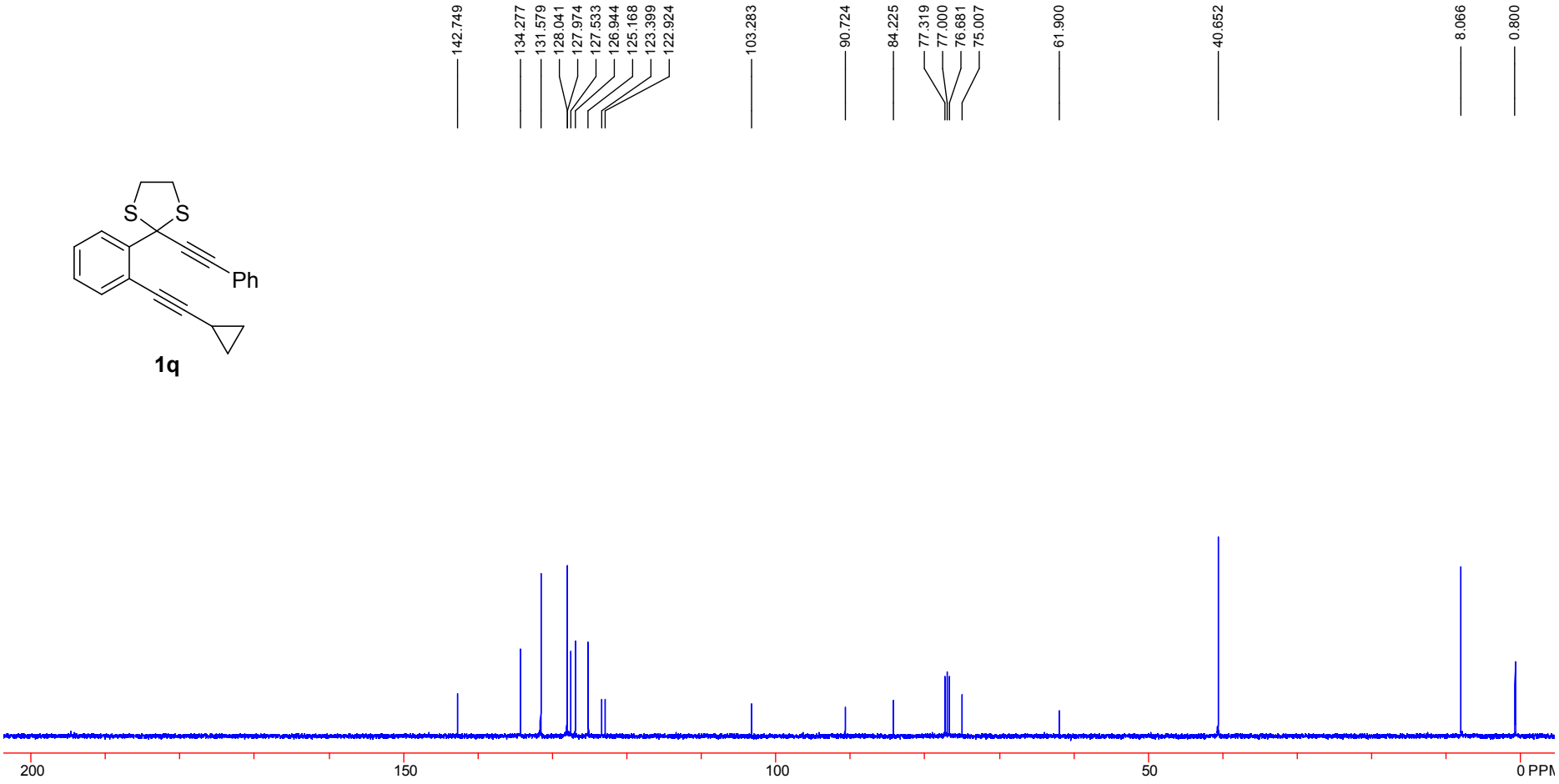
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50
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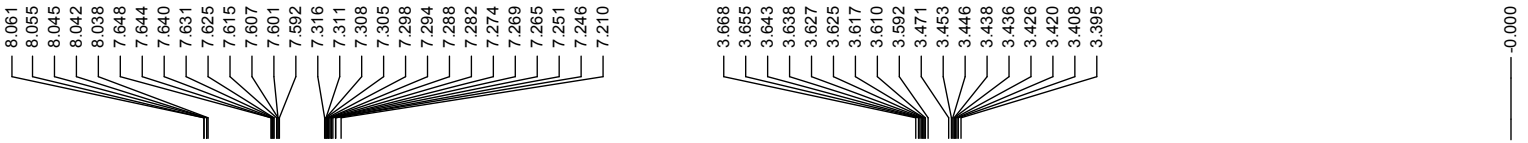
1q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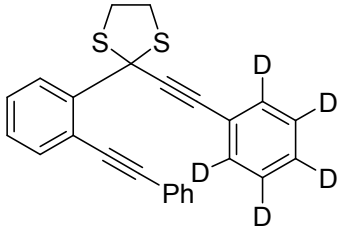
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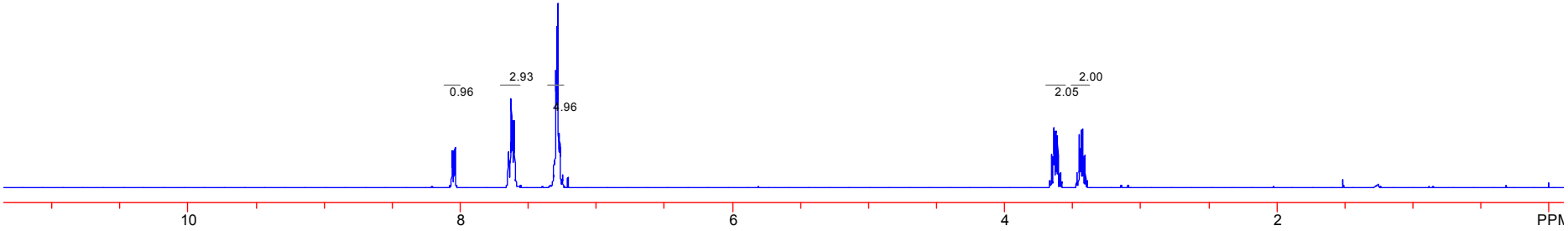
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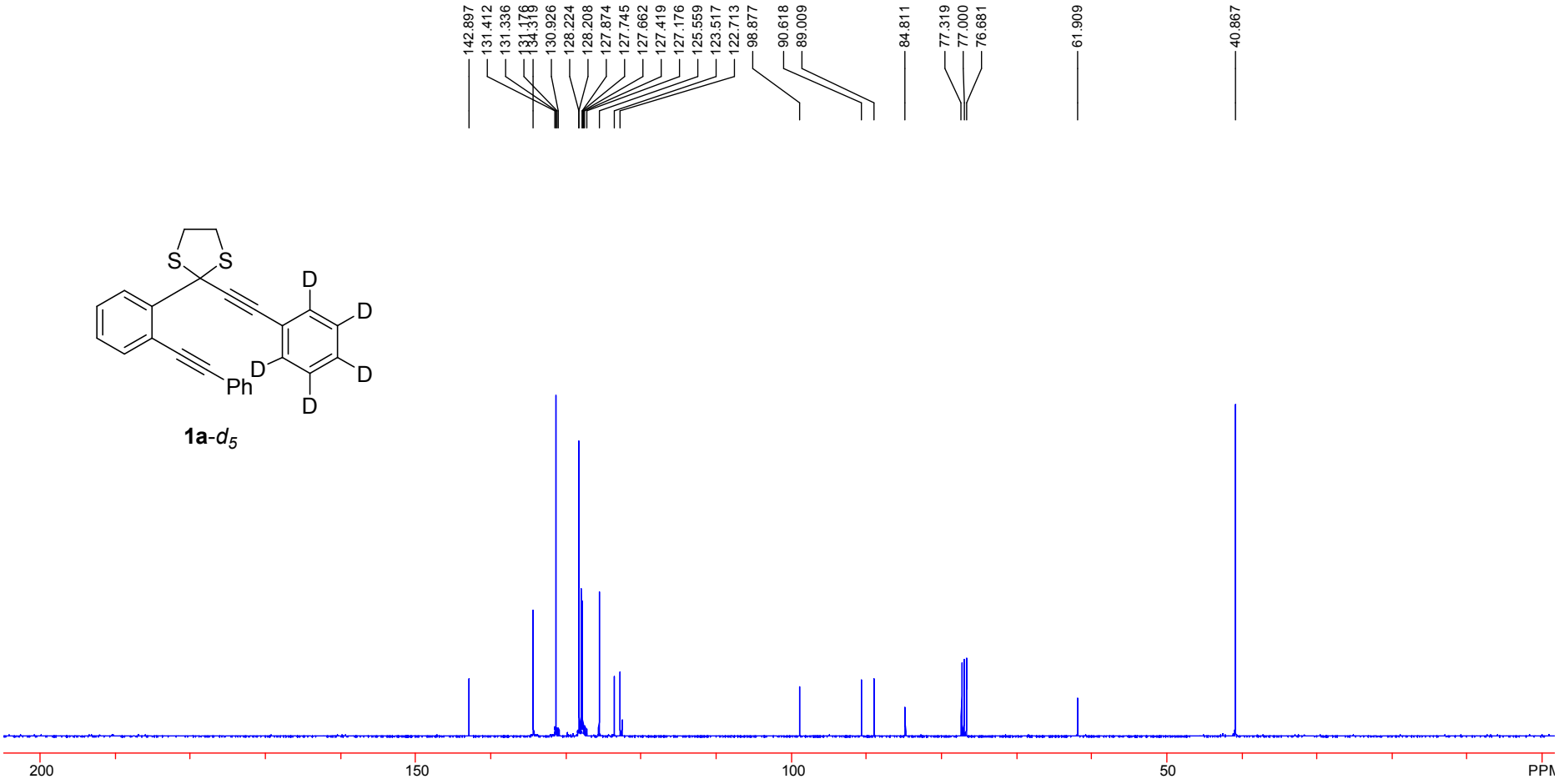
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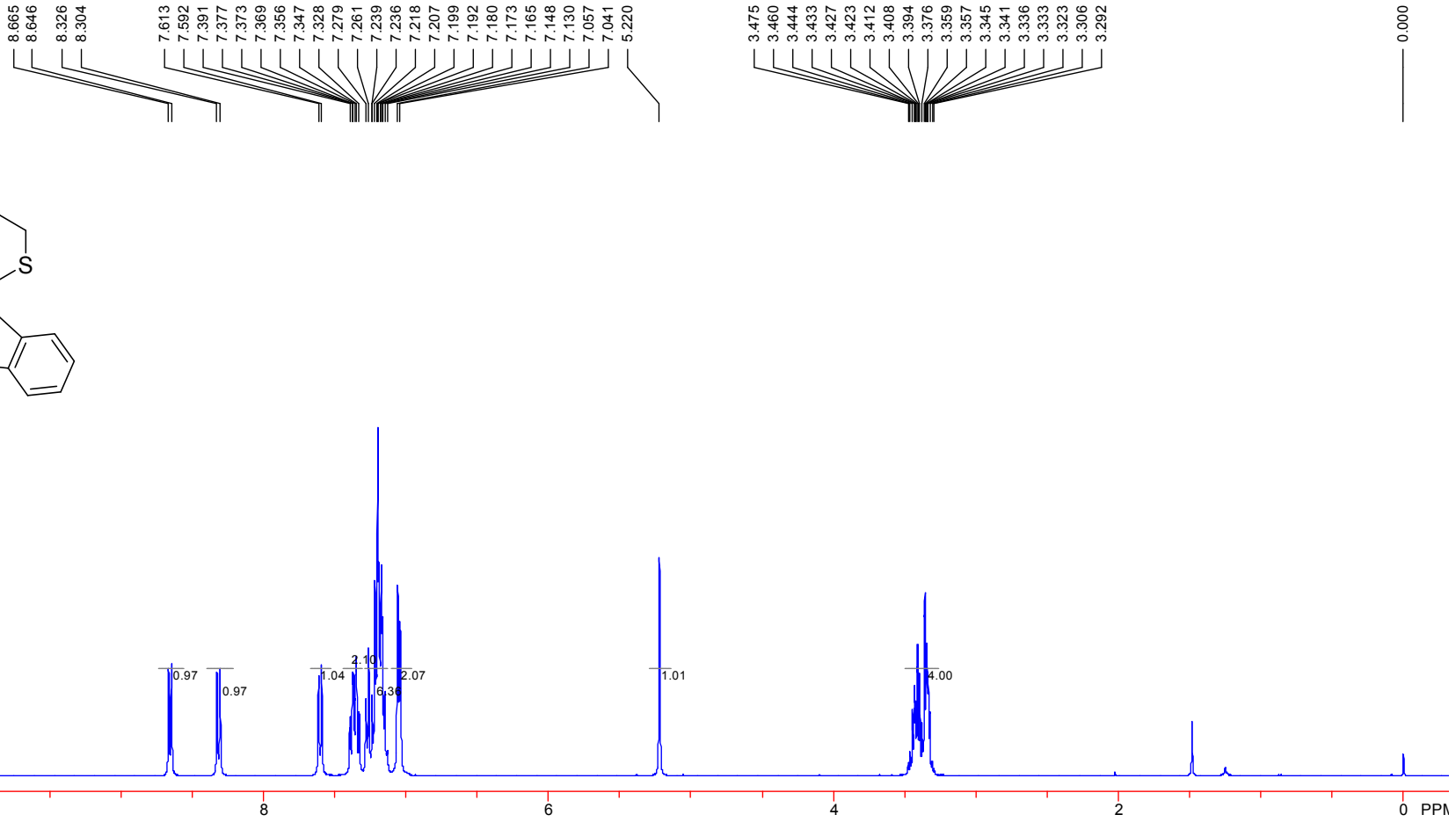
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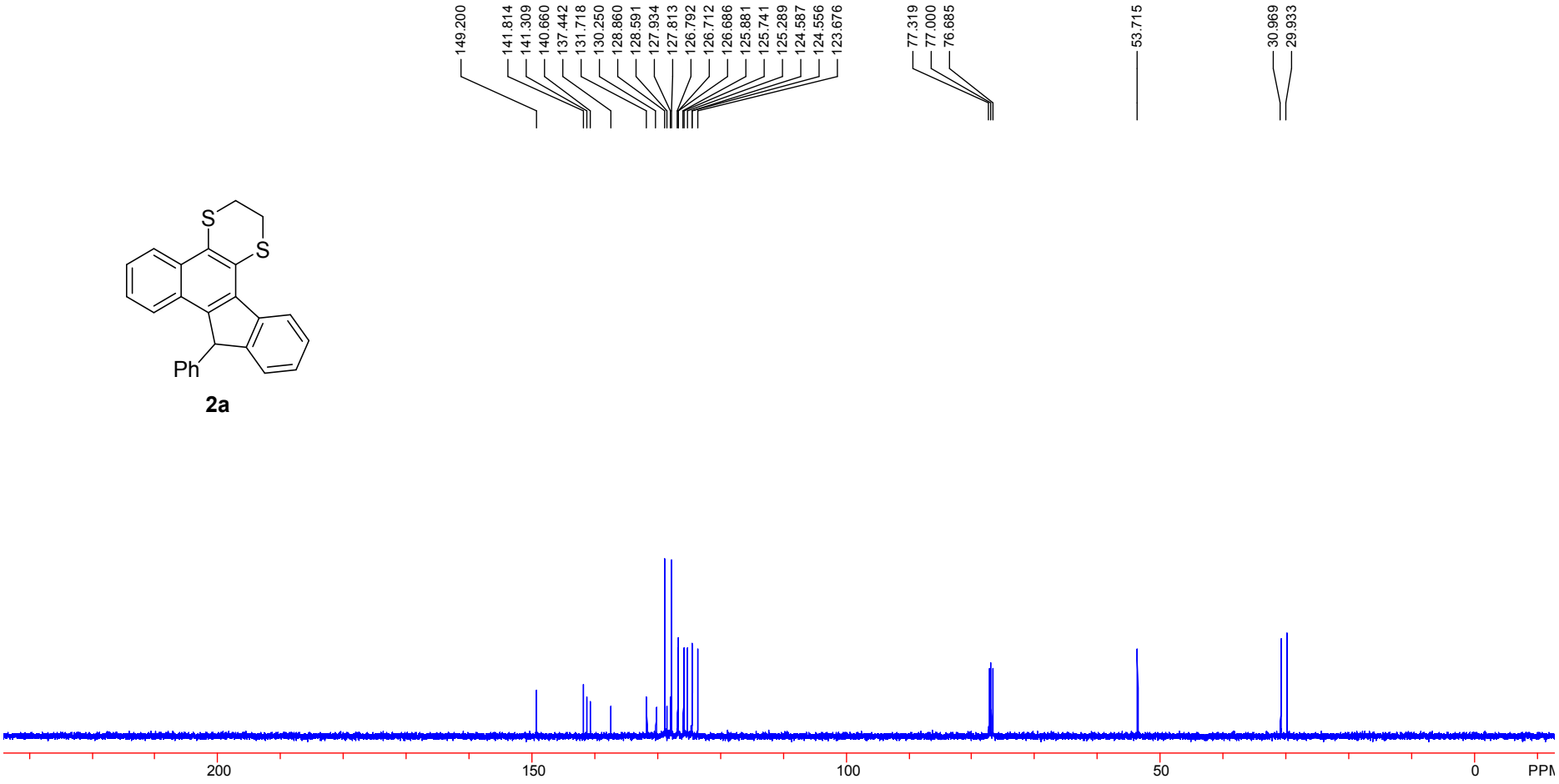
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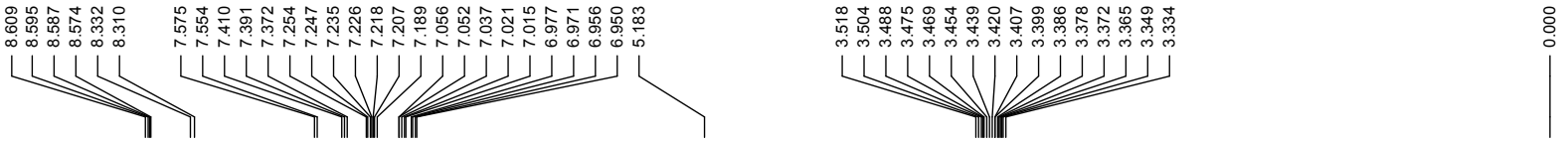
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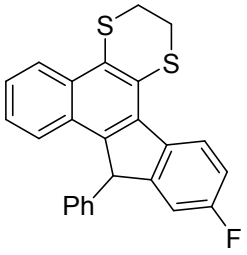
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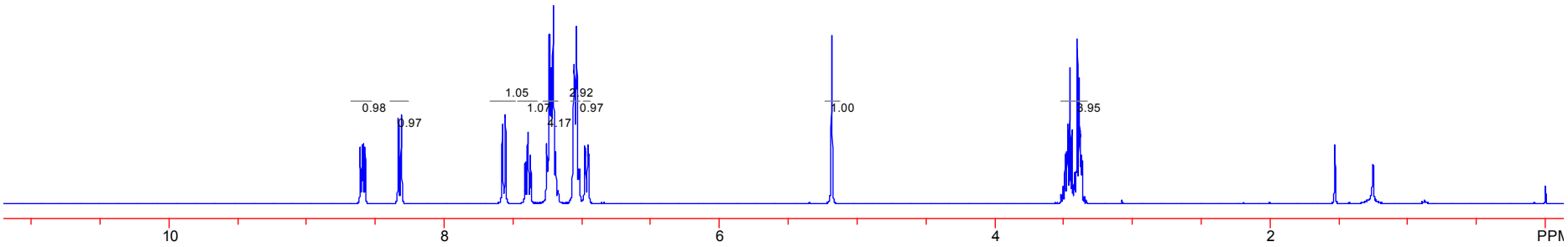
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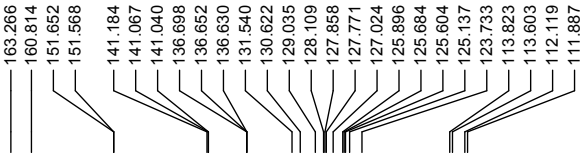
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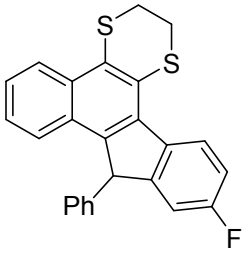
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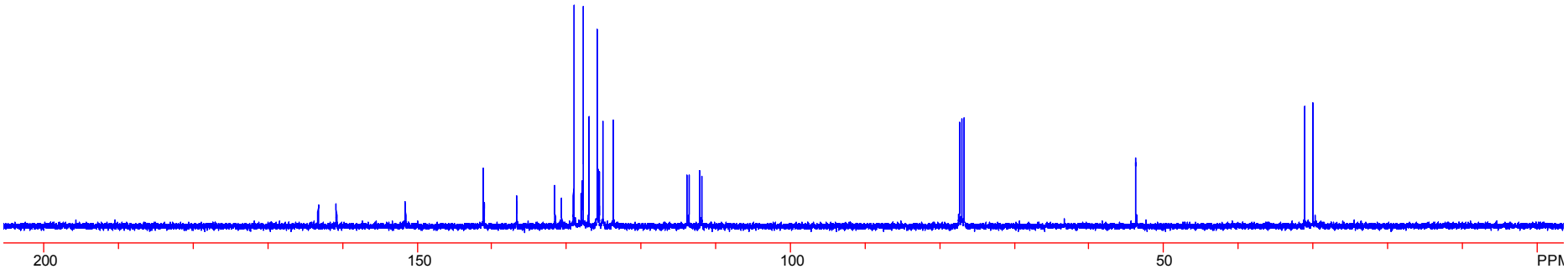
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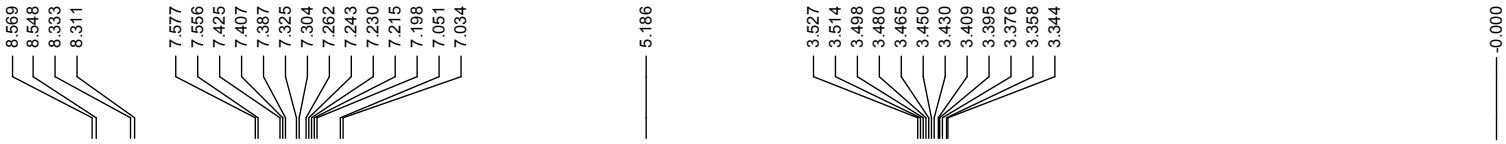
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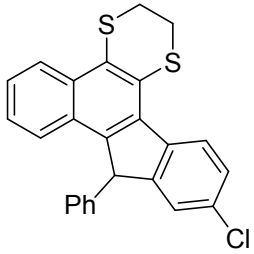
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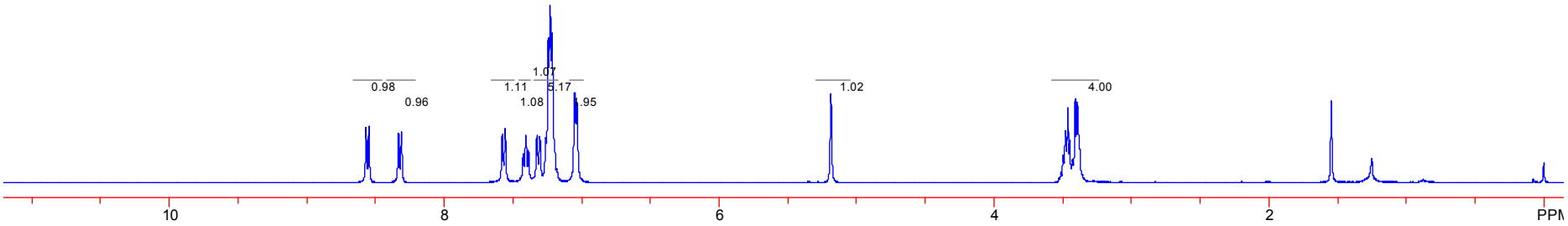
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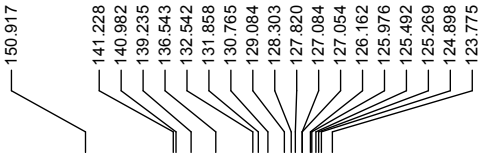
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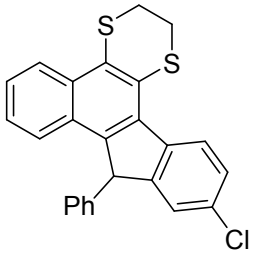
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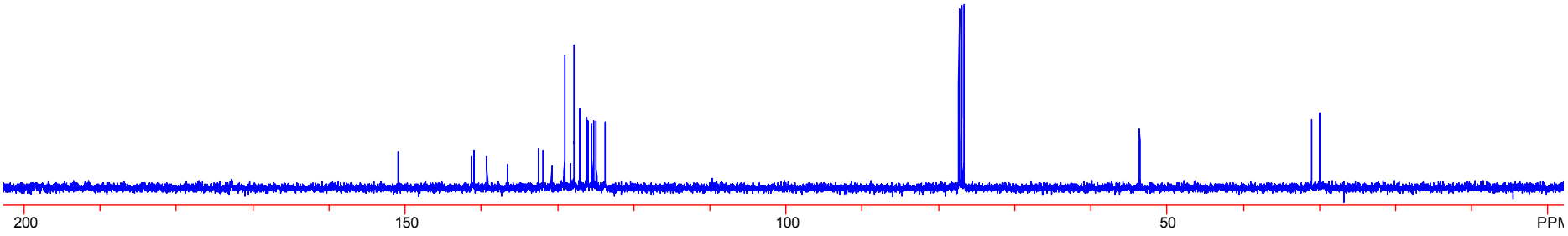
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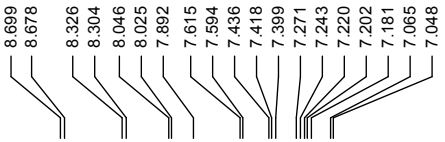
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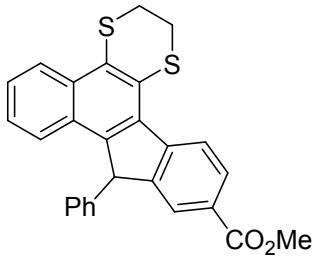
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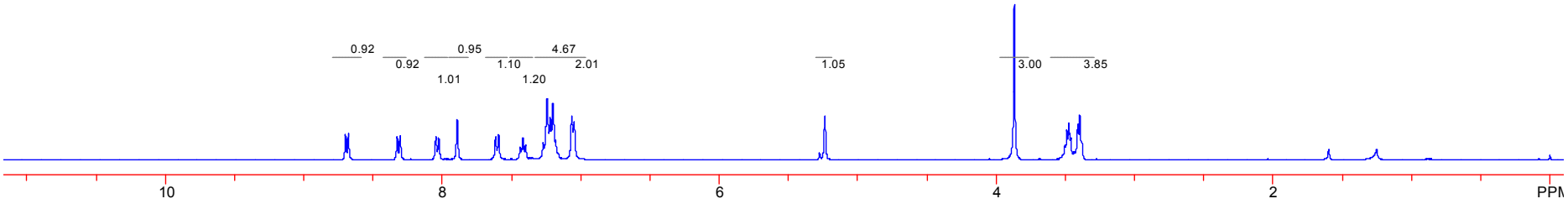
2d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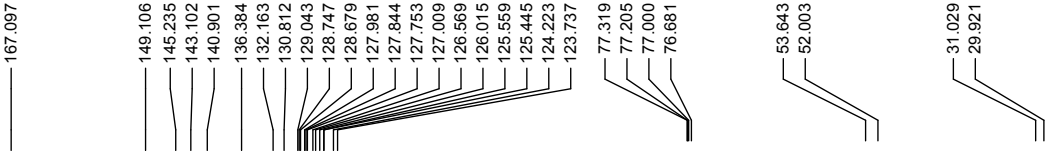
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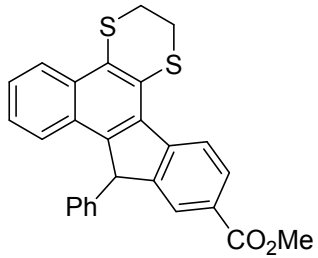
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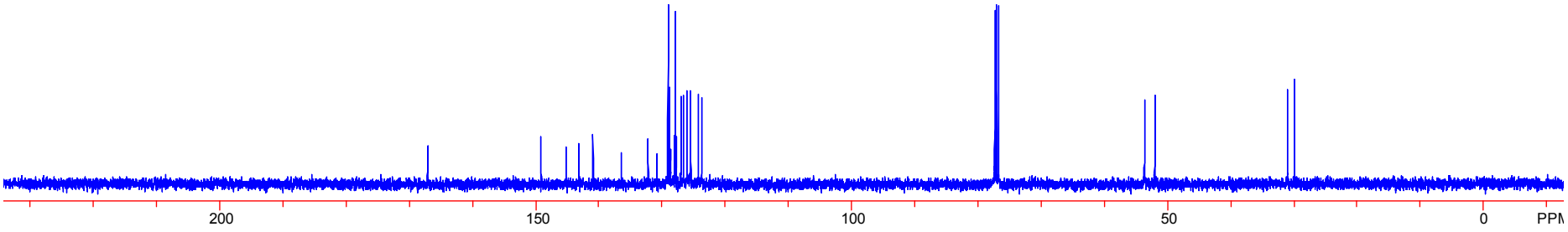
Ph
CO2Me

2d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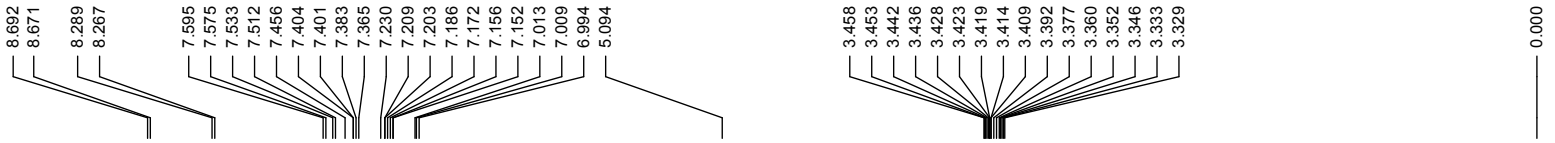
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7.172
7.156
7.152
7.013
7.009
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3.436
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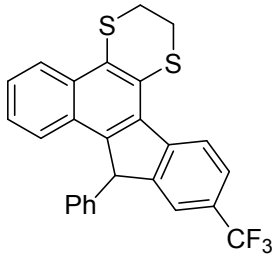
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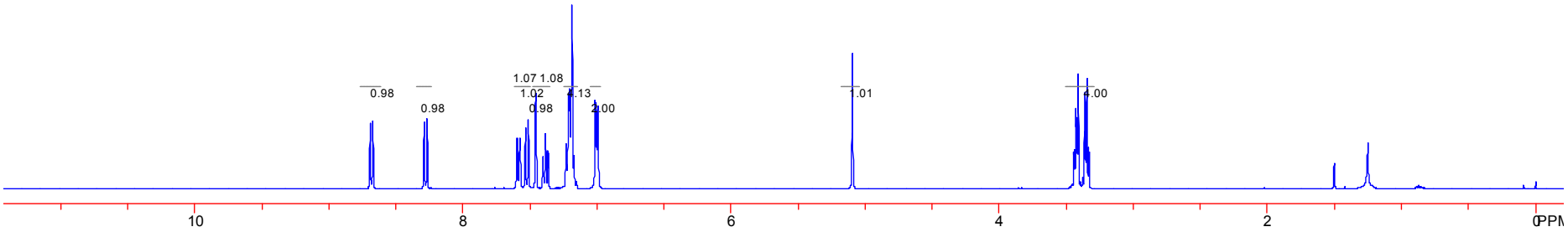
Ph
CF3

2e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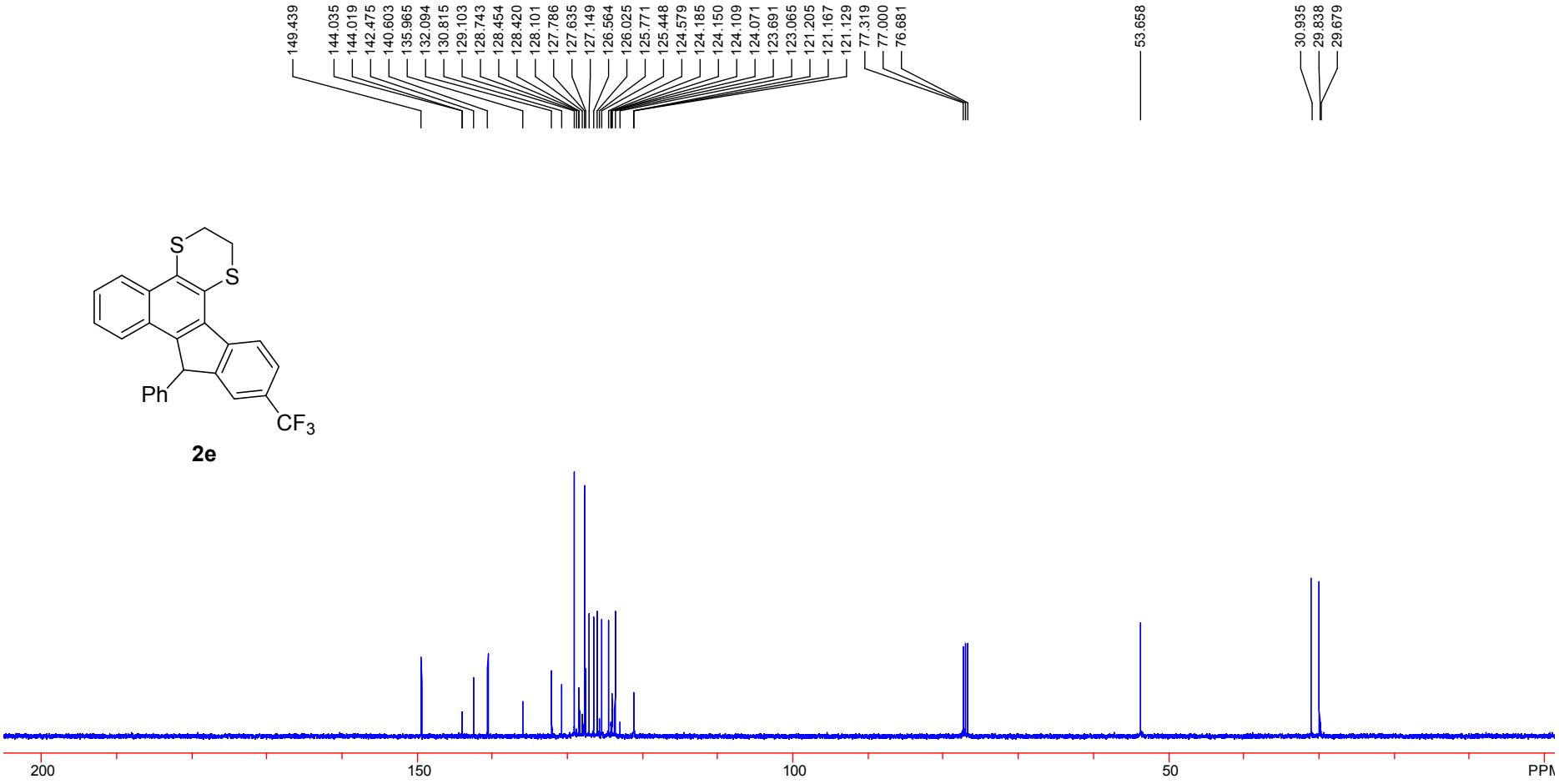
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CF3
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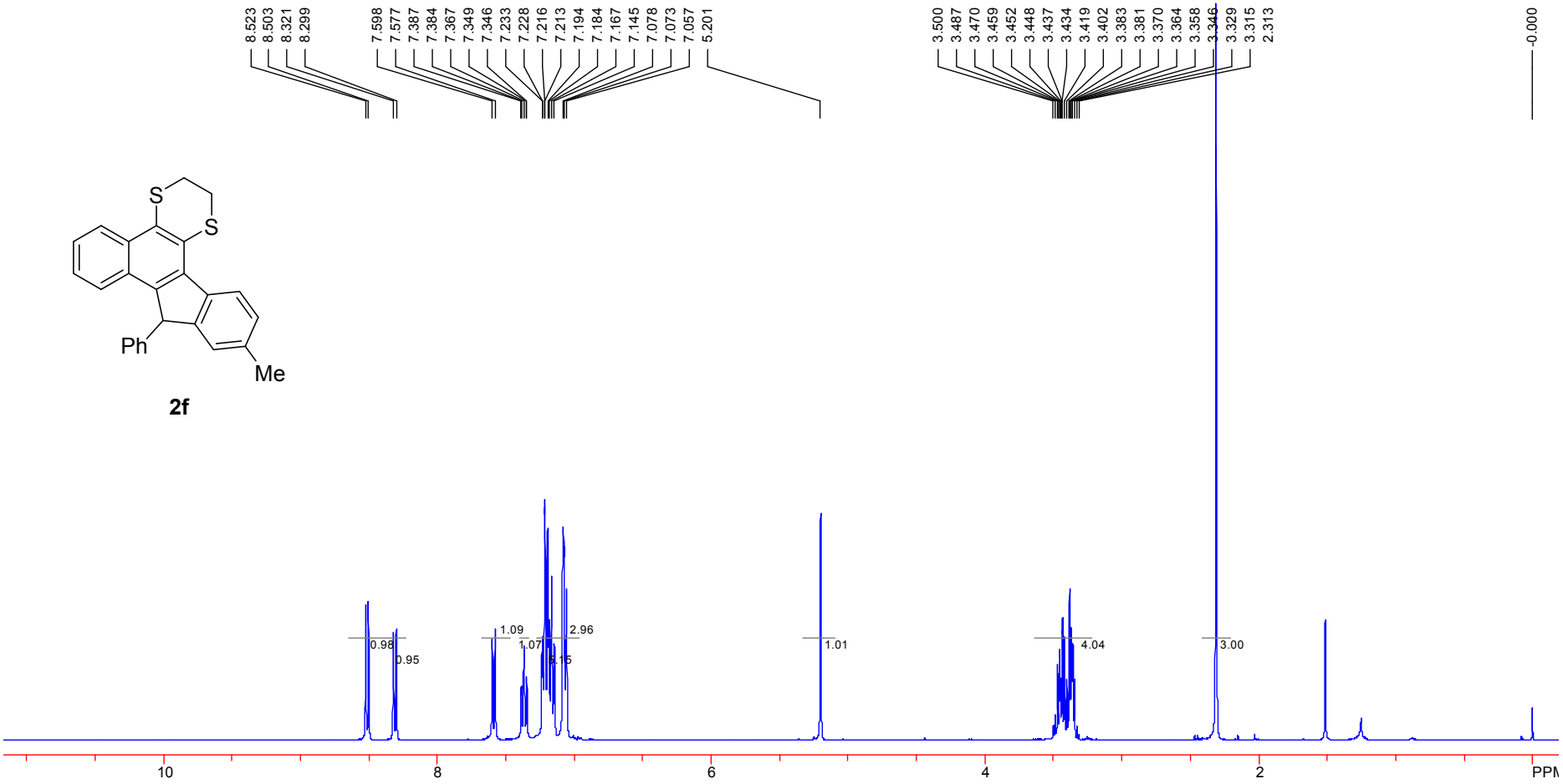
100
50
PPM

2e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3.459
3.452
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3.383
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3.329
3.315
2.313
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S
S
Ph
Me
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2
PPM

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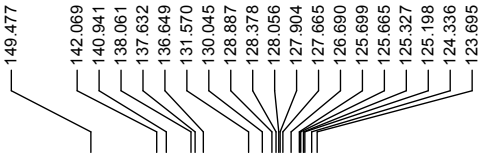
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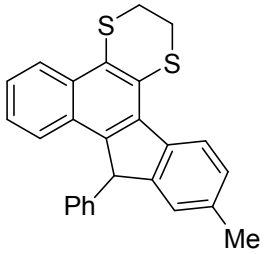
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Ph
Me

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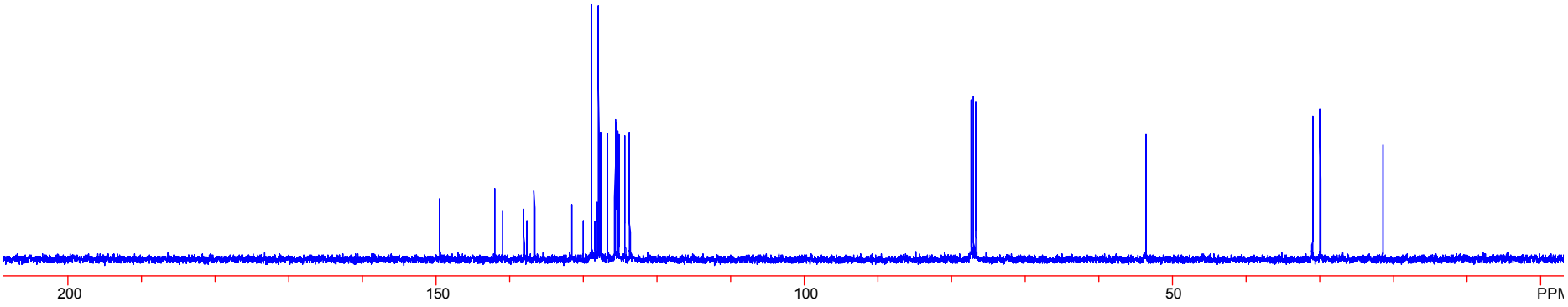
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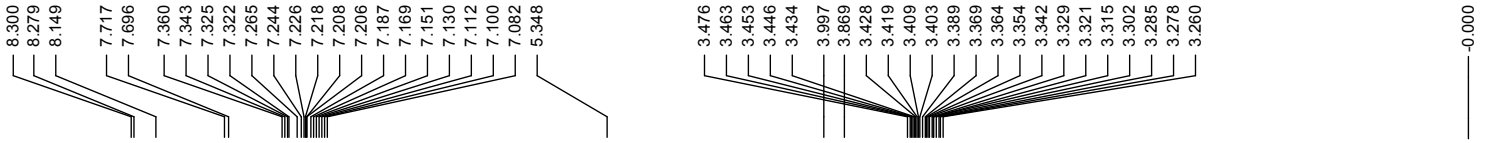
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7.187
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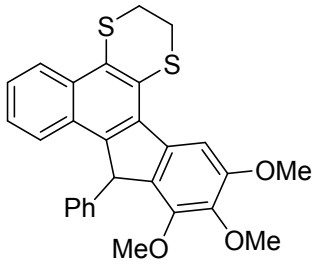
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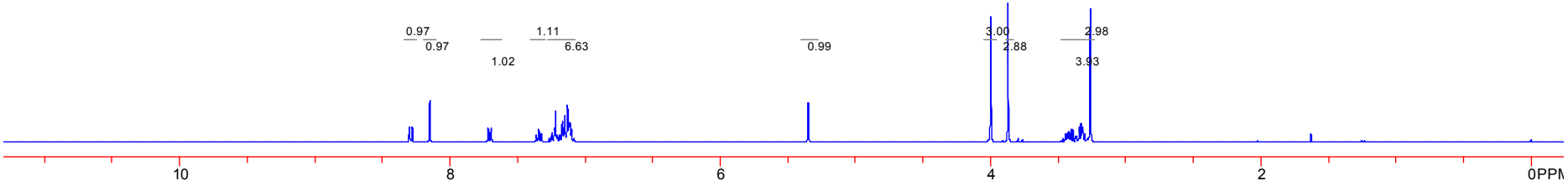
OMe
Ph
MeO
OMe

2g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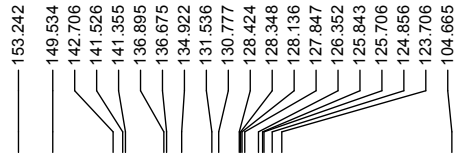
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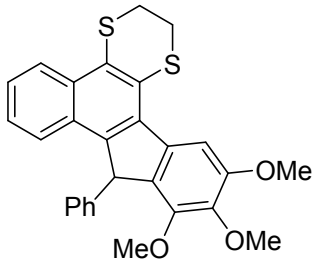
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Ph
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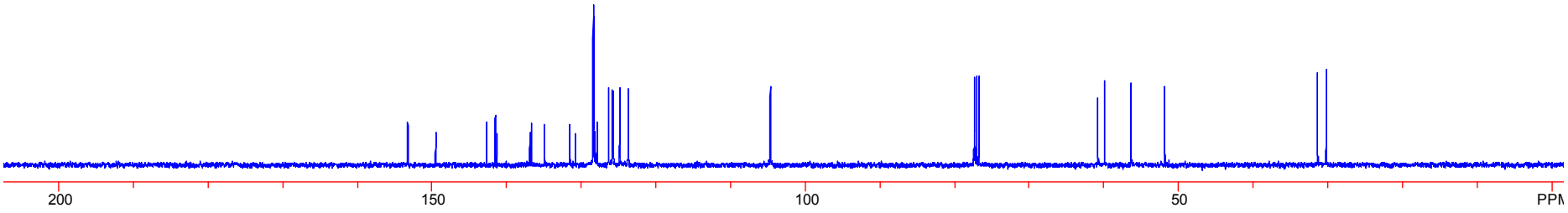
OMe

2g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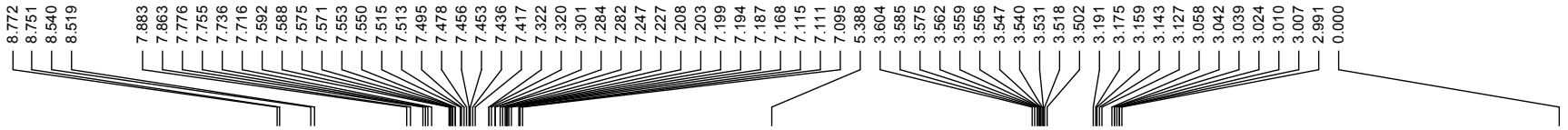
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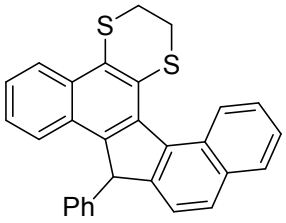
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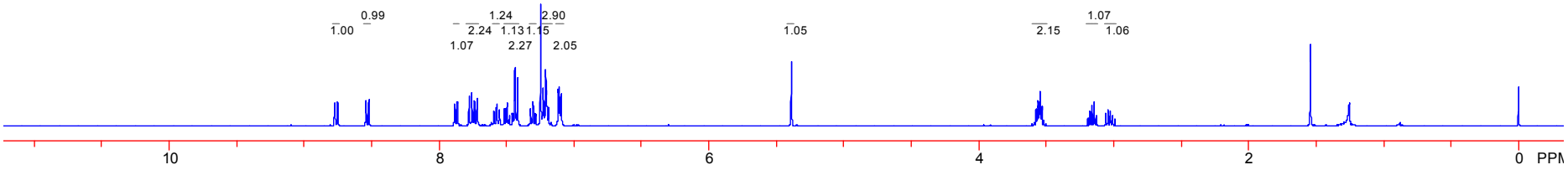
2h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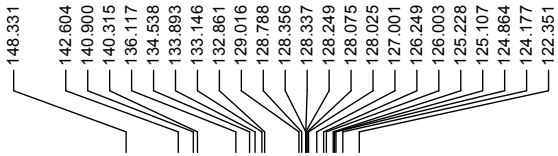
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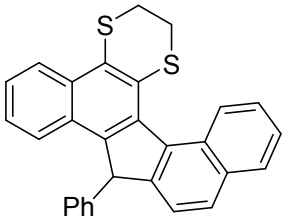
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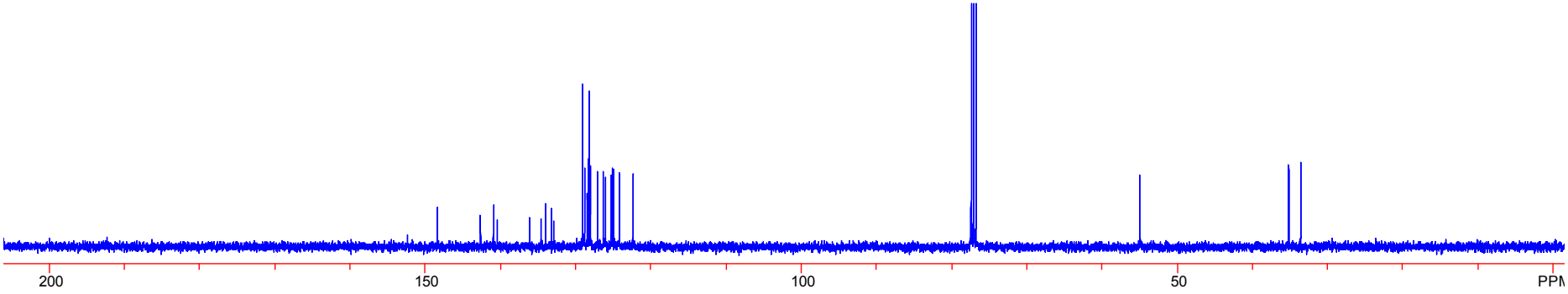
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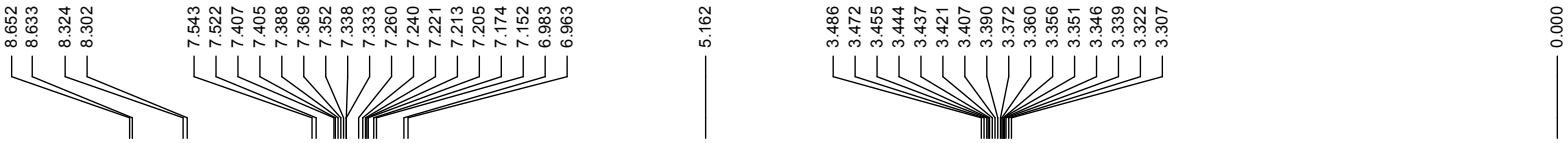
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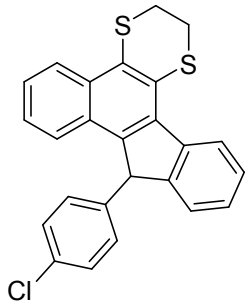
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Cl

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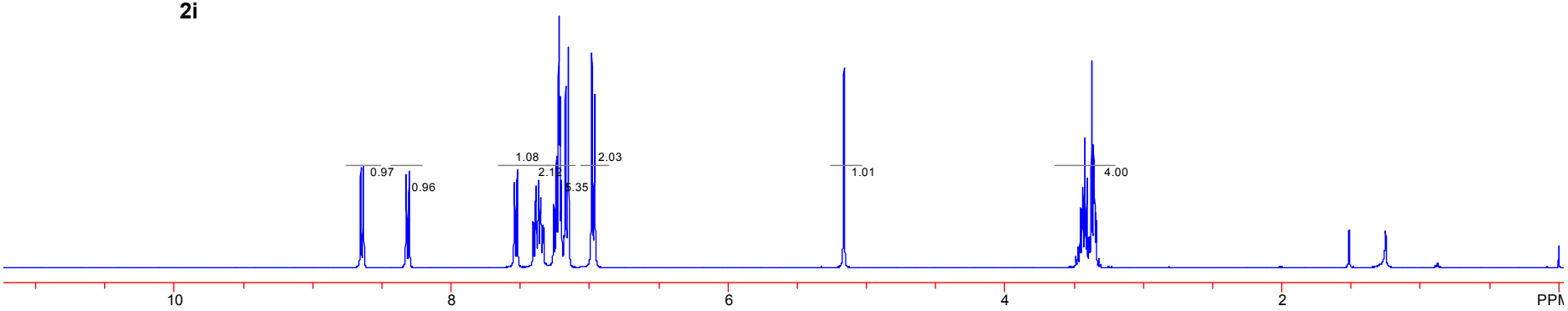
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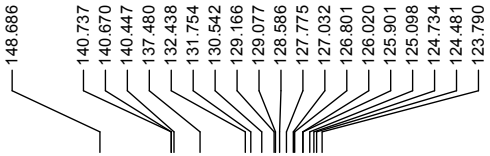
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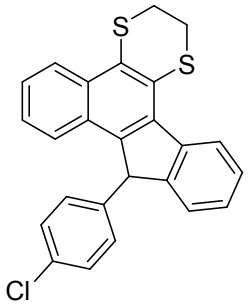
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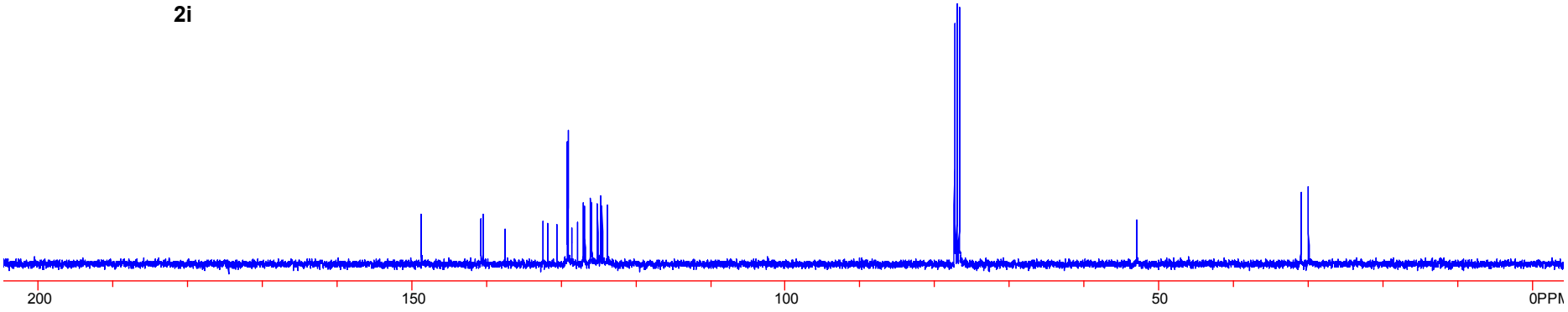
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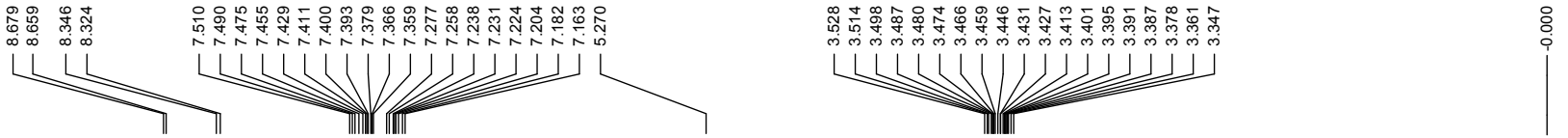
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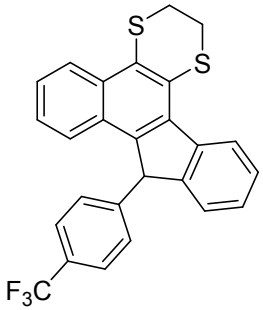
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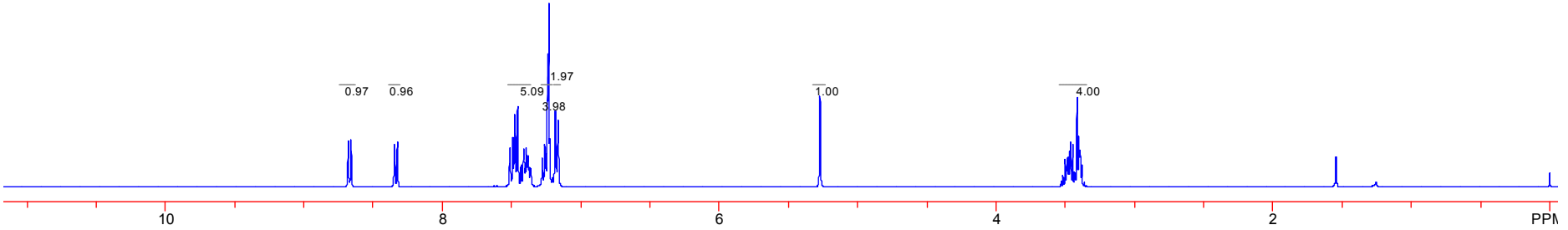
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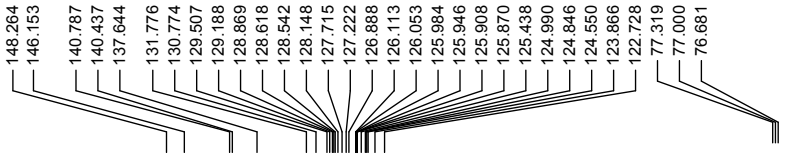
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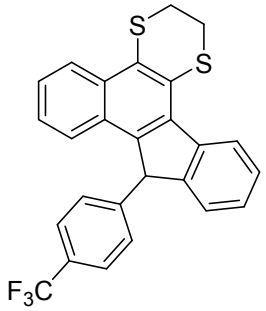
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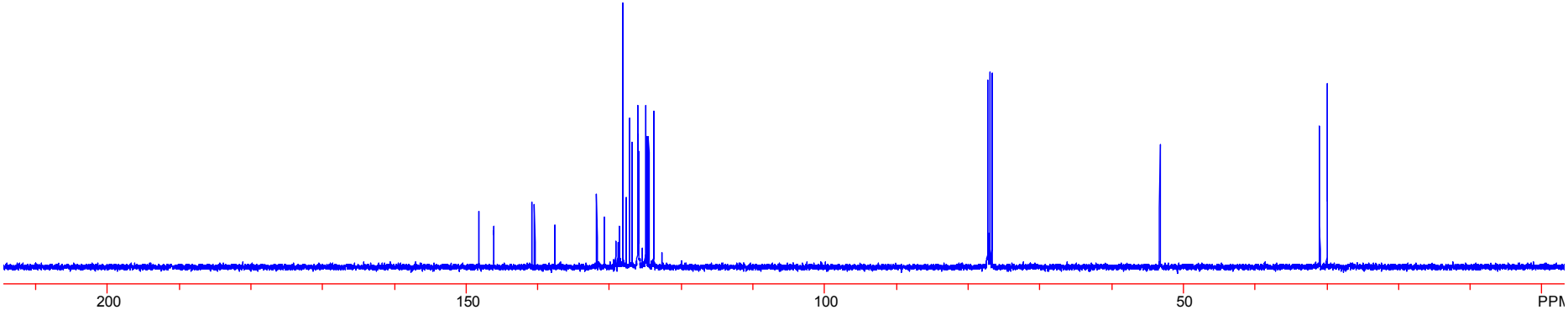
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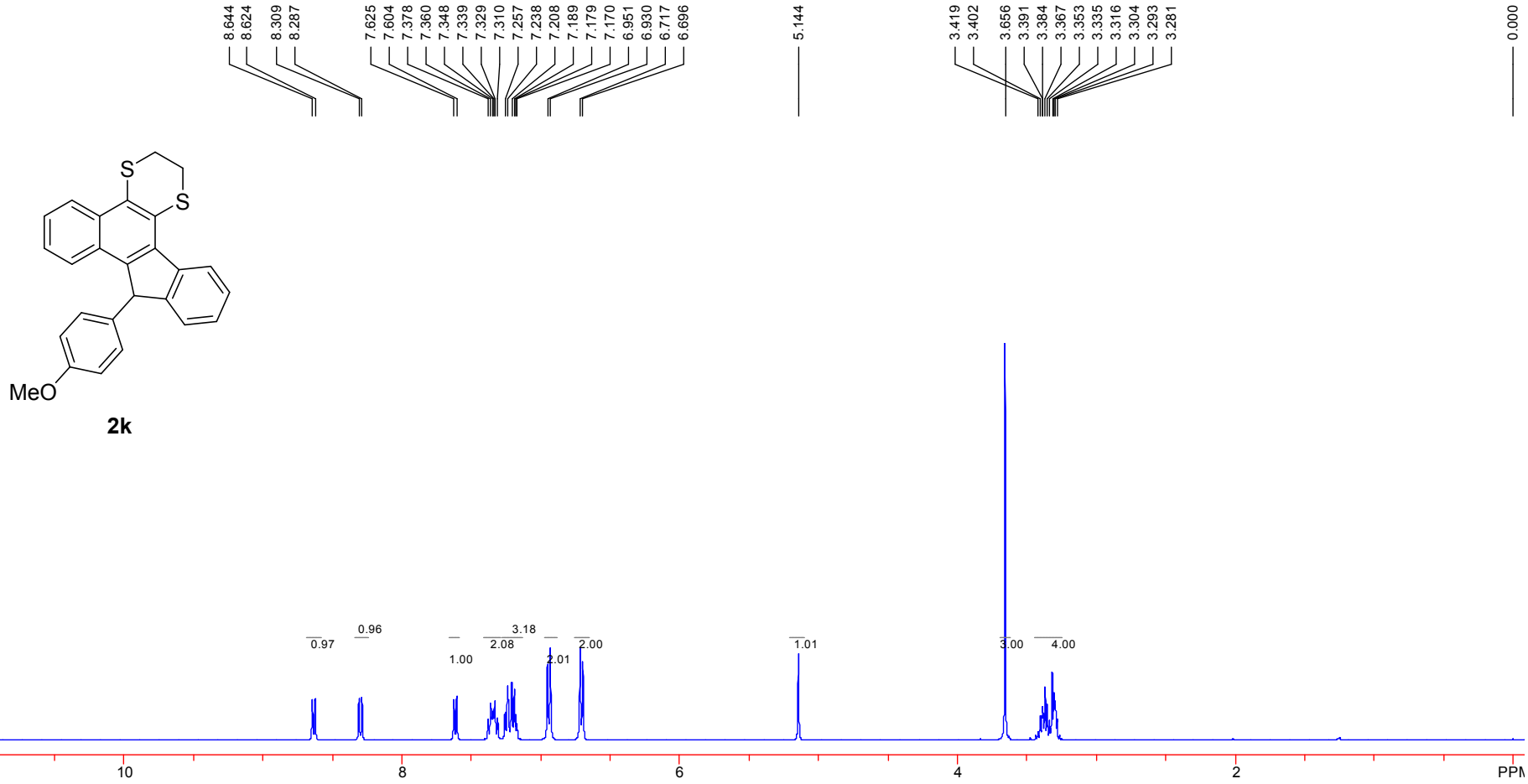
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7.360
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7.339
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7.257
7.238
7.208
7.189
7.179
7.170
6.951
6.930
6.717
6.696
5.144
3.419
3.402
3.656
3.391
3.384
3.367
3.353
3.335
3.316
3.304
3.293
3.281
0.000
S
S
MeO
2k
0.97
0.96
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3.18
2.01
2.00
1.01
3.00
4.00
10
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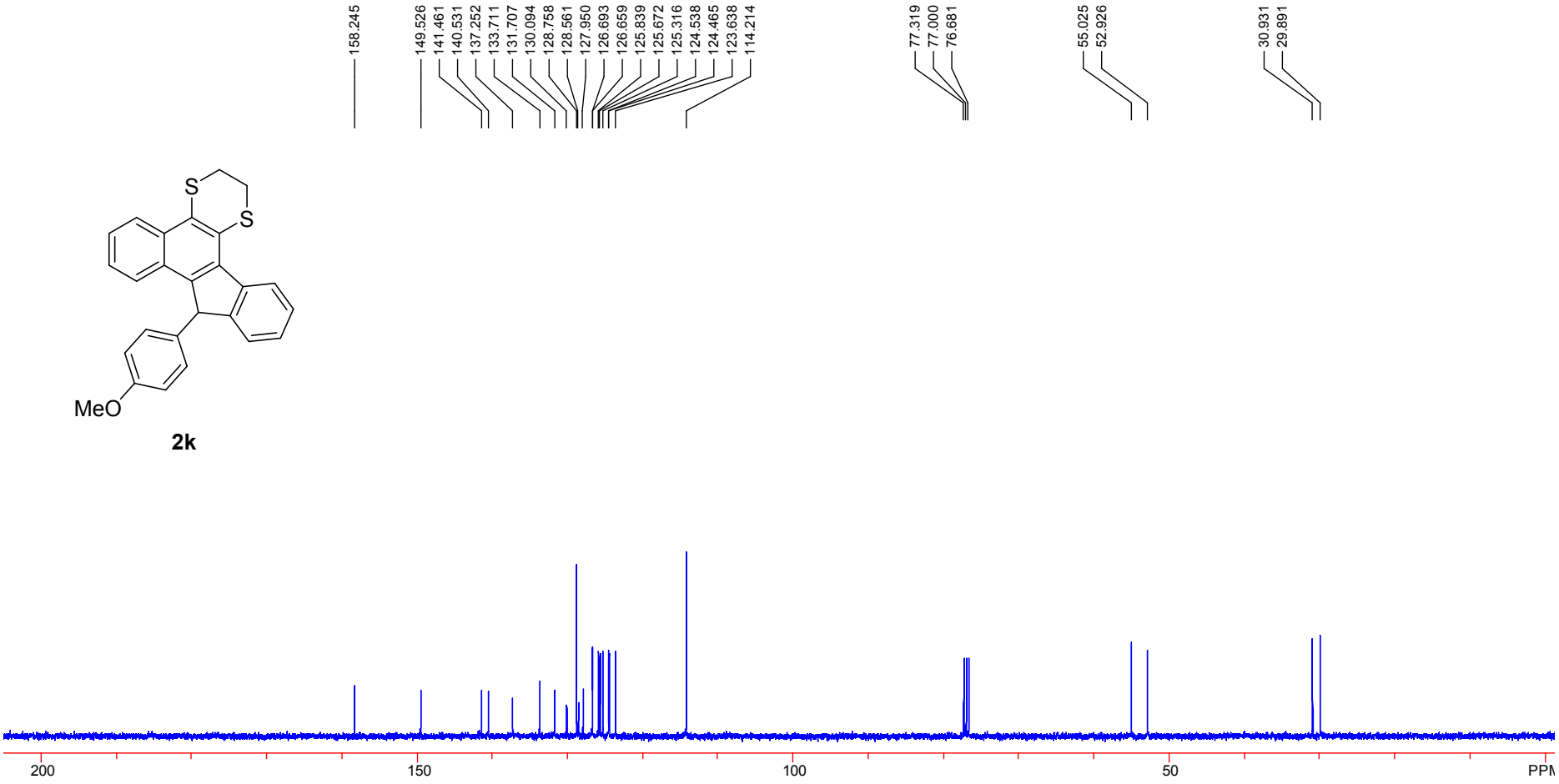
4
2
PPM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130.094
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127.950
126.693
126.659
125.839
125.672
125.316
124.538
124.465
123.638
114.214
77.319
77.000
76.681
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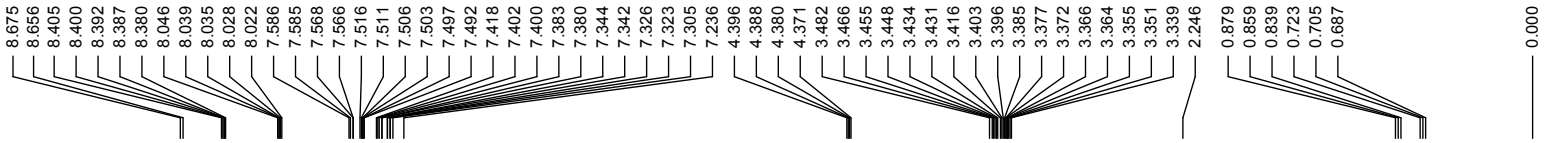
52.926
30.931
29.891
S
S
MeO
200
150
100
50
PPM

2k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8.035
8.028
8.022
7.586
7.585
7.568
7.566
7.516
7.511
7.506
7.503
7.497
7.492
7.418
7.402
7.400
7.383
7.380
7.344
7.342
7.326
7.323
7.305
7.236
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4.388
4.380
4.371
3.482
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3.455
3.448
3.434
3.431
3.416
3.403
3.396
3.385
3.377
3.372
3.366
3.364
3.355
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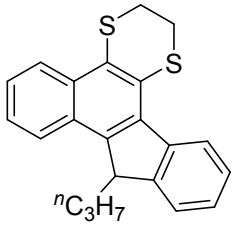
0.000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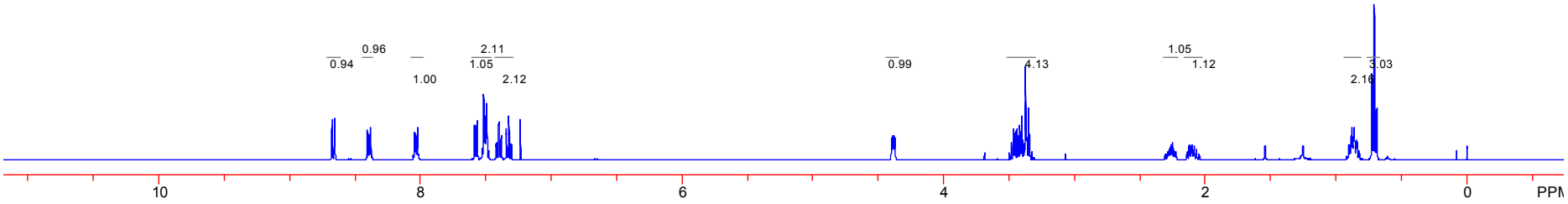
$^{n}C_3H_7$

2l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4.13
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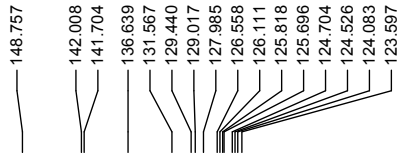
1.12
2.16
3.03
10
8
6
4
2
0
PPM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124.704
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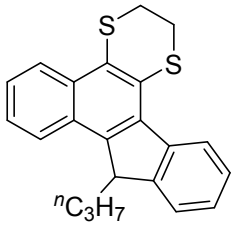
14.225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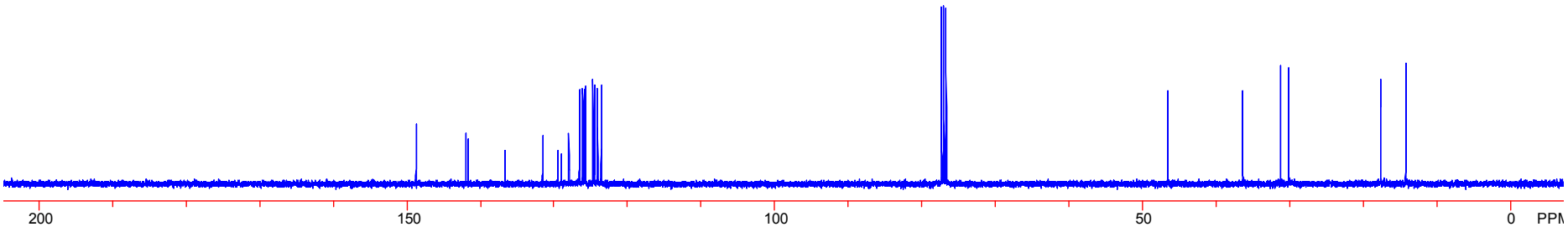
$^{n}C_3H_7$

2l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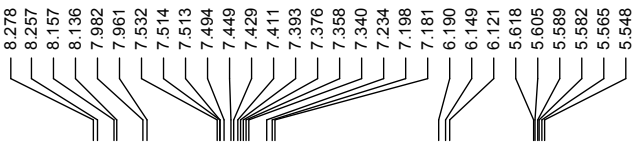
150
100
50
0
PPM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8.157
8.136
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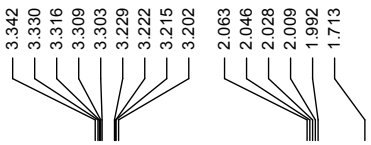
7.961
7.532
7.514
7.513
7.494
7.449
7.429
7.411
7.393
7.376
7.358
7.340
7.234
7.198
7.181
6.190
6.149
6.121
5.618
5.605
5.589
5.582
5.565
5.548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3.303
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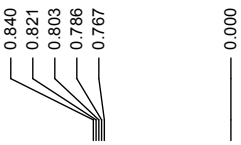
3.215
3.202
2.063
2.046
2.028
2.009
1.992
1.713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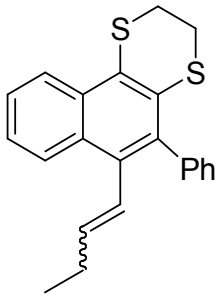
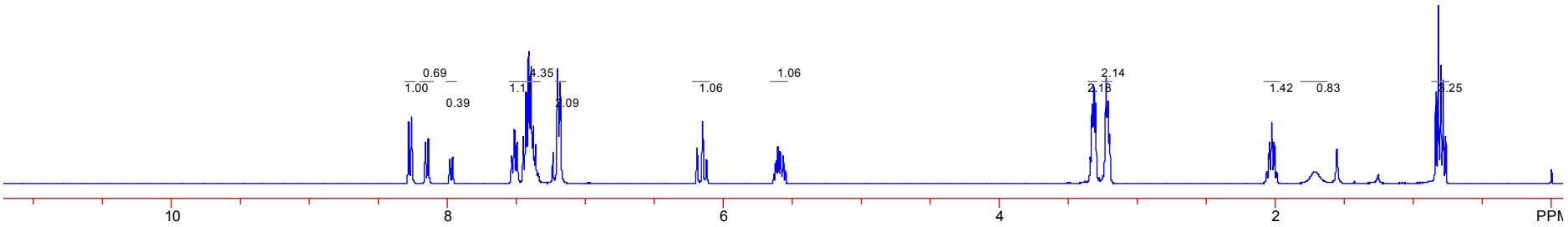
0.821
0.803
0.786
0.767

0.000


S
S
Ph

3l (*E*/*Z* = 1.8:1)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1.06
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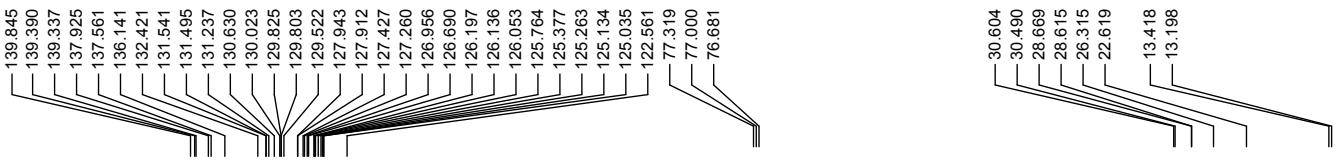
2.18
1.42
0.83
3.25
10
8
6
4
2
PPM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137.925
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136.141
132.421
131.541
131.495
131.237
130.630
130.023
129.825
129.803
129.522
127.943
127.912
127.427
127.260
126.956
126.690
126.197
126.136
126.053
125.764
125.377
125.263
125.134
125.035
122.561
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77.000
76.681
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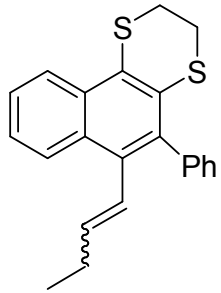
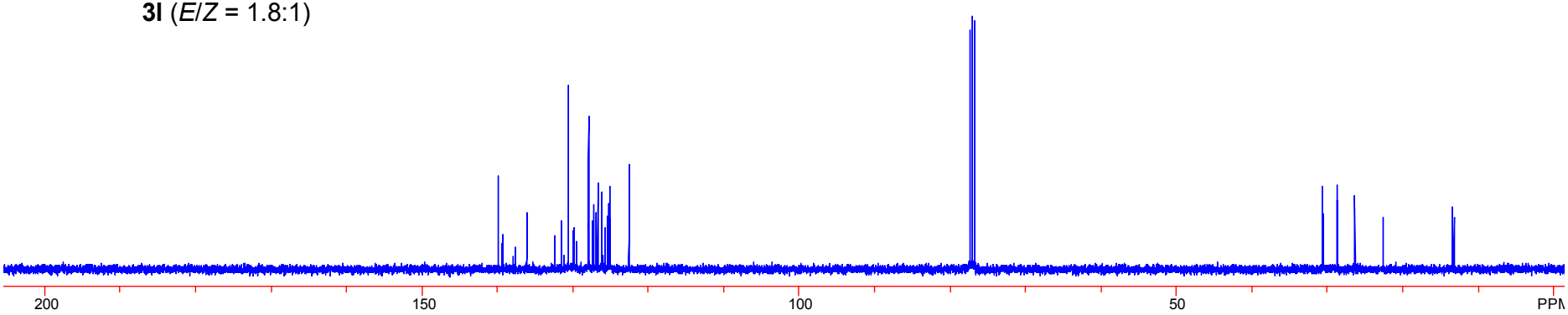
30.490
28.669
28.615
26.315
22.619
13.418
13.198


S
S
Ph

3l (*E*/*Z* = 1.8:1)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100
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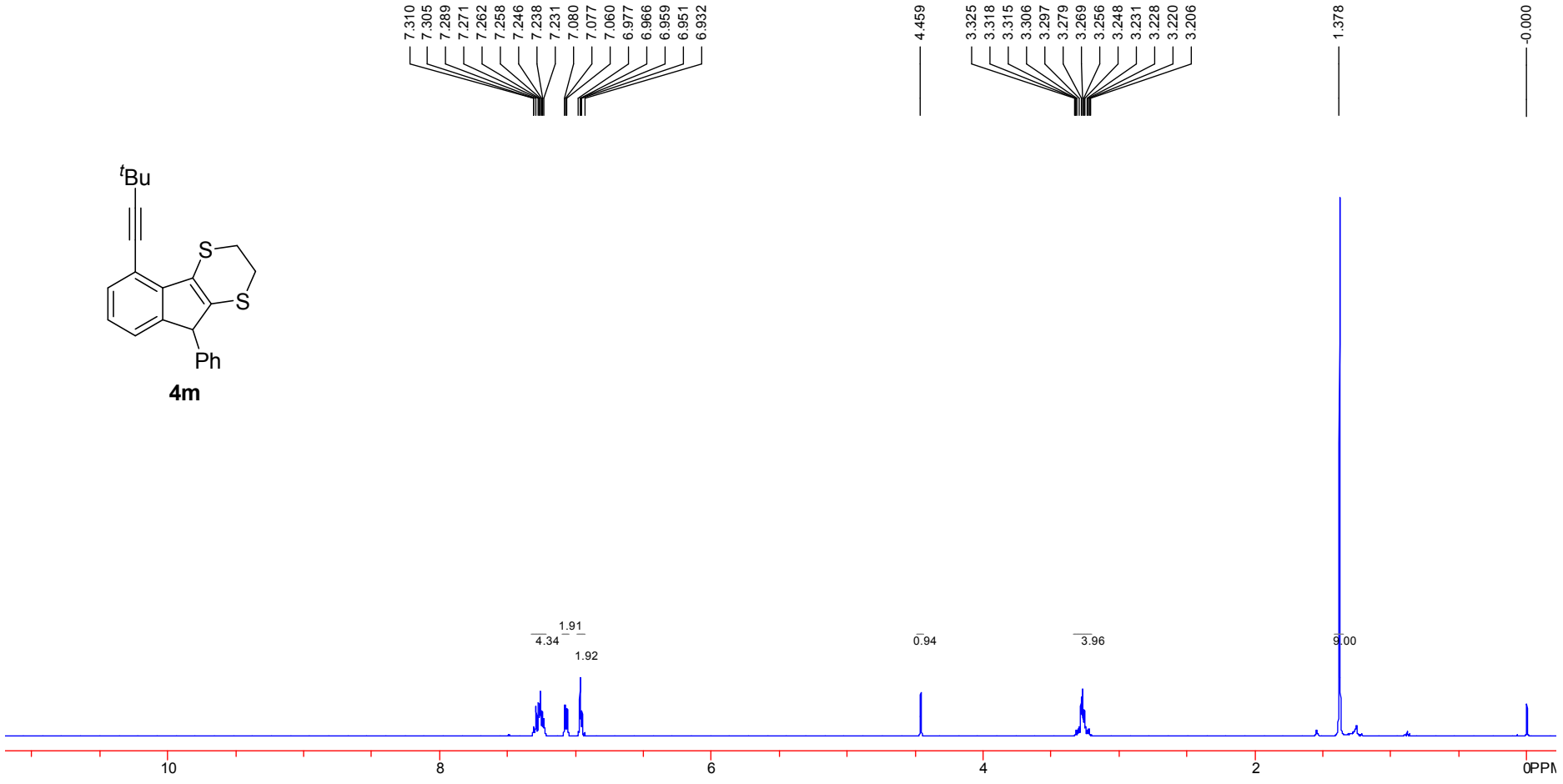
PPM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7.289
7.271
7.262
7.258
7.246
7.238
7.231
7.080
7.077
7.060
6.977
6.966
6.959
6.951
6.932
4.459
3.325
3.318
3.315
3.306
3.297
3.279
3.269
3.256
3.248
3.231
3.228
3.220
3.206
1.378
-0.000
tBu
S
S
Ph
4m
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1.92
0.94
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10
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6
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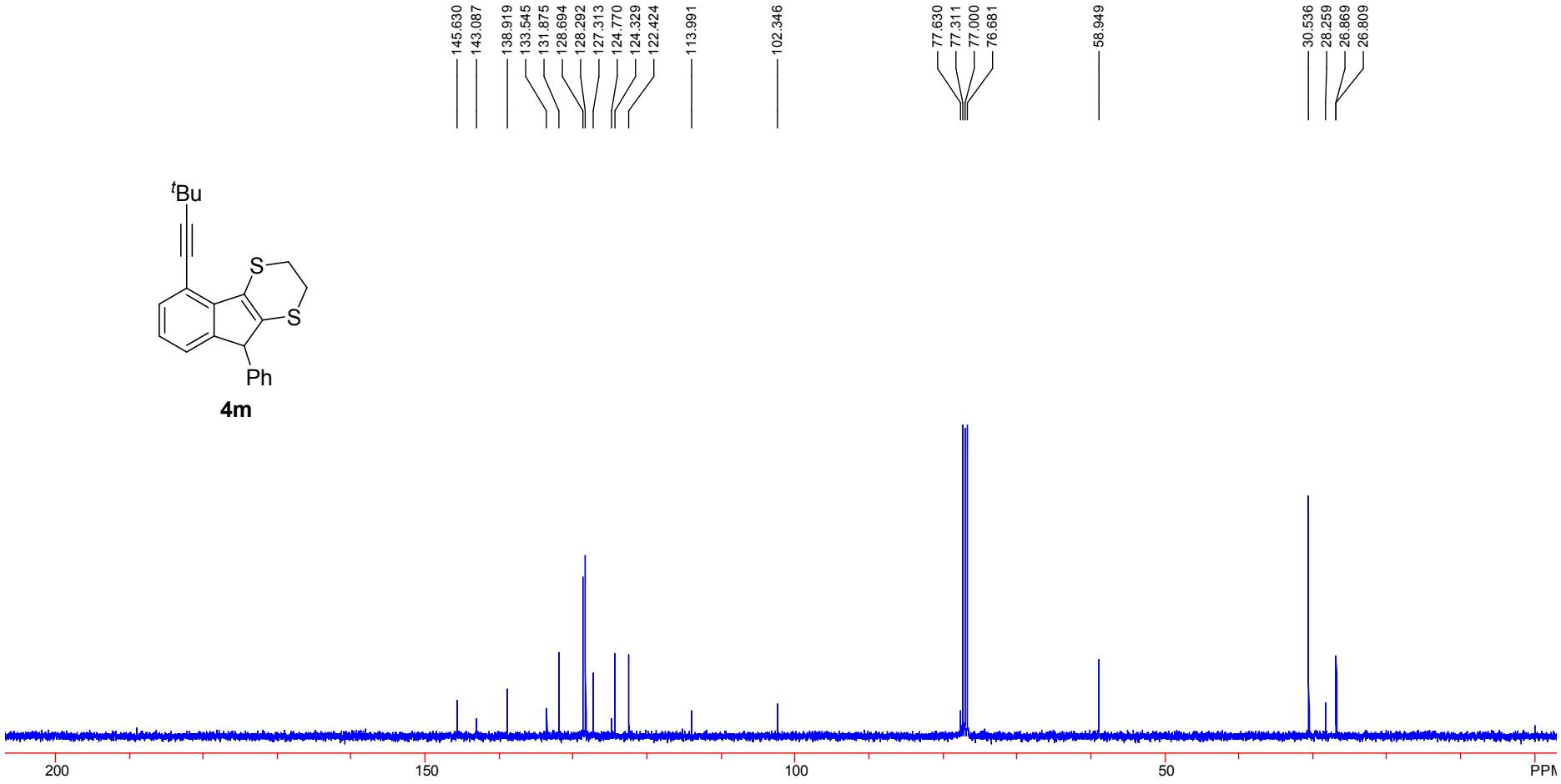
2
0
PPM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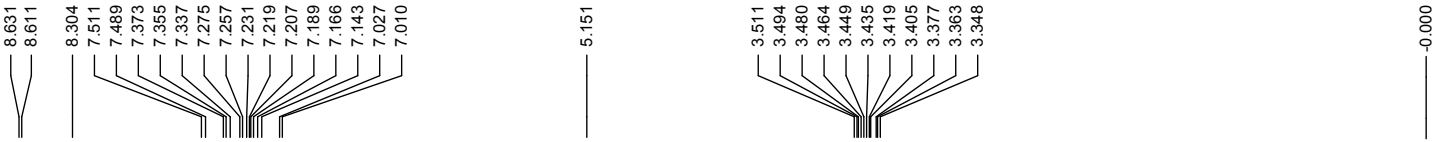
128.292
127.313
124.770
124.329
122.424
113.991
102.346
77.630
77.311
77.000
76.681
58.949
30.536
28.259
26.869
26.809
tBu
S
S
Ph
4m
200
150
100
50
PPM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7.489
7.373
7.355
7.337
7.275
7.257
7.231
7.219
7.207
7.189
7.166
7.143
7.027
7.010
5.151
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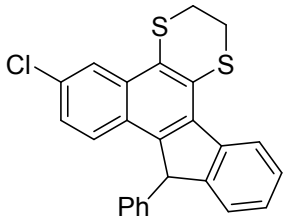
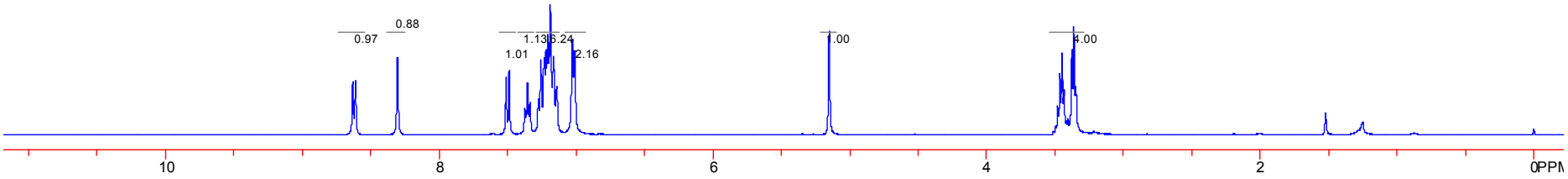
3.494
3.480
3.464
3.449
3.435
3.419
3.405
3.377
3.363
3.348
0.000


S
S
Cl
Ph

2n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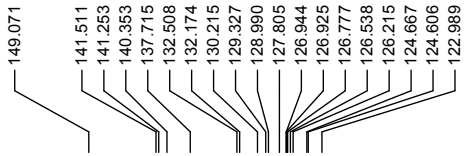
1.00
4.00
10
8
6
4
2
0
PPM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77.000
76.681
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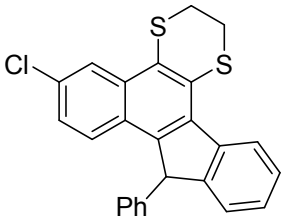
31.159
29.895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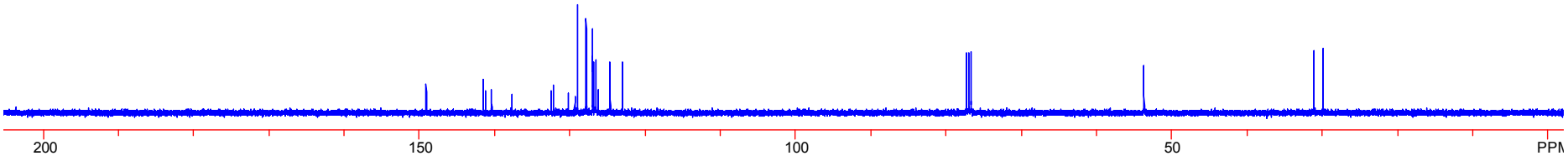
S
Cl
Ph

2n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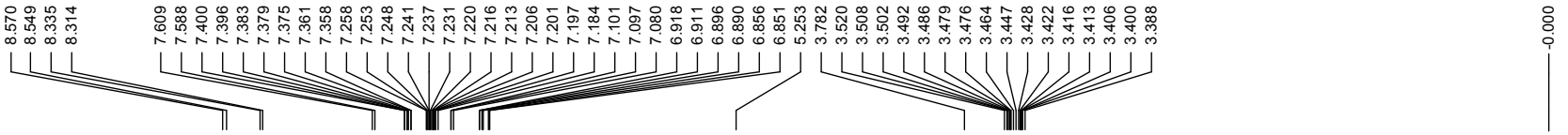
100
50
PPM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7.375
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7.358
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7.253
7.248
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7.237
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7.213
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7.101
7.097
7.080
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6.890
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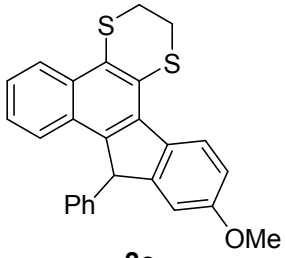
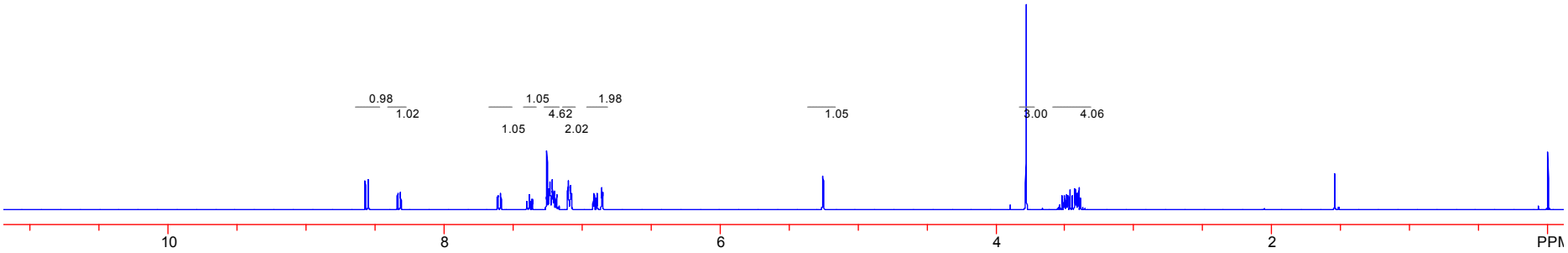

S
S
Ph
OMe

2o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1.05
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4.06
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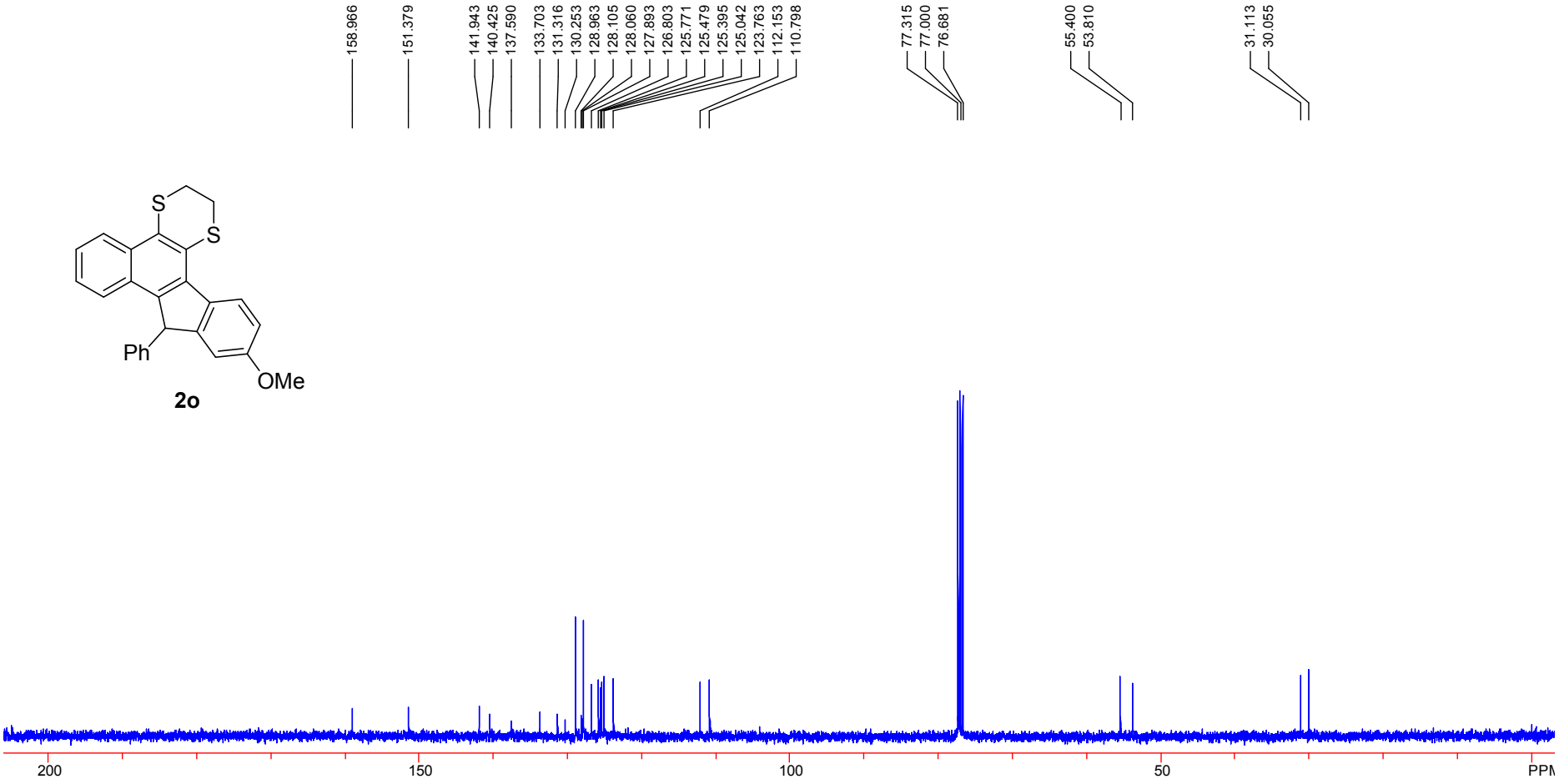
8
6
4
2
PPM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128.105
128.060
127.893
126.803
125.771
125.479
125.395
125.042
123.763
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110.798
77.315
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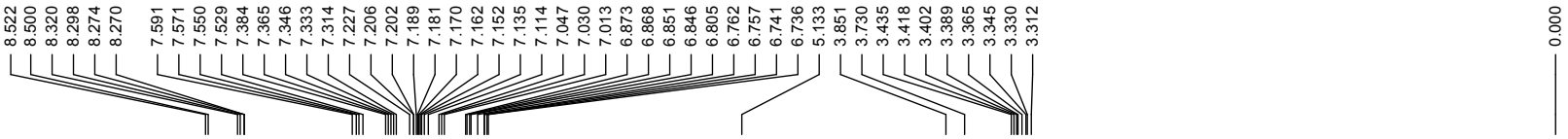
53.810
31.113
30.055
S
S
Ph
OMe
2o
200
150
100
50
PPM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7.189
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7.162
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7.047
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7.013
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6.805
6.762
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6.741
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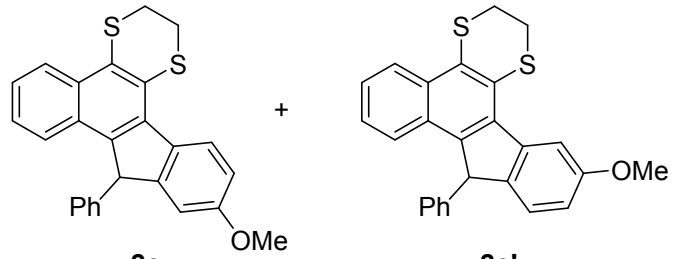
3.365
3.345
3.330
3.312
0.000


S
S
Ph
OMe

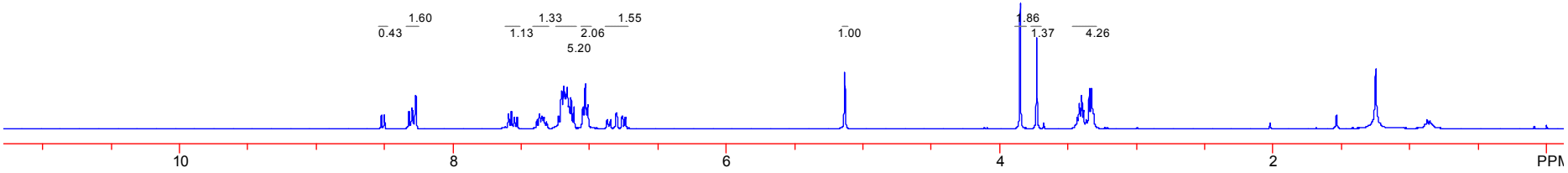
2o

+

S
S
Ph
OMe

2o'

1 : 1.4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1.86
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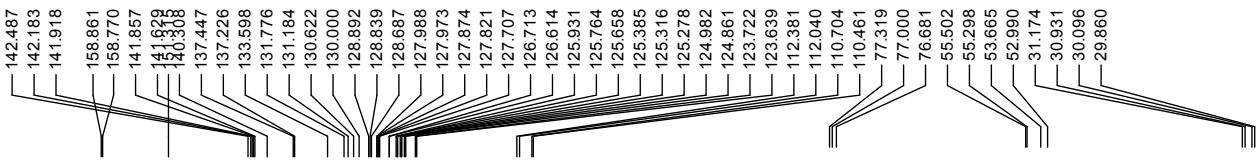
4.26
10
8
6
4
2
PPM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130.000
128.892
128.839
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127.988
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125.931
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125.658
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125.278
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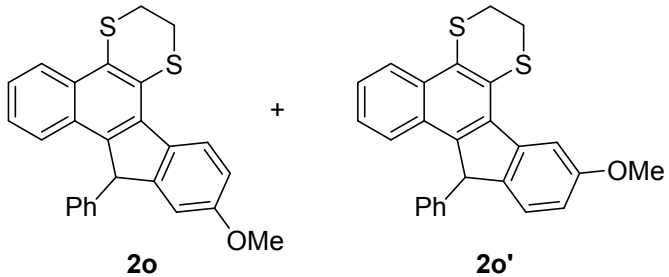
30.096
29.860


S
S
Ph
OMe

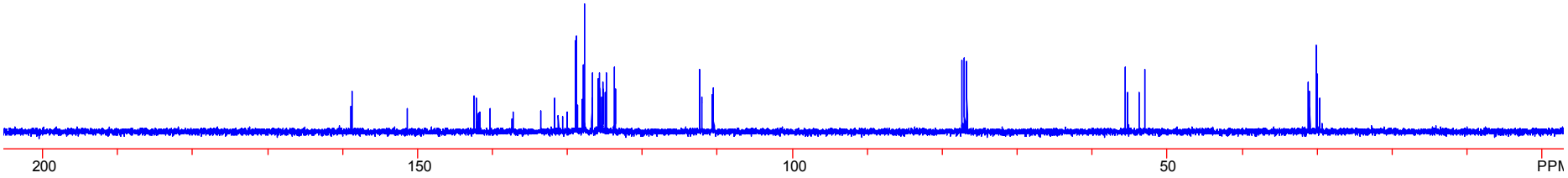
2o

+

S
S
Ph
OMe

2o'

1 : 1.4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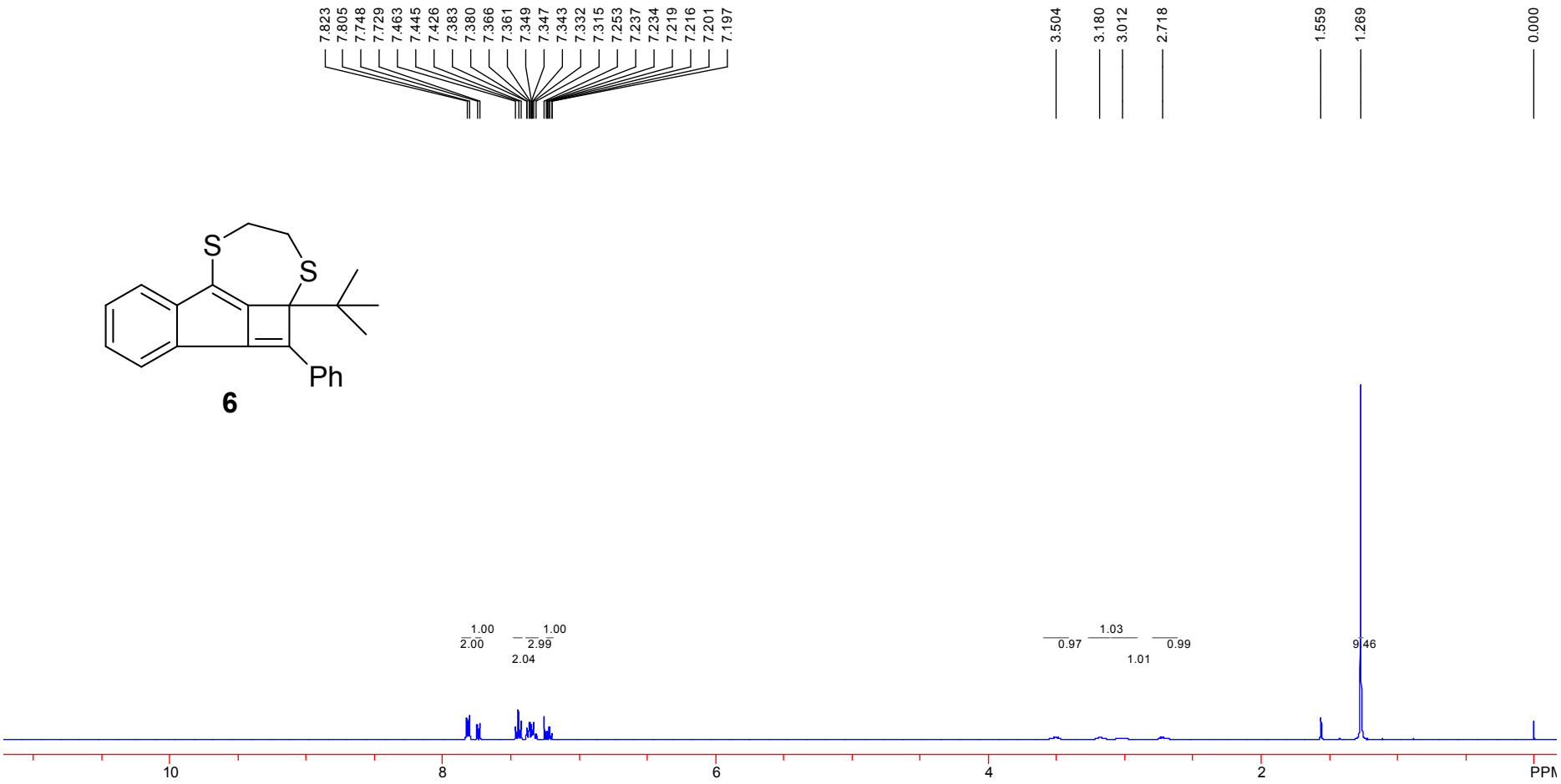
150
100
50
PPM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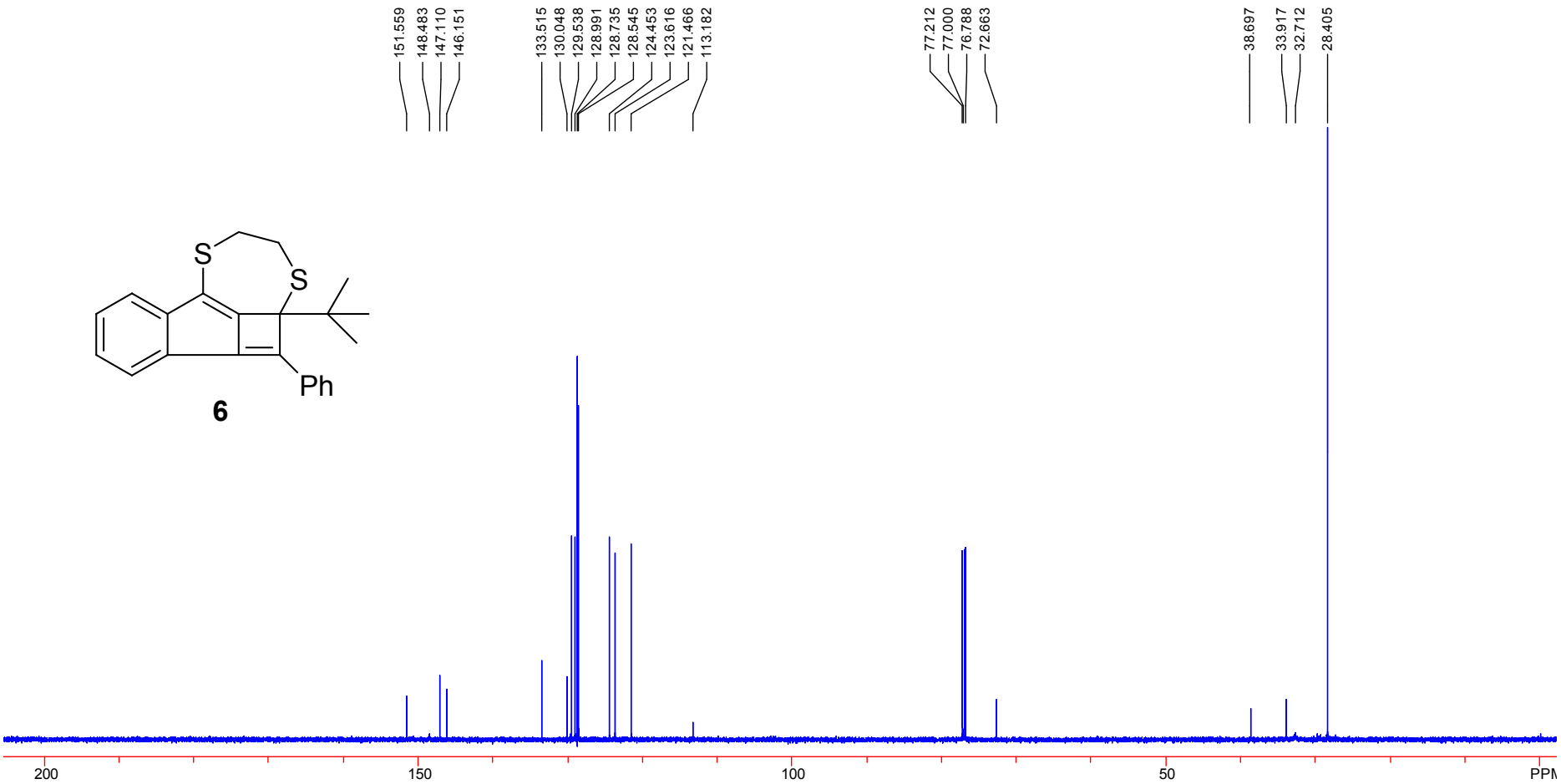
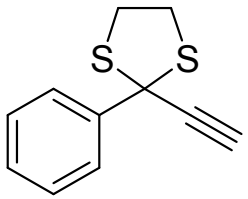
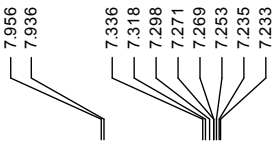
7.805
7.748
7.729
7.463
7.445
7.426
7.383
7.380
7.366
7.361
7.349
7.347
7.343
7.332
7.315
7.253
7.237
7.234
7.219
7.216
7.201
7.197
3.504
3.180
3.012
2.718
1.559
1.269
0.000
S
S
Ph
6
1.00
2.00
1.00
2.99
2.04
1.03
0.97
1.01
0.99
9.46
10
8
6
4
2
PPM


151.559
148.483
147.110
146.151
133.515
130.048
129.538
128.991
128.735
128.545
124.453
123.616
121.466
113.182
77.212
77.000
76.788
72.663
38.697
33.917
32.712
28.405
S
S
Ph
6
200
150
100
50
PPM


S
S

s-15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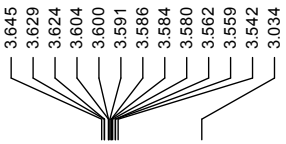
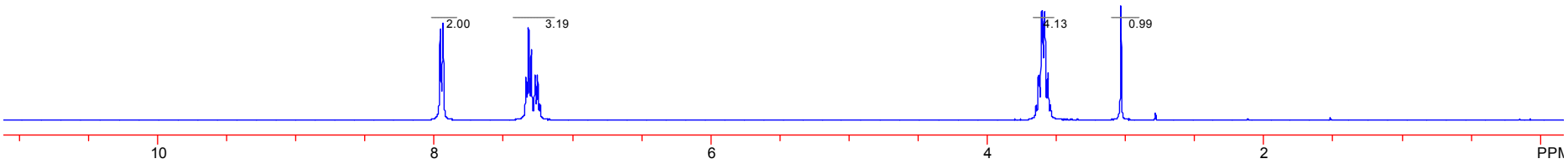
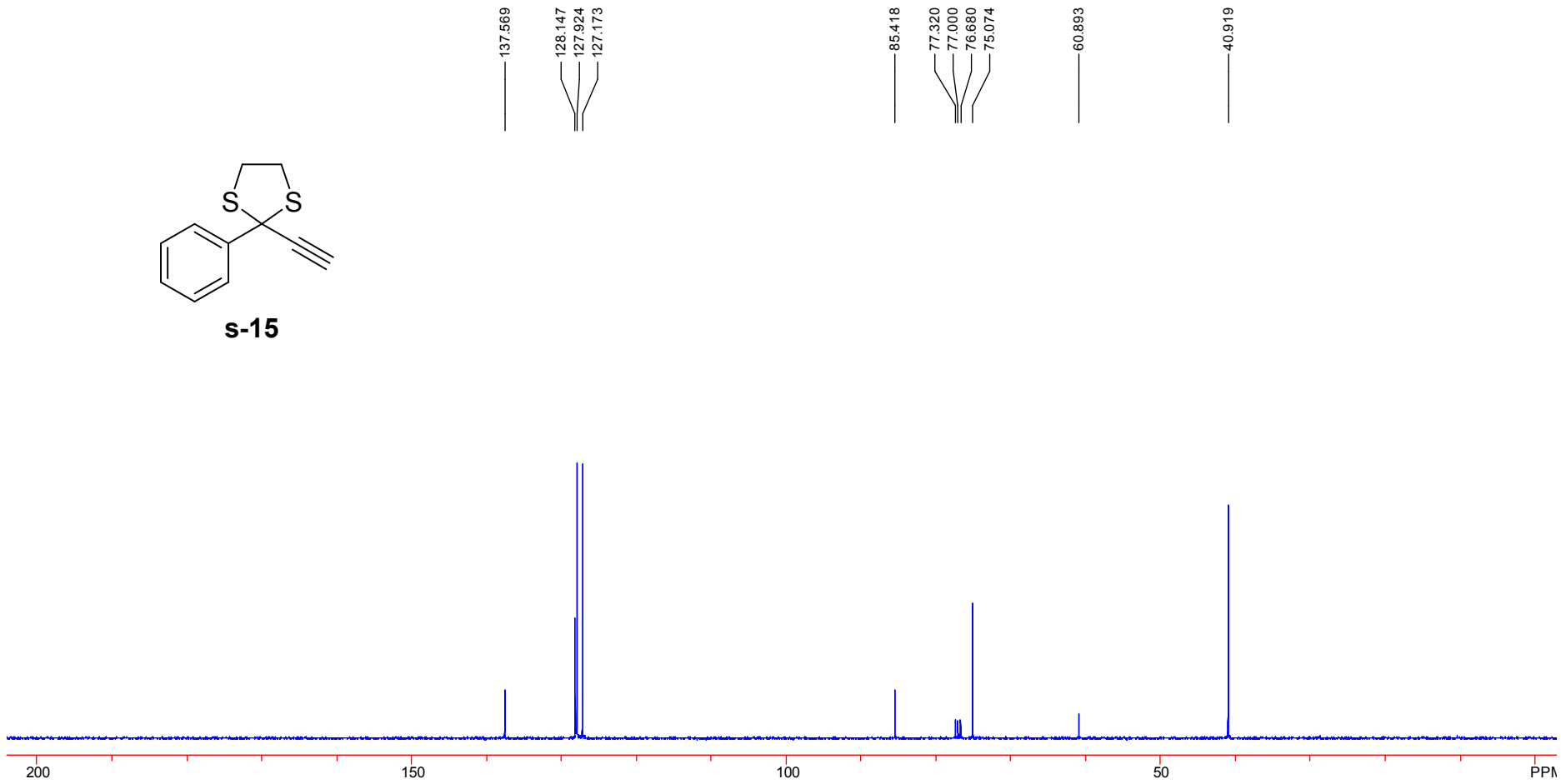
7.936
7.336
7.318
7.298
7.271
7.269
7.253
7.235
7.233

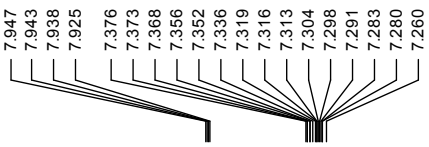

3.645
3.629
3.624
3.604
3.600
3.591
3.586
3.584
3.580
3.562
3.559
3.542
3.034

0.000


2.00
3.19
4.13
0.99
10
8
6
4
2
PPM


137.569
128.147
127.924
127.173
85.418
77.320
77.000
76.680
75.074
60.893
40.919
S
S
200
150
100
50
PPM

s-15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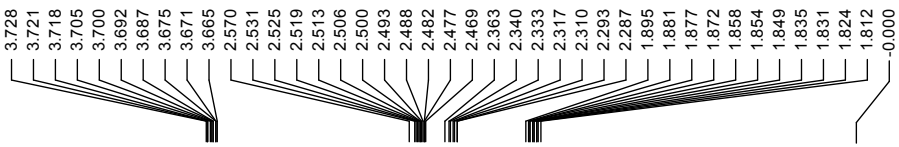
7.943
7.938
7.925
7.376
7.373
7.368
7.356
7.352
7.336
7.319
7.316
7.313
7.304
7.298
7.291
7.283
7.280
7.260


3.728
3.721
3.718
3.705
3.700
3.692
3.687
3.675
3.671
3.665
2.570
2.531
2.525
2.519
2.513
2.506
2.500
2.493
2.488
2.482
2.477
2.469
2.363
2.340
2.333
2.317
2.310
2.293
2.287
1.895
1.881
1.877
1.872
1.858
1.854
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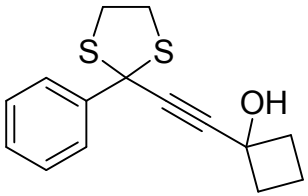
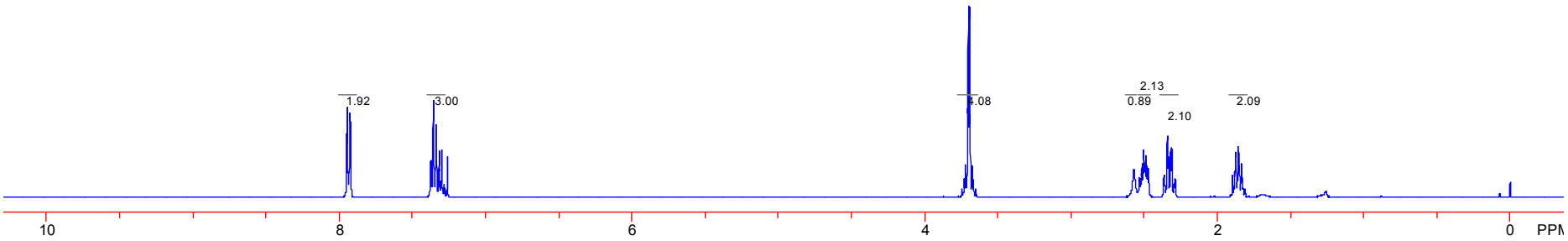
1.824
1.812
-0.000


S
S
OH

15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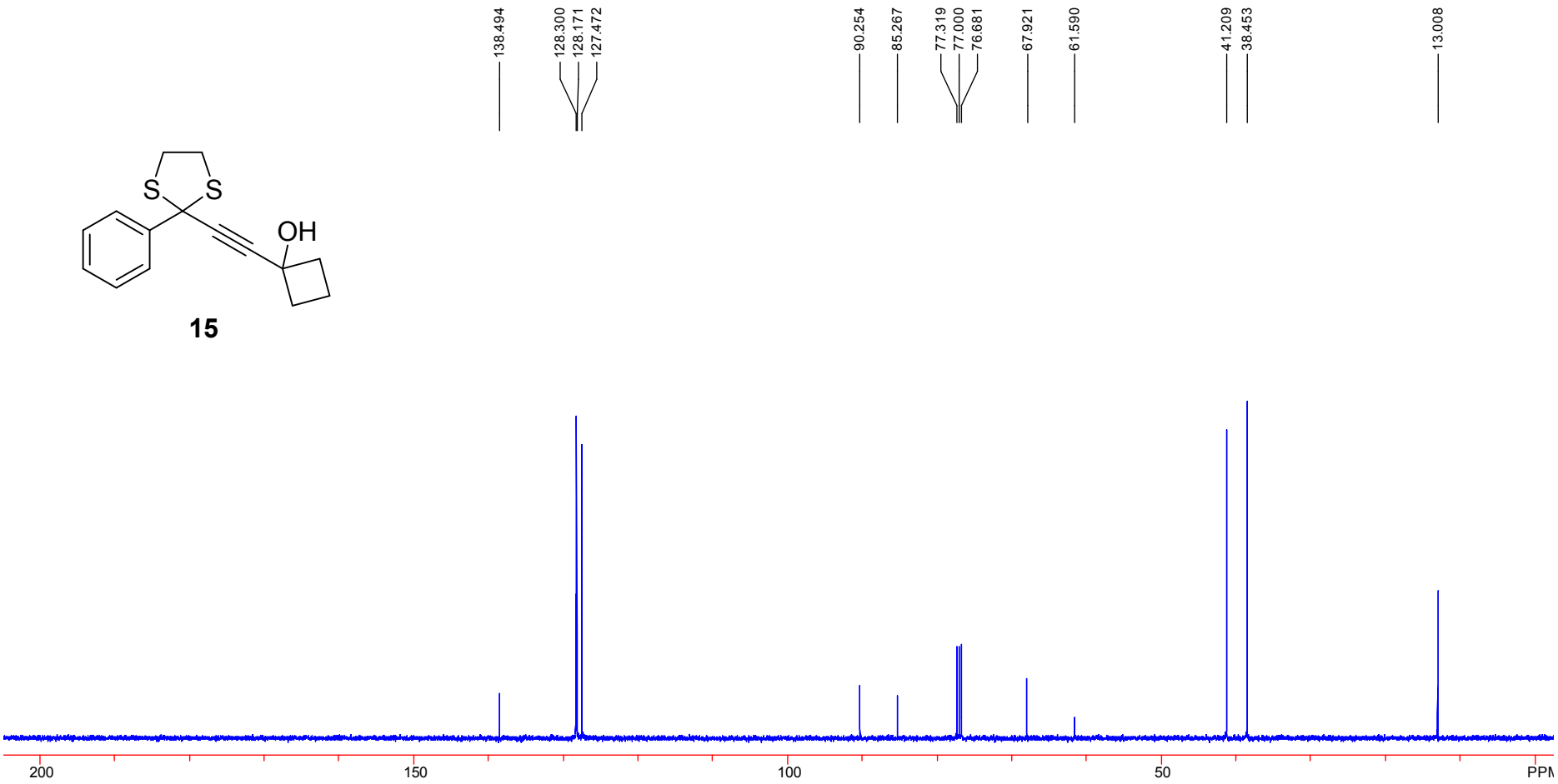
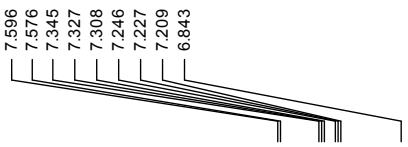
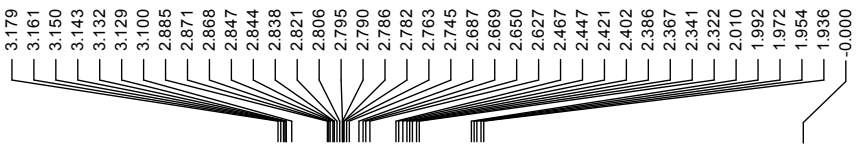
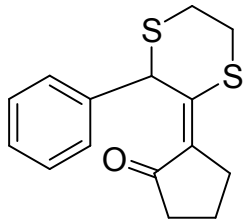
3.00
4.08
2.13
0.89
2.10
2.09
10
8
6
4
2
0
PPM


138.494
128.300
128.171
127.472
90.254
85.267
77.319
77.000
76.681
67.921
61.590
41.209
38.453
13.008
S
S
OH
200
150
100
50
PPM

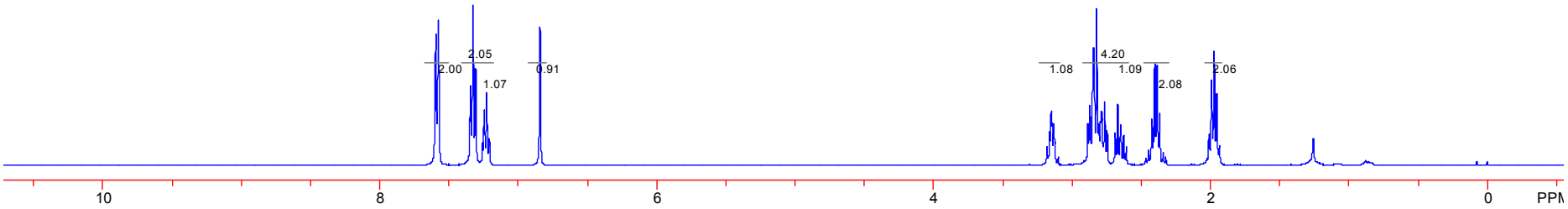
15

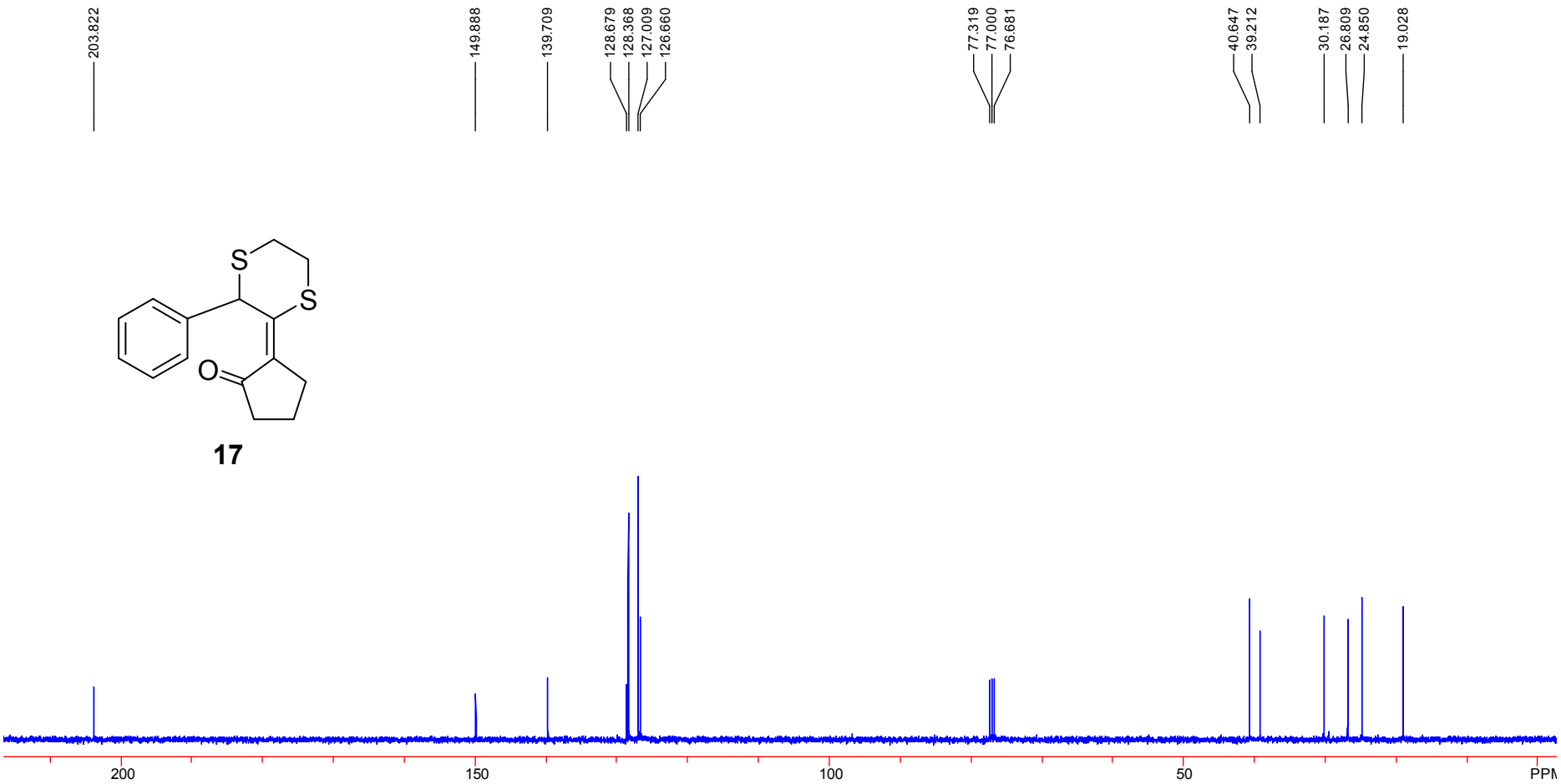

7.596
7.576
7.345
7.327
7.308
7.246
7.227
7.209
6.843


3.179
3.161
3.150
3.143
3.132
3.129
3.100
2.885
2.871
2.868
2.847
2.844
2.838
2.821
2.806
2.795
2.790
2.786
2.782
2.763
2.745
2.687
2.669
2.650
2.627
2.467
2.447
2.421
2.402
2.386
2.367
2.341
2.322
2.010
1.992
1.972
1.954
1.936
-0.000

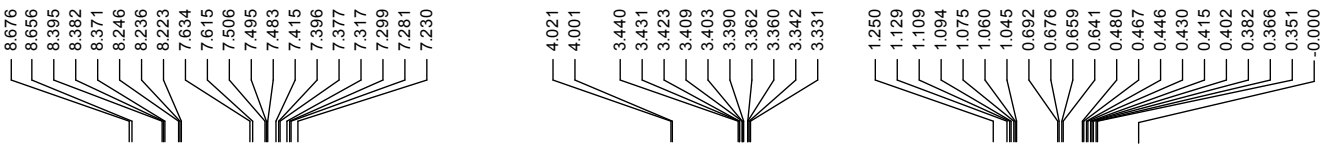

S
S
O

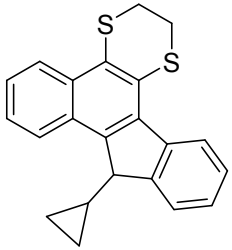
17


2.00
2.05
1.07
0.91
1.08
4.20
1.09
2.08
2.06
10
8
6
4
2
0
PPM

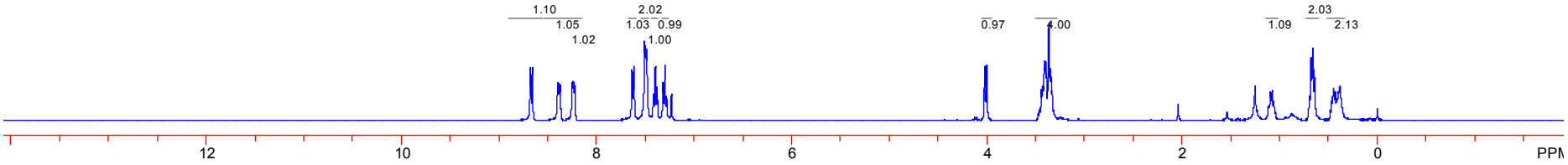

203.822
149.888
139.709
128.679
128.368
127.009
126.660
77.319
77.000
76.681
40.647
39.212
30.187
26.809
24.850
19.028
S
S
O
200
150
100
50
PPM

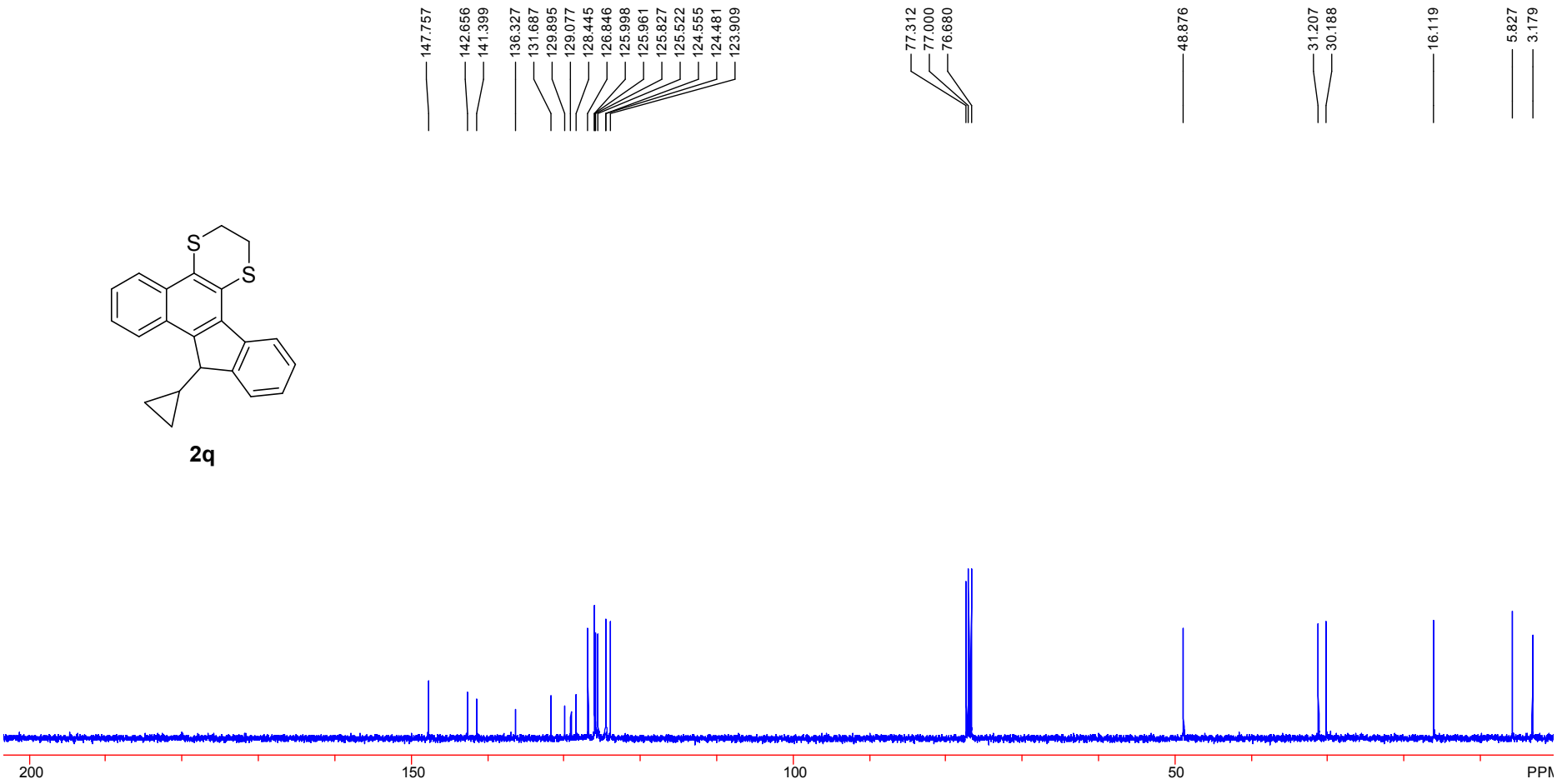
17


8.676
8.656
8.395
8.382
8.371
8.246
8.236
8.223
7.634
7.615
7.506
7.495
7.483
7.415
7.396
7.377
7.317
7.299
7.281
7.230
4.021
4.001
3.440
3.431
3.423
3.409
3.403
3.390
3.362
3.360
3.342
3.331
1.250
1.129
1.109
1.094
1.075
1.060
1.045
0.692
0.676
0.659
0.641
0.480
0.467
0.446
0.430
0.415
0.402
0.382
0.366
0.351
-0.000


S
S

2q


1.10
1.05
1.02
2.02
1.03
0.99
1.00
0.97
4.00
1.09
2.03
2.13
12
10
8
6
4
2
0
PPM


147.757
142.656
141.399
136.327
131.687
129.895
129.077
128.445
126.846
125.998
125.961
125.827
125.522
124.555
124.481
123.909
77.312
77.000
76.680
48.876
31.207
30.188
16.119
5.827
3.179
S
S
200
150
100
50
PPM

2q


8.291
8.278
8.273
8.258
7.539
7.521
7.503
7.501
7.470
7.451
7.432
7.419
7.405
7.402
7.271
7.265
7.252
7.248
7.240
5.962
3.341
3.328
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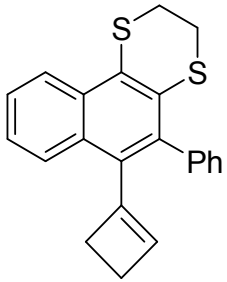
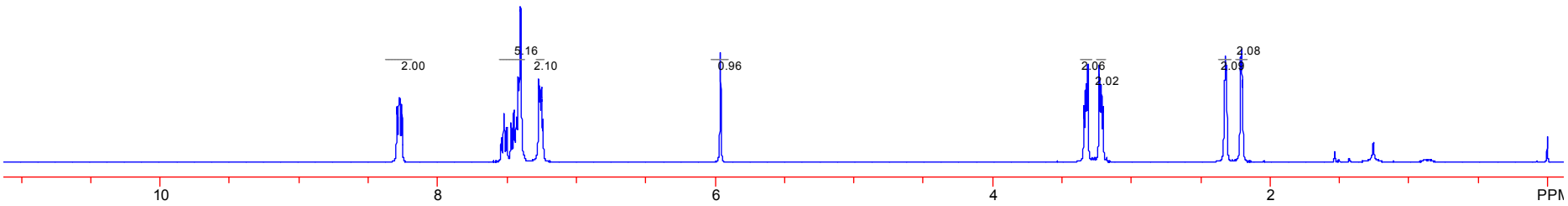
3.313
3.232
3.225
3.217
3.205
2.322
2.315
2.214
2.205
2.198
0.000


S
S
Ph

18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5.16
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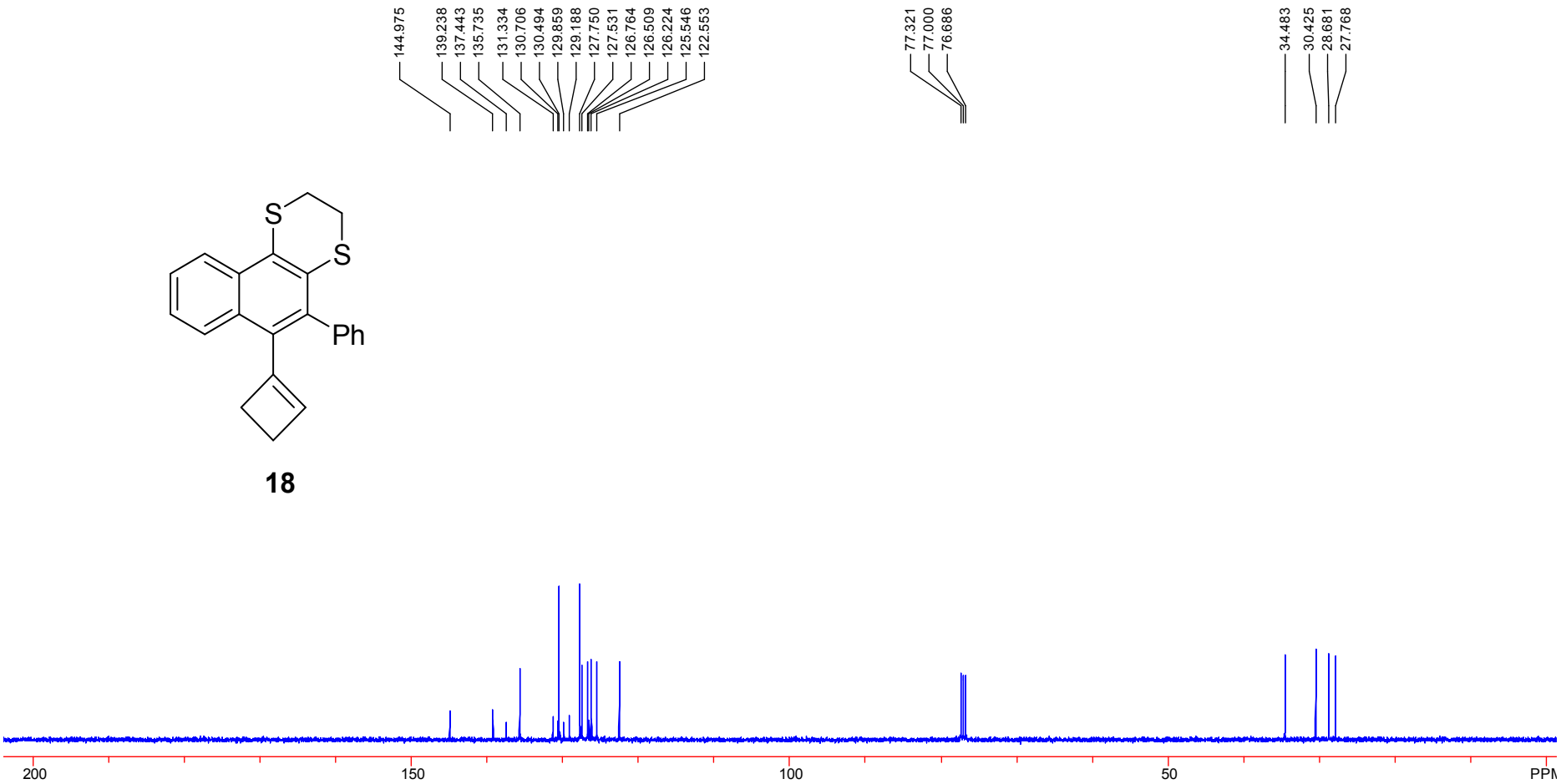
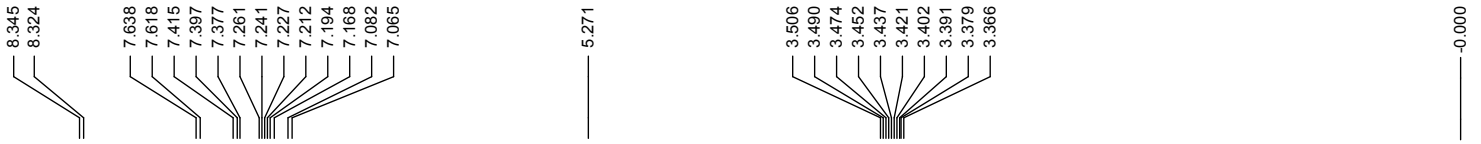
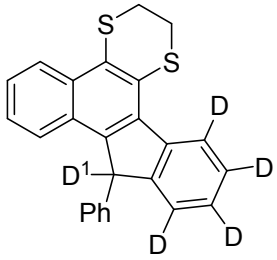
0.96
2.06
2.02
2.08
2.09
10
8
6
4
2
PPM

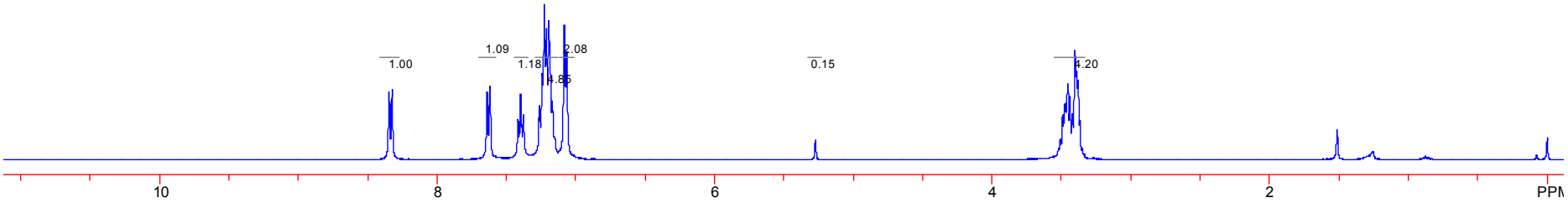

144.975
139.238
137.443
135.735
131.334
130.706
130.494
129.859
129.188
127.750
127.531
126.764
126.509
126.224
125.546
122.553
77.321
77.000
76.686
34.483
30.425
28.681
27.768
S
S
Ph
200
150
100
50
PPM

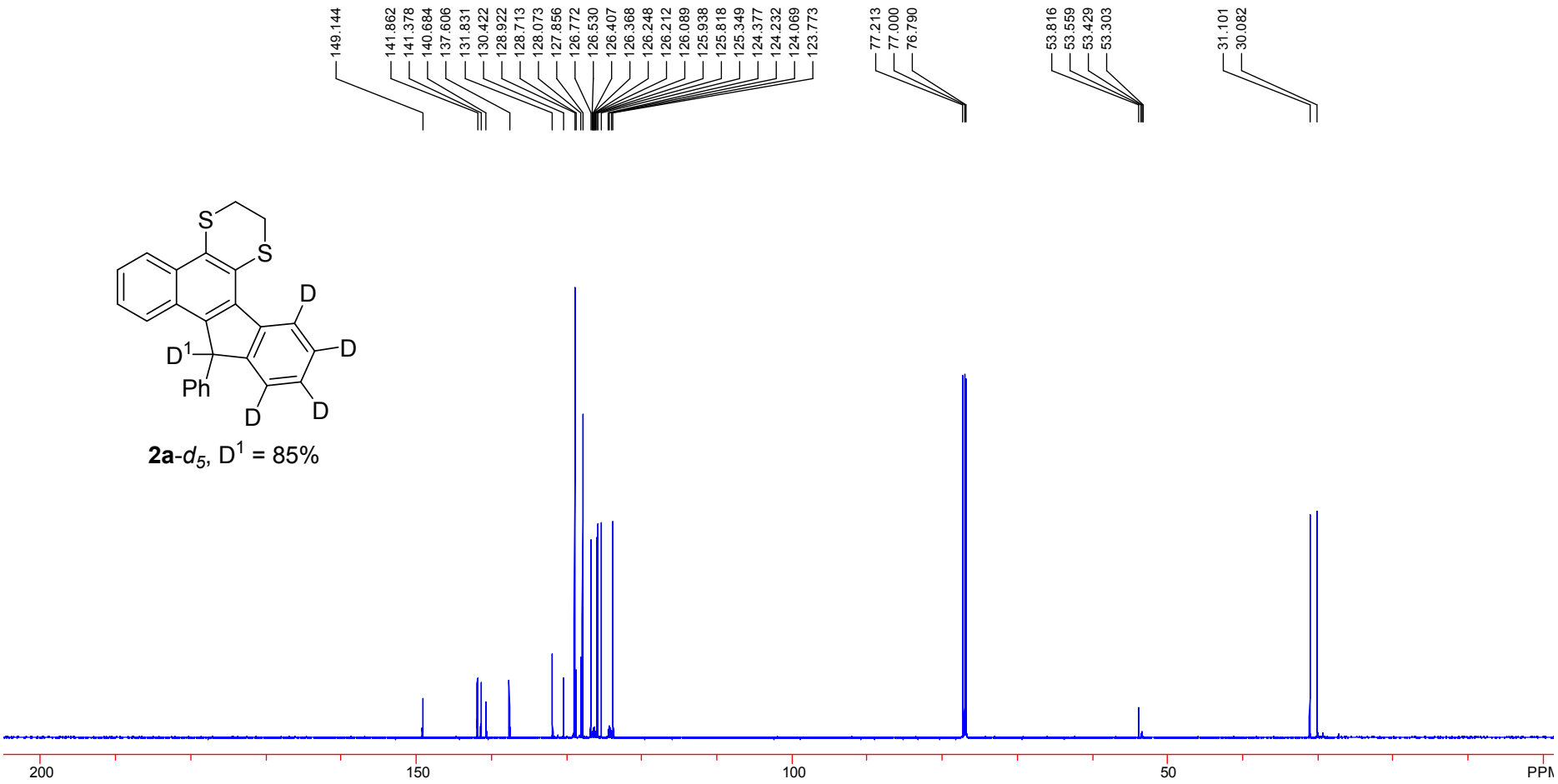
18


8.345
8.324
7.638
7.618
7.415
7.397
7.377
7.261
7.241
7.227
7.212
7.194
7.168
7.082
7.065
5.271
3.506
3.490
3.474
3.452
3.437
3.421
3.402
3.391
3.379
3.366
0.000


S
S
D
D
D1
Ph
D
D

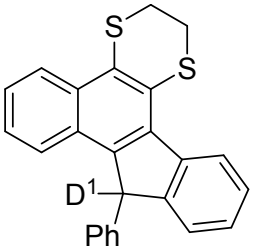
2a-d_5, D^1 = 85%


1.00
1.09
1.18
2.08
4.86
0.15
4.20
10
8
6
4
2
PPM

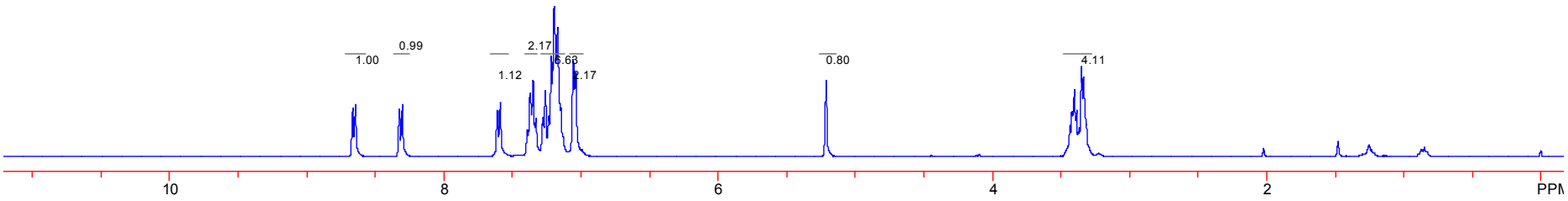

149.144
141.862
141.378
140.684
137.606
131.831
130.422
128.922
128.713
128.073
127.856
126.772
126.530
126.407
126.368
126.248
126.212
126.089
125.938
125.818
125.349
124.377
124.232
124.069
123.773
77.213
77.000
76.790
53.816
53.559
53.429
53.303
31.101
30.082
S
S
D
D
D1
Ph
D
D
200
150
100
50
PPM

2a-d_5, D^1 = 85%


8.663
8.644
8.323
8.302
7.609
7.588
7.389
7.370
7.349
7.328
7.277
7.259
7.234
7.215
7.196
7.193
7.170
7.146
7.056
7.038
5.212
3.435
3.423
3.418
3.413
3.401
3.386
3.368
3.349
3.337
3.315
-0.000


S
S
D1
Ph

2a-*d*$_1$, D^1 = 20%


1.00
0.99
1.12
2.17
5.63
2.17
0.80
4.11
10
8
6
4
2
PPM