**ELECTRONIC SUPPLEMENTARY INFORMATION**

**Polycyclic aromatic hydrocarbons and their adducts with solvents from Ag(II)SO4–based oxidative C–C coupling†,‡**

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**Experimental details**

All manipulations of highly reactive AgSO4 were done in Ar-filled glovebox (MBraun, O2, H2O< 1 ppm).

AgSO4 was obtained according to literature procedures.[[1]](#endnote-1) Commercial 9,9’-bianthrene was purchased from Fluorochem, while 9,9’-biphenantrene was purchased from Sigma Aldrich. All solvents used were from Sigma Aldrich.

IR spectra were measured on Bruker Vertex 80v FTIR spectrometer. MIR spectra were measured with samples in KBr pellets while for FIR range the samples were smeared on HDPE windows.

NMR spectra were recorded on Bruker AVANCE 500 MHz spectrometer. For GC-MS measurements Agilent 7890A & 5975 spectrometer (EI ionization) with standard HP-5MS column and NIST 08 database was used in all cases. Mass spectra were recorded in the range of 10-800 amu.

Raman spectra were recorded on Horiba-Jobin Yvon, T64000 spectrometer, 514 nm excitation line, 200 um confocal aperture, Rayleigh band cutoff via edge filter, monochromated with 1800 diffraction grating.

The crystals were measured on Agilent Supernova X-ray diffratometer with Cu-Kα radiation (microsource). Data collection and reduction was performed with CrysAlisPro software (v. 38.43).[[2]](#endnote-2) Structure solution: SHELXT,[[3]](#endnote-3) refinement against F2 in Shelxl-2013, with ShelXle[[4]](#endnote-4) or Olex[[5]](#endnote-5) as GUI software.

Crystal growth:

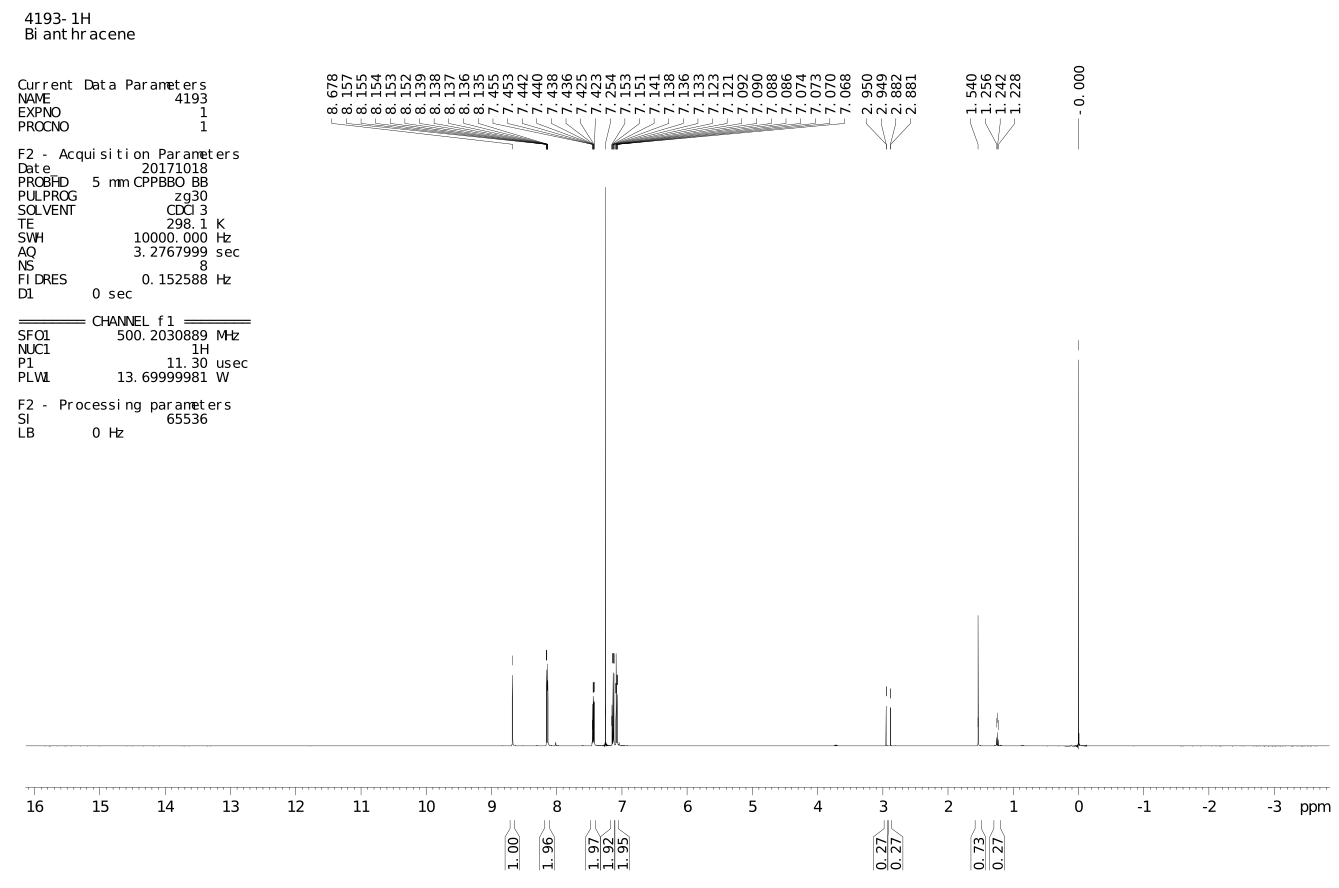
* pure 9,9'-bianthryl and 9,9'-biphenanthryl: 10 mg of the compound in 2 ml of m-xylene; slow crystallization at RT
* The inclusion compounds were prepared using 10 mg of bianthrene dissolved in ca. 2 ml of the corresponding solvent (benzene, toluene, o/p-xylene)using slow evaporation technique. Only 1:1 adduct of **1** and toluene was obtained by slow cooling of the RT-saturated solution of **1** in C7H8 to −30°C.

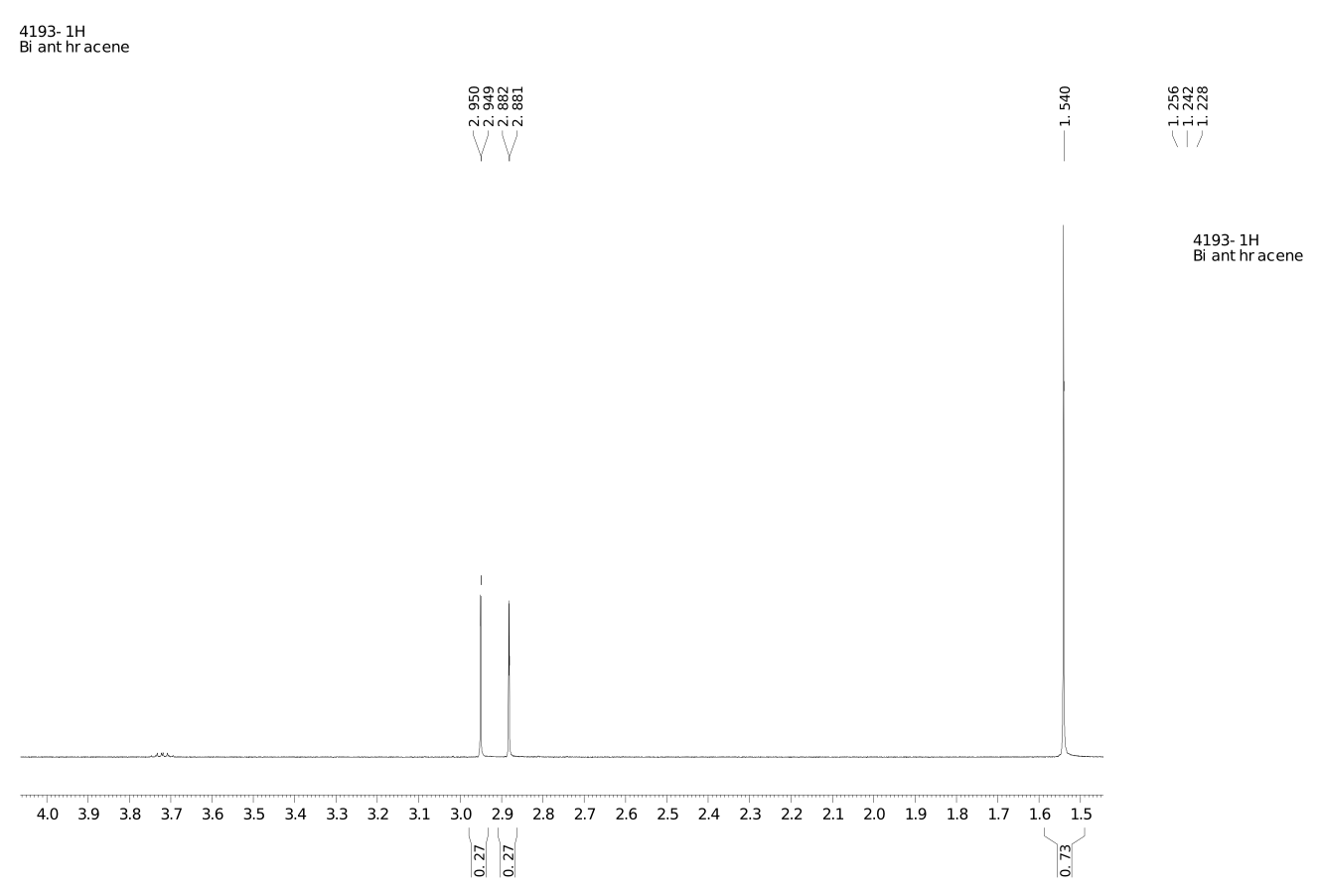
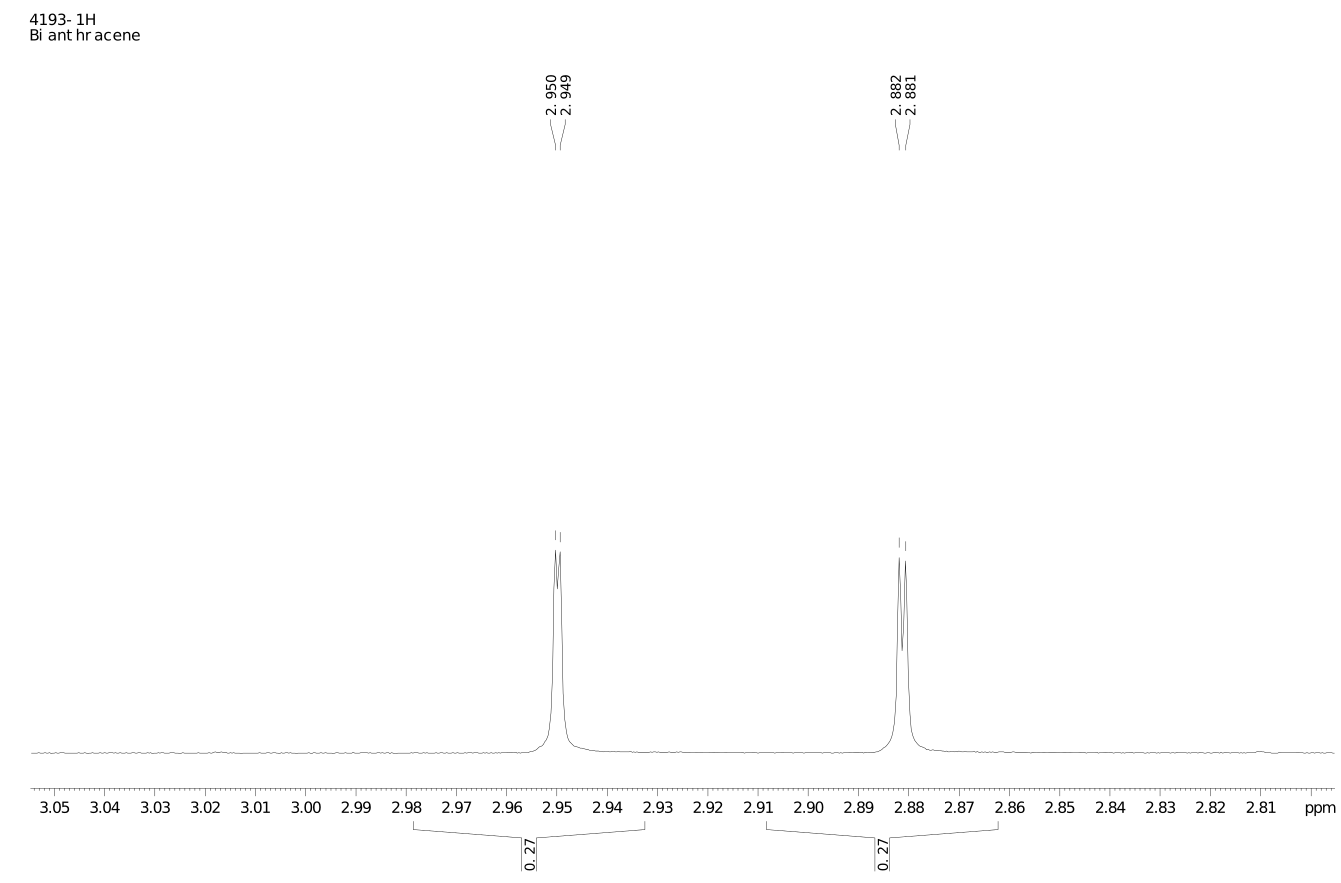
Hirschfeld surfaces were generated using Crystal Explorer software.[[6]](#endnote-6)

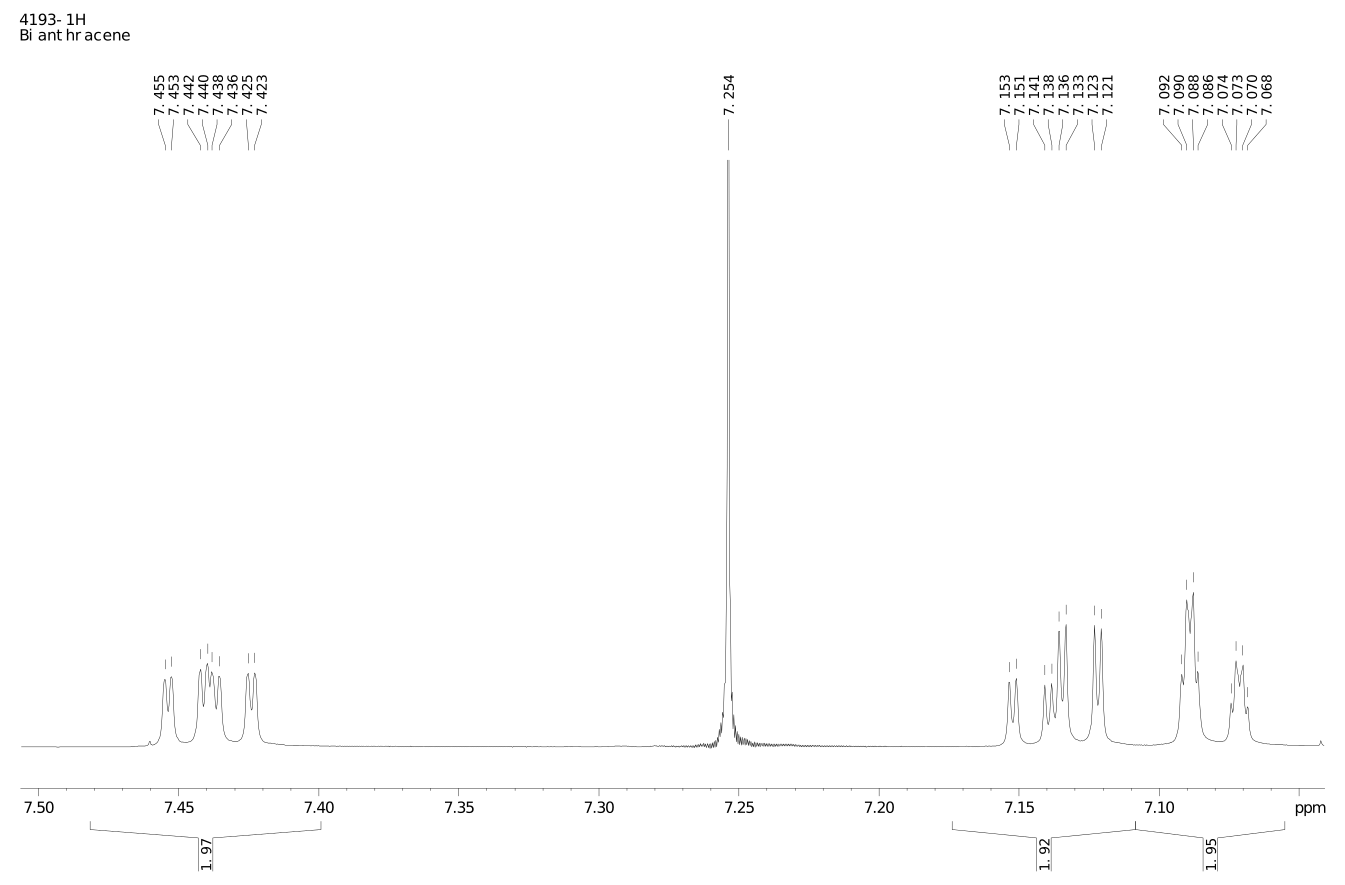
**The 1H, 13C and 1H *vs*. 13C HSQC NMR spectra, and IR spectra for 1 and 2**

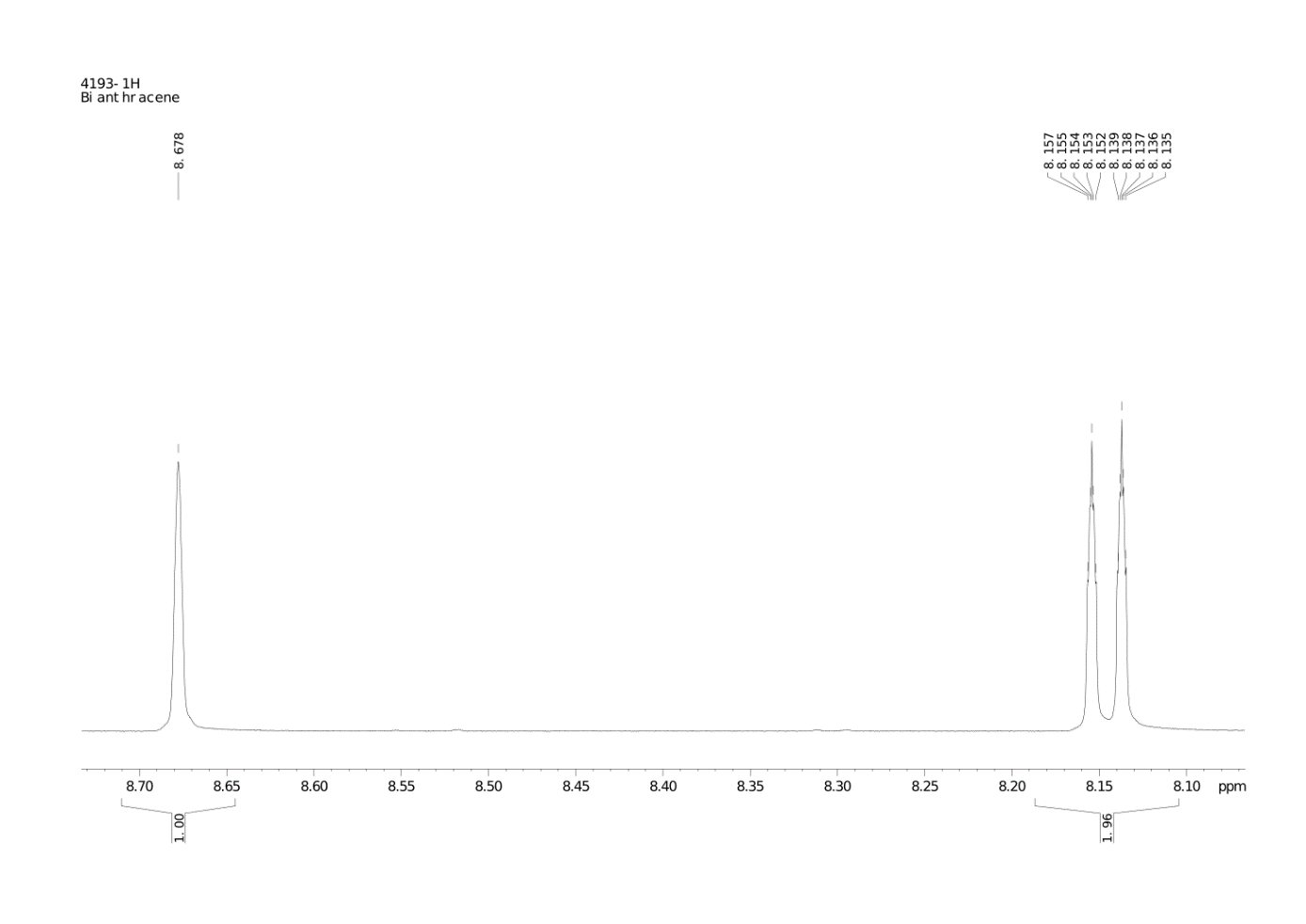
***9,9’-bianthryl (1) NMR spectra: C28H18***

***1H 500 MHz, 13C 125 MHz, 1H vs. 13C HSQC CDCl3 298 K***









***1H NMR:***

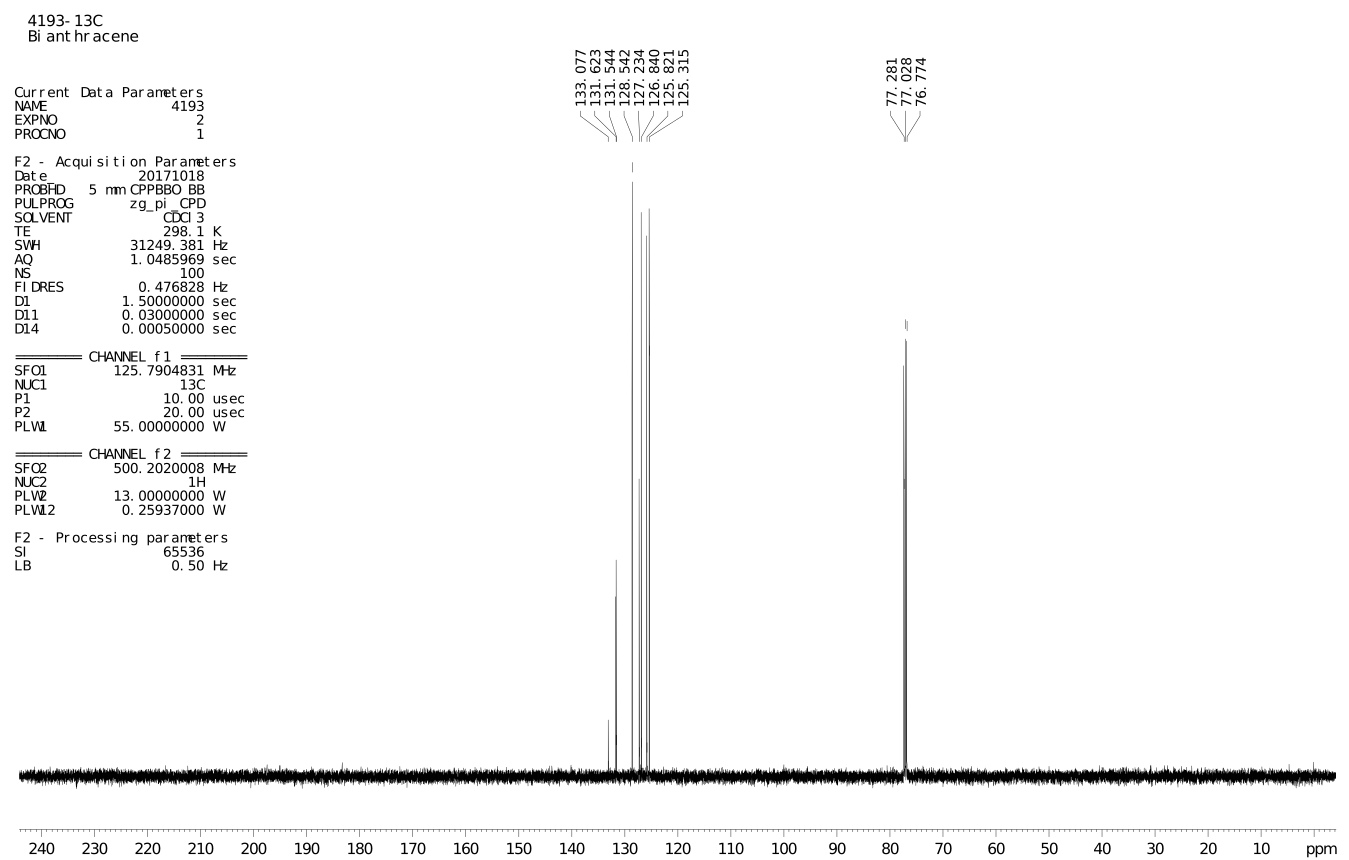
*7.092-7.068 ppm (4H dq J = 1 Hz)*

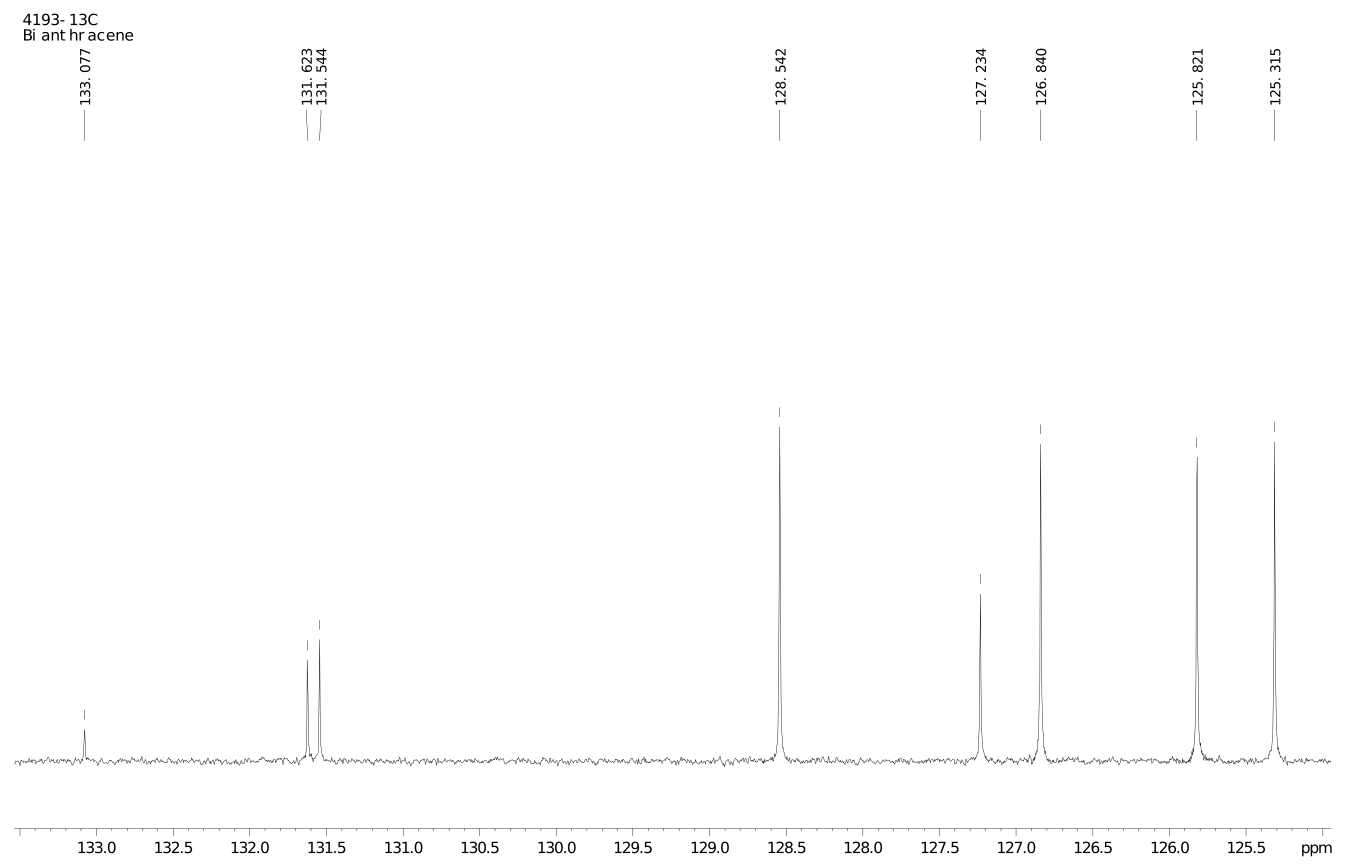
*7.153-7.121 ppm (4H dqd J = 1 Hz)*

*7.455-7.523 ppp (4H dqd J = 1 Hz)*

*8.157-8.135 ppm (4H dq J = 0.5 Hz)*

*8.678 ppm (2H s)*

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***13C NMR:***

*125.315 ppm*

*125.821 ppm*

*126.840 ppm*

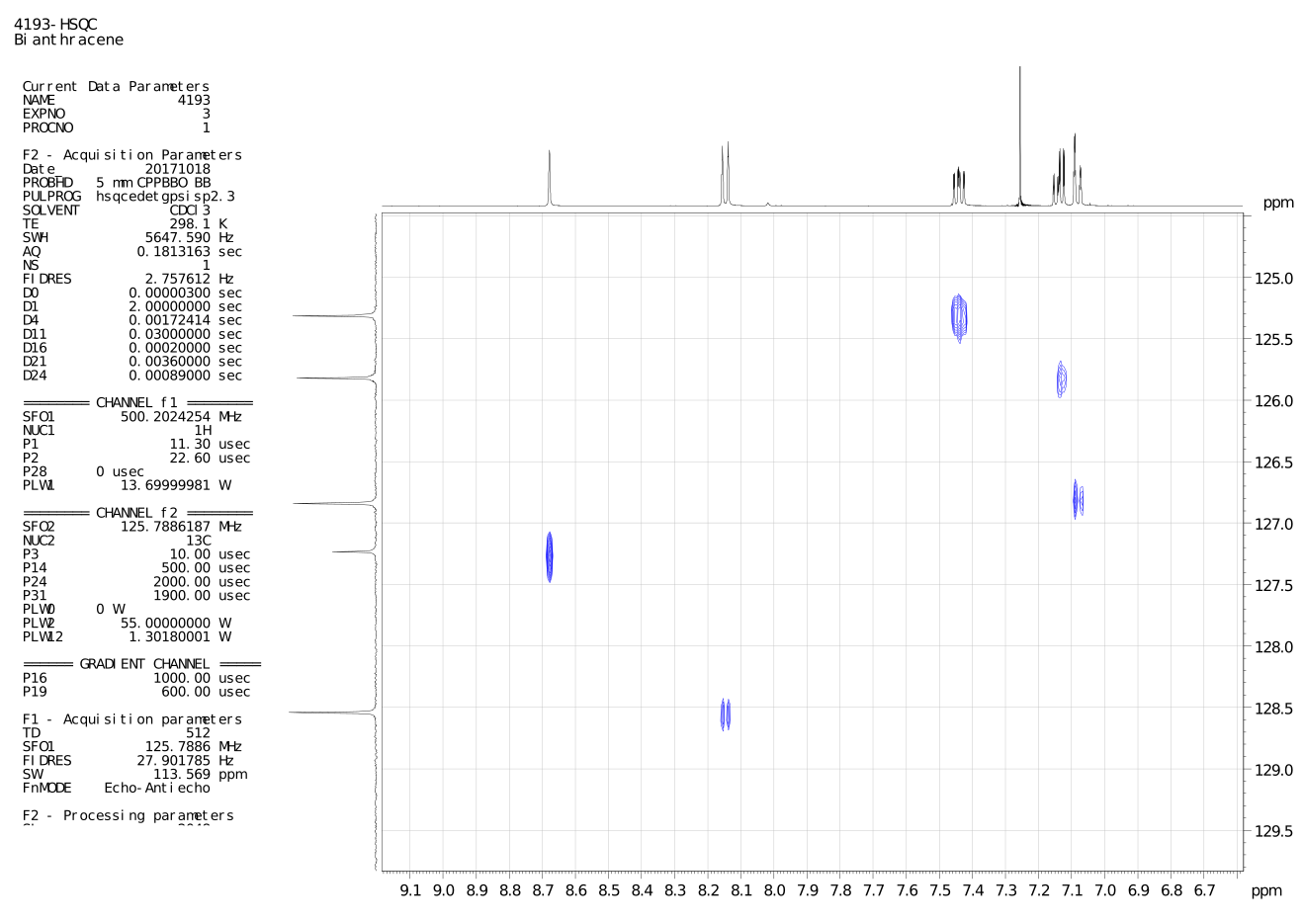
*127.234 ppm*

*128.542 ppm*

*131.544 ppm*

*131.623 ppm*

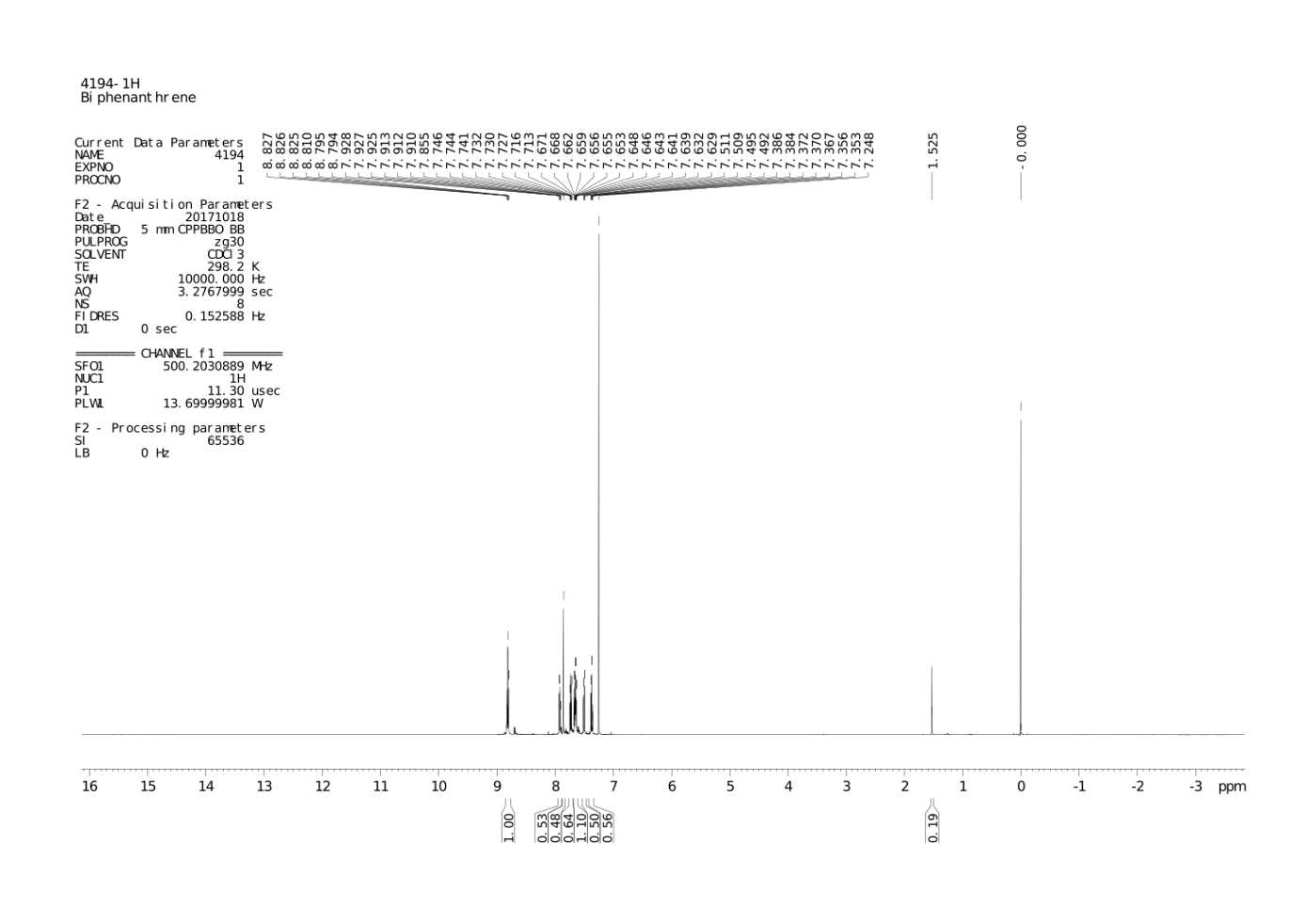
*133.077 ppm*

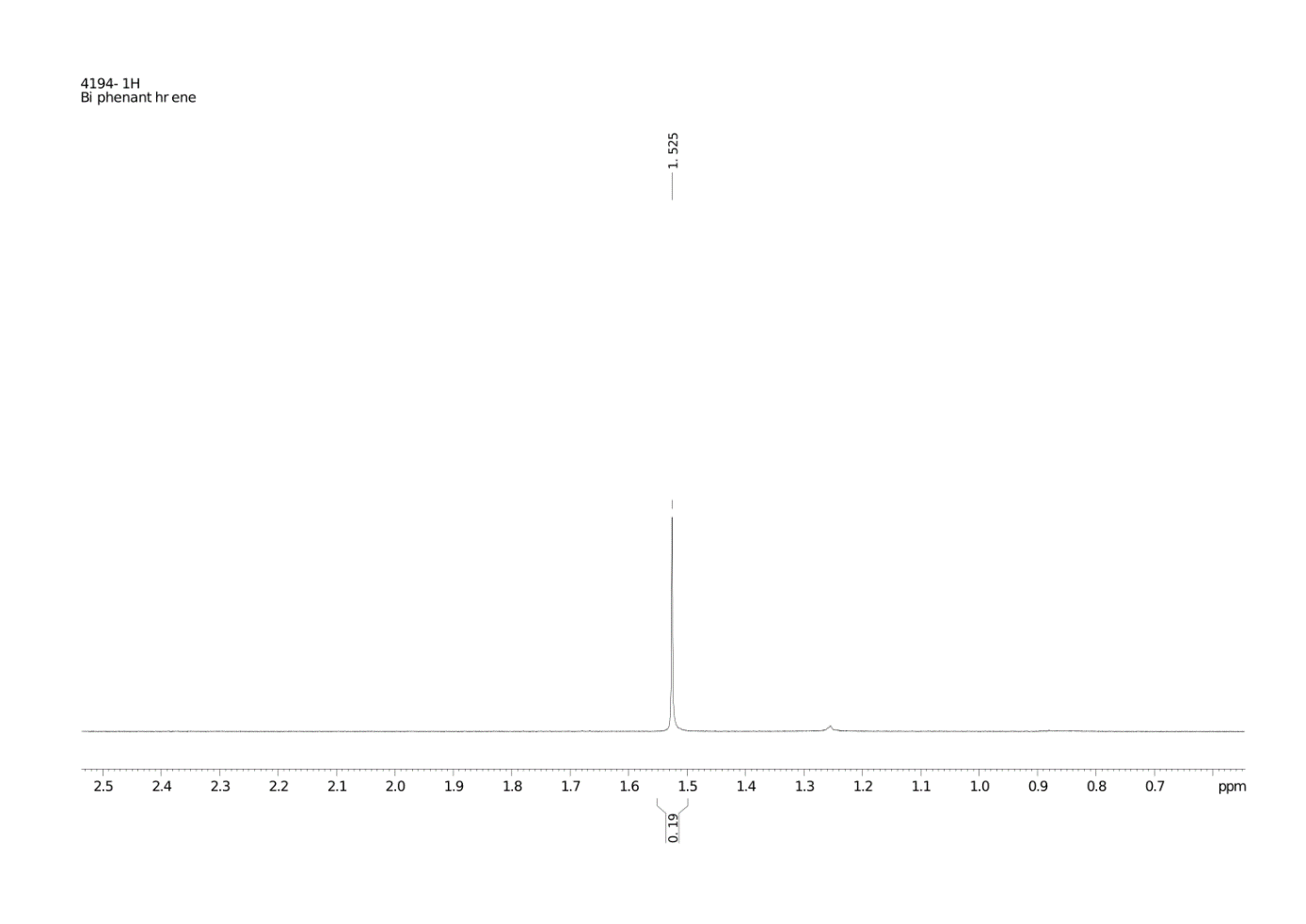
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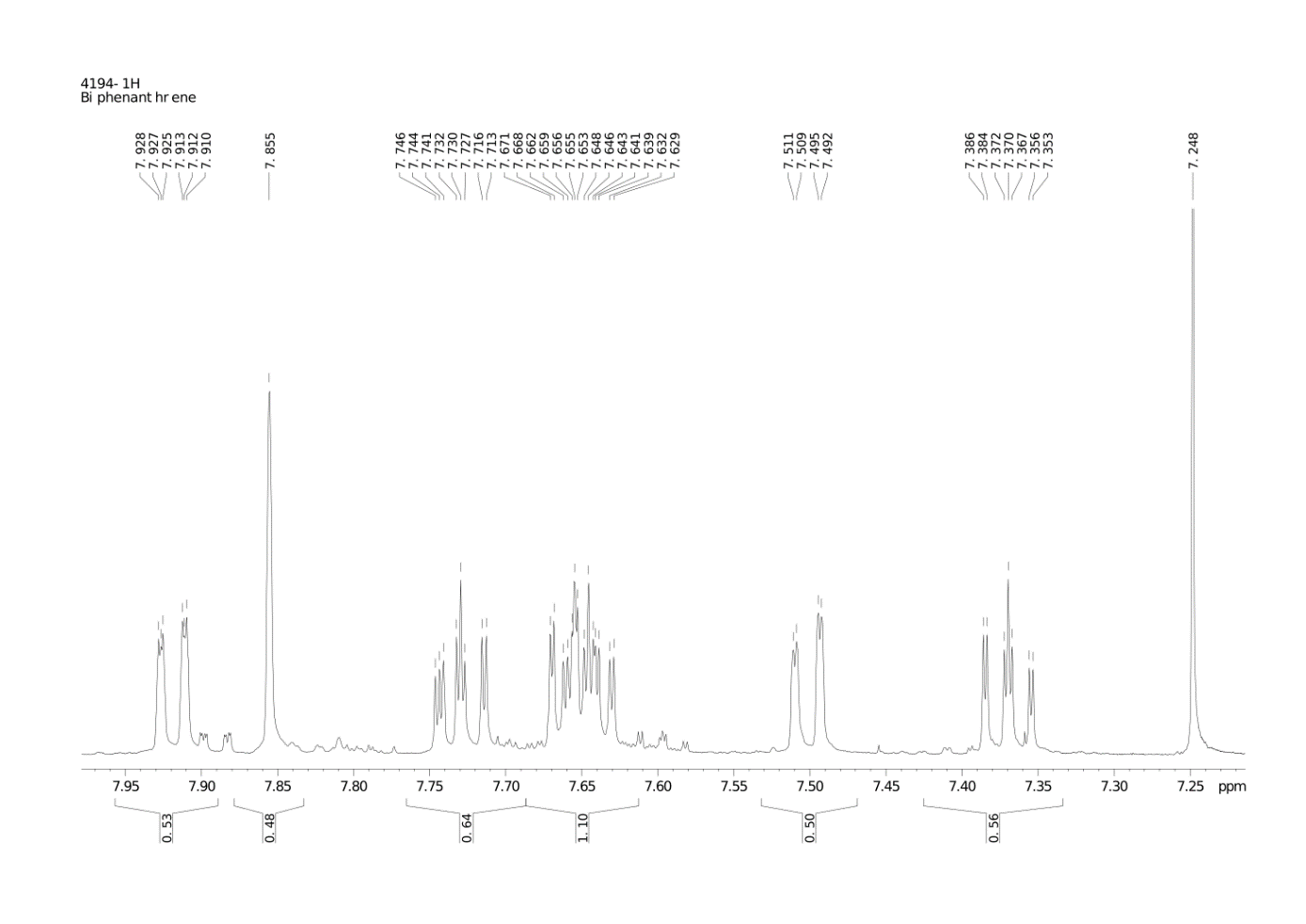
*Raman bands [cm−1]: 400, 1262, 1368, 1385, 1403, 1425, 1562, 1624*

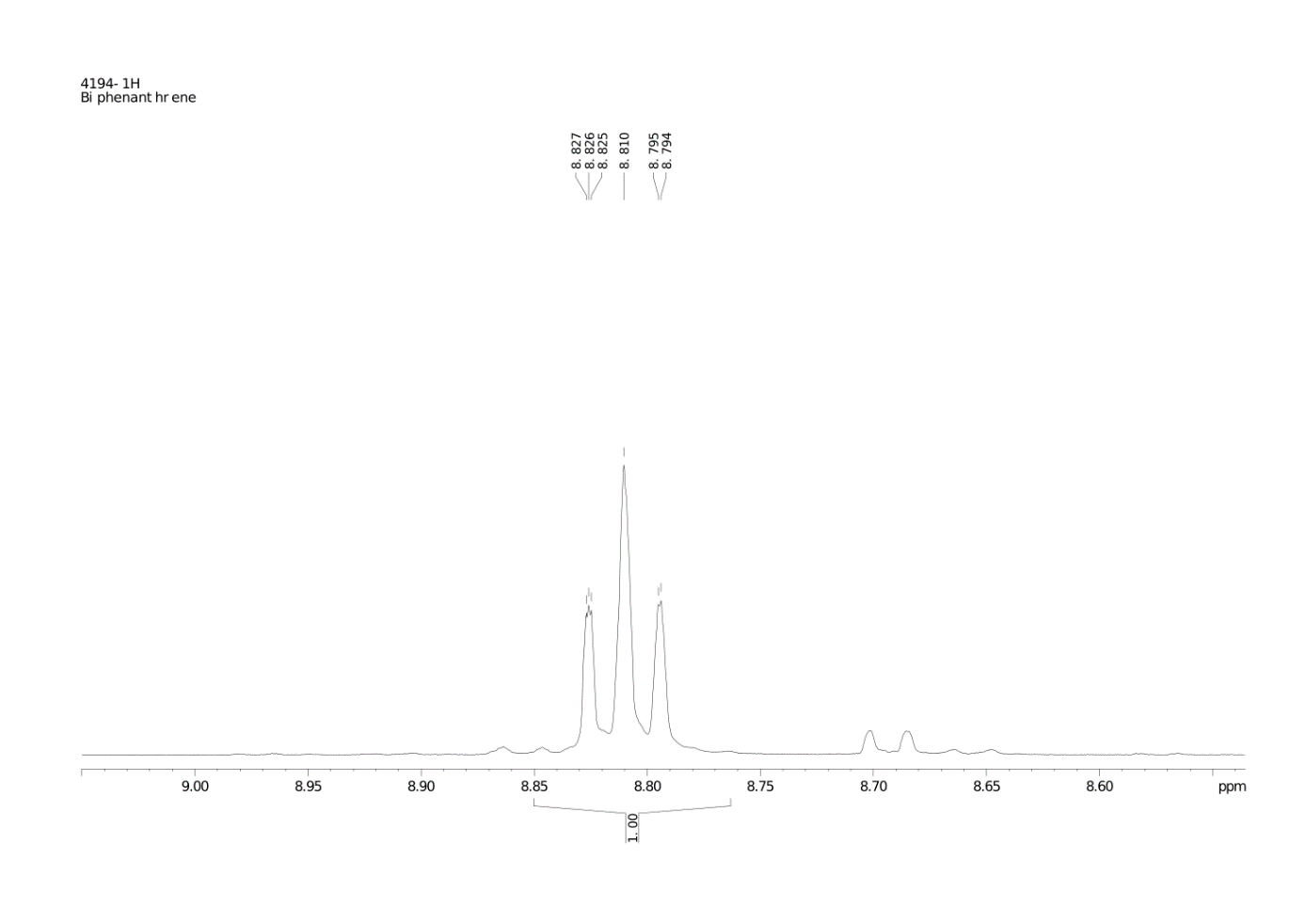
*IR bands [cm−1]: 425, 519, 563, 599, 602, 624, 641, 648, 730, 736, 760, 785, 789, 834, 837, 858, 885, 892, 909, 961, 1011, 1105, 1150, 1160, 1170, 1223, 1256, 1269, 1306, 1318, 1380, 1403, 1442, 1452, 1518, 1555, 1572, 1623, 1673, 1719, 1813, 1919, 1948, 2997, 3035, 3055, 3075****9,9’-biphenanthryl (2) NMR spectra: C28H18***

***1H 500 MHz, 13C 125 MHz, 1H vs. 13C HSQC CDCl3298 K***

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***1H NMR:***

*7.386-7.353 ppm (2H dtd J = 1 Hz)*

*7.511-7.492 ppm (2H dd J = 1 Hz)*

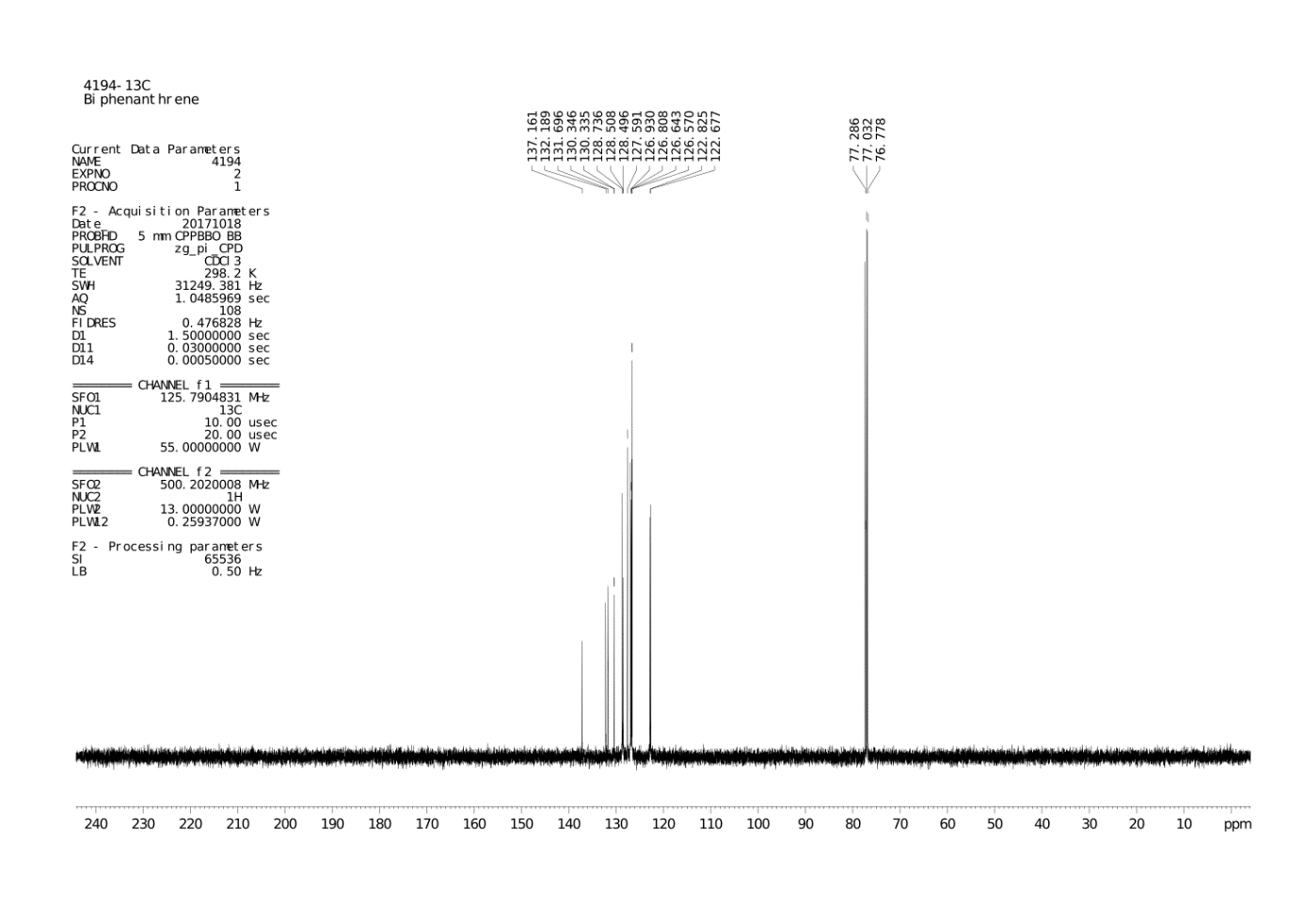
*7.671-7.629 ppm (4H dqqd J = 1Hz)*

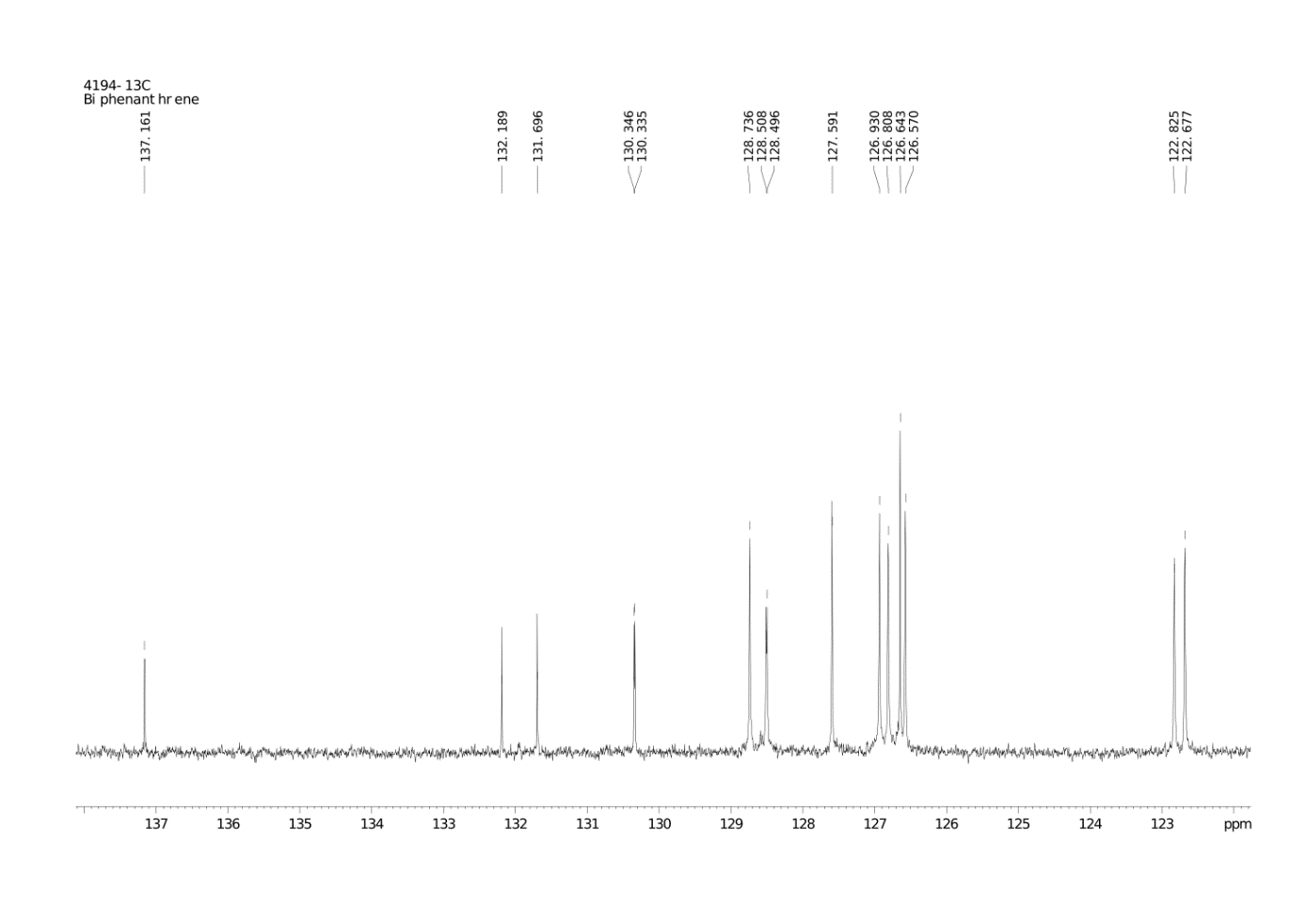
*7.746-7.713 ppm (2H ttd J = 1 Hz)*

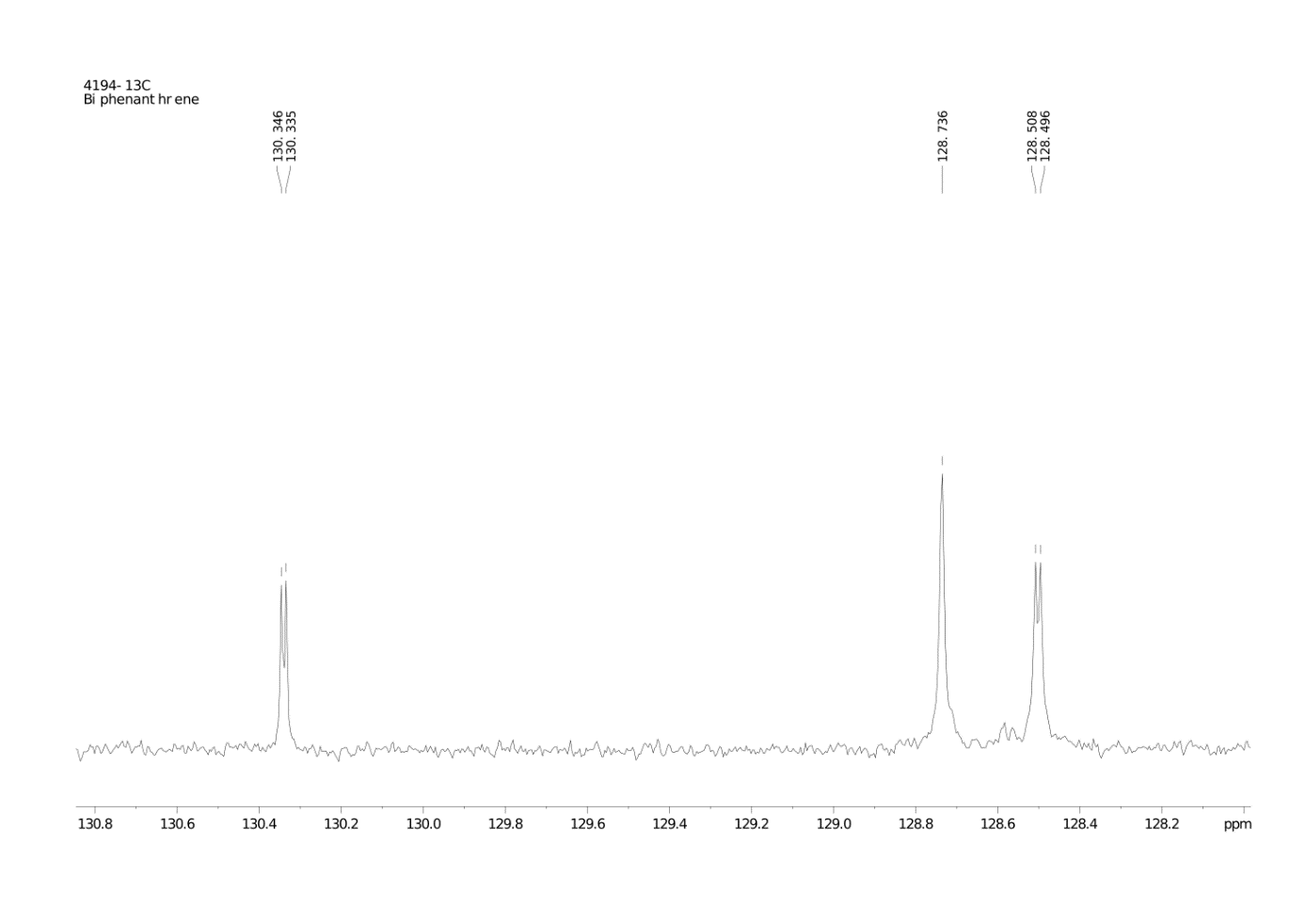
*7.855 ppm (2H s)*

*7.928-7.910 ppm (2H dt J = 1 Hz)*

*8.827-8.794 ppm (4H tsd J = 1 Hz)*

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***13C NMR:***

*122.677 ppm*

*122.825 ppm*

*126.570 ppm*

*126.643 ppm*

*126.808 ppm*

*126.930 ppm*

*127.591 ppm*

*128.496 ppm*

*128.508 ppm*

*128.736 ppm*

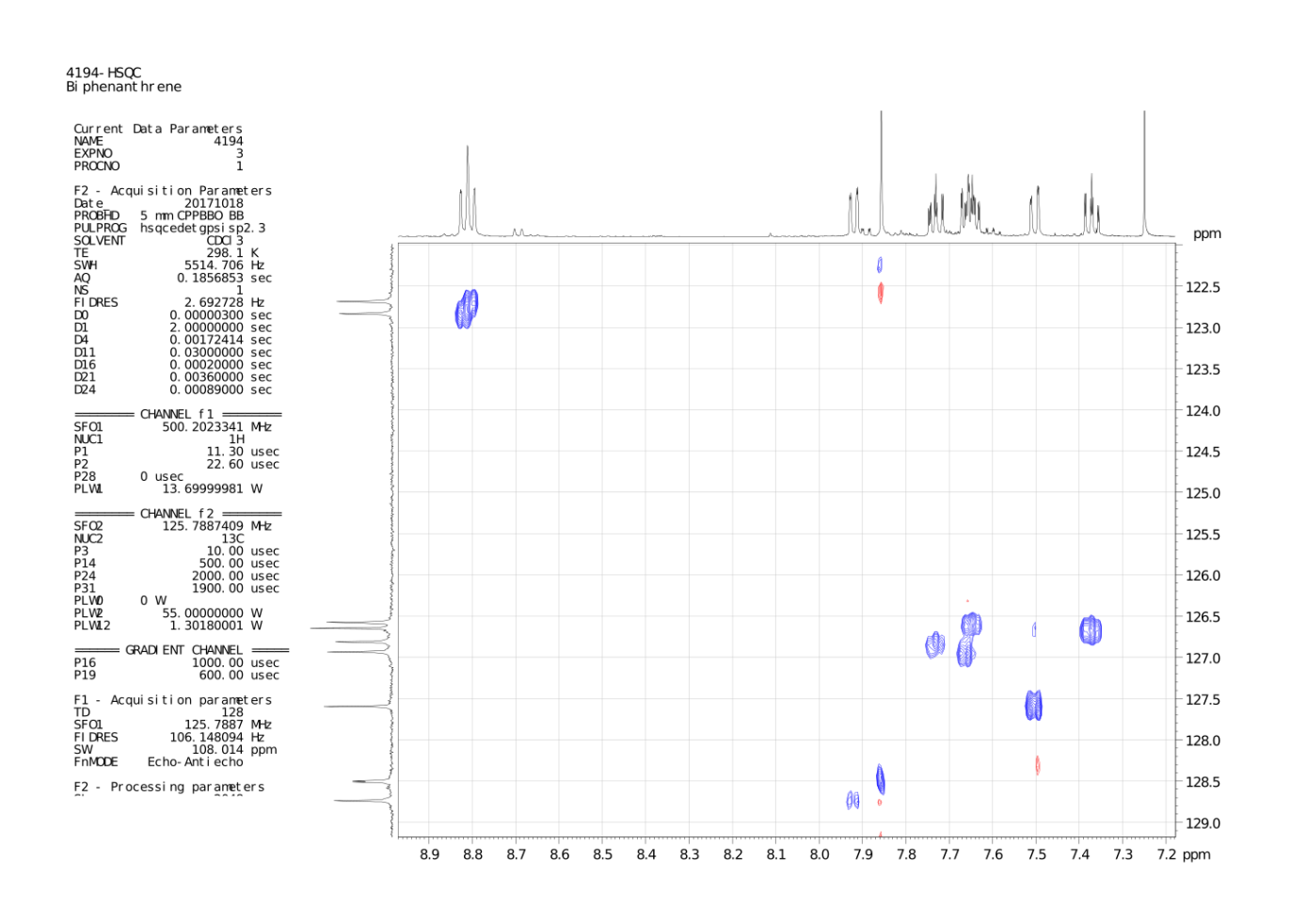
*130.335 ppm*

*130.346 ppm*

*131.696 ppm*

*132.189 ppm*

*137.161.ppm*



*Raman bands [cm−1]: 117, 188, 409, 714, 1036, 1247, 1347, 1382, 1421, 1447, 1459, 1528*

*IR bands [cm−1]: 408, 421, 426, 503.5, 548, 616.5, 726, 746.5, 766, 777, 789, 810, 832, 853, 866, 884, 896, 915, 942, 949, 976, 1002, 1020, 1039, 1100, 1142, 1155, 1165, 1187, 1206, 1230, 1243, 1263, 1291, 1372, 1381, 1421, 1428, 1440, 1449, 1480, 1493, 1526, 1573, 1592, 1916, 1946, 2930, 2965, 3016, 3029, 3051, 3056, 3072, 3101*

**TGA-DSC studies**



*Thermogravimetric (TGA) – calorimetric (DSC) profile of bianthryl-toluene 1:1 adduct at 5 K/min*

Toluene is released in two steps, 20–78.5 oC and 78.5–140 oC, with half mole of toluene released at each step from one mole of solvate. The total mass loss of ca. 18.9 % nicely corresponds to theoretical value (20.6 %). At 313 oC bianthryl melts or sublimes (the melting point of 316.6 oC was reported before [7]), and this is followed by vigorous evaporation of the liquid; at 400 oC all bianthryl is in the gas phase.



*Thermogravimetric (TGA) – calorimetric (DSC) profile of biphenanthryl at 5 K/min*

At 157.1 oC biphenanthryl melts and this is followed by evaporation of the liquid; the boiling point, determined from the maximum of the DSC peak, is 420 oC.

**References**

1. P. Połczyński, T.E. Gilewski, J. Gawraczyński, M. Derzsi, P.J. Leszczyński, W. Gadomski, Z. Mazej, R. Jurczakowski, W. Grochala, *Eur. J. Inorg. Chem.* 2016, **35**, 5401-5404. [↑](#endnote-ref-1)
2. Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, Oxfordshire, England. [↑](#endnote-ref-2)
3. G. M. Sheldrick, *Acta Cryst.* (2015) **A71**, 3–8. [↑](#endnote-ref-3)
4. C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr. (*2011) **44**,1281–1284. [↑](#endnote-ref-4)
5. L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, *Acta Cryst.* (2015) **A71**, 59-75. [↑](#endnote-ref-5)
6. M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, CrystalExplorer17 (2017). University of Western Australia. <http://hirshfeldsurface.net>.

   7 J. B. Kyzioł, J. Zaleski, *Acta Cryst.* (2007) **E63**, o1235–o1237. [↑](#endnote-ref-6)