Organic Syntheses

Synthesis of 1-Bromopyrene and 1-Pyrenecarbaldehyde

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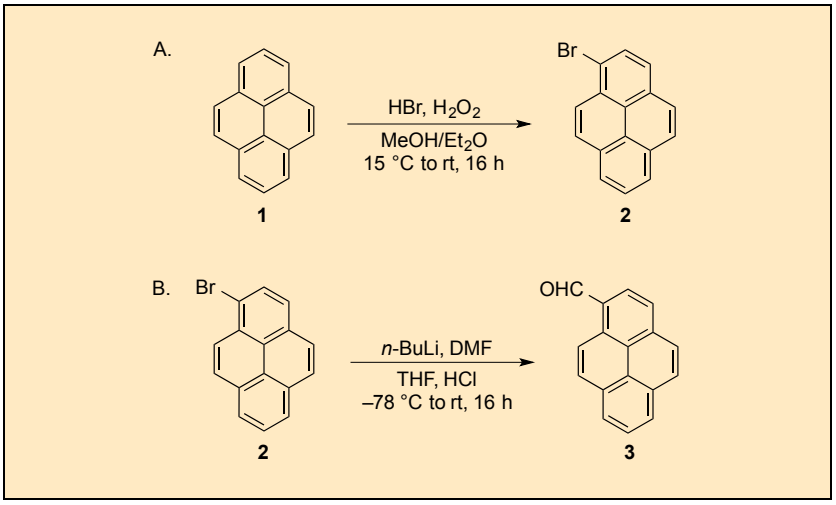

Procedure

A. *1-Bromopyrene* (**2**). A 500-mL, one-necked, round-bottomed flask was equipped with an octagonal Teflon-coated magnetic stirbar (25 mm x 10 mm), and a mixture of MeOH (Note 1) and Et_2O (250 mL, 1:1 v/v) (Note 2) is added. Pyrene (**1**) (20.0 g, 98.9 mmol, 1.00 equiv) (Note 3) is added with vigorous stirring, followed by addition of HBr (12.3 mL of 48% w/w aq solution, calculated to contain 8.8 g HBr, 109 mol, 1.1 equiv) (Note 4) *via* syringe. The round-

bottomed flask is equipped with a 25-mL pressure-equalizing addition funnel, which is then charged with H_2O_2 (30% w/w aq, 3.54 g, 10.4 mL, 104 mmol, 1.05 equiv) (Note 5). The reaction mixture is cooled to 15 °C using a water bath (Note 6), and the H_2O_2 slowly added over a period of 0.5 h (ca. 7 drops/min) (Note 7). The addition funnel is then replaced by a gas bubbler, the cooling bath removed, and the mixture stirred for 16 h at ambient temperature (Figure 1). Water (150 mL) is added, and the mixture is extracted with CH_2Cl_2 (2 x 250 mL) (Note 8) in a 1-L separatory funnel. The combined organic extracts are washed with NaOH (1 M aq, 150 mL) (Note 9) and saturated aq NaCl (2 x 150 mL) (Note 10) in a 1-L separatory

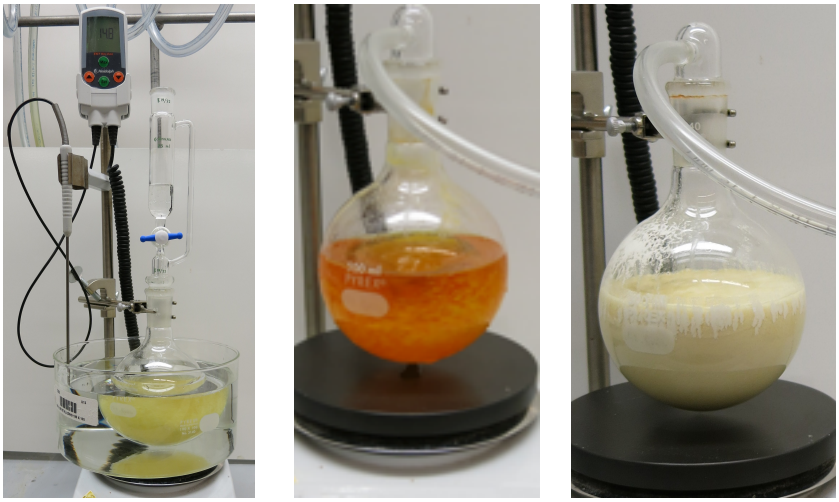

Figure 1. Reaction assembly for Step A before addition of H_2O_2, after addition of H_2O_2, and after mixture has stirred for 16 h

funnel, dried over $MgSO_4$ (20 g, 5 min) (Note 11), and filtered through a plug of silica gel (Note 12), which is rinsed with CH_2Cl_2 (2 x 100 mL) (Note 8). The solvent is removed by rotary evaporation (40 °C, 675–20 mmHg) and the resulting solid is dried *in vacuo* (0.01 mmHg) for 2 h. The crude material is placed in a Soxhlet extractor (Note 13) and extracted with *n*-pentane (750 mL) (Note 14) for 48 h (Figure 2). After cooling to room temperature, the *n*-pentane fraction, already containing crude precipitated pale yellow product, is concentrated by rotary evaporation (40 °C, 675 mmHg) to 500 ± 25 mL and placed in a refrigerator (ca. 2 °C) overnight. The formed precipitate is

collected by gravity filtration, dried *in vacuo* (0.01 mmHg) for 2 h, dissolved in boiling hexanes (1.0 L) (Note 15) in a 2-L, round-bottomed flask, and placed in a freezer (ca. –20 °C) overnight. The formed precipitate is collected by filtration on a Büchner funnel and dried *in vacuo* (0.01 mmHg) for 8 h to give 18.9 g of the title compound **2** as a pale yellow, air-stable powder. The mother liquor is concentrated to 400 ± 20 mL by rotary evaporation (40 °C, 315–245 mmHg) and cooled in a freezer (ca. –20 °C) overnight. The mixture is filtered using a Büchner funnel and the product dried *in vacuo* (0.01 mmHg) for 8 h to obtain 2.5 g of additional material. The combined yield from both recrystallizations is 21.4 g (77%) (Notes 16 and 17).

Figure 2. Soxhlet extraction assembly before extraction and after 48 h extraction.

B. *1-Pyrenecarbaldehyde* (*3*). A 500-mL, one-necked, round-bottomed Schlenk flask is equipped with an octagonal Teflon-coated magnetic stirbar (50 mm x 10 mm). After connecting to the vacuum/nitrogen line, 1-bromopyrene (**2**) (21.4 g, 0.076 mol, 1.0 equiv) is added, and the flask equipped with a rubber septum. The flask is evacuated under vacuum and purged with nitrogen (three times). Dry deoxygenated THF (300 mL) (Note 18) is added under a nitrogen atmosphere. After cooling to –78 °C (Note 19), *n*-BuLi (1.6 M in hexane, 62 mL, 0.99 mol, 1.3 equiv) (Note 20) is added *via* syringe under a nitrogen atmosphere over a period of 10 min to the light brown solution (Note 21). After stirring for 1 h, anhydrous DMF (7.6 g, 8.0 mL, 0.99 mol, 1.3 equiv) (Note 22) is added *via* syringe within 5 s (Note 23),

and the mixture is allowed to reach room temperature while stirring for 16 h overnight under a nitrogen atmosphere. The mixture is carefully poured over 10 min at room temperature into a rapidly stirred mixture of conc HCl and H_2O (500 mL, 1:1 v/v) (Note 24) in a 2-L one-necked, round-bottomed flask equipped with an octagonal Teflon-coated magnetic stirbar (50 mm x 10 mm) (Figure 3). Diethyl ether (500 mL) (Note 2) is added. The organic phase is separated in a 2-L separatory funnel and washed with H_2O (3 × 300 mL). After drying over $MgSO_4$ (10 g, 5 min) (Note 11), the mixture

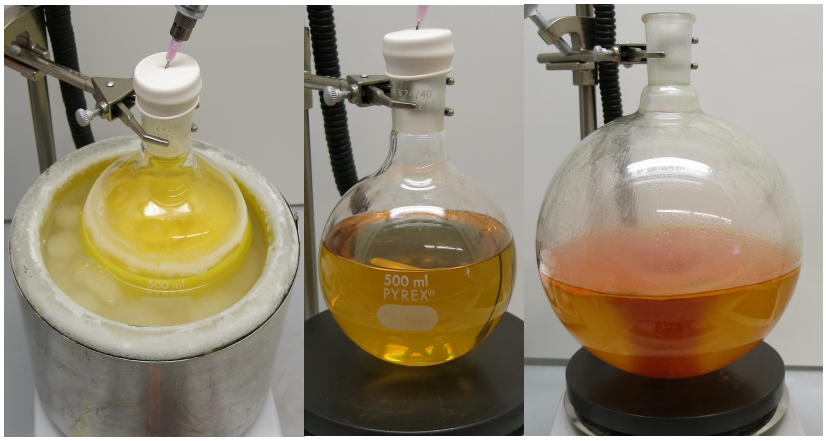

Figure 3. Reaction assembly for Step B after the addition of *n*-BuLi, after addition of DMF, and after mixture is poured into aqueous HCl

is filtered by gravity filtration, the solvent removed from the filtrate by rotary evaporation (40 °C, 650–10 mmHg) giving an orange solid, which is dried *in vacuo* (0.01 mmHg) for 2 h. The orange solid is dissolved in boiling EtOH (450 mL) (Note 25) in a 500-mL, one-necked, round-bottomed flask and after addition of H_2O (5 mL) *via* syringe and cooling to room temperature, the mixture is placed in a freezer (ca. –20 °C) overnight. The formed precipitate is collected by suction filtration using a medium porosity sintered glass funnel and dried *in vacuo* (0.01 mmHg) for 8 h to give 7.3 g of the title compound **3** as a dark yellow, crystalline, air-stable solid. The mother liquor is concentrated to 250 ± 15 mL by rotary evaporation (40 °C, 130 mmHg) and cooled in a freezer (ca. –20 °C) overnight. The formed precipitate is collected by suction filtration using a medium porosity sintered glass funnel and dried *in vacuo* (0.01 mmHg) for 8 h to obtain 3.3 g of additional material. The mother liquor is concentrated to 100 ± 10 mL and

placed in a freezer (ca. –20 °C) overnight. The precipitate is collected and dried as described above to obtain 2.4 g of additional material. The combined yield from the three recrystallizations is 13.0 g (74%) (Notes 26 and 27) (Figure 4).

Figure 4. Product of Step B

Notes

1. Methanol was purchased from Fisher (HPLC grade, 99.9% pure) and was used as received.
2. Diethyl ether was purchased from Fisher (99.9% BHT stabilized) and was used as received.
3. Pyrene (**1**) was purchased from Sigma-Aldrich (98%) and was used as received.
4. Hydrobromic acid (48% w/w aq) was purchased from Fluka (purum p.a.; ≥48%) and was used as received.
5. Hydrogen peroxide (30% w/w aq) was purchased from Sigma-Aldrich and was used as received.
6. To cool to 15 °C, the solution was stirred for 10 min with the round-bottomed flask immersed in a water/ice bath. Not all starting material is dissolved.
7. During addition of hydrogen peroxide the color of the reaction mixture darkens slightly to deep-yellow/orange and a colorless/grayish precipitate slowly starts to appear; the amount of precipitate increases while stirring for 16 h overnight.
8. Dichloromethane was purchased from Fisher (99.9% pure) and was used as received.
9. Sodium hydroxide was purchased from Macron (95% pure) and was used as received.

10. Sodium chloride was purchased from Sigma-Aldrich (>99.0% pure) and was used as received.
11. Magnesium sulfate (anhydrous) was purchased from Fisher (powder/certified) and was used as received.
12. The size of the silica plug was 5 cm (diameter) x 1 cm. Silica gel 60 (0.048–0.063 mm) was purchased from Silicycle.
13. Soxhlet apparatus: 19 cm length x 4.5 cm diameter on a 1-L, one-necked, round-bottomed flask filled with *n*-pentane (Note 14). The crude material was placed as a solid in the Soxhlet-cartridge and the *n*-pentane was heated to 50–55 °C *via* an oil bath.
14. *n*-Pentane was purchased from Fisher (99.6% pure) and was used as received.
15. Hexanes (isomeric mixture, 99.6%) was purchased from Fisher and was used as received.
16. When the reaction was performed on half scale, the isolated yield was 10.6 g (76%) with purity of >99%.
17. Physical properties and spectroscopic analysis of **2**: mp 93–94 °C (for both crops of material). IR (ATR) 3047, 1588, 1481, 1429, 178, 1015, 966, 835, 751, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99–8.06 (m, 3H), 8.09 (d, J = 8.9 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.20–8.24 (m, 3H), 8.43 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 120.0, 124.1, 125.6, 125.7, 125.9, 126.0, 126.1, 126.6, 127.2, 127.8, 129.1, 129.7, 130.1, 130.7, 131.1, 131.3. APCI HRMS *m/z* calcd. for $C_{16}H_9Br$ $[M+H]^+$ 279.9882, found 279.9885. Purity analysis of **2**: HPLC > 99 area % purity at 254 nm detection for both crops of material, using an Agilent 1260 Infinity instrument package (pump/autosampler/detector P4000/AS 3000/UV6000LP); HPLC conditions, Macherey-Nagel Nucleosil 100-5 C18 column (4.6 x 250 mm), 5 μM particle size, 1.00 mL/min flow; eluent (acetonitrile/water = 80/20); product elutes at 17.0 min. Residual pyrene (HPLC = <1 area % at 254 nm detection; product elutes at 9.0 min) was identified.
18. Tetrahydrofuran was purchased from Fisher (HPLC grade, 99.9% pure) and passed through an activated alumina column under an argon atmosphere prior to use.
19. The solution was cooled *via* a dry ice-acetone bath.
20. *n*-Butyllithium (1.6 M in hexane) was obtained from Acros Organics and stored at ca. 2 °C in a refrigerator. The reagent solution was used as received.
21. During addition of *n*-butyllithium, a yellow precipitate appears.

22. *N*,*N*-Dimethylformamide anhydrous, Drisolv® (water <50 ppm) was obtained from EMD Millipore and was used as received.
23. With the addition of *N*,*N*-dimethylformamide, the yellow precipitate disappears and transforms into a grey mixture, which changes color to brown by stirring overnight.
24. Hydrochloric acid (37.0%), obtained from Fisher, was used as received. Quenching the *N*,*N*-dimethylformamide complex with HCl/H_2O gives a brown organic phase and a yellow aqueous phase. The solution becomes warm during quenching and is cooled to room temperature prior to addition of diethyl ether.
25. Ethanol was purchased from Decon Labs (200 proof).
26. When the reaction was performed on half-scale, the isolated yield was 5.82 g (67%) with purity of 95%.
27. Physical properties and spectroscopic analysis of **3**: mp 125–126 °C (1st crop), 124–125 °C (2nd crop), 123–124 °C (3rd crop). IR (ATR) 3041, 2857, 2716, 1678, 1596, 1508, 1227, 1201, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, at 60 mg/mL, ^1H NMR is concentration dependent) δ: 7.89 (d, J = 8.9 Hz, 1H), 7.93–8.08 (m, 3H), 8.11 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 7.6 Hz, 2H), 8.23 (d, J = 7.9 Hz, 1H), 9.20 (d, J = 9.3 Hz, 1H), 10.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 123.2, 124.2, 124.7, 124.8, 126.7, 127.0, 127.2, 127.3, 127.5, 130.6, 130.9, 131.0, 131.1, 131.2, 131.5, 135.7,193.2. APCI HRMS *m*/*z* calcd. for $C_{17}H_{11}O$ $[M+H]^+$ 231.0804, found 231.0806. Purity analysis of **3**: HPLC 95 area % purity (1st crop), 97% area % purity (2nd crop), and 97% area % purity (3rd crop) at 254 nm detection, using an Agilent 1260 Infinity instrument package (pump/autosampler/detector P4000/AS 3000/UV6000LP); HPLC conditions, Macherey-Nagel Nucleosil 100-5 C18 column (4.6 x 250 mm), 5 μM particle size, 1.00 mL/min flow; eluent (acetonitrile/water = 80/20); product elutes at 7.6 min.

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http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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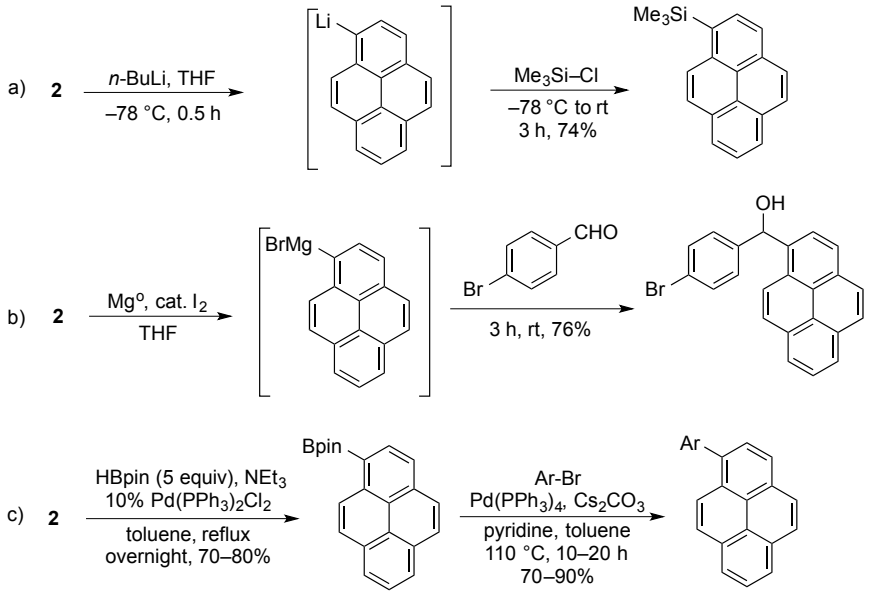
Discussion

Due to the useful photophysical attributes of pyrene (**1**),[2] it is a desirable component of many functional materials.[3] Thus, 1-bromopyrene (**2**) is a key building block for a large portion of the chemical community.[4] The first synthesis of **2** was described in 1937 by Lock, *via* the bromination of **1**.[5] Similar approaches have since been described using reagents such as NBS,[6] $CuBr_2$,[7] and HBr with H_2O_2.[8] The use of column chromatography in these protocols, however, limits the reaction scale.[8] Fulfilling the demand for 1-bromopyrene in larger amounts, a simple and chromatography free procedure has been reported in 1968 by Gumprecht.[9] Unfortunately, this procedure (and many others) require the use of CCl_4 as solvent,[5–7,9] which has been prohibited in many countries[10] due to toxicological[11] and environmental concerns.[12] Thus, there is considerable demand for a procedure with similar synthetic utility that does not require CCl_4 or column chromatography. Herein, we report such a protocol for the synthesis of **2** that has been reliably reproduced on a 10–20 g scale by

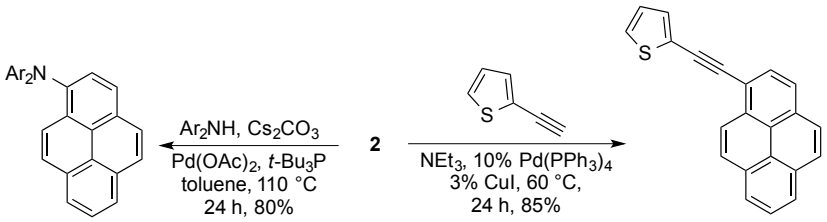
undergraduate students and that tolerates the use of inexpensive commercially available technical grade pyrene as precursor material.

For the design of functional materials, **2** can be easily transferred in analogy to other haloarenes into reactive species e.g., by lithiation,[13] magnesiation,[14] or borylation.[15] Consequently, **2** has been used in a large variety of reactions (Scheme 1).[13–15]



Scheme 1. Functionalization of 2 via reactive species using routes: a) lithiation,[13] b) Grignard reaction,[14] and c) borylation.[15]

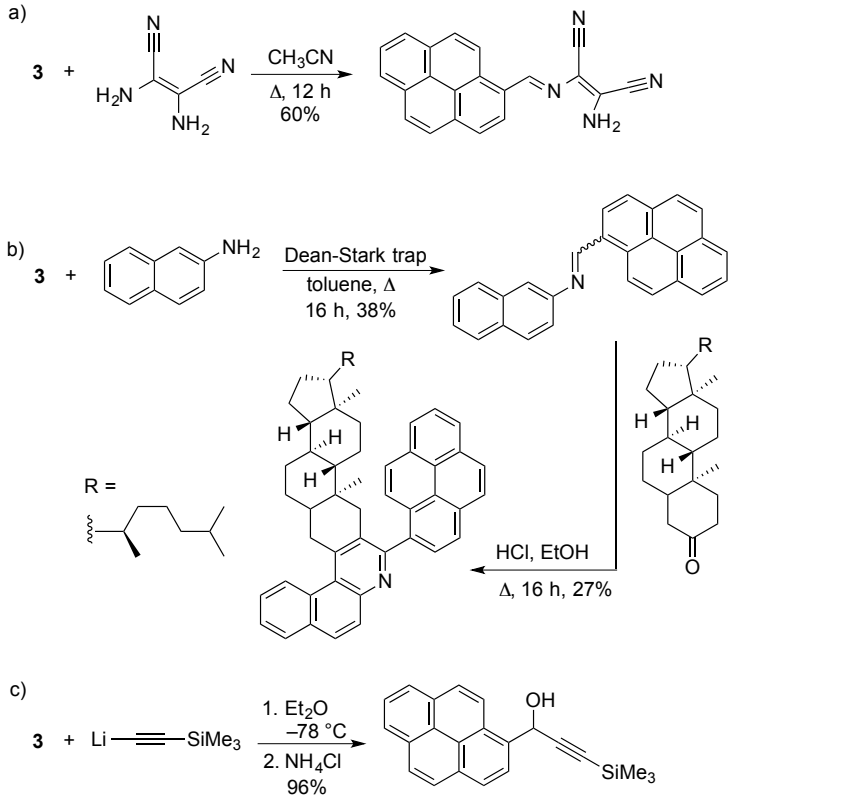
Bromide **2** can also be used directly in transition metal-catalyzed cross-coupling reactions. For example, heteroatomic or organic nucleophiles can be directly linked to **2** *via* Buchwald–Hartwig amination[16] or Sonogashira cross-coupling[17] (Scheme 2).



Scheme 2. Cross-coupling reactions of 2: Buchwald-Hartwig amination (Ar = *p*-OMePh)[16] (left) and Sonogashira reaction[17] (right).

Beside **2**, 1-pyrenecarbaldehyde (**3**) is also of considerable interest as building block for the synthesis of functional materials.[18,19] Several synthetic pathways toward **3** are already known. Vollmann reported the synthesis of **3** in 1937 starting from pyrene in a Vilsmeier-Haack[20] reaction with *N*-methylformanilide and $POCl_3$.[21] Other more recently reported methods use slightly modified Vilsmeier-Haack procedures,[18b,19c] or metal-catalyzed reactions with $AlCl_3$,[22] $TiCl_4$,[23] or a Ru-Co-Ce catalyst.[24] Most of these synthetic procedures, however, suffer from disadvantages, such as poor to moderate yields,[18b,19c,21,22] the necessity of toxic reagents (e.g., halo-ethers),[22,23,25] or the use of expensive metals.[24] With the interest of the chemical community in **3**,[18,19] we developed an inexpensive and facile synthesis, based on the lithiation of **2**,[13] and subsequent quenching with DMF. After acidic workup, aldehyde **3** is isolated in good yields by recrystallization. In combination with the synthesis of **2** described above, the preparation of **3** is efficiently conducted on a 10–15 g scale and does not require the use of expensive or toxic reagents.

Aldehyde **3** has been used as a building block for the synthesis of molecular sensors based on the unique UV-vis and emission characteristics of the pyrene chromophore.[18,19] These syntheses often rely on the use of an amine condensation reactions with **3**, as in Scheme 3a.[19a] Condensation reaction of aldehyde **3** with 2-naphthalenamine, followed by reaction with 5-α-cholestanone was used to form a benzoquinoline derivative (Scheme 3b).[26a] In this case, the pyrene moiety was designed to serve as an aromatic constituent of a petroleum model compound for thermal cracking experiments.[26b] Finally, the aldehyde moiety of **3** can serve as an electrophile in addition reactions toward the formation of carbon-rich molecules, for example, as in Scheme 3c.[27–29]



Scheme 3. Functionalization of 3 *via* a condensation reaction leading to a) a fluorescence sensor[19a] or b) a petroleum model compound.[26] c) Reaction of 3 with a Li-acetylide, toward formation of carbon-rich compounds.[27]

References

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Appendix
Chemical Abstracts Nomenclature (Registry Number)

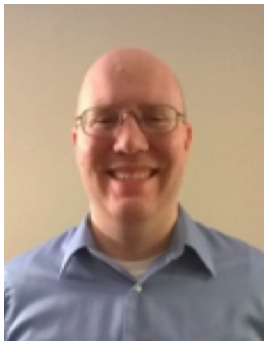
Pyrene: Benzo[*def*]phenanthrene; (129-00-0)
HBr: Hydrobromic acid; (10035-10-6)
H_2O_2: Hydrogen peroxide solution; (7722-84-1)
1-Bromopyrene; (1714-29-0)
n-BuLi: *n*-Butyllithium solution; (109-72-8)
DMF: *N*,*N*-Dimethylformamide; (68-12-2)
HCl: Hydrochloric acid; (7647-01-0)
1-Pyrenecarbaldehyde; (3029-19-4)

Matthias Schulze was born in Lauf a.d. Pegnitz (Germany) in 1986. He received his B. Sc. degree in chemistry in 2009 and his M. Sc. degree in 2011 from the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). He is currently a doctoral student at FAU under the supervision of Prof. Rik R. Tykwinski working on the synthesis of asphaltene model compounds and their supramolecular interactions.

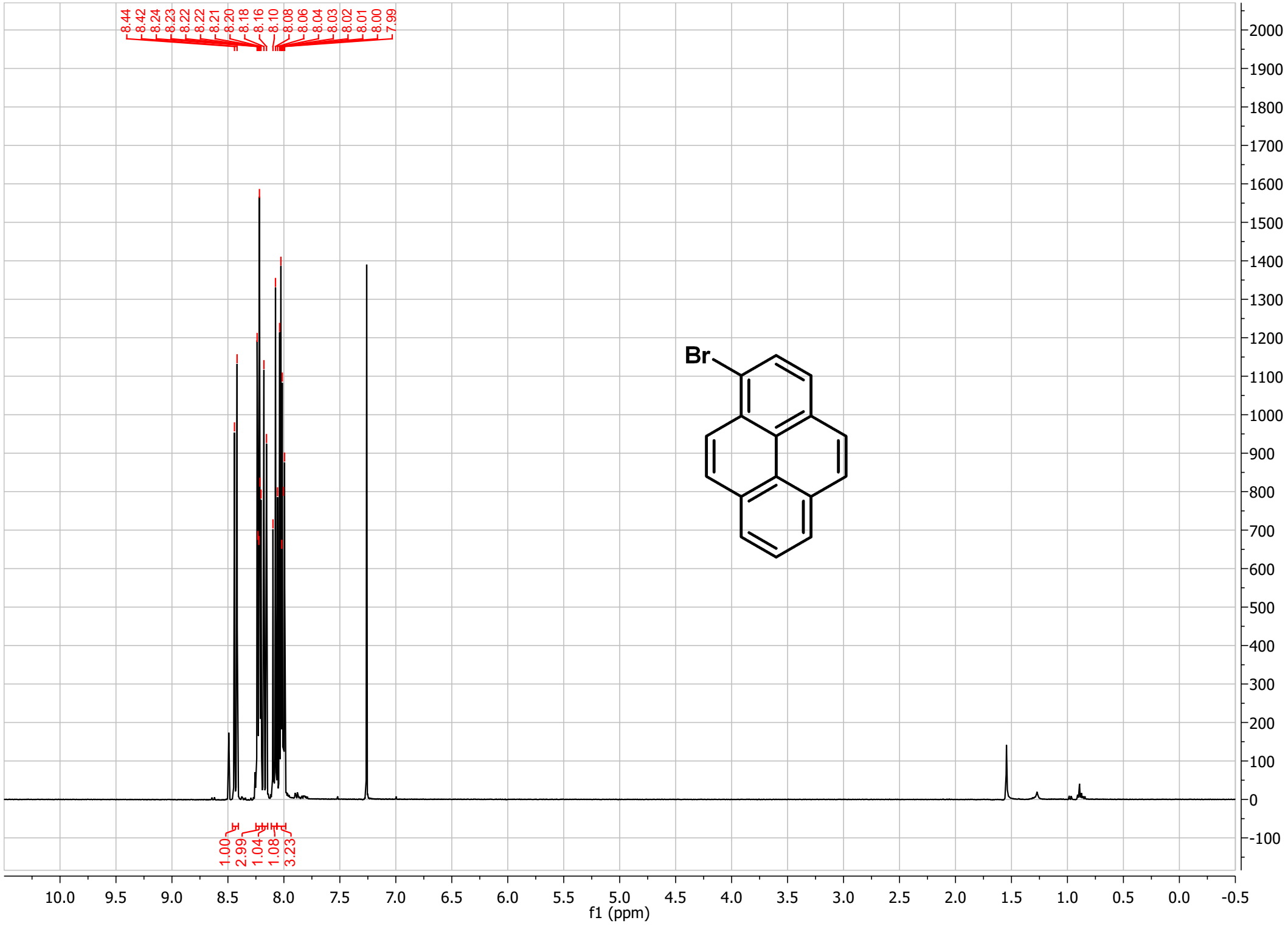
Alexander Scherer was born in Bamberg (Germany) in 1980. He received his diploma in chemistry in 2005 and his doctoral degree in chemistry in 2009 from the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). He was a post-doctoral researcher at the University of Alberta in Edmonton (Canada) and then at FAU (2009–2012), focusing on the aggregation of heavy oil, especially model compounds for the asphaltenes. In 2012 he became research associate (Akademischer Rat) at FAU.

Colin Diner was born in Boulder, Colorado in 1985. He received his B. S. in chemistry in 2009 from UW Madison and his doctorate in 2015 from the Stryker Group at the University of Alberta, Canada. He is currently a postdoctoral researcher at Stockholm University, Sweden under the supervision of Prof. Kalman Szábo. His research interests broadly include functional materials, asymmetric catalysis, and practical chemical synthesis. When not in the lab Colin can be found rock climbing, road cycling, and cooking.

Rik R. Tykwinski was born in Marshall, MN and completed his Ph. D. in 1994 at the University of Utah working with Prof. Peter Stang. He did post-doctoral research at ETH-Zürich with Prof. François Diederich (1994–1997), and in 1997 he joined the faculty at the University of Alberta. In 2009, he moved to the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) as Chair of Organic Chemistry. His interests focus on the development of synthetic methods for carbon-rich molecules and allotropes, characterization of their electronic properties, asphaltene model compounds, as well as mountain biking and entertaining his two sons.



Jeffrey Mighion was born in Concord, North Carolina in 1986. He received his B. S. in chemistry in 2008 from UNC Chapel Hill. In 2014, he completed his Ph. D. at Princeton University with Prof. Erik Sorensen in the area of natural products synthesis. He is currently a post-doctoral researcher at Emory University with Huw Davies where his research focuses on development and application of C-H functionalization.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8.16
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8.08
8.06
8.04
8.03
8.02
8.01
8.00
7.99
Br
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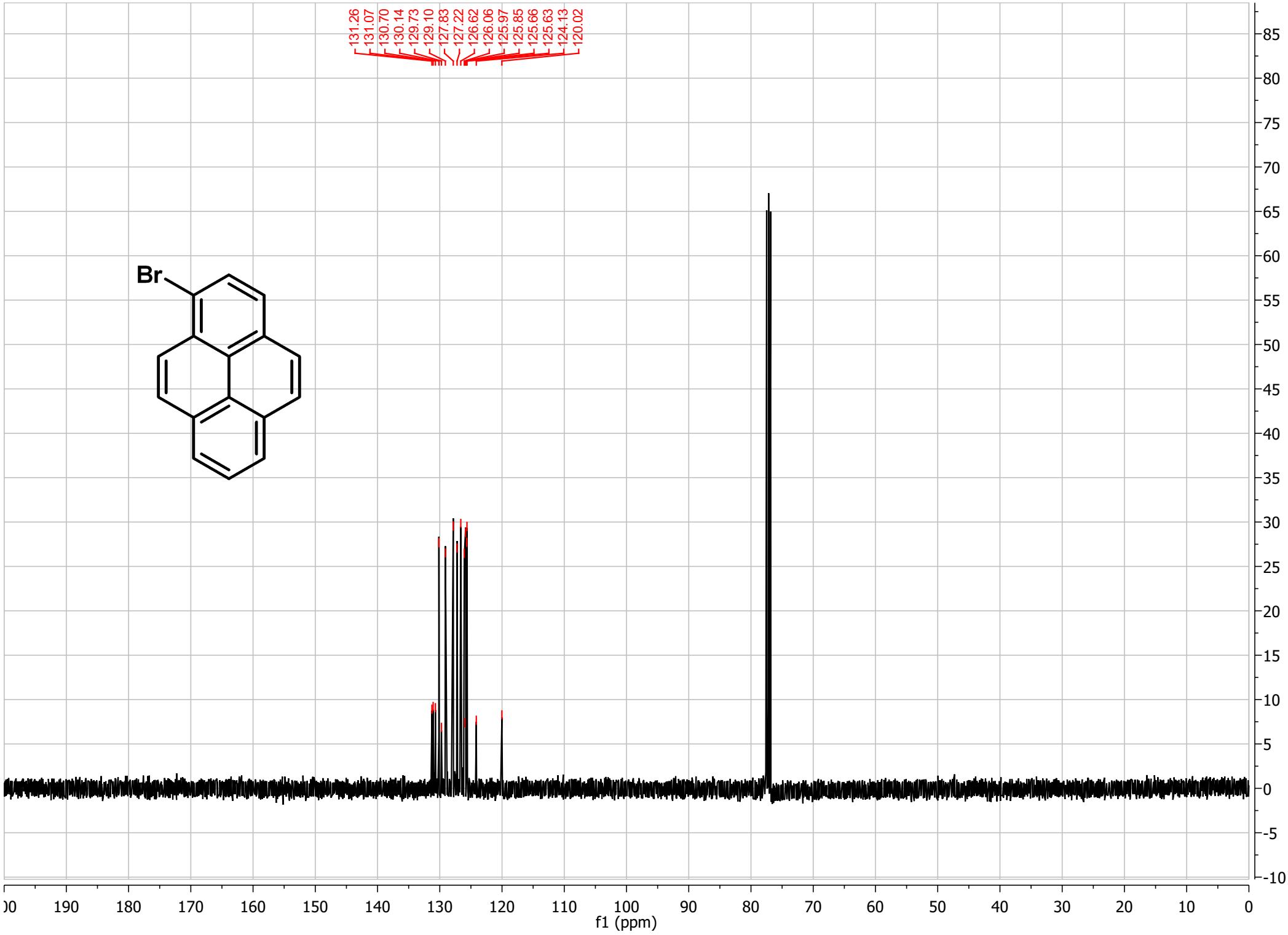
2.99
1.04
1.08
3.23
f1 (ppm)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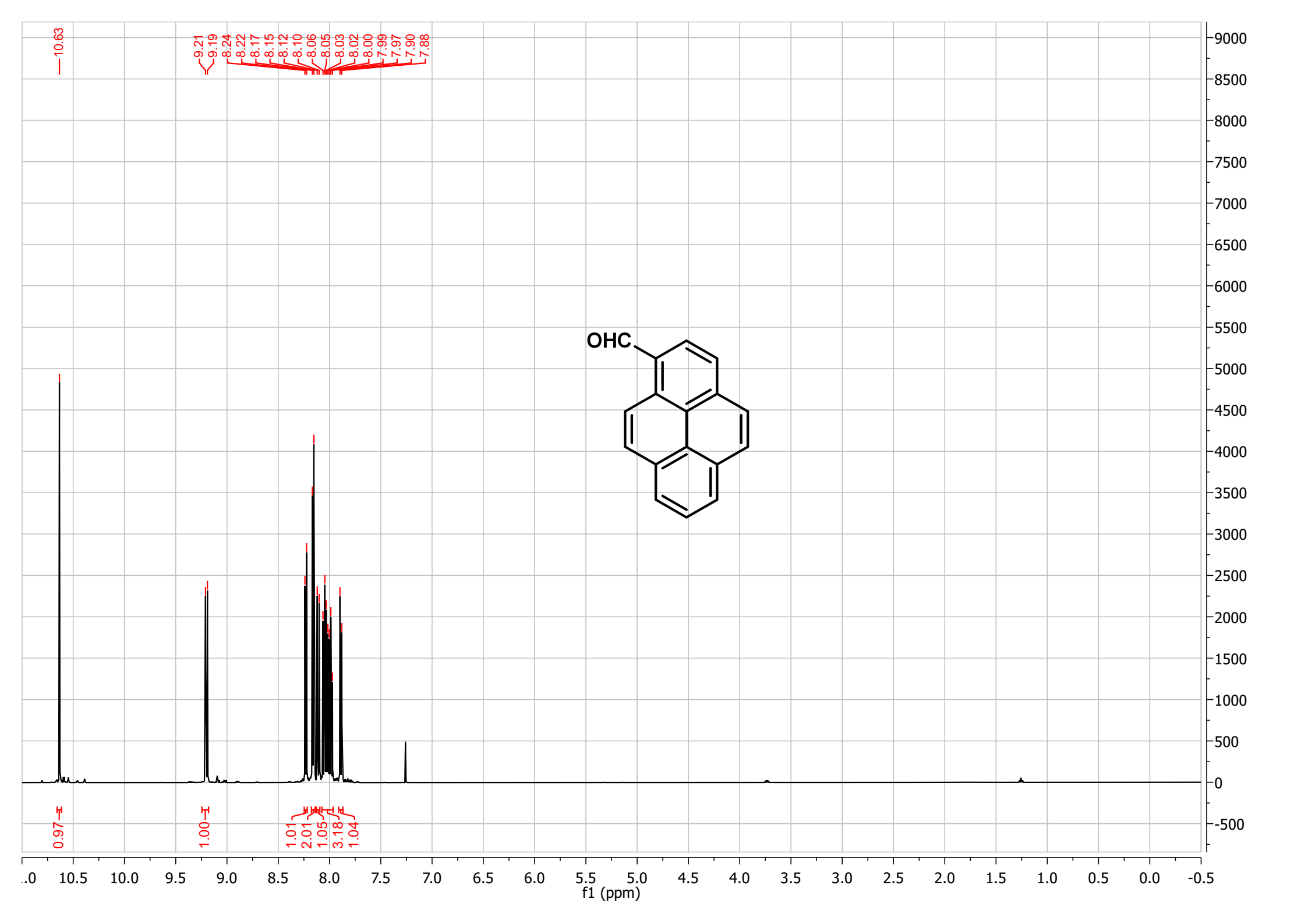
Br
f1 (ppm)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8.06
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8.02
8.00
7.99
7.97
7.90
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OHC
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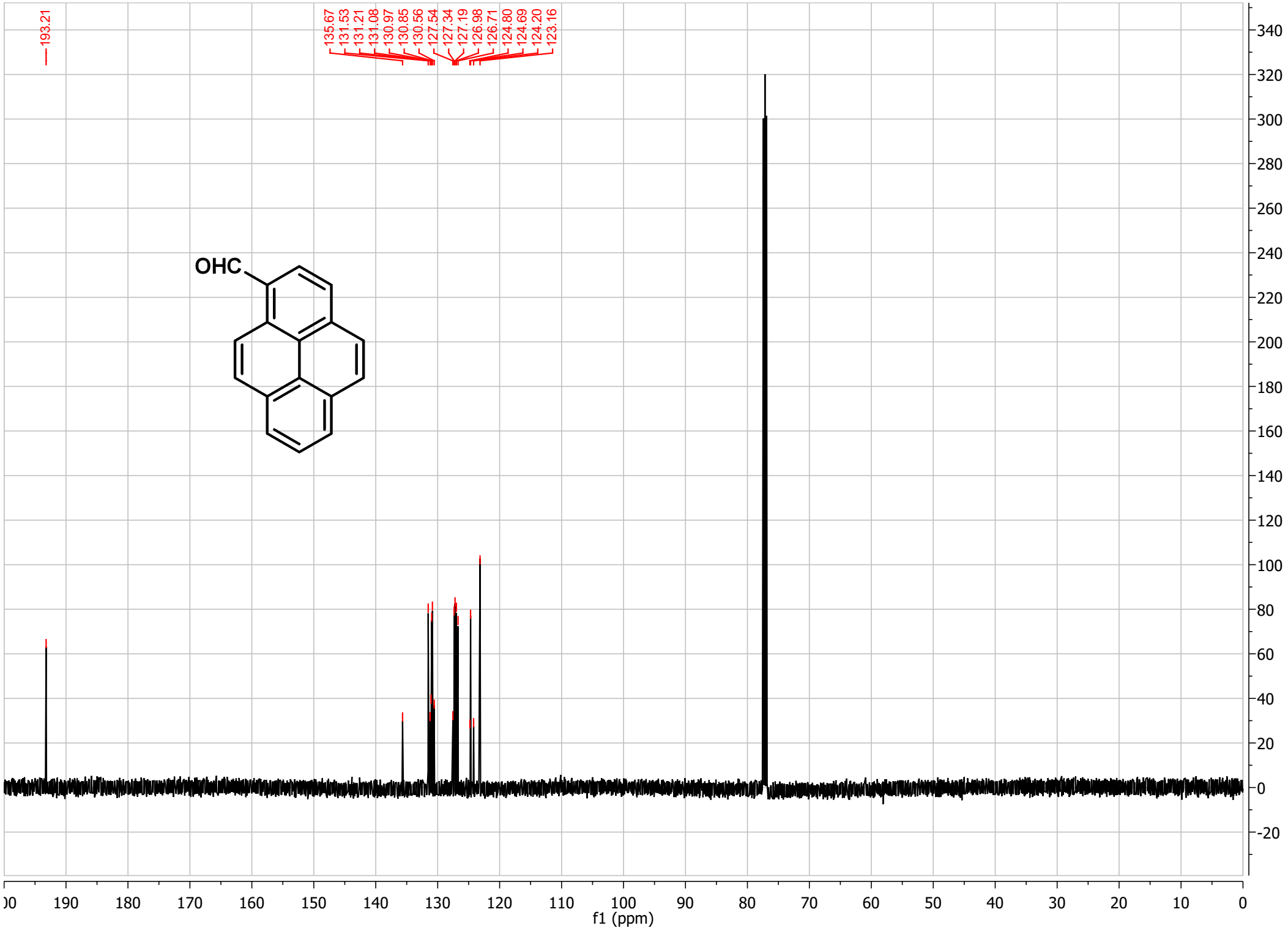
1.01
2.01
1.05
3.18
1.04
f1 (ppm)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124.80
124.69
124.20
123.16
OHC
f1 (ppm)