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Note

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Construction of Phenanthrenes and Chrysenes from β-Bromovinylarenes *via* Aryne Diels-Alder Reaction/Aromatization

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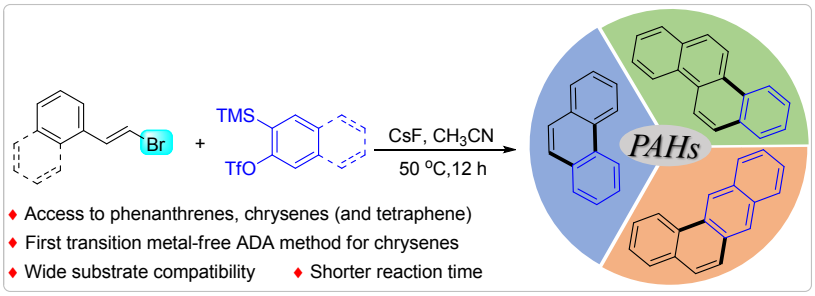
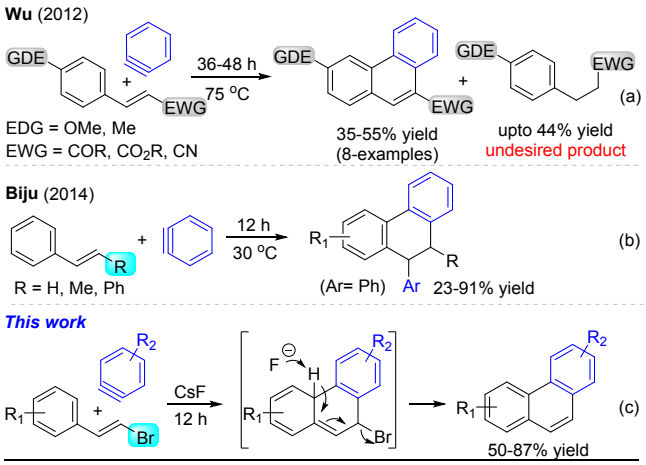


ABSTRACT: A highly efficient transition metal-free general method for the synthesis of polycyclic aromatic hydrocarbons (PAHs) like phenanthrenes and chrysenes (and tetraphene) from *β*-bromovinylarenes and arynes has been developed. The reactions proceed *via* Aryne Diels-Alder (ADA) reaction, followed by a facile aromatization. This is the first report on direct construction of chrysenes (and tetraphene) using ADA approach. Unlike the literature method which is limited to only 9/10-substituted derivatives, this method gives an access to a wide variety of functionalized phenanthrenes.

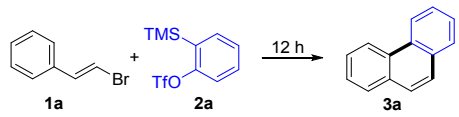
The preparation of phenanthrenes has received significant attention among the various polycyclic aromatic hydrocarbons (PAHs) because of their presence in natural products and pharmaceutics like antiviral, anticancer and antimalarial agents.[1] Apart from this, they also find a huge application in material chemistry due to their photochemical and electroluminescent properties.[2] Classically, phenanthrenes have been accessed *via* metal-catalyzed Ullman-McMurry,[3a] Pschorr,[3b] Mallory cyclization of stilbenes,[3c] radical coupling,[3d-e] photochemical cyclization,[3f-g] ring closing metathesis[3h], etc.[3i-n] On the other hand, arynes, unlike strain-free alkynes, have a high electrophilic reactivity due to a lower LUMO.[4] Therefore, the recent approach for phenanthrene synthesis includes co-cyclization of arynes with alkynes/allenes/halostyrenes/halobiaryls, biaryls, haloaryls, etc.[5] This approach, primarily driven by the groups of Larock, Guitian, Yamamoto, and Yao allows for the direct assembly of functionalized phenanthrenes.[5] Nevertheless, all these methods are transition metal-catalyzed, and often suffer from one or the other limitations like *cyclotrimerizations of arynes* due to their electrophilic nature, accessibility of the advanced starting materials, relatively lower overall yield, compatibility of functional groups, formation of undesired side products, etc.

Scheme 1. Preparation of PAHs from Arynes Under Transition Metal-Free Condition



In continuation of our work in developing (transition)metal-free reactions,[6] we were interested to prepare phenanthrenes under transition metal-free condition from arynes. The preparation

Table 1. Optimization of the Reaction Condition[a]



entry	F⁻ source	solvent	yield of **3a** (%)[b]
1	KF	CH_3CN	27
2[c]	KF	CH_3CN	43
3	TBAF	CH_3CN	<10
4	CsF	CH_3CN	71
5	CsF	1,4-dioxane	<10
6	CsF	THF	39
7	CsF	CH_2Cl_2	<10
8	CsF	toluene	<10
9[d]	CsF	CH_3CN	82
10[e]	CsF	CH_3CN	54

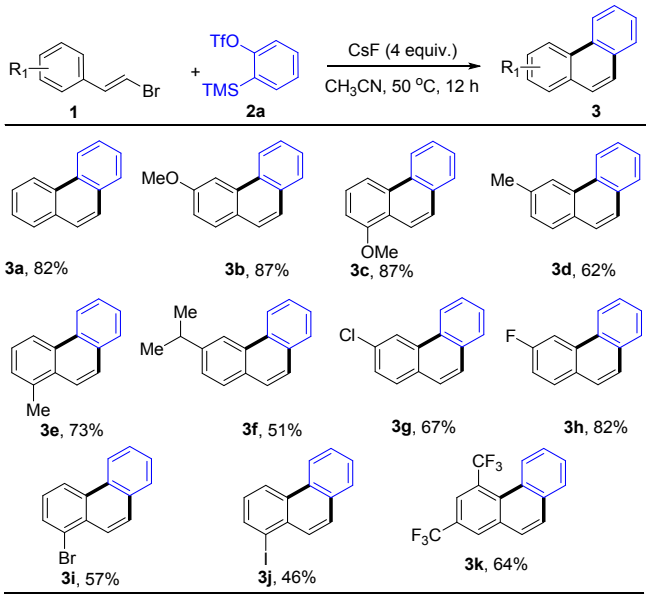
[a]Reaction conditions unless otherwise stated: **1a** (0.1 mmol), **2a** (0.2 mmol), fluoride source (0.4 mmol), solvent (2 ml) at rt for 12 h. [b]Isolated yield of **3a**. [c]3.0 equiv. of 18-crown-6 was used as an additive. [d]Reaction was performed at 50 °C. [e]0.12 mmol of **2a** was used.

of phenanthrenes from arynes under transition metal-free condition has scarcely been studied. The group of Wu established the preparation of 3,9-disubstituted phenanthrenes using styrenes compulsorily substituted with a strong electron donating group (EDG) at *para*-position on the aromatic ring and an electron-withdrawing group (EWG) such as keto, ester and cyanide at the *β*-position of the styrenes (Scheme 1a).[7a] This method afforded the desired products in 35-55% yield along with an undesired byproduct (saturated analog of the styrenes) in up to 44% yield at 75 °C and required 36-48 h of reaction time. Moreover, the substrate scope with respect to arynes has been less explored. Later, in 2014, Biju and co-workers reported the preparation of 9-aryldihydrophenanthrenes from arynes and *β*-unsubstituted styrenes (Scheme 1b).[7b] Therefore, in view of this very limited success to access phenanthrenes, a new transition metal-free method arising from arynes is interesting and desired.

We envisioned that styrenes substituted at *β*-position with a suitable good leaving group, but at the same time not so strong electron-withdrawing, would make a more facile substrate. We reasoned that such a group will facilitate the aromatization step without lowering the reactivity of the styrenes in the Diels-Alder reaction (Scheme 1c). Here in, we report an efficient transition metal-free method for the assembly of arynes and *β*-bromostyrenes to give phenanthrenes *via* Aryne Diels-Alder (ADA) reaction.

At the outset, we subjected bromostyrene **1a** to react with a benzyne precursor **2a** in CH_3CN (Table 1). With KF as the fluoride source, the desired product **3a** was obtained in 27% yield (entry 1). The use of 18-crown-6 in a condition identical to entry 1 improved the yield to 43% (entry 2). Switching to TBAF was detrimental to the reaction, generating only a trace amount of **3a** (entry 3). The yield improved dramatically in the presence of CsF, affording **3a** in 71% isolated yield (entry 4). With CsF as the common fluoride source, we screened several other solvents of varying polarity. Both polar as well as non-polar

Scheme 2. Substrate Scope for *β*-bromostyrenes 1[a]



[a]Isolated yields under the optimized condition as in entry 9, Table 1, unless otherwise mentioned.

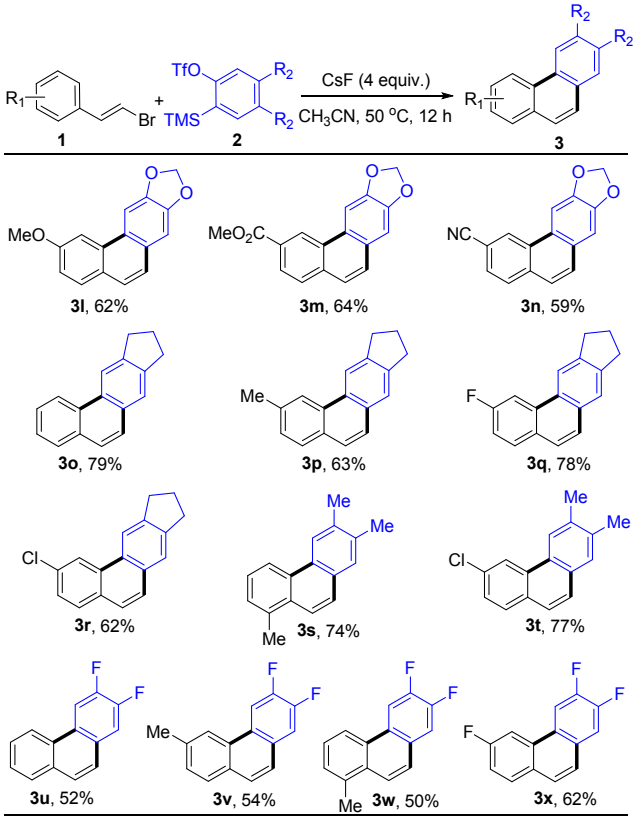
solvents were found unsuitable for this reaction. In most cases, the lower yield was due to an incomplete conversion of the substrates (entries 5-8), without formation of any side product. An elevation of the reaction temperature improved the reaction yield to 82% (entry 9). In addition, a lower loading of the benzyne precursor (1.2 equiv.) resulted the product in significantly diminished yield (entry 10). The manipulation of other parameters like higher temperature, base loading or co-bases like DBU, DMAP or NaH proved to be non-helpful.

With the optimized condition in hand, we next examined the substrate scope by using electron-rich as well electron-deficient bromostyrenes **1** (Scheme 2). The EDGs like -OMe and -Me were well tolerated at *para*- and *ortho*-position of the bromostyrenes to give 1- and 3-substituted phenanthrenes, respectively, in good to excellent yield (62-87%, **3b-3e**). A bulkier substitution like isopropyl group at *para*-position had a detrimental effect on the yield, giving the product in 51% yield (**3f**). Like the EDGs, the bromostyrenes substituted with EWGs, such as, halides (fluoro, chloro, bromo, iodo) at *ortho*- or *para*-position and 3,5-*bis*-trifluoromethyl also worked well (**3g-3k**). These halide-functionalities on phenanthrenes enable them as potential substrates for further manipulations. It is noteworthy mentioning that unsymmetrical *meta*-substituted bromostyrenes, e. g., *m*-methyl-*β*-bromostyrene also reacted well under the optimized condition, albeit, producing an inseparable mixture of regiomeric 2- and 4-methylphenanthrene in a 59:41 ratio and 72% overall yield (See page S68 in the Supporting Information). The synthetic utility of this method was further demonstrated using a larger scale of **1a** (0.457 g, 2.5 mmol) and **2a** (1.49 g, 5.0 mmol) under the optimized reaction condition. We were delighted to isolate **3a** in 76% yield along with the recovery of unreacted **1a** in 17% yield.

We next turned our attention towards different substituted arynes (Scheme 3). Various electron-rich benzynes, e. g., sesamol-, indanol and dimethyl-derived benzynes reacted

smoothly with both electron-rich and -deficient bromostyrenes to produce

Scheme 3. Substrate Scope for Aryne Precursors 2 with various *β*-bromostyrenes 1[a]

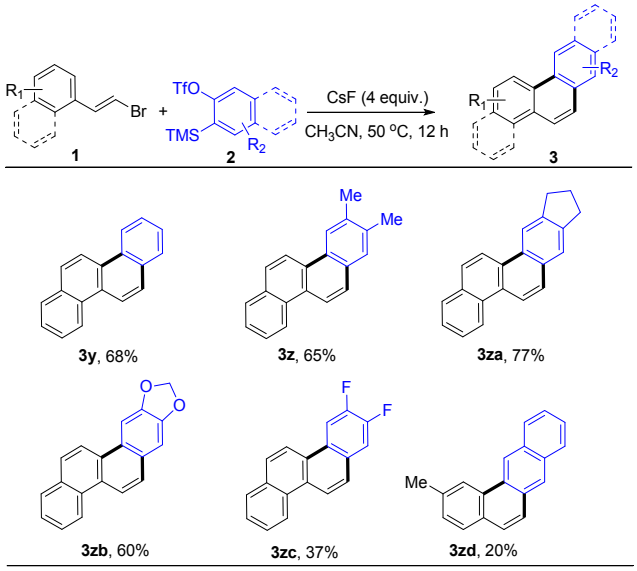


[a]Isolated yields under optimized condition (as in entry 9, Table 1) unless otherwise mentioned.

the desired product **(3l-3t)**. The electron deficient difluoro benzynes also coped well to give difluorinated phenanthrenes, albeit with a diminished yield **(3u-3x)**. The unsymmetrical mono-substituted arynes, e. g., the aryne derived from 4-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate in reaction with **1d**, resulted in an inseparable mixture (60:40) of regiomeric products in 53% overall yield (See page S69 in the Supporting Information).

We were next interested to prepare higher PAHs, such as chrysenes and tetraphenes. These class of molecules have emerged as the attractive targets because of their photophysical and electrochemical properties, for instance, narrow HOMO-LUMO gaps, low redox potential, extended π-conjugation, strong π-π stacking, and excellent chemical stability.[2,8] They have wide application in various optoelectronic devices such as organic chemosensors, organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic photovoltaic (OPVs) cells, etc.[9] These PAHs are generally obtained through transition metal-catalyzed multi step reactions.[10] The difficulty in accessing these materials is further elucidated by their high cost (USD 95/100 mg for **3y**, Sigma Aldrich). The group of Castedo obtained a mixture of trimers on subjecting 1,2-naphthynes to Pd-catalyst.[11] Therefore, a new transition metal-free direct approach to access these PAHs is significant and highly desired. To the best of our knowledge, there is no precedence on the preparation of these class of compounds *via* ADA approach. To our delight, different benzynes under the previously optimized condition reacted smoothly with *β*-bromovinyl naphthalene to produce various chrysene derivatives in good to

Scheme 4. Preparation of Chrysenes[a] and Tetraphene[a]



[a]Isolated yields under optimized condition (as in entry 9, Table 1) unless otherwise mentioned.

moderate yield (Scheme 4). Ingeneral, the electron-rich benzynes performed better than the corresponding electron-deficient ones (**3y**-**3zb** *vs* **3zc**). On the other hand, the use of naphthynes instead of benzynes produced 3-methyltetraphene (**3zd**) in a poor yield of 20% under the optimized condition. Repeating this reaction with a comparatively increased scale of bromostyrene **1d** (0.197 g, 1.0 mmol) and naphthynes **2f** (0.696 g, 2.0 mmol) moderately improved the yield to 31%.

In conclusion, we have successfully established the first transition metal-free general method for the construction of different class of PAHs like phenanthrenes and chrysenes (and tetraphene) through ADA reaction/aromatization. This method greatly improves the availability of differently substituted phenathrenes. The transition metal-free nature of the method advantageously avoids the undesired trimerization of the arynes.

EXPERIMENTAL SECTION

General Information: Aldehydes and other fine chemicals were obtained from commercial suppliers and used without purification. β-Bromovinylarenes[12] and aryne precursors[13] were prepared following the literature known procedures (see the Supporting Information for detailed method and related other citations). The melting points were recorded on Buchi M-560 meltiting point apparatus and are uncorrected. Solvents were dried and distilled following the standard procedures. TLC observation was carried out on precoated plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light or by charring the plates dipped in PMA/$KMnO_4$ solution. Flash chromatography was performed using silica gel (230-400 mesh) with distilled solvents. ^1H and $^{13}C\{^1H\}$ NMR for compounds were recorded at 400, 600 and 800 MHz instruments and 100, 150 and 200 MHz instrument, respectively, using $CDCl_3$ as the solvent unless stated otherwise. Chemical shifts were recorded

in parts per million (ppm, δ). ^{1}H and ^{13}C{^{1}H} NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), septet (sep), doublet of doublet (dd), doublet of triplet (dt), triplet of doublets (td), multiplet (m) etc. High resolution mass spectral analysis (HRMS) was performed on Q-TOF Premier mass spectrometer.

General procedure for the preparation of PAHs (3a-3zd): To a dry Schlenk tube equipped with a magnetic stirring bar, was added aryne precursor **2** (0.2 mmol, 2.0 equiv.) and β-bromovinylarene **1** (0.1 mmol, 1.0 equiv.). After addition of dry CH_3CN (2 mL), the reaction tube was flushed with argon, and CsF (0.4 mmol, 60.8 mg, 4.0 equiv.) was added. After stirring the reaction mixture at 50 ^{o}C in an oil bath for 12 h, solvent was removed under vacuum. The crude product was purified by silica gel column chromatography to obtain the pure desired product **3**.

*(E)-1-(2-Bromovinyl)-2-iodobenzene (**1j**)*: The title compound was prepared following literature protocol from 2-iodobenzaldehyde (10 mmol, 2.32 g) (see the Supporting Information).[12] The product was isolated in 35% yield over two step (1.08 g) as a mixture of E/Z (86:14) isomers. Pale yellow liquid, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (d, J = 8 Hz, 0.17H), 6.67 (d, J = 16 Hz, 1H), 6.33-6.99 (m, 1H), 7.01 (d, J = 8 Hz, 0.14H), 7.08 (d, J = 8 Hz, 0.19H), 7.25-7.35 (m, 3H), 7.37 (d, J = 8 Hz, 0.15H), 7.67 (d, J = 8 Hz, 0.17H), 7.82 (d, J = 8 Hz, 1H), 7.86 (d, J = 8 Hz, 0.18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 98.5, 109.2, 109.3, 126.6, 127.7, 128.5, 129.6, 129.6, 130.0, 136.5, 138.7, 139.0, 139.3, 139.6, 140.7; HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_8H_6BrINa^+$ 330.8590; found: 330.8607

*(E)-1-(2-Bromovinyl)-3,5-bis(trifluoromethyl)benzene (**1k**)*: The title compound was prepared following literature protocol from 3,5-*bis*(trifluoromethyl)benzaldehyde (10 mmol, 2.42 g).[12] The product was isolated in 40% yield over two steps (1.27 g) as a mixture of E/Z (93:7) isomers. Light yellow liquid, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J = 16 Hz, 1H), 7.18 (d, J = 13 Hz, 1H), 7.72 (s, 2H), 7.79 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 111.1, 121.5-121.9 (m), 123.1 (q, J = 270 Hz), 125.9, 132.4 (q, J = 30 Hz), 134.5, 137.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_5BrF_6Na^+$ 340.9371; found: 340.9364

*Phenanthrene (**3a**)*:[3g] The title compound was prepared according to the general procedure as described above, using **2a** (0.2 mmol, 59.6 mg, 2 equiv.), **1a** (0.1 mmol, 18.3 mg, 1.0 equiv.). The product was isolated in 82% yield (14.6 mg), colorless solid, eluent: hexane.

The product **3a** was obtained in 76% yield (0.338 g) along with the recovery of unreacted **1a** in 17% yield (0.077 g) when the reaction was run using **1a** (0.457 g, 2.5 mmol) and **2a** (1.490 g, 5.0 mmol) under the optimized reaction condition. *3-Methoxyphenanthrene (**3b**)*:[3g] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1b** (0.1 mmol, 21.3 mg, 21.3 mg, 1.0 equiv.). The product was isolated in 87% yield (18 mg), pale yellow solid, eluent: hexane.

*1-Methoxyphenanthrene (**3c**)*:[3m] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1c** (0.1 mmol, 21.3 mg, 19.7 mg, 1.0 equiv.). The product was isolated in 87% yield (18 mg), pale yellow solid, eluent: hexane.

*3-Methylphenanthrene (**3d**)*:[3g] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1d** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 62% yield (12 mg), white solid, eluent: hexane.

*1-Methylphenanthrene (**3e**)*:[3g] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1e** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 73% yield (14 mg), white solid, eluent: hexane.

*3-Isopropylphenanthrene (**3f**)*: The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1f** (0.1 mmol, 22.5 mg, 1.0 equiv.). The product was isolated in 51% yield (11 mg), colorless semi-solid, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (d, J = 8 Hz, 6H), 3.21 (sep, J = 8 Hz, 1H), 7.52 (dd, J = 8, 1.6 Hz, 1H), 7.57-7.75 (m, 4H), 7.83-7.91 (m, 2H), 8.53-8.54 (m, 1H), 8.73 (dd, J = 8, 0.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 24.2, 34.7, 119.7, 122.6, 125.7, 126.0, 126.3, 126.4, 126.7, 128.5, 130.2, 130.3, 130.4, 132.2, 147.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{17}^+$ 221.1325; found: 221.1324.

*3-Chlorophenanthrene (**3g**)*:[3g] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1g** (0.1 mmol, 21.7 mg, 1.0 equiv.). The product was isolated in 67% yield (14 mg), colorless solid, eluent: hexane.

*3-Fluorophenanthrene (**3h**)*:[3g] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1h** (0.1 mmol, 20.1 mg, 1.0 equiv.). The product was isolated in 82% yield (16 mg), colorless solid, eluent: hexane.

*1-Bromophenanthrene (**3i**)*:[3f] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1i** (0.1 mmol, 26.2 mg, 1.0 equiv.). The product was isolated in 57% yield (14.5 mg), white solid, eluent: hexane.

*1-Iodophenanthrene (**3j**)*: The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1j** (0.1 mmol, 30.9 mg, 1.0 equiv.). The product was isolated in 46% yield (14 mg), white solid, mp 96-98 ^{o}C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8 Hz, 1H), 7.61-7.72 (m, 2H), 7.82 (d, J = 8 Hz, 1H), 7.92 (d, J = 8 Hz, 1H), 8.07 (d, J = 8 Hz, 1H), 8.20 (d, J = 8 Hz, 1H), 8.68 (d, J = 8 Hz, 1H), 8.72 (d, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 100.6, 122.7, 123.3, 127.1, 127.2, 127.5, 128.7, 128.8, 130.0, 130.5, 131.5, 132.0, 132.9, 138.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_9INa^+$ 326.9641; found: 326.9669.

*2,4-Bis(trifluoromethyl)phenanthrene (**3k**)*: The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1k** (0.1 mmol, 31.9 mg, 1.0 equiv.). The product was isolated in 64% yield (20 mg), white solid, mp 105-107 ^{o}C eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.80 (m, 3H), 7.87-7.96 (m, 2H), 8.31 (d, J = 13 Hz, 2H), 8.84 (d, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 123.2-123.5 (m), 123.6 (q, J = 270 Hz), 124.9 (q, J = 273 Hz), 126.8 (d, J = 4 Hz), 127.1 (d, J = 4 Hz), 127.4 (d, J = 2 Hz), 127.9, 128.0 (d, J = 46 Hz), 128.3 (d, J = 8 Hz), 128.5, 128.6, 129.9, 130.3 (d, J =

4 Hz), 130.6, 133.8, 134.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_9F_6^+$ 315.0603; found: 315.0616.

*2-Methoxyphenanthro[2,3-d][1,3]dioxole (**3l**):* The title compound was prepared following the general procedure described above using **2b** (0.2 mmol, 68.5 mg, 2.0 equiv.) and **1b** (0.1 mmol, 21.3 mg, 1.0 equiv.). The product was isolated in 62% yield (15.6 mg), yellow solid, mp 136-137 °C eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (s, 3H), 6.10 (s, 2H), 7.17-7.22 (m, 2H), 7.49 (d, J = 8 Hz, 1H), 7.585 (d, J = 8 Hz, 1H), 7.75-7.82 (m, 2H), 7.93 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 55.4, 100.8, 101.3, 103.3, 105.7, 116.2, 124.1, 124.9, 125.7, 126.2, 128.8, 129.9, 131.3, 147.5, 147.7, 158.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}O_3^+$ 253.0860; found: 253.0878.

*1-(Phenanthro[2,3-d][1,3]dioxol-2-yl)ethanone (**3m**):* The title compound was prepared following the general procedure described above using **2b** (0.2 mmol, 68.5 mg, 2.0 equiv.) and **1l** (0.1 mmol, 24.1 mg, 1.0 equiv.). The product was isolated in 64% yield (18 mg), off white solid, mp 179-180 °C eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (s, 3H), 6.13 (s, 2H), 7.24 (s, 1H), 7.66 (d, J = 8 Hz, 1H), 7.72 (d, J = 8 Hz, 1H), 7.89 (d, J = 8 Hz, 1H), 8.11-8.15 (m, 2H), 9.22 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 52.3, 101.1, 101.5, 105.8, 124.7, 125.1, 125.5, 127.1, 127.5, 128.6, 128.7, 128.9, 129.4, 134.1, 147.9, 148.7, 167.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}O_4^+$ 281.0809; found: 281.0828.

*Phenanthro[2,3-d][1,3]dioxole-2-carbonitrile (**3n**):* The title compound was prepared following the general procedure described above using **2b** (0.2 mmol, 68.5 mg, 2.0 equiv.) and **1m** (0.1 mmol, 20.8 mg, 1.0 equiv.). The product was isolated in 59% yield (14.6 mg), yellow semi-solid, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (s, 2H), 7.25 (s, 1H), 7.63-7.70 (m, 2H), 7.76 (d, J = 8 Hz, 1H), 7.88-7.97 (m, 2H), 8.78 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 100.7, 101.8, 105.9, 109.4, 119.6, 124.5, 125.8, 126.8, 128.1, 128.9, 129.5, 129.7, 133.5, 148.5, 149.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{10}NO_2^+$ 248.0707; found: 248.0702.

*9,10-Dihydro-8H-cyclopenta[b]phenanthrene (**3o**):* The title compound was prepared following the general procedure described above using **2c** (0.2 mmol, 67.7 mg, 2.0 equiv.) and **1a** (0.1 mmol, 18.3 mg, 1.0 equiv.). The product was isolated in 79% yield (17 mg), yellow solid, mp 81-83 °C, eluent: hexane; ^{1}H NMR (800 MHz, $CDCl_3$): δ 2.21 (quin, J = 7.4 Hz, 2H), 3.12 (t, J = 7.4 Hz, 2H), 3.17 (t, J = 7.4 Hz, 2H), 7.54-7.58 (m, 1H), 7.61-7.64 (m, 1H), 7.66-7.71 (m, 2H), 7.72 (s, 1H), 7.88 (d, J = 8 Hz, 1H), 8.55 (s, 1H), 8.67 (d, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 26.1, 32.6, 33.1, 117.6, 122.5, 123.3, 125.8, 125.9, 126.2, 127.1, 128.4, 129.2, 130.4, 131.1, 131.8, 143.7, 143.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}^+$ 219.1169; found: 219.1165.

*2-Methyl-9,10-dihydro-8H-cyclopenta[b]phenanthrene (**3p**):* The title compound was prepared following the general procedure described above using **2c** (0.2 mmol, 67.7 mg, 2.0 equiv.) and **1d** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 63% yield (14.6 mg), yellow solid, mp 90-92 °C, eluent: hexane; ^{1}H NMR (800 MHz, $CDCl_3$): δ 2.20 (quin, J = 7.3 Hz, 2H), 2.62 (s, 3H), 3.11 (t, J = 7.3 Hz, 2H), 3.17 (t, J = 7.3 Hz, 2H), 7.39 (d, J = 7.9 Hz, 1H), 7.62 (s, 2H), 7.70 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 8.46 (s, 1H), 8.53(s, 1H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 26.1, 32.6, 33.1, 117.6, 122.5, 123.3, 125.7, 125.9, 126.1, 127.0, 128.4, 129.2, 130.4, 131.1, 131.8, 143.7, 143.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}^+$ 233.1325; found: 233.1318.

*2-Fluoro-9,10-dihydro-8H-cyclopenta[b]phenanthrene (**3q**):* The title compound was prepared following the general procedure described above using **2c** (0.2 mmol, 67.7 mg, 2.0 equiv.) and **1h** (0.1 mmol, 20.1 mg, 1.0 equiv.). The product was isolated in 78% yield (18.4 mg), white solid, mp 50-52, °C eluent: hexane; ^{1}H NMR (800 MHz, $CDCl_3$): δ 2.21 (quin, J = 7.3 Hz, 2H), 3.11 (t, J = 7.3 Hz, 2H), 3.17 (t, J = 7.3 Hz, 2H), 7.30 (td, J = 8.3, 2.4 Hz, 1H), 7.62-7.74 (m, 2H), 7.71 (s, 1H), 7.82-7.86 (m, 1H), 8.26 (dd, J = 11.2, 2.3 Hz, 1H), 8.39(s, 1H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 26.1, 32.7, 33.1, 107.5 (d, J = 18 Hz), 114.9, 115.0, 117.8, 123.4, 125.2, 126.2, 128.5, 128.7 (d, J = 4 Hz), 130.4 (d, J = 8 Hz), 131.3, 131.9 (d, J = 8 Hz), 144.2 (d, J = 80 Hz), 161.4 (d, J = 24 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}F^+$ 237.1075; found: 237.1065.

*2-Chloro-9,10-dihydro-8H-cyclopenta[b]phenanthrene (**3r**):* The title compound was prepared following the general procedure described above using **2c** (0.2 mmol, 67.7 mg, 2.0 equiv.) and **1g** (0.1 mmol, 21.7 mg, 1.0 equiv.). The product was isolated in 62% yield (15.6 mg), yellow solid, mp 96-98 °C, eluent: hexane; ^{1}H NMR (800 MHz, $CDCl_3$): δ 2.21 (quin, J = 7.4 Hz, 2H), 3.11 (t, J = 7.4 Hz, 2H), 3.16 (t, J = 7.4 Hz, 2H), 7.50 (dd, J = 8.4, 1.9 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.71 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 8.44 (s, 1H), 8.61 (d, J = 1.4 Hz, 1H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 25.9, 32.6, 33.1, 117.6, 122.2, 123.4, 125.1, 126.4, 127.3, 128.3, 129.8, 130.1, 131.3, 131.5, 132.1, 144.3, 144.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}Cl^+$ 253.0779; found: 253.0789.

*1,6,7-Trimethylphenanthrene (**3s**):* The title compound was prepared following the general procedure described above using **2d** (0.2 mmol, 65.3 mg, 2.0 equiv.) and **1e** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 74% yield (16.3 mg), white solid, mp 112-114 °C, eluent: hexane; ^{1}H NMR (800 MHz, $CDCl_3$): δ 2.51 (s, 3H), 2.57 (s, 3H), 2.79 (s, 3H), 7.45 (d, J = 8 Hz, 1H), 7.57 (t, J = 8 Hz, 1H), 7.69 (s, 1H), 7.74 (d, J = 8 Hz, 1H), 7.92 (d, J = 8 Hz, 1H), 8.50 (s, 1H), 8.61 (d, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 19.8, 19.9, 20.6, 120.6, 121.9, 123.2, 125.8, 126.1, 127.1, 128.5, 129, 130, 130.2, 130.5, 134.7, 135.7, 135.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}^+$ 221.1325; found: 221.1318.

*6-Chloro-2,3-dimethylphenanthrene (**3t**):* The title compound was prepared following the general procedure described above using **2d** (0.2 mmol, 65.3 mg, 2.0 equiv.) and **1g** (0.1 mmol, 21.7 mg, 1.0 equiv.). The product was isolated in 77% yield (18.5 mg), pale yellow solid, mp 80-82 °C, eluent: hexane; ^{1}H NMR (800 MHz, $CDCl_3$): δ 2.47 (s, 3H), 2.53 (s, 3H), 7.50 (dd, J = 8.3, 2 Hz, 1H), 7.60-7.66 (m, 3H), 7.78 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.59 (d, J = 1.5 Hz, 1H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 19.9, 20.5, 122.1, 122.9, 125.2, 126.4, 126.7, 127.6, 128.6, 129.8, 130.1, 130.7, 131.1, 132.2, 136.2, 136.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}Cl^+$ 241.0779; found: 241.0789.

*2,3-Difluorophenanthrene (**3u**):*[3n] The title compound was prepared following the general procedure described above using **2e** (0.2 mmol, 66.8 mg, 2.0 equiv.) and **1a** (0.1 mmol, 18.3 mg, 1.0 equiv.). The product was isolated in 52% yield (11 mg), white solid, eluent: hexane.

*6,7-Difluoro-1-methylphenanthrene (**3v**):* The title compound was prepared following the general procedure described above

using **2e** (0.2 mmol, 66.8 mg, 2.0 equiv.) and **1d** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 54% yield (12.3 mg), light yellow solid, mp 81-83 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.62 (s, 3H), 7.45 (dd, J = 8.1, 1.2 Hz, 1H), 7.55-7.60 (m, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 8.25 (s, 1H), 8.34-8.40 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.1, 110.2 (d, J = 18 Hz), 114.8 (d, J = 15 Hz), 122.4, 124.5-124.6 (m), 127.0 (dd, J = 7, 2 Hz), 127.3 (d, J = 2 Hz), 128.6, 128.7, 129.0 (dd, J = 7, 2 Hz), 129.5 (d, J = 4 Hz), 129.6 (d, J = 1 Hz), 136.9, 149.7 (dd, J = 248, 15 Hz), 150.0 (dd, J = 246, 14 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{11}F_2^+$ 229.0824; found: 229.0803.

*2,3-Difluoro-6-methylphenanthrene (**3w**):* The title compound was prepared following the general procedure described above using 2**e** (0.2 mmol, 66.8 mg, 2.0 equiv.) and **1e** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 50% yield (11.4 mg), off white solid, mp 124-126 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (s, 3H), 7.44-7.71 (m, 4H), 7.96 (d, J = 9.2 Hz, 1H), 8.34-8.44 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 19.9, 110.6 (d, J = 17 Hz) , 114.7 (d, J = 17 Hz), 120.8, 123.5 (d, J = 3 Hz), 125.2-125.3 (m), 126.6, 127.6-127.8 (m), 128.1, 128.6 (d, J = 9 Hz), 129.5 (d, J = 4 Hz), 130.5, 135.2, 149.9 (dd, J = 248, 15 Hz), 150.0 (dd, J = 247, 14 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for HRMS (ESI) cal. for $C_{15}H_{11}F_2^+$ 229.0824; found: 229.0822.

*2,3,6-Trifluorophenanthrene (**3x**):* The title compound was prepared following the general procedure described above using **2e** (0.2 mmol, 66.8 mg, 2.0 equiv.) and **1h** (0.1 mmol, 20.1 mg, 1.0 equiv.). The product was isolated in 62% yield (14.4 mg), light yellow solid, mp 106-108 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (td, J = 8.3, 2.4 Hz, 1H), 7.58-7.66 (m, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.85-7.91 (m, 1H), 8.06 (dd, J = 10.8, 2.4 Hz, 1H), 8.21-8.29 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 107.7 (d, J = 23 Hz), 110.5 (d, J = 19 Hz), 115.1, 116.1 (d, J = 24 Hz), 124.7, 126.6, 126.9, 128.3, 129.2, 129.3 (d, J = 2 Hz), 130.9 (d, J = 9 Hz), 149.9 (dd, J = 246, 12 Hz), 150.1 (dd, J = 248, 13 Hz), 161.7 (d, J = 245 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_8F_3^+$ 233.0573; found: 233.0561.

*Chrysene (**3y**):*[3g] The title compound was prepared following the general procedure described above using **2a** (0.2 mmol, 59.6 mg, 2.0 equiv.) and **1n** (0.1 mmol, 23.3 mg, 1.0 equiv.). The product was isolated in 68% yield (15.5 mg), white solid, eluent: hexane.

*2,3-Dimethylchrysene (**3z**):* The title compound was prepared following the general procedure described above using **2d** (0.2 mmol, 65.3 mg, 2.0 equiv) and **1n** (0.1 mmol, 23.3 mg, 1.0 equiv.). The product was isolated in 65% yield (16.6 mg), white solid, mp 204-206 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 2.58 (s, 3H), 7.59-7.64 (m, 1H), 7.67-7.72 (m, 1H), 7.75 (s, 1H), 7.92 (d, J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 2H), 8.5 (s, 1H), 8.64 (d, J = 8 Hz, 1H), 8.70 (d, J = 8 Hz, 1H), 8.77 (d, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 20.0, 20.7, 120.3, 121.2, 123.0, 123.2, 126.0, 126.5, 126.7, 127.0, 127.7, 127.8, 128.4, 128.5, 129.0, 130.7, 130.9, 132.0, 135.9, 136.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}^+$ 257.1325; found: 257.1315.

*9,10-Dihydro-8H-cyclopenta[b]chrysene (**3za**):* The title compound was prepared following the general procedure described above using **2c** (0.2 mmol, 67.7 mg, 2.0 equiv.) and **1n** (0.1 mmol, 23.3 mg, 1.0 equiv.). The product was isolated in 77% yield (20.6 mg), white solid, mp 198-200 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (quint, J = 8 Hz, 2H), 3.14 (t, J = 8 Hz, 2H), 3.21 (t, J = 8 Hz, 2H), 7.58-7.64 (m, 1H), 7.67-7.72 (m, 1H), 7.81 (s, 1H), 7.93-8.00 (m, 3H), 8.64 (d, J = 8 Hz, 2H), 8.71 (d, J = 8Hz, 1H), 8.77 (d, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 26.1, 32.6, 33.2, 117.9, 120.1, 121.4, 123.1, 123.1, 126.0, 126.5, 126.9, 127.3, 127.8, 128.2, 128.4, 129.7, 130.7, 131.4, 132.0; 143.7, 144.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}^+$ 269.1325; found: 269.1341.

*Chryseno[2,3-d][1,3]dioxole (**3zb**):* The title compound was prepared following the general procedure described above using **2b** (0.2 mmol, 68.5 mg, 2.0 equiv.) and **1n** (0.1 mmol, 23.3 mg, 1.0 equiv.). The product was isolated in 60% yield (16.3 mg), white solid, mp 218-220 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (s, 2H), 7.30 (s, 1H), 7.61 (t, J = 8 Hz, 1H), 7.69 (t, J = 8 Hz, 1H), 7.86 (d, J = 8 Hz, 1H), 7.95 (t, J = 8 Hz, 2H), 8.09 (s, 1H), 8.48 (d, J = 8 Hz, 1H), 8.60 (d, J = 8 Hz, 1H), 8.74 (t, J = 8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 100.9, 101.4, 105.3, 119.7, 121.3, 123.0, 126.1, 126.6, 126.7, 127.0, 127.1, 127.5, 127.9, 128.5, 129.0, 130.7, 131.7, 147.6, 148.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{13}O_2^+$ 273.0911; found: 273.0932.

*2,3-Difluorochrysene (**3zc**):*[3l] The title compound was prepared following the general procedure described above using **2e** (0.2 mmol, 66.8 mg, 2.0 equiv.) and **1n** (0.1 mmol, 23.3 mg, 1.0 equiv.). The product was isolated in 37% yield (9.7 mg), white solid, eluent: hexane.

*2-Methyltetraphene (**3zd**):* The title compound was prepared following the general procedure described above using **2f** (0.2 mmol, 69.6 mg, 2.0 equiv.) and **1d** (0.1 mmol, 19.7 mg, 1.0 equiv.). The product was isolated in 20% yield (4.8 mg).

Repeating this reaction with a comparatively increased scale of **1d** (0.197 g, 1.0 mmol) and **2f** (0.696 g, 2.0 mmol) moderately improved the yield to 31% (0.075 g), off white solid, mp 119-121 °C, eluent: hexane; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H), 7.45 (d, J = 8 Hz, 1H), 7.52-7.57 (m, 2H), 7.61 (d, J = 8 Hz, 1H), 7.72-7.77 (m, 2H), 8.03-8.06 (m, 1H), 8.11-8.15 (m, 1H), 8.35 (s, 1H), 8.64 (s, 1H), 9.16 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.1, 121.5, 123.0, 125.6, 125.7, 126.4, 126.7, 127.0, 127.7, 128.4, 128.5, 128.6, 128.9, 129.8, 130.6, 130.9, 131.9, 132.0, 136.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}^+$ 243.1169; found: 243.1158.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General information, experimental details, ^{1}H and ^{13}C{^{1}H} spectra (PDF)

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