Construction of Substituted [4]Acene Frameworks Based on Double Cationic Cyclizations of Fluoroalkenes

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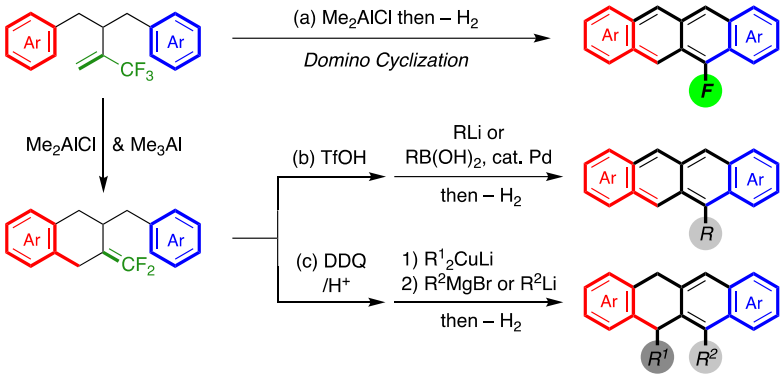
Dedicated to Professor Ferenc Fülöp in Honor of His 70th Birthday.



Received:
Accepted:
Published online:
DOI:

Abstract This study synthesized 5-substituted and 5,6-disubstituted [4]acenes based on the double cationic cyclization of fluoroalkenes. (a) After being treated with Me_2AlCl (1.2 equiv), 2-trifluoromethyl-1-alkenes bearing two aryl groups underwent domino Friedel–Crafts-type cyclization (two-ring construction) followed by dehydrogenation to synthesize 5-fluorinated [4]acenes. The same (trifluoromethyl)alkenes were treated with both Me_2AlCl (1.2 equiv) and Me_3Al (1.0 equiv), resulting in selective one-ring construction and the creation of bicyclic 1,1-difluoro-1-alkenes. (b) When treated with triflic acid, the bicyclic difluoroalkenes underwent regioselective protonation to generate CF_2 cations, whose Friedel–Crafts-type cyclization provided tetracyclic ketones. The obtained ketones act as an appropriate platform for the introduction of substituents at the 5-position of [4]acenes. (c) When treated with DDQ/H^+, the bicyclic difluoroalkenes underwent oxidative generation of allylic CF_2 cations, whose Friedel–Crafts-type cyclization produced tetracyclic enones. The enones were subjected to the double addition of carbanions to facilitate the introduction of two substituents at the 5- and 6-positions of the [4]acenes.

Key words acenes, cations, fluorine, cyclization, domino reactions

Polycyclic aromatic hydrocarbons (PAHs), particularly those comprising fused benzene rings in various configurations,[1] have attracted considerable attention mainly because of their utility as materials for organic electronics.[2] Among them, acenes, which have a linear benzene ring configuration, are of special importance and have long been used as base molecules for organic semiconducting materials (Figure 1).[3] In particular,

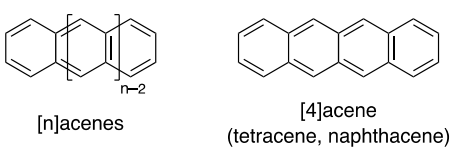


Figure 1 Structures of [n]acenes and [4]acene

substituted acenes, such as TIPS-pentacene[4] and rubrene,[5] have exhibited remarkable semiconducting properties. Therefore, the development of methods for synthesizing these compounds is highly desirable.[6]

Fluorine substituents stabilize carbocations at the α-position by donating its unshared electron pair to the vacant p orbital of the cationic center (Figure 2).[7] Based on this effect, we have already reported C–C bond formations in two types of fluoroalkenes (i.e., 2-trifluoromethyl-1-alkenes and 1,1-difluoro-1-alkenes) via stabilized CF_2 cations. (i) The treatment of 2-trifluoromethyl-1-alkenes with aluminium Lewis acids causes fluoride abstraction to generate allylic CF_2 cations, which in turn undergo intermolecular Friedel–Crafts-type arylation to produce 1,1-difluoro-1-alkenes [*S*$_N$*1'* reaction, Scheme 1(i)].[8] (ii) When aryl-bearing 1,1-difluoro-1-alkenes are treated with a superacid ($FSO_3H{\cdot}SbF_5$), regioselective protonation produces CF_2 cations; this facilitates intramolecular Friedel–Crafts-type arylation followed by dehydrofluorination and hydrolysis, which produce 1-tetralones [*S*$_N$*V*-type reaction, Scheme 1(ii)].[9,10]

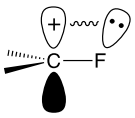
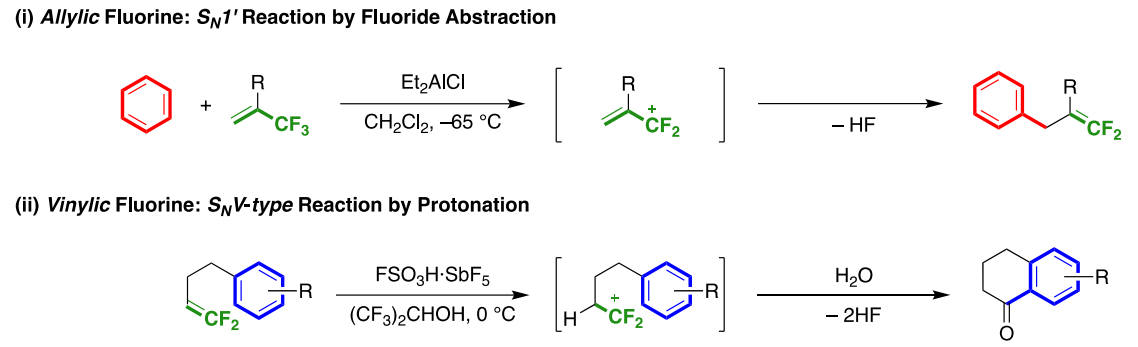
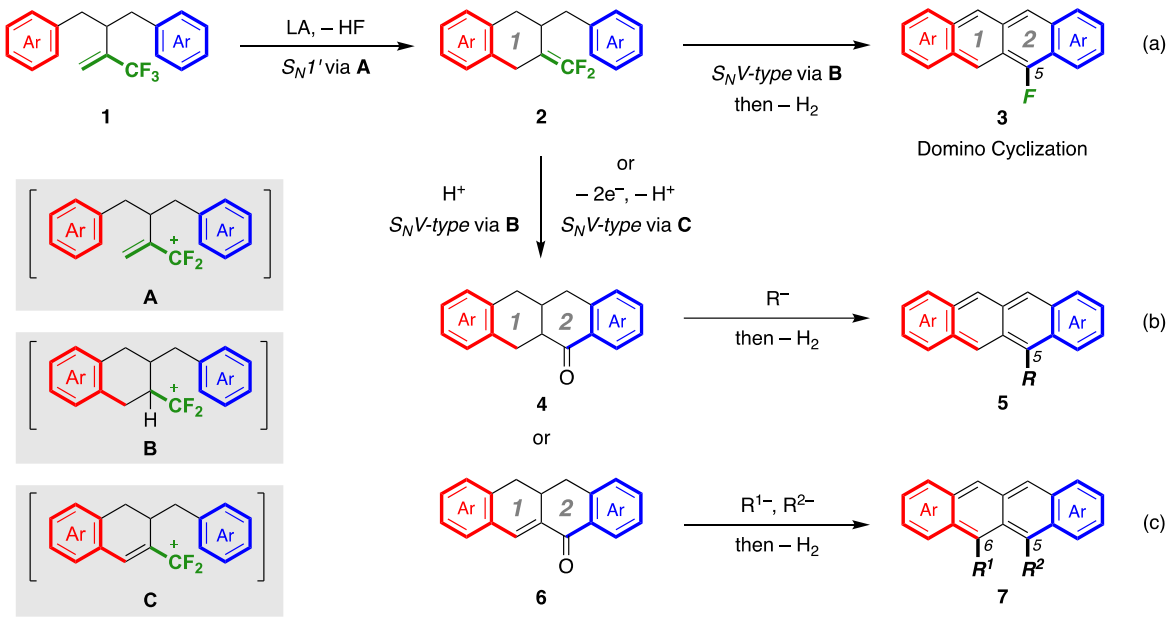


Figure 2 The α-cation stabilizing effect of fluorine

To construct the substructure of [4]acene (tetracene), this study combined the two aforementioned cationic arylations of fluoroalkenes (Scheme 1). Thus, (trifluoromethyl)alkenes **1** bearing two aryl groups were subjected to aluminium Lewis acids. The generated allylic CF_2 cations **A** underwent intramolecular arylation to produce bicyclic 1,1-difluoroalkenes **2** (first ring construction). Subsequent Friedel–Crafts-type arylation (second ring construction) was promoted via other CF_2



Scheme 1 Substitution for allylic and vinylic fluorines via CF_2 cations



Scheme 2 [S_N1' + S_NV-*type*] strategy and overview of substituted [4]acene synthesis

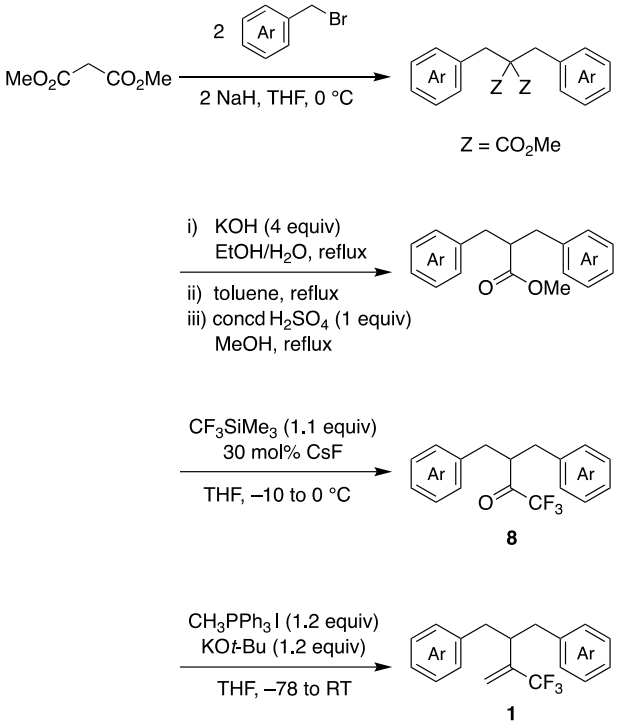
cations **B** by the acid liberated during the construction of the first ring. This was followed by dehydrofluorination and dehydrogenation, which produced 5-fluorinated [4]acenes **3** (domino cyclization, Scheme 2[a]).

Stepwise cyclization is suitable for the introduction of carbon substituents. Specifically, the treatment of 1,1-difluoroalkenes **2** with an appropriate acid (e.g., $FSO_3H{\cdot}SbF_5$) provides the corresponding tetralones **4**, whose ketone moiety can be utilized for the introduction of substituents (R) at the 5-position (**5**, Scheme 2[b]). In addition, the oxidative treatment of 1,1-difluoroalkenes **2** facilitates the introduction of two substituents, i.e., the removal of two electrons and a proton generates allylic CF_2 cations **C** (oxidative CF_2 cation generation), whose Friedel–Crafts-type cyclization produces tetracyclic enones **6**. The moiety of enones was used to introduce two substituents, R^1 and R^2, leading to the synthesis of 5,6-disubstituted [4]acenes **7** (Scheme 2[c]).

The starting (trifluoromethyl)alkenes were prepared from malonic diesters and benzyl bromides (Scheme 3).[11] Dimethyl malonate was dibenzylated with benzyl bromides under basic conditions. The formed diesters were decarboxylated and esterified again with methanol. Trifluoromethylation of the ester moiety was performed using trimethyl(trifluoromethyl)silane (Ruppert's reagent) and CsF.[12] The subsequent Wittig methylidenation of the resulting (trifluoromethyl)ketones **8** resulted in the desired (trifluoromethyl)alkenes **1**.

The Lewis acid-promoted intramolecular arylation of the (trifluoromethyl)alkenes **1** was investigated (Scheme 2[a]) using substrate **1a** with two phenyl groups as a model substrate (Table 1). (Trifluoromethyl)alkene **1a** was treated with various aluminium Lewis acids (1.2 equiv) in dichloromethane at −78°C before being warmed to room temperature. For the arylation, trimethylaluminium was less effective for providing bicyclic difluoroalkene **2a** in an 11% yield along with an 86% recovery of the initial **1a** (Entry 1).

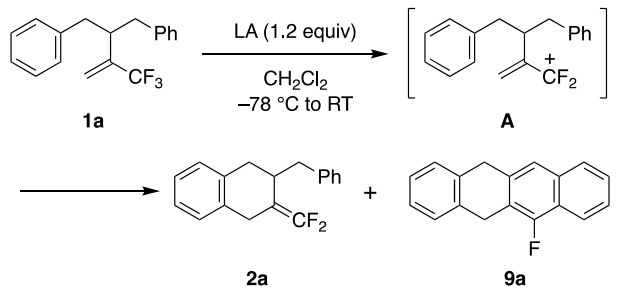
Among the chlorinated aluminium Lewis acids investigated (Entries 2–4), dimethylaluminium chloride (Entry 2), which was effective for the previous arylation (Scheme 1[i]),[8b] produced favorable results, with a 33% yield of the desired fluorine-containing domino product **9a** and a 46% yield of bicyclic difluoroalkene **2a**. $EtAlCl_2$ produced a 23% yield of **9a** and a 47%



Scheme 3 Preparation of 2-trifluoromethyl-1-alkenes **1**

yield of **2a**. Aluminium trichloride, which is insoluble in dichloromethane, was not suitable for both arylations (Entry 5). As above, the 5-fluorinated [4]acene derivative **9a** was obtained from (trifluoromethyl)alkene **1a** using Me_2AlCl (Entry 2).

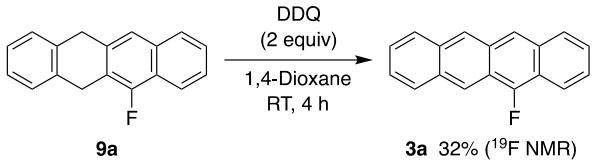
Table 1 Screening of Lewis acids (the first and second ring construction) [a]



Entry	Lewis Acid	Time (h)	Yield (%)		
			2a	**9a**	**1a** [b]
1	Me_3Al	1	11	–	86
2 [c]	Me_2AlCl	9	46	33	–
3 [d]	$MeAlCl_2$	0.25	38	13	10
4	$EtAlCl_2$	0.5	47	23	2
5	$AlCl_3$	1	12	5	–

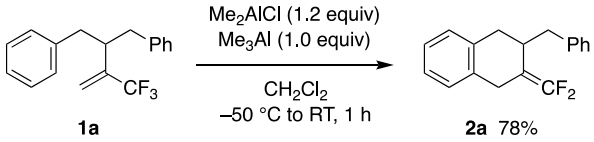
[a] ^{19}F NMR yield based on an internal standard $(CF_3)_2C(C_6H_4p\text{-}Me)_2$. [b] Recovery. [c] –50 to –20 °C. [d] –50 °C.

The dehydrogenation of the obtained **9a** was performed using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). The treatment of **9a** with DDQ (2 equiv) in 1,4-dioxane produced the desired 5-fluoro[4]acene (**3a**) in a 32% yield (^{19}F NMR yield based on $PhCF_3$, Scheme 4).[13] Thus, the domino synthesis of 5-fluoro[4]acenes **3** became available from (trifluoromethyl)alkenes **1** via the domino cyclization/dehydrogenation sequence.



Scheme 4 Synthesis of 5-fluoro[4]acene **3a** via dehydrogenation

As mentioned above, bicyclic difluoroalkene **2a** is a potential precursor for the preparation of tetracyclic ketone **4**, allowing the introduction of substituents at the 5-position (Scheme 2[b]). While being less effective, trimethylaluminium promoted arylation to provide **2a** selectively, thereby suppressing the formation of domino product **9a** (Table 1, Entry 1). Assuming that the methyl ligand of Me_3Al behaves as a base to remove a proton liberated during the construction of the first ring (reaction *S*$_N$*1'*), the intramolecular arylation with trimethylaluminium chloride was examined in the presence of a stoichiometric amount of Me_3Al (Scheme 5). The formation of domino product **9a** was completely suppressed, and the expected bicyclic difluoroalkene **2a** was obtained in a yield of 78%.

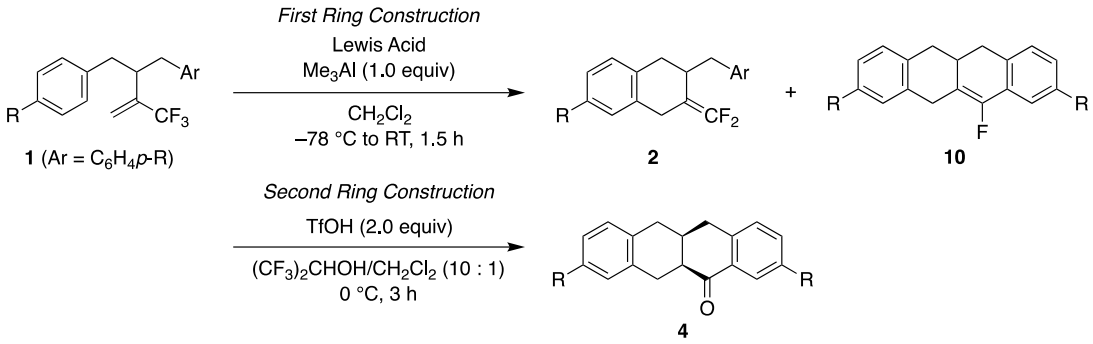


Scheme 5 Selective synthesis of bicyclic difluoroalkene **2a** (the first ring construction)

After the procedure to synthesize bicyclic difluoroalkenes **2** was established, the scope of the construction of the first ring was analyzed (Table 2). Unsubstituted **1a**, methylated **1b**, and phenylated **1c** provided the corresponding products **2a**–**c** in yields of 90%, 87%, and 89%, respectively (Entries 1–3). However, these isolated products contained small amounts of minor products (**10**), which were detected by GC-MS analysis. The first ring construction (arylation) with electron-deficient less-nucleophilic aryl groups in **1d** and **1e** was promoted by zirconium tetrachloride in the presence of Me_3Al to provide the corresponding products **2d** and **2e** in yields of 72% each (Entries 4 and 5). It is worth noting that there have been few reports of Friedel–Crafts-type reactions of electron-deficient arenes, such as halobenzenes.[14]

Acid-promoted *S*$_N$*V*-type arylation (second ring construction) was investigated (Table 3). At the outset, difluoroalkene **2a** was treated with 2 equiv of antimony pentafluoride in $(CF_3)_2CHOH$ (HFIP)/CH_2Cl_2 (10:1) at 0°C (Entry 1).[15] After the temperature was raised to room temperature, the desired tetracyclic ketone **4a** was obtained in a 48% yield as a diastereomeric mixture, the major isomer of which was determined to be *cis* (vide infra). An isolated mixture of **4a** (diastereomer ratio = 79:21) was subjected to sodium methoxide in methanol at room temperature (Scheme 6). Ketone **4a** was recovered in a yield of 97%, and its diastereomer ratio was changed to 25:75. The latter was considered to be a thermodynamically more stable *trans* isomer.[16] It is likely that the protonation of **2a** was effected by

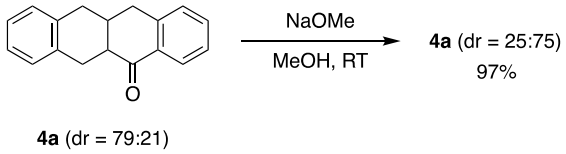
Table 2 Synthesis of tetracyclic ketones **4**.[a]



Entry	**1**	R	First Ring Construction (Arylation)		Second Ring Construction (Arylation)	
			Lewis Acid (equiv)	**2** + **10** (%) [b]	**4** (%)	*cis*/*trans* [c]
1	**1a**	H	Me_2AlCl (1.2)	**2a**+**10a** 90 (97:3)	**4a** 81[d]	88:12
2	**1b**	Me	Me_2AlCl (1.2)	**2b**+**10b** 87 [e]	**4b** 81	87:13
3	**1c**	Ph	Me_2AlCl (1.2)	**2c**+**10c** 89 (93:7)	**4c** 81	83:17
4	**1d**	Cl	$ZrCl_4$ (1.0)	**2d**+**10d** 72 (76:24)	**4d** 62 [f]	75:25
5	**1e**	Br	$ZrCl_4$ (1.0)	**2e**+**10e** 72 (81:19)	**4e** 52 [f]	77:23

[a] Isolated yield. [b] **2**/**10** ratio determined by ^{19}F NMR analysis is shown in parentheses. [c] *Cis*/*trans* ratio determined by ^{1}H NMR analysis is shown. [d] Table 3, Entry 5. [e] A trace amount of **10b** was observed by ^{19}F NMR analysis of the reaction mixture. [f] Reflux.

the acid generated from SbF_5 in HFIP by entering from the other side of the benzyl moiety and that subsequent Friedel–Crafts-type arylation predominantly provided *cis*-**4a** as a kinetic product.

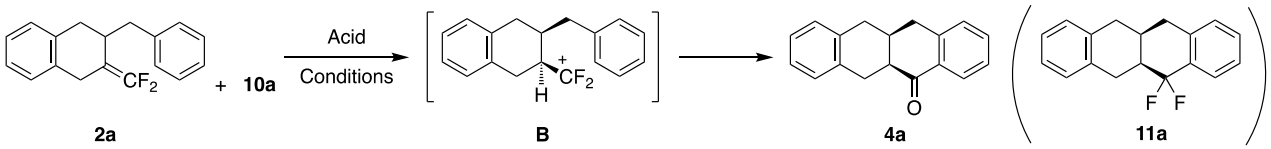


Scheme 6 Diastereomeric isomerization of ketone **4a**

While trifluoroacetic acid did not afford **4a** and resulted in a 53% recovery of the unreacted difluoroalkene **2a** (Table 3, Entry 2), triflic acid (TfOH) proved most effective for the synthesis of ketone **4a**. Thus, the use of TfOH in HFIP/CH_2Cl_2 (10:1) at room temperature increased the yield of **4a** to 70% (*cis*/*trans* = 85:15, Entry 4). The use of 2 equiv of TfOH further improved the yield of **4a** to 84% (*cis*/*trans* = 88:12, Entry 5). For all entries, tetracyclic difluoromethylene compound **11a** was not observed by the ^{19}F NMR analysis of the reaction mixture.[17]

TfOH was also used to synthesize other tetracyclic ketones **4** (Table 2). Difluoroalkenes **2a**–**c** containing **10a**–**c** were treated with 2 equiv of TfOH[18] in HFIP/CH_2Cl_2 (10:1) at 0°C (Entries 1–3). The desired ketones **4a**–**c** were afforded in an 81% yield each (*cis*/*trans* ratios of 83:17 to 88:12). The arylation with electron-deficient aryl groups in **2d** and **2e** proceeded at reflux; therefore, the corresponding **4d** and **4e** were obtained in yields of 62% (75:25) and 52% (77:23), respectively (Entries 4 and 5).

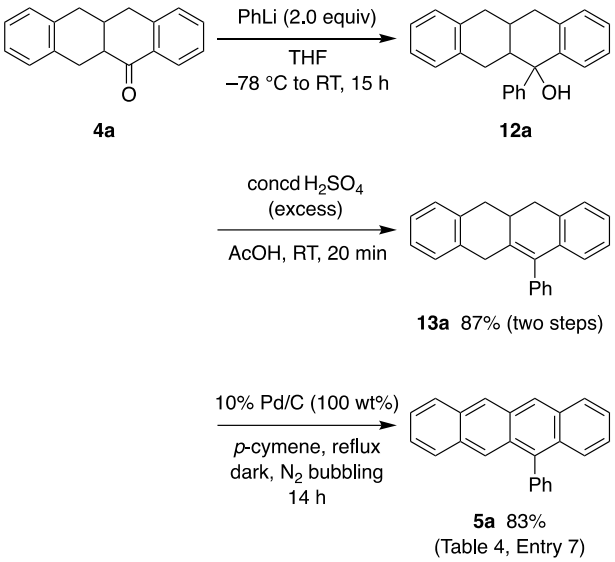
Table 3 Screening of acids (the acidic second ring construction) [a,b]



Entry	Acid (equiv)	Solvent	Conditions	Yield (%)	*cis*/*trans*
1	SbF_5 (2.0)	$(CF_3)_2CHOH/CH_2Cl_2$ (10:1)	0 °C to RT, 10 min	48	74:26
2	CF_3CO_2H (1.2)	$(CF_3)_2CHOH/CH_2Cl_2$ (10:1)	0 °C to RT, 2 h	– [c]	–
3	TfOH (2.0)	CH_2Cl_2	0 °C, 3 h	56	64:36
4	TfOH (1.1)	$(CF_3)_2CHOH/CH_2Cl_2$ (10:1)	RT, 18 h	70	85:15
5	TfOH (2.0)	$(CF_3)_2CHOH/CH_2Cl_2$ (10:1)	0 °C, 3 h	84	88:12

[a] ^{1}H NMR yield based on an internal standard $(CF_3)_2C(C_6H_4p\text{-}Me)_2$. [b] **2a**/**10a** = 95:5 to 97:3. [c] **2a** was recovered in 53% yield.

For the introduction of substituents, the obtained tetracyclic ketones **4** were subjected to nucleophilic addition followed by dehydration (Scheme 7, method A). The treatment of ketone **4a** with phenyllithium followed by sulfuric acid provided the corresponding cyclohexene **13a** in an 87% yield via tertiary alcohol **12a**.

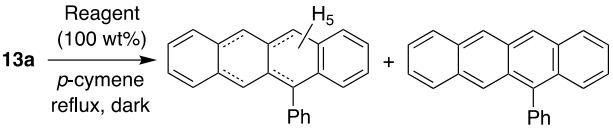


Scheme 7 Synthesis of 5-substituted [4]acene **5a** (method A)

Next, the dehydrogenation of **13a** was investigated. However, the previously described procedure for partially saturated PAHs with Pd/C[10b] was not satisfactory. When cyclohexene **13a** was treated with 100 wt% of Pd/C in refluxing *p*-cymene (Table 4, Entry 1), the complete conversion of **13a** required a long reaction time (24 h), providing the desired 5-phenyl[4]acene **5a** in a yield of only 59% (^{1}H NMR yields based on Ph_3CH). Other reagents, such as $Pd(OH)_2$, Pt/C, and PtO_2, provided low yields of **5a** (Entries 2–4) along with partially dehydrogenated product(s) **14** and initial **13a** (Entries 3 and 4).[19] The use of Rh/Al_2O_3 was also ineffective (Entry 5). Although the low mass balances (**14** + **5a** + **13a**, 13%–59% yields) and the long reaction times (5–24 h) for Entries 1–4 were improved by microwave irradiation, the issue of partial dehydrogenation (the formation of **14**) remained unsolved (Entry 6).[20] Finally, the dehydrogenation of **14** was completed by passing nitrogen gas through the reaction mixture during the reaction (Entry 7). The desired 5-phenyl[4]acene (**5a**) was obtained in a 90% yield (^{1}H NMR analysis) without the generation of **14**, and it was isolated in a yield of 83% (Scheme 7). The nitrogen stream likely removed the hydrogen that had been liberated from the Pd surface, which drove the dehydrogenation reaction to completion.[21]

A Pd-catalyzed cross-coupling reaction also facilitated the introduction of substituents and expanded the scope of [4]acene synthesis (Table 5, method B). Tetracyclic ketones **4a–e** were treated with trifluoromethanesulfonic anhydride (3.0 equiv) in the presence of 2,6-di(*t*-butyl)-4-methylpyridine (1.2 equiv, Entry 1)[22] to produce the corresponding vinyl triflates **15a–e** in 59% to quantitative yields (Entries 1–7). Vinyl triflates **15a–d** were subjected to Suzuki–Miyaura coupling with arylboronic acids to produce the desired 5-arylated cyclohexenes **13a–f** in

Table 4 Dehydrogenation of cyclohexene **10a** [a]



14 ($C_{24}H_{18}$) **5a** ($C_{24}H_{16}$)

Entry	Reagent	Time (h)	Yield (%)	
			14 + **5a** [b]	**13a**
1	10% Pd/C	24	59 (**5a** only)	–
2	$Pd(OH)_2$	11	13 (**5a** only)	–
3	5% Pt/C	5	26 (62:38)	27
4	PtO_2	5	16 (44:56)	30
5	5% Rh/Al_2O_3	5	4 (**14** only)	96
6 [c]	10% Pd/C	1	85 (44:56)	–
7	10% Pd/C, N_2 [d]	14	90 (**5a** only)	–

[a] ^{1}H NMR yield based on an internal standard Ph_3CH. [b] **14**/**5a** ratio is indicated in parentheses. [c] Microwave (130 W), 180 °C, closed. [d] 60 mL/min (bubbling through a glass filter).

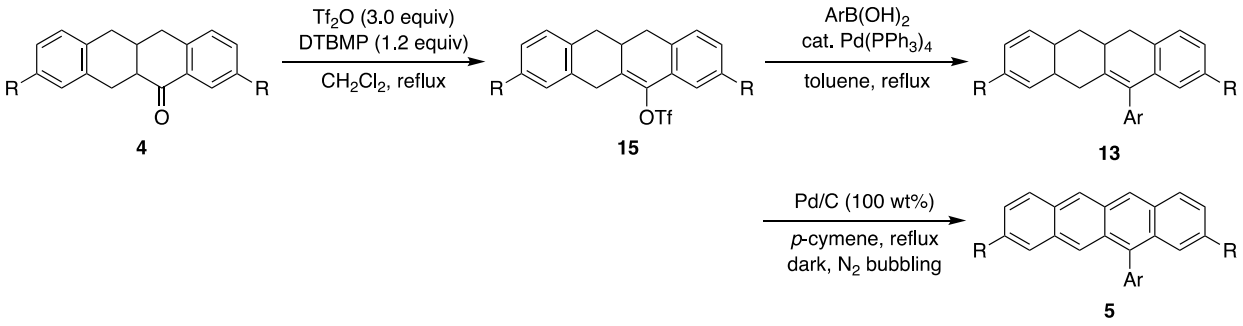
yields of 61–94% (Entries 1–6). In the case of bromine-bearing **15e**, phenylation was achieved using triflate-selective Kumada coupling (70% yield, **13g**, Entry 7).[23]

Cyclohexenes **13a–e** were finally dehydrogenated under the abovementioned conditions (Pd/C, N_2 stream) to provide the desired 5-arylated [4]acenes **5a–e** in 55%–83% yields. It is worth noting that chlorinated **13f** and brominated **13g** underwent hydrodehalogenation as well as dehydrogenation by Pd/C (not shown).[24] Although *p*-chloranil (tetrachloro-*p*-benzoquinone) was not effective, triphenylmethylium tetrafluoroborate (Ph_3CBF_4), which was effective in our previous synthesis of angular PAHs,[10c] provided **5g** from **13g** in a moderate yield. The yields of halogenated [4]acenes **5f** and **5g** were increased by the use of trityl cations, which were generated from triphenylmethyl alcohol in refluxing trifluoroacetic acid. Dichloro[4]acene **5f** and dibromo[4]acene **5g** were isolated in yields of 23% and 30%, respectively (Table 5, Entries 6 and 7).

The oxidative generation of CF_2 cations **C** from bicyclic difluoroalkenes was conducted to synthesize 5,6-disubstituted [4]acenes (Scheme 2c). While CF_2 cations **A** were generated by fluoride abstraction ($-F^-$) from (trifluoromethyl)alkenes (Scheme 2[a]) and CF_2 cations **B** by the protonation ($+H^+$) of difluoroalkenes (Scheme 2[b]) as described above, the generation of CF_2 cations **C** by the oxidation ($-e^-$) of difluoroalkenes (Scheme 2[c]) provides a new option, which allows the introduction of two substituents to the frameworks of [4]acene.

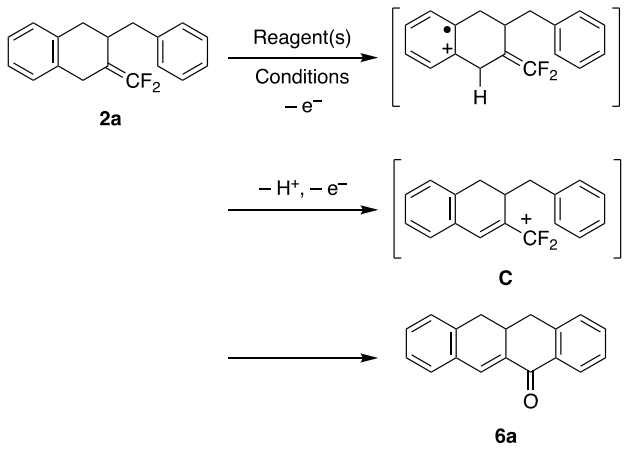
Scheme 8 depicts an explanation of the oxidative generation of CF_2 cations **C**. One-electron oxidation occurs on the benzene ring in **2a** to form a cation radical. Subsequent deprotonation followed by further one-electron oxidation generates **C**, leading to the cyclization to enone **6a**.

Table 5 Synthesis of 5-substituted [4]acenes **5** (method B) [a]



Entry	R	**4**	Yield (%) (Time)			
			15 (Triflation)	Ar	**13** (Coupling)	**5** (Dehydrogenation)
1	H	**4a**	**15a** 87 (4 h)	Ph	**13a** 61 (2 h)	**5a** 83 (14 h)
2	H	**4a**	**15a** 87 (4 h)	*p*-Tolyl	**13b** 94 (5 h)	**5b** 55 (12 h)
3	H	**4a**	**15a** 87 (4 h)	*p*-$CF_3C_6H_4$	**13c** 86 (5 h)	**5c** 60 (18 h)
4	Me	**4b**	**15b** 77 (4 h)	Ph	**13d** 93 (5 h)	**5d** 67 (12 h)
5	Ph	**4c**	**15c** Quant (4 h)	Ph	**13e** 80 (3 h)	**5e** 83 (24 h)
6	Cl	**4d**	**15d** 59 (15 h)	Ph	**13f** 89 (3 h)	**5f** 23 (44) [b] (12 h) [c]
7	Br	**4e**	**15e** 68 (1 h)	Ph	**13g** 70 (14 h) [d]	**5g** 30 (58) [b] (12 h) [c]

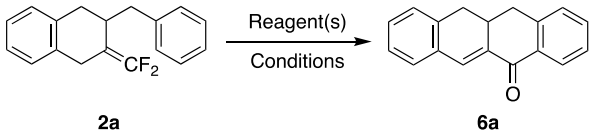
[a] Isolated yield. [b] ^{1}H NMR yield based on an internal standard CH_2Br_2. [c] Ph_3COH (2.0 equiv), CF_3CO_2H, reflux, dark. [d] 4 mol% $PdCl_2$(dppp), PhMgBr (1.4 equiv), LiBr (1.0 equiv), Et_2O, reflux.



Scheme 8 Generation of CF_2 cation **C** under oxidative conditions

The reaction conditions were examined using bicyclic difluoroalkene **2a** as a model substrate (Table 6). Treatment with iodobenzene diacetate (Entry 1) or iodobenzene bis(trifluoroacetate) (Entry 2) in HFIP at 0°C caused **2a** to undergo Friedel–Crafts-type cyclization to produce the desired tetracyclic enone **6a** in 2% and 9% yields, respectively (the oxidative second ring construction). Enone **6a** was not obtained using either Ph_3C^+ BF_4^- (Entry 3) or DDQ at 60°C (Entry 4). To enhance the oxidizing power of DDQ, the effects of acids were investigated. When the reaction was conducted with DDQ in the presence of *tert*-butyldimethylsilyl chloride (TBSCl) or aluminium chloride, **6a** was obtained in yields of 20% and 51%, respectively (Entries 5 and 6). However, oxidation in the presence of trifluoroacetic acid failed (Entry 7), while the use of TfOH at 0 °C successfully provided **6a** in an 87% yield (^{1}H NMR yield, isolated in 83%, Entry 8).[25] It should be noted that the treatment of ketone **4a** (*cis*/*trans* = 85:15) with DDQ (1.0 equiv)/TfOH (1.0 equiv) did not produce enone **6a** but instead resulted in the 63% recovery of **4a** (*cis*/*trans* = 94:6, HFIP, 0°C, 3 h, ^{1}H NMR yield). Thus, the pathway of the acid-mediated cyclization of **2a** to **4a** followed by dehydrogenation with DDQ can be ruled out for the formation of **6a**.

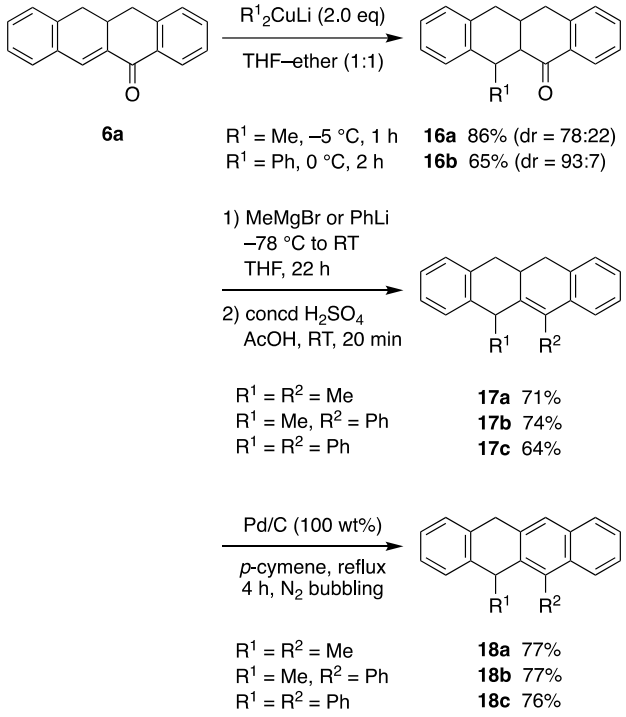
Table 6 Screening of oxidizing agents (the oxidative second ring construction) [a]



Entry	Reagent(s) (equiv)	Conditions	**6a** (%) [b]
1	$PhI(OAc)_2$ (1.0)	0 °C, 3 h	2
2	$PhI(OCOCF_3)_2$ (1.0)	0 °C, 4 h	9
3	Ph_3C^+ BF_4^- (1.0)	60 °C, 3 h	-
4	DDQ (1.0)	60 °C, 1 h	-
5	DDQ (1.0), TBSCl (1.0)	0 °C, 3 h	20
6	DDQ (1.0), $AlCl_3$ (1.7)	0 °C, 3 h	51
7	DDQ (1.0), CF_3CO_2H (1.0)	0 °C, 5 h	-
8	DDQ (1.0), TfOH (1.0)	0 °C, 3 h	87 (83) [c]

[a] ^{1}H NMR yield based on an internal standard CH_2Br_2. [b] **2a** was consumed completely in all Entries. [c] Isolated yield. TBS = Si(*t*-Bu)Me_2.

Therefore, the obtained tetracyclic enones **6a** are suitable intermediates for the double introduction of substituents (Scheme 9). First, the introduction of R^1 was conducted by the conjugate addition of organocuprates. When enone **6a** was treated with organocuprates (R^1 = Me and Ph), the desired conjugate addition products (tetracyclic ketones) **16a** and **16b** were obtained in yields of 86% (dr =78:22) and 65% (dr = 93:7), respectively. Second, the introduction of R^2 to **16a** and **16b** was performed in a similar way to **4a** (Scheme 7). Ketones **16a** and **16b** were treated with MeMgBr (R^2 = Me) or PhLi (R^2 = Ph) followed by dehydration with H_2SO_4 to realize disubstituted tetrahydro[4]acenes **17a–c** in yields of 64%–74%. Finally, the dehydrogenation of **17a–c** with Pd/C under an N_2 stream provided 5,6-disubstituted dihydro[4]acenes **18a–c** in yields of 76%–77%.[26]



Scheme 9 Synthesis of 5,6-substituted [4]acenes

In summary, this study synthesized 5-substituted and 5,6-disubstituted [4]acenes based on the domino and stepwise cyclizations of fluoroalkenes. (a) The treatment of 2-trifluoromethyl-1-alkenes bearing two aryl groups with Me_2AlCl resulted in domino Friedel–Crafts-type cyclization (two-ring construction). Subsequent dehydrogenation led to the synthesis of 5-fluorinated [4]acenes. However, the treatment of the same (trifluoromethyl)alkenes with Me_2AlCl in the presence of Me_3Al resulted in selective one-ring construction, providing bicyclic 1,1-difluoro-1-alkenes (the first ring construction). (b) When these bicyclic 1,1-difluoroalkenes were treated with TfOH, Friedel–Crafts-type cyclization provided tetracyclic ketones (the acidic second ring construction). The obtained ketones acted as a platform for the introduction of substituents at the 5-position of [4]acenes. (c) When the bicyclic difluoroalkenes were treated with DDQ/TfOH, allylic CF_2 cations were oxidatively generated, and Friedel–Crafts-type cyclization produced tetracyclic enones (the oxidative second ring construction). These enones were key sintermediates for the synthesis of [4]acenes bearing two substituents at the 5- and 6-positions.

Tetrahydrofuran (THF), dichloromethane, and toluene were dried by passing through a column of activated alumina followed by a column of Q-5 scavenger (Engelhard). *p*-Cymene was distilled with azeotropic removal of water and stored over molecular sieves 4A. Methanol was distilled from $Mg(OMe)_2$ and stored under MS 4A. $(CF_3)_2CHOH$ (HFIP) can be purchased from commercial suppliers such as Merck KGaA.

CF_3SiMe_3 (Ruppert's reagent) were supplied from TOSOH FINECHEM CORPORATION and used as received. TfOH and Tf_2O were supplied from Central Glass Co., Ltd. and used as received. These compounds can be purchased from commercial suppliers such as TOKYO CHEMICAL INDUSTRY CO., LTD.

2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) was purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and used as received.

1,1,1,3,3,3-Hexafluoro-2,2-di(4-methylphenyl)propane [$(CF_3)_2C(C_6H_4$*p*-$Me)_2$] as an internal standard for determination of ^{19}F and ^1H NMR yields was purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and used as received. PH_3CH and CH_2Br_2 as internal standards for determination of ^1H NMR yields was purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. and used as received.

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography). Purification was also performed by preparative HPLC (GPC), using a JAI LC-908 instrument (Jaigel-2H, $CHCl_3$).

IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR method). NMR spectra were recorded on Bruker Avance 500 or Jeol JNM ECS-400 spectrometers in $CDCl_3$ at 500 or 400 MHz (^1H NMR), at 126 or 101 MHz (^{13}C NMR), and at 470 or 376 MHz (^{19}F NMR). Chemical shifts were given in ppm relative to internal Me_4Si (for ^1H NMR: δ = 0.00), $CDCl_3$ (for ^{13}C NMR: δ = 77.0) and C_6F_6 (for ^{19}F NMR: δ = 0.0; C_6F_6 exhibits a ^{19}F NMR signal at –162.9 ppm vs. $CFCl_3$). High-resolution mass spectroscopy (HRMS) was conducted with Jeol JMS-T100GCV (EI/TOF) and JMS-T100CS (APCI/TOF) spectrometers. Elemental analysis (EA) was performed with a Yanako MT-3 CHN Corder apparatus.

Procedures and spectral data of compounds

Preparation of (trifluoromethyl)ketones 8. Preparation of (trifluoromethyl)ketone **8a** is described as a typical procedure. To a THF solution (45 mL) of methyl 2-benzyl-3-phenylpropionate (24.1 g, 91.6 mmol) and cesium fluoride (3.04 g, 20.0 mmol) was added CF_3SiMe_3 (16.5 mL, 112 mmol) dropwise over 2 h at –5°C. After being stirred for 12 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane/AcOEt = 20:1) to give (trifluoromethyl)ketone **8a** (21.7 g, 81% yield) as a colorless liquid.

Preparation of (trifluoromethyl)alkenes 1. Preparation of (trifluoromethyl)alkene **1a** is described as a typical procedure. To a THF solution (110 mL) of CH_3PPh_3I (10.7 g, 26.5 mmol) was added KO*t*-Bu (2.9 g, 26 mmol) at –78 °C. After stirring for 10 min, (trifluoromethyl)ketone **8a** (6.4 g, 22 mmol) was added at –78 °C. After being stirred at room temperature for 12 h, sat. aq. NH_4Cl was added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane) to give (trifluoromethyl)alkene **1a** (5.4 g, 87% yield) as a colorless liquid.

Synthesis of 5-fluoro[4]acenes 3. Synthesis of 5-fluoro[4]acene **3a** via 5-fluoro(dihydro)[4]acene **9a** is described. To a dichloromethane solution (10 mL) of (trifluoromethyl)alkene **1a** (361 mg, 1.00 mmol) was added a hexane solution of $AlMe_2Cl$ (1.00 mL, 1.0 M, 1.0 mmol) at –50 °C. After being gradually warmed to room temperature over 13 h, phosphate buffer

(pH 7) was added to quench the reaction. Organic materials were extracted with dichloromethane three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by GPC to give 5-fluoro(dihydro)[4]acene **9a** (111 mg, 36% yield) as a colorless liquid. To a 1,4-dioxane solution (6 mL) of DDQ (136 mg, 0.60 mmol) was added a 1,4-dioxane solution (4 mL) containing 0.30 mmol of fluoro(dihydro)[4]acene **9a** at room temperature. After being stirred for 4 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with $CHCl_3$ three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. ^{19}F NMR analysis of the sample indicated that fluoro[4]acene **3a** was formed in 32% yield.

Synthesis of tetracyclic ketones 4. Synthesis of tetracyclic ketone **4a** through bicyclic difluoroalkene **2a** intermediate is described as a typical procedure. To a CH_2Cl_2 solution (13 mL) of (trifluoromethyl)alkene **1a** (1.90 g, 6.54 mmol) were added a hexane solution of $AlMe_3$ (6.00 mL, 1.09 M, 6.54 mmol) and a hexane solution of $AlMe_2Cl$ (7.30 mL, 1.07 M, 7.81 mmol) at –78 C°. The reaction mixture was warmed to room temperature. After being stirred for 1 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane) as quickly as possible to give a mixture of bicyclic difluoroalkene **2a** and a small amount of **10a** (1.58 g, 90% yield, **2a**:**10a** = 97:3). To a HFIP/CH_2Cl_2 solution (11 mL, 10:1) of the obtained bicyclic difluoroalkene **2a** (1.58 g, 6.36 mmol, **2a**:**10a** = 97:3) was added TfOH (1.1 mL, 12 mmol) at 0 °C. After being stirred for 3 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by recrystallization (hexane/AcOEt = 10:1) to give tetracyclic ketone **4a** (1.28 g, 81% yield based on **2a**+**10a**, *cis*/*trans* = 88:12) as a yellow solid.

Synthesis of 5-substituted [4]acenes 5 via nucleophilic addition (method A). Synthesis of 5-substituted [4]acene **5a** through nucleophilic addition of organolithiums is described as a typical procedure. To a THF solution (10 mL) of PhLi, prepared from PhBr (0.32 mL, 3.0 mmol) and *n*-BuLi (1.6 M in hexane, 2.00 mL, 3.2 mmol) at –78 °C, was added tetracyclic ketone **4a** (495 mg, 2.00 mmol) at –78 °C. The reaction mixture was warmed to room temperature. After being stirred for 15 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials, containing tertiary alcohol **12a**, were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, AcOH (1 mL) and H_2SO_4 (0.1 mL) were added at room temperature. After being stirred for 20 min, water was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane) to give cyclohexene **13a** (504 mg, 82% yield) as a yellow solid.

To a *p*-cymene solution (5 mL) of cyclohexene **13a** (51 mg, 0.17 mmol) was added 10% Pd/C (50 mg, 100 wt%). After being refluxed for 14 h with passing nitrogen (60 mL/min) through a glass filter in the dark, the mixture was filtered through SiO_2 using $CHCl_3$ as an eluent. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane) to give 5-substituted [4]acene **5a** (41 mg, 83% yield) as a red solid.

Synthesis of 5-substituted [4]acenes 5 via cross coupling (method B). Synthesis of 5-substituted [4]acene **5b** through cross coupling is described as a typical procedure. To a CH_2Cl_2 solution (5 mL) of tetracyclic ketone **4a** (245 mg, 0.987 mmol) and DTBMP (241 mg, 1.17 mmol) was added Tf_2O (0.50 mL, 3.0 mmol) at room temperature. After being refluxed for 4 h, hexane was added and filtered through celite. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane/toluene = 10:1) to give triflate **15a** (335 mg, 89% yield) as a yellow liquid.

To a toluene/MeOH/water solution (10 mL, 5/2/3) of triflate **15a** (533 mg, 1.40 mmol) were added 4-methylphenyl boronic acid (255 mg, 1.88 mmol), $Pd(PPh_3)_4$ (80 mg, 0.071 mmol), and Na_2CO_3 (445 mg, 4.20 mmol) at room temperature. After being refluxed for 5 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane) to give cyclohexene **13b** (425 mg, 94% yield) as a yellow solid.

Treatment of cyclohexene **13b** (50 mg, 0.16 mmol) under the conditions similar to **13a** gave 5-substituted [4]acene **5b** (28 mg, 55% yield) as a red solid.

Synthesis of tetracyclic enones 6. Synthesis of tetracyclic enone **6a** is described as a typical procedure. To an HFIP solution (50 mL) of DDQ (1.2 g, 5.3 mmol) and TfOH (0.47 mL, 5.3 mmol) was added an HFIP solution (3 mL) of bicyclic difluoroalkene **2a** (1.4 g, 5.3 mmol) at 0 °C. After being stirred for 3 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane/AcOEt = 20:1) to give tetracyclic enone **6a** (1.1 g, 83% yield) as a yellow solid.

Synthesis of 5,6-disubstituted dihydro[4]acenes 18 via conjugate addition. Synthesis of 5,6-disubstituted dihydro[4]acene **18a** through conjugate addition of organocuprates is described as a typical procedure. To an Et_2O solution (5 mL) of CuI (384 mg, 2.02 mmol) was added an Et_2O solution of methyllithium (1.2 M, 3.5 mL, 4.1 mmol) at –5 °C. After being stirred for 1 h, a THF solution (5 mL) of enone **6a** (244 mg, 0.991 mmol) was added at –5 °C. After being stirred for 2 h, sat. aq. NH_4Cl was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on SiO_2 (hexane/AcOEt =20:1) to give conjugate addition product **16a** (225 mg, dr = 78:22, 86% yield) as a yellow solid. Thus-obtained tetracyclic ketone **16a** was subjected to the conditions described for tetracyclic ketone **4a** (method A) to give cyclohexene **17a** (149 mg, 71% yield) as a yellow solid. Cyclohexene **17a** was subjected to the conditions described for **13a** to give disubstituted dihydro[4]acene **18a** (292 mg, 77% yield) as a yellow solid.

3-Benzyl-4-phenyl-2-(trifluoromethyl)but-1-ene (1a)

5.4 g, 87% yield.

IR (neat): 3028, 1757, 1496, 1119, 752, 698 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.79 (dd, *J* = 13.8, 7.1 Hz, 2H, CH_2), 2.85 (dd, *J* = 13.8, 7.3 Hz, 2H, CH_2), 2.96 (tt, *J* = 7.3, 7.1 Hz, 1H, CH), 5.26 (br s, 1H, =CH_2), 5.75 (br s, 1H, =CH_2), 7.12 (d, *J* = 7.2 Hz, 4H, ArH), 7.19 (t, *J* = 7.6 Hz, 2H, ArH), 7.27 (dd, *J* = 7.6, 7.2 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 40.1 (CH_2), 42.9 (CH), 119.5 (q, J_{CF} = 6 Hz, =CH_2), 123.9 (q, J_{CF} = 275 Hz, CF_3), 126.2 (Ar), 128.2 (Ar), 129.2 (Ar), 139.2 (Ar), 140.0 (q, J_{CF} = 28 Hz, =C).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 94.3 (s, CF_3).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{17}F_3$: 290.1282; found: 290.1273.

4-(4-Methylphenyl)-3-(4-methylphenyl)methyl-2-(trifluoromethyl)but-1-ene (1b)

1.5 g, 79% yield.

IR (neat): 2925, 1516, 1163, 1117, 804 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.30 (s, 6H, CH_3), 2.72 (dd, *J* = 13.9, 7.2 Hz, 2H, CH_2), 2.78 (dd, *J* = 13.9, 7.2 Hz, 2H, CH_2), 2.92 (tt, *J* = 7.2, 7.2 Hz, 1H, CH), 5.21 (br s, 1H, =CH_2), 5.72 (d, *J* = 1.1 Hz, 1H, =CH_2), 6.99 (d, *J* = 7.9 Hz, 4H, ArH), 7.06 (d, *J* = 7.9 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.0 (CH_3), 39.6 (CH_2), 42.8 (CH), 119.3 (q, J_{CF} = 6 Hz, =CH_2), 123.9 (q, J_{CF} = 275 Hz, CF_3), 128.9 (Ar), 129.1 (Ar), 135.6 (Ar), 136.1 (Ar), 140.2 (q, J_{CF} = 28 Hz, =C).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 94.3 (s, CF_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{20}H_{21}F_3$: 318.1595; found: 318.1598.

4-(4-Phenylphenyl)-3-(4-phenylphenyl)methyl-2-(trifluoromethyl)but-1-ene (1c)

1.7 g, 65% yield.

IR (neat): 3028, 1487, 1165, 1117, 912, 735 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.85 (dd, *J* = 13.9, 7.0 Hz, 2H, CH_2), 2.92 (dd, *J* = 13.9, 7.2 Hz, 2H, CH_2), 3.04 (tt, *J* = 7.2, 7.0 Hz, 1H, CH), 5.30 (br s, 1H, =CH_2), 5.79 (br s, 1H, =CH_2), 7.20 (d, *J* = 8.3 Hz, 4H, ArH), 7.32 (tt, *J* = 7.4, 1.2 Hz, 2H, ArH), 7.42 (dd, *J* = 8.3, 7.4 Hz, 4H, ArH), 7.50 (d, *J* = 8.3 Hz, 4H, ArH), 7.58 (d, *J* = 8.3 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 39.7 (CH_2), 42.7 (CH), 119.6 (q, J_{CF} = 6 Hz, =CH_2), 123.9 (q, J_{CF} = 275 Hz, CF_3), 127.0 (Ar), 127.1 (Ar), 128.7 (Ar), 129.6 (Ar), 138.3 (Ar), 139.1 (Ar), 140.1 (q, J_{CF} = 28 Hz, =C), 140.9 (Ar).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 94.4 (s, CF_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{30}H_{25}F_3$: 442.1908; found: 442.1907.

4-(4-Chlorophenyl)-3-(4-chlorophenyl)methyl-2-(trifluoromethyl)but-1-ene (1d)

4.3 g, 92% yield.

IR (neat): 2935, 1493, 1163, 1117, 1014, 808 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.73 (dd, *J* = 13.8, 6.9 Hz, 2H, CH_2), 2.79 (dd, *J* = 13.8, 7.3 Hz, 2H, CH_2), 2.87 (tt, *J* = 7.3, 6.9 Hz, 1H, CH), 5.22 (br s, 1H, =CH_2), 5.76 (br s, 1H, =CH_2), 7.03 (d, *J* = 8.4 Hz, 4H, ArH), 7.24 (d, *J* = 8.4 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 39.4 (CH_2), 42.9 (CH), 132.2 (Ar), 119.9 (q, J_{CF} = 6 Hz, CH_2), 123.7 (q, J_{CF} = 275 Hz, CF_3), 128.5 (Ar), 130.5 (Ar), 137.4 (Ar), 139.5 (q, J_{CF} = 29 Hz, =C).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 94.3 (s, CF_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{18}H_{15}Cl_2F_3$: 358.0503; found: 358.0505.

4-(4-Bromophenyl)-3-(4-bromophenyl)methyl-2-(trifluoromethyl)but-1-ene (1e)

9.2 g, 69% yield.

IR (neat): 3026, 1487, 1163, 1113, 1072, 1011 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.71 (dd, *J* = 13.8, 6.9 Hz, 2H, CH_2), 2.78 (dd, *J* = 13.8, 7.3 Hz, 2H, CH_2), 2.87 (tt, *J* = 7.3, 6.9 Hz, 1H, CH), 5.21 (br s, 1H, =CH_2), 5.75 (br s, 1H, =CH_2), 6.96 (d, *J* = 8.2 Hz, 4H, ArH), 7.39 (d, *J* = 8.2 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 39.5 (CH_2), 42.9 (CH), 131.5 (Ar), 119.9 (q, J_{CF} = 6 Hz, CH_2), 120.3 (Ar), 123.7 (q, J_{CF} = 275 Hz, CF_3), 130.9 (Ar), 137.9 (Ar), 139.7 (q, J_{CF} = 28 Hz, =C).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 94.3 (s, CF_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{18}H_{15}Br_2F_3$: 447.9472; found: 447.9478.

2-Benzyl-3-difluoromethylidene-1,2,3,4-tetrahydronaphthalene (2a)

1.58 g, 90% (**2a** + **10a** mixture, 97:3).

IR (neat): 3026, 1749, 1225, 995, 741, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.49 (dd, *J* = 13.5, 9.0 Hz, 1H, CH_2), 2.60 (ddd, *J* = 15.6, 2.9, 2.9 Hz, 1H, CH_2), 2.65 (dd, *J* = 13.5, 6.8 Hz, 1H, CH_2), 2.77 (dd, *J* = 15.6, 5.4 Hz, 1H, CH_2), 3.04–3.11 (m, 1H, CH), 3.38 (ddd, *J* = 18.8, 3.8, 3.8 Hz, 1H, CH_2), 3.46 (dd, *J* = 18.8, 2.4 Hz, 1H, CH_2), 7.03 (d, *J* = 7.3 Hz, 1H, ArH), 7.08 (d, *J* = 7.5 Hz, 2H, ArH), 7.10–7.15 (m, 3H, ArH), 7.18 (t, *J* = 7.5 Hz, 1H, ArH), 7.25 (dd, *J* = 7.5, 7.3 Hz, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 25.3 (CH_2), 33.2 (CH_2), 33.8 (d, J_{CF} = 2 Hz, CH), 38.7 (dd, J_{CF} = 2, 2 Hz, CH_2), 87.8 (dd, J_{CF} = 17, 17 Hz, =C), 126.2 (Ar), 126.3 (Ar), 126.4 (Ar), 128.2 (Ar), 128.4 (Ar), 129.1 (Ar), 129.4(Ar), 134.0(Ar), 135.2(Ar), 139.8 (Ar), 152.0 (dd, J_{CF} = 284, 284 Hz, =CF_2).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 66.5 (br dd, *J* = 56 Hz, J_{FH} = 3 Hz, 1F, CF_2), 67.9 (d, *J* = 56 Hz, 1F, CF_2).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{18}H_{16}F_2$: 270.1220; found: 270.1224.

5-Fluoro[4]acene (3a)

32% yield (^{19}F NMR yield based on $PhCF_3$).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39–7.45 (m, 4H, ArH), 7.96–8.01 (m, 2H, ArH), 8.02–8.05 (m, 1H, ArH), 8.26 (d, *J* = 6.0 Hz, 1H, ArH), 8.45 (s, 1H, ArH), 8.65 (s, 1H, ArH), 8.90 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 154.0 (d, J_{CF} = 261 Hz, CF) (selected peak).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 32.0 (s).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{18}H_{11}F$: 246.0845; found: 246.0839.

6,11,11a,12-Tetrahydrotetracen-5(5a*H*)-one (4a, *cis*/*trans* = 88:12)

Colorless crystals, Mp. 109.8–110.7 °C, 1.0 g, 81% yield.

IR (neat): 2897, 1680, 1601, 1284, 742 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.33–2.42 (m, 1H*0.12), 2.61 (ddd, *J* = 12.6, 12.6, 5.7 Hz, 1H*0.12), 2.75 (dd, *J* = 16.8, 7.1 Hz, 1H*0.88, CH_2), 2.81–2.97 (m, 1H*0.88 + 3H*0.12), 2.93 (br d, *J* = 5.8 Hz, 1H*0.88), 2.96 (br d, *J* = 6.0 Hz, 1H*0.88), 3.01 (dd, *J* = 16.8, 7.3 Hz, 1H*0.88, CH_2), 3.08 (ddd, *J* = 6.7, 6.7, 4.8 Hz, 1H*0.88), 3.09 (dd, *J* = 16.5, 5.1 Hz, 1H*0.12, CH_2), 3.13 (dd, *J* = 16.5, 4.2 Hz, 1H*0.12, CH_2), 3.14 (dd, *J* = 16.8, 4.7 Hz, 1H*0.88, CH_2), 3.33 (dd, *J* = 16.8, 7.1 Hz, 1H*0.88, CH_2), 3.49 (ddd, *J* = 10.8, 5.8, 5.8 Hz, 1H*0.12), 7.03 (d, *J* = 6.3 Hz, 1H*0.88, ArH), 7.07–7.19 (m, 3H, ArH), 7.20–7.24 (m, 1H*0.12, ArH), 7.25 (d, *J* = 7.4 Hz, 1H*0.88, ArH), 7.28 (br d, *J* = 7.5 Hz, *J* = 1H*0.12, ArH), 7.31 (dd, *J* = 7.4, 7.4 Hz, 1H*0.88, ArH), 7.35 (dd, *J* = 7.5, 7.5 Hz, 1H*0.12, ArH), 7.49 (dd, *J* = 7.4, 7.4 Hz, 1H*0.88, ArH), 7.51 (dd, *J* = 7.5, 7.5 Hz, 1H*0.12, ArH), 8.04 (d, *J* = 7.4 Hz, 1H*0.88, ArH), 8.09 (d, *J* = 7.5 Hz, 1H*0.12, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 27.4 (*cis*), 29.7 (*trans*), 32.1 (*cis*), 32.6 (*cis*), 32.9 (*cis*), 36.1 (*trans*), 36.5 (*trans*), 37.2 (*trans*), 45.9 (*cis*), 48.0 (*trans*), 125.85 (*trans*, Ar), 125.85 (*cis*, Ar), 125.88 (*cis*, Ar), 126.0 (*trans*, Ar), 126.7 (*cis*, Ar), 126.8 (*trans*, Ar), 127.41 (*cis*, Ar), 127.42 (*trans*, Ar), 128.4 (*trans*, Ar), 128.5 (*trans*, Ar), 129.1 (*cis*, Ar), 129.3 (*trans*, Ar), 129.27 (*cis*, Ar), 129.30 (*cis*, Ar), 131.2 (*cis*, Ar), 132.1 (*trans*, Ar), 133.5 (*trans*, Ar), 133.5 (*cis*, Ar), 134.1 (*cis*, Ar), 134.3 (*cis*, Ar), 134.6 (*trans*, Ar), 135.3 (*trans*, Ar), 142.3 (*cis*, Ar), 142.9 (*trans*, Ar), 199.2 (*trans*, C=O), 199.2 (*cis*, C=O).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{18}H_{16}O$: 248.1201; found: 248.1210 (*cis*), 248.1207 (*trans*).

3,8-Dimethyl-6,11,11a,12-tetrahydrotetracen-5(5a*H*)-one (4b, *cis*/*trans* = 87:13)

0.56 g, 81% yield.

IR (neat): 2916, 1680, 1496, 1284, 814 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.27 (s, 3H*0.87, CH_3), 2.31 (s, 3H*0.13, CH_3), 2.35 (s, 3H*0.87, CH_3), 2.38 (s, 3H*0.13, CH_3), 2.57 (ddd, *J* = 12.7, 11.4, 5.7 Hz, 1H*0.13, CH_2), 2.69 (dd, *J* = 16.6, 6.8 Hz, 1H*0.87, CH_2), 2.73–2.99 (m, 4H), 3.00–3.11 (m, 2H), 3.25 (dd, *J* = 16.8, 7.4 Hz, 1H*0.87, CH_2), 3.44 (dd, *J* = 17.5, 5.7 Hz, 1H*0.13, CH_2), 6.90 (d, *J* = 7.1 Hz, 1H*0.87, ArH), 6.92 (d, *J* = 7.1 Hz, 1H*0.87, ArH), 6.96 (s, 1H*0.87, ArH), 6.83–6.96 (m 2H*0.13, ArH), 7.03 (d, *J* = 8.1 Hz, 1H*0.13, ArH), 7.13 (d, *J* = 8.0 Hz, 1H*0.87, ArH), 7.17 (d, *J* = 7.9 Hz, 1H*0.13, ArH), 7.28 (d, *J* = 8.0 Hz, 1H*0.87, ArH), 7.30 (d, *J* = 7.9 Hz, 1H*0.13, ArH), 7.84 (s, 1H*0.87, ArH), 7.89 (s, 1H*0.13, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.97 (*cis*, CH_3), 20.99 (*trans*, CH_3), 27.4 (*cis*, CH_3), 29.8 (*trans*, CH_3), 31.8 (*cis*), 32.2 (*cis*), 33.1 (*cis*), 36.2 (*trans*), 36.4 (*trans*), 36.9 (*trans*), 46.0 (*cis*), 48.2 (*trans*), 126.7 (*trans*, Ar), 126.8 (*cis*, Ar), 127.5 (*cis*, Ar), 128.3 (*trans*, Ar), 128.5 (*trans*, Ar), 129.2 (*cis*, Ar), 129.3 (*cis*, Ar), 129.6 (*cis*, Ar), 129.8 (*trans*, Ar), 131.0 (*cis*, Ar), 131.1 (*cis*, Ar), 131.6 (*trans*, Ar), 131.9 (*trans*, Ar), 134.2 (*cis*, Ar), 134.5 (*cis*, Ar), 135.2 (*trans*, Ar), 135.3 (*cis*, Ar), 135.6 (*trans*, Ar), 136.3 (*cis*, Ar), 136.5 (*trans*, Ar), 139.6 (*cis*, Ar), 140.2 (*trans*, Ar), 199.6 (*trans*, C=O), 199.7 (*cis*, C=O).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{20}H_{20}O$: 276.1514; found: 276.1517 (*cis*), 276.1512 (*trans*).

3,8-Diphenyl-6,11,11a,12-tetrahydrotetracen-5(5a*H*)-one (4c, *cis*/*trans* = 83:17)

0.63 g, 81% yield.

IR (neat): 2910, 1680, 1481, 758, 696 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.40–2.49 (m, 1H*0.17), 2.64–2.72 (m, 1H*0.17), 2.82 (dd, *J* = 16.7, 7.2 Hz, 1H*0.83, CH_2), 2.85–3.11 (m, 4H*0.83+3H*0.17), 3.12–3.24 (m, 2H), 3.43 (dd, *J* = 17.0, 6.8 Hz, 1H*0.83, CH_2), 3.59 (dd, *J* = 17.5, 5.5 Hz, 1H*0.17, CH_2), 7.12 (d, *J* = 8.0 Hz, 1H*0.83, ArH), 7.21 (d, *J* = 8.0 Hz, 1H*0.17, ArH), 7.30–7.48 (m, 9H, ArH), 7.53–7.65 (m, 4H*0.17, ArH), 7.56 (d, *J* = 7.7 Hz, 2H*0.83, ArH), 7.61 (d, *J* = 7.7 Hz, 2H*0.83, ArH), 7.74 (dd, *J* = 7.9, 1.9 Hz, 1H*0.83, ArH), 7.75–7.78 (m, 1H*0.17, ArH), 8.29 (d, *J* = 1.8 Hz, 1H*0.83, ArH), 8.32 (s, 1H*0.17, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 27.7 (*cis*), 29.9 (*trans*), 33.0 (*cis*), 31.9 (*cis*), 32.5 (*cis*), 36.2 (*trans*), 36.3 (*trans*), 37.0 (*trans*), 46.1 (*cis*), 48.2(*trans*), 124.6 (*trans*, Ar), 124.8 (*trans*, Ar), 124.9 (*cis*, Ar), 125.8 (*cis*, Ar), 126.96 (*cis*, Ar), 126.99 (*cis*, Ar), 127.03 (*cis*, Ar), 127.1 (*trans*, Ar), 127.57 (*cis*, Ar), 127.61 (*trans*, Ar), 127.8 (*cis*, Ar), 128.0 (*trans*, Ar), 128.67 (*cis*, Ar), 128.74 (*trans*, Ar), 128.8 (*cis*, Ar), 128.9 (*trans*, Ar), 129.2 (*trans*, Ar), 129.8 (*cis*, Ar), 130.0 (*cis*, Ar), 131.5 (*cis*, Ar), 132.2 (*cis*, Ar), 132.4 (*trans*, Ar), 133.4 (*cis*, Ar), 133.8 (*trans*, Ar), 134.7 (*cis*, Ar), 135.7 (*trans*, Ar), 139.0 (*cis*, Ar), 139.2 (*trans*, Ar), 139.8 (*cis*, Ar), 139.98 (*trans*, Ar), 140.00 (*cis*, Ar), 141.00 (*trans*, Ar), 141.9 (*trans*, Ar), 141.02 (*cis*, Ar), 141.2 (*cis*, Ar), 199.1 (*trans*, C=O), 199.2 (*cis*, C=O).

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{30}H_{25}O$: 401.1905; found: 401.1906.

3,8-Dichloro-6,11,11a,12-tetrahydrotetracen-5(5a*H*)-one (4d, *cis*/*trans* = 75:25)

0.83 g, 62% yield.

IR (neat): 2918, 1685, 1477, 1410, 1234 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.28–2.38 (m, 1H*0.25), 2.55–2.71 (m, 1H*0.75+1H*0.25), 2.75–3.00 (m, 4H*0.75+3H*0.25), 3.03–3.13 (m, 1H*0.75+2H*0.25), 3.17 (dd, *J* = 17.0, 4.2 Hz, 1H*0.75, CH_2), 3.34 (dd, *J* = 17.0, 6.0 Hz, 1H*0.75, CH_2), 3.44 (dd, *J* = 17.7, 5.8 Hz, 1H*0.25, CH_2), 6.93 (d, *J* = 8.4 Hz, 1H*0.75, ArH), 7.05–7.07 (m, 1H*0.75+1H*0.25, ArH), 7.11 (d, *J* = 8.2 Hz, 1H*0.25, ArH), 7.13–7.16 (m, 1H*0.75, ArH), 7.18–7.25 (m, 1H*0.75+2H*0.25, ArH), 7.45 (dd, *J* = 8.1, 2.4 Hz, 1H*0.75, ArH), 7.47 (dd, *J* = 8.2, 2.4 Hz, 1H*0.25, ArH), 7.98 (d, *J* = 2.4 Hz, 1H*0.75, ArH), 8.04 (d, *J* = 2.3 Hz, 1H*0.25, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 27.4 (*cis*), 29.5 (*trans*), 31.2 (*cis*), 32.4 (*cis*), 32.8 (*cis*), 35.8 (*trans*), 35.9 (*trans*), 36.5 (*trans*), 45.4 (*cis*), 47.5 (*trans*), 126.19 (*trans*, Ar), 126.24 (*cis*, Ar), 127.2 (*cis*, Ar), 127.3 (*trans*, Ar), 128.9 (*cis*, Ar), 129.0 (*trans*, Ar), 129.7 (*trans*, Ar), 130.2 (*trans*, Ar), 130.5 (*cis*, Ar), 131.0 (*cis*, Ar), 131.5 (*cis*, Ar), 131.7 (*trans*, Ar), 132.4 (*cis*, Ar), 132.5 (*cis*, Ar), 132.8 (*trans*, Ar), 133.1 (*cis*, Ar), 133.17 (*trans*, Ar), 133.21 (*trans*, Ar), 133.56 (*trans*, Ar), 133.61 (*cis*, Ar), 135.9 (*cis*, Ar), 136.9 (*trans*, Ar), 140.2 (*cis*, Ar), 141.0 (*trans*, Ar), 197.5 (*cis*, C=O), 197.7 (*trans*, C=O).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{18}H_{14}Cl_2O$: 316.0422; found 316.0422.

3,8-Dibromo-6,11,11a,12-tetrahydrotetracen-5(5a*H*)-one (4e, *cis*/*trans* = 83:17)

0.30 g, 52% yield.

IR (neat): 2916, 1685, 1475, 1234, 798, 756 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.57 (dd, *J* = 17.2, 9.8 Hz, 1H*0.17, CH_2), 2.64 (dd, *J* = 17.1, 9.7 Hz, 1H*0.83, CH_2), 2.72–2.86 (m, 2H), 2.87–2.95 (m, 2H), 3.01–3.09 (m, 1H), 3.10–3.18 (m, 1H), 3.34 (dd, *J* = 17.2, 11.0 Hz, 1H*0.83, CH_2), 3.43 (dd, *J* = 17.9, 10.5 Hz, 1H*0.17, CH_2), 6.87 (d, *J* = 8.2 Hz, 1H*0.83, ArH), 6.98 (d, *J* = 8.1 Hz, 1H*0.17, ArH), 7.12–7.17 (m, 1H, ArH), 7.17–7.22 (m, 1H, ArH), 7.30 (s, 1H*0.83, ArH), 7.35 (s, 1H*0.17, ArH), 7.57–7.63 (m, 1H, ArH), 8.13 (d, *J* = 2.2 Hz, 1H*0.83, ArH), 8.19 (d, *J* = 2.3 Hz, 1H*0.17, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 27.3 (*cis*), 29.4 (*trans*), 31.2 (*cis*), 32.4 (*cis*), 32.6 (*cis*), 35.7 (*trans*), 35.9 (*trans*), 36.6 (*trans*), 45.5 (*cis*), 47.5 (*trans*), 119.6 (*cis*), 119.7 (*trans*), 120.9 (*cis*) 121.0 (*trans*), 129.08 (*trans*), 129.12 (*cis*), 130.0 (*trans*), 130.2 (*cis*), 130.3 (*trans*), 130.4 (*trans*), 130.9 (*cis*), 131.3 (*cis*), 131.8 (*cis*), 131.9 (*trans*), 132.7, 133.0, 133.3 (*trans*), 133.4 (*trans*), 136.3, 136.4 (*trans*), 136.5 (*cis*), 137.3 (*trans*), 140.6 (*cis*), 141.4 (*trans*), 197.3 (*cis*), 197.5 (*trans*).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{18}H_{14}Br_2O$: 405.9391; found 405.9395 (*cis*), 405.9411 (*trans*).

Spectral data of 5-phenyl[4]acene **5a** met complete agreement with those in literature.[27]

5-(4-Methylphenyl)[4]acene (5b)

28 mg, 55% yield.

IR (neat): 3043, 3020, 1672, 1217, 893 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.58 (s, 3H, CH_3), 7.27–7.48 (m, 8H, ArH), 7.68 (d, *J* = 9.1 Hz, 1H, ArH), 7.81 (d, *J* = 8.6 Hz, 1H, ArH), 7.99 (d, *J* = 8.2 Hz, 1H, ArH), 8.03 (d, *J* = 8.2 Hz, 1H, ArH), 8.32 (s, 1H, ArH), 8.70 (s, 1H, ArH), 8.72 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.4 (CH_3), 124.8 (Ar), 124.9 (Ar), 125.0 (Ar), 125.2 (Ar), 125.7 (Ar), 126.3 (Ar), 126.5 (Ar), 126.9 (Ar), 127.9 (Ar), 128.5 (Ar), 128.7 (Ar), 129.2 (Ar), 129.5 (Ar), 129.7 (Ar), 130.0 (Ar), 131.1 (Ar), 131.2 (Ar), 131.29 (Ar), 131.32 (Ar), 135.9 (Ar), 137.0 (Ar), 137.1 (Ar).

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{25}H_{19}$: 319.1487; found: 319.1486.

5-[4-(Trifluoromethyl)phenyl][4]acene (5c)

31 mg, 60% yield.

IR (neat): 2925, 1321, 1122, 1065, 744 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.30 (dd, *J* = 8.6, 6.6 Hz, 1H, ArH), 7.34 (dd, *J* = 8.1, 6.7 Hz, 1H, ArH), 7.36–7.43 (m, 2H, ArH), 7.54 (d, *J* = 8.9 Hz, 1H, ArH), 7.63 (d, *J* = 7.6 Hz, 2H, ArH), 7.81 (d, *J* = 8.6 Hz, 1H, ArH), 7.91 (d, *J* = 7.6 Hz, 2H, ArH), 7.99 (d, *J* = 8.6 Hz, 1H, ArH), 8.04 (d, *J* = 8.5 Hz, 1H, ArH), 8.16 (s, 1H, ArH), 8.70 (s, 1H, ArH), 8.75 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 122.3 (q, J_{CF} = 272 Hz, CF_3), 124.9 (Ar), 125.3 (Ar), 125.50 (Ar), 125.53 (q, J_{CF} = 4 Hz, Ar), 125.7 (Ar), 126.2 (Ar), 126.7 (Ar), 127.4 (Ar), 128.0 (Ar), 128.62 (Ar), 128.64 (Ar), 129.0 (Ar), 129.5 (Ar), 129.8 (Ar), 129.9 (q, J_{CF} = 32 Hz, Ar), 131.0 (Ar), 131.2 (Ar), 131.6 (Ar), 131.9 (Ar), 134.9 (Ar), 143.0 (Ar).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 99.4 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{25}H_{15}F_3$: 372.1126; found: 372.1122.

2,9-Dimethyl-11-phenyl[4]acene (5d)

0.16 g, 67% yield.

IR (neat): 2914, 1626, 895, 731, 700 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.39 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 7.20 (br dd, *J* = 7.9, 7.9 Hz, 2H, ArH), 7.35 (s, 1H, ArH), 7.47–7.52 (m, 2H, ArH), 7.56 (s, 1H, ArH), 7.53–7.66 (m, 3H, ArH), 7.88 (d, *J* = 8.8 Hz, 1H, ArH), 7.92 (d, *J* = 8.8 Hz, 1H, ArH), 8.10 (s, 1H, ArH), 8.60 (s, 1H, ArH), 8.64 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.9 (CH_3), 22.3 (CH_3), 124.1 (Ar), 124.5 (Ar), 126.1 (Ar), 126.5 (Ar), 126.6 (Ar), 127.4 (Ar), 127.68 (Ar), 127.75 (Ar), 128.2 (Ar), 128.38 (Ar), 128.45 (Ar), 129.4 (Ar), 129.81 (Ar), 129.84 (Ar), 131.5 (Ar), 131.7 (Ar), 134.4 (Ar), 134.6 (Ar), 135.4 (Ar), 139.4 (Ar).

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{26}H_{21}$: 333.1643; found: 333.1642.

2,9,11-Triphenyl[4]acene (5e)

0.13 g, 83% yield.

IR (neat): 1466, 899, 756, 694 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (dd, *J* = 7.3, 7.3 Hz, 1H, ArH), 7.36 (dd, *J* = 7.3, 7.3 Hz, 1H, ArH), 7.42 (dd, *J* = 7.5, 7.5 Hz, 2H, ArH), 7.46 (dd, *J*= 7.5, 7.5 Hz, 2H, ArH), 7.55 (d, *J* = 6.7 Hz, 2H, ArH), 7.58–7.62 (m, 3H, ArH), 7.64 (d, *J* = 7.5 Hz, 2H, ArH), 7.68 (d, *J* = 8.4 Hz, 2H, ArH), 7.73 (d, *J* = 7.2 Hz, 2H, ArH), 7.85 (s, 1H, ArH), 8.02 (s, 1H, ArH), 8.06 (dd, *J* = 8.4, 8.4 Hz, 1H, ArH), 8.11 (dd, *J* = 8.4, 8.4 Hz, 1H, ArH), 8.32 (s, 1H, ArH), 8.69 (d, *J* = 7.2 Hz, 1H, ArH), 8.73 (d, *J* = 6.9 Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 124.3 (Ar), 125.2 (Ar), 125.6 (Ar), 126.0 (Ar), 126.1 (Ar), 126.3 (Ar), 126.5 (Ar), 127.1 (Ar), 127.28 (Ar), 127.33 (Ar), 127.4 (Ar), 127.7 (Ar), 128.6 (Ar), 128.79 (Ar), 128.81 (Ar), 129.2 (Ar), 129.9 (Ar), 130.0 (Ar), 130.2 (Ar), 130.37 (Ar), 130.42 (Ar), 131.5 (Ar), 131.6 (Ar), 137.2 (Ar), 137.3 (Ar), 137.4 (Ar), 138.9 (Ar), 140.8 (Ar), 141.2 (Ar).

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{36}H_{25}F_3$: 457.1956; found: 457.1957.

2,9-Dichloro-11-phenyl[4]acene (5f)

11 mg, 23% yield.

IR (neat): 1608, 1456, 912, 742 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.30 (dd, *J* = 7.2, 2.0 Hz, 1H, ArH), 7.32 (dd, *J* = 7.2, 2.0 Hz, 1H, ArH), 7.45 (d, *J* = 6.4 Hz, 1H, ArH), 7.46 (d, *J* = 6.4 Hz, 1H, ArH), 7.61–7.68 (m, 4H, ArH), 7.80 (s, 1H, ArH), 7.93 (d, *J* = 9.1 Hz, 1H, ArH), 7.97 (d, *J* = 9.1 Hz, 1H, ArH), 8.14 (s, 1H, ArH), 8.66 (s, 1H, ArH), 8.68 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 124.9 (Ar), 125.0 (Ar), 126.5 (Ar), 126.8 (Ar), 126.9 (Ar), 127.1 (Ar), 127.2 (Ar), 128.0 (Ar), 128.7 (Ar), 129.3 (Ar), 129.4 (Ar), 129.7 (Ar), 129.8 (Ar), 130.0 (Ar), 130.1 (Ar), 130.3 (Ar), 131.1 (Ar), 131.2 (Ar), 131.4 (Ar), 131.6 (Ar), 136.4 (Ar), 138.0 (Ar).

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{24}H_{15}Cl_2$: 372.1126; found: 372.1122.

2,9-Dibromo-11-phenyl[4]acene (5g)

7 mg, 30% yield.

IR (neat): 1593, 914, 887, 742, 702 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.39–7.48 (m, 4H, ArH), 7.59–7.68 (m, 3H, ArH), 7.81 (s, 1H, ArH), 7.85 (d, *J* = 9.0 Hz, 1H, ArH), 7.89 (d, *J* = 9.0 Hz, 1H, ArH), 8.00 (s, 1H, ArH), 8.14 (s, 1H, ArH), 8.63 (s, 1H, ArH), 8.66 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 119.6 (Ar), 120.1 (Ar), 125.0 (Ar), 127.1 (Ar), 127.3 (Ar), 128.0 (Ar), 128.5 (Ar), 128.70 (Ar), 128.74 (Ar), 129.1 (Ar), 129.3 (Ar), 129.4 (Ar), 129.6 (Ar), 129.8 (Ar), 129.9 (Ar), 130.2 (Ar), 130.3 (Ar), 130.6 (Ar), 131.2 (Ar), 132.2 (Ar), 136.4 (Ar), 137.9 (Ar).

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{24}H_{15}Br_2$: 462.9520; found: 462.9525.

11a,12-Dihydro[4]acen-5(11*H*)-one (6a)

1.1 g, 83% yield.

IR (neat): 1655, 1560, 1458, 1281, 760, 669 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.89–2.92 (m, 2H), 3.02–3.18 (m, 3H), 7.21–7.33 (m, 4H), 7.36 (d, *J* = 6.7 Hz, 1H, ArH), 7.39 (d, *J*= 7.4 Hz, 1H, ArH), 7.52 (dd, *J* = 7.4, 7.4 Hz, 1H, ArH), 7.86 (d, *J* = 3.9 Hz, 1H, ArH), 8.11 (d, *J* = 7.8 Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 32.3, 34.9, 35.8, 127.1, 127.2, 127.4, 127.9, 128.1, 129.4, 129.8, 132.8, 133.2, 133.8, 134.7, 135.3, 136.4, 142.0, 186.1 (C=O).

HRMS (APCI$^+$): *m/z* $[M]^+$ calcd for $C_{18}H_{14}O$: 246.1045; found: 246.1039.

3-Benzyl-1,1,1-trifluoro-4-phenylbutan-2-one (8a)

22 g, 81% yield.

IR (neat): 3030, 1757, 1496, 1147, 912, 742 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.77 (dd, *J* = 13.8, 6.7 Hz, 2H, CH_2), 3.06 (dd, *J* = 13.8, 7.6 Hz, 2H, CH_2), 3.56 (tt, *J* = 7.6, 6.7 Hz, 1H, CH), 7.11 (d, *J* = 7.2 Hz, 4H, ArH), 7.24 (t, *J* = 7.0 Hz, 2H, ArH), 7.30 (dd, *J* = 7.2, 7.0 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 37.2 (CH_2), 50.7 (CH), 115.3 (q, J_{CF} = 294 Hz, CF_3), 126.9 (Ar), 128.7 (Ar), 128.9 (Ar), 137.6 (Ar), 194.1 (q, J_{CF} = 35 Hz, C=O).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 82.8 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{15}F_3O$: 292.1075; found: 292.1065.

4-(4-Methylphenyl)-3-(4-methylphenyl)methyl-1,1,1-trifluorobutan-2-one (8b)

1.9 g, 47% yield.

IR (neat): 2925, 1757, 1516, 1211, 1147, 808 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.31 (s, 6H, CH_3), 2.71 (dd, *J* = 13.8, 6.7 Hz, 2H, CH_2), 3.00 (dd, *J* = 13.8, 7.4 Hz, 2H, CH_2), 3.51 (tt, *J* = 7.4, 6.7 Hz, 1H, CH), 6.98 (d, *J* = 7.9 Hz, 4H, ArH), 7.08 (d, *J* = 7.9 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.0 (CH_3), 36.7 (CH_2), 50.7 (CH), 115.4 (q, J_{CF} = 294 Hz, CF_3), 128.8 (Ar), 129.3 (Ar), 134.5 (Ar), 136.4 (Ar), 194.3 (q, J_{CF} = 35 Hz, C=O).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 82.6 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{19}F_3O$: 320.1388; found: 320.1389.

4-(4-Phenylphenyl)-3-(4-phenylphenyl)methyl-1,1,1-trifluorobutan-2-one (8c)

2.7 g, 90% yield.

IR (neat): 3032, 1753, 1487, 1167, 1153, 764 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.84 (dd, *J* = 13.8, 6.8 Hz, 2H, CH_2), 3.13 (dd, *J* = 13.8, 7.6 Hz, 2H, CH_2), 3.63 (tt, *J* = 7.6, 6.8 Hz, 1H, CH), 7.20 (d, *J* = 8.2 Hz, 4H, ArH), 7.34 (tt, *J* = 7.4, 1.0 Hz, 2H, ArH), 7.43 (dd, *J* = 8.1, 7.4 Hz, 4H, ArH), 7.52 (d, *J* = 8.2 Hz, 4H, ArH), 7.57 (d, *J* = 8.1 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 36.7 (CH_2), 50.5 (CH), 115.4 (q, J_{CF} = 293 Hz, CF_3), 127.0 (Ar), 127.3 (Ar), 127.4 (Ar), 128.8 (Ar), 129.4 (Ar), 136.6 (Ar), 139.8 (Ar), 140.6 (Ar), 194.1 (q, J_{CF} = 35 Hz, C=O).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 82.8 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{29}H_{23}F_3O$: 444.1701; found: 444.1704.

4-(4-Chlorophenyl)-3-(4-chlorophenyl)methyl-1,1,1-trifluorobutan-2-one (8d)

16 g, 98% yield.

IR (neat): 2931, 1759, 1493, 1217, 1149, 1093 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.72 (dd, *J* = 13.8, 6.7 Hz, 2H, CH_2), 3.02 (dd, *J* = 13.8, 7.7 Hz, 2H, CH_2), 3.47 (tt, *J* = 7.7, 6.7 Hz, 1H, CH), 7.03 (d, *J* = 8.6 Hz, 4H, ArH), 7.26 (d, *J* = 8.6 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 36.4 (CH_2), 50.4 (CH), 115.3 (q, J_{CF} = 293 Hz, CF_3), 128.9 (ArH), 130.3 (ArH), 133.0 (ArH), 135.7 (ArH), 193.6 (q, J_{CF} = 35 Hz, C=O).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 83.7 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{13}Cl_2F_3$: 360.0296; found: 360.0295.

4-(4-Bromophenyl)-3-(4-bromophenyl)methyl-1,1,1-trifluorobutan-2-one (8e)

14 g, 78% yield.

IR (neat): 3026, 1487, 1163, 1113, 1072, 1011 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 2.70 (dd, *J* = 13.5, 7.0 Hz, 2H, CH_2), 3.00 (dd, *J* = 13.5, 7.0 Hz, 2H, CH_2), 3.47 (tt, *J* = 7.0, 7.0 Hz, 1H, CH), 6.97 (d, *J* = 8.2 Hz, 4H, ArH), 7.41 (d, *J* = 8.2 Hz, 4H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 36.5 (CH_2), 50.2 (CH), 115.3 (q, J_{CF} = 293 Hz, CF_3), 121.1 (Ar), 130.6 (Ar), 131.9 (Ar), 136.3 (Ar), 193.5 (q, J_{CF} = 35 Hz, C=O).

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 82.6 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{13}Br_2F_3$: 447.9267; found: 447.9265.

6-Fluoro-5,12-dihydro[4]acene (9a)

111 mg, 36% yield.

IR (neat): 3024, 1373, 1327, 1279, 1034 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 4.08 (s, 2H, CH_2), 4.14 (s, 2H, CH_2), 7.19–7.25 (m, 2H, ArH), 7.35 (m, 1H, ArH), 7.35–7.38 (m, 1H, ArH), 7.43–7.48 (m, 2H, ArH), 7.52 (s, 1H, ArH), 7.75–7.79 (m, 1H, ArH), 8.03–8.07 (m, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 28.4 (d, J_{CF} = 4 Hz, CH_2), 36.4 (d, J_{CF} = 2 Hz, CH_2), 119.0 (d, J_{CF} = 17 Hz, Ar), 120.2 (d, J_{CF} = 5 Hz, Ar), 120.4 (d, J_{CF} = 4 Hz, Ar), 122.1 (d, J_{CF} = 17 Hz, Ar), 125.4 (Ar), 126.1 (Ar), 126.4 (d, J_{CF} =1 Hz, Ar), 126.9 (d, J_{CF} = 3 Hz, Ar), 127.4 (Ar), 127.7 (Ar), 133.1 (d, J_{CF} = 5 Hz, Ar), 135.5 (Ar), 136.4 (Ar), 136.49 (Ar), 136.52 (Ar), 154.8 (d, J_{CF} = 250 Hz, ArF),

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 32.7 (s, ArF).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{18}H_{13}F$: 248.1001; found: 248. 0999.

12-Phenyl-5,5a,6,11-tetrahydro[4]acene (13a)

41 mg, 83% yield.

IR (neat): 3018, 2927, 1483, 750, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.72–2.85 (m, 2H), 2.85–2.95 (m, 2H), 3.00 (dd, *J* = 13.6, 4.2 Hz, 1H, CH_2), 3.41 (d, *J* = 18.5 Hz, 1H, CH_2), 3.46 (d, *J* = 18.5 Hz, 1H, CH_2), 6.62 (d, *J* = 7.6 Hz, 1H, ArH), 6.98 (d, *J* = 7.0 Hz, 1H, ArH), 7.02 (d, *J* = 7.6 Hz, 1H, ArH), 7.07 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 1H, ArH), 7.10–7.26 (m, 6H, ArH), 7.38 (dddd, *J* = 7.4, 7.4, 1.3, 1.3 Hz, 1H, ArH), 7.43–7.49 (m, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 34.1, 35.6, 35.8, 36.0, 125.3, 126.0, 126.1, 126.29, 126.34, 126.8, 127.1, 127.3, 128.7, 130.0, 133.2, 134.8, 137.0, 137.6, 138.1, 139.7.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{24}H_{20}$: 308.1565; found: 308.1560.

12-(4-Methylphenyl)-5,5a,6,11-tetrahydro[4]acene (13b)

0.43 g, 94% yield.

IR (neat): 3018, 2924, 1483, 910, 766, 729 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.43 (s, 3H, CH_3), 2.70–2.82 (m, 2H), 2.85–2.92 (m, 2H), 2.98 (dd, *J* = 13.2, 3.6 Hz, 1H, CH_2), 3.41 (d, *J* = 18.6 Hz, 1H, CH_2), 3.47 (d, *J* = 18.6 Hz, 1H, CH_2), 6.64 (d, *J* = 7.5 Hz, 1H, ArH), 6.98 (d, *J* = 6.3 Hz, 1H, ArH), 7.01 (d, *J* = 7.5 Hz, 1H, ArH), 7.03–7.19 (m, 7H, ArH), 7.26 (d, *J* = 7.2 Hz, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.3, 34.1, 35.6, 35.9, 36.0, 125.3, 125.96, 126.04, 126.26, 126.31, 127.0, 127.3, 129.4, 129.9, 133.1, 134.9, 136.3, 136.6, 137.06, 137.14, 137.4, 138.1.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{25}H_{22}$: 322.1722; found: 322.1726.

12-[4-(Trifluoromethyl)phenyl]-5,5a,6,11-tetrahydro[4]acene (13c)

0.43 g, 86% yield.

IR (neat): 2931, 1323, 1122, 1066, 739 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.75 (dd, *J* = 13.6, 9.6 Hz, 1H, CH_2), 2.78–2.85 (m, 1H, CH), 2.87 (d, *J* = 14.2 Hz, 1H, CH_2), 2.93 (dd, *J* = 14.2, 6.6 Hz, 1H, CH_2), 3.01 (dd, *J* = 13.6, 4.2 Hz, 1H, CH_2), 3.37 (d, *J* = 19.9 Hz, 1H, CH_2), 3.41 (d, *J* = 19.9 Hz, 1H, CH_2), 6.53 (d, *J* = 7.5 Hz, 1H, ArH), 6.98 (d, *J* = 6.8 Hz, 1H, ArH), 7.02 (dd, *J* = 7.2, 7.2 Hz, 1H, ArH), 7.09 (ddd, *J* = 7.4, 7.4, 1.0 Hz, 1H, ArH), 7.13–7.21 (m, 4H, ArH), 7.27–7.38 (m, 2H, ArH), 7.72 (d, *J* = 7.4 Hz, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 34.1, 35.4, 35.6, 36.0, 124.3 (q, J_{CF} = 273 Hz, CF_3), 125.1, 125.7 (q, J_{CF} = 2 Hz, Ar),126.2, 126.4, 126.47, 126.50, 127.3, 127.4, 129.1 (q, J_{CF} = 32 Hz, Ar), 130.5, 132.1, 134.8, 136.3, 136.5, 137.9, 138.5, 143.6.

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 99.4 (s, CF_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{25}H_{19}F_3$: 376.1439; found: 376.1438.

2,9-Dimethyl-12-phenyl-5,5a,6,11-tetrahydro[4]acene (13d)

0.24 g, 93% yield.

IR (neat): 2922, 1491, 1441, 908, 810 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.15 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.67–2.80 (m, 2H), 2.81–2.88 (m, 2H), 2.94 (dd, *J* = 13.4, 3.8 Hz, 1H, CH_2), 3.38 (br s, 2H), 6.43 (s, 1H, ArH), 6.80 (s, 1H, ArH), 6.89 (d, *J* = 7.4 Hz, 1H, ArH), 6.95 (d, *J* = 7.6 Hz, 1H, ArH), 7.06 (d, *J* = 7.4 Hz, 2H, ArH), 7.11–7.29 (m, 2H, ArH), 7.38 (dd, *J* = 7.4, 7.4 Hz, 1H, ArH), 7.42–7.48 (m, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.0, 21.2, 34.1, 35.3, 35.4, 36.3, 126.0, 126.6, 126.7, 126.9, 127.2, 128.1, 128.6, 130.0, 131.9, 133.2, 135.0, 135.7, 135.8, 136.8, 137.8, 139.8.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{26}H_{24}$: 336.1878; found: 336.1878.

2,9,12-Triphenyl-5,5a,6,11-tetrahydro[4]acene (13e)

0.19 g, 80% yield.

IR (neat): 3028, 1481, 908, 760, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.81 (dd, *J* = 13.6, 9.9 Hz, 1H, CH_2), 2.83–2.91 (m, 1H), 2.93 (d, *J* = 14.4 Hz, 1H, CH_2), 2.98 (dd, *J* = 14.1, 6.0 Hz, 1H, CH_2), 3.06 (dd, *J* = 13.6, 4.0 Hz, 1H, CH_2), 3.50 (d, *J* = 19.0 Hz, 1H, CH_2), 3.55 (d, *J* = 19.0 Hz, 1H, CH_2), 6.87 (d, *J* = 1.6 Hz, 1H, ArH), 7.20–7.28 (m, 6H, ArH), 7.28–7.34 (m, 4H, ArH), 7.35–7.42 (m, 6H, ArH), 7.43–7.49 (m, 2H, ArH), 7.54 (d, *J* = 7.3 Hz, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 34.4, 35.3, 35.6, 36.1, 124.2, 124.8, 124.9, 126.2, 126.8, 126.96, 127.00, 127.5, 127.8, 128.55, 128.65, 128.8, 130.0, 133.4, 134.0, 137.2, 137.3, 137.9, 139.39, 139.43, 139.5, 141.1, 141.4.

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{36}H_{29}$: 461.2269; found: 461.2269.

2,9-Dichloro-12-phenyl-5,5a,6,11-tetrahydro[4]acene (13f)

0.23 g, 89% yield.

IR (neat): 2931, 1477, 904, 727, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.68 (dd, *J* = 13.8, 9.8 Hz, 1H, CH_2), 2.71–2.80 (m, 1H), 2.80 (dd, *J* = 13.8, 13.8 Hz, 1H, CH_2), 2.88 (dd, *J* = 13.8, 4.8 Hz, 1H, CH_2), 2.96 (dd, *J* = 13.5, 3.8 Hz, 1H, CH_2), 3.35 (d, *J* = 18.7 Hz, 1H, CH_2), 3.40 (d, *J* = 18.7 Hz, 1H, CH_2), 6.59 (d, *J* = 1.9 Hz, 1H, ArH), 6.97 (s, 1H, ArH), 7.04 (dd, *J* = 7.9, 1.9 Hz, 1H, ArH), 7.06–7.23 (m, 5H, ArH), 7.40 (dd, *J* = 7.1, 7.1 Hz, 1H, ArH), 7.44–7.53 (m, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 34.0, 34.8, 35.0, 35.8, 125.3, 126.0, 126.1, 127.3, 128.2, 128.6, 129.0, 129.8, 131.8, 132.1, 133.0, 136.2, 138.1, 138.4, 138.48, 138.52.

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}Cl_2$: 377.0864; found: 377.0867.

2,9-Dibromo-12-phenyl-5,5a,6,11-tetrahydro[4]acene (13g)

0.14 g, 70% yield.

IR (neat): 2929, 1473, 1074, 806, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.65 (dd, *J* = 13.8, 9.6 Hz, 1H, CH_2), 2.69–2.81 (m, 2H), 2.85 (dd, *J* = 13.4, 4.4 Hz, 1H, CH_2), 2.93 (dd, *J* = 13.8, 4.0 Hz, 1H, CH_2), 3.34 (d, *J* = 19.6 Hz, 1H, CH_2), 3.39 (d, *J* = 19.6 Hz, 1H, CH_2), 6.73 (d, *J* = 1.7 Hz, 1H, ArH), 7.02 (d, *J* = 7.2 Hz, 1H, ArH), 7.03 (d, *J* = 6.2 Hz, 1H, ArH), 7.08–7.21 (m, 2H, ArH), 7.12 (s, 1H, ArH), 7.19 (dd, *J* = 7.9, 1.9 Hz, 1H, ArH), 7.26 (dd, *J* = 8.0, 1.8 Hz, 1H, ArH), 7.40 (dd, *J* = 7.2, 7.2 Hz, 1H, ArH), 7.43–7.51 (m, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 34.0, 34.9, 35.1, 35.7, 119.9, 120.2, 127.3, 128.1, 128.6, 128.9, 129.0, 129.05, 129.07, 129.8, 130.2, 132.9, 133.5, 136.7, 138.1, 138.5, 138.8, 138.9.

HRMS (APCI$^+$): *m/z* $[M+H]^+$ calcd for $C_{24}H_{19}Br_2$: 466.9833; found: 466.9831.

6,11,11a,12-Tetrahydrotetracen-5-yl trifluoromethanesulfonate (15a)

0.11 g, 87% yield.

IR (neat): 2935, 1415, 1207, 1138, 972, 744 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.72–2.82 (m, 2H, CH_2), 2.85–2.96 (m, 3H, CH_2 + CH), 3.83 (d, *J* = 19.5 Hz, 1H, CH_2), 3.88 (d, *J* = 19.5 Hz, 1H, CH_2), 7.14–7.28 (m, 7H, ArH), 7.33 (d, *J* = 7.3 Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 30.6, 34.2, 34.9, 37.0, 118.5 (q, J_{CF} = 321 Hz, CF_3), 121.1, 126.6, 126.9, 127.0, 127.4, 127.5, 127.9, 128.3, 129.7, 133.2, 133.8, 134.9, 137.1, 139.8.

^{19}F NMR ($CDCl_3$, 476 MHz): δ = 88.1 (s, CF_3).

HRMS (EI): *m/z* $[M–SO_2CF_3]^+$ calcd for $C_{18}H_{15}O$: 247.1123; found: 247.1120.

6-Methyl-6,11,11a,12-tetrahydro[4]acen-5(5a*H*)-one (16a, dr = 78:22)

0.23 g, 86% yield.

IR (neat): 2922, 1680, 1603, 1282, 744 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.48 (d, *J* = 7.0 Hz, 3H*0.78, CH_3), 1.54 (d, *J* = 7.4 Hz, 3H*0.22, CH_3), 2.18–2.28 (m, 1H*0.78), 2.35 (dd, *J* = 13.8, 7.8 Hz, 1H*0.78, CH_2), 2.78–2.90 (m, 3H*0.22), 2.77–2.89 (m, 2H*0.78), 2.91–2.98 (m, 1H*0.78), 3.00 (dd, *J* = 6.1, 6.1 Hz, 1H*0.22), 3.08 (dd, *J* = 4.8, 4.8 Hz, 1H*0.22), 3.13 (dd, *J* = 16.5, 4.1 Hz, 1H*0.78, CH_2), 3.24–3.31 (m, 2H*0.22), 3.65 (qd, *J* = 7.1, 7.0 Hz, 1H*0.78, CH), 6.99 (d, *J* = 7.5 Hz, 1H*0.22), 7.07–7.12 (m, 1H*0.22, ArH), 7.10 (d, *J* = 6.4 Hz, 2H*0.78, ArH), 7.14–7.23 (m, 2H*0.22, ArH), 7.18–7.22 (m, 1H*0.78, ArH), 7.24– 7.28 (m, 1H*0.22, ArH), 7.25 (d, *J* = 8.5 Hz, 1H*0.78, ArH), 7.29–7.34 (m, 1H*0.22, ArH), 7.31 (d, *J* = 8.5 Hz, 1H*0.78, ArH), 7.33 (d, *J* = 8.0 Hz, 1H*0.78, ArH), 7.46–7.50 (m,

1H*0.22, ArH), 7.48 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H*0.78, ArH), 7.94 (d, *J* = 7.8 Hz, 1H*0.22, ArH), 8.06 (d, *J* = 8.0 Hz, 1H*0.78, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 19.2 (minor, CH_3), 26.5 (major, CH_3), 32.2 (major), 32.5 (minor), 34.5 (minor), 34.6 (minor), 35.6 (minor), 37.1 (major), 37.4 (major), 37.8 (major), 51.0 (minor), 57.2 (major), 125.3 (major, Ar), 125.8 (minor, Ar), 126.1 (minor, Ar), 126.6 (major, Ar), 126.6 (minor, Ar), 126.7 (major, Ar), 126.7 (minor, Ar), 126.9 (minor, Ar), 127.4 (major, Ar), 128.0 (major, Ar), 128.5 (major, Ar), 128.6 (major, Ar), 128.9 (minor, Ar), 129.3 (minor, Ar), 132.6 (minor, Ar), 133.3 (major, Ar), 133.9 (minor, Ar), 134.8 (major, Ar), 140.2 (minor, Ar), 141.5 (major, Ar), 141.7 (minor, Ar), 142.7 (major, Ar), 198.9 (major, C=O), 199.7 (minor, C=O).

HRMS (APCI$^+$): *m/z* [M]$^+$ calcd for $C_{19}H_{18}O$: 262.1358; found: 262.1365.

6-Phenyl-6,11,11a,12-tetrahydro[4]acen-5(5a*H*)-one (16b, dr = 93:7)

0.42 g, 65% yield.

IR (neat): 2906, 1684, 1601, 1284, 750 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.37–2.47 (m, 1H*0.07), 2.86–3.04 (m, 4H), 3.12–3.19 (m, 1H*0.93), 3.21 (d, *J* = 4.2 Hz, 1H*0.07), 3.37 (dd, *J* = 6.1, 4.8 Hz, 1H*0.93), 4.72 (d, *J* = 6.3 Hz, 1H*0.93, CH), 4.94 (d, *J* = 8.0 Hz, 1H*0.07), 6.97–7.05 (m, 4H*0.93, ArH), 6.97–7.05 (m, 3H*0.07, ArH), 7.08–7.23 (m, 5H*0.07, ArH), 7.10 (d, *J* = 7.9 Hz, 2H*0.93, ArH), 7.12–7.21 (m, 5H*0.93, ArH), 7.28 (d, *J* = 8.5 Hz, 1H*0.07, ArH), 7.29–7.33 (m, 2H*0.07, ArH), 7.31 (t, *J* = 7.4 Hz, 1H*0.93, ArH), 7.47 (t, *J* = 7.4 Hz, 1H*0.07, ArH), 7.80 (d, *J* = 7.9 Hz, 1H*0.93, ArH), 7.98 (d, *J* = 8.4 Hz, 1H*0.07, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 33.3 (major), 33.4 (major), 33.8 (major), 37.3 (minor), 37.80 (minor), 37.83 (minor), 43.8 (minor), 46.7 (major), 51.5 (major), 58.2 (minor), 125.7 (minor, Ar), 125.8 (minor, Ar), 126.0 (major, Ar), 126.3 (major, Ar), 126.7 (major, Ar), 126.7 (minor, Ar), 126.8 (minor, Ar), 127.0 (major, Ar), 127.5 (major, Ar), 127.9 (minor, Ar), 128.4 (minor, Ar), 128.5 (major, Ar), 128.5 (minor, Ar), 129.0 (minor, Ar), 129.1 (major, Ar), 129.6 (major, Ar), 130.4 (major, Ar), 130.7 (minor, Ar), 133.0 (major, Ar), 133.3 (minor, Ar), 135.3 (major, Ar), 137.9 (major, Ar), 139.6 (minor, Ar), 141.8 (major, Ar), 142.2 (major, Ar), 142.4 (minor, Ar), 148.8 (minor, Ar), 198.3 (minor, C=O), 199.9 (major, C=O).

HRMS (APCI$^+$): *m/z* [M]$^+$ calcd for $C_{24}H_{20}O$: 324.1514; found: 324.1514.

11,12-Dimethyl-5,5a,6,11-tetrahydro[4]acene (17a)

0.15 g, 71% yield.

IR (neat): 2922, 1485, 1450, 756, 729 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.36 (d, *J* = 7.4 Hz, 3H, CH_3), 2.16 (d, *J* = 2.5 Hz, 3H, CH_3), 2.43–2.53 (m, 1H), 2.70 (dd, *J* = 14.7, 14.7 Hz, 1H), 2.77 (d, *J* = 5.3 Hz, 1H), 2.78–2.84 (m, 2H), 4.01 (q, *J* = 7.4 Hz, 1H, CH), 7.10 (dd, *J* = 7.2, 1.2 Hz, 1H, ArH), 7.12–7.17 (m, 4H, ArH), 7.17–7.22 (m, 2H, ArH), 7.29 (d, *J* = 7.8 Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.1 (CH_3), 24.5, 34.7, 36.7, 36.9, 38.5, 122.6, 125.2, 125.8, 126.0, 126.4, 126.7, 126.8, 127.4, 127.6, 135.7, 137.2, 137.5, 141.1, 142.1.

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{20}H_{20}$: 260.1565; found 260.1566.

11-Methyl-12-phenyl-5,5a,6,11-tetrahydro[4]acene (17b)

A yellow solid, Mp. 134.9–135.9 °C, 0.13 g, 74% yield.

IR (neat): 2924, 1483, 1458, 766, 750, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.12 (d, *J* = 7.3 Hz, 3H, CH_3), 2.69–2.78 (m, 1H, ArH), 2.85–2.95 (m, 4H), 3.80 (q, *J* = 7.3 Hz, 1H, CH), 6.50 (d, *J* = 7.7 Hz, 1H, ArH), 6.98–7.02 (m, 2H, ArH), 7.08 (dd, *J* = 7.4, 7.4 Hz, 1H, ArH), 7.10–7.23 (m, 5H, ArH), 7.23–7.29 (m, 1H, ArH), 7.39 (dd, *J* = 7.4, 7.4 Hz, 1H, ArH), 7.41–7.50 (m, 2H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 24.4 (CH_3), 34.6, 36.79, 36.81, 38.4, 125.5, 126.1, 126.3, 126.77, 126.79, 126.82, 127.2, 127.7, 128.6, 130.3, 130.5, 133.9, 135.3, 137.0, 137.8, 139.7, 141.9, 142.7.

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{25}H_{22}$: 322.1722; found 322.1734.

11,12-Diphenyl-5,5a,6,11-tetrahydro[4]acene (17c)

Colorless crystals, Mp. 211.7–212.5 °C, 0.12 g, 64% yield.

IR (neat): 3020, 1491, 908, 729, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.57 (dd, *J* = 13.2, 13.2 Hz, 1H, CH_2), 2.76 (dd, *J* = 13.5, 4.8 Hz, 1H, CH_2), 2.82 (dd, *J* = 12.5, 4.8 Hz, 1H, CH_2), 2.91 (dd, *J* = 9.9, 5.0 Hz, 1H), 3.10 (dd, *J* = 15.6, 15.6 Hz, 1H, CH_2), 5.02 (s, 1H, CH), 6.63 (d, *J* = 7.2 Hz, 1H, ArH), 6.98 (br s, 1H, ArH), 7.01–7.06 (m, 2H, ArH), 7.10 (dd, *J* = 7.2, 7.2 Hz, 2H, ArH), 7.12–7.17 (m, 4H, ArH), 7.19 (ddd, *J* = 7.1, 7.1, 1.6 Hz, 1H, ArH), 7.21–7.33 (m, 6H, ArH), 7.43 (br s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 34.3, 35.9, 37.3, 48.6 (CH), 125.7, 126.1, 126.4, 126.5, 126.6, 126.7, 126.8, 127.0, 127.78, 127.83, 128.4, 130.1, 136.1, 136.3, 137.6, 138.3, 139.1, 139.3, 139.8, 143.5.

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{30}H_{24}$: 384.1878; found 384.1890.

5,6-Dimethyl-5,12-dihydro[4]acene (18a)

38 mg, 77% yield.

IR (neat): 2960, 1450, 1020, 874, 744 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.38 (d, *J* = 7.4 Hz, 3H, CH_3), 2.75 (s, 3H, CH_3), 4.01 (d, *J* = 17.6 Hz, 1H, CH_2), 4.29 (d, *J* = 17.6 Hz, 1H, CH_2), 4.56 (q, *J* = 7.4 Hz, 1H, CH), 7.17–7.23 (m, 2H, ArH), 7.30 (d, *J* = 6.8 Hz, 1H, ArH), 7.32 (d, *J* = 6.8 Hz, 1H, ArH), 7.38–7.45 (m, 2H, ArH), 7.60 (s, 1H, ArH), 7.74 (d, *J* = 7.7 Hz, 1H, ArH), 8.03 (d, *J* = 8.3 Hz, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.9 (CH_3), 21.9 (CH_3), 36.0, 39.0, 124.0 (Ar), 124.3 (Ar), 124.9 (Ar), 125.1 (Ar), 126.2 (Ar), 126.5 (Ar), 127.35 (Ar), 127.42 (Ar), 127.9 (Ar), 129.5 (Ar), 131.8 (Ar), 132.2 (Ar), 134.4 (Ar), 136.0 (Ar), 137.9 (Ar), 142.2 (Ar).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{20}H_{18}$: 258.1409; found 258.1404.

5-Methyl-6-phenyl-5,12-dihydro[4]acene (18b)

Colorless crystals, Mp. 136.5–137.1 °C, 22 mg, 77% yield.

IR (neat): 2964, 2925, 1506, 1030, 750 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.23 (d, *J* = 7.3 Hz, 3H, CH_3), 4.07 (q, *J* = 7.3 Hz, 1H, CH), 4.11 (d, *J* = 17.7 Hz, 1H, CH_2), 4.38 (d, *J* = 17.7 Hz, 1H, CH_2), 7.11 (d, *J* = 7.6 Hz, 1H, ArH), 7.13–7.20 (m, 2H, ArH), 7.21–7.24 (m, 1H, ArH), 7.25–7.29 (m, 2H, ArH), 7.33 (d, *J* = 6.7 Hz, 1H, ArH), 7.38–7.41 (m, 1H, ArH), 7.43 (d, *J* = 6.8 Hz, 1H, ArH), 7.47–7.57 (m, 3H, ArH), 7.80 (d, *J* = 8.0 Hz, 1H, ArH), 7.80 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 22.4 (CH_3), 36.1, 39.3, 125.12 (Ar), 125.15 (Ar), 125.7 (Ar), 126.1 (Ar), 126.4 (Ar), 126.5 (Ar), 127.0 (Ar), 127.16 (Ar), 127.20 (Ar), 127.5 (Ar), 128.2 (Ar), 128.5 (Ar), 130.1 (Ar), 130.6 (Ar), 132.0 (Ar), 132.1 (Ar), 134.6 (Ar), 136.0 (Ar), 136.9 (Ar), 138.1 (Ar), 139.3 (Ar), 142.4 (Ar).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{25}H_{20}$: 320.1565; found 320.1549.

5,6-Diphenyl-5,12-dihydro[4]acene (18c)

Colorless crystals, Mp. 202.7—203.2 °C, 40 mg, 76% yield.

IR (neat): 3057, 1502, 1261, 1030, 731 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.97 (s, 2H, CH_2), 5.27 (s, 1H, CH), 6.86 (d, *J* = 7.0 Hz, 2H, ArH), 7.03–7.10 (m, 3H, ArH), 7.12 (d, *J* = 7.6 Hz, 1H, ArH), 7.15–7.22 (m, 2H, ArH), 7.23–7.34 (m, 5H, ArH), 7.37–7.46 (m, 3H, ArH), 7.48 (dd, *J* = 8.2, 8.2 Hz, 1H, ArH), 7.85 (d, *J* = 8.0 Hz, 1H, ArH), 7.86 (s, 1H, ArH).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 36.9 (CH_2), 49.4 (CH), 125.3 (Ar), 125.5 (Ar), 125.76 (Ar), 125.83 (Ar), 126.3 (Ar), 126.5 (Ar), 126.7 (Ar), 127.27 (Ar), 127.30 (Ar), 127.57 (Ar), 127.60 (Ar), 127.9 (Ar), 128.0 (Ar), 128.1 (Ar), 128.3 (Ar), 130.1 (Ar), 130.3 (Ar), 131.9 (Ar), 132.4 (Ar), 135.5 (Ar), 136.1 (Ar), 137.3 (Ar), 138.2 (Ar), 138.8 (Ar), 140.9 (Ar), 142.4 (Ar).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{30}H_{22}$: 382.1722; found 382.1732.

Funding Information

This research was financially supported by JSPS KAKENHI Grant Number JP19H02707 (J.I.) in Grant-in-Aid for Scientific Research (B), JSPS KAKENHI Grant Number 20K21186 (J.I.) in Grant-in-Aid for Challenging Research (Exploratory), and JSPS KAKENHI Grant Number 20K05486 (K.F.) in Grant-in-Aid for Scientific Research (C).

Acknowledgment

TOSOH FINECHEM CORPORATION is acknowledged for the generous gift of Ruppert's reagent. Central Glass Co., Ltd. is acknowledged for the generous gifts of HFIP, TfOH, and Tf_2O. We thank Ms. K. Kudo for the collection of spectral data of compounds.

Supporting Information

YES

Primary Data

NO

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(20) Under microwave irradiation, partial dehydrogenation products **14** were obtained as a mixture of two isomers.

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