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Brønsted Acid-Mediated Domino One-Pot Dual C−C Bond Formation: Chemoselective Synthesis of Fused Tricyclic Ketones

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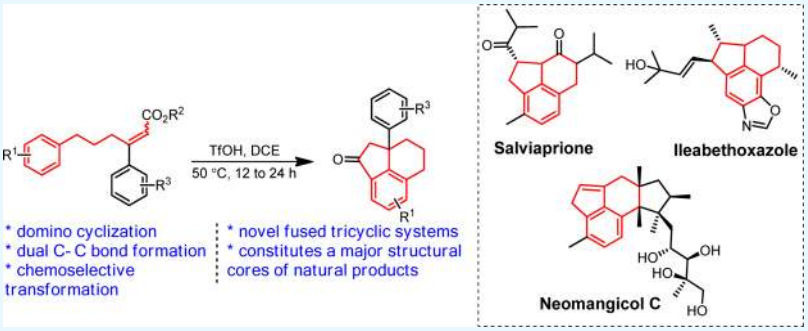
Supporting Information



ABSTRACT: A chemoselective synthesis of fused novel tricyclic motifs via a facile domino intramolecular cyclization is presented. The strategy enables the formation of dual C−C bond via intramolecular Friedel−Crafts alkylation followed by acylation to accomplish fused tricyclic ketones. Significantly, these fused tricyclic compounds are ubiquitous and constitute major structural cores of natural products.

INTRODUCTION

Domino one-pot strategies have become crucial for the construction of multiple bonds in a single reaction vessel. Friedel−Crafts reaction has been long known as one of the classical methods for the construction of C−C bonds.[1] This reaction is popular for the synthesis of alkyl arenes and aryl ketones through Friedel−Crafts alkylation and Friedel−Crafts acylation, respectively. Over the time, a broad range of Lewis and Brønsted acids in stoichiometric or sub-stoichiometric amounts have been employed toward aromatic electrophilic substitutions.[2−5] In particular, the Friedel−Crafts acylation, is an indispensible method for the synthesis of feedstock chemicals, useful synthons, and fine chemicals.[6] Of late, this facile method has been manipulated using novel precursors to afford varied annulated carbocyclic products. Among them, the fused tricyclic compounds[7] and the spirocyclic compounds[8] have been of great interest.

The fused tricyclic core is present as an integral part in a wide variety of naturally occurring compounds. For example, diterpenoid salviaprione,[9] diterpene alkaloid ileabethoxazole,[10] and sesteterpenoid neomangicol **C**[11] constitute a very distinctive fused tricyclic core part and are reported to show significant biological properties against bacillary dysentery, diarrhea, abdominal pain, influenza, and antibacterial properties. The research on *Incarvillea delavayi*by Zhang and his associates led to the isolation of incarviatone **A**, with a structurally unique natural product hybrid with a fused tricyclic core.[12] The fused tricyclic moiety also forms the part structure in some secondary metabolites such as hypoxylonol **B**,[13] daldinone **A**,[14] and hypoxylonol **C**[15] that exhibit cytotoxic activities and antiangiogenic activity against endothelial cells (Figure 1).

Owing to the significance of such scaffolds, numerous reports are described that utilized various transition metals as well as acid catalysis for the synthesis. Some interesting routes on the synthesis of tricyclic fused systems include cyclization of dienes, diynes, and enynes involving the transition metal catalysis.[16] Although acid-mediated approaches for various annulations are abundant,[17] in particular, pathways for the synthesis of tricyclic fused systems are scarcely explored.[18] In this context, highly efficient synthetic routes to obtain diverse tricyclic fused carbocycles from readily available starting materials are still in great demand.

Thus, owing to the omnipresence of the fused and spirocyclic compounds in the nature, we were inspired to develop a facile route toward the synthesis of fused tricyclic and spirocyclic compounds. In continuation to our interest on the development of domino one-pot processes,[19] particularly, using acid-mediated annulations,[20] recently, a practical strategy for novel spiro-tetracyclic compounds has been accomplished.[19a] Herein, we present an efficient chemoselective domino cyclization strategy for the synthesis of novel fused tricyclic ketones. This process effectively involves the formation of dual C−C bond via Friedel−Crafts alkylation and Friedel−Crafts acylation sequence. Notably, readily accessible and inert substituted cinnamic acid esters have been employed for this domino

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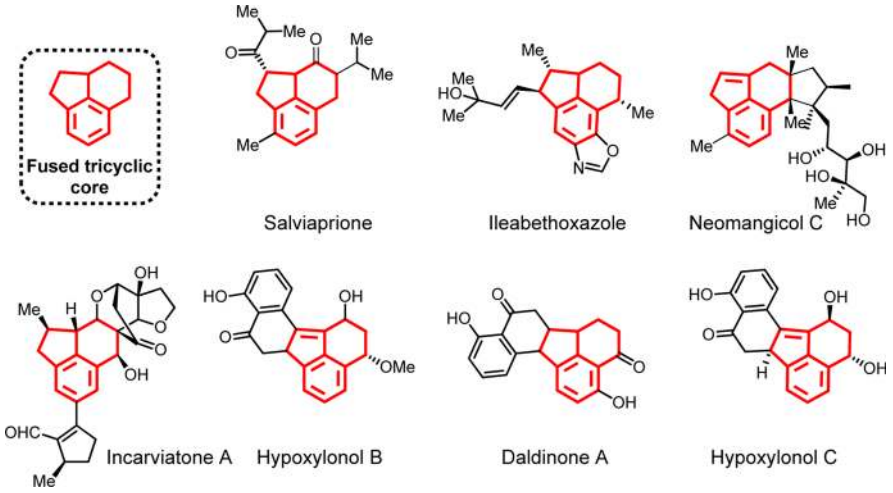
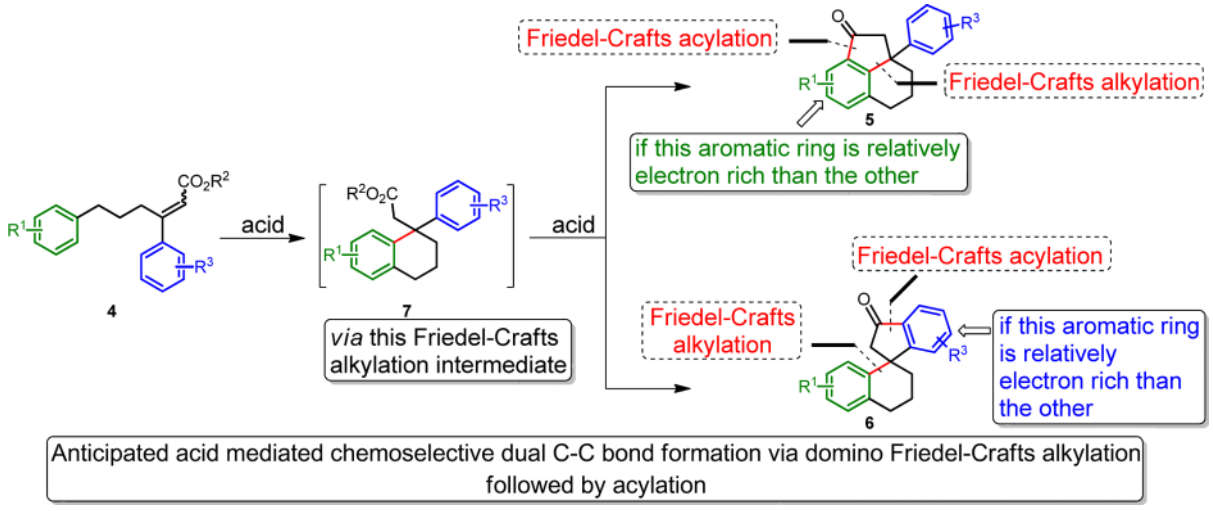


Figure 1. Representative examples of natural products comprising the fused tricyclic core part.

Scheme 1. Proposed Strategic Analysis for Chemoselective Synthesis of Novel Fused and Spirocyclic Compounds



strategy in the presence of Brønsted acid. Significantly, these fused tricyclic ketones constitute a major structural core of natural products of biological relevance.

RESULT AND DISCUSSION

We supposed that the electronic and steric effects of substituents on either aromatic rings of the cinnamic acid esters **4** would play a crucial role on the chemoselective outcome of the products. Thus, it was envisioned that the reaction of **4** in the presence of a strong acid would initially proceed via an intramolecular Friedel–Crafts alkylation to generate the bicyclic tetrahydronaphthalene intermediate **7**. It was contemplated that the formation of fused [5,6,6] tricyclic ketone **5** could be feasible, via a chemoselective intramolecular acylation from the intermediate **7**, if the aromatic ring of alkyl tether is relatively more electron rich than the β-aromatic ring of **4** (Scheme 1). Conversely, the reaction would also afford the spiro-tetracyclic ketone **6** from the same bicyclic intermediate **7**, if the β-aromatic ring is electron richer than the alkyl-tethered aromatic ring of **4** because the spirocyclic ketone **6** would be relatively more thermodynamically stable than the rigid fused [5,6,6] tricyclic ketones **5**. The required cinnamic acid esters **4** can be prepared using Heck coupling and Wittig–Horner–Wadsworth–Emmons protocol.

The synthesis of precursors, cinnamic acid ester derivatives **4** has been initiated from benzaldehydes. Thus, the reaction of benzaldehydes with allylzinc bromide, under sonochemically accelerated conditions, furnished the corresponding homo-allylic alcohols **2**, in near quantitative yields. The Heck coupling of homo-allylic alcohols **2** with iodoarenes **1** gave ketones **3**. Finally, the alkyl-tethered β-aryl-α,β-unsaturated esters **4** were accomplished from **3**, using standard Wittig–Horner–Wadsworth–Emmons conditions (Scheme 2). It is worth noting that the cinnamic acid esters **4** were isolated as an inseparable mixture of geometrical (E + Z) isomers.

To initiate the study for the feasibility of final intramolecular domino cyclization, we explored the reaction on the ester **4ca** with different acids. To begin with, the ester **4ca** was treated with stoichiometric amounts of the Lewis acids. During these trials, $FeCl_3$ in 1,2-dichloroethane (DCE) solvent under heating conditions was found to yield the required fused tricyclic product **5ca** in very poor yield (Table 1; entry 1), whereas $ZnCl_2$ and $AlCl_3$ did not furnish the desired product **5ca** and inconclusive multiple spots were seen on TLC (Table 1; entries 2 & 3). We realized the requirement for a much stronger acid and thus opted sulfuric acid for the task. The reaction was not progressive under ambient conditions (Table 1; entry 4), and in-spite of refluxing the reaction mixture, very minimum

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Scheme 2. Synthetic Strategy for the Formation of Esters 4 from the Corresponding Iodoarenes 1 and Homoallylic Alcohols 2 as Precursors

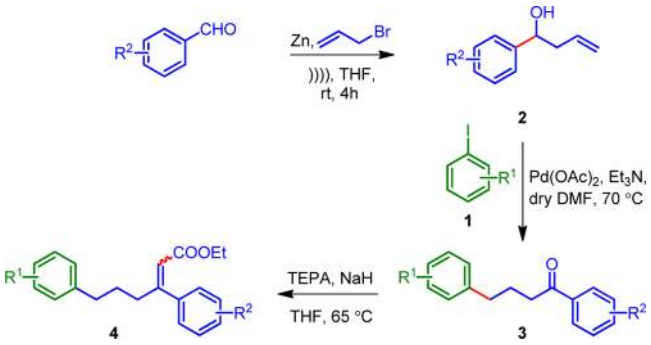
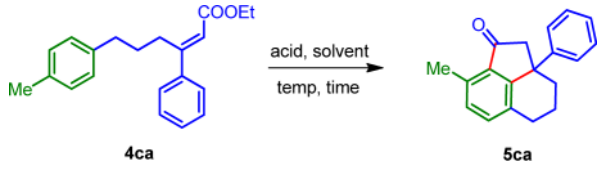


Table 1. Optimization for the Fused Tricyclic Compound 5ca[a,b]



Entry	Acid (equiv)	Solvent (2 mL)	Temp (°C)	Time (h)	Yield (%) 5ca
1	$FeCl_3$ (5)	DCE	80	24	20[c]
2	$ZnCl_2$ (5)	DCE	80	12	[d]
3	$AlCl_3$ (5)	DCE	80	12	[d]
4	H_2SO_4 (3)	DCE	rt	12	
5	H_2SO_4 (3)	DCE	80	24	[e]
6	*p*-TSA (3)	DCE	80	24	
7	CH_3SO_3H (5)	DCE	80	24	37
8	TfOH (1)	DCE	rt	24	
9	TfOH (1)	DCE	80	24	45[c]
10	TfOH (3)	DCE	80	24	55[c]
11	**TfOH (3)**	**DCE**	**50**	**24**	**86**
12	TfOH (3)	$CHCl_3$	50	30	35

[a]Reactions were performed on 0.5 mmol scale. [b]Yields are of chromatographically purified compounds. [c]Starting material was present and was not recovered. [d]Inconclusive multiple spots seen on TLC. [e]Very less conversion to product analyzed on TLC.

conversion to the product **5ca** was observed on TLC (Table 1; entry 5). However, the reaction with *p*-TSA also failed to show any progress in the reaction (Table 1; entry 6), whereas methanesulphonic acid gave product **5ca**, albeit in low yield (Table 1; entry 7). As we have worked extensively on Brønsted acid-mediated conversions, we checked the feasibility of the reaction with superacid triflic acid. Although under ambient conditions, no progress was noted (Table 1; entry 8), but delightfully, when refluxed, it led to product **5ca**, in moderate yield (Table 1; entry 9). Further increase in the triflic acid equivalence led to slight increase in the yield of product **5ca** accompanied with the formation of many other undesirable spots (Table 1; entry 10). In a view to obtain a cleaner conversion and improve the yield, the reaction with triflic acid was performed under slightly reduced temperature (50 °C). Gratifyingly, the fused tricyclic ketone product **5ca** was obtained in very good yield (Table 1; entry 11). When chloroform was used as a solvent, even under prolonged reaction time, the yield of product **5ca** was poor (Table 1; entry 12).

By employing these optimized conditions (Table 1, entry 11), we proceeded toward the study of the scope and applicability of the methodology and explored the strategy on various substituted iodoarenes **1** and on a variety of homoallylic alcohols **2**. It is worth to mention that in all the substrates, purposefully, it was ensured that the alkyl tethered aromatic ring is relatively more electron richer than *β*-aryl moiety of the cinnamic acid esters **4ca**−**4ch**. Thus, only this aromatic ring would chemoselectively compete in both cyclizations to give the desired fused tricyclic ketones **5**. To our delight, the scope of the methodology was observed to be wide and delivered the expected products **5ca**−**5ch**, in moderate to excellent yields (Table 2). Significantly, the method was amenable to the esters bearing simple to highly electron-rich aromatic rings of alkyl tether. The method was also studied on the variedly substituted *β*-aryl moiety of cinnamic acid esters. For example, even suitable with electron-deactivating groups like F, Cl, and Br substituents on the aromatic ring of the *β*-aryl moiety (Table 2; **5af**−**5ch**). Notably, the product **5ch** with Br substituent is interesting, as it could extend the strategy for the synthesis of various coupled products, under transition metal catalysis. Upon close observation, the formation of tricyclic ketone **5cd** from the ester **4cd** seems unusual. However, this can be explained from the fact that the aromatic ring of the bicyclic naphthalene intermediate is slightly electron rich than the *β*-para-tolyl group. Moreover, the methyl group of bicyclic intermediate is suitably situated at the orthoposition to the incoming acyl group, which favors the fused tricyclic ketone **5cd**. However, in the case of *β*-para-tolyl moiety, the methyl group is at the metaposition to the incoming acyl functionality that disfavors this cyclization. Significantly, all the tricyclic ketone products possess a dense substitution pattern on the aromatic ring of fused tricyclic systems (i.e. 1, 2, 3 or 1, 2, 3, 4 or 1, 2, 3, 4, 5 substitution pattern). This is very unusual to notice, as the steric thwart due to 1, 2, 3 ... substitutions is overcome, and this is probably due to the key role played by the electronic factors of the aromatic substituents. It is worth noting that in our previous results, the formation of tricyclic ketones were restricted because of severe conformational strain in fused [5,5,6] tricyclic system, rather selectively afforded the less strained spiro-tetracyclic ketones.[19a] However, the present strategy is based on the one carbon homologated alkyl-tethered cinnamic acid esters, in which it has become possible to achieve fused [5,6,6] tricyclic ketones. However, the formation of less strained spiro-tetracylic has been suppressed by taking into considerations the electronic effects of aromatic substituents.

In addition to the spectroscopic evidence for structural elucidation, the structure of the fused system **5dg** was further confirmed by the single crystal X-ray diffraction analysis (Table 2).

As we contemplated that the spiro-tetracyclic compounds could also be obtained, in the case when the *β*-aryl moiety is relatively more electron rich than the other arene, surprisingly, we observed the formation of spiro-tetracyclic ketone **6aa** when both aromatic rings are the same (i.e. phenyl). This may be due to the fact that both aromatic rings are not much different electronically even after achieving the bicyclic tetrahydronaphthalene intermediate **7aa** via initial Friedel−Crafts alkylation by alkyl tethered arene. Hence, in this case, thermodynamics would have been dominated to prefer the formation of thermodynamically stable spiro-tetracyclic ketone **6aa** (Table

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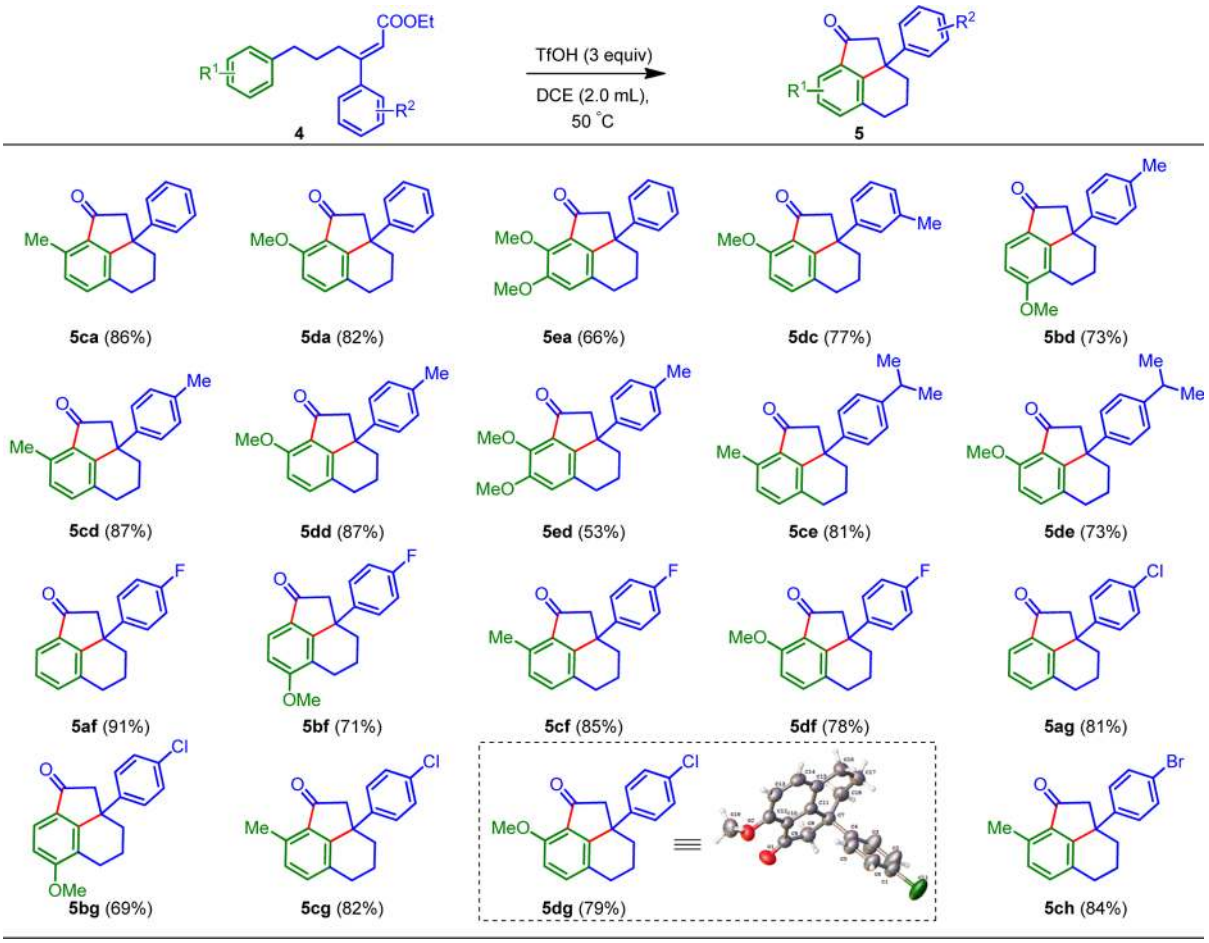
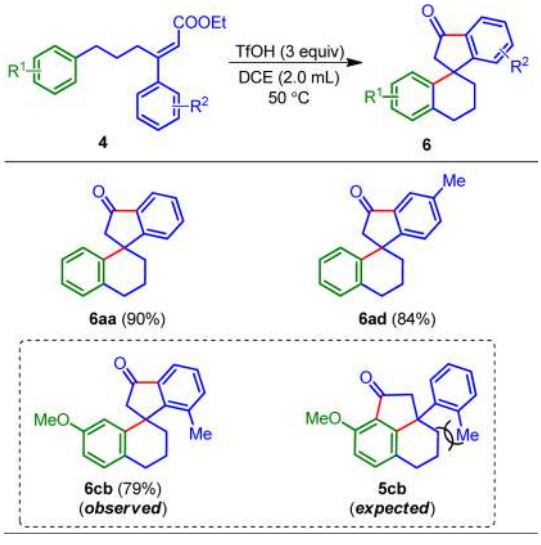
Table 2. Scope of the Synthesis of Fused Tricyclic Compounds 5 from Esters 4[a,b,c]



[a]All reactions were performed using 0.5 mmol of the ester **4**. [b]The yields correspond to the chromatographically isolated compounds. [c]Reaction was completed in 12 h (for OMe containing compounds).

3). As anticipated, the reaction of the cinnamic acid ester **4ad** with relatively more electron-rich β-para-tolyl group furnished the spiro-tetracyclic ketone **6ad** (Table 3). On the other hand, the ester **4cb** containing more electron-rich alkyl-tethered anisyl group preferred the spirocyclic ketone **6cb** (Table 3). At first glance, it looks like an exception, as the electron-rich alkyl-tethered arene must produce the fused tricyclic compound **5cb**. However, the formation of spiro-tetracyclic ketone **6cb** seems reasonable, as the anticipated fused tricyclic ketone **5cb** would suffer from steric thwart due to the ortho-methyl group of β-aryl moiety of ester **4cb**. This ortho-methyl steric effect might be compromised in the corresponding spirocompound, as the methyl group stays away from the cyclohexene residue, in which indanone bicyclic part lies in the right angle plane to that of the tetrahydronaphthalene portion.

Table 3. Formation of Spiro-Tetracyclic Compounds 6 from Esters 4



CONCLUSION

In conclusion, we have presented a chemoselective domino dual C−C bond formation for the synthesis of novel fused tricyclic ketones. The strategy proceeds through the intramolecular Friedel−Crafts alkylation and acylation sequence. These tricyclic motifs constitute the major structural core of naturally occurring compounds.

EXPERIMENTAL SECTION

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in a standard fashion with reference to either

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internal standard tetramethylsilane (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at room temperature in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2), and q = quartet (for CH_3). In the ^1H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet, and br. s = broad singlet. The assignment of signals was confirmed by ^1H, ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization modes. All small-scale dry reactions were carried out using Schlenk tubes under an inert atmosphere. Reactions were monitored by TLC on a silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. TfOH was purchased from local sources and used as received. Acme's silica gel (60−120 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material).

GP-1 (General Procedure for the Synthesis of Fused Tricyclic 5 and Spiro Tetracyclic Systems 6). In an oven-dried Schlenk tube were added ester **4** (147−184 mg, 0.5 mmol) and DCE (2.0 mL) followed by TfOH (0.13 mL, 1.5 mmol) at room temperature under nitrogen atmosphere and allowed the reaction mixture to stir at 50 °C for 12−24 h. The progress of the fused system **5**/spiro system **6** formation was monitored by TLC till the reaction is completed. Then, the mixture was quenched by the addition of aqueous $NaHCO_3$ solution and then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the fused tricyclic system **5**/spiro tetracyclic system **6** (53−91%) as viscous oil/semisolid/solid.

*8-Methyl-2a-phenyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5ca**).* **GP-1** was carried out with ester **4ca** (154 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5ca** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the fused tricyclic **5ca** (112.8 mg, 86%) as a pale yellow highly viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4ac**) = 0.50, R_f(**5ca**) = 0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2935, 1705, 1538, 1494, 1242, 702, cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (d, 1H, J = 7.8 Hz, ArH), 7.19 (dd, 2H, J = 7.8 and 7.3 Hz, ArH), 7.16−7.08 (m, 2H, ArH), 6.84 (d, 2H, J = 8.3 Hz, ArH), 2.99 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.82−2.65 (m, 2H, CH_2), 2.60 (s, 3H, $ArCH_3$), 2.60−2.52 (m, 1H, CH_aH_b), 1.87−1.70 (m, 2H, CH_2), 1.62−1.47 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 205.4 (s, C═O), 156.8 (s, ArC), 147.4 (s, ArC), 135.3 (s, ArC), 133.5 (s, ArC), 133.0 (s, ArC), 132.9 (d, ArCH), 130.2 (d, ArCH), 128.2 (d, 2C, 2 × ArCH), 127.1 (d, 2C, 2 × ArCH), 126.0 (d, ArCH), 56.7 (t, CH_2CO), 46.6 (s, C_q), 35.2 (t, CH_2), 24.6 (t, CH_2), 18.6 (t, CH_2), 17.7 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{19}O]^+$ = $[M + H]^+$: 263.1436; found, 263.1435.

*8-Methoxy-2a-phenyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5da**).* **GP-1** was carried out with ester **4da** (162 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5da** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5da** (114.1 mg, 82%) as a yellow semisolid. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**4da**) = 0.75, R_f(**5da**) = 0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2937, 1705, 1587, 1493, 1280, 1041, 702, cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.35 (d, 1H, J = 7.3 Hz, ArH), 7.19 (dd, 2H, J = 7.8 and 7.3 Hz, ArH), 7.12 (t, 1H, J = 7.3 Hz, ArH), 6.90−6.80 (m, 3H, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.97 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.86 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.72−2.62 (m, 2H, CH_2), 2.62−2.52 (m, 1H, CH_aH_b), 1.85−1.72 (m, 2H, CH_2), 1.60−1.45 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.2 (s, C═O), 158.4 (s, ArC), 155.4 (s, ArC), 147.0 (s, ArC), 135.5 (d, ArCH), 128.2 (d, 2C, 2 × ArCH), 127.8 (s, ArC), 127.0 (d, 2C, 2 × ArCH), 126.1 (d, ArCH), 123.2 (s, ArC), 110.4 (d, ArCH), 56.6 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 46.8 (s, C_q), 34.9 (t, CH_2), 24.1 (t, CH_2), 18.5 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{19}O_2]^+$ = $[M + H]^+$, 279.1385; found, 279.1383.

*7,8-Dimethoxy-2a-phenyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5ea**).* **GP-1** was carried out with ester **4ea** (177 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5ea** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 75:25) furnished the fused tricyclic **5ea** (101.6 mg, 66%) as a yellow viscous jelly liquid. [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**4ea**) = 0.70, R_f(**5ea**) = 0.34, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2935, 1706, 1488, 1445, 1264, 1117, 1019, 703 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.20 (dd, 2H, J = 7.8 and 7.3 Hz, ArH), 7.12 (t, 1H, J = 7.3 Hz, ArH), 6.97 (s, 1H, ArH), 6.86 (d, 2H, J = 7.8 Hz, ArH), 4.03 (s, 3H, $ArOCH_3$), 3.89 (s, 3H, $ArOCH_3$), 3.00 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.88 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.77−2.67 (m, 2H, CH_2), 2.57−2.47 (m, 1H, CH_aH_b), 1.85−1.72 (m, 2H, CH_2), 1.57−1.45 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.4 (s, C═O), 151.9 (s, ArC), 148.4 (s, ArC), 147.7 (s, ArC), 145.0 (s, ArC), 130.5 (d, ArCH), 128.5 (s, ArC), 128.2 (d, 2C, 2 × ArCH), 127.2 (s, ArC), 127.1 (d, 2C, 2 × ArCH), 126.1 (d, ArCH), 118.4 (d, ArCH), 62.6 (q, $ArOCH_3$), 57.2 (q, $ArOCH_3$), 56.8 (t, CH_2CO), 46.3 (s, C_q), 35.6 (t, CH_2), 25.0 (t, CH_2), 18.6 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{20}H_{21}O_3]^+$ = $[M + H]^+$, 309.1491; found, 309.1489.

*8-Methoxy-2a-(3-methylphenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5dc**).* **GP-1** was carried out with ester **4dc** (169 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5dc** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5dc** (122.9 mg, 84%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**4dc**) = 0.80, R_f(**5dc**) = 0.0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2939, 1700, 1591, 1457, 1239, 1070, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.35 (d, 1H, J = 8.3 Hz, ArH), 7.06 (dd, 1H, J = 7.8 and 7.3 Hz,

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ArH), 6.93 (d, 1H, J = 7.8 Hz, ArH), 6.84 (d, 1H, J = 8.3 Hz, ArH), 6.66 (s, 1H, ArH), 6.62 (d, 1H, J = 7.3 Hz, ArH), 3.95 (s, 3H, $ArOCH_3$), 2.96 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.70−2.62 (m, 2H, CH_2), 2.61−2.52 (m, 1H, CH_aH_b), 2.23 (s, 3H, $ArCH_3$), 1.85−1.72 (m, 2H, CH_2), 1.62−1.45 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.2 (s, C═O), 158.6 (s, ArC), 155.3 (s, ArC), 147.0 (s, ArC), 137.8 (d, ArCH), 135.4 (s, ArC), 128.0 (d, ArCH), 127.8 (d, ArCH), 127.7 (d, ArCH), 126.9 (d, ArCH), 124.2 (d, ArCH), 123.3 (s, ArC), 110.4 (d, ArCH), 56.7 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 46.8 (s, C_q), 34.9 (t, CH_2), 24.1 (q, $ArCH_3$), 21.5 (t, CH_2), 18.6 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{20}H_{21}O_2]^+ = [M + H]^+$, 293.1542; found, 293.1539.

*6-Methoxy-2a-(4-methylphenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5bd**).* **GP-1** was carried out with ester **4bd** (169 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5bd** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5bd** (106.4 mg, 73%) as a yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 85:15 R_f(**4bd**) = 0.70, R_f(**5bd**) = 0.0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2936, 1704, 1586, 1494, 1278, 1041, 728 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.34 (d, 1H, J = 8.3 Hz, ArH), 6.99 (d, 2H, J = 8.3 Hz, ArH), 6.83 (d, 1H, J = 8.3 Hz, ArH), 6.74 (d, 2H, J = 8.3 Hz, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.95 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.72−2.60 (m, 2H, CH_2), 2.57−2.50 (m, 1H, CH_aH_b), 2.25 (s, 3H, $ArCH_3$), 1.85−1.70 (m, 2H, CH_2), 1.62−1.47 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.2 (s, C═O), 158.7 (s, ArC), 155.3 (s, ArC), 144.1 (s, ArC), 135.6 (s, ArC), 135.4 (d, ArCH), 128.9 (d, 2C, 2 × ArCH), 127.8 (s, ArC), 126.9 (d, 2C, 2 × ArCH), 123.2 (s, ArC), 110.4 (d, ArCH), 56.7 (t, CH_2CO), 55.9 (q, $ArOCH_3$), 46.5 (s, C_q), 34.9 (t, CH_2), 24.1 (t, CH_2), 20.8 (q, $ArCH_3$), 18.6 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{20}H_{21}O_2]^+ = [M + H]^+$, 293.1542; found, 293.1539.

*8-Methyl-2a-(4-methylphenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5cd**).* **GP-1** was carried out with ester **4cd** (161 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5cd** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 93:7) furnished the fused tricyclic **5cd** (121.5 mg, 88%) as a pale yellow semisolid. [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**4cd**) = 0.70, R_f(**5cd**) = 0.50, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2934, 1703, 1582, 1241, 816 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.26 (d, 1H, J = 7.3 Hz, ArH), 7.13 (d, 1H, J = 7.3 Hz, ArH), 7.00 (d, 2H, J = 8.3 Hz, ArH), 6.73 (d, 2H, J = 8.3 Hz, ArH), 2.98 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.83 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.77−2.62 (m, 2H, CH_2), 2.59 (s, 3H, $ArCH_3$), 2.60−2.50 (m, 1H, CH_aH_b), 2.26 (s, 3H, $ArCH_3$), 1.85−1.67 (m, 2H, CH_2), 1.65−1.50 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 205.5 (s, C═O), 157.1 (s, ArC), 144.5 (s, ArC), 135.6 (s, ArC), 135.2 (s, ArC), 133.4 (s, ArC), 133.0 (s, ArC), 132.9 (d, ArCH), 130.1 (d, ArCH), 128.9 (d, 2C, 2 × ArCH), 127.0 (d, 2C, 2 × ArCH), 56.8 (t, CH_2CO), 46.3 (s, C_q), 35.1 (t, CH_2), 24.6 (t, CH_2), 20.8 (q, $ArCH_3$), 18.6 (t, CH_2), 17.7 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{20}H_{21}O]^+ = [M + H]^+$, 277.1592; found, 277.1593.

*8-Methoxy-2a-(4-methylphenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5dd**).* **GP-1** was carried out with ester **4dd** (169 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5dd** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5dd** (127.3 mg, 87%) as a pale yellow solid. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**4dd**) = 0.80, R_f(**5dd**) = 0.0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2936, 1702, 1597, 1453, 1245, 1061, 812 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.62 (d, 1H, J = 8.3 Hz, ArH), 6.99 (d, 2H, J = 7.8 Hz, ArH), 6.93 (d, 1H, J = 8.3 Hz, ArH), 6.73 (d, 2H, J = 8.3 Hz, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.97 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.84 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.67−2.58 (m, 2H, CH_2), 2.57−2.47 (m, 1H, CH_aH_b), 2.26 (s, 3H, $ArCH_3$), 1.87−1.72 (m, 2H, CH_2), 1.57−1.42 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.2 (s, C═O), 161.8 (s, ArC), 158.3 (s, ArC), 144.6 (s, ArC), 135.5 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 128.6 (s, ArC), 127.0 (d, 2C, 2 × ArCH), 124.1 (s, ArC), 122.6 (d, ArCH), 110.0 (d, ArCH), 56.5 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 46.5 (s, C_q), 34.8 (t, CH_2), 20.8 (q, $ArCH_3$), 20.2 (t, CH_2), 18.2 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{20}H_{21}O_2]^+ = [M + H]^+$, 293.1542; found, 293.1541. mp 178−179 °C.

*7,8-Dimethoxy-2a-(4-methylphenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5ed**).* **GP-1** was carried out with ester **4ed** (184 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5ed** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 75:25) furnished the fused tricyclic **5ed** (85.5 mg, 53%) as a dark yellow semisolid. [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**4ed**) = 0.75, R_f(**5ed**) = 0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2931, 1711, 1492, 1268, 1021, 817 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.01 (d, 2H, J = 8.3 Hz, ArH), 6.97 (s, 1H, ArH), 6.74 (d, 2H, J = 8.3 Hz, ArH), 4.03 (s, 3H, $ArOCH_3$), 3.90 (s, 3H, $ArOCH_3$), 2.98 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.86 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.77−2.60 (m, 2H, CH_2), 2.55−2.45 (m, 1H, CH_aH_b), 2.26 (s, 3H, $ArCH_3$), 1.85−1.70 (m, 2H, CH_2), 1.66−1.50 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.5 (s, C═O), 151.8 (s, ArC), 148.7 (s, ArC), 144.7 (s, ArC), 135.6 (s, ArC), 130.5 (s, ArC), 129.2 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 127.2 (s, ArC), 127.0 (d, 2C, 2 × ArCH), 118.4 (d, ArCH), 62.6 (q, $ArOCH_3$), 57.3 (q, $ArOCH_3$), 56.8 (t, CH_2CO), 45.9 (s, C_q), 35.4 (t, CH_2), 25.0 (t, CH_2), 20.8 (q, $ArOCH_3$), 18.6 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{21}H_{23}O_3]^+ = [M + H]^+$, 323.1647; found, 323.1645.

*2a-(4-Isopropylphenyl)-8-methyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5ce**).* **GP-1** was carried out with ester **4ce** (175 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5ce** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 93:7) furnished the fused tricyclic **5ce** (123.2 mg, 81%) as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4ce**) = 0.60, R_f(**5ce**) = 0.40, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2927, 1706, 1588, 1495, 1277, 1047, 827, 721 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (d, 1H, J = 7.8 Hz, ArH), 7.12 (d, 1H, J = 7.8 Hz, ArH), 7.04 (d, 2H, J = 8.3 Hz, ArH), 6.74 (d, 2H, J = 8.3 Hz, ArH), 2.99 (d, 1H, J = 17.1 Hz, CH_aH_bCO),

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2.86−2.64 [m, 3H, CH_2 and $CH(CH_3)_2$], 2.83 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.58 (s, 3H, $ArCH_3$), 2.60−2.50 (m, 1H, CH_aH_b), 1.87−1.70 (m, 2H, CH_2), 1.67−1.50 (m, 1H, CH_aH_b), 1.18 [d, 6H, J = 6.8 Hz, $CH(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 205.7 (s, C═O), 157.1 (s, ArC), 146.5 (s, ArC), 144.8 (s, ArC), 135.2 (s, ArC), 133.5 (s, ArC), 133.0 (s, ArC), 132.9 (d, ArCH), 130.1 (d, ArCH), 127.0 (d, 2C, 2 × ArCH), 126.2 (d, 2C, 2 × ArCH), 56.8 (t, CH_2CO), 46.3 (s, C_q), 35.2 (t, CH_2), 33.5 [d, $CH(CH_3)_2$], 24.7 (t, CH_2), 23.9 [2 × q, 2C, $ArCH_3$ and $CH(CH_3)_{2a}$], 18.7 (t, CH_2), 17.7 [q, $CH(CH_3)_{2b}$] ppm. HR-MS (ESI^+) m/z: calcd for $[C_{22}H_{25}O]^+ = [M + H]^+$, 305.1905; found, 305.1906.

*2a-(4-Isopropylphenyl)-8-methoxy-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5de**).* **GP-1** was carried out with ester **4de** (183 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5de** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5de** (116.7 mg, 73%) as a pale yellow semisolid. [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**4de**) = 0.75, R_f(**5de**) = 0.20, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2951, 1705, 1586, 1494, 1273, 1043, 827, 734 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.34 (d, 1H, J = 8.3 Hz, ArH), 7.03 (d, 2H, J = 8.3 Hz, ArH), 6.83 (d, 1H, J = 8.3 Hz, ArH), 6.73 (d, 2H, J = 8.3 Hz, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.97 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.85−2.75 [m, 1H, $CH(CH_3)_2$], 2.84 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.72−2.62 (m, 2H, CH_2), 2.57−2.50 (m, 1H, CH_aH_b), 1.85−1.70 (m, 2H, CH_2), 1.62−1.50 (m, 1H, CH_aH_b), 1.17 [d, 6H, J = 6.8 Hz, $CH(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.4 (s, C═O), 158.7 (s, ArC), 155.3 (s, ArC), 146.5 (s, ArC), 144.4 (s, ArC), 135.4 (s, ArC), 127.8 (s, ArC), 126.9 (d, 2C, 2 × ArCH), 126.2 (d, 2C, 2 × ArCH), 123.2 (s, ArC), 110.3 (d, ArCH), 56.7 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 46.5 (s, C_q), 34.9 (t, CH_2), 33.5 [d, $CH(CH_3)_2$], 24.1 (t, CH_2), 23.9 (q, CH_3), 23.8 (q, CH_3), 18.6 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{22}H_{25}O_2]^+ = [M + H]^+$, 321.1855; found, 321.1852.

*2a-(4-Fluorophenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5af**).* **GP-1** was carried out with ester **4af** (156 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5af** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 93:7) furnished the fused tricyclic **5af** (121.2 mg, 91%) as a pale yellow semisolid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4af**) = 0.60, R_f(**5af**) = 0.35, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2940, 1711, 1489, 1265, 1098, 827 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.60−7.54 (m, 1H, ArH), 7.45−7.35 (m, 2H, ArH), 6.88 (dd, 2H, J = 8.8 and 8.3 Hz, ArH), 6.82−6.75 (m, 2H, ArH), 2.98 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.86−2.70 (m, 2H, CH_2), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.64−2.50 (m, 1H, CH_aH_b), 1.90−1.72 (m, 2H, CH_2), 1.62−1.45 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.4 (s, C═O), 161.1 (d, J = 245.0 Hz, ArC), 156.3 (s, ArC), 143.0 (s, ArC), 136.5 (s, ArC), 135.5 (s, ArC), 133.6 (d, ArCH), 128.6 (d, ArCH), 128.5 (d, 2C, J = 7.9 Hz, 2 × ArCH), 120.8 (d, ArCH), 115.1 (d, 2C, J = 21.2 Hz, 2 × ArCH), 56.3 (t, CH_2CO), 46.6 (s, C_q), 35.1 (t, CH_2), 24.7 (t, CH_2), 18.4 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{18}H_{16}FO]^+ = [M + H]^+$, 267.1185; found, 267.1183.

*2a-(4-Fluorophenyl)-6-methoxy-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5bf**).* **GP-1** was carried out with ester **4bf** (171 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5bf** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5bf** (105.2 mg, 71%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**4bf**) = 0.65, R_f(**5bf**) = 0.20, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2939, 1709, 1590, 1494, 1278, 1045, 822 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.62 (d, 1H, J = 8.3 Hz, ArH), 6.93 (d, 1H, J = 8.3 Hz, ArH), 6.92−6.77 (m, 4H, ArH), 3.93 (s, 3H, $ArOCH_3$), 2.95 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.67−2.57 (m, 2H, CH_2), 2.55−2.45 (m, 1H, CH_aH_b), 1.90−1.72 (m, 2H, CH_2), 1.52−1.35 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.8 (s, C═O), 161.9 (s, ArC), 161.1 (d, J = 245.0 Hz, ArC), 157.7 (s, ArC), 143.2 (d, J = 3.4 Hz, ArC), 128.6 (d, 2C, J = 8.1 Hz, 2 × ArCH), 128.4 (s, ArC), 124.0 (s, ArC), 122.7 (d, ArCH), 114.9 (d, 2C, J = 21.3 Hz, 2 × ArCH), 110.1 (d, ArCH), 56.5 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 46.3 (s, C_q), 34.9 (t, CH_2), 20.1 (t, CH_2), 18.0 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}FO_2]^+ = [M + H]^+$, 297.1291; found, 297.1288.

*2a-(4-Fluorophenyl)-8-methyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5cf**).* **GP-1** was carried out with ester **4cf** (163 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5cf** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 93:7) furnished the fused tricyclic **5cf** (119.3 mg, 85%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4cf**) = 0.60, R_f(**5cf**) = 0.45, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2930, 1708, 1492, 1260, 1085, 833 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (d, 1H, J = 7.8 Hz, ArH), 7.14 (d, 1H, J = 7.8 Hz, ArH), 6.88 (d, 2H, J = 8.8 and 8.3 Hz, ArH), 6.84−6.76 (m, 1H, ArH), 2.96 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.80−2.67 (m, 2H, CH_2), 2.59 (s, 3H, $ArCH_3$), 2.57−2.47 (m, 1H, CH_aH_b), 1.87−1.75 (m, 2H, CH_2), 1.60−1.45 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 205.1 (s, C═O), 161.1 (d, J = 245.0 Hz, ArC), 156.5 (s, ArC), 143.2 (s, ArC), 135.4 (s, ArC), 133.3 (s, ArC), 133.1 (d, ArCH), 132.9 (s, ArC), 130.4 (d, ArCH), 128.6 (d, 2C, J = 8.1 Hz, 2 × ArCH), 114.9 (d, 2C, J = 21.3 Hz, 2 × ArCH), 56.7 (t, CH_2CO), 46.1 (s, C_q), 35.3 (t, CH_2), 24.5 (t, CH_2), 18.5 (t, CH_2), 17.6 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}FO]^+ = [M + H]^+$, 281.1342; found, 281.1342.

*2a-(4-Fluorophenyl)-8-methoxy-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5df**).* **GP-1** was carried out with ester **4df** (171 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5df** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5df** (115.4 mg, 78%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**4df**) = 0.70, R_f(**5df**) = 0.35, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2938, 1708, 1590, 1498, 1224, 1043, 836 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.36 (d, 1H, J = 8.3 Hz, ArH), 6.92−6.75 (m, 5H, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.93 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.86 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.72−2.62 (m, 2H, CH_2), 2.57−2.45 (m, 1H, CH_aH_b), 1.87−1.70 (m, 2H, CH_2), 1.58−1.40 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.8 (s, C═O), 161.1 (d, J = 245.0 Hz, ArC), 158.0 (s, ArC),

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155.4 (s, ArC), 142.8 (s, ArC), 135.6 (d, ArCH), 128.5 (d, 2C, J = 8.1 Hz, 2 × ArCH), 127.6 (s, ArC), 123.0 (s, ArC), 114.9 (d, 2C, J = 21.3 Hz, 2 × ArCH), 110.6 (d, ArCH), 56.7 (t, CH_2CO), 55.9 (q, $ArOCH_3$), 46.3 (s, C_q), 35.0 (t, CH_2), 24.0 (t, CH_2), 18.4 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}FO_2]^+ = [M + H]^+$, 297.1291; found, 297.1293.

*2a-(4-Chlorophenyl)-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5ag**).* **GP-1** was carried out with ester **4ag** (164 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5ag** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 93:7) furnished the fused tricyclic **5ag** (114.2 mg, 81%) as a yellow solid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4ag**) = 0.65, R_f(**5ag**) = 0.40, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2939, 1713, 1487, 1261, 1097, 827, 779 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.60−7.52 (m, 1H, ArH), 7.60−7.52 (m, 2H, ArH), 7.15 (d, 2H, J = 8.8 Hz, ArH), 6.77 (d, 2H, J = 8.8 Hz, ArH), 2.96 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.82−2.70 (m, 2H, CH_2), 2.62−2.50 (m, 1H, CH_aH_b), 1.92−1.75 (m, 2H, CH_2), 1.62−1.45 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.1 (s, C═O), 156.0 (s, ArC), 145.7 (s, ArC), 136.4 (s, ArC), 135.5 (s, ArC), 133.6 (d, ArCH), 132.0 (s, ArC), 128.7 (d, ArCH), 128.4 (d, 4C, 4 × ArCH), 120.7 (d, ArCH), 56.1 (t, CH_2CO), 46.7 (s, C_q), 34.9 (t, CH_2), 24.7 (t, CH_2), 18.3 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{18}H_{16}ClO]^+ = [M + H]^+$, 283.0890; found, 283.0887.

*2a-(4-Chlorophenyl)-6-methoxy-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5bg**).* **GP-1** was carried out with ester **4bg** (179 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5bg** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5bg** (107.6 mg, 69%) as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20), R_f(**4bg**) = 0.65, R_f(**5bg**) = 0.20, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2938, 1701, 1596, 1485, 1353, 1247, 1061, 818, 730 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.63 (d, 1H, J = 8.3 Hz, ArH), 7.15 (d, 2H, J = 8.8 Hz, ArH), 6.94 (d, 1H, J = 8.3 Hz, ArH), 6.77 (d, 2H, J = 8.8 Hz, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.93 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.69−2.56 (m, 2H, CH_2), 2.55−2.45 (m, 1H, CH_aH_b), 1.90−1.72 (m, 2H, CH_2), 1.55−1.35 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.5 (s, C═O), 162.0 (s, ArC), 157.4 (s, ArC), 146.1 (s, ArC), 132.0 (s, ArC), 128.5 (d, 2C, 2 × ArCH), 128.5 (s, ArC), 128.4 (d, 2C, 2 × ArCH), 124.0 (s, ArC), 122.8 (d, ArCH), 110.2 (d, ArCH), 56.3 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 46.5 (s, C_q), 34.8 (t, CH_2), 20.1 (t, CH_2), 18.1 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}ClO_2]^+ = [M + H]^+$, 313.0995; found, 313.0993.

*2a-(4-Chlorophenyl)-8-methyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5cg**).* **GP-1** was carried out with ester **4cg** (171 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5cg** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the fused tricyclic **5cg** (121.4 mg, 82%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4cg**) = 0.75, R_f(**5cg**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2938, 1701, 1596, 1485, 1247, 1061, 818, 730 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (d, 1H, J = 7.3 Hz, ArH), 7.20−7.10 (m, 3H, ArH), 6.77 (d, 2H, J = 8.8 Hz, ArH), 2.93 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.84 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.77−2.65 (m, 2H, CH_2), 2.58 (s, 3H, $ArCH_3$), 2.57−2.48 (m, 1H, CH_aH_b), 1.87−1.72 (m, 2H, CH_2), 1.57−1.42 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 205.0 (s, C═O), 156.3 (s, ArC), 146.0 (s, ArC), 135.5 (s, ArC), 133.4 (s, ArC), 133.2 (d, ArCH), 132.9 (s, ArC), 132.0 (s, ArC), 130.5 (d, ArCH), 128.6 (d, 2C, 2 × ArCH), 128.4 (d, 2C, 2 × ArCH), 56.6 (t, CH_2CO), 46.3 (s, C_q), 35.1 (t, CH_2), 24.6 (t, CH_2), 18.5 (t, CH_2), 17.7 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}ClO]^+ = [M + H]^+$, 297.1046; found, 297.1047.

*2a-(4-Chlorophenyl)-8-methoxy-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5dg**).* **GP-1** was carried out with ester **4dg** (179 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5dg** formation at 50 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the fused tricyclic **5dg** (123.6 mg, 79%) as a yellow solid. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**4dg**) = 0.75, R_f(**5dg**) = 0.30, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2936, 1707, 1587, 1491, 1277, 1042, 823 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.36 (d, 1H, J = 8.3 Hz, ArH), 7.15 (d, 2H, J = 8.8 Hz, ArH), 6.85 (d, 1H, J = 8.3 Hz, ArH), 6.79 (d, 2H, J = 8.8 Hz, ArH), 3.94 (s, 3H, $ArOCH_3$), 2.91 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.85 (d, 1H, J = 17.1 Hz, CH_aH_bCO), 2.72−2.62 (m, 2H, CH_2), 2.57−2.45 (m, 1H, CH_aH_b), 1.87−1.70 (m, 2H, CH_2), 1.60−1.40 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.6 (s, C═O), 157.7 (s, ArC), 155.4 (s, ArC), 145.6 (s, ArC), 135.7 (d, ArCH), 132.0 (s, ArC), 128.4 (d, 4C, 4 × ArCH), 127.6 (d, ArCH), 123.1 (s, ArC), 110.7 (d, ArCH), 56.4 (t, CH_2CO), 55.9 (q, $ArOCH_3$), 46.5 (s, C_q), 34.9 (t, CH_2), 24.0 (t, CH_2), 18.4 (t, CH_2) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}ClO_2]^+ = [M + H]^+$, 313.0995; found, 313.0997.

*2a-(4-Bromophenyl)-8-methyl-2a,3,4,5-tetrahydroacenaphthylen-1(2H)-one (**5ch**).* **GP-1** was carried out with ester **4ch** (193.5 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for fused tricyclic **5ch** formation at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the fused tricyclic **5ch** (143.2 mg, 84%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4ch**) = 0.80, R_f(**5ch**) = 0.60, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2942, 1705, 1598, 1482, 1243, 1059, 816, 725 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.28 (d, 2H, J = 8.3 Hz, ArH), 7.24 (d, 1H, J = 7.8 Hz, ArH), 7.11 (d, 1H, J = 7.8 Hz, ArH), 6.69 (d, 2H, J = 8.3 Hz, ArH), 2.90 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.82 (d, 1H, J = 16.6 Hz, CH_aH_bCO), 2.76−2.65 (m, 2H, CH_2), 2.56 (s, 3H, $ArCH_3$), 2.55−2.44 (m, 1H, CH_aH_b), 1.85−1.72 (m, 2H, CH_2), 1.57−1.40 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.9 (s, C═O), 156.1 (s, ArC), 146.6 (s, ArC), 135.5 (s, ArC), 133.3 (s, ArC), 133.1 (d, ArCH), 132.9 (s, ArC), 131.3 (d, 2C, 2 × ArCH), 130.5 (d, ArCH), 128.9 (d, 2C, 2 × ArCH), 120.1 (s, ArC), 56.5 (t, CH_2CO), 46.3 (s, C_q), 35.1 (t, CH_2), 24.5 (t, CH_2), 18.5 (t, CH_2), 17.7 (q, $ArCH_3$) ppm. HR-MS (ESI^+) m/z: calcd for $[C_{19}H_{18}BrO]^+ = [M + H]^+$, 341.0541; found, 341.0540.

*7′-Methoxy-7-methyl-3′,4′-dihydro-2′H-spiro[indene-1,1′-naphthalen]-3(2H)-one (**6cb**).* **GP-1** was carried out with ester **4cb** (169 mg, 0.5 mmol), DCE (2.0 mL), and TfOH (0.13 mL, 1.5 mmol) for spiro-tetracyclic **6cb** formation at 50 °C for 24 h.

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Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15) furnished the spiro-tetracyclic **6cb** (115.3 mg, 79%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**4cb**) = 0.75, R_f(**6cb**) = 0.60, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2931, 1711, 1492, 1268, 1120, 1021, 818 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (dd, 1H, J = 7.3 and 1.9 Hz, ArH), 7.38−7.27 (m, 2H, ArH), 7.05 (d, 1H, J = 8.8 Hz, ArH), 6.99 (dd, 1H, J = 8.3 and 2.9 Hz, ArH), 6.21 (d, 1H, J = 2.9 Hz, ArH), 3.59 (s, 3H, $ArOCH_3$), 2.99 (d, 1H, J = 19.1 Hz, CH_aH_bCO), 2.90−2.75 (m, 3H, CH_aH_bCO and CH_2), 2.16 (ddd, 1H, J = 13.7, 2.4 and 2.0 Hz, CH_aH_b), 2.07−1.97 (m, 1H, CH_aH_b), 1.87 (s, 3H, $ArCH_3$), 1.90−1.77 (m, 1H, CH_aH_b), 1.72−1.62 (m, 1H, CH_aH_b) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 206.5 (s, C═O), 160.5 (s, ArC), 158.4 (s, ArC), 142.7 (s, ArC), 137.9 (d, ArCH), 136.9 (s, ArC), 135.7 (s, ArC), 130.0 (d, ArCH), 128.8 (s, ArC), 128.1 (d, ArCH), 121.0 (d, ArCH), 112.2 (d, ArCH), 112.1 (d, ArCH), 56.7 (t, CH_2CO), 55.2 (q, $ArOCH_3$), 47.1 (s, C_q), 36.7 (t, CH_2), 29.0 (t, CH_2), 21.5 (t, CH_2), 18.4 (q, $ArCH_3$) ppm. HR-MS (ESI$^+$) m/z: calcd for $[C_{20}H_{21}O_2]^+$ = $[M + H]^+$, 293.1542; found, 293.1540.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01553.

Crystal data and copies of ^{1}H and ^{13}C spectra (PDF copies) of all the compounds (PDF)

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Notes

The authors declare no competing financial interest.

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