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Electrophilic Phosphonium Cations as Lewis Acid Catalysts in Diels−Alder Reactions and Nazarov Cyclizations

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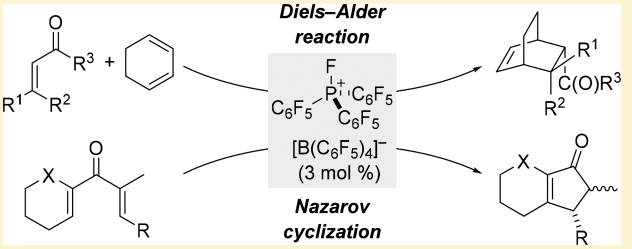
Supporting Information

ABSTRACT: The highly electrophilic fluorophosphonium cation $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ is shown to catalyze Diels−Alder reactions of challenging dienophile/enophile combinations and Nazarov cyclizations of various precursors. Several other electrophilic phosphonium cations (EPCs) have been tested for comparison. This systematic study demonstrates the power of these Lewis acids to act as catalysts for synthetically useful pericyclic reactions.



INTRODUCTION

Electrophilic phosphonium cations (EPCs) have long been known to act as Lewis acid catalysts.[1,2] Their use in catalytic carbon−carbon bond formation is one important application (Scheme 1), and this was started by Mukaiyama and co-workers three decades ago. Mukaiyama aldol reactions of aldehydes and silyl enol ethers or silyl ketene acetals were accomplished using the dicationic catalysts $[R_3POPR_3]^{2+}[OTf]_2^-$ (**1**, R = Bu; **2**, R = Ph).[3a] These catalysts were also shown to promote Michael reactions of enol ethers and allylic silanes as well as Mannich-type reactions of imines and silyl ketene acetals.[3] Recently, the groups of Stephan and Alcarazo reported the use of dicationic cyclopropenium- and pyridinium-substituted phosphonium salts such as $[Ph_3P(2\text{-}C_5H_4NMe)]^{2+}[B(C_6F_5)_4]_2^-$ (**3**) as competent catalysts for Mukaiyama aldol reactions.[4] Cyanosilylation of carbonyl groups is another area of application for EPCs. Single examples were realized with catalysts **1**[3a] and $[Ph_3PMe]^+[I]^-$ (**4**),[5] and slightly modified **4**, that is $[Ph_3PBn]^+[Cl]^-$ (**5**), showed broad substrate scope.[6]

Five years ago, Stephan and co-workers revived this field with the introduction of the highly electrophilic fluorophosphonium cation $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**).[7] Several strongly Lewis acidic EPCs have been developed since then.[1a] Applications include alkene hydroarylation[8] and various Friedel−Crafts alkylation reactions initiated by heterolytic C−F bond cleavage.[9] Given the high reactivity of Stephan's EPCs, we wondered whether these would be able to catalyze difficult Diels−Alder reactions with cyclohexa-1,3-diene as a dienophile. Of note, Terada and Kouchi had described the Diels−Alder reaction of cyclopentadiene and amide dienophiles with catechol-derived phosphonium salts such as **7** and **8** as catalysts.[10]

We disclose here EPC-catalyzed Diels−Alder reactions of challenging diene/dienophile combinations.[11] Moreover, the same EPC catalyst also promotes Nazarov cyclizations.

RESULTS AND DISCUSSION

EPC-Catalyzed Diels−Alder Reactions of Cyclohexa-1,3-diene and α,β-Unsaturated Ketones. We started our investigation with the Diels−Alder reaction of cyclohexa-1,3-diene (**10**) and (*E*)-chalcone (**9a**) to yield cycloadduct **11a** (Table 1). Catalyst **6**[7] had emerged as an optimal choice from an earlier screening of various EPCs (see the Supporting Information for further details). Additional examples include **12**−**18**,[4,12−16] and those highlighted in gray boxes performed similarly to **6** (Figure 1). **6** was eventually chosen for its easy accessibility.[17]

Catalyst **6** converted a 2:1 combination of **10** and **9a** into cycloadduct **11a** with 34% conversion after 24 h at room temperature; the *endo*:*exo* ratio was high (Table 1, entry 1). Successively increasing the amount of cyclohexa-1,3-diene (**10**) and then the catalyst loading led to enhanced conversion, reaching full conversion within 3 h with 8.0 equiv of **10** and 3.0 mol % of **6** (entries 2−6). Solvents other than 1,2-chlorobenzene resulted in lower conversions (entries 7−9).

The fact that a large excess of diene **10** is necessary to reach full conversion prompted us to look independently into the reactant/catalyst combinations by ^{1}H NMR spectroscopy. For this, we mixed cyclohexa-1,3-diene (**10**), $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**), and mesitylene as internal standard and analyzed this mixture after certain time intervals over a period of 24 h. The ^{1}H NMR analysis showed that two-thirds of **10** have been consumed after less than 1 h, and no **10** remained

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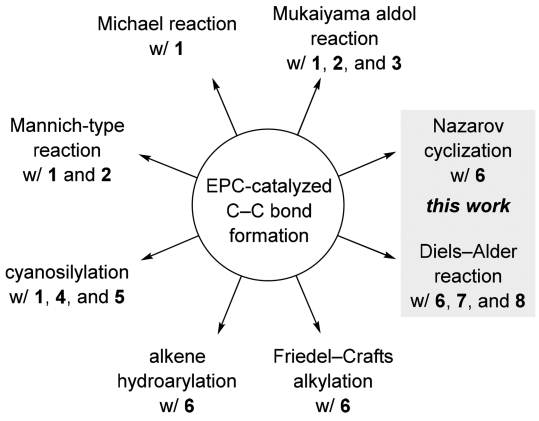
Scheme 1. EPC-Catalyzed Carbon–Carbon Bond-Forming Reactions and Representative Catalysts



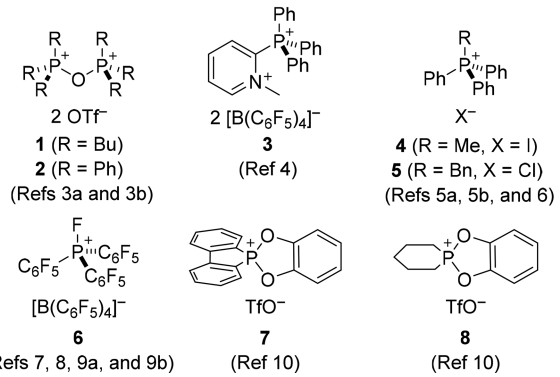
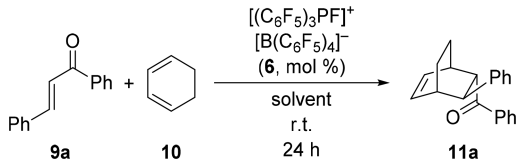


Table 1. Optimization of the EPC-Catalyzed Diels–Alder Reaction[a,b]



entry	diene **10** (equiv)	catalyst **6** (mol %)	solvent	conversn[c,d] (%)
1	2.0	1.0	1,2-$Cl_2C_6H_4$	34
2	3.0	1.0	1,2-$Cl_2C_6H_4$	79
3	5.0	1.0	1,2-$Cl_2C_6H_4$	89
4	5.0	3.0	1,2-$Cl_2C_6H_4$	95 (90)
5	6.0	3.0	1,2-$Cl_2C_6H_4$	100 (87)
6[e]	8.0	3.0	1,2-$Cl_2C_6H_4$	100
7	3.0	3.0	1,2-$Cl_2C_6H_4$	86
8	3.0	3.0	ClC_6H_5	73
9	3.0	3.0	CD_2Cl_2	54

[a]All reactions were performed according to General Procedure **GP1** (see the Experimental Section). [b]*endo*:*exo* ratio was determined by GLC analysis prior to purification. [c]Conversion of (*E*)-chalcone was determined by GLC analysis using mesitylene as internal standard. [d]Isolated yield after flash column chromatography in parentheses. [e]Full conversion already after 3 h.

after 24 h (see the Supporting Information for details). The obtained ^{1}H NMR spectra indicated oligomerization of diene **10**.[18] Another observed side reaction was the deoxygenation of **9a** by EPC **6**, affording $(C_6F_5)_3PF_2$ and $(C_6F_5)_3PO$.[19] Although these newly formed phosphorus compounds are not catalytically active, we observed formation of the cycloadduct **11a** even when cyclohexa-1,3-diene (**10**) was added to the dieneophile **9a** and the catalyst **6** after its full decomposition over several hours as monitored by ^{19}F and ^{31}P NMR spectroscopy. This experiment suggests that not only **6** but also in situ generated carbocations are potentially promoting this Diels–Alder reaction.[20]

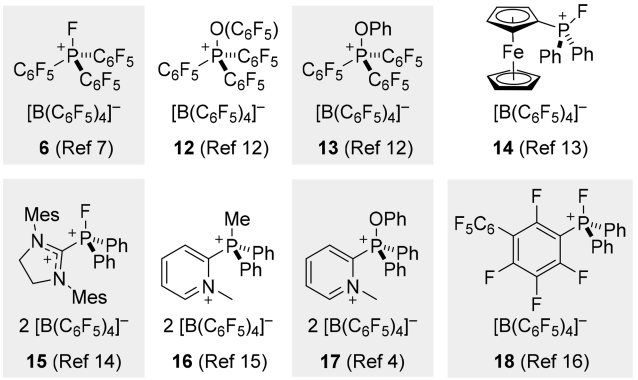


Figure 1. EPCs tested in challenging Diels–Alder reactions (see the Supporting Information for further details).

Although full conversion was achieved with 8.0 equiv of **10** after 3 h, we continued with using 6.0 equiv at a longer reaction time (see Table 1, entries 5 and 6). We then examined the scope of this Diels–Alder reaction for different *α,β*-unsaturated ketones **9b–h** (Scheme 2). Chalcone-derived **11a** had been obtained in 87% isolated yield before. An electron-rich anisyl group at the carbonyl carbon atom had no effect, and **11b** was obtained in 88% yield. Conversely, a mesitylene group thwarts the cycloaddition and **11c** only formed in trace amounts at a low conversion of 35%. The same trend was seen with naphthyl substituents: the yield was high with the *β*-naphthyl group (90% for **11d**), and a diminished yield was obtained for an *α*-naphthyl substituent (51% for **11e**). An alkyl group attached to the C=O unit was also tolerated, and **11f** was isolated in near-quantitative yield. Cyclic enones such as cyclopent-2-en-1-one (**9g**) and cyclohex-2-en-1-one (**9h**) are considered particularly poor dienophiles, but EPC **6** was still able to mediate their Diels–Alder reactions in decent yields of 63% (for **11g**) and 72% (for **11h**), respectively. Furthermore, we extended the method to 2,3-dimethylbuta-1,3-diene (**19**) as diene, and its reaction with **9a** yielded cycloadduct **20a** in good yield and with high *trans* selectivity (gray box, Scheme 2).

EPC-Catalyzed Nazarov Cyclization. The Nazaraov cyclization is another synthetically useful pericyclic reaction,[21] and no examples of EPC catalysis have been reported. We therefore tested catalyst **6** in the Nazarov cyclization with alkoxy-substituted dienone **21a**[22] as model substrate (Table 2). A catalyst loading of 3.0 mol % and a reaction time of 1 h at room temperature in dichloromethane was sufficient for full conversion (entry 1); the diastereoselectivity for **22a** slightly favoring *cis* was poor though. To increase the diastereoselectivity, we began testing different solvents. The use of benzene led mainly to the *trans* product (entry 2). While the increase from 43:57 to 84:16 was substantial, the ring closure was less clean. These impurities were reduced with 1,2-difluorobenzene as solvent, but the diastereomeric ratio dropped to 61:39 (entry 3). However, diastereocontrol was restored at a shorter reaction time (entry 4). Furthermore, a

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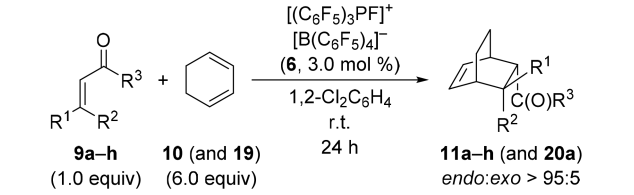
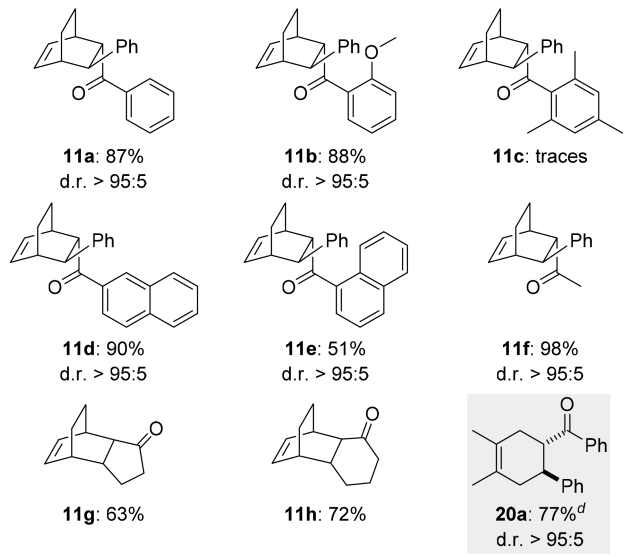
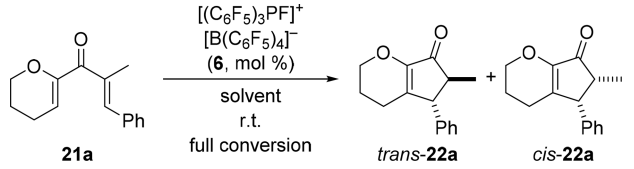
Scheme 2. Substrate Scope of the EPC-Catalyzed Diels–Alder Reaction of Cyclohexa-1,3-diene[a–c]





[a]All reactions were performed according to General Procedure **GP1** (see the Experimental Section). [b]*endo*:*exo* ratio was determined by GLC analysis prior to purification. [c]Diastereomeric ratio (*trans*:*cis*) was determined by GLC analysis prior to purification. [d]2,3-Dimethylbuta-1,3-diene (**19**) was used instead of cyclohexa-1,3-diene.

Table 2. Optimization of the EPC-Catalyzed Nazarov Reaction[a]



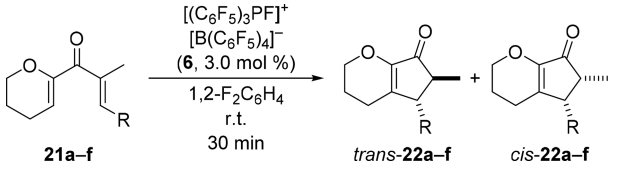
entry	catalyst **6** (mol %)	solvent	*t* (min)	dr[b]
1	3.0	CH_2Cl_2	60	43:57
2	3.0	C_6H_6	60	84:16
3	3.0	1,2-$F_2C_6H_4$	60	61:39
4	3.0	1,2-$F_2C_6H_4$	30	89:11
5	1.0	1,2-$F_2C_6H_4$	60	51:49
6	5.0	1,2-$F_2C_6H_4$	60	87:13

[a]All reactions were performed according to General Procedure **GP3** (see the Experimental Section). [b]*trans*:*cis* ratio was determined by ^{1}H NMR analysis prior to purification.

lower catalyst loading of 1.0 mol % was detrimental, while 5.0 mol % of **6** had no negative effect (entries 5 and 6).

We then examined the substrate scope under the optimized reaction conditions (Table 2, entry 4) with different (hetero)aromatic substituents in the *β*-position of alkoxy-substituted dienones **21a–f** (Table 3). The isolated yields of cyclized **22a–f** were rather low throughout; these ring closures proceeded essentially with no diastereocontrol. The ability of

Table 3. Substrate Scope of the EPC-Catalyzed Nazarov Cyclization of Activated Dienones[a]



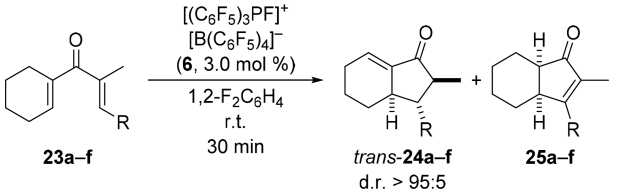
entry	precursor	R	dr[b]	yield[c,d] of **22** (%)
1	**21a**	Ph	63:37	23 (**22a**)
2	**21b**	4-BrC_6H_4	57:43	35 (**22b**)
3	**21c**	4-$(CF_3)C_6H_4$	45:55	41 (**22c**)
4	**21d**	4-$(OMe)C_6H_4$	35:65	30 (**22d**)
5	**21e**	fur-2-yl	55:45	26 (**22e**)
6	**21f**	thien-2-yl	51:49	28 (**22f**)

[a]All reactions were performed according to General Procedure **GP3** (see the Experimental Section). [b]*trans*:*cis* ratio was determined by ^{1}H NMR analysis prior to purification. [c]Combined isolated yield of both diastereomers after flash column chromatography on silica gel. [d]Isolated with inseparable unknown impurities.

EPC **6** to engage in deoxygenation[19] could be an explanation for the mediocre yields (see above). To verify this, we again performed independent NMR experiments with substrate/catalyst and product/catalyst combinations, respectively. Our assumption proved to be true, as we observed the deoxygenation of both cyclization precursor **21a** and cyclized product **22a**; catalyst **6** again decomposed to $(C_6F_5)_3PF_2$ and $(C_6F_5)_3PO$ (see the Supporting Information for details). It is important to mention that these new phosphorus compounds are not catalytically active in this Nazarov cyclization.

Unactivated dienones **23a–f**[23] are devoid of the ether oxygen atom present in **21a–f**, and these cyclization precursors showed higher yields in Nazarov cyclizations under otherwise identical reaction conditions (Table 4). In this ring closure, *trans*-**24a** was obtained along with regioisomer **25a**. For example, **23a** cyclized with a 85:15 regioisomeric ratio in 96% combined yield (entry 1). Related compounds **24b–d** and **25b–d** with an aromatic substituent in the *β*-position were

Table 4. Substrate Scope of the EPC-Catalyzed Nazarov Cyclization of Unactivated Dienones[a]



entry	precursor	R	**24**:**25**[b]	combined yield[c] of **24**/**25** (%)
1	**23a**	Ph	85:15	96 (**24a**/**25a**)
2	**23b**	4-BrC_6H_4	83:17	77 (**24b**/**25b**)
3	**23c**	4-$(CF_3)C_6H_4$	88:12	82 (**24c**/**25c**)
4	**23d**	4-$(OMe)C_6H_4$	84:16	59 (**24d**/**25d**)
5	**23e**	fur-2-yl	53:47	63 (**24e**/**25e**)
6	**23f**	thien-2-yl	64:36	80 (**24f**/**25f**)

[a]All reactions were performed according to General Procedure **GP3** (see the Experimental Section). [b]Regioisomeric ratio determined by ^{1}H NMR analysis prior to purification. [c]Combined isolated yield of both regioisomers after flash column chromatography on silica gel.

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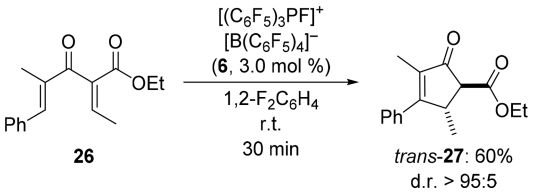
generally formed with a regioselectivity of approximately 85:15 (entries 2−4). The use of more electron donating groups such as fur-2-yl and thien-2-yl shifts the ratio more toward the regioisomers **25e,f** with the higher substituted double bond (entries 5 and 6). A reason for this could be the changed polarization in the divinyl ketone.[24] Again, the yields are lower of ether-oxygen-containing systems such as **23d,e** (entries 4 and 5); the effect is less pronounced, but yields dwindled from around 80% to 59% and 63%, respectively.

The Nazarov cyclization of precursor **26**[25] bearing an electron-withdrawing group in the α-position was successfully catalyzed by catalyst **6** to afford **27** in 60% yield (Scheme 3). The diastereoselectivity in favor of the *trans* isomer was high.

Scheme 3. Nazarov Cyclization of Divinyl Ketone with Electron-Withdrawing Group[a,b]



[a]The reaction was performed according to General Procedure **GP3** (see the Experimental Section). [b]*trans*:*cis* ratio was determined by ^{1}H NMR analysis prior to purification.

■ CONCLUSION

This systematic study shows that electrophilic phosphonium cations (EPCs) promote pericyclic reactions. The EPC **6** was identified as sufficiently Lewis acidic to catalyze difficult Diels−Alder reactions of cyclohexa-1,3-dienes as well as Nazarov cyclizations of activated and unactivated divinyl ketones.

■ EXPERIMENTAL SECTION

General Information. All reactions were performed in flame-dried glassware using an MBraun glovebox or conventional Schlenk techniques under a static pressure of argon (glovebox) or nitrogen. Liquids and solutions were transferred with syringes and cannulas. Solvents were dried and purified using standard procedures. Technical grade solvents for extraction or chromatography were distilled prior to use. C_6D_6, $CDCl_3$, and CD_2Cl_2 were dried over 4 Å molecular sieves. 1,2-$Cl_2C_6D_4$, cyclohexa-1,3-diene (**10**), and 2,3-dimethylbuta-1,3-diene (**19**) were dried over CaH_2, distilled, degassed, and stored under argon. Cyclopent-2-en-1-one and cyclohex-2-en-1-one were condensed, degassed, and stored under argon. Catalyst **6** was synthesized according to a literature procedure.[7] α,β-Unsaturated ketones **9a,d,e**[26,27] for Diels−Alder reactions as well as α,β-unsaturated aldehydes,[28] 1-bromocyclohex-1-ene,[29] diallyl alcohols,[22] their corresponding divinyl ketones **21a−f** and **23a−f**,[23] and divinyl ketone **26**[25] for Nazarov reactions were prepared according to literature procedures. Other chemicals not previously mentioned were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum sheets from Merck using the indicated solvents. Flash column chromatography was performed on silica gel 60 (40−63 μm, 230−400 mesh, ASTM) from Merck using the indicated solvents. ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, C_6D_6, or 1,2-$Cl_2C_6D_4$ on Bruker AV400 and Bruker AV500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$, δ 7.26 ppm for ^{1}H NMR; $CDCl_3$, δ 77.16 ppm for ^{13}C NMR; $CDHCl_2$, δ 5.32 ppm for ^{1}H NMR; CD_2Cl_2, δ 53.84 ppm for ^{13}C NMR; C_6D_5H, δ 7.16 ppm for ^{1}H NMR; C_6D_6, δ 128.06 ppm for ^{13}C NMR; 1,2-$Cl_2C_6D_3H$, δ 6.94 and 7.20 ppm for ^{1}H NMR; 1,2-$Cl_2C_6D_4$, δ 127.1, 130.1, and 132.5 ppm for ^{13}C NMR).[30] NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrophotometer equipped with an ATR unit and are reported as wavenumbers (cm^{-1}) (w = weak, m = medium, s = strong). Gas−liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph equipped with an HP-5 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) using the following program: N_2, carrier gas; injection temperature, 240 °C; detector temperature, 300 °C; flow rate, 1.74 mL/min; temperature program, start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Melting points (mp) were determined with a Stuart Scientific SMP20 melting point apparatus and are not corrected. High-resolution mass spectrometry (HRMS) was performed at the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

General Procedure for Diels−Alder Reactions Catalyzed by $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (6) (GP1). In a glovebox, a flame-dried GLC vial equipped with a magnetic stir bar was charged with the corresponding diene (0.49 mmol, 6.0 equiv), the indicated dienophile (82 μmol, 1.0 equiv), and 1,2-$Cl_2C_6H_4$ (0.1 mL). To this mixture was added a solution of $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 2.5 μmol, 3.0 mol %) in 1,2-$Cl_2C_6H_4$ (0.1 mL). After the reaction mixture was stirred for 24 h, the cycloadduct was purified by flash column chromatography on silica gel using a cyclohexane/dichloromethane or *n*-pentane/ethyl acetate mixture as eluent.

General Procedure for the Preparation of Divinyl Ketones (GP2). According to a procedure modified from that of Rawal,[23] *t*BuLi (1.70−1.82 M in pentane, 1.09−1.10 equiv) was added dropwise to a THF solution of 3,4-dihydro-2*H*-pyran or 1-bromocyclohex-1-ene (1.00 equiv) at −78 °C. After stirring of the reaction mixture for 30 min at 0 °C, a solution of the indicated aldehyde (1.10 equiv) in THF was added at −78 °C. The resulting mixture was stirred for 2 h at 0 °C, quenched with water (50 mL), and diluted with *tert*-butyl methyl ether (50 mL). After separation of the layers, the water phase was extracted with *tert*-butyl methyl ether (3 × 50 mL) and the combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The purification of the residue by flash column chromatography on silica gel using cyclohexane/ethyl acetate or cyclohexane/*tert*-butyl methyl ether mixtures as eluent afforded the corresponding diallyl alcohol. To a solution of the diallyl alcohol (1.0 equiv) in dichloromethane and pyridine was added successively Dess−Martin periodinane (1.1 equiv) at room temperature. After stirring of the mixture for 2 h at room temperature, the reaction was quenched by addition of a solution of aqueous NaOH (2 M, 50 mL). The resulting solution was stirred for 30 min. The layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a cyclohexane/ethyl acetate or *n*-pentane/*tert*-butyl methyl ether mixture as eluent.

General Procedure for Nazarov Cyclizations Catalyzed by $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (6) (GP3). In a glovebox, a flame-dried GLC vial equipped with a magnetic stir bar was charged with the corresponding divinyl ketone (0.082 mmol, 1.0 equiv) and 1,2-$F_2C_6H_4$ (0.1 mL). To this mixture was added a solution of $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 2.5 μmol, 3.0 mol %) in 1,2-$F_2C_6H_4$ (0.1 mL). After stirring of the reaction mixture for 30 min, the product was purified by flash column chromatography on silica gel using a cyclohexane/dichloromethane or cyclohexane/*tert*-butyl methyl ether mixture as eluent.

*endo-Phenyl(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (**11a**).* Prepared from (*E*)-chalcone (**9a**; 17 mg, 82 μmol, 1.0 equiv), cyclohexa-1,3-diene (**10**; 39 mg, 0.49 mmol, 6.0 equiv), and

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$[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP1**. The product **11a** (20.6 mg, 71.0 μmol, 87%) was obtained as a white solid after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 80/20) as eluent. R_f = 0.47 (cyclohexane/dichloromethane = 1/1). Mp: 118 °C (*n*-pentane). GLC (HP-5): t_R = 24.4 min. IR (ATR): $\tilde{\nu}$ 2926 (w), 2863 (w), 1672 (s), 1595 (w), 1446 (m), 1216 (m), 960 (m), 746 (s), 689 (s) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{21}H_{21}O^+$ [M + H]$^+$, 289.1587; found, 289.1582. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10−1.16 (m, 1H), 1.46−1.52 (m, 1H), 1.81−1.86 (m, 1H), 1.88−1.94 (m, 1H), 2.67−2.68 (m, 1H), 2.97−2.99 (m, 1H), 3.48−3.49 (m, 1H), 3.80−3.82 (m, 1H), 6.11−6.13 (m, 1H), 6.56−6.59 (m, 1H), 7.19−7.23 (m, 1H), 7.29−7.34 (m, 4H), 7.38−7.41 (m, 2H), 7.49−7.53 (m, 1H), 7.86−7.88 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 18.7, 26.6, 34.7, 36.6, 44.9, 51.1, 126.3, 128.3 (2C), 128.6 (4C), 128.6 (2C), 130.8, 132.8, 136.4, 136.6, 143.0, 200.9. The analytical and spectroscopic data are in accordance with those reported.[27]

*endo-(2-Methoxyphenyl)(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)-methanone (**11b**).* Prepared from (*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one (**9b**; 19.5 mg, 82.0 μmol, 1.00 equiv), cyclohexa-1,3-diene (**10**; 39 mg, 0.49 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP1**. The product **11b** (22.8 mg, 72.0 μmol, 88%) was obtained as a colorless oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 80/20 → 50/50) as eluent. R_f = 0.26 (cyclohexane/dichloromethane = 1/1). GLC (HP-5): t_R = 25.9 min. IR (ATR): $\tilde{\nu}$ 2938 (w), 2863 (w), 1672 (m), 1595 (m), 1483 (m), 1460 (m), 1434 (m), 1282 (m), 1242 (s), 1019 (m), 961 (m), 750 (s), 699 (s) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{22}H_{23}O_2^+$ [M + H]$^+$, 319.1693; found, 319.1686. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03−1.09 (m, 1H), 1.40−1.45 (m, 1H), 1.71−1.80 (m, 2H), 2.60−2.61 (m, 1H), 2.96−2.97 (m, 1H), 3.40−3.42 (m, 1H), 3.70 (s, 3H), 3.90−3.91 (m, 1H), 6.11−6.14 (m, 1H), 6.52−6.55 (m, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.95−6.97 (m, 1H), 7.17−7.20 (m, 1H), 7.25−7.32 (m, 4H), 7.35−7.39 (m, 1H), 7.43 (dd, *J* = 7.6 Hz, *J* = 1.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 18.7, 26.5, 33.5, 37.0, 44.8, 55.0, 55.4, 111.3, 120.8, 126.0, 128.3 (2C), 128.3 (2C), 129.3, 130.1, 131.3, 132.4, 136.6, 143.4, 157.4, 204.5. The analytical and spectroscopic data are in accordance with those reported.[27]

*endo-Naphthalen-2-yl(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)-methanone (**11d**).* Prepared from (*E*)-1-(naphthalen-2-yl)-3-phenylprop-2-en-1-one (**9d**; 21 mg, 82 μmol, 1.0 equiv), cyclohexa-1,3-diene (**10**; 39 mg, 0.49 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP1**. The product **11d** (24.9 mg, 74.0 μmol, 90%) was obtained as a yellow solid after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 80/20) as eluent. R_f = 0.53 (cyclohexane/dichloromethane = 1/1). Mp: 151 °C (*n*-pentane). GLC (HP-5): t_R = 33.0 min. IR (ATR): $\tilde{\nu}$ 2926 (w), 2863 (w), 1671 (s), 1451 (w), 1184 (w), 829 (m), 745 (s), 696 (s) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{25}H_{23}O^+$ [M + H]$^+$, 339.1743; found, 339.1739. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13−1.20 (m, 1H), 1.50−1.57 (m, 1H), 1.86−1.92 (m, 1H), 1.94−1.99 (m, 1H), 2.68−2.70 (m, 1H), 3.06−3.08 (m, 1H), 3.45 (m_c, 1H), 3.94 (m_c, 1H), 6.22 (m_c, 1H), 6.57 (m_c, 1H), 7.23−7.25 (m, 1H), 7.33−7.35 (m, 4H), 7.49 (m_c, 1H), 7.57 (m_c, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.97 (dd, *J* = 8.6 Hz, *J* = 1.7 Hz, 1H), 8.25 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 18.8, 26.4, 34.5, 36.7, 45.5, 51.7, 124.6, 126.4, 126.7, 127.8, 128.4 (4C), 128.7 (2C), 129.6, 130.2, 131.5, 132.6, 133.7, 135.5, 136.0, 143.2, 201.0. The analytical and spectroscopic data are in accordance with those reported.[27]

*endo-Naphthalen-1-yl(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)-methanone (**11e**).* Prepared from (*E*)-1-(naphthalen-1-yl)-3-phenylprop-2-en-1-one (**9e**; 21 mg, 82 μmol, 1.0 equiv), cyclohexa-1,3-diene (**10**; 39 mg, 0.49 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP1**. The product **11e** (14.2 mg, 42.0 μmol, 51%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 80/20) as eluent. R_f = 0.53 (cyclohexane/dichloromethane = 1/1). GLC (HP-5): t_R = 30.9 min. IR (ATR): $\tilde{\nu}$ 2925 (w), 2859 (w), 1681 (s), 1229 (w), 1100 (m), 802 (m), 777 (s), 750 (m), 698 (s) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{25}H_{23}O^+$ [M + H]$^+$, 339.1743; found, 339.1738. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04−1.12 (m, 1H), 1.38−1.45 (m, 1H), 1.75−1.82 (m, 2H), 2.65−2.66 (m, 1H), 2.92−2.93 (m, 1H), 3.55−3.56 (m, 1H), 3.76−3.78 (m, 1H), 6.17−6.21 (m, 1H), 6.60−6.64 (m, 1H), 7.21−7.25 (m, 1H), 7.28−7.38 (m, 5H), 7.51−7.53 (m, 3H), 7.85−7.87 (m, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 8.10−8.12 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 18.8, 26.4, 33.8, 37.0, 44.4, 55.3, 124.4, 125.5, 125.6, 126.3, 126.5, 127.5, 128.3 (2C), 128.5, 128.6 (2C), 130.6, 131.0, 131.3, 133.9, 137.0, 137.7, 143.0, 205.5. The analytical and spectroscopic data are in accordance with those reported.[27]

*endo-1-(3-Phenylbicyclo[2.2.2]oct-5-en-2-yl)ethan-1-one (**11f**).* Prepared from (*E*)-4-phenylbut-3-en-2-one (**9f**; 12 mg, 82 μmol, 1.0 equiv), cyclohexa-1,3-diene (**10**; 39 mg, 0.49 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP1**. The product **11f** (18.2 mg, 80.0 μmol, 98%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 2/1) as eluent. R_f = 0.37 (cyclohexane/dichloromethane = 1/1). GLC (HP-5): t_R = 18.6 min. IR (ATR): $\tilde{\nu}$ 2941 (w), 2866 (w), 1704 (s), 1353 (m), 1163 (m), 748 (m), 700 (s), 667 (m) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{16}H_{19}O^+$ [M + H]$^+$, 227.1430; found, 227.1426. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00−1.06 (m, 1H), 1.43−1.48 (m, 1H), 1.65−1.76 (m, 2H), 2.03 (s, 3H), 2.52−2.54 (m, 1H), 2.93−2.94 (m, 1H), 3.01−3.02 (m, 1H), 3.12−3.13 (m, 1H), 6.20−6.23 (m,1H), 6.46−6.49 (m, 1H), 7.22−7.25 (m, 1H), 7.28−7.29 (m, 2H), 7.33−7.36 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 18.5, 26.1, 28.5, 32.7, 37.3, 45.6, 56.6, 126.5, 128.2 (2C), 128.6 (2C), 131.6, 136.1, 142.8, 209.0. The analytical and spectroscopic data are in accordance with those reported.[27]

*endo-Tricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (**11g**).* Prepared from cyclopent-2-en-1-one (**9g**; 13 mg, 0.16 mmol, 1.0 equiv), cyclohexa-1,3-diene (**10**; 78 mg, 0.97 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 6.2 mg, 5.0 μmol, 3.0 mol %) according to **GP1**. The product **11g** (16.8 mg, 0.100 mmol, 63%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using *n*-pentane/ethyl acetate (40/1) as eluent. R_f = 0.27 (cyclohexane/ethyl acetate = 20/1). GLC (HP-5): t_R = 13.0 min. IR (ATR): $\tilde{\nu}$ 2931 (w), 2865 (w), 1726 (s), 1167 (m), 708 (s) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{11}H_{15}O^+$ [M + H]$^+$, 163.1117; found, 163.1115. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22−1.30 (m, 2H), 1.46−1.59 (m, 3H), 1.94−2.12 (m, 3H), 2.35−2.38 (m_c, 1H), 2.52−2.58 (m, 1H), 2.64−2.65 (m, 1H), 2.93−2.95 (m, 1H), 6.14−6.17 (m, 1H), 6.20−6.23 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 24.2, 24.9, 26.2, 32.6, 35.6, 38.3, 39.8, 52.5, 133.7, 133.9, 222.9. The analytical and spectroscopic data are in accordance with those reported.[11]

*endo-Tricyclo[6.2.2.0^{2,7}]dodec-9-en-3-one (**11h**).* Prepared from cyclohex-2-en-1-one (**9h**; 15 mg, 0.16 mmol, 1.0 equiv), cyclohexa-1,3-diene (**10**; 77 mg, 0.96 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 5.9 mg, 4.8 μmol, 3.0 mol %) according to **GP1**. The product **11h** (20.2 mg, 0.110 mmol, 69%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using *n*-pentane/ethyl acetate (40/1) as eluent. R_f = 0.28 (cyclohexane/ethyl acetate = 20/1); GLC (HP-5): t_R = 14.6 min. IR (ATR): $\tilde{\nu}$ 2931 (m), 2866 (w), 1700 (s), 713 (m) cm^{-1}. HRMS (APCI, *m*/*z*): calculated for $C_{12}H_{17}O^+$ [M + H]$^+$, 177.1274; found, 177.1269. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91−0.99 (m, 1H), 1.25−1.32 (m, 2H), 1.48−1.52 (m, 1H), 1.55−1.59 (m, 1H), 1.69−1.82 (m, 3H), 2.03−2.11 (m, 1H), 2.32−2.35 (m, 1H), 2.36−2.41 (m, 1H), 2.42−2.44 (m, 1H), 2.50 (m_c, 1H), 3.08 (m_c, 1H), 6.12 (m_c, 1H), 6.25 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 20.9, 24.1, 26.1, 29.7, 31.3, 36.0, 38.9, 42.3, 53.1, 133.2, 134.6, 214.6. The analytical and spectroscopic data are in accordance with those reported.[11]

*(3,4-Dimethyl-6-phenylcyclohex-3-en-1-yl)phenylmethanone (**20a**).* Prepared from (*E*)-chalcone (**9a**; 17 mg, 82 μmol, 1.0 equiv), 2,3-dimethylbuta-1,3-diene (**19**; 40 mg, 0.49 mmol, 6.0 equiv), and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according

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to **GP1**. The product **20a** (18.3 mg, 63.0 μmol, 77%) was obtained as a colorless oil after purification by flash column chromatography on silica gel using *n*-pentane/ethyl acetate (40/1) as eluent. R_f = 0.40 (cyclohexane/ethyl acetate = 20/1). GLC (HP-5): t_R = 24.0 min. IR (ATR): $\tilde{\nu}$ 2926 (w), 1673 (m), 1446 (m), 758 (m), 696 (s) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{21}H_{23}O^+$ $[M + H]^+$, 291.1743; found, 291.1735. ^1H NMR (500 MHz, $CDCl_3$): δ 1.69 (s, 6H), 2.25−2.37 (m, 4H), 3.30 (m_c, 1H), 4.00 (td, *J* = 10.7 Hz, *J* = 5.4 Hz, 1H), 7.06 (m_c, 1H), 7.14−7.20 (m, 4H), 7.38 (m_c, 2H), 7.48 (m_c, 1H), 7.81−7.83 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 18.8, 18.9, 37.1, 40.8, 43.2, 47.6, 124.3, 125.8, 126.3, 127.5 (2C), 128.2 (2C), 128.4 (2C), 128.6 (2C), 132.8, 137.5, 144.8, 203.6. The analytical and spectroscopic data are in accordance with those reported.[11]

(E)-1-(3,4-Dihydro-2H-pyran-6-yl)-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**21c**). Prepared from 3,4-dihydro-2*H*-pyran (0.46 g, 0.50 mL, 5.5 mmol, 1.0 equiv), *t*BuLi (1.7 M in pentane, 3.5 mL, 6.0 mmol, 1.1 equiv), and the crude (*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)acrylaldehyde (1.31 g, ∼1.11 equiv) in THF (3 mL) according to **GP2**. (*E*)-1-(3,4-Dihydro-2*H*-pyran-6-yl)-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (0.84 g, 2.8 mmol, 24% over two steps) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (20/1 → 10/1) as eluent. IR (ATR): $\tilde{\nu}$ 2931 (w), 2851 (w), 1613 (w), 1321 (s), 1160 (m), 1108 (s), 1063 (s), 1014 (m) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{16}H_{18}F_3O_2^+$ $[M + H]^+$, 299.1253; found, 299.1251. ^1H NMR (500 MHz, C_6D_6): δ 1.36−1.45 (m, 2H), 1.76−1.79 (m, 5H), 1.81−1.84 (m, 1H), 3.66 (m_c, 2H), 4.43 (m_c, 1H), 4.77 (t, *J* = 3.8 Hz, 1H), 6.62 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 14.4, 20.2, 22.6, 66.3, 77.5, 97.3, 125.2 (q, $^3J_{C,F}$ = 3.6 Hz, 2C), 125.4, 127.4 (q, $^1J_{C,F}$ = 288 Hz), 129.5 (2C), 140.6, 141.9, 154.0. One quaternary C atom could not be detected. $^{19}F\{^1H\}$ NMR (471 MHz, C_6D_6): δ = −62.1. The previously prepared diallyl alcohol (0.72 g, 2.4 mmol, 1.0 equiv) in dichloromethane (50 mL) was then reacted with pyridine (2 mL) and Dess−Martin periodinane (1.4 g, 3.3 mmol, 1.4 equiv) according to **GP2**. The product **21c** (0.41 g, 1.4 mmol, 58%) was obtained as a yellow solid after purification by flash column chromatography on silica gel using *n*-pentane/*tert*-butyl methyl ether (100/1 → 20/1) as eluent. IR (ATR): $\tilde{\nu}$ 1650 (m), 1615 (m), 1320 (s), 1256 (m), 1163 (m), 1110 (s), 1063 (s), 1012 (s), 908 (m), 843 (m) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{16}H_{16}F_3O_2^+$ $[M + H]^+$, 297.1097; found, 297.1091. ^1H NMR (500 MHz, $CDCl_3$): δ 1.89−1.96 (m, 2H), 2.12 (d, *J* = 1.4 Hz, 3H), 2.24−2.30 (m, 2H), 4.15−4.18 (m, 2H), 5.86 (t, *J* = 4.2 Hz, 1H), 7.20 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 15.0, 21.1, 21.7, 66.6, 113.7, 124.1 (q, $^1J_{C,F}$ = 271 Hz), 125.5 (q, $^3J_{C,F}$ = 3.5 Hz, 2C), 129.7 (2C), 130.1 (q, $^2J_{C,F}$ = 32.3 Hz), 136.4, 138.1, 139.6, 151.3, 193.3. $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$): δ −62.7.

(E)-1-(3,4-Dihydro-2H-pyran-6-yl)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-one (**21d**). Prepared from 3,4-dihydro-2*H*-pyran (0.37 g, 0.40 mL, 4.4 mmol, 1.0 equiv), *t*BuLi (1.8 M in pentane, 2.7 mL, 4.9 mmol, 1.1 equiv), and (*E*)-3-(4-methoxyphenyl)-2-methylacrylaldehyde (0.80 g, 4.5 mmol, 1.0 equiv) in THF (3 mL) according to **GP2**. (*E*)-1-(3,4-Dihydro-2*H*-pyran-6-yl)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-ol (0.62 g, 2.4 mmol, 55%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (100/1 → 10/1) as eluent. R_f = 0.19 (cyclohexane/*tert*-butyl methyl ether = 3/1). IR (ATR): $\tilde{\nu}$ 2928 (w), 2843 (w) 1673 (w), 1605 (m), 1508 (s), 1440 (w), 1296 (w), 1245 (s), 1175 (s), 1059 (s), 1031 (s) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{16}H_{21}O_3^+$ $[M + H]^+$, 261.1485; found, 261.1485. ^1H NMR (500 MHz, C_6D_6): δ 1.38−1.46 (m, 2H), 1.76−1.82 (m, 2H), 1.84 (d, *J* = 5.1 Hz, 1H), 1.97 (d, *J* = 1.3 Hz, 3H), 3.31 (s, 3H), 3.69 (m_c, 2H), 4.56 (d, *J* = 4.8 Hz, 1H), 4.86 (t, *J* = 3.7 Hz, 1H), 6.74 (s, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 14.4, 20.3, 22.7, 54.8, 66.3, 78.0, 96.7, 114.0 (2C), 126.8, 130.7 (2C), 130.9, 136.6, 154.5, 158.8. The previously prepared diallyl alcohol (0.50 g, 1.9 mmol, 1.0 equiv) in dichloromethane (50 mL) was then reacted with pyridine (2.0 mL), and Dess−Martin periodinane (0.90 g, 2.1 mmol, 1.1 equiv) according to **GP2**. The product **21d** (0.32 g, 1.2 mmol, 63%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (100/1 → 10/1) as eluent. R_f = 0.27 (cyclohexane/*tert*-butyl methyl ether = 3/1). IR (ATR): $\tilde{\nu}$ 1598 (s), 1508 (s), 1300 (m), 1249 (s), 1174 (s), 1057 (s), 1014 (s), 904 (m), 827 (m) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{16}H_{19}O_3^+$ $[M + H]^+$: 259.1329; found, 259.1331. ^1H NMR (500 MHz, C_6D_6): δ 1.31−1.37 (m, 2H), 1.72 (m_c, 2H), 2.21 (d, *J* = 1.3 Hz, 3H), 3.26 (s, 3H), 3.68−3.72 (m, 2H), 5.72 (t, *J* = 4.2 Hz, 1H), 6.71 (m_c, 2H), 7.21 (m_c, 2H), 7.54 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 14.7, 20.8, 22.0, 54.8, 66.0, 109.3, 114.2 (2C), 129.2, 131.7 (2C), 134.7, 139.4, 152.8, 160.1, 192.3.

(E)-1-(Cyclohex-1-en-1-yl)-2-methyl-3-(4-(trifluoromethyl)-phenyl)prop-2-en-1-one (**23c**). Prepared from 1-bromocyclohex-1-ene (1.00 g, 6.21 mmol, 1.00 equiv) in THF (4 mL), *t*BuLi (1.82 M in pentane, 3.70 mL, 6.77 mmol, 1.09 equiv), and (*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)acrylaldehyde (1.46 g, 6.83 mmol, 1.10 equiv) in THF (2 mL) according to **GP2**. (*E*)-1-(Cyclohex-1-en-1-yl)-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (0.59 g, 2.0 mmol, 32%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1 → 10/1) as eluent. R_f = 0.19 (cyclohexane/ethyl acetate = 90/10). GLC (HP-5): t_R = 20.0 min. IR (ATR): $\tilde{\nu}$ 3363 (w), 2925 (w), 2857 (w), 1613 (w), 1320 (s), 1161 (m), 1107 (s), 1065 (s), 1014 (m), 838 (w) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{17}H_{18}F_3^+$ $[M - OH]^+$, 279.1355; found, 279.1354. ^1H NMR (500 MHz, C_6D_6): δ 1.05 (s, 1H), 1.43−1.50 (m, 2H), 1.50−1.56 (m, 2H), 1.59 (d, *J* = 1.3 Hz, 3H), 1.75−1.80 (m, 1H), 1.92−1.96 (m, 3H), 4.21 (s, 1H), 5.69−5.71 (m, 1H), 6.55 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 14.3, 23.0, 23.1, 24.3, 25.4, 80.9, 124.1, 124.4, 125.2 (q, $^1J_{C,F}$ = 272 Hz), 125.3 (q, $^3J_{C,F}$ = 3.9 Hz, 2C), 129.5 (2C), 138.2, 141.2, 142.0. ^{19}F NMR (471 MHz, C_6D_6): δ −62.0. One quaternary C atom could not be detected. The previously prepared diallyl alcohol (0.500 g, 1.69 mmol, 1.00 equiv) in dichloromethane (25 mL) was then reacted with pyridine (1 mL) and Dess−Martin periodinane (0.790 g, 1.86 mmol, 1.10 equiv) according to **GP2**. The product **23c** (0.267 g, 0.910 mmol, 54%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.47 (cyclohexane/ethyl acetate = 10/1). GLC (HP-5): t_R = 20.0 min. IR (ATR): $\tilde{\nu}$ 2931 (w), 1629 (s), 1320 (s), 1235 (m), 1162 (m), 1119 (s), 1065 (s), 1005 (m), 821 (m) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{17}H_{18}F_3O^+$ $[M + H]^+$, 295.1304; found, 295.1306. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.64−1.69 (m, 2H), 1.69−1.74 (m, 2H), 2.08 (d, *J* = 1.5 Hz, 3H), 2.25−2.30 (m, 2H), 2.30−2.33 (m, 2H), 6.68−6.70 (m, 1H), 6.99 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 15.2, 22.1, 22.5, 24.5, 26.4, 124.7 (q, $^1J_{C,F}$ = 272 Hz), 125.6 (q, $^3J_{C,F}$ = 3.6 Hz, 2C), 129.7 (q, $^2J_{C,F}$ = 32 Hz), 130.0 (2C), 135.2, 138.5, 139.5, 140.5, 142.0, 200.3. ^{19}F NMR (471 MHz, CD_2Cl_2): δ −63.0.

(E)-1-(Cyclohex-1-en-1-yl)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-one (**23d**). Prepared from 1-bromocyclohex-1-ene (0.700 g, 4.35 mmol, 1.00 equiv) in THF (4 mL), *t*BuLi (1.82 M in pentane, 2.60 mL, 4.74 mmol, 1.09 equiv), and (*E*)-3-(4-methoxyphenyl)-2-methylacrylaldehyde (0.840 g, 4.79 mmol, 1.10 equiv) in THF (2 mL) according to **GP2**. (*E*)-1-(Cyclohex-1-en-1-yl)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-ol (0.272 g, 1.05 mmol, 24%) was obtained as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1 → 10/1) as eluent. R_f = 0.29 (cyclohexane/ethyl acetate = 90/10). GLC (HP-5): t_R = 23.0 min. IR (ATR): $\tilde{\nu}$ 3406 (w), 2923 (w), 2833 (w), 1602 (m), 1508 (s), 1439 (m), 1298 (w), 1244 (s), 1174 (s), 1031 (s), 830 (m), 804 (m) cm^{-1}. HRMS (APCI, *m/z*): calculated for $C_{17}H_{21}O^+$ $[M - OH]^+$, 241.1587; found, 241.1588. ^1H NMR (500 MHz, C_6D_6): δ 1.18 (s, 1H), 1.43−1.50 (m, 2H), 1.51−1.57 (m, 2H), 1.79 (d, *J* = 1.3 Hz, 3H), 1.82−1.89 (m, 1H), 1.96−2.00 (m, 3H), 3.33 (s, 3H), 4.33 (s, 1H), 5.81−5.83 (m, 1H), 6.64 (s, 1H), 6.80−6.83 (m, 2H), 7.22−7.25 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz,

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C_6D_6): δ 14.1, 23.1, 23.2, 24.8, 25.4, 54.8, 81.3, 114.0 (2C), 123.0, 125.8, 130.6 (2C), 131.0, 137.3, 138.5, 158.8. The previously prepared diallyl alcohol (0.236 g, 0.910 mmol, 1.00 equiv) in dichloromethane (20 mL) was then reacted with pyridine (0.7 mL) and Dess−Martin periodinane (0.420 g, 1.00 mmol, 1.10 equiv) according to **GP2**. The product **23d** (0.131 g, 0.510 mmol, 56%) was obtained as a white solid after purification by flash column chromatography on silica gel using cyclohexane/ethyl acetate (30/1) as eluent. R_f = 0.56 (cyclohexane/ethyl acetate = 90/10). Mp: 64 °C (*n*-pentane); GLC (HP-5): t_R = 23.3 min. IR (ATR): $\tilde{\nu}$ 2936 (w), 1598 (s), 1509 (s), 1438 (m), 1302 (s), 1246 (s), 1174 (s), 1124 (m), 1026 (s), 1003 (s), 835 (s), 803 (s) cm^{-1}. HRMS (ESI, *m*/*z*): calculated for $C_{17}H_{21}O_2^+$ $[M + H]^+$, 257.1536; found, 257.1543. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.63−1.68 (m, 2H), 1.68−1.74 (m, 2H), 2.09 (d, *J* = 1.5 Hz, 3H), 2.22−2.26 (m, 2H), 2.28−2.32 (m, 2H), 3.83 (s, 3H), 6.52−6.54 (m, 1H), 6.93 (m_c, 2H), 7.05 (m_c, 1H), 7.39 (m_c, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 14.9, 22.2, 22.6, 25.0, 26.2, 55.7, 114.2 (2C), 129.2, 131.6 (2C), 135.3, 138.4, 138.8, 139.8, 160.0, 201.0.

*6-Methyl-5-phenyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (**22a**).* Prepared from divinyl ketone **21a** (37 mg, 0.16 mmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 6.2 mg, 5.0 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (dr(*trans*:*cis*) = 63:37) afforded *trans*-**22a** and *cis*-**22a** (8.7 mg, 38 μmol, 23%, dr(*trans*:*cis*) = 65:35) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (80/20 → 50/50) as eluent. The ratio of *trans*-**22a** to *cis*-**22a** was determined by integration of baseline-separated signals at 3.34 and 4.02 ppm in the ^1H NMR spectrum.

*Analytical Data for trans-**22a**.* R_f = 0.45 (cyclohexane/*tert*-butyl methyl ether = 1/1). GLC (HP-5): t_R = 19.1 min (*cis*-**22a**), t_R = 20.7 min (*trans*-**22a**). HRMS (ESI, *m*/*z*): calculated for $C_{15}H_{17}O_2^+$ $[M + H]^+$, 229.1223; found, 229.1220. ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (d, *J* = 7.5 Hz, 3H), 1.90−1.98 (m, 2H), 2.08−2.12 (m, 2H), 2.22−2.29 (m, 1H), 3.34 (m_c, 1H), 4.16 (m_c, 2H), 7.12−7.15 (m, 2H), 7.27−7.29 (m, 1H), 7.32−7.36 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 15.0, 21.7, 22.2, 49.5, 53.4, 67.1, 127.3, 127.5 (2C), 129.1 (2C), 141.4, 145.4, 150.8, 202.7. The analytical and spectroscopic data are in accordance with those reported.[31]

*Selected Analytical Data for cis-**22a**.* R_f = 0.37 (cyclohexane/*tert*-butyl methyl ether = 1/1). ^1H NMR (500 MHz, $CDCl_3$): δ 0.69 (d, *J* = 7.6 Hz, 3H), 1.95−2.03 (m, 2H), 2.17−2.21 (m, 2H), 2.72−2.79 (m, 1H), 4.00−4.03 (m, 1H), 4.17−4.25 (m, 2H), 7.00−7.04 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 12.4, 21.8, 22.7, 43.4, 49.0, 67.2, 127.3, 128.6, 138.8, 144.9, 203.0. The analytical and spectroscopic data are in accordance with those reported.[23]

*5-(4-Bromophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]-pyran-7(2H)-one (**22b**).* Prepared from divinyl ketone **21b** (25 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (dr(*trans*:*cis*) = 57:43) afforded *trans*-**22b** (4.5 mg, 15 μmol, 18%, dr(*trans*:*cis*) = 96:4) as a colorless oil and *cis*-**22b** (4.2 mg, 14 μmol, 17%, dr(*trans*:*cis*) = 17:83) as a colorless oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (20/1 → 5/1) as eluent. The ratio of *trans*-**22b** to *cis*-**22b** was determined by integration of baseline-separated signals at 3.31 and 3.98 ppm in the ^1H NMR spectrum.

*Analytical Data for trans-**22b**.* R_f = 0.39 (cyclohexane/*tert*-butyl methyl ether = 1/1). GLC (HP-5): t_R = 23.9 min. HRMS (ESI, *m*/*z*): calculated for $C_{15}H_{16}BrO_2^+$ $[M + H]^+$, 307.0328; found, 307.0326. ^1H NMR (500 MHz, $CDCl_3$): δ 1.26 (d, *J* = 7.4 Hz, 3H), 1.91−1.99 (m, 2H), 2.06−2.11 (m, 2H), 2.17−2.23 (m, 1H), 3.31 (m_c, 1H), 4.15 (m_c, 2H), 7.01 (m_c, 2H), 7.47 (m_c, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 15.0, 21.7, 22.1, 49.4, 52.8, 67.1, 121.2, 129.2 (2C), 132.3 (2C), 140.4, 144.5, 151.1, 202.2.

*Selected Analytical Data for cis-**22b**.* R_f = 0.29 (cyclohexane/*tert*-butyl methyl ether = 1/1). GLC (HP-5): t_R = 24.4 min. ^1H NMR (500 MHz, $CDCl_3$): δ 0.69 (d, *J* = 7.6 Hz, 3H), 1.90−2.05 (m, 2H), 2.12−2.20 (m, 2H), 2.75 (m_c, 1H), 3.98 (m_c, 1H), 4.13−4.17 (m, 1H), 4.19−4.25 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.43−7.45 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 12.5, 21.8, 22.6, 43.2, 48.5, 67.3, 130.6 (2C), 131.8 (2C). The analytical and spectroscopic data are in accordance with those reported.[23]

*6-Methyl-5-(4-(trifluoromethyl)phenyl)-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (**22c**).* Prepared from divinyl ketone **21c** (24 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (dr(*trans*:*cis*) = 45:55) afforded *trans*-**22c** and *cis*-**22c** (10 mg, 34 μmol, 41%, dr(*trans*:*cis*) = 44:56) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 4/1 → 1/1) as eluent. The ratio of *trans*-**22c** to *cis*-**22c** was determined by integration of baseline-separated signals at 3.42 and 4.09 ppm in the ^1H NMR spectrum.

*Selected Analytical Data for trans-**22c**.* R_f = 0.22 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 20.9 min. HRMS (ESI, *m*/*z*): calculated for $C_{16}H_{16}F_3O_2^+$ $[M + H]^+$, 297.1097; found, 297.1096. ^1H NMR (500 MHz, $CDCl_3$): δ 1.28 (d, *J* = 7.4 Hz, 3H), 1.92−2.03 (m, 2H), 2.07−2.12 (m, 2H), 2.21−2.25 (m, 1H), 3.42 (m_c, 1H), 4.15−4.19 (m, 2H), 7.25−7.27 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 15.0, 21.6, 22.1, 49.3, 53.1, 67.1, 126.1−126.2 (m, 2C), 127.9 (2C), 144.2, 145.6, 151.3, 202.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ −62.5.

*Selected Analytical Data for cis-**22c**.* R_f = 0.16 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 20.4 min. ^1H NMR (500 MHz, $CDCl_3$): δ 0.68 (d, *J* = 7.7 Hz, 3H), 1.92−2.03 (m, 2H), 2.14−2.19 (m, 2H), 2.77−2.83 (m, 1H), 4.09 (d, *J* = 6.7 Hz, 1H), 4.14−4.19 (m, 1H), 4.21−4.26 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 12.5, 21.7, 22.6, 43.2, 48.8, 67.3, 124.2 (q, $^1J_{C,F}$ = 272 Hz, -CF_3), 125.6 (m_c, 2C), 129.3 (2C), 143.1, 143.8, 152.1, 202.3. ^{19}F NMR (471 MHz, $CDCl_3$): δ −62.5.

*5-(4-Methoxyphenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]-pyran-7(2H)-one (**22d**).* Prepared from divinyl ketone **21d** (21 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (dr(*trans*:*cis*) = 35:65) afforded *trans*-**22d** and *cis*-**22d** (6.4 mg, 25 μmol, 30%, dr(*trans*:*cis*) = 38:62) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 4/1 → 1/1) as eluent. The ratio of *trans*-**22d** to *cis*-**22d** was determined by integration of baseline-separated signals at 3.29 and 3.96 ppm in the ^1H NMR spectrum.

*Analytical Data for trans-**22d**.* R_f = 0.52 (cyclohexane/*tert*-butyl methyl ether = 1/1). GLC (HP-5): t_R = 23.8 min. HRMS (ESI, *m*/*z*): calculated for $C_{16}H_{19}O_3^+$ $[M + H]^+$, 259.1329; found, 259.1328. ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, *J* = 7.4 Hz, 3H), 1.89−2.02 (m, 2H), 2.09 (m_c, 2H), 2.20−2.24 (m, 1H), 3.29 (m_c, 1H), 3.80 (s, 3H), 4.13−4.23 (m, 2H), 6.86−6.89 (m, 2H), 7.03−7.06 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 15.0, 21.8, 22.2, 49.6, 52.6, 55.5, 67.0, 114.5 (2C), 128.5 (2C), 133.2, 145.6, 150.7, 158.9, 202.8.

*Analytical Data for cis-**22d**.* R_f = 0.42 (cyclohexane/*tert*-butyl methyl ether = 1/1). GLC (HP-5): t_R = 23.4 min. ^1H NMR (500 MHz, $CDCl_3$): δ 0.69 (d, *J* = 7.7 Hz, 3H), 1.89−2.02 (m, 2H), 2.16−2.19 (m, 2H), 2.72 (m_c, 1H), 3.80 (s, 3H), 3.96 (m_c, 1H), 4.13−4.23 (m, 2H), 6.83−6.86 (m, 2H), 6.94 (m_c, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 12.5, 21.9, 22.6, 43.6, 48.3, 55.4, 67.2, 114.5 (2C), 129.9 (2C), 130.7, 145.2, 151.6, 158.8, 203.2. The analytical and spectroscopic data are in accordance with those reported.[32]

*3-(Furan-2-yl)-2-methyl-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (**22e**).* Prepared from divinyl ketone **21e** (18 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (dr(*trans*:*cis*) = 55:45) afforded *trans*-**22e** and *cis*-**22e** (4.6 mg, 21 μmol, 26%, dr(*trans*:*cis*) = 54:46) as an orange oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 4/1 → 1/1) as eluent. The ratio of *trans*-**22e** to *cis*-**22e** was determined by integration of baseline-separated signals at 1.27 and 0.84 ppm in the ^1H NMR spectrum.

*Analytical Data for trans-**22e**.* R_f = 0.18 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 18.7 min. HRMS (ESI, *m*/*z*):

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calculated for $C_{13}H_{15}O_3^+$ [M + H]$^+$, 219.1016; found, 219.1015. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (d, J = 7.5 Hz, 3H), 1.94−2.00 (m, 2H), 2.20−2.22 (m, 2H), 2.46−2.51 (m, 1H), 3.50 (m$_c$, 1H), 4.13−4.15 (m, 2H), 6.13 (d, J = 3.3 Hz, 1H), 6.31−6.33 (m, 1H), 7.34−7.35 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 15.0, 21.7, 22.4, 45.6, 46.4, 67.0, 106.4, 110.5, 142.3, 142.7, 150.6, 153.8, 201.7. The analytical and spectroscopic data are in accordance with those reported.[32]

*Analytical Data for cis-**22e**.* R_f = 0.11 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 19.1 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (d, J = 7.6 Hz, 3H), 1.94−2.00 (m, 2H), 2.17−2.33 (m, 2H), 2.68−2.74 (m, 1H), 4.10−4.12 (m, 1H), 4.12−4.23 (m, 2H), 6.06 (m$_c$, 1H), 6.31−6.33 (m, 1H), 7.34−7.35 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 11.9, 21.8, 22.7, 42.7, 43.4, 67.2, 108.2, 110.3, 142.1, 142.2, 151.5, 152.8, 202.3. The analytical and spectroscopic data are in accordance with those reported.[23]

*6-Methyl-5-(thiophen-2-yl)-3,4,5,6-tetrahydrocyclopenta[b]-pyran-7(2H)-one (**22f**).* Prepared from divinyl ketone **21f** (19 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (dr(*trans*:*cis*) = 51:49) afforded *trans*-**22f** and *cis*-**22f** (5.3 mg, 23 μmol, 28%, dr(*trans*:*cis*) = 46:54) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 4/1 → 1/1) as eluent. The ratio of *trans*-**22f** to *cis*-**22f** was determined by integration of baseline-separated signals at 1.29 and 0.84 ppm in the ^{1}H NMR spectrum.

*Selected Analytical Data for trans-**22f**.* R_f = 0.35 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 20.6 min. HRMS (ESI, m/z): calculated for $C_{13}H_{15}O_2S^+$ [M + H]$^+$, 235.0787; found, 235.0786. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (d, J = 7.4 Hz, 3H), 1.93−2.01 (m, 2H), 2.12−2.37 (m, 2H), 2.37−2.42 (m, 1H), 3.68 (m$_c$, 1H), 4.14−4.24 (m, 2H), 6.88 (m$_c$, 1H), 6.95−6.99 (m, 1H), 7.18−7.22 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 15.0, 21.7, 22.2, 48.3, 49.9, 67.3, 124.5, 124.9, 127.2, 144.9, 201.7.

*Selected Analytical Data for cis-**22f**.* R_f = 0.26 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 21.1 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (d, J = 7.6 Hz, 3H), 1.93−2.01 (m, 2H), 2.12−2.37 (m, 2H), 2.74 (m$_c$, 1H), 4.14−4.24 (m, 2H), 4.31 (d, J = 6.6 Hz, 1H), 6.78 (m$_c$, 1H), 6.95−6.99 (m, 1H), 7.18−7.22 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 11.9, 21.8, 22.7, 43.9, 44.1, 67.1, 124.5, 126.4, 127.1, 142.7, 202.2. The analytical and spectroscopic data are in accordance with those reported.[23]

*(2S,3R,3aR)-2-Methyl-3-phenyl-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (trans-**24a**) and (3aS,7aR)-2-Methyl-3-phenyl-3a,4,5,6,7,7a-hexahydro-1H-inden-1-one (**25a**).* Prepared from divinyl ketone **23a** (19 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (*trans*-**24a**:**25a** = 85:15) afforded *trans*-**24a** (8.3 mg, 37 μmol, 45%) as a colorless oil and a product mixture (9.5 mg, 42 μmol, 51%, *trans*-**24a**:**25a** = 54:46) as a colorless oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 4/1 → 1/1) as eluent. The ratio of *trans*-**24a** to **25a** was determined by integration of baseline-separated signals at 6.80 and 3.33 ppm in the ^{1}H NMR spectrum.

*Analytical Data for trans-**24a**.* R_f = 0.63 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 19.7 min. IR (ATR): $\tilde{\nu}$ 2927 (w), 2868 (w), 1715 (s), 1650 (s), 1450 (m), 1174 (m), 922 (m), 759 (m), 698 (s) cm^{-1}. HRMS (ESI, m/z): calculated for $C_{16}H_{19}O^+$ [M + H]$^+$, 227.1430; found, 227.1428. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02−1.10 (m, 1H), 1.04 (d, J = 6.8 Hz, 3H), 1.50 (m$_c$, 1H), 1.83−1.88 (m, 1H), 1.95 (m$_c$, 1H), 2.15−2.25 (m, 1H), 2.28 (m$_c$, 1H), 2.31−2.38 (m, 1H), 2.46 (m$_c$, 1H), 2.58−2.65 (m, 1H), 6.80 (m$_c$, 1H), 7.25−7.26 (m, 1H), 7.27−7.29 (m, 2H), 7.34−7.38 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 12.2, 21.9, 25.8, 27.1, 44.3, 51.0, 56.7, 127.1, 127.6 (2C), 128.8 (2C), 133.0, 140.6, 141.2, 206.1. The analytical and spectroscopic data are in accordance with those reported.[23]

*Selected Analytical Data for **25a**.* R_f = 0.57 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 20.1 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.90 (d, J = 1.6 Hz, 3H), 2.58−2.65 (m, 1H), 3.30−3.36 (m, 1H), 7.39−7.49 (m, 5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 9.8, 21.3, 21.5, 23.0, 28.4, 41.6, 45.7, 127.8 (2C), 128.7 (2C), 129.1.

*(2S,3R,3aR)-3-(4-Bromophenyl)-2-methyl-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (trans-**24b**) and (3aS,7aR)-3-(4-Bromophenyl)-2-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-1-one (**25b**).* Prepared from divinyl ketone **23b** (25 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (*trans*-**23b**:**24b** = 83:17) afforded *trans*-**24b** and **25b** (19.3 mg, 63.0 μmol, 77%, *trans*-**24b**:**25b** = 83:17) as a colorless oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (20/1) as eluent. The ratio of *trans*-**24b** to **25b** was determined by integration of baseline-separated signals at 6.80 and 3.28 ppm in the ^{1}H NMR spectrum.

*Analytical Data for trans-**24b**.* R_f = 0.58 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 23.1 min. HRMS (ESI, m/z): calculated for $C_{16}H_{18}BrO^+$ [M + H]$^+$, 305.0536; found, 305.0536. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00−1.08 (m, 1H), 1.02 (d, J = 6.8 Hz, 3H), 1.45−1.54 (m, 1H), 1.83−1.94 (m, 2H), 2.15−2.26 (m, 2H), 2.31−2.37 (m, 1H), 2.37−2.43 (m, 1H), 2.53−2.61 (m, 1H), 6.80 (m$_c$, 1H), 7.12−7.15 (m, 2H), 7.46−7.49 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 12.1, 21.8, 25.7, 26.9, 44.2, 50.9, 56.2, 120.8, 129.3 (2C), 131.9 (2C), 133.4, 140.2 (2C), 205.5. The analytical and spectroscopic data are in accordance with those reported.[23]

*Selected Analytical Data for **25b**.* R_f = 0.42 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 23.4 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.87 (d, J = 1.6 Hz, 3H), 3.25−3.31 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 9.8, 21.3, 21.5, 22.9, 28.4, 41.4, 45.7, 129.4 (2C), 132.0 (2C).

*(2S,3R,3aR)-2-Methyl-3-(4-(trifluoromethyl)phenyl)-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (trans-**24c**) and (3aS,7aR)-2-Methyl-3-(4-(trifluoromethyl)phenyl)-3a,4,5,6,7,7a-hexahydro-1H-inden-1-one (**25c**).* Prepared from divinyl ketone **23c** (24 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (*trans*-**24c**:**25c** = 88:12) afforded a mixture of *trans*-**24c** and **25c** (19.9 mg, 68 μmol, 82%, *trans*-**24c**:**25c** = 88:12) as a colorless oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (20/1) as eluent. The ratio of *trans*-**24c** to **25c** was determined by integration of baseline-separated signals at 6.83 and 3.32 ppm in the ^{1}H NMR spectrum.

*Analytical Data for trans-**24c**.* R_f = 0.57 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 19.6 min. HRMS (ESI, m/z): calculated for $C_{17}H_{18}F_3O^+$ [M + H]$^+$, 295.1304; found, 295.1301. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (d, J = 6.7 Hz, 3H), 1.05−1.11 (m, 1H), 1.46−1.56 (m, 1H), 1.84−1.94 (m, 2H), 2.16−2.25 (m, 1H), 2.33−2.39 (m, 2H), 2.43−2.50 (m, 1H), 2.59−2.67 (m, 1H), 6.83 (m$_c$, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 12.2, 21.8, 25.7, 27.0, 44.2, 50.9, 56.5, 124.3 (q, $^1J_{C,F}$ = 272 Hz, -CF_3), 125.8 (q, $^3J_{C,F}$ = 3.7 Hz, 2C), 128.0 (2C), 129.5 (q, $^2J_{C,F}$ = 32 Hz), 133.6, 140.0, 145.4, 205.2. ^{19}F NMR (471 MHz, $CDCl_3$): δ −62.5.

*Selected Analytical Data for **25c**.* R_f = 0.57 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 19.7 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.88 (d, J = 1.7 Hz, 3H), 3.29−3.35 (m, 1H), 7.52 (m$_c$, 2H), 7.71 (m$_c$, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 9.7, 21.3, 21.4, 22.9, 28.2, 41.7, 45.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ −62.8.

*(2S,3R,3aR)-3-(4-Methoxyphenyl)-2-methyl-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (trans-**24d**) and (3aS,7aR)-3-(4-Methoxyphenyl)-2-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-1-one (**25d**).* Prepared from divinyl ketone **23d** (21 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (*trans*-**24d**:**25d** = 84:16) afforded *trans*-**24d** (8.6 mg, 34 μmol, 41%) as a yellow oil and a product mixture of *trans*-**24d** and **25d** (3.9 mg, 15 μmol, 18%, *trans*-**24d**:**25d** = 55:45) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl

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ether (20/1) as eluent. The ratio of *trans*-**24d** to **25d** was determined by integration of baseline-separated signals at 6.79 and 3.32 ppm in the ^{1}H NMR spectrum.

*Analytical Data for trans-**24d**.* R_f = 0.58 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 22.5 min. IR (ATR): $\tilde{\nu}$ 2928 (w), 2868 (w), 1715 (s), 1651 (s), 1510 (s), 1248 (s), 1174 (m), 1032 (m), 923 (m), 826 (m), 729 (s) cm^{-1}. HRMS (ESI, *m*/*z*): calculated for $C_{17}H_{21}O_2^+$ [M + H]$^+$, 257.1536; found 257.1534. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00−1.08 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.49 (m$_c$, 1H), 1.83−1.88 (m, 1H), 1.92−1.97 (m, 1H), 2.15−2.24 (m, 2H), 2.30−2.37 (m, 1H), 2.37−2.43 (m, 1H), 2.52−2.60 (m, 1H), 3.82 (s, 3H), 6.79 (m$_c$, 1H), 6.89−6.91 (m, 2H), 7.16−7.19 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 12.1, 21.9, 25.8, 27.0, 44.4, 51.1, 55.4, 55.9, 114.2 (2C), 128.5 (2C), 132.9, 133.1, 140.7, 158.7, 206.3.

*Selected Analytical Data for **25d**.* R_f = 0.50 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 23.1 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.93 (d, *J* = 1.5 Hz, 3H), 2.56−2.60 (m, 1H), 3.28−3.35 (m, 1H), 3.86 (s, 3H), 6.96−7.00 (m, 2H), 7.43−7.46 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 10.1, 21.4, 21.7, 23.0, 28.9, 41.2, 45.7, 55.5, 114.2 (2C), 129.6 (2C).

*(2S,3R,3aR)-3-(Furan-2-yl)-2-methyl-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (trans-**24e**) and (3aS,7aR)-3-(Furan-2-yl)-2-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-1-one (**25e**).* Prepared from divinyl ketone **23e** (18 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (*trans*-**24e**:**25e** = 53:47) afforded *trans*-**24e** (4.1 mg, 19 μmol, 23%, *trans*-**24e**:**25e** = 96:4) as a yellow oil and a product mixture of *trans*-**24e** and **25e** (7.1 mg, 33 μmol, 40%, *trans*-**24e**:**25e** = 26:74) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (30/1) as eluent. The ratio of *trans*-**24e** to **25e** was determined by integration of baseline-separated signals at 7.38 and 7.61 ppm in the ^{1}H NMR spectrum.

*Analytical Data for trans-**24e**.* R_f = 0.65 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 17.3 min. HRMS (ESI, *m*/*z*): calculated for $C_{14}H_{17}O_2^+$ [M + H]$^+$, 217.1223; found 217.1227. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06−1.12 (m, 1H), 1.14 (d, *J* = 6.7 Hz, 3H), 1.49−1.56 (m, 1H), 1.86−1.93 (m, 1H), 2.11−2.26 (m, 2H), 2.30−2.38 (m, 1H), 2.39−2.45 (m, 1H), 2.47−2.55 (m, 1H), 2.65−2.73 (m, 1H), 6.14 (d, *J* = 3.1 Hz, 1H), 6.35 (m$_c$, 1H), 6.79 (m$_c$, 1H), 7.38 (m$_c$, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 12.7, 21.8, 25.7, 27.5, 41.9, 48.9, 49.3, 105.8, 110.3, 133.5, 140.1, 141.8, 155.4, 205.7. The analytical and spectroscopic data are in accordance with those reported.[23]

*Analytical Data for **25e**.* R_f = 0.58 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 18.9 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98−1.07 (m, 1H), 1.15−1.22 (m, 1H), 1.28−1.38 (m, 1H), 1.54−1.63 (m, 2H), 1.63−1.71 (m, 1H), 2.04 (d, *J* = 0.9 Hz, 3H), 2.18−2.30 (m, 2H), 2.51−2.56 (m, 1H), 3.23−3.29 (m, 1H), 6.56 (m$_c$, 1H), 6.79 (d, *J* = 3.5 Hz, 1H), 7.61 (m$_c$, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 9.9, 22.2, 22.8 (2C), 31.7, 39.3, 46.1, 112.3, 113.8, 131.2, 144.6, 151.7, 157.6, 209.7.

*(2S,3R,3aR)-2-Methyl-3-(thiophen-2-yl)-2,3,3a,4,5,6-hexahydro-1H-inden-1-one (trans-**24f**) and (3aS,7aR)-2-methyl-3-(thiophen-2-yl)-3a,4,5,6,7,7a-hexahydro-1H-inden-1-one (**25f**).* Prepared from divinyl ketone **23f** (19 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. Purification of the crude product (*trans*-**24f**:**25f** = 64:36) afforded *trans*-**24f** (4.6 mg, 20 μmol, 24%) as a yellow oil and a product mixture of *trans*-**24f** and **25f** (10.7 mg, 46.0 μmol, 56%, *trans*-**24f**:**25f** = 49:51) as a yellow oil after purification by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether (30/1) as eluent. The ratio of *trans*-**24f** to **25f** was determined by integration of baseline-separated signals at 6.80 and 3.32 ppm in the ^{1}H NMR spectrum.

*Analytical Data for trans-**24f**.* R_f = 0.37 (cyclohexane/*tert*-butyl methyl ether = 10/1). GLC (HP-5): t_R = 19.7 min. IR (ATR): $\tilde{\nu}$ 2927 (w), 2865 (w), 1715 (s), 1651 (s), 1175 (w), 924 (m), 692 (s) cm^{-1}. HRMS (ESI, *m*/*z*): calculated for $C_{14}H_{17}OS^+$ [M + H]$^+$, 233.0995; found 233.0992. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05−1.12 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.50−1.56 (m, 1H), 1.87−1.92 (m, 1H), 2.11−2.18 (m, 1H), 2.18−2.25 (m, 1H), 2.32−2.38 (m, 1H), 2.38−2.44 (m, 1H), 2.56−2.65 (m, 2H), 6.80 (m$_c$, 1H), 6.92 (m$_c$, 1H), 6.99−7.00 (m, 1H), 7.22 (m$_c$, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 12.4, 21.8, 25.8, 27.2, 45.3, 51.6, 52.3, 123.6, 124.5, 127.1, 133.5, 140.1, 145.4, 205.2. The analytical and spectroscopic data are in accordance with those reported.[23]

*Analytical Data for **25f**.* R_f = 0.30 (cyclohexane/*tert*-butyl methyl ether = 10/1). GLC (HP-5): t_R = 21.0 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02−1.06 (m, 1H), 1.15−1.22 (m, 1H), 1.27−1.38 (m, 2H), 1.63−1.71 (m, 2H), 2.05 (d, *J* = 1.1 Hz, 3H), 2.23−2.30 (m, 2H), 2.58−2.61 (m, 1H), 3.32 (m$_c$, 1H), 7.19 (m$_c$, 1H), 7.46 (m$_c$, 1H), 7.58 (m$_c$, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 10.4, 22.4, 22.8, 22.9, 32.0, 41.6, 46.6, 127.8, 128.6, 129.5, 131.6, 138.9, 162.4, 209.4.

*Ethyl trans-2,4-Dimethyl-5-oxo-3-phenylcyclopent-3-ene-1-carboxylate (trans-**27**).* Prepared from divinyl ketone **26** (21 mg, 82 μmol, 1.0 equiv) and $[(C_6F_5)_3PF]^+[B(C_6F_5)_4]^-$ (**6**; 3.1 mg, 2.5 μmol, 3.0 mol %) according to **GP3**. The product *trans*-**27** (12.7 mg, 49.0 μmol, 60%) was obtained as a colorless oil after purification by flash column chromatography on silica gel using cyclohexane/dichloromethane (100/0 → 4/1) as eluent. R_f = 0.48 (cyclohexane/*tert*-butyl methyl ether = 3/1). GLC (HP-5): t_R = 19.7 min. HRMS (ESI, *m*/*z*): calculated for $C_{16}H_{19}O_3^+$ [M + H]$^+$, 259.1329; found 259.1329. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13 (d, *J* = 7.3 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.86 (d, *J* = 2.0 Hz, 3H), 3.14 (d, *J* = 2.7 Hz, 1H), 3.66−3.71 (m, 1H), 4.26 (m$_c$, 2H), 7.39−7.44 (m, 3H), 7.45−7.49 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 9.9, 14.4, 19.2, 40.3, 59.9, 61.7, 128.0 (2C), 128.8 (2C), 129.6, 134.7, 134.8, 169.4, 172.3, 201.8. The analytical and spectroscopic data are in accordance with those reported.[25]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00496.

Overview of screened catalysts and figures giving NMR spectra of compounds synthesized in this paper (PDF)

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The authors declare no competing financial interest.

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