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A Convenient Preparative Method for New 1,3-Bis(hetaryl)-2-chloropropen-1-ones Using β-Alkoxy-α-chloroalkenyllithium Compounds

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Keywords: 1-Aryl-2-chloro-1-ethoxyethene / 1,3-Biarylpropen-1-one / Alkenyllithium / Suzuki coupling

The 1,3-biaryl and 1,3-bis(hetaryl)propen-1-ones **14a–e**, **16**, **17a–c**, **19**, **20a** and the corresponding acetals **15a–d**, **18a** and **21a–d** were successfully synthesized by a stepwise process: the reaction of α-chloro-β-ethoxyethenyllithium compounds and aldehydes and ketones, and the successive hydration with TMSOTf. Further palladium-catalyzed arylation of 1,3-biaryl-2-chloroprop-2-enones proceeded with good yields.

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Introduction

2-Halopropen-1-ones (2-haloenones) have been utilized as an important intermediate in the syntheses of natural products having interesting biological activities such as prostacyclin,[1] α- and β-cuparenones,[2] pentalene and *epi*-pentalene.[3] Furthermore, the significant transformations of 2-chlorocyclopentenones to asymmetric cyclopentanones, dialkylcyclopentanones and 1-acetoxy-3-alkyl-2-chloropentenes have been reported by other groups.[4] In particular, 1,3-biaryl-2-halopropen-1-ones (2-halochalcones) have been much investigated and easily accessed by three general routes: condensation of aldehydes with α-chloroacetophenones,[5] chlorination followed by dehydrochlorination of chalcones,[6] and Wittig and Horner–Wadsworth–Emmons reactions;[7] however, the preparative methods for 1,3-bis(hetaryl)-2-chloropropen-1-ones have not been reported because it is difficult to prepare their precursors. Recently, much attention has been paid to 1-furyl-3-pyridylpropen-1-ones which show cyclooxygenase (COX)-inhibiting activity (nonsteroidal anti-inflammatory drugs).[8] For the development of new COX-inhibitors, the discovery of a new preparative method of 1,3-bis(hetaryl)-propen-1-ones is of much importance.[9] Fortunately, we were pleased to find that 1-aryl-2-chloro-1-ethoxyethenes could be conveniently generated by a simple reaction of aryllithiums with dichloroacetaldehyde diethyl acetals. The 1-hetaryl-2-chloro-1-ethoxyethenes could be used as new precursors of β-alkoxyalkenyllithiums bearing a chlorine atom and utilized for the synthesis of a wide variety of 1,3-bis-(hetaryl)-2-chloropropen-1-ones by the electrophilic reactions of aldehydes and ketones and successive hydration (Figure 1). We here report a new synthesis of 1,3-bis(hetaryl)-2-chloropropen-1-ones using α-chloroethoxyethenyllithiums bearing 2-thienyl, 2-furyl, and 2-pyridyl groups and their transformations to 1,2,3-triaryl- and 1,2,3-tris-(hetaryl)propen-1-ones.

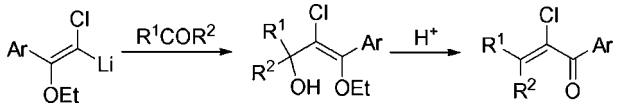
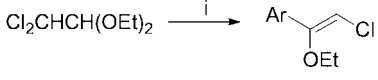


Figure 1. Synthesis of α-chloro-α,β-unsaturated aryl ketones using α-chloro-β-ethoxyalkenyllithiums.

We first prepared six kinds of 1-aryl-2-chloro-1-ethoxyethenes, **1**–**6**, according to our original method as shown in Scheme 1.[10] Next, we performed the lithiation of 2-(2-chloro-1-ethoxyethenyl)thiophene (**1**) and reaction with a variety of aldehydes and ketones. The lithiation of **1** with *n*BuLi proceeded at –78 °C, and the successive reaction with benzaldehyde gave (*Z*)-2-(2-chloro-1-ethoxy-3-hydroxy-3-phenylprop-1-enyl)thiophene (**7a**) in 85% yield. The reaction of **1** in the presence of 1.5 equiv. of *n*BuLi afforded **7a** in 45% yield, accompanied by 29% of the diol **8**, which was obtained by the further lithiation and alkylation of the intramolecular thiophene ring. We further performed the reactions of **1** with a variety of aldehydes and ketones as



1 (Ar = 2-thienyl) (82%)
2 (Ar = 5-methyl-2-thienyl) (71%)
3 (Ar = 2-furyl) (77%)
4 (Ar = 5-methyl-2-furyl) (50%)
5 (Ar = Ph) (82%)
6 (Ar = 2-pyridyl) (75%)

Reagent: i, ArLi/THF/-20 °C/15 min

Scheme 1. Synthesis of 1-aryl-2-chloro-1-ethoxyethenes.

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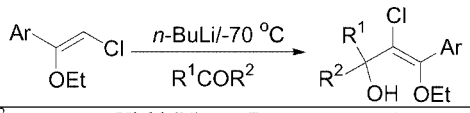
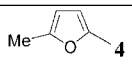
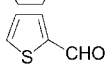
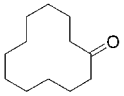
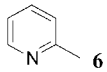
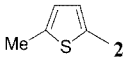
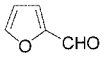
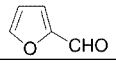
Table 1. Preparation of 3-aryl-2-chloroprop-2-en-1-ols from aldehydes and ketones using lithiated α-aryl-β-chloro-α-ethoxyethenes.



Entry	Ar	R^1COR^2	Yield (%)	Entry	Ar	R^1COR^2	Yield (%)
1	 **1**	PhCHO	**7a** (85)[a]	9	 **4**	*p*-ClC_6H_4CHO	**11a** (51)
2	**1**	*p*-ClC_6H_4CHO	**7b** (84)	10	**4**		**11b** (64)
3	**1**		**7c** (52)	11	**4**		**11c** (98)
4	**1**		**7d** (63)	12	**5 Ph**	*p*-$MeOC_6H_4CHO$	**12** (76)
5	**1**		**7e** (65)	13	 **6**	*p*-$MeOC_6H_4CHO$	**13a** (59)
6	**1**		**7f** (33)	14	**6**		**13b** (30)
7	 **2**		**9** (87)	15	**6**	(*E*)-PhCH=CHCHO	**13c** (53)
8	 **3**	*p*-$MeOC_6H_4CHO$	**10** (65)	16	**6**		**13d** (58)

[a] The dialkylated product, (*E*)-2-(2-chloro-1-ethoxy-3-phenylprop-1-enyl)-5-(hydroxyphenylmethyl)thiophene (**8**) was obtained in low yield.

shown in Table 1. 2-(2-Chloro-1-ethoxyethenyl)-5-methylthiophene **2**, the furyl derivatives **3**–**4**, phenyl derivative **5** and pyridyl derivative **6** also afforded the corresponding adducts **9**–**10**, **11a**–**c**, **12**, and **13a**–**d**, respectively, in moderate to high yields. The addition reaction of the alkenyllithiums proceeded with predominant *E* selectivity due to coordination of the β-alkoxy group with the lithium atom.

Next, we examined the hydrolysis of the thienyl alcohol **7a** using a variety of acids (Table 2, entries 1–4), beginning with trimethylsilyl trifluoromethanesulfonate (TMSOTf), which gave high yield at low temperature in CH_2Cl_2 (entry 1). The structure of **14a** was determined by the IR spectroscopic data, showing the absorption of the carbonyl group at $\tilde{\nu}$ = 1641 cm^{-1}, and the ^1H NMR spectroscopic data, exhibiting a singlet olefinic proton at δ = 7.66 ppm, and the MS and the elemental analytical data, showing the molecular formula of $C_{13}H_9ClS$. On the other hand, the usual acetalization process provided the α,β-unsaturated acetals **15a**–**b** in good yields (entry 2 and 5). *p*-Toluenesulfonic acid gave rise to a low yield of **14a**. Lewis acid-catalyzed formation of the α-chloro-α,β-unsaturated ketone **14a** using scandium triflate was successful (entry 4). 2-(*p*-Chlorophenyl-2-chloropropenyl)thiophene **7b** afforded α,β-unsaturated acetal **15b** (entry 5). Cycloalkanols also afforded the cycloalkylidene ketones **14c**–**e** and the corresponding acetal **15d**, respectively (entries 6–10); however, 2-cyclohexen-1-ol gave a complex mixture (entry 11). 5-Methylthienyl **9**, furyl **10** and 5-methylfuryl **11a**–**c** were transformed to the α,β-unsaturated ketones **16**, **17a**–**c**, and **18a** by the same method (entries 12–16). 2-Chloro-1-phenylprop-2-enone **19** was obtained in high yield (entry 17). The transformation of the pyridyl derivatives to the α,β-unsaturated ketones resulted in low yield of the product **20a** accompanied by recovery of the enol ethers (entry 18), while the usual acetalization improved the yield and provided the corresponding α,β-unsaturated acetal **21a** in up to 74% yield (entry 19). The other pyridyl ketones **21b**–**d** were also obtained as acetals in good yields

Having successfully determined a standard procedure for synthesizing 1,3-bis(hetaryl)-2-chloro-α,β-unsaturated ketones, we next examined the transformation of the α,β-unsaturated ketones bearing the chlorine atom and explored the preparation of 1,2,3-tris(aryl) or tris(hetaryl)propen-1-ones with arylboronic acids. A few palladium-catalyzed arylations of alkenyl halides with arylboronic acids have been reported:[11] one example is the cyclic system such as indole, benzo[*b*]thiophene and benzo[*b*]furan and another is the 2-iodo-2-alkenones. The arylation of 2-chloro-2-alkenones has not been reported. As illustrated in Table 3, the coupling reaction of **16a** with *p*-methoxyphenylboronic acid proceeded smoothly in the presence of Pd(dppb) as the best catalyst. Tetrakis(triphenylphosphane)palladium gave a low yield of the product. The palladium-catalyzed arylation of 1,3-biaryl-2-chloropropen-1-ones with some arylboronic acids was examined. The coupling reaction of **16** with *p*-chlorophenylboronic acid afforded **22b** in good yield; however, the method was not effective with 2-thienylboronic acid under the same conditions (entry 3). The phenyl derivative provided 2-(*p*-methoxyphenyl)-3-phenyl-1-(2-thienyl)-propen-1-one (**22d**) (entry 4). Pentamethylene derivative **22e** was also obtained in high yields; however, the 3-(2-furyl)-1-(2-pyridyl)propen-1-one **22f** was not. We performed the coupling reaction of the pyridyl acetal **21d**; however, the reaction did not proceed, and **21d** was recovered. The reac-

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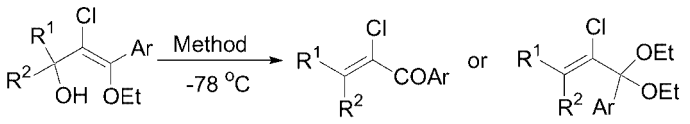
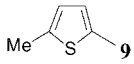
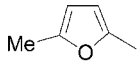
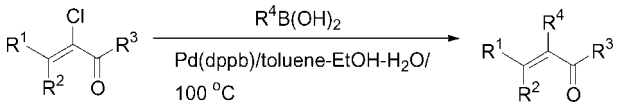
Table 2. Acid-mediated preparation of aryl 2-chloroprop-2-enyl ketones.



Entry	Ar	R^1	R^2	Conditions	Yield (%) of ketone	Yield (%) of acetal
1	 **7a**	Ph	H	TMSOTf / CH_2Cl_2 / –78 °C	**14a** (87)	
2	**7a**	Ph	H	$CH(OEt)_3$ / TsOH / EtOH / r.t.		**15a** (66)
3	**7a**	Ph	H	TsOH / $Cl(CH_2)_2Cl$ / r.t.	**14a** (43)	
4	**7a**	Ph	H	$Sc(OTf)_3$ (0.1 equiv.) / $Cl(CH_2)_2Cl$	**14a** (61)	
5	**7b**	$pClC_6H_4$	H	$CH(OEt)_3$ / TsOH / EtOH / r.t.		**15b** (41)
6	**7c**	$–(CH_2)_5–$		TMSOTf / CH_2Cl_2 / –78 °C	**14c** (99)	
7	**7c**	$–(CH_2)_5–$		$CH(OEt)_3$ / TsOH / EtOH / r.t.	**14c** (45)	
8	**7d**	$–(CH_2)_4–$		TMSOTf / CH_2Cl_2 / –78 °C	**14d** (95)	
9	**7d**	$–(CH_2)_4–$		$CH(OEt)_3$ / TsOH / EtOH / r.t.		**15d** (49)
10	**7e**	$–(CH_2)_{11}–$		TMSOTf / CH_2Cl_2 / –78 °C	**14e** (64)	
11	**7f**	$(CH_2)_3CH=CH$		TMSOTf / CH_2Cl_2 / –78 °C	–	–
12	 **9**	2-furyl	H	TMSOTf / CH_2Cl_2 / –78 °C	**16** (75)	
13	 **10**	$pMeOC_6H_4$	H	TMSOTf / CH_2Cl_2 / –78 °C	**17a** (87)	
14	 **11a**	$pClC_6H_4$	H	$CH(OEt)_3$ / TsOH / EtOH / r.t.		**18a** (60)
15	**11b**	$–(CH_2)_5–$		TMSOTf / CH_2Cl_2 / –78 °C	**17b** (56)	
16	**11c**	2-thienyl	H	TMSOTf / CH_2Cl_2 / –78 °C	**17c** (78)	
17	Ph **12**	$pMeOC_6H_4$	H	TMSOTf / CH_2Cl_2 / –78 °C	**19** (85)	
18	 **13a**	$pMeOC_6H_4$	H	TMSOTf / CH_2Cl_2 / –78 °C	**20a** (32)	
19	**13a**	$pMeOC_6H_4$	H	$CH(OEt)_3$ / TsOH / EtOH / –78 °C		**21a** (74)
20	**13a**	$pMeOC_6H_4$	H	$CH(OEt)_3$ / TsOH / EtOH / r.t.		**21a** (16)
21	**13b**	$–(CH_2)_5–$		$CH(OEt)_3$ / TsOH / EtOH / –78 °C		**21b** (75)
22	**13c**	*(E)*-PhCH=CH	H	$CH(OEt)_3$ / TsOH / EtOH / –78 °C		**21c** (82)
23	**13d**	2-furyl	H	$CH(OEt)_3$ / TsOH / EtOH / –78 °C		**21d** (77)

tions with *p*-methoxyphenylboronic acid proceeded during 4h, while the reactions with the *p*-chlorophenylboronic acid took over 12h. As a whole, the electron-donating substituents gave satisfactory results in the palladium-catalyzed coupling reactions of 1,3-bis(aryl) and 1,3-bis(hetaryl)-2-chloropropen-1-ones with arylboronic acids; however, the stereoselectivities were found to be very low. The details for these coupling reactions were not clear, therefore, we can not mention the reaction mechanisms and the stereoselectivities.

Table 3. Pd-catalyzed reaction of 1,3-biaryl-2-chloroprop-2-enone with arylboronic acids.



Entry	2-Chloropropenone	R^1	R^2	R^3	R^4	Yield (*E*:*Z*)
1	**16**	2-furyl	H	5-methyl-2-thienyl	p-$MeOC_6H_4$	**22a** (79 %) (71:29)
2	**16**	2-furyl	H	5-methyl-2-thienyl	p-ClC_6H_4	**22b** (72 %) (64:36)
3	**16**	2-furyl	H	5-methyl-2-thienyl	2-thienyl	**22c** (24 %) (100:0)
4	**19**	Ph	H	2-thienyl	p-$MeOC_6H_4$	**22d** (quant.) (58:42)
5	**14c**	$–(CH_2)_5–$		2-thienyl	p-$MeOC_6H_4$	**22e** (quant.)
6	**21d**	$–(CH_2)_5–$		2-pyridyl	p-$MeOC_6H_4$	**22f** (–)[a]

[a] 2-Chloro-3-furyl-1-(2-pyridyl)prop-2-enone (**21d**) was used as a starting material.

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Conclusion

We have described the first access to 1,3-bis(hetaryl)-2-chloropropenones from aldehydes and ketones using α-aryl-β-chloro-α-ethoxyethenyllithiums. The attractive features of this method include the versatility of the functional groups on the propenones by using a wide variety of β-alkoxyalkenyllithiums. Furthermore, the chloropropenones could be transformed into 1,2,3-triaryl- and 1,2,3-tris(hetaryl)propenones by the palladium-catalyzed coupling reactions with arylboronic acids. This process may be applied to the synthesis of multifunctionalized alkenes as potential cyclooxygenase inhibitors.

Experimental Section

General Experimental Methods: Melting points were determined on a J-Science Labo micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Center of Instrumentation of Gifu University. ^{1}H and ^{13}C NMR spectra were determined with Varian Inova 400 (400 MHz) and 500 (500 MHz) and JEOL ECA500 (500 MHz) spectrometers at Gifu University. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were determined with a JASCO FT-IR 460PLUS infrared spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained using a JEOL MS-700 spectrometer with a direct-insertion probe at 70 eV. All high-resolution mass spectra were obtained using a JMSD300 JMA2000 on-line system. The 2-chloro-1-ethoxyethenes **1**–**6** were prepared according to our previous method.[10] The stereochemistries of the alcohols **7a**–**f**, **9**, **10**, **11a**–**c**, **12**, **13a**–**d** and the propen-1-ones **14a**–**e**, **15a**–**d**, **16**, **17a**–**c**, **18a**, **19**, **20a**, **21a**–**d** were determined by the NOE experiments.

(*E*)-2-(2-Chloro-1-ethoxy-3-hydroxy-3-phenylprop-1-enyl)thiophene (7a). Typical Procedure: To a solution of (*E*)-2-(2-chloro-1-ethoxyethenyl)thiophene (**1**) (0.50 g, 2.65 mmol) in THF (6.0 mL) was added *n*BuLi (1.02 mL, 2.65 mmol) at –78 °C under Ar. After 10 min stirring, a solution of benzaldehyde (0.19 g, 1.77 mmol) in THF (1.0 mL) was added dropwise to the mixture. The resulting mixture was stirred for 10 min and then poured into water (50 mL). The usual work-up afforded compound **7a** (0.39 g, 85%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 3733 (OH), 1612, 1052 (C–O), 701 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, J = 7 Hz, 3 H, Me), 2.97 (br. s, 1 H, OH), 3.75–3.90 (m, 2 H, OCH_2), 6.20 (s, 1 H, C*H*OH), 7.04 (dd, J = 4, 5 Hz, 1 H, 4-H), 7.19–7.37 (m, 4 H, ArH), 7.45–7.48 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.23 (q), 68.71 (t), 70.23 (d), 124.18 (s), 125.90 (d × 2), 126.83 (d), 127.54 (d), 127.57 (d), 128.25 (d × 2), 129.50 (d), 135.37 (s), 140.83 (s), 146.44 (s) ppm. MS: m/z = 294 (M^+), 259 (M^+ – Cl). $C_{15}H_{15}ClO_2S$ (294.80): calcd. C 61.11, H 5.13; found C 60.89, H 5.10.

(*E*)-2-(2-Chloro-1-ethoxy-3-phenylprop-1-enyl)-5-(hydroxyphenylmethyl)thiophene (8): IR (KBr): $\tilde{\nu}$ = 3390 (OH), 1604, 1493, 1450, 1390, 1247, 1195, 1119, 1063, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, J = 7 Hz, 3 H, Me), 2.77 (br. s, 1 H, OH), 2.85 (br. s, 1 H, OH), 3.78–3.88 (m, 2 H, OCH_2), 5.97 (s, 1 H, CHO), 6.15 (s, 1 H, C*H*OH), 6.78 (d, J = 4 Hz, 1 H, ArH), 7.23–7.36 (m, 7 H, ArH), 7.41–7.44 (m, 4 H, ArH) ppm. MS: m/z = 400 (M^+), 382 ($M^+ – H_2O$).

(*Z*)- and (*E*)-2-[2-Chloro-3-(*p*-chlorophenyl)-1-ethoxyprop-1-enyl]thiophene (7b): IR (KBr): $\tilde{\nu}$ = 3427 (OH),1663, 1489, 710 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (t, J = 7 Hz, *Z*-Me), 1.34 (t, J = 7 Hz, *E*-Me), 2.70 (br. d, J = 6 Hz, *Z*-OH), 2.74 (br. s, *E*-OH), 3.76–4.14 (m, *Z*- and *E*-OCH_2), 5.99 (d, J = 3 Hz, *E*-C*H*OH), 6.17 (d, J = 7 Hz, *Z*-C*H*OH), 6.83 (d, J = 4 Hz, *E*-ArH), 7.07–7.09 (dd, J = 4, 5 Hz, *Z*-ArH), 7.25–7.54 (m, *Z*- and *E*-ArH) ppm. The isomer ratio is *E*/*Z* = 67:33. MS: m/z = 328 (M^+), 293 (M^+ – Cl); HRMS: calcd. for $C_{15}H_{14}Cl_2O_2S$ 328.0089; found 328.0056.

(*E*)-1-[1-Chloro-2-ethoxy-2-(2-thienyl)ethenyl]cyclohexanol (7c): IR (KBr): $\tilde{\nu}$ = 3502 (OH),1446 (thienyl), 704 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (t, J = 7 Hz, 3 H, Me), 1.57–1.58 (m, 2 H, CH_2), 1.65–1.90 (m, 6 H, CH_2), 1.92–1.95 (m, 2 H, CH_2), 3.74 (q, J = 7 Hz, 2 H, OCH_2), 4.47 (s, 1 H, OH), 7.03 (dd, J = 4, 5 Hz, 1 H, 5-H), 7.26 (dd, J = 1, 4 Hz, 1 H, 3-H), 7.37 (dd, J = 1, 5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.97 (q), 21.52 (t × 2), 25.31 (t), 36.39 (t × 2), 67.65 (t), 76.00 (s), 126.48 (d), 126.96 (d), 129.23 (s), 129.63 (d), 135.79 (s), 144.42 (s). MS: m/z = 286 (M^+), 251 (M^+ – Cl). $C_{14}H_{19}ClO_2S$ (286.82): calcd. C 58.63, H 6.33; found C 59.69, H 5.41.

(*E*)-1-[1-Chloro-2-ethoxy-2-(2-thienyl)ethenyl]cyclopentanol (7d): IR (KBr): $\tilde{\nu}$ = 3448 (OH), 2959, 2360, 1636, 1390, 1248, 1046, 851, 705 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, J = 7 Hz, 3 H, Me), 1.71–1.75 (m, 2 H, CH_2), 1.86–1.90 (m, 2 H, CH_2), 1.94–1.98 (m, 2 H, CH_2), 2.10–2.17 (m, 2 H, CH_2), 3.76 (q, J = 7 Hz, 2 H, OCH_2), 4.10 (s, 1 H, OH), 7.04 (dd, J = 4, 5 Hz, 1 H, ArH), 7.30 (dd, J = 1, 4 Hz, 1 H, ArH), 7.38 (dd, J = 1, 5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.96 (q), 23.64 (t × 2), 40.22 (t × 2), 67.73 (t), 84.84 (s), 126.50 (s), 126.93 (d), 126.99 (d), 129.53 (d), 135.79 (s), 145.08 (s). HRMS: calcd. for $C_{13}H_{17}ClO_2S$ 272.0638; found 272.0697.

(*E*)-1-[1-Chloro-2-ethoxy-2-(2-thienyl)ethenyl]cyclododecanol (7e): IR (KBr): $\tilde{\nu}$ = 3445 (OH), 2929, 1707, 1470, 1248, 1061, 702 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, J = 7 Hz, 3 H, Me), 1.26–1.31 (m, 4 H, CH_2), 1.38 (br. s, 10 H, CH_2), 1.49–1.51(m, 2 H, CH_2), 1.69–1.74 (m, 2 H, CH_2), 1.83–1.95 (m, 2 H, CH_2), 2.44–2.56 (m, 2 H, CH_2), 3.71 (q, J = 7 Hz, 2 H, OCH_2), 4.26 (s, 1 H, OH), 7.03 (br. t, J = 4 Hz, 1 H, 4-H), 7.23 (m, 1 H, 3-H), 7.39 (d, J = 4 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.96 (q), 19.77 (t), 22.02 (t), 22.29 (t), 22.49 (t), 24.17 (t), 24.55 (t), 24.69 (t), 26.08 (t), 26.32 (t), 34.83 (t), 40.30 (t), 67.18 (t), 78.32 (s), 126.48 (d), 126.95 (d), 128.45 (s), 129.63 (d), 135.41 (s), 144.88 (s) ppm. MS: m/z = 370 (M^+). $C_{20}H_{31}ClO_2S$ (370.98): calcd. C 64.75, H 8.42; found C 64.57, H 8.38.

(*E*)-1-[1-Chloro-2-ethoxy-2-(2-thienyl)ethenyl]cyclohex-2-en-1-ol (7f): IR (KBr): $\tilde{\nu}$ = 3448 (OH), 2933, 1617, 1246, 1041 (C–O), 851, 706 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (t, J = 7 Hz, 3 H, Me), 1.85–2.18 (m, 6 H, CH_2), 3.73–3.79 (m, 2 H, OCH_2), 4.56 (s, 1 H, OH), 5.82–5.83 (m, 1 H, olefinic H), 5.84–5.94 (m, 1 H, olefinic H), 7.05 (dd, J = 4, 5 Hz, 1 H, 4-H), 7.30 (dd, J = 1, 4 Hz, 1 H, ArH), 7.39 (dd, J = 1, 5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.92 (q), 18.48 (t), 24.58 (t), 35.86 (t), 67.82 (t), 74.15 (s), 126.55 (d), 127.10 (d), 127.44 (s), 129.65 (d), 129.71 (d), 130.51 (d), 135.63 (s), 145.19 (s) ppm. MS: m/z = 83 (thienyl). $C_{14}H_{17}ClO_2S$ (284.80): calcd. C 59.04, H 6.02; found C 58.88, H 5.97.

(*E*)-2-[2-Chloro-1-ethoxy-3-hydroxy-3-(2-furyl)prop-1-enyl]-5-methylthiophene (9): IR (KBr): $\tilde{\nu}$ = 3423 (OH), 2977, 1611, 1456, 1250, 1064, 806, 744 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30

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(t, J = 7 Hz, 3 H, Me), 2.49 (s, 3 H, Me), 3.00 (br. s, 1 H, OH), 3.86 (q, J = 7 Hz, 2 H, OCH_2), 6.12 (d, J = 8 Hz, 1 H, C*H*OH), 6.34 (dd, J = 2, 3 Hz, 1 H, ArH), 6.39–6.40 (m, 1 H, ArH), 6.72 (dd, J = 1, 4 Hz, 1 H, ArH), 7.28 (d, J = 4 Hz, 1 H, ArH), 7.37 (d, J = 1 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.07 (q), 15.17 (q), 65.64 (q), 68.90 (t), 106.94 (d), 110.23 (d), 120.65 (s), 125.14 (d), 129.74 (d), 132.70 (s), 142.09 (d), 142.54 (s), 146.99 (s), 153.56 (s) ppm. HRMS: calcd. for $C_{14}H_{15}ClO_3S$ 298.0430; found 298.0398.

(*E*)-2-[2-Chloro-1-ethoxy-3-hydroxy-3-(*p*-methoxyphenyl)prop-1-enyl]furan (10): IR (KBr): $\tilde{\nu}$ = 3443 (OH), 2932, 1612, 1511 (furyl), 1248, 1172, 1068, 1032 (C–O), 830, 748 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, J = 7 Hz, 3 H, Me), 2.84 (d, J = 7 Hz, 1 H, OH), 3.77 (s, 3 H, OMe), 3.79–3.89 (m, 2 H, OCH_2), 6.15 (d, J = 7 Hz, 1 H C*H*OH), 6.46 (dd, J = 2, 3 Hz, 1 H, ArH), 6.86–6.88 (m, 3 H, ArH), 7.38 (d, J = 8 Hz, 2 H, ArH), 7.47 (d, J = 2 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.17 (q), 55.14 (q), 68.54 (t), 69.53 (d), 111.11 (d), 113.59 (d × 2), 113.85 (d), 124.04 (s), 127.10 (d × 2), 132.94 (s), 142.62 (d), 142.92 (s), 146.51 (s) 158.96 (s). MS: m/z = 303.

(*E*)-2-[2-Chloro-3-(*p*-chlorophenyl)-1-ethoxyprop-1-enyl]-5-methylfuran (11a): IR (KBr): $\tilde{\nu}$ = 3434 (OH), 2360, 1595, 1489, 1265, 1088, 791, 730 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (t, J = 7 Hz, 3 H, Me), 2.34 (s, 3 H, Me), 2.79 (br. s, 1 H, OH), 3.79–3.97 (m, 2 H, OCH_2), 6.07–6.08 (m, 1 H, ArH), 6.15 (s, 1 H, CHO), 6.76 (d, J = 3 Hz, 1 H, ArH), 7.30 (d, J = 8 Hz, 2 H, ArH), 7.39 (d, J = 8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.66 (q), 15.22 (q), 68.56 (t), 69.45 (d), 107.48 (d), 115.41 (d), 121.79 (s), 127.34 (d × 2), 128.29 (d × 2), 133.20 (s), 139.49 (s), 143.55 (s), 144.35 (s), 153.03 (s) ppm. MS: m/z = 326 (M^+). $C_{16}H_{16}ClO_3$ (327.21): calcd. C 58.73, H 4.92; found C 58.44, H 4.71.

(*E*)-1-[1-Chloro-2-ethoxy-2-(5-methyl-2-furyl)ethenyl]cyclohexanol (11b): IR (KBr): $\tilde{\nu}$ = 3504 (OH), 2930, 2361, 1594 (furyl), 1447, 1392, 1267, 1066, 1028 (C–O), 964, 787 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, J = 7 Hz, 3 H, Me), 1.55–1.57 (m, 2 H, CH_2), 1.73–1.79 (m, 6 H, CH_2), 1.87–1.90 (m, 2 H, CH_2), 2.33 (s, 3 H, Me), 3.76 (q, J = 7 Hz, 2 H, OCH_2), 4.45 (s, 1 H, OH), 6.04 (brs, 1 H, 4-H), 6.61 (d, J = 4 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.63 (q), 15.02 (q), 21.53 (t × 2), 25.32 (t), 36.34 (t × 2), 67.82 (t), 75.87 (s), 106.95 (d), 114.87 (d), 128.00 (s), 142.10 (s), 144.75 (s), 152.26 (s). MS: m/z = 284 (M^+), 255 (M^+ – Et). $C_{15}H_{21}ClO_3$ (284.78): calcd. C 63.26, H 7.43; found C 62.98, H 7.17.

(*E*)-2-[2-Chloro-1-ethoxy-3-hydroxy-3-(2-thienyl)prop-1-enyl]-5-methylfuran (11c): IR (KBr): $\tilde{\nu}$ = 3434 (OH), 2978, 1594, 1438 (thienyl), 1266, 1073 (C–O), 704 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, J = 7 Hz, 3 H, Me), 2.35 (s, 3 H, Ar-Me), 2.80 (d, J = 9 Hz, 1 H, OH), 3.82–3.93 (m, 2 H, OCH_2), 6.09 (d, J = 3 Hz, 1 H, ArH), 6.31 (d, J = 9 Hz, 1 H, C*H*OH), 6.79 (d, J = 3 Hz, 1 H, ArH), 6.97 (t, J = 4 Hz, 1 H, ArH), 7.04 (d, J = 3 Hz, 1 H, ArH), 7.26 (d, J = 4 Hz, 1 H, ArH) ppm. MS: m/z = 298 (M^+), 263 (M^+ – Cl). $C_{14}H_{15}ClO_3S$ (298.79): calcd. C 56.28, H 5.06; found C 56.13, H 4.88.

(*E*)-2-Chloro-1-ethoxy-3-(*p*-methoxyphenyl)-1-phenylprop-1-en-3-ol (12): IR (KBr): $\tilde{\nu}$ = 3437 (OH), 1612, 1511, 1249, 1173, 1071, 831, 776, 701, 564 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, J = 7 Hz, 3 H, Me), 2.59 (br. s, 1 H, OH), 3.59–3.76 (m, 2 H, OCH_2), 3.81 (s, 3 H, OMe), 6.18 (d, J = 8 Hz, 1 H CHO), 6.91 (d, J = 8 Hz, 2 H, ArH), 7.35–7.43 (m, 5 H, ArH), 7.52 (d, J = 8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.12 (q), 55.26 (q), 66.24 (t), 69.90 (d), 113.70 (d × 2), 122.32 (s), 127.16 (d × 2), 128.16 (d × 2), 129.08 (d), 129.54 (d × 2), 132.76 (s), 133.52 (s), 151.59 (s), 159.05 (s) ppm. MS: m/z = 318 (M^+), 283 (M^+ – Cl). $C_{18}H_{19}ClO_3$ (318.80): calcd. C 67.82, H 6.01; found C 67.54, H 5.92.

(*E*)-2-[2-Chloro-1-ethoxy-3-hydroxy-3-(*p*-methoxyphenyl)prop-1-enyl]pyridine (13a): IR (KBr): $\tilde{\nu}$ = 3422 (OH), 3205, 1614, 1589, 1509 (pyridyl), 1468, 1434, 1299, 1242, 1084, 750 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (t, J = 7 Hz, 3 H, Me), 3.59 (d, J = 4 Hz, 1 H, OH), 3.61–3.71 (m, 2 H, OCH_2), 3.78 (s, 3 H, OMe), 6.29 (d, J = 4 Hz, 1 H, CHO), 6.89 (d, J = 9 Hz, 2 H, ArH), 7.24–7.27(m, 1 H, ArH), 7.48 (d, J = 9 Hz, 2 H, ArH), 7.57 (d, J = 8 Hz, 1 H, ArH), 7.70–7.74 (m, 1 H, ArH), 8.68–8.69 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.01 (q), 55.08 (q), 66.44 (t), 69.14 (d), 113.48 (d × 2), 123.38 (d), 124.55 (s), 125.58 (d), 127.13 (d × 2), 133.18 (s), 136.09 (d), 149.36 (d), 149.75 (s), 151.78 (s), 158.81 (s) ppm. MS: m/z = 319 (small M^+), 284 (M^+ – Cl). $C_{17}H_{18}ClNO_3$ (319.79): calcd. C 63.85, H 5.67, N 4.38; found C 63.60, H 5.58, N 4.36.

(*E*)-1-[1-Chloro-2-ethoxy-2-(2-pyridyl)ethenyl]cyclohexanol (13b): IR (KBr): $\tilde{\nu}$ = 3449 (OH), 2930, 2361, 1585 (pyridyl), 1430, 1390, 1294, 1071 (C–O), 966, 801, 749 (C–Cl), 636 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, J = 7 Hz, 3 H, Me), 1.57–2.05 (m, 10 H, CH_2), 3.58–3.63 (m, 2 H, OCH_2), 4.44 (s, 1 H, OH), 7.26–7.29 (m, 1 H, ArH), 7.50 (d, J = 8 Hz, 1 H, ArH), 7.73–7.76 (m, 1 H, ArH), 8.70 (d, J = 4 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.94 (q), 21.53 (t × 2), 25.35 (t), 36.08 (t × 2), 66.65 (t), 75.66 (s), 123.31 (d), 125.77 (d), 127.97 (s), 136.23 (d), 148.95 (s), 149.48 (d), 152.77 (s) ppm. HRMS: calcd. for $C_{15}H_{20}ClNO_2$ 281.1182; found 281.1098.

(1*E*,4*E*)-2-(2-Chloro-1-ethoxy-3-hydroxy-5-phenylpenta-1,4-dienyl)-pyridine (13c): IR (KBr): $\tilde{\nu}$ = 3399 (OH), 2978, 1587 (pyridyl), 1467, 1431, 1298, 1074 (C–O), 967, 789, 752 (C–Cl), 696 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23 (t, J = 7 Hz, 3 H, Me), 3.68 (q, J = 7 Hz, 2 H, OCH_2), 3.69 (br. s, 1 H, OH), 5.86 (s, 1 H, C*H*OH), 6.40 (dd, J = 5, 16 Hz, 1 H, olefinic H), 6.78 (dd, J = 1, 16 Hz, 1 H, olefinic H), 7.20–7.31 (m, 4 H, ArH), 7.40–7.42 (m, 2 H, ArH), 7.56–7.58 (m, 1 H, ArH), 7.69–7.73 (m, 1 H, ArH), 8.68–8.70 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.09 (q), 66.61 (t), 69.31 (d), 123.40 (s), 123.51 (d), 125.49 (d), 126.62 (d × 2), 127.70 (d), 128.32 (d), 128.47 (d × 2), 131.31 (d), 136.18 (d), 136.54 (s), 149.54 (d), 149.87 (s), 151.88 (s) ppm. HRMS: calcd. for $C_{18}H_{18}ClNO_2$ 315.1026; found 315.0988.

(*E*)-2-[2-Chloro-1-ethoxy-3-(2-furyl)-3-hydroxyprop-1-enyl]pyridine (13d): IR (KBr): $\tilde{\nu}$ = 3594 (OH), 2361, 1587, 1467, 1432, 1300, 1089, 746 (C–Cl) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, J = 7 Hz, 3 H, Me), 3.67 (q, J = 7 Hz, 2 H, OCH_2), 3.69 (br. s, 1 H, OH), 6.25 (br. s, 1 H, C*H*OH), 6.36 (t, J = 2 Hz, 1 H, ArH), 6.44 (d, J = 3 Hz, 1 H, ArH), 7.27–7.30 (m, 1 H, ArH), 7.40 (s, 1 H, ArH), 7.60 (d, J = 8 Hz, 1 H, ArH), 7.74–7.77 (m, 1 H, ArH), 8.70 (d, J = 5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.92 (q), 65.31 (t), 66.71 (d), 106.94 (d), 110.22 (d), 121.77 (s), 123.55 (d), 125.52 (d), 136.20 (d), 142.05 (d), 149.44 (d), 150.50 (s), 151.65 (s), 153.61 (s) ppm. MS: m/z = 279 (M^+). $C_{14}H_{14}ClNO_3$ (279.72): C 60.11, H 5.04, N 5.01; found C 59.92, H 5.03, N 5.00.

Preparation of (*Z*)-2-Chloro-3-phenyl-1-(2-thienyl)prop-2-enone (14a). Typical Procedure: To a solution of (*Z*)-2-(2-chloro-1-ethoxy-3-hydroxy-3-phenylprop-1-enyl)thiophene (**7a**, 84 mg, 0.32 mmol) in CH_2Cl_2 (2.0 mL) was added TMSOTf (72 mg, 0.32 mmol) at –78 °C under Ar. The reaction mixture was stirred for 10 min and then poured into a saturated $NaHCO_3$ solution (50 mL). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was puri-

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fied by column chromatography on silica gel, eluting with AcOEt/*n*-hexane (1:100) to give **14a** (70 mg, 87%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 1641, 1411 (thienyl), 1605, 1262, 1510, 1491, 1447, 1201, 763 (C–Cl), 730, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.17 (dd, J = 4, 5 Hz, 1 H, 4-H), 7.42–7.47 (m, 3 H, ArH), 7.66 (s, 1 H, olefinic H), 7.74 (dd, J = 1, 5 Hz, 1 H, 5-H), 7.85–7.87 (m, 3 H, ArH, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.95 (d), 128.56 (d × 2), 129.01 (s), 130.20 (d), 130.50 (d × 2), 132.85 (s), 134.54 (d), 134.74 (d), 137.07 (d), 141.49 (s), 182.25 (s) ppm. MS: m/z = 248 (M^+), 213 (M^+ – Cl). $C_{13}H_9ClOS$ (248.73): calcd. C 62.78, H 3.65; found C 62.64, H 3.56.

Preparation of (*Z*)-2-Chloro-1,1-diethoxy-3-phenyl-1-(2-thienyl)-prop-2-ene (15a). Typical Procedure for Acetalization: To a solution of **7a** (0.10 g, 0.34 mmol) in EtOH (1.0 mL) were added triethyl orthoformate (0.28 g, 1.90 mmol) and *p*-TsOH (7.0 mg, 0.04 mmol) at room temperature. The mixture was stirred for 30 min and then poured into $NaHCO_3$ (50 mL). The usual work-up afforded **15a** (72 mg, 66%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 2977, 2930, 2893, 1491, 1441, 1403, 1391, 1233, 1197, 1146, 1098, 1056, 983, 819, 787, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, J = 7 Hz, 6 H, Me), 3.54–3.58 (m, 4 H, OCH_2), 6.97 (t, J = 4 Hz, 1 H, 4-H), 7.13 (d, J = 4 Hz, 1 H, 3-H), 7.26–7.29 (m, 1 H, 5-H), 7.33–7.37 (m, 3 H, ArH), 7.49 (s, 1 H, olefinic H), 7.69–7.71 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.04 (q × 2), 58.10 (t × 2), 101.03 (s), 125.80 (d), 126.13 (d), 126.44 (d × 2), 128.15 (d × 3), 129.52 (d × 2), 133.09 (s), 134.37 (s), 144.26 (s). MS: m/z = 322 (M^+), 287 (M^+ – Cl). $C_{17}H_{19}ClO_2S$ (322.85): calcd. C 63.25, H 5.93; found C 62.97, H 5.79.

Reaction of 7a with *p*-TsOH in $ClCH_2CH_2Cl$: To a solution of **7a** (0.10 g, 0.38 mmol) in $ClCH_2CH_2Cl$ (2.0 mL) was added *p*-TsOH (6.5 mg, 0.04 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The usual work-up afforded **14a** (41 mg, 43%).

Reaction of 7a with $Sc(OTf)_3$: To a $EtOH/H_2O$ (1:1, 1.0 mL) solution of **7a** (0.10 g, 0.38 mmol) was added $Sc(OTf)_3$ (19 mg, 0.04 mmol) at room temperature. The reaction mixture was heated at reflux conditions for 70 min. The usual work-up afforded **14a** (61 mg, 61%).

(*Z*)-2-[2-Chloro-3-(*p*-chlorophenyl)-1,1-diethoxyprop-2-enyl]thiophene (15b): IR (KBr): $\tilde{\nu}$ = 3429, 2976, 1490 (thienyl), 1233, 1196, 1145, 1055 (C–O), 982, 818, 786, 702 (thienyl) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, J = 7 Hz, 6 H, Me), 3.44–3.46 (m, 4 H, OCH_2), 6.98 (dd, J = 3, 5 Hz, 1 H, 4′-H), 7.11 (dd, J = 1, 3 Hz, 1 H, 3′-H), 7.28 (dd, J = 1, 5 Hz, 1 H, 5′-H), 7.32 (d, J = 9 Hz, 2 H, ArH), 7.43 (s, 1 H, olefinic H), 7.64 (d, J = 9 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.02 (q × 2), 58.15 (t × 2), 100.98 (s), 125.26 (d), 125.90 (d), 126.19 (d), 126.48 (d), 128.35 (d × 2), 130.79 (d × 2), 132.82 (s), 133.83 (s), 133.89 (s), 144.04 (s) ppm. MS: m/z = 356 (M^+), 321 (M^+ – Cl). $C_{17}H_{18}Cl_2O_2S$ (357.30): calcd. C 60.51, H 5.08; found C 60.23, H 4.97.

2-Chloro-2-(cyclohexylidene)-1-(2-thienyl)ethanone (14c): IR (KBr): $\tilde{\nu}$ = 3448, 2932, 1645 (C=O), 1513, 1447, 1409 (thienyl), 1354, 1282, 1230, 1059, 985, 772 (C–Cl), 724 (C–Cl) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.52-1.72 (m, 6 H, CH_2), 2.21 (t, J = 6 Hz, 2 H, CH_2), 2.50 (t, J = 6 Hz, 2 H, CH_2), 7.15 (dd, J = 4, 5 Hz, 1 H, ArH), 7.72 (m, 1 H, 3-H), 7.75–7.76 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.90 (t), 26.93 (t), 27.49 (t), 30.66 (t), 32.11 (t), 117.81 (s), 128.26 (d), 134.95 (d), 135.39 (d), 142.56 (s), 142.74 (s), 183.94 (s) ppm. MS: m/z = 240 (M^+), 205 (M^+ – Cl). $C_{12}H_{13}ClOS$ (240.75): calcd. C 59.86, H 5.44; found C 59.63, H 5.41.

2-Chloro-2-(cyclopentylidene)-1-(2-thienyl)ethanone (14d): IR (KBr): $\tilde{\nu}$ = 3447, 2959, 1642 (C=O), 1411 (thienyl), 1353, 1267, 1064, 765 (C–Cl), 726 (C–Cl) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.75–1.78 (m, 4 H, CH_2), 2.55–2.59 (m, 4 H, CH_2), 7.12–7.13 (m, 1 H, 4-H), 7.67–7.68 (m, 1 H, 5-H), 7.90 (t, J = 3 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.13 (t), 27.67 (t), 33.99 (t), 34.71 (t), 118.63 (s), 127.88 (d), 134.48 (d), 134.54 (d), 142.45 (s), 155.86 (s), 182.51 (s) ppm. MS: m/z = 226 (M^+), 191 (M^+ – Cl). $C_{11}H_{11}ClOS$ (226.72): calcd. C 58.27, H 4.89; found C 57.98, H 4.81.

2-Chloro-1,1-diethoxy-1-(2-thienyl)-2-(cyclopentylidene)ethane (15d): IR (KBr): $\tilde{\nu}$ = 5746, 2973, 1637, 1231, 1058 (C–O), 699 (C–Cl) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, J = 7 Hz, 6 H, Me), 1.59–1.65 (m, 2 H, CH_2), 1.69–1.75 (m, 2 H, CH_2), 2.47 (t, J = 8 Hz, 2 H, CH_2), 2.73 (t, J = 7 Hz, 2 H, CH_2), 3.37–3.41 (m, 2 H, OCH_2), 3.48–3.51 (m, 2 H, OCH_2), 6.94–6.97 (m, 1 H, 4′-H), 7.07 (dd, J = 1, 3 Hz, 1 H, 3′-H), 7.24 (d, J = 5 Hz, 1 H, 5′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.98 (q × 2), 25.21 (t), 28.23 (t), 33.06 (t), 36.01 (t), 57.73 (t × 2), 102.30 (s), 123.85 (s), 125.16 (d), 125.24 (d), 126.24 (d), 145.43 (s), 145.55 (s) ppm. MS: m/z = 255 (M^+ – OEt). $C_{15}H_{21}ClO_2S$ (300.84): calcd. C 59.89, H 7.04; found C 59.65, H 6.96.

2-Chloro-2-(cycloundecylidene)-1-(2-thienyl)ethanone (14e): IR (KBr): $\tilde{\nu}$ = 3440, 2931, 1649, 1514, 1469, 1409 (thienyl), 1354, 1269, 723 (C–Cl) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.29–1.35 (m, 12 H, CH_2), 1.43–1.50 (m, 4 H, CH_2), 1.59–1.64 (m, 2 H, CH_2), 2.15 (t, J = 8 Hz, 2 H, CH_2), 2.43 (t, J = 8 Hz, 2 H, CH_2), 7.14 (t, J = 4 Hz, 1 H, 4′-H), 7.71–7.73 (m, 2 H, 5′-H and 3′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.97 (t), 22.41 (t), 22.73 (t), 22.79 (t), 22.86 (t), 23.88 (t), 25.55 (t), 25.58 (t), 25.73 (t), 28.34 (t), 29.59 (t), 121.14 (s), 128.16 (d), 135.04 (d), 135.29 (d), 142.35 (s), 143.80 (s), 183.94 (s) ppm. MS: m/z = 324 (M^+). $C_{18}H_{25}ClOS$ (324.91): calcd. C 66.54, H 7.76; found C 66.40, H 7.68.

(*Z*)-2-Chloro-3-(2-furyl)-1-(5-methyl-2-thienyl)propen-1-one (16): IR (KBr): $\tilde{\nu}$ = 3138, 1637, 1468, 1385, 1280, 1181, 1151, 1087, 1025, 944, 889, 827, 793, 766, 724, 686, 593, 459 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.56 (s, 3 H, Me), 6.50–6.61 (m, 1 H, ArH), 6.83–6.84 (m, 1 H, ArH), 7.34 (d, J = 3 Hz, 1 H, ArH), 7.59 (dd, J = 1, 2 Hz, 1 H, ArH), 7.65 (d, J = 4 Hz, 1 H, ArH), 7.67 (d, J = 1 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.91 (q), 112.79 (d), 116.77 (d), 125.75 (d), 126.37 (s), 126.68 (d), 134.93 (d), 139.11 (s), 144.87 (d), 149.25 (s), 150.73 (s), 180.65 (s) ppm. The molecular ion peak was not detected in the mass spectrum. $C_{12}H_9ClO_2S$ (252.72): calcd. C 57.03, H 3.59; found C 56.84, H 3.63.

(*Z*)-2-Chloro-3-(*p*-methoxyphenyl)-1-(2-furyl)propen-1-one (17a): IR (KBr): $\tilde{\nu}$ = 3435, 3133, 2934, 2839, 1644, 1597 (furyl), 1509, 1462, 1258, 1180, 1094, 1027 (C–O), 793 (C–Cl), 535 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OMe), 6.59 (dd, J = 2, 4 Hz, 1 H, 4′-H), 6.96 (d, J = 9 Hz, 2 H, ArH), 7.36 (d, J = 3 Hz, 1 H, ArH), 7.69–7.70 (m, 1 H, 5-H), 7.84 (s, 1 H, olefinic H), 7.89 (d, J = 9 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.41 (q), 112.25 (d), 114.12 (d × 2), 120.57 (d), 125.70 (s), 126.65 (s), 132.95 (d×2), 137.98 (d), 147.14 (d), 150.91 (s), 161.35 (s), 176.86 (s) ppm. MS: m/z = 262 (M^+), 227(M^+ – Cl). $C_{14}H_{11}ClO_3$ (262.69): calcd. C 64.01, H 4.22; found C 63.82, H 4.24.

(*Z*)-2-[2-Chloro-3-(*p*-chlorophenyl)-1,1-diethoxyprop-2-enyl]-5-methylfuran (18a): IR (KBr): $\tilde{\nu}$ = 3436, 2982, 1491 (furyl), 1254, 1051 (C–O), 948, 785 (C–Cl) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.24 (t, J = 7 Hz, 6 H, Me), 2.26 (s, 3 H, Me), 3.38–3.45 (m, 2 H, OCH_2), 3.50–3.95 (m, 2 H, OCH_2), 5.95 (br. s, 1 H, ArH), 6.47(d, J = 3 Hz, 1 H, ArH), 7.32 (d, J = 8 Hz, 2 H, ArH), 7.66 (d, J = 8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67 (q), 15.01 (q × 2), 57.90 (t × 2), 99.45 (s), 106.19 (d), 111.38 (d),

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126.29 (d), 128.31 (d × 2), 130.84 (d × 2), 131.75 (s), 132.88 (s), 133.77 (s), 149.34 (s), 152.16 (s) ppm. HRMS: calcd. for $C_{18}H_{20}Cl_2O_3$ 354.0789; found 354.0754.

2-Chloro-2-(cyclohexylidene)-1-(5-methyl-2-furyl)ethanone (17b): IR (KBr): $\tilde{\nu}$ = 3447, 2931, 1652 (C=O), 1509 (furyl), 1448, 1368, 1306, 1207, 1088, 1023, 787 (C–Cl), 734 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.35–1.61 (m, 4 H, CH_2), 1.65–1.81 (m, 2 H, CH_2), 2.21–2.23 (m, 2 H, CH_2), 2.42 (s, 3 H, Me), 2.47–2.49 (m, 2 H, CH_2), 6.21–6.22 (m, 1 H, 4′-H), 7.17 (d, J = 4 Hz, 1 H, 3′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.09 (q), 25.85 (t), 26.85 (t), 27.42 (t), 30.78 (t), 31.99 (t), 109.37 (d), 117.44 (s), 123.56 (d), 143.36 (s), 149.89 (s), 159.74 (s), 178.14 (s) ppm. MS: m/z = 238 (M^+), 203 (M^+ – Cl). $C_{13}H_{15}ClO_2$ (238.72): calcd. C 65.41, H 6.33; found C 65.15, H 6.31.

(*Z*)-2-Chloro-1-(5-methyl-2-furyl)-3-(2-thienyl)propen-1-one (17c): IR (KBr): $\tilde{\nu}$ = 3433, 1637 (C=O), 1509 (furyl), 1416, 1365, 1286, 1208, 1111, 1028, 860, 795 (C–Cl), 715 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, Me), 6.22 (d, J = 4 Hz, 1 H, ArH), 7.15 (dd, J = 4, 5 Hz, 1 H, ArH), 7.33 (d, J = 3 Hz, 1 H, ArH), 7.52 (d, J = 4 Hz, 1 H, ArH), 7.62–7.63 (m, 1 H, ArH), 8.14 (s, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.02 (q), 109.11 (d), 122.65 (d), 125.89 (s), 127.04 (d), 131.02 (d), 131.64 (d), 134.50 (d), 136.75 (s), 149.37 (s), 158.74 (s), 175.03 (s) ppm. MS: m/z = 252 (M^+), 217 (M^+ – Cl). $C_{12}H_9ClO_2S$ (252.72): calcd. C 57.03, H 3.59; found C 56.87, H 3.53.

(*Z*)-2-Chloro-3-(*p*-methoxyphenyl)-1-phenylpropen-1-one (19): IR (KBr): $\tilde{\nu}$ = 1656 (C=O), 1598, 1509, 1421, 1258, 1178, 1086, 1073, 1024, 828, 715, 655, 538 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OMe), 6.94 (d, J = 9 Hz, 2 H, ArH), 7.44 (s, 1 H, olefinic H), 7.45–7.48 (m, 2 H, ArH), 7.55–7.58 (m, 1 H, ArH), 7.73–7.75 (m, 2 H, ArH), 7.84 (d, J = 9 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.32 (q), 114.04 (d × 2), 125.42 (s), 128.27 (s), 128.32 (d × 2), 129.28 (d × 2), 132.08 (d), 132.80 (d × 2), 137.29 (s), 140.12 (d), 161.37 (s), 191.29 (s) ppm. MS: m/z = 272 (M^+), 237 (M^+ – Cl). $C_{16}H_{13}ClO_2$ (272.73): calcd. C 70.46, H 4.80; found C 70.32, H 4.82.

(*Z*)-2-Chloro-3-(*p*-methoxyphenyl)-1-(2-pyridyl)propen-1-one (20a): IR (KBr): $\tilde{\nu}$ = 1659 (C=O), 1593, 1509, 1259, 1178, 1096, 1029, 832, 672, 535 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OMe), 6.93 (d, J = 8 Hz, 2 H, ArH), 7.47–7.49 (m, 1 H, ArH), 7.87–7.93 (m, 4 H, ArH), 8.12 (s, 1 H, olefinic H), 8.70–8.71 (m, 1 H, ArH) ppm. HRMS: calcd. for $C_{15}H_{12}ClNO_2$ 273.0556; found 273.0539.

(*Z*)-2-[2-Chloro-1,1-diethoxy-3-(*p*-methoxyphenyl)prop-2-enyl]pyridine (21a): IR (KBr): $\tilde{\nu}$ = 3448, 2982, 2937, 2896, 2363, 1603, 1510, 1285, 1250, 1184, 1069, 833 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.28 (t, J = 7 Hz, 6 H, Me), 3.36–3.42 (m, 2 H, OCH_2), 3.53–3.60 (m, 2 H, OCH_2), 3.80 (s, 3 H, OMe), 6.87 (d, J = 8 Hz, 2 H, ArH), 7.20 (dd, J = 5, 8 Hz, 1 H, ArH), 7.55 (s, 1 H, olefinic H), 7.70–7.72 (m, 1 H, ArH), 7.71 (d, J = 8 Hz, 2 H, ArH), 7.86 (br. d, 1 H, J = 8 Hz, ArH), 8.63 (br. d, 1 H, J = 6 Hz, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.08 (q × 2), 55.15 (q), 57.87 (t × 2), 102.04 (s), 113.40 (d × 2), 122.85 (d), 123.20 (d), 126.78 (d), 126.93 (s), 129.51 (s), 131.04 (d × 2), 135.94 (d), 149.09 (d), 158.29 (s), 159.23 (s) ppm. MS: m/z = 347 (M^+), 318 (M^+ – Et), 302 (M^+ – OEt). $C_{19}H_{22}ClNO_3$ (347.84): calcd. C 65.61, H 6.38, N 4.03; found C 65.47, H 6.35, N 4.02.

2-[2-Chloro-2-(cyclohexylidene)-1,1-diethoxyethyl]pyridine (21b): IR (KBr): $\tilde{\nu}$ = 3435, 2928, 1586, 1432, 1390, 1270, 1226, 1064, 992, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, J = 7 Hz, 6 H, Me), 1.25–1.33 (m, 2 H, CH_2), 1.45–1.56 (m, 4 H, CH_2), 2.45 (t, J = 6 Hz, 2 H, CH_2), 2.56 (t, J = 6 Hz, 2 H, CH_2), 3.26–3.34 (m, 2 H, OCH_2), 3.50–3.58 (m, 2 H, OCH_2), 7.15–7.19 (m, 1 H, ArH), 7.64–7.68 (m, 1 H, ArH), 7.72 (d, J = 8 Hz, 1 H, ArH), 8.64 (d, J = 4 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.03 (q × 2), 26.32 (t), 27.44 (t), 27.58 (t), 31.17 (t), 34.05 (t), 57.48 (t × 2), 102.37 (s), 122.12 (d), 122.40 (d), 124.37 (s), 135.59 (d), 141.76 (s), 148.92 (d), 160.20 (s) ppm. MS: m/z = 263 (M^+ – EtOH). $C_{17}H_{24}ClNO_2$ (309.84): calcd. C 65.90, H 7.81, N 4.52; found C 65.85, H 7.78, N 4.49.

(2*Z*,4*E*)-2-(2-Chloro-1,1-diethoxy-5-phenylpenta-2,4-dienyl)pyridine (21c): IR (KBr): $\tilde{\nu}$ = 2977, 2360, 1585, 1436, 1170, 1057, 976, 752, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, J = 7 Hz, 6 H, Me), 3.32–3.40 (m, 2 H, OCH_2), 3.49–3.57 (m, 2 H, OCH_2), 6.83 (d, J = 16 Hz, 1 H, 5-H), 7.10 (dd, J = 11, 16 Hz, 1 H, 4-H), 7.15–7.36 (m, 5 H, 3-H ArH), 7.44–7.46 (m, 2 H, ArH), 7.68–7.73 (m, 1 H, ArH), 7.82–7.85 (m, 1 H, ArH), 8.63–8.64 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.05 (q × 2), 57.86 (t × 2), 101.79 (s), 122.90 (d), 123.05 (d), 123.43 (d), 126.69 (d × 2), 127.99 (d), 128.13 (d), 128.54 (d × 2), 132.90 (s), 135.97 (d), 136.49 (d), 136.97 (s), 149.15 (d), 158.08 (s) ppm. MS: m/z = 343 (M^+), 314 (M^+ – Et), 308 (M^+ – Cl), 298 (M^+ – EtO). $C_{20}H_{22}ClNO_2$ (343.85): calcd. C 69.86, H 6.45, N 4.07; found C 69.63, H 6.33, N 4.12.

(*Z*)-2-[2-Chloro-1,1-diethoxy-3-(2-furyl)prop-2-enyl]pyridine (21d): IR (KBr): $\tilde{\nu}$ = 2978, 1644, 1586, 1482, 1464, 1434, 1385, 1190, 1141, 1069, 960, 765, 692 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, J = 7 Hz, 6 H, Me), 3.35–3.39 (m, 2 H, OCH_2), 3.50–3.56 (m, 2 H, OCH_2), 6.43 (br. s, 1 H, ArH), 6.94 (d, J = 3 Hz, 1 H, ArH), 7.19–7.21 (m, 1 H, ArH), 7.43 (br. s, 1 H, olefinic H), 7.57 (s, 1 H, ArH), 7.71 (t, J = 8 Hz, 1 H, ArH), 7.84 (d, J = 7 Hz, 1 H, ArH), 8.63 (d, J = 4 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.01 (q × 2), 57.89 (t × 2), 101.79 (s), 111.45 (d), 111.63 (d), 117.61 (d), 122.92 (d), 123.04 (d), 129.63 (s), 135.98 (d), 142.12 (d), 149.15 (d), 150.00 (s), 157.97 (s) ppm. MS: m/z = 278 (M^+ – Et), 262 (M^+ – EtO). $C_{16}H_{18}ClNO_3$ (307.78): calcd. C 62.44, H 5.89, N 4.55; found C 62.32, H 5.80, N 4.52.

Palladium-Catalyzed Arylation of 16 with (*p*-Methoxyphenyl)-boronic Acid: To a solution of **16** (50 mg, 0.20 mmol) in toluene/EtOH (1:1, 3.0 mL) was added [1,4-bis(diphenylphosphanyl)butane]palladium dichloride (18.0 mg, 0.016 mmol), water (1.0 mL), Na_2CO_3 (34.0 mg, 0.32 mmol) and *p*-methoxyphenylboronic acid (72 mg, 0.47 mmol). The reaction mixture was heated for 1 h under reflux, and the usual work-up gave (*E*)-3-(2-furyl)-2-(*p*-methoxyphenyl)-1-(5-methyl-2-thienyl)propen-1-one (**22a**) (35 mg, 54%) and (*Z*)-**22a** (15 mg, 23%) as a yellow oil.

(*E*)-22a: IR (KBr): $\tilde{\nu}$ = 1637, 1511, 1449, 1352, 1290, 1249, 1229, 1181, 1032, 830, 741, 546 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.50 (s, 3 H, Me), 3.79 (s, 3 H, OMe), 6.30 (dd, J = 2, 4 Hz, 1 H, ArH), 6.35 (d, J = 3 Hz, 1 H, ArH), 6.68 (dd, J = 1, 3 Hz, 1 H, ArH), 6.76 (s, 1 H, olefinic H), 6.84 (d, J = 10 Hz, 2 H, ArH), 6.86–6.87 (m, 1 H, ArH), 7.26–7.27 (m, 1 H, ArH), 7.39 (d, J = 10 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.56 (q), 55.29 (q), 110.01 (d), 111.65 (d), 114.27 (d × 2), 114.62 (d), 127.03 (d), 127.19 (d × 2), 129.49 (s), 135.40 (d), 136.89 (s), 142.97 (d), 150.94 (s), 151.07 (s), 159.65 (s), 190.34 (s) ppm. HRMS: calcd. for $C_{19}H_{16}O_3S$ 324.0820; found 324.0785.

(*Z*)-22a: IR (KBr): $\tilde{\nu}$ = 1631 (C=O), 1607, 1574, 1510, 1448, 1390, 1362, 1087, 1065, 1027, 944, 885, 813, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, Me), 3.87 (s, 3 H, OMe), 5.95 (dd, J = 1, 3 Hz, 1 H, ArH), 6.29–6.30 (m, 1 H, ArH), 6.66 (d, J = 1, 4 Hz, 1 H, ArH), 6.97 (d, J = 9 Hz, 2 H, ArH), 7.10 (br. d, J = 4 Hz, 1 H, ArH), 7.27 (d, J = 9 Hz, 2 H, ArH), 7.38–7.39 (m, 1

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H, ArH), 7.45 (s, 1 H, olefinic H) ppm. The molecular ion peak was not detected in the mass spectrum.

Palladium-Catalyzed Arylation of 16 with (4-Chlorophenyl)boronic Acid: To a solution of **16** (50 mg, 0.20 mmol) in toluene/EtOH (1:1, 1.0 mL) was added [1,4-bis(diphenylphosphanyl)butane]palladium dichloride (12.0 mg, 0.02 mmol), water (1.0 mL), Na_2CO_3 (0.11 g, 1.00 mmol) and (*p*-chlorophenyl)boronic acid (93 mg, 0.59 mmol). The reaction mixture was heated for 12 h under reflux, and the usual work-up gave (*E*)-2-(*p*-chlorophenyl)-3-(2-furyl)-1-(5-methyl-2-thienyl)propen-1-one (**22b**) (30 mg, 46%) and (*Z*)-**22b** (17 mg, 26%).

(*E*)-22b: A yellow oil. IR (KBr): $\tilde{\nu}$ = 1637 (C=O), 1491, 1476, 1449, 1348, 1270, 1229, 1094, 1059, 1013, 930, 885, 857, 827, 808, 760, 742 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, Me), 6.32 (dd, *J* = 2, 3 Hz, 1 H, ArH), 6.42 (d, *J* = 3 Hz, 1 H, ArH), 6.69 (d, *J* = 3 Hz, 1 H, ArH), 6.90 (s, 1 H, ArH), 7.28 (br. s, 1 H, ArH), 7.29 (d, *J* = 9 Hz, 2 H, ArH), 7.38 (s, 1 H, olefinic H), 7.39 (d, *J* = 9 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.16 (q), 111.80 (d), 112.22 (d), 116.62 (d), 127.10 (d × 3), 128.99 (d × 2), 134.01 (s), 135.40 (s), 135.43 (d), 135.85 (s), 141.66 (s), 143.55 (d), 150.58 (s), 151.34 (s), 189.55 (s) ppm. MS: *m*/*z* = 328 (M^+). $C_{18}H_{13}ClO_2S$ (328.81): calcd. C 65.75, H 3.99; found C 65.49, H 3.95.

(*Z*)-22b: A yellow oil. IR (KBr): $\tilde{\nu}$ = 1631 (C=O), 1491, 1448, 1393, 1362, 1336, 1277, 1228, 1166, 1147, 1090, 1065, 1017, 943, 885, 802, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.50 (s, 3 H, Me), 6.02 (d, *J* = 3 Hz, 1 H, ArH), 6.32 (d, *J* = 2 Hz, 1 H, ArH), 6.70 (d, *J* = 4 Hz, 1 H, ArH), 7.17 (d, *J* = 4 Hz, 1 H, ArH), 7.30 (d, *J* = 9 Hz, 2 H, ArH), 7.37–7.41 (m, 3 H, ArH), 7.44 (s, 1 H, olefinic H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.92 (q), 112.23 (d), 114.98 (d), 126.60 (d), 126.90 (d), 128.99 (d × 2), 131.15 (d × 2), 134.27 (s), 134.62 (d), 135.25 (s), 141.74 (s), 143.57 (s), 144.36 (d), 150.18 (s), 150.85 (s), 185.65 (s) ppm HRMS: calcd. for $C_{18}H_{13}ClO_2S$ 328.0324; found 328.0321.

Palladium-Catalyzed Arylation of 16 with 2-Thienylboronic Acid: To a solution of **16** (50 mg, 0.20 mmol) in toluene/EtOH (1:1, 3.0 mL) was added [1,4-bis(diphenylphosphanyl)butane]palladium dichloride (12.0 mg, 0.02 mmol), water (1.0 mL), Na_2CO_3 (0.11 g, 1.00 mmol) and 2-thienylboronic acid (78 mg, 0.60 mmol). The reaction mixture was heated for 12 h under reflux, and the usual work-up gave (*E*)-3-(2-furyl)-1-(5-methyl-2-thienyl)-2-(2-thienyl)-propen-1-one (**22c**) (40 mg, 40%) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 1638, 1449, 1358, 1343, 1259, 1229, 1166, 1149, 1018, 927, 885, 806, 741, 700, 592 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, Me), 6.24 (dd, *J* = 2, 3 Hz, 1 H, ArH), 6.30 (d, *J* = 3 Hz, 1 H, ArH), 6.64 (d, *J* = 4 Hz, 1 H, ArH), 6.79 (s, 1 H, olefinic H), 6.84–6.88 (m, 2 H, ArH), 7.14 (d, *J* = 1 Hz, 1 H, ArH), 7.21 (d, *J* = 1 Hz, 1 H, ArH), 7.40 (d, *J* = 3 Hz, 1 H, ArH) ppm. HRMS: calcd. for $C_{16}H_{12}O_2S_2$ 300.0276; found 300.0256.

Palladium-Catalyzed Arylation of 19 with (*p*-Methoxyphenyl)-boronic Acid: To a solution of **19** (50 mg, 0.20 mmol) in toluene/EtOH (1:1, 3.0 mL) was added [1,4-bis(diphenylphosphanyl)butane]palladium dichloride (12.0 mg, 0.02 mmol), water (1.0 mL), Na_2CO_3 (0.11 g, 1.00 mmol) and (*p*-methoxyphenyl)boronic acid (91 mg, 0.60 mmol). The reaction mixture was heated for 12 h under reflux, and the usual work-up gave (*E*)- and (*Z*)-2-(*p*-methoxyphenyl)-3-phenyl-1-(2-thienyl)propen-1-one (**22d**) (64 mg, quant.) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 1634 (C=O), 1593, 1512, 1462, 1445, 1412, 1374, 1355, 1282, 1255, 1239, 1183, 918, 884, 857, 848, 826, 792, 758, 722, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, *Z*-OMe), 3.81 (s, *E*-OMe), 6.88 (d, *J* = 9 Hz, *E*-ArH), 6.94 (dd, *J* = 4, 5 Hz, *E*-ArH), 7.01 (t, *J* = 4 Hz, *Z*-ArH), 7.07 (s, *E*-olefinic H), 7.14–7.24 (m, *E*- and *Z*-ArH), 7.33 (d, *J* = 9 Hz, *E*-ArH), 7.39 (s, *Z*-olefinic H), 7.42–7.43 (m, *E*- and *Z*-ArH), 7.54–7.58 (m, *E*- and *Z*-ArH) ppm. Precipitation of (*E*)- and (*Z*)-**22d** afforded almost pure (*E*)-**22d**: ^1H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, OMe), 6.88 (d, *J* = 9 Hz, 2 H, ArH), 6.94 (dd, *J* = 4, 5 Hz, 1 H, ArH), 7.08 (s, 1 H, olefinic H), 7.14–7.23 (m, 3 H, ArH), 7.33 (d, *J* = 8 Hz, 2 H, ArH), 7.43 (d, *J* = 8 Hz, 2 H, ArH), 7.55 (d, *J* = 4 Hz, 1 H, ArH), 7.58 (dd, *J* = 1, 5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.24 (q), 114.20 (d × 2), 127.61 (d × 2), 127.78 (d), 128.18 (d), 128.38 (d × 2), 128.62 (d × 2), 130.28 (d), 131.15 (d), 134.95 (d), 135.07 (s), 135.56 (s), 140.14 (s), 144.11 (s), 159.69 (s), 191.61 (s) ppm. MS *m*/*z* 320 (M^+). $C_{20}H_{16}O_2S$ (320.41): calcd. C 74.97, H 5.03; found C 74.60, H 5.05.

Palladium-Catalyzed Arylation of 14c with (*p*-Methoxyphenyl)-boronic Acid: To a solution of **14c** (50 mg, 0.20 mmol) in toluene/EtOH (1:1, 3.0 mL) was added [1,4-bis(diphenylphosphanyl)butane]palladium dichloride (12.0 mg, 0.02 mmol), water (1.0 mL), Na_2CO_3 (0.11 g, 1.00 mmol) and (*p*-methoxyphenyl)boronic acid (91 mg, 0.60 mmol). The reaction mixture was heated for 12 h under reflux, and the usual work-up gave 2-(*p*-methoxyphenyl)-2-(cyclohexylidene)-1-(2-thienyl)ethanone (**22e**) (62 mg, quant.) as a yellow oil. IR (KBr): $\tilde{\nu}$ = 2929, 2853, 1638 (C=O), 1606, 1509, 1459, 1447, 1411, 1354, 1247, 1176, 1111, 1081, 1055, 1034, 984, 835, 799, 726 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.60–1.64 (m, 6 H, CH_2), 2.22 (br. s, 2 H, CH_2), 2.27–2.29 (m, 2 H, CH_2), 3.76 (s, 3 H, OMe), 6.84 (d, *J* = 9 Hz, 2 H, ArH), 7.05 (d, *J* = 4 Hz, 1 H, ArH), 7.23 (d, *J* = 9 Hz, 2 H, ArH), 7.58 (d, *J* = 5 Hz, 1 H, ArH), 7.64–7.65 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.28 (t), 28.05 (t), 28.14 (t), 30.83 (t), 33.08 (t), 55.09 (q), 113.74 (d × 2), 128.05 (d), 128.80 (s), 130.39 (d × 2), 133.20 (s), 133.98 (d), 134.19 (d), 142.53 (s), 144.88 (s), 158.71 (s), 191.18 (s) ppm. MS: *m*/*z* = 312 (M^+). $C_{19}H_{20}O_2S$ (312.43): calcd. C 73.04, H 6.45; found C 73.00, H 6.43.

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