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Inter- and Intramolecular Palladium-Catalyzed Allyl Cross-Coupling Reactions Using Allylindium Generated In Situ from Allyl Acetates, Indium, and Indium Trichloride

Dong Seomoon, Kooyeon Lee, Hyunseok Kim, and Phil Ho Lee*[a]

Abstract: Inter- and intramolecular palladium-catalyzed allyl cross-coupling reactions using allylindium generated in situ by treatment of allyl acetates with indium and indium trichloride in the presence of Pd^0 catalyst and nBuNMe$_2$ in DMF were successfully demonstrated. Allylindium species generated in situ by reductive transmetalation of π-allylpalladium(II) complexes, obtained from a variety of allyl acetates in the presence of Pd^0 catalyst together with indium and indium trichloride, were found to be capable of acting as effective nucleophilic coupling partners in Pd-catalyzed cross-coupling reactions. A variety of allyl acetates such as but-1-en-3-yl acetate, crotyl acetate, and 2-methylallyl acetate afforded the corresponding allylic compounds in good yields in cross-coupling reactions. Various electrophilic cross-coupling partners such as aryl iodides and vinyl bromides and triflates participate in these reactions. Not only intermolecular but also intramolecular Pd-catalyzed cross-coupling reactions work equally well to produce the desired allylic coupling products in good yields.

Keywords: allyl acetate · allylation · cross-coupling · indium · palladium

Introduction

The establishment of efficient methods for C–C bond formation is an important ongoing research subject in organic synthesis. Transition-metal-catalyzed cross-coupling reactions between organometallic reagents and a variety of electrophiles represent one of the most powerful methods through which to form C–C bonds.[1] Among these, reactions that make use of organoindium reagents have emerged as favorites, thanks to their reactivity and selectivity, ease of preparation and handling, operational simplicity, and low toxicity.[2] As a consequence of these desirable properties of organoindium species, we have previously reported Pd-catalyzed cross-coupling reactions and carbonylative cross-coupling reactions of allylindiums,[3] allenylindiums,[4] tri(organo)indiums,[5] and tetra(organo)indates[6] with a variety of electrophiles. In addition, it has been found that various organoindiums can serve as nucleophilic coupling partners in transition-metal-catalyzed cross-coupling reactions.[7] Because the widespread natural occurrence of the allyl group and its potential for further functionalization have promoted ongoing interest in synthetic methods for the introduction of allyl groups into organic compounds,[8] many allylation methods—such as Friedel–Crafts alkylation,[9] Claisen rearrangement,[10] and substitution reactions of allyl halides with various organometallic reagents[11]—have been developed. Moreover, Pd-catalyzed cross-coupling reactions have also attracted much attention in the area of allylation methods.[12] One of the most frequently used methods for allyl cross-coupling reactions involves the use of allylstannanes as nucleophilic coupling partners, these reagents having attracted much attention as a result of their availability, air- and moisture-stability, and compatibility with a variety of functional groups.[13] Although allylstannanes are generally obtainable, such procedures are sometimes restricted if the required allyl metals are difficult to produce, so direct conversion of readily accessible allylic substrates into allyl metal species is in demand. In general, the allylation reagents have been bound to allyl halides, particularly allyl bromides and iodides. Allyl chlorides have been used with iodide salts, via allyl iodide generated in situ. To overcome these drawbacks is therefore an imperative for the development of new allyl metals as cross-coupling partners. Recently, new methods for the preparation of allylindiums through reductive transmetalation[14] of π-allylpalladium(II) complexes from allyl alcohols and their derivatives have been investigated, and many successful examples of palladium- and indium-mediat-

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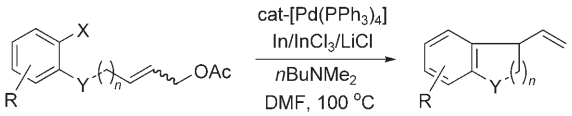
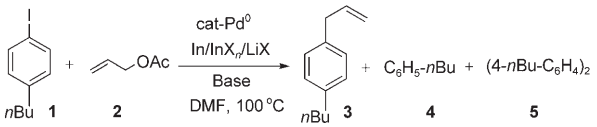
ed allylation of aldehydes,[15] imines,[16] and oximes[17] were then reported. In the context of our ongoing research interest in transition-metal-catalyzed cross-coupling reactions with the aid of a variety of organoindium reagents,[4,5a,6,18] we have reported Pd-catalyzed cross-coupling reactions between allylindiums—generated in situ from allyl halides and indium—and a variety of electrophilic coupling partners.[3] Our continuing endeavors in the area of indium chemistry resulted in our finding that allyl acetates, obtainable from easily available allyl alcohols, can be effectively used in intermolecular and intramolecular Pd-catalyzed allyl cross-coupling reactions via π-allylpalladium(II) complexes and their transmetalation with indium and indium trichloride in the presence of catalytic amounts of $[Pd(PPh_3)_4]$ (Scheme 1).[19]



n = 1, 2, 3
X = Br, I, OTf
Y = $C(CO_2Et)_2$, $CHCO_2Et$, NTs, CH_2ONBoc, $CH_2C(CO_2Et)_2$
$CH_2C(SO_2Ph)_2$, $CH_2C(CN)_2$, $CH_2C(CO_2Et)(SO_2Ph)$

Scheme 1. Inter- and intramolecular Pd-catalyzed allyl cross-coupling reactions.

Table 1. Optimization of Pd-catalyzed cross-coupling reactions between 4-*n*-butyl-1-iodobenzene and allyl acetate.[a]



1 2 3 4 5

Entry	In	InX_n	LiX	Base	Time [h]	Yield [%] 3[b]	4[c]	5[c]
1[d]	–	–	LiCl	Et_3N	48	(82)	0	0
2[d]	In	$InCl_3$	LiCl	–	18	21	74	0
3[e]	–	$InCl_3$	LiCl	Et_3N	42	14(28)	0	0
4	In	–	LiCl	Et_3N	18	58	15	15
5	In	$InCl_3$	LiCl	–	18	43	26	11
6	In	$InCl_3$	–	Et_3N	24	21	19	8
7	In	$InCl_3$	LiCl	Et_3N	6	54	11	27
8	In	$InBr_3$	LiCl	Et_3N	6	47	9	33
9	In	InI_3	LiCl	Et_3N	18	21(41)	10	23
10	In	$InCl_3$	LiBr	Et_3N	18	36	15	41
11	In	$InCl_3$	LiI	Et_3N	18	16(43)	29	6
12[f]	In	$InCl_3$	LiCl	K_2CO_3	18	21	35	33
13	–	InI	LiCl	–	16	2(95)	35	33
14	–	InI	LiCl	$nBuNMe_2$	16	30(55)	0	0
15	In	$InCl_3$	LiCl	$nBuNMe_2$	9	65	10	10
16[d]	In	$InCl_3$	LiCl	$nBuNMe_2$	16	31(52)	7	0

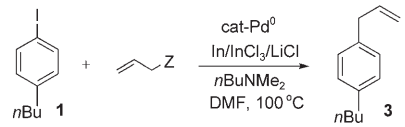
[a] Reactions performed in the presence of 10 mol% $[Pd(PPh_3)_4]$, 2.0 equivalents of In, 0.5 equivalents of InX_3, 3.0 equivalents of LiX, and 2.0 equivalents of base, unless otherwise noted. [b] Yield of isolated product. Numbers in parenthesis are recovered yields of **1**. [c] GC yields. [d] $[Pd(PPh_3)_4]$ (5 mol%) was used. [e] *trans*-1,3-Bis(4-*n*-butylphenyl)propene was obtained in 21% yield. [f] K_2CO_3 (1.0 equiv) was used.

Results and Discussion

Reaction optimization: Our initial study focused on Pd-catalyzed cross-coupling reactions between 1-*n*-butyl-4-iodobenzene (**1**) and allyl acetate (Table 1). DMF was the best solvent of several reaction media scrutinized (DMF, THF, CH_3CN, and THF/H_2O), while of the catalysts screened, $[Pd(PPh_3)_4]$ was the most satisfactory in terms of the yields, though other palladium catalysts such as $PdCl_2$, $Pd(OAc)_2$, $[Pd(CH_3CN)_2Cl_2]$, $[Pd(PhCN)_2Cl_2]$, and $[Pd_2(dba)_3CHCl_3]$/PPh_3 also produced 4-allyl-*n*-butylbenzene (**3**) in good yields. Combinations of indium and indium trihalide as reductive transmetalation reagents for π-allylpalladiums(II) gave the allyl cross-coupling product in good yield, while the use of indium iodide produced the desired product in only 30% yield (Table 1, entry 14). The cross-coupling reaction proceeded efficiently in the presence of LiCl as an additive (Table 1, entries 7, 10, and 11).[3,4] In addition, the presence of a tertiary alkylamine was necessary to reduce side products such as *n*-butylbenzene and 4,4′-di(*n*-butyl)biphenyl. Of the amines examined, *N*,*N*-dimethyl-*n*-butylamine gave the best result (Table 1, entries 5, 8, and 15).[12h,i,20] Use of inorganic bases such as potassium carbonate resulted in low yields (Table 1, entry 12). Of the reaction conditions examined, the best results were obtained with 10 mol% $[Pd(PPh_3)_4]$, 2.0 equivalents of In, 0.5 equivalents of $InCl_3$, 3.0 equivalents of LiCl, and 2 equivalents of *N*,*N*-dimethyl-*n*-butylamine in DMF at 100°C over 9 h, producing 4-allyl-*n*-butylbenzene (**3**) in 65% yield (Table 1, entry 15). These reactions do not take place in the absence of indium and indium trichloride (Table 1, entry 1).

In addition, various allylic compounds such as allyl alcohol, allyl acetate, allyl methyl carbonate, allyl trifluoromethyl carbonate, allyl phenyl ether, allyl methyl sulfide, allyl phenyl sulfone, allyl chloride, acrolein diethyl acetal, and allyl-*N*-cyclohexylcarbamate were also examined for their utility in cross-coupling reactions, and the results are shown in Table 2. Under the optimized conditions, allyl alcohol gave the desired compound in 5% yield (Table 2, entry 1), while in the case of allyl methyl carbonate, **3** was obtained in 59% yield together with **4** (34%; Table 2, entry 3). Treatment of allyl methyl sulfide and allyl phenyl sulfone under the optimum conditions produced **3** in low yields (7% and 10% yields, respectively; Table 2, entries 6 and 7), with the homocoupling product **5**[21] and the reduction product **4** being produced as major compounds in these reactions.

Table 2. Pd-catalyzed allyl cross-coupling reactions with various allylic compounds under the optimized reaction conditions.[a]



Entry	Z	Time [h]	Isolated yield			
			3	**4**	**5**[b]	**1**[b]
1	OH	7	5	55	40	0
2	OAc	9	65	10[b]	10	0
3	OCO_2CH_3	11	59	34	2	0
4	$OCOCF_3$	24	16	24[b]	13	47
5	OPh	16	38	17[b]	33	0
6	SMe	16	7	18[b]	76	0
7	SO_2Ph	14	10	78	9	0
8	Cl	20	32	18[b]	0	42
9	$(OEt)_2$	7	0	79	21	0
10	$OCONHC_6H_{11}$	8	44	4[b]	40	0

[a] Reactions performed in the presence of 10 mol% $[Pd(PPh_3)_4]$, 2.0 equivalents of In, 0.5 equivalents of $InCl_3$, 3.0 equivalents of LiCl, and 2.0 equivalents of nBuNMe$_2$. [b] GC yields.

Acrolein diethyl acetal did not act as a nucleophilic coupling partner in this reaction (Table 2, entry 9), while in the case of allyl carbamate the desired allyl cross-coupling product was produced in 44% yield together with **5** in 40% yield (Table 2, entry 10). Among the compounds examined, though, allyl acetate gave the best result (Table 2, entry 2).

Intermolecular cross-coupling reactions: To demonstrate the efficiency and scope of this method, we applied the catalytic system to a variety of allyl acetate and electrophilic coupling partners, and it was found that a diverse range of functional groups were compatible with the reaction conditions (Table 3). With allyl acetates as coupling partners, the presence of a methyl group at the α, β, or γ position had an effect both on reaction rates and on product yields. Allyl acetate (**2**), but-1-en-3-yl acetate (**23**), crotyl acetate (**24**), and 2-methylallyl acetate (**25**) afforded the corresponding allylic compounds in good yields in cross-coupling reactions. Treatment of 1-iodonaphthalene with allyl acetate gave 1-al-

Table 3. Intermolecular Pd-catalyzed allyl cross-coupling reactions.

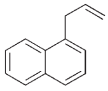
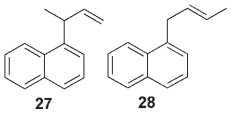
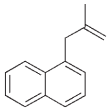
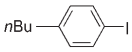
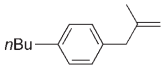
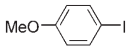
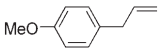
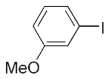
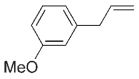
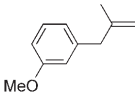
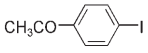
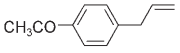
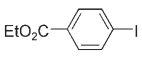
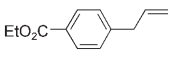
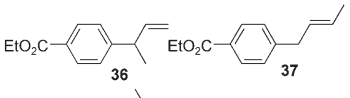
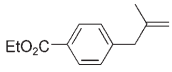
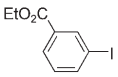
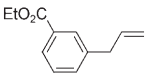
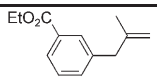
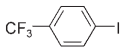
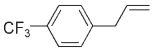
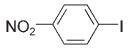
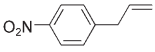
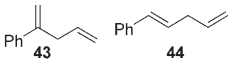
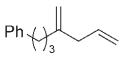
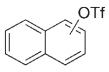
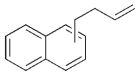
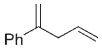
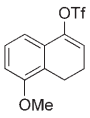
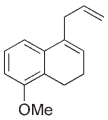
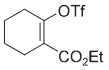
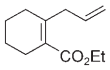
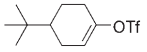
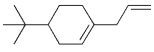
Entry	Starting material		Allyl acetate		Product		Isolated yield [%][a]
1		**6a** (X = Br)		**2**		**26**	35(41)
2		**6b** (X = I)	**2**				81
3	**6b**			**23**	 **27** **28**		57[b], 23[c], 7[d]
4	**6b**			**24**			46[e], 27[c], 18[d]
5	**6b**			**25**		**29**	74, 12[c], 3[d]
6		**7**	**25**			**30**	59[f], 10[c], 24,[d] 62, 14[c], 9[d]
7		**8**	**2**			**31**	66, 21[d]
8		**9**	**2**			**32**	75, 9[d]
9	**9**		**25**			**33**	61, 21[d]
10		**10**	**2**			**34**	64, 4[g], 21[h]
11		**11**	**2**			**35**	80[i], 12[d]
12	**11**		**23**		 **36** **37**		57[i,j], 17[d]
13	**11**		**25**			**38**	63[i], 19[d]
14		**12**	**2**			**39**	63[k], 12[c], 10[d] 80, 8[c]

Table 3. (Continued)

Entry	Starting material		Allyl acetate	Product		Isolated yield [%][a]
15		**12**	**25**		**40**	53[k], 29[d] 57, 22[d]
16		**13**	**2**		**41**	60[i], 20[d]
17		**14**	**2**		**42**	74[i,k,l]
18		**15**	**2**	 **43** **44**		66[m,o] (23)
19		**16**	**2**		**45**	74(19)[p]
20		**17** (1-TfO)	**2**		**26** (1-allyl)	33(50)
21		**18** (2-TfO)	**2**		**46** (2-allyl)	35(43)
22		**19**	**2**		**43**	61
23		**20**	**2**		**47**	91
24		**21**	**2**		**48**	81
25		**22**	**2**		**49**	84[o]

[a] Reactions performed in the presence of 10 mol% $[Pd(PPh_3)_4]$, 2.0 equivalents of In, 0.5 equivalents of $InCl_3$, 3.0 equivalents of LiCl, and 2.0 equivalents of nBuNMe$_2$ in DMF at 100°C over 2 h in substrates possessing electron-withdrawing groups and over 11 h in substrates possessing electron-donating groups, unless otherwise noted. Numbers in parentheses are recovered yields of starting material. [b] Ratio of **27** to **28** 3.7:1. [c] GC yields of reduction product of halide. [d] GC yields of homocoupling product. [e] Ratio of **27** to **28** 2.3:1. [f] Et_3N was used. [g] 2-(4-Allylpentyl)pent-4-en-2-ol. [h] 4,4′-Bis(2-hydroxypent-4-en-2-yl)-1,1′-biphenyl. [i] $[Pd(PPh_3)_4]$ (5 mol%) was used. [j] Ratio of **36** to **37** 2.9:1. [k] nBuNMe$_2$ was not used. [l] Reaction proceeded at 25°C. [m] Ratio of **43** to **44** 8.4:1. [o] Reaction time: 3 h. [p] Isolated yield of 5-phenylpent-1-ene.

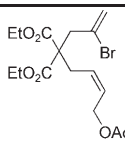
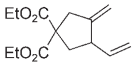
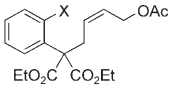
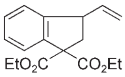
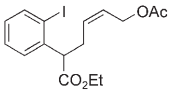
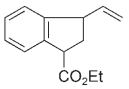
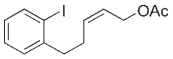
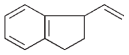
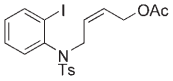
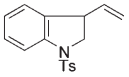
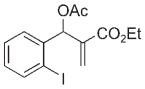
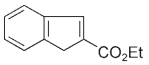
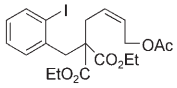
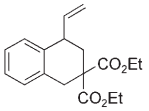
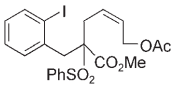
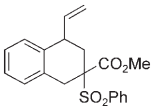
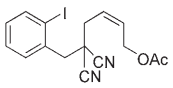
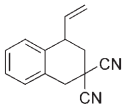
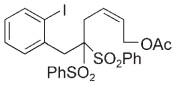
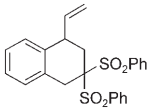
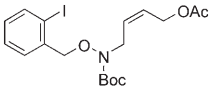
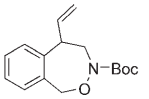
lylnaphthalene (**26**) in 81% yield under the optimized conditions (Table 3, entry 2), while exposure of 1-iodonaphthalene to the allylindium derived from **23** produced the desired products **27** and **28** in 57% yield, but with the product **27** resulting from α-attack predominating (α/γ 3.7:1) (Table 3, entry 3). Treatment of 1-iodonaphthalene with **24** gave the allyl cross-coupling product in 46% yield—the regioselectivity of this reaction being similar to that of **23**—to yield **27** as the major compound (Table 3, entry 4),[3] while treatment of 1-iodonaphthalene with **25** produced **29** in 74% yield (Table 3, entry 5). For electrophilic coupling partners such as aryl halides, aryl and vinyl triflate, and vinyl bromide, aryl iodides bearing *n*-butyl (Table 3, entry 6) and methoxy (Table 3, entries 7–9) substituents as electron-donating groups and acetyl (Table 3, entry 10), ethoxycarbonyl (Table 3, entries 11–15), trifluoromethyl (Table 3, entry 16), and nitro (Table 3, entry 17) substituents as electron-withdrawing groups smoothly reacted with allyl acetate under the optimum conditions to give the corresponding allylic aromatic compounds in moderate to good yields. These results suggest that the electron density on the aromatic ring does not seriously affect the efficiency of Pd-catalyzed cross-coupling reactions. Aryl iodides are more reactive than aryl bromides and give higher yields of the cross-coupling product (Table 3, entries 1 and 2). It should be noted that these conditions could be applied to aryl iodides containing carbonyl groups (Table 3, entries 10–15).

Treatment of α-bromostyrene with allyl acetate furnished a 59% yield of 2-phenylpenta-1,4-diene (**43**) and a 7% yield of *trans*-1-phenylpenta-1,4-diene (**44**) (Table 3, entry 18). Although the mechanism of the formation of **44** is not clear at present, we believe that the 1,4-diene **44** was produced through oxidative addition of Pd^0 to α-bromostyrene, dehydropalladation due to steric effects to produce phenylacetylene, and hydropalladation to form a β-styryl palladium complex, followed by the allyl cross-coupling reaction.[22] In the case of 2-bromo-5-phenylpent-1-ene (**16**), 4-methylene-7-phenylhept-1-ene (**45**) was produced in 74% yield, in a result that supports the mechanism of formation of **44** described above. The reactivities of naphthyl triflates derived from 1- or 2-naphthol are similar to that of 1-bromonaphthalene, producing 1- or 2-allylnaphthalene (**26** and **46**) in 33% and 35% yields, respectively, under the optimized conditions (Table 3, entries 20 and 21). However, treatment of vinyl triflates **19**–**22** with allylindium generated in situ from allyl acetate afforded the corresponding allylic compounds in good yields (Table 3, entries 22–25).

Intramolecular cross-coupling reactions: As the above results had provided encouragement, the intramolecular cross-

coupling reaction of **50** was selected for initial examination, as it was expected that cyclization of this substrate would be facilitated by the Thorpe–Ingold effect.[23] The results are summarized in Table 4. Treatment of **50** with Pd, In, and $InCl_3$ in the presence of *N*,*N*-dimethyl-*n*-butylamine and LiCl as an additive gave the desired compound **61** in 86% yield (Table 4, entry 1). Although allyl acetate **51a**, containing a bromophenyl group, gave the desired product **62** in only 22% yield (Table 4, entry 2), allyl acetate **51b**, with an iodophenyl group, was smoothly cyclized to produce **62** in 80% yield (Table 4, entry 3). These results suggest that the vinyl bromide group is a more reactive electrophilic coupling partner than the bromophenyl group in the cross-coupling reactions. Compound **52**, with one ethoxycarbonyl group on its backbone chain, was cyclized to produce **63** in 72% yield (Table 4, entry 4), while acetate **53** was also smoothly cyclized to give 1-vinylindane in 70% yield under the optimized conditions (Table 4, entry 5). These results imply that the presence of geminal Thorpe–Ingold buttressing is helpful but not a prerequisite for successful cyclization, as **53** partakes in the reaction. Accordingly, **54** had been converted into **65** in 56% yield together with *N*-phenyl-*p*-toluenesulfonamide in 13% yield after treatment at 100°C for 2 h (Table 4, entry 6). Treatment of allyl acetate **55**, derived from a secondary allyl alcohol, under the optimized conditions produced the desired product in 40% yield (Table 4, entry 7). Homologue **56** of **51** afforded the six-membered ring compound in 62% yield (Table 4,

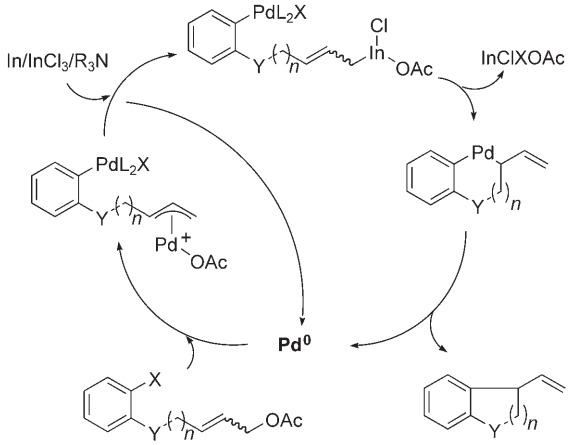
Table 4. Intramolecular Pd-catalyzed allyl cross-coupling reactions.

Entry	Starting material		Product		Isolated yield [%][a]
1		**50**		**61**	86
2		**51a** (X = Br)		**62**	22
3		**51b** (X = I)		**62**	80
4[b]		**52**		**63**	72 (1:1.2)[c]
5[b]		**53**		**64**	70 (10)[d]
6[b]		**54**		**65**	56 (13)[e]
7		**55**		**66**	40
8		**56**		**67**	62
9[b]		**57**		**68**	74 (16:1)[c]
10		**58**		**69**	64
11[b]		**59**		**70**	72
12		**60**		**71**	40

[a] Reactions performed in the presence of 10 mol% $[Pd(PPh_3)_4]$, 2.0 equivalents of In, 0.5 equivalents of $InCl_3$, 3.0 equivalents of LiCl, and 2.0 equivalents of $nBuNMe_2$ in DMF (0.25 M) at 100°C for 2 h, unless otherwise noted. [b] Reactions performed in the presence of 5 mol% $[Pd(PPh_3)_4]$, 1.0 equivalents of In, 0.25 equivalents of $InCl_3$, 3.0 equivalents of LiCl, and 1.0 equivalents of $nBuNMe_2$. [c] Diasteromeric ratio. [d] $[Pd_2(dba)_3CHCl_3]$ (5 mol%) and PPh_3 (40 mol%) were used. Mixture of 5-phenylpent-2-ene and 5-phenylpent-1-ene. [e] *N*-Phenyl-*p*-toluenesulfonamide.

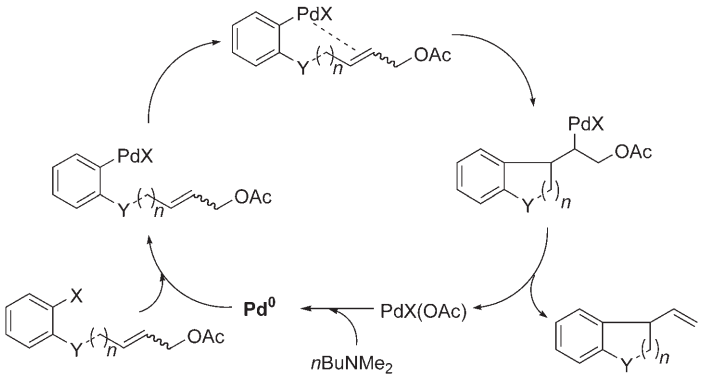
entry 8), while other homologues (**57**, **58**, and **59**) possessing phenylsulfonyl, methoxycarbonyl, and nitrile groups as electron-withdrawing groups also turned to out to be compatible with these reaction conditions, producing the desired compounds in good yields (Table 4, entries 9–11). We next applied these conditions to **60**, and the seven-membered ring compound **71** was then obtained in 40% yield (Table 4, entry 12).

Mechanism: Although the mechanism of this reaction has not yet been established, one possible reaction mechanism for a Pd/In-mediated allyl cross-coupling reaction of an aryl halide and vinyl triflate with allyl acetate is shown in Scheme 2. The π-allylpalladium(II) complex, initially



Scheme 2. Plausible mechanism for a Pd-catalyzed allyl cross-coupling reaction involving a π-allylpalladium(II) complex.

formed from allyl acetate in the presence of Pd^0 catalyst, undergoes reductive transmetallation by In and $InCl_3$ to give the allylindium(III) species,[24] which subsequently undergoes cross-coupling with aryl halide and vinyl triflate in the presence of Pd^0 catalyst to yield allyl arenes.[15c,j,n] Recently, Lautens reported Pd-catalyzed intramolecular coupling reactions between aryl iodides and allyl moieties[12i] and intermolecular Heck-type coupling reactions between aryl iodides and allylic acetates.[12j] Therefore, initial oxidation insertion of palladium into the aryl halide and vinyl triflate bond, followed by carbopalladation of olefin and elimination of the β-acetoxy group, could be postulated as another possible mechanism of this reaction (Scheme 3). However, the formation of isomeric mixtures from isomeric starting materials (Table 3, entries 3 and 4) suggests that the latter mechanism is not a dominant process.[12i] Also, the fact that these reactions do not take place in the absence of indium and indium trichloride supports the former mechanism. We expect that the tertiary amine, *N*,*N*-dimethyl-*n*-butylamine, generates Pd^0 from Pd^{II}.[20] This reaction is a good example in which the Pd^0 catalyst is simultaneously involved to two catalytic cycles in a one-pot reaction.



Scheme 3. Plausible mechanism for a Heck-type Pd-catalyzed allyl cross-coupling reaction.

Conclusion

In conclusion, inter- and intramolecular palladium-catalyzed allyl cross-coupling reactions based on the use of allylindium generated in situ from allyl acetates with indium and indium trichloride have been successfully demonstrated. Allylindium species generated in situ by reductive transmetalation of π-allylpalladium(II) complexes, obtained from a variety of allyl acetates in the presence of Pd^0 catalyst together with In and $InCl_3$, proved to be capable of acting as effective nucleophilic coupling partners in Pd-catalyzed cross-coupling reactions. A variety of materials—allyl acetate, but-1-en-3-yl acetate, crotyl acetate, and 2-methylallyl acetate—afforded the corresponding allylic compounds in good yields through cross-coupling reactions. Various electrophilic cross-coupling partners such as aryl iodides and vinyl bromides and triflates were found to participate in these reactions. These conditions work equally well not only intermolecularly, but also in intramolecular Pd-catalyzed cross-coupling reactions. This method thus represents an efficient synthetic route to a variety of both terminal and internal olefins, which can be easily be further functionalized. The method also complements existing synthetic methods as a result of advantageous features such as the easy availability of allyl acetates from allyl alcohols, easy preparation and handling, high reactivity and selectivity, operational simplicity, and the low toxicities of allylindium reagents. These results should immediately provide more opportunities for the elucidation of efficient new catalytic C–C bond forming reactions.

Experimental Section

General: Reactions were carried out under nitrogen in oven-dried glassware. All commercial reagents were used without purification, and all solvents were reaction grade. DMF was freshly distilled from CaH_2 and dried with molecular sieves (4 Å). All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography on Merck silica gel 60 F_{254} precoated glass plates, which were visualized under UV light and then developed by use either of iodine or of a solution of anisaldehyde. Flash column chromatography was carried out with Merck silica gel 60 (0.040–0.063 mm, 230–400 mesh). ^{1}H NMR and

^{13}C NMR spectra were recorded on a Brucker DPX FT (400 MHz) spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent ($\delta = 7.24$ ppm for ^{1}H and $\delta = 77.0$ ppm for ^{13}C). Infrared spectra were recorded with a JASCO FT/IR-460 plus FT-IR spectrometer, either as a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High-resolution mass spectra were recorded on an Autospec M363 series (Micromass).

Typical experimental procedure for the intermolecular cross-coupling reaction: *N,N*-Dimethylbutylamine (101.2 mg, 2.0 mmol) and allyl acetate (250.3 mg, 2.5 mmol) were added under nitrogen at 35 °C to a suspension of indium (114.8 mg, 1.0 mmol), indium(III) chloride (55.29 mg, 0.25 mmol), lithium chloride (63.5 mg, 1.5 mmol), and [Pd(PPh$_3$)$_4$] (10 mol %, 57.3 mg,) in DMF (1 mL). After 30 min, 1-iodonaphthalene (127.0 mg, 0.5 mmol) in DMF (1 mL) was added and the mixture was stirred at 100 °C for 9 h and then quenched with $Na_2S_2O_3$ (saturated aqueous). The aqueous layer was extracted with ether (3×20 mL) and the combined organics were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with *n*-hexane to give 1-allylnaphthalene (**26**, 68.5 mg, 81 %). $R_f = 0.4$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.01$ (d, $J = 8.08$ Hz, 1H), 7.83 (t, $J = 7.76$ Hz, 1H), 7.72 (d, $J = 6.89$ Hz, 1H), 7.50–7.42 (m, 2H), 7.39 (d, $J = 7.25$ Hz, 1H), 7.32 (d, $J = 6.89$ Hz, 1H), 6.16–6.65 (m, 1H), 5.11–5.06 (m, 2H), 3.82 ppm (d, $J = 6.30$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 135.13, 133.27, 132.01, 130.15, 126.84, 125.13, 124.44, 123.96, 123.77, 123.68, 122.19, 114.33, 35.43 ppm; IR (film): $\tilde{\nu} = 3003$, 2916, 1684, 1606, 1414, 1358 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{13}H_{12}$: 168.0939; found: 168.0934.

Typical experimental procedure for the intramolecular cross-coupling reaction: *N,N*-Dimethylbutylamine (101.2 mg, 2.0 mmol) and diethyl 2-iodophenyl *cis*-but-2-en-4-ethoxycarbonyl-1-yl malonate (237.1 mg, 0.5 mmol) in DMF (1 mL) were added to a suspension of indium (114.8 mg, 1.0 mmol), indium(III) chloride (55.29 mg, 0.25 mmol), lithium chloride (63.5 mg, 1.5 mmol), and [Pd(PPh$_3$)$_4$] (10 mol %, 57.3 mg) in DMF (1 mL). After the reaction mixture had been stirred at 100 °C for 1 h, it was quenched with $Na_2S_2O_3$ (saturated aqueous). The aqueous layer was extracted with ether (3×20 mL) and the combined organics were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with *n*-hexane to give 3-vinylindan-1,1-dicarboxylic acid diethyl ester (**62**, 155.3 mg, 80 %). $R_f = 0.3$ (hexane/EtOAc 10:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.58$ (d, $J = 6.96$ Hz, 1H), 7.32–7.26 (m, 3H), 7.16 (d, $J = 7.07$ Hz, 1H), 5.80 (ddd, $J = 17.46$, 9.59, 8.45 Hz, 1H), 5.23 (d, $J = 17.08$ Hz, 1H), 5.17 (d, $J = 10.02$ Hz, 1H), 4.26 (q, $J = 7.08$ Hz, 2H), 4.22–4.13 (m, 2H), 3.93 (q, $J = 8.30$ Hz, 1H), 3.04 (dd, $J = 13.29$, 5.63 Hz, 1H), 2.39 (dd, $J = 13.31$, 4.55 Hz, 1H), 1.30 (t, $J =$ 7.10, 3H), 1.24 ppm (t, $J = 7.17$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 170.62$, 170.32, 145.96, 139.83, 138.97, 128.71, 127.17, 126.59, 124.49, 116.35, 64.73, 61.72, 61.68, 47.08, 14.09, 13.98 ppm; IR (film): $\tilde{\nu} =$ 2982, 2929, 2900, 2878, 1732, 1475, 1367, 1250, 1186, 1098 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{17}H_{20}O_4$: 288.1362; found: 288.1361.

1-Allyl-4-butylbenzene (3): $R_f = 0.6$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.10$ (s, 4H), 5.96 (ddt, $J = 6.68$, 10.52, 16.94 Hz, 1H), 5.10–5.03 (m, 2H), 3.36 (d, $J = 6.69$ Hz, 2H), 2.58 (t, $J = 7.75$ Hz, 2H), 1.62–1.54 (m, 2H), 1.38–1.32 (m, 2H), 0.92 ppm (t, $J = 7.36$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 141.02$, 138.11, 137.57, 128.84, 128.79, 115.93, 40.25, 35.63, 34.13, 22.77, 14.36 ppm; IR (film): $\tilde{\nu} =$ 2957, 2929, 2858, 1638, 1514, 1466, 1433, 1419 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{13}H_8$: 174.1409; found: 174.1408.

1-(1-Methylprop-2-enyl)naphthalene (27): $R_f = 0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.11$ (d, $J = 8.27$ Hz, 1H), 7.83 (d, $J =$ 7.80 Hz, 1H), 7.70 (d, $J = 8.00$ Hz, 1H), 7.30–7.50 (m, 4H), 6.15 (ddd, $J =$ 5.57, 10.70, 15.64 Hz, 1H), 5.11 (m, $J = 16.08$ Hz, 1H), 5.10 (m, $J =$ 11.22 Hz, 1H), 4.28 (q, $J = 6.63$ Hz, 1H), 1.50 ppm (d, $J = 6.31$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 143.35$, 141.91, 134.46, 131.92, 129.38, 127.28, 126.21, 126.09, 125.83, 124.15, 123.98, 114.15, 38.34, 20.69 ppm; IR (film): $\tilde{\nu} = 3053$, 2986, 2395, 1421, 1270 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{14}$: 182.1096; found: 182.1097.

1-(*trans*-But-2-enyl)naphthalene (28): $R_f = 0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.02$ (t, $J = 7.42$ Hz, 2H), 7.83 (d, $J =$ 7.80 Hz, 2H), 7.78–7.74 (m, 1H), 7.30–7.50 (m, 9H), 5.49–5.70 (m, 4H), 3.82 (d, $J = 5.78$ Hz, 2H), 3.75 (d, $J = 6.29$ Hz, 2H), 1.79 (d, $J = 5.61$ Hz, 3H), 1.66 ppm (m, $J = 6.31$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 129.31$, 129.19, 127.23, 127.19, 126.24, 126.16, 125.98, 125.51, 124.39, 36.59, 31.14, 18.45, 13.50 ppm; IR (film): $\tilde{\nu} = 3053$, 2986, 2395, 1421, 1270 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{14}$: 182.1096; found: 182.1092 (*cis* isomer), 182.1096 (*trans* isomer).

1-(2-Methylallyl)naphthalene (29): $R_f = 0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.03$–8.00 (m, 1H), 7.86–7.34 (m, 1H), 7.74 (d, $J = 8.15$ Hz, 1H), 7.50–7.40 (m, 3H), 7.43 (d, $J = 6.94$ Hz, 1H), 4.86 (s, 1H), 4.62 (s, 1H), 3.78 (s, 3H), 1.78 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 145.04$, 136.145, 134.24, 132.83, 129.01, 127.58, 127.39, 126.10, 125.89, 125.86, 124.73, 112.66, 41.93, 23.21 ppm; IR (film): $\tilde{\nu} =$ 3067, 3045, 2970, 2934, 2907, 1651, 1597, 1509, 1444, 1396, 1374 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{14}$: 182.1096; found: 182.1096.

1-Butyl-4-(2-methylallyl)benzene (30): $R_f = 0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.09$ (s, 4H), 4.79 (s, 1H), 4.72 (s, 1H), 3.28 (s, 2H), 2.58 (t, $J = 7.76$ Hz, 2H), 1.67 (s, 3H), 1.62–1.54 (m, 2H), 1.38–1.32 (m, 2H), 0.92 ppm (t, $J = 7.36$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 145.82$, 141.01, 137.27, 129.13, 128.71, 112.06, 44.67, 35.67, 34.14, 22.81, 22.48, 14.39 ppm; IR (film): $\tilde{\nu} = 2957$, 2929, 2858, 1650, 1512, 1442, 1375 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{20}$: 188.1565; found: 188.1565.

1-Allyl-4-methoxybenzene (31): $R_f = 0.3$ (hexane/EtOAc 50:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.06$ (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J =$ 8.6 Hz, 2H), 6.01–5.81 (m, 1H), 5.06–4.97 (m, 2H), 3.70 (s, 3H), 3.28 ppm (d $J = 6.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 157.9, 137.8, 131.9, 129.3, 115.2, 113.7, 55.0, 39.2 ppm; IR (film): $\tilde{\nu} = 3030$, 1620, 1500 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{10}H_{12}O$: 148.0888; found: 148.0888.

1-Allyl-3-methoxybenzene (32): $R_f = 0.3$ (hexane/EtOAc 50:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.23$–7.19 (m, 1H), 6.80–6.76 (m, 3H), 6.74 (s, 1H), 5.96 (ddt, $J = 6.68$, 10.52, 16.94 Hz, 1H), 5.12–5.06 (m, 2H), 3.80 (s, 3H), 3.37 ppm (d, $J = 6.73$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 160.11$, 142.11, 137.64, 129.77, 121.37, 116.32, 114.66, 111.84, 55.56, 40.67 ppm; IR (film): $\tilde{\nu} = 2938$, 2912, 2835, 1601, 1584, 1489, 1259 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{10}H_{12}O$: 148.0888; found: 148.0888.

1-Methoxy-3-(2-methylallyl)benzene (33): $R_f = 0.3$ (hexane/EtOAc 50:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.23$–7.19 (m, 1H), 6.80–6.74 (m, 3H), 4.81 (s, 1H), 4.75 (s, 1H), 3.80 (s, 3H), 3.30 (s, 2H), 1.68 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 160.02$, 145.33, 141.79, 129.60, 121.78, 114.97, 112.44, 111.79, 56.50, 55.54, 45.09, 22.44 ppm; IR (film): $\tilde{\nu} = 2938$, 2913, 2834, 1601, 1584, 1488, 1258 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{11}H_{14}O$: 162.1045; found: 162.1045.

4-Allylacetophenone (34): $R_f = 0.3$ (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.89$ (d, $J = 8.20$ Hz, 2H), 7.28 (d, $J =$ 8.15 Hz, 2H), 5.99–5.90 (m, 1H), 5.12–5.08 (m, 2H), 3.44 (d, $J = 6.65$ Hz, 2H), 2.58 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 145.78$, 136.30, 135.29, 128.80, 128.59, 116.66, 40.12, 26.58 ppm; IR (film): $\tilde{\nu} =$ 3046, 3005, 2910, 1638, 1597 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{11}H_{12}O$: 160.0888; found: 160.0888.

Ethyl 4-allylbenzoate (35): $R_f = 0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.97$ (d, $J = 8.25$ Hz, 2H), 7.25 (d, $J =$ 7.87 Hz, 2H), 5.95 (ddt, $J = 6.68$, 10.52, 16.94 Hz, 1H), 5.09 (d, $J =$ 16.97 Hz, 1H), 5.07 (d, $J = 10.34$ Hz, 1H), 4.36 (q, $J = 7.02$ Hz, 2H), 3.43 (d, $J = 6.74$ Hz, 2H), 1.38 ppm (t, $J = 7.21$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 166.61$, 145.35, 137.66, 136.46, 129.73, 128.57, 116.53, 60.81, 40.15, 14.35 ppm; IR (film): $\tilde{\nu} = 3054$, 2986, 1713, 1421, 1269 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0991.

Ethyl 4-(1-methylprop-2-enyl)benzoate (36): $R_f = 0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.21$–8.02 (m, 4H), 5.90–6.02 (m, 1H), 5.01–5.11 (m, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.43–3.58

(m, 1H), 1.38 ppm (t, $J=7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=166.5$, 150.8, 142.3, 129.7, 129.0, 127.2, 113.8, 60.7, 43.1, 20.5, 14.3 ppm; IR (film): $\tilde{\nu}=2978$, 1726, 1610, 1587, 1415, 1392, 1367, 916, 584 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1146.

Ethyl 4-(but-2-enyl)benzoate (37): (*cis* and *trans* mixture): $R_f=0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=1.38$ (t, $J=7.1$ Hz, 3H), 1.69 (d, $J=4.75$ Hz, 3H; *trans*), 1.69 (d, $J=1.07$ Hz, 3H; *cis*), 3.35 (d, $J=4.61$ Hz, 2H; *trans*), 3.45 (d, $J=6.2$ Hz, 2H; *cis*), 4.36 (q, $J=7.13$ Hz, 2H), 5.53–5.58 (m, 2H), 7.21–7.98 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=166.6$, 146.5, 146.4, 129.7, 129.6, 129.0, 128.4, 128.2, 128.2, 128.0, 127.1, 125.6, 77.64, 77.01, 76.37, 60.70, 39.0 (*trans*), 33.12 (*cis*), 17.8 (*trans*), 14.3, 12.8 ppm (*cis*); IR (film): $\tilde{\nu}=$ 3023, 2856, 1716, 1610, 761, 701 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{16}O_2$ (264.12): C 76.4, H 7.9; found: C 76.3, H 7.8.

Ethyl 4-(2-methylprop-2-enyl)benzoate (38): $R_f=0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=1.39$ (t, $J=7.2$ Hz, 3H), 1.67 (s, 3H), 3.37 (s, 2H), 4.37 (q, $J=7.2$ Hz, 2H), 4.74 (s, 1H), 4.84 (s, 1H), 7.26 (d, $J=8.2$ Hz, 2H), 7.97 ppm (d, $J=8.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=14.3$, 22.0, 44.6, 60.8, 112.6, 128.4, 128.9, 129.6, 144.2, 145.1, 166.6 ppm; IR (film): $\tilde{\nu}=1711$, 1652, 706 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{16}O_2$ (204.12): C 76.4, H 7.9; found: C 76.2, H 7.9.

Ethyl 3-allylbenzoate (39): $R_f=0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.88$ (m, 2H), 7.36 (m, 2H), 5.97 (ddt, $J=6.61$, 9.22, 15.96 Hz, 1H), 5.09 (d, $J=15.62$ Hz, 1H), 5.10 (d, $J=$ 10.04 Hz, 1H), 4.37 (q, $J=7.10$ Hz, 2H), 3.44 (d, $J=6.64$ Hz, 2H), 1.39 ppm (t, $J=7.20$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=$ 167.12, 140.71, 137.22, 133.53, 131.03, 130.08, 127.85, 127.78, 116.76, 61.34, 40.34, 14.75 ppm; IR (film): $\tilde{\nu}=3054$, 2986, 1714, 1422, 1266 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{12}H_{14}O_2$: 190.0994; found: 190.0994.

Ethyl 3-(2-methylprop-2-enyl)benzoate (40): $R_f=0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.90$–7.87 (m, 2H), 7.38–7.34 (m, 2H), 4.84 (s, 1H), 4.73 (s, 1H), 4.38 (q, $J=7.10$ Hz, 2H), 3.37 (s, 2H), 1.68 (s, 3H), 1.68 (s, 3H), 1.40 ppm (t, $J=7.12$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=166.79$, 144.54, 140.05, 133.41, 130.53, 130.03, 128.29, 127.41, 112.44, 60.93, 44.36, 22.06, 14.35 ppm; IR (film): $\tilde{\nu}=2980$, 2937, 1719, 1281, 1191 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1158.

1-Allyl-4-trifluoromethylbenzene (41): $R_f=0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.69$ (d, $J=8.1$ Hz, 2H), 7.44 (d, $J=$ 8.1 Hz, 2H), 6.20–6.00 (m, 1H), 5.30–5.20 (m, 2H), 3.58 ppm (d, $J=$ 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=143.9$, 136.0, 128.9, 128.6, 124.1, 116.3, 39.6 ppm; IR (film): $\tilde{\nu}=3050$, 2960, 1650 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{10}H_9F_3$: 186.0656; found: 186.0656.

4-Allylnitrobenzene (42): $R_f=0.3$ (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=8.16$ (d, $J=8.72$ Hz, 2H), 7.35 (d, $J=$ 8.51 Hz, 2H), 5.95 (ddt, $J=6.68$, 10.52, 16.94 Hz, 1H), 5.18–5.10 (m, 2H), 3.49 ppm (d, $J=6.65$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=$ 147.79, 146.54, 135.46, 129.38, 123.68, 117.41, 39.89 ppm; IR (film): $\tilde{\nu}=$ 3080, 2919, 1604, 1519, 1494, 1347 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_9H_9NO_2$: 163.0633; found: 163.0636.

2-Phenylpenta-1,4-diene (43): $R_f=0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.44$ (d, $J=7.15$ Hz, 2H), 7.36–7.42 (m, 3H), 5.94–5.86 (m, 1H), 5.39 (s, 1H), 5.12 (d, $J=13.69$ Hz, 1H), 5.10 (s, 1H), 5.07 (d, $J=8.60$ Hz, 1H), 3.25 ppm (d, $J=6.49$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=146.33$, 140.94, 136.20, 128.25, 127.44, 125.99, 116.46, 113.15, 39.51 ppm; IR (film): $\tilde{\nu}=3053$, 2986, 2305, 1422, 1265 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{11}H_{12}$: 144.0939; found: 144.0935.

***trans*-1-Phenylpenta-1,4-diene (44)**: $R_f=0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.36$–7.19 (m, 5H), 6.41 (d, $J=$ 15.90 Hz, 1H), 6.23 (dt, $J=15.77$, 6.66 Hz, 1H), 5.96–5.86 (m, 1H), 5.11 (d, $J=17.13$ Hz, 1H), 5.07 (d, $J=10.12$ Hz, 1H), 2.96 ppm (t, $J=7.04$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=137.62$, 136.47, 130.85, 128.49, 128.18, 127.02, 126.04, 115.67, 37.00 ppm; IR (film): $\tilde{\nu}=3053$, 2986, 2395, 1421, 1270 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{11}H_{12}$: 144.0939; found: 144.0935.

(4-Methylenehept-6-enyl)benzene (45): $R_f=0.6$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.30$–7.26 (m, 2H), 7.19–7.16 (m, 3H), 5.81 (ddt, $J=16.95$, 10.12, 6.95 Hz, 1H), 5.07–5.02 (m, 2H), 4.78 (s, 2H), 2.76 (d, $J=6.88$ Hz, 2H), 2.61 (t, $J=7.69$ Hz, 2H), 2.07 (t, $J=$ 7.53 Hz, 2H), 1.77 ppm (quin, $J=7.68$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=147.89$, 142.49, 136.44, 128.43, 128.28, 125.69, 116.09, 110.16, 40.76, 35.54, 29.35 ppm; IR (film): $\tilde{\nu}=3049$, 2976, 2310, 1431, 1257 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{18}$: 186.1409; found: 186.1408.

2-Allylnaphthalene (46): $R_f=0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.86$–7.77 (m, 3H), 7.63 (s, 1H), 7.49–7.40 (m, 3H), 7.33 (dd, $J=8.46$, 1.42 Hz, 1H), 6.05 (ddt, $J=16.98$, 10.09, 6.77 Hz, 1H), 5.16–5.11 (m, 2H), 3.55 ppm (d, $J=6.66$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=137.55$, 137.32, 133.65, 132.12, 128.04, 127.62, 127.48, 127.39, 126.66, 125.93, 125.27, 40.36 ppm; IR (film): $\tilde{\nu}=3003$, 2916, 1684, 1606, 1414, 1358 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{13}H_{12}$: 168.0939; found 168.0934.

4-Allyl-8-methoxy-1,2-dihydronaphthalene (47): $R_f=0.5$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.15$ (d, $J=7.86$ Hz, 1H), 6.92 (d, $J=7.86$ Hz, 1H), 6.79 (d, $J=8.20$ Hz, 1H), 5.95 (ddt, $J=$ 16.70, 10.17, 6.35 Hz, 1H), 5.90–5.88 (m, 1H), 5.11 (dd, $J=17.16$, 1.58 Hz, 1H), 5.06 (dd, $J=10.07$, 1.58 Hz, 1H), 3.83 (s, 3H), 3.18 (dd, $J=6.36$, 1.28 Hz, 2H), 2.76 (t, $J=8.07$ Hz, 2H), 2.27–2.21 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=156.02$, 136.79, 135.91, 134.47, 126.17, 124.40, 115.96, 115.89, 109.46, 55.48, 37.37, 22.53, 19.89 ppm; IR (film): $\tilde{\nu}=3054$, 2986, 1573, 1422, 1263 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{16}O$: 200.1201; found 200.1202.

Ethyl 2-allylcyclohexene-1-carboxylate (48): $R_f=0.3$ (hexane/EtOAc 30:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=5.83$ (ddt, $J=16.95$, 10.11, 6.67 Hz, 1H), 5.07–4.99 (m, 2H), 4.19 (q, $J=7.11$ Hz, 2H), 3.10 (d, $J=6.63$ Hz, 2H), 2.33–2.25 (m, 2H), 2.26–2.08 (m, 2H), 1.63–1.57 (m, 4H), 1.29 ppm (t, $J=7.11$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=168.98$, 146.02, 136.10, 125.52, 115.68, 60.02, 39.89, 30.74, 26.55, 22.27, 22.25, 14.30 ppm; IR (film): $\tilde{\nu}=2991$, 1721, 1642, 1453, 1245 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{12}H_{18}O_2$: 194.1307; found 194.1306.

1-Allyl-4-(*tert*-butyl)cyclohexene (49): $R_f=0.5$ (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=5.80$ (ddt, $J=16.1$, 9.96, 6.89 Hz, 1H), 5.43 (d, $J=3.61$ Hz, 1H), 5.02 (d, $J=15.33$ Hz, 1H), 4.99 (d, $J=8.31$ Hz, 1H), 2.68 (d, $J=6.66$ Hz, 2H), 2.05–1.74 (m, 5H), 1.26–1.12 (m, 2H), 0.86 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=136.99$, 136.14, 122.08, 115.41, 44.15, 42.01, 32.20, 29.83, 27.25, 26.87, 24.26 ppm; IR (film): $\tilde{\nu}=3054$, 2862, 2305, 1637, 1423, 1267 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{13}H_{22}$: 178.1721; found: 178.1717.

3-Methylene-4-vinylcyclopentane-1,1-dicarboxylic acid diethyl ester (61): $R_f=0.5$ (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=5.09$–5.05 (m, 2H), 4.98 (d, $J=2.20$ Hz, 1H), 4.82 (d, $J=2.20$ Hz, 1H), 4.20 (q, $J=7.18$ Hz, 2H), 4.19 (q, $J=7.18$ Hz, 2H), 3.20–3.14 (m, 1H), 3.07 (d, $J=17.5$ Hz, 1H), 2.94 (dq, $J=17.5$, 2.30 Hz 1H), 2.57 (dd, $J=$ 13.0, 7.65 Hz, 1H), 2.00 (dd, $J=13.0$, 10.9 Hz, 1H), 1.26 (t, $J=7.08$ Hz, 3H), 1.25 ppm (t, $J=7.08$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=171.76$, 171.57, 150.62, 139.17, 116.01, 107.96, 61.55, 61.53, 58.58, 47.72, 40.18, 14.04 ppm; IR (film): $\tilde{\nu}=2982$, 1732, 1658, 1640, 1465, 1446, 1266, 1189 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{20}O_4$: 252.1362; found: 252.1361.

3-Vinylindan-1-carboxylic acid ethyl ester (63): $R_f=0.3$ (hexane/EtOAc 10:1); Isomer A ; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.39$ (d, $J=7.10$ Hz, 1H), 7.26–7.21 (m, 2H), 5.85 (ddd, $J=8.84$, 8.90, 17.26 Hz, 1H), 5.24–5.09 (m, 2H), 4.28–4.20 (m, 2H), 4.07–4.00 (m, 2H), 2.58 (ddd, $J=7.76$, 7.76, 12.87, Hz, 1H), 2.23 (ddd, $J=9.46$, 9.46, 12.86 Hz, 1H), 1.32 ppm (t, $J=7.11$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=$ 173.47, 145.52, 140.66, 140.59, 127.54, 127.01, 125.00, 124.48, 115.77, 60.89, 49.12, 48.73, 36.07, 14.35 ppm; Isomer B; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.39$ (d, $J=7.10$ Hz, 1H), 7.26–7.21 (m, 2H), 5.85 (ddd, $J=8.84$, 8.90, 17.26 Hz, 1H), 5.24–5.09 (m, 2H), 4.15 (q, $J=7.17$ Hz, 2H), 4.07–4.00 (m, 1H), 3.74 (q, $J=8.50$ Hz, 1H), 2.71 (ddd, $J=12.94$, 7.89, 3.68 Hz, 1H), 2.10 (ddd, $J=8.18$, 8.18, 13.05 Hz, 1H), 1.26 ppm (t, $J=$ 7.10 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta=173.72$, 145.79, 140.66, 140.39, 127.76, 127.01, 124.76, 124.48, 115.44, 60.81, 49.12, 48.67,

36.03, 14.24 ppm; IR (film): $\tilde{\nu}$ = 2980, 2938, 1734, 1475, 1258 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1153.

1-Vinylindan (64): R_f = 0.5 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.23–7.15 (m, 4 Hz), 5.86 (ddd, *J* = 17.07, 9.99, 8.22 Hz, 1H), 5.18–5.07 (m, 2H), 3.75 (q, *J* = 8.06 Hz, 1H), 2.99–2.84 (m, 2H), 2.40–2.28 (m, 1H), 2.15–2.04 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 141.18, 138.62, 128.46, 128.28, 125.75, 125.69, 114.78, 114.70, 49.85, 33.09, 31.62 ppm; IR (film): $\tilde{\nu}$ = 3063, 2934, 1605, 1486 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{11}H_{12}$: 144.2130; found: 144.2135.

1-(*p*-Toluenesulfonyl)-3-vinyl-2,3-dihydro-1*H*-indole (65): R_f = 0.3 (hexane/EtOAc 10:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.66 (t, *J* = 8.71 Hz, 3H), 7.22 (d, *J* = 8.03 Hz, 3H), 7.01 (d, *J* = 4.24 Hz, 2H), 5.53 (q, *J* = 8.82 Hz, 1H), 5.08 (dt, *J* = 11.62, 9.89 Hz, 2H), 4.14 (t, *J* = 9.86 Hz, 1H), 3.73 (q, *J* = 8.46 Hz, 1H), 3.59 (dd, *J* = 10.68, 7.87 Hz, 1H), 2.37 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 144.11, 141.69, 137.36, 133.87, 133.79, 129.65, 128.32, 127.35, 125.07, 123.89, 117.14, 115.10, 55.57, 44.85, 21.54 ppm; IR (film): $\tilde{\nu}$ = 3065, 2924, 1638, 1599, 1476, 1459, 1355, 1234, 1168, 1102, 1091, 1048, 926, 814, 755 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{17}H_{17}NO_2S$: 299.0980; found: 299.0982.

1*H*-Indene-2-carboxylic acid ethyl ester (66): R_f = 0.3 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.73 (s, 1H), 7.53–7.50 (m, 2H), 7.35–7.32 (m, 2H), 4.30 (q, *J* = 7.13 Hz, 2H), 3.69 (s, 2H), 1.37 ppm (t, *J* = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 165.08, 144.80, 142.78, 140.96, 137.51, 127.49, 126.85, 124.27, 123.34, 60.42, 38.36, 14.39 ppm; IR (film): $\tilde{\nu}$ = 3055, 2981, 2936, 2902, 1699, 1566, 1468, 1343, 1247, 757 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{12}H_{12}O_2$: 188.0837; found: 188.0839.

4-Vinyl-3,4-dihydro-1*H*-naphthalene-2,2-dicarboxylic acid diethyl ester (67): R_f = 0.2 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.18–7.13 (m, 4H), 5.77 (ddd, *J* = 17.06, 9.78, 9.30 Hz, 1H), 5.18 (dd, *J* = 16.89, 9.86 Hz, 2H), 4.20 (qq, *J* = 7.14, 7.11 Hz, 4H), 3.56–3.49 (m, 1H), 3.42–3.38 (m, 1H), 3.16 (d, *J* = 16.30 Hz, 1H), 2.59 (ddd, *J* = 13.50, 6.06, 2.10 Hz, 1H), 2.01 (dd, *J* = 13.50, 11.20 Hz, 1H), 1.27 (t, *J* = 7.14 Hz, 3H), 1.17 ppm (t, *J* = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 172.10, 171.10, 141.61, 136.68, 133.87, 129.22, 128.80, 126.86, 126.87, 116.88, 62.01, 61.76, 53.88, 41.84, 35.42, 35.41, 14.44, 14.38 ppm; IR (film): $\tilde{\nu}$ = 2985, 2930, 2904, 2888, 1712, 1465, 1347, 1253, 1185, 1095 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{18}H_{22}O_4$: 302.1518; found: 302.1501.

2-Benzenesulfonyl-4-vinyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (68): R_f = 0.4 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86 (d, *J* = 8.20 Hz, 2H), 7.73 (t, *J* = 7.11 Hz, 1H), 7.60 (t, *J* = 7.66 Hz, 2H), 7.15–7.10 (m, 4H), 5.72 (dt, *J* = 26.24, 17.35 Hz, 1H), 5.22 (dd, *J* = 17.05, 11.98 Hz, 2H), 3.59 (s, 3H), 3.56–3.40 (m, 4H), 2.67 (ddd, *J* = 12.9, 6.05, 2.37 Hz, 1H), 2.09 ppm (t, *J* = 12.32 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 167.55, 140.56, 135.40, 135.25, 134.45, 134.35, 131.84, 130.25, 129.21, 128.94, 128.85, 128.63, 126.82, 126.75, 117.30,72.25, 53.21, 41.86, 32.23, 31.90, 30.95 ppm; IR (film): $\tilde{\nu}$ = 3070, 2980, 2937, 1732, 1475, 1366, 1249, 1185, 1098, 1036, 744 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{20}H_{20}O_4S$: 356.1082; found: 356.1084.

4-Vinyl-3,4-dihydro-1*H*-naphthalene-2,2-dicarbonitrile (69): R_f = 0.2 (hexane/EtOAc 10:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.28–7.23 (m, 4H), 7.13 (d, *J* = 7.31 Hz, 1H), 5.75 (ddd, *J* = 17.04, 9.23, 7.66 Hz, 1H), 5.37 (dd, *J* = 14.47, 10.01 Hz, 2H), 3.86–3.79 (m, 1H), 3.49 (dt, *J* = 23.79, 7.52 Hz, 3H), 2.68 (ddd, *J* = 11.47, 6.02, 1.96 Hz, 1H), 2.19 ppm (dd, *J* = 13.32, 11.52 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.20, 134.51, 129.02, 128.91, 128.17, 128.10, 127.52, 119.03, 115.93, 114.92, 40.85, 38.26, 37.59, 30.45 ppm; IR (film): $\tilde{\nu}$ = 3079, 3026, 2979, 2868, 2250, 1640, 1488, 1425, 926, 743 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{14}H_{12}N_2$: 208.1000; found: 208.1003.

3,3-Bis-benzenesulfonyl-1-vinyl-1,2,3,4-tetrahydronaphthalene (70): R_f = 0.2 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.07 (d, *J* = 8.15 Hz, 2H), 7.95 (d, *J* = 8.18 Hz, 2H), 7.73 (t, *J* = 7.35 Hz, 1H), 7.67–7.58 (m, 3H), 7.51 (t, *J* = 7.75 Hz, 2H), 7.13 (t, *J* = 7.27 Hz, 1H), 7.09 (t, *J* = 6.42 Hz, 1H), 6.94 (d, *J* = 7.28 Hz, 1H), 5.8 (dt, *J* = 23.67, 16.96 Hz, 1H), 5.28 (d, *J* = 10.12 Hz, 1H), 5.19 (d, *J* = 17.04 Hz, 1H), 3.51 (d, *J* = 7.57 Hz, 1H), 3.47–3.42 (m, 1H), 2.78 (dd, *J* = 15.20, 4.74 Hz, 1H), 2.27 ppm (dd, *J* = 15.17, 11.82 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 138.02, 137.95, 136.49, 136.15, 134.72, 134.57, 134.42, 131.52, 131.38, 131.29, 131.16, 128.82, 128.73, 128.45, 128.08, 126.91, 126.87, 126.77, 118.34, 87.33, 41.11, 32.59, 31.28 ppm; IR (film): $\tilde{\nu}$ = 3065, 2978, 1642, 1583, 1447, 1310, 1145, 1077, 731, 688 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{24}H_{22}O_4S_2$: 438.0960; found: 438.0963.

9-Vinyl-8,9-dihydro-5*H*-6-oxa-7-azabenzocycloheptene-7-carboxylic acid *tert*-butyl ester (71): R_f = 0.2 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.29–7.20 (m, 4H), 6.15 (ddd, *J* = 22.79, 10.41, 5.76 Hz, 1H), 5.17 (dt, *J* = 14.02, 5.20 Hz, 2H), 5.00 (d, *J* = 13.99 Hz, 1H), 4.86 (d, *J* = 17.26 Hz, 1H), 4.19 (dd, *J* = 13.56, 5.85 Hz, 1H), 3.82 (d, *J* = 5.53 Hz, 1H), 3.76 (dd, *J* = 13.57, 5.85 Hz, 1H), 1.48 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.20, 140.67, 138.03, 137.24, 130.15, 129.06, 128.54, 127.34, 117.35, 81.62, 79.59, 53.32, 49.52, 28.76 ppm; IR (film): $\tilde{\nu}$ = 3056, 1701, 1652, 1481, 1433, 1307, 1182, 1104 1025, 998 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{16}H_{21}NO_3$: 275.1521; found: 275.1523.

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