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Tetrahedron
Tetrahedron 62 (2006) 9872–9882

Cyanoesterification of norbornenes catalyzed by palladium: facile synthetic methodology to introduce cyano and ester functionalities via direct carbon–carbon bond cleavage of cyanoformates

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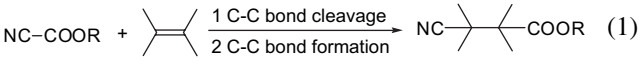
Received 26 July 2006; revised 7 August 2006; accepted 7 August 2006
Available online 1 September 2006

Abstract—Addition of cyanoformates (NC–COOR) to norbornene at 110 °C in the presence of $Pd(PPh_3)_4$ (10 mol %) as a catalyst affords with high selectivity the corresponding doubly functionalized polar norbornane derivatives bearing both cyano and ester groups. By using benzonorbornadiene and norbornadienes as the substrates, the reaction can be extended to synthesis of various functionalized norbornene derivatives in moderate to excellent yields. In most cases alkyl groups such as methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *tert*-butyl, and benzyl in the ester functionalities are applicable to the reactions. Oxidative addition of cyanoformates to Pd(0), insertion of norbornenes, and reductive elimination of the corresponding adducts constitute the proposed catalysis pathway.

1. Introduction

The transition metal-catalyzed direct carbon–carbon σ-bond cleavage and the subsequent simultaneous formation of two C–C bonds in regio-, stereo-, and chemoselective manners can supply products that have two newly constructed carbon–carbon bonds.[1] These can be fundamental skeletons in useful organic molecules.[2–4] Accordingly, addition reactions via carbon–carbon σ-bonds are highly advantageous and desirable from viewpoint of perfect atom economy provided they are attained efficiently. However, in most cases, the carbon–carbon σ-bond cleavage reaction is limited to the ring-opening, or elimination of small molecules, intramolecular rearrangement reactions, or metal complex formation of the intermediates.[5,6] Thus, the double functionalization of unsaturated organic molecules via C–C bond addition to unstrained molecules is quite rare.[7–9]

In view of the synthetic versatility of cyano and carbonyl functionalities, direct addition of C–C σ-bonds in cyanoformates (NC–COOR) is particularly useful. Several examples of synthetic methods for introduction of either cyano[10] or ester[11] groups into unsaturated organic molecules have been reported. But, to the best of our knowledge, there has been no precedent for cyanoesterification,[12] which, as depicted in Eq. 1, is a novel methodology for the simultaneous introduction of cyano and ester groups.



(1)

In view of the high reactivities of the nitrogen-containing cyano and oxygen-containing ester groups, neither of which can be readily introduced by conventional methods, the products are expected to allow a wide range of synthetic elaborations. We herein report the details of the efficient and highly stereoselective palladium-catalyzed addition of various cyanoformates across norbornene derivatives affording the corresponding doubly functionalized polar norbornenes bearing both cyano and ester groups.[13]

2. Results and discussion

2.1. Optimization of the reaction conditions in the palladium-catalyzed cyanoesterification using ethyl cyanoformate (1a) and norbornene (2)

We first screened catalyst systems effective for an equimolar reaction of ethyl cyanoformate (**1a**) with norbornene (**2**) and the results are summarized in Table 1. In a representative

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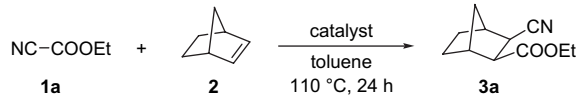
doi:10.1016/j.tet.2006.08.025

Table 1. Catalytic activity of palladium complexes in the addition reaction of ethyl cyanoformate (**1a**) across norbornene (**2**)[a]



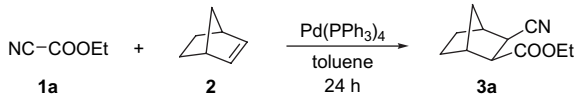
1a **2** **3a**

Entry	Catalyst	Yield % of **3a**[b]
1	$Pd(PPh_3)_4$	94 (80)
2	$Pd(dba)_2$/2 PPh_3[d]	82
3	$Pd(dba)_2$/2 $P(C_6H_4OMe\text{-}4)_3$	70
4	$Pd(dba)_2$/2 $P(C_6H_4F\text{-}4)_3$	58
5	$Pd(dba)_2$/2 $PMePh_2$	27
6	$Pd(dba)_2$/2 $P(t\text{-}Bu)_3$	11
7	$Pd(dba)_2$/2 PCy_3	0
8	$Pd(dba)_2$/2 $P(OPh)_3$	40
9	$Pd(dba)_2$/DPPE[e]	<1
10	$Pd(dba)_2$/DPPB[f]	0
11	$Pd(dba)_2$/DPPH[g]	6
12	$Pd(dba)_2$/DPPF[h]	13
13	$Pd(dba)_2$	0
14	$PdCl_2(NCPh)_2$	0
15[c]	$Pd(PPh_3)_4$	43

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), and a palladium catalyst (10 mol %) in toluene (2 mL).
[b] Determined by GC using dodecane as an internal standard. Isolated yield is shown in the parenthesis.
[c] Run in *n*-octane.
[d] dba=dibenzylideneacetone.
[e] DPPE=1,2-bis(diphenylphosphinoethane).
[f] DPPB=1,4-bis(diphenylphosphinobutane).
[g] DPPH=1,6-bis(diphenylphosphinohexane).
[h] DPPF=1,1′-bis(diphenylphosphinoferrocene).

catalytic reaction, a solution of a palladium catalyst (0.02 mmol, 10 mol %), **1a** (0.2 mmol), and **2** (0.2 mmol) in toluene (2 mL) was heated at 110 °C for 24 h. With $Pd(PPh_3)_4$, the addition reaction smoothly proceeded to afford the cyanoesterification adduct, (2*R**,3*S**)-ethyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (**3a**) in 94% GC yield (Table 1, entry 1). A similar but more practically useful catalyst was prepared in situ with the combination of $Pd(dba)_2$ (dba=dibenzylideneacetone) and various monodentate and bidentate phosphine ligands. However, various $Pd(dba)_2$–phosphine complexes ligated by one or two phosphines performed rather differently in the reaction of **1a** with **2**; the yield ranged from 0 to 82% (Table 1, entries 2–12). The reaction could take place in the presence of $Pd(dba)_2$–PPh_3 (P/Pd=2.0) and **3a** was obtained in 82% GC yield (Table 1, entry 2). We examined substituent effects on the aromatic ring in triarylphosphine, but the desired product **3a** was obtained in poorer yields (Table 1, entry 2 vs entries 3 and 4). More electron-rich monodentate phosphine ligands such as PMe_2Ph, $P(t\text{-}Bu)_3$, and PCy_3, which are suitable for the effective oxidative addition, gave unsatisfactory results (Table 1, entries 5–7). This propensity seems to indicate that electron-richness preferable for oxidative addition is not required for the present reaction. This hypothesis is supported by addition of $P(OPh)_3$ as a less electron-donating ligand, giving **3a**, albeit in 40% yield (Table 1, entry 8). Bidentate ligands such as DPPE, DPPB, DPPH, and DPPF were found to be inactive, suggesting that an appropriate coordination site for norbornenes is essential to proceed the reaction (Table 1, entries 9–12).[14] The high sensitivity of reaction performance to the nature of the phosphine ligands is presumably associated with the ease of insertion of **2**, which is envisaged to be the crucial step in the catalytic cycle (vide infra). $Pd(dba)_2$ alone and a palladium(II) complex showed no catalytic activity (Table 1, entries 13 and 14). Reaction catalyzed by $Pd(PPh_3)_4$ in octane at 110 °C produced the adduct in only 43% yield, indicating the importance of the solvent polarity, not the temperature (Table 1, entry 15). No addition reaction was observed in the absence of the palladium catalyst and other complexes such as $Ni(cod)_2$/2 PMe_3, which is known to be active catalyst for arylcyanation of alkynes,[8] $PdCl_2(PPh_3)_2$, $Pt(PPh_3)_4$, $RuCl_2(PPh_3)_2$, and $RhCl(PPh_3)_3$ did not show any catalytic activity under similar conditions.

Table 2. Addition of ethyl cyanoformate (**1a**) across norbornene (**2**)[a]



1a **2** **3a**

Entry	**1a**/mmol	**2**/mmol	$Pd(PPh_3)_4$/mmol	Temp/°C	Yield % of **3a**[b]
1	0.2	0.2	0.02	110	94
2	0.2	0.2	0.02	80	37
3	0.2	0.2	0.02	50	8
4	0.2	0.2	0.006	110	18
5	0.2	0.2	0.002	110	11
6	0.4	0.2	0.02	110	72
7	0.2	0.4	0.02	110	91[c]

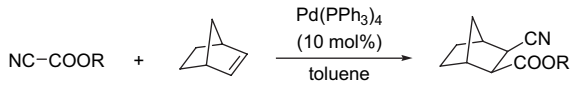
[a] The reactions were carried out at for 24 h in toluene (2 mL).
[b] Determined by GC using dodecane as an internal standard, based on **2**.
[c] Based on **1a**.

Using 10 mol % of $Pd(PPh_3)_4$ as a catalyst, other reaction conditions such as temperature, catalyst loading, and the ratio of reagents were varied. The results of the reactions conducted in toluene for 24 h are shown in Table 2. It appears reasonable that an elevated reaction temperature of 110 °C would enhance the addition reaction (Table 2, entry 1). Indeed, under otherwise the same conditions as in Table 1, entry 1, a significantly smaller amount (37%) of **3a** was formed (Table 2, entry 2) in reaction at 80 °C. However, no substantial change was observed in the yield of **3a** when the reaction temperature was raised over 110 °C. Since the catalyst loading of $Pd(PPh_3)_4$ is rather sensitive for the high-yield formation of **3a** (Table 2, entries 4 and 5), we adopted 10 mol % loading of $Pd(PPh_3)_4$ for the present reaction. Although we normally used an equimolar amount of **1a**, as for the reaction of Table 2, entry 1, the presence of excess **1a** appeared to suppress the desired reaction. For instance, when the quantity of **1a** was increased to 0.4 mmol (Table 2, entry 6), the total yield of **3a** decreased to 72%. An excess of **2** in the addition reaction was not necessary due to the occurrence of side reactions (Table 2, entry 7).

2.2. Reactions of various cyanoformates 1a–1g with norbornene (2) and benzonorbornadiene (4)

The generality of the cyanoesterification reaction was shown first by using various cyanoformates **1a**–**1g** and norbornene (**2**) in a 1:1 ratio under the optimum conditions, i.e., 10 mol % of $Pd(PPh_3)_4$ at 110 °C in toluene. The results are summarized in Table 3. Notable is the substantial effect of the ester substituents in the cyanoformates **1**, probably owing to the efficiency in oxidative addition of Pd(0) to the C–C

Table 3. Addition of cyanoformates **1a–1g** across norbornene (**2**)[a]



1 2 3

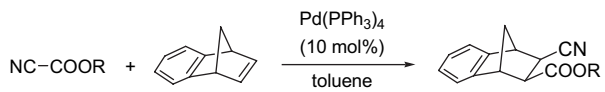
Entry	Cyanoformate **1**, R=	Time/h	Product	Yield %[b]
1	Et (**1a**)	6	**3a**	94 (80)
2	Me (**1b**)	6	**3b**	43[c] (28)
3	*n*-Pr (**1c**)	6	**3c**	72 (63)
4	*i*-Pr (**1d**)	12	**3d**	80 (63)
5	*n*-Bu (**1e**)	12	**3e**	67 (63)
6	*t*-Bu (**1f**)	24		0
7	Bn (**1g**)	3	**3g**	31 (14)

[a] The reactions were carried out at 110 °C, using **1** (1.0 equiv), **2** (1.0 equiv), and $Pd(PPh_3)_4$ (10 mol %) in toluene.
[b] Unless otherwise noted, determined by GC using dodecane as an internal standard. Isolated yields are shown in the parentheses.
[c] NMR yield using triphenylmethane as an internal standard.

bond of **1** and the subsequent insertion of norbornenes into the resulting intermediate. Most aliphatic cyanoformates, including Et, Me, ^{n}Pr, ^{i}Pr, and ^{n}Bu substituents react readily to afford the respective adducts in good to high yields (Table 3, entries 1–5). In contrast, a sterically demanding ^{t}Bu substituent interferes with the addition (Table 3, entry 6). These results strongly indicate that the low yield of adducts is associated with the steric bulk of cyanoformates. As expected, however, the reaction of less sterically hindered benzyl cyanoformate gave the desired adduct **3g**, albeit in 31% yield (Table 3, entry 7).

Accordingly, we employed 1,4-dihydro-1,4-methanonaphthalene (benzonorbornadiene) (**4**) as the coupling partner. Also, from the reactions of **4** with various alkyl cyanoformates **1a–1e**, the corresponding adducts **5a–5e** were produced in high to excellent yields (Table 4, entries 1–5). However, again with *tert*-butyl cyanoformate (**1f**), only a trace amount of the desired product **5f** was detected by GC (Table 4, entry 6). Compared to the reaction with norbornene (**2**) shown above, the isolated yield of **5g** from benzyl cyanoformate (**1g**) slightly increased to 22%, because benzonorbornadiene (**4**) seems to be more reactive for the present reaction.

Table 4. Addition of cyanoformates **1a–1g** across benzonorbornadiene (**4**)[a]



1 4 5

Entry	Cyanoformate **1**, R=	Time/h	Product	Yield %[b]
1	Et (**1a**)	3	**5a**	99 (83)
2	Me (**1b**)	3	**5b**	74 (65)
3	*n*-Pr (**1c**)	3	**5c**	83 (76)
4	*i*-Pr (**1d**)	3	**5d**	83 (68)
5	*n*-Bu (**1e**)	6	**5e**	87 (79)
6	*t*-Bu (**1f**)	3	**5f**	Trace
7	Bn (**1g**)	3	**5g**	(22)

[a] The reactions were carried out at 110 °C, using **1** (1.0 equiv), **4** (1.1 equiv), and $Pd(PPh_3)_4$ (10 mol %) in toluene.
[b] Determined by GC using dodecane as an internal standard. Isolated yields are shown in the parentheses.

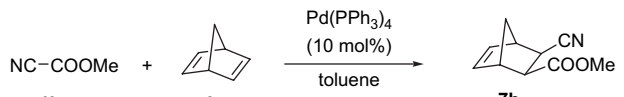
2.3. Reactions of various cyanoformates 1a–1g with norbornadiene (6)

Cyanoesterification of norbornadiene (**6**) would be synthetically valuable. The expected (2*R**,3*S**)-2-cyano-3-alkoxycarbonylbicyclo[2.2.1]hept-5-enes are potential precursors for polar functionalized cyclopentanes via further transformation and are interesting polar monomers for the transition metal-catalyzed ring-opening metathesis polymerization.[15] We carried out the reaction of **1b** with norbornadiene (**6**) in different ratios and the results are summarized in Table 5. An equimolar amount of **6** was used, an adduct **7b** was successfully isolated in 76% yield as a single product (Table 5, entry 1). Noteworthy is that the reaction of an excess of **1b** with **6** gave **7b** predominantly in 75% yield (Table 5, entry 3), suggesting that no double addition occurred. The structure of **7b** results from NMR spectroscopic data, in that the $^{13}C\{^1H\}$ NMR signals showed the presence of a C=C moiety along with a *C*N group at δ 120.2 and a *C*OOEt group at δ 171.8. We presume that once formed more sterically bulky **7b** is less reactive than the starting material **6** and retards the second cyanoesterification significantly. Overall, the ratio between **1b** and **6** little affected the yield of **7b**; thus, the reactions of various cyanoformates **1** with norbornadiene (**6**) were conducted in a 1:1 ratio.

Accordingly, reactions of a variety of cyanoformate **1a–1g** with norbornadiene (**6**) under the optimum conditions were exploited and the results are shown in Table 6. As was observed in the reactions of norbornene (**2**) and benzonorbornadiene (**4**), the reactions of alkyl cyanoformates **1a–1e** and **6** furnished the corresponding adducts **7a–7e** in good to high yields (Table 6, entries 1–5). A bulky cyanoformate **1f**, which is a poor coupling partner with norbornene and benzonorbornadiene, does produce the adduct **7f**, albeit in 13% yield (Table 6, entry 6). Thus, successful formation of cyanoesterification products requires starting materials to possess an appropriate steric factor to enhance the reaction. Phenyl cyanoformate (**1h**) furnished no desired product due to the competitive side reaction (vide infra).

Under the standard reaction conditions, 1-octene, styrene, methyl acrylate, cyclopentene, and cyclopenten-3-one did not react with the **1a**. Furthermore, ethylene (5 atm) was

Table 5. Addition of methyl cyanoformate (**1b**) across norbornadiene (**6**)[a]

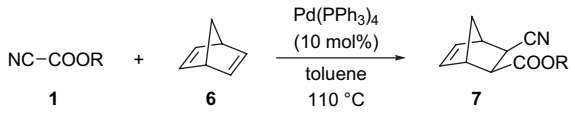


1b 6 7b

Entry	**1b**/mmol	**6**/mmol	Yield % of **7b**[b]
1	0.2	0.2	80 (76)
2	0.2	0.4	81 (76)
3	0.4	0.2	75[c]
4	0.2	0.3	81
5	0.2	0.24	72

[a] The reactions were carried out at 110 °C for 24 h in toluene (2 mL).
[b] Unless otherwise noted, GC yields were determined by using dodecane as an internal standard, based on **1b**. Isolated yields are shown in the parentheses.
[c] Based on **6**.

Table 6. Addition of cyanoformates **1a**–**1g** across norbornadiene (**6**)[a]



1 6 7

Entry	Cyanoformate **1**, R=	Time/h	Product	Yield %[b]
1	Et (**1a**)	3	**7a**	97 (78)
2	Me (**1b**)	3	**7b**	80 (76)
3	*n*-Pr (**1c**)	3	**7c**	89 (76)
4	*i*-Pr (**1d**)	3	**7d**	77 (62)
5	*n*-Bu (**1e**)	6	**7e**	86 (74)
6	*t*-Bu (**1f**)	6	**7f**	13 (12)
7	Bn (**1g**)	3	**7g**	84 (63)
8	Ph (**1h**)	24		0

[a] The reactions were carried out at 110 °C, using **1** (1.0 equiv), **6** (1.0 equiv), and $Pd(PPh_3)_4$ (10 mol %) in toluene.
[b] Determined by GC using dodecane as an internal standard. Isolated yields are shown in the parentheses.

also subjected to the reaction with **1a**, but no cyanoesterification occurred.[16]

2.4. Determination of stereochemistry of the adducts

The reaction of methyl cyanoformate (**1b**) with benzonorbornadiene (**4**) afforded the adduct **5b** as crystals of good quality. The 2-*exo*, 3-*exo* configuration[17] was unequivocally confirmed by X-ray crystallography (Fig. 1), which is consistent with the ^1H NMR spectra. The structure of norbornadiene adduct **7g** was also confirmed by X-ray crystallography (Fig. 2), showing the remained C=C bond in a molecule. These results suggest that cyanoformate **1** undergoes cis addition across norbornenes via coordination of a palladium center on a less hindered olefin face. From the viewpoint of electronic structure, the electron density of the *exo*-face of norbornenes is reportedly higher than that of the *endo*-face.[18]

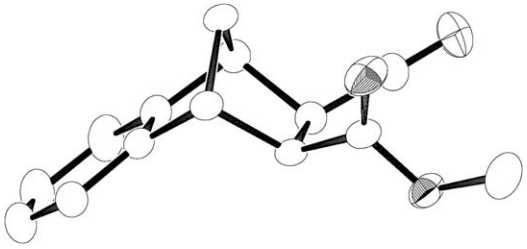


Figure 1. Molecular structure of **5b**.

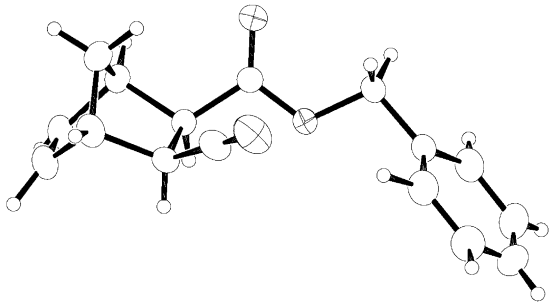
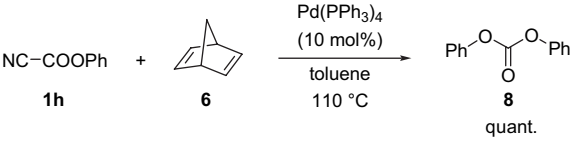


Figure 2. Molecular structure of **7g**.

It would also be responsible for the exclusive *exo*-selectivity. In all these reactions the *exo*-selectivity during the cyanoesterification reactions was found to be excellent, because no trace signal for the corresponding *endo*-isomer was detectable in the NMR measurements.

2.5. Reaction of norbornadiene (6) with phenyl cyanoformate (1h)

Phenyl cyanoformate (**1h**) reacts with equimolar amount of norbornadiene (**6**) in the presence of 10 mol % of $Pd(PPh_3)_4$ at 110 °C for 24 h leading to quantitative formation of diphenylcarbonate (**8**),[19] based on $Pd(PPh_3)_4$ (Eq. 2). Since the high-yield synthesis of *trans*-$Pd(CN)(CO_2Et)(PPh_3)_2$ (**9a**) and *trans*-$Pd(CN)(CO_2Me)(PPh_3)_2$ (**9b**) at room temperature has already suggested,[13] the C–C bond in phenyl cyanoformate (**1h**) is also postulated to react at room temperature with a palladium(0) complex to yield *trans*-$Pd(CN)(CO_2Ph)(PPh_3)_2$. As evidenced by the formation of diphenylcarbonate (**8**) in the catalytic reaction, *trans*-$Pd(CN)(CO_2Ph)(PPh_3)_2$ should be much more unstable than **9a** and **9b**. Decarbonylation from *trans*-$Pd(CN)(CO_2Ph)(PPh_3)_2$ generates the phenyloxopalladium complex, *trans*-$Pd(CN)(OPh)(PPh_3)_2$. This is followed by ligand exchange driven by nucleophilic attack of a phenyloxo group[20] between the unchanged *trans*-$Pd(CN)(CO_2Ph)(PPh_3)_2$ and the formed *trans*-$Pd(CN)(OPh)(PPh_3)_2$, which furnishes *trans*-$Pd(CN)_2(PPh_3)_2$[21] and *trans*-$Pd(OPh)(CO_2Ph)(PPh_3)_2$,[22] reductive elimination of which gives **8**. The thermal stabilities of complexes resulting from oxidative addition, relative to both decarbonylation and reductive elimination, are the key to make the present catalysis successful. The thermal stability of complex **9a** at 110 °C was examined in toluene and after heating for 12 h they afford *trans*-$Pd(CN)_2(PPh_3)_2$ in 43% yield, along with several unidentified compounds. Complex **9b** also behaved in much the same way as **9a** on thermolysis but appeared slightly more stable. Thus, we can safely conclude that the stability of complex **9** depends significantly on the electronic nature of the alkoxycarbonyl or aryloxycarbonyl ligands in that more electron-donating ones stabilize complex **9**. In the case of the phenoxycarbonyl group, the corresponding *trans*-$Pd(CN)(CO_2Ph)(PPh_3)_2$ derived from oxidative addition of phenyl cyanoformate (**1h**) appears to decompose rapidly at higher temperatures by decarbonylation as soon as it is generated even in the presence of norbornadiene (**6**).



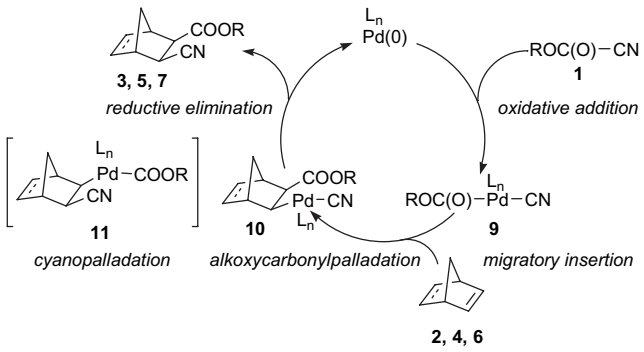
(2)

1h 6 8

quant.

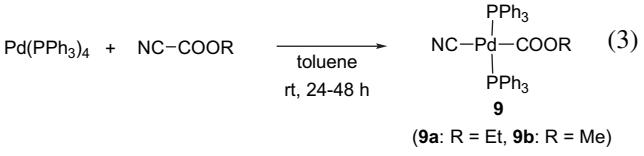
2.6. Reaction mechanism

The present catalysis is most likely to proceed via three fundamental processes: oxidative addition of the C–C bond of **1** to $Pd(PPh_3)_4$; insertion of a norbornene molecule into the resulting Pd–C bond; and subsequent C–C reductive elimination. Our proposed mechanism (Scheme 1) is substantiated by the observations described below. Initial attempts to



Scheme 1. A plausible catalytic cycle for the addition of cyanoformates across norbornene derivatives in the presence of a Pd(0) catalyst.

confirm this oxidative addition were made using $Pd(PPh_3)_4$ with **1a** at room temperature. Ethyl cyanoformate (**1a**) reacts readily with $Pd(PPh_3)_4$ even at room temperature; the reactivity of this oxidative addition is higher than with whole catalytic reaction conducted at 110 °C. For instance, when a pale yellow suspension of $Pd(PPh_3)_4$ in toluene was treated with 2.4 equiv of **1a**, the reaction mixture gradually became a white suspension in 48 h. The ^1H and $^{31}P\{^1H\}$ NMR spectroscopy suggested that *trans*-$Pd(CN)(CO_2Et)(PPh_3)_2$ (**9a**) was generated via oxidative addition of **1a** to $Pd(PPh_3)_4$ (Eq. 3). The Pd–P moiety in **9a** displayed a singlet in the $^{31}P\{^1H\}$ NMR spectrum, suggesting that the two phosphine ligands are in mutually trans positions. Both infrared (2126, 1638 cm^{-1}) and the $^{13}C\{^1H\}$ NMR (δ 137.2 and 192.6) spectra suggest the existence of cyano and alkoxycarbonyl groups. These and previous observations with related nickel complexes such as $Ni(CN)(CO_2Et)(triphos)$[23] led us to conclude that **9a** adopts the trans configuration. Careful recrystallization of the Me analogue **9b** from CH_2Cl_2–hexane furnished colorless crystals, allowing unequivocal confirmation of the structure by X-ray crystallography.[13] As expected from the NMR data, the coordination geometry at the palladium center is square planar with triphenylphosphine ligands in trans positions.



(3)

The cyanoesterification of **6** with **1a**, on the other hand, proceeded in the presence of complex **9a** (10 mol %) as the catalyst to give **7a** in 85% GC yield under the standard conditions. We thus conclude that the cyano(alkoxycarbonyl)palladium species **9** is involved in the catalytic cycle of the cyanoesterification process as shown in Scheme 1.

The most important fundamental process involved in this catalytic reaction is the insertion of the norbornene linkage. We presume, as in the cyanoesterification of norbornenes, that insertion into the Pd–COOR bond takes place by forming an intermediate such as **10** (alkoxycarbonylpalladation).[24] This eventually undergoes C–C reductive elimination to generate the adducts even though the experiments neither suggest the involvement of intermediate species such as **10** nor provide other details of the insertion process. An alternative possibility for the formation of **11** arises if a norbornene molecule is inserted into the Pd–CN bond of **9** (cyanopalladation). However, this possibility can be ruled out in view of the earlier reported observations that the Pd–CN bond cleavage from cyanopalladium(II) complexes normally requires very high temperatures.[25] Thus, in our catalytic reactions at 110 °C the insertion is envisaged to proceed through alkoxycarbonylpalladation. More detailed mechanistic aspects, such as the possible necessity of ligand dissociation before norbornene insertion, await further clarification.

3. Conclusion

In summary, we have developed an unprecedented palladium-catalyzed cyanoesterification of alkyl cyanoformates with norbornene, norbornadiene, and benzonorbornadiene, which proceeds in all cases with chemo- and stereoselectivity. This work offers another useful demonstration of the powerful transition metal catalysis to activate unstrained C–C σ-bonds with compatible functional groups. Investigations on the mechanism of insertion of norbornenes into cyano(alkoxycarbonyl)palladium(II) species **9** and further synthetic application in the construction of functionalized cyclopentanes bearing four stereo-defined carbon centers will be the subjects of forthcoming papers.

4. Experimental

4.1. General

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. The GC yields were determined using suitable hydrocarbon internal standards.

4.2. Measurements

^1H and ^{13}C NMR spectra were recorded on Varian INOVA 600 (600 MHz) or Mercury 300 (300 MHz) spectrometers at an ambient temperature with the chemical shifts being expressed in parts per million based on residual $CHCl_3$ as an internal standard. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. GC–MS analyses were carried out on a SHIMADZU GC-17A equipped with a SHIMADZU QP-5050 GC–MS system. Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. Elemental analyses were carried out with a Perkin–Elmer 2400 CHN elemental analyzer at Osaka City University.

4.3. Materials

Ethyl cyanoformate, methyl cyanoformate, and norbornadiene were purchased from Aldrich and used as received. $Pd(PPh_3)_4$,[26] cyanoformates (R=^{n}Pr,[27] ^{i}Pr,[27] ^{n}Bu,[27] ^{t}Bu,[28]

Bn,[27] and Ph[29]), and 1,4-dihydro-1,4-methanonapthalene (**4**)[30] were prepared according to the literature procedures. Dehydrated toluene, dichloromethane, hexane, and diethyl ether were purchased from Kanto Chemicals. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40–100 μm) from Kanto Chemicals.

4.4. General procedure for cyanoesterification

To a solution of $Pd(PPh_3)_4$ (580 mg, 0.5 mmol, 10 mol %) in toluene (50 mL) were added ethyl cyanoformate (**1a**) (490 μL, 5.0 mmol) and norbornene (**2**) (470 mg, 5.0 mmol) at room temperature. The reaction mixture was stirred for 24 h at 110 °C, quenched with 1 M hydrochloric acid (50 mL), and extracted with diethyl ether (25 mL×2). The combined ethereal layers were washed with brine and dried over $MgSO_4$. Filtration and evaporation afforded a pale yellow oil. Bulb to bulb distillation (135 °C/2.0 Torr) gave **3a** (773 mg, 80% yield) as a colorless oil.

4.4.1. (2*R,3*S**)-Ethyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (3a).** A colorless oil. Bp 135 °C/2.0 Torr. GC yield was 94%. Isolated yield was 80%. IR (neat, cm^{-1}): 2974 (s), 2882 (m), 2240 (m, *ν*CN), 1738 (s, *ν*CO), 1456 (m), 1375 (m), 1350 (m), 1290 (m), 1263 (m), 1222 (m), 1193 (s), 1154 (m), 1118 (m), 1040 (m), 926 (w), 853 (w), 748 (w). ^1H NMR ($CDCl_3$, 300 MHz, rt): *δ* 1.17–1.25 (m, 2H, ethylene C*H* (*endo*)), 1.28 (dt, *J*=7 Hz, 1 Hz, 3H, CH_3), 1.42 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*anti*)), 1.53–1.66 (m, 2H, ethylene C*H* (*exo*)), 1.95 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.62–2.65 (m, 3H, 2 bridgehead methine protons+C*H*COOEt), 2.83 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*CN), 4.18 (qd, *J*=7 Hz, 1 Hz, 2H, OCH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): *δ* 14.1 (*C*H_3), 27.8 (*C*H_2), 28.2 (*C*H_2), 36.6 (*C*H_2+*C*HCN), 39.0 (bridgehead carbon (CN side)), 41.9 (bridgehead carbon (COOEt side)), 49.9 (*C*HCOOEt), 61.1 (O*C*H_2), 119.7 (*C*N), 171.1 (*C*O). MS (El, *m*/*z* (relative intensity)): 193 (M^+, 6), 166 (18), 148 (29), 126 (64), 120 (74), 98 (100), 93 (46), 80 (27), 66 (95), 53 (20). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25%. Found: C, 68.24; H, 7.82; N, 6.94%.

4.4.2. (2*R,3*S**)-Methyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (3b).** A colorless oil. Bp 130 °C/1.6 Torr. NMR yield was 43%. Isolated yield was 28%. IR (neat, cm^{-1}): 2962 (s), 2882 (m), 2240 (m, *ν*CN), 1742 (s, *ν*CO), 1458 (m), 1437 (m), 1363 (m), 1290 (m), 1265 (m), 1224 (m), 1197 (s), 1154 (m), 1120 (m), 1040 (m), 934 (w), 870 (w), 770 (w). ^1H NMR ($CDCl_3$, 300 MHz, rt): *δ* 1.24 (m, 2H, ethylene C*H* (*endo*)), 1.43 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*anti*)), 1.62 (m, 2H, ethylene C*H* (*exo*)), 1.96 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.60–2.69 (m, 3H, 2 bridgehead methine protons+C*H*COOMe), 2.83 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*CN), 3.74 (s, 3H, OCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): *δ* 27.7 (*C*H_2), 28.2 (*C*H_2), 36.6 (*C*H_2+*C*HCN), 39.0 (bridgehead carbon (CN side)), 41.9 (bridgehead carbon (COOMe side)), 50.1 (*C*HCOOMe), 52.1 (O*C*H_3), 119.9 (*C*N), 171.8 (*C*O). MS (El, *m*/*z* (relative intensity)): 179 (M^+, 1), 164 (2), 148 (14), 134 (2), 120 (42), 112 (100), 98 (40), 93 (22), 80 (29), 67 (60), 53 (15). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%. Found: C, 67.23; H, 7.33; N, 7.86%.

4.4.3. (2*R,3*S**)-*n*-Propyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (3c).** A colorless oil. R_f=0.57 (hexane/ethyl acetate=7/3). GC yield was 72%. Isolated yield was 63%. IR (neat, cm^{-1}): 2968 (s), 2880 (s), 2238 (m, *ν*CN), 1734 (s, *ν*CO), 1356 (m), 1288 (m), 1264 (m), 1222 (m), 1191 (s), 1173 (m), 1152 (m), 1062 (m), 1027 (m). ^1H NMR ($CDCl_3$, 300 MHz, rt): *δ* 0.92–0.97 (t, *J*=8 Hz, 3H, $CH_2CH_2CH_3$), 1.21–1.24 (m, 2H, ethylene C*H* (*endo*)), 1.42 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*anti*)), 1.57–1.72 (m, 4H, ethylene C*H* (*exo*)+$CH_2CH_2CH_3$), 1.96 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.64–2.67 (m, 3H, 2 bridgehead methine protons+C*H*COO^{n}Pr), 2.83 (dd, *J*=9 Hz, 1 Hz, 1H, C*H*CN), 4.08 (t, 7 Hz, 2H, OCH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): *δ* 10.4 ($CH_2CH_2CH_3$), 21.8 ($CH_2CH_2CH_3$), 27.8 (*C*H_2), 28.2 (*C*H_2), 36.6 (*C*H_2+*C*HCN), 39.0 (bridgehead carbon (CN side)), 41.9 (bridgehead carbon (COO^{n}Pr side)), 50.1 (*C*HCOO^{n}Pr), 66.8 (O*C*H_2), 119.8 (*C*N), 171.4 (*C*O). MS (El, *m*/*z* (relative intensity)): 207 (M^+, 1), 179 (4), 166 (97), 148 (63), 140 (29), 120 (100), 104 (4), 98 (68), 93 (35), 80 (14), 77 (12), 72 (3), 66 (43). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76%. Found: C, 69.43; H, 8.33; N, 6.66%.

4.4.4. (2*R,3*S**)-*iso*-Propyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (3d).** A colorless oil. R_f=0.60 (hexane/ethyl acetate=7/3). GC yield was 80%. Isolated yield was 63%. IR (neat, cm^{-1}): 2979 (s), 2880 (s), 2238 (m, *ν*CN), 1729 (s, *ν*CO), 1455 (m), 1343 (m), 1301 (m), 1288 (m), 1264 (m), 1223 (m), 1195 (s), 1174 (m), 1153 (m), 1107 (m), 1017 (m). ^1H NMR ($CDCl_3$, 300 MHz, rt): *δ* 1.21–1.24 (m, 2H, ethylene C*H* (*endo*)), 1.25 (d, *J*=6 Hz, 3H, CH_3), 1.28 (d, *J*=6 Hz, 3H, CH_3), 1.41 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*anti*)), 1.52–1.72 (m, 2H, ethylene C*H* (*exo*)), 1.95 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.58 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*COO^{i}Pr), 2.63–2.64 (m, 2H, 2 bridgehead methine protons), 2.82 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*CN), 5.05 (sep, *J*=6 Hz, 1H, O*CH*); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): *δ* 21.7 (*C*H_3), 21.8 (*C*H_3), 27.7 (*C*H_2), 28.3 (*C*H_2), 36.6 (*C*H_2+*C*HCN), 39.0 (bridgehead carbon (CN side)), 42.0 (bridgehead carbon (COO^{i}Pr side)), 49.8 (*C*HCOO^{i}Pr), 66.8 (O*C*H), 119.7 (*C*N), 170.8 (*C*O). MS (El, *m*/*z* (relative intensity)): 207 (M^+, 1), 192 (9), 166 (47), 148 (71), 140 (24), 120 (100), 104 (7), 98 (33), 93 (35), 80 (18), 77 (12), 71 (2), 66 (79). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76%. Found: C, 69.56; H, 8.35; N, 6.69%.

4.4.5. (2*R,3*S**)-*n*-Butyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (3e).** A colorless oil. R_f=0.60 (hexane/ethyl acetate=7/3). GC yield was 67%. Isolated yield was 63%. IR (neat, cm^{-1}): 2961 (s), 2877 (s), 2238 (m, *ν*CN), 1735 (s, *ν*CO), 1465 (m), 1351 (m), 1288 (m), 1262 (m), 1222 (m), 1191 (s), 1152 (m). ^1H NMR ($CDCl_3$, 300 MHz, rt): *δ* 0.92 (sex, *J*=7 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.21–1.25 (m, 2H, ethylene C*H* (*endo*)), 1.35–1.45 (m, 3H, one of methylene (*anti*)+$CH_2CH_2CH_2CH_3$), 1.60–1.67 (m, 4H, ethylene C*H* (*exo*)+$CH_2CH_2CH_2CH_3$), 1.97 (dt, *J*=11 Hz, 1 Hz, 1H, one of methylene (*syn*)), 2.64–2.67 (m, 3H, 2 bridgehead methine protons+C*H*COO^{n}Bu), 2.83 (dd, *J*=10 Hz,

2 Hz, 1H, C*H*CN), 4.13 (m, 2H, OCH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 13.6 ($CH_2CH_2CH_2CH_3$), 19.1 ($CH_2CH_2CH_2CH_3$), 27.7 ($CH_2CH_2CH_2CH_3$), 28.3 (CH_2), 30.4 (CH_2), 36.6 (CH_2+CHCN), 39.0 (bridgehead carbon (CN side)), 41.9 (bridgehead carbon (COO^{n}Bu side)), 50.1 (CHCOO^{n}Bu), 65.1 (OCH_2), 119.8 (CN), 171.4 (CO). MS (El, *m*/*z* (relative intensity)): 221 (M^+, 1), 179 (7), 166 (100), 154 (31), 148 (43), 120 (95), 104 (4), 98 (53), 93 (32), 80 (12), 77 (11), 72 (5), 66 (39). Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33%. Found: C, 70.49; H, 8.76; N, 6.27%.

4.4.6. (2*R,3*S**)-Benzyl 3-cyanobicyclo[2.2.1]heptane-2-carboxylate (3g).** Off-white solid. R_f=0.57 (hexane/ethyl acetate=7/3). Mp=75–76 °C. GC yield was 31%. Isolated yield was 14%. IR (KBr, cm^{-1}): 2967 (s), 2877 (m), 2235 (s, νCN), 1731 (s, νCO), 1454 (m), 1383 (s), 1350 (m), 1302 (m), 1288 (m), 1222 (m), 1190 (s), 1167 (m), 1117 (m), 1029 (m). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 1.21–1.25 (m, 2H, ethylene C*H* (*endo*)), 1.45 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*anti*)), 1.59–1.67 (m, 2H, ethylene C*H* (*exo*)), 1.95 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.62–2.65 (m, 3H, 2 bridgehead methine protons+C*H*COOBn), 2.85 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*CN), 5.10 (d, *J*=12 Hz, 1H, OCH_2), 5.23 (d, *J*=12 Hz, 1H, OCH_2), 7.33–7.43 (m, 5H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 27.7 (CH_2), 28.2 (CH_2), 36.7 (CH_2+CHCN), 39.0 (bridgehead carbon (CN side)), 41.9 (bridgehead carbon (COOBn side)), 50.2 (CHCOOBn), 67.2 (OCH_2), 119.9 (CN), 128.4, 128.5, 128.7, 135.3, 171.2 (CO). MS (El, *m*/*z* (relative intensity)): 255 (M^+, 13), 237 (2), 227 (4), 148 (7), 120 (27), 107 (42), 91 (100), 79 (7), 77 (8), 66 (19). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%. Found: C, 74.87; H, 6.60; N, 5.10%.

4.4.7. (2*R,3*S**)-Ethyl 1,2,3,4-tetrahydro-3-cyano-1,4-methanonaphthalene-2-carboxylate (5a).** White solid. Mp 66–67 °C. GC yield was 99%. Isolated yield was 83%. IR (KBr, cm^{-1}): 2979 (s), 2886 (m), 2240 (s, νCN), 1739 (s, νCO), 1468 (m), 1374 (m), 1347 (m), 1312 (m), 1264 (m), 1240 (m), 1181 (s), 1156 (m), 1107 (m), 1036 (m), 951 (w), 857 (w), 754 (w). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 1.33 (t, *J*=7 Hz, 3H, CH_3), 2.02 (d of quintet, *J*=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 2.36 (dt, *J*=10 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.70 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*COOEt), 2.85 (dd, *J*=9 Hz, 2 Hz, 1H, C*H*CN), 3.72 (d, *J*=7 Hz, 2H, 2 bridgehead methine protons), 4.28 (qd, *J*=7 Hz, 4 Hz, 2H, OCH_2), 7.11–7.27 (m, 4H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 14.1 (CH_3), 34.9 (CHCN), 46.5 (bridgehead carbon (CN side)), 47.1 (CH_2), 48.8 (bridgehead carbon (COOEt side)+CHCOOEt), 61.6 (OCH_2), 119.7 (CN), 121.2, 121.7, 126.7, 127.3, 144.4, 146.0, 171.5 (CO). MS (El, *m*/*z* (relative intensity)): 241 (M^+, 4), 196 (2), 167 (6), 141 (7), 126 (5), 116 (100), 98 (10), 89 (3), 80 (5), 63 (4), 51 (3). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80%. Found: C, 74.48; H, 6.24; N, 5.63%.

4.4.8. (2*R,3*S**)-Methyl 1,2,3,4-tetrahydro-3-cyano-1,4-methanonaphthalene-2-carboxylate (5b).** A colorless liquid. Bp 75 °C/1.8 Torr. GC yield was 74%. Isolated yield was 65%. IR (neat, cm^{-1}): 3024 (m), 2956 (m), 2242 (m, νCN), 1740 (s, νCO), 1462 (m), 1437 (m), 1352 (m), 1311 (m), 1267 (m), 1238 (m), 1201 (s), 1183 (m), 1156 (m), 1110 (m), 1038 (m), 959 (w), 849 (w), 756 (w). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 2.02 (d of quintet, *J*=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 2.36 (dt, *J*=11 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.73 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*COOEt), 2.85 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*CN), 3.72 (d, *J*=6 Hz, 2H, 2 bridgehead methine protons), 3.82 (s, 3H, OCH_3), 7.11–7.27 (m, 4H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 34.9 (CHCN), 46.3 (bridgehead carbon (CN side)), 47.2 (CH_2), 48.9 (CHCOOMe), 49.1 (bridgehead carbon (COOMe side)), 52.5 (OCH_3), 119.8 (CN), 121.3, 121.8, 126.9, 127.5, 144.5, 146.0, 172.0 (CO). MS (El, *m*/*z* (relative intensity)): 227 (M^+, 5), 196 (2), 167 (5), 141 (6), 128 (3), 116 (100), 102 (1), 89 (3), 80 (5), 63 (4), 51 (3). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16%. Found: C, 73.74; H, 5.71; N, 6.02%.

4.4.9. (2*R,3*S**)-*n*-Propyl 1,2,3,4-tetrahydro-3-cyano-1,4-methanonaphthalene-2-carboxylate (5c).** A colorless oil. R_f=0.72 (hexane/ethyl acetate=7/3). GC yield was 83%. Isolated yield was 76%. IR (neat, cm^{-1}): 2970 (s), 2882 (s), 2238 (m, νCN), 1733 (s, νCO), 1470 (m), 1393 (m), 1352 (m), 1308 (s), 1265 (m), 1237 (m), 1194 (m), 1185 (m), 1109 (s). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 0.97 (td, *J*=8 Hz, 1 Hz, 3H, $CH_2CH_2CH_3$), 1.72 (td, *J*=8 Hz, 1 Hz, 2H, $CH_2CH_2CH_3$), 2.01 (dd, 1H, one of methylene (*anti*)), 2.36 (dd, *J*=10 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.70 (d, *J*=10 Hz, 1H, C*H*COO^{n}Pr), 2.85 (d, *J*=10 Hz, 1H, C*H*CN), 3.72 (d, *J*=8 Hz, 2H, 2 bridgehead methine protons), 4.17 (t, *J*=8 Hz, 2H, OCH_2), 7.10–7.26 (m, 4H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 10.4 ($CH_2CH_2CH_3$), 21.8 ($CH_2CH_2CH_3$), 34.9 (CHCN), 46.3 (bridgehead carbon (CN side)), 47.2 (CH_2), 48.9 (bridgehead carbon (COO^{n}Pr side), 49.0 (CHCOO^{n}Pr), 67.2 (OCH_2), 119.8 (CN), 121.3, 121.8, 126.8, 127.4, 144.5, 146.1, 171.6 (CO). MS (El, *m*/*z* (relative intensity)): 255 (M^+, 5), 196 (3), 168 (8), 153 (2), 141 (8), 128 (4), 116 (100), 98 (14), 89 (2), 80 (3), 65 (2). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%. Found: C, 75.32; H, 6.67; N, 5.21%.

4.4.10. (2*R,3*S**)-*iso*-Propyl 1,2,3,4-tetrahydro-3-cyano-1,4-methanonaphthalene-2-carboxylate (5d).** White solid. R_f=0.71 (hexane/ethyl acetate=7/3). Mp 90–91 °C. GC yield was 83%. Isolated yield was 68%. IR (KBr, cm^{-1}): 2986 (m), 2977 (m), 2239 (s, νCN), 1724 (s, νCO), 1473 (m), 1461 (s), 1366 (m), 1304 (s), 1237 (m), 1202 (m), 1104 (s), 1020 (m). ^1H NMR ($CDCl_3$, 300 MHz, rt): δ 1.30 (d, *J*=6 Hz, 3H, CH_3), 1.34 (d, *J*=6 Hz, 3H, CH_3), 2.01 (dd, *J*=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 2.35 (dd, *J*=10 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.64 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*COO^{i}Pr), 2.84 (dd, *J*=10 Hz, 2 Hz, 1H, C*H*CN), 3.71 (d, *J*=10 Hz, 2H, 2 bridgehead methine protons), 5.15 (sep, *J*=6 Hz, 1H, OC*H*), 7.10–7.26 (m, 4H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, rt): δ 21.7 (CH_3), 21.9 (CH_3), 34.9 (CHCN), 46.4 (bridgehead carbon (CN side)), 47.2 (CH_2), 48.8 (bridgehead carbon (COO^{i}Pr side)), 49.0 (CHCOO^{i}Pr), 69.4 (OCH), 119.8 (CN), 121.2, 121.8, 126.8, 127.4, 144.5, 146.2, 171.1 (CO). MS (El, *m*/*z* (relative intensity)): 255 (M^+, 6), 213 (2), 196 (6), 168 (14), 153 (2), 140 (10), 128 (5), 116 (100), 98 (17), 89 (3), 80 (3), 63 (2). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%. Found: C, 75.00; H, 6.73; N, 5.23%.

4.4.11. (2*R,3*S**)-*n*-Butyl 1,2,3,4-tetrahydro-3-cyano-1,4-methanonaphthalene-2-carboxylate (5e).** A colorless oil. R_f=0.71 (hexane/ethyl acetate=7/3). GC yield was 87%. Isolated yield was 79%. IR (neat, cm^{-1}): 2960 (s), 2936 (m), 2874 (s), 2238 (m, νCN), 1733 (s, νCO), 1470 (m), 1462 (m), 1390 (s), 1308 (s), 1265 (m), 1238 (m), 1194 (m), 1185 (m), 1109 (s), 1063 (m). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.94 (t, J=8 Hz, 3H, CH_3), 1.41 (sex, J=8 Hz, 2H, CH_2CH$_3$), 1.67 (sex, J=8 Hz, 2H, CH$_2$CH_2CH$_3$), 2.02 (dt, J=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 2.36 (dt, J=10 Hz, 1 Hz, 1H, one of methylene (*syn*)), 2.71 (d, J=10 Hz, 1H, C*H*COO^{n}Bu), 2.85 (d, J=10 Hz, 1H, C*H*CN), 3.72 (d, J=10 Hz, 2H, 2 bridgehead methine protons), 4.22 (t, J=8 Hz, 2H, OCH_2), 7.10–7.26 (m, 4H, aromatics); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 13.7 (*C*H$_3$), 19.1 (*C*H$_2$CH$_3$), 30.5 (*C*H$_2$CH$_2$CH$_3$), 34.9 (*C*HCN), 46.3 (bridgehead carbon (CN side)), 47.2 (*C*H$_2$), 48.9 (bridgehead carbon (COO^{n}Bu side)), 49.0 (*C*HCOO^{n}Bu), 65.6 (O*C*H$_2$), 119.8 (*C*N), 121.3, 121.8, 126.8, 127.4, 144.5, 146.1, 171.6 (*C*O). MS (El, *m*/*z* (relative intensity)): 269 (M^+, 5), 213 (1), 196 (2), 168 (7), 154 (3), 141 (8), 128 (4), 116 (100), 98 (16), 89 (2), 80 (3), 63 (2). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20%. Found: C, 75.51; H, 7.10; N, 5.07%.

4.4.12. (2*R,3*S**)-Benzyl 1,2,3,4-tetrahydro-3-cyano-1,4-methanonaphthalene-2-carboxylate (5g).** White solid. R_f=0.67 (hexane/ethyl acetate=7/3). Mp 102–103 °C. Isolated yield was 22%. IR (KBr, cm^{-1}): 2966 (s), 2950 (m), 2891 (s), 2238 (m, νCN), 1729 (s, νCO), 1454 (m), 1344 (m), 1307 (s), 1265 (m), 1238 (m), 1196 (m), 1187 (m), 1110 (s). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 2.03 (dt, J=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 2.39 (dt, J=10 Hz, 2 Hz, 1H, one of methylene (*syn*)), 2.76 (d, J=10 Hz, 1H, C*H*COOBn), 2.86 (d, J=10 Hz, 1H, C*H*CN), 3.74 (d, J=6 Hz, 2H, 2 bridgehead methine protons), 5.24 (q, J=12 Hz, 2H, OCH_2), 7.12–7.44 (m, 9H, aromatics); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 34.9 (*C*HCN), 46.3 (bridgehead carbon (CN side)), 47.2 (bridgehead carbon (COOBn side)), 48.9 (*C*HCOOBn), 49.1 (*C*H$_2$), 67.6 (O*C*H$_2$), 119.9 (*C*N), 121.3, 121.8, 126.8, 127.4, 128.5, 128.6, 128.8, 144.4, 145.9, 171.4 (*C*O). MS (El, *m*/*z* (relative intensity)): 303 (M^+, 5), 258 (2), 206 (2), 188 (27), 168 (6), 153 (2), 141 (8), 128 (5), 116 (69), 91 (100), 77 (4), 65 (9). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62%. Found: C, 78.95; H, 5.65; N, 4.68%.

4.4.13. (2*R,3*S**)-Ethyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7a).** A colorless liquid. Bp 135 °C/1.9 Torr. GC yield was 97%. Isolated yield was 78%. IR (neat, cm^{-1}): 2986 (m), 2240 (m, νCN), 1736 (s, νCO), 1460 (m), 1373 (m), 1344 (m), 1265 (m), 1243 (m), 1189 (s), 1160 (m), 1112 (m), 1038 (m), 907 (w), 822 (w), 772 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.31 (t, J=7 Hz, 3H, CH_3), 1.66 (dt, J=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 2.00 (d, J=10 Hz, 1H, one of methylene (*syn*)), 2.57 (dd, J=9 Hz, 2 Hz, 1H, C*H*COOEt), 2.68 (dd, J=9 Hz, 2 Hz, 1H, C*H*CN), 3.20 (br s, 1H, bridgehead methine proton (CN side)), 3.26 (br s, 1H, bridgehead methine proton (COOEt side)), 4.24 (m, 2H, OCH_2), 6.15 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 6.24 (dd, J=6 Hz, 3 Hz, 1H, =C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 14.3 (*C*H$_3$), 33.1 (*C*HCN), 45.0 (bridgehead carbon (CN side)), 46.5 (*C*H$_2$), 47.0 (*C*HCOOEt), 47.6 (bridgehead carbon (COOEt side)), 61.6 (O*C*H$_2$), 120.2 (*C*N), 135.9 (=*C*H), 138.4 (=*C*H), 171.8 (*C*O). MS (El, *m*/*z* (relative intensity)): 191 (M^+, 1), 146 (5), 126 (2), 118 (5), 98 (4), 90 (2), 80 (8), 66 (100), 52 (3). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32%. Found: C, 69.07; H, 6.74; N, 7.13%.

4.4.14. (2*R,3*S**)-Methyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7b).** A colorless oil. Bp 115–120 °C/2.8 Torr. GC yield was 80%. Isolated yield was 76%. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.59 (d, J=10 Hz, 1H, one of methylene (*anti*)), 1.92 (d, J=10 Hz, 1H, one of methylene (*syn*)), 2.54 (dd, J=9 Hz, 2 Hz, 1H, C*H*COOMe), 2.63 (dd, J=9 Hz, 2 Hz, 1H, C*H*CN), 3.12 (br s, 1H, bridgehead methine proton (CN side)), 3.18 (br s, 1H, bridgehead methane proton (CHCOOMe side)), 3.70 (s, 3H, CH_3), 6.10 (dd, J=5 Hz, 3 Hz, 1H, =C*H*), 6.18 (dd, J=5 Hz, 3 Hz, 1H, =C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 32.6 (*C*HCN), 44.7 (bridgehead carbon (CN side)), 46.0 (*C*H$_2$), 46.8 (*C*HCOOMe), 47.3 (bridgehead carbon (COOMe side)), 52.1 (O*C*H$_3$), 120.1 (*C*N), 135.8 (=*C*H), 138.1 (=*C*H), 172.2 (*C*O). MS (El, *m*/*z* (relative intensity)): 177 (M^+, 2), 146 (8), 118 (7), 112 (4), 91 (8), 80 (11), 66 (100). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90%. Found: C, 67.55; H, 6.22; N, 7.74%.

4.4.15. (2*R,3*S**)-*n*-Propyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7c).** A colorless oil. Bp 130–140 °C/3.0 Torr. GC yield was 89%. Isolated yield was 76% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.96 (t, J=7 Hz, 3H, CH$_2$CH$_2$CH_3), 1.66 (d, 1H, J=7 Hz, one of methylene (*anti*)), 1.72 (t, J=7 Hz, 2H, CH$_2$CH_2CH$_3$), 2.02 (d, J=9 Hz, 1H, one of methylene (*syn*)), 2.58 (dd, J=9 Hz, 2 Hz, 1H, C*H*COO^{n}Pr), 2.68 (dd, J=9 Hz, 2 Hz, 1H, C*H*CN), 3.19 (br s, 1H, bridgehead methine proton (CN side)), 3.26 (br s, 1H, bridgehead methane proton (CHCOO^{n}Pr side)), 4.14 (t, J=7 Hz, 2H, OCH$_2$), 6.15 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 6.25 (dd, J=6 Hz, 3 Hz, 1H, =C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 10.4 (CH$_2$CH$_2$*C*H$_3$), 21.8 (CH$_2$*C*H$_2$CH$_3$), 33.0 (*C*HCN), 45.0 (bridgehead carbon (CN side)), 46.4 (*C*H$_2$), 47.1 (*C*HCOO^{n}Pr), 47.6 (bridgehead carbon (COO^{n}Pr side)), 67.1 (*C*H$_2$CH$_2$CH$_3$), 120.3 (*C*N), 136.0 (=*C*H), 138.5 (=*C*H), 172.1 (*C*O). MS (El, *m*/*z* (relative intensity)): 205 (M^+, 1), 163 (2), 146 (10), 118 (13), 98 (9), 91 (7), 80 (11), 66 (100). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%. Found: C, 70.09; H, 7.45; N, 6.69%.

4.4.16. (2*R,3*S**)-*iso*-Propyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7d).** A colorless oil. Bp 130–140 °C/2.5 Torr. GC yield was 77%. Isolated yield was 62%. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.28 (d, J=11 Hz, 1H, CHCH$_3$CH_3), 1.30 (d, J=11 Hz, 1H, CHCH$_3$CH_3), 1.64 (d, 1H, J=9 Hz, one of methylene (*anti*)), 2.00 (d, J=9 Hz, one of methylene (*syn*)), 2.51 (dd, J=9 Hz, 2 Hz, 1H, C*H*COO^{i}Pr), 2.66 (dd, J=9 Hz, 2 Hz, 1H, C*H*CN), 3.18 (br s, 1H, bridgehead methine proton (CN side)), 3.25 (br s, 1H, bridgehead methane proton (CHCOO^{i}Pr side)), 5.11 (t, J=7 Hz, sept, 1H, C*H*CH$_3$CH$_3$), 6.14 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 6.24 (dd, J=6 Hz, 3 Hz, 1H, =C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 21.7 (one of CH*C*H$_3$CH$_3$), 21.8 (one of CHCH$_3$*C*H$_3$), 32.8 (*C*HCN), 44.9 (bridgehead carbon (CN side)), 46.3 (*C*H$_2$), 46.7 (*C*HCOO^{i}Pr), 47.5

(bridgehead carbon (COO^{i}Pr side)), 69.0 (*C*HCH$_3$CH$_3$), 120.1 (*C*N), 135.9 (=*C*H), 138.4 (=*C*H), 171.4 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%. Found: C, 70.20; H, 7.40; N, 6.85%.

4.4.17. (2*R,3*S**)-*n*-Butyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7e).** A colorless oil. Bp 135–150 °C/3.3 Torr. GC yield was 86%. Isolated yield was 74%. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 0.92 (t, J=7 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.39 (sex, 2H, J=7 Hz, $CH_2CH_2CH_2CH_3$), 1.60–1.70 (m, 3H, $CH_2CH_2CH_2CH_3$+one of methylene (*anti*)), 2.02 (d, J=9 Hz, 1H, one of methylene (*syn*)), 2.57 (dd, J=10 Hz, 2 Hz, 1H, C*H*COO^{n}Bu), 2.67 (dd, J=9 Hz, 2 Hz, 1H, C*H*CN), 3.18 (br s, 1H, bridgehead methine proton (CN side)), 3.24 (br s, 1H, bridgehead methane proton (CHCOO^{n}Bu side)), 4.17 (t, J=7 Hz, 2H, $CH_2CH_2CH_2CH_3$), 6.14 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 6.23 (dd, J=6 Hz, 3 Hz, 1H, =C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 13.3 ($CH_2CH_2CH_2CH_3$), 18.8 ($CH_2CH_2CH_2CH_3$), 30.1 ($CH_2CH_2CH_2CH_3$), 32.6 (*C*HCN), 44.7 (bridgehead carbon (CN side)), 46.0 (CH_2), 46.7 (*C*HCOO^{n}Bu), 47.2 (bridgehead carbon (COO^{n}Bu side)), 64.9 ($CH_2CH_2CH_2CH_3$), 120.0 (*C*N), 135.7 (=*C*H), 138.1 (=*C*H), 171.7 (*C*O). MS (El, *m*/*z* (relative intensity)): 219 (M$^+$, 1), 163 (4), 146 (5), 118 (13), 98 (9), 91 (6), 80 (10), 66 (100). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39%. Found: C, 71.20; H, 7.88; N, 6.36%.

4.4.18. (2*R,3*S**)-*tert*-Butyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7f).** White solid. Mp 47–48 °C. GC yield was 13%. Isolated yield was 12%. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.50 (s, 9H, CH_3), 1.63 (dt, J=10 Hz, 2 Hz, 1H, one of methylene (*anti*)), 1.97 (d, J=10 Hz, 1H, one of methylene (*syn*)), 2.45 (dd, J=10 Hz, 2 Hz, 1H, C*H*COO^{t}Bu), 2.64 (dd, J=10 Hz, 2 Hz, 1H, C*H*CN), 3.15 (br s, 1H, bridgehead methine proton (CN side)), 3.23 (br s, 1H, bridgehead methane proton (CHCOO^{t}Bu side)), 6.13 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 6.23 (dd, J=6 Hz, 3 Hz, 1H, =C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 28.0 (Me), 32.8 (*C*HCN), 45.0 (bridgehead carbon (CN side)), 46.4 (CH_2), 47.3 (*C*HCOO^{t}Bu), 47.6 (bridgehead carbon (COO^{t}Bu side)), 82.1 ($C(CH_3)_3$), 120.4 (*C*N), 135.9 (=*C*H), 138.6 (=*C*H), 171.0 (*C*O). MS (El, *m*/*z* (relative intensity)): 219 (M$^+$, 1), 205 (4), 163 (22), 146 (62), 118 (38), 104 (5), 98 (5), 91 (12), 80 (31), 66 (100). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39%. Found: C, 71.04; H, 7.80; N, 6.18%.

4.4.19. (2*R,3*S**)-Benzyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (7g).** White solid. Mp 81–82 °C. GC yield was 84%. Isolated yield was 63%. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 1.69 (dquin, 1H, J=10 Hz, 2 Hz, one of methylene (*anti*)), 2.05 (dt, J=10 Hz, 2 Hz, one of methylene (*syn*)), 2.63 (dd, J=10 Hz, 2 Hz, 1H, C*H*COOMe), 2.69 (dd, J=10 Hz, 2 Hz, 1H, C*H*CN), 3.23 (br s, 1H, bridgehead methine proton (CN side)), 3.28 (br s, 1H, bridgehead methane proton (CHCOOMe side)), 5.15 (d, J=12 Hz, 1H, one of CH_2Ph), 5.27 (d, J=12 Hz, 1H, one of CH_2Ph), 6.16 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 6.24 (dd, J=6 Hz, 3 Hz, 1H, =C*H*), 7.34–7.44 (m, 5H, C_6H_5); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, rt): δ 33.0 (*C*HCN), 45.0 (bridgehead carbon (CN side)), 46.4 (CH_2), 47.1 (*C*HCOOEt), 47.6 (bridgehead carbon (COOEt side)), 67.5 (CH_2Ph), 120.3 (*C*N), 128.4, 128.6, 128.8, 135.3, 136.1 (=*C*H), 138.4 (=*C*H), 171.9 (*C*O). MS (El, *m*/*z* (relative intensity)): 253 (M$^+$, 8), 209 (2), 187 (4), 146 (3), 118 (5), 107 (14), 91 (100), 80 (6), 77 (7), 66 (39). Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%. Found: C, 75.91; H, 5.92; N, 5.52%.

4.5. Reaction of norbornadiene (6) with phenyl cyanoformate (1h) in the presence of a catalytic amount of $Pd(PPh_3)_4$

To a solution of $Pd(PPh_3)_4$ (23 mg, 0.02 mmol, 10 mol %) in toluene (2 mL), were added phenyl cyanoformate (**1h**) (29.2 mg, 0.2 mmol) and norbornadiene (**6**) (21 μL, 0.2 mmol) at room temperature. The reaction mixture was stirred for 24 h at 110 °C. GC yield was calculated using commercially available **8**[19] as an authentic sample to be quantitatively, based on Pd. ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 7.25–7.32 (m, 3H, aromatic), 7.39–7.46 (m, 1H, aromatic).

4.5.1. Preparation of *trans*-Pd(PPh$_3$)$_2$(CN)(CO$_2$Et) (9a). To a toluene (20 mL) suspension of $Pd(PPh_3)_4$ (693 mg, 0.60 mmol) was added ethyl cyanoformate (142 μL, 1.44 mmol). The reaction mixture was stirred at room temperature. The initially pale yellow suspension became white suspension after 48 h. The solvents were evaporated under vacuum. The resulting off-white solid was washed with hexane (20 mL) two times. The product was extracted with dichloromethane (10 mL). Removal of the solvent from the extracts gave **9a** (430 mg, 0.59 mmol, 98%). Recrystallization from dichloromethane/hexane afforded colorless needles (308 mg, 0.42 mmol, 70%). Mp 131–132 °C (dec). IR (KBr, cm^{-1}): 2126 (w, νCN), 1638 (s, νCO). ^{1}H NMR (CD_2Cl_2, 300 MHz, rt): δ 0.52 (t, J=7 Hz, 3H, CH_3), 2.73 (q, J=7 Hz, 2H, CH_2), 7.38–7.51 (m, 18H, Ph), 7.66–7.78 (m, 12H, Ph); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz, rt): δ 13.2 (s, CH_3), 59.6 (s, OCH_2), 127.8 (t, J=5 Hz, *ortho*-PPh$_3$), 130.1 (s, *para*-PPh$_3$), 131.0 (t, J=24 Hz, *ipso*-PPh$_3$), 133.8 (t, J=7 Hz, *meta*-PPh$_3$), 137.2 (t, J=20 Hz, Pd–*C*N), 192.6 (t, J=3 Hz, Pd–*C*O); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, rt): δ 21.6 (s). Anal. Calcd for $C_{40}H_{35}NO_2P_2Pd$: C, 65.81; H, 4.83; N, 1.92%. Found: C, 65.78; H, 4.75; N, 1.88%.

4.5.2. Preparation of *trans*-Pd(PPh$_3$)$_2$(CN)(CO$_2$Me) (9b). To a toluene (20 mL) suspension of $Pd(PPh_3)_4$ (693 mg, 0.60 mmol) was added methyl cyanoformate (114 μL, 1.44 mmol). The reaction mixture was stirred at room temperature. The initially pale yellow suspension became white suspension after 24 h. The solvents were evaporated under vacuum. The resulting off-white solid was washed with hexane (20 mL) two times. The product was extracted with dichloromethane (10 mL). Removal of the solvent from the extracts gave the titled compound (416 mg, 0.58 mmol, 97%). Recrystallization from dichloromethane/hexane afforded colorless crystals of **9b** (364 mg, 0.51 mmol, 84%). Mp 163–164 °C (dec). IR (KBr, cm^{-1}): 2124 (w, νCN), 1663 (s, νCO). ^{1}H NMR (CD_2Cl_2, 300 MHz, rt): δ 2.44 (s, 3H, OCH_3), 7.39–7.55 (m, 18H, Ph), 7.67–7.79 (m, 12H, Ph); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz, rt): δ 50.0 (s, OCH_3), 127.8 (t, J=5 Hz, *ortho*-PPh$_3$), 130.2 (s, *para*-PPh$_3$), 130.9 (t, J=24 Hz, *ipso*-PPh$_3$), 133.8 (t, J=7 Hz, *meta*-PPh$_3$), 136.8 (t, J=20 Hz, Pd–*C*N), 192.9 (t, J=2 Hz, Pd–*C*O); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, rt): δ 21.8 (s).

Anal. Calcd for $C_{39}H_{33}NO_2P_2Pd$: C, 65.42; H, 4.65; N, 1.96%. Found: C, 65.46; H, 4.61; N, 1.84%.

4.5.3. Reaction of 1a with 2 in the presence of a catalytic amount of 9a. To a solution of **9a** (15 mg, 0.02 mmol, 10 mol %) in toluene (2 mL), were added **1a** (20 μL, 0.2 mmol) and norbornadiene (**6**) (19 mg, 0.2 mmol), and dodecane (46 μL, 0.2 mmol) as an internal standard. The reaction mixture was heated at 110 °C for 24 h to afford **7a** in 85% GC yield.

4.6. X-ray crystallography

Single crystals of **5b** were obtained by recrystallization from chloroform and crystals of **7g** were obtained by recrystallization from CH_2Cl_2–hexane. Single crystals were mounted on glass fibers. All the measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Cu Kα radiation (λ=1.54178 Å). The unit cells were determined and refined by a least-square method using the setting angles of 25 carefully centered reflections in the range $50.3<2\theta<57.7°$ for **5b** and $50.2<2\theta<59.1°$ for **7g**. The data were collected at room temperature using the $\omega-2\theta$ scan technique to a maximum 2θ value of 140°. The structures were solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF99). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Crystal structure analysis of **5b**: $C_{14}H_{13}NO_2$, FW=227.26, colorless, prismatic, 0.40×0.40×0.30 mm. Monoclinic, space group *C*2/*c* (no. 15). Cell parameters: a=22.208(2) Å, b=11.1961(9) Å, c=10.5569(5) Å, β=111.354(6)°, V=2444.6(3) Å^3; Z=8, D_{calcd}=1.235 g cm^{-3}, $R1$=0.060 ($I>2\sigma(I)$), $wR2$=0.176 (all reflections). Crystal structure analysis of **7g**: $C_{16}H_{15}NO_2$, FW=253.30, colorless, prismatic, 0.40×0.40×0.20 mm. Orthorhombic, space group $P2_12_12_1$ (no. 19). Cell parameters: a=10.4215(11) Å, b=14.858(2) Å, c=8.7585(9) Å, V=1356.2(3) Å^3; Z=4, D_{calcd}=1.240 g cm^{-3}, $R1$=0.057 ($I>2\sigma(I)$), $wR2$=0.165 (all reflections). CCDC-611071 (**5b**) and CCDC-611072 (**7g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors gratefully thank Prof. Hiroshi Nakazawa and Dr. Masumi Itazaki at Osaka City University for measurements of elemental analyses. Y.N. also acknowledges the Industrial Technology Research Grant Program in 2006 (No. 05A25502d) from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.08.025.

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