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1,3,2,4-Diazadiphosphetidines as new P–N ligands for palladium-catalyzed Heck reaction in water

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ABSTRACT

1,3,2,4-Diazadiphosphetidine-based phosphazane class have been used as a new generation of heterogeneous bidentate P(III) ligands containing nitrogen for base-free Pd(II) catalyzed C–C bond formation through Heck coupling reaction of aryl iodides, bromides and chlorides in water with styrene, *n*-butyl acrylate, 1-octene, and cyclohexene. The reactions occur heterogeneously in water and homogenously or partially heterogeneously in appropriate organic solvents. The ligand together with its Pd(0) complex is easily separated by filtration and reused for several runs.

1. Introduction

Cross-coupling reactions for carbon–carbon bond formation are among the most valuable synthetic methods developed over the past decade.[1] Apart from commonly used triarylphosphine ligands, and development of methods with non-phosphine ligands,[2] great progress has been achieved in the field of catalytic reactions and new phosphine ligands have been developed.[3–5] Due to the low toxicity and stability, nitrogen containing ligands based on aminophosphine,[6] diimine,[7] dipyridine,[8] hydrazone,[9] imidazole,[10] azetidin,[11] and pyridylbenzoimidazoles [12] have also found attention in the recent years. In all of the palladium-catalyzed coupling reactions, the use of an organic or inorganic base may be crucial to the performance of the reaction.

While a variety of media, such as ionic liquids,[13] fluorous solvents,[14] and supercritical carbon dioxide,[15] have been promoted as replacements to organic solvents in metal-catalyzed reactions, the use of water as the solvent is considered as a key characteristic from environmental, non-toxicity, industrial, and economical points of view.[16]

The synthesis and characterization of phosphorus(III) phosphazanes macromolecules containing P and N atoms with connectivity to other skeleton atoms is of considerable interest to inorganic chemists.[17] Reactions that might be expected to yield P(III) polyphosphazanes can also yield four-membered-ring 1,3,2,4-diazadiphosphetidines.[18,19] The 1,3,2,4-diazadiphosphetidine dimmer $[(PhNH)PNPh]_2$ (L_3), trimer $[(PhNH)PNPh]_3(L_2)$[20,21], oligomer $(PhNH)P_2(NPh)_2]_2NPh$ (L_1),[21,22] and (L_4),[23] which contain the *iso*-propylamino group, have been reported to be prepared from the reaction of $PC1_3$ with $PhNH_2$ or *iso*-propylamine under optimized reaction conditions. The ability of these compounds for complex formation have been demonstrated for L_1 and L_2 in their reactions with norbornadiene(nbd)-$Mo(CO)_4$.

It has been shown that $LMo(CO)_4$ ($L{=}L_1$ and L_2) is obtained in which only two of the phosphorous atoms of the ligands incorporated in the complex formation.[24]

The presence of phosphorous and nitrogen atoms in these compounds gives them interesting dual characteristics. They are very useful ligands in which their phosphorous sites bind to the metal and the same time, their nitrogen atoms act as base whenever a base is required in the reaction. The basicity of the nitrogen atoms in these compounds can also be increased by replacement of phenyl group with, for example, *iso*-propyl as it is demonstrated in L_4. The Heck reaction is among those reactions in which phosphine ligands in conjunction with an organic base, such as amines and Pd(II) as catalyst have been widely employed for cross-coupling reactions and therefore, employment of these compounds for this reaction as both ligand and base could be useful.

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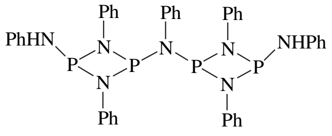
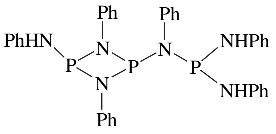


L_1



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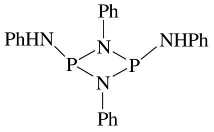
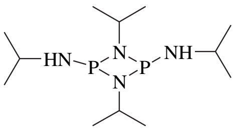


L_3



L_4

Herein, we report the use of easily prepared, oxygen, moisture, and thermally stable 1,3,2,4-diazadiphosphetidine compounds (L_{1-4}) as reusable ligands for Pd(II)-catalyzed Heck coupling reactions of aryl iodides, bromides, and chlorides under base-free condition in water.

2. Results and discussion

All the ligands (L_1–L_4) were prepared according to the literature from the reaction of PCl_3 and $PhNH_2$ or *iso*-propylamine.[20–23] The structure of the obtained phosphazanes depends critically upon the reaction conditions. Using $PhNH_2$–$PC1_3$ mole ratio of (4.7–4.9):1.0 at 110 °C in toluene, dinuclear 1,3,2,4-diazadiphosphetidine oligomer $[(PhNH)P_2(NPh)_2]_2NPh$ (L_1) is obtained in near quantitative yield.[22] At a slightly higher $PhNH_2$–$PC1_3$ ratio (5.0–5.1):1.0 and lower reaction temperature (25 °C), the main products of reaction are the two- and three-phosphorus phosphazane dimer and trimer $[(PhNH)PNPh]_2$ (L_3) and $[(PhNH)PNPh]_3$ (L_2).[22] Replacement of $PhNH_2$ with *iso*-propylamine yields L_4 as the major product.[23]

In a comparative study, we applied these compounds in conjunction with $PdCl_2$ as pre-catalyst for the Heck coupling reaction of bromobenzene and styrene in different organic solvents as well as in water at 100 °C (Fig. 1). Our preliminary studies showed that the coupling reaction can take place efficiently without adding any internally base.

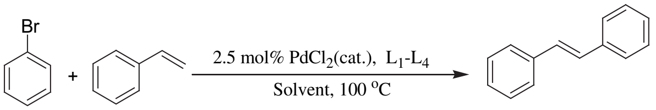


Figure 1. Reaction of bromobezene with styrene.

Results (Table 1) show that all four compounds (L_1–L_4) are very efficient and suitable ligands for the coupling reaction of bromobenzene and styrene in water with Pd(II) as pre-catalyst. On the basis of higher atom economy for L_1 compared to others, complete heterogeneous nature of its reaction and also higher yield for its preparation, this ligand was selected as the ligand of choice for this reaction in water. We then tried this reaction with L_1 in other solvents, such as DMF, DMSO, toluene, acetonitrile, and THF.

Table 1
Coupling of 1.0 mmol bromobezene with 1.5 mmol styrene in the presence of L_1–L_4 using 2.5 mol % of $PdCl_2$ without adding any internally base at 100 °C

Entry	Ligand	Solvent	Ligand[a] (mmol)	Time (h)	Condition	Conversion yield[b] %
1	L_1	H_2O	0.4	0.75	Heterogeneous	100
2	L_2	H_2O	0.53	0.75	Heterogeneous	95
3	L_3	H_2O	0.8	0.75	Partially soluble	95
4	L_4	H_2O	0.8	0.5	Partially soluble	100
5	L_1	Toluene	0.4	22	Homogeneous	90
6	L_1	DMF	0.4	4.5	Partially soluble	100
7	L_1	DMSO	0.4	6	Partially soluble	100
8	L_4	DMF	0.8	2	Partially soluble	100
8	L_1	Acetonitrile	0.4	20	Partially soluble	25
9	L_1	THF	0.4	20	Partially soluble	30

[a] Equal amounts of phosphorous are present in each reaction using L_1–L_4.
[b] Conversion yield is based on GC analysis using *n*-octane as internal standard.

Compared with the reaction on water, which takes 45 min, the coupling reaction of bromobenzene and styrene in the presence of L_1 in toluene is homogeneous and complete after 22 h. Use of DMF and DMSO provides shorter reaction times and the reactions completes in 4.5 and 6 h, respectively. Use of acetonitrile and THF is not successful and only 25 and 30% conversion yield was observed.

Among the solvents studied for this reaction, water was selected as the solvent of choice and we continued our studies using L_1 as the selected ligand and optimized the amount of ligand (L_1) and also Pd(II) pre-catalyst (Table 2).

Table 2
Optimization of the amounts of ligand (L_1) and $PdCl_2$ in the reaction of 1.0 mmol bromobenzene and 1.5 mmol styrene in refluxing water

	$PdCl_2$ (mmol)	Ligand (L_1) (mmol)	PhBr (mmol)	Styrene (mmol)	Time (h)	Coversion yield[a] %
1	0.05	0.6	1.0	1.1–1.5	0.5	100
2	0.05	0.4	1.0	1.1–1.5	0.5	100
3	0.05	0.3	1.0	1.1–1.5	1.0	90
4	0.05	0.2	1.0	1.1–1.5	1.5	90
5	0.05	0.1	1.0	1.1–1.5	1.5	80
6	0.025	0.25	1.0	1.1–1.5	1.5	80
7	0.025	0.4	1.0	1.1–1.5	0.75	100

[a] Conversion yield is based on GC analysis using *n*-octane as internal standard.

The optimized amounts of Pd(II) and the ligand (L_1) for the reaction of bromobenzene and styrene in water at 100 °C are shown in entry 7 of Table 2.

The effect of temperature on the reaction of bromobenzene and styrene in water using the optimized amounts of L_1 (0.4 mmol) and $PdCl_2$ (0.025 mmol) (Table 2, entry 7) was also studied and the results are shown in Table 3. As it indicates, complete conversion of the reaction can occur even at 70 °C after 5 h.

Table 3
Coupling of bromobenzene with styrene in water at different temperature

Temperature(°C)	100	80	70	50	40
Time (h)	0.75	2	5	8.0	10
Conversion (%)	100	100	100	80	0

Having optimized conditions (0.4 mmol of L_1, 0.025 mmol of $PdCl_2$, no internally added base and refluxing water), we applied these conditions to the coupling reactions of varieties of aryl iodides and bromides with styrene and also *n*-butyl acrylate (Fig. 2) in high yields. The reaction can also be successfully achieved with aryl chlorides but at harsher reaction conditions using sealed tube and 120 °C. The results are shown in Tables 4 and 5. The desired products were simply isolated by diethyl ether extraction.

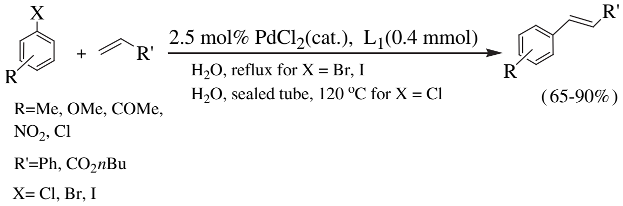
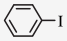
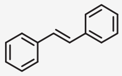
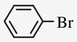
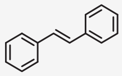
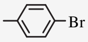
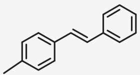
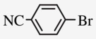
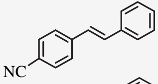
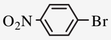
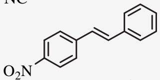
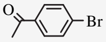
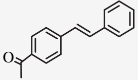
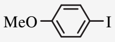
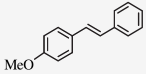
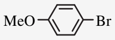
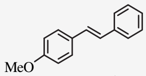
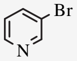
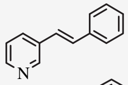
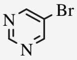
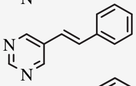
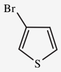
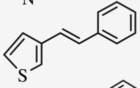
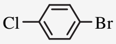
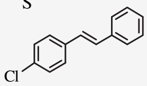
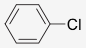
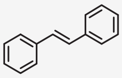
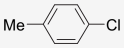
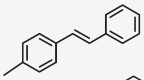
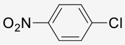
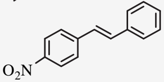


Figure 2.

This catalytic system proved efficient for a wide array of aromatic bromides and iodides. Complete conversion was achieved in the reactions of bromobenzene and 4-bromotoluene with styrene after 45 and 50 min, respectively (Table 4, entries 2, 3). 4-Iodoanisole, for example, was completely converted into the coupled products after

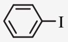
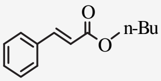
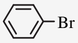
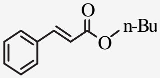
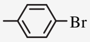
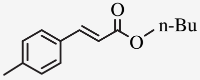
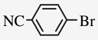
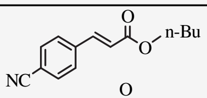
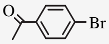
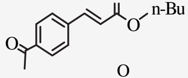
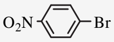
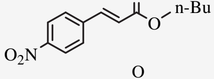
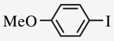
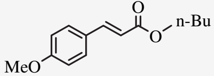
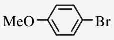
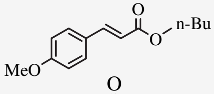
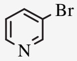
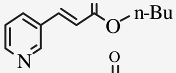
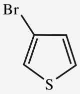
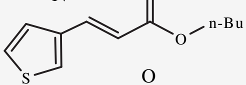
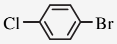
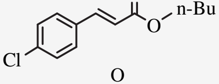
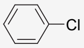
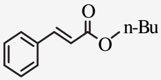
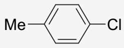
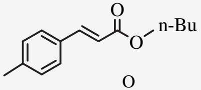
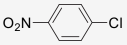
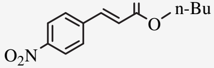
Table 4
Heck reaction of aryl halides and styrene in the presence of L_1 in refluxing water

Entry	Ar-X	Product[a]	Time (h)	Isolated yield (%)
1			0.5	91
2			0.75	90
3			1	89
4			5	82
5			15	85
6			12	75
7			1	90
8			2	87
9			3.5	70
10			4.5	75
11			0.5	90
12			4	80
13			10[b]	85
14			10[b]	83
15			10[b]	65

[a] All products are known compounds and were identified by comparison of their physical or spectroscopic data with those of known samples.[25–27]

[b] The reaction was placed in a sealed tube at 120 °C.

Table 5
Heck reaction between aryl halides and *n*-butyl acrylate in the presence of L_1

Entry	Ar-X	Product[a]	Time (h)	Isolated yield (%)
1			0.75	87
2			0.75	85
3			1.5	79
4			4.5	80
5			6	70
6			16	80
7			1.5	87
8			2.5	80
9			3	72
10			1	85
11			3.5	80
12			10[b]	85
13			10[b]	86
14			15[b]	65

(*continued on next page*)

Table 5 (*continued*)

[a] All products are known compounds and were identified by comparison of their physical or spectroscopic data with those for known samples.[25–27]

[b] The reaction was placed in a sealed tube at 120 °C.

1 h (Table 4, entry 7). With electron-deficient bromides, increasing reaction times were observed, along with a lowering of product yields (Table 4, entries 4–6). We thought that this could be due to the lower solubility of 4-bromobenzonitrile, 4-bromoacetophenone, and 1-bromo-4-nitrobenzene in water. We therefore repeated the reaction using an aqueous solution of SDS (10 mol %) instead of water. However, not appreciable improvement in the reaction yield was observed.

As illustrated in Table 4, entries 9–11, the Heck cross-coupling reactions were also applicable to heteroaryl halides. Use of 3-bromopyridine, 3-bromothiophene, and styrene as substrates gave a satisfactory result and the desired products were isolated in 70% and 90% yield, respectively.

The use of this system for coupling of aryl chlorides and styrene was also successful at 120 °C in sealed tube (Table 4, entries 13–15).

The coupling reactions with *n*-butyl acrylate were performed under the same reaction conditions as used for styrene and good to high yields of the coupled products were obtained (Table 5).

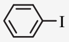
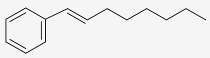
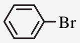
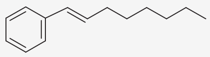
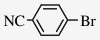
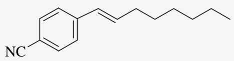
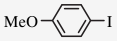
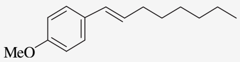
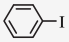
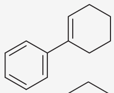
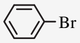
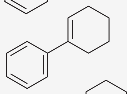
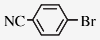
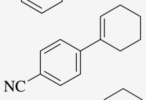
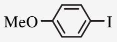
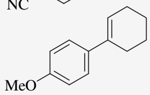
The trans products, as confirmed by ^{1}H NMR spectroscopic analysis, were obtained exclusively in all the cases that we present in this article. In the case of *n*-butyl acrylate, trace amounts of biphenyl (3–10%) was also observed as by-product.

Although the coupling reaction of aryl halides with styrene and electron-deficient alkenes have been widely studied, but the coupling reaction with unsubstituted olefins is rarely investigated.[28] In order to extend the applicability of L_1 in the Heck coupling reaction, we decided to study the behavior of simple olefins in this reaction.

We therefore performed the Heck coupling reaction of some aryl iodides and bromides with 1-octene in water at 100 °C employing L_1

as ligand in the absence of any external base. Interestingly, the reactions occurred successfully in the presence of catalytic amounts of $PdCl_2$ (0.025 mmol) and produced the coupled products. The desired products were obtained in high yields for the reactions of bromo and iodobenzene and also their substituted ones with 1-octene and cyclohexene under reflux condition in water (Table 6). The desired products were isolated simply by extraction with diethyl ether.

Table 6
Heck reactions of aryl halides with 1-octene and cyclohexene in the presence of L_1 in water using 2.5 mol % of $PdCl_2$

Entry	Ar-X	Product[a]	Time (h)	Isolated yield (%)
1			0.75	77
2			1	75
3			4	70
4			3.5	72
5			1. 5	71
6			0.83	70
7			4	69
8			3.5	70

[a] These products are known compounds and were identified by comparison of their physical or spectroscopic data with those of known samples.[28–30]

In order to gain some insight into the structure of the complex, we used mole ratio technique.[31] The use of this method for the complex formation between L_1 ligand and $PdCl_2$ suggests the possibility of having ML_2 structure for the pre-catalyst.

The presence of Pd(0) in the complex was studied by X-ray Powder Diffraction. The diffraction rings can be ascribed to the (111), (200), (220), and (311) crystallographic planes of the Pd(0) particles.[32] The same results were also obtained for the XRD patterns of the catalysts after its use in the coupling reaction of bromobenzene and styrene for atleast 10 cycles. This reveals the excellent stability and recovery of the catalysts.

As shown in (Fig. 3), the catalytic activity of ML_2 catalyst remained largely unchanged for 10 successive runs for the reaction of bromobenzene and styrene in water as solvent.

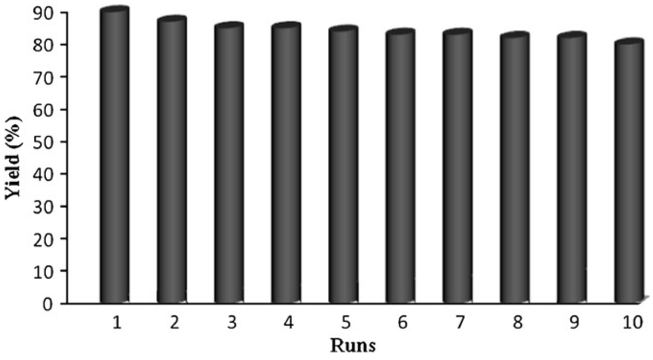


Figure 3. Recyclability of the catalyst in the synthesis of stilbene.

3. Conclusions

In summary, the use of 1,3,2,4-diazadiphosphetidine, oligomer $(PhNH)P_2(NPh)_2]_2NPh$ (L_1) as both the base and ligand in Pd(II) catalyzed Heck reaction of aryl halides with activated and non-activated double bonds provides a useful protocol for the efficient carbon–carbon bond formation. This can be regarded as the first synthetic application for this important class of phosphazanes. The ease of synthesis of L_1 in high yield from simple starting materials, and reusability of the ligand and its Pd(0) complex can also be considered as strong practical advantages of this method. The use of this ligand provides the possibility of performing the reaction in water under heterogeneous reaction conditions.

4. Experimental

4.1. General

Chemicals were obtained from Fluka or Merck chemical companies. The Progress of the reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates or by GC using a Shimadzu gas chromatograph GC-14A, equipped with a flame ionization detector and a 3-meter length glass column packed with DC-200 stationary phase and nitrogen as the carrier gas. IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 FT-NMR spectrometer. Melting points were determined with a Büchi 510 instrument in open capillary tubes and are uncorrected. All yields refer to the isolated products. Evaporation of solvents was performed at reduced pressure, with a Büchi rotary evaporator. The absorbance measurements as a function of time, at a fixed wavelength, were made with a Shimadzu UV 1601PC spectrophotometer.

4.2. Typical procedure for the Heck reaction between bromobenzene and styrene

$PdCl_2$ (0.025 mmol, 4.4 mg) was placed in a flask containing L_1 (0.4 mmol, 0.30 g) in water. The flask was placed in a 100 °C oil bath and stirred for 15 min. Then bromobenzene (1.0 mmol, 0.105 mL) and styrene (1.5 mmol, 0.16 mL) were added to the mixture. GC and TLC analysis of the reaction mixture showed the completion of the reaction after 45 min. After completion of reaction, the mixture was cooled to room temperature and *trans*-stilbene was extracted with diethyl ether (3×5 mL). Evaporation of the solvent followed by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate (5/1) as eluent gave, *trans*-stilbene (white solid; 90% yield (0.162 g). Mp lit.[26] 123–124 °C, found 121–123 °C; ^1H NMR (250 MHz, $CDCl_3$): δ=7.53 (d, J=7.5 Hz, 4H), 7.45 (t, J=7.5 Hz, 4H), 7.35 (t, J=7.5 Hz, 2H), 7.26 (s, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=139.5, 130.5, 128.5, 126.7, 128.5 ppm). (Table 4, entry 2).

4.3. Typical procedure for the Heck reaction between bromobenzene and *n*-butyl acrylate

To a flask containing L_1 (0.4 mmol, 0.30 g) in water, $PdCl_2$ (0.025 mmol, 4.4 mg) was added at 100 °C and stirred for 15 min. Then bromobenzene (1.0 mmol, 0.105 mL) and *n*-butyl acrylate (2.0 mmol, 0.28 mL) were added to the mixture. GC and TLC analysis of the reaction mixture showed the completion of the reaction after 45 min. After completion of reaction, the mixture was cooled to room temperature and butyl *trans*-cinnamate was extracted with diethyl ether (3×5 mL). Evaporation of the solvent followed by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate (5/1) as eluent gave, butyl *trans*-cinnamate (Colorless, oily; 85% yield (0.174 g). ^1H NMR (250 MHz, $CDCl_3$): δ=7.80 (d, J=16 Hz, 1H), 7.66 (m, 2H), 7.43 (m, 3H), 6.75 (d, J=16 Hz, 1H), 4.45 (t, J=6.8 Hz, 2H), 2.65 (m,

J=7.3 Hz, 2H), 1.80 (m, J=7.3 Hz, 2H), 1.05 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=170.5, 151.5, 140.8, 135.6, 130.2, 129.5, 120.8, 71.6, 35.0, 22.2, 15.5 ppm). (Table 5, entry 2).

4.4. Typical procedure for the Heck reaction between chlorobenzene and styrene in sealed tube

$PdCl_2$ (0.025 mmol, 4.4 mg) was placed in a glass tube containing L_1 (0.4 mmol, 0.30 g) in water (3 mL). Then, chlorobenzene (1.0 mmol, 0.101 mL) and styrene (1.5 mmol, 0.16 mL) were added to the mixture. The tube was placed in the liquid nitrogen, evacuated and was sealed simultaneously. The sealed tube was placed in a 120 °C oil bath. GC and TLC analysis of the reaction mixture after 10 h showed the completion of the reaction. After completion of reaction, the mixture was cooled to room temperature and *trans*-stilbene was extracted with diethyl ether (3×5 mL). Evaporation of the solvent followed by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate (5/1) as eluent gave, *trans*-stilbene (0.153 g, 85%) (Table 4, entry 13).

4.5. Characterization of the products

4.5.1. trans-Stilbene[26,27]. Table 4, entry 1; white solid; 90% yield (0.162 g). Mp lit.[26] 123–124 °C, found 121–123 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.53 (d, J=7.5 Hz, 4H), 7.45 (t, J=7.5 Hz, 4H), 7.35 (t, J=7.5 Hz, 2H), 7.26 (s, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=139.5, 130.5, 128.5, 126.7, 128.5 ppm.

4.5.2. 4-Methyl-trans-stilbene[27]. Table 4, entry 3; white plates; 90% yield (0.175 g). Mp lit.[27] 117–118 °C, found 116–118 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.42 (d, J=8.5 Hz, 2H), 7.31 (d, J=8.0 Hz, 2H), 7.20 (t, J=7.5 Hz, 2H), 7.15 (t, J=6.5 Hz, 1H), 7.05 (d, J=8.0 Hz, 2H), 6.96 (d, J=16.5 Hz, 1H), 6.90 (d, J=16.5 Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=136.7, 136.3, 134.2, 130.5, 129.8, 128.7, 127.8, 127.2, 126.0, 126.0, 23.0 ppm.

4.5.3. 4-Cyano-trans-stilbene[3e,33]. Table 4, entry 4; pale yellow plates; 80% yield (0.164 g). Mp lit.[33] 117.4–117.7 °C, found 118–119 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.45–7.60 (m, 6H), 7.49 (t, J=7.5 Hz, 2H), 7.40 (t, J=7.45 Hz, 1H), 7.20 (d, J=16.5 Hz, 1H), 7.02 (d, J=16.5 Hz, 1H) ppm.

4.5.4. 4-Nitro-trans-stilbene[3e,25–27]. Table 4, entry 5; yellow plates; 85% yield (0.191 g). Mp lit.[26] 156–157 °C, found 155–157 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.40 (d, J=9.3 Hz, 2H), 7.80 (d, J=9.3 Hz, 2H), 7.71 (d, J=7.3 Hz, 2H), 7.45–7.55 (m, 3H), 7.37 (d, J=16 Hz, 1H), 7.23 (d, J=16.5 Hz, 1H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=152.2, 149.9, 140.5, 135.5, 130.1, 129.0, 128.5, 128.0, 127.0, 125.5 ppm.

4.5.5. 4-Acetyl-trans-stilbene[3e,25–27]. Table 4, entry 6; white plates; 75% yield (0.166 g). Mp lit.[26] 138.7–144.8 °C, found 142–145 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.90 (d, J=8.0 Hz, 2H), 7.70 (d, J=8.0 Hz, 2H), 7.40 (d, J=8.0 Hz, 2H), 7.30–7.35 (m, 3H), 7.20 (d, J=16.5 Hz, 1H), 7.01 (d, J=16.5 Hz, 1H), 2.15 (s, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=194.5, 144.5, 137.9, 137.5, 130.7, 129.8, 129.8, 128.0, 127.8, 127.0, 125.0, 30.5 ppm.

4.5.6. 4-Methoxy-trans-stilbene[27]. Table 4, entry 7; pale yellow plates; 90% yield (0.189 g). Mp lit.[27] 135.4–137.1 °C, found 135–137 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.42 (d, J=7.5 Hz, 2H), 7.37 (d, J=8.5 Hz, 2H), 7.28 (t, J=7.5 Hz, 2H), 7.18 (t, J=6.5 Hz, 1H), 6.99 (d, J=16.0 Hz, 1H), 6.89 (d, J=16.5 Hz, 1H), 6.80 (d, J=8.5 Hz, 2H), 3.77 (s, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=160.5, 138.8, 130.9, 129.5, 128.0, 127.5, 127.0, 126.5, 126.0, 116.5, 57.5 ppm.

4.5.7. trans-3-Styrylpyridine[27]. Table 4, entry 9; pale yellow plates; 70% yield (0.127 g). Mp lit.[27] 78.6–81.6 °C, found 79–81 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.70 (s, 1H), 8.50 (d, J=4.8 Hz, 1H), 7.90 (d, J=8.3 Hz, 1H), 7.65 (d, J=7.3 Hz, 2H), 7.30 (t, J=7.3 Hz, 2H), 7.15–7.25 (m, 2H), 7.08 (d, J=16.5 Hz, 1H), 6.90 (d, J=16.0 Hz, 1H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=150.5, 149.5, 138.8, 135.0, 133.3, 130.0, 129.7, 127.6, 126.0, 125.0, 121.0 ppm.

4.5.8. 5-Styryl-pyrimidine[3e,25–27]. Table 4, entry 10; pale-yellow solid; 75% yield (0.137 g). Mp lit.[3e] 68–70 °C, found 69–70 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=9.01 (s, 1H), 8.79 (s, 2H), 7.45–7.48 (d, J=7.2, 2H), 7.23–7.48 (m, 3H), 7.17 (d, J=16.5, 1H), 6.92 (d, J=16.5, 1H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=156.9, 154.2, 132.9, 128.9, 128.4, 126.8, 120.9 ppm.

4.5.9. 3-Styryl-thiophene[3e,25–27]. Table 4, entry 11; brown solid; 90% yield (0.168 g). Mp lit.[34] 118–120 °C, found 117–118 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=6.85 (d, J=16.2, 1H), 7.04 (d, J=16.2, 1H), 7.15–7.28 (m, 5H), 7.38 (d, J=7.0, 2H), 7.40 (s, 1H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=140.1, 137.3, 128.6, 128.1, 127.4, 126.2, 125.6, 124.9, 122.9, 122.3 ppm.

4.5.10. 4-Chloro-trans–stilbene[3e,25–27]. Table 4, entry 12; white plates; 80% yield (0.172 g). Mp lit.[35] 127–130 °C, found 129–130 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.80 (d, J=7.3 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H), 7.30–7.44 (m, 5H), 7.20 (s, 2H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=140.0, 137.9, 135.5, 131.3, 129.9, 129.5, 128.2, 127.5, 127.0, 125.5 ppm.

4.5.11. trans-Cinnamic acid butyl ester[3e,25–27]. Table 5, entry 1; colorless, oily; 85% yield (0.174 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.80 (d, J=16 Hz, 1H), 7.66 (m, 2H), 7.43 (m, 3H), 6.75 (d, J=16 Hz, 1H), 4.45 (t, J=6.8 Hz, 2H), 2.65 (m, J=7.3 Hz, 2H), 1.80 (m, J=7.3 Hz, 2H), 1.05 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=170.5, 151.5, 140.8, 135.6, 130.2, 129.5, 120.8, 71.6, 35.0, 22.2, 15.5 ppm.

4.5.12. trans-4-Methyl-cinnamic acid butyl ester[3e,25–27]. Table 5, entry 3; pale-yellow liquid; 80% yield (0.175 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.87 (d, J=16 Hz, 1H), 7.55 (d, J=8.5 Hz, 2H), 7.25 (d, J=8.5 Hz, 2H), 6.60 (d, J=16 Hz, 1H), 4.90 (t, J=6.5 Hz, 2H), 2.80 (s, 3H), 1.99 (m, J=6 Hz, 2H), 1.20 (m, J=7.3 Hz, 2H), 0.88 (t, J=7.5 Hz, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=175.5, 150.6, 144.5, 130.0, 129.0, 128.5, 119.0, 70.5, 41.3, 25.7, 17.5, 13.0 ppm.

4.5.13. trans-4-Cyanocinnamic acid butyl ester[3e]. Table 5, entry 4; white plates; 80% yield (0.183 g). Mp lit.[27] 43.5–46.9 °C, found 44–46 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.82–7.69 (m, 5H), 6.90 (d, J=16 Hz, 1H), 5.45 (t, J=6.6 Hz, 2H), 2.23 (m, J=7.3 Hz, 2H), 1.99 (m, J=7.3 Hz, 2H), 1.07 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=184.5, 163.3, 151.2, 145.5, 133.7, 128.2, 121.9, 119.0, 86.5, 42.8, 25.5, 16.7 ppm.

4.5.14. trans-4-Acetylcinnamic acid butyl ester[25–27]. Table 5, entry 5; pale-yellow liquid; 70% yield (0.172 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.11 (d, J=8.5 Hz, 2H), 7.89 (d, J=15.5 Hz, 1H), 7.72 (d, J=8.5 Hz, 2H), 6.92 (d, J=16 Hz, 1H), 5.35 (t, J=7.5 Hz, 2H), 3.98 (s, 3H), 2.56 (m, J=7.5 Hz, 2H), 1.98 (m, J=7.5 Hz, 2H), 1.06 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ=195.5, 172.5, 155.0, 146.5, 141.5, 132.6, 130.8, 125.5, 88.3, 45.0, 33.4, 23.4, 16.0 ppm.

4.5.15. trans-4-Nitrocinnamic acid butyl ester[3e,27]. Table 5, entry 6; pale-yellow solid; 80% yield (0.199 g). Mp lit.[27] 59.6–64.4 °C, found 60–63 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.65 (d, J=8.7 Hz, 2H), 7.98–7.88 (m, 3H), 7.09 (d, J=15.5 Hz, 1H), 5.65 (t, J=7 Hz, 2H), 2.45 (m, J=7.8 Hz, 2H), 1.86 (m, J=7.5 Hz, 2H), 1.08 (t, J=7.5 Hz, 3H); ^{13}C NMR (60 MHz, CDCl$_3$): δ=184.0, 166.5, 155.5, 138.7, 133.5, 129.5, 123.3, 87.7, 54.4, 28.8, 15.5 ppm.

4.5.16. trans-4-Methoxycinnamic acid n-butyl ester[3e]. Table 5, entry 7; pale-yellow liquid; 85% yield (0.199 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=1.07 (t, J=7.5 Hz, 3H), 1.30–1.42 (m, 2H), 1.59–1.70 (m, 2H), 3.67 (s, 3H), 4.05 (t, J=6.7 Hz, 2H), 6.46 (d, J=16.0, 1H), 6.70–6.90 (m, 2H), 7.35–7.50 (m, 2H), 7.65 (d, J=16.0, 1H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=162.43, 159.091, 150.21, 126.72, 125.08, 118.05, 110.05, 60.19, 44.34, 35.67, 21.20, 12.05 ppm.

4.5.17. trans-3-(3-Pyridinyl)acrylic acid butyl ester[3e]. Table 5, entry 9; colorless, oily; 70% yield (0.144 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=8.85 (s, 1H), 8.72 (m, 1H), 7.75 (d, J=8.5 Hz, 1H), 7.57 (d, J=16 Hz, 1H), 7.24 (m, 1H), 6.79 (d, J=16.5 Hz, 1H), 5.09 (t, J=6.5 Hz, 2H), 2.23 (m, J=7.3 Hz, 2H), 1.78 (m, J=7.3 Hz, 2H), 1.04 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=187.5, 172.2, 159.9, 138.8, 135.5, 128.5, 123.3, 111.4, 89.9, 56.6, 39.9, 28.4, 15.0 ppm.

4.5.18. 1-Thiophen-3-yl-hept-1-en-3-one[3e,25–27]. Table 5, entry 10; brown liquid; 85% yield (0.179 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.57 (d, J=17.5 Hz, 1H), 7.41 (d, J=8.2 Hz, 1H), 7.27–7.18 (m, 2H), 6.17 (d, J=17.5 Hz, 1H), 4.11 (t, J=7.5 Hz, 2H), 1.62–1.54 (m, 2H), 1.42–1.31 (m, 2H), 0.87 (t, J=7.5 Hz, 3H), ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=166.2, 136.9, 136.5, 127.7, 126.9, 125.8, 116.9, 63.3, 29.7, 18.1, 12.7 ppm.

4.5.19. Butyl trans-4-chlorocinnamate[3e,27]. Table 5, entry 11; white plates; 80% yield (0.191 g). Mp lit.[36] 40 °C, found 38–40 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ=1.09 (t, J=7.4 Hz, 3H), 1.44–1.51 (m, 2H), 1.70–1.85 (m, 2H), 3.99 (t, J=6.7 Hz, 2H), 5.87 (d, J=16.0 Hz, 1H), 7.43–7.50 (m, 2H), 7.54–7.78 (m, 2H), 7.89 (d, J=16.0 Hz, 1H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=175.88, 152.13, 134.40, 130.14, 127.75, 125.50, 108.82, 74.66, 47.55, 25.15, 15.55 ppm.

4.5.20. Oct-1-enyl-benzene[28–30]. Table 6, entry 2; colorless oil; 75% yield (0.141 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.27–7.08 (m, 5H), 6.25–6.18 (m, 2H), 2.16–1.93 (m, 2H), 1.29–1.17 (m, 8H), 0.83–0.78 (t, 3H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=138.00, 133.61, 128.35, 128.24, 128.15, 125.94, 33.11, 32.40, 29.07, 22.63, 22.17, 14.11 ppm.

4.5.21. 4-Oct-1-enyl-benzonitrile[28,29]. Table 6, entry 3; pale yellow oil; 70% yield (0.149 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.58–7.53(m, 2H), 7.43–7.37 (m, 2H), 6.36–6.39 (m, 2H), 2.24–2.20 (m, 2H), 1.47–1.29 (m, 8H), 0.91–0.86 (t, 3H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=138.00, 133.54, 128.25, 128.14, 127.15, 125.86, 114.2, 33.17, 31.30, 29.17, 28.63, 22.37, 14.15 ppm.

4.5.22. 1-Methoxy-4-oct-1-enyl-benzene[28,29]. Table 6, entry 4; colorless oil; 72% yield (0.157 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.25–7.15 (m, 2H), 6.77–6.57 (m, 2H), 6.20–6.02 (m, 2H), 3.70 (s, 3H), 2.13–2.04 (m, 2H), 1.38–1.21 (m, 8H), 0.82–0.79 (t, 3H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=148.10, 132.54, 128.43, 128.27, 127.05, 113.94, 55.20, 32.91, 31.73, 29.67, 29.13, 22.77, 13.99 ppm.

4.5.23. Cyclohex-1-enyl-benzene[29]. Table 6, entry; colorless oil; 70% yield (0.111 g). ^{1}H NMR (300 MHz, CDCl3): δ=7.41–7.20 (m, 5H), 6.14 (br s, 1H), 2.43 (m, 2H), 2.23–2.22 (m, 2H), 1.82–1.76 (m, 2H), 1.71–1.66 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ=142.6, 136.5, 128.2, 126.5, 124.9, 124.8, 27.3, 25.9, 23.0, 22.1 ppm.

4.5.24. 4-Cyclohex-1-enyl-benzonitrile[29]. Table 6, entry 7; pale yellow oil; 69% yield (0.126 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ=7.04–7.09 (m, 2H), 6.75–6.80 (m, 2H), 5.94–5.96 (m, 1H), 3.71 (t, 3H), 2.07–2.67 (m, 4H), 1.48–1.69 (m, 4H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ=145.2, 136.5, 130.3, 129.1, 128.7, 124.3, 26.4, 21.6, 20.4, 19.3 ppm.

4.5.25. 1-Cyclohex-1-enyl-4-methoxy-benzene[29]. Table 6, entry 8; colorless oil; 70% yield (0.132 g); ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.34–7.30 (m, 2H), 6.86–6.83 (m, 2H), 6.05–6.02 (m, 1H), 3.80 (s, 3H), 2.40–2.36 (m, 2H), 2.22–2.16 (m, 2H), 1.79–1.74 (m, 2H), 1.69–1.63 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ=158.3, 135.8, 135.3, 125.9, 123.1, 113.5, 55.2, 27.4, 25.8, 23.1, 22.2 ppm.

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Supplementary data

Supplementary data that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.01.099.

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