Polystyrene-immobilised phenanthroline palladium(II) complex: a highly efficient and recyclable catalyst for oxidative Heck reactions

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Oxidative Heck coupling reactions of arylboronic acids with olefins were carried out in the presence of the polystyrene-immobilised phenanthroline palladium(II) complex using air as a co-oxidant to afford the Heck coupling products in high yields under base-free conditions. This heterogeneous palladium catalyst can be recovered by simple filtration and used for several times without loss of activity or selectivity.

Keywords: oxidative Heck coupling, supported palladium catalyst, phenanthroline palladium complex, arylboronic acid, heterogeneous catalysis

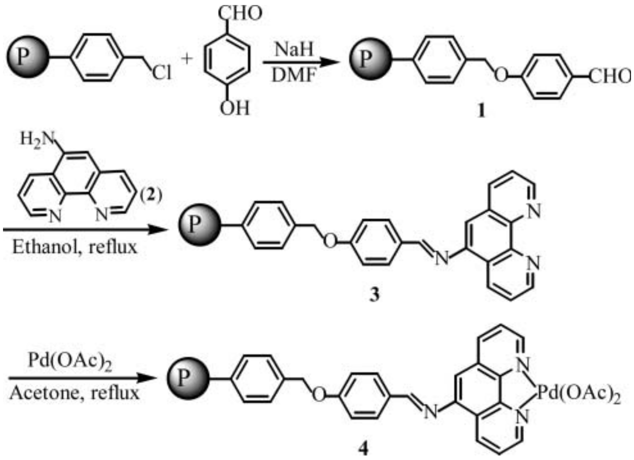
The palladium(II)-catalysed vinylic substitution reaction of arylboronic acids with olefins, known as oxidative Heck coupling, has received considerable attention of organic chemists in recent years.[1–9] The large diversity of readily accessible arylboronic acids, their relative stability in air and moisture, their low toxicity and the ease of boron-derived by-products removal have made oxidative Heck coupling useful tool for carbon-carbon bond formation. Usually, a metal salt such as $Cu(OAc)_2$[2,3] or molecular oxygen[3–7] are used as co-oxidants to reoxidise Pd(0) in the oxidative Heck reactions which, in turn, produces a stoichiometric amount of metal waste or causes problems associated with the use of handling pure oxygen gas. Recently, Larhed *et al.*[9] reported a base-free oxidative Heck reaction in the presence of air using palladium catalysts and nitrogen ligands.

The reported catalytic systems for the oxidative Heck reaction generally involve the use of homogeneous palladium complexes such as $Pd(OAc)_2$, which makes the recovery of the metal tedious if not impossible and might result in unacceptable palladium contamination of the product. From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction, for example, the use of a heterogeneous palladium catalyst would be desirable. Heterogeneous catalysis also helps to minimise wastes derived from reaction workup, contributing to the development of green chemical processes.[10–13] So far, supported palladium catalysts have successfully been used for the conventional Heck coupling reaction of aryl halides,[14–22] however, the heterogeneous palladium-catalysed oxidative Heck reaction has received less attention. In continuing our efforts to develop greener synthetic pathways for organic transformations, we now report a highly efficient and reusable polystyrene-immobilised phenanthroline palladium(II) complex catalyst for the oxidative Heck coupling reactions of arylboronic acids with olefins in the absence of external oxidants and under base-free conditions.

The polystyrene-immobilised phenanthroline palladium(II) complex was easily prepared starting from commercially available Merrifield resin according to Scheme 1. Firstly, Merrifield resin was reacted with 4-hydroxybenzaldehyde in the presence of NaH in anhydrous DMF in 90 °C to afford benzaldehyde-functionalised resin **1**. The resin **1** was subsequently treated with 5-amino-1,10-phenanthroline (**2**) in ethanol at 80 °C for 24 h. After the organics were filtered, the solid was washed with ethanol, diethyl ether and dried in vacuum to give the phenanthroline-functionalised resin **3**. Then the resin **3** was allowed to react with palladium acetate in acetone to generate the polystyrene-immobilised phenanthroline palladium complex catalyst **4** as a light yellow powder, the palladium content of the catalyst was determined by the ICP-AES to be 0.49 mmol/g.

In our initial screening experiments, the reaction between phenylboronic acid (**5a**) and butyl acrylate (**6a**) was investigated to optimise the reaction conditions, and the results are listed in Table 1. At first, the temperature effect was examined, and a significant temperature effect was observed. When the reaction was carried out at 80 °C, a too long reaction time was required although high yield and selectivity could be obtained (entry 1). The reaction rate increased with increase in reaction temperatures. For the temperatures evaluated [80, 90, 100, and 110 °C], 100 °C gave the best result (entry 3). Our next studies focused on the effect of solvent on the model reaction. Among the solvents examined, it turned out that DMF was the best choice (entry 3). While other solvents, such as CH_3CN, EtOH, toluene and DMSO were substantially less effective (entries 5–8). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of butyl-(*E*)-cinnamate **7a** (entry 9). Taken together, excellent result was obtained when the oxidative coupling reaction was carried out with 2.5 mol% of the palladium catalyst **4** in DMF at 100 °C under aerobic conditions (entry 3).

With this promising result in hand, we started to investigate the scope of this reaction under the optimised conditions. The scope of both arylboronic acids and olefins was explored, and the results are summarized in Table 2. From Table 2, it can be seen that the oxidative Heck coupling reactions of a variety of arylboronic acids with butyl acrylate could proceed smoothly under the optimised conditions to afford the corresponding substituted butyl-(*E*)-cinnamates in good to excellent yields (entries 2–9). The electronic effects of the substituents present



Scheme 1

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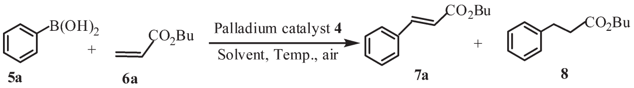
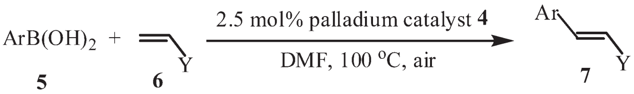
Table 1 Optimisation of reaction conditions for the oxidative Heck coupling of phenylboronic acid (**5a**) with butyl acrylate (**6a**)[a]



Entry	Solvent	Pd loading /mol%	Temperature /°C	Time /h	Yield[b] /%	Selectivity[c] (**7a**:**8**)
1	DMF	2.5	80	48	88	99:1
2	DMF	2.5	90	36	92	99:1
3	DMF	2.5	100	28	94	99:1
4	DMF	2.5	110	25	91	99:1
5	CH_3CN	2.5	80	48	79	99:1
6	EtOH	2.5	80	48	17	99:1
7	Toluene	2.5	110	48	12	99:1
8	DMSO	2.5	110	48	54	99:1
9	DMF	5	100	18	93	99:1

[a]Reaction conditions: phenylboronic acid (1 mmol), butyl acrylate (0.5 mmol), solvent (2.5 mL) under air. [b]Isolated yield of **7a** and **8**. [c]Determined by ^1H NMR and GC.

Table 2 Oxidative Heck coupling of arylboronic acids with olefins in the presence of the polystyrene-immobilised palladium catalyst[a]



Entry	Ar	Y	Time /h	Product	Yield /%[b]	Selectivity /%[c]
1	Ph	CO_2Bu	28	**7a**	94	99
2	4-MeC_6H_4	CO_2Bu	28	**7b**	93	92
3	4-ClC_6H_4	CO_2Bu	28	**7c**	96	98
4	4-$MeOC_6H_4$	CO_2Bu	30	**7d**	88	98
5	4-$O_2NC_6H_4$	CO_2Bu	28	**7e**	91	96
6	3-$O_2NC_6H_4$	CO_2Bu	28	**7f**	93	97
7	4-BrC_6H_4	CO_2Bu	28	**7g**	89	97
8	4-FC_6H_4	CO_2Bu	28	**7h**	88	98
9	4-$MeCOC_6H_4$	CO_2Bu	28	**7i**	91	99
10	Ph	Ph	40	**7j**	85	100
11	4-MeC_6H_4	Ph	40	**7k**	84	100
12	4-ClC_6H_4	Ph	40	**7l**	88	100
13	4-$MeOC_6H_4$	Ph	45	**7m**	81	100
14	4-$O_2NC_6H_4$	Ph	38	**7n**	87	100

[a]Reaction conditions: arylboronic acid (1 mmol), olefin (0.5 mmol), palladium catalyst **4** (2.5 mol%), DMF (2.5 mL) at 100 °C under air. [b]Isolated yield. [c]Selectivity of Heck coupling product determined by ^1H NMR and GC.

on the arylboronic acids do not have a significant effect on the reaction yields (entries 1–9). The selectivity to the Heck product varies between 92 and 99%, but we were not able to observe any direct relationship with the electronic nature of the arylboronic acids. The optimised reaction conditions were also applied to the oxidative Heck coupling of styrene with arylboronic acids. When we employed styrene in the oxidative Heck coupling reaction with phenylboronic acid, *trans*-stilbene was formed exclusively in high yield without any 1,4-addition product, but a longer reaction time was required (entry 10). A variety of arylboronic acids with electron-withdrawing or electron-donating groups were also coupled smoothly with styrene to afford the corresponding substituted *trans*-stilbenes in high yields with excellent selectivity (entries 10–14).

For a heterogeneous catalyst, it is important to examine its ease of separation, good of recoverability and reusability. The reusability of the polystyrene-immobilised phenanthroline palladium(II) catalyst **4** was tested through the repeated reaction of phenylboronic acid with butyl acrylate. After completion of reaction, the catalyst was separated by simple filtration and washed with DMF and acetone. After being air-dried, it can be reused directly without further purification. The recovered catalyst was used in the next run and almost consistent activity was observed for five consecutive cycles (Table 3). The result is important from a practical point of view.

In summary, we have described a novel polystyrene-immobilised phenanthroline palladium(II) complex catalyst whose preparation is simple and convenient. This heterogeneous palladium catalyst has not only high activity for the open air oxidative Heck coupling reaction of olefins with arylboronic acids under base-free conditions, but offers practical advantages such as easy handling, separation from the product and reuse.

Experimental

^1H NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Palladium acetate, Merrifield resin (1.0–1.3 mmol g^{-1}), arylboronic acids, butyl acrylate and styrene were purchased from Sigma-Aldrich and used as received. 5-Amino-1,10-phenanthroline (**2**) was prepared according to the literature procedure.[23]

*Synthesis of benzaldehyde-functionalised resin (***1***)*

A 100 mL, two-necked, round-bottom flask equipped with a magnetic stir bar, and argon was charged sequentially with dry DMF (35 mL), 4-hydroxybenzaldehyde (1.20 g) and sodium hydride (0.45 g). After the mixture was stirred at room temperature for 1 h, the Merrifield resin (4.0 g) was added and the reaction mixture was stirred at 90 °C for 6 h, cooled to room temperature and filtered. The solid product was washed with DMF (10 mL), distilled water (10 mL), and ethanol (3 × 10 mL) and dried under vaccum to afford 4.3 g of benzaldehyde-functionalised resin (**1**).

*Synthesis of phenanthroline-functionalised resin (***3***)*

A 50 mL, two-necked, round-bottom flask equipped with a magnetic stir bar, and argon was charged sequentially with dry ethanol (25 mL), benzaldehyde-functionalised resin **1** (2.0 g), and 5-amino-1,10-phenanthroline **2** (0.41 g, 5 mmol). The reaction mixture was refluxed for 24 h, cooled to room temperature and filtered. The solid product was washed with ethanol (10 mL), diethyl ether (10 mL), and dried under vaccum to give 2.11 g of phenanthroline-functionalised resin **3** as a light yellow powder. The nitrogen content of the resin **3** was determined to be 2.24 mmol/g by CHN microanalysis.

*Synthesis of polystyrene-immobilised phenanthroline palladium catalyst (***4***)*

Phenanthroline-functionalised resin **3** (1.5 g) was added to a solution of $Pd(OAc)_2$ (0.9 mmol) in acetone (50 mL). The mixture was heated at reflux under argon for 72 h. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under argon for 3 h to give 1.51 g of the light yellow polymeric palladium catalyst **4**. The nitrogen and palladium content was 2.03 mmol g^{-1} and 0.49 mmol g^{-1}, respectively.

Oxidative Heck coupling reaction; general procedure

In an oven-dried 15 mL round-bottomed flask, arylboronic acid (1 mmol), olefin (0.5 mmol), palladium catalyst **4** (2.5 mol%) and DMF (2.5 mL) were charged and the reaction mixture was stirred at

Table 3 Reusability study of the palladium catalyst **4** in oxidative Heck reaction of phenylboronic acid with butyl acrylate[a]

Cycle	1	2	3	4	5
Yield/%[b]	94	92	93	92	90

[a]Reaction conditions: phenylboronic acid (1 mmol), butyl acrylate (0.5 mmol), palladium catalyst **4** (2.5 mol%), DMF (2.5 mL) at 100 °C for 28 h under air. [b]Isolated yield.

100 °C under air. After completion of the reaction, as monitored by TLC, the catalyst was filtered, washed with DMF (3 × 10 mL) and acetone (2 × 10 mL), and reused in the next run. The filtrate was diluted with ethyl acetate and washed with 10% NaOH solution, followed by a saturated NaCl solution. The combined organic layer was concentrated under reduced pressure to give the crude product which was purified by flash chromatography on silica gel.

7a: Oil.[24] IR (film): ν (cm^{-1}) 3060, 2925, 2870, 1710, 1630, 1170, 825; ^{1}H NMR (CDCl$_3$): δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.53–7.17 (m, 5H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.12 (t, *J* = 6.4 Hz, 2H), 1.94–1.18 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H).

7b: Oil.[24] IR (film): ν (cm^{-1}) 3030, 2930, 2860, 1715, 1640, 1175, 830; ^{1}H NMR (CDCl$_3$): δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 1.93–1.17 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

7c: Oil.[24] IR (film): ν (cm^{-1}) 3060, 2930, 2865, 1725, 1643, 1173, 850; ^{1}H NMR (CDCl$_3$): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.22 (t, *J* = 6.4 Hz, 2H), 1.90–1.19 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H).

7d: Oil.[24] IR (film): ν (cm^{-1}) 3050, 2930, 2860, 1710, 1635, 1170, 830; ^{1}H NMR (CDCl$_3$): δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.22 (d, *J* = 16.0 Hz, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 3.68 (s, 3H), 1.93–1.18 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

7e: Yellow solid, m.p. 68-69 °C (lit.[24] m.p. 68–70 °C). IR (KBr): ν (cm^{-1}) 3070, 2920, 2860, 1710, 1640, 1515, 1340, 840; ^{1}H NMR (CDCl$_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 16.0 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 6.8 Hz, 2H), 1.96–1.27 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H).

7f: Yellow oil.[25] IR (film): ν (cm^{-1}) 3065, 2923, 2865, 1712, 1638, 1520, 1356, 970; ^{1}H NMR (CDCl$_3$): δ 8.12-7.47 (m, 5H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.4 Hz, 2H), 1.94–1.20 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

7g: Oil.[26] IR (film): ν (cm^{-1}) 3058, 2960, 2875, 1699, 1173, 851; ^{1}H NMR (CDCl$_3$): δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.8 Hz, 2H), 1.92-1.18 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H).

7h: Oil.[27] IR (film): ν (cm^{-1}) 3062, 2957, 2874, 1712, 1645, 1173, 850; ^{1}H NMR (CDCl$_3$): δ 7.52 (d, *J* = 15.6 Hz, 1H), 7.44–7.40 (m, 2H), 6.97–6.93 (m, 2H), 6.27 (d, *J* = 15.6 Hz, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 1.95–1.16 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H).

7i: Oil.[28] IR (film): ν (cm^{-1}) 3057, 2964, 2878, 1714, 1694, 1634, 1173, 830; ^{1}H NMR (CDCl$_3$): δ 7.98–7.94 (m, 2H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.63–7.60 (m, 2H), 6.51 (d, *J* = 15.6 Hz, 1H), 4.22 (t, *J* = 6.4 Hz, 2H), 2.62 (s, 3H), 1.95–1.19 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H).

7j: White solid, m.p. 124 °C (lit.[29] m.p. 124 °C). IR (KBr): ν (cm^{-1}) 3020, 1600, 1498, 760, 690; ^{1}H NMR (CDCl$_3$): δ 7.69–7.13 (m, 10H), 7.09 (s, 2H).

7k: White solid, m.p. 117-118 °C (lit.[30] m.p. 120 °C). IR (KBr): ν (cm^{-1}) 3030, 1596, 1490, 940, 825, 710; ^{1}H NMR (CDCl$_3$): δ 7.65–7.04 (m, 9H), 7.02 (s, 2H), 2.32 (s, 3H).

7l: White solid, m.p. 126–127 °C (lit.[31] m.p. 129 °C). IR (KBr): ν (cm^{-1}) 3060, 1590, 1495, 940, 814, 700; ^{1}H NMR (CDCl$_3$): δ 7.47–7.16 (m, 9H), 7.08 (s, 2H).

7m: White solid, m.p. 134–135 °C (lit.[32] m.p. 136 °C). IR (KBr): ν (cm^{-1}) 3050, 1601, 1500, 1250, 1170, 820, 750; ^{1}H NMR (CDCl$_3$): δ 7.58–7.20 (m, 7H), 7.02 (s, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H).

7n: Yellow solid, m.p. 156–157 °C (lit.[30] m.p. 157 °C). IR (KBr): ν (cm^{-1}) 3046, 1590, 1516, 1500, 1340, 840, 760, 690; ^{1}H NMR (CDCl$_3$): δ 8.32–8.18 (m, 2H), 7.78–7.25 (m, 7H), 7.18 (s, 2H).

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References

1 C.S. Cho and S. Uemura, *J. Organomet. Chem.*, 1994, **465**, 85.
2 X. Du, M. Suguro, K. Hirabayashi and A. Mori, *Org. Lett.*, 2001, **3**, 3313.
3 J.P. Parrish, Y.C. Jung, S.I. Shin and K.W. Jung, *J. Org. Chem.*, 2002, **67**, 7127.
4 M.M.S. Andappan, P. Nilsson and M. Larhed, *Chem. Commun.*, 2004, 218.
5 K.S. Yoo, C.H. Yoon and K.W. Jung, *J. Am. Chem. Soc.*, 2006, **128**, 16384.
6 C. Adamo, C. Amatore, I. Ciofini, A. Jutand and H. Lakmini, *J. Am. Chem. Soc.*, 2006, **128**, 6829.
7 P.A. Enquist, P. Nilsson, P. Sjoberg and M. Larhed, *J. Org. Chem.*, 2006, **71**, 8779.
8 P.A. Enquist, J. Lindh, P. Nilsson and M. Larhed, *Green Chem.*, 2006, **8**, 338.
9 J. Lindh, P.A. Enquist, A. Pilotti, P. Nilsson and M. Larhed, *J. Org. Chem.*, 2007, **72**, 7957.
10 M. Poliakoff, J.M. Fitzpatrick, T.R. Farren and P.T. Anastas, *Science*, 2002, **297**, 807.
11 A. Kirschnig, H. Monenschein and R. Wittenberg, *Angew. Chem. Int. Ed.*, 2001, **40**, 650.
12 N.E. Leadbeater and M. Marco, *Chem. Rev.*, 2002, **102**, 3217.
13 L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.
14 P.-W. Wang and M.A. Fox, *J. Org. Chem.*, 1994, **59**, 5358.
15 M.-Z. Cai, C.-S. Song and X. Huang, *Synthesis*, 1997, 521.
16 S.I. Khan and M.W. Grinstaff, *J. Org. Chem.*, 1999, **64**, 1077.
17 J.H. Clark, D.J. Macquarrie and E.B. Mubofu, *Green Chem.*, 2000, **2**, 53.
18 K. Yu, W. Sommer, J.M. Richardson, M. Week and C.W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161.
19 V. Farina, *Adv. Synth. Catal.*, 2004, **346**, 1553.
20 S.S. Prockl, W. Kleist, M.A. Gruber and K. Koehler, *Angew. Chem. Int. Ed.*, 2004, **43**, 1881.
21 A. Cwik, Z. Hell and F. Figueras, *Adv. Synth. Catal.*, 2006, **348**, 523.
22 M.L. Kantam, K.B.S. Kumar, P. Srinivas and B. Sreedhar, *Adv. Synth. Catal.*, 2007, **349**, 1141.
23 D. Stephanie, D. Eric, M. Cecile, K.-D.M. Andree and D. Pascal, *Tetrahedron Lett.*, 2003, **44**, 8379.
24 M. Miura, H. Hashimoto, K. Itoh and M. Nomura, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2207.
25 P.R. Likhar, M. Roy, S. Roy, M.S. Subhas, M.L. Kantam and B. Sreedhar, *Adv. Synth. Catal.*, 2008, **350**, 1968.
26 E.J. Farrington, J.M. Brown, C.F.J. Barnard and E. Rowsell, *Angew. Chem., Int. Ed.*, 2002, **41**, 169.
27 M. Feuerstein, H. Doucet and M. Santelli, *J. Org. Chem.*, 2001, **66**, 5923.
28 M.M.S. Andappan, P. Nilsson and M. Larhed, *Molecular Diversity*, 2003, **7**, 97.
29 Z.Y. Zhang, H.W. Hu and T.Y. Kao, *React. Polym., Ion Exch., Sorbents*, 1990, **12**, 229.
30 F. Bergmann and D. Schapira, *J. Org. Chem.*, 1947, **12**, 57.
31 A. Sekiguchi and W. Ando, *J. Org. Chem.*, 1979, **44**, 413.
32 A.R. George and R.G.W. Spickett, *J. Chem. Soc.*, 1949, 2724.