Electronic Supplementary Information

High efficiency of cavity-based *triaryl*-phosphines in nickel-catalysed Kumada-Tamao-Corriu cross coupling†

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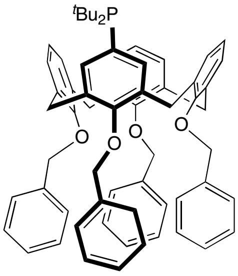
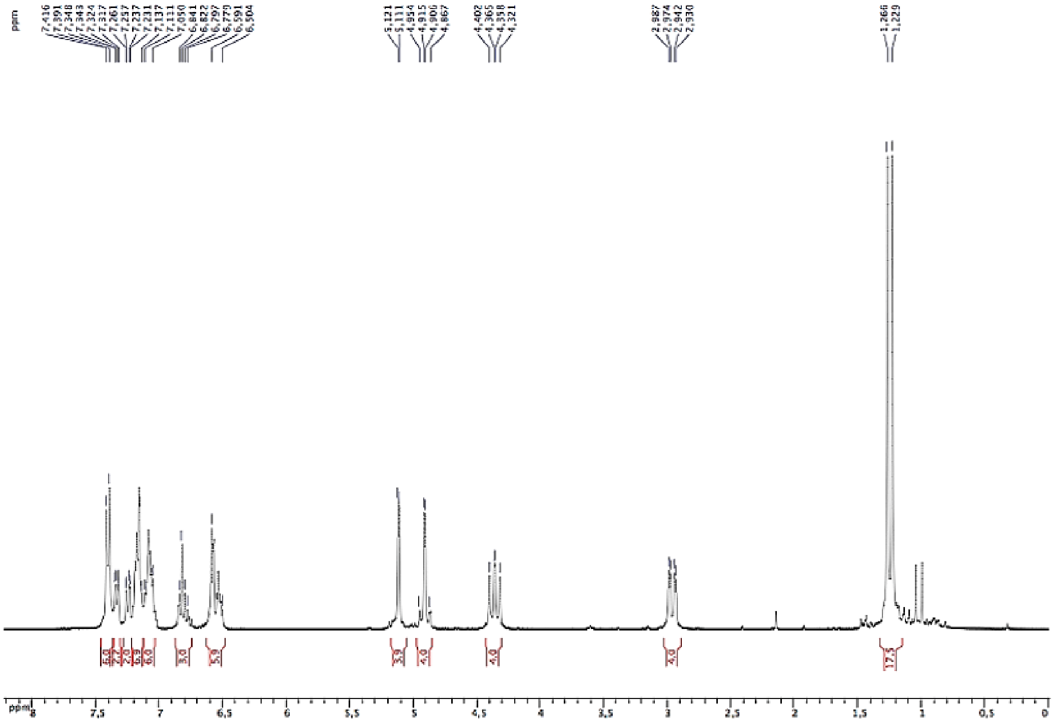
Synthesis of **6** *and characterising data*



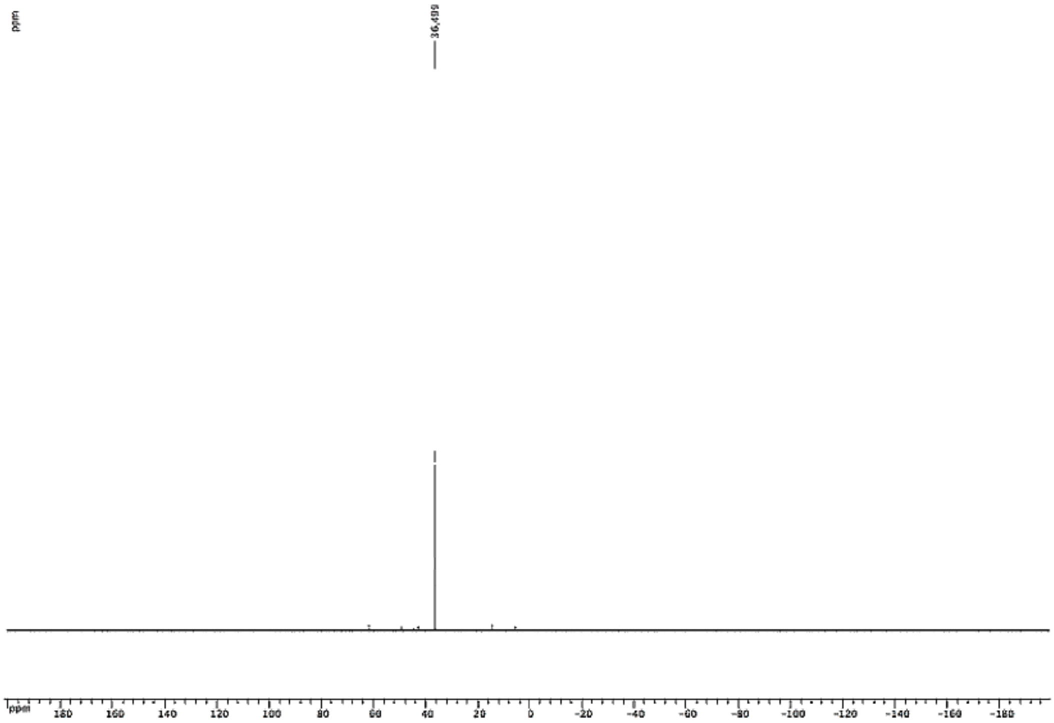
5-di-(*tert*-Butyl)phosphanyl-25,26,27,28-tetrabenzyloxy-calix[4]arene (**6**)

5-di-(*tert*-Butyl)phosphanyl-25,26,27,28-tetrabenzyloxy-calix[4]arene (**6**): *t*-Butyllithium (2.3 mmol) was slowly added to a solution of 5-bromo-25,26,27,28-tetrabenzyloxy-calix[4]arene (1.1 mmol) in THF (50 mL) at -78°C. After 0.5 h, the generated carbanion was quenched with chlorodi-*tert*-butylphosphine (2.3 mmol). The mixture was stirred at 50°C for 16 h. The reaction mixture was then evaporated. The resulting solid was extracted with toluene (20 mL) and the solution filtered through aluminium oxide. The aluminium oxide was washed with toluene (2 x 15 mL). The toluene solution was evaporated under reduced pressure. The calixarene monophosphane was purified by column chromatography on silica gel by using first CH_2Cl_2/hexane (50 : 50, *v*/*v*), then CH_2Cl_2/MeOH (95 : 5, *v*/*v*) as the eluents. Yield: 0.255 g, 25 %. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.40 (d, 6H, benzyl ArH, ^3J = 7.5 Hz), 7.33 (dd, 2H, benzyl ArH, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 7.25 (dd, 2H, benzyl ArH, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 7.19-7.14 (m, 6H, benzyl ArH), 7.11-7.03 (m, 6H, benzyl and calix ArH), 6.82 (t, 2H, calix ArH, ^3J = 7.5 Hz), 6.77 (t, 1H, calix ArH, ^3J = 7.4 Hz), 6.59-6.50 (m, 6H, calix ArH), 5.12 (s, 2H, CH_2Ph), 5.11 (s, 2H, CH_2Ph), 4.93 and 4.89 (AB spin system, 4H, CH_2Ph, ^2J = 11.7 Hz), 4.38 and 2.96 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.2 Hz), 4.34 and 2.95 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.2 Hz), 1.25 (d, 18H, $C(CH_3)_3$, $^3J_{PH}$ = 11.1 Hz) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 156.21, 155.59 and 155.10 (3s, Ar Cq-O), 137.96–122.68 (Ar C), 76.65 (s, OCH$_2$Ph), 76.34 (s, OCH$_2$Ph), 75.90 (s, OCH$_2$Ph), 31.62 (d, $C(CH_3)_3$, $^1J_{PC}$ = 22.2 Hz), 31.56 (s, ArCH_2Ar), 31.52 (s, ArCH_2Ar), 30.45 (d, $C(CH_3)_3$, $^2J_{PC}$ = 14.8 Hz) ppm. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ = 36.5 (s, P^{t}Bu$_2$) ppm.

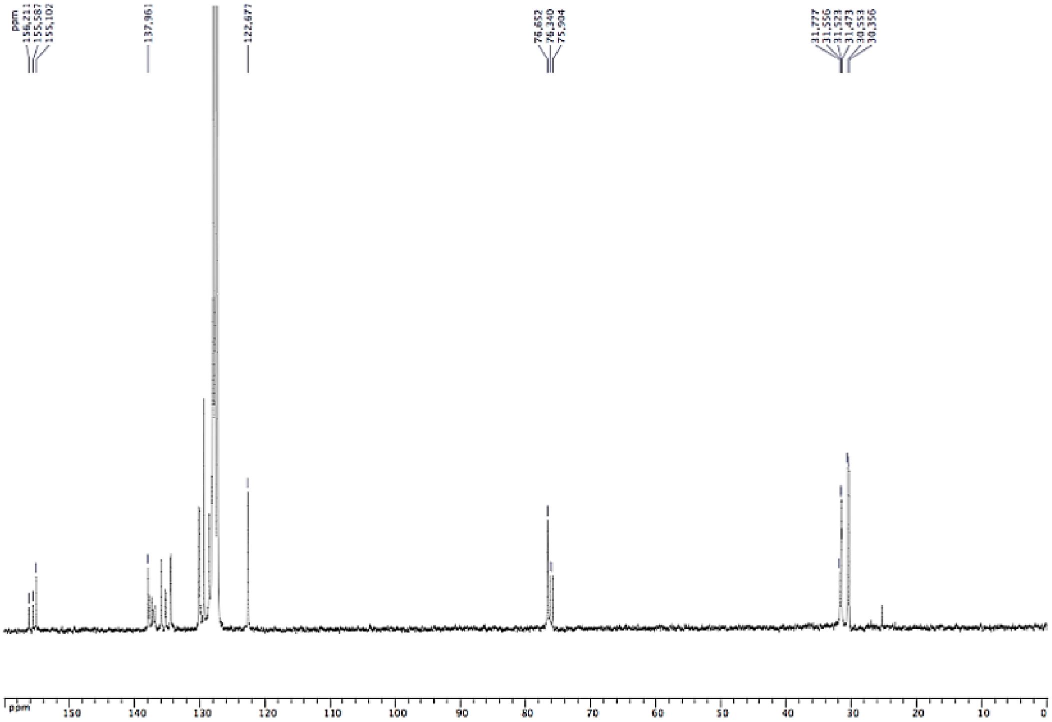
The following NMR spectra were recorded in C_6D_6 at 25 ºC.



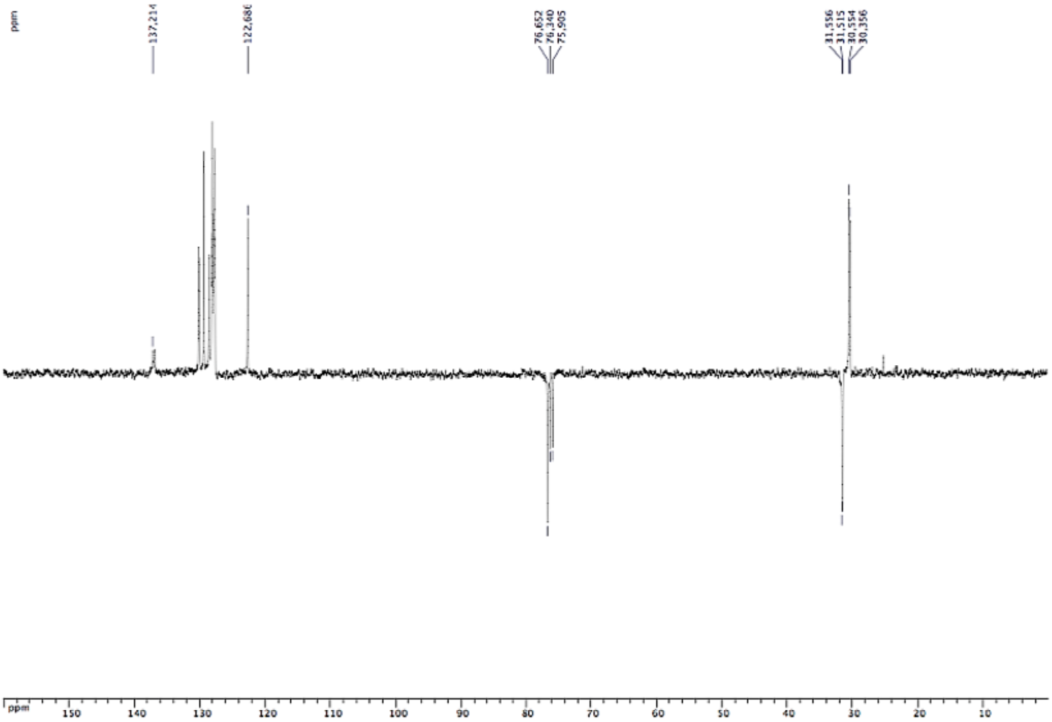
^{1}H NMR spectrum of **6**.



^{31}P NMR spectrum of **6**.



$^{13}C\{^1H\}$ NMR spectrum of **6**.



DEPT 135 spectrum of **6**.

Typical procedure for the nickel-catalysed cross–coupling reactions

In a Schlenk tube were successivily introduced a solution of [Ni(cod)$_2$] in dioxane, a solution of the ligand (2 equiv. / Ni) in dioxane, aryl halide (0.5 mmol), PhMgBr (1 mL, 1.0 mmol, 1 M solution in THF), decane (0.05 mL, internal reference) and a complementary amount of dioxane so that the total reaction volume was 1.5 mL. The reaction mixture was then heated for 1 h at 100°C. After cooling to room temperature, methanol (1 mL) was added and a small amount (0.5 mL) of the resulting solution was passed through a Millipore filter and analyzed by GC (Varian 3900, equipped with a WCOT fused-silica column (25 m x 0.25 mm)). All products, including Ph-Ph, were unambiguously identified by NMR after their isolation. The NMR spectra were compared to those reported in the literature.

In this study the following products were prepared:
4-methoxybiphenyl,[1] biphenyl,[1] 4-methylbiphenyl,[1] 4-cyanobiphenyl,[1] 4-nitrobiphenyl,[1] 2-methoxybiphenyl,[2] 1-phenylnaphthalene,[2] 2-methylbiphenyl,[2] 3-methylbiphenyl[2] and 2-methoxy-6-phenylnaphthalene.[3]

1. C. Röhlich, K. Köhler, Adv. Synth. Catal., 2010, 352, 2263-2274
2. X.-H. Fan, L.-M. Yang, Eur. J. Org. Chem., 2010, 2457-2460
3. W. Liu, H. Cao, A. Lei, Angew. Chem. Int. Ed., 2010, 49, 2004-2008

Table S-1 Optimising the ligand:nickel ratio[a]

Entry	**1**/Ni	Conversion (%)
1	1/1	79.3
2	1.5/1	85.4
3	2/1	82.7
4	2.5/1	77.8
5	5/1	69.4
6	10/1	65.2

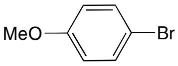
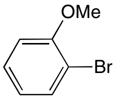
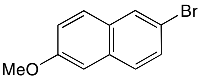
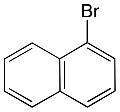
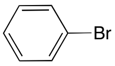
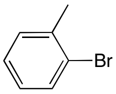
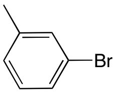
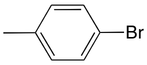
[a] Conditions: [Ni(cod)$_2$] (5 x 10^{-5} mmol, 1 x 10^{-2} mol %), phosphine **1**, 4-bromotoluene (0.5 mmol), PhMgBr (1 mmol), dioxane (1.50 mL), decane (0.05 mL), 100°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

Table S-2 Optimising the PhMgBr:ArBr ratio[a]

Entry	PhMgBr/ArBr	Conversion (%)
1	1/1	69.2
2	2/1	85.4
3	3/1	79.8

[a] Conditions: [Ni(cod)$_2$] (5 x 10^{-5} mmol, 1 x 10^{-2} mol %), ligand **1** (1 x 10^{-4} mmol), 4-bromotoluene (0.5 mmol), PhMgBr, dioxane (1.50 mL), decane (0.05 mL), 100°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

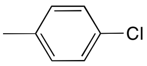
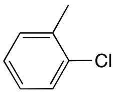
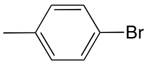
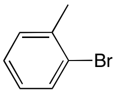
Table S-3 Kumada-Tamao-Corriu cross-coupling of aryl bromides applying a ArBr/Ni ratio of 100000[a]

Entry	ArBr		Monophosphane		
			1	**2**	**3**
1		conv. (%)	31.3	41.3	41.4
		PhPh:ArPh (%)	5.0	4.2	8.6
		TOF	31300	41300	41400
2		conv. (%)	20.1	24.0	25.5
		PhPh:ArPh (%)	7.1	5.9	9.0
		TOF	20100	24000	25500
3		conv. (%)	32.6	43.6	46.3
		PhPh:ArPh (%)	3.2	2.9	2.9
		TOF	32600	43600	46300
4		conv. (%)	79.8	89.4	86.4
		PhPh:ArPh (%)	1.3	1.6	3.4
		TOF	79800	89400	86400
5[b]		conv. (%)	38.6	43.9	42.6
		PhPh:ArPh (%)	3.1	4.0	5.2
		TOF	386000	439000	426000
6		conv. (%)	41.3	45.5	24.2
		PhPh:ArPh (%)	6.4	5.5	6.9
		TOF	41300	45500	29200
7		conv. (%)	17.1	23.0	17.2
		PhPh:ArPh	7.5	7.4	8.7
		(%)TOF	17100	23000	17200
8		conv. (%)	32.5	31.1	24.2
		PhPh:ArPh (%)	5.2	4.5	7.8
		TOF	32500	31100	24200
9		conv. (%)	35.8	41.2	30.6
		PhPh:ArPh (%)	7.6	6.1	8.9
		TOF	35800	41200	30600

[a] Conditions: [Ni(cod)$_2$] (5 x 10^{-6} mmol, 1 x 10^{-3} mol %), monophosphine (2 equiv. / Ni), ArBr (0.5 mmol), PhMgBr (1 mmol), dioxane (1.50 mL), decane (0.05 mL), 100°C, 1 h. The conversions were determined by GC, the calibrations being based on decane. The TOFs were expressed in mol(ArBr).mol(Ni)$^{-1}$.h^{-1}. [b] [Ni(cod)$_2$] (5 x 10^{-7} mmol, 1 x 10^{-4} mol %), monophosphine (2 equiv. / Ni). Performing this reaction with **5** led to a TOF of 253000 mol(naphtBr).mol(Ni)$^{-1}$.h^{-1}.

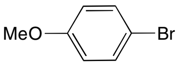
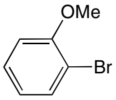
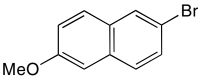
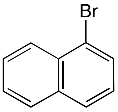
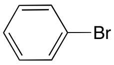
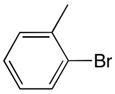
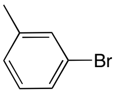
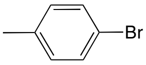
All the reactions shown in Table S-3 can go to complete conversions by increasing the reaction time.

Table S-4 Comparison between the catalytic properties of **1** and **6** (100°C, dioxane)[a]

Entry	ArX		Monophosphine	
			1	**6**
1[a]		conv. (%)	79.4	92.2
		PhPh:ArPh (%)	7.1	7.3
2[a]		conv. (%)	24.6	55.4
		PhPh:ArPh (%)	6.3	6.0
3[b]		conv. (%)	35.8	65.3
		PhPh:ArPh (%)	7.6	7.1
4[b]		conv. (%)	17.1	58.5
		PhPh:ArPh (%)	7.5	6.8

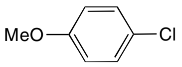
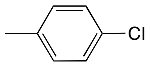
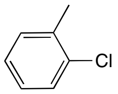
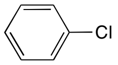
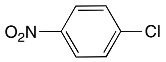
[a] Conditions: [Ni(cod)$_2$] (2.5 x 10^{-3} mmol, 1 mol %), monophosphine (2 equiv. / Ni), ArCl (0.25 mmol), PhMgBr (0.5 mmol), dioxane (0.75 mL), decane (0.025 mL), 100°C, 1 h. [b] Conditions: [Ni(cod)$_2$] (5 x 10^{-6} mmol, 1 x 10^{-3} mol %), monophosphine (2 equiv. / Ni), ArBr (0.5 mmol), PhMgBr (1 mmol), dioxane (1.50 mL), decane (0.05 mL), 100°C, 1 h. The conversions were determined by GC, the calibrations being based on decane.

Table 2 Kumada-Tamao-Corriu cross-coupling of aryl bromides using a ArBr/Ni ratio of 10000[a]

Entry	ArBr		Monophosphine		
			1	**2**	**3**
1		conv. (%)	86.4	89.4	88.4
		PhPh:ArPh (%)	5.6	5.1	8.1
2		conv. (%)	52.3	54.5	59.3
		PhPh:ArPh (%)	7.4	6.5	8.5
3		conv. (%)	85.3	88.9	86.8
		PhPh:ArPh (%)	3.8	4.2	4.0
4		conv. (%)	95.5	96.9	98.2
		PhPh:ArPh (%)	2.0	2.1	5.8
5		conv. (%)	80.8	96.3	49.3
		PhPh:ArPh (%)	6.8	5.9	7.1
6		conv. (%)	58.1	71.7	44.4
		PhPh:ArPh (%)	8.6	7.8	8.0
7		conv. (%)	76.2	85.7	73.6
		PhPh:ArPh (%)	6.1	5.1	6.7
8		conv. (%)	82.7	90.0	87.7
		PhPh:ArPh (%)	7.9	8.0	7.1

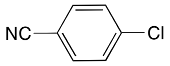
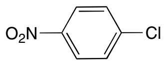
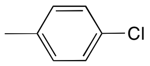
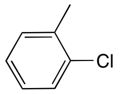
[a] Conditions: [Ni(cod)$_2$] (5 x 10^{-5} mmol, 1 x 10^{-2} mol %), phosphine (2 equiv. / Ni), ArBr (0.5 mmol), PhMgBr (1 mmol), dioxane (1.50 mL), decane (0.05 mL), 100°C, 1 h. Conversions by GC; calibrations based on decane.

Table 3 Kumada-Tamao-Corriu cross-coupling of arylchlorides catalyzed by $[Ni(cod)_2]$ / **1**[a]

Entry	ArCl	$[Ni(cod)_2]$ (mol %)	Reaction time (h)	Conversion (%)	PhPh:ArPh (%)
1		1	3	98.5	8.0
2		0.01	16	37.4	7.3
3		1	3	99.6	6.8
4		0.01	16	42.2	7.1
5		1	1	24.6	6.3
6		1	5	75.4	6.8
7		1	1	97.9	7.2
8		0.01	5	69.2	6.5
9		1	1	99.2	8.8
10		0.01	5	60.3	8.5

[a] Conditions: $[Ni(cod)_2]$, monophosphine **1** (2 equiv. / Ni), ArCl (0.25 mmol), PhMgBr (0.5 mmol), dioxane (0.75 mL), decane (0.025 mL), 100°C. The conversions were determined by GC, the calibrations being based on decane. At 100°C, the nitro group did not undergo nucleophilic attack.

Table 4 Kumada-Tamao-Corriu cross-coupling of aryl chlorides in the presence of monophosphines **1** and **6** at 25°C[a]

Entry	ArCl		Monophosphine	
			1	**6**
1		conv. (%) (6 h)	72.2	88.2
		PhPh:ArPh (%)	7.7	6.2
2		conv. (%) (6 h)	66.7	92.3
		PhPh:ArPh (%)	8.1	7.8
3		conv. (%) (24 h)	62.5	80.9
		PhPh:ArPh (%)	5.2	6.1
4		conv. (%) (24 h)	45.2	64.4
		PhPh:ArPh (%)	5.8	6.5

[a] Conditions: $[Ni(cod)_2]$ (7.5×10^{-3} mmol, 3 mol %), monophosphine (2 equiv. / Ni), ArCl (0.25 mmol), PhMgBr (0.5 mmol), dioxane (0.75 mL), decane (0.025 mL), 25°C. Conversions determined by GC; calibrations based on decane. At 25°C, neither the cyano nor the nitro groups were found to undergo nucleophilic attack.