Indium Trichloride-Catalyzed Imino Diels−Alder Reactions: Synthesis of New Indolylquinoline Derivatives

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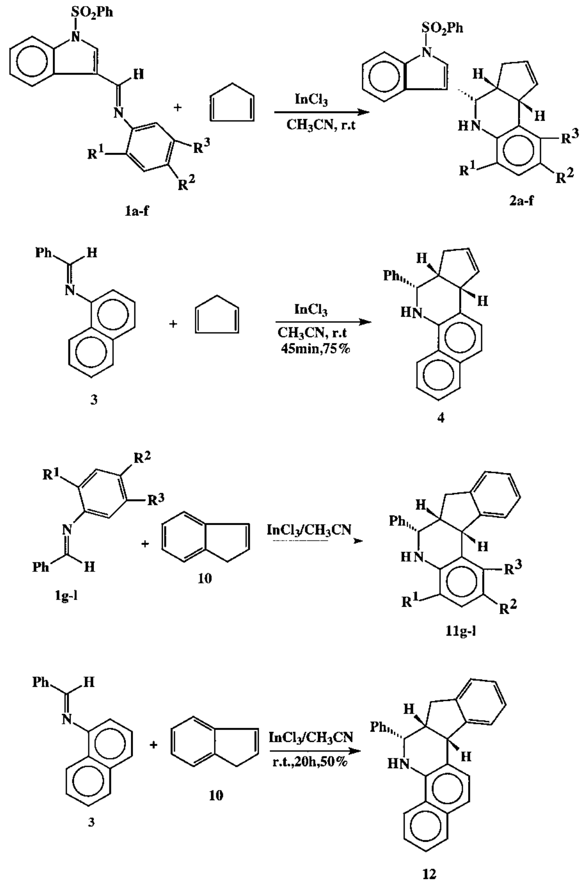
Abstract: Imino Diels−Alder reaction of *N*-arylaldimines with cyclopentadiene, 3,4-dihydro-*2H*-pyran and indene is efficiently catalyzed by indium trichloride to give new indolylquinoline derivatives in good yields.

Key words: catalysts, Diels−Alder reactions, indium trichloride, imines, quinolines, heterocycles



Scheme 1

The Diels−Alder reaction of imines is a powerful method for the construction of nitrogen heterocycles such as quinoline and pyridine derivatives.[1,2] Lewis acids such as $BF_3{\cdot}OEt_2$,[3] lanthanide triflates[4] and TFA[5] catalyzes the [4+2] cycloaddition of *N*-arylaldimines. Recently, we have found that indium trichloride is an efficient catalyst for the synthesis of quinoline and azabicycloalkanone derivatives by imino Diels−Alder reactions.[6−8] Literature survey reveals that indium trichloride also catalyzes the rearrangement of epoxides,[9] reductive Friedel−Crafts alkylation,[10] Prins reaction,[11] and Mukaiyama aldol reactions.[12]

In continuation of our research in imino Diels−Alder reactions for the synthesis of quinoline derivatives, we envisaged the synthesis of indolylquinoline derivatives. Compounds containing either the indole or the quinoline moiety possess wide range of biological activity. Few reports are available regarding compounds bearing both the indole and quinoline moiety[13−16] which possess a broad spectrum of biological activity. In this paper, we describe the convergent synthesis of new quinoline derivatives by imino Diels−Alder reactions catalyzed by indium trichloride.

In the presence of 20 mol% indium trichloride, *N*-arylaldimine **1a** was treated with cyclopentadiene in acetonitrile at room temperature (Scheme 1). After 1 hour, the imino Diels-Alder reaction had proceeded smoothly to afford the corresponding indolylquinoline derivative **2a** in 83% yield. *N*-Arylaldimines **1** having various substituents were reacted with cyclopentadiene in the presence of indium trichloride catalyst to afford indolylquinolines **2** in good yields (Table 1). The structures of the products were ascertained by the single crystal X-ray analysis of **2a** and **2c**[17a,b]. When we treated *N*-benzylidene-1-naphthylamine (**3**) with cyclopentadiene, benzo[*h*]cyclopentaquinoline **4** was obtained in 75% yield (Scheme 1).

Next, we planned to synthesise pyranoquinoline derivatives. The pyranoquinoline moiety is present in many alkaloids.[18] Pyranoquinoline derivatives possess a wide range of biological activities which includes psychotropic activity,[19] antiallergic activity,[20] antiinflammatory activity,[21] estrogenic activity[22] and are used as potential pharmaceuticals.[23] Few reports are available on their synthesis by imino Diels−Alder reactions. Acetic acid[24] and $BF_3{\bullet}OEt_2$[25] catalyze the Diels−Alder reaction of 3,4-dihydro-2*H*-pyran (**5**) with *N*-benzylidene aniline (**1g**) to afford pyranoquinolines; however, the yields are very low. When we treated *N*-benzylidene aniline (**1g**) with 3,4-dihydro-2*H*-pyran (**5**) in the presence of 20 mol% indium trichloride, after 30 minutes the reaction afforded the diastereomeric pyranoquinoline derivatives **6g** and **7g** in a ratio of 41:59 in an overall yield of 80% (Scheme 2).[26] *N*-Arylaldimines **1** having various substituents were reacted with 3,4-dihydro-2*H*-pyran (**5**) to afford pyranoquinoline derivatives in varying ratios (Table 2). The structures of the products were assigned based on the coupling con-

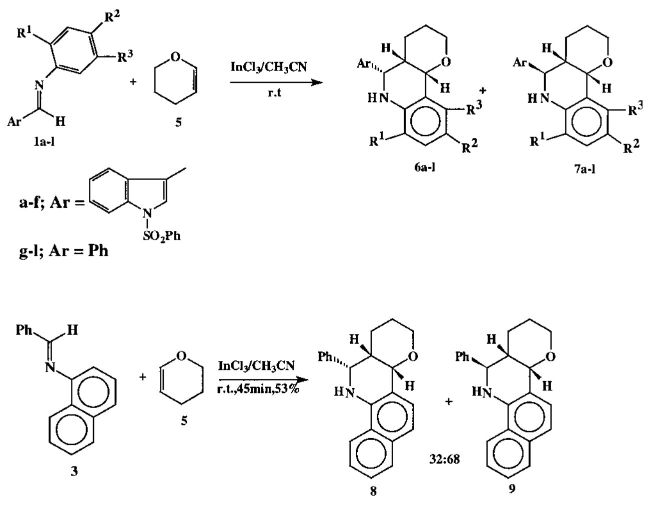
Table 1 Synthesis of Cyclopentaquinolines and Indenoquinolines Using 20 mol% $InCl_3$

Product	Substituents			Time (h)	Yield (%)[a]	mp (°C)	R_f Value
	R^1	R^2	R^3				
2a	H	H	H	0.5	83	165–166	0.48
2b	H	Me	H	0.5	60	65–66	0.52
2c	H	Cl	H	0.5	85	159–160	0.42
2d	Me	H	Me	0.5	87	93–95	0.44
2e	Me	Cl	H	0.5	79	72–73	0.41
4	–	–	–	0.75	75	–[b]	0.42
11g	H	H	H	6	40	134–135	0.74
11i	H	Cl	H	6	48	145–146	0.80
11j	H	OMe	H	24	30	113–114	0.70
11k	Me	Cl	H	12	48	138–139	0.76
11l	Me	H	Me	9 (reflux)	65	146–147	0.79
12	–	–	–	20	50	202–203	0.68

[a] All the compounds were recrystallised from EtOAc/petroleum ether.
[b] Isolated as dense liquid.

stants of the H-5 proton with the H-4a proton. From Table 2, it is evident that in the case of imines of 2,4- and 2,5-substituted anilines, pyranoquinoline derivative **7** was obtained as the major compound due to steric hindrance caused by the methyl protons in the ortho position. In the case of indole substituted imines, pyranoquinoline derivative **6** was obtained as major compound due to its bulky nature, which tends to be in (*E*)-form while reacting with 3,4-dihydro-2*H*-pyran (**5**). *N*-Benzylidene-1-naphthylamine (**3**) reacted with 3,4-dihydro-2*H*-pyran (**5**) to afford the benzo[*h*]pyranoquinolines **8** and **9** in a ratio of 32:68 in an overall yield of 53% (Scheme 2).

Indenoquinoline derivatives also possess a wide range of biological activities.[27–30] Reaction of *N*-benzylidene aniline (**1g**) with indene (**10**) in the presence of 20 mol% indium trichloride gave the indenoquinoline **11g** in 40%



Scheme 2

Table 2 Synthesis of Indolylpyranoquinolines and Phenylpyranoquinolines Using 20 mol % $InCl_3$

Imine	Substituents			Time (h)	Product Ratio[a]	Yield (%)	mp (°C)		R_f	
	R^1	R^2	R^3		**6 : 7**		**6**	**7**	**6**	**7**
1a	H	H	H	4	>99	68	149–150	–	0.93	–
1b	H	Me	H	6	71:29	55	174–175	139–140	0.87	0.67
1c	H	Cl	H	6	>99	65	182–183	–	0.63	–
1d	Me	H	Me	7	55:45	38	159–160	217–218	0.6	0.47
1f	H	OMe	H	8	99	50	129–130	–	0.75	–
1g	H	H	H	0.5	41:59	80 (25)[b]	123–124	94–95	0.62	0.47
1h	H	Me	H	2	68:32	70	128–129	–[d]	0.46	0.39
1i	H	Cl	H	0.5	34:66	50	154–155	122–123	0.51	0.31
1j	H	OMe	H	4	58:42	70 (54)[c]	146–147	–[d]	0.57	0.43
1k	Me	Cl	H	0.75	5:95	46	191–192	185–186	0.65	0.59
1l	Me	H	Me	3	5:95	45	111–112	106–107	0.59	0.49
3	–	–	–	0.75	32:68[e]	51	–[d,f]	–[d,g]	0.81[f]	0.59[g]

[a] Isolated yield based on products after column chromatography and recrystallised from EtOAc/petroleum ether.
[b] Yield reported in the literature.[25]
[c] Yield reported in the literature.[31]
[d] Isolated as dense liquid.
[e] Product ratio **8**:**9**.
[f] Product **8**.
[g] Product **9**.

Table 3 Spectral Data of Indolylcyclopentaquinolines, Indolylpyranoquinolines and Indolylindenoquinolines

Product[a]	IR (KBr) ν (cm^{-1})	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS *m/z*
2a	3409, 2949, 1480, 1401, 1385, 720	8.07−6.80 (m, 12 H), 6.72 (m, 1 H), 6.68 (d, 1 H, *J* = 7.8), 5.83 (m, 1 H), 5.61 (m, 1 H), 4.86 (d, 1 H, *J* = 2.6), 4.14 (d, 1 H, *J* = 8.1), 3.77 (br s, 1 H, NH), 3.22 (m, 1 H), 2.60 (m, 1 H), 1.69 (m, 1 H)	147.3, 137.9, 135.3, 135.2, 134.1, 133.7, 133.2, 132.6, 129.6, 127.2, 126.6, 126.5, 126.3, 125.1, 125.0, 124.0, 123.2, 119.4, 119.1, 116.0, 113.9, 113.7, 50.7, 45.7, 43.2, 32.4	426 (M^+)
2b	3400, 2950, 1450, 1380, 730	8.04−7.79 (m, 5 H), 7.26−7.24 (m, 5 H), 6.89 (s, 1 H), 6.83 (d, 1 H, *J* = 7.8), 6.56 (d, 1 H, *J* = 8.0), 5.81 (br s, 1 H), 5.60 (s, 1 H), 4.85 (d, 1 H, *J* = 10.9), 4.09 (d, 1 H, *J* = 8.4), 3.65 (br s, 1 H, NH), 3.10 (m, 1 H), 2.53 (m, 1 H), 2.27 (s, 3 H), 1.62 (m, 1 H)	142.7, 138.0, 135.3, 134.1, 133.7, 133.2, 130.0, 129.9, 129.3, 129.2, 129.1, 128.7, 127.2, 127.0, 126.7, 125.3, 125.0, 123.2, 122.3, 119.4, 113.9, 50.9, 45.8, 43.1, 32.0, 20.5	440 (M^+)
2c	3425, 3100, 2900, 1450, 1380, 750	8.03−7.85 (m, 5 H), 7.60−7.21 (m, 5 H),7.02 (s, 1 H), 6.92 (d, 1 H, *J* = 6.3), 6.56 (d, 1 H, *J* = 8.5), 5.75 (s, 1 H), 5.61 (m, 1 H), 4.80 (d, 1 H, *J* = 2.6), 4.06 (d, 1 H, *J* = 8.5), 3.77 (s, 1 H), 3.09 (m, 1 H), 2.48 (m, 1 H), 1.61 (m, 1 H)	143.8, 137.9, 135.5, 134.5, 133.9, 132.6, 130.4, 129.8, 127.9, 127.6, 126.4, 125.6, 124.8, 123.9, 123.7, 122.1, 120.6, 120.1, 117.9, 114.9, 112.9, 51.4, 49.9, 43.6, 32.2	462 (M^+ + 2), 460 (M^+)
2d	3459, 3110, 2910, 1460, 1381,754	8.05−7.89 (m, 3 H), 7.72−7.65 (m, 8 H), 6.84 (d, 1 H, *J* = 7.5), 6.59 (d, 1 H, *J* = 7.4), 5.79 (m, 1 H), 5.62 (m, 1 H), 4.70 (s, 1 H), 4.26 (d, 1 H, *J* = 8.7), 3.63 (br s, 1 H, NH), 2.72 (m, 1 H), 2.34 (s, 3 H), 2.14 (s, 3 H), 1.77 (m, 1 H)	144.6, 138.0, 135.4, 134.2, 133.7, 132.4, 130.3, 129.3, 129.2, 127.4, 126.7, 125.3, 125.1, 124.5, 123.3, 123.1, 122.2, 120.9, 120.5, 119.4, 114.0, 51.6, 45.1, 43.3, 32.8, 19.5, 17.0	454 (M^+)
2e	3400, 2900, 1475,1380, 720	8.04−7.86 (m, 3 H), 7.65−7.23 (m, 7 H), 6.92 (s, 1 H), 6.87 (s, 1 H), 5.76 (s, 1 H), 5.60 (s, 1 H), 4.81 (d, 1 H, *J* = 2.4), 4.10 (d, 1 H, *J* = 8.2), 3.64 (s, 1 H), 3.12 (m, 1 H), 2.53 (m, 1 H), 2.42 (s, 3 H), 1.61 (m, 1 H)	141.9,137.9,135.3,133.9,133.8,130.2, 129.2, 129.0, 127.2, 127.1, 126.6, 126.2, 125.2, 125.0, 124.6, 123.3, 123.1, 122.3, 119.4, 114.0, 50.7, 45.9, 43.0, 32.0, 17.0	463 (M^+ + 2), 461 (M^+)
4	3392,1485	7.90−7.32 (m, 11 H), 6.08 (m, 1 H), 5.79 (m, 1 H), 4.83 (d, 1 H, *J* = 2.4), 4.59 (br s, 1 H, NH), 4.39 (d, 1 H, *J* = 8.2), 3.25 (m, 1 H), 2.91 (m, 1 H), 2.04 (m, 1 H)	143.2, 139.9, 134.1, 132.7, 130.7, 128.7, 127.5, 126.8, 126.7,125.2, 125.1, 123.8, 120.3, 119.7, 118.9, 58.3, 47.1, 46.2, 31.5	297 (M^+)
6a	3457, 3395, 2929, 1608	8.04 (d, 1 H, *J* = 8.3), 7.90 (d, 1 H, *J* = 7.6), 7.62−7.11 (m, 10 H), 6.84 (d, 1 H, *J* = 7.4), 6.64 (d, 1 H, *J* = 7.9), 5.34 (d, 1 H, *J* = 5.3), 4.93 (s, 1 H), 3.86 (br s, 1 H, NH), 3.60 (m, 1 H), 3.41 (d, 1 H, *J* = 2.8), 2.27 (m, 1 H), 1.56−1.11 (m, 4 H)	144.8, 138.1, 135.5, 133.8, 132.0, 129.3, 128.9, 128.2, 127.7, 126.8, 126.1, 125.1, 123.4, 123.3, 123.1, 120.2, 119.6, 118.2, 114.6, 114.0, 72.0, 60.5, 52.2, 36.4, 25.3, 18.5	444 (M^+)
6b	3405, 3119, 2929, 1362, 717	8.04 (d, 1 H, *J* = 8.3), 7.91 (d, 1 H, *J* = 7.5), 7.90−7.04 (m, 9 H), 6.91 (d, 1 H, *J* = 8.0), 6.57 (d, 1 H, *J* = 8.1), 5.29 (d, 1 H, *J* = 5.4), 4.88 (s, 1 H), 3.61 (m, 3 H), 2.20 (s, 4 H), 1.54−1.12 (m, 4 H)	142.5, 138.1, 135.5, 133.8, 129.7, 129.2, 128.9, 128.8, 128.0, 127.8, 127.1, 126.9,126.7, 125.1, 123.3, 123.2, 120.1, 119.5, 114.7, 113.2, 72.3, 60.6, 52.3, 36.6, 25.3, 20.6, 18.5	458 (M^+)
7b	3451, 3380, 2929, 1362, 716	8.60−7.05 (m, 11 H), 6.92 (d, 1 H, *J* = 8.0), 6.45 (d, 1 H, *J* = 8.1), 4.95 (d, 1 H, *J* = 10.1), 4.35 (d, 1 H, *J* = 2.4), 4.09 (m, 2 H), 3.72 (m, 1 H), 2.23 (s, 4 H), 2.03−1.24 (m, 4 H)	137.1, 135.6, 135.2, 134.8, 133.0, 131.1, 130.1, 129.7, 129.2, 128.0, 127.3, 126.7, 125.0, 124.1, 123.2, 114.4, 113.9, 111.0, 74.4, 68.5, 48.2, 37.0, 24.3, 21.8, 20.2	458 (M^+)
6c	3452, 3385, 2924, 1383, 804	8.03 (d, 1 H, *J* = 8.2), 7.91 (d, 1 H, *J* = 7.5), 7.60 (s, 1 H), 7.53−7.32 (m, 8 H), 7.27 (d, 1 H, *J* = 1.9), 6.57 (d, 1 H, *J* = 8.4), 5.27 (d, 1 H, *J* = 5.4), 4.90 (s, 1 H), 3.82 (br s, 1 H, NH), 3.62−3.43 (m, 2 H), 2.31 (br s, 1 H) , 1.54−1.23 (m, 4 H)	144.0, 138.1, 134.2, 133.9, 133.1, 129.4, 129.2, 129.0, 128.1, 127.3, 126.7, 125.2, 123.4, 123.2, 122.6, 119.5, 115.9, 115.3, 114.0, 113.2, 71.9, 60.7, 52.2, 36.1, 25.2, 18.5	480 (M^+ + 2), 478 (M^+)
6d	3454, 3379, 2929, 1368, 717	8.05–7.11 (m, 10 H), 6.94 (d, 1 H, *J* = 7.1), 6.57 (d, 1 H, *J* = 7.2), 5.41 (d, 1 H, *J* = 5.1), 4.84 (s, 1 H), 3.65 (br s, 1 H, NH), 3.51 (d, 1 H, *J* = 10.2), 3.23 (m, 1 H), 2.38 (s, 4 H), 2.14 (s, 3 H),1.77–1.26 (m, 4 H)	143.9, 138.1, 137.3, 135.4, 133.7, 129.4, 129.1, 127.0, 126.7, 126.3, 125.1, 124.4, 123.5, 123.0, 120.9, 119.6, 119.4, 118.6, 113.9, 113.2, 72.1, 60.7, 52.0, 36.6, 30.1, 24.4, 21.5, 18.3	472 (M^+)

Table 3 (continued)

Product[a]	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS *m/z*
7b	3451, 3380, 2929, 1362, 716	8.60−7.05 (m, 11 H), 6.92 (d, 1 H, *J* = 8.0), 6.45 (d, 1 H, *J* = 8.1), 4.95 (d, 1 H, *J* = 10.1), 4.35 (d, 1 H, *J* = 2.4), 4.09 (m, 2 H), 3.72 (m, 1 H), 2.23 (s, 4 H), 2.03−1.24 (m, 4 H)	137.1, 135.6, 135.2, 134.8, 133.0, 131.1, 130.1, 129.7, 129.2, 128.0, 127.3, 126.7, 125.0, 124.1, 123.2, 114.4, 113.9, 111.0, 74.4, 68.5, 48.2, 37.0, 24.3, 21.8, 20.2	458 (M^+)
6c	3452, 3385, 2924, 1383, 804	8.03 (d, 1 H, *J* = 8.2), 7.91 (d, 1 H, *J* = 7.5), 7.60 (s, 1 H), 7.53−7.32 (m, 8 H), 7.27 (d, 1 H, *J* = 1.9), 6.57 (d, 1 H, *J* = 8.4), 5.27 (d, 1 H, *J* = 5.4), 4.90 (s, 1 H), 3.82 (br s, 1 H, NH), 3.62−3.43 (m, 2 H), 2.31 (br s, 1 H) , 1.54−1.23 (m, 4 H)	144.0, 138.1, 134.2, 133.9, 133.1, 129.4, 129.2, 129.0, 128.1, 127.3, 126.7, 125.2, 123.4, 123.2, 122.6, 119.5, 115.9, 115.3, 114.0, 113.2, 71.9, 60.7, 52.2, 36.1, 25.2, 18.5	480 (M^+ + 2), 478 (M^+)
6d	3454, 3379, 2929, 1368, 717	8.05−7.11 (m, 10 H), 6.94 (d, 1 H, *J* = 7.1), 6.57 (d, 1 H, *J* = 7.2), 5.41 (d, 1 H, *J* = 5.1), 4.84 (s, 1 H), 3.65 (br s, 1 H, NH), 3.51 (d, 1 H, *J* = 10.2), 3.23 (m, 1 H), 2.38 (s, 4 H), 2.14 (s, 3 H),1.77−1.26 (m, 4 H)	143.9, 138.1, 137.3, 135.4, 133.7, 129.4, 129.1, 127.0, 126.7, 126.3, 125.1, 124.4, 123.5, 123.0, 120.9, 119.6,119.4, 118.6, 113.9, 113.2, 72.1, 60.7, 52.0, 36.6, 30.1, 24.4, 21.5, 18.3	472 (M^+)
7d	3459, 3380, 2929, 1379, 715	8.05 (d, 1 H , *J* = 8.4), 8.02−7.18 (m, 9 H), 6.87 (d, 1 H, *J* = 7.2), 6.52 (d, 1 H, *J* = 7.3), 5.12 (d, 1 H, *J* = 10.3), 4.92 (s, 1 H), 3.71 (br s, 1 H, NH), 3.56 (d, 1 H, *J* = 10.3), 3.24 (m, 1 H), 2.33 (s, 4 H), 1.95 (s, 3 H), 1.82−1.24 (m, 4 H)	142.5, 138.1, 136.5, 134.7, 133.8, 129.9, 129.2, 127.1, 126.9, 126.4, 125.0, 124.6, 123.5, 123.2, 122.6, 121.3, 119.1, 118.7, 114.0, 113.2, 72.1, 68.7, 47.3, 37.2, 29.7, 21.8, 18.1, 17.1	472 (M^+)
6f	3436, 3385, 2934, 1368, 753	8.22 (m, 1 H), 8.03−7.03 (m, 10 H), 6.71 (d, 1 H, *J* = 2.7), 6.61 (d, 1 H, *J* = 8.6), 5.32 (d, 1 H, *J* = 5.5), 4.86 (s, 1 H), 3.77 (br s, 4 H), 3.55 (m, 2 H), 2.34 (br s, 1 H) ,1.57−1.24 (m, 4 H)	153.2, 138.7, 138.1, 136.1, 135.5, 134.7, 133.8, 129.7, 129.2, 127.1, 126.7, 125.1,123.4, 123.2, 122.6, 121.4, 119.6, 116.0, 115.1, 113.2, 72.4, 60.7, 55.8, 52.4, 36.6, 25.2, 18.4	474 (M^+)
6g	3378, 3316, 2936, 1605, 1485, 1071	7.41−7.24 (m, 6 H), 7.13 (m, 1 H), 6.83 (m, 1 H), 6.62 (d, 1 H, *J* = 7.6), 5.34 (d, 1 H, *J* = 4.5), 4.68 (br s, 1 H), 3.89 (br s, 1 H, NH), 3.61 (d, 1 H, *J* = 11.2), 3.44 (m, 1 H), 2.17 (m, 1 H), 1.75−1.31 (m, 4 H)	145.2, 141.1, 128.3, 128.0, 127.6, 127.5, 126.8, 119.8, 118.3, 114.4, 72.8, 60.6, 59.3, 38.9, 25.4, 18.0	265 (M^+)
7g	3374, 2928, 1610, 1489, 1077	7.43−7.34 (m, 5 H), 7.26 (d, 1 H, *J* = 7.0), 7.13 (m, 1 H), 6.75 (m, 1 H), 6.54 (d, 1 H, *J* = 7.8), 4.74 (d, 1 H, *J* = 10.6), 4.41 (br s, 1 H), 4.10 (m, 2 H), 3.78 (m, 1 H), 2.08 (m, 1 H), 1.89−1.31 (m, 4 H)	144.1, 141.7, 130.2, 128.7, 128.0, 127.2, 127.1, 120.0, 116.8, 113.5, 73.9, 68.0, 54.1, 38.2, 23.5, 21.4	265 (M^+)
6h	3387, 2940, 1512, 1019	7.48−7.26 (m, 6 H), 6.94 (d, 1 H, *J* = 7.6), 6.55 (d, 1 H, *J* = 7.8), 5.32 (d, 1 H, *J* = 4.2), 4.64 (br s, 1 H), 3.77 (br s, 1 H, NH), 3.62 (d, 1 H, *J* = 11.3 Hz), 3.48 (m, 1 H), 2.29 (s, 3 H), 2.16 (m, 1 H), 1.63−1.30 (m, 4 H)	142.7, 141.2, 128.6, 128.2, 127.6, 127.4, 127,3, 126.7, 119,7, 114.4, 72.7, 60.5, 59.3, 38.9, 25.2, 20.5, 17.8	279 (M^+)
7h	3367, 2927, 1509, 1261, 1086	7.48−7.24 (m, 5 H), 7.04 (s, 1 H), 6.92 (d, 1 H, *J* = 7.4), 6.46 (d, 1 H, *J* = 7.8), 4.70 (d, 1 H, *J* = 10.7), 4.35 (s, 1 H), 4.11 (d, 1 H, *J* = 10.5), 3.96 (br s, 1 H, NH), 3.75 (m, 1 H), 2.23 (s, 3 H), 2.08 (m, 1 H), 1.90−1.30 (m, 4 H)	142.2, 131.5, 130.6, 128.9, 127.7, 126.9, 126.3, 120.4, 114.8, 113.9, 74.0, 68.4, 54.9, 39.4, 24.0, 21.5, 19.4	279 (M^+)
7i	3348, 2934, 1494, 1265	7.37 (m, 5 H), 7.19 (s, 1 H), 7.03 (d, 1 H, *J* = 8.2), 6.45 (d, 1 H, *J* = 8.3), 4.67 (d, 1 H, *J* = 10.5), 4.33 (s, 1 H), 4.08 (m, 2 H), 3.73 (m, 1 H), 2.05 (m, 1 H), 1.83−1.31 (m, 4 H)	143.2, 141.8, 130.3, 129.1, 128.6, 127.9, 127.6, 121.8, 121.7, 115.2, 73.8, 68.4, 54.8, 38.6, 23.9, 22.0	301(M^+ + 2), 299 (M^+)
6j	3295, 2942, 1502, 1262, 1065	7.40−7.29 (m, 5 H), 7.03 (s, 1 H), 6.73 (d, 1 H, *J* = 8.2), 6.57 (d, 1 H, *J* = 8.4), 5.31 (d, 1 H, *J* = 5.4), 4.61 (s, 1 H), 3.73 (s, 3 H), 3.67 (br s, 1 H), 3.61−3.36 (m, 2 H), 2.15 (m, 1 H), 1.54−1.26 (m, 4 H)	152.8, 141.3, 139,1, 128.3, 127.4, 126.8, 121.1, 115.7, 115.0, 111.8, 72.9, 60.8, 59.5, 55.8, 39.1, 25.3, 17.9	295 (M^+)
7j	3361, 2938, 1504, 1255, 1032	7.43−7.27 (m, 5 H), 6.82 (s, 1 H), 6.75 (d, 1 H, *J* = 9.1), 6.49 (d, 1 H, *J* = 8.5), 4.62 (d, 1 H, *J* = 10.5), 4.38 (s, 1 H), 4.10 (m, 1 H), 3.75 (m, 5 H), 2.10 (m, 1 H), 1.84−1.30 (m, 4 H)	151.9, 142.2, 138.7, 128.1, 127.7, 121.3, 116.7, 115.5, 114.7, 74.5, 68.3, 55.7, 55.1, 38.8, 24.0, 21.9	295 (M^+)

Table 3 (continued)

Product[a]	IR (KBr) ν (cm^{-1})	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS *m/z*
6k	3384, 2936, 1493, 1263	7.45 (m, 5 H), 7.04 (s, 1 H), 6.98 (s, 1 H), 5.25 (s, 1 H), 4.64 (s, 1 H), 3.79 (br s, 1 H, NH), 3.62 (m, 1 H), 3.44 (m, 1 H), 2.12 (br s, 4 H), 1.80−1.31 (m, 4 H)	143.6, 140.5, 128.8, 127.7, 127.2, 126.9, 126.5, 126.0, 122.1, 115.4, 73.1, 60.5, 59.4, 39.1, 37.8, 25.2, 16.8	315 (M^+ + 2), 313 (M^+)
7k	3395, 2846, 1481, 1052	7.44−7.34 (m, 5 H), 7.10 (d, 1 H, *J* = 1.8), 6.97 (s, 1 H), 4.73 (d, 1 H, *J* = 10.7), 4.34 (d, 1 H, *J* = 2.4), 4.11 (d, 1 H, *J* = 8 .9), 3.88 (br s, 1 H, NH), 3.74 (m, 1 H), 2.11 (br s, 4 H), 1.90−1.32 (m, 4 H)	141.7, 140.9, 129.4, 128.3, 128.0, 127.6, 127.3, 122.5, 120.8, 120.7, 73.8, 68.1, 54.4, 38.1, 23.5, 21.5, 16.6	315 (M^+ + 2), 313 (M^+)
6l	3384, 2940, 1510, 1023	7.50 (m, 5 H), 6.92 (d, 1 H, *J* = 7.0), 6.51 (d, 1 H, *J* = 7.1), 5.31 (s, 1 H), 4.64 (s, 1 H), 3.76 (br s, 1 H, NH), 3.63 (d, 1 H, *J* = 11.2), 3.48 (m, 1 H), 2.35 (s, 3 H), 2.06 (br s, 4 H), 1.84−1.27 (m, 4 H)	142.6, 141.4, 128.7, 128.3, 127.7, 127.4, 127.3, 126.8, 119.7, 114.4, 71.7, 60.6, 59.4, 38.9, 25.3, 20.6, 17.8, 16.8	293 (M^+)
7l	3382, 2942, 1508, 1022	7.49−7.37 (m, 5 H), 6.91 (d, 1 H, *J* = 6.9), 6.52 (d, 1 H, *J* = 7.0), 4.76 (d, 1 H, *J* = 11.2), 4.50 (s, 1 H), 4.14 (d, 1 H, *J* = 10.3), 3.85 (br s, 1 H, NH), 3.73 (m, 1 H), 2.35 (s, 3 H), 2.08 (br s, 4 H), 1.93−1.27 (m, 4 H)	142.6, 142.5, 136.2, 129.7, 128.5, 127.8, 127.7, 118.8, 118.5, 118.3, 72.2, 68.6, 54.0, 39.4, 24.0, 21.8, 17.9, 16.9	293 (M^+)
8	3385, 2925, 1406, 1075	7.88−7.23 (m, 11 H), 5.50 (d, 1 H *J* = 5.5), 4.79 (s, 1 H), 4.50 (br s, 1 H), 3.62 (m, 1 H), 3.38 (m, 1 H), 2.26 (m, 1 H), 1.84−1.34 (m, 4 H)	141.2, 136.2, 134.4, 133.6, 129.7, 128.8, 128.3, 127.6, 126.9, 125.3, 122.8, 119.9, 118.1, 114.3, 72.8, 60.8, 59.5, 38.4, 25.3, 18.0	315 (M^+)
9	3413, 2937, 1721, 1494, 1216	7.76−7.21 (m, 11 H), 4.85 (d, 1 H, *J* = 10.7), 4.50 (s, 1 H), 4.14 (d, 1 H, *J* = 10.1), 3.76 (m, 1 H), 3.50 (m, 1 H), 2.20 (m, 1 H), 1.90−1.34 (m, 4 H)	142.2, 139.8, 134.3, 129.1, 128.1, 127.8, 127.4, 125.3, 124.0, 122.5, 119.7, 117.9, 116.5, 114.6, 74.7, 68.6, 55.2, 38.7, 25.4, 24.1	315 (M^+)
11g	3402, 1497	7.54−6.98 (m, 11 H), 6.76 (d, 1 H, *J* = 6.8), 6.62 (d, 1 H, *J* = 6.59), 4.76 (br s, 1 H), 4.59 (d, 1 H, *J* = 7.1), 3.91 (br s, 1 H, NH), 3.38−3.18 (m, 2 H), 2.43 (m, 1 H)	146.2, 145.1, 142.8, 142.5, 129.4, 128.5, 127.4, 126.8, 126.7, 126.5, 126.2, 124.9, 124.8, 123.7, 118.8, 115.5, 57.4, 48.1, 46.1, 31.0	297 (M^+)
11i	3381, 3032, 1499, 1308	7.51−7.09 (m, 10 H), 6.95 (d, 1 H, *J* = 7.9), 6.52 (d, 1 H, *J* = 8.1), 4.71 (br s, 1 H), 4.51 (d, 1 H, *J* = 6.7), 3.92 (br s, 1 H), 3.34−3.14 (m, 2 H), 2.42 (m, 1 H)	145.5, 143.7, 142.7, 142.1, 129.0, 128.6, 127.5, 127.1, 126.6, 126.5, 125.2, 124.8, 123.1, 116.6, 57.4, 47.8, 46.0, 30.9	333 (M^+ + 2), 331 (M^+)
11j	3398, 2947, 1515, 1160	7.55−6.52 (m, 12 H), 4.67 (s, 1 H), 4.56 (d, 1 H, *J* = 7.8), 3.86 (s, 1 H), 3.72 (s, 3 H), 3.35−3.12 (m, 2 H), 2.42 (m, 1 H)	152.6, 146.1, 143.0, 142.7, 139.1, 128.5, 128.3, 127.8, 126.9, 126.3, 125.2, 124.8, 124.0, 116.3, 115.4, 113.2, 57.8, 55.6, 48.1, 46.5, 30.9	327 (M^+)
11k	3387, 2950	7.55−6.86 (m, 11 H), 4.72 (s, 1 H), 4.54 (d, 1 H, *J* = 7.0), 3.80 (br s, 1 H, NH), 3.33−3.14 (m, 2 H), 2.42 (m, 1 H), 2.11 (s, 3 H)	145.8, 142.7, 142.4, 141.8, 129.0, 128.8, 128.5, 127.6, 127.5, 127.1, 126.5, 124.9, 124.6, 124.0, 122.3, 120.3, 57.3, 47.8, 46.2, 30.9, 17.2	347 (M^+ + 2), 345 (M^+)
11l	3385, 2930, 1495	7.42−6.71 (m, 11 H), 4.92 (d, 1 H, *J* = 6.0), 4.45 (d, 1 H, *J* = 4.2), 3.87 (br s, 1 H), 3.43−3.12 (m, 2 H), 2.85 (m, 1 H), 2.62 (s, 3 H), 2.15 (s, 3 H)	145.8, 145.4, 143.2, 142.5, 134.3, 128.8, 128.5, 127.5, 127.1, 126.2, 125.6, 124.8, 123.7, 123.3, 121.4, 119.7, 60.2, 46.6, 45.1, 33.8, 17.5, 16.1	325 (M^+)
12	3414, 3065, 1577	7.80−7.08 (m, 15 H), 4.85 (s, 1 H), 4.75 (d, 1 H, *J* = 7.2), 4.71 (br s, 1 H, NH), 3.47 (m, 2 H), 2.50 (m, 1 H)	146.2, 142.9, 142.7, 139.4, 132.6, 128.6, 128.5, 127.5, 127.3, 126.9, 126.7, 126.1, 125.2, 125.1, 125.0, 124.9, 122.2, 119.6, 118.5, 117.6, 57.7, 48.1, 46.8, 30.9	347 (M^+)

[a] Satisfactory microanalyses obtained: C ± 0.45; H ± 0.04; N ± 0.03.

yield (Scheme 1). Table 1 summarizes the results of reaction of indene with *N*-arylaldimines **1** having various substituents. Benzo[*h*]indenoquinoline **12** was obtained in 50% yield when *N*-benzylidene-1-naphthylamine (**3**) was treated with indene in the presence of indium trichloride.

In summary, the results demonstrated here reveal the wide utility of indium trichloride in the imino Diels−Alder reaction of *N*-arylaldimines to synthesise new quinoline derivatives.

Mass spectra were recorded on Varian VG 70-70H mass spectrometer. Melting points were measured in capillary tubes and are uncorrected. Analytical TLC was performed on precoated sheets of silica gel G of 0.25 mm thickness containing PF 254 indicator (Merck, Darmstadt). Column chromatography was performed with silica gel (60−120 mesh; SD Fine, Boisar). IR spectra were recorded as solids in KBr pellets on a Nicolet Impact-400 spectrometer. NMR spectra were obtained on a Bruker spectrometer. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and the chemical shifts are given in δ relative to the internal standard TMS. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ and the chemical shift was given in δ relative to the solvent (77.0). MeCN was distilled from CaH_2 and dried over 4 Å molecular sieves.

IndiumTrichloride-Catalyzed Diels−Alder Reaction of Imines 1a−l or 3 with Dienenophile; General Procedure

A mixture of imine **1** or **3** (2.5 mmol), $InCl_3$ (0.110 g, 20 mol%), dienenophiles [cyclopentadiene (5 mmol) or 3,4-dihydro-2*H*-pyran (5 mmol) or indene (2.5 mmol)] in MeCN (7 mL) was stirred at r.t. for the appropriate time. To the reaction mixture was added aq satd $NaHCO_3$ solution (5 mL) and the solution was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were washed with H_2O, brine, dried (Na_2SO4), filtered, and the solvent evaporated. The residue was purified by column chromatography eluting with 90:10 EtOAc/petroleum ether (bp 60-80°C) to afford the cycloadducts.

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