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An improved synthesis of arenedicarboximides by phosphine-assisted annulation of arene-1,2-dicarbaldehyde with *N*-substituted maleimide

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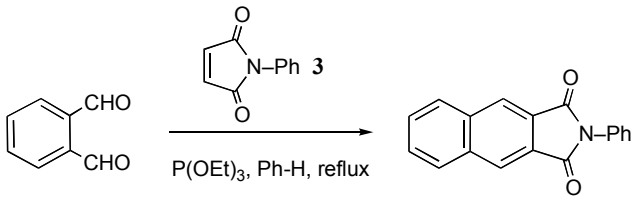
Abstract: Various arene-1,2-dicarbaldehydes react with *N*-substituted maleimides in the presence of trialkylphosphine in refluxing dioxane to afford the title compounds in good yields, which are better than those in a similar reaction using triethylphosphite reported by Haddadin *et al*. Many products were isolated by direct filtration from the reaction mixtures and washing with a suitable solvent. Application of the method to synthesis of diimides is also reported.

Keywords: Maleimides, Arene-1,2-Dicarbaldehydes, Morita-Baylis-Hillman Reaction, Intramolecular Wittig Reaction

1. Introduction

Arenedicarboximides show interesting photochemical behaviors, such as photoreduction [1,2] and photocycloaddition [3,4], and also unique photophysical properties [5–8]. Recently, Heagy *et al*. reported that dual fluorescent 2,3-naphthalenedicaboximides could be used in ratiometric DNA detection and as white organic light-emitting devices (OLEDs) [9], and syntheses of various di- and polydicarboximides for OLEDs and organic field-effect transistors have been continuously reported [10–12], indicating that arenedicarboximides are promising agents for biochemical reactions and electronic materials. *N*-Substituted arenedicarboximides can be obtained by various simple ways, such as condensation of arenedicarboxylic anhydride with amine [11,13–15] and Gabriel reaction of *N*-unsubstituted arenedicarboximide with alkyl or aryl halide [16-18]. When these anhydride and *N*-unsubstituted dicarboximide are commercially available or easily accessible, these methods are superior. Moreover, an approach by Diels-Alder reaction *via* arene-*o*-quinodimethane or isobenzofuran constructing concomitantly another benzene ring has been reliable [19–22]. Besides, Haddadin *et al.* reported an interesting synthetic reaction, in which *o*-phthaldehyde (1) condenses with *N*-phenylmaleimide (3) in the presence of triethylphosphite to give *N*-phenyl-2,3-naphthalenedicarboximide (2) in a satisfactory yield (62%) (Scheme 1) [23]. However, they also reported that the reaction of 2,3-naphthaldehyde under similar reaction conditions resulted in a low yield (35%) of the anthracenedicarboximide. Notwithstanding



1 **2**

Scheme 1. *A synthetic method of* ***2*** *by Haddadin et al.*

the fascinating methodology of Haddadin *et al*., there has been no work of its improvement reported for a long time. Herein we describe results of our effort to improve this reaction with various phosphorus reagents and solvents.

2. Results and Discussion

First, the reaction of 1 and 3 with various solvents and phosphorus reagents under refluxing conditions was examined.

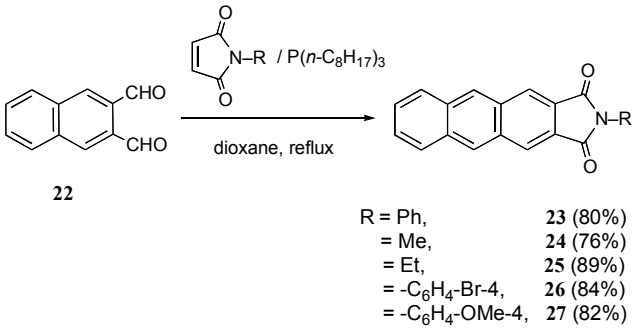
The results are presented in Table 1. It should be noted that the yields in the Table are ones isolated directly from reaction mixture just by filtration and washing with cold ether. Among solvents used, the reaction in dioxane gave a better yield than those in other solvents (Entry 1–5). Triphenylphosphine assisted the reaction as much as triethylphosphite (Entry 5), and bulky tri-*tert*-butyl and tri-*o*-tolylphosphines were entirely ineffective (Entry 6-7). The satisfactory yields were observed when tri-*n*-butyl-, tricyclohexyl-, and tri-*n*-octylphosphines were used (Entry 8–10). Under the conditions with a slight excess of tri-*n*-octylphosphine and 3, the product 2 was obtained in the best yield of 89% (Entry 11), which shows a clear improvement compared with the result of Haddadin *et al.*

Table 1. *Results of the reaction of 1 and 3*[a]

Entry	P reagent[b]	Solvent/reaction time	Yield of 2 (%)[c]
1	$P(OEt)_3$	benzene/15 min	62[d]
2	$P(OEt)_3$	CH_3CN/ 6 h	22
3	$P(OEt)_3$	EtOH/ 4 h	23
4	$P(OEt)_3$	dioxane/ 1.5 h	75
5	PPh_3	dioxane/ 2 h	74
6	P(*o*-tol)$_3$	dioxane/ 2 h	0
7	P(*t*-butyl)$_3$[e]	dioxane/ 2 h	0
8	P(*c*-hexyl)$_3$	dioxane/ 2 h	79
9	P(*n*-butyl)$_3$	dioxane/ 2 h	79
10	P(*n*-octyl)$_3$	dioxane/ 0.5 h	83
11	P(*n*-octyl)$_3$	dioxane/ 0.5 h	89[f]
12	P(*n*-octyl)$_3$	dioxane/ 0.5 h	88[g]

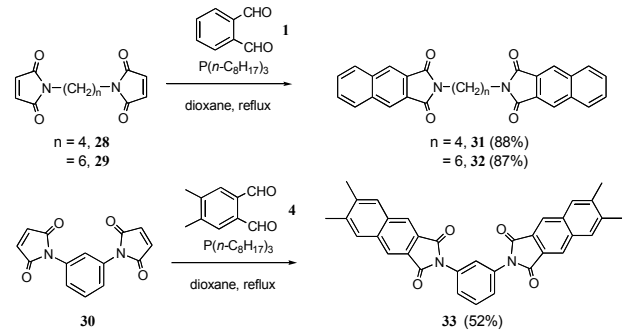
a) An equivalent of 3 to 1 was used, b) 1.2 equivalents of phosphorus reagent to 1 were used, c) isolated yield directly from reaction mixture, d) taken from ref. [22], e) P(*t*-butyl)$_3$HBF$_4$ salt was used in the presence of an equivalent of DBU, f) 1.1 equivalents of 3 to 1 were used, g) 1.2 equivalents of 3 and 1.3 equivalents of phosphine reagent to 1 were used

Secondly, various *N*-substituted maleimides were subjected to the reactions with 1, 4,5-dimethyl-*o*-phthaldehyde (4) [24] and 4,5-dichloro-*o*-phthaldehyde (5) [24,25] under the conditions of entry 11 in Table 1. Structures of the substituted 2,3-naphthalenedicarboximides synthesized are shown in Figure 1. The sixteen imide products were obtained in a range of 71–89% yields, indicating effectiveness of the improved procedure for a variety of naphthalenedicaboximides. The products were isolated mainly by filtration from the reaction mixture. However, some products soluble in dioxane to some extent were obtained partly by chromatography purification of the filtrate. We also applied our procedure to synthesis of 2,3-anthracenedicarboximides. The results are shown in Scheme 2. From 2,3-naphthaldehyde (22), the dicarboximides (23–27) were synthesized in good yields (Scheme 2). Particularly, the yield of 23 is more than twice of that



Scheme 2. *Synthesis of N-substituted 2,3-anthracenedicarboximides.*

reported by Haddadin *et al*. Furthermore, our protocol developed herein was applied to synthesis of diimides. Under the same conditions compounds 28 and 29 [26] react with 1 to give diimides 31 and 32 in good yields, respectively, and 30 reacts with 4 to give 33 in a moderate yield (Scheme 3).



Scheme 3. *Application to synthesis of diimide compounds 31–33.*

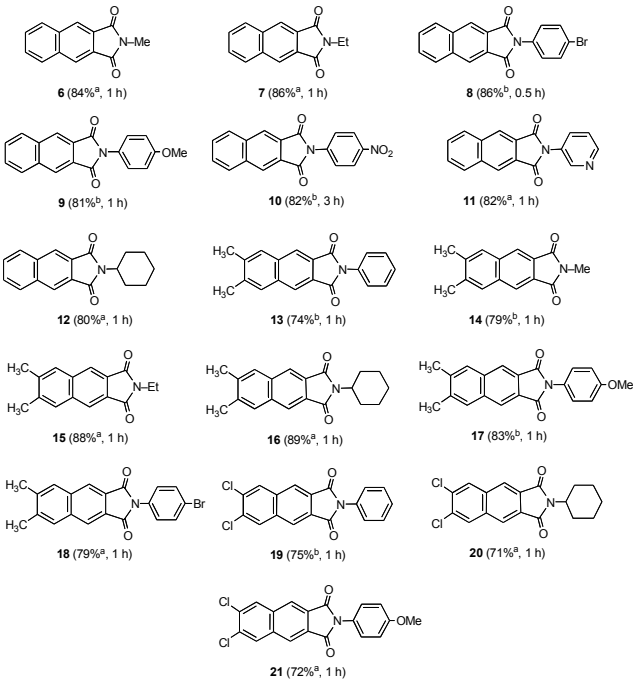
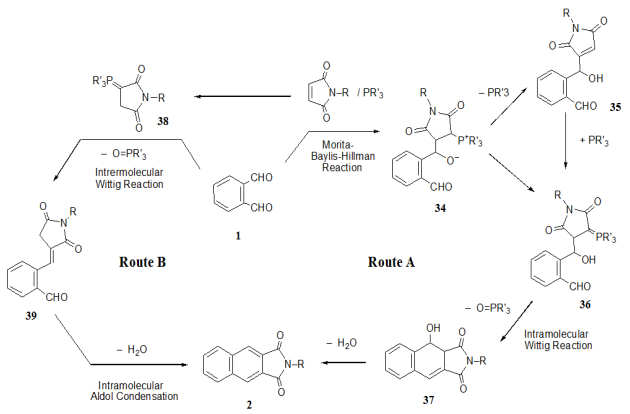


Figure 1. *Various dicarboximides obtained under reaction conditions of entry 12 in Table 1 with the corresponding dicarbaldehyde and N-substituted maleimides. Yield and reaction time are shown in parentheses.* [a)] *Isolated yield mainly by filtration from reaction mixture and partly by chromatography purification of the filtrate,* [b)] *isolated yield directly by filtration from reaction mixture and washing with cold ether..*

In Scheme 4, the possible reaction routes to 2 from 1 and *N*-substrtuted maleimide in the presence of phosphine are shown. As previously suggested by Haddadin *et al*., the reaction may proceed *via* the Morita-Baylis-Hillman reaction [27] to produce 36, followed by the intramolecular Wittig condensation (route A). Besides, route B involving intermolecular Wittig reaction of 1 with 38, being able to be formed from maleimide and phosphine, and subsequent intramolecular aldol condensation of 39 is possible. Since the reaction of the preformed Wittig reagent 38 [28] with 1 in refluxing dioxane was found to be very slow compared with the results in Table 1. Only a small amount of 2 (12% in a case with the tri-*n*-octylphosphorane reagent) was observed even after prolonged reaction times. Therefore, a process through the route B must be negligible at least under the conditions. Further mechanistic studies to obtain decisive evidences for the reaction mechanism are now under progress.



Scheme 4. *Possible reaction routes to 2 from 1 and N-substituted maleimide in the presence of phosphine.*

3. Experimental

3.1. General Remarks

Melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on JEOL Diamond-20 and JASCO FT/IR-4100 spectrometers. UV spectra were measured on a Shimadzu UV-2550 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL λ400 and ECA500 spectrometers. Chemical shift values of tetramethylsilane (δ= 0 ppm) for ^{1}H-NMR spectra and $CDCl_3$ (δ= 77.0 ppm) for ^{13}C-NMR spectra were used as internal standard. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was performed with Silica gel 60N from Kanto Chem. Dioxane was purchased from Kanto Chem. and was distilled over CaH_2. *o*-Phthalaldehyde, triethylphophite, triphenylphosphine, tricyclohexylphosphine, *N*-phenylmaleimide, *N*-methylmaleimide, *N*-ethylmaleimide, *N*-cyclohexylmaleimide, and *N,N'*-(*m*-phenylene)dimale-imide were purchased from Tokyo Chemical Industry, Inc. *N*-(3-Pyridyl)maleimide, *N*-(4-bromophenyl)maleimide, *N*-(4-methoxyphenyl)maleimide were prepared according to a procedure reported by Cava *et al.* [29] *N,N'*-Tetramethylene- and -hexamethylenedimaleimides are prepared by the method of Tona *et al.* [26] 2,3-Naphthaldehyde was prepared from phthalaldehyde and 2,5-dimethoxytetrahydrofuran by a method of Lepage *et al.* [30] 4,5-Dimethyl-*o*-phthalaldehyde (4) was prepared according to the method of Farooq. [24] 4,5-Dichloro-*o*-phthalaldehyde (5) was prepared by the method of Chen *et al.* [25]

3.2. General Procedure

To solution of dicarbaldehyde (0.5 mmol) and *N*-substituted maleimide (0.55 mmol) in 2 ml of dry dioxane was added tri-*n*-octylphosphine (0.60 mmol). The reaction mixture was refluxed on a preheated oil bath under nitrogen atmosphere for 0.5–3 h, and was cooled to ice-bath temperature. The crystals formed were collected by suction filtration and washed well with cold ether to give a product. If necessary, the filtrate was concentrated under vacuum and the residue was purified by silica gel chromatography with a solvent system of chloroform/ethyl acetate (or chloroform/ethanol).

3.3. N-Phenyl-2,3-naphthalimide (2)

Colorless prisms, m.p. 284–285 ˚C (lit. [23] 279–280 ˚C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (s, 2H), 8.11 (m, 2H), 7.74 (m, 2H), 7.54 (tm, J = 7.0 Hz, 2H), 7.50 (dm, J = 7.0 Hz, 2H), 7.43 (tm, J = 7.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 135.7, 131.9, 130.4, 129.4, 129.1, 128.2, 127.5, 126.7, 125.3.ppm.

3.4. N-Methyl-2,3-naphthalimide (6)

Colorless microcrystals, m.p. 239–242 ˚C (lit. [4] 215–217 ˚C, [31] 240–242 ˚C). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.32 (s, 2 H), 8.05 (m, 2H), 7.69 (m, 2H), 3.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1, 135.4, 130.3, 129.1, 127.9, 124.6, 24.2 ppm.

3.5. N-Ethyl-2,3-naphthalimide (7)

Colorless microcrystals, m.p. 185–186 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (s, 2 H), 8.05 (m, 2H), 7.69 (m, 2H), 3.82 (q, J = 7.0 Hz, 2H), 1.32 (q, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ= 167.9, 135.4, 130.2, 129.1, 128.0, 124.5, 33.1, 13.9 ppm. IR (KBr) ν=1760 (vs), 1707 (vs) cm^{-1}. UV (MeOH) λ = 215 (logε = 4.36), 239sh (4.38), 254 (4.57), 256 (4.58), 259 (4.58), 281 (3.78), 290 (3.79), 332sh (3.14), 344 (3.39), 357 (3.53) nm. MS *m/z* (%) = 225 (M^+, 57), 211 (14), 210 (100), 197 (7), 183 (7), 155 (13), 126 (16), 91 (10), 63 (7). HRMS Cald for $C_{14}H_{11}NO_2$ (M^+) 225.0790, found 225.0789.

3.6. N-(4-Bromophenyl)-2,3-naphthalimide (8)

Colorless microcrystals, m.p. >300 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.64 (s, 2 H), 8.32 (m, 2H), 7.82 (m, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ = 166.3, 135.1, 131.7, 131.3,

130.2, 129.33, 129.28, 127.3, 124.8, 121.0 ppm. IR (KBr) ν =1787 (s), 1719 (vs) cm^{-1}. UV (MeOH) λ = 203 (logε = 4.12), 217 (4.15), 245sh (4.25), 261 (4.37), 338 (2.98), 359 (2.77) nm. MS *m/z* (%) = 353 (M^+, 100), 351 (M^+, 100), 309 (23), 307 (23), 228 (22), 227 (14), 153 (8), 136 (19), 126 (48). HRMS Cald for $C_{18}H_{10}{}^{79}BrNO_2$ (M^+) 350.9895, found 350.9894.

3.7. N-(4-Methoxyphenyl)-2,3-naphthalimide (9) [6]

Yellowish microcrystals, m.p. 245–246 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 (s, 2H), 8.09 (m, 2H), 7.73 (m, 2H), 7.40 (dm, *J* = 8.4 Hz, 2H), 7.05 (dm, *J* = 8.4 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ =167.3, 159.3, 135.6, 130.3, 129.3, 127.9, 125.1, 124.5, 114.5, 55.5 ppm. UV (MeOH) λ = 217 (logε = 4.51), 225sh (4.43), 260 (4.72), 281sh (4.30), 342 (3.42), 358 (3.45) nm.

3.8. N-(4-Nitrophenyl)-2,3-naphthalimide (10)

Colorless solids, m.p. >300 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6 at 130 ˚C) δ = 8.59 (s, 2H), 8.37 (d, *J* = 8.8 Hz, 2H), 8.29 (m, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.81 (m, 2H) ppm. ^{13}CNMR (100 MHz, DMSO–d_6 at 130 ˚C) δ = 165.3, 146.1, 137.6, 134.9, 129.7, 128.9, 127.0, 126.6, 124.6, 123.3 ppm. IR (KBr) ν = 1771 (s,) 1749 (s,) 1723 (vs) cm^{-1}. MS *m/z* (%) = 318 (M^+, 100), 288 (19), 274 (25), 272 (14), 228 (25), 227 (9), 154 (9), 126 (52). HRMS calcd for $C_{18}H_{10}N_2O_4$ (M^+) 318.0641, found 318.0638.

3.9. N-(3-Pyridyl)-2,3-naphthalimide (11)

Colorless solids, m.p. 244–246 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.85 (dd, *J* = 2.5, 0.7 Hz, 1H), 8.66 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.48 (s, 2H), 8.12 (m, 2H), 7.90 (ddd, *J* = 8.2, 2.5, 1.7 Hz, 1H), 7.76 (m, 2H), 7.48 (ddd, *J* = 8.2. 4.9, 0.7 Hz, 1H) ppm. ^{13}CNMR (126 MHz, $CDCl_3$) δ = 166.5, 148.8, 147.4, 135.7, 133.6, 130.4, 129.6, 129.0, 127.0, 125.7, 123.6 ppm. IR (KBr) ν = 1784 (m), 1766 (m), 1715 (vs), 1709 (vs) cm^{-1}. UV (CH_3CN) λ = 261 (logε = 4.83), 294sh (3.99), 343 (3.42), 359 (3.57) nm. MS *m/z* (%) = 274 (M^+, 100), 229 (54), 126 (48). EA ($C_{17}H_{10}N_2O_2$) Calcd C; 74.44, H; 3.67, N; 10.21 %, Found C; 74.03, H; 3.72, N; 10.20 %.

3.10. N-Cyclohexyl-2,3-naphthalimide (12)

Colorless solids, m.p. 208–209 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 8.30 (s, 2H), 8.04 (m, 2H), 7.68 (m, 2H), 4.20 (tt, *J* = 12.3, 3.4 Hz, 1H), 2.28 (qd, *J* = 12.3, 3.4 Hz, 2H), 1.77 (dm, *J* = 12.3 Hz, 2H), 1.71 (dm, *J* = 12.3 Hz, 1H), 1.40 (qt, *J* = 12.3, 3.4 Hz, 2H), 1.32 (tt, *J* = 12.3, 3.4 Hz, 1H)ppm. ^{13}CNMR (126 MHz, $CDCl_3$) δ = 168.3, 135.6, 130.3, 129.1, 128.1, 124.4, 51.3, 29.9, 26.2, 25.3 ppm. IR (KBr) ν = 1761 (s), 1748 (m), 1700 (vs) cm^{-1}. MS *m/z* (%) = 279 (M^+, 55), 236 (28), 198 (100), 180 (30), 155 (10), 127 (10). HRMS calcd for $C_{18}H_{17}NO_2$ (M^+) 279.1259, found 279.1261.

3.11. 6,7-Dimethyl-N-phenyl-2,3-naphthalimide (13)

Colorless solids, m.p. >300 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$,) δ = 8.33 (s, 2H), 7.83 (s, 2H), 7.53 (tm, *J* = 7.2 Hz, 2H), 7.49 (dm, *J* = 7.2 Hz, 2H), 7.41 (tm, *J* = 7.2 Hz, 1H), 2.51 (s, 6H) ppm. ^{13}CNMR (126 MHz, $CDCl_3$ at 50 ^{o}C) δ = 167.4, 140.0, 134.8, 132.4, 130.1, 129.2, 128.2, 127.1, 126.8, 124.4, 20.5 ppm. UV (MeOH) λ = 218 (logε = 4.39), 257sh (4.48), 272 (4.72), 295sh (3.93), 321sh (3.44), 352 (3.32), 365 (3.46) nm. IR (KBr) ν = 1775 (m), 1763 (m), 1735 (s), 1712 (s) cm^{-1}. MS *m/z* (%) = 301 (M^+, 100), 257 (38), 242 (10), 154 (9). HRMS calcd for $C_{20}H_{15}NO_2$ (M^+) 301.1103, found 301.1101.

3.12. 6,7-Dimethyl-N-methyl-2,3-naphthalimide (14)

Colorless solids, m.p. 246–249 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 8.19 (s, 2H), 7.77 (s, 2H), 3.23 (s, 3H), 2.48 (s, 6H) ppm. ^{13}CNMR (126 MHz, $CDCl_3$) δ = 168.6, 139.7, 134.3, 130.0, 127.3, 123.7, 24.3, 20.5 ppm. IR (KBr) ν = 1770 (s), 1716 (vs), 1709 (vs) cm^{-1}. MS *m/z* (%) = 239 (M^+, 100), 211 (12), 195 (45), 154 (19), 139 (10). HRMS calcd for $C_{15}H_{13}NO_2$ (M^+) 239.0946, found 239.0947.

3.13. N-Ethyl-6,7-dimethyl-2,3-naphthalimide (15)

Colorless plates, m.p. 229–230 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$,) δ = 8.20 (s, 2H), 7.78 (s, 2H), 3.80 (q, *J* = 7.3 Hz, 2H), 2.48 (s, 6H), 1.31 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}CNMR (126 MHz, $CDCl_3$) δ= 168.4, 139.7, 134.4, 130.0, 127.4, 123.7, 33.2, 20.5, 14.1 ppm. IR (KBr) ν = 1769 (s), 1740 (s), 1717 (vs), 1708 (vs) cm^{-1}. MS *m/z* (%) = 253 (M^+, 64), 238 (100), 225 (13), 154 (11). HRMS calcd for $C_{16}H_{15}NO_2$ (M^+) 253.1103, found 253.1103.

3.14. N-Cyclohexyl-6,7-dimethyl-2,3-naphthalimide (16)

Colorless microcrystals, m.p. 252–253 ˚C. ^{1}HNMR ($CDCl_3$, 500 MHz) δ = 8.16 (s, 2H), 7.77 (s, 2H), 4.17 (tt, *J* = 12.7, 3.4 Hz, 1H), 2.27 (qd, *J* = 12.7, 3.4 Hz, 2H), 1.88 (dm, *J* = 12.7, 2H), 1.71 (dm, *J* = 12.7 Hz, 1H), 1.39 (qd, *J* = 12.7, 3.4 Hz, 2H), 1.30 (qd, *J* = 12.7, 3.4 Hz, 1H) ppm. ^{13}CNMR (126 MHz, $CDCl_3$) δ = 168.4, 139.3, 134.3, 129.7, 127.1, 123.3, 51.0, 29.8, 26.1, 25.2, 20.3 ppm. IR (KBr) ν = 1757 (s), 1701 (vs) cm^{-1}. MS *m/z* (%) = 307 (M^+, 73), 264 (33), 226 (100), 208 (26), 154 (13). HRMS calcd for $C_{20}H_{21}NO_2$ (M^+) 307.1572, found 307.1570.

3.15. N-(4-Methoxyphenyl)-6,7-dimethyl-2,3-naphthalimide (17)

Colorless microcrystals, m.p. 278–279 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 8.31 (s, 2H), 7.82 (s, 2H), 7.39 (dm, *J* = 9.1 Hz, 2H), 7.04 (dm, *J* = 9.1 Hz, 2H), 3.86 (s, 3H), 2.50 (s, 6H) ppm. ^{13}CNMR (126 MHz, $CDCl_3$ at 50 ^{o}C) δ = 167.5, 159.3, 139.7, 134.6, 129.9, 128.0, 127.0, 124.9, 124.1, 114.5, 55.6, 20.3 ppm. IR (KBr) ν = 1767 (m), 1739 (m), 1714 (vs) cm^{-1}. MS *m/z* (%) = 331 (M^+, 100), 316 (29), 287 (7), 316 (29), 208 (7), 154 (7). HRMS calcd for $C_{21}H_{17}NO_3$ (M^+) 331.1208, found 331.1207.

3.16. N-(4-Bromophenyl)-6,7-dimethyl-2,3-naphthalimide (18)

Faintly pink solids, m.p. >300 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 8.32 (s, 2H), 7.83 (s, 2H), 7.64 (dm, J = 8.7 Hz, 2H), 7.40 (dm, J = 8.7 Hz, 2H), 2.51 (s, 6H) ppm. ^{13}CNMR (125 MHz, $CDCl_3$) δ = 166.9, 140.0, 134.5, 132.2, 131.1, 129.9, 128.0, 127.0, 124.5, 121.7, 20.4 ppm. IR (KBr) ν = 1785 (s), 1719 (vs), 1709 (vs) cm^{-1}. MS *m/z* (%) = 381 (M^+, 100), 379 (M^+, 100), 337 (21), 335 (21), 154 (17), 153 (12), 152 (12), 150 (11), 143 (11), 139 (11). HRMS calcd for $C_{20}H_{14}{}^{79}BrNO_2$ (M^+) 379.0208, found 379.0210.

3.17. 6,7-Dichloro-N-phenyl-2,3-naphthalimide (19)

Yellowish powder, m.p. >300 ˚C. ^{1}HNMR (500 MHz, DMSO-d_6 at 140 ˚C) δ = 8.57 (s, 2H), 8.54 (s, 2H), 7.52 (t, J = 7.4 Hz, 2H), 7.48 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H) ppm. ^{13}CNMR (125 MHz, DMSO-d_6 at 140 ˚C) δ = 165.2, 133.8, 131.7, 131.6, 130.5, 128.1, 128.0, 127.3, 126.3, 123.2 ppm. IR (KBr) ν = 1772 (s), 1746 (s), 1718 (vs), 1702 (vs) cm^{-1}. MS *m/z* (%) = 345 (M^+, 12), 343 (M^+, 66), 341 (M^+, 100), 299 (27), 298 (40), 227 (19), 196 (20), 194 (30). HRMS calcd for $C_{18}H_9{}^{35}Cl_2NO_2$ (M^+) 341.0010, found 341.0007.

3.18. 6,7-Dichloro-N-cyclohexyl-2,3-naphthalimide (20)

Colorless powder, mp >300 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$) δ = 8.20 (s, 2H), 8.15 (s, 2H), 4.19 (tt, J = 12.4, 3.4 Hz, 1H), 2.26 (qd, J = 12.4, 3.4 Hz, 2H), 1.89 (dm, J = 12.4 Hz, 2H), 1.76 (dm, J = 12.4 Hz, 2H), 1.72 (dm, J = 12.4 Hz, 1H), 1.40 (qt, J = 12.4, 3.4 Hz, 2H), 1.30 (qt, J = 12.4, 3.4 Hz, 1H) ppm. ^{13}CNMR (125 MHz, $CDCl_3$) δ = 167.6, 134.4, 134.0, 131.0, 129.2, 123.2, 51.6, 29.9, 26.2, 25.3 ppm. UV (MeOH) λ = 213 (logε = 4.39), 245sh (4.52), 251sh (4.63), 261 (4.78), 267 (4.84), 280sh (4.13), 295 (4.04), 319 (3.31), 325 (3.29), 334 (3.19), 344 (3.37), 360 (3.47), 369 (3.15) nm. IR (KBr) ν = 1767 (s), 1703 (vs) cm^{-1}. MS *m/z* (%) = 350 (M^+, 5), 349 (M^+, 28), 347 (M^+, 42), 306 (16), 304 (24), 270 (11), 269 (10), 266 (100), 250 (16), 248 (23), 223 (10), 196 (10), 194 (15). HRMS calcd for $C_{18}H_{15}{}^{35}Cl_2NO_2$ (M^+) 347.0480, found 347.0480.

3.19. 6,7-Dichloro-N-(4-methoxyphenyl)-2,3-naphthalimide (21)

Yellow powder, m.p. >300 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$ at 50 ˚C) δ = 8.33 (s, 2H), 8.19 (s, 2H), 7.39 (d, J = 8.9 Hz, 2H), 7.03 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}CNMR (125 MHz, $CDCl_3$ at 50 ˚C) δ = 166.5, 159.6, 134.5, 134.4, 130.9, 128.9, 127.8, 124.5, 123.9, 114.6, 55.6 ppm. IR (KBr) ν = 1772 (m), 1725 (s), 1707 (vs) cm^{-1}. MS *m/z* (%) = 375 (M^+, 12), 373 (M^+, 66), 371 (M^+, 100), 358 (18), 356 (27), 194 (11). HRMS calcd for $C_{19}H_{11}{}^{35}Cl_2NO_3$ (M^+) 371.0116, found 371.0118.

3.20. N-Phenyl-2,3-anthracenedicarboximide (23) [32]

Yellow microcrystals, m.p. >300 ˚C (lit [19] 368–370 ˚C). ^{1}HNMR (400 MHz, DMSO-d_6) δ = 9.00 (s, 2H), 8.80 (s, 2H), 8.23 (m, 2H), 7.72 (m, 2H), 7.52 (m, 5H) ppm

3.21. N-Methyl-2,3-anthracenedicarboximide (24)

Yellow microcrystals, m.p. >300 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63 (s, 2H), 8.50 (s, 2H), 8.08 (m, 2H), 7.62 (m, 2H), 3.76 (s, 3H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$) δ = 168.0, 133.3, 131.9, 130.1, 128.5, 127.5, 126.8, 125.8, 24.3 ppm. IR (KBr) ν =1758 (s), 1701 (vs) cm^{-1}. UV (CH_3CN) λ_{max} = 211 (logε = 4.08), 239 (4.57), 276 (4.54), 287 (4.60), 290 (4.60), 291 (4.60), 293 (460), 307sh (4.40), 335sh (3.42), 322sh (3.55), 381 (3.73), 402 (3.78) nm. MS *m/z* (%) = 261 (M^+, 100), 217 (11), 204 (6), 176 (43), 116 (6), 88 (18). HRMS Calcd for $C_{17}H_{11}NO_2$ (M^+) 261.0790, found 261.0789

3.22. N-Ethyl-2,3-anthracenedicarboximide (25)

Yellow microcrystals, m.p. 271–272 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6 at 80 ˚C). δ = 8.99 (s, 2 H), 8.61 (s, 2 H), 8.17 (m, 2H), 7.67 (m, 2H), 3.71 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H) ppm ^{13}C NMR (100 MHz, DMSO-d_6 at 80 ˚C) δ = 166.6, 132.4, 131.3, 129.6, 128.0, 127.2, 126.3, 125.0, 32.4, 13.0 ppm. IR (KBr) ν =1759 (s), 1700 (vs) cm^{-1}. MS *m/z* (%) = 275 (M^+, 100), 260 (54), 247 (21), 233 (7), 205 (7), 176 (28), 130 (6), 116 (9), 102 (6), 88 (21). HRMS Calcd for $C_{18}H_{13}NO_2$ (M^+) 275.0946, found 275.0944.

3.23. N-(4-Bromophenyl)-2,3-anthracenedicarboximide (26) [32]

Yellow microcrystals, m.p. >300 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6 at 100 ˚C). δ = 8.96 (s, 2 H), 8.74 (s, 2 H), 8.20 (m, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.70 (m, 2H), 7.50 (d, J = 8.5 Hz, 2H) ppm IR (KBr) ν =1786 (m), 1742 (m), 1717 (vs), 1708 (vs) cm^{-1}. MS *m/z* (%) = 403 (M^+, 100), 401 (M^+, 100), 359 (34), 277 (17), 203 (29), 176 (88), 161 (30). HRMS Calcd for $C_{22}H_{12}{}^{79}BrNO_2$ (M^+) 401.0051, found 401.0052.

3.24. N-(4-Methoxyphenyl)-2,3-anthracenedicarboximide (27)

Yellow microcrystals, m.p. >300 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6 at 80 ˚C). δ = 8.95 (s, 2 H), 8.72 (s, 2 H), 8.20 (m, 2H), 7.69 (m, 2H), 7.41 (dm, J = 8.8 Hz, 2H), 7.09 (dm, J = 8.8 Hz, 2H), 3.84 (s, 3 H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6 at 100˚C) δ = 166.1, 159.6, 158.7, 132.4, 131.4, 129.6, 128.0, 127.9, 127.1, 125.4, 124.6, 113.9, 55.2 ppm. IR (KBr) ν =1762 (m), 1702 (vs) cm^{-1}. UV (CH_3CN) λ_{max} = 213 (logε = 4.25), 239 (4.66), 247 (4.66), 278sh (4.62), 291sh (4.74), 299 (4.80), 382 (3.80), 404 (3.82) nm. MS *m/z* (%) = 353 (M^+, 100), 338 (18), 309 (19), 266 (5), 230 (6), 203 (9), 176 (28). HRMS Calcd for $C_{23}H_{15}NO_3$ (M^+) 353.1052, found 353.1049.

3.25. N,N'-Tetramethylenebis(2,3-naphthalenedicarbox-imide) (31)

Colorless solids, m.p. >300 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$ at 50 ˚C) δ = 8.30 (s, 4H), 8.02 (m, 4H), 7.67 (m, 4H), 3.82

(m, 4H), 1.83 (m, 4H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$ at 50 ˚C) δ = 168.0, 135.6, 130.3, 129.1, 128.0, 124.6, 37.8, 26.1 ppm. IR (KBr) ν = 1762 (vs), 1717 (vs), 1710 (vs) cm^{-1}. UV ($CHCl_3$) λ_{max} = 246sh (logε = 4.73), 258sh (4.95), 262 (5.01), 283 (4.14), 293 (4.16), 304 (4.03), 325 (3.51), 343 (3.70), 359 (3.87) nm. MS *m/z* (%) = 448 (M^+, 60), 251 (14), 239 (11), 238 (65), 225 (11), 224 (18), 211 (36), 210 (100), 183 (11), 180 (10), 155 (17), 154 (11), 127 (28), 126 (24). HRMS calcd for $C_{28}H_{20}N_2O_4$ (M^+) 448.1423, found 448.1424.

3.26. N,N'-Hexamethylenebis(2,3-naphthalenedicarbox-imide) (32)

Colorless solids, m.p. 274-276 ˚C. ^{1}HNMR (500 MHz, $CDCl_3$ at 40 ˚C) δ = 8.30 (s, 4H), 8.03 (m, 4H), 7.67 (m, 4H), 3.74 (t, *J* = 7.0 Hz, 4H), 1.74 (quin, *J* = 7.0 Hz, 4H), 1.44 (quin, *J* = 7.0 Hz, 4H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$ at 40 ˚C) δ = 168.0, 135.5, 130.3, 129.0, 128.0, 124.5, 38.2, 28.4, 26.5 ppm. IR (KBr) ν = 1760 (s), 1708 (vs) cm^{-1}. UV ($CHCl_3$) λ_{max} = 244sh (logε = 4.70), 255sh (4.94), 262 (5.06), 281 (4.15), 293 (4.17), 303sh (4.03), 324 (3.48), 343 (3.71), 359 (3.89) nm. MS *m/z* (%) = 476 (M^+, 41), 266 (25), 238 (24), 224 (13), 211 (43), 210 (100), 180 (11), 155 (14), 127 (21), 126 (17). HRMS calcd for $C_{30}H_{24}N_2O_4$ (M^+) 476.1736, found 476.1738.

3.27. N,N'-(m-Phenylene)bis(6,7-dimethyl-2,3-naphtha-lene dicarboximide) (33) [32]

Orange solids, m.p. >300 ˚C. ^{1}HNMR (500 MHz, DMSO-d_6 at 150 ˚C) δ = 8.37 (s, 4H), 7.99 (s, 4H), 7.67 (m, 2H), 7.58 (dm, *J* = 7.6 Hz, 4H), 2.49 (s, 12H) ppm. IR (KBr) ν = 1766 (s), 1731 (s), 1714 (s) cm^{-1}. MS *m/z* (%) = 524 (M^+, 16), 368 (22), 120 (53), 97 (16), 88 (38), 56 (100). HRMS calcd for $C_{34}H_{24}N_2O_4$ (M^+) 524.1736, found 524.1738.

4. Conclusion

We have demonstrated a novel protocol for synthesis of arenedicarboximides. Our phosphine-assisted annulation resulted in much better yields of the products than those by the phosphite-assisted method reported by Haddadins *et al.* Also, we could successfully apply the method to the synthesis of some diimides.

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