SUPPORTING INFORMATION

Lewis Acid Promoted Annulation of *p*-Quinoneimides by Allylsilanes: A Facile Entry into Benzofused Heterocycles

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I. The remarkable sensitivity of the reaction towards the nature and amount of the Lewis acid used as well as to the temperature employed are depicted in the following schemes

A. at -41 °C, in presence of 2.4 eq. of Lewis acid

Lewis acid	Time	4a	1'
SnCl_4	3 h.	75%	<10%
$\text{BF}_3 \cdot \text{OEt}_2$	3 h.	38%	21%
Me_2AlCl	3 h.	<10%	54%
ZnCl_2	3 h.	<10%	<10%

Scheme S1

B. at room temperature, 1.1 eq. of Lewis acid

Lewis acid	Time	5a	1'
SnCl_4	3 h	-	<60%
$\text{BF}_3 \cdot \text{OEt}_2$	3 h.	74%	<10%
Me_2AlCl	3 h.	<10%	58%
ZnCl_2	3 h.	-	<10%

Scheme S2

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C. addition of p-quinone monoimides-insensitive to the nature of Lewis acid

Scheme S3

II. General Experimental Procedure

All reactions were carried out in oven-dried glasswares under argon atmosphere and the solvents used were dry. Allyltriisopropylsilane, allyltriphenylsilane, SnCl₄ (1M solution in heptane), BF₃.OEt₂ and Me₂AlCl were purchased from Aldrich. The quinoneimides were prepared according to literature reported procedures [a. Adams, R.; Nagarkatti, A. S. *J. Am. Chem. Soc.* **1950**, 72, 4601. b. Adams, R.; Looker, J. H. *J. Am. Chem. Soc.* **1951**, 73, 1145.] Progress of reactions were monitored by Thin Layer Chromatography while purification was effected using silica gel column chromatography. NMR data were collected at room temperature in CDCl₃ at operating frequency 300MHz. IR data were obtained by making pellets of compounds using KBr.

ZnCl₂ promoted reaction

Allyltriisopropylsilane (96 mg, 0.48 mmol) and quinoneimide (83 mg, 0.20 mmol) were taken in dry CH₂Cl₂ (8 mL), cooled to 0 °C and ZnCl₂ (66 mg, 0.48 mmol) was added. The reaction was allowed to attain room temperature gradually and stirred at that temperature for 72 h., quenched by adding ice-cold water and the mixture was extracted with CH₂Cl₂ (3x10 mL). The combined organic layer was washed with water (10 mL), brine (10 mL), and water (10 mL) and dried over anhyd. Na₂SO₄.

SnCl₄ and Me₂AlCl promoted reaction

A solution of allyltriisopropylsilane and quinoneimide in dry CH₂Cl₂ under argon atmosphere was treated with SnCl₄ for the indicated period of time at indicated

temperatures shown in respective schemes. The mixture was then quenched with sat. NH_4Cl solution and extracted with CH_2Cl_2 (3x10 mL). The combined organic layer was washed successively with water, brine and water and dried over Na_2SO_4 .

$\text{BF}_3 \cdot \text{OEt}_2$ Promoted reaction

Same experimental procedure for SnCl_4 promoted reaction except that sat. Na_2CO_3 was used for quenching the reaction.

III. Spectral Data

Data for **3a**

mp: 237-238 °C

IR (cm^{-1}): 2950, 2864, 1606, 1481, 1330, 1110, 1085, 843

^1H NMR (δ): 7.48 (d, **4H**, $J = 8.0$ Hz), 7.34 (s, **2H**), 7.15 (d, **4H**, $J = 8.0$ Hz), 4.52–4.46 (m, **2H**), 2.74 (dd, **2H**, $J = 15.4, 8.9$ Hz), 2.46–2.36 (m, **8H**), 1.43 (dd, **2H**, $J = 14.4, 3$ Hz), 1.24–1.10 (m, **38H**), 0.85–0.87 (m, **6H**)

^{13}C NMR (δ): 143.84, 137.80, 135.38, 132.25, 129.56, 126.90, 114.70, 62.10, 36.51, 21.53, 19.20, 18.82, 11.53

Anal. Calcd. for $\text{C}_{44}\text{H}_{68}\text{N}_2\text{O}_4\text{S}_2\text{Si}_2$: C, 65.30; H, 8.47; N, 3.46. Found: C, 65.18; H, 8.75; N, 3.51.

Single crystal X-ray structure for 3a

Data for **4a**

mp: 58-59 °C

IR (cm⁻¹): 3230, 2950, 2873, 1603, 1490, 1334, 1108, 1093, 883, 667

¹H NMR (δ): 7.59 (d, **2H**, $J = 7.8$ Hz), 7.47-7.41 (m, **3H**), 7.25-7.20 (m, **3H**), 7.13 (d, **2H**, $J = 7.8$ Hz), 6.90 (s, **1H**), 6.75 (s, **1H**, *exchangeable with D₂O*), 4.45-4.38 (m, **1H**), 2.68 (dd, **1H**, $J = 16.0, 9.0$ Hz), 2.41 (s, **3H**), 2.37 (s, **3H**), 1.38 (dd, **1H**, $J = 16.0, 3.0$ Hz), 1.07 (bs, **20H**), 0.85-0.88 (m, **3H**)

¹³C NMR (δ): 143.71, 143.62, 138.95, 136.13, 135.48, 133.60, 133.17, 129.52, 127.38, 126.95, 122.20, 120.02, 118.26, 61.58, 36.47, 21.60, 19.20, 18.84, 18.81, 11.46

Data for **4b**

mp: 108-109 °C

IR (cm⁻¹): 3318, 2994, 2867, 1614, 1589, 1493, 1338, 1110

¹H NMR (δ): 7.61 (d, **2H**, $J = 7.4$ Hz), 7.56-7.45 (m, **9H**), 7.38-7.33 (m, **12H**), 7.18 (d, **2H**, $J = 7.4$ Hz), 6.93 (s, **1H**), 6.98 (s, **1H**, *exchangeable with D₂O*), 4.51-4.51-4.42 (m, **1H**), 2.78 (dd, **1H**, $J = 15.6$ Hz, 8.7 Hz), 2.44 (s, **3H**), 2.39 (s, **3H**), 2.19 (dd, **1H**, $J = 14.4$ Hz, 6.1 Hz), 1.71 (dd, **1H**, $J = 14.4$ Hz, 7.9 Hz), 1.36 (dd, **1H**, $J = 15.6$ Hz, 4.1 Hz)

¹³C NMR (δ): 144.61, 144.13, 140.62, 139.87, 138.71, 135.83, 134.27, 133.39, 132.68, 130.54, 129.93, 128.1, 128.25, 128.14, 127.94, 122.08, 118.34, 116.71, 64.47, 37.54, 23.38, 22.35, 20.89.

Data for **4c**

mp: 86-87 °C

IR (cm⁻¹): 3320, 2958, 2879, 1601, 1474, 1342, 1158, 1092, 875, 664

¹H NMR (δ): : 7.77-7.75 (m, **2H**), 7.61-7.44 (m, **4H**), 7.39-7.26 (m, **4H**), 6.97 (s, **1H**), 6.75 (s, **1H**, *exchangeable with D₂O*), 4.46-4.43 (m, **1H**), 2.47 (s, **3H**), 1.78

(dd, **1H**, $J = 15.3, 7.0$ Hz), 1.65 (s, **3H**), 1.26 (dd, **1H**, $J = 15.3, 7.0$ Hz), 1.06-1.01 (m, **20H**), 0.78-0.73 (m, **3H**)

^{13}C NMR (δ): 143.71, 143.62, 138.95, 136.13, 135.48, 133.60, 133.17, 129.52, 127.38, 126.95, 122.20, 120.02, 118.26, 62.26, 35.95, 21.60, 19.20, 18.84, 18.81, 11.46

Data for **5a**

mp: 238-239 °C

IR (cm^{-1}): 3320, 3021, 2972, 1603, 1330, 1113, 976, 748

^1H NMR (δ): 7.57 (d, **4H**, $J = 7.9$ Hz), 7.17 (d, **4H**, $J = 7.9$ Hz), 7.09 (s, **2H**), 6.62 (bs, **2H**, *exchangeable with D_2O*), 2.62 (dd, **2H**, $J = 15.4, 9.4$ Hz), 2.37–2.34 (m, **8H**), 1.38 (m, **1H**), 1.06–0.93 (m, **21H**)

^{13}C NMR (δ): 143.65, 139.21, 136.90, 130.01, 129.59, 127.25, 122.61, 33.54, 21.62, 19.14, 18.88, 11.50

Data for **6a**

Mp: 99-101 °C

IR (cm^{-1}): 3269, 2947, 2872, 1620, 1491, 1332, 1218, 1165, 1095, 883, 725

^1H NMR (δ): 7.72 (d, **2H**, $J = 7.0$ Hz), 7.54-7.39 (m, **3H**), 6.96 (s, **1H**), 6.94 (s, **1H**, *exchangeable with D_2O*), 6.63 (d, **1H**, $J = 8.3$ Hz), 6.48 (d, **1H**, $J = 8.3$ Hz), 4.99-4.91 (m, **1H**), 3.25 (dd, **1H**, $J = 15.4, 8.2$ Hz), 2.76 (dd, **1H**, $J = 15.4, 7.8$ Hz), 1.35-1.25 (m, **2H**), 1.06 (s, **18H**), 0.87- 0.85 (m, **3H**)

^{13}C NMR (δ): 158.10, 139.15, 132.64, 128.63, 128.46, 128.20, 127.40, 124.46, 121.90, 109.16, 82.67, 38.51, 18.85, 18.08, 11.32

Data for **6b**

mp: 134-135 °C

IR (cm^{-1}): 3269, 3074, 2931, 1968, 1619, 1592, 1489, 1332, 1165, 1112, 1097, 731, 703

^1H NMR (δ): 7.67 (d, **2H**, $J = 7.6$ Hz), 7.54-7.47 (m, **6H**), 7.37-7.34 (m, **12H**), 6.83 (s, **1H**), 6.67 (s, **1H**, *exchangeable with D_2O*), 6.56 (d, **1H**, $J = 8.2$ Hz), 6.37 (d, **1H**, $J = 8.2$ Hz), 5.02-4.95 (m, **1H**), 2.90 (dd, **1H**, $J = 15.6, 8.5$ Hz), 2.57 (dd, **1H**, $J = 15.6, 7.6$ Hz), 2.16 (dd, **1H**, $J = 14.2, 5.8$ Hz), 1.73 (dd, **1H**, $J = 14.2, 8.5$ Hz)

^{13}C NMR (δ): 157.82, 139.18, 135.67, 134.20, 132.64, 129.72, 128.81, 128.37, 128.20, 128.02, 127.35, 124.31, 122.00, 109.27, 82.08, 37.90, 22.15