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SYNTHESIS OF 4,7-DIHYDRO-2*H*-ISOINDOLE DERIVATIVES *VIA* DIELS-ALDER REACTION OF TOSYLACETYLENE

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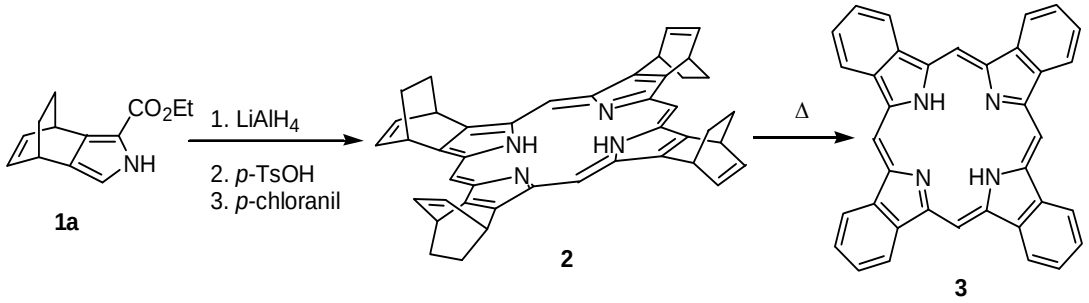
Dedicated to Professor S. M. Weinreb on the occasion of his 65th birthday.

Abstract –Diels-Alder reaction of ethynyl *p*-tolyl sulfone with 1,3-dienes gave the corresponding tosyl-1,4-cyclohexadienes. The resulting adducts could be converted into 4,7-dihydro-2*H*-isoindole derivatives including bicyclo[2.2.2]ocatadiene(BCOD)-fused pyrrole as an isoindole equivalent.

Tetrabenzoporphyrin and its derivatives have attracted much interest from many chemists because of their optical and electrical properties. Their chemistry has been investigated for the applications to photoelectronic materials and molecular devices.[1] Recently, π-conjugated organic compounds such as porphyrins, phthalocyanines, and pentacenes are the subject of considerable research interest in organic semiconductors with high performance.

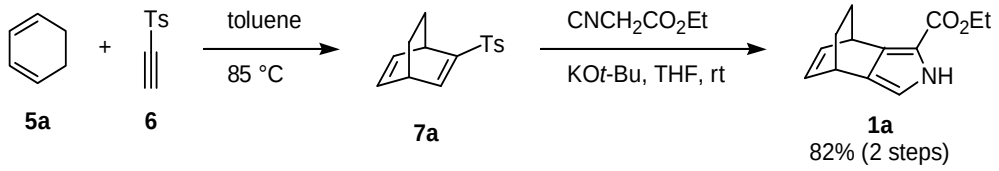
In the manipulation of such π-conjugated molecules, one serious problem is their poor solubility. We have reported the convenient and highly efficient synthesis of insoluble tetrabenzoporphyrin derivatives by the retro Diels-Alder reaction.[2] Insoluble tetrabenzoporphyrin (**3**) was prepared quantitatively by heating soluble bicyclo[2.2.2]octadiene(BCOD)-fused porphyrin (**2**) (Scheme 1). We have succeeded in preparation of a polycrystalline thin film of **3** by heating an amorphous thin film of **2** at 200 ºC following the spin coating of **2**. The thin film of **3** showed good transistor properties.[3] BCOD-fused pyrroles could be key compounds in the device fabrication of solution-processible organic semiconductor with π-expanded benzoporphyrin derivatives. In order to design the structure of benzoporphyrins as a high-performance organic semiconductor, development of preparation method of pyrroles is necessary.

Herein, we describe a new synthesis of 4,7-dihydroisoindoles based on the Diels-Alder reactions of conjugated dienes with tosylacetylene as a dienophile.



Scheme 1.

In the previous paper, we modified the preparative procedure of pyrrole (**1a**). The method *via* the Diels-Alder reaction of *trans*-1,2-bis(phenylsulfonyl)ethylene (**4**) is more convenient than the original one.[2] However, **4** is prepared by several steps: the reaction of *cis*-1,2-dichloroethylene with thiophenol, oxidation with H_2O_2 in the presence of diphenyl diselenide and *m*-CPBA, and isomerization into the *trans* form for 1-2 weeks under sunlight. Tosylacetylene (**6**) is readily prepared starting from bis(trimethylsilyl)acetylene.[4] The reaction of 1,3-cyclohexadiene (**5a**) with **6** gave the adduct (**7a**), which was converted into BCOD-fused pyrrole (**1a**) in high yield for 2 steps (Scheme 2). Now pyrrole (**1a**) which is important synthon of unstable isoindole[2a,5] can be prepared from readily available starting materials in shorter days.



Scheme 2.

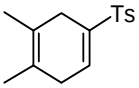
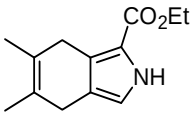
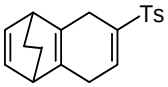
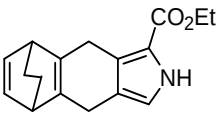
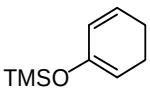
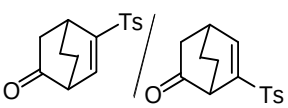
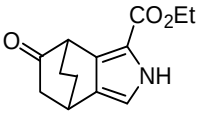
Chart 1.

To demonstrate the further utility of **6**, Diels-Alder reactions of **6** with 1,3-dienes (**5b**–**d**) were performed. The results are summarized in table 1. 2,3-Dimethyl-1,3-butadiene (**5b**) reacted with **6** at 130 ºC in an autoclave to give the adduct (**7b**) in 89% yield.[6] Tetrahydronaphthalene (**7c**) was obtained by the reaction of **6** with **5c** in 88% yield. The reaction of **6** with **5d** followed by hydrolytic removal of the silyl group resulted in formation of a mixture of **7d** and **7e** (ratio **7d**/**7e** 5/1).

The Diels-Alder adducts (**7**) were treated with ethyl isocyanoacetate in the presence of potassium *tert*-butoxide to afford the corresponding pyrroles (**1b**–**d**) as shown in table 1. Pyrroles (**1b** and **1c**) were obtained by the modified Barton-Zard reaction of **7b** and **7c** for 1 day in 49% and 76% yields, respectively.[7] The similar reaction of the adduct[8] of **5b** with β-sulfonylnitroethylene (**8**) did not give the desired dihydroisoindole. On the other hand, the formation of 1,2-dimethyl-4-nitrobenzene was observed in the treatment of the adduct with ethyl isocyanoacetate and potassium *tert*-butoxide by NMR. A similar result was obtained in the reaction of the adduct of **5c** with **4**. In the case of the adduct of **5c** with **4**, the reaction took very long time to give **1c** in 70% yield (7 days). Tosylbicyclo[2.2.2]octenone (**7d**/**7e**) reacted with ethylene glycol to give the corresponding acetal. The product was treated with ethyl isocyanoacetate and potassium *tert*-butoxide and then deprotected with 1 M HCl to give **1d** in 57% yield for 2 steps.

In summary, we have prepared the various 4,7-dihydroisoindoles (**1a**–**d**) utilizing the Diels-Alder adduct of tosylacetylene with conjugated dienes as the substrates in the Barton-Zard reaction. This method easily supplies pyrrole (**1a**) as an isoindole equivalent in the synthesis of tetrabenzoporphyrin in a large quantity. The pyrroles (**1b**–**d**) would be starting materials for substituted tetrabenzoporphyrins. Further investigation of synthesis of *meso*-free functionalized tetrabenzoporphyrins is under way.

Table 1. Diels-Alder Reaction of **6** with **5** and Synthesis of **1**

diene (**5**)	conditions	adduct (**7**)	pyrrole (**1**)
 **5b**	toluene, 130 °C, autoclave, 2 d	 **7b** (89%)	 **1b** (49%)
 **5c**	benzene, reflux, 22 h	 **7c** (88%)	 **1c** (76%)
 **5d**	benzene 70 °C, 1 week	 **7d**/**7e** (73%)	 **1d** (57%)[a]

[a] **1d** was obtained starting from **7d**/**7e** in 2 steps.

EXPERIMENTAL

General. Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. Mass spectra were measured on JEOL JMS-700 usually at 70 eV. ^{1}H NMR spectra (and ^{13}C

NMR spectra) were recorded on JEOL AL-400 at 400 MHz (100 MHz). Gel permeation chromatography (GPC) was performed on a JAIGEL 2.5-H. Elemental analyses were performed at Integrated Center for Sciences, Ehime University.

2-Tosylbicyclo[2.2.2]octa-2,5-diene (**7a**)

A solution of **5a** (0.30 mL, 3.1 mmol) and **6** (360 mg, 2.00 mmol) in dry toluene (10 mL) was heated at 85 ºC for 17 h under a N_2 atmosphere. The solvent was removed under a reduced pressure and the adduct was obtained as a pale yellow oil. The adduct (**7a**) was used in the next reaction without further purification.

pale yellow oil; MS (70 eV) *m*/*z* (rel intensity) 260 (M^+, 27%), 232 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H, $H^{2',6'}$), 7.31 (m, 2H, $H^{3',5'}$), 7.25 (m, 1H, H^3), 6.24 (m, 2H, $H^{5,6}$), 3.86 (m, 2H, $H^{1,4}$), 2.42 (s, 3H, 4'-Me), 1.35 (m, 2H, H^7 or H^8), 1.26 (m, 1H, H^7 or H^8), 1.17 (m, 1H, H^7 or H^8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5 (C^2), 144.0 (C^3), 143.8 ($C^{4'}$), 136.7 ($C^{1'}$), 133.3 (C^5 or C^6), 133.3 (C^5 or C^6), 129.6 ($C^{3',5'}$), 127.6 ($C^{2',6'}$), 38.1 (C^1 or C^4), 37.1 (C^1 or C^4), 25.1 (C^7 or C^8), 24.3 (C^7 or C^8), 21.6 (4'-Me); HRMS calcd for $C_{15}H_{16}O_2S$ 260.0871, found 260.0869.

Ethyl 4,7-dihydro-4,7-ethano-2*H*-isoindole-1-carboxylate (**1a**)

To a stirred solution of **7a** and ethyl isocyanoacetate (0.30 mL, 2.8 mmol) in THF (5 mL) was added a 1 M solution of potassium *tert*-butoxide in THF (5 mL) at 0 °C under a N_2 atmosphere. The resulting mixture was stirred at rt for 23 h. The reaction mixture was poured into 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with sat. aqueous $NaHCO_3$, water, and brine and dried with Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$/hexane to give **1a** (355 mg, 82% for 2 steps) as white crystals (mp 129-130 °C).

1,2-Dimethyl-4-tosyl-1,4-cyclohexadiene (**7b**)

A solution of **6** (3.60 g, 20.0 mmol) and **5b** (1.98 g, 24.1 mmol) in dry toluene (20 mL) was heated at 130 ºC in an autoclave for 2 d. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **7b** (4.68 g, 89%).

colorless needles; mp 110.9–111.8 °C; MS (70 eV) *m*/*z* (rel intensity) 262 (M^+, 100%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 2H, $H^{2',6'}$), 7.32 (m, 2H, $H^{3',5'}$), 6.98 (m, 1H, H^5), 2.85 (m, 2H, H^6), 2.71 (m, 2H, H^3), 2.43 (s, 3H, 4'-Me), 1.61 (s, 6H, 1,2-Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0 ($C^{4'}$), 137.7 (C^4), 136.1 ($C^{1'}$), 134.9 (C^5), 129.7 ($C^{3',5'}$), 128.0 ($C^{2',6'}$), 122.0 (C^1 or C^2), 121.4 (C^1 or C^2), 33.9 (C^6), 30.1 (C^3), 21.7 (4'-Me), 18.5 (1 or 2-Me), 18.0 (1 or 2-Me); Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.67; H,6.87.

1,4-Ethano-1,4,5,8-tetrahydro-6-tosylnaphthalene (**7c**)

A solution of **5c** (1.89 g, 14.3 mmol) and **6** (2.30 g, 12.8 mmol) in dry benzene (50 mL) was refluxed for 22 h under a N_2 atmosphere. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$/MeOH to give **7c** (3.49 g, 88%).

colorless needles; mp 152.7–153.2 °C (decomp); MS (70 eV) *m*/*z* (rel intensity) 312 (M^+, 87%), 285 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (m, 2H, $H^{2',6'}$), 7.32 (m, 2H, $H^{3',5'}$), 6.99 (m, 1H, H^7), 6.27 (m, 2H, $H^{2,3}$), 3.31 (m, 1H, H^1), 3.28 (m, 1H, H^4), 3.02 (m, 2H, H^8), 3.00 (m, 1H, H^5), 2.80 (m, 1H, H^5), 2.43 (s, 3H, 4'-Me), 1.26 (s, 4H, $H^{9,10}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1 ($C^{4'}$), 138.5 (C^6), 136.0 ($C^{1'}$), 135.5 (C^7), 133.99 (C^2 or C^3), 133.97 (C^2 or C^3), 132.7 (C^{4a} or C^{8a}), 132.1 (C^{4a} or C^{8a}), 129.7 ($C^{3',5'}$), 128.1 ($C^{2',6'}$), 40.5 (C^4), 40.1 (C^1), 29.3 (C^8), 26.1 (C^5), 25.14 (C^9 or C^{10}), 25.11 (C^9 or C^{10}), 21.6 (4'-Me); Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45. Found: C, 72.90; H, 6.47.

5-Tosylbicyclo[2.2.2]oct-5-en-2-one (**7d**)/**6-Tosylbicyclo[2.2.2]oct-5-en-2-one** (**7e**)

A solution of **5d** (1.0 mL, 5.3 mmol) and **6** (605 mg, 3.00 mmol) in dry benzene (80 mL) was heated at 70 ºC for a week under a N_2 atmosphere. After removal of the solvent *in vacuo*, the residue was dissolved in $CHCl_3$ and then stirred with silica gel at rt for 2 d. The silica gel was removed by filtration. The filtrate was concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give a mixture of **7d** and **7e** (ratio **7d**/**7e** 5/1 determined by ^{1}H NMR, 603 mg, 73%). Small amounts of pure **7d** and **7e** were obtained by GPC with $CHCl_3$ and characterized by spectral methods.

7d: colorless oil; MS (70 eV) *m*/*z* (rel intensity) 276 (M^+, 21%), 68 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 2H, $H^{2',6'}$), 7.35 (m, 2H, $H^{3',5'}$), 7.16 (dd, 1H, *J* = 6.8, 2.0 Hz, H^6), 3.44 (m, 1H, H^1), 3.33 (m, 1H, H^4), 2.45 (s, 3H, 4'-Me), 2.03 (dd, 1H, *J* = 18.5, 1.8 Hz, H^3), 1.96 (m, 1H, H^8), 1.75 (m, 1H, H^3), 1.71 (m, 2H, $H^{7,8}$), 1.44 (m, 1H, H^7); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5 (C^2), 148.0 (C^5), 144.7 ($C^{4'}$), 135.9 (C^6), 135.7 ($C^{1'}$), 130.0 ($C^{3',5'}$), 128.0 ($C^{2',6'}$), 50.1 (C^1), 39.5 (C^3), 33.2 (C^4), 24.6 (C^7), 22.9 (C^8), 21.7 (4'-Me); HRMS calcd for $C_{15}H_{16}O_3$ 276.0820, found 276.0820; **7e**: colorless oil; MS (70 eV) *m*/*z* (rel intensity) 276 (M^+, 23%), 234 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 2H, $H^{2',6'}$), 7.49 (dd, 1H, *J* = 6.8, 1.7 Hz, H^5), 7.33 (m, 2H, $H^{3',5'}$), 3.49 (m, 1H, H^1), 3.26 (m, 1H, H^4), 2.43 (s, 3H, 4'-Me), 2.09 (dd, 1H, *J* = 18.6, 2.4 Hz, H^3), 1.93 (ddd, *J* = 18.6, 2.7, 2.4 Hz 1H, H^3), 1.92 (m, 1H, H^8), 1.79 (m, 1H, H^7), and 1.55 (m, 2H, $H^{7,8}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5 (C^2), 144.7 ($C^{4'}$), 143.7 (C^5), 141.9 (C^6), 136.1 ($C^{1'}$), 130.0 ($C^{3',5'}$), 127.8 ($C^{2',6'}$), 48.1 (C^1), 38.5 (C^3), 33.1 (C^4), 24.0 (C^7), 23.1 (C^8), and 21.7 (4'-Me); HRMS calcd for $C_{15}H_{16}O_3S$ 276.0820, found 276.0824.

Ethyl 4,7-dihydro-5,6-dimethyl-2*H*-isoindole-1-carboxylate (**1b**)

To a stirred solution of **7b** (1.31 g, 5.01 mmol) and ethyl isocyanoacetate (0.80 mL, 7.5 mmol) in THF (15 mL) was added a 1.7 M solution of potassium *tert*-butoxide in THF (15 mL) at 0 °C under a N_2 atmosphere. The resulting mixture was stirred at rt for 24 h. The reaction mixture was poured into 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with sat. aqueous $NaHCO_3$, water, and brine and dried with Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$/MeOH to give **1b** (534 mg, 49%).

colorless needles; mp 173.8–175.2 °C; MS (70 eV) *m*/*z* (rel intensity) 220 (M^++1, 100%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (bs, 1H, NH), 6.68 (d, 1H, *J* = 2.9 Hz, H^3), 4.32 (q, 2H, *J* = 7.1 Hz, 1-CO_2Et), 3.36 (bs, 2H, H^7), 3.12 (bs, 2H, H^4), 1.79 (s, 3H, 5 or 6-Me), 1.76 (s, 3H, 5 or 6-Me), 1.36 (t, 3H, *J* = 7.1 Hz, 1-CO_2Et); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (1-CO_2Et), 126.1 (C^{7a}), 123.3 (C^5 or C^6), 122.6 (C^5 or C^6), 120.1 (C^{3a}), 117.7 (C^3), 116.8 (C^1), 59.8 (1-CO_2Et), 30.5 (C^7), 29.0 (C^4), 19.3 (5 or 6-Me), 19.3 (5 or 6-Me), 14.7 (1-CO_2Et); Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.18; H, 7.74; N, 6.37.

Ethyl 5,8-ethano-4,5,8,9-tetrahydro-2*H*-benz[*f*]isoindole-1-carboxylate (**1c**)

To a stirred solution of **7c** (942 mg, 3.01 mmol) and ethyl isocyanoacetate (1.0 mL, 9.3 mmol) in THF (10 mL) was added a 1 M solution of potassium *tert*-butoxide in THF (10 mL) at 0 °C under a N_2 atmosphere. The resulting mixture was stirred at rt for 22 h. The reaction mixture was poured into 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with sat. aqueous $NaHCO_3$, water, and brine and dried with Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **1c** (621 mg, 76%).

colorless needles; mp 160.9–162.5 °C (decomp); MS (70 eV) *m*/*z* (rel intensity) 269 (M^+, 85%), 241 (M^+-C_2H_4, 70), 212 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (bs, 1H, NH), 6.70 (d, 1H, *J* = 2.4 Hz, H^3), 6.37 (m, 2H, $H^{6,7}$), 4.32 (q, 2H, *J* = 7.1 Hz, 1-CO_2Et), 3.51 (m, 2H, H^9), 3.45 (m, 1H, H^5 or H^8), 3.38 (m, 1H, H^5 or H^8), 3.28 (m, 2H, H^4), 1.36 (t, 3H, *J* = 7.1 Hz, 1-CO_2Et), 1.30–1.39 (m, 4H, $H^{10,11}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (1-CO_2Et), 134.43 (C^6 or C^7), 134.42 (C^{4a} or C^{8a}), 134.3 (C^6 or C^7), 133.7 (C^{4a} or C^{8a}), 126.1 (C^{9a}), 120.1 (C^{3a}), 118.3 (C^3), 117.4 (C^1), 59.8 (1-CO_2Et), 41.41 (C^5 or C^8), 41.39 (C^5 or C^8), 26.2 (C^9), 25.6 (C^{10} or C^{11}), 25.5 (C^{10} or C^{11}), 24.5 (C^4), 14. 7 (1-CO_2Et); Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.51; H, 7.01; N, 5.18.

Ethyl 4,7-ethano-4,5,7-trihydro-6-oxoisoindole-1-carboxylate (**1d**)

To a solution of **7d**/**7e** (888 mg, 3.21 mmol) and ethylene glycol (0.50 mL, 8.9 mmol) in dry benzene (50 mL) was added TsOH (50 mg). Water was azeotropically removed by reflux for 21 h with a Dean-Stark apparatus under a N_2 atmosphere. The solvent was removed under a reduced pressure. The residue was

dissolved in $CHCl_3$. The solution was washed with water, sat. aqueous $NaHCO_3$, and brine and dried with Na_2SO_4. After removal of the solvent *in vacuo*, the residual acetal (900 mg) was dissolved in THF (10 mL). To a stirred solution of the acetal and ethyl isocyanoacetate (0.45 mL, 4.2 mmol) in THF was added a 1 M solution of potassium *tert*-butoxide in THF (5 mL) at 0 °C under a N_2 atmosphere. The resulting mixture was stirred at rt for 20 h. After an addition of 1 M HCl (10 mL), the mixture was stirred at rt for 19 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with sat. aqueous $NaHCO_3$, water, and brine and dried with Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$/hexane to give **1d** (424 mg, 57%). The other isomer was not obtained.

white crystals; mp 131.2–131.9 °C; MS (70 eV) *m*/*z* (rel intensity) 233 (M^+, 48%), 205 (M^+-C_2H_4, 25), 189 (100); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (bs, 1H, NH), 6.74 (d, 1H, *J* = 2.7 Hz, H^3), 4.32 (q, 1H, *J* = 7.1 Hz, 1-CO_2Et), 4.31 (q, 1H, *J* = 7.1 Hz, 1-CO_2Et), 4.12 (m, 1H, H^7), 3.42 (m, 1H, H^4), 2.34 (dd, 1H, *J* = 18.3, 2.4 Hz, H^5), 2.17 (ddd, 1H, *J* = 18.3, 3.2, 2.9 Hz, H^5), 2.09 (m, 1H, H^9), 1.91 (m, 1H, H^8), 1.76 (m, 1H, H^9), 1.61 (m, 1H, H^8), 1.36 (t, 3H, *J* = 7.1 Hz, 1-CO_2Et); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1(C^6), 161.4 (1-CO_2Et), 128.4 (C^{3a}), 126.3 (C^{7a}), 116.7 (C^3), 114.4 (C^1), 60.2 (1-CO_2Et), 46.5 (C^7), 43.6 (C^5), 29.8 (C^4), 26.1 (C^8), 24.2 (C^9), and 14.4 (1-CO_2Et); Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.83; H, 6.53; N, 6.02.

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REFERENCES

1. J. -H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow, and K. S. Suslick, 'The Porphyrin Handbook', Vol. 6, ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, Inc., San Diego, 1999, pp. 43-131.
2. (a) S. Ito, T. Murashima, H. Uno, and N. Ono, *Chem. Commun.*, 1998, 1661. (b) S. Ito, N. Ochi, H. Uno, T. Murashima, and N. Ono, *Chem. Commun.*, 2000, 893. (c) S. Ito, N. Ochi, T. Murashima, H. Uno, and N. Ono, *Heterocycles*, 2000, **52**, 399. (d) Y. Shimizu, Z. Shen, T. Okujima, H. Uno, and N. Ono. *Chem. Commun*. 2004, 374. (e) T. Okujima, N. Komobuchi, H. Uno, and N. Ono *Heterocycles*, 2006, **67**, 255.
3. S. Aramaki, Y. Sakai, and N. Ono, *Appl. Phys. Lett.*, 2004, **84**, 2085.
4. J. -P. Freeman, *Org. Synth. Coll. Vol.*, 1993, **8**, 282.
5. (a) Y. Inokuma, N. Ono, H. Uno, D. Y. Kim, S. B. Noh, D. Kim, and A. Osuka, *Chem. Commun.*,

2005, 3782. (b) Y. Inokuma, T. Matsunami, N. Ono, H. Uno, and A. Osuka, *Angew*. *Chem*. *Int*. *Ed*., 2005, **44**, 1856. (c) M. Graud-Roux, G. Ploni, K. Nakanishi, and N. Berova, *Heterocycles*, 2003, **61**, 417.

6. A. P. Davis and G. H. Whitham, *J*. *Chem*. *Soc*., *Chem*. *Commun*., 1980, 639.
7. (a) B. Bonnett, *Chem*. *Soc*. *Rev*., 1995, **24**, 19. (b) Y. Abel and F. -P. Montforts, *Tetrahedron Lett*. 1997, **38**, 1745. (c) Y. Abel, E. Haake, G. Haake, W. Schmidt, D. Struve, A. Walter, and F. -P. Montforts, *Helv*. *Chim*. *Acta*, 1998, **81**, 1978. (d) D. P. Arnold, L. Burgess-Dean, J. Hubbard, and M. A. Rahman, *Aust*. *J*. *Chem*., 1994, **47**, 969. (e) N. Ono, H. Hironaga, K. Shimizu, K. Ono, K. Kumano, and T. Ogawa, *J*. *Chem*. *Soc*., *Chem*. *Commun*., 1994, 1019.
8. (a) N. Ono, A. Kamimura, and A. Kaji, *Tetrahedron Lett*., 1986, **27**, 1595. (b) N. Ono, A. Kamimura, and A. Kaji, *J*. *Org*. *Chem*., 1988, **53**, 251.