[3+2] Cycloaddition of Metal-Containing Azomethine Ylides Derived from *N*-(*o*-Alkynyl)imines Bearing an Internal Alkyne Moiety: Highly Efficient Synthesis of Mitosene Skeleton

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General. All operations were performed under an argon atmosphere. ^1H and ^{13}C -NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^1H and 125 MHz for ^{13}C), a JEOL AL-400 (400 MHz for ^1H and 100 MHz for ^{13}C) or a JEOL Lambda-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer in CDCl_3 (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual CHCl_3 (δ_{H} 7.26) for ^1H spectra and CDCl_3 for ^{13}C (δ_{C} 77.0). IR spectra were recorded on a IR-810 or a FT/IR-460 plus (JASCO Co., Ltd.). Photoirradiation was performed with a 250W super high-pressure mercury lamp (USHIO INC.). Silica Gel 60 (Kanto Chemical Co., Inc.) or Aluminum Oxide 90 active neutral (activity I) (0.063-0.200 mm, Merck) was used for flash column chromatography. Merck Kieselgel 60 F254 (0.25 mm thickness, coated on glass 20 x 20 cm²) plate was used for thin layer chromatography (TLC), and Wakogel B-5F coated on glass in a thickness of 0.7 mm was used for preparative TLC. All solvents were distilled according to the usual procedures and stored over Molecular Sieves. MS4A and MS5A were heated by heat-gun under reduced pressure before use. High-resolution mass analyses (FAB) were performed on a JEOL JMS-700 mass spectrometer using 2-nitrophenyl octyl ether as a matrix. Elemental analyses were performed on a Perkin-Elmer 2400 instrument.

General Experimental Procedures

General procedure for the preparation of aldimines (1c**, **1g**) derived from 2-(1-alkynyl)anilines and benzaldehyde :**

(*E*)-*N*-benzylidene-2-(2-cyclohexylethynyl)aniline (1c**)**

To a stirred mixture of 2-(2-cyclohexylethynyl)aniline¹ (578 mg, 2.90 mmol) and MS5A (1.5 g) in toluene (2.0 mL) was added benzaldehyde (0.35 mL, 3.4 mmol) at room temperature. After 5 days, the reaction mixture was filtered through a short pad of Celite[®] and the filtrate was concentrated under reduced pressure. The resulting residue was purified by bulb-to-bulb distillation to give **1c** (786 mg, 2.71 mmol, 94%) as a single isomer. The geometry was confirmed to be *E* by the observation of an NOE between the aldimine proton and the aromatic proton on the 6-position.

IR (neat) 3061, 2929, 2223, 1633 cm⁻¹

^1H -NMR (400 MHz) δ = 1.20-1.35 (m, 3H), 1.37-1.55 (m, 3H), 1.61-1.84 (m, 4H), 2.54-2.65 (m, 1H), 7.02 (brd, J = 6.0 Hz, 1H), 7.11 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.27 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.42-7.60 (m, 4H), 7.89-7.97 (m, 2H), 8.47 (s, 1H).

^{13}C -NMR (100 MHz) δ = 24.6, 26.0, 29.7, 32.6, 78.3, 98.7, 116.6, 119.6, 124.8, 128.2, 128.6, 128.8, 131.3, 132.7, 136.1, 153.7, 161.7.

Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{N}$: C, 87.76; H, 7.36; N, 4.87. Found: C, 87.71, H, 7.38, N, 4.65.

Aldimine derivative **1g** was prepared according to the procedure described above. Preparative method and spectroscopic

data of other aldimine derivatives **1a**, **1b**, **1d** were described in our previous work².

2-(3-triisopropylsiloxyprop-1-ynyl)aniline (precursor of aldimine **1g**)

To a stirred mixture of 2-(3-hydroxyprop-1-ynyl) aniline³ (2.07 g, 14.1 mmol) and imidazole (2.39 g, 35.2 mmol) in DMF (5 mL) was added chlorotriisopropylsilane (3.1 mL, 14.5 mmol) at room temperature and the mixture was stirred for 1h. The reaction was quenched with 1N HCl, and then the aqueous layer was extracted with ether three times and the combined extracts were washed with brine, dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane-ethyl acetate = 5:1) to give 2-(3-triisopropylsiloxyprop-1-ynyl)aniline (4.00 g, 13.2 mmol, 94%).

IR (neat) 3478, 3384, 2943, 2866, 2225, 1615, 1493, 1090 cm⁻¹

¹H-NMR (400 MHz) δ = 1.08-1.23 (m, 21H), 4.13-4.27 (brs, 2H), 4.66 (s, 2H), 6.64-7.01 (m, 2H), 7.11 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.26 (dd, J = 7.6, 1.6 Hz, 1H).

¹³C-NMR (100 MHz) δ = 12.1, 18.0, 52.6, 81.1, 93.3, 107.6, 114.2, 117.7, 129.5, 132.2, 147.8.

Anal. Calcd for C₁₈H₂₉NOSi: C, 71.23; H, 9.63; N, 4.61. Found: C, 71.01, H, 9.42, N, 4.50.

(*E*)-*N*-benzylidene-2-(3-triisopropylsiloxyprop-1-ynyl)aniline (**1g**)

The geometry was confirmed to be *E* by the observation of an NOE between the aldimine proton and the aromatic proton on the 6-position.

IR (neat) 3063, 2941, 2230, 1633, 1190, 1106 cm⁻¹

¹H-NMR (400 MHz) δ = 1.01-1.16 (m, 21H), 4.57 (s, 2H), 7.01 (dd, J = 7.6, 1.2 Hz, 1H), 7.13 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.32 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.36-7.56 (m, 4H), 7.93 (dd, J = 7.6, 1.6 Hz, 2H), 8.44 (s, 1H).

¹³C-NMR (100 MHz) δ = 12.1, 18.0, 52.6, 82.1, 92.1, 115.9, 119.4, 124.9, 128.6, 128.9, 129.0, 131.4, 133.1, 136.0, 153.9, 161.8.

Anal. Calcd for C₂₅H₃₃NOSi: C, 76.67; H, 8.49; N, 3.58. Found: C, 76.38, H, 8.75, N, 3.42.

Preparation of imidate **1e**

(*E*)-Ethyl *N*-(2-(1-pentynyl)phenyl)formimidate (**1e**)

A mixture of 2-(pent-1-ynyl)aniline (437 mg, 2.74 mmol), triisopropyl orthoformate (2.5 mL, 11 mmol) and MS5A (4.2 g) in toluene (8.5 mL) was heated at 80 °C. After 15 h, the mixture was filtered through a short pad of Celite[®] and the filtrate was concentrated under reduced pressure. The resulting residue was purified by bulb-to-bulb distillation to give the imidate (**1e**) (547 mg, 2.38 mmol, 87%). The geometry was confirmed to be *E* by the observation of an NOE between the formimidic proton and the aromatic proton on the 6-position.

IR (neat) 2966, 2229, 1644 cm⁻¹

¹H-NMR (400 MHz) δ = 1.03 (t, J = 7.6 Hz, 3H), 1.39 (d, J = 6.0 Hz, 6H), 1.55-1.66 (m, 2H), 2.38 (t, J = 7.2 Hz, 2H), 5.19-5.33 (m, 1H), 6.84 (brd, J = 7.6 Hz, 1H), 7.01 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.19 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 7.6, 1.6 Hz, 1H), 7.65 (s, 1H).

^{13}C -NMR (100 MHz) δ = 13.6, 21.7, 21.8, 22.3, 69.4, 78.5, 93.7, 117.1, 120.9, 123.5, 128.2, 132.6, 149.6, 155.0.

Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.28, H, 8.48, N, 5.82.

General procedure for PtCl_2 - or AuBr_3 catalyzed reaction of imine derivatives **1a-1e** and **1g** with *tert*-butyl vinyl ether

5:

PtCl_2 or AuBr_3 (0.0030-0.030 mmol, 1-10 mol%) was added to a mixture of an imine derivative (0.30 mmol), *tert*-butyl vinyl ether (1.2-3.0 mmol, 4-10 eq.) and MS4A or MS5A (60 mg per 1 mL of toluene) in toluene (1.3-13 mL; 0.1 M for **1**) at room temperature, and then the mixture was stirred at room temperature or heated at 50 °C. After disappearance of the starting material, the reaction was quenched with saturated aq. NaHCO_3 and the reaction mixture was filtered through a short pad of Celite®. Organic layer was extracted with ethyl acetate three times and the combined organic layer was washed with brine, then dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative TLC (toluene : hexane = 2 : 1 – 5 : 1 or toluene : ethyl acetate = 40 : 1) to afford a polycyclic indole derivative.

These results were summarized in Table S1.

Table S1

entry	R ¹	R ²	cat. X / mol%	time / h	yield (cis : trans)
1	Ph	<i>n</i> -Pr	1a AuBr_3	3	2.5 4a 80 % (58 : 42)
2 ^a		<i>n</i> -Pr	1a	1	42 4a 81 % (56 : 44)
3		Me	1b	3	22 4b 81 % (55 : 45)
4		<i>c</i> -Hex	1c	3	2 4c 89 % (73 : 27)
5		Ph	1d	3	0.5 4d 62 % (49 : 51)
6 ^{a, b}	<i>O</i> - <i>t</i> -Pr	<i>n</i> -Pr	1e	10	1 4e 60 % (58 : 42)
7	Ph	<i>n</i> -Pr	1a PtCl_2	3	72 4a 81 % (54 : 46)
8 ^c		<i>n</i> -Pr	1a	3	6 4a 89 % (51 : 49)
9 ^{c, d}		<i>n</i> -Pr	1a	1	16.5 4a 74 % (38 : 62)
10 ^c		Me	1b	3	3.5 4b 88 % (51 : 49)
11 ^{b, c}		<i>c</i> -Hex	1c	3	35 4c 84 % (23 : 77)
12 ^c		Ph	1d	3	7 4d 84 % (33 : 67)
13 ^{b, e}	<i>O</i> - <i>t</i> -Pr	<i>n</i> -Pr	1e	3	2 4e 95 % (65 : 35)

^a Concentration of **1** was 0.03M. ^b 10 eq. of vinyl ether was used. ^c The reactions were carried out at 50 °C. ^d Concentration of **1** was 0.3M. ^e The reaction was carried out at 50 °C in the presence of MS5A.

1-*tert*-Butoxy-9-cyclohexyl-2,3-dihydro-3-phenyl-1*H*-pyrrolo[1,2-*a*]indole (**4c**)

The stereochemistry of the products were determined by the observation of NOE as shown below or by X-ray analysis.

cis-**4c**

IR (neat) 3046, 2972, 2924, 2850, 1456, 1363 cm^{-1}

^1H -NMR (500 MHz) δ = 1.39-1.48 (m, 3H), 1.34 (s, 9H), 1.75-1.81 (m, 1H), 1.86-2.05 (m, 6H), 2.47 (ddd, J = 13.2, 7.3, 5.2 Hz, 1H), 2.97-3.06 (m, 1H), 3.25 (ddd, J = 13.2, 7.3, 7.3 Hz, 1H), 5.16 (dd, J = 7.3, 7.3 Hz, 1H), 5.31 (dd, J = 7.3, 5.2 Hz, 1H), 6.66 (brd, J = 8.1 Hz, 1H), 6.89 (ddd, J = 8.1, 8.1, 1.0 Hz, 1H), 6.96 (ddd, J = 8.1, 8.1, 1.0 Hz, 1H), 7.27-7.37 (m, 3H), 7.37-7.41 (m, 2H), 7.70 (brd, J = 8.1 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 26.4, 27.37, 27.39, 28.9, 33.2, 33.9, 36.1, 49.7, 59.7, 68.0, 74.4, 110.5, 114.2, 118.4, 120.2, 120.6, 127.0, 127.7, 128.7, 131.8, 132.2, 140.3, 141.2.

Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{NO}$: C, 83.68; H, 8.58; N, 3.61. Found: C, 83.43; H, 8.56; N, 3.33.

trans-**4c**

The stereochemistry of *trans*-**4c** was determined by X-ray structure analysis as shown below.

Figure S1. ORTEP plot of *trans*-**4c** (hydrogen atoms are omitted for clarity). Full tables of data are provided in the .cif file.

IR (neat) 3047, 2973, 2926, 2850, 1455, 1364 cm^{-1}

^1H -NMR (500 MHz) δ = 1.32-1.50 (m, 3H), 1.33 (s, 9H), 1.77-1.82 (m, 1H), 1.87-2.03 (m, 6H), 2.70 (ddd, J = 12.6, 6.5, 6.4 Hz, 1H), 2.92-3.10 (m, 2H), 5.36 (dd, J = 6.4, 3.0 Hz, 1H), 5.54 (dd, J = 7.0, 6.5 Hz, 1H), 6.65 (brd, J = 8.1 Hz, 1H), 6.87-6.92 (m, 1H), 6.95-7.00 (m, 1H), 7.07-7.11 (m, 2H), 7.27-7.34 (m, 3H), 7.72 (brd, J = 8.1 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 26.4, 27.35, 27.37, 28.9, 33.3, 33.7, 36.4, 50.3, 59.2, 67.2, 74.5, 110.7, 114.2, 118.3, 120.4, 120.7, 126.3, 127.7, 128.8, 131.8, 132.3, 140.2, 141.6.

Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{NO}$: C, 83.68; H, 8.58; N, 3.61. Found: C, 83.42; H, 8.85; N, 3.33.

1-*tert*-Butoxy-2,3-dihydro-3-isopropoxy-9-propyl-1*H*-pyrrolo[1,2-*a*]indole (4e)

The stereochemistry of the products were determined by the observation of NOE as shown below.

cis-**4e**

IR (neat) 3050, 2972, 2930, 2870, 1456, 1365 cm^{-1}

$^1\text{H-NMR}$ (400 MHz) δ = 0.96 (t, J = 7.2 Hz, 3H), 1.06 (d, J = 6.0 Hz, 3H), 1.26 (d, J = 6.0 Hz, 3H), 1.35 (s, 9H), 1.63-1.78 (m, 2H), 2.42 (ddd, J = 14.0, 2.4, 2.4 Hz, 1H), 2.71-2.77 (m, 2H), 3.02 (ddd, J = 14.0, 7.0, 7.0 Hz, 1H), 4.02-4.12 (m, 1H), 5.06 (dd, J = 7.0, 2.4 Hz, 1H), 5.76 (dd, J = 7.0, 2.4 Hz, 1H), 7.08 (dd, J = 8.0, 8.0 Hz, 1H), 7.14 (dd, J = 8.0, 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H).

$^{13}\text{C-NMR}$ (100 MHz) δ = 14.3, 23.3, 23.5, 24.2, 26.1, 28.7, 46.7, 65.2, 68.1, 74.3, 83.8, 108.9, 110.4, 119.2, 119.3, 121.0, 132.0, 133.3, 140.0.

Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_2$: C, 76.55; H, 9.48; N, 4.25. Found: C, 76.27; H, 9.77; N, 3.97.

trans-**4e**

IR (neat) 3051, 2972, 2931, 2870, 1456, 1364 cm^{-1}

$^1\text{H-NMR}$ (500 MHz) δ = 0.98 (t, J = 7.4 Hz, 3H), 1.17 (d, J = 6.1 Hz, 3H), 1.24 (d, J = 6.1 Hz, 3H), 1.33 (s, 9H), 1.64-1.78 (m, 2H), 2.62 (ddd, J = 13.4, 6.5, 6.0 Hz, 1H), 2.75-2.80 (m, 2H), 2.82 (dd, J = 13.4, 6.5 Hz, 1H), 3.94-4.01 (m, 1H), 5.49 (dd, J = 6.5, 6.5 Hz, 1H), 5.88 (d, J = 6.0 Hz, 1H), 7.08 (dd, J = 7.9, 7.9 Hz, 1H), 7.13 (dd, J = 7.9, 7.9 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H).

$^{13}\text{C-NMR}$ (125 MHz) δ = 14.3, 22.5, 23.1, 24.4, 25.7, 28.6, 48.9, 67.0, 69.9, 74.3, 83.2, 109.6, 109.9, 119.1, 119.3, 121.0, 132.2, 133.6, 139.9.

Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_2$: C, 76.55; H, 9.48; N, 4.25. Found: C, 76.32; H, 9.70; N, 4.06.

1-tert-Butoxy-2,3-dihydro-9-triisopropylsiloxymethyl-3-phenyl-1H-pyrrolo[1,2-a]indole (4g)

The stereochemistry of *cis*-isomer was determined by the observation of NOE as shown below. Therefore, the major product was assigned to be the *trans* isomer.

cis-**4g** (minor)

IR (neat) 3049, 2965, 2942, 2865, 1456, 1364, 1192, 1060 cm^{-1}

^1H -NMR (400 MHz) δ = 1.09-1.31 (m, 21H), 1.34 (s, 9H), 2.45 (ddd, J = 12.8, 7.2, 6.0 Hz, 1H), 3.30 (ddd, J = 12.8, 7.2, 6.0 Hz, 1H), 5.09 (d, J = 12.0 Hz, 1H), 5.14 (d, J = 12.0 Hz, 1H), 5.22 (dd, J = 7.2, 7.2 Hz, 1H), 5.36 (dd, J = 6.0, 6.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.91 (dd, J = 8.0, 8.0 Hz, 1H), 7.02 (dd, J = 8.0, 8.0 Hz, 1H), 7.27-7.38 (m, 5H), 7.78 (d, J = 8.0 Hz, 1H)

^{13}C -NMR (100 MHz) δ = 12.2, 18.3, 28.8, 49.9, 56.9, 59.9, 67.8, 74.4, 108.0, 110.3, 119.1, 120.5, 120.7, 126.9, 127.8, 128.7, 132.0, 132.6, 140.9, 141.3.

Anal. Calcd for $\text{C}_{31}\text{H}_{45}\text{NO}_2\text{Si}$: C, 75.71; H, 9.22; N, 2.85. Found: C, 75.47; H, 9.45; N, 3.02.

trans-**4g** (major)

IR (neat) 3050, 2964, 2942, 2865, 1456, 1365, 1191, 1059 cm^{-1}

^1H -NMR (500 MHz) δ = 1.11-1.16 (m, 18H), 1.17-1.26 (m, 3H), 1.36 (s, 9H), 2.75 (ddd, J = 13.3, 6.7, 5.5 Hz, 1H), 2.95 (ddd, J = 13.3, 7.7, 3.7 Hz, 1H), 5.09 (d, J = 11.8 Hz, 1H), 5.15 (d, J = 11.8 Hz, 1H), 5.39 (dd, J = 6.7, 3.7 Hz, 1H), 5.58 (dd, J = 7.7, 5.5 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.94 (dd, J = 8.0, 8.0 Hz, 1H), 7.04 (dd, J = 8.0, 8.0 Hz, 1H), 7.07-7.12 (m, 2H), 7.27-7.35 (m, 3H), 7.80 (d, J = 8.0 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 12.2, 18.2, 28.7, 50.4, 57.1, 59.4, 67.0, 74.4, 108.2, 110.4, 119.1, 120.6, 120.9, 126.3, 127.7, 128.8, 132.2, 132.7, 141.4, 141.5.

Anal. Calcd for $\text{C}_{31}\text{H}_{45}\text{NO}_2\text{Si}$: C, 75.71; H, 9.22; N, 2.85. Found: C, 75.44; H, 9.49; N, 2.66.

PtCl₂-catalyzed reaction of an imidate derivative **1e with *p*-methoxybenzyl vinyl ether **6**:
2,3-Dihydro-3-isopropoxy-1-(4-methoxybenzyloxy)-9-propyl-1*H*-pyrrolo[1,2-*a*]indole (**4f**)**

To a mixture of *p*-methoxybenzyl vinyl ether **6** (82 mg, 5.0 mmol), activated MS5A (200 mg), and PtCl_2 (1.0 mg, 0.003 mmol) in toluene (2.5 mL) was added an imidate **1e** (28.5 mg, 0.125 mmol) in toluene (1.5 mL) over 2 h at 50 °C. After heating for further 6.5 h, the reaction was quenched with saturated aq. NaHCO_3 and the reaction mixture was filtered through a short pad of Celite®. Organic layer was extracted with ethyl acetate three times and the combined organic layer was washed with brine, and then dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative TLC (toluene : ethyl acetate = 40 : 1) to give **4f** (42.6 mg, 0.108 mmol, 87% (*cis:trans* = 45:55)).

The stereochemistry of the minor product was determined to be *cis* by the observed NOE shown below. Therefore, the major product was assigned to be the corresponding *trans* isomer.

cis-**4f** (minor)

IR (neat) 3050, 2959, 2930, 2869, 1612, 1514, 1455, 1328, 1247 cm^{-1}

^1H -NMR (500 MHz) δ = 0.98 (t, J = 7.3 Hz, 3H), 1.21 (d, J = 6.0 Hz, 3H), 1.25 (d, J = 6.0 Hz, 3H), 1.68-1.80 (m, 2H), 2.62 (brd, J = 14.1 Hz, 1H), 2.71-2.83 (m, 2H), 2.95 (ddd, J = 14.1, 6.8, 6.8 Hz, 1H), 3.81 (s, 3H), 4.08-4.17 (m, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.63 (d, J = 11.4 Hz, 1H), 5.08 (brd, J = 6.8 Hz, 1H), 5.76 (brd, J = 6.8 Hz, 1H), 6.89 (brd, J = 8.6 Hz, 2H), 7.12

(brdd, $J = 8.0, 8.0$ Hz, 1H), 7.20 (brdd, $J = 8.0, 8.0$ Hz, 1H), 7.31 (brd, $J = 8.6$ Hz, 2H), 7.38 (brd $J = 8.0$ Hz, 1H), 7.59 (brd, $J = 8.0$ Hz, 1H).

^{13}C -NMR (125 MHz) $\delta = 14.4, 22.8, 23.2, 23.6, 26.8, 43.7, 55.3, 69.1, 69.3, 71.0, 83.0, 110.3, 110.6, 113.7, 119.5, 119.8, 121.7, 129.3, 130.7, 132.7, 132.8, 138.9, 159.1$.

HRMS Calcd for. $\text{C}_{25}\text{H}_{31}\text{NO}_3$, M 393.2304. Found m/z 393.2300.

trans-**4f** (major)

IR (neat) 3050, 2960, 2930, 2869, 1612, 1514, 1456, 1328, 1248 cm^{-1}

^1H -NMR (500 MHz) $\delta = 0.99$ (t, $J = 7.4$ Hz, 3H), 1.23 (d, $J = 6.1$ Hz, 6H), 1.68-1.79 (m, 2H), 2.72-2.87 (m, 4H), 3.80 (s, 3H), 3.95-4.04 (m, 1H), 4.52 (d, $J = 11.2$ Hz, 1H), 4.55 (d, $J = 11.2$ Hz, 1H), 5.35 (dd, $J = 6.3, 4.9$ Hz, 1H), 5.95 (dd, $J = 5.4, 3.2$ Hz, 1H), 6.91 (brd, $J = 8.5$ Hz, 2H), 7.11 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.17 (dd, $J = 8.0, 8.0$ Hz, 1H), 7.31 (brd, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H).

^{13}C -NMR (125 MHz) $\delta = 14.3, 22.8, 23.0, 23.9, 26.5, 45.1, 55.3, 70.3, 70.4, 72.8, 84.2, 110.1, 110.3, 113.9, 119.3, 119.7, 121.4, 129.3, 130.3, 132.2, 133.2, 138.5, 159.3$.

HRMS Calcd for. $\text{C}_{25}\text{H}_{31}\text{NO}_3$, M 393.2304. Found m/z 393.2309.

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