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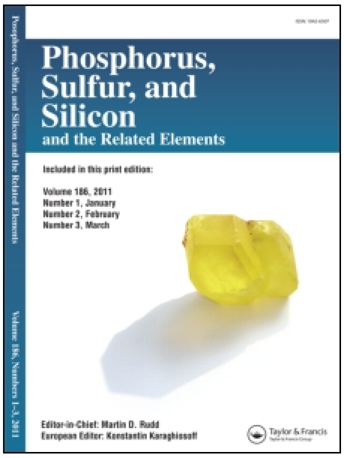

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REACTIONS OF CYCLIC AZA-YLIDES WITH β-DICARBONYL COMPOUNDS

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REACTIONS OF CYCLIC AZA-YLIDES WITH β-DICARBONYL COMPOUNDS

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The reactions of five- and six-membered cyclic iminophosphoranes, **3** and **4**, with β-dicarbonyl compounds gave enamino phosphine oxide derivatives **5a-h** in good yields. Compounds **5b** and **5e** were stereoselectively converted to 1,6- and 1,7-diene **9a** and **9b**.

Keywords: cyclic iminophosphoranes; β-dicarbonyl compounds; aza-Wittig reaction; Horner-Wittig Reaction

INTRODUCTION

Cyclic iminophosphoranes **3** and **4**[1] have two different kinds of nucleophilic atoms, i.e., carbon and nitrogen on the α position of the phosphorus atom. Recently, we reported tandem reactions with alkylating agents[2] using these two nucleophilic sites. Furthermore, the reactions of cyclic iminophosphoranes at the nitrogen nucleophilic site with α-diketones gave imino phosphine oxides in good yields. Also, the imino phosphine oxides were treated with LDA in THF to produce the cyclic imines[3].

In this paper, we describe the reactions of cyclic iminophosphoranes **3** and **4** with various β-dicarbonyl derivatives having an active methylene group.

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RESULTS AND DISCUSSION

A reaction of cyclic aza-ylide **3**, generated from aminophosphonium salt **1** in the presence of sodium hydride, with 2,4-pentanedione gave enaminophosphine oxide derivatives **5a** in 68% yields. Similarly, enaminophosphone oxide derivatives **5b**-**5f** were obtained in good yields. (TABLE I)

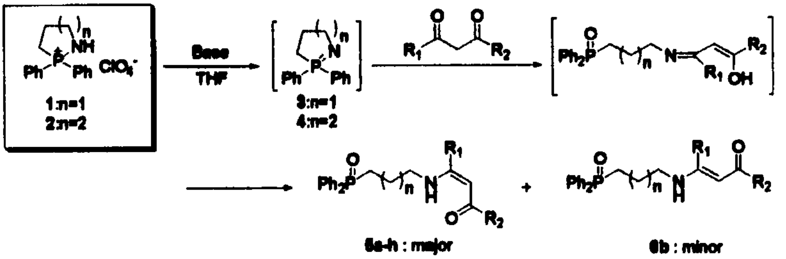


TABLE I Reaction of Cyclic Iminophosphoranes with β-dicarbonyl Derivatives

Entry	*Ylides*	*R_1*	*R_2*	*Base*	*Products*	*Yields*[a]	*ratio*[b]
1	3	CH_3	CH_3	NaH	**5a**	68	>99:1
2	3	CH_3	Ph	NaH	**5b**, **6b**	60	75:25
3	3	CH_3	p-$CH_3C_6H_4$	NaH	**5c**	61	>99:1
4	4	CH_3	CH_3	NaH	**5d**	66	>99:1
5	4	CH_3	Ph	NaH	**5e**	89	>99:1
6	4	CH_3	p-$CH_3C_6H_4$	NaH	**5f**	87	>99:1
7	3	CH_3	OEt	NaHMDS	**5g**	7	>99:1
8	3	CF_3	OEt	NaHMDS	**5h**	61	>99:1

a. Isolated Yields.
b. Determined by ^{1}H-NMR.

The structures of the products were determined from spectral data. Especially, the vinylic carbons of **5a** were observed at 96.02 and 163.3ppm in the ^{13}C-NMR spectrum. In the ^{1}H-NMR spectrum of the products **5a**, the amine proton appeared at about 10.87 ppm as a broad triplet signal. Furthermore, nuclear Overhauser effect was observed between methyl proton (R_1) and olefin proton. These results and literature data[5] suggest that the compound **5a** has an Z-enamine structure.

In the case of a reaction of **3** with benzoyl acetone, a mixture of isomers, **5b**and **6b**, was obtained in a ratio of 75:25. The major isomer **5b** showed an NH resonance at 11.49ppm in the ^1H-NMR spectrum, and the minor isomer did so at 10.79ppm. The downfield shift of the NH proton should be the result of a hydrogen bond between the amino hydrogen and the carbonyl oxygen[6]. The NOESY spectrum of a mixture of **5b** and **6b** indicated between methyl proton (R_1) and olefin proton of **5b**.

Furthermore, the carbonyl resonance of **5a** was observed at 195.4ppm in the ^{13}C-NMR spectra. On the other hand, that of **5b** was observed at 187.9ppm. The higher field signal of the carbonyl carbon is attributable the result of a phenyl-carbonyl resonance effect[7]. These results suggest the compound **5b** has a benzoyl group, not an acetyl group. The regiochemistry of the reactions might be the result of a steric effect of the phenyl group.

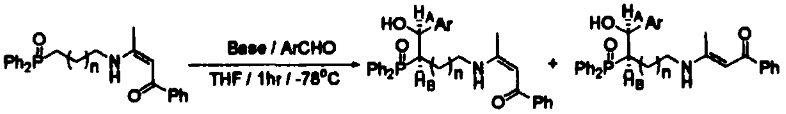
The reaction of **3** with ethyl acetoacetate provided **5g** in very low yield. (7%) The yield was improved to 61% when ethyl 4,4,4-trifluoroacetoacetate was used as a substrate. It was known that the great electrophilicity of fluoroalkyl carboxylic acid derivatives enables phosphorus ylides to add to the carbonyl group of esters[4] and even amides[8].

Treatment of a mixture of **5b** and **6b** with two equimolar amounts of LDA at 0°C gave a dark orange solution, which reacted with benzaldehyde to give the erythro alcohol **7a** in 8% yield. However, when using five equimolar amounts of LDA, the reaction progressed to form the product **7a** in 68% yield exclusively, after purification by column chromatography.

The structure and stereochemistry of **7a-c** were determined by ^1H-NMR and ^{13}C-NMR spectra. In the ^1H-NMR spectrum, the coupling constant was observed at $J_{AB}<1Hz$. The threo isomer ($J_{AB}=6$–$9Hz$) was not detected. Warren[9] and we[10] also have reported that reactions of alkyl or aryl (diphenyl) phosphine oxides with aldehydes gave preferentially erythro adducts.

Conversions of erythro adducts **7a, 8a** and **7c** into the 1,6- and 1,7-diene **9a** and **9b**with elimination of the diphenylphosphinate ion were performed by treatment with sodium hydride in N,N-dimethylformamide (SCHEME 1) The results indicated that elimination of the diphenylphosphinate ion proceeded with retention of the configuration in the alcohols **7a+8a** and **7c**.

In summary, cyclic 2-azaphosphonium salts can react with β-dicarbonyl compounds to give enamino phosphine oxide derivatives in good yields, and we showed that the two kinds of nucleophilic sites could be used for formation of a carbon-nitrogen bond and a stereoselective carbon-carbon double bond.



5b+6b : n=1
5e : n=2

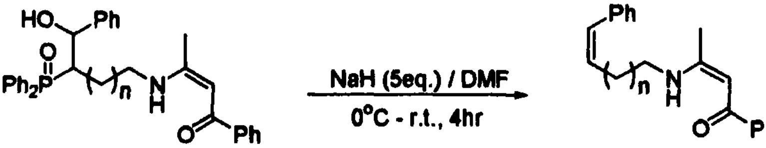
7a-c : major

8a,b : minor

TABLE II Reactions of Enamine Derivatives with Aldehydes

enamine	*Base*	*Ar*	*Products*	*Yield*[a]	*ratio*[b]
5b+6b	LDA(2eq.)	Ph	**7a**	8	n.d
5b+6b	LDA(5eq.)	Ph	**7a, 8a**	68	80:20
5b+6b	LDA(5eq.)	*p*-ClC$_6$H$_4$	**7b, 8b**	51	93:7
5b+6b	*n*-BuLi (5eq.)	Ph	**7a, 8a**	13	80:20
5e	LDA(5eq.)	Ph	**7c**	70	>99:1
5e	*n*-BuLi	Ph	**7c**	14	>99:1

a. Isolated Yields.
b. Determined by ^{1}H-NMR.



7a+8a : n=1
7c : n=2

9a : n=1, 66%
9b : n=2, 58%

SCHEME 1

EXPERIMENTAL SECTION

4-[3-(Diphenyl-phosphinoyl)-propylamino]-pent-3-en-2-one 5a

A mixture of sodium hydride (60% dispersion in mineral oil, 0.09 g, 2.25 mmol) and 1,1-diphenyl-2-azaphosphorinanium perchlorate **1** (0.68 g, 2 mmol) in dry THF (10 ml) was stirred for 30min at room temperature and 10min at reflux temperature. After cooling to room temperature, to this mixture was added dropwise a solution of 2,4-pentanedione (0.30 g, 3 mmol) in dry THF (5 ml) at room temperature and stirred for 20hr at reflux temperature. The reaction mixture was allowed to cool to room temperature. Water (10 ml) and dichloromethane (50 ml) were then added dropwise, and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give yellow crystals. (0.45 g, 66%): m.p. 139–140°C; IR (KBr) 3060, 2935, 1600, 1545, 1440, 1180, 1115 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.79–2.05 (m, 2H), 1.85 (s, 3H), 2.00 (s, 3H), 2.31–2.38 (m, 2H), 3.31–3.36 (m, 2H), 4.96 (s, 1H), 7.27–7.70 (m, 10H), 10.87 (brt, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$) δ 18.96 (s), 23.05 (d, $^2J_{PC}$=3.67Hz), 27.14 (d, $^1J_{PC}$=72.02Hz), 29.15 (s), 43.57 (d, $^3J_{PC}$=12.81Hz), 96.02 (s), 128.85–135.46 (m) 163.31 (s), 195.38 (s); MS m/z 342 (M^++1); HRMS calcd. for $C_{20}H_{25}NO_2P$ (M^++1) 342.1623, found 342.1617.

Compound 5b and 6b

Prepared as above. Yellow crystals (89% yield): m.p. 135–140°C; IR (KBr) 3050, 2930, 1590, 1575, 1540, 1430 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.75–2.02 (m, 2H), 1.97 (s, 2.25H), 2.08 (s, 0.75H), 2.24–2.29 (m, 0.5H), 2.35–2.42 (m, 1.5H), 3.18–3.21 (m, 0.5H), 3.39–3.44 (m, 1.5H), 5.05 (s, 0.25H), 5.66 (s, 0.75H), 7.43–7.85 (m, 15H), 10.79 (brt, 0.25H) 11.49 (brt, 0.75H,); ^{13}C-NMR 5b (100.61MHz, $CDCl_3$) δ 19.23 (s), 22.70 (d, $^2J_{PC}$=3.66Hz), 26.76 (d, $^1J_{PC}$=72.02Hz), 43.46 (d, $^3J_{PC}$=12.81Hz), 92.50 (s), 126.88–140.47 (m), 164.83 (s), 187.99 (s); **6b** δ 23.08 (s), 26.70 (d, $^1J_{PC}$=71.64Hz), 44.64 (d, $^3J_{PC}$=15.24Hz), 97.15 (s), 165.01(s), 195.95 (s); MS m/z 403 (M^+); HRMS calcd. for $C_{25}H_{26}NO_2P$ (M^+) 403.1701, found 403.1731.

Compound 5c

Prepared as above. Yellow crystals (87% yield): m.p. 162–164°C; IR (KBr) 3060, 2920, 1575, 1515, 1435, 1290, 1160, 1110 cm^{-1}; ^{1}H-NMR (89.56MHz, $CDCl_3$) δ 2.10–3.53 (m, 6H), 1.97 (s, 3H), 2.37 (s, 3H), 5.64

(s, 1H), 7.14–7.87 (m, 14H), 11.44 (brt, 1H); ^{13}C-NMR (22.39MHz, $CDCl_3$) δ 19.26 (s), 22.01 (d, $^{2}J_{PC}$=3.66Hz), 26.75 (d, $^{1}J_{PC}$=72.63Hz), 43.42 (d, $^{3}J_{PC}$=12.20Hz), 92.29 (s), 126.90–137.68 (m), 164.53 (s), 187.88 (s); MS m/z 418 (M^++1); HRMS calcd. for $C_{26}H_{29}NO_2P$(M^++1) 418.1921, found 418.1947.

Compound 5d

Prepared as above. Yellow crystals (68% yield): m.p. 96–98°C; IR (KBr) 3420, 3050, 2940, 1610, 1570, 1440, 1300, 1180, 1120 cm^{-1}; ^{1}H-NMR (89.56MHz, $CDCl_3$) δ 1.68–3.23 (m, 6H), 1.86 (s, 3H), 1.98 (s, 3H), 4.93 (s, 1H), 7.29–7.86 (m, 10H), 10.82 (brt, 1H); ^{13}C-NMR (22.39MHz, $CDCl_3$) δ 18.71 (s), 19.45 (d, $^{2}J_{PC}$=3.66Hz), 29.66 (d, $^{1}J_{PC}$=72.02Hz), 31.62 (d, $^{3}J_{PC}$=12.82Hz), 42.61 (s), 95.29 (s), 128.45–135.19 (m), 164.53 (s), 194.76 (s); MS m/z 356 (M^++1); HRMS calcd. for $C_{21}H_{27}NO_2P$ (M^++1) 356.1779, found 356.1765.

Compound 5e

Prepared as above. A yellow syrup (89% yield): IR (neat) 3380, 3050, 2940, 1610, 1570, 1440, 1300, 1180, 1120 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.71–1.78 (m, 4H), 2.01 (s, 3H), 2.03–2.35 (m, 2H), 3.27–3.31 (m, 2H), 5.65 (s, 1H), 7.28–7.90 (m, 15H), 11.44 (brt, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$) δ 19.22 (s), 19.33 (s), 29.38 (d, $^{1}J_{PC}$=71.64Hz), 31.18 (d, $^{3}J_{PC}$=12.95Hz), 42.85 (s), 92.11 (s), 126.84–140.39 (m), 164.80 (s), 187.61 (s); MS m/z 418 (M^++1); HRMS calcd. for $C_{26}H_{29}NO_2P$ (M^++1) 418.1936, found 418.1938.

Compound 5f

Prepared as above. A yellow syrup (61% yield): IR (neat) 3420, 3070, 2950, 1600, 1590, 1440, 1180, 1120 cm^{-1}; ^{1}H-NMR (89.56MHz, $CDCl_3$) δ 1.74–3.39 (m, 8H), 2.00 (s, 3H), 2.37 (s, 3H), 5.62 (s, 1H), 7.14–7.85 (m, 10H), 11.39 (brt, 1H); ^{13}C-NMR (22.39MHz, $CDCl_3$) δ 19.31 (s), 19.39 (s), 29.55 (d, $^{1}J_{PC}$=72.02Hz), 31.34 (d, $^{3}J_{PC}$=13.43Hz), 42.93 (s), 92.04 (s), 127.01–140.75 (m), 164.50 (s), 187.71 (s); MS m/z 432 (M^++1).

Compound 5g

To a suspension of 1,1-diphenyl-2-azaphospholanium perchlorate **1** (0.68 g, 2 mmol) in dry THF (10 ml) was added a 1 M solution of NaHMDS in THF (2.0 ml, 2.2 mmol) at room temperature with stirring. After 15 min, a solution of ethyl acetoacetate (0.26 g, 2 mmol) in THF (10 ml) was added to the mixture and stirred for 1hr. Ten of water was then added and extracted with dichloromethane. The organic layer was added over anhydrous sodium sulfate and concentrated in vacuo to give a yellow syrup **5** g(0.05 g, 7%): IR (neat) 3400, 2940, 1640, 1600, 1440, 1260, 1175, 1120 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.24 (t, 3H, J=7.0Hz), 1.83 (s, 3H), 1.89–2.42 (m, 4H), 3.14–3.19 (m, 2H), 4.08 (q, 2H, J=7.0Hz), 4.44 (s), 7.29–7.86 (m, 10H), 8.55 (m, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$) δ 15.20 (s), 19.67 (s), 23.70 (d, $^2J_{PC}$=3.66Hz), 27.39 (d, $^1J_{PC}$=72.02Hz), 43.88 (d, $^3J_{PC}$=13.3Hz), 58.83 (s), 83.73 (s), 127.47–132.54 (m), 162.14 (s), 171.19 (s); MS 385 m/z (M^+); HRMS calcd. for $C_{22}H_{28}O_3NP$ (M^+) 385.1806, found 385.1780.

Compound 5h

Prepared as above. Pale yellow crystals (61% yield): m.p. 78–79°C; IR (KBr) 3275, 2980, 1675, 1620, 1440, 1280, 1195, 1120 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.26 (t, 3H, J=7.4Hz), 1.86–1.93 (m, 2H), 2.28–2.35 (m, 2H), 3.34 (q, 2H, J_{HH}=6.60Hz, J_{HH}=6.56Hz), 4.15 (q, 2H, J=7.4Hz), 5.08 (s, 1H), 7.27–7.77 (m, 10H), 8.16 (brt, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$), δ 14.27 (s), 22.86 (d, $^2J_{PC}$=3.66Hz), 27.15 (d, $^1J_{PC}$=72.63Hz), 44.40 (d, $^3J_{PC}$=15.24Hz), 59.78 (s), 85.11 (d, $^3J_{CF}$=5.34Hz), 120.77 (q, $^1J_{CF}$=275.12Hz), 148.20 (q, $^2J_{CF}$=31.25Hz), 169.81 (s); MS 425 m/z (M^+); HRMS calcd. for $C_{21}H_{23}F_3NO_3P$ (M^+) 425.1367, found 425.1344.

3-[3-(Diphenyl-phosphinoyl)-4-hydroxy-4-phenyl-butylamino]-1-phen yl-but-2-en-1-one 7a

To an LDA solution (5.65 ml, 11.3 mmol) was added acyclic enamine phosphine oxides **5b, 6b** (0.910 g, 2.26 mmol) in 10 ml of dry THF solution at −78°C, and stirred for 10min at this temperature. A solution of benzaldehyde (0.288 g, 2.71 mmol) in THF was then added dropwise at same temperature. The mixture was stirred for 1hr at -78°C. After aqueous workup at room temperature, the mixture was extracted with ether, dried over anhydrous sodium sulfate, and concentrated to give the crude products. This crude product was purified by column chromatography of silica gel using ethyl acetate as the eluent to give **7a** as a yellow syrup. (0.770 g, 67%): IR (neat) 3350, 3050, 1595, 1540, 1435, 1320, 1285 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.41. (s, 2.4H), 1.71–2.87 (m, 5H), 2.13 (s, 0.6H), 4.73 (brs, 0.2H), 4.86 (brs, 0.8H), 4.90 (s, 0.2H), 5.27 (d, 0.2H, $^{3}J_{PH}$=9.36Hz) 5.31 (d, 0.8H, $^{3}J_{PH}$=8.84Hz), 5.50 (s, 0.8H), 7.19–8.04 (m, 20H), 10.52 (brt, 0.2H), 11.94 (brt, 0.8H); ^{13}C-NMR (100.61MHz, $CDCl_3$) **7a** δ 18.32 (s), 21.88 (s), 40.97 (d, $^{1}J_{PC}$=67.07Hz), 41.42 (d, $^{3}J_{PC}$=8.38Hz), 69.89 (s), 92.55 (s), 125.04–143.16 (m), 164.79 (s), 187.63 (s); **8a** δ 97.50 (s), 165.06 (s), 195.77 (s); MS 509 m/z (M^+); HRMS calcd. for $C_{32}H_{32}NO_3P$ (M^+) 509.2120, found 509.2090.

Compound 7b

Prepared as above. A yellow syrup (51% yield): IR (neat) 3380, 3050, 1595, 1580, 1540, 1435, 1320, 1260 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.46 (s, 3H), 1.73–2.84 (m, 5H), 4.93 (m, 1H), 5.20 (d, 0.07H, $^{3}J_{PH}$=9.32Hz), 5.26 (d, 0.93H, $^{3}J_{PH}$=8.84Hz), 5.27 (s, 0.07H), 5.53 (s, 0.93H), 7.23–8.04 (m, 19H), 10.50 (brt, 0.07H), 11.22 (brt, 0.93H); ^{13}C-NMR (100.61MHz, $CDCl_3$) **7b** δ 18.34 (s), 21.87 (s), 40.80 (d, $^{1}J_{PC}$=67.06Hz), 41.32 (d, $^{3}J_{PC}$=7.62Hz), 69.71 (s), 92.75 (s), 126.65–140.55 (m), 164.77 (s), 187.84 (s); **7b** δ 97.55 (s), 165.00 (s), 195.91 (s); MS m/z 558 (M^++1); HRMS calcd. for $C_{33}H_{34}NO_3PCl$ (M^++1) 558.1962, found 558.1969.

Compound 7c

Prepared as above. A yellow syrup (70% yield): IR (neat) 3380, 3050, 1595, 1580, 1540, 1435, 1320, 1260 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ. 0.84–0.93 (m, 1H), 1.07–1.13 (m, 1H), 1.58–1.71 (m, 1H), 1.69 (s, 3H), 1.88–1.98 (m, 1H), 2.51–2.55 (m, 1H), 2.72 (dt, 1H, JHH_C=7.04Hz, JHH_N=6.80Hz), 4.81 (brs, 1H), 5.28 (d, 1H, $^{3}J_{PH}$=9.12Hz), 5.53 (s, 1H), 7.20–8.04 (m, 20H), 11.22 (brt, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$) δ 19.02 (s), 19.04 (s), 30.19 (d, $^{3}J_{PC}$=6.10Hz), 42.99 (s), 44.41 (d, $^{1}J_{PC}$=66.30Hz), 70.61 (d,

$^{2}J_{PC}$=2.29Hz), 91.94 (s), 125.37–142.03 (m), 164.59 (s), 187.28 (s); MS m/z 523 (M^+); HRMS calcd. for $C_{33}H_{34}NO_3P$ (M^+) 523.2276, found 523.2248.

(Z)-1-Phenyl-3-(4-phenyl-3-butenylamino)-2-butene-1-one 9a

A solution of the alcohol **9a** (0.588 g, 1.12 mmol) in dry dimethylformamide (DMF) was added dropwise to a suspension of sodium hydride (60% dispersion in mineral oil, 0.225 g, 4.60 mmol) at 0°C, and the mixture was stirred at r.t. for 8h. After aqueous workup, the mixture was extracted with ether, and the organic layer was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated to give the crude product. The crude product was purified by column chromatography on silica gel with AcOEt as eluent to give **9a** as a yellow syrup (0.226 g, 66%): IR (neat) 3060, 3030, 1605, 1545, 1325, 1295 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.61–2.67 (m, 2H), 3.33–3.41 (m, 2H), 5.63–5.70 (m, 2H), 6.58 (d, 1H, J_{HH}=11.64Hz), 7.16–7.86 (m, 10H), 11.49 (brt, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$) δ 19.52 (s), 29.38 (s), 43.43 (s), 92.43 (s), 126.06–140.65 (m), 164.75 (s), 187.90 (s); MS m/z 291 (M^+); HRMS calcd. for $C_{20}H_{21}NO$ (M^+) 291.1623, found 291.1626.

Compound 9b

Prepared as above. A yellow syrup (58% yield): IR (neat) 3060, 3020, 2940, 1605, 1590, 1440, 1325, 1290 cm^{-1}; ^{1}H-NMR (400.13MHz, $CDCl_3$) δ 1.73–1.80 (m, 2H), 1.96 (s, 3H), 2.40–2.46 (m, 2H), 3.23–3.28 (m, 2H), 5.48–5.65 (m, 2H), 6.46 (d, 1H, J_{HH}=11.64Hz), 7.16–7.95 (m, 10H), 11.45 (brt, 1H); ^{13}C-NMR (100.61MHz, $CDCl_3$) δ 19.73 (s), 26.11 (s), 30.77 (s), 42.95 (s), 92.47 (s), 121.49–140.60 (m), 164.64 (s), 187.35 (s); MS m/z 306 (M^++1); HRMS calcd. for $C_{21}H_{24}NO$ (M^++1) 306.1858, found 306.1896.

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