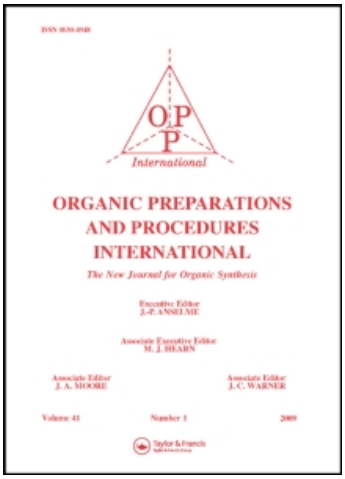

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FACILE AND HIGH-YIELD SYNTHESIS OF NEW 4-PHOSPHORANYLIDENE-4,5-DIHYDROPYRAZOL-5-ONES BY REACTION OF CONJUGATED AZOALKENES WITH PHOSPHINES

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FACILE AND HIGH-YIELD SYNTHESIS OF NEW 4-PHOSPHORANYLIDENE-4,5-DIHYDROPYRAZOL-5-ONES BY REACTION OF CONJUGATED AZOALKENES WITH PHOSPHINES

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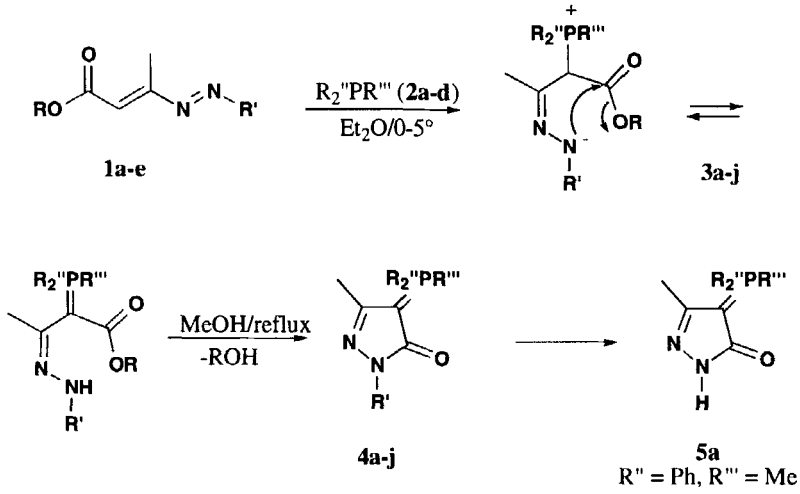
The Michael-type addition of triphenylphosphine to conjugated azoalkenes gave stable 1,5-zwitterionic species, which readily yielded interesting pyrazoles or 4-triphenylphosphoranylidene-4,5-dihydropyrazol-5-ones by two different internal heterocyclization pathways.[1] An X-ray diffraction study demonstrated that for 1-methoxycarbonylamino-2-methyl-3-ethoxycarbonyl-4-triphenylphosphoranylidene-4,5-dihydropyrrol-5-one the 1,4-dipolar canonical form, analogous to the zwitterionic phosphorus betaine intermediate in the Wittig reactions, is an important contributing structure to the resonance hybrid.[2] Such an electronic situation is clearly advantageous for further 1,4-additions and [4+2]-cycloadditions.[3] For these reasons, the aforementioned compounds represent both attractive products and useful intermediates in organic chemistry. Based on these facts and considering the different electron-donating effect of phenyl-, alkyl-, and alkylphenylphosphines,[4] we decided to investigate the reaction of conjugated azoalkenes and studied the reaction between conjugated azoalkenes **1a-e** and trimethylphosphine (**2a**), tributylphosphine (**2b**), dimethylphenylphosphine (**2c**) or methyldiphenylphosphine (**2d**).

An ice-cooled solution of azoalkenes **1a-e** reacts rapidly (10-30 min.) with phosphines **2a-d** in ether to give 1,4-adducts **3a-j** in excellent yields. Yields, reaction times and melting points of the 1,4-adducts **3a-j** are listed in Table 1. These 1,4-adducts precipitate from the reaction medium in satisfactory purity and after filtration afford 4-phosphoranylidene-4,5-dihydropyrazol-5-ones **4a-j** under reflux (4-18 hrs) in methanol by internal attack of the nitrogen atom on the carboxylate function with loss of an alcohol molecule. In the case of the 1,4-adduct **3i**, besides main product **4i** the pyrazole **5a**, from the hydrolytic N-CO bond cleavage, was also isolated (see Scheme). Yields, reaction times and melting points of the 4-phosphoranylidene-4,5-dihydropyrazol-5-ones **4a-j** and **5a** are listed in Table 2.

The findings confirm this procedure as a simple and versatile method for the synthesis of unknown polyfunctionalized pyrazolones from conjugated azoalkenes.[5]



a) R = R" = R'" = Me, R' = CO_2Bu*t* b) R = R" = R'" = Me, R' = $CONH_2$
c) R = R" = R'" = Me, R' = CONHPh d) R = Et, R' = CO_2*t*-Bu, R" = R'" = *t*-Bu
e) R = Et, R' = $CONH_2$, R" = R'" = *t*-Bu f) R = Et, R' = CONHPh, R" = R'" = *t*-Bu
g) R = R' = Me, R" = $CONH_2$, R'" = Ph h) R = R' = Me, R" = CONHPh, R'" = Ph
i) R = Et, R' = $CONH_2$, R" = Ph, R'" = Me j) R = R'" = Me, R' = CONHPh, R'" = Ph

TABLE 1. Data for 1,4-Adducts **3a-j**

Reactants 1	2	1,4-Adduct 3	R	R'	R''	R'''	Yield[a] (%)	Reaction time (hr)	Mp[b] (°C)
1a	**2a**	**3a**	Me	CO_2*t*-Bu	Me	Me	84	0.5	101-103
1b	**2a**	**3b**	Me	$CONH_2$	Me	Me	98	0.2	171-173
1c	**2a**	**3c**	Me	CONHPh	Me	Me	94	0.2	184-186
1d	**2b**	**3d**	Et	CO_2*t*-Bu	*t*-Bu	*t*-Bu	77	0.5	107-109
1b	**2b**	**3e**	Me	$CONH_2$	*t*-Bu	*t*-Bu	86	0.2	89-91
1c	**2b**	**3f**	Me	CONHPh	*t*-Bu	*t*-Bu	82	0.2	101-103
1b	**2c**	**3g**	Me	$CONH_2$	Me	Ph	91	0.2	125-127
1d	**2c**	**3h**	Me	CONHPh	Me	Ph	98	0.2	137-139
1e	**2d**	**3i**	Et	$CONH_2$	Ph	Me	91	0.2	129-130
1c	**2d**	**3j**	Me	CONHPh	Ph	Me	87	0.2	131-133

a) Yield of pure isolated product. b) Melting points are uncorrected.

TABLE 2. Data for 4-Phosphoranylidene-4,5-dihydropyrazol-5-ones **4a-j** and **5a**

Reactants 1	2	Products 4 and 5	R'	R"	R"'	Yield[a] (%)	Reaction time (hr)	mp[b] (°C)
1a	**2a**	**4a**	CO_2t-Bu	Me	Me	75	5.0	261-263
1b	**2a**	**4b**	$CONH_2$	Me	Me	89	5.0	217-219
1c	**2a**	**4c**	CONHPh	Me	Me	73	5.0	228-230
1d	**2b**	**4d**	CO_2t-Bu	*t*-Bu	*t*-Bu	72	12.0	177-179
1b	**2b**	**4e**	$CONH_2$	*t*-Bu	*t*-Bu	82	18.0	147-149
1c	**2b**	**4f**	CONHPh	*t*-Bu	*t*-Bu	93	18.0	136-138
1b	**2c**	**4g**	$CONH_2$	Me	Ph	93	5.0	157-159
1d	**2c**	**4h**	CONHPh	Me	Ph	79	4.0	162-164
1e	**2d**	**4i**	$CONH_2$	Ph	Me	68	4.0	268-270
1c	**2d**	**4j**	CONHPh	Ph	Me	83	4.0	207-209
-	-	**5a**	H	Ph	Me	10	–	286-285

a) Yield of pure isolated product. b) Melting points are uncorrected.

EXPERIMENTAL SECTION

Alkoxycarbonylazoalkenes (R' = CO_2Bu-*t*)[6] and aminocarbonylazoalkenes (R" = $CONH_2$, CONHPh)[7] were prepared as previously reported. Methyldiphenylphosphine (Janssen), dimethylphenylphosphine, trimethylphosphine and tributylphosphine (Aldrich) were commercial materials and were used without further purification. Melting points were determined in capillary tubes with a Büchi apparatus and are uncorrected. The products often decompose at melting point. IR spectra were obtained for nujol mull with a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra at 60 MHz were recorded on a Varian EM-360L spectrometer and at 200 MHz were recorded on a Bruker AC-200 in $CDCl_3$. Chemical shifts (δ) are reported in ppm downfield from internal TMS. Mass spectra were recorded on a Hewlett Packard HP- 5995. Macherey-Nagel precoated silica gel SIL G-25UV$_{254}$ plates (0.25 mm) were employed for analytical thin layer chromatography (TLC) and Baker silica gel (0.063-0.200 mm) for column chromatography.

General Procedure for the Synthesis of 1,4-Adduct 3a-j. - To a stirred, ice-cooled solution of conjugated azoalkene **1a-e** (1 mmol), in diethyl ether (5 ml), was added dropwise a solution of phosphine **2a-d** (1 mmol) in diethyl ether (3 ml). After 10-30 minutes, the conjugated azoalkene completely disappeared (monitored by silica gel TLC) and a white precipitate formed. The 1,4-adducts **3a-j** were collected and showed satisfactory purity and were used without further purification.

Compound 3a: IR: 3400, 3130, 1685, 1620 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.49 (9H, s, *t*-Bu), 1.82 (9H, d, $^2J_{P\text{-}H}$ = 13.8 Hz, PMe), 2.09 (3H, s, Me), 3.58 (3H, s, OMe), 7.15 (1H, br s, NH, D_2O ex) ppm. EI/MS: m/e: 304 (M^+), 248, 204 (M^+-CO_2t-Bu), 189 (M^+-$NHCO_2t$-Bu).

Anal. Calcd. for $C_{13}H_{25}N_2O_4P$: C, 51.31; H, 8.28; N, 9.21. Found: C, 51.15; H, 8.54; N, 9.32.

Compound 3b: IR: 3460, 3300, 3160, 1730, 1680, 1625 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.54 and 1.96 (9H, 2d, $^2J_{P\text{-}H}$ = 13.8 Hz, PMe), 2.08 and 2.22 (3H, 2s, Me), 3.57 and 3.61 (3H, 2s, OMe),

5.36 (2H, br s, NH_2, D_2O ex), 7.45 and 7.85 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 247 (M^+), 204 (M^+-$CONH_2$), 173, 157.

Anal. Calcd. for $C_9H_{18}N_3O_3P$: C, 43.72; H, 7.34; N, 17.0. Found: C, 43.91; H, 7.09; N, 17.21.

Compound 3c: IR: 3180, 1710 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.53 and 1.81 (9H, 2d, $^2J_{P-H}$ = 13.8 Hz, PMe), 2.13 and 2.23 (3H, 2s, Me), 3.58 and 3.64 (3H, 2s, OMe), 6.95-7.73 (6H, m, Ph, NH), 7.88 and 8.20 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 323 (M^+), 288, 231 (M^+-NHPh), 199.

Anal. Calcd. for $C_{15}H_{22}N_3O_3P$: C, 55.72; H, 6.86; N, 13.0. Found: C, 55.51; H, 7.12; N, 13.21.

Compound 3d: IR: 3230, 3140, 1685, 1620 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.73-1.12 (9H, m, Me), 1.15-1.75 (15H, m, CH_2, Me), 1.53 (9H, s, *t*-Bu), 1.87-2.50 (12H, m, PCH_2, Me), 4.03 (2H, q, J = 7.0 Hz, OCH_2), 7.17 and 8.22 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 444 (M^+), 399, 359, 344 (M^+-CO_2t-Bu), 328 (M^+-$NHCO_2t$-Bu).

Anal. Calcd. for $C_{23}H_{45}N_2O_4P$: C, 62.14; H, 10.2; N, 6.3. Found: C, 62.23; H, 10.09; N, 6.55.

Compound 3e: IR: 3460, 3180, 3140, 1740, 1690, 1635 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.71-1.17 (9H, m, Me), 1.22-1.83 (12H, m, CH_2), 1.85-2.53 (9H, m, PCH_2, Me), 3.70 (3H, s, OMe), 5.62 (2H, br s, NH_2, D_2O ex), 8.53 and 8.79 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 373 (M^+), 330 (M^+-$CONH_2$), 298, 269.

Anal. Calcd. for $C_{19}H_{38}N_3O_3P$: C, 58.89; H, 9.88; N, 10.84. Found: C, 59.01; H, 9.63; N, 11.01.

Compound 3f: IR: 3360, 3200, 1690, 1635 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.64-1.16 (9H, m, Me), 1.16-1.75 (12H, m, CH_2), 1.78-2.40 (9H, m, PCH_2, Me), 3.61 (3H, s, OMe), 6.87-7.16 (6H, m, Ph, NH), 7.99 and 8.12 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 449 (M^+), 357 (M^+-NHPh), 231, 218.

Anal. Calcd. for $C_{24}H_{40}N_3O_3P$: C, 64.12; H, 8.97; N, 9.35. Found: C, 63.88; H, 8.86; N, 9.61.

Compound 3g: IR: 3470, 3260, 3200, 1730, 1685, 1625 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.74 and 2.00 (6H, 2d, $^2J_{P-H}$ = 13.8 Hz, PMe), 1.89 and 2.18 (3H, 2s, Me), 3.54 and 3.60 (3H, 2s, OMe), 4.81 (2H, br s, NH_2, D_2O ex), 7.35-7.94 (5H, m, Ph), 7.98 and 8.28 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 309 (M^+), 278, 234 (278-$CONH_2$), 195.

Anal. Calcd. for $C_{14}H_{20}N_3O_3P$: C, 54.37; H, 5.52; N, 13.59. Found: C, 54.18; H, 6.77; N, 13.75.

Compound 3h: IR: 3340, 3180, 1680, 1640 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.74 and 2.04 (6H, 2d, $^2J_{P-H}$ = 13.8 Hz, PMe), 1.92 and 2.20 (3H, 2s, Me), 3.56 and 3.84 (3H, 2s, OMe), 6.70-7.90 (11H, m, Ph, NH), 7.83 and 7.92 (1H, 2br s, NH, D_2O ex) ppm. EI/MS: m/e: 265 (M^+-CONHPh), 245, 231, 194.

Anal. Calcd. for $C_{20}H_{24}N_3O_3P$: C, 62.33; H, 6.28; N, 10.9. Found: C, 62.58; H, 6.15; N, 10.76.

Compound 3i: IR: 3480, 3330, 3180, 1735, 1670 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.07 (3H, t, J=7.0 Hz, Me), 1.93 and 2.10 (3H, 2s, Me), 2.28 (3H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 3.97 (2H, q, J = 7.0 Hz, CH_2), 4.57 and 5.30 (2H, 2br s, NH_2, D_2O ex), 7.33-8.25 (11H, m, Ph, NH) ppm. EI/MS: m/e: 385 (M^+), 342 (M^+-$CONH_2$), 326 (M^+-$NHCONH_2$), 297, 269.

Anal. Calcd. for $C_{20}H_{24}N_3O_3P$: C, 62.33; H, 6.28; N, 10.9. Found: C, 62.15; H, 6.54; N, 10.64.

Compound 3j: IR: 3370, 3350, 3200, 1730, 1680 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 1.93 and 2.10

(3H, 2s, Me), 2.30 (3H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 3.53 (3H, s, OMe), 6.63-8.23 (17H, m, Ph, NH) ppm. EI/MS: m/e: 328 (M^+-CONHPh), 299, 290, 270.

Anal. Calcd. for $C_{25}H_{26}N_3O_3P$: C, 67.1; H, 5.86; N, 9.39. Found: C, 67.38; H, 5.75; N, 9.27.

General Procedure for the Synthesis of 4-Phosphoranylidene-4,5-dihydropyrazol-5-ones (4a-j and 5a).- A solution of 1,4-adduct **3a-j** (1 mmol), in methanol (5 ml), was heated under reflux (4-18 hrs) until 1,4-adduct completely disappeared (monitored by silica gel TLC). After evaporation of the solvent under reduced pressure the crude product was isolated by chromatography on a silica gel column (elution with ethyl acetate-methanol mixture). 4-Phosphoranylidene-4,5-dihydropyrazol-5-ones **4a-j** and **5a** were further purified by crystallization from ethyl acetate-petroleum ether (bp. 40-60 °).

Compound 4a: IR: 3420, 1735 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.63 (9H, s, *t*-Bu), 1.93 (9H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 2.17 (3H, s, Me) ppm. EI/MS: m/e: 272 (M^+), 199, 172 (M^+-CO_2*t*-Bu), 157.

Anal. Calcd. for $C_{12}H_{21}N_2O_3P$: C, 52.93; H, 7.77; N, 10.29. Found: C, 52.77; H, 8.03; N, 10.14.

Compound 4b: IR: 3470, 3300, 3150, 1730, 1700 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.96 (9H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 2.22 (3H, s, Me), 5.06 and 8.81 (2H, 2br s, NH_2, D_2O ex) ppm. EI/MS: m/e: 172 (M^+-$CONH_2$), 157, 141, 129.

Anal. Calcd. for $C_8H_{14}N_3O_2P$: C, 44.65; H, 6.56; N, 19.53. Found: C, 44.91; H, 6.4; N, 19.76.

Compound 4c: IR: 3170, 1710 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.98 (9H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 2.24 (3H, s, Me), 6.91-7.81 (5H, m, Ph), 11.35 (1H, br s, NH, D_2O ex) ppm. EI/MS: m/e: 172 (M^+-CONHPh), 119, 115, 91.

Anal. Calcd. for $C_{14}H_{18}N_3O_2P$: C, 57.73; H, 6.23; N, 14.43. Found: C, 57.63; H, 6.0; N, 14.71.

Compound 4d: IR: 1730, 1620 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.94 (9H, t, J = 7.0 Hz, Me), 1.34-1.60 (12H, m, CH_2), 1.62 (9H, s, *t*-Bu), 2.06-2.29 (9H, m, PCH_2, Me) ppm. EI/MS: m/e: 398 (M^+), 325, 298 (M^+-CO_2*t*-Bu), 281, 269.

Anal. Calcd. for $C_{21}H_{39}N_2O_3P$: C, 63.29; H, 9.86; N, 7.03. Found: C, 63.14; H, 9.72; N, 7.17.

Compound 4e: IR: 3310, 3170, 1710, 1680 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.81-1.18 (9H, m, Me), 1.31-1.67 (12H, m, CH_2), 1.99-2.39 (9H, m, PCH_2, Me), 5.38 and 8.88 (2H, 2br s, NH_2, D_2O ex) ppm. EI/MS: m/e: 298 (M^+-$CONH_2$), 269, 242, 225, 213.

Anal. Calcd. for $C_{17}H_{32}N_3O_2P$: C, 59.8; H, 9.45; N, 12.31. Found: C, 59.66; H, 9.71; N, 12.21.

Compound 4f: IR: 3200, 1700 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 0.75-1.24 (9H, m, Me), 1.24-1.84 (12H, m, CH_2), 1.99-2.48 (9H, m, PCH_2, Me), 6.90-7.77 (5H, m, Ph), 11.44 (1H, br s, NH, D_2O ex) ppm. EI/MS: m/e: 417 (M^+), 298 (M^+-CONHPh), 271, 242.

Anal. Calcd. for $C_{23}H_{36}N_3O_2P$: C, 66.16; H, 8.69; N, 10.06. Found: C, 66.06; H, 8.94; N, 10.2.

Compound 4g: IR: 3460, 3260, 3180, 1735, 1690 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.92 (3H, s, Me), 2.22 (6H, 2d, $^2J_{P-H}$ = 13.8 Hz, PMe), 5.21 and 8.86 (2H, 2br s, NH_2, D_2O ex), 7.17-8.07 (5H, m, Ph) ppm. EI/MS: m/e: 277 (M^+), 234 (M^+-$CONH_2$), 219, 177.

Anal. Calcd. for $C_{13}H_{16}N_3O_2P$: C, 56.32; H, 5.82; N, 15.16. Found: C, 56.47; H, 5.68; N, 15.42.

Compound 4h: IR: 3410, 3170, 1715 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.93 (3H, s, Me), 2.24 (6H, 2d, $^2J_{P-H}$ = 13.8 Hz, PMe), 6.93-7.83 (5H, m, Ph), 11.43 (1H, br s, NH, D_2O ex) ppm. EI/MS:

m/e: 353 (M^+), 295, 234 (M^+-CONHPh), 219.

Anal. Calcd. for $C_{19}H_{20}N_3O_2P$: C, 64.58; H, 5.7; N, 11.89. Found: C, 64.33; H, 5.91; N, 11.72.

Compound 4i: IR: 3480, 3330, 3170, 1730, 1700 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.52 (3H, s, Me), 2.58 (3H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 5.13 and 8.87 (2H, 2br s, NH_2, D_2O ex), 7.44-7.81 (10H, m, Ph) ppm. EI/MS: m/e: 296 (M^+-$CONH_2$), 279, 239, 215.

Anal. Calcd. for $C_{18}H_{18}N_3O_2P$: C, 63.71; H, 5.35; N, 12.38. Found: C, 63.96; H, 5.20; N, 12.47.

Compound 4j: IR: 3180, 1725 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.53 (3H, s, Me), 2.60 (3H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 6.78-7.94 (15H, m, Ph), 11.41 (1H, br s, NH, D_2O ex) ppm. EI/MS: m/e: 415 (M^+), 296 (M^+-CONHPh), 281, 239.

Anal. Calcd. for $C_{24}H_{22}N_3O_2P$: C, 69.39; H, 5.34; N, 10.11. Found: C, 69.24; H, 5.26; N, 10.37.

Compound 5a: IR: 3200, 3080, 1715 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.45 (3H, s, Me), 2.59 (3H, d, $^2J_{P-H}$ = 13.8 Hz, PMe), 7.44-7.91 (10H, m, Ph), 8.53 (1H, br s, NH, D_2O ex) ppm. EI/MS: m/e: 296 (M^+), 215, 201, 183.

Anal. Calcd. for $C_{17}H_{17}N_2OP$: C, 68.91; H, 5.78; N, 9.45. Found: C, 68.76; H, 5.92; N, 9.68.

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