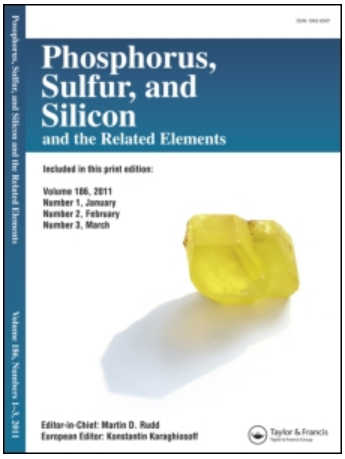

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An Efficient One-Pot Synthesis of Sulphur-Containing Phosphorus Ylides

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AN EFFICIENT ONE-POT SYNTHESIS OF SULPHUR-CONTAINING PHOSPHORUS YLIDES

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Protonation of the reactive 1:1 intermediate produced in the reaction between dialkyl acetylenedicarboxylates and triphenylphosphine by arylsulfonamides leads to vinylphosphonium salts, which undergoes Michael addition with the conjugate base of the NH-acid to produce highly functionalized, salt-free phosphorus ylides in good yields. These stable ylides exist as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partial double bond, resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords: Acetylenic esters; arylsulfonamides; NH-acids; stabilized ylides; triphenylphosphine

INTRODUCTION

Organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom, are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic uses.[1–10] As a result a large number of methods have appeared describing novel synthesis of organophosphorus compounds. Phosphorus ylides are reactive intermediates, which take part in valuable reactions in the synthesis of organic products. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually obtained from the phosphine and an alkyl halide. Phosphonium salts are also prepared by Michael addition of trivalent phosphorus nucleophiles to activated olefins and in other ways. The phosphorus salts are most often converted to the ylide by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. We present an efficient synthetic route to sterically congested sulphur-containing phosphorus ylide **3** using

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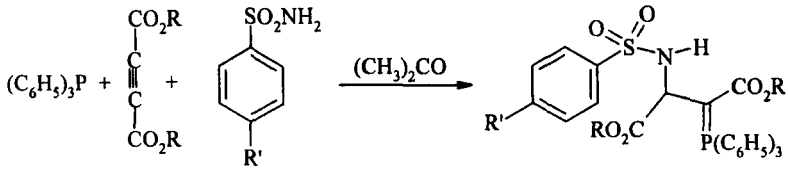
triphenylphosphine, dialkyl acetylenedicarboxylates **1** and a nitrogen acid, such as arylsulfonamides **2** in good yields (see Scheme 1).



1	R
a	Me
b	Et
c	^{t}Bu

2	R'
a	H
b	Me

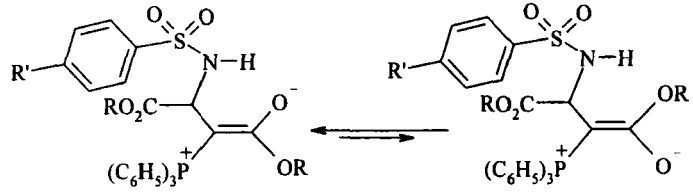
3	R	R'	%Yield
a	Me	H	76
b	Et	H	76
c	^{t}Bu	H	73
d	Me	Me	78
e	Et	Me	75
f	^{t}Bu	Me	73

SCHEME 1

RESULTS AND DISCUSSION

The structures of compounds **3a–f** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these ylides are fairly similar and display molecular ion peaks. Any other fragmentation involved the loss of the ester moieties.

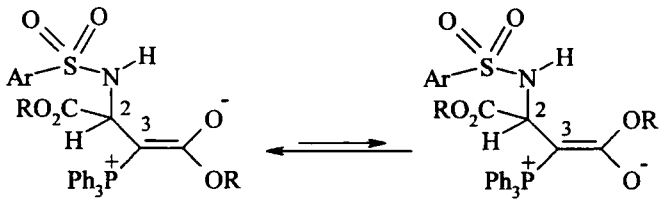
The NMR spectra of ylides **3a–f** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in (***E***)-**3** and (***Z***)-**3** geometrical isomers and is slow on the NMR time scale at ambient temperature. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–f** are shown in Table I. Assignment of configuration (*Z*) to the major geometrical isomer is based on the ^{1}H chemical shift of the OR moiety, which is expected to be shielded as a result of the anisotropic effect of the phenyl groups (see Scheme 2). The



(*Z*)-**3**; Major (*E*)-**3**; Minor

SCHEME 2

TABLE I Selected ^{1}H, ^{13}C and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, N-H, C-2 and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds **3a–f**



(*Z*)-**3** (*E*)-**3**

Compound	Isomer (%)	^{1}H NMR spectroscopic data				^{13}C NMR data		^{31}P NMR
		H-2 ($^{3}J_{PH}$, $^{3}J_{HH}$)	N-H ($^{3}J_{HH}$)	OR	CO_2R	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	
3a	M (60)	3.94 (15.0, 9.1)	6.85 (9)	3.11	3.47	56.1 (17.4)	43.7 (127.0)	23.26
3a	m (40)	3.93 (14.6, 9.2)	6.07 (9)	3.54	3.48	55.3 (17.4)	44.8 (132.8)	24.24
3b	M (72)	4.07 (14.9, 9.1)	6.88 (9)	3.70[a]	3.95[a]	56.0 (17.8)	43.3 (127.0)	22.67
3b	m (28)	4.06 (14.8, 9.1)	6.07 (9)	3.96[a]	3.89[a]	55.4 (17.8)	44.8 (136.0)	22.69
3c	M (70)	3.66 (15.3, 9.0)	6.89 (9)	0.90	1.26	55.90 (18.2)	42.15 (128.8)	21.65
3c	m (30)	3.53 (9.4)	6.08 (9)	1.40	1.23	54.78 (18.2)	44.68 (136.3)	21.23
3d	M (55)	3.93 (15.7, 9.2)	6.79 (9)	3.11	3.49	56.0 (17.3)	43.6 (127.1)	22.73
3d	m (45)	4.38 (13.3, 9.3)	6.02 (9)	3.54	3.49	55.2 (17.2)	44.2 (135.9)	23.69
3e	M (70)	4.07 (15.1, 9.2)	6.79 (9)	3.67[a]	4.00[a]	55.8 (17.7)	43.3 (127.1)	22.64
3e	m (30)	4.06 (15.1, 9.1)	6.04 (9)	3.99[a]	3.86[a]	55.2 (17.5)	44.9 (136.0)	23.65
3f	M (68)	3.63 (15.0, 8.9)	6.78 (9)	0.89	1.26	55.81 (18.4)	42.57 (127.8)	24.78
3f	m (32)	3.52 (16.5, 8.9)	6.02 (9)	1.40	1.23	54.69 (18.2)	44.69 (135.4)	24.87

[a]The methylene group of the OR moiety.

TABLE II Selected Proton Chemical Shifts (at 90 MHz, in ppm, Me_4Si) and Activation Parameters (k $Jmol^{-1}$) for **3a** and **3d** in 1,2-Dichlorobenzene

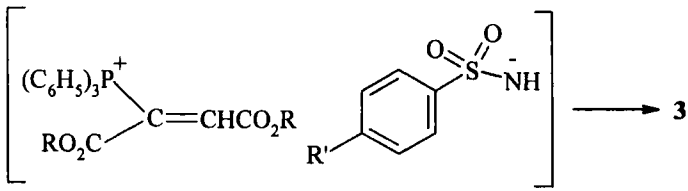
Compound	Temp (°C)	Resonance (P-C-CO_2CH_3)		$\Delta\nu$ (Hz)	k (s^{-1})	T_c (K)	$\Delta G^{\neq}$
3a	5	3.58	3.13	40	89	338	70.4 ± 2
	120	3.24					
3d	5	3.54	3.14	36	79	340	71.2 ± 2
	120	3.25					

possibility of hydrogen-bond formation between the negatively-charged oxygen atom and the NH group may also play some role in stabilization of **(Z)-3**.

The most noteworthy feature of the ^1H NMR spectra of **3a** and **3d** in $CDCl_3$ at ambient temperature (25°C) is in the methoxy region which, for each compound, exhibits two sharp singlets for the CO_2CH_3 groups of (*E*) and (*Z*) isomers and two fairly broad singlets for the methoxy groups (see Table I). Near 5°C the broad lines become sharper. The ^1H NMR spectra **3a** and **3d** in 1,2-dichlorobenzene at 5°C is similar to those measured in $CDCl_3$. Increasing the temperature results in coalescence of the methoxy resonances (see Table II). At 100°C, a fairly broad singlet was observed for the OCH_3 group, while the CO_2CH_3 protons appear as a sharp single resonance.

Although an extensive line-shape analysis in relation to the dynamic ^1H NMR effects observed for **3a** and **3d** was not undertaken, the variable temperature spectra allowed to calculate[11] the free energy barrier (if not the enthalpy and entropy of activation) for the dynamic NMR processes in these ylides (see Table II). The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ are not large.[12]

Although we have not yet established the mechanism of the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of arylsulfomides in an experimental manner, a possible explanation is proposed in Scheme 3. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles[1–10] it is



SCHEME 3

reasonable to assume that ylide **3** results from an initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the arylsufonamide. Then, the positively charged ion might be attacked by the conjugate base of the NH-acid to form stable ylide **3** (see Scheme 3).

In summary, sulphur-containing phosphorus ylides **3a–f** may be considered as potentially useful synthetic intermediates. The procedure described here may be an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR 460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a BRUKER DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1, 125.8, and 202.4 MHz, respectively. Dynamic NMR studies were carried out using a JEOL-EX90 Fourier transform spectrometer at 90 MHz. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Triphenylphosphine and dialkyl acetylenedicarboxylates **1**, were obtained from Fluka (Buchs, Switzerland) and used without further purification.

Preparation of Dimethyl 2-(benzenesulfonylamino)-3-(triphenylphosphanylidene)-succinate 3a

General Procedure

To a magnetically stirred solution of benzenesulfonamide (0.314 g, 2 mmol) and triphenylphosphine (0.512 g, 2 mmol) in acetone (7 mL) was added dropwise, a mixture of dimethyl acetylenedicarboxylate (0.284 g, 2 mmol) in acetone (3 mL) at −5°C over 10 min. After 6 h stirring at room temperature, the white solid product was filtered, washed with diethyl ether (2 × 5 mL), and recrystallized from ethanol. White powder, m.p. 161–162°C. IR (KBr) (ν_{max}, cm^{-1}): 3280 (N-H), 1730 (C=O), 1629 (C=C). Analyses: Calcd. for $C_{30}H_{28}NO_6PS$ (561.6): 64.16; H, 5.03; N, 2.49%. Found C, 64.2; H, 5.0; N, 2.6%. MS (*m/z*, %): 561 (M, 1); 469 (M-Ph, CH_3, 5); 425 (M-Ph, CO_2Me, 7); 141 ($PhSO_2$, 20); 77 (Ph, 85). ^{1}H, ^{13}C, and ^{31}P NMR data for the major (60%) isomer (*Z*)-**3a**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.11 and 3.47 (6 H, 2 s, 2 OCH_3), 3.94 (1 H, dd, $^{3}J_{HH}$ = 9.1 Hz, $^{3}J_{PH}$ = 15.0 Hz, CH), 6.85 (1 H, br d, $^{3}J_{HH}$ = 9 Hz,

NH), 7.3–7.7 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 43.7 (d, $^1J_{PC}$ = 127.0 Hz, P-*C*=C), 49.6 and 52.6 (2 OCH_3), 56.1 (d, $^2J_{PC}$ = 17.4 Hz, N-CH), 126.4 (d, $^1J_{PC}$ = 93.1 Hz, P-C_{ipso}), 127–135 (CH arom), 141.84 (C-S), 170.51 (d, $^2J_{PC}$ = 13.2 Hz, C=*C*-O), 173.08 (d, $^3J_{PC}$ = 6.4 Hz, C=O).^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.26 (Ph_3P^+-C). ^1H, ^{13}C, and ^{31}P NMR data for the minor (40%) isomer (***E***)-**3a**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.48 and 3.54 (6 H, 2 s, 2 OCH_3), 3.93 (1 H, dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{PH}$ = 14.6 Hz, CH), 6.07 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.3–7.7 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 44.8 (d, $^1J_{PC}$ = 132.8 Hz, P-*C*=C), 50.6 and 52.7 (2 OCH_3), 55.3 (d, $^2J_{PC}$ = 17.4 Hz, N-CH), 126.0 (d, $^1J_{PC}$ = 92.6 Hz, P-C_{ipso}), 127–135 (CH arom), 141.30 (C-S), 170.35 (d, $^2J_{PC}$ = 16.7 Hz, C=*C*-O), 173.02 (d, $^3J_{PC}$ = 7.5 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.24 (Ph_3P^+-C).

Selected Data for Diethyl 2-(benzenesulfonylamino)-3-(triphenylphosphanylidene)-succinate 3b

White powder, m.p. 158–159°C. IR (KBr) (ν_{max}, cm^{-1}): 3270 (N-H), 1724 (C=O), 1629 (C=C). Analyses: Calcd. for $C_{32}H_{32}NO_6PS$ (589.6): C, 65.18; H, 5.47; N, 2.38%. Found: C, 65.3; H, 5.4; N, 2.5%. MS (*m/z*, %): 589 (M, 1); 419 (M-$PhSO_2$, Et, 5); 227 ($PhSO_2NHCHCO_2$, 4); 156 ($PhSO_2NH$, 3); 141 ($PhSO_2$, 20); 77 (Ph, 90). ^1H, ^{13}C, and ^{31}P NMR data for the major (72%) isomer (*Z*)-**3b**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 0.43 and 1.05 (6 H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_2CH_3), 3.70 and 3.95 (4 H, 2 ABX_3 system, 2 OCH_2), 4.07 (1 H, dd, $^3J_{HH}$ = 9.1 Hz, $^3J_{PH}$ = 14.9 Hz, CH), 6.88 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.30–7.60 (20 H, m, 4 C_6H_5).^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.3 and 14.4 (2 CH_2CH_3), 43.3 (d, $^1J_{PC}$ = 127.0 HZ, P-*C*=C), 56.0 (d, $^2J_{PC}$ = 17.8 Hz, N-CH), 58.0 and 61.6 (2 OCH_2), 126.6 (d, $^1J_{PC}$ = 92.3 Hz, P-C_{ipso}), 127.0–134.0 (CH arom), 141.85 (C-S), 170 (d, $^2J_{PC}$ = 12.6 Hz, P-C=*C*-O), 172.3 (d,$^3J_{PC}$ = 6.5 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.67 (Ph_3P^+-C). ^1H, ^{13}C, and ^{31}P NMR data for the minor (28%) isomer (***E***)-**3b**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.11 and 1.18 (6 H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_2CH_3), 3.89 and 3.96 (4 H, 2 ABX_3 system, 2 OCH_2), 4.07 (1H, dd, $^3J_{HH}$ = 9.1 Hz, $^3J_{PH}$ = 14.8 Hz, CH), 6.07 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.2–7.6 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.6 and 15.4 (2 CH_2CH_3), 44.8 (d,$^1J_{PC}$ = 136.0 Hz, P-*C*=C), 55.4 (d, $^2J_{PC}$ = 17.8 Hz, N-CH), 58.6 and 61.7 (2 OCH_2), 126.1 (d, $^1J_{PC}$ = 92.6 Hz, P-C_{ipso}), 127.0–134.0 (CH arom), 141.2 (C-S), 170.0 (d,$^2J_{PC}$ = 19.0 Hz, P-C=*C*-O), 172.5 (d, $^3J_{PC}$ = 8.3 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.69 (Ph_3P^+-C).

Selected Data for Di-Tert Buthyl 2-(benzenesulfonylamino)-3-(triphenylphosphanylidene)-succinate 3c

White powder, m.p. 163–164°C. IR (KBr) (ν_{max}, cm^{-1}): 3245 (N-H), 1728 (C=O), 1597 (C=C). Analyses: Calcd. for $C_{36}h_{40}NO_6PS$ (645.8): C, 66.96; H, 6.24; N, 2.17%. Found: C, 66.8; H, 6.1; N, 2.1%. MS (*m/z*, %): 645 (M, 1): 156 ($PhSO_2NH$, 27); 141 ($PhSO_2$, 15); 77 (Ph, 90). ^1H, ^{13}C, and ^{31}P NMR data for the major (70%) isomer (***Z***)-**3c**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 0.90 and 1.26 (18 H, 2 s, 2 *CMe*$_3$), 3.66 (1 H, dd, $^3J_{HH} = 9.0$ Hz, $^3J_{PH} = 15.3$ Hz, CH), 6.86 (1 H, br d, $^3J_{HH} = 9$ Hz, NH), 7.20–7.65 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 27.62 and 27.79 (2*CMe*$_3$), 42.15 (d, $^1J_{PC} = 128.0$ Hz, P-*C*=C), 55.90 (d, $^2J_{PC} = 18.2$ Hz, N-CH), 77.2 and 81.6 (2 O*C*Me$_3$), 126.5 (d, $^1J_{PC} = 81.0$ Hz, P-C$_{ipso}$), 127.0–134.0 (CH arom), 133.80 (C-S), 168.75 (d, $^2J_{PC} = 12.2$ Hz, P-C=*C*-O), 170.34 (d, $^3J_{PC} = 7.4$ Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 21.65 (Ph_3P^+-C). ^1H, ^{13}C, and ^{31}P NMR data for the minor (30%) isomer (***E***)-**3c**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.23 and 1.40 (18 H, 2 s, 2 *CMe*$_3$), 3.53 (1 H, dd, $^3J_{HH} = 9.4$ Hz, $^3J_{PH} = 16.5$ Hz, CH), 6.08 (1 H, br d, $^3J_{HH} = 9$ Hz, NH), 7.30–7.60 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 27.79 and 28.05 (2 C*Me*$_3$), 44.68 (d, $^1J_{PC} = 136.3$ Hz, P-*C*=C), 54.78 (d, $^2J_{PC} = 18.2$ Hz, N-CH), 80.41 and 81.45 (2 OCMe$_3$), 126.59 (d, $^1J_{PC} = 92.2$ Hz, P-C$_{ipso}$), 127.0–134.0 (CH arom), 133.71 (C-S), 168.75 (d, $^2J_{PC} = 12.2$ Hz, P-C=*C*-O), 170.24 (d, $^3J_{PC} = 8.7$ Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 21.23 (Ph_3P^+-C).

Selected Data for Dimethyl 2-(toluene-4-sulfonylamino)-3-(triphenylphosphanylidene)-succinate 3d

White powder, m.p. 166–167°C. IR (KBr) (ν_{max}, cm^{-1}): 3145 (N-H), 1736 (C=O), 1610 (C=C). Analyses: Calcd. for $C_{31}H_{30}NO_6PS$ (575.6) C, 64.70; H, 5.08; N, 2.44%. Found: C, 64.7; H, 5.1; N, 2.5%. MS (*m/z*, %): 575 (M, 1); 516 (M-CO_2Et, 3); 484 (M-PhMe, 3); 183 ($ArSO_2NHCH$, 30); 155 ($ArSO_2$, 23); 91 ($PhCH_2$, 37). ^1H, ^{13}C, and ^{31}P NMR data for the major (55%) isomer (***Z***)-**3d**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.36 (3 H, s, CH_3), 3.11 and 3.49 (6 H, 2 s, 2 OCH_3), 3.93 (1 H, dd, $^3J_{HH} = 9.2$ Hz, $^3J_{PH} = 15.7$ Hz, CH), 6.79 (1 H, br d, $^3J_{HH} = 9$ Hz, NH), 7.3–7.7 (19 H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.8 (CH_3), 43.6 (d, $^1J_{PC} = 127.1$ Hz, P-*C*=C), 49.5 and 52.6 (2 OCH_3), 56.0 (d, $^2J_{PC} = 17.3$ Hz, N-CH), 126.4 (d, $^1J_{PC} = 92.6$ Hz, P-C$_{ipso}$), 129.0–134.0 (CH arom), 138.88 (*C*-CH_3), 142.88 (C-S), 170.4 (d, $^2J_{PC} = 12.2$ Hz, P-C=*C*-O), 173.1 (d, $^3J_{PC} = 7.2$ Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.73 (Ph_3P^+-C). ^1H, ^{13}C, and ^{31}P NMR data for the minor (45%) isomer

(*E*)-**3d**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.36 (3 H, s, CH_3), 3.49 and 3.54 (6 H, 2 s, 2 OCH_3), 4.38 (1 H, dd, $^3J_{HH}$ = 9.3 Hz, $^3J_{PH}$ = 13.3 Hz, CH), 6.02 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.3–7.7 (19 H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.7 (CH_3), 44.2 (d, $^1J_{PC}$ = 135.9 Hz, P-*C*=C), 50.5 and 52.7 (2 OCH_3), 55.2 (d, $^2J_{PC}$ = 17.2 Hz, N-CH), 125.8 (d, $^1J_{PC}$ = 92.4 Hz, P-C_{ipso}), 129.0–134.0 (CH arom), 138.52 (C-CH_3), 143.05 (C-S), 170.3 (d, $^2J_{PC}$ = 16.7 Hz, P-C=*C*-O), 173.1 (d, $^3J_{PC}$ = 7.2 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.69 (Ph_3P^+-C).

Selected Data for Diethyl 2-(toluene-4-sulfonylamino)-3-(triphenylphosphanylidene)-succinate 3e

White powder, m.p. 168–169°C. IR (KBr) (ν_{max}, cm^{-1}): 3250 (N-H), 1720 (C=O), 1623 (C=C). Analyses: Calcd. for $C_{33}H_{34}NO_6PS$ (603.7): C, 65.66; H, 5.68; N, 2.32%. Found: C, 65.8; H, 5.6; N, 2.4% MS (*m/z*, %): 603 (M, 1): 433 (M-$ArSO_2NH$, 10); 347 ($EtO_2CC{=}PPh_3$, 6); 183 ($ArSO_2NHCH$, 70); 155 ($ArSO_2$, 45); 91 ($PhCH_2$, 85). ^{1}H, ^{13}C, and ^{31}P NMR data for the major (70%) isomer (*Z*)-**3e**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.43 and 1.06 (6 H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_2CH_3), 2.35 (3 H, s, CH_3), 3.67 and 4.00 (4 H, 2 ABX_3 system, 2 CH_2CH_3), 4.07 (1 H, dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{PH}$ = 15.1 Hz, CH), 6.79 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.0–7.7 (19 H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.3 and 14.4 (2 CH_2CH_3), 21.8 (CH_3), 43.3 (d, $^1J_{PC}$ = 127.1 Hz, P-*C*=C), 55.8 (d, $^2J_{PC}$ = 17.7 Hz, N-CH), 57.9 and 61.5 (2 OCH_2), 126.6 (d, $^1J_{PC}$ = 93.4 Hz, P-C_{ipso}), 127.0–134.0 (CH arom), 138.87 (*C*-CH_3), 142.83 (C-S), 169.9 (d, $^2J_{PC}$ = 12.6 Hz, P-C=*C*-O), 172.3 (d, $^3J_{PC}$ = 6.8 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.64 (Ph_3P^+-C). ^{1}H, ^{13}C, and ^{31}P NMR data for the minor (30%) isomer (*E*)-**3e**: ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.11 and 1.17 (6 H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_2CH_3), 2.34 (3 H, s, CH_3), 3.86 and 3.99 (4H, 2 ABX_3 system, 2CH_2CH_3), 4.06 (1 H,dd, $^3J_{HH}$ = 9.1 Hz, $^3J_{PH}$ = 15.1 Hz, CH), 6.04 (1 H, br d, $^3J_{HH}$ = 9.0 Hz, NH), 7.0–7.7 (19 H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.5 and 15.4 (2 CH_2CH_3), 21.6 (CH_3), 44.9 (d, $^1J_{PC}$ = 136.0 Hz, P-*C*=C), 55.2 (d, $^2J_{PC}$ = 17.5 Hz, N-CH), 58.6 and 61.6 (2 OCH_2), 126.2 (d, $^1J_{PC}$ = 92.6 Hz, P-C_{ipso}), 127.0–134.0 (CH arom), 138.21 (*C*-CH_3), 142.07 (C-S), 170.0 (d, $^2J_{PC}$ = 17.9 Hz, P-C=*C*-O), 172.5 (d, $^3J_{PC}$ = 8.0 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.65 (Ph_3P^+-C).

Selected Data for di-tert-butyl 2-(toluenesulfonylamino)-3-(triphenylphosphanylidene)-succinate 3f

White powder, m.p. 178–179°C. IR (KBr) (ν_{max}, cm^{-1}): 3250 (N-H), 1728 (C=O), 1605 (C=C). $C_{37}H_{42}NO_6PS$ (659.8): C, 67.36; H, 6.42; N, 2.12%. Found: C67.21; H6.38; N2.23%. MS (*m/z*, %): 659 (M, 1); 432 (M-^{t}Bu,

$ArSO_2NH$, 10); 183 ($ArSO_2NHCH$, 65); 91 ($PhCH_2$, 80). ^1H, ^{13}C, and ^{31}P NMR data for the major (68%) isomer (***Z***)-**3f**: ^1H NMR (500.1 MHz, $CDCl_3$): δ 0.89 and 1.26 (18 H, 2 s, 2 CMe_3), 2.34 (3 H, s, CH_3), 3.63 (1 H, dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{PH}$ = 15.0 Hz, CH), 6.78 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.0–7.7 (19 H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.24 (CH_3), 27.23 and 27.79 (2 CMe_3), 42.57 (d, $^1J_{PC}$ = 127.8 Hz, P-*C*=C), 55.81 (d, $^2J_{PC}$ = 18.4 Hz, N-CH), 77.15 and 81.42 (2 CMe_3), 126.55 (d, $^1J_{PC}$ = 92.2 Hz, P-C_{ipso}), 127.0–132.0 (CH arom), 134.74 (*C*-Me), 142.90 (C-S), 168.50 (d, $^2J_{PC}$ = 12.5 Hz, P-C=*C*-O), 170.34 (d, $^3J_{PC}$ = 7.8 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.78 (Ph_3P^+-C). ^1H, ^{13}C, and ^{31}P NMR data for the minor (32%) isomer (***E***)-**3f**: ^1H NMR (500 MHz, $CDCl_3$): δ 1.23 and 1.40 (18 H, 2 s, 2 CMe_3), 2.30 (3 H, s, CH_3), 3.52 (1 H, dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{PH}$ = 16.5 Hz, CH), 6.02 (1 H, br d, $^3J_{HH}$ = 9 Hz, NH), 7.01–7.67 (19 H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.15 (CH_3), 27.58 and 28.04 (2 CMe_3), 44.69 (d, $^1J_{PC}$ = 135.4 Hz, P-*C*=C), 54.69 (d, $^2J_{PC}$ = 18.2 Hz, N-CH), 80.30 and 81.55 (2 CMe_3), 126.68 (d, $^1J_{PC}$ = 92.3 Hz, P-C_{ipso}), 127.0–132.0 (CH arom), 134.82 (*C*-Me), 141.83 (C-S), 168.40 (d, $^2J_{PC}$ = 15.5 Hz, P-C=*C*-O), 170.34 (d, $^3J_{PC}$ = 7.8 Hz, C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.87 (Ph_3P^+-C).

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