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Supporting Information for:

A More Critical Role for Silicon in the Catalytic Staudinger Amidation: Silanes as Non-Innocent Reductants

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Contents

1. General Information

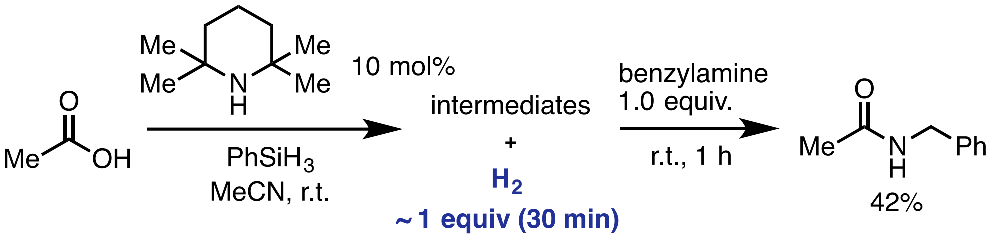
Glassware was dried in an oven overnight before use. All reactions were carried out under an argon balloon atmosphere. All solvents and reagents were used as supplied unless otherwise stated. Benzyl azide was supplied by Alfa Aesar at 94% purity. Thin layer chromatography was carried out on Polgram SIL G/UV254 silica-aluminium plates and plates were visualized using ultra-violet light (254 nm) or $KMnO_4$ solution. For flash column chromatography, fluorochem silica gel 60, 35–70 mesh was used. NMR data was collected at 400 MHz for ^1H; 101 MHz for ^{13}C; 162 MHz for ^{31}P and; 79 MHz for ^{29}Si. Data was manipulated directly from the spectrometer or via a networked PC with appropriate software. Reference values for residual solvent were taken as $\boldsymbol{\delta}$=7.26 ($CDCl_3$) for ^1H NMR; $\boldsymbol{\delta}$=77.00 ($CDCl_3$) for ^{13}C NMR; $\boldsymbol{\delta}$=7.16 (C_6D_6) for ^1H NMR; $\boldsymbol{\delta}$=128.06 (C_6D_6) for ^{13}C NMR. ^{31}P-NMR shifts are reported relative to phosphoric acid at 0.0 ppm. ^{29}Si-NMR shifts are proton decoupled and reported relative to tetramethylsilane at 0.0 ppm. NMR-yields were calculated relative to one equivalent of 1,1,2,2-tetrachloroethane as an internal standard where appropriate; ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (s, 2H). Multiplicities for coupled signals are designated using the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, sex=sextet, br=broad signal and ap=apparent. The coupling constants are reported in Hertz. High-resolution mass spectrometry data were quoted to four decimal places (0.1 mDa) with error limits for acceptance of ±5.0 ppm (defined as calcd/found mass 10^{-6}). Mass spectra were acquired on a VG micromass 70E, VG autospec or micromass LCTOF. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR instrument as dilute chloroform solutions. Melting points were recorded on a Stuart manual melting point apparatus.

2.1 Base-Catalysed Silyl Ester Formation

The formation of silyl esters from phenylsilane and carboxylic acids is a base-catalysed procedure.[1] *The following supporting experiments demonstrate this reactivity.*

Rudimentary hydrogen gas volume measuring experiments were performed by connecting a stirring sealed flask containing the reagents to an upturned water-filled measuring cylinder in a reservoir containing water, which was displaced upon gas evolution. The volume of gas collected was read off the cylinder. The tube connecting the flask to the cylinder was packed with calcium chloride to hinder the passage of water vapour back up the tube. The volume of 1 mole of hydrogen was approximated as 23 dm^3. The identity of the gas was confirmed as hydrogen by observing the characteristic combustion of a lit splint in the presence of the gas and the resulting water condensation on the walls of the vessel as well as its ^{1}H-NMR shift of 4.57 ppm in d3-MeCN.

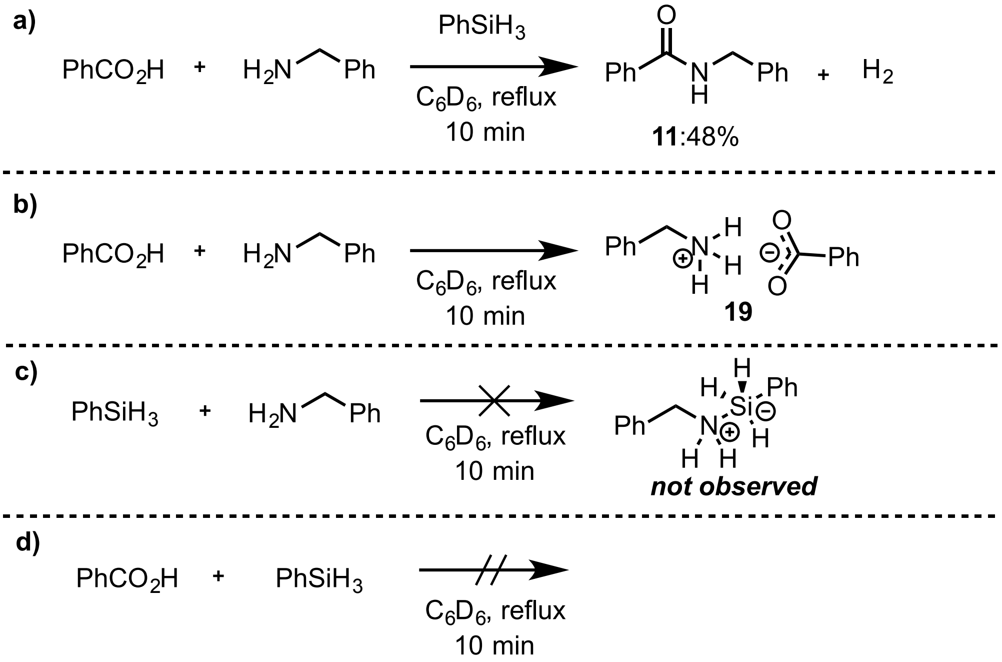
2.10 The base-catalysed dehydrogenative coupling reaction of carboxylic acid and phenylsilane leads to species able to mediate amidation



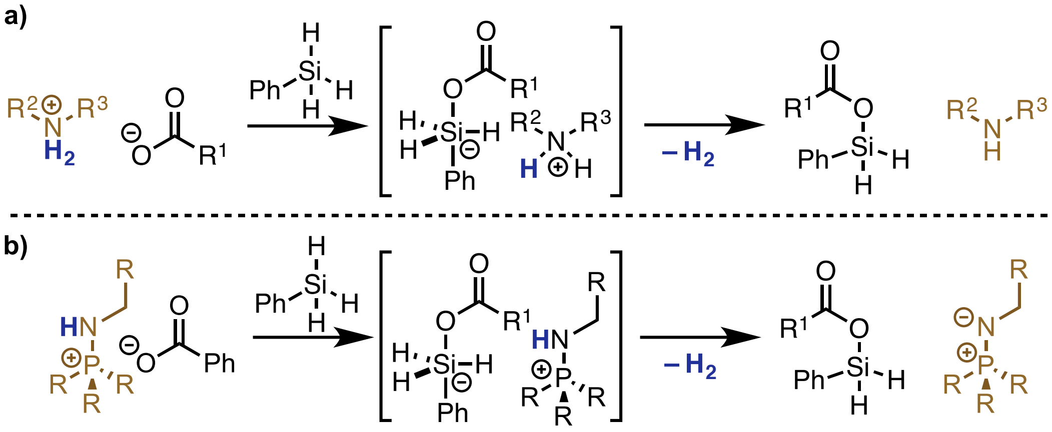
MeCN-D_3 was filtered through magnesium sulfate into a dry flask under argon and acetic acid (9.1 µL, 0.16 mmol) and 2,2,6,6-tetramethylpiperidine (2.2 µL, 0.016 mmol) were added and the reaction mixture was stirred at room temperature. Phenylsilane (19.7 µL, 0.160 mmol) was then added and the flask sealed immediately with an adaptor as described above. The volume of displaced water was measured over 21 h, with 3.7 cm^3 gas approximately equivalent to 1 equivalent of hydrogen. One equivalent of hydrogen was released within 30 min, corresponding to the complete formation of silyl esters. Due to adventitious water, 2.5 equivalents had been collected after 21 hr. Benzylamine (17.5 µL, 0.160 mmol) was then added and the reaction stirred at r.t. for 1 h. ^{1}H-NMR showed 42% yield of *N*-benzylacetamide relative to TCE as internal standard.

2.11 A base-catalyst is required for the generation of silyl esters

Benzoic acid, benzylamine and phenylsilane (0.38 mmol scale) were combined stoichiometrically in all permutations in C_6D_6 (0.63 mL) and refluxed for 10 minutes. After this time, the solutions were transferred to a dry NMR tube and the ^{1}H-NMR spectrum recorded. For ***a***, 48% amide was observed (relative to amine). For ***b***, only the ammonium carboxylate salt was observed. For ***c***, no species were observed at all, and both phenylsilane and benzylamine remained unreacted. For ***d***, no new species were observed either.



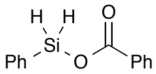
2.12 Proposed reactivity of basic iminophosphoranes is analogous to demonstrated role of basic amine: an aminophosphonium carboxylate acts like an ammonium carboxylate



2.2 Generation and Characterisation of Iminophosphorane 1 and Silyl Ester 8

The following reactions were conducted in oven-dried 5 mL flasks under an argon balloon, and fitted with a water condenser when heating is used.

Phenylsilyl benzoate (8)

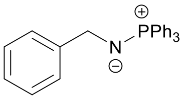


Chloro(phenyl)silane (21.3 µL, 0.160 mmol) was added to a refluxing suspension/solution of potassium benzoate (25.6 mg, 0.160 mmol) in C_6D_6 (0.5 mL) for 30-60 min. The solution, containing solid potassium chloride, was used without further manipulation (filtration leads to hydrolysis of the sensitive silyl ester species). The major species was assigned as phenylsilylbenzoate with the following signals selected from the NMR spectra:

^{1}H NMR (400MHz, C_6D_6) δ ppm 8.07 - 8.03 (m, 2H), 7.73 - 7.67 (m, 2H), 7.13 - 7.04 (m, 4H), 6.99 - 6.94 (m, 2H), 5.36 (SiH_2, s, 2H); **^{13}C NMR** (101 MHz, C_6D_6) 167.3, 135.8, 133.4, 131.3, 130.7, 130.6, 130.5, 128.6, 128.5; **^{29}Si NMR** (79 MHz, C_6D_6) δ −19.9.

1,3-diphenyldisiloxane, formed from the reaction of adventitious water, was also present, typically up to 15%.

N-benzyl-1,1,1-triphenyl-λ^5-phosphanimine (iominophosphorane/ylide)[3] (1)

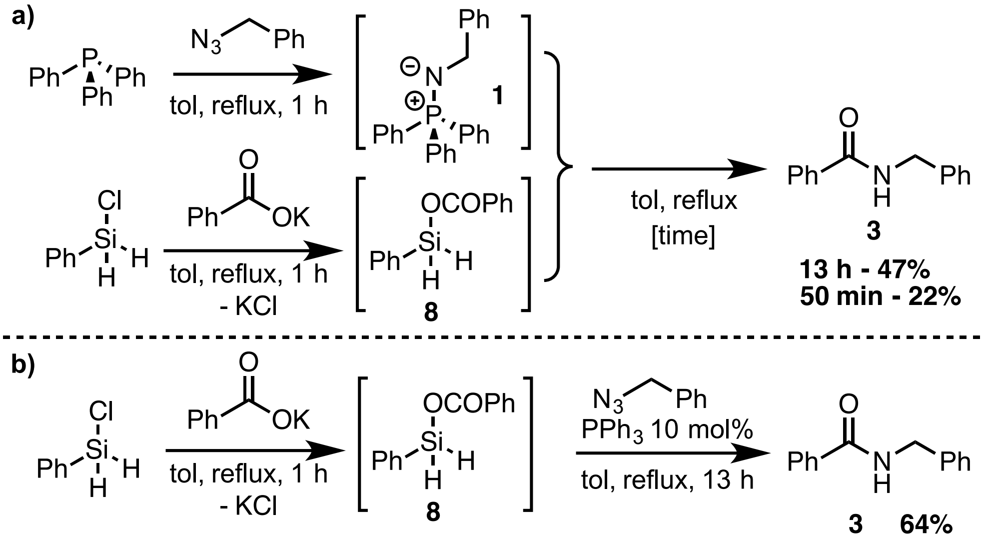


Commercial benzyl azide (Alfa-Aesar, 94%) (12.5 µL, 0.100 mmol) was added to a solution of triphenylphosphine (0.100 mmol, 26.2 mg) in C_6D_6 (0.5 mL) and the reaction refluxed for 1 h. The ^{31}P-NMR spectrum of the solution indicated a 1:87:11 ratio (by integration) of phosphine oxide(25.0 ppm): iminophosphorane(6.0 ppm):phosphine(-5.2 ppm). The solution was used in further transformations without further manipulation.

^{1}H NMR (400 MHz, C_6D_6) δ 7.90 - 7.81 (m, 2H), 7.81 - 7.68 (m, 6H), 7.43 - 7.36 (m, 1H), 7.36 - 7.29 (m, 2H), 7.08 - 7.00 (m, 9H), 4.71 (d, *J*= 15.2 Hz, 2H); **^{31}P NMR** (162 MHz, C_6D_6) δ 6.0.

2.3 Deconstructed Staudinger Ligation NMR Experiments

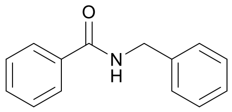
2.31 Amide formation *via* independent preformation of iminophosphorane (1) and silyl ester (8)



Stoichiometric (a): The iminophosphorane (ylide) was preformed by stirring benzyl azide (22.0 μL, 0.176 mmol) in toluene (0.5 mL) at reflux for 1 h in the presence of triphenylphosphine (40.0 mg, 0.153 mmol). Phenylsilylbenzoate **8** was preformed as described above, in toluene (0.5 mL), with 0.153 mmol of each component. The solution of iminophosphorane was then added to the silyl ester and the reaction stirred at toluene reflux for 13 h. After this time, the reaction was cooled, quenched with methanol and concentrated *in vacuo*. The yield of amide was determined to be 47% amide by ^{1}H-NMR by comparison to tetrachloroethane as an internal standard. When the reaction was run for 50 min, 22% amide was observed by ^{1}H-NMR, and ^{31}P-NMR showed 98% phosphine and 2% phosphine oxide.

Catalytic (b) (SCHEME 4C in manuscript)**:** The silyl ester **8** (0.153 mmol) was preformed as described above, in toluene (1.0 mL). Triphenylphosphine (4.0 mg, 10 mol%) was added, and allowed to dissolve before adding the benzyl azide (22.0 μL, 0.176 mmol). The reaction stirred at reflux for 13 h. After this time, the reaction was cooled, quenched with methanol and concentrated *in vacuo*. The yield of amide was determined to be 64% amide by comparison to 1,1,2,2-tetrachloroethane as an internal standard.

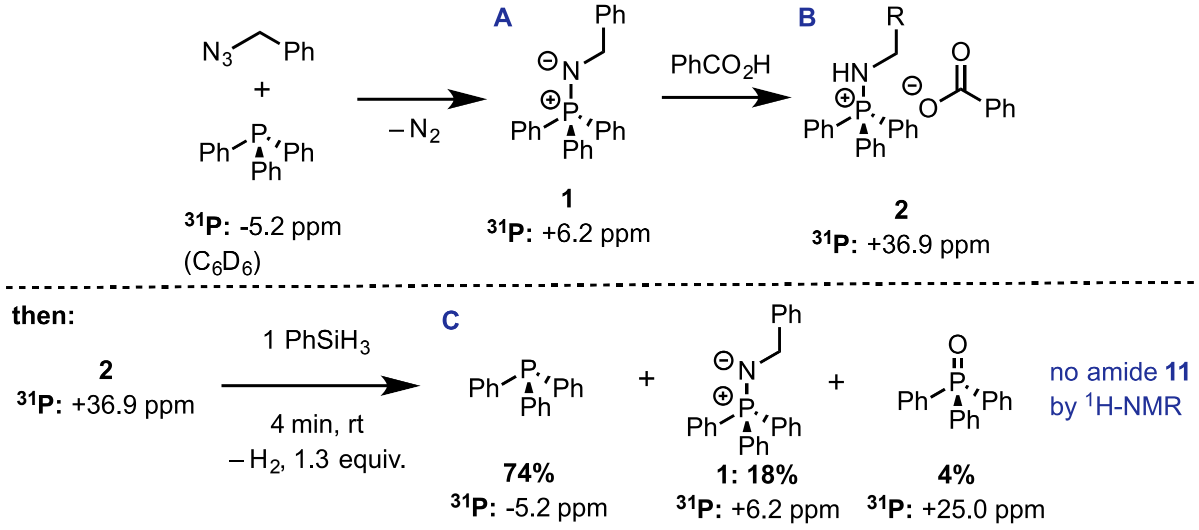
N-benzylbenzamide[2] (3)



The amide product was isolated and characterised as follows; the solvent was concentrated and the residue taken up in ethyl acetate, washed once with each aqueous HCl (1 M), saturated aqueous sodium carbonate and brine. The organics were dried over magnesium sulfate, concentrated, and purified by flash column chromatography (8-20% EtOAc in petrol) to give a white solid, consistent with literature data.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.73 (m, 2H), 7.53 - 7.46 (m, 1H), 7.46 - 7.39 (m, 2H), 7.37 - 7.27 (m, 5H), 6.69 - 6.29 (m, 1H), 4.64 (d, *J*= 5.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 138.2, 134.3, 131.5, 128.7, 128.6, 127.9, 127.6, 126.9, 44.1; **HRMS** (ESI+): Exact mass calcd for $C_{14}H_{13}NNaO$ [M+Na], 234.0889. Found 234.0893, σ = 0.0087; **IR** (cm^{-1}) ($CDCl_3$) 3452, 3011, 1658, 1519, 1487; **Mp** 101-102 ºC (lit.[3] 100-101 ºC).

2.32 Phenylsilane rapidly reduces the aminophosphonium carboxylate (Scheme 3 in manuscript)



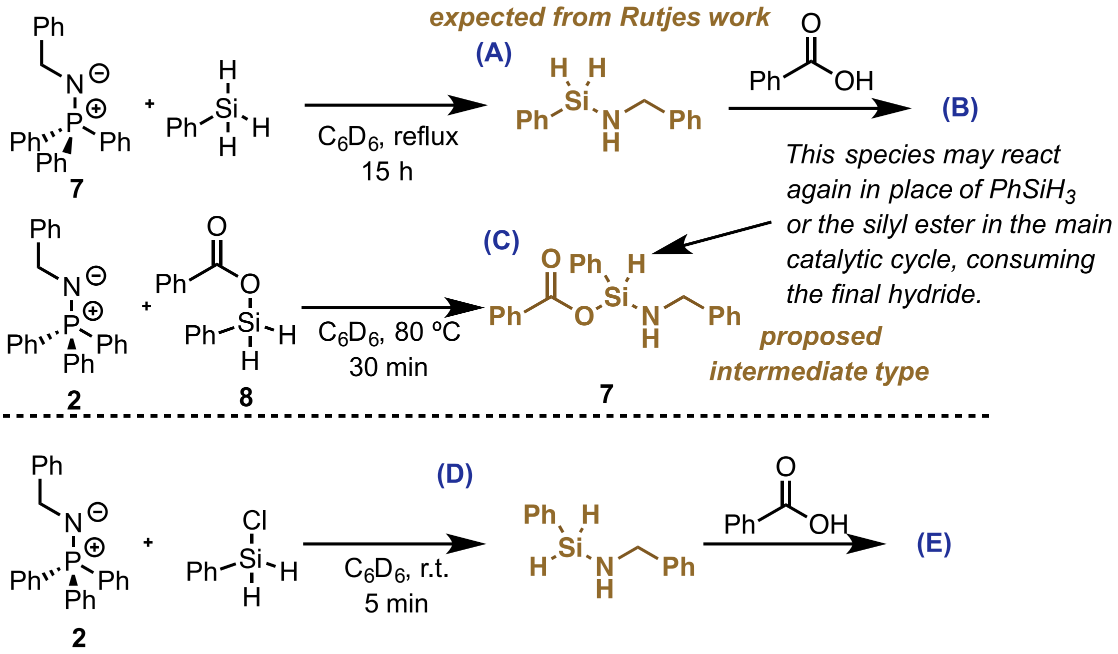
In all cases, the components were prepared as above (0.38 mmol scale), and combined in oven-dried flasks (5 mL) in C_6D_6 (0.63 mL) under an argon atmosphere.

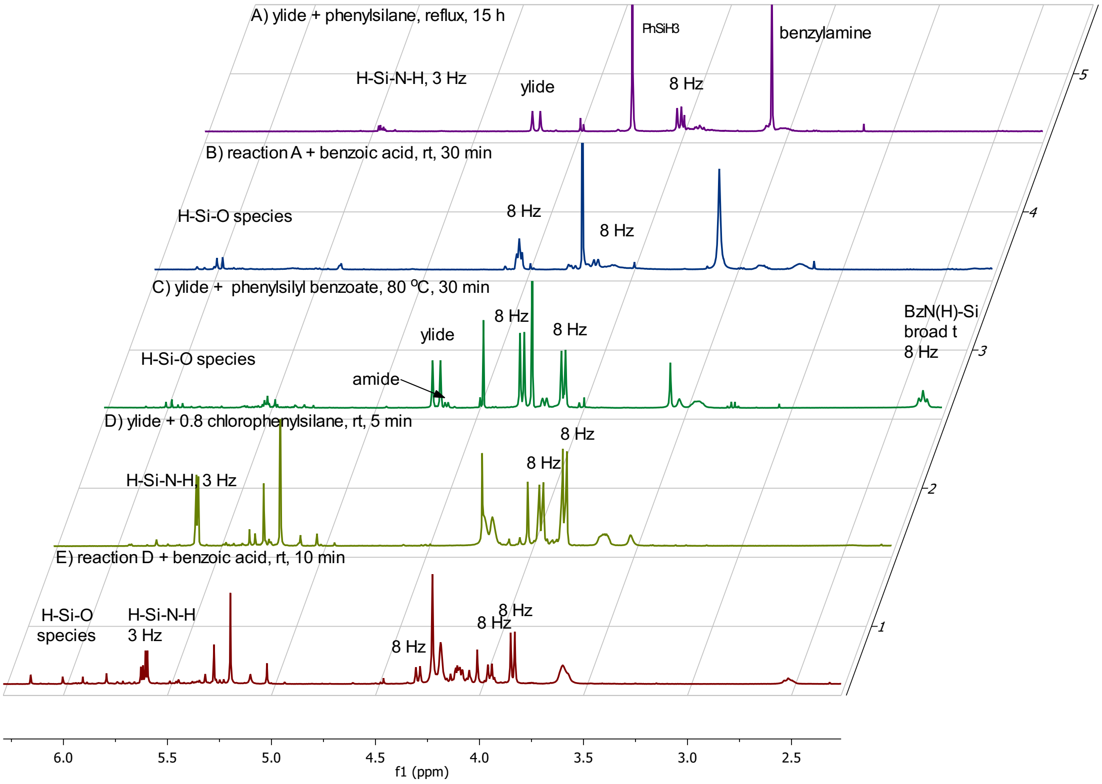
The iminophosphorane of benzyl azide (**1**) and triphenylphosphine was formed as described above (^{31}P-NMR, δ +6.2 ppm). Added was benzoic acid (1 equivalent) and the solution in C_6D_6 was cooled to room temperature once the benzoic acid had dissolved. At this point, ^{31}P NMR showed the aminophosphonium carboxylate complex **2** (^{31}P-NMR, δ +36.9 ppm). Addition of phenylsilane (1 equivalent) at room temperature was accompanied by 1.3 equivalents of hydrogen gas evolution within 4 min, measured as described above. At this point, ^{31}P-NMR showed oxide:iminophosphorane:phosphine (7:18:74) (δ 25.0 : 6.8 : -5.2 ppm). No amide or the known monobenzoxysilyl ester was observed. After standing at room temperature overnight in the NMR tube, the ^{1}H-NMR of the sample showed 53% amide **3** and 47% benzylamine.

2.33 Thermal amidation (Scheme 2 in manuscript)

Preformed iminophosphorane **1** and benzoic acid were combined stoichiometrically (0.38 mmol scale) in toluene (0.63 mL). NMR analysis demonstrated formation of aminophosphonium carboxylate **2**. The reaction was refluxed over 20 h, taking aliquots for NMR at 4 stages and mixing with enough C_6D_6 for solvent locking. The spectra are shown in SCHEME 2 in the main text, and demonstrate the formation of amide and phosphine oxide over 20 h; 81% amide was formed after 20 h (with losses due to hydrolysis.)

2.34 Orthogonal formation of mixed silanamines and acyloxysilanamines





(A) Preformed iminophosphorane **1** and phenylsilane were combined stoichiometrically (0.38 mmol scale) in C_6D_6 (0.63 mL) in a 5 mL flask and heated at reflux for 15 h. After this time, a ^{1}H-NMR spectrum was recorded. Some iminophosphorane remained, and some benzylamine was also present. A species with 8 Hz (silanamine) was also visible at ~4 ppm. These data are in agreement with the catalytic Staudinger reduction reaction described by

Rutjes and co-workers.[4] Added to this mixture was benzoic acid, and the reaction stirred at rt for 30 min. Another NMR spectrum was recorded, which showed two new 8 Hz doublets had formed with higher shifts, likely mixed species of type **7**. (B)

(C) Preformed iminophosphorane **1** and preformed silyl ester **8** were combined stoichiometrically (0.38 mmol scale) in C_6D_6 (0.63 mL) in an NMR tube, and a ^{1}H-NMR recorded after 30 min at 80 °C. Several 8 Hz doublets are visible.

(D) Preformed iminophosphorane **1** and chlorophenylsilane were combined stoichiometrically (0.38 mmol scale) in C_6D_6 (0.63 mL) in an NMR tube, and a ^{1}H-NMR recorded. This time the silyl hydrides are visible as 3 Hz doublets. Benzoic acid was added at room temperature and an NMR recorded after 10 min (E) generating further species.

All the 8 Hz species formed are various benzylaminosilicon species. Note that, in the reaction mixture, the ammonium carboxylate salt **2** may react with the acyloxysilanamine species (e.g. of type **7**) rather than with a silyl ester, which will expend the final hydride and generate a range of species of type **7**.

2.4 Supporting Information from the Literature

2.41 Comparison of literature assignments supporting the current assignments

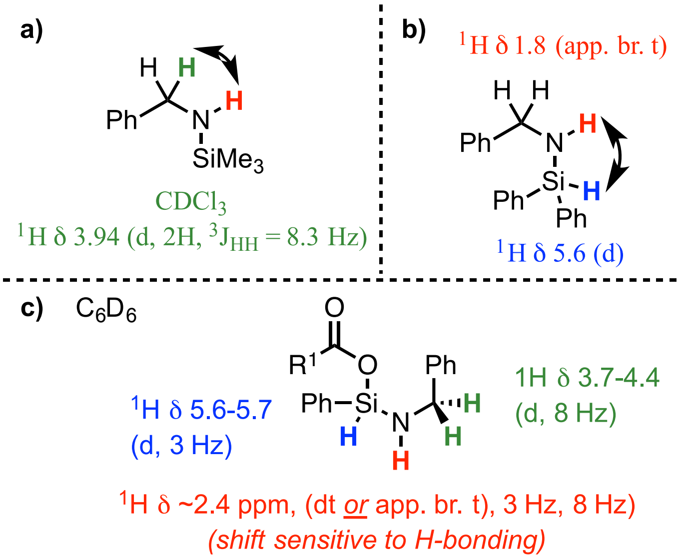
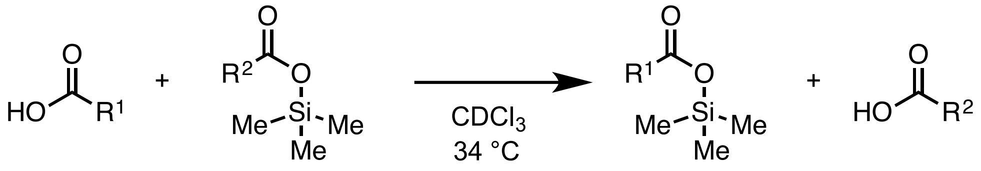


Figure S1: (a) and (b) Literature shifts for known compounds; (c) Some NMR shifts and J values for typical species proposed to be acyloxysilanamines.[5,6]

2.42 Literature examples of silyl ester and silanamine exchange[7–10]

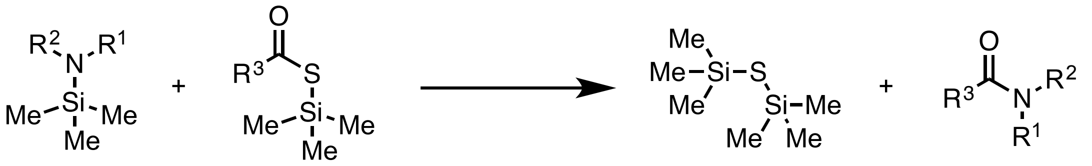
The final acyloxysilanamine species of type **7** may undergo various exchange reactions under the thermal/acidic conditions. Some known examples are shown below.

a) Kozuka: Rates measured for exchange by monitoring ^{1}H-NMR Me signal

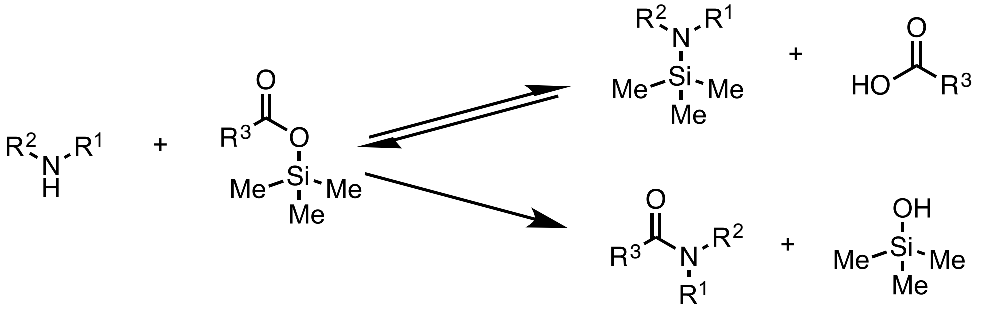


base-catalysis accelerates rate of exchange (> x 700 for acetoxy to chloroacetoxy)

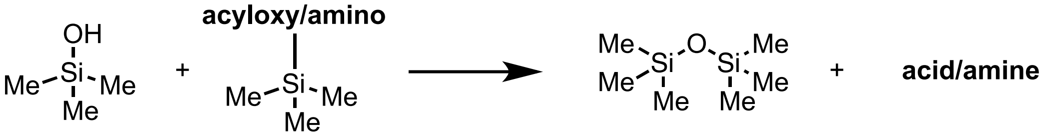
b) Rühlmann: Bimolecular exchange reactions of thioesters and silanamines



c) Rühlmann: Amidation and exchange reactions of silyl esters and silanamines



d) Rühlmann: Silanol or water degradation of sensitive amino/acyloxysilanes



3. Computational Details

Calculations were performed using Spartan ’10[11] (PC version) using the B3LYP/6-31G* theoretical model in the gas phase. Stationary points were characterised by frequency calculations. Structures **4** and **5** (minima) had no imaginary frequency. Structure TS **6** (transition structure) has a single imaginary frequency. The energies reported in Scheme 2C of the manuscript are relative electronic energies with zero point energy correction. Coordinates are given below.

4

P	-0.051027	-0.205653	-0.417022
C	1.138439	-1.582887	-0.082733
C	2.968772	-3.679105	0.309657
C	0.881604	-2.859858	-0.601206
C	2.323735	-1.369593	0.636915
C	3.237878	-2.405752	0.815869
C	1.785567	-3.904079	-0.391475
C	0.673862	1.474204	-0.615543
C	1.811779	3.983880	-1.149563
C	1.974987	1.572267	-1.135912
C	-0.058057	2.644761	-0.385117
C	0.510169	3.890630	-0.659491
C	2.545269	2.819530	-1.385544
C	-1.863020	-0.435798	-0.132080
C	-4.613564	-0.880135	0.245581
C	-2.538946	-1.421174	-0.872988
C	-2.584865	0.327327	0.797054
C	-3.953267	0.113647	0.967901
C	-3.899886	-1.650803	-0.672164
O	0.177265	0.043285	1.591519
C	0.074935	0.985632	2.496751
O	-0.610341	2.005724	2.421797
N	-0.121457	-0.624698	-2.137656
C	-0.772629	0.261758	-3.103808
H	-1.815194	0.422159	-2.814428
H	-0.774826	-0.219854	-4.088356
H	-0.291954	1.246963	-3.200875
H	0.793870	-0.911726	-2.472829
H	-1.058306	2.593955	0.023201
H	2.552634	0.676136	-1.346112
H	-0.070080	4.790708	-0.476091
H	2.251809	4.956900	-1.350924
H	3.559615	2.878672	-1.771278
H	2.522572	-0.395199	1.064466
H	4.156188	-2.219329	1.366296
H	3.675796	-4.489669	0.464736
H	1.560636	-4.892119	-0.784046
C	0.910654	0.696474	3.740865
H	1.977574	0.757833	3.494521
H	0.682341	1.420427	4.525643
H	0.718823	-0.320652	4.097170
H	-1.999570	-1.994346	-1.616538
H	-4.400665	-2.428898	-1.242104
H	-2.083324	1.083291	1.392033
H	-4.499026	0.724155	1.682312
H	-5.676313	-1.052637	0.395346
H	-0.022883	-3.046714	-1.167567

5

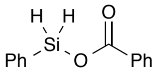
P	-0.027144	-0.016225	-0.588734
C	-0.817777	-1.428078	0.286905
C	-1.958516	-3.662516	1.535804
C	-1.091346	-2.588629	-0.450371
C	-1.127949	-1.389779	1.651602
C	-1.691929	-2.506702	2.270509
C	-1.661634	-3.699851	0.172031
H	-0.855751	-2.624930	-1.510518
H	-0.964478	-0.483733	2.221787
H	-1.932899	-2.465552	3.329314
H	-1.872802	-4.593470	-0.409583
H	-2.400755	-4.528346	2.021486
C	0.227968	1.577609	0.313195
C	0.740407	4.015719	1.604989
C	-0.122908	2.790519	-0.293195
C	0.860668	1.600520	1.563334
C	1.092342	2.811395	2.215631
C	0.144103	4.002304	0.343492
H	-0.616277	2.785773	-1.259139
H	1.182495	0.675213	2.030978
H	1.562241	2.812546	3.195580
H	-0.126310	4.936069	-0.142733
H	0.934304	4.959680	2.107413
C	1.800075	-0.586259	-0.346129
C	4.524197	-1.323921	-0.119459
C	2.831033	0.271077	-0.777874
C	2.174640	-1.820595	0.204466
C	3.520593	-2.184219	0.320781
C	4.173591	-0.090390	-0.673181
H	2.581308	1.245407	-1.191755
H	1.417507	-2.514456	0.552374
H	3.779133	-3.146875	0.754996
H	4.945651	0.594159	-1.016088
H	5.569657	-1.607674	-0.030093
N	0.170786	-0.120665	-2.259755
H	1.095635	-0.431540	-2.518298
C	-0.740782	0.106317	-3.384413
H	-1.074410	1.145260	-3.443551
H	-1.625276	-0.531949	-3.329594
H	-0.189132	-0.134660	-4.299594
O	-1.796028	0.563725	-1.066434
C	-2.750916	0.936210	-0.224465
O	-2.630928	1.050489	0.985529
C	-4.064133	1.213073	-0.943553
H	-3.912180	1.933528	-1.754403
H	-4.800473	1.598189	-0.235905
H	-4.440248	0.288864	-1.396728

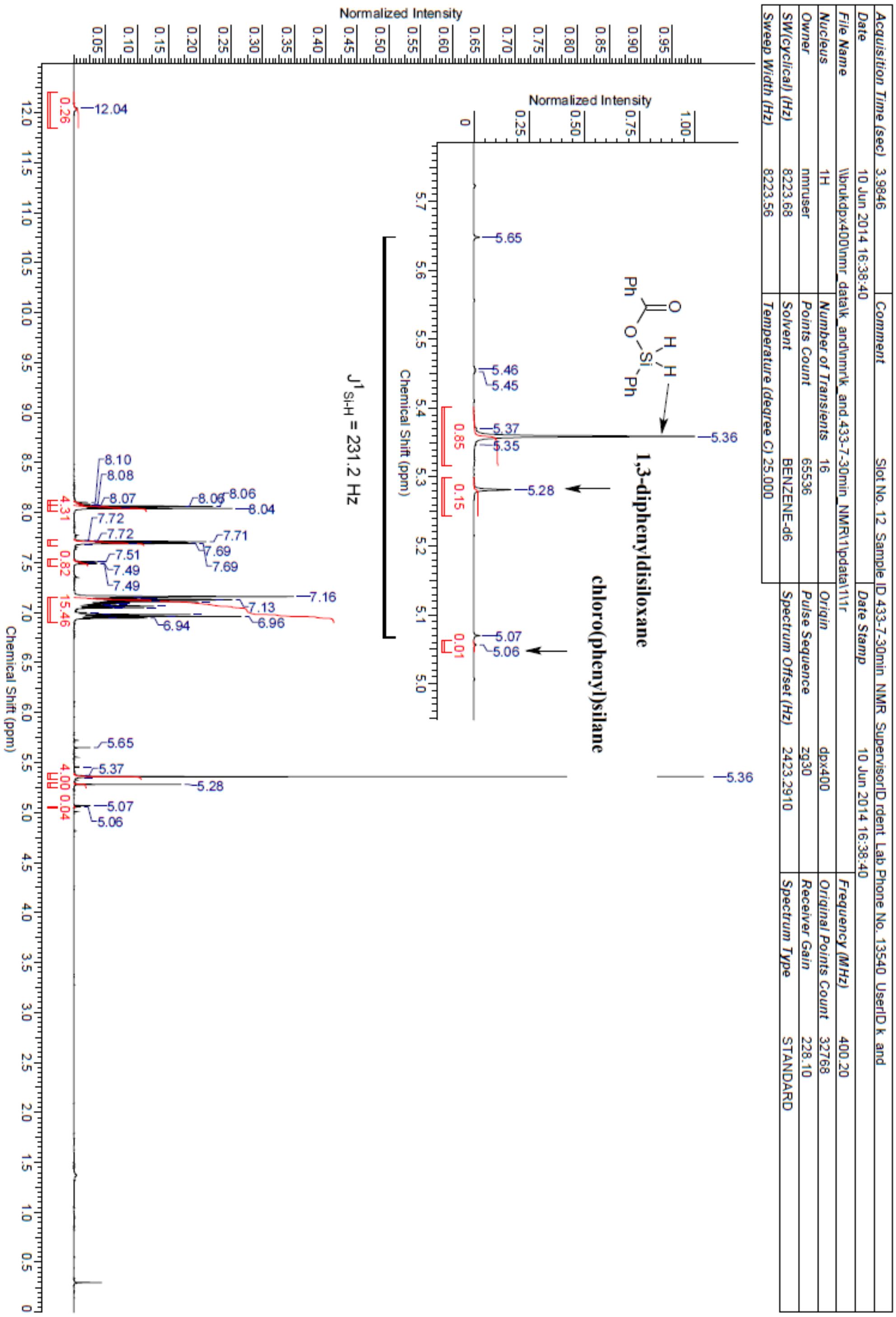
TS 6

P	0.077343	0.315117	0.230199
O	-0.044071	0.855779	1.786657
O	-1.048802	2.902360	2.026938
N	0.606276	2.169562	-0.081142
C	1.268874	2.724241	2.661182
C	1.905740	2.672415	-0.512762
C	-0.001905	2.293807	1.970288
H	1.380925	3.807734	2.579244
H	1.970720	3.747343	-0.293126
H	1.175868	2.468401	3.724295
H	2.152521	2.222673	2.265364
H	2.111048	2.538821	-1.585875
H	2.710760	2.173435	0.033974
H	-0.126694	2.671522	-0.576577
C	1.668017	-0.294719	-0.476904
C	4.143826	-1.187788	-1.445587
C	2.594042	-0.893882	0.388321
C	1.993929	-0.146391	-1.831241
C	3.220205	-0.605299	-2.315341
C	3.831318	-1.324986	-0.091912
H	2.340667	-1.038400	1.434926
H	1.291419	0.329987	-2.508618
H	3.456554	-0.498161	-3.370600
H	4.544667	-1.779982	0.589869
H	5.102211	-1.535141	-1.821978
C	-1.340315	0.515024	-0.942323
C	-3.566930	0.780666	-2.629510
C	-2.355860	1.436060	-0.635206
C	-1.461851	-0.283318	-2.088590
C	-2.562028	-0.138830	-2.934341
C	-3.464504	1.557280	-1.474839
H	-2.288848	2.044060	0.264402
H	-0.709159	-1.030971	-2.318344
H	-2.638391	-0.756581	-3.825366
H	-4.250145	2.263879	-1.220424
H	-4.428627	0.883909	-3.283462
C	-0.530007	-1.402667	0.839682
C	-1.639710	-3.895325	1.597757
C	-0.159857	-2.593839	0.193598
C	-1.481734	-1.494298	1.871414
C	-2.027957	-2.721977	2.246994
C	-0.704083	-3.825515	0.566247
H	0.571208	-2.576886	-0.609151
H	-1.792200	-0.595256	2.391868
H	-2.757778	-2.760629	3.052318
H	-0.390313	-4.729942	0.050116
H	-2.062765	-4.852576	1.891827

4. NMR spectra

^{1}H NMR (400 MHz, C_6D_6): **Phenylsilyl benzoate (18)** (formed *in situ*, major species)

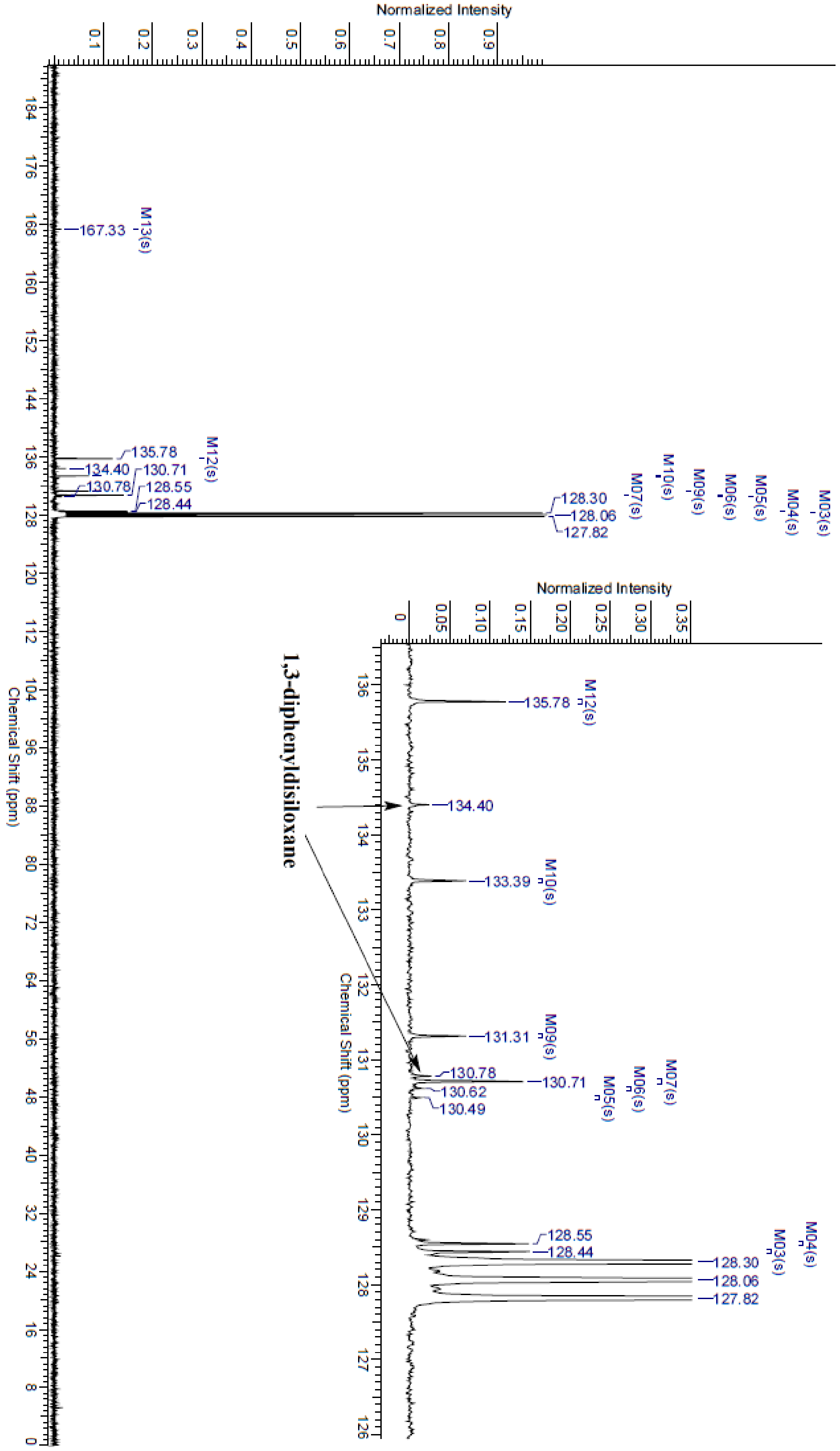




Acquisition Time (sec)	3.9846	*Comment*	Slot No. 12 Sample ID 433-7-30min NMR SupervisorID rdent Lab Phone No. 13540 UserID k and				
Date	10 Jun 2014 16:38:40			*Date Stamp*	10 Jun 2014 16:38:40		
File Name	\\brukdpx400\nmr_data\k and\nmr\k and.433-7-30min_NMR\1\pdata\1\1r					*Frequency (MHz)*	400.20
Nucleus	1H	*Number of Transients*	16	*Origin*	dpx400	*Original Points Count*	32768
Owner	nmruser	*Points Count*	65536	*Pulse Sequence*	zg30	*Receiver Gain*	228.10
SW(cyclical) (Hz)	8223.68	*Solvent*	BENZENE-d6	*Spectrum Offset (Hz)*	2423.2910	*Spectrum Type*	STANDARD
Sweep Width (Hz)	8223.56	*Temperature (degree C)*	25.000				

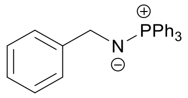
^{13}**C NMR** (101 MHz, C_6D_6): **Phenylsilyl benzoate (18)** (formed *in situ*, major species)

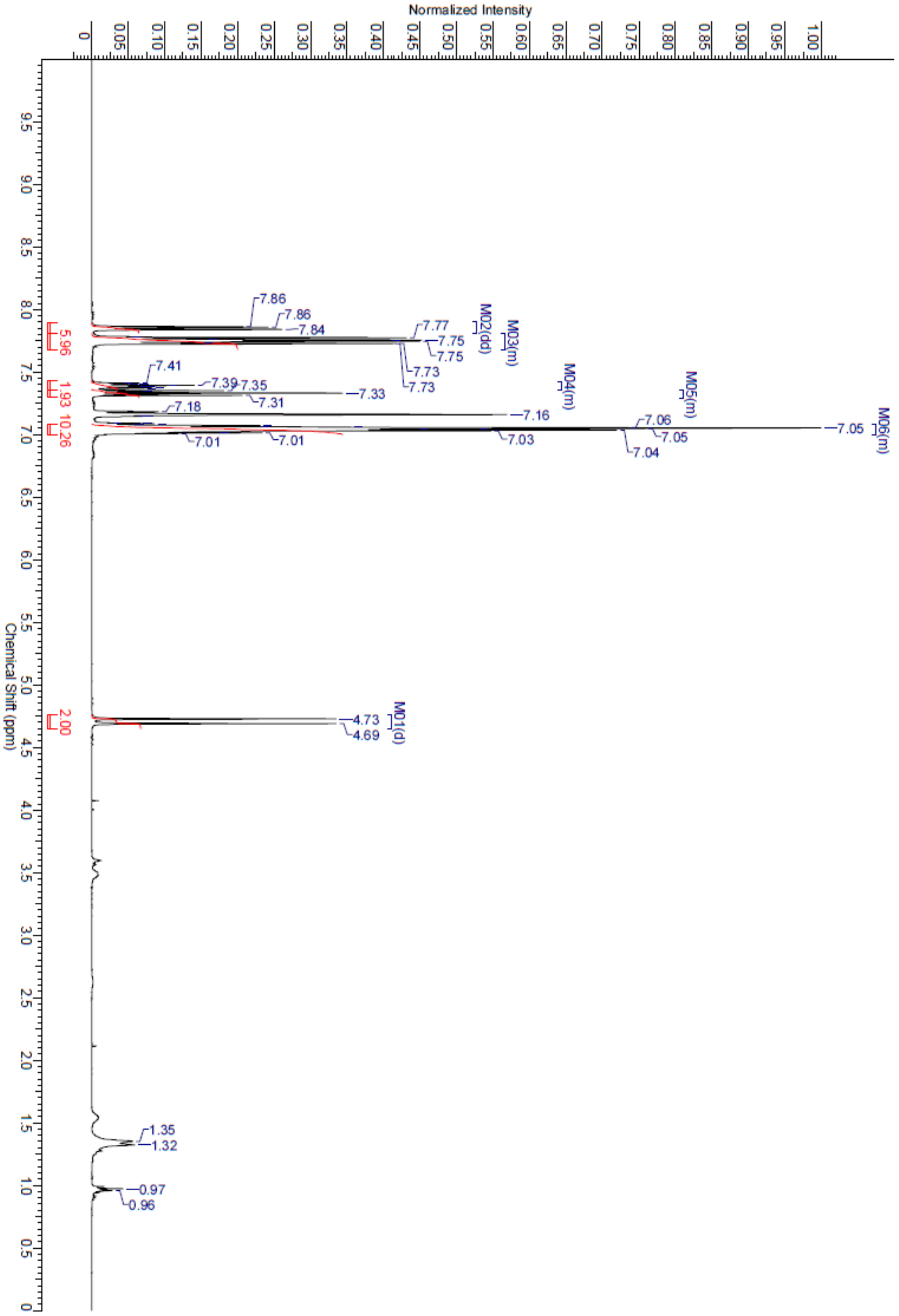
Acquisition Time (sec)	0.6521	*Comment*	Slot No. 12 Sample ID 433-7-30min NMR C SupervisorID rdent Lab Phone No. 13540 UserID k and				
Date	10 Jun 2014 17:17:04			*Date Stamp*	10 Jun 2014 17:17:04		
File Name	\\brukdpx400\nmr_data\k_and\nmr\k_and.433-7-30min_NMR_C\1\pdata\1\1r					*Frequency (MHz)*	100.63
Nucleus	13C	*Number of Transients*	128	*Origin*	dpx400	*Original Points Count*	16384
Owner	nmruser	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	14596.50
SW(cyclical) (Hz)	25125.63	*Solvent*	BENZENE-d6	*Spectrum Offset (Hz)*	11094.3926	*Spectrum Type*	STANDARD
Sweep Width (Hz)	25124.86	*Temperature (degree C)*	25.100				



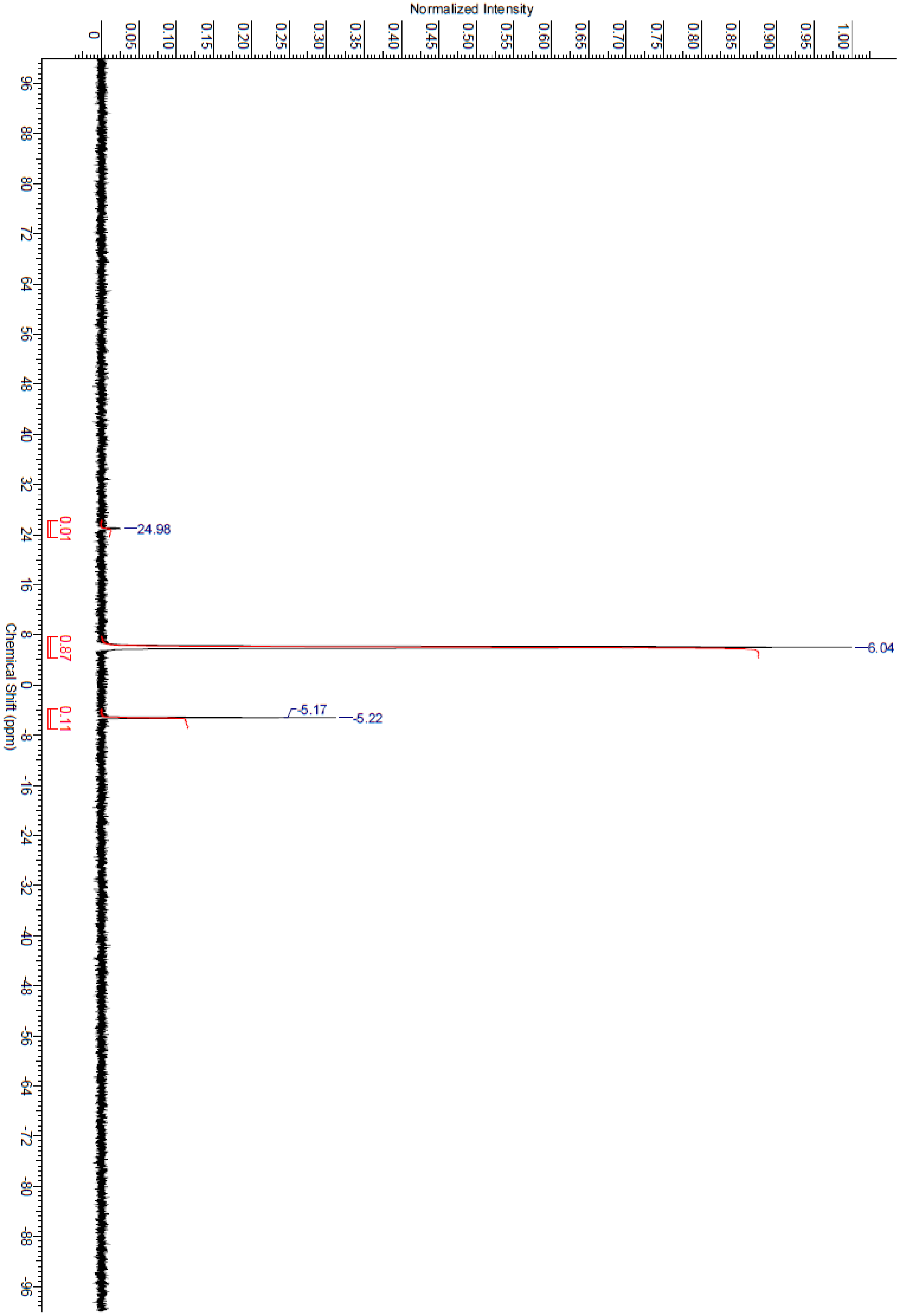
^{1}H NMR (400 MHz, C_6D_6): ***N*-benzyl-1,1,1-triphenyl-λ^5-phosphanimine (ylide) (7)**

(formed *in situ*: contains traces of triphenylphosphine oxide and triphenylphosphine (slight excess used in formation of iminophosphorane.))

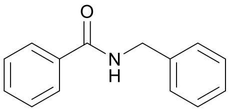


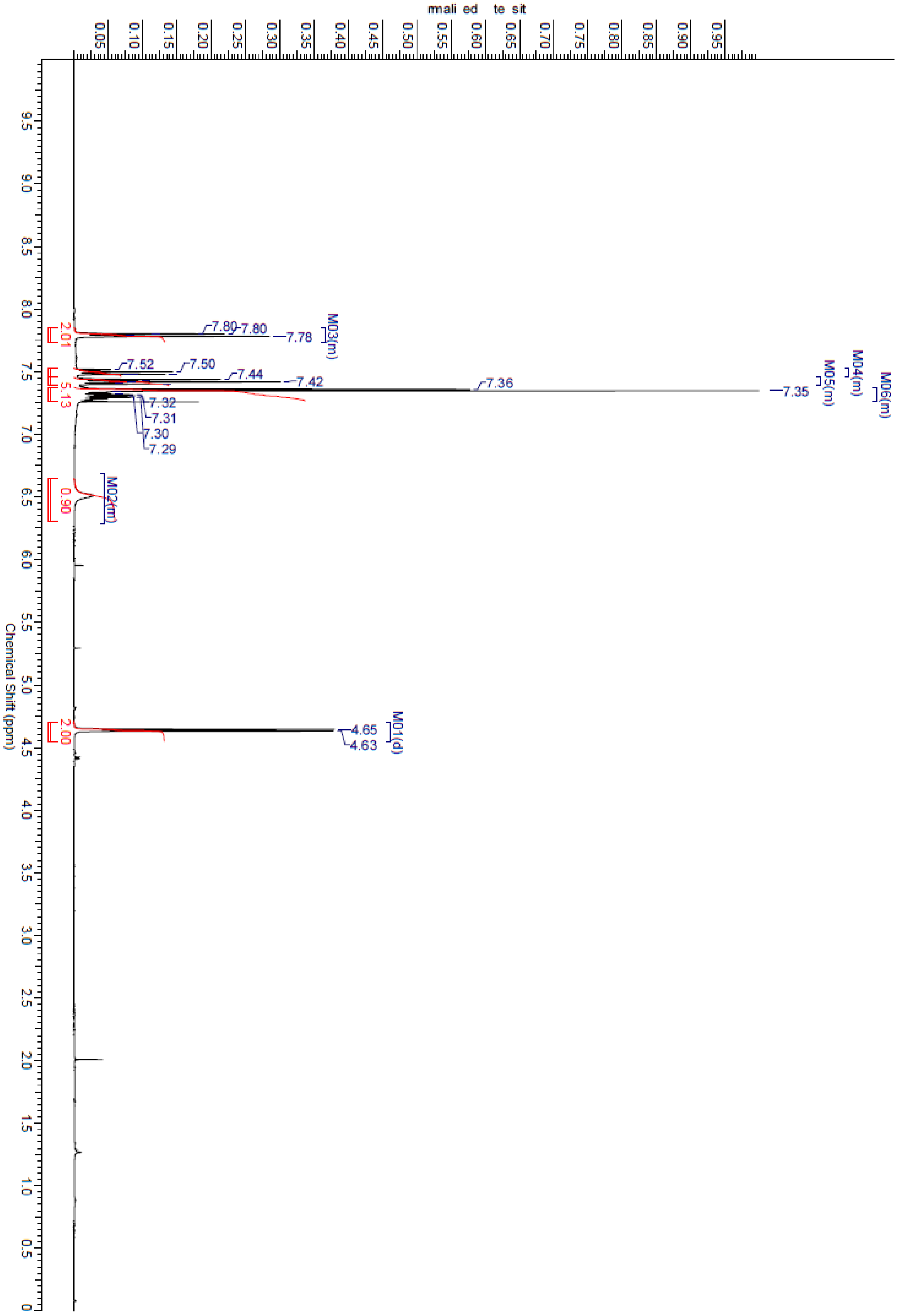


^{31}**P NMR** (162 MHz, C_6D_6): ***N*-benzyl-1,1,1-triphenyl-λ^5-phosphanimine (ylide) (7)**

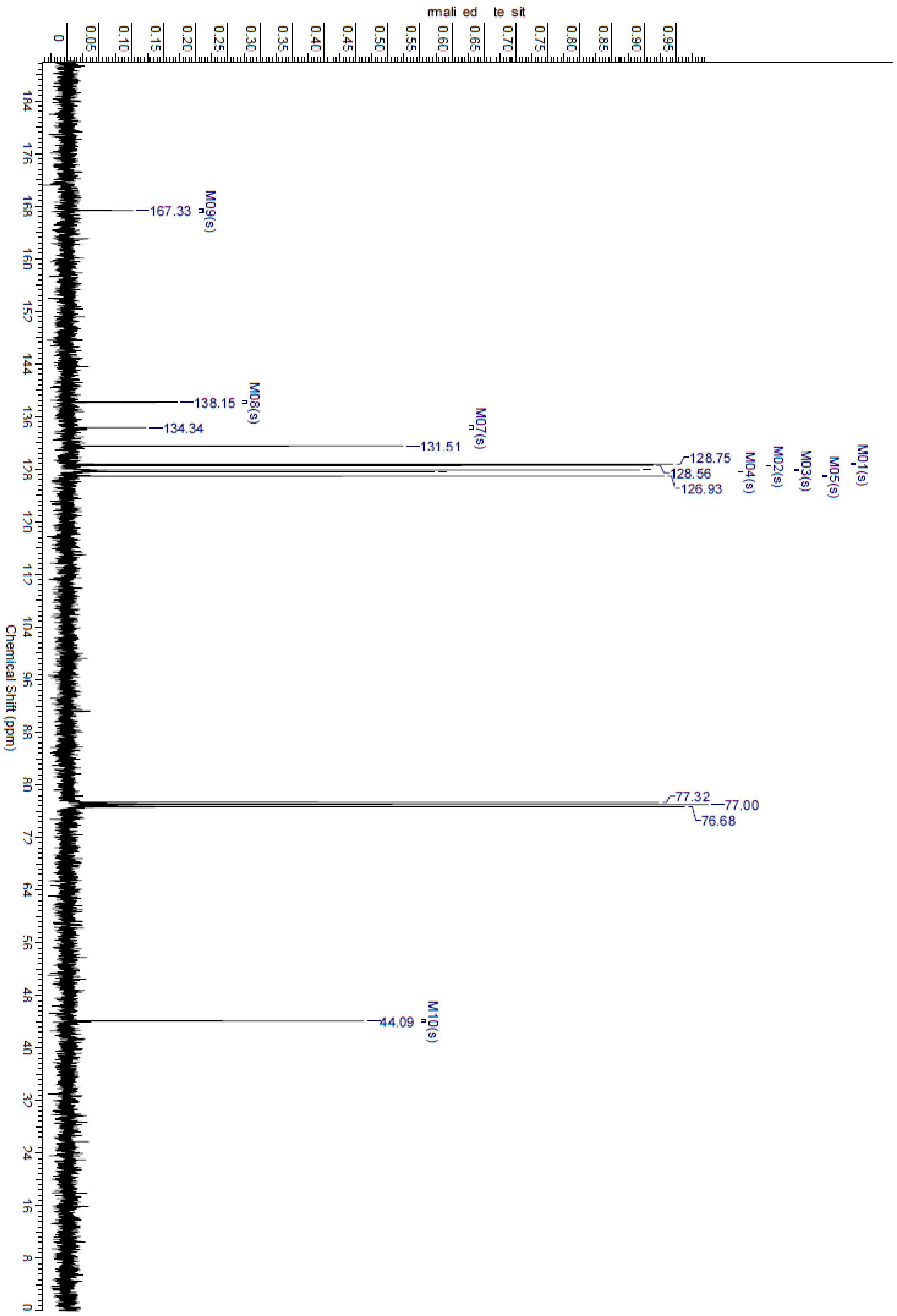


^{1}H NMR (400 MHz, CDCl$_3$): *N*-benzylbenzamide (11)





^{13}**C NMR** (101 MHz, CDCl$_3$): ***N*-benzylbenzamide (11)**



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