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Supplementary Information

Disilanes as Oxygen Scavengers and Surrogates of Hydrosilanes Suitable for Selective Reduction of Nitroarenes, Phosphine Oxides and other Valuable Substrates

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General considerations

Commercially available starting materials, reagents, catalysts and anhydrous and degassed solvents were used without further purification. Flash column chromatography was performed with Merck silica gel 60 (230-400 mesh). The solvents for column chromatography were distilled before use. Thin layer chromatography was carried out using Merck TLC Silica gel 60 F₂₅₄ and visualized by short-wavelength ultraviolet light or by treatment with potassium permanganate (KMnO₄) stain. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker 250 and 500 MHz at 20°C. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for CHCl₃ (7.26 ppm) and DMSO (2.50 ppm). All ¹³C NMR spectra were reported in ppm relative to residual CHCl₃ (77.00 ppm) or DMSO (39.70 ppm) and were obtained with ¹H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). Gas chromatographic analyses was performed on Gas Chromatograph Mass Spectrometer GCMS-QP2010 Ultra instrument.

Optimization details

The optimal reaction conditions were identified by Microscale High-Throughput Experimentation Screening. Parallel synthesis was accomplished in an MBraun glovebox operating with a constant Ar-purge (oxygen and water <5 ppm). Screening reactions were carried out in 1 mL V-type pressure vials using suitable heating blocks. Liquid chemicals were dosed using gas tight microsyringes.

General experimental procedure on the instance of base screening

The reactions were set up inside of glovebox under an argon atmosphere. The heating block containing 1 mL V-type pressure vials were loaded with 4-nitroanisole (1 equiv., 0.3 mmol), hexamethyldisilane (4 equiv.), appropriate base (4 equiv.), TBAB (1 equiv.) and toluene (2 mmol). Afterwards, the V-type pressure vials were sealed and stirred outside the glovebox for 18h at 100°C. Further, the reaction mixtures were cooled to room temperature, opened to air and a solution of biphenyl in DCM was syringed into each vial. Using a gas tight microsyringe, portions of each reaction mixture (10 μ L) were transferred into vials prefilled with 600 μ L of DCM. The vials were sealed with a stopper and analysed by Gas Chromatograph Mass Spectrometer GCMS-QP2010 Ultra instrument.

Table S1. Screening of bases.^a

MeO 1a	NO ₂ +	Me Me Me-Si-Si-Me Me Me 2a	base (4 equiv.), TBAB (1 equiv.) Toluene, 100°C, 18h	MeO I
	entry	base	conversion 1a (%)	b yield $\mathbf{I} (\%)^{b}$
	1	NaF	13	0
	2	LiF	8	0
	3	KF	23	18
	4	CsF	100	88 (79) ^c
	5	AgF	100	62
	6	$\mathrm{TBAF}^{\mathrm{d}}$	100	76
	7	TBAF x 3H ₂ O ^d	23	0
	8	NaOH	86	43
	9	КОН	93	56
	10	K_2CO_3	6	0
	11	Cs_2CO_3	8	0
	12	K ₃ PO ₄	5	0
	13	KOAc	2	0
	14	KO <i>t</i> Bu	100	23
	15	NaOMe	100	0
	16	Pyridine	3	0
	17	No base	2	0

^a Reaction conditions: **1a** (0.3 mmol), **2a** (4 equiv.), base (4 equiv.), TBAB (1 equiv.), Toluene (2 mmol), 100°C, 18h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield. ^d In this case TBAB was not used.

Table S2. Screening of solvents.^a



^a Reaction conditions: **1a** (0.3 mmol), **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.), solvent (2 mmol), 100°C, 18h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield. ^d OR = OEt, the reaction was performed at 120°C, within 72h.

Table S3. Screening of ammonium salts.^a



^a Reaction conditions: **1a** (0.3 mmol), **2a** (4 equiv.), CsF (4 equiv.), ammonium salt (1 equiv.), Toluene (2 mmol), 100°C, 18h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield. ^d In this case CsF was not used.

Table S4. Screening of the reaction temperature.^a



^a Reaction conditions: **1a** (0.3 mmol), **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.), Toluene (2 mmol), T ^oC, 18h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield.

Table S5. Screening of duration of the reaction.^a



^a Reaction conditions: **1a** (0.3 mmol), **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.), Toluene (2 mmol), 100°C, h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield.

Table S6. Blank experiments, synthesis of azo compounds I.^a

MeO	NO ₂ 1a	² Me I + Me-Si-Si Me I 2a	Me CsF TBA Me T Me 10	(4 equiv.), B (1 equiv.) oluene, 0°C, 18h	MeO	OMe
entry	2a	CsF	TBAB	Toluene	conversion 1a (%) ^b	yield I (%) ^b
1	\checkmark	\checkmark	\checkmark	\checkmark	100	88 (79) ^c
2	Х	\checkmark	\checkmark	\checkmark	3	0
3	\checkmark	X	\checkmark	\checkmark	2	0
4	\checkmark	\checkmark	X	\checkmark	2	0
5	\checkmark	\checkmark	\checkmark	Х	100	83

^a Reaction conditions: **1a** (0.3 mmol), **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.), Toluene (2 mmol), 100°C, 18h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield.

Table S7. Blank experiments, synthesis of anilines II.^a

	MeO ^{~~}	NO ₂	Me + Me-Si Me	Me i-Si-Me Me 2a	Pd/C (2 mol%). CsF (4 equiv.), TBAB (1 equiv.) EtOH, 120°C, 72h	MeO II	2
entry	2a	Pd/C	CsF	TBAB	EtOH	conversion 1a (%) ^b	yield II (%) ^b
1	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	100	98 (86) ^c
2	Х	\checkmark	\checkmark	\checkmark	\checkmark	8	0
3	\checkmark	Х	\checkmark	\checkmark	\checkmark	100	7
4	\checkmark	\checkmark	Х	\checkmark	\checkmark	16	0
5	\checkmark	\checkmark	\checkmark	Х	\checkmark	12	0
6	\checkmark	\checkmark	\checkmark	\checkmark	X	100	0

^a Reaction conditions: **1a** (0.3 mmol), **2a** (6 equiv.), CsF (4 equiv.), TBAB (1 equiv.), Pd/C (2 mol%), EtOH (2 mmol), 120°C, 72h. ^b Conversion and yield determined by GC using biphenyl as an internal standard. ^c Isolated yield.

Scheme S1. Synthesis of indazoles from 2-nitrotoluene derivatives.



General procedures

Unless otherwise stated, commercial reagents were used without purification. Compounds **3a**,¹ **3b**,² **3c**,³ **3d**,³ **3e**,⁴ **3f**,⁵ **3g**,⁶ **4e**,⁷ **5c**,⁸ **6a**,⁹ **6b**,¹⁰ **6c**,¹¹ **6d**,¹² **6e**,¹³ **6f**,¹⁰ **6g**,¹³ **6h**,¹⁴ **6i**,¹⁰ **6j**,¹⁵ **7a**,¹⁶ **7b**,¹⁰ **7c**,¹⁷ **8a**,¹⁵ **8b**,¹⁸ **8c**,¹⁵ **9a**,¹⁹ **9b**,¹⁹ **9c**,²⁰ **9d**,²¹ **10a**,²² **10b**,²⁰ **10c**,²⁰ **10d**,²³ **11a**,²⁴ **11b**,²⁵ **11c**,²⁶ **11d**,²⁸ **11e**,²⁷ **11f**,²⁸ **11g**,²⁵ **11h**,²⁹ are known. Enamine Ltd. Company (Ukraine) kindly provided phosphine oxides.

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Method A: synthesis of symmetrical azobenzenes. Preparation of compounds 3a-h. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding nitrobenzene **1** (1 equiv.), hexamethyldisilane **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (3 mL for 4 mmol of starting nitrobenzene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired azobenzene.



Method A: synthesis of unsymmetrical azobenzenes. Preparation of compounds 4a-f. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding nitroarene 1 (1 equiv.), nitrobenzene 1* (3 equiv.), hexamethyldisilane 2a (8 equiv.), CsF (8 equiv.), TBAB (2 equiv.) and Toluene (3 mL for 2 mmol of starting nitroarene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired azobenzene.



Method A: synthesis of Schiff bases. Preparation of compounds 5a-c. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding nitroarene 1 (1 equiv.), carbonyl compound 1* (3 equiv.), hexamethyldisilane 2a (8 equiv.), CsF (8 equiv.), TBAB (2 equiv.) and Toluene (3 mL for 2 mmol of starting nitroarene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired Schiff base.



Method B: synthesis of anilines. Preparation of compounds 6a-j. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding nitrobenzene **1** (1 equiv.), hexamethyldisilane **2a** (6 equiv.), Pd/C (2 mol%), CsF (4 equiv.), TBAB (1 equiv.) and ethanol (3 mL for 2 mmol of starting nitrobenzene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was treated with water. The water phase was extracted by DCM. The

organic layer was dried and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired aniline.



Method B: reduction of dinitro compounds. Preparation of compounds 7a-c. Under inert atmosphere (glovebox operating with a constant Arpurge) corresponding nitrobenzene **1** (1 equiv.), hexamethyldisilane **2a** (12 equiv.), Pd/C (4 mol%), CsF (8 equiv.), TBAB (2 equiv.) and ethanol (3 mL for 1 mmol of starting nitrobenzene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was treated with water. The water phase was extracted by DCM. The organic layer was dried and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired aniline.



Method B: reduction of nitroalkanes. Preparation of compounds 8a-c. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding nitroalkane 1 (1 equiv.), hexamethyldisilane 2a (6 equiv.), Pd/C (2 mol%), CsF (4 equiv.), TBAB (1 equiv.) and ethanol (3 mL for

2 mmol of starting nitroalkane) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and treated with a dilute solution of hydrochloric acid. Afterwards, the aqueous layer was separated, washed with DCM, neutralized and then treated with aqueous solution of NaOH. The resulting solution was extracted with DCM; the organic layers were combined and dried. Afterwards, the DCM was removed by distillation under atmospheric pressure that was followed by distillation of aliphatic amine using a dephlegmator.



Method A: multigram synthesis of 4a. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding nitropyrazole (10 mmol), nitrobenzene (30 mmol), hexamethyldisilane (80 mmol), CsF (80 mmol), TBAB (20 mmol) and Toluene (15 mL) were weighed and placed into a round bottom flask (volume 100 mL) equipped with a magnetic stir bar, which then was capped with a rubber septum. Afterwards, the reaction vessel was connected with an argon balloon and heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired azo compound.



Method B: multigram synthesis of 6f. Under inert atmosphere (glovebox operating with a constant Ar-purge) 3-nitrobenzotrifluoride (10 mmol), hexamethyldisilane (60 mmol), Pd/C (2 mol%), CsF (40 mmol), TBAB (10 mmol) and ethanol (15 mL) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was treated with water. The water phase was extracted by DCM. The organic layer was dried and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired aniline.



Method B: the Pd-catalysed reduction of *N*-oxides. Preparation of compounds 9a-d. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding *N*-oxide (1 equiv.), hexamethyldisilane 2a (6 equiv.), Pd/C (2 mol%), CsF (4 equiv.), TBAB (1 equiv.) and ethanol (3 mL for 2 mmol of starting *N*-oxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was treated with water. The water phase was extracted by DCM. The organic layer was dried and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired pyridine derivative.



Method A: the metal-free reduction of *N***-oxides. Preparation of compounds 9a-d.** Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding *N*-oxide (1 equiv.), hexamethyldisilane **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (3 mL for 4 mmol of starting *N*-oxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired pyridine derivative.



Method B: the Pd-catalysed reduction of sulfoxides. Preparation of compounds 10a-d. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding sulfoxide (1 equiv.), hexamethyldisilane **2a** (6 equiv.), Pd/C (2 mol%), CsF (4 equiv.), TBAB (1 equiv.) and ethanol (3 mL for 2 mmol of starting sulfoxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired sulfide.



Method A: the metal-free reduction of sulfoxides. Preparation of compounds 10a-d. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding sulfoxide (1 equiv.), hexamethyldisilane **2a** (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (3 mL for 4 mmol of starting sulfoxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired sulfide.



Method A: the metal-free reduction of phosphine oxides. Preparation of compounds 11a-c. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding phosphine oxide (1 equiv.), hexamethyldisilane 2a (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (3 mL for 4 mmol of starting phosphine oxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 48 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using degassed hexane/ethyl acetate mixtures to provide the desired phosphine.



Method A: the metal-free reduction of phosphine oxides. Preparation of compounds 11d-h. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding phosphine oxide (1 equiv.), hexamethyldisilane 2a (8 equiv.), CsF (6 equiv.), TBAB (2 equiv.) and Toluene (3 mL for 2 mmol of starting phosphine oxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 48 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using degassed hexane/ethyl acetate mixtures to provide the desired phosphine.



General procedure for the synthesis of indazoles from derivatives of 2-nitrotoluene. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding derivatives of 2-nitrotoluene (1 equiv.), hexamethyldisilane (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (3 mL for 4 mmol of starting derivatives of 2-nitrotoluene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 110°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired indazole.



Method B: the reduction of corresponding intermediates to aniline. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding intermediate (1 equiv.), hexamethyldisilane (6 equiv.), Pd/C (2 mol%), CsF (4 equiv.), TBAB (1 equiv.) and ethanol (3 mL for 2 mmol of starting intermediate) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was treated with water. The water phase was extracted by DCM. The organic layer was dried and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired aniline.



Method A: the synthesis of azobenzene from suitable intermediates. Under inert atmosphere (glovebox operating with a constant Ar-purge) corresponding intermediate (1 equiv.), hexamethyldisilane (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (3 mL for 4 mmol of starting intermediate) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired azobenzene.



Competitive experiment between nitrobenzene and *p***-toluidine.** Under inert atmosphere (glovebox operating with a constant Ar-purge) nitrobenzene (1 equiv., 0.3 mmol), *p*-toluidine (3 equiv.), hexamethyldisilane (4 equiv.), CsF (4 equiv.), TBAB (1 equiv.) and Toluene (2 mmol) were weighed and placed into the V-type pressure vial equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and analysed by GC/MS which indicated that the only product is azobenzene in addition to corresponding diphenyldiazene oxide.



Competitive experiment between nitrobenzene and nitrosobenzene. Under inert atmosphere (glovebox operating with a constant Ar-purge) nitrobenzene (1 equiv., 0.3 mmol), appropriate nitrosobenzene (3 equiv.), hexamethyldisilane (8 equiv.), CsF (8 equiv.), TBAB (2 equiv.) and Toluene (2 mmol) were weighed and placed into the V-type pressure vial equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 100°C for 18 h. Upon completion, the reaction was cooled to room temperature and analysed by GC/MS which showed the formation of a mixture of three different azobenzenes and diphenyldiazene oxide.



General procedure for the synthesis of aniline from nitrobenzene using dimethyl(phenyl)silane. Under inert atmosphere (glovebox operating with a constant Ar-purge) nitrobenzene (1 equiv.), dimethyl(phenyl)silane (6 equiv.), Pd/C (2 mol%) and ethanol (3 mL for 2 mmol of starting nitrobenzene) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired aniline.



General procedure for the synthesis of isoquinoline from isoquinoline *N*-oxide using dimethyl(phenyl)silane. Under inert atmosphere (glovebox operating with a constant Ar-purge) isoquinoline *N*-oxide (1 equiv.), dimethyl(phenyl)silane (6 equiv.), Pd/C (2 mol%) and ethanol (3 mL for 2 mmol of starting isoquinoline *N*-oxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired isoquinoline.



General procedure for the synthesis of diphenyl sulfide from diphenyl sulfoxide using dimethyl(phenyl)silane. Under inert atmosphere (glovebox operating with a constant Ar-purge) diphenyl sulfoxide (1 equiv.), dimethyl(phenyl)silane (6 equiv.), Pd/C (2 mol%) and ethanol (3 mL for 2 mmol of starting diphenyl sulfoxide) were weighed and placed into an Ace Pressure Tube equipped with a magnetic stir bar, which then was capped with a stopper. Afterwards, the reaction mixture was heated to 120°C for 72 h. Upon completion, the reaction was cooled to room temperature, filtered through a celite pad and concentrated under vacuum. The residue was purified by column chromatography typically using hexane/ethyl acetate mixtures to provide the desired diphenyl sulfide.

Characterization of products



1,2-Bis(4-methoxyphenyl)diazene (3a).

Yield = 79% (0.191g). The product is an intense yellow solid. mp 139-141°C. ¹H NMR (500 MHz, CDCl₃): δ 3.88 (s, 6H, OMe), 6.99-7.02 (m, 4H, CH_{Ar}), 7.88-7.90 (m, 4H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.5, 114.1, 124.3, 147.0, 161.5.

Anal. calcd. for C14H14N2O2: C, 69.41; H, 5.82; N, 11.56. Found: C, 70.33; H, 5.73; N, 11.62.



1,2-Bis(4-ethoxyphenyl)diazene (3b).

Yield = 77% (0.208g). The product is a yellow solid. mp 151-152°C. ¹H NMR (500 MHz, CDCl₃): δ 1.46 (t, 6H, ³*J* = 7.4 Hz, OCH₂CH₃), 4.10 (q, 4H, ³*J* = 6.9 Hz, OCH₂CH₃), 6.98-7.00 (m, 4H, CH_{Ar}), 7.86-7.87 (m, 4H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 14.8, 63.7, 114.6, 124.3, 146.9, 161.0.

Anal. calcd. for C₁₆H₁₈N₂O₂: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.21; H, 6.66; N, 10.42.

1,2-Diphenyldiazene (3c).

Yield = 86% (0.157g). The product is an orange solid. mp 68-69°C. ¹H NMR (500 MHz, CDCl₃): δ 7.50-7.53 (m, 2H, CH_{Ar}), 7.55-7.59 (m, 4H, CH_{Ar}), 8.00-8.02 (m, 4H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 122.8, 129.0, 130.9, 152.6. Anal. calcd. for C₁₂H₁₀N₂: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.17; H, 5.61; N, 15.41.

N NN

1,2-Di(naphthalen-1-yl)diazene (3d).

Yield = 62% (0.175g). The product is a brown solid. mp more than 200°C. ¹H NMR (200 MHz, CDCl₃): δ 7.74-7.99 (m, 8H, CH_{Ar}), 8.09-8.13 (m, 2H, CH_{Ar}), 8.37-8.42 (m, 2H, CH_{Ar}), 9.80-9.84 (m, 2H, CH_{Ar}).

¹³C NMR due to bed solubility it was not possible to measure.

Anal. calcd. for C₂₀H₁₄N₂: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.22; H, 5.08; N, 9.78.



1,2-Bis(4-phenoxyphenyl)diazene (3e).

Yield = 67% (0.245g). The product is a yellow solid. mp 139-141°C. ¹H NMR (500 MHz, CDCl₃): δ 7.08-7.09 (m, 4H, CH_{Ar}), 7.10-7.11 (m, 4H, CH_{Ar}), 7.18 (tt, 2H, ³*J* = 7.4 Hz, ⁴*J* = 0.9 Hz, CH_{Ar}), 7.38-7.41 (m, 4H, CH_{Ar}), 7.89-7.91 (m, 4H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 118.4, 119.7, 124.1, 124.5, 130.0, 148.3, 156.3, 159.8. Anal. calcd. for C₂₄H₁₈N₂O₂: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.71; H, 5.03; N, 7.72.



1,2-Bis(3-(trifluoromethyl)phenyl)diazene (3f).

Yield = 88% (0.280g). The product is a yellow solid. mp 82-84°C. ¹H NMR (500 MHz, CDCl₃): δ 7.68 (t, 2H, ³*J* = 8.2 Hz, CH_{Ar}), 7.77 (d, 2H, ³*J* = 7.3 Hz, CH_{Ar}), 8.13 (d, 2H, ³*J* = 8.2 Hz, CH_{Ar}), 8.22 (s, 2H, CH_{Ar}).

¹³**C NMR** (126 MHz, CDCl₃): δ 119.7 (q, ³*J*_{CF} = 3.5 Hz), 123.8 (q, ¹*J*_{CF} = 272.1 Hz), 126.5, 127.8, 127.9, 129.8, 131.8 (q, ²*J*_{CF} = 33.6 Hz), 152.2. Anal. calcd. for C₁₄H₈F₆N₂: C, 52.84; H, 2.53; N, 8.80. Found: C, 52.72; H, 2.48; N, 8.64.



1,2-Bis(4-methoxy-2-methylphenyl)diazene (3g).

Yield = 42% (0.113g). The product is a yellow solid. mp 158-160°C. ¹H NMR (500 MHz, CDCl₃): δ 2.72 (s, 6H, 2xMe), 3.06 (s, 6H, 2xOMe), 6.77-6.83 (m, 4H, CH_{Ar}), 7.68 (d, 2H, ³*J* = 8.8 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 17.9, 55.4, 112.3, 115.2, 117.3, 139.9, 145.5, 161.2. Anal. calcd. for C₁₆H₁₈N₂O₂: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.22; H, 6.62; N, 10.42.



1,2-Bis(1-phenethyl-1H-pyrazol-4-yl)diazene (3h).

Yield = 72% (0.266g). The product is an orange solid. mp 139-141°C. ¹H NMR (500 MHz, CDCl₃): δ 3.20 (t, 4H, ³*J* = 7.0 Hz, CH₂), 4.36 (t, 4H, ³*J* = 7.0 Hz, CH₂), 7.10-7.11 (m, 4H, CH_{Ar}), 7.26-7.29 (m, 6H, CH_{Ar}), 7.65 (s, 2H, Pyrazole), 7.93 (s, 2H, Pyrazole). ¹³C NMR (126 MHz, CDCl₃): δ 36.6, 54.3, 125.8, 126.9, 128.6, 128.69, 128.7, 132.6, 137.6, 141.3. Anal. calcd. for C₂₂H₂₂N₆: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.53; H, 5.78; N, 22.61.



1-Phenethyl-4-(phenyldiazenyl)-1H-pyrazole (4a).

Yield = 78% (0.215g). The product is an orange solid. mp 78-80°C. ¹H NMR (500 MHz, CDCl₃): δ 3.23 (t, 2H, ³*J* = 7.5 Hz, CH₂), 4.36 (t, 2H, ³*J* = 7.5 Hz, CH₂), 7.12-7.14 (m, 2H, CH_{Ar}), 7.23-7.30 (m, 3H, CH_{Ar}), 7.49 (m, 3H, CH_{Ar}), 8.16 (s, 1H, Pyrazole), 8.22-8.25 (m, 2H, CH_{Ar}), 8.54 (s, 1H, Pyrazole).

¹³**C NMR** (126 MHz, CDCl₃): δ 36.6, 54.2, 121.8, 126.7, 126.8, 131.0, 137.5, 139.3, 146.9. Anal. calcd. for C₁₇H₁₆N₄: C, 73.89; H, 5.84; N, 20.27. Found: C, 73.77; H, 5.78; N, 20.13.



4-((4-Methoxyphenyl)diazenyl)-1-phenethyl-1H-pyrazole (4b).

Yield = 69% (0.211g). The product is an orange solid. mp 93-95°C. ¹H NMR (500 MHz, CDCl₃): δ 3.22 (t, 2H, ³*J* = 7.4 Hz, CH₂), 3.87 (s, 3H, OMe), 4.39 (t, 2H, ³*J* = 7.6 Hz, CH₂), 6.94-6.96 (m, 2H, CH_{Ar}), 7.12-7.14 (m, 2H, CH_{Ar}), 7.22-7.30 (m, 3H, CH_{Ar}), 8.12 (s, 1H, Pyrazole), 8.18-8.20 (m, 2H, CH_{Ar}), 8.50 (s, 1H, Pyrazole).

¹³C NMR (126 MHz, CDCl₃): δ 36.6, 54.2, 55.7, 113.7, 123.4, 126.5, 126.8, 128.6, 128.7, 128.8, 137.6, 139.1, 140.3, 161.7. Anal. calcd. for C₁₈H₁₈N₄O: C, 70.57; H, 5.92; N, 18.29. Found: C, 70.49; H, 5.73; N, 18.36.



1-Phenethyl-4-((3-(trifluoromethyl)phenyl)diazenyl)-1H-pyrazole (4c).

Yield = 76% (0.261g). The product is an orange solid. mp 77-79°C. ¹H NMR (500 MHz, CDCl₃): δ 3.24 (t, 2H, ³*J* = 7.5 Hz, CH₂), 4.10 (t, 2H, ³*J* = 7.5 Hz, CH₂), 7.11-7.13 (m, 2H, CH_{Ar}), 7.23-7.30 (m, 3H, CH_{Ar}), 7.64 (t, 1H, ³*J* = 7.9 Hz, CH_{Ar}), 7.77 (d, 1H, ³*J* = 7.9 Hz, CH_{Ar}), 8.10 (s, 1H, Pyrazole), 8.44 (d, 1H, ³*J* = 8.3 Hz, CH_{Ar}), 8.52 (s, 1H, Pyrazole), 8.55 (s, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 36.6, 54.3, 119.2 (q, *J*_{CF} = 3.9 Hz), 123.4 (q, ¹*J*_{CF} = 272.1 Hz, CF₃), 125.1, 126.9, 127.0, 127.6 (q, *J*_{CF} = 3.0 Hz),

128.5, 128.7, 128.8, 129.6, 131.5 (q, ${}^{2}J_{CF}$ = 34.0 Hz, CCF₃), 137.4, 139.,5, 143.1, 147.0.

Anal. calcd. for C₁₈H₁₅F₃N₄: C, 62.79; H, 4.39; N, 16.27. Found: C, 62.61; H, 4.47; N, 16.35.



(E)-3-((3-(Trifluoromethyl)phenyl)diazenyl)pyridine (4d).

Yield = 56% (0.141g). The product is an orange oil. ¹**H NMR** (500 MHz, CDCl₃): δ 7.46-7.49 (m, 1H, CH_{Ar}), 7.68 (t, 1H, ³*J* = 8.3 Hz, CH_{Ar}), 7.75 (d, 1H, ³*J* = 7.8 Hz, CH_{Ar}), 8.13 (d, 1H, ³*J* = 8.3 Hz, CH_{Ar}), 8.17 (dt, 1H, ³*J* = 8.2 Hz, ⁴*J* = 1.8 Hz, CH_{Ar}), 8.21 (br. s, 1H, CH_{Ar}), 8.74 (dd, 1H, ³*J* = 4.6 Hz, ⁴*J* = 1.8 Hz, CH_{Ar}), 9.23 (d, 1H, ⁴*J* = 2.0 Hz, CH_{Ar}).

¹³**C NMR** (126 MHz, CDCl₃): δ 119.8 (q, J_{CF} = 4.0 Hz), 123.9 (q, ${}^{1}J_{CF}$ = 231.4 Hz, CF₃), 124.1, 126.4, 127.0, 128.0 (q, J_{CF} = 3.1 Hz), 129.8, 131.7 (q, ${}^{2}J_{CF}$ = 33.3 Hz, CCF₃), 147.6, 148.9, 152.4.

Anal. calcd. for C12H8N3F3: C, 57.37; H, 3.21; N, 16.73. Found: C, 57.48; H, 3.32; N, 16.58.



3-(Phenyldiazenyl)pyridine (4e).

Yield = 65% (0.119g). The product is an orange solid. mp 56-59°C. ¹H NMR (500 MHz, CDCl₃): δ 7.42-7.45 (m, 1H, CH_{Ar}), 7.50-7.55 (m, 3H, CH_{Ar}), 7.93-7.95 (m, 2H, CH_{Ar}), 8.13-8.15 (m, 1H, CH_{Ar}), 8.69-8.70 (m, 1H, CH_{Ar}), 9.19-9.20 (m, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 120.4, 123.0, 123.9, 126.8, 129.2, 131.8, 147.4, 151.7. Anal. calcd. for C₁₁H₉N₃: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.02; H, 5.03; N, 22.84.



3-((4-Methoxyphenyl)diazenyl)pyridine (4f).

Yield = 81% (0.119g). The product is an orange solid. mp 66-68°C. ¹H NMR (500 MHz, CDCl₃): δ 3.89 (s, 3H, OMe), 7.01 (dt, 2H, ³*J* = 9.0 Hz, ⁴*J* = 2.1 Hz, CH_{Ar}), 7.40-7.42 (m, 1H, CH_{Ar}), 7.93 (dt, 2H, ³*J* = 8.9 Hz, ⁴*J* = 2.0 Hz, CH_{Ar}), 8.08-8.11 (m, 1H, CH_{Ar}), 8.65 (dd, 1H, ³*J* = 4.7 Hz, ⁴*J* = 1.6 Hz, CH_{Ar}), 9.14 (d, 1H, ⁴*J* = 2.0 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 55.6, 114.3, 123.9, 125.1, 126.7, 146.9, 147.1, 147.9, 151.0, 162.6.

Anal. calcd. for C₁₂H₁₁N₃O: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.71; H, 5.25; N, 19.71.



N-(1-Phenethyl-1H-pyrazol-4-yl)-1,1-diphenylmethanimine (5a).

Yield = 68% (0.239g). The product is a green oil. ¹**H NMR** (500 MHz, CDCl₃): δ 3.05 (t, 2H, ³*J* = 7.2 Hz, CH₂), 4.17 (t, 2H, ³*J* = 7.4 Hz, CH₂), 6.57 (s, 1H, Pyrazole), 6.87 (s, 1H, Pyrazole), 7.02-7.04 (m, 2H, CH_{Ar}), 7.17-7.18 (m, 2H, CH_{Ar}), 7.23-7.29 (m, 3H, CH_{Ar}), 7.35-7.40 (m, 3H, CH_{Ar}), 7.44-7.46 (m, 3H, CH_{Ar}), 7.71-7.73 (m, 2H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 36.6, 53.7, 125.0, 126.6, 127.7, 128.1, 128.3, 128.5, 128.6, 128.8, 129.2, 130.0, 132.4, 135.7, 137.9, 138.5, 139.7, 165.1.

Anal. calcd. for C₂₄H₂₁N₃: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.89; H, 5.93; N, 12.03.



N-(4-Ethoxyphenyl)-1-(4-(trifluoromethyl)phenyl)methanimine (5b).

Yield = 44% (0.219g). The product is a green solid. mp 137-139°C. ¹H NMR (500 MHz, CDCl₃): δ 1.42 (t, 3H, ³*J* = 6.8 Hz, OCH₂CH₃), 4.05 (q, 2H, ³*J* = 6.8 Hz, OCH₂CH₃), 6.92 (dt, 2H, ³*J* = 8.9 Hz, ⁴*J* = 2.2 Hz, CH_{Ar}), 7.25 (dt, 2H, ³*J* = 8.9 Hz, ⁴*J* = 2.2 Hz, CH_{Ar}), 7.70 (d, 2H, ³*J* = 8.2 Hz, CH_{Ar}), 7.98 (d, 2H, ³*J* = 8.0 Hz, CH_{Ar}), 8.52 (s, 1H, NCH).

¹³**C NMR** (126 MHz, CDCl₃): δ 14.9, 63.7, 115.0, 122.4, 123.9 (q, ¹*J*_{CF} = 271.7 Hz, CF₃), 125.6 (q, *J*_{CF} = 3.9 Hz), 128.7, 132.2 (q, ²*J*_{CF} = 30.2 Hz, CCF₃), 139.6, 143.9, 156.1, 158.2.

Anal. calcd. for C₁₆H₁₄F₃NO: C, 65.52; H, 4.81; N, 4.78. Found: C, C, 65.42; H, 4.95; N, 4.69.



N,1-Di-p-tolylmethanimine (5c).

Yield = 42% (0.089g). The product is a yellow solid. mp 95-97°C. ¹H NMR (500 MHz, CDCl₃): 2.38 (s, 3H, Me), 2.42 (s, 3H, Me), 7.13 (d, 2H, ${}^{3}J = 8.4$ Hz, CH_{Ar}), 7.19 (d, 2H, ${}^{3}J = 8.0$ Hz, CH_{Ar}), 7.27 (d, 2H, ${}^{3}J = 8.0$ Hz, CH_{Ar}), 7.79 (d, 2H, ${}^{3}J = 8.0$ Hz, CH_{Ar}), 8.44 (s, 1H, NCH). ¹³C NMR (126 MHz, CDCl₃): δ 21.0, 21.6, 120.8, 128.7, 129.4, 129.7, 133.7, 135.6, 141.6, 149.6, 159.6. Anal. calcd. for C₁₅H₁₅N: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.22; H, 7.18; N, 6.73.



4-Methoxyaniline (6a).

Yield = 86% (0.105g). The product is a yellow solid. mp 56-58°C. ¹H NMR (500 MHz, CDCl₃): δ 3.40 (br. s, 2H, NH₂), 3.74 (s, 3H, OMe), 6.63 (dt, 2H, ³J = 8.9 Hz, ⁴J = 2.3 Hz, CH_{Ar}), 6.74 (dt, 2H, ³J = 8.8 Hz, ⁴J = 2.2 Hz, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 55.6, 114.7, 116.3, 139.9, 152.7.

Anal. calcd. for C₇H₉NO: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.33; H, 7.31; N, 11.30.



4-Ethoxyaniline (6b).

Yield = 83% (0.114g). The product is a slightly yellow liquid. ¹**H NMR** (500 MHz, CDCl₃): δ 1.37 (t, 3H, ³*J* = 7.0 Hz, OCH₂CH₃), 3.35 (br. s, 2H, NH₂), 3.95 (q, 2H, ³*J* = 7.0 Hz, OCH₂CH₃), 6.63-6.65 (m, 2H, CH_{Ar}), 6.73-6.75 (m, 2H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 15.0, 64.0, 115.6, 116.4, 139.8, 152.1. Anal. calcd. for C₈H₁₁NO: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.22; H, 8.21; N, 10.07.



Aniline (6c).

Yield = 91% (0.085g). The product is a colorless liquid. ¹**H NMR** (500 MHz, CDCl₃): δ 3.60 (br. s, 2H, NH₂), 6.69-6.72 (m, 2H, CH_{Ar}), 6.79 (t, 1H, ³*J* = 7.4 Hz, CH_{Ar}), 7.16-7.20 (m, 2H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 115.1, 118.5, 129.2, 146.3.

Anal. calcd. for C₆H₇N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.21; H, 7.62; N, 15.18.

 NH_2

Naphthalen-1-amine (6d).

Yield = 64% (0.092g). The product is a colorless soloid. mp 48-50°C. ¹H NMR (500 MHz, CDCl₃): δ 4.14 (br. s, 2H, NH₂), 6.79 (dd, 1H, ³*J* = 7.1 Hz, ⁴*J* = 1.5 Hz, CH_{Ar}), 7.31-7.37 (m, 2H, CH_{Ar}), 7.46-7.52 (m, 2H, CH_{Ar}), 7.83-7.85 (m, 2H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 109.6, 118.9, 120.8, 123.6, 124.8, 125.8, 126.3, 128.5, 134.3, 142.0. Anal. calcd. for C₁₀H₉N: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.92; H, 6.26; N, 9.72.



 N^1 , N^1 -Dimethylbenzene-1, 4-diamine (6e).

Yield = 68% (0.092g). The product is a dark red solid. mp 52-53°C. ¹H NMR (500 MHz, CDCl₃): δ 2.83 (s, 6H, NMe₂), 3.30 (br. s, 2H, NH₂), 6.66 (d, 2H, ³*J* = 8.6 Hz, CH_{Ar}), 6.70 (d, 2H, ³*J* = 8.6 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 42.2, 115.6, 116.5, 138.0, 144.6. Anal. calcd. for C₈H₁₂N₂: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.36; H, 8.81; N, 20.67.



3-(Trifluoromethyl)aniline (6f).

Yield = 87% (0.140g). The product is a yellowish oil. ¹**H NMR** (500 MHz, CDCl₃): δ 3.82 (br. s, 2H, NH₂), 6.81 (dd, 1H, ³*J* = 8.0 Hz, ⁴*J* = 2.1 Hz, CH_{Ar}), 6.89 (br. s, 1H, CH_{Ar}), 6.99 (d, 1H, ³*J* = 7.7 Hz, CH_{Ar}), 7.23 (d, 1H, ³*J* = 7.9 Hz, CH_{Ar}).

¹³**C NMR** (126 MHz, CDCl₃): δ 111.3 (q, ³*J*_{CF} = 4.0 Hz), 114.9 (q, ³*J*_{CF} = 4.0 Hz), 118.0, 124.2 (q, ¹*J*_{CF} = 271 Hz, CF₃), 129.7, 131.6 (q, ²*J*_{CF} = 32.2 Hz), 146.7.

Anal. calcd. for C₇H₆F₃N: C, 52.18; H, 3.75; N, 8.69. Found: C, 52.22; H, 3.69; N, 8.56.



o-Toluidine (6g).

Yield = 75% (0.080g). The product is a light brown liquid. ¹**H NMR** (500 MHz, CDCl₃): δ 2.19 (s, 3H, Me), 3.59 (br. s, 2H, NH₂), 6.69 (d, 1H, ³*J* = 7.4 Hz, CH_{Ar}), 6.73 (t, 1H, ³*J* = 7.4 Hz, CH_{Ar}), 7.04-7.08 (m, 2H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 17.3, 114.9, 118.6, 122.3, 126.9, 130.4, 144.5. Anal. calcd. for C₇H₉N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.51; H, 8.52; N, 13.00.



2-Bromoaniline (6h).

Yield = 63% (0.108g). The product is a white solid. mp 25-26°C. ¹H NMR (500 MHz, CDCl₃): δ 4.08 (br. s, 2H, NH₂), 6.61-6.65 (m, 1H, CH_{Ar}), 6.76 (dd, 1H, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, CH_{Ar}), 7.10-7.13 (m, 1H, CH_{Ar}), 7.41 (dd, 1H, ³*J* = 8.0 Hz, ⁴*J* = 1.3 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 109.3, 115.7, 119.3, 128.3, 132.5, 144.0. Anal. calcd. for C₆H₆BrN: C, 41.89; H, 3.52; N, 8.14. Found: C, 41.79; H, 3.58; N,8.23.



[1,1'-Biphenyl]-2-amine (6i).

Yield = 61% (0.103g). The product is a colorless solid. mp 45-46°C. ¹H NMR (500 MHz, CDCl₃): δ 3.75 (br. s, 2H, NH₂), 6.78 (dd, 1H, ³*J* = 7.4 Hz, ⁴*J* = 1.1 Hz, CH_{Ar}), 6.84 (dt, 1H, ³*J* = 8.0 Hz, ⁴*J* = 0.8 Hz, CH_{Ar}), 7.13-7.18 (m, 2H, ³*J* = 11.2 Hz, CH_{Ar}), 7.34-7.37 (m, 1H, CH_{Ar}), 7.44-7.48 (m, 4H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 115.6, 118.7, 127.2, 127.6, 128.5, 128.8, 129.1, 130.4, 139.5, 143.4.

Anal. calcd. for C₁₂H₁₁N: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.09; H, 6.78; N, 8.31.



4-Aminopyridine (6j).

Yield = 67% (0.063g). The product is a white solid. mp 155-156°C. ¹**H NMR** (500 MHz, *DMSO-d*₆): δ 5.98 (br. s, 2H, NH₂), 6.44-6.45 (m, 2H, Pyridine), 7.95-7.97 (m, 2H, Pyridine).

¹³C NMR (126 MHz, *DMSO-d*₆): δ 108.9, 149.5, 154.2.

Anal. calcd. for C₅H₆N₂: C, 63.81; H, 6.43; N, 29.77. Found: C, 63.71; H, 6.48; N, 29.83.


Benzene-1,2-diamine (7a).

Yield = 72% (0.078g). The product is a colorless solid. mp 102-103°C. ¹**H NMR** (500 MHz, CDCl₃): δ 3.43 (br. s, 4H, 2xNH₂), 6.71-6.75 (m, 4H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 116.7, 120.2, 134.7.

Anal. calcd. for C₆H₈N₂: C, 66.64; H, 7.46; N, 25.90. Found: C, 66.81; H, 7.22; N, 25.83.



Benzene-1,4-diamine (7b).

Yield = 77% (0.083g). The product is a white solid. mp 145-146°C. ¹H NMR (500 MHz, *DMSO-d*₆): δ 4.18 (br. s, 4H, 2xNH₂), 6.36 (br. s, 4H, CH_{Ar}).

¹³C NMR (126 MHz, *DMSO-d*₆): δ 115.4, 139.0.

Anal. calcd. for C₆H₈N₂: C, 66.64; H, 7.46; N, 25.90. Found: C, 66.52; H, 7.39; N, 25.99.



2,2'-(Ethane-1,2-diyl)dianiline (7c).

Yield = 69% (0.146g). The product is a white solid. mp 72-74°C. ¹H NMR (500 MHz, CDCl₃): δ 2.82 (s, 4H, 2xCH₂), 3.59 (br. s, 4H, 2xNH₂), 6.69 (dd, 2H, ³*J* = 7.8 Hz, ⁴*J* = 0.9 Hz, CH_{Ar}), 6.78 (dt, 2H, ³*J* = 7.4 Hz, ⁴*J* = 1.1 Hz, CH_{Ar}), 7.06-7.10 (m, 4H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 30.9, 115.8, 119.0, 126.2, 127.2, 129.4, 144.3. Anal. calcd. for C₁₄H₁₆N₂: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.36; H, 7.72; N, 13.28.

 NH_2

Cyclohexanamine (8a).

Yield = 79% (0.078g). The product is a yellowish liquid. ¹H NMR (500 MHz, CDCl₃): δ 0.98-1.04 (m, 2H, Cyclohexyl), 1.08-1.13 (m, 1H, Cyclohexyl), 1.19-1.28 (m, 4H, NH₂, Cyclohexyl), 1.55-1.59 (m, 1H, Cyclohexyl), 1.66-1.70 (m, 2H, Cyclohexyl), 1.77-1.80 (m, 2H, Cyclohexyl), 2.56-2.62 (m, 1H, Cyclohexyl). ¹³C NMR (126 MHz, CDCl₃): δ 25.1, 25.7, 36.9, 50.4.

 10 C NMR (126 MHZ, CDCl₃): 0 25.1, 25.7, 30.9, 50.4.

Anal. calcd. for C₆H₁₃N: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.72; H, 13.16; N, 14.23.

 NH_2 Me、 Me

2-Methylpropan-2-amine (8b).

Yield = 67% (0.049g). The product is a colorless liquid. ¹**H NMR** (500 MHz, CDCl₃): δ 1.12 (s, 9H, *t*Bu), 1.18 (br. s, 2H, NH₂). ¹³**C NMR** (126 MHz, CDCl₃): δ 32.5, 47.3. Anal. calcd. for C₄H₁₁N: C, 65.69; H, 15.16; N, 19.15. Found: C, 65.52; H, 15.26; N, 19.02.

 Me^{NH_2}

Propan-1-amine (8c).

Yield = 49% (0.026g). The product is a colorless liquid. ¹**H NMR** (500 MHz, CDCl₃): δ 0.89 (t, 3H, ³*J* = 7.5 Hz, C*H*₃CH₂CH₂NH₂), 1.15 (br. s, 2H, CH₃CH₂CH₂NH₂), 1.41-1.45 (m, 2H, CH₃CH₂CH₂NH₂), 2.63 (t, 2H, ³*J* = 7.5 Hz, CH₃CH₂CH₂NH₂). ¹³C NMR (126 MHz, CDCl₃): δ 11.3, 26.9, 44.1.

Anal. calcd. for C₃H₉N: C, 60.96; H, 15.35; N, 23.70. Found: C, 60.90; H, 15.38; N, 23.72.

Me

2-Methylquinoline (9a).

Yield = 81% (0.116g), 93% (0.133g). The product is a colorless oil. ¹**H NMR** (500 MHz, CDCl₃): δ 2.74 (s, 3H, Me), 7.26 (d, 1H, ³*J* = 8.1 Hz, CH_{Ar}), 7.45-7.48 (m, 1H, CH_{Ar}), 7.65-7.69 (m, 1H, CH_{Ar}), 7.75 (d, 1H, ³*J* = 8.1 Hz, CH_{Ar}), 8.02 (dd, 2H, ³*J* = 8.2 Hz, ⁴*J* = 3.6 Hz, CH_{Ar}). ¹³**C NMR** (126 MHz, CDCl₃): δ 25.3, 122.0, 125.6, 126.4, 127.5, 128.6, 129.4, 136.1, 147.8, 158.9. Anal. calcd. for C₁₀H₉N: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.97; H, 6.41; N, 9.69.



Isoquinoline (9b).

Yield = 76% (0.098g), 89% (0.115g). The product is a yellow oil. ¹**H NMR** (500 MHz, CDCl₃): δ 7.59-7.62 (m, 1H, CH_{Ar}), 7.64 (d, 1H, ³*J* = 5.8 Hz, CH_{Ar}), 7.68-7.71 (m, 1H, CH_{Ar}), 7.81 (d, 1H, ³*J* = 7.6 Hz, CH_{Ar}), 7.97 (dd, 1H, ³*J* = 8.1 Hz, ⁴*J* = 0.7 Hz, CH_{Ar}), 8.52 (d, 1H, ³*J* = 5.7 Hz, CH_{Ar}), 9.26 (s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 120.4, 126.5, 127.2, 127.6, 128.7, 130.3, 135.8, 143.0, 152.5.

Anal. calcd. for C₉H₇N: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.77; H, 5.50; N, 10.76.



2,6-Dimethylpyridine (9c).

Yield = 71% (0.076g) 84% (0.090g). The product is a yellowish oli. ¹H NMR (500 MHz, CDCl₃): δ 2.49 (s, 6H, 2xMe), 6.91 (d, 2H, ³*J* = 7.4 Hz, CH_{Ar}), 7.42 (d, 1H, ³*J* = 7.9 Hz, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 24.5, 120.1, 136.4, 157.6. Anal. calcd. for C₇H₉N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.61; H, 8.41; N, 13.16.



2-Phenylpyridine (9d).

Yield = 77% (0.119g), 91% (0.141g). The product is a colorless oil. ¹**H NMR** (500 MHz, CDCl₃): δ 7.22-7.25 (m, 1H, CH_{Ar}), 7.40-7.44 (m, 1H, CH_{Ar}), 7.47-7.50 (m, 2H, CH_{Ar}), 7.73-7.78 (m, 2H, CH_{Ar}), 7.98-8.00 (m, 2H, CH_{Ar}), 8.70-8.71 (m, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 120.6, 122.1, 127.0, 128.8, 129.0, 136.8, 139.4, 149.7, 157.5. Anal. calcd. for C₁₁H₉N: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.22; H, 5.81; N, 9.00.

Diphenylsulfane (10a).

Yield = 82% (0.153g), 96% (0.179g). The product is a colorless liquid. ¹H NMR (500 MHz, CDCl₃): δ 7.23-7.27 (m, 2H, CH_{Ar}), 7.30-7.32 (m, 4H, CH_{Ar}), 7.35-7.36 (m, 4H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 127.0, 129.2, 131.0, 135.8. Anal. calcd. for C₁₂H₁₀S: C, 77.38; H, 5.41. Found: C, 77.43; H, 5.61.



Methyl(phenyl)sulfane (10b).

Yield = 66% (0.082g), 85% (0.105g). The product is a colorless liquid. ¹**H NMR** (500 MHz, CDCl₃): 2.78 (s, 3H, Me), 7.11-7.15 (m, 1H, Ph), 7.25-7.28 (m, 4H, Ph).

¹³C NMR (126 MHz, CDCl₃): δ 15.8, 125.0, 126.6, 128.8, 138.4.

Anal. calcd. for C₇H₈S: C, 67.69; H, 6.49. Found: C, 67.52; H, 6.38.



Methyl(p-tolyl)sulfane (10c).

Yield = 70% (0.097g), 87% (0.120g). The product is a colorless liquide. ¹**H NMR** (500 MHz, CDCl₃): 2.32 (s, 3H, Me), 2.47 (s, 3H, SMe), 7.10 (d, 2H, ${}^{3}J$ = 7.9 Hz, CH_{Ar}), 7.18 (d, 2H, ${}^{3}J$ = 7.9 Hz, CH_{Ar}). ¹³**C NMR** (126 MHz, CDCl₃): δ 16.5, 20.9, 127.2, 129.6, 134.7, 135.0.

Anal. calcd. for C₈H₁₀S: C, 69.51; H, 7.29. Found: C, 69.57; H, 7.31.



Dibenzylsulfane (10d).

Yield = 67% (0.143g), 78% (0.167g). The product is a white solid. mp 49-50°C. ¹H NMR (500 MHz, CDCl₃): δ 3.94 (br. s, 4H, 2xCH₂), 7.27-7.37 (m, 10H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 35.5, 127.0, 128.4, 129.0, 138.1.

Anal. calcd. for C₁₄H₁₄S: C, 78.46; H, 6.58. Found: C, 78.55; H, 6.41.

Ph P Ph

Triphenylphosphane (11a).

Yield = 87% (0.228g). The product is a white solid. mp 80-81°C. ¹H NMR (500 MHz, CDCl₃): δ 7.33-7.37 (m, 15H, CH_{Ar}).

³¹**P NMR** (81 MHz, CDCl₃): -5.4.

¹³**C NMR** (126 MHz, CDCl₃): δ 128.5 (d, J_{CP} = 7 Hz), 128.7, 133.7, 133.8, 137.1 (d, J_{CP} = 10.2 Hz).

Anal. calcd. for C₁₈H₁₅P: C, 82.43; H, 5.76. Found: C, 82.49; H, 5.86.



Tri-o-tolylphosphane (11b).

Yield = 85% (0.258g). The product is a white solid. mp 123-124°C. ¹H NMR (500 MHz, CDCl₃): δ 2.42 (s, 9H, 3xMe), 6.74-6.76 (m, 3H, CH_{Ar}), 7.08-7.11 (m, 3H, CH_{Ar}), 7.24-7.30 (m, 6H, CH_{Ar}).

³¹**P NMR** (81 MHz, CDCl₃): -29.5.

¹³**C NMR** (126 MHz, CDCl₃): δ 21.1, 21.3, 126.1, 128.7, 130.0 (d, $J_{CP} = 4.7$ Hz), 133.0, 134.4 (d, ${}^{2}J_{CP} = 10.5$ Hz), 134.5, 142.7 (d, ${}^{1}J_{CP} = 25.1$ Hz).

Anal. calcd. for C₂₁H₂₁P: C, 82.87; H, 6.95. Found: C, 82.93; H, 7.00.



Dicyclohexyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphane (11c).

Yield = 79% (0.376g). The product is a white solid. mp 187-189°C. ¹H NMR (500 MHz, CDCl₃): δ 0.96 (s, 3H, Me), 0.97 (s, 3H, Me), 1.15-1.23 (m, 8H, Cy), 1.18 (s, 3H, Me), 1.23 (s, 3H, Me), 1.30 (s, 3H, Me), 1.31 (s, 3H, Me), 1.58-1.86 (m, 14H, Cy), 2.41 (q, 2H, ³*J* = 6.9 Hz, 2xC*H*Me₂), 2.93 (q, 1H, ³*J* = 6.9 Hz, C*H*Me₂), 7.00 (s, 2H, CH_{Ar}), 7.14-7.16 (m, 1H, CH_{Ar}), 7.31-7.34 (m, 2H, CH_{Ar}), 7.59-7.60 (m, 1H, CH_{Ar}). ³¹P NMR (81 MHz, CDCl₃): -12.4.

¹³**C NMR** (126 MHz, CDCl₃): δ 22.9, 24.0, 25.9, 26.5, 27.3 (d, $J_{CP} = 8.6$ Hz), 27.5 (d, $J_{CP} = 11.4$ Hz), 29.3 (d, $J_{CP} = 12.1$ Hz), 30.6, 30.8 (d, $J_{CP} = 15.7$ Hz), 34.0, 34.5 (d, $J_{CP} = 15.0$ Hz), 120.3, 126.1, 127.6, 131.5 (d, $J_{CP} = 5.7$ Hz), 132.3 (d, $J_{CP} = 2.3$ Hz), 136.4-136.6 (m), 145.9, 147.6, 147.7 (d, $J_{CP} = 31.8$ Hz).

Anal. calcd. for C₃₃H₄₉P: C, 83.14; H, 10.36. Found: C, 83.25; H, 10.28.



2,2'-Bis(diphenylphosphanyl)-1,1'-binaphthalene (11d).

Yield = 82% (0.510g). The product is a white solid. mp above 200°C. ¹**H NMR** (500 MHz, CDCl₃): δ 6.83 (d, 2H, ³*J* = 8.5 Hz, CH_{Ar}), 6.90-6.93 (m, 2H, CH_{Ar}), 7.04-7.19 (m, 20H, CH_{Ar}), 7.33-7.36 (m, 2H, CH_{Ar}), 7.45 (dd, 2H, ³*J* = 8.4 Hz, ⁴*J* = 2.5 Hz, CH_{Ar}), 7.83 (d, 2H, ³*J* = 8.1 Hz, CH_{Ar}), 7.89 (d, 2H, ³*J* = 8.6 Hz, CH_{Ar}).

³¹**P NMR** (81 MHz, CDCl₃): -15.6.

¹³**C NMR** (126 MHz, CDCl₃): δ 125.8, 126.5, 127.5 (d, $J_{CP} = 9.0$ Hz), 127.7, 128.0-128.1 (m), 128.4, 130.5, 132.8-133.0 (m), 133.2, 134.1-134.3 (m).

Anal. calcd. for C₄₄H₃₂P₂: C, 84.87; H, 5.18. Found: C, 84.96; H, 5.22.



(9,9-Dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphane) (11e).

Yield = 78% (0.451g). The product is a white solid. mp above 200°C. ¹**H** NMR (500 MHz, CDCl₃): δ 1.68 (s, 6H, 2xMe), 6.57-6.59 (m, 2H, CH_{Ar}), 6.98 (t, 2H, ³*J* = 7.6 Hz, CH_{Ar}), 7.19-7.29 (m, 20, CH_{Ar}), 7.42 (dd, 2H, ³*J* = 7.8 Hz, ⁴*J* = 1.4 Hz, CH_{Ar}). ³¹**P** NMR (81 MHz, CDCl₃): -18.0. ¹³**C NMR** (126 MHz, CDCl₃): δ 31.8, 123.3, 125.7-125.9 (m), 126.3, 128.1-128.8 (m), 129.9, 132.1, 133.9 (t, $J_{CP} = 10.8$ Hz), 137.4 (t, $J_{CP} = 5.8$ Hz), 152.5 (t, $J_{CP} = 8.9$ Hz).

Anal. calcd. for C₃₉H₃₂OP₂: C, 80.95; H, 5.57. Found: C, 81.00; H, 5.61.

Ph₂P PPh₂

Bis(diphenylphosphanyl)methane (11f).

Yield = 74% (0.284g). The product is a white solid. mp 117-119°C. ¹**H NMR** (500 MHz, CDCl₃): δ 2.84 (t, 2H, ³*J* = 1.4 Hz, CH₂), 7.32 (t, 12H, ³*J* = 3.4 Hz, CH_{Ar}), 7.44-7.48 (m, 8H, CH_{Ar}).

³¹**P NMR** (81 MHz, CDCl₃): -22.5.

¹³**C NMR** (126 MHz, CDCl₃): δ 28.0 (t, ¹*J_{CP}* = 22.6 Hz), 128.4 (t, *J_{CP}* = 3.4 Hz), 128.7, 132.8 (t, ²*J_{CP}* = 10.3 Hz), 138.7.

Anal. calcd. for C₂₅H₂₂P₂: C, 78.12; H, 5.77. Found: C, 78.03; H, 5.56.



1,3-Bis(diphenylphosphanyl)propane (11g).

Yield = 69% (0.284g). The product is a white solid. mp 62-65°C. ¹H NMR (500 MHz, CDCl₃): δ 1.61-1.67 (m, 2H CH₂CH₂CH₂), 2.22 (t, 4H, ³J = 8.0 Hz, CH₂CH₂CH₂), 7.31-7.32 (m, 12H, CH_{Ar}), 7.37-7.40 (m, 8H, CH_{Ar}).

³¹**P NMR** (81 MHz, CDCl₃): -17.5.

¹³C NMR (126 MHz, CDCl₃): δ 22.3 (t, J_{CP} = 15.9 Hz), 29.5 (t, J_{CP} = 11.2 Hz), 128.3 (d, J_{CP} = 6.6 Hz), 128.5, 132.7 (d, J_{CP} = 18.3 Hz), 138.3 (d, J_{CP} = 11.9 Hz).

Anal. calcd. for C₂₇H₂₆P₂: C, 78.63; H, 6.35. Found: C, 78.86; H, 6.39.

1,4-Bis(diphenylphosphanyl)butane (11h).

Yield = 61% (0.260g). The product is a white solid. mp 132-134°C. ¹H NMR (500 MHz, CDCl₃): δ 1.57-1.58 (m, 4H CH₂CH₂CH₂CH₂), 2.25 (t, 4H, ³*J* = 7.2 Hz, CH₂CH₂CH₂CH₂), 7.32-7.35 (m, 12H, CH_{Ar}), 7.39-7.42 (m, 8H, CH_{Ar}). ³¹P NMR (81 MHz, CDCl₃): -16.1. ¹³C NMR (126 MHz, CDCl₃): δ 27.4-27.7 (m), 128.4 (d, *J*_{CP} = 6.7 Hz), 128.6, 132.6 (d, *J*_{CP} = 18.7 Hz), 138.4 (d, *J*_{CP} = 11.2 Hz).

Anal. calcd. for $C_{28}H_{28}P_2$: C, 78.96; H, 6.62. Found: C, 78.73; H, 6.58.



2-(o-Tolyl)-2H-indazole (12a).

Yield = 69% (0.144g). The product is an orange oil. ¹**H NMR** (500 MHz, CDCl₃): δ 2.26 (s, 3H, Me), 6.82-6.84 (m, 1H, CH_{Ar}), 7.14-7.17 (m, 1H, CH_{Ar}), 7.34-7.45 (m, 4H, CH_{Ar}), 7.75 (d, 1H, ³*J* = 8.3 Hz, CH_{Ar}), 7.81 (dd, 1H, ³*J* = 8.0 Hz, ⁴*J* = 0.8 Hz, CH_{Ar}), 8.10 (s, 1H, CH_{Ar}). ¹³C NMR (126 MHz, CDCl₃): δ 17.8, 117.8, 120.2, 121.9, 122.1, 124.3, 126.3, 126.5, 126.6, 129.1, 131.2, 133.9, 140.3, 149.2. Anal. calcd. for C₁₄H₁₂N₂: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.81; H, 6.12; N, 13.25.



6-Methoxy-2-(4-methoxy-2-methylphenyl)-2H-indazole (12b).

Yield = 52% (0.131g). The product is a yellow solid. mp 108-110°C. ¹H NMR (500 MHz, CDCl₃): δ 2.18 (s, 3H, Me), 3.86 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.82-6.84 (m, 1H, CH_{Ar}), 6.85-6.86 (m, 1H, CH_{Ar}), 6.93-6.94 (m, 1H, CH_{Ar}), 7.04 (dd, 1H, ³*J* = 9.3 Hz, ⁴*J* = 2.4 Hz, CH_{Ar}), 7.32 (d, 1H, ³*J* = 7.5 Hz, CH_{Ar}), 7.67 (d, 1H, ³*J* = 9.0 Hz, CH_{Ar}), 7.90 (s, 1H, CH_{Ar}).

¹³C NMR (126 MHz, CDCl₃): δ 18.0, 55.4, 55.5, 96.3, 111.5, 116.1, 119.2, 121.2, 121.7, 123.6, 127.7, 133.7, 135.5, 146.0, 155.2, 159.7. Anal. calcd. for C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.69; H, 6.15; N, 10.30.

Copies of spectra



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Compound 3a



Compound 3b

SpinWorks 4: AG 232-1 1H



transmitter freq.: 500.134001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130025 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 203.206 ppm/cm: 0.40630

Compound 3b



Compound 3c

SpinWorks 4: SM 109 1H







The: F: VMapO VMMK (500 VMK (1303 / 1/h expt: <2g30 > transmitter freq.: 500.134001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 32 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 182.830 ppm/cm: 0.36556

Compound 3c

SpinWorks 4: SM 109 13C 120.423 122.791 128.617 129.010 130.919 152.549 76.744 76.998 77.252 N²N²N LI PPM 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 file: F:\Napo\NMR\500\mkr11303\2\fid expt: <zgpg30> freq. of 0 ppm: 125.757812 MHz transmitter freq.: 125.772879 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt Hz/cm: 1442.308 ppm/cm: 11.46756 number of scans: 170

Compound 3d

SpinWorks 4: AG 91A-3B







Compound 3e

SpinWorks 4: AG 289 1H



file: F:\Napo\MR\500\mkr10702\l\fid expt: <zg30> transmitter freq.: 500.134001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 24 freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 179.002 ppm/cm: 0.35791

Compound 3e



Compound 3f

SpinWorks 4: AG 177 -1 1H







Compound 3f

SpinWorks 4: AG 177-1 13C



Compound 3g



Compound 3g



Compound 3h

SpinWorks 4: AG 93-2 1H





time domain size: 65536 points width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 32

LB: 0.300 GF: 0.0000 Hz/cm: 199.902 ppm/cm: 0.39970 Ph

N-

Ph

Compound 3h



Compound 4a



number of scans: 24

Hz/cm: 180.606 ppm/cm: 0.36112

Compound 4a



Compound 4b



Compound 4b



Compound 4c



Compound 4c

SpinWorks 4: AG 393-1 13C



Compound 4d

SpinWorks 4: AG 402 1H







Compound 4d

SpinWorks 4: AG 402 13C



Compound 4e

SpinWorks 4: AG 403-1 1H







Compound 4e

SpinWorks 4: AG 403-1 13C


Compound 4f

SpinWorks 4: R 404 1H



Compound 4f



Compound 5a

SpinWorks 4: AG 426-1 1H



Compound 5a

SpinWorks 4: AG 426-1 13C



Compound 5b



Compound 5b



Compound 5c

SpinWorks 4: AG 436 1H



Compound 5c



Compound 6a



Compound 6a



Compound 6b



Compound 6b



Compound 6c

SpinWorks 4: SM 104 1H 3.598 ~~~~~ 0000000000 164 171 183 184 195 203 .692 .697 .710 .713 .713 .713 .715 .772 .772 .772 .772 LLLLLLL NH_2 PPM 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 2.000 1.995 2.090 1 (Lili PPM 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 freq. of 0 ppm: 500.130023 MHz file: F:\Napo\NMR\500\gev10603\7\fid expt: <zg30> processed size: 65536 complex points transmitter freq.: 500.134001 MHz LB: 0.300 GF: 0.0000 time domain size: 65536 points Hz/cm: 198.250 ppm/cm: 0.39639 width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt

number of scans: 32

Compound 6c



Compound 6d

SpinWorks 4: SM 228 1H $\begin{array}{c} 66.793\\ 6.807\\ 6.807\\ 6.807\\ 7.3213\\ 7.32560\\ 7.32560\\ 7.32560\\ 7.32560\\ 7.3253\\ 7.3256\\ 7.4481\\ 7.4464\\ 7.4477\\ 7.4464\\ 7.4490\\ 7.4497\\ 7.4490\\ 7.4491\\ 7.853\\ 7.5163\\ 7.853\\ 7.$ 4.148 NH₂ PPM 15.0 14.0 13.0 12.0 11.0 10.0 9.0 2.042 2.08 2.308 00 T 1 PPM 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 file: F:\Napo\NMR\500\mkr12803\3\fid expt: <zg30> freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points transmitter freq.: 500.133001 MHz LB: 0.300 GF: 0.0000 time domain size: 65536 points width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt Hz/cm: 198.800 ppm/cm: 0.39749

number of scans: 32

Compound 6d

SpinWorks 4: SM 228 13C 118.916 120.761 123.596 124.815 125.810 126.308 128.512 134.341 142.039 109.633 76.766 77.020 77.274 NH_2 PPM 185 175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 file: F:\Napo\NMR\500\mkr12803\4\fid expt: <zgpg30> freq. of 0 ppm: 125.757802 MHz processed size: 32768 complex points transmitter freq.: 125.772879 MHz LB: 2.000 GF: 0.0000 time domain size: 65536 points

width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt

number of scans: 1024

Hz/cm: 998.025 ppm/cm: 7.93514

Compound 6e

SpinWorks 4: SM 108 1H



Compound 6e





SpinWorks 4: SM 105 1H



Compound 6f







Compound 6g



Compound 6h

4.075

SpinWorks 4: AG 172-1 1H



1 1 PPM 16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.(



width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 24

Hz/cm: 198.800 ppm/cm: 0.39749

Compound 6h

SpinWorks 4: AG 172-1 13C 128.290 132.518 115.709 119.348 144.013 109.259 76.766 77.020 77.274 NH₂ PPM 180 160 140 120 100 80 60 40 20 file: F:\Napo\NMR\500\mkr11502\4\fid expt: <zgpg30> freq. of 0 ppm: 125.757802 MHz processed size: 32768 complex points transmitter freq.: 125.772879 MHz LB: 2.000 GF: 0.0000 time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt Hz/cm: 1007.684 ppm/cm: 8.01193 number of scans: 1024

Compound 6i

SpinWorks 4: AG 332-2 1H



Compound 6i

SpinWorks 4: AG 332-2 13C



file: F:\Napo\NMR\500\mkr11502\6\fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 1024 freq. of 0 ppm: 125.757794 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 1001.245 ppm/cm: 7.96074





Compound 6j



Compound 7a



Compound 7a



Compound 7b



Compound 7b



Compound 7c



Compound 7c



Compound 8a



Compound 8a

SpinWorks 4: SM 102 13C


Compound 8b



Compound 8b

SpinWorks 4: SM 91 13C 32.529 47.348 3222228 NH₂ 1 Т Т PPM 185 175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 file: F:\Napo\NMR\500\mkr10103\4\fid expt: <zgpg30> freq. of 0 ppm: 125.757793 MHz transmitter freq.: 125.772879 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 time domain size: 65536 points Hz/cm: 986.757 ppm/cm: 7.84555 width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 260

Compound 8c







Compound 9a

7.260 7.454 7.454 7.454 7.454 7.484 7.484 7.654 7.654 7.654 7.654 7.654 8.018 8.018 8.018 2.741 L'ILLILLY Me 14.0 13.0 12.0 11.0 10.0 9.0 PPM IY 1.113 1.020 1.869 2.000 3.227 1 1 1 1 1 1 1 1 1 1 PPM 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 file: F:\Napo\NMR\500\mkr10603\7\fid expt: <zg30> freq. of 0 ppm: 500.130023 MHz transmitter freq.: 500.134001 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 time domain size: 65536 points Hz/cm: 199.351 ppm/cm: 0.39860 width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 24

SpinWorks 4: SM 72 1H

Compound 9a



Compound 9b



Compound 9b

SpinWorks 4: SM 74 13C 142.981 120 126 127 127 128 130 76.766 77.020 77.274 .447 · THE PPM 185 175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 file: F:\Napo\NMR\500\mkr10702\10\fid expt: <zgpg30> freq. of 0 ppm: 125.757795 MHz processed size: 32768 complex points transmitter freq.: 125.772879 MHz LB: 2.000 GF: 0.0000 time domain size: 65536 points Hz/cm: 999.635 ppm/cm: 7.94794 width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 1536

Compound 9c



Compound 9c



Compound 9d

SpinWorks 4: SM 68-1 1H



Compound 9d



Compound 10a

SpinWorks 4: AG 327 1H





Compound 10a

SpinWorks 4: ag 327





Compound 10b



Compound 10b



Compound 10c

SpinWorks 4: SM 112 1H



Compound 10c



Compound 10d

SpinWorks 4: SM 96-1 1H



Compound 10d



Compound 11a

SpinWorks 4: sm 225 1H



Compound 11a

SpinWorks 4: SM 225 CDCl3



Compound 11a

SpinWorks 4: SM 225 13C



Compound 11b

SpinWorks 4: sm 115 1H



132

Compound 11b

SpinWorks 4: SM 115-1 CDCl3



Compound 11b



Compound 11c

SpinWorks 4: SM 226 1H



Compound 11c

SpinWorks 4: SM 226 CDCI3



Compound 11c

SpinWorks 4: SM 226 13C



Compound 11d

SpinWorks 4: SM 116 1H



Compound 11d

SpinWorks 4: SM 116 CDCl3







Compound 11d

SpinWorks 4: SM 116 13C



Compound 11e

SpinWorks 4: SM 117 1H



141

Compound 11e

SpinWorks 4: SM 117 CDCl3



	44				****	an dan bahar bahar			******			a e ster dan sê de di se da	1999				****	****
1							1									-		
PPM	80	70	60	50	40	30	20	10	C	-10	-20	-30	-40	-50	-60	-70	-80	-90
file: F:\Na transmitte time doma width: 364 number of	po\NMR\S er freq.: 81 ain size: 32 496.35 Hz f scans: 16	M 117\2 .028303 2768 poi = 450.4	\fid exp 8 MHz nts 148 ppm	ot: <zgj n = 1.11</zgj 	og30> 13780 Ha	z/pt				freq. of 0 processed LB: 2.000 Hz/cm: 64	ppm: 81.0 size: 163 GF: 0.0 1.945 p	026243 84 comp 0000 opm/cm	MHz blex poin 7.92248	ts 8				

Compound 11e

SpinWorks 4: SM 117 13C



file: F:\Napo\NMR\500\gre12303\2(fid expt: <zgpg30> transmitter freq.: 125.772879 MHz time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt number of scans: 256 freq. of 0 ppm: 125.757795 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 Hz/cm: 999.635 ppm/cm: 7.94794

Compound 11f

SpinWorks 4: SM 222 1H



file: F:\Napo\MMR\500\gre12303\5\fid expt: <zg30> transmitter freq.: 500.134001 MHz time domain size: 65536 points width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 32 freq. of 0 ppm: 500.130024 MHz processed size: 65536 complex points LB: 0.300 GF: 0.0000 Hz/cm: 196.597 ppm/cm: 0.39309
Compound 11f



Compound 11f



Compound 11g

SpinWorks 4: SM 221 1H



Compound 11g



Compound 11g



Compound 11h

SpinWorks 4: SM 220 1H



Compound 11h

-16.116

SpinWorks 4: SM 220 CDCl3



Compound 11h

SpinWorks 4: SM 220 13C







Compound 12a

SpinWorks 4: AG 244-1 1H $\begin{array}{c} \textbf{7.141}\\ \textbf{7.154}\\ \textbf{7.154}\\ \textbf{7.1556}\\ \textbf{7.1556}\\ \textbf{7.1556}\\ \textbf{7.3399}\\ \textbf{7.3351}\\ \textbf{7.3405}\\ \textbf{7.4054}\\ \textbf{7.4438}\\ \textbf{8.1064}\\ \textbf{8.106$ 2.257 0.348 N Me PPM 15.0 14.0 13.0 12.0 11.0 10.0 9.0 1.025 1:838 -1.073 5.321 1 1 1 1 1 PPM 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 file: F:\Napo\NMR\500\mkr11302\3\fid expt: <zg30> freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points transmitter freq.: 500.134001 MHz LB: 0.300 GF: 0.0000 time domain size: 65536 points width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt Hz/cm: 198.250 ppm/cm: 0.39639

number of scans: 24

Compound 12a

149.200 $\begin{array}{c} 1117\\1120\\1221\\122\\1226\\126\\126\\126\\126\\126\\123\\133\\133\end{array}$ 76.766 77.020 77.274 17.840 N~N′ Me PPM 180 160 140 120 100 80 60 40 20 file: F:\Napo\NMR\500\mkr11302\4\fid expt: <zgpg30> freq. of 0 ppm: 125.757800 MHz transmitter freq.: 125.772879 MHz processed size: 32768 complex points LB: 2.000 GF: 0.0000 time domain size: 65536 points width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt Hz/cm: 1006.074 ppm/cm: 7.99913 number of scans: 260

SpinWorks 4: mkrtchvan ag 244-2

Compound 12b

3.736 3.856 3.861 2.164 2.170 2.188 111111111111000000000 900 MeO N-Me PPM 15.0 14.0 13.0 12.0 11.0 10.0 9.0 OMe 6.870 4.016 HN .000 .050 .027 .028 PPM 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 8.0 7.6 7.2 6.8 6.4 file: F:\Napo\NMR\500\mkr11302\5\fid expt: <zg30> freq. of 0 ppm: 500.130023 MHz processed size: 65536 complex points transmitter freq.: 500.134001 MHz LB: 0.300 GF: 0.0000 time domain size: 65536 points Hz/cm: 153.643 ppm/cm: 0.30720 width: 12335.53 Hz = 24.6644 ppm = 0.188225 Hz/pt number of scans: 24

SpinWorks 4: AG 243-1 1H

Compound 12b



Competitive experiments between nitrobenzene and p-toluidine





Spectrum







Competitive experiments between nitrobenzene and nitrosobenzene











Spectrum





m/z

Detection of the analogue of hexamethyldisiloxane





