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Acceptorless Dehydrogenative Construction of C=N and C=C bond through Catalytic Aza-Wittig and Wittig Reaction in the Presence of Air-stable Ruthenium Pincer Complex

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The construction of C=N bond has been achieved by the dehydrogenative coupling of alcohol and azide via aza-Wittig type reaction. The reaction is catalyzed by acridine derived ruthenium pincer complex and it does not use any oxidant. The present protocol offers a wide range of substrate scope including aliphatic, aryl or heteroaryl alcohol/azide. This expeditious protocol has also been successfully applied to construct a C=C bond directly from alcohol via dehydrogenative Wittig reaction. Furthermore, the synthesis of structurally important Pyrrolo[1,4]benzodiazepines derivatives has also been achieved by the use of this methodology.

Introduction

Though Staudinger and Meyers first reported the synthesis of phosphazines,[1] it was only after the work of Wittig,[2] the phosphazines have been applied in the construction of C=N bonds and become popular as aza-Wittig reagents. Since then, the Wittig and aza-Wittig reactions have experienced remarkable development and have become a powerful tool for the construction of nitrogen-containing heterocycles.[3] An effective 'borrowing hydrogen' method to synthesize alkane directly from alcohol, through indirect Wittig reaction catalysed by iridium or ruthenium complex, was first developed by William and co-workers.[4] Recently, Milstein and co-workers have shown the selective synthesis of alkene[5a] directly from alcohol through catalytic oxidant-free Wittig reaction[5] or Julia olefination[6] in presence of phosphine based-ruthenium pincer complex. A few years ago, William and co-worker[7] developed a method to convert alcohols into N-alkyl anilines *via* aza-Wittig type reaction[8] in presence of iridium catalyst. However, the selective formation of C=N bond[9] and C=C bond directly from alcohol through catalytic aza-Wittig and Wittig reaction is highly important and would be a significant advance if this could be performed by air stable pincer complexes.

Recently pincer based ruthenium complexes have attracted much attention due to their tremendous application towards the development of environmentally benign, atom-economical sustainable methodologies for the synthesis of useful building blocks.[10-14] Most of these highly active metal complexes involve pyridine,[11] bipyridine,[12] acridine[13] and diethyl amino[14] based phosphine pincer ligands. Although these phosphine based pincer ligands have shown significant applications in the area of homogeneous catalysis, they have encountered well-known drawbacks associated with their air and moisture sensitivities and cost-effectiveness. Thus, the search for new air-stable pincer ligands and their applicability in the catalysis have attracted much attention in the recent time.[15,16,17] In this regard, N-heterocyclic carbenes (NHC) based ligand [18] is found to be one of the best alternatives and even can exhibit a different type of catalytic applicability compared to the phosphine analogue.[16] Very recently, Gusev and co-workers showed the superior activity of $HN(C_2H_4SEt)_2$ ligand over the phosphine analog.[17] Herein we have synthesized new air and moisture stable NNS- and SNS-ruthenium pincer complexes (Fig. 1) and investigated their catalytic applicability towards dehydrogenative aza-Wittig and Wittig-reaction for the construction of C=N and C=C bond.

Results and discussion

First, the acridine-based SNS ligand was prepared by nucleophilic substitution reaction of 4,5-bis(bromomethyl)acridine with the corresponding thiolate.[19]

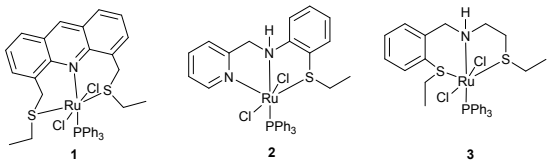

Fig. 1 Ruthenium pincer complexes

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† Electronic Supplementary Information (ESI) available: copies of ^{1}H NMR and ^{13}C NMR spectra of all the compounds. CCDC 1847040, 1865785 and 1865803. For ESI and crystallographic data in CIF or other electronic format see DOI: See DOI: 10.1039/x0xx00000x

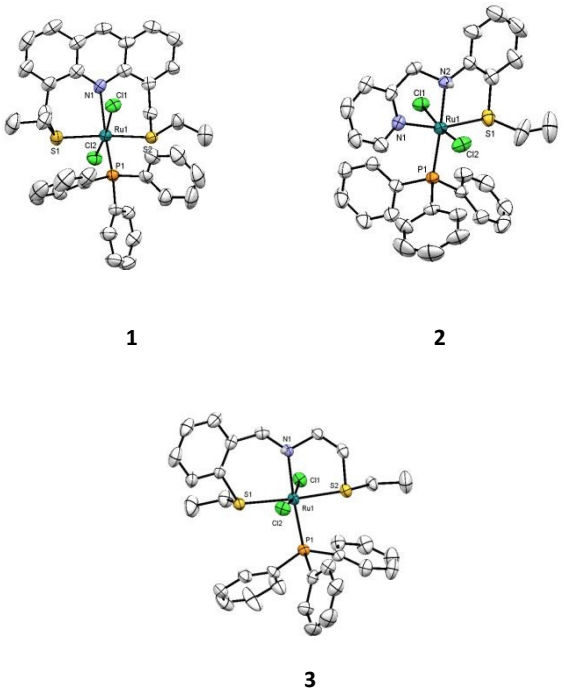
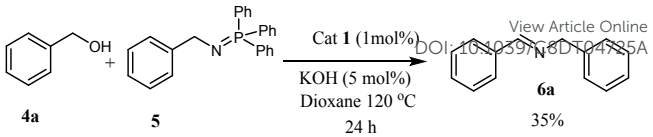


Fig. 2. Molecular structure of complex 1 (thermal ellipsoid 50% probability level), **2** and **3** (thermal ellipsoid 30% probability level).

The complex **1** was synthesized by stirring $RuCl_2(PPh_3)_3$ with the ligand in CH_2Cl_2 for 12 h. The brown colored single crystal suitable for X-ray diffraction was developed by layering the solution of the complex **1** in mixture of dichloromethane and acetonitrile with diethyl ether under air. Crystal structure (Fig. 2) showed the geometry of the Ru center to be pseudo-octahedral type with an elongated Ru-N bond (2.56 Å). This bond length is slightly longer than the one observed in case of acridine PNP based ruthenium pincer complex reported by Milstein (Ru-N: 2.479 Å) [13c] or Hofmann (Ru-N: 2.488 Å) [13d]. The complexes **2** and **3** were prepared by refluxing the $RuCl_2(PPh_3)_3$ with the corresponding tridentate ligand in THF. ^{1}H- and ^{31}P{1H}-NMR spectral analysis reveals that the complex **2** exists as one pure isomer in solution whereas complex **3** exists in solution as an isomeric mixture (60:40) at room temperature. The complex **2** and **3** were crystallized by layering their solution in $CHCl_3$ with diethyl ether and hexane respectively at ambient temperature. The solid-state structure of both **2** and **3** was found to be *trans-(meri-)* dichloride complex (Fig. 2).

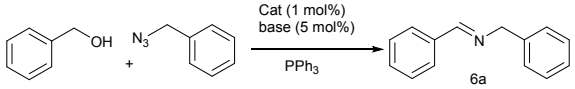
Initially, the catalytic activity of the complexes towards the synthesis of imines directly from alcohol and phosphazines was investigated. To explore the feasibility of the catalytic aza-Wittig reaction, a dioxane solution containing benzyl alcohol (1 mmol) and $PhCH_2N{=}PPh_3$ (1 mmol) was refluxed at 120 °C (bath temperature) for 24 h in presences of 0.01 mmol of complex **1** and 0.05 mmol of KOH under argon atmosphere. 35% (E)-N-benzylidene-1-phenylmethanamine was isolated (Scheme 1). Encouraged by the initial attempt, we thought to prepare the aza-Wittig reagent *in situ*. Thus a mixture of benzyl alcohol (1 mmol), benzyl azide (1 mmol) and triphenyl phosphine (1 mmol) in dioxane (5 mL) was refluxed (Bath temperature 120 °C) in presence of 0.01 mmol of complex **1** and 0.05 mmol of KOH.



Scheme 1 Catalytic oxidant free aza-Wittig reaction in presence of acridine SNS based ruthenium pincer complex.

36% (E)-N-benzylidene-1-phenylmethanamine was obtained after 24 h and 64% benzyl alcohol remained unreacted (Table 1, entry 1). As the reaction showed similar activity, we decided to proceed further through the protocol with *in situ* generated phosphazine. Thus, when toluene was used as a solvent, 46% desired imine was formed only after 18 h (Table 1, entry 2). Upon increasing the reaction temperature (bath temperature 135 °C), the yield of the desired (E)-N-benzylidene-1-phenylmethanamine was improved to 91% with the complete consumption of benzyl alcohol as indicated by NMR. Pure imine was obtained (87%) after column chromatography. Under the similar reaction conditions, complex **2** or **3** gave an inferior yield of the desired imine (Table 1, entries 4 and 5). However, when 0.05 mol% of catalyst **1** was used, keeping other conditions unaltered, only 70% desired imine was obtained after 36 h. The effect of the base has been studied and KOH is found more effective than ^{t}BuOK or K_2CO_3 (Table 1**,** entries 7 and 8). The catalyst failed to give any desired imine without a catalytic amount of base. The reaction under air gave 83% yield of the desired imine after 24 h, which was slightly lower compared to the inert reaction condition (Table 1, entry 15).

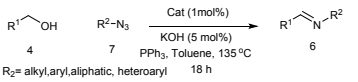
Table 1 Optimization of the reaction condition for the catalytic aza-Wittig reaction.[a]

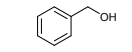
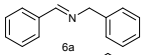
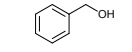
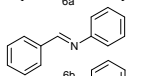
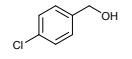
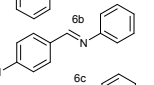
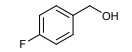
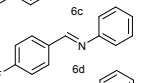
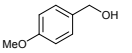
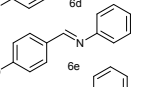
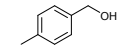
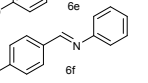
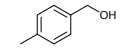
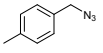
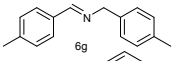
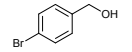
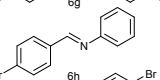
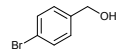
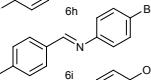
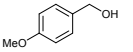
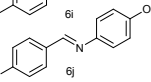
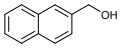
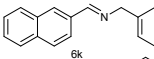
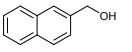
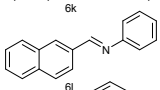
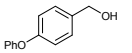
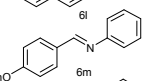


Entry	Cat.	Base	Solvent	Bath temperature (°C)	Time (h)	Yield[b] [%]
1	1	KOH	Dioxane	120	24	36
2	1	KOH	Toluene	120	18	46
3	1	KOH	Toluene	135	18	91
4	2	KOH	Toluene	135	18	30
5	3	KOH	Toluene	135	18	60
6	1	-	Toluene	135	18	trace
7	1	^{t}BuOK	Toluene	135	18	52
8	1	K_2CO_3	Toluene	135	18	43
9	1	KOH	THF	76	24	10
10	1	KOH	Et_2O	55	24	5
11	1	KOH	Toluene	135	4	52
12[c]	1	KOH	Toluene	135	36	70
13	[(p-Cymene) $RuCl_2]_2$	KOH	Toluene	135	24	27
14	$RuCl_2(PPh_3)_3$	KOH	Toluene	135	24	30
15[d]	1	KOH	Toluene	135	24	83

[a] Reaction conditions: Benzyl alcohol (1 mmol), benzyl azide (1 mmol), PPh_3 (1mmol), solvent (5 mL). [b] NMR yield using dioxane or CH_3CN as internal standard. [c] 0.5 mol% catalyst loading. [d] under air

Table 2 Catalytic Aza-Wittig type reaction directly from alcohol and azide.[a]



Entry	Alcohol	Azide	Product	Yield[b] (%)
1			 6a	91(87)
2			 6b	85(80)
3			 6c	90(85)
4			 6d	87(80)
5			 6e	87(84)
6			 6f	(86)
7			 6g	(84)
8			 6h	(80)
9			 6i	(82)
10			 6j	(85)
11			 6k	(90)
12			 6l	(88)
13			 6m	91
14[c]			6n	65(55)
15			6o	(54)
16[d]			6p	(75)
17			6q	(74)
18			6r	(80)
19			6s	(79)
20			6t	(60)
21			6u	(65)
22[e]			6v	83(68)
23			6w	(65)

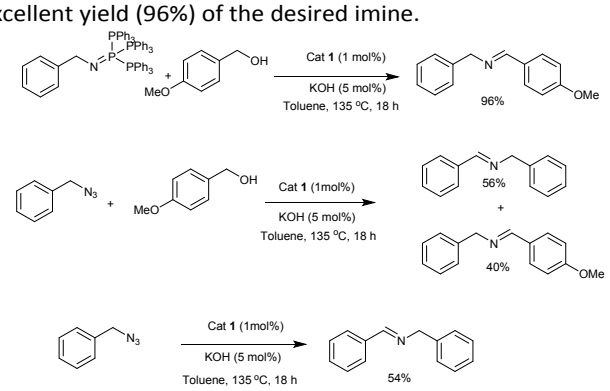
[a] Reaction conditions: Alcohol (1 mmol), benzyl azide (1 mmol), PPh_3 (1mmol), Toluene (5 mL), Cat **1** (1 mol%), KOH (5 mol%). [b] NMR yield, the yield in the parenthesis-isolated yield. [c] 48 h. [d] Phenyl azide (2 mmol), PPh_3 (2 mmol). [e] 24 h.

Under the similar condition, $[(p\text{-Cymene})RuCl_2]_2$ or $RuCl_2(PPh_3)_3$ gave substantially lower yield of the desired product (Table 1, entries 13-14).

To study the scope of the reaction with respect to aromatic azides, the optimized reaction conditions were applied to the reaction of benzyl alcohol and phenyl azide. 85% yield of the desired (E)-N-benzylidenebenzenamine was obtained after 18 h (Table 2, entry 2). Encouraged by this result, we wanted to expand the scope of the reaction. Thus, the reactions of differentially substituted benzyl alcohol with variously substituted aromatic or benzyl azide were studied. It has been observed that both electron-withdrawing and electron-donating substituents in the aromatic ring gave excellent yield in this catalytic dehydrogenative aza-Wittig reaction methodology. Exploring the scope of the reaction with regard to secondary alcohol, 1-Phenylethanol was reacted with phenyl azide. The yield of the desired imine was 65% (Table 2, entry 14) even after 48 h, which is probably due to the lower reactivity of ketones towards the aza-Wittig reaction. In this reaction, 35% of acetophenone was also observed. Secondary azide, reacting with benzyl alcohol also gave moderate yield (54%). Delightfully, no dehalogenation reaction was observed when 4-chlorobenzyl alcohol or 4-bromobenzyl alcohol was used as substrates. It is interesting to note that 75% of (E)-N-(2-aminobenzylidene)benzenamine were achieved when 2-amino benzyl alcohol was reacted with 2 equivalent of phenyl azide and triphenyl phosphine (Table 2, entry 16). 2-Nitrobenzylzlcohol and phenyl azide gave (E)-N-(2-nitrobenzylidene) benzenamine in 74% yield. A small amount (15%) of (E)-N-(2-aminobenzylidene) benzenamine was also obtained due to the reduction of the nitro group under the reaction condition (Table 2, entry 17). The reaction methodology was successfully extended to heterocyclic alcohols; both 2-thiophenemethanol and 2-pyridinemethanol gave moderate to good yields of the desired imine under the optimized reaction conditions. To expand the scope of the reaction with regard to aliphatic alcohols or aliphatic azide, the optimized reaction conditions were applied to the reaction of hexanol with hexyl azide. An excellent yield (83%) of the desired imine was obtained only after 24 h (Table 2, entry 22). Similarly, octanol reacted smoothly with benzyl azide to give a mixture of (E)-N-octyl-1-phenylmethanimine (71%) and (E)-N-benzyloctan-1-imine (14%). Here the initially formed (E)-N-benzyloctan-1-imine was isomerized to form the more stable (E)-N-octyl-1-phenylmethanimine under the reaction conditions and has been isolated (65%).

To understand whether the reaction is going through the aza-Wittig type reaction pathway or through the *in situ* formation of amine [20] by hydrogen auto-transfer reaction, we performed the reaction of 4-methoxy benzyl alcohol and benzyl azide in the absence of PPh_3. Only 40 % desired imine was observed together with 56% of (E)-N-benzylidene-1-phenylmethanamine (Scheme 2). Next, we treated the benzyl azide with the catalyst and base, under the same conditions and we observed the formation of (E)-N-benzylidene-1-phenylmethanamine (54%).[21] In sharp contrast, the reaction of (benzylimino)triphenylphosphorane with 4-methoxybenzyl

alcohol under the optimized reaction condition gave an excellent yield (96%) of the desired imine.



Scheme 2. Control experiments

Thus, we can conclude that the reaction was proceeding mainly through the aza-Wittig type reaction pathway via the rapid *in situ* formation of the aza-Wittig reagent.

It was of interest to us to expand the catalytic activity of the Ru-complex towards the oxidant-free Wittig reactions of alcohols for the construction of C=C bond. Table **3** summarizes the ruthenium catalysed olefination reaction between alcohol and Wittig-salt. The reaction works well with different benzylic or heteroaryl alcohols and in most of the cases the E isomer is the major product together with a very small amount of Z product (1-2 %). The reaction is slower and moderate yield was obtained when aliphatic alcohol or aliphatic phosphonium salt was used as substrates (Table 3, entries 11 and 12). ^{1}H NMR analysis of the crude mixture of the reaction between butyltriphenylphosphonium bromide with benzyl alcohol and 1-phenyl ethanol showed that E:Z isomers were formed in 30:70 ratio.

Finally, we tried to apply our methodology to synthesize structurally important heterocyclic compounds. There is a wide range of biologically important compounds having pyrrolo[1,4]benzodiazepines (PBDs) as a core structural unit.[22] Thus, we wanted to apply our methodology to synthesize PBDs. Therefore we have synthesized (S)-(2-azidophenyl)(2-(hydroxymethyl) pyrrolidin-1-yl)methanone **12** by the reaction of 2-azidobenzoyl chloride and L-prolinol. When a toluene solution containing 1:1 mixture of (S)-(2-azidophenyl)(2-(hydroxymethyl) pyrrolidin-1-yl)methanone and triphenylphosphine was refluxed in the presence of 1 mol% cat **1**, 5 mol% KOH, (S)-1,2,3,10,11,11a-hexahydro-5H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one was obtained after 20 h (Scheme 2). Interestingly no racemization was observed as the reaction was performed under almost neutral reaction condition. The imine formed was hydrogenated *in situ* to the corresponding amine **13**. Thus to obtain (S)-1,2,3,11a-tetrahydro-5H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one, **14** we have treated (S)-(2-azidophenyl)(2-(hydroxymethyl)pyrrolidin-1-yl) methanone, **12** with equimolar amount of triphenylphosphine in the presence of 0.01 mmol of KOH and diphenyl acetylene as H_2 acceptor. Gratifyingly, good yield of the desired product was obtained.

Table 3 Catalytic Wittig type reaction directly from alcohol and Wittig salt.

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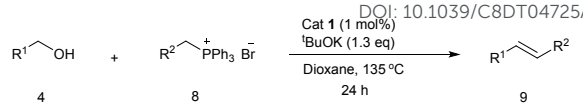
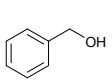
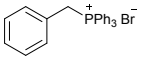
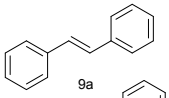
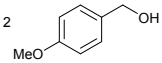
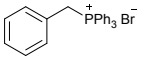
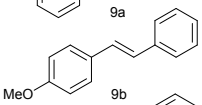
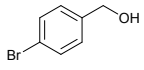
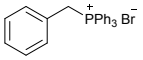
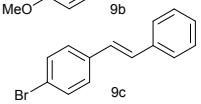
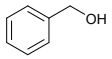
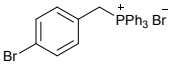
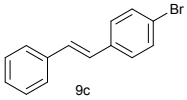
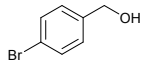
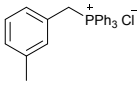
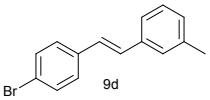
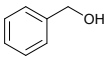
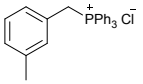
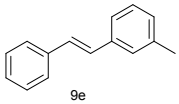
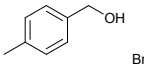
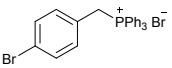
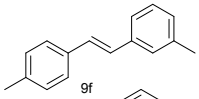
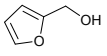
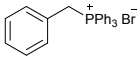
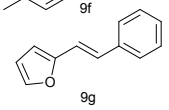
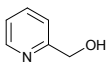
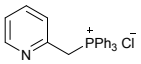
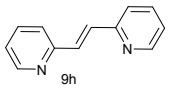
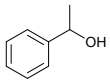
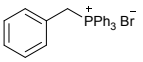
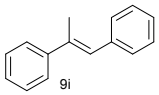
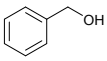
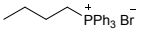
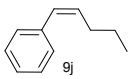
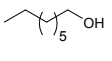
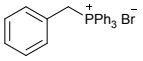
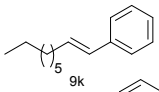
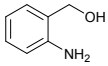
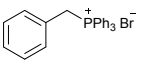


R_1, R_2= aryl, alkyl, heteroaryl

Entry	Alcohol	Wittig Salt	Product	Yield (%)[b]
1			 9a	75
2			 9b	86
3			 9c	88
4			 9c	90
5			 9d	80
6			 9e	83
7			 9f	81
8			 9g	76
9			 9h	60
10[c]			 9i	40
11[d]			 9j	54
12[e]			 9k	45
13[f]			9l	75

[a] Reaction conditions: Alcohol (1 mmol), phosphonium salt (1.2 mmol), dioxane (5 mL), Cat **1** (1 mol%), ^{t}BuOK (1.3 mmol). [b] Isolated yield, [c] E/Z 54:46, acetophenone left (35%). [d] E/Z 30:70, [e] 48 h, [f] Wittig salt (2 mmol).

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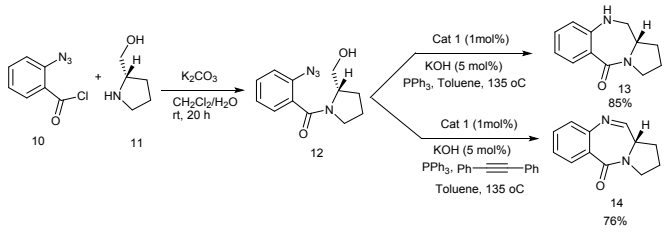

Scheme 3 Application of catalytic aza-Wittig reaction to synthesize benzodiazepines derivatives.

Conclusions

In conclusion, we have developed a catalytic route for the formation of C=N bond directly from alcohol and azide. The reaction strategy involves in situ preparation of aza-Wittig reagent and dehydrogenative coupling of aza-Wittig reagent with alcohol in presence of acridine derived air stable ruthenium pincer complex. This reaction showed a wide range of substrate scope. This efficient method has also been applied to the olefination reaction of alcohol and phosphonium salt. As a highlight, we successfully applied our protocol devising the synthesis of structurally important Pyrrolo[1,4] benzodiazepines.

Experimental section

General Informations: Unless otherwise mentioned, all the chemicals were purchased from common commercial sources and used as received. $RuCl_2(PPh_3)_3$ was purchased from Sigma-Aldrich. All solvents were dried by using standard procedure.[23] Solvent such as toluene were predried using CaH_2 and dried over Na with benzophenone indicator. The preparation of catalyst was carried out under argon atmosphere with freshly distilled dry THF or dichloromethane. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600 and 400 spectrometers were used to record ^{1}H, ^{13}C NMR and ^{31}P NMR. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane; spin−spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. IR spectra were recorded on Perkin Elmer Instrument at room temperature making KBr pellet. MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520. X-ray crystallographic data were collected using Agilent Super Nova (Single source at offset, Eos) diffractometer and Bruker Nonius SMART APEX CCD diffractometer equipped with a graphite monochromator. Data refinement and cell reduction were carried out by CrysAlisPro. Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F2 using SHELXL-97. All of the non-H atoms were refined anisotropically. SQUEEZE was used to reduce contribution of solvent molecule (diethylether/ acetonitrile) to the overall electron density. Column chromatography was done with SRL Silica gel 100-200 mesh. Organic azides should be handled under proper safety precautions such as i) chlorinated solvent should not be used as reaction media ii) organic azides should not be distilled iii) azides should be kept in dark at low temperature. [24]

Synthesis of 4,5-bis(ethylthiomethyl)acridine: NaOH (0.47g, 12 mmol) was taken in 5 mL of water and the resulting NaOH solution was added dropwise to a solution of ethanethiol (0.62g, 10 mmol) in ethanol (50 mL). Then the resulting mixture was refluxed for 30 min and then 4,5-bis(bromomethyl)acridine (1.8 g, 5 mmol) in tetrahydrofuran (10 mL), was added to it. After that, the reaction mixture was refluxed for another 2 h. After cooling to room temperature, the reaction mixture was poured into distilled water (100 mL) and extracted with 80 mL of chloroform. The extract was washed with water (3 × 25 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure on a rotary evaporator and the crude mixture was purified by silica gel column chromatography using hexane: ethyl acetate (9.5:0.5) to afford the pure ligand as a yellow solid (Yield: 1.3 g, 80%. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.71 (s, 1H), 7.89 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.76 (dd, *J* = 6.9, 1.3 Hz, 2H), 7.48 (dd, *J* = 8.4, 6.7 Hz, 2H), 4.60 (s, 4H), 2.60 (q, *J* = 7.4 Hz, 4H), 1.31 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 146.52, 137.76, 136.42, 129.40, 127.33, 126.89, 125.54, 31.80, 26.55, 14.76. HRMS (ESI) calcd for $C_{19}H_{21}NS_2$ [M + H]$^+$ 328.1194, Found 328.1192.

Synthesis of (2-(ethylthio)-N-(pyridin-2-ylmethyl)aniline: Pyridine-2-carboxaldehyde (0.721 g, 6.7 mmol) and 2-(ethylthio)aniline (1.0 g, 6.5 mmol) were dissolved in dry MeOH (25 mL) and the resulting mixture was refluxed for 24 h. After cooling the reaction, $NaBH_4$ (1.228 g, 32.5 mmol) was added portion wise in stirring condition at 0 °C and the stirring was continued for 6 hours at room temperature. Then the solvent was evaporated and 25 ml water was added and neutralized by acetic acid. After that, it was extracted by CH_2Cl_2 (40 mL×3) and the combined organic phase was dried over Na_2SO_4. Then, the solvent was evaporated to get the crude product, which was purified further by silica gel column chromatography using 10-30 % ethyl acetate in hexane. Brown liquid (Yield 1.308 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62-8.58 (m, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.20-7.10 (m, 2H), 6.64 (td, *J* = 7.5, 1.3 Hz, 1H), 6.54 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.02 (brs, 1H), 4.54 (s, 2H), 2.79 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.89, 149.43, 148.87, 136.78, 136.23, 130.01, 122.15, 121.23, 117.88, 117.09, 110.54, 49.44, 29.18, 15.05. HRMS (ESI) calcd for $C_{14}H_{16}N_2S$ [M + H]$^+$: 245.1112; found, 245.1119.

Synthesis of 2-(ethylthio)-N-(2-(ethylthio)benzyl)ethan-1-amine: A solution of 2-(ethylthio)benzaldehyde (2.127g, 12.79 mmol) and 2-(ethylthio)ethan-1-amine compound (1.282 g, 12.18 mmol) in 45 mL dry MeOH was refluxed for overnight. Then, the reaction mixture was cooled to room temperature and $NaBH_4$ (1.154 g, 30.5 mmol) was added portion wise in stirring condition at 0 ˚C and the stirring was continued for 6 hours at room temperature. Then the solvent was evaporated and 60 ml water was added and neutralized by acetic acid. The

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aqueous layer was then extracted with CH_2Cl_2 (80 mL × 3) and the combined organic phase was dried over Na_2SO_4. Then the solvent was evaporated to get the crude product, which was purified further by silica gel column chromatography using 10-30 % ethyl acetate in hexane. White solid. (Yield 2.958 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.7, 2.2 Hz, 1H), 7.45-7.42 (m, 1H), 7.36 (ddt, *J* = 9.3, 7.7, 1.5 Hz, 1H), 7.32-7.27 (m, 1H), 4.37 (s, 2H), 3.52-3.43 (m, 1H), 3.08 (t, *J* = 7.3 Hz, 2H), 3.03-2.93 (m, 4H), 2.48 (q, *J* = 7.4 Hz, 2H), 1.33 (td, *J* = 7.3, 1.5 Hz, 3H), 1.22 (td, *J* = 7.4, 0.9 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 137.03, 131.87, 131.08, 130.65, 130.26, 127.39, 48.39, 45.60, 29.01, 27.69, 25.88, 14.76, 14.35. HRMS (ESI) calcd for $C_{13}H_{22}NS_2$ [M + H]$^+$: 256.1194; found, 256.1197.

Synthesis of acridine derived (SNS) ruthenium pincer complex 1: To a solution of 4,5-bis(ethylthiomethyl)acridine (0.235 g, 0.721 mmol) in dry CH_2Cl_2 (10 mL) was added a solution of $RuCl_2(PPh_3)_3$ (0.553g, 0.576 mmol) in dry CH_2Cl_2 (10 mL) and stirred 12 h at room temperature under argon. The solvent was evaporated and the brown solid was washed with diethyl ether several times and dried under vacuum, resulting in the pure complex as a brown solid (Yield 0.372 g, 85%). The single crystal was grown by slow diffusion of diethyl ether in the $CHCl_3$/CH_3CN solution of the complex.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.02 (s, 1H), 8.10 (d, *J* = 8.04 Hz, 2H), 7.77 (t, *J* = 9 Hz, 6H), 7.72 (d, *J* = 6.24 Hz , 2H), 7.50 (t, *J* = 7.32 Hz , 3H), 7.35-7.29 (m, 8H), 5.69 (d, *J* = 13.02 Hz, 2H), 4.29 (d, *J* = 13.08 Hz, 2H), 1.53-1.47 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 6H), 0.60-0.54 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 149.74, 143.22, 134.90 (d, *J* = 8.37 Hz), 134.62 (d, *J* = 46.48 Hz), 134.32, 130.85, 130.73, 129.35, 128.63, 127.25 (d, *J* = 9.36 Hz), 124.34, 35.54, 22.49, 12.46; ^{31}P{^{1}H} δ (ppm) 54.84; Anal. Calc. for $C_{37}H_{36}Cl_2NPRuS_2$ C, 58.34; H, 4.76; N, 1.84 found C, 58.35; H, 4.71; N, 1.84; HRMS (ESI) calcd for $C_{37}H_{36}Cl_2NPRuS_2$ [M - Cl]$^+$: 726.0759; found, 726.0757.

Synthesis of ruthenium pincer complex 2: Ligand, 2-(ethylthio)-N-(pyridin-2-ylmethyl)aniline (0.030g, 0.13 mmol) was taken in 1 mL dry THF and was added dropwise to the solution of $[RuCl_2(PPh_3)_3]$ (0.107g, 0.11 mmol) in 4 mL degassed dry THF under argon. Then, it was refluxed for 6 hours. After cooling it down to the room temperature, 20 ml diethyl ether was added. The resulting precipitate was thoroughly washed with diethyl ether and dried under vacuum to get brown solid (Yield 0.046g, 83%). The single crystal was grown by slow diffusion of diethyl ether in the $CHCl_3$ solution of the complex.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.68 (d, *J* = 5.6 Hz, 1H), 7.70 (q, *J* = 8.4, 7.1 Hz, 6H), 7.61 – 7.56 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.30 (m, 12H), 6.91 (t, *J* = 6.6 Hz, 1H), 5.46 (t, *J* = 12.6 Hz, 1H), 5.17-5.13 (m, 1H), 2.71-2.66 (m, 1H), 2.41-2.36 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 163.13, 157.24, 146.37, 140.09, 135.67 (d, *J*= 10.5 Hz), 135.45, 134.92 (d, *J* = 9.8 Hz), 133.77, 129.82, 129.24, 127.67 (d, *J* = 9.1 Hz), 127.58, 124.33, 123.47, 121.58, 57.01, 35.04, 13.49. ^{31}P{^{1}H} δ (ppm) 50.15; Anal. Calc. for $C_{32}H_{31}Cl_2N_2PRuS$ C, 56.64; H, 4.60; N, 4.13 found C, 56.69; H, 4.60; N, 4.12; HRMS (ESI) calcd for $C_{32}H_{31}Cl_2N_2PRuS_2$ [M - Cl]$^+$: 643.0678; found, 643.0650.

Synthesis of ruthenium pincer complex 3: Ligand, 2-(ethylthio)-N-(2-(ethylthio)benzyl)ethan-1-amine (0.058 g, 0.22 mmol) was taken in 3 mL dry THF and was added dropwise to the solution of $[RuCl_2(PPh_3)_3]$ (0.181g, 0.18 mmol) in 5 mL degassed dry THF. Then, it was refluxed for 6 hours under argon atmosphere. After cooling it down to the room temperature, the solvent was evaporated to obtain the residue, which was thoroughly washed with diethyl ether and dried under vacuum to get yellow solid (Yield 0.103g, 81%). The single crystal was grown by slow diffusion of hexane in the $CHCl_3$ solution of the complex.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1st dias. (Cis-isomer) (60%) 7.77-7.19 (m, 19H), 5.10 (t, *J* = 10.7 Hz, 1H), 3.94 (t, *J* = 11.8 Hz, 1H), 3.67-2.10 (m, 7H), 1.5-0.8 (m, 5H), 0.63 (t, *J* = 7.1 Hz, 3H). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2nd dias. (trans isomer) (40%) 7.77-7.19 (m, 19H), 4.89 (t, *J* = 10.8 Hz, 1H), 4.22 (t, *J* = 11.2 Hz, 1H), 3.67-2.10 (m, 7H), 1.5-0.8 (m, 5H), 0.69 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 1st+2nd dias. 140.75, 139.95, 136.94, 136.56, 136.29, 135.96, 135.90, 134.77, 134.67, 132.19, 131.06, 130.33, 130.16, 129.07, 128.75, 128.70, 127.51, 127.46, 127.43, 127.37, 54.97, 54.66, 51.89, 51.51, 35.57, 32.01, 31.04, 30.73, 30.03, 29.54, 26.00, 12.95, 12.88, 12.67. ^{31}P{^{1}H} δ (ppm) 45.23 and 43.41. Anal. Calc. for $C_{31}H_{36}Cl_2NPRuS_2$ C, 53.99; H, 5.26; N, 2.03 found C, 53.53; H, 5.38; N, 2.22; HRMS (ESI) calcd for $C_{31}H_{36}Cl_2NPRuS_2$ [M - Cl]$^+$: 654.0759; found, 654.0759.

Representative procedure for the catalytic aza-Wittig type reaction of alcohol and azide.

In a two necked round bottom flask, equipped with a condenser, complex (0.01 mmol), KOH (0.05 mmol) and dry toluene (3 ml) were added under argon atmosphere. To this suspension alcohol (1 mmol), azide (1 mmol) and PPh_3 (1 mmol) in dry toluene (2 ml) were subsequently added under argon atmosphere. The solution was refluxed to 135 ˚C (bath temperature) with stirring under argon atmosphere for the specified time. Then the reaction mixture was allowed to cool to the room temperature and was filtered through celite. After that, the solvent was removed and 1,4-dioxane or acetonitrile was added as internal standard to the reaction mixture and take ^{1}H NMR in $CDCl_3$ to get the NMR yield. Purification was done by column chromatography over silica gel using 0.5:10 mixture of ethyl acetate-hexane containing 2 % triethylamine as eluent to afforded pure imine product. Characterization data of the products are given below.

Representative procedure for the catalytic Wittig type reaction of alcohol and phosphonium salt.

In a two-necked round bottom flask, equipped with a condenser, complex (0.01 mmol), alcohol (1 mmol), phosphonium salt (1.2 mmol), ^{t}BuOK (1.3 mmol) and dry dioxane (5 ml) were added under argon atmosphere. The solution was then refluxed to 135 ˚C (bath temperature) with stirring under argon for the specified time. Then the reaction mixture was allowed to cool to the room temperature and was filtered through celite and the solvent was removed. The crude product was analyzed by ^{1}H NMR to determine the E/Z. Purification was done by column chromatography over silica gel using hexane or 0.5:10 mixture of ethyl acetate-hexane as eluent to afforded pure alkene product.

Synthesis of (S)-1,2,3,10,11,11a-hexahydro-5H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one (13). In a two-

necked round bottom flask, the complex (0.005 mmol), (S)-(2-azidophenyl)(2-(hydroxymethyl)pyrrolidin-1-yl)methanone (0.5 mmol) (8), PPh_3 (0.5 mmol), KOH (5 mol%) and dry toluene (5 ml) were placed under Argon atmosphere. The mixture was stirred at 135 ˚C for 18 h under argon atmosphere. After that, the reaction mixture was cooled to room temperature and filtered through celite. Then the solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography (silica gel; 75% ethyl acetate and hexane).

(S)-1,2,3,11a-tetrahydro-5H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one (14). In a two-necked round bottom flask, the complex (0.005 mmol), (S)-(2-azidophenyl)(2-(hydroxymethyl)pyrrolidin-1-yl)methanone (0.5 mmol) (8), PPh_3 (0.5 mmol), KOH (5 mol %), diphenylacetylene (0.75 mmol) and dry toluene (5 ml) were placed under argon atmosphere. The mixture was stirred at 135 ˚C for 18 h under argon atmosphere. After the reaction finished, the reaction mixture was cooled to room temperature and filtered through celite. Then the solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography (silica gel; 75% ethyl acetate and hexane).

N-benzylidene-1-phenylmethanamine ***(6a)***.[25] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.43 (s, 1H), 7.83-7.81 (m, 2H), 7.46-7.45 (m, 3H), 7.38-7.37 (m, 4H), 7.31-7.27 (m, 1H), 4.83 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 162.14, 139.40, 136.27, 130.90, 128.73, 128.62, 128.41, 128.11, 127.12, 65.19.

N-benzylideneaniline ***(6b)***.[26] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.49 (s, 1H), 7.95-7.94 (m, 2H), 7.52- 7.51 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.29-7.24 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 160.57, 152.21, 136.33, 131.52, 129.28, 128.94, 128.91, 126.07, 121.00.

N-(4-chlorobenzylidene)aniline ***(6c)***.[26] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.34 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.34-7.31 (m, 2H), 7.18-7.13 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 158.98, 151.80, 137.51, 134.83, 130.09, 129.34, 129.22, 126.34, 120.98.

N-(4-Fluorobenzylidene)aniline ***(6d)***.[27] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.33 (s, 1H), 7.83-7.81 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.17-7.14 (m, 1H), 7.12 (dd, *J* = 7.3 Hz, 1.1 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 164.82(d, *J* = 250 Hz), 158.95, 151.97, 132.70 (d, *J* = 3.03 Hz), 130.91 (d, *J* = 8.74 Hz), 129.31, 126.15, 120.96, 116.06 (d, *J* = 21.85 Hz).

N-(4-methoxybenzylidene)aniline ***(6e)***.[25] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.42 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.43 (t, *J* = 8.3 Hz, 2H), 7.26-7.25 (m, 3H), 7.02 (d, *J* = 8.8 Hz) 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 162.29, 159.75, 152.40, 130.57, 129.31, 129.17, 125.63, 120.95, 114.24, 55.45.

N-(4-bromobenzylidene)aniline ***(6h)***.[26] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.42- 7.38 (m, 2H), 7.22-7.20 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 158.99, 151.81, 137.52, 134.83, 130.10, 129.34, 129.22, 126.34, 120.99.

4-Bromo-N-[(4-bromophenyl)methylene]benzenamine ***(6i)***.[28] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 159.47, 150.68, 134.93, 132.40, 132.25, 130.34, 126.36, 122.70, 119.78.

4-Methoxy-N-[(4-methoxyphenyl)methylene]benzenamine ***(6j)***.[26] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.41 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 162.08, 158.07, 158.03, 145.34, 130.36, 129.55, 122.19, 114.44, 114.25, 55.60, 55.53.

N-(2-Naphthalenylmethylene)benzenemethanamine ***(6k)***.[29] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.53 (s, 1H), 8.07- 8.04 (m, 2H), 7.90-7.83 (m, 3H), 7.52-7.50 (m, 2H), 7.39-7.24 (m, 5H), 4.88 (s, 2H) ; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 162.18, 139.44, 134.89, 133.98, 133.22, 130.25, 128.75, 128.66, 128.61, 128.17, 128.01, 127.30, 127.16, 126.59, 124.08, 65.27

N-(2-Naphthalenylmethylene)benzenamine ***(6l)***.[26] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 1H), 8.20 -8.16 (m, 2H), 7.95- 7.87 (m, 3H), 7.56 -7.53 (m, 2H), 7.44 -7.40 (m, 2H), 7.28-7.25 (m, 3H) ; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 160.52, 152.26, 135.18, 134.10, 133.25, 131.40, 129.34, 128.93, 128.83, 128.09, 127.70, 126.77, 126.15, 124.07, 121.08.

N-(1-Phenylethylidene)benzenamine ***(6n)***.[30] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, *J* = 8.1 Hz, 2H), 7.47-7.44 (m, 3H), 7.35 (t, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 2H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 165.64, 151.83, 139.63, 130.61, 129.09, 128.51, 127.31, 123.36, 119.52, 17.54.

N-Benzylidene-α-methylbenzylamine ***(6o)***.[31] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (s, 1H), 7.78-7.76 (m, 2H), 7.43-7.42 (m, 2H), 7.39-7.38 (m, 3H), 7.33 (t, *J* = 5.1 Hz, 2H), 7.23 (t, *J* = 4.8 Hz, 1H), 4.53 (q, *J* = 6.6 Hz, 1H), 1.59 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): 159.62, 145.25, 136.45, 130.69, 128.64, 128.53, 128.37, 126.94, 126.74, 69.87, 24.96.

N-[(2-Aminophenyl)methylene]benzenamine ***(6p)***:[32] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H), 7.34-7.25 (m, 3H), 7.16- 7.11 (m, 4H), 6.66 (t, *J* = 7.88 Hz, 2H); 6.46 (brs, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 163.29, 152.07, 148.95, 134.53, 131.96, 129.30, 125.67, 121.10, 117.81, 116.40, 115.94. HRMS (ESI) calcd for $C_{14}H_{13}N_2$ $[M + H]^+$: 197.1079; found, 197.1073.

N-[(2-Nitrophenyl)methylene]benzenamine ***(6q)***.[33] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.95 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H) 7.75 (t, *J* = 8.2 Hz, 1H), 7.64-7.60 (m, 1H), 7.43 (t, *J* = 7.92 Hz, 2H), 7.30- 7.26 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 156.02, 151.22, 149.47, 133.75, 131.34, 130.28, 129.91, 129.44, 127.08, 124.70, 121.34.

3-Hydroxybenzalaniline ***(6r)***.[34] White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.37 (s, 1H), 7.46 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ (ppm) 161.49, 156.62, 151.38, 137.14, 130.22, 129.39, 126.44, 122.31, 121.13, 119.50, 114.51. HRMS (ESI) calcd for $C_{13}H_{11}NO$ $[M + H]^+$: 198.0919; found, 198.0911.

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N-(2-Thienylmethylene)benzenemethanamine ***(6s)***.[26] Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.50 (s, 1H), 7.45-7.37 (m, 6H), 7.35-7.32 (m, 1H), 7.12 (t, *J* = 6.6 Hz, 1H), 4.85 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): 155.17, 142.44, 139.07, 130.67, 129.04, 128.49, 128.02, 127.37, 127.01, 64.42.

N-(2-Pyridinylmethylene)benzenemethanamine ***(6t)***.[35] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.66 (d, *J* = 6 Hz, 1H), 8.56 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.75-7.62 (m, 2H), 7.42-7.33 (m, 2H), 7.18 (m, 1H), 5.01 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 164.08, 158.85, 154.51, 149.63, 149.50, 136.83, 136.70, 125.07, 122.51, 122,28, 121.64, 66.70.

N-(2-Pyridinylmethylene)benzenamine ***(6u)***.[36] Light Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.64 (d, *J* = 6.5 Hz, 1H), 8.53 (s, 1H), 8.13 (d, *J* = 11.8 Hz, 1H), 7.74 (t, *J* = 11.5 Hz, 1H), 7.36-7.28 (m, 3H), 7.23-7.19 (m, 3H) ; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 160.77, 154.70, 151.10, 149.84, 136.80, 129.36, 126.85, 125.27, 122.02, 121.23.

N-Hexyllidenehexane-1-amine ***(6v)***.[25] Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (s, 1H), 3.31 (t, *J* = 6.9 Hz, 3H), 2.20-2.18 (m, 2H), 1.56-1.51 (m, 2H), 1.50-1.46 (m, 2H), 1.30-1.25 (m, 10H), 0.88-0.84 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 165.02, 61.53, 35.90, 31.72, 31.58, 30.82, 27.00, 25.93, 22.73, 22.57, 14.16, 14.08.

N-octyl-1-phenylmethanimine ***(6w)***.[37] Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 1H), 7.73-7.71 (m, 2H), 7.41-7.39 (m, 3H), 3.60 (t, *J* = 8.0 Hz, 2H), 1.71-1.68 (m, 2H), 1.33-1.27 (m, 10H), 0.88 (t, *J* = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 160.85, 130.56, 128.70, 128.15, 61.97, 31.99, 31.06, 29.56, 29.41, 27.50, 22.80, 14.24.

E-stilbene ***(9a)***.[38] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58-7.56 (m, 4H), 7.44-7.40 (m, 4H), 7.34-7.31 (m, 2H), 7.17 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 137.49, 128.86, 128.82, 127.75, 126.66.

E-1-Methoxy-4-styryl-benzene ***(9b)***.[38] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (d, *J* = 5.1 Hz, 2H), 7.38 (d, *J* = 5.3 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.17-7.15 (m, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 159.39,137.75.130.24, 128.78, 128.31, 127.84, 127.35, 126.71, 126.37, 114.24, 55.47.

E-1-Bromo-4-styryl-benzene ***(9c)***.[39] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44-7.40 (m, 4H), 7.31-7.2 (m, 4H), 7.22-7.18 (m, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.95 (d, *J* = 16.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 137.11, 136.45, 131.93, 129.59, 128.89, 128.12, 128.05, 127.56, 126.71, 121.46.

E-1-(4-bromostyryl)-3-methylbenzene ***(9d)***.[40] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J*= 7.5 Hz, 2H), 7.30-7.17 (m, 5H), 7.03-7.01 (m, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 138.45, 137.06, 136.56, 131.92, 129.72, 128.89, 128.78, 128.09, 127.41, 127.36, 123.92, 121.37, 21.56.

E-1-Methyl-3-styryl-benzene ***(9e)***.[41] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 (d, *J* = 7.3 Hz, 2H), 7.34-7.28 (m, 4H), 7.24-7.20 (m, 2H), 7.06-7.04 (m, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 138.36, 137.61, 137.44, 128.98, 128.81, 128.72, 128.66, 128.60, 127.68, 127.36, 126.63, 123.86, 21.57.

(E)-1-Methyl-3-(4-methylstyryl)benzene ***(9f)***.[42] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, *J* = 7.96 Hz, 2H), 7.32 (d, *J* = 9.8 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.12-7.02 (m, 3H), 2.38 (s, 3H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 138.32, 137.63, 137.56, 134.83, 129.53, 128.69, 128.59, 128.38, 127.99, 127.25, 126.55, 123.74, 21.57, 21.37.

E-2-Styryl-furan ***(9g)***.[38] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45-7.19 (m, 6H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.85 (d, *J* = 16.3 Hz, 1H), 6.39-6.38 (m, 1H), 6.31 (d, *J* = 3.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 153.46, 142.28, 137.20, 128.83, 127.72, 127.32, 126.48, 116.71, 111.78, 108.68.

E-1,2-bis(2-pyridyl)ethylene ***(9h)***.[43] Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.55 (d, *J* = 5.6 Hz, 2H), 7.62-7.57 (m, 4H), 7.38-7.35 (m, 2H), 7.12-7.09 (m, 2H), $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 155.14, 149.87, 136.77, 131.89, 123.40, 122.77.

(E/Z)-1,2-Diphenylprop-1-ene ***(9i)***.[44] White solid. 7.52 (d, *J* = 7.88 Hz, 2H), 7.40-7.36 (m, 6H), 7.31-7.25 (m, 2H), 6.84 (s, 1H, E-isomer), 6.48 (s, 1H, Z-isomer), 2.29 (s, 3H, E-isomer), 2.21 (s, 3H, Z-isomer). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) (E) 144.15, 138.53, 137.59, 129.30, 128.6, 128.47, 127.98, 127.87, 126.61, 126.16, 17.62. (Z) 142.28, 138.9, 137.78, 129.08, 128.60, 127.98, 127.04, 126.72, 126.67, 126.22, 27.25.

Z-1-Penten-1-ylbenzene ***(9j)***.[45] Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27-7.19 (m, 4H), 7.14-7.08 (m, 1H), 6.35-6.28 (m, 1H), 6.18-5.55 (m, 1H), 2.24-2.20 (m, 2H), 1.43-1.39 (m, 2H), 0.87-0.84 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 138, 133.17, 129.01, 128.91, 128.23, 126.55, 30.83, 23.30, 13.98.

E-1-Penten-1-ylbenzene ***(9j)***.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27-7.19 (m, 4H), 7.14-7.08 (m, 1H), 6.35-6.28 (m, 1H), 2.11 (q, *J* = 7.2 Hz, 1H), 1.43-1.39 (m, 2H), 0.87-0.84 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 138.12, 133.17, 131.10, 130.06, 128.60, 126.89, 126.06, 35.27, 22.70, 13.86.

E-non-1-en-1-ylbenzene ***(9k)***.[5] Colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42-7.33 (m, 4H), 7.27-7.23 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.33-6.28 (m, 1H), 2.27 (td, J = 7.9, 1.1 Hz, 1H), 1.41-1.33 (m, 10H), 0.96 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 138.14, 131.42, 129.83, 128.60, 126.87, 126.05, 33.20, 32.00, 29.85, 29.55, 29.35, 22.82, 14.24.

E-2-styrylaniline ***(9l)***.[46] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.31-7.27 (m, 1H), 7.20 (d, J = 16.1 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.02 (d, *J* = 16.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 144.14, 137.77, 130.53, 128.85, 127.72, 127.43, 126.59, 124.47, 124.17, 119.33, 116.41.

(S)-1,2,3,11a-tetrahydro-5H-pyrrolo[1,2-a][1,4]benzodiazepin-5-one ***(14)***.[47] White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 4.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 8.6 Hz, 2H), 3.89-3.83 (m, 1H), 3.76-3.72 (m, 1H), 3.60-3.53 (m, 1H), 2.35-2.30 (m, 2H), 2.10-2.04 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 165.07, 164.56, 145.82, 131.54, 130.40, 127.77, 126.93, 126.70, 53.65, 46.97, 29.70, 24.32. $[\alpha]_d^{24.6}$ +354 (c 0.02, $CHCl_3$); HRMS (ESI) calcd for $C_{12}H_{12}N_2O$ $[M + H]^+$: 201.1028; found, 201.1033.

(S)-1,2,3,10,11,11a-hexahydro-5H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one ***(13)***.[48] Yellow oil. ^{1}H NMR (600 MHz,

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$CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 3.85-3.81 (m, 1H), 3.78-3.74 (m, 1H), 3.64-3.60 (m, 1H), 3.49 (m, 1H), 3.29-3.26 (m, 1H), 2.21- 2.15 (m, 1H), 1.88-1.86 (m, 1H), 1.82-1.77 (m, 1H), 1.67-1.62 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 166.85, 145.37, 133.00, 131.93, 119.20, 118.05, 118.00, 57.00, 53.24, 48.18, 30.75, 22.91. $[\alpha]_d^{19.2}$ +368 (c 0.02, $CHCl_3$); HRMS (ESI) calcd for $C_{12}H_{14}N_2O$ $[M + H]^+$: 203.1184; found, 203.1184.

Conflicts of interest

There are no conflicts to declare.

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