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PAPER

A convenient approach to β-heteroarylated (C–N bond) ketones from Cs_2CO_3 promoted reaction between propargyl alcohols and nitrogen-heterocycles†‡

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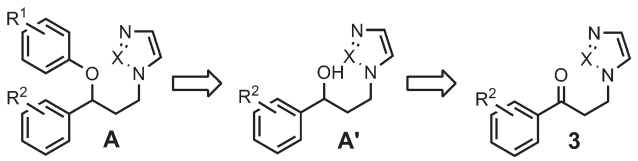
An efficient and direct approach to β-heteroarylated (C–N bond) ketones is demonstrated. Base promoted redox isomerization of propargyl alcohol to α,β-unsaturated ketone followed by conjugate addition to NH-heteroarenes affords a wide range of β-heteroarylated ketones in good to excellent yields. Aryl, heteroaryl, alkyl C(sp), and terminal alkynes containing unactivated propargyl alcohols effectively undergo redox-isomerization conjugate addition (RICA) with NH-heteroarenes. Reaction of 3-substituted pyrazoles or indazole with propargyl alcohols enables highly regioselective products. A diverse range of NH-bearing nucleophiles such as: pyrazoles, imidazole, triazoles, pyrrole, indoles and aniline participate in this reaction and deliver the corresponding β-heteroarylated ketones.

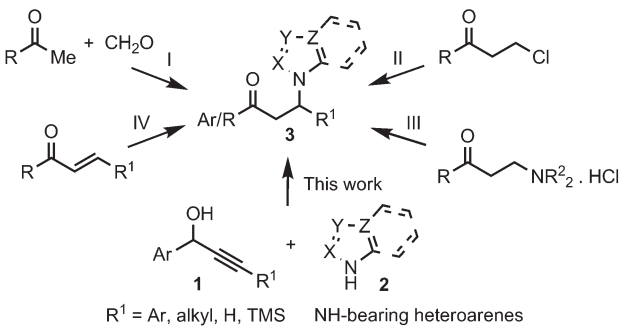
Introduction

Because of their unique structures, inherent properties and interesting reactivities, nitrogen-containing heteroarenes are often found in various natural products, materials and biologically active compounds of pharmaceutical interest.[1] Obviously, development of simple and efficient processes to N-heteroarenes has always attracted considerable attention.[2] The azole-bearing compounds ketoconazole, econazole, miconazole, fluconazole, posaconazole are potential antifungal agents and are already in the market.[3] Structure–activity relationship (SARs) studies reveal that the 1-[3-aryloxy-3-aryl)propyl]-1*H*-imidazoles (**A**) are lead structural units, showing potent activity against *Candida albicans* and dermatophytes.[3] Compounds of type **A** can be easily prepared from β-heteroarylated ketones (**3**) *via* the reduction of the carbonyl group followed by O-arylation (Scheme 1).[5a]

A brief overview of synthetic methods for the preparation of β-heteroarylated (C–N bond) ketones (**3**) is shown in Scheme 2. A multi-component reaction between ketones, formaldehyde and NH-azoles is a convenient approach, however, this transformation has limited substrate scope (path I).[4] Nucleophilic displacement of β-chloro ketones or β-dialkyl ammonium salt with nitrogen heterocycles is an alternate route (path II, III), unfortunately, hazardous wastes such as acids and quaternary amines are produced.[5,6] The most preferred and atom-efficient strategy is the conjugate addition of NH-bearing nucleophiles to activated α,β-unsaturated ketones (path IV),[7] however, multiple steps are invariably required for the preparation of starting materials.[8] In addition, most of the strategies lack generality and have a narrow reaction-scope.[4,6] Therefore, discovering a practicable, and efficient method for the construction of β-heteroarylated (C–N bond) ketones (**3**) from readily available starting materials is always desirable.[9]



Scheme 1 Synthetic strategy to azole derivatives **A**.



Scheme 2 Overview of β-heteroarylated ketone synthesis.

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†Dedicated to Professor Goverdhan Mehta, University of Hyderabad, India, for his outstanding contribution to organic synthesis and his 70th birthday.

‡Electronic supplementary information (ESI) available: Detailed optimization studies and ^{1}H and ^{13}C NMR spectra for all new compounds. CCDC reference numbers : 863901 and 863903. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25165e

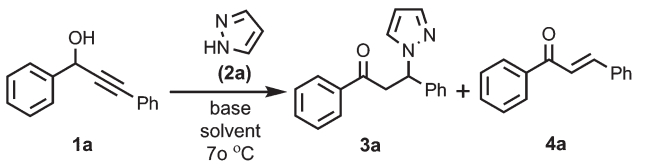
An elegant method to α,β-unsaturated carbonyl compounds from propargyl alcohols (**1**) through Ru-catalyzed redox-isomerization has been demonstrated by Trost and Livingston.[10f] Exploration of this strategy to O- and N-bearing heterocycles involving intramolecular conjugate addition of the heteroatom to α,β-unsaturated carbonyls derived from the propargyl alcohols has been well-investigated.[10c,d] A direct and chemoselective synthesis of β-heteroarylated (C–C) ketones involves the addition of indoles/furans to propargyl alcohols *via* a Ru/In catalyzed tandem redox-isomerization conjugate addition (RICA) sequence.[10a,e] These results reveal the effective use of the transiently formed α,β-unsaturated carbonyl compounds from propargyl alcohols through redox-isomerization.[10] Moreover, propargyl alcohols are highly-stable and easily fabricated by addition of terminal alkynes into the carbonyl compounds in a single step.[21e]

Recently, we have shown atom-efficient syntheses of arylvinyl ethers and α-acyloxy methyl ketones;[11] unactivated alkynes are the key-structural units employed in these useful transformations and a library of new molecular entities has been created.[11] Inspired by the above results and our current interest in finding new atom-economical transformations, we envisioned exploring a direct and efficient approach to β-heteroarylated ketones. We presume that the conjugate addition of NH-heteroarenes to transiently formed α,β-unsaturated carbonyls derived from propargyl alcohols through redox-isomerization sequence would create β-heteroarylated ketones directly. Reisch has shown the addition of aniline to propargyl alcohols in the presence of K_2CO_3 and piperidine, when refluxed in xylene.[12c] DBU catalyzed redox isomerization of activated propargyl alcohol followed by aza-Michael attack of the nitrogen heterocycle is one mild method to β-heteroarylated ketone synthesis.[12b] To the best of our knowledge, intermolecular addition of various NH-heteroarenes to aryl, alkyl, TMS substituted and terminal alkynes containing unactivated propargyl alcohols remains elusive.[12a] Herein we report a practical, efficient, and highly-regioselective single-step reaction strategy to β-heteroarylated ketones *via* Cs_2CO_3 promoted RICA between propargyl alcohols and NH-bearing heteroarenes (Scheme 2).

Results and discussion

To probe the viability of the intermolecular addition of NH-heteroarenes to propargyl alcohols, the reaction between 1,3-diphenylprop-2-yn-1-ol (**1a**) and pyrazole (**2a**) in the presence of different bases was investigated at first. Table 1 summarizes the results of the optimization studies.[13] The reaction proceeds sluggishly at temperatures below 70 °C. Progress of the reaction was monitored after stirring overnight (12 h) at 70 °C. Redox isomerization of **1a** to α,β-unsaturated ketone (**4a**) was exclusively observed albeit in poor yield, when the reaction was performed in K_2CO_3 in toluene (entry 1, Table 1). Organic base i-Pr_2NEt proved futile, producing only a negligible amount of **4a** (entry 2). Gratifyingly, reaction of **1a** in the presence of K_3PO_4 delivered the desired 1,3-diphenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (**3a**) and **4a** in 68% and 9% yields, respectively (entry 3). To our delight, Cs_2CO_3 base gave the best results and the yield of the desired redox isomerization conjugate addition (RICA) product

Table 1 Optimization of reaction conditions[a]



Entry	**2a** (equiv)	Base	Solvent	Time (h)	Yield[b] (%) **3a**	**4a**
1	2.0	K_2CO_3	Toluene	12	00	17
2	2.0	i-Pr_2NEt	Toluene	12	00	08
3	2.0	K_3PO_4	Toluene	12	68	09
4	2.0	Cs_2CO_3	Toluene	12	95	05
5	2.0	Cs_2CO_3	THF	12	88	12
6	2.0	Cs_2CO_3	Dioxane	12	81	19
7	2.0	Cs_2CO_3	CH_3CN	12	81	19
8	2.0	Cs_2CO_3	DMF	12	74	26
9	2.0	DBU	CH_2Cl_2	12	49	16
10	**2.0**	**Cs_2CO_3**	**Toluene**	**01**	**95**	**05**
11	1.5	Cs_2CO_3	Toluene	01	92	08
12	1.2	Cs_2CO_3	Toluene	01	88	12
13	1.0	Cs_2CO_3	Toluene	01	85	15

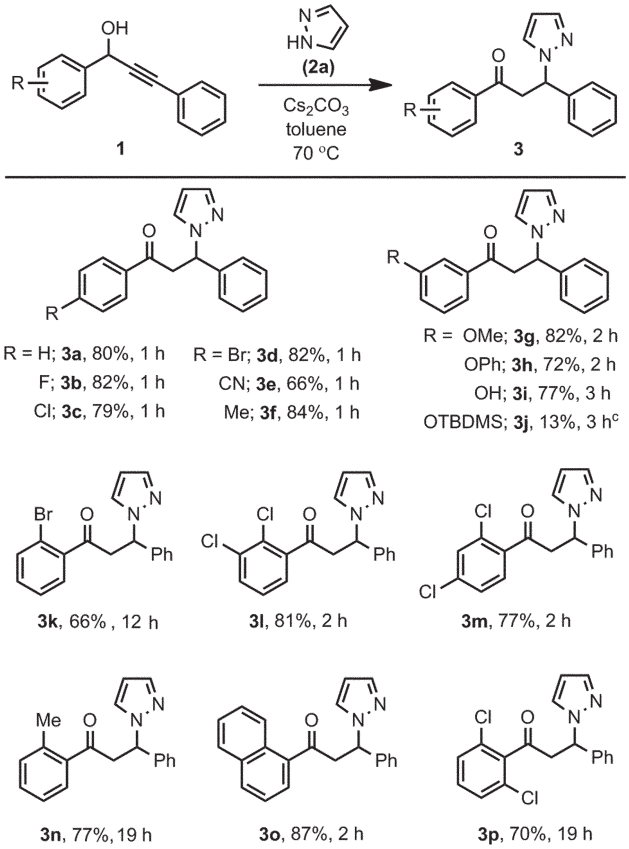
[a] Reactions were carried out using **1a** (0.5 mmol), base (0.5 mmol) in solvent (1.0 mL). [b] NMR yield.

3a was calculated as 95% by NMR (entry 4). With a selective base in hand, the effect of solvent on this reaction was then examined. Polar-aprotic solvents did not affect the progress of the reaction; however, undesired **4a** was detected in a substantial amount (entries 5–8). For example: use of the solvents such as: THF, dioxane, CH_3CN and DMF led to the formation of **4a** in 12%, 19%, 19% and 26% yields, respectively (entries 5–8). Among various solvents screened, toluene was found to be the best (entry 4). Reaction between activated 4-aryl-4-hydroxy-2,3-alkynyl esters and NH-heterocycles in the presence of DBU in CH_2Cl_2 provides 2-heterocycle-(C–N bond)-substituted-4-oxo-4-arylbutanoates efficiently;[12b] however, a moderate yield of **3a** was noticed under this reaction condition (entry 9). To our delight, quantitative formation of **3a** and complete consumption of **1a** was observed even within 1 h, when the reaction was performed in Cs_2CO_3 in toluene at 70 °C (entry 10). This demonstrates the efficiency of the optimized condition. Next, the amount of pyrazole required for this RICA transformation was pursued. Loading of reduced amounts of pyrazole resulted in producing the more of the redox isomerized product **4a** (entries 11–13). Moreover, the use of 2.0 equiv of pyrazole was found to be optimum.

Reaction scope

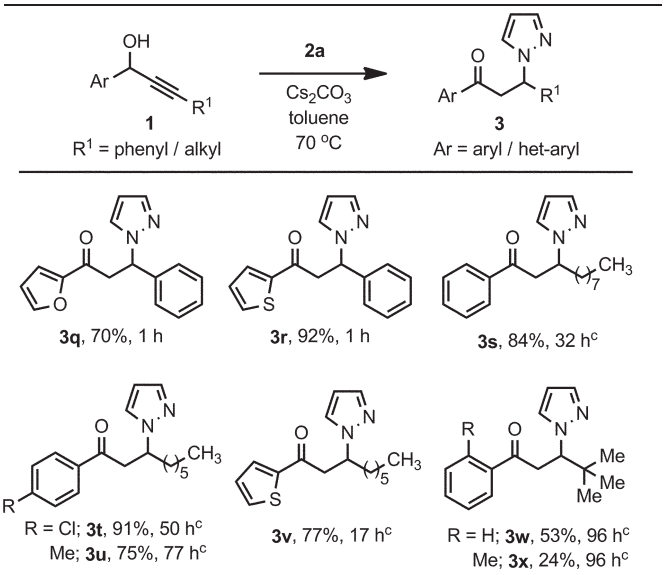
To explore the generality of the reaction and the synthesis of new RICA products **3**, reactions between a variety of propargyl alcohols and pyrazole (**2a**) were investigated under the optimized conditions (1 equiv of Cs_2CO_3 in toluene at 70 °C). The effect of substitution on the aryl-moiety at the propargyl position of the propargyl alcohol, 1-aryl-3-phenylprop-2-yn-1-ol (**1**), on the RICA with **2a** was examined at first (Table 2). As observed in

Table 2 Effect of arenes at the propargyl position of propargyl alcohols to the RICA with **2a**[a,b]



[a] Reactions were carried out using **1** (1.0 mmol), **2a** (2.0 mmol), Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) at 70 °C. [b] Isolated yield. [c] Cleavage of O-TBDMS protecting group was observed; the corresponding –OH bearing product **3i** was obtained in 64% yield.

Table 3 RICA of heteroarenes/arenes and/or C(sp)-alkyls containing propargyl alcohols with **2a**[a,b]

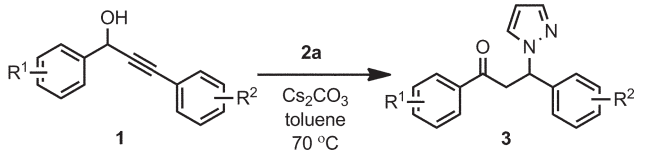


[a] Reactions were carried out using **1** (1.0 mmol), **2a** (2.0 mmol), Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) at 70 °C. [b] Isolated yield. [c] At 80 °C.

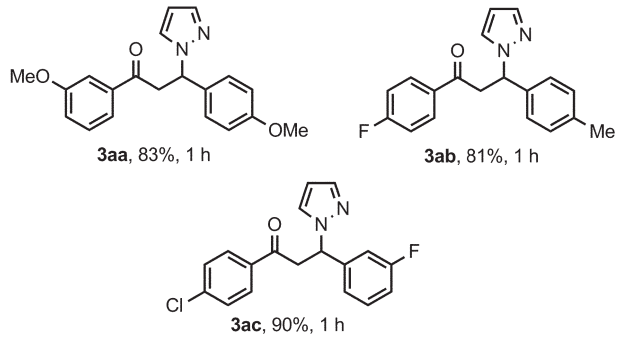
the optimization studies, electronically neutral substrate **1a** reacted efficiently with **2a** to give **3a** in 80% isolated yield.[12d] The Cu-assisted or the base-mediated replacement of aromatic halo-groups by pyrazole is a well-established phenomenon.[14] Surprisingly fluoro, chloro and bromo groups survived to this reaction condition and the corresponding products **3b–d** were isolated in good yields. Transition-metal catalyzed functionalization of the halo groups would generate new heteroaryl-bearing valuable substrates. Interestingly, cyano group is survived; however, trace of moisture in the system hydrolyses the cyano-group partially, producing **3e** in moderate yield.[15] Propargyl alcohols having the electron-donating substitutions methyl, methoxy or phenoxy groups at the 3- and/or 4-position on aromatic ring reacted efficiently with **2a** and the corresponding products **3f–h** are produced in excellent yields. Next, we examined the RICA of propargyl alcohol containing free phenol-OH moiety with **2a**. A report of Liu group describes the synthesis of benzofurans from Lewis-acid assisted annulation of phenols with propargyl alcohols.[16] The phenoxide ion generated *in situ* with the aid of the base is expected to undergo conjugate addition to the α,β-unsaturated ketones.[10c] Gratifyingly, we did not observe the participation of the free phenol-OH group in the reaction and **3i** was exclusively obtained in 77% yield in 3 h. Generally, silyl protected hydroxyl groups are sensitive to acidic and basic reagents.[15] To assess the relative stability of the silyl-protecting groups; the –OTBDMS containing precursor **1j** was subjected to the reaction condition. As anticipated, the TBDMS group was partial survived and the corresponding silicon protected and de-protected products **3j** and **3i** were isolated in 13%, 64% yields, respectively. The optimized procedure was subsequently applied to a range of propargyl alcohols having *ortho*-substituted arenes, to assess the steric effect in this RICA reaction sequence (Table 2). The *ortho*-halo groups on the aryl moiety are inert to the reaction condition, displaying good reactivity and appreciable yields (**3k–m**). Incomplete conversion of **1n** was observed to the synthesis of **3n** (77% yield) even with prolonged reaction time. 1-Naphthyl substituted propargyl alcohol underwent RICA with **2a** efficiently (**3o**). The more sterically demanding propargyl alcohol **1p** having two *ortho*-substitutions on aryl group did not affect the product-formation, although the reaction requires longer time for completion, producing **3p** in slightly lower yield. These experimental results reveal that the electronic as well as steric effect on the aryl group at the propargyl position in propargyl alcohol did not influence much to the reaction outcome.

Next, the RICA reactions of **2a** with heteroaryl bearing propargyl alcohols were surveyed (Table 3). The nucleophilic β-carbon and the acidic α-hydrogen of furan and thiophene would lead to C-alkylation product with propargyl alcohols.[17] Fortunately, the furyl- and thienyl-2-substituted propargyl alcohols (**1q** and **1r**) reacted efficiently with **2a** and afforded the corresponding β-pyrazolyl ketones **3q** and **3r** in 70% and 92% yields, respectively. We then turned our attention to examine the effect of alkyl-substitution at the C(sp)-center of the propargyl alcohols on the RICA with **2a**. The results are shown in Table 3. It is obvious that the inductively donating alkyl group enhances the electron density on the alkynes. As a consequence, slow

Table 4 Electronic effect of aryl-groups of propargyl alcohols on the RICA with **2a**[a,b]



R^1, R^2 = *m*-OMe, *p*-OMe (**1aa**); R^1 = *p*-F, R^2 = *p*-Me (**1ab**); R^1 = *p*-Cl, R^2 = *m*-F (**1ac**)

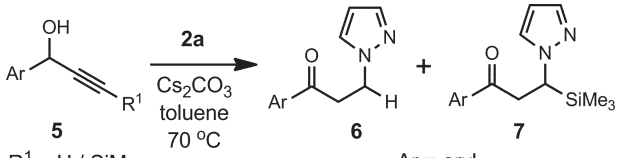


[a] Reactions were carried out using **1** (1.0 mmol), **2a** (2.0 mmol), Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) at 70 °C. [b] Isolated yield.

redox-iosmerization of the propargyl alcohol to the α,β-conjugated ketone is expected. To overcome this problem, we therefore performed the reactions at a higher temperature and a relatively longer time. Gratifyingly, product **3s** was isolated in 84% yield, when the reaction between C(sp)-octyl substituted propargyl alcohol **1s** and **2a** was conducted at 80 °C for 32 h. Even though the reaction took 50 h at 80 °C, an excellent yield of the desired **3t** was isolated with the survival of the chloro group. The electron-rich propargyl alcohol **1u** smoothly participated in the RICA reaction and furnished the ketone **3u** in good yield. Similarly, the propargyl alcohol having thienyl and C(sp)-alkyl moieties reacted with **2a** and produced **3v** in 77% yield. Importantly, the sterically encumbered C(sp)-*t*-butyl containing propargyl alcohol underwent RICA with **2a**. Incomplete conversion of **1w** was noticed and the corresponding β-pyrazolyl ketone **3w** was isolated in 53% yield, even though the reaction was continued for 4 days. The more sterically congested product **3x** was obtained albeit in poor yield from the RICA between **1x** and **2a** under the optimized condition.

Encouraged by the excellent performance of the RICA between **1** and pyrazole, the effect of electronic groups on both the arene-moieties attached at the propargyl and C(sp) positions in propargyl alcohols was next investigated, and the results are shown in Table 4. The presence of electron donating methoxy substituents on both arenes did not affect the reaction efficiency, and the desired RICA product **3aa** was isolated in 83% yield. Propargyl alcohol bearing an electron-withdrawing (–F) and electron donating (–Me) group at *para*-position on both the aryl moieties reacted with **2a**, affording **3ab** in 81% yield. Efficient reaction and excellent yield of the corresponding β-pyrazolyl ketone **3ac** was obtained from the RICA between the electron-deficient **1ac** and **2a**. These results show that the electronic variation of the propargyl alcohol did not display a pronounced effect on the reaction efficiency.

Table 5 RICA of terminal/TMS substituted propargyl alcohols with **2a**[a]



R^1 = H / $SiMe_3$ Ar = aryl

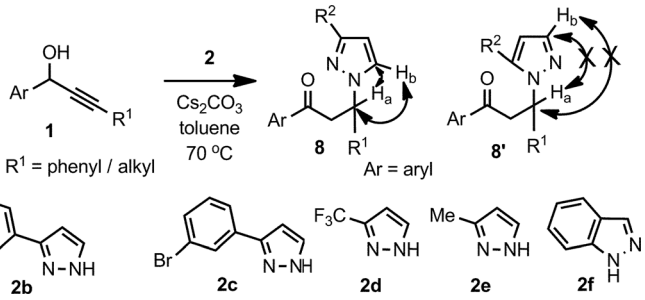
Entry	R^1	Ar	5	Time (h)	Yield[b] (%) 6	7
1	H	C_6H_5	**5a**	1	96	—
2	H	4-Me-C_6H_5	**5b**	1	93	—
3	H	4-Cl-C_6H_5	**5c**	1	73	—
4	H	1-Naphthyl	**5d**	2	68	—
5	Me_3Si	4-Me-C_6H_5	**5e**	1	87	04
6	Me_3Si	4-Cl-C_6H_5	**5f**	1	65	17
7	Me_3Si	1-Naphthyl	**5g**	1	72	07

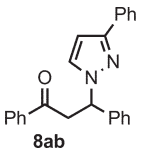
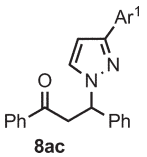
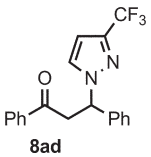
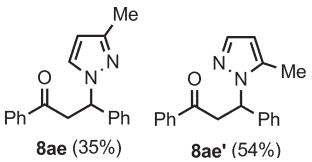
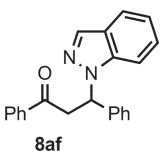
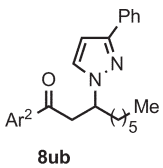
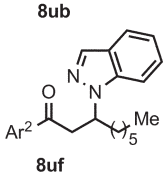
[a] Reactions were carried out using **5** (1.0 mmol), **2a** (2.0 mmol), Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) at 70 °C. [b] Isolated yield.

Next, exploration of terminal and alkynyl-C-TMS protected propargyl alcohols in the RICA with **2a** was pursued and the results are detailed in Table 5. Generally, base promotes the generation of the acetylides from terminal alkynes.[18] We speculate that the formation of the corresponding ketones will occur through the conjugate addition of the C-nucleophile (acetylide) to α,β-unsaturated ketones, obtained from the base induced redox isomerization of propargyl alcohol.[19] This would inhibit the formation of the desired β-heteroarylated ketones. To probe this assumption, the terminal propargyl alcohol **5a** and **2a** were exposed to the optimized conditions. To our surprise, the β-pyrazolyl ketone **6a** was exclusively obtained in 96% yield (entry 1, Table 5). Similarly, an excellent yield of product **6b** was isolated from the reaction of electron-rich propargyl alcohol **5b** with **2a** (entry 2). An electron withdrawing group at the *p*-position in the alcohol **5c** underwent RICA with **2a** efficiently (entry 3). Reaction of **2a** with naphthalene-containing propargyl alcohol **5d** was performed and **6d** was isolated in reasonable yield. Generally, deprotection of the silyl protecting groups occurs under basic media at ambient temperature.[15] With this fact in mind, we intend to test the reaction condition for the alkynyl-TMS protected propargyl alcohols and the results are summarized in Table 5. Although the reaction between **5e** and **2a** proceeded efficiently, the corresponding C-TMS containing β-heteroarylated ketone **7e** was obtained in poor yield (4%) and the silyl-deprotected product **6b** isolated in 87% yield (entry 5). Similar trends of the product-selectivity were also noticed in case of the RICA of 4-chlorophenyl and 1-naphthyl substituted alkynyl-TMS containing propargyl alcohols (entries 6 and 7). We therefore conclude that this optimized reaction condition did not tolerate the C-TMS group up to our expectations.

To broaden the reaction scope, we then investigated the RICA between various substituted pyrazoles and propargyl alcohols. Table 6 summarizes the results of this study. The reaction of 3-substituted-pyrazole with the propargyl alcohol usually provides a mixture of two regioisomers. For example, addition of 3-

Table 6 RICA between propargyl alcohols and pyrazole derivatives (**2**)[a]

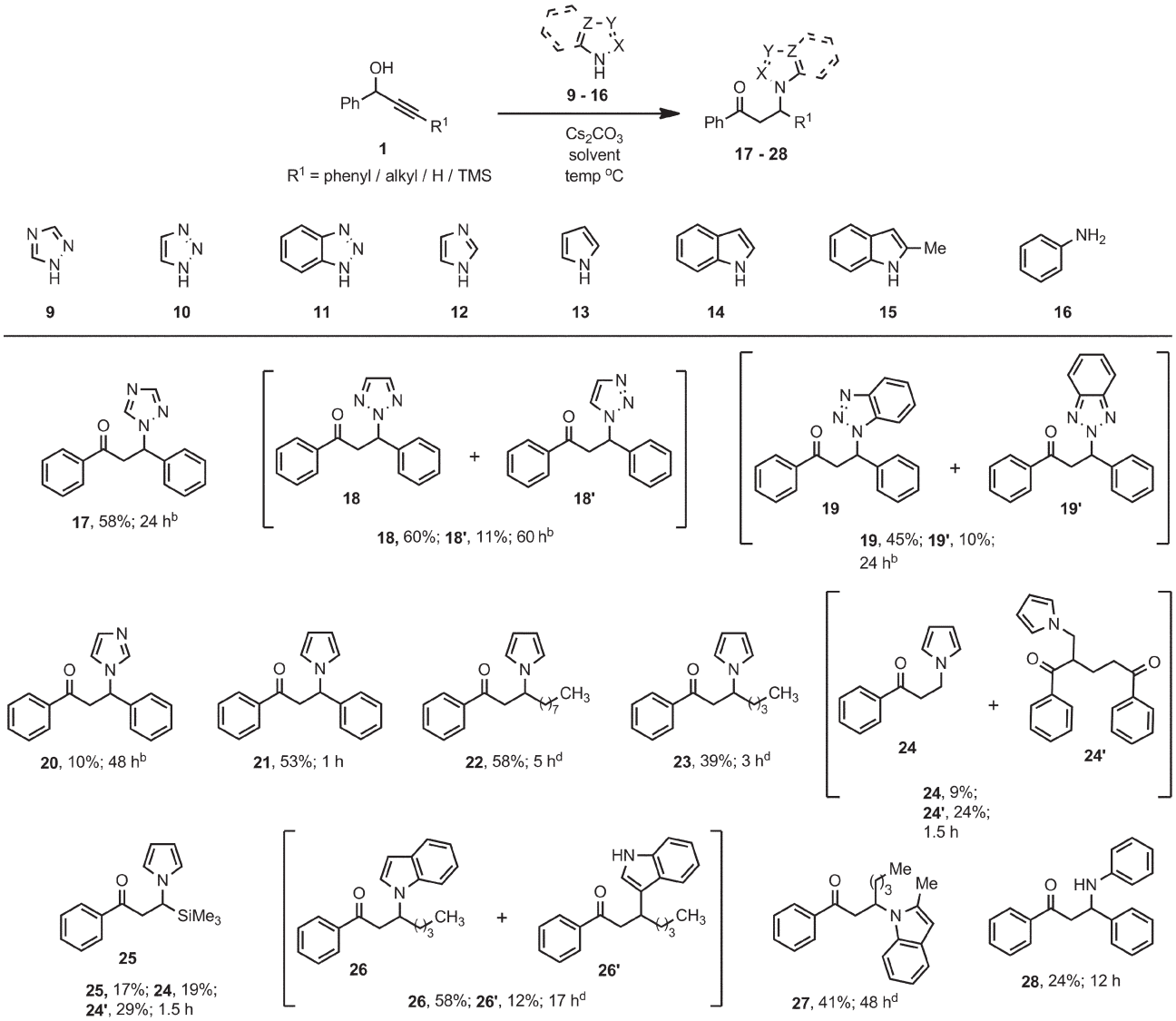


Entry	1	2	8	Time (h)	Yield[b] (%) 8
1	**1a**	**2b**	 **8ab**	05	83
2	**1a** Ar^1 = 3-Br-C_6H_5	**2c**	 **8ac**	05	93
3	**1a**	**2d**	 **8ad**	05	79[c]
4	**1a**	**2e**	 **8ae** (35%) **8ae'** (54%)	05	89
5	**1a**	**2f**	 **8af**	05	92
6	**1u** Ar^2 = 4-Me-C_6H_5	**2b**	 **8ub**	92	32[c]
7	**2u**	**2f**	 **8uf**	60	65[c]

[a] Reactions were carried out using **1** (1.0 mmol), **2** (2.0 mmol), Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) at 70 °C. [b] Isolated yield. [c] At 80 °C.

substituted pyrazole or indazole to 4-aryl-4-hydroxy-2,3-alkynyl esters in the presence of DBU in CH_2Cl_2 gave two non-separable regioisomers of the corresponding β-heteroarylated ketones.[12b] To examine the amount of regioselective product formation in the reaction, RICA between 3-phenyl pyrazole (**2b**) and **1a** was performed in the presence of Cs_2CO_3 (1.0 equiv) in toluene at 70 °C. To our surprise, single regioisomer **8ab** was exclusively produced (entry 1). The structure of **8ab** was confirmed based on X-ray crystallographic analysis.[13] Similarly, reaction of 3-(3-bromophenyl)-1*H*-pyrazole (**2c**) with **1a** led to only **8ac** in excellent yield. Heteronuclear multiple bond correlation (HMBC) studies to **8ac** reveal a strong correlation between C_a and H_b, H_a

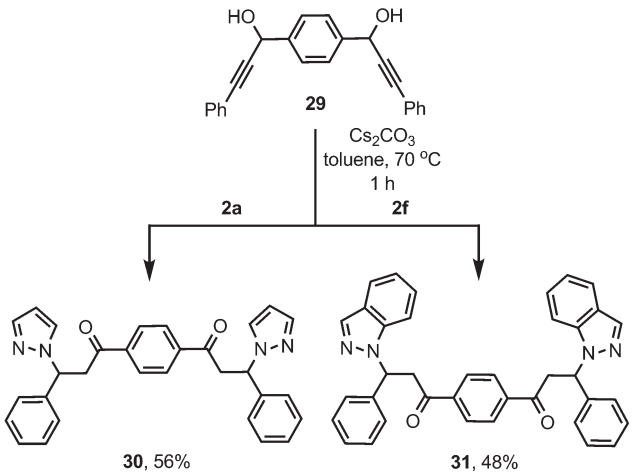
Table 7 RICA between propargyl alcohols and other NH-heteroarenes[a,c]



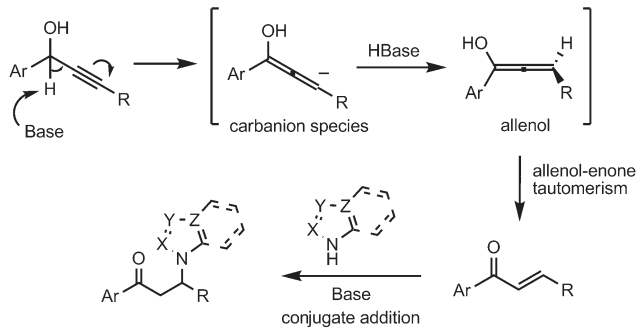
[a] Reactions were carried out using **1** (1.0 mmol), **9–16** (2.0 mmol), Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) at 70 °C. [b] Reactions were carried out using toluene (1.5 mL) + DMF (0.5 mL) at 80 °C. [c] Isolated yields. [d] At 80 °C.

and C_b whereas the correlation between H_a and C_d are not seen.[13] Based on this observation, the structure of **8ac** is established; furthermore, the X-ray crystallographic analysis data supports its structure (entry 2).[13] We assume that the steric nature of the substituent and the relatively milder reaction conditions are detrimental to this high regioselectivity. Electron-poor and relatively small 3-CF_3-substituted pyrazole (**2d**) reacted efficiently with **1a** at 80 °C, affording the desired β-heteroarylated ketone **8ad** in 79% yield; a trace of the other regioisomer (*ca.* ~3% by GC) was also noticed (entry 3). Based on the HMBC studies, the structure of **8ad** is confirmed.[13] However, RICA between 3-methyl pyrazole (**2e**) and **1a** gave a mixture of regioisomers; both the isomers are separated by flash chromatography resulting **8ae** and **8ae′** in 35% and 54% yields, respectively (entry 4). Once again, the structures of **8ae** and **8ae′** are confirmed through detailed HMBC studies.[13] Divergence in the behaviour of the observed regioselectivity is interesting; however, the factors responsible for this effect are unclear. It appears that the steric and electronic nature of the C-3-substitution in pyrazole contribute to the regioselectivity. Gratifyingly, a single isomer **8af** in excellent yield was obtained from the RICA between **1a** and indazole (**2f**) (entry 5). Similarly, **2b** and **2f** were independently reacted with 1-*p*-tolylnon-2-yn-1-ol (**1u**) and the corresponding β-heteroarylated ketones **8ub** and **8uf** are isolated in 32% and 65% yields, respectively; incomplete conversion of **1u** was observed even with the extended reaction time (entries 6 and 7).[13] Poor reactivity and the moderate product yields are the consequences of the alkyl-substitution of the propargyl alcohols.

To widen the synthetic utility of this methodology, various NH-bearing heterocycles such as triazoles, imidazole, pyrrole, indole, aniline and its derivatives were tested in the RICA reaction with propargyl alcohols. The results of this survey are



Scheme 3 RICA of propargyl alcohol (**29**) with **2a**/**2f**.



Scheme 4 Plausible mechanism.

detailed in Table 7. Conjugate addition of triazole to the propargyl alcohol in the presence of DBU was unsuccessful.[12b] Under the optimized conditions, addition of triazoles with **1a** led to little conversion of **1a** even though the reaction continued for 4 days. This failure inspired us to find suitable conditions for this transformation. In order to improve the product yield and reaction efficiency, we at first surveyed mixtures of different solvents for this RICA reaction. Interestingly, complete conversion of **1a** has been observed, when a toluene (1.5 mL) and DMF (0.5 mL) mixture was employed and the reaction was heated at 80 °C. A moderate yield of **17** was obtained from the RICA between 1,2,4-triazole (**9**) and **1a** under the modified reaction conditions. Although reaction of 1,2,3-triazole (**10**) with **1a** was sluggish, the corresponding regioisomers **18** and **18′** (6 : 1) were isolated in satisfactory overall yields.[7d,12b] However, in case of the benzotriazole, a reverse trend of the regioisomer selectivity **19** and **19′** (1 : 4.5; 55% yield) was noticed.[7c] The reaction between imidazole (**12**) and **1a** was complex, however, the product **20** was obtained in only 10% yield. The pyrrole-building block has been widely found in biologically active molecules.[20a,b] However, owing to the better reactivity, pyrrole tended to polymerize at an elevated temperature.[20c,d] Therefore, we are interested in examining the reactivity of pyrrole (**13**) with various propargyl alcohols. Interestingly, pyrrole reacted with **1a** sluggishly under the optimized reaction conditions (shown in entry 10, Table 1) and a moderate amount of product **21** was produced in 53% yield. Relatively poor-reactive C(sp)-alkyl substituted propargyl alcohols **1s** and 1-phenylhept-2-yn-1-ol (**1y**) successfully underwent RICA with pyrrole at 80 °C and delivered the corresponding β-pyrrolyl ketones **22** and **23** albeit in moderate yields. Surprisingly, a fast reaction between **13** and terminal propargyl alcohol **5a** has been observed, the addition product 1-phenyl-3-(1*H*-pyrrol-1-yl)propan-1-one (**24**) was obtained in only 9% yield. Interestingly, a Michael adduct **24′**, obtained through the conjugate addition of the carbanion (α-to carbonyl) of **24** to the α,β-unsaturated ketone, was isolated in 24% yield. The products **25**, **24**, **24′** has been isolated in overall good yield, when **13** reacted with 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ol (**5h**).

Because of the nucleophilic character of NH– and the C-3 center of indole, C–C and C–N bond formations with the redox isomerized product of the propargyl alcohol are possible.[10a,12b] Thus, RICA between indole (**14**) and **1y** was performed; the β-indolyl-(C–N bond)-ketone (**26**) and C-3 functionalized β-indolyl-(C–C bond)-ketone (**26′**) (5 : 1) are obtained in overall good yields. However, 2-methyl indole underwent RICA with **1y** and exclusively produced the β-indolyl-(C–N bond)-ketone **27**; the ^{1}H spectrum of crude reaction mixture did not show any trace of the corresponding β-indolyl-(C–C bond)-ketone. A recent report from the Trost group describes the synthesis of β-indolyl-(C–C bond)-ketones from RICA between substituted indole derivatives and propargyl alcohols.[10a] Therefore, RICA between propargyl alcohols and indoles under different reaction conditions can generate two distinct products. Importantly, the $-NH_2$ group of aniline participated in this RICA to **1a** and the product **28** was generated in only 24% yield. Unfortunately, electron-rich indole or aniline failed to react with ethyl 4-hydroxy-4-phenylbut-2-ynoate.[12b] Therefore, we believe that our optimized reaction conditions are better because they show a broader reaction scope.

To enlarge the molecular diversity by incorporating more heteroarenes in the molecule, compound **29** having two propargyl alcohol units was prepared. The pyrazole (**2a**) and indazole (**2f**) were independently exposed to **29** under the optimized conditions and the desired β-heteroarylated ketone **30** and **31** resulted albeit in reasonable yields (Scheme 3).

Based on the precedence, the reaction is likely to proceed through the following mechanism, as shown in Scheme 4.[21] The first step is the formation of the carbanion *via* the abstraction of the acidic benzylic C–H proton in the presence of base.[21e,f] Stabilization of carbanion through delocalization followed by protonation with the conjugate acid delivers the corresponding allenol. Allenol–enone tautomerism gives the reactive α,β-unsaturated carbonyl compound. Finally, base mediated conjugate addition of NH-heteroarenes with enones produces the desired β-heteroarylated ketones.[7b,d,e,g]

Conclusion

In conclusion, a direct, practicable and efficient approach to β-heteroarylated ketones is demonstrated. The reaction proceeds through the base induced redox-isomerization of easily accessible propargyl alcohols followed by conjugate addition of NH-heteroarenes in one-step. This reaction displays broad scope and tolerates a variety of reactive functional groups. Aryl, heteroaryl,

alkyl C(sp), and terminal alkynes containing unactivated propargyl alcohols undergo RICA with the pyrazole efficiently. Notably, the RICA of 3-substituted pyrazoles or indazole with propargyl alcohols delivers the products with a better level of regioselectivity. RICA between propargyl alcohols and a range of NH-bearing compounds such as: 1,2,4-triazole, 1,2,3-triazole, imidazole, pyrrole, indoles and aniline are successfully demonstrated. Current effort is directed towards exploring the synthetic application of this methodology.

Experimental section

General procedure for the preparation of 1 from aldehydes (1′) (GP-1)

A solution of terminal-alkyne (1.2 equiv) in THF (50 mL) was stirred in a 100 mL oven-dried two-necked round bottom flask under an argon atmosphere at −70 °C. n-Butyllithium (1.2 equiv, 1.60 M in THF) was introduced over 30 minutes at −70 °C. After an additional 1 h stirring, a solution of aldehyde (**1′**, 1.0 equiv) in THF (5 mL) was added at −70 °C. The resulting mixture was stirred for 1 h and warmed to room temperature slowly and stirring continued for 30 minutes. The reaction mixture was quenched with saturated NH_4Cl aqueous solution (20 mL) at 0 °C. The organic layer was separated; the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined extracts were washed with water (2 × 20 mL), brine (25 mL) and dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel. The desired propargyl alcohols are obtained in good yields. Physical characterization data is exactly matching with the reported values for the respective compounds **1a–h**,[22] **1k–s**,[22,23] **1u–w**,[24] **1ab**,[25] **1y**[26] and **29**,[27] whereas **1i–j**, **1t**, **1x**, **1aa** and **1ac** are new.

3-(1-Hydroxy-3-phenylprop-2-ynyl)phenol (1i). Following the literature procedure,[28] $LiOAc{\cdot}2H_2O$ (52 mg, 10 mol%) was added to a solution of 1-(3-(*tert*-butyldimethylsilyloxy)phenyl)-3-phenylprop-2-yn-1-ol (**1j**, 2.7 g, 8.0 mmol) in DMF–H_2O. The resulting mixture was heated at 70 °C under an inert atmosphere. Upon complete consumption of starting material, the reaction mixture was extracted with ethyl acetate. After usual work up, the crude material was purified using silica gel column chromatography. The product **1i** was isolated in 1.43 g, 80% yield as a pale yellow thick oil. R_f = 0.28 (4 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.43 (m, 2H), 7.38–7.23 (m, 4H), 7.19–7.10 (m, 2H), 6.86–6.81 (m, 1H), 5.72 (bs, 1H), 5.64 (s, 1H), 2.34 (bs, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.8, 143.9, 131.7 (2C), 129.7, 129.1 (2C), 129.0, 122.8, 117.6, 115.0, 113.8, 91.9, 84.7, 63.3; IR (Neat) ν_{max} 3337, 3155, 2220, 1602, 1466, 1311, 1259, 1163, 1020, 902, 752 cm^{-1}; MS (EI) *m*/*z* (%) 225 (M^+ + 1, 100), 207 (2), 174 (2); Anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.15; H, 5.31.

1-(3-(*tert*-Butyldimethylsilyloxy)phenyl)-3-phenylprop-2-yn-1-ol (1j). Following the general procedure (GP-1), reaction of 3-(*tert*-butyldimethylsilyloxy)benzaldehyde (**1′j**; 1.89 g, 8.00 mmol), phenyl acetylene (980 mg, 9.60 mmol) and n-BuLi (6.0 mL, 1.6 M in THF, 9.60 mmol) gave **1j** (1.63 g, 60% yield) as a light yellow thick oil. R_f = 0.42 (4 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2H), 7.38–7.20 (m, 5H), 7.13 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.64 (s, 1H), 2.32 (bs, 1H), 1.00 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 142.2, 131.8 (2C), 129.7, 128.6, 128.3 (2C), 122.4, 120.1, 119.6, 118.5, 88.7, 86.6, 64.9, 25.7 (3C), 18.2, −4.4 (2C); IR (KBr) ν_{max} 3441, 3065, 2932, 2887, 2197, 1643, 1599, 1485, 1439, 1286, 939, 839 cm^{-1}; MS (EI) *m*/*z* (%) 339 (M^+ + 1, 10), 321 (100), 229 (2); Anal. calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74. Found: C, 74.45; H, 7.71.

1-(4-Chlorophenyl)non-2-yn-1-ol (1t). Following the general procedure (GP-1), reaction of 4-chlorobenzaldehyde (**1′t**; 1.40 g, 10.0 mmol), 1-octyne (1.32 g, 12.0 mmol) and n-BuLi (7.5 mL, 1.6 M in THF, 12.0 mmol) gave **1t** (2.18 g, 87% yield) as a colorless oil. R_f = 0.45 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 5.43 (d, *J* = 5.6 Hz, 1H), 2.27 (td, *J* = 1.6, 6.8 Hz, 2H), 2.12 (d, *J* = 6.0 Hz, 1H), 1.57–1.50 (m, 2H), 1.43–1.32 (m, 2H), 1.32–1.23 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 133.9, 128.6 (2C), 128.0 (2C), 88.1, 79.6, 64.0, 31.2, 28.6, 28.5, 22.5, 18.8, 14.0; IR (Neat) ν_{max} 3368, 2930, 2858, 1489, 1091, 1014, 779 cm^{-1}; MS (EI) *m*/*z* (%) 203 (M^+ + 1, 100), 167 (8), 139 (27), 91 (8); Anal. calcd for $C_{15}H_{19}ClO$: C, 71.84; H, 7.64. Found: C, 71.94; H, 7.69.

4,4-Dimethyl-1-*o*-tolylpent-2-yn-1-ol (1x). Following the general procedure (GP-1), reaction of 2-methylbenzaldehyde (**1′x**; 960 mg, 8.0 mmol), 3,3-dimethylbut-1-yne (788 mg, 9.6 mmol) and n-BuLi (6.0 mL, 1.6 M in THF, 9.6 mmol) gave **1x** (389 mg, 72% yield) as a colorless oil. R_f = 0.40 (32 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 4.0 Hz, 1H), 7.26–7.20 (m, 2H), 7.20–7.16 (m, 1H), 5.60 (d, *J* = 5.6 Hz, 1H), 2.45 (s, 3H), 1.99 (d, *J* = 5.6 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 136.1, 130.7, 128.2, 126.5, 126.1, 95.1, 78.3, 62.6, 31.0 (3C), 27.5, 19.0; IR (Neat) ν_{max} 3368, 2968, 1460, 983, 750 cm^{-1}; MS (EI) *m*/*z* (%) 203 (M^+ + 1, 100), 167 (8), 139 (27), 91 (8); Anal. calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 8.92.

1-(3-Methoxyphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-ol (1aa). Following the general procedure (GP-1), reaction of 3-methoxybenzaldehyde (**1′g**; 500 mg, 3.78 mmol), 1-ethynyl-4-methoxybenzene (599 mg, 4.53 mmol) and n-BuLi (2.8 mL, 1.6 M in THF, 4.53 mmol) gave **1aa** (730 mg, 72% yield) as a yellow thick oil. R_f = 0.28 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.26 (m, 3H), 7.25–7.12 (m, 2H), 6.95–6.75 (m, 3H), 5.65 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.60 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (2C), 142.5, 133.3 (2C), 129.7, 119.0, 114.5, 114.0, 113.9 (2C), 112.2, 87.4, 86.6, 65.1, 55.3 (2C); IR (Neat) ν_{max} 3385, 3011, 2968, 2930, 2843, 1606, 1510, 1248, 1170, 1030, 831 cm^{-1}; MS (EI) *m*/*z* (%) 269 (M^+ + 1, 100), 186 (13), 137 (23); Anal. calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.23; H, 6.10.

1-(4-Chlorophenyl)-3-(3-fluorophenyl)prop-2-yn-1-ol (1ac). Following the general procedure (GP-1), reaction of 4-chlorobenzaldehyde (**1′c**; 1.00 g, 7.14 mmol), 1-ethynyl-3-fluorobenzene (1.03 g, 8.56 mmol) and n-BuLi (5.0 mL, 1.6 M in THF, 8.56 mmol) gave **1ac** (1.40 g, 75% yield) as a colorless solid.

mp 59–60 °C; R_f = 0.45 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.33–7.23 (m, 2H), 7.16 (d, J = 9.6 Hz, 1H), 7.06 (t, J = 8.8 Hz, 1H), 5.67 (d, J = 6.0 Hz, 1H), 2.36 (d, J = 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 248 Hz), 138.7, 134.2, 129.9 (d, J = 8.7 Hz), 128.7 (2C), 128.0 (2C), 127.5 (d, J = 3.2 Hz), 123.8 (d, J = 9.4 Hz), 118.4 (d, J = 23.1 Hz), 116.1(d, J = 21.2 Hz), 89.1, 85.5 (d, J = 3.3 Hz), 64.1; IR (KBr) ν_{max} 3341, 2874, 1571, 1487, 1168, 1016, 785, 680 cm^{-1}; MS (EI) m/z (%) 203 (M^+ + 1, 100), 167 (8), 139 (27), 91 (8); Anal. calcd for $C_{15}H_{10}ClFO$: C, 69.11; H, 3.87. Found: C, 69.25; H, 3.83.

General procedure for the synthesis of 5 from 1′ (GP-2)

A solution of trimethylsilylacetylene (1.2 equiv) in THF (50 mL) was stirred in a 100 mL oven-dried two-necked round bottom flask under an argon atmosphere at −70 °C. n-Butyllithium (1.2 equiv, 1.60 M in THF) was introduced over 30 minutes at −70 °C. After an additional 1 h stirring, a solution of aldehyde (**1′**, 1.0 equiv) in THF (5 mL) was added at −70 °C. The resulting mixture was stirred for 1 h and warmed to room temperature slowly and stirring continued for 30 minutes. The reaction mixture was quenched with saturated NH_4Cl aqueous solution (20 mL) at 0 °C. The organic layer was separated; the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined extracts were washed with water (2 × 20 mL), brine (25 mL) and dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was subsequently used for the desilylation reaction.

Methanol (15 mL) and K_2CO_3 (2.5 equiv) was introduced to the crude residue obtained in the above reaction and the heterogeneous mixture was stirred under an argon atmosphere at ambient temperature overnight. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (2 × 20 mL) and brine (10 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel. Physical characterization data is exactly matching with the reported values for the respective compounds **5a–h**.[29–34]

General procedure for the RICA between propargyl alcohols and NH-heteroarenes (GP-3)

Propargyl alcohol **1** (1.0 mmol), NH-heteroarene (2.0 mmol) and cesium carbonate (326 mg, 1.0 mmol) were taken in an oven-dried Schlenk flask under an argon atmosphere. Toluene (2 mL) was added to this mixture. The resulting solution was stirred at 70 °C as per the time shown in the representative tables. Upon complete consumption of **1**, the reaction mixture was diluted with dichloromethane (10 mL), and filtered over a small pad of Celite. The solvent was evaporated under reduced pressure and the crude reaction mixture was purified using column chromatography on silica gel.

1,3-Diphenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3a). 220 mg, 80% yield; light yellow solid; mp 79–80 °C; R_f = 0.31 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.2 Hz, 2H), 7.60–7.50 (m, 3H), 7.45 (t, J = 7.6 Hz, 2H), 7.37–7.32 (m, 4H), 7.31–7.26 (m, 1H), 6.24 (s, 1H), 6.13 (dd, J = 5.6, 8.4 Hz, 1H), 4.50 (dd, J = 8.4, 17.6 Hz, 1H), 3.65 (dd, J = 5.2, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 140.8, 139.3, 136.5, 133.4, 129.8, 128.8 (2C), 128.6 (2C), 128.2 (2C), 128.0, 126.7 (2C), 105.6, 60.8, 44.2; IR (KBr) ν_{max} 3032, 2925, 1682, 758, 563 cm^{-1}; MS (EI) m/z (%) 278 (M^+ + 2, 54), 241 (27), 209 (100), 105 (8), 69 (8); Anal. calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.09; H, 5.76; N, 10.25.

1-(4-Fluorophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3b). 241 mg, 82% yield; colorless solid; mp 42–43 °C; R_f = 0.38 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.94 (m, 2H), 7.53 (s, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.37–7.25 (m, 5H), 7.08 (t, J = 8.4 Hz, 2H), 6.24 (t, J = 2.0 Hz, 1H), 6.12 (dd, J = 5.2, 8.4 Hz, 1H), 4.50 (dd, J = 8.8,17.6 Hz, 1H), 3.58 (dd, J = 4.8, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 165.6 (d, J = 255 Hz), 140.5, 139.0, 132.7, 130.7 (d, J = 10.1 Hz, 2C), 129.6, 128.6 (2C), 127.8, 126.4 (2C), 115.5 (d, J = 21.2 Hz, 2C), 105.5, 60.6, 43.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −104.58 to −104.66 (m); IR (KBr) ν_{max} 3111, 3034, 2920, 1682, 1599, 1157, 991, 756, 628 cm^{-1}; MS (EI) m/z (%) 296 (M^+ + 2, 51), 295 (M^+ + 1, 100), 259 (24), 227 (70), 123 (11), 101 (11), 69 (14); Anal. calcd for $C_{18}H_{15}FN_2O$: C, 73.45; H, 5.14; N, 9.52. Found: C, 73.35; H, 5.21; N, 9.66.

1-(4-Chlorophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3c). 246 mg, 79% yield; colorless solid; mp 74–75 °C; R_f = 0.25 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 10.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.39–7.23 (m, 5H), 6.22 (s, 1H), 6.08 (dd, J = 4.8, 8.0 Hz, 1H), 4.49 (dd, J = 8.8, 17.6 Hz, 1H), 3.57 (dd, J = 4.8, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 140.6, 139.9, 139.3, 134.9, 129.8, 129.7 (2C), 128.9 (2C), 128.8 (2C), 128.1, 126.6 (2C), 105.7, 60.8, 44.1; IR (KBr) ν_{max} 3042, 2924, 1684, 1087, 750 cm^{-1}; MS (EI) m/z (%) 313 (M^+ + 2, 54), 312 (M^+ + 1, 54), 311 (M^+, 100), 139 (19), 107 (3); Anal. calcd for $C_{18}H_{15}ClN_2O$: C, 69.57; H, 4.86; N, 9.01. Found: C, 69.37; H, 4.81; N, 9.12.

1-(4-Bromophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3d). 291 mg, 82% yield; pale yellow solid; mp 81–82 °C; R_f = 0.40 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.47 (dd, J = 1.6, 12.8 Hz, 2H), 7.36–7.22 (m, 5H), 6.21 (s, 1H), 6.07 (dd, J = 4.8, 8.4 Hz, 1H), 4.45 (dd, J = 8.8, 17.6 Hz, 1H), 3.53 (dd, J = 4.8, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 140.4, 139.0, 135.0, 131.7 (2C), 129.6, 129.5 (2C), 128.6 (2C), 128.3, 127.9, 126.4 (2C), 105.5, 60.5, 43.9; IR (KBr) ν_{max} 3108, 1684, 1585, 1070, 752, 702 cm^{-1}; MS (EI) m/z (%) 357 (M^+ + 2, 97), 355 (M^+, 100), 287 (32), 209 (30), 101 (20), 69 (16); Anal. calcd for $C_{18}H_{15}BrN_2O$: C, 60.86; H, 4.26; N, 7.89. Found: C, 60.75; H, 4.31; N, 7.79.

4-(3-Phenyl-3-(1*H*-pyrazol-1-yl)propanoyl)benzonitrile (3e). 198 mg, 66% yield; yellow solid; mp 117–118 °C; R_f = 0.50 (3 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.39–7.22 (m, 5H), 6.22 (s, 1H), 6.07 (dd, J = 4.8, 8.8 Hz, 1H), 4.55 (dd, J = 8.8, 17.6 Hz, 1H), 3.53 (dd, J = 4.8, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 140.3, 139.4, 139.1,

132.4 (2C), 129.7, 128.8 (2C), 128.5 (2C), 128.1, 126.5 (2C), 117.8, 116.4, 105.8, 60.6, 44.3; IR (KBr) ν_{max} 3074, 2922, 2227, 1687, 754, 696, 625 cm^{-1}; MS (EI) *m/z* (%) 303 (M^+ + 2, 41), 302 (100), 130 (5), 69 (16); Anal. calcd for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.94. Found: C, 75.61; H, 5.10; N, 13.86.

3-Phenyl-3-(1*H*-pyrazol-1-yl)-1-*p*-tolylpropan-1-one (3f). 224 mg, 84% yield; colorless solid; mp 41–42 °C; R_f = 0.37 (6 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 12.8 Hz, 2H), 7.33–7.24 (m, 4H), 7.24–7.19 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.18 (s, 1H), 6.10 (dd, *J* = 5.2, 8.0 Hz, 1H), 4.42 (dd, *J* = 8.4, 17.2 Hz, 1H), 3.58 (dd, *J* = 5.2, 17.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 143.9, 140.6, 139.0, 133.8, 129.5, 129.0 (2C), 128.5 (2C), 128.1 (2C), 127.7, 126.5 (2C), 105.3, 60.6, 43.8, 21.4; IR (KBr) ν_{max} 3032, 2920, 1682, 1454, 817, 752, 628 cm^{-1}; MS (EI) *m/z* (%) 292 (M^+ + 2, 59), 291 (M^+ + 1, 100), 255 (14), 223 (59), 119 (14), 91 (8); Anal. calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.47; H, 6.32; N, 9.55.

1-(3-Methoxyphenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3g). 251 mg, 82% yield; light yellow thick liquid; R_f = 0.36 (6 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.47 (bd, *J* = 5.6 Hz, 2H), 7.35–7.21 (m, 6H), 7.07 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.21 (s, 1H), 6.09 (dd, *J* = 5.2, 8.0 Hz, 1H), 4.45 (dd, *J* = 8.8, 18.0 Hz, 1H), 3.78 (s, 3H), 3.64 (dd, *J* = 5.2, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 159.5, 140.5, 138.9, 137.5, 129.4, 129.3, 128.5 (2C), 127.7, 126.4 (2C), 120.6, 119.7, 111.9, 105.3, 60.5, 55.0, 43.9; IR (Neat) ν_{max} 3065, 2939, 1682, 1454, 1045, 754, 626 cm^{-1}; MS (EI) *m/z* (%) 308 (M^+ + 2, 80), 271 (39), 239 (100), 135 (19), 101 (16), 69 (14); Anal. calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.36; H, 5.98; N, 9.25.

1-(3-Phenoxyphenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3h). 265 mg, 72% yield; yellow solid; mp 62–63 °C; R_f = 0.68 (6 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H) 7.49 (s, 1H), 7.46 (s, 1H), 7.41–7.22 (m, 8H), 7.18 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.21 (s, 1H), 6.07 (dd, *J* = 5.2, 8.0 Hz, 1H), 4.44 (dd, *J* = 8.8, 18.0 Hz, 1H), 3.58 (dd, *J* = 5.2, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 157.5, 156.3, 140.5, 139.0, 138.1, 129.8, 129.7 (2C), 129.5, 128.6 (2C), 127.8, 126.4 (2C), 123.6, 123.3, 122.8, 118.9 (2C), 117.7, 105.4, 60.5, 44.1; IR (KBr) ν_{max} 3032, 2916, 1687, 1581, 1240, 752, 696 cm^{-1}; MS (EI) *m/z* (%) 370 (M^+ + 2, 51), 369 (M^+ + 1, 100), 333 (35), 301 (76), 197 (11), 101 (11), 69 (8); Anal. calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.32; H, 5.43; N, 7.52.

1-(3-Hydroxyphenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3i). 225 mg, 77% yield; colorless solid; mp 129–130 °C; R_f = 0.53 (2 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.70–8.00 (bs, –OH, 1H), 7.55 (dd, *J* = 2.0, 16.4 Hz, 2H), 7.40–7.36 (m, 1H), 7.35 (bt, *J* = 2.4 Hz, 1H), 7.31–7.24 (m, 5H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.91 (dd, *J* = 2.4, 8.0 Hz, 1H), 6.27 (t, *J* = 2.4 Hz, 1H), 6.10 (dd, *J* = 5.2, 8.4 Hz, 1H), 4.42 (dd, *J* = 8.8, 18.0 Hz, 1H), 3.63 (dd, *J* = 5.2, 18.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 156.7, 140.1, 139.3, 137.5, 130.5, 129.6, 128.8 (2C), 128.1, 126.6 (2C), 120.8, 119.9, 115.1, 105.9, 60.9, 43.8; IR (KBr) ν_{max} 3112, 1684, 1587, 1280, 750, 698, 625 cm^{-1}; MS (EI) *m/z* (%) 294 (M^+ + 2, 100), 257 (5), 225 (27), 121 (11), 101 (19), 69 (27); Anal. calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.85; H, 5.48; N, 9.68.

1-(3-(*tert*-Butyldimethylsilyloxy)phenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3j). 53 mg, 13% yield; brown color thick liquid; R_f = 0.55 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 10.8 Hz, 2H), 7.42 (s, 1H), 7.38–7.23 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.24 (bd, *J* = 1.2 Hz, 1H), 6.10 (t, *J* = 7.6 Hz, 1H), 4.45 (dd, *J* = 8.0, 17.6 Hz, 1H), 6.63 (dd, *J* = 4.8, 17.6 Hz, 1H), 0.99 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 160.0, 140.7, 139.3, 138.0, 129.7, 129.6, 128.8 (2C), 128.0, 126.7 (2C), 125.2, 121.3, 119.4, 105.5, 60.8, 44.3, 25.6 (3C), 18.1, −4.4 (2C); IR (Neat) ν_{max} 3065, 2957, 1687, 1581, 1280, 931, 837, 625 cm^{-1}; MS (EI) *m/z* (%) 408 (M^+ + 1, 35), 390 (23), 376 (100), 344 (100), 316 (8), 288 (8), 79 (10), 65 (6); Anal. calcd for $C_{24}H_{30}N_2O_2Si$: C, 70.90; H, 7.44; N, 6.89. Found: C, 71.21; H, 7.48; N, 6.75.

1-(2-Bromophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3k). 234 mg, 66% yield; yellow thick liquid; R_f = 0.31 (12 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 2H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.39–7.20 (m, 8H), 6.26 (t, *J* = 2.0 Hz, 1H), 6.08 (dd, *J* = 5.2, 9.6 Hz, 1H), 4.38 (dd, *J* = 9.2, 17.2 Hz, 1H), 3.63 (dd, *J* = 4.8, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 140.7, 140.0, 139.0, 133.4, 131.7, 129.6, 129.0 (2C), 128.7, 128.0, 127.2, 126.5 (2C), 118.5, 105.6, 60.9, 47.9; IR (Neat) ν_{max} 3030, 2918, 1699, 1284, 875 cm^{-1}; MS (EI) *m/z* (%) 358 (M^+ + 3, 30), 357 (M^+ + 2, 100), 356 (M^+ + 1, 30), 355 (M^+, 100), 321 (8), 319 (8), 289 (30), 287 (30), 185 (14), 183 (14), 101 (8); Anal. calcd for $C_{18}H_{15}BrN_2O$: C, 60.86; H, 4.26; N, 7.89. Found: C, 60.75; H, 4.32; N, 7.68.

1-(2,3-Dichlorophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3l). 279 mg, 81% yield; pale yellow thick liquid; R_f = 0.30 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.48 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.44 (s, 1H), 7.38–7.22 (m, 6H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.24 (s, 1H), 6.06 (dd, *J* = 4.8, 9.2 Hz, 1H), 4.35 (dd, *J* = 10.0, 17.6 Hz, 1H), 3.57 (dd, *J* = 4.4, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 141.0, 139.8, 138.9, 133.6, 132.0, 129.5, 128.6 (2C), 128.5, 127.9, 127.4, 126.8, 126.4 (2C), 105.6, 60.9, 48.2; IR (Neat) ν_{max} 3065, 2924, 1701, 1410, 736, 625 cm^{-1}; MS (EI) *m/z* (%) 347 (M^+ + 2, 84), 346 (M^+ + 1, 38), 345 (M^+, 100), 277 (14), 173 (22), 69 (11); Anal. calcd for $C_{18}H_{14}Cl_2N_2O$: C, 62.62; H, 4.09; N, 8.11. Found: C, 62.48; H, 4.15; N, 8.25.

1-(2,4-Dichlorophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3m). 265 mg, 77% yield; yellow thick liquid; R_f = 0.33 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (bd, *J* = 1.2 Hz, 1H), 7.38 (dd, *J* = 2.8, 11.6 Hz, 3H), 7.34–7.19 (m, 6H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.02 (dd, *J* = 4.8, 9.6 Hz, 1H), 4.35 (dd, *J* = 9.6, 17.2 Hz, 1H), 3.53 (dd, *J* = 4.8, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 140.0, 138.9, 137.4,

136.8, 131.9, 130.6, 130.1, 129.6, 128.7 (2C), 128.0, 127.1, 126.4 (2C), 105.7, 61.0, 48.1; IR (Neat) ν_{max} 3063, 2926, 1697, 1375, 750, 625 cm^{-1}; MS (EI) *m/z* (%) 347 (M^+ + 2, 84), 346 (M^+ + 1, 41), 345 (M^+, 100), 277 (11), 173 (24), 147 (8), 69 (8); Anal. calcd for $C_{18}H_{14}Cl_2N_2O$: C, 62.62; H, 4.09; N, 8.11. Found: C, 62.71; H, 4.03; N, 8.07.

3-Phenyl-3-(1*H*-pyrazol-1-yl)-1-*o*-tolylpropan-1-one (3n). 223 mg, 77% yield; pale yellow thick liquid; R_f = 0.43 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.46 (s, 1H), 7.37–7.16 (m, 8H), 6.22 (s, 1H), 6.06 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.36 (dd, *J* = 9.2, 17.6 Hz, 1H), 3.51 (dd, *J* = 5.2, 17.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 140.4, 139.0, 137.9, 137.5, 131.7, 131.3, 129.5, 128.6 (2C), 128.4, 127.8, 126.5 (2C), 125.5, 105.4, 60.9, 46.8, 20.8; IR (Neat) ν_{max} 3063, 2966, 1689, 1494, 1089, 750, 625 cm^{-1}; MS (EI) *m/z* (%) 292 (M^+ + 2, 75), 255 (59), 223 (100), 119 (16), 91 (12), 69 (10); Anal. calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.66; H, 6.21; N, 9.58.

1-(Naphthalen-1-yl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3o). 283 mg, 87% yield; pale yellow solid; mp 77–78 °C; R_f = 0.21 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.49 (s, 1H), 7.48–7.40 (m, 3H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.33–7.17 (m, 5H), 6.19 (s, 1H), 6.15 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.50 (dd, *J* = 9.2, 17.2 Hz, 1H), 3.61 (dd, *J* = 4.8, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 140.4, 139.1, 135.3, 133.6, 132.7, 129.9, 129.6, 128.6 (2C), 128.2, 127.9, 127.8, 127.7, 126.5 (2C), 126.3, 125.5, 124.2, 105.5, 61.1, 47.3; IR (KBr) ν_{max} 3036, 1743, 1682, 1396, 752 cm^{-1}; MS (EI) *m/z* (%) 328 (M^+ + 2, 100), 291 (27), 259 (95), 155 (49), 144 (11), 69 (3); Anal. calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.75; H, 5.51; N, 8.49.

1-(2,6-Dichlorophenyl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3p). 241 mg, 70% yield; pale yellow liquid; R_f = 0.33 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.8 Hz, 2H), 7.45–7.36 (m, 3H), 7.36–7.19 (m, 5H), 6.25 (s, 1H), 6.11 (t, *J* = 7.2 Hz, 1H), 4.27 (dd, *J* = 8.0, 18.8 Hz, 1H), 3.72 (dd, *J* = 5.2, 18.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 139.6, 139.3, 138.5, 130.6, 130.3, 129.5 (2C), 128.5 (2C), 128.1 (2C), 127.9, 126.8 (2C), 105.3, 59.8, 48.9; IR (Neat) ν_{max} 3067, 2916, 1712, 1431, 779, 625 cm^{-1}; MS (EI) *m/z* (%) 347 (M^+ + 2, 86), 345 (M^+, 100), 309 (49), 277 (22), 173 (22), 69 (16); Anal. calcd for $C_{18}H_{14}Cl_2N_2O$: C, 62.62; H, 4.09; N, 8.11. Found: C, 62.51; H, 4.15; N, 8.21.

1-(Furan-2-yl)-3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (3q). 187 mg, 70% yield; light brown solid; mp 98–99 °C; R_f = 0.28 (6 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (d, *J* = 16.8 Hz, 2H), 7.32 (bs, 4H), 7.31–7.25 (m, 1H), 7.22 (bd, *J* = 3.2 Hz, 1H), 6.52 (bt, *J* = 1.6 Hz, 1H), 6.22 (s, 1H), 6.07 (dd, *J* = 5.6, 8.4 Hz, 1H), 4.30 (dd, *J* = 8.8, 16.8 Hz, 1H), 3.53 (dd, *J* = 5.2, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.1, 152.0, 146.6, 140.2, 139.1, 129.5, 128.6 (2C), 127.8, 126.5 (2C), 117.7, 112.2, 105.4, 60.2, 43.6; IR (KBr) ν_{max} 3115, 2922, 1653, 756, 698, 625 cm^{-1}; MS (EI) *m/z* (%) 268 (M^+ + 2, 86), 231 (7), 199 (100), 157 (9), 101 (3), 69 (14); Anal. calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.28; H, 5.36; N, 10.

3-Phenyl-3-(1*H*-pyrazol-1-yl)-1-(thiophen-2-yl)propan-1-one (3r). 259 mg, 92% yield; brown solid; mp 42–43 °C; R_f = 0.18 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (bd, *J* = 3.6 Hz, 1H), 7.58 (bd, *J* = 4.8 Hz, 1H), 7.48 (dd, *J* = 1.2, 17.6 Hz, 2H), 7.35–7.22 (m, 5H), 7.07 (bt, *J* = 3.6 Hz, 1H), 6.21 (s, 1H), 6.07 (dd, *J* = 5.6, 8.4 Hz, 1H), 4.38 (dd, *J* = 8.4, 16.8 Hz, 1H), 3.59 (dd, *J* = 5.2, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 143.5, 140.3, 139.3, 134.1, 132.4, 129.7, 128.7 (2C), 128.1, 127.9, 126.6 (2C), 105.5, 60.6, 44.6; IR (KBr) ν_{max} 3103, 2924, 1662, 1053, 750, 625 cm^{-1}; MS (EI) *m/z* (%) 284 (M^+ + 2, 35), 283 (100), 247 (5), 215 (35), 111 (3); Anal. calcd for $C_{16}H_{14}N_2OS$: C, 68.06; H, 5.00; N, 9.92. Found: C, 68.15; H, 5.12; N, 9.86.

1-Phenyl-3-(1*H*-pyrazol-1-yl)undecan-1-one (3s). Reaction was performed at 80 °C. 262 mg, 84% yield; colorless solid; mp 43–44 °C; R_f = 0.52 (19 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.54 (bt, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 13.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.15 (bt, *J* = 2.0 Hz, 1H), 4.91–4.79 (m, 1H), 3.80 (dd, *J* = 7.2, 17.2 Hz, 1H), 3.32 (dd, *J* = 5.2, 17.6 Hz, 1H), 2.12–2.01 (m, 1H), 1.87–1.74 (m, 1H), 1.29–1.18 (m, 11 H), 1.12–0.97 (m, 1H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 139.5, 136.6, 133.3, 130.0, 128.5 (2C), 128.0 (2C), 104.2, 58.0, 44.0, 35.3, 31.7, 29.3, 29.1, 29.0, 26.1, 22.6, 14.0; IR (KBr) ν_{max} 3102, 2918, 1674, 1446, 1095, 760, 625 cm^{-1}; MS (EI) *m/z* (%) 314 (M^+ + 2, 49), 313 (M^+ + 1, 100), 277 (11), 245 (19), 101 (3), 69 (6); Anal. calcd for $C_{20}H_{28}N_2O$: C, 76.88; H, 9.03; N, 8.97. Found: C, 76.81; H, 9.08; N, 8.85.

1-(4-Chlorophenyl)-3-(1*H*-pyrazol-1-yl)nonan-1-one (3t). Reaction was performed at 80 °C. 290 mg, 91% yield; colorless liquid; R_f = 0.45 (9 : 1 hexane–EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.46 (dd, *J* = 1.5, 22 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 6.13 (bt, *J* = 2.0 Hz, 1H), 4.84–4.80 (m, 1H), 3.78 (dd, *J* = 7.5, 17.0 Hz, 1H), 3.24 (dd, *J* = 5.0, 17.5 Hz, 1H), 2.13–1.99 (m, 1H), 1.87–1.73 (m, 1H), 1.33–1.13 (m, 7H), 1.09–0.98 (m, 1H), 0.84 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 139.7, 139.5, 134.8, 130.0, 129.4 (2C), 128.8 (2C), 104.3, 58.0, 43.8, 35.3, 31.5, 28.6, 25.9, 22.4, 13.9; IR (Neat) ν_{max} 2926, 1687, 1589, 1091, 831, 750 cm^{-1}; MS (EI) *m/z* (%) 322 (M^+ + 3, 11), 321 (M^+ + 2, 51), 320 (M^+ + 1, 38), 319 (M^+, 100), 146 (5), 69 (3); Anal. calcd for $C_{18}H_{23}ClN_2O$: C, 67.81; H, 7.27; N, 8.79. Found: C, 67.71; H, 7.21; N, 8.68.

3-(1*H*-Pyrazol-1-yl)-1-*p*-tolylnonan-1-one (3u). Reaction was performed at 80 °C. 223 mg, 75% yield; pale yellow thick liquid; R_f = 0.41 (12 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.50 (dd, *J* = 1.2, 15.6 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.16 (bs, 1H), 4.92–4.78 (m, 1H), 3.77 (dd, *J* = 7.6, 17.2 Hz, 1H), 3.32 (dd, *J* = 5.2, 17.2 Hz, 1H), 2.39 (s, 3H), 2.13–2.02 (m, 1H), 1.89–1.78 (m, 1H), 1.35–1.13 (m, 7H), 1.11–0.96 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 144.1, 139.5, 134.2, 130.0, 129.2 (2C), 128.2 (2C), 104.2, 58.2, 44.0, 35.4, 31.6, 28.8, 26.1, 22.5, 21.6, 14.0; IR (Neat) ν_{max} 3103, 2928, 1682, 1574, 1043, 812,

748, 625 cm^{-1}; MS (EI) *m/z* (%) 300 (M^+ + 2, 62), 299 (M^+ + 1, 100), 263 (8), 231 (27), 179 (3), 91 (3); Anal. calcd for $C_{19}H_{26}N_2O$: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.58; H, 8.68; N, 9.21.

3-(1*H*-Pyrazol-1-yl)-1-(thiophen-2-yl)nonan-1-one (3v). Reaction was performed at 80 °C. 223 mg, 77% yield; pale yellow thick liquid; R_f = 0.38 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 1.2, 22 Hz, 2H), 7.51 (d, *J* = 1.2 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.10–7.06 (m, 1H), 6.14 (dd, *J* = 1.6, 3.2 Hz, 1H), 4.87–4.73 (m, 1H), 3.71 (dd, *J* = 7.6, 16.4 Hz, 1H), 3.27 (dd, *J* = 5.2, 16.4 Hz, 1H), 2.15–2.00 (m, 1H), 1.86–1.74 (m, 1H), 1.35–1.08 (m, 7H), 1.08–0.93 (m, 1H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 144.0, 139.6, 134.1, 132.5, 130.1, 128.2, 104.3, 58.3, 44.8, 35.3, 31.6, 28.7, 26.0, 22.5, 14.0; IR (Neat) ν_{max} 3103, 2926, 1660, 1516, 1047, 748, 625 cm^{-1}; MS (EI) *m/z* (%) 292 (M^+ + 2, 51), 291 (M^+ + 1, 100), 255 (8), 223 (35), 101 (5), 69 (8); Anal. calcd for $C_{16}H_{22}N_2OS$: C, 66.17; H, 7.64; N, 9.65. Found: C, 66.32; H, 7.61; N, 9.59.

4,4-Dimethyl-1-phenyl-3-(1*H*-pyrazol-1-yl)pentan-1-one (3w). Reaction was performed at 80 °C. 136 mg, 53% yield; colorless solid; mp 37–38 °C; R_f = 0.43 (9 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 6.4 Hz, 2H), 7.59–7.50 (m, 1H), 7.50–7.40 (m, 4H), 6.14 (bt, *J* = 1.6 Hz, 1H), 4.68 (dd, *J* = 2.0, 8.0 Hz, 1H), 4.23 (dd, *J* = 8.0, 14.0 Hz, 1H), 3.20 (dd, *J* = 2.0, 14.0 Hz, 1H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 138.8, 136.9, 133.1, 131.7, 128.5 (2C), 128.1 (2C), 103.8, 66.0, 38.3, 35.4, 27.2 (3C); IR (KBr) ν_{max} 3109, 2959, 1684, 1402, 754, 626 cm^{-1}; MS (EI) *m/z* (%) 258 (M^+ + 2, 43), 257 (M^+ + 1, 100), 221 (16), 189 (43), 101 (11), 69 (8); Anal. calcd for $C_{16}H_{20}N_2O$: C, 74.97; H, 7.86; N, 10.93. Found: C, 74.85; H, 7.95; N, 11.07.

4,4-Dimethyl-3-(1*H*-pyrazol-1-yl)-1-*o*-tolylpentan-1-one (3x). Reaction was performed at 80 °C. 65 mg, 24% yield; colorless oil; R_f = 0.40 (32 : 1 hexane–EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.0 Hz, 1H), 7.46 (dd, *J* = 2.0, 11 Hz, 2H), 7.34 (td, *J* = 1.0, 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.16 (bt, *J* = 2.0 Hz, 1H), 4.36 (dd, *J* = 8.0, 11 Hz, 1H), 4.10 (dd, *J* = 11, 17 Hz, 1H), 3.12 (dd, *J* = 3.0, 17 Hz, 1H), 2.28 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 138.8, 138.3, 137.7, 131.7 (2C), 131.2, 128.3, 125.6, 103.9, 66.5, 41.2, 35.3, 27.1 (3C), 20.7; IR (Neat) ν_{max} 2962, 1687, 1093, 750, 625 cm^{-1}; MS (EI) *m/z* (%) 272 (M^+ + 2, 22), 271 (M^+ + 1, 100), 228 (3), 186 (11), 141 (5), 109 (11); Anal. calcd for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found: C, 75.39; H, 8.26; N, 10.45.

1-(3-Methoxyphenyl)-3-(4-methoxyphenyl)-3-(1*H*-pyrazol-1-yl)-propan-1-one (3aa). 278 mg, 83% yield; pale yellow solid; mp 62–63 °C; R_f = 0.42 (3 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.46 (s, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.30–7.23 (m, 2H), 7.09 (dd, *J* = 1.6, 8.0 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.21 (s, 1H), 6.04 (bt, *J* = 7.2 Hz. 1H), 4.40 (dd, *J* = 8.0, 17.6 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.64 (dd, *J* = 5.6, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 159.7, 159.2, 139.2, 137.8, 132.5, 129.5, 129.4, 128.0 (2C), 120.8, 120.0, 114.0 (2C), 112.1, 105.4, 60.3, 59.3, 55.2, 44.2; IR (KBr) ν_{max} 3057, 2939, 1682, 1612, 739 cm^{-1}; MS (EI) *m/z* (%) 338 (M^+ + 2, 57), 337 (M^+ + 1, 100); Anal. calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.56; H, 6.12; N, 8.21.

1-(4-Fluorophenyl)-3-(1*H*-pyrazol-1-yl)-3-*p*-tolylpropan-1-one (3ab). 249 mg, 81% yield; yellow thick liquid; R_f = 0.52 (6 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 4.8, 10.4 Hz, 2H), 7.47 (dd, *J* = 1.6, 12.8 Hz, 2H), 7.17 (dd, *J* = 8.0, 26 Hz, 4H), 7.08 (t, *J* = 4.8 Hz, 2H), 6.21 (t, *J* = 2.0 Hz, 1H), 6.05 (dd, *J* = 5.2, 8.4 Hz, 1H), 4.40 (dd, *J* = 8.4, 17.2 Hz, 1H), 3.57 (dd, *J* = 5.2, 17.6 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 165.8 (d, *J* = 256 Hz), 139.2, 137.8, 137.5, 133.0 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 9.5 Hz, 2C), 129.6, 129.4 (2C), 126.6 (2C), 115.6 (d, *J* = 22.0 Hz, 2C), 105.5, 60.6, 44.0, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −104.63 to −104.70 (m); IR (Neat) ν_{max} 3105, 2922, 1684, 1599, 1508, 841, 752 cm^{-1}; MS (EI) *m/z* (%) 311 (M^+ + 3, 89), 309 (M^+ + 1, 100), 299 (57), 277 (73), 243 (5), 209 (14), 173 (3); Anal. calcd for $C_{19}H_{17}FN_2O$: C, 74.01; H, 5.56; N, 9.08. Found: C, 74.16; H, 5.49; N, 9.15.

1-(4-Chlorophenyl)-3-(3-fluorophenyl)-3-(1*H*-pyrazol-1-yl)-propan-1-one (3ac). 296 mg, 90% yield; colorless solid; mp 108–109 °C; R_f = 0.55 (6 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.34–7.24 (m, 1H), 7.05 (dd, *J* = 8.0, 20 Hz, 2H), 6.97 (t, *J* = 8.4 Hz, 1H), 6.24 (s, 1H), 6.08 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.46 (dd, *J* = 8.8, 17.6 Hz, 1H), 3.55 (dd, *J* = 5.2, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 162.9 (d, *J* = 247 Hz), 143.1 (d, *J* = 6.1 Hz), 140.0, 139.5, 134.6, 130.3 (d, *J* = 8.1 Hz), 129.9, 129.6 (2C), 128.9 (2C), 122.2, 115.0 (d, *J* = 21.2 Hz), 113.7 (d, *J* = 22.2 Hz), 105.9, 60.2, 44.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.80 to −111.86 (m); IR (KBr) ν_{max} 3061, 2968, 1680, 1589, 1400, 758, 522 cm^{-1}; MS (EI) *m/z* (%) 332 (M^+ + 3, 41), 331 (M^+ + 2, 76), 330 (M^+ + 1, 100), 264 (11), 258 (11); Anal. calcd for $C_{18}H_{14}ClFN_2O$: C, 65.76; H, 4.29; N, 8.52. Found: C, 65.81; H, 4.23; N, 8.45.

1-Phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one (6a).[35] 192 mg, 96% yield; pale yellow solid; mp 45–46 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.52 (s, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.23 (s, 1H), 4.63 (t, *J* = 6.4 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 139.5, 136.3, 133.4, 130.0, 128.6 (2C), 128.0 (2C), 105.2, 46.5, 38.8; IR (KBr) ν_{max} 3111, 3063, 2953, 1682, 1448, 1217, 750, 619 cm^{-1}; MS (EI) *m/z* (%) 202 (M^+ + 2, 8), 201 (48), 157 (100), 143 (6), 69 (8).

3-(1*H*-Pyrazol-1-yl)-1-*p*-tolylpropan-1-one (6b). 199 mg, 93% yield; pale yellow thick liquid; R_f = 0.23 (4 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 2.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.20 (bt, *J* = 2.0 Hz, 1H), 4.58 (t, *J* = 6.4 Hz, 2H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 144.3, 139.4, 133.8, 130.0, 129.2 (2C), 128.0 (2C), 105.1, 46.6, 38.6, 21.6; IR (Neat) ν_{max} 3032, 2951, 1682, 1398, 1089, 978, 752 cm^{-1}; MS (EI) *m/z* (%) 216 (M^+ + 2, 35), 215 (M^+ + 1, 100), 147 (8), 101 (3),

91 (3), 69 (6); Anal. calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.91; H, 6.51; N, 13.15.

1-(4-Chlorophenyl)-3-(1*H*-pyrazol-1-yl)propan-1-one (6c). 171 mg, 73% yield; colorless solid; mp 76–77 °C; R_f = 0.14 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.50 (s, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.21 (s, 1H), 4.59 (t, J = 6.8 Hz, 2H), 3.56 (t, J = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 139.9, 139.6, 134.6, 130.0, 129.4 (2C), 128.9 (2C), 105.2, 46.4, 38.7; IR (KBr) ν_{max} 3103, 2924, 1689, 1589, 1400, 754, 617 cm^{-1}; MS (EI) m/z (%) 238 (M^+ + 3, 11), 237 (M^+ + 2, 65), 236 (M^+ + 1, 30), 235 (M^+, 100), 167 (3), 101 (12), 69 (19); Anal. calcd for $C_{12}H_{11}ClN_2O$: C, 61.41; H, 4.72; N, 11.94. Found: C, 61.52; H, 4.66; N, 11.85.

1-(Naphthalen-1-yl)-3-(1*H*-pyrazol-1-yl)propan-1-one (6d). 171 mg, 68% yield; pale yellow thick liquid; R_f = 0.14 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.86 (dd, J = 7.6, 12.8 Hz, 2H), 7.60 (dtd, J = 1.6, 1.2, 8.2 Hz, 1H), 7.57–7.52 (m, 3H), 7.47 (t, J = 7.2 Hz, 1H), 6.24 (t, J = 2.0 Hz, 1H), 4.68 (t, J = 6.4 Hz, 2H), 3.68 (t, J = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 139.6, 134.8, 133.8, 133.1, 130.0, 129.9, 128.4, 128.1, 128.0, 126.4, 125.6, 124.3, 105.2, 46.9, 41.8; IR (Neat) ν_{max} 3049, 2951, 1678, 1510, 777, 619 cm^{-1}; MS (EI) m/z (%) 252 (M^+ + 2, 38), 251 (M^+ + 1, 100), 215 (19), 183 (19), 165 (16), 101 (11), 69 (11); Anal. calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.62; H, 5.58; N, 11.25.

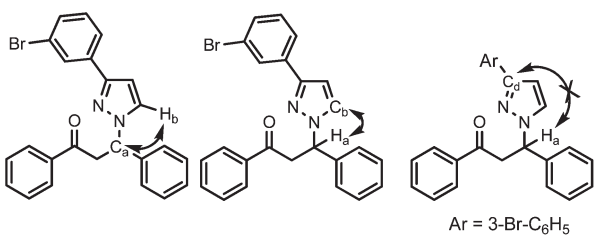
3-(1*H*-Pyrazol-1-yl)-1-*p*-tolyl-3-(trimethylsilyl)propan-1-one (7e). 11 mg, 4% yield; pale yellow liquid; R_f = 0.74 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 12.8 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.09 (t, J = 2.0 Hz, 1H), 4.51 (dd, J = 3.2, 10.0 Hz, 1H), 3.92 (dd, J = 10.0, 17.6 Hz, 1H), 3.10 (dd, J = 3.2, 17.6 Hz, 1H), 2.39 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 144.1, 138.9, 134.3, 130.5, 129.2 (2C), 128.2 (2C), 104.2, 49.4, 39.2, 21.6, −2.9 (3C); IR (Neat) ν_{max} 2951, 1684, 1506, 1182, 844, 748 cm^{-1}; MS (EI) m/z (%) 288 (M^+ + 2, 51), 287 (M^+ + 1, 100), 251 (19), 219 (32), 101 (5), 69 (5); Anal. calcd for $C_{16}H_{22}N_2OSi$: C, 67.09; H, 7.74; N, 9.78. Found: C, 67.22; H, 7.69; N, 9.71.

1-(4-Chlorophenyl)-3-(1*H*-pyrazol-1-yl)-3-(trimethylsilyl)propan-1-one (7f). 52 mg, 17% yield; colorless liquid; R_f = 0.66 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 2H), 7.41 (bd, J = 1.6 Hz, 1H), 7.39–7.33 (m, 3H), 6.08 (bt, J = 2.2 Hz, 1H), 4.47 (dd, J = 2.8, 10.4 Hz, 1H), 3.93 (dd, J = 10.4, 17.2 Hz, 1H), 3.04 (dd, J = 2.8, 17.2 Hz, 1H), 0.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 139.6, 139.0, 135.0, 130.5, 129.5 (2C), 128.8 (2C), 104.3, 49.5, 39.2, −3.0 (3C); IR (Neat) ν_{max} 3103, 2955, 1689, 1589, 1091, 845, 696 cm^{-1}; MS (EI) m/z (%) 310 (M^+ + 3, 24), 309 (M^+ + 2, 76), 308 (M^+ + 2, 59), 307 (M^+, 100), 239 (5), 223 (110, 101 (3), 69 (11); Anal. calcd for $C_{15}H_{19}ClN_2OSi$: C, 58.71; H, 6.24; N, 9.13. Found: C, 58.62; H, 6.21; N, 9.21.

1-(Naphthalen-1-yl)-3-(1*H*-pyrazol-1-yl)-3-(trimethylsilyl)propan-1-one (7g). 23 mg, 7% yield; pale yellow liquid; R_f = 0.62 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.59–7.42 (m, 4H), 7.40 (bd, J = 1.6 Hz, 1H), 6.13 (bt, J = 1.6 Hz, 1H), 4.60 (dd, J = 3.2, 11.2 Hz, 1H), 4.06 (dd, J = 10.8, 16.8 Hz, 1H), 3.14 (dd, J = 3.2, 16.8 Hz, 1H), 0.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 139.0, 136.0, 133.8, 132.6, 130.6, 129.9, 128.3, 127.8, 127.6, 126.4, 125.5, 124.3, 104.3, 50.1, 42.9, −3.0 (3C); IR (Neat) ν_{max} 3051, 2955, 1682, 1249, 844, 750, 623 cm^{-1}; MS (EI) m/z (%) 325 (M^+ + 2, 32), 324 (100), 288 (5), 255 (27), 165 (27), 101 (5), 69 (14); Anal. calcd for $C_{19}H_{22}N_2OSi$: C, 70.77; H, 6.88; N, 8.69. Found: C, 70.65; H, 6.91; N, 8.61.

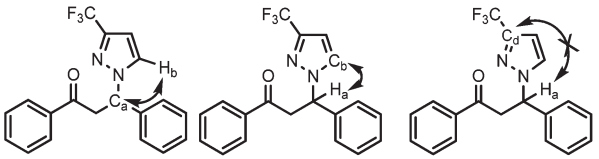
1,3-Diphenyl-3-(3-phenyl-1*H*-pyrazol-1-yl)propan-1-one (8ab). 293 mg, 83% yield; colorless solid; mp 110–111 °C; R_f = 0.51 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.49–7.42 (m, 3H), 7.42–7.37 (m, 2H), 7.34 (td, J = 1.6, 6.4 Hz, 4H), 7.29–7.22 (m, 2H), 6.52 (bd, J = 2.0 Hz, 1H), 6.11 (dd, J = 5.2, 8.8 Hz, 1H), 4.61 (dd, J = 8.4, 17.2 Hz, 1H), 3.56 (dd, J = 5.2, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 150.8, 140.7, 136.6, 133.7, 133.2, 130.9, 128.7 (2C), 128.5 (2C), 128.3 (2C), 128.1 (2C), 127.9, 127.3, 126.7 (2C), 125.5 (2C), 102.9, 61.2, 44.2; IR (KBr) ν_{max} 3063, 2920, 1684, 1454, 750, 694 cm^{-1}; MS (EI) m/z (%) 354 (M^+ + 2, 51), 353 (M^+ + 1, 100), 263 (5); Anal. calcd for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.59. Found: C, 81.65; H, 5.76; N, 7.88. X-Ray crystallographic analysis confirms the structure of **8ab**.[13]

3-(3-(3-Bromophenyl)-1*H*-pyrazol-1-yl)-1,3-diphenylpropan-1-one (8ac). 401 mg, 93% yield; colorless solid; mp 105–106 °C; R_f = 0.42 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 1.2 Hz, 1H), 1.57 (dd, J = 8.0, 17.2 Hz, 2H), 7.51–7.41 (m, 3H), 7.41–7.25 (m, 6H), 7.17 (t, J = 8.0 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.10 (dd, J = 4.8, 8.8 Hz, 1H), 4.58 (dd, J = 8.8, 17.6 Hz, 1H), 3.52 (dd, J = 4.8, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 149.3, 140.4, 136.5, 135.7, 133.2, 131.1, 130.1, 129.9, 128.7 (2C), 128.5 (2C), 128.3, 128.1 (2C), 128.0, 126.6 (2C), 124.0, 122.5, 103.1, 61.3, 44.1; IR (KBr) ν_{max} 3063, 2918, 1684, 1452, 995, 752, 688 cm^{-1}; MS (EI) m/z (%) 434 (M^+ + 2, 30), 433 (M^+ + 1, 100), 431 (M^+, 100), 257 (8), 255 (8), 209 (67), 145 (16); Anal. calcd for $C_{24}H_{19}BrN_2O$: C, 66.83; H, 4.44; N, 6.49. Found: C, 66.75; H, 4.51; N, 6.41.



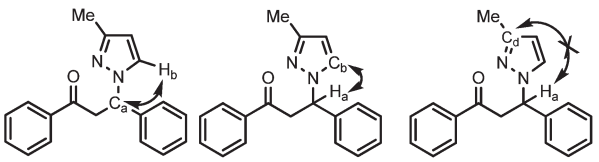
The structure of **8ac** is established based on the heteronuclear multiple bond correlation (HMBC) studies; correlations between C_a (61.3 ppm) and H_b (7.43 ppm), H_a (6.20 ppm) and C_b (131.1 ppm) are quite significant whereas the correlation between H_a and C_d (149.3 ppm) is not seen. Furthermore, the X-ray crystallographic analysis data supports the structure of **8ac**.[13]

1,3-Diphenyl-3-(3-(trifluoromethyl)-1*H*-pyrazol-1-yl)propan-1-one (8ad). Reaction was performed at 80 °C. 272 mg, 79% yield; colorless solid; mp 80–81 °C; R_f = 0.38 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 0.8, 6.4 Hz, 2H), 7.56 (tt, J = 1.2, 6.8 Hz, 1H), 7.50 (bd, J = 1.6 Hz, 1H), 7.45 (bt, J = 8.0 Hz, 2H), 7.36–7.27 (m, 5H), 6.47 (bd, J = 2.0, 1H), 6.11 (dd, J = 5.2, 8.4 Hz, 1H), 4.49 (dd, J = 8.4, 17.6 Hz, 1H), 3.61 (dd, J = 4.8, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 142.2 (q, J = 58.3 Hz), 139.5, 136.3, 133.5, 131.1, 128.9 (2C), 128.6 (2C), 128.4, 128.1 (2C), 126.7 (2C), 121.3 (d, J = 270 Hz), 104.4, 61.8, 44.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.54; IR (KBr) ν_{max} 3151, 2947, 1693, 1242, 773, 688 cm^{-1}; MS (EI) m/z (%) 346 (M^+ + 2, 41), 345 (M^+ + 1, 100), 195 (11), 165 (5), 91 (3); Anal. calcd for $C_{19}H_{15}F_3N_2O$: C, 66.27; H, 4.39; N, 8.14. Found: C, 66.15; H, 4.46; N, 8.21.



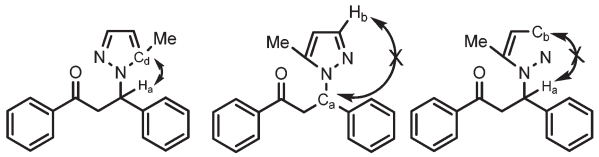
The structure of **8ad** is established based on the HMBC studies; correlations between C_a (61.8 ppm) and H_b (7.50 ppm), H_a (6.11 ppm) and C_b (131.1 ppm) are quite significant whereas the correlation between H_a and C_d (142.3 ppm) is not seen.[13]

3-(3-Methyl-1*H*-pyrazol-1-yl)-1,3-diphenylpropan-1-one (8ae). 101 mg, 35% yield; pale yellow thick liquid; R_f = 0.35 (12 : 1 hexane–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 5.5 Hz, 2H), 7.35 (d, J = 2.5 Hz, 1H), 7.31 (d, J = 4.5 Hz, 4H), 7.28–7.24 (m, 1H), 6.02 (dd, J = 5.5, 8.0 Hz, 1H), 5.98 (d, J = 2.0 Hz, 1H), 4.41 (dd, J = 8.0, 17.5 Hz, 1H), 3.65 (dd, J = 5.5, 17.5 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 148.5, 140.9, 136.7, 133.3, 130.4, 128.7 (2C), 128.6 (2C), 128.3 (2C), 127.9, 126.7 (2C), 105.1, 60.7, 44.3, 13.8; IR (Neat) ν_{max} 2926, 1685, 1450, 1203, 752 cm^{-1}; MS (EI) m/z (%) 292 (M^+ + 2, 20), 291 (M^+ + 1, 100), 219 (3), 97 (3); Anal. calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.45; H, 6.31; N, 9.58.



The structure of **8ae** is established based on the HMBC studies; correlations between C_a (60.7 ppm) and H_b (7.38 ppm), H_a (6.05 ppm) and C_b (130.4 ppm) are quite significant whereas the correlation between H_a and C_d (148.5 ppm) is not seen.[13]

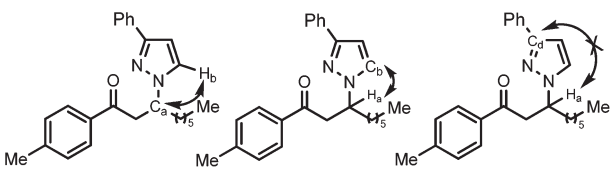
3-(5-Methyl-1*H*-pyrazol-1-yl)-1,3-diphenylpropan-1-one (8ae′). 157 mg, 54% yield; pale yellow thick liquid; R_f = 0.35 (12 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.42 (d, J = 1.6 Hz, 1H), 7.37–7.31 (m, 2H), 7.31–7.25 (m, 3H), 6.08 (dd, J = 4.4, 8.8 Hz, 1H), 6.03 (s, 1H), 4.66 (dd, J = 9.2, 17.6 Hz, 1H), 3.57 (dd, J = 4.4, 17.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 141.0, 138.8, 138.1, 136.6, 133.2, 128.7 (2C), 128.5 (2C), 128.2 (2C), 127.6, 126.5 (2C), 105.5, 57.0, 44.7, 11.0; IR (Neat) ν_{max} 3030, 2922, 1685, 1448, 752, 698 cm^{-1}; MS (EI) m/z (%) 292 (M^+ + 2, 35), 291 (M^+ + 1, 100), 241 (22), 209 (81), 115 (22), 83 (22); Anal. calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.49; H, 6.21; N, 9.76.



The structure of **8ae′** is established based on the HMBC studies; correlation between C_d (138.8 ppm) and H_a (6.08 ppm) is quite significant whereas correlations between C_a (57.0 ppm) and H_b (7.42 ppm), H_a and C_b (138.1 ppm) are not seen.[13]

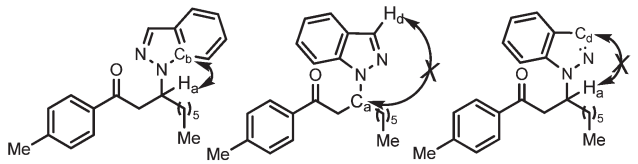
3-(1*H*-Indazol-1-yl)-1,3-diphenylpropan-1-one (8af). 301 mg, 92% yield; colorless solid; mp 92–93 °C; R_f = 0.42 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.98 (s, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.37–7.20 (m, 6H), 7.10 (t, J = 8.0 Hz, 1H), 6.46 (dd, J = 5.2, 8.8 Hz, 1H), 4.67 (dd, J = 8.8, 18.0 Hz, 1H), 3.74 (dd, J = 4.8, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 140.7, 139.5, 136.4, 133.1, 132.9, 128.6 (2C), 128.4 (2C), 128.0 (2C), 127.6, 126.5 (2C), 126.2, 124.1, 120.8, 120.7, 109.4, 57.3, 44.2; IR (KBr) ν_{max} 3061, 2916, 1682, 1018, 750, 696 cm^{-1}; MS (EI) m/z (%) 328 (M^+ + 2, 41), 327 (M^+ + 1, 100), 241 (5), 209 (67), 151 (3), 119 (14); Anal. calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.85; H, 5.51; N, 8.65. X-Ray crystallographic analysis elucidates the structure of **8af**.[13]

3-(3-Phenyl-1*H*-pyrazol-1-yl)-1-*p*-tolylnonan-1-one (8ub). Reaction was performed at 80 °C. 120 mg, 32% yield; pale yellow thick liquid; R_f = 0.63 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.76 (dd, J = 1.2, 8.4 Hz, 2H), 7.46 (d, J = 2.0 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.24 (tt, J = 1.2, 7.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 6.42 (d, J = 2.0 Hz, 1H), 4.86–4.80 (m, 1H), 3.83 (dd, J = 7.2, 17.2 Hz, 1H), 3.30 (dd, J = 5.2, 17.2 Hz, 1H), 2.34 (s, 3H), 2.18–2.07 (m, 1H), 1.88–1.78 (m, 1H), 1.37–1.18 (m, 7H), 1.17–1.07 (m, 1H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 151.4, 144.0, 134.3, 134.0, 131.1, 129.2 (2C), 128.4 (2C), 128.2 (2C), 127.2, 125.6 (2C), 101.6, 58.5, 43.9, 35.2, 31.6, 28.7, 26.1, 22.5, 21.5, 14.0; IR (Neat) ν_{max} 3034, 2928, 1682, 1606, 1458, 750, 694 cm^{-1}; MS (EI) m/z (%) 376 (M^+ + 2, 54), 375 (M^+ + 1, 100), 263 (3), 231 (19), 177 (11), 145 (19), 91 (3); Anal. calcd for $C_{25}H_{30}N_2O$: C, 80.17; H, 8.07; N, 7.48. Found: C, 80.06; H, 8.12; N, 7.56.



The structure of **8ub** is established based on the NMBC studies; correlations between C_a (58.5 ppm) and H_b (7.51 ppm), H_a (4.83 ppm) and C_b (131.1 ppm) are quite significant whereas the correlation between H_a and C_d (151.4 ppm) is not seen.[13]

3-(1*H*-Indazol-1-yl)-1-*p*-tolylnonan-1-one (8uf). Reaction was performed at 80 °C. 226 mg, 65% yield; pale yellow thick liquid; R_f = 0.47 (9 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.39 (td, J = 0.8, 6.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 5.23–5.32 (m, 1H), 3.85 (dd, J = 7.2, 17.6 Hz, 1H), 3.46 (dd, J = 5.6, 17.2 Hz, 1H), 2.38 (s, 3H), 2.24–2.13 (m, 1H), 2.00–1.87 (m, 1H), 1.30–1.13 (m, 7H), 1.05–0.93 (m, 1H), 0.82 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 144.1, 140.2, 134.2, 133.3, 129.2 (2C), 128.2 (2C), 126.1, 123.4, 120.8, 120.4, 109.4, 54.1, 43.8, 35.5, 31.5, 28.8, 26.1, 22.5, 21.6, 13.9; IR (Neat) ν_{max} 3059, 2928, 1682, 1608, 1014, 740 cm^{-1}; MS (EI) m/z (%) 350 (M^+ + 2, 62), 349 (M^+ + 1, 100), 263 (14), 231 (57), 151 (11), 119 (19); Anal. calcd for $C_{23}H_{28}N_2O$: C, 79.27; H, 8.10; N, 8.04. Found: C, 79.45; H, 8.06; N, 8.12.



The structure of **8uf** is established based on the HMBC studies; correlation between C_b (140.2 ppm) and H_a (5.31 ppm) is quite significant whereas correlations between C_a (54.1 ppm) and H_d (8.01 ppm), H_a and C_d (133.3 ppm) are not seen.[13]

1,3-Diphenyl-3-(1*H*-1,2,4-triazol-1-yl)propan-1-one (17).[36] Reaction was performed in toluene (1.5 mL) + DMF (0.5 mL) mixture at 80 °C. 162 mg, 58% yield; pale yellow solid; mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.92 (s, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.50–7.32 (m, 7H), 6.20 (dd, J = 4.8, 9.2 Hz, 1H), 4.44 (dd, J = 8.8, 17.6 Hz, 1H), 3.63 (dd, J = 4.4, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 151.6, 143.5, 138.7, 136.0, 133.7, 129.0 (2C), 128.7 (2C), 128.6, 128.1 (2C), 126.9 (2C), 58.9, 43.7; IR (KBr) ν_{max} 2922, 1685, 1502, 1006, 754, 690 cm^{-1}; MS (EI) m/z (%) 279 (M^+ + 2, 30), 278 (M^+ + 1, 100), 241 (16), 209 (57), 105 (8), 70 (8).

1,3-Diphenyl-3-(2*H*-1,2,3-triazol-2-yl)propan-1-one (18).[7d] Reaction was performed in toluene (1.5 mL) + DMF (0.5 mL) mixture at 80 °C. 166 mg, 60% yield; colorless solid; mp 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.59–7.49 (m, 3H), 7.41 (t, J = 8.0 Hz, 2H), 7.35–7.22 (m, 5H), 6.51 (dd, J = 5.2, 9.2 Hz, 1H), 4.51 (dd, J = 9.2, 18.0 Hz, 1H), 3.69 (dd, J = 5.2, 18.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 139.3, 136.2, 134.0 (2C), 133.3, 128.7 (2C), 128.5 (2C), 128.1, 128.0 (2C), 126.5 (2C), 63.8, 43.8; IR (KBr) ν_{max} 3063, 2908, 1682, 1332, 960, 750, 687 cm^{-1}; MS (EI) m/z (%) 279 (M^+ + 2, 15), 278 (M^+ + 1, 52), 241 (6), 209 (100), 79 (5), 68 (5).

1,3-Diphenyl-3-(1*H*-1,2,3-triazol-1-yl)propan-1-one (18′).[7d] Reaction was performed in toluene (1.5 mL) + DMF (0.5 mL) mixture at 80 °C. 31mg, 11% yield; colorless solid; mp 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.68 (s, 1H), 7.61 (s, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.39–7.29 (m, 5H), 6.32 (dd, J = 4.8, 8.4 Hz, 1H), 4.65 (dd, J = 8.4, 17.6 Hz, 1H), 3.74 (dd, J = 5.2, 18.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 139.0, 136.1, 133.8, 133.6, 129.0 (2C), 128.7 (2C), 128.1 (2C), 127.1, 126.8 (2C), 124.2, 60.3, 44.2; IR (KBr) ν_{max} 3097, 1682, 1213, 752, 690, 549 cm^{-1}; MS (EI) m/z (%) 280 (M^+ + 3, 14), 279 (M^+ + 2, 35), 278 (M^+ + 1, 100), 156 (3), 123 (5).

3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1,3-diphenylpropan-1-one (19).[7c] Reaction was performed in toluene (1.5 mL) + DMF (0.5 mL) mixture at 80 °C. 147 mg, 45% yield; light yellow solid; mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.53 (s, 1H), 7.51 (t, J = 3.6 Hz, 1H), 7.45–7.35 (m, 5H), 7.35–7.22 (m, 4H), 6.60 (dd, J = 4.8, 8.8 Hz, 1H), 4.86 (dd, J = 8.8, 18 Hz, 1H), 3.89 (dd, J = 4.8, 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 145.9, 138.9, 135.9, 133.4, 132.8, 128.8 (2C), 128.5 (2C), 128.3, 128.0 (2C), 127.1, 126.5 (2C), 123.9, 119.6, 109.8, 58.1, 44.2; IR (KBr) ν_{max} 3061, 2924, 1687, 1267, 920, 746 cm^{-1}; MS (EI) m/z (%) 228 (M^+ + 1, 100), 196 (46), 183 (14), 100 (6).

3-(2*H*-Benzo[*d*][1,2,3]triazol-2-yl)-1,3-diphenylpropan-1-one (19′).[7c] Reaction was performed in toluene (1.5 mL) + DMF (0.5 mL) mixture at 80 °C. 33 mg, 10% yield; yellow thick liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.30 (m, 14 H), 6.78 (dd, J = 5.0, 9.0 Hz, 1H), 4.73 (dd, J = 9.0, 18.0 Hz, 1H), 3.89 (dd, J = 5.0, 18.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 144.1 (2C), 138.8, 136.2, 133.5, 130.9, 128.9 (2C), 128.7 (2C), 128.2 (2C), 126.8 (2C), 126.2 (2C), 118.2 (2C), 65.7, 44.1; IR (KBr) ν_{max} 3063, 2930, 1582, 1332, 960, 700, 687 cm^{-1}; MS (EI) m/z (%) 328 (M^+ + 1, 100), 277 (14), 191 (22), 108 (6), 67 (6).

3-(1*H*-Imidazol-1-yl)-1,3-diphenylpropan-1-one (20).[37] Reaction was performed in toluene (1.5 mL) + DMF (0.5 mL) mixture at 80 °C. 28 mg, 10% yield; pale yellow solid; mp 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 8.0 Hz, 3H), 7.35–7.23 (m, 4H), 7.23–7.16 (m, 1H), 6.90 (s, 2H), 4.84 (t, J = 6.8 Hz, 1H), 4.22 (dd, J = 7.6, 18.0 Hz, 1H), 3.58 (dd, J = 6.0, 18.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 149.4, 141.6, 136.6, 133.2 (2C), 128.8 (2C), 128.5 (2C), 128.1 (2C), 128.0 (2C), 127.1 (2C), 44.1, 40.0; IR (KBr) ν_{max} 3040, 1682, 1462, 752, 688, 553 cm^{-1}; MS (EI) m/z (%) 278 (M^+ + 2, 46), 277 (M^+ + 1, 100), 209 (3), 157 (5), 69 (2).

1,3-Diphenyl-3-(1*H*-pyrrol-1-yl)propan-1-one (21). 146 mg, 53% yield; pale yellow solid; mp 89–90 °C; R_f = 0.57 (6 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 8.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.37–7.25 (m, 3H), 7.22 (d, J = 7.2 Hz, 2H), 6.79 (s, 2H), 6.17 (s, 2H), 5.99 (t, J = 6.8 Hz, 1H), 3.96 (dd, J = 7.2, 17.2 Hz, 1H), 3.80 (dd, J = 6.4, 17.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 141.1, 136.5, 133.5, 128.8 (2C), 128.7 (2C), 128.0 (2C), 127.8, 126.4 (2C), 119.7 (2C), 108.4 (2C), 58.2, 44.6; IR (KBr)

ν_{max} 3059, 2924, 1680, 1269, 723, 634 cm^{-1}; MS (EI) *m/z* (%) 277 (M^+ + 2, 5), 276 (M^+ + 1, 24), 156 (100), 129 (13), 105 (15), 97 (33); Anal. calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.75; H, 6.28; N, 5.15.

1-Phenyl-3-(1*H*-pyrrol-1-yl)undecan-1-one (22). Reaction was performed at 80 °C. 180 mg, 58% yield; brown color solid; mp 41–42 °C; R_f = 0.52 (19 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.2 Hz, 2H), 7.56 (bt, J = 7.6 Hz, 1H), 7.44 (bt, J = 7.6 Hz, 2H), 6.72 (s, 2H), 6.11 (s, 2H), 4.63 (bt, J = 7.2 Hz, 1H), 3.46 (dd, J = 6.4, 17.2 Hz, 1H), 3.32 (dd, J = 6.8, 17.2 Hz, 1H), 1.81 (bd, J = 6.4 Hz, 2H), 1.35–1.15 (m, 12 H), 0.86 (t, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 136.7, 133.2, 128.6 (2C), 128.0 (2C), 118.9 (2C), 107.8 (2C), 55.7, 45.7, 36.2, 31.8, 29.3, 29.2 (2C), 26.1, 22.6, 14.1; IR (KBr) ν_{max} 3130, 2922, 1680, 758 cm^{-1}; MS (EI) *m/z* (%) 312 (M^+ + 1, 49), 311 (100), 269 (8), 210 (3); Anal. calcd for $C_{21}H_{29}NO$: C, 80.98; H, 9.38; N, 4.50. Found: C, 80.78; H, 9.41; N, 4.61.

1-Phenyl-3-(1*H*-pyrrol-1-yl)heptan-1-one (23). Reaction was performed at 80 °C. 99 mg, 39% yield; brown color solid; mp 47–48 °C; R_f = 0.47 (19 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.75 (t, J = 2.4 Hz, 2H), 6.14 (t, J = 2.0 Hz, 2H), 4.72–4.59 (m, 1H), 3.49 (dd, J = 6.4, 17.2 Hz, 1H), 3.34 (dd, J = 6.8, 17.2 Hz, 1H), 1.93–1.76 (m, 2H), 1.43–1.19 (m, 3H), 1.19–1.05 (m, 1H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 136.7, 133.3, 128.6 (2C), 127.9 (2C), 118.9 (2C), 107.8 (2C), 55.7, 45.7, 35.9, 28.3, 22.2, 13.9; IR (KBr) ν_{max} 3059, 2957, 1682, 1448, 725, 690 cm^{-1}; MS (EI) *m/z* (%) 257 (M^+ + 2, 35), 256 (100), 238 (51), 189 (5), 136 (11), 80 (8); Anal. calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.85; H, 8.32; N, 5.41.

1-Phenyl-3-(1*H*-pyrrol-1-yl)propan-1-one (24).[38] 18 mg, 9% yield; brown color semi-solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 6.73 (s, 2H), 6.16 (s, 2H), 4.39 (t, J = 6.8 Hz, 2H), 3.46 (t, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 136.4, 133.4, 128.7 (2C), 127.9 (2C), 120.7 (2C), 108.3 (2C), 44.2, 40.5; IR (Neat) ν_{max} 3057, 2935, 1678, 1498, 1284, 1089, 748, 621 cm^{-1}; MS (EI) *m/z* (%) 201 (M^+ + 2, 24), 200 (M^+ + 1, 100), 182 (5), 156 (3), 80 (8).

2-((1*H*-Pyrrol-1-yl)methyl)-1,5-diphenylpentane-1,5-dione (24′). 39 mg, 24% yield; brown thick liquid; R_f = 0.34 (12 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91–7.82 (m, 4H), 7.54 (t, J = 7.2 Hz, 2H), 7.42 (t, J = 7.6 Hz, 4H), 6.63 (t, J = 1.6 Hz, 2H), 6.06 (t, J = 2.0 Hz, 2H), 4.38 (q, J = 9.6 Hz, 1H), 4.15–4.04 (m, 2H), 3.01–2.89 (m, 1H), 2.89–2.76 (m, 1H), 2.29–2.18 (m, 1H), 2.10–2.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 199.1, 136.7, 136.5, 133.5, 133.1, 128.7 (2C), 128.5 (2C), 128.1 (2C), 127.9 (2C), 120.9 (2C), 108.5 (2C), 51.2, 47.3, 35.0, 25.1; IR (Neat) ν_{max} 3061, 2928, 1680, 1448, 1089, 727, 690 cm^{-1}; MS (EI) *m/z* (%) 332 (M^+ + 1, 50), 314 (100), 265 (40), 212 (16), 200 (20), 194 (25); Anal. calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.65; H, 6.31; N, 4.35.

1-Phenyl-3-(1*H*-pyrrol-1-yl)-3-(trimethylsilyl)propan-1-one (25). 47 mg, 17% yield; light brown liquid; R_f = 0.66 (12 : 1 hexane–EtOAc); along with **24** (39 mg, 19% yield), and **24′** (49 mg, 29% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 3.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.63 (s, 2H), 6.08 (s, 2H), 4.34 (dd, J = 4.4, 9.6 Hz, 1H), 3.63 (dd, J = 9.6, 17.2 Hz, 1H), 3.21 (dd, J = 4.4, 17.2 Hz, 1H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 136.7, 133.1, 128.6 (2C), 128.0 (2C), 120.4 (2C), 107.5 (2C), 46.9, 40.4, −3.0 (3C); IR (Neat) ν_{max} 2957, 1687, 1251, 979, 842, 721, 628 cm^{-1}; MS (EI) *m/z* (%) 274 (M^+ + 3, 16), 273 (M^+ + 2, 51), 272 (M^+ + 1, 100), 254 (11), 237 (110, 205 (14), 152 (110, 93 (3); Anal. calcd for $C_{16}H_{21}NOSi$: C, 70.80; H, 7.80; N, 5.16. Found: C, 70.58; H, 7.76; N, 5.21.

3-(1*H*-Indol-1-yl)-1-phenylheptan-1-one (26). Reaction was performed at 80 °C. 177 mg, 58% yield; pale yellow thick liquid; R_f = 0.43 (19 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.54–7.44 (m, 2H), 7.39 (bt, J = 7.6 Hz, 2H), 7.23–7.16 (m, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 5.15–5.05 (m, 1H), 3.55–3.40 (m, 2H), 2.04–1.90 (m, 2H), 1.36–1.18 (m, 3H), 1.13–1.01 (m, 1H), 0.80 (t, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 136.5, 135.9, 133.3, 128.6 (2C), 128.5, 127.9 (2C), 124.7, 121.4, 120.9, 119.3, 109.8, 101.9, 52.2, 44.7, 34.9, 28.3, 22.3, 13.8; IR (Neat) ν_{max} 3055, 2957, 1658, 1460, 1307, 740, 690 cm^{-1}; MS (EI) *m/z* (%) 307 (M^+ + 2, 46), 306 (M^+ + 1, 100), 236 (5), 209 (8), 91 (10); Anal. calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.45; H, 7.65; N, 4.51.

3-(1*H*-Indol-3-yl)-1-phenylheptan-1-one (26′). Reaction was performed at 80 °C. 36 mg, 12% yield; brown color thick liquid; R_f = 0.13 (19 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.93 (bs, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.01 (s, 1H), 3.72–3.61 (m, 1H), 3.42 (dd, J = 6.4, 16.0 Hz, 1H), 3.34 (dd, J = 7.2, 16.4 Hz, 1H), 1.91–1.77 (m, 2H), 1.33–1.23 (m, 4H), 0.82 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 137.3, 136.5, 132.8, 128.4 (2C), 128.0 (2C), 126.6, 121.8, 121.2, 119.5, 119.4, 119.1, 111.2, 45.3, 35.2, 32.9, 29.9, 22.7, 14.0; IR (Neat) ν_{max} 3416, 3057, 2928, 1682, 1454, 740 cm^{-1}; MS (EI) *m/z* (%) 307 (M^+ + 2, 46), 306 (100), 236 (5), 209 (8), 91 (10); Anal. calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.71; H, 7.52; N, 4.65.

3-(2-Methyl-1*H*-indol-1-yl)-1-phenylheptan-1-one (27). Reaction was performed at 80 °C. 132 mg, 41% yield; brown color thick liquid; R_f = 0.27 (12 : 1 hexane–EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (bs, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.81–7.73 (m, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.31–7.23 (m, 1H), 7.21–7.13 (m, 2H), 3.73–3.60 (m, 2H), 3.46 (dd, J = 8.8, 18.4 Hz, 1H), 2.37 (s, 3H), 2.15–2.02 (m, 1H), 1.98–1.85 (m, 1H), 1.45–1.20 (m, 4H), 0.89 (t, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 137.2, 135.5, 132.6, 131.4, 128.3 (2C), 127.9 (2C), 127.0, 120.3, 118.8, 118.6, 113.4, 110.5, 44.6, 34.7, 32.8, 30.2, 22.5, 13.9, 11.8; IR (Neat) ν_{max} 3055, 2928, 1680, 1462, 742, 690 cm^{-1}; MS (EI) *m/z* (%)

320 (M^+ + 1, 100), 232 (38), 199 (65), 200 (100), 144 (65), 132 (5); Anal. calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.59; H, 7.81; N, 4.43.

1,3-Diphenyl-3-(phenylamino)propan-1-one (28).[39] 72 mg, 24% yield; colorless solid; mp 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.87 (m, 2H), 7.57 (tt, J = 1.2, 7.2 Hz, 1H), 7.51–7.41 (m, 4H), 7.34 (t, J = 8.0 Hz, 2H), 7.29–7.22 (m, 1H), 7.15–7.05 (m, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.57 (dd, J = 0.8, 8.4 Hz, 2H), 5.02 (dd, J = 5.2, 7.6 Hz, 1H), 4.57 (bs, 1H), 3.52 (dd, J = 5.2, 16.0 Hz, 1H), 3.43 (dd, J = 7.6, 16.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 147.0, 142.9, 136.7, 133.4, 129.1 (2C), 128.8 (2C), 128.7 (2C), 128.2 (2C), 127.3, 126.3 (2C), 117.7, 113.8 (2C), 54.8, 46.3; IR (KBr) ν_{max} 3385, 3024, 2918, 1670, 1599, 1290, 744, 686 cm^{-1}; MS (EI) m/z (%) 300 (M^+ − 1, 100), 284 (5).

1,1′-(1,4-Phenylene)bis(3-phenyl-3-(1*H*-pyrazol-1-yl)propan-1-one) (30). 265 mg, 56% yield; light brown solid; mp 173–174 °C; R_f = 0.28 (3 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 4H), 7.47 (dd, J = 1.6, 10.0 Hz, 4H), 7.42–7.30 (m, 10H), 6.22 (t, J = 2.0 Hz, 2H), 6.08 (dd, J = 4.8, 8.4 Hz, 2H), 4.52 (dd, J = 8.8, 17.6 Hz, 2H), 3.58 (dd, J = 5.2, 17.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2 (2C), 140.4 (2C), 139.8 (2C), 139.2 (2C), 129.7 (2C), 128.8 (4C), 128.4 (4C), 128.1 (2C), 126.6 (4C), 105.7 (2C), 60.7 (2C), 44.5 (2C); IR (KBr) ν_{max} 3063, 2918, 1687, 1398, 754, 626 cm^{-1}; MS (EI) m/z (%) 476 (M^+ + 2, 16), 474 (M^+, 61), 473 (41), 406 (51), 353 (51), 338 (100), 238 (3), 96 (3); Anal. calcd for $C_{30}H_{26}N_4O_2$: C, 75.93; H, 5.52; N, 11.81. Found: C, 75.86; H, 5.49; N, 11.68.

1,1′-(1,4-Phenylene)bis(3-(1*H*-indazol-1-yl)-3-phenylpropan-1-one) (31). 276 mg, 48% yield; yellow thick liquid; R_f = 0.50 (3 : 1 hexane–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.02 (m, 6H), 7.72 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.41–7.25 (m, 12 H), 7.15 (t, J = 7.6 Hz, 2H), 6.49 (dd, J = 4.4, 8.8 Hz, 2H), 4.75 (dd, J = 8.8, 17.6 Hz, 2H), 3.74 (dd, J = 4.4, 17.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2 (2C), 140.5 (2C), 139.7 (2C), 139.5 (2C), 133.0 (2C), 128.7 (4C), 128.3 (4C), 127.8 (2C), 126.5 (4C), 126.3 (2C), 124.2 (2C), 120.9 (2C), 120.8 (2C), 109.4 (2C), 57.4 (2C), 44.6 (2C); IR (Neat) ν_{max} 3061, 2924, 1687, 1498, 1024, 740 cm^{-1}; MS (EI) m/z (%) 576 (M^+ + 1, 14), 575 (M^+, 35), 457 (20), 339 (100), 151 (51), 119 (82); Anal. calcd for $C_{38}H_{30}N_4O_2$: C, 79.42; H, 5.26; N, 9.75. Found: C, 79.52; H, 5.21; N, 9.68.

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